Division 101 Appendix 1

Best Pollution Prevention Practices For Abrasive Blast Media Waste From Shipyard Repair Activities

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Based on Best Management Practices Manual for the Shipbuilding and Repair Industry, The Commonwealth of Virginia State Water Control Board.

FORWARD

There has been increasing concern in recent years about pollutants generated by the shipbuilding and repair industry. In particular, abrasive blast media, metals, metal related compounds, petroleum associated hydrocarbons and antifouling ingredients in paints have come under scrutiny. One reason for concern with pollutants generated by ship repair activities is the close proximity to water and the potential to pollute this resource. Technical inspections and toxics monitoring of shipyard effluent show that significant levels of pollutants are generated by shipbuilding, repair and maintenance operations. Inspections demonstrate a continuing effort by the DEQ to prevent shipyard-related pollutants from entering State waters, particularly to sensitive bays and estuaries.

As a result of these inspections, it was evident that Best Pollution Prevention Practices (BPP's) for the ship and boat repair industry were necessary. In 1993, the DEQ proceeded with the identification of general BPP's applicable to this industry. National Pollutant Discharge Elimination System (NPDES) permits were written to include BPP language, however, the permit wording was later determined to be too general. It was apparent that BPP's were needed that would contain practical hazardous sandblast grit containment methods .

This manual was developed through literature search, yard inspections and discussions between DEQ and the marine industry, and is designed to serve as an introduction to pollution prevention for repair facilities that do abrasive blasting. Implementation of BPP's described herein should provide significant and economical pollution control at boat yard and repair facilities.

Because the Department of Environmental Quality is not responsible for the implementation and maintenance of the BPP's described in this manual, and does not have daily control over each facility's particular use of the BPP's, the Department will not guarantee or warrant the performance or results that may be obtained by the implementation of the BPP's described herein; only that the BPP's will perform substantially in accordance with the specifications and constraints set forth in this manual, assuming they are properly installed and maintained.

BPP's are intended to complement, not substitute, existing Federal and State regulations.

INTRODUCTION

The shipbuilding and repair industry presents a unique problem in terms of applying pollution control techniques. Although a given facility may not compare exactly with another facility in terms of repair capabilities, type and size of docks, and so on, there are enough similarities between facilities to describe pollution control techniques that can be adapted to suit a specific site.

There are several different functions that occur at ship and boat repair facilities. Some facilities employ a few people, while others employ many people, including various

subcontractors, blacksmiths, boilermakers, chemists, carpenters, electricians, laborers, machinists, welders, painters, sandblasters, riggers, pipe fitters and a number of administrative and managerial staff.

Each of these facilities and associated shipyard services create their own unique set of potential environmental concerns. A tremendous amount of spent blast abrasive dust and grit is generated daily. Millions of gallons of vessel discharges are piped, collected, tested, treated, recycled or transported. Air pollution, noise pollution and water pollution can occur simultaneously with the variety of operations that take place.
There are hundreds of smaller shipyards and marinas which service small commercial and private boats, in addition to large shipyards which service everything from small vessels and marine equipment to super structures.

Abrasive blasting at repair facilities presents an especially challenging task in terms of pollution control because this activity results in a very fine airborne dust which is difficult to contain, it is generated in large volumes, and it takes place near water resources. Add to this complexity, antifouling ingredients which can be deadly to water organisms. Abrasive blasting clearly is what is known as a "cross media" pollutant which affects air, water and land.

While there are a variety of pollutants that may result from activities at repair facilities: abrasive blast and paint, lubricants and oils, solvents, vessel discharge, storm water runoff, etc., all of which need to be properly managed to insure protection of the environment, this manual focuses on one of the biggest problems in the shipyard industry: controlling the pollutants associated with paint removal operations.

SECTION ONE

ABRASIVE BLASTING AND ANTIFOULING PAINT

There are a variety of abrasive blast materials that can be used in air or water blasting processes used to remove paint from vessels and marine structures. Blast material particles, also referred to as "grit", are about 1/8" in diameter. These normally jagged, or sharp-edged particles become rounded and somewhat reduced in size after being blasted against a vessel's hull, for example, to remove paint.

Vessels, depending on the size, can use an enormous amount of grit for both interior and exterior blasting. One large supertanker, for example, may require up to 40,000 tons of grit just to do interior blasting. The amount of grit needed to remove paint from a vessel's exterior depends on the surface condition of the hull (i.e., was the previous paint put on bare metal, or over existing paint), the nozzle diameter of the hose used in abrasive blasting, and the number of coats to be removed and other contract specifications.

Some of the brand names of abrasive blast material include: Black Blast, Black Beauty, Fines Blast and Green Diamond. The constituents of abrasive blast varies somewhat, but in general the primary components with approximate percentages are:

Silicon Dioxide	20-50%
Iron Oxide	15-40%
Aluminum Oxide	0-25%
Calcium Oxide	0-25%

These four components comprise up to 90 percent of the abrasive grit composition. Other abrasive grits may contain as much as 10-15 percent zinc oxide or 20-25 percent magnesium oxide. Trace elements in these abrasive grits include: potassium oxide, sodium oxide, copper, titanium and sulfur.

Spent abrasive blast material may contain a variety of pollutants. Fresh, or unused abrasive blast media is even considered a "dangerous" or "special" waste in some states due to gill abrasion which can be fatal to some fish; therefore, abrasive blast media, used or unused, should not be discharged into State waters.
When hydroblasting, rust inhibitors such as sodium nitrite or diamonium phosphate may be used. In certain situations, antifreeze may also be part of the water jet to reduce ice formations.

Antifouling paints are used on vessels and marine structures to control the growth and attachment of "fouling" organisms such as barnacles, seaweed and algae. This is the intended effect of antifouling ingredients in paint. However, some antifouling ingredients, such as Tributyltin (TBT) can have a deadly effect on species other than fouling organisms. TBT is highly toxic in small concentrations to fish, oysters, clams and other forms of water life, so proper management of TBT-containing paint, and while blasting vessels that have been painted with TBT paint, is extremely important.

How does Tributyltin, and other antifoulants get into the environment?

Here are some of the most common ways:

- External blasting out of dry docks or contained areas
- Uncovered or loosely covered sandblast waste piles where grit blows away, or rainwater leaches antifoulant into nearby surface water or groundwater
- Sweeping or hosing sandblast grit waste into water
- Submerging dry docks with grit waste on them
- Overspray of TBT or other antifouling paints

Not only can mismanagement of waste containing antifoulants kill water organisms, but mismanagement of antifouling paints is a violation of hazardous and solid waste regulations.

The following section provides suggested Best Pollution Prevention Practices that are intended to be used as general guidelines to achieve the underlying objective of protecting the air, water and land from abrasive blast media, which may or may not contain antifouling ingredients.

SECTION TWO

ABRASIVE BLASTING: BEST POLLUTION PREVENTION PRACTICES

It is easy to understand the magnitude of controlling the pollutants associated with paint removal operations when the multitude of marine paints, which contain hazardous and toxic chemicals, is considered. And this is just one aspect of the activities that go on in ship repair. Besides blasting operations which are ongoing, there is the potential for large quantities of paints, thinners and solvents to enter State waters, either by accidental spills, poor cleaning procedures or improper disposal. When these paints are blasted off of vessels and marine structures, thousands of tons of grit waste are generated. The following Best Pollution Prevention Practices describe various methods of containing abrasive blasting:

BPP ONE: SHROUDING

Vessel maintenance generally involves some amount of abrasive blasting with copper, nickel or some other type of slag, or steel shot. These operations may be carried out on the ship's interior tanks and compartments or on the exterior hull and upper decks. The use of blast abrasive or paint represents a major pollutant source which may be lost, directly or indirectly to the water during the repair work.

While performing abrasive blasting or painting operations in floating dry docks, wet slips and marine railways, or other areas where blast material may reach State water, shroud material should be erected to prevent the loss or scattering of these potential pollutants. Shroud material should be used in graving docks as well, particularly extending from the ship sides to the top of the graving dock walls. In addition, shrouding should be incorporated with all blasting or painting performed on super structures.

BPP OBJECTIVE:

The use of shrouds can reduce or prevent the loss of abrasive blast grit and paint to the water surface. Shrouding can also reduce the scattering effects of wind and localize the area needing cleanup.

CRITERIA:

The shroud must be large enough the adequately enclose or segregate the working area. The bottom of the shroud should be fastened to the dock floor.

The shroud must be sufficiently supported to withstand minor wind stress. Support structures should be used in conjunction with the shroud.

With the shrouding in place the drydock space beneath the shrouding would be considered a confined space. To comply with OSHA 1915 standards, fresh air respirators for all personnel is required and proper ventilation, blowers, fans and all electrical equipment must be intrinsically safe.

Floating Drydocks

It is recommended that lightweight, polyethylene shroud be used for vertical hanging. Small sections of the material can be tied together to form larger shrouds for hanging at the aft and bow sections of the dock. The shroud may have screened flaps or openings to lessen wind stresses. The material can also be manufactured with grommets and securing (spring type) hooks which are used to hang the shroud. Typically the shroud can be fastened to cables connected to dock wing walls or cables which are strung from the top of one wing wall to the other wing wall. Ropes or cables can be fastened to grommets on the center of the shrouds to enhance vertical hanging stability.

The material can also be used to shroud the larger sally ports of some docks. For work on upper sides of vessels, the shroud should be fastened from the ship decks to the dock wing walls. The bottom of the shroud should hang sufficiently upon the dock floor to allow it to be weighted down or fastened. Straw bales should be placed on the floor behind the bottom of the shroud. Periodically, scattered abrasive will be blown and trapped under the shroud. This material needs to be swept up daily to prevent it from escaping into the water. Shrouding, combined with other Best Pollution Prevention Practices should provide an effective method for controlling blast abrasive and paint overspray on floating dry docks.

Graving Docks

The primary concern at these facilities involves using shrouds to prevent blast abrasives and paint overspray from exiting the top of the dock. Therefore, shrouds should be erected between the vessel deck to the dock walls. Vessel deck abrasive blasting and painting activities should be shrouded in a dome-like fashion to prevent the scatter and loss of pollutants.

Marine Railways

Marine railways present a different problem in controlling spent abrasive blast material. These are areas that are essentially uncontained and open to the effects of the wind. Two methods are suggested to control abrasive scatter at railways. The first technique involves erecting poles or masts at each end of the railway in a semicircular fashion. The poles can hold rolled-up shrouds that are lowered when needed. Shroud is also hung vertically from the railway wing wall scaffold to prevent abrasive loss on the railway sides. The top is then protected by stringing shroud from the vessel deck to the side wall scaffolds. Some railways may not have side wall scaffolds, It is then necessary to erect masts which encircle the entire railway work area.

Another acceptable technique involves segregating the water surface from the railway work area. Masts are erected along the shoreline which hold the shrouds. The vessel is raised and the shrouds are strung to form a barrier between the water surface and the work area. A portable scaffold is then placed around the immediate work area of the vessel. The scaffold is covered with shroud material. The workman is required to work within the shroud scaffold, which must be moved as the workman moves along the length of the vessel. Abrasive material that escapes the shrouding scaffold will be further confined to the work area by the shoreline shrouding. Timely cleanup and railway underpaving play an important and equal role in ensuring that the pollutants will not enter State waters. A lighter may be required in conjunction with shrouding for ships that overhang a marine railway, or on the pier side of a vessel in a wet slip.

Wet Slip

Wet slips are the most difficult locations to attempt to control abrasive scatter and paint overspray. Such work in this area will most likely result in the loss of pollutants to the water surface. To properly conduct blasting and painting operations at wet slips, it will be necessary to use the pier, scaffolding, lighters and the vessel to erect shrouds. Only small sections of a vessel should generally be worked on at any time. Protecting surface waters from wet slip blasting and painting is a time consuming and difficult task which must conform to the varying size and shape of each vessel. This task can be made more efficient by erecting masts along the pier and by using magnets against the vessel hull to hold the shroud in place. The lighters and the pier should be cleaned up at the end of each work shift.

CONCERNS
To be effective, the shrouding must be properly designed, constructed positioned and erected.

The use of magnets to hold shrouding may be acceptable if sensitive electronic equipment is on board the vessel. Enhance lighting outline in OSHA 1915.92 standards and forced supply and exhaust ventilation may be required for the shrouded work areas.

While certain concentrations of blast dust are airborne and during all painting evolutions, the concentrations of fumes and dust will require continuous monitoring for the LEL and 02 contents by a Marine Chemist or OSHA Certified Competent Person.

BPP TWO: OVERWATER PROTECTION

General work and repairs are continually being performed around or adjacent to wet slip piers, floating dry docks, marine railways and the exterior and interior sides and the upper decks of ships. Much of this work generates trash and pollutants of various forms which potentially may fall onto the water surface below. The use and proper positioning of lighters (pontoons, small floating decks or barges, etc.) can enhance the ability to retrieve pollutants prior to inadvertent loss to surface waters.

BPP:
Provide and position a lighter adjacent to ships, floating dry docks, piers and marine railways. These work platforms provide a catch surface for trash, paint spray, grit, paint slop, oil slop, etc.

Lighters should be used to protect the water surface underneath and adjacent to vessels in wet slips and vessels which overhang marine railways and floating dry docks.

BPP OBJECTIVE:
The primary objective is to catch the waste pollutant material prior to being lost to the water surface where cleanup becomes more difficult. The lighters need not necessarily be used primarily for workmen or machinery support but rather to catch discarded materials and pollutants.

Lighters also provide a surface for performing work related operations. The lighter should carry a drip pan in which all fluids (paints, solvents, oils, etc.) are contained. A drop cloth should be placed under the drip pan to catch fluid "slosh" over the pan rim due to wave action or transport. Following use of the drip pan, it must be removed from the lighter and cleaned. The waste fluids should be placed in proper storage containers for subsequent disposal.

For abrasive blasting and painting operations, lighters are to be used in conjunction with shrouding. Booms and/or absorbent devices are to be placed around the lighter to contain contaminants which reach the water surface.

CRITERIA:
Proper positioning of the lighter is of utmost importance to prevent pollutants from reaching surface waters. The lighter must be large enough to catch falling pollutants and stable enough to support workmen and required equipment. A tarpaulin or other protective coverings should be employed if the spacing between flooring boards is great enough to allow pollutants to fall through. The mixing of paints, solvents, or other hazardous materials should not be permitted on the lighter. This should be performed at a designated mixing area.

CONCERNS:
Use of a lighter requires that cleanup operations are periodically performed. Cleanup of the lighter should occur daily, and if, possibly, after every work shift. Cleanup procedures include sweeping or vacuuming spent abrasive and trash and placing the debris into designated disposal containers.

BPP THREE: WATER BLASTING, HYDROBLASTING, WATER-CONE BLASTING AND SLURRY BLASTING

Water blasting, hydroblasting, water-cone blasting and slurry blasting is performed to either clean sediment and marine growth from vessel hulls or to remove the top layers of

hull paint. These techniques will generate large volumes of water with the potential of transporting existing pollutants to surface water.

BPP:
Water blasting, hydroblasting, slurry blasting and/or water-cone blasting should not be conducted unless prior cleanup of the dry dock or marine railway floor is complete.

Water blasting runoff should be channeled into floor sumps where the wastewater will be pumped to grit removal basins/sedimentation tanks for settling treatment. The effluent discharge from the sedimentation treatment must be NPDES permitted.

Prior to entering floor drains and sumps, water blasting runoff may also be channeled through straw bales and/or sand bags which will catch most of the particles of paint and marine growth. Once the floor is dry the collected particles may be removed employing graving dock and floating dry dock clean-up methods.

BPP OBJECTIVE:
Water blasting techniques produce a scattered water pattern which is difficult to control or immediately contain. Unless prior cleanup of the dock or marine railway floor has been conducted, it is difficult to prevent water blast from contacting pollutants.

CRITERIA:
Runoff generated from water blasting, hydroblasting, slurry blasting and/or water-cone blasting should not be allowed to discharge directly into surface waters from graving docks, floating dry docks, or marine railway work areas.

The design flow of the collection and treatment system must be adequate to receive the water blasting runoff flow rates. Special consideration should be given to pumping and treatment of slurry blast runoff.

CONCERNS:
All pump connections, valves, meters and couplings must be watertight. Leaks must be immediately repaired when discovered.

BPP FOUR: ABRASIVE BLAST MATERIAL CONTAINMENT

Abrasive blasting is generally one of the preliminary tasks performed when a vessel is docked for repairs and maintenance. The task typically involves blasting the vessel hull or upper decks with nickel, copper or some other type of slag or steel shot to remove layers of old paint. Blasting generates a tremendous volume of spent abrasive which must be cleaned up and contained on a frequent basis.

BPP:
Spent abrasive blast must be stored in proper containment vessels or structures while on the shipyard site. Containment bins, tanks or hoppers must have covers to prevent rainwater from entering the structure and percolating through the stored abrasive.

BPP OBJECTIVE:
The objective is to store all spent abrasive in appropriate containment vessels until ultimate disposal off site. Proper containment involves not allowing any stormwater runoff or accidental discharges to come into contact with the abrasive. This method eliminates the typical procedure of storing voluminous piles of spent abrasive on bare ground. Storing the abrasive in yard stockpiles promotes pollutant runoff.

CRITERIA:
The containment structures may consist of specifically designated hoppers for holding abrasive; metal bins with covers, or a concrete containment pit or slab (three-walled) with runoff channels to sedimentation treatment units.

CONCERNS:
Treatment units which provide a discharge must be NPDES permitted. The NPDES permit may require more advanced treatment than sedimentation.

There must be an appropriate storage volume available on site to contain all spent abrasive.

BPP FIVE: RECORD KEEPING

Due to the nature of the shipyard repair business, BPP installations are in constant need of repair, replacement, inspection and cleanup. Records indicating a history of maintenance should be kept to provide a good indication of the current reliability of existing BPP's.

BPP:
Records should be maintained to document BPP's at the facility. The type of records which should be maintained include, but are not limited to, the following:

1. Quantities of abrasive which are used for blasting and quantities which are retrieved through cleanup.

2. Date of installation of a BPP control, inspections and subsequent repairs or replacements to the BPP including such items as how often straw bales, absorbent booms and other filtering
devices are replaced and/or cleaned.

3. A listing of BPP equipment, and supplies.

4. Date, time, description and action taken for any chemical spills.

5. The location, quantities, destination and hauler of vessel discharge waters and spent abrasive material.

6. Waste inventory records.

CRITERIA:
Record keeping should be maintained by designated individuals responsible for the task. The records should be kept at a specified location for review upon request.

BPP SIX: BPP TRAINING

BPP:
Shipyard management should provide all employees with regularly scheduled Best Pollution Prevention Practices seminars and discussions related to shipyard pollutants and pollutant runoff. The training should emphasize procedure, BPP techniques and supervisory responsibility and accountability. Subcontracting firms in the shipyard should be strongly encouraged to participate in the BPP program.

BPP OBJECTIVE:
Training each employee about the fundamentals of BPP control lessens the chance of recurrent pollutant discharges. Providing each officer, manager, supervisor, dock master, etc., with a strong sense of BPP commitment ensures solutions for recurring problems.

CONCERNS:
The primary concern is that not enough emphasis is given to teaching employees about the rudimentary aspects of Best Pollution Prevention Practices. Each new employee should be made aware of the BPP's as part of new employee training.

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OAR 340-016-0075 Equations

340-016-0075(3)(c) – Table 1 Equation

$$\text{ROI Factor} = \frac{1 - (1 + \text{Facility ROI}) - \text{UL}}{\text{Facility ROI}}$$

Where:

- ROI Factor – as set forth in subsection (3)(b)
- Facility ROI – ROI percentages from 0 to 36 in increments of 0.25% - Table 1
- UL – is the Useful Life of the facility

340-016-0075(3)(e)(B) – Percentage of Facility Costs Allocable to Pollution Control

$$\text{PA} = \frac{(\text{National ROI} - \text{Facility ROI}) \text{ X } 100}{\text{National ROI}}$$

Where:

- PA: Is the percentage of actual facility cost properly allocable to pollution control represented as a percentage, rounded off to the nearest whole number
- National ROI: As set forth in subsection (3)(d)
- Facility ROI: As set forth in subsection (3)(c)

340-016-0075(4)(d)(B) – Percentage of Facility Costs Allocable to Pollution Control

$$\text{PA} = \frac{(\text{National ROI} - \text{Industry AP}) \text{ X } 100}{\text{National ROI}}$$

Where:

- PA: Is the percentage of actual costs properly allocable to pollution control in percent, rounded off to the nearest whole number
- National ROI: As set forth in subsection (4)(b)
- Industry AP: As set forth in subsection (4)(c)

340-016-0075(5)(b)(H) – Percentage of Actual Costs Allocable to Pollution Control

$$PA = \frac{(\text{National ROI} - IRR) \times 100}{\text{National ROI}}$$

Where:

- PA: Is the percentage of actual costs properly allocable to pollution control in percent, rounded off to the nearest whole number
- IRR: Is the Internal Rate of Return for the claimed facility
- National ROI: As set forth in subsection (4)(b) of this rule

State of Oregon Department of Environmental Quality

OAR 340-016-0290 Attachments

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DRAFT

GENERIC VERIFICATION PROTOCOL FOR DIESEL EXHAUST CATALYSTS, PARTICULATE FILTERS, AND ENGINE MODIFICATION CONTROL TECHNOLOGIES FOR HIGHWAY AND NONROAD USE DIESEL ENGINES

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1.0 INTRODUCTION

1.1 Environmental Technology Verification

The U.S. Environmental Protection Agency (EPA) through its Office of Research and Development (EPA-ORD) has instituted the Environmental Technology Verification (ETV) Program to verify the performance of innovative and improved technical solutions to problems that threaten human health or the environment. EPA created the ETV Program to substantially accelerate the entrance of new and improved environmental technologies into the domestic and international marketplaces. It is a voluntary, non-regulatory program. Its goal is to verify the environmental performance characteristics of commercial-ready technologies through the evaluation of objective and quality-assured data so that potential purchasers and permitters are provided with an independent and credible assessment of what they are buying and permitting.

The ETV Program does not conduct technology research or development. ETV test results are always publically available, and the applicants are strongly encouraged to ensure, prior to beginning an ETV test, that they are satisfied with the performance of their technologies. Within the ETV Program, this state of development is characterized as "commercial-ready ," and the ETV test is conducted on production units or prototypes having the major characteristics of commercial units.

The provision of high-quality performance data on fully-developed commercial technology encourages more rapid implementation of those technologies and consequent protection of the environment with better and less expensive approaches. The ETV Program is conducted by six ETV centers that span the breadth of environmental technologies.

1.2 Air Pollution Control Technology Verification Center

EPA's partner in the Air Pollution Control Technology Verification Center (APCTVC) is RTI, a non-profit contract research organization with headquarters in Research Triangle Park, NC. The APCTVC verifies the performance of commercial-ready technologies used to control air pollutant emissions. The emphasis of the APCTVC is currently on technologies for controlling particulate matter, volatile organic compounds, nitrogen oxides (NO_x), and hazardous air pollutants from both mobile and stationary sources. The activities of the APCTVC are conducted with the assistance of stakeholders from various interested parties. Overall APCTVC guidance is provided by the Stakeholders Advisory Committee (SAC), while the detailed development of individual technology ETV protocols is conducted with input from Technical Panels (TP) focused on each technology area.

The APCTVC develops generic verification protocols and specific test/quality assurance (test/QA) plans, conducts independent testing of technologies, and prepares ETV test reports and statements for broad dissemination. Testing costs are ultimately borne by the technology applicants, although initial tests within a given technology area may be partially supported with government funds.

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1.3 Mobile Sources Air Pollution Control Technologies

Control of emissions from mobile sources continues to be of great national importance. Several areas of the country are not able to attain ambient air quality standards. The mobile source provisions of the 1990 Clean Air Act Amendments (CAAA) are intended to reduce most vehicle-related air pollutants by more than 40 percent for 1996 and later model year vehicles and engines. Earlier engine models emit pollutants at higher levels, and as these engine are durable and have long useful lives, they will continue to emit pollutants at higher levels many years into the future. For these reasons, the EPA funded and the APCTVC SAC recommended inclusion of air pollution control technologies for mobile sources as a priority for ETV.

One important group of mobile source air pollution control initiatives is concerned with highway and nonroad use diesel engines. The diesel particulate standard for urban buses was reduced in 1993 by 60 percent, from 0.33 to 0.13 g/kWh (0.25 to 0.10 g/bhp-hr). The standard, which applies to urban transit buses, dropped to 0.094 g/kWh (0.070 g/bhp-hr) in 1994 and to 0.067 g/kWh (0.050 g/bhp-hr) in 1996. While existing engine technologies can meet these standards, future standards are expected to be increasingly stringent and will require the use of post-combustion emissions control technologies. New technologies are being developed to meet these goals. In addition, since a NO_x emission level below the level mandated allows the generation of credits through the Voluntary Diesel Retrofit Program (VDRP), pollution prevention becomes more cost effective, and innovations in less-polluting alternatives and control technologies are encouraged.

Retrofit mobile source control technologies are principally exhaust treatment emission control devices and engine modifications. Some require no mechanical changes to engines, while others will involve some modification of the engine or its control system.

Filters for particulate matter (PM) control and diesel exhaust catalysts (DECs) may make use of or require some integration with engines. Engine modifications, in the context of this protocol, refer to pollution reduction technologies integral to the engine or the engine control systems. All these technologies have the potential to affect engine performance, and the concurrence of the engine manufacturer that the changes are compatible with safe, efficient, and reliable operation in the engine is an important element in demonstrating commercial readiness and suitability for ETV. The technologies and their testing are discussed in more detail below.

Selective Catalytic Reduction (SCR) nitrogen oxides (NO_x) control technologies, fuels, fuel additives, reformulated fuels, and lubricants are specifically excluded from consideration under this protocol for testing as retrofit emissions control devices. Protocols for these technologies may be developed in the future.

1.4 The APCTVC Mobile Sources Verification Program

This generic verification protocol (GVP) provides the requirements for APCTVC's ETV of the performance of DEC, PM filter, and engine modification air pollution control technologies applied to highway and nonroad use diesel engines. Other technologies will be addressed

similarly. Other organizations [e.g., EPA's Office of Transportation and Air Quality (EPA-OTAQ) and the California Air Resources Board] also 'verify' the performance of mobile source emissions control devices under different protocols to meet the needs of those organizations. Specifically, EPA-OTAQ has established, for applicants who meet particular criteria, a generally parallel path that does not require the level of external QA that is required for APCTVC ETV. The technology applicant should discuss the intended application of the technology with the appropriate regulatory body to determine the most suitable path for "verification."

This GVP is intended to apply only to DECs, PM filters, and engine modifications and their combinations. The APCTVC reserves the right to evaluate each technology submitted for ETV and to determine the applicability of this protocol to that specific technology. Special testing may be required in some cases to maintain the integrity and credibility, and, therefore, the value of ETVs. The critical data quality objectives (DQOs) in this document were chosen to provide emissions measurements sufficient to support the VDRP and its emissions credit provisions. Emissions credit allowances will be set by the appropriate state regulatory authority or EPA-OTAQ. (As stated above, the VDRP approving agencies may have data requirements that are in addition to the ETV test report.)

This protocol was developed and has been reviewed by a technical panel composed of a broad group of stakeholders who have expertise in mobile source controls and come from the vendor, user, and regulatory spheres. Technical panel membership is dynamic, and its composition is expected to change over time as technical emphases change. The APCTVC will maintain membership balance on the panel.

The basic APCTVC ETV test will measure and report baseline emissions concentrations and rates for an engine prior to use of the retrofit technology and also the emissions concentrations and rates for this engine following retrofit. It will be conducted at an independent, third-party test laboratory. The data quality requirements of this generic protocol will be applied at approved test laboratories through the preparation of test-specific test/QA plans. Other laboratory-, application-, or technology-specific information may also need to be addressed in the test/QA plan, which is described in Section 10.0. In general, test/QA plans prepared by test laboratories will not be reviewed by the entire technical panel. However, because specific technology areas may require special expertise or emphasis, input and review will be obtained from an ad hoc subcommittee of the technical panel and/or outside experts when deemed appropriate by the APCTVC. Test results will be presented as ETV reports and statements.

1.5 Quality Management Documents

Management and testing in this APCTVC program are performed in accordance with procedures and protocols defined by the following:

1) EPA's ETV Quality and Management Plan (ETV QMP) (EPA, 1998a or the quality management plan current at the time of testing),
2) the APCT Quality Management Plan (QMP) (RTI, 1998),

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3) the Generic Verification Protocol for Diesel Exhaust Catalysts, Particulate Filters, and Engine Modification Control Technologies for Highway and Nonroad Use Diesel Engines (this document), and
4) the test/QA plan prepared for each specific test or group of tests.

EPA's ETV QMP lays out the definitions, procedures, processes, inter-organizational relationships, and outputs that will ensure the quality of both the data and the programmatic elements of the ETV Program. Part A of the ETV QMP contains the specifications and guidelines that are applicable to common or routine quality management functions and activities necessary to support the ETV Program. Part B of the ETV QMP contains the specifications and guidelines that apply to test-specific environmental activities involving the generation, collection, analysis, evaluation, and reporting of test data.

APCT's QMP describes the quality systems in place for the overall APCTVC. It was prepared by RTI and approved by EPA. Among other quality management items, it defines what must be covered in the GVPs and test/QA plans for technologies undergoing ETV testing.

Generic Verification Protocols (GVPs) are prepared to describe the general procedures to be used for testing a type of technology and define the critical data quality objectives (critical DQOs). The GVP for retrofit air pollution control technologies for highway and nonroad use diesel engines was written by the APCTVC with input from a technical panel and approved by EPA.

A test/QA plan is prepared for each test or group of tests. The test/QA plan describes, in detail, how the testing organization will implement and meet the requirements of the GVP. The test/QA plan also sets DQOs for any planned measurements that were not set in the GVP. The test/QA plan addresses issues such as the test organization's management structure, the test schedule, test procedures and documentation, analytical methods, record keeping requirements, and instrument calibration and traceability, and it specifies the QA and quality control (QC) requirements for obtaining ETV data of sufficient quantity and quality to satisfy the DQOs of the generic verification protocol. Section 10 of this GVP addresses requirements for the test/QA plan.

Because multiple testing organizations will be conducting the tests and the desirability to ensure comparability, the APCTVC will develop a prototype test/QA plan (not part of this GVP) for each type of technology. This prototype will be customized by the testing organization to meet its specific implementation of the Federal Test Procedures (FTPs) as defined in 40 CFR Parts 86 and 89, and the secondary measurements, subject to approval by the APCTVC and EPA-ORD. Testing arrangements that do not meet the requirements of the FTP will not be approved, and test instrumentation or test procedures that the APCTVC determines will compromise data reliability or comparability between testing organizations will not be approved.

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2.0 OBJECTIVE AND SCOPE

2.1 Objective

The objective of this GVP is to establish the parameters within which DECs, PM filters, and engine modification air pollution control technologies for highway and nonroad use diesel engines will be tested to verify their performance with uniform and consistent methodologies within the APCTVC. The protocol addresses the requirements for technology submission, outlines the test conditions and procedures to be used, and states the critical DQOs for ETV and states reporting requirements. The control technologies will be verified within a specified range of applicability, and ETV reports and statements will be produced for dissemination to the public.

2.2 Scope

APCTVC testing will be performed to quantify the effectiveness of commercially ready emissions control technologies that are intended for use on diesel engines considered mobile sources of air pollutants. Emissions testing under this ETV Program is based on the applicable FTPs for highway and nonroad engines. As performed by manufacturers to certify their engines, FTPs are fully defined by the regulations and consist of the engine-appropriate cold- and hot-start engine dynamometer tests conducted under specified load cycles. For purposes of this protocol, the number and type of FTP tests may be different from certification requirements, as determined by the applicant and the APCTVC to best verify the performance of the technology under consideration. However, the individual FTP test module -- the cold-start test or the hot-start test -- will be performed completely in accordance with the regulations. (The low NO_x and PM emissions from post-2001 engines are prompting development of new test procedures better suited to these emission levels. As these test procedures become standardized and acceptable to EPA, they will be acceptable for use in ETVs.) The pollutants of major interest are NO_x, hydrocarbons (HCs), PM, and carbon monoxide (CO). Other measurements will also be made of emissions (for instance, carbon dioxide[CO_2]) and operating parameters of the test engine and the control technology. Additional measurements may also be required if the technology might be reasonably expected to generate secondary emissions. Emissions will be measured along with other data useful for evaluating the performance of the technologies and the technologies' associated environmental and efficiency impacts. In this context, the effects of control technologies on fuel economy and engine performance and power will be of particular interest.

Also fundamental to this ETV protocol is providing emissions control efficiency information needed for applicants to participate in the EPA Voluntary Diesel Retrofit Program (VDRP). The VDRP is managed by EPA-OTAQ. The data quality objectives given in Section 2.3 were set to provide emissions control device performance data that can be used in submittals to the VDRP. VDRP determinations are made by EPA-OTAQ, which may require information not included in the ETV.

The APCTVC will consider applications for ETV of air pollution control technologies on test engines specified by the applicant. Depending on the expected application, the data collected,

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and the test design, the results obtained may be valid only for that single engine or to groupings of multiple engines. If application of single engine test results to an engine group is made by the regulatory body, the decision will be based on an expectation that the control device, if appropriately sized, will perform similarly on all the engines in that group. Generally, similar emissions control performance is expected from engines that have the same engine technology and use. The sensitivity of emissions control performance to engine type and usage is not known to be the same for all technologies, and the applicability decision will be made separately for each technology type and possibly for each technology. Previously obtained performance data may affect the decision. In all cases, the decision regarding applicability will be made by EPA-OTAQ, which should be contacted at the time a technology is submitted to obtain current information.

Implicit in the potential use of single engine ETV tests as predictive of performance over segments of the total engine population is the availability of non-proprietary application sizing information and that the technology be labeled. The purpose of this requirement is to allow the APCTVC and the potential technology user to evaluate the applicability of the verified technology to other applications. Applicants who utilize application sizing charts must verify their technologies on an engine at the most challenging end of the range of applicability. ETV reports and statements will report the results and the design guidance required to independently extend application of the technology to other engines in the same engine grouping.

To request ETV, the applicant applies to the APCTVC for the technology to be tested and proposes the test engine(s) to be used. The APCTVC will review the application and provide input as required to ensure that the engine(s) proposed are suitable and that the emission control equipment sizing is clear and correct. The equipment/technology will be applied to the engine(s) according to the applicant's instructions. ETV test results for the engine(s) will be reported in the ETV report and statement. The results will provide the emissions performance data required for the VDRP reviewing regulatory authority to determine the emission reduction capability of the technology.

2.2.1 Highway Engines

Applicants may choose to have their technologies verified on a single highway engine or multiple selected engines, depending on the applicant's intended use of the data. EPA-OTAQ will determine the extent of applicability of data from any given engine and should be consulted by the applicant for that purpose. Testing of emissions control technology intended to control emissions from highway diesel engines will be conducted generally under the provisions of 40 CFR, Part 86, Subpart N. The primary emissions measurements will be of NO_x, PM, HC, CO, and other FTP requirements. CO_2 and the engine operating parameters are required secondary measurements. Each engine in the test will be loaded by a dynamometer as described in the transient FTP. Each ETV test will consist of at least a single full FTP test (cold- and hot-start) and two additional hot-start tests (total of three hot-starts) on an emission-stabilized baseline engine and on the engine with the control technology in use. Additional hot-start tests may also be required to meet the number of test requirements described in Section 5, or the applicant may wish to run additional tests to narrow the confidence interval on the result. [An ETV

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requirement for multiple hot-start tests may be met using the hot-start results from full FTP test data (both cold- and hot-start), at the applicant's option.] Durability testing , which consists of ETV of aged control technology units as described in Section 5.2.9, is part of the ETV process. Emissions reductions will be computed relative to the baseline engine emissions.

2.2.2 Nonroad Engines

As with highway engines, applicants select the nonroad engines on which to test their technologies. The ETV testing of emissions from nonroad diesel engines will be conducted generally within the requirements of 40 CFR, Part 89, Subpart E. As for highway engines, the primary emissions measurements for nonroad engines will be of NO_x, PM, HC, CO, and other FTP requirements. CO_2 and engine operating parameters are required secondary measurements. The ETV testing will consist of three or more nonroad steady-state mode tests (40 CFR, Part 89, Subparts D and E), as described in Section 5. (Concerns about transient emissions from nonroad engines are prompting development of new test procedures. As these test procedures become standardized and are codified in the FTP, they will be included in the ETV test protocol.) The test must be conducted over all applicable modes of the test cycle appropriate to the engine (e.g., 8-mode test cycle for variable speed engines or 5-mode cycle for constant speed engines) or may be conducted over all modes at the applicant's request. The ETV report will reflect the extent of the test conducted. Each ETV test will consist of the same assemblage of FTP tests on the broken-in baseline engine and the engine with the control technology in use. Durability testing is required as described in Section 5.2.9. Composite emissions reductions are computed relative to the baseline engine emissions. In addition, the emissions results will be reported in composite and mode-by-mode to allow flexibility in use of the data for different engine applications.

2.2.3 Control Technologies

This GVP is specifically intended to include the following emissions control technologies:

1) DECs regenerated continuously or periodically,
2) PM filters, and
3) Engine modifications.

The basic ETV test remains the same for all emissions control technologies. However, the technologies interact differently with the various engines. Therefore, the engine grouping concept may be applied differently by EPA-OTAQ depending of the nature of the technology. In addition, where technologies require particular fuel characteristics or have other restrictions or interactions, applicants must specify these and any associated requirements in their ETV applications.

In all cases, the ETV test will be designed to reasonably isolate the effects of the retrofit technology from coincident engine adjustments and tune-ups. For example, a retrofit technology that required an engine tune-up following installation would be tested against a tuned-up baseline engine.

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Some technologies, by their nature, may reasonably require engine adjustments following installation. To be allowed, such adjustments must be part of the description of the technology, be included in the installation instructions, be described in the application, and be made by the laboratory technician and not by the applicant. They will be examined to determine the effect of those engine adjustments alone, and the baseline engine may be tuned to the same operating condition if the adjustments alone are considered to have a positive effect on emissions. This requires that the APCTVC and the testing laboratory be provided with a full disclosure of the working principles of the technology prior to developing the test. In these cases, the ETV report and statement will define the retrofit technology as consisting of both the device and the engine adjustments, with both required to achieve any emissions reduction observed.

2.2.4 Relationship of ETV Program to EPA-OTAQ VDRP Verified Technology List

EPA-OTAQ is charged with establishing a Verified Technology List of technologies capable of providing emissions reductions. The test results EPA-OTAQ will utilize to evaluate a technology may be generated following the ETV process, with the ETV report and verification statement serving as the data package to EPA-OTAQ. Other paths to the verified technology list also exist. The VDRP program is described and appropriate contacts are identified at http://www.epa.gov/otaq/retrofit/. The technology applicant should discuss the intended application of the technology with EPA-OTAQ to determine the most suitable evaluation path for the applicant's technology.

As of the date of this protocol, emissions test data from a full FTP test (whether highway or nonroad), that was generated by a manufacturer to obtain a certificate of conformity may be determined by EPA-OTAQ to constitute a valid data set for VDRP purposes. Certification data do not pass though the ETV Program. The certification and VDRP technology listing processes are independently performed by EPA-OTAQ. In addition, EPA-OTAQ has established for some applicants a technology evaluation pathway whose test requirements parallel those of this GVP, but with reduced QA requirements.

2.3 Data Quality Objectives (DQOs)

The data of primary interest in this ETV are the reduction in emissions of NO_x, HC, PM, and CO. (Numerous other measurements, including CO_2 emissions, will also be made as described in later sections. However, these are not considered critical, and the methods and data quality objectives will be stated in the test/QA plan for each technology.) The DQOs of this GVP are the requirements of the test methods specified in 40CFR Parts 86 or 89 for highway or nonroad diesel engines, respectively, when conducting the number and type of FTP tests called for by the approved test/QA plan for the technology. ETV tests that do not meet the FTP QA requirements must be repeated.

The number of and type of FTP tests (cold- and/or hot-start) required for ETV is determined from the following criteria:

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First, a minimum of three tests is required to provide the basic ETV result of a mean emission reduction and the 95% confidence interval on that mean based on measured variability for each of the measured emissions and test parameters. For highway engines this minimum is satisfied with one cold start test and three hot start tests. For nonroad engines three replicates of the appropriate test sequence (i.e., three 8-mode tests, or three 6-mode tests) are required. A three test minimum is currently the same as is required by the State of California for verification.

Second, additional tests may be required to meet the ETV requirement that the test/QA plan provide a 90% probability of detecting the expected emissions reductions when computed using the expected experimental errors for the various measurements. These criteria become controlling for low emissions reductions and/or high test variability. This is a planning requirement for the test/QA plan. The procedure to determine the appropriate number of tests is given in Section 5.

Third, additional tests may be desired by the applicant to reduce the width of the 95% confidence interval on the mean emission reduction. Section 5 provides additional explanation and example scenarios. This third criterion is a consequence of applying standard statistical procedures to the ETV test design and data analysis. At a fixed measurement variability, normal statistical procedures lead to a small number of tests giving a broader 95% confidence interval than a larger number of tests. To any regulator or potential technology user, an emission reduction of 40% ± 5% is better than 40% ± 20% and will be given more credence.

An applicant may conduct privately sponsored tests at a test laboratory for development purposes with the same test engine prior to and/or after conducting ETV tests. Such testing is understood to be common and important to ensure the technology is properly adjusted and tuned to the application. However, two important principles of ETV are that the verified technology be commercial ready when tested and that all data obtained under the ETV process be reported.

Therefore, preparation for the ETV test (submittal of the technology to the APCTVC, discussion of engine selection, and preparation of the test/QA plan) must be completed prior to conducting the ETV test itself. In particular, declaration of the test run which is to be the ETV test must be made prior to starting the test, the engine must be brought to a starting point in accordance with the test/QA plan, and the results of that test will be documented and reported in accordance with the test/QA plan. The data from all ETV tests will be retained and reported to the APCTVC, including invalid FTP test results. Data that meet the QA requirements of the FTP are considered valid and will be used to compute emissions reductions for ETV purposes. Section 8.0 addresses a technology applicant's options should the technology perform below expectations.

Tests conducted at qualified laboratories will be accepted as ETV tests provided the technology is submitted to the APCTVC and all requirements of this GVP are met, including approval of the test/QA plan prior to testing. This requires that the technology be submitted

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to the APCTVC, that a test/QA plan be prepared by the laboratory in conjunction with the APCTVC, and that the test/QA plan be approved by the APCTVC prior to testing. All QA requirements of the FTP methods must be met, and the test and test laboratory must meet the QA requirements of ETV as established in this GVP and the test/QA plan.

Engine emissions are expressed in grams of pollutant per kilowatt-hour (g/kWh) or in units of grams per brake horsepower-hour (g/bhp-hr). The primary measurement of HC and NO_x is normally concentration in the exhaust stream in parts per million by volume (ppmv), which is then converted to g/kWh in accordance with the FTP. For calculation of the technology's removal efficiency, the baseline emissions of the tested engine must also be known. The control technology performance will be reported as both absolute emissions in g/kWh and as percentage emissions reduction for a specific engine or engine family. The percentage emission reduction reported will be the mean emission reduction (relative to the baseline emission) with attendant upper and lower 95% confidence limits on that mean.

3.0 ETV TESTING RESPONSIBILITIES

This ETV program is conducted by the APCTVC under the sponsorship of the EPA-ORD and with the participation of technology applicants. The APCTVC is operated under a cooperative agreement by RTI, EPA's ETV partner. RTI's role as ETV partner is to provide technical and administrative leadership and either conduct or manage the conduct of ETV testing and reporting. Various subcontractors have roles in the APCTVC under RTI's management.

ETV tests are conducted by qualified test laboratories as contractors to RTI. Test laboratory-specific ETV test/QA plans are prepared by the testing laboratories to meet the requirements of the GVP.

The test/QA plan includes a chart that presents the test program organization and major lines of communication. The organizations involved in the ETV of mobile diesel engine air pollution control technologies are the EPA, RTI, testing laboratory, and technology applicant.

The primary responsibilities for each organization involved in the test program are:

1) The EPA-ORD, following its procedures for ETV, reviews and approves GVPs, test/QA plans, ETV reports and statements, and conducts QA audits.
2) The APCTVC prepares the GVP, provides oversight of the testing organization, provides a template for test/QA plans, and jointly with EPA-ORD reviews and approves the ETV reports and statements.
3) The testing organization prepares the test/QA plan in accordance with the GVP, coordinates test details and schedules with the applicants, conducts the tests, and prepares and revises draft ETV reports and statements. The testing organization QA staff is responsible for conducting internal QA on test results and reports.
4) EPA-ORD and/or APCTVC QA staff, at their discretion, will conduct assessments of the test organization's technical and quality systems.

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5) The technology applicant provides complete, commercial-ready equipment for ETV testing; provides logistical and technical support, as required; and assists the testing organization with operation and monitoring of the equipment during the ETV testing. The applicant's responsibilities are defined by a contract or letter of agreement with RTI..

4.0 TECHNOLOGY CAPABILITIES AND DESCRIPTION

This section outlines the information to be submitted by the ETV applicant, who is the basic source of the information regarding its mobile source air pollution control technology. This information is used by the test laboratory and APCTVC to prepare and review a test/QA plan that meets the requirements of the applicant and potential users of the ETV. No general outline can anticipate the data requirements for all possible technologies, so the applicant may be requested to supplement this outline when additional information is needed. This protocol has been developed with an awareness of the California Air Resources Board (CARB) "verification" program, and an application to CARB for retrofit "verification" is expected to provide adequate information. The basic application form to be used for ETV is that posted by EPA-OTAQ for the voluntary retrofit program, which can be found at:

http://www.epa.gov/otaq/retrofit/documents/forms.xls (as an Excel file)
http://www.epa.gov/otaq/retrofit/documents/forms.wk4 (as a Quattro file)

EPA-OTAQ has also posted application form guides, which can be found by replacing "forms" with "forms_guide" in the links above. The ETV test/QA plan will summarize this information in a form that clearly describes the technology being verified and states, for potential users of the technology, it's intended range of applicability as stated by the applicant. The test/QA plan will also include a draft ETV statement, based on Appendix A, customized to the specific technology being verified and measurements being made. The balance of this section independently describes the information requirements that led to development of these forms.

4.1 Basic Technology Identification and ETV Requirements

The basic technology identification should be a concise description of the technology that describes what is being verified and summarizes the emissions control performance expected. This information will be used to describe the technology in the ETV statement.

It should include such information as: technology name, model number, manufacturer's name and address, serial number or other unique identification, warning and caution statements, capacity or throughput rate, specific installation instructions, adjustments, limits on flow, temperature, pressure, and other information necessary to describe the specific technology and its intended use. Warranty information on the technology should be provided, including a sample warranty statement.

In addition, the applicant must state the goal of the ETV in terms of range of applicability

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(single or multiple engine, fuel requirements, equipment sizing, etc.), expected emissions reduction, and anticipated data use. This information will be used to develop the ETV test/QA plan.

4.2 Technology Descriptive Information

This section of the application is intended to describe the technology more fully. It will be used to prepare the test/QA plan and as a more complete description of the technology in the ETV report.

The applicant should describe the technology in a brief (300 word) statement, referring to the scientific principles of the technology's operation. Depending on the complexity of the technology, this may be followed by more extensive information. When applicable, the inclusion of schematic drawings explaining operation of the technology is encouraged. Examples of descriptive information that should be included are:

> Installation requirements. Space occupied, installation time, any physical modifications, placement issues, identification of ancillary equipment, if any, recommended duration of degreening as well as any special start-up procedures, and any other special requirements.
> Operation. Description to include identification of any favorable or unfavorable operating conditions and their effect on performance, fuel requirements (such as fuel sulfur limit), consequences of misfueling, identification of any chemicals or other consumable reactants, regeneration requirements, and expected engine back-pressure. Any requirement for energy sources (e.g., heat, electricity, compressed air, hydraulic fluid, pressure) external to the engine must be identified so they can be accounted for in the test/QA plan.
> Maintenance and warranty. Identification of recommended maintenance procedures, cleaning instructions, and spare parts and supplies. The warranty being offered should be stated.
> Operator or mechanic qualifications/training/safety. Qualifications needed to operate and service the technology, amount and type of training needed for operation and maintenance, and special safety considerations. Use of personal protective equipment (eyeglasses, hearing protection, etc.) should be noted.
> Secondary emissions. Identification of any secondary emission to the air that impacts water quality, or liquid or solid waste.
> Technology's life expectancy. Special attention should be given to the technology's regeneration requirements, if any, including a description of the regeneration process, any operating condition requirements for successful regeneration (e.g., temperature), and any manual or computer control of regeneration.

In the case of combinations of independent technologies that are being submitted for ETV, the description of the combined technology should completely identify and describe those technologies being combined and fully state the nature of the combined test and expected result.

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4.3 Technology Performance

The technology applicant must quantify the performance expected from the technology and support that expectation with background test data, including both initial performance and technology durability test descriptions and results. In general, these data will not be used to verify the performance of the technology, but will be used to develop an ETV test/QA plan that can adequately support the expected performance. The level of descriptive detail required for existing tests and their results cannot be generally stated because it is dependent on the ETV goals. Applicants are encouraged to supply pertinent data supporting their claims, which will include test facility descriptions, procedures, quality assurance and control, and any deviations from the FTP.

All aspects of the technology's performance should be addressed, beginning with performance during routine steady-state operation, but also including unsteady or unfavorable operation such as extended idling periods, uncontrolled regeneration, in-place maintenance, etc. Any known or expected impact the technology might have on the character of the emissions (gas composition, temperature, particle size or composition, etc.) should be identified.

4.4 Technology/Engine Interactions

The applicant must describe interactions between the proposed engine(s) and the technology, to include the known or expected effects of the technology on the engine(s). Backpressure, additional parasitic loads, fuel consumption, effects on engine durability, and oil consumption are of special concern. The relationship of the technology, engine control logic, and engine operation should be addressed for the engine(s) under consideration.

The applicant should defend the applicability of the technology to the applicable engine(s) by including exhaust temperature profiles, duty cycles, and other relevant performance information. The operating conditions that are favorable for the control technology should be compared with those of the engine.

The opinion of the engine(s)'s manufacturers regarding compatibility of the technology with their engine should be solicited, summarized, and the correspondence included in the application. Any known or anticipated impact of the technology on engine warranty is to be identified. The relationship between technology warranty and engine warranty should be discussed.

5.0 ETV TESTING

As stated in Section 2.3, Data Quality Objectives, an ETV test consists of a minimum of three FTP tests, and may include additional FTP tests to differentiate a low emission reduction technology from zero or to narrow the confidence limit on the mean emission reduction. Section 5.1 presents the methods that are used to design an ETV test to accomplish the applicant's goal, beginning from an expected emissions reduction for a

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particular pollutant and progressing through the methods used to generate the 95% confidence interval on the mean emission redutions. Section 5.2 presents other general ETV test considerations that apply to most retrofit air pollution control technologies. The remaining sections of this chapter are specific to the indicated types of technologies.

5.1 ETV Test Design

The data of primary interest in this ETV are the reduction in emissions of NO_x, HC, PM, and CO. (Numerous other measurements, including CO_2 emissions, will also be made as described in later sections. However, these are not considered critical, and the methods and data quality objectives will be stated in the test/QA plan for each technology.) NO_x emissions will be used to compute the number of tests required unless the applicant specifically requests that the reduction in another of the pollutants be used to control test design.

The number of and type of FTP tests required for ETV will be as follows:

A minimum of three tests is required to provide a mean emission reduction and the 95% confidence interval on that mean based on measured variability for each of the measured emissions and test parameters. For highway engines this minimum is satisfied with one cold start test and three hot start tests. For nonroad engines the minimum is satisfied with three replicates of the test sequence appropriate for the engine classification for which the technology is intended (i.e., three 8-mode tests for applicable engines, three 5-mode test for constant speed engines, three 6-mode test for variable speed engines under 19 kW.)

Additional tests may be required to meet the ETV requirement that the test/QA plan provide a 90% probability of detecting the expected emissions reductions when computed using the expected experimental errors for the various measurements. These criteria become controlling for low emissions reductions and/or high test variability for the controlling pollutant, which will be NO_x unless another pollutant is selected. This is a planning requirement for the test/QA plan. Section 5.1.1 describes the calculation procedure.

Relative to the minimum number, additional tests may be desired by the applicant to reduce the width of the 95% confidence interval on the mean emission reduction. Section 5.2 provides additional explanation and example scenarios.

5.1.1 Determination of Number of Tests Required to Meet ETV Requirements

Minimizing the cost of ETV testing is important, and reducing the number of tests conducted is one way to minimize cost. However, if too few tests are conducted, normal experimental variability could prevent the ETV from producing a useful outcome. For measurements having known variability and for stated expected reductions in emissions, the probability that a given number of tests can detect the expected reduction can be computed from statistical theory based on normal distributions. This ETV protocol requires that all ETV test/QA plans

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include sufficient tests to have a high probability of detecting the emissions reductions expected by the applicant. This requirement was implemented to ensure, as much as was practical, that the ETV test would accomplish the applicant's goals. This requirement will generally only be important to ETV test design for low emissions reductions and/or measurements having high variability. Specifically, the ETV test is to be designed such that there is 95% confidence that there is a 90% probability of detecting the emission reductions expected by the applicant, computed from the expected experimental variability for the various measurements. In this context, "detecting" means that the 95% confidence interval does not include zero emissions reduction. (This requirement is for test design purposes, and does not require that the test/QA plan be modified should actual test data show that the assumptions that went into the calculation were incorrect. However, as explained below, insufficient replication can result in inability to issue a verification and publication of an ETV report stating that a technology had no statistically significant benefit.)

An equation was derived to explicitly compute the number of tests required for normally distributed measurements having known standard deviations. Some results of applying that calculation are presented in Table 1 for PM and NO_x emission reductions. The equation used to compute the number of tests required is presented in Appendix B.

In Table 1 the baseline engine is assumed to be at a fixed emission value (the 1990 certification emission level for highway diesel engines) for PM (top of table) and NOx (bottom three rows). PM and NO_x measurements are used in Table 1 because the measurement standard deviations were known for one laboratory. The results in Table 1 are limited by the requirement in the derivation that the measurements be normally distributed with known variability. As will be shown in Section 5.1.2, the determination of the measurement variability from data, as will be done during the ETV data analysis, leads to a broadening of the confidence interval. Consequently, more tests than shown in Table 1 may be required under those conditions, and careful examination of the number of tests needed will be required during test/QA plan development.

The column headings in the first row of the PM and NO_x sections of the table give the assumption that installing the control technology gives emissions reductions of 5%, 20%, 50%, or 85% from the baseline emissions levels, which might be the applicant's estimate of emission reduction for different technologies. The second row gives the constant and known baseline engine (without control technology) variability when emitting at the 1990 certification level. The third row is the known measurement variability for the baseline engine after having been fitted with control technology that achieves the reduction shown in the column heading. (Variability is expressed as the known standard deviation at the emission level divided by the corresponding baseline engine mean emission and multiplied by 100%.) The variability increases as the emission reduction increases from left to right because the absolute error is roughly constant, while the magnitude is decreasing. The fourth row gives the calculated number of tests required to have 90% confidence that the 95% confidence interval about the mean expected emission reduction would not include zero.

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Table 1. Number of replicate tests (on both baseline and controlled engine) to achieve a 90% probability of detecting a PM emission reduction at a confidence level of 95%

Expected emission reduction (relative to the respective 1990 certification levels for PM and NO_x, respectively)	5%	20%	50%	85%
Variability for baseline engine PM measurement at 1990 levels	2%	2%	2%	2%
PM measurement variability at specified emission reduction	2%	2%	3%	10%
Number of tests required to have 90% probability (ETV requirement) of detecting expected PM emission reduction[a]	3	1	1	1
Variability for baseline engine NO_x measurement at 1990 levels	2%	2%	2%	2%
NO_x measurement variability at specified emission reduction	2%	2%	7%	NA[b]
Number of tests required to have 90% probability (ETV requirement) of detecting expected NOx emission reduction[a]	3	1	1	NA[b]

[a] Computed under the assumption of normally distributed measurements having known variability. Additional tests may be required for sample standard deviations obtained during ETV.

[b] NA = Not Available.

The fifth through the seventh rows (shaded) repeat the calculation for the NO_x measurement. No estimate of variability was available for the NO_x measurement at an 85% reduction from the 1990 level. Table 1 shows that, for both PM and NO_x, three tests are sufficient to distinguish between zero and emissions reductions as low as 5%, provided the estimates of measurement variability are met in the actual ETV. One test would be sufficient to detect the other emissions reductions, but three are required by ETV to provide a measured standard deviation. No specific estimates of variability for HC emissions were available, but at high emissions reductions (low absolute levels) the HC variability may be on the order of 30%. Three tests would not be sufficient in that case. In the development of the test/QA plan, the test laboratory will report its known measurement variability, and the expected number of tests required. This estimate will be reviewed by the APCTVC.

Appendix C presents a sensitivity analysis for additional levels of measurement variability. As explained in section 5.1.2, below, the number of tests may be increased further if an applicant desires to reduce the width of the confidence interval on the mean emission reduction.

5.1.2 Confidence Interval on the ETV Result

A consequence of the unavoidable variability in emissions measurements is that the mean of a small number of measurements has a small probability of giving the true emission reduction. In some cases it may not be possible to make a statistically-significant determination that the measured emission reduction is different from zero. The results of ETV measurements will be presented in verification statements and reports as the mean and

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95% confidence interval on that mean, calculated using the sample standard deviations determined from the ETV test data. Because sample standard deviations are available, the t-statistic is applied to compute the confidence intervals. This results in a broader error distribution than indicated in Table 1.

Table 2 illustrates the results that would be obtained for the PM emissions measurement variability numbers that were presented in Table 1 should those results be obtained during an ETV. Two additional 20% reduction columns have been added as examples of the effects of still higher variability at moderate reductions. (As was true in Table 1, the measurement variability in Table 2 is expressed as a measurement standard deviation divided by the baseline engine mean emission. However, relative to Table 1, the use of the t-distribution broadens the confidence interval.) The first three rows of Table 2 are the same as those in Table 1. Rows 5 through 7 give the two-sided 95% confidence intervals on the indicated mean percent emissions reduction from the 1990 certification emission value for three, six, and nine tests. For the 5% reduction column, Table 2 shows that the three test ETV minimum does not detect the 5% reduction in that a zero reduction is within the 95% confidence interval of -1.7 to 11.7% reduction. Six tests do detect the difference. Therefore, between three and six tests would be required.

The fourth and fifth columns of Table 2 illustrate the effects of higher variability levels for the controlled engine than were presented in Table 1 for a 20% emissions reduction, and more clearly show the potential benefits of additional testing. This hypothetical additional variability would arise from some interaction between the engine and the control device, because the variability of the test method is affected by modest changes in emissions levels such as are contemplated here. With 3 tests and an 8% test variability, the confidence interval on the mean reduction would be ± 16.4%. Obtaining the same mean from 6 tests, at the same variability, would give a confidence interval of ±6.9%, less than half the width of that with 3 tests.

Table 2. 95% confidence intervals on example mean emission reductions relative to baseline engine emissions at 1990 certification value.

Emission reduction, % of baseline engine emission	**5**	**20**	**20**	**20**	**50**	**85**
PM measurement variability for baseline engine, % of baseline engine emission	2	2	2	2	2	2
PM measurement variability for controlled engine, % of baseline engine emission	2	2	4	8	3	10
Number of replicate verification tests	**95% confidence intervals on emission reduction, % of baseline engine emission**					
3	5±6.7	20±5.6	20±8.9	20±16.4	50±4.5	85±3.8
6	5±2.8	20±2.4	20±3.8	20±6.9	50±1.9	85±1.6
9	5±2.1	20±1.7	20±2.8	20±5.1	50±1.4	85±1.2

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When planning a test, the ETV program will use the applicant's estimated emissions reduction, available test results, and experience with similar technologies to design an ETV that is capable of detecting the emission reduction expected and meeting the applicant's goals for confidence interval. However, the technology may not perform as expected. Section 8.0 addresses these circumstances.

5.2 General ETV Test Considerations

Unless specified otherwise, the general test considerations in this section will apply to all technologies covered by this protocol.

5.2.1 Submittal of Technologies and ETV Sequence

The ETV process begins with the applicant indicating to the APCTVC or to a test laboratory an interest in the ETV process. In either case, the second step is agreement between the APCTVC, the applicant, and the test laboratory regarding the general form of the ETV process and the responsibilities of all parties. This second step culminates with a formal application for ETV to the APCTVC, providing the information about the technology described in Section 4. The approximate cost of the ETV will be estimated and a contractual relationship between the APCTVC and the applicant will be started.

The test laboratory will then develop the ETV test/QA plan, reviewing it with the applicant and the APCTVC to ensure that it meets the requirements of the APCTVC, and, to the extent possible, accomplishes the applicant's goals for ETV. The test/QA plan will then be reviewed formally by the APCTVC and EPA. Test/QA plan development consists of a series of sequential activities, and the test/QA plan must be approved before testing begins.

The applicant will provide the technology to be tested. The applicant has the responsibility to arrange for provision of the engine on which the test will be conducted. Scheduling of the ETV test will be done by the test lab. De-greening of the technology is the applicant's responsibility, as is providing a de-greened unit and an aged unit for durability testing. The applicant must also provide any special ancillary equipment required for operation of the technology.

The applicant may choose to conduct private, proprietary test work at the test lab during the same time period the ETV is taking place. Such arrangements are between the test lab and the applicant. However, a clear differentiation is required between such private test work and the ETV test itself. In addition, the APCTVC must have adequate notice regarding an ETV test to be able to audit those tests if desired. The manner in which the start and end of the ETV test will be established and when the APCTVC will be notified must be specified in the test/QA plan. All ETV data must be reported.

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Following the ETV test, the test lab will report the data to the APCTVC, which will incorporate those data into the ETV report and statement. These documents will be reviewed with the test lab and the applicant to address comments and concerns as appropriate. The draft report will then be submitted to the multi-step EPA review and revised as needed. The ETV report and signed statement will be provided by the APCTVC to the applicant and EPA, and posted on the ETV and APCTVC websites.

5.2.2 Highway Engine ETV

Testing of technology intended to control emissions from highway diesel engines will be conducted generally under the provisions of 40 CFR Part 86 Subpart N. The primary emissions measurements will be of NOx, PM, HCs, CO, and other FTP specified emissions. CO_2 and other emissions and measurements described by this protocol are secondary measurements. Each ETV test will consist of the same number of tests on the baseline broken-in engine, the de-greened emission control technology, and the technology after aging. The number of tests will include a single cold- and hot-start highway transient FTP engine dynamometer test and may include additional hot-start tests in numbers determined using the test design procedure described above. The emissions reductions will be reported as the composite of the cold and mean of the hot starts, as required by the FTP, and as the mean and confidence interval on multiple hot-start tests. The smoke test is not required. The test parameters will be derived from the baseline engine mapping procedure. Emissions reductions will be computed relative to the baseline engine emissions using the same test cycle used during the baseline testing. As required by the FTP, tests that do not meet the FTP QA requirements must be repeated.

The test/QA plan for a specific technology will specify the engines that will be tested and any other aspects of the test that are specific to the technology or the test laboratory.

5.2.3 Highway Test Engines

The emissions characteristics of diesel engines of the same PM certification level are arguably similar because the engine technologies required to achieve those certification levels are likely to be similar. The emissions characteristics are also similar for engine families that have a breadth of technology similar to the tested engine. These similarities may provide an opportunity to group engines and reduce the ETV testing burden on applicants. As of the date of this protocol, EPA-OTAQ has proposed allowing the ETV test results from a single engine test to apply to multiple engines of different manufacturers. This is a decision that has been reserved by EPA-OTAQ, who should be consulted for details regarding the engines required to be tested as part of the ETV, the applicability of that ETV, and the magnitude of the associated emissions reduction credit under the VDRP.

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5.2.4 ETV Testing of Nonroad Engines - General

The basic ETV test for nonroad engines will consist of the nonroad steady-state mode tests as described in 40 CFR, Part 89, Subpart E. The primary emissions measurements will be of NO_x, PM, HC, CO and other FTP required measurements. CO_2 emissions and other measurements described by this protocol are required secondary measurements. Each ETV test will consist of one or more full steady-state multimode FTP test(s) on the baseline broken-in engine, the de-greened technology, and the technology after aging. The test condition will be derived from the baseline engine mapping procedure. The test may be conducted over all modes of the Part 89 test or over portions selected by the applicant. The emissions reductions will be reported as the composite mean and confidence interval of the multiple test modes, computed as stated in the FTP.

Composite emissions reductions are computed relative to the composite baseline engine emissions and will be reported in composite and mode-by-mode to allow flexibility in use of the data for different engine applications.

5.2.5 Nonroad Test Engines

Following an approach similar to that used for the highway engines, the results of ETVs conducted on individual nonroad engines may be applicable to broader groups of engines. Technology applicants may select the engines on which to test their technologies. Coordination with EPA-OTAQ is encouraged because the decision regarding acceptable engine grouping has been reserved by EPA-OTAQ, who should be consulted regarding the engines required to be tested as part of the ETV, the applicability of that ETV, and the magnitude of the associated emissions reduction credit under the VDRP.

5.2.6 De-greening

For many hardware technologies, a brief period of use (de-greening) is needed to achieve a stable emissions reduction that allows representative testing. For instance, the pressure drop across a continuously regenerating PM filter reaches an equilibrium value. The de-greening time period required varies for different technologies, but is on the order of 25 to 125 hours. In all cases, the technology applicant must propose and justify the extent of the de-greening process in the ETV application. The APCTVC office will review and comment on this proposal, advise regarding the documentation requirements, and append the de-greening process description to the technology test/QA plan. When complete, the actual process used must be documented. A description of the de-greening process will be included in the ETV report.

For purposes of this protocol, the de-greening time requirement will be specified by the technology applicant as indicated by either previous testing or the requirements of the data user. To allow flexibility for the applicant, de-greening is not required to be conducted at the test lab. It may be done and documented by the applicant or conducted by the test lab by arrangement with the applicant. In either case, the applicant will ensure that such de-

greening activity documentation as start and stop date and time, engine and fuel description, and operating conditions are available and signed by the person responsible for the activity.

De-greening may occur in a laboratory or during in-use field operations on an engine that is equivalent to the proposed ETV test engine, or another engine of the same size which utilizes the same engine technology (and thus falls within the range of the technology's stated applicability).

5.2.7 Regeneration

Emissions control devices whose normal operation includes a periodic regeneration will be tested over sufficient test cycles (described below) until a test cycle includes a "regeneration" event. The verified emissions rate and emissions reduction achieved will be computed as the time-weighted average of the emissions rate and reduction achieved over this complete operating cycle.

Technologies that are continuously regenerated in normal operation are not the subject of this paragraph. Continuous cleaning PM filters should reach a stable operating range (as evidenced by near constant pressure drop) before testing, which may be accomplished in the de-greening activity.

5.2.8 Device Scaling

The performance of most retrofit air pollution control technologies is affected by the relative sizes of the tested technologies and the engines. Therefore, the use of single engine ETV tests as predictive of performance over segments of the total engine population requires the availability of non-proprietary application sizing information and that the technology be labeled. Sizing information may be provided in sizing charts [e.g., model AA1 is suitable for 37 to 74 kW (50 to 100 hp) engines, model AA2 to 74 to 112 kW (100 to 150 hp) engines] or through the release of basic design information (e.g., space velocity, catalyst loading). The purpose of this requirement is to allow the APCTVC and the potential technology user (the public) to evaluate the applicability of the verified technology to other applications. Applicants who utilize application sizing charts must verify their technologies on an engine at the most challenging end of the range of applicability. ETV reports and statements will report the results and the design guidance required to independently extend application of the technology to other engines in the same engine grouping. Device scaling and engine selection decisions will be explained and documented in the test/QA plan to the extent possible and will be reported in the ETV report. The ETV report and statement will report the results and the design guidance required to independently extend application of the technology to other engines in the same engine grouping.

5.2.9 Durability

The emissions reductions measured for the de-greened air pollution control device will not account for changes in product performance that may occur as the device ages. For

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participation in the VDRP, additional testing of an "aged" control device is required by EPA-OTAQ. If done as part of the ETV program, the "aged" device test will meet the same data requirements as a new device test. This testing is followed by extrapolation of the "initial de-greened" and "aged" verified performance measurement to the end of the warranted life of the control technology using a method determined by EPA-OTAQ. The aging process details and the extrapolation of the data to an "end of life point" are not part of this protocol. Provided for information only, the description below is current as of December, 2001 and may change. The details should be confirmed prior to ETV.

1) Aging entails subjecting the control device to operating conditions that cause normal wear equivalent to at least 33% of the Minimum Durability Testing Period established in the California "verification" procedure for diesel retrofit systems (CARB, 2001). Table 3 provides the testing periods that were current as of the date of this protocol. The applicant should verify the testing period current at the date of ETV. The technology applicants must conduct the aging process on their technology. They have discretion to tailor this process to product requirements. Applicants may age an exhaust catalyst by using it during real-world operation, or through accelerated bench testing. It is expected that applicants will submit identical parts (one in a de-greened state, one aged to at least 33% expected full-life) so that testing with the baseline may occur sequentially. However, applicants may conduct the de-greened and aged technology tests as separate tests, in which case the baseline engine test must be repeated. All aging protocols must accompany the ETV application and explain the technical basis for stating the aging protocol results in at least 33% full-life aging. If real-world aging is performed, the application must describe and provide documentation of the usage and maintenance history of the aged unit as well as the engine with which it was aged.
2) Emissions testing using the aged device will be part of the ETV process and will follow the same procedures applied to the de-greened technology. First, baseline emissions testing shall be conducted, followed by testing with the de-greened device, and then finally testing the aged device with a re-test of the baseline engine if technically feasible. An applicant may elect to age a unit to its full useful life prior to testing and request ETV on that basis.

3) The full useful-life reduction capabilities will be estimated by EPA-OTAQ following procedures they will provide to applicants.

5.2.10 Standard Diesel Test Fuel

The standard diesel test fuel for highway engines should meet the EPA specifications outlined in 40 CFR Part 86.1313-98 with the exception of the sulfur content. For nonroad engines, the test fuel

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Table 3. Minimum durability testing periods (CARB, 2001)

Engine Type	Engine Size	Minimum Durability Testing Period	
Highway	Light heavy-duty, generally 70 to 170 hp, GVWR[a] normally less than 19,500 lb.	5 yr or 60,000 miles (or equivalent time in hours)	
	Medium heavy-duty, generally 170 to 250 hp, GVWR[a] normally from 19,500 to 33,000 lb.	5 yr or 100,000 miles (or equivalent time in hours)	
	Heavy heavy-duty, generally exceeds 250 hp, GVWR[a] normally exceeds 33,000 lb.	5 yr or 150,000 miles (or equivalent time in hours)	
Nonroad and Stationary	Under 25 hp and for constant speed engines rated under 50 hp with rated speeds greater than or equal to 3,000 rpm	3 yr	1,600 hr operation
	At or above 25 hp and under 50 hp	4 yr	2,600 hr operation
	At or above 50 hp	5 yr	4,200 hr operation

[a]GVWR = Gross Vehicle Weight Rating

should be that described in 40 CFR Part 89.330 or another fuel as specified by the control technology applicant. Because the performance and durability of many types of diesel retrofit technologies are affected by the sulfur content of the diesel fuel, applicants should specify the maximum sulfur level of the fuel for which their technologies are designed. The sulfur content of the ETV test fuel should be no less than 66% of the stated maximum sulfur content. (Because refinery and blending operations are such that very low sulfur content control is difficult, test fuel with a sulfur content of 15 ppm or below is not constrained to the "66% rule". The actual sulfur content of the test fuel batch is to be reported.) Other test fuels should meet the applicable EPA specifications outlined in 40CFR Part 86.1313. Adding sulfur to the fuel by the test laboratories is permissible if necessary to achieve the required fuel sulfur content for either baseline or controlled engine tests.
During ETVs, baseline engines should be fueled with the standard fuels that are representative of nominal in-use fuels and controlled engines with low sulfur versions of the standard fuels that are representative of the applicant's recommended or required fuel.

5.2.11 Engine Performance and Power

Engine performance and power will be measured and reported for both the baseline engine (without the control device installed) and the engine with the control technology. Engine performance measurements will be made with the engine operating at maximum power (rated conditions) and at peak torque as defined in the applicable FTP.

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5.2.12 Fuel Consumption

Fuel consumption will be measured for both the baseline engine (without the control device installed) and the engine with the control device installed to determine the effect of the technology on fuel consumption. The engine fuel consumption measurements will be made at maximum power at rated conditions and at peak torque at intermediate speed. Multiple tests, if available, will be averaged. The results will be reported as a fractional increase or decrease relative to the baseline engine. Also reported will be fuel economy and brake specific fuel consumption from testing by the applicable FTP.

5.2.13 Back-pressure

Within the test cell, baseline engine back-pressure will be set to the value required by the applicable FTP (highway or nonroad). Once installed for the ETV test, the back-pressure of the retrofit control technology may be greater than the FTP requirement. If so, the ETV test will be conducted without adding additional back-pressure; if not, the test cell will be adjusted to meet the FTP requirements. Because back-pressure of a retrofit control technology may affect the performance of an engine, the ETV test will measure and report back-pressure with the control device at full-load and rated speed. Back-pressure will be measured and reported for both the baseline engine (as set for the FTP test without the technology installed) and the engine with the de-greened or aged control technology installed.

5.2.14 Control Technology Operating Temperature

Inlet (engine exhaust) and discharge temperatures must be measured for technologies that are either dependent on specific operating temperature ranges or affected by engine or exhaust temperatures.

5.2.15 Other Measurements and Conditions

ETV of technologies that may produce secondary pollutants or have other secondary effects must include measurement of those pollutants in the ETV test. CO_2 emissions, while not primary, must be measured using instrumentation and/or estimated from a carbon balance from the fuel usage. ETV must include the appropriate measurements for technologies that require other specific operating conditions or affect emissions over only a limited range of a particular pollutant. For example, because the long-term operation of DECs and PM filters is affected by the soluble organic fraction (SOF) of the PM, SOF must be measured during ETV testing for these and similar technologies. The details of these non-critical measurements and their QA goals will be part of the test/QA plan.

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5.3 ETV of DECs and PM Filters

5.3.1 Technology Description

For the purposes of this GVP, DECs are defined as devices made of active catalyst material (often containing precious metal) deposited on a support medium. The engine exhaust passes through the device, where the pollutants catalytically react and more environmentally acceptable reaction products are exhausted. PM filters mechanically trap PM emissions and subsequently oxidize them. Filters may also employ a catalyst for gaseous emissions control and to enhance the oxidation of the collected PM.

Physically, DECs and PM filters have the general appearance of a large muffler and are placed in the engine exhaust at approximately the same location. They are therefore well-suited to retrofit applications. No external liquid or gaseous reactants are required for them to function.

DECs have been reported to decrease HC and CO emissions by over 50%. They decrease PM emissions by about 20%. PM filters have been reported to decrease PM and HC emissions by 80% or more and to decrease CO at about the level achieved by exhaust catalysts. NOx emissions may be decreased slightly by exhaust catalysts.

Operational issues with DECs and PM filters are primarily achieving or maintaining adequate temperature within the device to complete the reactions and functioning satisfactorily with an accumulation of catalyst poisons and/or non-combustible lubricant ash residue. Lubricant ash and wear metals can largely be removed by infrequent “blowing” with compressed air. Guidance on technique and frequency of such cleaning should be provided in the ETV application.

5.3.2 Test Considerations Specific to DECs and PM Filters

The general considerations in Section 5.2 apply to DEC and PM filter ETV testing. ETVs of DECs and PM filters require measurement of the SOF content of the exhaust stream prior to entering the DEC. (The SOF may be measured for PM collected during the baseline engine test. The method to be used is the *Test Method for Soluble Organic Fraction (SOF) Extraction* [CARB, 1989] or a equivalent method recognized by EPA-OTAQ.) Both DECs and PM filters require measurements of inlet and outlet temperatures.

5.4 ETV of Engine Modifications

5.4.1 Technology Description for Engine Modifications

Engine modifications are defined as a change integral to an engine (e.g., component modifications or change or engine control system calibration change) that is proposed as an emissions reduction technology.

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5.4.2 Test Considerations Specific to Engine Modifications

The general considerations in Section 5.2 apply to engine modification ETV. Baseline engine performance will be measured prior to modification, followed by modification of the baseline engine in accordance with the application instructions, operation for a de-greening/stabilization period, and then measurement of the de-greened technology's performance. An aged engine modification technology's emissions performance will be evaluated as described in Section 5.2.9. However, there is no requirement to re-run the baseline engine which was modified. It cannot be shown that a modified engine can be returned to its original state to again serve as a baseline.

Engine modifications whose use is warranted by engine manufacturers will be taken to have no adverse impact on engine durability, and that endorsement will be noted in the verification report (VR) and verification statement (VS) along with the verified emissions reductions for the aged engine. The lack of any verified knowledge regarding the impact on engine durability of technologies not warranted by the engine manufacturer will similarly be noted.

6.0 REPORTING AND DOCUMENTATION

This section describes the procedures for reporting data in the VR and VS. The specifics of what data must be included and the format in which the data must be included are addressed in this section (e.g., QA/QC summary forms, raw data collected, photographs/slides/video tapes). The VR for each technology will include near it's beginning the VS. The VS is a short summary of the ETV results. An example draft is attached as Appendix A. The VR, including the VS, will be written by the APCTVC based on the test report submitted by the testing organization. The VR and VS will be reviewed by the APCTVC and the technology applicant before being submitted to EPA for review and approval as specified in the ETV QMP.

6.1 Reports

Based on the test report from the laboratory, the APCTVC will prepare the draft VR, which includes the following topics:

1) VS;
2) Introduction;
3) Description and identification of product tested;
4) Procedures and methods used in testing;
5) Statement of operating range over which the test was conducted;
6) Summary and discussion of results as required to:
    a) Support the VS,
    b) Explain and document necessary deviations from test plan, and
    c) Discuss QA issues;
7) Conclusions and recommendations;
8) References; and

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9) Appendices:
   a) QA/QC activities and results,
   b) Raw test data, and
   c) Equipment calibration results.

The VS will include the following:

10) Technology applicant's name and technology's descriptive information,
11) Summary of ETV test program,
12) Results of the ETV test,
13) Any limitations of the ETV results, and
14) Brief QA statement.

Review and approval of the draft ETV report and statement are as described in Section 3.0. A draft VS is attached to this protocol as Appendix A.

6.2 Data Reduction

Data from measurements made as part of the ETV test will be reported as emissions rates in g/kWh (g/bhp-hr) and as percentage emission reductions from the baseline engine. The confidence limits will be presented as well as the mean emissions reduction, as discussed in Section 5.1.2. When they would be helpful to the mobile sources community because of established usage, the appropriate English Engineering units will be supplied parenthetically.

7.0 DISSEMINATION OF ETV REPORTS AND STATEMENTS

After a retrofit control technology has been tested and the draft VR and VS received from the testing organization, the APCTVC will send a draft of both to the applicant for review prior to submission to EPA-ORD and release of the approved report to the public. This gives the applicant opportunity to review the results, test methodology, and report terminology while the drafts remain working documents and are not publically accessible. The applicant may submit comments and revisions on the draft statement and report to the APCTVC. The APCTVC will consider these comments and may suggest revisions of its own.

After incorporating appropriate revisions, the draft final VR and VS will be submitted to EPA-ORD for review and approval. A signed original VS and VR will be filed and retained by the APCTVC, and signed originals will also be provided to the applicant and to EPA. Three additional paper copies of the ETV report will be provided to the applicant. Further distribution of the ETV report, if desired, is at the applicant's discretion and responsibility. However, approved VSs and VRs will be posted on the ETV web site for public access without restriction. The VR report appendices will not be posted on the website, but will be publically available from the APCTVC.

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8.0 APPLICANT'S OPTIONS SHOULD A TECHNOLOGY PERFORM BELOW EXPECTATIONS

ETV is not a technology research and development program; technologies submitted for ETV are to be commercial-ready and with well-understood performance. Tests that meet the ETV data quality requirements (a valid FTP test) are considered valid and suitable for publishing. However, a technology may fail to meet the applicant's expectations. Based on limited testing, for instance, the applicant might expect an emission reduction of 30% ± 7% result. However, the actual ETV result from the more complex FTP test cycle might be 20% ± 15%. The APCTVC will use its experience to avoid this situation, but it is possible. In this case, the applicant may choose to schedule additional tests, may accept the result and complete the verification, or may request that a VS not be issued. However, ETV reports are always in the public domain. VRs will be written and will be available from EPA-ORD for review by the public regardless of a request not to issue a verification statement, and summaries of the results of ETV testing may be published by ETV and/or EPA-OTAQ.

Another example of a technology not meeting expectations would be an expected result of a mean of 10% reduction with a confidence interval of ± 5% reduction, but an actual ETV mean reduction of 5% with a confidence interval of ± 7% reduction. In this case, the data are insufficient for ETV to verify that the technology does anything at all. Additional tests must be scheduled and a statistically significant reduction obtained for a VS to be issued. Inability to detect a statistically significant emission reduction (equivalently, failure to have sufficient tests) will prevent completion of the ETV, and the results of the ETV will be reported publically stating that performance could not be distinguished from 0% reduction. An ETV statement will not be issued in these cases.

In either of these cases, the applicant may improve the product and resubmit it under a new model identification for ETV testing. ETV Statements for acceptable tests of the new product will be issued as they are processed by the APCTVC and EPA-ORD (except that the results for several identical tests performed in rapid succession will all be released at the same time).

9.0 LIMITATIONS ON TESTING AND REPORTING

To avoid having multiple ETV reports for the same product and to maintain the ETV testing as a cooperative effort with the applicant, the following restrictions apply to ETV testing under this protocol:

1) Applicants may submit only products they manufacture or whose distribution they control. Applicants may not submit for ETV testing control devices whose use is not in their control except with the agreement of the manufacturer or vendor.
2) For a given product (e.g., brand and model), APCTVC policy is that only one ETV report and statement will be issued for any single application.
3) Air pollution control technology frequently performs differently in different

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applications. Applicants may request additional tests of essentially identical technology if it is being applied to pollution sources that are clearly different from those for which ETVs have been obtained.

10.0 REQUIREMENTS FOR TEST/QA PLAN

10.1 Quality Management

All testing organizations participating in this ETV Program must meet the QA/QC requirements defined below and have an adequate quality system to manage the quality of work performed. Documentation and records management must be performed according to the *ETV Quality and Management Plan for the Pilot Period (1995-2000)* (ETV QMP, EPA, 1998a). Testing organizations must also perform assessments and allow audits by the APCTVC (headed by the APCT QA Officer) and EPA corresponding to those in Section 11.

All testing organizations participating in the Retrofit Air Pollution Control Technologies for Highway and Nonroad Use Diesel Engines Program must have an ISO 9000-accredited (ISO, 1994) or ANSI E4-compliant (ANSI, 1994) quality system and an EPA- or APCTVC-approved QMP.

10.2 Quality Assurance (QA)

All ETV testing will be done following an approved test/QA plan that meets *EPA Requirements for Quality Assurance Project Plans* (EPA, 2001a) and Part B, Section 2.2.2 of EPA's ETV QMP (EPA, 1998a). These documents establish the requirements for test/QA plans and the common guidance document, *Guidance for Quality Assurance Project Plans* (EPA, 1998b), provides guidance on how to meet these requirements. The APCT Quality Management Plan (RTI, 1998) implements this guidance for the APCTVC.

ETVs conducted under this generic protocol utilize test procedures described in the FTP (40 CFR Part 86 for highway engines and 40 CFR Part 89 for nonroad engines). The test/QA plan must describe, in adequate detail, how the FTP test methods are implemented by the testing organization. Replication of the FTP text is neither expected nor desired. The test/QA plan should reference the FTP in detail, by section and subsection, as appropriate for the topic under consideration. Any deviations from the FTP must be identified and explained. Internal standard operating procedures (SOPs) may be referenced provided they are available for audit review. (SOPs need not be incorporated into the test/QA plan except by reference. If considered proprietary to the test organization, they should be clearly marked.) When the FTP offers alternative test procedures or equipment, the test/QA plan must identify the alternative implemented. Similarly, if a range of operating parameters is allowed by the FTP, the specifics of the particular implementation must be provided. For a test organization with multiple test cells, these details may be tabulated and incorporated by attaching a table and identifying the test cell on the test report. Steps the testing organization will take to ensure acceptable data quality in the test results are also identified in the test/QA plan. As above, detailed reference to SOPs, the calibration portions of the FTP, or other

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available documents is encouraged. Any needed SOPs will be developed in accordance with *Guidance for Preparing Standard Operating Procedures (SOPs)* (EPA, 2001b.)

The testing organization must prepare a test/QA plan and submit it for approval by the APCTVC. The test/QA plan must be approved before the test organization can begin ETV testing.

A test/QA plan contains the elements listed below, the contents of which may be stand alone or include references to the FTP or other widely distributed and publically available sources. Legible hand-notated diagrams from the FTP are acceptable. If specific elements are not included, an explanation for not including them must be provided.

1) Title and approval sheet;
2) Table of contents, distribution list;
3) Test description and test objectives;
4) Identification of the critical measurements, data quality objectives (DQOs) and indicators, test schedule, and milestones;
5) Organization of test team and responsibilities of members of that team;
6) Documentation and records;
7) Test design;
8) Sampling procedures;
9) Sample handling and custody;
10) Analytical procedures;
11) Test-specific procedures for assessing data quality indicators;
12) Calibrations and frequency;
13) Data acquisition and data management procedures;
14) Internal systems and performance audits;
15) Corrective action procedures;
16) Assessment reports to EPA;
17) Data reduction, data review, data validation, and data reporting procedures;
18) Reporting of data quality indicators for critical measurements;
19) Limitations of the data; and
20) Any deviations from methods from this generic verification protocol.

The APCTVC will provide a test/QA plan template that illustrates it's expectations.

10.3 Additional Requirements to be Included in the Test/QA Plan

The test/QA plan must include or reference a diagram and description of the extractive gaseous measurement system to be used for the testing and a list of the reference analyzers and measurement ranges to be used for quantifying the concentrations of all gaseous compounds to be measured, including both primary and ancillary pollutants.

The test/QA plan must include or reference a schematic drawing showing all sample and test locations, including the inlet and outlet to the technology sampling locations. The location of

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flow disturbances and the upstream and downstream distances from the sampling ports to those flow disturbances must be noted. The number of traverse points that will be sampled must be provided.

The test/QA plan must include or reference the appropriately detailed descriptions of all measuring devices that will be used during the test.

The test/QA plan must explain or reference the specific techniques to be used for monitoring process conditions appropriately for the source being tested. It must also note the techniques that will be used to estimate any other operational parameters.

The test/QA plan must include and document estimates of historical measurement variability that will be used, as discussed in Section 5.1.1, to compute the number of tests required and provide confidence intervals on single test ETVs.

11.0 ASSESSMENT AND RESPONSE

Each independent test laboratory must conduct internal assessments of its quality and technical systems and must allow external assessments of these systems by the APCTVC QA personnel and by EPA QA personnel. After an assessment, the test laboratory will be responsible for developing and implementing corrective actions in response to the assessment's findings.

As appropriate, the APCTVC and/or EPA will conduct assessments to determine the testing organization's compliance with its test/QA plan. The requirement to conduct assessments is specified in EPA's *Quality and Management Plan for the Pilot Period (1995 - 2000)* (EPA, 1998a), and in RTI's QMP (RTI, 1998). EPA will assess RTI's compliance with RTI's test/QA plans. RTI will assess the compliance of other organizations with their test/QA plans. The assessments will be conducted according to *Guidance on Technical Audits and Related Assessments for Environmental Data Operations* (EPA, 2000) and *Guidance on Assessing Quality Systems* (EPA, 2001.)

11.1 Assessment Types

Quality system assessment - Qualitative assessment of a particular quality system to establish whether the prevailing quality management structure, policies, practices, and procedures meet EPA requirements and are adequate for ensuring that the type and quality of measurements needed are obtained.

Technical systems audit - Qualitative on-site audit of the physical setup of the test. The auditors determine the compliance of testing personnel with the test/QA plan.

Performance evaluation audit - Quantitative audit in which measurement data are independently obtained and compared with routinely obtained data to evaluate the accuracy (bias and precision) of a measurement system.

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Audit of data quality - Qualitative and quantitative audit in which data and data handling are reviewed and data quality and data usability are assessed.

Surveillance audit - Observation of ongoing work to document conformance with specified requirements and/or procedures, such as those given in a test/QA plan or SOP.

11.2 Assessment Frequency

Activities performed during ETV performance operations that affect the quality of the data shall be assessed regularly and the findings reported to management to ensure that the requirements stated in the generic verification protocols and the test/QA plans are being implemented as prescribed.

The types and minimum frequency of assessments for the ETV Program are listed in Part A Section 9.0 of EPA's *Quality and Management Plan for the Pilot Period (1995 - 2000).* Tests conducted by the APCTVC will have at a minimum the following types and numbers of assessments:

1) Technical systems audits and surveillance audits: Self-assessments (qualitative) by test laboratory as provided for in the test/QA plans and at least one independent assessment of the test laboratory.
2) Performance evaluation audits: Self-assessments (quantitative) by test laboratory as provided for in the test/QA plans and at least one independent assessment of the test laboratory.
3) Audits of data quality: Self-assessments (quantitative and qualitative) by the test laboratory of at least 10% of all the ETV data with detailed reports of the audit results to be included in the data packages sent to the APCTVC for review.
4) Assessements of quality systems: Self-assessments by the test laboratory as provided for in the test/QA plans and at least one independent assessment of the test laboratory.

The independent assessments of tests conducted by RTI will be performed by EPA. The independent assessments of other organizations will be by RTI.

11.3 Response to Assessment

When needed, appropriate corrective actions shall be taken and their adequacy verified and documented in response to the findings of the assessments. Data found to have been taken from non-conforming technology shall be evaluated to determine its impact on the quality of the required data. The impact and the action taken shall be documented. Assessments are conducted according to procedures contained in the APCT QMP. Findings are provided in audit reports. Responses by the test laboratory to adverse findings are required within 10 working days of receiving the audit report. Follow up by the auditors and documentation of responses are required.

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12.0 SAFETY MEASURES

12.1 Safety Responsibilities

The test laboratory's project leader is responsible for ensuring compliance with all applicable occupational health and safety requirements. Each individual staff member is expected to follow the requirements and identify personnel who deviate from them and report such action to their supervisor.

12.2 Safety Program

The test company must maintain a comprehensive safety program and ensure that all test personnel are familiar with and follow it.

13.0 REFERENCES

ASQC. *AMERICAN NATIONAL STANDARD Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Programs*. ANSI/ASQC E4-1994. American Society for Quality Control. Milwaukee, WI. 1994.

CARB. *Proposed Regulation Order (DRAFT) Verification Procedure for Diesel Retrofit Systems*. http://www.arb.ca.gov/msprog/mailouts/msc0114/msc0114att1.pdf, California Air Resources Board, El Monte, CA. August, 2001.

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EPA. *Guidance on Technical Audits and Related Assessments for Environmental Data Operations, EPA QA/G-7*, EPA/600/R-99/080, http://www.epa.gov/quality/qs-docs/g7-final.pdf, Office of Environmental Information, U.S. Environmental Protection Agency. Washington, DC. January 2000.

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RTI. *Verification Testing of Air Pollution Control Technology - Quality Management Plan*. Air Pollution Control Technology Program. J. R. Farmer, Program Director, Research Triangle Institute, Research Triangle Park, NC. 1998.

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APPENDIX A: EXAMPLE VERIFICATION STATEMENT

Appendix A is an example verification statement written for a generic PM filter control technology. The technology is assumed to be directed at a highway use engine. It is assumed to be an efficient control device, requiring only a single test by the minimum-number-of-tests calculation. The PM values in Table A-2 are taken from the 85% reduction column of Table 3, while the other values are completely hypothetical.

This generic verification statement is intended only to show the form of a verification statement. It will require modification for each technology verified, depending on the details of that technology's design, construction, and operation. The test/QA plan written for each test will include a draft verification statement customized for the technology actually being tested. The text of that specific verification statement will address the significant parameters that apply to the technology tested.

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THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

U.S. Environmental Protection Agency

ETV Joint Verification Statement

TECHNOLOGY TYPE:	**MOBILE DIESEL ENGINE AIR POLLUTION CONTROL**
APPLICATION:	**CONTROL OF EMISSIONS FROM MOBILE DIESEL ENGINES IN (*HIGHWAY*) (*NONROAD*) USE BY (*TECHNOLOGY TYPE*)**
TECHNOLOGY NAME:	**TECHNOLOGY NAME**
COMPANY:	**COMPANY NAME**
ADDRESS:	**ADDRESS** **PHONE: (000) 000-0000**
	CITY, STATE ZIP **FAX: (000) 000-0000**
WEB SITE:	**http://www.company.com**
E-MAIL:	**some.one@company.com**

The U.S. Environmental Protection Agency (EPA) has created the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative or improved environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high quality, peer reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized standards and testing organizations; stakeholder groups which consist of buyers, vendor organizations, permitters, and other interested parties; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The Air Pollution Control Technology Verification Center (APCTVC), one of six centers under the ETV Program, is operated by the RTI, in cooperation with EPA's National Risk Management Research Laboratory. The APCTVC has evaluated the performance of a *TYPE* emission control technology for mobile diesel engines, the *TECHNOLOGY* by *COMPANY NAME*.

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ETV TEST DESCRIPTION

All tests were performed in accordance with the APCTVC *Generic Verification Protocol for Diesel Exhaust Catalysts, PM Filters, and Engine Modification Technologies for Highway and Nonroad Use Diesel Engines* and the specific technology test plan "ETV Test/QA Plan for *TECHNOLOGY NAME*" These documents include requirements for quality management, quality assurance, procedures for product selection, auditing of the test laboratories, and test reporting format.

The mobile diesel engine air pollution control technology was tested at *TEST LABORATORY*. The performance verified was the percentage emission reduction achieved by the technology for particulate matter (PM), nitrogen oxides (NO_x), hydrocarbons (HCs), and carbon monoxide (CO) relative to the performance of the same baseline engine without the technology in place. Operating conditions were documented and ancillary performance measurements were also made. The basic modules of the test procedure are found in the federal test procedures (FTPs) for highway engines (40CFR, Part 86, Subpart N) and nonroad engines (40CFR, Part 89, Subpart E). For highway use, a single full FTP test was conducted, augmented by additional hot start transient tests as needed to meet the requirements of the generic verification protocol (GVP). For nonroad use, one or more multimode tests were conducted as described in the GVP. A summary description of the ETV test is provided in Table A-1.

Table A-1. Summary of the conditions for ETV test of *TECHNOLOGY NAME* on ENGINE DESCRIPTION.

Test Conducted	Highway Transient FTP
Engine Family	*ENGINE MFGR NAME* Series *XXXYYY*, ??? operating hours prior to test
Engine Size	YYY kW (XXX hp)
Technology	ACME Mark II PM Trap, Model AA1 for diesel engines up to 150 hp on standard fuel
Technology description	Honeycomb PM filter packaged in an muffler-sized can for retrofit installation by a moderately skilled mechanic. No engine modifications required.
Test cycle or mode description	1 full FTP test (1 cold start and 1 hot start)
Test fuel description	EPA standard diesel per 40 CFR Part 86.1313-98
Critical measurements	PM, NOx, HCs, and CO per the FTP
Ancillary measurements	CO_2, backpressure at engine exhaust port, exhaust temperature, fuel consumption, regeneration requirements

VERIFIED TECHNOLOGY DESCRIPTION

This verification statement is applicable to the *TECHNOLOGY NAME* (to include model number and other identifying information as needed), which is an cordierite-based PM filter manufactured by *MANUFACTURER NAME*. *TECHNOLOGY NAME* is packaged and marketed for particular engine families (for example, Model AA1 is properly sized for the A1A1 engine) or as a unit suitable for use on engines below a particular diesel power rating. The unit whose performance was verified was the Model AA1, which is rated for engines up to YYY kW (XXX hp) fueled by standard diesel fuel.

This verification statement describes the performance of *TECHNOLOGY NAME* on the diesel engine

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identified in Table A-1. The retrofit device, *TECHNOLOGY NAME*, is expected to provide similar emissions control performance on other engines having similar exhaust stream characteristics (similar fuel and engine technology) when properly sized for the application.

VERIFICATION OF PERFORMANCE

TECHNOLOGY NAME achieved the emissions reduction shown in Table A-2 at the stated conditions. The number of required ETV tests was estimated to be one complete FTP test, and this

Table A-2. Verified emissions reductions for hypothetical *TECHNOLOGY NAME*

Test Engine: **Manufacturer name Model No. AA1**	**Degreened (XX hours) Technology Test**			**Aged (XXXX hours) Technology Test**		
	Baseline Engine	Controlled Engine	Emissions Reduction %[a]	Baseline Engine	Controlled Engine	Emissions Reduction %[a]
Critical Measurements of Emissions						
Hot Start PM, g/bkWh (g/bhp-hr)	0.804 (0.600)	0.012 (0.090)	85±3	0.790 (0.590)	0.012 (0.091)	84.6±3
Composited PM, g/bkWh (g/bhp-hr)						
Hot Start NO_x, g/bkWh (g/bhp-hr)						
Composited NO_x, g/bkWh (g/bhp-hr)						
Composited HC, g/bkWh (g/bhp-hr)						
Composited CO, g/bkWh (g/bhp-hr)						
Ancillary Measurements						
Engine Power, kW (hp)						
Peak Torque, N-m (lb_f-ft)						
Composited CO_2, g/bkWh (g/bhp-hr)						
PM SOF, g/bkWh (g/bhp-hr)						
Exhaust Flow, L/min (ft^3/min)						
Exhaust Temperature, °C (°F)						
Backpressure, kPa (in. Hg)						
Fuel Usage, % reduction						
Technology In/Out Temp., °C (°F)						
Regeneration	brief description					
Maintenance Schedule	brief description					
Comments						

[a] units of rows as indicated except shaded columns in %

estimate was confirmed by the ETV test results. Table A-2 may include ETV results for both the initial operation (degreened) and for the technology following the stated period of aging. For the

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purposes of determining the status of the technology in regard to EPA's voluntary retrofit program, the prospective user is encouraged to contact EPA-Office of Transportation and Air Quality (OTAQ) or visit the retrofit program web site at http://www.epa.gov/otaq/retrofit/.

The APCT QA Officer has reviewed the test results and quality control data and has concluded that the data quality objectives given in the generic verification protocol and test/QA plan have been attained.

During the ETV tests, EPA or APCTVC quality assurance staff conducted technical assessments at the test laboratory. These confirm that the ETV tests were conducted in accordance with the test laboratory's EPA-approved test/QA plan.

This verification statement verifies the emissions characteristics of *TECHNOLOGY NAME* within the stated range of application. Extrapolation outside that range should be done with caution and an understanding of the scientific principles that control the performance of *TECHNOLOGY NAME*. This verification focused on emissions. Potential technology users may obtain other types of performance information from the manufacturer.

In accordance with the generic verification protocol, this verification statement is valid commencing on *DATE* indefinitely for application of *TECHNOLOGY NAME* within the range of applicability of the statement.

E. Timothy Oppelt Date
Director
National Risk Management Research Laboratory
Office of Research and Development
United States Environmental Protection Agency

Jack R. Farmer Date
Program Director
Air Pollution Control Technology Verification Center
RTI

NOTICE: ETV verifications are based on an evaluation of technology performance under specific, predetermined criteria and the appropriate quality assurance procedures. EPA and RTI make no expressed or implied warranties as to the performance of the technology and do not certify that a technology will always operate as verified. The end user is solely responsible for complying with any and all applicable federal, state, and local requirements. Mention of commercial product names does not imply endorsement.

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APPENDIX B: EXAMPLE CALCULATION OF NUMBER OF TESTS REQUIRED

This appendix presents example calculations to illustrate calculation of the minimum number of tests for ETV.

The calculation is based on:

1) PM and NO_x hot-start FTP emissions measurement variability experience for a diesel emissions laboratory, which is a function of both the type of measurement and the emissions level. The emissions variability is taken to be known for the population of measurements. Therefore the normal distribution value is appropriately used in the calculations. Eq. B-1 is not strictly applicable for a set of measurements for which only sample standard deviations are available;
2) A known baseline mean emission; and
3) A mean controlled emission (the product of the baseline emission and the expected emissions reduction).

The criterion being used is that the minimum number of hot-start FTP tests required for ETV is the number of tests required to have a 90% probability of detecting the specified emission reduction at the 95% confidence level. The basic equation being used for the calculation is:

$$n \approx (z_\alpha + z_\beta)^2 [\sigma^2_1 + (1 - \delta/100)^2 \cdot \sigma^2_2] / \delta^2 \qquad \text{(B-1)}$$

where:

n	=	sample size in each group, rounded up to the next integer;
z_α	=	normal distribution value corresponding to upper-tail probability of α; and
z_β	=	normal distribution value corresponding to upper-tail probability of β.
$1-\alpha$	=	confidence coefficient on comparison of means (0.95 minimum for ETV);
$1-\beta$	=	probability of detection of reduction (0.90 minimum for ETV);
σ^2_1	=	squared standard deviation of baseline-engine emission data, expressed as a percent of the baseline emission value;
σ^2_2	=	squared standard deviation of controlled-engine emission data, expressed as a percent of the baseline emission value;
δ	=	difference between baseline and controlled engine emissions mean, expressed as a percent of the baseline emission value;

Note that σ_1, σ_2, and δ, are expressed as percentages of the baseline emission. This transformation was used to simplify the equation and allow its use for Table 1. For Table 1, the baseline emission value was chosen as the 1990 EPA certification value. The parameter 'z' is tabulated under different names in statistics reference texts. It is the 'z' value corresponding to 'the tail area of the unit normal distribution' in Box, Hunter, and Hunter (1978). In the Standard Mathematical Tables (CRC, 1968), 'z' is known as 'x', and the tail area is labeled '1 - F(x)', where F(x) is the cumulative distribution function of a standardized normal random variable. To obtain the value of 'z' from the statistical tables, α (or β) is the probability (ranging from 0.5000 to 0.0000) in the body of the table, and 'z' is read (or interpolated) from the appropriate column and/or row, ranging from 0.00 to 4.00 over that

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range. The value 'z' can be calculated within an EXCEL® or QUATTRO PRO® spreadsheet as the absolute value of the function returning the inverse of the standard normal cumulative distribution, NORMSINV(probability), by setting probability equal to α or β, as appropriate.

Table B-1 gives a step-by-step calculation example drawn from Table 1 for a 90% probability ($\beta = 0.10$) of detecting a 5% and a 50% emission reduction at the 95% confidence level ($\alpha = 0.05$).

Table B-1. Example calculation of minimum number of ETV tests.

	Table 1, Col.1	Table 1, Col. 3
Emission reduction relative to baseline (certification) emission, δ, %	5	50
Known measurement variability at specified emission reduction, σ_2, %	2	3
Known measurement variability for baseline engine, σ_1, %	2	2
α	0.05	0.05
z_α	1.645	1.645
β	0.10	0.10
z_β	1.282	1.282
$(\sigma^2_1 + (1 - \delta/100)^2 \cdot \sigma^2_2) / \delta^2$	0.304	0.0016
$(z_\alpha + z_\beta)^2 (\sigma^2_1 + (1 - \delta/100)^2 \cdot \sigma^2_2) / \delta^2$	2.61	0.014
Number of tests required[a], n	3	1[a]

Note: [a] The minimum number of ETV tests is three. If 'n' is less than three, 'n' equals three.

Substitution of the t-statistic for z in Equation B-1 implicitly violates some of the assumptions made in the derivation and is therefore not strictly valid. An iterative calculation results, and it may not converge. However, it does provide a number of tests estimate that is larger and closer to the result of the population statistics confidence interval described in Section 5.1.2.

References for Appendix B

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APPENDIX C: SENSITIVITY OF NUMBER OF TESTS CALCULATION TO MEASUREMENT VARIABILITY

Table C-1 presents the results of a sensitivity analysis of the calculation of the required number of tests in the particular cases of high (85%) and low (10% and 5%) reductions in emissions. The number of tests reported in the final column is the number required to have a 90% probability of detecting the emissions reduction with 95% confidence. The equation in Appendix B was used to compute the required number of tests. As in these sections, all calculations utilize the normal distribution under the assumption that the test measurement error is known and constant.

Within Table C-1, the variability of the baseline engine measurement ranges from 2 to 30%, and the controlled engine measurement variability from 10 to 30%. All of the percentage numbers in the table are referenced to a baseline engine emission. To convert the percentages to an absolute emission rate, they must be multiplied by a baseline engine emission rate, and at 30% variability the standard deviations are twice the emission rate in g/bhp-hr. The emissions and standard deviations in Table C-1 have all been calculated for a baseline engine emitting PM at the 1990 certification level of 0.6 g/bhp-hr. For example, from the first row, an 85% reduction means an absolute PM emission of 0.09 g/bhp-hr. A 10% controlled engine measurement variability means the standard deviation for that measurement is 0.06 g/bhp-hr. For the baseline engine, the variability is 2%, so the baseline engine standard deviation is 0.012 g/bhp-hr. The same approach can be used to make a similar table for any other emission rate by multiplying the percentages by the desired baseline emission rate.

While the number of required tests increases as the test variability increases, Table C-1 shows that the increase is modest at high emissions reduction levels. While higher variability is expected at higher levels of control because the absolute emissions concentrations are low, the large reduction in emissions is easily detected.

On the other hand, lower variability is expected for low emissions reductions, but the smaller changes are harder to detect and more tests are required. Therefore even modest variability levels (relative to those in the top block of Table C-1) lead to very large numbers of tests.

As was discussed in Section 5.1.2, calculation of the confidence intervals on the mean emissions reduction will be based on population statistics and will utilize the t-distribution. Thus the number of tests calculated using Equation B-1 (population statistics) may be fewer than will be required by the data itself based on sample statistics. As mentioned in Appendix B, an approximate calculation can be made for sample variability utilizing the Student's t-distribution rather than the normal (z-distribution) in Equation B-1. This use of Equation B-1 is not strictly valid, but may be useful for low emission reduction and/or high variability test designs to make a better estimate of the number of tests required.

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Table C-1. Sensitivity of number of tests to measurement variability

Expected emissions reduction, %	Controlled engine emissions, g/bhp-hr, relative to a baseline engine at the 1990 PM certification emission limit	Controlled engine variability, % of baseline engine	Controlled engine standard deviation, g/bhp-hr for baseline emission of 0.6 g/bhp-hr	Baseline engine variability, %, with the 1990 certification limit as baseline	Baseline engine standard deviation, g/bhp-hr, for1990 emission limit baseline emission of 0.6 g/bhp-hr	Number[a] of tests to achieve 90% probability of detecting reduction with 95% confidence
85	0.09	10	0.06	2	0.012	1
85	0.09	15	0.09	2	0.012	1
85	0.09	20	0.12	2	0.012	1
85	0.09	30	0.18	2	0.012	1
85	0.09	10	0.06	10	0.060	1
85	0.09	15	0.09	10	0.060	1
85	0.09	20	0.12	10	0.060	1
85	0.09	30	0.18	10	0.060	1
85	0.09	10	0.06	30	0.150	2
85	0.09	15	0.09	30	0.150	2
85	0.09	20	0.12	30	0.150	2
85	0.09	30	0.18	30	0.150	2
10	0.54	2	0.012	2	0.012	1
10	0.54	4	0.024	4	0.024	3
10	0.54	6	0.036	6	0.036	6
10	0.54	8	0.048	8	0.048	10
10	0.54	10	0.06	10	0.060	16
5	0.57	2	0.012	2	0.012	3
5	0.57	4	0.024	4	0.024	11
5	0.57	6	0.036	6	0.036	24
5	0.57	8	0.048	8	0.048	42
5	0.57	10	0.06	10	0.060	66

Note: [a] For ETV, the minimum number of tests is three.

Item E 000076

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September 2003

Environmental Technology Verification Protocol

DETERMINATION OF EMISSIONS REDUCTIONS OBTAINED BY USE OF ALTERNATIVE OR REFORMULATED LIQUID FUELS, FUEL ADDITIVES, FUEL EMULSIONS, AND LUBRICANTS FOR HIGHWAY AND NONROAD USE DIESEL ENGINES AND LIGHT DUTY GASOLINE ENGINES AND VEHICLES

Prepared by:

RTI INTERNATIONAL

Under a Cooperative Agreement with

U. S. Environmental Protection Agency

ETV ETV ETV

Revision No.: 03
Date: September 2003

GENERIC VERIFICATION PROTOCOL FOR DETERMINATION OF EMISSIONS REDUCTIONS OBTAINED BY USE OF ALTERNATIVE OR REFORMULATED LIQUID FUELS, FUEL ADDITIVES, FUEL EMULSIONS, AND LUBRICANTS FOR HIGHWAY AND NONROAD USE DIESEL ENGINES AND LIGHT DUTY GASOLINE ENGINES AND VEHICLES

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ABBREVIATIONS AND ACRONYMS

APCT	air pollution control technology
APCTVC	Air Pollution Control Technology Verification Center
BSFC	brake-specific fuel consumption
CARB	California Air Resources Board
CBI	confidential business information
CFR	Code of Federal Regulations
CI	confidence interval
CO	carbon monoxide
CO_2	carbon dioxide
CTM	conditional test method
DEC	diesel exhaust catalyst
DQO	data quality objective
EGR	exhaust gas recirculation
EPA	Environmental Protection Agency
ETV	Environmental Technology Verification Program
FM	fuel modification
FTIR	Fourier transform infrared
FTP	federal test procedure
g/bhp-hr	grams per brake horsepower-hour
g/kWh	grams per kilowatt-hour
GVP	generic verification protocol
HAP	hazardous air pollutant
HC	hydrocarbon
HHD	heavy-heavy duty
hp	horsepower
LDV	light duty vehicle
LHD	light-heavy duty
MHD	medium-heavy duty
MIL	maintenance indicator light
NH_3	ammonia
NMHC	non-methane hydrocarbon
NO_X	nitrogen oxides
OBD	on-board detection
OEM	original equipment manufacturer
ORD	Office of Research and Development
OTAQ	Office of Transportation and Air Quality
PCV	positive crankcase ventilation
PM	particulate matter
ppm	parts per million
QA	quality assurance
QC	quality control
QMP	quality management plan
RFG	reformulated gasoline
RTI	Research Triangle Institute
SAC	stakeholders advisory committee
SCR	selective catalytic reduction

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SET	Supplemental Emissions Test (40 CFR 86.1360)
SOP	standard operating procedure
ULSD	ultralow sulfur diesel
VDRP	Voluntary Diesel Retrofit Program
VOC	volatile organic compound

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1.0 INTRODUCTION

This protocol describes the Environmental Technology Verification (ETV) Program's considerations and requirements for verification of emissions reduction provided by fuel and lubricant technologies. For purposes of this protocol, all such technologies will be identified as fuel modifications (FMs). The basis of the verification will be comparison of the emissions and performance of well-maintained, conventionally fueled (or lubricated) engines or vehicles to the same engines or vehicles with FMs. The protocol applies to diesel- and gasoline-fueled engines and light-duty vehicles in mobile source applications and describes the requirements for a single engine or vehicle ETV having narrow application and for a multiple engine or vehicle ETV to evaluate fleet-wide emissions reductions.

ETV provides verified emissions reduction data for FM technologies. It may be part of an overall process that leads to inclusion of FMs on the U.S. Environmental Protection Agency (EPA) mobile sources retrofit emissions reduction verified technology list. This protocol describes the ETV portions of that process in detail. Table 1 provides an overview of mobile source FM ETV and its interface with the EPA retrofit emissions reduction program.

Table 1. Overview of Mobile Source ETV Process and Participants' Responsibilities

Step in Process	Applicant	ETV		EPA-OTAQ[b]	EPA-ORD[c]
		APCTVC[a]	Testing Org.		
Preparation of preliminary application (without ETV data)	Primary	None	None	Advise	Access
Preliminary test dialog	Participate	Organize & participate	Participate	Participate	Access
Test/quality assurance (QA) plan	Review	Shared preparation, APCTVC approve		Review	Review & approve
Acceptance of ETV test/QA plan, and terms and payment	Primary	Advise	Advise	Access	Access
Conduct ETV test	Access	Audit	Primary	Access	Audit
Prepare test report	Access	Review	Primary	Access	Access
Publish ETV report & statement	Review	Primary	Review	Access	Review & approve

[a] APCTVC = Air Pollution Control Technology Verification Center at RTI.
[b] EPA-OTAQ = EPA's Office of Transportation and Air Quality.
[c] EPA-ORD = EPA's Office of Research and Development, the ETV sponsor.

1.1 Environmental Technology Verification

EPA through its Office of Research and Development (EPA-ORD) has instituted the ETV Program to verify the performance of innovative and improved technical solutions to problems that threaten human health or the environment. EPA created the ETV Program to accelerate the entrance of new and improved environmental technologies into the marketplace. It is a voluntary, nonregulatory program. Its goal is to verify the environmental performance characteristics of commercially ready technologies through the evaluation of objective and quality-assured data so that potential purchasers and permitters are provided with an independent and credible assessment of what they are buying and permitting.

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The ETV Program does not conduct technology research or development. ETV test results are always publicly available, and the applicants are strongly encouraged to ensure prior to beginning an ETV test that they are satisfied with the performance of their technologies. Within the ETV Program, this state of development is characterized as "commercially ready."

The provision of high-quality performance data on a commercial technology encourages more rapid implementation of that technology and consequent protection of the environment with better and less expensive approaches. The ETV Program is conducted by seven ETV centers that span the breadth of environmental technologies.

1.2 Air Pollution Control Technology Verification Center

EPA's partner in the Air Pollution Control Technology Verification Center (APCTVC) is RTI International,[1] a nonprofit contract research organization with headquarters in Research Triangle Park, NC. The APCTVC verifies the performance of commercially ready technologies used to control air pollutant emissions. The emphasis of the APCTVC is currently on technologies for controlling particulate matter (PM), volatile organic compounds (VOCs), nitrogen oxides (NO_X), and hazardous air pollutants (HAPs) from both mobile and stationary sources. The activities of the APCTVC are conducted with the assistance of stakeholders from various interested parties. Overall, APCTVC guidance is provided by the Stakeholders Advisory Committee (SAC), whereas the detailed development of individual technology ETV protocols is conducted with input from technical panels focused on each technology area.

The APCTVC develops generic verification protocols and specific test/quality assurance (QA) plans, conducts independent testing of technologies, and prepares ETV test reports and statements for broad dissemination. Testing costs are ultimately borne by the technology applicants, although initial tests within a given technology area may be partially supported with government funds.

1.3 The APCTVC Mobile Sources Verification Program

The various retrofit technologies have been divided into three groups to facilitate ETV:

- Retrofit diesel mobile source control devices,
- FMs, and
- Selective catalytic reduction (SCR) devices.

Retrofit mobile diesel control devices include exhaust treatment emission control devices, other retrofit devices, and engine modifications. Some require no mechanical changes to engines, whereas others will involve some modification of the engine or its control system. Filters for PM control and diesel exhaust catalysts (DECs) may make use of or require some integration with engines. Engine modifications, in this context, refer to pollution reduction technologies integral to the engine or the engine control systems. All these technologies have the potential to affect engine performance, and the concurrence of the engine manufacturer that the changes are compatible with safe, efficient, and reliable operation in the engine is an important element in demonstrating commercial readiness and suitability for ETV. ETV of these technologies is guided by *Generic Verification Protocol for Diesel Exhaust Catalysts, Particulate*

[1]RTI International is a trade name of Research Triangle Institute.

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Filters, and Engine Modification Control Technologies for Highway and Nonroad Use Engines (RTI, 2002).

SCR NO_X control technologies are also retrofit technologies, but they require more integration with the controlled engine than most other retrofit devices and therefore are being treated as a separate category (for which a separate verification protocol is being developed).

This generic verification protocol (GVP) provides the requirements for APCTVC's verification of the performance of FMs applied to mobile source diesel and gasoline engines. Other organizations (e.g., EPA's Office of Transportation and Air Quality [EPA-OTAQ] and the California Air Resources Board) also verify the performance of FMs under different protocols to meet the needs of those organizations. The technology applicant should discuss the intended application of the FM with EPA-OTAQ to determine the most suitable path for verification.

This GVP is intended to apply only to FMs. The APCTVC reserves the right to evaluate each technology submitted for verification and to determine the applicability of this protocol to that specific technology. Regulatory authorities (EPA-OTAQ and others) may also have requirements. Special testing may be required in some cases to maintain the integrity and credibility and, therefore, the value of verifications. The critical data quality objectives (DQOs) in this document were chosen to provide emissions measurements sufficient to support the vendor's application for emissions credits under the Voluntary Diesel Retrofit Program (VDRP).

This protocol was developed and has been reviewed by a technical panel composed of a broad group of stakeholders who have expertise in mobile source controls and come from the vendor, user, and regulatory spheres. Technical panel membership is dynamic, and its composition is expected to change over time as technical emphases change. The APCTVC will maintain membership balance on the panel.

The basic FM verification will measure and report baseline emissions concentrations and rates using the Federal Test Procedures (FTPs) applicable to a particular engine or vehicle on a baseline fuel compared to that same engine or vehicle using the FM. The test requirements will differ depending on whether the FM provides its full emissions reduction immediately (immediate-effect FM) or requires operation for some period of time to reach full effect (cumulative-effect FM). The engines or vehicles required to be tested will depend on the intended use and applicability of the FM. The tests will be conducted at an independent, third-party testing organization that has been qualified and audited by the APCTVC. The data quality requirements of this GVP will be applied at approved testing organizations through the preparation of an FM-specific test/QA plan. Other laboratory-, application-, or technology-specific information may also need to be addressed in the test/QA plan, which is described in Section 10.0. Because specific technology areas may require special expertise or emphasis, input and review will be obtained from an ad hoc subcommittee of the technical panel and/or outside experts when deemed appropriate by the APCTVC. Test results will be presented as ETV reports and statements.

This generic protocol will be revised as necessary. Changes to the protocol will not affect products that have been verified. However, such changes will be reflected in test/QA plans not yet finalized regardless of the applicant's application status. Test/QA plans that are being carried out when a protocol change is enacted will be examined to determine whether any modifications must be made.

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1.4 Quality Management

Management and testing in the APCTVC program are performed in accordance with procedures and protocols defined by the following:

- EPA's ETV Quality and Management Plan (QMP) (U.S. EPA, 2002a or the QMP current at time of testing);
- APCTVC Quality Management Plan (RTI, 1998);
- *Generic Verification Protocol for Determination of Emissions Reductions Obtained by Use of Alternative or Reformulated Liquid Fuels, Fuel Additives, Fuel Emulsions, Lubricants, and Lubricant Additives for Highway and Nonroad Use Diesel Engines and Light Duty Gasoline Engines and Vehicles* (this document); and
- Test/QA plan prepared for each FM test or group of tests.

EPA's ETV QMP lays out the definitions, procedures, processes, interorganizational relationships, and outputs that will ensure the quality of both the data and the programmatic elements of the ETV Program. Part A of the ETV QMP contains the specifications and guidelines that are applicable to common or routine quality management functions and activities necessary to support the ETV Program. Part B of the ETV QMP contains the specifications and guidelines that apply to test-specific environmental activities involving the generation, collection, analysis, evaluation, and reporting of test data.

The APCTVC QMP describes the quality systems in place for the overall APCTVC. It was prepared by RTI and approved by EPA. Among other quality management items, it defines what must be covered in the GVPs and test/QA plans for technologies undergoing ETV testing.

Generic Verification Protocols are prepared to describe the general procedures to be used for testing a type of technology and to define the critical DQOs. The GVPs for retrofit air pollution control technologies for highway and nonroad use engines were written by the APCTVC with input from a technical panel and approved by EPA.

A test/QA plan is prepared for each test or group of tests. The test/QA plan describes, in detail, how the testing organization will implement and meet the requirements of the GVP. The test/QA plan also sets DQOs for any planned measurements that were not set in the GVP for a particular technology. The test/QA plan addresses issues such as the testing organization's management structure, the test schedule, test procedures and documentation, analytical methods, recordkeeping requirements, and instrument calibration and traceability, and it specifies the QA and quality control (QC) requirements for obtaining ETV data of sufficient quantity and quality to satisfy the DQOs of the GVP. Testing organizations will be audited by the APCTVC against the approved GVP and test/QA plan they are expected to follow. Section 10 of this GVP addresses requirements for the test/QA plan.

Because multiple testing organizations may be conducting the tests, the APCTVC will develop a prototype test/QA plan (not part of this GVP) for each type of technology to ensure comparability. This prototype will be customized by the testing organization to meet its specific implementation of the FTPs as defined in 40 Code of Federal Regulations (CFR) Parts 86 and 89, and the secondary measurements, subject to approval by the APCTVC and EPA-ORD. Testing arrangements that do not meet the requirements of the FTP will not be approved, and test instrumentation or test procedures that the APCTVC determines will compromise data reliability or comparability between testing organizations will not be approved.

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2.0 OBJECTIVE AND SCOPE

2.1 Objective

The objective of this GVP is to establish the parameters within which FMs to diesel or gasoline engines will be tested to verify their emissions control performance with uniform and consistent methods.

2.2 Scope

This protocol describes the considerations and requirements for ETV of emissions reduction by FMs. The FMs to which it applies are

- Alternative diesel and gasoline fuels,
- Reformulated diesel and gasoline fuels,
- Additives to standard diesel and gasoline fuels,
- Alternative lubricants for diesel- and gasoline-fueled engines, and
- Lubricant additives and systems for diesel- and gasoline-fueled engines.

Although FMs may achieve similar emissions reductions on many engines, each ETV test is conducted on and reported for the actual test conditions: engine (vehicle), base fuel, and FM test conditions. The base engine (vehicle) will be well maintained and will produce emissions at levels consistent with a well-maintained engine (vehicle) of its age and use. FMs may be combined with other technologies for verification testing as a single entity emissions control system. Before systems can be accepted for verification,

- the controlling interests in each technology must be in agreement to pursue ETV (in this context, low sulfur diesel fuels are considered commodities available to all, not technologies, and therefore no permission is required),
- the applicant must be a single organization with authority to pay for the applicant's cost, and
- the applicant must show that each component of the system has a credible impact on emissions.

Verification testing for a system will incorporate into the test/QA plan elements from the protocols applicable to the individual technologies. In general, the test for a system will include the more stringent aspects of each protocol where they differ. Each test may be different, and the APCTVC should be consulted for assistance.

For purposes of ETV, the emission reduction effects of FMs are classified as either of two types:

1. Immediate effect—FMs whose emissions reduction effect is immediate for a well-maintained, base-fueled engine. No long-term residual effect is expected from an immediate-effect FM. The applicant agrees and the test confirms that reproducible results can be obtained for both the base and FM fuels on the same engine with an alternating fuel test pattern, allowing only for fuel flushing and a brief stabilization period (as many as three preconditioning cycles [EPA Urban Dynamometer Driving Schedule 40 CFR 86.132-90] for a light duty vehicle (LDV) and 1 hour of engine operation for a diesel) between tests.
2. Cumulative effect—FMs that require more than 10 hours of engine operation for a diesel or 500 miles of driving for a LDV on the FM for the product to reach its full effectiveness. Cumulative-effect FMs are expected to have residual effects on the test engine, and repeated base-fueled tests

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separated by FM tests would not be meaningful. Return to base fuel emissions rates is expected only after an extended period of operation or manual cleaning and rebuild.

FMs may be evaluated based on either of these categories. The applicant's requests and the product's performance mechanism will be considered. For example, an applicant may have a fuel additive that reaches its full potential only after an extended period of time, but the applicant may prefer to evaluate the additive with the immediate-effect procedure. The applicant must recognize and accept the implied liability for selecting the appropriate test program.

Emissions testing under this protocol is based on the FTPs for emissions certification of diesel highway engines (40 CFR Part 86), diesel nonroad engines (40 CFR Part 89), and light duty gasoline engines (40 CFR Part 86). For diesel nonroad engines, emissions testing under this protocol will also include the nonroad transient test cycle as published in the NPRM (Notice of Proposed Rulemaking) for "Control Emissions of Air Pollution from Nonroad Diesel Engines and Fuel" on May 23, 2003. (New test procedures become standardized and are incorporated into the FTPs from time to time. Verifications are to be conducted under the current applicable FTP.)

2.3 Applicability

2.3.1 Applicability of ETV Results to Other Engines and Engine Families

The basic ETV test remains the same for all FMs and engines; however, the FMs may interact differently with the various engines. The extension of emissions reductions from one engine or engine family to another requires engineering analysis of the data and may require additional testing. Determination of the applicability of single-engine tests to other engines is an EPA-OTAQ decision and not part of ETV.

2.3.2 Relationship of ETV Program to EPA-OTAQ VDRP Verified Technology List

EPA-OTAQ is charged with establishing a verified list of technologies capable of providing emissions reductions. The test results EPA-OTAQ will use to evaluate a technology may be generated following the ETV process, with the ETV report and verification statement submitted by the vendor as the data package to EPA-OTAQ. Other paths to the verified technology list also exist. The VDRP program is described and appropriate contacts are identified at http://www.epa.gov/otaq/retrofit/. The technology applicant should discuss the intended application of the technology with EPA-OTAQ to determine the most suitable evaluation path for the applicant's technology.

2.3.3 Assignment of Emissions Benefits to FMs

The emissions from engines vary as engines age and progress through the cycle of routine maintenance. The intent of ETV under this GVP is to determine the emissions reductions provided by FMs, exclusive of oil and filter changes, engine tune-ups, and similar scheduled maintenance that, by themselves, may provide emissions benefits. Emissions benefits may also accrue from tuning an engine to lower power output or other operating points different from those recommended by the engine manufacturer. The ETV test will be designed to isolate the effects of the FMs from coincident engine adjustments and tune-ups to the extent possible. Baseline engines will be tuned and set to the engine manufacturer's recommendations, and the baseline emissions are expected to be consistent with the age and usage history of the engine (near certification levels for diesel engines; in conformance with the expected model year standard for gasoline vehicles).

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Engine modifications may be appropriate for particular FMs that have different energy contents than standard fuels, and these will be implemented on the required test engines provided they are part of the description of the FM as a single technology.

2.4 Data Quality Objectives

The data of primary interest in this verification are the reduction in emissions of the FTP primary pollutants: NO_X, hydrocarbons (HCs), PM, and carbon monoxide (CO). The DQOs of this GVP are the requirements of the test methods specified in 40 CFR Part 86 (light duty gasoline and diesel highway engines) or 89 (nonroad diesel engines) when conducting the number and type of FTP tests called for by the approved test/QA plan for the FM. ETV tests that do not meet the FTP QA requirements are invalid.

The number and type of FTP tests (cold- and/or hot-start) required for ETV is determined from the following criteria:

First, a minimum of three tests is required to provide the basic ETV result of a mean emission reduction and the 95% confidence interval on that mean based on measured variability for each of the measured emissions and test parameters. For highway engines this minimum is satisfied with one cold start test and three hot start tests. For nonroad engines three replicates of the appropriate test sequence (i.e., three 8-mode tests, or three 6-mode tests) are required. A three test minimum is currently the same as is required by the State of California for its program.

Second, additional tests may be required to meet the ETV requirement that the test/QA plan provide a 90% probability of detecting the expected emissions reductions when computed using the expected experimental errors for the various measurements. These criteria become controlling for low emissions reductions and/or high test variability. This is a planning requirement for the test/QA plan. The procedure to determine the appropriate number of tests is given in Appendix B.

Third, additional tests may be desired by the applicant to reduce the width of the 95% confidence interval on the mean emission reduction. Section 5 provides additional explanation and example scenarios. This third criterion is a consequence of applying standard statistical procedures to the ETV test design and data analysis. At a fixed measurement variability, normal statistical procedures lead to a small number of tests giving a broader 95% confidence interval than a larger number of tests. To any regulator or potential technology user, an emission reduction of 40% ± 5% is better than 40% ± 20% and will be given more credence.

Noncritical measurements, including carbon dioxide (CO_2) emissions, fuel utilization, and power, will also be made as described in later sections. These are not considered critical, and the methods and DQOs will be stated in the test/QA plan.

The FTP tests referenced above are conducted following test cycles specified in 40 CFR. As discussed in Section 5, other test cycles may also be required for verification of an FM. A single test data set would consist of a single FTP test cycle and any other special cycle required for the FM. The requirements for the emissions tests remain the same in both cases.

An applicant may conduct privately sponsored tests at a testing organization for development purposes with the same test engine prior to or after conducting verification tests. Such testing is understood to be

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common and important to ensure the technology is properly adjusted and tuned to the application. The ETV data quality objectives do not apply to privately sponsored testing. However, the applicant and testing organization must coordinate the entire testing effort with the APCTVC so that:

- Preparation for the ETV test (submittal of the technology to the APCTVC, discussion of engine selection, and preparation of the test/QA plan) is completed prior to conducting the ETV test itself;
- The APCTVC is notified of the ETV test dates in time to schedule QA activities at the discretion of the APCTVC; and
- Declaration of the test run that is to be the ETV test is made prior to starting the test, the engine must be brought to a starting point in accordance with the test/QA plan, and the results of that test are documented and reported in accordance with the test/QA plan.

An applicant may desire to run the base-fueled ETV test, conduct private developmental testing, and then complete the ETV tests following the private testing. This approach may be acceptable provided the base-fueled run is considered to remain valid for the duration of and for the activities that occur during the private testing. If not, the base-fuel case will have to be rerun.

The data from all ETV tests will be retained and reported to the APCTVC, including invalid FTP test results. Data that meet the QA requirements of the FTP are considered valid and will be used to compute emissions reductions for ETV purposes.

The FM emissions reduction performance will be reported as both absolute emissions in the appropriate units (per applicable FTP) for the base-fueled and FM-fueled cases, and as percentage emissions reduction for a specific engine or engine family. The percentage emissions reduction reported will be the mean emissions reduction (relative to the baseline emission) with attendant upper and lower 95% confidence limits on that mean.

3.0 ETV RESPONSIBILITIES

The primary responsibilities for each organization involved in the FM ETV verification program were summarized in Table 1. Additional comments are provided below:

- The technology applicant provides the complete, commercially ready product for ETV testing, and logistical and technical support, as required, during the ETV testing. The applicant's responsibilities are defined by a contract or letter of agreement with the APCTVC (RTI.) The preliminary application (Table 1, Row 1) provides relevant background data and technology information to facilitate test/QA plan development. The applicant must pay the portion of the verification cost required at the time its contractual relationship with the APCTVC begins.
- In addition to the items in Table 1, the APCTVC prepares the GVP (this document); qualifies, approves, and audits the testing organization; provides a template for test/QA plans; prepares the ETV reports and statements from the laboratory test reports; and, jointly with EPA-ORD, reviews and approves the ETV reports and statements.
- Qualified testing organizations conduct ETV verifications under contract to the APCTVC. The order of activities in Table 1 is mandatory, with the test/QA plan being prepared and approved before testing. The testing organization also conducts internal QA on test results and reports.

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4.0 APPLICATION AND TECHNOLOGY DESCRIPTION

The ETV applicant is the basic source of information regarding its technology, information which is provided to the APCTVC and EPA-OTAQ through an application form. This information is used by the testing organization and APCTVC to prepare and review a test/QA plan that meets the requirements of the applicant and by EPA-OTAQ and other users to verify data. In keeping with the voluntary nature of ETV, the applicant must control the technology within the United States to submit it for verification.

For the applicant's convenience, the application form used by the EPA-OTAQ retrofit program can also be used for ETV. The applicant should complete as much of the form as possible and submit it to OTAQ and the APCTVC. ETV will provide test data that will allow completion of the form for submission to EPA-OTAQ and participation in the VDRP. The form can be obtained from the APCTVC and is also posted on the EPA-OTAQ retrofit website at http://www.epa.gov/otaq/retrofit/retrofittech.htm. Both Microsoft Excel and Lotus 123 versions are provided. Alternatively, an applicant who is not participating in the VDRP can use the APCTVC's shorter general application form.

The VDRP application consists of four worksheets: (1) Manufacturer Information, (2) Product Information, (3) Test Information, and (4) Component Information. There is a separate spreadsheet containing directions and examples for completing the forms. This guidance document begins with a page of general instructions for the entire form. Since no general form can anticipate the data requirements for all possible FMs, the applicant should use the applicable portions of the form. Additional information will be requested to supplement this form if needed.

The mobile sources ETV program is intended to provide independent and quality-assured performance data to potential users of technologies through a documented public process. Existing data (whether Confidential Business Information [CBI] or not) cannot be used to substitute for ETV tests, although they can be used to help design the ETV test. The ETV documents (protocol, test/QA plans, reports, and verification statements) are publicly available. For these reasons, the submittal of CBI to the APCTVC is unlikely to be necessary. The application form **is not** intended to convey CBI to the APCTVC and none should be included in the form. Any applicant who believes that CBI is required to provide input to the ETV process should explain that belief in a cover letter to the APCTVC. It should be noted that all information submitted on the application is subject to the Freedom of Information Act.

4.1 Manufacturer Information

This first page of the application requests background and contact information for the applicant who is seeking product verification. Guidance and examples supporting its use are provided on the second page of the guidance form.

4.2 Fuel Modification Descriptive Information

The second page of the application is used to describe the FM fully and concisely. It will be used to prepare the test/QA plan and as a more complete description of the technology in the ETV report. It requires a concise (300-word or less) description of the FM being verified and requests a number of operating details that summarize the emissions control performance expected, along with the product's operation. All questions may not apply. Instructions for completing this page can be found in the "Explan_Prod" page of the guidance document.

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In the case where combinations of independent technologies are being submitted for verification, the description of the combined technology should completely identify and describe those technologies being combined and fully state the nature of the combined test and expected result.

4.3 Test Information

Results of verification testing on the applicant FM are to be detailed on the third sheet of the application form. Completion of this page is not required for application to the APCTVC for verification of a technology because the verification itself will be providing the test results. However, the applicant is encouraged to report all available test data, which can be used by the APCTVC to better plan the ETV test program for the applicant's technology. These existing test data will not be included in the verification report. The Explan_Tests page of the guidance document provides information for completing this page.

4.4 Component Information

The last page of the application form, Component Information, lists the major components of the technology system. For fuels and fuel additives, it is expected that few components will need to be listed here, although for combined systems this will be an important document. Directions are given in the Explan_Components page of the guidance.

5.0 ETV TESTING

This section gives the test requirements for verification of FMs. It also describes reduction of the data to produce the emissions reduction measures that are the product of the tests. Section 5.1 gives an overview of the testing and data analysis as it applies to all FMs. Section 5.2 gives ETV testing details for FMs intended for use in diesel engines. Section 5.3 gives the detailed test requirements for ETV of FMs intended for use in gasoline vehicles and engines. Section 5.4 gives detailed test requirements for ETV of lubricants.

5.1 Test Design and Data Analysis for ETV of FMs

5.1.1 Overview of Testing Requirements

The data of primary interest in this verification testing are the reduction in emissions of NO_X, HC, PM, and CO. Emissions reductions are defined as the percentage reduction obtained between a base case and the FM candidate case or the natural log equivalent. For all engine and vehicle types, emissions measurements are made using the FTP certification test cycles applicable to the engine or vehicle for which the FM is intended. Additional special test cycles are sometimes also required in addition to the FTP certification test. The details of the tests are different for different engines and vehicles and are given below.

A simple test of an engine without a control device installed followed by one with the device installed is not considered to be adequate for all FM ETVs. Emissions from engines or vehicles may increase over their service life, particularly for gasoline-fueled engines or vehicles. FMs may require significant service life to have their full effect. These characteristics require that the ETV test for FMs be designed to provide emissions reductions with a changing baseline emission.

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Testing conducted under this protocol utilizes individual FTP and special tests that measure emission rates, *E*, of various pollutants. Replicate tests are conducted at a particular test point in the service life of an engine or vehicle, fueled or lubricated by either the base or the FM candidate. The FTP and special tests are combined to give a combined emissions rate for each pollutant. The complete ETV test sequence includes several test points, each of which gives a combined emissions rate for either the base engine or the candidate FM engine. The combined emissions rates from all valid data are then used to estimate the emissions reduction, *ER*, for each pollutant.

The requirements for testing diesel and gasoline FMs for immediate and cumulative effects in highway and nonroad diesel applications will be discussed in greater detail in the following sections. Table 2 summarizes the tests required at each test point in the test sequence.

ETV provides engine emissions reductions from which EPA-OTAQ or others estimate fleet emissions reductions. Estimation of fleet-wide emissions reductions from single engine emissions reductions requires knowledge of the composition of the entire fleet, identification of the number and kind of representative engines or vehicles, and numerous other assumptions. All of these considerations factor into the experimental design. Making these assumptions is uniquely the responsibility of the agency evaluating the data.

Table 2. Summary of Tests Required at Each Test Point

Type	Effect	Engine	Sequence of Test Points[1]	Tests at Each Point[2]	Reference
Diesel FMs	Immediate	Highway	BCCB or BCBC	(Cold + 3 hots + SET)	5.2.3.4, 5.2.4.1
Diesel FMs	Immediate	Nonroad	BCCB or BCBC	3 (multi-mode steady-state) + NTTC[3]	5.2.3.4, 5.2.4.1
Diesel FMs	Cumulative	Highway	BBBBCCBB	(Cold + 3 hots + SET)	Fig. 1, 5.1.3.4
Diesel FMs	Cumulative	Nonroad	BBBBCCBB	3 (multi-mode steady-state) + NTTC	Fig. 1
Gasoline FMs	Immediate	Highway	BCCB	3 (Cold + hot + US06)[4]	5.3.3.2, 5.3.4
Gasoline FMs	Immediate	Nonroad	BCCB	3 (multi-mode steady-state)	5.3.3.2, 5.3.4
Gasoline FMs	Cumulative	Highway	BBBBCCBB	3 (Cold + hot + US06)[4]	5.3.3.2, 5.1.3.4
Gasoline FMs	Cumulative	Nonroad	BBBBCCBB	3 (multi-mode steady-state)	5.3.3.2, 5.1.3.4
Lubricant FM	*(diesel)*	Highway	BBBBCCCCBBBB	(Cold + 3 hots + SET)	Fig. 2, Table 7
Lubricant FM	*(diesel)*	Nonroad	BBBBCCCCBBBB	3 (multi-mode steady-state) + NTTC	Fig. 2, Table 7
Lubricant FM	*(gasoline)*	Highway	BBBBCCCCBBBB	3 (Cold + hot + US06)	Fig. 2, Table 7
Lubricant FM	*(gasoline)*	Nonroad	BBBBCCCCBBBB	3 (multi-mode steady-state)	Fig. 2, Table 7

[1] B = Baseline condition; C = Candidate technology.
[2] Minimum requirement. When emissions reductions are expected to be low, more tests may be required to achieve the 95% confidence interval.
[3] Nonroad transient test cycle.
[4] Highway fuel economy test, cold CO, and evaporative emissions testing will be required on any FM that may reasonably be expected to affect fuel volatility.

5.1.2 Test Design Requirement for Single Engine Verification

Minimizing the cost of ETV testing is important, and limiting the amount of testing required is one way to lower costs. However, if too few tests are conducted, normal experimental variability could prevent the ETV from finding a significant result. All ETV test/QA plans for FMs are required to include

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sufficient tests to have a high probability of detecting the emissions reductions expected by the applicant. In addition to other requirements, each FM ETV test plan is to be designed to have at least a 90% probability of detecting the emission reductions expected by the applicant. This requirement was adopted to ensure, as much as practical, that the ETV test would accomplish the applicant's goals.

In this context, detecting means that the 95% confidence interval on the emission reduction does not include zero. (This requirement is for test design purposes and does not require that the test/QA plan be modified should actual test data show that the assumptions that went into the calculation were incorrect. However, insufficient replication can result in the inability to verify any emissions reduction and publication of an ETV report stating that a technology had no statistically significant benefit.) The test/QA plan prepared for the FM will reflect this requirement, based on the applicant's knowledge of his product and the testing organization's estimates of test variability.

At each test point, a minimum of three tests are required. More may be necessary for low emission reduction technologies. The definition of a single test depends on the technology. For diesel engines, for instance, one FTP cold start, three FTP hot starts, and one additional cycle are considered three tests when combined. Depending on the FM technology and test engine or vehicle, a complete single engine ETV may require as few as two or as many as 12 base and FM test points. Sections 5.2 (diesel engines), 5.3 (gasoline vehicles), and 5.4 (lubricants) provide the details of these requirements.

5.1.3 Analysis of Combined Emissions Data

5.1.3.1 Data analysis for single engine tests of immediate effect FMs. Immediate effect FMs produce their emission reduction as soon as they are fully flushed through the fuel system and are expected to have no residual effect. The emissions reduction can therefore be determined without concern for test engine drift or deterioration. Verification of immediate effect FMs requires a single base case test point followed closely in time by a single candidate FM test point and is very similar to that used to test retrofit devices. This section describes the data analysis procedure that will be used to calculate the emission reductions for immediate effect FMs.

The first steps are the calculation of the combined test emission results for each test and each pollutant for the base and candidate FM tests. E_B and E_F are understood to refer to a single pollutant in the equations below. Calculation of E_B and E_F from individual test results differs for diesel and gasoline engines and for LDVs and is described in the respective sections below. Once the E values for the test points are available, the sample means and standard deviations (s_B and s_F) are computed using Equations 1 and 2.

$$\overline{E_B} = \frac{\sum_{1}^{n_B} E_{B,i}}{n_B} \qquad \textit{and} \qquad \overline{E_F} = \frac{\sum_{1}^{n_F} E_{F,i}}{n_F} \tag{1}$$

where:

$\overline{E_B}$ = mean emission rate for base for a single pollutant,
$\overline{E_F}$ = mean emission rate for FM for a single pollutant,
$E_{B,i}$ = emission results for a single base (B) test for a single pollutant,
$E_{F,i}$ = emission results for a single FM (F) test for a single pollutant,

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n_B and n_F = number of base (B) and FM (F) tests, and
s_B and s_F = standard deviations of base (B) and FM (F) tests.

$$s_B = \sqrt{\sum_{1}^{n_B}\left(E_{B,i} - \overline{E_B}\right)^2 \Big/ \left(n_B - 1\right)} \quad and \quad s_F = \sqrt{\sum_{1}^{n_F}\left(E_{F,i} - \overline{E_F}\right)^2 \Big/ \left(n_F - 1\right)} \tag{2}$$

The raw emission reduction for each pollutant, ER_{RAW}, is then computed as the difference between the combined emission results for the base and candidate FM case, divided by the base case emission, as shown in Equation 3.

$$ER_{RAW} = \left(\overline{E_B} - \overline{E_F}\right) \Big/ \overline{E_B} \tag{3}$$

The upper and lower bounds of the approximate confidence interval (*CI*) around ER_{RAW} are computed using Equations 4a and 4b.

$$CI\ (upper\ bound) = ER_{RAW} + \left\{ \left(t_{\alpha/2} \bullet \sqrt{\frac{s_B^2}{n_B} + \left(1 - ER_{RAW}\right)^2 \frac{s_F^2}{n_F}} \right) \Big/ \overline{E_B} \right\} \tag{4a}$$

$$CI\ (lower\ bound) = ER_{RAW} - \left\{ \left(t_{\alpha/2} \bullet \sqrt{\frac{s_B^2}{n_B} + \left(1 - ER_{RAW}\right)^2 \frac{s_F^2}{n_F}} \right) \Big/ \overline{E_B} \right\} \tag{4b}$$

where $t_{\alpha/2}$ is $t_{0.025}$ in tables of the critical values (alternatively, tail area probability) of the t-distribution, with degrees of freedom, *v*, given by Equation 5 (rounded down):

$$v = \frac{\left[s_B^2 / n_B + \left(1 - ER_{RAW}\right)^2 s_F^2 / n_F \right]^2}{\left[\left(s_B^2 / n_B \right)^2 / \left(n_B - 1\right) \right] + \left(1 - ER_{RAW}\right)^4 \left[\left(s_F^2 / n_F \right)^2 / \left(n_F - 1\right) \right]} \tag{5}$$

The fractional values of emission reduction and the confidence intervals are converted to percentages by multiplying by 100%.

Although ER_{RAW} is the observed value of the data for the single engine tested, there is significant potential for the true emission reduction achieved in the field to be lower due to measurement errors. Therefore, an environmentally conservative discounted single engine emission reduction, ER_{DSCT}, is also reported as the lower bound of the confidence interval using Equation 6.

$$ER_{DSCT} = 100\%\ CI\ (lower\ bound\ from\ Equation\ 4b) \tag{6}$$

For example, if ER_{RAW} was 0.15 (15% emissions reduction) with a confidence interval of ± 0.05 (± 5%), ER_{DSCT} would have a value of 0.1 (10%).

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5.1.3.2 Calculation of fleet-wide emissions reductions for immediate effect FMs. For immediate effect FMs, the fleet emissions reduction (ER_{FLEET}) is computed by EPA-OTAQ for gasoline engines as the unweighted (gasoline) mean or as the weighted mean (diesel engines) of the discounted single engine emissions reductions. Emissions reductions are computed separately for each pollutant.

5.1.3.3 General treatment of cumulative effect FMs. ETV of cumulative effect FMs requires additional testing. Because the technology must be in use for an extended period to take full effect, the total duration of the testing can be long. Therefore, the base engine emissions may change as the engine/vehicle ages, or because ambient conditions change, or because test cell instrumentation requires recalibration. This situation leads to uncertainty about the cause of a measured emission change. Cumulative effect technologies also have a residual effect after use ceases. This characteristic prevents immediately re-running the baseline at the end of the test to quantify any drift.

Figure 1 illustrates the expected FM performance and testing model used in this protocol to evaluate a cumulative effect FM having residual effects on emissions. Increasing emissions with increasing service is assumed based on the known behavior of gasoline vehicles and their catalytic emissions control systems. Over the life of the vehicle, the emissions steadily increase as shown by the solid line, which represents the base case. Some of the deterioration is caused by changes in the engine, and some is caused by the emissions control system's deterioration. The slope and intercept of the deterioration line varies from gasoline vehicle to gasoline vehicle and from within and across vehicle's type and manufacturer. For the purposes of this protocol, the deterioration factor is assumed to be linear and unknown. Over the service life of diesel engines (when not controlled by catalytic systems), the deterioration factor is low and may be zero within the time frame of ETV tests. After changing to the candidate FM, the emissions are assumed to become lower. The shape of the curve during the transition is not important to this analysis.

The goal of the cumulative effects testing and data analysis is to separate the change in emissions due to the FM from the other changes. The emission reduction is assumed to be proportional to total emissions. That is, regardless of total emissions, the percent emissions reduction is assumed constant as implied by the natural log transformation of the emissions rate (vertical scale in Figure 1). As shown in Appendix C, the use of a log-scale analysis produces results nearly identical to using a percentage change in the native units when the measurement errors and effects to be detected are relatively small. The analysis is thus conceptually consistent with that for an immediate-effect FM.

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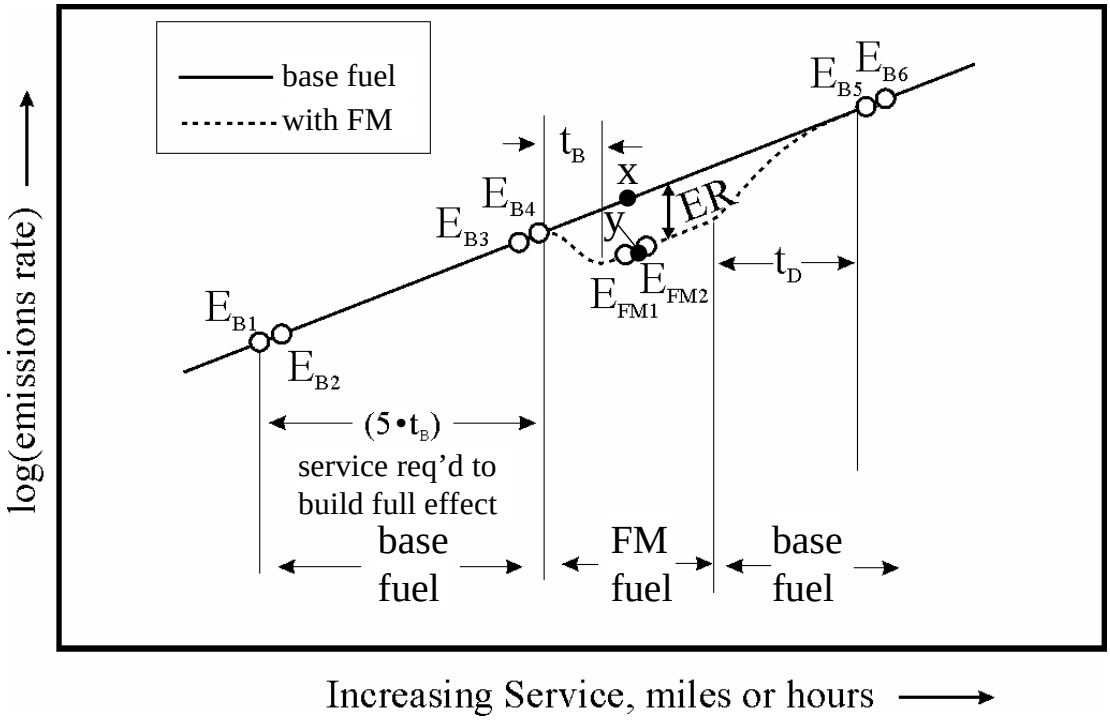

Figure 1. Performance Model and Testing for Cumulative Effects FMs

The candidate FM is assumed to be characterized by a known time for the emissions reduction to have full effect, t_B. Determining t_B is not part of this protocol and is assumed to be known and specified by the applicant. As shown in Figure 1, the test procedure requires a run-in period equal to five times t_B. The service accumulation cycle is required to be appropriate for the engine/vehicle (40 CFR 86.090-26), to be the same for both base fuel and candidate FM, and for an entire cycle to be completed before beginning a test sequence. Figure 1 shows two base case emissions test sequences carried out in duplicate at the beginning (E_{B1} and E_{B2}) and end (E_{B3} and E_{B4}) of the run-in period to provide a good estimate of the deterioration rate. FMs in diesel engines may not require both.

Following the completion of emissions test sequence E_{B4}, the FM fuel is flushed through the system, and a period of operation on candidate FM fuel begins. Use of candidate FM fuel continues for the period t_B, after which two FM test sequences, E_{FM1} and E_{FM2}, are carried out. Once E_{FM2} has been determined, the engine/vehicle is returned to base case fuel. The base fuel is used for the period required to return the engine to the base emission line. This time period, t_D, is also assumed to be known and specified by the applicant before ETV testing, and determination of t_D is not part of the ETV test. After operating on base fuel for the time required for the effect of the FM fuel's use to completely decay, the fifth and sixth base case emissions sequences are carried out to obtain E_{B5} and E_{B6}, which confirm the deterioration line.

Although the verification process does not require testing beyond point E_{B6}, the applicant may wish to generate additional data if the FM is expected to provide a benefit that would not be fully evaluated through a single FM test period, or to evaluate different pollutants or increase confidence in results. In keeping with ETV procedures, all verification testing must be planned and included in the test/QA plan.

The ETV test must be conducted in the order shown in Figure 1: base, candidate FM, base. Before all testing, the engine must be conditioned on the test fuel (base or candidate) to purge any remaining old

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fuel before each map or cold start procedure. The reference cycle map used for the candidate diesel fuel must be the same as determined for the base fuel. The oil and oil filter are to be changed immediately prior to test sequences E_{B1}, E_{FM1}, and E_{B5}.

The data analysis of the cumulative effect FMs described in the following sections is based on an assumption that Figure 1 represents the true behavior of FM, with t_B and t_D known so that there is no confounding between the base and FM fuel cases. These procedures are those recommended and preferred by EPA-OTAQ.

Because the data analysis approach in this protocol is specific to the technology performance and experimental design assumed in Figure 1, an applicant may propose a verification applying another experimental design. In this case, the applicant's proposal must include a detailed justification and demonstrate quantitatively its superiority to the ETV protocol's approach; the applicant's proposal will be evaluated and tested by ETV statisticians regarding the reasonableness of the design and the engine/vehicle selection. The test/QA plan will include an appendix describing development of the experimental design to be used for testing.

5.1.3.4 Data analysis for single engine cumulative effect FMs. The emission reduction is computed from the two FM measurements (E_{FM1} and E_{FM2}) and from the estimated base emissions at the same service (hours or miles). In Figure 1, this would be the intersection of a vertical line rising between E_{FM1} and E_{FM2} and the base case performance line (i.e., difference in rates at points X and Y). The base fueled emissions at that point are estimated from a linear least-squares regression of the natural logarithm of emissions [ln(E)] versus service accumulation for the six base case emissions measurements (E_{B1}, E_{B2}...E_{B6}). Appendix D develops this approach to analyzing the data, presents equations that allow calculation of the estimated effect of the FM and the variance of that estimate, and provides some suggestions to maximize the power of the experiment.

5.2 ETV Testing for Diesel FMs

This section applies to FMs used in compression-ignition engines.

5.2.1 Diesel Base Fuels

Applicants may choose from among the following two FM base fuel alternatives, which are described in more detail in Table 3:

1. The nationwide average base fuel for nationwide application of the FM.
2. FMs intended for California (or an area in which California-type fuel is the dominant available diesel fuel) may be tested using California-type fuel as the base fuel.

Applicants who intend to market FMs in specific markets (regional, specific, or other) may propose alternate base fuels for use during ETV testing. A proposal for an alternate base fuel must be accompanied by evidence that the fuel truly is a "base" that is in use and from which the candidate FM will reduce emissions. If acceptable, the fuel supplied by the applicant will be tested and reported as the base fuel in the ETV report and statement. ETV can make no representation regarding possible extension of the data to other base fuels.

In all these cases, the ETV report and statement will report the test conditions, the FM tested, and the results obtained.

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Note that the ranges given in Table 3 for the properties of the base fuels are not as broad as those for the fuel allowed in emissions certification tests, and that the sulfur level has been limited to 15 ppm. The ranges were narrowed to reduce test-to-test variations in the emissions reductions measurements, whereas the ultra-low sulfur diesel (ULSD) is proposed as the test case. Refinery diesel product streams must be used to produce the base fuels for tests. They cannot be blended from purified chemicals. Because oxygenates are rarely used in diesel, neither the California nor the national average fuel may contain oxygenates. Although additives are not used consistently in diesel, it is permissible for the California and/or the national average fuel to contain a registered additive or additives designed to maintain fuel quality during transport and storage, such as an antioxidant and/or corrosion inhibitor.

Table 3. Properties of Base Fuel for ETV of Diesel FMs

Property	Nationwide Average Fuel	California Fuel	Applicant-Choice Base fuel[a]	ASTM Test
Accepted by EPA-OTAQ	Yes	Yes	No[a]	
Cetane number	43 to 46	51 to 54		D 613
Aromatics, volume %	32 to 36	20 to 24		D 5186
Specific gravity	0.84 to 0.86	0.83 to 0.85		D 1298
Additives	minimal[b]	minimal[b]		
Sulfur, ppm				
Highway	0 to 15	0 to 15		D 6428
Nonroad	2500 to 3500[c]	100 to 160		D 2622
Distillation range				
10% point, °F	410 to 430	410 to 430		D 86
50% point, °F	490 to 520	490 to 520		D 86
90% point, °F	585 to 620	595 to 630		D 86

[a] Testing of FMs using a base fuel chosen by the applicant is possible within this protocol.
[b] Cetane improvers and some other additives cannot be avoided in refinery products. However, these are to be minimized, and no additional additives are to be used.
[c] Use of highway diesel sulfur levels allowed in accordance with 40 CFR part 89.330.

5.2.2 Selection of Engines for ETV Testing

The applicant may select one of three targets for the candidate diesel FM: (1) a specific engine family as represented by a single test engine, (2) the entire on-highway diesel fleet, or (3) some portion of the on-highway diesel fleet. A candidate FM ETV can be conducted on any single engine meeting the requirements of Section 5.2.2.1.

5.2.2.1 General criteria for diesel engine selection. Test engines must be in good operating condition and representative of in-use engines. Standard engines proposed for testing must be in a certified configuration. The engines are to be "as delivered, without any added technologies, and are to be tuned to the manufacturer's specifications. (Specially prepared engines [such as future technology engines that are not commonly available] may also be tested under this protocol, and will be identified as such. However, the acceptability of such a verification to EPA-OTAQ should be explored by the applicant prior to beginning verification if VDRP listing is desired.) For engines manufactured before implementation of emission standards, the engine must be representative of normal production engines.

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Engines must have a minimum of 125 hours of use before beginning an ETV test and exhibit stable operation. Emissions control components must be sufficiently broken in so that they exhibit stable operation over the course of the test program. Because residual effect FMs may have been used in an engine before its use in the ETV program, the engine owner (testing organization or applicant) must establish that the engine can be considered a reasonable baseline for the engine family of interest, either through replicate baseline tests showing a stable baseline or documentation of its fueling history. On the base fuel, the test engine must not exceed 110% of its applicable emission standards. For engines manufactured before emission standards, the engine must not exceed 150% of the first standards for that engine category.

Rebuilt engines will be allowed so long as they represent a certified configuration, produce emissions at the certification standard when fueled by the base fuel (within limits given above), and meet other applicable criteria.

5.2.3 Test Procedures—General Requirements

5.2.3.1 Engine maintenance. All equipment used in the testing must be maintained and operated in accordance with applicable FTP regulations. To the extent practical, the engine and test conditions should be maintained the same between the base and candidate FM tests. This consideration applies to all aspects of engine operation and maintenance. Routine engine maintenance must be performed before beginning a verification test and, once testing has started, routine engine maintenance is not allowed. If use of an FM requires that an engine be tuned for the fuel, this requirement must be detailed in the test/QA plan and will be included in the report as a requirement for use of the FM. Resumption of testing following engine or test stand breakdown and repair will be evaluated by the APCTVC on a case-by-case basis and will be allowable only for brief shutdowns for which no emissions impact is considered likely. A full fuel analysis is required on both base and candidate FM fuel.

5.2.3.2 Test data format and retention. Raw test results will be retained by the testing laboratory in the electronic format required for EPA certification tests and made available to the APCTVC on request. Results for cold and hot starts will be reported both independently and appropriately weighted. Emissions during steady-state testing are to be reported mode-by-mode as well as in the final weighted form. Torque curves will be provided electronically for each engine map. Brake-specific fuel consumption (BSFC) will be measured during each engine map and provided with the map.

5.2.3.3 Fuel conditioning. When switching fuels, a conditioning cycle will be run to purge old fuel and stabilize engine operation on the new fuel. The conditioning cycle must represent normal engine operation and will be specified in the test/QA plan. The engine must be mapped prior to performing a test sequence each time a new test fuel (base fuel or candidate fuel) is used. Engine mapping is conducted following conditioning. The most recently generated engine map on base fuel shall be used in transient testing. The supplemental emissions test (SET) will be performed with the most recently conducted map.

5.2.3.4 ETV test procedures. For on-highway engines, the FTP is described at 40 CFR Part 86. The minimum immediate effects FM emission reduction ETV on-highway engine test at a single test point consists of one cold start FTP test, three hot start FTP tests, and one SET. The weighted cold start results shall be applied to each of the weighted hot start results to provide three (3) transient sets of data for each regulated pollutant and BSFC. Additional testing at each test point may be required to detect the expected emissions reduction, as described in Section 5.1.2.

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The SET for on-highway engines is specified at 40 CFR 86.1360. The SET is a 13-mode steady-state test cycle. The test sequence shall consist of using the FTP to perform one cold start and three hot start transient tests followed by one SET.

For nonroad engines, the FTP is described at 40 CFR Part 89. In most cases, nonroad engines will be verified with both the applicable steady-state cycle and the nonroad transient cycle. However, constant speed engines, such as for generators, may be tested using only the steady-state cycles. For nonroad engines, the basic minimum immediate emission reduction ETV test requires triplicate multimode FTP tests plus the diesel nonroad transient cycle. Additional testing at each test point may be required to detect the expected emissions reduction, as described in Section 5.1.2.

For locomotive engines, the FTP is described at 40 CFR Part 92. The marine engine FTP is described in 40 CFR Part 94. Additional testing at each test point may be required to detect the expected emissions reduction, as described in Section 5.1.2.

Future revisions to the applicable FTP or new procedures adopted in applicable regulations are incorporated in this protocol. Unless otherwise described in this document or identified in the approved test/QA plan, the FTP is to be followed in its entirety. In accordance with this protocol, any deviations from the test/QA plan will be noted and throughly documented by the testing organization in its report.

Requests for the use of alternate or special test procedures to better predict emissions and/or engine operation will not be rejected without consideration. All data quality and QA requirements of this protocol must be met by any alternate test, and this protocol relies on the QA incorporated in the FTP. Significant modification of the FTP sampling and analysis system is unlikely to be acceptable. Changes in the FTP that amount to re-arrangement of existing portions of the test procedure and retain the existing QA steps are more likely to be acceptable.

With these constraints, alternate or special test procedures may be proposed in the application for the technology and will be reviewed with the APCTVC for conformance to this generic protocol before test/QA plan preparation.

Existing data of any kind and chassis and in-use field (e.g., on-road testing devices) data are not acceptable as the basis for ETV.

5.2.4 ETV of Diesel FMs Delivering Immediate Emission Reductions

5.2.4.1 ETV testing sequence. Emission testing on the base fuel must be conducted first. For an arbitrary engine choice for which no historical emissions performance information is available, the base/candidate test points may be conducted in either sequence of base/candidate/base/candidate (BCBC), or base/candidate/ candidate/ base (BCCB). Each test point (B or C) is to include the same number of tests. For the special case of an engine having a substantial documented emissions history (explained further below), a test sequence of BBCC is permitted.

Table 4 outlines the minimum single highway diesel engine test for an immediate emissions reduction FM using the BCCB sequence. The minimum number of tests required at each point in the test sequence is given in Equation B-3. For example purposes, the FM being evaluated in Table 4 is assumed to be one whose expected emissions reduction is large enough that the minimum test set (one cold test, three hot starts, and one SET) at each test point provides a sufficiently narrow confidence interval. Other diesel engine applications would run the appropriate FTP test sequence.

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After the base fuel is used to conduct the prescribed minimum number of tests for the expected emission reduction, candidate fuel testing should be performed. After conducting the minimum number of prescribed tests on the candidate fuel, emission results for each pollutant should be analyzed. If the emission reduction achieved is less than expected, the applicant may run additional tests to support fuel performance. If additional testing on the candidate fuel is desired by the applicant, all testing on the candidate fuel should be completed before switching fuels.

Diesel engines are not expected to exhibit emissions deterioration such as is shown in Figure 1. However, for an unknown FM in an arbitrary engine, it is possible. Potential drift by the test diesel engine (Table 4, Step 11) is to be evaluated as follows:

1. By comparing base fuel emissions at the beginning and end of the test program. Initial and final base fuel results that are not statistically different indicate no deterioration and a zero slope emissions line.
2. By choosing an engine with a documented test history for which at least two baseline emissions measurements show constant emissions over a period that exceeds the expected total ETV test duration. The FM application should propose the engine and provide the requisite evidence of constant emissions so that the test/QA plan can be properly prepared. If the initial ETV baseline emissions result (Table 4, Step 3) is not statistically different from the previous two measurements for the engine, the final baseline test (Table 4, Step 10) may be conducted, on a separate day, prior to use of the FM, and the average emissions of the two will serve as the base-fuel emissions. That is, Step 10 becomes a new Step 3a.

Table 4. Minimum ETV Test Program for Single On-highway Diesel Engine and Immediate Effect FM

1.	Select representative engine and stabilize operation on base fuel.
2.	Map engine on base fuel and practice cycles.
3.	Conduct cold start, three hot starts, and SET on base-fueled engine with base fuel map.
4.	Switch to candidate FM, purge base fuel, and operate and stabilize engine.
5.	Map engine with FM. Practice cycles using base fuel map.
6.	Conduct cold start, three hot starts (using base fuel map), and SET (with FM map) on FM-fueled engine.
7.	Repeat cold start, three hot starts (using base fuel map), and SET (with FM map) on FM-fueled engine.
8.	Switch back to base fuel, purge FM fuel, and operate and stabilize engine.
9.	Perform second map using base fuel. Perform practice cycles using new base map.
10.	Using new base fuel map, conduct cold start, three hot starts, and SET.
11.	Compare initial and final base fuel emissions results for statistical differences.

5.2.4.2 Data reduction for immediate effects diesel FM. For highway diesel engines, emissions tests results are recorded at each test point for HC, CO, NO_X, PM and the other measured pollutants. For each pollutant, the single cold start emissions measurement (e_C) is combined with each of up to three hot start emission measurements (e_H) to obtain up to three composite emissions rates [$(E_{COMP})_m$] following the normal fractional calculation for highway engines:

$$(E_{comp})_m = \frac{(1/7)(e_c) + (6/7)(e_H)_m}{(1/7)(W_c) + (6/7)(W_H)_m} \quad (7)$$

where:

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(E_{COMP}) = weighted mass emission level in grams per brake horsepower-hour and, if appropriate, the weighted mass total hydrocarbon equivalent, in grams per brake horsepower-hour,

m = hot start test 1, 2, or 3,

e_c = mass emission level in grams or grams carbon mass equivalent, measured during the cold start test,

e_H = mass emission level in grams or grams carbon mass equivalent, measured during the hot start test,

W_C = total brake horsepower-hour (brake horsepower integrated over time) for the cold start test,

W_H = total brake horsepower-hour (brake horsepower integrated over time) for the hot start test.

Hot start tests that are combined with a cold start test must be obtained sequentially following that cold start, and no more than three hot starts may be combined with a single cold start or single SET. The composited FTP highway transient emission for each pollutant, E_{COMP}, is combined with a single SET as follows to obtain the combined tests emission rate (E) for each pollutant for each of the n tests at the test point:

$$(E)_i = 0.85 \bullet (E_{COMP})_i + 0.15 \bullet E_{SET} \quad (8)$$

for i = 1 to n tests required at each test point.

As an example, suppose a total of five $(E)_k$ measurements were required to be calculated at each test point to provide enough data. As stated by Equation 8, $(E_{COMP})_1$, $(E_{COMP})_2$ and $(E_{COMP})_3$ would be computed from the first cold start and the first three valid hot starts following the cold start. $(E_{COMP})_4$ and $(E_{COMP})_5$ would be computed from the second cold start and next two valid hot starts, giving the required total of five E_{COMP} values. One SET would be required for the first three E_{COMP} values and a second SET for the last two E_{COMP} values. Then the SET results would be combined with the E_{COMP} values to obtain five E_T values according to Equation 9. (The APCTVC recognizes that the emissions results generated in this way are not fully independent. This approach is a compromise allowed to reduce cost.)

The same process would be applied to both the base case and the candidate FM case.

The same general approach is applied to nonroad engines. Instead of combining a cold and hot start test result, E_{COMP} for nonroad tests is obtained from the nonroad multimode test following the weightings in Appendix B to Subpart E of 40 CFR Part 89 as appropriate for the intended nonroad use as shown in Equation 10.

$$(E_{COMP})_i = \sum_{j=1}^{k} f_j \bullet E_j \quad (9)$$

where:

$(E_{COMP})_i$ = combined emissions rate for test i of n tests required at test point,

k = total number of modes for intended application per 40 CFR 89,

f_j = mode weighting factor from 40 CFR 89, Subpart E, Appendix B, for j = 1,2, …, k modes,

E_j = pollutant emissions rate for j=1,2,..., k modes.

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The nonroad transient test cycle takes the place of the SET for nonroad applications. Only a single nonroad transient test is required at each test point. The nonroad transient cycle emissions are combined with the combined multimode test emissions as follows:

$$E_i = \boldsymbol{X} \bullet (E_{COMP})_i + \boldsymbol{Y} \bullet E_{NTTC} \text{ for } i = 1 \text{ to } n \text{ tests required at each test point} \quad (10)$$

where: $\boldsymbol{X}$ = constant determined by EPA-OTAQ,
$\boldsymbol{Y}$ = constant determined by EPA-OTAQ,
E_{NTTC} = emissions from nonroad transient test cycle.

The emissions reductions for both highway and nonroad engines are then calculated using Equations 1 through 6 from Section 5.1.3.1.

5.2.5 FMs Delivering Cumulative Emission Reductions

5.2.5.1 ETV of single diesel engine tests of cumulative effect FMs. The general procedure discussed in Section 5.1.3.4 is applied for single engine tests.

5.3 ETV of Gasoline FMs

This section applies to fuels and fuel additives used in spark-ignition engines.

5.3.1 Base Fuels

The general requirement for a base gasoline fuel within ETV is that it be widely and consistently available within the region where the FM will be marketed and defined narrowly enough to give consistent test results. As part of the ETV test, the base fuel will be analyzed and the result reported in the ETV report and verification statement. The applicant will specify the desired base fuel in his application, with his choice based on the intended market.

5.3.2 Test Vehicles

5.3.2.1 General requirements. The gasoline FM applicant may select as the target of the verification results a specific engine family. The APCTVC specifies the general requirements for vehicles that will be used in the test and provides the single engine test protocol. General ETV requirements for gasoline test vehicles are as follows:

1. Test vehicles must be in their certified condition, have no obvious signs of tampering, and be in reasonably good repair. Vehicles may have no new emission control components.
2. Whether for single or multiple vehicle verification, the test/QA plan must specify the vehicle selection criteria and procurement method. Test vehicles must have at least 10,000 miles on their engines, be in good working condition, and not have been screened for sensitivity to the candidate FM.
3. All prior maintenance and repair information must be documented.
4. Rebuilt engines are not allowed.
5. Vehicles must not exceed 110% of the applicable emissions certification standard during baseline testing. Exceeding any emissions standard must be the result of the normal distribution of emissions; that is, the vehicle and emission control system must be operating properly, with no obvious reason for the non-compliance.

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5.3.2.2 Number of test vehicles. For single LDV family verification, the specific LDV is the applicant's choice. The application for the FM should state the desired vehicle, and the characteristics of that vehicle will be included in the test/QA plan. If eventually seeking full U.S. fleet verification, the applicant is required to coordinate with EPA-OTAQ.

5.3.2.3 Nonroad use gasoline engines for FM verification. Gasoline FMs may be verified for emissions reductions in nonroad gasoline engines. The applicant recommends the desired test engine, which must meet the general criteria in Section 5.3.2.1.

5.3.3 General Test Procedures

All equipment used in the ETV testing must be maintained and operated in accordance with applicable FTPs. Raw test results are to be retained by the testing organization in the electronic format required for certification tests and made available to the APCTVC if requested. Results for each test phase are to be reported separately as well as with final weighted FTP test results.

5.3.3.1 Vehicle preparation and maintenance. Prior to baseline testing, test vehicles must have normal maintenance performed such as oil and air filter changes. Other recommended maintenance, such as positive crankcase ventilation (PCV), spark plugs, crankcase filter, etc., shall be performed if the normally recommended interval is due or would become due during the test program. Vehicles will be checked for trouble codes and maintenance indicator lights (MILs) and repairs performed before beginning the ETV test. No trouble codes may be stored when beginning ETV testing. Trouble codes set during testing must be recorded and described in the test records.

To the extent practical, the engine and test conditions should be maintained the same between the base and candidate FM tests. This consideration applies to all aspects of engine operation and maintenance. Routine engine maintenance must be performed before beginning a verification test and, once testing has started, routine engine maintenance is generally not allowed. If use of an FM requires that an engine be tuned for the FM, this requirement must be detailed in the test/QA plan and will be included in the report as a requirement for use of the FM. Resumption of testing following engine or test stand breakdown and repair will be evaluated by the APCTVC on a case-by-case basis and will be allowable only for brief shutdowns for which no emissions impact is considered likely. A full fuel analysis is required on both base and candidate FM fuel.

Before initiating ETV testing, the fuel tank(s) shall be drained, base fuel added to the 40% full level, and a triple preparation (three 505-second hot-start tests per the EPA Dynamometer Procedure 40 CFR 86.135-90) performed.

5.3.3.2 Required test procedures. For on-road vehicles and engines, the FTP is described by 40 CFR Part 86. For nonroad engines, the FTP is described by 40 CFR Part 90. The FTP applicable at the time of the test is to be used. Whenever an FTP test is performed on a light duty vehicle or light duty truck, it will be followed by a US06 test (40 CFR 86.159-00). Heavy duty gasoline engines are tested on an engine dynamometer (40 CFR 86 Subpart N).

The highway fuel economy test, cold CO test, and evaporative emission testing will be required of any FM that may reasonably be expected to affect fuel volatility. When evaporative emission testing is not being performed, the heat build portion of the test will not be required after adding fuel.

Requests by applicants to use alternate or special gasoline vehicle or engine test procedures to better predict emissions and/or engine operation in use will not be rejected without consideration. They must

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be proposed in the application and will be discussed before preparing the test/QA plan, which must incorporate a complete description of the ETV test. The ETV testing data quality and QA requirements of this protocol must be met by any alternate test. Significant modification of the FTP sampling and analysis system is unlikely to be acceptable. Alternate test procedures that amount to rearrangements of existing portions of the FTP test for which the existing test descriptions and QA procedures remain valid are more likely to be acceptable. Specific modes of operation may be required to assess emission reductions for particular in-use operating conditions. Existing data may be used for test design.

5.3.4 Gasoline FMs Delivering Immediate Emission Effects

A single gasoline LDV test point consists of a complete composite FTP test (cold start test plus a valid hot start test) and the US06 test. In accordance with 40 CFR 86.137-94, emissions from the gasoline FTP tests are measured and recorded for all pollutants (HC, CO, NO_X, PM) for both phases of the cold start (transient and stabilized) and for the transient phase of the hot start. A minimum of three test points is required for both the base fuel and the candidate FM. After the base fuel is used to conduct the prescribed minimum number of tests for the expected emission reduction, candidate fuel testing should be performed. After conducting the minimum number of prescribed tests on the candidate fuel, emission results for each pollutant should be analyzed. If the emission reduction achieved is less than expected, the applicant may run additional tests to support better FM performance. If additional testing on the candidate fuel is desired by the applicant, all testing on the candidate fuel should be completed before switching fuels.

Additional testing may be conducted if the minimum testing requirements do not demonstrate the targeted emission reductions by continuing to test with the candidate fuel and then performing a corresponding number of tests with the base fuel.

The weighted FTP mass emission rate E_{comp} for each pollutant is obtained as described in 40 CFR 86.144-94 as the sum of 43% of the cold start emissions per mile (E_C) and 57% of the hot start emissions per mile (E_H).

$$E_{comp} = 0.43 \bullet E_C + 0.57 \bullet E_H \quad (11)$$

The combined emissions for each pollutant from a single test, E, are computed as follows:

$$E = 0.72 \bullet E_{comp} + 0.28 \bullet E_{US06} \quad (12)$$

where: E_{US06} = emission rate for the US06 test.

Each value of E_T is computed from separate FTP and US06 measurements. Therefore, if three tests are required to have sufficient data at a test point, a total of three full FTP tests and three US06 tests are required.

Calculation of the single engine emissions reduction is completed using Equations 1 through 6, with the combined emissions for each pollutant, E, for the base case being substituted for E_B, and E for the FM case being substituted for E_F.

The same general approach is applied to nonroad gasoline engines. Instead of combining a cold and hot start test result, E for nonroad tests is obtained from the multimode nonroad test following the weightings in 40 CFR Part 90 as appropriate for the intended nonroad use as shown in Equation 16.

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$$E_i = \sum_{j=1}^{k} f_j \bullet E_j \qquad (13)$$

where:

E_i = emissions rate for test *i* of *n* tests required at each test point,
k = total number of modes for intended application per 40 CFR 90, for j = 1,2, …, k modes,
f_j = mode weighting factor from 40 CFR 90,
E_j = pollutant emissions rate for j=1,2,...k modes.

5.3.5 ETV of Gasoline Cumulative Effect FMs

5.3.5.1 ETV of single gasoline vehicle with cumulative effect FMs. The general procedure discussed in Section 5.1.3.4 is applied for single engine tests.

5.3.5.2 ETV of multiple gasoline vehicles with cumulative effect FMs. For fleet-wide emissions reductions, the emissions reduction for each pollutant is computed from a linear regression on the data from the tested vehicles (as for diesel engines) as described in Appendix D.

5.4 ETV of Lubricant FMs

This protocol was developed to verify the performance of lubricant FMs that are straightforward replacements of conventional crankcase lubricants. Lubricant FMs tested are expected to provide equivalent or better performance than those recommended by the original equipment manufacturer (OEM) for the test engine(s). By providing emissions control and unchanged maintenance requirements, these FMs may provide a net emission reduction.

If a candidate lubricant is not a straightforward replacement for conventional crankcase lubricants or cannot meet the performance specifications required by the OEM, the applicant must provide an appropriate means to demonstrate that any emission reductions identified will be achieved in-use. For example, if the FM candidate lubricant cannot maintain the oil change interval recommended by the OEM, the applicant must provide a compliance and enforcement plan that will verify that the new interval will be followed in use to assure projected emission reductions are achieved in use. This plan will then be considered an integral part of the technology and the verification will be for the lubricant and its written plan for use.

If a candidate lubricant requires a special oil filter or other companion technology to function, the application must specify the requirement. The test will then be designed for both the FM lubricant and the companion technology, and the ETV verification will be for both technologies as a system.

As with the other FMs, verification of emissions reductions for lubricants is based on comparison of emissions during a base case test with those during a test using the candidate lubricant. For the base case and candidate lubricant test, the duration is approximately one oil change cycle, with emissions tests conducted periodically during that cycle. Tests done under this protocol do not evaluate the long term engine and emission control system deterioration/improvement from candidate lubricants; the applicant should be confident of and have conducted adequate tests to confirm the long term effects of the lubricant.

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The applicant is responsible for providing necessary information on candidate and base lubricants as well as OEM specifications for lubricants and their change intervals for each test engine. All applicable specifications and ratings must be fully referenced and documented by the applicant. All additives contained in the candidate lubricant must be fully described. Any exceptions to the applicable specifications must be noted for discussion with the APCTVC and/or EPA-OTAQ. Additionally, the application must describe the lubricant, its source, all additives, and provide information showing that the candidate lubricant does not contribute to increased engine or emission control system deterioration. Where procedures are not specified in this section, applicable procedures in the gasoline or diesel sections must be followed.

5.4.1 Candidate Lubricants

The suitability of candidate lubricants for the proposed application will be evaluated based on comparison of the candidate FM's properties to those of a base lubricant for the tests referenced in Table 5. The lubricant FM application must report results for the tests in Table 5 (or their latest revision) for all grades proposed for use in the ETV verification. This table suggests ranges of results for these tests. Because test procedures and property standards may change, the protocol will not require compliance with these ranges. Instead, a verification will indicate how a candidate lubricant compares with an expected performance standard. All additives in the candidate lubricant must be fully described. This includes measurements of all properties listed in Table 5. The presence of additives or of performance specifications related to emission control system deterioration (such as phosphorus) will be specifically noted in the verification report because these could cause decreased emission control system durability or a reduced emission benefit after long term use.

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Table 5. FM Lubricant Properties and Tests[a]

Test	ASTM Number	Description	Range of Result
Kinematic viscosity @ 100 °C	ASTM D 445	Measures flow resistance of fluid to gravity	3.5 (SAE 0W) to 16.5 cSt (SAE 50)
Pour point	ASTM D 97	Measures temperature at which fluid sample will no longer flow by gravity	-25 to - 45 °C
Noack volatility	ASTM D 5800	Measures evaporation of fluid at 250 °C for 1 hr	0 to 30%
Flash point	ASTM D 92 or D 93	Temperature at which a spark will ignite a flame in the vapor space over test fluid	120 °C minimum
Rotating bomb oxidation test (RBOT)	ASTM D 2272	Measures time for uptake of 100 psi oxygen gas (by pressure drop) of fluid at 100 °C in closed, rotating vessel	30 minutes minimum
Chemical analysis	ICP Spectra or XRF	Quantitative analysis of elements	No halogens, Pb, catalyst poisons
Phosphorus content	ICP Spectra or XRF	Quantitative analysis of elements	1500 ppm maximum
Copper corrosion	ASTM D 130	Grades color change of copper surface after immersion in fluid for 3 hr at 100 °C	1B maximum
Rust prevention	ASTM D 665 A&B	Counts size and number of rust spots on fluid-treated steel surface in fresh water (A) and sea water (B)	Pass A
Foam control	ASTM D 892 Sequence I-IV	Measures foam head on fluid into which air is sparged under various conditions (Sequence I-IV)	None after 10 minutes in all sequences
Four ball wear	ASTM D 4172	Measures diameter of spot worn on stationary ball bearings by a driven ball bearing under 20 kg load	0.5 mm maximum
Falex pin and vee block	ASTM D 3233	Measures friction and wear on a pin spinning between blocks under measured clamping load	Steady state coeff. of friction = 0.15 max

[a] Society of Automotive Engineers (SAE) Document J300, Viscosity Grades for Engine Oils, December, 1999.

The applicant must provide a single mixed batch of the candidate lubricant FM(s) in sufficient quantity for the entire program. The ETV report will list the lubricant grades tested and the emissions reduction obtained.

5.4.2 Base Lubricant and Test Fuel

The applicant must recommend potential base lubricating oils for the ETV verification. They are to be widely distributed, conventional technology lubricants, and are expected to be petroleum- based. The base lubricant must meet the most recent performance specifications for each engine or vehicle model. Where OEM specifications have been superseded by a new grade, the new grade must be used as the base lubricant. From the recommended list, the APCTVC will choose one brand of base lubricant for all ETVs, and the verification report will note emission reductions relative to that base lubricant.

If the applicant knows that the candidate lubricant may be affected by fuel properties, this should be described in the application, will be factored into the test design, and will be reported as characteristic of

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the FM. As described in more detail below, the ETV test includes periodic emissions test sequences separated by mileage (time) accumulation periods. Test fuels meeting the base fuel specifications in the gasoline or diesel sections must be used at each test sequence of the program. Commercial fuel may be used for mileage accumulation, provided it is used consistently throughout the entire test. The test/QA plan will identify specific fuel properties for all phases of the program, and the ETV will report the measured emissions reduction specifically for the gasoline or diesel fuel used during the test.

The base lubricant and the test fuel must be obtained and prepared as needed such that both are available in sufficient quantities for the entire program.

5.4.3 Highway Use Test Engines or Vehicles

Test vehicle(s) or engine(s) used in the lubricant FM tests must be stable as described in the applicable gasoline and diesel FM sections. The base and candidate lubricants must meet the lubricant specifications for the test vehicle(s) or engine(s). Documentation of these specifications must be provided for each vehicle or engine.

5.4.3.1 Types of vehicles. The types of test vehicles shall be selected in accordance with the gasoline and/or diesel FM sections. Where more than one vehicle or engine will be tested, an effort should be made to maximize the diversity of engine characteristics, such as engine speed and operating temperatures, that might affect oil performance.

5.4.4 Nonroad Engine Selection

The general requirements for engine selection for ETV of modified fuels remains applicable for lubricant FMs intended for nonroad applications. The applicant may propose test engines in his application, and these recommendations will be reviewed by the APCTVC.

5.4.5 General Test Procedures

To minimize carryover effects between the lubricants, a purge of the test vehicle (engine) shall be performed each time the oil type is changed. If the base or candidate oil is clearly labeled with a specific purge step as standard operating procedure (SOP), that SOP will be incorporated in the test/QA plan. If a purge SOP is not provided, the test vehicle or engine must be operated for a full oil change interval on the new lubricant before the oil change interval during which emission testing will occur. This operation will help insure that a normal residual amount of used oil (base or FM lubricant) is in the test vehicle when testing is conducted. Whenever the oil is changed or added, the volume of all oil added or removed must be recorded. Prior to making any oil changes (removal or addition), the crankcase oil level and condition must be recorded.

5.4.5.1 Vehicle preparation and maintenance. All test vehicles/engines are to be in good operating condition and to have been maintained in accordance with OEM requirements. Vehicle information must be recorded and maintenance documented through shop records. Prior to beginning the ETV test sequence, the crankcase oil level and condition must be recorded. After the engine/vehicle start condition has been noted, normally scheduled maintenance that is due or may become due during the test program should be performed; and, if so equipped, spark plugs, PCV valve, and air and breather filters are to be changed. The condition of the parts removed is to be noted and these parts are to be retained. An oil sample may be obtained to determine oil condition. No MIL/OBD fault codes are to be present. This vehicle information must be reviewed for acceptability prior to beginning testing.

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Similarly, at the end of the testing program, spark plugs, PCV valve, and air and breather filters will be removed, retained, and their condition noted. The vehicle/engine will be inspected, and any MIL/OBD faults noted. The condition of the vehicle/engine, indications of oil deposits, leaking, or any other oil-related potential concerns will be noted and described in detail in the verification report.

For replacement lubricant FMs, the same brand and part number of oil filters (as specified by the vehicle or engine original equipment manufacturer) must be used throughout the program. The number of filters required for the entire ETV program must be procured prior to its beginning, and the oil filter used at any time randomly selected from that stock.

Base and candidate oils must each be batch-mixed to have enough for the entire program. All special mixing and/or handling procedures must be consistent with good engineering judgment and fully described in the test/QA plan. All storage, mixing, and/or handling instructions for the candidate oil must be fully described in the application.

5.4.5.2 Required test procedures. The required emission tests are described in the applicable gasoline and diesel FM test sections. Equipment and reporting requirements, are specified in the applicable federal regulations. If an oil analysis is performed on any oil from a test vehicle, the results of that analysis will be included in the verification report.

5.4.5.3 Service accumulation. The test/QA plan will specify a service accumulation schedule for each vehicle to follow over the oil change interval. The OEM oil change interval should be used unless a longer interval is needed to evaluate changes over a longer period of operation such as if the oil were not changed in time. An applicant may request a shorter oil change interval. Where more than one vehicle or engine will be tested, the service accumulation schedules for different vehicles should include severe and normal operation to confirm performance of the candidate oil over a broad range of operation. In all cases, the service accumulation on the base oil and candidate oil must be the same over the oil change interval.

5.4.6 Lubricant FM ETV Test Sequences

Figure 2 shows the form of lubricant FM effects that are contemplated in the GVP data analysis in its most complex form with both short-term and long-term deterioration. The same analysis applies in cases exhibiting no deterioration in either the short term (over a single oil change) or the long term, and with different slopes for the base and FM cases. The estimated log (emission reduction) is the difference between the base case and FM case emissions at the midpoint of the FM case service. The analysis is simplest when the test points are symmetrical as shown in Figure 2.

The ETV test for a single vehicle/engine consists of a purge with the new lubricant and alternating test sequences and mileage/hours accumulation periods. As implied in Figure 2, it is assumed within this protocol that the emissions effect will be measurable during the first oil change of the candidate oil (following the purge step). If cumulative effects are expected, additional mileage accumulation may be incorporated into the test/QA plan and steps taken to return the vehicle/engine to baseline operation as described in Section 5.1. The applicant will be expected to provide the mileage/hours required for the FM to reach full effectiveness and the time required to return the vehicle/engine to baseline operation.

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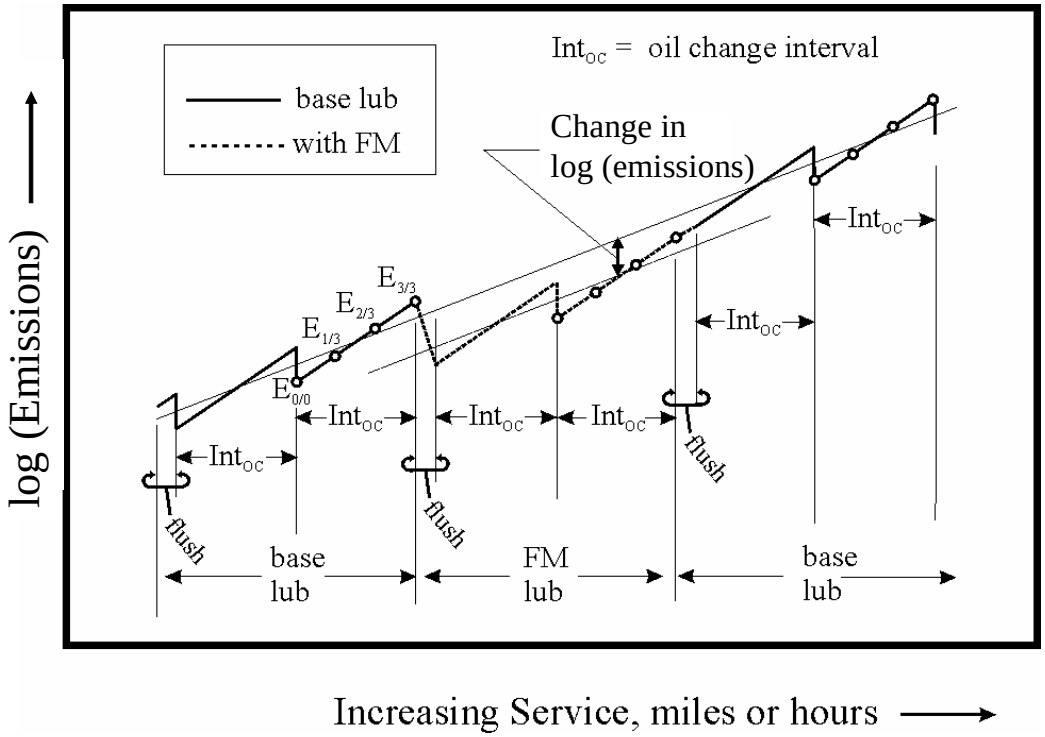

Figure 2. Lubricant FM Testing

The lubricant FM tests for light duty gasoline and all diesel engines are essentially the same as those described above for FMs. Figure 2 provides a graphic overview of the lubricant FM ETV test, and Table 6 gives the testing procedure for lubricant FMs. Details of the testing at the individual test points are as described in Sections 5.2 and 5.3 for diesel engines and gasoline vehicles, respectively.

5.4.7 Evaluating Results

Table 6. Lubricant FM Test Sequences

Light Duty Gasoline-Vehicle Test Sequence[a]
Fuel drain and 40% fill. Triple preparation
Fuel drain and 40% fill. Conduct FTP and US06 tests per Section 5.3.
Fuel drain and 40% fill. Conduct FTP and US06 tests per Section 5.3.
Fuel drain and 40% fill. Conduct FTP and US06 tests per Section 5.3.
Assign weight and combine results as described in Sections 5.3.5 and 5.3.6 to obtain the fully combined emission rates for each pollutant.
Heavy Duty Engine Test Sequence
Map engine.
Practice FTP cycles.
Run cold start test.
Run up to three hot start tests without running another cold start.
Run the SET.
Weight and combine emissions results as described in Sections 5.2.4 and 5.2.5 to obtain the fully composited emission rate for each pollutant.

[a] Highway fuel economy testing is optional; but, if used, it must be performed after required tests and consistently in each test sequence to maintain test uniformity.

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5.4.7.1 Single engine test data analysis. If there is no indication of emission system deterioration (the means of the base case test are the same), the single engine data may be analyzed applying Equations 1 through 6 as described in Section 5.1.3.1. All eight base case tests should be averaged to generate the base case mean. The resulting emission reduction for each pollutant will be reported.

If comparison of the two base case test series shows a measurable increase in emissions, a least-squares line should be fitted to the data applying the principles given in Appendix E. For an experiment in with a symmetrical design (Figure 2), the mean emission reduction, $\hat{\Delta}$, is

$$\hat{\Delta}_j = \overline{E2_j} - \frac{\overline{E1_j} + \overline{E3_j}}{2} \tag{14}$$

where:

$\overline{E1}$ = the mean of the first four base case tests (in log-scale units) for the pollutant of interest,

$\overline{E2}$ = the mean of the four FM tests (in log-scale units) for the pollutant of interest,

$\overline{E3}$ = is the mean of the second four base case tests (in log-scale units) for the pollutant of interest.

Equation 18 is a recast version of Equation E-5 in Appendix E. As a percentage, the emission reduction is computed as

$$ER = (1 - e^{\hat{\Delta}_j}) \times 100\% \tag{15}$$

For non-symmetrical designs, the general form of the analysis in Appendix D will be applied.

5.4.7.2 Cumulative effect lubricant FM data analysis. The analysis of cumulative effect lubricant FM emission reductions is highly dependent on the type of cumulative effect caused by the FM. As of the date of this protocol, no data or theory were available describing the probable effect of cumulative effect FMs. As is shown in Appendix E, the effect of a lubricant FM is totally confounded with a long-term quadratic effect for a 12-test experimental design such as is shown in Figure 2. Therefore, more complex data analyses are not likely to bear fruit. In addition, no cumulative effect lubricant FM vendor has applied to ETV and no such effects have been postulated to the APCTVC. Therefore, all lubricant FM technologies will be treated as providing an immediate effect for the purposes of this protocol.

Should an applicant propose a cumulative effect lubricant, the APCTVC and the testing organization will develop a specific experimental design that applies the test design criteria stated or implied in this protocol for the other technologies.

6.0 REPORTING AND DOCUMENTATION

This section describes the procedures for reporting data in the verification report and verification statement. The specifics of what data must be included and the format in which the data must be included are addressed in this section (e.g., QA/QC summary forms, raw data collected, photographs/slides/video tapes). The verification report for each technology will include near the

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beginning a verification statement that summarizes the ETV results. An example draft is attached as Appendix A. The verification report, including the verification statement, will be written by the APCTVC based on the test report submitted by the testing organization. The verification report and verification statement will be reviewed by the APCTVC and the technology applicant before being submitted to EPA for review and approval as specified in the ETV QMP.

6.1 Reports

Based on the test report from the laboratory, the APCTVC will prepare the draft verification report, which includes the following topics:

1. Verification statement;
2. Introduction;
3. Description and identification of product tested;
4. Procedures and methods used in testing;
5. Statement of operating range over which the test was conducted;
6. Summary and discussion of results as required to
    a. support the verification statement,
    b. explain and document necessary deviations from the test plan, and
    c. discuss QA issues;
7. References; and
8. Appendices:
    a. QA/QC activities and results,
    b. Raw test data, and
    c. Equipment calibration results.

The verification statement will include the following:

9. Technology applicant's name and technology's descriptive information,
10. Summary of ETV test program,
11. Results of the ETV test,
12. Notice of control device warranty and any limitations of the ETV results, and
13. Brief QA statement.

Review and approval of the draft ETV report and statement are described in Section 3.0.

6.2 Data Reduction

Data from measurements made as part of the ETV test will be reported as emissions rates in grams/kilowatt-hour (g/kW-h) (grams/brake horsepower-hour [g/bhp-hr]) or grams/mile (g/mi) and as percentage emission reductions from the baseline engine. The confidence limits will be presented as well as the mean emissions reduction, as discussed in Section 5.1.2. When they would be helpful to the mobile sources community because of established usage, the appropriate English engineering units will be supplied parenthetically.

7.0 DISSEMINATION OF ETV REPORTS AND STATEMENTS

After an FM technology has been tested and the draft verification report and verification statement prepared by the APCTVC, the APCTVC will send a draft of both to the applicant for review prior to

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submission to EPA and release of the approved report to the public. This gives the applicant the opportunity to review the results, test methodology, and report terminology while the drafts remain working documents and are not publicly accessible. The applicant may submit comments and revisions on the draft statement and report to the APCTVC. The APCTVC will consider these comments and may suggest revisions of its own.

After incorporating appropriate revisions, the draft final verification report and verification statement will be submitted to EPA for review and approval. A signed original verification statement within the verification report will be filed and retained by the APCTVC, and signed originals will also be provided in verification reports to the applicant and to EPA. Three additional paper copies of the ETV report will be provided to the applicant. Further distribution of the ETV report, if desired, is at the applicant's discretion and responsibility. However, approved verification statements and verification reports will be posted on the ETV Web site for public access without restriction. The verification report report appendices will not be posted on the Web site, but will be publicly available from the APCTVC.

8.0 APPLICANT'S OPTIONS SHOULD A TECHNOLOGY PERFORM BELOW EXPECTATIONS

ETV is not a technology research and development program; technologies submitted to ETV are to be commercially ready and with well-understood performance. Tests that meet the ETV data quality requirements (a valid FTP test) are considered valid and suitable for publishing; however, a technology may fail to meet the applicant's expectations. Based on limited testing, for instance, the applicant might expect an emission reduction of 30% ± 7% result. However, the actual ETV result from the more complex FTP test cycle might be 20% ± 15%. The APCTVC will use its experience to avoid this situation, but it is possible. In this case, the applicant may choose to schedule additional tests, may accept the result and complete the verification, or may request that a verification statement not be issued. However, ETV reports are always in the public domain and will be posted on the ETV Web site. Verification reports will be written and will be available from EPA for review by the public regardless of a request not to issue a verification statement.

As another example, an applicant might expect a mean of 10% reduction with a confidence interval of ±5%, but testing results in an actual verification shows a mean reduction of 5% with a confidence interval of ±7% reduction. In this case, the ETV data are insufficient to verify that the technology provided any reduction at all. Additional tests must be scheduled and a statistically significant reduction obtained for a verification statement to be issued. Inability to detect a statistically significant emission reduction (or failure to have sufficient tests) will prevent completion of the ETV, and the results of the ETV will be reported publicly stating that performance could not be distinguished from 0% reduction. A verification statement will not be issued in this case.

In either of the above cases, the applicant may improve the product and resubmit it under a new model identification for ETV testing. ETV reports and statements for acceptable tests of the new product will be issued as they are processed by the APCTVC and EPA (except that the results for several identical tests performed in rapid succession will be released simultaneously).

9.0 LIMITATIONS ON TESTING AND REPORTING

To avoid having multiple ETV reports for the same product and to maintain the ETV testing as a cooperative effort with the applicant, the following restrictions apply to ETV testing under this protocol:

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- Applicants may submit only products they manufacture or whose distribution they control. Applicants may not submit for ETV testing control systems whose use is not in their control except with the agreement of the manufacturer or vendor.
- For a given product (e.g., brand and model), APCTVC policy is that only one ETV report and statement will be issued for any single application.
- Air pollution control technology frequently performs differently in different applications. Applicants may request additional tests of essentially identical technology if it is being applied to pollution sources that are clearly different from those for which verifications have been obtained.

10.0 REQUIREMENTS FOR TEST/QA PLAN

10.1 Quality Management

All testing organizations participating in this ETV Program must meet the QA/QC requirements defined below and have an adequate quality system to manage the quality of work performed. Documentation and records management must be performed according to the ETV QMP (U.S. EPA, 2002a) or its superceding document. Testing organizations must also perform assessments and allow audits by the APCTVC (headed by the APCT QA Officer) and EPA corresponding to those in Section 11.

All testing organizations participating in the Retrofit Air Pollution Control Technologies for Highway and Nonroad Use Diesel Engines Program must have an ISO 9000-accredited (ISO, 1994) or ANSI E4-compliant (ANSI, 1994) quality system and an EPA- or APCTVC-approved QMP.

10.2 Quality Assurance

All ETV testing will be done following an approved test/QA plan that meets *EPA Requirements for Quality Assurance Project Plans* (U.S. EPA, 2001c) and Part B, Section 2.2.2 of EPA's ETV QMP (U.S. EPA, 2002a). These documents establish the requirements for test/QA plans and the common guidance document, *Guidance for Quality Assurance Project Plans* (U.S. EPA, 2002b), provides guidance on how to meet these requirements. The APCT Quality Management Plan (RTI, 1998) implements this guidance for the APCTVC.

ETVs conducted under this generic protocol utilize test procedures described in the FTP (40 CFR Part 86 for highway engines and 40 CFR Part 89 for nonroad engines). The test/QA plan must describe in adequate detail how the FTP test methods are implemented by the testing organization. Replication of the FTP text is neither expected nor desired. The test/QA plan should reference the FTP in detail, by section and subsection, as appropriate for the topic under consideration. Any deviations from the FTP must be identified and explained. Internal SOPs may be referenced provided they are available for audit review. (SOPs need not be incorporated into the test/QA plan except by reference. If considered proprietary to the testing organization, they should be clearly marked.) When the FTP offers alternative test procedures or equipment, the test/QA plan must identify the alternative implemented. Similarly, if a range of operating parameters is allowed by the FTP, the specifics of the particular implementation must be provided. For a testing organization with multiple test cells, these details may be tabulated and incorporated by attaching a table and identifying the test cell on the test report. Steps the testing organization will take to ensure acceptable data quality in the test results are also identified in the test/QA plan. Detailed reference to SOPs, the calibration portions of the FTP, or other available documents is encouraged. Any needed SOPs will be developed in accordance with *Guidance for Preparing Standard Operating Procedures (SOPs)* (U.S. EPA, 2001b.)

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The testing organization must prepare a test/QA plan and submit it for approval by the APCTVC. The test/QA plan must also be approved by EPA before the testing organization can begin ETV testing.

A test/QA plan contains the 24 elements listed below, the contents of which may be stand-alone or include references to the FTP or other widely distributed and publicly available sources. Legible hand-notated diagrams from the FTP are acceptable. If specific elements are not included, an explanation for not including them must be provided.

Group A Elements: Project Management

A1 Title and Approval Sheet
A2 Table of Contents
A3 Distribution List
A4 Project/Task Organization
A5 Problem Definition/Background
A6 Project/Task Description
A7 Quality Objectives and Criteria
A8 Special Training/Certifications
A9 Documentation and Records

Group B Elements: Data Generation and Acquisition

B1 Sampling Process Design (Experimental Design)
B2 Sampling Methods
B3 Sample Handling and Custody
B4 Analytical Methods
B5 Quality Control
B6 Instrument/Equipment Testing, Inspection, and Maintenance
B7 Instrument/Equipment Calibration and Frequency
B8 Inspection/Acceptance of Supplies and Consumables
B9 Non-direct Measurements
B10 Data Management

Group C Elements: Assessment and Oversight

C1 Assessments and Response Actions
C2 Reports to Management

Group D Elements: Data Validation and Usability

D1 Data Review, Verification, and Validation
D2 Verification and Validation Methods
D3 Reconciliation with User Requirements

The APCTVC will provide a test/QA plan template that illustrates its expectations.

10.3 Additional Requirements To Be Included in Test/QA Plan

The test/QA plan must include or reference a diagram and description of the extractive gaseous measurement system to be used for the testing and a list of the reference analyzers and measurement ranges to be used for quantifying the concentrations of all gaseous compounds to be measured, including both primary and ancillary pollutants.

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The test/QA plan must include or reference a schematic drawing showing all sample and test locations, including the inlet and outlet to the technology sampling locations. The location of flow disturbances and the upstream and downstream distances from the sampling ports to those flow disturbances must be noted. The number of traverse points that will be sampled must be provided.

The test/QA plan must include or reference the appropriately detailed descriptions of all measuring devices that will be used during the test.

The test/QA plan must explain or reference the specific techniques to be used for monitoring process conditions appropriately for the source being tested. It must also note the techniques that will be used to estimate any other operational parameters.

The test/QA plan must include and document estimates of historical measurement variability that will be used, as discussed in Section 5.1.1 and Appendix B, to compute the number of tests required and provide confidence intervals on single-test ETVs.

The test/QA plan must include a list of data quality indicator goals for individual measurements that conform to those specified in the relevant sections of the FTP and the corresponding acceptance criteria.

11.0 ASSESSMENT AND RESPONSE

Each independent testing organization must conduct internal assessments of its quality and technical systems and must allow external assessments of these systems by APCTVC QA personnel and by EPA QA personnel. After an assessment, the testing organization will be responsible for developing and implementing corrective actions in response to the assessment's findings.

As appropriate, the APCTVC and/or EPA will conduct assessments to determine the testing organization's compliance with its test/QA plan. The requirement to conduct assessments is specified in EPA's ETV QMP (U.S. EPA, 2002a), and in RTI's APCTVC QMP (APCTVC, 1998). EPA will assess RTI's compliance with APCTVC's test/QA plans. APCTVC will assess the compliance of other organizations with their test/QA plans. The assessments will be conducted according to *Guidance on Technical Audits and Related Assessments for Environmental Data Operations* (U.S. EPA, 2000) and *Guidance on Assessing Quality Systems* (U.S. EPA, 2001a.)

11.1 Assessment Types

Quality system assessment—Qualitative assessment of a particular quality system to establish whether the prevailing quality management structure, policies, practices, and procedures meet EPA requirements and are adequate for ensuring that the type and quality of measurements needed are obtained.

Technical systems audit—Qualitative on-site audit of the physical setup of the test. The auditors determine the compliance of testing personnel with the test/QA plan.

Performance evaluation audit—Quantitative audit in which measurement data are independently obtained and compared with routinely obtained data to evaluate the accuracy (bias and precision) of a measurement system.

Audit of data quality—Qualitative and quantitative audit in which data and data handling are reviewed and data quality and data usability are assessed.

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11.2 Assessment Frequency

Activities performed during verifications performance operations that affect the quality of the data will be assessed regularly and the findings reported to management to ensure that the requirements stated in the generic verification protocols and the test/QA plans are being implemented as prescribed.

The types and minimum frequency of assessments for the ETV Program are listed in Part A Section 9.0 of EPA's ETV QMP (U.S. EPA, 2002a). Tests conducted by the APCTVC will have, at a minimum, the following types and numbers of assessments:

- Quality system audit: Self-assessments by the testing organization at least once, and at least one independent assessment of the testing organization.
- Technical systems audits: Self-assessments (qualitative) by the testing organization at least once per test, and at least one independent assessment of the testing organization.
- Performance evaluation audits: Self-assessments (quantitative) by the testing organization on each test, and at least one independent assessment of the testing organization.
- Audits of data quality: Self-assessments (quantitative and qualitative) by the testing laboratory of at least 10% of all the ETV data with detailed reports of the audit results to be included in the data packages sent to the APCTVC for review.

The independent assessments of tests conducted by RTI for the APCTVC will be performed by EPA. The independent assessments of other organizations will be performed by the APCTVC.

11.3 Response to Assessment

When needed, appropriate corrective actions shall be taken and their adequacy verified and documented in response to the findings of the assessments. Data found to have been taken from nonconforming technology shall be evaluated to determine its impact on the quality of the required data. The impact and the action taken shall be documented. Assessments are conducted according to procedures contained in the APCT QMP. Findings are provided in audit reports. Responses by the testing organization to adverse findings are required within 10 working days of receiving the audit report. Followup by the auditors and documentation of responses are required.

12.0 SAFETY MEASURES

12.1 Safety Responsibilities

The testing organization's project leader is responsible for ensuring compliance with all applicable occupational health and safety requirements. Each individual staff member is expected to follow the requirements and identify personnel who deviate from them and report such action to their supervisor.

12.2 Safety Program

The testing organization must maintain a comprehensive safety program and ensure that all test personnel are familiar with and follow it.

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13.0 REFERENCES

APCTVC. *Verification Testing of Air Pollution Control Technology – Quality Management Plan*. Air Pollution Control Technology Program. Research Triangle Institute, Research Triangle Park, NC. 1998.

APCTVC. *Generic Verification Protocol for Diesel Exhaust Catalysts, Particulate Filters, and Engine Modification Control Technologies for Highway and Nonroad Use Engines*. Air Pollution Control Technology Program. Research Triangle Institute, Research Triangle Park, NC. 2002.

ASQC (American Society for Quality Control). *Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Programs* ANSI/ASQC E4-1994. American Society for Quality Control, Milwaukee, WI. 1994.

ASTM. *Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry* ASTM D 2622. ASTM International, West Conshohocken, PA. 1998.

ASTM. *Standard Test Methods for Measurement of Extreme Pressure Properties of Fluid Lubricants (Falex Pin and Vee Block Methods)* ASTM D 3233. ASTM International, West Conshohocken, PA. 1998a.

ASTM. *Standard Test Method for Wear Preventive Characteristics of Lubricating Fluid (Four-Ball Method)* ASTM D 4172. ASTM International, West Conshohocken, PA. 1999.

ASTM. *Standard Test Method for Determination of Aromatic Content and Polynuclear Aromatic Content of Diesel Fuels and Aviation Turbine Fuels by Supercritical Fluid Chromatography* ASTM D 5186. ASTM International, West Conshohocken, PA. 1999a.

ASTM. *Standard Test Method for Density. Relative Density (Specific Gravity). or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method* ASTM D 1298. ASTM International, West Conshohocken, PA. 1999b.

ASTM. *Test Method for Total Sulfur in Liquid Aromatic Hydrocarbons and Their Derivatives by Oxidative Combustion and Electrochemical Detection* ASTM D 6428. ASTM International, West Conshohocken, PA. 1999c.

ASTM. *Standard Test Method for Evaporation Loss of Lubricating Oils by the Noack Method* ASTM D 5800. ASTM International, West Conshohocken, PA. 2000.

ASTM. *Standard Test Method for Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test* ASTM D 130. ASTM International, West Conshohocken, PA. 2000a.

ASTM. *Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure* ASTM D 86. ASTM International, West Conshohocken, PA. 2001.

ASTM. *Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (the Calculation of Dynamic Viscosity)* ASTM D 445. ASTM International, West Conshohocken, PA. 2001a.

ASTM. *Standard Test Method for Cetane Number of Diesel Fuel Oil* ASTM D 613. ASTM International, West Conshohocken, PA. 2001b.

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ASTM. *Standard Test Method for Flash and Fire Points by Cleveland Open Cup Tester* ASTM D 92. ASTM International, West Conshohocken, PA. 2002.

ASTM. *Standard Test Methods for Flash-Point by Pensky-Martens Closed Cup Tester* ASTM D 93. ASTM International, West Conshohocken, PA. 2002a.

ASTM. *Standard Test Method for Pour Point of Petroleum Products* ASTM D 97. ASTM International, West Conshohocken, PA. 2002b.

ASTM. *Standard Test Method for Rust-Preventing Characteristics of Inhibited Mineral Oil in the Presence of Water* ASTM D 665. ASTM International, West Conshohocken, PA. 2002c.

ASTM. *Standard Test Method for Foaming Characteristics of Lubricating Oils* ASTM D 892. ASTM International, West Conshohocken, PA. 2002d.

ASTM. *Standard Test Method for Oxidation Stability of Steam Turbine Oils by Rotating Pressure Vessel* ASTM D 2272. ASTM International, West Conshohocken, PA. 2002e.

CARB. *Test Method for Soluble Organic Fraction (SOF) Extraction.* California Air Resources Board, El Monte, CA. April, 1989.

CARB. *Proposed Regulation Order (DRAFT) Verification Procedure for Diesel Retrofit Systems*. http://www.arb.ca.gov/msprog/mailouts/msc0114/msc0114att1.pdf, California Air Resources Board, El Monte, CA. August, 2001.

ISO. *ISO 9001-1994, Quality Systems Model for Quality Assurance in Design, Development, Production, Installation, and Servicing*. International Organization for Standardization. Geneva, Switzerland. In USA, American National Standards Institute, New York, NY. 1994.

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U.S. EPA (Environmental Protection Agency). *Strategies and Issues in Correlating Diesel Fuel Properties with Emissions*. EPA 420-P-01-001. Office of Transportation and Air Quality. U.S. Environmental Protection Agency. Washington, DC. July 2001.

U.S. EPA (Environmental Protection Agency). *Guidance on Assessing Quality Systems (Quality Staff Draft)*. EPA QA/G-3. Office of Environmental Information, U.S. Environmental Protection Agency. Washington, DC. August, 2001a.

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U.S. EPA (Environmental Protection Agency). *Environmental Technology Verification Program, Quality and Management Plan*. EPA 600/R-03/021. National Risk Management Research Laboratory – National Exposure Research Laboratory, Office of Research and Development, National Homeland Security Research Center, U.S. Environmental Protection Agency. Cincinnati, OH. December 2002a.

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APPENDIX A: EXAMPLE VERIFICATION STATEMENT

Appendix A is an example verification statement written for a generic fuel modification intended to reduce engine emissions from mobile diesel engines. The technology is assumed to have an immediate effect and to be directed at a highway use engine. It is assumed to provide sufficiently large emissions reductions, requiring only the minimum number of tests by the minimum-number-of-tests calculation.

This generic verification statement is intended only to show the form of a verification statement. It will require modification for each technology verified, depending on the details of that technology's design, construction, and operation. The test/QA plan written for each test will include a draft verification statement customized for the technology actually being tested. The text of that specific verification statement will address the significant parameters that apply to the technology tested.

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U.S. Environmental Protection Agency

ETV Joint Verification Statement

TECHNOLOGY TYPE:	**MOBILE DIESEL ENGINE FUEL MODIFICATION INTENDED TO PROVIDE EMISSIONS REDUCTIONS**		
APPLICATION:	**CONTROL OF EMISSIONS FROM MOBILE DIESEL ENGINES IN (*HIGHWAY*) (*NONROAD*) USE BY (*TECHNOLOGY TYPE*)**		
TECHNOLOGY NAME:	**TECHNOLOGY NAME**		
COMPANY:	**COMPANY NAME**		
ADDRESS:	**ADDRESS**	**PHONE:**	**(000) 000-0000**
	CITY, STATE ZIP	**FAX:**	**(000) 000-0000**
WEB SITE:	**http://www.company.com**		
E-MAIL:	**some.one@company.com**		

The U.S. Environmental Protection Agency (EPA) has created the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative or improved environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high quality, peer reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized standards and testing organizations; stakeholder groups which consist of buyers, vendor organizations, permitters, and other interested parties; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The Air Pollution Control Technology Verification Center (APCTVC), one of six centers under the ETV Program, is operated by RTI, in cooperation with EPA's National Risk Management Research Laboratory. The APCTVC has evaluated the performance of a _____*TYPE*_____ fuel modification for mobile diesel engines, the *TECHNOLOGY* by *COMPANY NAME*.

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ETV TEST DESCRIPTION

All tests were performed in accordance with the APCTVC ***Generic Verification Protocol for Determination of Emissions Reductions Obtained by Use of Alternative or Reformulated Liquid Fuels, Fuel Additives, Fuel Emulsions, and Lubricants for Highway and Nonroad Use Diesel Engines*** *and Light Duty Gasoline Engines* and the specific technology test plan "ETV Test/QA Plan for *TECHNOLOGY NAME*" These documents include requirements for quality management, quality assurance, procedures for product selection, auditing of the testing organizations, and test reporting format.

The mobile diesel engine air pollution control technology was tested at *TESTING ORGANIZATION*. The performance verified was the percentage emission reduction achieved by the fuel modification for particulate matter (PM), nitrogen oxides (NO_X), hydrocarbons (HCs), and carbon monoxide (CO) relative to the performance of the same engine on base fuel. Operating conditions were documented and ancillary performance measurements were also made. The basic modules of the test procedure are found in the Federal Test Procedures (FTPs) for emissions certification of diesel highway engines (40 CFR Part 86), diesel nonroad engines (40 CFR Part 89), and light-duty gasoline engines (40 CFR Part 86). Multiple replicate tests are required, depending on the type of fuel modification (FM) and the expected emissions reductions. A summary description of the ETV test is provided in Table A-1.

Table A-1. Summary of the Conditions for ETV Test of *TECHNOLOGY NAME* on ENGINE DESCRIPTION

Test conducted	Highway Transient Federal Test Procedure (FTP)
Engine family	*ENGINE MFGR NAME* Series *XXXYYY*, ??? operating hours prior to test
Engine size	YYY kW (XXX hp)
Technology	ACME Mark II Fuel Additive blended into CA 15 ppm ultra-low sulfur diesel fuel (ULSD)
Technology description	Additive is blended at the terminal with the base fuel at 0.02% by weight.
Test cycle or mode description	For both the base and FM-fueled tests, duplicate test sequences were run, each consisting of 1 cold start, 3 hot starts, and 1 highway steady-state (SET) cycle.
Base fuel description	EPA standard diesel per 40 CFR Part 86.1313-98
Critical measurements	PM, NO_X, HCs, and CO per the FTP
Ancillary measurements	CO_2, exhaust temperature, fuel consumption

VERIFIED TECHNOLOGY DESCRIPTION

This verification statement is applicable to the *TECHNOLOGY NAME* (to include model number and other identifying information as needed), which is a proprietary fuel additive manufactured by *MANUFACTURER NAME*. *TECHNOLOGY NAME* is distributed to fuel terminals and is blended into diesel fuel at the time all other additives are blended.

This verification statement describes the performance of *TECHNOLOGY NAME* on the diesel engine identified in Table A-1. The fuel additive, *TECHNOLOGY NAME*, is expected to provide similar emissions control performance on other engines having similar exhaust stream characteristics (similar fuel and engine technology) when properly sized for the application.

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VERIFICATION OF PERFORMANCE

TECHNOLOGY NAME achieved the emissions reduction shown in Table A-2 at the stated conditions. The number of required ETV tests required was estimated to be the minimum test, consisting of one cold start, three hot starts, and one SET for each of six baseline tests and two candidate FM tests. This estimate was confirmed by the ETV test results. For the purposes of determining the status of the technology in regard to EPA's voluntary retrofit program, the prospective user is encouraged to contact EPA-Office of Transportation and Air Quality (OTAQ) or visit the retrofit program web site at http://www.epa.gov/otaq/retrofit/.

Table A-2. Verified Emissions Reductions for *TECHNOLOGY NAME*

Test Engine: Manufacturer's Name and Model No. AA1	Technology Test			
			Emissions Reduction, %[a]	
	Base Fuel	Candidate FM	Raw[b]	Discounted[c]
Critical Measurements of Emissions				
Hot start PM, g/bkWh (g/bhp-hr)or g/mi				
Composited PM, g/bkWh (g/bhp-hr)				
Hot start NO_X, g/bkWh (g/bhp-hr)				
Composited NO_X, g/bkWh (g/bhp-hr)				
Composited HC, g/bkWh (g/bhp-hr)				
Composited CO, g/bkWh (g/bhp-hr)				
Ancillary Measurements				
Engine power, kW (hp)				
Peak torque, N-m (lb_f-ft)				
Composited CO_2, g/bkWh (g/bhp-hr)				
Exhaust flow, L/min (ft^3/min)				
Exhaust temperature, °C (°F)				
Backpressure, kPa (in. Hg)				
Fuel usage,[d] % reduction				
Technology in/out temperature, °C (°F)				
Comments				

[a]Units of measure in rows are as indicated, except shaded columns in %.
[b]ER_{RAW} from Equation 3 of the GVP.
[c]ER_{DSCT} from Equation 6 of the GVP.
[d](Candidate PM-base fuel)/Base fuel x 100.

The APCT QA Officer has reviewed the test results and quality control data and has concluded that the DQOs given in the generic verification protocol and test/QA plan have been attained.

During the ETV tests, EPA or APCTVC QA staff conducted technical assessments at the testing organization. These confirm that the ETV tests were conducted in accordance with the testing organization's EPA-approved test/QA plan.

This verification statement verifies the emissions characteristics of *TECHNOLOGY NAME* within the stated range of application. Extrapolation outside that range should be done with

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caution and an understanding of the scientific principles that control the performance of *TECHNOLOGY NAME*. This verification focused on emissions. Potential technology users may obtain performance information from the manufacturer.

In accordance with the generic verification protocol, this verification statement is valid commencing on *DATE* indefinitely for application of *TECHNOLOGY NAME* within the range of applicability of the statement.

Hugh W. McKinnon, MD MPH Date
Director
National Risk Management Research Laboratory
Office of Research and Development
United States Environmental Protection Agency

Jack R. Farmer Date
Program Director
Air Pollution Control Technology Verification Center
RTI

NOTICE: ETV verifications are based on an evaluation of technology performance under specific, predetermined criteria and the appropriate quality assurance procedures. EPA and RTI make no expressed or implied warranties as to the performance of the technology and do not certify that a technology will always operate as verified. The end user is solely responsible for complying with any and all applicable federal, state, and local requirements. Mention of commercial product names does not imply endorsement.

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APPENDIX B: DETERMINING MINIMUM NUMBER OF TESTS REQUIRED AT EACH TEST POINT

The ETV program for mobile source emissions requires that a testing program for a given technology attempt to achieve the following for each vehicle tested:

- The emissions reduction (ER) is to be tested using a t-test with significance level of 0.05; the null hypothesis is that the FM produces no reduction, and the alternative is that it reduces emissions.
- For the applicant's expected ER, a statistical power of 0.90 is desired.

For FM, the t-test can be formulated in terms of a confidence interval as in equation (4) of the protocol document, or as the ratio (observed ER)/(square root of variance of ER). The goal of this appendix is to derive the sample size needed for this statistical test to achieve the desired level of power.

An approximate variance expression for the emissions reduction is embedded in eq. (4) of the protocol document. This variance is

$$Var(ER) \approx \left(\frac{1}{\bar{E}_B}\right)^2 \left[\frac{s_F^2}{n_F} + (1-ER)^2 \frac{s_B^2}{n_B}\right] \qquad \text{(B-1)}$$

where $\bar{E}_B$ = the mean of the baseline emissions
s_F^2 = the variance of the FM emissions
s_B^2 = the variance of the baseline emissions
n_F = the number of emissions measurements in the FM sample
n_B = the number of emissions measurements in the baseline sample

To get an initial sample size, assume that

$$n = n_B = n_F \text{ and } s_B^2 = s_F^2 = s^2 .$$

Then (B-1) becomes

$$Var(ER) = \frac{1}{n}\frac{s^2}{E_B{}^2}\left[1 + (1-ER)^2\right] \qquad \text{(B-2)}$$

Let μ_B and μ_F denote the true mean emissions level for the given vehicle under baseline and FM conditions, respectively. Assume that we want to have a probability of 1-β of declaring significance if the FM results in an emissions level equal to $k\mu_B$, where, for instance, k might be 0.95. The true ER would then be given by $\frac{\mu_B - \mu_F}{\mu_B} = 1-k,$ or 0.05. Then, if we want n to be

large enough to detect an true ER of (1-k) with power (1-β), an approximate formula for n would be given by,

$$n \geq \frac{\left(z_{1-\alpha} + z_{1-\beta}\right)^2 \left(\sigma^2 / \mu_B^2\right)\left[1+k^2\right]}{(1-k)^2} + \frac{z_{1-\alpha}^2}{2} \qquad \text{(B-3)}$$

where μ_B = the true population mean baseline emissions rate

σ^2 = the true population measurement-error variance (for both baseline and fuel additive emissions)

$Z_{1-\alpha}$ = the standard normal deviate associated with probability 1-α

$Z_{1-\beta}$ = the standard normal deviate associated with probability 1-β.

The n calculated in (B-3) is the sample size for both FM and baseline tests (i.e., the total number of tests is 2n); the calculated n should be rounded up to next highest integer. The first term in (B-3) is based on a modification of the standard sample size formula for a one sided z-test; note that it depends on the magnitude of the effect to be detected (k), the relative measurement-error variance (in the parentheses), and the specified error rates (α and β). The second term is a correction factor that accounts for the fact that a t-test rather than z-test (i.e., normal-distribution-based test) is used, since n will generally be small. A derivation of the correction factor is available in Appendix A of the EPA G-4 guidance document (*Guidance on the Data Quality Objectives Process* (EPA/600/R-96/055)).

As an example of applying (B-3), assume the following:
α=0.05, so $z_{1-\alpha}$=1.645;
β=0.10 when k=0.95, so $z_{1-\beta}$=1.282;
relative measurement error standard deviation = 0.02 (i.e., 2%).

Then substituting into (B-3) yields

$$n \geq \frac{(1.645+1.282)^2 (0.02)^2 [1+(0.95)^2]}{(1-0.95)^2} + \frac{(1.645)^2}{2} = 2.61 + 1.35 = 3.96 \qquad \text{(B-4)}$$

In this situation, 4 baseline and 4 FM tests would be sufficient to demonstrate the emissions reduction with the desired confidence.

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APPENDIX C: USE OF LOG SCALE TO TEST EMISSIONS REDUCTIONS

Let 100δ represent the true percentage reduction in emissions due to a candidate FM relative to the baseline emissions. That is, if there were no measurement error and no temporal variation associated with measurements, then we would expect the baseline emissions, E_B, and the FM-based emissions, E_F, to be related as

$$\delta = \frac{E_B - E_F}{E_B} \quad . \tag{C-1}$$

This implies that

$$E_B \delta = E_B - E_F \tag{C-2}$$

or

$$E_F = E_B (1 - \delta) \, . \tag{C-3}$$

Now suppose there is a series of n measurements for each type emission (E_{Bi} and E_{Fi}, $i=1,2,...,n$) and that these are summed. Then, from Equation C-3, the sums would be expected to be related as

$$\sum_{i=1}^{n} E_{Fi} = \left(\sum_{i=1}^{n} E_{Bi} \right) (1 - \delta) \, . \tag{C-4}$$

This suggests that a natural estimator for (1-δ) would be the ratio of the sums, or equivalently, that an estimator $\hat{\delta}$ for δ is

$$\hat{\delta} = 1 - \frac{\sum_{i=1}^{n} E_{Fi}}{\sum_{i=1}^{n} E_{Bi}} \quad . \tag{C-5}$$

This is the estimator described in Equation 3 of Section 5.1.3.1 of this generic verification protocol. It was proposed for use in simple before-versus-after analyses in which no residual effects were anticipated. In that context, confidence intervals for δ were developed which were used for testing the null hypothesis, H_0: δ = 0, versus the alternative hypothesis, H_A: δ > 0.

Elsewhere in this generic verification protocol, the use of a log-scale for assessing emission reductions is advocated. In particular, in testing fuel additives and lubricants where carry-over effects may occur and where phase-in periods are needed, it is not practical to test the baseline and FM conditions at essentially the same mileage or hours of engine operation. A log-scale

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model is proposed for estimating baseline emissions at that point where the FM tests are conducted. This is appropriate for several reasons.

First, the log-scale analysis is much easier to deal with statistically. Defining an estimator of δ in a manner analogous to Equation C-5 would result in complex variance formulas and complex formulas for approximate degrees of freedom because, in the original scale, measurement error variances are likely to change with varying emission levels. Use of the log scale, which presumes that standard deviations of measured emissions are approximately proportional to their magnitude, allows the relevant variances to be calculated in a simple fashion and for degrees of freedom to be determined exactly.

Second, when measurement errors are relatively small (e.g., relative standard deviations [RSDs] less than 20%) and when effects to be detected are relatively small (e.g., 5% or 10%, rather than 50%), the log-scale analysis will produce results nearly identical to that implied by Equation C-5. To see this, the log-scale equivalents of the above relationships are defined. Note that Equation C-3 implies (all logs are natural logarithms)

$$\ln(E_F) = \ln(E_B) + \ln(1-\delta). \tag{C-6}$$

For a series of measurements, then

$$\ln(1-\delta) = \mu_F - \mu_B \quad , \tag{C-7}$$

where μ_F and μ_B are the true ln-scale mean emissions for FM and base respectively.

A natural estimator of ln(1-δ) is therefore the difference in the observed ln-scale means from a series of measurements:

$$\ln(1-\delta) \cong \overline{Y}_F - \overline{Y}_B, \tag{C-8}$$

where $\overline{Y}_F$ and $\overline{Y}_B$ are the observed log-scale means. This implies that the $\tilde{\delta}$ can be estimated in terms of the ratio of the geometric means (GMs):

$$\tilde{\delta} = 1 - \frac{\exp(\overline{Y}_F)}{\exp(\overline{Y}_B)} \equiv 1 - \frac{GM_F}{GM_B} \quad . \tag{C-9}$$

Note that the hypotheses expressed in Equation C-6 can be equivalently stated in log-scale units as

$$H_0: \ln(1-\delta) = 0 \text{ versus } H_A: \ln(1-\delta) < 0 \tag{C-10}$$

or

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$$H_0: \mu_F = \mu_B \text{ versus } H_A: \mu_F < \mu_B \,. \qquad \text{(C-11)}$$

The similarity of the results obtained via the alternate approaches for estimating, and testing for, emission reductions is demonstrated by the simulation results given in Table C-1. Three different sample sizes were considered. In each case, a log-scale measurement error standard deviation of 0.1 (essentially a 10% RSD) was used. The true effects shown in column 2 were used to generate normally distributed "data." The estimated values of the effects and the results of the respective t tests are very similar, especially for the smaller effect sizes.

Table C-1. Summary of Simulation Results

	True Effects		Estimated Effects			Standard Errors (*s.e.*s) of Estimates		p Values from t Tests[b]	
Total *n*[a]	ln (1-δ)	δ	$\hat{\delta}$	$\hat{\mu}_F - \hat{\mu}_B$	$\tilde{\delta}$	$s.e.[\hat{\delta}]$	$s.e.[\hat{\mu}_F - \hat{\mu}_B]$	p_1	p_2
400	-0.03	0.030	0.027	-0.028	0.027	0.010	0.011	0.004	0.005
	-0.05	0.049	0.051	-0.053	0.052	0.010	0.010	0.000	0.000
	-0.10	0.095	0.086	-0.091	0.087	0.009	0.010	0.000	0.000
	-0.15	0.139	0.152	-0.164	0.152	0.008	0.010	0.000	0.000
	-0.20	0.181	0.166	-0.182	0.167	0.009	0.010	0.000	0.000
	-0.25	0.221	0.203	-0.227	0.203	0.008	0.010	0.000	0.000
	-0.30	0.259	0.260	-0.299	0.259	0.007	0.010	0.000	0.000
60	-0.03	0.030	0.014	-0.015	0.015	0.025	0.026	0.290	0.276
	-0.05	0.049	0.029	-0.028	0.028	0.024	0.025	0.116	0.135
	-0.10	0.095	0.056	-0.062	0.060	0.023	0.025	0.010	0.008
	-0.15	0.139	0.143	-0.155	0.144	0.021	0.024	0.000	0.000
	-0.20	0.181	0.158	-0.172	0.158	0.021	0.026	0.000	0.000
	-0.25	0.221	0.185	-0.206	0.186	0.017	0.021	0.000	0.000
	-0.30	0.259	0.273	-0.315	0.270	0.019	0.026	0.000	0.000
8	-0.03	0.030	0.108	-0.116	0.109	0.053	0.059	0.047	0.048
	-0.05	0.049	0.021	-0.019	0.019	0.058	0.059	0.368	0.381
	-0.10	0.095	0.135	-0.143	0.133	0.038	0.044	0.019	0.008
	-0.15	0.139	0.138	-0.148	0.138	0.045	0.052	0.014	0.015
	-0.20	0.181	0.289	-0.343	0.290	0.035	0.049	0.000	0.000
	-0.25	0.221	0.223	-0.253	0.223	0.017	0.021	0.000	0.000
	-0.30	0.259	0.111	-0.117	0.111	0.030	0.035	0.007	0.008

[a] $n/2$ observations each for FM and for baseline.

[b] p_1 is for t test based on $\hat{\delta}$. p_2 is for t test based on $\hat{\mu}_F - \hat{\mu}_B$.

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APPENDIX D: DATA ANALYSIS FOR CUMULATIVE EFFECT FMs

Assume that a series of emission measurements are made at each of four mileage points as indicated in Figure 1 of this generic verification protocol. In particular, assume that the third mileage point is for the candidate FM and that the other three points represent baseline measurements. Let X denote the mileage and let Y denote the natural log of the emissions for a given contaminant. Let $\overline{X}_{Fj}$ and $\overline{X}_{Bj}$ denote the average mileages associated with the FM measurements and baseline measurements, respectively, for vehicle *j*. For a single vehicle, the FM effect, Δ_j, is defined as the difference in ln(emissions) occurring at $\overline{X}_{Fj}$. The value $\hat{\Delta}_j$, which is an approximation of Δ_j, can be estimated as

$$\hat{\Delta}_j = \hat{Y}_{Fj}(\overline{X}_{Fj}) - \hat{Y}_{Bj}(\overline{X}_{Fj}) \tag{D-1}$$

where $\hat{Y}_{Fj}(\overline{X}_{Fj})$ is the predicted FM-based emissions at the (average) mileage associated with those measurements, and $\hat{Y}_{Bj}(\overline{X}_{Fj})$ is the predicted baseline emissions at that same mileage. With the measurement design indicated above, $\hat{Y}_{Fj}(\overline{X}_{Fj})$ is simply the average of the FM-based ln{emissions):

$$\hat{Y}_{Fj}(\overline{X}_{Fj}) = \overline{Y}_{Fj} = \frac{1}{n_F}\sum_{i=1}^{n_F} y_{ij} \tag{D-2}$$

where n_F is the number of FM-based measurements, y_{ij} = i^{th} observed ln(emission) for vehicle *j*, and the summation is over the FM-based measurements. On the other hand, $\hat{Y}_{Bj}(\overline{X}_{Fj})$ must be estimated based on the assumed baseline relationship between Y and X. If this relationship is assumed to be linear, then a statistical model for simultaneously estimating Δ_j and the parameters of the linear baseline relationship is the following:

$$y_{ij} = \alpha_j + \Delta_j Z_{ij} + \beta_j(x_{ij} - \overline{X}_{Fj}) + \varepsilon_{ij} \tag{D-3}$$

where

y_{ij} = i^{th} observed ln(emission) for vehicle *j*,
x_{ij} = mileage associated with i^{th} observation for vehicle *j*,
Z_{ij} = 1 if i^{th} observation for j^{th} vehicle is for FM-based condition,
= 0, otherwise,
ε_{ij} = random error for i^{th} observation for vehicle *j*, and

α_j, Δ_j, and $+\beta_j(x)$ are parameters to be estimated. With the model parameters defined in this way, the resulting estimates from a least squares regression are as follows:

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$\hat{\alpha}_j = \hat{Y}_{Bj}(\overline{X}_{Fj})$ = estimated baseline (ln-scale) emissions at the mileage where the FM-based tests are conducted,

$\hat{\Delta}_j$, as defined by Equation (D-1), is the estimated effect of the FM, and

$\hat{\beta}_j = \dfrac{\sum_{i=1}^{n_B} x_{ij} y_{ij} - n_B \overline{X}_{Bj} \overline{Y}_{Bj}}{\sum_{i=1}^{n_B} x_{ij}^2 - n_B \overline{X}_{Bj}^2}$ = estimated deterioration rate under baseline conditions,

where n_B is the total number of baseline measurements and $\overline{Y}_{Bj}$ is the mean of the n_B baseline measurements. It should be noted that this slope estimate is identical to the least squares estimate that would be obtained if only baseline data were included in the regression. Standard multiple regression software can therefore be used to produce both an estimate of the desired FM effect and of its standard error. Hence, confidence interval estimates for $\hat{\Delta}_j$ (or hypothesis tests) are straightforward. The variance of the estimated effect can be estimated as

$$Var[\hat{\Delta}_j] = s_j^2 \left[\frac{1}{n_F} + \frac{1}{n_B} + \frac{(\overline{X}_{Fj} - \overline{X}_{Bj})^2}{\sum_{i=1}^{n_B} x_{ij}^2 - n_B \overline{X}_{Bj}^2} \right] \quad \text{(D-4)}$$

where s_j^2 is the residual variance from the multiple regression performed on the vehicle *j* data. (If the model is accurate, then s_j^2 is an estimate of the measurement error variance of the emissions.) The degrees of freedom associated with Equation D-4 is $n_F + n_B - 3$.

The primary single-vehicle hypothesis of interest is the following:

$$H_0: \Delta_j = 0 \text{ vs. } H_A: \Delta_j < 0 \quad \text{(D-5)}$$

This is tested by computing a t statistic on the estimated effect, $\hat{\Delta}_j$,

$$t = \frac{\hat{\Delta}_j}{\sqrt{Var(\hat{\Delta}_j)}} \quad \text{(D-6)}$$

and comparing the result to t_C, the 5th percentage point of a t distribution with $n_F + n_B - 3$ degrees of freedom (e.g., if the total sample size is 24, then $t_C = -1.721$). The null hypothesis, H_0, is rejected if $t < t_C$.

To achieve the desired ETV confidence level (95%) and level of statistical power (90% at the applicant's anticipated effect level) for testing this hypothesis, one must ensure that the variance

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in Equation (D-4) is sufficiently small. Clearly, the magnitude on Equation (D-4) depends not only on the sample sizes and the underlying measurement error variance, but also on the design – namely, the spacing of the mileage points and the amount of replicate testing at each of those points. In general, smaller variance will be achieved by increasing the dispersion of the baseline mileage points used in the regression and/or by decreasing the absolute difference between $\overline{X}_{Fj}$ and $\overline{X}_{Bj}$. Note that all of the quantities appearing inside the brackets of Equation (D-4) depend solely on the particular design used. Hence, for any given design, the power of the test can be determined as follows.

- First determine the degrees of freedom and critical value, t_C, of the test, as defined above (e.g., select the 95th percentage point from a table of percentage points of the t distribution).

- Based on prior data, assume a value for the true underlying measurement error variance; denote this quantity as σ^2.

- Then compute a noncentrality parameter, *D*, as

$$D = \frac{\delta}{\sqrt{\sigma^2 K_j}} \qquad \text{(D-7)}$$

  where δ is the anticipated effect (in ln-scale units, or relative difference) and K_j is the quantity inside the brackets in Equation (C-4). (Given the formulation of the hypothesis test, δ should be negative.)

- The power (the probability of rejecting the null hypothesis when a true effect is equal to δ) is then determined as

$$\Pr[T(D) < t_C] \qquad \text{(D-8)}$$

  where T(D) denotes a random variable following a noncentral t distribution with noncentrality parameter D and $n_F + n_B - 3$ degrees of freedom. (Standard statistical software packages such as S-Plus or SAS have built-in functions for calculating such percentage points from noncentral t distributions.)

- By varying the design and/or the sample sizes, one can determine when Equation (D-8) exceeds 0.90, the desired power.

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APPENDIX E: SINGLE VEHICLE TESTS FOR LUBRICANTS

Assume that emission measurements are made at each of four mileage points within each of three phases, as indicated in Figure 2 of the generic verification protocol. In particular, assume that phase 2 consists of tests for the candidate FM and that phases 1 and 3 consist of baseline measurements. Note the following characteristics regarding the mileage scale of the design:

- The within-phase designs are the same for each phase. They can be characterized by a variable *U*, which is the mileage since oil change. Let U_{ijk} = the mileage since last oil change for measurement *i* within phase *k* for vehicle *j*, and let $\overline{U_{ik}}$ denote the average of these mileages for phase *k* of vehicle *j*. Let $u_{ijk} = U_{ijk} - \overline{U}_{jk}$ be the deviation of these mileages from their respective phase-specific means. (Nominally, the mileages within a phase are equally spaced, so that the four *U* values are proportional to 0, 1, 2, and 3; hence the deviations are proportional to -3, -1, 1, and 3.)

- In terms of the mileage scale, phase 2 is centered between phases 1 and 3. Hence, a continuous variable representing phase (with values of 1, 2, and 3) is in fact equivalent, apart from a scale factor and location factor, to a mileage variable. (That is, if the average mileages for the phases are denoted as $\overline{X}_{kj}$ and if deviations from the phase 2 mean are computed, then these deviations will be proportional to -1, 0, and 1, respectively, for phases 1, 2, and 3. This is the same variable as can be obtained by subtracting 2 from the phase indicator, *k*.)

An important consequence of the second bullet is that *the effect of the lubricant FM is totally confounded with a long-term quadratic deterioration effect*. To see this, *assume for the moment that phase 2 also involves baseline measurements* and assume that (a) within-phase deterioration effects are linear, and (b) that long-term (i.e., across phases or oil changes) deterioration effects are potentially quadratic. This corresponds to a saw-toothed curve with linear segments within phases that are connected at their midpoints by a second-order curve.

The statistical model for such a situation can be expressed as

$$y_{ijk} = \alpha_{jk} + \beta_{jk} u_{ijk} + \lambda_j L_{ijk} + \Delta_j Q_{ijk} + \epsilon_{ijk} \qquad \text{(E-1)}$$

where

y_{ijk} = i[th] observed ln(emission) for vehicle *j* and phase *k*,
u_{ijk} = within-phase mileage deviation (standardized, if desired [as described above], to take on values of -3, -1, +1, and +3),
L_{ijk} = -1 for phase 1 observations,
= 0 for phase 2 observations,
= +1 for phase 3 observations,
Q_{ijk} = -1/3 for phase 1 observations,
= +2/3 for phase 2 observations,
= -1/3 for phase 3 observations,
ε_{ijk} = random error for i[th] observation for phase *k* and vehicle *j*, and

α_{jk}, β_{jk}, λ_j, and Δ_j are parameters to be estimated.

With the model terms defined in this way, the resulting estimates, indicated by a ^, from a least-squares regression on the vehicle *j* data are as follows:

$$\hat{\alpha}_{jk} = \overline{Y}_{jk} = \text{average ln(emissions) for phase } k \text{ and vehicle } j, \quad \text{(E-2)}$$

$$\hat{\beta}_{jk} = \frac{\sum_{i=1}^{4} u_{ijk} y_{ijk}}{\sum_{i=1}^{4} u_{ijk}^2} = \text{within-phase deterioration factor for vehicle } j, \text{ phase k(expressed in thousand-mile [K] units, where 6K is the number of miles between the first and last tests within a phase),} \quad \text{(E-3)}$$

$$\hat{\lambda}_j = 0.5(\overline{Y}_{j3} - \overline{Y}_{j1}) = \text{linear component of long-term deterioration factor (expressed in phase units), and} \quad \text{(E-4)}$$

$$\hat{\Delta}_j = \overline{Y}_{j2} - \frac{\overline{Y}_{j1} + \overline{Y}_{j3}}{2} = \text{quadratic component of long-term deterioration factor (expressed in phase units).} \quad \text{(E-5)}$$

Now assume that the phase 2 measurements are for the lubricant FM rather than for baseline. Also assume that the long-term deterioration for baseline measurements is linear. This latter assumption is necessary if the effect of the FM for a given vehicle is to be defined as the "average FM emissions for phase 2 minus the baseline emissions that are predicted for phase 2," since we cannot isolate the effect of the FM from the quadratic component of the long-term baseline deterioration factor. For these assumptions, the model of Equation (E-1) still applies, but now Δ_j represents the effect of the FM and its estimate is given by Equation (E-5).

For the given design and the above model, fitting the model of Equation (E-1) to the data for a single vehicle will result in a variance for the estimated FM effect, $\hat{\Delta}_j$, as

$$Var[\hat{\Delta}_j] = 3s_j^2 / 8 \quad \text{(E-6)}$$

where s_j^2 is the residual variance from the multiple regression performed on the vehicle *j* data. (If the model is accurate, then s_j^2 is an estimate of the measurement error variance of the emissions.) The degrees of freedom associated with this variance is 4. The model of Equation (E-1) can also be fit using data from all tested vehicles; in that case, the variance of the estimated FM effect for vehicle *j* is

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$$Var[\hat{\Delta}_j] = 3s_P^2 / 8 \quad \text{(E-7)}$$

where s_P^2 is the (pooled) residual variance from the multiple regression performed on the *m* vehicles in the fleet. The degrees of freedom associated with Equation (E-7) is 4*m*.

Standard multiple regression software can therefore be used to produce both an estimate of the desired FM effect and of its standard error. Hence, confidence interval estimates for Δ_j (or hypothesis tests) are straightforward. The primary single-vehicle hypothesis of interest is the null hypothesis, H_0:$\Delta_j = 0$, versus the alternative hypothesis, H_A:$\Delta_j<0$.

This is tested by computing a t statistic, on the estimated effect, Δ_j,

$$t = \frac{\hat{\Delta}_j}{\sqrt{Var(\hat{\Delta}_j)}} \quad \text{(E-8)}$$

and comparing the result to t_C, the 5th percentage point of a t distribution with 4 or 4*m* degrees of freedom. The null hypothesis, H_0, is rejected if $t < t_C$.

To achieve the desired ETV confidence level (95%) and level of statistical power (90% at the applicant's anticipated effect level) for testing this hypothesis, one must ensure that the variance in Equations (E-6) or (E-7) is sufficiently small. The power of the test can be determined as follows:

- First determine the degrees of freedom and critical value, t_C, of the test, as defined above (e.g., select the 95th percentage point from a table of percentage points of the t distribution).
- Based on prior data, assume a value for the true underlying measurement error variance; denote this quantity as σ^2.
- Then compute a noncentrality parameter as

$$D = \frac{\delta}{\sqrt{\sigma^2 (3/8)}} \quad \text{(E-9)}$$

where δ is the anticipated effect (in ln-scale units, or relative difference). (Given the formulation of the hypothesis test, δ should be negative.)

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- The power, the probability of rejecting the null hypothesis when a true effect is equal to δ, is then determined as

$$\Pr[T(D) < t_C] \qquad \text{(E-10)}$$

where T(D) denotes a random variable following a noncentral t distribution with noncentrality parameter D and 4 or 4*m* degrees of freedom. (Standard statistical software packages such as S-Plus or SAS have built-in functions for calculating such percentage points from noncentral t distributions.)

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APPENDIX F: SENSITIVITY OF NUMBER OF TESTS CALCULATION TO MEASUREMENT VARIABILITY

Table F-1 presents the results of a sensitivity analysis of the calculation of the required number of tests in the particular cases of high (85%) and low (10% and 5%) reductions in emissions. The number of tests reported in the final column is the number required to have a 90% probability of detecting the emissions reduction with 95% confidence. Equation B-3 in Appendix B was used to compute the required number of tests. As in these sections, all calculations utilize the normal distribution under the assumption that the test measurement error is known and constant.

Within Table F-1, the variability of the baseline engine measurement ranges from 2 to 30%, and the controlled engine measurement variability from 10 to 30%. All of the percentage numbers in the table are referenced to a baseline engine emission. To convert the percentages to absolute emission rates, they must be multiplied by a baseline engine emission rate, and at 30% variability the standard deviations are twice the emission rates in g/bhp-hr. The emissions and standard deviations in Table F-1 have all been calculated for a baseline engine emitting PM at the 1990 certification level of 0.6 g/bhp-hr. For example, from the first row, an 85% reduction means an absolute PM emission of 0.09 g/bhp-hr. A 10% controlled engine measurement variability means the standard deviation for that measurement is 0.06 bhp-hr. For the baseline engine, the variability is 2%, so the baseline engine standard deviation is 0.012 bhp-hr. The same approach can be used to make a similar table for any other emission rate by multiplying the percentages by the desired baseline emission rate.

While the number of required tests increases as the test variability increases, Table F-1 shows that the increase is modest at high emissions reduction levels. While higher variability is expected at higher levels of control because the absolute emissions concentrations are low, the large reduction in emissions is easily detected.

On the other hand, lower variability is expected for low emissions reductions, but the smaller changes are harder to detect and more tests are required. Therefore even modest variability levels (relative to those in the top block of Table F-1) lead to very large numbers of tests.

As was discussed in Section 5.1.2, calculation of the confidence intervals on the mean emissions reduction will be based on population statistics and will utilize the t-distribution. Thus, the number of tests calculated using Equation B-3 (population statistics) may be fewer than will be required by the data itself based on sample statistics. As mentioned in Appendix B, an approximate calculation can be made for sample variability utilizing the Student's t-distribution rather than the normal (z-distribution) in Equation B-3. This use of Equation B-3 is not strictly valid, but may be useful for low emission reduction and/or high variability test designs to make a better estimate of the number of tests required.

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Table F-1. Sensitivity of Number of Tests to Measurement Variability

Expected emissions reduction, %	Controlled engine emissions, g/bhp-hr, relative to a baseline engine at the 1990 PM certification emission limit	Controlled engine variability, % of baseline engine	Controlled engine standard deviation, g/bhp-hr for baseline emission of 0.6 g/bhp-hr	Baseline engine variability, %, with the 1990 certification limit as baseline	Baseline engine standard deviation, g/bhp-hr, for1990 emission limit baseline emission of 0.6 g/bhp-hr	Number[a] of tests to achieve 90% probability of detecting reduction with 95% confidence
85	0.09	10	0.06	2	0.012	1
85	0.09	15	0.09	2	0.012	1
85	0.09	20	0.12	2	0.012	1
85	0.09	30	0.18	2	0.012	1
85	0.09	10	0.06	10	0.060	1
85	0.09	15	0.09	10	0.060	1
85	0.09	20	0.12	10	0.060	1
85	0.09	30	0.18	10	0.060	1
85	0.09	10	0.06	30	0.150	2
85	0.09	15	0.09	30	0.150	2
85	0.09	20	0.12	30	0.150	2
85	0.09	30	0.18	30	0.150	2
10	0.54	2	0.012	2	0.012	1
10	0.54	4	0.024	4	0.024	3
10	0.54	6	0.036	6	0.036	6
10	0.54	8	0.048	8	0.048	10
10	0.54	10	0.06	10	0.060	16
5	0.57	2	0.012	2	0.012	3
5	0.57	4	0.024	4	0.024	11
5	0.57	6	0.036	6	0.036	24
5	0.57	8	0.048	8	0.048	42
5	0.57	10	0.06	10	0.060	66

[a] For ETV, the minimum number of tests is three.

US EPA ARCHIVE DOCUMENT

Final Regulation Order

California Code of Regulations, Title 13, Division 3

Chapter 14. Verification Procedure, Warranty and In-Use Compliance Requirements for In-Use Strategies to Control Emissions from Diesel Engines

§ 2700. Applicability.

These procedures apply to in-use strategies which, through the use of sound principles of science and engineering, control emissions of particulate matter (PM) and oxides of nitrogen (NOx) from diesel-fueled diesel engines. These strategies may include but are not limited to, diesel particulate filters, diesel oxidation catalysts, fuel additives, selective catalytic reduction systems, exhaust gas recirculation systems, and alternative diesel fuels. To be verified under these procedures, a strategy must either reduce emissions of PM or both PM and NOx. A strategy that reduces emissions of NOx alone may be verified only for use with on-road diesel engines certified to a PM emissions standard of 0.01 grams per brake-horsepower hour (g/bhp-hr) or less, or off-road diesel engines certified to a PM emissions standard of 0.03 g/bhp-hr or less. A strategy that reduces emissions of NOx alone may be verified for use with other diesel engines provided that they are not regulated by ARB in-use fleet regulations or Airborne Toxic Control Measures that require PM emissions control, or provided that they would otherwise potentially not be retrofit with PM emission control strategies.

NOTE: Authority cited: Sections 39002, 39003, 39500, 39600, 39601, 39650-39675, 40000, 43000, 43000.5, 43011, 43013, 43018, 43105, 43600 and 43700, Health and Safety Code. Reference: Sections 39650-39675, 43000, 43009.5, 43013, 43018, 43101, 43104, 43105, 43106, 43107 and 43204-43205.5 Health and Safety Code; and Title 17 California Code of Regulations Section 93000.

§ 2701. Definitions.

(a) The definitions in Section 1900(b), Chapter 1, Title 13 of the California Code of Regulations are incorporated by reference herein. The following definitions shall govern the provisions of this chapter:
  (1) “15 ppmw or less sulfur fuel” means diesel fuel with a sulfur content equal to or less than 15 parts per million by weight (ppmw).
  (2) “Advertise” means to provide any notice, announcement, information, publication, catalog, listing for sale or lease, or other statement concerning a product or service to the public for the purpose of furthering the sale or lease of the product or service.
  (3) “Alternative Diesel Fuel” means any fuel used in diesel engines that is not commonly or commercially known, sold or represented as diesel fuel No. 1-D or No. 2-D, pursuant to the specifications in ASTM Standard Specification for Diesel Fuel Oils D975-81 and does not require engine or

fuel system modifications for the engine to operate, although minor modifications (e.g. recalibration of the engine fuel control) may enhance performance. Examples of alternative diesel fuels include, but are not limited to, biodiesel, Fischer Tropsch fuels, and emulsions of water in diesel fuel. Natural gas is not an alternative diesel fuel. An emission control strategy using a fuel additive will be treated as an alternative diesel fuel based strategy unless:

(A) The additive is supplied to the vehicle or engine fuel by an on-board dosing mechanism, or

(B) The additive is directly mixed into the base fuel inside the fuel tank of the vehicle or engine, or

(C) The additive and base fuel are not mixed until vehicle or engine fueling commences, and no more additive plus base fuel combination is mixed than required for a single fueling of a single engine or vehicle.

(4) "Approach Light System with Sequenced Flasher Lights in Category 1 and Category 2 Configurations" (ALSF-1 and ALSF-2) mean high intensity approach lighting systems with sequenced flashers used at airports to illuminate specified runways during category II or III weather conditions, where category II means a decision height of 100 feet and runway visual range of 1,200 feet, and category III means no decision height or decision height below 100 feet and runway visual range of 700 feet.

(5) "Applicant" means the entity that has applied for or has been granted verification under this Procedure.

(6) "Auxiliary Emission Control Device" (AECD) means any device or element of design that senses temperature, vehicle speed, engine revolutions per minute (RPM), transmission gear, manifold vacuum, or any other parameter for the purpose of activating, modulating, delaying, or deactivating the operation of the emission control system.

(7) "Average" means the arithmetic mean.

(8) "Backpressure Monitor" means a device that includes a sensor for measuring the engine backpressure upstream of a hardware-based diesel emission control system or component thereof installed in the exhaust system and an indicator to notify the operator when the backpressure exceeds specified high and in some cases low backpressure limits, as defined by the engine manufacturer or the applicant for verification of a diesel emission control strategy.

(9) "Baseline" means the test of a vehicle or engine without the diesel emission control strategy implemented.

(10) "Cold Start" means the start of an engine only after the engine oil and water temperatures are stabilized between 68 and 86 degrees Fahrenheit for a minimum of 15 minutes.

(11) "Common ownership fleet" means all off-road and on-road vehicles and stationary engines being owned or managed day to day by the same person, corporation, partnership, or association. Vehicles managed by the same directors, officers, or managers, or by corporations controlled

by the same majority stockholders are considered to be under common ownership or control even if their title is held by different business entities. For purposes of this regulation, on-road, off-road vehicles and stationary engines are to be considered separate fleets.

(12) "Component Swapping" means the movement of designated parts between different vehicles/applications utilizing the same DECS.

(13) "Diesel emission control strategy" or "Diesel emission control system" means any device, system, or strategy employed with an in-use diesel vehicle or piece of equipment that is intended to reduce emissions. Examples of diesel emission control strategies include, but are not limited to, particulate filters, diesel oxidation catalysts, selective catalytic reduction systems, fuel additives used in combination with particulate filters, alternative diesel fuels, and combinations of the above.

(14) "Diesel Emission Control Strategy Family Name." See Section 2706(j)(2).

(15) "Diesel Engine" means an internal combustion engine with operating characteristics significantly similar to the theoretical diesel combustion cycle. The primary means of controlling power output in a diesel cycle engine is by limiting the amount of fuel that is injected into the combustion chambers of the engine. A diesel cycle engine may be petroleum-fueled (i.e., diesel-fueled) or alternate-fueled.

(16) "Distributor" means any person or entity to whom a diesel emission control strategy is sold, leased or supplied for the purposes of resale or distribution in commerce.

(17) "Donor Vehicle/engine" means any vehicle/engine whose installed DECS device has been removed for the purpose of re-designation or component swapping.

(18) "Durability" means the ability of the applicant's diesel emission control strategy to maintain a level of emissions below the baseline and maintain its physical integrity over some period of time or distance determined by the Executive Officer pursuant to these regulations. The minimum durability testing periods contained herein are not necessarily meant to represent the entire useful life of the diesel emission control strategy in actual service.

(19) "Emergency Standby Engine" means a diesel engine operated solely for emergency use, except as otherwise provided in airborne toxic control measures adopted by the ARB.

(20) "Emergency Use" means using a diesel engine to provide electrical power or mechanical work during any of the following events and subject to the following conditions:

(A) The failure or loss of all or part of normal electrical power service or normal natural gas supply to the facility,

(B) The failure of a facility's internal power distribution system,

(C) The pumping of flood water or sewage to prevent or mitigate a flood or sewage overflow,

(D) The pumping of water for fire suppression or protection,

(E) The powering of ALSF-1 and ALSF-2 airport runway lights under category II or III weather conditions,
(F) Other conditions as specified in airborne toxic control measures adopted by the ARB.

(21) “Emission control group” means a set of diesel engines and applications determined by parameters that affect the performance of a particular diesel emission control strategy. The exact parameters depend on the nature of the diesel emission control strategy and may include, but are not limited to, certification levels of engine emissions, combustion cycle, displacement, aspiration, horsepower rating, duty cycle, exhaust temperature profile, and fuel composition. Verification of a diesel emission control strategy and the extension of existing verifications are done on the basis of emission control groups.

(22) “End user” means any individual or entity that owns or operates a vehicle or piece of equipment that has a verified diesel emission control system installed.

(23) “Executive Officer” means the Executive Officer of the Air Resources Board or the Executive Officer’s designee.

(24) “Executive Order” means the document signed by the Executive Officer that specifies the verification level of a diesel emission control strategy for an emission control group and includes any enforceable conditions and requirements necessary to support the designated verification.

(25) “Fuel Additive” means any substance designed to be added to fuel or fuel systems or other engine-related systems such that it is present in-cylinder during combustion and has any of the following effects: decreased emissions, improved fuel economy, increased performance of the entire vehicle or one of its component parts, or any combination thereof; or assists diesel emission control strategies in decreasing emissions, or improving fuel economy or increasing performance of a vehicle or component part, or any combination thereof. Fuel additives used in conjunction with diesel fuel may be treated as an alternative diesel fuel. See Section 2701 (a)(3) .

(26) “Hot Start” means the start of an engine within four hours after the engine is last turned off. The first hot start test run should be initiated 20 minutes after the cold start for Federal Test Procedure testing following Section 86.1327-90 of the Code of Federal Regulations, Title 40, Part 86.

(27) “Installer” means any individual or entity that equips any vehicle, engine or equipment with a diesel emission control strategy.

(28) “Portable Engine” means an engine designed and capable of being carried or moved from one location to another, except as defined in section 2701(a)(33). Engines used to propel mobile equipment or a motor vehicle of any kind are not portable. Indicators of portability include, but are not limited to, wheels, skids, carrying handles, dolly, trailer, or platform. A portable engine cannot remain at the same facility location for more than 12 consecutive rolling months or 365 rolling days, whichever occurs first, not including time spent in a storage facility. If it

does remain at the facility for more than 12 months, it is considered to be a stationary engine. The definitions in Title 13 California Code of Regulations section 2452(g) and section 2452(x) are incorporated by reference herein.

(29) "Re-designation" means the movement of a used verified DECS from an appropriate engine/application and installation to another engine/application meeting the terms and conditions of the DECS Executive Order within the same common ownership fleet.

(30) "Regeneration" in the context of diesel particulate filters, means the periodic or continuous combustion of collected particulate matter that is trapped in a particulate filter through an active or passive mechanism. Active regeneration requires a source of heat other than the exhaust itself to regenerate the particulate filter. Examples of active regeneration strategies include, but are not limited to, the use of fuel burners and electrical heaters. Passive regeneration does not require a source of heat for regeneration other than the exhaust stream itself. Examples of passive regeneration strategies include, but are not limited to, the use of fuel additives and the catalyst-coated particulate filter. In the context of NOx reduction strategies, "regeneration" means the desorption and reduction of NOx from NOx adsorbers (or NOx traps) during rich operation conditions.

(31) "Revoke" means to cancel the verification status of a diesel emission control strategy. If a diesel emission control strategy's verification status is revoked by the Executive Officer, the applicant must immediately cease and desist selling the diesel emission control strategy to end-users.

(32) "Seller" means any person or entity that sells, leases or supplies a diesel emission control strategy.

(33) "Stationary Engine" means an engine that is designed to stay in one location, or remains in one location. An engine is stationary if any of the following are true:

(A) The engine or its replacement is attached to a foundation, or if not so attached, will reside at the same location for more than 12 consecutive months. Any engine that replaces engine(s) at a location, and is intended to perform the same or similar function as the engine(s) being replaced, will be included in calculating the consecutive time period. In that case, the cumulative time of all engine(s), including the time between the removal of the original engine(s) and installation of the replacement engine(s), will be counted toward the consecutive time period; or

(B) The engine remains or will reside at a location for less than 12 consecutive months if the engine is located at a seasonal source and operates during the full annual operating period of the seasonal source, where a seasonal source is a stationary source that remains in a single location on a permanent basis (at least two years) and that operates at that single location at least three months each year; or

(C) The engine is moved from one location to another in an attempt to circumvent the residence time requirements [Note: The period during which the engine is maintained at a storage facility shall be excluded from the residency time determination.] The definitions in Title 13 California Code of Regulations Section 2452(g) and Section 2452(x) are incorporated by reference herein.

(34) "Unidirectional Device Design and Installation" means that an emission control device must be appropriately designed, manufactured and labeled to prevent reverse flow installation.

(35) "Used Verified Device" means any verified DECS which has been sold or leased to an end user and installed on an engine/application.

(36) "Verification" means a determination by the Executive Officer that a diesel emission control strategy meets the requirements of this Procedure. This determination is based on both data submitted or otherwise known to the Executive Officer and engineering judgment.

(37) "Warrantable Condition" means any condition of the diesel emission control strategy, vehicle, or engine which triggers the responsibility of the applicant to take corrective action pursuant to Section 2707.

NOTE: Authority cited: Sections 39002, 39003, 39500, 39600, 39601, 39650-39675, 40000, 43000, 43000.5, 43011, 43013, 43018, 43105, 43600 and 43700, Health and Safety Code. Reference: Sections 39650-39675, 43000, 43009.5, 43013, 43018, 43101, 43104, 43105, 43106, 43107 and 43204-43205.5, Health and Safety Code; and Title 17 California Code of Regulations Section 93000.

§ 2702. Application Process.

(a) Overview. Before submitting a final application for the verification of a diesel emission control strategy for use with an emission control group, the applicant must submit a preliminary verification application (pursuant to Section 2702(b)) at the Executive Officer's discretion in the format shown in 2702(d). To obtain verification, the applicant must conduct emission reduction testing (pursuant to Section 2703), durability testing (pursuant to Section 2704), a field demonstration (pursuant to Section 2705), and submit the results along with comments and other information (pursuant to Sections 2706 and 2707) in a final verification application to the Executive Officer, in the format shown in Section 2702(d). If the Executive Officer grants verification of a diesel emission control strategy, it will issue an Executive Order to the applicant identifying the verified emission reduction and any conditions that must be met for the diesel emission control strategy to function properly. After the Executive Officer grants verification of a diesel emission control strategy, the applicant must provide a warranty, conduct in-use compliance testing of the strategy after having sold or leased a specified number of units, and report the results to the Executive Officer (pursuant to Section 2709). A diesel emission control strategy that employs two or more individual systems or

components must be tested and submitted for evaluation as one system. A verified diesel emission control strategy may not be installed on an engine with another diesel emission control strategy that is not included in the Executive Order. Applicants seeking verification of an alternative diesel fuel must follow the procedure described in Section 2710.

(b) Preliminary Verification Application. Before formally submitting a final application for the verification of a diesel emission control strategy, the applicant must submit a preliminary verification application at the Executive Officer's discretion. The Executive Officer shall use the information in the preliminary verification application to help determine whether the strategy relies on sound principles of science and engineering to control emissions, the need for additional analyses, and the appropriateness of allowing alternatives to the prescribed requirements. The preliminary verification application must follow the format shown in Section 2702(d) and at a minimum provide the information required in sections 1. through 5., and section 8.A.5, where applicable. In addition, the preliminary verification application must include the following information:

(1) Identification of the contact persons, phone numbers, names and addresses of the responsible party submitting the preliminary verification application.

(2) Description of the diesel emission control strategy's principles of operation. A schematic depicting operation must be included. It is the responsibility of the applicant to demonstrate that its product relies on sound principles of science and engineering to achieve emission reductions.

(A) If, after reviewing the preliminary verification application, the Executive Officer determines that the applicant has not made a satisfactory demonstration that its product (diesel emission control strategy) relies on sound principles of science and engineering to achieve emission reductions, the Executive Officer shall notify the applicant of the determination in writing within 30 days of receiving the preliminary verification application. The applicant may choose to withdraw from the verification process or submit additional materials and clarifications. The additional submittal must be received by the Executive Officer no later than 60 days from the date of the notification letter or the application may be suspended.

(B) If, after reviewing the additional submittal, the Executive Officer determines that the applicant has not yet made a satisfactory demonstration that its product relies on sound principals of science and engineering to achieve emission reductions, the preliminary verification application shall be suspended. If a preliminary verification application has been suspended, it may only be reactivated at the discretion of the Executive Officer.

(C) If at any time, the Executive Officer has reason to doubt the scientific or engineering soundness of a product, the Executive Officer shall notify the applicant in writing and may require the applicant to submit

additional supporting materials and clarifications no later than 60 days from the date of the notification letter. If the additional submittal is not received by the Executive Officer by the deadline established in the notification letter, the preliminary or final application may be suspended or the existing verification may be revoked. In deciding whether to suspend a preliminary or final application or revoke an existing verification the Executive Officer will review submittals as provided in subsection (B) above.

(3) Preliminary parameters for defining emission control groups that are appropriate for the diesel emission control strategy. The Executive Officer will work with the applicant to determine appropriate emission control group parameters.

(4) The applicant's proposed test plan for meeting the requirements of Sections 2702-2706. Existing test data may be submitted for the Executive Officer's consideration. The preliminary verification application must focus on verification of the diesel emission control strategy for use with a single emission control group.

(5) A brief statement that the applicant acknowledges and agrees to do the following:

(A) Provide a warranty pursuant to the requirements of Section 2707.

(B) Submit in-use compliance information pursuant to the requirements of Section 2709.

(C) Keep records until the in-use compliance requirements are completed that contain information per Section 2702 (m) including:

1. Updated end user contact information.
2. A description of the vehicles or equipment on which the applicant's products are installed.
3. A description of the engines on which the applicant's products are installed.

(c) When an applicant submits a preliminary verification application, the Executive Officer shall, within 30 days of its receipt, determine whether the applicant has identified the information necessary to support an application for verification and notify the applicant in writing that it may submit an application for verification. The Executive Officer may suggest modifications to the proposed preliminary verification application to facilitate verification of the diesel emission control strategy. All applications, correspondence, and reports must be submitted in writing to:

Chief, Heavy-Duty Diesel In-Use Strategies Branch
Air Resources Board
1001 I Street
Sacramento, CA 95814

(d) Application Format. The preliminary and final verification applications must be submitted in writing to the address shown in subsection (c) above. Electronic mail and verbal submissions do not constitute acceptable application formats. Supporting data in electronic format may be accepted as part of the application at the discretion of the Executive Officer. The preliminary and final verification applications for a diesel emission control strategy must follow the format shown below. If a section asks for information that is not applicable to the diesel emission control strategy, the applicant must indicate "not applicable." If the Executive Officer concurs with the applicant's judgment that a section is not applicable, the Executive Officer may waive the requirement to provide the information requested in that section. Final verification applications must include all of the information provided in the preliminary verification application as described in Section 2702(b), including any additional information, updates, or changes, and all additional information shown below.

1. Introduction

1.1 Identification of applicant, manufacturer, and product
1.2 Identification of type of verification being sought
- 1.2.1 Description of emission control group selected
- 1.2.2 Emission reduction claim
- 1.2.3 Description of intended applications (examples of in-use vehicles or equipment, typical duty cycles, fuel requirements, etc.)

2. Diesel Emission Control Strategy Information

2.1 General description of the diesel emission control strategy
- 2.1.1 Detailed discussion of principles of operation and system design
- 2.1.2 Description of inducement method if applicable
- 2.1.3 Schematics depicting operation (as appropriate)
- 2.1.4 A list identifying all the parts of the diesel emission control strategy as described in Section 2706(o)
- 2.1.5 Detailed description of measures taken to prevent reverse flow installation

2.2 Description of regeneration method
- 2.2.1 Operating condition requirements for regeneration
- 2.2.2 Thresholds and control logic to activate regeneration
- 2.2.3 Description of backpressure monitor including thresholds and control logic

2.3 Favorable operating conditions
2.4 Unfavorable operating conditions and associated reductions in performance
2.5 Fuel and lubricating oil requirements and misfueling considerations
2.6 Identification of failure modes and associated consequences

2.7 Complete discussion of potential safety issues *(e.g., uncontrolled regeneration, lack of proper maintenance, unfavorable operating conditions, etc.)*
2.8 Installation requirements
2.9 Maintenance requirements
2.9.1 Detailed description of all normal maintenance requirements for the diesel emission control system
2.9.2 A copy of the language that will instruct the end user of proper handling of spent components and/or materials cleaned from the diesel emission control system, identify any hazardous materials, and provide procedures for resetting any backpressure monitors after maintenance procedures are completed.
2.10 Description of noise level control compliance

3. Alternative Diesel Fuel and Fuel Additive Information.
(Use of an alternative diesel fuel/fuel additive requires a multimedia evaluation as required by Section 43830.8 California Health and Safety Code)
3.1 Additional information from Section 2710(b), 2710(c), 2710(f), and 2710(g)
3.2 Emission control group compatibility considerations
3.3 Misfueling prevention strategies
3.4 Multimedia evaluation
3.4.1 Additional test data and information required for multimedia evaluation

4. Diesel Emission Control Strategy and Emission Control Group Compatibility
4.1 Compatibility with the engine
4.1.1 Discussion on calibrations and design features that may vary from engine to engine
4.1.2 Effect on overall engine performance
4.1.3 Effect on engine backpressure
4.1.4 Additional load on the engine
4.1.5 Effect on fuel consumption
4.1.6 Engine oil consumption considerations
4.2 Compatibility with the application
4.2.1 Dependence of calibration and other design features on application characteristics
4.2.2 Presentation of typical exhaust temperature profiles and other relevant field-collected data from representative applications within the emission control group
4.2.3 Comparison of field-collected application data with operating conditions suitable for the diesel emission control strategy

5. Testing Information
5.1 Emission reduction testing
5.1.1 Test facility identification including capabilities and identification of all analytical instruments

5.1.2 Description of test vehicle and engine *(make, model year, engine family name, PM and NOx certification levels if applicable, etc.)*
5.1.3 Statement indicating whether the test engine is in a proper state of maintenance, and/or has been rebuilt or modified from the original engine manufacturer configuration
5.1.4 Description of test fuel
5.1.5 Discussion of effects of elevated NOx emissions on diesel emission control strategy (effects on emission reduction performance, durability, safety, and control strategy response)
5.1.6 Test procedure description *(-pre-conditioning period, test cycle, etc.)*
5.1.7 Test results and comments
5.1.8 Incomplete and aborted test data and explanations

5.2 Durability testing
5.2.1 Test facility identification including capabilities and identification of all analytical instruments
5.2.2 Description of field application (where applicable)
5.2.3 Description of test vehicle and engine *(make, model year, engine family name, PM and NOx certification levels if applicable, etc.)*
5.2.4 Analysis of emissions test fuel
5.2.5 Analysis of durability test fuel
5.2.6 Test procedure description *(field or bench, test cycle, etc.)*
5.2.7 Test Procedure demonstrating durability of monitoring and notification system
5.2.8 Description of maintenance during durability testing
5.2.9 Test results and comments
5.2.10 Summary of evaluative comments from third-party for in-field durability demonstration *(e.g., driver or fleet operator)*

5.3 Field demonstration (where applicable)
5.3.1 Field application identification
5.3.2 Description of test vehicle and engine *(make, model year, engine family name, PM and NOx certification levels if applicable, etc.)*
5.3.3 Engine backpressure and exhaust temperature graphs with comments
5.3.4 Summary of evaluative comments from third-party *(e.g., driver or fleet operator)*
5.3.5 Description of test failures

*6***.** *Warranty and In-Use Compliance Requirements*

6.1 Statement that the applicant agrees to provide annual warranty reports and to follow the warranty requirements per Section 2707
6.2 Statement that the applicant agrees to follow the in-use compliance requirements per Section 2709
6.3 Statement that the applicant agrees to keep the required end user information per Section 2702(m)

7. *References*

8. *Appendices*

A. Laboratory test report information *(for all tests, including incomplete, aborted and failed tests)*
   - A.1 Actual laboratory test data
   - A.2 Plots of engine backpressure and exhaust temperature
   - A.3 Driving traces for chassis dynamometer tests
   - A.4 Quality assurance and quality control information
   - A.5 Testing equipment information and indication that testing equipment meets specifications and calibrations given in the Code of Federal Regulations, Title 40, Part 86 (See Sections 2703(m), 2706(a)(2))

B. Third-party letters or questionnaires describing in-field performance
C. Diesel emission control system label
D. Copy of the Owner's manual (as described in Section 2706 (l))
E. Copy of the Installation Manual
F. Sample diesel emission control system label (See Section 2706(j))
G. Other supporting documentation

(e) Within 30 days of receipt of the preliminary application, the Executive Officer shall notify the applicant whether the application is complete.

(f) Within 60 days after a final application has been deemed complete, the Executive Officer shall determine whether the diesel emission control strategy merits verification and shall classify it as shown in Table 1:

Table 1. Verification Classifications for Diesel Emission Control Strategies

Pollutant	Reduction	Classification
PM	< 25%	Not verified
		Level 0* (see note below)
	≥ 25%	Level 1
		Level 1 Plus**
	≥ 50%	Level 2
		Level 2 Plus**
	≥ 85%, or ≤ 0.01 g/bhp-hr	Level 3
		Level 3 Plus**
NOx	< 25%	Not verified
	≥ 25%	Mark 1
	≥ 40%	Mark 2
	≥ 55%	Mark 3
	≥ 70%	Mark 4
	≥ 85%	Mark 5

*A diesel emission control strategy that reduces emissions of PM by less than 25 percent may be verified as a Level 0 strategy if it reduces emissions of NOx by at least 25 percent and meets the other criteria in section 2700.
**The diesel emission control strategy complies with the 20 percent NO_2 limit before January 1, 2009 (and after January 1, 2007).

The applicant and the Executive Officer may mutually agree to a longer time period for reaching a decision, and additional supporting documentation may be submitted by the applicant before a decision has been reached. The Executive Officer shall notify the applicant of the decision in writing and specify the verification level for the diesel emission control strategy and identify any terms and conditions that are necessary to support the verification.

(g) Extensions of an Existing Verification. If the applicant has verified a diesel emission control strategy with one emission control group and wishes to extend the verification to include additional emission control groups, it may apply to do so using the original test data, additional test data, engineering justification and analysis, or any other information deemed necessary by the Executive Officer to address the differences between the emission control

group already verified and the additional emission control group(s). Processing time periods follow sections (e) and (f) above.

(h) Conditional Extensions of an Existing Verification for On-road Applications. If an applicant has an ARB verified diesel emission control strategy and wishes to extend the verification to include new on-road emission control groups, the applicant may apply to receive a conditional extension. If the Executive Officer determines that the diesel emission control strategy is technologically sound and appropriate for the intended application, the applicant may be granted a conditional extension for up to one year. Upon receiving a conditional extension, the applicant may sell the diesel emission control strategy as a verified product for the duration of the conditional extension period. To obtain full verification, the applicant must complete the requirements set forth by the Executive Officer according to the requirements of the regulation. In granting a conditional extension, the Executive Officer may consider all relevant information including, but not limited to, the following: the design of the diesel emission control strategy, original test data, other relevant test data, the duty cycle of the prospective emission control group, and field experience. For the time period it is effective, a conditional extension is equivalent to a verification for the purposes of satisfying the in-use compliance requirements. Emission control strategies that are conditionally verified for off-road and stationary applications are not eligible for conditional extensions (See Section 2704(k)).

(i) Design Modifications. If an applicant modifies the design of a diesel emission control strategy that has already been verified or is under consideration for verification by the Executive Officer, the modified version must be evaluated under this Procedure. The applicant must provide a detailed description of the design modification along with an explanation of how the modification will change the operation and performance of the diesel emission control strategy. To support its claims, the applicant must submit additional test data, engineering justification and analysis, or any other information deemed necessary by the Executive Officer to address the differences between the modified and original designs. Processing time periods follow sections (e) and (f) above.

(j) Verification Transfers. If an applicant wishes to sell, lease, or supply another manufacturer's previously verified diesel emission control system, the applicant must do the following:
   (1) Submit a letter of consent from the manufacturer that legally holds the original verification. The letter must give the applicant the right to hold a verification for the diesel emission control system and, if applicable, to use information that was previously submitted as support in the application for the original verification.
   (2) Submit an application(s) per Section 2702 of this Procedure. If previously submitted information is included, necessary additional information must

be submitted that satisfies all applicable requirements of this Procedure (e.g. testing data, warranty statement, label, owner's manual, etc.).

(3) Submit a description of the diesel emission control strategy's principles of operation. The applicant must demonstrate understanding of how the product relies on sound principles of science and engineering to achieve emissions reductions.

(k) Emission Control Systems Approved under Other Verification Programs. Any applicant with a diesel emission control system that is verified under another diesel emission control verification program that wishes to receive ARB verification must submit an application that contains the information requested in part (d) above. Pre-existing data and information submitted in support of verification approval from other programs may be submitted, but the applicant must meet requirements that are unique to this Procedure including, but not limited to, a system label compliant with Section 2706(j), a California owner's manual compliant with Section 2706(l), a warranty compliant with Section 2707, in-use compliance requirements per Section 2709, and multimedia evaluation if applicable. The Executive Officer may evaluate all information submitted including additional information required by this Procedure to determine if a diesel emission control strategy merits ARB verification.

(l) Treatment of Confidential Information. Information submitted to the Executive Officer by an applicant may be claimed as confidential, and such information shall be handled in accordance with the procedures specified in Title 17, California Code of Regulations, Sections 91000-91022. The Executive Officer may consider such confidential information in reaching a decision on a verification application.

(m) Applicants that receive verifications, conditional verifications (See Section 2704(k), or conditional extensions must keep records that have valid end user contact information (name, address, phone number), a description of the vehicles or equipment the units are applied to (type of vehicle/equipment, make, model year, vehicle identification number), and a description of the engines the units are applied to (make, model, model year, engine serial number, engine family name). The applicant must keep these records for each diesel emission control strategy family until the in-use compliance requirements of the diesel emission control strategy family are completed. Applicants that receive conditional extensions or conditional verifications must submit these records to the Executive Officer one year after receiving the conditional extension or conditional verification. Applicants that receive verifications must submit these records upon request by the Executive Officer to an agent or employee of ARB. The Executive Officer may request that such records be made available at any time. The applicant must provide these records within 30 days of the request by the ARB. Failure to submit these records may result in revocation or suspension of the verification

and/or any other remedy available under Part 5, Division 26 of the Health and Safety Code.

(n) The Executive Officer may at any time with respect to any diesel emission control strategy sold, leased, offered for sale, intended for sale, or manufactured for sale in California, order the applicant or manufacturer to submit records pertaining to the diesel emission control strategy, at the applicant's expense, to a location specified by the Executive Officer.

(o) Applicants that receive verifications, conditional verifications, or conditional extensions must demonstrate sales or the active pursuit of sales of their diesel emission control systems in California upon request of the Executive Officer. If an applicant fails to provide such proof, the Executive Officer will evaluate whether the verification should be revoked.

(p) The Executive Officer may, with respect to any diesel emission control strategy sold, leased, offered for sale, intended for sale, or manufactured for sale in California, order the applicant or strategy manufacturer to make available for testing and/or inspection a reasonable number of diesel emission control systems, and may direct that they be delivered at the applicant's expense to the state board at the Haagen-Smit Laboratory, 9528 Telstar Avenue, El Monte, California or where specified by the Executive Officer. The Executive Officer may also, with respect to any diesel emission control strategy being sold, leased, offered for sale, intended for sale, or manufactured for sale in California, have an applicant test and/or inspect under the supervision of the Executive Officer a reasonable number of units at the applicant's or manufacturer's facility or at any test laboratory accepted by the Executive Officer. All such testing and inspection is confirmatory in nature. If the Executive Officer finds performance that is not consistent with either an existing or requested verification, the applicant must address and resolve the inconsistency to the satisfaction of the Executive Officer in order to maintain or receive verification. Any testing and inspection done by ARB cannot be used as a substitute for emissions test data or other support required in an application for verification.

(q) The Executive Officer may lower the verification level or revoke the verification status of a verified diesel emission control strategy family, a conditionally verified system, or a system with a conditional extension or suspend all review of pending verification applications if the Executive Officer determines that there are errors, omissions, inaccurate information, fraudulent submittals, or a deficiency of required submittals in the application for verification, supporting information, warranty report, or in-use compliance testing. Additionally, penalties may be assessed under Part 5, Division 26 of the Health and Safety Code. The Executive Officer may suspend the review of all other applications sent by an applicant if that applicant fails to submit warranty reports or other requested information. The Executive Officer may

also seek remedial action against the applicant if it is determined that the verified diesel emission control strategy does not comply with the requirements or provisions of the Executive Order.

NOTE: Authority cited: Sections 39002, 39003, 39500, 39600, 39601, 39650-39675, 40000, 43000, 43000.5, 43011, 43013, 43018, 43105, 43600 and 43700, Health and Safety Code. Reference: Sections 39650-39675, 43000, 43009.5, 43013, 43018, 43101, 43104, 43105, 43106, 43107 and 43204-43205.5, Health and Safety Code; and Title 17 California Code of Regulations Section 93000.

§ 2703. Emission Testing Requirements.

(a) The applicant must test the diesel emission control strategy on an emission control group basis and identify the emission control group. The applicant must identify the test engines and vehicles, if applicable, by providing the engine family name, make, model, model year, and PM and NOx certification levels if applicable. The applicant must also describe the applications for which the diesel emission control strategy is intended to be used by giving examples of in-use vehicles or equipment, characterizing typical duty cycles, indicating any fuel requirements, and/or providing other application-related information.

(b) Test Engine Requirements and Pre-conditioning. The applicant may tune-up or rebuild test engines prior to, but not after, baseline testing unless rebuilding the engine is an integral part of the diesel emission control strategy. All testing should be performed with the test engine in a proper state of maintenance. Emissions of NO_2 from the test engine must not exceed 15 percent of the total baseline NOx emissions by mass. If there is a special category of engines with NO_2 emission levels that normally exceed 15 percent, this requirement may be adjusted for those engines at the discretion of the Executive Officer.

(c) Diesel Emission Control System Pre-conditioning. The engine or vehicle installed with a diesel emission control system must be operated for a break-in period of between 25 and 125 hours before emission testing. Note that special pre-conditioning requirements may apply. See section 2706(a)(4) for details.

(d) Test Fuel.
(1) The test fuel must meet the specifications in the California Code of Regulations (Sections 2280 through 2283 of Title 13), with the exception of the sulfur content or other properties previously identified by the applicant and approved by the Executive Officer. The Executive Officer may approve test fuel(s) that do not comply with Sections 2280 through 2283 of Title 13 of the California Code of Regulations if the fuel(s) are

determined to be, based on sound science and engineering, representative of commercially available fuel typically used for the intended application(s).

(2) If operation or performance of a diesel emission control strategy is affected by fuel sulfur content, the sulfur content of the test fuel must be no less than 66 percent of the stated maximum sulfur content for the diesel emission control strategy, unless
   (A) the testing is performed with fuel containing 15 ppmw or less sulfur for verification on 15 ppmw or less sulfur diesel fuel, or
   (B) the testing is performed with diesel fuel commercially available in California for verification on CARB diesel fuel (i.e., fuel meeting the specifications in Title 13, California Code of Regulations, Sections 2280 through 2283).

(3) Baseline testing may be conducted with commercially available diesel fuel or diesel fuel with 15 ppmw or less sulfur. Baseline and control tests must be performed using the same fuel unless the control fuel is specified as a component of the emission control strategy.

(4) The test fuel (or batch of fuel purchased) must be analyzed using American Society for Testing and Materials (ASTM) test methods listed in Table 6 (See Section 2710), which are incorporated herein by reference. At a minimum, sulfur content, aromatic content, polycyclic aromatic hydrocarbons, nitrogen content, and cetane number must be reported. The Executive Officer may ask for additional properties to be reported if evidence suggests those properties may affect functioning of the diesel emission control strategy.

(e) Test Cycle. The diesel emission control strategy must be tested using the test cycles indicated in subparagraphs 1-3 below (summarized in Table 2) or with an alternative cycle(s) approved by the Executive Officer pursuant to subsection (f) below. The Executive Officer may require the applicant to conduct additional testing if such information is necessary for a complete evaluation of the control technology.

Table 2. Test Cycles for Emission Reduction Testing*

Test Type	On-Road	Off-Road (including portable engines)	Stationary
Engine	FTP Heavy-duty Transient Cycle (1 cold-start and 3 hot-starts)	Steady-state test cycle from ARB off-road regulations until December 31, 2008 with Executive Officer approval, otherwise; Transient test cycle from ARB off-road regulations (3 hot-starts either cycle)	Discrete mode test cycle from ARB off-road regulations (3 hot-starts)
Chassis	UDDS (3 hot-starts) and a low-speed test cycle per 2703 (e)(1)(B)2. (3 hot-starts).	Not Applicable	Not Applicable

FTP = Federal Test Procedure; UDDS = Urban Dynamometer Driving Schedule

(1) On-road Engines and Vehicles. For on-road diesel-fueled vehicles, the applicant may choose between engine dynamometer testing and chassis dynamometer testing, subject to the following conditions. Engine testing may be used for verification of an absolute engine emissions level or a percent emission reduction. Chassis testing may be used only to verify a percent emission reduction. The applicant may use emission test data to satisfy the durability test data requirement, but must follow the same testing option for the remaining durability tests (see Section 2704).

(A) Engine testing must consist of one cold-start and at least three hot-start tests using the Federal Test Procedure (FTP) Heavy-duty Transient Cycle for engines used in on-road applications, in accordance with the provisions in the Code of Federal Regulations, Title 40, Part 86, Subpart N.

(B) The applicant must conduct all chassis tests in accordance with the provisions of the Code of Federal Regulations, Title 40, Part 86, Subpart N insofar as they pertain to chassis dynamometer testing. Chassis testing must include two separate test cycles as follows:

1. At least three hot-start tests using the Urban Dynamometer Driving Schedule (UDDS) (see Code of Federal Regulations, Title 40, Part 86, appendix I (d)).
2. Three hot-start tests using a low-speed chassis test cycle representing urban stop-and-go traffic operation. The test cycle must include a repetitive series of idling periods immediately

followed by events of maximum vehicle acceleration. The applicant can propose, for Executive Officer approval, a low-speed cycle as applicable to the type of vehicle and vehicle operation for which the diesel emission control strategy is intended. The Executive Officer will provide examples (e.g., New York Bus Cycle) of appropriate test cycles upon request by the applicant during the verification process. The applicant may request that the Executive Officer waive the requirement to conduct the low-speed chassis test. In reviewing this request, the Executive Officer may consider all relevant information including, but not limited to, characteristics of the duty cycles in the emission control group and the principles of operation of the diesel emission control strategy.

3. The driver must follow the test cycles as closely as possible and must not deviate beyond the following tolerances (See Code of Federal Regulation, Part 86, Subpart M, 86.1215-85).
   a. The upper limit is 4 miles per hour higher than the highest point on the trace within 1 second of the given time.
   b. The lower limit is 4 miles per hour lower than the lowest point on the trace within 1 second of the given time.
   c. Speed variations greater than the tolerances (such as may occur during gear changes or braking spikes) are acceptable, provided they occur for less than 2 seconds on any occasion and are clearly documented as to the time and speed at that point of the test cycle.
   d. Speeds lower than those prescribed are acceptable, provided the vehicle is operated at maximum available power during such occurrences.

(C) For any diesel emission control strategy intended to reduce NOx from on-road applications, the applicant must identify and discuss the effects of elevated NOx emissions on the diesel emission control strategy (emissions of NOx that are significantly greater than certified levels are said to be elevated, and may result, for example, from the activation of an AECD that advances fuel injection timing under cruise conditions). The applicant's discussion must include effects on emission reduction performance, durability, and safety considerations, how the strategy would respond to elevated NOx emissions that do not occur at the time the strategy is calibrated, and must be supported by engineering justification and any pertinent data.

(2) Off-road Engines and Equipment (including portable engines). For off-road diesel-fueled vehicles and equipment, the applicant must follow the transient test procedures outlined in the ARB off-road regulations (California Code of Regulations, Title 13, Section 2423 and the incorporated California Exhaust Emissions Standards and Test Procedures for New 2008 and Later Tier 4 Off-Road Compression-Ignition Engines, Part I-C). For all variable speed engines, a minimum of three

hot-start tests must be conducted using the Nonroad Transient Composite Cycle (NRTC).

(A) The Executive Officer may require the applicant to follow another test cycle if the Executive Officer determines that it is more representative of the in-use duty cycle of the off-road application for which the applicant seeks verification.

(B) An applicant may follow the steady state test procedure outlined in the ARB off-road regulations (California Code of Regulations, Title 13, Section 2423 and the incorporated California Exhaust Emission Standards and Test Procedures for New 2000 and Later Tier 1, Tier 2, and Tier 3 Off-Road Compression-Ignition Engines, Part I-B) only if the applicant has submitted a complete preliminary verification application by October 1, 2008 and has received a letter of notification from the Executive Officer, dated no later than December 31, 2008 that the application is complete. In addition, the applicant must submit a complete final verification application that is consistent with the terms of the approved preliminary verification application by July 1, 2010. If the applicant fails to submit a complete final verification application by July 1, 2010, the applicant must test using the NRTC.

(C) An applicant with a system verified after October 19, 2007 using the steady state test procedure outlined in the ARB off-road regulations (California Code of Regulations, Title 13, Section 2423 and the incorporated California Exhaust Emission Standards and Test Procedures for New 2000 and Later Tier 1, Tier 2, And Tier 3 Off-Road Compression-Ignition Engines, Part I-B) must submit emissions test data using the NRTC by January 1, 2013. The Executive Officer will reassess and potentially revise the verification status of the system, claimed emissions reductions, and compliance with NO_2 emissions requirements based on the submitted data. Appropriate testing must include a pre-conditioned unit, an aged unit, and a baseline test. If such data are not received and approved by the Executive Officer by January 1, 2013, the verification will be revoked. A verification awarded prior to October 19, 2007, is not subject to this requirement. A verification for which the Executive Officer determines the NRTC is not appropriate per section 2703(e)(2)(A) is not subject to this requirement.

(D) Applicants may request that the Executive Officer consider alternative test cycles, as described in subsection (f).

(3) Stationary Engines. For stationary engines, the applicant must follow the discrete mode test procedures outlined in the ARB off-road regulations (as referenced in (2) above). A minimum of three hot-start tests must be conducted using the specified test cycle. Applicants may request that the Executive Officer consider alternative test cycles and methods, as described in subsection (f).

(f) Alternative Test Cycles and Methods. The applicant may request the Executive Officer to approve an alternative test cycle or method in place of a required test cycle or method. In reviewing this request, the Executive Officer will consider all relevant information including, but not limited to, the following:
(1) Test procedures specified in airborne toxic control measures adopted by the ARB, e.g. the Airborne Toxic Control Measure for Stationary Compression Ignition Engines,
(2) Similarity of average speed, percent of time at idle, average acceleration, and other characteristics to the specified test cycle or method and in-use duty cycle,
(3) Body of existing test data generated using the alternative test cycle or method,
(4) Technological necessity, and
(5) Technical ability to conduct the required test.

(g) Test Run. The number of tests indicated in Table 2 must be run for both baseline (without the diesel emission control strategy implemented) and control configurations. For strategies that include exhaust aftertreatment, engine backpressure and exhaust temperature must be measured and recorded on a second-by-second basis (1 Hertz) during at least one baseline run and each of the control test runs. For strategies that use a chemical reductant to reduce emissions of NOx from on-road or off-road applications, the amount of reductant consumed during each control test run must be measured and recorded.

(h) Emissions During Particulate Filter Regeneration Events. For any diesel emission control strategy that has a distinct regeneration event, emissions that occur during the event must be measured and taken into account when determining the net emission reduction efficiency of the system. If a regeneration event will not occur during emission testing, applicants may pre-load the diesel emission control system with diesel PM to force such an event to occur during testing, subject to the approval of the Executive Officer. Applicants must provide data or engineering analysis indicating when events occur on test cycles and in actual operation (e.g., backpressure data).

(i) Results. For all valid emission tests used to support emission reduction claims, the applicant must report emissions of total PM, non-methane hydrocarbons or total hydrocarbons (whichever is used for the relevant engine or vehicle certification), oxides of nitrogen, nitrogen dioxide, carbon monoxide, and carbon dioxide.
(1) For mobile sources, or for engines tested using an engine dynamometer, emissions must be reported in grams/mile (g/mile) or grams/brake horsepower-hour (g/bhp-hr).
(2) For stationary engines, gaseous and particulate matter emissions must be reported as required by the test methods approved by the Executive Officer.

(j) Incomplete and Aborted Tests. The applicant must identify all incomplete and aborted tests and explain why those tests were incomplete or aborted.

(k) Additional Analyses. The Executive Officer may require the applicant to perform additional analyses if there is reason to believe that the use of a diesel emission control strategy may result in the increase of toxic air contaminants, other harmful compounds, or a change in the nature or amount of the emitted particulate matter.
  (1) In its determination, the Executive Officer may consider all relevant data, including but not limited to the following:
    (A) The addition of any substance to the fuel, intake air, or exhaust stream,
    (B) Whether a catalytic reaction is known or reasonably suspected to increase toxic air contaminants or ozone precursors,
    (C) Results from scientific literature,
    (D) Field experience, and
    (E) Any additional data.
  (2) These additional analyses may include, but are not limited to, measurement of the following:
    (A) Benzene
    (B) 1,3-butadiene
    (C) Formaldehyde
    (D) Acetaldehyde
    (E) Polycyclic aromatic hydrocarbons (PAH)
    (F) Nitro-PAH
    (G) Dioxins
    (H) Furans
  (3) The Executive Officer will determine appropriate test methods for additional analyses in consultation with the applicant.

(l) Quality Control of Test Data. The applicant must provide information on the test facility, test procedure, and equipment used in the emission testing. For data gathered using on-road and off-road test cycles and methods, applicants must provide evidence establishing that the test equipment used meets the specifications and calibrations given in the Code of Federal Regulations, Title 40, Part 86, subpart N. The testing information must be approved by the Executive Officer.

(m) The Executive Officer may, with respect to any diesel emission control strategy sold, leased, offered for sale, or manufactured for sale in California, order the applicant or strategy manufacturer to make available for testing and/or inspection a reasonable number of diesel emission control systems, and may direct that they be delivered at the applicant's expense to the state board at the Haagen-Smit Laboratory, 9528 Telstar Avenue, El Monte, California or where specified by the Executive Officer. The Executive Officer

may also, with respect to any diesel emission control strategy being sold, leased, offered for sale, or manufactured for sale in California, have an applicant test and/or inspect a reasonable number of units at the applicant or manufacturer's facility or at any test laboratory under the supervision of the Executive Officer.

NOTE: Authority cited: Sections 39002, 39003, 39500, 39600, 39601, 39650-39675, 40000, 43000, 43000.5, 43011, 43013, 43018, 43105, 43600 and 43700, Health and Safety Code. Reference: Sections 39650-39675, 43000, 43009.5, 43013, 43018, 43101, 43104, 43105, 43106, 43107 and 43204-43205.5 Health and Safety Code; Title 17 California Code of Regulations Section 93000.

§ 2704. Durability Testing Requirements

(a) The applicant must demonstrate, to the satisfaction of the Executive Officer, the durability of the applicant's diesel emission control strategy through an actual field or laboratory-based demonstration combined with chassis or engine dynamometer-based emission tests. If the applicant chooses a laboratory-based durability demonstration, an additional field demonstration will be required to demonstrate in-field compatibility (pursuant to Section 2705). If the applicant has demonstrated the durability of the identical system in a prior verification or has demonstrated durability through field experience, the applicant may request that the Executive Officer accept the previous demonstration in fulfillment of this requirement. In evaluating such a request, the Executive Officer may consider all relevant information including, but not limited to, the similarity of baseline emissions and application duty cycles, the relationship between the emission control group used in previous testing and the current emission control group, the number of engines tested, evidence of successful operation and user acceptance, and published reports.

(b) Engine Selection. Subject to the approval of the Executive Officer, the applicant may choose the engine and application to be used in the durability demonstration. The engine and application must be representative of the emission control group for which verification is sought. The selected engine need not be the same as the engine used for emission testing, but if the applicant does use the same engine, the emission testing may also be used for the initial durability tests. Emissions of NO_2 from the emissions test engine must not exceed 15 percent of the total baseline NOx emissions by mass. If there is a special category of engines with NO_2 emission levels that normally exceed 15 percent, this requirement may be adjusted for those engines at the discretion of the Executive Officer.

(c) Test Fuel.
(1) The test fuel must meet the specifications in the California Code of Regulations (Sections 2280 through 2283 of Title 13), with the exception

of the sulfur content or other properties previously identified by the applicant and approved by the Executive Officer. The Executive Officer may approve test fuel(s) that do not comply with Sections 2280 through 2283 of Title 13 of the California Code of Regulations if the fuel(s) are determined to be, based on sound science and engineering, representative of commercially available fuel typically used for the intended application(s).

(2) If operation or performance of a diesel emission control strategy is affected by fuel sulfur content, the sulfur content of the test fuel must be no less than 66 percent of the stated maximum sulfur content for the diesel emission control strategy, unless
   (A) the testing is performed with fuel containing 15 ppmw or less sulfur for verification on 15 ppmw or less sulfur diesel fuel, or
   (B) the testing is performed with diesel fuel commercially available in California for verification on CARB diesel fuel (i.e., fuel meeting the specifications in Title 13, California Code of Regulations, Sections 2280 through 2283).

(3) Baseline testing may be conducted with commercially available diesel fuel or diesel fuel with 15 ppmw or less sulfur. Baseline and control tests must be performed using the same fuel unless the control fuel is specified as a component of the emission control strategy.

(4) The test fuel (or batch of fuel purchased) must be analyzed using American Society for Testing and Materials (ASTM) test methods listed in Table 6 (See Section 2710), which are incorporated herein by reference. At a minimum, sulfur content, aromatic content, polycyclic aromatic hydrocarbons, nitrogen content, and cetane number must be reported. The Executive Officer may ask for additional properties to be reported if evidence suggests those properties may affect functioning of the diesel emission control strategy.

(d) Service Accumulation. The durability demonstration consists of an extended service accumulation period in which the diesel emission control strategy is implemented in the field or in a laboratory accepted by the Executive Officer, with emission reduction testing before and after the service accumulation. Service accumulation begins after the first emission test and concludes before the final emission test. The pre-conditioning period required in Section 2703 (c) cannot be used to meet the service accumulation requirements.

(1) Minimum Durability Demonstration Periods. The minimum durability demonstration periods are shown in Table 3, below.

Table 3. Minimum Durability Demonstration Periods

Engine Type	Minimum Durability Demonstration Period
On-Road	50,000 miles or 1000 hours
Off-Road (including portable engines) and Stationary	1000 hours
Stationary Emergency Standby Engines	500 hours

(2) Temperature and Backpressure Measurement Requirements. For strategies that include exhaust aftertreatment, engine backpressure and exhaust temperature must be measured and recorded for 1000 hours or over the entire durability period (whichever is shorter). The applicant must propose a measurement and recording protocol for approval by the Executive Officer. The protocol may include, but is not limited to, measurement and recording of values once every few seconds, or higher frequency measurement with recording of averages, minima, and maxima over longer time intervals. Data must be submitted electronically in columns as a text file or another format approved by the Executive Officer.

(3) NOx Emissions Measurement Requirements. For strategies that include exhaust aftertreatment to reduce emissions of NOx, the mass emissions of NOx both upstream and downstream of the aftertreatment device must be measured and recorded for at least the first and last 100 hours of the durability period. The applicant must propose a measurement method for approval by the Executive Officer. The method may include, but is not limited to, the use of NOx sensors before and after the device. Measurements of NOx emissions must occur on at least a 1 Hertz basis. Data must be recorded as averages over time intervals no greater than 10 seconds. Data must be submitted electronically in columns as a text file or another format approved by the Executive Officer.

(4) Fuel for Durability Demonstrations. The fuel used during durability demonstrations should be equivalent to the test fuel, or a fuel with properties less favorable to the durability of the emission control strategy. Durability demonstrations may, at the applicant's option and with the Executive Officer’s approval, include intentional misfueling events so that data on the effects of misfueling may be obtained.

(e) Third-Party Statement for In-field Durability Demonstrations. For in-field durability demonstrations, the applicant must provide a written statement from

an Executive Officer approved third party, such as the owner or operator of the vehicle or equipment used, at the end of the durability period. The statement must describe overall performance, maintenance required, problems encountered, and any other relevant comments. The results of a visual inspection conducted by the third party at the end of the demonstration period must also be described. The description should comment on whether the diesel emission control strategy is physically intact, securely mounted, leaking any fluids, and should include any other evaluative observations.

(f) Test Cycle. Testing requirements are summarized in Table 4. Note that the same cycle(s) must be used for both the initial and final tests.
(1) On-Road Applications. The applicant must perform either chassis or engine dynamometer-based testing before beginning and after completion of the service accumulation as specified in Table 4. A minimum of three hot-start tests are required for chassis testing while a minimum of one cold-start and three hot-start tests are required for engine testing. Chassis testing requires an additional three hot-starts on a low-speed cycle as described in Section 2703(e)(1)(B)2. As indicated in Section 2703(e)(1)(B)2., the applicant may request the Executive Officer to waive the tests on a low-speed cycle. If a field durability demonstration is selected, the applicant must perform chassis dynamometer testing, or request that the Executive Officer consider engine dynamometer testing. In reviewing the request, the Executive Officer may consider all relevant information, including, but not limited to the following:
(A) Similarity of the field vehicle's engine to the laboratory engine, and
(B) Similarity of the diesel emission control system's calibration and set-up when installed on the field vehicle to that when installed on the laboratory engine.
(2) Off-road and Stationary Applications. The applicant must use the same cycle for the emission reduction testing as defined in Section 2703. A minimum of three hot-start tests is required.

(g) Test Run. The requirements for emissions reduction testing are summarized in Table 4, below. Note that special pre-conditioning requirements may apply. See section 2706(a)(4) for details.
(1) The diesel emission control strategy must undergo one set of emission tests before beginning and after completion of the service accumulation. Baseline testing with test repetitions as indicated in Table 4 must be conducted before and after the service accumulation. If baseline testing after the service accumulation is not technically feasible, the applicant may request the Executive Officer to waive the requirement. If there are substantial test data from previous field studies or field demonstrations, applicants may request that the Executive Officer consider these in place of the initial emission tests.
(2) As an alternative to testing a single unit before and after the service accumulation period, the applicant may request that the Executive Officer

consider the testing of two identical units, one that has been pre-conditioned and another that has completed the service accumulation period. In reviewing the request, the Executive Officer may consider all relevant information, including, but not limited to, the following:

(A) The effect of the diesel emission control strategy on engine operation over time. Strategies that cause changes in engine operation are likely not to qualify for this testing option.

(B) The quality of the evidence the applicant can provide to support that the two units are identical,

(C) Previous experience with similar or related technologies, and

(D) Whether the applicant is participating in the U.S. EPA verification process and has made an agreement with U.S. EPA to test two units.

(3) For strategies that include exhaust aftertreatment, engine backpressure and exhaust temperature must be measured and recorded on a second-by-second basis (1 Hertz) during at least one baseline run and each of the control test runs.

(4) For strategies that use a chemical reductant to reduce emissions of NOx from on-road or off-road applications, the amount of reductant consumed during each control test run must be measured and recorded.

Table 4. Emission Tests Required for Durability Demonstrations

Application	Test Type	Initial Test (prior to service accumulation) Final Test (after completion of 100% of the service accumulation)
On-Road	Engine	FTP Heavy-duty Transient Cycle (1 cold and 3 hot-starts)
	Chassis	UDDS (3 hot-starts) and a low-speed cycle per 2703 (e)(1)(B)2.(3 hot-starts)
Off-Road and portable engines	Engine	Steady-state test cycle from ARB off-road regulations or an alternative cycle (3 hot-starts)
Stationary	Engine	Steady-state test cycle from ARB off-road regulations or an alternative cycle (3 hot-starts)

(h) Maintenance During Durability Demonstration. Except for emergency engine repair, only scheduled maintenance on the engine and diesel emission control system and re-fill of additives (if any) may be performed during the durability

demonstration. If normal maintenance includes replacement of any component of the diesel emission control system, the time (miles, years, or hours) between component change or refill must be reported with the results of the demonstration.

(i) Functional Testing of Monitoring and Notification Systems. The applicant must demonstrate the durability of all monitoring and notification systems employed by the diesel emission control strategy. Such systems include, but are not limited to, backpressure monitors, reductant level monitors, malfunction indicator systems, and mechanisms to de-rate an engine's maximum power output. The applicant must propose test procedures to demonstrate the durability of the monitoring and notification systems on a diesel emission control strategy that has completed the service accumulation period.

(j) Performance Requirements. The diesel emission control strategy must meet the following requirements throughout the durability demonstration period:
(1) If the applicant claims a percent emission reduction, the percent emission reduction must meet or exceed the initial verified percent emission reduction level.
(2) If the applicant claims to achieve 0.01 g/bhp-hr for PM, the PM emission level must not exceed 0.01 g/bhp-hr.
(3) The diesel emission control system must maintain its physical integrity. Its physical structure and all of its components not specified for regular replacement during the durability demonstration period must remain intact and fully functional.
(4) The diesel emission control strategy must not cause any damage to the engine, vehicle, or equipment.
(5) The backpressure caused by the diesel emission control strategy should not exceed the engine manufacturer's specified limits, or must not result in any damage to the engine.
(6) No maintenance of the diesel emission control system beyond that specified in its owner's manual will be allowed without prior Executive Officer approval.

(k) Conditional Verification for Off-road and Stationary Applications. If the Executive Officer determines that the diesel emission control strategy is technologically sound and appropriate for the intended application, he may grant a conditional verification for off-road and stationary applications upon completion of 33 percent of the minimum durability period. In making this determination, the Executive Officer may consider all relevant information including, but not limited to, the following: the design of the diesel emission control system, filter and catalyst substrates used, similarity of the system under consideration to verified systems, the intended application of the diesel emission control system, other relevant testing data, and field experience. Where conditional verification is granted, full verification must be obtained by completing the durability testing and all other remaining requirements. These

requirements must be completed within a year after receiving conditional verification. For the aforementioned time period, conditional verification is equivalent to verification for the purposes of satisfying the requirements of in-use emission control regulations.

(l) Failure During the Durability Demonstration Period. If the diesel emission control strategy fails to maintain its initial verified percent emission reduction or emission level for any reason, the Executive Officer may downgrade the strategy to the verification level which corresponds to the lowest degraded performance observed in the durability demonstration period. If the diesel emission control strategy fails to maintain at least a 25 percent PM reduction or 25 percent NOx reduction at any time during the durability period, the diesel emission control strategy will not be verified. If the diesel emission control strategy fails in the course of the durability demonstration period, the applicant must submit a report explaining the circumstances of the failure within 90 days of the failure. The Executive Officer may then determine whether to deny verification or allow the applicant to correct the failed diesel emission control strategy and either continue the durability demonstration or begin a new durability demonstration.

NOTE: Authority cited: Sections 39002, 39003, 39500, 39600, 39601, 39650-39675, 40000, 43000, 43000.5, 43011, 43013, 43018, 43105, 43600 and 43700, Health and Safety Code. Reference: Sections 39650-39675, 43000, 43009.5, 43013, 43018, 43101, 43104, 43105, 43106, 43107 and 43204-43205.5 Health and Safety Code; and Title 17 California Code of Regulations Section 93000.

§ 2705. Field Demonstration Requirements.

(a) The applicant must demonstrate compatibility of its diesel emission control strategy in the field with at least one vehicle or piece of equipment belonging to the initial emission control group for which it seeks verification. Note that if the durability demonstration selected by the applicant is in-field, it may be used to satisfy the field demonstration requirement for that emission control group.

(1) Compatibility is determined by the Executive Officer based on the third-party statement (see part (c) of this section) and any other data submitted including backpressure data. A diesel emission control strategy is compatible with the chosen application if it:

(A) Does not cause damage to the engine or engine malfunction

(B) Does not cause backpressure outside of the engine manufacturer's specified limits or which results in any damage to the engine

(C) Does not hinder or detract from the vehicle or equipment's ability to perform its normal functions

(D) Is physically intact and well mounted with no signs of leakage or other visibly detectable problems

(2) To determine whether additional emission control groups require separate field demonstrations, the Executive Officer may consider all relevant information, including, but not limited to existing field experience and engineering justification and analysis.

(b) Test Period.
(1) For on- and off-road engines, and stationary engines not used in emergency generators, a vehicle or piece of equipment must be operated with the diesel emission control strategy installed for a minimum period of 200 hours or 10,000 miles, whichever occurs first.
(2) For stationary emergency standby engines, the emission control system must remain in the field for at least 30 days and operation must include:
(A) 12 maintenance runs (allowing for engine cool down between runs), and
(B) a minimum of two separate 4 hour sessions where the engine is operated under load (allowing engine cool down between runs).

(c) Reporting Requirements.
(1) Temperature and Backpressure Measurement Requirements. For strategies that include exhaust aftertreatment, engine backpressure and exhaust temperature must be measured and recorded over the entire demonstration period. The applicant must propose a measurement and recording protocol for approval by the Executive Officer. The protocol may include, but is not limited to, measurement and recording of values once every few seconds, or higher frequency measurement with recording of averages, minima, and maxima over longer time intervals. Data must be submitted electronically in columns as a text file or another format approved by the Executive Officer.
(2) NOx Emissions Measurement Requirements. For strategies that include exhaust aftertreatment to reduce emissions of NOx, the mass emissions of NOx both upstream and downstream of the aftertreatment device must be measured and recorded over the entire demonstration period. The applicant must propose a measurement method for approval by the Executive Officer. The method may include, but is not limited to, the use of NOx sensors before and after the device. Measurements of NOx emissions must occur on at least a 1 Hertz basis. Data must be recorded as averages over time intervals no greater than 10 seconds. Data must be submitted electronically in columns as a text file or another format approved by the Executive Officer.
(3) Third Party Statement. The applicant must provide a written statement from a third party approved by the Executive Officer, such as the owner or operator of the vehicle or equipment used in the field demonstration. The written statement must be provided at the end of the test period and must describe the following aspects of the field demonstration: overall performance of the test application and the diesel emission control strategy, maintenance performed, problems encountered, and any other

relevant information. The results of a visual inspection conducted by the third party at the end of the demonstration period must also be described. The description should comment on whether the diesel emission control strategy is physically intact, securely mounted, leaking any fluids, and should include any other evaluative observations.

(d) Failure During the Field Demonstration. If the diesel emission control strategy fails in the course of the field demonstration, the applicant must submit a report explaining the circumstances of the failure within 90 days of the failure. The Executive Officer may then determine whether to deny verification or allow the applicant to correct the failed diesel emission control strategy and either continue the field demonstration or begin a new demonstration.

NOTE: Authority cited: Sections 39002, 39003, 39500, 39600, 39601, 39650-39675, 40000, 43000, 43000.5, 43011, 43013, 43018, 43105, 43600 and 43700, Health and Safety Code. Reference: Sections 39650-39675, 43000, 43009.5, 43013, 43018, 43101, 43104, 43105, 43106, 43107 and 43204-43205.5 Health and Safety Code; and Title 17 California Code of Regulations Section 93000.

§ 2706. Other Requirements.

(a) Limit and Procedure for Measuring Nitrogen Dioxide (NO_2).
(1) In order for a diesel emission control strategy to be verified, effective January 1, 2007, the diesel emission control strategy must not increase emissions of NO_2 by more than an increment equivalent in mass to 30 percent of the baseline NOx emission level. Effective January 1, 2009, the increment is reduced to 20 percent of the baseline NOx emission level. The average of NO_2 emission levels from both the initial and final emissions tests described in Section 2704(g) is used to determine compliance with the NO_2 limit. For chassis dynamometer testing, only the NO_2 emission level over the UDDS cycle is used. The first NO_2 emission limit takes effect beginning on January 1, 2007. Diesel emission control strategies verified and installed prior to January 1, 2007 are exempted from this requirement. Those verified prior to January 1, 2007 will no longer be allowed for installation after January 1, 2007 unless they meet the appropriate NO_2 emission limit. After January 1, 2007, all diesel emission control strategies verified and installed must meet this requirement.
(2) NO_2 emissions are to be quantified by one of the following methods:
(A) Two chemiluminescence analyzers,
(B) A dual-path chemiluminescence analyzer, or
(C) An alternative method approved by the Executive Officer.
(3) Analyzer configuration and determination of NO_2 emission level. For (2)(A) and (2)(B), the analyzers are to be fed from a heated and conditioned sample path. If two chemiluminescence analyzers are

employed, they are to be simultaneously fed from a common heated sample path. One instrument (or path) shall be set to NOx mode, while the second shall be set to nitric oxide (NO) mode. The instrument (or path) set to NOx mode receives a sample that has passed through an NO_2-to-NO converter, and the resultant concentration is designated as total NOx ($NO+NO_2$) in the sample. The instrument (or path) that is set to NO mode receives a sample that has not passed through the converter and quantifies the amount of NO only. The difference between NO and NOx is the amount of NO_2 in the sample. Both NO and NOx signals are recorded by an external data acquisition system at 1 Hertz. Using the average concentrations of NO and NOx over the entire test cycle, the conventional equation for calculating total NOx (Code of Federal Regulations, Title 40, part 86, Subpart N) is then used to generate a gram per mile or g/bhp-hr value for both NO and NOx. The resulting value for NO is then subtracted from that for NOx to determine the gram per mile or g/bhp-hr value for NO_2. The instrument for measuring NO and NOx must be calibrated in accordance with the NOx calibration procedure as described in the Code of Federal Regulations, Title 40, part 86, Subpart N.

(4) Pre-conditioning requirements. If the Executive Officer determines that a diesel emission control system has a propensity to increase emissions of NO_2 and that NO_2 emissions from a diesel emission control system could be affected by the presence of particulate matter or ash (as with a catalyzed diesel particulate filter), the system must be preconditioned according to the following procedure:

(A) Initial test (prior to service accumulation). Before conducting the initial emissions test, the unit being tested must be pre-conditioned as follows:

1. Install a new, unused unit on an engine that is an appropriate size for the unit, in a good state of maintenance, and certified to a PM standard equal to or more stringent than that of the engines in the emission control group for which the applicant seeks verification.
2. Operate the engine on one of the test cycles specified below for 25 to 30 hours. For on-road verifications, use either the FTP (hot-start) or UDDS cycle as identified in 2703(e), or the 13-mode Supplemental Emissions Test (SET) in the Code of Federal Regulations, Title 40, Part 86. For off-road and stationary verifications, use either the steady-state test cycle or the Nonroad Composite Transient Cycle (NRTC) (California Code of Regulations, Title 13, Section 2423 and the incorporated California Exhaust Emissions Standards and Test Procedures for New 2008 and Later Tier 4 Off-Road Compression-Ignition Engines, Part I-C) from ARB off-road regulations. For up to 10 hours of the 25 to 30 hour period, beginning after at least the first three test cycle repetitions or ending before at least the last three test cycle repetitions, an applicant may alternatively:

a. Run the engine at high load such that the exhaust temperature is between 350 and 450 degrees Celsius, or
b. Alternate back and forth between high and low loads such that the exhaust temperature never exceeds 525 degrees Celsius and the low load operation does not result in significant soot accumulation at the end of the pre-conditioning period.

3. Measure and record the backpressure and exhaust temperature on a second-by-second basis (1 Hertz) for the duration of the 25 to 30 hour pre-conditioning period. Determine the average backpressure for at least the first three and last three test cycle repetitions.
4. Following the 25 to 30 hour period of operation, remove the unit from the pre-conditioning engine and install it on the emissions test engine, if applicable. Proceed with the initial emissions test and determine NO_2^i, as defined in section 2706(a)(5). Determine the average backpressure over each of the emissions test repetitions and then average those values. The resulting average backpressure is compared with that of the aged unit per subsection (B), below.

(B) Final test (after the service accumulation). Before conducting the final emissions test, the aged unit may need to be pre-conditioned if the backpressure is too high. The applicant may either first perform the backpressure check described below or directly proceed with the final emissions test with the understanding that the test must be repeated if the backpressure is too high.

1. Backpressure check. Run one hot-start of the emissions test cycle with the aged unit installed on the emissions test engine. If using a chassis dynamometer, run the UDDS. Measure and record the backpressure on a second-by-second basis (1 Hertz) and determine the average. No pollutant measurements are necessary. Proceed with the emissions test as described in subsection (B)(3.) below if either the average backpressure is within 30 percent of the average backpressure recorded for the initial test unit or, for transient test cycles, the backpressure does not exceed 60 inches of water for more than two percent of the time, or, for steady-state test cycles, the backpressure never exceeds 60 inches of water. Otherwise, pre-condition the aged unit as described in subsection (B)(2.) below.
2. If the backpressure of the aged unit does not comply with the appropriate criterion described in subsection (B)(1.) above, burn off excess soot or clean out excess ash as necessary. Run an additional repetition of the emissions test cycle (hot-start) to check if the unit complies with the backpressure criterion. Repeat as necessary.
3. Conduct emissions testing with the aged unit. Determine NO_2^f, as defined in section 2706(a)(5.). If the backpressure does not comply with the appropriate criterion described in subsection (B)(1.) above,

pre-condition the unit in accordance with subsection (B)(2.) and retest. If the backpressure check in subsection (B)(1.) was conducted prior to emissions testing and the unit was brought into compliance at that time, do not retest.

(C) In-use compliance testing. Before conducting the first phase of in-use compliance emissions testing, the test units may need to be pre-conditioned. Using the required test cycle, measure and record the backpressure on a second-by-second basis (1 Hertz) over one hot-start test with a cleaned (or pre-conditioned per subsection (A) above) reference unit installed on the engine to be used for in-use compliance testing. The reference unit must be identical to the test units. Measure and record the backpressure of the test units retrieved from the field using the same engine and test cycle (one hot-start) as used with the reference unit. If the backpressure of a given test unit is either within 30 percent of the average backpressure recorded for the reference unit or, for transient test cycles, the backpressure does not exceed 60 inches of water for more than two percent of the time, or, for steady-state test cycles, the backpressure never exceeds 60 inches of water, it does not require pre-conditioning. Otherwise, the test units must be pre-conditioned following subsection (B) above. Other units may not be substituted for the selected test units.

(D) Determination of backpressure. The applicant must submit the actual recorded backpressure in an electronic format as measured on a second-by-second basis over each test run and over the 25 to 30 hour pre-conditioning period. Prior to calculating the average backpressure over a given test run, however, any negative values caused by the draw of the dilution tunnel must first be zeroed.

(5) Determination of compliance with the NO_2 limit. Compliance with the NO_2 limit is based on the average incremental increase in NO_2 emissions as determined by the following equation:

$$\text{Percent Increase} = 100\% \times 0.5 \times [(NO_2^{i} - NO_2^{b}) + (NO_2^{f} - NO_2^{b})] / NOx^{b}$$

Where "NO_2" and "NOx" stand for the mass-based emission rates of NO_2 and NOx, respectively, as determined in subsection (a)(3) above, and the superscripts "i", "f", and "b" stand for "initial test", "final test", and "baseline test", respectively. For in-use compliance testing, the equation is:

$$\text{Percent Increase} = 100\% \times (NO_2^{c} - NO_2^{b}) / NOx^{b}$$

Where the superscript "c" stands for the in-use compliance emissions testing conducted with the unit installed on the test engine.

(6) Alternative Method to Measure NO_2. The applicant may request the Executive Officer to approve an alternative method in place of the required

methods. In reviewing this request, the Executive Officer may consider all relevant information including, but not limited to, the following:
(A) Correlation of the alternative method with the methods stated in 2(A) or 2(B).
(B) Body of existing data generated using the alternative method.

(b) Limits on Other Pollutants.
(1) Limits on non-methane hydrocarbon (NMHC) and NOx. In order for a diesel emission control strategy to be verified, the applicant must comply with one of the following:
(A)The diesel emission control strategy must not increase the emissions of either NMHC or NOx by more than ten percent of the baseline emissions level as reported under section 2708 (a), or
(B)For strategies verified prior to July 1, 2006, the applicant must provide sufficient evidence to demonstrate that the sum of NMHC and NOx emissions with the strategy implemented does not exceed the baseline emission level sum of NMHC and NOx as reported under Section 2708 (a); or
(C) For strategies verified on or after July 1, 2006, the applicant must provide atmospheric modeling data which indicates that widespread use of the strategy will not result in an increase in exposure of the public to ozone. The atmospheric model employed must be approved in advance by the Executive Officer.
(2) Limit on CO.
(A) On-road and Off-road (including portable) Engines. In order for a diesel emission control strategy to be verified, the diesel emission control strategy must not increase the emissions of CO greater than the current CO emission standards for new diesel engines adopted by the Air Resources Board and in effect at the time of verification.
(B) Stationary Engines. In order for a diesel emission control strategy to be verified, the diesel emission control strategy must either:
1. Meet the applicable CO standard for off-road engines of the same model year and maximum rated power as specified in the Off-Road Compression-Ignition Engine Standards (title 13, CCR, section 2423). If no standards have been established for an off-road engine of the same model year and maximum rated power as the stationary diesel-fueled CI engine, then the stationary diesel-fueled CI engine shall meet the Tier 1 standard in title 13, CCR, section 2423 for an off-road engine of the same maximum rated power, irrespective of the stationary diesel-fueled CI engine's model; Or
2. Not increase the emissions of CO by more than 10 percent of the baseline emissions level as reported under Section 2708(a).
(3) Limit on Ammonia (NH_3). In order for a diesel emission control strategy to be verified, the diesel emission control strategy must not increase the emissions of ammonia to a level greater than 25 parts per million by

volume at the tailpipe on average over any test cycle used to support emission reduction claims.

(A) Emissions of ammonia are to be quantified with a method subject to approval by the Executive Officer which employs Fourier Transform Infrared (FTIR) spectroscopy. The applicant may request the Executive Officer to approve an alternative method in place of the required method. In reviewing this request, the Executive Officer may consider all relevant information including, but not limited to, consistency with the method required by U.S. EPA and the body of existing data generated using the alternative method.

(B) If an applicant does not expect its diesel emission control strategy to increase emissions of ammonia, the applicant may request that the Executive Officer waive the requirement to conduct testing for ammonia emissions. In reviewing the request, the Executive Officer may consider all relevant information including, but not limited to, the principles of operation of the diesel emission control strategy, the existence of a mechanism for ammonia formation, and published emissions data from similar technologies.

(C) The strategy must be in compliance with applicable federal, state, and local government requirements relating to ammonia emissions, which may be more stringent than the limit presented here.

(4) Other Pollutants. In order for a diesel emission control strategy to be verified, the diesel emission control strategy must not increase the emissions of other pollutants by more than ten percent of the baseline emission level as reported under Section 2708(a).

(c) Fuel Additives. Diesel emission control strategies that use fuel additives must comply with Section 2710 and meet the following additional requirements for verification. Fuel additives must be used in combination with a level 3 diesel particulate filter unless they can be proven to the satisfaction of the Executive Officer to be safe for use alone. In addition, the applicant must meet the following requirements:

(1) The applicant must submit the exact chemical formulation of the fuel additive,

(2) Diesel emission control systems employing the dosing of an additive in conjunction with a diesel particulate filter must include an on-board monitor of the additive level in the reservoir, integrated with the diesel particulate filter. The on-board monitor for fuel additive must include indicators to notify the operator when the additive level becomes low and when the additive tank is empty. In addition, the on-board monitor must be capable of shutting off the supply of additive, if there is a detected diesel particulate filter problem,

(3) The applicant must submit to the Executive Officer environmental, toxicological, epidemiological, and other health-related data pertaining to the fuel additive every two years. The Executive Officer will review the data, including any new information, and may revoke the verification if the

data indicate that the fuel additives cause, or are linked, to negative environmental, or health consequences.

(4) The applicant must conduct additional emission tests of fuel additives.

(A) Except as provided in (B) below, the additional emission tests must follow the same test procedures, test cycles, and number of test runs as indicated in Section 2703, except that the concentration of the additive must be at least 50 ppm or 10 times higher than that specified for normal use, whichever is highest. In all other respects, the additive in the high concentration test solutions must be identical to that in the fuel additive submitted for verification.

(B) The applicant may petition to use a concentration less than that required in (A), above, if the higher dose would result in catastrophic damage to the engine. The applicant must supply information on the failure modes, and the level of the additive that would trigger failure. The applicant must also supply information and data supporting the highest feasible dose for testing. An increase in emissions is not by itself sufficient to justify a dose lower than that required in (A), above, and must be correlated to potential engine damage. After reviewing this information and any other relevant information, the Executive Officer shall determine if testing at a lower level could be accepted, or if testing must be conducted at 50 ppm or ten times the specified dose rate as required in (A).

(5) Fuel additives must be in compliance with applicable federal, state, and local government requirements. This requirement includes, but is not limited to, registration of fuel additives with the U.S. EPA.

(d) Alternative Diesel Fuels. Alternative diesel fuels must be in compliance with applicable federal, state, and local government requirements. This requirement includes, but is not limited to registration of the alternative diesel fuel with the U.S. EPA. The applicant must conduct additional emission tests of alternative diesel fuels if the Executive Officer determines that such tests are necessary. The Executive Officer may consider all factors including, but not limited to, fuel components that could adversely affect emissions reductions and/or the applications to which they are applied.

(e) Selective Catalytic Reduction (SCR) Systems. A diesel emission control strategy that uses an SCR system to reduce emissions of NO_x has the following additional requirements:

(1) The diesel emission control strategy must include a system to monitor the amount of reductant available and notify the operator when the level is low. The notification must occur and be clearly visible to the operator while the vehicle or equipment is in use.

(2) The diesel emission control strategy must include a strong inducement to ensure that the operator maintains a constant supply of reductant to the SCR system. For example, the diesel emission control strategy may include a mechanism to de-rate the engine's maximum power output if the

operator fails to refill the reductant tank. The inducement must be both resistant to tampering and strong enough to ensure an uninterrupted supply of reductant. The applicant must propose an inducement for approval by the Executive Officer.

(3) The diesel emission control strategy must include a means to ensure that the reductant present in the tank meets the specifications necessary for the SCR system to function properly. The applicant must propose a quality control strategy for approval by the Executive Officer.

(f) Engine Backpressure and Monitoring. During the emission and durability testing, the applicant must demonstrate that the backpressure caused by its diesel emission control system is within the engine manufacturer's specified limits, or will not result in any damage to the engine. Furthermore,

(1) If operation of the engine with the diesel emission control system installed will result in a gradual build-up of backpressure exceeding the engine's specified limits over time (such as due to the accumulation of ash in a filter), information describing how the backpressure will be reduced must be included.

(2) All filter-based diesel emission control systems must be installed with a backpressure monitor to notify the operator when the high backpressure limit, as specified by the engine manufacturer or included in the verification, is approached. The notification must occur and be clearly visible to the operator while the vehicle or equipment is in use. The applicant must identify the high backpressure limits of the system in its application for verification.

(3) The Executive Officer reserves the right to require monitors that identify low backpressure limits in those cases where failures leading to low backpressure are unlikely to be detected, or have the potential to cause environmental damage beyond that caused by the engine prior to being equipped with the emission control strategy (e.g., systems that introduce additives into the fuel).

(g) Fuel and Oil Requirements. The applicant must specify the fuel and lubricating oil requirements necessary for proper functioning of the diesel emission control system. The applicant must also specify any consequences that will be caused by failure to comply with these requirements, as well as methods for reversing any negative consequences.

(h) Maintenance Requirements. The applicant must identify all normal maintenance requirements for the diesel emission control system. The applicant must specify the recommended intervals for cleaning and/or replacing components. Any components to be replaced within the defects warranty period must be covered with the original diesel emission control system package or provided free of charge to the customer at the appropriate maintenance intervals. Any normal maintenance items that the applicant does not intend to provide free of charge must be approved by the Executive

Officer (the applicant is not required to submit cost information for these items). In addition, the applicant must specify procedures for proper handling of spent components and/or materials cleaned from the diesel emission control system. If any such materials are hazardous, the applicant must identify them as such in the owner's manual. For filter-based diesel emission control strategies, the applicant must include procedures for resetting any backpressure monitors after maintenance procedures are completed.

(i) Component Swapping and Re-Designation Practices

(1) End User Device Component Swapping Practices. Applicants may authorize end users to move components of their verified control systems from the original installed configuration and transfer them on to other vehicles or equipment, but only within a common ownership fleet, provided the following provisions are met:

(A) Applicants must first receive written approval outlining the specific component eligible to be moved from the Executive Officer prior to approving any transfers.

(B) Recipient vehicle must be fitted with the same DECS.

(C) Component swapping must also comply with the requirements as described in subsection (i)(3).

(D) Donor vehicle/engine whose component has been moved must remain in compliance with the terms and conditions of the applicable Executive Order and have all DECS components present and functional.

(2) Device Re-Designation Practices. Applicants may authorize end users to completely remove their verified control systems from the original installed configuration and install them on other vehicles or equipment within the end user's commonly owned fleet, provided the following provisions are met:

(A) Applicants must receive written approval from the Executive Officer prior to approving a DECS re-designation.

(B) Any party which removes a verified DECS from an engine/application must remove the verified DECS engine label. If the engine label cannot be removed whole, it must be destroyed.

(C) Any party which re-designates a device to another engine/application which was never previously retrofit with that exact DECS must obtain and properly install an appropriate DECS engine label.

(D) Any party which removes a verified DECS from an engine/application must ensure the engine/application returns to its original factory configuration.

(E) DECS which are more than 10 years old based on the month and date of manufacture listed on the device label, or devices of unknown age, are not legal candidate systems for re-designation to a new engine/application.

(F) DECS system re-designation must also comply with the requirements as described in subsection (i)(3)

(3) Additional Component Swapping and Re-designation Requirements. In addition to the specific requirements in subparts (1) and (2), the following requirements must be met prior to the approval of a component swap or device re-designation:
(A) Applicants must provide written information on approved practices and, compliance with warranty and in-use compliance,
(B) Applicants must provide instructions for assessing if the system still meets its verified emissions reductions (for PM and/or NOx), instructions for device movement to prevent installation on an inappropriate vehicle, and other information required by the EO to assess the request.
(C) The end user must verify that the new recipient vehicle is within the scope of the original verification.
(D) Applicants must specify acceptable end user installation and reinstallation practices in the owner's manual and the installation manual (see section 2706(l) and 2706(n)) and possible repercussions to the end user if such practices are done in an inappropriate manner. (See section 2706(i)).
(E) The applicant must agree to honor the original warranty and warranty period (see sections 2702 and 2707) and must provide a written statement to the EO confirming continued support of the original warranty.
(4) Any device installed under the device re-designation provisions above must be compliant with the warranty requirements in section 2707 of the verification procedure. However, if the original device warranty has expired, the installer must issue a warranty to guard against potential installation defects for a period of one year from the date of installation (see section 2707). Any transfer of a device by an installer that does not offer this installation warranty will not be considered a valid installation. No party shall advertise, sell, lease, or offer for sale or lease, a used verified DECS.

(j) System Labeling.
(1) The applicant must ensure that identical, legible, and durable labels are affixed on both the diesel emission control system and the engine (or an alternate location approved by the Executive Officer) on which the diesel emission control system is installed except as noted in (3) below. The required labels must identify the name, address, and phone number of the manufacturer, the diesel emission control strategy family name (defined in (2) below) of the installed system, a unique serial number, and the month and year of manufacture. The month and year of manufacture are not required on the label if this information can be readily obtained from the applicant by reference to the serial number. The applicant and installer must ensure that the label is affixed such that it is resistant to tampering and degradation from the conditions of its environment. The applicant and/or installer must ensure that the label is visible after installation. In the event that the original system label is damaged or destroyed by the end-

user, the device manufacturer shall issue a replacement. The replacement label must be identical to the original label with the exception of the words "REPLACEMENT LABEL" which must be included at the bottom line of information. A sample scale drawing of the original and replacement labels must be submitted with the verification application. Unless an alternative is approved by the Executive Officer, the label information must be in the following format:

Name, Address, and Phone Number of Manufacturer
Diesel Emission Control Strategy Family Name
Product Serial Number
ZZ-ZZ (Month and Year of manufacture, e.g., 06-02)
REPLACEMENT LABEL*

* "Replacement Label" to be used only when a replacement of the original label has been issued by the device manufacturer.

(2) Diesel Emission Control Strategy Family Name. Each diesel emission control strategy shall be assigned a family name defined as below:

CA/MMM/YYYY/PM#/N##/APP/XXXXX

CA:	Designates a diesel emission control strategy verified in California
MMM:	Manufacturer code (assigned by the Executive Officer)
YYYY:	Year of verification
PM#:	PM verification level 0, 1, 1+, 2, 2+, 3, or 3+ (e.g., PM3 means a level 3 PM emission control system).
N##:	NOx verified reduction level in percent, if any (e.g., N25 means NOx reduction of 25 percent).
APP:	Verified application which may include a combination of On-road (ON),Off-road (OF),or Stationary (ST)
XXXXX:	Five alphanumeric character code issued by the Executive Officer

(3) The applicant may request that the Executive Officer approve an alternative label format. In reviewing this request, the Executive Officer may consider all relevant information including, but not limited to, the informational content of an alternative label as proposed by the applicant.

(k) Additional Information. The Executive Officer may require the applicant to provide additional information about the diesel emission control strategy or its

implementation when such information is needed to assess environmental impacts associated with its use.

(l) Owner's Manual. The applicant must provide a copy of the diesel emission control system owner's manual, which must clearly specify at least the following information:
(1) Warranty statement including the warranty period over which the applicant is liable for any defects.
(2) Installation procedure and maintenance requirements for the diesel emission control system.
(3) Possible backpressure range imposed on the engine.
(4) Fuel consumption penalty, if any.
(5) Fuel requirements including sulfur limit, if any.
(6) Handling and supply of additives, if any.
(7) Instructions for reading and resetting the backpressure monitor.
(8) Requirements for lubrication oil quality and maximum lubrication oil consumption rate.
(9) Contact information for replacement components and cleaning agents.
(10) Contact information to assist an end-user to determine proper ways to dispose of waste generated by the diesel emission control strategy (e.g., ash accumulated in filter-based systems). At a minimum, the owner's manual should indicate that disposal must be in accordance with all applicable Federal, State and local laws governing waste disposal.
(11) Appropriate methods of removing the diesel emission control system from the original installed configuration and installing the system on a different vehicle or piece of equipment, if such practices are allowed. The applicant must state possible repercussions to the end user if such practices are done in an inappropriate manner. (See section 2706(i))
(12) Parts List.

(m) Noise Level Control. Any diesel emission control system that replaces a muffler must continue to provide at a minimum the same level of exhaust noise attenuation as the muffler with which the vehicle was originally equipped by the vehicle or engine manufacturer. Applicants must ensure that the diesel emission control system complies with all applicable noise limits contained in Part 205, Title 40, Code of Federal Regulations and California Vehicle Code, Sections 27150, 27151 and 27200 through 27207, for the gross vehicle weight rating and year of manufacture of the vehicle for which the diesel emission control strategy is intended. All diesel emission control systems must be in compliance with applicable local government requirements for noise control.

(n) Installation Manual. The applicant must provide a copy of the diesel emission control system installation manual that the applicant intends to provide to installers and/or owners.

(o) Parts List. The applicant must include a list of all of the component parts of the diesel emission control system. All primary components must be listed, including, but not limited to, substrates, electronic control units, sensors, injectors, pumps, blowers, storage tanks, and notification lights. Brackets, fasteners, and wiring need not be included. For each listed component, the applicant must give a description and identification number. The applicant must also clearly specify which parts, if any, are not covered by the warranty. Parts that may be excluded from warranty coverage are subject to approval by the Executive Officer.

(p) Multimedia Assessment for Fuel Strategies. Diesel emission control strategies which rely on fuel changes either through use of additives or through use of alternative diesel fuels must undergo an evaluation of the multimedia effects. No diesel emission control strategy that relies on the use of an additive or an alternative fuel may be verified unless a multimedia evaluation of the additive or alternative fuel has been conducted and the California Environmental Policy Council established by Public Resources Code section 71017 has determined that such use will not cause a significant adverse impact on the public health or the environment, pursuant to Health and Safety Code section 43830.8. No person shall sell, offer for sale, supply or offer for supply an alternative fuel or a diesel fuel in California that contains an additive for use in a verified diesel emission control strategy unless such a multimedia evaluation has been conducted and resulted in a determination that use of the alternative fuel or additive will not cause a significant adverse impact on the public health and the environment. The applicant shall bear the expense of conducting the multimedia assessment.

(q) Sales and Installation. No person or entity shall advertise, sell, lease, supply, offer for sale, represent, or install any device, apparatus, mechanism, or fuel based system as a verified diesel emission control strategy for or on any engine, vehicle or equipment that does not meet the terms and conditions of the strategy's Executive Order. The applicant, distributor, and/or installer must ensure that each verified diesel emission control strategy is supplied, sold, leased, and installed pursuant to the provisions of the Executive Order. Failure to follow the provisions of the Executive Order may result in revocation or suspension of the verification and/or any other remedy available under Part 5, Division 26 of the Health and Safety Code.

(r) Aftertreatment Devices. Any control strategy that is installed on or after January 1, 2010 that includes an aftertreatment device such as a diesel particulate filter, must be designed such that the aftertreatment device can only be installed on the application in one unique direction. Any new aftertreatment device installed in the period between February 19, 2009 and December 31, 2009 must indicate the proper direction of exhaust flow so the end user or installer can clearly see how to properly install the device.

(s) Verification of a diesel emission control strategy by the Air Resources Board does not release the applicant from complying with all other applicable legal requirements.

NOTE: Authority cited: Sections 39002, 39003, 39500, 39600, 39601, 39650-39675, 40000, 43000, 43000.5, 43011, 43013, 43018, 43105, 43600, 43700 and 43830.8, Health and Safety Code. Reference: Sections 39650-39675, 43000, 43009.5, 43013, 43018, 43101, 43104, 43105, 43106, 43107, 43204-43205.5 and 43830.8, Health and Safety Code; Section 71017, Public Resources Code; and Title 17 of Regulations Section 93000.

§ 2707. Warranty Requirements.

(a) (1) Product Warranty.

(A) The applicant must warrant to all owners, for ownership within the warranty period and lessees, for lease contracts within the warranty period, that its verified diesel emission control strategy is free from defects in design, materials, workmanship, or operation of the diesel emission control strategy which cause the diesel emission control strategy to fail to conform to the emission control performance level it was verified to, or to the other requirements of Sections 2700-2706, and 2710 for the minimum periods shown in Table 5, provided the operation of and conditions of use for the vehicle, equipment, engine, and diesel emission control strategy conform with the operation and conditions specified in the ARB's Executive Order.

(B) For each engine type and size listed in Table 5, the minimum defects warranty period is terminated by that listed event which occurs first. The warranty must cover the full repair or replacement cost of the diesel emission control strategy, including parts and labor.

(C)The warranty must also cover the full repair or replacement cost of returning engine components to the condition they were in prior to the failure, including parts and labor, for damage to the engine proximately caused by the verified diesel emission control strategy. Repair or replacement of any warranted part, including the engine must be performed at no charge to the vehicle or engine owner. This includes only those relevant diagnostic expenses in the case in which a warranty claim is valid. The applicant may, at its option, instead pay the fair market value of the engine prior to the time the failure occurs.

(D)The repair or replacement of any warranted part otherwise eligible for warranty coverage may be excluded from such warranty coverage if the diesel emission control strategy, vehicle or engine has been abused, neglected, or improperly maintained, and that such abuse, neglect, or improper maintenance was the direct cause of the need for the repair or replacement of the part.

(E) Failure of the vehicle or engine owner to ensure scheduled maintenance or to keep maintenance records for the vehicle, equipment, engine, or diesel emission control strategy may, but shall not per se, be grounds for disallowing a warranty claim.

(2) Installation Warranty

(A) A person or company who installs a verified diesel emission control strategy must warrant that the installation is free from defects in workmanship or materials which cause the diesel emission control strategy to fail to conform to the emission control performance level it was verified to or the other requirements of sections 2700-2706 for the minimum time periods shown in Table 5.

(B) For each engine type and size listed in Table 5, the minimum defects warranty period is terminated by that listed event whichever occurs first. The extent of the warranty coverage provided by installers must be the same as the warranty provided by the applicant as established in subsection (a)(1) and the same exclusions must apply.

Table 5. Minimum Warranty Periods

Engine Type	Engine Size	Minimum Warranty Period
On-Road	Light heavy-duty, 70 to 170 hp, Gross Vehicle Weight Rating (GVWR) less than 19,500 lbs.	5 years or 60,000 miles
	Medium heavy-duty, 170 to 250 hp, GVWR from 19,500 lbs. to 33,000 lbs.	5 years or 100,000 miles
	Heavy heavy-duty, exceeds 250 hp, GVWR exceeds 33,000 lbs.	5 years or 150,000 miles
	Heavy heavy-duty, exceeds 250 hp, GVWR exceeds 33,000 lbs., and the truck is: 1. Typically driven over 100,000 miles per year, and 2. Has less than 300,000 miles on the odometer at the time of installation.	2 years, unlimited miles
Off-Road (includes portable engines) and Stationary	Under 25 hp, and for constant speed engines rated under 50 hp with rated speeds greater than or equal to 3,000 rpm	3 years or 1,600 hours
	At or above 25 hp and under 50 hp	4 years or 2,600 hours
	At or above 50 hp	5 years or 4,200 hours

(b)(1) Product Warranty Statement. The applicant must furnish a copy of the following statement in the owner's manual. The applicant may include descriptions of circumstances that may result in a denial of warranty coverage, but these descriptions shall not limit warranty coverage in any way.

YOUR WARRANTY RIGHTS AND OBLIGATIONS

(Applicant's name) must warrant the diesel emission control system in the application for which it is sold or leased to be free from defects in design, materials, workmanship, or operation of the diesel emission control system which cause the diesel emission control system to fail to conform to the emission control performance level it was verified to, or to the requirements in the California Code of Regulations, Title 13, Sections 2700 to 2706, and 2710, for the periods of time listed below, provided there has been no abuse, neglect, or improper maintenance of your diesel emission control system, vehicle or equipment, as specified in the owner's manuals. Where a warrantable condition exists, this warranty also covers the engine from damage caused by the diesel emission control system, subject to the same exclusions for abuse, neglect or improper maintenance of your vehicle or equipment. Please review your owner's manual for other warranty information. Your diesel emission control system may include a core part (e.g., particulate filter, diesel oxidation catalyst, selective catalytic reduction converter) as well as hoses, connectors, a back pressure monitor (if applicable), and other emission-related assemblies. Where a warrantable condition exists, (applicant's name) will repair or replace your diesel emission control system at no cost to you including diagnosis, parts, and labor.

WARRANTY COVERAGE:

For a (engine size) engine used in a(n) (type of application) application, the warranty period will be (years or hours or miles of operation) whichever occurs first. If any emission-related part of your diesel emission control system is defective in design, materials, workmanship, or operation of the diesel emission control system thus causing the diesel emission control system to fail to conform to the emission control performance level it was verified to, or to the requirements in the California Code of Regulations, Title 13, Sections 2700 to 2706, and 2710, within the warranty period, as defined above, (Applicant's name) will repair or replace the diesel emission control system, including parts and labor.

In addition, (applicant's name) will replace or repair the engine components to the condition they were in prior to the failure, including parts and labor, for damage to the engine proximately caused by the verified diesel emission control strategy. This also includes those relevant diagnostic expenses in the case in which a warranty claim is valid.

(Applicant‘s name) may, at its option, instead pay the fair market value of the engine prior to the time the failure occurs.

OWNER’S WARRANTY RESPONSIBILITY

As the (vehicle, engine, equipment) owner, you are responsible for performing the required maintenance described in your owner’s manual. (Applicant’s name) recommends that you retain all maintenance records and receipts for maintenance expenses for your vehicle, engine, or equipment, and diesel emission control system. If you do not keep your receipts or fail to perform all scheduled maintenance, (applicant’s name) may have grounds to deny warranty coverage. You are responsible for presenting your vehicle, equipment, or engine, and diesel emission control system to a (applicant’s name) dealer as soon as a problem is detected. The warranty repair or replacement should be completed in a reasonable amount of time, not to exceed 30 days. If a replacement is needed, this may be extended to 90 days should a replacement not be available, but must be performed as soon as a replacement becomes available.

If you have questions regarding your warranty rights and responsibilities, you should contact (Insert chosen applicant’s contact) at 1-800-xxx-xxxx or the California Air Resources Board at 9528 Telstar Avenue, El Monte, California 91731, or (800) 363-7664, or electronic mail: helpline@arb.ca.gov.

(2) Installation Warranty Statement. The installer must furnish the owner with a copy of the following statement.

YOUR WARRANTY RIGHTS AND OBLIGATIONS

(Installer’s name) must warrant that the installation of a diesel emission control system is free from defects in workmanship or materials which cause the diesel emission control system to fail to conform to the emission control performance level it was verified to, or to the requirements in the California Code of Regulations, Title 13, Sections 2700 to 2706. The warranty period and the extent of the warranty coverage provided by (installer’s name) must be the same as the warranty provided by the product manufacturer, and the same exclusions must apply.

OWNER’S WARRANTY RESPONSIBILITY

As the vehicle, engine, or equipment owner, you are responsible for presenting your vehicle, engine, or equipment, and diesel emission control system to (installer’s name) as soon as a problem with the installation is detected.

If you have questions regarding your warranty rights and responsibilities, you should contact (Insert chosen installer’s contact) at 1-800-xxx-xxxx or the California Air Resources Board at 9528 Telstar Avenue, El Monte,

California 91731, or (800) 363-7664, or electronic mail: helpline@arb.ca.gov.

(c) Diesel Emission Control Strategy Warranty Report. The applicant must submit a warranty report to the Executive Officer by April 1 of each calendar year. The applicant must also submit a warranty report within 30 calendar days if warranty claims exceed four percent of the number of diesel engines using the diesel emission control strategy. The warranty report must include the following information:

(1) Annual and cumulative sales, and annual and cumulative leases of diesel emission control systems (California only).

(2) Annual and cumulative production of diesel emission control systems (California only).

(3) Annual summary of warranty claims (California only). The summary must include:

(A) A description of the nature of the claims and of the warranty replacements or repairs. The applicant must categorize warranty claims for each diesel emission control strategy family by the component(s) replaced or repaired.

(B) The number and percentage of diesel emission control systems of each model for which a warranty replacement or repair was identified.

(C) A short description of the diesel emission control system component that was replaced or repaired under warranty and the most likely reason for its failure.

(4) Date the warranty claims were filed and the engine family and application the diesel emission control systems were used with.

(5) Delineate the reason(s) for any instances in which warranty service is not provided to end-users that file warranty claims.

NOTE: Authority cited: Sections 39002, 39003, 39500, 39600, 39601, 39650-39675, 40000, 43000, 43000.5, 43011, 43013, 43018, 43105, 43600 and 43700, Health and Safety Code. Reference: Sections 39650-39675, 43000, 43009.5, 43013, 43018, 43101, 43104, 43105, 43106, 43107, and 43204-43205.5 Health and Safety Code; Title 17 California Code of Regulations Section 93000.

§ 2708. Determination of Emissions Reduction.

(a) Calculation of Emissions Reduction. The emissions reduction verified for a diesel emission control strategy is based on the average of all valid test results before (baseline) and after (control) implementation of the diesel emission control strategy. Test results from both emission testing and durability testing are to be used. If the applicant chooses to perform either the initial or the final durability baseline test, but not both, it must use those results to calculate the reductions obtained in both the initial and final control tests.

(1) Percentage Reduction. The percentage reduction for a given pair of baseline and control test sets (where a "set" consists of all test cycle repetitions, e.g., the test set of 3 hot-start UDDS tests) is the difference between the average baseline and average control emissions divided by the average baseline emissions, multiplied by 100 percent. The average of all such reductions, as shown in the equation below, is used in the verification of a diesel emission control strategy.

$$\text{Percentage Reduction} = 100\% \times \frac{\Sigma\,[(\text{baseline}_{AVG} - \text{control}_{AVG})/\text{baseline}_{AVG}]}{\text{Number of control test sets}}$$

Where:

Σ = sum over all control test sets

baseline_{AVG} or control_{AVG} = average of emissions from all baseline or control test repetitions within a given set

(A) For any test set involving cold and hot starts, the time weighted emission result is to be calculated by weighting the cold-start emissions by one-seventh (1/7) and the hot-start emissions by six-sevenths (6/7) as shown below.

Weighted Emission Result = 1/7* average cold-start emissions + 6/7* average hot-start emissions

(B) For applicants seeking verification of NOx reductions from on-road applications, weighted test results from the additional test set described in subsection 2703(e)1(C) are included in the percentage reduction equation above. The Executive Officer shall determine an appropriate weighting factor in consultation with the applicant based on factors including, but not limited to, the amount of time that vehicles within the selected emission control group have elevated NOx emissions and the breadth of engines and applications encompassed by the emission control group.

(2) The absolute emission level is the average control emission level, as defined in the following equation:

$$\text{Absolute Emission Level} = \frac{\Sigma\,(\text{control}_{AVG})}{\text{Number of control test sets}}$$

(b) Categorization of the Diesel Emission Control Strategy. The Executive Officer shall categorize diesel emission control strategies to reduce PM and NOx emissions based on their verified emission reductions. Diesel emission control strategies that reduce NOx will be assigned their verified emission reduction (Mark 1, 2, 3, 4, or 5) in 15 percent increments starting at 25 percent (See Table 1 in section 2702). Diesel emission control strategies are categorized by their PM reductions as follows:

(1) Level zero: the system has been demonstrated under these procedures to reduce PM emissions by less than 25 percent from the baseline emission level and to reduce NOx emissions by at least 25 percent from the baseline emission level.

(2) Level one: the system has been demonstrated under these procedures to reduce PM emissions by at least 25 percent from the baseline emission level.

(3) Level two: the system has been demonstrated under these procedures to reduce PM emissions by at least 50 percent from the baseline emission level.

(4) Level three: the system has been demonstrated under these procedures to reduce PM emissions by at least 85 percent from the baseline emission level, or to achieve PM emission levels of 0.01 grams per brake-horsepower-hour (g/bhp-hr) or less.

Diesel emission control strategies are categorized by their NOx reductions as follows:

(1) Mark 1: the system has been demonstrated under these procedures to reduce NOx emissions by at least 25 percent from the baseline emission level.

(2) Mark 2: the system has been demonstrated under these procedures to reduce NOx emissions by at least 40 percent from the baseline emission level.

(3) Mark 3: the system has been demonstrated under these procedures to reduce NOx emissions by at least 55 percent from the baseline emission level.

(4) Mark 4: the system has been demonstrated under these procedures to reduce NOx emissions by at least 70 percent from the baseline emission level.

(5) Mark 5: the system has been demonstrated under these procedures to reduce NOx emissions by at least 85 percent from the baseline emission level.

NOTE: Authority cited: Sections 39002, 39003, 39500, 39600, 39601, 39650-39675, 40000, 43000, 43000.5, 43011, 43013, 43018, 43105, 43600 and 43700, Health and Safety Code. Reference: Sections 39650-39675, 43000, 43009.5, 43013, 43018, 43101, 43104, 43105, 43106, 43107 and 43204-43205.5, Health and Safety Code; and Title 17 California Code of Regulations Section 93000.

§ 2709. In-Use Compliance Requirements.

(a) Applicability. These in-use compliance requirements apply to all diesel emission control strategies for on-road, off-road, and stationary applications. It is the responsibility of the applicant to perform in-use compliance testing for each verified diesel emission control strategy family (see Section 2706 (j) (2)). Testing is required when 50 units within a given diesel emission control strategy family have been sold or leased in the California market. Applicants must submit an in-use compliance testing proposal for approval by the Executive Officer prior to the in-use compliance testing. Applicants who have sold 50 units or more but have less than 50 units installed may submit a request for the Executive Officer to delay the in-use compliance deadlines specified in this section.

(b) Test Phases. In-use compliance testing, as described below in subsections (d), (e), (f), and (g), must be conducted per an approved in-use compliance testing proposal at two different phases for each diesel emission control strategy family:
(1) Phase 1. Applicants must obtain and test diesel emission control systems once they have been operated for at least 25 percent of their minimum warranty period or for one year, whichever comes first.
(2) Phase 2. Applicants must obtain and test diesel emission control systems once they have been operated between 60 and 80 percent of their minimum warranty period. For all systems used with heavy heavy-duty vehicles, the 60 to 80 percent window must be applied to the 5 year or 150,000 mile minimum warranty period.

(c) In-Use Compliance Testing Proposal. The applicant must submit to the Executive Officer a Phase 1 in-use compliance testing proposal no later than 90 days after selling the 50^{th} unit. The applicant must submit a Phase 2 in-use compliance testing proposal to the Executive Officer no later than 3 years after the 50^{th} unit is sold. The following information must be included in both testing proposals:
(1) Applicant identification.
(2) Diesel emission control strategy family name.
(3) Parties to be involved in conducting in-use compliance tests.
(4) Test facility identification and description.
(5) Quality control and quality assurance procedures for the test equipment.
(6) List of candidate test units (at least 10 choices per phase) with the following information for each: vehicle/equipment information on which the unit is installed (make, model, model year), location, engine information (family name, make, series, model year, displacement), date of manufacture, date of installation, and cleaning/repair history.
(7) Cumulative sales of the emission control strategy family in each application.

(8) Predicted mileage or hours of use each diesel emission control system will have accrued by the time it is obtained by the applicant of diesel emission control strategy testing.
(9) Description of test vehicles and engines (engine family name, make, model, model year, displacement)
(10) Testing plan for meeting the requirements of part (g) below.

Within 45 days of receipt of the completed testing proposal, the Executive Officer shall determine whether the applicant has an appropriate testing proposal to support in-use compliance testing. The in-use testing proposal will not be considered approved until the Executive Officer issues the applicant a letter of approval. If the Executive Officer determines that the testing proposal is insufficient or inappropriate, the applicant must, within 30 days, submit a revised testing proposal.

(d) Selection of Diesel Emission Control Systems for Testing. For each diesel emission control strategy family and for both test phases, the applicant must propose a representative sample of installed diesel emission control systems for in-use compliance testing based on information provided per Section 2709(c) to be approved by the Executive Officer. The selected diesel emission control systems should come from a representative sample of engines or vehicles equipped with the control systems. The engines or vehicles equipped with the selected diesel emission control systems must have good maintenance records and may receive a tune-up or normal maintenance prior to the applicant obtaining the diesel emission control systems for testing. The applicant must obtain information from the end users regarding the diesel emission control systems' accumulated mileage or hours of usage, maintenance records (to the extent practicable), operating conditions and a description of any unscheduled maintenance that may affect the emission results.

(e) Selection of Test Engines. The Executive Officer must approve the appropriate test engines or vehicles for in-use compliance testing. The applicant must provide candidate test vehicles/engines for the Executive Officer's review. If the Executive Officer determines that a diesel emission control system affects the performance of the engine, the Executive Officer may require the applicant to test the selected diesel emission control system with the engine on which it is installed. The applicant may tune-up or rebuild test engines prior to, but not after, baseline testing unless rebuilding the engine is an integral part of the diesel emission control strategy. All testing should be performed with the test engine in a proper state of maintenance. Emissions of NO_2 from the test engine must not exceed 15 percent of the total baseline NOx emissions by mass. If there is a special category of engines with NO_2 emission levels that normally exceed 15 percent, this requirement may be adjusted for those engines at the discretion of the Executive Officer.

(f) Number of Diesel Emission Control Systems to be Tested. The number of diesel emission control systems an applicant must test in each of the two test phases will be determined as follows:

(1) A minimum of four diesel emission control systems in each diesel emission control strategy family must be tested. For every system tested that does not reduce emissions by at least 90 percent of the lower bound of its initial verification level (or does not achieve an emission level less than or equal to 0.011 g/bhp-hr of PM) or does not meet the NO_2 requirement in section 2709(k), two more diesel emission control systems from the same family must be obtained and tested. The total number of systems tested shall not exceed ten per diesel emission control strategy family.

(2) At the discretion of the Executive Officer, applicants may begin by testing more than the minimum of four diesel emission control systems. Applicants may concede failure of an emission control system before testing a total of ten diesel emission control systems.

(g) In-use Compliance Emission Testing. Applicants must follow the testing procedure used for emission reduction verification as described in Section 2703 (both baseline and control tests are required). As provided in Section 2709(h), the applicant may request the Executive Officer to review and approve an alternative testing procedure. If a diesel emission control strategy verified by U.S. EPA must perform engine dynamometer testing with the Heavy-duty Transient FTP cycle to fulfill the in-use compliance requirements of that program, but was verified by the Executive Officer with chassis dynamometer testing, the Executive Officer will also accept testing with the Heavy-duty Transient FTP cycle for the in-use compliance requirements of this Procedure.

(h) Alternative Test Cycles and Methods. The Executive Officer may consider, on a case by case basis, an alternative test plan or method for applicants to satisfy the in-use compliance requirements of this section. The proposed alternative test plan must be as scientifically sound as the testing described in Section 2709(g) of the Procedure and it must produce accurate results that will indicate if the emission control system reduces emissions to the level for which it was verified. Use of an alternative test procedure must be approved by the Executive Officer.

(i) In-Use Compliance Report. The applicant must submit an in-use compliance report to the Executive Officer after each phase of testing. The applicant must submit the phase 1 report within 18 months from when the 50^{th} unit is sold. The phase 2 report must be submitted within 4 years from when the 50^{th} unit is sold. The following information must be reported for each of the minimum of four diesel emission control systems tested:

(1) Parties involved in conducting the in-use compliance tests.

(2) Quality control and quality assurance information for the test equipment.

(3) Diesel emission control strategy family name and manufacture date.
(4) Vehicle or equipment and type of engine (engine family name, make, model year, model, displacement, etc.) the diesel emission control system was applied to.
(5) Mileage or hours the diesel emission control system was in use.
(6) Results of all emission testing.
(7) Summary of all maintenance, adjustments, modifications, and repairs performed on the diesel emission control system.

(j) The Executive Officer may request the applicant to perform additional in-use testing if the warranty claims exceed four percent of the number of diesel engines using the diesel emission control strategy, or based on other relevant information. As noted in Section 2707(c), if warranty claims exceed four percent of the number of diesel engines using the diesel emission control strategy, the applicant must notify the Executive Officer and submit a warranty report within 30 calendar days of that time.

(k) Conditions for Passing In-Use Compliance Testing. For a diesel emission control strategy to pass in-use compliance testing, emission test results must indicate that the strategy reduced emissions by at least 90 percent of the lower bound of the emission reduction level the Executive Officer originally verified it to. In addition, the strategy must meet the requirements of section 2706(a) with the exception that the strategy must not increase emissions of NO_2 by more than an increment equivalent in mass to 33 or 22 percent of the baseline NOx emission level for systems verified under the 30 or 20 percent NO_2 limits, respectively. If the first four diesel emission control systems tested within a diesel emission control strategy family meet both of these standards, the diesel emission control strategy passes in-use compliance testing. If any of the first four diesel emission control systems tested within a diesel emission control strategy family fail to meet either of these standards, and more than four units are tested, at least 70 percent of all units tested must meet both standards for the diesel emission control strategy family to pass in-use compliance testing. For each failed test, for which the cause of failure can be attributed to the product and not to maintenance or other engine-related problems, two additional units must be tested, up to a total of ten units per diesel emission control strategy family. Within 30 days of a test unit failing, the applicant must submit to the Executive Officer for approval a testing proposal for the additional test units that is compliant with part (c) above. The testing proposal must include an investigative report detailing the causes of the failure. The Executive Officer shall, within 45 days of its receipt, determine whether the test plan is acceptable. After receiving approval from the Executive Officer, the applicant must complete testing.

(l) Failure of In-use Compliance Testing. If a diesel emission control strategy family does not meet the minimum in-use compliance requirements of this

section, the applicant must submit a remedial report within 90 days after the in-use compliance report is submitted. The remedial report must include:
(1) Summary of the in-use compliance report.
(2) Detailed analysis of the failed diesel emission control systems and possible reasons for failure.
(3) Remedial measures to correct or replace failed diesel emission control systems as well as the rest of the in-use diesel emission control systems.

(m) The Executive Officer shall evaluate the remedial report, annual warranty report, and all other relevant information to determine if the diesel emission control strategy family satisfies the in-use compliance requirements. The Executive Officer may request additional information from the applicant. Based on this review, the Executive Officer may lower the verification level or revoke the verification status of a verified diesel emission control strategy family. The Executive Officer may also lower the verification level or revoke the verification status of a verified diesel emission control strategy family, if the applicant does not conduct in-use compliance testing in accordance with this section, or if the Executive Officer conducts in-use compliance testing in accordance with this section (including alternative testing) and the diesel emission control strategy family does not pass the standards in this section.

(n) The Executive Officer may lower the verification level or revoke the verification status of a verified diesel emission control strategy family if the applicant fails to observe the requirements of Sections 2706 or 2707. The Executive Officer must allow the applicant an opportunity to address the possible lowering or revocation of the verification level in a remedial report to the Executive Officer and the Executive Officer may make this determination based on all relevant information.

NOTE: Authority cited: Sections 39002, 39003, 39500, 39600, 39601, 39650-39675, 40000, 43000, 43000.5, 43011, 43013, 43018, 43105, 43600 and 43700, Health and Safety Code. Reference: Sections 39650-39675, 43000, 43009.5, 43013, 43018, 43101, 43104, 43105, 43106, 43107 and 43204-43205.5, Health and Safety Code; and Title 17 California Code of Regulations Section 93000.

§ 2710. Verification of Emission Reductions for Alternative Diesel Fuels and Fuel Additives

(a) Applicability. This section applies to in-use strategies that include emission reductions from the use of alternative diesel fuels or fuel additives. The requirements in this section are in addition to those in Sections 2700-2709, except as specifically noted.

(b) Alternative Diesel Fuel and Fuel Additive Proposed Test Protocol. The applicant must submit a proposed test protocol which includes:

(1) References to criteria pollutant and toxic emissions sampling and analyses that are consistent with the requirements of Section 2703.
(2) Description and Parameters of Alternative Diesel Fuels and Fuel Additives.
  (A) The applicant must describe the applicability of the alternative diesel fuel or fuel additive to diesel engines and identify any requirements for engine or fuel system modifications.
  (B) The applicant must provide a general description of the alternative diesel fuel or fuel additive that includes the fuel type, fuel characteristics, fuel properties, fuel formulation, and chemical composition. The applicant for the candidate alternative diesel fuel or fuel additive must specify the following:
    1. Identity, chemical composition, and concentration of fuel additives
    2. Sulfur content
    3. Total aromatic content
    4. Total polycyclic aromatic hydrocarbon content
    5. Nitrogen content
    6. API gravity (density)
    7. Distillation temperature distribution information, initial boiling point (IBP),
    8. 10% recovered (REC), 5O% REC, 90% REC, and end point (EP)
  (C) The applicant must provide information on the candidate alternative diesel fuel or fuel additive that may affect engine performance, engine wear, and safety. The applicant for the candidate alternative diesel fuel or fuel additive must specify the following:
    1. Viscosity (engine performance)
    2. Fuel volatility (engine performance)
    3. Ignition quality (engine performance)
    4. Fuel operating temperatures (engine performance)
    5. Engine wear tendencies (engine wear)
    6. Corrosion (engine wear)
    7. Lubricity (engine wear)
    8. Fuel flash point (safety)
  (D)The applicant must provide information on the candidate alternative diesel fuel or fuel additive to determine if there are chemicals in the fuel or fuel additive that may increase levels of toxic compounds or potentially form toxic compounds in the fuel or fuel additive. The applicant will conduct an analysis for metals and elements by a method specified by the applicant. Copper, iron, cerium, lead, cadmium, chromium, and phosphorus must be included in the analysis. Additional analysis for other toxic compounds may be required after reviewing the chemical composition of the candidate alternative diesel fuel and its additives or fuel additive (Note: For alternative diesel fuels or fuel additives that are in part comprised of standard diesel fuel, such as emulsified diesel fuels, a toxic analysis of the diesel base fuel is not necessary).

(E) With the approval of the Executive Officer or designee, an applicant may also specify different fuel parameters and test methods that are appropriate to better characterize the candidate alternative diesel fuel or fuel additive.

(3) Upon review of the proposed test protocol, the Executive Officer or designee may require additional fuel components, parameters, and specifications to be determined.

(4) Reference Fuel Specifications. The reference fuel used in the comparative testing described in Section 2710(d) allows the applicant three options in selecting a reference fuel.

(A) Option (1). The first option is to use a 10 percent aromatic California diesel reference fuel. The reference fuel must be produced from straight-run California diesel fuel by a hydrodearomatization process and must have the characteristics set forth below under "Reference Fuel Specifications" (the listed ASTM methods are incorporated herein by reference).

(B) Option (2). The second option is to make the reference fuel from a custom blend using a "like" California diesel fuel made from a straight-run California diesel fuel by a hydroaromatization process and must have the characteristics set forth below under "Reference Fuel Specifications". In addition the reference fuel must exhibit the bell shaped distillation curve characteristic of diesel fuel and no chemical feedstocks or pure chemicals such as solvents can be used as blend stocks. Details of the source and specifications of the feedstocks must be provided in the protocol and the processes and diesel feedstocks used to make the reference fuel must be reviewed and approved by the Executive Officer.

(C) Option (3). For alternative diesel fuels and fuel additives that contain diesel as a base fuel such as emulsified diesel fuel and 80:20 biodiesel fuel (80 percent diesel/20 percent biodiesel), the base diesel fuel used to make the alternative diesel fuel or fuel additive can be used in place of the 10 percent aromatic California diesel reference fuel. The base diesel fuel must be a certified, commercially available diesel fuel sold in California. The sulfur content, aromatic hydrocarbon content, polycyclic aromatic hydrocarbon content, nitrogen content, natural cetane number, API gravity, viscosity, and distillation specifications must be provided for the base diesel fuel used for the reference fuel.

Table 6. Fuel Test Methods and Reference Fuel Specifications

Property	General Reference Fuel Specifications	ASTM Test Method
Sulfur Content	15 ppm max	D5453-93
Aromatic Hydrocarbon content, Vol. %	10% max	D5186-96
Polycyclic Aromatic Hydrocarbon content %	1.4% max	D5186-96
Nitrogen Content	10 ppm max	D4629-96
Natural Cetane Number	48 min	D613-84
Gravity, API	33-39	D287-82
Viscosity at 40^{o}, cSt	2.0-4.1	D445-83
Flash point, ^{o}F	130	D93-80
Distillation, ^{o}F IBP 10%REC 50%REC 90%REC EP	 340-420 400-490 470-560 550-610 580-660	D86-96

(5) The identity of the entity proposed to conduct the tests described in Section 2710(d);
(6) Reasonably adequate quality assurance and quality control procedures;
(7) Notification of any outlier identification and exclusion procedure that will be used, and
(8) A demonstration that any procedure meets generally accepted statistical principles.

(c) Application for Alternative Diesel Fuel and Fuel Additive Emission Reduction Verification. Upon completion of the tests, the applicant may submit an application for verification to the Executive Officer or designee. The application must follow the format in Section 2702(d) as applicable and include:
(1) The approved test protocol,
(2) All of the test data,
(3) Copy of the complete test log prepared in accordance with Section 2710(d)(3)(B),
(4) A demonstration that the candidate alternative diesel fuel or fuel additive meets the requirements for verification set forth in this section, and
(5) Such other information as the Executive Officer or designee may reasonably require.

(d) Emissions Test Procedures for Particulates, Nitrogen Oxides, Soluble Organic Fraction, Hydrocarbons, and Toxics.
(1) Criteria pollutants test requirements. In each test of a fuel, exhaust emissions of NO_x, NO_2 (pursuant to Section 2706(a)(2)), total PM, carbon

monoxide, carbon dioxide, and hydrocarbons must be measured. In addition, for each test the soluble organic fraction (SOF) of the particulate matter in the exhaust emissions must be determined in accordance with the Air Resources Board's "Test Method for Soluble Organic Fraction (SOF) Extraction" dated April 1989, which is incorporated herein by reference.

(2) Toxic emissions sampling and analysis requirements. Exhaust emissions of formaldehyde, acetaldehyde, benzene, toluene, ethyl benzene, xylenes, butadiene, and polycyclic aromatic hydrocarbons are to be sampled and analyzed as specified in Table 7 for a minimum of three test samples collected from separate emission test repetitions.

Table 7. Toxics sampling and analysis [1,2]

Toxics	Method
Formaldehyde and acetaldehyde	ARB SOP 104
Benzene toluene, ethyl benzene, xylenes, and butadiene	ARB SOP 102/103
Polycyclic aromatic hydrocarbons	ARB method 429[3]

[1]Additional toxics sampling may be required depending on the chemical composition of the additives in the fuel.
[2]At a minimum tunnel blanks are required prior to and after conducting toxic emissions sampling for the reference fuel and candidate alternative diesel fuel or fuel additive.
[3]PAH sampling consists of a filter to collect particulate PAHs and XAD resin to collect volatile PAHs. The sampling protocol needs to be included in the test protocol. Analysis of the samples will be performed by ARB method 429.

(3) Emission test requirements and test sequence for emissions test program.

(A) The applicant must follow the emission test requirements from Section 2703 subsections (a), (b), (k), (l), and (m). For all on-road diesel vehicles and equipment, the applicant must conduct engine dynamometer testing using the Federal Test Procedure (FTP) Heavy-duty Transient Cycle, in accordance with the provisions in the Code of Federal Regulations, Title 40, Part 86, Subpart N. For all off-road and stationary diesel vehicles and equipment, the applicant must conduct engine dynamometer testing in accordance with Section 2703(e)(2) and 2703(e)(3). The applicant must use one of the following test sequences:

1. If both cold start and hot start exhaust emission tests are conducted, a minimum of five exhaust emission tests must be performed on the engine with each fuel, using either of the following sequences, where "R" is the reference fuel and "C" is the candidate

alternative diesel fuel or fuel additive: RC CR RC CR RC (and continuing in the same order) or RC RC RC RC RC (and continuing in the same order). The engine mapping procedures and a conditioning transient cycle must be conducted with the reference fuel before each cold start procedure using the reference fuel. The reference cycle used for the candidate alternative diesel fuel or fuel additive must be the same as determined for the reference fuel.

2. If only hot start exhaust emission tests are conducted, one of the following test sequences must be used throughout the testing, where "R" is the reference fuel and "C" is the candidate alternative diesel fuel or fuel additive :

   Alternative 1: RC CR RC CR (continuing in the same order for a given calendar day; a minimum of twenty individual exhaust emission tests must be completed with each fuel)

   Alternative 2: RR CC RR CC (continuing in the same order for a given calendar day; a minimum of twenty individual exhaust emission tests must be completed with each fuel)

   Alternative 3: RRR CCC RRR CCC (continuing in the same order for a given calendar day: a minimum of twenty-one individual exhaust emission tests must be completed with each fuel)

   For all alternatives, an equal number of tests must be conducted using the reference fuel and the candidate alternative diesel fuel or fuel additive on any given calendar day. At the beginning of each calendar day, the sequence of testing must begin with the fuel that was tested at the end of the preceding day. The engine mapping procedures and a conditioning transient cycle must be conducted at the beginning of each day for the reference fuel. The reference cycle used for the candidate alternative diesel fuel or fuel additive must be the same as determined for the reference fuel.

3. Alternative test sequence. The applicant may request the Executive Officer to approve an alternative test sequence in place of the above test sequences. In reviewing this request, the Executive Officer may consider all relevant information including, but not limited to, the following:
   a. Statistical and scientific equivalence to 1. or 2., and
   b. Body of existing test data using the alternative test sequence.

(B) The applicant must submit a test schedule to the Executive Officer or designee at least one week prior to commencement of the tests. The test schedule must identify the days on which the tests will be conducted, and must provide for conducting test consecutively without substantial interruptions other than those resulting from the normal

hours of operations at the test facility. The Executive Officer or designee should be permitted to observe any tests. The party conducting the tests must maintain a test log which identifies all tests conducted, all engine mapping procedures, all physical modifications to or operational tests of the engine, all recalibrations or other changes to the test instruments, and all interruptions between tests, and the reason for each interruption. The party conducting the tests or the applicant must notify the Executive Officer or designee by telephone and in writing of any unscheduled interruption resulting in a test delay of 48 hours or more, and the reason for such delay. Prior to restarting the test, the applicant or person conducting the tests must provide the Executive Officer or designee with a revised schedule for the remaining tests. All tests conducted in accordance with the test schedule, other than any test rejected in accordance with an outlier identification and exclusion procedure included in the approved test protocol, must be included in the comparison of emissions.

(C) Upon approval of the Executive Officer or designee, the applicant may specify an alternative test sequence to Section 2710(d)(3)(A). The applicant must provide the rationale demonstrating that the alternative test sequence better characterizes the average emissions difference between the reference fuel and the alternative diesel fuel or fuel additive.

(e) Durability.

(1) The applicant must meet the durability demonstration requirements in Section 2704 subsections (a), (b), (d), (e), and (h) with the exceptions of emission testing and fuel requirements. If the applicant's diesel emission control strategy includes hardware components in addition to the alternative diesel fuel or fuel additive, then the emission testing requirements in Section 2704 apply.

(2) The applicant must provide test data obtained after completion of the service accumulation, described in Section 2704(d), showing that the candidate alternative diesel fuel or fuel additive does not adversely affect the performance and operation of diesel engines or cause premature wear or cause damage to diesel engines. This must include but is not limited to lubricity, corrosion, and damage to engine parts such as fuel injector tips. The applicant must provide data showing under what temperature and conditions the candidate alternative diesel fuel or fuel additive remains stable and usable in California.

(f) Multimedia Assessment for Fuel Strategies. Diesel emission control strategies which rely on fuel changes either through use of additives or through use of alternative diesel fuels must undergo an evaluation of the multimedia effects. No diesel emission control strategy that relies on the use of an additive or an alternative fuel may be verified unless a multimedia evaluation of the additive or alternative fuel has been conducted and the California Environmental

Policy Council established by Public Resources Code section 71017 has determined that such use will not cause a significant adverse impact on the public health or the environment, pursuant to Health and Safety Code section 43830.8. No person shall sell, offer for sale, supply or offer for supply an alternative fuel or a diesel fuel in California that contains an additive for use in a verified diesel emission control strategy unless such a multimedia evaluation has been conducted and resulted in a determination that use of the alternative fuel or additive will not cause a significant adverse impact on the public health and the environment. The applicant shall bear the expense of conducting the multimedia assessment.

(g) Other Requirements.
(1) The candidate alternative diesel fuel or fuel additive must be in compliance with applicable federal, state, and local government requirements.
(2) Applicants planning to market fuel in California must contact and register with the U.S. EPA and the California Dept. of Food and Agriculture. Contacts are listed below.

Office of Transportation and Air Quality
U.S. EPA Head Quarters
Ariel Rios Blvd.
1200 Pennsylvania Ave, N.W.
Washington DC 20468
Phone (202) 564-9303

Petroleum Products/Weighmaster Enforcement Branch
Division of Measurement Standards
Dept. of Food and Agriculture
8500 Fruitridge Road, Sacramento CA 95826
Phone (916) 229-3000

(3) Additional government agencies such as the California Energy Commission, Area Council of Governments, and Local Air Quality Management Districts may be contacted to facilitate the marketing of alternative diesel fuel in California.

(h) Conditional Verification.
(1) The Executive Officer may grant a conditional verification for an alternative diesel fuel or fuel additive for off-road or stationary applications only after the conditional verification for on-road application is granted. The Executive Officer may grant a conditional verification for on-road application if the applicant meets the following conditions:
(A) The applicant has applied for U.S. EPA registration of the alternative diesel fuel or fuel additive ;

(B) The U.S. EPA has granted a research and development exemption or otherwise granted permission for the alternative diesel fuel or fuel additive to be used, and;
(C) All relevant requirements of Sections 2700-2710 have been met with the exception that registration with the U.S. EPA has not been completed.
(D) Multimedia Assessment as specified in Section 2710 (f).

(2) Where conditional verification is granted, full verification must be obtained by completing the U.S. EPA registration process within a year after receiving conditional verification. During that year, conditional verification is equivalent to verification for the purposes of satisfying the requirements of in-use emission control regulations.

(i) Extensions of an Existing Verification. See Section 2702 (g). The applicant may request the Executive Officer to approve a reduced number of emission tests when extending an existing verification to other emission control groups. In reviewing this request, the Executive Officer may consider all relevant information including, but not limited to, the following:
(1) Variability in the test results used for the existing verification,
(2) Characteristics of the duty cycles in the other emission control groups,
(3) The mechanism by which the alternative diesel fuel or fuel additive reduces emissions, and
(4) Body of existing test data.

NOTE: Authority cited: Sections 39002, 39003, 39500, 39600, 39601, 39650-39675, 40000, 43000, 43000.5, 43011, 43013, 43018, 43105, 43600, 43700 and 43830.8 Health and Safety Code. Reference: Sections 39650-39675, 43000, 43009.5, 43013, 43018, 43101, 43104, 43105, 43106, 43107, 43204-43205.5 and 43830.8, Health and Safety Code; Section 71017, Public Resources Code, and Title 17 California Code of Regulations Section 93000.

State of Oregon Department of Environmental Quality

OAR 340-040-0020 Numerical Groundwater Quality Reference Levels

11/14/97

Table 1 – Inorganic Contaminants Numerical Groundwater Quality Reference Level[1]	
Contaminants	**Reference Level (mg/L)**
Arsenic	0.05
Barium	1.0
Cadmium	0.01
Chromium	0.05
Fluoride	4.0
Lead	0.05
Mercury	0.002
Nitrate-N	10.0
Selenium	0.01
Silver	0.05

[1]All reference levels are for total (unfiltered) concentrations unless otherwise specified by the Department.

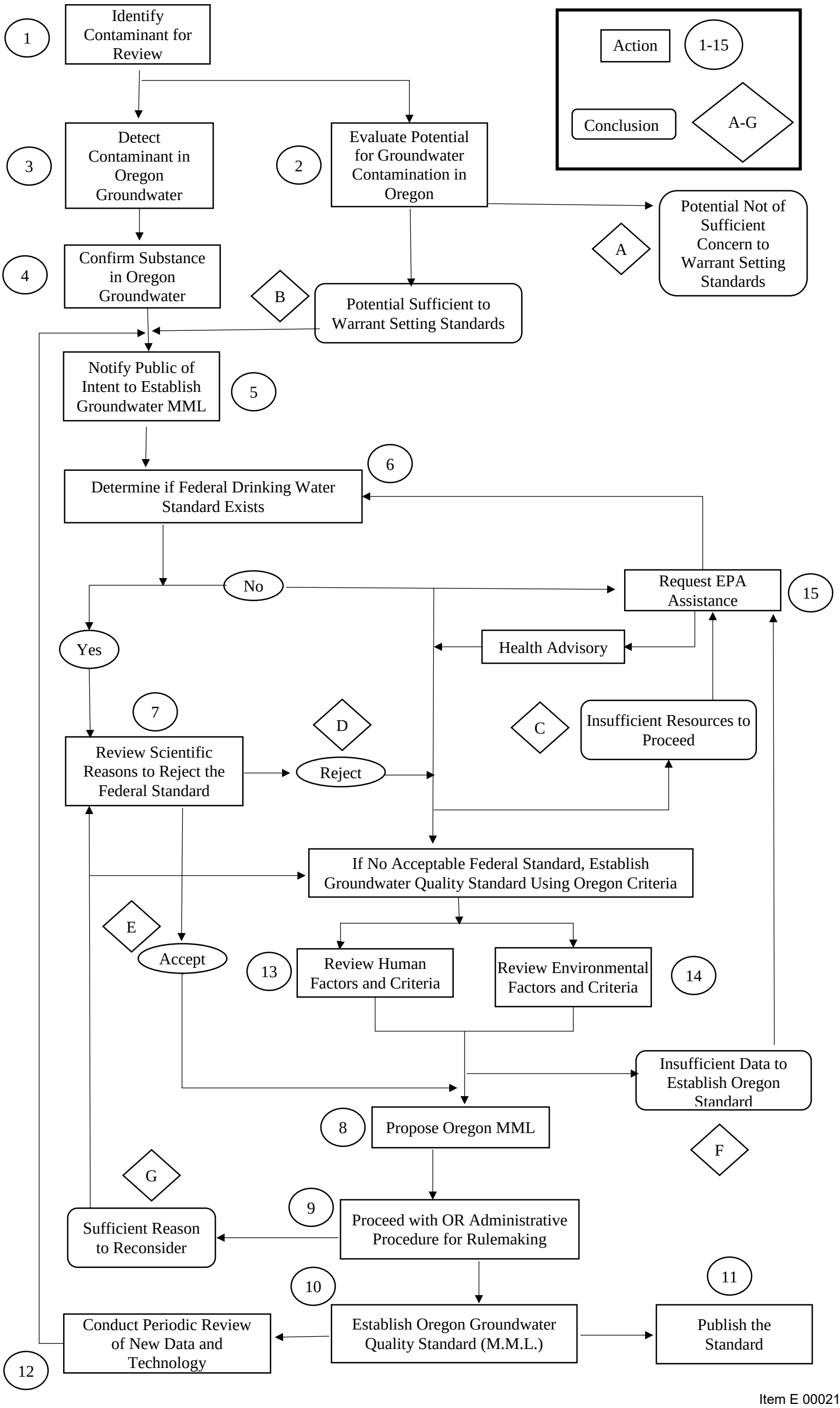
Table 2 – Organic Contaminants Numerical Groundwater Quality Reference Level[1]	
Contaminants	**Reference Level (mg/L)**
Benzene	0.005
Carbon Tetrachloride	0.005
p-Dichlorobenzene	0.075
1,2-Dichloroethane	0.005
1,1-Dichloroethylene	0.007
1,1,1-Trichloroethane	0.200
Trichloroethylene	0.005
Total Trihalomethanes (the sum of concentrations bromodichloromethane, dibromochloromethane, tribromomethane (bromoform), and trichloromethane (chloroform))	0.100
Vinyl Chloride	0.002
2,4-D	0.100
Endrin	0.0002
Lindane	0.004
Methoxychlor	0.100
Toxaphene	0.005
2,4,5-TP Silvex	0.010
[1]All reference levels are for total (unfiltered) concentrations unless otherwise specified by the Department.	

Table 3 – Miscellaneous Contaminants Numerical Groundwater Quality Guidance Levels[1]	
Contaminants	**Guidance Level (mg/L)[2]**
Chloride	250
Color	15 Color Units
Copper	1.0
Foaming agents	0.5
Iron	0.3
Manganese	0.05
Odor	3 Threshold odor number
pH	6.5 – 8.5
Sulfate	250
Total dissolved solids	500
Zinc	5.0

[1] All guidance levels except total dissolved solids are for total (unfiltered) concentrations unless the Department specifies otherwise.
[2] Unless otherwise specified, except pH.

OAR 340-040-0108 – Appendix 1

Method Outline for Determining Oregon Groundwater Quality Standards



State of Oregon Department of Environmental Quality

OAR 340-040-0125
EPA National Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses

PB85-227049

Guidelines for Deriving Numerical National Water Quality Criteria for the Protection Of Aquatic Organisms and Their Uses

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Notices

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication.

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This document is available the public to through the National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield, VA 22161.

Special Note

This December 2010 electronic version of the 1985 Guidelines serves to meet the requirements of Section 508 of the Rehabilitation Act. While converting the 1985 Guidelines to a 508-compliant version, EPA updated the taxonomic nomenclature in the tables of Appendix 1 to reflect changes that occurred since the table were originally produced in 1985. The numbers included for Phylum, Class and Family represent those currently in use from the Integrated Taxonomic Information System, or ITIS, and reflect what is referred to in ITIS as Taxonomic Serial Numbers. ITIS replaced the National Oceanographic Data Center (NODC) taxonomic coding system which was used to create the original taxonomic tables included in the 1985 Guidelines document (NODC, Third Addition - see Introduction). For more information on the NODC taxonomic codes, see http://www.nodc.noaa.gov/General/CDR-detdesc/taxonomic-v8.html.

The code numbers included in the reference column of the tables have not been updated from the 1985 version. These code numbers are associated with the old NODC taxonomic referencing system and are simply replicated here for historical purposes. Footnotes may or may not still apply.

EPA is working on a more comprehensive update to the 1985 Guidelines, including new taxonomic tables which better reflect the large number of aquatic animal species known to be propagating in U.S. waters.

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Executive Summary

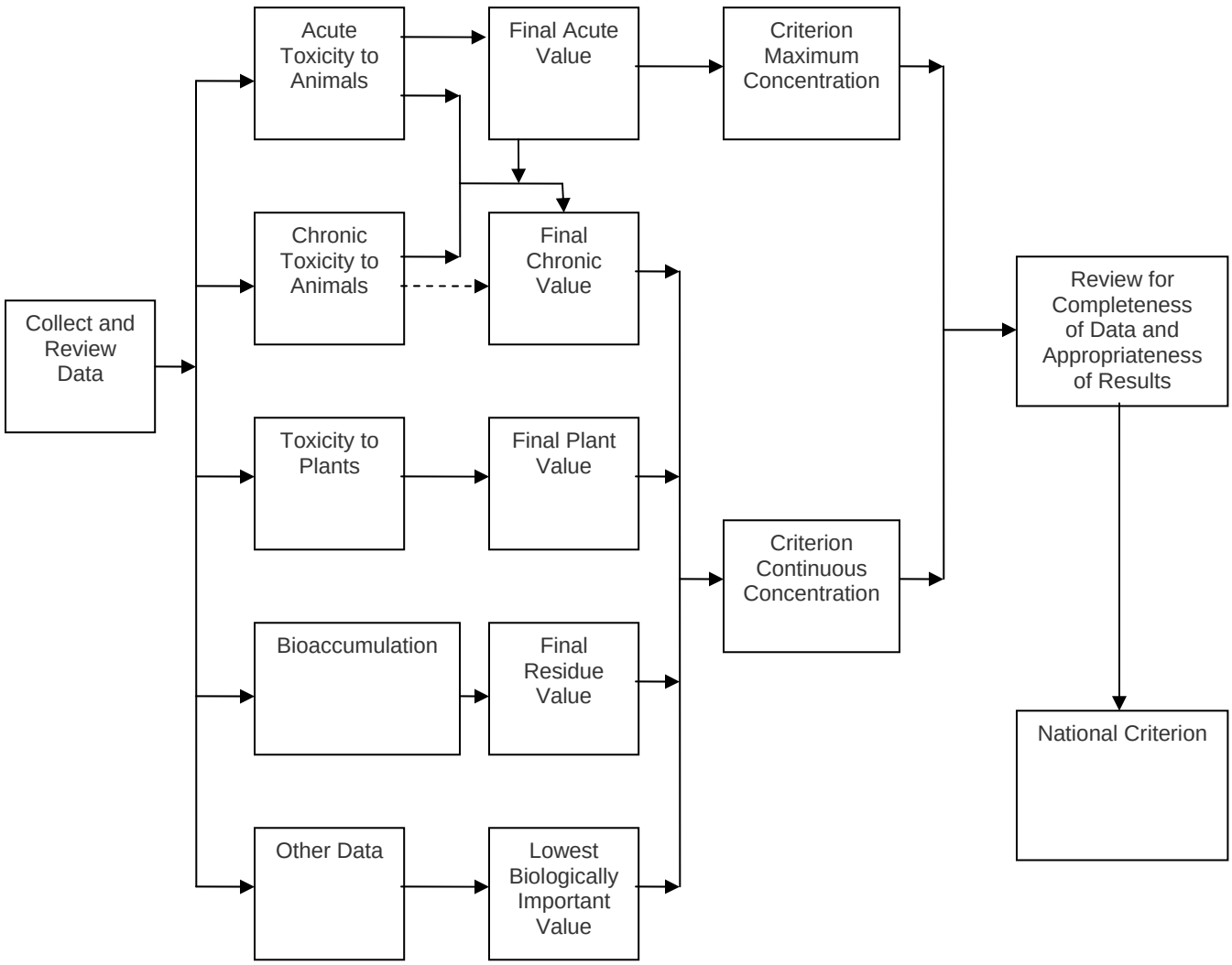
Derivation of numerical national water quality criteria for the protection of aquatic organism and their uses is a complex process (Figure 1) that uses information from many areas of aquatic toxicology. After a decision is made that a national criterion is needed for a particular material, all available information concerning toxicity to, and bioaccumulation by, aquatic organisms is collected, reviewed for acceptability, and sorted. If enough acceptable data on acute toxicity to aquatic animals are available, they are used to estimate the highest one-hour average concentration that should not result in unacceptable effects on aquatic organisms and their uses. If justified, this concentration is made a function of a water quality characteristic such as pH, salinity, or hardness. Similarly, data on the chronic toxicity of the material to aquatic animals are used to estimate the highest four-daily average concentration that should not cause unacceptable toxicity during a long-term exposure. If appropriate, this concentration is also related to a water quality characteristic.

Data on toxicity to aquatic plants are examined to determine whether plants are likely to be unacceptably affected by concentrations that should not cause unacceptable effects on animals. Data on bioaccumulation by aquatic organisms are used to determine if residues might subject edible species to restrictions by the U.S. Food and Drug Administration or if such residues might harm some wildlife consumers of aquatic life. All other available data are examined for adverse effects that might be biologically important.

If a thorough review of the pertinent information indicates that enough acceptable data are available, numerical national water quality criteria are derived for fresh water or salt water or both to protect aquatic organisms and their uses from unacceptable effects due to exposures to high concentrations for short periods of time, lower concentrations for longer periods of time, and combinations of the two.

Figure 1

Derivation of Numerical National Water Quality Crtieria for the Protection of Aquatic Organisms and Their Uses



Introduction

Of the several possible forms of criteria, the numerical form is the most common, but the narrative (e.g., pollutants must not be present in harmful concentrations) and operational (e.g., concentrations of pollutants must not exceed one-tenth of the 96-hr LC50) forms can be used if numerical criteria are not possible or desirable. If it were feasible, a freshwater (or saltwater) numerical aquatic life national criterion* for a material should be determined by conducting field tests on a wide variety of unpolluted bodies of fresh (or salt) water. It would be necessary to add various amounts of the material to each body of water in order to determine the highest concentration that would not cause any unacceptable long-term or short-term effect on the aquatic organisms or their uses. The lowest of these highest concentrations would become the freshwater (or saltwater) national aquatic life water quality criterion for that material, unless one or more of the lowest concentrations were judged to be outliers. Because it is not feasible to determine national criteria by conducting such field tests, these Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses (hereafter referred to as the National Guidelines) describe an objective, internally consistent, appropriate, and feasible way of deriving national criteria, which are intended to provide the same level of protection as the infeasible field testing approach described above.

Because aquatic ecosystems can tolerate some stress and occasional adverse effects, protection of all species at all times and places is not deemed necessary. If acceptable data are available for a large number of appropriate taxa from an appropriate variety of taxonomic and functional groups, a reasonable level of protection will probably be provided if all except a small fraction of the taxa are protected, unless a commercially or recreationally important species is very sensitive. The small fraction is set at 0.05 because other fractions resulted in criteria that seemed too high or too low in comparison with the sets of data from which they were calculated. Use of 0.05 to calculate a Final Acute Value does not imply that this percentage of adversely affected taxa should be used to decide in a field situation whether a criterion is too high or too low or just right.

Determining the validity of a criterion derived for a particular body of water, possibly by modification of a national criterion to reflect local conditions [1, 2, 3], should be based on an operation definition of "protection of aquatic organisms and their uses" that takes into account the practicalities of field monitoring programs and the concerns of the public. Monitoring programs should contain sampling points at enough times and places that all unacceptable changes, whether caused directly or indirectly, will be detected. The programs should adequately monitor the kinds of species of concern to the public, i.e., fish in fresh water and fish and macroinvertebrates in salt water. If the kinds of species of concern cannot be adequately monitored at a reasonable cost, appropriate surrogate species should be monitored. The kinds of species most likely to be good surrogates are those that either (a) are a major food of the desired kinds of species or (b) utilize the same food as the desired species or (c) both. Even if a major adverse effect on appropriate surrogate species does not directly result in an unacceptable effect on the kinds of species of concern to the public, it indicates a high probability that such an effect will occur.

* The term "national criteria" is used herein because it is more descriptive than the synonymous term "section 304(a) criteria", which is used in the Water Quality Standards Regulation [1].

To be acceptable to the public and useful in field situations, protection of aquatic organisms and their uses should be defined as prevention of unacceptable long-term short-term effects on (1) commercially, recreationally, and other important species and (2) (a) fish and benthic invertebrate assemblages in rivers and streams, and (b) fish, benthic invertebrate, and zooplankton assemblages in lakes, reservoirs, estuaries, and oceans. Monitoring programs intended to be able to detect unacceptable effects should be tailored to the body of water of concern so that necessary samples are obtained at enough times and places to provide adequate data on the populations of the important species, as well as data directly related to the reasons for their being considered important. For example, for substances that are residue limited, species that are consumed should be monitored for contaminants to ensure that wildlife predators are protected, FDA action levels are not exceeded, and flavor is not impaired. Monitoring programs should also provide data on the number of taxa and number of individuals in the above-named assemblages that can be sampled at reasonable cost. The amount of decrease in the number of taxa or number of individuals in an assemblage that should be considered unacceptable should take into account appropriate features of the body of water and its aquatic community. Because most monitoring programs can only detect decreases of more than 20 percent, any statistically significant decrease should usually be considered unacceptable. The insensitivity of most monitoring programs greatly limits their usefulness for studying the validity of criteria because unacceptable changes can occur and not be detected. Therefore, although limited field studies can sometimes demonstrate that criteria are underprotective, only high quality field studies can reliably demonstrate that criteria are not underprotective.

If the purpose of water quality criteria were to protect only commercially and recreationally important species, criteria specifically derived to protect such species and their uses from the direct adverse effects of a material would probably, in most situations, also protect those species from indirect adverse effects due to effects of the material on other species in the ecosystem. For example, in most situations either the food chain would be more resistant than the important species and their uses or the important species and their food chains would be adaptable enough to overcome effects of the material on portions of the food chains.

These National Guidelines have been developed on the theory that effects which occur on a species in appropriate laboratory tests will generally occur on the same species in comparable field situations. All North American bodies of water and resident aquatic species and their uses are meant to be taken into account, except for a few that may be too atypical, such as the Great Salt Lake, brine shrimp, and the siscowet subspecies of lake trout, which occurs in Lake Superior and contains up to 67% fat in the fillets [4]. Derivation of criteria specifically for the Great Salt Lake or Lake Superior might have to take brine shrimp and siscowet, respectively, into account.

Numerical aquatic life criteria derived using these National Guidelines are expressed as two numbers, rather than the traditional one number, so that the criteria more accurately reflect toxicological and practical realities. If properly derived and used, the combination of a maximum concentration and a continuous concentration should provide an appropriate degree of protection of aquatic organisms and their uses from acute and chronic toxicity to animals, toxicity to plants, and bioaccumulation by aquatic organisms, without being as restrictive as a one-number criterion would have to be in order to provide the same degree of protection.

Criteria produced by these Guidelines are intended to be useful for developing water quality standards, mixing zone standards, effluent limitations, etc. The development of such standards

and limitations, however, might have to take into account such additional factors as social, legal, economic, and hydrological considerations, the environmental and analytical chemistry of the material, the extrapolation from laboratory data to field situations, and relationships between species for which data are available and species in the body of water of concern. As an intermediate step in the development of standards, it might be desirable to derive site-specific criteria by modification of national criteria to reflect such local conditions as water quality, temperature, or ecologically important species [1, 2, 3]. In addition, with appropriate modifications these National Guidelines can be used to derive criteria for any specific geographical area, body of water (such as the Great Salt Lake), or group of similar bodies of water, if adequate information is available concerning the effects of the material of concern on appropriate species and their uses.

Criteria should attempt to provide a reasonable and adequate amount of protection with only a small possibility of considerable overprotection or underprotection. It is not enough that a national criterion be the best estimate that can be obtained using available data; it is equally important that a criterion be derived only if adequate appropriate data are available to provide reasonable confidence that it is a good estimate. Therefore, these National Guidelines specify certain data that should be available if a numerical criterion is to be derived. If all the required data are not available, usually a criterion should not be derived. On the other hand, the availability of all required data does not ensure that a criterion can be derived.

A common belief is that national criteria are based on "worst case" assumptions and that local considerations will raise, but not lower, criteria. For example, it will usually be assumed that if the concentration of a material in a body of water is lower than the national criterion, no unacceptable effects will occur and no site-specific criterion needs to be derived. If, however, the concentration of a material in a body of water is higher than the national criterion, it will usually be assumed that a site-specific criterion should be derived. In order to prevent the assumption of the "worst case" nature of national criteria from resulting in the underprotection of too many bodies of water, national criteria must be intended to protect all or almost all bodies of water. Thus, if bodies of water and the aquatic communities in them do differ substantially in their sensitivities to a material, national criteria should be at least somewhat overprotective for a majority of the bodies of water. To do otherwise would either (a) require derivation of site-specific criteria even if the site-specific concentration were substantially below the national criterion or (b) cause the "worst case" assumption to result in the underprotection of numerous bodies of water. On the other hand, national criteria are probably underprotective of some bodies of water.

The two factors that will probably cause the most difference between national and site-specific criteria are the species that will be exposed and the characteristics of the water. In order to ensure that national criteria are appropriately protective, the required data for national criteria include some species that are sensitive to many materials and national criteria are specifically based on tests conducted in water relatively low in particulate matter and organic matter. Thus, the two factors that will usually be considered in the derivation of site-specific criteria from national criteria are used to help ensure that national criteria are appropriately protective.

On the other hand, some local conditions might require that site-specific criteria be lower than national criteria. Some untested locally important species might be very sensitive to the material of concern, and local water quality might not reduce the toxicity of the material. In addition,

aquatic organisms in field situations might be stressed by diseases, parasites, predators, other pollutants, contaminated or insufficient food, and fluctuating and extreme conditions of flow, water quality, and temperature. Further, some materials might degrade to more toxic materials, or some important community functions or species interactions might be adversely affected by concentrations lower than those that affect individual species.

Criteria must be used in a manner that is consistent with the way in which they were derived if the intended level of protection is to be provided in the real world. Although derivation of water quality criteria for aquatic life is constrained by the ways toxicity and bioconcentration tests are usually conducted, there are still many different ways that criteria can be derived, expressed, and used. The means used to derive and state criteria should relate, in the best possible way, the kinds of data that are available concerning toxicity and bioconcentration and the ways criteria can be used to protect aquatic organisms and their uses.

The major problem is to determine the best way that the statement of a criterion can bridge the gap between the nearly constant concentrations used in most toxicity and bioconcentration tests and the fluctuating concentrations that usually exist in the real world. A statement of a criterion as a number that is not to be exceeded any time or place is not acceptable because few, if any, people who use criteria would take it literally and few, if any, toxicologists would defend a literal interpretation. Rather than try to reinterpret a criterion that is neither useful nor valid, it is better to develop a more appropriate way of stating criteria.

Although some materials might not exhibit thresholds, many materials probably do. For any threshold material, continuous exposure to any combination of concentrations below the threshold will not cause an unacceptable effect (as defined on pages 1 and 2) on aquatic organisms and their uses, except that the concentration of a required trace nutrient might be too low. However, it is important to note that this is a threshold of unacceptable effect, not a threshold of adverse effect. Some adverse effect, possibly even a small reduction in the survival, growth, or reproduction of a commercially or recreationally important species, will probably occur at, and possibly even below, the threshold. The Criterion Continuous Concentration (CCC) is intended to be a good estimate of this threshold of unacceptable effect. If maintained continuously, any concentration above the CCC is expected to cause an unacceptable effect. On the other hand, the concentration of a pollutant in a body of water can be above the CCC without causing an unacceptable effect if (a) the magnitudes and durations of the excursions above the CCC are appropriately limited and (b) there are compensating periods of time during which the concentration is below the CCC. The higher the concentration is above the CCC, the shorter the period of time it can be tolerated. But it is unimportant whether there is any upper limit on concentrations that can be tolerated instantaneously or even for one minute because concentrations outside mixing zones rarely change substantially in such short periods of time.

An elegant, general approach to the problem of defining conditions (a) and (b) would be to integrate the concentration over time, taking into account uptake and depuration rates, transport within the organism to a critical site, etc. Because such an approach is not currently feasible, an approximate approach is to require that the average concentration not exceed the CCC. The average concentration should probably be calculated as the arithmetic average rather than the geometric mean [5]. If a suitable averaging period is selected, the magnitudes and durations of concentrations above the CCC will be appropriately limited, and suitable compensating periods below the CCC will be required.

In the elegant approach mentioned above, the uptake and depuration rates would determine the effective averaging period, but these rates are likely to vary from species to species for any particular material. Thus the elegant approach might not provide a definitive answer to the problem of selecting an appropriate averaging period. An alternative is to consider that the purpose of the averaging period is to allow the concentration to be above the CCC only if the allowed fluctuating concentrations do not cause more adverse effect than would be caused by a continuous exposure to the CCC. For example, if the CCC caused a 10% reduction in growth of rainbow trout, or a 13% reduction in survival of oysters, or a 7% reduction in reproduction of smallmouth bass, it is the purpose of the averaging period to allow concentrations above the CCC only if the total exposure will not cause any more adverse effect than continuous exposure to the CCC would cause.

Even though only a few tests have compared the effects of a constant concentration with the effects of the same average concentration resulting from a fluctuating concentration, nearly all the available comparisons have shown that substantial fluctuations result in increased adverse effects [5, 6]. Thus if the averaging period is not to allow increased adverse effects, it must not allow substantial fluctuations. Life-cycle tests with species such as mysids and daphnids and early life-stage tests with warmwater fishes usually last for 20 to 30 days. An averaging period that is equal to the length of the test will obviously allow the worst possible fluctuations and would very likely allow increased adverse effects.

An averaging period of four days seems appropriate for use with the CCC for two reasons. First, it is substantially shorter than the 20 to 30 days that is obviously unacceptable. Second, for some species it appears that the results of chronic tests are due to the existence of a sensitive life stage at some time during the test [7], rather than being caused by either long-term stress or long-term accumulation of the test material in the organism. The existence of a sensitive life stage is probably the cause of acute-chronic ratios that are not much greater than 1, and is also possible when the ratio is substantially greater than 1. In addition, some experimentally determined acute-chronic ratios are somewhat less than 1, possibly because prior exposure during the chronic test increased the resistance of the sensitive life stage [8]. A four-day averaging period will probably prevent increased adverse effects on sensitive life stages by limiting the durations and magnitudes of exceedences[*] of the CCC.

The considerations applied to interpretation of the CCC also apply to the CMC. For the CMC the averaging period should again be substantially less than the lengths of the tests it is based on, i.e., substantially less than

48 to 96 hours. One hour is probably an appropriate averaging period because high concentrations of some materials can cause death in one to three hours. Even when organisms do not die within the first hour or so, it is not known how many might have died due to delayed effects of this short of an exposure. Thus it is not appropriate to allow concentrations above the CMC to exist for as long as one hour.

The durations of the averaging periods in national criteria have been made short enough to restrict allowable fluctuations in the concentration of the pollutant in the receiving water and to restrict the length of time that the concentration in the receiving water can be continuously above

[*] Although "exceedence" has not been found in any dictionary, it is used here because it is not appropriate to use "violation" in conjunction with criteria, no other word seems appropriate, and all appropriate phrases are awkward.

a criterion concentrations. The statement of a criterion could specify that the four-day average should never exceed the CCC and that the one-hour average should never exceed the CMC. However, one of the most important uses of criteria is for designing waste treatment facilities. Such facilities are designed based on probabilities and it is not possible to design for a zero probability. Thus, one of the important design parameters is the probability that the four-day average or the one-hour-average will be exceeded, or, in other words, the frequency with which exceedences will be allowed.

The frequency of allowed exceedences should be based on the ability of aquatic ecosystems to recover from the exceedences, which will depend in part on the magnitudes and durations of the exceedences. It is important to realize that high concentrations caused by spills and similar major events are not what is meant by an "exceedence", because spills and other accidents are not part of the design of the normal operation of waste treatment facilities. Rather, exceedences are extreme values in the distribution of ambient concentrations and this distribution is the result of the usual variations in the flows of both the effluent and the receiving water and the usual variations in the concentrations of the material of concern in both the effluent and in the upstream receiving water. Because exceedences are the result of usual variation, most of the exceedences will be small and exceedences as large as a factor of two will be rare. In addition, because these exceedences are due to random variation, they will not be evenly spaced. In fact, because many receiving waters have both one-year and multi-year cycles and many treatment facilities have daily, weekly, and yearly cycles, exceedences will often be grouped, rather than being evenly spaced or randomly distributed. If the flow of the receiving water is usually much greater than the flow of the effluent, normal variation and the flow cycles will result in the ambient concentration usually being below the CCC, occasionally being near the CCC, and rarely being above the CCC. In addition, exceedences that do occur will be grouped. On the other hand, if the flow of the effluent is much greater than the flow of the receiving water, the concentration might be close to the CCC much of the time and rarely above the CCC, with exceedences being randomly distributed.

The abilities of ecosystems to recover differ greatly, and depend on the pollutant, the magnitude and duration of the exceedence, and the physical and biological features of the ecosystem. Documented studies of recoveries are few, but some systems recover from small stresses in six weeks whereas other systems take more than ten years to recover from severe stress [3]. Although most exceedences are expected to be very small, larger exceedences will occur occasionally. Most aquatic ecosystems can probably recover from most exceedences in about three years. Therefore, it does not seem reasonable to purposely design for stress above that caused by the CCC to occur more than once every three years on the average, just as it does not seem reasonable to require that these kinds of stresses only occur once every five or ten years on the average.

If the body of water is not subject to anthropogenic stress other than the exceedences of concern and if exceedences as large as a factor of two are rare, it seems reasonable that most bodies of water could tolerate exceedences once every three years on the average. In situations in which exceedences are grouped, several exceedences might occur in one or two years, but then there will be, for example, 10 to 20 years during which no exceedences will occur and the concentration will be substantially below the CCC most of the time. In situations in which the concentration is often close to the CCC and exceedences are randomly distributed, some adverse effect will occur regularly, and small additional, unacceptable effects will occur about every

third year. The relative long-term ecological consequences of evenly spaced and grouped exceedences are unknown, but because most exceedences will probably be small, the long-term consequences should be about equal over long periods of time.

The above considerations lead to a statement of a criterion in the frequency-intensity-duration format that is often used to describe rain and snow fall and stream flow, e.g., how often, on the average, does more than ten inches of rain fall in a week? The numerical values chosen for frequency (or average recurrence interval), intensity (i.e., concentration), and duration (of averaging period) are those appropriate for national criteria. Whenever adequately justified, a national criterion may be replaced by a site-specific criterion [1], which may include not only site-specific criterion concentrations [2], but also site-specific durations of averaging periods and site-specific frequencies of allowed exceedences [3].

The concentrations, durations, and frequencies specified in criteria are based on biological, ecological, and toxicological data, and are designed to protect aquatic organisms and their uses from unacceptable effects. Use of criteria for designing waste treatment facilities requires selections of an appropriate wasteload allocation model. Dynamic models are preferred for the application of water quality criteria, but a steady-state model might have to be used instead of a dynamic model in some situations. Regardless of the model that is used, the durations of the averaging periods and the frequencies of allowed exceedences must be applied correctly if the intended level of protection is to be provided. For example, in the criterion statement frequency refers to the average frequency, over a long period of time, of rare events (i.e., exceedences). However, in some disciplines, frequency is often thought of in terms of the average frequency, over a long period of time, of the years is which rare events occur, without any consideration of how many rare events occur within each of those eventful years. The distinction between the frequency of events and the frequency of years in important for all those situations in which the rare events, e.g., exceedences, tend to occur in groups within the eventful years. The two ways of calculating frequency produce the same results in situations in which each rare event occurs in a different year because then the frequency of events is the same as the frequency of eventful years.

Because fresh water and salt water have basically different chemical compositions and because freshwater and saltwater (i.e., estuarine and true marine) species rarely inhabit the same water simultaneously, these National Guidelines provide for the derivation of separate criteria for these two kinds of water. For some materials sufficient data might not be available to allow derivation of criteria for one or both kinds of water. Even though absolute toxicities might be different in fresh and salt waters, such relative data as acute-chronic ratios and bioconcentration factors often appear to be similar in the two waters. When data are available to indicate that these ratios and factors are probably similar, they are used interchangeably.

The material for which a criterion is desired is usually defined in terms of a particular chemical compound or ion, or a group of closely related compounds or ions, but it might possibly be defined in terms of an effluent. These National Guidelines might also be useful for deriving criteria for temperature, dissolved oxygen, suspended solids, pH, etc., if the kinds of data on which the Guidelines are based are available.

Because they are meant to be applied only after a decision has been made that a national water quality criterion for aquatic organisms is needed for a material, these National Guidelines do not

address the rationale for making that decision. If the potential for adverse effects on aquatic organisms and their uses is part of the basis for deciding whether an aquatic life criterion is needed for a material, these Guidelines will probably be helpful in the collection and interpretation of relevant data. Such properties as volatility might affect the fate of a material in the aquatic environment and might be important when determining whether a criterion is needed for a material; for example, aquatic life criteria might not be needed for materials that are highly volatile or highly degradable in water. Although such properties can affect how much of the material will get from the point of discharge through any allowed mixing zone to some portion of the ambient water and can also affect the size of the zone of influence in the ambient water, such properties do not affect how much of the material aquatic organisms can tolerate in the zone of influence.

This version of the National Guidelines provides clarifications, additional details, and technical and editorial changes from the previous version [9]. These modifications are the result of comments on the previous version and subsequent drafts [10], experience gained during the U.S. EPA's use of previous versions and drafts, and advances in aquatic toxicology and related fields. Future versions will incorporate new concepts and data as their usefulness is demonstrated. The major technical changes incorporated into this version of the National Guidelines are:

1. The requirement for acute data for freshwater animals has been changed to include more tests with invertebrate species. The taxonomic, functional, and probably the toxicological, diversities among invertebrate species are greater than those among vertebrate species and this should be reflected in the required data.

2. When available, 96-hr EC50s based on the percentage of fish immobilized plus the percentage of fish killed are used instead of 96-hr LC50s for fish; comparable EC50s are used instead of LC50s for other species. Such appropriately defined EC50s better reflect the total severe acute adverse impact of the test material on the test species than do LC50s or narrowly defined EC50s. Acute EC50s that are based on effects that are not severe, such as reduction in shell deposition and reduction in growth, are not used in calculating the Final Acute Value.

3. The Final Acute Value is now defined in terms of Genus Mean Acute Values rather than Species Mean Acute Values. A Genus Mean Acute Value is the geometric mean of all the Species Mean Acute Values available for species in the genus. On the average, species within a genus are toxicologically much more similar than species in different genera, and so the use of Genus Mean Acute Values will prevent data sets from being biased by an overabundance of species in one or a few genera.

4. The Final Acute Value is now calculated using a method [11] that is not subject to the bias and anomalous behavior that the previous method was. The new method is also less influenced by one very low value because it always gives equal weight to the four values that provide the most information about the cumulative probability of 0.05. Although the four values receive the most weight, the other values do have a substantial effect on the Final Acute Value (see examples in Appendix 2).

5. The requirements for using the results of tests with aquatic plants have been made more stringent.

6. Instead of being equal to the Final Acute Value, the Criterion Maximum Concentration is now equal to one-half the Final Acute Value. The Criterion Maximum Concentration is intended to protect 95 percent of a group of diverse genera, unless a commercially or recreationally important species is very sensitive. However, a concentration that would severely harm 50 percent of the fifth percentile or 50 percent of a sensitive important species cannot be considered to be protective of that percentile or that species. Dividing the Final Acute Value by 2 is intended to result in a concentration that will not severely adversely affect too many of the organisms.

7. The lower of the two numbers in the criterion is now called the Criterion Continuous Concentration, rather than the Criterion Average Concentration, to more accurately reflect the nature of the toxicological data on which it is based.

8. The statement of a criterion has been changed (a) to include durations of averaging periods and frequencies of allowed exceedences that are based on what aquatic organisms and their uses can tolerate, and (b) to identify a specific situation in which site-specific criteria [1, 2, 3] are probably desirable.

In addition, Appendix 1 was added to aid in determining whether a species should be considered resident in North America and its taxonomic classification. Appendix 2 explains the calculation of the Final Acute Value.

The amount of guidance in these National Guidelines has been increased, but much of the guidance is necessarily qualitative rather than quantitative; much judgment will usually be required to derive a water quality criterion for aquatic organisms and their uses. In addition, although this version of the National Guidelines attempts to cover all major questions that have arisen during use of previous versions and drafts, it undoubtedly does not cover all situations that might occur in the future. All necessary decisions should be based on a thorough knowledge of aquatic toxicology and an understanding of these Guidelines and should be consistent with the spirit of these Guidelines, i.e., to make best use of the available data to derive the most appropriate criteria. These National Guidelines should be modified whenever sound scientific evidence indicates that a national criterion produced using these Guidelines would probably be substantially overprotective or underprotective of the aquatic organisms and their uses on a national basis. Derivation of numerical national water quality criteria for aquatic organisms and their uses is a complex process and requires knowledge in many areas of aquatic toxicology; any deviation from these Guidelines should be carefully considered to ensure that it is consistent with other parts of these Guidelines.

I. Definition of Material of Concern

A. Each separate chemical that does not ionize substantially in most natural bodies of water should usually be considered a separate material, except possibly for structurally similar organic compounds that only exist in large quantities as commercial mixtures of various compounds and apparently have similar biological, chemical, physical, and toxicological properties.

B. For chemicals that do ionize substantially in most natural bodies of water (e.g., some phenols and organic acids, some salts of phenols and organic acids, and most

inorganic salts and coordination complexes of metals), all forms that would be in chemical equilibrium should usually be considered one material. Each different oxidation state of a metal and each different nonionizable covalently bonded organometallic compound should usually be considered a separate material.

C. The definition of the material should include an operational analytical component. Identification of a material simply, for example, as "sodium" obviously implies "total sodium", but leaves room for doubt. If "total" is meant, it should be explicitly stated. Even "total" has different operational definitions, some of which do not necessarily measure "all that is there" in all samples. Thus, it is also necessary to reference or describe the analytical method that is intended. The operational analytical component should take into account the analytical and environmental chemistry of the material, the desirability of using the same analytical method on samples from laboratory tests, ambient water, and aqueous effluents, and various practical considerations, such as labor and equipment requirements and whether the method would require measurement in the field or would allow measurement after samples are transported to a laboratory.

The primary requirements of the operational analytical component are that it be appropriate for use on samples of receiving water, that it be compatible with the available toxicity and bioaccumulation data without making extrapolations that are too hypothetical, and that it rarely result in underprotection or overprotection of aquatic organisms and their uses. Because an ideal analytical measurement will rarely be available, a compromise measurement will usually have to be used. This compromise measurement must fit with the general approach that if an ambient concentration is lower than the national criterion, unacceptable effects will probably not occur, i.e., the compromise measurement must not err on the side of underprotection when measurements are made on a surface water. Because the chemical and physical properties of an effluent are usually quite different from those of the receiving water, an analytical method that is acceptable for analyzing an effluent might not be appropriate for analyzing a receiving water, and vice versa. If the ambient concentration *calculated* from a measured concentration in an effluent is higher than the national criterion, an additional option is to *measure* the concentration after dilution of the effluent with receiving water to determine if the measured concentration is lowered by such phenomena as complexation or sorption. A further option, of course, is to derive a site-specific criterion [1, 2, 3]. Thus, the criterion should be based on an appropriate analytical measurement, but the criterion is not rendered useless if an ideal measurement either is not available or is not feasible.

NOTE: The analytical chemistry of the material might have to be taken into account when defining the material or when judging the acceptability of some toxicity tests, but a criterion should not be based on the sensitivity of an analytical method. When aquatic organisms are more sensitive than routine analytical methods, the proper solution is to develop better analytical methods, not to underprotect aquatic life.

II. Collection of Data

A. Collect all available data on the material concerning (a) toxicity to, and bioaccumulation by, aquatic animals and plants, (b) FDA action levels [12], and (c) chronic feeding studies and long-term field studies with wildlife species that regularly consume aquatic organisms.

B. All data that are used should be available in typed, dated, and signed hard copy (publication, manuscript, letter, memorandum, etc.) with enough supporting information to indicate that acceptable test procedures were used and that the results are probably reliable. In some cases it may be appropriate to obtain additional written information from the investigator, if possible. Information that is confidential or privileged or otherwise not available for distribution should not be used.

C. Questionable data, whether published or unpublished, should not be used. For example, data should usually be rejected if they are from tests that did not contain a control treatment, tests in which too many organisms in the control treatment died or showed signs of stress or disease, and tests in which distilled or deionized water was used as the dilution water without addition of appropriate salts.

D. Data on technical grade materials may be used if appropriate, but data on formulated mixtures and emulsifiable concentrates of the material of concern should not be used.

E. For some highly volatile, hydrolyzable, or degradable materials it is probably appropriate to use only results of flow-through tests in which the concentrations of test material in the test solutions were measured often enough using acceptable analytical methods.

F. Data should be rejected if they were obtained using:

1. Brine shrimp, because they usually only occur naturally in water with salinity greater than 35 g/kg.

2. Species that do not have reproducing wild populations in North America (see Appendix 1).

3. Organisms that were previously exposed to substantial concentrations of the test material or other contaminants.

G. Questionable data, data on formulated mixtures and emulsifiable concentrates, and data obtained with non-resident species in North America or previously exposed organisms may be used to provide auxiliary information but should not be used in the derivation of criteria.

III. Required data

A. Certain data should be available to help ensure that each of the four major kinds of possible adverse effects receives adequate consideration. Results of acute and chronic toxicity tests with representative species of aquatic animals are necessary so that data available for tested species can be considered a useful indication of the sensitivities of

appropriate untested species. Fewer data concerning toxicity to aquatic plants are required because procedures for conducting tests with plants and interpreting the results of such tests are not as well developed. Data concerning bioaccumulation by aquatic organisms are only required if relevant data are available concerning the significance of residues in aquatic organisms.

B. To derive a criterion for freshwater aquatic organisms and their uses, the following should be available:

1. Results of acceptable acute tests (see Section IV) with at least one species of freshwater animal in at least eight different families such that all of the following are included:

    a. the family Salmonidae in the class Osteichthyes

    b. a second family in the class Osteichthyes, preferably a commercially or recreationally important warmwater species (e.g., bluegill, channel catfish, etc.)

    c. a third family in the phylum Chordata (may be in the class Osteichthyes or may be an amphibian, etc.)

    d. a planktonic crustacean (e.g., cladoceran, copepod, etc.)

    e. a benthic crustacean (e.g., ostracod, isopod, amphipod, crayfish, etc.)

    f. an insect (e.g., mayfly, dragonfly, damselfly, stonefly, caddisfly, mosquito, midge, etc.)

    g. a family in a phylum other than Arthropoda or Chordata (e.g., Rotifera, Annelida, Mollusca, etc.)

    h. a family in any order of insect or any phylum not already represented.

2. Acute-chronic ratios (see Section VI) with species of aquatic animals in at least three different families provided that one of the three species:

    - at least one is a fish
    - at least one is an invertebrate
    - at least one is an acutely sensitive freshwater species (the other two may be saltwater species).

3. Results of at least one acceptable test with a freshwater alga or vascular plant (see Section VIII). If plants are among the aquatic organisms that are most sensitive to the material, results of a test with a plant in another phylum (division) should also be available.

4. At least one acceptable bioconcentration factor determined with an appropriate freshwater species, if a maximum permissible tissue concentration is available (see Section IX).

C. To derive a criterion for saltwater aquatic organisms and their uses, the following should be available:

1. Results of acceptable acute tests (see Section IV) with at least one species of saltwater animal in at least eight different families such that all of the following are included:

    a. two families in the phylum Chordata

    b. a family in a phylum other than Arthropoda or Chordata

    c. either the Mysidae or Penaeidae family

    d. three other families not in the phylum Chordata (may include Mysidae or Penaeidae, whichever was not used above)

    e. any other family.

2. Acute-chronic ratios (see Section VI) with species of aquatic animals in at least three different families provided that of the three species:

    - at least one is a fish
    - at least one is an invertebrate
    - at least one is an acutely sensitive saltwater species (the other two may be freshwater species).

3. Results of at least one acceptable test with a saltwater alga or vascular plant (see Section VIII). If plants are among the aquatic organisms most sensitive to the material, results of a test with a plant in another phylum (division) should also be available.

4. At least one acceptable bioconcentration factor determined with an appropriate saltwater species, if a maximum permissible tissue concentration is available (see Section IX).

D. If all the required data are available, a numerical criterion can usually be derived, except in special cases. For example, derivation of a criterion might not be possible if the available acute-chronic ratios vary by more than a factor of ten with no apparent pattern. Also, if a criterion is to be related to a water quality characteristic (see Sections V and VII), more data will be necessary.

Similarly, if all required data are not available, a numerical criterion should not be derived except in special cases. For example, even if not enough acute and chronic data are available, it might be possible to derive a criterion if the available data

clearly indicate that the Final Residue Value should be much lower than either the Final Chronic Value or Final Plant Value.

E. Confidence in a criterion usually increases as the amount of available pertinent data increases. Thus, additional data are usually desirable.

IV. Final Acute Value

A. Appropriate measures of the acute (short-term) toxicity of the material to a variety of species of aquatic animals are used to calculate the Final Acute Value. The Final Acute Value is an estimate of the concentration of the material corresponding to a cumulative probability of 0.05 in the acute toxicity values for the genera with which acceptable acute tests have been conducted on the material. However, in some cases, if the Species Mean Acute Value of a commercially or recreationally important species is lower than the calculated Final Acute Value, then that Species Mean Acute Value replaces the calculated Final Acute Value in order to provide protection for that important species.

B. Acute toxicity tests should have been conducted using acceptable procedures [13].

C. Except for test with saltwater annelids and mysids, results of acute tests during which the test organisms were fed should not be used, unless data indicate that the food did not affect the toxicity of the test material.

D. Results of acute tests conducted in unusual dilution water, e.g., dilution water in which total organic carbon or particulate matter exceeded 5 mg/L, should not be used, unless a relationship is developed between acute toxicity and organic carbon or particulate matter or unless data show that organic carbon, particulate matter, etc., do not affect toxicity.

E. Acute values should be based on endpoints which reflect the total severe acute adverse impact of the test material on the organisms used in the test. Therefore, only the following kinds of data on acute toxicity to aquatic animals should be used:

1. Tests with daphnids and other cladocerans should be started with organisms less than 24 hours old and tests with midges should be started with second- or third-instar larvae. The result should be the 48-hr EC50 based on percentage of organisms immobilized plus percentage of organisms killed. If such an EC50 is not available from a test, the 48-hr LC50 should be used in place of the desired 48-hr EC50. An EC50 or LC50 of longer than 48 hr can be used as long as the animals were not fed and the control animals were acceptable at the end of the test.

2. The result of a test with embryos and larvae of barnacles, bivalve molluscs (clams, mussels, oysters, and scallops), sea urchins, lobsters, crabs, shrimp, and abalones, should be the 96-hr EC50 based on the percentage of organisms with incompletely developed shells plus the percentage of organisms killed. If such an EC50 is not available from a test, the lower of the 96-hr EC50 based on the percentage of organisms with incompletely developed shells and the 96-hr LC50

should be used in place of the desired 96-hr EC50. If the duration of the test was between 48 and 96 hr, the EC50 or LC50 at the end of the test should be used.

3. The acute values from tests with all other freshwater and saltwater animal species and older life stages of barnacles, bivalve molluscs, sea urchins, lobsters, crabs, shrimps, and abalones should be the 96-hr EC50 based on the percentage of organisms exhibiting loss of equilibrium plus the percentage of organisms immobilized plus the percentage of organisms killed. If such an EC50 is not available from a test, the 96-hr LC50 should be used in place of the desired 96-hr EC50.

4. Tests with single-celled organisms are not considered acute tests, even if the duration was 96 hours or less.

5. If the tests were conducted properly, acute values reported as "greater than" values and those which are above the solubility of the test material should be used, because rejection of such acute values would unnecessarily lower the Final Acute Value by eliminating acute values for resistant species.

F. If the acute toxicity of the material to aquatic animals apparently has been shown to be related to a water quality characteristic such as hardness or particulate matter for freshwater animals or salinity or particulate matter for saltwater animals, a Final Acute Equation should be derived based on that water quality characteristic. Go to Section V.

G. If the available data indicate that one or more life stages are at least a factor of two more resistant than one or more other life stages of the same species, the data for the more resistant life stages should not be used in the calculation of the Species Mean Acute Value because a species can only be considered protected from acute toxicity if all life stages are protected.

H. The agreement of the data within and between species should be considered. Acute values that appear to be questionable in comparison with other acute and chronic data for the same species and for other species in the same genus probably should not be used in calculation of a Species Mean Acute Value. For example, if the acute values available for a species or genus differ by more than a factor of 10, some or all of the values probably should not be used in calculations.

I. For each species for which at least one acute value is available, the Species Mean Acute Value (SMAV) should be calculated as the geometric mean of the results of all flow-through tests in which the concentrations of test material were measured. For a species for which no such result is available, the SMAV should be calculated as the geometric mean of all available acute values, i.e., results of flow-through tests in which the concentrations were not measured and results of static and renewal tests based on initial concentrations (nominal concentrations are acceptable for most test materials if measured concentrations are not available) of test material.

NOTE: Data reported by original investigators should not be rounded off. Results of all intermediate calculations should be rounded [14] to four significant digits.

NOTE: The geometric mean of N numbers is the Nth root of the product of the N numbers. Alternatively, the geometric mean can be calculated by adding the logarithms of the N numbers, dividing the sum by N, and taking the antilog of the quotient. The geometric mean of two numbers is the square root of the product of the two numbers, and the geometric mean of one number is that number. Either natural (base e) or common (base 10) logarithms can be used to calculate geometric means as long as they are used consistently within each set of data, i.e., the antilog used must match the logarithm used.

NOTE: Geometric means, rather than arithmetic means, are used here because the distributions of sensitivities of individual organisms in toxicity tests on most materials and the distributions of sensitivities of species within a genus are more likely to be lognormal than normal. Similarly, geometric means are used for acute-chronic ratios and bioconcentration factors because quotients are likely to be closer to lognormal than normal distributions. In addition, division of the geometric mean of a set of numerators by the geometric mean of the set of corresponding denominators will result in the geometric mean of the set of corresponding quotients.

J. For each genus for which one or more SMAVs are available, the Genus Mean Acute Value (GMAV) should be calculated as the geometric mean of the SMAVs available for the genus.

K. Order the GMAVs from high to low.

L. Assign ranks, R, to the GMAVs from "1" for the lowest to "N" for the highest. If two or more GMAVs are identical, arbitrarily assign them successive ranks.

M. Calculate the cumulative probability, P, for each GMAV as R/(N+1).

N. Select the four GMAVs which have cumulative probabilities closest to 0.05 (if there are less than 59 GMAVs, these will always be the four lowest GMAVs).

O. Using the selected GMAVs and Ps, calculate

$$S^2 = \frac{\sum((\ln GMAV)^2) - ((\sum \ln GMAV))^2 / 4}{\sum (F) - ((\sum(\sqrt{P}))^2 / 4)}$$

$$L = (\sum (\ln GMAV) - S(\sum(\sqrt{P}))) / 4$$

$$A = S(\sqrt{0.05}) + L$$

$$FAV = e^A$$

(See [11] for development of the calculation procedure and Appendix 2 for an example calculations and computer program.)

NOTE: Natural logarithms (logarithms to base e, denoted as ln) are used herein merely because they are easier to use on some hand calculators and computers than common (base 10) logarithms. Consistent use of either will produce the same result.

P. If for a commercially or recreationally important species the geometric mean of the acute values from ~~the~~ flow-through tests in which the concentrations of test material were measured is lower than the calculated Final Acute Value, then that geometric mean should be used as the Final Acute Value instead of the calculated Final Acute Value.

Q. Go to Section VI.

V. Final Acute Equation

A. When enough data are available to show that acute toxicity to two or more species is similarly related to a water quality characteristic, the relationship should be taken into account as described in Sections B-G below or using analysis of covariance [15, 16]. The two methods are equivalent and produce identical results. The manual method described below provides an understanding of this application of covariance analysis, but computerized versions of covariance analysis are much more convenient for analyzing large data sets. If two or more factors affect toxicity, multiple regression analysis should be used.

B. For each species for which comparable acute toxicity values are available at two or more different values of the water quality characteristic, perform a least squares regression of the acute toxicity values on the corresponding values of the water quality characteristic to obtain the slope and its 95% confidence limits for each species.

NOTE: Because the best documented relationship is that between hardness and acute toxicity of metals in fresh water and a log-log relationship fits these data, geometric means and natural logarithms of both toxicity and water quality are used in the rest of this section. For relationships based on other water quality characteristics, such as pH, temperature, or salinity, no transformation or a different transformation might fit the data better, and appropriate changes will be necessary throughout this section.

C. Decide whether the data for each species is useful, taking into account the range and number of the tested values of the water quality characteristic and the degree of agreement within and between species. For example, a slope based on six data points might be of limited value if it is based only on data for a very narrow range of values of the water quality characteristic. A slope based on only two data points, however, might be useful if it is consistent with other information and if the two points cover a broad enough range of the water quality characteristic. In addition, acute values that appear to be questionable in comparison with other acute and chronic data available for the same species and for other species in the same genus probably should not be used. For example, if after adjustment for the water quality characteristic, the acute values available for a species or genus differ by more than a factor of 10, rejection of some or all of the values is probably appropriate. If useful slopes are not available for at least one fish and one invertebrate or if the available slopes are too dissimilar or if too few data are available to adequately define the relationship between acute toxicity and the water quality characteristic, return to Section IV.G., using the results of tests

conducted under conditions and in waters similar to those commonly used for toxicity tests with the species.

D. Individually for each species calculate the geometric mean of the available acute values and then divide each of the acute values for a species by the mean for the species. This normalizes the acute values so that the geometric mean of the normalized values for each species individually and for any combination of species is 1.0.

E. Similarly normalize the values of the water quality characteristic for each species individually.

F. Individually for each species perform a least squares regression of the normalized acute toxicity values on the corresponding normalized values of the water quality characteristic. The resulting slopes and 95% confidence limits will be identical to those obtained in Section B above. Now, however, if the data are actually plotted, the line of best fit for each individual species will go through the point 1,1 in the center of the graph.

G. Treat all the normalized data as if they were all for the same species and perform a least squares regression of all the normalized acute values on the corresponding normalized values of the water quality characteristic to obtain the pooled acute slope, V, and its 95% confidence limits. If all the normalized data are actually plotted, the line of best fit will go through the point 1,1 in the center of the graph.

H. For each species calculate the geometric mean, W, of the acute toxicity values and the geometric mean, X, of the values of the water quality characteristic. (These were calculated in steps D and E above.)

I. For each species calculate the logarithm, Y, of the SMAV at a selected value, Z, of the water quality characteristic using the equation:

$$Y = \ln W - V(\ln X - \ln Z).$$

J. For each species calculate the SMAV at Z using the equation: $SMAV = e^{Y}$.

NOTE: Alternatively, the SMAVs at Z can be obtained by skipping step H above, using the equations in steps I and J to adjust each acute value individually to Z, and then calculating the geometric mean of the adjusted values for each species individually. This alternative procedure allows an examination of the range of the adjusted acute values for each species.

K. Obtain the Final Acute Value at Z by using the procedure described in Section IV.J-O.

L. If the SMAV at Z of a commercially or recreationally important species is lower than the calculated Final Acute Value at Z, then that SMAV should be used as the Final Acute Value at Z instead of the calculated Final Acute Value.

M. The Final Acute Equation is written as: Final Acute Value = $e^{(V[\ln(\text{water quality characteristic})] + \ln A - V[\ln Z])}$, where V = pooled acute slope and A = Final Acute Value at Z. Because

V, A, and Z are known, the Final Acute Value can be calculated for any selected value of the water quality characteristic.

VI. Final Chronic Value

A. Depending on the data that are available concerning chronic toxicity to aquatic animals, the Final Chronic Value might be calculated in the same manner as the Final Acute Value or by dividing the Final Acute Value by the Final Acute-Chronic Ratio. In some cases it may not be possible to calculate a Final Chronic Value.

NOTE: As the name implies, the acute-chronic ration (ARC) is a way of relating acute and chronic toxicities. The acute-chronic ratio is basically the inverse of the application factor, but this new name is better because it is more descriptive and should help prevent confusion between "application factors" and "safety factors". Acute-chronic ratios and application factors are ways of relating the acute and chronic toxicities of a material to aquatic organisms. Safety factors are used to provide an extra margin of safety beyond the known or estimated sensitivities of aquatic organisms. Another advantage of the acute-chronic ratio is that it will usually be greater than one; this should avoid the confusion as to whether a large application factor is one that is close to unity or one that has a denominator that is much greater than the numerator.

B. Chronic values should be based on results of flow-through (except renewal is acceptable for daphnids) chronic tests in which the concentrations of test material in the test solutions were properly measured at appropriate times during the test.

C. Results of chronic tests in which survival, growth, or reproduction in the control treatment was unacceptably low should not be used. The limits of acceptability will depend on the species.

D. Results of chronic tests conducted in unusual dilution water, e.g., dilution water in which total organic carbon or particulate matter exceeded 5 mg/L, should not be used, unless a relationship is developed between chronic toxicity and organic carbon or particulate matter or unless data show that organic carbon, particulate matter, etc., do not affect toxicity.

E. Chronic values should be based on endpoints and lengths of exposure appropriate to the species. Therefore, only results of the following kinds of chronic toxicity tests should be used:

1. Life-cycle toxicity tests consisting of exposures of each of two or more groups of individuals of a species to a different concentration of the test material throughout a life cycle. To ensure that all life stages and life processes are exposed, tests with fish should begin with embryos or newly hatched young less than 48 hours old, continue through maturation and reproduction, and should end not less than 24 days (90 days for salmonids) after the hatching of the next generation. Tests with daphnids should begin with young less than 24 hours old and last for not less than 21 days. Tests with mysids should begin with young less than 24 hours old and continue until 7 days past the median time of first brood release in the

controls. For fish, data should be obtained and analyzed on survival and growth of adults and young, maturation of males and females, eggs spawned per female, embryo viability (salmonids only), and hatchability. For daphnids, data should be obtained and analyzed on survival and young per female. For mysids, data should be obtained and analyzed on survival, growth, and young per female.

2. Partial life-cycle toxicity tests consisting of exposures of each of two or more groups of individuals of a species of fish to a different concentration of the test material through most portions of a life cycle. Partial life-cycle tests are allowed with fish species that require more than a year to reach sexual maturity, so that all major life stages can be exposed to the test material in less than 15 months. Exposure to the test material should begin with immature juveniles at least 2 months prior to active gonad development, continue through maturation and reproduction, and end not less than 24 days (90 days for salmonids) after the hatching of the next generation. Data should be obtained and analyzed on survival and growth of adults and young, maturation of males and females, eggs spawned per female, embryo viability (salmonids only), and hatchability.

3. Early life-stage toxicity tests consisting of 28- to 32-day (60 days post hatch for salmonids) exposures of the early life stages of a species of fish from shortly after fertilization through embryonic, larval, and early juvenile development. Data should be obtained and analyzed on survival and growth.

   NOTE: Results of an early life-stage test are used as predictions of results of life-cycle and partial life-cycle tests with the same species. Therefore, when results of a life-cycle or partial life-cycle test are available, results of an early life-stage test with the same species should not be used. Also, results of early life-stage tests in which the incidence of mortalities or abnormalities increased substantially near the end of the test should not be used because results of such tests are possibly not good predictions of the results of comparable life-cycle or partial life-cycle tests.

F. A chronic value may be obtained by calculating the geometric mean of the lower and upper chronic limits from a chronic test or by analyzing chronic data using regression analysis. A lower chronic limit is the highest tested concentration (a) in an acceptable chronic test, (b) which did not cause an unacceptable amount of adverse effect on any of the specified biological measurements, and (c) below which no tested concentration caused an unacceptable effect. An upper chronic limit is the lowest tested concentration (a) in an acceptable chronic test, (b) which did cause an unacceptable amount of adverse effect on one or more of the specified biological measurements, and (c) above which all tested concentrations also caused such an effect.

   NOTE: Because various authors have used a variety of terms and definitions to interpret and report results of chronic tests, reported results should be reviewed carefully. The amount of effect that is considered unacceptable is often based on a statistical hypothesis test, but might also be defined in terms of a specified percent reduction from the controls. A small percent reduction (e.g., 3%) might be

considered acceptable even if it is statistically significantly different from the control, whereas a large percent reduction (e.g., 30%) might be considered unacceptable even if it is not statistically significant.

G. If the chronic toxicity of the material to aquatic animals apparently has been shown to be related to a water quality characteristic such as hardness or particulate matter for freshwater animals or salinity or particulate matter for saltwater animals, a Final Chronic Equation should be derived based on that water quality characteristic. Go to Section VII.

H. If chronic values are available for species in eight families as described in Sections III.B.1 or III.C.1, a Species Mean Chronic Value (SMCV) should be calculated for each species for which at least one chronic value is available by calculating the geometric mean of all chronic values available for the species, and appropriate Genus Mean Chronic Values should be calculated. The Final Chronic Value should then be obtained using the procedure described in Section IV.J-O. Then go to Section VI.M.

I. For each chronic value for which at least one corresponding appropriate acute value is available, calculate an acute-chronic ratio, using for the numerator the geometric mean of the results of all acceptable flow-through (except static is acceptable for daphnids) acute tests in the same dilution water and in which the concentrations were measured. For fish, the acute test(s) should have been conducted with juveniles. The acute test(s) should have been part of the same study as the chronic test. If acute tests were not conducted as part of the same study, acute tests conducted in the same laboratory and dilution water, but in a different study, may be used. If no such acute tests are available, results of acute tests conducted in the same dilution water in a different laboratory may be used. If no such acute tests are available, an acute-chronic ratio should not be calculated.

J. For each species, calculate the species mean acute-chronic ratio as the geometric mean of all acute-chronic ratios available for that species.

K. For some materials the acute-chronic ratio seems to be the same for all species, but for other materials the ratio seems to increase or decrease as the Species Mean Acute Value (SMAV) increases. Thus the Final Acute-Chronic Ratio can be obtained in four ways, depending on the data available:

1. If the species mean acute-chronic ratio~~s~~ seems to increase or decrease as the SMAV increases, the Final Acute-Chronic Ratio should be calculated as the geometric mean of the acute-chronic ratios for species whose SMAVs are close to the Final Acute Value.

2. If no major trend is apparent and the acute-chronic ratios for a number of species are within a factor of ten, the Final Acute-Chronic Ratio should be calculated as the geometric mean of all the species mean acute-chronic ratios available for both freshwater and saltwater species.

3. For acute tests conducted on metals and possibly other substances with embryos and larvae of barnacles, bivalve molluscs, sea urchins, lobsters,

crabs, shrimp, and abalones (see Section IV.E.2), it is probably appropriate to assume that the acute-chronic ratio is 2. Chronic tests are very difficult to conduct with most such species, but it is likely that the sensitivities of embryos and larvae would determine the results of life-cycle tests. Thus, if the lowest available SMAVs were determined with embryos and larvae of such species, the Final Acute-Chronic Ratio should probably be assumed to be 2, so that the Final Chronic Value is equal to the Criterion Maximum Concentration (see Section XI.B).

4. If the most appropriate species mean acute-chronic ratios are less than 2.0, and especially if they are less than 1.0, acclimation has probably occurred during the chronic test. Because continuous exposure and acclimation cannot be assured to provide adequate protection in field situations, the Final Acute-Chronic Ratio should be assumed to be 2, so that the Final Chronic Value is equal to the Criterion Maximum Concentration (see Section XI.B).

If the available species mean acute-chronic ratios do not fit one of these cases, a Final Acute-Chronic Ratio probably cannot be obtained, and a Final Chronic Value probably cannot be calculated.

L. Calculate the Final Chronic Value by dividing the Final Acute Value by the Final Acute-Chronic Ratio. If there was a Final Acute Equation rather than a Final Acute Value, see also Section VII.A.

M. If the Species Mean Chronic Value of a commercially or recreationally important species is lower than the calculated Final Chronic Value, then that Species Mean Chronic Value should be used as the Final Chronic Value instead of the calculated Final Chronic Value.

N. Go to Section VIII.

VII. Final Chronic Equation

A. A Final Chronic Equation can be derived in two ways. The procedure described here in Section A will result in the chronic slope being the same as the acute slope. The procedure described in Sections B-N will usually result in the chronic slope being different from the actual slope.

1. If acute-chronic ratios are available for enough species at enough values of the water quality characteristic to indicate that the acute-chronic ratio is probably the same for all species and is probably independent of the water quality characteristic, calculate the Final Acute-Chronic Ratio as the geometric mean of the available species mean acute-chronic ratios.

2. Calculate the Final Chronic Value at the selected value Z of the water quality characteristic by dividing the Final Acute Value at Z (see Section V.M.) by the Final Acute-Chronic Ratio.

3. Use V = pooled acute slope (see section V.M.) as L = pooled chronic slope.

4. Go to Section VII.M.

B. When enough data are available to show that chronic toxicity to at least one species is related to a water quality characteristic, the relationship should be taken into account as described in Sections B-G below or using analysis of covariance [15, 16]. The two methods are equivalent and produce identical results. The manual method described below provides an understanding of this application of covariance analysis, but computerized versions of covariance analysis are much more convenient for analyzing large data sets. If two more factors affect toxicity, multiple regression analysis should be used.

C. For each species for which comparable chronic toxicity values are available at two or more different values of the water quality characteristic, perform a least squares regression of the chronic toxicity values on the corresponding values of the water quality characteristic to obtain the slope and its 95% confidence limits for each species.

NOTE: Because the best documented relationship is that between hardness and acute toxicity of metals in fresh water and a log-log relationship fits these data, geometric means and natural logarithms of both toxicity and water quality are used in the rest of this section. For relationships based on other water quality characteristics, such as pH, temperature, or salinity, no transformation or a different transformation might fit the data better, and appropriate changes will be necessary throughout this section. It is probably preferable, but not necessary, to use the same transformation that was used with the acute values in Section V.

D. Decide whether the data for each species is useful, taking into account the range and number of the tested values of the water quality characteristic and the degree of agreement within and between species. For example, a slope based on six data points might be of limited value if it is based only on data for a very narrow range of values of the water quality characteristic. A slope based on only two data points, however, might be useful if it is consistent with other information and if the two points cover a broad enough range of the water quality characteristic. In addition, chronic values that appear to be questionable in comparison with other acute and chronic data available for the same species and for other species in the same genus probably should not be used. For example, if after adjustment for the water quality characteristic, the chronic values available for a species or genus differ by more than a factor of 10, rejection of some or all of the values is probably appropriate. If a useful chronic slope is not available for at least one species or if the available slopes are too dissimilar or if too few data are available to adequately define the relationship between chronic toxicity and the water quality characteristic, it might be appropriate to assume that the chronic slope is the same as the acute slope, which is equivalent to assuming that the acute-chronic ratio is independent of the water quality characteristic. Alternatively, return to Section VI.H, using the results of tests

conducted under conditions and in waters similar to those commonly used for toxicity tests with the species.

E. Individually for each species calculate the geometric mean of the available chronic values and then divide each chronic value for a species by the mean for the species. This normalizes the chronic values so that the geometric mean of the normalized values for each species individually and for any combination of species is 1.0.

F. Similarly normalize the values of the water quality characteristic for each species individually.

G. Individually for each species perform a least squares regression of the normalized chronic toxicity values on the corresponding normalized values of the water quality characteristic. The resulting slopes and the 95% confidence limits will be identical to those obtained in Section B above. Now, however, if the data are actually plotted, the line of best fit for each individual species will go through the point 1,1 in the center of the graph.

H. Treat all the normalized data as if they were all for the same species and perform a least squares regression of all the normalized chronic values on the corresponding normalized values of the water quality characteristic to obtain the pooled chronic slope, L, and its 95% confidence limits. If all the normalized data are actually plotted, the line of best fit will go through the point 1,1 in the center of the graph.

I. For each species calculate the geometric mean, M, of the toxicity values and the geometric mean, P, of the values of the water quality characteristic. (These were calculated in steps E and F above.)

J. For each species calculated the logarithm, Q, of the Species Mean Chronic Value at a selected value, Z, of the water quality characteristic using the equation: $Q = \ln M - L(\ln P - \ln Z)$.

NOTE: Although it is not necessary, it will usually be best to use the same value of the water quality characteristic here as was used in Section V.I.

K. For each species calculate a Species Mean Chronic Value at Z using the equation: $SMCV = e^{Q}$.

NOTE: Alternatively, the Species Mean Chronic Values at Z can be obtained by skipping step J above, using the equations in steps J and K to adjust each acute value individually to Z and then calculating the geometric means of the adjusted values for each species individually. This alternative procedure allows an examination of the range of the adjusted chronic values for each species.

L. Obtain the Final Chronic Value at Z by using the procedure described in Section IV.J-O.

M. If the Species Mean Chronic Value at Z of a commercially or recreationally important species is lower than the calculated Final Chronic Value at Z, then that Species Mean

N. The Final Chronic Equation is written as: Final Chronic Value = $e^{(L[\ln(\text{water quality characteristic})] + \ln S - L[\ln Z])}$, where L = pooled chronic slope and S = Final Chronic Value at Z. Because L, S and Z are known, the Final Chronic Value can be calculated for any selected value of the water quality characteristic.

VIII. Final Plant Value

A. Appropriate measures of the toxicity of the material to aquatic plants are used to compare the relative sensitivities of aquatic plants and animals. Although procedures for conducting and interpreting the results of toxicity tests with plants are not well developed, results of tests with plants usually indicate that criteria which adequately protect aquatic animals and their uses will probably also protect aquatic plants and their uses.

B. A plant value is the result of a 96-hr test conducted with an alga or a chronic test conducted with an aquatic vascular plant.

NOTE: A test of the toxicity of a metal to a plant usually should not be used if the medium contained an excessive amount of a complexing agent, such as EDTA, that might affect the toxicity of the metal. Concentrations of EDTA above about 200 µg/L should probably be considered excessive.

C. The Final Plant Value should be obtained by selecting the lowest result from a test with an important aquatic plant species in which the concentrations of test material were measured and the endpoint was biologically important.

IX. Final Residue Value

A. The Final Residue Value is intended to (a) prevent concentrations in commercially or recreationally important aquatic species from affecting marketability because of exceedance of applicable FDA action levels and (b) protect wildlife, including fishes and birds, that consume aquatic organisms from demonstrated unacceptable effects. The Final Residue Value is the lowest of the residue values that are obtained by dividing maximum permissible tissue concentrations by appropriate bioconcentration or bioaccumulation factors. A maximum permissible tissue concentration is either (a) an FDA action level [12] for fish oil or for the edible portion of fish or shellfish, or (b) a maximum acceptable dietary intake based on observations on survival, growth, or reproduction in a chronic wildlife feeding study or a long-term wildlife field study. If no maximum permissible tissue concentration is available, go to Section X because no Final Residue Value can be derived.

B. Bioconcentration factors (BCFs) and bioaccumulation factors (BAFs) are quotients of the concentration of a material in one or more tissues of an aquatic organism divided by the average concentration in the solution in which the organism had been living. A BCF is intended to account only for net uptake directly from water, and thus almost

has to be measured in a laboratory test. Some uptake during the bioconcentration test might not be directly from water if the food sorbs some of the test material before it is eaten by the test organisms. A BAF is intended to account for the net uptake from both food and water in a real-world situation. A BAF almost has to be measured in a field situation in which predators accumulate the material directly from water and by consuming prey that itself could have accumulated the material from both food and water. The BCF and BAF are probably similar for a material with a low BCF, but the BAF is probably higher than the BCF for materials with high BCFs. Although BCFs are not too difficult to determine, very few BAFs have been measured acceptably because it is necessary to make enough measurements of the concentration of the material in water to show that it was reasonably constant for a long enough period of time over the range of territory inhabited by the organisms. Because so few acceptable BAFs are available, only BCFs will be discussed further. However, if an acceptable BAF is available for a material, it should be used instead of any available BCFs.

C. If a maximum permissible tissue concentration is available for a substance (e.g., parent material, parent material plus metabolites, etc.), the tissue concentration used in the calculation of the BCF should be for the same substance. Otherwise~~,~~ the tissue concentration used in the calculation of the BCF should be that of the material and its metabolites which are structurally similar and are not much more soluble in water than the parent material.

D.

1. A BCF should be used only if the test was flow-through, the BCF was calculated based on measured concentrations of the test material in tissue and in the test solution, and the exposure continued at least until either apparent steady-state or 28 days was reached. Steady-state is reached when the BCF does not change significantly over a period of time, such as two days or 16 percent of the length of the exposure, whichever is longer. The BCF used from a test should be the highest of (a) the apparent steady-state BCF, if apparent steady-state was reached, (b) the highest BCF obtained, if apparent steady-state was not reached, and (c) the projected steady-state BCF, if calculated.

2. Whenever a BCF is determined for a lipophilic material, the percent lipids should also be determined in the tissue(s) for which the BCF was calculated.

3. A BCF obtained from an exposure that adversely affected the test organisms may be used only if it is similar to a BCF obtained with unaffected organisms of the same species at lower concentrations that did not cause adverse effects.

4. Because maximum permissible tissue concentrations are almost never based on dry weights, a BCF calculated using dry tissue weights must be converted to a wet tissue weight basis. If no conversion factor is reported with the BCF, multiply the dry weight BCF by 0.1 for plankton and by 0.2 for individual species of fishes and invertebrates [17].

5. If more than one acceptable BCF is available for a species, the geometric mean of the available values should be used, except that if the BCFs are from different lengths of exposure and the BCF increases with length of exposure, the BCF for the longest exposure should be used.

E. If enough pertinent data exist, several residue values can be calculated by dividing maximum permissible tissue concentrations by appropriate BCFs:

1. For each available maximum acceptable dietary intake derived from a chronic feeding study or a long-term field study with wildlife, including birds and aquatic organisms, the appropriate BCF is based on the whole body of aquatic species which constitute or represent a major portion of the diet of the tested wildlife species.

2. For an FDA action level for fish or shellfish, the appropriate BCF is the highest geometric mean species BCF for the edible portion (muscle for decapods, muscle with or without skin for fishes, adductor muscle for scallops, and total soft tissue for other bivalve molluscs) of a consumed species. The highest species BCF is used because FDA action levels are applied on a species-by-species basis.

F. For lipophilic materials, it might be possible to calculate additional residue values. Because the steady-state BCF for a lipophilic material seems to be proportional to percent lipids from one tissue to another and from one species to another [18, 19, 20], extrapolations can be made from tested tissues or species to untested tissues or species on the basis of percent lipids.

1. For each BCF for which the percent lipids is known for the same tissue for which the BCF was measured, normalize the BCF to a one percent lipid basis by dividing the BCF by the percent lipids. This adjustment to a one percent lipid basis is intended to make all the measured BCFs for a material comparable regardless of the species or tissue with which the BCF was measured.

2. Calculate the geometric mean normalized BCF. Data for both saltwater and freshwater species should be used to determine the mean normalized BCF, unless the data show that the normalized BCFs are probably not similar.

3. Calculate all possible residue values by dividing the available maximum permissible tissue concentrations by the mean normalized BCF and by the percent lipids values appropriate to the maximum permissible tissue concentrations, i.e.,

$$\text{Residue Value} = \frac{(\text{maximum permissible tissue concentration})}{(\text{mean normalized BCF})\,(\text{appropriate percent lipids})}$$

a. For an FDA action level for fish oil, the appropriate percent lipids value is 100.

b. For an FDA action level for fish, the appropriate percent lipids value is 11 for freshwater criteria and 10 for saltwater criteria because FDA action levels are applied on a species-by-species basis to commonly consumed species. The highest lipid contents in the edible portions of important consumed species are about 11 percent for both the freshwater chinook salmon and lake trout and about 10 percent for the saltwater Atlantic herring [21].

c. For a maximum acceptable dietary intake derived from a chronic feeding study or a long-term field study with wildlife, the appropriate percent lipids is that of an aquatic species or group of aquatic species which constitute a major portion of the diet of the wildlife species.

G. The Final Residue Value is obtained by selecting the lowest of the available residue values.

NOTE: In some cases the Final Residue Value will not be low enough. For example, a residue value calculated from an FDA action level will probably result in an average concentration in the edible portion of a fatty species that is at the action level. Some individual organisms, and possibly some species, will have residue concentrations higher than the mean value but no mechanism has been devised to provide appropriate additional protection. Also, some chronic feeding studies and long-term field studies with wildlife identify concentrations that cause adverse effects but do not identify concentrations which do not cause adverse effects; again no mechanism has been devised to provide appropriate additional protection. These are some of the species and uses that are not protected at all times in all places.

X. Other Data

Pertinent information that could not be used in earlier sections might be available concerning adverse effects on aquatic organisms and their uses. The most important of these are data on cumulative and delayed toxicity, flavor impairment, reduction in survival, growth, or reproduction, or any other adverse effect that has been shown to be biologically important. Especially important are data for species for which no other data are available. Data from behavioral, biochemical, physiological, microcosm, and field studies might also be available. Data might be available from tests conducted in unusual dilution water (see IV.D and VI.D), from chronic tests in which the concentrations were not measured (see VI.B), from tests with previously exposed organisms (see II.F), and from tests on formulated mixtures or emulsifiable concentrates (see II.D). Such data might affect a criterion if the data were obtained with an important species, the test concentrations were measured, and the endpoint was biologically important.

XI. Criterion

A. A criterion consists of two concentrations: the Criterion Maximum Concentration and the Criterion Continuous Concentration.

B. The Criterion Maximum Concentration (CMC) is equal to one-half the Final Acute Value.

C. The Criterion Continuous Concentration (CCC) is equal to the lowest of the Final Chronic Value, the Final Plant Value, and the Final Residue Value, unless other data (see Section X) show that a lower value should be used. If toxicity is related to a water quality characteristic, the CCC is obtained from the Final Chronic Equation, the Final Plant Value, and the Final Residue Value by selecting the one, or the combination, that results in the lowest concentrations in the usual range of the water quality characteristic, unless other data (see Section X) show that a lower value should be used.

D. Round [14] both the CMC and the CCC to two significant digits.

E. The criterion is stated as:

The procedures described in the "Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses" indicate that, except possibly where a locally important species is very sensitive, (1) aquatic organisms and their uses should not be affected unacceptably if the four-day average concentration of (2) does not exceed (3) μg/L more than once every three years on the average and if the one-hour average concentration does not exceed (4) μg/L more than once every three years on the average.

where (1) = insert "freshwater" or "saltwater"

(2) = insert name of material

(3) = insert the Criterion Continuous Concentration

(4) = insert the Criterion Maximum Concentration.

XII. Final Review

A. The derivation of the criterion should be carefully reviewed by rechecking each step of the Guidelines. Items that should be especially checked are:

1. If unpublished data are used, are they well documented?
2. Are all required data available?
3. Is the range of acute values for any species greater than a factor of 10?
4. Is the range of Species Mean Acute Values for any genus greater than a factor of 10?
5. Is there more than a factor of ten difference between the four lowest Genus Mean Acute Values?
6. Are any of the four lowest Genus Mean Acute Values questionable?

7. Is the Final Acute Value reasonable in comparison with the Species Mean Acute Values and Genus Mean Acute Values?

8. For any commercially or recreationally important species, is the geometric mean of the acute values from flow-through tests in which the concentrations of test material were measured lower than the Final Acute Value?

9. Are any of the chronic values questionable?

10. Are chronic values available for acutely sensitive species?

11. Is the range of acute-chronic ratios greater than a factor of 10?

12. Is the Final Chronic Value reasonable in comparison with the available acute and chronic data?

13. Is the measured or predicted chronic value for any commercially or recreationally important species below the Final Chronic Value?

14. Are any of the other data important?

15. Do any data look like they might be outliers?

16. Are there any deviations from the Guidelines? Are they acceptable?

B. On the basis of all available pertinent laboratory and field information, determine if the criterion is consistent with sound scientific evidence. If it is not, another criterion, either higher or lower, should be derived using appropriate modifications of these Guidelines.

References

[1] U.S. EPA. 1983. Water Quality Standards Regulation. Federal Register 48: 51400-51413. November 8.

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Appendix 1. Resident North American Species of Aquatic Animals Used in Toxicity and Bioconcentation Tests

Introduction

These lists identify species of aquatic animals which have reproducing wild populations in North America and have been used in toxicity or bioconcentration tests. "North America" includes only the 48 contiguous states, Canada, and Alaska; Hawaii and Puerto Rico are not included. Saltwater (i.e., estuarine and true marine) species are considered resident in North America if they inhabit or regularly enter shore waters on or above the continental shelf to a depth of 200 meters. Species do not have to be native to be resident. Unlisted species should be considered resident North American species if they can be similarly confirmed or if the test organisms were obtained from a wild population in North America.

The sequence for fishes is taken from A List of Common and Scientific Names of Fishes from the United States and Canada. For other species, the sequence of phyla, classes, and families is taken from the NODC Taxonomic Code, Third Edition, National Oceanographic Data Center, NOAA, Washington, DC 20235, July, 1981, and the numbers given are from that source to facilitate verification. Within a family, genera are in alphabetical order, as are species in a genus.

The references given are those used to confirm that the species is a resident North American species. (The NODC Taxonomic Code contains foreign as well as North American species.) If no such reference could be found, the species was judged to be nonresident. No reference is given for organisms not identified to species; these are considered resident only if obtained from wild North American populations. A few nonresident species are listed in brackets and noted as "nonresident" because they were mistakenly identified as resident in the past or to save other investigators from doing literature searches on the same species.

Special Note

This December 2010 electronic version of the 1985 Guidelines serves to meet the requirements of Section 508 of the Rehabilitation Act. While converting the 1985 Guidelines to a 508-compliant version, EPA updated the taxonomic nomenclature to reflect changes that occurred since the tables were originally produced in 1985. The numbers included for Phylum, Class and Family represent those currently in use from the Integrated Taxonomic Information System, or ITIS, and reflect what is referred to in ITIS as Taxonomic Serial Numbers. ITIS replaced the National Oceanographic Data Center (NODC) taxonomic coding system which was used to create the original taxonomic tables included in the 1985 Guidelines document (NODC, Third Addition - see Introduction). For more information on the NODC taxonomic codes, see http://www.nodc.noaa.gov/General/CDR-detdesc/taxonomic-v8.html.

The code numbers included in the reference column of the tables have not been updated from the 1985 version. These code numbers are associated with the old NODC taxonomic referencing system and are simply replicated here for historical purposes. Footnotes may or may not still apply.

EPA is working on a more comprehensive update to the 1985 Guidelines, including new taxonomic tables which better reflect the large number of aquatic animal species known to be propagating in U.S. waters.

Freshwater Species Table

Synonyms appear after the official Scientific Name and are marked with an asterisk (*).
Non-resident species are noted in the Reference column and are marked with a dagger (†)

Class	Family	Species		Reference
		Common Name	Scientific Name	
Phylum: Porifera (46861)				
Demospongiae 47528	Spongillidae 47691	Sponge	*Ephydatia fluviatilis*	P93
Phylum: Cnidaria (48738)				
Hydrozoa 48739	Hydridae 50844	Hydra	*Hydra oligactis*	E318, P112
		Hydra	*Hydra littoralis*	E321, P112
Phylum: Platyhelminthes (53963)				
Turbellaria 53964	Planariidae 54502	Planarian	*Dugesia dorotocephala*	D22
		Planarian	*Dugesia lugubris* *Dugesia polychroa*‡	D24
		Planarian	*Planaria gonocephala*	[1]
		Planarian	*Polycelis felina*§	nonresident
	Dendrocoelidae 54469	Planarian	*Procotyla fluviatilis* *Dendrocoelum lacteum**	E334, P132, D63
Phylum: Gastrotricha (57597)				
Chaetonotida 57822	Chaetonotidae 57823	Gastrotrich	*Lepidodermella squamata* *Lepidodermella squamatum**	E413
Phylum: Rotifera (58239)				
Eurotatoria (Formerly Bdelloidea) 654070	Philodinidae 58266	Rotifer	*Philodina acuticornis*	Y
		Rotifer	*Philodina roseola*	E487
Eurotatoria (Formerly Monogononta) 654070	Brachionidae 58344	Rotifer	*Keratella cochlearis*	E442, P188
		Rotifer	*Keratella sp.*	[2]
Phylum: Annelida (64357)				
Polychaeta (Formerly Archiannelida) 64358	Aeolosomatidae 68423	Worm	*Aeolosoma headleyi*	E528, P284
Clitellata (Formerly Oligochaeta) 568832	Lumbriculidae 68440	Worm	*Lumbriculus variegatus*	E533, P290
	Tubificidae 68585	Tubificid worm	*Branchiura sowerbyi*	E534, P289, GG
		Tubificid worm	*Limnodrilus hoffmeisteri*	E536, GG
		Tubificid worm	*Quistadrilus multisetosus* *Peloscolex multisetosus**	E535, GG
		Tubificid worm	*Rhyacodrilus montanus*	GG
		Tubificid worm	*Spirosperma ferox* *Peloscolex ferox**	GG
		Tubificid worm	*Spirosperma nikolskyi* *Peloscolex variegatus**	E534, GG
		Tubificid worm	*Stylodrilus heringianus*	GG

‡ Synonym
§ Non-resident species

Class	Family	Species		Reference
		Common Name	Scientific Name	
		Tubificid worm	*Tubifex tubifex*	E536, P289, GG
		Tubificid worm	*Varichaeta pacifica*	GG
	Naididae 68854	Worm	*Nais sp.*	2
		Worm	*Paranais sp.*	2
		Worm	*Pristina sp.*	2
Clitellata (Formerly Hirudinea) 568832	Erpobdellidea 69438	Leech	*Erpobdella octoculata*	Formerly nonresident (BB16)
Phylum: Mollusca (69458)				
Gastropoda 69459	Viviparidae 70304	Snail	*Campeloma decisum*	P731, M216
	Bithyniidae (Amnicolidae) (Bulimidae) (Hydrobiidae) 70745	Snail	*Amnicola sp.*	2
	Pleuroceridae 71541	Snail	*Goniobasis livescens*	P732
		Snail	*Elimia virginica* *Goniobasis virginica*[*]	E1137
		Snail	*Leptoxis carinata* *Nitocris carinata*[*] *Mudalia carinata*[*]	X, E1137
		Snail	*Nitocris sp.*	2
	Lymnaeidae 76483	Snail	*Lymnaea acuminata*[†]	nonresident
		Snail	*Lymnaea catascopium* *Lymnaea emerginata*[*] *Stagnicola emerginata*[*]	M328
		Snail	*Lymnaea elodes* *Lymnaea palustris*[*]	E1127, M351
		Snail	*Lymnaea luteola*[†]	nonresident M266
		Snail	*Lymnaea stagnalis*	E1127, P728, M296
		Snail	*Lymnaea sp.*	2
	Planorbidae 76591	Snail	*Biomphalaria glabrata*	Formerly nonresident (M390)
		Snail	*Gyraulus circumstriatus*	P729, M397
		Snail	*Helisoma campanulatum*	M445
		Snail	*Helisoma trivolvis*	P729, M452
	Physidae 76676	Snail	*Aplexa hypnorum*	E1126, P727, M373
		Snail	*Physa fontinalis*[†]	nonresident M373
		Snail	*Physa gyrina*	E1126, P727, M373
		Snail	*Physa heterostropha*	M378
		Snail	*Physa integra*	P727
		Snail	*Physa sp.*	2
Bivalvia (Pelecypoda) 79118	Margaritiferidae 79914	Mussel	*Margaritifera margaritifera*	E1138, P748, J11
	Unionidae (Formerly Amblemidae) 79913	Mussel	*Amblema plicata*	AA122
	Unionidae	Mussel	*Anodonta imbecillis*	J72, AA122

Class	Family	Species		Reference
		Common Name	Scientific Name	
	79913	Mussel	*Carunculina parva* *Toxolasma texasensis*[*]	J19, AA122
		Mussel	*Cyrtonaias tampicoenis*	P759, AA122
		Mussel	*Elliptio complanata*	J13
	Corbiculidae 81381	Asiatic clam	*Corbicula fluminea*	E1159
		Asiatic clam	*Corbicula manilensis*	P749
	Pisidiidae Sphaeriidae[*] 81388	Fingernail clam	*Eupera cubensis* *Eupera singleyi*[*]	E1158, P763, G9
		Fingernail clam	*Musculium transversum* *Sphaerium transversum*[*]	M160, G11
		Fingernail clam	*Sphaerium corneum*	G12
Phylum: Arthropoda (82696)				
Branchiopoda (Formerly Crustacea) 83687	Lynceidae 83769	Conchostracan	*Lynceus brachyurus*	E580, P344
	Sididae 83834	Cladoceran	*Diaphanosoma sp.*	2
	Daphniidae 83872	Cladoceran	*Ceriodaphnia acanthina*	E618
		Cladoceran	*Ceriodaphnia reticulata*	E618, P368
		Cladoceran	*Daphnia ambigua*	E607, P369
		Cladoceran	*Daphnia carinata*	[3]
		Cladoceran	*Daphnia cucullata*[†]	nonresident
		Cladoceran	*Daphnia galeata mendotae*	E610, P370
		Cladoceran	*Daphnia hyalina*	[4]
		Cladoceran	*Daphnia longispina*	[5]
		Cladoceran	*Daphnia magna*	E605, P367
		Cladoceran	*Daphnia parvula*	E611
		Cladoceran	*Daphnia pulex*	E613, P367
		Cladoceran	*Daphnia pulicaria*	A
		Cladoceran	*Daphnia similis*	E606, P367
		Cladoceran	*Simocephalus serrulatus*	E617, P370
		Cladoceran	*Simocephalus vetulus*	E617, P370
	Moinidae (Formerly Daphnidae) 84162	Cladoceran	*Moina macrocopa*	E622, P372
		Cladoceran	*Moina rectirostris*	E623
	Bosminidae 83935	Cladoceran	*Bosmina longirostris*	E624, P373
	Polyphemidae 83959	Cladoceran	*Polyphemus pediculus*	E599, P385
Ostracoda (Formerly Crustacea) 84195	Cyprididae Cypridae[*] 84462	Ostracod	*Cypretta kawatai*[†]	nonresident U
		Ostracod	*Cypridopsis vidua*	E770, P430
Maxillopoda (Formerly Crustacea) 621145	Diaptomidae 85779	Copepod	*Eudiaptomus padanus*[†]	nonresident
	Temoridae 85855	Copepod	*Epischura lacustris*	E751, P407
	Cyclopidae 88634	Copepod	*Cyclops abyssorum*[†]	nonresident
		Copepod	*Cyclops bicuspidatus*	E807, P405
		Copepod	*Cyclops vernalis*	E804, P405
		Copepod	*Cyclops viridis* *Acanthocyclops viridis*[*]	E803, P397

Class	Family	Species		Reference
		Common Name	Scientific Name	
		Copepod	*Acanthocyclops sp.*	2
		Copepod	*Diacyclops sp.*	2
		Copepod	*Eucyclops agilis*	P403
		Copepod	*Mesocyclops leuckarti*	E812, P403
Malacostraca (Formerly Crustacea) 89787	Asellidae 92657	Isopod	*Asellus aquaticus*†	nonresident (I2)
		Isopod	*Caecidotea bicrenata* (Formerly *Asellus bicrenata)*	HH (I1,2)
		Isopod	*Asellus brevicaudus*	E875, P447, I
		Isopod	*Asellus communis*	E875, P448, I
		Isopod	*Asellus intermedius*	E875, P448, I
		Isopod	*Asellus meridionalis*† *Asellus meridianus**†	nonresident
		Isopod	*Asellus racovitzai*	P449, I
		Isopod	*Lirceus alabamae*	P875, I
	Crangonyctidae (Formerly Gammaridae) 95080	Amphipod	*Crangonyx pseudogracilis*	P459, T68, FF23
	Gammaridae 93745	Amphipod	*Gammarus fasciatus*	E877, P458, T53
		Amphipod	*Gammarus lacustris*	E877, P458, FF23
		Amphipod	*Gammarus pseudolimnaeus*	E877, P458, T48
		Amphipod	*Gammarus pulex*†	nonresident
		Amphipod	*Gammarus tigrinus*	L51, FF17
		Amphipod	*Gammarus sp.*	2
	Hyalellidae (Talitridae) 94022	Amphipod	*Hyalella azteca* *Hyalella knickerbockeri**	E876, P457, T154
	Palaemonidae 96213	Prawn	*Macrobrachium lamarrei*†	nonresident
		Prawn	*Macrobrachium rosenbergii*	[6]
		Prawn	*Palaemonetes kadiakensis*	E881, P484
	Cambaridae (Formerly Astacidae) 97336	Crayfish	*Cambarus latimanus*	E897
		Crayfish	*Faxonella clypeata*	E890
		Crayfish	*Orconectes immunis*	E894, P482
		Crayfish	*Orconectes limosus*	E893, P482
		Crayfish	*Orconectes propinquus*	E894, P482
		Crayfish	*Orconectes nais*	E894
		Crayfish	*Orconectes rusticus*	E893, P482
		Crayfish	*Orconectes virilis*	E894, P483
		Crayfish	*Pacifastacus trowbridgii*	E883
		Crayfish	*Procambarus acutus*	P482
		Crayfish	*Procambarus clarki* *Procambarus clarkii**	E885, P482
		Crayfish	*Procambarus simulans*	E888, P482
		Crayfish	*Procambarus sp.*	2
Insecta 99208	Heptageniidae 100504	Mayfly	*Maccaffertium ithaca* *Stenonema ithaca**	S173, O205
		Mayfly	*Maccaffertium modestum* *Stenonema rubrum**	S178, O205
	Baetidea	Mayfly	*Callibaetis skokianus*	S116, N9

Class	Family	Species		Reference
		Common Name	Scientific Name	
	100755	Mayfly	*Callibaetis sp.*	2
		Mayfly	*Cloeon dipterum*	O173
	Leptophlebiidae 101095	Mayfly	*Paraleptophlebia praepedita*	S89, O233
	Ephemerellidae 101232	Mayfly	*Drunella doddsii* *Ephemerella doddsi*[*]	O245
		Mayfly	*Drunella grandis* *Ephemerella grandis*[*]	O245
		Mayfly	*Ephemerella subvaria*	N9, O248, S71
		Mayfly	*Ephemerella sp.*	2
	Caenidea 101467	Mayfly	*Caenis diminuta*	S51, O268
	Ephemeridae 101525	Mayfly	*Ephemera simulans*	S36, N9, O283
		Mayfly	*Hexagenia bilineata*	N9, S39, O290
		Mayfly	*Hexagenia rigida*	O290, S41, N9
		Mayfly	*Hexagenia sp.*	2
	Libellulidae 101797	Dragonfly	*Pantala hymenaea* *Pantala hymenea*[*]	N15, V603
	Coenagrionidae Agrionidae[*] Coenagriidae[*] 102077	Damselfly	*Enallagma aspersum*	DD
		Damselfly	*Ischnura elegans*[†]	nonresident
		Damselfly	*Ischnura verticalis*	N15, E918
		Damselfly	*Ischnura sp.*	2
	Pteronarcyidae (Formerly Pteronarcidae) Pleronarcyidae[*] 102470	Stonefly	*Pteronarcella badia*	L172
		Stonefly	*Pteronarcys californica*	L173
		Stonefly	*Pteronarcys dorsata*	E947
		Stonefly	*Pteronarcys sp.*	2
	Nemouridae 102517	Stonefly	*Nemoura cinerea*[†]	nonresident
	Perlidae 102914	Stonefly	*Acroneuria lycorias*	N4, E953
		Stonefly	*Acroneuria pacifica*	E953, L180
		Stonefly	*Claassenia sabulosa*	E953
		Stonefly	*Agnetina capitata* *Neophasganophora capitata*[*] *Phasganophora capitata*[*]	E953, CC407
	Perlodidae 102994	Stonefly	*Skwala americana* *Arcynopteryx parallela*[*]	E954
	Nepidae 103747	Water Scorpion	*Ranatra elongate*[†] (Species cannot be confirmed in ITIS)	nonresident
	Dytiscidae 111963	Beetle	-	2
	Elmidae Elminthidae[*] 114093	Beetle	*Stenelmis sexlineata*	W21
	Hydropsychidae 115398	Caddisfly	*Arctopsyche grandis*	L251, II98
		Caddisfly	*Hydropsyche betteni*	N24
		Caddisfly	*Hydropsyche californica*	L253
		Caddisfly	*Hydropsyche sp.*	2
	Limnephilidae 115933	Caddisfly	*Clistoronia magnifica*	II206
		Caddisfly	*Philarctus quaeris*	II272

Class	Family	Species		Reference
		Common Name	Scientific Name	
	Brachycentridae 116905	Caddisfly	*Brachycentrus sp.*	2
	Tipulidae 118840	Crane fly	*Tipula sp.*	2
	Ceratopogonidae 127076	Biting midge	-	2
	Culicidae 125930	Mosquito	*Aedes aegypti*	EE3
		Mosquito	*Culex pipiens*	EE3
	Chironomidae 127917	Midge	*Chironomus plumosus* *Tendipas plumosus*[*]	L423
		Midge	*Chironomus tentans*	Q
		Midge	*Chironomus thummi*[†]	nonresident
		Midge	*Chironomus sp.*	2
		Midge	*Paratanytarsus parthenogeneticus*	[7]
		Midge	*Paratanytarsus dissimilis* *Tanytarsus dissimilis*[*]	R11
	Athericidae (Formerly Rhagionidae) Leptidae[*] 130928	Snipe fly	*Atherix sp.*	2
Phylum: Ectoprocta (155470)				
Phylactolaemata 156688	Pectinatellidae (Formerly Pectinatelcidae) 156729	Bryozoan	*Pectinatella magnifica*	E502, P269
	Lophopodidae 156714	Bryozoan	*Lophopodella carteri*	E502, P2671
	Plumatellidae 156690	Bryozoan	*Plumatella emarginata*	E505, P272
Phylum: Chordata (158852)				
Agnatha 159693	Petromyzontidae 159697	Sea lamprey	*Petromyzon marinus*	F11
Actinopterygii (Formerly Osteichthyes) 161061	Anguillidae 161125	American eel	*Anguilla rostrata*	F15
	Salmonidae 161931	Pink salmon	*Oncorhynchus gorbuscha*	F18
		Coho salmon	*Oncorhynchus kisutch*	F18
		Sockeye salmon	*Oncorhynchus nerka*	F19
		Chinook Salmon	*Oncorhynchus tshawytscha*	F19
		Mountain whitefish	*Prosopium williamsoni*	F19
		Golden Trout	*Oncorhynchus aguabonita* (Formerly *Salmo aguabonita)*	F19
		Cutthroat trout	*Oncorhynchus clarki* (Formerly *Salmo clarki)*	F19
		Rainbow trout Steelhead trout[*]	*Oncorhynchus mykiss* (Formerly *Salmo gairdneri)*	F19
		Atlantic salmon	*Salmo salar*	F19
		Brown trout	*Salmo trutta*	F19
		Brook trout	*Salvelinus fontinalis*	F19
		Lake trout	*Salvelinus namaycush*	F19

Class	Family	Species		Reference
		Common Name	Scientific Name	
	Esocidae 162137	Northern pike	*Esox lucius*	F20
	Cyprinidae 163342	Chiselmouth	*Acrocheilus alutaceus*	F21
		Longfin dace	*Agosia chrysogaster*	F21
		Central stoneroller	*Campostoma anomalum*	F21
		Goldfish	*Carassius auratus*	F21
		Common carp	*Cyprinus carpio*	F21
		Zebra danio Zebrafish*	*Danio rerio*† *Brachydanio rerio*†*	nonresident F96
		Silverjaw minnow	*Notropis buccatus* *Ericymba buccata**	F21
		Golden shiner	*Notemigonus crysoleucas*	F23
		Pugnose shiner	*Notropis anogenus*	F23
		Emerald shiner	*Notropis atherinoides*	F23
		Striped shiner	*Luxilus chrysocephalus* *Notropis chrysocephalus**	F23
		Common shiner	*Luxilus cornutus* *Notropis cornutus**	F23
		Pugnose minnow	*Opsopoeodus emiliae* *Notropis emiliae**	F24
		Spottail shiner	*Notropis hudsonius*	F24
		Red shiner	*Cyprinella lutrensis* *Notropis lutrensis**	F24
		Spotfin shiner	*Cyprinella spiloptera* *Notropis spilopterus**	F25
		Sand shiner	*Notropis stramineus*	F25
		Steelcolor shiner	*Cyprinella whipplei* *Notropis whipplei**	F25
		Northern redbelly dace	*Phoxinus eos*	F25
		Bluntnose minnow	*Pimephales notatus*	F25
		Fathead minnow	*Pimephales promelas*	F25
		Northern squawfish	*Ptychocheilus oregonensis*	F25
		Blacknose dace	*Rhinichthys atratulus*	F25
		Speckled dace	*Rhinichthys osculus*	F25
		Bitterling	*Rhodeus sericeus*	F26
		Rudd	*Scardinius erythrophthalmus*	F26
		Creek chub	*Semotilus atromaculatus*	F26
		Pearl dace	*Margariscus margarita* *Semotilus margarita**	F26
		Tench	*Tinca tinca*	F26
	Catostomidae 163892	White sucker	*Catostomus commersoni*	F26
		Mountain sucker	*Catostomus platyrhynchus*	F26
	Ictaluridae 163995	Black bullhead	*Ameiurus melas* *Ictalurus melas**	F27
		Yellow bullhead	*Ameiurus natalis* *Ictalurus natalis**	F27
		Brown bullhead	*Ameiurus nebulosus* *Ictalurus nebulosus**	F27
		Channel catfish	*Ictalurus punctatus*	F27

Class	Family	Species		Reference
		Common Name	Scientific Name	
	Clariidae 164118	Walking catfish	*Clarias batrachus*	F28
	Adrianichthyidae (Formerly Oryziidae) 165623	Medaka	*Oryzias latipe*[†]	nonresident F96
	Cyprinodontidae 165629	Banded killifish	*Fundulus diaphanus*	F33
		Flagfish	*Jordanella floridae*	F33
	Poeciliidae 165876	Mosquitofish	*Gambusia affinis*	F33
		Amazon molly	*Poecilia formosa*	F34
		Sailfin molly	*Poecilia latipinna*	F34
		Molly	*Poecilia sp.*	
		Guppy	*Poecilia reticulata* *(Lebistes reticulatus,* Obs.*)*	F34
		Southern platyfish	*Xiphophorus maculatus*	F34
	Gasterosteidae 166363	Brook stickleback	*Culaea inconstans*	F35
		Threespine stickleback	*Gasterosteus aculeatus*	F35
		Ninespine stickleback	*Pungitius pungitius*	F35
	Percichthyidae 170315	White perch	*Morone americana* *(Roccus americanus,* Obs.*)*	F36
		Striped bass	*Morone saxatilis* *(Roccus saxatilis,* Obs.*)*	F36
	Centrarchidae 168093	Rock bass	*Ambloplites rupestris*	F38
		Green sunfish	*Lepomis cyanellus*	F38
		Pumpkinseed	*Lepomis gibbosus*	F38
		Orangespotted sunfish	*Lepomis humilis*	F38
		Bluegill	*Lepomis macrochirus*	F38
		Longear sunfish	*Lepomis megalotis*	F38
		Redear sunfish	*Lepomis microlophus*	F38
		Smallmouth bass	*Micropterus dolomieui*	F39
		Largemouth bass	*Micropterus salmoides*	F39
		White crappie	*Pomoxis annularis*	F39
		Black crappie	*Pomoxis nigromaculatus*	F39
	Percidae 168356	Rainbow darter	*Etheostoma caeruleum*	F39
		Johnny darter	*Etheostoma nigrum*	F40
		Orangethroat darter	*Etheostoma spectabile*	F40
		Yellow perch	*Perca flavescens*	F41
		Walleye	*Sander vitreus* *Stizostedion vitreum vitreum*[*]	F41
	Sciaenidae 169237	Freshwater drum	*Aplodinotus grunniens*	F45
	Cichlidae 169770	Oscar	*Astronotus ocellatus*	F47
		Blue tilapia	*Tilapia aurea*	F47
		Mozambique tilapia	*Oreochromis mossambicus* *Tilapia mossambica*[*]	F47
	Cottidae 167196	Mottled sculpin	*Cottus bairdi*	F60
Amphibia 173420	Ranidae 173433	Bullfrog	*Rana catesbeiana*	B206
		Green frog	*Rana clamitans*	B206

Class	Family	Species		Reference
		Common Name	Scientific Name	
		Pig frog	*Lithobates grylio* *Rana grylio*[*]	B206
		River frog	*Rana heckscheri*	B206
		Leopard frog	*Rana pipiens*	B205
		Wood frog	*Rana sylvatica*	B206
		Frog	*Rana temporia*[†]	nonresident
		Leopard frog	*Lithobates sphenocephalus sphenocephalus* (Formerly *Rana spenocephala)*	JJ
	Microhylidae 173465	Eastern narrow-mouthed toad	*Gastrophryne carolinensis*	B192
	Bufonidae 173471	American toad	*Anaxyrus americanus americanus* *Bufo americanus*[*]	B196
		Toad	*Bufo bufo*[†]	nonresident
		Green toad	*Anaxyrus debilis debilis* *Bufo debilis*[*]	B197
		Fowler's toad	*Anaxyrus fowleri* *Bufo fowleri*[*]	B196
		Red-spotted toad	*Anaxyrus punctatus* *Bufo punctatus*[*]	B198
		Woodhouse's toad	*Anaxyrus woodhousii woodhousii* *Bufo woodhousii*[*]	B196
	Hylidae 173497	Northern cricket frog	*Acris crepitans*	B203
		Southern gray treefrog	*Hyla chrysoscelis*	B201
		Spring creeper	*Pseudacris crucifer* *Hyla crucifer*[*]	B202
		Barking treefrog	*Hyla gratiosa*	B201
		Squirrel treefrog	*Hyla squirella*	B201
		Gray treefrog	*Hyla versicolor*	B200
		Northern chorus frog	*Pseudacris triseriata*	B202
	Pipidae 173547	African clawed frog	*Xenopus laevis*	Z16
	Ambystomatidae 173588	Spotted salamander	*Ambystoma maculatum*	B176
		Mexican axolotl	*Ambystoma mexicanum*[†]	nonresident
		Marbled salamander	*Ambystoma opacum*	B176
	Salamandridae 173613	Newt	*Notophthalmus viridescens* *Triturus viridescens*[*]	B179

Footnotes for Freshwater Species

[1] Apparently this is an outdated name (D19, 20). Organisms identified as such should only be used if they were obtained from North America.

[2] Apparently this is an outdated name (D19, 20). Organisms identified as such should only be used if they were obtained from North America.

[3] If from North America, it is resident and should be called *D. similis* (C). If not from North America, it should be considered nonresident.

[4] If from North America, it is resident and may be any one of a number of species such as *D. laevie, D. dubia,* or *D. galeate mendoca* (C). If not from North America, it should be considered nonresident.

[5] If from North America, it is resident and may be any one of a number of species such as *D. ambigua*, *D. longiremis*, or *D. rosea* (C). If not from North America, it should be considered nonresident.

[6] This species might be established in portions of the southern United States.

[7] The taxonomy of this species and this and similar genera has not been clarified, but this species should be considered resident.

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Saltwater Species Table

Synonyms appear after the official Scientific Name and are marked with an asterisk (*).
Non-resident species are noted in the Reference column and are marked with a dagger (†)

Class	Family	Species		Reference
		Common Name	Scientific Name	
Phylum: Cnidaria (Coelenterata) (48738)				
Hydroza 48739	Campanulariidae 49470	Hydroid	*Campanularia flexiosa* *Campanularia flexuosa***	B122, E81
		Hydroid	*Laomedea loveni*††	nonresident
		Hydromedusa	*Phialidium sp.*	[1] (E81)
	Campanulinidae 49756	Hydroid	*Eirene viridula*†	nonresident
Phylum: Ctenophora (53856)				
Tentaculata 53858	Pleurobrachiidae 53860	Ctenophore	*Pleurobrachia pileus*	B218, E162
	Mnemiidae 53915	Ctenophore	*Mnemiopsis mccradyi*	C39, I94
Phylum: Nemertea (Rhynchocoela) (57411)				
Heteronemertea 57438	Lineidae 57443	Nemertine worm	*Cerebratulus fuscus*	B252
Phylum: Rotifera (Rotatoria) (58239)				
Monogononta 58342	Brachionidae 58344	Rotifer	*Brachionus plicatilis*	B272
Phylum: Annelida (64357)				
Polychaeta 64358	Phyllodocidae 65228	Polychaete worm	*Phyllodoce maculata* *Anaitides maculata** *Nereiphylla maculata**	E334
	Nereididae (Nereidae) 65870	Polychaete worm	*Neanthes arenaceodentata* *Nereis arenaceodentata**	E377
		Polychaete worm	*Neanthes vaali*†	nonresident
		Polychaete worm	*Nereis diversicolor* *Neanthes diversicolor**	E337, F527
		Sand worm	*Nereis virens* *Neanthes virens**	B317, E337, C58
		Polychaete worm	*Nereis sp.*	
	Dorvilleidae 66478	Polychaete worm	*Ophryotrocha diadema*	P23
		Polychaete worm	*Ophryotrocha labronica*† *Ophryotrocha labrunica**†	nonresident
	Spionidae 66781	Polychaete worm	*Polydora websteri*	E338
	Cirratulidae 67116	Polychaete worm	*Cirriformia spirabranchia*	G253
	Ctenodrilidae 67217	Polychaete worm	*Ctenodrilus serratus*	G275
	Capitellidae 67413	Polychaete worm	*Capitella capitata*	B358, E337
	Arenicolidae 67500	Polychaete worm	*Arenicola marina*	B369, E337

** Synonym
†† Non-resident species

Class	Family	Species		Reference
		Common Name	Scientific Name	
	Sabellidae 68076	Polycheate worm	*Eudistylia vancouveri*	DD
Oligochaeta 68422	Tubificidae 68585	Oligochaete worm	*Limnodriloides verrucosus*	Z
		Oligochaete worm	*Monopylephorus cuticulatus*	Z
		Oligochaete worm	*Peloscolex gabriellae* *Tubificoides gabriellae*[*]	Z
Phylum: Mollusca (69458)				
Gastropoda 69459	Haliotididae 566897	Black abalone	*Haliotis cracherodii*	C88, D17
		Red abalone	*Haliotis rufescens*	D18
	Calyptraeidae 72611	Common Atlantic slippershell	*Crepidula fornicata*	C90, D141
	Muricidae 73236	Oyster drill	*Urosalpinx cinerea* *Urosalpinx cinereus*[*]	B646, D179, E264
	Melongenidae (Neptuneidae) 74069	Channeled whelk	*Busycotypus canaliculatus* *(Formerly Busycon canaliculatum)*	B655, D223, E264
	Nassariidae (Nassidae) 74102	Mud snail	*Nassarius obsoletus* *Nassa obsoleta*[*] *Icyanassa obsoleta*[*]	B649, D226, E264
Bivalvia (Pelecypoda) 79118	Mytilidae 79451	Northern horse mussel	*Modiolus modiolus*	D434
		Blue mussel	*Mytilus edulis*	B566, C101, D428, E299
		Mediterranean mussel	*Mytilus galloprovincialis*[†]	nonresident
	Pectinidae 79611	Bay scallop	*Argopecten irradians*	D447
	Ostreidae 79866	Pacific oyster	*Crassostrea gigas*	C102, D456, E300
		Eastern oyster	*Crassostrea virginica*	D456, E300
		Oyster	*Crassostrea sp.*	1
		Oyster	*Ostrea edulis*	E300
	Cardiidae 80865	Cockle	*Cerastoderma edule*[†] *Cardium edule*[*†]	nonresident
	Mactridae 80942	Clam	*Mulinia lateralis*	D491
		Common rangia	*Rangia cuneata*	D491, E301
		Surf clam	*Spisula solidissima*	B599, D489, E301
	Tellinidae 81032	Clam	*Macoma inquinata*	D507
		Bivalve	*Tellina tenuis*[†]	nonresident
	Veneridae 81439	Quahog clam	*Mercenaria mercenaria*	D523, E301
		Common Pacific littleneck	*Protothaca staminea*	D526
		Japanese littleneck clam	*Tapes philippinarum*	D527
	Myidae 81688	Soft-shell clam	*Mya arenaria*	B602, D536, E302
Phylum: Arthropoda (82696)				
Merostomata 82698	Limulidae 82701	Horseshoe crab	*Limulus polyphemus*	B533, E403, H30
Branchiopoda (Formerly Crustacea) 83687	Artemiidae 83689	Brine shrimp	*Artemia salina*[†]	[2] nonresident
Maxillopoda (Formerly Crustacea) 621145	Calanidae 85259	Copepod	*Calanus helgolandicus*	Q25
		Copepod	*Undinula vulgaris*	Q29
	Eucalanidae 85299	Copepod	*Eucalanus elongatus*	AA
		Copepod	*Subeucalanus pileatus* *Eucalanus pileatus*[*]	AA
	Pseudocalanidae 85351	Copepod	*Pseudocalanus minutus*	E447, I155, Q43

Class	Family	Species		Reference
		Common Name	Scientific Name	
	Euchaetidae 85524	Copepod	*Euchaeta marina*	Q63
	Metridinidae (Formerly Metridiidae) 593501	Copepod	*Metridia pacifica*	X179, Y
	Pseudodiaptomidae 85847	Copepod	*Pseudodiaptomus coronatus*	E447, I154, Q101
	Temoridae 85855	Copepod	*Eurytemora affinis*	E450, I155, Q111
	Pontellidae 86038	Copepod	*Labidocera scotti*	R157
	Acartiidae 86083	Copepod	*Acartia clausi*	E447
		Copepod	*Acartia tonsa*	E447, I154
	Harpacticidae 86329	Copepod	*Tigriopus californicus*	J78
		Copepod	*Tigriopus japanicus*†	nonresident
	Tisbidae 86444	Copepod	*Tisbe holothuriae*	BB
	Ameiridae (Formerly Canthocamptidae) 86999	Copepod	*Nitokra spinipes* *Nitocra spinipe**	Q240
	Archaeobalanidae (Formerly Balanidae) 89681	Barnacle	*Semibalanus balanoides* *Balanus balanoides**	B424, E457
	Balanidae 89599	Barnacle	*Balanus crenatus*	B426, E457
		Barnacle	*Balanus eburneus*	B424, E457
		Barnacle	*Balanus improvisus*	B426, E457
Malacostraca (Formerly Crustacea) 89787	Mysidae 89856	Mysid	*Heteromysis formosa*	E513, K720
		Mysid	*Americamysis bahia* *Mysidopsis bahia**	U173
		Mysid	*Americamysis bigelowi* *Mysidopsis bigelowi**	E513, K720
		Mysid	*Neomysis sp.*	1
	Idoteidae 92564	Isopod	*Idotea balthica* *Idothea baltica**	B446, E483
		Isopod	*Idotea emarginata*†	nonresident
		Isopod	*Idotea neglecta*†	nonresident
	Janiridae 92810	Isopod	*Jaera albifrons*†	nonresident
		Isopod	*Jaera albifrons sensu*†	nonresident
		Isopod	*Jaera nordmanni*†	nonresident
	Ampeliscidae 93320	Amphipod	*Ampelisca abdita*	E488, L136
	Eusiridae (Pontogeneiidae) 93681	Amphipod	*Pontogeneia sp.*	1
	Gammaridae 93745	Amphipod	*Gammarus duebeni*	L56
		Amphipod	*Gammarus oceanicus*	E489, L50
		Amphipod	*Gammarus tigrinus*	L51
		Amphipod	*Gammarus zaddachi*†	nonresident
		Amphipod	*Marinogammarus obtusatus*	L58
	Uristadae (Formerly Lysianassidae) 621432	Amphipod	*Anonyx sp.*	1
	Euphausiidae (Thysanopodidae) 95500	Euphausiid	*Euphausia pacifica*	M15
	Penaeidae	Brown shrimp	*Penaeus aztecus*	E518, N17

Class	Family	Species		Reference
		Common Name	Scientific Name	
	95602	Pink shrimp	*Penaeus duorarum*	E518, N17
		White shrimp	*Penaeus setiferus*	E518, N17
		Blue Shrimp	*Penaeus stylirostris*†	nonresident
	Palaemonidae 96213	Shrimp	*Leander paucidens*†	nonresident
		Prawn	*Leander squilla*† *Palaemon elegans**†	nonresident
		Prawn	*Macrobrachium rosenbergii*	[3]
		Korean shrimp	*Palaemon macrodactylus*	T380
		Grass shrimp	*Palaemonetes pugio*	E521, N59
		Grass shrimp	*Palaemonetes vulgaris*	B500, E521, N56
	Hippolytidae 96746	Sargassum shrimp	*Latreutes fucorum*	N78
	Pandalidae 96965	Coon stripe shrimp	*Pandalus danae*	T306, W163
		Shrimp	*Pandalus goniurus*	W163
		Pink shrimp	*Pandalus montagui*	B494, E522, W163
	Crangonidae 97106	Sand shrimp	*Crangon crangon*†	nonresident
		Bay shrimp	*Crangon franciscorum* *Crago franciscorum**	V176, W164
		Shrimp	*Crangon nigricauda*	V176, W164
		Sand shrimp	*Crangon septemspinosa*	B500, E522
	Nephropidae (Homaridae) 97307	American lobster	*Homarus americanus*	B502, E532
		European lobster	*Homarus gammarus*†	nonresident
	Paguridae 97774	Hermit crab	*Pagurus longicarpus*	B514, E537, N125
	Cancridae 98670	Rock crab	*Cancer irroratus*	B518, E543, N175
		Dungeness crab	*Cancer magister*	T166, V185, W177
	Portunidae 98689	Blue crab	*Callinectes sapidus*	B521, C80, E543, N168
		Green crab	*Carcinus maenas*	C80, E543
	Xanthidae (Pilumnidae) 98748	Mud crab	*Eurypanopeus depressus*	B522, E543, N195
		Crab	*Leptodius floridanus*	S80
		Mud crab	*Rhithropanopeus harrisii*	E543, N187
	Varunidae (formerly Grapsidae) 621521	Shore crab	*Hemigrapsus nudus*	CC
		Shore crab	*Hemigrapsus oregonensis*	CC
	Sesarmidae (formerly Grapsidae) 621520	Drift line crab	*Armases cinereum* *(Sesarma cinereum)*	B526, E544, N222
		Crab	*Sesarma haematocheir*†	nonresident
	Ocypodidae 99080	Fiddler crab	*Uca pugilator*	B526, E544, N232
Phylum: Echinodermata (156857)				
Asteroidea 156862	Asteriidae 157212	Starfish	*Asterias forbesi*	B728, E578, O392
Ophiuroidea 157325	Ophiothricidae 157792	Brittle star	*Ophiothrix spiculata*	O672, T526
Echinoidea 157821	Arbaciidae 157904	Sea urchin	*Arbacia lixula*†	nonresident
		Sea urchin	*Arbacia punctulata*	B762, E572
	Toxopneustidae 157919	Sea urchin	*Lytechinus pictus*	T253
		Sea urchin	*Pseudocentrotus depressus*†	nonresident
	Echinidae 157940	[chinoderm	*Paracentrotus lividus*†	nonresident
	Echinometridae 157955	Coral reef echinoid	*Echinometra mathaei*†	nonresident [Hawaii only]

Class	Family	Species		Reference
		Common Name	Scientific Name	
	Strongylocentrotidae 157965	Sea urchin	*Strongylocentrotus purpuratus*	O574, T202
	Dendrasteridae 158008	Sand dollar	*Dendraster excentricus*	O537, V363
Phylum: Chaetognatha (158650)				
Sagittoidea 158655	Sagittidae 158726	Arrow worm	*Ferosagitta hispida* *Sagitta hispida*[*]	E218
Phylum: Chordata (158852)				
Chondrichthyes 159785	Rajidae 160845	Thornback ray	*Raja clavata*[†]	nonresident
Actinopterygii (Formerly Osteichthyes) 161061	Anguillidae 161125	American eel	*Anguilla rostrata*	A15
	Clupeidae 161700	Atlantic menhaden	*Brevoortia tyrannus*	A17
		Gulf menhaden	*Brevoortia patronus*	A17
		Atlantic herring	*Clupea harengus* *Clupea harengus harengus*[*]	A17
		Pacific herring	*Clupea pallasii* *Clupea harengus pallasii*[*]	A17
		Herring	*Clupea harengus*	A17
	Engraulidae 553173	Northern anchovy	*Engraulis mordax*	A18
		Nehu	*Encrasicholina purpurea*[†] *tolephorus purpureus*[*†]	nonresident [Hawaii only]
	Salmonidae 161931	Pink salmon	*Oncorhynchus gorbuscha*	A18
		Chum salmon	*Oncorhynchus keta*	A18
		Coho salmon	*Oncorhynchus kisutch*	A18
		Sockeye salmon	*Oncorhynchus nerka*	A19
		Chinook salmon	*Oncorhynchus tshawytscha*	A19
		Rainbow trout (Steelhead trout)	*Oncorhynchus mykiss* (Formerly *Salmo gairdneri)*	A19
		Atlantic salmon	*Salmo salar*	A19
	Gadidae 164701	Atlantic cod	*Gadus morhua*	A30
		Haddock	*Melanogrammus aeglefinus*	A30
	Cyprinodontidae 165629	Sheepshead minnow	*Cyprinodon variegatus*	A33
		Mummichog	*Fundulus heteroclitus*	A33
		Striped killifish	*Fundulus majalis*	A33
		Longnose killifish	*Fundulus similis*	A33
	Poeciliidae 165876	Mosquitofish	*Gambusia affinis*	A33
		Sailfin molly	*Poecilia latipinna*	A34
	Atherinidae 165984	Inland silverside	*Menidia beryllina*	A34
		Atlantic silverside	*Menidia menidia*	A34
		Tidewater silverside	*Menidia peninsulae*	A34
	Gasterosteidae 166363	Threespine stickleback	*Gasterosteus aculeatus*	A35
		Fourspine stickleback	*Apeltes quadracus*	A35
	Syngnathidae 166443	Northern pipefish	*Syngnathus fuscus*	A36
	Percichthyidae 170315	Striped bass	*Morone saxatilis* (*Roccus saxatilis,* Obs.*)*	A36
	Kuhliidae 168083	Mountain bass	*Kuhlia sandvicensis*[†]	nonresident [Hawaii only]
	Carangidae 168584	Florida Pompano	*Trachinotus carolinus*	A43

Class	Family	Species		Reference
		Common Name	Scientific Name	
	Sparidae 169180	Pinfish	*Lagodon rhomboides*	A45
	Sciaenidae 169237	Spot	*Leiostomus xanthurus*	A46
		Atlantic croaker	*Micropogonias undulatus*	A46
		Red drum	*Sciaenops ocellatus*	A46
	Embiotocidae 169735	Shiner perch	*Cymatogaster aggregata*	A47
		Dwarf perch	*Micrometrus minimus*	A48
	Pomacentridae 170044	Blacksmith	*Chromis punctipinnis*	A48
	Labridae 170477	Cunner	*Tautogolabrus adspersus*	A49
		Bluehead	*Thalassoma bifasciatum*	A49
	Mugilidae 170333	Mullet	*Aldrichetta forsteri*†	nonresident
		Striped mullet	*Mugil cephalus*	A49
		White mullet	*Mugil curema*	A49
	Ammodytidae 171670	Pacific sand lance	*Ammodytes hexapterus*	A53
	Gobiidae 171746	Longjaw mudsucker	*Gillichthys mirabilis*	A54
		Naked goby	*Gobiosoma bosci*	A54
	Cottidae 167196	Tidepool sculpin	*Oligocottus maculosus*	A61
	Bothidae 172714	Speckled sanddab	*Citharichthys stigmaeus*	A64
		Summer Flounder	*Paralichthys dentatus*	A64
	Pleuronectidae 172859	Dab	*Limanda limanda*†	nonresident
		Plaice	*Pleuronectes platessa*†	nonresident
		English sole	*Parophrys vetulus*	A65
		Winter flounder	*Pseudopleuronectes americanus*	A65
	Balistidae 173128	Planehead filefish	*Monacanthus hispidus*	A66
	Tetraodontidae 173283	Northern puffer	*Sphoeroides maculatus*	A66

Footnotes for Saltwater Species

[1] Organisms not identified to species are considered resident only if obtained from wild populations in North America.

[2] This species should not be used because it might be too atypical.

[3] This species might be established in portions of the southern United States.

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Appendix 2. Example Calculation of Final Acute Value, Computer Program, and Printouts

A. Example Calculation

N = total number of MAVs in data set = 8

Rank	MAV	ln(MAV)	$\ln(MAV)^2$	P = R / (N+1)	$\sqrt{P}$
4	6.4	1.8563	3.4458	0.44444	0.66667
3	6.2	1.8245	3.3290	0.33333	0.57735
2	4.8	1.5686	2.4606	0.22222	0.47140
1	0.4	-0.9163	0.8396	0.11111	0.33333
Sum		4.3331	10.0750	1.11110	2.04875

$$S^2 = \frac{10.0750 - (4.3331)^2 / 4}{1.11110 - (2.04875)^2 / 4} = 87.134$$

$S = 9.3346$

$L = [\ 4.3331 - (9.3346)(2.04875)] / 4 = -3.6978$

$A = (9.3346)\ (\sqrt{0.05}\ ) - 3.6978 = -1.6105$

$FAV = e^{-1.6105} = 0.1998$

B. Example Computer Program in BASIC Language for Calculating the FAV

```
10    REM This program calculates the FAV when there are less than
20    REM 59 MAVs in the data set
30    X = 0
40    X2 = 0
50    Y = 0
60    Y2 = 0
70    PRINT "How many MAVs are in the data set?"
80    INPUT N
90    PRINT "What are the four lowest MAVs?"
100   FOR R = 1 TO 4
110         INPUT V
```

```
120         X = X + LOG(V)
130         X2 = X2 + (LOG(V)) * (LOG(V))
140         P = R / (N + 1)
150         Y2 = Y2 + P
160         Y = Y + SQR((X2 – X * X / 4))
170   NEXT R
180   S = SQR((X2 – X * X / 4) / (Y2 – Y * Y / 4))
190   L = (X – S * Y) / 4
200   A = S * SQR(0.05) + L
210   F = EXP(A)
220   PRINT "FAV = " F
230   END
```

C. Example Printouts from Program

```
How many MAVs are in the data set?
? 8
What are the four lowest MAVs?
? 6.4
? 6.2
? 4.8
? .4
FAV = 0.1998


How many MAVs are in the data set?
? 16
What are the four lowest MAVs?
? 6.4
? 6.2
? 4.8
? .4
FAV = 0.4365
```

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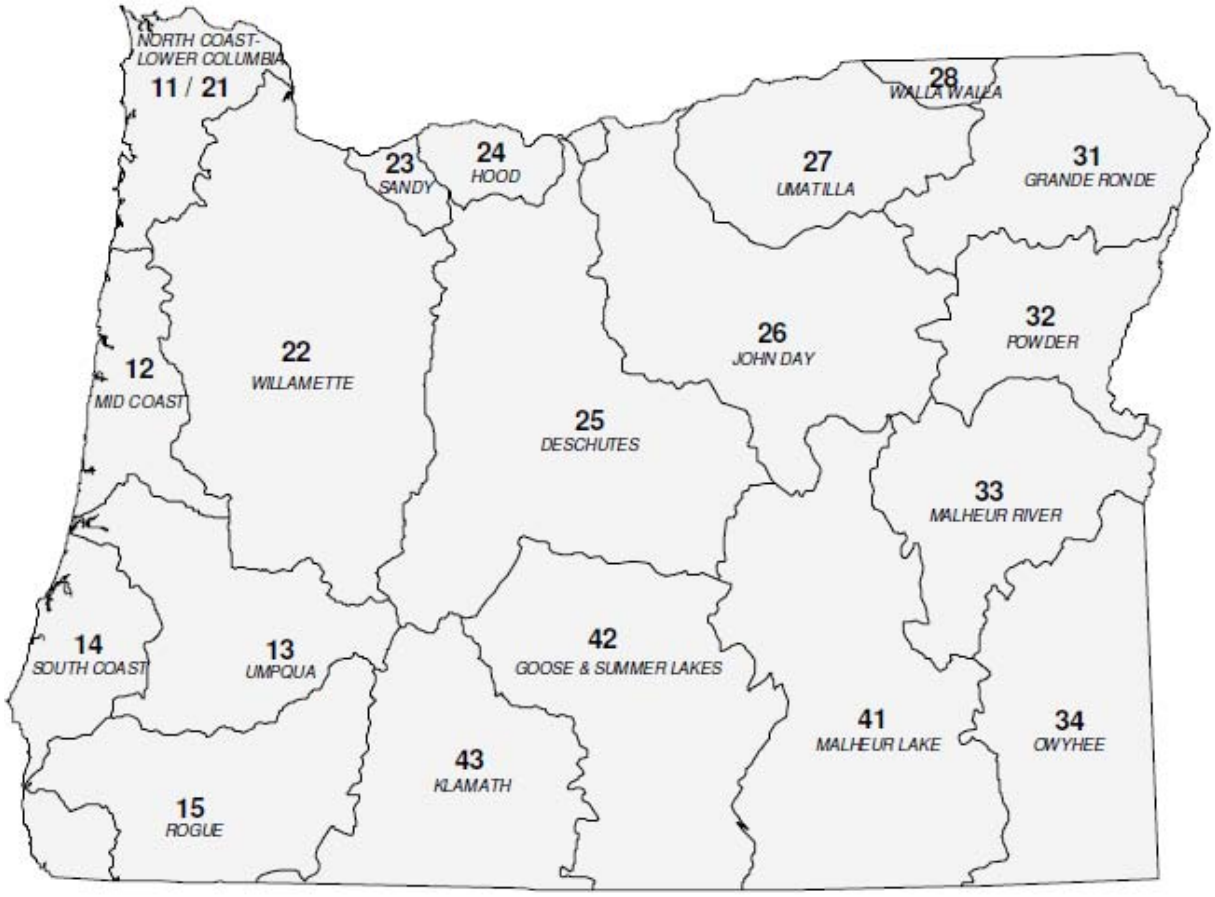
OAR 340-041-0101
Tables and Figures
Basin-Specific Criteria, Beneficial Uses to be Protected in the Main Stem Columbia River

Figure 1: Oregon Basin Index Map



n Name	Basin #	OAR #
S	25	340-041-0130
UMMER LKS	42	340-041-0140
ONDE	31	340-041-0151
	24	340-041-0160
	26	340-041-0170
	43	340-041-0180
LAKE	41	340-041-0190
RIVER	33	340-041-0201
	12	340-041-0220
AST-LWR COL	11-21	340-041-0230
	34	340-041-0250
	32	340-041-0260
	15	340-041-0271
	23	340-041-0286
AST	14	340-041-0300
A	27	340-041-0310
	13	340-041-0320
ALLA	28	340-041-0330
TTE	22	340-041-0340

OAR 340-041-0101
Table 101A
Designated Beneficial Uses
Main stem Columbia River

(November 2003)

Beneficial Uses	Columbia River Mouth to RM 86	Columbia River RM 86 to 309
Public Domestic Water Supply[1]	X	X
Private Domestic Water Supply[1]	X	X
Industrial Water Supply	X	X
Irrigation	X	X
Livestock Watering	X	X
Fish & Aquatic Life[2]	X	X
Wildlife & Hunting	X	X
Fishing [3]	X	X
Boating	X	X
Water Contact Recreation[3]	X	X
Aesthetic Quality	X	X
Hydro Power		X
Commercial Navigation & Transportation	X	X

[1] With adequate pretreatment and natural quality to meet drinking water standards.

[2] See also Table 101B for fish use designations for this river.

[3] See also Figure 101A for coastal water contact use and shellfish harvesting designations.

OAR 340-041-0101
Table 101B
Beneficial Use Designations – Fish Uses
Main stem Columbia River

(November 2003)

Geographic Extent of Use	Salmon and Steelhead Migration Corridors (20°C)	Salmon and Steelhead Spawning through Fry Emergence	Shad and Sturgeon Spawning and Rearing
Mainstem Columbia River			
Beacon Rock to Upstream of Ives Island (RM 141,5 to RM 143.5)		October 15 – March 31	
Columbia River, mouth to WA border (RM 309)	X		
Columbia River (RM 146 to RM 203)			X

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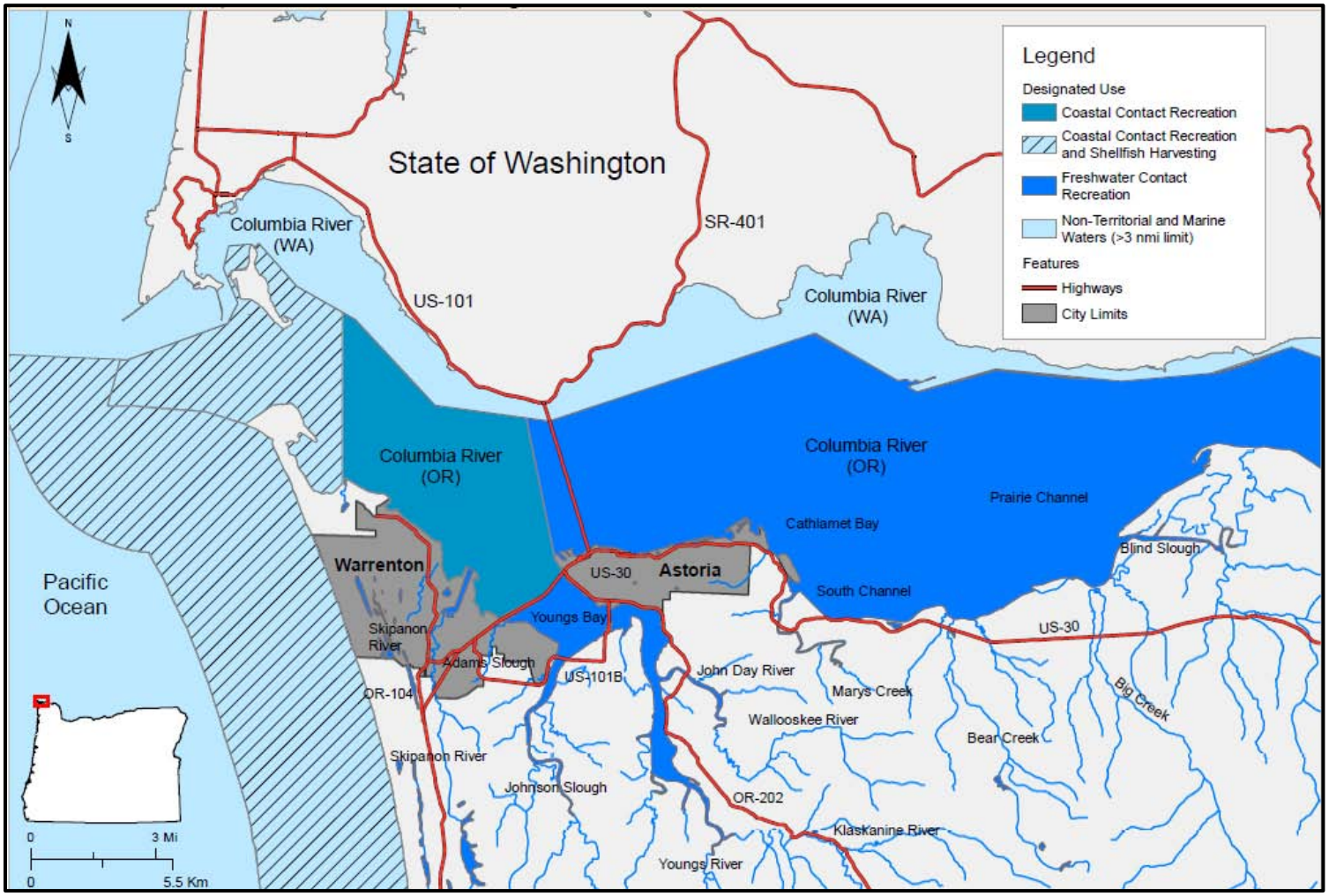
OAR 340-041-0101

Figure 101A - Water Contact Recreation and Shellfish Harvesting Designated Uses, Columbia River, Columbia River Basin, Oregon



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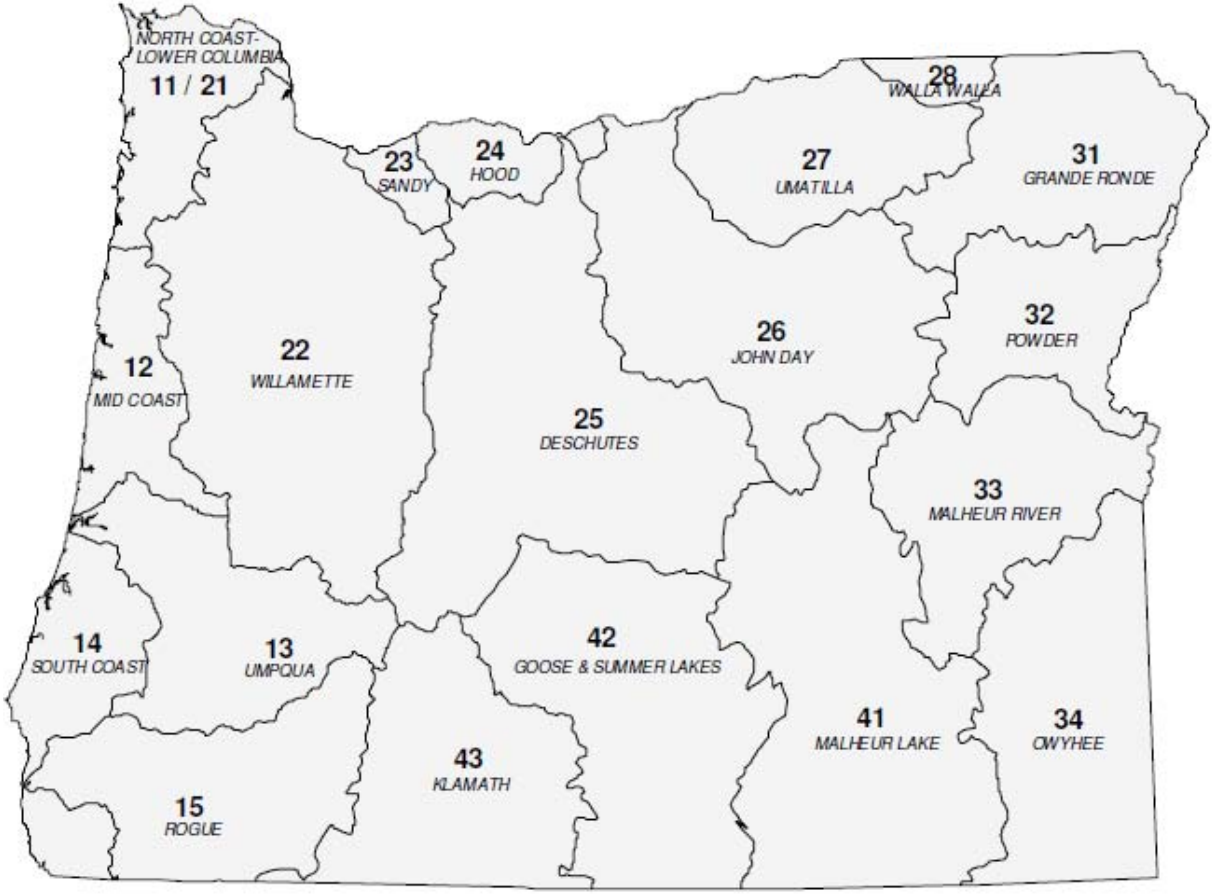
OAR 340-041-0121
Tables and Figures

Figure 1: Oregon Basin Index Map



Basin Name	Basin #	OAR #
DESCHUTES	25	340-041-0130
GOOSE & SUMMER LKS	42	340-041-0140
GRANDE RONDE	31	340-041-0151
HOOD	24	340-041-0160
JOHN DAY	26	340-041-0170
KLAMATH	43	340-041-0180
MALHEUR LAKE	41	340-041-0190
MALHEUR RIVER	33	340-041-0201
MD COAST	12	340-041-0220
NORTH COAST-LWR COL	11-21	340-041-0230
OWYHEE	34	340-041-0250
POWDER	32	340-041-0260
ROGUE	15	340-041-0271
SANDY	23	340-041-0286
SOUTH COAST	14	340-041-0300
UMATILLA	27	340-041-0310
UMPQUA	13	340-041-0320
WALLA WALLA	28	340-041-0330
WILLAMETTE	22	340-041-0340

OAR 340-041-0121
Table 121A
Designated Beneficial Uses
Mainstem Snake River

Beneficial Uses	Snake River RM 176 to 409
Public Domestic Water Supply[1]	X
Private Domestic Water Supply[1]	X
Industrial Water Supply	X
Irrigation	X
Livestock Watering	X
Fish & Aquatic Life[2]	X
Wildlife & Hunting	X
Fishing	X
Boating	X
Water Contact Recreation	X
Aesthetic Quality	X
Hydro Power	X
Commercial Navigation & Transportation	X

[1] With adequate pretreatment and natural quality that meets drinking water standards.

[2] See also Table 121B for fish use designations for this river.

OAR 340-041-0121
Table 121B
Beneficial Use Designations - Fish Uses
Mainstem Snake River

Geographic Extent of use	Salmon and Steelhead Migration Corridors (20°C)	Redband or Lahontan Cutthroat Trout (20°C)	Salmon and Steelhead Spawning Through Fry Emergence
Mainstem Snake River			
Oregon/Washington Border to Hells Canyon Dam (RM 169 to 247.5)	X		October 23-April 15
Hells Canyon Dam to Idaho Border (RM 247.5 to RM 409)		X	

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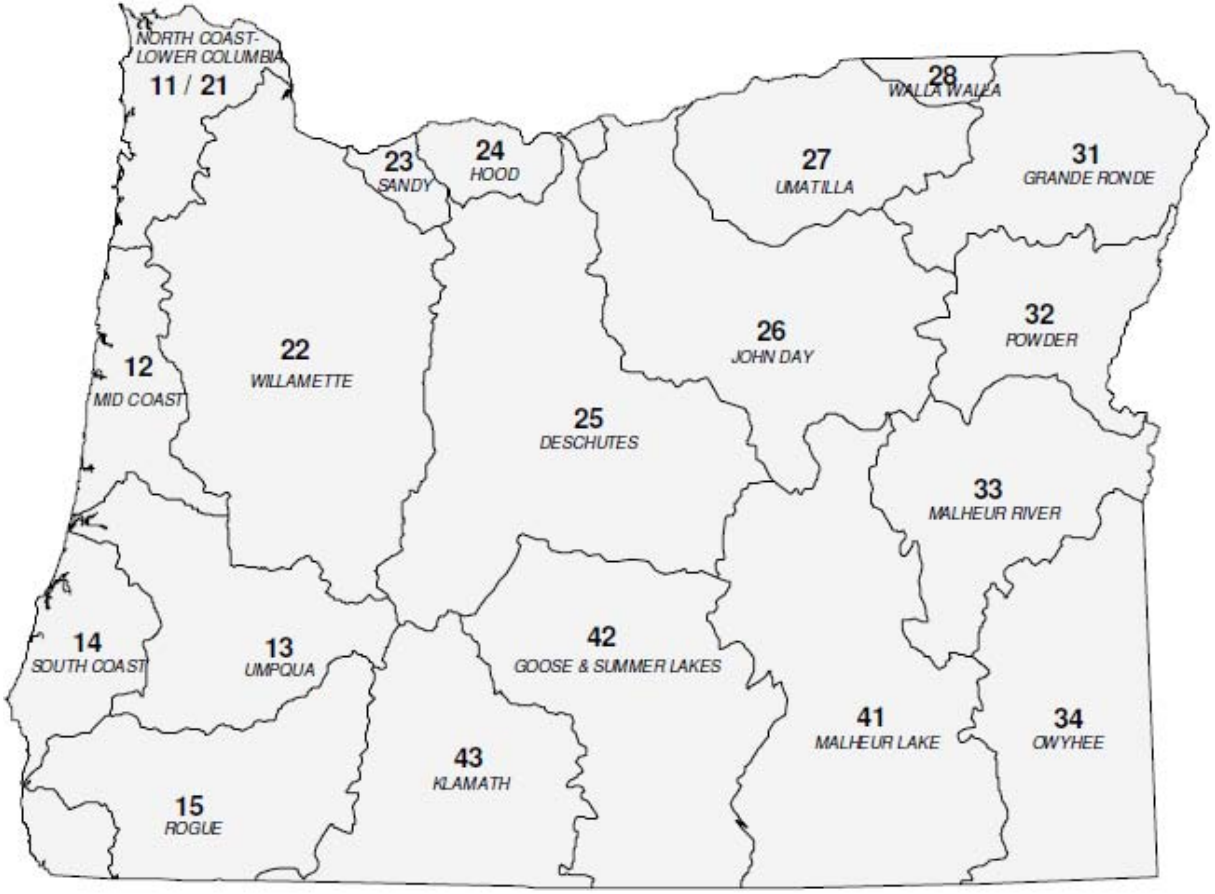
OAR 340-041-0130
Tables and Figures

Figure 1: Oregon Basin Index Map



Basin Name	Basin #	OAR #
DESCHUTES	25	340-041-0130
GOOSE & SUMMER LKS	42	340-041-0140
GRANDE RONDE	31	340-041-0151
HOOD	24	340-041-0160
JOHN DAY	26	340-041-0170
KLAMATH	43	340-041-0180
MALHEUR LAKE	41	340-041-0190
MALHEUR RIVER	33	340-041-0201
MD COAST	12	340-041-0220
NORTH COAST-LWR COL	11-21	340-041-0230
OWYHEE	34	340-041-0250
POWDER	32	340-041-0260
ROGUE	15	340-041-0271
SANDY	23	340-041-0286
SOUTH COAST	14	340-041-0300
UMATILLA	27	340-041-0310
UMPQUA	13	340-041-0320
WALLA WALLA	28	340-041-0330
WILLAMETTE	22	340-041-0340

OAR 340-041-0130
Table 130A
Designated Beneficial Uses
Deschutes Basin

Beneficial Uses	Deschutes River Main Stem from Mouth to Pelton Regulating Dam	Deschutes River Main Stem from Pelton Regulating Dam to Bend Diversion Dam and for the Crooked River Main Stem	Deschutes River Main Stem above Bend Diversion Dan & for the Metolious River Main Stem	All Other Basin Stems
Public Domestic Water Supply[1]	X	X	X	X
Private Domestic Water Supply[1]	X	X	X	X
Industrial Water Supply	X	X	X	X
Irrigation	X	X	X	X
Livestock Watering	X	X	X	X
Fish & Aquatic Life[2]	X	X	X	X
Wildlife & Hunting	X	X	X	X
Fishing	X	X	X	X
Boating	X	X	X	X
Water Contact Recreation	X	X	X	X
Aesthetic Quality	X	X	X	X
Hydro Power		X		
Commercial Navigation & Transportation				

[1] With adequate pretreatment (filtration and disinfection) and natural quality that meets drinking water standards.

[2] See also Figures 130A and 130B for fish use designations for this river.

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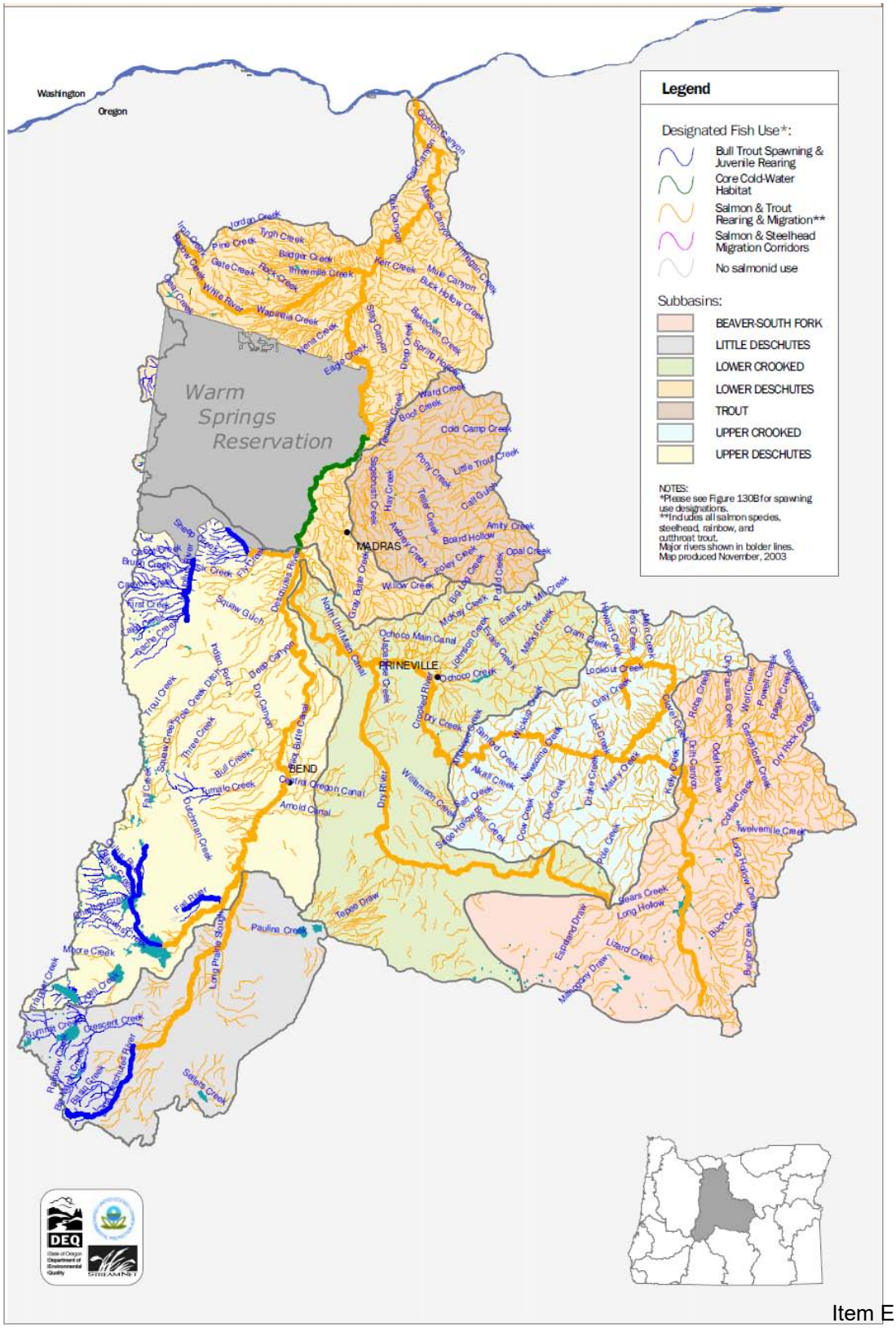
OAR 340-041-0130 – Figure 130A

Fish Use Designations
Deschutes Basin, Oregon



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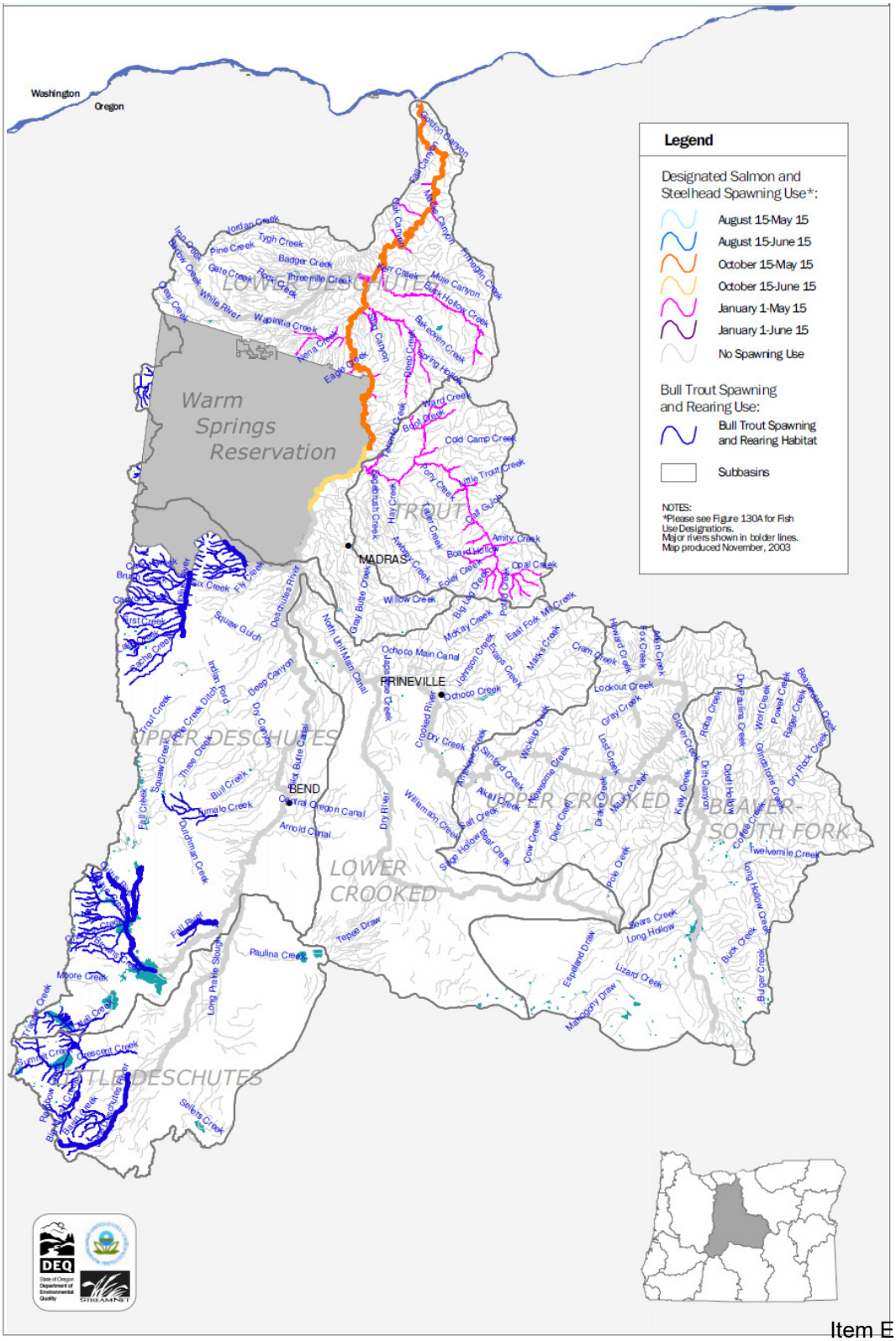
OAR 340-041-0130 – Figure 130B

Salmon and Steelhead Spawning Use Designations
Deschutes Basin, Oregon



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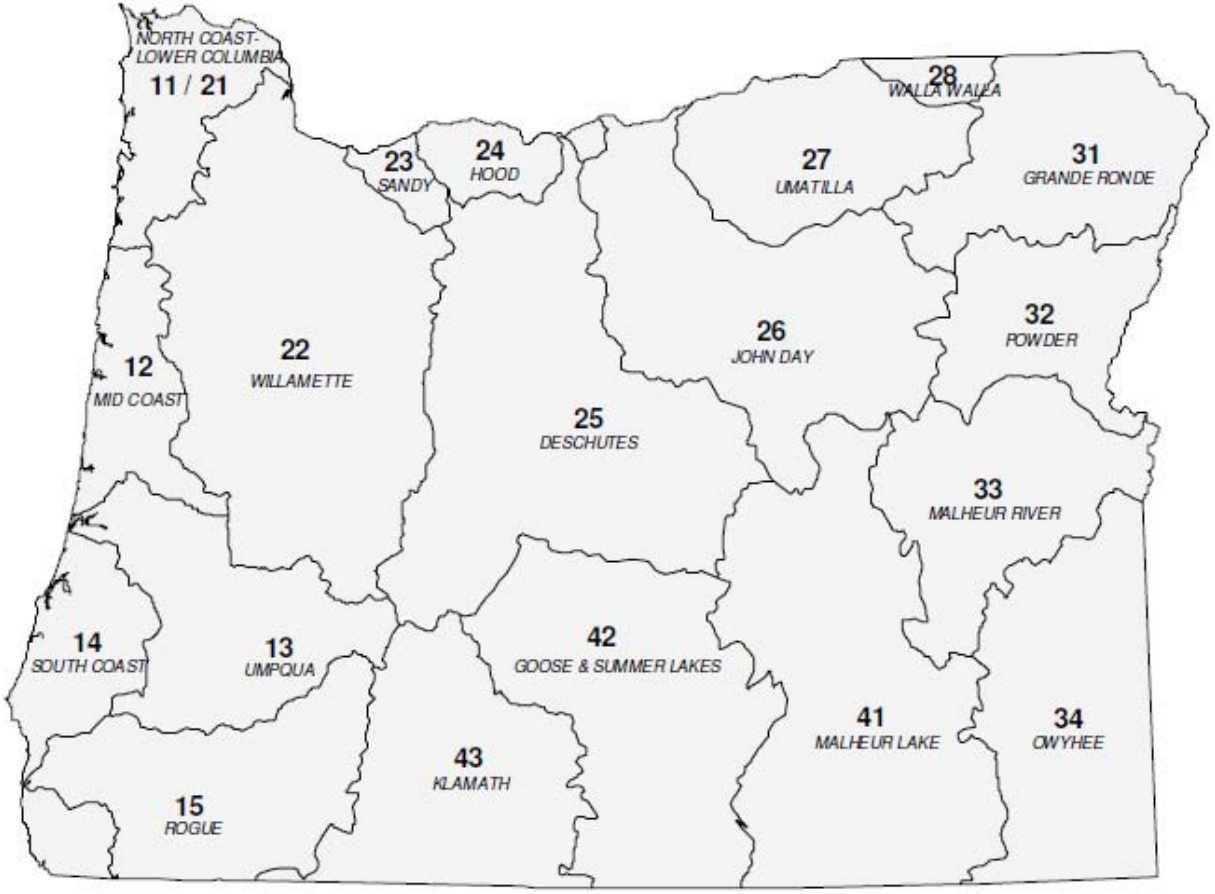
OAR 340-041-0140
Tables and Figures

Figure 1: Oregon Basin Index Map



Basin Name	Basin #	OAR #
DESCHUTES	25	340-041-0130
GOOSE & SUMMER LKS	42	340-041-0140
GRANDE RONDE	31	340-041-0151
HOOD	24	340-041-0160
JOHN DAY	26	340-041-0170
KLAMATH	43	340-041-0180
MALHEUR LAKE	41	340-041-0190
MALHEUR RIVER	33	340-041-0201
MD COAST	12	340-041-0220
NORTH COAST-LWR COL	11-21	340-041-0230
OWYHEE	34	340-041-0250
POWDER	32	340-041-0260
ROGUE	15	340-041-0271
SANDY	23	340-041-0286
SOUTH COAST	14	340-041-0300
UMATILLA	27	340-041-0310
UMPQUA	13	340-041-0320
WALLA WALLA	28	340-041-0330
WILLAMETTE	22	340-041-0340

OAR 340-041-0140
Table 140A
Designated Beneficial Uses
Goose and Summer Lakes Basin

Beneficial Uses	Goose Lake	Freshwater Lakes & Reservoirs	Highly Alkaline & Saline Lakes	Freshwater Streams
Public Domestic Water Supply[1]		X		X
Private Domestic Water Supply[1]		X		X
Industrial Water Supply		X	X	X
Irrigation		X		X
Livestock Watering	X	X		X
Fish & Aquatic Life[2]	X	X	X	X
Wildlife & Hunting	X	X	X	X
Fishing	X	X	X	X
Boating	X	X	X	X
Water Contact Recreation	X	X	X	X
Aesthetic Quality	X	X	X	X
Hydro Power				
Commercial Navigation & Transportation				

[1] With adequate pretreatment (filtration and disinfection) and natural quality to meet drinking water standards.

[2] See also Table 140B for fish use designations for this basin.

OAR 340-041-0140
Table 140B
Beneficial Use Designations – Fish Uses
Goose and Summer Lakes Basin, Oregon

Geographic Extent of Use	Redband or Lahontan Cutthroat Trout (20°C)	Cool Water Species (No Salmonid Use)
Summer Lake Subbasin		
Ft. Rock subbasin*: Silver Creek, Buck Creek and Bridge Creek	X	
Ft. Rock subbasin*: all other streams		X
Alkali Lake subbasin*		X
All other Summer Lake subbasin streams	X	
All other Goose and Summer Lakes basin streams within Oregon	X	
All other Highly Alkaline & Saline Lakes in this basin.		X

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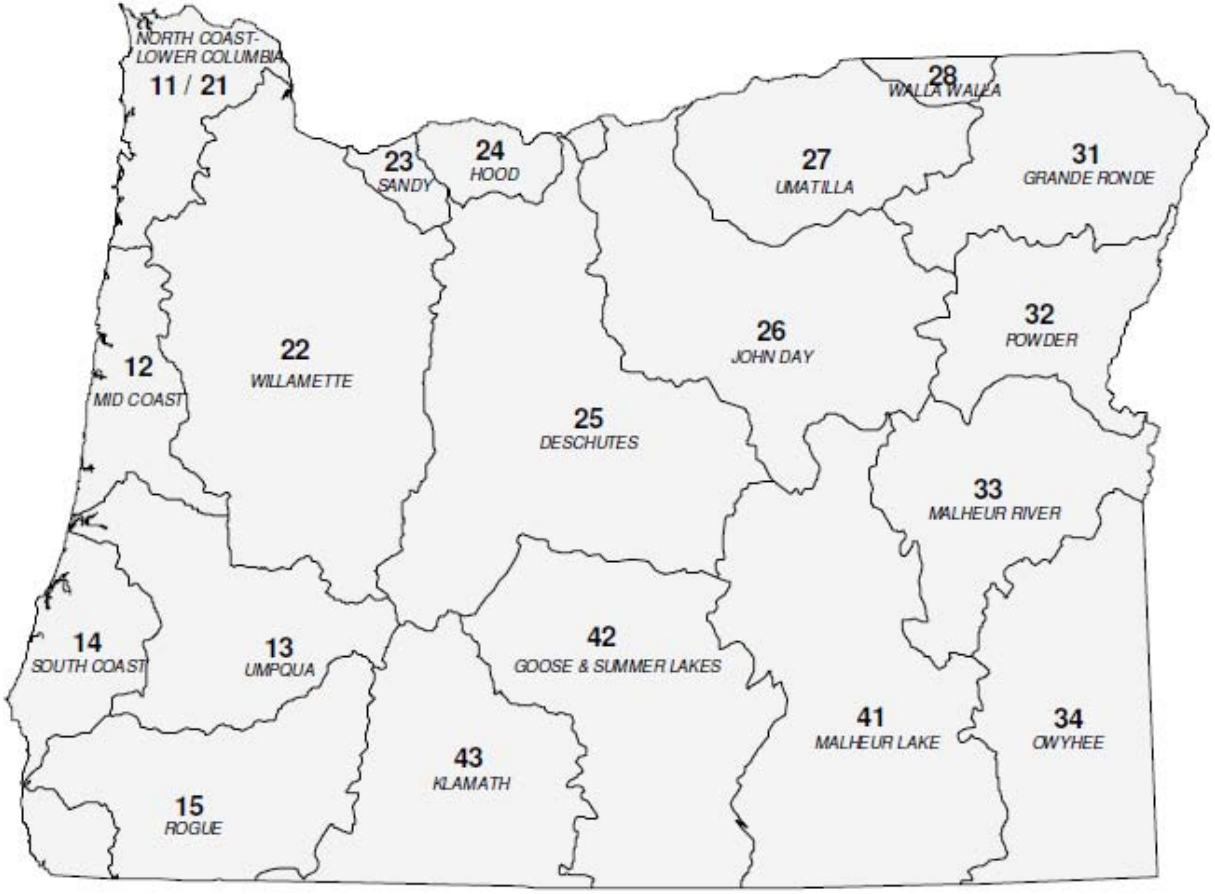
OAR 340-041-0151
Tables and Figures

Figure 1: Oregon Basin Index Map



Basin Name	Basin #	OAR #
DESCHUTES	25	340-041-0130
GOOSE & SUMMER LKS	42	340-041-0140
GRANDE RONDE	31	340-041-0151
HOOD	24	340-041-0160
JOHN DAY	26	340-041-0170
KLAMATH	43	340-041-0180
MALHEUR LAKE	41	340-041-0190
MALHEUR RIVER	33	340-041-0201
MD COAST	12	340-041-0220
NORTH COAST-LWR COL	11-21	340-041-0230
OWYHEE	34	340-041-0250
POWDER	32	340-041-0260
ROGUE	15	340-041-0271
SANDY	23	340-041-0286
SOUTH COAST	14	340-041-0300
UMATILLA	27	340-041-0310
UMPQUA	13	340-041-0320
WALLA WALLA	28	340-041-0330
WILLAMETTE	22	340-041-0340

OAR 340-041-0151
Table 151A
Designated Beneficial Uses
Grand Ronde Basin

Beneficial Uses	Main Stem Grand Ronde River (RM 39 to 165)	All Other Basin Waters
Public Domestic Water Supply[1]	X	X
Private Domestic Water Supply[1]	X	X
Industrial Water Supply	X	X
Irrigation	X	X
Livestock Watering	X	X
Fish & Aquatic Life[2]	X	X
Wildlife & Hunting	X	X
Fishing	X	X
Boating	X	X
Water Contact Recreation	X	X
Aesthetic Quality	X	X
Hydro Power	X	X
Commercial Navigation & Transportation		

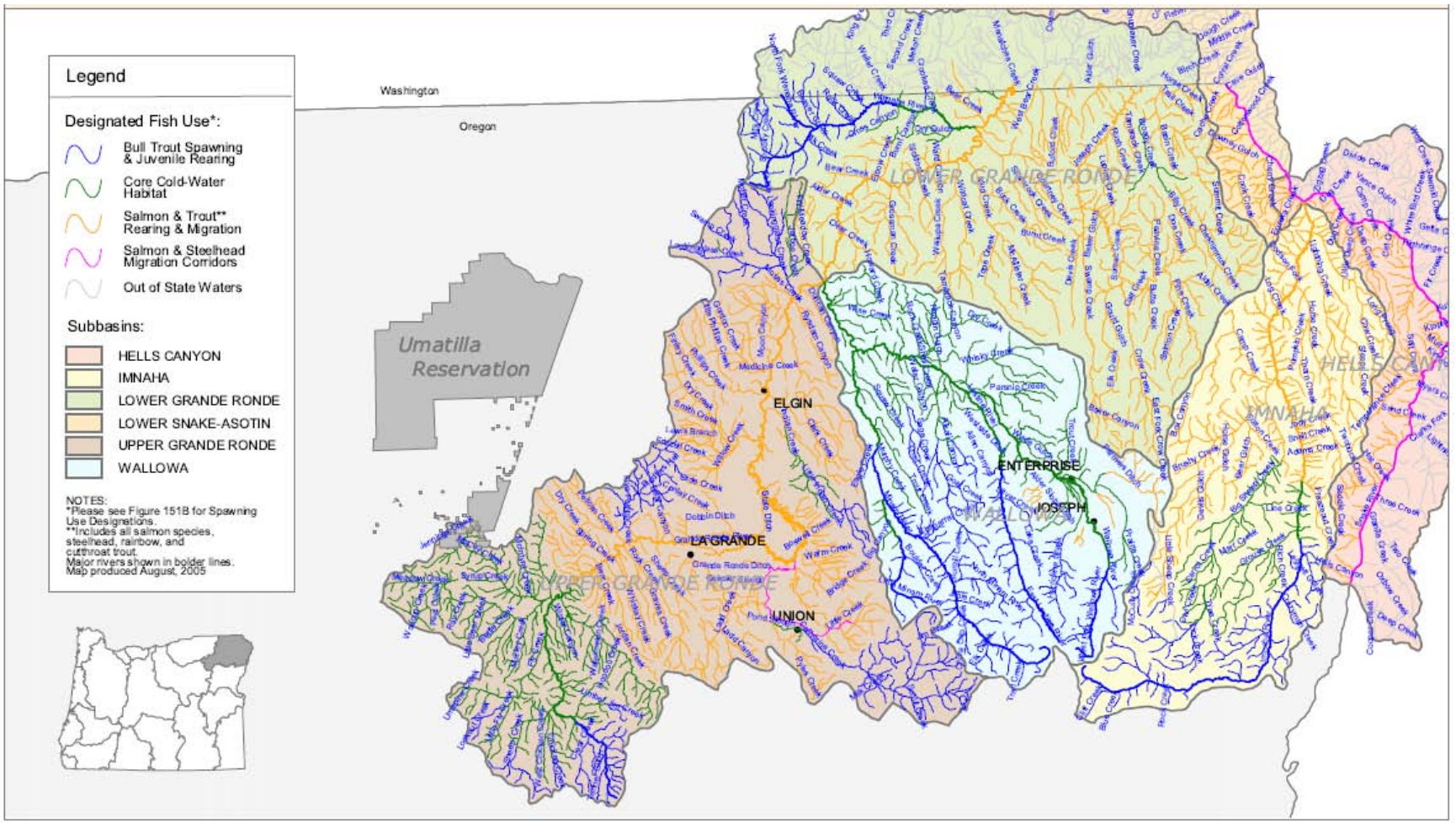
[1] With adequate pretreatment (filtration and disinfection) and natural quality to meet drinking water standards.

[2] See also Figures 151A and 151B for fish use designations for this basin.

State of Oregon Department of Environmental Quality

OAR 340-041-0151

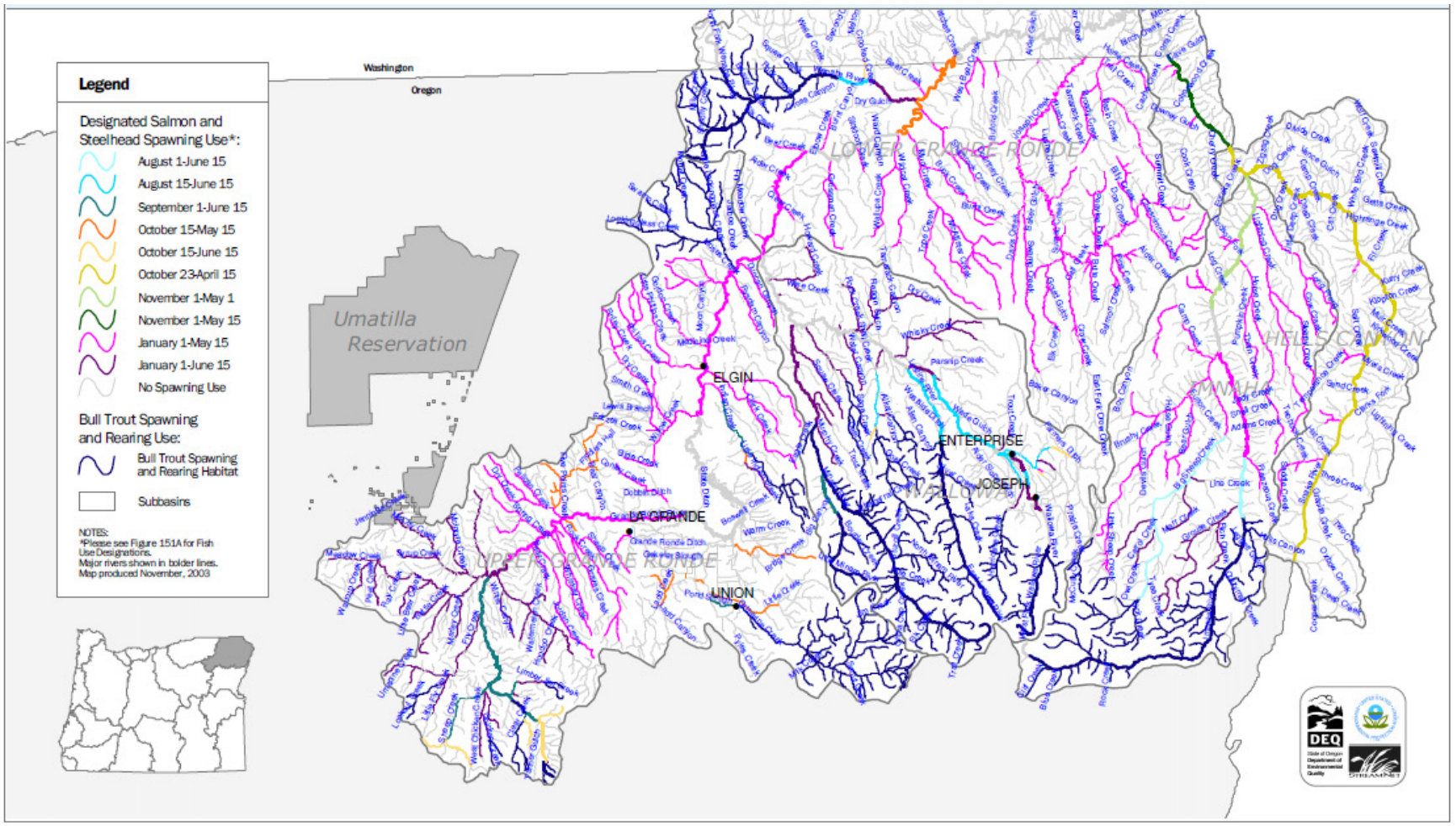
Figure 151A: Fish Use Designations*
Grande Ronde Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0151

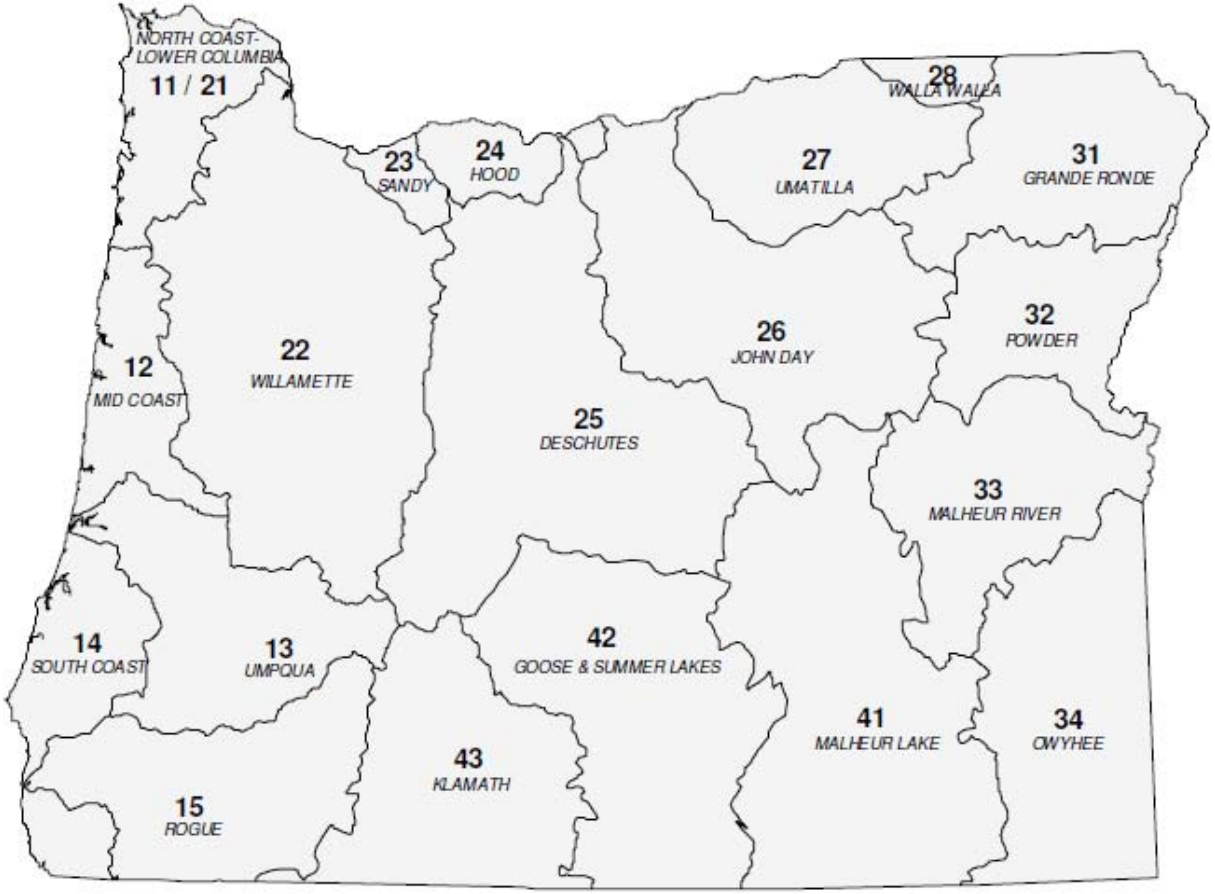
Figure 151B: Salmon and Steelhead Use Designations*
Grande Ronde Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0160
Tables and Figures

Figure 1: Oregon Basin Index Map



Basin Name	Basin #	OAR #
DESCHUTES	25	340-041-0130
GOOSE & SUMMER LKS	42	340-041-0140
GRANDE RONDE	31	340-041-0151
HOOD	24	340-041-0160
JOHN DAY	26	340-041-0170
KLAMATH	43	340-041-0180
MALHEUR LAKE	41	340-041-0190
MALHEUR RIVER	33	340-041-0201
MD COAST	12	340-041-0220
NORTH COAST-LWR COL	11-21	340-041-0230
OWYHEE	34	340-041-0250
POWDER	32	340-041-0260
ROGUE	15	340-041-0271
SANDY	23	340-041-0286
SOUTH COAST	14	340-041-0300
UMATILLA	27	340-041-0310
UMPQUA	13	340-041-0320
WALLA WALLA	28	340-041-0330
WILLAMETTE	22	340-041-0340

OAR 340-041-0160
Table 160A
Designated Beneficial Uses
Hood Basin

Beneficial Uses	Hood River Basin Streams
Public Domestic Water Supply[1]	X
Private Domestic Water Supply[1]	X
Industrial Water Supply	X
Irrigation	X
Livestock Watering	X
Fish & Aquatic Life[2]	X
Wildlife & Hunting	X
Fishing	X
Boating	X
Water Contact Recreation	X
Aesthetic Quality	X
Hydro Power	X
Commercial Navigation & Transportation	

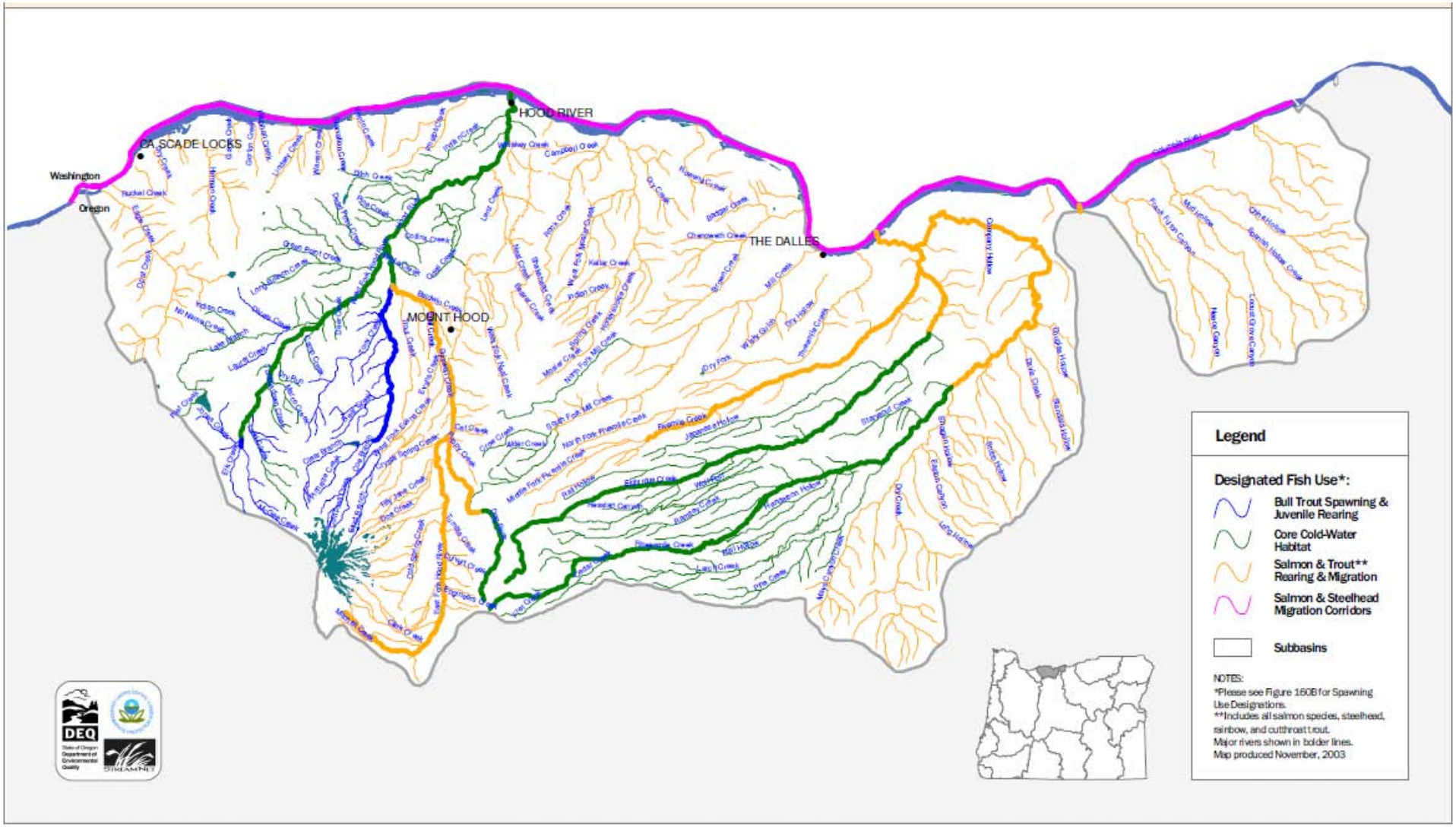
[1] With adequate pretreatment (filtration & disinfection) and natural quality to meet drinking water standards.

[2] See also Figures 160A and 160B for fish use designations for this basin.

State of Oregon Department of Environmental Quality

OAR 340-041-0160

Figure 160A: Fish Use Designations*
Hood Basin, Oregon



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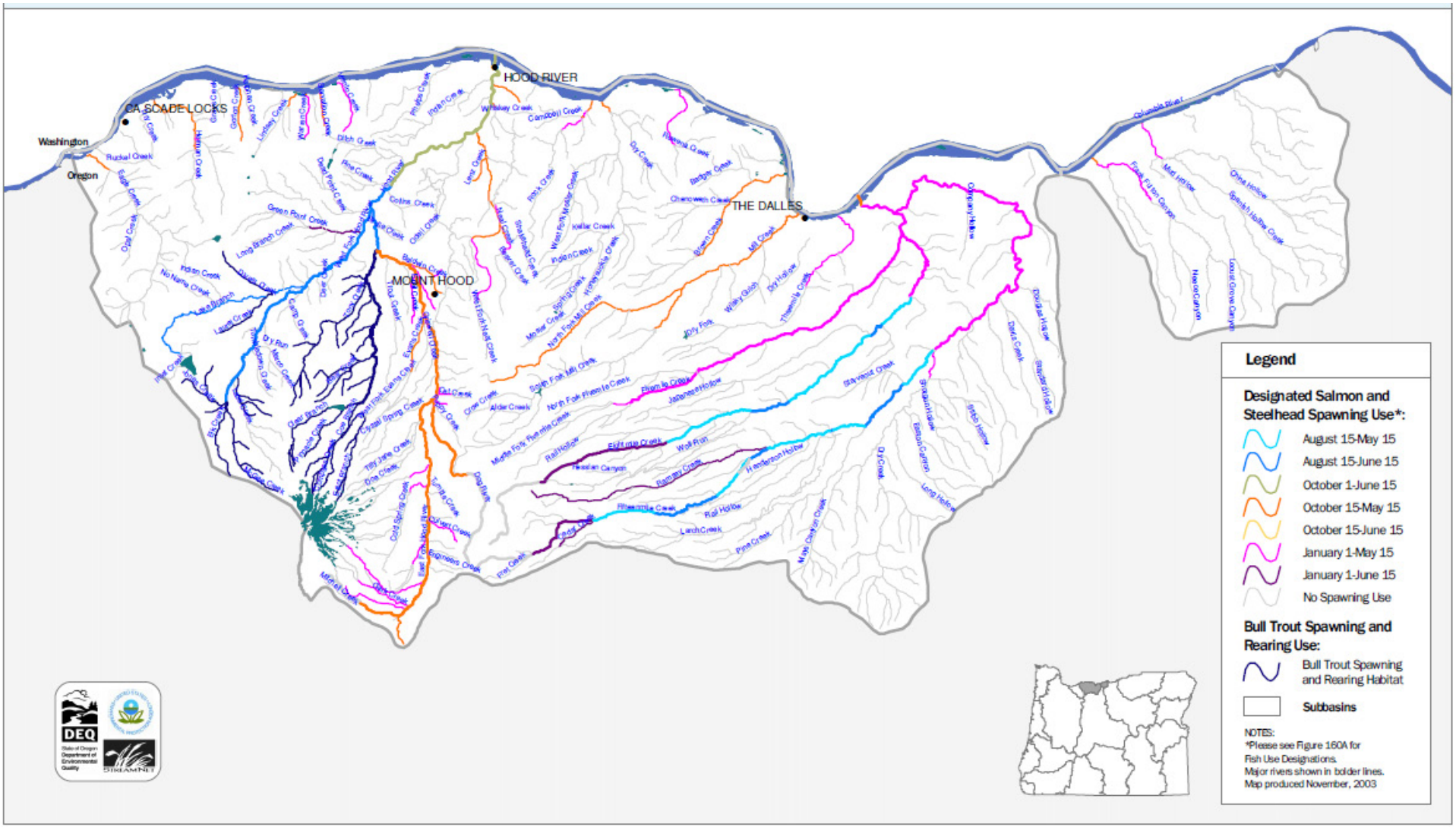
OAR 340-041-0160

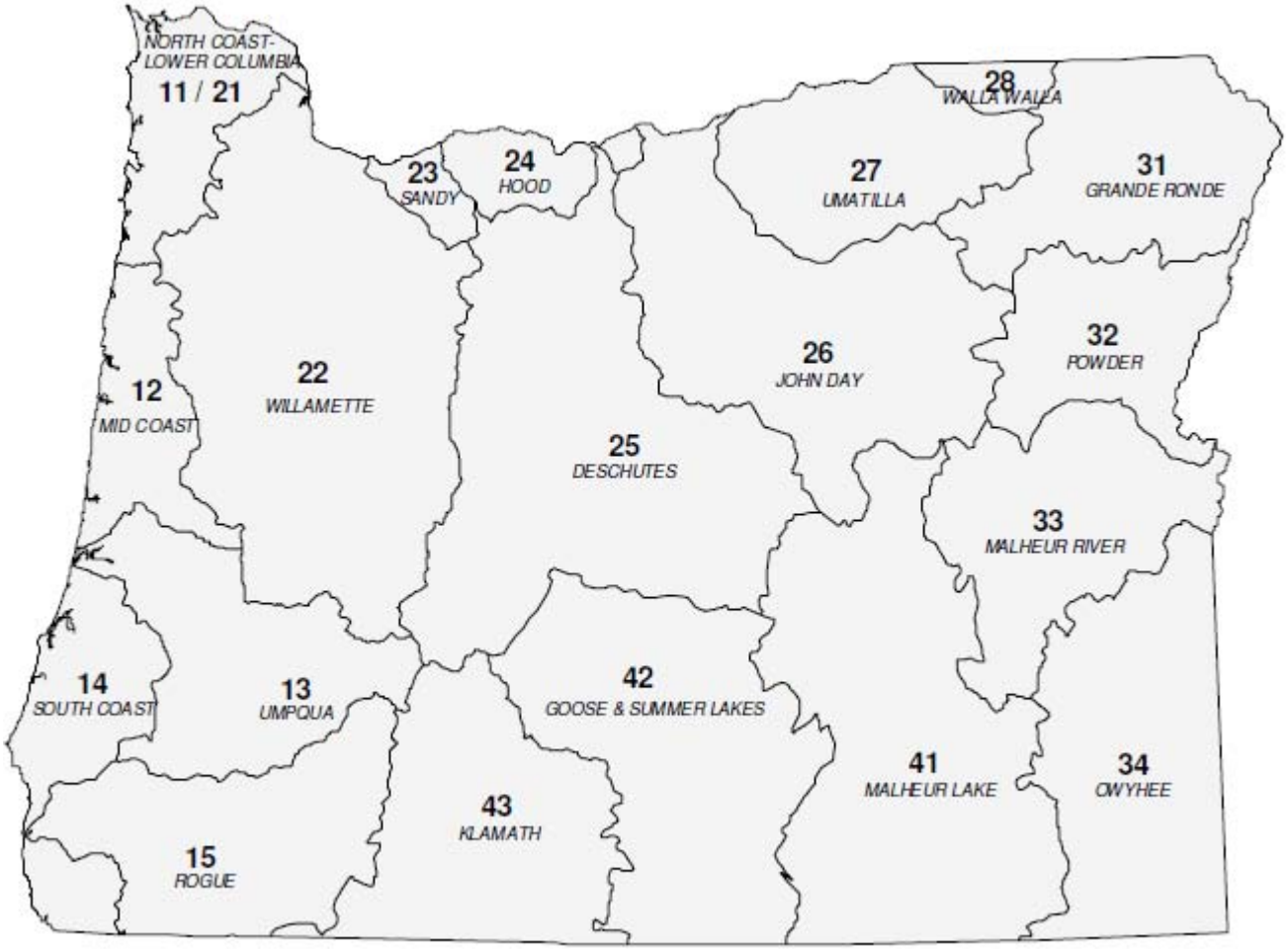
Figure 160B: Salmon and Steelhead Spawning Use Designations*
Hood Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0170
Tables and Figures

Figure 1: Oregon Basin Index Map

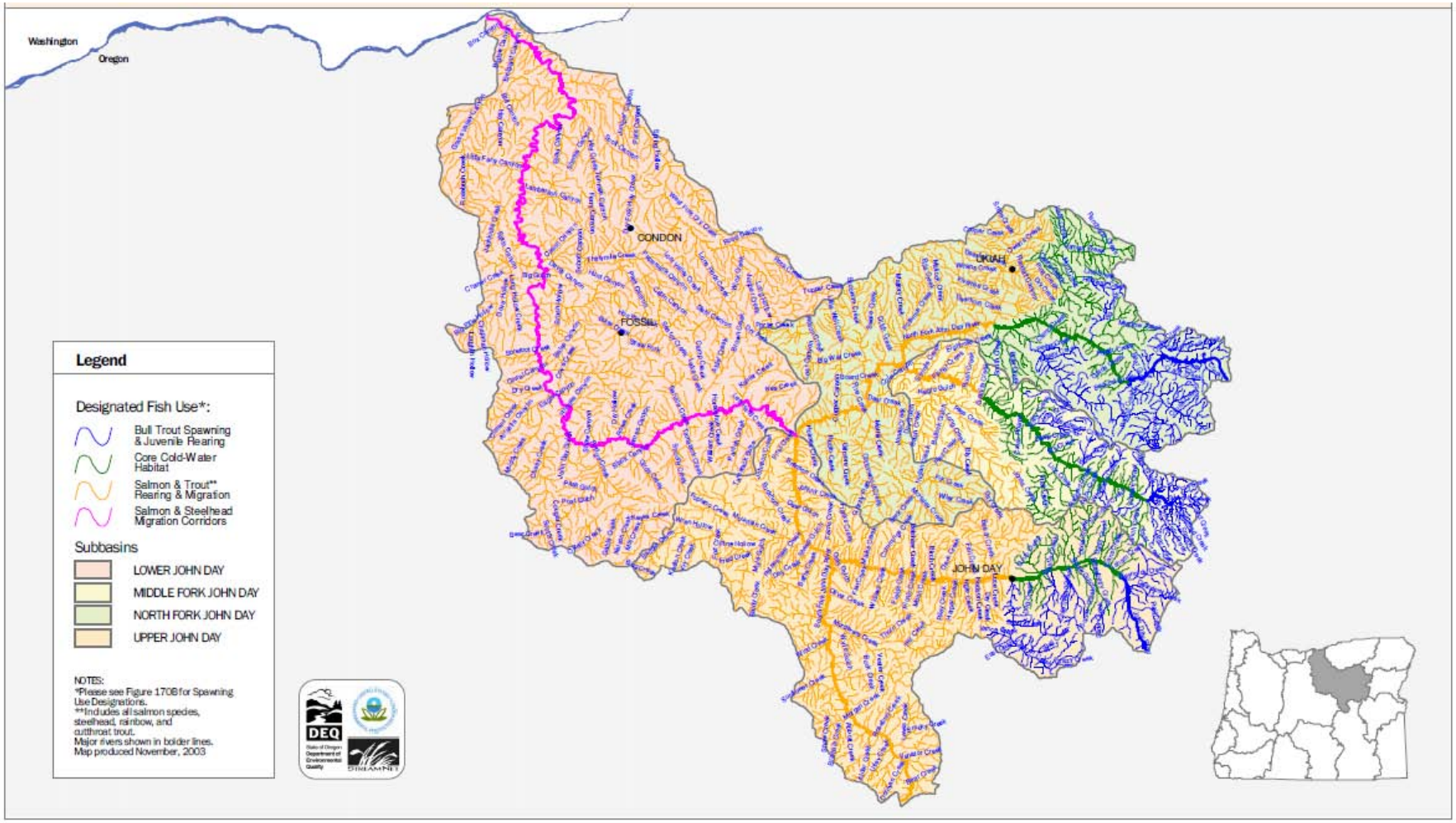


Basin Name	Basin #	OAR #
DESCHUTES	25	340-041-0130
GOOSE & SUMMER LKS	42	340-041-0140
GRANDE RONDE	31	340-041-0151
HOOD	24	340-041-0160
JOHN DAY	26	340-041-0170
KLAMATH	43	340-041-0180
MALHEUR LAKE	41	340-041-0190
MALHEUR RIVER	33	340-041-0201
MD COAST	12	340-041-0220
NORTH COAST-LWR COL	11-21	340-041-0230
OWYHEE	34	340-041-0250
POWDER	32	340-041-0260
ROGUE	15	340-041-0271
SANDY	23	340-041-0286
SOUTH COAST	14	340-041-0300
UMATILLA	27	340-041-0310
UMPQUA	13	340-041-0320
WALLA WALLA	28	340-041-0330
WILLAMETTE	22	340-041-0340

State of Oregon Department of Environmental Quality

OAR 340-041-0170

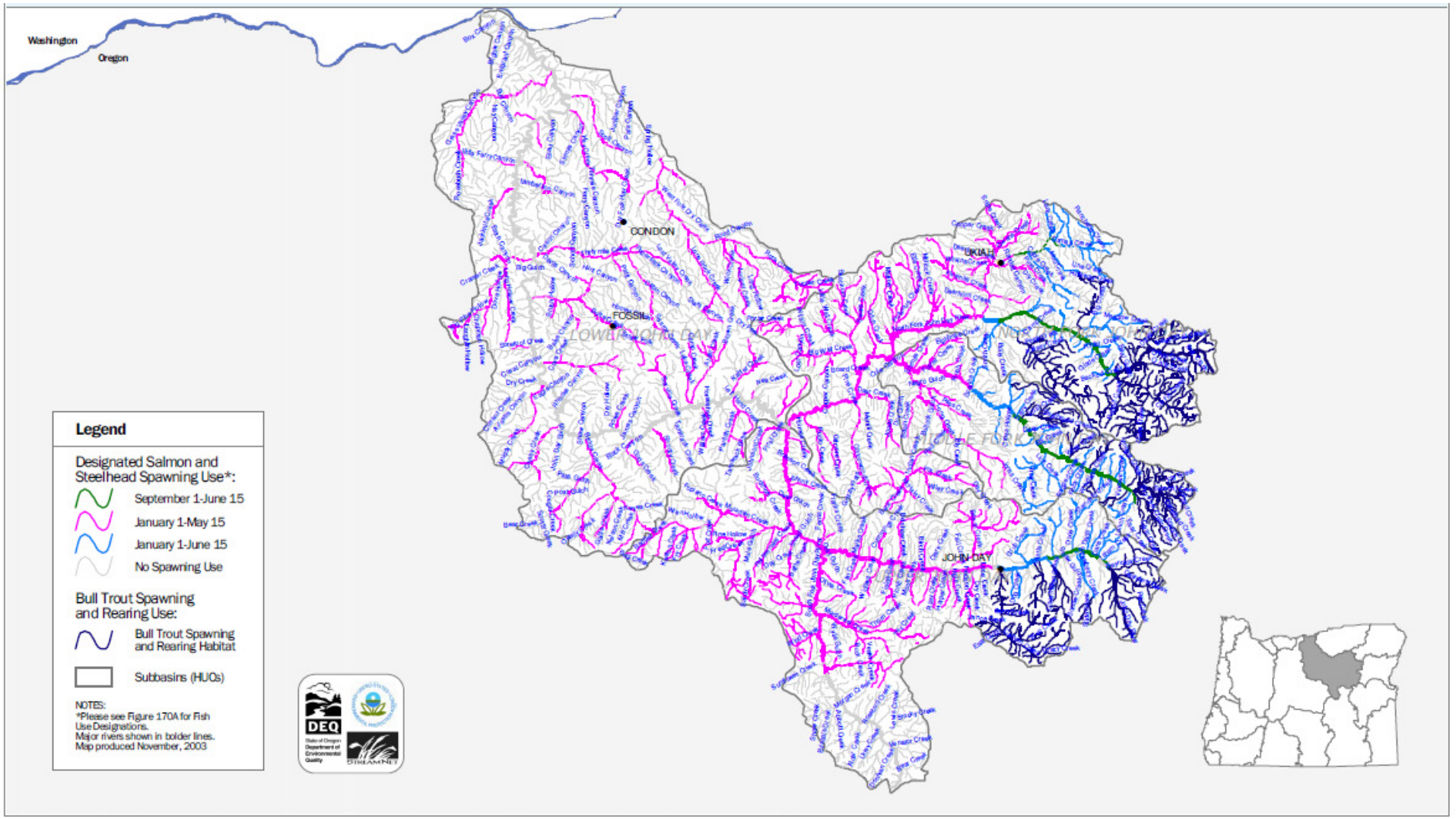
Figure 170A: Fish Use Designations*
John Day Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0170

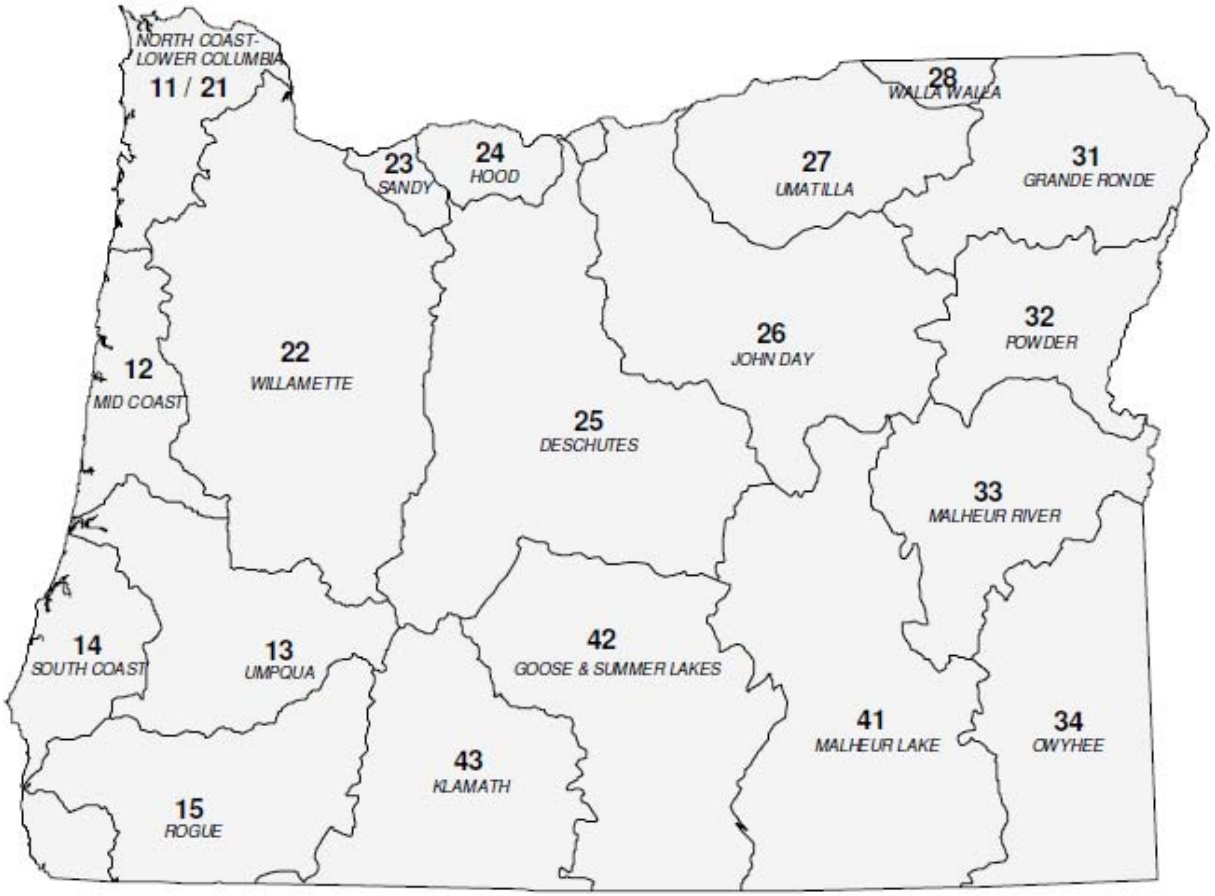
Figure 170B: Salmon and Steelhead Use Designations*
John Day Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0180
Tables and Figures

Figure 1: Oregon Basin Index Map



Basin Name	Basin #	OAR #
DESCHUTES	25	340-041-0130
GOOSE & SUMMER LKS	42	340-041-0140
GRANDE RONDE	31	340-041-0151
HOOD	24	340-041-0160
JOHN DAY	26	340-041-0170
KLAMATH	43	340-041-0180
MALHEUR LAKE	41	340-041-0190
MALHEUR RIVER	33	340-041-0201
MD COAST	12	340-041-0220
NORTH COAST-LWR COL	11-21	340-041-0230
OWYHEE	34	340-041-0250
POWDER	32	340-041-0260
ROGUE	15	340-041-0271
SANDY	23	340-041-0286
SOUTH COAST	14	340-041-0300
UMATILLA	27	340-041-0310
UMPQUA	13	340-041-0320
WALLA WALLA	28	340-041-0330
WILLAMETTE	22	340-041-0340

OAR 340-041-0180
Table 180A
Designated Beneficial Uses
Klamath Basin

Beneficial Uses	Klamath River from Klamath Lake to Keno Dam (RM 255 to 232.5)	Lost River (Rm 5 to 65) & Lost River Diversion Channel	All Other Basin Waters
Public Domestic Water Supply[1]	X	X	X
Private Domestic Water Supply[1]	X	X	X
Industrial Water Supply	X	X	X
Irrigation	X	X	X
Livestock Watering	X	X	X
Fish & Aquatic Life[2]	X	X	X
Wildlife & Hunting	X	X	X
Fishing	X	X	X
Boating	X	X	X
Water Contact Recreation	X	X	X
Aesthetic Quality	X	X	X
Hydro Power	X		
Commercial Navigation & Transportation	X		

[1] With adequate pretreatment (filtration & disinfection) and natural quality to meet drinking water standards.

[2] See also Figure 180A for fish use designations for this basin.

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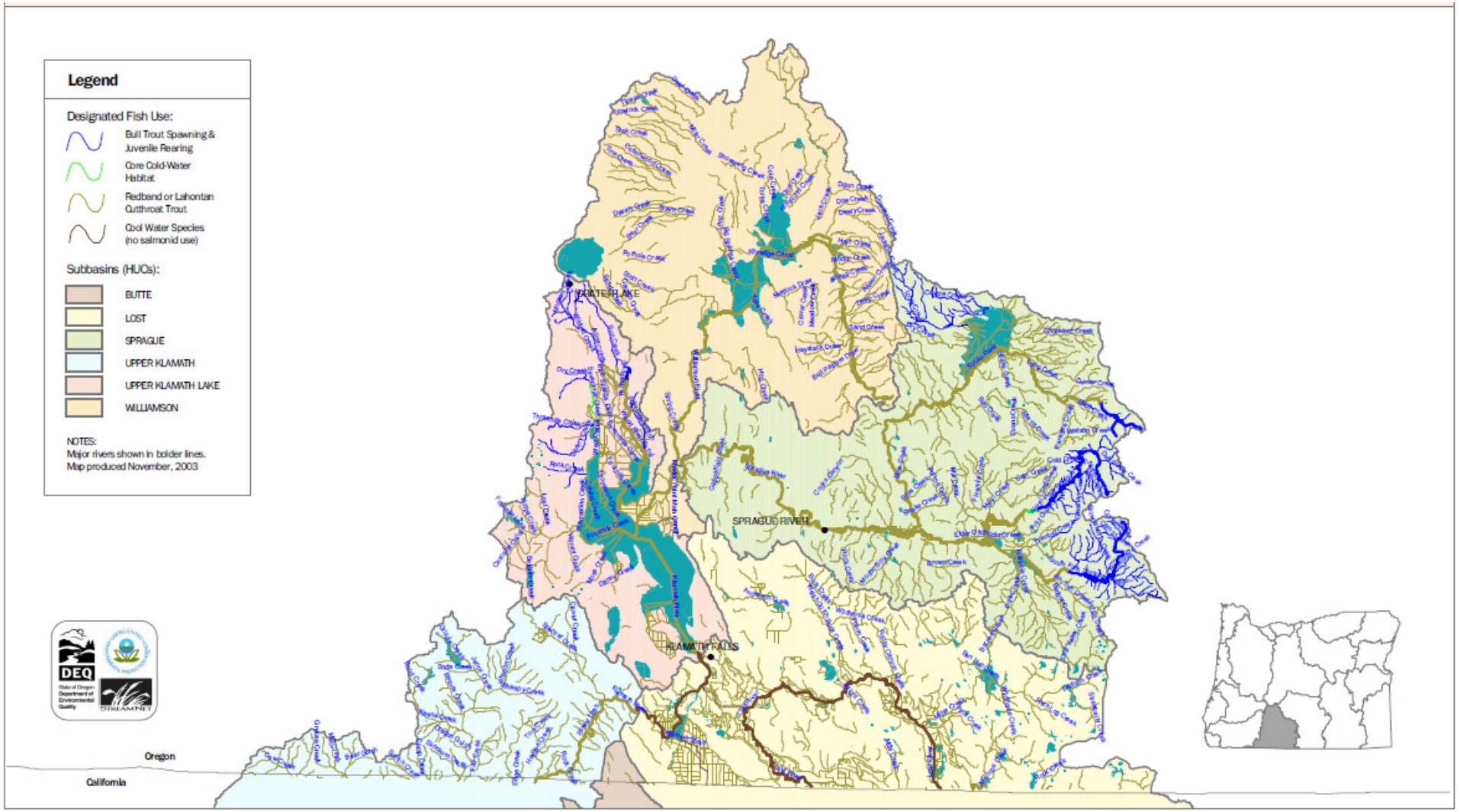
OAR 340-041-0180

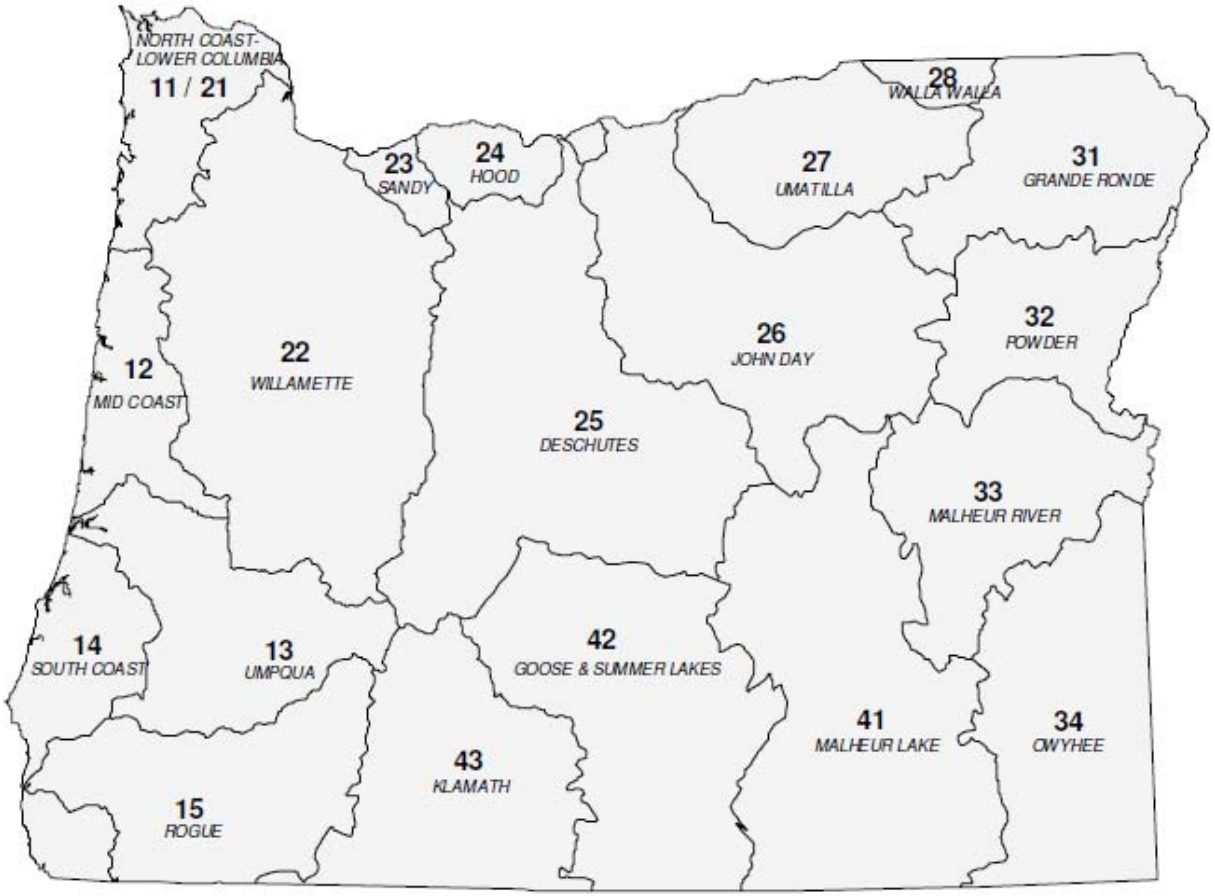
Figure 180A: Fish Use Designations Klamath Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0190
Tables and Figures

Figure 1: Oregon Basin Index Map



Basin Name	Basin #	OAR #
DESCHUTES	25	340-041-0130
GOOSE & SUMMER LKS	42	340-041-0140
GRANDE RONDE	31	340-041-0151
HOOD	24	340-041-0160
JOHN DAY	26	340-041-0170
KLAMATH	43	340-041-0180
MALHEUR LAKE	41	340-041-0190
MALHEUR RIVER	33	340-041-0201
MD COAST	12	340-041-0220
NORTH COAST-LWR COL	11-21	340-041-0230
OWYHEE	34	340-041-0250
POWDER	32	340-041-0260
ROGUE	15	340-041-0271
SANDY	23	340-041-0286
SOUTH COAST	14	340-041-0300
UMATILLA	27	340-041-0310
UMPQUA	13	340-041-0320
WALLA WALLA	28	340-041-0330
WILLAMETTE	22	340-041-0340

OAR 340-041-0190
Table 190A
Designated Beneficial Uses
Malheur Lake Basin

Beneficial Uses	Natural Lakes	All Rivers & Tributaries
Public Domestic Water Supply[1]		X
Private Domestic Water Supply[1]		X
Industrial Water Supply		X
Irrigation	X	X
Livestock Watering	X	X
Fish & Aquatic Life[2]	X	X
Wildlife & Hunting	X	X
Fishing	X	X
Boating	X	X
Water Contact Recreation	X	X
Aesthetic Quality	X	X
Hydro Power		
Commercial Navigation & Transportation		

[1] With adequate pretreatment (filtration & disinfection) and natural quality to meet drinking water standards.
[2] See also Table 190B for fish use designations for this basin.

OAR 340-041-0190 - Table 190B
Beneficial Use Designations – Fish Uses Malheur Lake Basin, Oregon

Geographic Extent of Use	Redband and Hybrid Trout (20°C)	Lahontan Trout* (20°C)	Borax Lake Chub	Cool Water Species (no salmonid use)
Alvord Lake Subbasin				
Waters associated with Borax Lake and Lower Borax Lake, including lake outflows, Harney County, Oregon.			X	
Willow Creek from headwaters to the Willow Creek Well.		X		
Little Whitehorse Creek from headwaters to confluence with Whitehorse Creek		X		
Whitehorse Creek from headwaters to confluence with East Channel; including upper tributaries Little Whitehorse Creek, Cottonwood Creek and Doolittle Creek		X		
Antelope Creek from headwaters to confluence with unnamed tributary, approximately 4 RM upstream of confluence with Little Antelope Creek		X		
Denio Creek from headwaters to mouth		X		

OAR 340-041-0190 - Table 190B
Beneficial Use Designations – Fish Uses Malheur Lake Basin, Oregon

Geographic Extent of Use	Redband and Hybrid Trout (20°C)	Lahontan Trout* (20°C)	Borax Lake Chub	Cool Water Species (no salmonid use)
Alvord Lake Subbasin				
Van Horn Creek from headwaters to mouth		X		
Group of streams NE of Alvord Desert: Pike Creek, Little Alvord Creek, Big Alvord Creek, Cottonwood, Willow Creek, Mesquito Creek, Bueno Vista Creek, and Little McCoy Creek		X		
Mann Creek from headwaters to mouth, House Creek from headwaters to mouth	X			
Little Trout Creek and Big Trout Creek from headwaters to confluences with Trout Creek	X			
Segment of Trout Creek from confluence with Big Trout Creek to confluence with Stoney Creek	X			
Pueblo Slough, from Tum-Tum Lake to Van Horn Creek				X (Alvord Chub)

OAR 340-041-0190 - Table 190B
Beneficial Use Designations – Fish Uses Malheur Lake Basin, Oregon

Geographic Extent of Use	Redband and Hybrid Trout (20°C)	Lahontan Trout* (20°C)	Borax Lake Chub	Cool Water Species (no salmonid use)
Alvord Lake Subbasin				
Segment of Trout Creek from confluence with Stoney Creek to approximately 12 RM upstream of Alvord Lake; Segment of South Fork Trout Creek from confluence with Trout Creek upstream approximately 2 RM; Alvord Lake				X (Alvord Chub)
All other Alvord Lake subbasin waters				X (no fish use)
Upper Quinn Subbasin				
Indian Creek from approximately 1.3 RM below headwaters to approximately .25 RM below confluence with Spring Creek (approximately 5.1 RM total)	X			
Sage Creek from headwaters to mouth		X		

OAR 340-041-0190 - Table 190B
Beneficial Use Designations – Fish Uses Malheur Lake Basin, Oregon

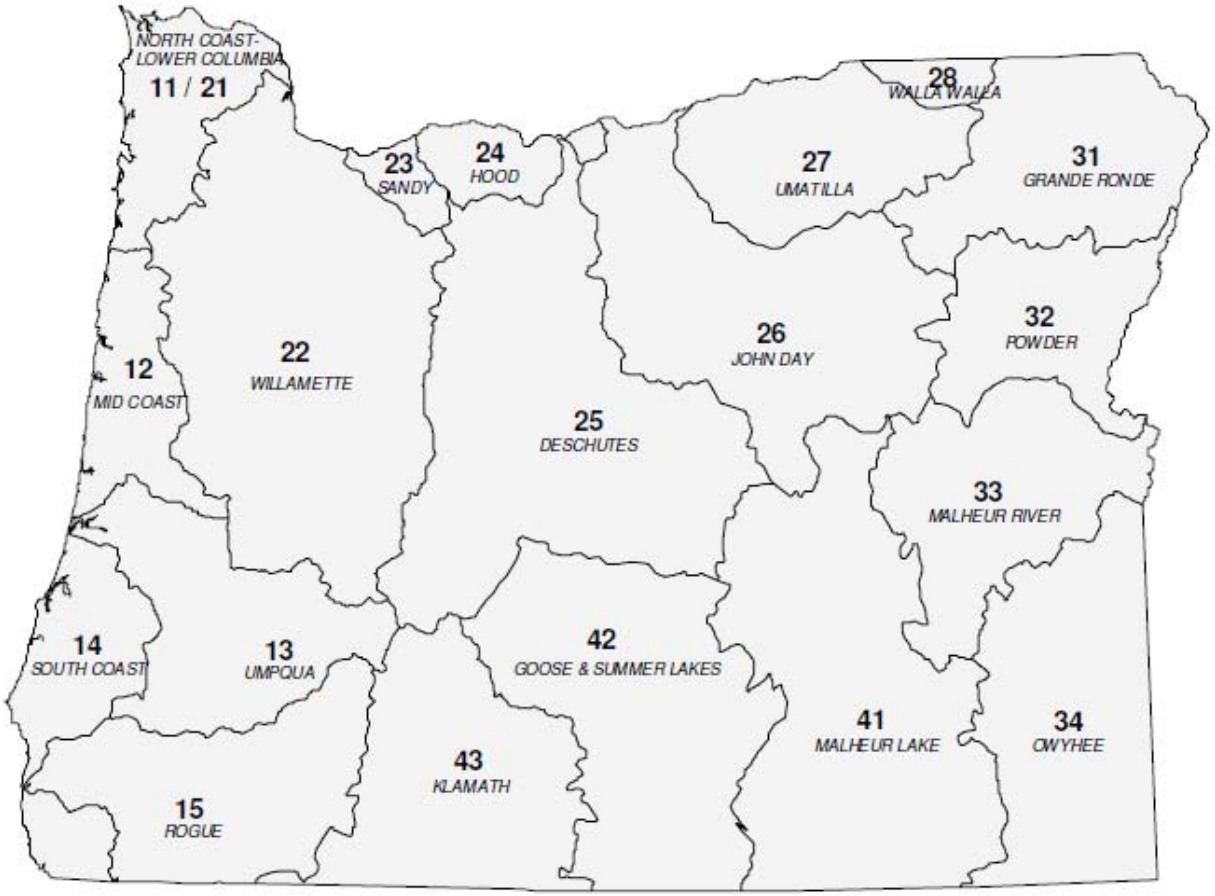
Geographic Extent of Use	Redband and Hybrid Trout (20°C)	Lahontan Trout* (20°C)	Borax Lake Chub	Cool Water Species (no salmonid use)
Upper Quinn Subbasin				
Line Canyon Creek from headwaters to mouth		X		
All other Upper Quinn subbasin waters				X
All Other				
All other Malheur Lake Basin Waters (includes the Silver, Silvies, Harney-Malheur, Donner and Blitzen, Guano, and Thousand-Virgin subbasins)	X			

*Spawning in these reaches occurs April 1-July 15.

State of Oregon Department of Environmental Quality

OAR 340-041-0201
Tables and Figures

Figure 1: Oregon Basin Index Map



Basin Name	Basin #	OAR #
DESCHUTES	25	340-041-0130
GOOSE & SUMMER LKS	42	340-041-0140
GRANDE RONDE	31	340-041-0151
HOOD	24	340-041-0160
JOHN DAY	26	340-041-0170
KLAMATH	43	340-041-0180
MALHEUR LAKE	41	340-041-0190
MALHEUR RIVER	33	340-041-0201
MD COAST	12	340-041-0220
NORTH COAST-LWR COL	11-21	340-041-0230
OWYHEE	34	340-041-0250
POWDER	32	340-041-0260
ROGUE	15	340-041-0271
SANDY	23	340-041-0286
SOUTH COAST	14	340-041-0300
UMATILLA	27	340-041-0310
UMPQUA	13	340-041-0320
WALLA WALLA	28	340-041-0330
WILLAMETTE	22	340-041-0340

OAR 340-041-0201
Table 201A
Designated Beneficial Uses
Malheur River Basin

Beneficial Uses	Malheur River (Namorf to Mouth) Willow Creek (Brogan to Mouth) Bully Creek (Reservoir to Mouth)	Willow Creek (Malheur Reservoir to Brogan) Malheur River (Beulah Dam & Warm Springs Dams to Namorf)	RESERVOIRS Malheur Bully Creek Beulah Warm Springs	Malheur River & Tributaries Upstream from Reservoirs
Public Domestic Water Supply[1]	X	X	X	X
Private Domestic Water Supply[1]	X	X	X	X
Industrial Water Supply	X	X	X	X
Irrigation	X	X	X	X
Livestock Watering	X	X	X	X
Fish & Aquatic Life[2]	X	X	X	X
Wildlife & Hunting	X	X	X	X
Fishing	X	X	X	X
Boating	X	X	X	X
Water Contact Recreation	X	X	X	X
Aesthetic Quality	X	X	X	X
Hydro Power				
Commercial Navigation & Transportation				

[1] With adequate pretreatment (filtration & disinfection) and natural quality to meet drinking water standards.
[2] See also Figure 201A for fish use designations for this basin.

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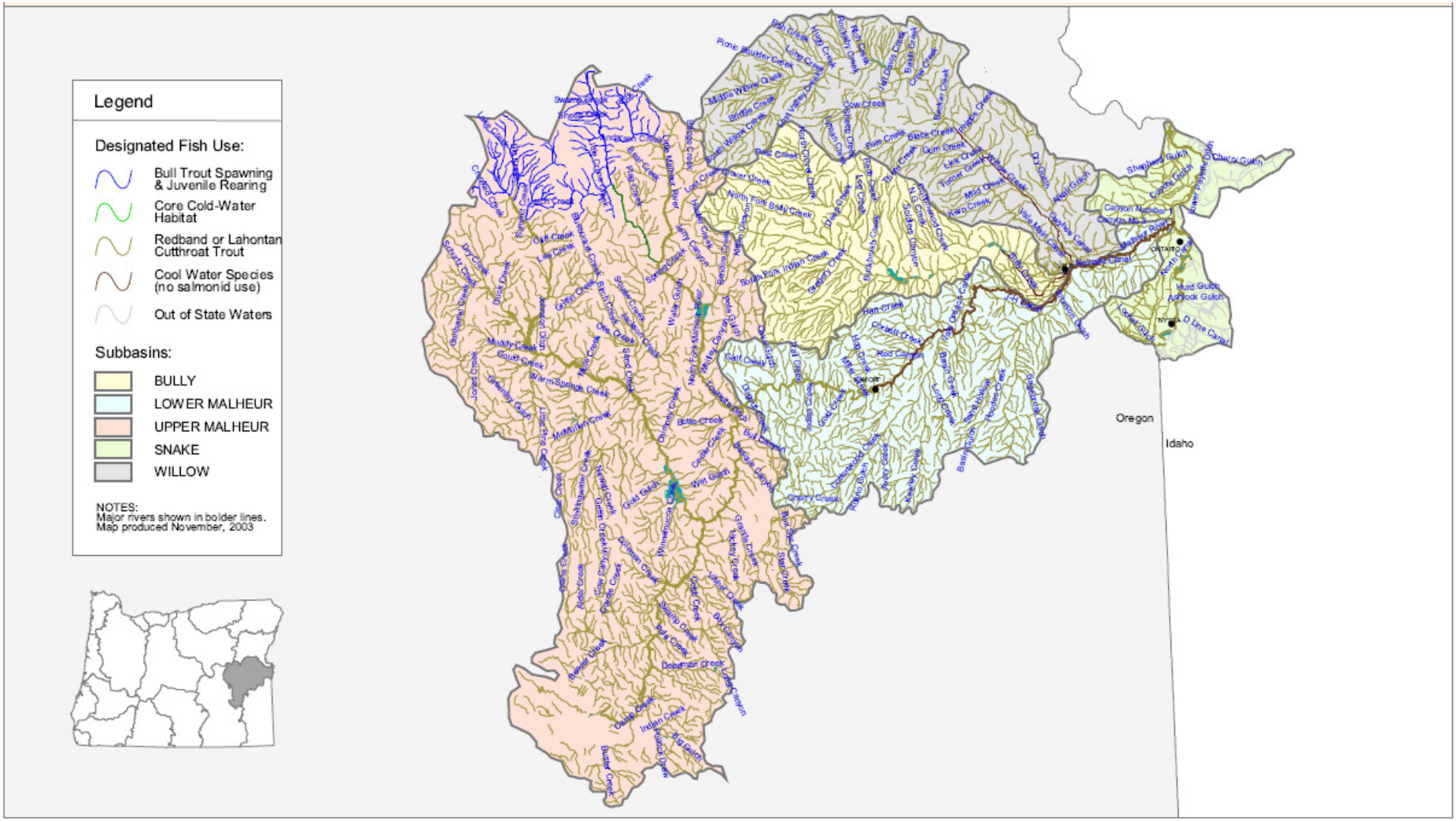
OAR 340-041-0201

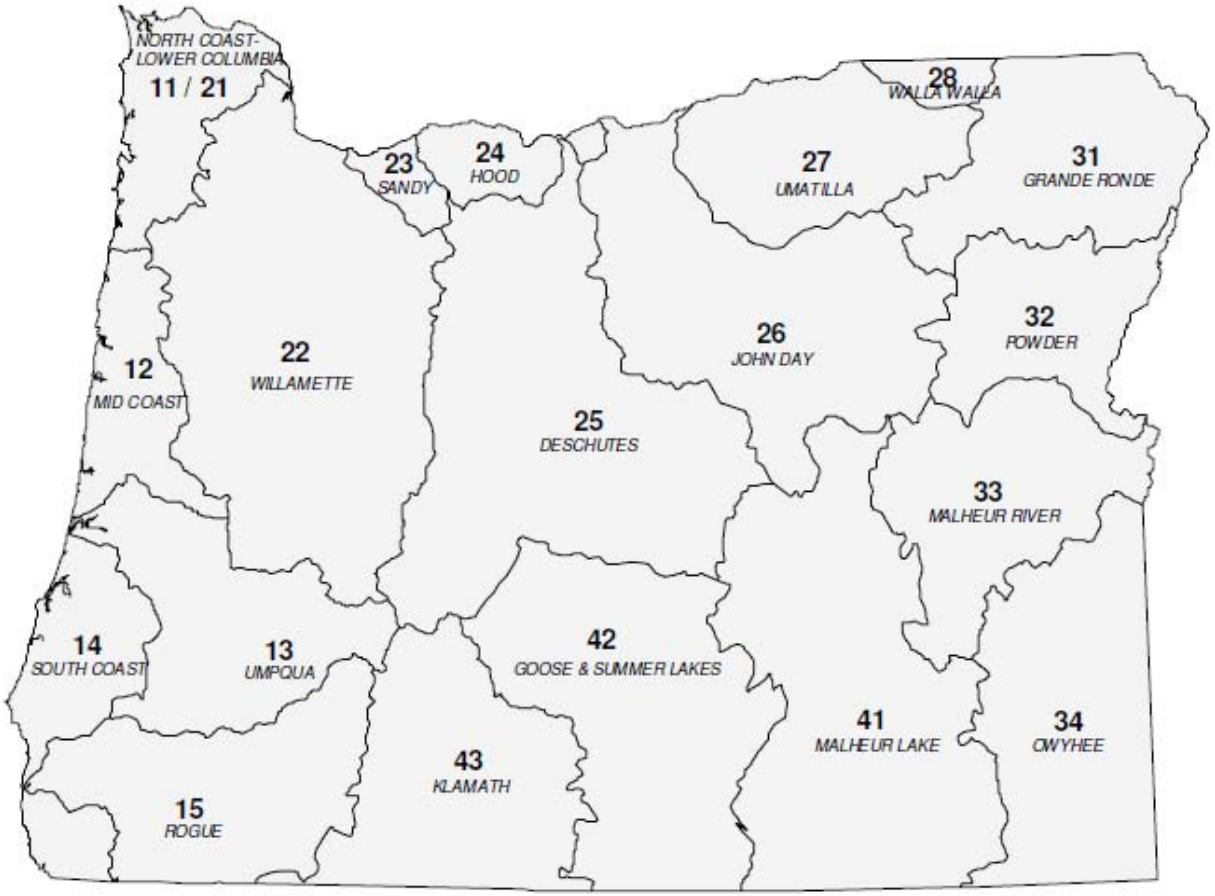
Figure 201A: Fish Use Designations
Malheur River Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0220
Tables and Figures

Figure 1: Oregon Basin Index Map



Basin Name	Basin #	OAR #
DESCHUTES	25	340-041-0130
GOOSE & SUMMER LKS	42	340-041-0140
GRANDE RONDE	31	340-041-0151
HOOD	24	340-041-0160
JOHN DAY	26	340-041-0170
KLAMATH	43	340-041-0180
MALHEUR LAKE	41	340-041-0190
MALHEUR RIVER	33	340-041-0201
MD COAST	12	340-041-0220
NORTH COAST-LWR COL	11-21	340-041-0230
OWYHEE	34	340-041-0250
POWDER	32	340-041-0260
ROGUE	15	340-041-0271
SANDY	23	340-041-0286
SOUTH COAST	14	340-041-0300
UMATILLA	27	340-041-0310
UMPQUA	13	340-041-0320
WALLA WALLA	28	340-041-0330
WILLAMETTE	22	340-041-0340

OAR 340-041-0220
Table 220A
Designated Beneficial Uses - Mid Coast Basin

Beneficial Uses	Estuaries & Adjacent Marine Waters	All Steams & Tributaries Thereto
Public Domestic Water Supply[1]		X
Private Domestic Water Supply[1]		X
Industrial Water Supply	X	X
Irrigation		X
Livestock Watering		X
Fish & Aquatic Life[2]	X	X
Wildlife & Hunting	X	X
Fishing[3]	X	X
Boating	X	X
Water Contact Recreation[3]	X	X
Aesthetic Quality	X	X
Hydro Power		X
Commercial Navigation & Transportation	X	

[1] With adequate pretreatment (filtration & disinfection) and natural quality to meet drinking water standards.

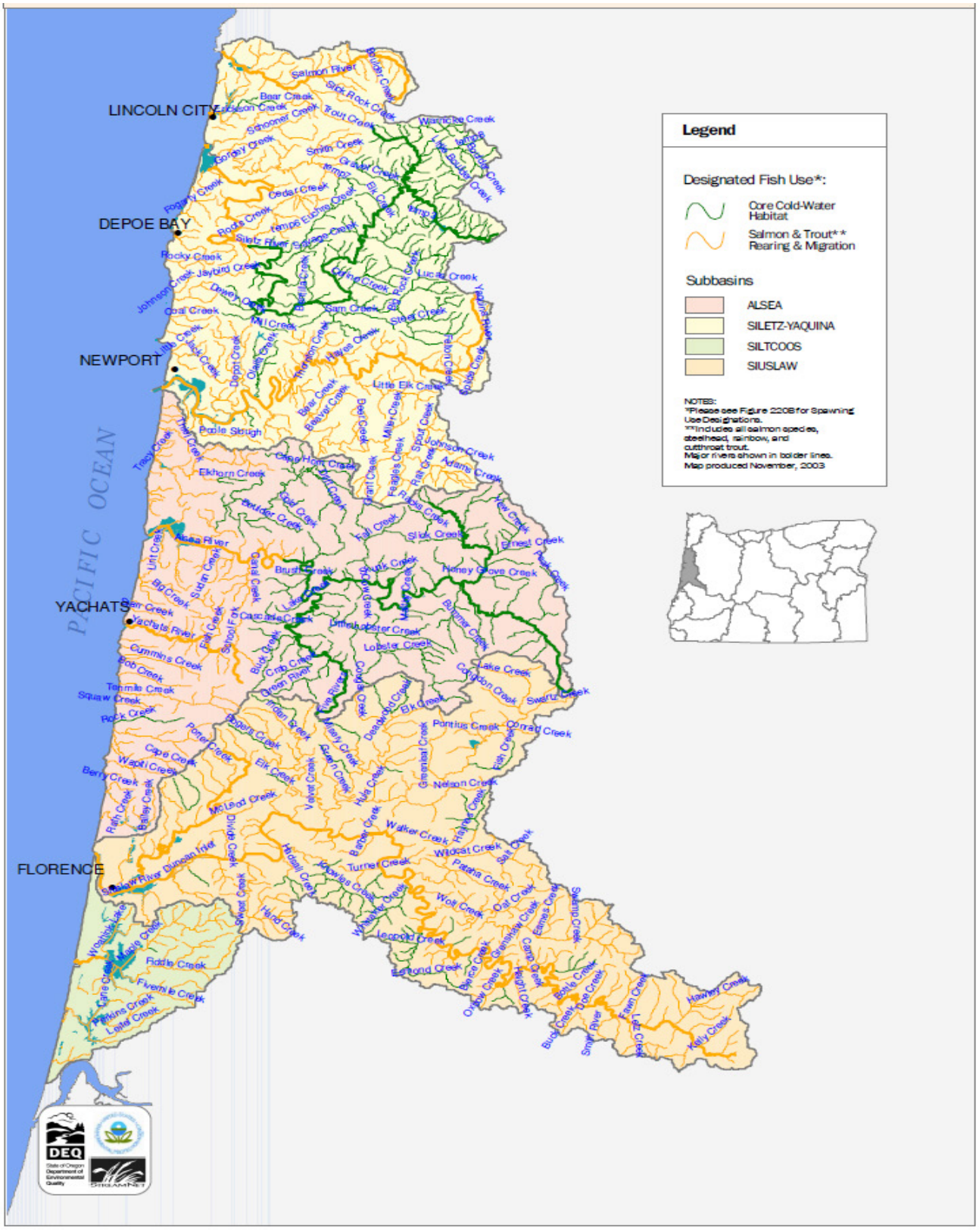
[2] See also Figures 230A and 230B for fish use designations for this basin.

[3] For coastal water contact recreation and shellfish harvesting uses, see also Figures 220C (Salmon River Estuary), 220D (Siletz Bay), 220E (Yaquina Bay), 220F (Alsea River Estuary), 220G (Yachats River Estuary), and 220H (Siuslaw River Estuary)

State of Oregon Department of Environmental Quality

OAR 340-041-0220 – Figure 220A

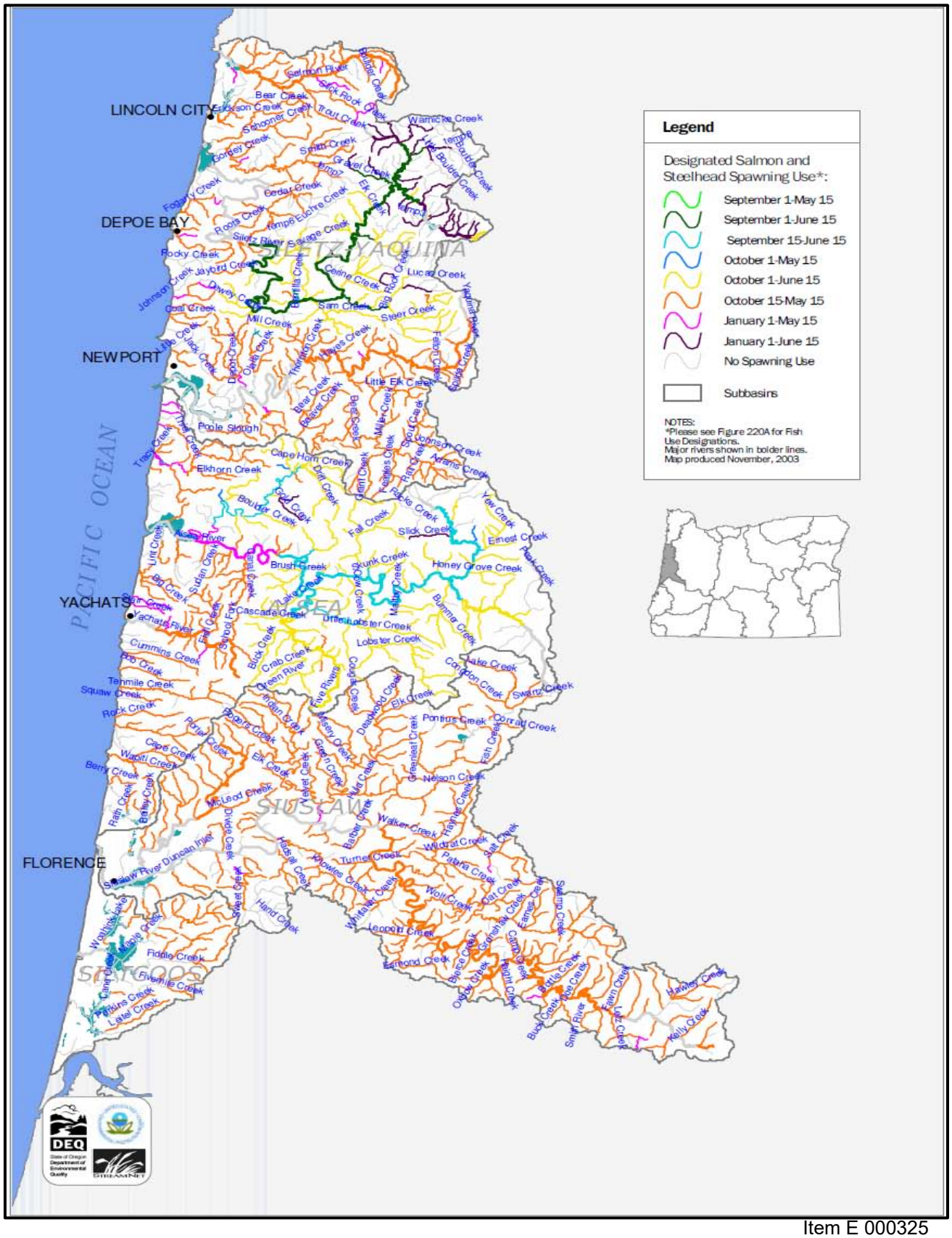
Fish Use Designations* - Mid Coast Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0220 – Figure 220B

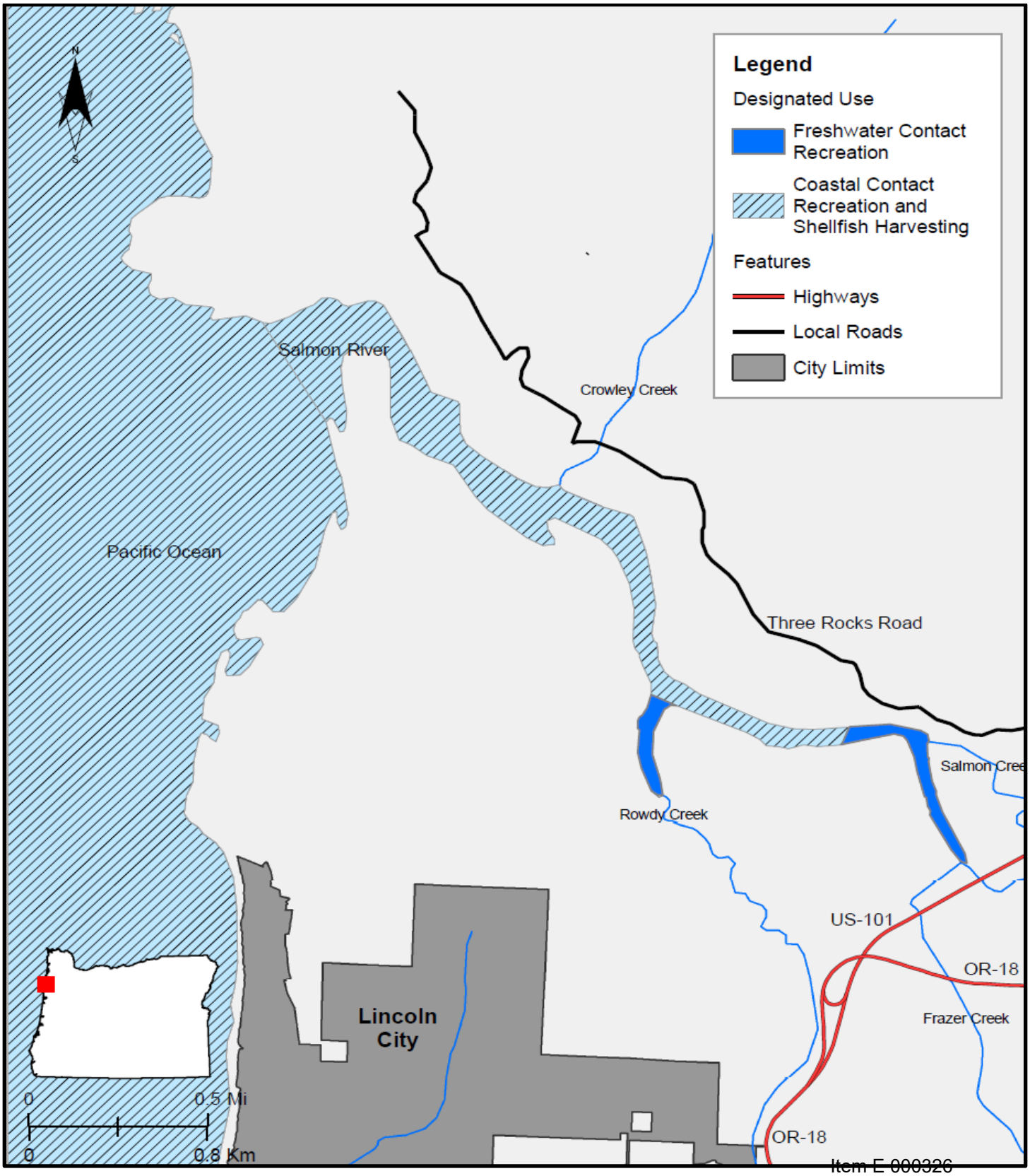
Salmon and Steelhead Use Designations* - Mid Coast Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0220 – Figure 220C

Water Contact Recreation and Shellfish Harvesting Designated Uses
Mid Coast Basin, Oregon



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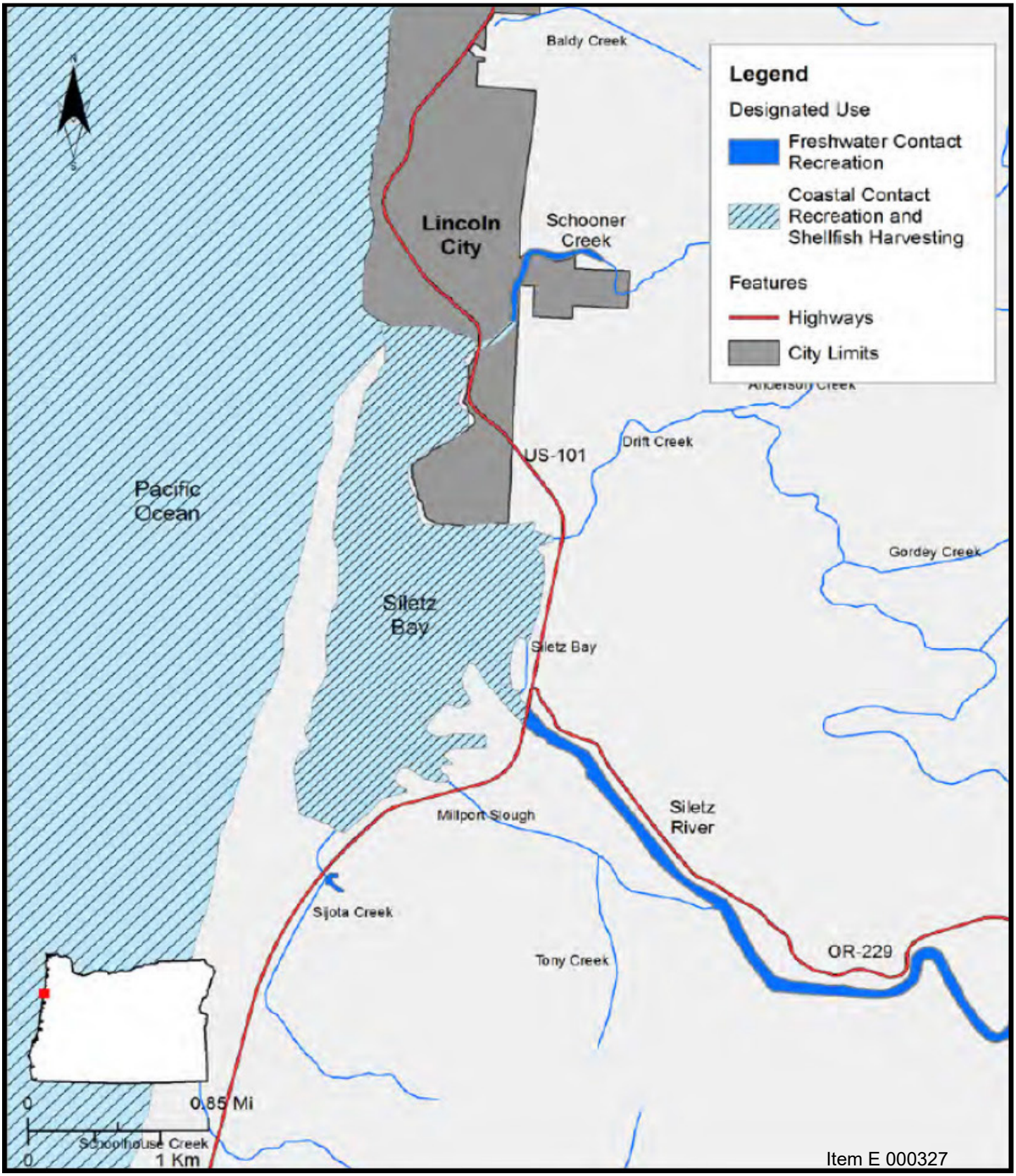
OAR 340-041-0220 – Figure 220D

Water Contact Recreation and Shellfish Harvesting Designated Uses
Siletz River, Mid Coast Basin, Oregon



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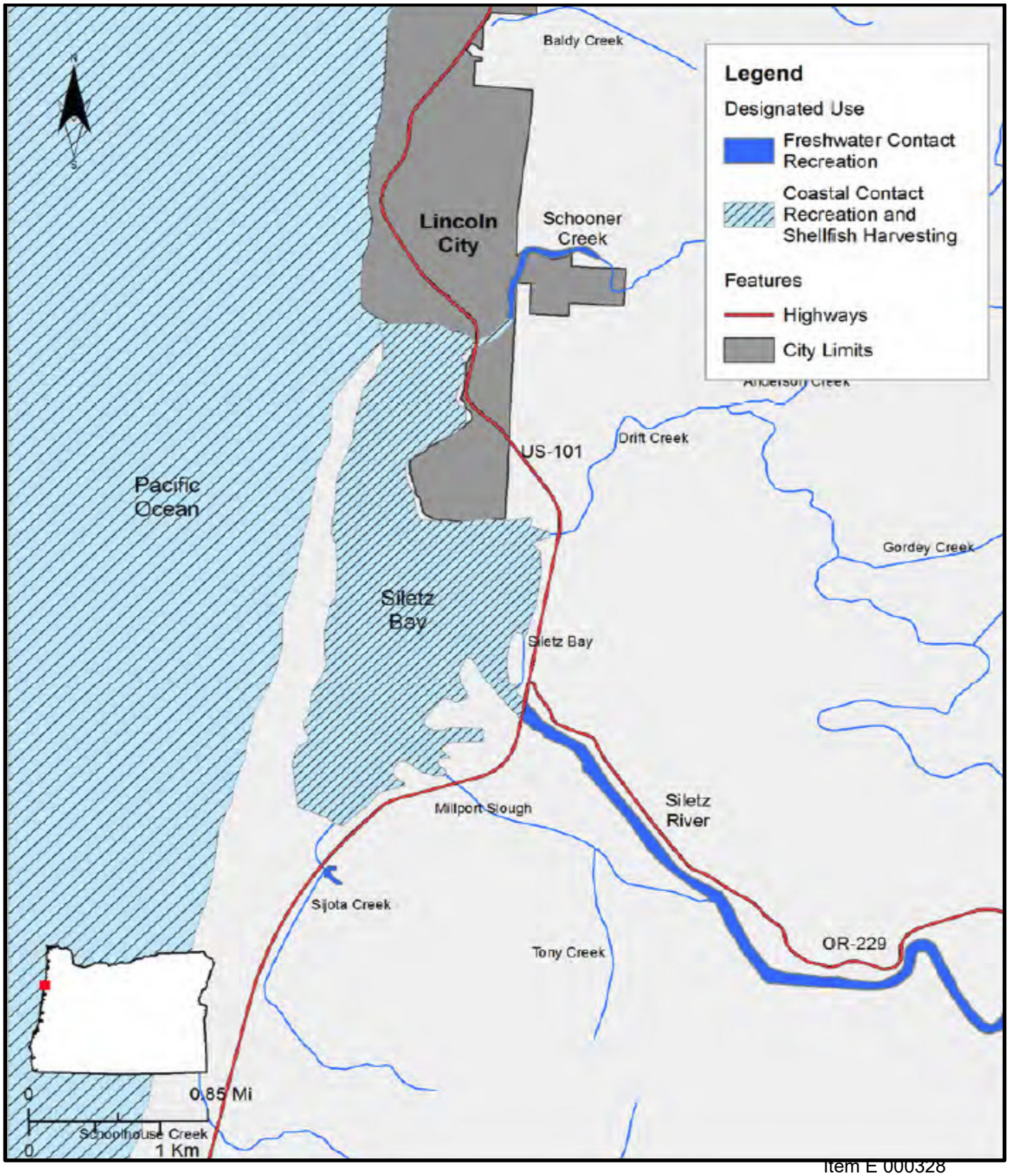
OAR 340-041-0220 – Figure 220E

Water Contact Recreation and Shellfish Harvesting Designated Uses
Yaquina Bay, Mid Coast Basin, Oregon



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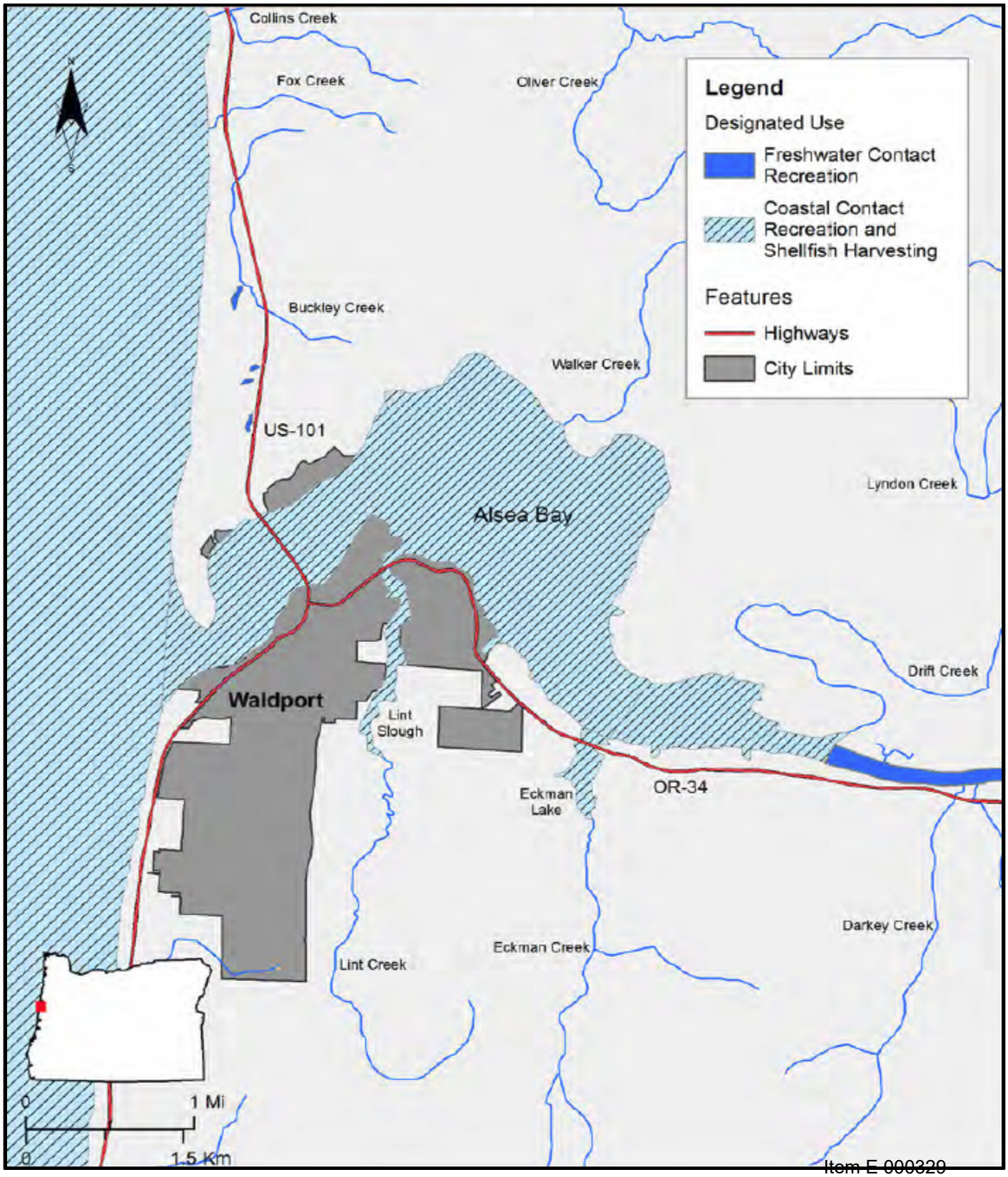
OAR 340-041-0220 – Figure 220F

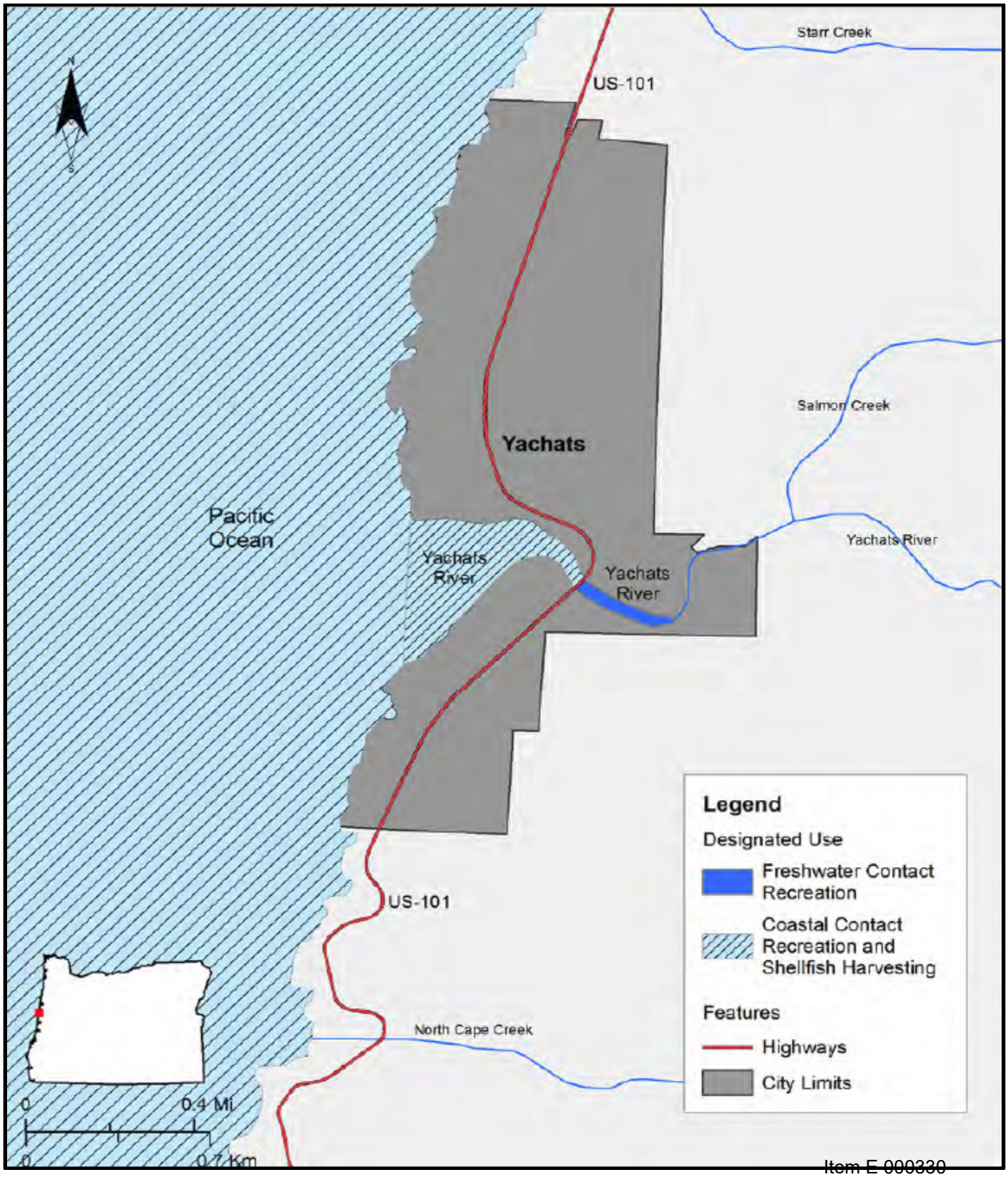
Water Contact Recreation and Shellfish Harvesting Designated Uses
Alsea River, Mid Coast Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0220 – Figure 220G

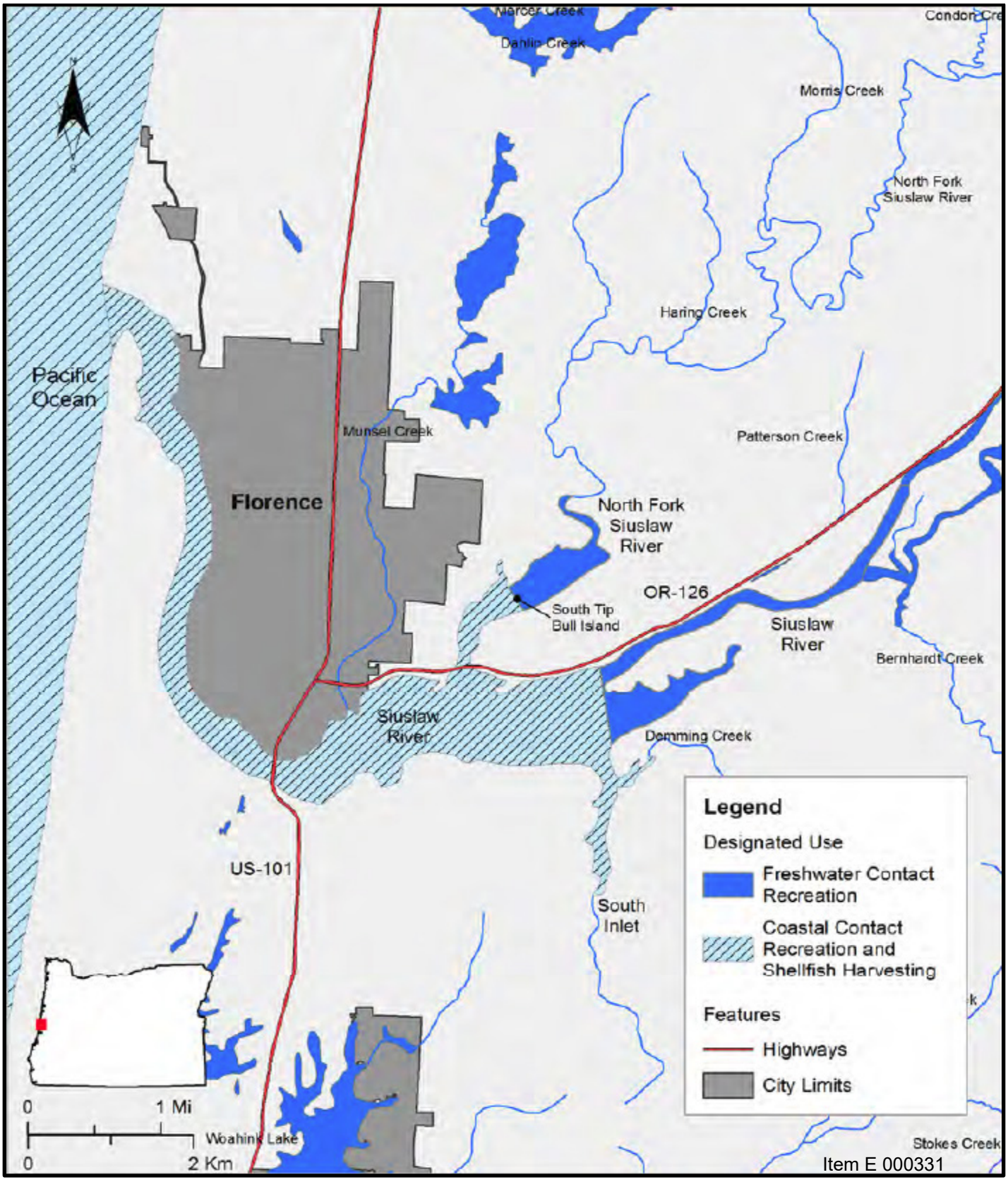
Water Contact Recreation and Shellfish Harvesting Designated Uses
Yachats River, Mid Coast Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0220 – Figure 220H

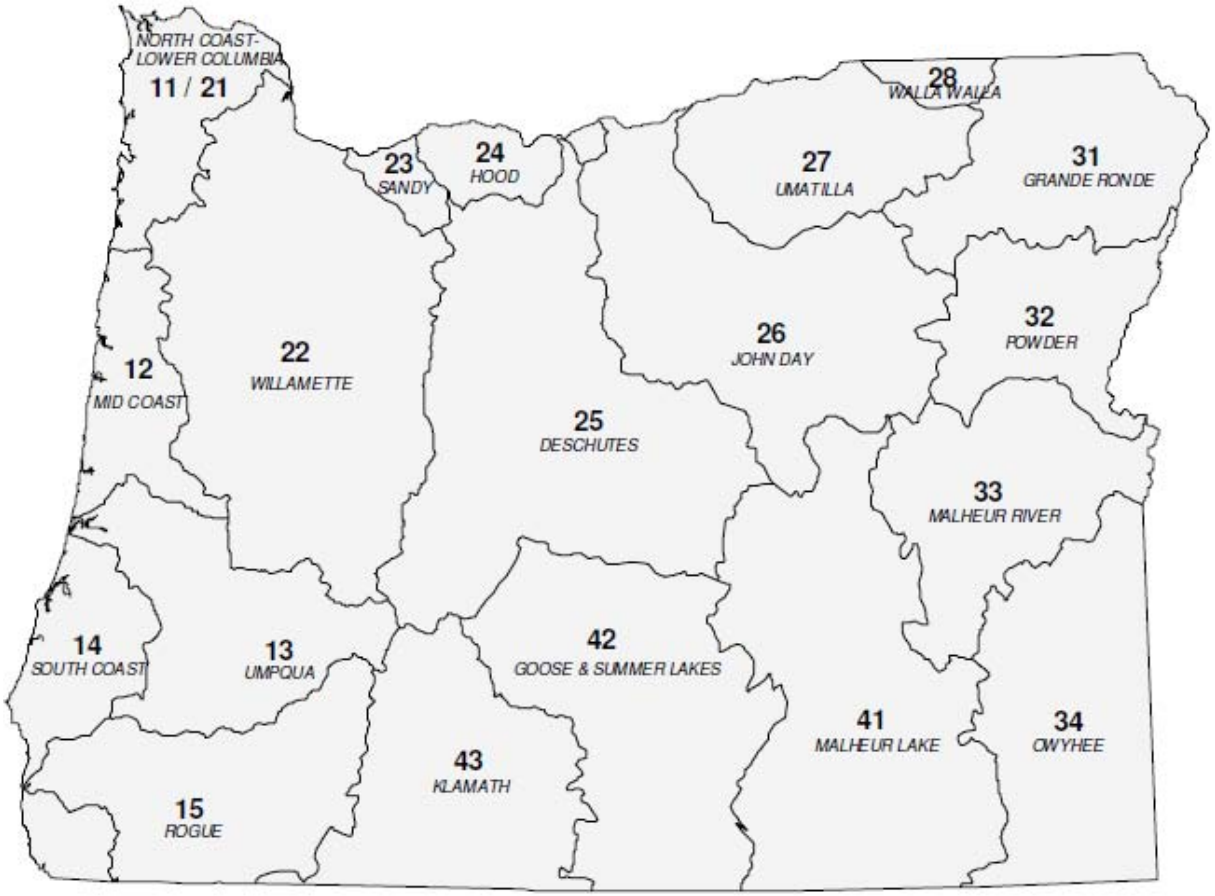
Water Contact Recreation and Shellfish Harvesting Designated Uses
Siuslaw River, Mid Coast Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0230
Tables and Figures

Figure 1: Oregon Basin Index Map



Basin Name	Basin #	OAR #
DESCHUTES	25	340-041-0130
GOOSE & SUMMER LKS	42	340-041-0140
GRANDE RONDE	31	340-041-0151
HOOD	24	340-041-0160
JOHN DAY	26	340-041-0170
KLAMATH	43	340-041-0180
MALHEUR LAKE	41	340-041-0190
MALHEUR RIVER	33	340-041-0201
MD COAST	12	340-041-0220
NORTH COAST-LWR COL	11-21	340-041-0230
OWYHEE	34	340-041-0250
POWDER	32	340-041-0260
ROGUE	15	340-041-0271
SANDY	23	340-041-0286
SOUTH COAST	14	340-041-0300
UMATILLA	27	340-041-0310
UMPQUA	13	340-041-0320
WALLA WALLA	28	340-041-0330
WILLAMETTE	22	340-041-0340

OAR 340-041-0230
Table 230A
Designated Beneficial Uses
North Coast Basin

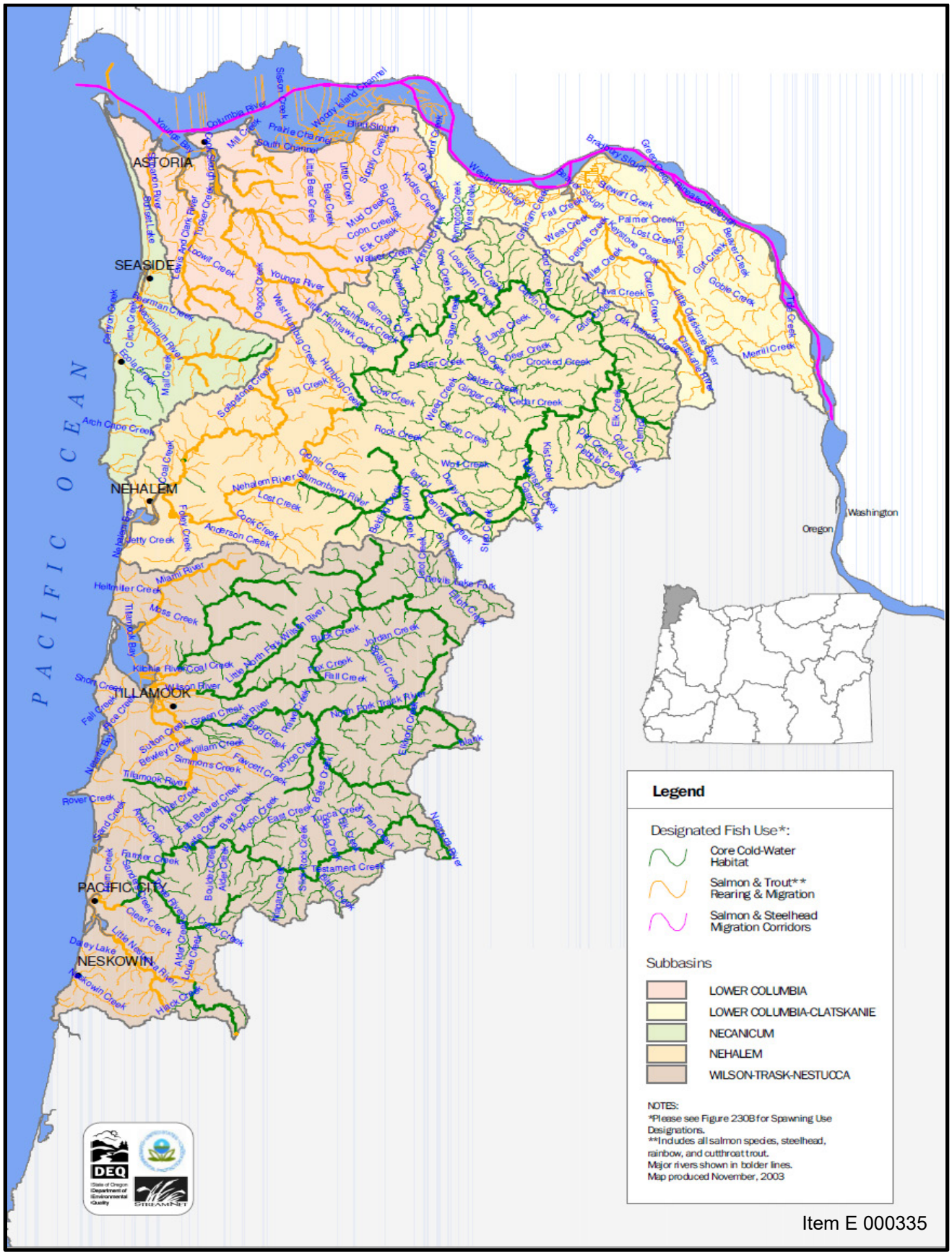
Beneficial Uses	Estuaries & Adjacent Maine Waters	All Steams & Tributaries Thereto
Public Domestic Water Supply[1]		X
Private Domestic Water Supply[1]		X
Industrial Water Supply	X	X
Irrigation		X
Livestock Watering		X
Fish & Aquatic Life[2]	X	X
Wildlife & Hunting	X	X
Fishing	X	X
Boating	X	X
Water Contact Recreation	X	X
Aesthetic Quality	X	X
Hydro Power		
Commercial Navigation & Transportation	X	

[1] With adequate pretreatment (filtration & disinfection) and natural quality to meet drinking water standards.
[2] See also Figures 230A and 230B for fish use designations for this basin.

State of Oregon Department of Environmental Quality

OAR 340-041-0230 – Figure 230A

Fish Use Designations* - North Coast Basin, Oregon

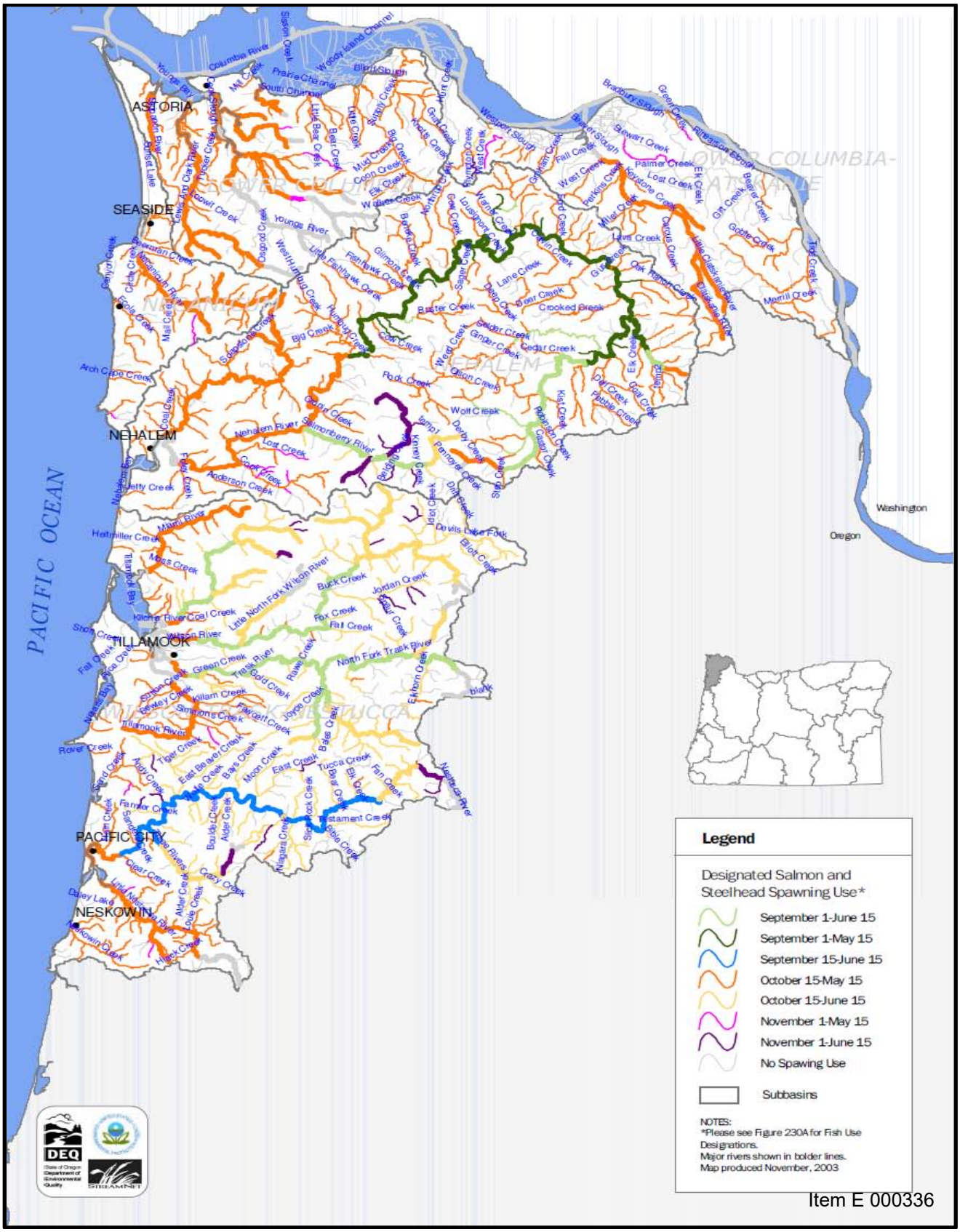


Item E 000335

State of Oregon Department of Environmental Quality

OAR 340-041-0230 – Figure 230B

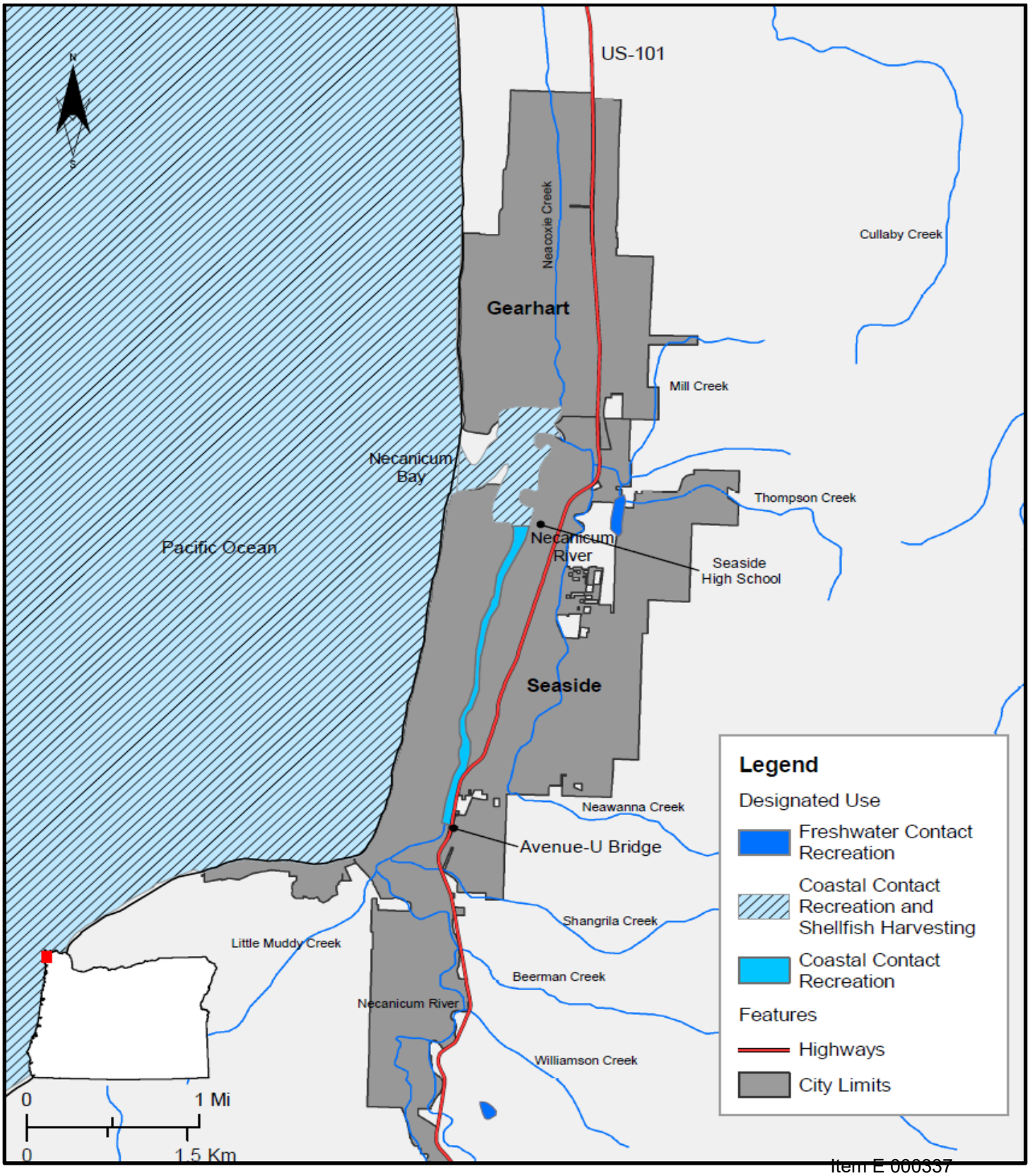
Salmon and Steelhead Spawning Use Designations*
North Coast Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0230 – Figure 230C

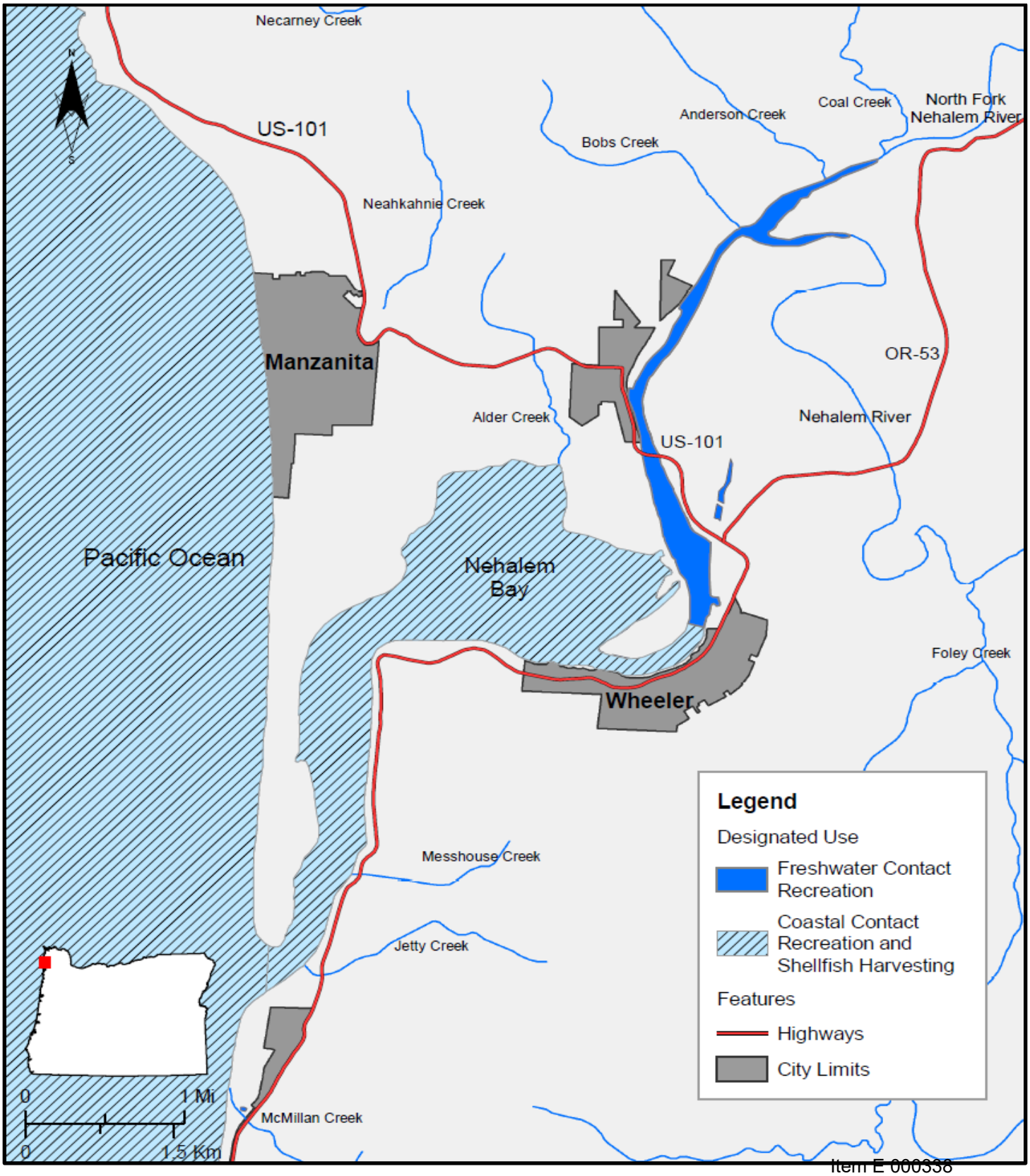
Water Contact Recreation and Shellfish Harvesting Designated Uses
Necanicum Bay, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0230 – Figure 230D

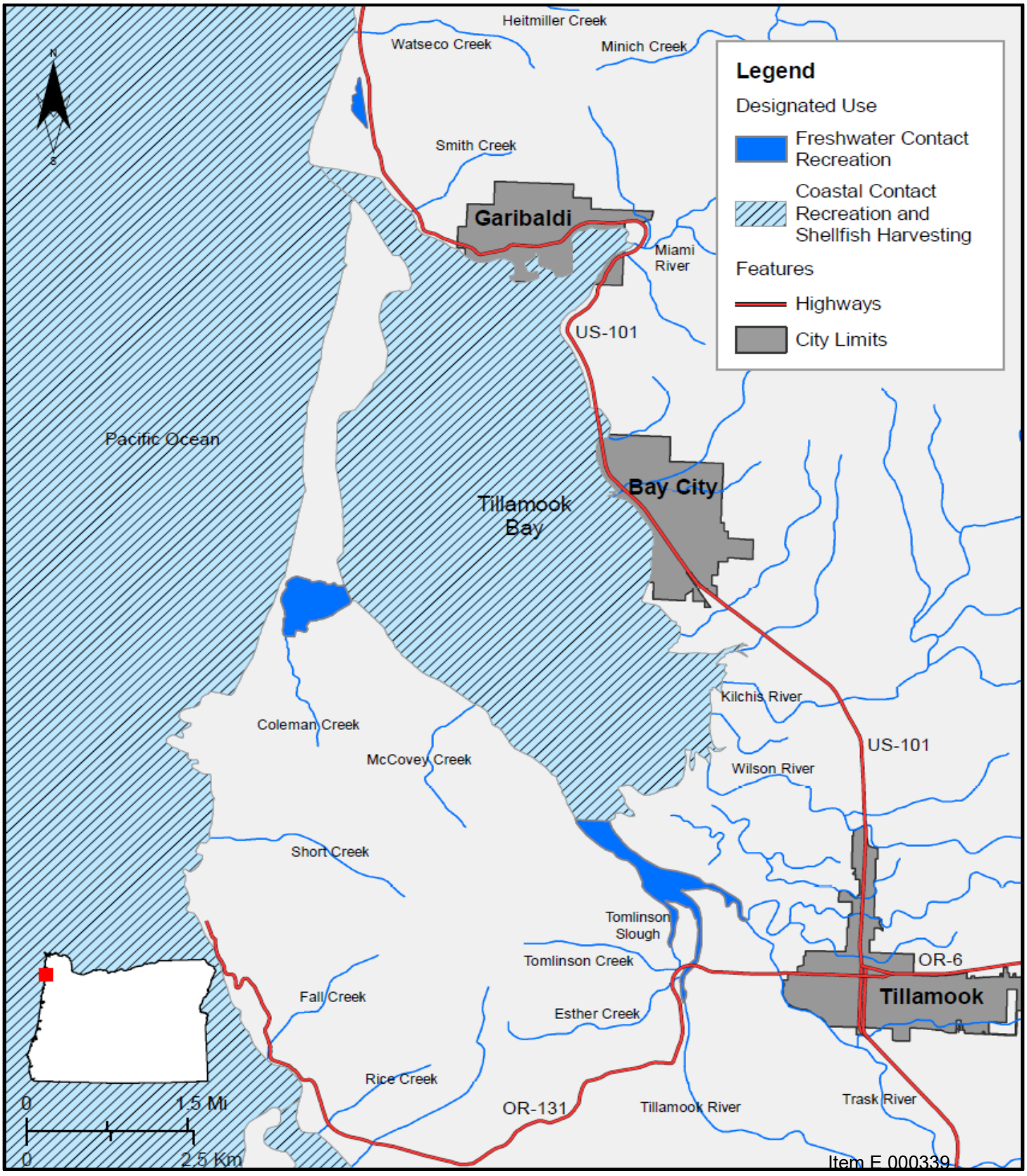
Water Contact Recreation and Shellfish Harvesting Designated Uses
Nehalem Bay, North Coast Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0230 – Figure 230E

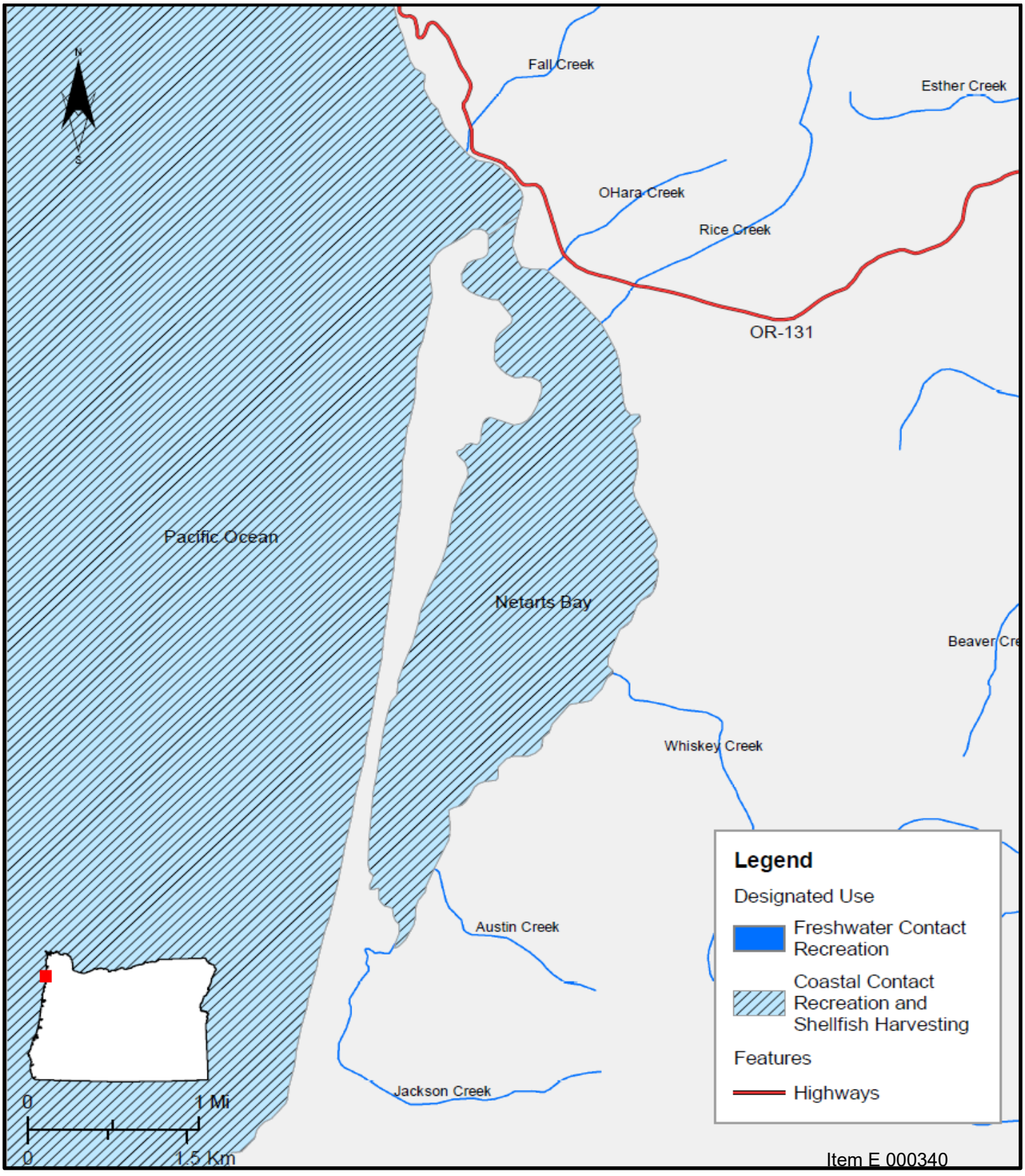
Water Contact Recreation and Shellfish Harvesting Designated Uses
Tillamook Bay, North Coast Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0230 – Figure 230F

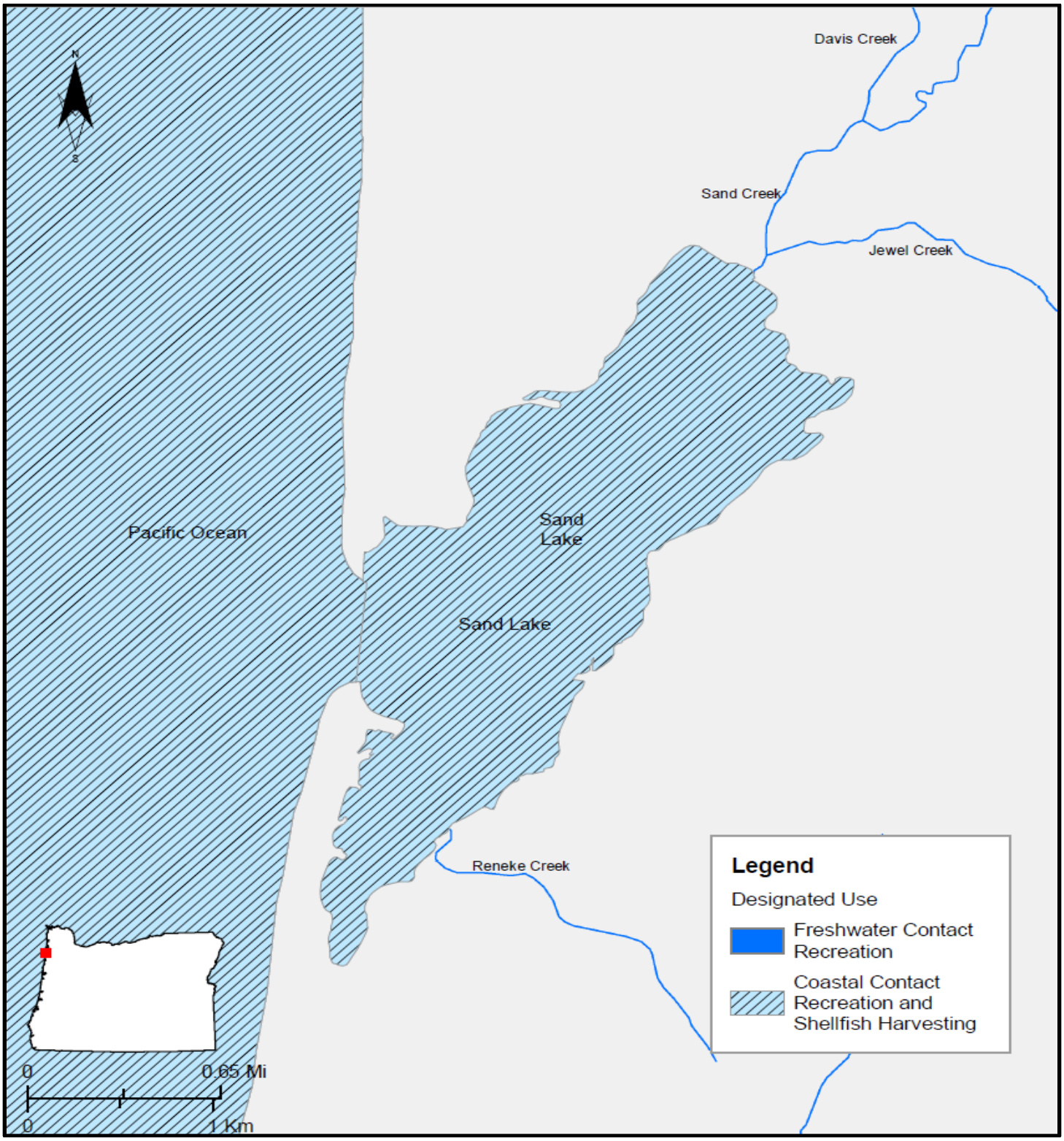
Water Contact Recreation and Shellfish Harvesting Designated Uses
Netarts Bay, North Coast Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0230 – Figure 230G

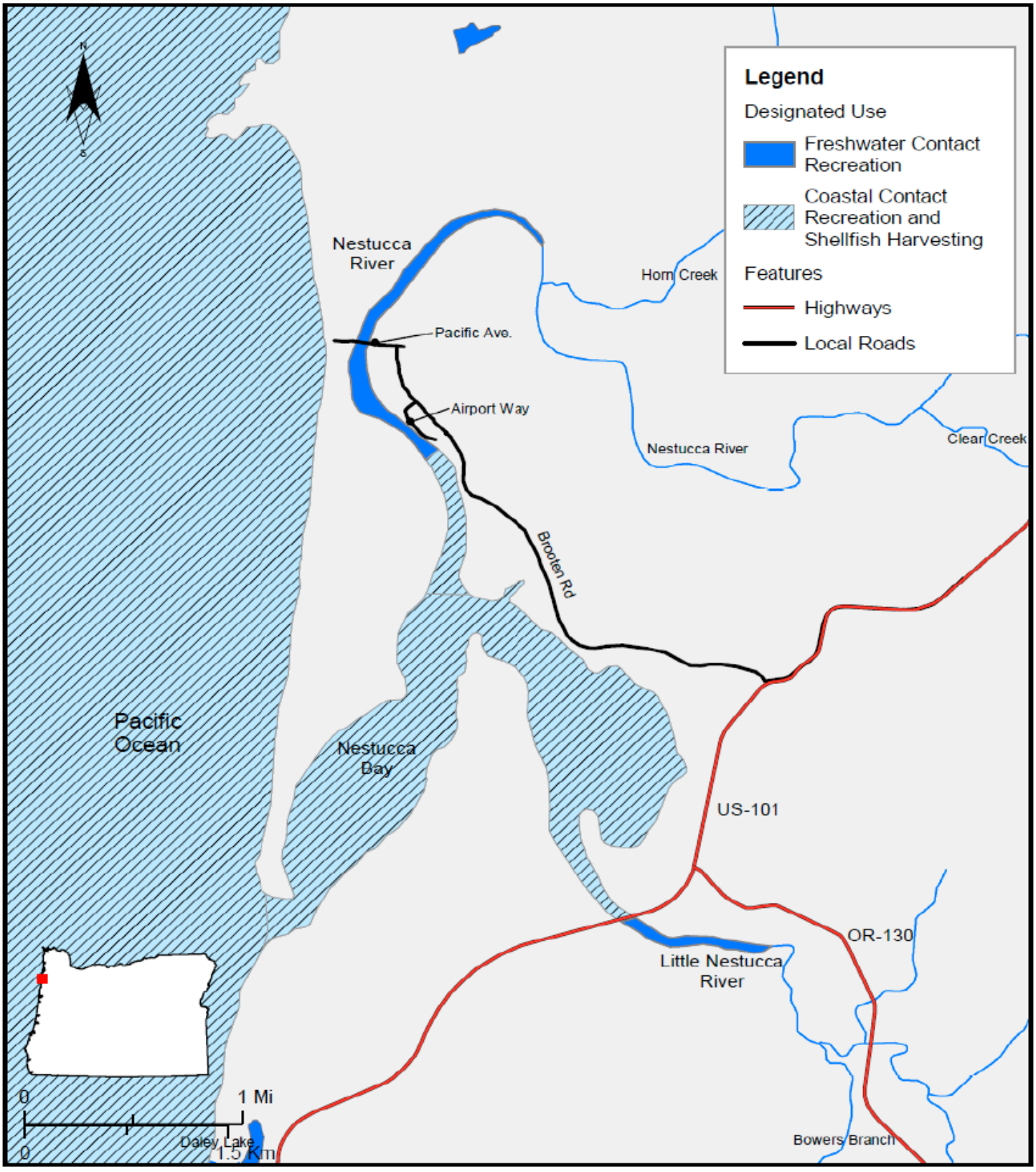
Water Contact Recreation and Shellfish Harvesting Designated Uses
Sand Lake, North Coast Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0230 – Figure 230H

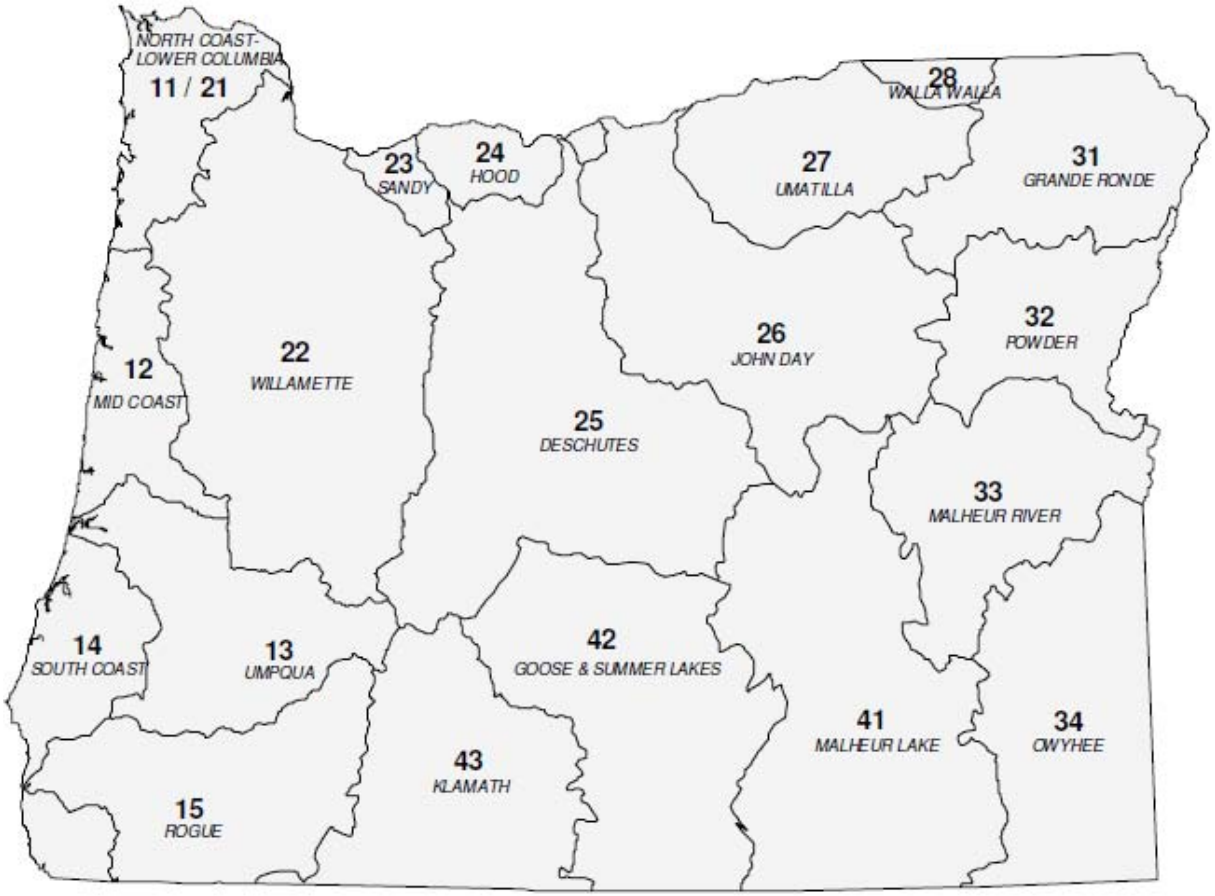
Water Contact Recreation and Shellfish Harvesting Designated Uses
Nestucca Bay, North Coast Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0250
Tables and Figures

Figure 1: Oregon Basin Index Map



Basin Name	Basin #	OAR #
DESCHUTES	25	340-041-0130
GOOSE & SUMMER LKS	42	340-041-0140
GRANDE RONDE	31	340-041-0151
HOOD	24	340-041-0160
JOHN DAY	26	340-041-0170
KLAMATH	43	340-041-0180
MALHEUR LAKE	41	340-041-0190
MALHEUR RIVER	33	340-041-0201
MD COAST	12	340-041-0220
NORTH COAST-LWR COL	11-21	340-041-0230
OWYHEE	34	340-041-0250
POWDER	32	340-041-0260
ROGUE	15	340-041-0271
SANDY	23	340-041-0286
SOUTH COAST	14	340-041-0300
UMATILLA	27	340-041-0310
UMPQUA	13	340-041-0320
WALLA WALLA	28	340-041-0330
WILLAMETTE	22	340-041-0340

OAR 340-041-0250
Table 250A
Designated Beneficial Uses
Owyhee Basin

Beneficial Uses	Owyhee River (RM 0-18)	Owyhee River (RM 18-Dam)	Reservoirs Antelope Cow Creek Owyhee	Owyhee River & Tributaries Upstream from Owyhee Reservoir	Designated Scenic Waterway[3]
Public Domestic Water Supply[1]	X	X	X	X	X
Private Domestic Water Supply[1]	X	X	X	X	X
Industrial Water Supply	X	X	X	X	
Irrigation	X	X	X	X	
Livestock Watering	X	X	X	X	X
Fish & Aquatic Life[2]	X	X	X	X	X
Wildlife & Hunting	X	X	X	X	X
Fishing	X	X	X	X	X
Boating	X	X	X	X	X
Water Contact Recreation	X	X	X	X	X
Aesthetic Quality	X	X	X	X	X
Hydro Power					
Commercial Navigation & Transportation					

[1] With adequate pretreatment (filtration & disinfection) and natural quality to meet drinking water standards.
[2] See also Table 250B for fish use designations for this basin.
[3] The mainstem of the South Fork of the Owyhee River from the Oregon-Idaho River border to Three Forks (the confluence of the North, Middle and South Forks Owyhee River) and the mainstem Owyhee River form Crooked Creek (river mile 22) to the mouth of Birch Creek (river mile 76) is designated by statute as a Scenic Waterway.

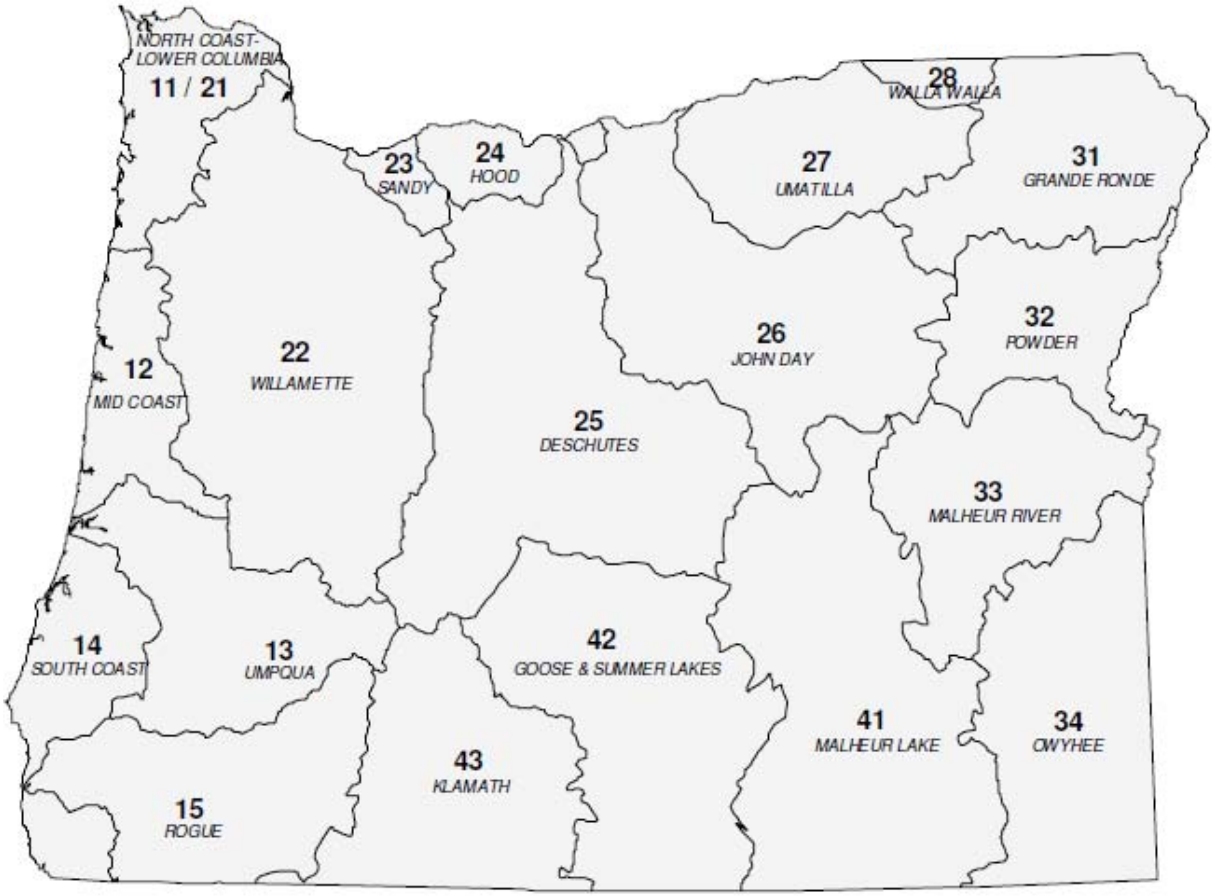
OAR 340-041-0250
Table 250B
Beneficial Use Designations – Fish Uses
Owyhee Basin, Oregon

Geographic Extent of Use	Redband or Lahontan Cutthroat Trout (20°C)	Cool Water Species (No Salmonid Use)
Lower Owyhee River Subbasin		
Mainstem Owyhee River from the mouth to the confluence with Snively Gulch (RM 18).		X
All other Lower Owyhee subbasin waters.	X	
All other Owyhee Basin waters within Oregon		
	X	

State of Oregon Department of Environmental Quality

OAR 340-041-0260
Tables and Figures

Figure 1: Oregon Basin Index Map



Basin Name	Basin #	OAR #
DESCHUTES	25	340-041-0130
GOOSE & SUMMER LKS	42	340-041-0140
GRANDE RONDE	31	340-041-0151
HOOD	24	340-041-0160
JOHN DAY	26	340-041-0170
KLAMATH	43	340-041-0180
MALHEUR LAKE	41	340-041-0190
MALHEUR RIVER	33	340-041-0201
MD COAST	12	340-041-0220
NORTH COAST-LWR COL	11-21	340-041-0230
OWYHEE	34	340-041-0250
POWDER	32	340-041-0260
ROGUE	15	340-041-0271
SANDY	23	340-041-0286
SOUTH COAST	14	340-041-0300
UMATILLA	27	340-041-0310
UMPQUA	13	340-041-0320
WALLA WALLA	28	340-041-0330
WILLAMETTE	22	340-041-0340

OAR 340-041-0260
Table 260A
Designated Beneficial Uses
Powder/Burnt Basin

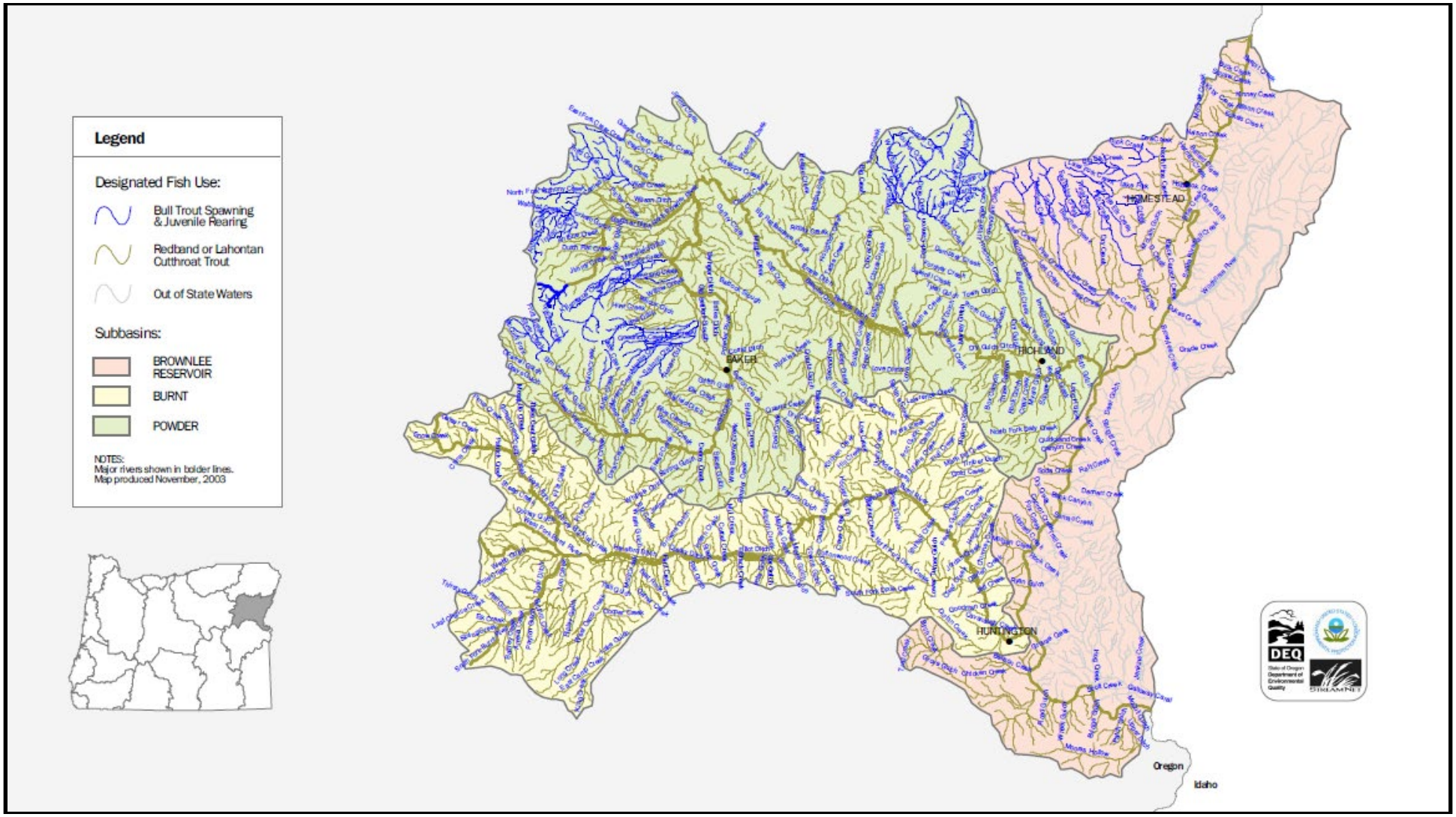
Beneficial Uses	All Basin Waters
Public Domestic Water Supply[1]	X
Private Domestic Water Supply[1]	X
Industrial Water Supply	X
Irrigation	X
Livestock Watering	X
Fish & Aquatic Life[2]	X
Wildlife & Hunting	X
Fishing	X
Boating	X
Water Contact Recreation	X
Aesthetic Quality	X
Hydro Power	
Commercial Navigation & Transportation	

[1] With adequate pretreatment (filtration & disinfection) and natural quality to meet drinking water standards.
[2] See also Figure 260A for fish use designations for this basin.

State of Oregon Department of Environmental Quality

OAR 340-041-0260 – Figure 260A

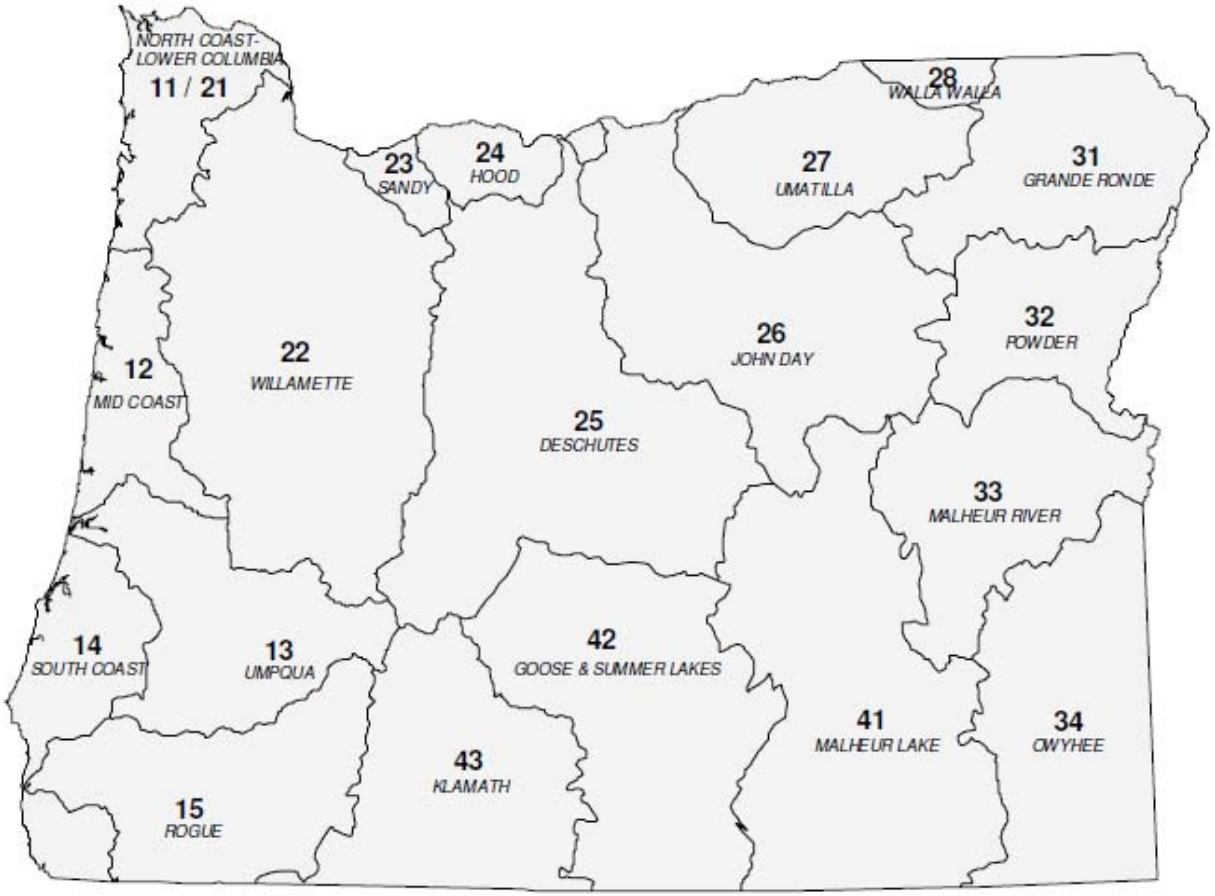
Fish Use Designations – Powder Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0271
Tables and Figures

Figure 1: Oregon Basin Index Map



Basin Name	Basin #	OAR #
DESCHUTES	25	340-041-0130
GOOSE & SUMMER LKS	42	340-041-0140
GRANDE RONDE	31	340-041-0151
HOOD	24	340-041-0160
JOHN DAY	26	340-041-0170
KLAMATH	43	340-041-0180
MALHEUR LAKE	41	340-041-0190
MALHEUR RIVER	33	340-041-0201
MD COAST	12	340-041-0220
NORTH COAST-LWR COL	11-21	340-041-0230
OWYHEE	34	340-041-0250
POWDER	32	340-041-0260
ROGUE	15	340-041-0271
SANDY	23	340-041-0286
SOUTH COAST	14	340-041-0300
UMATILLA	27	340-041-0310
UMPQUA	13	340-041-0320
WALLA WALLA	28	340-041-0330
WILLAMETTE	22	340-041-0340

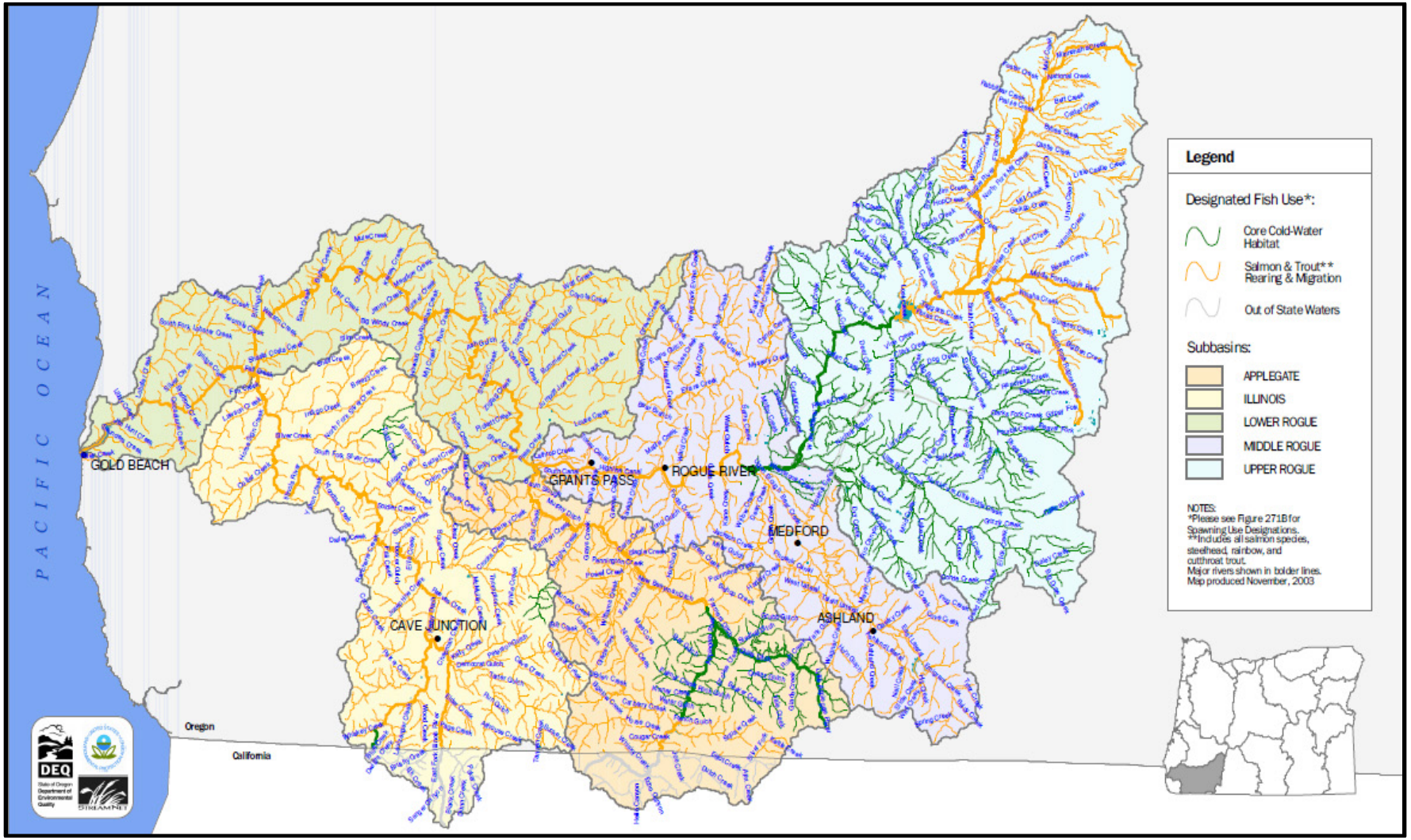
OAR 340-041-0271
Table 271A
Designated Beneficial Uses
Rogue Basin

Beneficial Uses	Rogue River Estuary & Adjacent Marine Waters	Rogue River Main Stem from Estuary to Lost Creek Dam	Rogue River Main Stem above Lost Dam & Tributaries	Bear Creek Main Stem	All Other Tributaries to Rogue River & Bear Creek
Public Domestic Water Supply[1]		X	X	*	X
Private Domestic Water Supply[1]		X	X		X
Industrial Water Supply	X	X	X	X	X
Irrigation		X	X	X	X
Livestock Watering		X	X	X	X
Fish & Aquatic Life[2]	X	X	X	X	X
Wildlife & Hunting	X	X	X	X	X
Fishing	X	X	X	X	X
Boating	X	X	X	X	X
Water Contact Recreation	X	X	X	X	X
Aesthetic Quality	X	X	X	X	X
Hydro Power			X		X
Commercial Navigation & Transportation	X	X			

[1] With adequate pretreatment (filtration & disinfection) and natural quality to meet drinking water standards
[2] See also Figures 271A and 271B for fish use designations for this basin.
* Designation for this use is presently under study

State of Oregon Department of Environmental Quality

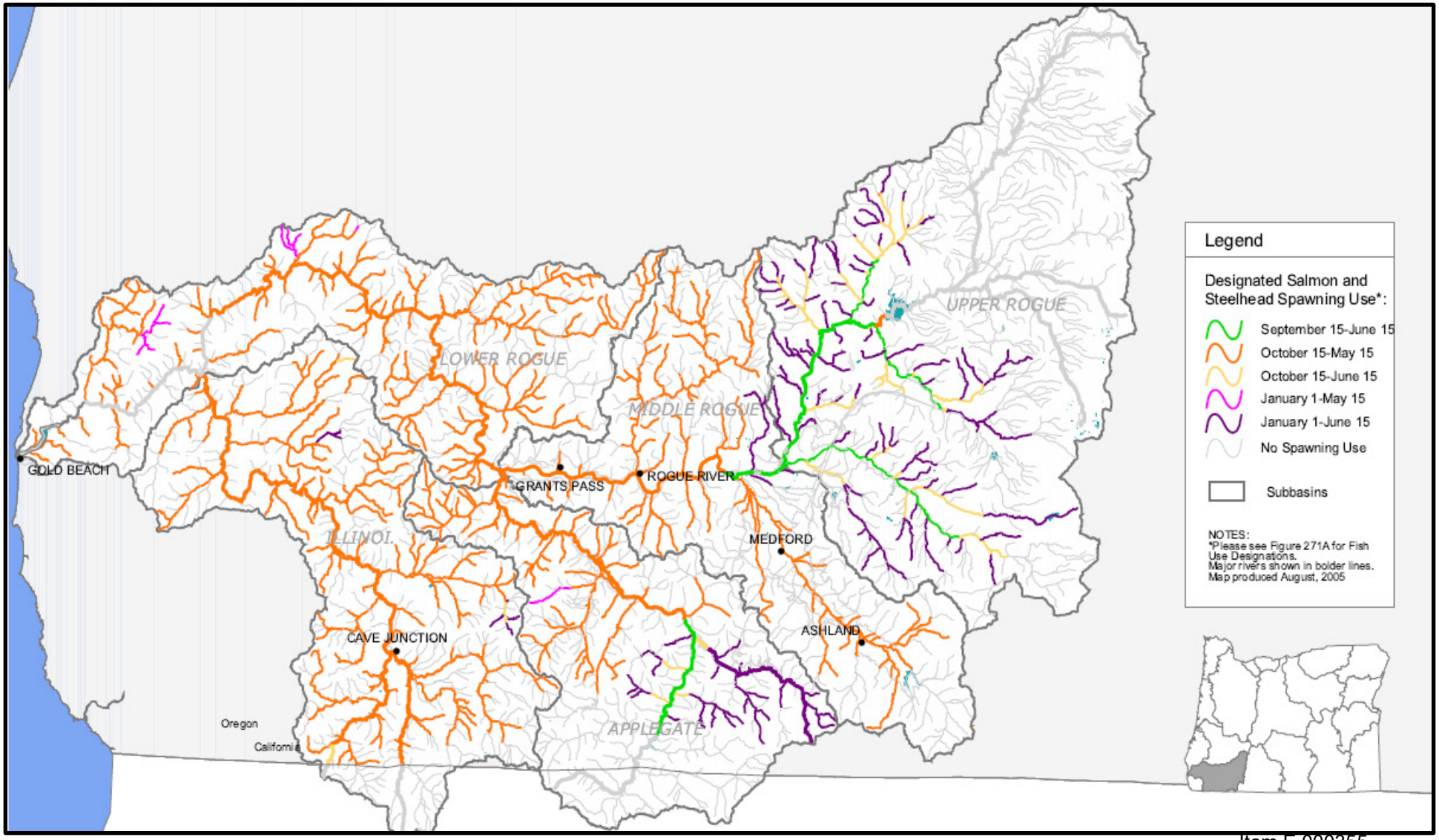
OAR 340-041-0271 – Figure 271A
Fish Use Designations* - Rogue Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0271 – Figure 271B

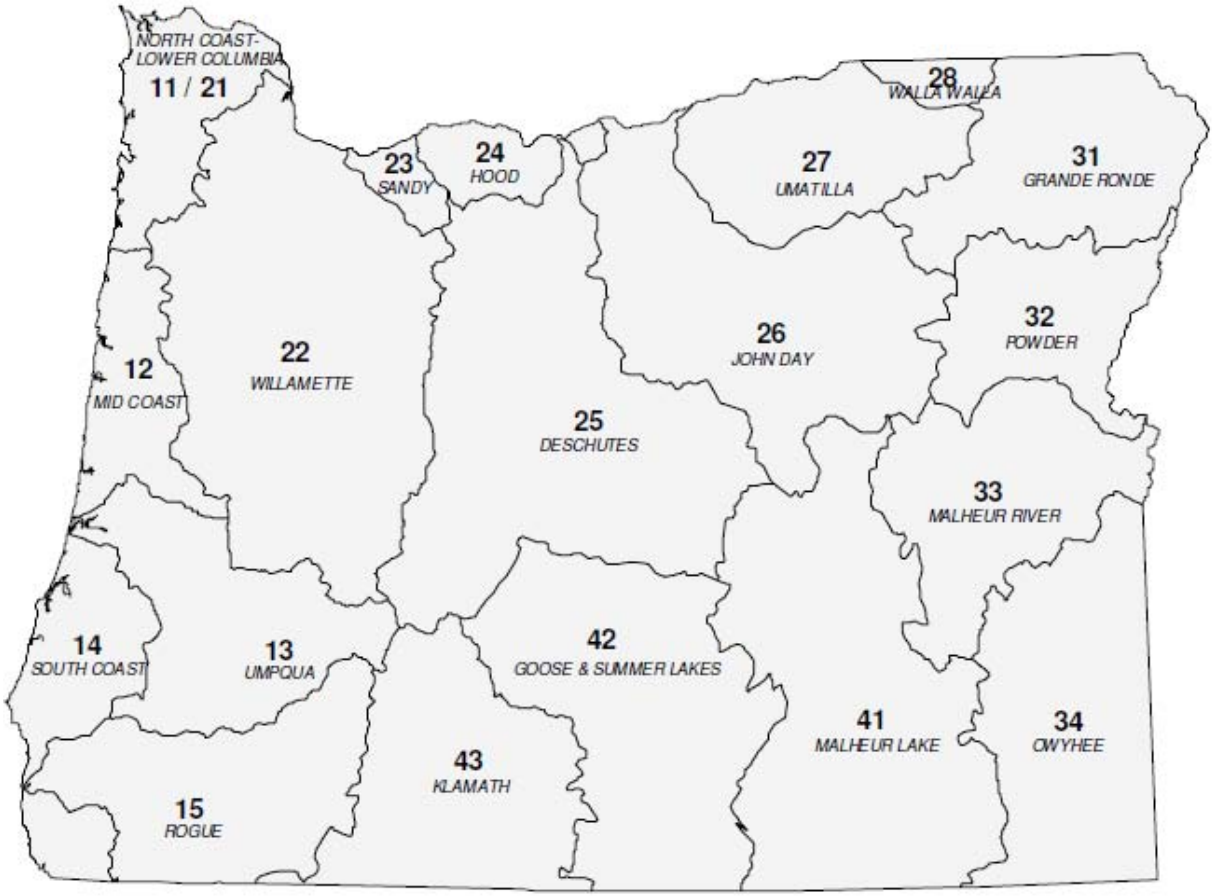
Salmon and Steelhead Spawning Use Designations*
Rogue Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0286
Tables and Figures

Figure 1: Oregon Basin Index Map



Basin Name	Basin #	OAR #
DESCHUTES	25	340-041-0130
GOOSE & SUMMER LKS	42	340-041-0140
GRANDE RONDE	31	340-041-0151
HOOD	24	340-041-0160
JOHN DAY	26	340-041-0170
KLAMATH	43	340-041-0180
MALHEUR LAKE	41	340-041-0190
MALHEUR RIVER	33	340-041-0201
MD COAST	12	340-041-0220
NORTH COAST-LWR COL	11-21	340-041-0230
OWYHEE	34	340-041-0250
POWDER	32	340-041-0260
ROGUE	15	340-041-0271
SANDY	23	340-041-0286
SOUTH COAST	14	340-041-0300
UMATILLA	27	340-041-0310
UMPQUA	13	340-041-0320
WALLA WALLA	28	340-041-0330
WILLAMETTE	22	340-041-0340

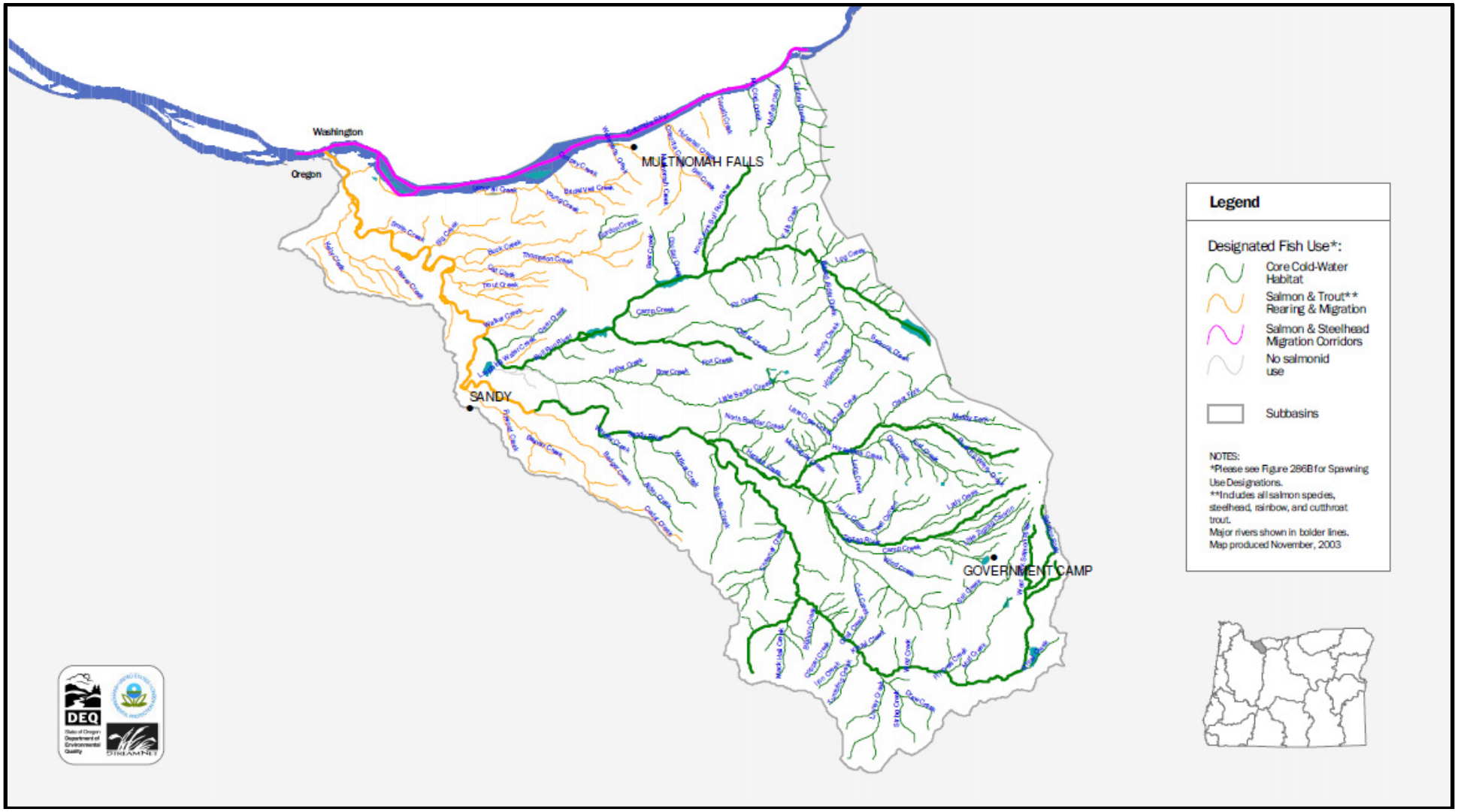
OAR 340-041-0286
Table 286A
Designated Beneficial Uses
Sandy Basin

Beneficial Uses	Streams Forming Waterfalls Near Columbia River Highway	Sandy River	Bull Run River and all Tributaries	All Other Tributaries to Sandy River
Public Domestic Water Supply[1]		X	X	X
Private Domestic Water Supply[1]		X		X
Industrial Water Supply		X		X
Irrigation		X		X
Livestock Watering		X		X
Fish & Aquatic Life[2]	X	X	X	X
Wildlife & Hunting	X	X		X
Fishing	X	X		X
Boating		X		X
Water Contact Recreation	X	X		X
Aesthetic Quality	X	X	X	X
Hydro Power		X	X	X
Commercial Navigation & Transportation				

[1] With adequate pretreatment (filtration & disinfection) and natural quality to meet drinking water standards.
[2] See also Figures 286A and 286B for fish use designations for this basin.

State of Oregon Department of Environmental Quality

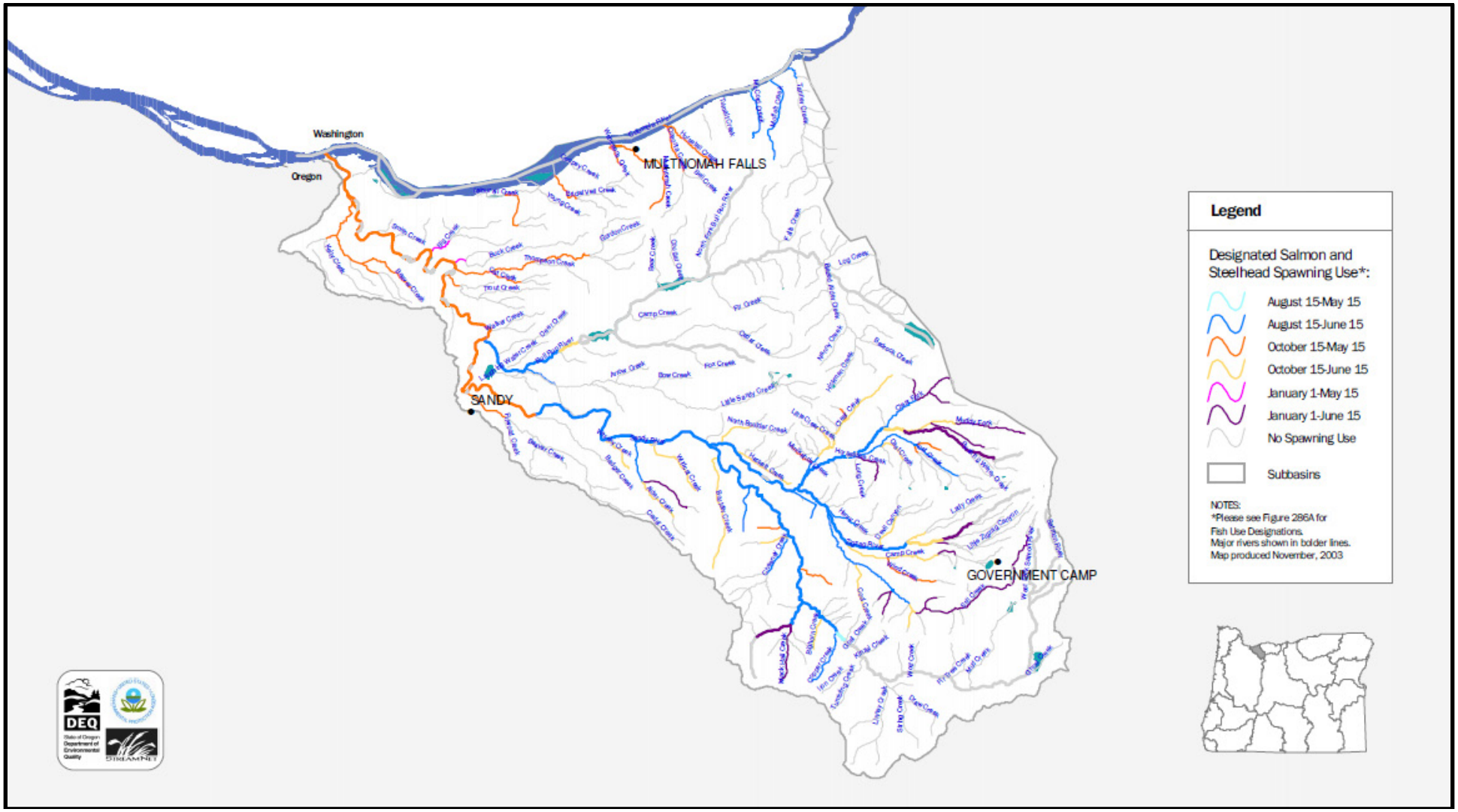
OAR 340-041-0286 - Figure 286A
Fish Use Designations* - Sandy Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0286 - Figure 286B

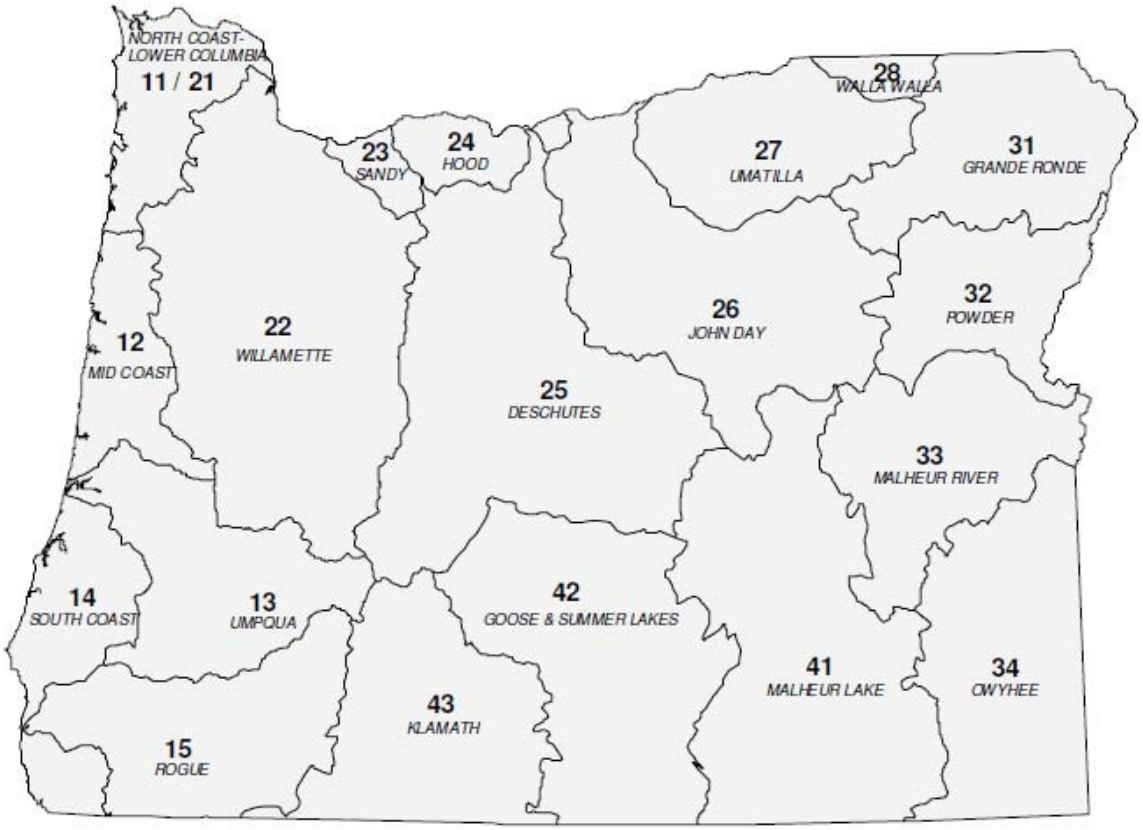
Salmon and Steelhead Spawning Use Designations*
Sandy Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0300 – Tables and Figures

Figure 1: Oregon Basin Index Map



Basin Name	Basin #	OAR #
DESCHUTES	25	340-041-0130
GOOSE & SUMMER LKS	42	340-041-0140
GRANDE RONDE	31	340-041-0151
HOOD	24	340-041-0160
JOHN DAY	26	340-041-0170
KLAMATH	43	340-041-0180
MALHEUR LAKE	41	340-041-0190
MALHEUR RIVER	33	340-041-0201
MD COAST	12	340-041-0220
NORTH COAST-LWR COL	11-21	340-041-0230
OWYHEE	34	340-041-0250
POWDER	32	340-041-0260
ROGUE	15	340-041-0271
SANDY	23	340-041-0286
SOUTH COAST	14	340-041-0300
UMATILLA	27	340-041-0310
UMPQUA	13	340-041-0320
WALLA WALLA	28	340-041-0330
WILLAMETTE	22	340-041-0340

340-041-0300
Table 300A
Designated Beneficial Uses
South Coast Basin
(November 2003)

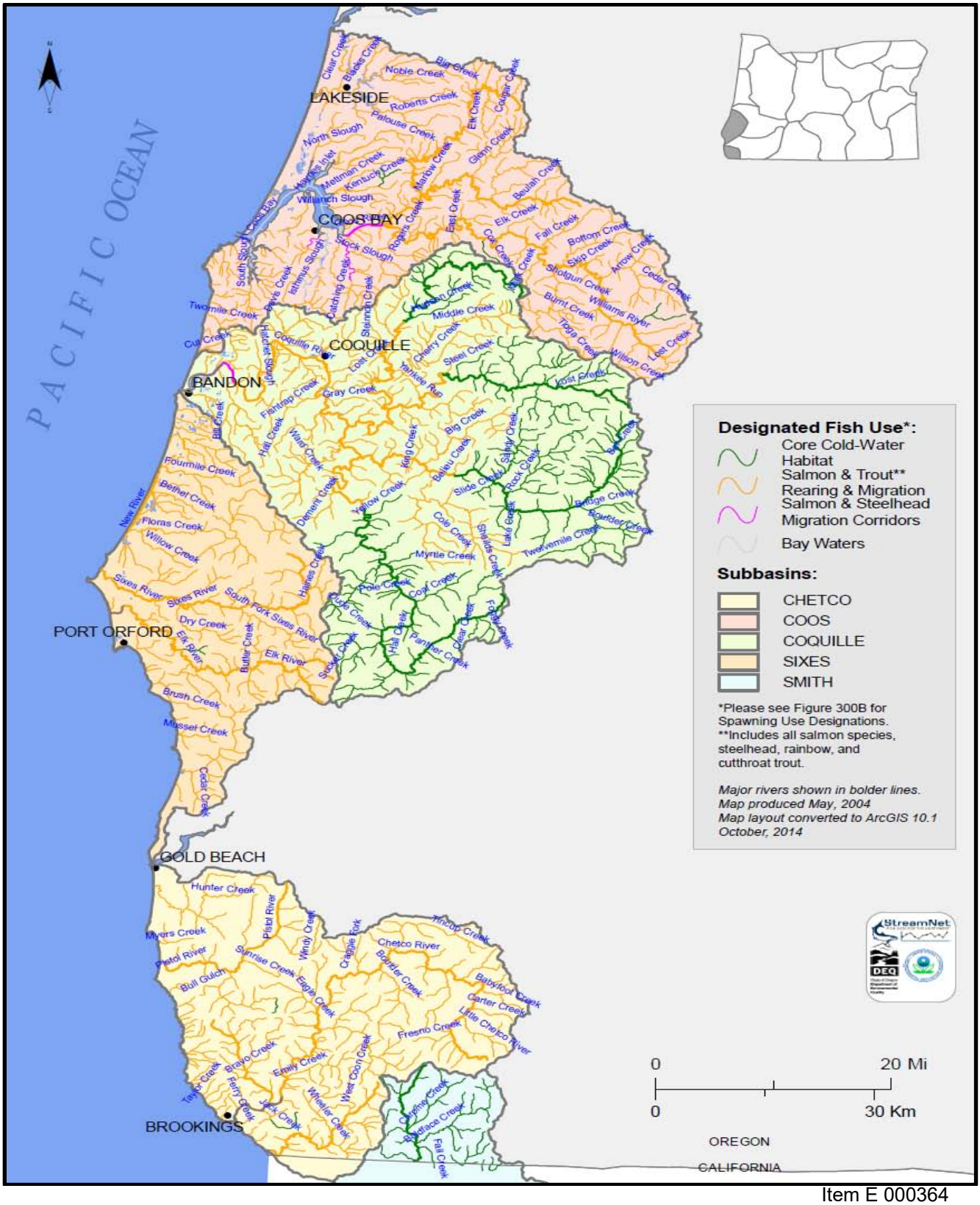
Beneficial Uses	Estuaries & Adjacent Marine Waters	All Streams & Tributaries Thereto
Public Domestic Water Supply[1]		X
Private Domestic Water Supply[1]		X
Industrial Water Supply	X	X
Irrigation		X
Livestock Watering		X
Fish & Aquatic Life[2]	X	X
Wildlife & Hunting	X	X
Fishing[3]	X	X
Boating	X	X
Water Contact Recreation[3]	X	X
Aesthetic Quality	X	X
Hydro Power		X
Commercial Navigation & Transportation	X	

[1] With adequate pretreatment (filtration & disinfection) and natural quality to meet drinking water standards.
[2] See also Figures 300A and 300B for fish use designations for this basin.
[3] For coastal water contact recreation and shellfish harvesting uses, see also Figures 300C (Coos Bay) and 300D (Coquille River Estuary).

State of Oregon Department of Environmental Quality

OAR 340-041-0300 – Figure 300A

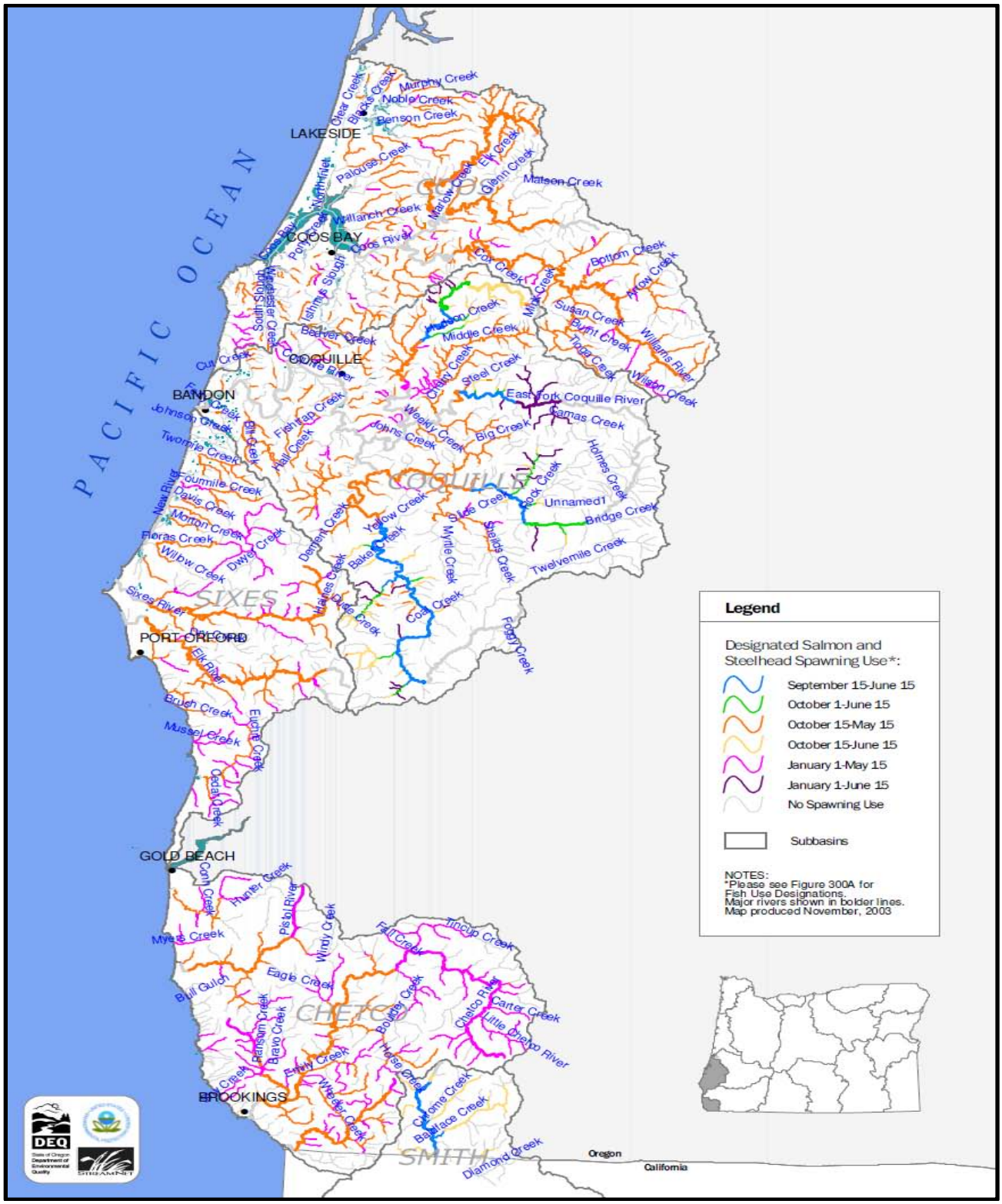
Fish Use Designations* - South Coast Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0300 – Figure 300B

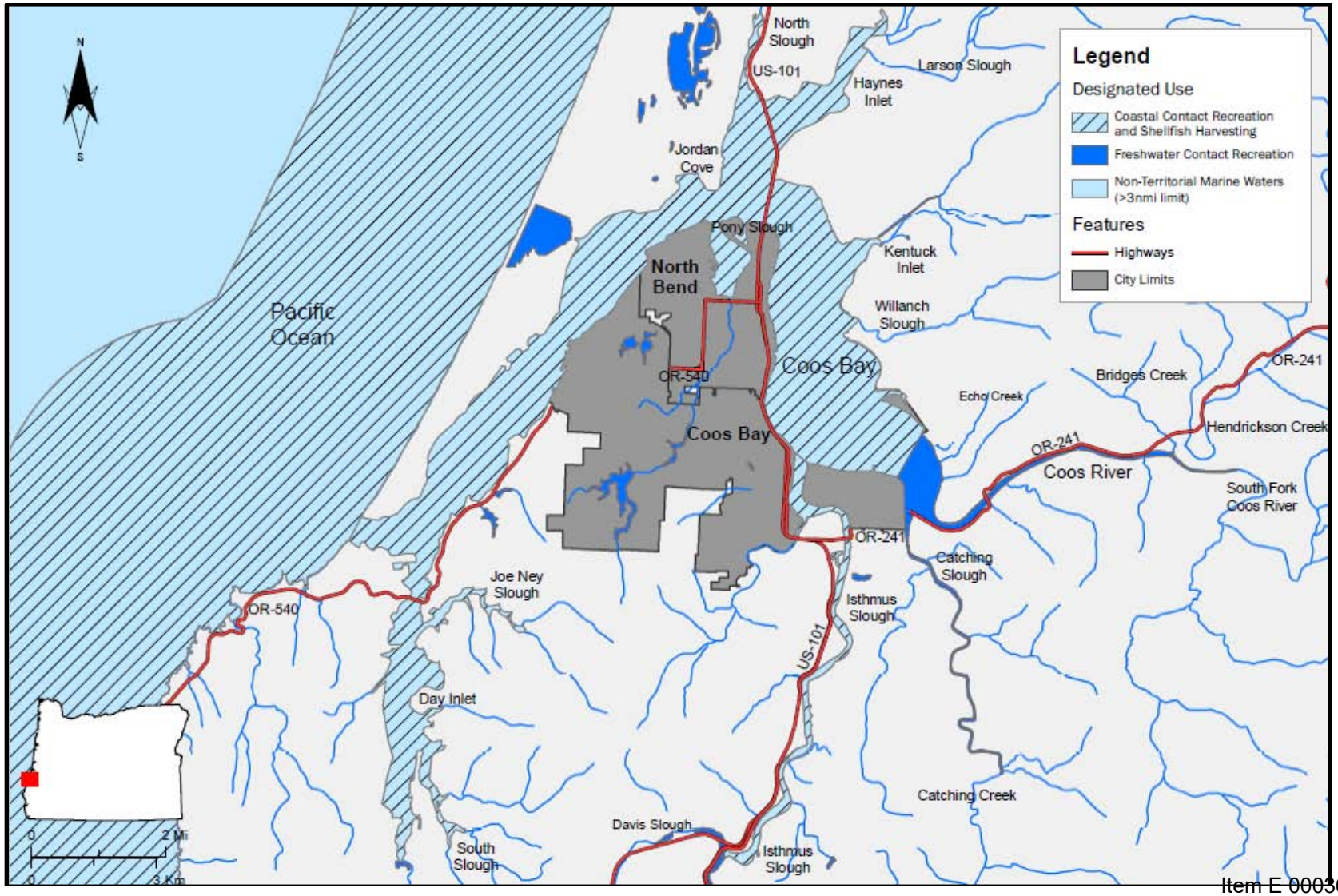
Salmon and Steelhead Spawning Use Designations*
South Coast Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0300 – Figure 300C

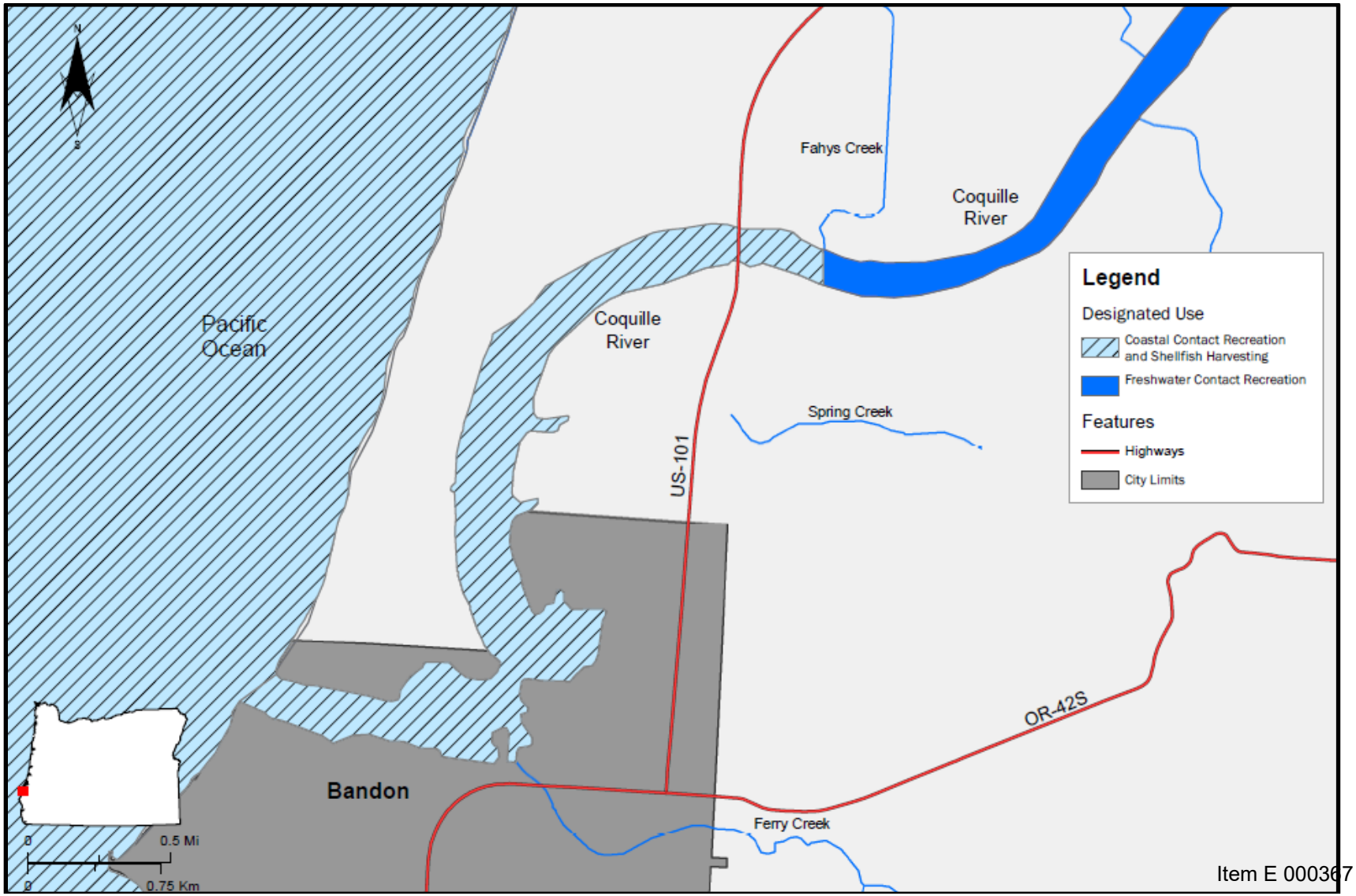
Water Contact Recreation and Shellfish Harvesting Designated Uses
Coos Bay, South Coast Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0300 – Figure 300D

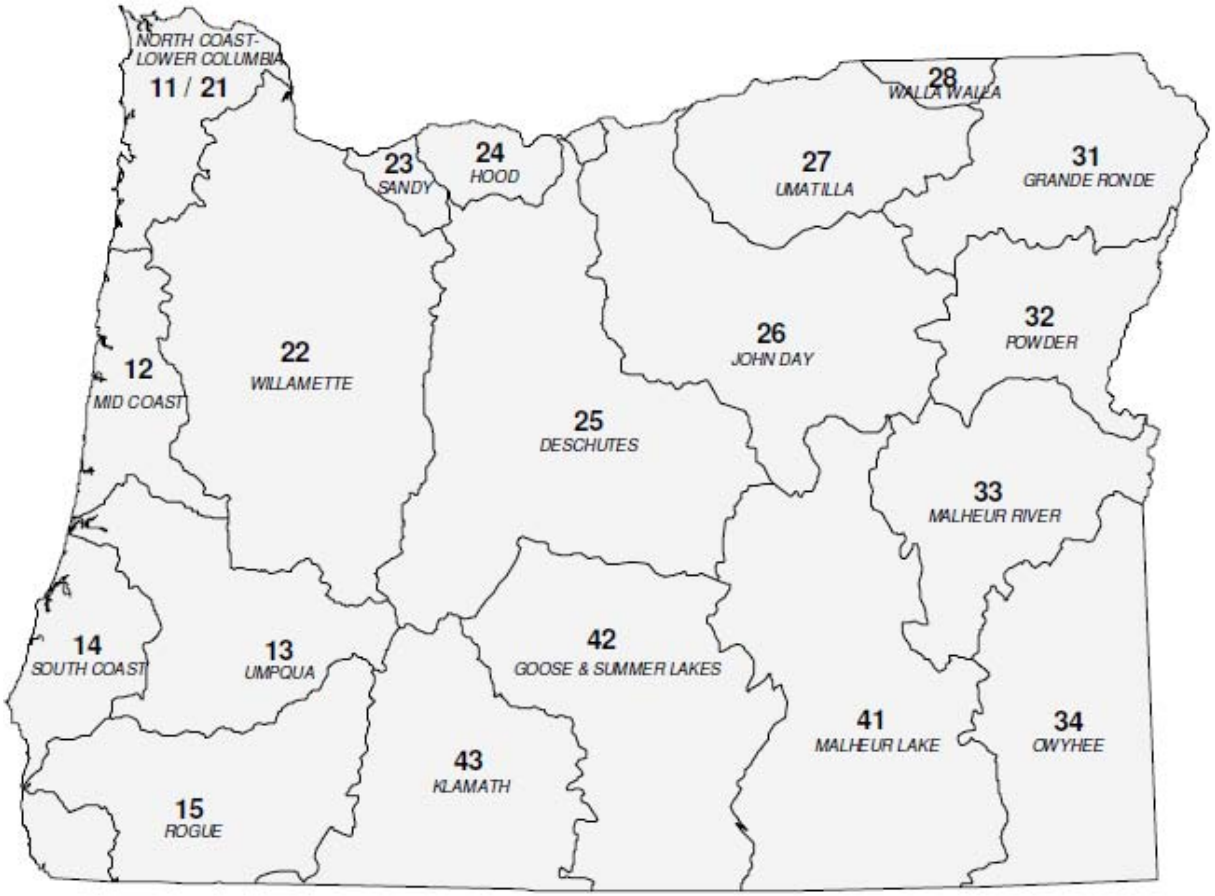
Water Contact Recreation and Shellfish Harvesting Designated Uses
Coquille River, South Coast Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0310
Tables and Figures

Figure 1: Oregon Basin Index Map



Basin Name	Basin #	OAR #
DESCHUTES	25	340-041-0130
GOOSE & SUMMER LKS	42	340-041-0140
GRANDE RONDE	31	340-041-0151
HOOD	24	340-041-0160
JOHN DAY	26	340-041-0170
KLAMATH	43	340-041-0180
MALHEUR LAKE	41	340-041-0190
MALHEUR RIVER	33	340-041-0201
MD COAST	12	340-041-0220
NORTH COAST-LWR COL	11-21	340-041-0230
OWYHEE	34	340-041-0250
POWDER	32	340-041-0260
ROGUE	15	340-041-0271
SANDY	23	340-041-0286
SOUTH COAST	14	340-041-0300
UMATILLA	27	340-041-0310
UMPQUA	13	340-041-0320
WALLA WALLA	28	340-041-0330
WILLAMETTE	22	340-041-0340

OAR 340-041-0310
Table 310A
Designated Beneficial Uses
Umatilla Basin

Beneficial Uses	Umatilla Subbasin	Willow Creek Subbasin	West Division Main Canal – constructed channel[3]	West Division Main Canal – overflow channels[3]
Public Domestic Water Supply[1]	X	X		
Private Domestic Water Supply[1]	X	X		
Industrial Water Supply	X	X	X	X
Irrigation	X	X	X	X
Livestock Watering	X	X	X	X
Fish & Aquatic Life[2]	X	X		X
Wildlife & Hunting	X	X	X	X
Fishing	X	X		X
Boating	X	X (at mouth)		
Water Contact Recreation	X	X	X	X
Aesthetic Quality	X	X	X	X
Hydro Power	X	X	X	X
Commercial Navigation and Transportation				

[1]With adequate pretreatment (filtration & disinfection) and natural quality to meet drinking water standards.

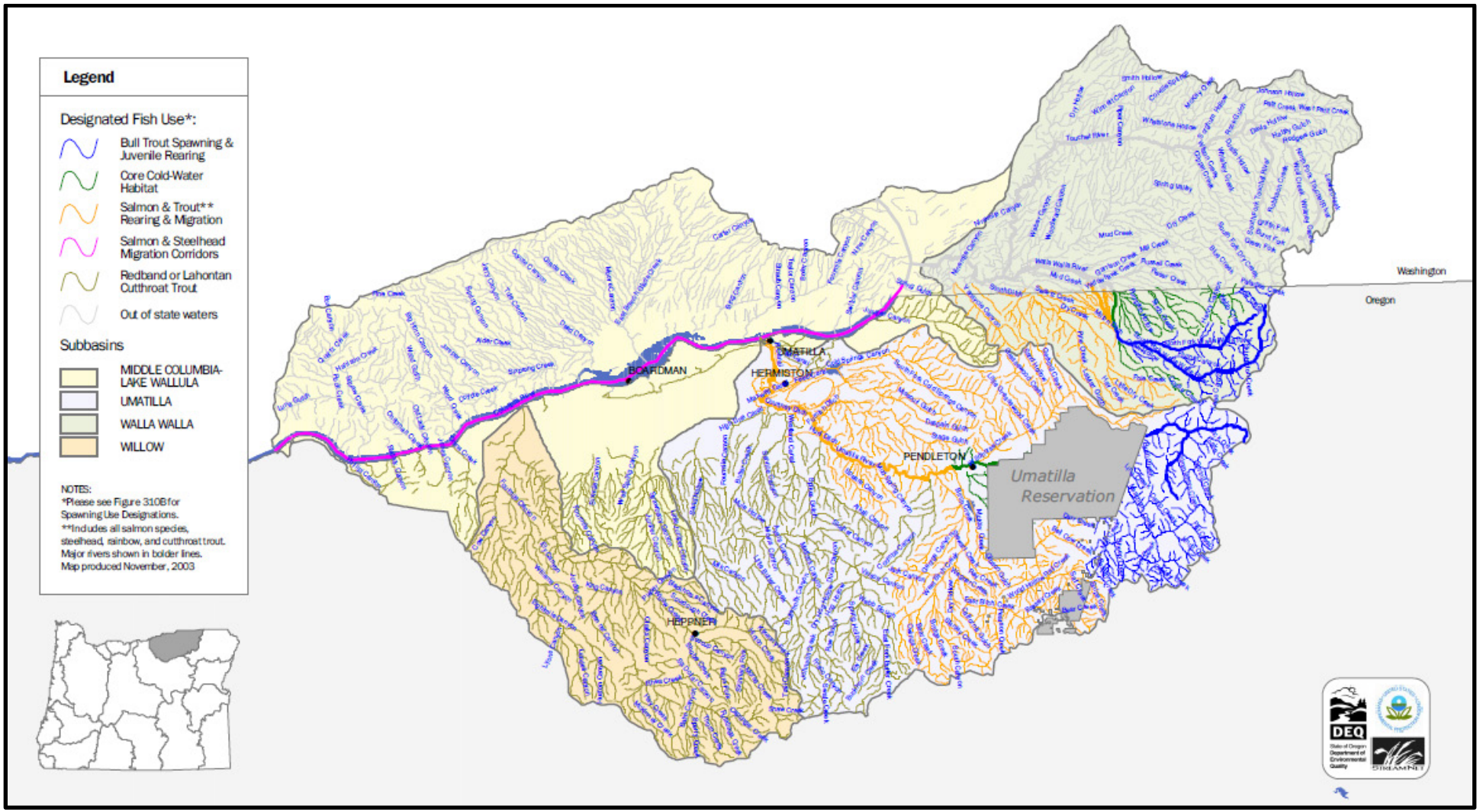
[2]See also Figures 310A and 310B for fish use designations for this basin. Note: The fish & aquatic life use designations for the "constructed channel" segment of the West Division Main Canal in this table supersede Figure 310A, which incorrectly identifies Redband trout use in that portion of the canal.

[3]The West Division Main Canal extends from the point of diversion from the Umatilla River to the confluence with the Columbia River. The canal consists of two segments. The constructed channel segment extends from the Umatilla River 27 miles down gradient to the flow control gate at the end of the concrete structure as it was originally built (concrete-lining was later added to parts of the overflow channels). The overflow channels segment extends from the lower end of the constructed channel to the outflow to the Columbia River.

State of Oregon Department of Environmental Quality

OAR 340-041-0310 – Figure 310A

Fish Use Designations* – Umatilla Basin, Oregon

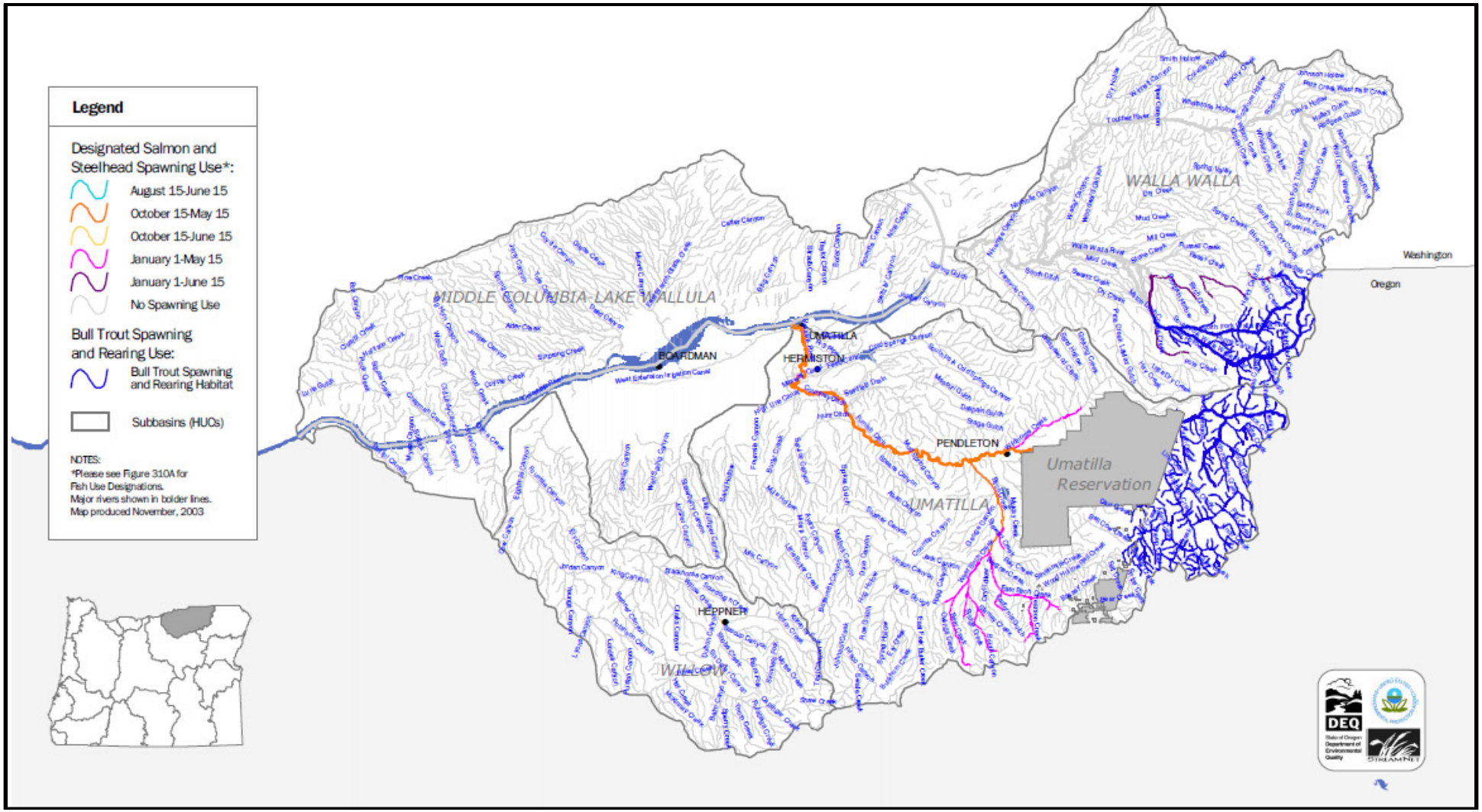


State of Oregon Department of Environmental Quality

OAR 340-041-0310 – Figure 310B

Salmon and Steelhead Spawning Use Designations*

Umatilla Basin, Oregon



OAR 340-041-0315
Table 315
Water Quality Criteria
Constructed Channel Segment
West Division Main Canal, Umatilla Basin

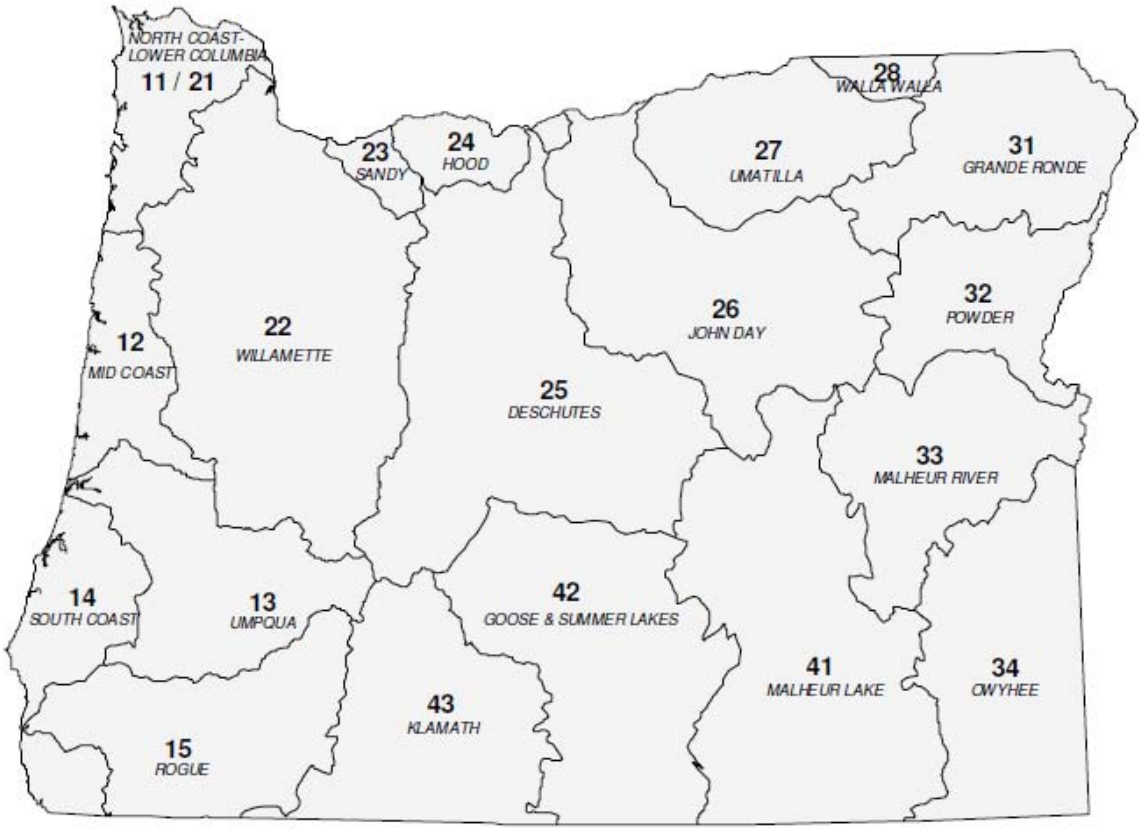
Parameter	For Irrigation (mg/l, metals as dissolved)	For Livestock Watering (mg/l, metals as dissolved)
Total dissolved solids	450	
Arsenic (inorganic)	0.1	0.2
Beryllium	0.1	
Cadmium	0.01	0.05
Chromium	0.1	1
Copper	0.2	0.5
Lead	5	0.1
Mercury		0.01
Nickel	0.2	
Selenium	0.02	0.05
Zinc	2	25

Table Revised January 2015

State of Oregon Department of Environmental Quality

OAR 340-041-0320
Tables and Figures

Figure 1: Oregon Basin Index Map



Basin Name	Basin #	OAR #
DESCHUTES	25	340-041-0130
GOOSE & SUMMER LKS	42	340-041-0140
GRANDE RONDE	31	340-041-0151
HOOD	24	340-041-0160
JOHN DAY	26	340-041-0170
KLAMATH	43	340-041-0180
MALHEUR LAKE	41	340-041-0190
MALHEUR RIVER	33	340-041-0201
MD COAST	12	340-041-0220
NORTH COAST-LWR COL	11-21	340-041-0230
OWYHEE	34	340-041-0250
POWDER	32	340-041-0260
ROGUE	15	340-041-0271
SANDY	23	340-041-0286
SOUTH COAST	14	340-041-0300
UMATILLA	27	340-041-0310
UMPQUA	13	340-041-0320
WALLA WALLA	28	340-041-0330
WILLAMETTE	22	340-041-0340

OAR 340-041-0320
Table 320A
Designated Beneficial Uses
Umpqua Basin
(November 2003)

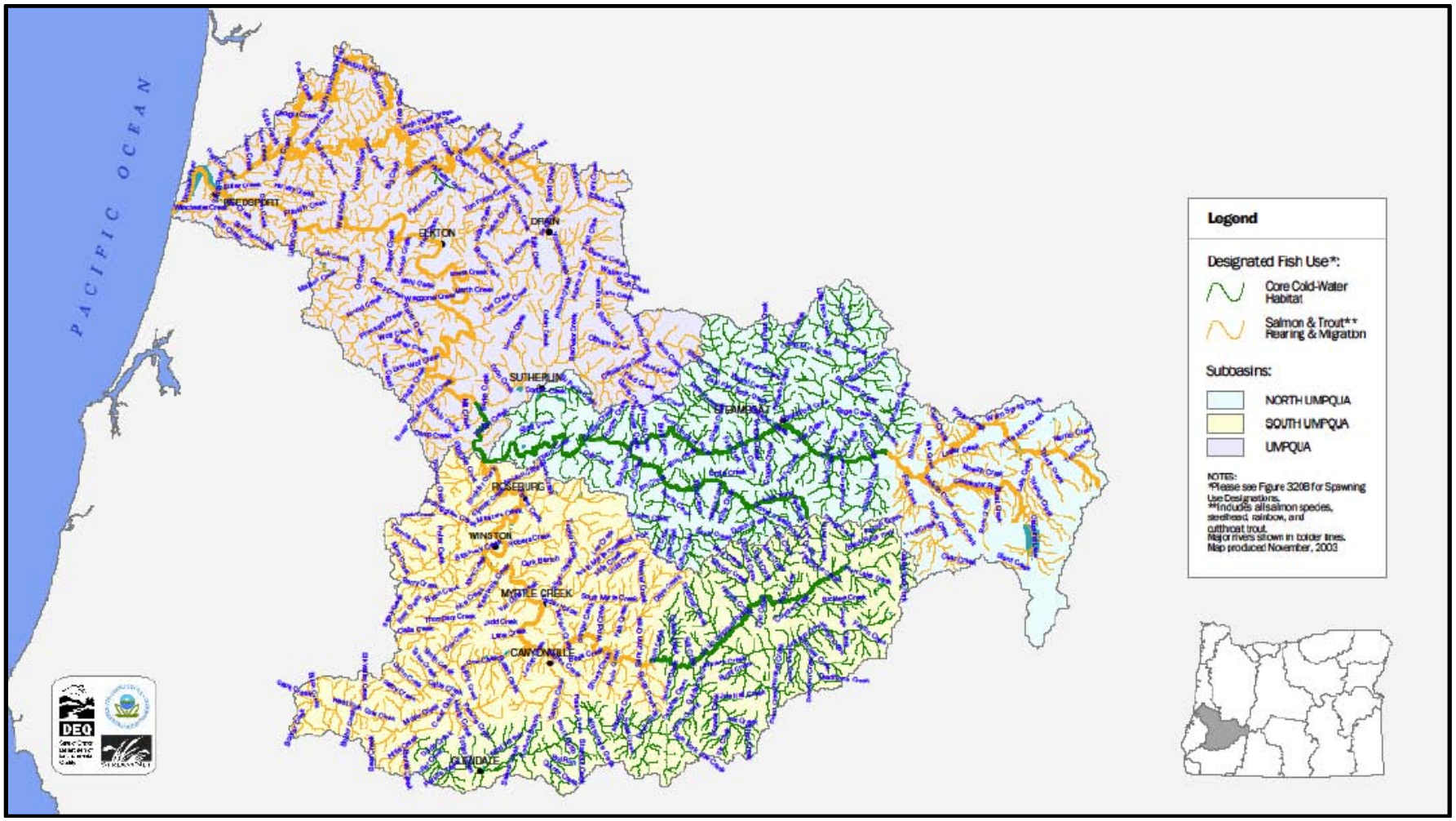
Beneficial Uses	Umpqua R. Estuary to Head of Tidewater and Adjacent Marine Waters	Umpqua R. Main from Head of Tidewater to Confluence of N. and S. Umpqua Rivers	North Umpqua River Main Stem	South Umpqua River Main Stem	All Other Tributaries to Umpqua, North and South Umpqua Rivers
Public Domestic Water Supply[1]		X	X	X	X
Private Domestic Water Supply[1]		X	X	X	X
Industrial Water Supply	X	X	X	X	X
Irrigation		X	X	X	X
Livestock Watering		X	X	X	X
Fish & Aquatic Life[2]	X	X	X	X	X
Wildlife & Hunting	X	X	X	X	X
Fishing	X[3]	X	X	X	X
Boating	X	X	X	X	X
Water Contact Recreation	X[3]	X	X	X	X
Aesthetic Quality	X	X	X	X	X
Hydro Power			X	X	X
Commercial Navigation & Transportation	X				

[1] With adequate pretreatment (filtration and disinfection) and natural quality to meet drinking water standards.
[2] See also Figures 320A and 320B for fish use designations for this basin.
[3] For coastal water contact recreation and shellfish harvesting uses in the Umpqua River Estuary and Adjacent Marine Waters, see also Figure 320C.

State of Oregon Department of Environmental Quality

OAR 340-041-0320 – Figure 320A

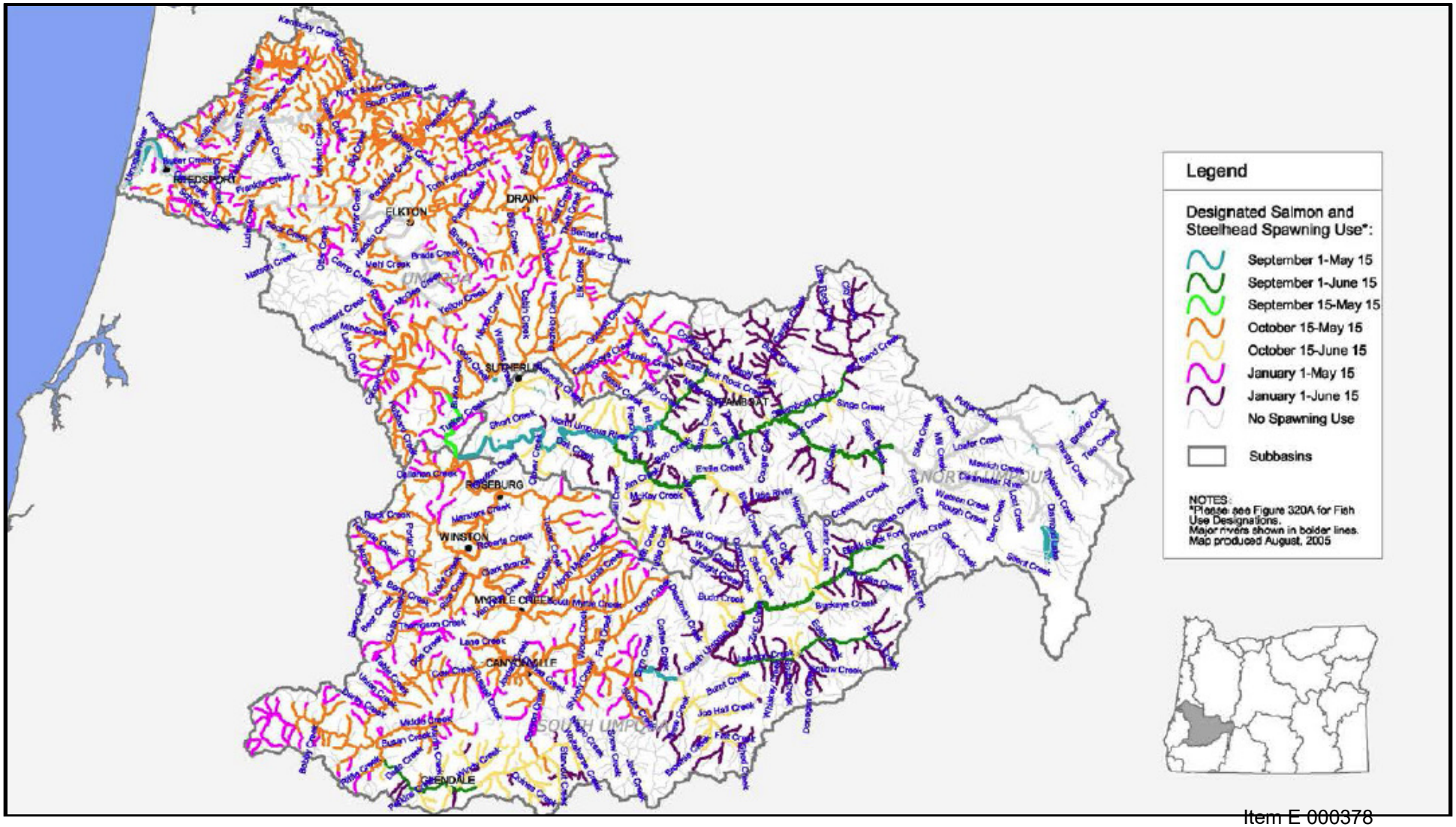
Fish Use Designations* - Umpqua Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0320 – Figure 320B

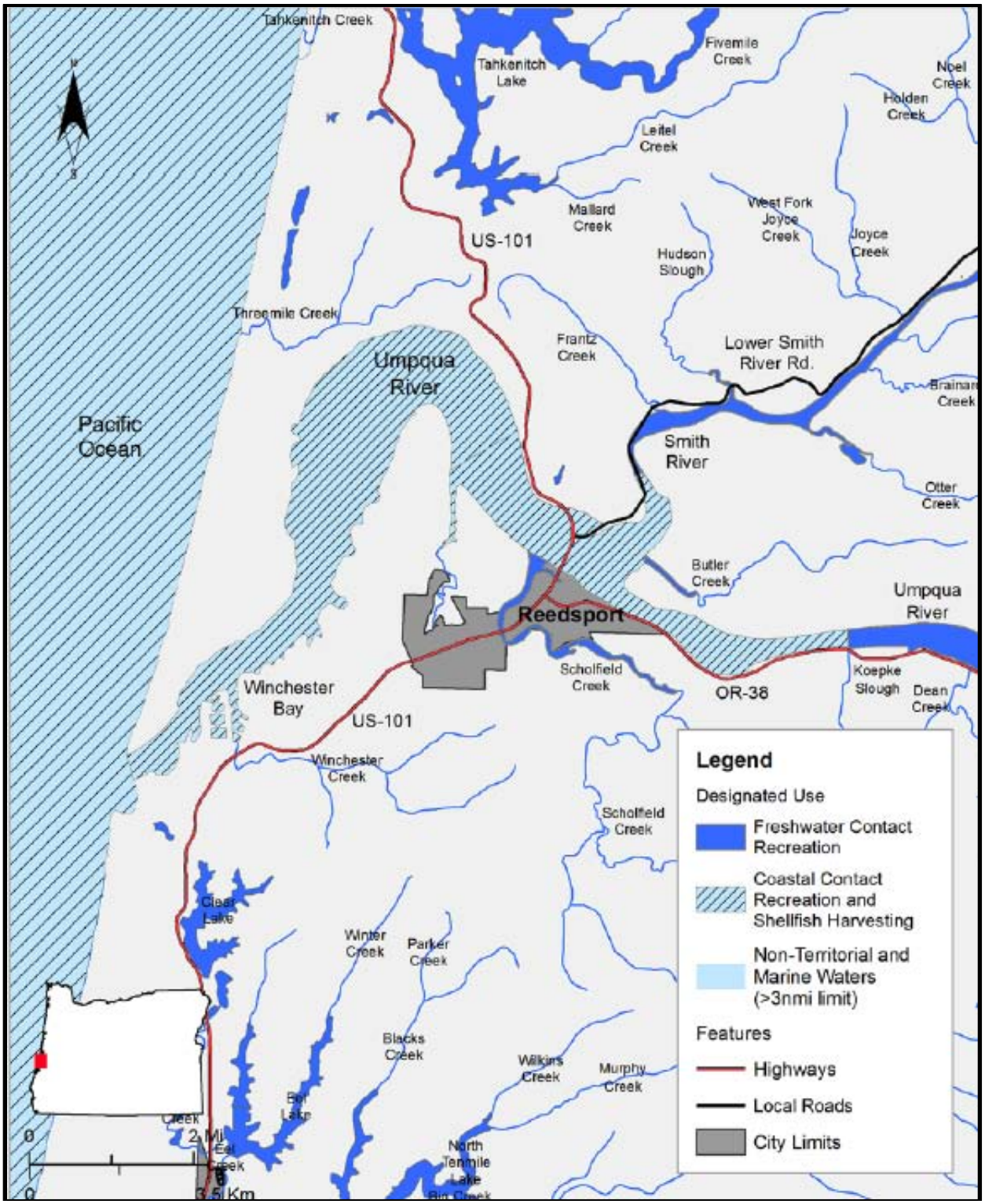
Salmon and Steelhead Spawning Use Designations*
Umpqua Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0320 – Figure 320C

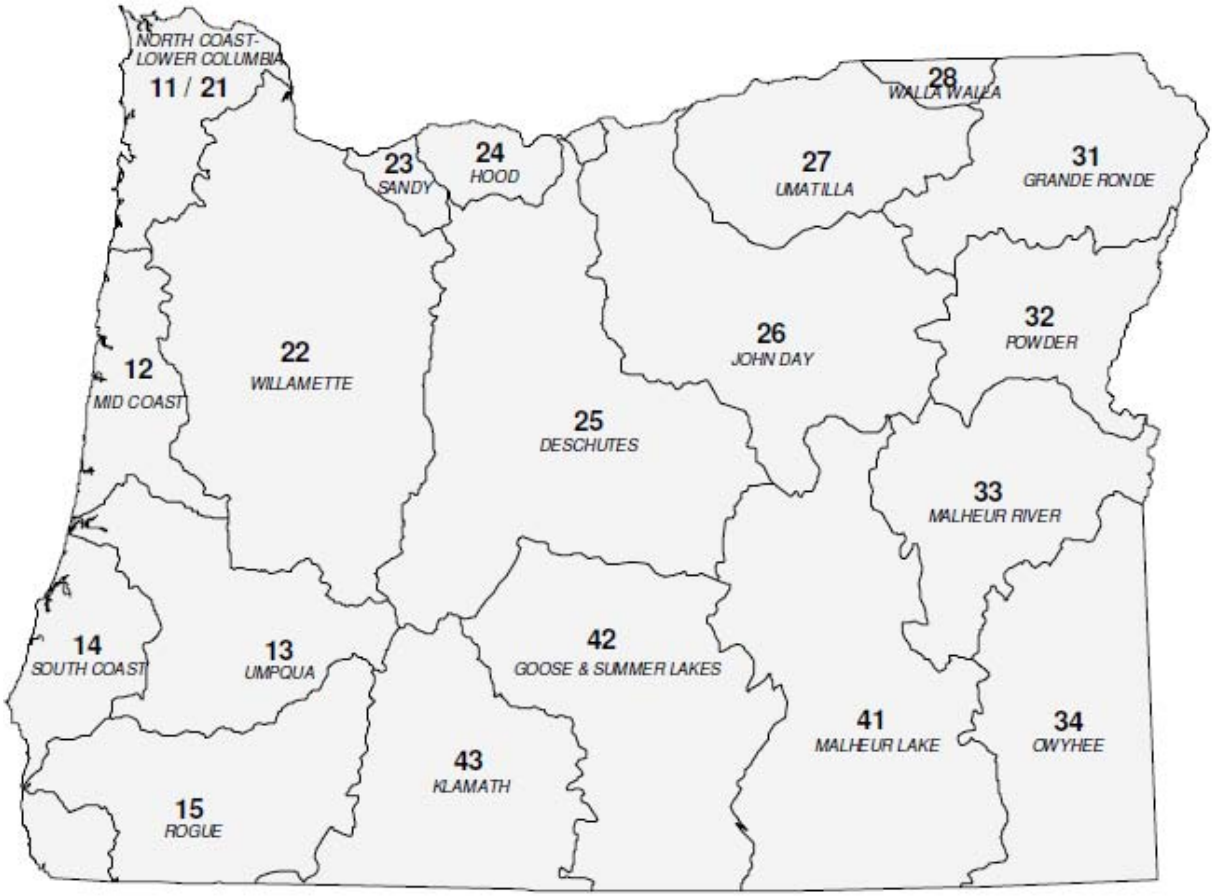
Water Contact Recreation and Shellfish Harvesting Designated Uses Umpqua Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0330
Tables and Figures

Figure 1: Oregon Basin Index Map



Basin Name	Basin #	OAR #
DESCHUTES	25	340-041-0130
GOOSE & SUMMER LKS	42	340-041-0140
GRANDE RONDE	31	340-041-0151
HOOD	24	340-041-0160
JOHN DAY	26	340-041-0170
KLAMATH	43	340-041-0180
MALHEUR LAKE	41	340-041-0190
MALHEUR RIVER	33	340-041-0201
MD COAST	12	340-041-0220
NORTH COAST-LWR COL	11-21	340-041-0230
OWYHEE	34	340-041-0250
POWDER	32	340-041-0260
ROGUE	15	340-041-0271
SANDY	23	340-041-0286
SOUTH COAST	14	340-041-0300
UMATILLA	27	340-041-0310
UMPQUA	13	340-041-0320
WALLA WALLA	28	340-041-0330
WILLAMETTE	22	340-041-0340

OAR 340-041-0330
Table 330A
Designated Beneficial Uses
Walla Walla Basin

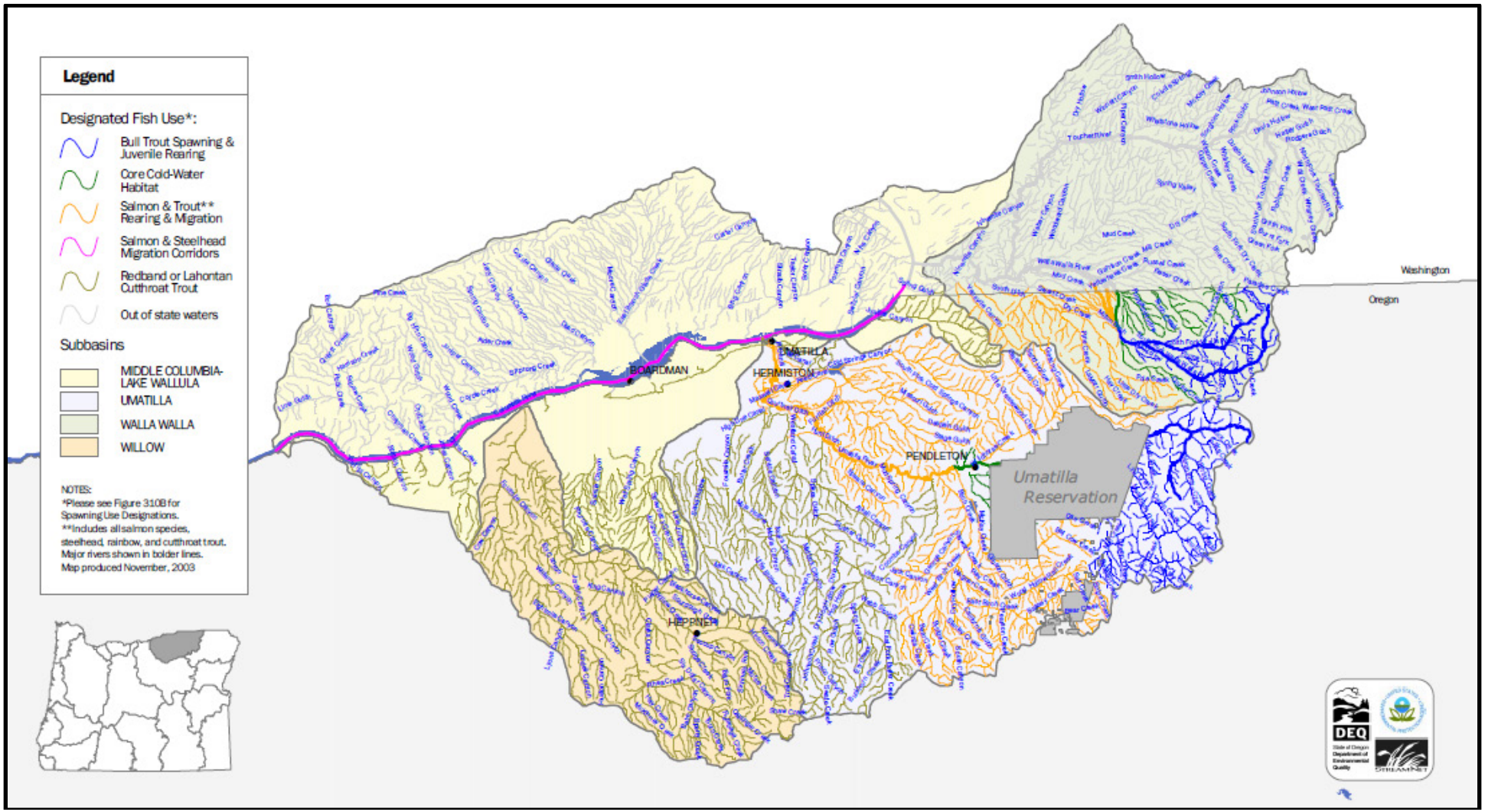
Beneficial Uses	Walla Walla River Main Stem from Confluence of North & South Forks to State Line	All Other Basin Streams
Public Domestic Water Supply[1]	X	X
Private Domestic Water Supply[1]	X	X
Industrial Water Supply	X	
Irrigation	X	X
Livestock Watering	X	X
Fish & Aquatic Life[2]	X	X
Wildlife & Hunting	X	X
Fishing	X	X
Boating	X	X
Water Contact Recreation	X	X
Aesthetic Quality	X	X
Hydro Power		X
Commercial Navigation & Transportation		

[1] With adequate pretreatment (filtration & disinfection) and natural quality to meet drinking water standards.
[2] See also Figures 310A and 310B for fish use designations for this basin.

State of Oregon Department of Environmental Quality

OAR 340-041-0330 – Figure 310A

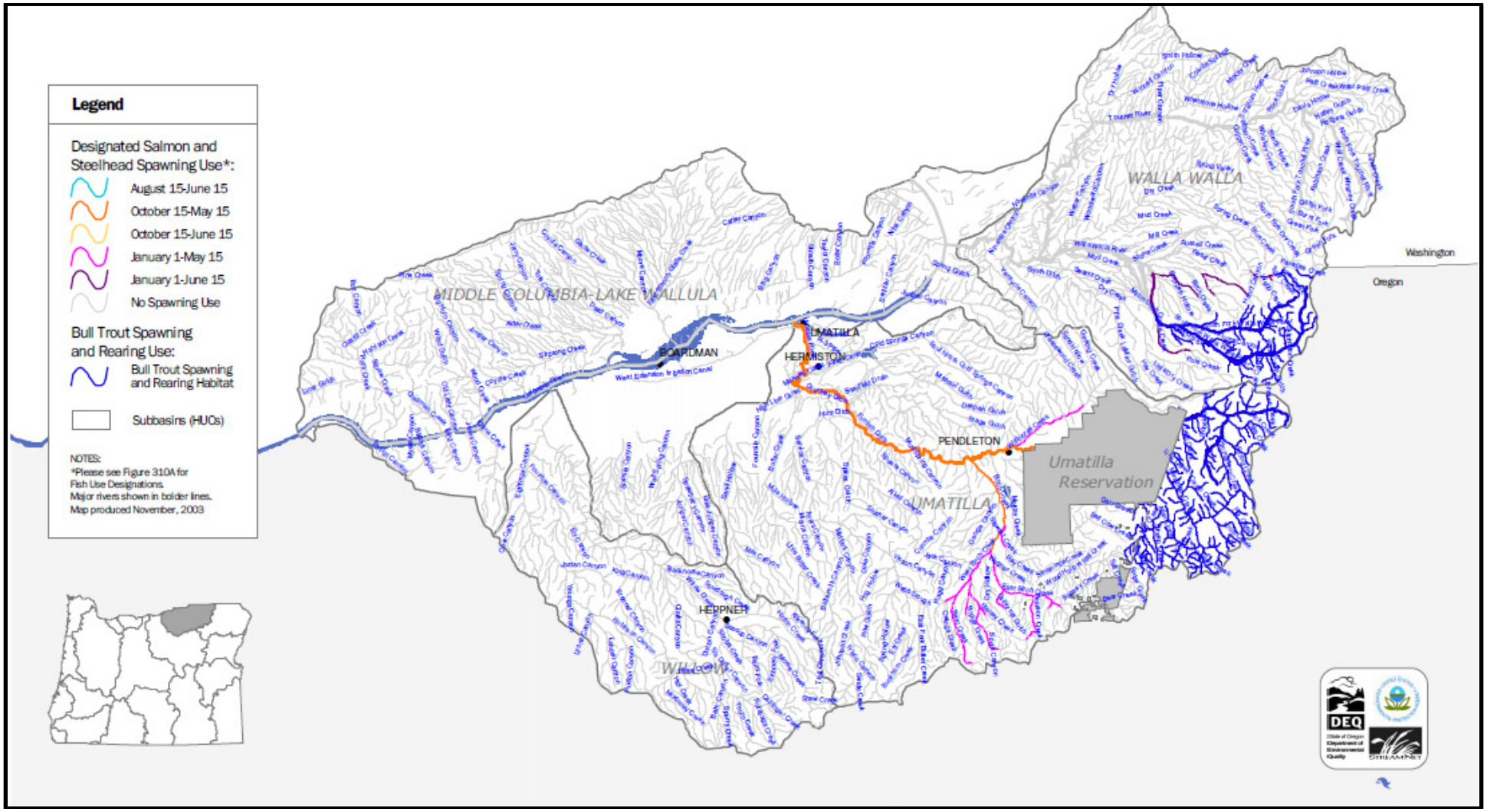
Fish Use Designations* - Umatilla Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0330 – Figure 310B

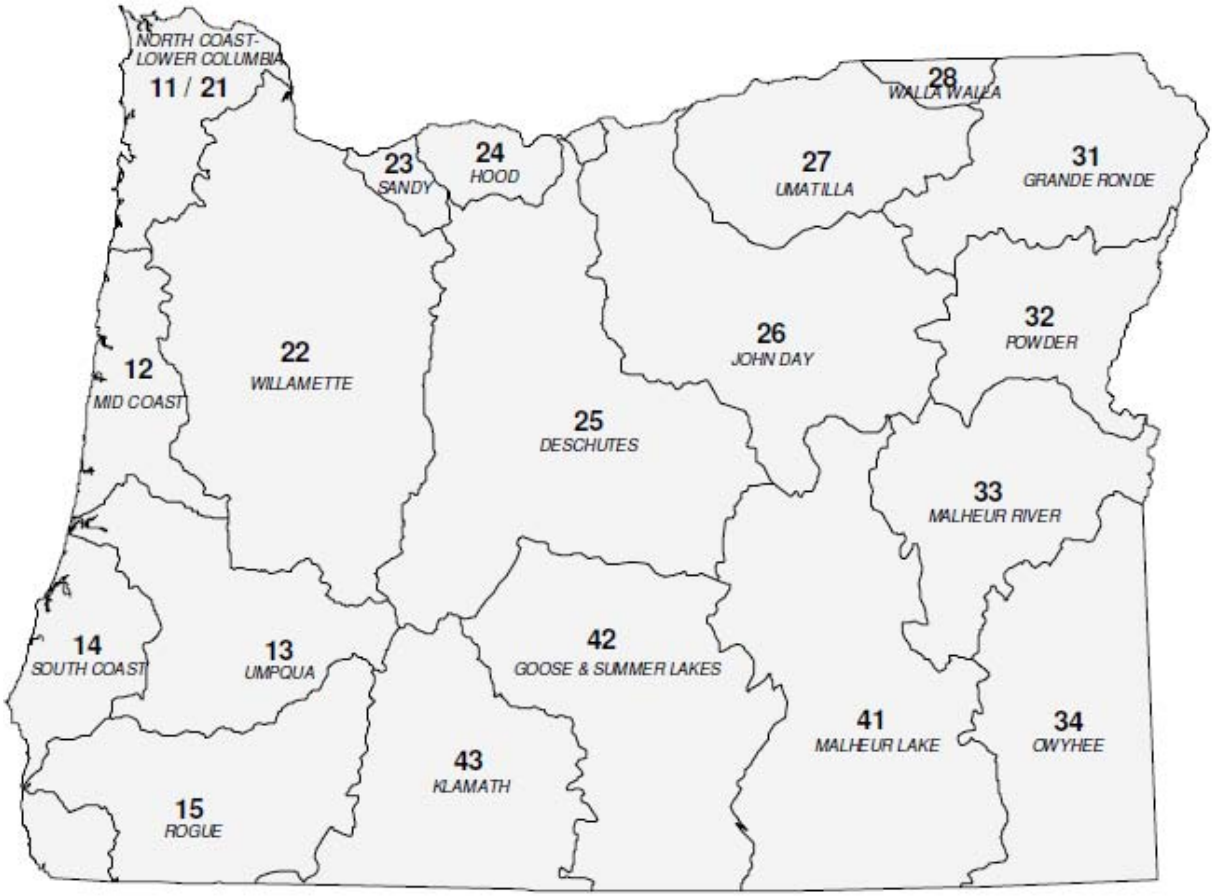
Salmon and Steelhead Spawning Use Designations*
Umatilla Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0340 – Tables and Figures

Figure 1: Oregon Basin Index Map

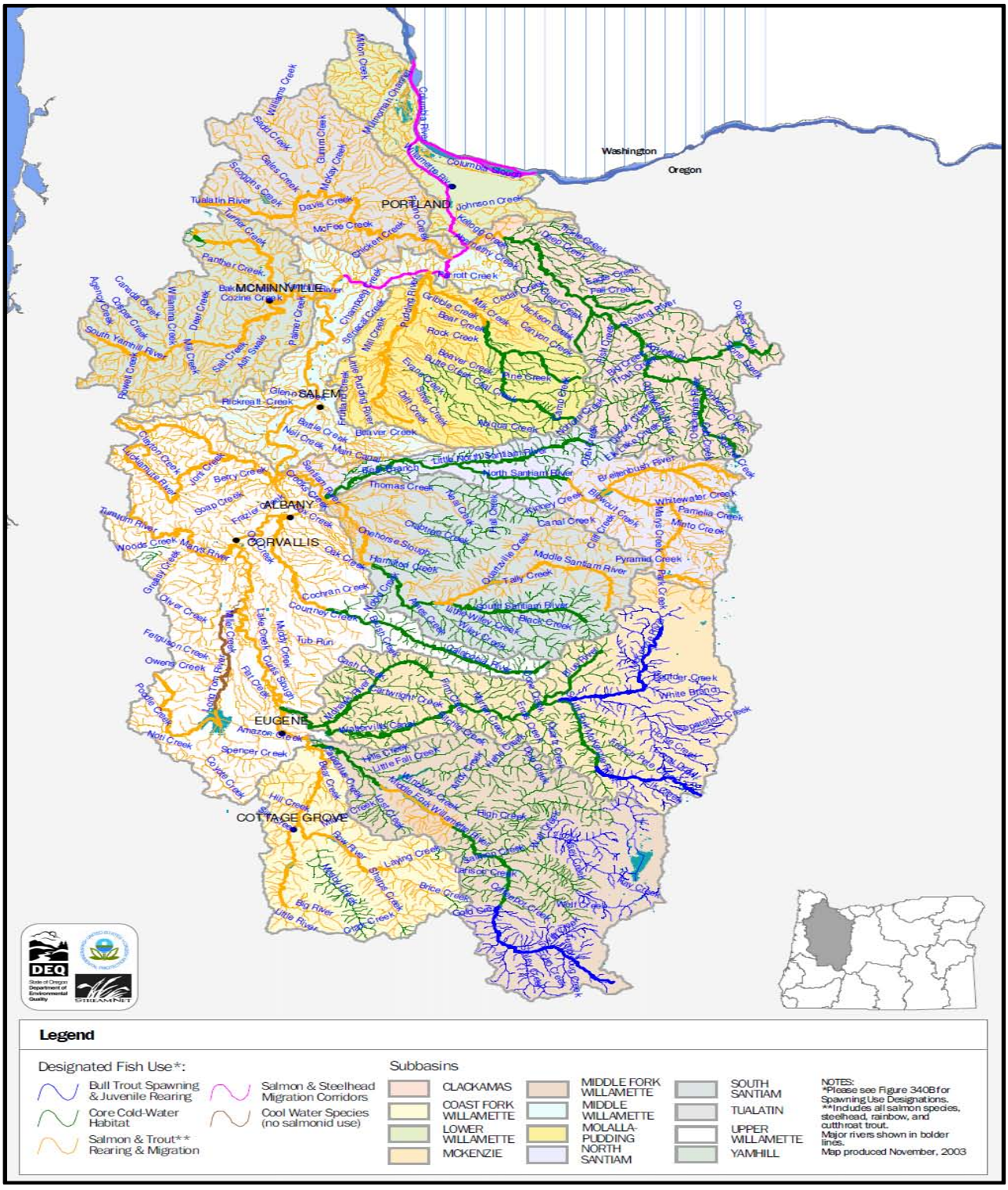


Basin Name	Basin #	OAR #
DESCHUTES	25	340-041-0130
GOOSE & SUMMER LKS	42	340-041-0140
GRANDE RONDE	31	340-041-0151
HOOD	24	340-041-0160
JOHN DAY	26	340-041-0170
KLAMATH	43	340-041-0180
MALHEUR LAKE	41	340-041-0190
MALHEUR RIVER	33	340-041-0201
MD COAST	12	340-041-0220
NORTH COAST-LWR COL	11-21	340-041-0230
OWYHEE	34	340-041-0250
POWDER	32	340-041-0260
ROGUE	15	340-041-0271
SANDY	23	340-041-0286
SOUTH COAST	14	340-041-0300
UMATILLA	27	340-041-0310
UMPQUA	13	340-041-0320
WALLA WALLA	28	340-041-0330
WILLAMETTE	22	340-041-0340

State of Oregon Department of Environmental Quality

OAR 340-041-0340 – Figure 340A

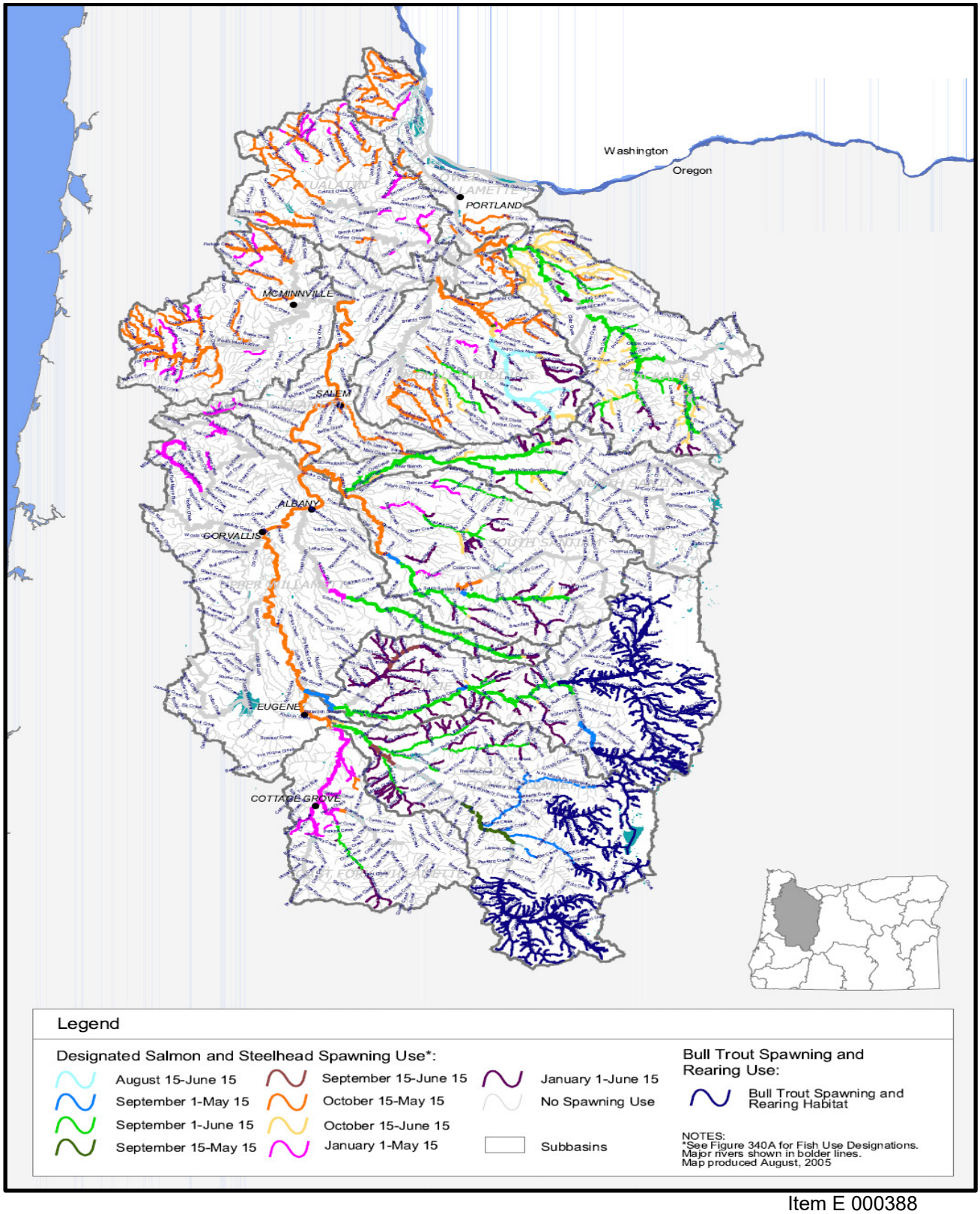
Fish Use Designations* - Willamette Basin, Oregon



State of Oregon Department of Environmental Quality

OAR 340-041-0340 – Figure 340B

Salmon and Steelhead Spawning Use Designations*
Willamette Basin, Oregon



OAR 340-041-8033
Table 30
Aquatic Life Water Quality Criteria for Toxic Pollutants

The concentration for each compound listed in Table 30 is a criterion established for waters of the state in order to protect aquatic life. The aquatic life criteria apply to waterbodies where the protection of fish and aquatic life is a designated use. All values are expressed as micrograms per liter (µg/L). Compounds are listed in alphabetical order with the corresponding information: the Chemical Abstract Service (CAS) number, whether there is a human health criterion for the pollutant (i.e. "y"= yes, "n" = no), and the associated aquatic life freshwater and saltwater acute and chronic criteria. *Italicized* pollutants are not identified as priority pollutants by EPA. Dashes in the table column indicate that there is no aquatic life criterion.

Unless otherwise noted in the table below, the acute criterion is the Criterion Maximum Concentration (CMC) applied as a one-hour average concentration, and the chronic criterion is the Criterion Continuous Concentration (CCC) applied as a 96-hour (4 days) average concentration. The CMC and CCC criteria may not be exceeded more than once every three years. Footnote A, associated with eleven pesticide pollutants in Table 30, describes the exception to the frequency and duration of the toxics criteria stated in this paragraph.

OAR 340-041-8033
Table 30
Aquatic Life Water Quality Criteria for Toxic Pollutants

No.	Pollutant	CAS Number	Human Health Criterion	Freshwater (µg/L)		Saltwater (µg/L)	
				Acute Criterion (CMC)	Chronic Criterion (CCC)	Acute Criterion (CMC)	Chronic Criterion (CCC)
1	Aldrin	309002	y	3 [A]	--	1.3 [A]	--
[A] *See expanded endnote A at bottom of Table 30 for alternate frequency and duration of this criterion.*							
2	*Alkalinity*		n	--	20,000 [B]	--	--
[B] *Criterion shown is the minimum (i.e. CCC in water may not be below this value in order to protect aquatic life).*							

OAR 340-041-8033
Table 30
Aquatic Life Water Quality Criteria for Toxic Pollutants

No.	Pollutant	CAS Number	Human Health Criterion	Freshwater (µg/L)		Saltwater (µg/L)	
				Acute Criterion (CMC)	Chronic Criterion (CCC)	Acute Criterion (CMC)	Chronic Criterion (CCC)
3	*Ammonia*	7664417	n	*The ammonia criteria are pH and temperature dependent — See ammonia criteria Tables 30(a)-(c) at end of Table 30.*[M]		*The ammonia criteria are pH, temperature and salinity dependent. Values for saltwater criteria (total ammonia) can be calculated from the tables specified in Ambient Water Quality Criteria for Ammonia (Saltwater)—1989 (EPA 440/5-88-004) See DEQ's calculator for calculating saltwater ammonia criteria at: http://www.deq.state.or.us/wq/standards/toxics.htm*	
[M] *The acute criteria in Table 30(a) apply in waterbodies where salmonids are a designated use in OAR 340-041-0101 through OAR 340-041-0340. The acute criteria in Table 30(b) apply in waterbodies where salmonids are not a designated use. The chronic criteria in Table 30(c) apply where fish and aquatic life is a designated use. It is not necessary to account for the presence or absence of salmonids or the presence of any early life stage of fish for the chronic criteria. Refer to DEQ's beneficial use website at: http://www.deq.state.or.us/wq/standards/uses.htm for additional information on salmonid beneficial use designations, including tables and maps.*							
4	Arsenic	7440382	y	340 [C, D]	150 [C, D]	69 [C, D]	36 [C, D]
[C] *Criterion is expressed in terms of "dissolved" concentrations in the water column.* [D] *Criterion is applied as total inorganic arsenic (i.e. arsenic (III) + arsenic (V)).*							
5	BHC Gamma (Lindane)	58899	y	0.95	0.08 [A]	0.16 [A]	--
[A] *See expanded endnote A at bottom of Table 30 for alternate frequency and duration of this criterion.*							
6	Cadmium	7440439	n	*See* **E**	*See* **C, F**	40 [C]	8.8 [C]
[C] *Criterion is expressed in terms of "dissolved" concentrations in the water column.*							

OAR 340-041-8033
Table 30
Aquatic Life Water Quality Criteria for Toxic Pollutants

No.	Pollutant	CAS Number	Human Health Criterion	Freshwater (µg/L)		Saltwater (µg/L)	
				Acute Criterion (CMC)	Chronic Criterion (CCC)	Acute Criterion (CMC)	Chronic Criterion (CCC)
E *The freshwater criterion for this metal is expressed as "total recoverable" and is a function of hardness (mg/L) in the water column. To calculate the criterion, use formula under expanded endnote E at bottom of Table 30.*							
F *The freshwater criterion for this metal is expressed as a function of hardness (mg/L) in the water column. To calculate the criterion, use formula under expanded endnote F at bottom of Table 30.*							
7	Chlordane	57749	y	2.4 **A**	0.0043 **A**	0.09 **A**	0.004 **A**
A *See expanded endnote A at bottom of Table 30 for alternate frequency and duration of this criterion.*							
8	*Chloride*	16887006	n	860,000	230,000	--	--
9	*Chlorine*	7782505	n	19	11	13	7.5
10	*Chlorpyrifos*	2921882	n	0.083	0.041	0.011	0.0056
11	Chromium III	16065831	n	*See* **C, F**	*See* **C, F**	--	--
C *Criterion is expressed in terms of "dissolved" concentrations in the water column.* **F** *The freshwater criterion for this metal is expressed as a function of hardness (mg/L) in the water column. To calculate the criterion, use formula under expanded endnote F at bottom of Table 30.*							
12	Chromium VI	18540299	n	16 **C**	11 **C**	1100 **C**	50 **C**
C *Criterion is expressed in terms of "dissolved" concentrations in the water column.*							
13	Copper	7440508	y	*See* **C, N**	*See* **C, N**	4.8 **C**	3.1 **C**
C *Criterion is expressed in terms of "dissolved" concentrations in the water column.* **N** *The freshwater criterion for copper is a function of the concentration of ions, alkalinity, organic carbon, pH and temperature in the water column. To calculate the criterion, use the Biotic Ligand Model referenced in endnote N at the bottom of Table 30. The acute copper criterion (CMC) is applied as a one-hour average concentration. The chronic criterion (CCC) is applied as a 96-hour (4 days) average concentration. See endnote N also for procedures and information.*							

OAR 340-041-8033
Table 30
Aquatic Life Water Quality Criteria for Toxic Pollutants

No.	Pollutant	CAS Number	Human Health Criterion	Freshwater (µg/L)		Saltwater (µg/L)	
				Acute Criterion (CMC)	Chronic Criterion (CCC)	Acute Criterion (CMC)	Chronic Criterion (CCC)
*[**Note**: The Environmental Quality Commission adopted these revised copper criteria on 11/02/2016. However, the revised criteria become effective for federal Clean Water Act purposes upon approval by the U.S. Environmental Protection Agency.]*							
14	Cyanide	57125	y	22 [J]	5.2 [J]	1 [J]	1 [J]
[J] *This criterion is expressed as µg free cyanide (CN)/L.*							
15	DDT 4,4'	50293	y	1.1 [A, G]	0.001 [A, G]	0.13 [A, G]	0.001 [A, G]
[A] *See expanded endnote A at bottom of Table 30 for alternate frequency and duration of this criterion.* [G] *This criterion applies to DDT and its metabolites (i.e. the total concentration of DDT and its metabolites should not exceed this value).*							
16	*Demeton*	8065483	n	--	0.1	--	0.1
17	Dieldrin	60571	y	0.24	0.056	0.71[A]	0.0019[A]
[A] *See expanded endnote A at bottom of Table 30 for alternate frequency and duration of this criterion.*							
18	Endosulfan	115297	n	0.22 [A, H]	0.056 [A, H]	0.034 [A, H]	0.0087 [A, H]
[A] *See expanded endnote A at bottom of Table 30 for alternate frequency and duration of this criterion.* [H] *This value is based on the criterion published in Ambient Water Quality Criteria for Endosulfan (EPA 440/5-80-046) and should be applied as the sum of alpha- and beta-endosulfan.*							
19	Endosulfan Alpha	959988	y	0.22 [A]	0.056 [A]	0.034 [A]	0.0087 [A]
[A] *See expanded endnote A at bottom of Table 30 for alternate frequency and duration of this criterion.*							
20	Endosulfan Beta	33213659	y	0.22 [A]	0.056 [A]	0.034 [A]	0.0087 [A]
[A] *See expanded endnote A at bottom of Table 30 for alternate frequency and duration of this criterion.*							
21	Endrin	72208	y	0.086	0.036	0.037 [A]	0.0023 [A]
[A] *See expanded endnote A at bottom of Table 30 for alternate frequency and duration of this criterion.*							
22	*Guthion*	86500	n	--	0.01	--	0.01

OAR 340-041-8033
Table 30
Aquatic Life Water Quality Criteria for Toxic Pollutants

No.	Pollutant	CAS Number	Human Health Criterion	Freshwater (µg/L)		Saltwater (µg/L)	
				Acute Criterion (CMC)	Chronic Criterion (CCC)	Acute Criterion (CMC)	Chronic Criterion (CCC)
23	Heptachlor	76448	y	0.52 [A]	0.0038 [A]	0.053 [A]	0.0036 [A]
[A] *See expanded endnote A at bottom of Table 30 for alternate frequency and duration of this criterion.*							
24	Heptachlor Epoxide	1024573	y	0.52 [A]	0.0038 [A]	0.053 [A]	0.0036 [A]
[A] *See expanded endnote A at bottom of Table 30 for alternate frequency and duration of this criterion.*							
25	*Iron (total)*	7439896	n	--	1000	--	--
26	Lead	7439921	n	*See* **C , F**	*See* **C , F**	210 [C]	8.1 [C]
[C] *Criterion is expressed in terms of "dissolved" concentrations in the water column.* [F] *The freshwater criterion for this metal is expressed as a function of hardness (mg/L) in the water column. To calculate the criterion, use formula under expanded endnote F at bottom of Table 30.*							
27	*Malathion*	121755	n	--	0.1	--	0.1
28	Mercury (total)	7439976	n	2.4	0.012	2.1	0.025
29	*Methoxychlor*	72435	y	--	0.03	--	0.03
30	*Mirex*	2385855	n	--	0.001	--	0.001
31	Nickel	7440020	y	*See* **C , F**	*See* **C , F**	74 [C]	8.2 [C]
[C] *Criterion is expressed in terms of "dissolved" concentrations in the water column.* [F] *The freshwater criterion for this metal is expressed as a function of hardness (mg/L) in the water column. To calculate the criterion, use formula under expanded endnote F at bottom of Table 30.*							
32	*Parathion*	56382	n	0.065	0.013	--	--
33	Pentachlorophenol	87865	y	*See* **I**	*See* **I**	13	7.9
[I] *Freshwater aquatic life values for pentachlorophenol are expressed as a function of pH, and are calculated as follows: CMC=(exp(1.005(pH)-4.869); CCC=exp(1.005(pH)-5.134).*							
34	*Phosphorus Elemental*	7723140	n	--	--	--	0.1

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Table 30
Aquatic Life Water Quality Criteria for Toxic Pollutants

No.	Pollutant	CAS Number	Human Health Criterion	Freshwater (µg/L)		Saltwater (µg/L)	
				Acute Criterion (CMC)	Chronic Criterion (CCC)	Acute Criterion (CMC)	Chronic Criterion (CCC)
35	Polychlorinated Biphenyls (PCBs)	NA	y	2 [K]	0.014 [K]	10 [K]	0.03 [K]
[K] *This criterion applies to total PCBs (e.g.* determined as Aroclors or congeners)							
36	Selenium	7782492	y	*See* **C , L**	4.6 [C]	290 [C]	71 [C]
[C] *Criterion is expressed in terms of "dissolved" concentrations in the water column.* [L] *The CMC=(1/[(f1/CMC1)+(f2/CMC2)]µg/L) * CF where f1 and f2 are the fractions of total selenium that are treated as selenite and selenate, respectively, and CMC1 and CMC2 are 185.9 µg/L and 12.82 µg/L, respectively. See expanded endnote F for the Conversion Factor (CF) for selenium.*							
37	Silver	7440224	n	*See* **C , F**	0.10 [C]	1.9 [C]	--
[C] *Criterion is expressed in terms of "dissolved" concentrations in the water column.* [F] *The freshwater acute criterion for this metal is expressed as a function of hardness (mg/L) in the water column. To calculate the criterion, use formula under expanded endnote F at bottom of Table 30.*							
38	*Sulfide Hydrogen Sulfide*	7783064	n	--	2	--	2
39	Toxaphene	8001352	y	0.73	0.0002	0.21	0.0002
40	*Tributyltin (TBT)*	688733	n	0.46	0.063	0.37	0.01
41	Zinc	7440666	y	*See* **C , F**	*See* **C , F**	90 [C]	81 [C]
[C] *Criterion is expressed in terms of "dissolved" concentrations in the water column.* [F] *The freshwater criterion for this metal is expressed as a function of hardness (mg/L) in the water column. To calculate the criterion, use formula under expanded endnote F at bottom of Table 30.*							

Expanded Endnotes A, E, F, N

Endnote A: Alternate Frequency and Duration for Certain Pesticides

This criterion is based on EPA recommendations issued in 1980 that were derived using guidelines that differed from EPA's 1985 Guidelines which update minimum data requirements and derivation procedures. The CMC may not be exceeded at any time and the CCC may not be exceeded based on a 24-hour average. The CMC may be applied using a one hour averaging period not to be exceeded more than once every three years, if the CMC values given in Table 30 are divided by 2 to obtain a value that is more comparable to a CMC derived using the 1985 Guidelines.

Endnote E: Equation for Hardness-Dependent Freshwater Cadmium Acute Criteria

The freshwater criterion for this metal is expressed as total recoverable with two significant figures, and is a function of hardness (mg/L) in the water column. Criteria values based on hardness are calculated using the following formula (CMC refers to the acute criterion):

$$\mathbf{CMC} = (\exp(m_A*[\ln(\text{hardness})] + b_A))$$

Chemical	m_A	b_A	m_C	b_C
Cadmium	1.128	-3.828	N/A	N/A

Endnote F: Equations for Hardness-Dependent Freshwater Metals Criteria and Conversion Factor Table

The freshwater criterion for this metal is expressed as dissolved with two significant figures, and is a function of hardness (mg/L) in the water column. Criteria values based on hardness are calculated using the following formulas (CMC refers to the acute criterion; CCC refers to the chronic criterion):

$$\textbf{CMC} = (\exp(m_A*[\ln(\text{hardness})] + b_A))*CF$$

$$\textbf{CCC} = (\exp(m_C*[\ln(\text{hardness})] + b_C))*CF$$

"CF" is the conversion factor used for converting a metal criterion expressed as the total recoverable fraction in the water column to a criterion expressed as the dissolved fraction in the water column.

Values for Calculating Hardness-Dependent Metals Criteria				
Chemical	**m_A**	**b_A**	**m_C**	**b_C**
Cadmium	N/A	N/A	0.7409	-4.719
Chromium III	0.8190	3.7256	0.8190	0.6848
Lead	1.273	-1.460	1.273	-4.705
Nickel	0.8460	2.255	0.8460	0.0584
Silver	1.72	-6.59	--	--
Zinc	0.8473	0.884	0.8473	0.884

The conversion factors (CF) below must be used in the equations above for the hardness-dependent metals in order to convert total recoverable metals criteria to dissolved metals criteria. For metals that are not hardness-dependent (i.e. arsenic, chromium VI, selenium, and silver (chronic)), or are saltwater criteria, the criterion value associated with the metal in Table 30 already reflects a dissolved criterion based on its conversion factor below.

Conversion Factor (CF) Table for Dissolved Metals				
Chemical	Freshwater		Saltwater	
	Acute	Chronic	Acute	Chronic
Arsenic	1.000	1.000	1.000	1.000
Cadmium	N/A	1.101672-[(ln hardness)(0.041838)]	0.994	0.994
Chromium III	0.316	0.860	--	--
Chromium VI	0.982	0.962	0.993	0.993
Copper	N/A	N/A	0.83	0.83
Lead	1.46203-[(ln hardness)(0.145712)]	1.46203-[(ln hardness)(0.145712)]	0.951	0.951
Nickel	0.998	0.997	0.990	0.990
Selenium	0.996	0.922	0.998	0.998
Silver	0.85	0.85	0.85	--
Zinc	0.978	0.986	0.946	0.946

Endnote N: Deriving freshwater copper criteria

The freshwater copper criteria at any time are the Biotic Ligand Model (BLM) derived Instantaneous Water Quality Criteria (IWQC) output based on a concurrently measured set of model input parameter values. The Biotic Ligand Model uses multiple ambient water quality parameters to derive 1-hour acute exposure (CMC) and 96-hour chronic exposure (CCC) water quality criteria (IWQC) for copper based on the site specific water chemistry that determines the toxicity of copper to aquatic life. If measured data for one or more of the model input parameters used to derive the acute and chronic IWQC is not available, the procedures in section (1) or (2) of this endnote will be used as specified to substitute an estimate or a default value for the missing input parameter. BLM results (IWQC) based on sufficient measured input parameter data are more accurate and supersede results based on estimates or default values. The acceptable BLM software to calculate the IWQC include version 2.2.3, referenced in "Aquatic Life Ambient Freshwater Quality Criteria – Copper": EPA-822-R-07-001, February 2007, and version 2.2.4. The criteria are expressed as dissolved copper in micrograms per liter (to the nearest one-tenth).

(1) Input Parameter Substitution and Estimation Procedures to Derive BLM Criteria (IWQC)

If the measured value for any input parameter needed to derive an IWQC using the BLM is not available, DEQ will substitute an estimated input parameter value according to the procedures described in this section [Endnote N (1)]. If the data required to determine the estimated parameter value is not available, DEQ will use default values derived according to the procedures in Endnote N (2).

(a) Total recoverable concentration measurements will be substituted for dissolved concentration measurements that are not available. For alkalinity, calcium, chloride, magnesium, potassium, sodium and sulfate, total recoverable concentration measurements will be used as a direct substitute for dissolved concentration measurements. Total organic carbon (TOC) measurements will be multiplied by 0.83 to convert the TOC value to an equivalent dissolved organic carbon (DOC) value; except where sufficient TOC and DOC data are available for a site, DEQ will calculate and apply a site-specific translator in place of 0.83 to convert TOC values to DOC for use in the BLM.

(b) Alkalinity, calcium, chloride, magnesium, potassium, sodium and sulfate:
If data for any of these BLM input parameters are missing from a particular dataset, DEQ will estimate its value based on the relationship of the ion or alkalinity to specific conductance measurements for that data set using the regression analysis equations in Table 1. Specific conductance measurements must be concurrent with the other BLM input parameters dataset.

Table N-1	
Parameter	**Regression Equation**
Alkalinity	$Alk. = \exp^{(0.88 \cdot [\ln(SpC)] - 0.41)}$
Calcium	$Ca = \exp^{(0.96 \cdot [\ln(SpC)] - 2.29)}$
Chloride	$Cl = \exp^{(1.15 \cdot [\ln(SpC)] - 3.82)}$
Magnesium	$Mg = \exp^{(0.91 \cdot [\ln(SpC)] - 3.09)}$
Potassium	$K = \exp^{(0.84 \cdot [\ln(SpC)] - 3.74)}$
Sodium	$Na = \exp^{(0.86 \cdot [\ln(SpC)] - 2.22)}$
Sulfate	$SO_4 = \exp^{(1.45 \cdot [\ln(SpC)] - 5.59}$

Where, "SpC" is a measurement of specific conductance in μmhos/cm, "ln" is the natural logarithm, and "exp" is a mathematical constant that is the base of the natural logarithm.

(c) pH
If concurrent pH data is missing from the sample dataset, DEQ will use a representative pH value determined by interpolating from data available for the site or proximate monitoring locations where conditions (such as type of water body, stream flow and geology) are similar to the site. DEQ will use the available data and methods to produce the best practicable estimate of pH for the site and time for which the IWQC is being derived.

(d) Temperature
If concurrent temperature data is missing from the sample dataset, DEQ will use a monthly mean temperature based on data available for the site or proximate monitoring locations where conditions (such as type of water body and stream flow) are similar to the site.

(e) Humic Acid
If sufficient high quality data on the percentage of humic acid as a proportion of DOC is available for a site, DEQ will use that value in the BLM in place of the default value of 10% used in the model.

(2) Default Action Values

If the measured value for DOC, alkalinity, calcium, chloride, magnesium, potassium, sodium or sulfate is not available to derive an IWQC using the BLM, and the parameter value cannot be estimated as specified in section (1) above, DEQ will use a conservative input value for the missing parameter as described in this section [Endnote N (2)] to derive a default action value using the Biotic Ligand Model. The default action value will be used for Clean Water Act purposes until measured or estimated input parameter data are available to derive accurate copper criteria (IWQC) based on site specific water chemistry.

(a) The default input parameter values for DOC, alkalinity calcium, chloride, magnesium, potassium, sodium and sulfate will be the percentile value from the distribution of the high quality data available for surface waters in the region as shown in Table N-2.

Table N-2
Percentile of data distribution to be used as default value by region

Region	DOC percentile	Alkalinity and Ions percentile
Willamette	20th	20th
Coastal	20th	20th
Cascades	20th	20th
Eastern	15th	15th
Columbia River	20th	20th

(b) The regional default values for each parameter and region will be updated periodically as additional high quality data becomes available and is added to DEQ's database.
(c) The regional default values for each parameter are available on DEQ's website.
(d) The regions listed in Table N-2 are comprised of the following EPA Level III ecoregions or waterbody:
(i) Willamette: the Willamette Valley
(ii) Coastal: Coast Range and Klamath Mountains
(iii) Cascades: Cascades
(iv) Eastern: Eastern Cascades Slopes and Foothills, Columbia Plateau, Blue Mountains, Northern Basin and Range and Snake River Plain
(v) Columbia River: Columbia River mainstem in Oregon

(3) General Policies
(a) The copper BLM derives instantaneous criteria results (IWQC) that vary at a site over time reflecting the effect of local water chemistry on copper toxicity to aquatic organisms. DEQ will apply the BLM criteria for Clean Water Act purposes to protect the water body during the most bioavailable or toxic conditions.
(b) For assessing waters of the state, DEQ will use approaches that give preference to the use of BLM criteria derived with site-specific measured input parameter data.

Table 30(a): Ammonia Acute Criteria Values (One-hour Average)—Salmonid Species Present
Temperature and pH-Dependent and expressed as Total Ammonia Nitrogen (mg/L TAN)

Criteria cannot be exceeded more than once every three years

$$Acute\ Criterion = MIN\left(\left(\frac{0.275}{1+10^{7.204-pH}}+\frac{39.0}{1+10^{pH-7.204}}\right),\left(0.7249\times\left(\frac{0.0114}{1+10^{7.204-pH}}+\frac{1.6181}{1+10^{pH-7.204}}\right)\times\left(23.12\times 10^{0.036\times(20-T)}\right)\right)\right)$$

	Temperature (°C)																
pH	**0-14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**
6.5	33	33	32	29	27	25	23	21	19	18	16	15	14	13	12	11	9.9
6.6	31	31	30	28	26	24	22	20	18	17	16	14	13	12	11	10	9.5
6.7	30	30	29	27	24	22	21	19	18	16	15	14	13	12	11	9.8	9.0
6.8	28	28	27	25	23	21	20	18	17	15	14	13	12	11	10	9.2	8.5
6.9	26	26	25	23	21	20	18	17	15	14	13	12	11	10	9.4	8.6	7.9
7.0	24	24	23	21	20	18	17	15	14	13	12	11	10	9.4	8.6	8.0	7.3
7.1	22	22	21	20	18	17	15	14	13	12	11	10	9.3	8.5	7.9	7.2	6.7
7.2	20	20	19	18	16	15	14	13	12	11	9.8	9.1	8.3	7.7	7.1	6.5	6.0
7.3	18	18	17	16	14	13	12	11	10	9.5	8.7	8.0	7.4	6.8	6.3	5.8	5.3
7.4	15	15	15	14	13	12	11	9.8	9.0	8.3	7.7	7.0	6.5	6.0	5.5	5.1	4.7
7.5	13	13	13	12	11	10	9.2	8.5	7.8	7.2	6.6	6.1	5.6	5.2	4.8	4.4	4.0
7.6	11	11	11	10	9.3	8.6	7.9	7.3	6.7	6.2	5.7	5.2	4.8	4.4	4.1	3.8	3.5
7.7	9.6	9.6	9.3	8.6	7.9	7.3	6.7	6.2	5.7	5.2	4.8	4.4	4.1	3.8	3.5	3.2	3.0
7.8	8.1	8.1	7.9	7.2	6.7	6.1	5.6	5.2	4.8	4.4	4.0	3.7	3.4	3.2	2.9	2.7	2.5
7.9	6.8	6.8	6.6	6.0	5.6	5.1	4.7	4.3	4.0	3.7	3.4	3.1	2.9	2.6	2.4	2.2	2.1
8.0	5.6	5.6	5.4	5.0	4.6	4.2	3.9	3.6	3.3	3.0	2.8	2.6	2.4	2.2	2.0	1.9	1.7
8.1	4.6	4.6	4.5	4.1	3.8	3.5	3.2	3.0	2.7	2.5	2.3	2.1	2.0	1.8	1.7	1.5	1.4
8.2	3.8	3.8	3.7	3.5	3.1	2.9	2.7	2.4	2.3	2.1	1.9	1.8	1.6	1.5	1.4	1.3	1.2
8.3	3.1	3.1	3.1	2.8	2.6	2.4	2.2	2.0	1.9	1.7	1.6	1.4	1.3	1.2	1.1	1.0	0.96
8.4	2.6	2.6	2.5	2.3	2.1	2.0	1.8	1.7	1.5	1.4	1.3	1.2	1.1	1.0	0.93	0.86	0.79
8.5	2.1	2.1	2.1	1.9	1.8	1.6	1.5	1.4	1.3	1.2	1.1	0.98	0.90	0.83	0.77	0.71	0.65
8.6	1.8	1.8	1.7	1.6	1.5	1.3	1.2	1.1	1.0	0.96	0.88	0.81	0.75	0.69	0.63	0.59	0.54
8.7	1.5	1.5	1.4	1.3	1.2	1.1	1.0	0.94	0.87	0.80	0.74	0.68	0.62	0.57	0.53	0.49	0.45
8.8	1.2	1.2	1.2	1.1	1.0	0.93	0.86	0.79	0.73	0.67	0.62	0.57	0.52	0.48	0.44	0.41	0.37
8.9	1.0	1.0	1.0	0.93	0.85	0.79	0.72	0.67	0.61	0.56	0.52	0.48	0.44	0.40	0.37	0.34	0.32
9.0	0.88	0.88	0.86	0.79	0.73	0.67	0.62	0.57	0.52	0.48	0.44	0.41	0.37	0.34	0.32	0.29	0.27

Table 30(b): Ammonia Acute Criteria Values (One-hour Average*)—Salmonid Species Absent
Temperature and pH-Dependent and expressed as Total Ammonia Nitrogen (mg/L TAN)

Criteria cannot be exceeded more than once every three years

$$Acute\ Criterion = 0.7249 \times \frac{0.0114}{1+10^{7.204-pH}} + \frac{1.6181}{1+10^{pH-7.204}} \times MIN\left(51.93, 23.12 \times 10^{0.036\times(20-T)}\right)$$

	Temperature (ºC)																				
pH	**0-10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**
6.5	51	48	44	41	37	34	32	29	27	25	23	21	19	18	16	15	14	13	12	11	9.9
6.6	49	46	42	39	36	33	30	28	26	24	22	20	18	17	16	14	13	12	11	10	9.5
6.7	46	44	40	37	34	31	29	27	24	22	21	19	18	16	15	14	13	12	11	9.8	9.0
6.8	44	41	38	35	32	30	27	25	23	21	20	18	17	15	14	13	12	11	10	9.2	8.5
6.9	41	38	35	32	30	28	25	23	21	20	18	17	15	14	13	12	11	10	9.4	8.6	7.9
7.0	38	35	33	30	28	25	23	21	20	18	17	15	14	13	12	11	10	9.4	8.6	7.9	7.3
7.1	34	32	30	27	25	23	21	20	18	17	15	14	13	12	11	10	9.3	8.5	7.9	7.2	6.7
7.2	31	29	27	25	23	21	19	18	16	15	14	13	12	11	9.8	9.1	8.3	7.7	7.1	6.5	6.0
7.3	27	26	24	22	20	18	17	16	14	13	12	11	10	9.5	8.7	8.0	7.4	6.8	6.3	5.8	5.3
7.4	24	22	21	19	18	16	15	14	13	12	11	9.8	9.0	8.3	7.7	7.0	6.5	6.0	5.5	5.1	4.7
7.5	21	19	18	17	15	14	13	12	11	10	9.2	8.5	7.8	7.2	6.6	6.1	5.6	5.2	4.8	4.4	4.0
7.6	18	17	15	14	13	12	11	10	9.3	8.6	7.9	7.3	6.7	6.2	5.7	5.2	4.8	4.4	4.1	3.8	3.5
7.7	15	14	13	12	11	10	9.3	8.6	7.9	7.3	6.7	6.2	5.7	5.2	4.8	4.4	4.1	3.8	3.5	3.2	2.9
7.8	13	12	11	10	9.3	8.5	7.9	7.2	6.7	6.1	5.6	5.2	4.8	4.4	4.0	3.7	3.4	3.2	2.9	2.7	2.5
7.9	11	9.9	9.1	8.4	7.7	7.1	6.6	3.0	5.6	5.1	4.7	4.3	4.0	3.7	3.4	3.1	2.9	2.6	2.4	2.2	2.1
8.0	8.8	8.2	7.6	7.0	6.4	5.9	5.4	5.0	4.6	4.2	3.9	3.6	3.3	3.0	2.8	2.6	2.4	2.2	2.0	1.9	1.7
8.1	7.2	6.8	6.3	5.8	5.3	4.9	4.5	4.1	3.8	3.5	3.2	3.0	2.7	2.5	2.3	2.1	2.0	1.8	1.7	1.5	1.4
8.2	6.0	5.6	5.2	4.8	4.4	4.0	3.7	3.4	3.1	2.9	2.7	2.4	2.3	2.1	1.9	1.8	1.6	1.5	1.4	1.3	1.2
8.3	4.9	4.6	4.3	3.9	3.6	3.3	3.1	2.8	2.6	2.4	2.2	2.0	1.9	1.7	1.6	1.4	1.3	1.2	1.1	1.0	0.96
8.4	4.1	3.8	3.5	3.2	3.0	2.7	2.5	2.3	2.1	2.0	1.8	1.7	1.5	1.4	1.3	1.2	1.1	1.0	0.93	0.86	0.79
8.5	3.3	3.1	2.9	2.7	2.4	2.3	2.1	1.9	1.8	1.6	1.5	1.4	1.3	1.2	1.1	0.98	0.90	0.83	0.77	0.71	0.65
8.6	2.8	2.6	2.4	2.2	2.0	1.9	1.7	1.6	1.5	1.3	1.2	1.1	1.0	0.96	0.88	0.81	0.75	0.69	0.63	0.58	0.54
8.7	2.3	2.2	2.0	1.8	1.7	1.6	1.4	1.3	1.2	1.1	1.0	0.94	0.87	0.80	0.74	0.68	0.62	0.57	0.53	0.49	0.45
8.8	1.9	1.8	1.7	1.5	1.4	1.3	1.2	1.1	1.0	0.93	0.86	0.79	0.73	0.67	0.62	0.57	0.52	0.48	0.44	0.41	0.37
8.9	1.6	1.5	1.4	1.3	1.2	1.1	1.0	0.93	0.85	0.79	0.72	0.67	0.61	0.56	0.52	0.48	0.44	0.40	0.37	0.34	0.32
9.0	1.4	1.3	1.2	1.1	1.0	0.93	0.86	0.79	0.73	0.67	0.62	0.57	0.52	0.48	0.44	0.41	0.37	0.34	0.32	0.29	0.27

Table 30(c): Ammonia Chronic Criteria Values (30-day Rolling Average*)

Temperature and pH-Dependent and expressed as Total Ammonia Nitrogen (mg/L TAN)

* The highest four-day average within the 30-day averaging period must not be more than 2.5 times the chronic value

Criteria cannot be exceeded more than once every three years

$$Chronic\ Criterion = 0.8876 \times \left(\frac{0.0278}{1+10^{7.688-pH}} + \frac{1.1994}{1+10^{pH-7.688}}\right) \times \left(2.126 \times 10^{0.028\times(20-MAX(T,7))}\right)$$

	Temperature (ºC)																							
pH	**0-7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**
6.5	4.9	4.6	4.3	4.1	3.8	3.6	3.3	3.1	2.9	2.8	2.6	2.4	2.3	2.1	2.0	1.9	1.8	1.6	1.5	1.5	1.4	1.3	1.2	1.1
6.6	4.8	4.5	4.3	4.0	3.8	3.5	3.3	3.1	2.9	2.7	2.5	2.4	2.2	2.1	2.0	1.8	1.7	1.6	1.5	1.4	1.3	1.3	1.2	1.1
6.7	4.8	4.5	4.2	3.9	3.7	3.5	3.2	3.0	2.8	2.7	2.5	2.3	2.2	2.1	1.9	1.8	1.7	1.6	1.5	1.4	1.3	1.2	1.2	1.1
6.8	4.6	4.4	4.1	3.8	3.6	3.4	3.2	3.0	2.8	2.6	2.4	2.3	2.1	2.0	1.9	1.8	1.7	1.6	1.5	1.4	1.3	1.2	1.1	1.1
6.9	4.5	4.2	4.0	3.7	3.5	3.3	3.1	2.9	2.7	2.5	2.4	2.2	2.1	2.0	1.8	1.7	1.6	1.5	1.4	1.3	1.2	1.2	1.1	1.0
7.0	4.4	4.1	3.8	3.6	3.4	3.2	3.0	2.8	2.6	2.4	2.3	2.2	2.0	1.9	1.8	1.7	1.6	1.5	1.4	1.3	1.2	1.1	1.1	0.99
7.1	4.2	3.9	3.7	3.5	3.2	3.0	2.8	2.7	2.5	2.3	2.2	2.1	1.9	1.8	1.7	1.6	1.5	1.4	1.3	1.2	1.2	1.1	1.0	0.95
7.2	4.0	3.7	3.5	3.3	3.1	2.9	2.7	2.5	2.4	2.2	2.1	2.0	1.8	1.7	1.6	1.5	1.4	1.3	1.3	1.2	1.1	1.0	0.96	0.90
7.3	3.8	3.5	3.3	3.1	2.9	2.7	2.6	2.4	2.2	2.1	2.0	1.8	1.7	1.6	1.5	1.4	1.3	1.3	1.2	1.1	1.0	0.97	0.91	0.85
7.4	3.5	3.3	3.1	2.9	2.7	2.5	2.4	2.2	2.1	2.0	1.8	1.7	1.6	1.5	1.4	1.3	1.3	1.2	1.1	1.0	0.96	0.90	0.85	0.79
7.5	3.2	3.0	2.8	2.7	2.5	2.3	2.2	2.1	1.9	1.8	1.7	1.6	1.5	1.4	1.3	1.2	1.2	1.1	1.0	0.95	0.89	0.83	0.78	0.73
7.6	2.9	2.8	2.6	2.4	2.3	2.1	2.0	1.9	1.8	1.6	1.5	1.4	1.4	1.3	1.2	1.1	1.1	0.98	0.92	0.86	0.81	0.76	0.71	0.67
7.7	2.6	2.4	2.3	2.2	2.0	1.9	1.8	1.7	1.6	1.5	1.4	1.3	1.2	1.1	1.1	1.0	0.94	0.88	0.83	0.78	0.73	0.68	0.64	0.60
7.8	2.3	2.2	2.1	1.9	1.8	1.7	1.6	1.5	1.4	1.3	1.2	1.2	1.1	1.0	0.95	0.89	0.84	0.79	0.74	0.69	0.65	0.61	0.57	0.53
7.9	2.1	1.9	1.8	1.7	1.6	1.5	1.4	1.3	1.2	1.2	1.1	1.0	0.95	0.89	0.84	0.79	0.74	0.69	0.65	0.61	0.57	0.53	0.50	0.47
8.0	1.8	1.7	1.6	1.5	1.4	1.3	1.2	1.1	1.1	1.0	0.94	0.88	0.83	0.78	0.73	0.68	0.64	0.60	0.56	0.53	0.50	0.44	0.44	0.41
8.1	1.5	1.5	1.4	1.3	1.2	1.1	1.1	0.99	0.92	0.87	0.81	0.76	0.71	0.67	0.63	0.59	0.55	0.52	0.49	0.46	0.43	0.40	0.38	0.35
8.2	1.3	1.2	1.2	1.1	1.0	0.96	0.90	0.84	0.79	0.74	0.70	0.65	0.61	0.57	0.54	0.50	0.47	0.44	0.42	0.39	0.37	0.34	0.32	0.30
8.3	1.1	1.1	0.99	0.93	0.87	0.82	0.76	0.72	0.67	0.63	0.59	0.55	0.52	0.49	0.46	0.43	0.40	0.38	0.35	0.33	0.31	0.29	0.27	0.26
8.4	0.95	0.89	0.84	0.79	0.74	0.69	0.65	0.61	0.57	0.53	0.50	0.47	0.44	0.41	0.39	0.36	0.34	0.32	0.30	0.28	0.26	0.25	0.23	0.22
8.5	0.80	0.75	0.71	0.67	0.62	0.58	0.55	0.51	0.48	0.45	0.42	0.40	0.37	0.35	0.33	0.31	0.29	0.27	0.25	0.24	0.22	0.21	0.20	0.18
8.6	0.68	0.64	0.60	0.56	0.53	0.49	0.46	0.43	0.41	0.38	0.36	0.33	0.31	0.29	0.28	0.26	0.24	0.23	0.21	0.20	0.19	0.18	0.16	0.15
8.7	0.57	0.54	0.51	0.47	0.44	0.42	0.39	0.37	0.34	0.32	0.30	0.28	0.27	0.25	0.23	0.22	0.21	0.19	0.18	0.17	0.16	0.15	0.14	0.13
8.8	0.49	0.46	0.43	0.40	0.38	0.35	0.33	0.31	0.29	0.27	0.26	0.24	0.23	0.21	0.20	0.19	0.17	0.16	0.15	0.14	0.13	0.13	0.12	0.11
8.9	0.42	0.39	0.37	0.34	0.32	0.30	0.28	0.27	0.25	0.23	0.22	0.21	0.19	0.18	0.17	0.16	0.15	0.14	0.13	0.12	0.12	0.11	0.10	0.09
9.0	0.36	0.34	0.32	0.30	0.28	0.26	0.24	0.23	0.21	0.20	0.19	0.18	0.17	0.16	0.15	0.14	0.13	0.12	0.11	0.11	0.10	0.09	0.09	0.08

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TABLE 31
Aquatic Life Water Quality Guidance Values for Toxic Pollutants

Effective April 18, 2014

Water Quality Guidance Values Summary [A]

The concentration for each compound listed in Table 31 is a guidance value that DEQ may use in application of Oregon's Toxic Substances Narrative (340-041-0033(2)) to waters of the state in order to protect aquatic life. All values are expressed as micrograms per liter (µg/L) except where noted. Compounds are listed in alphabetical order with the corresponding EPA number (from National Recommended Water Quality Criteria: 2002, EPA-822-R-02-047), corresponding Chemical Abstract Service (CAS) number, aquatic life freshwater acute and chronic guidance values, and aquatic life saltwater acute and chronic guidance values.

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Table 31
Aquatic Life Water Quality Guidance Values for Toxic Pollutants

EPA No.	Pollutant	CAS Number	Freshwater		Saltwater	
			Acute	Chronic	Acute	Chronic
56	Acenaphthene	83329	1,700	520	970	710
17	Acrolein	107028	68	21	55	
18	Acrylonitrile	107131	7,550	2,600		
1	Antimony	7440360	9,000	1,600		
19	Benzene	71432	5,300		5,100	700
59	Benzidine	92875	2,500			
3	Beryllium	7440417	130	5.3		
19 B	BHC (Hexachlorocyclohexane-Technical)	319868	100		0.34	
21	Carbon Tetrachloride	56235	35,200		50,000	

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Table 31
Aquatic Life Water Quality Guidance Values for Toxic Pollutants

EPA No.	Pollutant	CAS Number	Freshwater		Saltwater	
			Acute	Chronic	Acute	Chronic
	Chlorinated Benzenes		250	50	160	129
	Chlorinated naphthalenes		1,600		7.5	
	Chloroalkyl Ethers		238,000			
26	Chloroform	67663	28,900	1,240		
45	Chlorophenol 2-	95578	4,380	2,000		
	Chlorophenol 4-	106489			29,700	
52	Methyl-4-chlorophenol 3-	59507	30			
5a	Chromium (III)	16065831			10,300	
109	DDE 4,4'-	72559	1,050		14	
110	DDD 4,4'-	72548	0.06		3.6	
	Diazinon	333415	0.08	0.05		
	Dichlorobenzenes		1,120	763	1,970	
29	Dichloroethane 1,2-	107062	118,000	20,000	113,000	
	Dichloroethylenes		11,600		224,000	
46	Dichlorophenol 2,4-	120832	2,020	365		
31	Dichloropropane 1,2-	78875	23,000	5,700	10,300	3,040
32	Dichloropropene 1,3-	542756	6,060	244	790	
47	Dimethylphenol 2,4-	105679	2,120			
	Dinitrotoluene		330	230	590	370
16	Dioxin (2,3,7,8-TCDD)	1746016	0.01	38 pg/L		
85	Diphenylhydrazine 1,2-	122667	270			

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Table 31
Aquatic Life Water Quality Guidance Values for Toxic Pollutants

EPA No.	Pollutant	CAS Number	Freshwater		Saltwater	
			Acute	Chronic	Acute	Chronic
33	Ethylbenzene	100414	32,000		430	
86	Fluoranthene	206440	3,980		40	16
	Haloethers		360	122		
	Halomethanes		11,000		12,000	6,400
89	Hexachlorobutadiene	87683	90	9.3	32	
90	Hexachlorocyclopentadiene	77474	7	5.2	7	
91	Hexachloroethane	67721	980	540	940	
93	Isophorone	78591	117,000		12,900	
94	Naphthalene	91203	2,300	620	2,350	
95	Nitrobenzene	98953	27,000		6,680	
	Nitrophenols		230	150	4,850	
26 B	Nitrosamines	35576911	5,850		3,300,000	
	Pentachlorinated ethanes		7,240	1,100	390	281
54	Phenol	108952	10,200	2,560	5,800	
	Phthalate esters		940	3	2,944	3.4
	Polynuclear Aromatic Hydrocarbons				300	
	Tetrachlorinated Ethanes		9,320			
37	Tetrachloroethane 1,1,2,2-	79345		2,400	9,020	
	Tetrachloroethanes		9,320			

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Table 31
Aquatic Life Water Quality Guidance Values for Toxic Pollutants

EPA No.	Pollutant	CAS Number	Freshwater		Saltwater	
			Acute	Chronic	Acute	Chronic
38	Tetrachloroethylene	127184	5,280	840	10,200	450
	Tetrachlorophenol 2,3,5,6					440
12	Thallium	7440280	1,400	40	2,130	
39	Toluene	108883	17,500		6,300	5,000
	Trichlorinated ethanes		18,000			
41	Trichloroethane 1,1,1-	71556			31,200	
42	Trichloroethane 1,1,2-	79005		9,400		
43	Trichloroethylene	79016	45,000	21,900	2,000	
55	Trichlorophenol 2,4,6-	88062		970		

The following chemicals/compounds/classes are of concern due to the potential for toxic effects to aquatic organisms; however, no guidance values are designated. If these compounds are identified in the waste stream, then a review of the scientific literature may be appropriate for deriving guidance values.

- Polybrominated diphenyl ethers (PBDE)
- Polybrominated biphenyls (PBB)
- Pharmaceuticals
- Personal care products
- Alkyl Phenols
- Other chemicals with Toxic effects

Footnotes:

A Values in Table 31 are applicable to all basins.

B This number was assigned to the list of non-priority pollutants in National Recommended Water Quality Criteria: 2002 (EPA-822-R-02-047).

OAR 340-041-8033
TABLE 40
Human Health Water Quality Criteria for Toxic Pollutants

Effective April 18, 2014

Human Health Criteria Summary

The concentration for each pollutant listed in Table 40 was derived to protect Oregonians from potential adverse health impacts associated with long-term exposure to toxic substances associated with consumption of fish, shellfish, and water. The "organism only" criteria are established to protect fish and shellfish consumption and apply to waters of the state designated for fishing. The "water + organism" criteria are established to protect the consumption of drinking water, fish, and shellfish, and apply where both fishing and domestic water supply (public and private) are designated uses. All criteria are expressed as micrograms per liter (µg/L), unless otherwise noted. Pollutants are listed in alphabetical order. Additional information includes the Chemical Abstract Service (CAS) number, whether the criterion is based on carcinogenic effects (can cause cancer in humans), and whether there is an aquatic life criterion for the pollutant (i.e. "y"= yes, "n" = no). All the human health criteria were calculated using a fish consumption rate of 175 grams per day unless otherwise noted. A fish consumption rate of 175 grams per day is approximately equal to 23 8-ounce fish meals per month. For pollutants categorized as carcinogens, values represent a cancer risk of one additional case of cancer in one million people (i.e. 10^{-6}), unless otherwise noted. All metals criteria are for total metal concentration, unless otherwise noted. Italicized pollutants represent non-priority pollutants. The human health criteria revisions established by OAR 340-041-0033 and shown in Table 40 do not become applicable for purposes of ORS chapter 468B or the federal Clean Water Act until approved by EPA pursuant to 40 CFR 131.21 (4/27/2000).

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Table 40
Human Health Water Quality Criteria for Toxic Pollutants

No.	Pollutant	CAS Number	Carcinogen	Aquatic Life Criterion	Human Health Criteria for the Consumption of:	
					Water + Organism (µg/L)	Organism Only (µg/L)
1	Acenaphthene	83329	n	n	95	99
2	Acrolein	107028	n	n	0.88	0.93
3	Acrylonitrile	107131	y	n	0.018	0.025
4	Aldrin	309002	y	y	0.0000050	0.0000050
5	Anthracene	120127	n	n	2900	4000
6	Antimony	7440360	n	n	5.1	64
7	Arsenic (inorganic) [A]	7440382	y	y	2.1	2.1(freshwater) 1.0 (saltwater)
[A] *The arsenic criteria are expressed as total inorganic arsenic. The "organism only" freshwater criterion is based on a risk level of approximately 1 x 10^{-5}, and the "water + organism" criterion is based on a risk level of 1 x 10^{-4}.*						
8	Asbestos [B]	1332214	y	n	7,000,000 fibers/L	--
[B] *The human health risks from asbestos are primarily from drinking water, therefore no "organism only" criterion was developed. The "water + organism" criterion is based on the Maximum Contaminant Level (MCL) established under the Safe Drinking Water Act.*						
9	*Barium* [C]	7440393	n	n	1000	--
[C] *The human health criterion for barium is the same as originally published in the 1976 EPA Red Book which predates the 1980 methodology and did not utilize the fish ingestion BCF approach. This same criterion value was also published in the 1986 EPA Gold Book. Human health risks are primarily from drinking water, therefore no "organism only" criterion was developed. The "water + organism" criterion is based on the Maximum Contaminant Level (MCL) established under the Safe Drinking Water Act.*						
10	Benzene	71432	y	n	0.44	1.4
11	Benzidine	92875	y	n	0.000018	0.000020
12	Benz(a)anthracene	56553	y	n	0.0013	0.0018
13	Benzo(a)pyrene	50328	y	n	0.0013	0.0018

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Table 40
Human Health Water Quality Criteria for Toxic Pollutants

No.	Pollutant	CAS Number	Carcinogen	Aquatic Life Criterion	Human Health Criteria for the Consumption of:	
					Water + Organism (µg/L)	Organism Only (µg/L)
14	Benzo(b)fluoranthene 3,4	205992	y	n	0.0013	0.0018
15	Benzo(k)fluoranthene	207089	y	n	0.0013	0.0018
16	BHC Alpha	319846	y	n	0.00045	0.00049
17	BHC Beta	319857	y	n	0.0016	0.0017
18	BHC Gamma (Lindane)	58899	n	y	0.17	0.18
19	Bromoform	75252	y	n	3.3	14
20	Butylbenzyl Phthalate	85687	n	n	190	190
21	Carbon Tetrachloride	56235	y	n	0.10	0.16
22	Chlordane	57749	y	y	0.000081	0.000081
23	Chlorobenzene	108907	n	n	74	160
24	Chlorodibromomethane	124481	y	n	0.31	1.3
25	Chloroethyl Ether bis 2	111444	y	n	0.020	0.053
26	Chloroform	67663	n	n	260	1100
27	Chloroisopropyl Ether bis 2	108601	n	n	1200	6500
28	Chloromethyl ether, bis	542881	y	n	0.000024	0.000029
29	Chloronaphthalene 2	91587	n	n	150	160
30	Chlorophenol 2	95578	n	n	14	15
31	Chlorophenoxy Herbicide (2,4,5,-TP) [D]	93721	n	n	10	--

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Table 40
Human Health Water Quality Criteria for Toxic Pollutants

No.	Pollutant	CAS Number	Carcinogen	Aquatic Life Criterion	Human Health Criteria for the Consumption of:	
					Water + Organism (µg/L)	Organism Only (µg/L)
[D] *The Chlorophenoxy Herbicide (2,4,5,-TP) criterion is the same as originally published in the 1976 EPA Red Book which predates the 1980 methodology and did not utilize the fish ingestion BCF approach. This same criterion value was also published in the 1986 EPA Gold Book. Human health risks are primarily from drinking water, therefore no "organism only" criterion was developed. The "water + organism" criterion is based on the Maximum Contaminant Level (MCL) established under the Safe Drinking Water Act.*						
32	Chlorophenoxy Herbicide (2,4-D) [E]	94757	n	n	100	--
[E] *The Chlorophenoxy Herbicide (2,4-D) criterion is the same as originally published in the 1976 EPA Red Book which predates the 1980 methodology and did not utilize the fish ingestion BCF approach. This same criterion value was also published in the 1986 EPA Gold Book. Human health risks are primarily from drinking water, therefore no "organism only" criterion was developed. The "water + organism" criterion is based on the Maximum Contaminant Level (MCL) established under the Safe Drinking Water Act.*						
33	Chrysene	218019	y	n	0.0013	0.0018
34	Copper [F]	7440508	n	y	1300	--
[F] *Human health risks from copper are primarily from drinking water, therefore no "organism only" criterion was developed. The "water + organism" criterion is based on the Maximum Contaminant Level (MCL) established under the Safe Drinking Water Act.*						
35	Cyanide [G]	57125	n	y	130	130
	[G] *The cyanide criterion is expressed as total cyanide (CN)/L.*					
36	DDD 4,4'	72548	y	n	0.000031	0.000031
37	DDE 4,4'	72559	y	n	0.000022	0.000022
38	DDT 4,4'	50293	y	y	0.000022	0.000022
39	Dibenz(a,h)anthracene	53703	y	n	0.0013	0.0018
40	Dichlorobenzene(m) 1,3	541731	n	n	80	96
41	Dichlorobenzene(o) 1,2	95501	n	n	110	130

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Table 40
Human Health Water Quality Criteria for Toxic Pollutants

No.	Pollutant	CAS Number	Carcinogen	Aquatic Life Criterion	Human Health Criteria for the Consumption of:	
					Water + Organism (µg/L)	Organism Only (µg/L)
42	Dichlorobenzene(p) 1,4	106467	n	n	16	19
43	Dichlorobenzidine 3,3'	91941	y	n	0.0027	0.0028
44	Dichlorobromomethane	75274	y	n	0.42	1.7
45	Dichloroethane 1,2	107062	y	n	0.35	3.7
46	Dichloroethylene 1,1	75354	n	n	230	710
47	Dichloroethylene trans 1,2	156605	n	n	120	1000
48	Dichlorophenol 2,4	120832	n	n	23	29
49	Dichloropropane 1,2	78875	y	n	0.38	1.5
50	Dichloropropene 1,3	542756	y	n	0.30	2.1
51	Dieldrin	60571	y	y	0.0000053	0.0000054
52	Diethyl Phthalate	84662	n	n	3800	4400
53	Dimethyl Phthalate	131113	n	n	84000	110000
54	Dimethylphenol 2,4	105679	n	n	76	85
55	Di-n-butyl Phthalate	84742	n	n	400	450
56	Dinitrophenol 2,4	51285	n	n	62	530
57	*Dinitrophenols*	25550587	n	n	62	530
58	Dinitrotoluene 2,4	121142	y	n	0.084	0.34
59	Dioxin (2,3,7,8-TCDD)	1746016	y	n	0.00000000051	0.00000000051

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Table 40
Human Health Water Quality Criteria for Toxic Pollutants

No.	Pollutant	CAS Number	Carcinogen	Aquatic Life Criterion	Human Health Criteria for the Consumption of:	
					Water + Organism (µg/L)	Organism Only (µg/L)
60	Diphenylhydrazine 1,2	122667	y	n	0.014	0.020
61	Endosulfan Alpha	959988	n	y	8.5	8.9
62	Endosulfan Beta	33213659	n	y	8.5	8.9
63	Endosulfan Sulfate	1031078	n	n	8.5	8.9
64	Endrin	72208	n	y	0.024	0.024
65	Endrin Aldehyde	7421934	n	n	0.030	0.030
66	Ethylbenzene	100414	n	n	160	210
67	Ethylhexyl Phthalate bis 2	117817	y	n	0.20	0.22
68	Fluoranthene	206440	n	n	14	14
69	Fluorene	86737	n	n	390	530
70	Heptachlor	76448	y	y	0.0000079	0.0000079
71	Heptachlor Epoxide	1024573	y	y	0.0000039	0.0000039
72	Hexachlorobenzene	118741	y	n	0.000029	0.000029
73	Hexachlorobutadiene	87683	y	n	0.36	1.8
74	*Hexachlorocyclo-hexane-Technical*	608731	y	n	0.0014	0.0015
75	Hexachlorocyclopentadiene	77474	n	n	30	110
76	Hexachloroethane	67721	y	n	0.29	0.33
77	Indeno(1,2,3-cd)pyrene	193395	y	n	0.0013	0.0018

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Table 40
Human Health Water Quality Criteria for Toxic Pollutants

No.	Pollutant	CAS Number	Carcinogen	Aquatic Life Criterion	Human Health Criteria for the Consumption of:	
					Water + Organism (µg/L)	Organism Only (µg/L)
78	Isophorone	78591	y	n	27	96
79	Manganese [H]	7439965	n	n	--	100
[H] *The "fish consumption only" criterion for manganese applies only to salt water and is for total manganese. This EPA recommended criterion predates the 1980 human health methodology and does not utilize the fish ingestion BCF calculation method or a fish consumption rate.*						
80	Methoxychlor [I]	72435	n	y	100	--
[I] *The human health criterion for methoxychlor is the same as originally published in the 1976 EPA Red Book which predates the 1980 methodology and did not utilize the fish ingestion BCF approach. This same criterion value was also published in the1986 EPA Gold Book. Human health risks are primarily from drinking water, therefore no "organism only" criterion was developed. The "water + organism" criterion is based on the Maximum Contaminant Level (MCL) established under the Safe Drinking Water Act.*						
81	Methyl Bromide	74839	n	n	37	150
82	Methyl-4,6-dinitrophenol 2	534521	n	n	9.2	28
83	Methylene Chloride	75092	y	n	4.3	59
84	Methylmercury (mg/kg) [J]	22967926	n	n	--	0.040 mg/kg
[J] *This value is expressed as the fish tissue concentration of methylmercury. Contaminated fish and shellfish is the primary human route of exposure to methylmercury.*						
85	Nickel	7440020	n	y	140	170
86	Nitrates [K]	14797558	n	n	10000	--
[K] *The human health criterion for nitrates is the same as originally published in the 1976 EPA Red Book which predates the 1980 methodology and did not utilize the fish ingestion BCF approach. This same criterion value was also published in the 1986 EPA Gold Book. Human health risks are primarily from drinking water, therefore no "organism only" criterion was developed. The "water + organism" criterion is based on the Maximum Contaminant Level (MCL) established under the Safe Drinking Water Act.*						
87	Nitrobenzene	98953	n	n	14	69

OAR 340-041-8033
Table 40
Human Health Water Quality Criteria for Toxic Pollutants

No.	Pollutant	CAS Number	Carcinogen	Aquatic Life Criterion	Human Health Criteria for the Consumption of:	
					Water + Organism (µg/L)	Organism Only (µg/L)
88	Nitrosamines	35576911	y	n	0.00079	0.046
89	Nitrosodibutylamine, N	924163	y	n	0.0050	0.022
90	Nitrosodiethylamine, N	55185	y	n	0.00079	0.046
91	Nitrosodimethylamine, N	62759	y	n	0.00068	0.30
92	Nitrosodi-n-propylamine, N	621647	y	n	0.0046	0.051
93	Nitrosodiphenylamine, N	86306	y	n	0.55	0.60
94	Nitrosopyrrolidine, N	930552	y	n	0.016	3.4
95	Pentachlorobenzene	608935	n	n	0.15	0.15
96	Pentachlorophenol	87865	y	y	0.15	0.30
97	Phenol	108952	n	n	9400	86000
98	Polychlorinated Biphenyls (PCBs) [L]	NA	y	y	0.0000064	0.0000064
[L] *This criterion applies to total PCBs (e.g. determined as Aroclors or congeners).*						
99	Pyrene	129000	n	n	290	400
100	Selenium	7782492	n	y	120	420
101	Tetrachlorobenzene, 1,2,4,5-	95943	n	n	0.11	0.11
102	Tetrachloroethane 1,1,2,2	79345	y	n	0.12	0.40
103	Tetrachloroethylene	127184	y	n	0.24	0.33
104	Thallium	7440280	n	n	0.043	0.047

OAR 340-041-8033
Table 40
Human Health Water Quality Criteria for Toxic Pollutants

No.	Pollutant	CAS Number	Carcinogen	Aquatic Life Criterion	Human Health Criteria for the Consumption of:	
					Water + Organism (µg/L)	Organism Only (µg/L)
105	Toluene	108883	n	n	720	1500
106	Toxaphene	8001352	y	y	0.000028	0.000028
107	Trichlorobenzene 1,2,4	120821	n	n	6.4	7.0
108	Trichloroethane 1,1,2	79005	y	n	0.44	1.6
109	Trichloroethylene	79016	y	n	1.4	3.0
110	Trichlorophenol 2,4,6	88062	y	n	0.23	0.24
111	Trichlorophenol, 2, 4, 5-	95954	n	n	330	360
112	Vinyl Chloride	75014	y	n	0.023	0.24
113	Zinc	7440666	n	y	2100	2600

State of Oregon Department of Environmental Quality

OAR 340-043-0120 – Tables and Figures

OAR 340-043-0120
Table 1
Heap-Leach Liquid Storage Data

Component	Pregnant-Solution Pond	Barren-Solution Pond
Operating volume	Minimum necessary to maintain recirculation	Minimum necessary to maintain recirculation
Operational surge	Anticipated draindown and rinse volume	Anticipated draindown and rinse volume
Climatic surge	100 year 24 hour storm plus 10 year snowmelt	100 year 24 hour storm plus 10 year snowmelt
Safety factor	2 feet dry freeboard	2 feet dry freeboard

OAR 340-043-0120
Table 2
Required Responses to Leakage Detected from the Leach Pad and Processing Chemical Storage Ponds

Leakage Category	Response
Zero leakage to 200 gallons/day-acre	Notify DEQ; increase pumping and monitoring
Leakage from 200 gallons/day-acre to 400 gallons/day-acre	Change operating practices to reduce leakage
Leakage in excess of 400 gallons/day-acre	Repair leaks under DEQ schedule

State of Oregon Department of Environmental Quality

OAR 340-043-0150
EPA Guidance Document

Final Covers on Hazardous Waste Landfills and Surface Impoundments

United States Environmental Protection Agency | Office of Solid Waste and Emergency Response Washington DC 20460 | EPA 530-SW-89-047 July 1989 | PB89-233480

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Technical Guidance Document:

Final Covers on Hazardous Waste Landfills and Surface Impoundments

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16. ABSTRACT

This document recommends and describes a design for landfill covers that will meet the requirements of RCRA regulations. It is a multilayered system consisting, from the top down, of:

- a top layer of at least 60 cm of soil, either vegetated or armored at the surface;
- a granular or geosynthetic drainage layer with a hydraulic transmissivity no less than 3×10^{-5} cm^2/sec; and
- a two-component low permeability layer comprised of (1) a flexible membrane liner installed directly on (2) a compacted soil component with an hydraulic conductivity no greater than 1×10^{-7} cm/sec.

Optional layers may be added, e.g., a biotic barrier layer or a gas vent layer, depending on the need.

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TECHNICAL GUIDANCE DOCUMENT

FINAL COVERS ON HAZARDOUS WASTE LANDFILLS AND SURFACE IMPOUNDMENTS

Office of Solid Waste and Emergency Response
U.S. Environmental Protection Agency
Washington, DC 20460

In cooperation with

RISK REDUCTION ENGINEERING LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

DISCLAIMER

The preparation of this document has been funded wholly by the United States Environmental Protection Agency. It has been subjected to the Agency's peer and admininistrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Risk Reduction Engineering Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs, and regulations of the U.S. Environmental Protection Agency; the permitting and other responsibilities of State and local governments; and the needs of both large and small businesses in handling their wastes responsibility and economically.

This document provides design guidance on final cover systems for hazardous waste landfills and surface impoundments. We believe that the final cover, if properly designed and constructed, can provide long-term protection of the unit from moisture infiltration due to precipitation. The cover system presented herein is a multilayer design consisting of a vegetated top layer, drainage layer, and low-permeability layer. Optional layers which may be required for site-specific conditions are also discussed. Rationale is provided for the design parameters to give designers and permit writers background information and an understanding of cover systems.

This document is intended for use by organizations involved in permitting, designing, and constructing hazardous waste land disposal facilities.

E. Timothy Oppelt, Director
Risk Reduction Engineering Laboratory

PREFACE

Subtitle C of the Resource Conservation and Recovery Act (RCRA) requires the U.S. Environmental Protection Agency (EPA) to establish a Federal hazardous waste management program. This program must ensure that hazardous wastes are handled safely from generation until final disposition. EPA issued a series of hazardous waste regulations under Subtitle C of RCRA that are published in Title 40 Code of Federal Regulations (40 CFR). The principal 40 CFR Part 264 and 265 regulations were issued on July 26, 1982 for treatment, storage, and disposal (TSD) facilities and establish performance standards for hazardous waste landfills, surface impoundments, land treatment units, and waste piles. The regulations have been amended several times since then.

In support of the regulations, EPA has been developing three types of documents to assist preparers and reviewers of RCRA permit applications for hazardous waste TSD facilities. These include RCRA Technical Guidance Documents, Permit Guidance Manuals, and Technical Resource Documents (TRDs).

RCRA Technical Guidance Documents, such as this one, present design and operating parameters or design evaluation techniques that generally comply with, or demonstrate compliance with, the Design and Operating Requirements and the Closure and Post-Closure Requirements of 40 CFR Part 264.

The Permit Guidance Manuals are being developed to describe the permit application information the Agency seeks, and to provide guidance to applicants and permit writers in addressing information requirements. These manuals will include a discussion of each set of specifications that must be considered for inclusion in the permit.

The Technical Resource Documents present summaries of state-of-the-art technologies and evaluation techniques determined by the Agency to constitute good engineering designs, practices, and procedures. They support the RCRA Technical Guidance Documents and Permit Guidance Manuals in certain areas (i.e., liners, leachate management, final covers, and water balance) by describing current technologies and methods for designing hazardous waste facilities, or for evaluating the performance of a facility design. Although emphasis is given to hazardous waste facilities, the information presented in these TRDs may be used

for designing and operating nonhazardous waste TSD facilities as well. Whereas the RCRA Technical Guidance Documents and Permit Guidance Manuals are directly related to the regulations, the information in these TRDs covers a broader perspective and should not be used to interpret the requirements of the regulations.

This document is a Technical Guidance Document prepared by the Risk Reduction Engineering Laboratory of EPA's Office of Research and Development in cooperation with the Office of Solid Waste and Emergency Response. The document has undergone extensive technical review and has been revised accordingly. With the issuance of this document, all previous drafts are obsolete and should be discarded.

Comments are welcome at any time on the accuracy and usefulness of the information in this document. Comments will be evaluated, and suggestions will be incorporated, wherever feasible, before publication of any future revisions. Written comments should be addressed to EPA RCRA Docket (OS-305), 401 M Street S.W., Washington, DC 20460. The document for which comments are being provided should be identified by title and number.

ABSTRACT

The owner or operator of a landfill, or a surface impoundment closed as a landfill, must meet the closure requirements specified under 40 CFR 264.310 (permitted units) or 40 CFR 265.310 (interim status units).

This guidance document addresses landfill covers and recommends a multilayer final cover design that includes the following elements, from top to bottom:

- a top layer consisting of two components: (1) a vegetated or armored surface component, either of which is selected to minimize erosion and, to the extent possible, promote drainage off the cover, and (2) a soil component with a minimum thickness of 60 cm [24 in.] comprised of topsoil and/or fill soil as appropriate, the surface of which slopes uniformly at least 3 percent but not more than 5 percent;

- a soil drainage layer with a minimum thickness of 30 cm (12 in.) and a minimum hydraulic conductivity of 1×10^{-2} cm/sec that will effectively minimize water infiltration into the low-permeability layer, and a final bottom slope of at least 3 percent after settlement and subsidence; or the drainage layer may consist of geosynthetic materials with equivalent performance characteristics; the drainage layer also serves as a protective cover for the flexible membrane liner (FML) component of the underlying low-permeability layer;

- a two-component low-permeability layer, that limits water infiltration into the underlying wastes to a rate less than or equal to the rate of leachate migration out of the bottom liner system and consists of (1) a 20-mil minimum thickness [or greater depending on the material and design] FML component and (2) a 60-cm [24-inch] minimum thickness compacted soil component with an in-place saturated hydraulic conductivity no less than 1×10^{-7} cm/sec. (NOTE: The requirement for FMLs in the cover are for all permitted units and interim status units with an FML in the bottom. For interim status units with only a clay bottom liner, an FML may not be required.)

Optional layers that may be used on a site-specific basis include (1) a gas vent layer to remove gases produced within the wastes, and/or (2) a biotic barrier layer to protect the cover from animal or plant intrusion.

The Agency recommends a detailed construction quality assurance (CQA) program for each layer of the final cover system. CQA records should document quality and demonstrate compliance with plans and specifications. The cover design process must consider many site-specific factors, such as precipitation, construction materials, freeze-thaw phenomena, waste characteristics, potential subsidence, and other environmental factors.

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1. INTRODUCTION

1.1 PURPOSE

This document provides design guidance on final covers for hazardous waste units. The recommended design satisfies the requirements of 40 CFR 264 and 265 Subparts G (closure and post-closure), K (surface impoundments), and N (landfills). The Environmental Protection Agency (hereafter referred to as "the Agency") emphasizes that recommendations are guidance only and not regulations. The Agency acknowledges that other final cover designs may be acceptable, depending upon site-specific conditions and upon a determination by the Agency that an alternative design adequately fulfills the regulatory requirements. It is, however, the responsibility of the facility owner or operator to prove that the alternate design will provide a level of performance that is at least equivalent to that of the final cover system described in this document.

The Agency's liquids management strategy for landfills, and the role that final covers serve in that strategy, are outlined in general terms for background. Regulatory requirements for landfill and surface impoundment covers are also outlined, as well as differences in requirements between interim status and permitted units. The Agency-recommended final cover system design is presented in detail, as well as considerations for construction quality assurance. Attention is given to erosion, settlement, and subsidence, and their potential cover-damaging effects.

A separate section of this document is devoted to the design details of each layer of the recommended cover. A discussion of the rationale for the recommended specifications is included.

1.2 CLOSURE AND POST-CLOSURE REGULATIONS

All of the regulations dealing with hazardous waste landfill and surface impoundment cover requirements are found in Title 40, Parts 264 and 265, of the Code of Federal Regulations (40 CFR 264 and 40 CFR 265). Part 264 deals with permitted facilities and Part 265 with interim status facilities. Interim status facilities are, in general, those facilities that were in existence on November 19, 1980. Three Subparts of each of Parts 264 and 265 deal with general closure requirements: Subpart G - Closure and Post-Closure; Subpart K - Surface Impoundments; and

Subpart N - Landfills. Each Subpart contains several sections important to cover planning, design, and construction, as outlined in Table 1.

There are few difference between permitted and interim status unit closure and post-closure regulations under Subpart G of Parts 264 and 265. The major difference is that, for interim status units, public notice for changes to the approved closure and post-closure plans is not required. Changes to plans for permitted units require permit modifications which, in turn, require public notice and comment.

There are three significant differences between permitted and interim status unit final cover regulations under Subparts K and N of Parts 264 and 265. Part 264.303 requires monitoring and inspection to ensure that synthetic and soil materials used in the cover are watertight and structurally uniform. Such a requirement was not included in Part 265 for interim status units. The Agency recommends that a Construction Quality Assurance (CQA) program, establishing inspection activities, be utilized for covers being built at both permitted and interim status units. The Agency believes that a site-specific CQA inspection program is necessary to ensure that cover design specifications are met.

A second difference in requirements is that, while leachate collection and removal activities are required after closure under 40 CFR 264.310, for permitted units, they are not required under Part 265 for interim status units. The absence of a stated post-closure leachate collection and removal requirement makes cover performance for interim status units even more important. It should be noted that, under the broader performance standards of 40 CFR 265.111, the Agency may still require leachate collection during post-closure at an interim site.

The third, and perhaps most significant, difference is in the requirements of 40 CFR 264.310(b)(1)(v) and 40 CFR 265.310 (b)(1)(v). These subsections require that the cover have a permeability less than or equal to any bottom liner or natural subsoil present. For interim status units, without an engineered liner, the cover could presumably be of relatively permeable materials. But here again, the Agency may impose the standards of 40 CFR 265.111, and require a more impermeable cover.

For permitted landfills, to meet the requirements of 40 CFR 264.310, the cover must have a permeability no greater than that of the double liner required under 40 CFR 264.301(c). The Agency does not consider this to mean that the final cover for a permitted unit must actually contain a double liner. Rather, the Agency recommends that the final cover include a layer whose liquid-rejection performance is equal to or better than the

Table 1. Closure and Post-Closure Regulatory Requirements

Section	Part 264	Part 265
	Subpart G - Closure and Post-Closure	
111	Closure performance standard.	Closure performance standard.
112	Closure plan; amendment of plan.	Closure plan; amendment of plan.
113	Time allowed for closure.	Time allowed for closure.
115	Certification of closure.	Certification of closure.
116	Survey plat.	Survey plat.
117	Post-closure care.	Post-closure care.
118	Post-closure plan; amendment of plan.	Post-closure plan; amendment of plan.
120	Certificate of completion of postclosure care.	Certificate of completion of post-closure care.
	Subpart K - Surface Impoundments	
226	Monitoring and inspection.	Inspections.
228	Closure and post-closure care.	Closure and post-closure care.
	Subpart N - Landfills	
301	Design and operating requirements.	Design requirements.
302	N/A	General operating requirements.
303	Monitoring and inspection.	N/A
310	Closure and post-closure care.	Closure and post-closure care.

bottom composite liner (flexible membrane liner [FML] underlain, and in full contact with, compacted soil) of the double-liner system detailed in the "Minimum Technology Guidance on Double Liner Systems for Landfills and Surface Impoundments - Design, Construction and Operation" (EPA, 1987i). The Agency-recommended design for the cover does, in fact, include a composite barrier layer as outlined in Section 4. In all cases where a FML is used in the bottom liner, one should also be used in the cover. This does not mean, however, that the Agency necessarily recommends the use of exactly the same barrier materials in both the liner and cover. For example, different FML materials of equivalent performance may be used, such as high density polyethylene for the bottom liner and polyvinyl chloride in the cover.

The Agency also recommends using the composite FML/clay barrier in interim status unit covers. However, for interim status units, compacted clay with a permeability equal to or less than 1×10^{-7} cm/sec may be used without a FML if the clay is less permeable than the landfill bottom liner or natural subsoil beneath the site. While 40 CFR 265.310(a)(5) might allow a less effective design, we believe the long-term protection from infiltration provided by the recommended cover design justifies its use for all units. With the Agency-recommended composite design, it is more certain that the cover will be no more permeable than the bottom of the unit. In addition, the installation of the composite design on interim status units takes advantage of the practical opportunity to more effectively minimize water infiltration, leachate generation, and leachate migration.

1.3 LIQUIDS MANAGEMENT STRATEGY

The general closure performance standards are specified in 40 CFR 264.111 and 265.111 (Subpart G) for permitted and interim hazardous waste disposal facilities, respectively. The standards state that:

"The owner or operator must close the facility in a manner that:

a. Minimizes the need for further maintenance; and

b. Controls, minimizes, or eliminates, to the extent necessary to protect human health and the environment, post-closure escape of hazardous waste, hazardous constituents, leachate, contaminated runoff, or hazardous waste decomposition products to the ground or surface waters or to the atmosphere . . "

The requirements apply to hazardous waste landfills and to hazardous waste surface impoundments closed as landfills.

Landfill closure requirements are based on a two-part liquids management strategy of (1) minimizing the leachate generation by keeping liquids out of the unit, and (2) detecting, collecting, and removing leachate within the unit. Closure requirements are specified in 40 CFR 264.310 and 40 CFR 265.310 and include a final cover and post-closure care.

The Agency considers keeping water out of the unit to be the prime element of the strategy. Thus, the Agency believes that a properly designed and constructed cover becomes, after closure, the most important feature of the landfill structure. The Agency requires that the cover be designed and constructed to provide long-term minimization of the movement of water from the surface into the closed unit. Where the waste mass lies entirely above the zone of ground-water saturation, a properly designed and maintained cover can prevent, for all practical purposes, the entry of water into the closed unit, and thus minimize the formation and migration of leachate. In the absence of damage, the cover design recommended here, including the FML/soil low-permeability layer, should restrict infiltration, to the extent of the design, for the long term.

1.4 GENERAL COVER SYSTEM RECOMMENDATIONS

The cover system should be a major consideration during site selection, planning, and initial design of the landfill containment structure. Factors for consideration include location and availability of low-permeability soil, stockpiling of topsoil, restricting height to provide stable slopes, and site use beyond the post-closure care period.

1.4.1 Design Recommendations

The final cover recommended in this guidance document is a multilayer design (Figure 1) comprised as follows, from top to bottom:

- a top layer consisting of two components: (1) either a vegetated or armored surface component, selected to minimize erosion and, to the extent possible, promote drainage off the cover, and (2) a soil component with a minimum thickness of 60 cm [24 in.], comprised of topsoil and/or fill soil as appropriate, the surface of which slopes uniformly at least 3 percent but not more than 5 percent; a soil component of greater thickness may be required to assure that the underlying low-permeability layer is below the frost zone;

- either a soil drainage (and FML-protective bedding) layer with minimum thickness of 30 cm (12 in.) and a minimum hydraulic conductivity of 1 x 10^{-2} cm/sec that

will effectively minimize water infiltration into the low-permeability layer, and will have a final slope of at least 3 percent after settlement and subsidence; or a drainage layer consisting of geosynthetic materials with equivalent performance characteristics; and

- a two-component low-permeability layer, lying wholly below the frost zone, that provides long-term minimization of water infiltration into the underlying wastes, consisting of (1) a 20-mil [0.5 mm] minimum thickness flexible membrane liner [FML] component and (2) a compacted soil component with a minimum thickness of at least 60 cm [24 in.] and a maximum in-place saturated hydraulic conductivity of 1×10^{-7} cm/sec.

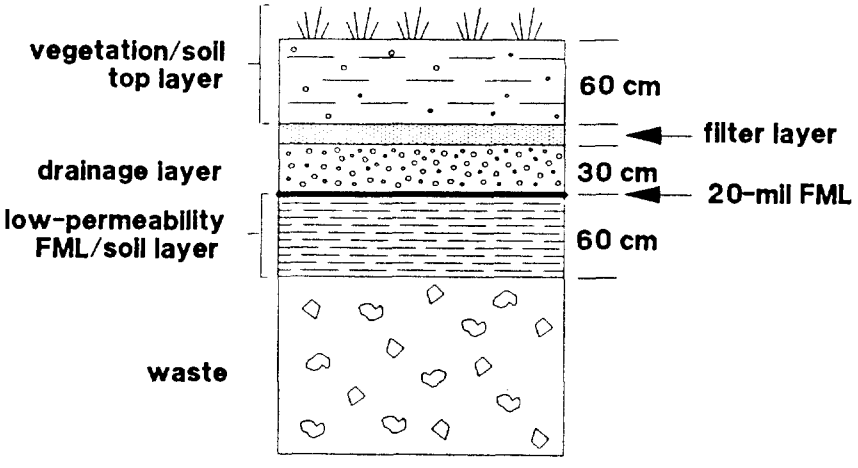

Figure 1. EPA-recommended cover design.

Optional layers may be used on a site-specific basis. Figure 2 depicts a cover design that includes optional layers. Two such layers include (1) a gas vent layer to remove gases that are produced within the wastes, and/or (2) a biotic barrier layer to protect the cover from animal or plant intrusion. Geosynthetic filter materials may also be used to prevent migration of fine materials from one layer into another or to prevent clogging of the drainage layer.

The Agency recognizes, for specific cases, that alternative designs (e.g., fewer layers or optional layers) may be applicable. For instance, in extremely arid regions, a gravel-armored top surface component might serve to compensate for a naturally reduced vegetation coverage and the erosion control that it provides. Also, in arid regions the drainage layer might not be required. In areas where burrowing animals may damage the

low-permeability layer, the damage may be prevented by use of an overlying "biotic barrier" layer of large-size material, such as cobbles. A gas vent layer between the waste and the low-permeability layer may be installed, as shown in Figure 2, at units that produce gases.

Alternative designs must provide long-term performance at least equivalent to the recommended design outlined in this guidance. All alternative designs must be approved by the appropriate Regional Administrator of the Agency.

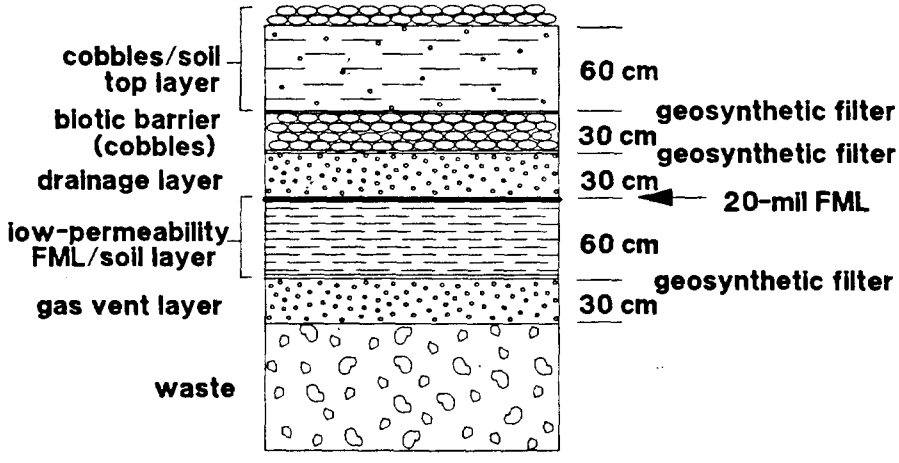

Figure 2. EPA-recommended cover design with optional layers.

In some cases, where the waste is of such character that vertical migration of gases is impeded, full-depth vent structures to the bottom of the waste mass may be needed. These structures would be designed to prevent the horizontal migration of gases out of the landfill into the surrounding soil. Active rather than passive systems may be required in some cases to adequately remove accumulated gases.

Filter layers are likely to be needed above the drainage layer and between layers that are comprised of soils of greatly different particle sizes, to prevent one from migrating into the other. The filters may be constructed of soils of intermediate grain size, or they may be geosynthetic materials. Three between-layer locations where geosynthetic filters may be appropriate are shown in Figure 2.

Table 2 presents a synopsis of the Agency-recommended components of a landfill and their principal design parameters.

1.4.2 Construction Quality Assurance (CQA)

The Agency believes that the landfill owner or operator should implement a detailed construction quality assurance (CQA) program for the final cover system based on written plans for inspecting the quality of construction materials and the construction practices employed in their placement. The Agency believes that use of a CQA program is essential for determining, with a reasonable degree of certainty, whether a completed final cover system meets or exceeds all design criteria, plans, and specifications. The Agency has issued technical guidance that includes final cover CQA (EPA, 1987i).

The Agency has proposed CQA rules for both permitted and interim status units (EPA, 1987b). These proposed rules would require a CQA program for installing the following components of landfills, surface impoundments and waste piles: foundations; low-permeability soils; FMLs; dikes; leachate detection, collection, and removal systems; and final covers. The CQA plan would be site-specific. It should address activities such as inspecting, monitoring, and sampling of the individual components. For the cover, the CQA plan should provide assurance that: 1) all layers of the final cover are uniform and damage-free; 2) the materials for each layer are as specified in the design specifications; and 3) each layer is constructed as specified in the design.

1.4.3 Settlement and Subsidence

Settlement within a closed hazardous waste landfill can disrupt the integrity and function of the final cover system. Settlement of the waste may be uniformly distributed and may occur primarily before placement of the final cover. Subsidence, however, is considered to be an unevenly distributed settlement (i.e., differential settlement) after closure that can disrupt the integrity of the final cover by creating depressions and cracks. In addition, subsidence due to the collapse of drums (this will occur mainly in older units), the leaching of soluble waste constituents, or biodegradation of organic matter in the waste, may not begin until several years after closure or it may occur gradually over decades.

To reduce the potential for damage from settlement and subsidence, the final cover should be designed and constructed to allow for the total estimated settlement. The final grade after subsidence of the cover should be at the actual desired design elevation. The cover design process used to establish the final grade elevation should include consideration of the following:

- consolidation of all waste layers (the primary consideration) and daily and intermediate soil covers;

Table 2. Synopsis of Minimum Technology Guidance for Covers

Layer	Thickness	Slope	Requirements
Top Layer			
Vegetation	--	--	Persistent, drought-resistant, adapted to local conditions.
OR			
Surface Armor	5-10 in. (13-25 cm)		Cobbles, gravel.
ON			
Soil	$\geq$ 24 in. ($\geq$ 60 cm)	3-5%	Erosion rate <2 ton/acre/yr (5.5 MT/ha/yr).
Drainage Layer			
Soil	$\geq$ 12 in. ($\geq$ 30 cm)	$\geq$ 3%	SP (USCS) soil $K > 1 \times 10^{-2}$ cm/s; gravel toe drain.
OR			
Geosynthetic	variable	$\geq$ 3%	Performance equivalent to soil, hydraulic transmissivity $\geq 3 \times 10^{-5}$ m^2/sec.
Low-Permeability Layer			
FML	$\geq$ 20 mils ($\geq$ 0.5 mm)	$\geq$ 3%	In EPA Report No. EPA 600/2-88-052.
ON			
Low-Permeability Soil	$\geq$ 24 in. ($\geq$ 60 cm)	$\geq$ 3%	In-place $K < 1 \times 10^{-7}$ cm/s and test fill.
Optional Layers (site-specific design)			
Gas Vent Layer	$\geq$ 12 in. ($\geq$ 30 cm)	$\geq$ 2%	Similar to drainage layer.
Biotic Barrier	animal or root-dependent	--	Large materials, e.g., cobbles.

- consolidation of soils and foundation materials underlying the site;
- consolidation of liner and leachate collection systems; and
- consolidation of all final cover components.

The Agency has published two technical research reports on cover settlement and subsidence (EPA, 1985c and 1987d) that address both the theoretical and practical aspects.

Interim covers have been proposed when a significant amount of settlement and subsidence is expected in a fairly short time (say 2-5 years) that could result in the premature failure of a final cover. An interim cover could be maintained until settling is judged to be virtually complete. After settlement occurs, the interim cover could be removed and replaced or overlain by a new final cover. If components of the interim cover can meet the CQA requirements for the final cover, the interim cover could be made an integral part of the final design.

In no case can an interim cover be used that does not satisfy the performance standards of 40 CFR 264.111 to protect human health and the environment. Use of an interim cover on a permitted unit will generally result in a longer closure period during which the stipulations of 40 CFR 264.113 must be met, i.e., the applicant must take all necessary steps "to prevent threats to human health and the environment from the unclosed but not operating hazardous waste management unit or facility, including compliance with all applicable permit requirements."

2. TOP LAYER

The Agency recommends a two-component top layer for a landfill cover system (Figure 1). The upper component should be vegetation or other surface treatment, designed to impede erosion but allowing surface runoff from major storm events. The Agency believes that, in most cases, vegetation underlain by soil, at least part of which is topsoil, will best accomplish these objectives. However, in some areas the prevailing climate may inhibit the establishment and maintenance of vegetation, or a planned alternative use of the site may preclude vegetation. In those cases, an armored surface without vegetation (Figure 2), and underlain by fill soil, might be used if it will minimize erosion and abrasion of the cover and allow, to the maximum practicable extent, surface drainage off the cover.

2.1 DESIGN

The Agency recommends that the vegetation component of the top layer meet the following specifications:

- Locally adapted perennial plants.
- Resistant to drought and temperature extremes.
- Roots that will not disrupt the low-permeability layer.
- Capable of thriving in low-nutrient soil with minimum nutrient addition.
- Sufficient plant density to minimize cover soil erosion to no more than 2 tons/acre/year (5.5 MT/ha/yr), calculated using the USDA Universal Soil Loss Equation.
- Capable of surviving and functioning with little or no maintenance.

In landfill situations where the environment or other considerations make it inappropriate for maintaining sufficiently dense vegetation, armoring material may be substituted as the upper component of the top layer or in rare cases the whole layer. It is recommended that the material possess the following characteristics:

- capable of remaining in place and minimizing erosion of itself and the underlying soil component during extreme weather events of rainfall and/or wind;

- capable of accommodating settlement of the underlying material without compromising the purpose of the component;

- surface slope approximately the same as the underlying soil (at least 3 percent slope); and

- capable of controlling the rate of soil erosion from the cover to no more than 2 tons/acre/year (5.5 MT/ha/yr), calculated by using the USDA Universal Soil Loss Equation.

Agency-recommended specifications for the lower soil component of the top layer include the following:

- for vegetation support, a minimum thickness of 60 cm (24 in.) including at least 15 cm (6 in.) of topsoil (soil of lower quality may be used beneath an armored surface); greater total thickness where required, e.g., where maximum frost penetration exceeds this depth, or where greater plant-available water storage is necessary or desirable;

- medium texture to facilitate seed germination and plant root development;

- final top slope, after allowance for settling and subsidence, of at least 3 percent, but no greater than 5 percent, to facilitate runoff while minimizing erosion; and

- minimum compaction to facilitate root development and sufficient infiltration to maintain growth through drier periods.

The owner or operator of the landfill should prepare a separate section specific to monitoring construction of the top layer to be included in the construction quality assurance (CQA) plan.

2.2 DISCUSSION

2.2.1 Upper Component of Top Layer

As noted in the design recommendations above, the upper component of the top layer may be vegetation (Agency-preferred where possible) or other erosion-impeding materials. These are discussed separately below.

2.2.1.1 Vegetation

Plant species is an important consideration in the establishment of vegetation when it is selected as the upper component of the top layer. The use of shrubs and trees is usually inappropriate because the root systems extend to a depth that would normally invade the drainage layer or the low-permeability layer. A large number of suitable plant species such as grasses and low-growing plants are available for various climates (EPA, 1983c and 1987c). The timing of seeding is also very important to successful vegetation establishment.

The Agency advises landfill owners or operators to contact a consulting agronomist, Cooperative Extension Service agent, or local university for recommendations of adapted plant varieties and other guidance on local crop cultivation. Several references provide lists of available vegetation and discussions on site-selection criteria (EPA, 1976, 1979, 1983a, 1983c, 1985a, and 1987c; Lee, et al., 1984; Thornburg, 1979; and Wright, 1976). These references provide essential information about plant species, seeding rate, time of seeding, and areas of adaptation.

2.2.1.2 Other Erosion-Impeding Materials

In areas where vegetation is inappropriate or difficult to establish and maintain, other materials may be selected as the upper component of the top layer. The materials should be selected to prevent erosion of the cover and yet allow, as much as practicable, for surface drainage. Several materials have been suggested for use in lieu of vegetation, including broken rock or cobbles that may prevent deterioration of the cap due to wind, heavy rain, or temperature extremes (EPA, 1982b and 1985a; Nyhan, et al., 1985; Pertusa, 1980). An example of such an upper component is a layer several (perhaps eight or more) inches thick comprised of 5- to 10-cm (2- to 4-in.) cobbles of hard durable rock. The cobbles allow infiltration of rain water but retard erosion due to water and wind action (see Figure 2). Asphalt or concrete might be used if promoting runoff is a prime objective, but they are likely to deteriorate, for example, by cracking due to thermal effects and subsidence deformation (EPA, 1979 and 1987a) thus causing concern for their long-term performance. Substantial maintenance could be expected for these materials. Asphalt can be very permeable unless special attention is given to eliminating the air voids during mixing and application (Repa, et al., 1987).

A surface armor component of very coarse materials promotes infiltration rather than runoff. Thus, it may be more applicable in arid areas. In those areas, leachate generation due to water infiltration may not be a major concern, but it can happen during infrequent short-duration storms of great intensity (EPA, 1987c).

2.2.2 Lower Component of Top Layer

When the upper component of the top layer is vegetation, the EPA recommends that the associated lower component be composed of at least 60 cm (24 in.) of soil. The soil should be capable of indefinitely sustaining plant species that will minimize erosion. The minimum thickness of the soil component is based upon the Agency's judgment that:

- it accommodates the root systems of most non-woody plant species (EPA, 1983c);
- for most locales, it provides adequate water-holding capacity to attenuate rainfall infiltration to the drainage layer and to sustain vegetation through dry periods; and
- it provides sufficient soil thickness to allow for expected long-term erosional losses.

A layer thicker than 60 cm (24 in.) may be required to prevent freezing and thawing from damaging the low-permeability layer, or to increase plant-available water storage capacity in drier climates.

Medium-textured soils such as loam soils, have the best overall characteristics for seed germination and plant root system development. Fine-textured soils, such as clays, are often fertile but may be beset by management problems such as puddling of water on the surface or difficulty in initial establishment of plant cover during wet periods. Sandy soils are often a problem due to low water retention and loss of nutrients by leaching. It may be cost-effective to stockpile the topsoil initially removed from a site for later use during cover construction. Where only a minimum amount of native topsoil can be saved by stockpiling, the remainder needed to provide at least the minimum thickness of 60 cm (24 in.) may be made up by selecting local borrow material having appropriate qualities.

The Agency recommends that the lower component of the top layer (and thus the entire top layer) be slightly convex, or be low in height above the surrounding terrain and uniformly sloped. In non-level terrain, diversion structures should be installed to prevent the run-on of surface water onto the cover. To prevent ponding of rainwater due to irregularities of the surface of the lower component, the final slope should be uniform and at least 3 percent, after allowance for settlement and subsidence (EPA, 1982a, p. 42). Slopes greater than 5 percent, however, are likely to promote erosion unless controls are included in the design. The design of surface water controls is well-documented (EPA, 1979 and 1982b). The Agency believes that slopes greater than 5 percent will increase erosion, decrease slope stability,

and, in general, increase the long-term maintenance of the cover system. Owners and operators using final slopes based on site-specific conditions should determine that the slopes will not result in the formation of erosion rills and gullies and will limit total erosion to less than 2.0 tons/acre/year (5.5 MT/ha/yr). The U.S. Department of Agriculture's Universal Soil Loss Equation (USLE) is recommended as the tool for use in evaluating erosion potential (EPA, 1982a). The Agency believes that a maximum erosion rate of 2.0 tons/acre/year (5.5 MT/ha/yr) is realistically achievable for a wide range of soils, climates, and vegetation. The Agency also believes that reliance on this criterion will minimize gully development and cover maintenance.

3. DRAINAGE LAYER

The recommended final cover design includes a drainage layer for the removal of water which infiltrates through the top layer (see Figures 3a and 3b). The drainage layer should be designed to minimize the amount and residence time of water coming into contact with the low-permeability layer, thereby decreasing the potential for leachate generation. In other words, the drainage layer construction materials and configuration should facilitate the rapid and efficient removal of water to an exit drain.

The drainage layer should be designed, constructed, and operated to function without clogging. Physical clogging may be prevented by incorporating a filter layer of soil or geosynthetic material between the top layer and the drainage layer. The prevention of biological clogging may range from limiting vegetation to shallow-rooted species to the installation of a biotic barrier (see Figure 2). Any or all of these features may be included in a single cover design.

In arid locations, the need for, and design of, a drainage layer should be based on consideration of precipitation event frequency and intensity, and sorptive capacity of other soil layers in the cover system. It may be possible to construct a top layer that will absorb most, if not all, of the precipitation that infiltrates into that layer, eliminating the need for a drainage layer.

3.1 DESIGN

If composed of granular material such as sand (Figure 3a), the Agency recommends that the cover drainage layer meet the following specifications:

- Minimum thickness of 30 cm (12 in.) and minimum slope of 3 percent at the bottom of the layer; greater thickness and/or slope if necessary to provide sufficient drainage flow as determined by site-specific hydrologic (e.g., HELP) modeling.

- Hydraulic conductivity of drainage material should be no less than 1×10^{-2} cm/sec (hydraulic transmissivity no less than 3×10^{-5} m^2/sec) at the time of installation.

- Granular material should be no coarser than 3/8 inch (0.95 cm), and classified as SP; it should be smooth and rounded and should contain no debris that could damage the underlying flexible membrane liner (FML), nor should it contain fines that might lessen permeability.

- A filter layer (granular or geosynthetic) should be included between the drainage layer and top layer if necessary to prevent clogging of the drainage layer by fine particles.

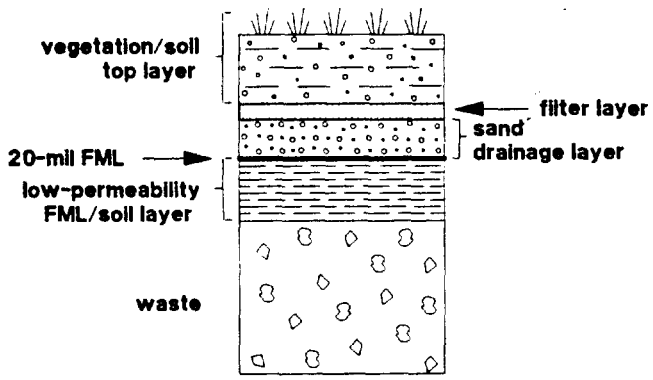

Figure 3a. Cover with sand drainage layer.

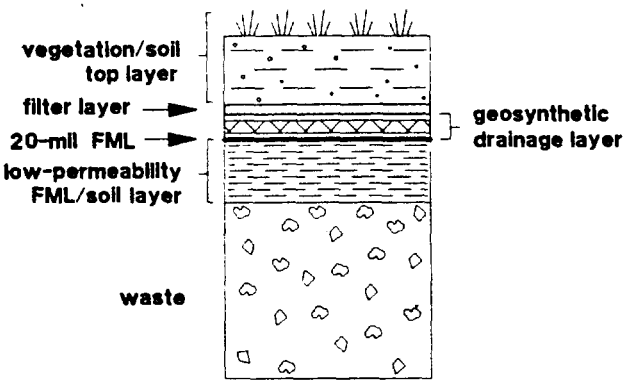

Figure 3b. Cover with geosynthetic drain layer.

If composed of geosynthetic materials (Figure 3b), the Agency recommends that the drainage layer meet the following specifications:

- Same minimum flow capabilility as a granular drainage layer in the same situation; hydraulic transmissivity no less than 3 x 10^{-5} m^2/sec under anticipated overburden for the design life.

- Inclusion of a geosynthetic filter layer above the drainage material to prevent intrusion and clogging by the overlying top layer soil material.

- Inclusion of geosynthetic bedding beneath the drainage layer, if necessary, to increase friction and minimize slippage between the drainage layer and the underlying FML, and to prevent intrusion, by deformation, of the FML into the net or grid of the drainage layer.

The owner or operator should prepare a written construction quality assurance (CQA) plan to be used during construction and installation of the drainage layer (see EPA, 1987b).

3.2 DISCUSSION

The primary functions of the drainage layer are to intercept water that percolates through the top layer and to transport the water out of the cover (for example, by gravity flow to an outlet at the toe of the cover). The Agency believes that the criteria presented above are the minimums required to provide cover drainage and FML protection. The criteria for permeability and FML bedding are equivalent to those cited in "Minimum Technology Guidance on Double Liner Systems for Landfills and Surface Impoundments -- Design, Construction and Operation" (EPA, 1987i) for the leachate detection, collection, and removal system.

The recommended 30-cm (12-in.) minimum thickness of the drainage layer allows sufficient cross-sectional area for transport of drainage in most situations and for protection of the FML during construction. In some cases, particularly where unusually long drainage slopes may be part of the design, drainage layers thicker than 30 cm (12 in.) and/or slopes greater than 3 percent may be necessary. The minimum value of 1×10^{-2} cm/sec for permeability was chosen because granular materials widely used as drainage media (i.e., SP soils) can provide this minimum hydraulic conductivity. In situations where the minimum criteria are insufficient or questionable, the design should utilize flow modelling in arriving at the flow-controlling design parameters. The HELP model (EPA, 1984a) can be of assistance for this purpose.

Rounded grains with a maximum size of 3/8 inch (0.95 cm) have been recommended, because they have been shown to be non-damaging to most FMLs when in direct contact with them (EPA, 1984b). Crushed stone would not normally be appropriate due to sharpness of the particles.

The drainage layer must slope to an exit drain which allows percolated water to be efficiently removed. An example of an exit drain is shown in Figure 4. Further information is provided in EPA (1985a) and Bureau of Reclamation (1977) publications. Care should be taken in the design to control the velocity of the exiting water, within and beyond the exit drains, to prevent soil loss and destabilization. Large safety factors may be needed to accommodate unexpected events.

Materials used to construct the drainage layer should be washed or screened prior to construction to remove fines that may promote clogging. To further prevent clogging of the drainage

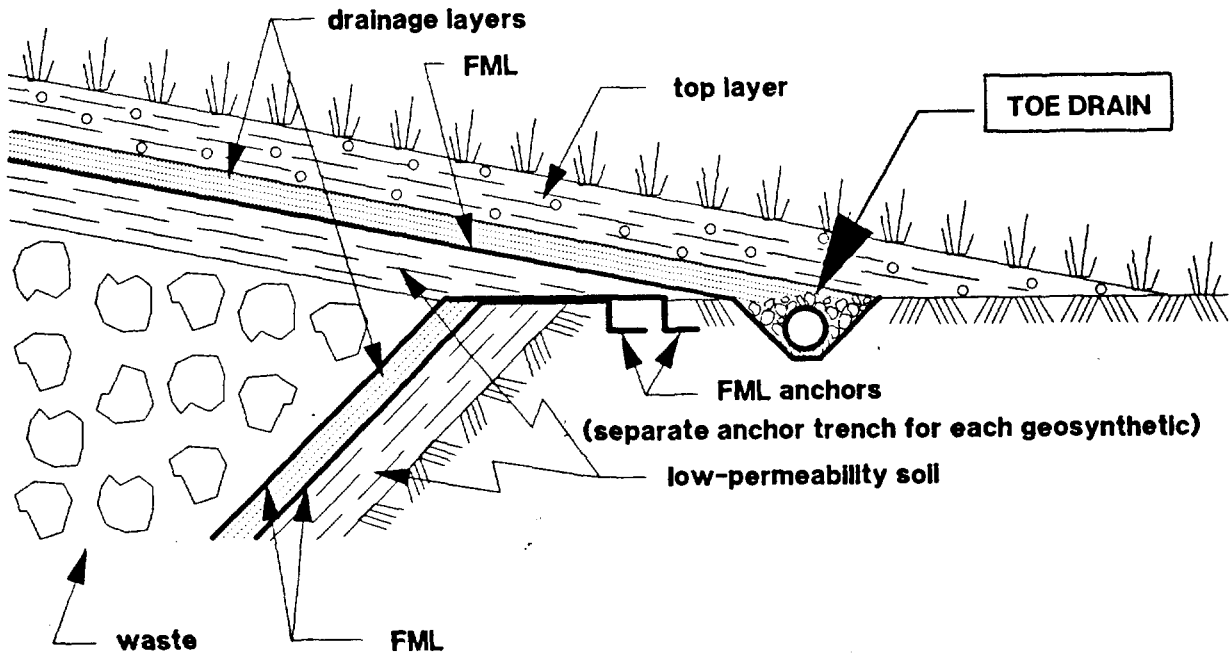

Figure 4. Cover and liner edge configuration with example toe drain.

layer, the Agency recommends that a granular or geosynthetic filter be placed directly over the drainage layer to minimize the migration of fines from the overlying topsoil into the drainage layer. If a graded granular filter is used, care should be taken to design the relationship of grain sizes according to the criteria presented below (Cedergren, 1967).

To prevent piping:

$$\frac{D_{15}\ \text{Filter}}{D_{85}\ \text{Top soil layer}} < 4\text{-}5, \text{ and}$$

$$\frac{D_{15}\ \text{Drainage layer}}{D_{85}\ \text{Filter}} < 4\text{-}5$$

To maintain permeability:

$$\frac{D_{15}\ \text{Filter}}{D_{15}\ \text{Top soil layer}} > 4\text{-}5, \text{ and}$$

$$\frac{D_{15}\ \text{Drainage layer}}{D_{15}\ \text{Filter}} > 4\text{-}5$$

To achieve uniformity of grain size distribution curves among top soil layer, filter, and drainage layer:

$$\frac{D_{50}\ \text{Filter}}{D_{50}\ \text{Top soil layer}} < 25, \text{ and}$$

$$\frac{D_{50}\ \text{Drainage layer}}{D_{50}\ \text{Filter}} < 25$$

These criteria are cited by the Army Corps of Engineers for selection of a filter layer in relation to a soil to prevent the soil from piping through the filter. D_{85} refers to the size of particle in the gradation, below which 85 percent by weight of the particles have a smaller particle size. D_{15} and D_{50} have similar definitions. The criteria must be satisfied for all layers or media in the drainage system, including protected soil, filter media, and drainage media. Criteria for granular and geotextile filter design are found in numerous references (Horz, 1984; Bureau of Reclamation, 1984 and 1977; EPA, 1987e; and Koerner, 1989).

Innovative drainage systems, such as those using geosynthetic materials (see Figure 3b), may be used if it can be shown that they are at least equivalent to the recommended granular system in hydraulic transmissivity, in performance longevity (transmissivity must be maintained for cover's design life), and in their ancillary function as FML bedding. Criteria which should be addressed in determining equivalence of geosynthetic and soil drainage materials include, but are not limited to, the following:

- hydraulic transmissivity (the rate at which liquid can be removed) no less than 3×10^{-5} m^2/sec;
- compressibility (the ability to maintain open pore space and thus transmissivity, under expected overburden);
- deformation characteristics (the ability to conform to changes in the shape of the surrounding materials);
- mechanical compatibility with the FML (the tendency for the drainage material and the FML to deform each other);
- useful life of the system; and
- ability to resist physical, chemical and biological clogging.

Geosynthetic drainage materials are manufactured in a variety of configurations, which continue to evolve with experience in manufacturing and use. "Geonets" and "geogrids" are drainage components designed for rapid flowthrough. They are manufactured as single components that usually must be separated from overlying and underlying soils that could clog them. The separating materials are also geosynthetics in the form of filter fabric. The geogrid, and top and bottom filters (which may also serve as protective bedding and slide-resistant materials), may all be factory-bonded together in one unit. These bonded-together materials, one form of "geocomposites," may be applied in one operation as the entire drainage layer. The various forms of geocomposites are well-described by Koerner (1989). In geosynthetic materials are continually being improved by the manufacturers for durability and design.

4. LOW-PERMEABILITY LAYER

The final cover system is required by 40 CFR 264.228, 264.310, and 265.310 to provide long-term minimization of migration of liquids through the closed land disposal unit and to have a permeability less than or equal to the permeability of the bottom liner system or natural subsoils present. The Agency has interpreted this to mean that the cover should contain a FML/soil composite layer (Figure 5) similar in concept (but not necessarily identical construction materials) to the composite bottom liner detailed in "Minimum Technology Guidance on Double Liner Systems for Landfills and Surface Impoundments -- Design, Construction and Operation" (EPA, 1987i) and in proposed regulations (EPA, 1987a). The two components (FML and soil) of the low-permeability layer recommended in this document are considered to function as one system. They should be designed, constructed, and operated to maximize removal of water by the

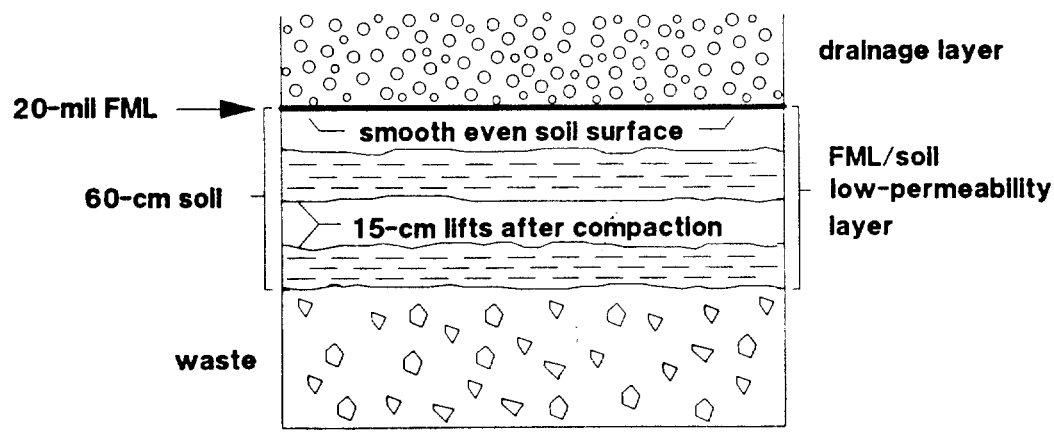

Figure 5. Detail of FML/soil composite low-permeability layer.

overlying drainage layer and to minimize infiltration of water into the waste. The low-permeability layer should require little or no maintenance during and after the post-closure period. The Agency recommends the same design for both permitted and interim status units, although it may not be required for some interim status units.

4.1 DESIGN

The Agency recommends that the low-permeability layer be located below the maximum depth of frost penetration and, at a minimum, consist of the following two components:

1. An upper FML component with the following characteristics:

   a. The FML should be at least 20 mils (0.5 mm) in thickness, but some units and/or some FML materials may require a greater thickness to prevent failure under potential stress of the post-closure care period, or during construction. The Agency recognizes that some types of FMLs must be thicker to accommodate unique seamability requirements, or to increase long-term durability (e.g., increase resistance to puncture).

   b. The surface of the FML should have a minimum 3 percent slope after allowance for settlement.

   c. There should be no surface unevenness, local depressions, or small mounding that create depressions capable of containing or otherwise impeding the rapid flow and drainage of infiltrating water.

   d. The Agency recommends the use of material and seam specifications such as those in "Lining of Waste Containment and other Impoundment Facilities" (EPA, 1987h).

   e. The FML should be protected by an overlying drainage layer of at least 30 cm (12 in.) of soil material no coarser than 3/8-in. (0.95-mm) particle size, Unified Soil Classification System (USCS) SP sand, free of rock, fractured stone, debris, cobbles, rubbish, roots, and sudden changes in grade (slope) that may impair the FML. The overlying drainage layer should suffice as bedding in most cases, but care should be taken that any included drainage pipes are not placed in a way that will damage the FML.

   f. The FML should be in direct contact with the underlying compacted soil component and should be installed on a smoothed soil surface.

g. The number of penetrations of the FML by designed structures (e.g., gas vents) should be minimized. Where penetrations are necessary, the FML should be sealed securely around the structure.

h. Bridging or similar stressed conditions in the FML should be avoided by providing slack allowances for temperature-induced shrinkage of the FML during installation and during the period prior to placement of the protective layer or drainage layer.

i. Slack should not be excessive to the extent that folds are created that later may crack.

2. A bottom low-permeability soil component with the following characteristics:

a. The soil should be at least 60 cm (24 in.) of compacted, low-permeability soil with an in-place saturated hydraulic conductivity of 1×10^{-7} cm/sec or less.

b. The compacted soil must be free of clods, rock, fractured stone, debris, cobbles, rubbish, and roots, etc., that would increase the hydraulic conductivity or serve to promote preferential water flow paths.

c. The upper surface of the compacted soil (which is in contact with the FML) should have a minimum slope of 3 percent after allowance for settlement.

d. The soil layer should be constructed so that it will be entirely below the maximum depth of frost penetration upon completion of the cover system.

The written CQA plan prepared by the owner/operator should include a separate section specific to monitoring the installation of both the FML and compacted soil liner (see EPA, 1987i).

4.2 DISCUSSION

The Agency believes that the recommended two-component low-permeability layer design (Figure 5) is the best practicable, in most cases, to minimize infiltration of surface water into the underlying waste. Both the FML and the compacted soil components have excellent characteristics to prevent infiltration into underlying waste over the long term when properly designed, installed, and operated in accordance with site-specific conditions. Their characteristics tend to complement each other,

so that the long-term effectiveness of the two components together is greater than each alone. A summary discussion of the comparative effectiveness of the composite liner in the bottom liner application appears in a Federal Register notice (EPA, 1987f). A more complete discussion appears in "Background Document on Bottom Liner Performance in Double-Lined Landfills and Surface Impoundments" (EPA, 1987g). In short, the FML will tend to roof over the inconsistencies in the underlying compacted soil, while the compacted soil will tend to significantly impede the flow of any leakage through a hole in the overlying FML. In addition, each component tends to back up the other in the event of a failure of either.

In the past, due to lack of data on durability, the Agency has considered the FML to be short-lived compared to compacted soil. Thus, the Agency has thought of the FML as fulfilling a function of "short-term prevention" of infiltration, while the soil provides for "long-term minimization." With increasing knowledge of FML characteristics and performance, and the increasing technical ability to custom-tailor FML materials to the containment need, it is now the consensus that they, too, can be made to last for very long periods of time (EPA, 1988a). Of course, this implies that care be taken in the construction, and later operation of the facility, that all design requirements are met, that certain waste consolidation conditions are met to minimize settlement problems, and that physical damage does not occur. The same implication applies to the soil component even though the design requirements and potential physical damage are significantly different.

The following subsections provide more detail on the design rationale for each of the two components of the low-permeability layer.

4.2.1 FML Component

The Agency recommends that, in no case, should the thickness of the FML be less than 20 mils (0.5 mm). The Agency believes that this is the minimum acceptable thickness to meet cover objectives and still be sufficiently rugged to withstand expected stresses during construction and operation. In many, if not most, cases the thickness should be greater. The adequacy of the selected thickness should be demonstrated by an evaluation considering the type, strength, and durability of the proposed FML material, its seamability, and site-specific factors such as: steepness of slopes, physical compatibility with the material used in the underlying and overlying layers, stresses of installation, expected overburden, climatic conditions, settlement, and subsidence.

FML failure mechanisms are discussed in several reports (EPA 1985a, 1983b, 1987h). Most failures result from inadequacies in the design and construction processes. It follows then that most failures can be prevented if a strict quality assurance program is adhered to during the construction process. The Agency has placed great emphasis on construction quality assurance, particularly in the construction of barrier layers, and has published guidance in that area for landfill waste containment liners (EPA, 1986).

One of the causes of FML failure in landfill and surface impoundment lining systems is chemical incompatibility. However, the FML in a final cover should not come in direct contact with any wastes and chemical incompatibility should not be of concern. This makes it possible to accept a wider range of FML materials in cover systems. It should be remembered here that it was not the Agency's intent in the regulations that the bottom liner and cover barrier necessarily be constructed of the same material.

Another of the primary causes of FML failure is damage during installation or operation. To aid in preventing damage, such as punctures, rips and tears, at least 30 cm (12 in.) of bedding material above and below the membrane is recommended. Since the FML is in direct contact with the low-permeability soil layer, that layer will serve as the underlying FML bedding. In most cases, the drainage layer above the membrane will suffice as the overlying FML bedding. A minimum underlying bedding thickness of 30 cm (12 in.) is recommended, the same as for the drainage layer. The actual bedding thickness should, however, be based upon consideration of failure mechanisms and construction methods potentially harmful to the FML (e.g., if construction equipment or methods are capable of penetrating the 30-cm [12-in.] drainage layer and tearing, ripping or puncturing the FML, then the thickness should be increased). If the design thicknesses for drainage and bedding differ, then the greater thickness should be used. Geosynthetic drainage materials may also serve as protective bedding if they can provide equivalent protection for the design life of the cover system.

Penetration of the FML by gas vents or drainage pipes should be minimized. Where a vent is necessary, it is essential to obtain a secure, liquid-tight seal between the structure and the FML to prevent leakage of water around the vent (see Section 5). Settlement of the material around the structure may create destructive stresses in the FML, which should be taken into account in the design of both the structure and the FML collar.

Differential settlement across the cover may also cause disruptive stresses that should be accounted for in the FML design. Care should be taken to make allowance for these and other stresses. For example, wrinkles and folds might be created

intentionally to reduce stress, but they may, in turn, result in stresses in the folds that can lead to long-term failure of the FML (EPA, 1988b).

The subgrade for the FML must be carefully prepared and smoothed so that no small-scale stress points are created due to protrusions of rocks or other materials. In most cases, this should cause no difficulty, since the subgrade will be the low-permeability soil component, comprised of fine material.

Field-seaming of the FML must be done carefully by technicians qualified and experienced in seaming the particular FML being installed. Holes can result from discontinuous seams or those not sufficiently sturdy to withstand unavoidable stresses. Some FMLs require destructive surface preparation (e.g., grinding) prior to seaming; all will expand and shrink with temperature changes. These characteristics may promote later leakage if not carefully considered in the construction process. All of the potential failure causes can be minimized or prevented by using expert installers and adhering to a strict construction quality assurance program (EPA, 1986).

4.2.2. Low-Permeability Compacted Soil Component

The Agency believes that a compacted soil component beneath, and in direct contact with, the FML will:

- minimize, over the long term, liquid migration into the waste in the event of FML failure or through imperfections (holes, tears, etc.) inadvertently left during the construction process;
- provide a firm foundation for the overlying layers of the cover system;
- serve as bedding material for protection of the overlying FML; and
- in conjunction with the FML, satisfy the regulatory requirement for the cover to be no more permeable than the bottom liner of the facility.

The design of the soil layer will depend on site-specific factors including the properties and engineering characteristics of the soil being compacted, the degree of compaction attainable, the total expected load, and the expected precipitation.

The Agency recommends a minimum thickness of 60 cm (24 in.) for the low-permeability soil component. The minimum thickness is based upon constructability considerations and the ability to provide uniformity in overall permeability. Sixty centimeters allows for the installation of four lifts (see Figure 5),

considered sufficient to overcome any inconsistencies in the underlying surface. The four lifts also allow the localized inconsistencies in permeability in one lift to be "sealed" by the overlying lift.

As in the case of landfill liners, the Agency recommends the use of a test fill (EPA, 1986, 1987i, and 1988c) prior to actual construction of the soil component. The purpose is to demonstrate, where appropriate soil is available, that the compacted soil component actually can be constructed to an hydraulic conductivity no greater than 1×10^{-7} cm/sec. (Most of the ensuing discussion assumes that soil will be available that can meet the 1×10^{-7} criterion.) The Agency believes that construction of a test fill utilizing the soil, equipment, and procedures to be used in construction of the low-permeability layer will ensure that design specifications are attainable with the available materials and equipment.

The test fill need not be constructed on the waste. The Agency believes that, if the waste consolidation or compressive strength of the waste is insufficient to allow adequate compaction of the low-permeability soil component, that problem should be corrected before installation of the compacted soil. One of the possible solutions is to install an interim cover, as noted earlier for the mitigation of subsidence. If components of the interim cover can meet the CQA requirements for the final cover, the interim cover could be made an integral part of the final design.

Potential failure mechanisms that must be considered in evaluating the design of the compacted soil component include subsidence, dessication cracking, and freeze-thaw cycling. Subsidence has been discussed in the Introduction. The main factor of concern in design to counter subsidence is the consolidation potential remaining at the time of cover installation. That potential is difficult to estimate, but, in the estimation, information regarding the presence of voids and compressible materials in the underlying waste is all-important. Ordinarily, most of the consolidation that will take place in hazardous waste landfills has occurred by the time of cessation of waste placement (EPA, 1985c and 1987d). An important benefit is the ability of the compacted soil component to deform somewhat without rupturing, a desirable characteristic related to the soil's compressive and tensile strengths under expected field conditions of moisture, density, etc.

The potential for desiccation of the compacted clay component will depend on the physical properties of the clay, design moisture content, local climatology, and moisture content of the underlying waste. The actual clay-size particle content of the soil, the type of clay, and properties such as liquid

limit, plasticity, and shrinkage should be used to select a soil with low cracking potential or in determining placement procedures to reduce cracking potential (RTI, 1983; EPA, 1979).

Compaction of the soil component wet of optimum is recommended by the Agency to assure that the lowest permeability may be attained with standard Proctor densities (RTI, 1983). To guard against drying in this case, the applicant may propose immediate installation of the FML above the soil. If this is done, it must first be assured that the installation of the soil is complete, including a smooth surface on which to directly apply the FML.

Freeze-thaw conditions are an important potential source of damage to the soil component of the low-permeability layer. Cycles of freezing and thawing may cause material cracking, lessening of density, and loss of strength. This is brought about by volume expansion of liquids in pore spaces during freezing which, after thawing, increases the accessibility of liquids to the pore spaces (EPA, 1983b). Cracking may be created due to the expansion associated with freezing. For these reasons, the Agency recommends that, upon completion of cover system construction, the low-permeability layer be entirely below the maximum depth of frost penetration estimated for the area in which the facility is constructed. In other words, the top layer and drainage layer of the cover together should be thicker than the maximum depth of frost penetration. In northern areas of the United States this recommendation would necessitate a top layer thicker than the recommended 60-cm (24-in.) minimum.

Figure 6 is provided to show the variability of mean frost penetration across the United States (Stewart, et. al., 1975). The figure is provided only for perspective. It should not be used to find the maximum depth of frost penetration at any particular site. In determining the site-specific maximum depth of frost penetration, advice may be sought from the Soil Conservation Service, utility companies, construction contractors, and universities in the area of concern.

Penetration of the low-permeability soil component by gas vents or drainage pipes should be minimized. Adequate attention must be given to the design of seals for such penetrations and possible complications induced by differential settlement of natural and man-made materials at penetration points. The Agency has no information specific to the adequacy of seals in the soil component of the low-permeability layer.

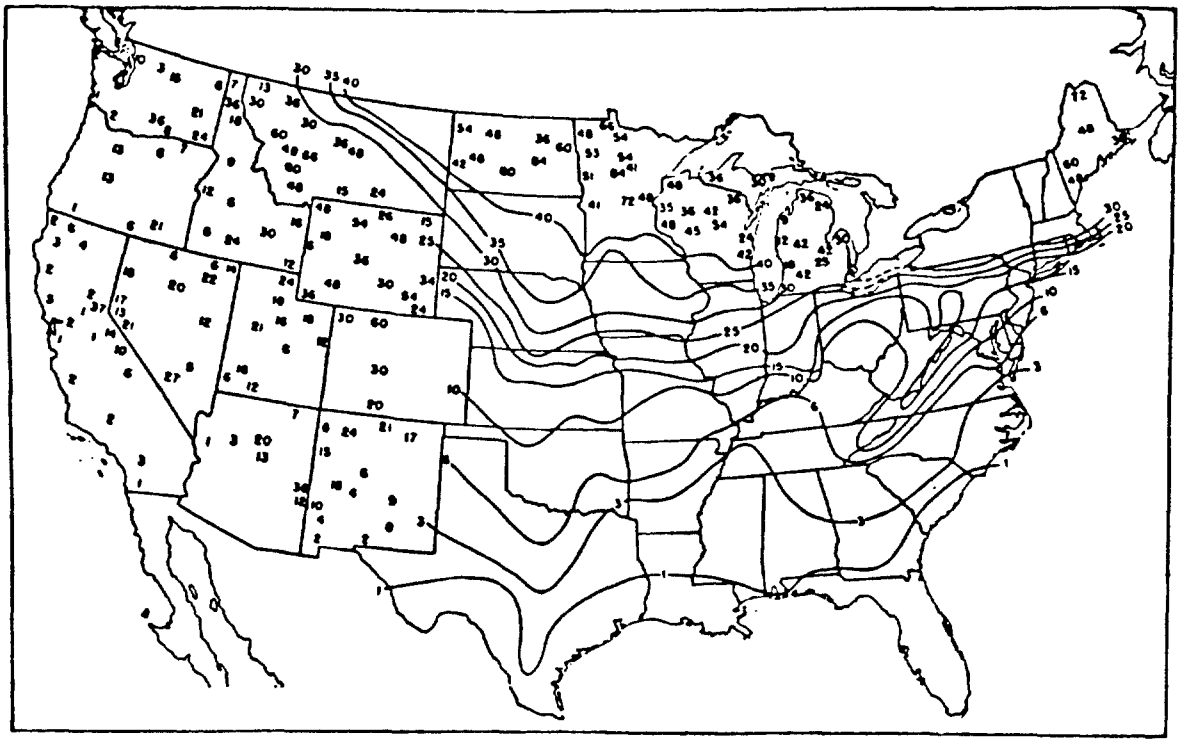

Figure 6. Regional average depth of frost penetration in inches (Stewart, et al., 1975).

5. OPTIONAL LAYERS

The optional layers discussed in this section are the gas vent and biotic barrier layers. Other layers may be needed on a site-specific basis. The Agency does not have information on the performance of these layers in full-scale multilayer cover systems.

5.1 GAS VENT LAYER

The function of a gas vent layer (Figure 7) is to control combustible or toxic gases released from wastes buried in a disposal facility. Hazardous waste disposal facilities that are most likely to require a gas vent layer are co-disposal facilities that receive organic waste material such as that found in municipal waste. However, certain chemicals may also emit gases or vapors in sufficient quantity to require venting.

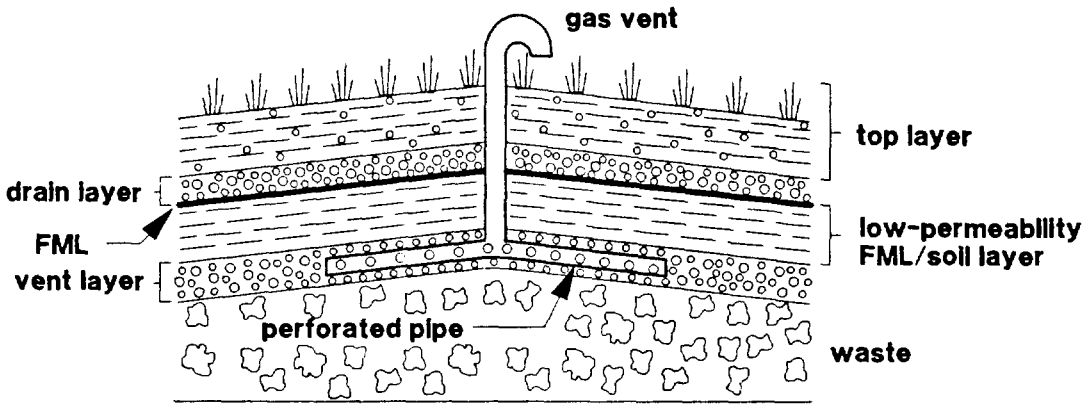

Figure 7. Cover with gas vent outlet and vent layer.

5.1.1 Design

The Agency offers the following design recommendations, based upon engineering judgment, for a gas vent layer:

- The layer should be a minimum of 30 cm (12 in.) thick and should be located between the low-permeability soil liner and the waste layer (see Figure 2).

- Materials used in construction of the gas vent layer should be coarse-grained, porous materials such as those used in the drainage layer.

- Geosynthetic materials may be substituted for granular materials in the vent layer if equivalent performance can be shown.

- Venting to an exterior collection point for disposal or treatment should be provided by means such as horizontal perforated pipes, patterned laterally throughout the gas vent layer, which channel gases to vertical risers.

- The number of vertical risers through the cover should be minimized and located at high points in the cross-section, and designed to prevent water infiltration through and around them.

An alternative design, particularly useful for layered landfills where vertical migration is impeded, may include perforated vertical collector pipes penetrating to the bottom of the landfill. In this case, several cover penetrations may be required, one for each standpipe. Here again, the pipes should be securely sealed to the low-permeability layer. The standpipes may be 30 cm (12 in.) or more in diameter and may be dual purpose, serving also to provide access for measurement of leachate levels.

The written CQA plan prepared by the owner/operator should contain a specific section which covers monitoring the construction and installation of the gas vent system.

5.1.2 Discussion

Materials used in construction of the gas vent layer should have specifications similar to the granular material used for the drainage layer. The materials should be chosen and placed in a way that facilitates the emplacement and compaction of the overlying low-permeability soil component. Once placed, the granular material should allow free movement of gases to collection pipes and/or outlet points.

The outlets may consist of pipes or vents allowing the gas to be collected, vented, or treated. The vent layer and outlet should be designed to minimize cover penetrations which could allow possible liquid infiltration through the cover. Outlet vents should be constructed through the barrier layer at the highest elevation of the gas vent layer to allow maximum evacuation of gas (see Figure 7).

A minimum thickness of 30 cm (12 in.) is recommended to assure that a continuous layer of reasonable thickness (to allow free movement of gases) is provided after placement on a non-uniform waste surface.

In addition to providing gas removal, the gas vent layer may provide a protective foundation upon which to construct the compacted soil liner. The vent layer must be placed over the waste up to design elevation, allowing for estimated settlement, prior to placement and compaction of the soil liner. A filter, either granular or geotextile, may be required between the gas vent layer and the low-permeability soil to prevent clogging.

Alternative gas layer designs (e.g., using geosynthetic materials) may be considered if it can be shown that they provide a level of performance equivalent to a 30-cm (12-in.) granular layer. Equivalence is based upon the ability of the design to efficiently remove any gases produced, resist clogging, prevent infiltration, withstand expected overburden pressures, and function under the stresses of construction and operation.

Designs for gas vent layers can be found in several EPA publications (EPA 1979, EPA 1985a).

Alternative, vertical standpipe gas collectors are constructed of perforated sections, being built up as the unit is filled with waste. They may be constructed of concrete and wrapped with geosynthetic filter material to prevent clogging of the perforations.

5.2 BIOTIC BARRIER LAYER

Plant roots or burrowing animals (collectively described as biointruders) may disrupt the integrity of the drainage and low-permeability layers. The drainage layer may be especially susceptible to the intrusion of plant roots, which could interfere with the drainage capability of the material. The danger of FML penetration by plant intrusion has not been proven. Burrowing animals may be a greater threat to FMLs, if a threat indeed exists. In the absence of an FML, the low-permeability soil layer could be exposed to both root and animal penetration.

Physical barriers, such as layers of cobbles or coarse gravel beneath the top layer, and chemical barriers, have been proposed to discourage or reduce the threat of biointrusion.

5.2.1 Design

The Agency knows of no full-scale application that would prove the effectiveness of a biotic barrier in a landfill situation. Therefore, the design of such a barrier must rely on the results of small-scale field experiments. Experiments with

barrier layers of cobbles have been carried out in arid or semi-arid situations, with plants unique to such habitats (Cline, 1979 and Cline, et al, 1982). Some research suggests that three feet (90 cm) of cobbles, or six inches (15 cm) of gravel over 30 inches (75 cm) of cobbles, may be effective in stopping root penetration of some deep-rooted plants (DePoorter, 1982). It may also be effective in stopping the invasion of burrowing animals. The biotic barrier layer would directly underlie the soil component of the top layer, perhaps separated by a geosynthetic filter layer.

A polymeric herbicide carrier/delivery (PCD) system, used to release herbicide, as discussed by Cline, et al. (1981), might be installed within a cover, also just above the drainage layer to stop the intrusion of roots below the system. The PCD system would contain an herbicide designed to be released slowly over many years. Note here the probable reluctance of the Agency in approving this alternative, because it may introduce a hazardous waste to the cover system, and/or it may not last through the 30-year post-closure period.

5.2.2 Discussion

Research by Cline (1979) and Hokanson (1986) found that if objects, such as cobbles, placed in a burrowing animal's path are too large or tightly packed, the animal's progress is effectively stopped. Hokanson also found that large void spaces, which lack water and nutrients, within the layer of stone, reduced the intrusion of plant roots. On the other hand, the layer of very coarse materials, at least in arid areas, may favor the growth of grasses by impeding the downward percolation of moisture, thus helping to retain it in the top soil layer.

Cline et al. (1982) also looked at the effectiveness of several phytotoxins impregnated into polymeric sheets and buried in soil. Some of them met the goal of being effective in stopping the downward progress of root growth, with no other effects. Some of the phytotoxins killed the plants when the roots encountered the sheet, while others had no effect. Obviously, a chemical biotic barrier must be chosen carefully, if at all, to avoid potentially adverse environmental effects.

Most of the research on the effectiveness of biotic barriers has been done in arid areas. Thus, the results must be used with caution in areas of greater precipitation. The design and resulting effectiveness of a biotic barrier are site-specific and dependent upon the overlying topsoil layer, biotic barrier material, natural precipitation, and anticipated biointruders.

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OAR 340-045-0100
Table A – Persistent Pollutants

For the pollutants listed in italics below, the initiation level is the 2009 National Primary Drinking Water Standards Maximum Contaminant Level (MCL).

CASRN	Chemical Name	Initiation Level (µg/L)
120-12-7	Anthracene	0.01
7440-38-2	*Arsenic Compounds*	10
56-55-3	Benz(a)anthracene	0.02
50-32-8	*Benzo(a)pyrene*	0.2
205-99-2	Benzo(b)fluoranthene	0.5
191-24-2	Benzo(g,h,i)perylene	2
207-08-9	Benzo(k)fluoranthene	0.002
98-07-7	Benzotrichloride [trichloromethylbenzene]	0.03
82657-04-3	Bifenthrin	0.02
56-35-9	Bis (tributyltin) oxide [TBTO, hexabutyldistannoxane]	0.008
7440-43-9	*Cadmium Compounds*	5
5103-71-9	*Chlordane, cis-*	2
5103-74-2	*Chlordane, trans-*	2
143-50-0	Chlordecone [Kepone]	0.5
2921-88-2	Chlorpyrifos	0.04
57-88-5	Cholesterol	0.06
218-01-9	Chrysene [benzo(a)phenanthrene]	2
360-68-9	Coprostanol	0.04
541-02-6	Cyclopentasiloxane, decamethyl- [D5]	16
556-67-2	Cyclotetrasiloxane, octamethyl- [D4]	7
72-54-8	DDD, 4,4'-	0.1
72-55-9	DDE, 4,4'-	0.1
50-29-3	DDT, 4,4'-	0.001
434-90-2	Decafluorobiphenyl	18
52918-63-5	Deltamethrin [decamethrin]	0.0004
333-41-5	Diazinon	0.2
53-70-3	Dibenz(a,h)anthracene	0.04
115-32-2	Dicofol	6
60-57-1	Dieldrin	0.002
56-53-1	Diethylstilbestrol	87
88-85-7	*Dinoseb*	7
1746-01-6	*Dioxins/furans [as 2,3,7,8-TCDD TEQ]*	3 □□10^{-5}

OAR 340-045-0100
Table A – Persistent Pollutants

For the pollutants listed in italics below, the initiation level is the 2009 National Primary Drinking Water Standards Maximum Contaminant Level (MCL).

CASRN	Chemical Name	Initiation Level (µg/L)
1031-07-8	Endosulfan sulfate	0.1
72-20-8	*Endrin*	2
66230-04-4	Esfenvalerate	0.02
13356-08-6	Fenbutatin-oxide	0.5
120068-37-	Fipronil	15
206-44-0	Fluoranthene [benzo(j,k)fluorine]	0.04
1222-05-5	Galaxolide [HHCB]	29
76-44-8	*Heptachlor*	0.4
1024-57-3	*Heptachlor epoxide*	0.2
32241-08-0	Heptachloronaphthalene	0.4
25637-99-4	Hexabromocyclododecane [HBCD]	7
118-74-1	*Hexachlorobenzene [HCB]*	1
319-84-6	Hexachlorocyclohexane, alpha-	0.006
319-85-7	Hexachlorocyclohexane, beta-	0.04
58-89-9	*Hexachlorocyclohexane, gamma-*	0.2
1335-87-1	Hexachloronaphthalene	1.4
70-30-4	Hexachlorophene	2
193-39-5	Indeno(1,2,3-cd)pyrene	0.5
465-73-6	Isodrin	0.6
91465-08-6	Lambda-cyhalothrin	0.01
7439-92-1	*Lead Compounds*	15
330-55-2	Linuron	0.09
22967-92-6	Methylmercury	0.004
832-69-9	Methylphenanthrene, 1-	0.7
2381-21-7	Methylpyrene, 1-	20
2385-85-5	Mirex	0.001
15323-35-0	Musk indane	10
81-14-1	Musk ketone	30
145-39-1	Musk tibetene	4
81-15-2	Musk xylene	100
88671-89-0	Myclobutanil	200
5103-73-1	Nonachlor, cis-	2
39765-80-5	Nonachlor, trans-	2
29082-74-4	Octachlorostyrene	0.2

OAR 340-045-0100
Table A – Persistent Pollutants

For the pollutants listed in italics below, the initiation level is the 2009 National Primary Drinking Water Standards Maximum Contaminant Level (MCL).

CASRN	Chemical Name	Initiation Level (µg/L)
27304-13-8	Oxychlordane, single isomer	0.4
42874-03-3	Oxyfluorfen	1.3
5436-43-1	PBDE-047 [2,2',4,4'-Tetrabromodiphenyl	0.7
60348-60-9	PBDE-099 [2,2',4,4',5-	0.7
189084-64-	PBDE-100 [2,2',4,4',6-	0.7
68631-49-2	PBDE-153 [2,2',4,4',5,5'-hexabromodiphenyl ether]	1
1163-19-5	PBDE-209 [decabromodiphenyl ether]	0.1
7012-37-5	*PCB-028 [2,4,4'-trichlorobiphenyl]*	0.5
35693-99-3	*PCB-052 [2,2',5,5'-tetrachlorobiphenyl]*	0.5
32598-13-3	*PCB-077 [3,3',4,4'-tetrachlorobiphenyl]*	0.5
70362-50-4	*PCB-081 [3,4,4',5-tetrachlorobiphenyl]*	0.5
37680-73-2	*PCB-101 [2,2',4,5,5'-*	0.5
32598-14-4	*PCB-105 [2,3,3',4,4'-*	0.5
74472-37-0	*PCB-114 [2,3,4,4',5-pentachlorobiphenyl]*	0.5
31508-00-6	*PCB-118 [2,3',4,4',5-*	0.5
65510-44-3	*PCB-123 [2',3,4,4',5-*	0.5
57465-28-8	*PCB-126 [3,3',4,4',5-*	0.5
35065-28-2	*PCB-138 [2,2',3,4,4',5'-*	0.5
35065-27-1	*PCB-153 [2,2',4,4',5,5'-*	0.5
38380-08-4	*PCB-156 [2,3,3',4,4',5-*	0.5
69782-90-7	*PCB-157 [2,3,3',4,4',5'-*	0.5
52663-72-6	*PCB-167 [2,3',4,4',5,5'-*	0.5
32774-16-6	*PCB-169 [3,3',4,4',5,5'-*	0.5
35065-29-3	*PCB-180 [2,2',3,4,4',5,5'-*	0.5
39635-31-9	*PCB-189 [2,3,3',4,4',5,5'-*	0.5
40487-42-1	Pendimethalin	6
1825-21-4	Pentachloroanisole [2,3,4,5,6-	35
608-93-5	Pentachlorobenzene	6
1321-64-8	Pentachloronaphthalene	4
82-68-8	Pentachloronitrobenzene	20
375-85-9	Perfluoroheptanoic acid [PFHpA]	300
375-95-1	Perfluorononanoic acid [PFNA]	1
754-91-6	Perfluorooctane sulfonamide [PFOSA]	0.2

OAR 340-045-0100
Table A – Persistent Pollutants

For the pollutants listed in italics below, the initiation level is the 2009 National Primary Drinking Water Standards Maximum Contaminant Level (MCL).

CASRN	Chemical Name	Initiation Level (µg/L)
1763-23-1	Perfluorooctane sulfonic acid [PFOS]	300
335-67-1	Perfluorooctanoic acid [PFOA]	24
85-01-8	Phenanthrene	0.4
2062-78-4	Pimozide	3
67747-09-5	Prochloraz	2
129-00-0	Pyrene	0.03
80214-83-1	Roxithromycin	710
7782-49-2	*Selenium Compounds]*	50
83-45-4	Sitostanol, beta- [stigmastanol]	75
83-46-5	Sitosterol, beta-	25
92-94-4	Terphenyl, p-	11
79-94-7	Tetrabromobisphenol A [TBBPA]	980
1335-88-2	Tetrachloronaphthalene	14
1321-65-9	Trichloronaphthalene	43
95-95-4	Trichlorophenol, 2,4,5-	18
88-06-2	Trichlorophenol, 2,4,6-	2
3380-34-5	Triclosan [2,4,4'-trichloro-2'-hydroxydiphenyl ether]	70
1582-09-8	Trifluralin	1.1
732-26-3	Tris-(1,1-dimethylethyl)phenol, 2,4,6-	6

State of Oregon Department of Environmental Quality

OAR 340-050-0035 Attachments

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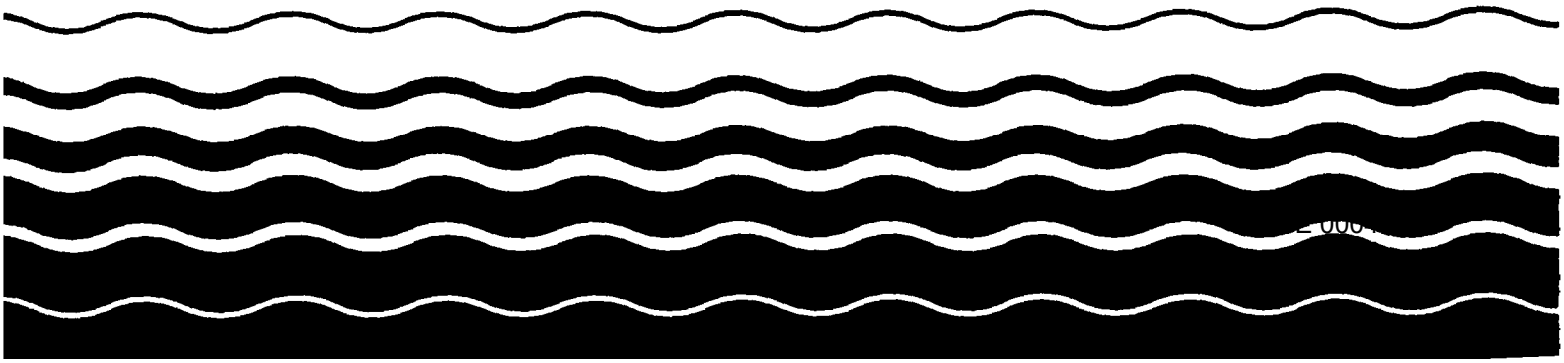
EPA

POTW Sludge Sampling And Analysis Guidance Document



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1. INTRODUCTION

The passage of the 1987 amendments to the Clean Water Act brought about significant changes in the regulation of the use and disposal of municipal sewage sludge. Although the Clean Water Act had required since 1977 that EPA develop technical standards for sludge use and disposal, the 1987 amendments required that these standards, when promulgated, be implemented through permits. The amendments also state that prior to promulgation of the technical standards, EPA must include sludge conditions in NPDES permits issued to publicly-owned treatment works or take other appropriate measures to protect public health and the environment from pollutants in sewage sludge. This requirement has initiated a program for "case-by-case" permitting to ensure protection of the environment prior to the issuance of final sludge standards which are scheduled for promulgation in October 1991.

This focus on sludge permitting places increased emphasis on the need to assess sewage sludge quality. In policy and guidance documents that EPA has developed for implementing the sludge requirements of the Clean Water Act, the Agency has recommended that POTWs sample and analyze their sludge at least annually to determine if the sludge quality is such that the sludge may be safely reused and recycled or disposed. Accurate characterization of sludge composition spots operational problems at the treatment works and may also signal adverse environmental impacts. In addition, sludge sample and analysis is needed to assess compliance with current requirements (e.g., 40 CFR Part 257 requirements for cadmium and PCBs).

In view of the variability of municipal sludge quality, appropriate procedures must be followed to collect and analyze samples that accurately represent each POTW's sludge quality. This manual was developed to provide that guidance to POTW operators, engineers, managers, chemists and permit writers. It was intended to provide guidance in developing and implementing a sampling and analysis program, to gather information on sludge quality and determine compliance with permit conditions. This manual is based on current, state-of-the-art field and laboratory practices and therefore is recommended for all sludge sampling and analysis programs.

2. SLUDGE SAMPLING

2.1 BACKGROUND INFORMATION

Depending on the use or disposal practice, it may be necessary to sample various sludge types throughout a given POTW. In order to sample a sludge stream effectively, it is necessary for sampling personnel to be aware of the physical characteristics of the sludge stream(s) at intended sampling locations.

2.1.1 Solids Content and Viscosity

Two important physical characteristics of sludge with respect to sampling and analysis are viscosity and solids content. Solids content is the percent, by weight, of solid material in a given volume of sludge. Sludges have a much higher solids content than most wastewaters. Solids content and solids settling characteristics determine whether a given sludge will separate into different fractions which increases the potential of obtaining a nonrepresentative sample.

Viscosity is the degree to which a fluid resists flow under an applied force. The viscosity of a sludge is only somewhat proportional to solids content. This property affects the ability to automatically sample a liquid, since friction through pipes is proportional to liquid viscosity. In general, sludges of up to 20 percent solids may be conveyed by means of a pump. Sludge with a greater solids content, often referred to as sludge cake, must be conveyed by mechanical means. Automatic samplers that rely on pumps may be useful only for liquid sludges with a solids content of less than 20 percent. However, sludge cakes require manual grab sampling. Other problems created by sludge

solids (see Section 2.3.1) generally preclude the use of automatic samplers.

Solids content is also significant from an analytical standpoint. Increased solids content may require sample dilution and cause a corresponding increase in experimental error and detection limits. Also, water removal through dewatering can either concentrate parameters of interest in the sludge and increase analytical accuracy, or carry away pollutants and decrease pollutant concentration and analytical accuracy. Analytical precision (repeatability) and accuracy (closeness to true value) may also decrease as the concentration of interfering compounds and matrix effects increase, due to higher solids content after dewatering.

2.1.2 Processed Sludge Characteristics

The quantity and quality of sludge generated depends on raw wastewater characteristics and the sludge treatment practices. The sludge to be sampled may be in the form of a liquid, dewatered cake, compost product, or dried powder. Some of the physical characteristics of each sludge type are described below.

2.1.2.1 Anaerobically Digested Sludge

Anaerobically digested sludge is a thick slurry of dark-colored particles and entrained gases. When well digested, it dewaters easily and has a non-offensive odor. The addition of chemicals coagulates a digested sludge prior to mechanical dewatering. The dry residue of digested sludge contains 30 to 60 percent volatile solids. Depending on the mode of digester operation, the percent solids of digested sludges ranges from 4 to 8 percent.

2.1.2.2 Aerobically Digested Sludge

Aerobically digested sludge is a dark-brown, flocculent, relatively inert waste produced by long-term aeration of sludge. The suspension is bulky and generally difficult to thicken. The odor of aerobically digested sludge is not offensive. The percent solids of aerobically digested sludge is less than that of the influent sludge (if not decanted), because approximately 50 percent of the volatile solids are converted to gaseous end products during aerobic digestion.

2.1.2.3 Dewatered Sludges

Dewatering converts sludge from a flowing mixture of liquids and solids to a cake-like substance more readily handled as a solid. The characteristics of dewatered sludge depend on the type of sludge, chemical conditioning, and treatment processes employed. The percent solids content of dewatered cake ranges from 15 to >40 percent. Cake with a lower percent solids is similar to a wet manure, while cake with a higher percent solids is a chunky solid.

2.1.2.4 Compost Product

Composting is a process in which organic material undergoes biological degradation to a stable end product. Properly composted sludge is a sanitary, nuisance-free, humus-like material containing 75 to 80 percent solids. Approximately 20 to 30 percent of the volatile solids are converted to carbon dioxide and water.

2.1.2.5 Dried Powder

Dried powder is the residue from heat drying processes. Sludge drying reduces water content by vaporization of water to permit sludge grinding, weight reduction, and to prevent

continued biological action. The moisture content of dried sludge is less than 10 percent.

Incinerator ash is a product of the incineration of sewage sludge. Ash is therefore not covered under the sampling or analysis of sewage sludge. It is covered under RCRA Subtitle C if it is a hazardous waste and if not it falls under Subtitle D.

2.2 SAMPLE POINT SELECTION

2.2.1 General Considerations

NPDES, pretreatment and sludge program officials need sludge quality data in order to determine whether sludge use or disposal may pose a threat to public health or the environment. Thus, as a general rule, sludge samples should be drawn from an appropriate sampling point and in such a manner that the sample represents, as well as possible, the quality of the sludge as it will be disposed of or used. When selecting a specific sample point, the following two factors should be carefully considered:

- Does the sample point represent the entire sludge stream?
- Are the sludge stream flow or mass flux data available?

The following paragraphs examine both factors and present recommendations on means to address each factor.

2.2.1.1 Sample Point Representation of the Entire Sludge Stream

Often it is not possible to obtain a wholly representative sample of a given wastestream at any one time. Effort must be made, however, to ensure that a sample is obtained that is as representative as possible. Three concerns that need to be

addressed to ensure that the sample points selected will provide representative samples of the entire sludge stream are: obtaining samples that are representative of the cross-section of the entire flow; obtaining well mixed samples; and obtaining samples of multiple sludge streams.

A particular concern in any sampling program is to obtain samples which represent the entire flow past the sample point throughout the sample period. Each discrete sample should represent the cross-section of the entire flow at the sampling point. Each composite sample of multiple contributory streams should represent the cross-section of the entire flow of the combined stream.

Samples should be obtained from points where the sludge is well-mixed. While some pollutant parameters are predominantly associated with the solids fraction (particularly precipitated metals), others are more associated with the liquid-fraction (many dissolved organics). Failure to acquire a sample with representative solid/liquid fractions can significantly affect the analytical results of a given sample. This is particularly true of sludge streams with high percent solids and large floc particles. Since turbulence ensures mixed samples, these recommendations should be followed:

- In sludge processing trains, samples from taps on the discharge side of sludge pumps are well mixed since flow at this point in the system is turbulent with no solids separation within the flow stream.
- If a sample is drawn from a tap on a pipe containing sludge which is distant from the sludge pumps, the average flow velocity through the pipe should be greater than 2 feet per second (fps). Average velocities of less than 2 fps result in solids separation and settling, and affect sample solids content, depending on the location of the tap (top,

side or bottom of the pipe). Given a choice, a tap on the side of the pipe is preferable. In addition, the tap should be a large size to encourage draw from the entire cross-section of flow when fully open.

At times it may be necessary to sample a poorly mixed open channel flow. If this cannot be avoided, then each sample must be a composite consisting of grabs taken at several levels (1/4, 1/2 and 3/4 depth, for example) in order to minimize sample bias caused by solids stratification. For sampling solid sludges (i.e. dewatered cake, compost, etc.), stratification can be avoided by not only sampling at various depths, but at numerous locations over the entire sludge pile.

Although it is preferable to sample sludge just prior to its exit from the treatment plant in a combined stream, sometimes that is not possible. Therefore, a consideration in many sludge sampling situations is the need to produce a composite sample from confluent streams. An example is the sampling of sludge flows from several parallel sources which later combine downstream in an unsafe or inaccessible location. Several options exist to accommodate multiple streams. The most appropriate choice depends on the sludge flow and solids flux information available, the parameters being sampled and the purpose of the generated data. Several options are as follows:

- The simplest option is to withdraw equal volumes of sample from each of the multiple sludge streams to create a composite sample. This approach is justified in the case of identical units receiving equal flow and generating equal sludge amounts.
- A second option is to weight the grab samples in each composite according to the wastewater flow to each unit (or in the case of filter cake, the thickened sludge flow to each unit). This approach recognizes that for different sized units with different design flows, the volume of sludge produced will theoretically be

proportional to the influent flow to the unit. However, factors such as unequal loading rates, differences in sludge collection mechanisms, etc. can affect solids removal rates and sludge generation rates by unequal, parallel treatment units. This option particularly applies to situations where no sludge flow or solids data exists for unequal parallel flow streams.

- The third option is to weight grabs from individual streams based on sludge flow data or solids flux data. Whether to use sludge flow or solids flux will depend on the sample streams, the parameters of interest, and the planned use of the resulting data. For example, if filter cake is being monitored for compliance with land application limits, solids flux data would be used as the criteria for proportioning grabs from parallel dewatering systems, since most land application limits are based on dry weight application rates.

2.2.1.2 Availability of Flow Data and/or Solids Flux Data

The availability of accurate solids flux data (weight/time) or accurate flow data (volume/time) is an important consideration in planning a sludge sampling program. Most information requirements relating to sludge characteristics involve, at least in part, the need for data on the solids flux of pollutant parameters found in sludge discharged from a POTW. The percent solids should be determined on sludge samples.

Portable flow monitoring devices are not well suited to high-solids flow streams, and most sludge processing streams are not designed in a manner which is physically conducive to the use of these devices. Thus, in most cases, it is necessary to rely on existing integrated flow monitoring equipment. Due to difficulties in monitoring sludge flows, flow meters are high maintenance items. Frequent calibration of sludge flowmeters is necessary in order to ensure accurate flow measurement. This data should be cross-checked against mass balance data. When ultimate use or disposal practices dictate monitoring sludge with

a high solids content, liquid flow meters are replaced by gross weight scales. Table 2.1 summarizes the types of flow measurement equipment employed to monitor various sludge flows.

2.2.2 Sludge Sample Points

The determination of the appropriate sludge sampling point is dependent on the rationale behind the sampling. For permits and regulation enforcement, sludge samples must come from the treatment unit process immediately preceding disposal or use. For example, if a POTW disposes of its dewatered filter cakes in a sanitary landfill, then sampling activity focuses on the output sludge stream from the dewatering device (i.e., vacuum filter, belt filter, etc.). The sludge treatment processes commonly employed are stabilization, dewatering, drying, composting, and thermal reduction. Table 2.2 summarizes sampling points for these processes. Other sludges sampling points may be necessary to examine the origin or fate of pollutants within a POTW, (i.e., additional sludge samples from influent and output of other processes may be needed).

2.3 SAMPLE COLLECTION

Having selected appropriate sampling points for a sludge sampling program, it is then necessary to determine the method and equipment by which sampling will be carried out. In doing so, the following objectives should be considered:

- Each grab sample, or aliquot of a composite sample, must be as representative as possible of the total stream flow passing the sampling point
- Effort must be made to minimize the possibility of sample contamination
- The selected sampling method should be safe, convenient and efficient.

TABLE 2.1. SLUDGE FLOW MEASUREMENT DEVICES

Application	Measurement Means
Stabilized Sludge	Venturi Flow Tube Magnetic Meter Positive Displacement Pump
Thickener	Magnetic Meter Positive Displacement Pump
Dewatering	Belt press scales
Drying Composting Thermal Reduction	Bulk container or truck scales

TABLE 2.2. SLUDGE SAMPLING POINTS

Sludge Type	Sampling Point
Anaerobically Digested -	Sample from taps on the discharge side of positive displacement pumps.
Aerobically Digested -	Sample from taps on discharge lines from pumps. If batch digestion is used, sample directly from the digester. Two cautions are in order concerning this practice: (1) If aerated during sampling, air entrains in the sample. Volatile organic compounds may purge with escaping air. (2) When aeration is shut off, solids separate rapidly in well digested sludge.
Thickened Sludges -	Sample from taps on the discharge side of positive displacement pumps.

TABLE 2.2. SLUDGE SAMPLING POINTS
(continued)

Sludge Type	Sampling Point
Heat Treatment	Sample from taps on the discharge side of positive displacement pumps <u>after</u> decanting. Be careful when sampling heat treatment sludge because of: (1) High tendency for solids separation (2) High temperature of sample (frequently >60°C as sampled) can cause problems with certain sample containers due to cooling and subsequent contraction of entrained gases.
Dewatered, Dried, Composted, or Thermally Reduced various depths.	Sample from material collection conveyors and bulk containers. Sample from many locations within the sludge mass and at
Dewatered:	
Belt Filter Press, Centrifuge, Vacuum Filter Press	Sample from sludge discharge chute.
Sludge Press (plate and frame)	Sample from the storage bin; select four points within the storage bin, collect equal amount of sample from each point and combine.
Drying Beds	Divide bed into quarters, grab equal amounts of sample from the center of each quarter and combine to form a grab sample of the total bed. Each grab sample should include the entire depth of the sludge (down to the sand).
Compost piles	Sample directly from front-end loader as the sludge is being loaded into trucks to be hauled away.

Except for limitations on the use of automatic sampling devices, the actual sampling techniques for sludges are similar to those found in wastewater sampling. The following sections describe two important considerations for selecting appropriate sludge sampling methods: sampling equipment and proper sampling practices.

2.3.1 Sampling Equipment

In general, automatic sampling devices, which are widely used for wastewater streams, do not work well for sludge streams because of the solids content and viscosity of sludges. Automatic samplers which use pumps to draw samples up a suction tube cause solids separation if flow velocity in the suction and discharge tube is too low. This increases pump head requirements and limits the range of tubing diameter. A second problem which occurs in the use of automatic samplers is fouling of tubing and/or pump structure by sludge solids. This results in contamination of subsequent aliquots during composite sampling. Sludge particles may also plug the sample tube or pumping mechanism and interrupt sample collection. Therefore, it is preferable to sample liquid sludge streams manually, particularly if sample taps can be provided on pump discharge lines.

Sampling equipment must be made of materials which will not contaminate or react with the sludge. The best material choices are Teflon, glass, and stainless steel because they are relatively inert. When the cost of Teflon and stainless steel equipment prohibits or restricts their use, plastic, steel and/or aluminum may be substituted for most sampling activities. (If steel equipment is used, ensure that galvanized or zinc coated items are not used because these materials will readily release zinc into the sample.)

Graduated glass or plastic pitchers or cylinders are used to draw grabs for manually composted samples. Stainless steel pitchers are also commercially available, and are used to grab samples from taps and also can be affixed to lengths of conduit to sample from open channel flows. Only aluminum conduits should be used since most commercially available steel conduit is galvanized. In addition, only stainless steel clamps should be used to attach the sample container to the conduit.

2.3.2 Proper Sampling Practices

Listed below are practices that should be followed when sampling sludges:

- Clean all sampling equipment between each sample period to prevent cross-contamination. Cleaning consists of thorough washing with a laboratory detergent, thorough rinsing with tap water and then with at least three distilled water rinses.
- Sample aliquots should be composted directly into sample containers. Sample containers, preservation of sample and allowable holding time prior to analysis are discussed in Section 2.5.
- When collecting samples for oil and grease analysis, sample directly into the sample container since oil and grease tend to adhere to surfaces. Sample composites should be sent to the laboratory as a series of grab samples.
- Sample collection procedures should be adequately documented, as discussed in Section 2.7.
- When collecting samples for organic volatiles or semi-volatiles, carefully pour liquid sludge into container so as to avoid entrapping air within sample. Fill container to overflowing and screw on lid. Check air bubbles by turning container upside down and tapping lid. If air bubbles rise, open container and fill with additional sample. For sludge cake, care-fully pack sludge into container so as to avoid air spaces. Fill the container to overflowing and screw on lid.

- When collecting samples for dioxin/furan, fill the container to 4/5 full to enable expansion of samples when they are frozen.

- When collecting samples for pesticides/PCBs/herbicides, metals and nonconventionals, fill container to within 1/2 inch of the top to provide room for expansion should there be any gas production during sample shipment.

When sampling liquid sludges:

- To draw a fresh representative sludge sample from a tap:

  a) Allow sufficient time following pump start up to clear line of stagnant sludge, and

  b) Allow sludge to flow for several seconds from tap prior to sampling in order to flush out stagnant sludge and solids accumulated in the tap.

- Before drawing a sludge sample, rinse each piece of sampling equipment 3 times with sample to reduce the chance of contamination from the previous grab.

- To prevent solids separation in the sample, use glass, Teflon-coated stirring rods, or stainless steel spoons to mix the sample before splitting or transferring any portion of it to another container(s).

When sampling solid sludges:

- For either dewatered cakes, dried powder or compost product, combine equal amounts collected at various locations/depths for each grab sample to obtain a more representative sample.

  a) To produce a sample from multiple sample locations (e.g., two or more dewatering units), combine the grab samples from each location (equal amounts or weighted based on flow or solids flux data) in a plastic or stainless steel pail and thoroughly mix the sample (with a scoop or spoon), then transfer it to sample containers. This is not appropriate for volatile or microbial samples.

b) When sampling drying beds, divide each bed into quarters. From the center of each quarter, collect a single core sample through the entire depth of the sludge using a coring device. Usually a small amount of sand will be collected; avoid large amounts of sand. Combine and thoroughly mix in plastic or stainless steel pail and transfer to sample containers.

2.4 SAMPLE SIZE, SAMPLE TYPE, AND SAMPLING FREQUENCY

Sample Size

A proper sample is small enough to transport conveniently and handle carefully in the laboratory, but large enough to accurately represent the characteristics of the whole material. Minimum sample sizes required for accurate analysis are specified in each analytical method. Table 2.3 lists minimum sample sizes for some common analytical methods. For methods not listed here, consult an analytical methods reference or the laboratory for further guidance.

Sample Type

A grab sample collected at a particular time and location can represent the composition of the source only at that time and location. In the case of most sludges, single grab samples will adequately represent only the instantaneous composition of the material being sampled. The quality of a grab sample will be improved if it is comprised of several smaller samples taken over a period of a few minutes.

A composite sample gives a better reflection of the time- and location-weighted average concentrations that are found in the sludge flow stream. In most cases, the term "composite sample" refers to a mixture of grab samples collected at the same sampling point at different times. Although a 24-hour composite

TABLE 2.3

CONTAINERS, PRESERVATION, HOLDING TIMES, AND MINIMUM SAMPLE VOLUMES[1]

Parameter	Wide-mouthed Container	Preservative[2]	Maximum Holding Time[2]	Minimum Sample Volume[3]
Inorganic Compounds				
Asbestos	P,	None	None	2000 mL
Metals				
Chromium VI	P,G	Cool, 4°C	24 hours	300 mL
Mercury	P,G	HNO_3 to pH<2	28 days	500 mL
Metals except above	P,G	HNO_3 to pH<2	6 months	1000 mL
Organic Compounds				
Extractables (including phthalates, nitrosamines, nitroaromatics, isophorone, polynuclear aromatic HC, haloethers, chlorinated HC and TCDD)	G, teflon-lined cap P, for dioxin and furan only	Cool, 4°C 0.008% $Na_2S_2O_3$	7 days (u) 40 days (a)	1000 mL
Extractable (phenols)	G, teflon-lined cap	Cool, 4°C H2SO4 to pH<2 0.008% Na2S2O3	7 days (u) 40 days (a)	1000 mL
Purgeables (Halocarbons and Aromatics)	G, teflon lined septa	Cool 4°C 0.008% $Na_2S_2O_3$ 1:1HCl to pH 2	7 days (w/o) 14 days in darkness	>20 mL
Purgeables (Acrolein and Acrylonitrile)	G, teflon lined septa	Cool 4°C 0.008% $Na_2S_2O_3$ pH to 4 or 3	14 days	>20 mL

TABLE 2.3 (Continued)

CONTAINERS, PRESERVATION, HOLDING TIMES, AND MINIMUM SAMPLE VOLUMES[1]

Wide-mouthed Parameter	Container	Preservative[2]	Maximum Holding Time[2]	Minimum Sample Volume[3]
Pesticides & PCBs	G, teflon-lined septa	Cool 4°C 0.008% $Na_2S_2O_3$	7 days (u) 40 days (a)	1000 mL

(1) 40 CFR Part 136

(2) Preservatives should be added to sampling containers prior to actual sampling episodes. Holding times commence upon addition of sample to sampling container. Shipping of pre-preserved containers to the sample sites may be regulated under DOT hazardous materials regulations. Shipping of preserved samples to the laboratory is generally not regulated as a hazardous material.

(3) Varies with analytical method. Consult 40 CFR Part 136.

P = Plastic (Polyethylene)

G = Glass (Non-etched Pyrex)

(a) After extraction

(u) Before extraction

(w/o) Without preservatives

sample (consisting of a number of time- or flow-weighted grab samples) is more representative than a grab sample, it can give a picture of only one day's sludge quality. Historical data is necessary to truly represent the sludge quality. A composite for volatile components analysis is produced in the lab from grab samples collected in the field.

Sampling Frequency

As sludge quality is directly related to wastewater influent quality (which can vary from day to day and hour to hour), a POTW should sample and analyze its sludge frequently to obtain representative data. Collection of representative sludge data is crucial because the permitting authority will use the resultant analytical data to establish permit monitoring parameters and frequencies, and thereafter, to assess compliance with the permit and to ascertain if there is a potential for adverse environmental impacts. POTW operators should be aware that EPA's "Strategy for Interim Implementation in Permits Issued to POTWs" (draft June 1988) to be finalized during the fourth quarter of 1989) sets forth minimum recommended monitoring frequencies to be included in the NPDES permit when it is reissued. The Interim Strategy is scheduled to be finalized in the summer of 1989. The NPDES permit writer may decide based on his/her best professional judgment (BPJ) that more frequent monitoring is needed. The sampling frequency will be set out in the POTW's permit.

To the extent practicable, the POTW should have a sludge sampling program which adequately addresses random and cyclic variation within the system and the potential for human exposure to sludge once it is disposed of or used.

- Anticipated cyclical variation in pollutant loadings - although they are difficult to accurately predict, anticipated cycles include daily industrial production

cycles, weekly industrial production cycles, and other known or suspected production cycles, particularly those associated with intermittent batch discharges by significant industries. Longer-term production cycles, including seasonal and annual/multi-year production cycles (e.g., business cycles), do not need to be considered in determining monitoring frequency unless they are known to affect short-term variation in sludge quality.

- **Risk of environmental exposures** - As the risk of environmental exposure from sludge use/disposal increases, a POTW should increase its sampling frequency to provide better information about potential variation in sludge quality. For example, a sludge that is applied to food-chain croplands should be sampled more frequently than sludge that is disposed of in a landfill that has an impermeable liner and a groundwater monitoring system.

Other factors that should be considered in determining sampling frequency include:

- **Size** - As influent flow increases, day-to-day sludge variability increases, as does outflow volume. Thus, where high volumes exist, the risk of adverse exposure is higher. Since variability and potential impact are major considerations, many sampling programs are based on size alone (e.g. 40 CFR Part 503 proposed rule). Size is also an easy factor to measure.

- **Percentage of industrial flow** - While sludge quality variability is directly related to the individual characteristics of each POTW, POTWs with little or no commercial/industrial contributors in the system can expect relatively small variation in sludge quality. POTWs with significant industrial contributions can expect to have monthly, weekly and even daily variation in sludge quality.

- **Treatment plant characteristics** - As either detention time or mixing increases within a treatment plant, sampling frequency can be reduced since treatment processes will effectively composite sludge to a greater degree. For example, high rate digestion and storage/blending facilities will provide mechanical mixing of sludge. Other plant technologie , such as anaerobic digestion, aerobic digestion and storage,

provide longer sludge detention times, enabling greater mixing through physical processes such as diffusion, convection, etc. For combined sewer systems, a sampling strategy may be designed to monitor the effects of storm events on sludge quality.

Another consideration is the type(s) of information a POTW wishes to collect. If, for example, a POTW desires to measure daily variation over a typical week, the POTW may collect and analyze seven or more 24-hour composite samples for the pollutant. Similarly, if a POTW wishes to measure variation within a single day, the POTW may collect and analyze several grab samples taken at different times during the day.

2.5 SAMPLE PREPARATION AND PRESERVATION

There is the potential for errors of varying severity to be introduced during sample collection and storage which affect analytical determinations. To avoid potential errors and maintain sample integrity, POTW operators should carefully consider the following:

- Sample Container Material
- Sample Container Preparation
- Sample Preservation
- Holding Time Prior to Analysis.

Table 2.3 lists recommended container materials, preservatives, holding times, and minimum sample volumes for the analysis of sludges. For method-specific details concerning all facets of sample preparation and preservation, consult the references cited in 40 CFR Part 136, "Guidelines for Establishing Test Procedures for the Analysis of Pollutants."

2.5.1 Sample Container Material

The requirements for sample containers are method-specific, but containers are usually made of Teflon, glass or polyethylene. Sample containers should be wide-mouthed for sludge sampling, particularly for solids (cake) sampling. Teflon containers are typically supplied with Teflon caps. Glass containers frequently are supplied with caps which can cause sample contamination (phenol, phthalate compounds). For organic parameters, these glass container caps should be fitted with Teflon liners; aluminum liners could be used but they must be fitted precisely within the circumference of the cap to prevent tearing and possible sample leakage.

2.5.2 Sample Container Preparation

Proper sample container preparation is necessary to prevent contamination of the sample by material left from the container manufacturing process or that has otherwise been introduced into the unused sample containers. All containers should be washed with a good quality laboratory detergent, thoroughly rinsed with tap water, and then rinsed at least 3 times with distilled water prior to air drying. Additional container preparations for analysis of particular parameters are described below:

- **Extractable Organics** - Use glass containers with Teflon-lined caps only. Wash containers as above and rinse with solvent (typically methylene chloride); air-dry.
- **Volatile Organics** - Prepare containers by washing and rinsing as described above, and then bake both vials and septums at 105°C until dry. Cool in an organic-free atmosphere.
- **Metals** - Wash and rinse as described above. Then rinse with dilute acid (1 part deionized, distilled water to 1 part nitric acid (HNO_3)), followed by two rinses with deionized, distilled water.

2.5.3 Sample Preservation

Table 2.3 presents U.S. EPA's recommended preservation protocols. These protocols are primarily intended for effluent monitoring; however, they are generally applicable to liquid sludge sampling.

The following are specific recommendations regarding sample preservation:

- In instances where it is desirable to split one composite sample into several fractions, each having incompatible preservation requirements, it is acceptable to chill the entire sample to 4°C during compositing. Following the sample period, the composite is then cautiously mixed and split into various fractions, each of which is appropriately preserved. This does not apply to samples for analysis of volatile, semivolatile or microbial contaminants.

- If processing of microbial samples cannot occur within one hour of collection, iced coolers should be used for storage during transport to the lab. Samples should be held below 10°C during the maximum transport time of 6 hours. Note: these samples must be immediately refrigerated and processed at the lab within 2 hours of receipt.

- Whenever possible, sample containers should be pre-preserved. Thus, grab samples are preserved upon sampling and composite samples are preserved during compositing. This is not appropriate, however, when sampling for metals or pathogens.

- In general, all samples should be chilled (4°C) during compositing and holding.

- For solid sludge samples (cake), adding chemical preservative is generally not useful since the preservative usually does not penetrate the sludge matrix. Preservation consists of chilling to 4°C.

- When sampling and holding sludges, particularly biologically active sludges, gas production in the sealed container may cause an explosion unless the pressure is periodically released. This should not be

done however if volatile or semivolatile pollutants are to be analyzed.

2.5.4 Holding Time Prior to Analysis

Table 2.3 lists the maximum holding times for various pollutant samples. Table 2.4 lists some potential interferences that may affect samples during shipping and storage. There are many more interferences associated with particular analytical methods, which are discussed further in chapter 3 as well as in the particular methodology.

2.6 PACKAGING AND SHIPPING

When analysis will be performed away from the sampling locale, samples must be packaged and transported.

2.6.1 Packaging

Sample containers must be packaged in order to protect them and to reduce the risk of leakage. Containers should be held upright and cushioned from shock. In addition, sufficient insulation and/or artificial refrigerant ("blue ice") should be provided to maintain a sample temperature of 4°C for the duration of transportation.

2.6.2 Transportation Regulations

The following guidelines control the shipment of wastewater and sludge samples:

- Unpreserved normal (i.e., not heavily contaminated) environmental samples are not regulated under DOT Hazardous Material Regulations. These samples may be shipped following the packaging guidelines in Section 2.6.1, and using a commercial carrier, etc. To assure proper sample temperature, transit time should be held to less than 24 hours.

TABLE 2.4

POTENTIAL INTERFERENCES ASSOCIATED WITH
SAMPLE SHIPPING AND STORAGE

Parameter	Interferences[1]	Prevention
Acidity	Carbon dioxide loss	Fill container completely
Ammonia	Chlorine Volatilization	Sodium thiosulfate Fill container completely
Cyanide	Sulfides	Cadmium nitrate, tetrahydrate
Chromium VI	Reducing agents	Minimize holding time
Phenols	Hydrogen sulfide, Sulfur dioxide Oxidizing agents	Aerate Ferrous sulfate
Silica	---	Avoid freezing
Sulfide	Aeration, agitation	Fill container completely
Sulfite	Aeration, agitation	Fill container completely
Organic Chemicals	Photodegradation	Use brown glass container

1 Other than those addressed by protocols shown in Table 2.3

- When environmental samples are preserved as recommended (see Table 2.5), they may be shipped as non-hazardous samples.

The guidelines above assume no material is present in the samples at concentrations which would result in a "hazardous" DOT rating. Should hazardous material (as defined by DOT) be present, DOT regulations concerning packaging, transportation and labeling must be followed (see 49 CFR Parts 172, 173 and 178). A material is considered hazardous by DOT if it fails one of the four characteristic tests of: corrosivity, ignitability, reactivity and EP Toxicity [see "Test Methods for Evaluating Solid Waste, SW 846, 1986 for exact methods]. Municipal sewage sludges labeled as hazardous are usually from failed EP Toxicity tests and occasionally from reactivity tests.

2.7 DOCUMENTATION

Adequate documentation of sludge sampling activities (1) is important for general program quality assurance/quality control, and (2) is required by most monitoring regulations. Proper sampling activity documentation includes proper sample labeling, chain-of-custody procedures and a log book of sampling activities. The number of people in the chain of custody should be kept to a minimum to limit the possibility of contamination and to increase accountability.

2.7.1 Sample Labeling

It is important that each sample label include the following information (items in bold text are minimum elements):

- Sampling Organization Name
- **Facility Name (being sampled)**
- Bottle Number (specific to container

TABLE 2.5

STANDARD PRESERVATIVES LISTED IN THE HAZARDOUS MATERIALS TABLE (49 CFR 172.101) USED BY EPA FOR PRESERVATION OF WATER, EFFLUENT, BIOLOGICAL, SEDIMENT, AND SLUDGE SAMPLES

Sample Type/ Parameter	Preservative	pH Recommendation	Quantity of Preservative Added Per Liter*	WT. % of Preservative
Organic Carbon	Hydrochloric acid	<2 ->1	2 ml of 1:1	0.04%
Nitrogen Species	Mercuric chloride	N.A.	40 mg	0.004%
Metals, Hardness**	Nitric acid	<2 - >1	5 ml of Conc. (70%)	0.35%
Nitrogen Species COD, Oil & Grease, P (hydrolyzable) Organic Carbon	Sulfuric acid	<2 - >1	2 ml of 36N	0.35%
Cyanides	Sodium hydroxide	>12 - <13	2 ml of 10N	0.080%
Phenolics	Ortho-phosphoric acid	<4 - >2	to yield desired pH	
Biological - Fish & Shellfish Tissue***	Freezing $0^{o}C$ (Dry Ice)	N.A.	N.A.	N.A.

* Sample dilution must be avoided. The volume of washings must be minimized and any dilution that does occur must be documented and the data corrected for the dilution.

** The sample may be initially preserved by cooling and immediately shipping it to the laboratory. Upon receipt in the laboratory, the sample must be acidified with conc. HNO_3 to pH<2. At time of analysis, sample container should be thoroughly rinsed with 1:1HNO_3; washings should be added to sample.

*** Dry ice is classified as an ORM-A hazard by DOT. There is no labeling requirement for samples preserved with dry ice, but each package must be plainly and durably marked on at least one side or edge with the designation ORM-A. Advance arrangements which must be met to ship dry ice are found in DOT regulation 49 CFR 173.616.

- Sample Number (specific to sampling event i.e. location)
- Type of sample, i.e., grab, 24 hour composite, etc.
- Date, Time (24 hour time is preferable, i.e., 1600 vs. 4:00 p.m.)
- Sample Location
- Preservatives
- Analytical Parameter(s)
- Collector
- Special Conditions or Remarks.

Labels and ink should be waterproof. Fix labels to containers with clear waterproof tape. Tape completely around container and over label to prevent accidental label loss or ink smear during shipping and handling.

2.7.2 Chain-of-Custody

Each sample shipment requires a chain-of-custody record. A chain-of-custody document provides a record of sample transfer from person to person. This document helps protect the integrity of the sample by ensuring that only authorized persons have custody of the sample. In addition, the chain-of-custody procedure ensures an enforceable record of sample transfer which is necessary if the sample results are to be used in a judicial proceeding alleging violations of sludge standards. This document shall record each sample's collection and handling history from time of collection until analysis as well as the information listed on each sample bottle. All personnel handling the sample shall sign, date and note the time of day on the chain-of-custody document. A sample chain-of-custody document is provided in Appendix A.

2.7.3 Sampling Log Book

All sampling activities should also be documented in a bound log book. This book duplicates all information recommended for the chain-of-custody document above, and notes all relevant observations regarding sample stream conditions.

2.8 SAFETY CONSIDERATIONS

Safety is important in sludge sampling, especially since many sampling points preclude direct collection of grab samples. Several safety considerations are noteworthy given the potential health-related effects of sewage and sludge, and the hazards associated with treatment plant equipment (water, electricity, moving components, etc.).

Personal hygiene is important for all personnel involved in sludge sampling efforts. Sludge presents a unique health hazard, not only because of the potential presence of toxic substances, but also because of the abundance of pathogens (bacteria, viruses and worms). As a precautionary measure, inoculations are recommended for all personnel who have direct contact with sludge (as well as any wastewater) samples. As a minimum, inoculation should include diseases such as typhoid and tetanus. Avoidance of direct sludge contact is preferred and is possible if proper precautions are taken. Wear rubber or latex gloves at all times, especially while collecting or handling samples, and use waterproof garments when the risk of splashing exists. Wash any cuts or scrapes thoroughly and treat immediately.

Gas production from biologically active sludge samples may cause pressure build up, especially if the samples are not stored at 4°C as recommended in Table 2.3. Treating samples with the appropriate preservatives (e.g., acids for metals samples) as

well as refrigeration will significantly suppress biological activity and therefore gas evolution. However, except for volatile and semi-volatile analysis samples, pressure may need to be periodically released to prevent explosions of the sealed sampling containers. The field control sample should also be vented to expose it to the same potential contaminants.

There are several universal safety precautions that are applicable to sludge sampling as well. When sampling sludge in confined areas, particularly around anaerobic digesters, dangerous gases may be present. These gases may include either explosive vapors (methane), poisonous mixtures (including hydrogen sulfide), or oxygen-deprived atmospheres (carbon dioxide). Explosive vapors require care to avoid sparks and possible ignition. These situations necessitate adequately ventilated equipment, gas detection meters and backup breathing apparatus. Exercise care around open pits or uncovered holes. Proper lighting increases the visibility of such hazards. Loose or dangling garments (ties, scarves, etc.) should not be worn around equipment with moving parts, especially pumps. Exercise extra awareness around pumps controlled by intermittent timers. Finally, be very careful when sampling high pressure sludge lines or lines containing high temperature, thermally-conditioned sludges (i.e., Zimpro or Porteus) in order to avoid injury by either high pressure streams or burns.

3. ANALYTICAL PROCEDURES

Sewage sludge is compositionally diverse, rich in organic matter, and highly variable in physical and chemical properties. Sewage sludge analysis is difficult because of the inherent complexity of sludge matrices. Matrix complexity often results in significant analytical interference which can lead to poor analytical accuracy and precision with a resultant loss of data reliability. For example, matrix interference, which is exacerbated in sludges, can both mask the identity of analytes by suppressing instrumental response, or falsely contribute to a positive response.

Variations in the physical and chemical properties of sewage sludge often make it difficult to obtain samples which represent the material as a whole. The diversity of sludge characteristics, coupled with the heterogeneous nature of sludges, presents a considerable challenge to precise and accurate determinations of trace levels of pollutants in sludges. Often sludge samples must be diluted to attain analytical results. A tenfold sample dilution means a tenfold increase in the detection limit (e.g., 1 ppm to 10 ppm). This increases the complexity of attaining accurate, precise data.

The following sections provide a summary of the analytical techniques available for characterization of the sewage sludge and soil constituents considered important in the selection of use or disposal options. Analytical techniques for conventional pollutants, inorganics, priority pollutant metals, priority pollutant organics, and pathogenic organisms are discussed.

3.1 CONVENTIONAL AND INORGANIC POLLUTANT PARAMETERS

Conventional pollutant parameters have historically been the focal point of sewage sludge analyses. The parameters normally associated with this group include total suspended solids, pH, oil and grease, BOD and fecal coliform. Inorganics, which have also been of concern, include phosphorus species, nitrogen species, phenolics, and total cyanide. As Table 3.1 indicates, the analytical protocols commonly employed for these analyses are adaptations of gravimetric or colorimetric techniques developed for aqueous samples.

Existing federal regulations (40 CFR Part 257) require POTWs that apply sludge to food-chain croplands to measure the pH of the sludge-soil mixture and background soil cation exchange capacity (CEC). Soil pH should be measured using a 1:1 solution of sludge-soil mixture and deionized water (see Table 3.1). For distinctly acid soils, CEC should be measured using the summation method (see Table 3.1). For neutral, saline, or calcareous soils, the sodium acetate method should be used (see Table 3.1).

Another inorganic of more recent concern is asbestos. Asbestos is a generic term which refers to naturally occurring, commercially useful fibrous silicate mineral. There are two types. Chrysotile, which comprises 93 percent of the current asbestos production, is a hydrated magnesium silicate which exhibits a much higher cancer risk for textile workers. Amphibole, which occurs in five forms, crocidolite, amosite, actinolite, tremolite and anthrophyllite, is a hydrated silica associated with various lung carcinogenic trace metals (nickel, chromium, aluminum and iron). Crocidolite poses the greatest health risk of all asbestos types and is the riskiest to miners and millers.

TABLE 3.1

ANALYTICAL TECHNIQUES FOR CONVENTIONAL AND INORGANIC POLLUTANTS IN SLUDGE

Parameter	Preparation Techniques	Analytical Technique (a)	QA/QC (b)	Aqueous Detection Limit (mg/l)	Comments	Method
Phos-phorous (Ortho & Total)	Acidic Digestion Turbid samples must be filtered after digestion	C	B St Sp	0.001	- High iron concentration can cause precipitation and loss of phosphorous - Turbidity interference - 24 hr-holding time	(1) 365.3
Total Kjeldahl Nitrogen	H_2SO_4 digestion	C	B St	0.05	- Digestion solution 2 times for sludge - 24 hr-holding time - Fe + Cr catalyze; Cu inhibits reaction	(1) 351.2, 3
Ammonia	Colorimetric reaction	C ISE	Sp	0.05	- Hg can complex with NH_4 - Filter sample - Distillation required prior to analysis	(1) 350.1 350.2, 3 (2) 417A, B, D, E, G
Nitrate	Reaction to brucine sulfate or Nitrate-nitrite N minus Nitrite N	C		0.1	- Dissolved organic matter	(1) 352.1 (3) 9200
Nitrate-Nitrite	Hydrazine or Cd reduction	C		0.05	- Filter sample for Cd - Strong oxidizing or reducing agents - Suspended matter in reduction column - Samples which contain high conc. of metals or organics	(1) 353.1, or 353.2
Nitrite	Diazotization	S		0.5		(1) 354.1 (2) 419

TABLE 3.1 (Continued)

ANALYTICAL TECHNIQUES FOR CONVENTIONAL AND INORGANIC POLLUTANTS IN SLUDGE

Parameter	Preparation Techniques	Analytical Technique (a)	QA/QC (b)	Aqueous Detection Limit (mg/l)	Comments	Method
Cyanide	CN converted to HCN by reflux-distillation	C	B St Sp	0.02	- Fatty acids and sulfides interfere	(1) 335.2 (3) 9010, or 9012
Phenolics	Distillation and extraction	C	B St Sp	0.002	- 24 hr-holding time - Sulphur compounds and oxidizing agents interfere	(1) 420.1 (2) 510A or C (3) 9065, 9066, 9067
Total Organic Carbon	Inorganic carbon removal	Catalytic combustion & dispersive IR	B St Sp	1.0	- Carbonate + bicarbonate interfere	(1) 415.1 (2) 505A (3) 9060
Chemical Oxygen Demand	Oxidation to potassium dichromate and HCl	Titration	B St Sp	5.0	- Possible loss of volatiles - Chloride oxidation could be an interference	(1) 410.1, (Block digestion) (2) 1508 A or B
Biochemical Oxygen Demand	Incubation	Measurement of reduction in DO	B St Sp	2.0	- 5-day incubator	(1) 405.1 (2) 507
Oil and Grease	Solvent extraction	G	B Sp	5.0		(1) 413.1,2 (2) 503A, D (3) 9070, or 9071
pH	Solution in suspension with fluid	ISE	St	---	- Interference from solids and oily residues	(1) 150.1 (3) 9040 (4) p. 900, 57-4
CEC	$BaCl_2$/treatment (acid exchange) (base exchange)	T C	None cited in references		- Acid soils	(3) 9080 (4) Ibid.

TABLE 3.1 (Continued)

ANALYTICAL TECHNIQUES FOR CONVENTIONAL AND INORGANIC POLLUTANTS IN SLUDGE

Parameter	Preparation Techniques	Analytical Technique (a)	QA/QC (b)	Aqueous Detection Limit (mg/l)	Comments	Method
CEC	Na acetate sludge sol'n, isopropanol wash, NH_4 acetate exchange	Emission or absorption AAS	One B per batch	No data available	- Neutral, saline, or calcareous soils	(3) 9081 (4) p. 891
Solids	Filtration	Gravimetric	B	4.0-10.0		(1) 160.1 or .5
% Solids	Evaporation	Gravimetric	B	N/A		(1) 160.3 (2) 209A

(1) Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983.

(2) Standard Methods for the Examination of Water and Wastewater, 16th Edition, Mary Ann Franson, managing ed., American Public Health Association, Washington, DC, 1985.

(3) Test Methods for Evaluating Solid Waste, Third Edition, (SW-846), EPA, September 1986.

(4) "Methods of Soil Analysis", Agronomy Monograph Number 9, C.A. Black, ed., American Society of Agronomy, Madison, Wisconsin, 1965.

(a) C Colorimetric; DO - Dissolved Oxygen; G - Gravimetric; IR - Infrared; ISE - Ion Selective Electrode; S - Spectrophotometric; T - Titration

(b) B - Blank(s); St - Standards; Sp - Spike(s)

In certain cases, such as when large scale asbestos removal is/will occur during the permit term or in municipalities where asbestos industries are located, the permit writer or the permittee may feel that sampling the sewage sludge for asbestos is warranted. Consult Table 2.4 for the appropriate sample sizes, containers, preservatives and holding times. Unless sample preparation will be within 48 hours, the sample should be refrigerated or stored in the dark to prevent bacterial growth.

Although there are tests which differentiate between the various asbestos types, current research does not associate health risk with specific types. The risk from asbestos is directly proportional to the concentration of airborne respirable particles. Thus current recommended analytical detection methods count fibers per area. Respirable particles are those with a diameter (length in this case) of less than 2 microns, which can only be detected using transmission electron microscopy (TEM). The polarized light microscopy (PLM) method does not detect respirable particles.

3.2 METALS

There are several analytical techniques used for the determination of metals in sewage sludge, with variations in both the sample preparation and analysis steps. A discussion of these techniques follows.

3.2.1 Analyte Isolation/Preparation Overview

Two approaches are currently used to evaluate the concentrations of metal contaminants in sludges. The most frequently used approach involves determination of the total metal content or other materials of interest, without regard to chemical form. The analytical techniques for such determinations

are designed to solubilize all of the metal species (bound to organic particulates and mineralogically bound). In the other approach, often referred to as the "leachate approach," the proportion of the total contaminant loading which will become available or mobilized under environmental conditions is determined. Thus, leachate techniques are designed to mimic a given environmental scenario. With either approach, the complexity and variability of sludge matrices has made the development of sample preparation techniques a great analytical challenge.

The two primary steps for sample preparation of metals in sewage sludge are (1) dissolution of the sample portion containing the metal components of interest, and (2) elimination of inorganic and organic interferences. The preparation procedure must be capable of effectively liberating the analytes from the solid constituents, solubilizing the elemental species, homogenizing the sample phase(s) of interest, as well as completely oxidizing the associated organics. Sludge matrices are challenging in this regard because of the high organic levels and solids loadings characteristics.

All state-of-the-art sample preparation procedures for <u>total</u> metal determinations depend on acid-mediated digestions and chemical or physical oxidation techniques. The approach involves the use of strong acid and elevated temperature digestion procedures in combination with chemical or physical oxidants. The modifications which have been used include variations in acids, oxidation reagents, physical oxidation techniques, reaction conditions, and/or the sequence in which components are employed. Acids used most frequently include nitric acid (HNO_3), hydrofluoric acid (HF), hydrochloric acid (HCL), and perchloric acid ($HCLO_4$); while hydrogen peroxide and perchloric acid are

common oxidizing reagents. High temperature (550°0C) combustion and low temperature plasma ashing (LTPA) have been used successfully as physical oxidants. Closed system digestion procedures are also used successfully.

Two closely related techniques to estimate the amount of inorganic and organic contaminants which may be leached from the sludge after disposal in landfills or surface impoundments are the Extraction Procedure protocol and the Toxicity Characteristic Leachate Procedure. In both procedures the sludge is maintained in an aqueous slurry under a given set of conditions, after which contaminant levels are measured on the filtered aqueous media. The Extraction Procedure (EP) test developed by EPA (in response to RCRA legislation) to evaluate the impact of landfill waste disposal practices on subsurface and surface waters (40 CFR Part 261 Appendix II) evaluates criteria for 8 metals and 6 pesticides. The proposed Toxicity Characteristic Leaching Procedure (TCLP) 51 Federal Register 21648 is expected to be promulgated in August/September of 1989. The TCLP test which evaluates the same 8 metals and 6 pesticides and an additional 38 compounds will replace the EP test after promulgation.

3.2.2 Analytical Techniques for Metals

3.2.2.1 Sample Preparation/Digestion

Table 3.2 shows the sample preparation/digestion technique recommended by the USEPA. Method 3050 (SW-846, 3rd ed.) is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectroscopy (FLAA and GFAA, respectively) or by inductively coupled argon plasma spectroscopy (ICAP). Samples prepared by this method may be analyzed by ICAP for all the metals listed below, or by FLAA or GFAA as indicated:

FLAA		GFAA	
Aluminum	Lead	Arsenic	Manganese
Antimony	Magnesium	Beryllium	Nickel
Barium	Manganese	Cadmium	Selenium
Beryllium	Nickel	Chromium	Silver
Cadmium	Potassium	Cobalt	Zinc
Calcium	Silver	Copper	Thallium
Chromium	Sodium	Iron	Vanadium
Cobalt	Thallium	Lead	
Copper	Tin		
Iron	Vanadium		
	Zinc		

Method 3050 prepares samples for analysis of total metals (except mercury, silver and antimony) determination through vigorous digestion in nitric acid and hydrogen peroxide followed by dilution with either nitric or hydrochloric acid. This method is not appropriate for mercury, silver, and antimony because of potential for volatilization. For the digestion and analysis procedures for mercury, silver and antimony, see section 3.2.2.2.

3.2.2.2 Analytical Detection Methods

Metals should be analyzed using either Atomic Absorption Spectrometry (AAS) or Inductively Coupled Argon Plasma (ICAP). The following discussion generally describes both methods.

Inductively Coupled Argon Plasma is a form of optical emission spectroscopy which uses an argon plasma to excite ions and atoms. This process causes the ions and atoms to emit light which is measured as a signal. The signal response is proportional to concentration level, and each element emits a uniquely characteristic light. This technique poses several advantages. A linear relationship between concentration and signal response can be expected over 4-6 orders of magnitude. Detection limits are low (although not as low as AAS, and not strongly inhibited by matrix variation); costs are moderate since

TABLE 3.2.

RECOMMENDED PREPARATION TECHNIQUE
FOR ELEMENTAL ANALYSIS OF SLUDGE SAMPLES

METHOD 3050[1]

1) Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh to the nearest 0.01 g and transfer to a conical beaker a 1.00- to 2.00-g portion of sample.

2) Add 10 ml of 1:1 HNO_3, mix the slurry, and cover with a watch glass. Heat the sample to 95°C and reflux for 10 to 15 min without boiling. Allow the sample to cool, add 5 ml of concentrated HNO_3, replace the watch glass, and reflux for 30 min. Repeat this last step to ensure complete oxidation. Using a ribbed watch glass, allow the solution to evaporate to 5 ml without boiling, while maintaining a layer of solution over the bottom of the beaker.

3) After Step 2 has been completed and the sample has cooled, add 2 ml of Type II water and 3 ml of 30% H_2O_2. Cover the beaker with a watch glass and return the covered beaker to the hot plate for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the beaker.

4) Continue to add 30% H_2O_2 in 1-ml aliquots while warming until the effervescence is minimal or until the general sample appearance is unchanged.
NOTE: Do not add more than a total of 10 ml 30% H_2O_2.

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(1) USEPA "TEST METHODS FOR EVALUATING SOLID WASTE: VOLUME 1A" SW-846 3rd EDITION, NOVEMBER 1986. CHAPTER 3, PP. 3050-1,5.

many elements may be determined at once; and analysis time is fairly rapid. The primary drawbacks are: matrix interferences (as with all analyses); the fact that solid samples cannot be analyzed directly as in AAS; and the high cost of purchasing ICAP instruments (more than $100,000).

The basic principle behind atomic absorption spectroscopy is the opposite of the emission method, ICAP. In AAS, the analyte (metal) is dissociated into atoms in a flame or furnace, and passed through a light beam from the reference source. This reference source emits a beam of the characteristic atomic spectrum of the analyte. The analyte in the sample will absorb this energy thus decreasing the original signal to the detector from the reference beam. Since absorption is directly proportional to concentration, the analyte concentration can be determined. Selection of a specific wavelength which corresponds to one of the more intense characteristic line of the analyte's spectra allows for high element specificity. For this reason, AAS is more responsive than ICAP to lower concentrations of metals in sludge. However, this very precise nature of AAS is also the cause of its major drawback: only one elemental determination per sample is possible at a time. Thus, the total analysis time of AAS is significantly greater than that of ICAP when many metals are present in the sample.

In sewage sludge applications, it is important to realize that both of these analytical techniques are reliable tools and neither offers a significant technical advantage over the other. However, ICAP's capability to simultaneously analyze multiple elements is a tremendous advantage in terms of sample throughput and labor savings, which may outweigh the noted limitations. For sludge applications, EPA recommends either method and leaves the

final decision to individual POTWs. Table 3.3 summarizes the relative advantages and disadvantages of ICAP and AAS.

TABLE 3.3

COMPARISON SUMMARY OF ICAP AND AAS

	ICAP	AAS
Cost for Instrument	-	+
Cost per Sample	+	-
Detection Limits	-	+
Precision	+	+
Linear Working Range	-	-
Sensitivity	-	+-
Number of Elements/Sample	-	-
Analysis Time	+	-
Spectral Interference	-	+
Matrix Interference	-	-

\- disadvantage
\+ advantage
++ extra advantage

ICAP Method 6010

EPA recommends Method 6010 for the determination of metals in solution by Inductively Coupled Argon Plasma atomic emission spectroscopy (ICAP). This method can be found in the USEPA manual "Test Methods for Evaluating Solid Waste," (SW-846, Nov. 1986, 3rd Ed., Vol 1A, pp. 6010-1,7). The method is applicable to a large number of metals and wastes. All matrices, including ground water, aqueous samples, EP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis. EPA recommends digestion Method 3050 (SW-846, 3rd Ed. - see Section 3.2.2.1).

Elements for which Method 6010 is applicable are listed in Table 3.4. Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and model of spectrometer. The data shown in Table 3.4 provide concentration ranges for clean (interference-free) aqueous samples. Due to matrix interferences, the detection limits in typical sludge samples will be somewhat higher. Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

Atomic Absorption Methods

EPA recommends use of the methods listed in the manual "Test Methods for Evaluating Solid Waste" (SW-846, Nov. 1986, 3rd Ed., Vol 1A) for the determination of metals in solution by atomic absorption spectroscopy. A complete set of procedures for each metal-specific method may be found on pages 7000-1 to 7950-3. These methods are simple, rapid, and applicable to a large number of metals in drinking, surface, and saline waters as well as domestic and industrial wastes. Ground water, aqueous samples other than drinking water, EP extracts, industrial wastes, soils, sludges, sediments, and other wastes require digestion prior to analysis. EPA recommends digestion Method 3050 (SW-846, 3rd Ed. - see section 3.2.2.1).

Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and models of atomic absorption spectrometers. The data shown in Table 3.5 provide some indication of the detection limits obtainable by direct aspiration and by furnace techniques. Due to the matrix

[1] For drinking water and other non-sludge applications, priority pollutant scans may require very low contaminant detection levels. Therefore, there may be no choice except to rely on the lower detection limit capability of graphite furnace AAS. This, in turn, will determine the digestion method used.

TABLE 3.4

RECOMMENDED INDUCTIVELY COUPLED WAVELENGTHS
AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Element	Wavelength[a] (nm)	Wastewater Estimated Detection Limit[b] (ug/L)	EMSL's Best SLUDGE Detection Limit[c] (ug/L)	EMSL's Estimate of Routine SLUDGE Limit (ug/L)
Aluminum	308.215	45	--	--
Antimony	206.833	32	--	--
Arsenic	193.696	53	--	--
Barium	455.403	2	--	--
Beryllium	313.042	0.3	--	--
Boron	249.773	5	--	--
Cadmium	226.502	4	1	5
Calcium	317.933	10	--	--
Chromium	267.716	7	--	--
Cobalt	228.616	7	--	--
Copper	324.754	6	5	10
Iron	259.940	7	--	--
Lead	220.353	42	20	50
Magnesium	279.079	30	--	--
Manganese	257.610	2	--	--
Molybdenum	202.030	8	10	30
Nickel	231.604	15	--	--
Potassium	766.491	See note d	--	--

TABLE 3.4 (cont.)

RECOMMENDED INDUCTIVELY COUPLED WAVELENGTHS
AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Element	Wavelength[a] (nm)	Wastewater Estimated Detection Limit[b] (ug/L)	EMSL's Best SLUDGE Detection Limit[c] (ug/L)	EMSL's Estimate of Routine SLUDGE Limit (ug/L)
Selenium	196.026	75	75	100
Silicon	288.158	58	--	--
Silver	328.068	7	--	--
Sodium	588.995	29	--	--
Thallium	190.864	40	100	150
Vanadium	292.402	8	--	--
Zinc	213.856	2	5	15

Reference: Test Methods for Evaluating Solid Waste: SW-846.

a The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference. In time, other elements may be added as more information becomes available and as required.

b The estimated instrumental detection limits are shown. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

c EPA's Environmental Monitoring Support Laboratory detection limit ranges.

d Highly dependent on operating conditions and plasma position.

TABLE 3.5

ATOMIC ABSORPTION FLAME AND FURNACE INSTRUMENTAL DETECTION AND SENSITIVITY LIMITS FOR WASTEWATER SAMPLES

Metal	Direct Aspiration Detection Limit (mg/L)	Direct Aspiration Sensitivity (mg/L)	Furnace Procedure[a,c] Detection Limit (ug/L)
Aluminum	0.1	1	--
Antimony	0.2	0.5	3
Arsenic[b]	0.002	--	1
Barium(p)	0.1	0.4	--
Beryllium	0.005	0.025	0.2
Cadmium	0.005	0.025	0.1
Calcium	0.01	0.08	--
Chromium	0.05	0.25	1
Cobalt	0.05	0.2	1
Copper	0.02	0.1	--
Iron	0.03	0.12	--
Lead	0.1	0.5	1
Magnesium	0.001	0.007	--
Manganese	0.01	0.05	--
Mercury[d]	0.0002	--	--
Molybdenum(p)	0.1	0.4	1
Nickel(p)	0.04	0.15	--
Potassium	0.01	0.04	--
Selenium[b]	0.002	--	2
Silver	0.01	0.06	--
Sodium	0.002	0.015	--
Thallium	0.1	0.5	1
Tin		0.8	4--
Vanadium(p)	0.2	0.8	4
Zinc		0.005	0.02--

Reference: Test Methods for Evaluating Solid Waste: SW-846.

NOTE: The symbol (p) indicates the use of pyrolytic graphite with the furnace procedure.

a For furnace sensitivity values, consult instrument operating manual.

b Gaseous hydride method.

c The listed furnace values are those expected when using a 20-uL injection and normal gas flow, except in the cases of arsenic and selenium, where gas interrupt is used.

d Cold vapor technique.

interferences, the detection limits for typical sludge samples will be somewhat higher.

Mercury Analysis

The physical-chemical characteristics of mercury are not amenable to digestion by the generally recommended technique, Method 3050. For the determination of total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge material, EPA recommends using Method 7471, a cold-vapor atomic absorption spectrometry. This method appears in the EPA manual "Test Methods for Evaluating Solid Waste." (SW-846, Nov. 1986, 3rd Ed., pp. 7471-1,10). Prior to analysis, the solid or semi-solid samples must be prepared according to the procedures discussed in this method. The typical detection limit for this method is 0.0002 mg/L.

Antimony and Silver Analysis

The procedures for preparation of antimony and silver samples are given in Method 3005. Method 3005, a soft digestion, is presently the only digestion procedure recommended for antimony. It yields better recoveries than either Method 3010 or 3050. There is no hard digestion for antimony at this time (SW-846, Nov. 1986, 3rd Ed., p. 7041-2). Samples prepared by Method 3005 are amenable to determination by either ICAP Method 6010 or the atomic absorption furnace technique, Method 7041. (SW-846, 3rd Ed. - see pp 7041-1 through 7041-4). Detection limits for Method 7041 are 3 ug/L for antimony and 10 mg/l for silver.

3.3 ORGANICS

The evolution of analytical techniques for organic contaminants has involved a number of modifications to a basic method in order to widen potential applications. Because the instrumentation is complex and the number of possible analytes is large, quality control is difficult to monitor and several analytical techniques are required. As with analyses for metals and other elements, the organic-rich complex matrices characteristic of sewage sludges often mean that analyte extraction/isolation procedures play a significant role in the reliability of the resultant analytical data.

3.3.1 Overview of Analyte Extraction and Isolation

For a number of reasons, EPA has focused regulatory attention on two categories of contaminants: volatile organics and semi-volatile organics. While the classification of these groups is founded upon inherent physical/chemical properties, extraction and isolation techniques are the functional basis for the distinction.

Volatile Organics

Two methods are available for extraction and isolation of volatile organics in aqueous and solid matrices: headspace techniques and purge and trap techniques. Several versions of these procedures have been sanctioned by regulatory agencies and/or developed for use in specific applications. For POTW sludge sampling and analysis, EPA recommends two analytical methods (1624C, 624-S) which both extract via purge and trap (see Section 3.3.2).

Purge and trap requires moderate sample preparation. The method relies upon a stripping process in which an inert gas is bubbled through the sample to remove the volatile organics. The volatilized organics are transferred from the aqueous/solid phase to the gaseous phase and subsequently trapped on a solid adsorbent column. The adsorbent column is then heated and the trapped organics are thermally desorbed and swept into the analytical instrument.

Semi-volatile Organics

The first step in all procedures for determination of semi-volatile organics is solvent extraction. (Note: For extraction procedures recommended by EPA for sludge analysis see Section 3.3.2). The sample material is mixed and agitated with a solvent, causing the organic analytes to be preferentially partitioned into the solvent phase. Extractions are typically performed at both acidic and basic pH ranges to facilitate extraction of ionizable organics. Modifications to the extraction method are usually based upon the manner in which the sample-solvent mixture is agitated and post-extraction cleanup procedures.

The organic solvent used most frequently for extraction of semi-volatile analytes is methylene chloride, either singly or in combination with a more polar solvent. Extraction techniques which are applicable to sludge and solid matrices include:

- Sonication extraction
- Continuous liquid-liquid extractors
- Soxhlet extraction
- Mechanical agitation (shaker table, homogenization, or wrist-action shaker).

Sonication relies on the mechanical energy developed from ultra-sonic devices to affect agitation and solvent-solid contact. The best approach involves the use of a sonication horn which is immersed into the solvent-sample mixture, rather than a sonication bath. This technique has also been proven effective in sludge and sediment applications.

Continuous liquid-liquid extractors and Soxhlet extractors employ the same basic principle of operation. The extraction solvent is distilled from a reservoir, condensed above the sample material, and subsequently rains down through the sample. The distillation-condensation process continues until a volume of solvent has collected sufficient force to establish a siphon, at which point the extraction solvent is siphoned back into the reservoir. The cycle is repeated with freshly distilled solvent and is generally allowed to occur for 12-24 hours. The continuous liquid-liquid extraction procedure can only be used on low solids (<5%) sludges, while the Soxhlet technique is most useful for materials with low water content.

A variety of mechanical agitation techniques have been used for extractable organics determinations, including homogenization, wrist-action shakers and platform shakers (shaker tables). The objective of each technique is to maximize the contact between the extraction solvent and the solid particles. Wrist-action and platform shakers have both proven adequate, with wrist-action shakers generally preferable for smaller sample containers and platform shakers preferable for larger extraction vessels. Homogenization relies on agitation of the solvent-solid mixture, rather than agitation of the entire extraction vessel. This technique has been used quite successfully in sludge applications as a result of its superior agitation. However,

sand, a fairly common constituent of sewage sludge, literally chews up high speed homogenizers.

As a result of the complexity of sludge matrices, fractionation and/or cleanup procedures are often required after sample extraction to minimize interference. The basic concept used in virtually all cleanup techniques is selective adsorption of the interfering components. Although a variety of cleanup procedures have been developed for specific analytes, the techniques commonly employed for the listed applications include:

- Gel permeation resins - broad spectrum cleanup and higher molecular weight biogenic organics
- Activated carbon - fractionation and general purpose cleanup
- Alumina adsorbent - inorganic adsorbent
- Florisil adsorbent - inorganic adsorbent
- Silica gel adsorbent - inorganic adsorbent
- Copper and mercury - removal of sulfur-containing compounds.

Cleanup procedures can be used individually or in combination with other procedures, depending upon the need of the particular application and the complexity of the sample.

For more detail regarding extraction and isolation techniques, consult the references cited in 40 CFR Part 136, "Guidelines for Establishing Test Procedures for the Analysis of Pollutants."

3.3.2 Recommended Analytical Techniques for Organics

For determining concentrations of organic pollutants in sludge, EPA recommends two methods designed for qualitative and quantitative analysis of municipal and industrial wastewater treatment sludges:

- Volatile Organics - 624-S (EPA 1984b) or 1624C (EPA 1988a)
- Semi-Volatile Organics - 625-S (EPA 1984b) or 1625C (EPA 1988a)

Each of these two methods employ gas chromatography/mass spectrometry (GC/MS).

GC/MS is a combination of two microanalytical techniques: gas chromatography (a separation technique) and mass spectrometry (an identification technique). A sample aliquot is prepared for extraction, extracted, then introduced to the GC/MS system. The extract is vaporized quickly at an elevated temperature and carried by an inert gas (mobile phase) through a coated column (stationary phase). Separation of the extract components is effected by their differential partitioning between stationary and mobile phases. The separated components exit the column and enter the mass spectrometer (MS) where they are decomposed to specific unimolecular species. The manner in which a component fragments is characteristic of that component and is the basis for identification. The MS detector quantifies a compound by responding with a signal proportional to the detected amount of the compound.

The GC/MS system is calibrated by measuring signal response to three to five analyte standard solutions of various concentrations (e.g., 20-160 ng/ml). The solutions are carefully

prepared mixtures of pollutants suspected to be present in the sample, as well as a few labeled pollutant analogs known as internal standards. The accumulated measurements form an instrument response curve. Samples are spiked with the same internal standards at a fixed concentration immediately prior to analysis. If the MS detects any sample-originated pollutants, the generated signal for each pollutant is measured against both the internal standard and the response curve.

GC/MS analysis affords several advantages over other techniques:

- Provides qualitative and quantitative information about a wide range of organic compounds.
- Confirms specific information from a small sample size.
- Produces a spectrum with a fragmentation pattern, or fingerprint, which can be used to identify an unknown.

3.3.2.1 Methods 1624C and 1625C

Methods 1624C and 1625C are draft methods for analyzing volatile organics (Method 1624C) and base/neutral, non and semi-volatile organics (Method 1625C) in sludge. These methods were developed by the USEPA Office of Water Industrial Technology Division, and are derived from previous methods 1624 and 1625 (see 40 CFR Part 136) for analyzing wastewaters.

The 1624C/1625C (and 1624/1625) test procedures are isotope dilution techniques. In conventional GC/MS, up to six internal standards are used to quantify the response of perhaps several dozen analytes. Isotope dilution GC/MS employs stable, isotopically labeled analogs of the compounds of interest, which is analogous to providing a separate internal standard for each analyte. The result is that isotope dilution GC/MS is sensitive

to even minute contaminant concentrations. Methods 1624C/1625C and 1624/1625 are similar in this respect but differ in sample preparation.

Method 1624C sample preparation for sludge samples consists of the following three routes, depending on the percent (%) solids content of the sludge. If the solids content is less than one percent, stable isotopically labeled analogs of the compounds of interest are added to a 5 gram sample and the sample is purged in a chamber designed for soil or water samples. If the solids content is 30 percent or less, the sample is diluted to one percent solids with reagent water, and labeled compounds are added to a 5 gram aliquot of the sludge/water mixture. The mixture is then purged. If the solids content is greater than 30 percent, five ml of reagent water and the labeled compounds are added to a 5 gram aliquot of sample. The mixture is then purged.

Method 1625c sample preparation for sludge samples consists of the following three routes, depending on the percent (%) solids content of the sludge. If the solids content is less than one percent, a one liter sample is extracted with methylene chloride using continuous extraction techniques. If the solids content is 30 percent or less, the sample is diluted to one percent solids with reagent water, homogenized ultrasonically, and extracted. If the solids content is greater than 30 percent, the sample is extracted using ultrasonic techniques. Each extract is subjected to a gel permeation chromatography (GPC) cleanup.

These methods are currently undergoing revision at EPA's Environmental Monitoring and Support Laboratory for problems relating to the sample preparation portions. They are the

methods used in the National Sewage Sludge Survey (which EPA is conducting to provide a current data base to be used to set pollutant limits, evaluate risks of use and disposal practices, and evaluate the impacts of the proposed rule) and also are discussed in the 40 CFR Part 503 regulation proposed on February 6, 1989 and now out for comment. Depending on the results of the comment period, the isotope dilution methods may be exclusively required for priority pollutant organics analysis when 40 CFR Part 503 is finalized.

3.3.2.2 Methods 624-S and 625-S

Methods 624-S and 625-S are existing methods for the measurement of organic priority pollutants in sludges. These test procedures were derived from previously developed methods 624 and 625 for analyzing wastewaters (see 40 CFR Part 136). The 624-S/625-S techniques are conventional GC/MS and operate as described in Section 3.3.2. Method 624-S is used to analyze for volatile organic compounds. Method 625-S is used for semi-volatile or nonvolatile organics.

In Method 624-S, an inert gas is bubbled through a 10-ml sludge aliquot contained in a purging chamber at ambient temperature. The purgeable compounds are transferred from the aqueous phase to the vapor phase. The vapor is carried through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeables into a gas chromatographic column. The gas chromatograph is temperature programmed to separate the purgeables which are then detected with a mass spectrometer.

Method 625-S uses repetitive solvent extraction (see section 3.3.1) aided by a high-speed homogenizer. The extract is

separated by centrifugation and removed with a pipette or syringe. Extracts containing base/neutral compounds are cleaned by silica gel or florisil chromatography or by gel permeation chromatography (GPC). Extracts containing the acidic compounds are cleaned by GPC. The organic priority pollutants are determined in the cleaned extracts by capillary column or packed column GC/MS. Option A, i.e., extract cleanup by silica gel or florisil chromatography and analysis by capillary column GC/MS (HRGC/MS) is preferred since HRGC/MS allows easier data interpretation.

While Methods 1624C/1625C provide lower detection limits, in some cases, than Methods 624-S/625-S, these methods are also more costly. Presently, Methods 1624C/1625C cost about $2,200-$2,400 per sample, which is approximately $200-$400 more than a similar analysis by Methods 624-S/625-S. The extra cost reflects the Method 1634/1635 isotope spikes and approximately two weeks of work necessary to prepare additional spectral libraries.

Neither Methods 624-S/625-S or Methods 1624C/1625C detect pesticides at very low concentrations. Without megabore column analysis, which may cost an additional $1,000, none of these methods will do better than the detection limits, 20-50 ppb. For some highly mixed pesticides such as chlordane, these methods can only detect 200-300 ppb. At this time, EPA is not recommending megabore column pesticide analysis nationally. However, in situations where lower detection limits are crucial such as in PCB or pesticide analysis, megabore column analysis is necessary.

3.4 PATHOGENIC MICROORGANISMS

A pathogen or pathogenic agent is any biological species that can cause disease in the host organism (primarily humans). These organisms fall into four broad categories: viruses,

bacteria, parasites, and fungi. From these categories, species commonly found in sewage sludge include fecal coliforms, fecal streptococci, salmonella, and ascaris (helminth). Wastewater sludge disinfection, the destruction or inactivation of pathogenic organisms in the sludge, is carried out to minimize public health concerns regarding these and other microbial agents.

The 40 CFR Part 257 regulations issued under joint authority of Subtitle D of the Resource Conservation and Recovery Act (RCRA) and Section 405(d) of the Clean Water Act establish requirements for the disposal of solid waste which include pathogens in sewage sludge. The regulations (40 CFR Part 257.3-6) require that sewage sludges applied to the land surface or incorporated into the soil be treated by a Process to Significantly Reduce Pathogens (PSRP). Public access must be controlled for at least twelve months after sludge applications and grazing by animals whose products are consumed by humans must be prevented for at least one month after application. Treatment by a Process to Further Reduce Pathogens (PFRP) is required for sewage sludge applied to the land surface or incorporated into the soil if crops for direct human consumption are grown within eighteen months after application, if the edible portion of the crop will touch the sludge.

Rather than requiring a specific reduction or concentration for given pathogens, the process-based regulation (see Appendix II of 40 CFR Part 257) describes and sets numerical requirements for unit processes and operating conditions that qualify as PSRP and PFRP (e.g., criteria for process time and temperature and for volatile solids reduction). Thus permit compliance is based on meeting process requirements, not pathogen reduction per se. Appendix II of 40 CFR Part 257 allows methods or operating

conditions other than those listed under PSRP or PFRP if pathogens and vector attraction are reduced commensurate with the reductions attainable from listed methods. Appendix II (of 40 CFR Part 257) does not prescribe the operation mode (i.e., batch or continuous) for digesters. The regulation also does not specify a method for calculating volatile solids reduction. For a comprehensive discussion of the ways that volatile solids reduction may be calculated and their limitations, refer to Appendix B of this guidance document.

Although the 40 CFR Part 257 regulations are based on specific processes rather than on meeting specific pathogen reduction levels, the regulations do provide that other processes "may be acceptable if pathogens are reduced to an extent equivalent to the listed processes." In order to provide guidance on the equivalence of these other methods EPA has a panel of experts, the Pathogen Equivalency Committee (PEC), which evaluates the acceptability of the process based on the level of pathogen reduction, as determined by standardized analytical tests. For more comprehensive information on pathogen and guidance on whether alternative processes provide equivalent levels of pathogen reduction consult the draft "Guidance for Controlling Pathogens in Municipal Wastewater Sludge" PEC/EPA May 1989 (to be finalized July/August 1989).

Sampling techniques for determining pathogens in sewage sludge are no different than for other tests except that no preservatives are used. In the absence of definitive sludge methods for determining bacteria concentrations, modified standard wastewater methods are often utilized. The analytical methods for analysis of pathogens and indicator organisms are provided in Table 3.6. Unfortunately no standardized methods exist for parasitic determinations.

TABLE 3.6

ANALYTICAL TECHNIQUES FOR DETERMINATION OF PATHOGENIC MICROORGANISMS IN SEWAGE SLUDGE

Pathogen	Preparation Technique	Culture Media	Reference
Fecal Coliform		---	A(908 or 909)
Fecal streptococcus/ enterococci		---	A(910A) or B
E. Coli	Centrifugation and filtration	M-PC broth membrane filters	A(912E)
Salmonella sp.	Filtration	Brilliant green-xylose lysine desoxycholate agars	A(912C.1) or C
Animal Viruses	Centrifugation, elutriation, filtration, and flocculation	Tissue culture	D
Helminth Ova	Filtration	---	A(917) or E
Protozoa	Filtration	---	A(917) or E

A) APHA-AWWA-WPCF Standard Methods for the Examination of Water and Wastewater. 16th Ed.

B) Slantely, L.W. and Bartley, "Numbers of enterococci in water, sewage, and feces determined by the membrane filter technique with an improved medium", J. Bacteriology 74: 591-595 (1957).

C) Kenner, B.A., and Clark, "Detection and enumeration of Salmonella and Pseudomonas aeruginosa", J. Water Pollution Control Federation 46(9): 2163-2171 (1974).

D) "The Manual of Methods for Virology", EPA/600/4-84/013 (February 1984) as revised.

E) Fox, J.C., Fitzgerald, and Lue-Hing, "Sewage Organisms: A Color Atlas", Lewis Publishers, Chelsea, Michigan (1981).

The effectiveness of many PSRPs and PFRPs for reducing pathogens can be estimated by measuring the effects on fecal indicator organism densities (e.g., fecal coliform and/or fecal streptococcus). These tests are less expensive and easier to run than tests for specific pathogens and also provide good control data.

4. QUALITY ASSURANCE/QUALITY CONTROL

An essential part of a sampling and analysis program includes a well designed quality assurance/quality control (QA/QC) program. The extent of the QA/QC program should mirror the intent and purpose of the sampling effort. It should be noted that the facility is ultimately responsible for the quality of the data even if a contractor is used. Therefore, it behooves the POTW to have a good QA/QC program.

If the purpose of the sampling and analysis program is to determine compliance with permit conditions, or to provide critical data for making a major cost decision, then the QA/QC program should be extensive and be able to demonstrate the precision, accuracy, representativeness, comparability and completeness of the data. The determination of these QA/QC parameters and their definitions are as follows:

- QA is an overall program which guarantees the quality of the product. It includes a QC auditing process to prevent future defects. QA is synonymous with process control, continuous improvement and prevention of poor quality. QC is the examination of the product to determine if it meets the specifications of the QA program. QC is part of the overall QA program. QC is synonymous with appraisal after the fact. An example of QC is that lab duplicate results must be within a certain percentage of each other or else the whole batch must be redone.

- Laboratory QA includes prevention of data contamination during laboratory procedures. Contamination may be due to various other tests that are run in the lab at any given time. In order to assure that any sample contamination that does occur does not contaminate lab data, a lab QA sample, usually a deionized water "blank" (or other "clean" appropriate material), is run along with the actual field samples. Lab QA also includes doing duplicates and spikes of the actual samples. Field QA serves the same purpose, to prevent data from being erroneous. However, it is virtually

impossible to prevent contamination of the samples since the sampling environment is not controllable. Therefore, the field blanks are subject to the same conditions as the samples, i.e., the containers are exposed to the environment as long as the sample containers are open, the sample and field "blank" are transported together.

- Accuracy, which is closeness to actual values, of all sample testing and analyses should be evaluated at a minimum frequency of 5 percent of the samples tested (i.e., at least one in every 20 samples), using spiked samples. Accuracy is calculated from the known and analytically derived values of spiked parameters, and expressed as percent recovery. The accuracy required in the quality assurance program for the analyses is specified in each of the EPA methods (e.g., EPA 600 or 1600 Series or EPA Methods for Chemical Analysis of Water and Wastes).

- Precision, which is repeatability of results, of sample analyses should be evaluated at a minimum frequency of 5 percent (i.e., at least one in every 20 samples), using spiked samples in duplicate. Precision is calculated from the analytical results of the spiked analytes in each set of duplicate samples, and expressed as percent relative standard deviation. The precision required in the quality assurance program for the analyses is specified in each of the EPA Methods (e.g., EPA 600 or 1600 series or EPA Methods for Chemical Analysis of Water and Wastes).

- Completeness is calculated as the ratio of valid measurements obtained to the number of valid measurements needed to reach a predefined statistical level of confidence in the resulting data. Completeness is determined and evaluated on the basis of data sets for each specific measurement process. Data are considered to be valid if both the accuracy and precision of the measurements meet the data quality objective (i.e., accuracy, precision, and compliance with analysis method protocol).

- All sampling should be performed using methods, procedures, and controls that ensure the collection of representative samples which thus ensures that the analytical results are representative of the media and the conditions being measured.

- Comparability is a more qualitative QA measurement. All analytical data must be calculated and reported in units consistent with those specified in the applicable permit. Previously developed data generated for each facility about to be inspected is reviewed to ensure that no difficulties of data comparability will be encountered by following the specifications of the permit. If no previous data exist and the permit requirements are incomplete or ambiguous, data should be reported in the standard units prescribed in the appropriate EPA Methods (e.g., EPA 600 or 1600 series or EPA Methods for Chemical Analysis of Water and Wastes).

These QA/QC procedures are necessary for ensuring data quality. On the other hand, if the purpose of the sampling effort is to monitor plant performance for routine operation and maintenance (O&M) decisions, a simplified QA program that includes sample replicates and a field blank might suffice.

Sludge sampling and analysis programs for determining compliance with permit conditions should include a written QA Plan. EPA guidance for the development of a QA Program (EPA Quality Assurance Project Plans (QAPP), 1983) identifies 16 elements which should be addressed in a QA plan:

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Performance and System Audits

Preventive Maintenance

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Corrective Action

Quality Assurance Reports to Management

In preparing a QAPP, the QA parameters and specifications of the analytical program should be dictated by the analytical parameters. The QA parameters are specified in each analytical protocol. There are situations (particularly for enforcement actions) in which more stringent protocols will be desired.

In preparing the QA plans, the collection of field blanks (blanks to reflect sample handling effects) and sample replicates should be addressed. At a minimum, field blanks should be collected every day that sampling is performed. Field blanks should be prepared at the beginning of each sampling event, at each discrete sampling site, by pouring American Society for Testing and Materials (ASTM) Type II reagent-water into prepared sample bottles. These sample bottles are randomly selected from the supply of prepared sample bottles; a sample container should be selected that is appropriate for each type of analysis for which environmental samples are being collected (see Table 2.4). The field blanks should be handled and analyzed in the same manner as environmental samples. Because field blanks and environmental samples are collected under the same conditions, field blanks analyses should be used to indicate the presence of

external contaminants that may have been introduced into samples during collection.

One field replicate for every 20 samples or less should be collected at a preselected POTW monitoring point. Field replicates should be collected at the same time and in the same manner as the other environmental samples. Results of the field replicate analyses should be used primarily to assess the precision of the field sampling methods.

In preparing and evaluating the analytical report, attention should be given to the data quality, and the impact of both the sampling and analysis data quality to the overall interpretation of the analytical results. Both the data from the field QA samples and the laboratory QA samples should be evaluated for the presence of contaminants. Additionally, statistical procedures should be used for the determination of precision, accuracy and completeness. The QAPP 1983 document provides a description of the statistical procedures and their applications. All reports of analytical data should contain a separate section which assesses the quality of the reported data.

The sample procedures and frequency section of the quality assurance plans should address, among other elements, sample holding times, sample preservation procedures, and sample chain-of-custody. Maximum sample holding times are presented in Table 2.4. Section 2.5.3 addresses sample preparation. Section 2.7.2 addresses sample chain-of-custody.

The section of the quality assurance plan on internal quality control checks specifically discuss how the following activities will be addressed:

Organic Priority Pollutants

- Instrument tuning and calibration
- Method blank analysis
- Surrogate spike analysis
- Matrix spike/matrix spike duplicate analysis
- Internal standards analysis

Inorganic Priority Pollutants

- Initial calibration verification
- Continuing calibration verification
- Instrument response and linearity verification
- Calibration and preparation blank analyses
- Interference check sample analyses
- Spike sample analyses
- Duplicate sample analyses
- Quality control sample analyses
- Serial dilution analyses (if applicable)
- Instrument detection limit determination
- Method of standard additions application.

5. SAMPLING AND ANALYTICAL COSTS

The cost of carrying out a sludge sampling program can vary depending on the number and type of samples, parameters analyzed, and whether analytical services are contracted out. The following discussion examines sampling and analytical costs as of April 1989.

5.1 MANPOWER REQUIREMENTS

Manpower requirements fall into two categories: (1) supervisory and program development, and (2) sampling/analytical. All sampling programs should be designed and supervised by qualified personnel. Developmental and supervisory needs will vary according to the following factors:

- Type and number of samples
- Number of streams to be sampled
- Number of facilities/locations
- Availability of suitable sample points
- Parameters to be analyzed
- Experience and qualifications of field and laboratory personnel.

The number of factors influencing supervisory needs makes estimating average costs for these needs impractical. Costs will vary according to the hours needed for each program and according to the salary range of qualified personnel within a given organization.

Sampling manpower needs will also vary widely depending on the conditions listed above. For 24-hour composite sampling, a

two shifts (more likely three) are required. The actual time spent sampling during the shifts will depend on how frequently grab samples are collected (one per hour or once every 4 hours) during the 24-hour sampling period. In addition to the manpower required to actually collect the sample, additional time is required for sample preparation and handling. On-the-job training is generally acceptable for sampling procedures.

Estimates of some of these needs are presented below:

TABLE 5.1

Activity	Manpower
o Automatic Sampler Setup[1]	0.5 - 4 manhours
o Sample Container Preparation[2]	2 - 15 man-minutes / sample
o Sample Documentation[3]	2 - 15 man-minutes / sample
o Sample Handling[4]	2 - 60 man-minutes / sample

1 Depending on sample point characteristics.
2 Depending on parameter.
3 Depending on parameter, ultimate data use and number of points sampled simultaneously.
4 Depending on parameters sampled and whether samples are analyzed on site, are delivered or shipped.

5.2 IN-HOUSE ANALYTICAL COSTS

If any analytical work is done in-house, manpower, equipment/facility and operating (i.e., electrical, chemical supplies, etc.) costs will be incurred. Real costs will vary according to what extent the analytical load imposed by the sludge sampling is marginal to the laboratory's operational

capacity. Two extremes serve as examples of this cost variability.

A plant electing to do in-house analysis which has no laboratory would need to make a sizable expenditure for an adequate facility and the necessary analytical equipment and supplies. In addition, qualified (B.S. Chemistry or equivalent) laboratory personnel must be put on the payroll. Given these circumstances, it would generally not be practical to do in-house analysis. Instead, it is likely that this plant would contract out for analytical services.

A second plant, conducting a similar sludge sampling program, also elects to do all related analytical work in-house. This plant, however, has an analytical laboratory in place which is capable of performing all analyses required. In addition, the laboratory is presently operating below capacity. The additional load imposed by the sludge sampling program will not require any capital expenditure, and will require little, if any, additional laboratory manpower (any additional manpower needs can be accommodated by limited overtime rather than new employee hires). In the case of this plant, in-house analysis for a sludge sampling program can be accomplished at a very low real cost.

Because of the wide range of real costs possible for sampling and in-house analytical work, no attempt is made herein to quantify these costs on a dollars per sample basis. Rather, each sampling program must be analyzed in light of applicable salary scales, sampling program complexity and in-house analytical capabilities.

5.3 CONTRACT ANALYTICAL COSTS

Many sludge sampling programs, particularly those conducted by small municipalities or authorities, will utilize contract laboratories for analytical work. In contrast to sampling costs, which vary greatly due to a wide variety of factors, contract analytical costs fall within a relatively narrow range. Table 5.2 presents typical analytical costs for parameters commonly run on sludge samples. These cost estimates were obtained in a March 1988 and 1989 telephone survey of analytical laboratories.

Two factors must be considered in estimating contract analytical costs for sludge sampling programs. The first is the need, depending on parameters, for additional preparation of sludge samples prior to analysis. Many laboratories charge an additional fee for this preparation, which can be as much as $100, depending on the parameters to be run.

The second factor impacting analytical costs is the practice by most laboratories of offering discounts on per sample prices for multiple sample analysis. These discounts vary from laboratory to laboratory, and can be substantial depending on the number of samples involved. Of particular importance is the number of samples being received simultaneously by the laboratory (i.e., a greater discount will typically be offered for 10 samples if all are to be analyzed at one time rather than if one is to be delivered to the lab each week for 10 weeks).

5.4 SAMPLING EQUIPMENT COSTS

The cost of sampling equipment and containers is typically a relatively small fraction of the overall cost of a sludge sampling program. In general, the manual collection methods used for sludge sampling require only simple, relatively inexpensive

TABLE 5.2

TYPICAL CONTRACT ANALYTICAL COSTS FOR
COMMONLY ANALYZED SLUDGE PARAMETERS

	ANALYSIS COST RANGE ($/SAMPLE)			
	Washington State	District of Columbia	California	Massachusetts
Priority Pollutants				
Organics Methods:				
1624C/1625C		2200-2400		
Office of Solid Waste #8240			250	
624-S/625-S		1800-2200	425	550
Acid Fraction Only		N/A	N/A	225
Base Neutral Only		N/A	N/A	325
Metals:				
ICAP or AAS		25-200/metal	240/(13)	290/(13)
Others:				
Cyanide		20-30	75	60
Phenols		20-30	75	50
Total PCBs		60-150	200	175
Pesticides			included in above	150
Total for Priority Scan without Dioxin		2225-5210	1265	1275
Other Non Priority Pollutants				
Oil & Grease		15-25		
" total grav.				60
" HC "				80
" HC & tot "				130
" IR method				100
Ammonia, as N		10-20		35
Tot Kjeldahl N		10-20		35
Tot Suspend Sol		10-20		15
Tot % Solids		10-20		15
Tot Phosphorus		10-20		35
Phosphate		10-50		35
Potassium		20-30		15
Tot Org Halides		50-100		80
EP Toxicity				
extraction		N/A	100	75
8 metals			140	185
2 pest.			100	150
4 herb.			150	175
TOTAL EP	$ 420		$490	$585

equipment. The following paragraphs highlight the primary equipment cost items in a typical sludge sampling program.

- **Sample Containers** - Sample container costs are related to: (1) the number of containers needed, and (2) the type of container needed, depending on parameter(s) to be analyzed. The following are typical per-container prices for some commonly used containers:

Container	Size	Approx. Price
Teflon	1 liter	$ 35 - 40
Graduated Glass (w/Teflon-lined cap)	1 liter	$ 3 - 4
Polypropylene	1 liter	$ 2
Polypropylene	0.5 liter	$ 1.50
Polypropylene	10 liter	$ 15
Glass (w/Teflon lined cap)	0.5 liter	$ <1 - 2

  As with analytical costs, suppliers of containers often offer substantial discounts for volume purchases.

- **Automatic Samplers** - In most sludge sampling programs the use of automatic sampling equipment will be precluded due to sample characteristics. If automatic sampling is utilized in a given sampling program, automatic sampler costs will typically constitute the majority of sampling equipment costs. Portable, battery-powered peristaltic-type samplers typically cost from $1000 to $3000, depending on features such as computerized controls, etc. Pneumatically operated plunger-type samplers will vary in price according to application and capacity.

- **Manual Sampling Equipment** - In general, equipment costs for manual sludge sampling are minimal. Stainless steel pitchers (2 liter), which are useful for sampling from either a tap or an open channel flow, are available for approximately $20. Polypropylene pitchers typically cost about 1/2 of the price of stainless steel. Stainless steel scoops used for sludge cake sampling cost approximately $40 (depending on size), while aluminum scoops of similar size are available for less than $10.

- **Preservatives** - Reagent grade chemicals should be used as preservatives. Since each sample will typically

require very small amounts of preservatives, cost on a per sample basis is negligible.

5.5 OPPORTUNITIES FOR COST SAVINGS

To provide a representation of sludge quality over a fixed duration, sewage sludge can be composited (i.e. mixed), reducing the number of samples to be analyzed. In light of the high costs associated with analysis of priority pollutant organics in sewage sludge, compositing samples provides an opportunity to substantially lower analytical costs. Field compositing is not an appropriate technique to use when the sample will be analyzed for volatile components. Lab personnel can composite grab samples in the lab.

When interested in daily variation in sludge constituents, a POTW can collect and analyze 24-hour composite samples, each consisting of six or more grab samples. This represents a significant cost savings when compared to separately analyzing many individual, non-composited samples. Smaller POTWs, with less variation in sludge quality, may elect to composite samples over several days as opposed to 24-hour composites. The suitability of a multi-day compositing procedure will depend upon whether the specific sludge constituent can be adequately preserved in the sludge sample. Table 2.3 shows the recommended preservatives and maximum sample holding times for organic and metal pollutants.

Another way to reduce costs would be to sample more frequently for parameters that are relatively inexpensive to analyze such as metals, nitrogen, phosphorus, and potassium, and to test for organic pollutants (expensive) less frequently, so long as some data are available indicating that the levels of organic contaminants in the sludge are acceptable.

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APPENDIX A

CHAIN OF CUSTODY RECORD

Chain of Custody Record

W.O. No.	Project Name			Sample Type	Number and Type of Containers						Remarks
Samplers: (Signature)											
Sta. No.	Date	Time	Station Description								

Relinquished By: (Signature)	Date	Time	Received By: (Signature)	(Print)	Comments

Source: 1987 EPA Document "Preparation Aid for HWERL's Category II Quality Assurance Project Plans"

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APPENDIX B

DETERMINATION OF VOLATILE SOLIDS

DETERMINATION OF VOLATILE SOLIDS REDUCTION IN DIGESTION[1]

By J.B. Farrell

INTRODUCTION

When sewage sludge is utilized on land, Federal regulations require that it be treated by a "process to significantly reduce pathogens" (PSRP) or a "process to further reduce pathogens" (PFRP). A requirement of both of these steps is a reduction in "vector attraction" of the sludge. If the PSRP or PFRP is anaerobic or aerobic digestion, the requirement for vector attraction reduction is achieved if volatile solids are reduced by 38 percent. As Fischer[1] has noted, the Federal regulation[2] does not specify a method for calculating volatile solids reduction. Fischer observed that the United Kingdom has a similar requirement for volatile solids reduction for digestion (40 percent), but also failed to prescribe a method for calculating volatile solids reduction. Fischer has provided a comprehensive discussion of the ways that volatile solids reduction may be calculated and their limitations. He presents the following equations for determining volatile solids reduction:

1. Full mass balance equation
2. Approximate mass balance equation
3. "Constant ash" equation
4. Van Kleeck equation

The full mass balance equation is the least restricted but requires more information than is currently collected at a wastewater treatment plant. The approximate mass balance equation assumes steady state conditions. The "constant ash" equation requires the assumption of steady state conditions as well as the assumption that ash input rate equals ash output rate. The Van Kleeck equation, which is the equation generally suggested in publications originating in the United States[3] is equivalent to the "constant ash" equation. Fischer calculates volatile solids reduction using a number of

[1] Source: "Control of Pathogens in Municipal Wastewater Sludge," EPA, to be published August, 1989.

examples of considerable complexity and illustrates that the different methods frequently yield different results. He closes with the recommendation, obviously directed to rulemakers, that "if it is necessary to specify a particular value for FVSR (fractional volatile solids reduction) then the specification should indicate the method of calculation of FVSR."

Fischer's paper is extremely thorough and is highly recommended for someone trying to develop a deep understanding of potential complexities in calculating volatile solids reduction. However, it was not written as a guidance document for field staff faced with the need to calculate volatile solids reduction in their own plant. The nomenclature is precise but so detailed that it makes comprehension difficult. In addition, two important troublesome situations that complicate the calculation of volatile solids reduction--grit deposition in digesters and decantate removal--are not explicitly discussed. Consequently, this presentation has been prepared to present guidance that describes the major pitfalls likely to be encountered in calculating volatile solids reduction and assists the practitioner of digestion to the best route to take for his situation.

The recommendation of this presentation is not the same as Fischer's. He suggests that the authorities should have provided a calculation method when they required specific volatile solids reductions. From a review of Fischer's results and this presentation, it will be clear that sometimes very simple calculations will give correct results and in other cases the simple methods will yield results seriously in error. Selecting one method and requiring that it be followed is excessively restrictive. The best solution is to require that the calculation be done correctly and then provide adequate guidance. This presentation attempts, belatedly, to provide that adequate guidance.

It is important to note that the calculations of volatile solids reduction will only be as accurate as the measurement of volatile solids content in the sludge streams. The principal cause of error is poor sampling. Samples should be representative, covering t'e entire charging and withdrawal periods. Averages should cover extended periods of time during which changes in process conditions are minimal. For some plants it is expected that

periodic checks of volatile solids reduction will produce results so erratic that no confidence can be placed in them. In this case, adequacy of stabilization can be verified by the method suggested in the text--periodically batch digest the product for 40 days. If VS reduction is less than 15%, the product is sufficiently stable.

The Equations for FVSR

The equations for fractional volatile solids reduction (FVSR) that will be discussed below are the same as developed by Fischer[1], except for omission of his "constant ash" equation. This equation gives identical results to the Van Kleek equation so it is not shown. Fischer's nomenclature has been avoided or replaced with simpler terms. The material balance approaches are called "methods" rather than "equations." The material balances are drawn to fit the circumstances. There is no need to formalize the method with a rigid set of equations.

In the derivations and calculations that follow, both VS (total volatile solids content of the sludge or decantate on dry solids basis) and FVSR are expressed throughout as fractions to avoid the frequent confusion that occurs when these terms are expressed as percentages. "Decantate" is used in place of the more commonly used "supernatant" to avoid the use of "s" in subscripts. Similarly, "bottoms" is used in place of "sludge" to avoid use of "s" in subscripts.

The "full mass balance" method

The "full mass balance" method must be used when steady conditions do not prevail over the time period chosen for the calculation. The chosen time period must be substantial, at least twice the nominal residence time in the digester (nominal residence time = average volume of sludge in the digester ÷ average volumetric flow rate. Note: when there is supernatant withdrawal, volume of sludge withdrawn should be used to calculate average volumetric flow rate). The reason for the long time period is to reduce the influence of short-term fluctuations in feed or product flow rates or compositions. If input compositions have been relatively constant for a long period of time, then the time period can be shortened.

An example where the full mass balance method would be needed is an aerobic digester operated as follows:

1. Started with the digester 1/4 full (Time zero).
2. Raw sludge is fed to the digester daily until digester is full.
3. Supernatant is periodically decanted and raw sludge is charged into the digester until not enough settling occurs to accommodate daily feeding. (Hopefully this will not occur until enough days have passed for adequate digestion.)
4. Draw down the digester to about 1/4 full (final time), discharging the sludge to sand beds.

The full mass balance is written as follows:

Sum of total volatile solids inputs in feed streams during the entire digestion period = sum of volatile solids outputs in withdrawals of decantate and bottoms + loss of volatile solids + accumulation of volatile solids in the digester. (1)

Loss of volatile solids is calculated from Equation 1. FVSR is calculated by Equation 2:

$$FVSR = \frac{\text{loss in volatile solids}}{\text{sum of volatile solids inputs}} \quad (2)$$

The accumulation of volatile solids in the digester is the final volume in the digester after the drawdowns times final volatile solids concentration less the initial volume at time zero times the initial volatile solids concentration.

To properly determine FVSR by the full mass balance method requires determination of all feed and withdrawal volumes, initial and final volumes in the digester and determination of volatile solids concentrations on all streams. In some cases, which will be discussed later, simplifications are possible.

The "approximate mass balance" method

If volumetric inputs and outputs are relatively constant on a daily basis, and there is no substantial accumulation of volatile solids in the digester over the time period of the test, an approximate mass balance (AMB) may be used. The basic relationship is stated simply:

volatile solids input rate = volatile solids output rate + loss of volatile solids. (3)

The FVSR is given by Equation 2.

No decantate, no grit accumulation - Calculation of FVSR is illustrated for Problem 1 in Table 1 which represents a simple situation with no decantate removal and no grit accumulation. An approximate mass balance is applied to the digester operated under constant flow conditions. Since no decantate is removed volumetric flow rate of sludge leaving the digester equals flow rate of sludge entering. Applying Equations 3 and 2,

$$FY_f = BY_b + \text{loss} \quad (4)$$

$$\text{Loss} = 100\ (50-30) = 2000 \quad (5)$$

$$FVSR = \frac{\text{Loss}}{FY_f} \quad (6)$$

$$FVSR = \frac{2000}{(100)(50)} = 0.40 \quad (7)$$

Nomenclature is given in Table 1. Note that the calculation did not require use of the fixed solids concentrations.

The calculation is so simple that one wonders why it is so seldom used. One possible reason is that the input and output volatile solids concentrations (Y_f and Y_b) may show greater coefficients of variation (standard deviation ÷ arithmetic average) than the fraction volatile solids (VS, fraction of the sludge solids that is volatile--note the difference between VS and Y).

Grit deposition - Grit deposition can be a serious problem in both aerobic and anaerobic digestion. The biological processes that occur in digestion dissolve or destroy the substances suspending the grit and it tends to settle. If agitation is inadequate to keep the grit particles in suspension they will accumulate in the digester. The approximate mass balance can be used to estimate accumulation of fixed solids.

For Problem 1, the balance yields the following:

$$FX_f = BX_b + \text{loss} \quad (8)$$

$$(100)(17) = (100)(17) + \text{Fixed Solids Loss} \quad (9)$$

$$\text{Fixed Solids Loss} = 0 \quad (10)$$

The material balance compares fixed solids in output with input. If some fixed solids are missing this loss term will be a positive number. Since we know that digestion does not consume fixed solids, we assume that the fixed solids are accumulating in the digester. As Equation 10 shows, the fixed solids loss equals zero. Note that for this case where input and output sludge flow rates are equal, the fixed solids concentrations are equal when there is no grit accumulation.

The calculation of fixed solids is repeated for Problem 2. Conditions in Problem 2 have been selected to show grit accumulation. Parameters are the same as in Problem 1 except for the fixed solids concentration (X_b) and parameters related to it. Fixed solids concentration in the digested sludge is lower than in Problem 1. Consequently, VS is higher and mass flow rate of solids (input rate = output rate + rate of loss of fixed solids) is presented in Equation 11-13.

$$FX_f = BX_b + \text{Fixed Solids Loss} \quad (11)$$

$$\text{Fixed Solids Loss} = FX_f - BX_b \quad (12)$$

$$\text{Fixed Solids Loss} = (100)(17) - (100)(15) = 200 \text{ kg/d} \quad (13)$$

The material balance, which only looks at inputs and outputs, informs us that 200 kg/d of fixed solids have not appeared in the outputs as expected. We know that fixed solids are not destroyed and conclude that they are accumulating in the bottom of the digester. The calculation of FVSR for Problem 2 is exactly the same as for Problem 1 (see Equations 4-7) and yields the same result. The accumulation of solids does not change the result.

Decantate withdrawal, no grit accumulation - In Problem 3, supernatant is withdrawn daily. Volatile and fixed solids concentrations are known for all streams but the volumetric flow rates are not known for decantate and bottoms. It is impossible to calculate FVSR without knowing the relative volume balance and a fixed solids balance, provided it can be assumed that loss of fixed solids (i.e., accumulation in the digester) is zero.

Selecting a basis for F of 100 m^3/d,

$$\text{Volume balance:} \quad 100 = B + D \tag{11}$$

$$\text{Fixed solids balance:} \quad 100\,X_f = BX_b + DX_d \tag{12}$$

Since the three Xs are known, B and D can be found.

Substituting 100-D for B and the values for the Xs from Problem 3 and solving for D and B.

$$(100)(17) = (100 - D)(23.50) + (D)(7.24) \tag{13}$$

$$D = 40.0\ m^3/d,\ B = 60.0\ m^3/d \tag{14}$$

The FVSR can now be calculated by drawing a volatile solids balance:

$$FY_f = BY_b + DY_d + \text{loss} \tag{15}$$

$$FVSR = \frac{\text{loss}}{FY_f} = \frac{FY_f - BY_b - DY_d}{FY_f} \tag{16}$$

$$FVSR = \frac{(100)(50) - (60)(41.42) - (40)(12.76)}{(100)(50)} = 0.40 \tag{17}$$

Unless information is available on actual volumes of decantate and sludge, there is no way to determine whether grit is accumulating in the digester. If it is accumulating, the calculated FVSR will be in error.

When we make the calculation shown in Equation 15-17, we assume that the volatile solids that are missing from the output streams are consumed by biological reactions that convert them to carbon dioxide and methane. We assume accumulation is negligible. Volatile solids are less likely to accumulate than fixed solids but it can happen. In poorly mixed digesters, the scum layer that collects at the surface is an accumulation of volatile solids. FVSR calculated by Equations 15-17 will be overestimated if volatile solids accumulation rate is substantial.

Decantate withdrawal and grit accumulation - In Problem 4, there is suspected grit accumulation. The quantity of B and D can no longer be calculated by Equations 11 and 12 because Equation 12 is no longer correct. The values of B and D must be measured. All parameters in Problem 4 are the same as Problem 3 except measured values for B and D are introduced into Problem 4. Values of B and D calculated assuming no grit accumulation (Problem 3--see previous section), and measured quantities are compared below:

	Calculated	Measured
B	60	49.57
D	40	50.43

The differences in the values of B and D are not large but they make a substantial change in the numerical value of FVSR. The FVSR for Problem 4 is calculated below:

$$FVSR = \frac{(100)(50) - (49.57)(41.42) - (50.43)(12.76)}{(100)(50)} = 0.461 \qquad (18)$$

If it had been assumed that there was no grit accumulation, FVSR would equal 0.40 (see Problem 3). It is possible to determine the amount of grit accumulation that has caused this change. A material balance on fixed solids is drawn:

$$FX_f = BX_b + DX_d + \text{Fixed Solids Loss} \qquad (19)$$

The fractional fixed solids loss due to grit accumulation is found by rearranging this equation:

$$\frac{\text{Fixed Solids Loss}}{FX_f} = \frac{FX_f - BX_6 - DX_d}{FX_f} \quad (20)$$

Substituting in the parameter values for Problem 4.

$$\frac{\text{Fixed Solids Loss}}{FX_f} = \frac{(100)(17) - (49.57)(23.50) - (50.43)(7.24)}{(100)(17)} \quad (21)$$

$$= 0.100$$

If this fixed solids loss of 10 percent had not been accounted for, the calculated FVSR would have been 13 percent lower than the correct value of 0.461. Note that if grit accumulation occurs and it is ignored, calculated FVSR will be lower than the actual value.

The Van Kleeck Equation

Van Kleeck first presented his equation without derivation in a footnote for a review paper on sludge treatment processing in 1945[4]. The equation is easily derived from total solids and volatile solids mass balances around the digestion system. Consider a digester operated under steady state conditions with decantate and bottom sludge removal. A total solids mass balance and a volatile solids mass balance are:

$$M_f = M_b + M_d + (\text{Loss of total solids}) \quad (22)$$

$$M_f \cdot VS_f = M_b \cdot VS_b + M_d \cdot VS_d + (\text{Loss of volatile solids}) \quad (23)$$

The masses must be mass of solids rather than total mass of liquid and solid because VS is an unusual type of concentration unit--it is "mass of volatile solids per unit mass of total solids."

It is now assumed that fixed solids are not destroyed and there is no grit deposition in the digester. The losses in Equations 22 and 23 then comprise only volatile solids so the losses are equal. It is also assumed that the VS of the decantate and of the bottoms are the same. This means that the bottoms may have a much higher solids content than the decantate but the

proportion of volatile solids to fixed solids is the same for both streams. Assuming then that VS_b equals VS_d and making this substitution in the defining equation for FVSR (Equation 2),

$$FVSR = \frac{\text{Loss of vol. solids}}{M_f \cdot VS_f} = 1 - \frac{(M_b + M_d)\, VS_b}{M_f \cdot VS_f} \tag{24}$$

From Equation 22, recalling that we have assumed that loss of total solids equals loss of volatile solids,

$$M_b + M_d = M_f - \text{loss of vol. solids} \tag{25}$$

Substituting for $M_b + M_d$ into Equation 24,

$$FRVS = 1 - \frac{(M_f - \text{Loss of vol. solids})}{M_f \cdot VS_f} \cdot VS_b \tag{26}$$

Simplifying further,

$$FRVS = 1 - \left(\frac{1}{VS_f} - FRVS\right) \cdot VS_b \tag{27}$$

Solving for FRVS,

$$FRVS = \frac{VS_f - VS_b}{VS_f - VS_f \cdot VS_b} \tag{28}$$

This is the form of the Van Kleeck Equation found in WPCF's Manual of Practice No. 16[3]. Van Kleeck[4] presented the equation in the following equivalent form:

$$FRVS = 1 - \frac{VS_b \cdot (1 - VS_f)}{VS_f \cdot (1 - VS_b)} \tag{29}$$

The Van Kleeck Equation is applied below to Problems 1-4 in Table 1 and compared to the approximate mass balance equation results:

	1	2	3	4
Approximate Mass Balance (AMB)	0.40	0.40	0.40	0.461
Van Kleeck (VK)	0.40	0.318	0.40	0.40

Problem 1: No decantate and no grit accumulation. Both methods give correct answers.

Problem 2: No decantate but grit accumulation. VK is invalid and incorrect.

Problem 3: Decantate but no grit accumulation. AMB method is valid VK method is valid only if $VS_b = VS_d$.

Problem 4: Decantate and grit acumulation. AMB method valid only if B and D are measured. VK method is invalid.

The Van Kleeck equation is seen to have serious shortcomings when applied to certain practical problems. The AMB method can be completely reliable whereas the Van Kleeck method is useless under some circumstances.

Review and Discussion of Calculation Methods and Results

Complete Mass Balance Method - The complete mass balance method allows calculation of volatile solids reduction of all approaches to digestion, even processes where final volumes in the digester does not equal initial volume and where daily flows are not steady. A serious drawback is the need for volatile solids concentration and volumes of all streams added to or withdrawn from the digester as well as initial and final volumes and concentrations in the digester. This can be a daunting task particularly for the small plants which are most likely to run their digesters in other than steady flow modes. For plants of this kind, an "equivalent" method that shows that the sludge has undergone the proper volatile solids reduction is likely to be a better choice than trying to demonstrate 38 percent volatile solids reduction. An aerobic sludge has received treatment equivalent to a 38 percent volatile solids reduction if specific oxygen uptake rate is below a specified maximum.

Anaerobically digested sludge has received treatment equivalent to a 38 percent volatile solids reduction if volatile solids reduction after batch digestion of the product sludge for 40 days is less than a specified maximum[5].

Approximate Mass Balance (AMB) Method - The approximate mass balance method assumes that daily flows are steady and reasonably uniform in composition, and that digester volume and composition does not vary substantially from day to day. Results of calculations and an appreciation of underlying assumptions show that the method is accurate for all cases, including withdrawal of decantate and deposition of grit, provided that in addition to composition of all streams the quantity of decantate and bottoms (the digested sludge) are known. If the quantities of decantate and bottoms are not known, the accumulation of grit cannot be determined. If accumulation of grit is substantial and FVSR is calculated assuming it to be negligible, FVSR will be lower than the true value. The result is conservative and could be used to show that minimum volatile solids reductons are being achieved.

The Van Kleeck Equation - The Van Kleeck Equation has underlying assumptions that should be made clear wherever the equation is presented. It is never valid when there is grit accumulation because it assumes the fixed solids input equals fixed solids output. Fortunately, it produces a conservative result in this case. Unlike the AMB method it does not provide a convenient way to check for accumulation of grit. It can be used when decantate is withdrawn provided VS_b equals VS_d. Just how big the difference between these VS values can be before an appreciable error in FVRS occurs is unknown, although it could be determined by making up a series of problems with increasing differences between the VS values, calculating FRVS using the AMB method and a Van Kleeck equation, and comparing results.

The shortcomings of the Van Kleeck equation are substantial and may eventually lead to a recommendation not to use it. However, it has one strong point. The VS of the various sludge and decantate streams are likely to show much lower coefficients of variation (standard deviation ÷ arithmetic average) than volatile solids and fixed solids concentration. Review of data are needed to determine how seriously the variation in concentrations affect the confidence interval of FVSR calculated by both methods. A hybrid approach may

turn out to be advantageous. The AMB method could be used first to determine if grit accumulation is occurring. If grit is not accumulating, the Van Kleeck equation could be used. If decantate is withdrawn, the Van Kleeck equation still cannot be used unless VS_b is nearly equal to VS_d.

Average Values - The concentrations and VS values used in the equations will all be averages. For the material balance methods, the averages should be weighted averages according to the mass of solids in the stream in question. The example below shows how to average the volatile solids concentration for four consecutive sludge additions.

Addition	Volume	Volatile Solids Concentration
1	10 m^3	50 kg/m^3
2	7 m^3	45 kg/m^3
3	15 m^3	40 kg/m^3
4	12 m^3	52 kg/m^3

$$Y_{av} = \frac{10 \times 50 + 7 \times 45 + 15 \times 40 + 12 \times 52}{10 + 7 + 15 + 12} = 46.3 \text{ kg/m}^3 \qquad (30)$$

For the Van Kleeck equation, the averages of VS are required. Properly they should be weighted averages based on the weight of the solids in each component of the average although an average weighted by the volume of the component or an arithmetic average may be sufficiently accurate if variation in VS is small. The following example demonstrates the calculation of all three averages.

Addition	Volume	Total Solids Concentration	VS
1	12 m^3	72 kg/m^3	0.75
2	8 m^3	50 kg/m^3	0.82
3	13 m^3	60 kg/m^3	0.80
4	10 m^3	55 kg/m^3	0.77

Weighted by Mass

$$VS\ av = \frac{12 \times 72 \times 0.75 + 8 \times 50 \times 0.82 + 13 \times 60 \times 0.80 + 10 \times 55 \times 0.77}{12 \times 72 + 8 \times 50 + 13 \times 60 + 10 \times 55} = 0.795 \quad (31)$$

Weighted by Volume

$$VS\ av = \frac{12 \times 0.75 + 8 \times 0.82 + 13 \times 0.80 + 10 \times 0.77}{12 + 8 + 13 + 10} = 0.783 \quad (32)$$

Arithmetic Average

$$VS\ av = \frac{0.75 + 0.82 + 0.80 + 0.77}{4} = 0.785 \quad (33)$$

In this example the arithmetic average was nearly as close as the volume-weighted average to the mass-weighted average, which is the correct value.

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2. U.S. EPA, Code of Federal Regulations, Title 40, part 257 (40 CFR 257), "Part 257--Criteria for Classification of Solid Waste Disposal Facilities and Practices."

3. Water Pollution Control Federation, Manual of Practice No. 16, "Anaerobic Sludge Digestion," pub. Water Pollution Control Federation, Washington, DC (1968).

4. Van Kleeck, L.W., Sewage Works J., 17 (6), 1240-1255 (1945), "Operation of sludge drying and gas utilization units," Refer to footnote on p 1241.

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TABLE 1

QUANTITATIVE INFORMATION FOR EXAMPLE PROBLEMS [1,2,3]

Parameter	Symbol	Units	Problem Statement Number 1	2	3	4
Nominal residence time	Θ	d	20	20	20	20
Time period for averages		d	60	60	60	60
Feed Sludge						
Volumetric flow rate	F	m^3/d	100	100	100	100
Volatile solids concentration	Y_f	kg/m^3	50	50	50	50
Fixed solids concentration	X_f	kg/m^3	17	17	17	17
Fraction volatile solids	VS_f	kg/kg	0.746	0.746	0.746	0.746
Mass flow rate of solids	M_f	kg/d	6700	6700	6700	6700
Digested Sludge (Bottoms)						
Volumetric flow rate	B	m^3/d	100	100		49.57
Volatile solids concentration	Y_b	kg/m^3	30	30	41.42	41.42
Fixed solids concentration	X_b	kg/m^3	17	15	23.50	23.50
Fraction volatile solids	VS_b	kg/kg	0.638	0.667	0.638	0.638
Mass flow rate of solids	M_b	kg/d	4700	4500		
Decantate						
Volumetric flow rate	D	m^3/d	0	0		50.43
Volatile solids concentration	Y_d	kg/m^3	-	-	12.76	12.76
Fixed solids concentration	X_d	kg/m^3	-	-	7.24	7.24
Fraction volatile solids	VS_d	kg/kg	-	-	0.638	0.638
Mass flow rate of solids	M_d	kg/d	-	-		

1. Conditions are steady state; all daily flows are constant. Volatile solids are not accumulating in the digester, although grit may be settling out in the digester.

2. Numerical values are given at 3 or 4 significant figures. This is unrealistic considering the expected accuracy in measuring solids concentrations and sludge volumes. The purpose of extra significant figures is to allow more understandable comparisions to be made of the different calculation methods.

3. All volatile solids concentrations are based on the total solids, not merely on the suspended solids.

United States
Environmental Protection
Agency

Environmental Regulations and Technology

Control of Pathogens and Vector Attraction in Sewage Sludge

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Revised July 2003

Environmental Regulations and Technology

Control of Pathogens and Vector Attraction in Sewage Sludge

(Including Domestic Septage)
Under 40 CFR Part 503

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Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threaten human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

Hugh W. McKinnon, Director
National Risk Management Research Laboratory

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Chapter 1
Introduction

1.1 What is Sewage Sludge?

Sewage sludge - the residue generated during treatment of domestic sewage (Figure 1-1) - is often used as an organic soil conditioner and partial fertilizer in the United States and many other countries. It is applied to agricultural land (pastures and cropland), disturbed areas (mined lands, construction sites, etc.), plant nurseries, forests, recreational areas (parks, golf courses, etc.), cemeteries, highway and airport runway medians, and home lawns and gardens (see photographs, pages 2 and 3). Certain treatment works (POTWs) own or have access to land dedicated solely to disposal of sewage sludge, a practice referred to as surface disposal. The U.S. Environmental Protection Agency (EPA), the primary federal agency responsible for sewage sludge management, encourages the beneficial use of sewage sludge through land application (Figure 1-2), after it has been appropriately treated for its intended use. In 1995 it was found that 54% of sewage sludge generated in the United States was land applied (Bastian, 1997).

Sewage sludge has beneficial plant nutrients and soil conditioning properties; however, it may also contain pathogenic bacteria, viruses, protozoa, parasites, and other microorganisms that can cause disease. Land application and surface disposal of untreated sewage sludge create a potential for human exposure to these organisms through direct and indirect contact. To protect public health from these organisms and from the pollutants that some sewage sludge contains, many countries now regulate the use and disposal of sewage sludge.

"Sewage Sludge" vs. "Biosolids"

Throughout the wastewater and sewage sludge industry, the term "sewage sludge" has largely been replaced by the term "biosolids." "Biosolids" specifically refers to sewage sludge that has undergone treatment and meets federal and state standards for beneficial use. The distinction between untreated sewage sludge and biosolids that have undergone processing and analysis will be made throughout this document.

What is Beneficial Use?

For the purposes of this document, land application is considered to be beneficial use. The document specifically deals with land application and the issues related to the pathogen and vector attraction reduction requirements for

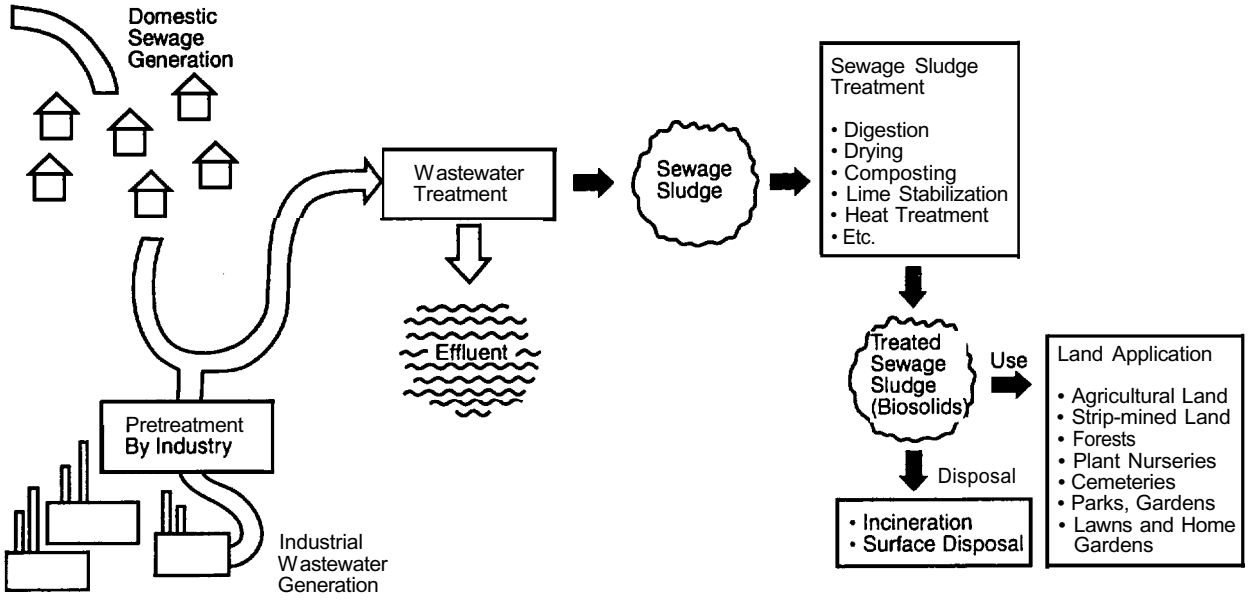

Figure 1-1. Generation, treatment, use, and disposal of sewage sludge.

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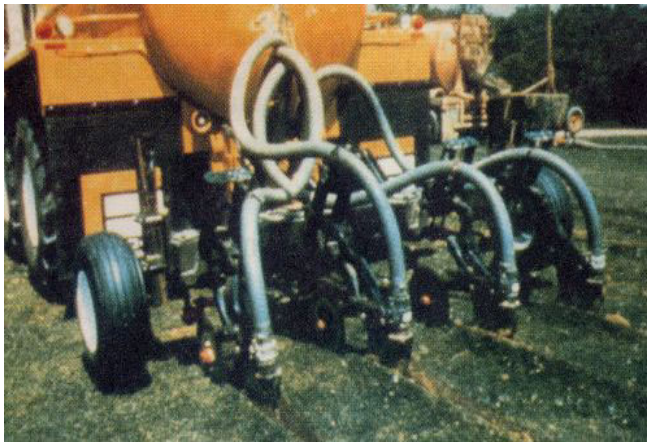
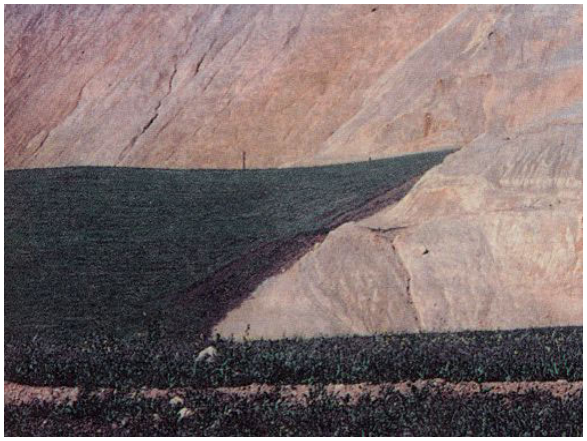
Highway median strip in Illinois after land application of dried sludges.
(Photo courtesy of Metropolitan Water Reclamation District of Greater Chicago)

Flower beds amended with sludge compost at the Betty Ford Alpine Gardens, Vail, CO.

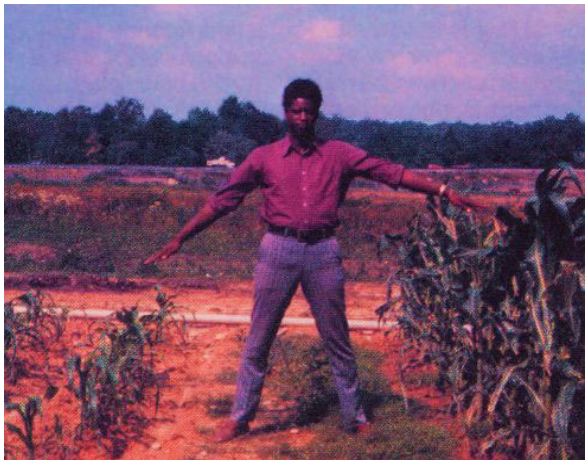


Injection of liquid sludge into sod.

Oat field showing sludge-treated (right) and untreated (left) areas.
(Photo courtesy of City of Tulsa, Oklahoma)



Reclaimed mine spoil land. Kennecott Copper near Salt Lake City, Utah.



Corn grown on sludge-treated soil (right) and untreated soil (left).

Mine spoil land sludge treatment. Note lush vegetative cover on reclaimed soil which will support grazing. (Photo courtesy of City of Tulsa, Oklahoma)

Cross-sectlon of popular trees showing how sludge application increases tree growth. Both cross sections are 8 years old; the larger is aprox. 8 inches in diameter.
(Photo courtesy of Mike VanHam, British Columbia, Canada)

The U.S. Environmental Protection Agency (EPA) will actively promote those municipal sludge management practices that provide for the beneficial use of sewage sludge while maintaining or improving environmental quality and protecting human health. To implement this policy, EPA will continue to issue regulations that protect public health and other environmental values. The Agency will require states to establish and maintain programs to ensure that local governments utilize sewage sludge management techniques that are consistent with federal and state regulations and guidelines. Local communities will remain responsible for choosing among alternative programs; for planning, constructing, and operating facilities to meet their needs; and for ensuring the continuing availability of adequate and acceptable disposal or use capacity.

Figure 1-2. EPA policy on sewage sludge management. Source: EPA, 1984.

land applied biosolids. For more information on the pathogen and vector attraction reduction requirements for the surface disposal of biosolids, please refer to Section 503.25 of the regulation.

1.2 U.S. Regulation of Treated Sewage Sludge (Biosolids)

In the United States, the use and disposal of treated sewage sludge (biosolids), including domestic septage, are regulated under 40 CFR Part 503[1] .This regulation, promulgated on February 19, 1993, was issued under the authority of the Clean Water Act (CWA) as amended in 1977 and the 1976 Resource Conservation and Recovery Act (RCRA). For most sewage sludge[2], the new regulation replaces 40 CFR 257, the original regulation governing the use and disposal of sewage sludge, which has been in effect since 1979.

The EPA policy shown below was developed in response to specific language in the CWA and RCRA federal policy statements in order to facilitate and encourage the beneficial reuse of sewage sludge (U.S. EPA, 1984).

Protection of Public Health and the Environment

Subpart D of the Part 503 regulation protects public health and the environment through requirements designed to reduce the potential for contact with the disease-bearing microorganisms (pathogens) in sewage sludge applied to the land or placed on a surface disposal site. These requirements are divided into:

- Requirements designed to control and reduce pathogens in treated sewage sludge (biosolids)
- Requirements designed to reduce the ability of the treated sewage sludge (biosolids) to attract vectors (insects and other living organisms that can transport biosolids pathogens away from the land application or surface disposal site)

Subpart D includes both performance and technology based requirements. It is designed to provide a more flexible approach than the approach in the Part 257, which required sewage sludge to be treated by specific listed or approved treatment technologies. Under Part 503, treatment works may continue to use the same processes they used under Part 257, but they now also have the freedom to modify conditions and combine processes with each other, as long as the applicable Part 503 requirements are met.

Environmental Effects of Pathogens in Sewage Sludge

Because of concern over the effect of pathogens from biosolids on animal health (certain human pathogens can cross species lines and infect animals, particularly warm blooded animals) the 503 regulations require that sewage sludge undergo pathogen treatment prior to land application. For sewage sludge subject to Class B pathogen treatment site restrictions are also required. While relatively little research has been conducted on specific inter-species crossover to wildlife, more information is available for grazing animals which are more likely to have a greater exposure to biosolids than wildlife. Available information on the impact of biosolids pathogens on grazing animals suggests that the Part 503 Subpart D requirements for pathogen control (which include restrictions on grazing) protect grazing animals (EPA, 1992). References regarding the impact of biosolids application on both wild and domestic animals are included at the end of this chapter.

1.3 Implementation Guidance

This document is not regulatory in nature. A complete copy of Subpart D of the Part 503 Regulation appears in Appendix B. This document is only intended to serve as a guide to pathogen and vector attraction reduction for anyone who is involved with the treatment of sewage sludge for land application. This includes:

- Owners and operators of domestic sewage treatment works
- Developers or marketers of sewage sludge treatment processes
- Groups that distribute and market biosolids products
- Individuals involved in applying biosolids to land
- Regional, state, and local government officials responsible for implementing and enforcing the Part 503 Subpart D regulation

[1] Because domestic septage is a form of sewage sludge, any use of the term "sewage sludge" in this document includes domestic septage.

[2] Sewage sludge generated at an industrial facility during the treatment of domestic sewage commingled with industrial wastewater in an industrial wastewater treatment facility is still covered under 40 CFR Part 257 if the sewage sludge is applied to the land.

- Consultants to these groups
- Anyone interested in understanding the federal requirements concerning pathogens in sewage sludge

This guide was previously released in 1993. The updates and amendments to this document are a product of comments and suggestions from the regulatory and sewage sludge management community. This edition of the document includes clarification of many of the sampling and monitoring issues and reflects the increased understanding of analytical issues. There are additional operational guidelines and examples of how a variety of facilities have complied with the Part 503 requirements. Some of the notable additions to this edition include:

- Clarification of Class A processes
- More specific guidelines for the operation of composting facilities
- More information on site restrictions including permit conditions which may apply to specific crops
- Recommendation for the use of the Kenner and Clark methodology for *Salmonella* sp. bacteria analysis
- Guidelines for retesting biosolids products that have been stored or remixed
- More information on public health and pathogens
- More information on sampling and monitoring protocols
- Updates on the Pathogen Equivalency Committee and approved processes

Other publications related to pathogen or vector attraction issues include the "Technical Support Document for Reduction of Pathogens and Vector Attraction in Sewage Sludge" (U.S. EPA, 1992) and "Part 503 Implementation Guidance" (U.S. EPA, 1995). Although the federal regulation under 40 CFR Part 503 includes restrictions for pollutant concentrations and application rates, this document is intended to clarify pathogen and vector related requirements and does not discuss pollutant limits.

This document does not discuss the general requirements and management practices which must be followed for land application of all biosolids except in the case of "exceptional quality" biosolids which have met certain pollutant limits and pathogen and vector attraction reduction requirements. In addition to meeting the regulation set forth in this document, bulk biosolids application must be conducted in accordance with agronomic rates, and biosolids appliers must ensure that applied biosolids are not applied within 10 meters of any water body, do not enter surface waters or wetlands without the approval of the appropriate permitting authority, and do not adversely affect endangered or threatened species or their habitats.

It should be noted that the Part 503 regulation and the sampling and monitoring requirements outlined in the regulation were developed as minimum requirements. EPA supports the beneficial use of treated sewage sludge (biosolids) and encourages facility operators and generators of biosolids products to develop sampling and monitoring plans that go beyond the minimum regulatory requirements as needed to ensure consistent product quality.

For most states, the authority for implementing the Part 503 regulation currently remains with the Regional EPA offices. A guide to EPA offices and relevant contacts can be found in Appendix A.

1.4 Definitions

The sections of this document that discuss specific regulatory requirements utilize the same terminology used throughout the Part 503 regulation in order to maintain consistency between the regulation and this guidance document. However, in some parts of this document, particularly in sections which discuss operational parameters and other issues related to biosolids management, terms which are not formally defined by the regulations are used. The following glossary has been provided in order to prevent confusion about the intent and jurisdiction of the Part 503 regulation.

Applier - The applier is the individual or party who land applies treated sewage sludge (biosolids). This may include farmers, municipalities, and private enterprises that land apply or their contractors.

Biosolids - Sewage sludge that has been treated and meets state and federal standards for land application.

Control - Some of the regulatory requirements make a distinction based on whether the biosolids preparer (see below) has "control" over the material. A preparer loses control over material when it is sold or given away. Until that point, the material is still within the control of the preparer even if the treatment process has ended and the material is in storage on or off-site.

Detectable Limits - Minimum concentration at which an analyte can be measured. The detectable limit for any given analyte varies depending on the lab methodology used and the volume of material analyzed. As such, detectable limits may fluctuate. Throughout this document, the term "detectable limit" refers to the limits as they are defined in the allowable lab methodologies outlined in the Appendices.

Exceptional Quality (EQ) Biosolids - The term "EQ" is not used in the Part 503 regulation, but it has become a useful description for regulators and biosolids preparers when referring to biosolids that meet the pollutant concentration limits of Table 3 of Section 503.13, Class A pathogen reduction, and one of the first eight treatment processes for meeting vector attraction reduction standards. Biosolids that fall into this category are not subject to the Part 503 general requirements and management practices for land application.

Preparer - The person(s) who generate biosolids from the treatment of domestic sewage in a treatment works or change the quality of the sewage sludge received from the generator. This includes facilities that derive a material from sewage sludge prior to land application of the material which could include wastewater treatment facilities, composting or other sewage sludge processing operations, and soil blenders who handle non-EQ biosolids materials. A soil blender who takes EQ biosolids and mixes them with other (non-sewage sludge) materials for land application is not a preparer. However, a soil blender that takes non-EQ biosolids and mixes it with other materials for land application is a preparer.

Product - This may include materials such as composted, heat-dried, lime stabilized, alkaline stabilized, or otherwise processed biosolids which have met the requirements of the Part 503. The term "product" is sometimes used in this document in discussions regarding material distribution. The term "sludge derived material" is used in the Part 503 to refer to these materials.

Sewage Sludge - The solid, semi-solid, or liquid residue generated during the treatment of municipal sewage in a treatment works. The term "biosolids" refers to sewage sludge which has undergone treatment and meets state and federal requirements for land application. The distinction between untreated sewage sludge and treated biosolids is made throughout this document.

1.5 Pathogen Equivalency Committee

The Pathogen Equivalency Committee (PEC) is made up of U.S. EPA experts who review pathogen and vector attraction reduction issues and make recommendations to the appropriate permitting authority. The primary role of the PEC is to review proposals for Processes to Significantly Reduce Pathogens (PSRP) and Processes to Further Reduce Pathogens (PFRP) equivalency determinations and to offer guidance on the issues associated with pathogen and vector attraction reduction.

More information on the PEC and the process of applying for equivalency is presented in Chapter 11.

1.6 What is in this Document?

Chapter 2 of this document provides basic information about pathogens and describes why pathogen control is required to protect public health and the environment, and Chapters 3 through 5 discuss the current federal requirements under Subpart D of Part 503. Chapters 6 and 7 review the different PFRP and PSRP processes, and Chapter 8 discusses vector attraction reduction issues. Chapters 9 and 10 summarize sampling and analysis protocols used to meet the quantitative requirements of Part 503. Chapter 11 outlines the process for applying for equivalency and discusses the kind of support EPA's Pathogen Equivalency Committee can provide to permitting authorities. Chapter 12 lists general references and additional resources related to biosolids use; specific references related to particular topics are also included at the end of each chapter.

The Appendices provide additional information on:

- Determination of volatile solids and residence time for digestion
- Sample preparation and analytical methods for meeting the Part 503 pathogen reduction requirements
- Tests for demonstrating vector attraction reduction
- Additional references on pathogen research and technical background to regulations

Appendix A lists EPA and state sewage sludge coordinators, and Appendix B contains Subpart D of the Part 503 regulation.

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Chapter 2
Sewage Sludge Pathogens

2.1 What are Pathogens?

A pathogen is an organism or substance capable of causing disease. The Part 503 regulation only discusses pathogenic organisms, and throughout this document, "pathogen" refers only to living organisms, except where specified. Pathogens infect humans through several different pathways including ingestion, inhalation, and dermal contact. The infective dose, or the number of a pathogenic organism to which a human must be exposed to become infected, varies depending on the organism and on the health status of the exposed individual.

Pathogens that propagate in the enteric or urinary systems of humans and are discharged in feces or urine pose the greatest risk to public health with regard to the use and disposal of sewage sludge. Pathogens are also found in the urinary and enteric systems of other animals and may propagate in non-enteric settings. However, because this document is concerned with the regulation of sewage sludge, this chapter focuses on the pathogens most commonly found in the human enteric system.

2.2 Pathogens in Sewage Sludge

What pathogens can be found in sewage sludge?

The four major types of human pathogenic (disease-causing) organisms (bacteria, viruses, protozoa, and helminths) all may be present in domestic sewage. The actual species and quantity of pathogens present in the domestic sewage from a particular municipality (and the sewage sludge produced when treating the domestic sewage) depend on the health status of the local community and may vary substantially at different times. The level of pathogens present in treated sewage sludge (biosolids) also depends on the reductions achieved by the wastewater and sewage sludge treatment processes.

The pathogens in domestic sewage are primarily associated with insoluble solids. Primary wastewater treatment processes concentrate these solids into sewage sludge, so untreated or raw primary sewage sludges have higher quantities of pathogens than the incoming wastewater. Biological wastewater treatment processes such as lagoons, trickling filters, and activated sludge treatment may substantially reduce the number of pathogens in the wastewater (EPA, 1989). These processes may also reduce the number of pathogens in sewage sludge by creating adverse conditions for pathogen survival.

Nevertheless, the resulting biological sewage sludges may still contain sufficient levels of pathogens to pose a public health and environmental concern. Part 503 Regulation thus requires sewage sludge to be treated by a Class A pathogen treatment process or a Class B process with site restrictions. These requirements prevent disease transmission. Table 2-1 lists some principal pathogens of concern that may be present in wastewater and sewage sludge. These organisms and other pathogens can cause infection or disease if humans and animals are exposed to sufficient levels of the organisms or pathogens. The levels, called infectious doses, vary for each pathogen and each host.

As mentioned in Chapter 1, one concern is the potential effect of some human pathogens on animals. Enteric viruses can cross species lines, and animal life, particularly warm blooded animals, can be affected if they are exposed to some of the pathogens found in sewage sludge. Domestic animals are protected by site restrictions which limit grazing on sludge amended land.

How could exposure to these pathogens occur?

If improperly treated sewage sludge was illegally applied to land or placed on a surface disposal site, humans and animals could be exposed to pathogens directly by coming into contact with the sewage sludge, or indirectly by consuming drinking water or food contaminated by sewage sludge pathogens. Insects, birds, rodents, and even farm workers could contribute to these exposure routes by transporting sewage sludge and sewage sludge pathogens away from the site. Potential routes of exposure include:

Direct Contact

- Touching the sewage sludge.
- Walking through an area - such as a field, forest, or reclamation area - shortly after sewage sludge application.
- Handling soil from fields where sewage sludge has been applied.

Table 2-1. Principal Pathogens of Concern in Domestic Sewage and Sewage Sludge

Organism	Disease/Symptoms
Bacteria	
Salmonella sp.	Salmonellosis (food poisoning), typhoid fever
Shigella sp.	Bacillary dysentery
Yersinia sp.	Acute gastroenteritis (including diarrhea, abdominal pain)
Vibrio cholerae	Cholera
Campylobacter jejuni	Gastroenteritis
Escherichia coli (pathogenic strains)	Gastroenteritis
Enteric Viruses	
Hepatitis A virus	Infectious hepatitis
Norwalk and Norwalk-like viruses	Epidemic gastroenteritis with severe diarrhea
Rotaviruses	Acute gastroenteritis with severe diarrhea
Enteroviruses	
Polioviruses	Poliomyelitis
Coxsackieviruses	Meningitis, pneumonia, hepatitis, fever, cold-like symptoms, etc.
Echoviruses	Meningitis, paralysis, encephalitis, fever, cold-like symptoms, diarrhea, etc.
Reovirus	Respiratory infections, gastroenteritis
Astroviruses	Epidemic gastroenteritis
Caliciviruses	Epidemic gastroenteritis
Protozoa	
Cryptosporidium	Gastroenteritis
Entamoeba histolytica	Acute enteritis
Giardia lamblia	Giardiasis (including diarrhea, abdominal cramps, weight loss)
Balantidium co/i	Diarrhea and dysentery
Toxoplasma gondii	Toxoplasmosis
Helminth Worms	
Ascaris lumbricoides	Digestive and nutritional disturbances, abdominal pain, vomiting, restlessness
Ascaris suum	May produce symptoms such as coughing, chest pain, and fever
Trichuris trichiura	Abdominal pain, diarrhea, anemia, weight loss
Toxocara canis	Fever, abdominal discomfort, muscle aches, neurological symptoms
Taenia saginafa	Nervousness, insomnia, anorexia, abdominal pain, digestive disturbances
Taenia solium	Nervousness, insomnia, anorexia, abdominal pain, digestive disturbances
Necator americanus	Hookworm disease
Hymenolepis nana	Taeniasis

Source: Kowal (1985) and EPA (1989).

- Inhaling microbes that become airborne (via aerosols, dust, etc.) during sewage sludge spreading or by strong winds, plowing, or cultivating the soil after application.

Indirect Contact

- Consumption of pathogen-contaminated crops grown on sewage sludge-amended soil or of other food products that have been contaminated by contact with these crops or field workers, etc.
- Consumption of pathogen-contaminated milk or other food products from animals contaminated by grazing in pastures or fed crops grown on sewage sludge-amended fields.
- Ingestion of drinking water or recreational waters contaminated by runoff from nearby land application sites or by organisms from sewage sludge migrating into ground-water aquifers.
- Consumption of inadequately cooked or uncooked pathogen-contaminated fish from water contaminated by runoff from a nearby sewage sludge application site.
- Contact with sewage sludge or pathogens transported away from the land application or surface disposal site by rodents, insects, or other vectors, including grazing animals or pets.

The purpose of the Part 503 regulation is to place barriers in the pathway of exposure either by reducing the number of pathogens in the treated sewage sludge (biosolids) to below detectable limits, in the case.of Class A treatment, or, in the case of Class B treatment, by preventing direct or indirect contact with any pathogens possibly present in the biosolids.

Each potential pathway has been studied to determine how the potential for public health risk can be alleviated. The references listed at the end of this chapter include some of the technical writings which summarize the research on which the Part 503 regulation is based.

For example, the potential for public health impacts via inhalation of airborne pathogens was examined. Pathogens may become airborne via the spray of liquid biosolids from a splash plate or high-pressure hose, or in fine particulate dissemination as dewatered biosolids are applied or incorporated. While high-pressure spray applications may result in some aerosolization of pathogens, this type of equipment is generally used on large, remote sites such as forests, where the impact on the public is minimal. Fine particulates created by the application of dewatered biosolids or the incorporation of biosolids into soil may cause very localized fine particulate/dusty conditions, but particles in dewatered biosolids are too large to travel far, and the fine particulates do not spread beyond the immediate area. The activity of applying and incorporating biosolids may create dusty conditions. However, the biosolids are moist materials and do not add to the dusty conditions, and by the time biosolids have dried sufficiently to create fine particulates, the pathogens have been reduced (Yeager and Ward, 1981)

The study of each pathway and the potential for public health risk resulted in site restrictions that are protective of public health and the environment and that must be followed when Class B biosolids are land applied. While the site restrictions provided in the Part 503 rule are sufficient to protect the public from health impacts, workers exposed to Class B biosolids might benefit from several additional precautions. For example, dust masks should be worn for the spreading of dry materials, and workers should wash

their hands carefully after working with sewage sludge or biosolids. Other recommended practices for workers handling biosolids or sewage sludge include:

- Wash hands before eating, drinking, smoking or using the restroom.
- Use gloves when touching biosolids or sewage sludge or surfaces exposed to biosolids or sewage sludge.
- Remove excess sewage sludge or biosolids from shoes prior to entering an enclosed vehicle.
- Keep wounds covered with clean, dry bandages.
- If contact with biosolids or sewage sludge occurs, wash contact area thoroughly with soap and water.

Table 2-2 shows the various pathways of exposure and how the process requirements and site restrictions of the Part 503 regulation protect public health for each pathway.

Table 2-2. Pathways of Exposure and Applicable Site Restrictions (Class B Biosolids Only)

Pathways	Part 503 Required Site Restriction
Handling soil from fields where sewage sludge has been applied	No public access* to application sites until at least 1 year after Class B biosolids application.
Handling soil or food from home gardens where sewage sludge has been applied	Class B biosolids may not be applied on home gardens.
Inhaling dust**	No public access to application sites until at least 1 year after Class B biosolids application.
Walking through fields where sewage sludge has been applied*	No public access to fields until at least 1 year after Class B biosolids application.
Consumption of crops from fields on which sewage sludge has been applied	Site restrictions which prevent the harvesting of crops until environmental attenuation has taken place.
Consumption of milk or animal products from animals grazed on fields where sewage sludge has been applied	No animal grazing for 30 days after Class B biosolids have been applied.
Ingestion of water contaminated by runoff from fields where sewage sludge has been applied	Class B biosolids may not be applied within 10 meters of any waters in order to prevent runoff. from biosolids amended land from affecting surface water.
Ingestion of inadequately cooked fish from water contaminated by runoff from fields where sewage sludge has been applied	Class B biosolids may not be applied within 10 meters of any waters in order to prevent runoff from biosolids amended land from affecting surface water.
Contact with vectors which have been in contact with sewage sludge	All land applied biosolids must meet one of the Vector Attraction Reduction options (see Chapter 8).

*Public access restrictions do not apply to farm workers. If there is low probability of public exposure to an application site, the public access restrictions apply for only 30 days. However, application sites which are likely to be accessed by the public, such as ballfields, are subject to 1 year public access restrictions.

**Agricultural land is private property and not considered to have a high potential for public access. Nonetheless, public access restrictions still are applied.

2.3 General Information on Pathogens

The EPA has attempted, through this and other documents, to provide the public with a broad understanding of the risk assessment and scientific basis of the Part 503 regulation. The regulation is based on the results of extensive research and experience with land application of treated sewage sludge (biosolids). However, as for all regulations, proper interpretation and implementation of the regulation are the most important aspects of protecting public health and the environment.

Biosolids preparers should have a basic knowledge of microbiology so that they can:

- Understand the goals of the Part 503 regulation and what is expected to meet the requirements
- Address questions regarding pathogens and the protection of public health and the environment
- Design appropriate testing/sampling programs to meet the Part 503 requirements
- Make informed decisions about laboratory and analytical methodology selection

This section outlines some of the generic issues of pathogen testing and quantification. References related to these issues are listed at the end of this chapter as well as in Chapter 12. Other chapters discuss sampling and sample preservation as well as meeting the Part 503 requirements in more detail.

Survivability of Pathogens

Wastewater generally contains significantly high concentrations of pathogens which may enter the wastewater system from industries, hospitals, and infected individuals. The wastewater treatment process tends to remove pathogens from the treated wastewater, thereby concentrating the pathogens in the sewage sludge. Like any other living organisms, pathogens thrive only under certain conditions. Outside of these set conditions, survivability decreases. Each pathogen species has different tolerance to different conditions; pathogen reduction requirements are therefore based on the need to reduce all pathogenic populations. Some of the factors which influence the survival of pathogens include pH, temperature, competition from other microorganisms, sunlight, contact with host organisms, proper nutrients, and moisture level.

The various Class A and Class B pathogen reduction processes as well as the site restrictions for the land appli-

cation of Class B biosolids are based on research regarding the survivability of pathogens under specific treatment conditions. Table 2-3 shows a comparison of the survival of bacteria, viruses, and parasites in different sewage sludge treatments. Table 2-4 shows the survival time of various pathogens on soil or plant surfaces after land application of biosolids.

Identification of Pathogens

Some of the pathogens of concern that appear in domestic sewage and sewage sludge are shown in the photographs on pages 12 and 13. These include ascarids *(Ascaris lumbricoides* and *Toxacara),* whipworms *(Trichuris* sp.), tapeworms *(Hymenolepis* sp. and *Taenia* sp.), amoeba (*Entamoeba coli*), and giardia *(Giardia lamblia).* As shown in these photographs, several color staining procedures are needed to identify the organisms and the different structures within the organisms. The photograph of *Giardia lamblia* depicts specimens stained with Lugol's iodine solution, showing two nuclei, a median body, and axonemes in each. In addition, scientists use a blue filter when photographing the pathogenic organisms through a microscope. This filter is necessary to show the natural color of the organisms.

What Units are Used to Measure Pathogens?

Density of microorganisms in Part 503 is defined as number *of microorganisms per unit mass of total solids (dry weight).* Ordinarily, microorganism densities are determined as number per 100 milliliters of wastewater or sewage sludge. While the use of units of volume is sensible for wastewater, it is less sensible for sewage sludge. Many microorganisms in sewage sludge are associated with the solid phase. When sewage sludge is diluted, thickened, or filtered, the number of microorganisms per unit volume changes markedly, whereas the number per unit mass of solids remains almost constant. This argues for reporting their densities as the number present per unit mass of solids, which requires that sewage sludge solids content always be determined when measuring microorganism densities.

A second reason for reporting densities per unit mass of total solids is that biosolids application to the land is typically measured and controlled in units of mass of dry solids per unit area of land. If pathogen densities are measured as numbers per unit mass of total solids, the rate of pathogen application to the land is directly proportional to the mass of dry biosolids applied.

Table 2-3. Summary of the Effects of Sewage Sludge Treatment on Pathogens (Log Reductions Shown*)

PSRP Treatment	Bacteria	Viruses	Parasites (protozoa and helminths)
Anaerobic Digestion	0.5-4.0	0.5-2.0	0.5
Aerobic Digestion	0.5-4.0	0.5-2.0	0.5
Composting (PSRP)	2.0-4.0	2.0-4.0	2.0-4.0
Air Drying	0.5-4.0	0.5-4.0	0.5-4.0
Lime Stabilization	0.5-4.0	4.0	0.5

*A 1-log reduction (10-fold) is equal to a 90% reduction. Class B processes are based on a 2-log reduction.

Table 2-4. Survival Times of Pathogens in Soil and on Plant Surfaces[a]

	Soil		Plants	
Pathogen	Absolute Maximum[a]	Common Maximum	Absolute Maximum[b]	Common Maximum
Bacteria	1 year	2 months	6 months	1 month
Viruses	1 year[c]	3 months	2 months	1 month
Protozoan cysts[d]	10 days	2 days	5 days	2 days
Helminth ova	7 years	2 years	5 months	1 month

[a] For survival rates, see Sorber and Moore (1986).
[b] Absolute maximum survival times are possible under unusual conditions such as consistently low temperatures or highly sheltered conditions (e.g., helminth ova below the soil in fallow fields) (Kowal, 1985).
[c] Solisey and Shields, 1987.
[d] Little, if any, data are available on the survival times of Giardia cysts and Cryptosporidium oocysts.
Source: Kowal, 1985.

Different Methods for Counting Microorganisms

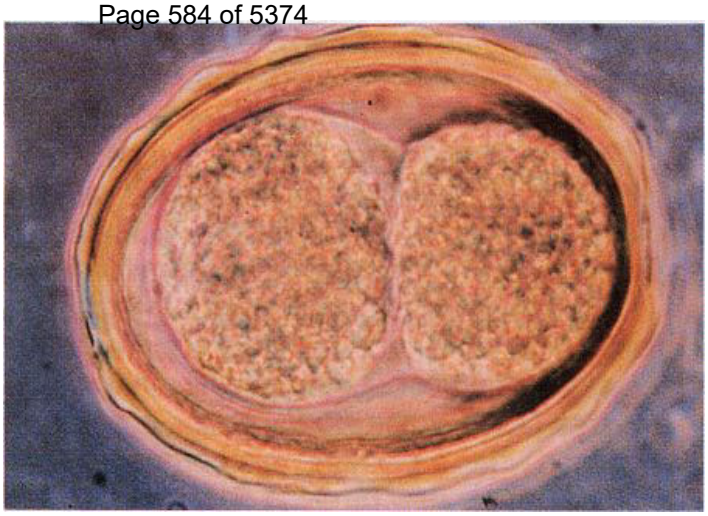
The methods and units used to count microorganisms vary depending on the type of microorganism. Viable helminth ova are observed and counted as individuals (numbers) under a microscope. Viruses are usually counted in plaque-forming units (PFU). Each PFU represents an infection zone where a single infectious virus has invaded and infected a layer of animal cells. For bacteria, the count is in colony-forming units (CFU) or most probable number (MPN). CFU is a count of colonies on an agar plate or filter disk. Because a colony might have originated from a clump of bacteria instead of an individual, the count is not necessarily a count of separate individuals. MPN is a statistical estimate of numbers in a sample. The sample is diluted at least once into tubes containing nutrient medium. The tubes are maintained under conditions favorable for bacterial growth. The original bacterial density in the sample is estimated based on the number of tubes that show growth and the level of dilution in those tubes.

Part 503 Density Limits

Under Part 503, the density limits for the pathogens are expressed as numbers of PFUs, CFUs, or MPNs per 4 grams dry weight sewage sludge. This terminology came about because most of the tests started with 100 ml of sewage sludge which typically contained 4 grams of sewage sludge solids. Also, expressing the limits on a "per gram" basis would have required the use of fractions (i.e., 0.25/g or 0.75/g). Density limits for fecal coliforms, the indicator organisms, however, are given on a "per gram" basis because these organisms are much more numerous than pathogens.

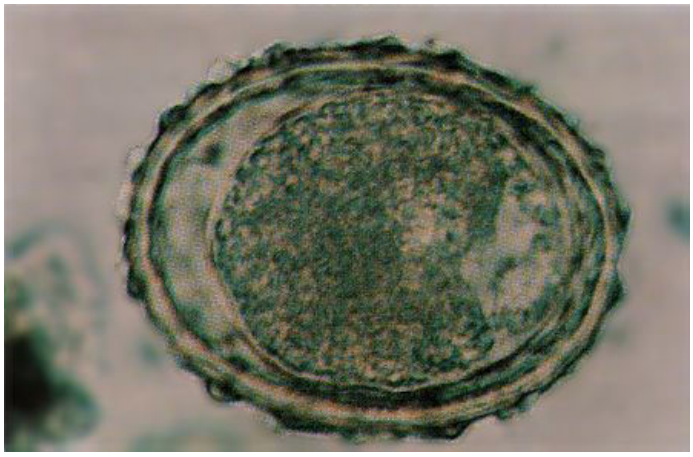
2.4 Protecting Public Health - The Part 503

The Part 503 regulation protects public health by limiting the potential for public exposure to pathogens. This is



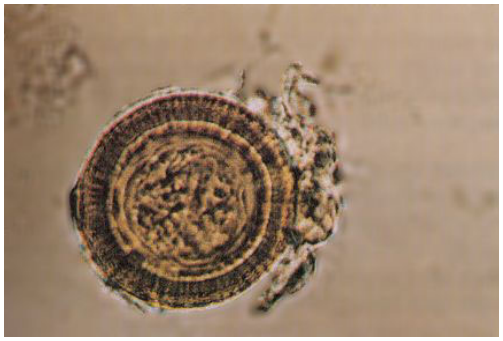
Ascaris lumbricoides **(or var. suum) eggs, 66 µm, from anaerobically digested sludge. Two-cell stage.** (Photos on this page courtesy of Fox et al., 1981)

Toxocara **sp. egg, 90 µm from raw sewage.**



Ascaris lumbricoides **(or var. suum) eggs, 65 µm, from anaerobically digested sludge.**

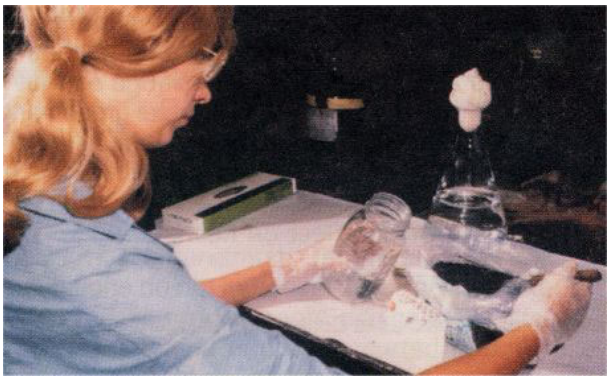
Trichuris sp. **egg, 60 µm from anaerobically digested sludge.**



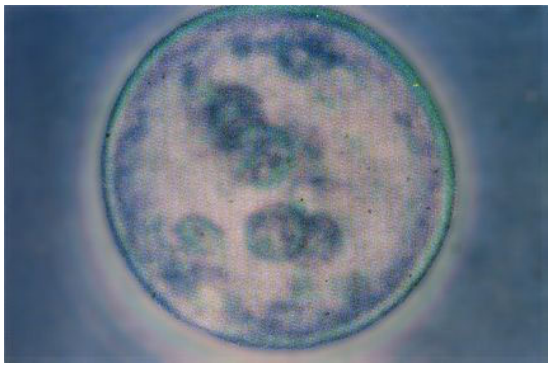
Taenia sp. ovum. (Photo courtesy of Fox et al., 1981)

***Giardia lamblia* cysts.** (Photo courtesy of Frank Schaefer, U.S. EPA, National Risk Management Research Laboratory, Cincinnati, Ohio)

***Hymenolepis* (tapeworm) ova.** (Photo courtesy of Fox et al., 1981)



Preparing compost for pathogen analysis. (Photo courtesy of U.S. Department of Agriculture, Beltsville, Maryland)



***Entamoeba coli* cysts, 15 µm from anaerobically digested sludge.** (Photo courtesy of Fox et al., 1981)

accomplished through treatment of the sewage sludge or through a combination of sewage sludge treatment and restrictions on the land application site that prevent exposure to the pathogens in the biosolids and allow time for the environment to reduce the pathogens to below detectable levels. The Part 503 vector attraction reduction requirements also help reduce the spread of pathogens by birds, insects, and other disease carriers (i.e. vectors) by requiring that all sewage sludge that is to be land applied undergo vector attraction reduction.

The Part 503 regulation also establishes the analytical protocol for pathogen analysis. More information on the quantification of pathogens and how pathogen reduction is measured is included in Chapter 10 and in the Appendices.

Reducing the Number of Pathogens

Pathogen reduction can be achieved by treating sewage sludge prior to use or disposal and through environmental attenuation. Many sewage sludge treatment processes are available that use a variety of approaches to reduce pathogens and alter the sewage sludge so that it becomes a less effective medium for microbial growth and vector attraction (Table 2-5). Processes vary significantly in their effectiveness. For example, some processes (e.g. lime stabilization) may effectively reduce bacteria and viruses but have little or no effect on helminth eggs. The effectiveness of a particular process can also vary depending on the conditions under which it is operated. For example, the length of time and the temperature to which sewage sludge is heated is critical to the effectiveness of heat-based treatment processes.

Part 503 lists sewage sludge treatment technologies that are judged to produce biosolids with pathogens sufficiently reduced to protect public health and the environment. The regulation also allows the use of any other technologies that produce biosolids with adequately reduced pathogens as demonstrated through microbiological monitoring. The Part 503 establishes two classifications of biosolids based on the level of pathogen reduction the biosolids have undergone. Class A biosolids are treated to the point at which pathogens are no longer detectable. For Class B biosolids, a combination of treatment and site restrictions are designed to protect public health and the environment.

Monitoring Indicator Species

Sewage sludge may contain numerous species of pathogenic organisms, and analyzing for each species is not practical. The microbiological requirements of the Part 503 are therefore based on the use of an indicator organism for the possible presence of pathological bacteria and both the representative and the hardiest of known species for viruses and helminths to represent the larger set of pathogenic organisms. The indicator and representative organ-

Table 2-5. General Approaches to Controlling Pathogens and Vector Attraction in Sewage Sludge

Approach	Effectiveness	Process Example [a]
Application of high temperatures (temperatures may be generated by chemical, biological, or physical processes).	Depends on time and temperature. Sufficient temperatures maintained for sufficiently long time periods can reduce bacteria, viruses, protozoan cysts, and helminth ova to below detectable levels. Helminth ova are the most resistant to high temperatures.	Composting (using biological processes to generate heat). Heat drying and heat treatment (use physical processes to generate heat, e.g., hot gases, heat exchangers). Pasteurization (physical heat, e.g., hot gases, heat exchangers). Aerobic digestion (biological heat)[b] Anaerobic digestion (physical heat)[b]
Application of radiation	Depends on dose. Sufficient doses can reduce bacteria, viruses, protozoan cysts, and helminth ova to below detectable levels. Viruses are most resistant to radiation.	Gamma and high-energy electron beam radiation.
Application of chemical disinfectants	Substantially reduces bacteria and viruses and vector attraction. Probably reduces protozoan cysts. Does not effectively reduce helminth ova unless combined with heat.	Lime stabilization
Reduction of the sewage sludge's volatile organic content (the microbial food source).	Reduces bacteria. Reduces vector attraction.	Aerobic digestion Anaerobic digestion Composting[b]
Removal of moisture from the sludge	Reduces viruses and bacteria. Reduces vector attraction as long as the sewage sludge remains dry. Probably effective in destroying protozoan cysts. Does not effectively reduce helminth ova unless combined with other processes such as high temperature.	Air or heat drying

[a] See Chapters 6 and 7 for a description of these processes. Many processes use more than one approach to reduce pathogens.
[b] Effectiveness depends on design and operating conditions.

isms are ones that have been found to respond to treatment processes and environmental conditions in a manner similar to other organisms. Monitoring the levels of these organisms, therefore, provides information about the survival of the larger group.

For example, for helminth ova, tests are employed to determine their presence and viability. The only helminth ova viability that can be determined is that of *Ascaris* sp. *Ascaris* is the hardiest of known helminths; thus, if conditions are such that it cannot survive, it is not possible for other helminth species *(Toxacara, Trichuris,* and *Hymenolepis)* to survive.

For viruses, a test is available that simultaneously monitors for several enterovirus species (a subset of enteric viruses - see Table 2-1), which are presumed to be good representatives for other types of enteric viruses.

Salmonella sp. are bacteria of great concern as well as good representatives of reduction of other bacterial pathogens because they are typically present in higher densities than are other bacterial pathogens and are at least as hardy.

Fecal coliforms are enteric bacteria that are used as indicators of the likelihood of the presence of bacterial pathogens. Although fecal coliforms themselves are usually not harmful to humans, their presence indicates the presence of fecal waste which may contain pathogens. These bacteria are commonly used as indicators of the potential presence of pathogens in sewage sludges. They are abundant in human feces and therefore are always present in untreated sewage sludges. They are easily and inexpensively measured, and their densities decline in about the same proportion as enteric bacterial pathogens when exposed to the adverse conditions of sludge processing (EPA, 1992).

In the case of Class B biosolids, the microbiological limit for meeting Alternative 1 is 2 million MPN fecal coliforms per gram dry weight. Because untreated sewage sludge generally contains up to 100 million MPN fecal coliforms per gram dry weight, this limit assumes an approximate 2-log reduction in the fecal coliform population. Studies of anaerobic or aerobic digestion of sludges have shown that the corresponding reduction in the pathogen population will be significant and sufficient so that environmental attenuation can reduce pathogen levels to below detection limit within the time period of site restrictions (Farrell et al.1985; Martin et al. 1990).

For some processes, fecal coliforms may be an overly conservative indicator. Because bacteria may proliferate outside of a host, reintroduction of fecal coliforms into treated biosolids may result in their growth. Concentrations may exceed the Class A fecal coliform limit even though pathogens are not present. In these cases, because fecal coliforms themselves are not a concern, testing directly for *Salmonella* sp. as an indicator of pathogen survival is permissible. Another issue with fecal coliforms is that the tests for these bacteria may overestimate the number of coliforms from human species. This is of particular concern when additives such as wood chips or other bulking agents have been added to biosolids (Meckes, 1995). In this case also, it is advisable to test directly for *Salmonella* sp.

It must however be noted that high counts of fecal coliforms may also indicate that a process is not being operated correctly. While a preparer may meet the regulatory requirements by testing for and meeting the regulatory limits for *Salmonella* sp., it is recommended that the pathogen reduction process be reviewed to determine at what point fecal coliforms are potentially not being reduced or are being reintroduced into treated biosolids, and ensure that process requirements are being fulfilled.

Regrowth of Bacteria

One of the primary concerns for biosolids preparers is regrowth of pathogenic bacteria. Some bacteria are unique among sewage sludge pathogens in their ability to multiply outside of a host. The processes outlined in the Part 503 regulation and in this document have been demonstrated to reduce pathogens, but even very small populations of certain bacteria can rapidly proliferate under the right conditions, for example, in sewage sludges in which the competitive bacterial populations have been essentially eliminated through treatment (see Section 4.3). Viruses, helminths, and protozoa cannot regrow outside their specific host organism(s). Once reduced by treatment, their populations do not increase. The Part 503 regulation contains specific requirements designed to ensure that regrowth of bacteria has not occurred prior to use or disposal.

Preventing Exposure

Exposure to pathogens in Class B biosolids is limited by restricting situations in which the public may inadvertently come into contact with biosolids and by limiting access to biosolids by vectors which may carry pathogens from the sewage sludge.

Site Restrictions

In the case of land application of Class B biosolids, site restrictions are sometimes required in order to protect public health and the environment. The potential pathways of exposure to Class B biosolids or to pathogens which may exist in Class B biosolids, are listed in Table 2.2 along with a description of how site restrictions impose barriers to exposure pathways. Site restrictions, discussed in detail in Chapter 5, place limits on crop harvesting, animal grazing, and public access on land where Class B biosolids have been applied.

The goal of site restrictions is to limit site activities such as harvesting and grazing until pathogens have been reduced by environmental conditions such as heat, sunlight, desiccation, and competition from other microorganisms. Table 2-3 summarizes the survival rates of four types of pathogenic organisms on soil and on plants. As shown,

helminths have the longest survival time; consequently, the duration of some of the site restrictions is based on helminth survival potential.

Vector Attraction Reduction

Insects, birds, rodents, and domestic animals may transport sewage sludge and pathogens from sewage sludge to humans. Vectors are attracted to sewage sludge as a food source, and the reduction of the attraction of vectors to sewage sludge to prevent the spread of pathogens is a focus of the Part 503 regulation. Vector attraction reduction can be accomplished in two ways: by treating the sewage sludge to the point at which vectors will no longer be attracted to the sewage sludge and by placing a barrier between the sewage sludge and vectors. The technological and management options for vector attraction reduction are discussed in Chapter 8.

2.5 Frequently Asked Questions

Because land application of biosolids has increased dramatically in the past several years, and because of some well publicized incidents of pathogen contamination (not necessarily related to biosolids), there have been many questions about the level to which public health is protected. Although it is not possible for every issue to be considered, the following section includes some of the questions which are most frequently asked. In addition, references are included at the end of this chapter and in Chapter 12.

Can biosolids carry the pathogen that causes mad cow disease?

It has been found that Bovine Spongiform Encephalopathy (BSE), or Mad Cow disease, is caused by a prion protein, or the resistant beta form of protein. The pathway for transmission is through the ingestion of tissue from infected animals. There has been no evidence that the BSE prion protein is shed in feces or urine. There have been no known cases of BSE in the United States, and the Food and Drug Administration (FDA) has taken various measures to prevent spread of the disease to or within the United States. For example, the primary route for infection, the use of animal carcasses in animal feed, is banned in this country. These measures have been effective, and BSE has not become a public health concern in the U.S. with regard to ingestion of beef or other exposure routes. Thus there should be no risk of BSE exposure from biosolids. (Tan, et al. 1999)

Is there any risk of HIV infection from biosolids?

The HIV virus is contracted through contact with blood or other body fluids of an infected individual. Feces and urine do not carry the HIV virus, but contaminated fluids may be discharged in minor amounts to the sewerage system. The conditions in the wastewater system are not favorable for the virus's survival. Separation from the host environment, dilution with water, chemicals from household and industrial sewer discharges, and the length of time from discharge to treatment all impede the survival of the virus (WEF/U.S. EPA Fact Sheet, 1997). HIV is seldom detected in wastewater, and the additional treatment that wastewater goes through, producing an effluent and sewage sludge which undergoes treatment to become Class A or B biosolids, makes it virtually impossible that biosolids would contain the HIV virus. (Lue-Hing, et al. 1999)

Wastewater treatment workers may come into contact with contaminated objects (bandages, condoms, etc.), but common sense hygiene practices already in place at wastewater treatment plants including the use of protective clothing and gloves greatly reduce the potential for exposure. The U.S. Department of Health and Human Services stated in 1990 that ". . .these workers (wastewater treatment workers) have no increased potential of becoming infected by blood borne infectious agents. Therefore, medical waste discarded to the sanitary sewer is not likely to present any additional public health effects to the wastewater workers or to the general public." (Johnson, et al. 1994)

What is a bioaerosol?

Bioaerosols are airborne water droplets containing microorganisms. These may include pathogenic microorganisms. Bioaerosols are a potential public health concern with regard to Class B biosolids because if pathogens are contained in the biosolids, they may become airborne and infect workers or the public through direct inhalation or through contact after settling on clothing or tools. It has been found that aerosolization of protozoa and helminths is unlikely, but bacteria or bacterial components (endotoxin) and viruses may become airborne and disperse from an application source depending on local meteorological and topographical conditions. However, Class B biosolids are rarely applied dry enough to become airborne; applying wet biosolids, particularly when the biosolids are incorporated or injected into the land, makes it highly unlikely that bioaerosols will be dispersed from land application.

The public access restrictions for land-applied Class B biosolids are based on the various pathways by which pathogens may impact public health. Site restrictions are adequate for the protection of public health, but site workers who are present during the application of Class B biosolids should follow standard hygiene precautions such as washing their hands after contacting biosolids and wearing dust masks if applying extremely dry material. More information on aerosolization of pathogens from land application can be found in the references following this chapter.

What is Aspergillus fumigatus?

Aspergillus fumigatus is a pathogenic fungus which is found in decaying organic matter such as sewage sludge, leaves, or wood. Because the fungus is heat resistant, and because sewage sludge composting facilities often use wood chips as a bulking agent, *A. fumigatus* has been associated with composting. Inhalation of *A. fumigatus* spores

may result in allergenic effects including irritation of the mucous membranes and asthma. However, *A. fumigatus* is a secondary, or opportunistic pathogen, and infection from *A. fumigatus* ("Aspergillosis") is limited to debilitated or immuno-compromised individuals. Studies of the health status of compost facility workers, the population most likely to be exposed to *Aspergillus fumigatus,* have not shown any negative health impacts (Millner, et al. 1994).

A. fumigatus is a ubiquitous fungus and has been found in homes, gardens, and offices at considerable levels. Numerous studies have been conducted to determine the level of the fungus in the areas surrounding active compost sites and compare this level to background concentrations of *Aspergillus fumigatus.* In general, it has been found that concentrations of *A. fumigatus* drop to background levels within 500-1000 feet of site activity. *A. fumigatus* is not covered in the Part 503.

There have been several incidents in which fruit has been contaminated with pathogens. Was this due to the land application of biosolids?

No. Pathogens such as *Salmonella* sp. and pathogenic strains of *E. coli* are typically associated with animal products (meat and eggs), but outbreaks have been known to occur as a result of vegetable or fruit contamination from the use of animal manures. Some of the well-publicized incidents include cases in which the consumption of fresh apple juice and cider resulted in widespread illness and the death of a child (Center for Disease Control, 1996). One case was found to be due to contamination from *E. coli* found in bovine feces, and the other was due to *Cryptosporidium* sp., also suspected to be from contact with animal manure. Other cases have involved the contamination of berries, melons, and alfalfa sprouts.

The Part 503 regulation applies only to the land application of biosolids. Education of field workers, regulation of working conditions, both domestically and abroad, and the use of animal manure products are beyond the scope of this document.

What is the Fate of Giardia and Cryptosporidium During Sewage Sludge Treatment?

Giardia lamblia and *Cryptosporidium parvurn* are protozoan parasites that can infect the digestive tract of humans and other warm blooded animals. Semi-aquatic mammals can serve as hosts, transmitting the disease to humans who consume contaminated water. Domestic mammals (particularly ruminants) can serve as infective hosts and contaminate a drinking water supply. It is currently believed that at least 7% of the diarrheal cases in the United States are caused by *Cryptosporidium* sp.

West (1991) notes that human protozoan parasites such as *Cryptosporidium* sp. and *Giardia* sp. possess several traits which facilitate waterborne transmission. They can (1) be excreted in feces in large numbers during illness; (2) persist through conventional sewage treatment; (3) survive in an environmentally robust form or demonstrate resilience to inactivation while in aquatic environments; (4) be resistant to commonly used disinfectants in the treatment of drinking water; and (5) require low numbers to elicit infection in susceptible hosts consuming or exposed to contaminated water.

Stadterman et al. (1995) reported on an anaerobic digestion study which spiked *Cryptosporidium* sp. oocysts into the digester and then periodically removed samples to determine the die-off. They found that conventional anaerobic digestion produces about a 2-log removal or a better log reduction on this protozoan than it does on bacteria and viruses, but it does not reduce densities to the low values needed for Class A for this pathogen. The reported survival of some protozoa after anaerobic digestion at 35°C is a cause for concern.

Jenkins et al. (1998) reported that ammonia inactivates these oocysts, depending on the concentration. High pH processes that increase the free ammonia concentration can inactivate these oocysts (although pH by itself does little).

A conservative conclusion from the limited research performed is that Class B processes can only be expected to reduce protozoan pathogens by about a factor of ten. The restrictions written into the regulation (access control, growing only certain crops, restrictions on root crops, etc.) are necessary to prevent exposure to these pathogens. The Class A processes reduce protozoa to below detectable limits.

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Chapter 3
Overview of Part 503 Subpart D Requirements, Their Applicability, and Related Requirements

3.1 Introduction

The Subpart D (pathogen and vector attraction reduction) requirements of the 40 CFR Part 503 regulation apply to sewage sludge (both bulk sewage sludge and sewage sludge that is sold or given away in a bag or other container for application to the land) and domestic septage applied to the land or placed on a surface disposal site. The regulated community includes persons who generate or prepare sewage sludge for application to the land, as well as those who apply it to the land. Included is anyone who:

- Generates treated sewage sludge (biosolids) that is land applied or placed on a surface disposal site
- Derives a material from treated sewage sludge (biosolids)
- Applies biosolids to the land
- Owns or operates a surface disposal site

Sewage sludge cannot be applied to land or placed on a surface disposal site unless it has met, among other things, the two basic types of requirements in Subpart D:

- Requirements to ensure reduction of pathogens.
- Requirements to reduce the potential of the sewage sludge to attract vectors (rodents, birds, insects, and other organisms that can transport pathogens).

These two types of requirements are separated in Part 503 (they were combined in an earlier regulation, Part 257), which allows flexibility in how they are achieved. Compliance with the two types of requirements must be demonstrated separately. Therefore, demonstration that a requirement for reduced vector attraction has been met does not imply that a pathogen reduction requirement also has been met, and vice versa.

This chapter provides an overview of the Subpart D requirements, their applicability, and the requirements related to frequency of monitoring and recordkeeping. Where relevant, the titles of the sections in this chapter include the number of the Subpart D requirement discussed in the section. Chapters 4 through 8 provide detailed information on the pathogen and vector attraction reduction requirements.

Some of the pathogen and vector attraction reduction alternatives are suitable only for biosolids which have been processed by particular methods, such as by aerobic or anaerobic digestion or composting. Chapters 4 and 5 contain examples of how some facilities have met Part 503 requirements using appropriate pathogen and vector attraction reduction protocols, and Chapter 8 discusses each vector attraction option in detail.

3.2 Pathogen Reduction Requirements

Sewage Sludge [503.32(a) and (b)]

The pathogen reduction requirements for sewage sludge are divided into two categories: Class A and Class B. These requirements use a combination of technological and microbiological requirements to ensure reduction of pathogens.

The implicit goal of the Class A requirements is to reduce the pathogens in sewage sludge (including enteric viruses, pathogenic bacteria, and viable helminth ova) to below detectable levels, as defined in the 1992 regulation.

The implicit goal of the Class B requirements is to reduce pathogens in sewage sludge to levels that are unlikely to pose a threat to public health and the environment under the specific use conditions. For Class B biosolids that are applied to land, site use restrictions are imposed to minimize the potential for human or animal exposure to Class B biosolids for a period of time following land application and until environmental factors (e.g. sunlight, desiccation) have further reduced pathogens. Both Class A treatment of the sewage sludge which reduces pathogens to below detectable levels and the combination of Class B sewage sludge treatment and use restrictions on the land application site protect public health and the environment.

"Exceptional quality" (EQ) biosolids are biosolids which have met the Part 503 pollutant concentration limits (Table 3 of Section 503.13) as well as Class A pathogen reduction requirements and one of the first eight vector attraction reduction options listed in 503.33(b)(1) through (b)(8). EQ biosolids may be land applied without site restrictions.

Application of Class B biosolids must be conducted in compliance with site restrictions. Because it is not possible for regulators to follow the land application of biosolids applied on lawns and home gardens, Class B biosolids cannot be sold or given away in bags or other containers or applied on lawns and home gardens.

The testing requirements outlined throughout this document are minimum standards for compliance with the Part 503 rule. It should be pointed out that biosolids are properly distributed under the most recent test results. However, facilities which distribute biosolids between sampling events may wish to enhance their sampling programs to better ensure compliance with pathogen reduction requirements and to enhance public confidence in biosolids quality. More frequent testing should also enable the biosolids generators and preparers to better detect any changes in operations that might affect compliance and slow more rapid correction in any adverse changes. It should be noted that when additional determinations are made, even though they are in excess of Part 503 regulatory requirements, all these analytical results and records must be retained in the generator's, preparer's or land applier's files or reported to the regulatory authority depending on the classification of the operation or the regulatory authority's wishes.

Domestic Septage [503.32(c)]

As stated in Chapter 1, domestic septage is a form of sewage sludge. The requirements for domestic septage vary depending on how it is used or disposed. Domestic septage applied to a public contact site, lawn, or home garden must meet the same requirements as treated sewage sludge (biosolids) applied to these types of land (Class A requirements). Separate, less-complicated requirements for pathogen reduction apply to domestic septage applied to agricultural land, forests, or reclamation sites. These requirements include site restrictions to reduce the potential for human exposure to domestic septage and to allow for pH adjustment or environmental attenuation with site restrictions only on harvesting crops. No pathogen requirements apply if domestic septage is placed on a surface disposal site.

3.3 Vector Attraction Reduction (VAR) Requirements [503.33]

Subpart D provides 12 options to demonstrate vector attraction reduction. These are referred to in this document as Options 1 through 12. Table 8-2 summarizes these options, and Chapter 8 provides more detailed information on the options.

Reduction through Treatment

Options 1 through 8 apply to sewage sludge that has been treated in some way to reduce vector attraction (e.g., aerobic or anaerobic digestion, composting, alkali addition, drying). These options consist of either operating conditions or tests to demonstrate that vector attraction has been reduced in the treated sewage sludge. Option 12 is a requirement to demonstrate reduced vector attraction in domestic septage through elevated pH. This option applies only to domestic septage.

Reduction through Barriers

Options 9 through 11 are "barrier" methods. These options require the use of soil as a physical barrier (i.e., by injection, incorporation, or as cover) to prevent vectors from coming in contact with the land applied biosolids. They include injection of biosolids below the land surface, incorporation of biosolids into the soil, and placement of a cover over the biosolids. Options 9 through 11 apply to both biosolids and domestic septage. Option 11 may only be used at surface disposal sites.

Timing of Pathogen and Vector Attraction Reduction

In the case of Class A biosolids, pathogen reduction must take place before or at the same time as vector attraction reduction unless VAR Option 6, 7, or 8 is used. More information is provided in Section 4.2.

3.4 Applicability of the Requirements [503.15 and 503.25]

The applicability of the pathogen and vector attraction reduction requirements is covered in 503.15 and 503.25. Tables 3-1 to 3-3 summarize the applicability of the Subpart D requirements to sewage sludge and domestic septage.

Table 3-1. Subpart D Requirements for the Land Application of Bulk Biosolids[1]

	Applied to Agricultural Land, a Forest, a Public Contact Site[2], or a Reclamation Site[3]	Applied to a Lawn or Home Garden
Pathogen Requirements	Class A or Class B with site restrictions	Class A[4]
Vector Attraction Reduction Requirements	Options 1-10[5]	Options 1-8[5,6]

[1] Bulk biosolids are biosolids that are not sold or given away in a bag or other container for application to the land.
[2] Public contact site is land with a high potential for contact by the public, e.g., public parks, ball fields, cemeteries, plant nurseries, turf farms, and golf courses.
[3] Reclamation site is drastically distrubed land (e.g., strip mine, construction site) that is reclaimed using biosolids.
[4] The regulation does not permit use of biosolids meeting Class B requirements on lawns or home gardens, because it would not be feasible under these circumstances to impose the site restrictions that are an integral part of the Class B requirements.
[5] See Chapter 8 for a description of these options.
[6] The two vector attraction reduction requirements that cannot be met when bulk biosolids are applied to a lawn or a home garden are injection of the bulk biosolids below the land surface and incorporation of bulk biosolids into the soil. Implementation of these requirements for bulk biosolids applied to a lawn or a home garden would be difficult, if not impossible.

Table 3-2. Subpart D Requirements for Biosolids Sold or Given Away in a Bag or Other Container for Application to the Land

	Land Application
Pathogen Requirements	Class A[1]
Vector Attraction Reduction Requirements	Options 1-8[2]

[1]Class B biosolids cannot be sold or given away for use on home gardens or lawns because it is not feasible to impose the Class B site restrictions for these uses.
[2]Only the treatment-related options for vector attraction reduction apply to biosolids that are sold or given away in bags or other containers for application to the land, because of the barrier options, which are implemented at the site of application, would be impossible. See Chapter 8 for a description of these options.

Table 3-3. Subpart D Requirements for Domestic Septage Applied to Agricultural Land, a Forest, or a Reclamation Site[1] or Placed on a Surface Disposal Site

	Application to Agricultural Land, a Forest, or a Reclamation Site[2]	Surface Disposal
Pathogen Reduction Requirements	Class B site restrictions only or a pH adjustment (pH > 12 for 30 minutes) plus restrictions concerning crop harvesting	No pathogen requirements[3]
Vector Attraction Reduction Requirements	Options 9, 10, 12[4]	Options 9-12[4]

[1]For application to all other types of land, domestic septage must meet the same requirements as other forms of sewage sludge (see Tables 3-1 and 3-2).
[2]Reclamation site is drastically disturbed land (e.g., strip mine, construction site) that is reclaimed using biosolids.
[3]There is no pathogen requirement for domestic septage placed on a surface disposal site because site restrictions for grazing of animals, public access, and crop growing are already imposed by the Part 503, Subpart C management practices to reduce exposure to pollutants in domestic septage placed on a surface disposal site.
[4]See Chapter 8 for a description of these options.

Table 3-4. Frequency of Monitoring for Land Application and Surface Disposal

Amount of Biosolids[1] (metric tons dry solids per 365-day period)	Minimum Frequency
Greater than zero but less than 290[2]	Once per year
Equal to or greater than 290 but less than 1,500[2]	Once per quarter (four times per year)
Equal to or greater than 1,500 but less than 15,000[2]	Once per 60 days (six times per year)
Equal to or greater than 15,000[2]	Once per month (12 times per year)

[1]Either the amount of bulk biosolids applied to the land, or the amount of sewage sludge received by a person who prepares biosolids that are sold or given away in a bag or other container for application to the land (dry weight basis), or the amount of biosolids (excluding domestic septage) placed on a surface disposal site.
[2]290 metric tons = 320 tons (approximately 0.9 tons/day for a year).
1,500 metric tons = 1,653 tons (approximately 4.5 tons/day for a year).
15,000 metric tons = 16,534 tons (approximately 45 tons/day for a year).

3.5 Frequency of Monitoring

Sewage Sludge [503.16(a) and 503.26(a)]

The Class A and Class B pathogen requirements and the vector attraction reduction Options 1 through 8 (the treatment related methods) all involve some form of monitoring. The minimum frequency of monitoring for these requirements is given in Part 503.16(a) for land application and Part 503.26(a) for surface disposal. The frequency depends on the amount of biosolids used or disposed annually (see Table 3-4). The larger the amount used or disposed, the more frequently monitoring is required.

In addition to monitoring frequency, a sampling plan should address the minimum number of samples per sampling event that are necessary to adequately represent biosolids quality. Both of these issues are addressed in Chapter 9.

As stated throughout this document, the monitoring requirements set forth in the Part 503 and this document are the minimum requirements. Persons or facilities that generate and distribute biosolids are encouraged to go beyond the minimum required programs as necessary.

Domestic Septage [503.16(b) and 503.26(b)]

One of the requirements that can be used for demonstrating both pathogen reduction and vector attraction reduction in domestic septage is to elevate pH to 12 for 30 minutes (see Sections 5.6 and 8.13). When this requirement is to be met, each container of domestic septage (e.g., each tank truckload) applied to the land or placed on a surface disposal site must be monitored for pH over 30 minutes.

3.6 Sampling Stockpiled or Remixed Biosolids

In many cases there are several steps of preparation before biosolids are actually used or distributed. For example, some products such as composted biosolids may be prepared and then mixed with other materials to create a soil blend. Other biosolids products may be prepared and then stored either on site or at a field until the material can be applied. In some cases, resampling and/or re-establishment of the biosolids quality may be necessary. Whether or not biosolids must undergo additional sampling or processing depends on the classification of the biosolids and on whether the biosolids remain in the control of the preparer or if they have been distributed or sold.

EQ Biosolids

If the biosolids are classified as exceptional quality (EQ) (see Section 3.2), they may be distributed for land application without site restriction. EQ is an industry term rather than a regulatory term. Land application of EQ biosolids is not regulated by the Part 503 once the biosolids leave the control of the biosolids preparer. Therefore, soil blenders or other (non-preparer) users who take EQ biosolids may store the biosolids or mix the EQ biosolids with other (non-sewage sludge) materials without resampling the product.

Conversely, if EQ biosolids remain within the control of the preparer, they are still considered biosolids and are still covered by the Part 503. Like all Class A products, they must undergo microbiological testing at the last possible point before being distributed. In addition, if the preparer mixes the EQ biosolids or otherwise changes the quality of the biosolids, the new biosolids product must again comply with pathogen reduction, vector attraction reduction, and microbiological requirements.

Non-EQ Class A Biosolids

Class A biosolids are not necessarily classified as EQ biosolids; if pollutant levels exceed the Table 3 limits or if one of the first eight vector attraction options has not been met, the Class A biosolids are not considered EQ. All Class A biosolids must undergo microbiological testing just before they are distributed, so testing for fecal coliforms or *Salmonella* sp. must take place after storage. In addition, if the preparer mixes the Class A biosolids with other materials or otherwise changes the quality of the biosolids, the new biosolids product must comply with pathogen reduction, vector attraction reduction, and microbiological requirements.

Non-EQ Class A biosolids must also be monitored after they are distributed. For example, if a Class A compost which does not meet one of the EQ pollutant limits is sold to a vendor who mixes the compost with soil, the soil blender becomes a biosolids preparer, and must therefore comply with all Part 503 regulations. The new biosolids product must comply with pathogen reduction, vector attraction reduction, and microbiological requirements.

Class B Biosolids

Class B biosolids can meet pathogen reduction requirements at any point; there is no requirement that Class B biosolids be tested just before distribution. Therefore, biosolids which have met the Class B pathogen reduction requirements can be stored on site without retesting. However, if the Class B biosolids are mixed with other materials or the quality of the biosolids are otherwise altered, the new biosolids product must meet pathogen reduction and vector attraction reduction requirements.

The same is true for Class B biosolids that are distributed and no longer under the control of the preparer. Stored Class B biosolids do not have to be retested for pathogen reduction, unless the quality of the biosolids is somehow altered through mixing or further processing.

3.7 Recordkeeping Requirements [503.17 and 503.27]

Recordkeeping requirements are covered in Part 503.17 for land application and Part 503.27 for surface disposal. Records are required for both biosolids and domestic septage that are used or disposed. All records must be retained for 5 years except when the cumulative pollutant loading rates (CPLRs) in Subpart B (Land Application) of the Part 503 are used[1]. If CPLRs are used, records of pollutant loading at each site must be kept indefinitely. All records must be retained and made available to the regulatory authority upon request (see Section 3.8).

Land Application

Records must be kept to ensure that the biosolids meet the applicable pollutant limits, management practices[2], one of the pathogen requirements, one of the vector attraction reduction requirements and, where applicable, the site restrictions associated with land application of Class B biosolids. When biosolids are applied to land, the person preparing the biosolids for land application and the person applying bulk biosolids must keep records[3, 4]. The person applying biosolids that were sold or given away does not have to keep records.Table 3-5 summarizes the recordkeeping requirements for land application.

Surface Disposal

When biosolids are placed on a surface disposal site, the person preparing the biosolids and the owner/operator of the surface disposal site must keep records. In the case of domestic septage applied to agricultural land, forest, or a reclamation site or placed on a surface disposal site, the person applying the domestic septage and the owner/operator of the surface disposal site may be subject to pathogen record keeping requirements, depending on which vector attraction reduction option is met. Table 3-6 summarizes the pathogen-related recordkeeping requirements for surface disposal.

Certification Statement

In every case, recordkeeping involves signing a certification statement that the requirement has been met. Parts 503.17 and 503.27 of the regulation contain the required certification language.

3.8 Reporting Requirements for Sewage Sludge [503.18 and 503.28]

Reporting requirements for sewage sludge are found in Part 503.18 for land application and Part 503.28 for surface disposal. These requirements apply to Class I sludge management facilities[5] and to publicly owned treatment

[1]Cumulative pollutant loading rates are not related to pathogen control and therefore are not covered in this document.

[2]Pollutant limits and management practices are not related to the pathogen requirements and therefore are not covered in this document.

[3]Person as defined under Part 503.9 may be an individual, association, partnership, corporation, municipality, state or federal agency, or an agent or employee of a state or federal agency.

[4]When biosolids are prepared by one person, and another person who places it in a bag or other container for sale or give-away for application to the land changes the quality of that biosolids, both persons must keep the records required of preparers (see Table 3-5 and Section 3.6).

[5]A Class I sewage sludge management facility is any publicly owned treatment works (POTW) required to have an approved pretreatment program under 40 CFR 403.8(a) [including any POTW located in a state that has assumed local program responsibilities under 40 CFR 403.1 (e)] and any treatment works treating domestic sewage classified as a Class I sludge management facility by EPA or the state sludge management program because of the potential for its sewage sludge use or disposal practices to adversely affect public health and the environment.

Table 3-5. Summary of Pathogen and Vector Attraction Reduction Recordkeeping Requirements for Land Application of Biosolids[1]

	Description of How Class A Pathogen Requirement Was Met	Description of How Class B Pathogen Requirement Was Met	Description of How the Class B Site Restrictions Were Met at Each Site Where Sewage Sludge Was Applied	Description of How Pathogen Requirement for Domestic Septage Applied to Agricultural Land, a Forest, or a Reclamation Site Was Met	Description of How Vector Attraction Requirement Was Met	Certification Statement that the Requirement Was Met
Biosolids - Pathogen Requirements						
Person preparing Class A bulk biosolids	√					√
Person preparing Class A biosolids for sale or give away in a bag or other container	√					√
Person preparing Class B biosolids		√				√
Person applying Class B biosolids			√			√
Biosolids - Vector-Attraction Reduction Requirements						
Person preparing biosolids that meet one of the treatment-related vector attraction reduction requirements (Options 1-8)					√	√
Person applying biosolids if a barrier-related option (Options 9-11) is used to meet the vector attraction reduction requirement					√	√
Domestic Septage						
Person applying domestic septage to agricultural land, a forest, or a reclamation site				√	√	√

[1]Other recordkeeping requirements, not covered in this document; apply to pollutant limits and management practices.

Table 3-6. Summary of Pathogen and Vector Attraction Reduction Recordkeeping Requirements for Surface Disposal of Biosolids[1]

	Required Records		
	Description of How Class A or B Pathogen Requirement was Met	Description of How Vector Attraction Requirement was Met	Certification Statement that the Requirement was Met
Biosolids - Pathogen Requirements			
Person preparing the biosolids	√		√
Sewage Sludge - Vector Attraction Reduction Requirements			
Person preparing biosolids that meet one of the treatment-related vector attraction reduction requirements (Options 1-8)		√	√
Owner/operator of the surface disposal site if a barrier-related option (Options 9-11) is used to meet the vector attraction reduction requirement		√	√

continued

Table 3-6. (Continued)

	Required Records		
	Description of How Class A or B Pathogen Requirement was Met	Description of How Vector Attraction Requirement was Met	Certification Statement that the Requirement was Met
Domestic Septage			
Person who places domestic septage on the surface disposal site if the domestic septage meets Option 12 for vector attraction reduction		√	√
Owner/operator of the surface disposal site if a barrier-related option (Options 9-11) is used to meet the vector attraction reduction requirement		√	√

[1]Other recordkeeping requirements, not covered in this document, apply to pollutant limits and management practices.

works either with a design flow rate equal to or greater than 1 million gallons per day or that serve 10,000 or more people, or if specifically required by the permitting authority. Reports must be submitted to the regulatory authority (see Tables 3-5 and 3-6) and/or as the owner/operators of surface disposal sites (see Table 3-6) on February 19 of each year. There are no reporting requirements associated with the use or disposal of domestic septage, but records must be kept and made available to the regulatory authority upon request.

3.9 Permits and Direct Enforceability [503.3]

Permits

Under Part 503.3(a), the requirements in Part 503 may be implemented through (1) NPDES permits issued to treatment works treating domestic sewage by EPA permits issued by states with an EPA-approved sludge management program, and (2) by permits issued under Subtitle C of the Solid Waste Disposal Act; Part C of the Safe Drinking Water Act; the Marine Protection, Research, and Sanctuaries Act of 1972; or the Clean Air Act. Treatment works treating domestic sewage should submit a permit application[6] to the approved state program, or, if there is no such program, to the EPA Regional Sludge Coordinator (see Appendix A).

Direct Enforceability

Under Part 503.3(b), the requirements of Part 503 automatically apply and are directly enforceable even when no federal permit has been issued for the use or disposal of biosolids.

[6] See 40 CFR Parts 122/123, and 501; 54 FR 18716/May 2,1989; and 58 FR 9404/February 19, 1993, for regulations establishing permit requirements and procedures, as well as requirements for states wishing to implement approved sewage sludge management programs as either part of their NPDES programs or under separate authority.

Chapter 4
Class A Pathogen Requirements

4.1 Introduction

This chapter principally discusses the Class A pathogen requirements in Subpart D of the 40 CFR Part 503 regulation. Biosolids that are sold or given away in a bag or other container for application to land **must** meet these requirements (see Section 3.4). Bulk biosolids applied to a lawn or home garden also **must** meet these requirements. Bulk biosolids applied to other types of land **must** meet these requirements if site restrictions are not met (see Chapter 5 for guidance on Class B biosolids). Some discussion is, however, presented of vector attraction reduction.

There are six alternative methods for demonstrating Class A pathogen reduction. Two of these alternatives provide continuity with 40 CFR Part 257 by allowing use of Processes to Further Reduce Pathogens (PFRPs) and equivalent technologies (see Sections 4.8 and 4.9). Any one of these six alternatives may be met for the sewage sludge to be Class A with respect to pathogens. The implicit objective of all these requirements is to reduce pathogen densities to below detectable limits which are:

Salmonella sp.	less than 3 MPN per 4 grams total solids biosolids (dry weight basis)
Enteric viruses[1]	less than 1 PFU per 4 grams total solids biosolids (dry weight basis)
Viable helminth ova	less than 1 viable helminth ova/ 4 gram total solids biosolids (dry weight basis)

One of the vector attraction reduction requirements (see Chapter 8) also must be met when biosolids are applied to the land or placed on a surface disposal site. To meet the Part 503 regulatory requirements, pathogen reduction must be met before vector attraction reduction or at the same time vector attraction reduction is achieved.

For the following sections, the title of each section provides the number of the Subpart D requirement discussed in the section. The exact regulatory language can be found in Appendix B, which is a reproduction of Subpart D. Chapters 9 and 10 provide guidance on the sampling and analysis needed to meet the Class A microbiological monitoring requirements.

[1] Enteric viruses are monitored using a method that detects several enterovirus species--a subset of enteric viruses. This method is presumed to be a good indicator of enteric viruses. Since the objective of the Part 503 regulation is to reduce all enteric viruses to less than 1 PFU per 4 grams total solids sewage sludge, this document refers to "enteric viruses" when discussing this requirement, although, in reality, the detection method enumerates only enteroviruses.

4.2 Vector Attraction Reduction to Occur With or After Class A Pathogen Reduction [503.32(a)(2)]

Although vector attraction reduction and pathogen reduction are separate requirements, they are often related steps of a process. Chapter 8 discusses the vector attraction reduction options in greater detail.

The order of Class A pathogen reduction in relation to the reduction of vector attraction is important when certain vector attraction reduction options are used. Part 503.32(a)(2) requires that Class A pathogen reduction be accomplished before or at the same time as vector attraction reduction, except for vector attraction reduction by alkali addition [503.33(b)(6)] or drying [503.33(b)(7) and (8)] (see Chapter 8).

This requirement is necessary to prevent the growth of bacterial pathogens after sewage sludge is treated. Contamination of biosolids with a bacterial pathogen after one of the Class A pathogen reduction alternatives has been conducted may allow extensive bacterial growth unless: a) an inhibitory chemical is present, b) the biosolids are too dry to allow bacterial growth, c) little food remains for the microorganisms to consume, or d) an abundant population of non-pathogenic bacteria is present. Vegetative cells of non-pathogenic bacteria repress the growth of pathogenic bacteria by "competitive inhibition" which is in substantial part due to competition for nutrients. It should be noted that vector attraction reduction by alkali addition [503.3(b)(6)] or drying [503.3(b)(7)] and (8) is based on the characteristic of the biosolids (pH or total solids) remaining elevated. Should the pH drop or the biosolids absorb moisture, the biosolids may be more hospitable to microorganisms, and pathogenic bacteria, if introduced, may grow. Therefore it is recommended that biosolids treated with these methods be stored appropriately.

Biological treatment processes like anaerobic digestion, aerobic digestion, and composting produce changes in the

sewage sludge so that it satisfies one of the vector attraction reduction requirements [503.3(b)(1) through (5)]. They repress bacterial growth by minimizing the food supply and providing competition for the remaining food from non-pathogenic organisms. The pathogen reduction alternative must precede the vector attraction reduction process; otherwise, the large number of non-pathogenic bacterial cells would be killed and growth of pathogenic bacteria could occur. Certain pathogen reduction processes such as composting accomplish vector attraction reduction by a biological process simultaneously with thermal reduction of pathogens. A non-pathogenic bacterial community survives which adequately suppresses growth of pathogenic bacteria.

In the case of Class B biosolids, a population of non-pathogenic bacteria is retained and inhibits the growth of pathogenic bacteria through competition, and site restrictions are imposed with their land application to reduce the risk of exposure to pathogens. Therefore, bacterial growth is not a concern for Class B biosolids, and vector attraction reduction and pathogen reduction for compliance with the Part 503 Rule requirements may be met in any order.

4.3 Monitoring of Fecal Coliform or *Salmonella* sp. to Detect Growth of Bacterial Pathogens [503.32(a)(3)-(8)]

The goal of Class A processes is to reduce the level of pathogens to below detectable levels and below the level at which they are infectious. The Class A processes have been shown to sufficiently reduce pathogen levels in biosolids, and studies to date have not found that the growth of pathogenic bacteria may occur in materials after processes take place or during storage. Favorable conditions for the growth of pathogenic bacteria would be: adequate moisture, absence of an inhibitory chemical, and inadequate reduction of nutritive value of the sewage sludges.

Because Class A biosolids may be used without site restrictions, all Class A material must be tested to show that the microbiological requirements are met at the time when *it is ready to be used or disposed.* In addition to meeting process requirements, Class A biosolids must meet one of the following requirements:

- Either the density of fecal coliforms in the sewage sludge be less than 1,000 MPN[2] per gram total solids (dry weight basis).
- Or the density of *Sa/mone//a* sp. bacteria in the sewage be less than 3 MPN per 4 grams of total solids (dry weight basis).

Although the Part 503 regulation does not specify the number of samples that should be taken to show compliance with Class A density requirements, sampling programs should provide adequate representation of the biosolids generated. Chapter 9 provides guidance for calculating the number of samples that should be taken per sampling event. Unlike Class B biosolids, compliance with Class A requirements is not based on an average value. **Each sample analyzed must comply with the numerical requirements.**

The microbiological requirement must be met either:

- At the time of use or disposal[3], or
- At the time the biosolids are prepared for sale or give away in a bag or other container for land application, or
- At the time the biosolids or material derived from the biosolids is prepared to meet the requirements in 503.10(b), 503. 10(c), 503. 10(e), or 503. 10(f)[4].

If a facility stores material before it is distributed for use or disposal, microbiological testing should take place after storage.

In each case, the timing represents the last practical monitoring point before the biosolids are applied to the land or placed on a surface disposal site. Biosolids that are sold or given away cannot be monitored just prior to actual use or disposal; instead monitoring is required as it is prepared for sale or give away. Biosolids that meet the 503.10(b, c, d, or e) requirements are considered "Exceptional Quality" and are therefore not subject to further control (see Section 1.4). For this reason, the microbiological requirements must be met at the time the biosolids are prepared to meet the 503.10 requirements, which in most cases is the last time the biosolids are under the control of a biosolids preparer.

As discussed in Chapter 9, the timing of pathogen sampling is also a function of laboratory turnaround time. Obtaining results for fecal coliform and *Salmonella* sp. analysis may take several days if tests are performed in-house, but commercial labs may require more time to process and report results. It is not unusual for laboratories to have a turnaround time of 2 weeks, even for simple tests such as fecal coliform. If this is the case, this time should be factored into the sampling program so that results can be obtained before biosolids are distributed for use or disposal.

Monitoring Fecal Coliforms or Salmonella sp.

Fecal coliforms are used in the Part 503 as an indicator organism, meaning that they were selected to be monitored because reduction in fecal coliforms correlates to reduction in *Sa/mone//a* sp. and other organisms. The re-

[2]The membrane filter method is not allowed for Class A because, at the low fecal coliform densities expected, the filter would have too high a loading of sewage sludge solids to permit a reliable count of the number of fecal coliform colonies.

[3]Minus the time needed to test the biosolids and obtain the test results prior to use or disposal (see Chapter 10).

[4]The 503.10(b)(c)(e) and (f) requirements are not discussed in this document.

quirements were based on experimental work by Yanko (1987) and correlations developed from Yanko's data by Farrell (1993) which show that this level of fecal coliforms correlate with a very low level of *Salmonella* sp. detection in composted sewage sludge (EPA, 1992).

Anecdotal reports suggest that some composting facilities may have difficulty meeting this requirement even when *Salmonella* sp. are not detected. This might be expected under several circumstances. For example, very severe thermal treatment of sewage sludge during composting can totally eliminate *Salmonella* sp. yet leave residual fecal coliforms. If the sewage sludge has been poorly composted and thus is a good food source, fecal coliforms may grow after the compost cools down from thermophilic temperatures. Because the *Salmonella* sp. are absent, they cannot grow. An even more probable circumstance could occur if the sewage sludge is treated with lime before composting. Lime effectively destroys *Salmonella* sp. in sewage sludge and leaves surviving fecal coliforms (Farrell et al., 1974). Under conditions favorable for growth, the fecal coliforms can regrow to levels higher than 1,000 MPN per gram. Research has shown that detection of *Salmonella* sp. is much rarer in composted sewage sludge that has been lime treated and composted than detection of fecal coliforms. *Fecal coliform densities maybe high therefore compared to pathogen densities in such cases and maybe overly conservative.* For this reason, all of the Part 503 Class A alternatives allow the direct measurement of *Salmonella* sp. or fecal coliform analysis, but do not require both.

4.4 Alternative 1: Thermally Treated Sewage Sludge [503.32(a)(3)]

This alternative may be used when the pathogen reduction process uses specific time-temperature regimes to reduce pathogens. Under these circumstances, time-consuming and expensive tests for the presence of specific pathogens can be avoided. It is only necessary to demonstrate that:

- Either fecal coliform densities are below 1,000 MPN per gram of total solids (dry weight basis), or *Salmonella* sp. bacteria are below detection limits (3 MPN per 4 grams total solids [dry weight basis]) at the time the sewage sludge is used or disposed, at the time the sewage sludge is prepared for sale or given away in a bag or other container for land application, **or** at the time the sewage sludge or material derived from the sewage sludge is prepared to meet the requirements in 503.10(b), 503.10(c), 503.10(e), or 503.10(f).

- And the required time-temperature regimes are met.

Time-Temperature Requirement

Four different time-temperature regimes are given in Alternative 1. Each regime is based on the percent solids of the sewage sludge and on operating parameters of the treatment process. Experimental evidence (EPA, 1992) demonstrates that these four time-temperature regimes reduce the pathogenic organisms to below detectable levels.

The four time-temperature regimes are summarized in Table 4-1. They involve two different time-temperature equations. The equation used in Regimes A through C results in requirements that are more stringent than the requirement obtained using the equation in Regime D. For any given time, the temperature calculated for the Regime D equation will be 3 Celsius degrees (5.4 Fahrenheit degrees) lower than the temperature calculated for the Regimes A through C equation.

The time-temperature relationships described for Alternative 1 are based on extensive research conducted to correlate the reduction of various pathogens in sewage sludge to varying degrees of thermal treatment. The resulting time-temperature relationship which is the basis for Alternative 1 is shown in Figure 4-1. These requirements are similar to the FDA requirements for treatment of eggnog, a food product with flow characteristics similar to those of liquid sewage sludge. The Regimes A through D differ depending on the characteristics of sewage sludge treated and the type of process used because of the varying efficiency of heat transfer under different conditions.

It is important to note that **it is mandatory for all sewage sludge particles to meet the time-temperature regime.** Therefore, testing of temperatures throughout the sewage sludge mass and agitating the material to ensure uniformity would be appropriate. For processes such as thermophilic digestion, it is important that the digester design not allow for short circuiting of untreated sewage sludge. One approach that has been used to overcome this problem has been to draw off treated sewage sludge and charge feed intermittently with a sufficient time period between draw-down and feeding to meet the time-temperature requirement of Alternative 1. Another option would be to carry out the process in two or more vessels in series so as to prevent bypassing.

These time-temperature regimes are not intended to be used for composting (the time-temperature regime for composting is covered in Alternative 5: Processes to Further Reduce Pathogens).

A more conservative equation is required for sewage sludges with 7% or more solids (i.e., those covered by Regimes A and B) because these sewage sludges form an internal structure that inhibits the mixing that contributes to uniform distribution of temperature. The more stringent equation is also used in Regime C (even though this regime applies to sewage sludges with less than 7% solids) because insufficient information is available to apply the less stringent equation for times less than 30 minutes.

The time-temperature requirements apply to every particle of sewage sludge processed. Time at the desired temperature is readily determined for batch or plug flow operations, or even laminar flow in pipes. Time of contact also can be calculated for a number of completely mixed

Table 4-1. The Four Time-Temperature Regimes for Alternative 1 (Thermally Treated Sewage Sludge) [503.32(a)(3)]

Regime	Part 503 Section	Applies to	Required Time-Temperature[1]
A	503.32(a)(3)(ii)(A)	Sewage sludge with at least 7% solids (except those covered by Regime B)	$D = 131{,}700{,}000/10^{0.1400t}$ $t \geq 50°C$ (122°F)[2] $D \geq 0.0139$ (i.e., 20 minutes)[3]
B	503.32(a)(3)(ii)(B)	Sewage sludge with at least 7% solids that are small particles heated by contact with either warmed gases or an immiscible liquid[4]	$D = 131{,}700{,}000/10^{0.1400t}$ $t \geq 50°C$ (122°F)[2] $D \geq 1.74 \times 10^{-4}$ (i.e., 15 seconds)[5]
C	503.32(a)(3)(ii)(C)	Sewage sludge with less than 7% solids treated in processes with less than 30 minutes contact time	$D = 131{,}700{,}000/10^{0.1400t}$ 1.74×10^{-4} (i.e., 15 seconds) $\leq D \leq 0.021$ (i.e. 30 minutes)[6]
D	503.32(a)(3)(ii)(D)	Sewage sludge with less than 7% solids treated in processes with at least 30 minutes contact time	$D = 50{,}070{,}000/10^{0.1400t}$ $t \geq 50°C$ (122°F)[2] $D \geq 0.021$ (i.e. 30 minutes)[7]

[1]D = time in days; t = temperature (°C).
[2]The restriction to temperatures of at least 50°C (122°F) is imposed because information on the time-temperature relationship at lower temperatures is uncertain.
[3]A minimum time at 20 minutes is required to ensure that the sewage sludge has been uniformly heated.
[4]Two examples of sewage sludge to which this requirement applies are:
- Sewage sludge cake that is mixed with previously dried solids to make the entire mass a mixture of separate particles, and is then dried by contact with a hot gas stream in a rotary drier.
- Sewage sludge dried in a multiple-effect evaporator system in which the system sludge particles are suspended in a hot oil that is heated by indirect heat transfer with condensing steam.

[5]Time-at-temperature of as little as 15 seconds is allowed because, for this type of sewage sludge, heat transfer between particles and the healing fluid is excellent. Note that the temperature is the temperature achieved by the sewage sludge particles, not the temperature of the carrier medium.
[6]Time-at-temperature of as little as 15 seconds is allowed because heat transfer and uniformity of temperature is excellent in thiswage sludge. The maximum time of 30 minutes is specified because a less stringent regime (D) applies when time-at-temperature is 30 minutes or more.
[7]Time-at-temperature of at least 30 minutes is required because information on the effectiveness of this time-temperature regime for reducing pathogens at temperatures of less than 30 minutes is uncertain.

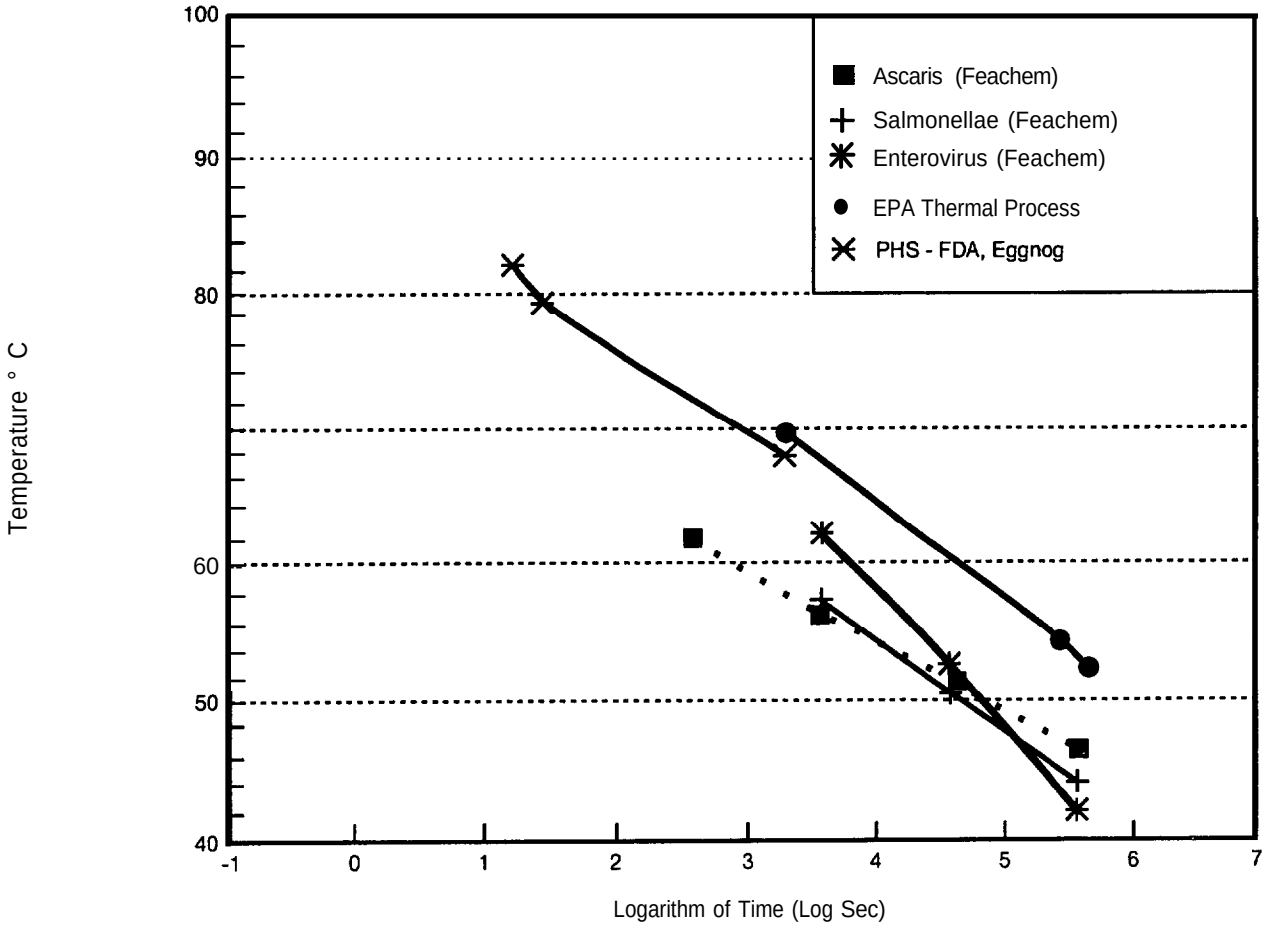

Figure 4-1. EPA's time-temperature relationship for thermal disinfection compared with other time-temperature relationships.

reactors in series (Schafer, et al, 1994). However, there are concerns that flow-through systems may permit some sludge to pass through without adequate treatment. It is recommended that facilities wishing to use this alternative for a flow-through system conduct tracer studies to demonstrate that sewage sludge is treated at the required temperature for sufficient time.

Vector Attraction Reduction

Thermally treated sewage sludge must be treated by an additional vector attraction reduction process since thermal treatment does not necessarily break down the volatile solids in sewage sludge. Vector attraction reduction can be met by further processing the sewage sludge with pH adjustment or heat drying (Options 6 and 7), or by meeting one of the other options (Options 8 – 11). Options 1 through 5 would not be applicable to thermally treated sludge unless the sludge was subject to biological digestion after or during thermal treatment.

Example of Meeting Class A Pathogen and Vector Attraction Reduction Requirements

Type of Facility	Thermophilic Anaerobic Digester Class A
	Digested sewage sludge is retained for at least 5 days at 50°C (Regime D). Sewage sludge is agitated regularly to ensure thorough mixing, and temperatures are monitored continually in a batch mode of operation.
Testing	Sewage sludge is sampled 6 times each year for pollutants and fecal coliforms. Compliance with vector attraction reduction is also monitored.
Vector Attraction Reduction	VAR is met by reducing volatile solids by over 38 percent. Five samples of input and output sewage sludge from each batch are analyzed for volatile solids content over a period of two weeks.
Use or Disposal	The Class A biosolids are land applied.

Microbiological Requirement

Microbiological monitoring for either fecal coliforms or *Salmonella* sp. is required to ensure that growth of bacterial pathogens has not occurred.

4.5 Alternative 2: Sewage Sludge Treated in a High pH-High Temperature Process (Alkaline Treatment) [503.32(a)(4)]

This alternative describes conditions of a high temperature-high pH process that has proven effective in reducing pathogens to below detectable levels. The process conditions required by the Part 503 regulation are:

- Elevating pH to greater than 12 and maintaining the pH for more than 72 hours.
- Maintaining the temperature above 52°C (126°F) throughout the sewage sludge for at least 12 hours during the period that the pH is greater than 12.
- Air drying to over 50% solids after the 72-hour period of elevated pH.

The hostile conditions of high pH, high temperature, and reduced moisture for prolonged time periods allow a variance to a less stringent time-temperature regime than for the thermal requirements under Alternative 1. The pH of the sewage sludge is measured at 25°C (77°F) or an appropriate correction is applied (see Section 10.7).

Example of Meeting Class A Pathogen and Vector Attraction Reduction

Type of Process Class	Alkaline Treatment
Pathogen Reduction	Alkaline material is used to bring sewage sludge pH to 12 for 72 hours during which time temperatures are above 52°C for 72 hours. Sewage sludge is agitated during the heat pulse phase to maintain even distribution, and temperature and pH are measured at multiple points within the sewage sludge. The sewage sludge is then moved to piles and maintained until moisture is reduced to 50 percent.
Testing	Piles are tested quarterly for pollutants and *Salmonella* sp. Samples are taken from stockpiled material, and material is not distributed for use or disposal until test results are received
Vector Attraction Reduction	VAR Option 6,pH adjustment; pH is to remain elevated until use/disposal.
Use or Disposal	During winter months (Nov-March), biosolids remain on site. In the spring, biosolids are re-tested for pathogens before being distributed.

Operational Issues

Because the elevated pH and temperature regimes must be met by the entire sewage sludge mass, operational protocols which include monitoring pH and temperature at various points in a batch and agitating the sewage sludge during operations to ensure consistent temperature and pH are appropriate.

Vector Attraction Reduction

The pH requirement of vector attraction reduction Option 6 is met when Alternative 2 is met. Compliance with Alternative 2 exceeds the pH requirements of Option 6.

Microbiological Requirements

As with all the Class A alternatives, microbiological monitoring for fecal coliforms or *Salmonella* sp. is required (see Section 4.3) to ensure that pathogens have been reduced and growth of pathogenic bacteria has not occurred.

4.6 Alternative 3: Sewage Sludge Treated in Other Processes [503.32(a)(5)]

This alternative applies to sewage sludge treated by processes that do not meet the process conditions required by Alternatives 1 and 2. This requirement relies on comprehensive monitoring of bacteria, enteric viruses and viable helminth ova to demonstrate adequate reduction of pathogens:

- Either the density of fecal coliforms in the sewage sludge must be less than 1000 MPN per gram of total solids (dry weight basis), or the *Salmonella* sp. bacteria in sewage sludge must be less than 3 MPN per 4 grams of total solids (dry weight basis) at the time the sewage is used or disposed, at the time the sewage sludge is prepared for sale or given away in a bag or other container for land application, or at the time the sewage sludge or material derived from the sewage sludge is prepared to meet the requirements in 503.10(b), 503.10(c), 503.10(e), or 503.10(f).
- The density of enteric viruses in the sewage sludge after pathogen treatment must be less than 1 PFU per 4 grams of total solids (dry weight basis).
- The density of viable helminth ova in the sewage sludge after pathogen treatment must be less than 1 per 4 grams of total solids (dry weight basis).

Testing for enteric viruses and viable helminth ova can be complicated by the fact that they are sometimes not present in the untreated sewage sludge. In this case, an absence of the organisms in the treated sewage sludge does not demonstrate that the process can reduce them to below detectable limits. For this reason, Alternative 3 requires that the feed sewage sludge be analyzed for enteric viruses and viable helminth ova. If these organisms are not detected in the feed sewage sludge, the sewage sludge is presumed to be acceptable as a Class A material until the next monitoring episode. Monitoring is continued until enteric viruses and/or viable helminth ova are detected in the feed sewage sludge (i.e., the density of enteric viruses is greater than or equal to 1 PFU per 4 grams total solids (dry weight basis) and/or the density of viable helminth ova is greater than or equal to 1 per 4 grams total solids (dry weight basis). At this point, the treated sewage sludge is analyzed to see if these organisms survived treatment. If enteric viruses densities are below detection limits, the sewage sludge meets Class A requirements for enteric viruses, and will continue to do so as long as the treatment process is operated under the same conditions that successfully reduced the enteric virus densities. If the viable helminth ova densities are below detection limits, the process meets the Class A requirements for enteric viruses and will continue to do so as long as the treatment process is operated under the same conditions that successfully reduced the viable helminth ova densities. Thus, it is essential to monitor and document operating conditions until adequate enteric virus and helminth ova reduction has been successfully demonstrated. Samples of untreated and treated sewage sludge must correspond (see Section 7.4).

Enteric Virus and Viable Helminth Ova Testing

Tests for enteric viruses and viable helminth ova take substantial time: 4 weeks to determine whether helminth ova are viable, and 2 weeks or longer for enteric viruses. The treatment works operator does not know whether the feed sewage sludge has enteric viruses or helminth ova until at least 2 to 4 weeks after the first samples for testing feed densities are taken. This works with rapid processes but long-term process systems need to have temporally related samples. In such cases, it may be feasible to obtain results within the processing time constraints. For enteric viruses, the sewage sludge should be stored frozen, unless the sample can be processed within 24 hours, in which case the samples may be stored at 4°C (39°F). For viable helminth ova, the sewage sludge should be stored at 4°C (39°F) (see Section 9.6).

Finding a laboratory that performs viable helminth ova and virus testing has been difficult for some sewage sludge preparers. Chapter 9 has more information on how to select a laboratory. State and Regional EPA sludge coordinators should also be contacted for information on qualified labs in the region.

Since this option relies on testing, rather than process and testing, to protect public health additional testings should be completed. At a minimum, a detailed sampling plan should be submitted to the permitting authority for review.

Vector Attraction Reduction

For both Alternatives 3 and 4, meeting vector attraction reduction depends on the process by which pathogen reduction is met. For example, sewage sludge subject to long-term storage may meet vector attraction reduction through volatile solids reduction (Options 1 – 3). Sewage sludges may also undergo additional processing or be applied following the requirements in Options 8 – 11.

Microbiological Requirements

As with all the Class A alternatives, microbiological monitoring for fecal coliforms or *Salmonella* sp. is required (see Section 4.3) to ensure that pathogens have been reduced and growth of pathogenic bacteria has not occurred.

4.7 Alternative 4: Sewage Sludge Treated in Unknown Processes [503.32(a)(6)]

The sewage sludge must meet the following limits at the time the biosolids (or material derived from sludge) are used or disposed, at the time the sewage sludge is prepared for sale or given away in a bag or other container for land application, or at the time the sewage sludge or material derived from the sewage sludge is prepared to meet the requirements in 503.10(b), 503.10(c), 503.10(e), or 503.10(f):

- The density of enteric viruses in the sewage sludge must be less than 1 PFU per 4 grams of total solids (dry weight basis).
- The density of viable helminth ova in the sewage sludge must be less than 1 per 4 grams of total solids (dry weight basis).

In addition, as for all Class A biosolids, the sewage sludge must meet fecal coliform or *Salmonella* sp. limits. As with Alternative 3, Alternative 4 depends on a successful sampling program that provides accurate representation of the sewage sludge's microbial quality (see Chapter 9).

Example Of Meeting Class A Pathogen Vector Attraction Reduction

Type of Facility	Unknown Process
Class	A
Pathogen Reduction	Sewage sludge is digested and retained in a lagoon up to 2 years. Sewage sludge is then moved to a stockpiling area where it may stay for up to 2 years.
Testing	Before sewage sludge is distributed, each pile, representing approximately 1 year of sewage sludge production, is tested for *Salmonella* sp., viable helminth ova, and enteric viruses. Since quarterly testing is mandated, based on the amount of sewage sludge which is used or disposed, four samples per pile are submitted
Vector Attraction Reduction	VAR is demonstrated by showing a 38 percent reduction in volatile solids. Records of incoming material and volume, bulk density, and percent volatile solids of outgoing material are used to calculate the reduction.
Distribution	Biosolids are distributed for land application and agricultural land.

Examples of situations where Alternative 4 may be used:

- Sewage sludge treatment process is unknown.
- The sewage sludge was produced with the process operating at conditions less stringent than the operating conditions at which the sewage sludge could qualify as Class A under other alternatives.

Enteric Virus and Viable Helminth Ova Testing

Tests for enteric viruses and viable helminth ova take substantial time: 4 weeks to determine whether helminth ova are viable, and 2 weeks or longer for enteric viruses. The treatment works operator does not know whether the feed sewage sludge has enteric viruses or helminth ova until at least 2 to 4 weeks after the first samples for testing feed densities are taken. This option works with rapid processes but long-term process systems need to have temporally related samples. In such cases, it may be feasible to obtain results within the processing time constraints. For enteric viruses, the sewage sludge should be stored frozen, unless the sample can be processed within 24 hours, in which case the samples may be stored at 4°C (39°F). For viable helminth ova, the sewage sludge should be stored at 4°C (39°F) (see Section 9.6).

Finding a laboratory that performs viable helminth ova and virus testing has been difficult for some sewage sludge preparers. Chapter 9 has more information on how to select a laboratory. State and Regional EPA sludge coordinators should also be contacted for information on qualified labs in the region.

Since this option relies on testing, rather than process and testing, to protect public health additional testings should be completed. At a minimum, a detailed sampling plan should be submitted to the permitting authority for review.

Vector Attraction Reduction

For both Alternatives 3 and 4, meeting vector attraction reduction depends on the process by which pathogen reduction is met. For example, sewage sludge subject to long-term storage may meet vector attraction reduction through volatile solids reduction (Options 1-3). Sewage sludges may also undergo additional processing or be applied following the requirement in Options 8-11.

4.8 Alternative 5: Use of PFRP [503.32(a)(7)]

Alternative 5 provides continuity with the 40 CFR Part 257 regulation. This alternative states that sewage sludge is considered to be Class A if:

- It has been treated in one of the Processes to Further Reduce Pathogens (PFRPs) listed in Appendix B of the regulation, and
- Either the density of fecal coliforms in the sewage sludge is less than 1,000 MPN per gram total solids (dry weight basis), or the density of *Salmonella* sp. bacteria in the sewage sludge is less than 3 MPN per 4 grams total solids (dry weight basis) at the time the sewage sludge is used or disposed, at the time the sewage sludge is prepared for sale or give away in a bag or other container for land application, or at the

time the sewage sludge or material derived from the sewage sludge is prepared to meet the requirements in 503.10(b), 503.10(c), 503.10(e), or 503.10(f).

To meet this requirement, the sewage sludge treatment processes must be operated according to the conditions listed in Appendix B of the regulation.

The Appendix B list of PFRPs is reproduced in Table 4-2. This list is very similar to the PFRP technologies listed in 40 CFR Part 257, with two major differences:

- All requirements related to vector attraction reduction have been removed.
- All the "add-on" processes listed in Part 257 are now full-fledged PFRPs.

Under this Alternative, treatment processes classified as PFRP under 40 CFR Part 257 can continue to be operated; however, microbiological monitoring must now be performed to ensure that the pathogen density levels are below detection limits and to ensure that growth of *Salmonella* sp. bacteria does not occur between treatment and use or disposal.

For all PFRP processes, the goal of temperature monitoring should be to represent all areas of a batch or pile and to ensure that temperature profiles from multiple points in the process all meet mandated temperatures. In some instances it may be possible to monitor representative areas of a batch or pile or a reasonable worst case area to ensure compliance. Chapter 7 contains more guidelines about the operation of PFRP processes.

4.9 Alternative 6: Use of a Process Equivalent to PFRP [503.32(a)(8)]

The 40 CFR Part 257 regulation allowed any treatment process to be determined *equivalent* to a PFRP. Under Alternative 6, sewage sludge is considered to be a Class A sewage sludge if:

- It is treated by any process equivalent to a PFRP, **and**
- Either the density of fecal coliforms in the sewage sludge is less than 1,000 MPN per gram total solids (dry weight basis), or the density of *Salmonella* sp. bacteria in the sewage sludge is less than 3 MPN per 4 grams total solids (dry weight basis) at the time the sewage sludge is used or disposed, at the time the sewage sludge is prepared for sale or give away in a bag or other container for land application, or at the time the sewage sludge or material derived from the sewage sludge is prepared to meet the requirements in 503.10(b), 503.10(c), 503.10(e), or 503.10(f).

Facilities that meet Alternative 6 for pathogen reduction must still meet vector attraction reduction requirements.

Processes Already Recommended as Equivalent

Processes recommended to be equivalent to PFRP are shown in Table 11.2. Products of all equivalent processes must still meet the Class A fecal coliform or *Salmonella* sp. requirements.

Who Determines Equivalency?

Part 503 gives the permitting authority responsibility for determining equivalency under Alternative 6. The EPA's Pathogen Equivalency Committee (PEC) is available as a resource to provide guidance and recommendations on equivalency determinations to both the permitting authority and the regulated community (see Chapter 11).

4.10 Frequency of Testing

The Part 503 regulation sets forth minimum sampling and monitoring requirements. Table 3-4 in Chapter 3 de-

Table 4-2. Processes to Further Reduce Pathogens (PFRPs) Listed in Appendix B of 40 CFR Part 503[1]

Composting	Using either the within-vessel composting method or the static aerated pile composting method, the temperature of sewage sludge is maintained at 55°C (131°F) or higher for 3 consecutive days. Using the windrow composting method, the temperature of the sewage sludge is maintained at 55°C (131°F) or higher for 15 consecutive days or longer. During the period when the compost is maintained at 55°C (131°F) or higher, there shall be a minimum of five turnings of the windrow.
Heat Drying	Sewage sludge is dried by direct or indirect contact with hot gases to reduce the moisture content of the sewage sludge to 10% or lower. Either the temperature of the sewage sludge particles exceeds 80°C (176°F) or the wet bulb temperature of the gas in contact with the sewage sludge as the sewage sludge leaves the dryer exceeds 80°C (176°F).
Heat Treatment	Liquid sewage sludge is heated to a temperature of 180°C (356°F) or higher for 30 minutes.
Thermophilic Aerobic Digestion	Liquid sewage sludge is agitated with air or oxygen to maintain aerobic conditions and the mean cell residence time (i.e., the solids retention time) of the sewage sludge is 10 days at 55°C (131°F) to 60°C (140°F).
Beta Ray Irradiation	Sewage sludge is irradiated with beta rays from an electron accelerator at dosages of at least 1.0 megarad at room temperature (ca. 20°C [68°F]).
Gamma Ray Irradiation	Sewage sludge is irradiated with gamma rays from certain isotopes, such as Cobalt 60 and Cesium 137, at dosages of at least 1.0 megarad at room temperature (ca. 20°C [68°F]).
Pasteurization	The temperature of the sewage sludge is maintained at 70°C (158°F) or higher for 30 minutes or longer.

[1]Chapter 7 provides a detailed description of these technologies.

scribes the minimum frequency at which the sewage sludge must be sampled and analyzed for pathogens or vector attraction reduction in order to meet regulatory requirements. In addition to meeting these minimal requirements, the EPA recommends that sewage sludge generators and preparers also consider the potential public health impact pathways and possible liability issues when designing a sampling program. In some cases, it may be appropriate to sample more frequently than the required minimum.

Classification of biosolids as Class A or Class B is based on the most recent test results available. For example, if a facility produces a Class A compost, and sampling is performed once each quarter, the compost produced after each test result verifying Class A is returned is also assumed to be Class A, assuming that the same process continues to be followed. If a test result indicates that compost is not achieving Class A, all compost subsequently generated would be classified as Class B (assuming it meets Class B requirements). The Class B classification would remain until a test result confirming Class A quality is returned.

This raises several issues. Land application of Class B biosolids without site restrictions is a violation of the 503 regulation. In addition, if material is mistakenly classified as EQ biosolids and land applied without restriction to the public, the biosolids preparer may be inadvertently creating a public health risk as well as opening the facility to liability. The key issues to consider are:

At what point between the two sampling events does the material change from Class A to C/ass B? This depends on the particular situation. The Class B test result may be an exception – the result of cross contamination or faulty sampling or monitoring for one pile. On the other hand, the test result could be indicative of an operation which is not adequately reducing pathogens. The piles which were actually sampled may have been used or distributed under the classification of the previous lab results while lab results were pending (it generally takes 2 weeks to get lab results back). Because distribution of this material as Class A would constitute a violation of the Part 503 regulation, it is recommended that material generated during and subsequent to a sampling event remain on site until lab results are available.

What can you do if you suspect Class B biosolids have been distributed as Class A biosolids? The first question to answer is: has this material created a public health risk. The material should be resampled to determine if it is indeed Class B and not Class A. The Part 503 requires that Class A biosolids meet either the fecal coliform or the *Salmonella* sp. requirements (except for Alternatives 3 and 4). If the material is out of compliance for fecal coliforms, it should immediately be tested for *Salmonella* sp. (and vice versa). In addition, the validity of the test results should be checked by contacting the lab and reviewing the data.

Material distribution should then be tracked to determine where material has been used. Businesses and individuals to whom material has been distributed should be notified and informed of the potential quality issue. If material is stockpiled at distribution points such as at a soil blender or landscaper, the material should be retested for pathogen levels, and distribution be curtailed until the process is reviewed and acceptable results are achieved. The facility may even consider recalling the biosolids from the users.

If material has already been distributed to public access areas, including homes, gardens, parks, or other public areas, the biosolids preparer may consider testing the soil. If the testing indicates problems, corrective actions may be necessary.

How can a situation like this be avoided? There are several sampling practices that a facility should follow in order to avoid a situation like this.

First, sampling should take place close enough to the time of distribution so that results accurately reflect material quality.

If possible, material sampled and subsequently produced material should not be distributed until the results are available; there is usually a 2-week waiting period for lab results for fecal coliform or *Salmonella* sp. analysis.

More frequent sampling can help pinpoint when operational conditions change. This may allow more rapid correction of operations.

Stockpile biosolids in discrete batches and take multiple samples per sampling event. This will allow better identification of which piles may be out of compliance and will allow for the distribution of material that is identified as Class A.

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Chapter 5
Class B Pathogen Requirements and Requirements for Domestic Septage Applied to Agricultural Land, a Forest, or a Reclamation Site

5.1 Introduction

Class B pathogen requirements can be met in three different ways. The implicit objective of all three alternatives is to ensure that pathogenic bacteria and enteric viruses are reduced in density, as demonstrated by a fecal coliform density in the treated sewage sludge (biosolids) of 2 million MPN or CFU per gram total solids biosolids (dry weight basis)[1]. Viable helminth ova are not necessarily reduced in Class B biosolids.

Unlike Class A biosolids, which are essentially pathogen free, Class B biosolids may contain some pathogens. Site restrictions that restrict crop harvesting, animal grazing, and public access for a certain period of time are required. This allows environmental factors to further reduce pathogens. Where appropriate, these restrictions are designed to ensure sufficient reduction in viable helminth ova, one of the hardiest of pathogens, since these pathogens may not have been reduced during sewage sludge treatment.

The Class B requirements apply to bulk biosolids that are land applied to such areas as agricultural land, forests, public contact sites, or reclamation sites. Biosolids that are placed on a surface disposal site also must meet the Class B pathogen requirements, unless the active biosolids unit on which the biosolids are placed is covered at the end of each operating day (see Table 3-1). Because the use of Class B biosolids must be closely monitored, Class B biosolids cannot be given away or sold in bags or other containers.

Domestic septage applied to agricultural land, forest, or a reclamation site must meet all of the Class B site restrictions under 503.32(b)(5) unless the domestic septage has met specific pH requirements (see Section 5.6).

Class B biosolids and domestic septage also must meet one of the vector attraction reduction requirements (see Chapter 8). Note that the choice of vector attraction options may affect the duration of site restrictions in some cases. Specifically, if Option 9 or 10 (injection or incorporation) is used to reduce vector attraction, the restriction on harvesting for food crops grown below the soil surface (potatoes, carrots, etc.) is increased from 20 months to 38 months.

Sections 5.2 to 5.4 discuss the three alternative Class B pathogen requirements for sewage sludge. Section 5.5 discusses the site restrictions for land applied Class B biosolids, and Section 5.6 presents the requirements for domestic septage applied to agricultural land, forests, or reclamation sites. The title of each section provides the number of the Subpart D requirement discussed in the section. A copy of Subpart D can be found in Appendix B. Chapters 9 and 10 provide guidance on the sampling and analysis necessary to meet the Class B microbiological requirements.

5.2 Sewage Sludge Alternative 1: Monitoring of Fecal Coliform [503.32(b)(2)]

Alternative 1 requires that seven samples of treated sewage sludge (biosolids) be collected and that the geometric mean fecal coliform density of these samples be less than 2 million CFU or MPN per gram of biosolids (dry weight basis). This approach uses fecal coliform density as an indicator of the average density of bacterial and viral pathogens. Over the long term, fecal coliform density is expected to correlate with bacterial and viral pathogen density in biosolids treated by biological treatment processes (EPA, 1992).

Use of at least seven samples is expected to reduce the standard error to a reasonable value. The standard deviation can be a useful predictive tool. A relatively high standard deviation for the fecal coliform density indicates a wide range in the densities of the individual samples. This may be due to sampling variability or variability in the laboratory analysis, or it may indicate that the treatment process is not consistent in its reduction of pathogens. A high standard deviation can therefore alert the preparer that the sampling, analysis, and treatment processes should be reviewed.

[1]Farrell et al. (1985) have shown that if a processed sewage sludge is processed by aerobic or anaerobic digestion it has a fecal coliform density of 2 million MPN or CFU per gram, enteric viruses and bacteria are significantly reduced. A comparison of suspended solids densities in entering wastewater to suspended solids densities in treated sewage sludge shows that this density of fecal coliform in treated sewage sludge represents a 100-fold (Z-log) reduction in fecal coliform density, and is expected to correlate with an approximately 1.5 log (approximately 32-fold) reduction in *Salmonella* sp. density and an approximately 1.3 log (20-fold) reduction in the density of enteric viruses.

Each of the multiple samples taken for fecal coliform analysis should be taken at the same point in the process so that treatment of each sample has been equal. Samples must be handled correctly and analyzed within 24 hours in order to minimize the effect of the holding time of the sample on the microbial population.

Laboratory sampling should follow Standard Methods as outlined in the Appendix of this document. Standard QA/QC practices, including duplicates to verify laboratory protocols should be followed. Generally a log standard deviation between duplicate samples under 0.3 is acceptable for lab analyses.

Calculating the Geometric Mean for Class B Alternative 1

- Take seven samples over a 2-week period.
- Analyze samples for fecal coliform using the membrane filter or MPN dilution method.
- Take the log (Base 10) of each result.
- Take the average (arithmetic) of the logs.
- Take the anti-log of the arithmetic average. This is the geometric mean of the results.

Example: The results of analysis of seven samples of sewage sludge are shown below. The second column of the table shows the log of each result.

	Fecal Coliform (MPN/dry gram sewage sludge)	Log
Sample 1	6.4×10^6	6.81
Sample 2	4.8×10^4	4.68
Sample 3	6.0×10^5	5.78
Sample 4	5.7×10^5	5.76
Sample 5	5.8×10^5	5.76
Sample 6	4.4×10^6	6.64
Sample 7	6.2×10^7	7.80
Average (Arithmetic)		6.18
Antilog (geometric mean)		1.5×10^6
Log standard deviation		1.00*

Note that this sewage sludge would meet Class B fecal coliform requirements even though several of the analysis results exceed the 2.0×10^6/dry gram limit.
*Duplicate analyses on the same sample would give a much lower standard deviation. Variability is inflated by differences in feed and product over a 2-week sampling period.

Process parameters including retention time and temperature should be examined in order to verify that the process is running as specified. Monitoring equipment should be calibrated regularly.

The seven samples should be taken over a 2-week period in order to represent the performance of the facility under a range of conditions. For small facilities that are required to sample infrequently, sampling should be performed under worst case conditions, for example, during the winter when the climatic conditions are the most adverse.

It has been found that* for *Class B compliance, the MPN dilution method for fecal coliform analysis is more appropriate than the membrane filtration test. This is because colloidal and suspended solids may interfere with media transport through the membrane filter. Furthermore, concentration of toxic or inhibitory substances at the filter surface may affect results. It is therefore recommended that the membrane filter procedure be used *only after demonstrating comparability between the membrane filter test and the MPN method for a given sewage sludge.*

Example of Meeting Class B Pathogen Vector Attraction Reduction Requirements

Type of Facility	Extended Aeration
Class	B
Pathogen Reduction	----------
Testing	Quarterly testing for pollutants and for fecal coliform to determine if Class B Alternative 1 requirements are met.
Vector Attraction Reduction	The SOUR test is used to demonstrate compliance with VAR Option 4
Use or Disposal	The Class B biosolids are delivered to farmers along with information regarding analysis and site restrictions

5.3 Sewage Sludge Alternative 2: Use of a Process to Significantly Reduce Pathogens (PSRPs) [503.32(b)(3)]

The PSRP Class B alternative provides continuity with the 40 CFR Part 257 regulation. Under this Alternative, treated sewage sludge (biosolids) is considered to be Class B if it is treated in one of the "Processes to Significantly Reduce Pathogens" (PSRPs) listed in Appendix B of Part 503. The biological PSRP processes are sewage sludge treatment processes that have been demonstrated to result in a 2-log reduction in fecal coliform density. See Chapter 7.

The PSRPs in the Part 503 are reproduced in Table 5-1 and described in detail in Chapter 6. They are similar to the PSRPs listed in the Part 257 regulation, except that all conditions related to reduction of vector attraction have been removed. Under this alternative, sewage sludge treated by processes that are PSRPs under 40 CFR Part 257 are Class B with respect to pathogens. Unlike the comparable Class A requirement (see Section 4.8), this Class B alternative does not require microbiological monitoring.

However, monitoring of process requirements such as time, temperature, and pH is required.

Table 5-1. Processes to Significantly Reduce Pathogens (PSRPs) Listed in Appendix B of 40 CFR Part 503

1. Aerobic Digestion	Sewage sludge is agitated with air or oxygen to maintain aerobic conditions for a specific mean cell residence time (i.e., solids retention time) at a specific temperature. Values for the mean cell residence time and temperature shall be between 40 days at 20°C (68°F) and 60 days at 15°C (59°F).
2. Air Drying	Sewage sludge is dried on sand beds or on paved or unpaved basins. The sewage sludge dries for a minimum of 3 months. During 2 of the 3 months, the ambient average daily temperature is above 0°C (32°F).
3. Anaerobic Digestion	Sewage sludge is treated in the absence of air for a specific mean cell residence time (i.e., solids retention time) at a specific temperature. Values for the mean cell residence time and temperature shall be between 15 days at 35°C to 55°C (131°F) and 60 days at 20°C (68°F).
4. Composting	Using either the within-vessel, static aerated pile, or windrow composting methods, the temperature of the sewage sludge is raised to 40°C (104°F) or higher and remains at 40°C (104°F) or higher for 5 days. For 4 hours during the 5 day period, the temperature in the compost pile exceeds 55°C (131°F).
5. Lime Stabilization	Sufficient lime is added to the sewage sludge to raise the pH of the sewage sludge to 12 for ≥2 hours of contact.

5.4 Sewage Sludge Alternative 3: Use of Processes Equivalent to PSRP [503.32(b)(4)]

The Part 257 regulation allowed the sewage sludge to be treated by a process determined to be equivalent to a PSRP. Under Class B Alternative 3, sewage sludge treated by any process determined to be equivalent to a PSRP is considered to be Class B biosolids. A list of processes that have been recommended as equivalent to PSRP are shown in Table 11.1.

Part 503 gives the regulatory authority responsibility for determining equivalency. The Pathogen Equivalency Committee is available as a resource to provide guidance and recommendations on equivalency determinations to the regulatory authorities (see Chapter 11).

5.5 Site Restrictions for Land Application of Biosolids [503.32(b)(5)]

Potential exposure to pathogens in Class B biosolids via food crops is a function of three factors: first there must be pathogens in the biosolids; second, the application of Class B biosolids to food crops must transfer the pathogens to the harvested crop, and third, the crop must be ingested before it is processed to reduce the pathogens. Elimination of one of these steps eliminates the pathway by which public health may be affected. The use of Class A biosolids protects public health by reducing pathogens in sewage sludge to below detectable levels. Biosolids that meet the Class B requirements may contain reduced but still significant densities of pathogenic bacteria, viruses, protozoans, and viable helminth ova. Thus, site restrictions are to allow time for further reduction in the pathogen population. Harvest restrictions are imposed in order to reduce the possibility that food will be harvested and ingested before pathogens which may be present on the food have died off. Harvest restrictions vary, depending on the type of crop, because the amount of contact a crop will have with biosolids or pathogens in biosolids varies.

The site restrictions are primarily based in the survival rates of viable helminth ova, one of the hardiest of pathogens that may be present on sewage sludge. The survival of pathogens, including the helminth ova, depends on exposure to the environment. Some of the factors that affect pathogen survival include pH, temperature, moisture, cations, sunlight, presence of soil microflora, and organic material content. On the soil surface, helminth ova has been found to die off within 4 months, but survival is longer if pathogens are within the soil. Helminth ova have been found to survive in soil for several years (Smith, 1997; Kowal 1985). Site restrictions take this into account by making a distinction between biosolids that are applied to the land surface, biosolids that are incorporated into the soil after at least 4 months on the soil surface, and biosolids that are incorporated into the soil within 4 months of being applied.

Site restrictions also take the potential pathways of exposure into account. For example, crops that do not contact the soil, such as oat or wheat, may be exposed to biosolids, but pathogens on crop surfaces have been found to be reduced very quickly (30 days) due to exposure to sunlight, desiccation, and other environmental factors. Crops that touch the soil, such as melons or cucumbers, may also come into contact with biosolids particles, but pathogens in this scenario are also subject to the harsh effects of sunlight and rain and will die off quickly. Crops grown in soil such as potatoes are surrounded by biosolids amended soil, and pathogen die-off is much slower below the soil surface.

These pathways should be considered when determining which site restriction is appropriate for a given situation. The actual farming and harvesting practices as well as the intended use of the food crop should also be considered. For example, oranges are generally considered a food crop that does not touch the ground. However, some oranges grow very low to the ground and may come into contact with soil. If the oranges that have fallen to the ground or grew touching the ground are harvested for direct consumption without processing, the 14-month harvest restriction for crops that touch the soil should be followed. Orange crops which do not touch the ground at all would not fall under the 14-month harvest restriction; harvest would be restricted for 30 days under 503.32(b)(5)(iv)

which covers food crops that do not have harvested parts in contact with the soil. For similar situations, the potential for public health impacts must be considered. Harvest practices such as the use of fallen fruit or washing or processing crops should be written into permits so that restrictions and limits are completely clear. Figure 5-1 illustrates the steps of exposure that should be considered when making a decision about harvest and site restrictions. In addition, several examples of permit conditions are included. The site restrictions for land applied Class B biosolids are summarized below. The regulatory language is given in italics. Note that the restrictions apply only to the harvesting of food crops, but not to the planting or cultivation of crops.

Food Crops with Harvested Parts That Touch the Sewage Sludge/Soil Mixture

503.32(b)(5)(i): Food crops with harvested parts that touch the sewage sludge/soil mixture and are totally above the land surface shall not be harvested for 14 months after application of sewage sludge.

This time frame is sufficient to enable environmental conditions such as sunlight, temperature, and desiccation to further reduce pathogens on the land surface. Note that the restriction applies only to harvesting. Food crops can be planted at any time before or after biosolids application, as long as they are not harvested within 14 months

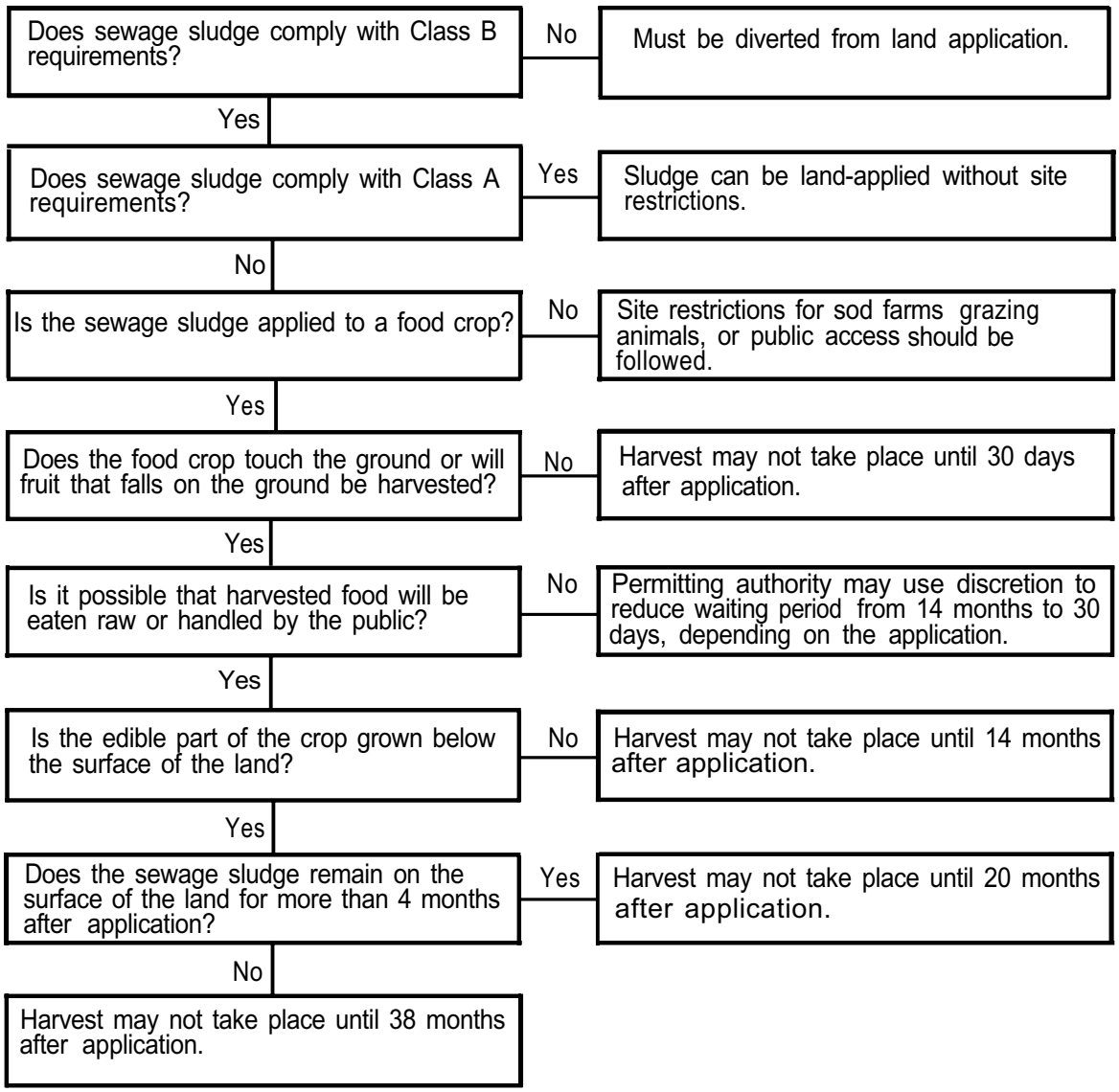

Figure 5-1. Decision tree for harvesting and site restrictions.

after sludge application. Examples of food crops grown on or above the soil surface with harvested parts that typically touch the sewage sludge/soil mixture include lettuce, cabbage, melons, strawberries, and herbs. Land application should be scheduled so that crop harvests are not lost due to harvest restrictions.

Food Crops with *Harvested Parts Below the Land Surface*

503.32(b)(5)(ii): Food crops with harvested parts below the surface of the land shall not be harvested for 20 months after application of sewage sludge when the sewage sludge remains on the land surface for 4 months or longer prior to incorporation into the soil.

Pathogens on the soil surface will be exposed to environmental stresses which greatly reduce their populations. Helminth ova have been found to die off after 4 months on the soil surface (Kowal, 1994). Therefore, a distinction is made between biosolids left on the soil surface for 4 months and biosolids which are disced or plowed into soil more quickly.

For a September 1999 harvest, biosolids could be applied to the soil surface up to the end of December 1997, plowed or disced into the soil in April 1998, and the crop planted in order to allow it to be harvested in September 1999. Examples of crops with harvested parts below the land surface are potatoes, radishes, beets, onions and carrots.

Examples of Site Restrictions for Questionable Food Crop Situations

Tree Nut Crops - Nuts which are washed hulled, and dehydrated before being distributed for public consumption must follow the 30-day restriction. Nuts which are harvested from the ground and sold in their shell without processing are subject to the 14-month restriction.

Sugar Beets - Sugar beets aren't expected to be eaten raw. If the beets are transported off site and considerable biosolids amended soil is carried off with them, the restrictions apply. If biosolids are left on the soil surface for 4 months or longer before being incorporated, the 20-month restriction applies. If biosolids are incorporated within 4 months of application, the 38-month restriction applies.

Tomatoes (and peppers) - Fruit often comes in contact with the ground. Tomatoes are sold both to processors and to farm stands. Tomatoes may be eaten raw by the public without further processing. The 14-month restriction applies.

503.32(b)(5)(iii): Food crops with harvested parts below the surface of the land shall not be harvested for 38 months after application of sewage sludge when the sewage sludge remains on the land surface for less than 4 months prior to incorporation into the soil.

Exposure of the surface of root crops such as potatoes and carrots to viable helminth ova is a principal concern under these circumstances. Four months is considered the minimum time for environmental conditions to reduce viable helminth ova in biosolids on the land surface. Class B biosolids incorporated into the soil surface less than 4 months after application may contain significant numbers of viable helminth ova. Once incorporated into the soil, die-off of these organisms proceeds much more slowly; therefore, a substantially longer waiting period is required to protect public health. Thirty-eight months after biosolids application is usually sufficient to reduce helminth ova to below detectable levels.

Food Crops, Feed Crops, and Fiber Crops

503.32(b)(5)(iv): Food crops, feed crops, and fiber crops shall not be harvested for 30 days after application of sewage sludge.

This restriction covers food crops that are not covered by 503.32(b)(I-iii). This would include crops with harvested parts that do not typically touch the biosolids/soil mixture and which are not collected from the ground after they have fallen from trees or plants. The restriction also applies to all feed and fiber crops. These crops may be exposed to pathogens when biosolids are applied to the land. Harvesting of these crops could result in the transport of biosolids pathogens from the growing site to the outside environment. After 30 days, however, any pathogens in biosolids that may have adhered to the crop during application will likely have been reduced to non-detectable levels. Hay, corn, soybeans, or cotton are examples of a crop covered by this restriction.

Animal Grazing

503.32(b)(5)(v): Animals shall not be allowed to graze on the land for 30 days after application of sewage sludge.

Biosolids can adhere to animals that walk on biosolids amended land and thereby be brought into potential contact with humans who come in contact with the animals (for example, horses and milking cows allowed to graze on a biosolids amended pasture). Thirty days is sufficient to substantially reduce the pathogens in surface applied biosolids, thereby significantly reducing the risk of human and animal contamination.

Turf Harvesting

503.32(b)(5)(vi): Turf grown on land where sewage sludge is applied shall not be harvested for 1 year after application of the sewage sludge when the harvested turf is placed on either land with a high potential for public exposure or a lawn, unless otherwise specified by the permitting authority.

The 1-year waiting period is designed to significantly reduce pathogens in the soil so that subsequent contact

of the turf layer will not pose a risk to public health and animals. A permitting authority may reduce this time period in cases in which the turf is not used on areas with high potential for public access.

Public Access

503.32(b)(5)(vii): Public access to land with a high potential for public exposure shall be restricted for 1 year after application of the sewage sludge.

As with the turf requirement above, a 1-year waiting period is necessary to protect public health and the environment in a potential high-exposure situation. A baseball diamond, playground, public park, or a soccer field are examples of land with a high potential for public exposure. The land gets heavy use and contact with the soil is substantial (children or ball players fall on it and dust is raised which is inhaled and ingested).

503.32(b)(5)(viii): Public access to land with a low potential for public exposure shall be restricted for 30 days after application of the sewage sludge.

A farm field used to grow corn or soybeans is an example of land with low potential for public exposure. Even farm workers and family members walk about very little on such fields. Public access restrictions do not apply to farm workers, but workers should be aware of the public health implications of land application and the land application schedule, and should follow good hygiene practice during the 30-day period. For example, workers should be instructed to wash their hands after handling soil or crops that come into contact with soil. Protective clothing and footwear are recommended for workers who work on fields that have recently been applied with Class B biosolids. More safety recommendations for workers handling biosolids are included in Section 2.2.

5.6 Domestic Septage [503.32(c)]

Under Part 503.32(c), pathogen reduction in domestic septage applied to agricultural land, forest, or reclamation sites[2] may be reduced in one of two ways:

- Either all the Class B site restrictions under 503.32(b)(5) --see Section 5.5--must be met,
- Or the pH of the domestic septage must be raised to 12 or higher by alkali addition and maintained at pH 12 or higher for 30 minutes without adding more alkali, and the site restrictions on crop harvesting in 503.32(b)(5)(I-iv) must be met (see Section 5.5). The Part 503 regulation uses the term alkali in the broad sense to mean any substance that causes an increase in pH.

Vector attraction reduction can be met with Option 9, 10, or 13. Domestic septage can be incorporated or injected into the soil to prevent vector attraction, or the pH of the domestic septage can be adjusted as outlined in Option 12 (see Section 8). pH adjustment can fulfill both pathogen and vector attraction reduction.

The pH requirement applies to every container of domestic septage applied to the land, which means that the pH of each container must be monitored. The first alternative reduces exposure to pathogens in land applied domestic septage while environmental factors attenuate pathogens. The second alternative relies on alkali treatment to reduce pathogens and contains the added safeguard of restricting crop harvesting, which prevents exposure to crops grown on domestic septage amended soils.

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[2] Class B sewage sludge requirements apply to domestic septage applied to all other types of land. No pathogen-related requirements apply to domestic septage placed on a surface disposal site.

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Chapter 6
Processes to Significantly Reduce Pathogens (PSRPs)

6.1 Introduction

Processes to Significantly Reduce Pathogens (PSRPs) are listed in Appendix B of Part 503. There are five PSRPs: aerobic and anaerobic digestion, air drying, composting, and lime stabilization. Under Part 503.32(b)(3), sewage sludge meeting the requirements of these processes is considered to be Class B with respect to pathogens (see Section 5.3). When operated under the conditions specified in Appendix B, PSRPs reduce fecal coliform densities to less than 2 million CFU or MPN per gram of total solids (dry weight basis) and reduce *Salmonella* sp. and enteric virus densities in sewage sludge by approximately a factor of 10 (Farrell, et al., 1985).

This level of pathogen reduction is required, as a minimum, by the Part 503 regulation if the sewage sludge is applied to agricultural land, a public contact site, a forest, or a reclamation site or placed on a surface disposal site[1]. Because Class B biosolids may contain some pathogens, land application of Class B biosolids is allowed only if crop harvesting, animal grazing, and public access are limited for specific periods of time following application of Class B biosolids so that pathogens can be further reduced by environmental factors (see Section 5.5).

The PSRPs listed in Part 503 are essentially identical to the PSRPs that were listed under the 40 CFR Part 257 regulation, except that all requirements related solely to reduction of vector attraction have been removed. Vector attraction reduction is now covered under separate requirements (see Chapter 8) that include some of the requirements that were part of the PSRP requirements under Part 257, as well as some new options for demonstrating vector attraction reduction. These new options provide greater flexibility to the regulated community in meeting the vector attraction reduction requirements.

Although theoretically two or more PSRP processes, each of which fails to meet its specified requirements, could be combined and effectively reduce pathogens (i.e. partial treatment in digestion followed by partial treatment by air drying) it cannot be assumed that the pathogen reduction contribution of each of the operations will result in the 2-log reduction in fecal coliform necessary to define the combination as a PSRP. Therefore, to comply with Class B pathogen requirements, one of the PSRP processes must be conducted as outlined in this chapter, or fecal coliform testing must be conducted in compliance with Class B Alternative 1. The biosolids preparer also has the option of applying for PSRP equivalency for the combination of processes. Achieving PSRP equivalency enables the preparer to stop monitoring for fecal coliform density.

This chapter provides detailed descriptions of the PSRPs listed in Appendix B. Since the conditions for the PSRPs, particularly aerobic and anaerobic digestion, are designed to meet pathogen reduction requirements, they are not necessarily the same conditions as those traditionally recommended by environmental engineering texts and manuals.

6.2 Aerobic Digestion

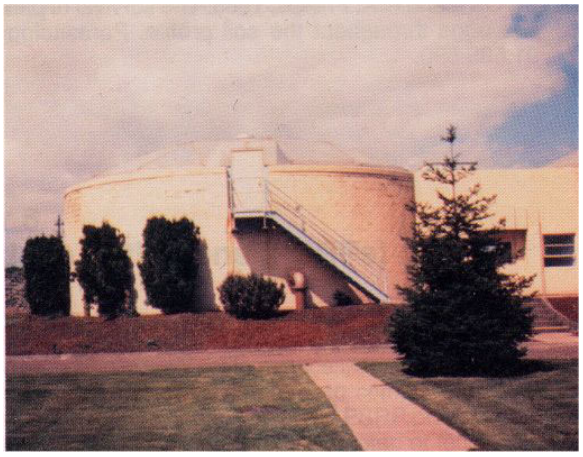
In aerobic digestion, sewage sludge is biochemically oxidized by bacteria in an open or enclosed vessel (see photo). To supply these aerobic microorganisms with enough oxygen, either the sewage sludge must be agitated by a mixer, or air must be forcibly injected (Figure 6-1). Under proper operating conditions, the volatile solids in sewage sludge are converted to carbon dioxide, water, and nitrate nitrogen.

Aerobic systems operate in either batch or continuous mode. In batch mode, the tank is filled with untreated sewage sludge and aerated for 2 to 3 weeks or longer, depending on the type of sewage sludge, ambient temperature, and average oxygen levels. Following aeration, the stabilized solids are allowed to settle and are then separated from the clarified supernatant. The process is begun again by inoculating a new batch of untreated sewage sludge with some of the solids from the previous batch to supply the necessary biological decomposers. In continuous mode, untreated sewage sludge is fed into the digester once a day or more frequently; thickened, clarified solids are removed at the same rate.

The PSRP description in Part 503 for aerobic digestion is:

- Sewage sludge is agitated with air or oxygen to maintain aerobic conditions for a specific mean cell resi-

[1]Unless the active biosolids surface disposal unit is covered at the end of each operating day, in which case no pathogen requirement applies.



Digester in Vancouver, Washington.

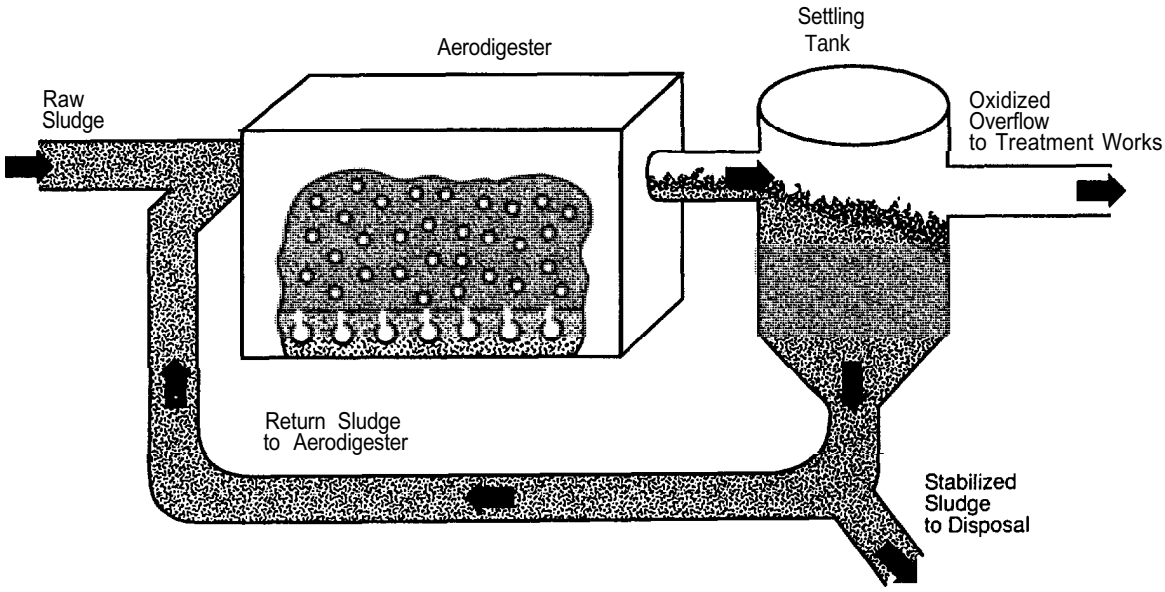


Figure 6-1. Aerobic digestion.

dence time at a specific temperature. Values for the mean cell residence time and temperature shall be between 40 days at 20°C (68°F) and 60 days at 15°C (59°F).

For temperatures between 15°C (59°F) and 20°C (68°F) use the relationship between time and temperature provided below to determine the required mean cell residence time.

$$\frac{\text{Time @T°C}}{40\ \text{d}} = 1.08\ (20\text{-}T)$$

The regulation does not differentiate between batch, intermittently fed, and continuous operation, so any method is acceptable. The mean cell residence time is considered the residence time of the sewage sludge solids. The appropriate method for calculating residence time depends on the type of digester operation used (see Appendix E).

Continuous-Mode, No Supernatant Removal For continuous-mode digesters where no supernatant is removed, nominal residence times may be calculated by dividing liquid volume in the digester by the average daily flow rate in or out of the digester.

Continuous-Mode, Supernatant Removal In systems where the supernatant is removed from the digester and recycled, the output volume of sewage sludge can be much less than the input volume of sewage sludge. For these systems, the flow rate of the sewage sludge out of the digester is used to calculate residence times.

Continuous-Mode Feeding, Batch Removal of Sewage Sludge For some aerobic systems, the digester is initially filled above the diffusers with treated effluent, and sewage sludge is wasted daily into the digester. Periodically, aeration is stopped to allow solids to settle and supernatant to be removed. As the supernatant is drawn off, the solids content in the digester gradually increases. The process is complete when either settling or supernatant removal is inadequate to provide space for the daily sewage sludge wasting requirement, or sufficient time for digestion has been provided. The batch of digested sewage sludge is then removed and the process begun again. If the daily mass of sewage sludge solids introduced has been constant, nominal residence time is one-half the total time from initial charge to final withdrawal of the digested sewage sludge.

Batch or Staged Reactor Mode A batch reactor or two or more completely-mixed reactors in series are more effective in reducing pathogens than is a single well-mixed reactor at the same overall residence time. The residence time required for this type of system to meet pathogen reduction goals may be 30% lower than the residence time required in the PSRP definition for aerobic digestion (see Appendix E). However, since lower residence times would not comply with PSRP conditions required for aerobic digestion in the regulation, approval of the process as a PSRP by the permitting authority would be required.

Other Digesters are frequently operated in unique ways that do not fall into the categories above. Appendix E provides information that should be helpful in developing a calculation procedure for these cases. Aerobic digestion carried out according to the Part 503 requirements typically reduces bacterial organisms by 2-log and viral pathogens by 1-log. Helminth ova are reduced to varying degrees, depending on the hardiness of the individual species. Aerobic digestion typically reduces the volatile solids content (the microbes' food source) of the sewage sludge by 40% to 50%, depending on the conditions maintained in the system.

Vector Attraction Reduction

Vector attraction reduction for aerobically digested sewage sludges is demonstrated either when the percent volatile solids reduction during sewage sludge treatment equals or exceeds 38%, or when the specific oxygen uptake rate (SOUR) at 20°C (68°F) is less than or equal to 1.5 mg of oxygen per hour per gram of total solids, or when additional volatile solids reduction during bench-scale aerobic batch digestion for 30 additional days at 20°C (68°F) is less than 15% (see Chapter 8).

Thermophilic aerobic systems (operating at higher temperatures) capable of producing Class A biosolids are described in Section 7.5.

6.3 Anaerobic Digestion

Anaerobic digestion is a biological process that uses bacteria that function in an oxygen-free environment to convert volatile solids into carbon dioxide, methane, and ammonia. These reactions take place in an enclosed tank (see Figure 6-2) that may or may not be heated. Because the biological activity consumes most of the volatile solids needed for further bacterial growth, microbial activity in the treated sewage sludge is limited. Currently, anaerobic digestion is one of the most widely used treatments for sewage sludge treatment, especially in treatment works with average wastewater flow rates greater than 19,000 cubic meters/day (5 million gallons per day).

Most anaerobic digestion systems are classified as either standard-rate or high-rate systems. Standard-rate systems take place in a simple storage tank with sewage sludge added intermittently. The only agitation that occurs comes from the natural mixing caused by sewage sludge gases rising to the surface. Standard-rate operation can be carried out at ambient temperature, though heat is sometimes added to speed the biological activity.

High-rate systems use a combination of active mixing and carefully controlled, elevated temperature to increase the rate of volatile solids destruction. These systems sometimes use pre-thickened sewage sludge introduced at a uniform rate to maintain constant conditions in the reactor. Operating conditions in high-rate systems foster more efficient sewage sludge digestion.

The PSRP description in Part 503 for anaerobic digestion is:

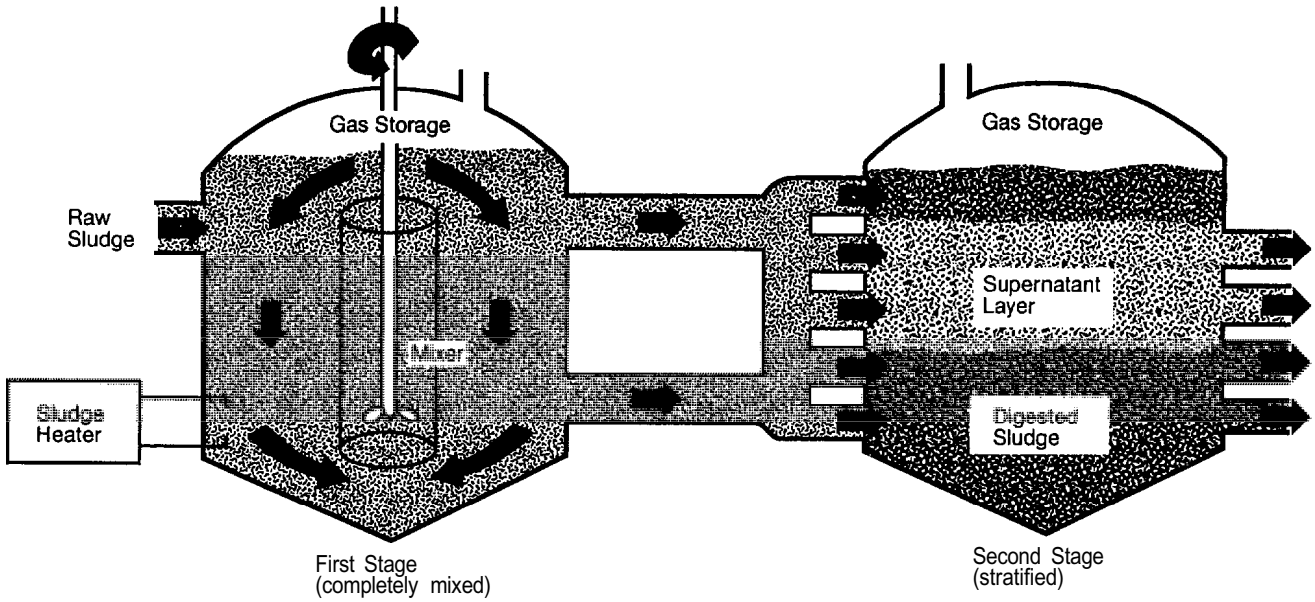


Figure 6-2. Two-stage anaerobic digestion (high rate).

- Sewage sludge is treated in the absence of air for a specific mean cell residence time at a specified temperature. Values for the mean cell residence time and temperature shall be between 15 days at 35°C to 55°C (95°F to 131°F) and 60 days at 20°C (68°F).

Straight-line interpolation to calculate mean cell residence time is allowable when the temperature falls between 35°C and 20°C.

Section 6.2 provides information on calculating residence times. Anaerobic digestion that meets the required residence times and temperatures typically reduces bacterial and viral pathogens by 90% or more. Viable helminth ova are not substantially reduced under mesophilic conditions (32°C to 38°C [90°F to 100°F]) and may not be completely reduced at temperatures between 38°C (100°F) and 50°C (122°F).

Anaerobic systems reduce volatile solids by 35% to 60%, depending on the nature of the sewage sludge and the system's operating conditions. Sewage sludges produced by systems that meet the operating conditions specified under Part 503 will typically have volatile solids reduced by at least 38%, which satisfies vector attraction reduction requirements. Alternatively, vector attraction reduction can be demonstrated by Option 2 of the vector attraction reduction requirements, which requires that additional volatile solids loss during bench-scale anaerobic batch digestion of the sewage sludge for 40 additional days at 30°C to 37°C (86°F to 99°F) be less than 17% (see Section 8.3). The SOUR test is an aerobic test and cannot be used for anaerobically digested sewage sludge.

6.4 Air Drying

Air drying allows partially digested sewage sludge to dry naturally in the open air (see photo). Wet sewage sludge is usually applied to a depth of approximately 23 cm (9 inches) onto sand drying beds, or even deeper on paved or unpaved basins. The sewage sludge is left to drain and dry by evaporation. Sand beds have an underlying drainage system; some type of mechanical mixing or turning is frequently added to paved or unpaved basins. The effectiveness of the air drying process depends very much on the local climate: drying occurs faster and more completely in warm, dry weather, and slower and less completely in cold, wet weather. During the drying/storage period in the bed, the sewage sludge is undergoing physical, chemical, and biological changes. These include biological decomposition of organic material, ammonia production, and desiccation.

Sludge drying operation. (Photo credit: East Bay Municipal Utility District)

The PSRP description in Part 503 for air drying is:

- Sewage sludge is dried on sand beds or on paved or unpaved basins. The sewage sludge dries for a minimum of 3 months. During 2 of the 3 months, the ambient average daily temperature is above 0°C (32°F).

Although not required by the Part 503, it is advisable to ensure that the sewage sludge drying beds are exposed to the atmosphere (i.e., not covered with snow) during the 2 months that the daily temperature is above 0°C (32°F). Also, the sewage sludge should be at least partially digested before air drying. Under these conditions, air drying will reduce the density of pathogenic viruses by 1-log and bacteria by approximately 2-log. Viable helminth ova also are reduced, except for some hardy species that remain substantially unaffected.

Vector Attraction Reduction

Frequently sand-bed drying follows an aerobic or anaerobic digestion process that does not meet the specified process requirements and does not produce 38% volatile solids destruction. However, it may be that the volatile solids reduction produced by the sequential steps of digestion and drying will meet the vector attraction reduction requirement of 38% volatile solids reduction. If this is the case, vector attraction reduction requirements are satisfied.

Example of Meeting PSRP and Vector Attraction Reduction Requirements

Type of Facility	Air Drying
Class	B
Pathogen Reduction	Partially digested sewage sludge is thickened and spread in drying beds. Filling of beds starts in June, and the beds accommodate sewage sludge generated over 1 full year. Beds are then emptied the following September so that all sewage sludge is retained over an entire summer (>0°C ambient temperatures).
Testing	Sewage sludge is tested for pollutants 2 weeks before material is removed and distributed.
Vector Attraction Reduction	Biosolids are land applied and plowed immediately into the soil.
Use or Disposal	Biosolids are delivered to local farmers. Farmers are given information on site restrictions, and must follow harvest, grazing, and public access restrictions.

Vector Attraction Reduction

Air-dried sewage sludge typically is treated by aerobic or anaerobic digestion before it is placed on drying beds. Usually, the easiest vector attraction reduction requirement to meet is a demonstration of 38% reduction in volatile solids (Option 1, See Section 8.2), including the reduction that occurs during its residence on the drying beds.

In dry climates, vector attraction reduction can be achieved by moisture reduction (see Option 7 in Section 8.8, and Option 8 in Section 8.9).

6.5 Composting

Composting involves the aerobic decomposition of organic material using controlled temperature, moisture, and oxygen levels. Several different composting methods are currently in use in the United States. The three most common are windrow, aerated static pile, and within-vessel composting. These are described below.

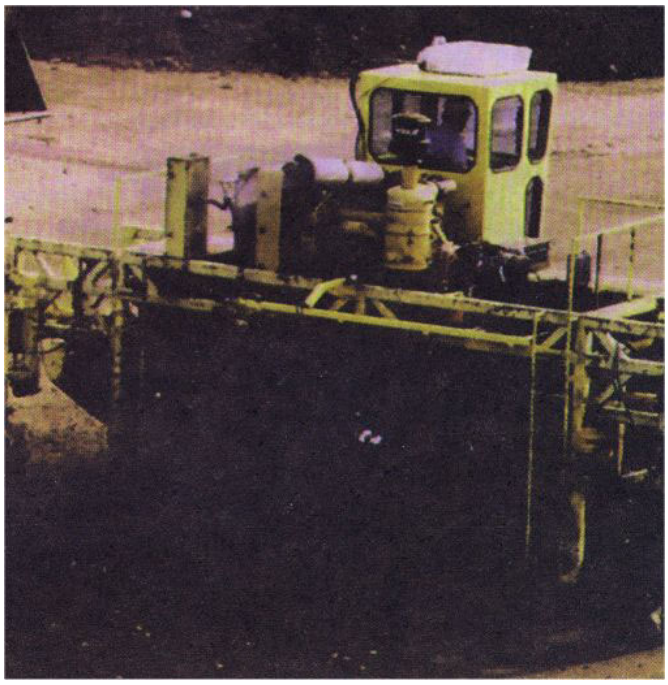
Composting can yield either Class A or Class B biosolids, depending on the time and temperature variables involved in the operation.

All composting methods rely on the same basic processes. Bulking agents such as wood chips, bark, sawdust, straw, rice hulls, or even-finished compost are added to the sewage sludge to absorb moisture, increase porosity, and add a source of carbon. This mixture is stored (in windrows, static piles, or enclosed tanks) for a period of intensive decomposition, during which temperatures can rise well above 55°C (131°F). Depending on ambient temperatures and the process chosen, the time required to reduce pathogens and produce Class B biosolids can range from 3 to 4 weeks. Aeration and/or frequent mixing or turning are needed to supply oxygen and remove excess heat. Following this active stage, bulking agents may or may not be screened from the completed compost for recycling (see photo), and the composted biosolids are “cured” for an additional period.

Windrow composting involves stacking the sewage sludge/bulking agent mixture into long piles, or windrows, generally 1.5 to 2.7 meters high (5 to 9 feet) and 2.7 to 6.1 meters wide (9 to 20 feet). These rows are regularly turned or mixed with a turning machine or front-end loader to fluff up the material and increase porosity which allows better convective oxygen flow into the material. Turning also breaks up compacted material and reduces the moisture content of the composting media (see photo, next page). Active windrows are typically placed in the open air, except in areas with heavy rainfall. In colder climates, winter weather can significantly increase the amount of time needed to attain temperatures needed for pathogen reduction.

Aerated static pile composting uses forced-air rather than mechanical mixing (see Figure 6-3) to both supply sufficient oxygen for decomposition and carry off moisture. The sewage sludge/bulking agent mixture is placed on top of

Composted sludge is screened to remove the bulking agent prior to land application



Compost mixing equipment turns over a windrow of compost for solar drying prior to screening [Photo credit: East Bay Municipal Utility District)

either (1) a fixed underlying forced aeration system, or (2) a system of perforated piping laid on the composting pad surface and topped with a bed of bulking agent. The entire pile is covered with a layer of cured compost for insulation and odor control. Pumps are used to blow air into the compost pile or suck air through it. The latter provides greater odor control because the compost air can be easily collected and then filtered or scrubbed.

Within-vessel composting systems vary greatly in design, but they share two basic techniques: the process takes place in a reactor vessel where the operating conditions can be carefully controlled (see photo page 49), and active aeration meets the system's high oxygen demand. Agitated bed systems (one type of within-vessel composting) depend on continuous or periodic mixing within the vessel, followed by a curing period.

Pathogen reduction during composting depends on time and temperature variables (see photo page 49). Part 503 provides the following definition of PSRP requirement for pathogen reduction during composting:

- Using either the within-vessel, static aerated pile, or windrow composting methods, the temperature of the sewage sludge is raised to 40°C (104°F) or higher and remains at 40°C (104°F) or higher for 5 days. For 4 hours during the 5-day period, the temperature in the compost pile exceeds 55°C (131°F).

These conditions, achieved using either within-vessel, aerated static pile, or windrow methods, reduce bacterial pathogens by 2-log and viral pathogens by 1-log.

A process time of only 5 days is not long enough to fully break down the volatile solids in sewage sludge, so the composted sewage sludge produced under these conditions will not be able to meet any of the requirements for reduced vector attraction. In addition, sewage sludge that has been composted for only 5 days may still be odorous. Breakdown of volatile solids may require 14 to 21 days for within-vessel; 21 or more days for aerated static pile; and 30 or more days for windrow composting. Many treatment works allow the finished sewage sludge compost to further mature or cure for at least several weeks following active composting during which time pile turning or active aeration may continue.

Composting is most often used to meet Class A requirements. More guidance for composting operations and how to meet Class A time and temperature requirements is provided in Chapter 7.

Vector Attraction Reduction

Vector attraction reduction must be conducted in accordance with Option 5, or compost must be incorporated into soil when land applied. This option requires aerobic treatment (i.e., composting) of the sewage sludge for at least 14 days at over 40°C (104°F) with an average temperature of over 45°C (113°F).

6.6 Lime Stabilization

The lime stabilization process is relatively straightforward: lime — either hydrated lime, $Ca(OH)_2$; quicklime, CaO; or lime containing kiln dust or fly ash — is added to sewage sludge in sufficient quantities to raise the pH above 12 for 2 hours or more after contact, as specified in the Part 503 PSRP description for lime stabilization:

- Sufficient lime is added to the sewage sludge to raise the pH of the sewage sludge to 12 after 2 hours of contact.

For the Class B lime stabilization process, the alkaline material must be a form of lime. Use of other alkaline ma-

Taulman Weiss in-vessel composting facility in Portland, Oregon.

Compost operator measures compost pile temperature as part of process monitorlng. (Photo credit: East Bay Municipal Utility District, Oakland, California)

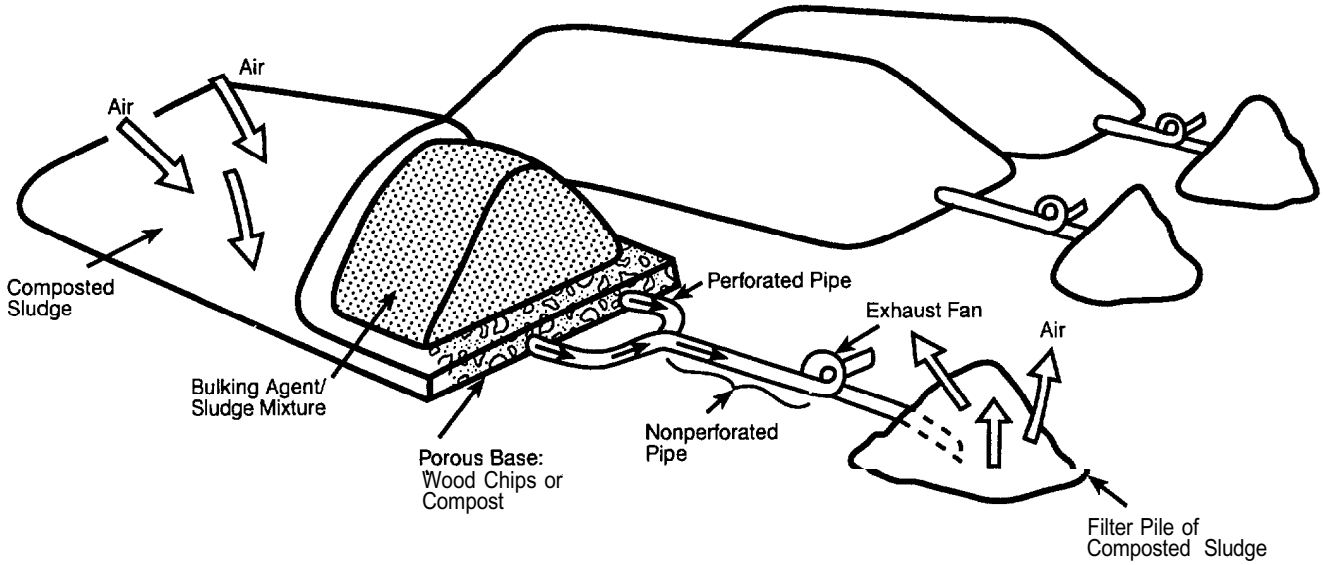


Figure 6-3. Static aerated pile composting.

terials must first be demonstrated to be equivalent to a PSRP. Elevation of pH to 12 for 2 hours is expected to reduce bacterial and viral density effectively.

Lime may be introduced to liquid sewage sludge in a mixing tank or combined with dewatered sewage sludge, providing the mixing is complete and the sewage sludge cake is moist enough to allow aqueous contact between the sewage sludge and lime.

Mixing must be sufficient to ensure that the entire mass of sewage sludge comes into contact with the lime and undergoes the increase in pH and to ensure that samples are representative of the overall mixture (see Chapter 9). pH should be measured at several locations to ensure that the pH is raised throughout the sewage sludge.

A variety of lime stabilization processes are currently in use. The effectiveness of any lime stabilization process for controlling pathogens depends on maintaining the pH at levels that reduce microorganisms in the sewage sludge. Field experience has shown that the application of lime stablized material after the pH has dropped below 10.5 may, in some cases, create odor problems. Therefore it is

recommended that biosolids application take place while the pH remains elevated. If this is not possible, and odor problems develop, alternate management practices in the field include injection or incorporation or top dressing the applied biosolids with additional lime. Alternate management practices if the biosolids have not yet left the wastewater treatment plant may include adding additional lime to maintain the elevated pH or additional treatment through drying or composting. Lime stabilization can reduce bacterial and viral pathogens by 99% or more. Such alkaline conditions have little effect on hardy species of helminth ova, however.

Vector Attraction Reduction

For lime-treated sewage sludge, vector attraction reduction is best demonstrated by Option 6 of the vector attraction reduction requirements. This option requires that the sewage sludge pH remain at 12 or higher for at least 2 hours, and then at 11.5 or more for an additional 22 hours (see Section 8.7).

Lime stabilization does not reduce volatile solids. Field experience has shown that the application of lime stabilized material after the pH has dropped below 10.5 may create odor problems. Therefore it is recommended that land application of biosolids take place as soon as possible after vector attraction reduction is completed and while pH remains elevated.

6.7 Equivalent Processes

Table 11.1 in Chapter 11 lists some of the processes that the EPA's Pathogen Equivalency Committee has recommended as being equivalent to PSRP under Part 257. Information on the PEC and how to apply for equivalency are discussed in Chapter 11.

References and Other Resources

Berg, G. and D. Berman. 1980. Destruction by anaerobic mesophilic and thermophilic digestion of viruses and indicator bacteria indigenous to domestic sludges. Appl. Envir. Microbiol. 39(2):361-368.

Farrell, J.B., G. Stern, and A.D. Venosa. 1990. Microbial destructions achieved by full-scale anaerobic digestion. Paper presented at Municipal Wastewater Sludge Disinfection Workshop. Kansas City, MO. Water Pollution Control Federation, October 1995.

U.S. EPA. 1992. Technical support document for reduction of pathogens and vector attraction in sewage sludge. EPA/822/R-93/004.

Chapter 7
Processes to Further Reduce Pathogens (PFRPs)

7.1 Introduction

Processes to Further Reduce Pathogens (PFRPs) are listed in Appendix B of the Part 503. There are seven PFRPs: composting, heat drying, heat treatment, thermophilic aerobic digestion, beta ray irradiation, gamma ray irradiation, and pasteurization. When these processes are operated under the conditions specified in Appendix B, pathogenic bacteria, enteric viruses, and viable helminth ova are reduced to below detectable levels. The PFRPs listed in Part 503 are essentially identical to the PFRPs listed under the 40 CFR Part 257 regulation, except that all requirements related solely to reduction of vector attraction have been removed.

This chapter provides detailed descriptions of the seven PFRPs listed in Part 503. Because the purpose of these processes is to produce Class A biosolids, the pathogen reduction process must be conducted concurrent to or prior to the vector attraction reduction process (see Section 4.2).

Under Part 503.32(a)(7), sewage sludge treated in these processes is considered to be Class A with respect to helminth ova, enteric viruses, and pathogenic bacteria. In addition, Class A biosolids must be monitored for fecal coliform or *Salmonella* sp. bacteria at the time of use on disposal, at the time the biosolids are prepared for sale or give away in a bag or other container for land application, or at the time the biosolids are prepared to meet the requirements for "exceptional quality" sludge (see Chapter 2) in 503.10(b), 503.10(c), 503.10(e), or 503.10(f) to ensure that growth of bacteria has not occurred (see Section 4.3). Guidelines regarding the frequency of pathogen sampling and sampling protocols are included in Chapter 9.

7.2 Composting

Composting is the controlled, aerobic decomposition of organic matter which produces a humus-like material. Sewage sludge which is to be composted is generally mixed with a bulking agent such as wood chips which increases porosity in the sewage sludge, allowing air to more easily pass through the composting material and maintain aerobic conditions. There are three commonly used methods of composting: windrow, static aerated pile, and within-vessel.

To be considered a PFRP under Part 503, the composting operation must meet certain operating conditions:

- Using either the within-vessel composting method or the static aerated pile composting method, the temperature of the sewage sludge is maintained at 55°C (131°F) or higher for 3 consecutive days.
- Using the windrow composting method, the temperature of the sewage sludge is maintained at 55°C (131°F) or higher for 15 consecutive days or longer. During the period when the compost is maintained at 55°C (131°F) or higher, there shall be a minimum of five turnings of the windrow.

For aerated static pile and in-vessel composting processes, temperatures should be taken at multiple points at a range of depths throughout the composting medium. Points which are likely to be slightly cooler than the center of the pile, such as the toes of piles, also should be monitored. Because the entire mass of sewage sludge must attain the required temperatures for the required duration, the temperature profiles from every monitoring point, not just the average of the points, should reflect PFRP conditions.

It has been found that points within 0.3 m (1 foot) of the surface of aerated static piles may be unable to reach PFRP temperatures, and for this reason, it is recommended that a 0.3 m (1 foot) or greater layer of insulating material be placed over all surfaces of the pile. Finished compost is often used for insulation. It must be noted that because the insulation will most likely be mixed into the composted material during post-processing or curing, compost used as an insulation material must be a Class A material so as not to reintroduce pathogens into the composting sewage sludge.

For windrow composting, the operational requirements are based on the same time-temperature relationship as aerated static pile and in-vessel composting. The material in the core of the windrow attains at least 55°C and must remain at that temperature for 3 consecutive days. Windrow turning moves new material from the surface of the windrow into the core so that this material may also undergo pathogen reduction. After five turnings, all material in the windrow must have spent 3 days at the core of the pile. The time-temperature regime takes place over a period of at least 15 consecutive days during which time the temperature in the core of the windrow is at least 55°C. See Appendix J for additional guidance.

Pathogen reduction is a function of three parameters:

- Ensuring that all sewage sludge is mixed into the core of the pile at some point during active composting
- Ensuring that all sewage sludge particles spend 3 consecutive days in the core during which time the temperatures are at 55°C
- Preventing growth of pathogenic bacteria in composted material

The first issue, ensuring that all material is mixed into the core of the pile, depends on the configuration of the windrows and the turning methodology. Pile size and shape as well as material characteristics determine how much of the pile is in the "hot zone" at any given time. Additional turning and maintenance of temperatures after the mandated 15 days are recommended, depending on the windrow configuration. For example, the Los Angeles County Sanitation District found that as many as 12-15 turnings were necessary to reduce pathogens in windrow composted sewage sludge (Personal Communication, Ross Caballero, Los Angeles County Sanitation District, 1998).

Second, it is important that once that material is in the pile core it be subject to the full time-temperature regime necessary to reduce pathogens. Therefore, the turning schedule and the recovery of the core zone to 55°C are important factors. If pile turning is not evenly distributed throughout the 15-day period, some material may not spend adequate time in the core of the pile. Additionally, pile temperatures generally drop off immediately after turning; if temperatures in the pile core do not quickly recover to 55°C (within 24 hours), the necessary pathogen reduction period of 3 days will not be achieved.

Because of the operational variability, pathogen reduction in windrow composting has been found to be less predictable than pathogen reduction in aerated static pile or in-vessel composting. In order to improve pathogen reduction, the following operational guidelines are recommended.

- Windrow turning should take place after the pile core has met pathogen reduction temperatures for 3 consecutive days. Windrow turnings should be evenly spaced within the 15 days so that all material remains in the core zone for 3 consecutive days; allowing additional time as needed for the core temperature to come up to 55°C.
- Pathogen reduction temperatures (55°C) must be met for 15 consecutive days at the pile core.
- Temperatures should be taken at approximately the same time each day in order to demonstrate that 55°C has been reached in the pile core within 24 hours after pile turning.
- Testing frequency should be increased; a large sewage sludge windrow composting operation recommends testing each windrow for *Salmonella* sp. before piles are distributed (Personal Communication, Ross Caballero, Los Angeles County Sanitation District, 1998). Samples are taken after turning is completed, and piles which do not comply with Class A requirements are retained on site for further composting.

Vector Attraction Reduction (VAR)

The options for demonstrating vector attraction reduction for both PFRP and PSRP composting are the same. Option 5 is the most appropriate for composting operations. This option requires aerobic treatment (e.g. composting) of the sewage sludge for at least 14 consecutive days at over 40ºC (104°F) with an average temperature of over 45ºC (113°F). This is usually easily attained by sewage sludge composting.

The PFRP and VAR requirements can be met concurrently in composting. For within-vessel or aerated static pile composting, the temperature profile should show PFRP temperatures at each of the temperature monitoring points for 3 consecutive days, followed by a minimum of 11 more days during which time the average temperature of the pile complies with VAR requirements. For windrow piles, the compliance with PFRP temperatures will also fulfill VAR requirements.

PFRP temperatures should be met before or at the same time that VAR requirements are fulfilled in order to reduce the potential for pathogen regrowth. However, continued curing of the composting material will most likely further prevent the growth of pathogenic bacteria from taking place.

Like all microbiological processes, composting can only take place with sufficient moisture (45-60%). Excessive aeration of composting piles or arid ambient condition may dry composting piles to the point at which microbial activity slows or stops. The cessation of microbial activity results in lowered pile temperatures which can easily be mistaken for the end-point of composting. Although composting may appear to have ended, and compost may even meet vector attraction reduction via Option 7, overly dried compost can cause both odor problems and vector attraction if moisture is reintroduced into the material and microbial activity resumes. It is therefore recommended that the composting process be maintained at moisture levels between 45-60% (40-55% total solids) (Epstein, 1997).

Microbiological Requirements

If the conditions specified by the Part 503 regulation are met, all pathogenic viruses, bacteria, and parasites will be reduced to below detectable levels. However, it may be difficult to meet the Class A microbiological requirement for fecal coliforms even when *Salmonella* sp. bacteria are not present. Biological sewage sludge treatment processes involving high temperatures, such as composting, can reduce *Salmonella* sp. to below detectable levels while leaving some surviving fecal coliforms. If sufficient nutrients remain in the sewage sludge, bacteria can later grow to

significant numbers. It may be preferable, therefore, to test composted sewage sludge directly for *Salmonella* sp., rather than using fecal coliforms as an indicator of pathogen control.

Although not mandated by the Part 503 regulation, compost is usually maintained on site for longer than the required PFRP and VAR duration. In order to produce a high-quality, marketable product, it has been found that a curing period, or the period during which the volatile solids in the sewage sludge continue to decompose, odor potential decreases, and temperatures decrease into the mesophilic (40-45°C) range, is necessary. Depending on the feedstock and the particular process, the curing period may last an additional 30 - 50 days after regulatory requirements are met.

In general, compost is not considered marketable until the piles are no longer self-heating. It is important to note that compost piles that are cooled by excessive aeration or that do not self-heat because the material is too dry to support microbial activity may not actually be fully decomposed.

It has been found that further reduction of organic material takes place during the curing phase of composting (Epstein, 1997). Therefore microbiological testing should take place at the end of the curing process when compost is prepared for sale or distribution. Compost which is stored on site for extended periods of time until it can be sold or distributed must be tested for compliance with microbiological limits when it is to be used or disposed.

7.3 Heat Drying

Heat drying is used to reduce both pathogens and the water content of sewage sludge. The Part 503 PFRP description of heat drying is:

- Sewage sludge is dried by direct or indirect contact with hot gases to reduce the moisture content to 10% or lower. Either the temperature of the sewage sludge particles exceeds 80°C (176°F) or the wet bulb temperature of the gas in contact with the sewage sludge as it leaves the dryer exceeds 80°C (176°F).

Properly conducted heat drying will reduce pathogenic viruses, bacteria, and helminth ova to below detectable levels. Four processes are commonly used for heat drying sewage sludge: flash dryers, spray dryers, rotary dryers, and steam dryers. Flash dryers used to be the most common heat drying process installed at treatment works, but current practice favors rotary dryers. These processes are briefly described below. More detailed descriptions are provided in EPA's Process Design Manual (EPA, 1979).

Flash Dryers

Flash dryers pulverize sewage sludge in the presence of hot gases. The process is based on exposing fine sewage sludge particles to turbulent hot gases long enough to attain at least 90% solids content.

Spray Dryers

A spray dryer typically uses centrifugal force to atomize liquid sewage sludge into a spray that is directed into a drying chamber. The drying chamber contains hot gases that rapidly dry the sewage sludge mist. Some spray drying systems use a nozzle to atomize sewage sludge.

Rotary Dryers

Rotary dryers function as horizontal cylindrical kilns. The drum rotates and may have plows or louvers that mechanically mix the sewage sludge as the drum turns. There are many different rotary kiln designs, utilizing either direct heating or indirect heating systems. Direct heating designs maintain contact between the sewage sludge and the hot gases. Indirect heating separates the two with steel shells.

Steam Dryers

Indirect steam dryers utilize steam to heat the surface of the dryers which will come into contact with the sewage sludge. The heat transfer surface may consist of discs or paddles, which rotate to increase their contact with the sewage sludge.

Vector Attraction Reduction

No further processing is required because the PFRP requirements for heat drying also meet the requirements of Option 8 for vector attraction reduction (the percent solids must be at least 90% before mixing the sewage sludge with other materials). This fulfills the requirement of Option 7 if the sewage sludge being dried contains no unstabilized solids.

Drying of sewage sludge to 90% solids deters the attraction of vectors, however, unstabilized dried biosolids which are rewet may become odorous and attract vectors. Therefore, it is recommended that materials be used or disposed while the level of solids remains high and that dried material be stored and maintained under dry conditions.

Some operators have found that maintaining stored material at solids levels above 95% helps to deter reheating because microbiological activity is halted. However, storage of materials approaching 90% total solids can lead to spontaneous combustion with subsequent fires and risk of explosion. While there is little likelihood of an explosion occurring with storage of materials like pellets, precautionary measures such as maintaining proper oxygen levels and minimizing dust levels in storage silos and monitoring temperatures in material can reduce the risk of fires.

Microbiological Requirements

Heat dried biosolids must be tested for fecal coliform or *Salmonella* sp. at the last point before being used or disposed. For example, biosolids should be tested immediately before they are bagged or before they leave the site for bulk distribution. If material is stored for a long period of time, it should be re-tested, even if previous testing has

shown the biosolids to have met the Part 503 regulation. This is particularly important if material has been rewetted.

7.4 Heat Treatment

Heat treatment processes are used to disinfect sewage sludge and reduce pathogens to below detectable levels. The processes involve heating sewage sludge under pressure for a short period of time. The sewage sludge becomes sterilized and bacterial slime layers are solubilized, making it easier to dewater the remaining sewage sludge solids. The Part 503 PFRP description for heat treatment is:

- Liquid sewage sludge is heated to a temperature of 180°C (356°F) or higher for 30 minutes.

Two processes have principally been used for heat treating sludge in preparation for dewatering: the Porteous and the Zimpro process. In the Porteous process the sewage sludge is preheated and then injected into a reactor vessel. Steam is also injected into the vessel under pressure. The sewage sludge is retained in the vessel for approximately 30 minutes after which it is discharged to a decant tank. The resulting sewage sludge can generally be concentrated and dewatered to high solids concentrations. Further dewatering may be desirable to facilitate sewage sludge handling.

The Zimpro process is similar to the Porteous process. However, air is injected into the sewage sludge before it enters the reactor and the vessel is then heated by steam to reach the required temperature. Temperatures and pressures are approximately the same for the two processes.

Vector Attraction Reduction

Heat treatment in most cases must be followed by vector attraction reduction. Vector attraction reduction Options 6 to 11 (pH adjustment, heat drying, or injection, incorporation, or daily cover) may be used (see Chapter 8). Options 1 through 5 would not typically be applicable to heat treated sludge unless the sludge was digested or otherwise stabilized during or after heat treatment (e.g. through the use of wet air oxidation during heat treatment).

Microbiological Requirements

When operated according to the Part 503 requirements, the process effectively reduces pathogenic viruses, bacteria, and viable helminth ova to below detectable levels. Sewage sludge must be properly stored after processing because organic matter has not been reduced, and therefore, growth of bacteria can occur.

Heat treated sewage sludge must be tested for fecal coliform or *Salmonella* sp. at the time of use or disposal or as it is prepared for sale or distribution. If heat treated biosolids are subsequently composted or otherwise treated, pathogen testing should take place after that processing is complete.

7.5 Thermophilic Aerobic Digestion

Thermophilic aerobic digestion is a refinement of the conventional aerobic digestion processes discussed in Section 6.2. In this process, feed sewage sludge is generally pre-thickened and an efficient aerator is used. In some modifications, oxygen is used instead of air. Because there is less sewage sludge volume and less air to carry away heat, the heat released from biological oxidation warms the sewage sludge in the digester to as high as 60°C (140°F).

Because of the increased temperatures, this process achieves higher rates of organic solids reduction than are achieved by conventional aerobic digestion which operates at ambient air temperature. The biodegradable volatile solids content of the sewage sludge can be reduced by up to 70% in a relatively short time. The digested sewage sludge is effectively pasteurized due to the high temperatures. Pathogenic viruses, bacteria, viable helminth ova and other parasites are reduced to below detectable limits if the process is carried out at temperatures exceeding 55°C (131°F).

This process can either be accomplished using auxiliary heating of the digestion tanks or through special designs that allow the energy naturally released by the microbial digestion process to heat the sewage sludge. The Part 503 PFRP description of thermophilic aerobic digestion is:

- Liquid sewage sludge is agitated with air or oxygen to maintain aerobic conditions and the mean cell residence time of the sewage sludge is 10 consecutive days at 55°C to 60°C (131°F to 140°F).

The thermophilic process requires significantly lower residence times (i.e., solids retention time) than conventional aerobic processes designed to qualify as a PSRP, which must operate 40 to 60 days at 20°C to 15°C (68°F to 59°F), respectively. Residence time is normally determined by dividing the volume of sewage sludge in the vessel by the volumetric flow rate. Facility operation should minimize the potential for bypassing by withdrawing treated sewage sludge before feeding, and feeding no more than once a day.

In the years following the publication of the Part 503 regulation, advances in thermophilic digestion have been made. It should be noted, however, that complete-mix reactors with continuous feeding may not be adequate to meet Class A pathogen reduction because of the potential for bypassing or short-circuiting of untreated sewage sludge.

Vector Attraction Reduction

Vector attraction reduction must be demonstrated. Although all options, except Options 2, 4, and 12 are possible, Options 1 and 3 which involve the demonstration of volatile solids loss are the most suitable. (Option 2 is appropriate only for anaerobically digested sludge, and Option 4 is not possible because it is not yet known how to translate SOUR measurements obtained at high temperatures to 20°C [68°F].)

Thermophilically aerobically digested biosolids must be tested for fecal coliform or *Salmonella* sp. at the time of

use or disposal or as it is prepared for sale or distribution. If digested biosolids are subsequently composted or otherwise treated, pathogen testing for either fecal coliform or *Salmonella* sp. should take place after processing is complete.

7.6 Beta Ray and Gamma Ray Radiation

Radiation can be used to disinfect sewage sludge. Radiation destroys certain organisms by altering the colloidal nature of the cell contents (protoplasm). Gamma rays and beta rays are the two potential energy sources for use in sewage sludge disinfection. Gamma rays are high-energy photons produced by certain radioactive elements. Beta rays are electrons accelerated in velocity by electrical potentials in the vicinity of 1 millions volts. Both types of radiation destroy pathogens that they penetrate if the doses are adequate. The Part 503 PFRP descriptions for irradiation systems are:

Beta Ray Irradiation

- Sewage sludge is irradiated with beta rays from an accelerator at dosages of at least 1.0 megarad at room temperature (ca. 20°C [68°F]).

Gamma Ray Irradiation

- Sewage sludge is irradiated with gamma rays from certain isotopes, such as Cobalt 60 and Cesium 137 [at dosages of at least 1.0 megarad] at room temperature (ca. 20°C [68°F]).

The effectiveness of beta radiation in reducing pathogens depends on the radiation dose, which is measured in rads. A dose of 1 megarad or more will reduce pathogenic viruses, bacteria, and helminths to below detectable levels. Lower doses may successfully reduce bacteria and helminth ova but not viruses. Since organic matter has not been destroyed with processing, sewage sludge must be properly stored after processing to prevent contamination.

Although the two types of radiation function similarly to inactivate pathogens, there are important differences. Gamma rays can penetrate substantial thicknesses of sewage sludge and can therefore be introduced to sewage sludge by either piping liquid sewage sludge into a vessel that surrounds the radiation source (Figure 7-1) or by carrying composted or dried sewage sludge by hopper conveyor to the radiation source. Beta rays have limited penetration ability and therefore are introduced by passing a thin layer of sewage sludge under the radiation source (Figure 7-2).

Vector Attraction Reduction

Radiation treatment must be followed by vector attraction reduction. The appropriate options for demonstrating vector attraction reduction are the same as for heat treatment (see Section 7.4), namely Options 6 to 11. Options 1-5 are not applicable unless the sewage sludge is subsequently digested.

Microbiological Requirements

Irradiated sewage sludge must be tested for fecal coliform or *Salmonella* sp. at the time of use or disposal or as it is prepared for sale or distribution.

7.7 Pasteurization

Pasteurization involves heating sewage sludge to above a predetermined temperature for a minimum time period. For pasteurization, the Part 503 PFRP description is:

- The temperature of the sewage sludge is maintained at 70°C (158°F) or higher for 30 minutes or longer.

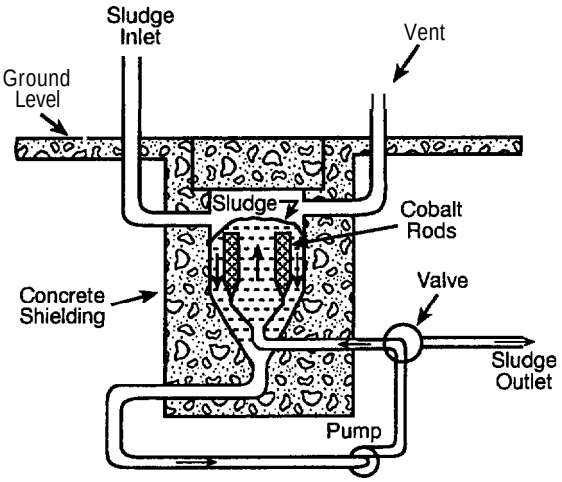


Figure 7-1. Schematic representation of cobalt-60 (gamma ray) irradiation facility at Geiselbullach, Germany. Source: EPA. 1979.

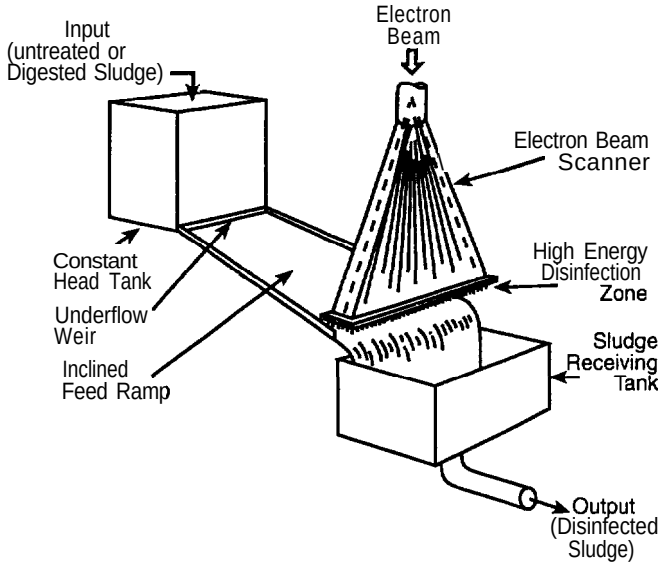


Figure 7-2. Beta ray scanner and sludge spreader. Source: EPA,1979.

Pasteurization reduces bacteria, enteric viruses, and viable helminth ova to below detectable values. Sewage sludge can be heated by heat exchangers or by steam injection. Although sewage sludge pasteurization is uncommon in the United States, it is widely used in Europe. The steam injection method is preferred because it is more effective at maintaining even temperatures throughout the sewage sludge batch being processed. Sewage sludge is pasteurized in batches to prevent recontamination that might occur in a continuous process. Sewage sludge must be properly stored after processing because the organic matter has not been stabilized and therefore odors and growth of pathogenic bacteria can occur if sewage sludge is re-inoculated.

In theory, quicklime can be used to meet the requirements for pasteurization of sewage sludge. The water in the sludge slakes the lime, forming calcium hydroxide, and generates heat. However, it is difficult to ensure that the entire mass of sewage sludge comes into contact with the lime and achieves the required 70°C for 30 minutes. This is particularly true for dewatered sewage sludges. Processes must be designed to 1) maximize contact between the lime and the sewage sludge, 2) ensure that adequate moisture is present, 3) ensure that heat loss is minimal, and 4) if necessary, provide an auxiliary heat source. Pasteurization cannot be accomplished in open piles.

In addition, in order for pasteurization to be conducted properly, facility operators must be trained with regard to 1) the proper steps to be taken to ensure complete hydration of the alkaline reagent used, 2) the evaluation of the slaking rate of the lime-based alkaline material required for their particular process, specifying the reactivity rate required, 3) the proper measurement of pH, 4) an awareness of the effect of ammonia gassing off and how this affects the lime dose, and 5) the necessity for maintaining sufficient moisture in the sewage sludge/alkaline mixture during the mixing process to ensure the complete hydration of the quicklime and migration of hydroxyl ions throughout the sewage sludge mass. This is to ensure that the entire sewage sludge mass is disinfected.

EPA-sponsored studies showed that pasteurization of liquid sewage sludge at 70°C (158°F) for 30 minutes inactivates parasite ova and cysts and reduces the population of measurable viruses and pathogenic bacteria to below detectable levels (U.S. EPA, 1979). This process is based on the pasteurization of milk which must be heated to at least 63°C (145°F) for at least 30 minutes.

Vector Attraction Reduction

Pasteurization must be followed by a vector attraction reduction process unless the vector attraction reduction conditions of Option 6 (pH adjustment) have been met. The options appropriate for demonstrating vector attraction reduction are the same as those for heat treatment (see Section 10.4), namely Options 6 to 11. Options 1 to 5 are not applicable unless the sludge is subsequently digested.

Microbiological Requirements

Pasteurized sludge must be tested for fecal coliform or *Salmonella* sp. at the time of use or disposal or as it is prepared for sale or distribution. In Europe, serious problems with regrowth of *Salmonella* sp. have occurred, so pasteurization is rarely used now as a terminal treatment process. Pre-pasteurization followed by mesophilic digestion has replaced the use of pasteurization after digestion in many European communities.

7.8 Equivalent Processes

Under Class A Alternative 6, sewage sludge treated in processes that are determined to be equivalent to PFRP are considered to be Class A with respect to pathogens (assuming the treated sewage sludges also meet the Class A microbiological requirement). Table 11-2 in Chapter 11 lists some of the processes that were found, based on the recommendation of EPA's Pathogen Equivalency Committee, to be equivalent to PFRP under Part 257. Chapter 11 discusses how the PEC makes a recommendation of equivalency.

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Chapter 8
Requirements for Reducing Vector Attraction

8.1 Introduction

The pathogens in sewage sludge pose a disease risk only if there are routes by which the pathogens are brought into contact with humans or animals. A principal route for transport of pathogens is vector transmission. Vectors are any living organism capable of transmitting a pathogen from one organism to another either mechanically (by simply transporting the pathogen) or biologically by playing a specific role in the life cycle of the pathogen. Vectors for sewage sludge pathogens would most likely include insects, rodents, and birds.

Suitable methods for measuring vector attraction directly are not available. Vector attraction reduction is accomplished by employing one of the following:

- Biological processes which breakdown volatile solids, reducing the available food nutrients for microbial activities and odor producing potential
- Chemical or physical conditions which stop microbial activity
- Physical barriers between vectors and volatile solids in the sewage sludge

At the present time there is no vector attraction equivalency committee that evaluates other options for vector attraction reduction. The creation of one is being considered. The specific options outlined in the Part 503 regulation are currently the only available means for demonstrating vector attraction reduction.

The term “stability” is often used to describe sewage sludge. Although it is associated with vector attraction reduction, stability is not regulated by the Part 503 Rule. With regard to sewage sludge, stability is generally defined as the point at which food for rapid microbial activity is no longer available. Sewage sludge which is stable will generally meet vector attraction reduction (VAR) requirements. The converse is not necessarily true; meeting VAR requirements does not ensure sewage sludge stability. Because stability is also related to odor generation and the continued degradation of sewage sludge, it is often considered an important parameter when producing biosolids for sale or distribution. Table 8-1 lists some of the common methods for measuring stability.

Table 8-1. Stability Assessment

Process	Monitoring Methods
Composting	CO_2 respiration, O_2 uptake
Heat Drying	Moisture content
Alkaline Stabilization	pH; pH change with storage; moisture; ammonia evolution; temperature
Aerobic Digestion	SOUR; volatile solids reduction, additional volatile solids reduction
Anaerobic Digestion	Gas production; volatile solids reduction, additional volatile solids reduction

More information on stability can be found in the WERF publication, “Defining Biosolids Stability: A Basis for Public and Regulatory Acceptance” (1997).

The Part 503 regulation contains 12 options, described below and summarized in Table 8-2, for demonstrating a reduction in vector attraction of sewage sludge. These requirements are designed to either reduce the attractiveness of sewage sludge to vectors (Options 1 through 8 and Option 12) or prevent the vectors from coming in contact with the sewage sludge (Options 9 through 11).

Guidance on when and where to sample sewage sludge to meet these requirements is provided in Chapter 10.

As mentioned in Chapter 3, meeting the vector attraction reduction requirements must be demonstrated separately from meeting the pathogen reduction requirements. Therefore, demonstration of vector attraction reduction (e.g., through reduction of volatile solids by 38% as described below) does not demonstrate achievement of pathogen reduction. It should be noted that for Class A biosolids, vector attraction reduction must be met after or concurrent with pathogen reduction to prevent growth of pathogenic bacteria.

8.2 Option 1: Reduction in Volatile Solids Content [503.33(b)(1)]

This option is intended for use with biological treatment systems only. Under Option 1, reduction of vector attraction is achieved if the mass of volatile solids in the sewage sludge is reduced by at least 38%. This is the percentage

Table 8-2. Vector Attraction Reduction Options

Requirement	What is Required?	Most Appropriate For:
Option 1 503.33(b)(1)	At least 38% reduction in volatile solids during sewage sludge treatment	Sewage sludge processed by: Anaerobic biological treatment Aerobic biological treatment
Option 2 503.33(b)(2)	Less than 17% additional volatile solids loss during bench-scale anaerobic batch digestion of the sewage sludge for 40 additional days at 30°C to 37°C (86°F to 99°F)	Only for anaerobically digested sewage sludge that cannot meet the requirements of Option 1
Option 3 503.33(b)(3)	Less than 15% additional volatile solids reduction during bench-scale aerobic batch digestion for 30 additional days at 20°C (68°F)	Only for aerobically digested liquid sewage sludge with 2% or less solids that cannot meet the requirements of Option 1 — e.g., sewage sludges treated in extended aeration plants. Sludges with 2% solids must be diluted
Option 4 503.33(b)(4)	SOUR at 20°C (68°F) is ≤1.5 mg oxygen/hr/g total sewage sludge solids	Liquid sewage sludges from aerobic processes run at temperatures between 10 to 30°C. (should not be used for composted sewage sludges)
Option 5 503.33(b)(5)	Aerobic treatment of the sewage sludge for at least 14 days at over 40°C (104°F) with an average temperature of over 45°C (113°F)	Composted sewage sludge (Options 3 and 4 are likely to be easier to meet for sewage sludges from other aerobic processes)
Option 6 503.33(b)(6)	Addition of sufficient alkali to raise the pH to at least 12 at 25°C (77°F) and maintain a pH ≥12 for 2 hours and a pH≥11.5 for 22 more hours	Alkali-treated sewage sludge (alkaline materials include lime, fly ash, kiln dust, and wood ash)
Option 7 503.33(b)(7)	Percent solids ≥ 75% prior to mixing with other materials	Sewage sludges treated by an aerobic or anaerobic process (i.e., sewage sludges that do not contain unstabilized solids generated in primary wastewater treatment)
Option 8 503.33(b)(8)	Percent solids ≥90% prior to mixing with other materials	Sewage sludges that contain unstabilized solids generated in primary wastewater treatment (e.g., heat-dried sewage sludges)
Option 9 503.33(b)(9)	Sewage sludge is injected into soil so that no significant amount of sewage sludge is present on the land surface 1 hour after injection, except Class A sewage sludge which must be injected within 8 hours after the pathogen reduction process	Sewage sludge applied to the land or placed on a surface disposal site. Domestic septage applied to agricultural land, a forest, or a reclamation site, or placed on a surface disposal site
Option 10 503.33(b)(10)	Sewage sludge is incorporated into the soil within 6 hours after application to land or placement on a surface disposal site, except Class A sewage sludge which must be applied to or placed on the land surface within 8 hours after the pathogen reduction process	Sewage sludge applied to the land or placed on a surface disposal site. Domestic septage applied to agricultural land, forest, or a reclamation site, or placed on a surface disposal site
Option 11 503.33(b)(11)	Sewage sludge placed on a surface disposal site must be covered with soil or other material at the end of each operating day	Sewage sludge or domestic septage placed on a surface disposal site
Option 12 503.33(b)(12)	pH of domestic septage must be raised to ≥12 at 25°C (77°F) by alkali addition and maintained ≥ 12 for 30 minutes without adding more alkali	Domestic septage applied to agricultural land, a forest, or a reclamation site or placed on a surface disposal site

of volatile solids reduction that can generally be attained by the "good practice" recommended conditions for anaerobic digestion of 15 days residence time at 35°C [95°F] in a completely mixed high-rate digester. The percent volatile solids reduction can include any additional volatile solids reduction that occurs before the biosolids leave the treatment works, such as might occur when the sewage sludge is processed on drying beds or in lagoons.

The starting point for measuring volatile solids in sewage sludge is at the point at which sewage sludge enters a sewage sludge treatment process. This can be problem-

atic for facilities in which wastewater is treated in systems like oxidation ditches or by extended aeration. Sewage sludges generated in these processes are already substantially reduced in volatile solids content by their long exposure to oxidizing conditions in the process. If sewage sludge removed from these processes is further treated by anaerobic or aerobic digestion to meet VAR requirements, it is unlikely that the 38% reduction required to meet Option 1 can be met. In these cases, use of Options 2, 3, or 4 is more appropriate.

The end point where volatile solids are measured to calculate volatile solids losses can be at any point in the process. Because volatile solids continue to degrade throughout sewage sludge treatment, it is recommended that samples be taken at the end point of treatment.

Volatile solids reduction is calculated by a volatile solids balance around the digester or by the Van Kleeck formula (Fisher, 1984). Guidance on methods of calculation is provided in Appendix C.

Volatile solids reduction is typically achieved by anaerobic or aerobic digestion. These processes degrade most of the biodegradable material to lower activity forms. Any biodegradable material that remains characteristically degrades so slowly that vectors are not drawn to it.

8.3 Option 2: Additional Digestion of Anaerobically Digested Sewage Sludge [503.33(b)(2)]

Under this option, an *anaerobically* digested sewage sludge is considered to have achieved satisfactory vector attraction reduction if it loses less than 17% additional volatile solids when it is anaerobically batch-digested in the laboratory in a bench-scale unit at 30°C to 37°C (86°F to 99°F) for an additional 40 days. Procedures for this test are presented in Appendix D. As noted in Appendix D, the material balance method for calculating additional volatile solids reduction will likely show greater reductions than the Van Kleeck method.

Frequently, return activated sludges have been recycled through the biological wastewater treatment section of a treatment works or have resided for long periods of time in the wastewater collection system. During this time they undergo substantial biological degradation. If they are subsequently treated by anaerobic digestion for a period of time, they are adequately reduced in vector attraction, but because they entered the digester with volatile solids already partially reduced, the volatile solids reduction after treatment is frequently less than 38%. The additional digestion test is used to demonstrate that these sewage sludges are indeed satisfactorily reduced in vector attraction.

It is not necessary to demonstrate that Option 1 cannot be met before using Option 2 or 3 to comply with VAR requirements.

This additional anaerobic digestion test may have utility beyond use for sewage sludge from the classical anaerobic digestion process. The regulation states that the test can be used for a previously anaerobically digested sewage sludge. One possible application is for sewage sludge that is to be removed from a wastewater lagoon. Such sewage sludge may have been stored in such a lagoon for many years, during which time it has undergone anaerobic digestion and lost most of its volatile solids. It is only recognized by the regulations as a sewage sludge when it is removed from the lagoon. If it were to be further processed by anaerobic digestion, the likelihood of achieving 38% volatile solids reduction is very low. The additional anaerobic digestion test which requires a long period of batch digestion at temperatures between 30°C and 37°C would seem to be an appropriate test to determine whether such a sewage sludge has the potential to attract vectors.

8.4 Option 3: Additional Digestion of Aerobically Digested Sewage Sludge [503.33(b)(3)]

Under this option, an *aerobically* digested sewage sludge with 2% or less solids is considered to have achieved satisfactory vector attraction reduction if it loses less than 15% additional volatile solids when it is aerobically batch-digested in the laboratory in a bench-scale unit at 20°C (68°F) for an additional 30 days. Procedures for this test and the method for calculating additional volatile solids destruction are presented in Appendix D. The test can be run on sewage sludges up to 2% solids and does not require a temperature correction for sewage sludges not initially digested at 20°C (68°F). Liquid sludges with greater than 2% solids can be diluted to 2% solids with unchlorinated effluent, and the test can then be run on the diluted sludge. This option should not be used for non-liquid sewage sludge such as dewatered cake or compost.

This option is appropriate for aerobically digested sewage sludges that cannot meet the 38% volatile solids reduction required by Option 1. These include sewage sludges from extended aeration and oxidation ditch processes, where the nominal residence time of sewage sludge leaving the wastewater treatment processes section generally exceeds 20 days. In these cases, the sewage sludge may already have been substantially reduced in biological degradability prior to aerobic digestion.

As was suggested for the additional anaerobic digestion test, the additional aerobic digestion test may have application to sewage sludges that have been aerobically treated by other means than classical aerobic digestion.

8.5 Option 4: Specific Oxygen Uptake Rate (SOUR) for Aerobically Digested Sewage Sludge [503.33(b)(4)]

For an aerobically digested sewage sludge with a total solids content equal to or less than 2% which has been processed at a temperature between 10°- 30°C, reduction in vector attraction can also be demonstrated using the SOUR test. The SOUR of the sewage sludge to be used or disposed must be less than or equal to 1.5 mg of

oxygen per hour per gram of total sewage sludge solids (dry weight basis) at 20°C (68°F).[1] This test is based on the fact that if the aerobically treated sewage sludge consumes very little oxygen, its value as a food source for vectors is very low and therefore vectors are unlikely to be attracted to it. Frequently aerobically digested sewage sludges are circulated through the aerobic biological wastewater treatment process for as long as 30 days. In these cases, the sewage sludge entering the aerobic digester is already partially digested, which makes it difficult to demonstrate the 38% reduction required by Option 1.

The oxygen uptake rate depends on the conditions of the test and, to some degree, on the nature of the original sewage sludge before aerobic treatment. The SOUR test should not be used on sewage sludge products such as heat or air dried sludge or compost. Because of the reduction of microbial populations that occur in these processes, the SOUR results are not accurate and should not be used. SOUR testing on sewage sludges with a total solids content below 0.5% may give inaccurately high results. Farrell, et al. (1996) cite the work of several investigators indicating such an effect. Farrell, et al. (1996) also note that storage for up to two hours did not cause a significant change in the SOUR measurement. It is therefore suggested that a dilute sewage sludge could be thickened to a solids content less than 2% solids and then tested, provided that the thickening period is not in excess of two hours.

The SOUR test requires a poorly defined temperature correction at temperatures differing substantially from 20°C (68°F). SOUR cannot be applied to sewage sludges digested outside the 10-30°C range (50-86°F). The actual temperature of the sewage sludge tested cannot be adjusted because temperature changes can cause short-term instability in the oxygen uptake rate (Benedict, et al. (1973); Farrell, et al. [1996]), and this would invalidate the results of the test. Guidance on performing the SOUR test and on sewage sludge-dependent factors are provided in Appendix D.

It should be noted that the limit on the use of the SOUR test for sewage sludges at different solids and temperature levels is due to the lack of research and data on different sewage sludges. EPA encourages the collection of SOUR data for different sewage sludges so that at some point, Option 4 may be expanded to include more sewage sludge materials.

[1] SOUR is defined in Part 503 as the mass of oxygen consumed per unit time per unit mass of total solids (dry weight basis) in the sewage sludge. SOUR is usually based on total suspended volatile solids rather than total solids because it is assumed that it is the volatile matter in the sewage sludge that is being oxidized. The SOUR definition in Part 503 is based on the total solids primarily to reduce the number of different determinations needed and for consistency with application rates, which are measured in total solids per unit area. Generally, the range in the ratio of volatile solids to total solids in aerobically digested sewage sludges is not large. The SOUR based on total solids will merely be slightly lower than if it had been based on volatile suspended solids to indicate the same endpoint.

8.6 Option 5: Aerobic Processes at Greater Than 40°C [503.33(b)(5)]

The sewage sludge must be aerobically treated for 14 days or longer during which time the temperature must be over 40°C (104°F) and the average temperature higher than 45°C (113°F). This option applies primarily, but not exclusively, to composted sewage sludge. These processed sewage sludges generally contain substantial amounts of partially decomposed organic bulking agents, in addition to sewage sludge. This option must be used for composted sewage sludge; other options are either not appropriate or have not adequately been investigated for use with compost.

The Part 503 regulation does not specifically mention or limit this option to composting. This option can be applied to sewage sludge from other aerobic processes such as aerobic digestion as long as temperature requirements can be met and the sewage sludge is maintained in an aerobic state for the treatment period, but other methods such as Options 3 and 4 are likely to be easier to meet for these sewage sludges.

If composting is used to comply with Class A pathogen requirements, the VAR time-temperature regime must be met along with or after compliance with the pathogen reduction time-temperature regime.

8.7 Option 6: Addition of Alkali [503.33(b)(6)]

Sewage sludge is considered to have undergone adequate vector attraction reduction if sufficient alkali is added to:

- Raise the pH to at least 12
- Maintain a pH of at least 12 without addition of more alkali for 2 hours
- Maintain a pH of at least 11.5 without addition of more alkali for an additional 22 hours

pH should be measured in a slurry at 25°C. For more information on making a slurry, see Section 10.7. Either sewage sludge samples may be taken and heated or cooled to 25°C or results can be adjusted based on the ambient temperature where pH is measured and the following calculation:

$$\text{Correction Factor} = \frac{0.03 \text{ pH units} \times (T_{meas} - 25°C)}{1.0°C}$$

Actual pH = Measured pH +/- the Correction Factor

T = Temperature measured

Example of Using the pH Correction Factor

If the measured pH is 12.304 at 30°C, the actual pH can be calculated as follows:

Correction Factor = 0.03 x (30-25) = +0.15
Actual pH = 12.304 + 0.15 = 12.454

It should be noted that temperature compensation devices on pH meters correct only for variations in the conductance of pH probes, and not for the variability in solution concentration. Therefore, the temperature correction noted above should be applied to pH measurements, even if a pH meter with temperature settings is used.

As noted in Section 5.6, the term "alkali" means a substance that causes an increase in pH. Raising sewage sludge pH through alkali addition reduces vector attraction by reducing or stopping biological activity. However, this reduction in biological activity is not permanent. If the pH drops, surviving bacteria become biologically active and the sewage sludge will again putrefy and potentially attract vectors. The more soluble the alkali, the less likely it is that there will be an excess present when a pH of 12 is reached. Consequently, the subsequent drop in pH with time will be more rapid than if a less soluble alkali is used.

The conditions required under this option are designed to ensure that the sewage sludge can be stored for at least several days at the treatment works, transported, and applied to soil without the pH falling to the point where biological activity results in vector attraction. The requirement of raising the pH to 12 increases the probability that the material will be used before pH drops to a level at which putrefaction can occur. The requirements for pH adjustment of domestic septage are less stringent because it is unlikely that septage haulers will hold domestic septage for long periods of time.

Raising the pH to 12 and maintaining this pH for two hours and a pH of 11.5 for an additional 22 hours ensures that the pH will stay at adequately high levels to prevent putrefaction before disposal in all but unusual cases. In any event, it is prudent in a timely manner to apply sludge in a thin layer or incorporate it into the soil for the prevention of odors and vector attraction.

More information on alkali addition and measurement of pH are included in Chapter 10.

8.8 Option 7: Moisture Reduction of Sewage Sludge Containing No Unstabilized Solids [503.33(b)(7)]

Under this option, vector attraction is considered to be reduced if the sewage sludge does not contain unstabilized solids generated during primary wastewater treatment and if the solids content of the sewage sludge is at least 75% before the sewage sludge is mixed with other materials. Thus, the reduction must be achieved by removing water, not by adding inert materials.

It is important that the sewage sludge not contain unstabilized solids because the partially degraded food scraps likely to be present in such a sewage sludge could attract birds, some mammals, and possibly insects, even if the solids content of the sewage sludge exceeds 75%.

The way dried sewage sludge is handled or stored before use or disposal can create or prevent vector attraction. If dried sewage sludge is exposed to high humidity, the outer surface of the sewage sludge could equilibrate to a lower solids content and attract vectors. Proper management should be conducted to prevent this from happening.

8.9 Option 8: Moisture Reduction of Sewage Sludge Containing Unstabilized Solids [503.33(b)(8)]

Vector attraction of any sewage sludge is considered to be reduced if the solids content of the sewage sludge is increased to 90% or greater. This extreme desiccation deters vectors in all but the most unusual situations. As noted for Option 7, the solids increase should be achieved by removal of water and not by dilution with inert solids. Drying to this extent severely limits biological activity and strips off or decomposes the volatile compounds that attract vectors.

Because sewage sludge meeting vector attraction reduction with this option may contain unstabilized solids, material that absorbs moisture or is rewet may putrefy and attract vectors. Proper storage and use of this material should be considered in order to prevent potential pathogen growth and vector attraction.

8.10 Option 9: Injection [503.33(b)(9)]

Vector attraction reduction can be achieved by injecting the sewage sludge below the ground. Under this option, no significant amount of the sewage sludge can be present on the land surface within 1 hour after injection, and, if the sewage sludge is Class A with respect to pathogens, it must be injected within 8 hours after discharge from the pathogen-reduction process.

Injection of sewage sludge beneath the soil places a barrier of earth between the sewage sludge and vectors. The soil quickly removes water from the sewage sludge, which reduces the mobility and odor of the sewage sludge. Odor is usually present at the site during the injection process, but it quickly dissipates when injection is complete.

The special restriction requiring injection within 8 hours for Class A sewage sludge is needed because these sewage sludges are likely devoid of actively growing bacteria and are thus an ideal medium for growth of pathogenic bacteria (see Section 4.3). If pathogenic bacteria are present (survivors or introduced by contamination), their numbers increase slowly for the first 8 hours after treatment, but after this period, their numbers can rapidly increase. This kind of explosive growth is not likely to happen with Class B sludge because high densities of nonpathogenic bacteria are present which suppresses the growth of pathogenic bacteria. In addition, the use of Class B biosolids requires site restrictions which reduce the risk of public exposure to pathogens. Consequently, this special requirement is not needed for Class B biosolids

8.11 Option 10: Incorporation of Sewage Sludge into the Soil [503.33(b)(10)]

Under this option, sewage sludge applied to the land surface or placed on a surface disposal site must be incorporated into the soil within 6 hours after application to or placement on the land. If the sewage sludge is Class A with respect to pathogens, the time between processing and incorporation after application or placement must not exceed 8 hours -- the same as for injection under Option 9.

When applied at agronomic rates, the loading of sewage sludge solids typically is about 1/100th or less of the mass of soil in the plow layer (approximately the top six inches of soil). If mixing is reasonably good, the dilution of sewage sludge in the soil surface is equivalent to that achieved with soil injection. Odor will be present and vectors will be attracted temporarily, as the sewage sludge dewaters on the soil surface. This attraction diminishes and is virtually eliminated when the sewage sludge is mixed with the soil. The mixing method applies to liquid sewage sludges, dewatered sewage sludge cake, and even to dry sewage sludges that have not already met the vector attraction reduction requirements of the regulation by one of the other options.

The 6 hours allowed to complete the mixing of sewage sludge into the soil should be adequate to allow for proper incorporation. As a practical matter, it may be wise to complete the incorporation in a much shorter time. Clay soils tend to become unmanageably slippery and muddy if the liquid sewage sludge is allowed to soak into the first inch or two of topsoil.

8.12 Option 11: Covering Sewage Sludge [503.33(b)(11)]

Under this option, sewage sludge placed on a surface disposal site must be covered with soil or other material at the end of each operating day. Daily covering reduces vector attraction by creating a physical barrier between the sewage sludge and vectors, while environmental factors work to reduce pathogens.

8.13 Option 12: Raising the pH of Domestic Septage [503.33(b)(12)]

This option applies only to domestic septage applied to agricultural land, forest, a reclamation site, or surface disposal site. Vector attraction is reduced if the pH is raised to at least 12 through alkali addition and maintained at 12 or higher for 30 minutes without adding more alkali. (These conditions also accomplish pathogen reduction for domestic septage--see Section 5.6.) When this option is used, every container (truckload) must be monitored to demonstrate that it meets the requirement. As noted in Section 5.6, “alkali” refers to a substance that causes an increase in pH.

This vector attraction reduction requirement is slightly less stringent than the alkali addition requirement for sewage sludge. The method is geared to the practicalities of the use or disposal of domestic septage, which is typically treated by lime addition in the domestic septage hauling truck. The treated septage is typically applied to the land shortly after lime addition. During the very short time interval, the pH is unlikely to fall to a level at which vector attraction could occur.

If domestic septage is not applied soon after pH adjustment, it is recommended that pH be retested, and additional alkali be added to the domestic septage to raise the pH to 12 if necessary. Alternatively, if pH has dropped and the domestic septage begins to putrefy, it is advisable to cover or incorporate the domestic septage in order to prevent vector attraction.

8.14 Number of Samples and Timing

Unlike pathogenic bacteria, volatile solids cannot regenerate once they are destroyed, so samples can be taken at any point along the process. However, since volatile solids are destroyed throughout treatment, it is recommended that samples be taken at the end of processing.

Facilities which use Option 2 or 3 to demonstrate vector attraction reduction must schedule sampling to leave ample time to complete the laboratory tests before sewage sludge is used or disposed. A suggested procedure would be to take several samples at evenly spaced time intervals during the period between the required monitoring dates and calculate running averages comprised of at least four volatile solids results. This has the advantage of not basing the judgement that the process is performing adequately (or inadequately) on one or two measurements that could be erroneous because of experimental error or a poorly chosen sample inadvertently taken during a brief process upset. It also provides an important quality control measure for process operations. Since the Part 503 regulations do not specify a sampling program, it is recommended that sewage sludge preparers consult with the regulatory authority with regard to sampling schedules.

8.15 Vector Attraction Reduction Equivalency

Many of the vector attraction reduction tests are time consuming and inconvenient, particularly for small treatment plants that do not have a laboratory. Efforts to define new, simpler methods for measuring vector attraction are on-going.

Since it is infeasible to measure the actual attraction of vectors, given the large number of variables, methodology development must continue to focus on the cause of vector attraction, namely the availability of a food source (volatile solids) or odor. The tests to measure the attractants may vary depending on the technology by which the sewage sludge is processed.

Some of the parameters which might be used to measure vector attraction may include gas production or measures of microbial activity. For example, several methods

which measure carbon dioxide evolution or reheating potential are currently in use to measure compost stability, but these methods must be examined more closely to determine if they can be applied to other forms of sewage sludge and if results can be adequately correlated to vector attraction.

The responsibility to eventually develop additional vector attraction reduction test protocols lies with the scientific community and the sewage sludge industry. Since there is currently no standard procedure for considering VAR equivalency, new methods must be submitted to the EPA for consideration and potential inclusion in the next rulemaking effort.

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Chapter 9
Sampling Procedures and Analytical Methods

9.1 Introduction

Many of the Part 503 Subpart D pathogen and vector attraction reduction requirements call for monitoring and analysis of the sewage sludge to ensure that microbiological quality and vector attraction reduction meet specified requirements (see Chapters 4 to 6 for a description of the requirements).The purpose of this chapter is to describe procedures for obtaining representative samples and ensuring their quality and integrity. It also summarizes the analytical methods required under Part 503, and directs the reader to other sections of this document that describe some of those methods.

Sampling personnel will also benefit from reading expanded presentations on the subject. “Standard Methods” (APHA, 1992), “Principles of Environmental Sampling” (Keith, 1988), “Samplers and Sampling Procedures for Hazardous Waste Streams” (EPA, 1980), "Sludge Sampling and Analysis Guidance Document” (EPA, 1993) and ASTM Standard E 300-86, “Standard Practice for Sampling Industrial Chemicals” (ASTM, 1992a) are highly recommended. The latter publication provides an in-depth description of available sampling devices and procedures.

When referring to other publications, it is important to note that most guidance on specific sampling techniques is directed toward chemical analysis. Procedures described may be inappropriate for microbiological sampling because they expose the samples to possible contamination, or may be appropriate only after some modification to reduce the risk of microbial contamination during sampling.

9.2 Laboratory Selection

A very important, but often overlooked component of pathogen and vector attraction monitoring is selecting an appropriate analytical laboratory. The analysis of sewage sludge or biosolids for indicator and pathogenic organisms is more complex than water analysis. Solid samples such as biosolids are prepared differently than water samples and also typically contain a much higher background microbial population than water contains. Biosolids products such as compost can be very heterogeneous, requiring special sample preparation procedures. It is therefore important to use a laboratory that has developed an expertise through the routine analysis of biosolids products. Regional and state sludge coordinators should be contacted for assistance in selecting a qualified laboratory.

To ensure that a laboratory has adequate experience with biosolids analyses, the following information should be obtained and reviewed.

- For how long has the laboratory been analyzing biosolids for the specified parameters?
- Approximately how many biosolids samples does the laboratory analyze per week or month?
- For how many wastewater treatment facilities is the laboratory conducting the specified analyses?
- A list of references.
- Does the laboratory have a separate and distinct microbiology lab?
- Does the laboratory have microbiologists on staff? Request and review their resumes.
- Who will actually perform the analyses?
- Is the laboratory familiar with the analytical procedures including sample preparation, holding times, and QA/QC protocols?

A laboratory tour and reference check are also recommended. A good laboratory should be responsive, providing requested technical information in a timely manner. It is the biosolids generator’s responsibility to provide accurate analytical results. Consequently, the selection of an appropriate laboratory is an important component of developing a biosolids monitoring plan.

9.3 Safety Precautions

Sewage sludges that are being sampled should be presumed to contain pathogenic organisms, and should be handled appropriately. Both the sampler and the person carrying out the microbiological analysis must take appropriate precautions. Safety precautions that should be taken when sampling and when analyzing the samples are discussed in Standard Methods (APHA, 1992) in Sections 1060A and 1090C.

Individuals performing sampling (usually employees of wastewater treatment works) should receive training in the microbiological hazards of sewage sludge and in safety

precautions to take when sampling. Laboratory personnel should be aware that the outside of every sample container is probably contaminated with microorganisms, some of which may be pathogens. Personal hygiene and laboratory cleanliness are also extremely important. Several safety practices that should be standard procedures during sample collection and analysis are:

- Gloves should be worn when handling or sampling untreated sewage sludge or treated biosolids.
- Personnel taking the samples should clean sample containers, gloves, and hands before delivering the samples to others.
- Hands should be washed frequently and always before eating, smoking, and other activities that involve hand-to-mouth contact.
- Photocell-activated or foot-activated hand washing stations are desirable to reduced spreading of contamination to others.
- Employees should train themselves to avoid touching their lips or eyes.
- Mouth pipetting should be forbidden.
- Smoking should not be allowed inside the lab.

Employees involved in sample collection (or any other activity where they are exposed to wastewater or sewage sludges) should review their immunization history. At a minimum, employees should be immunized against tetanus. However, employees should consider immunization for other diseases, particularly hepatitis A and B. Employees should also consider having a blood sample analyzed to determine if they still have active antibodies for the various immunizations they received as children.

Personnel analyzing sewage sludge or biosolids samples should receive training in awareness and safety concerning biohazards. Because microbiological laboratories have safety programs, this subject is not covered in depth here. A facility's sampling plan should include a section on microbiological hazards and appropriate safety practices or, alternatively, refer the reader to another document where this information is presented.

9.4 Requirements for Sampling Equipment and Containers

Containers

Sampling containers may be of glass or plastic that does not contain a plasticizer (Teflon, polypropylene, and polyethylene are acceptable). Plastic bags are especially useful for thick sewage sludges and free-flowing solids. Presterilized bags are available. Stainless steel containers are acceptable, but steel or zinc coated steel vessels are not appropriate. In addition to providing guidance on appropriate containers for specific analyses, private analytical laboratories will typically provide sample containers at no cost. Sampling containers used for microbiological analyses should be sterile. Sampling tools that come in contact with the actual sample should be constructed of stainless steel, which is easily cleaned, and sterilized. Tools made of wood, which is difficult to sterilize because of porosity, should not be used.

Equipment

The sampling equipment used is primarily dependent on the type of material being sampled. For relatively high solids content biosolids, a hand trowel or scoop may be adequate, whereas, collecting stratified samples from a lagoon requires more sophisticated and specialized equipment. Automated sampling equipment, as commonly used for wastewater, should not be used. Such equipment can cause solids separation during sampling and is difficult to clean, resulting in cross contamination. Sampling equipment should be constructed of non-corrosive materials, such as stainless steel, Teflon, or glass, that can be thoroughly cleaned. Sampling equipment should be dedicated for this task and should not be used for other applications. Equipment should be cleaned well with detergent and a nylon scrub brush after each use and stored inside in a dedicated location. The types of sampling equipment and their applications are presented in Table 9-1. The use of this equipment is discussed in greater detail in Sections 9.6 and 9.7.

Sterilization

The containers and tools used for sampling must be sterilized if the biosolids product is to be analyzed for Class A microbiological parameters. Alternatively, pre-sterilized, disposable scoops, and other sampling devices can be purchased, alleviating the need to sterilize sampling equipment. Conservative microbiological practice also requires sterilization of containers and sampling tools used for collecting samples to be tested for meeting the Class B requirements. Sample containers and equipment should be scrupulously cleaned prior to actual sample collection. After the samples are collected, the sampling equipment should be cleaned well with soap and water and put away until the next sampling event. Equipment should be dedicated to sampling and not used for other activities. Only equipment that touches the actual sample must be sterilized. Equipment such as shovels or heavy equipment used to access a sludge pile interior does not need to be sterilized, but should be clean, as long as another sterile sample collection device (such as a hand trowel) is used to access and collect the actual sample. Sterilization is not required when collecting samples of sewage sludge to be used in vector attraction reduction tests, but all equipment must be clean.

Either steam or a sterilizing solution such as sodium hypochlorite (household bleach) should be used for sterilizing equipment. If bleach is used, equipment must be rinsed thoroughly in order to prevent residual bleach from having an effect on the microbial population in the sample. Equipment should be thoroughly washed with water, soap, and a brush prior to sterilization. If an autoclave or large

Table 9-1. Equipment Used for Collecting Sewage Sludge Samples

Equipment	Application
Composite Liquid Waste Sampler (Coliwasa)	The Coliwasa is a device employed to sample free-flowing sewage sludges contained in drums, shallow tanks, pits, and similar containers. It is especially useful for sampling wastes that consist of several immiscible liquid phases. The Coliwasa consists of a glass, plastic, or metal tube equipped with an end closure that can be opened and closed while the tube is submerged in the material to be sampled.
Weighted Bottle	This sampling device consists of a glass or plastic bottle, sinker, stopper, and a line that is used to lower, raise, and open the bottle. The weighted bottle is used for sampling free flowing sewage sludges and is particularly useful for obtaining samples at different depths in a lagoon. A weighted bottle with line is built to the specifications in ASTM Method D270 and E300.
Dipper	The dipper consists of a glass or plastic beaker clamped to the end of a two- or three-piece telescoping aluminum or fiberglass pole that serves as the handle. A dipper is used for obtaining samples of free flowing sewage sludges that are difficult to access. Dippers are not available commercially and must be fabricated.
Sampling Thief	A thief consists of two slotted concentric tubes, usually made of stainless steel or brass. The outer tube has a conical pointed tip that permits the sampler to penetrate the material being sampled. The inner tube is rotated to open and close the sampler. A thief is used to sample high solids content materials such as composted and heat dried biosolids for which particle diameter is less than one-third the width of the slots. Thief samplers are available from laboratory supply companies.
Trier	A trier consists of a tube cut in half lengthwise with a sharpened tip that allows the sampler to cut into sticky materials such as dewatered cake and lime stabilized biosolids. A trier samples moist or sticky solids with a particle diameter less than one-half the diameter of the trier. Triers 61 to 100 cm long and 1.27 to 2.54 cm in diameter are available from laboratory supply companies
Auger	An auger consists of sharpened spiral blades attached to a hard metal central shaft. An auger can be used to obtain samples through a cross section of a biosolids stockpile. Augers are available at hardware and laboratory supply stores.
Scoops and Shovels	Scoops are used to collect samples from sewage sludge or biosolids stockpiles, shallow containers, and conveyor belts. Stainless steel or disposable plastic scoops are available at laboratory supply houses. Due to the difficulty of sterilizing shovels and other large sampling equipment, this type of equipment should only be used for accessing the center of stockpiles and should not be used for collecting the actual sample.

pressure cooker is available, enclose the sampling tool in a kraft paper bag and place the bag in the autoclave. A minimum period of 30 minutes at a temperature of 121°C is required for sterilization. The kraft paper bag keeps the sampling device from becoming contaminated in the field. A steam cleaner can also be used to sterilize sampling equipment. Place the equipment in a heat resistant plastic bucket and direct steam onto the equipment for a minimum of 10 minutes. When done, place the sterilized equipment in a kraft paper bag.

Many facilities do not have an autoclave or steam cleaning equipment and will need to use a sterilizing solution to sterilize equipment. A 10% household bleach solution (1 part bleach, 9 parts water) is readily available and works well. However, bleach is corrosive and may also affect the microbial population of a sample and does need to be adequately removed from the equipment prior to sample collection. Make up the 10% solution in a clean plastic bucket. Immerse each piece of clean equipment in the solution for a minimum contact time of a minute. Rinse the equipment in another bucket containing sterile or boiled water. Let the equipment air dry for a few minutes or dry with sterile paper or cloth towels. After drying, place the equipment in a paper bag. Sterile plastic bags obtained from a scientific equipment supplier can also be used for short-term sterile equipment storage.

9.5 Sampling Frequency and Number of Samples Collected

The primary objective of biosolids monitoring is to assure that all of the biosolids produced meet the regulatory requirements related to land application. It is obviously not feasible to sample and analyze every load of biosolids leaving a facility, nor is it necessary. However, a sampling plan does need to adequately account for the variability of the biosolids. This entails collecting samples at an adequate frequency and analyzing a sufficient number of samples. The minimum sampling frequency and number of samples to be analyzed are shown in 40 CFR Part 503. As shown in Table 3-4, the sample collection frequency is determined by the amount of biosolids used or disposed.

The number of samples which must be analyzed for compliance with Class A microbiological parameters is not specified, however, it is strongly recommended that multiple samples per sampling event be analyzed for biosolids. The number of samples taken must be sufficient to adequately represent biosolids quality. It must be noted that for Class A biosolids, analytical results are not averaged: every sample analyzed must meet the Class A requirements.: “Either the density of fecal coliform in the sewage sludge must be less than 1,000 MPN per gram of total solids (dry weight basis), or the density of *Salmonella* sp.

bacteria in sewage sludge must be less than 3 MPN per 4 grams of total solids (dry weight basis)."

To meet Class B Alternative 1 requirements, seven samples must be taken and the geometric mean of results must meet the 2.0×10^6 MPN fecal coliform per dry gram limit (see Chapter 5). It is recommended that the samples be taken over a two-week period in order to adequately represent variability in the sewage sludge.

The actual sampling and analysis protocol is typically developed by the facility and reported to the regulatory authority, which can require a more stringent sampling and analysis protocol than that stipulated in the Part 503 regulation. In some cases, the regulatory authority may initially require a more stringent monitoring schedule which may be relaxed once product consistency is established. The biosolids preparer should carefully consider the treatment process, analytical variability, end-use, and other factors when determining the frequency and number of samples to be analyzed. Collecting samples more frequently or analyzing more samples will help to ensure the product meets the regulatory criteria and that pathogen and vector attraction reduction goals have been met. More information on this subject is available in Chapter 10.

It is recommended that additional sampling be conducted for heterogeneous biosolids products. A single grab sample may adequately represent the sewage sludge in a digester that is being mixed, but might not adequately represent several hundred yards of compost product stored in several stockpiles. Likewise, a facility that conducts a single annual analysis should consider more frequent monitoring, particularly if the analytical results from the annual analysis are near the regulatory limit. It is a facility's responsibility and in the facility's best interest to develop a monitoring plan that assures product quality.

9.6 Sampling Free-Flowing Sewage Sludges

Sewage sludges below about 7% solids behave, at worst, like moderately viscous liquids such as an SAE 20 lubricating oil. They flow freely under small pressure gradients, and flow readily into a sample bottle. They are heterogeneous, and concentration gradients develop upon standing. Generally settling is slow and is overcome by good mixing.

Liquid sewage sludges may be flowing in pipes, undergoing processing, or stored in concrete or metal tanks, in tank cars or tank trucks, or in lagoons. This section describes procedures for sampling from these various situations, except for lagoons, which are discussed in Section 9.7.

Filling Containers

Liquid sewage sludge samples are usually transferred into wide mouth bottles or flexible plastic containers. Sewage sludges can generate gases, and pressure may build up in the container. Consequently, the bottle or container is generally not filled. If the sewage sludge is to be used for the oxygen uptake test, the sample bottle should not be more than half full, to provide some oxygen for respiration of the microorganisms in the sewage sludge. Conversely, if the sewage sludge is to be used for the additional anaerobic digestion test for vector attraction reduction, it is important that it not be exposed to oxygen more than momentarily. Consequently, sample bottles must be completely filled to the top. Bottles should have closures that can pop off, or else be made of flexible plastic that can both stretch and assume a spherical shape to relieve any internal pressure that develops.

The containers used to collect the samples can be widemouth bottles that can be capped, or pails. If a pail is used and only part of its contents will be taken as a sample, the sample should be transferred to a bottle at the sampling location. Preferably, the transfer should be made by use of a ladle rather than by pouring, since some settling can occur in the pail, particularly with primary or mixed sewage sludges of solids contents below about 3%.

Collecting Liquid Sewage Sludge Samples

If liquid sewage sludges are to be sampled, it is most desirable to sample them as they are being transferred from one vessel to another. Preferably this is done downstream of a pump that serves to mix the sewage sludge thoroughly. Ideally, the sample is taken through a probe facing upstream in the center of the discharge pipe and is withdrawn at the velocity of the liquid at the center-line of the pipe. This approach generally is not possible with sewage sludge, because fibrous deposits can build up on the probe and plug up the pipeline.

Sampling through a side tap off the main discharge pipe is adequate only if the flow is turbulent and the sample point is over ten pipe diameters downstream from the pipe inlet (e.g., for a 3-inch [7.6-cm] pipe, 30 inches [76 cm] downstream) or the tap is downstream from a pump. For any kind of a slurry, the fluid at the wall contains fewer particles than the bulk of the fluid in the pipe. The sample should be withdrawn fast enough so that it minimizes the amount of thinned-out fluid from the outside pipe wall that enters the sample.

If the sewage sludge discharges into the open as it is transferred from one vessel to another, it can be sampled by passing a sample container through the discharge. The container should be large enough to catch the whole discharge during the sampling interval, rather than, for example, just sampling the center or the edge of the discharge. The sample container could be a pail or a beaker at the end of an extension arm. Sample volume should be about three times what is needed for the analyses planned.

The collection of a representative sample often requires the use of time compositing procedures. For example, if a digester is being sampled during a withdrawal that takes about 15 minutes, a sample can be taken during the first, second, and third 5-minute period. The three separate

samples should be brought back to the laboratory and composited into a single sample. If the sample is being analyzed for bacteria, viruses, or vector attraction reduction, the composite should be prepared within an hour of collecting the first individual grab sample. A longer time period might allow microbiological changes to occur in the first sample taken. Composite sampling over 24 hours is possible for viable helminth ova analysis, provided that the ova in the sample are not exposed to chemical or thermal stress such as temperatures above 40°C (104°F) or certain chemicals such as ammonia, hydroxides, and oxidants.

Sampling Sewage Sludge in Tanks

The purpose of the sampling is to determine the properties of the entire mass of the sewage sludge, rather than, for example, to find out if there is a gradient in the property at various points in the tank. This requires that the tank be well-mixed, otherwise many subsamples must be taken throughout the tank and composited. Large tanks, even if they are well-mixed, have the potential for developing gradients in composition. An enclosed tank such as an anaerobic digester must be sampled through pipelines entering the digester. A minimum of three taps on a side wall of the enclosed tank is recommended. The sample tap pipe should project several feet into the tank. Precautions must be taken to minimize contamination from sample collection lines. When a sample is taken, enough material must be withdrawn to thoroughly flush the line before the sample is collected. This helps flush any contaminants in the sample line and assure that a representative sample is collected from the tank. The sample line should be backflushed with water after the sample is withdrawn to clean out residual sewage sludge and prevent microbial growth. Sampling should be conducted when the tank is being agitated. An open tank such as an aerobic digester can be sampled by drawing a vacuum on a vacuum-filtering flask connected to a rigid tube lowered to the desired level in the tank. A weighted sampling bottle may also be used to sample the liquid at the desired depth in the tank (see ASTM E30086, Par. 21, in ASTM [1992a]).

9.7 Sampling Thick Sewage Sludges

If sewage sludges are above 7% solids, they take on "plastic" flow properties; that is, they require a finite shear stress to cause flow. This effect increases as the solids content increases. Solids may thicken in lagoons to 15% solids. At these concentrations, they will not flow easily and require a substantial hydrostatic head before they will flow into a sample bottle.

Sampling of sewage sludge stored in lagoons may be very difficult, depending on the objectives of sampling and the nature of the sewage sludge in the lagoon. The thickened sewage sludge solids are generally nonuniformly distributed in all three dimensions. It is desirable first to map the distribution of depth with length and width to determine where the sampling should be concentrated. A length-width grid should be established that takes the nonuniformity of the solids deposit into account. ASTM E300-86, Figure 19 (ASTM, 1992a), shows a grid for sampling a uniform deposit in a railroad car.

The layer of water over the sewage sludge complicates the use of many types of tube samplers because the overlying water should not be included in the sample. A thief sampler (ASTM, 1992a) that samples only the sewage sludge layer may be useful. Weighted bottle samplers (ASTM, 1992a) that can be opened at a given depth can be used to collect samples at a desired depth. Samples at three depths can be taken and composited. Most likely the sewage sludge will be as much as twice as high in solids content at the bottom of the sewage sludge layer as at the top. Compositing of equal volumes of samples from top, middle, and bottom produces an excellent mass-average sample and adjusts for this difference in solids content. Generally there is no point in determining the gradient with depth for microbiological and VAR parameters, because there is no practical way of separately removing layers of sewage sludge from a lagoon. Determining whether there are gradients with length and width makes more sense because, if desired, sewage sludge could be removed selectively from part of a lagoon, leaving behind the unacceptable material.

Sewage sludges from dewatering equipment such as belt filter presses and centrifuges can have a solids content up to 35% and even higher following some conditioning methods. High solids content sewage sludges are easy to sample if they are on moving conveyors, as described in Section 9.5. However, if the sewage sludge is stored in piles, obtaining a representative sample requires more planning and a greater overall effort. As a result of the different environment between the pile surface and interior a gradient will develop over time in the sewage sludge storage pile. The sampling methodology used needs to address this potential gradient between the pile surface and interior. Sampling devices such as augers (a deeply threaded screw) are used on high solids cakes (ASTM, 1992a) to collect a cross sectional sample. The auger is "turned into the pile and then pulled straight out. The sample is removed from the auger with a spatula or other suitable device." Alternatively, a shovel can be used to collect subsamples for compositing from the pile interior. The pile should be sampled in proportion to its mass; more samples are taken where the pile is deeper.

9.8 Sampling Dry Sewage Sludges

For purposes of this discussion, "dry" sewage sludges contain as much as 60% water. They include heat dried and composted sewage sludges, and sewage sludges from dewatering processes, such as pressure filtration, that produce a cake which is usually handled by breaking it up into pieces. Some centrifuge cakes are dry enough that they are comprised of small pieces that remain discrete when piled.

Dry sewage sludges are best sampled when they are being transferred, usually on conveyors. Preferably material across the entire width of the conveyor is collected for

a short period of time. Several of these across-width samples are collected and combined into a time-composite sample. If the entire width of the conveyor cannot be sampled, the sample is collected from various points across the breadth of the conveyor, and a space and time-composited sample is collected.

Collecting a representative sample from a stockpile containing a dried sewage sludge product poses a greater challenge than collecting the sample from a conveyor. The settling and classification of the material and the different environments between the pile edge and interior must be considered. When a material comprised of discrete particles is formed into a pile, classification occurs. If the particles are homogeneous in size and composition, a representative sample can be easily obtained (assuming the sample is collected within 24 hours of pile construction). However if the particles are of a different size or composition, an unequal distribution of the particles may result during settling. For example, a composted sewage sludge may be heterogeneous, with respect to particle composition, even when oversized bulking agents have been removed. It is important that the edges and interior of such piles are properly weighted as part of the sample collection procedure. A sampling grid that prevents bias, such as that presented in ASTM E300-86, Item 31.4 (ASTM, 1992a), should be used.

The heterogeneous nature and presence of large particles in some composted sewage sludges cause another problem in sampling. For example, most augers and sampling thiefs will be ineffective in getting a representative sample from the interior of a pile containing large wood chips and fine composted sewage sludge. There may be no substitute for digging with a shovel to get to the desired location.

Stockpile sampling is also made more difficult by the constant evolution of the characteristics of stored material. Immediately after a sewage sludge stockpile is constructed, physical, chemical, and biological changes begin to occur within and on the surface of the stockpile. Within a period as short as 24 hours, the characteristics of the surface and outer part of the pile can differ substantially from that of the pile interior. The outer part of a pile tends to remain at or near ambient temperature, loses moisture through evaporation, and volatilizes some compounds such as ammonia. In contrast, pile interiors retain heat (achieving temperatures that can be 40°C greater than the pile surface), but lose little moisture or chemical compounds through evaporation and volatilization. As a result, the level of microbial growth and activity within the pile and on the pile surface will also differ. The potential for growth of fecal coliform bacteria in mesophilic regions of the pile is of particular concern. If a sewage sludge stockpile is more than one day old, the sample should be collected from a pile cross section. This is especially important when there is a large temperature gradient between the pile surface and interior.

9.9 Control of Temperature, pH, and Oxygenation After Sample Collection Samples for Microbial Tests

Table 9-2 summarizes the maximum holding times and temperatures for sewage sludge samples taken for microbial analyses. All samples should be cooled to appropriate temperatures immediately after they are collected to minimize changes in indicator organism and pathogen populations. For example, enteric viral and bacterial densities are noticeably reduced by even 1 hour of exposure to temperatures of 35°C (95°F) or greater. The requirement for cooling limits the practical size of the sample collection container. A gallon sample bottle takes much longer to cool than a quart bottle. Use of bottles no larger than a quart is recommended for most samples, particularly if the sewage sludge being sampled is from a process operated at above ambient temperature. Granular solids and thick sewage sludges take a long time to cool, so use of containers smaller than one quart is advised. For rapid cooling, place the sample container in a slurry of water and ice. Placing the sample container in a cooler containing bagged ice or "blue ice" is effective in maintaining low temperatures but several hours can elapse before this kind of cooling reduces sample temperature to below 10°C (50°F) (Kent and Payne, 1988). The same is true if warm samples are placed in a refrigerator. The presence or absence of oxygen is not a serious concern for the microbiological tests if the samples are promptly cooled.

Table 9-2. Analytical Methods Required Under Part 503

Analysis	Methodology	Maximum Holding Time[3]/Temperature
Enteric Viruses	American Society for Testing and Materials Method D 4994-89 (ASTM, 1992b)[1]	-18°C (0°F); up to 2 weeks
Fecal Coliform	Standard Methods Part 9221 E or Part 9222 D (APHA, 1992)[2]	4°C (39.2°F) (do not freeze); 24 hours
Salmonella sp. Bacteria	Standard Methods Part 9260D (APHA,1992)[2] or Kenner and Clark (1974) (see Appendix G of this document)	4°C (39.2°F) (do not freeze); 24 hours
Viable Helminth Ova	Yanko (1987) (see Appendix I of this document)	4°C (39.2°F) (do not freeze); 1 month
Specific Oxygen Uptake Rate (SOUR)	Standard Methods Part 27108 (APHA,1992)	20°C (sewage sludge must be digested in the 10-30°C range); 2 hours
Total, Fixed, and Volatile Solids	Standard Methods Part 2540G (APHA.,1992)	NA
Percent Volatile Solids Reduction	Appendlix C of this document	NA

[1] Appendix H of this document presents a detailed discussion of this method.

[2] Method SM-9221 E, the MPN procedure, is required for analysis of Class A biosolids and recommended for Class B biosolids. Method SM-9221 D, the membrane filtration procedure is also allowable for Class B biosolids. See Appendix F of this document for recommended sample preparation procedures and a discussion of the reporting of results.

[3] Time between sampling and actual analysis, including shipping time.

Standard Methods (APHA, 1992) states that if analysis for bacterial species (fecal coliform and *Salmonella* sp.) will commence within 1 hour after sample collection, no temperature adjustment is required. If analysis will commence between 1 and 6 hours after collection,the sample should be immediately cooled to at least 10°C. If analysis will commence between 6 and 24 hours after collection the sample should be immediately cooled to 4°C. The sample should never be frozen and analysis must commence within 24 hours of collection.

Proper planning and coordination with the courier service and analytical laboratory are essential if bacterial analyses are to be conducted within 24 hours of sample collection. The laboratory needs to be notified several days in advance so they can be prepared to initiate the analysis within several hours of receiving the sample. If they are not notified, the laboratory may not be adequately prepared and another day may lapse before the samples are analyzed. Actual sample collection should be conducted in the afternoon, within a few hours of the sample courier's arrival. If the samples are collected in the morning, a greater than 24-hour period may pass before the laboratory actually begins the analysis.

Follow-up with the laboratory is important to determine the actual sample holding time and temperature of the sample when it was received. This information can be used to improve the overall sample collection and transfer procedure. Feedback received from the lab regarding sample condition and holding times may also provide an explanation for erroneous or unexpected test results.

The requirement for prompt chilling of samples is appropriate for viruses as well as bacteria. There are far fewer laboratories capable of carrying out virus tests than can conduct bacterial analyses, so time between sample collection and analysis can routinely exceed 24 hours. Fortunately, viruses are not harmed by freezing. Typically, virology laboratories store samples at -70°C (-94°F) before analysis. Samples can be frozen in a -18°C (0°F) freezer and stored for up to 2 weeks without harm. Samples should be frozen, packed in dry ice, and shipped overnight to the analytical laboratory.

Viable helminth ova are only slightly affected by temperatures below 35°C (95°F), provided chemicals such as lime, chlorine, or ammonia are not utilized in the treatment process. Nevertheless, chilling to 4°C (39.2°F) is advised. If the samples are held at this temperature, a period of a month can elapse between sampling and analysis. Freezing should be avoided because the effect of freezing on helminth ova is not well understood.

Vector Attraction Reduction Tests

For the vector attraction reduction tests that measure oxygen uptake, or additional anaerobic or aerobic digestion (see Appendix D), the samples must be kept at the temperature at which they were collected. This sometimes can be done just by collecting a large sample in a large container. Covering the sample with an insulating blanket or placing it in an insulated box provides adequate protection against temperature change in most cases. Desired temperature can be maintained in the box by adding a "hot water bottle" or a bag of blue ice.

Depending on whether the sewage sludge is from an aerobic process or anaerobic digestion, the presence or lack of oxygen will determine which vector attraction reduction test is appropriate and therefore how the sample should be handled. For aerobic sewage sludges, a lack of oxygen will interfere with the metabolic rate of the aerobic microorganisms in the sample. Similarly, presence of oxygen will seriously affect or even kill the anaerobic organisms that convert organic matter to gases in anaerobic digestion. With samples taken for SOUR analysis, it has been the experience of some investigators that if the test is not run almost immediately after collection (within about 15 minutes), that erroneous results are obtained. The additional aerobic digestion test is more "forgiving" (because it is a long-term test and shocked bacteria can revive); up to 4 hours of shortage of oxygen can be tolerated. For the additional anaerobic digestion test, the sample containers should be filled to exclude air. In any subsequent operations where there is a freeboard in the sample or testing vessel, that space should be filled with an inert gas such as nitrogen.

No pH adjustment is to be made for any of the vector attraction reduction tests. For those vector attraction processes that utilize lime, the only requirement is to measure pH after the time periods indicated in the vector attraction reduction option (see Section 8.7).

9.10 Sample Compositing and Size Reduction

The amount of sample collected in the field generally far exceeds the amount needed for analysis. The field sample must therefore be reduced to a manageable size for the analyst to handle. As for all sample handling, sample size reduction is more difficult for microbial samples than for samples taken for vector attraction reduction tests because of the potential for microbial contamination. The laboratory may be better equipped to perform subsampling than samplers in the field.

Microbial Tests

Freely flowing liquid samples can be adequately mixed in the sample bottles by shaking the bottles. There must be room in the bottle for adequate mixing. Compositing of smaller samples is accomplished by pouring them into a larger bottle with adequate freeboard and mixing it by shaking or stirring it thoroughly with a sterile paddle. Pouring off a portion of the contents of a large container into a smaller bottle is not an acceptable procedure because the top layer of any slurry always contains fewer solids than do lower layers. Sampling with a pipette with a wide bore is an acceptable alternative, provided the bore of the pipette does not restrict the entry of solid particles. The

sample should be drawn into the pipette slowly and the tip moved through the sample to minimize selective collection of liquid over solid particles.

Sample size reduction for thick sewage sludges is difficult, because they cannot be mixed by shaking. Stirring with a mechanical mixer or a paddle is often inadequate (recall how long it takes to mix a can of paint). A satisfactory approach is to hand mix a composite of subsamples, and then take a large number of small grabs from the composited sample to form the smaller sample for the analyst.

Dry solids samples can generally be mixed adequately by shaking if there is sufficient head space in the sample container, but the individual particles are frequently large and must be reduced in size to get a representative sample. If the particles are large and a number of subsamples must be combined into a large composite, it may be necessary to reduce the particle size before they are composited. This can be done in a sterile covered chopper, blender, or grinder. The individual subsamples are then combined and mixed by shaking, rotating, and tumbling. A smaller composite is then prepared by combining a number of grabs from all parts of the combined sample. Many facilities do not have adequate equipment needed to perform this size reduction procedure. However, most analytical laboratories have this capability and will typically perform this procedure at a nominal cost. Coordination with the analytical laboratory regarding subsampling is an important part of the sampling and analysis procedure that should not be ignored. Some other sample size reduction methods, such as "coning and quartering" (ASTM, 1992a) may be use only if aseptic handling practices are observed. It should be noted that particle size reduction is not appropriate if the large pieces in the sample are not sewage sludge but are other materials which have been added to the sewage sludge for processing purposes. For the purpose of microbial or volatile solids reduction testing, additives such as wood chips should be removed from the sample before size reduction or sample preparation (see Section 10.5). It is recommended in these cases that a one-quarter inch mesh sieve be used for this purpose.

Vector Attraction Reduction Tests

The lack of a need to prevent microbial contamination makes compositing and size reduction easier for vector attraction reduction tests than for the microbial tests. However, there is a need to keep the aerobic samples aerobic and to prevent the anaerobic samples from coming into contact with air. Subsamples for the anaerobic tests can be collected into individual bottles at the sampling location. As noted above, these sample bottles should be filled completely and capped. A brief exposure to air will not cause a problem, but any prolonged exposure, such as might occur when several subsamples are being blended together and reduced in size for a representative composite sample, must be avoided. One acceptable sample size reduction procedure is to flush a large sterile bottle with nitrogen, then pour in the subsamples and blend them together with nitrogen still bleeding into the vessel. Alternatively, the nitrogen-filled vessel could be flushed with more nitrogen after the admission of the subsamples, capped, and then shaken thoroughly to accomplish the blending. Analytical laboratories generally can perform this size reduction procedure.

9.11 Packaging and Shipment

Proper packaging and shipment are important to ensure that the samples arrive in good condition (proper temperature, no spillage) within the specified time frame.

Sealing and Labeling Sample Containers

Sample containers should be securely taped to avoid contamination, and sealed (e.g., with gummed paper) so it is impossible to open the container without breaking the seal. Sealing ensures that sample integrity is preserved until the sample is opened in the laboratory. A permanent label should be affixed to each sample container. At a minimum the following information should be provided on each sample container:

- Type of analysis to be performed (e.g., *Salmonella* sp., fecal coliform bacteria, enteric virus, or viable helminth ova)
- Sample identification code (if used) or a brief description of the sample (that distinguishes it from other samples) if no sample code system is used
- Sample number (if more than one sample was collected at the same point on the same day)

Other information may include:

- Facility name, address and telephone number
- Date and time the sample was taken
- Facility contact person

This information should also be included on an enclosed chain of custody form.

Shipment Container

A soundly constructed and insulated shipment box is essential to provide the proper environment for the preserving sample at the required temperature and to ensure the sample arrives intact. Small plastic cased coolers are ideal for sample shipping. It is recommended that the outside of the shipment container be labeled with the following information:

- The complete address of the receiving laboratory (including the name of the person responsible for receiving the samples and the telephone number)
- Appropriate shipping label that conforms to the courier's standards
- Number of samples included (i.e. "This cooler contains 10 samples")

- The words “Fragile” and “This End Up”

To maintain a low temperature in the shipment box, a blue-ice type of coolant in a sealed bag should be included in the box. If the blue ice has been stored in a 0°F (-18°C) freezer (e.g., a typical household freezer), the coolant should be “tempered” to warm it up to the melting point of ice (0°C [32°F]) before it is placed around the sample. Additional packing material (bubble wrap, Styrofoam peanuts, balled-up newspaper) should be placed in the shipping container to fill in empty space to prevent sample containers from moving and potentially breaking or spilling during shipping. It is also recommended that the courier be contacted in order to determine if there are any special requirements for the shipping of this type of sample.

Adherence to Holding and Shipment Times

Adherence to sample preservation and holding time limits described in Section 9.6 is critical. Samples that are not processed within the specified time and under the proper conditions can yield erroneous results, especially with the less stable microorganisms (i.e., bacteria). Make sure the analytical laboratory reports the date and time when the samples arrived, and total holding time (period from when the sample was collected to the initiation of analysis). This information will be valuable for improving future sample events and maintaining quality control.

9.12 Documentation

Sampling Plan

It is recommended that all procedures used in sample collection, preparation, and shipment be described in a sampling plan. At a minimum, a sampling plan should provide the following information:

- Sample collection locations
- Volume of sample to be collected
- Sample compositing procedures
- Days and times of collection
- Required equipment
- Instructions for labeling samples and ensuring chain of custody
- A list of contact persons and telephone numbers in case unexpected difficulties arise during sampling

If a formal sampling plan is not available, a field log that includes instructions and a sample collection form may be used (EPA, 1980).

Sampling Log

All information pertinent to a sampling event should be recorded in a bound log book, preferably with consecutively numbered pages. At a minimum, the following information should be recorded in the log book.

- Purpose of sampling event
- Date and time of sample collection
- Location where samples were collected
- Grab or composite sample (for composite samples, the location, number, and volume of subsamples should be included)
- Name of the person collecting the sample(s)
- Type of sewage sludge
- Number and volume of the sample taken
- Description of sampling point
- Date and time samples were shipped

Chain of Custody

To establish the documentation necessary to trace sample possession from the time of collection, it is recommended that a chain-of-custody record be filled out and accompany every sample. This record is particularly important if the sample is to be introduced as evidence in litigation. Suggested information for the chain-of-custody record includes, at a minimum:

- Collector’s name
- Signature of collector
- Date and time of collection
- Place and address of collection
- Requested preprocessing (subsampling, compositing, particle size reduction)
- Requested analyses
- Sample code number for each sample (if used)
- Signatures of the persons involved in the chain of possession

A good rule of thumb is to record sufficient information so that the sampling situation can be reconstructed without reliance on the collector’s memory. Chain-of-custody forms can be obtained from the laboratory and should be used even if the laboratory is on-site and part of the treatment facility.

9.13 Analytical Methods

Part 503.8(b) of the Part 503 regulation specifies methods that must be used when analyzing for enteric viruses; fecal coliform; *Salmonella* sp.; viable helminth ova; specific oxygen uptake rate; and total, fixed, and volatile solids. Table 9-2 lists the required methods. Complete references for these methods can be found in Chapter 12, and recommended sample preparation and analytical methods can be found in the appendix as listed below.

Calculating volatile solids reduction	Appendix C
Conducting additional digestion and specific oxygen uptake rate (SOUR) tests	Appendix D
Determination of residence time in digesters	Appendix E
Sample preparation — fecal coliform and *Salmonella* sp. analysis	Appendix F
Analytical method — *Salmonella* sp.	Appendix G
Analytical method — enteroviruses in sewage sludge	Appendix H
Analytical method — viable helminth ova	Appendix I

As of the time of publication of this document, the allowable analytical methodologies are as listed above. However, in the case of fecal coliform analysis for Class B-Alternative 1, it is recommended that the MPN method be used instead of the membrane filter test (the MPN method is required for Class A fecal coliform analysis), and that the Kenner and Clark methodology be used for *Salmonella* sp. analysis.

9.14 Quality Assurance

Quality assurance involves establishing a sampling plan and implementing quality control measures and procedures for ensuring that the results of analytical and test measurements are correct. A complete presentation of this subject is beyond the scope of this manual. A concise treatment of quality assurance is found in Standard Methods (APHA, 1992) and is strongly recommended. Parts 1000 to 1090 of Standard Methods are relevant to the entire sampling and analysis effort. Part 1020 discusses quality assurance, quality control, and quality assessment. Standard Methods (Part 1020B) states that "a good quality control program consists of at least seven elements: certification of operator competence, recovery of known additions, analysis of externally supplied standards, analysis of reagent blanks, calibration with standards, analysis of duplicates, and maintenance of control charts." For most of the tests to be carried out to meet the pathogen and vector attraction reduction requirements of the Part 503 regulation, these elements cannot be met completely, but they should be kept in mind as a goal.

Microbial Tests

For the microbiological tests, quality assurance is needed to verify precision and accuracy. Quality assurance for microbiological methods is discussed in Part 9020 of Standard Methods. The quality control approach suggested is recommended for the microbiological tests required by the Part 503 regulation. In Part 9020B-4, Analytical Quality Control Procedures, it is suggested that precision be initially established by running a number of duplicates, and that thereafter duplicates (5% of total samples) be run to determine whether precision is being maintained.

Spiking and recovery tests are an important part of quality assurance. Yanko (1987) has found that spiking is useful for the viable helminth ova test, but that testing recovery effectiveness on unspiked sewage sludge is more useful for quality assurance for bacterial or viral tests. With either method, the density of the measured pathogens should be at levels that are relevant to the Part 503 regulation. For example, for viable helminth ova, samples should be spiked to density levels of approximately 100 per gram. Recovery of bacteria and viruses should be conducted on primary sewage sludges that typically contain viruses at low but consistent levels (such as primary sewage sludges from large cities).

For both commercial and in-house laboratories, quality assurance procedures should be incorporated into the analytical method and assessed routinely. Communication with the analytical personnel is an important part of developing a good sampling and analysis protocol. The sewage sludge preparer should review quality assurance data along with analysis results to ensure that laboratory performance is acceptable.

Vector Attraction Reduction Tests

It is not possible to test for accuracy for any of the vector attraction reduction tests, because standard sewage sludges with consistent qualities do not exist. Standard Methods gives guidance on precision and bias. However, for some of the vector attraction reduction options, this information was not available or was approximate. Section 10.7 provides guidance on the number of samples to take. The procedures for three of the vector attraction options developed for the Part 503 regulation (additional anaerobic and aerobic digestion and the specific oxygen uptake rate test), which are presented in Appendix D, have internal quality control procedures that include replication. Since the tests are newly proposed, the data are insufficient to judge whether agreement between replicates is adequate. This kind of information will be communicated as experience with these options accumulates.

References and Additional Resources

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Chapter 10
Meeting the Quantitative Requirements of the Regulation

10.1 Introduction

The Part 503 regulation contains operational standards for pathogen and vector attraction reduction. It provides only minimal guidance on the amount of information that must be obtained during a monitoring event to prove that a standard has been met or to demonstrate that process conditions have been maintained. This document provides more detailed information for regulators and facilities on how to adequately satisfy the regulatory requirements. Some frequently asked questions and answers are also included at the end of this chapter.

In general, it has been found that the daily, weekly, and seasonal fluctuations that occur in wastewater treatment works and sludge quality make it difficult to adequately represent sludge quality with minimum sampling. It is therefore recommended that multiple samples be taken for any sampling event and that samples be taken over a minimum 2-week period in order to best represent the performance of a sludge treatment process. Although extensive-sampling is time consuming and facility operators are often under pressure to reduce costs, it is strongly recommended that multiple samples be included in a sampling plan so that the variable quality of sludge can fully be understood.

There are many types of wastewater treatment plants and sludge management practices. This document addresses some of the many operational variables and provides some examples of how to demonstrate compliance with the regulations. The final decision about what to monitor and how frequently to monitor it lies with the permitting authority who may impose permit conditions based on specific parameters including the type of sludge produced, its intended usage, and/or the history of the facility.

10.2 Process Conditions

Sufficient information must be collected about sludge processing conditions and made available to the permitting authority and any other interested parties to enable a qualified reviewer to determine if the Part 503 requirements have been met. How this information is collected and how much information is needed depend on the process. The following example illustrates the type of information and the level of detail that may be included in a permit application. Consider the case of a treatment works that meets the pathogen reduction requirement for a Class B sludge by using anaerobic digestion conducted at the PSRP conditions of 35°C (95°F) with a 15-day residence time. To meet the pathogen reduction requirement, the monitoring results must demonstrate that the 35°C (95°F) temperature and 15-day residence time are maintained whenever the process is being used. The example below illustrates some of the factors to be considered in assuring compliance with the regulation. In addition, a contingency plan in case the conditions are not met, and product usage should be specified.

Example

Facility	Clarksdale Wastewater Treatment Facility Anaerobic Digestion
Size:	300 dry metric tons per year
Class:	B

Sewage sludge is treated in two digesters, operated in parallel, fed by constant displacement progressive cavity pumps. The facility complies with PSRP requirements by maintaining sludge at a temperature at or above 35°C for a minimum of 15 consecutive days.

- Temperature — During the first six months of operation under this permit, the permittee shall perform temperature scans throughout the volume of the digester to establish the location of the zone at which temperature is at a minimum. Scans will be conducted under the expected range of operating conditions. Once the location of the zone is established, the permittee will continuously measure digester temperature in the zone of minimum temperature. Temperatures will be recorded continuously or at intervals of eight hours. The temperature measuring device will be calibrated on a monthly basis.

- Retention Time — The permittee shall calculate the working volume of the digester to determine residence time. The permittee shall provide evidence that the digester has been cleaned within the last two years, or alternatively, determine the levels of grit and scum accumulation. Residence time must be at least 15 days. Flow rate and residence time will be measured and calculated each year.

- Vector Attraction Reduction - The facility will comply with vector attraction reduction via management practices. After digestion, the sludge will be dewatered and transported to farm land where it will be land applied and disked immediately (within six hours) into the soil (see below). Sludge will not be stored at application sites.

- Reporting- The data collected throughout the year will be summarized and submitted to the permitting authority annually. Reports will include temperature and residence time records as well as records of all application sites and sludge application rates.

- Contingency Plan -If the facility fails to meet the 35° C/15-day requirement, it has several options. The facility can try to meet the Class B time/temperature requirement with lower temperatures and longer residence times as determined by a linear interpolation between 35ºC (95°F) and 15 days and 20ºC (68°F) and 60 days. If the facility does not have the flexibility to maintain sludge in the digester for longer than 15 days, it can meet Class B requirements by sampling the sludge for fecal coliform and demonstrating that the sludge contains less than 2 million CFU or MPN per gram of sludge on a dry weight basis. Alternatively, the facility can dispose of the sludge by means other than land application. In the case that the facility cannot meet the time/temperature requirements, the permitting authority must be contacted so that a sampling plan which adequately represents sludge quality and demonstrates Class B pathogen reduction can be designed. If the facility decides to divert the sludge from land application, it must notify the regulatory agency of its plans.

- Product Use - The sludge will be land applied in accordance with all Part 503 restrictions. The facility will distribute the Class B sludge to local fruit farmers. The facility will notify applicators of sludge quality and relevant site restrictions. Crop harvesting will be restricted in accordance with Part 503 site restrictions. In the case of application to fruit trees, the farmer will wait a minimum of 30 days after application to harvest the fruit. If fruit that has fallen off the trees or otherwise touched the ground will also be harvested, the farmer will wait 14 months after sludge application to harvest the fruit. If there is any question about the waiting period or if the facility wishes to distribute sludge to farmers of crops which touch the ground, the facility should notify the regulator. Site restrictions for crops which touch the soil or which grow below the soil surface are subject to longer waiting periods.

The number and the level of detail of a permit's conditions vary depending on the type of process. Facilities that handle sludge or septage from more than one source should be subject to more frequent testing until they can demonstrate that the product consistently meets quality standards. The permitting authority must determine at what point the facility has adequately demonstrated consistency and can reduce the level of sampling.

For example, consider a treatment facility that collects liquid sewage sludge and septage from several different sources. Although all of the sludge collected undergoes standard treatment for Class B pathogen reduction, the quality of the sludge generated may vary depending on the particular feedstock received. Initially, the permitting authority may require this facility to monitor every batch of sludge in order to demonstrate that it consistently produces sludge in compliance with regulatory and permit requirements. Eventually, if enough data is available showing that the treated sewage sludge is rarely off specification, the sampling frequency could be reduced.

For other processes, such as static pile composting, a sampling plan might specify that one of several piles constructed in a day could be monitored, probably with several thermocouples at different elevations and locations in the pile, to demonstrate conformance for the whole day's production.

At times, processes do not conform to process conditions. In such cases, the operator should keep records showing that the treated sludge produced was either recycled to be processed again or diverted in some manner for use or disposal consistent with its quality (e.g., disposal in a landfill with daily cover or, if the sludge meets the Class B requirements, application as a Class B [rather than as a Class A] biosolids).

10.3 Schedule and Duration of Monitoring Events

For purposes of this discussion:

- A sampling event is defined as the period during which samples are collected. Samples may include several independently analyzed subsamples taken during the sampling event.

- A monitoring event includes the sampling period and the period to analyze the samples and provide the results needed to determine compliance.

Monitoring events are intended to reflect the typical usual performance of the treatment works. Conditions should be as stable as possible before the monitoring event. Day-to-day variations in feed rate and quality are inevitable in sewage sludge treatment, and the processes are designed to perform satisfactorily despite these variations. However, major process changes should be avoided before monitoring events, because long periods of time --as much as 3 months if anaerobic digestion is part of the process train-- are required before steady state operation is reestablished.

Monitoring for Microbiological Quality

To meet the Part 503 pathogen reduction requirements, sewage sludges may have to be monitored to determine densities of fecal coliforms, *Salmonella* sp., enteric viruses,

and/or viable helminth ova. Monitoring for these microorganisms presents special problems, primarily caused by the length of time it takes to obtain microbiological test results. This is a function of the time it takes to deliver the samples to a laboratory, have the tests conducted, and obtain the results. Microbiological analyses require a substantially longer period than conventional physical and chemical analyses. The approximate time to complete specific microbiological analyses is summarized as follows.

Fecal coliform (MPN), 4 days
Salmonella sp. (MPN) 5 to 7 days
Enteric viruses, 14 days
Viable helminth ova, 28 days

Variations in the microbiological quality of the treated sludge and intrinsic variation in the analytical methods are generally large enough that a single measurement of a microbiological parameter is inadequate to determine whether a process meets or fails to meet a requirement. The Pathogen Equivalency Committee recommends that the monitoring event include at least seven samples taken over a period of approximately 2 weeks (see Section 10.7). Based on the reliability of the treatment process and historic test results, there may be times when a reduction in this monitoring recommendation is justified.

Thus, the time required for a monitoring event could range from 3 to 7 weeks. During this time, the quality of the treated sewage sludge generated is unknown. As discussed in Section 4.10, classification of sludge as Class A or B is based on the most recent test results available. Therefore, material can continue to be distributed under its classification as Class A or B until more recent analytical results are available. However, it is recommended that material generated during the monitoring event be retained on site until results from the monitoring event are available. This will prevent misclassified sludge from being erroneously distributed.

For example, consider a facility producing a Class A sludge that is sampled for *Salmonella* sp. analysis every quarter. All historic data has shown the facility to be in compliance with Class A standards including the most recent set of lab analyses from the January monitoring event. Under these results, materials are distributed as Class A products even throughout April when a subsequent monitoring event takes place. This is acceptable because material is still classified under the most recent available lab result. However, suppose the April results show non-compliance with Class A standards. Despite the fact that the preparer complied with regulations, it is possible that some Class B material was inadvertently distributed for Class A use.

In order to avoid this situation, it is recommended that the sludge processed during the monitoring event either be stored until it is demonstrated that the processed sludge meets the quality requirements for use as a Class A or B sludge, or - if the sludge is being monitored for Class A requirements - used or disposed as a Class B sludge (provided it meets the Class B requirements). This may take up to 3 weeks in the case of fecal coliform or *Salmonella* sp. analysis and much longer if sludge is being analyzed for helminth ova or viruses. Contingencies for this type of situation should be discussed with the regulatory authority and included in permit conditions and operational plans. (For more discussion on the timing of sampling and distribution, see Section 4.10.)

Monitoring for Vector Attraction Reduction

Not all the vector attraction reduction options listed in the regulation (see Chapter 8) require lab testing. Four of the methods (treatment of sewage sludge in an aerobic process for 14 days or longer, injection below the surface of the land, incorporation of sludge into the land, and placement of sludge on a surface disposal site and covering it at the end of each day) are technology descriptions. These technologies have to be maintained throughout the year in the manner described in the regulation. Examples of the kind of information needed to demonstrate adequate performance are provided in Section 10.2.

The remaining vector attraction reduction options are based on laboratory testing for volatile solids reduction, moisture content, or oxygen uptake reduction. Some of the options can only be used with certain sludge processes. For example, the oxygen uptake rate test is only appropriate for a sludge from any aerobic digestion or wastewater treatment process. Other options, such as the 38 percent reduction in volatile solids, can be applied to a variety of biological sludge treatment processes. In any case, the technology aspect of the option, or the process by which vector attraction reduction is being attained, must be documented in the manner described in Section 10.2. Monitoring for vector attraction reduction should be performed at a minimum according to the required monitoring schedule.

Some tests for vector attraction reduction can be conducted within a few hours while others can take more than a month. For the tests that can be conducted within a few hours, the sampling event must be more than a few hours to account for the variability in the material tested and the performance of the vector attraction reduction process as affected by the changes in feedstock.

It is suggested in Section 8.14 that facilities maintain a sampling program that involves sampling at evenly spaced time intervals throughout an established monitoring period. The on-going samples can be used to calculate running averages of volatile solids reduction which are more representative than single samples or an attempt to correlate feed sludge and sludge product. As is the case for the microbiological tests, these vector attraction reduction tests should be conducted over approximately 2 weeks to minimize the expected effect of these variations. The 2-week period can be the same 2-week period during which the microbiological parameters are being determined.

The longer VAR tests present a similar problem as monitoring for microbiological quality. Some of the tests - such as the additional digestion tests - take more than a month to complete. Unless the treatment works has several sets of duplicate testing equipment, it will be impossible to run these tests on enough samples during a 2-week sampling period to assess the variability in the performance of the treatment process. Storing samples taken during this period until the equipment becomes available is not an option, because samples cannot be stored for more than a limited time period (see Section 9.6.) In such circumstances, the preparer may wish to run the vector attraction reduction tests more frequently than required in order to demonstrate on-going compliance with the requirements. More frequent testing will indicate if the facility is performing consistently and will reduce the need for multiple samples during the sampling period.

The preparer may wish to conduct composite sampling which combines samples taken within a 24-hour period to better represent sludge quality. (See Section 10.6). Since some of the bench scale tests may be affected by long-term storage of samples, compositing should be limited to a 24-hour period. If composting is done, the composite should be held at 5°C during compositing, and the assay must begin immediately upon completion of the composite.

Preparers should discuss specific facility parameters with the permitting authority to design a sampling program that is appropriate.

10.4 Comparison of Feed Sludge and Sludge Product Samples

The enteric virus and viable helminth ova analytical requirements to demonstrate that an existing or new sludge treatment process is equivalent to a PFRP one and some of the vector attraction reduction methods (e.g., percent volatile solids reduction) involve taking input and output samples that correspond (i.e., they are “before processing” and “after processing” samples of the same batch of sludge). The comparison of input and output samples allows for the determination of whether enteric viruses and helminth ova levels are being reduced to adequate levels and/or percent volatile solids reduction.

Obtaining samples that correspond can be difficult for sewage sludge treatment processes, such as anaerobic digestion, that characteristically treat sludge in fully mixed reactors with long residence times. For example, as mentioned in Section 10.3, it can take up to 3 months for an anaerobic digester to achieve steady state operation after some substantive change in feed sludge or process condition is made. Samples taken only after the process has reached steady state operation are considered as corresponding.

Many of the treatment processes that might be considered for demonstrating equivalency to PFRP are either batch or plug flow processes. In theory it is relatively simple to obtain corresponding samples - it is only necessary to calculate the time for the input material to pass through the system and sample the downstream sludge at that time. Achieving accurate correspondence in practice, however, is seldom easy. Consider, for example, the difficulty of obtaining good correspondence of feed and treated sludge for a composting operation in which the feed sewage sludge is to be compared to composted sludge that has been stored for 3 months.

Taking multiple samples and appropriately compositing the samples of feed and treated sludge averages out the composition of these sewage sludges and reduces the correspondence problem. It is the regulatory authority’s task to determine how many samples should be taken and how much data is necessary to demonstrate reduction of microorganisms in corresponding samples. As indicated in Section 10.6, limitations on the periods of time over which microbiological samples can be collected limit the utility of compositing.

10.5 The Effect of Sludge Processing Additives on Monitoring

Many sewage sludge dewatering and stabilization processes introduce other substances into the sludge. With the exception of large bulky additives such as wood chips, there is no need to modify sampling and analytical procedures. As discussed below, additives such as wood chips can complicate sample preparation and analysis and are best removed prior to analysis.

Polymers, lime, ferric chloride, paper pulp, and recycled sludge ash are frequently used to aid in dewatering. Disinfection by alkaline treatment requires the addition of lime or other alkaline materials to increase the temperature of the sewage sludge cake to disinfecting temperature. These materials also reduce the microbial densities by dilution and increased solids content. However, the change in microbial density caused by dilution may not be substantial. For example, an increase in mass of 20% would result in a reduction in the log density of a microbiological parameter of only 0.079.

The exposure risk to human health is directly related to the mass of treated sludge. So the achievement of pathogen reduction requirements and safe end-use is dictated by the population of pathogenic organisms in the final product. This is the approach taken by the Part 503 regulation, which requires that the treated sludge, regardless of the mass of other materials added, meet the standards for Class A or Class B sludge.

For some sludges, particularly those treated by composting (these usually will be Class A biosolids), the amount of additive can be considerable. Nevertheless, the regulation requires that the biosolids meet the standard, which means that no correction need be made for dilution.

The issues of sampling and analytical procedures for employment are different when considering wood chips or other materials which are often added to sludge as a bulk-

ing agent for composting. Compost product may be given away or sold as a screened or unscreened product, and although regulations require that the treated sludge, as it is applied, meets 503 standards, in the case of wood chips and other large particle size bulking materials, it is appropriate to remove large pieces before analysis takes place.

Large additives are removed in order to improve the accuracy of the microbial measurements. The wood chips are so big (typically 4 cm x 4 cm x 1 cm) that a very large sample would have to be taken and blended to get a representative subsample. Sample reliability is reduced when the sample consists of a mix of sludge solids and fibrous wood-chip residue from blending. Another reason for removing the wood chips prior to microbial analysis is that the exposure of users to the compost is related to the fine particle content and not to large, physically distinct wood chips. For example, a user who handles the compost gets his or her hands covered with compost particles. Similarly, the user might breathe in a dust of compost particles. In both cases, it is the "fines" of the compost, not the wood chips that the user is exposed to.

In order to ensure that wood chips are not included in the lab's subsample, the facility should remove wood chips after sampling, being careful not to contaminate, with a sterilized sieve. The size of the sieve needed depends on the dimensions of the wood chips, but the same sieve size should be used for each sampling event. Alternatively, the laboratory should be asked to remove wood chips from samples before subsampling or analyses are conducted. Again, the sieve size should be established so that a standard size is used.

10.6 Collecting Representative Samples

Sludge quality varies depending on the inputs to the wastewater system. In addition, the process is subject to ambient conditions which vary daily as well as seasonally. The goal of a sampling program is to adequately represent the quality of sludge. Therefore, both the frequency of sampling and the number of samples taken in any one sampling event must be considered carefully. This section discusses the issue of variability and how sampling frequency and composite sampling can improve the quality of data collected. A sampling plan is recommended for all sampling events to assure representative samples.

Random Variability

Virtually all sewage sludge treatment processes will experience a certain amount of short-term random or cyclic variation in the feed sludge and in process performance. Evaluation of average performance over a 2-week time period is suggested as a reasonable approach to account for these variations. Cyclic variation can be minimized by sampling on randomly selected days and time-of-day in a given week. In the case of Class B fecal coliform analysis **ONLY** variability is minimized by taking the geometric mean of analytical results. In the case of Class A, all samples must meet the fecal coliform or *Salmonella* sp. numerical limit.

Seasonal Variability

For some sewage sludge treatment processes, performance is poorer during certain parts of the year due to seasonal variations in such factors as temperature, sunshine, and precipitation. For example, aerobic digestion and some composting operations can be adversely affected by low ambient temperature. In such cases, it is critical that process performance be evaluated during the time of year when poorest performance is expected. If a treatment works is evaluated four or more times a year at intervals of 2 or 3 months, there is no problem, because all seasons of the year will be covered. For small treatment works that are evaluated only once or twice a year, it is important to monitor in the time of year where performance is expected to be poorest, to avoid approving a process that is not performing adequately for much of the year. It may also be beneficial to initially conduct sampling more frequently than the required minimum, perhaps on a quarterly basis, in order to determine the range of sludge quality. Process criteria of PSRPs and PFRPs should be discussed by the facility with the regulatory authority, and specific requirements should be included in permit conditions.

Composite Sampling

Composite sampling, or the combination of several grab samples to better represent a large quantity of sludge, is frequently practiced in wastewater treatment. Composites may consist of grab samples taken over time (typically for continuous flow processes) or from random locations in a vessel or pile (typically for batch processes). Since the purpose of composite sampling is to provide representation of a large quantity of sludge, the number and distribution of grab samples, the locations from where they are taken, and the process of combining grab samples to create a composite sample are important to consider.

The following is an example of a sampling procedure for compositing a continuous flow process. A small stream of wastewater or sludge is drawn off at rate proportional to the flow of the main stream being sampled and collected as a single sample. Typically, times of collection are for one shift (8 hours) or one day (24 hours). In this case, the accumulated sample represents a volume-average sample over the period of time the sample is drawn. The sample is chilled during the period it is being collected to prevent chemical/microbiological change until it can be brought back to the laboratory for analysis.

Composite sampling from stockpiled solid material involves taking multiple grab samples from a range of locations in the stockpile. Samples should be taken from different interior sections of the pile which may represent material produced in different time periods. Grab samples should all be of the same size so that the composite is an equal representation of all of the grab samples. The grab samples should be mixed thoroughly and a subsample pulled from the mixture.

Composite sampling is useful for any type of sampling, but the protocol must be modified when microbial analy-

ses are intended. Samples must be taken over a shorter period of time so that microbial populations do not undergo significant changes during the sampling event. For example, a composite time-average sample can be obtained by combining a series of small samples taken once every 5 minutes for a period of an hour. A composite sample for bacterial and viral testing could be taken over an hour or less under most circumstances without compromising the results. Composite sampling over 24 hours, or even longer if special precautions are taken, is possible for viable helminth ova provided the ova in the sample are not exposed to thermal or chemical stress (e.g., temperatures above 40°C [104°F] or the addition of certain chemicals such as ammonia, hydroxides, and oxidants). In addition to limiting the sampling period, sterile equipment must be used when taking grab samples or compositing the samples for microbiological analysis in order to prevent introducing pathogenic bacteria.

Composite sampling may be possible for samples to be used in some of the procedures to determine whether vector attraction reduction is adequate. It may not be appropriate for those procedures that depend on bacterial respiration (i.e., aerobic or anaerobic digestion). This subject is discussed in Appendix D which presents procedures for three methods to demonstrate reduced vector attraction.

10.7 Regulatory Objectives and Number of Samples that Should be Tested

Overall, it is recommended that numerous samples be taken over a period of 2 weeks in order to represent the average characteristics of a sludge stream. Unfortunately, sampling for microbial and vector attraction reduction parameters is more complicated than sampling for heavy metals because of the time limits and contamination issues involved. In addition, the results of microbial testing must be handled differently. The following is a review of the primary sampling and monitoring issues that relate to particular pathogen and vector attraction reduction parameters.

Class B: Monitoring for Fecal Coliform Densities

Part 503 requires that seven samples be taken to demonstrate compliance with the fecal coliform levels required of Class B biosolids. Under the Class B requirements seven samples also means seven analyses. Seven samples were judged adequate to account for the short-term fluctuations in treated sludge quality and allow determination of average performance. Variance of fecal coliform determinations is known to be high, but analysis (presented below) showed that if seven samples are averaged, the error band about the mean value is sufficiently compressed that treatment works with adequately treated sludge would not have difficulty meeting the standard. If the mean value does not meet the standard, the material is not a Class B biosolids and must be disposed of otherwise until the standard is met.

The regulation requires that the geometric mean fecal coliform density of the seven samples be less than 2 million CFU or MPN per gram of total solids sewage sludge (dry weight basis). If a treatment works were producing a treated sewage sludge with a true mean density of exactly 2 million fecal coliform per gram, measured values of the fecal coliform density would cluster around 2 million per gram, but half would be below and half would be above it. Half the time, the treatment works would appear not to be meeting the requirement. The true mean density must be below 2 million per gram to be confident that the experimentally determined average will be below 2 million per gram. Just how much below depends on the standard error of the average.

Use of at least seven samples is expected to reduce the standard error to a reasonable value. In tests on extended aeration sludges, Farrell et al. (1990) obtained a standard deviation of the logarithm of the fecal coliform density (s) of 0.3 using the membrane filter method. This included the variability in the analysis as well as variability over time (approximately a year). Standard error for the average of seven measurements (S.E.= $s/(n^{1/2})$)is 0.11. Using the normal probability distribution, the true mean must be below 1.30 million if the geometric mean of seven measurements is to be below 2 million 95% of the time (see Table 10-1 for details of this calculation). If the standard deviation were higher, the true mean would have to be even lower to be reasonably confident that the geometric mean would be below 2 million per gram. Thus, efforts should be made to reduce variability. Steps that can be taken are:

- Reduce the standard error by increasing the number of measurements used to determine the geometric mean.
- Reduce process variability.
- Improve sampling and analytical techniques.

What action to take to reduce the geometric mean depends on the process. For anaerobic or aerobic digestion, some suggested steps are to increase temperature, increase residence time, use a draw-and-fill feeding procedure rather than fill-and-draw or continuous feeding, and increase the time between withdrawal and feeding. After an attempt at improvement, the evaluation should be repeated. If the process continues to fail, more substantial changes to the process may be appropriate.

Class A: Monitoring for Fecal Coliform or Salmonella sp. *Densities*

Part 503 requires that, to qualify as a Class A sludge, sewage sludge must be monitored for fecal coliform or *Salmonella* sp. and have a density of less than 1,000 MPN fecal coliform per gram of total solids sewage sludge (dry weight basis) or *Salmonella* sp. densities below detection limits (3 MPN/4 g). The regulation does not specify the number of samples that have to be taken during a monitoring event. One sample is not enough to properly represent the sewage sludge. It is recommended that multiple

Table 10-1. True Geometric Mean Needed If Standard Fecal Coliform Density of 2 Million CFU Per Gram is to be Rarely Exceeded

Assumptions

- The fecal coliform densities of the sewage sludge are log normally distributed. (The arithmetic mean of the logarithms of the fecal coliform densities is the mean of the distribution. The geometric mean is the antilog of the arithmetic mean of the log values.)
- The goal is to ensure that the measured mean value does not exceed the density requirement more than once in 20 monitoring events.
- The standard deviation of the log density is 0.30.

Calculation

To predict the expected frequency of a measurement using the normal probability distribution, the variable x is converted to the standard measure (u - see below) and its probability of occurrence is obtained from tabulated values of the probability distribution. In this case, the reverse is carried out. A certain probability of occurrence is desired and the value of the standard measure is read from the tables. From the normal distribution table (single-sided), u is 1.645 when P = 0.05 (one in 20),

Where:
P = the proportion of the area under the curve to the right of u relative to the whole area under the curve.
and:
$u = (\bar{x} - \mu)/S_{\bar{x}}$ (Equation 1)
Where:
μ = true log mean
$\bar{x}$ = log mean of the measurements
$S_{\bar{x}} = s/n^{1/2}$
n = number of measurements that are averaged
s = standard deviation of a single measurement of log mean density

The logarithm of the fecal coliform density requirement (2 million CFU/g) is $\bar{x}$ ($\bar{x}$ = 6.301). This is the number that should not be exceeded more than once in 20 monitoring episodes. Substituting into Equation 1 and calculating μ,

$1.645 = (6.301-\mu)/(0.3/7^{1/2})$
$\mu = 6.114$
Antilog 6.114 = 1.3 million CFU/g.

samples (≥7) be taken over a period of two weeks in order to adequately represent sludge quality. Based on the reliability of the treatment process and historic test results, there may be time when a reduction in this monitoring recommendation is justified. In the case of Class A, analytical results from multiple samples are not averaged together; instead, all results must be in compliance with Class A limits.

The measured fecal coliform density provides an estimate of the likelihood of *Salmonella* sp. detection and, if detected, the expected density. Yanko (1987) obtained a good correlation between fecal coliform density and *Salmonella* sp. detections in his extensive investigation of composts derived from sewage sludge. The fraction detected is less than 10% when fecal coliform density is less than 1,000 MPN/g. Yanko also obtained a good correlation between fecal coliform density and *Salmonella* sp. density for those samples for which *Salmonella* sp. were detected. That correlation predicts that, for fecal coliform densities less than 1,000 MPN/g,*Sa/mone//a* sp. densities will be less than 1.0 MPN/g. Thus, at fecal coliform densities 4,000 MPN/g, *Salmonella* sp. detections will be infrequent and, if detected, densities are expected to be below 1 MPN/g.

The Part 503 a!lows the monitoring of either fecal coliform or *Salmonella* sp. in order to demonstrate compliance with Class A microbiological requirements. The *Salmonella* sp. determination is somewhat similar to the fecal coliform test, but it is much more expensive and requires a high experience level. In all likelihood, the *Salmonella* sp. tests would have to be carried out by a contract laboratory.

The standard deviation for Class A sludges will most likely be lower than for Class B. This is due to the fact that we have many more organisms present in Class B sludges which are not equally distributed within the biosolids. Therefore you have greater variability and hence a higher S.D.

What action to take to further reduce pathogens in case the fecal coliform requirement is not met depends on the process. In general, verification of retention times and temperatures as well as elimination of cross-contamination between feed and treated sludge or opportunities for reintroduction of pathogens into treated sludge are recommended. For aerated deep-pile composting, thicker insulating layers on the pile and longer maturing times are suggested.

Class A: Monitoring for and Demonstration of Enteric Virus and Viable Helminth Ova Reduction

The accuracy of monitoring results demonstrating the absence of enteric viruses and helminth ova is influenced by the variability in the influent to the treatment works and the inherent error in the experimental method. Information

on method error for both enteric viruses and helminth ova is available only on standard deviations calculated from duplicate samples. Goyal et al. (1984) report that, in their comparison of methods for determining enteroviruses, the log standard deviation for the virus determination in sewage sludge was 0.26 (47 degrees of freedom). A review of the work of Reimers et al. (1989) indicates that, in the range of 5 to 100 viable Ascaris ova per 10 grams sewage sludge solids, standard deviation was about half the number of viable ova. This is equivalent to a log density of 0.3, which is about the same as for fecal coliform. Thus, there is no unusually high variability in the basic test methods that would require an increased number of samples to minimize this effect.

Deciding how many samples to take for enteric viruses and viable helminth ova is more difficult than for fecal coliform and *Salmonella* sp. because enteric viruses and viable helminth ova often may not be present in untreated sludge. For this reason, the interpretation of the density determinations for these organisms in treated sludge depends on the quality of the feed sludge. If no enteric viruses or viable helminth ova are detected in the feed sludge, then the absence of these organisms in corresponding samples of treated sludge does not indicate in any way whether the process is or is not capable of reducing these organisms to below detectable limits. The ability of a process to reduce these organisms to below detectable limits is indicated when analysis shows that these organisms were present in the feed sludge and were not present in corresponding samples of treated sludge. One important questions is: What fraction of the total pairs of corresponding samples must show positive in the feed sludge and negative in the treated sludge to provide convincing evidence that the process consistently reduces enteric viruses and viable helminth ova to below detectable levels? This is a difficult question to answer.

Because viable helminth ova are relatively stable microorganisms, compositing is suggested as a way to obtain meaningful representative samples and analytical results. If precautions are taken, such as cooling the sample promptly to close to 0°C (32°F) and destroying or neutralizing any added chemicals such as strong bases that were added as part of the pathogen-reducing process, composites can be collected over a 2-week period. Corresponding composites of feed and treated sludge can be compared, with a much lower likelihood of not finding viable helminth ova in the feed sewage sludge. Because the analytical method itself has a high variance (see above), a minimum of four duplicates of the composite should be tested.

For enteric viruses, the same approach may be used as suggested above for viable helminth ova. Precautions are taken to cool the sample and destroy or neutralize any chemicals added in the pathogen-reducing process. Samples are collected on separate days and are promptly frozen at 0°F (-18°C), or -94°F (-70°C) if samples will be stored for more than 2 weeks. When the samples are to be analyzed, the individual samples are thawed and composited, and viral densities determined.

The density of both viable helminth ova and enteric viruses in processed sludge must be based on the results of several measurements. Most of these measurements are expected to show below detectable densities. If any one sample is above 1 PFU (for viruses) or 1 viable helminth ovum (for helminths) per 4 grams, the process does not meet the Part 503 operational standard.

Vector Attraction Reduction Tests

Reduction in Volatile Solids

One way to demonstrate reduction in volatile solids requires measurement of volatile solids of the sewage sludge before and after sludge treatment. The sampling point for the "after treatment" measurement can be immediately leaving the processing unit or at the point of use or disposal, provided there has been no significant dilution downstream with inert solids.

Farrell et al. (1996) have determined the standard deviation of the percent volatile solids (%VS) determination for separate samples withdrawn from pilot-scale digesters to be 0.65% (total solids content ranged from 2% to 5%). Conventional statistical procedures (see Davies and Goldsmith, 1972) were used to calculate the standard error of the percent volatile solids reduction (%VSR), which is calculated from the %VS of the untreated and treated sludge. The standard error of the %VSR when calculated by the Van Kleeck equation (see Appendix D) is 2.0% in the range of interest (38% VSR). The 95% confidence limits of the %VSR are ±4%, which is excessive. If the %VSR is the average of seven determinations, the confidence interval is reduced to ±1.5%, which is a more acceptable value.

The most difficult problem with the %VSR determination, as discussed above in Section 10.4, is getting correspondence of the influent sludge with the effluent sludge. If there has been a significant change in an inlet concentration or flow rate, achieving correspondence can require several months of monitoring inlet and outlet volatile solids concentrations. If conditions have been steady and feed compositions have been fluctuating about an average value for a long period, data taken over a 2-week period would be adequate to establish steady state performance.[1] This implies that data have been collected beforehand that demonstrate that sewage sludge composition has reached steady state for a long period before the 2-week sampling period. It appears that regular collection of data for some months before the sampling period is unavoidable to demonstrate steady state performance before the testing period. Fortunately, the total and volatile solids determinations are not costly, and they provide valuable operating information as well.

Total and volatile solids content of a sample do not change significantly over the course of a day, particularly if

[1]Note that, unlike the plug flow case, there should be no displacement in time between comparisons of input and output for fully mixed reactors. Only when there has been a significant change is it necessary to wait a long time before the comparisons can be made.

the sludge is cooled. Time composites collected over a course of a day can be used for these determinations. Seven or more determinations are recommended to reduce the error band around the mean to minimize the chance that a process that actually has a greater volatile solids reduction than 38% might show an average that is below this value.

Additional Digestion Tests

The essential measurement in the additional digestion tests for aerobic and anaerobic sludges (see Sections 8.3 and 8.4) is the percent volatile solids content (%VS) from which the percent volatile solids reduction is calculated (%VSR). Using the standard deviation of 0.65% determined by Farrell et al. (see above), the standard error of the %VSR when calculated by the Van Kleeck equation (see Appendix D) is 2.5% in the range of interest (15% VSR). The 95% confidence limits of the %VSR are ± 5%. The tests (see Appendix D) require substantial internal replication which shrinks these confidence limits. Samples should also be taken to account for the variability in the process. The 2-week sampling period suggested for the Class A disinfection microbiological tests may be excessively restrictive if several samples are to be evaluated. The equipment needed for the test is not expensive but the units take up substantial bench space. It is unlikely that a treatment works will want to have more than two sets of test equipment. Since the tests take 30 to 40 days, it is not possible to run more than one set of tests (two in a set) within a monitoring event. It is suggested that these tests be routinely carried out during the year and the results be considered applicable to the monitoring period. It is estimated on a best judgment basis that five tests are needed to account for variability in the feed sludge and in the treatment process itself.

Specific Oxygen Uptake Rate Test

The Oxygen uptake measuring part of the specific oxygen uptake rate test (SOUR, see Appendix D) can be completed in the laboratory or field in a few minutes, so there is no difficulty in completing the test during a monitoring event. The test requires the SOUR determination to be made on two subsamples of a given sample. Farrell et al. (1996) found that, in the target SOUR value of 1.5 mg O_2/hr/g, sludge solids replicates agreed within about ± 0.1 mg O_2/hr/g. Since the test is easy to run, it is suggested that seven tests within the 2-week sampling event will adequately define the SOUR. Labs performing this test should demonstrate that they too can achieve this level of precision for replicates (±0.1 mg O_2/hr/g). Arithmetic average of the tests should be computed and compared against the Part 503 SOUR value.

Raising the pH to 12

There are two options in the regulation that reduce vector attraction by pH adjustment. In the first, sludge is raised in pH by alkali addition so that pH is ≥12 for 2 hours after alkali addition and, without further alkali addition, remains at pH ≥11.5 for an additional 22 hours (see Section 8.7). The second method is for domestic septage. The pH is raised to pH ≥12 by alkali addition and, without further addition of alkali, remains at ≥12 for 30 minutes (see Section 8.13). As noted in Section 5.6, the term alkali is used in the broad sense to mean any substance that increases pH.

The pH requirement in the regulation was established using data obtained at room temperature (Counts and Shuckrow, 1975; Ronner and Cliver, 1987), which is presumed to have been 25°C (77°F). Consequently, pH should be measured at 25°C (77°F) or measured at the existing temperature and converted to 25°C (77°F) by use of a temperature-versus-pH conversion table determined experimentally for a treated sludge that meets the pH requirements. The correction is not trivial for alkaline solutions; it is about -0.03 pH units/°C (-0.017 pH units/°F) for aqueous calcium hydroxide with a pH of about 12, and should not be ignored. Note that temperature-compensated pH meters only adjust instrument parameters and do not compensate for the effect of temperature on the pH of the solution.

pH Adjustment and Septage

Each container of domestic septage being treated with alkali addition must be monitored. The pH is monitored just after alkali addition and a half hour or more after alkali addition. Bonner and Cliver (1987) suggest that alkali (they used slaked lime) be added to the septic tank or to the septic tank truck while domestic septage is being pumped from a septic tank into the tank truck. If slaked lime is used, a dose of 0.35 lb per 10 gallons (4.2 g per liter) is sufficient to raise the pH to 12 for a typical domestic septage of about 1% solids content. The agitation from the high velocity incoming stream of septage distributes the lime and mixes it with the domestic septage. The pH is measured when the truck loading is complete. The truck then moves to the use or disposal site. Agitation generated by the motion of the truck may help in mixing and distributing the lime however, supplemental mixing in the tank may be needed. The pH is again measured at the use or disposal site. The second pH measurement should be at least a half hour after the addition of lime. The sample may be obtained through the top entry of the tank truck, using, for example, a stainless steel cup welded to a long handle to collect the sample. The pH is most conveniently measured with alkaline pH paper in the pH range of 11 to 13. The pH paper can age and become contaminated. It is best to use strips from two separate containers. If they do not agree, compare with a third batch and reject the one that disagrees with the others. Accuracy of these measurements is within ± 0.1 pH unit. If the pH is below 12, either initially or after 30 minutes, more lime should be added and mixed in. After an additional waiting period of at least 30 minutes, the pH must again be measured to ensure that it is greater than 12.

pH Adjustment and Sewage Sludges

For addition of alkali to sewage sludges, the pH requirement is part of both the PSRP process description (see Section 5.3) and the requirement of a vector attraction option (see Section 8.7). Monitoring is required from 1 to 12 times a year (see Table 3-4 in Chapter 3), and the pro-

cess must meet the prescribed operating conditions throughout the year.

Alkali is sometimes added to liquid sludge and sometimes to dewatered sludge. The pH requirements as stated in the regulation apply in the same way for both liquid and dewatered sludge. For the first measurement of pH in liquid sludge 2 hours after addition of alkali, it is assumed that the alkali and the sludge have been mixed together for a sufficient time to reach equilibrium (not considering the gradual changes that occur over substantial periods of time). Consequently, the pH measurement can be made directly in the liquid sludge. The pH measurement is made preferably with a pH meter equipped with a temperature compensation adjustment and a low-sodium glass electrode for use at pH values over 10. The pH electrode is inserted directly in the sludge for the reading. The second measurement is made 24 hours after addition of alkali. If the sludge is still in the liquid state, the pH measurement is made in the same fashion. However, if the process includes a dewatering step immediately following the alkali addition and the sludge is now a dewatered cake, the cake must be made into a slurry for the pH measurement. Acceptable procedures for preparing the sample and measuring pH are given by EPA (1986). The procedure requires adding 20 mL of distilled water (containing 0.01 M $CaCl_2$) to 10 g of sludge cake, mixing occasionally for half an hour, waiting for the sample to clarify if necessary, and then measuring pH. The important step is the mixing step that allows the alkali-treated dewatered sludge to come into equilibrium with the added water.

Number of Samples

The accuracy of pH meters and of pH paper is within ± 0.1 pH unit. More than one sample is necessary if the domestic septage or sludge is not well mixed. If the lime has been added gradually over the period in which septage is being pumped into a tank truck is considered adequate and a single measurement taken at the top of the tank truck is sufficient. If alkali has been added to liquid sludge in a tank at a treatment plant, tests are easily run to establish how much mixing is required to produce a uniform pH in the sludge. If this adequate mixing time is used, a single sample withdrawn from the tank for pH measurement is sufficient.

If alkali is added to sludge cake, more sampling is suggested. Typically, alkali (usually lime) is added to sludge cake in a continuous process. The sludge from the dewatering process discharges continuously to a mixer, from which it discharges to a pile or to a storage bin. Lime is metered into the mixer in proportion to the sludge flow rate. The flow rate and compositions of the sewage sludge can vary with time. To demonstrate compliance on a given day, several time-composite samples each covering about 5 minutes should be collected, and the pH measured. This procedure should be repeated several times during the course of a 2-week sampling event.

For sludge cake, the composites collected for pH measurement must be reduced in size for the pH measurement. The alkaline-treated sludge may be discharged from the mixing devices in the form of irregular balls that can be up to 5 to 7.6 cm (2 or 3 inches) in diameter. It is important that the biosolids to which the environment will be exposed have been treated to reduce pathogens and vector attraction to the desired level. If the discharged biosolids are ball shaped and the alkali has not penetrated the entire ball, one or both of these goals is not met for the material inside the ball. The entire ball should be at the proper pH. It is suggested that the composite be thoroughly mixed and that a subsample be taken for analysis from the mixed composite. An even more conservative approach is to sample only the interior of the balls.

Percent Solids Greater Than or Equal to 75% and 90%

The monitoring requirement for these vector attraction options (see Sections 8.8 and 8.9) is simply measurement of total solids. This measurement is described in Standard Methods (APHA [1992], Standard Method 2540 G). Standard Methods states that duplicates should agree within ± 0.5% of their average. For 75% solids, this would be ± 3.8%. For a continuous process, a time-composite sample can be taken over the course of a day, and duplicate analyses carried out on this composite. This is possible because biological activity essentially ceases at high solids content, and decomposition will not occur. Approximately seven such composites over the course of a 2-week sampling period would provide adequate sampling.

Some drying processes such as drying sludge on sand drying beds are batch processes. In such cases, it may be desirable to ascertain that the sludge meets the vector attraction reduction requirements before removing the sludge from the drying area. This can be done by taking two separate space-composites from the dried sludge, analyzing each of them in duplicate, and removing the sludge only if it meets the required solids content.

Frequently Asked Questions

How many samples should be submitted for each monitoring event for Class A pathogen tests? How many grab samples should be taken for each composite?

The 503 regulations do not specify a minimum number of samples per sampling event for Class A sludge, but it is strongly recommended that enough samples be taken to adequately represent the mass of material which is to be distributed. A minimum of seven samples, as required for Class B fecal coliform testing is recommended, but the number of samples, and the number of grab samples which each composite should represent, depends on the size of the facility and the volume of sludge product that is distributed. A sampling plan should be developed and submitted to the permitting authority for review.

Are you out of compliance for Class A if you take more than one sample, and one result is over the limit?

Yes, In order to meet Class A standards, all material must meet pathogen standards. Although Class B pathogen standards are based on a geometric mean of analytical results, geometric (or arithmetic) means are not acceptable for compliance with Class A standards. Therefore, if several samples are submitted for analysis during one monitoring event, and one sample is found to be out of compliance with Class A pathogen standards, the entire batch must be considered Class B (assuming it meets Class B standards).

For batch processes, one way to prevent one 'out of compliance' sample from affecting the classification of a large volume of finished product is to maintain smaller separate storage piles and to sample from segregated areas. For example, finished compost could be separated into piles based on when composting was completed. If one result shows non-compliance with the Class A standards, but other samples are within the Class A limits, it would be relatively simple to separate out the non-compliance material and reprocess it or distribute it as Class B material.

Continuous flow operations can reduce the probability that one outlying result will cause their process to fail by taking multiple samples over a 24-hour period and compositing the samples. The composite sample can then be analyzed in duplicate to provide more data.

Averaging lab results is allowable as a means to eliminate laboratory variability; however, all data must be reported to the permitting authority for review. For example, if a lab runs duplicate fecal coliform analyses on one sample, the results from these analyses can be averaged together for one result. This is not intended to allow facilities to rerun analyses on out-of-compliance samples in the hope of lowering average results.

Pathogen testing on our Class A sludge product has shown that we consistently reduce *Salmonella* sp. to below detectable limits, but fecal coliform levels are sometimes over 1000 MPN per gram. Should we be concerned about this? Should we be concerned if the fecal coliform level in our Class A material is occasionally as high as 990 MPN/gram?

According to the regulations, neither situation is a problem. You are required to comply with either the *Salmonella* sp. or the fecal coliform standards, not both. However, the level of fecal coliform in the product may indicate that there is incomplete pathogen destruction or some regrowth in your product, in which case you should examine your pathogen and vector attraction reduction processes to ensure that you are complying fully with the requirements and are not contaminating the product. The high fecal coliform counts may also be due to the presence of other, non-fecal coliforms in the sludge. These coliforms, which share some characteristics with fecal coliforms, may be detected in fecal coliform testing. They are particularly likely to appear in compost samples since they tend to be found in woody materials.

In addition, certain processes have been found to leave a residual population of fecal coliform which can repopulate the sludge. It is possible that testing would find fecal coliform over the Class A limits even when the pathogenic bacteria for which fecal coliform are intended to serve as indicators have been reduced below detectable levels. Composting and lime treatment are two of these processes. It is therefore recommended that if properly operated Class A facilities yield high populations of fecal coliform in finished solids that *Salmonella* sp. be used as the indicator organism for these types of facilities.

Can we distribute finished material before getting pathogen test results back? If yes, what do you do if results later show that material was not Class A?

This issue is covered extensively in Section 4.10. Sludge classification is based on the most recent available lab data, and therefore, material generated during a sampling period can be distributed before results from that sampling period are available (based on the results of the previous sampling event). However, it is recommended that materials generated during the sampling period be held on site until results are available in order to prevent a situation in which material is erroneously classified and distributed as Class A.

If composting piles are monitored for temperatures at three different points, do all three points have to meet PFRP at the same time?

All particles of sludge must undergo the PFRP time and temperature regime. For aerated static pile and in-vessel composting, the entire pile must meet the temperature requirements concurrently. If one point is found to be below the 55°C level during the temperature monitoring period, the entire pile is considered to be out of compliance, and the three consecutive day PFRP period must start over again. However, if temperatures are taken in distinct piles or cells of an in-vessel system, each section can meet the PFRP requirements separately.

Our facility often stockpiles composted sewage sludge over the winter. In the spring, we may have as much as four months' production of compost on site. How should sampling be conducted?

After material is stored on site, it must be resampled in order to determine if regrowth of pathogens has taken place. The number of samples should correspond to the time period that the stockpile represents and the mandated frequency of sampling based on the facility's size. For example, if a facility is required to sample sludge every month, and there are four months' worth of compost on site, a minimum of four samples (therefore, 4 times 7 or 28 analysis) from appropriate sections of the stockpile must be submitted. Ideally, material will be stored in segregated piles so that each month's production of compost can be sampled separately.

This applies to other long-term sludge storage such as lagoons. The number of samples taken from lagoons should be based on the time period that the lagoon(s) repre-

sent and the frequency of sampling that a facility is obligated to follow because of the rate of sludge generation.

What should we do if our process changes or expands?

Permits are granted based on particular operational parameters. Therefore, any projected changes in the operation or expanded flow should be discussed with the permitting authority before changes are made, even if you do not have a permit.

Can we be permitted for operation only during certain months?

If your operation will only meet pathogen or vector attraction reduction standards during part of the year, your permit can contain conditions which allow distribution only during these times. Permits can also be written to take ambient conditions into account; for example, some "low-impact" composting facilities are required to retain material over two summers. It may also be practical to limit storage and utilization of particular types of sludges to some seasons.

Can we combine two PSRP processes that individually do not meet the specified process requirements to produce a Class B product? Can time in extended aeration be added to digester time?

The only way to evaluate the effectiveness of pathogen reduction through a combination of two or more PSRP processes is by testing the sludge for fecal coliform density. If sufficient pathogen reduction can be demonstrated consistently, the preparer also may consider applying for a PSRP equivalency for the combined processes in order to eliminate the need for fecal coliform testing.

In general, extended aeration cannot be considered a PSRP or part of a PSRP because raw sewage is continually being added to the aerator and blending with the mixed liquor. Specific cases in which extended aeration is not subject to short-circuiting and is thought to contribute significantly to the pathogen reduction process should be evaluated by testing the resulting sludge for fecal coliform density and by the SOUR test or extended aerobic digestion one for addressing VAR requirements.

If I produce an "exceptional quality" (EQ) product and mix the product with topsoil before distribution, does the mix have to be tested for 503 compliance?

Regulations regarding "exceptional quality" material, or material which complies with the highest levels of pathogen and vector attraction reduction as well as heavy metals limits, are based on when the sludge preparer loses control of the material. If the EQ material is still within your control (i.e. on-site or owned by the preparer) when it is mixed, the new product must undergo pathogen and vector attraction reduction processes and be analyzed for Part 503 parameters including pathogens, vector attraction reduction, and heavy metals. This may be problematic for some facilities since a mix of stable compost and soil, for example, is unlikely to meet/undergo PFRP time and temperature requirements. You may have to test the mix for helminth ova and enteric viruses in order to demonstrate compliance with Class A pathogen reduction. If, however, the EQ material has left your control (i.e. is sold to a soil blender), the material falls out of the jurisdiction of the Part 503, and any subsequent blending of the material with other products is not covered by these regulations. Non-EQ materials are always subject to the Part 503, and storage or mixing of non-EQ materials with soil, yard waste, or other additives must be followed with re-testing and re-classification. The party responsible for the sludge mixing is considered a sludge preparer and is therefore subject to all Part 503 requirements.

Our sludge product meets vector attraction reduction requirements because the level of total solids in the material is greater than 75 percent. If stored material becomes wet because of rainfall, is the material still in compliance with the requirements?

The vector attraction reduction requirement stipulates that the material be processed to greater than 75 percent (or 90 percent when unstabilized solids are present) total solids. If dried sewage sludge (biosolids) is stored at your facility and becomes wet, it still meets the vector attraction reduction criteria as long as the facility has testing documentation that the biosolids were processed to ≥75 or 90 percent solids prior to the time the material became wet. It is a good management practice however to prevent dried biosolids from getting wet while it is being stored at the facility.

In the case of vector attraction reduction Option 6, it is required that the pH of the sludge be raised to ≥12 for 2 hours and ≥11.5 for 22 hours. It is not required that the sludge be maintained at the elevated pH once the material has fulfilled the vector attraction reduction requirement. However, it is important to note that the sludge which appears to be stable under the elevated conditions may become odorous and attract vectors if the pH declines. It is recommended that sludge be utilized before the pH drops below 10.5 in order to prevent odors or vector attraction which may result in a public nuisance.

Can Alternative 1 be used to demonstrate pathogen reduction for composting if the compost piles do not attain 55°C for 3 consecutive days?

Alternative 1 is based on similar time/temperature relationships as the composting process. Regime A ($D=131{,}700{,}000/10^{0.1400t}$ in which $t \geq 50°C$ and $D \geq 0.0139$ days) can apply to composting. The table below shows some points on the time/temperature curve that would comply with the regime.

Time (Days)	Temperature (°C)
0.02 (30 min)	70
0.04 (1 hour)	68
0.08 (2 hours)	66
1	58
2	56
3	55

As shown, it is theoretically possible that a compost pile could comply with Alternative 1 by reaching very high temperatures for a short period of time. **Alternative 1 is based on the assumption that all particles of sludge are attaining these temperatures uniformly.** This may be difficult in a compost pile unless the compost pile is completely enclosed and well insulted. In addition, excessive temperatures in a composting process may result in anaerobic conditions and subsequent odors.

Our facility is planning to expand next year, and we would like to implement a new process for pathogen reduction. We will submit our request for equivalency to the PEC this year, but, given the current turn around time for applications, do not expect to have equivalency granted for 2 more years. What should we do in the interim?

Depending on the class of sludge you are hoping to produce, you have two options. If you are producing a Class B sludge, you should continue to do fecal coliform testing in order to demonstrate compliance with the Class B limit of 2 million CFU or MPN per dry gram of sludge. If you are producing a Class A sludge, you could follow Alternative 4 and test the sludge product for helminth ova and enteric viruses as well as either fecal coliform or *Salmonella* sp. In either case, an application for equivalency will require data demonstrating pathogen reduction, so this data will be useful in that respect.

You may also wish, in the case of Class A sludge, to test the feed sludge for enteric virus and helminth ova. Adequate demonstration that the process reduces these pathogens on a consistent basis may qualify the process as a PFRP equivalent one (Class A, Alternative 6). You should consult with the permitting authority to determine an acceptable sampling protocol. Demonstration of helminth ova and virus reduction is difficult, particularly if the density of these pathogens in the influent is low or sporadic. The sampling program must demonstrate that actual reduction is taking place, not just that the pathogen density in the treated sludge is low. Once pathogen reduction has been sufficiently demonstrated, testing for enteric viruses and helminth ova are no longer necessary as long as the process is conducted in compliance with specified conditions for PFRP equivalency.

Our facility distributes Class B lime stabilized sludge to farmers who use the sludge on a variety of crops. Is it our responsibility to keep track of how this sludge is used?

You are required to provide the farmers with all sludge quality data as well as regulatory information which will allow them to comply with the appropriate site restrictions. The applicator, and/or the POTW, is then responsible for following the correct site and harvest restrictions. However, given that any problems with land application will most likely affect the public perception of sludge reuse and this may in turn affect your facility, it is recommended that you work closely with farmers to ensure that the regulations are being followed. In addition, the permitting authority may choose to include conditions related to site and harvest restrictions in your permit.

Is there any limit of how long Class B sludge can be stored before it is used?

Part 503 Rule defines storage as "the placement of sewage sludge: on land on which the sewage sludge remains for two years or less." It does not include placement of sewage sludge on the land for treatment. After two years the storage site is considered a final disposal one. The permitting authority may include storage conditions in your permit which mandates usage of the material while it still retains certain characteristics (moisture content) or within a certain time period. It is recommended that storage of Class B material be limited to 30 days and be conducted under similar site restrictions as usage of Class B material. For example, public contact and access to the storage site should be restricted.

If the vector attraction reduction requirements have been fulfilled under Option 6, is there any need for the sludge to remain at an elevated pH?

In the case of vector attraction reduction Option 6, it is required that the pH of the sludge be raised to ≥12 for 2 hours and ≥11.5 for 22 hours. It is not required that the sludge be maintained at the elevated pH once the material has fulfilled the vector attraction reduction requirement. However, it is important to note that sludge that appears to be stable under the elevated conditions may become odorous and attract vectors if the pH declines. It is recommended that sludge be utilized before the pH drops below 10.5 in order to prevent odors or vector attraction that may result in a public nuisance.

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Chapter 11
Role of EPA's Pathogen Equivalency Committee in Providing Guidance Under Part 503

11.1 Introduction

One way to meet the pathogen reduction requirements of the Part 503 is to treat sewage sludge in a process "equivalent to" the PFRP or PSRP processes listed in Appendix B of the Part 503 regulation (see Tables 4-2 and 5-1 for a list of these processes):

- Under Class A Alternative 6, sewage sludge that is treated in a process equivalent to PFRP and meets the Class A microbiological requirement (see Section 4.3) is considered to be a Class A biosolids with respect to pathogens (see Section 4.9).

- Under Class B Alternative 3, sewage sludge treated by a process equivalent to PSRP is considered to be a Class B biosolids with respect to pathogens (see Section 5.4).

These alternatives provide continuity with the Part 257 regulation, which required that sewage sludge be treated by a PSRP, PFRP, or equivalent process prior to use or disposal. There is one major difference between Part 257 and Part 503 with respect to equivalency. Under Part 257, a process had to be found equivalent in terms of both pathogen reduction and vector attraction reduction. Under Part 503, equivalency pertains only to pathogen reduction. However, like all Class A and B biosolids, sewage sludges treated by equivalent processes must also meet a separate vector attraction reduction requirement (see Chapter 8).

What Constitutes Equivalency?

To be equivalent, a treatment process must be able to consistently reduce pathogens to levels comparable to the reduction achieved by the listed PSRPs or PFRPs. (These levels, described in Section 11.3, are the same levels required of all Class A and B biosolids.) The process continues to be equivalent as long as it is operated under the same conditions (e.g., time, temperature, pH) that produced the required reductions. Equivalency may be site-specific; equivalency applies only to that particular operation run at that location under the specified conditions, and cannot be assumed for the same process performed at a different location, or for any modification of the process. Processes that are able to consistently produce the required pathogen reductions under the variety of conditions that may be encountered at different locations across the country may qualify for a recommendation of national equivalency (a recommendation that the process will be equivalent wherever it is operated in the United States).

Who Determines Equivalency?

The permitting authority is responsible for determining equivalency under Part 503. The permitting authority and facilities are encouraged to seek guidance from EPA's Pathogen Equivalency Committee (PEC) in making equivalency determinations. The PEC makes both site-specific and national equivalency recommendations.

What Are the Benefits of Equivalency?

A determination of equivalency can be beneficial to a facility, because it reduces the microbiological monitoring burden in exchange for greater monitoring of process parameters. For example a facility meeting Class A requirements by sampling for enteric viruses and viable helminth ova in compliance with Alternative 4 may be able to eliminate this monitoring burden if they are able to demonstrate that their treatment process adequately reduces these pathogens on a consistent basis[1]. Similarly, a facility meeting Class B Alternative 1 requirements by analyzing sewage sludge for fecal coliform may be able to eliminate the need for testing if the process is shown to reduce pathogens to the same extent as all PSRP processes. Equivalency is also beneficial to facilities which may have low cost, low technology systems capable of reducing pathogen populations. Options such as long-term storage, air drying, or low technology composting have been considered by the PEC.

Because equivalency status allows a facility to eliminate or reduce microbiological sampling, it is imperative that the treatment processes deemed equivalent undergo rigorous review to ensure that the Part 503 requirements are met. Obtaining a recommendation of equivalency necessitates a thorough examination of the process and an ex-

[1]A determination of PFRP equivalency will not reduce the monitoring required for *Salmonella* sp. or fecal coliform because all Class A biosolids, even biosolids produced by equivalent processes, must be monitored for *Salmonella* sp. or fecal coliform (see Section 4.3).

tensive sampling and monitoring program. The time needed to review an application is contingent on the completeness of the initial application. Sewage sludge preparers wishing to apply for equivalency should review this chapter carefully and discuss the issue with the regulatory authority in order to determine if equivalency is appropriate for their situation.

Figure 11-1 indicates when application for equivalency may be appropriate.

Recommendation of National Equivalency

The PEC can also recommend that a process be considered equivalent on a national level if the PEC finds that the process consistently produces the required pathogen reductions under the variety of conditions that may be encountered at different locations across the country. A recommendation of national equivalency can be useful for treatment processes that will be marketed, sold, or used at different locations in the United States. Such a recom-

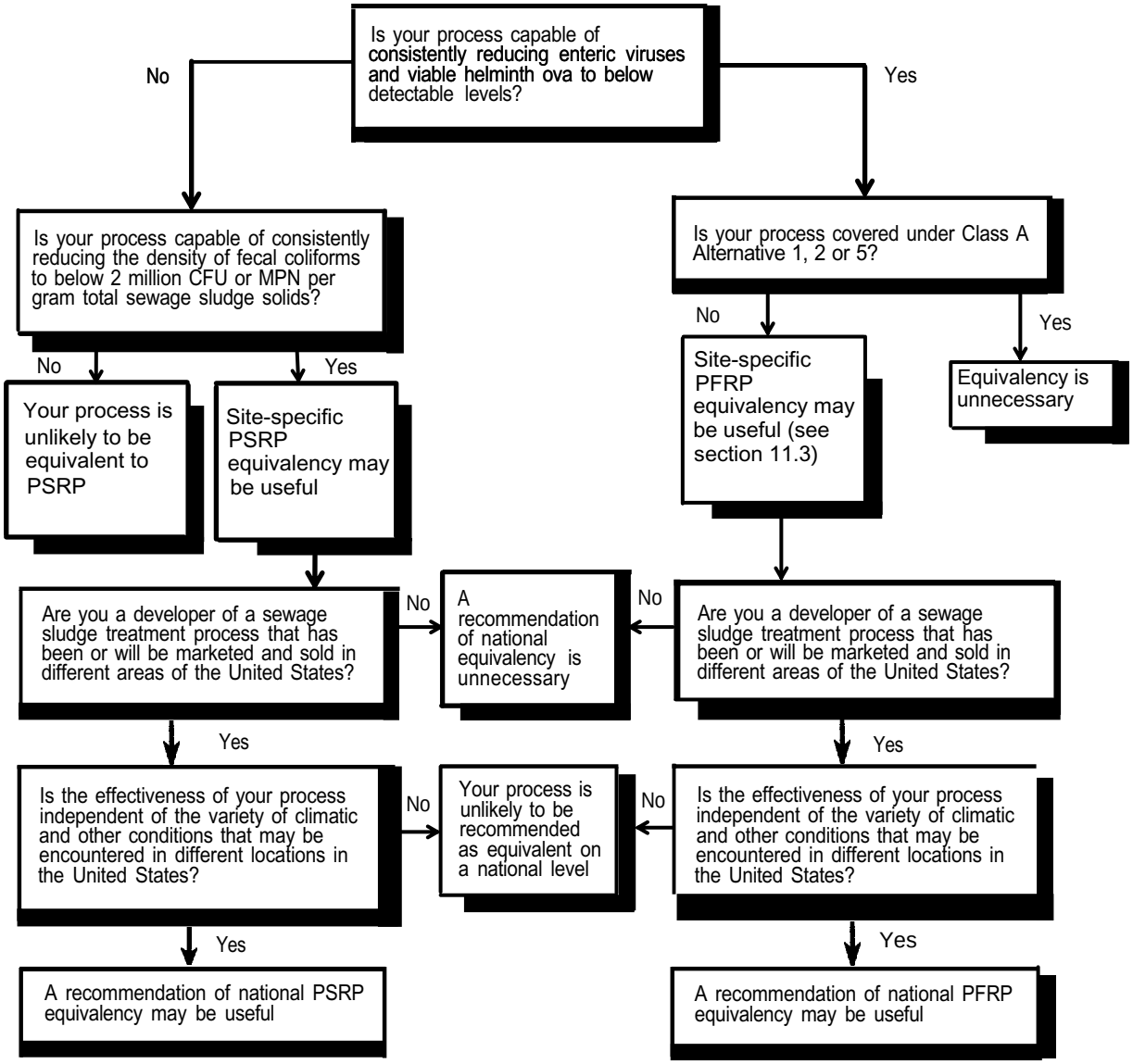

Figure 11-1. When is application for PFRP or PSRP equivalency appropriate?

Item E 000677

mendation may be useful in getting PFRP or PSRP equivalency determinations from different permitting authorities across the country.

Role of the Pathogen Equivalency Committee

The U.S. Environmental Protection Agency created the Pathogen Equivalency Committee (PEC) in 1985 to make recommendations to EPA management on applications for PSRP and PFRP equivalency under Part 257 (Whittington and Johnson, 1985). The PEC consists of approximately ten members with expertise in bacteriology, virology, parasitology, environmental engineering, medical and veterinary sciences, statistics, and sewage sludge regulations. It includes representatives from EPA's Research and Development Office, the Office of Water, and the regional offices. The 1993 memorandum included at the end of this chapter describes the role of the PEC.

Guidance and Technical Assistance on Equivalency Determinations

The PEC continues to review and make recommendations to EPA management on applications for equivalency under Part 503. Its members also provide guidance to applicants on the data necessary to determine equivalency, and to permitting authorities and members of the regulated community on issues (e.g., sampling and analysis) related to meeting the Subpart D (pathogen and vector attraction reduction) requirements of Part 503. It is not necessary to consult the PEC with regard to sampling and monitoring programs if a protocol is already approved under one of the Class A alternatives. Figure 11-2 elaborates on the role of the PEC under Part 503.

What's in This Chapter?

This chapter explains how the PEC makes equivalency recommendations and describes how to apply for PEC guidance. The guidance in this chapter may also prove useful for permitting authorities in establishing the information they will need to make equivalency determinations.

11.2 Overview of the PEC's Equivalency Recommendation Process

The first point of contact for any equivalency determination, recommendation, or other guidance is usually the permitting authority. This is the regional EPA office or the State in cases in which responsibility for the Part 503 program has been delegated to the state. Appendix A provides a list of EPA Regional and state Contacts. If PEC involvement is appropriate, the permitting authority will coordinate contact with the PEC.

The PEC considers each equivalency application on a case-by-case basis. Applicants submit information on sewage sludge characteristics, process characteristics, climate, and other factors that may affect pathogen reduction or process efficiency as described in Section 11.5. The committee evaluates this information in light of current knowledge concerning sewage sludge treatment and pathogen reduction, and recommends one of five decisions about the process or process sequence:

- It is equivalent to PFRP.
- It is not equivalent to PFRP.
- It is equivalent to PSRP.
- It is not equivalent to PSRP.
- Additional data or other information are needed.

Site-specific equivalency is relevant for many applications; to receive a recommendation for national equivalency, the applicant must demonstrate that the process will produce the desired reductions in pathogens under the variety of conditions that may be encountered at different locations across the country. Processes affected by local climatic conditions or that use materials that may vary significantly from one part of the country to another are unlikely to be recommended as equivalent on a national basis unless specific material specifications and process procedure requirements can be identified.

If the PEC recommends that a process is equivalent to a PSRP or PFRP, the operating parameters and any other conditions critical to adequate pathogen reduction are specified in the recommendation. The equivalency recommendation applies only when the process is operated under the specified conditions.

If the PEC finds that it cannot recommend equivalency, the committee provides an explanation for this finding. If additional data are needed, the committee describes what those data are and works with the permitting authority and the applicant, if necessary, to ensure that the appropriate data are gathered in an acceptable manner. The committee then reviews the revised application when the additional data are submitted.

11.3 Basis for PEC Equivalency Recommendations

As mentioned in Section 11.1, to be determined equivalent, a treatment process must consistently and reliably reduce pathogens in sewage sludge to the same levels achievable by the listed PSRPs or PFRPs. The applicant must identify the process operating parameters (e.g., time, temperature, pH) that result in these reductions.

PFRP Equivalency

To be equivalent to a PFRP, a treatment process must be able to consistently reduce sewage sludge pathogens to below detectable limits. For purposes of equivalency, the PEC is concerned only with the ability of a process to demonstrate that enteric viruses and viable helminth ova have been reduced to below detectable limits. This is because Part 503 requires ongoing monitoring of all Class A biosolids for fecal coliform or *Salmonella* sp. (see Section

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON. D.C. 20460

JUN 15 1993

OFFICE OF WATER

MEMORANDUM

SUBJECT: The Role of the Pathogen Equivalency Committee Under the Part 503 ***Standards for the Use or Disposal of Sewage Sludge***

FROM: **Michael B. Cook, Director**
Office of Wastewater Enforcement & Compliance

James A. Hanlon, Acting Director
Office of Science & Technology

TO: Water Division Directors
Regions I - X

PURPOSE

This memorandum explains the role of the **Pathogen Equivalency Committee (PEC)** in providing technical assistance and recommendations regarding pathogen reduction equivalency in implementing the Part 503 ***Standards for the Use or Disposal of Sewage.*** The PEC is an Agency resource available to assist your permit writers and regulated authorities. This information should be sent to your Regional Sludge Coordinators, Municipal Construction Managers, Permits and Enforcement Coordinators, and Solid Waste Offices, State Sludge Management Agencies and others concerned with sewage sludge management.

BACKGROUND

The PEC Under Part 257

The Criteria for Classification of Solid Waste Facilities and Practices (44 FR 53438, September 13, 1979), in 40 CFR Part 257 required that sewage sludge disposed on the land be treated by either a ***Process to Significantly Reduce Pathogens*** **(PSRP)** or a ***Process to Further Reduce Pathogens (PFRP).*** A list of PSRPs and PFRPs were included in Appendix II to Part 257.

In 1985, the PEC was formed to provide technical assistance and recommendations on whether sewage sludge treatment processes not included in Appendix II to Part 257 were equivalent to PSRP or PFRP. Under Part 257, the PEC provided technical assistance to both the permitting authority and to members of the regulated

Figure 11-2. Role of the PEC under Part 503.

A series of options are provided in the Part 503 regulation for meeting the specific requirements for the two classes of pathogen reduction. One of the Class A alternatives is to treat the sewage sludge by a process equivalent to a PFRP and one of the Class B alternatives is to treat the sewage sludge by a process equivalent to a PSRP. The permitting authority must decide whether a process is equivalent to a PFRP or a PSRP, which is the same approach used under Part 257.

THE PEC UNDER 503

Part 503 provides specific criteria and procedures for evaluating bacterial indicators (Fecal coliforms and ***Salmonella*** sp.), enteric virus and viable helminth ova as well as vector attraction reduction. The PEC will continue to support the permitting authority and members of the regulated community under the new Part 503 regulation in evaluating equivalency situations and providing technical assistance in matters such as sampling and analysis. Specifically the PEC:

- will continue to provide technical assistance to the permitting authority and regulated community, including recommendations to the permitting authority about process equivalency. The PEC also will make both site-specific and national (i.e., a process that is equivalent anywhere in the United States where it is installed and operated) recommendations on *process* equivalency .

- will submit recommendations on process equivalency to the Director, Health and Ecological Criteria Division, Office of Science and Technology, who will review those recommendations and then notify the applicant and appropriate permitting authorities of our recommendation.

For site-specific recommendations, requests for **PEC** review or assistance should be made through the appropriate Federal permitting authority (e.g., the State sludge regulatory authority for delegated programs or the EPA Regional Sludge Coordinator for non-delegated programs). For national recommendations, requests for **PEC** review or assistance can also be made through the Director, Health and Ecological Criteria Division (4304T), Office of Science & Technology, **1200 Pennsylvania Avenue, Washington, DC 20460** or directly to the PEC Chairman. The current **PEC** Chairman is: Dr. James *E.* Smith, Jr., U.S. EPA, NRMRL, (National Risk Management Research Laboratory) 26 W Martin Luther King Dr., Cincinnati, OH 45268 (Tele: 513/569-7355).

Additional information and guidance to supplement the pathogen reduction requirements of Part 503 and the procedures to use to reach the **PEC** and the assistance provided by the PEC is provided in "Control of Pathogens and Vector Attraction in Sewage

Figure 11-2. Role of the PEC under Part 503 (continued).

community. The PEC membership has included representatives from the Office of Research & Development (ORD), Office of Wastewater Enforcement & Compliance (OWEC), and the Office of Science & Technology (OST) with extensive experience in microbiology, sludge process engineering, statistics and regulatory issues. The PEC recommendations regarding the equivalency of processes were forwarded to the Office of Science and Technology, which notified applicants about the PEC's recommendations. Final decisions on equivalency were made by the permitting authority.

The Part 503 Sewage Sludge Standards

The 40 CFR Part 503 Standards for the Use or Disposal of Sewage Sludge were published in the **Federal Register** on February 19, 1993 (58 **FR 9248)** under the authority of section **405** of the Clean Water Act, as amended. Part 503 establishes requirements for sewage sludge applied to the land, placed on a surface disposal site, or fired in a sewage sludge incinerator. Along with the 40 CFR Part 258 Municipal Solid Waste (MSW) Landfill Regulation (56 **FR** 50978, October 9, 1991), which established requirements for materials placed in MSW landfills, the Part 503 requirements for land application of sewage sludge and placement of sewage sludge on a surface disposal site, replaces the requirements for those practices, including the requirement to treat the sewage sludge in either a PSRP or a PFRP, in Part 257.

The Part 503 regulation addresses disease-causing organisms (i.e., pathogens) in sewage sludge by establishing requirements for sewage sludge to be classified either as Class A or Class B with respect to pathogens as an operational standard. Class A requirements are met by treating the sewage sludge to reduce pathogens to below detectable limits, while the Class B requirements rely on a combination of treatment and site restrictions to reduce pathogens. The site restrictions prevent exposure to the pathogens and rely on Natural Environmental processes to reduce the pathogens in the sewage sludge to below detectable levels. In addition to pathogen reduction, a vector attraction reduction requirement has to be met when sewage sludge is applied to the land or placed on a surface disposal site.

Vector attraction reduction requirements are imposed under Part 503 to reduce the potential for spreading of infectious disease agents by vectors (i.e., flies, rodents, and birds). A series of alternative methods for meeting the vector attraction reduction requirement are provided in the rule.

All sewage sludges that are to be sold or given away in a bag or other container for land application, or applied to lawns or home gardens must meet Class A pathogen control and vector attraction reduction requirements. All sewage sludge intended for land application must meet at least the Class B pathogen control and vector attraction reduction requirements. Surface disposal of sewage sludge reguires that Class A or Class B requirements, along with one of the vector attraction reduction practices, be met unless the sewage sludge is covered with soil or other material daily.

Figure 11-2. Role of the PEC under Part 503 (continued).

Sludge" (EPA 625/R-92/013), which will-be updated from **time to time by the PEC. This document is an update of the 1989 document** "Control of Pathogens in Municipal Wastewatsr Sludge" **(EPA/625/l0-89/006),** and is available from CERI.

If there are any questions about this memorandum, **please contact Bob Bastian *from*** OWM **at** 202/564-0635 **or *Dr.* Smith from NRMRL at 513-569-7355..**

Figure 11-2. Role of the PEC under Part 503 (continued).

4.3) to ensure that *Salmonella* sp. are reduced to below detectable limits (i.e., to less than 3 MPN per 4 grams total solids sewage sludge [dry weight basis]) and that growth of pathogenic bacteria has not occurred. Thus, to demonstrate PFRP equivalency, the treatment process must be able to consistently show that enteric viruses and viable helminth ova are below the detectable limits, shown below:

There are two ways these reductions can be demonstrated:

- Direct monitoring of treated and untreated sewage sludge for enteric viruses and viable helminth ova
- Comparison of the operating conditions of the process with the operating conditions of one of the listed PFRPs.

The process comparison approach to demonstrating equivalency is discussed in Section 11.4.

PSRP Equivalency

To be equivalent to PSRPs, a process must consistently reduce the density of pathogenic viruses and bacteria (number per gram of biosolids (dry weight basis)) in mixed sludge from a conventional plant by equal to or greater than 1 log (base 10). Data indicate that, for conventional biological and chemical treatment processes (e.g. ,digestion and lime treatment) a reduction of 1 log (base 10) in pathogenic virus and bacteria density correlates with a reduction of 1 to 2 logs (base 10) in the density of indicator organisms (Farrell et al., 1985, Farrah et al., 1986). On this basis a 2-log (base 10) reduction in fecal indicator density is accepted as satisfying the requirement to reduce pathogen density by 1 log (base 10) for these types of processes (EPA, 1989c). Specifically, the applicant must demonstrate a 2-log (base 10) reduction (number per gram of biosolids (dry weight basis)) in fecal coliforms.

There is substantial data to indicate that sludge produced by conventional wastewater treatment and anaerobic digestion at 35°C for more than 15 days contains fecal coliforms at average log (base 10) densities (number per gram of biosolids (dry weight basis)) of less than 6.0 (Farrell, 1988). Thus, for processes or combinations of processes that do not depart radically from conventional treatment (gravity thickening, anaerobic or aerobic biological treatment, dewatering, air drying and storage of liquid or sludge cake), or for any process where there is a demonstrated correlation between pathogenic bacteria and virus reduction and indicator organisms reduction, the PEC accepts an average log (base 10) density (no./g. TSS) of fecal coliforms and fecal streptococci of less than 6.0 in the treated sludge as indicating adequate viral and bacterial pathogen reduction. (The average log density is the log of the geometric mean of the samples taken. Calculations of average log density should be based on data from approximately nine sludge samples to account for the natural variability and the variability of the microbiological tests.)

The data submitted must be scientifically sound in order to ensure that the process can reliably produce the required reductions under all the different types of conditions that the process may operate. For example, for processes that may be affected by daily and seasonal variations in the weather, four or more sets of samples taken at different times of the year and during different precipitation conditions (including worst-case conditions) will be needed to make this demonstration.

For national equivalency recommendations, the demonstration must show that the process can reliably produce the desired reductions under the variety of climatic and other conditions that may be encountered at different locations in the United States.

11.4 Guidance on Demonstrating Equivalency for PEC Recommendations

Many of the applicants seeking equivalency do not receive a recommendation from the PEC. The most common reason for this is incomplete applications or insufficient microbiological data. The review process can be both lengthy and expensive, but it can be expedited and simplified if the applicant is aware of the type of data that will be required for the review and submits a complete plan for demonstrating equivalency in a timely fashion.

As described below, equivalency can be demonstrated in one of two ways:

- By comparing operating conditions to existing PFRPs or PSRPs.
- By providing performance and microbiological data.

Comparison to Operating Conditions for Existing PSRPs or PFRPs

If a process is similar to a PSRP or PFRP described in the Part 503 regulation (see Tables 4-2 and 5-1), it may be possible to demonstrate equivalency by providing performance data showing that the process consistently meets or exceeds the conditions specified in the regulation. For example, a process that consistently produces a pH of 12 after 2 hours of contact (the PSRP condition required in Part 503 for lime stabilization) but uses a substance other than lime to raise pH could possibly qualify as a PSRP equivalent. In such cases, microbiological data may not be necessary to demonstrate equivalency.

Process-Specific Performance Data and Microbiologic Data

In all other cases, both performance data and microbiological data (listed below) are needed to demonstrate process equivalency:

- A description of the various parameters (e.g., sewage sludge characteristics, process operating parameters, climatic factors) that influence the microbiological char-

acteristics of the treated sewage sludge (see Section 11.5 for more detail on relevant parameters).

- Sampling and analytical data to demonstrate that the process has reduced microbes to the required levels (see Section 11.3 for a description of levels).
- Discussion of the ability of the treatment process to consistently operate within the parameters necessary to achieve the appropriate reductions.

Sampling and Analytical Methods

Sewage sludge should be sampled using accepted, state-of-the-art techniques for sampling and analyzed using the methods required by Part 503 (see Chapter 9). The sampling program should demonstrate the quality of the sewage sludge that will be produced under a range of conditions. Therefore, sampling events should include a sufficient number of samples to adequately represent product quality, and sampling events should be designed to reflect how the operation might be affected by changes in conditions including climatic and sewage sludge quality variability.

Data Quality

The quality of the data provided is an important factor in EPA's equivalency recommendation. The following steps can help ensure data quality:

- Use of accepted, state-of-the-art sampling techniques (see Chapter 9).
- Obtaining samples that are representative of the expected variation in sewage sludge quality.
- Developing and following quality assurance procedures for sampling.
- Using an independent, experienced laboratory to perform the analysis.

Since processes differ widely in their nature, effects, and processing sequences, the experimental plan to demonstrate that the process meets the requirements for PSRP or PFRP equivalency should be tailored to the process. The permitting authority will evaluate the study design, the accuracy of the data, and the adequacy of the results for supporting the conclusions of the study.

Can Pilot-Scale Data Be Submitted?

Operation of the process at a full-scale facility is desirable. However, if a pilot-scale operation truly simulates full-scale operation, testing on this reduced scale is possible. The permitting authority and the PEC should be contacted to discuss this possibility before testing is initiated. In such cases, it is important to indicate that the data were obtained from a pilot-scale operation, and to discuss why and to what extent this simulates full-scale operation. Any data available from existing full-scale operations would be useful.

The conditions of the pilot-scale operation should be at least as severe as those of a full-scale operation. The arrangement of process steps, degree of mixing, nature of the flow, vessel sizing, proportion of chemicals used, etc. are all part of the requirement. Any substantial degree of departure in the process parameters of the full-scale operation that might reduce the severity of the procedure will invalidate any PEC equivalency recommendations and permitting authority equivalency determinations and will require a retest under the new condition.

11.5 Guidance on Application for Equivalency Recommendations

The following outline and instructions are provided as guidance for preparing applications for equivalency recommendations by EPA's Pathogen Equivalency Committee.

Summary Fact Sheet

The application should include a brief fact sheet that summarizes key information about the process. Any important additional facts should also be included.

Introduction

The full name of the treatment works and the treatment process should be provided. The application should indicate whether it is for recommendation of:

- PSRP or PFRP equivalency.
- Site-specific or national equivalency.

Process Description

The type of sewage sludge used in the process should be described, as well as other materials used in the process. Specifications for these materials should be provided as appropriate. Any terms used should be defined.

The process should be broken down into key steps and graphically displayed in a quantified flow diagram of the wastewater and sewage sludge treatment processes. Details of the wastewater treatment process should be provided and the application should precisely define which steps constitute the beginning and end of sewage sludge treatment.[2] The earliest point at which sewage sludge treatment can be defined as beginning is the point at which the sewage sludge is collected from the wastewater treatment process. Sufficient information should be provided for a mass balance calculation (i.e., actual or relative volumetric flows and solids concentration in and out of all streams, additive rates for bulking agents or other additives). A description of process parameters should be provided for each step of the process, giving typical ranges and mean values where appropriate. The specific process parameters that should be discussed will depend on the type of process and should include any of the following that affect pathogen reduction or process reliability:

Sewage Sludge Characteristics

- Total and volatile solids content of sewage sludge before and after treatment

[2] When defining which steps constitute the "treatment process," bear in mind that all steps included as part of a process equivalent to PSRP or PFRP must be continually operating according to the specifications and conditions that are critical to pathogen reduction.

- Proportion and type of additives (diluents) in sewage sludge
- Chemical characteristics (as they affect pathogen survival/destruction, e.g., pH)
- Type(s) of sewage sludge (unstabilized vs. stabilized, primary vs. secondary, etc.)
- Wastewater treatment process performance data (as they affect sewage sludge type, sewage sludge age, etc.)
- Quantity of treated sewage sludge
- Sewage sludge age
- Sewage sludge detention time

Process Characteristics

- Scale of the system (e.g., reactor size, flow rate)
- Sewage sludge feed process (e.g., batch vs. continuous)
- Organic loading rate (e.g., kg volatile solids/cubic meter/day)
- Operating temperature(s) (including maximum, minimum, and mean temperatures)
- Operating pressure(s) if greater than ambient
- Type of chemical additives and their loading rate
- Mixing
- Aerobic vs. anaerobic
- Duration/frequency of aeration
- Dissolved oxygen level maintained
- Residence/detention time
- Depth of sewage sludge
- Mixing procedures
- Duration and type of storage (e.g., aerated vs. nonaerated)

Climate

- Ambient seasonal temperature range
- Precipitation
- Humidity

The application should include a description of how the process parameters are monitored including information on monitoring equipment. Process uniformity and reliability should also be addressed. Actual monitoring data should be provided whenever appropriate.

Description of Treated Sewage Sludge

The type of treated sewage sludge (biosolids) should be described, as well as the sewage sludge monitoring program for pathogens (if there is one). How and when are samples taken? For what parameters are the samples analyzed? What protocols are used for analysis? What are the results? How long has this program been in operation?

Sampling Technique(s)

The PEC will evaluate the representativeness of the samples and the adequacy of the sampling techniques. For a recommendation of national PFRP equivalency, samples of untreated and treated sewage sludge are usually needed (see Sections 11.3, 4.6, and 10.4). The sampling points should correspond to the beginning and end of the treatment process as defined previously under Process Description above. Chapters 9 and 10 provide guidance on sampling. Samples should be representative of the sewage sludge in terms of location of collection within the sewage sludge pile or batch. The samples taken should include samples from treatment under the least favorable operating conditions that are likely to occur (e.g., wintertime). Information should be provided on:

- Where the samples were collected from within the sewage sludge mass. (If samples were taken from a pile, include a schematic of the pile and indicate where the subsamples were taken.)
- Date and time the samples were collected. Discuss how this timing relates to important process parameters (e.g., turning over, beginning of drying).
- Sampling method used.
- How any composite samples were compiled.
- Total solids of each sample.
- Ambient temperature at time of sampling.
- Temperature of sample at time of sampling.
- Sample handling, preservation, packaging, and transportation procedures.
- The amount of time that elapsed between sampling and analysis.

Analytical Methods

Identify the analytical techniques used and the laboratory(ies) performing the analysis.

Analytical Results

The analytical results should be summarized, preferably in tabular form. A discussion of the results and a summary of major conclusions should be provided. Where appropriate, the results should be graphically displayed. Copies of original data should be provided in an appendix.

Quality Assurance

The application should describe how the quality of the analytical data has been ensured. Subjects appropriate to address are: why the samples are representative; the quality assurance program; the qualifications of the in-house or contract laboratory used; and the rationale for selecting the sampling technique.

Rationale for Why Process Should Be Determined Equivalent

Finally, the application should describe why, in the applicant's opinion, the process qualifies for PSRP or PFRP equivalency. For example, it may be appropriate to describe or review particular aspects of the process that contribute to pathogen reduction, and why the process is expected to operate consistently. Complete references should be provided for any data cited. Applications for a recommendation of national equivalency should discuss why the process effectiveness is expected to be independent of the location of operation.

Appendices

A copy of the complete laboratory report(s) for any sampling and analytical data should be attached as an appendix. Any important supporting literature references should also be included as appendices.

11.6 Pathogen Equivalency Committee Recommendations

Tables 11.1 and 11.2 list processes that the PEC has recommended for use nationally as equivalent to PSRP or PFRP, respectively. Space in the tables limits the detail given for each of the processes. As such individuals having an interest in any of the processes are encouraged to contact either the PEC or the applicant for greater detail on how the process must be operated to be PSRP or PFRP, respectively.

Table 11-1. Processes Recommended as Equivalent to PSRP

Applicant	Process	Process Description
N-Viro Energy Systems, Ltd., Toledo, Ohio	Alkaline Addition to achieve *Lime Stabilization*	Use of cement kiln dust and lime kiln dust (instead of lime) to treat sludge by raising the pH. Sufficient lime or kiln dust is added to sludge to produce a pH of 12 for at least 12 hours of contact
Synox Corp., Jacksonville, FL	OxyOzonation	Batch process where sludge is acidified to pH 3.0 by sulfuric acid; exposed to 1 lb. Ozone/1000 gallons of treated sludge under 60 psig pressure for 60 minutes; depressurized; mixed with 100 mg/l of sodium nitrite and held for ≥2 hours; and stored at ≤ pH 3.5. Limitations imposed were for total solids to be ≤ 4%; temperature must be ≥20°C; and total solids must be ≤ 6.2% before nitrite addition.

11.7 Current Issues

The PEC is continuing to develop methodologies and protocols for the monitoring of pathogen and vector attraction reduction. Current issues include:

- Establishment of a vector attraction reduction equivalency process
- Conducting round robin laboratory testing for pathogens in sewage sludge and biosolids

In addition, the PEC continues to recommend interpretations of the Part 503 with regard to the sampling and monitoring requirements set forth in this document.

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Table 11-2. Processes Recommended as Equivalent to PFRP

Applicant	Process	Process Description
CBI Walker, Inc., Aurora, Illinois	ATP™ Two Stage Sludge Stabilization Process	Sludge is introduced intermittently into a vessel, amounting to 5 to 20% of its volume, where it is heated by both external heat exchange and by the bio-oxidation which results from vigorously mixing air with the sludge (pasteurized) and has a nominal residence time of 18 to 24 hours. Time between feedings of unprocessed sludge can range from 1.2 (@ ~ 65°C) to 4.5 (@ > 60°C) hours. Exiting sludge is heat exchanged with incoming unprocessed sludge. Thus the sludge is cooled before it enters a mesophilic digester. Time and temperature in the first vessel are critical and controlled by the equation below for sludges of ≤ 7% solids, times ≥ 30 minutes, and temperatures ≥50°C. Operations of the reaction vessel during the time-temperature period must be either plug flow or batch mode. $D = 50{,}070{,}000 / 10^{0.1400t}$ where D = time required in days; t = temperature in °C
Fuchs Gas und Wassertechnik, Gmbh, Mayen, Germany	Autothermal Thermophilic Aerobic Digestion	ATAD is a two-stage, autothermal aerobic digestion process. The stages are of equal volume. Treated sludge amounting to 1/3 the volume of a stage is removed every 24 hours from the second stage as product. An equal amount then is taken from the first stage and fed to the second stage. Similarly, an equal amount of untreated sludge is then fed to the first stage. In the 24-hour period between feedings, the sludge in both stages is vigorously agitated and contacted with air. Bio-oxidation takes place and the heat produced increases the temperature. Sludge temperature in the reactors averages between 56 and 57°C for ≥ a 16-hour period, while the overall hydraulic residence time is 6 days.
International Process Systems, Inc., Glastonbury, Connecticut	Type of Composting Process	40 CFR 503.32(a)(7) states that when the within-vessel composting method is employed, the sludge is to be maintained at operating conditions of 55°C or greater for three days, for the product to be PFRP. IPS Process' operation is to further be controlled so that the composting mass passes through a zone in the reactor in which the temperature of the compost is at least 55°C throughout the entire zone, and the time of contact in this zone is at least three days.
K-F Environmental Technologies, Inc., Pompton Plains, NJ	Sludge Drying	Sludge is heated to a minimum temperature of 100°C and indirectly dried to below 10% moisture using oil as a heat transfer medium. The final discharge product has exceeded a temperature of 80°C and is granular dry pellet that can be land applied, incinerated or landfilled. In addition the following conditions must be met: *Dewatered sludge cake is dried by direct or indirect contact with hot gases, and moisture content is reduced to 10% or lower. Sludge particles reach temperatures well in excess of 80°C or the* wet *bulb* temperature *of the gas stream in contact with* the *sludge at the point where it leaves the dryer is in excess of 80°C.*
Lyonnaise des Eaux, Le Pecz-Sur-Seine, France	Two-Phase Thermo-Meso Feed Sequencing Anaerobic Digestion*	Sewage sludge is treated in the absence of air in an acidogenic thermophilic reactor and a mesophilic methanogenic reactor connected in series. The mean cell residence time shall be at least 2.1 days (± 0.05 d) in the acidogenic thermophilic reactor followed by 10.5 days (± 0.3 d) in the mesophilic methanogenic reactor. Feeding of each digester shall be intermittent and occurring 4 times per day every 6 hours. The mesophilic methanogenic reactor shall be fed in priority from the acidogenic thermophilic reactor. Between two consecutive feedings temperature inside the acidogenic thermophilic reactor should be between 49°C and 55°C with 55°C maintained during at least 3 hours. Temperature inside the mesophilic methanogenic reactor shall be constant and at least 37°C.
ATW, Inc. Santa Barbara, CA	Alkaline Stabilization	Manchak process uses quicklime to simultaneously stabilize and pasteurize biosolids. Quicklime, or a combination of quicklime and flyash, is mixed with dewatered biosolids at a predetermined rate in a confined space. An instant exothermic reaction is created in the product wherein the pH is raised in excess of 12 after two hours of contact, in addition, the temperature is raised in excess of 70°C for > 30 minutes.

(continued)

Table 11-2. Continued.

Applicant	Process	Process Description
N-Viro Energy Systems, Ltd., Toledo, OH	Advanced Alkaline stabilization with subsequent accelerated drying	**Alternative 1:** Fine alkaline materials (cement kiln dust, lime kiln dust, quicklime fines, pulverized lime, or hydrated lime) are uniformly mixed by mechanical or aeration mixing into liquid or dewatered sludge to raise the pH to >12 for 7 days. If the resulting sludge is liquid, it is dewatered. The stabilized sludge cake is then air dried (while pH remains >12 for ≥ 7 days) for >30 days and until the cake is ≥ 65% solids. A solids concentration of ≥ 60% is achieved before the pH drops below 12. The mean temperature of the air surrounding the pile is > 5°C (41°F) for the first 7 days. **Alternative 2:** Fine alkaline materials (cement kiln dust, lime kiln dust, quicklime fines, pulverized lime, or hydrated lime) are uniformly mixed by mechanical or aeration mixing into liquid or dewater sludge to raise the pH to > 12 for ≥ 72 hours. If the resulting sludge is liquid, it is dewatered. The sludge cake is then heated, while the pH > 12, using exothermic reactions or other thermal processes to achieve temperatures of ≥ 52°C (126°F) throughout the sludge for ≥ 12 hours. The stabilized sludge is then air dried (while pH > 12 for ≥ 3 days) to ≥ 50% solids.
Synox Corp., Jacksonville, FL	OxyOzonation	Operation occurs in a batch mode and under the following conditions: sludge temperature of > 20°C; sludge solids of < 6% TSS; pH during ozonation of 2.5 - 3.1 and during nitrite contact of 2.6 - 3.5; sludge ORP after ozonation of > 100 mV; nitrite dose of ≥ 670 mg (NO_2)/1 sludge or 16 g (NO_2)/kg sludge solids, whichever is greater is to be mixed into the ozonated sludge. Ozonation takes place in a pressure vessel operating at 60 psig.
Ultraclear, Marlboro, NJ	Microbiological Conditioning and Drying Process (MVCD)	In this process, sludge cake passes through several aerobic-biological type stages (Composting is an example) where different temperatures are maintained for varying times. Stage 1 occurs at 35°C for 7-9 hours; stage 2 occurs at 35-45°C for 8-10 hours; stage 3 occurs at 45-65°C for 7-10 hours; and the last stage is pasteurization at 70-80°C for 7-10 hours. In addition one of two conditions described below must be met: **Condition 1:** *Dewatered sludge cake is dried by direct or indirect contact with hot gases, and moisture content is reduced to 10% or lower. Sludge particles reach temperatures we// in excess of 80°C or the wet bulb temperature of the gas stream in contact with the sludge at the point where it leaves the dryer is in excess of 80°C. OR* **Condition** *2:* A) *Using the within-vessel, static aerated pile, or windrow composting methods, the sludge is maintained at minimum operating conditions of 40°C for 5 days. For 4 hours during the period the temperature exceeds 55°C; {Note: another PSRP-type process should be substituted for that* of *composting};* and B) *Sludge is maintained for at least 30 minutes at a minimum temperature of 70°C.*

*Currently a site specific recommendation. Undergoing further study for national equivalency.

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Appendix B
Subpart D of the Part 503 Regulation

[Code of Federal Regulations]
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TITLE 40 - PROTECTION OF ENVIRONMENT

CHAPTER I - ENVIRONMENTAL PROTECTION AGENCY (Continued)

PART 503 - STANDARDS FOR THE USE OR DISPOSAL OF SEWAGE SLUDGE-Table of Contents

Subpart D-Pathogens and Vector Attraction Reduction

Sec. 503.30 Scope.

(a) This subpart contains the requirements for a sewage sludge to be classified either Class A or Class B with respect to pathogens.

(b) This subpart contains the site restrictions for land on which a Class B sewage sludge is applied.

(c) This subpart contains the pathogen requirements for domestic septage applied to agricultural land, forest, or a reclamation site.

(d) This subpart contains alternative vector attraction reduction requirements for sewage sludge that is applied to the land or placed on a surface disposal site.

Sec. 503.31 Special definitions.

(a) Aerobic digestion is the biochemical decomposition of organic matter in sewage sludge into carbon dioxide and water by microorganisms in the presence of air.

(b) Anaerobic digestion is the biochemical decomposition of organic matter in sewage sludge into methane gas and carbon dioxide by microorganisms in the absence of air.

(c) Density of microorganisms is the number of microorganisms per unit mass of total solids (dry weight) in the sewage sludge.

(d) Land with a high potential for public exposure is land that the public uses frequently. This includes, but is not limited to, a public contact site and a reclamation site located in a populated area (e.g., a construction site located in a city).

(e) Land with a low potential for public exposure is land that the public uses infrequently. This includes, but is not limited to, agricultural land, forest, and a reclamation site located in an unpopulated area (e.g., a strip mine located in a rural area).

(f) Pathogenic organisms are disease-causing organisms. These include, but are not limited to, certain bacteria, protozoa, viruses, and viable helminth ova.

(g) pH means the logarithm of the reciprocal of the hydrogen ion concentration.

(h) Specific oxygen uptake rate (SOUR) is the mass of oxygen consumed per unit time per unit mass of total solids (dry weight basis) in the sewage sludge.

(i) Total solids are the materials in sewage sludge that remain as residue when the sewage sludge is dried at 103 to 105 degrees Celsius.

(j) Unstabilized solids are organic materials in sewage sludge that have not been treated in either an aerobic or anaerobic treatment process.

(k) Vector attraction is the characteristic of sewage sludge that attracts rodents, flies, mosquitos, or other organisms capable of transporting infectious agents.

(l) Volatile solids is the amount of the total solids in sewage sludge lost when the sewage sludge is combusted at 550 degrees Celsius in the presence of excess air.

Sec. 503.32 Pathogens.

(a) Sewage sludge-Class A. (1) The requirement in Sec. 503.32(a)(2) and the requirements in either Sec. 503.32(a)(3), (a)(4), (a)(5), (a)(6) (a)(7) or (a)(8) shall be met for a sewage sludge to be classified Class A with respect to pathogens.

(2) The Class A pathogen requirements in Sec. 503.32 (a)(3) through (a)(8) shall be met either prior to meeting or at the same time the vector attraction reduction requirements in Sec. 503.33, except the vector attraction reduction requirements in Sec. 503.33 (b)(6) through (b)(8), are met.

(3) Class A-Alternative 1. (i) Either the density of fecal coliform in the sewage sludge shall be less than 1000 Most Probable Number per gram of total solids (dry weight basis), or the density of *Salmonella* sp. bacteria in the sewage sludge shall be less than three Most Probable Number per four grams of total solids (dry weight basis) at the time the sewage sludge is used or disposed; at the time the sewage sludge is prepared for sale or give away in a bag or other container for application to the land; or at the time the sewage sludge or material derived from sewage sludge is prepared to meet the requirements in Sec. 503.10 (b), (c), (e), or (f).

(ii) The temperature of the sewage sludge that is used or disposed shall be maintained at a specific value for a period of time.

(A) When the percent solids of the sewage sludge is seven percent or higher, the temperature of the sewage sludge shall be 50 degrees Celsius or higher; the time period shall be 20 minutes or longer; and the temperature and time period shall be determined using equation (2), except when small particles of sewage sludge are heated by either warmed gases or an immiscible liquid.

$$D = \frac{131{,}700{,}000}{10^{0.1400t}} \qquad \text{Eq. (2)}$$

Where,
D=time in days.
t=temperature in degrees Celsius.

(B) When the percent solids of the sewage sludge is seven percent or higher and small particles of sewage sludge are heated by either warmed gases or an immiscible liquid, the temperature of the sewage sludge shall be 50 degrees Celsius or higher; the time period shall be 15 seconds or longer; and the temperature and time period shall be determined using equation (2).

(C) When the percent solids of the sewage sludge is less than seven percent and the time period is at least 15 seconds, but less than 30 minutes, the temperature and time period shall be determined using equation (2).

(D) When the percent solids of the sewage sludge is less than seven percent; the temperature of the sewage sludge is 50 degrees Celsius or higher; and the time period is 30 minutes or longer, the temperature and time period shall be determined using equation (3).

$$D = \frac{50{,}070{,}000}{10^{0.1400t}} \qquad \text{Eq.3}$$

Where,
D=time in days.
t=temperature in degrees Celsius.

(4) Class A - Alternative 2. (i) Either the density of fecal coliform in the sewage sludge shall be less than 1000 Most Probable Number per gram of total solids (dry weight basis), or the density of *Salmonella* sp. bacteria in the sewage sludge shall be less than three Most Probable Number per four grams of total solids (dry weight basis) at the time the sewage sludge is used or disposed; at the time the sewage sludge is prepared for sale or give away in a bag or other container for application to the land; or at the time the sewage sludge or material derived from sewage sludge is prepared to meet the requirements in Sec. 503.10 (b), (c), (e), or (f).

(ii)(A) The pH of the sewage sludge that is used or disposed shall be raised to above 12 and shall remain above 12 for 72 hours.

(B) The temperature of the sewage sludge shall be above 52 degrees Celsius for 12 hours or longer during the period that the pH of the sewage sludge is above 12.

(C) At the end of the 72 hour period during which the pH of the sewage sludge is above 12, the sewage sludge shall be air dried to achieve a percent solids in the sewage sludge greater than 50 percent.

(5) Class A - Alternative 3. (i) Either the density of fecal coliform in the sewage sludge shall be less than 1000 Most Probable Number per gram of total solids (dry weight basis), or the density of *Salmonella* sp. bacteria in sewage sludge shall be less than three Most Probable Number per four grams of total solids (dry weight basis) at the time the sewage sludge is used or disposed; at the time the sewage sludge is prepared for sale or give away in a bag or other container for application to the land; or at the time the sewage sludge or material derived from sewage sludge is prepared to meet the requirements in Sec. 503.10 (b), (c), (e), or (f).

(ii)(A) The sewage sludge shall be analyzed prior to pathogen treatment to determine whether the sewage sludge contains enteric viruses.

(B) When the density of enteric viruses in the sewage sludge prior to pathogen treatment is less than one Plaque-forming Unit per four grams of total solids (dry weight basis), the sewage sludge is Class A with respect to enteric viruses until the next monitoring episode for the sewage sludge.

(C) When the density of enteric viruses in the sewage sludge prior to pathogen treatment is equal to or greater

than one Plaque-forming Unit per four grams of total solids (dry weight basis), the sewage sludge is Class A with respect to enteric viruses when the density of enteric viruses in the sewage sludge after pathogen treatment is less than one Plaque-forming Unit per four grams of total solids (dry weight basis) and when the values or ranges of values for the operating parameters for the pathogen treatment process that produces the sewage sludge that meets the enteric virus density requirement are documented.

(D) After the enteric virus reduction in paragraph (a)(5)(ii)(C) of this section is demonstrated for the pathogen treatment process, the sewage sludge continues to be Class A with respect to enteric viruses when the values for the pathogen treatment process operating parameters are consistent with the values or ranges of values documented in paragraph (a)(5)(ii)(C) of this section.

(iii)(A) The sewage sludge shall be analyzed prior to pathogen treatment to determine whether the sewage sludge contains viable helminth ova.

(B) When the density of viable helminth ova in the sewage sludge prior to pathogen treatment is less than one per four grams of total solids (dry weight basis), the sewage sludge is Class A with respect to viable helminth ova until the next monitoring episode for the sewage sludge.

(C) When the density of viable helminth ova in the sewage sludge prior to pathogen treatment is equal to or greater than one per four grams of total solids (dry weight basis), the sewage sludge is Class A with respect to viable helminth ova when the density of viable helminth ova in the sewage sludge after pathogen treatment is less than one per four grams of total solids (dry weight basis) and when the values or ranges of values for the operating parameters for the pathogen treatment process that produces the sewage sludge that meets the viable helminth ova density requirement are documented.

(D) After the viable helminth ova reduction in paragraph (a)(5)(iii)(C) of this section is demonstrated for the pathogen treatment process, the sewage sludge continues to be Class A with respect to viable helminth ova when the values for the pathogen treatment process operating parameters are consistent with the values or ranges of values documented in paragraph (a)(5)(iii)(C) of this section.

(6) Class A - Alternative 4. (i) Either the density of fecal coliform in the sewage sludge shall be less than 1000 Most Probable Number per gram of total solids (dry weight basis), or the density of *Salmonella* sp. bacteria in the sewage sludge shall be less than three Most Probable Number per four grams of total solids (dry weight basis) at the time the sewage sludge is used or disposed; at the time the sewage sludge is prepared for sale or give away in a bag or other container for application to the land; or at the time the sewage sludge or material derived from sewage sludge is prepared to meet the requirements in Sec. 503.10 (b), (c), (e), or (f).

(ii) The density of enteric viruses in the sewage sludge shall be less than one Plaque-forming Unit per four grams of total solids (dry weight basis) at the time the sewage sludge is used or disposed; at the time the sewage sludge is prepared for sale or give away in a bag or other container for application to the land; or at the time the sewage sludge or material derived from sewage sludge is prepared to meet the requirements in Sec. 503.10 (b), (c), (e), or (f), unless otherwise specified by the permitting authority.

(iii) The density of viable helminth ova in the sewage sludge shall be less than one per four grams of total solids (dry weight basis) at the time the sewage sludge is used or disposed; at the time the sewage sludge is prepared for sale or give away in a bag or other container for application to the land; or at the time the sewage sludge or material derived from sewage sludge is prepared to meet the requirements in Sec. 503.10 (b), (c), (e), or (f), unless otherwise specified by the permitting authority.

(7) Class A - Alternative 5. (i) Either the density of fecal coliform in the sewage sludge shall be less than 1000 Most Probable Number per gram of total solids (dry weight basis), or the density of *Salmonella* sp. bacteria in the sewage sludge shall be less than three Most Probable Number per four grams of total solids (dry weight basis) at the time the sewage sludge is used or disposed; at the time the sewage sludge is prepared for sale or given away in a bag or other container for application to the land; or at the time the sewage sludge or material derived from sewage sludge is prepared to meet the requirements in Sec. 503.10 (b), (c), (e), or (f).

(ii) Sewage sludge that is used or disposed shall be treated in one of the Processes to Further Reduce Pathogens described in Appendix B of this part.

(8) Class A - Alternative 6. (i) Either the density of fecal coliform in the sewage sludge shall be less than 1000 Most Probable Number per gram of total solids (dry weight basis), or the density of *Salmonella*, sp. bacteria in the sewage sludge shall be less than three Most Probable Number per four grams of total solids (dry weight basis) at the time the sewage sludge is used or disposed; at the time the sewage sludge is prepared for sale or given away in a bag or other container for application to the land; or at the time the sewage sludge or material derived from sewage sludge is prepared to meet the requirements in Sec. 503.10 (b), (c), (e), or (f).

(ii) Sewage sludge that is used or disposed shall be treated in a process that is equivalent to a Process to Further Reduce Pathogens, as determined by the permitting authority.

(b) Sewage sludge-Class B. (1)(i) The requirements in either Sec. 503.32(b)(2), (b)(3), or (b)(4) shall be met for a sewage sludge to be classified Class B with respect to pathogens.

(ii) The site restrictions in Sec. 503.32(b)(5) shall be met when sewage sludge that meets the Class B pathogen requirements in Sec. 503.32(b)(2), (b)(3), or (b)(4) is applied to the land.

(2) Class B - Alternative 1. (i) Seven samples of the sewage sludge shall be collected at the time the sewage sludge is used or disposed.

(ii) The geometric mean of the density of fecal coliform in the samples collected in paragraph (b)(2)(i) of this section shall be less than either 2,000,000 Most Probable Number per gram of total solids (dry weight basis) or 2,000,000 Colony Forming Units per gram of total solids (dry weight basis).

(3) Class B - Alternative 2. Sewage sludge that is used or disposed shall be treated in one of the Processes to Significantly Reduce Pathogens described in Appendix B of this part.

(4) Class B - Alternative 3. Sewage sludge that is used or disposed shall be treated in a process that is equivalent to a Process to Significantly Reduce Pathogens, as determined by the permitting authority.

(5) Site restrictions. (i) Food crops with harvested parts that touch the sewage sludge/soil mixture and are totally above the land surface shall not be harvested for 14 months after application of sewage sludge.

(ii) Food crops with harvested parts below the surface of the land shall not be harvested for 20 months after application of sewage sludge when the sewage sludge remains on the land surface for four months or longer prior to incorporation into the soil.

(iii) Food crops with harvested parts below the surface of the land shall not be harvested for 38 months after application of sewage sludge when the sewage sludge remains on the land surface for less than four months prior to incorporation into the soil.

(iv) Food crops, feed crops, and fiber crops shall not be harvested for 30 days after application of sewage sludge.

(v) Animals shall not be allowed to graze on the land for 30 days after application of sewage sludge.

(vi) Turf grown on land where sewage sludge is applied shall not be harvested for one year after application of the sewage sludge when the harvested turf is placed on either land with a high potential for public exposure or a lawn, unless otherwise specified by the permitting authority.

(vii) Public access to land with a high potential for public exposure shall be restricted for one year after application of sewage sludge.

(viii) Public access to land with a low potential for public exposure shall be restricted for 30 days after application of sewage sludge.

(c) Domestic septage. (1) The site restrictions in Sec. 503.32 (b)(5) shall be met when domestic septage is applied to agricultural land, forest, or a reclamation site; or (2) The pH of domestic septage applied to agricultural land, forest, or a reclamation site shall be raised to 12 or higher by alkali addition and, without the addition of more alkali, shall remain at 12 or higher for 30 minutes and the site restrictions in Sec. 503.32 (b)(5)(i) through (b)(5)(iv) shall be met.

Sec. 503.33 Vector attraction reduction.

(a)(1) One of the vector attraction reduction requirements in Sec. 503.33 (b)(1) through (b)(10) shall be met when bulk sewage sludge is applied to agricultural land, forest, a public contact site, or a reclamation site.

(2) One of the vector attraction reduction requirements in Sec. 503.33 (b)(1) through (b)(8) shall be met when bulk sewage sludge is applied to a lawn or a home garden.

(3) One of the vector attraction reduction requirements in Sec. 503.33 (b)(1) through (b)(8) shall be met when sewage sludge is sold or given away in a bag or other container for application to the land.

(4) One of the vector attraction reduction requirements in Sec. 503.33 (b)(1) through (b)(11) shall be met when sewage sludge (other than domestic septage) is placed on an active sewage sludge unit.

(5) One of the vector attraction reduction requirements in Sec. 503.33 (b)(9), (b)(10), or (b)(12) shall be met when domestic septage is applied to agricultural land, forest, or a reclamation site and one of the vector attraction reduction requirements in Sec. 503.33 (b)(9) through (b)(12) shall be met when domestic septage is placed on an active sewage sludge unit.

(b)(1) The mass of volatile solids in the sewage sludge shall be reduced by a minimum of 38 percent (see calculation procedures in "Environmental Regulations and Technology - Control of Pathogens and Vector Attraction in Sewage Sludge," EPA/625/R-92/013,1992, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268).

(2) When the 38 percent volatile solids reduction requirement in Sec. 503.33 (b)(1) cannot be met for an anaerobically digested sewage sludge, vector attraction reduction can be demonstrated by digesting a portion of the previously digested sewage sludge anaerobically in the laboratory in a bench-scale unit for 40 additional days at a temperature between 30 and 37 degrees Celsius. When at the end of the 40 days, the volatile solids in the sewage sludge at the beginning of that period is reduced by less than 17 percent, vector attraction reduction is achieved.

(3) When the 38 percent volatile solids reduction requirement in Sec. 503.33 (b)(1) cannot be met for an aerobically digested sewage sludge, vector attraction reduction can be demonstrated by digesting a portion of the previously digested sewage sludge that has a percent solids of two percent or less aerobically in the laboratory in a bench-scale unit for 30 additional days at 20 degrees Celsius. When at the end of the 30 days, the volatile solids in the sewage sludge at the beginning of that period is reduced

by less than 15 percent, vector attraction reduction is achieved.

(4) The specific oxygen uptake rate (SOUR) for sewage sludge treated in an aerobic process shall be equal to or less than 1.5 milligrams of oxygen per hour per gram of total solids (dry weight basis) at a temperature of 20 degrees Celsius.

(5) Sewage sludge shall be treated in an aerobic process for 14 days or longer. During that time, the temperature of the sewage sludge shall be higher than 40 degrees Celsius and the average temperature of the sewage sludge shall be higher than 45 degrees Celsius.

(6) The pH of sewage sludge shall be raised to 12 or higher by alkali addition and, without the addition of more alkali, shall remain at 12 or higher for two hours and then at 11.5 or higher for an additional 22 hours.

(7) The percent solids of sewage sludge that does not contain unstabilized solids generated in a primary wastewater treatment process shall be equal to or greater than 75 percent based on the moisture content and total solids prior to mixing with other materials.

(8) The percent solids of sewage sludge that contains unstabilized solids generated in a primary wastewater treatment process shall be equal to or greater than 90 percent based on the moisture content and total solids prior to mixing with other materials.

(9)(i) Sewage sludge shall be injected below the surface of the land.

(ii) No significant amount of the sewage sludge shall be present on the land surface within one hour after the sewage sludge is injected.

(iii) When the sewage sludge that is injected below the surface of the land is Class A with respect to pathogens, the sewage sludge shall be injected below the land surface within eight hours after being discharged from the pathogen treatment process.

(10)(i) Sewage sludge applied to the land surface or placed on a surface disposal site shall be incorporated into the soil within six hours after application to or placement on the land.

(ii) When sewage sludge that is incorporated into the soil is Class A with respect to pathogens, the sewage sludge shall be applied to or placed on the land within eight hours after being discharged from the pathogen treatment process.

(11) Sewage sludge placed on an active sewage sludge unit shall be covered with soil or other material at the end of each operating day.

(12) The pH of domestic septage shall be raised to 12 or higher by alkali addition and, without the addition of more alkali, shall remain at 12 or higher for 30 minutes.

Appendix C
Determination of Volatile Solids Reduction by Digestion

Introduction

Under 40 CFR Part 503, the ability of sewage sludge to attract vectors must be reduced when sewage sludge is applied to the land or placed on a surface disposal site. One way to reduce vector attraction is to reduce the volatile solids in the sewage sludge by 38% or more (see Section 8.2 of this document). Typically, volatile solids reduction is accomplished by anaerobic or aerobic digestion. Volatile solids reduction also occurs under other circumstances, such as when sewage sludge is stored in an anaerobic lagoon or is dried on sand beds. To give credit for this extra loss in volatile solids, the regulation allows the untreated sewage sludge to be compared with the treated sewage sludge that leaves the treatment works, which should account for all of the volatile solids reduction that could possibly occur. For most processing sequences, the processing steps downstream from the digester, such as short-term storage or dewatering, have no influence on volatile solids content. Consequently, the appropriate comparison is between the sewage sludge entering the digester and the sewage sludge leaving the digester. The remainder of the discussion is limited to this circumstance, except for the final section of this appendix, which compares incoming sewage sludge with the sewage sludge leaving the treatment works.

The Part 503 regulation does not specify a method for calculating volatile solids reduction. Fischer (1984) observed that the United Kingdom has a similar requirement for volatile solids reduction for digestion (40%), but also failed to prescribe a method for calculating volatile solids reduction. Fischer has provided a comprehensive discussion of the ways that volatile solids reduction may be calculated and their limitations. He presents the following equations for determining volatile solids reduction:

- Full mass balance equation
- Approximate mass balance equation
- "Constant ash" equation
- Van Kleeck equation

The full mass balance equation is the least restricted approach but requires more information than is currently collected at a wastewater treatment plant. The approximate mass balance equation assumes steady state conditions. The "constant ash" equation requires the assumption of steady state conditions as well as the assumption that the ash input rate equals the ash output rate. The Van Kleeck equation, which is the equation generally suggested in publications originating in the United States (WPCF, 1968), is equivalent to the constant ash equation. Fischer calculates volatile solids reduction using a number of examples of considerable complexity and illustrates that different methods frequently yield different results.

Fischer's paper is extremely thorough and is highly recommended for someone trying to develop a deep understanding of potential complexities in calculating volatile solids reduction. However, it was not written as a guidance document for field staff faced with the need to calculate volatile solids reduction. The nomenclature is precise but so detailed that it makes comprehension difficult. In addition, two important troublesome situations that complicate the calculation of volatile solids reduction - grit deposition in digesters and decantate removal - are not explicitly discussed. Consequently, this presentation has been prepared to present guidance that describes the major pitfalls likely to be encountered in calculating percent volatile solids reduction.

It is important to note that the calculation of volatile solids reduction is only as accurate as the measurement of volatile solids content in the sewage sludge. The principal cause of error is poor sampling. Samples should be representative, covering the entire charging and withdrawal periods. Averages should cover extended periods of time during which changes in process conditions are minimal. For some treatment, it is expected that periodic checks of volatile solids reduction will produce results so erratic that no confidence can be placed in them. In this case, adequacy of stabilization can be verified by the method described under Options 2 and 3 in Chapter 8 --periodically batch digest anaerobically digested sewage sludge for 40 additional days at 30°C (86°F) to 37°C (99°F), or aerobically digested sewage sludge for 30 additional days at 20°C (68°F). If the additional VS reduction is less than 17% for the anaerobically digested sewage sludge or less than 15% for the aerobically digested sewage sludge, the sewage sludge is sufficiently stable (see Sections 8.3 and 8.4).

Equations for FVSR

The equations for fractional volatile solids reduction (FVSR) that will be discussed below are the same as those developed by Fischer (1984), except for omission of his constant ash equation. This equation gives identical results to the Van Kleeck equation so it is not shown. Fischer's nomenclature has been avoided or replaced with simpler terms. The material balance approaches are called methods rather than equations. The material balances are drawn to fit the circumstances. There is no need to formalize the method with a rigid set of equations.

In the derivations and calculations that follow, both VS (total volatile solids content of the sewage sludge or decantate on a dry solids basis) and FVSR are expressed throughout as fractions to avoid the frequent confusion that occurs when these terms are expressed as percentages. "Decantate" is used in place of the more commonly used "supernatant" to avoid the use of "s" in subscripts. Similarly, "bottoms" is used in place of "sludge" to avoid use of "s" in subscripts.

Method Full Mass Balance

The full mass balance method must be used when steady conditions do not prevail over the time period chosen for the calculation. The chosen time period must be substantial, at least twice the nominal residence time in the digester (nominal residence time equals average volume of sludge in the digester divided by the average volumetric flow rate. Note: when there is decantate withdrawal, volume of sewage sludge withdrawn should be used to calculate the average volumetric flow rate). The reason for the long time period is to reduce the influence of short-term fluctuations in sewage sludge flow rates or compositions. If input compositions have been relatively constant for a long period of time, then the time period can be shortened.

An example where the full mass balance method would be needed is where an aerobic digester is operated as follows:

- Started with the digester 1/4 full (time zero)
- Raw sewage sludge is fed to the digester daily until the digester is full
- Supernatant is periodically decanted and raw sewage sludge is charged into the digester until settling will not occur to accommodate daily feeding (hopefully after enough days have passed for adequate digestion)
- Draw down the digester to about 1/4 full (final time), discharging the sewage sludge to sand beds

The full mass balance is written as follows:

Sum of total volatile solids inputs in feed streams during the entire digestion period = sum of volatile solids outputs in withdrawals of decantate and bottoms + loss of volatile solids + accumulation of volatile solids in the digester. (1)

Loss of volatile solids is calculated from Equation 1. FVSR is calculated by Equation 2:

$$FVSR = \frac{\text{loss in volatile solids}}{\text{sum of volatile solids inputs}} \quad (2)$$

The accumulation of volatile solids in the digester is the final volume in the digester after the drawdown times final volatile solids concentration less the initial volume at time zero times the initial volatile solids concentration.

To properly determine FVSR by the full mass balance method requires determination of all feed and withdrawal volumes, initial and final volumes in the digester, and volatile solids concentrations in all streams. In some cases, which will be presented later, simplifications are possible.

Approximate Mass Balance Method

If volumetric inputs and outputs are relatively constant on a daily basis, and there is no substantial accumulation of volatile solids in the digester over the time period of the test, an approximate mass balance (AMB) may be used. The basic relationship is stated simply:

volatile solids input rate = volatile solids output rate + rate of loss of volatile solids. (3)

The FVSR is given by Equation 2.

No Decantate, No Grit Accumulation (Problem 1)

Calculation of FVSR is illustrated for Problem 1 in Table C-1, which represents a simple situation with no decantate removal and no grit accumulation. An approximate mass balance is applied to the digester operated under constant flow conditions. Because no decantate is removed, the volumetric flow rate of sewage sludge leaving the digester equals the flow rate of sewage sludge entering the digester.

Applying Equations 3 and 2,

$$FY_f = BY_b + \text{loss} \quad (4)$$

$$\text{Loss} = 100(50-30) = 2000 \quad (5)$$

$$FVSR = \frac{\text{Loss}}{FY_f} \quad (6)$$

$$FVSR = \frac{2000}{(100)\ (50)} = 0.40 \quad (7)$$

Nomenclature is given in Table C-1. Note that the calculation did not require use of the fixed solids concentrations.

The calculation is so simple that one wonders why it is so seldom used. One possible reason is that the input and output volatile solids concentrations (Y_f and Y_b) typically will show greater coefficients of variation (standard) deviation divided by arithmetic average) than the fractional volatile solids (VS is the fraction of the sewage sludge solids

Table C-1. Quantitative Information for Example Problems [1,2,3]

Parameter	Symbol	Units	Problem Statement Number 1	2	3	4
Nominal Residence Time	θ	d	20	20	20	20
Time period for averages	—	d	60	60	60	60
Feed Sludge						
Volumetric flow rate	F	m^3/d	100	100	100	100
Volatile solids concentration	Y_f	kg/m^3	50	50	50	50
Fixed solids concentration	X_f	kg/m^3	17	17	17	17
Fractional volatile solids	VS_f	kg/kg	0.746	0.746	0.746	0.746
Mass flow rate of solids	M_f	kg/d	6700	6700	6700	6700
Digested Sludge (Bottoms)						
Volumetric flow rate	B	m^3/d	100	100		49.57
Volatile solids concentration	Y_b	kg/m^3	30	41.42	41.42	41.42
Fixed solids concentration	X_b	kg/m^3	17	15	23.50	23.50
Fractional volatile solids	VS_b	kg/kg	0.638	0.667	0.638	0.638
Mass flow rate of solids	M_b	kg/d	4700	4500		
Decantate						
Volumetric flow rate	D	m^3/d	0	0		50.43
Volatile solids concentration	Y_d	kg/m^3	—	—	12.76	12.76
Fixed solids concentration	X_d	kg/m^3	—	—	7.24	7.24
Fractional volatile solids	VS_d	kg/kg	—	—	0.638	0.638
Mass flow rate of solids	M_d	kg/d	—	—		

[1]Conditions are steady state; all daily flows are constant. Volatile solids are not accumulating in the digester, although grit may be settling out in the digester.
[2]Numerical values are given at 3 or 4 significant figures. This is unrealistic considering the expected accuracy in measuring solids concentrations and sludge volumes. The purpose of extra significant figures is to allow more understandable comparisons to be made of the different calculation methods.
[3]All volatile solids concentrations are based on total solids, not merely on suspended solids.

that is volatile-note the difference between VS and Y). If this is the case, the volatile solids reduction calculated by the approximate mass balance method from several sets of Y_f-Y_b data will show larger deviations than if it were calculated by the Van Kleeck equation using VS_f -VS_b data.

Grit deposition can be a serious problem in both aerobic and anaerobic digestion. The biological processes that occur in digestion dissolve or destroy the substances suspending the grit, and it tends to settle. If agitation is inadequate to keep the grit particles in suspension, they will accumulate in the digester. The approximate mass balance can be used to estimate accumulation of fixed solids.

For Problem 1, the balance yields the following:

$$FX_f = BX_b + \text{fixed solids loss} \quad (8)$$

$$(100)(17) = (100)(17) + \text{Fixed Solids Loss} \quad (9)$$

$$\text{Fixed Solids Loss} = 0 \quad (10)$$

The material balance compares fixed solids in output with input. If some fixed solids are missing, this loss term will be a positive number. Because digestion does not consume fixed solids, it is assumed that the fixed solids are accumulating in the digester. As Equation 10 shows, the fixed solids loss equals zero. Note that for this case, where input and output sewage sludge flow rates are equal, the fixed solids concentrations are equal when there is no grit accumulation.

Grit Deposition (Problem 2)

The calculation of fixed solids is repeated for Problem 2. Conditions in Problem 2 have been selected to show grit accumulation. Parameters are the same as in Problem 1 except for the fixed solids concentration (X_b) and parameters related to it. Fixed solids concentration in the sewage sludge is lower than in Problem 1. Consequently, VS is higher and the mass flow rate of solids leaving is lower than in Problem 1. A mass balance on fixed solids (input rate = output rate + rate of loss of fixed solids) is presented in Equations 11-13.

$$FX_f = BX_b + \text{Fixed Solids Loss} \quad (11)$$

$$\text{Fixed Solids Loss} = FX_f - BX_b \quad (12)$$

$$\text{Fixed Solids Loss} = (100)(7) - (100)(15) = 200 \text{ kg/d} \quad (13)$$

The material balance, which only looks at inputs and outputs, informs us that 200 kg/d of fixed solids have not appeared in the outputs as expected. Because fixed solids are not destroyed, it can be concluded that they are accumulating in the bottom of the digester. The calculation of FVSR for Problem 2 is exactly the same as for Problem 1 (see Equations 4 through 7) and yields the same result. The approximate mass balance method gives the

correct answer for the FVSR despite the accumulation of solids in the digester. As will be seen later, this is not the case when the Van Kleeck equation is used.

Decantate Withdrawal, No Grit Accumulation (Problem 3)

In Problem 3, decantate is withdrawn daily. Volatile and fixed solids concentrations are known for all streams but the volumetric flow rates are not known for decantate and bottoms. It is impossible to calculate FVSR without knowing the relative volumes of these streams. However, they are determined easily by taking a total volume balance and a fixed solids balance, provided it can be assumed that loss of fixed solids (i.e., accumulation in the digester) is zero.

Selecting a basis for F of 100 m^3/d

$$\text{Volume balance: } 100 = B + D \tag{14}$$

$$\text{Fixed solids balance: } 100\,X_f + BX_b + DX_d \tag{15}$$

Because the three Xs are known, B and D can be found. Substituting 100-D for B and the values for the Xs from Problem 3 and solving for D and B,

$$(100)(17) = (100 - D)(23.50) + (D)(7.24) \tag{16}$$

$$D = 40.0\ m^3/d,\ B = 60.0\ m^3/d \tag{17}$$

The FVSR can now be calculated by drawing a volatile solids balance:

$$FY_f = BY_b + DY_d + \text{loss} \tag{18}$$

$$FVSR = \frac{\text{loss}}{FY_f} = \frac{FY_f - BY_b - DY_d}{FY_f} \tag{19}$$

$$FVSR = \frac{(100)(50) - (60)(41.42) - (40)(12.76)}{(100)(50)} = 0\,40 \tag{20}$$

Unless information is available on actual volumes of decantate and sewage sludge (bottoms), it is not possible to deterrnine whether grit is accumulating in the digester. If it is accumulating, the calculated FVSR will be in error.

When the calculations shown in Equations 18 through 20 are made, it is assumed that the volatile solids that are missing from the output streams are consumed by biological reactions that convert them to carbon dioxide and methane. Accumulation is assumed to be negligible. Volatile solids are less likely to accumulate than fixed solids, but it can happen. In poorly mixed digesters, the scum layer that collects at the surface is an accumulation of volatile solids. FVSR calculated by Equations 18 through 20 wiIl be overestimated if the volatile solids accumulation rate is substantial.

Decantate Withdrawal and Grit Accumulation (Problem 4)

In Problem 4, there is suspected grit accumulation. The quantity of B and D can no longer be calculated by Equations 14 and 15 because Equation 15 is no longer correct. The values of B and D must be measured. All parameters in Problem 4 are the same as in Problem 3 except that measured values for B and D are introduced into Problem 4. Values of B and D calculated assuming no grit accumulation (Problem 3--see previous discussion), and measured quantities are compared below:

	Calculated	Measured
B	60	49.57
D	40	50.43

The differences in the values of B and D are not large but they make a substantial change in the numerical value of FVSR. The FVSR for Problem 4 is calculated below:

$$FVSR = \frac{(100)(50) - (49.57)(41.42) - (50.43)(12.76)}{(100)(50)} = 0.461 \tag{21}$$

If it had been assumed that there was no grit accumulation, FVSR would equal 0.40 (see Problem 3). It is possible to determine the amount of grit accumulation that has caused this change. A material balance on fixed solids is drawn:

$$FX_f = BX_b + DX_d + \text{Fixed Solids Loss} \tag{22}$$

The fractional fixed solids loss due to grit accumulation is found by rearranging this equation:

$$\frac{\text{Fixed Solids Loss}}{FX_f} = \frac{FX_f - BX_b - Dx_d}{FX_f} \tag{23}$$

Substituting in the parameter values for Problem 4,

$$\frac{\text{Fixed Solids Loss}}{FX_f} = \frac{(100)(17) - (49.57)(23.50) - (50.43)(7.24)}{(100)(17)} = 0.100 \tag{24}$$

If this fixed solids loss of 10 percent had not been accounted for, the calculated FVSR would have been 13% lower than the correct value of 0.461. Note that if grit accumulation occurs and it is ignored, calculated FVSR will be lower than the actual value.

The Van Kleeck Equation

Van Kleeck first presented his equation without derivation in a footnote for a review paper on sewage sludge treatment processing in 1945 (Van Kleeck, 1945). The equation is easily derived from total solids and volatiie solids mass balances around the digestion system. Consider a digester operated under steady state conditions with decantate and bottom sewage sludge removal. A total solids mass balance and a volatile solids mass balance are:

$$M_f = M_b + M_d + (\text{loss of total solids}) \tag{25}$$

$$M_f \cdot VS_f = M_b \cdot VS_b + M_d \cdot VS_d + (\text{loss of volatile solids}) \quad (26)$$

where
M_f, M_b, and M_d are the mass of solids in the feed, bottoms, and decantate streams.

The masses must be mass of solids rather than total mass of liquid and solid because VS is an unusual type of concentration unit-it is "mass of volatile solids per unit mass of total solids."

It is now assumed that fixed solids are not destroyed and there is no grit deposition in the digester. The losses in Equations 25 and 26 then comprise only volatile solids so the losses are equal. It is also assumed that the VS of the decantate and of the bottoms are the same. This means that the bottoms may have a much higher solids content than the decantate but the proportion of volatile solids to fixed solids is the same for both streams. Assuming then that VS_b equals VS_d, and making this substitution in the defining equation for FVSR (Equation 2),

$$FVSR = \frac{\text{Loss of vol. solids}}{M_f \times VS_f} = 1 - \frac{(M_b + M_d)\, VS_b}{M_f \times VS_f} \quad (27)$$

From Equation 25, recalling that we have assumed that loss of total solids equals loss of volatile solids,

$$M_b + M_d + M_f - \text{loss of vol. solids} \quad (28)$$

Substituting for $M_b + M_d$ into Equation 27,

$$FVSR = 1 - \frac{(M_f - \text{loss of vol. solids}) \cdot VS_b}{M_f \cdot VS_f} \quad (29)$$

Simplifying further,

$$1 - (1/VS_f - FVSR) \cdot VS_b \quad (30)$$

Solving for FVSR,

$$FVSR = \frac{VS_f - VS_b}{VS_f - (VS_f \cdot VS_b)} \quad (31)$$

This is the form of the Van Kleek equation found in WPCF Manual of Practice No. 16 (WPCF, 1968). Van Kleeck (1945) presented the equation in the following equivalent form:

$$FVSR = 1 - \frac{VS_b \times (1 - VS_f)}{VS_f \times (1 - VS_b)} \quad (32)$$

The Van Kleeck equation is applied below to Problems 1 through 4 in Table C-1 and compared to the approximate mass balance equation results:

	1	2	3	4
Approximate Mass Balance (AMB)	0.40	0.40	0.40	0.461
Van Kleeck (VK)	0.40	0.318	0.40	0.40

Problem 1: No decantate and no grit accumulation. Both methods give correct answer.

Problem 2: No decantate but grit accumulation. VK is invalid and incorrect.

Problem 3: Decantate but no grit accumulation. AMB method is valid. VK method is valid only if VS_b equals VS_d.

Problem 4: Decantate and grit accumulation. AMB method valid only if B and D are measured. VK method is invalid.

The Van Kleeck equation is seen to have serious shortcomings when applied to certain practical problems. The AMB method can be completely reliable, whereas the Van Kleeck method is useless under some circumstances.

Average Values

The concentrations and VS values used in the equations will all be averages. For the material balance methods, the averages should be weighted averages according to the mass of solids in the stream in question. The example below shows how to average the volatile solids concentration for four consecutive sewage sludge additions

Addition	Volume	Total Solids Concentration	VS
1	12 m^3	72 kg/m3	0.75
2	8 m^3	50 kg/m3	0.82
3	13 m^3	60 kg/m3	0.80
4	10 m^3	55 kg/m3	0.77

(33)

Weighted by Mass

$$VS\ av = \frac{12 \times 72 \times 0.75 + 8 \times 50 \times 0.82 + 13 \times 60 \times 0.80 + 10 \times 55 \times 0.77}{12 \times 72 + 8 \times 50 + 13 \times 60 + 10 \times 55} = 0.795 \quad (34)$$

Weighted by Volume

$$VS\ av = \frac{12 \times 0.75 + 8 \times 0.82 + 13 \times 0.80 + 10 \times 0.77}{12+8+13+10} = 0.783 \quad (35)$$

Arithmetic Average

$$VS\ av = \frac{0.75 + 0.82 + 0.80 + 0.77}{4} = 0.785 \quad (36)$$

In this example the arithmetic average was nearly as close as the volume-weighted average to the mass-weighted average, which is the correct value.

Which Equation to Use?

Full Mass Balance Method

The full mass balance method allows calculation of volatile solids reduction for all approaches to digestion, even

processes in which the final volume in the digester does not equal the initial volume and where daily flows are not steady. A serious drawback to this method is the need for volatile solids concentration and the volumes of all streams added to or withdrawn from the digester, as well as initial and final volumes and concentrations in the digester. This can be a daunting task, particularly for the small treatment works that is most likely to run digesters in other than steady flow modes. For treatment works of this kind, an "equivalent" method that shows that the sewage sludge has undergone the proper volatile solids reduction is likely to be a better approach than trying to demonstrate 38% volatile solids reduction. An aerobic sewage sludge has received treatment equivalent to a 38% volatile solids reduction if the specific oxygen uptake rate is below a specified maximum. Anaerobically digested sewage sludge has received treatment equivalent to a 38% volatile solids reduction if volatile solids reduction after batch digestion of the sewage sludge for 40 days is less than a specified maximum (EPA, 1992).

Approximate Mass Balance Method

The approximate mass balance method assumes that daily flows are steady and reasonably uniform in composition, and that digester volume and composition do not vary substantially from day to day. Results of calculations and an appreciation of underlying assumptions show that the method is accurate for all cases, including withdrawal of decantate and deposition of grit, provided that in addition to composition of all streams the quantities of decantate and bottoms (the digested sewage sludge) are known. If the quantities of decantate and bottoms are not known, the accumulation of grit cannot be determined. If accumulation of grit is substantial and FVSR is calculated assuming it to be negligible, FVSR will be lower than the true value. The result is conservative and could be used to show that minimum volatile solids reductions are being achieved.

Van Kleeck Method

The Van Kleeck equation has underlying assumptions that should be made clear wherever the equation is presented. The equation is never valid when there is grit accumulation because it assumes the fixed solids input equals fixed solids output. Fortunately, it produces a conservative result in this case. Unlike the AMB method it does not provide a convenient way to check for accumulation of grit. It can be used when decantate is withdrawn, provided VS_b equals VS_d. Just how significant the difference between these VS values can be before an appreciable error in FVSR occurs is unknown, although it could be determined by making up a series of problems with increasing differences between the VS values, calculating FVSR using the AMB method and a Van Kleeck equation, and comparing the results.

The shortcomings of the Van Kleeck equation are substantial, but the equation has one strong point: The VS of the various sewage sludge and decantate streams are likely to show much lower coefficients of variation (standard deviation divided by arithmetic average) than volatile solids and fixed solids concentrations. Reviews of data are needed to determine how seriously the variation in concentrations affect the confidence interval of FVSR calculated by both methods. A hybrid approach may turn out to be advantageous. The AMB method could be used first to determine if grit accumulation is occurring. If grit is not accumulating, the Van Kleeck equation could be used. If decantate is withdrawn, the Van Kleeck equation is appropriate, particularly if the decantate is low in total solids. If not, and if VS_d differs substantially from VS_b, it could yield an incorrect answer.

Volatile Solids Loss Across All Sewage Sludge Treatment Processes

For cases when appreciable volatile solids reduction can occur downstream from the digester (for example, as would occur in air drying or lagoon storage), it is appropriate to calculate the volatile solids loss from the point at which the sewage sludge enters the digester to the point at which the sewage sludge leaves the treatment works. Under these circumstances, it is virtually never possible to use the approximate mass balance approach, because flow rates are not uniform. The full mass balance could be used in principle, but practical difficulties such as measuring the mass of the output sewage sludge (total mass, not just mass of solids) that relates to a given mass of entering sewage sludge make this also a practical impossibility. Generally then, the only option is to use the Van Kleeck equation, because only the percent volatile solids content of the entering and exiting sewage sludge is needed to make this calculation. As noted earlier, this equation will be inappropriate if there has been a selective loss of high volatility solids (e.g., bacteria) or low volatility solids (e.g., grit) in any of the sludge processing steps.

To make a good comparison, there should be good correspondence between the incoming sewage sludge and the treated sewage sludge to which it is being compared (see Section 10.4). For example, when sewage sludge is digested for 20 days, then dried on a sand bed for 3 months, and then removed, the treated sludge should be compared with the sludge fed to the digester in the preceding 3 or 4 months. If no selective loss of volatile or nonvolatile solids has occurred, the Van Kleeck equation (see Equation 31) can be used to calculate volatile solids reduction.

References

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Appendix D
Guidance on Three Vector Attraction Reduction Tests

This appendix provides guidance for the vector attraction reduction Options 2,3, and 4 to demonstrate reduced vector attraction (see Chapter 8 for a description of these requirements).

1. Additional Digestion Test for Anaerobically Digested Sewage Sludge

Background

The additional digestion test for anaerobically digested sewage sludge is based on research by Jeris et al. (1985). Farrell and Bhide (1993) explain in more detail the origin of the time and volatile solids reduction requirements of the test.

Jeris et al. (1985) measured changes in many parameters including volatile solids content while carrying out additional digestion of anaerobically digested sludge from several treatment works for long periods. Samples were removed from the digesters weekly for analysis. Because substantial amount of sample was needed for all of these tests, they used continuously mixed digesters of 18 liters capacity. The equipment and procedures of Jeris et al., although not complex, appear to be more elaborate than needed for a control test. EPA staff (Farrell and Bhide, 1993) have experimented with simplified tests and the procedure recommended is based on their work.

Recommended Procedure

The essentials of the test are as follows:

- Remove, from the plant-scale digester, a representative sample of the sewage sludge to be evaluated to determine additional volatile solids destruction. Keep the sample protected from oxygen and maintain it at the temperature of the digester. Commence the test within 6 hours after taking the sample.

- Flush fifteen 100-mL volumetric flasks with nitrogen, and add approximately 50 mL of the sludge to be tested into each flask. Frequently mix the test sludge during this operation to assure that its composition remains uniform. Select five flasks at random, and determine total solids content and volatile solids content, using the entire 50 mL for the determination. Seal each of the remaining flasks with a stopper with a single glass tube through it to allow generated gases to escape.

- Connect the glass tubing from each flask through a flexible connection to a manifold. To allow generated gases to escape and prevent entry of air, connect the manifold to a watersealed bubbler by means of a vertical glass tube. The tube should be at least 30-cm long with enough water in the bubbler so that an increase in atmospheric pressure will not cause backflow of air or water into the manifold. Maintain the flasks containing the sludge at constant temperature either by inserting them in a water bath (the sludge level in the flasks must be below the water level in the bath) or by placing the entire apparatus in a constant temperature room or box. The temperature of the additional digestion test should be the average temperature of the plant digester, which should be in the range of 30°C to 40°C (86°F to 104°F). Temperature should be controlled within + 0.15°C (0.27°F).

- Each flask should be swirled every day to assure adequate mixing, using care not to displace sludge up into the neck of the flask. Observe the water seal for the first few days of operation. There should be evidence that gas is being produced and passing through the bubbler.

- After 20 days, withdraw five flasks at random. Determine total and volatile solids content using the entire sample for the determination. Swirl the flask vigorously before pouring out its contents to minimize the hold up of thickened sludge on the walls and to assure that any material left adhering to the flask walls will have the same average composition as the material withdrawn. Use a consistent procedure. If holdup on walls appears excessive, a minimal amount of distilled water may be used to wash solids off the walls. Total removal is not necessary, but any solids left on the walls should be approximately of the same composition as the material removed.

- After 40 days, remove the remaining five flasks. Determine total and volatile solids content using the entire sample from each flask for the determination. Use the same precautions as in the preceding step to remove virtually all of the sludge, leaving only material with the same approximate composition as the material removed.

Total and volatile solids contents are determined using the procedures of Method 2540 G of Standard Methods (APHA, 1992).

Mean values and standard deviations of the total solids content, the volatile solids content, and the percent volatile solids are calculated. Volatile solids reductions that result from the additional digestion periods of 20 and 40 days are calculated from the mean values by the Van Kleeck equation and by a material balance (refer to Appendix C for a general description of these calculations). The results obtained at 20 days give an early indication that the test is proceeding satisfactorily and will help substantiate the 40-day result.

Alternative approaches are possible. The treatment works may already have versatile bench-scale digesters available. This equipment could be used for the test, provided accuracy and reproducibility can be demonstrated. The approach described above was developed because Farrell and Bhide (1993) in their preliminary work experienced much difficulty in withdrawing representative samples from large digesters even when care was taken to stir the digesters thoroughly before sampling. If an alternative experimental setup is used, it is still advisable to carry out multiple tests for the volatile solids content in order to reduce the standard error of this measurement, because error in the volatile solids content measurement is inflated by the nature of the equation used to calculate the volatile solids reduction.

Variability in flow rates and nature of the sludge will result in variability in performance of the plant-scale digesters. It is advisable to run the additional digestion test routinely so that sufficient data are available to indicate average performance. The arithmetic mean of successive tests (a minimum of three is suggested) should show an additional volatile solids reduction of $\leq$ 17%.

Calculation Details

Appendix C, Determination of Volatile Solids Reduction by Digestion, describes calculation methods to use for digesters that are continuously fed or are fed at least once a day. Although the additional anaerobic digestion test is a batch digestion, the material balance calculations approach is the same. Masses of starting streams (input streams) are set equal to masses of ending streams (output streams).

The test requires that the fixed volatile solids reduction (FVSR) be calculated both by the Van Kleeck equation and the material balance method. The Van Kleeck equation calculations can be made in the manner described in Appendix C.

The calculation of the volatile solids reduction (and the fixed fractional solids reduction [FFSR]) by the mass balance method shown below has been refined by subtracting out the mass of gas lost from the mass of sludge at the end of the digestion step. For continuous digestion, this loss of mass usually is ignored, because the amount is small in relation to the total digesting mass, and mass before and after digestion are assumed to be the same. Considering the inherent difficulty in matching mass and composition entering to mass and composition leaving for a continuous process, this is a reasonable procedure. For batch digestion, the excellent correspondence between starting material and final digested sludge provides much greater accuracy in the mass balance calculation, so inclusion of this lost mass is worthwhile.

In the equations presented below, concentrations of fixed and volatile solids are mass fractions--mass of solids per unit mass of sludge (mass of sludge includes both the solids and the water in the sludge)-- and are indicated by, the symbols lowercase y and x. This is different from the usage in Appendix C where concentrations are given in mass per unit volume, and are indicated by the symbols uppercase y and x. This change has been made because masses can be determined more accurately than volumes in small-scale tests.

In the material balance calculation, it is assumed that as the sludge digests, volatile solids and fixed solids are converted to gases that escape or to volatile compounds that distill off when the sludge is dried. Any production or consumption of water by the biochemical reactions in digestion is assumed to be negligible. The data collected (volatile solids and fixed solids concentrations of feed and digested sludge) allow mass balances to be drawn on volatile solids, fixed solids, and water. As noted, it is assumed that there is no change in water mass -- all water in the feed is present in the digested sludge. Fractional reductions in volatile solids and fixed solids can be calculated from these mass balances for the period of digestion. Details of the calculation of these relationships are given by Farrell and Bhide (1993). The final form of the equations for fractional volatile solids reduction (mass balance [m.b.] method) and fractional fixed solids reduction (m.b. method) are given below:

$$FVSR(m.b.) = \frac{y_f(1-x_b)-y_b(1-x_f)}{y_f(1-x_b-y_b)} \quad (1a)$$

$$FFSR(m.b.) = \frac{x_f(1-y_b)-x_b(1-y_f)}{x_f(1-x_b-y_b)} \quad (1b)$$

where:

y = mass fraction of volatile solids in the liquid sludge
x = mass fraction of fixed solids in the liquid sludge
f = indicates feed sludge at start of the test
b = indicates "bottoms" sludge at end of the test

If the fixed solids loss is zero, these two equations are reduced to Equation 2 below:

$$FVSR(m.b.) = (y_f - y_b)/y_f\,(1-y_b) \quad (2)$$

If the fixed solids loss is not zero but is substantially smaller than the volatile solids reduction, Equation 2 gives surprisingly accurate results. For five sludges batch-digested by Farrell and Bhide (1993), the fixed solids reduc-

tions were about one-third of the volatile solids reductions. When the FVSR(m.b.) calculated by Equation 1a averaged 15%, the FVSR(m.b.) calculated by Equation 2 averaged 14.93%, which is a trivial difference.

The disappearance of fixed solids unfortunately has a relatively large effect on the calculation of FVSR by the Van Kleeck equation. The result is lower than it should be. For five sludges that were batch-digested by Farrell and Bhide (1993), the FVSR calculated by the Van Kleeck method averaged 15%, whereas the FVSR (m.b.) calculated by Equation 1a or 2 averaged about 20%. When the desired endpoint is an FVSR below 17%, this is a substantial discrepancy.

The additional digestion test was developed for use with the Van Kleeck equation, and the 17% requirement is based on results calculated with this equation. In the future, use of the more accurate mass balance equation may be required, with the requirement adjusted upward by an appropriate amount. This cannot be done until more data with different sludge become available.

2. Specific Oxygen Uptake Rate

Background

The specific oxygen uptake rate of a sewage sludge is an accepted method for indicating the biological activity of an activated sewage sludge mixed liquor or an aerobically digesting sludge. The procedure required by the Part 503 regulation for this test is presented in Standard Methods (APHA, 1992) as Method 2710 B, Oxygen-Consumption Rate.

The use of the specific oxygen uptake rate (SOUR) has been recommended by Eikum and Paulsrud (1977) as a reliable method for indicating sludge stability provided temperature effects are taken into consideration. For primary sewage sludges aerobically digested at 18°C (64°F), sludge was adequately stabilized (i.e., it did not putrefy and cause offensive odors) when the SOUR was less than 1.2 mg O_2/hr/g VSS (volatile suspended solids). The authors investigated several alternative methods for indicating stability of aerobically digested sludges and recommended the SOUR test as the one with the most advantages and the least disadvantages.

Ahlberg and Boyko (1972) also recommend the SOUR as an index of stability. They found that, for aerobic digesters operated at temperatures above 10°C (50°F), SOUR fell to about 2.0 mg O_2/hr/g VSS after a total sludge age of 60 days and to 1.0 mg O_2/hr/g VSS after about 120 days sludge age. These authors state that a SOUR of less than 1.0 mg O_2/hr/g VSS at temperatures above 10°C (50°F) indicates a stable sludge.

The results obtained by these authors indicate that long digestion times--more than double the residence time for most aerobic digesters in use today--are needed to eliminate odor generation from aerobically digested sludges. Since the industry is not being deluged with complaints about odor from aerobic digesters, it appears that a higher SOUR standard can be chosen than they suggest without causing problems from odor (and vector attraction).

The results of long-term batch aerobic digestion tests by Jeris et al. (1985) provide information that is helpful in setting a SOUR requirement that is reasonably attainable and still protective. Farrell and Bhide (1993) reviewed the data these authors obtained with four sewage sludges from aerobic treatment processes and concluded that a standard of 1.5 mg O_2/hr/g TS at 20°C (68°F) would discriminate between adequately stabilized and poorly stabilized sludges. The "adequately digested" sludges were not totally trouble-free, i.e., it was possible under adverse conditions to develop odorous conditions. In all cases where the sludge was deemed to be adequate, minor adjustment in plant operating conditions created an acceptable sludge.

The SOUR requirement is based on total solids rather than volatile suspended solids. This usage is preferred for consistency with the rest of the Part 503 regulation where all loadings are expressed on a total solids basis. The use of total solids concentration in the SOUR calculation is rational since the entire sludge solids and not just the volatile solids degrade and may exert some oxygen demand. Making an adjustment for the difference caused by basing the requirement on TS instead of VSS, the standard is about 1.8 times higher than Eikum and Paulsrud's recommended value and 2.1 times higher than Ahlberg and Boykos' recommendation.

Unlike anaerobic digestion, which is typically conducted at 35°C (95°F), aerobic digestion is carried out without any deliberate temperature control. The temperature of the digesting sludge will be close to ambient temperature, which can range from 5°C to 30°C (41°F to 86°F). In this temperature range, SOUR increases with increasing temperature. Consequently, if a requirement for SOUR is selected, there must be some way to convert SOUR test results to a standard temperature. Conceivably, the problem could be avoided if the sludge were simply heated or cooled to the standard temperature before running the SOUR test. Unfortunately, this is not possible, because temperature changes in digested sludge cause short-term instabilities in oxygen uptake rate (Benedict and Carlson [1973], Farrell and Bhide [1993]).

Eikum and Paulsrud (1977) recommend that the following equation be used to adjust the SOUR determined at one temperature to the SOUR for another temperature:

$$(SOUR)_{T1} / (SOUR)_{T2} = \theta^{(T1-T2)} \quad (3)$$

where:

$(SOUR)_{T1}$ = specific oxygen uptake rate at T_1
$(SOUR)_{T2}$ = specific oxygen uptake rate at T_2
θ = the Streeter-Phelps temperature sensitivity coefficient

These authors calculated the temperature sensitivity coefficient using their data on the effect of temperature on the rate of reduction in volatile suspended solids with time during aerobic digestion. This is an approximate approach, because there is no certainty that there is a one-to-one relationship between oxygen uptake rate and rate of volatile solids disappearance. Another problem is that the coeffficient depends on the makeup of each individual sludge. For example, Koers and Mavinic (1977) found the value of θ to be less than 1.072 at temperatures above 15°C (59°F) for aerobic digestion of waste activated sludges, whereas Eikum and Paulsrud (1977) determined θ to equal 1.112 for primary sludges. Grady and Lim (1980) reviewed the data of several investigators and recommended that θ = 1.05 be used for digestion of waste-activated sludges when more specific information is not available. Based on a review of the available information and their own work, Farrell and Bhide (1993) recommend that Eikum and Paulsruds' temperature correction procedure be utilized, using a temperature sensitivity coefficient in the range of 1.05 to 1.07.

Recommended Procedure for Temperature Correction

A SOUR of 1.5 mg O_2/hr/g total solids at 20°C (68°F) was selected to indicate that an aerobically digested sludge has been adequately reduced in vector attraction.

The SOUR of the sludge is to be measured at the temperature at which the aerobic digestion is occurring in the treatment works and corrected to 20°C (68°F) by the following equation:

$$SOUR_{20} = SOUR_T \times \theta^{(20-T)} \quad (4)$$

where
θ = 1.05 above 20°C (68°F)
1.07 below 20°C (68°F)

This correction may be applied only if the temperature of the sludge is between 10°C and 30°C (50°F and 86°F). The restriction to the indicated temperature range is required to limit the possible error in the SOUR caused by selecting an improper temperature coefficient. Farrell and Bhide's (1993) results indicate that the suggested values for θ will give a conservative value for SOUR when translated from the actual temperature to 20°C (68°F).

The experimental equipment and procedures for the SOUR test are those described in Part 2710 B, Oxygen Consumption Rate, of Standard Methods (APHA, 1992). The method allows the use of a probe with an oxygen-sensitive electrode or a respirometer. The method advises that manufacturer's directions be followed if a respirometer is used. No further reference to respirometric methods will be made here. A timing device is needed as well as a 300-mL biological oxygen demand (BOD) bottle. A magnetic mixer with stirring bar is also required.

The procedure of Standard Method 2710 B should be followed with one exception. The total solids concentration instead of the volatile suspended solids concentration is used in the calculation of the SOUR. Total solids concentration is determined by Standard Method 2540 G. Method 2710 B cautions that if the suspended solids content of the sludge is greater than 0.5%, additional stirring besides that provided by the stirring bar be considered. Experiments by Farrell and Bhide (1993) were carried out with sludges up to 2% in solids content without difficulty if the SOUR was lower than about 3.0 mg O_2/g/h. It is possible to verify that rnixing is adequate by running repeat measurements at several stirrer bar speeds. If stirring is adequate, oxygen uptake will be independent of stirrer speed.

The inert mineral solids in the wastewater in which the sludge particles are suspended do not exert an oxygen demand and probably should not be part of the total solids in the SOUR determination. Ordinarily, they are such a small part of the total solids that they can be ignored. If the ratio of inert dissolved mineral solids in the treated wastewater to the total solids in the sludge being tested is greater than 0.15, a correction should be made to the total solids concentration. Inert dissolved mineral solids in the treated wastewater effluent is determined by the method of Part 2540 B of Standard Methods (APHA, 1992). This quantity is subtracted from the total solids of the sludge to determine the total solids to be used in the SOUR calculation.

The collection of the sample and the time between sample collection and measurement of the SOUR are important. The sample should be a composite of grab samples taken within a period of a few minutes duration. The sample should be transported to the laboratory expeditiously and kept under aeration if the SOUR test cannot be run immediately. The sludge should be kept at the temperature of the digester from which it was drawn and aerated thoroughly before it is poured into the BOD bottle for the test. If the temperature differs from 20°C (68°F) by more than ±10°C (±18°F), the temperature correction may be inappropriate and the result should not be used to prove that the sewage sludge meets the SOUR requirement.

Variability in flow rates and nature of the sludge will result in variability in performance of the plant-scale digesters. It is advisable to run the SOUR test routinely so that sufficient data are available to indicate average performance. The arithmetic mean of successive tests-a minimum of seven over 2 or 3 weeks is suggested-should give a SOUR of ≤ 1.5 mg O_2/hr/g total solids.

3. Additional Digestion Test for Aerobically Digested Sewage Sludge

Background

Part 503 lists several options that can be used to demonstrate reduction of vector attraction in sewage sludge. These options include reduction of volatile solids by 38% and demonstration of the SOUR value discussed above (see also Chapter 8). These options are feasible for many, but not all, digested sludges. For example, sludges from extended aeration treatment works that are aerobically di-

gested usually cannot meet this requirement because they already are partially reduced in volatile solids content by their exposure to long aeration times in the wastewater treatment process.

The specific oxygen uptake test can be utilized to evaluate aerobic sludges that do not meet the 38% volatile solids reduction requirement. Unfortunately, this test has a number of limitations. It cannot be applied if the sludges have been digested at temperatures lower than 10°C (50°F) or higher than 30°C (86°F). It has not been evaluated under all possible conditions of use, such as for sludges of more than 2% solids.

A straightforward approach for aerobically treated sludges that cannot meet either of the above criteria is to determine to what extent they can be digested further. If they show very little capacity for further digestion, they will have a low potential for additional biodegradation and odor generation that attracts vectors. Such a test necessarily takes many days to complete, because time must be provided to get measurable biodegradation. Under most circumstances, this is not a serious drawback. If a digester must be evaluated every 4 months to see if the sewage sludge meets vector attraction reduction requirements, it will be necessary to start a regular assessment program. A record can be produced showing compliance. The sludge currently being produced cannot be evaluated quickly but it will be possible to show compliance over a period of time.

The additional digestion test for aerobically digested sludges in Part 503 is based on research by Jeris et al. (1985), and has been discussed by Farrell et al. (EPA, 1992). Farrell and Bhide (1993) explain in more detail the origin of the time and volatile solids reduction requirements of the test.

Jeris et al. (1985) demonstrated that several parameters--volatile solids reduction, COD, BOD, and SOUR--declined smoothly and approached asymptotic values with time as sludge was aerobically digested. Any one of these parameters potentially could be used as an index of vector attraction reduction for aerobic sludges. SOUR has been adopted (see above) for this purpose. Farrell and Bhide (1993) have shown that the additional volatile solids reduction that occurs when sludge is batch digested aerobically for 30 days correlates equally as well as SOUR with the degree of vector attraction reduction of the sludge. They recommend that a sewage sludge be accepted as suitably reduced in vector attraction when it shows less than 15% additional volatile solids reduction after 30 days additional batch digestion at 20°C (68°F). For three out of four sludges investigated by Jeris et al. (1985), the relationship between SOUR and additional volatile solids reduction showed that the SOUR was approximately equal to 1.5 mg O_2/hr/g (the Part 503 requirement for SOUR) when additional volatile solids reduction was 15%. The two requirements thus agree well with one another.

Recommended Procedure

There is considerable flexibility in selecting the size of the digesters used for the additional aerobic digestion test. Farrell and Bhide (1993) used a 20-liter fish tank. A tank of rectangular cross-section is suggested because sidewalls are easily accessible and are easily scraped clean of adhering solids. The tank should have a loose-fitting cover that allows air to escape. It is preferable to vent exhaust gas to a hood to avoid exposure to aerosols. Oil and particle-free air is supplied to the bottom of the digester through porous stones at a rate sufficient to thoroughly mix the sewage sludge. This will supply adequate oxygen to the sludge, but the oxygen level in the digesting sludge should be checked with a dissolved oxygen meter to be sure that the supply of oxygen is adequate. Oxygen level should be at least 2 mg/L. Mechanical mixers also were used to keep down foam and improve mixing.

If the total solids content of the sewage sludge is greater than 2%, the sludge must be diluted to 2% solids with secondary effluent at the start of the test. The requirement stems from the results of Reynolds (1973) and Malina (1966) which demonstrate that rate of volatile solids reduction decreases as the feed solitis concentration increases. Thus, for example, a sludge with a 2% solids content that showed more than 15% volatile solids reduction when digested for 30 days might show a lower volatile solids reduction and would pass the test if it were at 4%. This dilution may cause a temporary change in rate of volatile solids reduction. However, the long duration of the test should provide adequate time for recovery and demonstration of the appropriate reduction in volatile solids content.

When sampling the sludge, care should be taken to keep the sludge aerobic and avoid unnecessary temperature shocks. The sludge is digested at 20°C (68°F) even if the digester was at some other temperature. It is expected that the bacterial population will suffer a temporary shock if there is a substantial temperature change, but the test is of sufficient duration to overcome this effect and show a normal volatile solids reduction. Even if the bacteria are shocked and do not recover completely, the test simulates what would happen to the sludge in the environment. If it passes the test, it is highly unlikely that the sludge will attract vectors when used or disposed to the environment. For example, if a sludge digested at 35°C (95°F) has not been adequately reduced in volatile solids and is shocked into biological inactivity for 30 days when its temperature is lowered to 20°C (68°F), it will be shocked in the same way if it is applied to the soil at ambient temperature. Consequently, it is unlikely to attract vectors.

The digester is charged with about 12 liters of the sewage sludge to be additionally digested, and aeration is commenced. The constant flow of air to the aerobic digestion test unit will cause a substantial loss of water from the digester. Water loss should be made up every day with distilled water.

Solids that adhere to the walls above and below the water line should be scraped off and dispersed back into the sludge daily. The temperature of the digesting sludge should be approximately 20°C (68°F). If the temperature of the labora-

tory is maintained at about 22°C (72°F), evaporation of water from the digester will cool the sludge to about 20°C (68°F).

Sewage sludge is sampled every week for five successive weeks. Before sampling, makeup water is added (this will generally require that air is temporarily shut off to allow the water level to be established), and sludge is scraped off the walls and redistributed into the digester. The sludge in the digester is thoroughly mixed with a paddle before sampling, making sure to mix the bottom sludge with the top. The sample is comprised of several grab samples collected with a ladle while the digester is being mixed. The entire sampling procedure is duplicated to collect a second sample.

Total and volatile solids contents of both samples are determined preferably by Standard Method 2540 G (APHA, 1992). Percent volatile solids is calculated from total and volatile solids content. Standard Methods (APHA, 1992) states that duplicates should agree within 5% of their average. If agreement is substantially poorer than this, the sampling and analysis should be repeated.

Calculation Details

Fraction volatile solids reduction is calculated by the Van Kleeck formula (see Appendix C) and by a mass balance method. The mass balance (m.b.) equations become very simple, because final mass of sludge is made very nearly equal to initial mass of sludge by adjusting the volume by adding water. These equations for fractional volatile solids reduction (FVSR) and fractional fixed solids reduction (FFSR) are:

$$FVSR(m.b.) = (y_f - y_b) / y_f \quad (5a)$$

$$FFSR(m.b.) = (x_f - x_b) / x_f \quad (5b)$$

where:

y and x = mass fraction of volatile and fixed solids, respectively (see previous section on "Calculation details" for explanation of "mass fraction")

f and b = subscripts indicating initial and final sludges

This calculation assumes that initial and final sludge densities are the same. Very little error is introduced by this assumption.

The calculation of the fractional fixed solids reduction is not a requirement of the test, but it will provide useful information.

The test was developed from information based on the reduction in volatile solids content calculated by the Van Kleeck equation. As noted in the section on the additional anaerobic digestion test, for batch processes the material balance procedure for calculating volatile solids reduction is superior to the Van Kleeck approach. It is expected that the volatile solids reduction by the mass balance method will show a higher volatile solids reduction than the calculation made by using the Van Kleeck equation.

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Appendix E
Determination of Residence Time for Anaerobic and Aerobic Digestion

Introduction

The PSRP and PFRP specifications in 40 CFR 257 for anaerobic and aerobic digestion not only specify temperatures but also require minimum mean cell residence times of the sludge in the digesters. The mean cell residence time is the time that the sludge particles are retained in the digestion vessel under the conditions of the digestion. The calculation of residence time is ordinarily simple but it can become complicated under certain circumstances. This appendix describes how to make this calculation for most of the commonly encountered modes for operating digesters.

Approach

The discussion has to be divided into two parts: residence time for batch operation and for plug flow, and residence time for fully mixed digesters. For batch operation, residence time is obvious--it is the duration of the reaction. For plug flow, the liquid--solid mixture that is sludge passes through the reactor with no backward or forward mixing. The time it takes the sludge to pass through the reactor is the residence time. It is normally calculated by the following equation:

$$\theta = V/q \quad (1)$$

where
θ = plug flow solids residence time
V = volume of the liquid in the reactor
q = volume of the liquid leaving the reactor

Normally the volume of liquid leaving the reactor will equal the volume entering. Conceivably, volume leaving could be smaller (e.g., because of evaporation losses) and residence time would be longer than expected if θ were based on inlet flow. Ordinarily, either inlet or outlet flow rate can be used.

For a fully mixed reactor, the individual particles of the sludge are retained for different time periods--some particles escape very soon after entry whereas others circulate in the reactor for long periods before escaping. The average time in the reactor is given by the relationship:

$$\theta_n = \frac{\Sigma(\delta s \times \theta)}{\Sigma(\delta s)} \quad (2)$$

where
δs = an increment of sludge solids that leaves the reactor
θ = time period this increment has been in the reactor
θ_n = nominal average solids residence time

When the flow rates of sludge into and out of the completely mixed vessel are constant, it can be demonstrated that this equation reduces to:

$$\theta_n = \frac{VC_v}{qC_q} \quad (3)$$

where
V = reactor volume
q = flow rate leaving
C_v = concentration of solids in the reactor
C_q = concentration of solids in exiting sewage sludge

It is important to appreciate that q is the flow rate leaving the reactor. Some operators periodically shut down reactor agitation, allow a supernatant layer to form, decant the supernatant, and resume operation. Under these conditions, the flow rate entering the reactor is higher than the flow rate of sludge leaving.

Note that in Equation 3, VC_v is the mass of solids in the system and qC is the mass of solids leaving. Ordinarily C_v equals C_q and these terms could be canceled. They are left in the equation because they show the essential form of the residence time equation:

$$\theta_n = \frac{\text{mass of solids in the digester}}{\text{mass flow rate of solids leaving}} \quad (4)$$

Using this form, residence time for the important operating mode in which sludge leaving the digester is thickened and returned to the digester can be calculated.

In many aerobic digestion installations, digested sludge is thickened with part of the total volume returned to increase residence time and part removed as product. The calculation follows Equation 4 and is identical with the SRT (solids retention time) calculation used in activated sludge process calculations. The focus here is on the solids in the digester and the solids that ultimately leave the system. Applying Equation 4 for residence time then leads to Equation 5:

$$\theta_n = \frac{VC_v}{pC_p} \quad (5)$$

where

p = flow rate of processed sludge leaving the system
C_p = solids concentration in the processed sludge

The subscript p indicates the final product leaving the system, not the underflow from the thickener. This approach ignores any additional residence time in the thickener since this time is relatively short and not at proper digestion conditions.

Sample Calculations

In the following paragraphs, the equations and principles presented above are used to demonstrate the calculation of residence time for several commonly used digester operating modes:

Case 1

- Complete-mix reactor
- Constant feed and withdrawal at least once a day
- No substantial increase or decrease in volume in the reactor (V)
- One or more feed streams and a single product stream (q)

The residence time desired is the nominal residence time. Use Equation 3 as shown below:

$$\theta_n = \frac{VC_v}{qC_q} = \frac{V}{q}$$

The concentration terms in Equation 4 cancel out because C_v equals C_q.

Case 2a

- Complete-mix reactor
- Sludge is introduced in daily batches of volume (V_i) and solids concentration (C_i)
- Vessel contains a "heel" of liquid sludge (V_f) at the beginning of the digestion step
- When final volume (V_f) is reached, sludge is discharged until V_h remains and the process starts again

Some aerobic digesters are run in this fashion. This problem is a special case involving a batch reaction. Exactly how long each day's feeding remains in the reactor is known, but an average residence time must be calculated as shown in Equation 2:

$$\theta_n = \frac{\Sigma v_i C_i \times \text{time that batch i remains in the reactor}}{\Sigma v_i C_i}$$

The following problem illustrates the calculation:

Let V_h = 30 m^3 (volume of "heel")
V_d= 130 m^3 (total digester volume)
V_i = each day 10 m3 is fed to the reactor at the beginning of the day
C_i =12 kg/m^3
V_f is reached in 10 days. Sludge is discharged at the end of Day 10.

$$\text{Then } \theta_n = \frac{(10\cdot12\cdot10+10\cdot12\cdot9+\ldots+10\cdot12\cdot1)}{(10\cdot12+10\cdot12+\ldots 10\cdot12)}$$

$$\theta_n = \frac{10\cdot12\cdot55}{10\cdot12\cdot10} = 5.5 \text{ days}$$

Notice that the volume of the digester or of the "heel" did not enter the calculation.

Case 2b

Same as Case 2a except:

- The solids content of the feed varies substantially from day to day
- Decantate is periodically removed so more sludge can be added to the digester

The following problem illustrates the calculation:

Let V_h = 30m^3, and V_d = 130m^3

Day	V_i (m^3)	Solids Content (kg/m^3)	Decantate (m^3)
1	10	10	0
2	10	15	0
3	10	20	0
4	10	15	0
5	10	15	0
6	10	10	0
7	10	20	0
8	10	25	0
9	10	15	10
10	10	10	0
11	10	15	10
12	10	20	0

$$\theta_n = \frac{(10\cdot10\cdot12+10\cdot15\cdot11+10\cdot20\cdot10+\ldots+10\cdot10\cdot3+10\cdot15\cdot2+10\cdot20\cdot1)}{(10\cdot10+10\cdot15+10\cdot20+\ldots+10\cdot10+10\cdot15+10\cdot20}$$

θ_n = 11,950/1,900 = 6.29d

The volume of "heel" and sludge feedings equaled 150 m^3, exceeding the volume of the digester. This was made possible by decanting 20 m^3.

Case 3

Same as Case 2 except that after the digester is filled it is run in batch mode with no feed or withdrawals for several days.

A conservative θ_n can be calculated by simply adding the number of extra days of operation to the θ_n calculated

for Case 2. The same applies to any other cases followed by batch mode operation.

Case 4

- Complete-mix reactor
- Constant feed and withdrawal at least once a day
- No substantial increase or decrease of volume in the reactor
- One or more feed streams, one decantate stream returned to the treatment works, one product stream; the decantate is removed from the digester so the sludge in the digester is higher in solids than the feed

This mode of operation is frequently used in both anaerobic and aerobic digestion in small treatment works.

Equation 3 is used to calculate the residence time:

Let V=100 m^3
q_f = 10 m^3/d (feed stream)
C_f = 40 kg solids/m^3
q = 5 m^3/d (existing sludge stream)
C_v = 60 kg solids/m^3

$$\theta_n = \frac{100 \times 60}{5 \times 60} = 20 \text{d}$$

Case 5

- Complete-mix reactor
- Constant feed and withdrawal at least once a day
- Volume in digester reasonably constant
- One or more feed streams, one product stream that is thickened, some sludge is recycled, and some is drawn off as product

This mode of operation is sometimes used in aerobic digesters. Equation 5 is used to calculate residence time.

Let V = 100 m^3
Feed flow rate = 10 m^3/d
Feed solids content = 10 kg/m^3
Flow rate from the digester = 12 m^3/d
Solids content of sludge from the digester = 13.3 kg/m^3
Flow rate of sludge from the thickener = 4 m^3/d
Solids content of sludge from the thickener = 40 kg/m^3
Flow rate of sludge returned to the digester = 2 m^3/d
Flow rate of product sludge = 2 m^3/d

$$\theta_n = \frac{100 \times 13.3}{2 \times 40} = 16.6 \text{ d}$$

The denominator is the product of the flow rate leaving the system (2 m^3/d) and the concentration of sludge leaving the thickener (40 kg/m^3). Notice that flow rate of sludge leaving the digester did not enter into the calculation.

Comments on Batch and Staged Operation

Sludge can be aerobically digested using a variety of process configurations (including continuously fed single- or multiple-stage completely mixed reactors), or it can be digested in a batch mode (batch operation may produce less volatile solids reduction for a primary sludge than the other options because there are lower numbers of aerobic microorganisms in it). Single-stage completely mixed reactors with continuous feed and withdrawal are the least effective of these options for bacterial and viral destruction, because organisms that have been exposed to the adverse condition of the digester for only a short time can leak through to the product sludge.

Probably the most practical alternative to use of a single completely mixed reactor for aerobic digestion is staged operation, such as use of two or more completely mixed digesters in series. The amount of slightly processed sludge passing from inlet to outlet would be greatly reduced compared to single-stage operation. If the kinetics of the reduction in pathogen densities are known, it is possible to estimate how much improvement can be made by staged operation.

Farrah et al. (1986) have shown that the declines in densities of enteric bacteria and viruses follow first-order kinetics. If first-order kinetics are assumed to be correct, it can be shown that a one-log reduction of organisms is achieved in half as much time in a two-stage reactor (equal volume in each stage) as in a one-stage reactor. Direct experimental verification of this prediction has not been carried out, but Lee et al. (1989) have qualitatively verified the effect.

It is reasonable to give credit for an improved operating mode. Since not all factors involved in the decay of microorganisms densities are known, some factor of safety should be introduced. It is recommended then that for staged operation using two stages of approximately equal volume, the time required be reduced to 70% of the time required for single-stage aerobic digestion in a continuously mixed reactor. This allows a 30% reduction in time instead of the 50% estimated from theoretical considerations. The same reduction is recommended for batch operation or for more than two stages in series. Thus, the time required would be reduced from 40 days at 20°C (68°F) to 28 days at 20°C (68°F), and from 60 days at 15°C (59°F) to 42 days at 15°C (59°F). These reduced times are also more than sufficient to achieve adequate vector attraction reduction.

If the plant operators desire, they may dispense with the PSRP time-temperature requirements of aerobic digestion but instead demonstrate experimentally that microbial levels in the product from their sludge digester are satisfactorily reduced. Under the current regulations, fecal coliform densities must be less than or equal to 2,000,000 CFU or MPN per gram total solids. Once this performance is demonstrated, the process would have to be operated between monitoring episodes at time-temperature conditions at least as severe as those used during their tests.

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Appendix F
Sample Preparation for Fecal Coliform Tests and *Salmonella* sp. Analysis

1. Sample Preparation for Fecal Coliform Tests

1.1 Class B Alternative 1

To demonstrate that a given domestic sludge sample meets Class B Pathogen requirements under alternative 1, the density of fecal coliform from at least seven samples of treated sewage sludge must be determined and the geometric mean of the fecal coliform density must not exceed 2 million Colony Forming Units (CFU) or Most Probable Number (MPN) per gram of total solids (dry weight basis). The solids content of treated domestic sludge can be highly variable. Therefore, an aliquot of each sample must be dried and the solids content determined in accordance with procedure 2540 G. of the 18th edition of Standard Methods for the Examination of Water and Wastewater (SM).

Sludge samples to be analyzed in accordance with SM 9221 E. Fecal Coliform MPN Procedure and 9222 D. Fecal Coliform Membrane Filter Procedure may require dilution prior to analysis. An ideal sample volume will yield results which accurately estimate the fecal coliform density of the sludge. Detection of fecal coliform in undiluted samples could easily exceed the detection limits of these procedures. Therefore, it is recommended that the following procedures be used (experienced analysts may substitute other dilution schemes as appropriate).

For Liquid Samples:

1. Use a sterile graduated cylinder to transfer 30.0 mL of well mixed sample to a sterile blender jar. Use 270 mL of sterile buffered dilution water (see Section 9050C) to rinse any remaining sample from the cylinder into the blender. Cover and blend for two minutes on high speed. 1.0 mL of this mixture is 0.1 mL of the original sample or $1.0X10^{-1}$.

2. Use a sterile pipette to transfer 11.0 mL of the blended sample mixture to 99 mL of sterile buffered dilution in a sterile screw cap bottle and mix by vigorously shaking the bottle a minimum of 25 times. This is dilution "A." 1.0 mL of this mixture is 0.010 mL of the original sample or $1.0X10^{-2}$.

3. Use a sterile pipette to transfer 1.0 mL of dilution "A" to a second screw cap bottle containing 99 mL of sterile buffered dilution water, and mix as before. This is dilution "B." 1.0 mL of this mixture is 0.00010 mL of the original sample or $1.0X10^{-4}$.

4. Use a sterile pipette to transfer 1.0 mL of dilution "B" to a sterile screw cap bottle containing 99 mL of sterile buffered dilution water, and mix as before. This is dilution "C." Go to step 5 for MPN analysis (preferred) or 7 for MF analysis.

5. For MPN analysis, follow procedure 9221 E. in SM. Four series of 5 tubes will be used for the analysis. Inoculate the first series of 5 tubes each with 10.0 mL of dilution "B." This is a 0.0010 mL of the original sample. The second series of tubes should be inoculated with 1.0 mL of dilution "B" (0.00010). The third series of tubes should receive 10.0 mL of "C" (0.000010). Inoculate a fourth series of 5 tubes each with 1.0 mL of dilution "C" (0.0000010). Continue the procedure as described in SM.

6. Refer to Table 9221.IV. in SM to estimate the MPN index/100 mL. Only three of the four series of five tubes will be used for estimating the MPN. Choose the highest dilution that gives positive results in all five tubes, and the next two higher dilutions for your estimate. Compute the MPN/g according to the following equation:

$$\text{MPN Fecal Coliform/g} = \frac{10 \times \text{MPN Index/100 mL}}{\text{largest volume} \times \% \text{ dry solids}}$$

Examples:

In the examples given below, the dilutions used to determine the MPN are underlined. The number in the numerator represents positive tubes; that in the denominator, the total number of tubes planted; the combination of positives simply represents the total number of positive tubes per dilution.

Example	0.0010 mL	0.00010 mL	0.000010 mL	0.0000010 mL	Combination of positives
a	5/5	5/5	3/5	0/5	5-3-0
b	5/5	3/5	1/5	0/5	5-3-1
c	0/5	1/5	0/5	0/5	0-1-0

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For each example we will assume that the total solids content is 4.0%.

For example a:

The MPN index/100 mL from Table 9221.4 is 80. Therefore:

$$MPN/g = \frac{10 \times 80}{0.00010 \times 4.0} = 2.0 \times 10^6$$

For example b:

The MPN index/100 mL from Table 9221.4 is 110. Therefore:

$$MPN/g = \frac{10 \times 110}{0.0010 \times 4.0} = 2.8 \times 10^5$$

For example c:

The MPN index/100 mL from Table 9221.4 is 2. Therefore:

$$MPN/g = \frac{10 \times 2}{0.0010 \times 4.0} = 5.0 \times 10^3$$

5. Alternately the membrane filter procedure may be used to determine fecal coliform density. This method should only be used if comparability with the MPN procedure has been established for the specific sample medium. Three individual filtrations should be conducted in accordance with SM 9222 D. using 10.0 mL of dilution "C," and 1.0 mL and 10.0 mL of dilution "B." These represent 0.000010, 0.00010, and 0.0010 mL of the original sample. Incubate samples, and count colonies as directed. Experienced analysts are encouraged to modify this dilution scheme (e.g. half log dilutions) in order to obtain filters which yield between 20 and 60 CFU.

6. Compute the density of CFU from membrane filters which yield counts within the desired range of 20 to 60 fecal coliform colonies:

$$\text{coliform colonies/g} = \frac{\text{coliform colonies counted} \times 100}{\text{mL sample} \times \% \text{ dry solids}}$$

For Solid Samples:

1. In a sterile dish weigh out 30.0 grams of well mixed sample. Whenever possible, the sample tested should contain all materials which will be included in the sludge. For example, if wood chips are part of a sludge compost, some mixing or grinding means may be needed to achieve homogeneity before testing. One exception would be large pieces of wood which are not easily ground and may be discarded before blending. Transfer the sample to a sterile blender. Use 270 mL of sterile buffered dilution water to rinse any remaining sample into the blender. Cover and blend on high speed for two minutes. One milliliter of this sample contains 0.10 g of the original sample.

2. Use a sterile pipette to transfer 11.0 mL of the blender contents to a screw cap bottle containing 99 mL of sterile buffered dilution water and shake vigorously a minimum of 25 times. One milliliter of this sample contains 0.010 g of the original sample. This is dilution "A."

3. Follow the procedures for "Liquid Samples" starting at Step 3.

Examples:

Seven samples of a treated sludge were obtained prior to land spreading. The solids concentration of each sample was determined according to SM. These were found to be:

Sample No.	Solids Concentration (%)
1	3.8
2	4.3
3	4.0
4	4.2
5	4.1
6	3.7
7	3.9

The samples were liquid with some solids. Therefore the procedure for liquid sample preparation was used. Furthermore, the membrane filter technique was used to determine if the fecal coliform concentration of the sludge would meet the criteria for Class B alternative 1. Samples were prepared in accordance with the procedure outlined above. This yielded 21 individual membrane filters (MF) plus controls. The results from these tests are shown in Table 1

Table 1. Number of Fecal Coliform Colonies on MF Plates

Sample No.	0.000010 mL Filtration	0.00010 mL Filtration	0.0010 mL Filtration
1	0	1	23
2	2	18	TNTC
3	0	8	65
4	0	5	58
5	0	1	17
6	0	1	39
7	0	1	20

The coliform density is calculated using only those MF plates which have between 20 and 60 blue colonies whenever possible. However, there may be occasions when the total number of colonies on a plate will be above or below the ideal range. If the colonies are not discrete and appear to be growing together results should be reported as "too numerous to count" (TNTC). If no filter has a coliform count falling in the ideal range (20 - 60), total the coliform counts on all countable filters and report as coliform colonies/g. For sample number 2 the fecal coliform density is:

$$\text{coliform colonies/g} = \frac{(2+18)\times 100}{(0.000010 + 0.00010) \times 4.3} = 4.2 \times 10^6$$

Sample number 3 has two filters which have colony counts outside the ideal range also. In this case both countable plates should be used to calculate the coliform density/g. For sample number 3, the fecal coliform density is:

$$\text{coliform colonies/g} = \frac{(8 + 65) \times 100}{(0.00010 + 0.0010) \times 4.0} = 1.6 \times 10^6$$

Except for sample number 5, all of the remaining samples have at least one membrane filter within the ideal range. For these samples, use the number of colonies formed on that filter to calculate the coliform density. For sample number 1, the fecal coliform density is:

$$\text{coliform colonies/g} = \frac{23\times 100}{0.0010 \times 3.8} = 6.0 \times 10^5$$

Coliform densities of all the samples were calculated and converted to $\log_{10}$ values to compute a geometric mean. These calculated values are presented in Table 2.

Table 2. Coliform Density of Sludge Samples

Sample No.	Coliform Density	$\log_{10}$
1	6.0×10^5	5.78
2	4.2×10^6	6.63
3	1.6×10^6	6.22
4	1.4×10^5	6.14
5	4.0×10^5	5.60
6	1.0×10^6	6.02
7	5.1×10^5	5.71

The geometric mean for the seven samples is determined by averaging the $\log_{10}$ values of the coliform density and taking the antilog of that value.

$(5.78 + 6.63 + 6.22 + 6.14 + 5.60 + 6.02 + 5.71)/7 = 6.01$

The antilog of $6.01 = 1.03 \times 10^6$

Therefore, the geometric mean fecal coliform density is below 2 million and the sludge meets Class B Pathogen requirements under alternative 1.

1.2 Class A Alternative 1

Part 503 requires that, to qualify as a Class A sludge, treated sewage sludge must be monitored for fecal coliform (or *Salmonella* sp. and have a density of less than 1,000 MPN fecal coliform per gram of total solids (dry weight basis). The regulation does not specify total number of samples. However, it is suggested that a sampling event extend over two weeks and that at least seven samples be collected and analyzed. The membrane filter procedure may not be used for this determination. This is because the high concentration of solids in such sludges may plug the filter or, render the filter uncountable. The total solids content for each sample must be determined in accordance with procedure 2540 G. of SM.

For Liquid Samples:

1. Follow procedure 9221 E. in SM. Inoculate at least four series of five tubes using ten fold serial dilutions. Prepare the sample as described for "Class B Alternative 1, Liquid Samples," except inoculate each of the first series of tubes with 10.0 mL of the blender contents (the concentration of the enrichment broth must be adjusted to compensate for the volume of added sample). This is equivalent to adding 1.0 mL of sludge to the first series of tubes. Inoculate the remaining tubes and complete the analysis in accordance with SM.

2. Calculate the MPN as directed in Step 4 above.

For Solid Samples:

1. Follow procedure 9221 E. in SM. Inoculate at least four series of five tubes using ten fold serial dilutions. Prepare the sample as described for "Class B Alternative 1, Solid Samples," except inoculate each of the first series of tubes with 10.0 mL of the blender contents (the concentration of the enrichment broth must be adjusted to compensate for the volume of added sample). This is equivalent to adding 1.0 g of sludge (wet wieght) to the first series of tubes. Inoculate the remaining tubes and complete the analysis in accordance with SM.

2. Calculate the MPN as directed in step 4 above.

2. Sample Preparation for *Salmonella* sp. Analysis

Salmonella sp. quantification may be used to demonstrate that a sludge meets Class A criteria, instead of analyzing for fecal coliforms. Sludges with *Salmonella* sp. densities below 3 MPN/4 g total solids (dry weight basis) meet Class A criteria. The analytical method described in Appendix F of this document describes the procedure used to identify *Salmonella* sp. in a water sample. Similarly, the procedures for analysis of *Salmonella* sp. in SM (Section 9260 D) do not address procedures for sludges, the sample preparation step described here should be used, and the total solids content of each sample must be determined according to method 2540 G in SM.

For Liquid Samples:

1. Follow the same procedure used for liquid sample preparation for fecal coliform analysis described under "Class A Alternative 1." However, the enrichment medium used for this analysis should be dulcitol selenite broth (DSE) as described in Appendix G of this document or dulcitol selenite or tetrathionate broth as described in SM. Only three series of five tubes should be used for this MPN procedure. Use a sterile open tip pipette to transfer 10.0 mL of well mixed sample to each tube in the first series. These tubes should contain 10.0 mL of double strength enrichment broth. Each tube in the second series should contain 10.0 mL of double strength enrichment broth. These tubes should each receive 10.0

mL of the blended mixture. The final series of tubes should contain 10.0 mL of single strength enrichment broth. These tubes should each receive 1.0 mL of the blended mixture. Complete the MPN procedure as described in Appendix G or SM as appropriate.

2. Refer to Table 9221.IV. in SM to estimate the MPN index/100 mL. Calculate the MPN/4 g according to the following equation:

$$\textit{Salmonella}\text{ sp. MPN/4 g} = \frac{\text{MPN Index/100 mL x 4}}{\text{\% dry solids}}$$

For example:

If one tube in the first series was identified as being positive for *Salmonella* sp. and no other tubes were found to be positive, from Table 9221.IV one finds that a 1-0-0 combination of positives has an MPN index/100 mL of 2. If the percent of dry solids for the sample was 4.0, then:

$$\textit{Salmonella}\text{ sp. MPN/4g} \qquad \frac{2 \text{ x } 4}{4.0} = 2$$

For Solid Samples:

1. Follow the procedure for solid sample preparation for fecal coliform analysis described under Class A Alternative 1 above. However, the enrichment medium used for this analysis should be dulcitol selenite broth (DSE) as described in Appendix G or dulcitol selenite or tetrathionate broth as described in SM, and only three series of five tubes should be used for this MPN procedure. Use aseptic technique to weigh out and transfer 10.0 g of well mixed sample to each screw cap tube in the first series, shake vigorously to mix. These tubes should contain 10.0 mL of double strength enrichment broth. Likewise, each tube in the second series should contain 10.0 mL of double strength enrichment broth. These tubes should receive 10.0 mL of the blended mixture. The final series of tubes should contain 10.0 mL of single strength enrichment broth. These tubes should receive 1.0 mL of the blended mixture. Alternately, because the calculated detection limit is dependent upon the total solids content of the sample, samples with total solids contents >28% can be blended as described above and the blender contents can be used for inoculating the initial series of tubes. When this option is chosen, the final series of tubes will contain 0.1 mL of the blender contents. Complete the MPN procedure as described in Appendix G or SM as appropriate.

2. Refer to Table 9221.IV. in SM to estimate the MPN index/100 mL. Calculate the MPN/4 g according to the following equation:

$$\textit{Salmonella}\text{ sp. MPN/4g} = \frac{\text{MPN Index/1 00mL x 4}}{\text{\% dry solids}}$$

Appendix G
Kenner and Clark (1974) Analytical Method for *Salmonella* sp. Bacteria*

Detection and enumeration of *Salmonella* and *Pseudomonas aeruginosa*

BERNARD A. KENNER AND HAROLD P. CLARK

THE FEDERAL WATER POLLUTION CONTROL AMENDMENTS of 1972 [1-4] may well require the quantification and enumeration of pathogens such as *Salmonella* species in all classes of waters. The requirements are described by Shedroff. [5]

One of the continuing programs of the Environmental Protection Agency (EPA) is a research project concerned with the development of practical laboratory methods for the isolation, quantification, and enumeration of pathogens from polluted waters. This paper reports a monitoring method developed for the simultaneous isolation and enumeration of *Salmonella* species and *Pseudomonas aeruginosa* from potable waters, reuse waters, treatment plant effluents, receiving waters, and sludges.

The method described herein, and developed by Kenner,[6] is practical because readily available bacteriological media, chemicals, and equipment are all that are required to obtain the desired results. These results are the establishment of the absence or presence of *Salmonella* species (pathogenic hazardous bacteria) and/or *Pseudomonas aeruginosa* (potential pathogens) that affect persons who are in a debilitated condition and are very common as infectious agents in hospitals because of their resistance to antibiotic therapy.[7-9] Potable waters have also been shown to contain *Ps. aeruginosa.*[6,10] The sources of these potential pathogens are human and animal feces and wastewaters.[11,12]

When the monitoring method was used, it was found that 100 percent of municipal wastewaters and treatment plant sludges contained both of these potential pathogens. *Ps. aeruginosa* has been found in potable water supplies of large and small municipalities where insufficient residual chlorine is evident. Also important is the fact that these organisms may be found in the absence of fecal coliforms, whereas negative indicator tests may give a false sense of security. It is believed by the authors that these organisms may be better indicators than fecal coliforms of pollution in potable, direct reuse, bathing, and recreational waters.

MATERIALS AND METHODS

The monitoring method uses a multiple tube (MPN) procedure in which dulcitol selenite broth (DSE) [13] is used for primary enrichment medium, and is modified by the use of sodium acid selenite (BBL). The formula is proteose peptone (Bacto), 0.4 percent; yeast extract (Bacto), 0.15 percent; dulcitol, 0.4 percent; BBL, 0.5 percent; Na_2HPO_4, 0.125 percent; and KH_2PO_4, 0.125 percent in distilled water. The constituents are dissolved in a sterile flask, covered with foil, and heated to 88°C in a water bath to obtain a clear sterile medium that does not require adjustment of pH. Productivity for *Salmonella* species is enhanced by the addition of an 18-hr, 37°C culture of *Salmonella paratyphi* A (10 percent by volume) in single-strength DSE broth, killed by heating to 88°C.

Concentration of bacteria from large volumes of water is necessary when potable, direct reuse, receiving waters, and treatment effluents are being monitored.

TABLE I.-Retentive Characteristics of Several Glass Fiber Filter Papers* Compared with Membrane Filters

Filter	Total Bacteria † Filtered	Number Passing Filter	Percentage Retention
Millipore (MF) HAWG 047 HA 0.45 μ, white, grid, 47 mm, Millipore Filter Corp.	1,376	0	100
984H Ultra Glass Fiber Filter, 47 mm, Reeve Angel Corp.	1,229	25	98
GF/F Glass Paper Whatman, ‡47 mm, Reeve Angel Corp.	2,698	6	99.8
GF/D Glass Paper Whatman,‡ 47 mm, Reeve Angel Corp.	2,622	2,166	17.4
934AH Glass Fiber Filter, 47 mm, Reeve Angel Corp.	1,049	198	81
GF/A Glass Paper Whatman, 47 mm, Reeve Angel Corp.	1,066	680	36

* The 984H Ultra Glass Fiber Filter is flexible when wet, readily allows filtration of large volumes of water, can readily be bent double with forceps, and, when placed into primary enrichment broth, disintegrates when tube is shaken and releases entrapped bacteria.

† Enteric bacteria. *E. coli*, 0.5 X 1-3 μ

‡ A new paper filter GF/F has better retentive properties than the 984H, and has same properties (tested Oct. 1973).

Concentration is attained by filtration through glass fiber filters* in a membrane filter apparatus. After the desired volume of water is filtered through the ultra filter, the flexible filter is folded double with sterile forceps and inserted into a suitable volume of single-strength DSE medium contained in a test tube located in the first row of the multiple tube setup. The tube should then be shaken to cause filter to disintegrate (Table I and Figure 1). To obtain MPN results per one l or per 10 l, 100 ml or 1,000 ml of sample, respectively, are filtered for each tube of DSE medium in the first row of the five-tube MPN setup. Additional dilutions are made by transferring material from tubes in the first row to tubes farther back in the setup.

Obtaining results on a per 1-gal (3.8-l) basis requires filtration of 380 ml, and on a per l0-gal (38-1) basis requires filtration of 3,600 ml for each tube in the first row. Where concentration of bacteria is not usually required, as in municipal wastewaters, sludges, or primary effluents, the regular transfer of 10 ml of sample to each tube in the first row of the setup into 10 ml of double-strength DSE is made, 1 ml of sample in 9 ml of single-strength DSE in the second row, and so on. The MPN table in "Standard Methods"[14] is used to read directly the results per volume of sample.

Incubation temperature of 40° ± 0.2°C for 1 and 2 days is critical to obtain optimum recovery of *Salmonella* sp. and *Pseudomonas aeruginosa* when DSE broth is used for primary enrichment. After primary incubation at 40°C surface loopfuls (scum) (7 mm platinum or nichrome wire loop) are removed from each multiple-tube culture and streaked on each of two sections of a divided plate of Xylose lysine desoxycholate agar (XLD)[15] in order to isolate colonial growth. The numbered plates are inverted and incubated at 37°C for a period not to exceed 24 hr.

Commercial dehydrated XLD agars (BBL and Difco) are satisfactory if they are reconstituted in distilled water in sterile foil-covered flasks and heated to 88° or 92°C, respectively. The agar is then cooled to 55° to 60°C and distributed in sterile petri dishes. This laboratory prefers l0-ml portions in each section of a divided sterile disposable plastic dish (Figure 1).

* Reeve Angel 984H ultra glass fiber filter, 47 mm Reeve Angel & Co., Inc., Clifton, N. J. Mention of trade names does not constitute endorsement or recommendation by EPA.

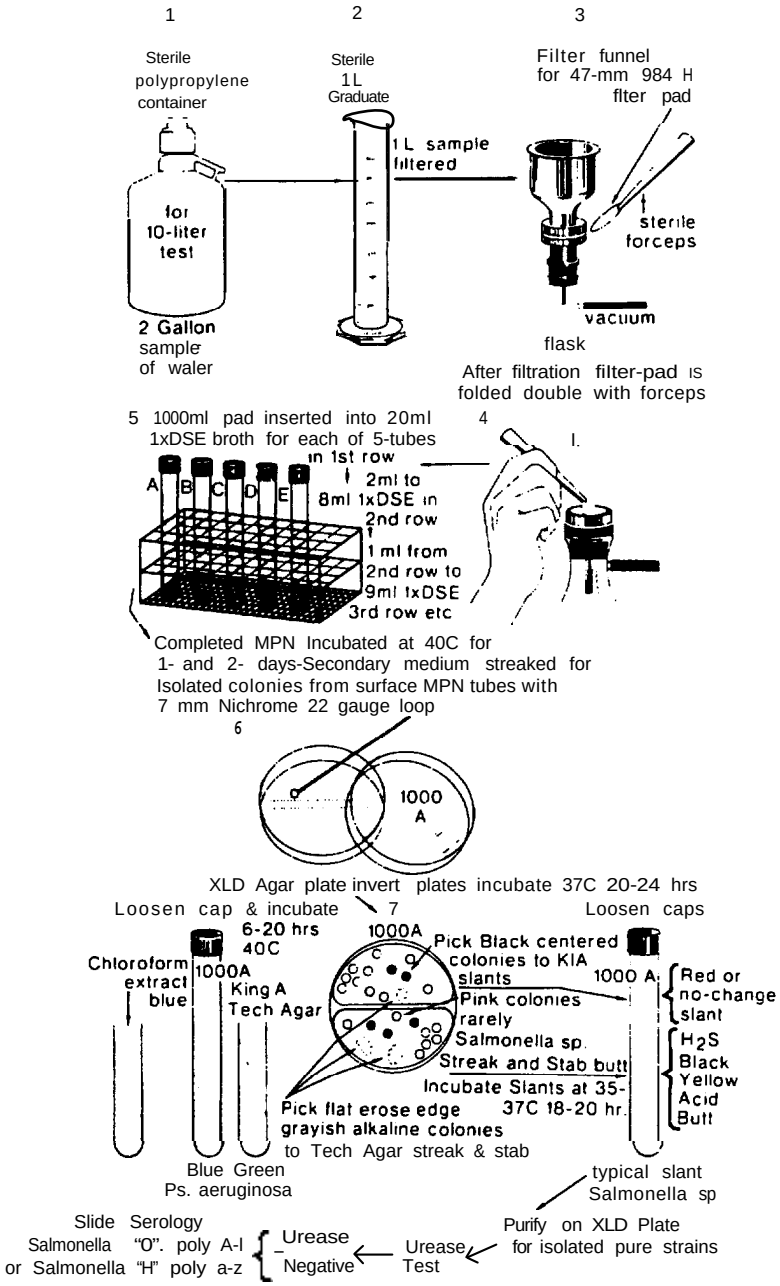

FIGURE I.--Procedure for isolation of pathogens.

Positive incubated XLD plate cultures contain typical clear, pink-edged, black-centered *Salmonella* colonies, and flat, mucoid, grayish alkaline, pink erose-edged *Ps. aeruginosa.* The *Salmonella* colonies are picked to Kligler iron agar (KIA) or Triple sugar iron agar slants for typical appearance, purification, and identity tests. *Ps. aeruginosa* colonies are picked to King A agar slants (Tech agar BBL) for ohtaining the bluegreen pyocyanin confirmation at 40°C (Figure 1).

Typically, *Salmonella* sp. slant cultures (streaked and stabbed), incubated over-

TABLE II.-Advantage of Ultra-filter 984H Use in Monitoring Suspected Waters for *Salmonella* species

Type of Sample	*Salmonella* (no./100 ml)	Serotypes Found (no./100ml)	*Salmonella* (no./gal)	Serotypes Found (no./gal)
Stormwater runoff	4.5	S. bareilly[7]	210	*S. kottbus*[10] *S. bareilly*[11]
Stormwater runoff	<3.0	none	7.3	S. *java*[4] *S. muenchen*[2]
Activated sludge effluent	<3.0	none	3.6	S. group G[4]
Municipal wastewater	6.2	Arizona[3]	1,500	Arizona[4] *S. anatum*[2] *S. newport*[4] *S. san diego*[7] *S. worthington*[2]
Municipal wastewater	<3.0	none	110	*S. anatum*[3] *S. derby*[1] *S. newport*[3]
Activated sludge effluent	<3.0	none	28	*S. blockley*[7] *S. newport*[3]
Mississippi River water, mile 403.1	43	*S. ohio*[10]	>11,000	*S. ohio*[19] *S. derby*[2] *S. meleagridis*[6]
Municipal wastewater	3.0	*S. cholerasuis* var. kunzendorf[2]	21	*S. cholerasuis* var. kunzendorf[5] *S. newport*[6]

night at 37°C, give an unchanged or alkaline red-appearing slant; the butt is blackened by H_2S, is acid-yellow, and has gas bubbles, except for rare species. Typical-appearing slant cultures are purified by transferring them to **XLD** agar plates for the development of isolated colonies. The flat or umbonated-appearing colonies with large black centers and clear pink edges then are picked to **KIA** slants (streaked and stabbed), incubated at 37°C, and urease tested before the identification procedure (Figure 1). Urease-negative tubes are retained for presumptive serological tests and serotype identification.

Typical Tech agar slant cultures for *Ps. aeruginosa* that are incubated at 40°C overnight turn a bluegreen color from pyocyanin, a pigment produced onIy by this species. A reddish-blue color is caused by the additional presence of pyorubin. The blue pigment is extractable in chloroform and is light blue in color after a few hours at room temperature. No further tests are necessary. The count is read directly from the MPN table.

JUSTIFICATION FOR PROCEDURES

Choice of primary enrichment medium and secondary isolation agar. Most of the enrichment media described in contemporary literature were designed for the isolation of pathogens from clinical specimens from ill persons or from samples of suspected foods, and they work quite well for those types of samples. When they are used, however, for the isolation of pathogens from polluted waters and other types of environmental samples, such as soils, they do not prove adequate. Enrichment media that were tested and found wanting in regard to detection and selectivity were tetrathionate broth (**TT**), with and without brilliant green at 41.5°C; selenite cystine broth at 37°C; selenite F broth at 37°C; selenite brilliant green, with and without sulfa, at 37° and 41.5°C; and Gram-negative broth (**GN**) at 40°C and 41.5°C.

None of the media named worked well at 37°C for the isolation of *Salmonella* sp., and isolation from wastewaters only oc-

TABLE III.-Percentage of Colony Picks from DSE-XLD Combination Positive for *Salmonella* species

Liquid Samples	No.	Total Picks from XLD	No. Positive	No. Negative	Percentage Positive	Range of *Salmonella* counts/100 ml
Municipal wastewater	15	315	250	65	79	3.0-1,500
Stockyard wastewater	1	36	36	0	100	2,100
Rivers						
Mississippi						
Ohio	8	110	84	26	76	1.5->300
Stormwater runoffs	2	18	14	4	78	0.2-1.5
Activated sludge biological effluent	20	386	306	80	79	0.1-1,100
Trickling filter effluent	7	103	78	25	76	0.35-140
Package plant effluent	6	83	55	28	66	1.8-620
Package plant sludge	2	41	37	4	90	43-240
Chlorinated primary outfall	2	17	13	4	76	3-43
Creek 1 mile (1.6 km) below package plant outfall	2	37	16	21	43	4.5-12
Home cisterns	2	17	10	7	59	0.26-1.1
Dupont R-O						
Feed	1	20	14	6	70	4.3
Reject	1	16	8	8	50	0.91
Product-negative						
Raw primary sludge	4	80	66	14	83	13-700
Primary activated sludge	1	15	13	2	87	23
Anaerobic digester sludge	3	78	65	13	83	79-170
Anaerobic digester sludge (28 days)	1	9	3	6	33	2
Activated secondary sludge	6	189	155	34	82	11->11,000
Total	84	1,570	1,223	347	average 78	

curred by chance and was purely qualitative. Of the above-named media used in preliminary tests, selenite brilliant green sulfa broth (SBGS) at 41.5°C gave the best isolation of *Salmonella* sp. from wastewaters (with and without the addition of S. *typhimurium* in known numbers). Of thirteen wastewater samples tested in SBGS at 41.5°C, six contained *Salmonella* or 46 percent were positive. With DSE broth at 40°C, 28 of 28, or 100 percent of wastewater samples, gave positive results.

Studies were not continued on SBGS medium when it was noted that some lots of commercially available SBGS seemed to be selective for *Salmonella* sp. while others were not. The medium was then prepared according to the original formula[16] with six different lots of brilliant green (certified), only one of which was selective. The use of brilliant green agar as a selective medium is subject to the same variability, according to Read and Reyes.[17]

The main reasons for rejection of TT, with and without brilliant green, and for selenite broth's using brilliant green agar and XLD agar as secondary media are not only fewer isolations of *Salmonella* sp., but also the poor selectivity of these combinations when they are used for monitoring polluted waters. These combinations' poor selectivity at 41.5°C is apparent in the results of Dutka and Bell,[18] where the TT broth-XLD combination yielded 26 percent confirmation of colonial picks, and selenite broth-BGA and selenite broth-XLD gave 55 and 56 percent confirmations, respectively. The authors had similar results. The GN-XLD combination was poorest for water samples at 40° and 41.5°C yielding less than 10 percent isolations from wastewaters.

Effect of incubation temperature on isolation of *Salmonella* sp. In a study of 26 wastewater samples that was conducted with the DSE multiple tube setups at three

TABLE IV.-Serotypes of *Salmonella* Found in Polluted Waters

Serotype	No. of Strains	Rank in Water Isolations	Rank in Human Occurrence*
1 *typhimurium**	375	1	1 and 6†
2 *derby*	287	2	12
3 *cubana*	223	3	20
4 *chester*	203	4	19
5 *newport*	188	5	4
6 *koltbus*	158	6	—‡
7 *blockley*	157	7	11
8 *infantis*	141	8	9
9 *enteritidis*	128	9	5
10 *anatum*	127	10	13
11 *heidelberg*	110	11	6
12 *manhattan*	97	12	14
13 *paratyphi* B	91	13	17
14 *illinois*	77	14	—‡
15 *thompson*	63	15	3
16 *livingstone*	52	16	—‡
17 *montevideo*	47	17	16
18 *muenchen*	45	18	18
19 *oranienberg*	44	19	15
20 *san diego*	44	19	18
21 *barielly*	42	20	23
22 *tshiongwe*	41	21	—
23 *orion*	41	21	—‡
24 *senftenberg*	39	22	25
25 *schwarzengrund*	37	23	—‡
26 *lexington*	33	24	—‡
27 *cholerasuis*	30	25	—‡
28 *binza*	29	26	24
29 *cholerasuis* var. kunzendorf	29	26	—‡
Other serotypes:			
30 *albany*	20	31	—‡
31 *benfica*	10	40	—‡
32 *braenderup*	13	38	—‡
33 *brancaster*	1		—‡
34 *bredeney*	8		23
35 *california*	2		—‡
36 *drypool*	14	37	—‡
37 *friedenau*	4		—
38 *give*	25	29	22
39 *grumpensis*	10	40	—‡
40 *haifa*	2		—‡
41 *hartford*	2		—‡
42 *havana*	16	35	—‡
43 *indiana*	10	40	—‡
44 *java*	15	36	7
45 *javiana*	13	38	8
46 *litchfield*	17	34	21
47 *lomita*	26	28	—‡
48 *meleagridis*	18	33	25
49 *mission*	14	37	—‡
50 *newington*	2		—‡
51 *newlands*	8		—‡
52 *norwich*	14	37	—‡
53 *ohio*	19	32	—‡
54 *preston*	2		—
55 *reading*	26	28	—‡
56 *rubislaw*	15	36	—‡
57 *saint paul*	21	30	10
58 *schleissheim*	12	39	—
59 *simsbury*	9		—‡
60 *taksony*	16	35	—‡
61 *tennessee*	12	39	20
62 *typhi-suis* var. voldagsen	2		—
63 *uzaramo*	28	27	—‡
64 *wil*	3		—
65 *worthington*	10	40	24
Sub total	3,417		
Arizona	151		
Incomplete serology	232		
Total	3,800		

* Rank in human occurrence Table I, Martin and Ewing.[19]

† Separation of *S. typhimurium* and var. copenhagen not done after initial identifications.

‡ Serotypes occurring in humans, 1965-1971, Center for Disease Control, Salmonella Surveillance, Annual Summary 1971, Table IX, U. S. DHEW, PHS DHEW Publ. No. (HSM) 73-8184 (Oct. 1972).

different temperatures, it was found that 100 percent of the samples contained *Salmonella* sp. and ***Ps. aeruginosa*** at 40°C. At 41.5°C, however, only 50 percent or 13 of the samples yielded ***Salmonella*** sp., and at 37°C only 8 percent or 2 of the samples yielded ***Salmonella*** sp.

Effect of enhancement of DSE broth with a killed culture of S. *paratyphi* A. In a study of 84 samples of activated sludge effluents, trickling filter effluents, package plant effluents, and stream waters, **DSE** broth enhanced with a killed culture of *S. paratyphi* A in **DSE** broth (10 percent by volume) yielded isolations in 64 samples or 74 percent isolated *Salmonella* sp., compared with 48 samples or 57 percent isolations when the **DSE** broth was used without enhancement. An improved isolation of 17 percent was achieved with enhanced **DSE** broth.

Ultra-filter. The advantages of ultrafilter use in testing water samples are illustrated in Table II.

RESULTS AND DISCUSSION

Of importance to those who must use bacteriological tests to obtain *Salmonella* sp. and ***Ps. aeruginosa*** counts from waters is the amount of work that must be done to secure accurate results. Table III presents the percentage of colony picks made with the described method that proved to be *Salmonella* sp. If there are black-centered colonies on the **XLD** plates, more than 75 percent of the picks will prove to be *Salmonella* sp.; thus, the method leads to less unproductive work. When other methods were used, the authors have at times had to pick 50 black-centered colonies to obtain only 5 *Salmonella* sp. strains. This type of unproductive work has given the search for pathogens in the environment an undeserved bad reputation, and it has caused some to give up.

In Table II it may readily be seen that in many cases the fault with many tests has been the testing of an insufficient volume of sample. Many people think that it involves too much work, and that only expensive fluorescent antibody techniques will work. The problem is, however, to

TABLE V.-Percentage of Various Types of Water Samples Positive for *Salmonella* species

Type of Sample	Number of Samples	Number Positive	Number Negative	Percentage Positives
Municipal wastewaters	28	28	0	100.0
Municipal primary efflucnts (chlorinated)	9	5	4	56.0
Activated sludge effluents (clarified)	40	29	11	72.5
Activated sludge effluents Before chlorination	5	4	1	80.0
After chlorination, 1.4-2.0 mg/l residual, 5 min contact	8	0	8	0.0
Trickling filter effluents	26	15	11	57.7
Package plant effluents	15	7	8	46.7
Creek 1 mile (1.6 km) below package plant	3	3	0	100.0
Ohio River above Cincinnati public landing	20	9	11	45.0
Wabash River	4	3	1	75.0
Mississippi River	4	3	1*	75.0
Streams collective	31	18	13	58.0
Stormwater runoff after heavy rain	6	3†	3‡	50.0
Farm wells	4	0	4	0.0
Home cisterns suburban	5	2	3	40.0
Septic tank sludges	6	3	3	50.0
Totals	183	114	69	

* Municipal intake.
† Positive by per-gallon technique.
‡ Negative by per-100 ml technique.

concentrate the bacteria in a 10-gal (38-l) sample or a l00-gal (380-l) sample of potable or reuse water to obtain results, and still not require even more expensive filtration or centrifugation equipment. It also seems unrealistic to test only extremely small samples of the water being examined, because they may not be representative.

Table IV contains a list of *Salmonella* serotypes isolated from polluted waters and ranked according to the frequency of serotype isolations. It will be noted that all of the serotypes except S. ***typhi*** were isolated from environmental samples by the monitoring method, and that only 6 of the 65 serotypes reported were not reported as occurring in humans in the U. S. over the period from 1965 to 1971.

Table V summarizes the percentage of various types of water samples positive for *Salmonella* sp. Of interest is the fact that 100 percent of the municipal wastewaters tested contain *Salmonella* sp., that 56 percent of chlorinated primary effluents tested contain the pathogens, and that 100 percent of chlorinated secondary effluents are negative for pathogens. There are more studies scheduled for testing of secondary and tertiary effluents to obtain minimal chlorine residuals. Calabro et al.[20] reported that more than 50 attempts at isolating *Salmonella* sp. from septic tank samples using SBGS-BGSA combinations were unsuccessful.

Table VI summarizes the isolation of ***Ps. aeruginosa*** from potable water supply, that is, wells, cisterns, and small municipal water supply. It should be noted that fecal coliforms were not detected in most of these samples. Fecal streptococci counts were higher than fecal coliform counts where both tests were used. ***Ps. aeruginosa*** were present in all but three of the tests, and *Salmonella* sp. were isolated from two different cistern samples.

It is of importance to the user of pathogen tests that the test be quantitative. In initial studies on the DSE-XLD combination, it was important to know if the enrichment broth would support the growth of a wide

TABLE VI.-Isolation of *Pseudomonas aeruginosa* from Potable Water Supply

Type of Sample	*Ps. aeruginosa* Isolation	Indicators/100 ml		
		Total Coliforms	Fecal Coliforms	Fecal Streptococci
Well 8/16/71	+	4	—	—
Well 8/25/71	+	22	—	—
Well 3/27/72	+	—	<1	—
Well 3/27/72 (chlorinated)	+	—	<1	—
Well 8/23/72	+	—	0.25	62
Well 10/ 4/72	+	—	<2	46
Suburban cisterns				
8/ 4/72	+	—	180	—
10/ 9/72*	+	—	15	156
11/ 6/72*	+	—	<2	22
11/ 6/72	+	—	<2	2
11/26/72	+	—	3	28
Municipal supplies				
Population served 54,700				
3/17/71	+	—	<1	—
6/21/71	+	—	<1	—
7/19/71	+	—	<1	—
6/19/72	+	—	0.26	—
10/ 9/72	+	—	<1	<1
5/ 8/72	0	—	<1	—
Population served 14,000				
5/ 8/72	0	—	<1	—
10/24/72	+	—	<1	18
Population served < 10,000				
11/27/72	0	—	<1	<1

* *Salmonella* sp. also present in samples.

range of ***Salmonella*** serotypes. Laboratory cultures of ***S. paratyphi*** A, ***S. typhimurium, S. bredeney, S. oranienberg, S. pullorum, S. anatum, S. give,*** and S. ***worthington*** were tested in three enrichment broths. The time required to isolate each of the above cultures from an estimated 10 to 20 organisms/l00 ml in buffer water was 48 to 72 hr for ***S. paratyphi*** A in TT broth, 24 hr for DSE broth, and 36 to 48 hr for SBGS broth. The rest of the cultures were isolated in estimated numbers in 14 to 24 hr in TT and DSE broths. In SBGS broth, ***S. typhimurium, S. bredeney, S. anatum, S.*** give, and S. ***worthington*** required 36 to 48 hr incubation, and ***S. pullorum*** and S. ***oranienberg*** required 48 to 72 hr incubation.

It is impossible to know if 100 percent of ***Salmonella*** sp. in a polluted water sample are isolated. In tests where laboratory cultures have been added in low numbers to wastewater and treatment effluent samples, all of the numbers added were detected, as well as the ***Salmonella*** sp. that were naturally occurring. The higher the quality of the water (for example, secondary or tertiary treatment effluent, or even potable waters), the better the possibility of isolation of all the *Salmonella* serotypes present, as well as Ps. ***aeruginosa,*** a potential pathogen.

SUMMARY

A practical laboratory method is presented for the simultaneous isolation and enumeration of ***Salmonella*** sp. and *Pseudomonas* ***aeruginosa*** from all classes of waters, including potable water supplies, with a minimum of interfering false positive isolations. The method allows for the testing

of large volumes of high quality waters, wherein the absence of indicator bacteria (that is, total coliforms, fecal coliforms, and fecal streptococci), may give a false sense of security because of the low volumes of water usually tested. Justification for each step of the procedural method is presented.

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Credits. The technical assistance of Pauline C. Haley in performing the necessary serology for identifying many of the *Salmonella* serotypes reported is gratefully acknowledged.

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Appendix H
Method for the Recovery and Assay of Total Culturable Viruses from Sludge

1. Introduction

1.1. Scope

This chapter describes the method that must be followed to produce Class A sludge when virus monitoring under 40 CFR Part 503 is required. The method is designed to demonstrate that sludges meet the requirement that human enteric viruses (i.e., viruses that are transmitted via the fecal-oral route) are less than one plaque-forming unit (PFU) per 4 g of total dry solids.

1.2. Significance

More than 100 different species of pathogenic human enteric viruses may be present in raw sludge. The presence of these viruses can cause hepatitis, gastroenteritis and numerous other diseases. Hepatitis A virus and noroviruses are the primary human viral pathogens of concern, but standard methods for their isolation and detection have not been developed. The method[1] detailed in this chapter detects total culturable viruses, which primarily include the human enteroviruses (e.g., polioviruses, coxsackieviruses, echoviruses) and reoviruses.

1.3. Safety

The sludges to be monitored may contain pathogenic human enteric viruses. Laboratories performing virus analyses are responsible for establishing an adequate safety plan and must decontaminate and dispose of wastes according to their safety plan and all applicable regulations. Aseptic techniques and sterile materials and apparatus must be used throughout the method.

2. Sample Collection

For each batch of sludge that must be tested for viruses, prepare a composite sample by collecting ten representative samples of 100 mL each (1,000 mL total) from different locations of a sludge pile or at different times from batch or continuous flow processes. Combine and mix thoroughly all representative samples for a composite. Batch samples that cannot be assayed within 24 hours of collection must be frozen at -70°C; otherwise, they should be held at 4°C until processed. If representative samples must be frozen before they can be combined, then thaw, combine and mix them thoroughly just prior to assay. Then remove a 50 mL portion from each composite sample for solids determination as described in section 3. The remaining portion is held at 4°C while the solids determination is being performed or frozen for later processing if the assay cannot be initiated within 8 hours.

Freeze/thawing biosolids may result in some virus loss.

3. Determination of Total Dry Solids[2]

3.1. Weigh a dry weighing pan that has been held in a desiccator and is at a constant weight. Place the 50 mL sludge portion for solids determination into the pan and weigh again.

3.2. Place the pan and its contents into an oven maintained at 103-105°C for at least one hour.

3.3. Cool the sample to room temperature in a desiccator and weigh again.

3.4. Repeat the drying (1 h each), cooling and weighing steps until the loss in weight is no more than 4% of the previous weight.

3.5. Calculate the fraction of total dry solids (T) using the formula:

$$T = \frac{(A - C)}{(B - C)}$$

where A is the weight of the sample and dish after drying, B is the weight of the sample and dish before drying, and C is the weight of the dish. Record the fraction of dry solids (T) as a decimal (e.g., 0.04).

4. Total Culturable Virus Recovery from Sludge

4.1. Introduction

Total culturable viruses in sludge will primarily be associated with solids. Although the fraction of virus associated with the liquid portion will usually be small, this fraction may vary considerably with different sludge types. To correct for this variation, samples will first be treated to

[1]Method D4994-89, ASTM (1992)

[2]Modified from EPA/600/4-84/013(R7), September 1989 Revision (section 3). This and other cited EPA publications may be requested from the Biohazard Assessment Research Branch, National Exposure Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio, USA 45268.

bind free virus to solids. Virus is then eluted from the solids and concentrated prior to assay.

4.2. Conditioning of Suspended Solids

Conditioning of sludge binds unadsorbed total culturable viruses present in the liquid matrix to the sludge solids.

Each analyzed composite sample (from the portion remaining after solids determination) must have an initial total dry solids content of at least 16 g. This amount is needed for positive controls and for storage of a portion of the sample at -70°C as a backup in case of procedural mistakes or sample cytotoxicity.

4.2.1 Preparation

(a) Apparatus and Materials

(a.1) Refrigerated centrifuge capable of attaining 10,000 ×*g* and screw-capped centrifuge bottles with 100 to 1000 mL capacity.

Each bottle must be rated for the relevant centrifugal force.

(a.2) A pH meter with an accuracy of at least 0.1 pH unit, equipped with a combination-type electrode.

(a.3) Magnetic stirrer and stir bars.

(b) Media and Reagents

Analytical Reagent or ACS grade chemicals (unless specified otherwise) and deionized, distilled water (dH_2O) should be used to prepare all reagents. All water used must have a resistance of greater than 0.5 megohms-cm, but water with a resistance of 18 megohms-cm is preferred.

(b.1) Hydrochloric acid (HCl) — 1 and 5 M.

Mix 10 or 50 mL of concentrated HCl with 90 or 50 mL of dH_2O, respectively.

(b.2) Aluminum chloride ($AlCl_3 \cdot 6H_2O$) — 0.05 M.

Dissolve 12.07 g of aluminum chloride in a final volume of 1000 mL of dH_2O. Autoclave at 121°C for 15 minutes.

(b.3) Sodium hydroxide (NaOH) — 1 and 5 M.

Dissolve 4 or 20 g of sodium hydroxide in a final volume of 100 mL of dH_2O, respectively.

(b.4) Beef extract (Difco Product No. 0115-17-3 or equivalent).

Prepare buffered 10% beef extract by dissolving 10 g beef extract, 1.34 g $Na_2HPO_4 \cdot 7H_2O$ and 0.12 g citric acid in 100 mL of dH_2O. The pH should be about 7.0. Dissolve by stirring on a magnetic stirrer. Autoclave for 15 minutes at 121°C.

Do not use paste beef extract (Difco Laboratories Product No. 0126) for virus elution. This beef extract tends to elute cytotoxic materials from sludges.

(b.5) HOCl — 0.1%

Add 19 mL of household bleach (Clorox, The Clorox Co., or equivalent) to 981 mL of dH_2O and adjust the pH of the solution to 6-7 with 1 M HCl.

(b.6) Thiosulfate — 2% and 0.02%

Prepare a stock solution of 2% thiosulfate by dissolving 20 g of thiosulfate in a total of 1 liter of dH_20. Sterilize the solution by autoclaving at 121°C for 15 minutes. Prepare a working solution of 0.02% thiosulfate just prior to use by mixing 1 mL of 2% thiosulfate with 99 mL of sterile dH_2O.

4.2.2 Conditioning Procedure

Figure 1 gives a flow diagram for the procedure to condition suspended solids.

(a) Calculate the amount of sample to condition.

Use a graduated cylinder to measure the volume. If the volumes needed are not multiples of 100 mL (100, 200, 300 mL, etc.), add sterile water to bring the volume to the next multiple of 100 mL. Each sample should then be aliquoted into 100 mL portions before proceeding. Samples must be mixed vigorously just before aliquoting because solids begin to settle out as soon as the mixing stops. Each aliquot should be placed into a 250 mL beaker containing a stir bar.

CAUTION: Always avoid the formation of aerosols by slowly pouring samples down the sides of vessels.

(a.1) Calculate the amount needed to measure the endogenous total culturable virus in a composite sludge sample using the formula:

$$Xts = \frac{12}{T}$$

where Xts equals the milliliters of sample required to obtain 12 g of total solids and T equals the fraction of total dry solids (from section 3).[3]

(a.2) Calculate the amount needed for a recovery control for each sludge composite from the formula:

$$Xpc = \frac{4}{T}$$

where Xpc equals the milliliters of sample required to obtain 4 g of total solids.

Add 400 plaque forming units (PFU) of a Sabin poliovirus stock to the recovery control sample. Use a virus stock that has been filtered through a 0.2 µm filter (see Section 4.3.1) prior to assay to remove clumped virus particles.

(a.3) Place 30 mL of 10% buffered beef extract and 70 mL of dH_2O into a 250 mL beaker with stir bar to serve as a negative process control.

(a.4) Freeze any remaining composite sample at -70°C for backup purposes.

[3]This formula is based upon the assumption that the density of the liquid in sludge is 1 g/mL. If the fraction of total dry solids is too low (e.g., less than 0.02), then the volume of sludge collected must be increased.

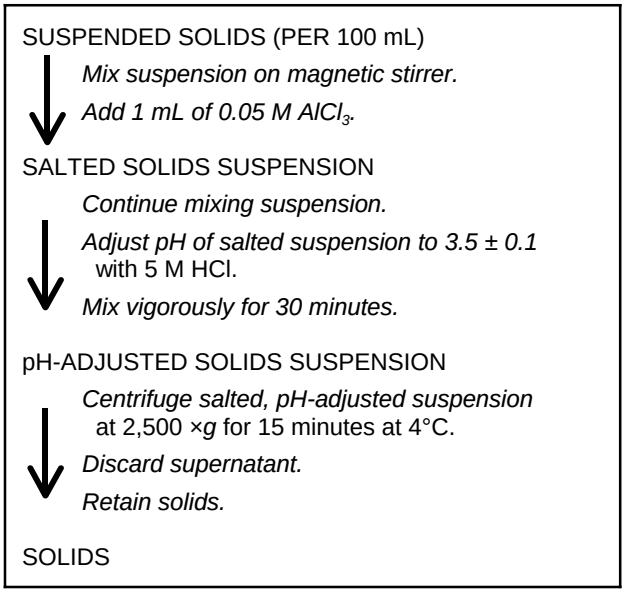

Figure 1. Flow diagram of method for conditioning suspended solids

(b) Perform the following steps on each 100 mL aliquot from steps 4.2.2a.1 to 4.2.2a.3.

(b.1) Place the beaker on a magnetic stirrer, cover loosely with aluminum foil, and stir at a speed sufficient to develop vortex. Add 1 mL of 0.05 M $AlCl_3$ to the mixing aliquot.

The final concentration of $AlCl_3$ in each aliquot is approximately 0.0005 M.

(b.2) Place a combination-type pH electrode into the mixing aliquot. Adjust the pH of the aliquot to 3.5 ± 0.1 with 5 M HCl. Continue mixing for 30 minutes.

The pH meter must be standardized at pH 7 and 4. When solids adhere to an electrode, clean it by moving up and down gently in the mixing aliquot.

After adjusting the pH of each sample, rinse the electrode with dH_2O and sterilize it with 0.1% HOCl for five minutes. Neutralize the HOCl by submerging the electrode in sterile 0.02% thiosulfate for one to five minutes.

The pH of the aliquot should be checked at frequent intervals. If the pH drifts up, readjust it to 3.5 ± 0.1 with 5 M HCl. If the pH drifts down, readjust it with 5 M NaOH. Use 1 M acid or base for small adjustments. Do not allow the pH to drop below 3.4.

(b.3) Pour the conditioned aliquot into a centrifuge bottle and centrifuge at 2,500 ×*g* for 15 minutes at 4°C.

To prevent the transfer of the stir bar into the centrifuge bottle when decanting the aliquot, hold another stir bar or magnet against the bottom of the beaker. Solids that adhere to the stir bar in the beaker may be removed by manipulation with a pipette. It may be necessary to pour the aliquot back and forth several times from the centrifuge bottle to the beaker to obtain all the solids in the bottle. If a large enough centrifuge bottle is available, the test sample aliquots may be combined into a single bottle at this step. If there is more than one recovery control aliquot, they may also be combined into another centrifuge bottle.

(b.4) Decant the supernatant into a beaker and discard. Replace the cap onto the centrifuge bottle. Elute the solids by following the procedure described in section 4.3.

4.3. Elution of Viruses from Solids

4.3.1 Apparatus and Materials

In this and following sections only apparatus and materials which have not been described in previous sections are listed.

(a) Membrane filter apparatus for sterilization — 47 mm diameter Swinnex filter holder and 60 mL slip-tip syringe (Millipore Corp. Product No. SX00 047 00 and Becton Dickinson Product No. 1627 or equivalent).

(b) Disc filters, 47 mm diameter — 3.0, 0.45, and 0.2 µm pore size filters (Mentec America, Filterite Div., Duo- Fine series, Product No. 8025-030, 8025-034 and 8025-037 or equivalent). Filters may be cut to the proper diameter from sheet filters.

Disassemble a Swinnex filter holder. Place the filter with a 0.2 µm pore size on the support screen of the filter holder and stack the remaining filters on top in order of increasing pore size. Reassemble and tighten filter holder. Wrap filter stack in foil and sterilize by autoclaving at 121°C for 15 min.

Filters stacked in tandem as described tend to clog more slowly when turbid material is filtered through them. Prepare several filter stacks.

4.3.2 Elution Procedure

A flow diagram of the virus elution procedure is given in Figure 2.

(a) Place a stir bar and 100 mL of buffered 10% beef extract into the centrifuge bottle containing the solids (from section 4.2.2b.4).

If the test and control samples are divided into more than one centrifuge bottles, the solids should be combined at this step.

Place the centrifuge bottle on a magnetic stirrer, and stir at a speed sufficient to develop a vortex for 30 min at room temperature.

To minimize foaming (which may inactivate viruses), do not mix faster than necessary to develop vortex.

(b) Remove the stir bar from each bottle with a long sterile forceps or a magnet retriever and centrifuge the solids-eluate mixture at 10,000 ×*g* for 30 minutes at 4°C. Decant supernatant fluid (eluate) into a beaker and discard the solids.

Determine if the centrifuge bottle is appropriate for the centrifugal force that will be applied.

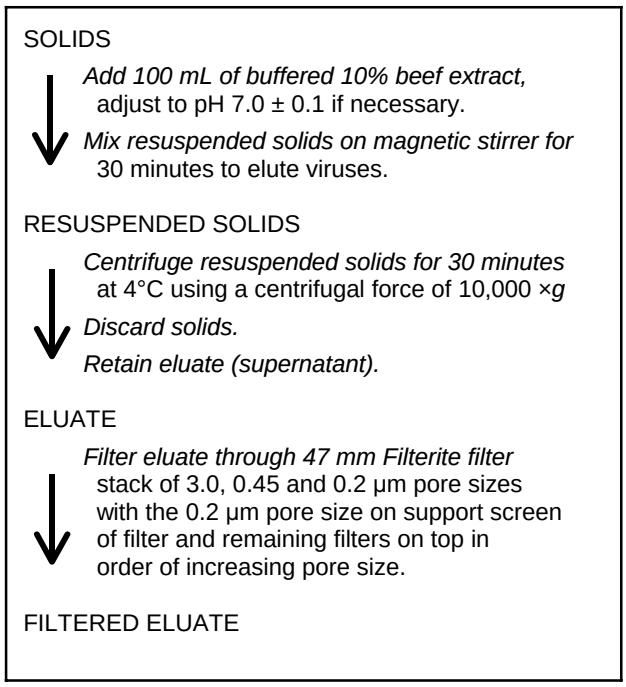

Figure 2. Flow diagram of method for elution of virus from solids.

Centrifugation at 10,000 ×g is normally required to clarify the sludge samples sufficiently to force the resulting supernatant through the filter stacks.

(c) Place a filter holder that contains filter stacks (from section 4.3.1b) onto a 250 mL Erlenmeyer receiving flask. Load 50 mL syringes with the supernatants from step 4.3.2c. Place the tip of the syringe into the filter holder and force the supernatant through the filter stacks into 250 mL receiving flasks.

Prior to use, pass 15 mL of 3% beef extract through each filter holder to minimize non-specific adsorption of viruses. Prepare 3% beef extract by mixing 4.5 mL of 10% beef extract and 10.5 mL of dH_2O. Take care not to break off the tip of the syringe and to minimize pressure on the receiving flask because such pressure may crack or topple the flask. If the filter stack begins to clog badly, empty the loaded syringe into the beaker containing unfiltered eluate, fill the syringe with air, and inject air into filter stack to force residual eluate from the filters. Continue the filtration procedure with another filter holder and filter stack. Discard contaminated filter holders and filter stacks. This procedure may be repeated as often as necessary to filter the entire volume of supernatant. Disassemble each filter holder and examine the bottom 0.2 µm filters to be certain they have not ruptured. If a bottom filter has ruptured, repeat the step with new filter holders and filter stacks.

Proceed immediately to section 4.4.

4.4. Organic Flocculation

This organic flocculation concentration procedure (Katzenelson et al., 1976) is used to reduce the number of cell cultures needed for assays by concentrating total culturable viruses in the eluate. The step significantly reduces costs associated with labor and materials.

Floc formation capacity of the beef extract reagent must be pretested. Because some beef extract lots may not produce sufficient floc, each new lot must be pretested to determine virus recovery. This may be performed by spiking 100 mL of dH_2O with a known amount of poliovirus in the presence of a 47 mm nitrocellulose filter. This sample should be conditioned using section 4.2 above to bind virus to the filter. Virus should then be eluted from the filter using the procedure in section 4.3, and concentrated and assayed using the following procedures. Any lot of beef extract not giving a overall recovery of at least 50% should not be used.

4.4.1 Media and Reagents

In this and following sections only media and reagents which have not been described in previous sections are listed.

(a) Sodium phosphate, dibasic ($Na_2HPO_4 \cdot 7H_2O$) — 0.15 M.

Dissolve 40.2 g of sodium phosphate in a final volume of 1000 mL. Autoclave at 121°C for 15 minutes.

4.4.2 Virus Concentration Procedure

A flow diagram for the virus concentration procedure is given in Figure 3.

(a) Pour the filtered eluates from the test sample, recovery control and negative process control from section 4.3.2d into graduated cylinders, and record their volumes. Transfer the samples into separate 600 mL beakers and cover them loosely with aluminum foil.

(b) For every 3 mL of beef extract eluate, add 7 mL of dH_2O to the 600 mL beakers. Add stir bars to each beaker.

The concentration of beef extract is now 3%. This dilution is necessary because 10% beef extract often does not process well by the organic flocculation concentration procedure.

(c) Record the total volume of the diluted eluates. Place the beakers onto a magnetic stirrer, cover loosely with aluminum foil, and stir at a speed sufficient to develop vortex.

To minimize foaming (which may inactivate viruses), do not mix faster than necessary to develop vortex.

(d) For each diluted, filtered beef extract, insert a sterile combination-type pH electrode and then add 1 M HCl slowly until the pH of the extract reaches 3.5 ± 0.1. Continue to stir for 30 minutes at room temperature.

The pH meter must be standardized at pH 4 and 7. Sterilize the electrode by treating it with 0.1% HOCl for five minutes. Neutralize the HOCl by treating the electrode with 0.02% sterile thiosulfate for one to five minutes.

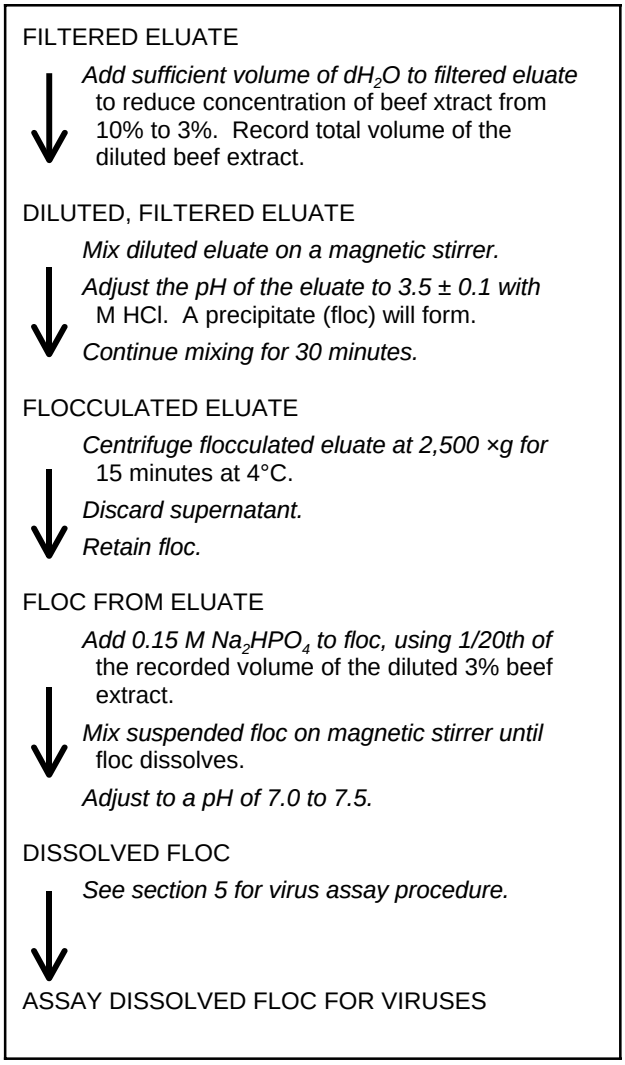

Figure 3. Flow diagram of method for concentration of viruses from beef extract eluate.

A precipitate will form. If the pH is accidentally reduced below 3.4, add 1 M NaOH until it reaches 3.5 ± 0.1. Avoid reducing the pH below 3.4 because some inactivation of virus may occur.

(e) Pour the contents of each beaker into 1,000 mL centrifuge bottles. Centrifuge the precipitated beef extract suspensions at 2,500 ×*g* for 15 minutes at 4°C. Pour off and discard the supernatants.

To prevent the transfer of the stir bar into a centrifuge bottle, hold another stir bar or magnet against bottom of the beaker when decanting contents.

(f) Place stir bars into the centrifuge bottles that contains the precipitates. To each, add a volume of 0.15 M $Na_2HPO_4 \cdot 7H_2O$ equal to exactly 1/20 of the volume recorded in step 4.4.2c. If the precipitate from a sample is in more than one bottle, divide the 1/20th volume equally among the centrifuge bottles containing that sample. Place the bottles onto a magnetic stirrer, and stir slowly until the precipitates have dissolved completely.

Support the bottles as necessary to prevent toppling. Avoid foaming which may inactivate or aerosolize viruses. The precipitates may be partially dissipated with sterile spatulas before or during the stirring procedure.

(g) Measure the pH of the dissolved precipitates.

If the pH is above or below 7.0-7.5, adjust to that range with either 1 M HCl or 1 M NaOH.

(h) Freeze exactly one half of the dissolved precipitate test sample (but not the positive and negative controls) at -70°C. This sample will be held as a backup to use should the sample prove to be cytotoxic. Record the remaining test sample volume (this volume represents 6 g of total dry solids). Refrigerate the remaining samples immediately at 4°C until assayed in accordance with the instructions given in section 5 below.

If the virus assay cannot be undertaken within 24 hours, store the remaining samples at -70°C.

5. Assay for Plaque-forming Viruses[4]

5.1. Introduction

This section outlines procedures for the detection of viruses in sludge by use of the plaque assay system. The system uses an agar medium to localize virus growth following attachment of infectious virus particles to a cell monolayer. Localized lesions of dead cells (plaques) developing some days after viral infection are visualized with the vital stain, neutral red, which stains only live cells. The number of circular unstained plaques are counted and reported as plaque forming units, whose number is proportional to the amount of infectious virus particles inoculated.

The detection methodology presented in this section is geared towards laboratories with a small-scale virus assay requirement. Where the quantities of cell cultures, media and reagents set forth in the section are not sufficient for processing the test sample concentrates, the prescribed measures may be increased proportionally to meet the demands of more expansive test regimes.

5.2. Plaque Assay Procedure

5.2.1 Apparatus and materials.

(a) Waterbath set at 50 ± 1°C.

Used for maintaining the agar temperature (see section 5.2.2j).

5.2.2 Media and Reagents.

(a) ELAH — 0.65% lactalbumin hydrolysate in Earle's base.

Dissolve 6.5 g of tissue culture, highly soluble grade lactalbumin hydrolysate (Gibco BRL Product No. 11800 or

[4]Modified from EPA/600/4-84/013(R11), March 1988 Revision

equivalent) in 1 L of Earle's base (Gibco BRL Product No. 14015 or equivalent) prewarmed to 50-60°C. Sterilize ELAH through a 0.22 μm filter stack and store for up to two months at 4°C.

(b) Wash medium — Add 1 mL of penicillin-streptomycin stock (see section 6.4.2e.1 for preparation of antibiotic stocks), 0.5 mL of tetracycline stock and 0.2 mL of fungizone stock per liter to ELAH immediately before washing of cells.

(c) HEPES — 1 M (Sigma Chemical Product No. H-3375 or equivalent).

Prepare 50 mL of a 1 M solution by dissolving 11.92 g of HEPES in a final volume of 50 mL dH_2O. Sterilize by autoclaving at 121°C for 15 min.

(d) Sodium bicarbonate ($NaHCO_3$) — 7.5% solution.

Prepare 50 mL of a 7.5% solution by dissolving 3.75 g of sodium bicarbonate in a final volume of 50 mL dH_2O. Sterilize by filtration through a 0.22 μm filter.

(e) Magnesium chloride ($MgCl_2 \cdot 6H_20$) — 1.0% solution.

Prepare 50 mL of a 1.0% solution by dissolving 0.5 g of magnesium chloride in a final volume of 50 mL dH_2O. Sterilize by autoclaving at 121°C for 15 min.

(f) Neutral red solution — 0.333%, 100 mL volume (GIBCO BRL Product No. 630-5330 or equivalent).

Procure one 100 mL bottle.

Some neutral red solutions are cytotoxic. All new solutions should be tested prior to their use for assaying sludge samples. Testing may be performed by assaying a stock of poliovirus with known titer using this plaque assay procedure.

(g) Bacto skim milk (Difco Laboratories Product No. 0032-01 or equivalent).

Prepare 100 mL of 10% skim milk in accordance with directions given by manufacturer.

(h) Preparation of Medium 199.

The procedure described is for preparation of 500 mL of Medium 199 (GIBCO BRL Product No. 400-1100 or equivalent) at a 2X concentration. This procedure will prepare sufficient medium for at least fifty 6 oz glass bottles or eighty 25 cm^2 plastic flasks.

(h.1) Place a three inch stir bar into a one liter flask. Add the contents of a 1 liter packet of Medium 199 into the flask. Add 355 mL of dH_2O. Rinse medium packet with three washes of 20 mL each of dH_2O and add the washes to the flask.

Note that the amount of dH_2O is 5% less than desired final volume of medium.

(h.2) Mix on a magnetic stirrer until the medium is completely dissolved. Filter the reagent under pressure through a filter stack (see section 6.2.6).

Test each lot of medium to confirm sterility before the lot is used (see section 6.5). Each batch may be stored for two months at 4°C.

(i) Preparation of overlay medium for plaque assay.

The procedure described is for preparation of 100 mL of overlay medium and will prepare sufficient media for at least ten 6 oz glass bottles or twenty 25 oz plastic flasks when mixed with the agar prepared in section 5.2.2j.

(i.1) Add 79 mL of Medium 199 (2X concentration) and 4 mL of serum to a 250 mL flask.

(i.2) Add the following to the flask in the order listed, with swirling after each addition: 6 mL of 7.5% $NaHCO_3$, 2 mL of 1% $MgCl_2$, 3 mL of 0.333% neutral red solution, 4 mL of 1 M HEPES, 0.2 mL of penicillin-streptomycin stock (see section 6.4.2e for a description of antibiotic stocks), 0.1 mL of tetracycline stock, and 0.04 mL of fungizone stock.

(i.3) Place flask with overlay medium in waterbath set at 36 ± 1°C.

(j) Preparation of overlay agar for plaque assay.

(j.1) Add 3 g of agar (Sigma Chemical Product No. A-9915 or equivalent) and 100 mL of dH_2O to a 250 mL flask. Melt by sterilizing the agar solution in an autoclave at 121°C for 15 min.

(j.2) Cool the agar to 50°C in waterbath set at 50 ± 1°C.

(k) Preparation of agar overlay medium.

(k.1) Add 2 mL of 10% skim milk to overlay medium prepared in section 5.2.2i.

(k.2) Mix equal portions of overlay medium and agar by adding the medium to the agar flask.

To prevent solidification of the liquified agar, limit the portion of agar overlay medium mixed to that volume which can be dispensed in 10 min.

5.2.3 Procedure for Inoculating Test Samples.

Section 6.6 provides the procedures for the preparation of cell cultures used for the virus assay in this section.

BGM cell cultures used for virus assay are generally found to be at their most sensitive level between the third and sixth days after initiation. Those older than seven days or which are not 100% confluent should not be used.

(a) Decant and discard the growth medium from previously prepared cell culture test vessels.

To prevent splatter, a gauze-covered beaker may be used to collect spent medium.

The medium is changed from one to four hours before cultures are to be inoculated and carefully decanted so as not to disturb the cell monolayer.

(b) Replace discarded medium with an equal volume of wash medium (from section 5.2.2b) on the day the cultures are to be inoculated.

Table 1. Guide for Virus Inoculation, Suspended Cell Concentration and Overlay Volume of Agar Medium

Vessel Type	Volume of Virus Inoculum (mL)	Volume of Agar Overlay Medium (mL)	Total Number of Cells
1 oz glass bottle[1]	0.1	5	1×10^7
25 cm^2 plastic flask	0.1-0.5	10	2×10^7
6 oz glass bottle	0.5-1.0	20	4×10^7
75 cm^2 plastic flask	1.0-2.0	30	6×10^7

[1]Size is given in oz only when it is commercially designated in that unit.

To reduce shock to cells, prewarm the wash medium to 36.5 ± 1°C before placing it onto the cell monolayer.

To prevent disturbing cells with the force of the liquid against the cell monolayer, add the wash medium to the side of cell culture test vessel opposite the cell monolayer.

(c) Identify cell culture test vessels by coding them with an indelible marker. Return the cell culture test vessels to a 36.5 ± 1°C incubator and hold at that temperature until the cell monolayers are to be inoculated.

(d) Decant and discard the wash medium from cell culture test vessels.

Do not disturb the cell monolayer.

(e) Inoculate BGM cultures with the test sample and positive and negative process control samples from section 4.4.2h. Divide each sample onto a sufficient number of BGM cultures to ensure that the inoculum volume is no greater than 1 mL for each 40 cm^2 of surface area. Use Table 1 as a guide for inoculation size.

Avoid touching either the cannula or the pipetting device to the inside rim of the cell culture test vessels to avert the possibility of transporting contaminants to the remaining culture vessels.

If the samples are frozen, thaw them rapidly by placing them in warm water. Samples should be shaken during the thawing process and removed from the warm water as soon as the last ice crystals have dissolved.

(e.1) Inoculate BGM cultures with the entire negative process control sample using an inoculum volume per vessel that is appropriate for the vessel size used.

(e.2) Inoculate two BGM cultures with an appropriate volume of 0.15 M $Na_2HPO_4 \cdot 7H_2O$ preadjusted to pH 7.0-7.5 and seeded with 20-40 PFU of poliovirus. These cultures will serve as a culture sensitivity control.

(e.3) Remove a volume of the test sample concentrate exactly equal to 1/6th (i.e., 1 g of total dry solids) of the volume recorded in section 4.4.2h. Seed this subsample with 20-40 PFU of poliovirus. Inoculate the subsample onto one or more BGM cultures using a inoculum volume per vessel that is appropriate for the vessel size used. These cultures will serve as controls for cytotoxicity (see section 5.2.5b).

(e.4) Inoculate BGM cultures with the entire recovery control sample using an inoculum volume per vessel that is appropriate for the vessel size used.

(e.5) Record the volume of the remaining 5/6th portion of the test sample. This remaining portion represents a total dry solids content of 5 g. Inoculate the entire remaining portion (even if diluted to reduce cytotoxicity) onto BGM cultures using an inoculum volume per vessel that is appropriate for the vessel size used. Inoculation of the entire volume is necessary to demonstrate a virus density level of less than 1 PFU per 4 g total dry solids.

(f) Rock the inoculated cell culture test vessels gently to achieve uniform distribution of inoculum over the surface of the cell monolayers. Place the cell culture test vessels on a level stationary surface at room temperature (22- 25°C) so that the inoculum will remain distributed evenly over the cell monolayer.

(g) Incubate the inoculated cell cultures at room temperature for 80 min to permit viruses to adsorb onto and infect cells and then proceed immediately to section 5.2.4.

It may be necessary to rock the vessels every 15-20 min during the 80 min incubation to prevent cell death in the middle of the vessels from dehydration.

5.2.4 Procedure for Overlaying Inoculated Cultures with Agar.

If there is a likelihood that a test sample will be toxic to cell cultures, the cell monolayer should be treated in accordance with the method described in section 5.2.5b.

(a) To each cell culture test vessel, add the volume of warm (42-46°C) agar overlay medium appropriate for the cell surface area of the vessels used (see Table 1).

The preparation of the overlay agar and the agar overlay medium must be made far enough in advance so that they will be at the right temperature for mixing at the end of the 80 min inoculation period.

To prevent disturbing cells with the force of the liquid against the cell monolayer, add the agar overlay medium to the side of the cell culture test vessel opposite the cell monolayer.

(b) Place cell culture test vessels, monolayer side down, on a level stationary surface at room temperature (22-25°C) so that the agar will remain evenly distributed as it solidifies. Cover the vessels with a sheet of aluminum foil, a tightly woven cloth, or some other suitable cover to reduce the light intensity during solidification and incubation. Neutral red can damage or kill tissue culture cells by light-induced crosslinking of nucleic acids.

Care must be taken to ensure that all caps on bottles and flasks are tight; otherwise, the gas seal will not be complete and an erroneous virus assay will result.

Agar will fully solidify within 30 min.

(c) After 30 min, invert the cell culture test vessels and incubate them covered in the dark at 36.5 ± 1°C.

5.2.5 Plaque Counting Technique.

(a) Count, mark and record plaques in cell culture test vessels on days one, two, three, four after adding the agar overlay medium. Plaques should be counted quickly using a lightbox (Baxter Product No. B5080-1 or equivalent) in a darkened room. Most plaques should appear within 1 week.

Depending on the virus density and virus types present in the inoculated sample, rescheduling of virus counts at plus or minus one day may be necessary. Virus titers are calculated from the total plaque count. Note that not all plaques will be caused by viruses.

(b) Determine if samples are cytotoxic by macroscopic examination of the appearance of the cell culture monolayer (compare negative, positive and recovery controls from section 5.2.3e with seeded and unseeded test samples) after one to four days of incubation at 36.5 ± 1°C. Samples show cytotoxicity if cell death is observed on test and recovery control samples prior to its development on positive controls. Cytotoxicity should be suspected when the agar color is more subdued, generally yellow to yellow-brown. This change in color results in a mottled or blotchy appearance instead of the evenly diffused "reddish" color observed in "healthy" cell monolayers. Cytotoxicity may also cause viral plaques to be reduced in number or to be difficult to distinguish from the surrounding monolayer. To determine if this type of cytotoxicity is occurring, compare the two types of positive controls (section 5.2.3e). If samples are cytotoxic, do not proceed to the next steps. Re-assay a small amount of the remaining sample using 1:2, 1:4 and 1:8 dilutions. Then re-assay the remaining sample as specified in section 5.2.3 using the dilution which removes cytotoxicity and the specified number of flasks times the reciprocal of the dilution.

A small amount of sample may be tested for cytotoxicity prior to a full assay.

(c) Examine cell culture test vessels as in step 5.2.5a on days six, eight, twelve and sixteen.

If no new plaques appear at 16 days, proceed with step 5.2.6; otherwise continue to count, mark and record plaques every two days until no new plaques appear between counts and then proceed with step 5.2.6.

Inoculated cultures should always be compared to uninoculated control cultures so that the deterioration of the cell monolayers is not recorded as plaques. If experience shows that cultures start to deteriorate prior to 16 days, a second layer of agar can be added after 7 days as described in section 5.2.4.

If negative process controls develop plaques or if positive controls fail to develop plaques, stop all assays until the source of the problem is corrected.

Samples giving plaque counts that are greater than 2 plaques per cm^2 should be diluted and replated.

5.2.6 Virus Plaque Confirmation Procedure

The presence of virus in plaques must be confirmed for all plaques obtained from sludge samples. Where more than ten plaques are observed, it is allowable to confirm at least ten well-separated plaques per sample or 10% of the plaques in a sample, whichever is greater. Flasks may be discarded after samples are taken for plaque confirmation.

(a) Apparatus, Materials and Reagents

(a.1) Pasteur pipettes, disposable, cotton plugged — 229 mm (9 inches) tube length and rubber bulb — 1 mL capacity.

Flame each pipette gently about 2 cm from end of the tip until the tip bends to an approximate angle of 45°. Place the pipettes into a 4 liter beaker covered with aluminum foil and sterilize by autoclaving or by dry heat.

(a.2) 16 x 150 mm cell culture tubes containing BGM cells.

See section 6.6 for the preparation of cell culture tubes.

(a.3) Tissue culture roller apparatus — 1/5 rpm speed (New Brunswick Scientific Product No. TC-1 or equivalent) with culture tube drum for use with roller apparatus (New Brunswick Scientific Product No. ATC-TT16 or equivalent).

(a.4) Freezer vial, screw-capped (with rubber insert) or cryogenic vial — 0.5-1 dram capacity.

(b) Procedure for obtaining viruses from plaque.

In addition to plaques from sludge samples, perform the procedure on at least three negative regions of negative process control flasks and at least three plaques from positive control flasks.

(b.1) Place a rubber bulb onto the upper end of a cotton-plugged Pasteur pipette and then remove the screw-cap or stopper from a plaque bottle.

(b.2) Squeeze the rubber bulb on the Pasteur pipette to expel the air and penetrate the agar directly over the edge of a plaque with the tip of the pipette. Gently force the tip of the pipette through the agar to the surface of the vessel, and scrape some of the cells from the edge of the plaque.

Repeatedly scratch the surface and use gentle suction to insure that virus-cell-agar plug enters the pipette.

(b.3) Remove the pipette from the plaque bottle and tightly replace the cap or stopper.

(c) Procedure for inoculating cell cultures with agar plugs from negative control samples and from plaques.

(c.1) Prepare plaque conformation maintenance medium by adding 5 mL of serum and 5 mL of dH_2O per 90 mL of wash medium (section 5.2.2b) on day samples are to be tested.

(c.2) Pour the spent medium from cell culture tubes and discard the medium. Replace the discarded medium with 2

mL of the plaque conformation maintenance medium. Label the tubes with sample and plaque isolation identification information.

To prevent splatter, a gauze-covered beaker may be used to collect spent medium.

To reduce shock to cells, warm the maintenance medium to 36.5 ± 1°C before placing on cell monolayer.

To prevent disturbing cells with the force of the liquid against the cell monolayer, add the maintenance medium to the side of cell culture test tube opposite the cell monolayer. Note that cells will be only on the bottom inner surface of the culture tube relative to their position during incubation.

(c.3) Remove the cap from a cell culture tube and place the tip of a Pasteur pipette containing the agar plug from section 5.2.6b.3 into the maintenance medium in the cell culture tube. Force the agar plug from the Pasteur pipette by gently squeezing the rubber bulb. Withdraw and discard the pipette, and replace and tighten down the screw-cap on the culture tube.

Tilt cell culture tube as necessary to facilitate the procedure and to avoid scratching the cell sheet with the pipette.

Squeeze bulb repeatedly to wash contents of pipette into the maintenance medium.

(c.4) Place the cell culture tubes in the drum used with the tissue culture roller apparatus. Incubate the cell cultures at 36.5 ± 1°C while rotating at a speed of 1/5 rpm. Examine the cells daily microscopically for 1 week for evidence of cytopathic effects (CPE).

CPE may be identified as cell disintegration or as changes in cell morphology. Rounding-up of infected cells is a typical effect seen with enteric virus infections. However, uninfected cells round up during mitosis and a sample should not be considered positive unless there are significant clusters of rounded-up cells over and beyond what is observed in the uninfected controls. If there is any doubt about the presence of CPE or if CPE appears late (i.e., on day 6 or 7), the conformation process should be repeated by transferring 0.2 mL of the medium in the culture tube to a freshly prepared tube.

Incubation of BGM cells in roller apparatus for periods greater than 1 week is not recommended as cells under these conditions tend to die-off if held longer.

If tubes receiving agar plugs from negative controls develop CPE or tubes receiving agar plugs from positive controls fail to develop CPE, stop all assays until the source of the failure is identified and corrected.

Tubes developing CPE may be stored in a -70°C freezer for additional optional tests (e.g., the Lim Benyesh-Melnick identification procedure.[5]

(c.5) Determine the fraction of confirmed plaques (C) for each sludge sample tested. Calculate "C" by dividing the number of tubes inoculated with agar plugs from plaques that developed CPE by the total number of tubes inoculated (i.e., if CPE was obtained from 17 of 20 plaques, C = 0.85).

5.2.7 Calculation of virus titer.

If more than one composite sample was assayed, average the titer of all composite samples and report the average titer and the standard deviation for each lot of sludge tested.

(a) If the entire remaining portion of a test sample was inoculated onto BGM cultures as described in section 5.2.3e.5, calculate the virus titer (V) in PFU per 4 g of total dry solids according to the formula:

$$V = 0.8 \times P \times C$$

where P is the total number of plaques in all test vessels for that sample and C equals the fraction of confirmed plaques.

(b) If the sample was diluted due to high virus levels (e.g., when the virus density of the input to a process is being determined; see section 5.2.5c), calculate the virus titer (V) in PFU per 4 g total dry solids with the formula:

$$V = 0.8 \times \frac{P}{I} \times D \times S \times C$$

where P is the total number of plaques in all test vessels for dilution series, I is the volume (in mL) of the dilution inoculated, D is reciprocal of the dilution made on the inoculum before plating, S is the volume of the remaining portion of the test sample (as recorded in section 5.2.3e.5) and C is the fraction of confirmed plaques.

5.2.8 Calculate the percent of virus recovery (R) using the formula:

$$R = \frac{P}{400} \times 100$$

where P is the total number of plaques on all test vessels inoculated with the recovery control.

6. Cell Culture Preparation and Maintenance[6]

6.1. Introduction

This section outlines procedures and media for culturing the Buffalo Green monkey (BGM) kidney cell line and is intended for the individual who is experienced in cell culture preparation. BGM cells are a continuous cell line derived from African Green monkey kidney cells. The characteristics of this line were described by Barron et al. (1970). Use of BGM cells for recovering viruses from environmental samples was described by Dahling et al. (1974). The media and methods recommended are the results of the BGM cell line optimization studies by Dahling and Wright (1986). The BGM cell line can be obtained by qualified laboratories from the Biohazard Assessment Research Branch, National Exposure Research Laboratory, U. S. Environmental Protection Agency, Cincinnati, Ohio, USA 45268. Although BGM

[5]For more information see EPA/600/4-84/013(R12), May 1988 Revision

[6]Modified from EPA/600/4-84/013(R9), January 1987 Revision

cells will not detect all enteric viruses that may be present in sludges, the use of this cell line alone is sufficient to meet the requirements of 40 CFR Part 503.

6.2. Apparatus and Materials

6.2.1 Glassware, Pyrex (Corning Product No. 1395 or equivalent).

Storage vessels must be equipped with airtight closures.

6.2.2 Autoclavable inner-braided tubing with metal quick-connect connectors or with screw clamps for connecting tubing to equipment to be used under pressure.

Quick-connect connectors can be used only after equipment has been properly adapted.

6.2.3 Positive pressure air, nitrogen or 5% CO_2 source equipped with pressure gauge.

Pressure sources from laboratory air lines and pumps must be equipped with an oil filter. The source must not deliver more pressure to the pressure vessel than is recommended by manufacturer.

6.2.4 Dispensing pressure vessel — 5 or 20 liter capacity (Millipore Corp. Product No. XX67 00P 05 and XX67 00P 20 or equivalent).

6.2.5 Disc filter holders — 142 mm or 293 mm diameter (Millipore Corp. Product No. YY30 142 36 and YY30 293 16 or equivalent).

Use only pressure type filter holders.

6.2.6 Sterilizing filter stacks — 0.22 µm pore size (Millipore Corp. Product No. GSWP 142 50 and GSWP 293 25 or equivalent). Fiberglass prefilters (Millipore Corp. Product No. AP15 142 50 or AP15 293 25 and AP20 142 50 or AP20 293 25 or equivalent).

Stack AP20 and AP15 prefilters and 0.22 µm membrane filter into a disc filter holder with AP20 prefilter on top and 0.22 µm membrane filter on bottom.

Always disassemble the filter stack after use to check the integrity of the 0.22 µm filter. Refilter any media filtered with a damaged stack.

6.2.7 Positively-charged cartridge filter — 10 inch (Zeta plus TSM, Cuno Product No. 45134-01-600P or equivalent). Holder for cartridge filter with adaptor for 10 inch cartridge (Millipore Corp. Product No. YY16 012 00 or equivalent).

6.2.8 Culture capsule filter (Gelman Sciences Product No. 12140 or equivalent).

6.2.9 Cell culture vessels — Pyrex, soda or flint glass or plastic bottles and flasks or roller bottles (e.g., Brockway Product No. 1076-09A, 1925-02, Corning Product No. 25100-25, 25110-75, 25120-150, 25150-1750 or equivalent).

Vessels must be made from clear glass or plastic to allow observation of the cultures and be equipped with airtight closures. Plastic vessels must be treated by the manufacturer to allow cells to adhere properly.

6.2.10 Screw caps, black with rubber liners (Brockway Product No. 24-414 for 6 oz bottles[7] or equivalent).

Caps for larger culture bottles usually supplied with bottles.

6.2.11 Roller apparatus (Bellco Product No. 7730 or equivalent).

6.2.12 Incubator capable of maintaining the temperature of cell cultures at 36.5 ± 1°C.

6.2.13 Waterbath, equipped with circulating device to assure even heating at 36.5 ± 1°C.

6.2.14 Light microscope, with conventional light source, equipped with lenses to provide 40X, 100X, and 400X total magnification.

6.2.15 Inverted light microscope equipped with lenses to provide 40X, 100X, and 400X total magnification.

6.2.16 Cornwall syringe pipettors, 2, 5 and 10 mL sizes (Curtin Matheson Scientific Product No. 221-861, 221-879, and 221-887 or equivalent).

6.2.17 Brewer-type pipetting machine (Curtin Matheson Scientific Product No. 138-107 or equivalent).

6.2.18 Phase contrast counting chamber (hemocytometer) (Curtin Matheson Scientific Product No. 158-501 or equivalent).

6.2.19 Conical centrifuge tubes, sizes 50 mL and 250 mL.

6.2.20 Rack for tissue culture tubes (Bellco Product No. 2028 or equivalent).

6.2.21 Bottles, aspirator-type with tubing outlet, size 2,000 mL.

Bottles for use with pipetting machine.

6.2.22 Storage vials, size 2 mL.

Vials must withstand temperatures to -70°C.

6.3. Media and Reagents

6.3.1 Sterile fetal calf, gammagobulin-free newborn calf or iron-supplemented calf serum, certified free of

[7]Size is given in oz only when it is commercially designated in that unit.

viruses, bacteriophage and mycoplasma (GIBCO BRL or equivalent).

Test each lot of serum for cell growth and toxicity before purchasing. Serum should be stored at -20°C for long-term storage. Upon thawing, each bottle should be heat-inactivated at 56°C for 30 min and stored at 4°C for short term use.

6.3.2 Trypsin, 1:250 powder (Difco Laboratories Product No. 0152-15-9 or equivalent) or trypsin, 1:300 powder (BBL Microbiology Systems Product No. 12098 or equivalent).

6.3.3 Sodium (tetra) ethylenediamine tetraacetate powder (EDTA), technical grade, (Fisher Scientific Product No. S657-500 or equivalent).

6.3.4 Thioglycollate medium (Difco Laboratories Product No. 0257-01-9 or equivalent).

6.3.5 Fungizone (amphotericin B, Sigma Chemical Product No. A-9528 or equivalent), Penicillin G (Sigma Chemical Product No. P-3032 or equivalent), dihydrostreptomycin sulfate (ICN Biomedicals Product No. 100556 or equivalent), and tetracycline (ICN Biomedicals Product No. 103011 or equivalent).

Use antibiotics of at least tissue culture grade.

6.3.6 Eagle's minimum essential medium (MEM) with Hanks' salts and L-glutamine, without sodium bicarbonate (GIBCO BRL Product No. 410-1200 or equivalent).

6.3.7 Leibovitz's L-15 medium with L-glutamine (GIBCO BRL Product No. 430-1300 or equivalent).

6.3.8 Trypan blue (Sigma Chemical Product No. T-6146 or equivalent).

Note: This chemical is on the EPA list of proven or suspected carcinogens.

6.3.9 Dimethyl sulfoxide (DMSO; Sigma Chemical Product No. D-2650 or equivalent).

6.3.10 Mycoplasma testing kit (Irvine Scientific Product No. T500-000 or equivalent).

6.4. Preparation of Cell Culture Media

6.4.1 General Principles

(a) Equipment care — Carefully wash and sterilize equipment used for preparing media before each use.

(b) Disinfection of work area — Thoroughly disinfect surfaces on which the medium preparation equipment is to be placed. Many commercial disinfectants do not adequately kill total culturable viruses. To ensure thorough disinfection, disinfect all surfaces and spills with either a solution of 0.5% (5 g per liter) iodine in 70% ethanol or 0.1% HOCl.

(c) Aseptic technique — Use aseptic technique when preparing and handling media or medium components.

(d) Dispensing filter-sterilized media — To avoid post-filtration contamination, dispense filter-sterilized media into storage containers through clear glass filling bells in a microbiological laminar flow hood. If a hood is unavailable, use an area restricted solely to cell culture manipulations.

(e) Coding media — Assign a lot number to and keep a record of each batch of medium or medium components prepared. Place the lot number, the date of preparation, the expiration date, and the initials of the person preparing the medium on each bottle.

(f) Sterility test — Test each lot of medium and medium components to confirm sterility as described in section 6.5 before the lot is used for cell culture.

(g) Storage of media and medium components — Store media and medium components in clear airtight containers at 4°C or -20°C as appropriate.

(h) Sterilization of $NaHCO_3$-containing solutions — Sterilize media and other solutions that contain $NaHCO_3$ by positive pressure filtration.

Negative pressure filtration of such solutions increases the pH and reduces the buffering capacity.

6.4.2 Media Preparation Recipes

(a) Sources of cell culture media — Commercially prepared liquid cell culture media and medium components are available from several sources. Cell culture media can also be purchased in powder form that requires only dissolution in dH_2O and sterilization. Media from commercial sources are quality-controlled. The conditions specified by the supplier for storage and expiration dates should be strictly observed. However, media can also be prepared in the laboratory directly from chemicals. Such preparations are labor intensive, but allow quality control of the process at the level of the preparing laboratory.

(b) Procedure for the preparation of EDTA-trypsin.

The procedure described is for the preparation of 10 liters of EDTA-trypsin reagent. It is used to dislodge cells attached to the surface of culture bottles and flasks. This reagent, when stored at 4°C, retains its working strength for at least four months. The amount of reagent prepared should be based on projected usage over a four-month period.

(b.1) Add 30 g of trypsin (1:250) or 25 g of trypsin (1:300) and two liters of dH_2O to a six liter flask containing a three inch stir bar. Place the flask onto a magnetic stirrer and mix the trypsin solution rapidly for a minimum of one hour.

Trypsin remains cloudy.

(b.2) Add four liters of dH_2O and a three-inch stir bar into 20 liter clear plastic carboy. Place the carboy onto a magnetic stirrer and stir at a speed sufficient to develop a vortex while adding the following chemicals: 80 g NaCl, 12.5 g

EDTA, 50 g dextrose, 11.5 g $Na_2HPO_4 \cdot 7H_2O$, 2.0 g KCl, and 2.0 g KH_2PO_4.

Each chemical does not have to be completely dissolved before adding the next one.

(b.3) Add four more liters of dH_2O to carboy.

Continue mixing until all chemicals are completely dissolved.

(b.4) Add the two liters of trypsin from step 6.4.2b.1 to the prepared solution in step 6.4.2b.3 and mix for a minimum of one hour. Adjust the pH of the EDTA-trypsin reagent to 7.5 - 7.7.

(b.5) Filter reagent under pressure through a disc filter stack and store the filtered reagent in tightly stoppered or capped containers at 4°C.

The cartridge prefilter (section 6.2.7) can be used in line with the culture capsule sterilizing filter (section 6.2.8) as an alternative to a filter stack (section 6.2.6).

(c) Procedure for the preparation of MEM/L-15 medium.

The procedure described is for preparation of 10 liters of MEM/L-15 medium.

(c.1) Place a three inch stir bar and four liters of dH_2O into 20 liter carboy.

(c.2) Place the carboy onto a magnetic stirrer. Stir at a speed sufficient to develop a vortex and then add the contents of a five liter packet of L-15 medium to the carboy. Rinse the medium packet with three washes of 200 mL each of dH_2O and add the rinses to the carboy.

(c.3) Mix until the medium is evenly dispersed.

L-15 medium may appear cloudy as it need not be totally dissolved before proceeding to step 6.4.2c.4.

(c.4) Add three liters of dH_2O to the carboy and the contents of a five liter packet of MEM medium to the carboy. Rinse the MEM medium packet with three washes of 200 mL each of dH_2O and add the rinses to the carboy. Add 800 mL of dH_2O and 7.5 g of $NaHCO_3$ and continue mixing for an additional 60 min.

(c.5) Transfer the MEM/L-15 medium to a pressure can and filter under positive pressure through a 0.22 µm sterilizing filter. Collect the medium in volumes appropriate for the culturing of BGM cells (e.g., 900 mL in a 1 liter bottle) and store in tightly stoppered or capped containers at 4°C.

Medium may be stored for periods of up to two months.

(d) Procedure for preparation of trypan blue solution.

The procedure described is for the preparation of 100 mL of trypan blue solution. It is used in the direct determination of the viable cell counts of the BGM stock cultures. As trypan blue is on the EPA suspect carcinogen list, particular care should be taken in its preparation and use so as to avoid skin contact or inhalation. The wearing of rubber gloves during preparation and use is recommended.

(d.1) Add 0.5 g of trypan blue to 100 mL of dH_2O in a 250 mL flask. Swirl the flask until the trypan blue is completely dissolved.

(d.2) Sterilize the solution by autoclaving at 121°C for 15 minutes and store in a screw-capped container at room temperature.

(e) Procedure for preparation of stock antibiotic solutions.

If not purchased in sterile form, stock antibiotic solutions must be filter-sterilized by the use of 0.22 µm membrane filters. It is important that the recommended antibiotic levels not be exceeded when planting cells as the cultures are particularly sensitive to excessive concentrations at this stage.

Antibiotic stock solutions should be placed in screw-capped containers and stored at -20°C until needed. Once thawed, they may be refrozen; however, repeated freezing and thawing of these stock solutions should be avoided by distributing them in quantities that are sufficient to support a week's cell culture work.

(e.1) Preparation of penicillin-streptomycin stock solution.

The procedure described is for preparation of ten 10 mL aliquots of penicillin-streptomycin stock solution at concentrations of 1,000,000 units of penicillin and 1,000,000 µg of streptomycin per 10 mL unit. The antibiotic concentrations listed in step 6.4.2e.1.1 may not correspond to the concentrations obtained from other lots or from a different source.

(e.1.1) Add appropriate amounts of penicillin G and dihydrostreptomycin sulfate to a 250 mL flask containing 100 mL of dH_2O. Mix the contents of the flasks on magnetic stirrer until the antibiotics are dissolved.

For penicillin supplied at 1435 units per mg, add 7 g of the antibiotic.

For streptomycin supplied at 740 mg per g, add 14 g of the antibiotic.

(e.1.2) Sterilize the antibiotics by filtration through 0.22 µm membrane filters and dispense in 10 mL volumes into screw-capped containers.

(e.2) Preparation of tetracycline stock solution. Add 1.25 g of tetracycline hydrochloride powder and 3.75 g of ascorbic acid to a 125 mL flask containing 50 mL of dH_2O. Mix the contents of the flask on a magnetic stirrer until the antibiotic is dissolved. Sterilize the antibiotic by filtration through a 0.22 µm membrane filter and dispense in 5 mL volumes into screw-capped containers.

(e.3) Preparation of amphotericin B (fungizone) stock solution. Add 0.125 g of amphotericin B to a 50 mL flask containing 25 mL of ddH_2O. Mix the contents of the flask on a magnetic stirrer until the antibiotic is dissolved. Sterilize the antibiotic by filtration through 0.22 µm membrane filter and dispense 2.5 mL volumes into screw-capped containers.

6.5. Procedure for Verifying Sterility of Liquids

There are many techniques available for verifying the sterility of liquids such as cell culture media and medium components. The two techniques described below are standard in many laboratories. The capabilities of these techniques are limited to the detection of microorganisms that grow unaided on the test medium utilized. Viruses, mycoplasma, and microorganisms that possess fastidious growth requirements or that require living host systems will not be detected. Nonetheless, with the exception of a few special contamination problems, the test procedures and microbiological media listed below should prove adequate. Do not add antibiotics to media or medium components until after sterility of the antibiotics, media and medium components has been demonstrated. BGM cell lines should be monitored every six months for mycoplasma contamination according to test kit instructions. Cells that are contaminated should be discarded.

6.5.1 Procedure for Verifying Sterility of Small Volumes of Liquids. Inoculate 5 mL of the material to be tested for sterility into 5 mL of thioglycollate broth. Shake the mixture and incubate at 36.5 ± 1°C. Examine the inoculated broth daily for seven days to determine whether growth of contaminating organisms has occurred.

Vessels that contain thioglycollate medium must be tightly sealed before and after medium is inoculated.

6.5.2 Visual Evaluation of Media for Microbial Contaminants. Incubate media at 36.5 ± 1°C for at least one week prior to use. Visually examine and discard any media that lose clarity.

A clouded condition that develops in the media indicates the occurrence of contaminating organisms.

6.6. Procedures for Preparation and Passage of BGM Cell Cultures

A laminar flow biological safety cabinet should be used to process cell cultures. If a biological safety cabinet is not available, cell cultures should be prepared in controlled facilities used for no other purposes. Viruses or other microorganisms must not be transported, handled, or stored in cell culture transfer facilities.

6.6.1 Vessels and Media for Cell Growth

(a) The BGM cell line grows readily on the inside surfaces of glass or specially treated, tissue culture grade plastic vessels. 16 to 32 oz (or equivalent growth area) flat-sided, glass bottles, 75 or 150 cm^2 plastic cell culture flasks, and 690 cm^2 glass or 850 cm^2 plastic roller bottles are usually used for the maintenance of stock cultures. Flat-sided bottles and flasks that contain cells in a stationary position are incubated with the flat side (cell monolayer side) down. If available, roller bottles and roller apparatus units are preferable to flat-sided bottles and flasks because roller cultures require less medium than flat-sided bottles per unit of cell monolayer surface. Roller apparatus rotation speed should be adjusted to one-half revolution per minute to ensure that cells are constantly bathed in growth medium.

(b) Growth and maintenance media should be prepared on the day they will be needed. Prepare growth medium by supplementing MEM/L-15 medium with 10% serum and antibiotics (100 mL of serum, 1 mL of penicillin-streptomycin stock, 0.5 mL of tetracycline stock and 0.2 mL of fungizone stock per 900 mL of MEM/L-15). Prepare maintenance medium by supplementing MEM/L-15 with antibiotics and 2% or 5% serum (20 or 50 mL of serum, antibiotics as above for growth medium and 70 or 50 mL of dH_2O, respectively).

6.6.2 General Procedure for Cell Passage

Pass stock BGM cell cultures at approximately seven day intervals using growth medium.

(a) Pour spent medium from cell culture vessels, and discard the medium.

To prevent splatter, a gauze-covered beaker may be used to collect spent medium.

Before discarding, autoclave all media that have been in contact with cells or that contain serum.

(b) Add to the cell cultures a volume of warm EDTA-trypsin reagent equal to 40% of the volume of medium replaced.

See Table 2 for the amount of reagents required for commonly used vessel types.

To reduce shock to cells, warm the EDTA-trypsin reagent to 36.5 ± 1°C before placing it on cell monolayers. Dispense the EDTA-trypsin reagent directly onto the cell monolayer.

(c) Allow the EDTA-trypsin reagent to remain in contact with the cells at either room temperature or at 36.5 ± 1°C until cell monolayer can be shaken loose from inner surface of cell culture vessel (about five min).

If necessary, a sterile rubber policeman (or scraper) may be used to physically remove the cell sheet from the bottle. However, this procedure should be used only as a last resort because of the risk of cell culture contamination inherent in such manipulations. The EDTA-trypsin reagent should remain in contact with the cells no longer than necessary as prolonged contact can alter or damage the cells.

(d) Pour the suspended cells into centrifuge tubes or bottles.

To facilitate collection and resuspension of cell pellets, use tubes or bottles with conical bottoms. Centrifuge tubes and bottles used for this purpose must be able to withstand the g-force applied.

(e) Centrifuge cell suspension at 1,000 ×*g* for 10 min to pellet cells. Pour off and discard the supernatant.

Do not exceed this speed as cells may be damaged or destroyed.

TABLE 2. Guide for Preparation of BGM Stock Cultures

Vessel Type	EDTA-Trypsin Volume (mL)[1]	Media Volume (mL)[2]	Total No. Cells to Plate per Vessel
16 oz glass flat bottles[3]	10	25	2.5×10^6
32 oz glass flat bottles	20	50	5.0×10^6
75 cm^2 plastic flat flask	12	30	3.0×10^6
150 cm^2 plastic flat flask	24	60	6.0×10^6
690 cm^2 glass roller bottle	40	100	7.0×10^7
850 cm^2 plastic roller bottle	50	120	8.0×10^7

[1]The volume required to remove cells from vessels.
[2]Serum requirements: growth medium contains 10% serum; maintenance medium contains 2-5% serum. Antibiotic requirements: penicillin-streptomycin stock solution, 1.0 mL/ liter; tetracycline stock solution, 0.5 mL/liter; fungizone stock solution, 0.2 mL/liter.
[3]Size is given in oz only when it is commercially designated in that unit.

(f) Suspend the pelleted cells in growth medium (see section 6.6.1b) and perform a viable count on the cell suspension according to procedures in section 6.7.

Resuspend pelleted cells in sufficient volumes of medium to allow thorough mixing of the cells (to reduce sampling error) and to minimize the significance of the loss of the 0.5 mL of cell suspension required for the cell counting procedure. The quantity of medium used for resuspending pelleted cells varies from 50 to several hundred mL, depending upon the volume of the individual laboratory's need for cell cultures.

(g) Dilute the cell suspension to the appropriate cell concentration with growth medium and dispense into cell culture vessels with either a Cornwall-type syringe or Brewer-type pipetting machine dispenser.

Calculate the dilution factor requirement using the cell count established in section 6.7 and the cell and volume parameters given in Table 2 for stock cultures and in Table 3 for virus assay cultures.

As a general rule, the BGM cell line can be split at a 1:3 ratio. However, a more suitable inoculum is obtained if low passages of the line (passages 100-150) are split at a 1:2 ratio and higher passages (generally above passage 250) are split at a 1:4 ratio. To plant two hundred 25 cm^2 cell culture flasks weekly from a low-level passage of the line would require the preparation of six roller bottles (surface area 690 cm^2 each): two to prepare the six roller bottles and four to prepare the 25 cm^2 flasks.

(h) Except during handling operations, maintain BGM cells at 36.5 ± 1°C in airtight cell culture vessels.

6.6.3 Procedure for Changing Medium on Cultured Cells — Cell monolayers normally become 95 to 100% confluent three to four days after seeding with an appropriate number of cells, and growth medium becomes acidic. Growth medium on confluent stock cultures should then be replaced with maintenance medium containing 2% serum. Maintenance medium with 5% serum should be used when monolayers are not yet 95% to 100% confluent but the medium in which they are immersed has become acidic. The volume of maintenance medium should equal the volume of discarded growth medium.

6.7. Procedure for Performing Viable Cell Counts

With experience a fairly accurate cell concentration can be made based on the volume of packed cells. However, viable cell counts should be performed periodically as a quality control measure.

6.7.1 Add 0.5 mL of cell suspension (or diluted cell suspension) to 0.5 mL of 0.5% trypan blue solution in a test tube.

To obtain an accurate cell count, the optimal total number of cells per hemocytometer section should be between 20 and 50. This range is equivalent to between 6.0 × 10^5 and 1.5 × 10^6 cells per mL of cell suspension. Thus, a dilution of 1:10 (0.5 mL of cells in 4.5 mL of growth medium) is usually required for an accurate count of a cell suspension.

6.7.2 Disperse cells by repeated pipetting.

Avoid introducing air bubbles into the suspension, because air bubbles may interfere with subsequent filling of the hemocytometer chambers.

6.7.3 With a capillary pipette, carefully fill a hemocytometer chamber on one side of a slip-covered hemocytometer slide. Rest the slide on a flat surface for about one min to allow the trypan blue to penetrate the cell membranes of nonviable cells.

Do not under or over fill the chambers.

6.7.4 Under 100X total magnification, count the cells in the four large corner sections and the center section of the hemocytometer chamber.

Include in the count cells lying on the lines marking the top and left margins of the sections, and ignore cells on the lines marking the bottom and right margins. Trypan blue is excluded by living cells. Therefore, to quantify viable cells, count only cells that are clear in color. Do not count cells that are blue.

Table 3. Guide for Preparation of Virus Assay Cell Cultures

Vessel Type	Volume of Medium (mL)[1]	Final Cell Count per Bottle
1 oz glass bottle[2]	4	9.0×10^5
25 cm^2 plastic flask	10	3.5×10^6
6 oz glass bottle	15	5.6×10^6
75 cm^2 plastic flask	30	1.0×10^7
16 mm × 150 mm tubes	2	4.0×10^4

[1]Serum requirements: growth medium contains 10% serum; maintenance medium contains 2-5% serum. Antibiotic requirements: penicillin-streptomycin stock solution, 1.0 mL/liter; tetracycline stock solution, 0.5 mL/liter; fungizone stock solution, 0.2 mL/liter.
[2]Size is given in oz only when it is commercially designated in that unit.

6.7.5 Calculate the average number of viable cells in each mL of cell suspension by totaling the number of viable cells counted in the five sections, multiplying this sum by 4000, and where necessary, multiplying the resulting product by the reciprocal of the dilution.

6.8. Procedure for Preservation of BGM Cell Line

An adequate supply of BGM cells must be available to replace working cultures that are used only periodically or become contaminated or lose virus sensitivity. Cells have been held at -70°C for more than 15 years with a minimum loss in cell viability.

6.8.1 Preparation of Cells for Storage

The procedure described is for the preparation of 100 cell culture vials. Cell concentration per mL must be at least 1 x 10^6.

Base the actual number of vials to be prepared on usage of the line and the anticipated time interval requirement between cell culture start-up and full culture production.

(a) Prepare cell storage medium by adding 10 mL of DMSO to 90 mL of growth medium (see section 6.6.1b). Sterilize cell storage medium by passage through an 0.22 µm sterilizing filter.

Collect sterilized medium in 250 mL flask containing a stir bar.

(b) Harvest BGM cells from cell culture vessels as directed in section 6.6.2. Count the cells according to the procedure in section 6.7 and resuspend them in the cell storage medium at a concentration of 1×10^6 cells per mL.

(c) Place the flask containing suspended cells on a magnetic stirrer and slowly mix for 30 min. Dispense 1 mL volumes of cell suspension into 2 mL vials.

6.8.2 Procedure for Freezing Cells

The freezing procedure requires slow cooling of the cells with the optimum rate of -1°C per min. A slow cooling rate can be achieved using the following method or by using the recently available freezing containers (e.g., Nalge Company Product No. 5100-0001 or equivalent) as recommended by the manufacturers.

(a) Place the vials in a rack and place the rack in refrigerator at 4°C for 30 min, in a -20°C freezer for 30 min, and then in a -70°C freezer overnight. The transfers should be made as rapidly as possible.

To allow for more uniform cooling, wells adjoining each vial should remain empty.

(b) Rapidly transfer vials into boxes or other containers for long-term storage.

To prevent substantial loss of cells during storage, temperature of cells should be kept constant after -70°C has been achieved.

6.8.3 Procedure for Thawing Cells

Cells must be thawed rapidly to decrease loss in cell viability.

(a) Place vials containing frozen cells into a 36°C water bath and agitate vigorously by hand until all ice has melted. Sterilize the outside surface of the vials with 0.5% iodine in 70% ethanol.

(b) Add BGM cells to either 6 oz tissue culture bottles or 25 cm^2 tissue culture flasks containing an appropriate volume of growth medium (see Table 3). Use two vials of cells for 6 oz bottles and one vial for 25 cm^2 flasks.

(c) Incubate BGM cells at 36.5 ± 1°C. After 18 to 24 h replace the growth medium with fresh growth medium and then continue the incubation for an additional five days. Pass and maintain the new cultures as directed in section 6.6.

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Appendix I
Test Method for Detecting, Enumerating, and Determining the Viability of *Ascaris* Ova in Sludge

1.0 Scope

1.1 This test method describes the detection, enumeration, and determination of viability of *Ascaris* ova in water, wastewater, sludge, and compost. These pathogenic intestinal helminths occur in domestic animals and humans. The environment may become contaminated through direct deposit of human or animal feces or through sewage and wastewater discharges to receiving waters. Ingestion of water containing infective *Ascaris* ova may cause disease.

1.2 This test method is for wastewater, sludge, and compost. It is the user's responsibility to ensure the validity of this test method for untested matrices.

1.3 This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. For specific hazard statements, see section 9.

2.0 Referenced Documents

***2.1 ASTM Standards**:*

- D 1129 Terminology Relating to Water[1]
- D 1193 Specification for Reagent Water[2]
- D 2777 Practice for Determination of Precision and Bias of Applicable Methods of committee D-19 on Water[3]

3.0 Terminology

(Definitions and Descriptions of Terms must be approved by the Definitions Advisor.)

3.1 Definitions - For definitions of terms used in this test method, refer to Terminology D 1129.

3.2 Descriptions of Terms Specific to This Standard:

3.2.1 The normal nematode life cycle consists of the egg, 4 larval stages and an adult. The larvae are similar in appearance to the adults; that is, they are typically worm-like in appearance.

3.2.2 Molting (*ecdysis*) of the outer layer *(cuticle*) takes place after each larval stage. Molting consists of 2 distinct processes, the deposition of the new cuticle and the shedding of the old one or exsheathment. The cuticle appears to be produced continuously, even throughout adult life.

3.2.3 A molted cuticle that still encapsulates a larva is called a *sheath*.

3.2.4 Ascarid egg shells are commonly comprised of layers. The outer tanned, bumpy layer is referred to as the *mammillated* layer and is useful in identifying *Ascaris* eggs. The mammillated layer is sometimes absent. Eggs that do not possess the mammillated layer are referred to as *decorticated* eggs.

3.2.5 A potentially infective *Ascaris* egg contains a third stage larva[4] encased in the sheaths of the first and second larval stages.

4.0 Summary of Test Method

4.1 This method is used to concentrate pathogenic *Ascaris* ova from wastewater, sludge, and compost. Samples are processed by blending with buffered water containing a surfactant. The blend is screened to remove large particulates. The solids in the screened portion are allowed to settle out and the supernatant is decanted. The sediment is subjected to density gradient centrifugation using magnesium sulfate (specific gravity 1.20). This flotation procedure yields a layer likely

[1]Annual Book of ASTM Standards, Vol 11.01.
[2]Annual Book of ASTM Standards, Vol 11.01.
[3]Annual Book of ASTM Standards, Vol 11.01.

[4]P.L. Geenen, J. Bresciani, J. Boes, A. Pedersen, L. Eriksen, H.P. Fagerholm, and P. Nansen (1999)The morphogenesis of Ascaris suum to the infective third-stage larvae within the egg, J. Parasitology 85(4):616-622.

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to contain *Ascaris* and some other parasitic ova, if present, in the sample. Small particulates are removed by a second screening on a small mesh size screen.[5] The resulting concentrate is incubated at 26EC until control *Ascaris* eggs are fully embryonated. The concentrate is then microscopically examined for the categories of *Ascaris* ova on a Sedgwick-Rafter counting chamber.

5.0 Significance and Use

5.1 This test method is useful for providing a quantitative indication of the level of *Ascaris* ova contamination of wastewater, sludge, and compost.

5.2 This test method will not identify the species of *Ascaris* detected nor the host of origin.

5.3 This method may be useful in evaluating the effectiveness of treatment.

6.0 Interferences

6.1 Freezing of samples will interfere with the buoyant density of *Ascaris* ova and decrease the recovery of ova.

7.0 Apparatus

7.1 A good light microscope equipped with brightfield, and preferably with phase contrast and/or differential contrast optics including objectives ranging in power from 10X to 45X.

7.2 Sedgwick-Rafter cell.

7.3 Pyrex beakers, 2 L. Coat with organosilane.

7.4 Erlenmeyer flask, 500 mL. Coat with organosilane.

7.4 A centrifuge that can sustain forces of at least 660 X G with the rotors listed below.

7.4.1 A swinging bucket rotor to hold 100 or 250 ml centrifuge glass or plastic conical bottles.

7.4.2 A swinging bucket rotor to hold 15 ml conical glass or plastic centrifuge tubes.

7.5 Tyler sieves.

7.5.1 20 or 50 mesh.

7.5.2 400 mesh, stainless steel, 5 inch in diameter.

7.5.3 A large plastic funnel to support the sieve. Coat with organosilane.

7.6 Teflon spatula.

7.7 Incubator set at 26EC.

7.8 Large test tube rack to accommodate 100 or 250 mL centrifuge bottles.

7.9 Small test tube rack to accommodate 15 mL conical centrifuge tubes.

7.10 Centrifuge bottles, 100 or 250 mL. Coat with organosilane.

7.11 Conical centrifuge tubes, 15 mL. Coat with organosilane.

7.12 Pasteur pipettes. Coat with organosilane.

7.13 Vacuum aspiration apparatus.

7.13.1 Vacuum source.

7.13.2 Vacuum flask, 2 L or larger.

7.13.3 Stopper to fit vacuum flask, fitted with a glass or metal tubing as a connector for 1/4 inch tygon tubing.

7.14 Spray bottles (16 fl oz.) (2).

7.14.1 Label one “Water”.

7.14.2 Label one “1% 7X”.

8.0 Reagents and Materials

8.1 Purity of Reagents — Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society[6]. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

[5]This method is based on a protocol published by Bowman, D.D., M.D. Little, and R.S. Reimers (2003) Precision and accuracy of an assay for detecting *Ascaris* eggs in various biosolid matrices. Water Research **37**(9):2063-2072.

[6]Reagent Chemicals, American Chemical Specifications, American Chemical Society, Washington, D.C. For suggestions on testing of Reagents not listed by the American Chemical Society, see Analar Standards for Laboratory Chemicals, BHD Ltd., Poole, Dorset, U.K. and the United States Pharmacopeia and National Formulary, U.S. Pharmaceutical Convention, Inc. (USPC).

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8.2 Purity of Water — Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type I.

8.3 Preparation of Reagents — Prepare reagents in accordance with Practice E200.

8.3.1 Phosphate-buffered water (1 L = 34.0 g KH_2PO_4, pH adjusted to 7.2 ± 0.5 with 1 N NaOH).

8.3.2 1% (v/v) 7X ("ICN" laboratory detergent) (1 L = 999 mL phosphate-buffered water, 1 mL 7X "ICN", Adjust pH to 7.2 ± 0.1 with 1N NaOH).

8.3.3 Magnesium sulfate, sp. gr. 1.20. (1 L = 215.2 g $MgSO_4$, check specific gravity with a hydrometer; adjust as necessary to reach 1.20).

8.3.4 Organosilane. For coating glassware. Coat all glassware according to manufacturer's instructions.

8.3.5 Fresh *Ascaris* ova for positive control, purified from *Ascaris* infected pig fecal material.

9.0 Precautions

9.1 When handling *Ascaris* ova and biosolids, personal protective measures must be employed to prevent infection. Prevention of infection in humans is a matter of good personal hygiene. Wear a laboratory coat at all times in the laboratory. In addition, latex or nitrile gloves and splash protection safety glasses should always be worn in the laboratory. Mouth pipetting is strictly forbidden. Contaminated pipettes are never laid down on the bench top but are immediately placed in a pipette discard container which has disinfectant in it. Contaminated equipment is separated as it is used into containers for disposable materials and containers for re-cycling. After these containers which are always autoclave pans, are full, they are autoclaved for 30 minutes at 121EC and 15 pounds/in^2. Contaminated glassware is never washed until after it has been autoclaved. Eating, drinking, and smoking in the laboratory is not permitted. Likewise, refrigerators are not to be used for storing lunches or other items for human consumption. If infective *Ascaris* ova are ingested they may cause disease.

10.0 Sampling

10.1 Collect 1 liter of compost, wastewater, or sludge in accordance with Practice D 1066, Specification D 1192, and Practices D 3370, as applicable.

10.2 Place the sample container(s) on wet ice or around chemical ice and ship back to the laboratory for analysis within 24 hours of collection.

10.3 Store the samples in the laboratory refrigerated at 2 to 5EC. Do not freeze the samples during transport or storage.

11.0 Preparation of Apparatus

11.1 Test the centrifuge with a tachometer to make sure the revolution's per minute correlate with the speed gauge.

11.2 Calibrate the incubator temperature with a NIST traceable thermometer.

11.3 Microscope.

11.3.1 Clean the microscope optics.

11.3.2 Adjust the condenser on the microscope, so Köhler illumination is established.

12.0 Procedure

12.1 The percentage moisture of the sample is determined by analyzing a separate portion of the sample, so the final calculation of ova per gram dry weight can be determined. The concentration of ova in liquid sludge samples may be expressed as ova per unit volume.

12.2 Initial preparation:

12.2.1 Dry or thick samples: Weigh about 300 g (estimated dry weight) and place in about 500 ml water in a beaker and let soak overnight at 4 - 10EC. Transfer to blender and blend at high for one minute. Divide sample into four beakers.

12.2.2 Liquid samples: Measure 1,000 ml or more (estimated to contain at least 50 g dry solids) of liquid sample. Place one half of sample in blender. Add about 200 mL water. Blend at high speed for one minute transfer to a beaker. Repeat for other half of sample.

12.3 Pour the homogenized sample into a 1000 mL tall form beaker and using a wash bottle, thoroughly rinse blender container into beaker. Add 1% 7X to reach 900 ml final volume.

12.4 Allow sample to settle four hours or overnight at 4 - 10EC. Stir occasionally with a wooden applicator, as needed to ensure that material floating on the surface settles. Additional 1% 7X may be added, and the mixture stirred if necessary.

12.5 After settling, vacuum aspirate supernatant to just above the layer of solids. Transfer sediment to blender and add water to 500 ml, blend again for one minute at high speed.

12.6 Transfer to beaker, rinsing blender and add 1% 7X to reach 900 ml. Allow to settle for two hours at 4 - 10EC, vacuum aspirate supernatant to just above the layer of solids.

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12.7 Add 300 ml 1% 7X and stir for five minutes on a magnetic stirrer.

12.8 Strain homogenized sample through a 20 or 50 mesh sieve placed in a funnel over a tall beaker. Wash sample through sieve with a spray of 1% 7X from a spray bottle.

12.9 Add 1% 7X to 900 mL final volume and allow to settle for two hours at 4 - 10EC.

12.10 Vacuum aspirate supernatant to just above layer of solids. Mix sediment and distribute equally to 50 mL graduated conical centrifuge tubes. Thoroughly wash any sediment from beaker into tubes using water from a wash bottle. Bring volume in tubes up to 50 ml with water.

12.11 Centrifuge for 10 minutes at 1000 X G. Vacuum aspirate supernatant from each tube down to just above the level of sediment. (The packed sediment in each tube should not exceed 5 mL. If it exceeds this volume, add water and distribute the sediment evenly among additional tubes, repeat centrifugation, and vacuum aspirate supernatant.)

12.12 Add 10 to 15 mL of $MgSO_4$ solution (specific gravity 1.20) to each tube and mix for 15 to 20 seconds on a vortex mixer. (Use capped tubes to avoid splashing of mixture from the tube.)

12.13 Add additional $MgSO_4$ solution (specific gravity 1.20) to each tube to bring volume to 50 mL. Centrifuge for five to ten minutes at 800 to 1000 X g. DO NOT USE BRAKE.

12.14 Allow the centrifuge to coast to a stop without the brake. Pour the top 25 to 35 mL of supernatant from each tube through a 400 mesh sieve supported in a funnel over a tall beaker.

12.15 Using a water spray bottle, wash excessive flotation fluid and fine particles through sieve.

12.16 Rinse sediment collected on the sieve into a 100 mL beaker by directing the stream of water from the wash bottle onto the upper surface of the sieve.

12.17 After thoroughly washing the sediment from the sieve, transfer the suspension to the required number of 15 mL centrifuge tubes, taking care to rinse the beaker into the tubes. Usually one beaker makes one tube.

12.18 Centrifuge the tubes for three minutes at 800 X G, then discard the supernatant.

12.19 If more than one tube has been used for the sample, transfer the sediment to a single tube, fill with water, and repeat centrifugation.

12.20 Aspirate the supernatant above the solids.

12.21 Resuspend the solids in 4 mL 0.1 N H_2SO_4 and pour into a 20-mL polyethylene scintillation vial or equivalent with loose caps.

12.22 Before incubating the vials, mark the liquid level in each vial with a felt tip pen. Incubate the vials, along with control vials containing *Ascaris* ova mixed with 4 mL 0.1 N H_2SO_4, at 26EC for three to four weeks. Every day or so, check the liquid level in each vial. Add reagent grade water up to the initial liquid level line as needed to compensate for evaporation. After 18 days, suspend, by inversion and sample small aliquots of the control cultures once every 2 - 3 days. When the majority of the control *Ascaris* ova are fully embryonated, samples are ready to be examined.

12.23 Examine the concentrates microscopically using a Sedgwick-Rafter cell to enumerate the detected ova. Classify the ova as either unembryonated, embryonated to the first, second, or third larval stage. In some embryonated *Ascaris* ova the larva may be observed to move. See Figure 1 for examples of various *Ascaris* egg categories.

13.0 Calculation

13.1 Calculate % total solids using the % moisture result:

$$\% \text{ Total solids} = 100\% - \% \text{ moisture}$$

13.2 Calculate catagories of ova/g dry weight in the following manner:

$$\text{Ova/g dry wt} = \frac{(NO) \times (CV) \times (FV)}{(SP) \times (TS)}$$

Where:

NO = no. ova
CV = chamber volume(= 1 mL)
FV = final volume in mL
SP = sample processed in mL or g
TS = % total solids

14.0 Report

14.1 Report the results as the total number of *Ascaris* ova, number of unembryonated *Ascaris* ova, number of 1st, 2nd, or 3rd stage larva; reported as number of *Ascaris* ova and number of various larval *Ascaris* ova per g dry weight.

15.0 Keywords

Ascaris, ova, embryonation, viability assay, helminth.

Item E 000755

Notice

The PEC was consulted in a recent (1998-1999) pilot study by Lyonnaise des Eaux concerning the use of a microscope in making helminth ova counts for different types of sludge. Solids and debris present in the sludge being viewed with the microscope were found to impair ones ability to count. Dilution of raw sludge and digested sludge, however, with phosphate-buffered water prior to analyzing them significantly improved the number of ova that could be counted. Raw sludges were diluted by a factor of 20 and digested sludges by a factor of 5. QA/QC procedures were followed to validate this procedure. The PEC should be consulted for more details.

[revised May 15, 2003]

Figure A1.1. *Ascaris* ovum: potentially non-fertile, note bumpy mammilated outer layer.

Figure A1.2. *Ascaris* ovum: fertile, note the bumpy outer mammilated layer.

Figure A1.3. *Ascaris* ovum: decorticated, unembryonated. Note the outer mammilated layer is gone

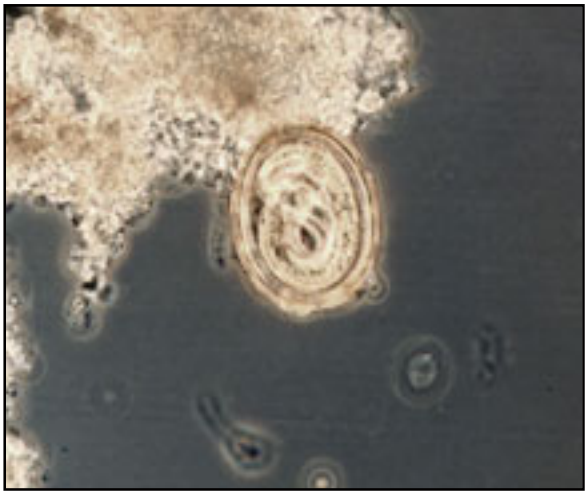


Figure A1.4. *Ascaris* ovum: decorticated and embryonated.

Figure A1.5. *Ascaris* ovum: decorticated, embryonated.

Figure A1.6. *Ascaris* ovum with second stage larva; note the first stage larval sheath at the anterior end of the worm

Appendix J
The Biosolids Composting Process

Introduction

Composting is the biological decomposition of organic matter under controlled aerobic conditions. The objectives of composting are to reduce pathogens to below detectable levels, degrade volatile solids, and produce a usable product. Pathogen reduction is a function of time and temperature. Composted biosolids is one way to meet 40 CFR Part 503 pathogen (and vector attraction) reduction requirements. Composted biosolids can meet either a "Process to Significantly Reduce Pathogens" (PSRP/Class B) or a "Process to Further Reduce Pathogens" (PFRP/Class A) standard, depending upon the operating conditions maintained at the facility. Process and operational considerations must be taken into account when a facility desires to meet the pathogen and vector attraction requirements of 40 CFR 503. The 40 CFR Part 503 regulations require composted biosolids applied to the land to meet specific pollutant limits, site restrictions, management practices, and pathogen and vector attraction reduction processes, depending upon whether they: 1) are applied to agricultural land, forest, a public contact site, or a reclamation site; 2) are sold or given away in a bag or other container; or 3) are applied to a lawn or home garden. Discussions provided here are presented in summary form; it is recommended that the facility seek additional details in developing a compost operation.

Composting Process Description

The addition of a bulking agent to sewage sludge provides optimum conditions for the composting process, which usually lasts 3 to 4 weeks. A bulking agent acts as a source of carbon for the biological process, increases porosity, and reduces the moisture level. The composting process has several phases, including the active phase, the curing phase, and the drying phase.

Active phase. During the active or stabilization phase, the sewage sludge/bulking agent mix is aerated and the sewage sludge is decomposed due to accelerated biological activity. The biological process involved in composting can raise the temperature up to 60°C or more. At these high temperatures, all of the disease-causing pathogens are destroyed. Windrow systems must meet this condition by achieving 55°C for a minimum of 15 consecutive days during which time the windrow is turned five times. The critical requirement is that the material in the core of the compost pile be maintained at the required temperatures (55°C) for the required time (3 days). Therefore, the first phase typically lasts 21 days. Aeration is accomplished in one of two ways: 1) by mechanically turning the mixture so that the sewage sludge is exposed to oxygen in the air; or 2) by using blowers to either force or pull air through the mixture.

Curing phase. After the active phase, the resulting material is cured for an additional 30 days to 180 days. At this time, additional decomposition, stabilization, pathogen destruction, and degassing takes place. Composting is considered complete when the temperature of the compost returns to ambient levels. Depending upon the extent of biodegradation during the active phase and the ultimate application of the finished product, the curing phase may not be carried out as a separate process.

Drying phase. After curing, some operations add another step called the drying phase which can vary from days to months. This stage is necessary if the material is to be screened to either recover the unused bulking agent for recycling or for an additional finished product. If the product is to be marketable, the final compost should be 50% to 60% solids.

There are two main process configurations for the composting process:

Unconfined composting. This process is conducted in long piles (windrows) or in static piles. Operations using unconfined composting methods may provide oxygen to the compost by turning the piles by hand or machine or by using air blowers which may be operated in either a positive (blowing) or negative (suction) mode. For windrows without blower aeration, it is typical to turn the windrow two or three times a week, using a front-end loader. Properly operating aerated static piles do not require turning.

Confined (in-vessel) composting. This process is carried out within an enclosed container, which minimizes odors and process time by providing better control over the process variables. Although in-vessel composting has been effective for small operations, typically these operations are proprietary and therefore will not be described any further in this fact sheet.

Operational Considerations

The key process variables for successful composting are the moisture content and carbon to nitrogen (C:N) ratio of the biosolids/bulking agent mixture, and temperature and aeration of the compost pile. Other process parameters such as volatile solids content, pH, mixing and the materials used in the compost also affect the process.

Bioso/ids/Bu/king Agent Mixture Moisture Content. Moisture control is an important factor for effective composting. Water content must be controlled for effective stabilization, pathogen inactivation, odor control and finished compost quality (Benedict, 1988). The optimum moisture content of the mix is between 40% and 60%. At less than 40% water, the material is too fluid, has reduced porosity and has the potential for producing septic conditions and odors; above 60% solids, the lack of moisture may slow down the rate of decomposition. Since typical dewatered sewage sludge or biosolids are often in the range of 15% to 20% solids for vacuum filtered sewage sludge or biosolids and 20% to 35% solids for belt press or filter pressed sewage sludge or biosolids, the addition of drier materials (bulking agents) is usually essential.

Biosolids/Bulking Agent Mixture Carbon to Nitrogen Ratio. Microorganisms need carbon for growth and nitrogen for protein synthesis. For efficient composting, the carbon to nitrogen (C:N) ratio of the biosolids/bulking agent mixture should be in the range of 25:1 to 35:1

Oxygen /eve/s. For optimum aerobic biological activity, air within the pile should have oxygen levels of between 5% and 15%. Lower levels of oxygen will create odors and reduce the efficiency of the composting. Excessive aeration will cool the pile, slow the composting process, and will not provide the desired pathogen and vector attraction reduction.

Conventional windrows obtain necessary oxygen through the natural draft and ventilation induced from the hot, moist air produced during active composting and from the periodic windrow turning. Where blowers are used for aeration, it is typical to provide at least one blower per pile.

Biosolids/Bulking Agent Mixture Volatile Solids Con tent. The volatile solids content of the biosolids/bulking agent mix should be greater than 50% for successful composting (EPA, 1985). This parameter is an indicator of the energy available for biological activity and therefore compostability.

Bioso/ids/Bu/king Agent Mixture pH. The pH of the biosolids/bulking agent mix should be in the range of 6 to 9 for efficient composting (EPA, 1985). Higher pH mixtures may result if lime stabilized biosolids are used. They can be composted; however, it may take longer for the composting process to achieve the temperatures needed to reduce pathogens.

Biosolids and Bulking Agent Mixing. Uniform mixing is necessary in order to assure that moisture concentration is constant through the pile and that air can flow throughout.

Type of Biosolids. The type of biosolids used may have an effect on the composting process. Composting can be accomplished with unstabilized biosolids, as well as anaerobically and aerobically digested biosolids. Raw sludge has a greater potential to cause odors because they have more energy available and will, therefore, degrade more readily. This may cause the compost pile to achieve higher temperatures faster unless sufficient oxygen is provided and may also cause odors (EPA, 1985).

Material for Bulking Agents. Materials such as wood chips, sawdust and recycled compost are usually added as "bulking agents" or "amendments" to the compost mixture to provide an additional source of carbon and to control the moisture content of the mixture. Other common bulking agents used by facilities around the country include wood waste, leaves, brush, manure, grass, straw, and paper (Goldstein, 1994). Because of their cost, wood chips are often screened out from the matured compost, for reuse. Although sawdust is frequently used for in-vessel composting, coarser materials such as wood chips, wood shavings, and ground-up wood are often preferred because they permit better air penetration and are easier to remove. Recycled compost is often used as a bulking agent in windrows, especially if bulking agents must be purchased. However, its use is limited because the porosity decreases as the recycle ages (EPA, 1989). The amount of biosolids and bulking agent which must be combined to make a successful compost is based on a mass balance process considering the moisture contents, C:N ratio, and volatile solids content.

Compost Pile Size. In general, assuming adequate aeration, the larger the pile the better. A larger pile has less surface area per cubic yard of contents and therefore retains more of the heat that is generated and is less influenced by ambient conditions. In addition, less cover and base material (recycled compost, wood chips, etc.) is needed as well as the overall land requirements for the compost operation. Larger piles tend to retain moisture longer. The surface area to volume ratio has an effect on the temperature of the pile. Assuming other factors are constant (e.g., moisture, composition, aeration), larger piles (with their lower surface area to volume ratio), retain more heat than smaller piles. Ambient temperatures have a significant impact on composting operations (Benedict, 1988).

A typical aerated static pile for a large operation would be triangularly shaped in cross section about 3 meters(m) high by 4.5 to 7.5 m wide (15 to 25 feet) at the base by 12 to 15 m long (39 to 50 feet) (Haug, 1980). One survey study indicates that extended aerated static pile (where piles are formed on the side of older piles) heights were typically 12 to 13 feet high. Minimum depths of base and cover materials (recycled compost, wood chips, etc.) were 12 and 18 inches, respectively (Benedict, 1988).

In windrow composting, the compost mix is stacked in long parallel rows. In cross section, windrows may range from rectangular to trapezoidal to triangular, depending

upon the material and the turning equipment. Atypical trapezoidal windrow might be 1.2 m (4 feet) high by 4.0 m (13 feet) at its base and 1.0 m (3 feet) across the top (Haug, 1980).

Monitoring and Sampling of the Compost Pile

Unless the entire composting mass is subject to the pathogen reduction temperatures, organisms may survive and repopulate the mass once the piles or windrows are cooled. Therefore it is crucial that temperatures be attained throughout the entire pile. For aerated static piles or in-vessel systems using static procedures such as tunnels or silos, temperature monitoring should represent points throughout the pile, including areas which typically are the coolest. In aerated static piles this is usually the toes of the pile (Figure 1). Temperatures should be taken at many locations and at various depths to be assured that the core of the pile maintains the required temperature. Records of the temperature, date, and time should be maintained and reviewed on an ongoing basis. Microbial analysis should at a minimum be taken in a matter to represent the entire compost pile. Operational parameters such as moisture, oxygen as well as the others should be monitored at a frequency necessary to assure that the compost operation is operating within acceptable ranges.

For composting, vector attraction reduction (VAR) is achieved through the degradation of volatile solids. The extent to which the volatile solids are degraded is often referred to as compost stability. Stabilization requires sufficient time for the putrescible organic compounds and for other potential food sources for vectors to decompose. Under this vector attraction reduction option, the Part 503 requires that biosolids be maintained under aerobic conditions for at least 14 days, during which time temperatures are over 40°C (104°F), and the average temperature is over 45°C (113°F) (503.33(b)(5). These criteria are based on studies which have shown that most of the highly putrescible compounds are decomposed during the first 14 days of composting and that significant stability is achieved at mesophilic (<45°C) temperatures.

Recommendations for Specific Technologies

Aerated static pile – Aerated static piles should be covered with an insulation layer of sufficient thickness to ensure that temperatures throughout the pile, including the pile surface, reach 55°C. It is recommended that the insulation layer be at least 1 foot thick. Screened compost is a more effective insulation than unscreened compost or wood chips. Screened compost also provides more odor control than the other two materials.

Air flow rate and the configuration of an aeration system are other factors which affect temperature. Air flow must be sufficient to supply oxygen to the pile, but excessive aeration removes heat and moisture from the composting material. The configuration of an aeration system is also important. Aeration piping too close to pile edges may result in uneven temperatures in the pile and excessive cooling at the pile toes. If holes in the perforated piping are too large or not distributed properly, portions of the pile may receive too much air and be too cool as a result.

Windrows – Compliance with the pathogen reduction requirements for windrows depends on proper windrow size and configuration. If windrows are too small, the high surface area to volume ratio will result in excessive heat loss from the pile sides. Turning must ensure that all material

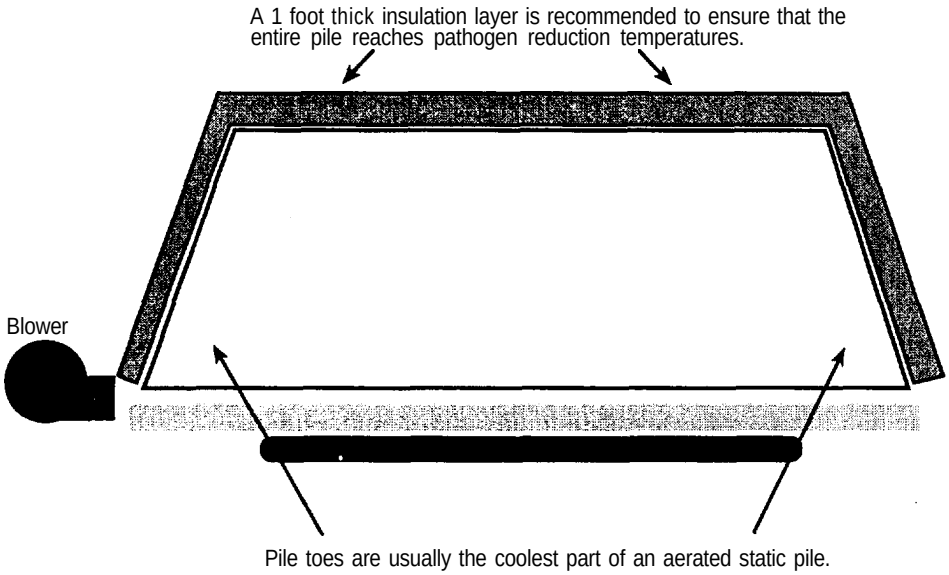
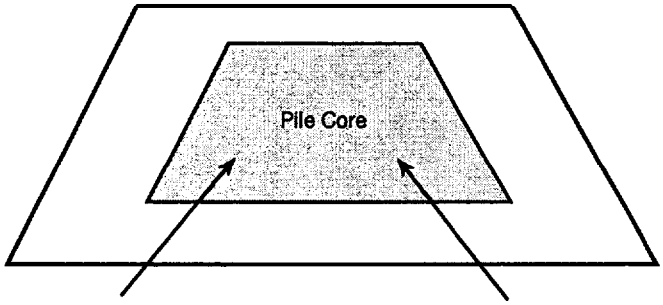


Figure 1a. Aerated static pile.



Material turned into the pile core reaches pathogen reduction temperatures. Operations must ensure that all material is turned into the core at some point during composting and that core temperatures rise to 55 degrees after turning.

Figure 1b. Windrow.

in a windrow be introduced into the pile core and raised to pathogen reduction temperatures. This is most easily achieved with a windrow turning machine.

In-Vessel systems- It is difficult to provide guidance for these systems as there are numerous types with varying configurations. Two key factors that apply to all in-vessel systems are aeration and available carbon. As with aerated static piles, the air flow configuration and rate can affect the distribution of aeration to different parts of a composting mass and the temperature profile of a pile. Many in-vessel systems use sawdust as an amendment. This may not provide sufficient energy if the volatile solids in the biosolids are low.

Requirements for Class A/Class B Compost

For class A biosolids, aerated static pile, conventional windrow and in-vessel composting methods must meet the PFRP requirements, including the following temperature/ time requirements:

- Aerated static piles and in-vessel systems must be maintained at a minimum operating temperature of 55°C (131°F) for at least 3 days; and
- Windrow piles must be maintained at a minimum operating temperature of 55°C (131°F) for 15 days or longer. The piles must be turned five times during this period.

For class B biosolids, aerated static pile, conventional windrow and in-vessel composting methods must meet the PSRP requirements, including the following temperature/ time requirements:

- The compost pile must be maintained at a minimum of 40°C for at least five days; and
- During the five-day period, the temperature must rise above 55°C for at least four hours to ensure pathogen destruction. This is usually done near the end of the active composting phase in order to prevent inactivating the organic destroying bacteria.

To meet 40 CFR Part 503 vector attraction reduction requirements using the "aerobic process" alternative, composting operations must ensure that the process lasts for 14 days or longer at a temperature greater than 40°C. In addition, the average temperature must be higher than *45°C.*

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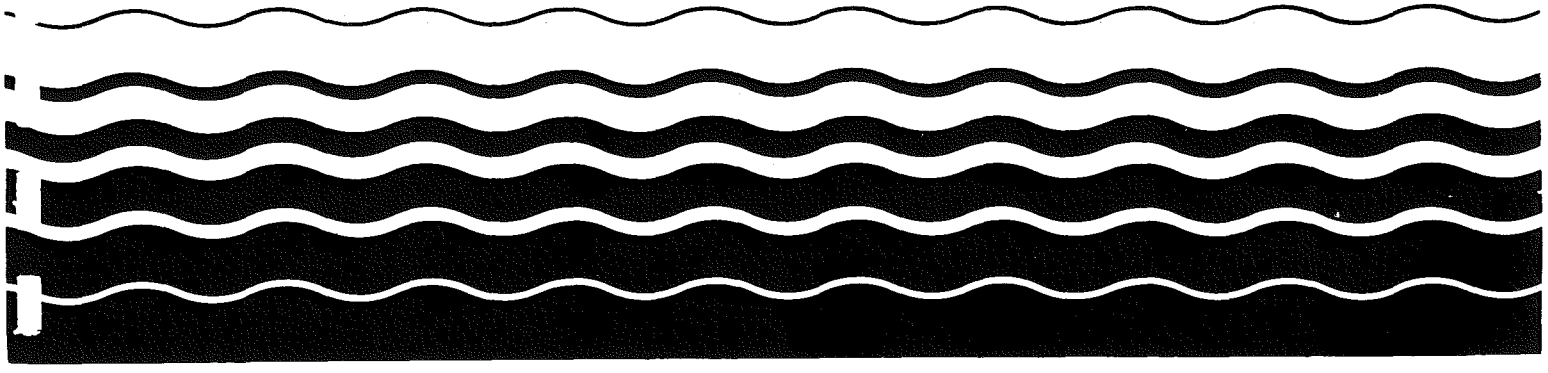
Sampling Procedures and Protocols for the National Sewage Sludge Survey



SAMPLING PROCEDURES AND PROTOCOLS FOR THE NATIONAL SEWAGE SLUDGE SURVEY

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Appendix A - Commonly Used Sewage Sludge Sampling Points

Appendix B - Sample Control Center: Sample Scheduling and Shipment Instructions

NATIONAL SEWAGE SLUDGE SURVEY
SAMPLING PROCEDURES AND PROTOCOLS

1.0 PROJECT DESCRIPTION

This document presents the sampling procedures and protocols for the National Sewage Sludge Survey.

The objective of this sampling project is to visit and collect samples of sewage sludge from a variety of Publicly Owned Treatment Works (POTWs) in an effort to identify the presence and level of toxic pollutants contained in municipal sewage sludge (hereinafter referred to as sludge). After collection and icing, samples will be shipped to laboratories for preservation and analysis. Laboratory tests will be performed for: 1) those analytes listed in The 1987 Industrial and Technology Division List Of Analytes, and 2) the following non-conventional pollutants:

Fluoride
TKN
Nitrate
Nitrite
Phosphorous
Percent solids
Cyanide

2.0 SAMPLE METHOD SELECTION

Representative sampling may be performed using either grab samples or long-term composite samples.

Grab sampling consists of collecting a single sample for each different and segregated sludge product produced during a POTW's normal daily operations. A grab sample is a sample collected over a short period (usually less than 15 minutes) during the daily operation of a POTW. This is the quickest and least expensive way of collecting reliable sludge samples.

Composite sampling consists of consecutively collecting samples (weekly, monthly, etc.) over a period of time and requires considerably more man-hours to accomplish. Long-term sampling incorporates the effects of seasonal climatic changes, POTW operating procedures, long-term industrial production cycles, and the number and type of POTW collection system connections (domestic/industrial) on the sludge pollutant concentrations. A long-term sampling program is of more benefit in describing the changes associated with POTW sludge production over extended periods.

The quickest and most cost effective, yet representative, sample collection method for the purpose of this study is short-term sampling. Grab samples are adequate to characterize the quality of sludges prior to final disposal, because the long sludge detention times found at POTWs reduces the variability of the sludge characteristics. Processes which produce sludge and/or add to a POTW's sludge detention time include:

A. Primary Clarification: Located at the head of the treatment plant, easily settleable and floatable materials are removed from the wastewater. Sludge mixing is minimal until the primary sludge is pumped to digesters and thickeners for mixing with other process sludges.

B. Activated Sludge/Secondary Clarification: The constant recycling of biomass within the process generates sludges with process ages (sludge detention times) of 5 to 30 days. Sludge detention times vary dependent upon process modifications.

C. Other Biological Treatment Processes: Trickling filters, rotating biological contactors and other fixed media systems have intermittent sloughing off of biomass which cause sludge to vary in quality and quantity.

D. Chemical Precipitation/Coagulation: After secondary treatment (where 80% to 90% of the pollutants have been removed), chemicals such as aluminum hydroxide, ferric chloride, lime and polymers are added to further treat the wastewater. Some sludge is recycled and detention times reach 1 to 2 days. These sludges are frequently difficult to dewater and are normally mixed with digested or undigested biological sludges prior to further processing.

E. Sludge Holding/Gravity Thickeners/Elutriation Tanks: Due to process constraints such as septicity, sludge detention time is normally no more than 1 to 2 days.

F. Aerobic/Anaerobic Digesters: Detention times of 20 to 30 days normally are found in these sludge stabilization processes.

G. Miscellaneous Stabilization Processes: Additional sludge stabilization processes, such as lime stabilization, chlorine oxidation, heat treatment, and wet air oxidation, can drastically change a sludge's characteristics but have a very small effect on its detention time.

A POTW may use one or more of the above processes to treat wastewater and to condition sludge before dewatering, composting, and final use/disposal. The combined detention times: 1)

disperse and dilute any slugs or otherwise non-representative concentrations of pollutants, and 2) produce a consistently homogenous mixture of sludge. For this reason, a grab sample could adequately represent a 20- or 30-day composite sample.

A short-term effect on sludge quality may be felt during dewatering. Equipment used in the process (belt presses, centrifuges, vacuum filters) does not generate a product of constant dryness. The percent solids (or percent moisture) may vary, depending on chemical feed rates, septicity of incoming liquid sludge, and differences among machines. As the percent solids of the final product varies so will the amount of water soluble pollutants. This can be avoided to some degree by sampling only during normal operating hours (i.e., never during a dewatering facilities start-up mode).

Under these controlled sampling circumstances, short-term sampling will provide representative samples of sewage sludges.

3.0 SAMPLE COLLECTION

This section provides the rationale for selecting sampling locations and describes the protocols to be used for sample collection and handling.

3.1 Sample Point Identification

3.1.1 Sample Type Classification

All samples to be collected will be grab samples of the final sludge product or products produced by the POTW. The final sludge product will be defined as sewage sludge after all conditioning, dewatering, etc., but before disposal (i.e., before land application, incineration, landfill, distribution and marketing, permanent lagooning or ocean disposal). In cases where a sewage treatment plant's sludge is transported to another facility for further processing, the sample will be collected at the facility of origin, before transfer.

Individual samples will be collected for each distinct type of sludge segregated and disposed of by the POTW. Individual sludge types may be classified in two categories: liquid and solid. Liquid sludge is defined as any sludge which has the capacity to flow and is conveyed via pump. Solid sludge is defined as any sludge which does not meet the liquid sludge definition.

Liquid and solid subcategories may evolve when sludges produced during various plant processes are segregated, treated, and disposed of individually, as opposed to being blended before treatment and disposal. Each of these final sludge products will be considered as a different and individual sample. Therefore, a POTW may have a variety of final sludge products, liquid and/or solid, combined or individual. Each type will require an

individual grab sample. However, grab samples will be collected and combined when similar dewatering devices are used for the same type of sludge.

The following is a description of an imaginary POTW to demonstrate the classification of various final sludge types.

EXAMPLE

POTW "X" (refer to "Generic" POTW flow diagram, Figure 1) consists of primary clarification, activated sludge and secondary clarification, chemical treatment/precipitation, aerobic digestion, sludge thickening and dewatering through the use of one centrifuge, two belt presses and a drying bed.

Primary clarifier sludge and secondary clarifier sludge (i.e., waste activated sludge) are sent to the aerobic digester for stabilization. Sludge from the aerobic digester is then dewatered using a centrifuge, belt press #1, and the drying bed. The solid sludge is landfilled.

Sludge produced in the chemical treatment/precipitation unit is mixed with additional aerobically digested sludge in the thickener. Half of this mixture is dewatered using belt press #2 and landfilled. The other half is hauled away as a liquid and applied to farmland.

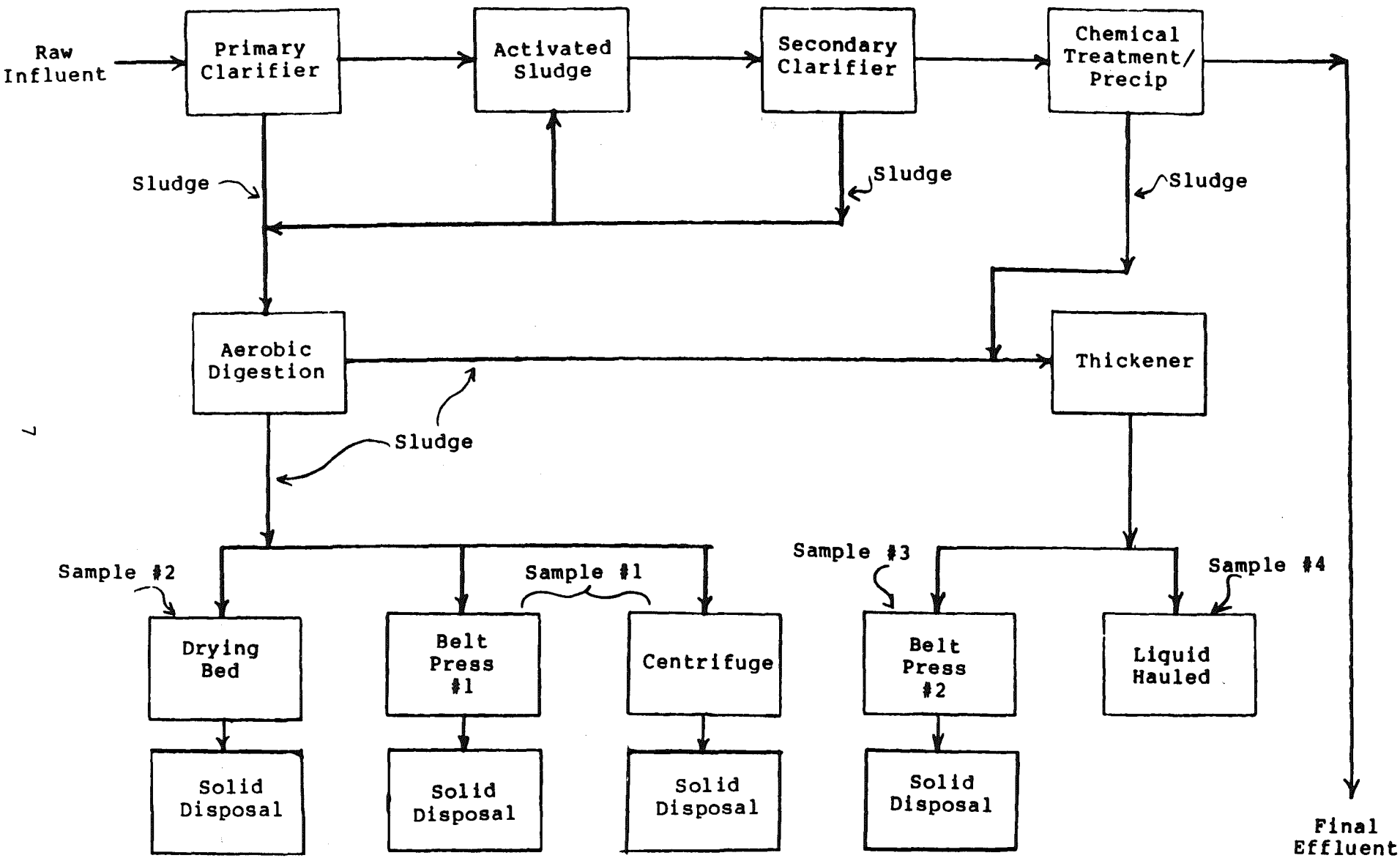


Figure 1. POTW "Generic" Flow Diagram

The individual sludge samples that should be collected at this imaginary POTW are as follows:

Sample #1 - Aerobically digested sludge from the centrifuge and belt press #1: Both the centrifuge and belt press #1 are dewatering the same type of sludge. A grab sample would be collected from each machine and combined to form a single representative sample.

Sample #2 - Aerobically digested sludge from the drying bed: This is a separate sample. Aerobically digested sludge in Sample #2 is being dewatered in a radically different way than in Sample #1. Drying beds reduce the moisture content of a sludge much more than centrifuges and belt presses. Also chemical and physical changes in the sludge occur due to the long holding time and exposure to elements while on a drying bed. Grab samples of different areas of the drying bed (as described in Section 3.2.1.C) would be collected and combined to form a representative sample.

Sample #3 - The chemical and aerobically digested sludge mixture dewatered on belt press #2: This is a different sludge type from Samples #1 and #2. A separate grab sample would be collected.

Sample #4 - The chemical and aerobically digested sludge mixture hauled away as a liquid: This is the same sludge as in Sample #3, except in liquid form. The liquid is treated as a different sludge type, and a grab sample is collected.

Sampling points for the above samples are shown in Figure 1.

3.1.2 Sample Collection Point Selection

The following procedures should be followed to select the appropriate collection point necessary for representative grab samples once each individual sludge type has been identified. Appendix A, taken from the U.S. EPA POTW Sludge Sampling and Analysis Guidance Document, contains additional information on commonly used sludge sampling points.

Solid Sludge Collection Point

Samples of solid sludge should be collected directly from the final sludge treatment processes. These processes include, but are not limited to, belt filter press (continuous), plate and frame sludge press (batch), centrifuge, vacuum filter, compost pile and drying beds (sand beds, cement pads, drying lagoons, vacuum assisted drying beds).

A. Belt Filter Press/Centrifuge/Vacuum Filter: Each process dewaters sludge continuously. The sample should be collected from the sludge discharge chute.

B. Sludge Press (plate and frame): This is a batch process and discharges sludge cake intermittently. Sludge is dewatered in the press until plates are full. The unit is then opened and sludge cake is dropped into a bin. Samples should be collected directly from the storage bin.

C. Drying Beds (drying lagoons, cement pads, sand beds, vacuum assisted drying beds): Drying beds are also a batch process. Each bed should be divided into quarters. One grab sample should be collected from the center of each quarter and all grabs combined from all beds to form a complete sample. Sludge should not be sampled until ready for removal from beds. The criteria for removal vary from facility to facility. Sludge should be collected from beds which are ready for clearing, as deemed by the facility's manager. Drying beds are normally encountered at smaller POTWs, where sludge production is variable. Therefore, sample scheduling must be coordinated to take place when sludge is available and ready for removal.

D. Compost Piles: This is an additional conditioning process in which the dewatered sludge (from one of the previous processes) is mixed with a bulking agent such as wood chips, aerated in large piles, and allowed to stabilize. This process takes a few weeks. The sample should be collected from piles which have completed composting and are ready for disposal. A representative sample scheme should be determined through discussions with the compost facility manager.

Liquid Sludge Collection Point

Liquid sludge normally is transported off the POTW site in tanker trucks. The sampling point should be as close to the truck loading point as possible. The ideal liquid sludge sample point would be at the end of the hose or pipe that is used to fill the tanker truck. If this is inaccessible, optional sampling points such as taps on sludge process piping should be used. When locating a sampling point within the process piping, the

following procedures should be followed to ensure that representative samples are obtained.

A. In sludge treatment process trains the most representative sample typically is obtained from a tap on the discharge side of sludge pumps. Flow at this point in the system is turbulent and the sludge is well mixed.

B. If a sample is drawn from a tap on a pipe containing sludge that is distant from the sludge pump, the average flow velocity of the sludge in the pipe should be determined. Average velocities of less than 2 feet per second are likely to result in solids separation and settling, with an attendant effect on sample solids content, depending on the location of the tap (top, side or bottom of the pipe). Given a choice, a tap on the side of the pipe is preferable.

3.2 Sample Collection Procedures

The following general steps are to be taken by the sampling team for proper sample collection:

A. The sampling team leader, through consultation with the POTW Manager, should establish the number of sludge types leaving the plant for final disposal and the sample points for each sludge type as designated in Section 3.1. The percent solids of each type also must be established. Sludges with solid contents more than 2 percent should use the sample volumes shown in Table 1; sludges with solid contents less than 2 percent should use the sample volumes listed in Table 2. This information, along with contacts, phone numbers, facility address, directions to facility, and necessary safety equipment required (hard hat, safety shoes, etc.), should be written up in a pre-sampling report. One copy each should go to the project manager, sample team, and file.

   If unexpected difficulties are encountered on site when locating sludge sample points, or if sampling is impossible, the project manager should be notified immediately and sampling plan modifications made.

B. To remove any sample contamination potential, all sampling equipment is to be made of polyethylene or polypropylene, used only once, and discarded.

TABLE 1
SAMPLE CONTAINER DESCRIPTIONS

Sludge Samples Containing >2% Solids

SAMPLE TYPE	VOLUME REQUIRED	TYPE OF CONTAINER
GC/MS for:		
Semi-volatile Org	2 each 500ml	G
Volatile Organics	2 each 4oz	G
GC/MS for:		
Dioxin/Furan	500ml	G
GC for:		
Pesticides/PCBs	2 each 500ml	G
Herbicides	500ml	G
ICP & AA for:		
27 IFB metals	500ml	P
Non-conventionals:	4 each 500ml	P
Fluoride		
TKN		
Nitrate		
Nitrite		
Phosphorous		
% Solids		
Cyanide		

G - glass
P - polyethylene

TABLE 2
SAMPLE CONTAINER DESCRIPTIONS

Sludge Samples Containing <2% Solids

SAMPLE TYPE	VOLUME REQUIRED	TYPE OF CONTAINER
GC/MS for:		
Semi-volatile Org	4 each 500ml	G
Volatile Organics	4 each 4oz	G
GC/MS for:		
Dioxin/Furan	500ml	G
GC for:		
Pesticides/PCBs	4 each 500ml	G
Herbicides	2 each 500ml	G
ICP & AA for:		
27 IFB metals	500ml	P
Non-conventionals:	4 each 500ml	P
Fluoride		
TKN		
Nitrate		
Nitrite		
Phosphorous		
% Solids		
Cyanide		

G - glass
P - polyethylene

Polyethylene gloves also must be worn to prevent sample contamination and to provide for worker safety.

C. Prior to sample collection, each sample container should be labeled with a sample number. A set of sample numbers (all identical) should be used for one sample point and discarded. Each sample number label should have the sample type written on it (i.e., metals, classicals, dioxin/furan, extractables, VOA unpreserved, VOA unpreserved duplicate, VOA trip blank, VOA trip blank duplicate, pesticides/PCB's or herbicides). Some labels are preprinted; others will require the sample type to be written in. After the sample number is applied to the container, a piece of wide clear type should be applied to protect the label from dirt and liquids. If a label is mis-marked, it should be replaced; do not write over a mistake. Dioxin/furan samples should be labeled on both the inside glass sample container and outside plastic secondary container. Only one metals sample is collected and the label used may say ICP or AA.

D. At each sampling point, the required amount of sample should be collected, following procedures as described in this document.

E. Fifteen percent of the samples are to have duplicates collected. Duplicate samples are to be identified with a new sample number. There should be no written reference to the duplication of samples on traffic reports.

F. Organic volatile trip blanks should be used to determine the extent of contamination, if any, arising from sample container handling and field conditions encountered during the POTW visits. Trip blanks are organic-free samples of reagent grade water prepared by a designated laboratory before the sampling trip. These blanks are to be handled and shipped with the collected sludge samples to the laboratory for analysis. These blanks should not be opened until arrival at the laboratory. One set of two trip blanks will be used at 15 percent of the sites.

G. All sample containers (including trip blanks) should be sealed by applying a piece of clear wide tape around the top, thus preventing the lid from popping off or unscrewing. Each glass sample container should be wrapped with a piece of bubble wrap. The bubble wrap should be secured with a piece of shipping tape.

H. After all containers have been taped and wrapped, they should be packed into their respective coolers. All material (except one layer of bubble wrap on the bottom of the cooler) should be removed from the cooler and the cooler lined with a large trash bag. Each sample container then should be packed into the cooler, and ice should be applied to the samples. All ice should be packed in zip-lock bags to help prevent any leaking during shipment. With sample containers and ice inside the cooler, the trash bag should be tied closed (also to help prevent leaks). More bubble wrap should be added to fill the remaining space in the cooler, the pink and gold copies of trip report enclosed on top, and the cooler closed and wrapped with shipping tape.

I. Refer to Appendix B for instructions on completing traffic reports and other pertinent information about the Sample Control Center.

J. Each cooler should be shipped via overnight delivery service. The Sample Control Center should be called to provide them with sample collection information.

K. The sampling team also will record site information. These data will be recorded on a preprinted log sheet and will include at least: date, POTW name and address, name of POTW contact, sample identification number and sample point description, basic descriptions of POTW sludge treatment processes and final sludge disposal method(s).

3.2.1 Solid Sludge Sample Collection

At the sample point(s), a sample of solid sludge will be collected using a polyethylene pail and polypropylene scoop.

A. Belt Press/Centrifuge/Vacuum Filter: These sludge dewatering processes are continuous. When one or a combination of these dewatering devices are encountered and used to dewater the same sludge type, then only one sample is collected.

1. If just one dewatering unit is present, a sufficient amount of solid sludge is collected (refer to sample amounts in Table 1) in the polyethylene pail directly from the sludge discharge chute. The sample is thoroughly mixed with the polypropylene scoop and/or coring device (Figure 2). The sludge should be transferred to

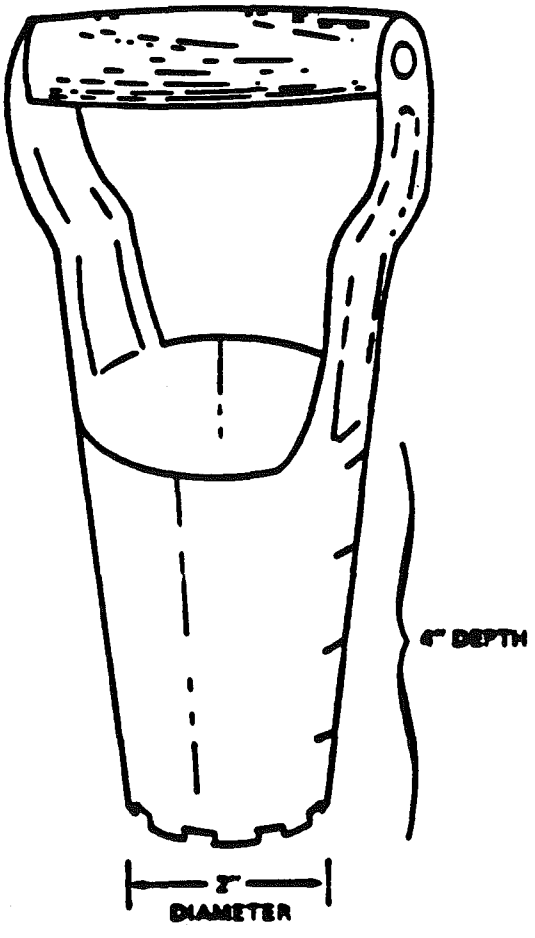


FIGURE 2. Coring Device

*These devices do very well at mixing and reducing particle size of samples, as well as the actual sample collection.

the required sample containers by means of the polypropylene scoop as described in Section 3.2.2.

2. If two or more dewatering units (any combination) machines are present (dewatering the same sludge type), equal amounts of solid sludge are to be collected from each discharge point and combined in the polyethylene pail, the sample thoroughly mixed with the polypropylene scoop and/or coring device, and the sludge transferred to the required sample containers by means of the polypropylene scoop as described in Section 3.2.2.

B. Sludge Press (plate and frame): To collect a representative sample, at least four points within the sludge bin must be selected. An equal amount of sample is collected (refer to Table 1) from each point and combined in the polyethylene pail. The sample is thoroughly mixed with the polypropylene scoop and/or coring device, and the sludge is transferred to the required sample containers by means of the polypropylene scoop as described in Section 3.2.2.

C. Drying Beds: The sludge must be sufficiently dry before sampling may take place. The sludge dryness will vary based on the particular POTW's circumstances. The sampling visit should be scheduled to coincide with a POTW's decision that a drying bed is ready for cleaning. Sludge should be collected from only those beds deemed ready for cleaning. The POTW Manager's assistance should be used for scheduling.

1. To collect the sample, the bed is divided into quarters and equal amounts of sample are grabbed from the center of each quarter using a coring device. Enough sample should be collected to fill the sample containers (refer to Table 1). The sample should include the entire depth of sludge on the bed. Care must be taken not to include large amounts of the drying bed sand when the sample is collected. A small amount of sand is allowable though, as this would be representative of the fact that during normal sludge removal, small amounts of sand are usually taken. The four grabs should be combined in the polyethylene pail, the sample thoroughly mixed with the polypropylene scoop and/or coring device, and the sludge transferred to the required sample containers by means of the polypropylene scoop as described in Section 3.2.2.

2. If more than one drying bed is used to dewater the same sludge type, the above sampling technique should be used on each bed. All the samples should be combined in the polyethylene pail, the sample thoroughly mixed with the polypropylene scoop and/or coring device, and the sludge transferred to the required sample containers by means of the polypropylene scoop as described in Section 3.2.2.

D. Compost Pile: A grab sample should be collected from a compost pile or piles that are ready for disposal using the polyethylene pail, scoop and corer (refer to Table 1 for total amount of sample needed). The compost pile should be divided into equal sections. Using the coring device, equal amounts of sample should be collected from each section to form a complete grab sample. The sample should be thoroughly mixed with the polypropylene scoop and/or coring device and the sludge transferred to the required sample containers by means of the polypropylene scoop as described in Section 3.2.2.

3.3.2 Solid Sludge Handling

The following describes the procedures for the handling of solid sludge samples and filling of sample containers. Refer to Table 1 for sample volumes.

A. Organic Volatiles/Semi-volatiles: The sludge should be thoroughly mixed in the sample pail, using the polypropylene scoop, and the labeled sample container filled. The sludge should be carefully packed into the container so as to avoid air spaces. Covering one's hand in a clean polyethylene glove and packing the sludge with the fingers seems to be the easiest method. The labeled container should be filled to overflowing, and the lid screwed on, wrapped, and sealed with clear tape.

B. Dioxin/Furan: The sludge should be thoroughly mixed in the sample pail, using the polypropylene scoop, and the labeled sample containers filled to four-fifths full. This is to enable expansion of the samples when they are stored at <0°C. Storing at <0°C preserves the samples and prevents biological activity that may change the chemical characteristics of the sludge. Air

spaces are of no concern. The lid should be wrapped and sealed with clear tape. These samples are to be frozen to facilitate a longer holding time before analysis.

C. Pesticides/PCBs/Herbicides, Metals and Non-Conventionals: The sludge should be thoroughly mixed in the sample pail, using the polypropylene scoop, and each labeled sample container filled to within 1/2 inch of top. This provides room for expansion should there be any gas production due to biological activity. Air spaces within the sludge are of no concern. The lid should be wrapped and sealed with clear tape.

3.2.3 Liquid Sludge Sample Collection

At the sample point, liquid sludge should be collected directly into the 14-quart polyethylene pail. Enough sample should be collected to fill the sample container (refer to the appropriate table, Table 1 or Table 2). When drawing the liquid sludge from:

A. Completely Mixed Tank:

1. The POTW operator should start and run the pump for 5 minutes to clear the line of stagnant sludge.

2. Sludge must be allowed to flow for several seconds from the tap (or sample outlet) prior to sampling in order to flush out stagnant sludge and solids that may have accumulated in the tap.

3. The polyethylene pail should then be filled.

B. Unmixed Tank:

1. An unmixed tank will have a sludge layer and supernatant layer; the sludge pump must draw from the sludge layer.

2. The POTW operator should start and run pump for 5 minutes to clear the line of stagnant sludge.

3. Sludge must be allowed to flow for several seconds from the tap (or sample outlet) prior to sampling in order to flush out stagnant sludge and solids that may have accumulated in the tap.

4. The polyethylene pail should then be filled.

Before transferring liquid sludge into sample containers (see Section 3.2.4), the liquid sludge should be manually agitated in the pail with a polyethylene ladle until thoroughly mixed.

3.2.4 Liquid Sludge Handling

The following describes the procedures for the handling of liquid sludge samples and filling of sample containers. Refer to Table 1 or Table 2 for sample volumes (this will be based on the expected percent solids of the sample).

A. Organic Volatiles/Semi-volatiles: The sludge should be thoroughly mixed in the sample pail, using the polyethylene ladle, and each labeled sample container filled. The sludge should be carefully side-poured into the container so as to avoid entrapping air within the sample. The container should be filled to overflowing and the lid screwed down. The sample should be checked for air bubbles. To do this, the container is turned up-side-down and the lid tapped. If air bubbles rise up, the container should be opened and filled with additional sample. When there are no further air bubbles, the container should be wrapped and the lid sealed with clear tape.

B. Dioxin/Furan: The sludge should be thoroughly mixed in the polyethylene pail, using the polyethylene ladle, and each labeled sample container filled to four-fifths full; this allows for sample expansion at <0°C. Storing at <0°C will preserve the samples and prevent any biological activity. Air spaces in the sample container are of no concern. The lid should be wrapped and sealed with clear tape. These samples are to be frozen to facilitate a longer holding time before analysis.

C. Pesticides/PCBs/Herbicides, Metals and Non-Conventionals: The sludge should be thoroughly mixed in the polyethylene pail, using the polyethylene ladle, and each sample container filled to within 1/2 inch of the top. This will provide room for expansion should there be any gas production due to biological activity. Air spaces in the sample containers are of no concern. The lid should be wrapped and sealed with clear tape.

4.0 SAMPLE HANDLING AND CUSTODY

This section describes the procedures for sample handling and shipment.

4.1 Sample Handling

Except for mixing of samples in the sample pail, no modifications to the structure or content (removal of plastics, paper, etc.) of the samples will be performed. Sample transfer will be kept to a minimum. The sludge will be placed in polyethylene or glass sample containers which have been analyzed for quality control by the supplier and which are certified to meet U.S. EPA cleanliness specifications.

4.2 Sample Preservation

Once a sample is collected, steps will be taken to preserve the chemical and physical integrity of the sample during transport and storage prior to analysis. All samples will be immediately cooled to a temperature of 4°C or less using regular (wet) ice (which has been purchased and sealed in zip-lock bags prior to the sampling visit) and shipped promptly to the designated

laboratories. Upon arrival at the laboratories, samples will be preserved further or analysis begun as appropriate within 48 hours of the sample collection.

4.3 Sample Shipment

All samples will be shipped from the field on the day of collection using an overnight commercial delivery service. If circumstances prohibit this, samples will be kept on ice and shipped in the most expedient method available.

The shipment box will be of sturdy construction and insulated to provide the proper environment for preserving the samples at <4°C (in this case a regular, 28-quart cooler). Each sample container will be sealed with clear tape to prevent lid removal or leakage. All glass sample containers will be enclosed in bubble wrap. All sample containers will be securely packed in the shipment box with additional bubble wrap. On the outside of the shipment container the following should be placed: 1) a shipping label with the complete address of the receiving laboratory including the responsible laboratory person receiving the samples, 2) a designated box number to indicate to the receiver exactly how many sample boxes are included in the shipment, and 3) "Fragile" and "This End-Up" labels.

4.4 Field Custody Procedures

Each sample container will have a label attached (Figure 3) and covered with clear plastic tape to prevent solvent attack. Shipment record forms will be written for each group of samples shipped to a particular laboratory. These forms will be the standard Sample Control Center Organics Traffic Report, Metals Traffic Report, and (generic) Sample Traffic Report shown in Figures 4, 5 and 6. The pink and gold copies of each form will accompany sample shipment to the laboratory. The yellow copy of each form will remain in the custody of the sample team. The white copy will be delivered directly to the Sample Control Center. Additional details are provided in Appendix B.

5.0 SAMPLING EQUIPMENT

This section lists the sampling supplies and equipment to be used by the sampling team while in the field. Two sets of clean equipment will be saved for an equipment blank analysis. The study will consist of soaking each piece of equipment for 72 hours in laboratory water and analyzing the water for contaminants which may have leached from the sample equipment.

5.1 Sampling Equipment

-Sample kit (to be prepared prior to sampling visits)

Sampling kits will be prefabricated and ready for use before sampling begins. The kits will contain:

-High impact plastic coolers with lids

-Sample containers (see Table 1 and/or Table 2)

EXAMPLE OF SAMPLE NUMBER LABELS

16272-C Composite	16272
16272-CB Composite Blank	16272
16272-G Grab	16272
16272-V1 VOA Preserved	16272
16272-V2 VOA Preserved Dup	16272
16272-V3 VOA Unpreserved	16272
16272-V4 VOA Unpreserved Dup	16272
16272-VB1 VOA Trip Blank	16272
16272-VB2 VOA Trip Blank Dup	16272
16272-Other	16272

16272-M1 Metals ICP	16272
16272-M2 Metals AA	16272
16272-Other	16272

Figure 3.

USEPA INDUSTRIAL TECHNOLOGY DIVISION
SAMPLE CONTROL CENTER
P.O. BOX 1407
ALEXANDRIA, VA 22313
703/557-5040 / FTS-8-557-5040

EPISODE NO:
RANGE OF SAMPLE NOS: —

ORGANICS TRAFFIC REPORT

INDUSTRIAL FIRM SAMPLED:	SAMPLING DATE
	BEGIN:
CITY:	END:
STATE:	SHIPPING INFORMATION
INDUSTRIAL CATEGORY:	SHIP TO:
	ATTN:
CONFIDENTIAL: ____ YES ____ NO	
SAMPLING OFFICE:	CARRIER:
	AIRBILL NO:
SAMPLER:	DATE SHIPPED:

	SAMPLE POINT DESCRIPTION								SAMPLE TYPE										
SAMPLE NUMBER	RAW WATER (CITY, RIVER, WELL)	IN LINE PROCESS	UNTREATED EFFLUENT (RAW WASTE WATER)	TREATED EFFLUENT	OTHER (SPECIFY)	ADDITIONAL SAMPLE DESCRIPTION	PH LEVEL	SAMPLE POINT FLOW UNITS: ____	C COMPOSITE (EXTRACTABLE ORGANICS)	CB COMPOSITE BLANK	G GRAB (EXTRACTABLE ORGANICS)	V1 VOA PRESERVED	V2 VOA PRESERVED (DUPLICATE)	V3 VOA UNPRESERVED	V4 VOA UNPRESERVED (DUPLICATE)	VB1 VOA TRIP BLANK	VB2 VOA TRIP BLANK ((DUPLICATE)	OTHER SPECIFY:	

WHITE — SCC COPY YELLOW — SAMPLER COPY PINK — LAB COPY FOR RETURN TO SCC GOLD — LAB COPY

Figure 4.

USEPA/INDUSTRIAL TECHNOLOGY DIVISION
SAMPLE CONTROL CENTER
P.O. BOX 1407
ALEXANDRIA, VA 22313
703/557-5040 / FTS-8-557-5040

EPISODE NO:
RANGE OF SAMPLE NOS: —

METALS TRAFFIC REPORT

INDUSTRIAL FIRM SAMPLED:	SAMPLING DATE
	BEGIN:
CITY:	END:
STATE:	SHIPPING INFORMATION
INDUSTRIAL CATEGORY:	SHIP TO:
	ATTN:
CONFIDENTIAL: ____ YES ____ NO	
SAMPLING OFFICE:	CARRIER:
	AIRBILL NO:
SAMPLER:	DATE SHIPPED:

	SAMPLE POINT DESCRIPTION								SAMPLE TYPE		
SAMPLE NUMBER	RAW WATER (CITY, RIVER, WELL)	IN LINE PROCESS	UNTREATED EFFLUENT (RAW WASTE WATER)	TREATED EFFLUENT	OTHER (SPECIFY)	ADDITIONAL SAMPLE DESCRIPTION	PH LEVEL	SAMPLE POINT FLOW UNITS:	M1 METALS TASK I (ICP ONLY)	M2 METALS TASK II (AA)	METALS OTHER (SPECIFY)

WHITE — SCC COPY YELLOW — SAMPLER COPY PINK — LAB COPY FOR RETURN TO SCC GOLD — LAB COPY

Figure 5.

USEPA INDUSTRIAL TECHNOLOGY DIVISION
SAMPLE CONTROL CENTER
P.O. BOX 1407
ALEXANDRIA, VA 22313
703/557-5040 / FTS-8-557-5040

EPISODE NO:

RANGE OF SAMPLE NOS: —

TRAFFIC REPORT

INDUSTRIAL FIRM SAMPLED: _____

CITY: _____

STATE: _____

INDUSTRIAL CATEGORY: _____

CONFIDENTIAL: ____ YES ____ NO

SAMPLING OFFICE: _____

SAMPLER: _____

SAMPLING DATE

BEGIN: _____

END: _____

SHIPPING INFORMATION

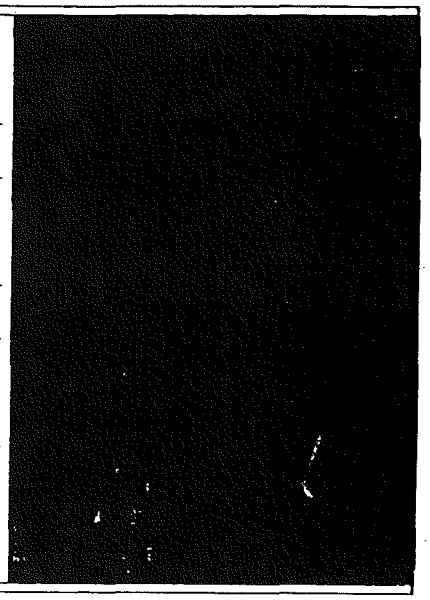
SHIP TO: _____

ATTN: _____

CARRIER: _____

AIRBILL NO: _____

DATE SHIPPED: _____



SAMPLE NUMBER	SAMPLE POINT DESCRIPTION: RAW WATER (CITY, RIVER, WELL)	IN LINE PROCESS	UNTREATED EFFLUENT (RAW WASTE WATER)	TREATED EFFLUENT	OTHER (SPECIFY)	ADDITIONAL SAMPLE DESCRIPTION	PH LEVEL	SAMPLE POINT FLOW UNITS: ____	SAMPLE TYPE				

WHITE — SCC COPY YELLOW — SAMPLER COPY PINK — LAB COPY FOR RETURN TO SCC GOLD — LAB COPY

Figure 6.

5.0 SAMPLING EQUIPMENT

This section lists the sampling supplies and equipment to used by the sampling team in the field to collect samples.

5.1 Sampling Equipment

-Sample kit (to be prepared prior to sampling visits)

-Disposable 14 quart polyethylene pails

-Disposable polyethylene gloves

-Disposable polypropylene scoops

-Disposable stainless steel corers

-Disposable polyethylene ladles

5.2 Miscellaneous

-Clear tape (to seal sample containers)

-Packing tape

-Writing tools

-Clear plastic zip-lock bags

-Shipping materials

-Shipping instructions and appropriate shipping forms

-Trash bags

6.0 SAMPLING KITS

Sampling kits will be prefabricated and ready for use before sampling begins. The kits will contain;

-High impact plastic coolers with lids

-sample containers (refer to Table I)

all sample containers will be certified to meet USEPA cleanliness specifications and will have been quality control analyzed by the supplier

-packing materials (bubble wrap, peanuts, etc.)

TABLE I
SAMPLE CONTAINER DESCRIPTIONS

SAMPLE TYPE	VOLUME REQUIRED	TYPE OF CONTAINER
GC/MS for:		
Semi-volatile Org	500ml	G
Volatile Organics	2 each 4oz	G
GC/MS for:		
Dioxin/Furan	500ml	P
GC for:		
Pesticides/PCBs	2 each 500ml	G
Herbicides	500ml	G
ICP & AA for:		
27 IFB metals	500ml	P
Non-conventionals:	4 each 500ml	P
Fluoride		
TKN		
Nitrate		
Nitrite		
Phosphorous		
% Solids		
Cyanide		

G - glass
P - polyethylene

APPENDIX A

COMMONLY USED SEWAGE SLUDGE SAMPLING POINTS

Sludge Type	Sampling Point
Primary Sludge -	Most frequently sampled from taps on the discharge side of positive displacement pumps. Difficult to sample from wells or pits due to solids separation.
Activated Sludge -	Sampled from taps on lines or from open channel flows. Open channel flow can be considered an acceptable sample point if the flow is well mixed.
Trickling Filter Humus -	Sampled at taps on discharge lines from pumps or from wells, pits or channels. Care should be taken to assure adequate mixing, since humus has a greater tendency for solids separation than activated sludge.
Anaerobically Digested Sludge -	Typically sampled from taps on the discharge side of positive displacement pumps.
Aerobically Digested Sludge -	Frequently sampled from taps on discharge lines from pumps. In some cases, particularly where batch digestion is used, sludge may be sampled directly from the digester. Two cautions are in order concerning this practice: (1) If aerated during sampling, significant air will be entrained in the sample. Depending on parameters to be analyzed, this may affect sample integrity. (2) If aeration is shut off, solids separation will occur rapidly in well digested sludge, affecting sample representativeness.
Thickened Sludges -	Typically sampled from taps on the discharge side of positive displacement pumps.
Heat Treatment Sludge -	Generally sampled from taps on the discharge side of positive displacement pumps after decanting. Particular care should be taken when sampling heat treatment sludge due to: (1) High tendency for solids separation, and (2) High temperature of sample (frequently 60°C+ as sampled) can cause problems with certain sample containers due to cooling and subsequent contraction of entrained gases.
Dewatered Sludges (Cake) -	Generally sampled from the conveyors on which dewatered sludge is collected. If sampled from bulk containers, sample should be taken from several locations within the sludge mass.

APPENDIX B

USEPA INDUSTRIAL TECHNOLOGY DIVISION
SAMPLE CONTROL CENTER
SAMPLE SCHEDULING AND SHIPMENT INSTRUCTIONS

Sample Scheduling

To schedule a sampling site, an authorized requestor should call the Sample Control Center (SCC) with the following information:

- Name and affiliation and the telephone number of the individual requesting the analysis
- The analyses requested
- Facility name and location
- Industrial Category
- Industrial Sub Category
- Scheduled sampling and shipping dates
- Sampling organization, contact, and telephone number
- Number and types of samples to be collected

When an authorized requestor schedules the sampling site, the SCC assigns an Episode number for the site (an Episode refers to a group of samples collected at a given plant or location within the same calendar week) and prepares a packet of materials to send to the Sampler. The packet normally contains the following:

- Episode Number assignments
- Laboratory assignments
- Traffic Report(s)
- Adhesive Sample Number Labels

SCC then creates a hardcopy Episode file and enters the scheduling information in the SAMTRAC (Sample Tracking) System.

Instructions for Completing Traffic Report

A separate Traffic Report (TR) (see Attachment 1), is to be completed for each shipment of samples to a laboratory. For samples going to EPA Contract laboratories use the TR provided by the SCC.

First, enter the Episode number on the top right corner of the TR form, where indicated. The Episode number is the identifying number that was assigned by SCC at the time the sampling was scheduled. This is followed by the Range of Sample numbers, which are assigned by the sampler when samples are packed for shipment to the laboratory(s).

Next, complete header information, excluding the grey areas on the top right of the form.

Along with the TR forms, the sampler will receive sequentially numbered sample labels from SCC. In order to protect the labels from water or solvent attack, labels on the sample container should be covered with clear, waterproof tape.

Enter the Sample numbers (from the labels) on the lower left side of the TR where indicated. Record all Sample numbers for samples included within the shipment. Extra numbered labels should be discarded and new strips of labels should be used for the next Episode of samples.

For each sample, indicate sample point description by checking the appropriate box. If additional sample point information is required enter it in the box labeled "Additional Sample Description" located in the center of the TR. Next record the physical parameters of the site at the time of sampling (i.e. pH, effluent flow, etc.). In the remaining boxes indicate what type of analysis the laboratory is to perform on a sample. Note: Analyses must be approved by EPA and requested through SCC at the time sampling is scheduled, to ensure that proper arrangements can be made in advance to accommodate the request.

The bottom two copies of the completed TR (pink and gold copies) must be included with the sample shipment to the laboratory. The TR should be enclosed in a clear plastic bag and securely taped to the underside of the lid of the shipping cooler.

Following sample shipment, distribute remaining TR copies as follows:

- Mail the top (white) copy to SCC at the address shown on the top of the TR form.
- The second (yellow) copy of TR form is retained by the sampler as the Region's file copy.

Procedures for Coordinating Sample Shipment

Immediately following sample shipment, call SCC and provide the following information:

- Sampler name and phone number
- Episode number
- Sampling date
- Sample numbers for samples included in each shipment
- Number of coolers per shipment
- Date of shipment
- Courier name and airbill number
- Type of shipment (e.g., overnight, two-day)
- Laboratory samples shipped to
- Any irregularities or anticipated problems with the samples
- Status of sampling project (e.g., final shipment, update of future shipping schedule)

SCC notifies the laboratory that samples are in transit and confirms arrival of the samples at the receiving laboratory. SCC assists in resolution of any problems concerning the samples, coordinating with the appropriate sampling personnel.

Upon sample receipt, the laboratory completes designated sections of the TR, recording date of sample receipt and sample condition, signs the TR, and returns the copy to SCC. SCC retains the laboratory-signed TR as written confirmation of sample receipt.

If you have any questions or comments regarding this information please call or write the Sample Control Center.

USEPA ITD
Sample Control Center
P.O. Box 1407
Alexandria, Virginia 22314
Phone (703) 557-5040

State of Oregon Department of Environmental Quality

OAR 340-052-0020
Appendices

APPENDIX A

SEWER PIPELINES

(1) MINIMUM REQUIREMENTS FOR SEWER - PIPELINES

(a) Capacity:

Sewers shall be of such diameter as to pass without overflow, bypass, or back flow onto damageable property of a user the design peak flow including sewage and infiltration. All unavoidable inflow from roof, surface, footing, foundation, or other groundwater or surface water sources shall be excluded from capacity allowance.

(b) Velocity:

Sewers shall be designed to have a velocity to "self clean" or transport constituent solids to the treatment facility or the owner shall periodically service sewers to flush, transport, or remove solids from sewers with minimal velocity.

(2) GUIDELINES FOR SEWER PIPELINES

(a) Capacity:

(A) Collection sewers should be designed for the ultimate development of the tributary areas as determined by master sewerage and land use plans of the owner.

(B) The design of sewers should be based upon initial and ultimate flows. Flows should be broken down into domestic, industrial, and infiltration/inflow fractions. A peaking factor should be applied to domestic and industrial fractions.

(C) Domestic flows should be between 50 and 100 gallons per capita per day (gpcd). Peaking factors should be between 1.8 and 4.0. Infiltration allowance should be normally less than 2,000 gallons per acre per day; any greater allowance should be justified. Any significant inflow allowance should be justified.

(D) The minimum diameter of sewers should be 8 inches for maintenance purposes. Short nonextendable 6 inch sections of up to 250 feet are permissible.

(E) Replacement sewers should be designed commensurate with flow conditions.

(b) Velocity:

(A) Sewers should be laid on a gradient which will produce a mean velocity, when flowing full or half full, of at least (2) two feet per second, based upon the Manning formula with "n", the coefficient of roughness, valued at 0.013.

(b) Sewers with minimal flow such as upper

reaches of laterals or those sewers serving few dwellings should be steepened and/or reduced in diameter to approach a (2) two feet per second selfcleaning velocity. Actual flows during initial years of use should be carefully evaluated in this regard.

(C) Force mains and inverted siphons should be designed for (3) three feet per second at average flows.

(D) The minimum gradient for 8 inch sewers should be no less than 0.4 percent regardless of pipe material.

(E) The minimum gradient for 6 inch sewers should be no less than 0.6 percent, preferably 0.75 percent.

(F) The flow channel(s) through manhole bases should be smooth and conform to the shape and slope of the inlet sewer(s).

(G) Intersecting sewers, sewer connections, etc., should be made without causing backup into the smaller sewer. For intersecting unequal sized sewers in manholes, the elevation at 0.8 of full depth of flow in each sewer should match.

(c) Watertightness:

Completed sewer construction shall result in limited infiltration/exfiltration through pipe walls, joints, fittings, and connection fittings, etc., and no inflow. The limit shall be consistent with the pipe and manhole materials and with what is obtainable at the time by the construction industry on representative jobs for the same type of construction using high quality materials and state-of-the-art methods of workmanship. All completed sewer lines in new work shall be tested for watertightness using either recognized air or water testing requirements and procedures.

(c) Watertightness:

(A) Watertightness begins with good material and finally depends upon sound field practices. Good inspection and tests should be supplemented with an initial television inspection after trench backfilling is complete. Since many defects do not appear initially, an eleventh month final inspection should be performed where that capability is available and determined necessary to obtain acceptable in-place work. If only one television inspection is considered, the eleventh month inspection is recommended.

(B) Exfiltration testing or the low pressure air test for sanitary sewers should be a pres-

sure at least 6 feet greater than the groundwater conditions which the sewer is subject to at test time.

(C) Pipe materials, joints, fittings, and appurtenances should be selected for their watertight capabilities.

(D) Acceptance or performance standards should not necessarily be uniform for all pipe materials since average testing results with good workmanship for work will vary depending upon pipe materials. The range of allowable exfiltration/infiltration for work acceptance should be between 50 and 200 gallons per day per inch-of-diameter per mile (gpdidm). Nonporous (non-airpermeable) pipe should sustain pressure for twice the computed time for the same one pound per square inch (psi) air pressure drop required by the air test. Test sections should be from manhole-to-manhole or about 700 feet maximum.

(E) The watertightness of all building sewers should conform to the State Plumbing Code and be tested without exception.

(F) Manholes should be water tested for exfiltration during construction and/or visually inspected during first wet weather season after construction for infiltration. Leaks should be promptly repaired.

(G) Curved sewers should be as watertight as other sewers and be tested. While not recommended, horizontal/vertical curves at times may be allowed but should be limited in use. When used, the minimum radius of curvature should be not less than 200 feet and the maximum computed joint opening no more than 3/8 inch. Complete and accurate records should be kept of the exact location of such curved sewers for future reference. Reasonable field control should be exercised to not compound joint deflections and compromise watertightness.

(d) Structural Strength:

The completed installation including the excavated trench, the pipe, the bedding, and the pipe zone materials shall resist imposed loads from backfill, impact, and live loads (construction and design) without pipe failure through crushing, loss of watertightness, settlement, or significant capacity loss.

(d) Structural Strength:

(A) Bedding material should be placed full trench width from at least 4 inches under to spring line of all pipe for a leveling course and proper pipe support. Hand shaping of the native trench bottom for rigid pipe is not recommended but may be allowed, if appropriate, and uniform pipe support can be obtained and grade/ alignment can be maintained.

(B) Cantilevering of nonreinforced rigid pipe at manholes should be limited to the least distance practicable to make a flexible connection. A flexible joint should be within 12 inches of manhole for smaller pipe sizes. A second flexible joint should be provided within 4 feet of the manhole.

(C) Where cover from top of pipe to finished grade is less than 36 inches, special design and/or construction requirements should be considered including, but not limited to, raising finish grade, increasing class of pipe and/or pipe bedding, use of ductile iron, concrete encasement and restriction of construction equipment from travel over partially backfilled trench.

(e) Ability to Pass Solids:

Sewer systems shall be free of depressions, sharp edges, roughness, side sewer projections, obstructions, restrictions, displaced "0" rings, etc., which can cause solids to accumulate or deposit.

(e) Ability to Pass Solids:

(A) New sewers should be thoroughly flushed and visually inspected for accumulated debris prior to use.

(B) Building sewer connections should be made with fittings which prevent any projection into the main sewer. The main sewer should not be cracked, crushed, or otherwise damaged in making taps. All taps should be watertight.

(C) A tolerance for vertical deviation from true grade line should be plus or minus 0.02 feet. Depressions for solids deposition should be avoided. Similarly, the horizontal tolerance for deviation from line should be plus or minus 3/8 inch.

(D) Drop manhole piping should be easily maintained, self cleaning or able to "overflow" into the manhole. Pressure sewer piping connections, flow measuring devices, etc., in manholes should be designed to not obstruct flow.

(E) Flow channels in manholes should slope at least 0.1 feet from inlet to outlet.

(f) Durability:

(A) The materials and details of construction shall provide an inplace sewerage system which will resist corrosion of the pipe and manhole materials caused by any source or condition. Any corrosive effect shall be consistent with the design life of the sewer.

(B) Resistance to erosion of surfaces by grit, high velocity flow, etc., shall be addressed if appropriate.

(C) Temperature effect upon thermoplastic materials shall be appropriate.

(f) Durability:

(A) Sewers should be constructed of materials resistant to or protected from biological degradation, acid and alkaline solutions, normal sewer temperature variations, abrasion and industrial wastes (where applicable), or other harmful service conditions which may exist in the sewerage system.

The owner should have a user ordinance which restricts discharge of harmful substances into the sewerage system.

(B) Velocities over 15 feet per second in sewers should have special consideration for erosion control.

(g) Stability:

(A) Line and Grade: Horizontal alignment and vertical grade of inplace sewers upon construction completion and construction acceptance shall be relatively stable.

Design considerations, construction specifications, inspections, etc., shall preclude pipe settlement, shifting, or flotation such that capacity, watertightness structural integrity, ability to pass solids, maintainability, etc., are not compromised either at construction or any later time.

(B) Diameter: Rigid, flexible and

(g) Stability:

(A) Appropriate foundation stabilization or soils should be employed in unstable soils. Back fill should be in small lifts and compacted uniformly to specified density along and around the pipe.

(B) The Soil Class and density for bedding and pipe zone materials should be carefully selected and then compacted in the field to the required in-place density.

PVC and ABS composite sewer pipe should be deflection tested upon construction completion prior to acceptance with an approved nine blade go-no-go gauge. Initial deflection at construction completion should be no more than the following:

semiflexible pipes tend to lose minimum inside diameter if not designed and/or installed properly. Design considerations, construction specifications, field inspections, etc., shall preclude diameter loss such that capacity, watertightness, structural integrity, ability to pass solids, maintainability, etc., are not compromised either at construction or any later time.

(i) PVC (ASTM D-3034) sewer pipe should deflect no more than 4 to 5 percent based upon inside base diameters of 7.76, 9.71, 11.56 and 14.14 inches for 8, 10, 12, and 15 inch nominal pipe respectively.

(ii) ABS (ASTM D-2680) composite sewer pipe should deflect no more than 2 to 3 percent based upon inside average diameters of 7.75, 9.75, 11.75 and 14.75 inches for 8, 10, 12, and 15 inch nominal pipe respectively.

(C) Sewers on slopes over 25 percent should be evaluated for slippage or pipe bedding depending upon soil type, groundwater presence, construction conditions, etc. Appropriate anchors should be provided if necessary.

(h) Operation, Maintenance, and Safety:

Sewer systems require periodic and unscheduled maintenance for sustained operation. Designs shall conform to requirements of the sewage works owner for manhole construction, spacing, size, details and easements. All parts of the sewerage system shall be readily accessible. The minimum inside bottom diameter of manholes shall be 42 inches.

(h) Operation, Maintenance. and Safety:

(A) Access to the sewer by the sewer owner is essential to perform maintenance tasks. Easements should be granted along the sewer line to the system owner for any sewer for emergency repairs. Manholes and cleanouts are necessary for routine access. Structures should not be located over sewers.

(B) Owners should review own procedures, equipment, construction standards, etc., for sewer maintenance. Requirements of the owner should be obtained by designers upon start of sewer design since the owner must assume all future maintenance. Stricter standards of the owner should prevail if in conflict with these guidelines.

(C) General Manhole/Cleanout Standards for Sewers:

(i) The minimum inside bottom diameter should be no less than 48 inches. The least inside dimension may be reduced 38 inches where an integral

inside drop is acceptable to the owner. No more than one inside drop should be installed in a manhole.

(ii) Minimum cover opening diameter should be 22 inches.

(iii) Manholes should be located at:

(I) Every change in grade or alignment of sewer.

(II) Every point of change in size or elevation of sewer.

(III) Each intersection or junction of sewers.

(IV) Upper end of a lateral sewer.

(V) At intervals of 500 feet or less except for 24 inch and larger sewers.

(iv) Cleanouts should not be substituted for manholes except at the upper end of lateral sewers 250 feet or less in length.

(v) Channel width and depth should be equal pipe diameter. Manhole base ledges should be sloped to drain at least I in 12.

(vi) Access to manholes may be by portable ladder. Manhole rungs and in-place ladders which are subject to considerable corrosion and sliming are not recommended.

(vii) Where free fall of sewage into a manhole exceeds 24 inches from inlet pipe invert to manhole invert, an approved drop manhole should be used.

(D) Inverted Siphons:

Inverted siphons should include at least two pipe lines of such size and hydraulic gradient as to maintain a velocity of at least 3 feet per second in one pipe under conditions of average dry weather flow. Control manholes must be provided at both ends of the inverted siphon line. The inlet and outlet details shall be so arranged that the normal flow is diverted to either barrel so that the other barrel may be removed from service for maintenance.

(i) Separation of Water and Sewer Lines:

Protection of the water supply, be it distribution system, production facilities or source is not only prudent but mandatory and absolutely necessary.

Sanitary sewers and appurtenances thereto shall not physically connect to a public or private potable water supply system so as to permit the passage of any sewage or polluted water into the potable supply.

Sewer construction shall not disturb, degrade, or decrease the watertightness of any existing water supply line.

(i) Separation of Water and Sewer Lines:

(A) Parallel Water and Sewer Lines:

(i) Sewer lines should conform to Figure A-1.

(ii) Common trench construction for water and sewer should be avoided where practical. Where used, the minimum pipe separations of Figure A-1 should be maintained.

(B) Vertical Separation at Crossings of Water and Sewer Lines:

No special precautions should be necessary where top of sewer line is at least 1.5 feet below bottom of waterline and adequate structural protection for each line is provided.

(C) Exceptions: Use of Pressure Pipe Material for Sewer Line:

(i) Where the above horizontal or vertical separations cannot be maintained, the following pressure pipe materials should be used in addition to whatever waterline improvements or reconstruction that may be advisable or required for protection of water. The use of these pressure pipe materials from manhole-to-manhole is encouraged to avoid discontinuity

of materials.

(I) Ductile iron pipe, class 50, ANSI Standard A21.51 (AWWA C- 15 1) with either Push-on or mechanical rubber gasket joints in accordance with ANSI Standard A21. 11 (AWWA-C I 11).

(II) PVC pressure pipe, ASTM D-2241, SDR 32.5, (125 psi) with rubber-gasket joint in accordance with UNI-Bell Plastic Pipe Association recommended Standard Specification UNI-B-1 for a pressure-joint assembly.

(III) Asbestos-Cement pressure pipe, class 100, ASTMC-296 (AWWA C-400) with rubberring gaskets in accordance with ASTM D-1869

(IV) High density polyethylene pipe (Driscopipe 1000) PE 3406, minimum SDR 32.5, with butt fused joints.

(V) Other materials approved by the State Health Division.

(ii) At crossings requiring pressure pipe materials, the following should apply with one standard length of special pressure pipe centered over the waterline in all cases:

Pipe Material	Standard Pipe Length	Minimum Laying Length Each Side of Waterline Crossing
Ductile Iron	18 Feet	18 Feet
PVC	20 Feet	20 Feet
Asbestos-Cement	13 Feet	19 Feet
High-Density Polyethylene	38 Feet	19 Feet

(D) Soil Restoration at Crossings:

Soil removed in sewer line trench construction at waterline crossings where sewer crosses over water should be replaced in all areas to as near natural densities as possible through mechanical compaction to restore any natural resistance to groundwater movement which did exist prior to construction. Soil should include no rock fragments over 1-1/2 inch in the pipe zone.

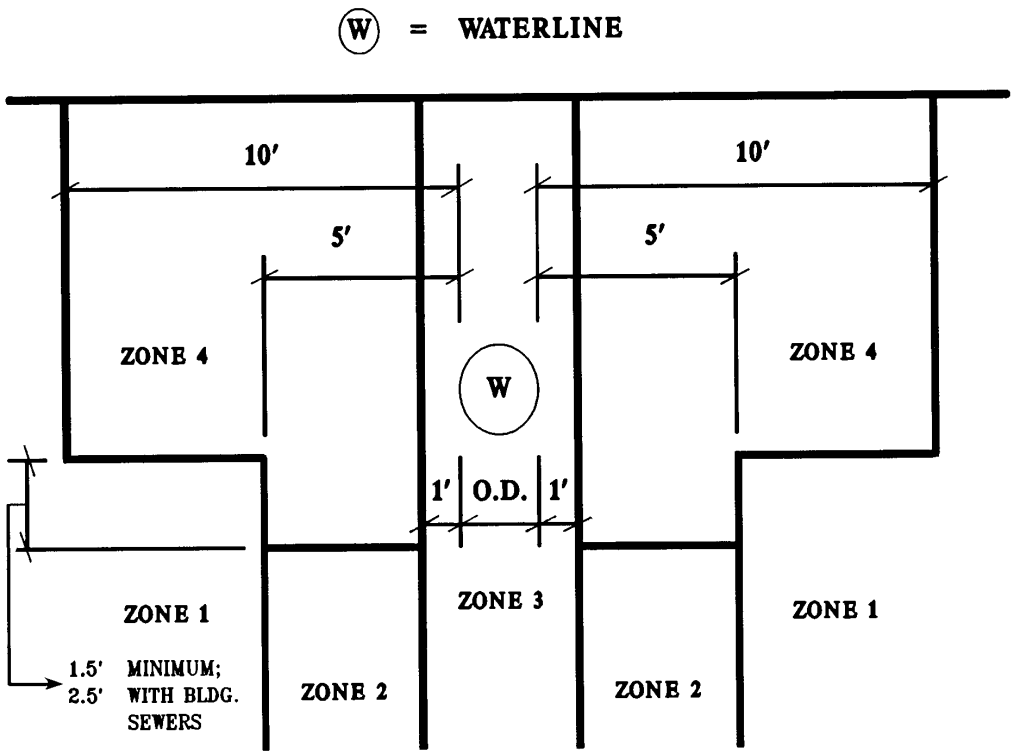
(E) Well Protection:

No sewer pipe should be laid less than 50 feet from any well without specific Health Division approval. Pressure pipe materials should be used to protect wells where minimum setbacks are not obtainable or where additional protection is required as determined by the State Health Division.

(F) Pipe Testing:

Whenever a pressure pipe material is used for any of the above purposes of separation, an appropriate pressure test should be conducted on the pressure pipe to confirm watertightness. Test pressures should be no less than 15 psig where use will be for a gravity sewer and higher where use will be for a pressure sewer (force main).

(G) Other Exceptions should be resolved jointly with the water purveyor and the State Health Division.



SEWER LINE ZONES

ZONE 1 SEWER LINE CAN BE LAID IN THIS AREA WITH NO SPECIAL REQUIREMENTS OF EITHER CONSTRUCTION OR MATERIALS.

ZONE 2 INSTALLING A SEWER LINE IN THIS ZONE IS NOT ADVISABLE AND MUST BE JUSTIFIED IN EACH CASE. WATER LINE SHOULD BE LOCATED ON A BENCH OF UNDISTURBED EARTH WHEN CONSTRUCTED CONCURRENTLY IN A COMMON TRENCH WITH SEWER LINE.

ZONE 3 INSTALLING A SEWER MAIN DIRECTLY OVER A WATER MAIN OR DIRECTLY UNDER A WATER MAIN IN THIS ZONE IS PROHIBITED SINCE TAPPING AND O. & M. OF EACH LINE WOULD BE IMPAIRED.

ZONE 4 SEWER LINE CONSTRUCTION IN THIS ZONE WOULD GENERALLY NOT BE PERMITTED. EACH INSTALLATION MUST BE JUSTIFIED. IF CONSTRUCTION WAS PERMITTED, PRESSURE PIPE MATERIALS FOR THIS SEWER LINE WOULD BE REQUIRED.

Effective 9/1/81

FIGURE A-1
SEPARATION OF PARALLEL WATER-SEWER LINES

APPENDIX B

RAW SEWAGE LIFT STATIONS

(1) MINIMUM REQUIREMENTS FOR RAW SEWAGE LIFT STATIONS

(a) Capacity:

Stations shall pass peak hourly flow including domestic, industrial and infiltration/inflow allowance.

(b) Solids Handling:

Pumping equipment shall pass at least 2-1/2 inch spheres. Valves, fittings etc., shall be capable of passing at least 3 inch spheres. Minimum force main size shall be 3 inches.

(c) Reliability:

(A) Mechanical reliability shall be achieved by redundant lift units such that the peak hourly flow can be passed with the largest unit out of service. Redundancy shall include check and gate valves and other 'common mode' failure sensitive items such as vacuum pumps or compressors on control systems.

(B)(i) Power outages shall result in no raw sewage discharges or bypasses to waters of the state based upon a predictable maximum period of power outage which will occur from year-to-year. Where such reliability does not exist, facilities and/or procedures shall be provided to prevent the discharge or bypass.

(2) GUIDELINES FOR RAW SEWAGE LIFT STATIONS

(a) Capacity:

Lift stations should be sized for the immediate flow requirement and expandable to the longrange (ultimate) requirement. Alternatively interim lift stations may be proposed if the date of expansion is unknowable or beyond the useful life of the lift station.

(b) Solids Handling:

All equipment should be sized to handle at least a 3-inch spheres. Force mains should be at least 4 inches in diameter.

(c) Reliability:

(A) Where no specific records exist, a four (4) hour minimum electrical power outage should be assumed.

(B) Events which should be excluded from design considerations are those which are rare, unusual, and cataclysmic in nature.

Means to prevent discharge or by pass include, but are not limited to, the following:

(i) Electric generator:

- Stationary or portable.
- Automatically or manually started.

(ii) Auxiliary fuel fired pump:

- Stationary or portable.

(C) Failure of prudent Operation and maintenance shall not be considered a valid reason for a station failure and resultant discharge or bypass.

(D) (i)Alarms shall be provided to all stations to announce at least high wet well conditions.

(ii) Telemetering to location with a 24-hour attendant shall be required in sensitive areas.

(d) Operation and Maintenance:

(A) Lift equipment shall be easily removable. Screwed fittings shall not be used for equipment removal. Lifting eyes or hoists shall be provided for equipment removal as appropriate.

(B) (i) A means to wash down wet wells shall be provided for all stations.

(ii) Potable water piped into wells or dry wells shall be equipped with a reduced pressure backflow prevention device.

(C) Wet wells shall have 'hopper

(iii) Storage:

- Sewer lines and manholes.
- Wet well.
- External basin.

(iv) Water supply reduction.

(C) (Future)

(D) (i) Alarms signals should be relayed to the sewer system owner in an effective manner.

(ii) Alarm should be actuated independently of the station control system. Example: Pumps are controlled by pneumatic system and separate float actuated alarm is provided.

(iii) Alarm power should have a battery powered backup electrical source.

(d) Operation and Maintenance:

(A) Flanged or bolted compressions fittings should be used for pump removal.

(B) Frequent wet well washdown should be assumed for all stations. A source of high volume wash water through a nozzle should be provided for this purpose at or on finish grade.

bottoms' at a slope of no flatter than one to one (1: 1), and flat bottom area shall be minimized to prevent deposition of solids.

(e) Safety:

(A) Wet and dry wells of all lift stations shall be considered manholes which will be entered by the owner's personnel.

(B) Each dry well shall have permanently installed ladder, lights, and forced fresh (out-side) air supply to the bottom of the well. Air supply shall be activated with light switch and intermittently operated with a timer.

(C) Wet wells including single well lift stations, shall have either installed or portable equipment for access, lighting, ventilation, etc., to be used when entered.

(e) Safety:

(A) No amount of safety equipment should replace basic safety procedures, knowledge, training and precautions.

(B) (i) Designers should follow appropriate safety codes.

(ii) Air supply should be sized for a least 30 air changes per hour where installed.

(C) (i) Frequently entered wet wells should have permanently installed equipment for access, lighting and ventilation, etc.

(ii) Infrequently entered wet wells may be served with portable equipment.

OAR 340-053-0080
Table 1
Design Flows for Graywater Reuse and Disposal Systems

Type of Establishment		Gallons Per Unit Per Day	Minimum Gallons Per Establishment Per Day
Airports		2.4 (per passenger)	72
Bathhouses and swimming pools		4.8 (per person)	144
Camps: (4 Persons per Campsite, where Applicable)	Campground with central comfort stations	16.8 (per person)	336
	With flush toilets, no showers	12 (per person)	240
	Construction camps — semi-permanent	24 (per person)	480
	Day camps — no meals served	7.2 (per person)	144
	Resort camps (night and day) with limited plumbing	24 (per person)	480
	Luxury camps	48 (per person)	960
Churches		2.4 (per seat)	72
Country clubs		4.8 (per resident member)	960
		12 (per nonresident member present)	
Dwellings:	Boarding houses	72 (per bedroom)	288
	Boarding houses – additional for nonresidential boarders	4.8 (per person)	—
	Rooming houses	38.4 (per person)	240
	Condominiums, Multiple family dwellings — including apartments	144 (per unit)	432
	Single family dwellings	36 (per bedroom for third & each succeeding bedroom)	216
Factories (exclusive of industrial wastes — with shower facilities)		16.8 (per person per shift)	144

OAR 340-053-0080
Table 1
Design Flows for Graywater Reuse and Disposal Systems

Type of Establishment		Gallons Per Unit Per Day	Minimum Gallons Per Establishment Per Day
Factories (exclusive of industrial wastes — without shower facilities)		7.2 (per person per shift)	72
Hospitals		120 (per bed space)	1200
Hotels with private baths		57.6 (per room)	288
Hotels without private baths		48 (per room)	240
Institutions other than hospitals		60 (per bed space)	600
Laundries — self-service		400 (per machine)	2000
Mobile home parks		120 (per space)	360
Motels — with bath, toilet, and kitchen wastes		48 (per bedroom)	240
Motels — without kitchens		38.4 (per bedroom)	192
Picnic Parks — toilet wastes only		0 (per picnicker)	0
Picnic Parks — with bathhouses, showers, and flush toilets		4.8 (per picnicker)	144
Restaurants		19.2 (per seat)	384
Restaurants — single-service		0.96 (per customer)	144
Restaurants — with bars and/or lounges		24 (per seat)	480
Schools:	Boarding	48 (per person)	1440
	Day — without gyms, cafeterias, or showers	7.2 (per person)	216
	Day — with gyms, cafeterias and showers	12 (per person)	360
	Day — with cafeteria, but without gyms or showers	9.6 (per person)	288
Service Stations		4.8 (per vehicle served)	240

OAR 340-053-0080
Table 1
Design Flows for Graywater Reuse and Disposal Systems

Type of Establishment		Gallons Per Unit Per Day	Minimum Gallons Per Establishment Per Day
Swimming pools and bathhouses		4.8 (per person)	144
Theaters:	Movie	2.4 (per seat)	144
	Drive-In	9.6 (per car space)	480
Travel trailer parks — without individual water and sewer hookups		24 (per space)	144
Travel trailer parks — with individual water and sewer hookups		48 (per space)	240
Workers:	Construction — as semi-permanent camps	24 (per person)	480
	Day — at schools and offices	7.2 (per shift)	72

OAR 340-053-0090
Table 2
Minimum Horizontal Separation Distances (in feet)

Feature requiring setback	Graywater storage or surge tank	Point of graywater discharge to landscape for irrigation or edge of landscape pond		
		Type 1	Type 2	Type 3
Groundwater supplies and wells	50	100	50	50
Springs	50	100	50	50
Surface waters of the state, excluding springs	50	50	25	25
Stormwater management structures, collection systems, and catch basins	10	10	10	10
Underground Injection Control Systems (UICs)	10	10	10	10
Property boundaries	5	2	2	*
Building structures	0	0	0	*

* Where sprinkler irrigation is used, there must be 10 feet from the edge of the site used for irrigation and the property boundary and graywater must not be sprayed within 10 feet of an area where food is being prepared or served, or where a drinking fountain is located.

State of Oregon Department of Environmental Quality

OAR 340-071-0800 Tables

OAR 340-071-0220
TABLE 1
MINIMUM SEPARATION DISTANCES

(ALL MEASUREMENTS IN FEET UNLESS OTHERWISE NOTED)

Items Requiring Setback		From Subsurface Absorption Area Including Replacement Area	From Septic Tank and Other Treatment Units, Effluent Sewer and Distribution Units
1. Groundwater Supplies and Wells		*100	50
2. Springs	Upgradient	50	50
	Downgradient	100	50
**3. Surface Public Waters	Year round	100	50
	Seasonal	50	50
4. Intermittent Streams	Piped (watertight not less than 20' from any part of the onsite system)	20	20
	Unpiped	50	50
5. Groundwater Interceptors	On a slope of 3% or less	20	10
	On a slope greater than 3%: Upgradient	10	5
	On a slope greater than 3%: Downgradient	50	10
6. Irrigation Canals	Lined (watertight canal) : Downgradient	25	25
	Unlined: Upgradient	25	25
	Unlined: Downgradient	50	50

OAR 340-071-0220
TABLE 1
MINIMUM SEPARATION DISTANCES

(ALL MEASUREMENTS IN FEET UNLESS OTHERWISE NOTED)

Items Requiring Setback		From Subsurface Absorption Area Including Replacement Area	From Septic Tank and Other Treatment Units, Effluent Sewer and Distribution Units
7. Manmade Cuts Down - Gradient in Excess of 30 Inches (top of downslope cut)	Which Intersect Layers that Limit Effective Soil Depth Within 48 Inches of Surface	50	25
	Which Do Not Intersect Layers that Limit Effective Soil Depth	25	10
8. Downgradient Escarpments	Which Intersect Layers that Limit Effective Soil Depth	50	10
	Which Do Not Intersect Layers that Limit Effective Soil Depth	25	10
9. Property Lines		10	5
10. Water Lines		10	10
11. Foundation Lines of any Building, Including Garages and Out Buildings.		10	5
12. Underground Utilities.		10	—

* 50-foot setback for wells constructed with special standards granted by WRD.
**This does not prevent stream crossings of pressure effluent sewers.

OAR 340-071-0220
TABLE 2
QUANTITIES OF SEWAGE FLOWS

Type of Establishment		Column 1 Gallons Per Day	Column 2 Minimum Gallons Per Establishment Per Day
Airports		5 (per passenger)	150
Bathhouses and swimming pools		10 (per person)	300
Camps: (4 Persons per Campsite, where Applicable)	Campground with central comfort stations	35 (per person)	700
	With flush toilets, no showers	25 (per person)	500
	Construction camps — semi-permanent	50 (per person)	1000
	Day camps — no meals served	15 (per person)	300
	Resort camps (night and day) with limited plumbing	50 (per person)	1000
	Luxury camps	100 (per person)	2000
Churches		5 (per seat)	150
Country clubs		100 (per resident member)	2000
Country clubs		25 (per non-resident member present)	—
Dwellings:	Boarding houses	150 (per bedroom)	600
	Boarding houses – additional for non-residential boarders	10 (per person)	—
	Rooming houses	80 (per person)	500
	Condominiums, Multiple family dwellings — including apartments	300 (per unit)	900
	Single family dwellings	300 (not exceeding 2 bedrooms)	450*
	Single family dwellings — with more than 2 bedrooms	75 (for third & each succeeding bedroom)	450
Factories (exclusive of industrial wastes — with shower facilities)		35 (per person per shift)	300
Factories (exclusive of industrial wastes — without shower facilities)		15 (per person per shift)	150
Hospitals		250 (per bed space)	2500
Hotels with private baths		120 (per room)	600

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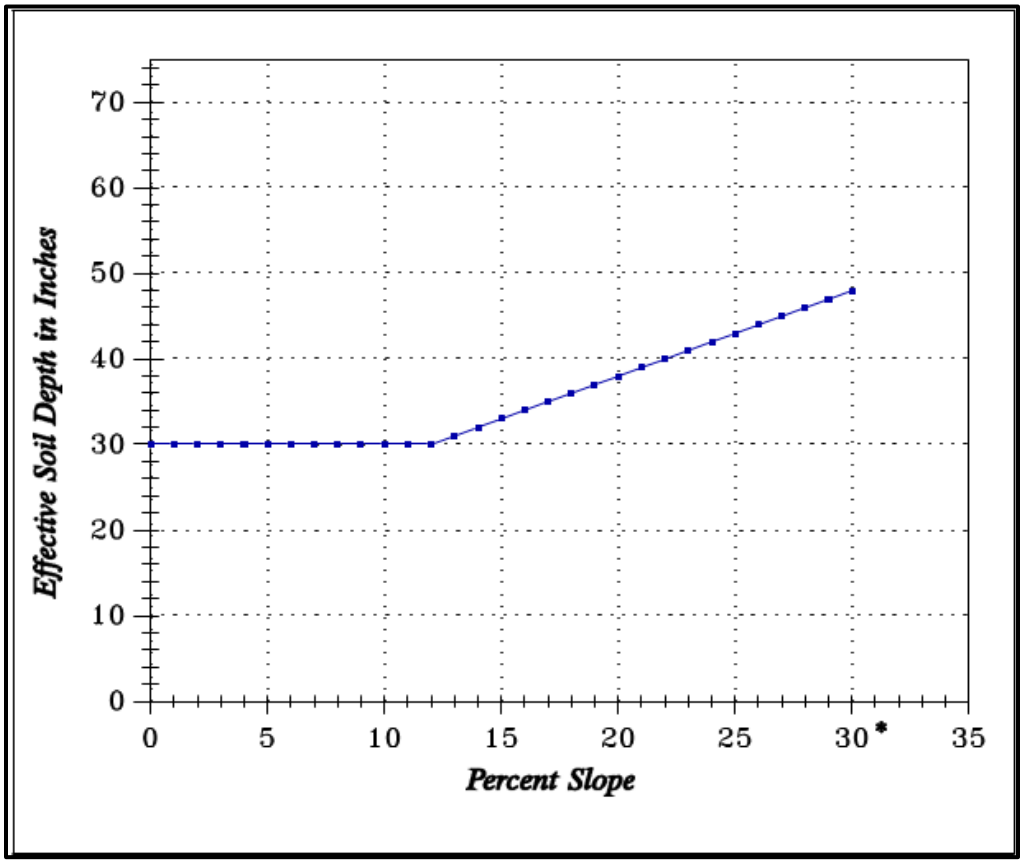
TABLE 2
QUANTITIES OF SEWAGE FLOWS

Type of Establishment		Column 1 Gallons Per Day	Column 2 Minimum Gallons Per Establishment Per Day
Hotels without private baths		100 (per room)	500
Institutions other than hospitals		125 (per bed space)	1250
Laundries — self-service		500 (per machine)	2500
Mobile home parks		250 (per space)	750
Motels — with bath, toilet, and kitchen wastes		100 (per bedroom)	500
Motels — without kitchens		80 (per bedroom)	400
Picnic Parks — toilet wastes only		5 (per picnicker)	150
Picnic Parks — with bathhouses, showers, and flush toilets		10 (per picnicker)	300
Restaurants		40 (per seat)	800
Restaurants — single-service		2 (per customer)	300
Restaurants — with bars and/or lounges		50 (per seat)	1000
Schools:	Boarding	100 (per person)	3000
	Day — without gyms, cafeterias, or showers	15 (per person)	450
	Day — with gyms, cafeterias and showers	25 (per person)	750
	Day — with cafeteria, but without gyms or showers	20 (per person)	600
Service Stations		10 (per vehicle served)	500
Swimming pools and bathhouses		10 (per person)	300
Theaters:	Movie	5 (per seat)	300
	Drive-In	20 (per car space)	1000
Travel trailer parks — without individual water and sewer hookups		50 (per space)	300
Travel trailer parks — with individual water and sewer hookups		100 (per space)	500
Workers:	Construction — as semi-permanent camps	50 (per person)	1000
	Day — at schools and offices	15 (per shift)	150

* Except as otherwise provided in these rules.

OAR 340-071-0220
TABLE 3
SLOPE, EFFECTIVE SOIL DEPTH RELATIONSHIP



OAR 340-071-0220
TABLE 4

Minimum length of absorption trench (linear feet) required per 150 gallons projected daily sewage flow determined from soil texture versus effective soil depth.

Effective Soil Depth	Soil Group		
	A	B	C
18" to Less than 24"	125	150	175
24" to Less than 36"	100	125	150
36" to Less than 48	75	100	125
48" or more	50	75	125

* Soil Group A — Sand, Loamy Sand, Sandy Loam.
* Soil Group B — Sandy Clay Loam, Loam, Silt Loam, Silt, Clay Loam. Soil Group C — Silty Clay Loam, Sandy Clay, Silty Clay, Clay.
* If sand grains are fine or very fine, site according to Group B soils.

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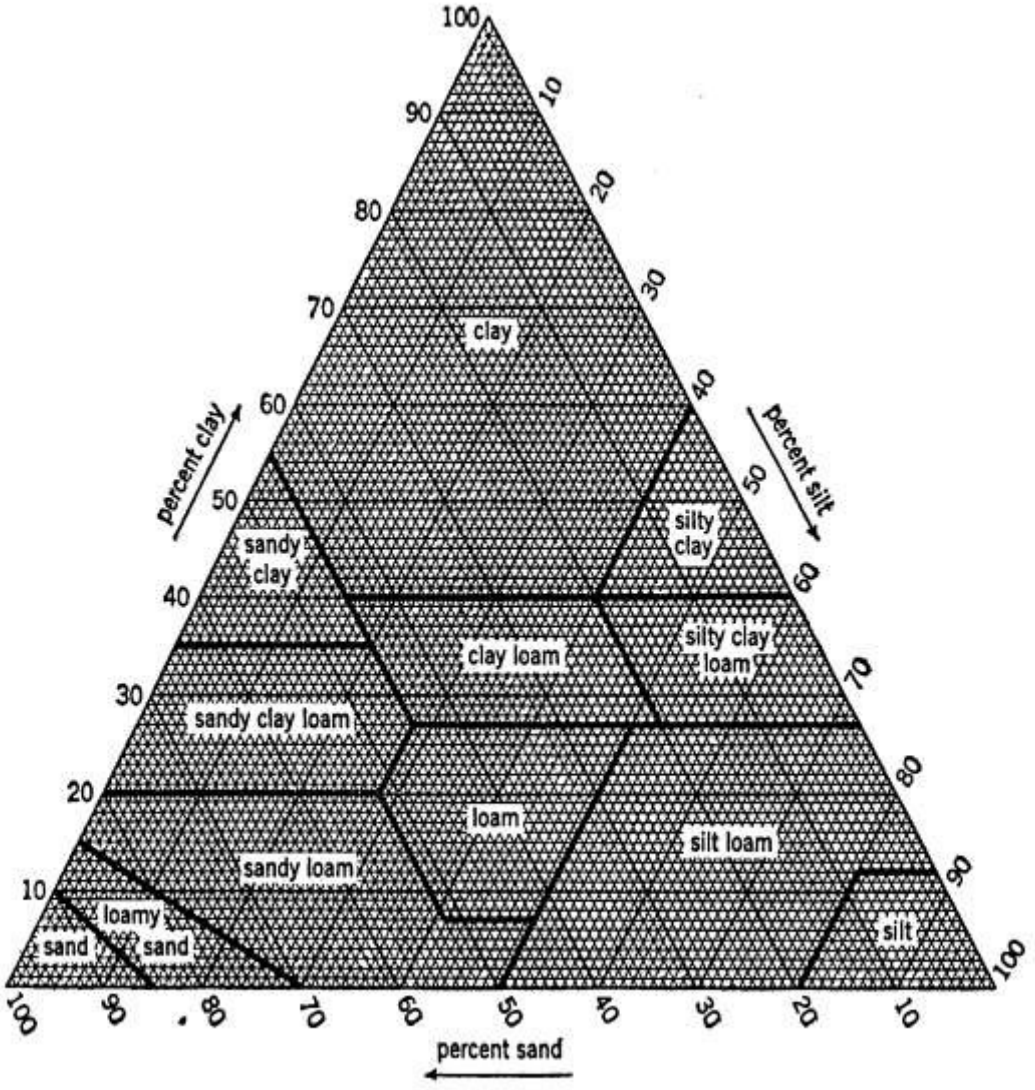
TABLE 5

Minimum length of absorption trench (linear feet) required per 150 gallons projected daily sewage flow determined from soil texture versus depth to temporary groundwater.

Depth to Temporary Groundwater	Soil Group		
	A	B	C
24" to Less than 48"	100	125	150
48" or More	50	75	125

* Soil Group A — Sand, Loamy Sand, Sandy Loam.
* Soil Group B — Sandy Clay Loam, Loam, Silt Loam, Silt, Clay Loam. Soil Group C — Silty Clay Loam, Sandy Clay, Silty Clay, Clay.
* If sand grains are fine or very fine, site according to Group B soils.

OAR 340-071-0100
TABLE 6
SOIL TEXTURAL CLASSIFICATION CHART



OAR 340-071-0100 TABLE 7 USDA SOIL CLASSIFICATION SIZES OF SOIL SEPARATES		
Material	**Sieve Sizes**	**Millimeters**
Clay		.002
Silt	270	.050
Very Fine Sand	200 140	.075 .1
Fine Sand	60	.25
Medium Sand	35	.5
Coarse Sand	18	1.0
Very Coarse Sand	10	2.0
Fine Gravel	4 3/8” 1/2	4.75 9.5 12.5
Course Gravel	3”	76.2
Cobbles		

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TABLE 8
MINIMUM SEPARATION DISTANCES FOR NONWATER-CARRIED WASTE DISPOSAL FACILITIES

	Self-Contained Nonwater-Carried Waste Disposal	Unsealed Earth Type Privies, Graywater Waste Disposal Sump and Seepage Chambers
Groundwater supplies including springs and cisterns	50'	100'
Surface public waters, excluding intermittent streams	50'	100'
Intermittent streams	50'	50'
Property line	25'	25'

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TABLE 9A

SITE EVALUATION AND EXISTING SYSTEM EVALUATION FEES

New Site Evaluation Fees. Fees in this section apply to each system for which site suitability is evaluated.	
Single family dwelling - First lot	$700
Single family dwelling - Each additional lot evaluated during initial visit	$700
Commercial facility with a design capacity of 1,000 gpd or less	$700
Commercial facility with a design capacity of 1,001-1,500 gpd	$882
Commercial facility with a design capacity of 1,501-2,000 gpd	$1,063
Commercial facility with a design capacity of 2,001-2,500 gpd	$1,244
Commercial facility s with a design capacity of 2,501-3,000 gpd	$1,426
Commercial facility with a design capacity of 3,001-3,500 gpd	$1,607
Commercial facility with a design capacity of 3,501-4,000 gpd	$1,788
Commercial facility with a design capacity of 4,001-4,500 gpd	$1,969
Commercial facility with a design capacity of 4,501-5,000 gpd	$2,151
Commercial facility with a design flow greater than 5,000 gpd	$2,373
Site Evaluation Report Review fee	$659
Existing System Evaluation Report fee	$659

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TABLE 9B

PERMITTING FEES FOR SYSTEMS NOT SUBJECT TO WPCF PERMITS

Type of Fee		System Type					Plan Review fees for Commercial Facility Systems
		A	B	C	D	E	
Construction-Installation Permit Fees	For systems with a design capacity of less than 600 gpd	$461	$890	$1,038	$1,272	$1,566	$0
	For systems with a design capacity of 601-1,000 gpd	$461	$890	$1,038	$1,272	$1,566	$379
	For systems with a design capacity of 1,001-1,500 gpd	$560	$989	$1,137	$1,352	$1,710	$445
	For systems with a design capacity of 1,501-2,000 gpd	$659	$1,088	$1,236	$1,433	$1,763	$511
	For systems with a design capacity of 2,001-2,500 gpd	$758	$1,187	$1,335	$1,513	$1,862	$577
Reinspection fee		$103	$103	$103	$103	$103	$103
Pump Evaluation fee. For all permits that specify the use of a pump or dosing siphon except for sand filter, Alternative treatment technologies, Recirculating gravel filter, and pressurized distribution systems		$66	$66	$66	$66	$66	$66

System Type Key:
Type A = Gray Water waste disposal sumps
Type B = Holding tanks
Type C = Standard subsurface, Absorption trenches in saprolite, Redundant, Seepage trench, Steep slope
Type D = Alternative treatment technologies, Capping fill, Pressurized distribution, Tile dewatering
Type E = Recirculating gravel filter, Sand filter (commercial or residential)

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TABLE 9C

OTHER PERMITTING FEES FOR SYSTEMS NOT SUBJECT TO WPCF PERMITS

Type	Fee	Field Visit required	No Field Visit required
Minor Alteration Permit	$272		
Major Alteration Permit	$569		
Minor Repair Permit - Single Family Dwelling	$264		
Major Repair Permit - Single Family Dwelling	$551		
Minor Repair Permit - Commercial Facility	$478		
Major Repair Permit - Commercial Facility	$1,038		
Permit Denial Review	$363		
Permit Transfer, Reinstatement, or Renewal		$536	$157
Authorization Notice		$643	$165
Authorization Notice Denial Review	$659		
Renewal of hardship authorization for temporary dwelling		$340	$103
Alternative system inspection - Holding tanks	$396		
Variance from onsite system rules	$2,142		
Land use clearance	$52		
Annual report evaluation - Holding tanks – hard copy submittal	$31		
Annual report evaluation - Holding tanks – online submittal	$26		
Alternative system inspection - Other alternative systems listed in Table 9B	$544		
Annual report evaluation - Sand filters, pressurized distribution systems, recirculating gravel filters, and alternative treatment technology – hard copy submittal	$62		

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TABLE 9C

OTHER PERMITTING FEES FOR SYSTEMS NOT SUBJECT TO WPCF PERMITS

Type	Fee	Field Visit required	No Field Visit required
Annual report evaluation - Sand filters, pressurized distribution systems, recirculating gravel filters, and alternative treatment technology – online submittal	$52		

OAR 340-071-0140
TABLE 9D
WPCF PERMIT FEES

	Application filing fee (all systems)	Permit processing fees for onsite systems with a design capacity of 1,200 gpd or less	Permit processing fees for onsite systems with a design capacity over 1,200 gpd
New application	$91	$732	$3,655
Permit renewal (involving request for effluent limit modifications)	$91	$364	$1,830
Permit renewal (without request for effluent limit modifications)	$91	$184	$913
Permit modification (involving increase in effluent limitations)	$91	$364	$1,830
Permit modification (not involving an increase in effluent limits)	$91	$274	$913
Plan Review fee			
For commercial facilities with a design capacity less than 600 gpd	$0		
For commercial facilities with a design capacity of 601 - 1,000 gpd	$349		
For commercial facilities with a design capacity of 1,001 - 1,500 gpd	$411		
For commercial facilities with a design capacity of 1,501 - 2,000 gpd	$473		
For commercial facilities with a design capacity of 2,001 - 2,500 gpd	$533		
For commercial facilities with a design capacity of 2,501 - 3,000 gpd	$625		
For commercial facilities with a design capacity of 3,001 - 3,500 gpd	$686		
For commercial facilities with a design capacity of 3,501 - 4,000 gpd	$747		

OAR 340-071-0140 TABLE 9D WPCF PERMIT FEES	
For commercial facilities with a design capacity of 4,001 - 4,500 gpd	$806
For commercial facilities with a design capacity of 4,501 - 5,000 gpd	$868
Commercial facilities with a design capacity greater than 5,000 gpd	$913
Single family dwelling	$184
Annual Compliance Determination fee	
Onsite sewage lagoon with no discharge	$1,096
Treatment Standard 1 or better systems with design capacities less than 2,500 gpd	$457
Treatment Standard 1 or better systems with design capacities of 2,501 - 20,000 gpd	$913
Holding tanks, if by the date specified by DEQ, the owner does not submit written certification to DEQ that the holding tank has been operated the previous calendar year in full compliance with the permit or that the previous year's service logs for the holding tanks are not available for inspection by the DEQ	$364
Holding tanks, if by the date specified by DEQ, the owner submits written certification to DEQ that the holding tank has been operated the previous calendar year in full compliance with the permit and that the previous year's service	$40
Other systems with design capacities less than 20,000 gpd	$457

OAR 340-071-0140 TABLE 9D WPCF PERMIT FEES	
Other systems with design capacities greater than 20,000 gpd	$913

OAR 340-071-0140 TABLE 9E SEWAGE DISPOSAL SERVICE LICENSE AND TRUCK INSPECTION FEES	
New 3-year business license	$438 per year
Renewal of business license	$330 per year
Additional license fee for additional pumper vehicles	$16/vehicle
Transfer of or amendments to license	$206
Reinstatement of suspended license	$258
Pumper truck inspections - First vehicle, each inspection	$103
Pumper truck inspections - Each additional vehicle, each inspection	$52

OAR 340-071-0140 TABLE 9F OTHER FEES	
Innovative or Alternative Technology Review	$1,648
Alternative Technology Review (greater than 1,500 gpd)	$3,296
Alternative Treatment Technology Annual Compliance Determination Fee (per listed model)	$515
Material Plan Review	$494
Department Surcharge	$100

State of Oregon Department of Environmental Quality

OAR 340-090-0360

Recycled Content Calculation Formula

The calculation for determining recycled content described in OAR 340-090-0360(2)(b) can be stated as the following formula:

$$\frac{\text{Recycled Material}}{\text{Total Plastic Material}} \text{ X } 100 = \text{Recycled Content}$$

OAR 340-093-0270
Standing Beneficial Use Determinations

Solid Waste	Beneficial Use	Conditions on Use
(a) Asphalt pavement or asphalt grindings from road projects	As asphalt and aggregate in new asphalt pavement or as fill within road prisms	Asphalt grindings must be compacted when used within road prisms
(b) Asphalt shingle waste from roof tear-offs and manufacturer scrap	As asphalt binder in asphalt mixtures	The waste does not contain asbestos or other non-asphalt shingle materials from roof tear-offs, such as nails, metal flashing, paper, or wood waste
(c) Dredged sediment approved by the department's water quality program for unconfined in-water placement based on chemical screening	Non-residential construction fill, surcharge, utility trench fill, or roadbase; habitat improvement, beach nourishment or other similar uses	A person using the material must submit a report to the Department in accordance with section (4) of this rule
(d) Dredged sediment not approved by the department's water quality program for in-water placement	Non-residential construction fill, utility trench fill, or roadbase	Concentrations of hazardous substances are below the higher of Department-approved human health occupational risk-based screening levels or naturally occurring background; placed where it will not be in contact with or adversely impact waters of the state; covered in a manner that minimizes exposure to ecological receptors; and a person using the material must submit a report to the Department in accordance with section (4) of this rule
(e) Foundry sand produced by iron, steel, or aluminum foundries	As aggregate in asphalt mixtures, concrete, Portland cement, or masonry mortar	None specified beyond the requirements of this rule
(f) Foundry sand produced by iron, steel, or aluminum foundries	Non-residential construction fill, utility trench fill, or roadbase	Concentrations of hazardous substances are below the higher of Department-approved human health occupational risk-based screening levels or naturally occurring background; placed where it will not be in contact with or adversely impact waters of the state; covered in a manner that minimizes exposure to ecological receptors; and a person using the material must submit a report to the Department in accordance with section (4) of this rule

OAR 340-093-0270
Standing Beneficial Use Determinations

Solid Waste	Beneficial Use	Conditions on Use
(g) Soil from cleanup sites	Non-residential construction fill, utility trench fill, or roadbase	Concentrations of hazardous substances are below the higher of Department-approved human health occupational risk-based screening levels or naturally occurring background; placed where it will not be in contact with or adversely impact waters of the state; covered in a manner that minimizes exposure to ecological receptors; the use is approved through Department Cleanup or Tanks Program cost recovery oversight; and a person using the material must submit a report to the Department in accordance with section (4) of this rule
(h) Soil from petroleum cleanup sites	As aggregate in asphalt mixtures	Petroleum contamination from releases of heating oil or motor fuel only
(i) Steel slag	As aggregate in asphalt mixtures, concrete, or Portland cement	None specified beyond the requirements of this rule
(j) Street sweeping fines	Spill response absorbent	After use of the waste a hazardous waste determination must be conducted and the material disposed at an appropriate permitted disposal site
(k) Street sweeping sand from winter storm applications	Road sanding	Swept up within 6 months of application or being re-exposed on the road after snowmelt; and the sand is separated from the street sweepings
(l) Wood-derived bottom ash, boiler rock, or clinkers, including rock, sand, dirt, and fused wood ash, from wood and wood waste fired boilers	As aggregate in asphalt mixtures, concrete, or Portland cement	None specified beyond the requirements of this rule

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State of Oregon Department of Environmental Quality

OAR 340-094-0040

Toxicity Characteristic Leaching Procedure

METHOD 1311

TOXICITY CHARACTERISTIC LEACHING PROCEDURE

1.1 SCOPE AND APPLICATION

1.2 The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes.

1.3 If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the TCLP need not be run.

1.4 If an analysis of any one of the liquid fractions of the TCLP extract indicates that a regulated compound is present at such high concentra- tions that, even after accounting for dilution from the other fractions of the extract, the concentration would be above the regulatory level for that compound, then the waste is hazardous and it is not necessary to analyze the remaining fractions of the extract.

1.5 If an analysis of extract obtained using a bottle extractor shows that the concentration of any regulated volatile analyte exceeds the regulatory level for that compound, then the waste is hazardous and extraction using the ZHE is not necessary. However, extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the regulatory level.

2.1 SUMMARY OF METHOD

2.2 For liquid wastes (i.e., those containing less than 0.5% dry solid material), the waste, after filtration through a 0.6 to 0.8 µm glass fiber filter, is defined as the TCLP extract.

2.3 For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatile analytes (see Table 1 for a list of volatile compounds). Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 µm glass fiber filter.

2.4 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3.1 INTERFERENCES

3.2 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.1 APPARATUS AND MATERIALS

4.2 Agitation apparatus: The agitation apparatus must be capable of rotating the extraction vessel in an end-over-end fashion (see Figure 1) at 30 ± 2 rpm. Suitable devices known to EPA are identified in Table 2.

4.3 Extraction Vessels

4.3.1 Zero-Headspace Extraction Vessel (ZHE). This device is for use only when the waste is being tested for the mobility of volatile analytes (i.e., those listed in Table 1). The ZHE (depicted in Figure 2) allows for liquid/solid separation within the device, and effectively precludes headspace. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel (see Section 4.3.1). The vessels shall have an internal volume of 500-600 mL, and be equipped to accommodate a 90-110 mm filter. The devices contain VITON®[1] O-rings which should be replaced frequently. Suitable ZHE devices known to EPA are identified in Table 3.

For the ZHE to be acceptable for use, the piston within the ZHE should be able to be moved with approximately 15 psi or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for TCLP analyses and the manufacturer should be contacted.

The ZHE should be checked for leaks after every extraction. If the device contains a built-in pressure gauge, pressurize the device to 50 psi, allow it to stand unattended for 1 hour, and recheck the pressure. If the device does not have a built-in pressure gauge, pressurize the device to 50 psi, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted.

Some ZHEs use gas pressure to actuate the ZHE piston, while others use mechanical pressure (see Table 3). Whereas the volatiles procedure (see Section 7.3) refers to pounds per square inch (psi), for the mechanically actuated piston, the pressure applied is measured in torque-inch-pounds. Refer to the manufacturer's instructions as to the proper conversion.

[1] VITON® is a trademark of Du Pont.

4.3.2 Bottle Extraction Vessel. When the waste is being evaluated using the nonvolatile extraction, a jar with sufficient capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel.

The extraction bottles may be constructed from various materials, depending on the analytes to be analyzed and the nature of the waste (see Section 4.3.3). It is recommended that borosilicate glass bottles be used instead of other types of glass, especially when inorganics are of concern. Plastic bottles, other than polytetrafluoroethylene, shall not be used if organics are to be investigated. Bottles are available from a number of laboratory suppliers. When this type of extraction vessel is used, the filtration device discussed in Section 4.3.2 is used for initial liquid/solid separation and final extract filtration.

4.4 Filtration Devices: It is recommended that all filtrations be performed in a hood.

4.4.1 Zero-Headspace Extractor Vessel (ZHE): When the waste is evaluated for volatiles, the zero-headspace extraction vessel described in Section 4.2.1 is used for filtration. The device shall be capable of supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation (50 psi).

NOTE: When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.

4.4.2 Filter Holder: When the waste is evaluated for other than volatile analytes, any filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psi or more. The type of filter holder used depends on the properties of the material to be filtered (see Section 4.3.3). These devices shall have a minimum internal volume of 300 mL and be equipped to accommodate a minimum filter size of 47 mm (filter holders having an internal capacity of 1.5 L or greater, and equipped to accommodate a 142 mm diameter filter, are recommended). Vacuum filtration can only be used for wastes with low solids content (<10%) and for highly granular, liquid-containing wastes. All other types of wastes should be filtered using positive pressure filtration. Suitable filter holders known to EPA are shown in Table 4.

4.4.3 Materials of Construction: Extraction vessels and filtration devices shall be made of inert materials which will not leach or absorb waste components. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride (PVC) may be used only when evaluating the mobility of metals. Borosili-

water glass bottles are recommended for use over other types of glass bottles, especially when inorganics are analytes of concern.

4.5 Filters: Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6 to 0.8 µm, or equivalent. Filters known to EPA which meet these specifications are identified in Table 5. Pre-filters must not be used. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 1N nitric acid followed by three consecutive rinses with deionized distilled water (a minimum of 1 L per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

4.5 pH Meters: The meter should be accurate to ± 0.05 units at 25 °C.

4.6 ZHE Extract Collection Devices: TEDLAR®[2] bags or glass, stainless steel or PTFE gas-tight syringes are used to collect the initial liquid phase and the final extract of the waste when using the ZHE device. The devices listed are recommended for use under the following conditions:

4.6.1 If a waste contains an aqueous liquid phase or if a waste does not contain a significant amount of nonaqueous liquid (i.e., <1% of total waste), the TEDLAR® bag or a 600 mL syringe should be used to collect and combine the initial liquid and solid extract.

4.6.2 If a waste contains a significant amount of nonaqueous liquid in the initial liquid phase (i.e., >1% of total waste), the syringe or the TEDLAR® bag may be used for both the initial solid/liquid separation and the final extract filtration. However, analysts should use one or the other, not both.

4.6.3 If the waste contains no initial liquid phase (is 100% solid) or has no significant solid phase (is 100% liquid), either the TEDLAR® bag or the syringe may be used. If the syringe is used, discard the first 5 mL of liquid expressed from the device. The remaining aliquots are used for analysis.

4.7 ZHE Extraction Fluid Transfer Devices: Any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is acceptable (e.g., a positive displacement or peristaltic pump, a gas tight syringe, pressure filtration unit (see Section 4.3.2), or other ZHE device).

4.8 Laboratory Balance: Any laboratory balance accurate to within ± 0.01 grams may be used (all weight measurements are to be within ± 0.1 grams).

4.9 Beaker or Erlenmeyer flask, glass, 500 mL.

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[2] TEDLAR® is a registered trademark of Du Pont.

4.10 Watchglass, appropriate diameter to cover beaker or Erlenmeyer flask.

4.11 Magnetic stirrer.

5.1 REAGENTS

5.2 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.3 Reagent Water. Reagent water is defined as water in which an interferant is not observed at or above the method's detection limit of the analyte(s) of interest. For nonvolatile extractions, ASTM Type II water or equivalent meets the definition of reagent water. For volatile extractions, it is recommended that reagent water be generated by any of the following methods. Reagent water should be monitored periodically for impurities.

5.3.1 Reagent water for volatile extractions may be generated by passing tap water through a carbon filter bed containing about 500 grams of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.3.2 A water purification system (Millipore Super-Q or equivalent) may also be used to generate reagent water for volatile extractions.

5.3.3 Reagent water for volatile extractions may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the water temperature at 90 $\pm$ 5 degrees C, bubble a contaminant-free inert gas (e.g. nitrogen) through the water for 1 hour. While still hot, transfer the water to a narrow mouth screw-cap bottle under zero-headspace and seal with a Teflon-lined septum and cap.

5.4 Hydrochloric acid (1N), HCl, made from ACS reagent grade.

5.5 Nitric acid (1N), HNO_3, made from ACS reagent grade.

5.6 Sodium hydroxide (1N), NaOH, made from ACS reagent grade.

5.7 Glacial acetic acid, CH_3CH_2OOH, ACS reagent grade.

5.8 Extraction fluid.

5.8.1 Extraction fluid # 1: Add 5.7 mL glacial CH_3CH_2OOH to 500 mL of reagent water (See Section 5.2), add 64.3 mL of 1N NaOH, and dilute to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 4.93 $\pm$ 0.05.

5.8.2 Extraction fluid # 2: Dilute 5.7 mL glacial CH_3CH_2OOH with reagent water (See Section 5.2) to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 2.88 $\pm$ 0.05.

NOTE: These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid shall be discarded and fresh extraction fluid prepared.

5.9 Analytical standards shall be prepared according to the appropriate analytical method.

6.1 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.2 All samples shall be collected using an appropriate sampling plan.

6.3 The TCLP may place requirements on the minimal size of the field sample, depending upon the physical state or states of the waste and the analytes of concern. An aliquot is needed for preliminary evaluation of which extraction fluid is to be used for the nonvolatile analyte extraction procedure. Another aliquot may be needed to actually conduct the nonvolatile extraction (see Section 1.4 concerning the use of this extract for volatile organics). If volatile organics are of concern, another aliquot may be needed. Quality control measures may require additional aliquots. Further, it is always wise to collect more sample just in case something goes wrong with the initial attempt to conduct the test.

6.3 Preservatives shall not be added to samples before extraction.

6.4 Samples may be refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

6.5 When the waste is to be evaluated for volatile analytes, care shall be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g., samples should be collected in Teflon-lined septum capped vials and stored at 4 °C. Samples should be opened only immediately prior to extraction).

6.6 TCLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH < 2, unless precipitation occurs (see Section 7.2.14 if precipitation occurs). Extracts should be preserved for other analytes according to the guidance given in the individual analysis methods. Extracts or portions of extracts for organic analyte determinations shall not be allowed to come into contact with the atmosphere (i.e., no headspace) to prevent losses. See Section 8.0 (QA requirements) for acceptable sample and extract holding times.

7.2 Preliminary Evaluations

Perform preliminary TCLP evaluations on a minimum 100 gram aliquot of waste. This aliquot may not actually undergo TCLP extraction. These preliminary evaluations include: (1) determination of the percent solids (Section 7.1.1);
(2) determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration (Section 7.1.2); (3) determination of whether the solid portion of the waste requires particle size reduction (Section 7.1.3); and (4) determination of which of the two extraction fluids are to be used for the nonvolatile TCLP extraction of the waste (Section 7.1.4).

7.1.1 Preliminary determination of percent solids: Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below.

7.1.1.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solids) proceed to Section 7.1.3.

7.1.1.2 If the sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device described in Section 4.3.2 and is outlined in Sections 7.1.1.3 through 7.1.1.9.

7.1.1.3 Pre-weigh the filter and the container that will receive the filtrate.

7.1.1.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

7.1.1.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight.

7.1.1.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.1.1.7 Quantitatively transfer the waste sample to the filter holder (liquid and solid phases). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room temperature then allow the sample to warm up to room temperature in the device before filtering.

NOTE: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Section 7.1.1.5 to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within any 2 minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.1.1.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Section 7.1.1.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.1.1.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (see Section 7.1.1.3) from the total weight of the filtrate-filled container. Determine the weight of the solid phase of the waste sample by subtracting the weight of the liquid phase from the weight of the total waste sample, as determined in Section 7.1.1.5 or 7.1.1.7.

Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\text{Percent solids} = \frac{\text{Weight of solid (Section 7.1.1.9)}}{\text{Total weight of waste (Section 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2 If the percent solids determined in Section 7.1.1.9 is equal to or greater than 0.5%, then proceed either to Section 7.1.3 to

determine whether the solid material requires particle size reduction or to Section 7.1.2.1 if it is noticed that a small amount of the filtrate is entrained in wetting of the filter. If the percent solids determined in Section 7.1.1.9 is less than 0.5%, then proceed to Section 7.2.9 if the nonvolatile TCLP is to be performed and to Section 7.3 with a fresh portion of the waste if the volatile TCLP is to be performed.

7.1.2.1 Remove the solid phase and filter from the filtration apparatus.

7.1.2.2 Dry the filter and solid phase at 100 ± 20 °C until two successive weighing yield the same value within ± 1%. Record the final weight.

NOTE: Caution should be taken to ensure that the subject solid will not flash upon heating. It is recommended that the drying oven be vented to a hood or other appropriate device.

7.1.2.3 Calculate the percent dry solids as follows: (Wt. of dry waste + filter) - tared wt. of filter

$$\text{Percent dry solids} = \frac{\text{(Wt. of dry waste + filter) - tared wt. of filter}}{\text{Initial wt. of waste (Section 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2.4 If the percent dry solids is less than 0.5%, then proceed to Section 7.2.9 if the nonvolatile TCLP is to be performed, and to Section 7.3 if the volatile TCLP is to be performed. If the percent dry solids is greater than or equal to 0.5%, and if the nonvolatile TCLP is to be performed, return to the beginning of this Section (7.1) and, with a fresh portion of waste, determine whether particle size reduction is necessary (Section 7.1.3) and determine the appropriate extraction fluid (Section 7.1.4). If only the volatile TCLP is to be performed, see the note in Section 7.1.4.

7.1.3 Determination of whether the waste requires particle size reduction (particle size is reduced during this step): Using the solid portion of the waste, evaluate the solid for particle size. Particle size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1 cm^2, or is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm (0.375 inch) standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above. If the solids are prepared for organic volatiles extraction, special precautions must be taken (see Section 7.3.6).

NOTE: Surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet

the criteria, sample specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

7.1.4 Determination of appropriate extraction fluid: If the solid content of the waste is greater than or equal to 0.5% and if the sample will be extracted for nonvolatile constituents (Section 7.2), determine the appropriate fluid (Section 5.7) for the nonvolatiles extraction as follows:

NOTE: TCLP extraction for volatile constituents uses only extraction fluid #1 (Section 5.7.1). Therefore, if TCLP extraction for nonvolatiles is not required, proceed to Section 7.3.

7.1.4.1 Weigh out a small subsample of the solid phase of the waste, reduce the solid (if necessary) to a particle size of approximately 1 mm in diameter or less, and transfer 5.0 grams of the solid phase of the waste to a 500 mL beaker or Erlenmeyer flask.

7.1.4.2 Add 96.5 mL of reagent water to the beaker, cover with a watchglass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is <5.0, use extraction fluid #1. Proceed to Section 7.2.

7.1.4.3 If the pH from Section 7.1.4.2 is >5.0, add 3.5 mL 1N HCl, slurry briefly, cover with a watchglass, heat to 50 °C, and hold at 50 °C for 10 minutes.

7.1.4.4 Let the solution cool to room temperature and record the pH. If the pH is <5.0, use extraction fluid #1. If the pH is >5.0, use extraction fluid #2. Proceed to Section 7.2.

7.1.5 If the aliquot of the waste used for the preliminary evaluation (Sections 7.1.1 - 7.1.4) was determined to be 100% solid at Section 7.1.1.1, then it can be used for the Section 7.2 extraction (assuming at least 100 grams remain), and the Section 7.3 extraction (assuming at least 25 grams remain). If the aliquot was subjected to the procedure in Section 7.1.1.7, then another aliquot shall be used for the volatile extraction procedure in Section 7.3. The aliquot of the waste subjected to the procedure in Section 7.1.1.7 might be appropriate for use for the Section 7.2 extraction if an adequate amount of solid (as determined by Section 7.1.1.9) was obtained. The amount of solid necessary is dependent upon whether a sufficient amount of extract will be produced to support the analyses. If an adequate amount of solid remains, proceed to Section 7.2.10 of the nonvolatile TCLP extraction.

7.2 Procedure When Volatiles are not Involved

A minimum sample size of 100 grams (solid and liquid phases) is recommend- ed. In some cases, a larger sample size may be appropriate, depending on the

solids content of the waste sample (percent solids, See Section 7.1.1), whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of TCLP extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single TCLP extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

7.2.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solid, see Section 7.1.1), weigh out a subsample of the waste (100 gram minimum) and proceed to Section 7.2.9.

7.2.2 If the sample is liquid or multiphasic, liquid/solid separation is required. This involves the filtration device described in Section 4.3.2 and is outlined in Sections 7.2.3 to 7.2.8.

7.2.3 Pre-weigh the container that will receive the filtrate.

7.2.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (see Section 4.4).

NOTE: Acid washed filters may be used for all nonvolatile extractions even when metals are not of concern.

7.2.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight. If the waste contains <0.5% dry solids (Section 7.1.2), the liquid portion of the waste, after filtration, is defined as the TCLP extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required of the TCLP extract. For wastes containing >0.5% dry solids (Sections 7.1.1 or 7.1.2), use the percent solids information obtained in Section 7.1.1 to determine the optimum sample size (100 gram minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the TCLP extract.

7.2.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the waste is centrifuged, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.2.7 Quantitatively transfer the waste sample (liquid and solid phases) to the filter holder (see Section 4.3.2). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at

room temperature, then allow the sample to warm up to room temperature in the device before filtering.

NOTE: If waste material (>1% of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Section 7.2.5, to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within a 2 minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.2.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase may now be either analyzed (See Section 7.2.12) or stored at 4 °C until time of analysis.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Section 7.2.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the extraction as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.2.9 If the waste contains <0.5% dry solids (see Section 7.1.2), proceed to Section 7.2.13. If the waste contains >0.5% dry solids (see Section 7.1.1 or 7.1.2), and if particle size reduction of the solid was needed in Section 7.1.3, proceed to Section 7.2.10. If the waste as received passes a 9.5 mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to Section 7.2.11.

7.2.10 Prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described in Section 7.1.3. When the surface area or particle size has been appropriately altered, quantitatively transfer the solid

material into an extractor bottle. Include the filter used to separate the initial liquid from the solid phase.

NOTE: Sieving of the waste is not normally required. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended. If sieving is necessary, a Teflon coated sieve should be used to avoid contamination of the sample.

7.2.11 Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (Section 7.1.1)} \times \text{weight of waste filtered (Section 7.2.5 or 7.2.7)}}{100}$$

Slowly add this amount of appropriate extraction fluid (see Section 7.1.4) to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal), secure in rotary agitation device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at 23 ± 2 °C during the extraction period.

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of wastes (e.g., limed or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

7.2.12 Following the 18 ± 2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in Section 7.2.7. For final filtration of the TCLP extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filter(s) shall be acid-washed (see Section 4.4) if evaluating the mobility of metals.

7.2.13 Prepare the TCLP extract as follows:

7.2.13.1 If the waste contained no initial liquid phase, the filtered liquid material obtained from Section 7.2.12 is defined as the TCLP extract. Proceed to Section 7.2.14.

7.2.13.2 If compatible (e.g., multiple phases will not result on combination), combine the filtered liquid resulting from Section 7.2.12 with the initial liquid phase of the waste obtained in Section 7.2.7. This combined liquid is defined as the TCLP extract. Proceed to Section 7.2.14.

7.2.13.3 If the initial liquid phase of the waste, as obtained from Section 7.2.7, is not or may not be compatible with the filtered liquid resulting from Section 7.2.12, do not combine these liquids. Analyze these liquids, collectively defined as the TCLP extract, and combine the results mathematically, as described in Section 7.2.14.

7.2.14 Following collection of the TCLP extract, the pH of the extract should be recorded. Immediately aliquot and preserve the extract for analysis. Metals aliquots must be acidified with nitric acid to pH <2. If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses shall not be acidified and the extract shall be analyzed as soon as possible. All other aliquots must be stored under refrigeration (4 °C) until analyzed. The TCLP extract shall be prepared and analyzed according to appropriate analytical methods. TCLP extracts to be analyzed for metals shall be acid digested except in those instances where digestion causes loss of metallic analytes. If an analysis of the undigested extract shows that the concentration of any regulated metallic analyte exceeds the regulatory level, then the waste is hazardous and digestion of the extract is not necessary. However, data on undigested extracts alone cannot be used to demonstrate that the waste is not hazardous. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to $\pm$ 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phase (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.2.15 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

7.3 Procedure When Volatiles are Involved

Use the ZHE device to obtain TCLP extract for analysis of volatile compounds only. Extract resulting from the use of the ZHE shall not be used to evaluate the mobility of nonvolatile analytes (e.g., metals, pesticides, etc.).

The ZHE device has approximately a 500 mL internal capacity. The ZHE can thus accommodate a maximum of 25 grams of solid (defined as that fraction of a

sample from which no additional liquid may be forced out by an applied pressure of 50 psi), due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase.

Charge the ZHE with sample only once and do not open the device until the final extract (of the solid) has been collected. Repeated filling of the ZHE to obtain 25 grams of solid is not permitted.

Do not allow the waste, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any manipulation of these materials should be done when cold (4 °C) to minimize loss of volatiles.

7.3.1 Pre-weigh the (evacuated) filtrate collection container (See Section 4.6) and set aside. If using a TEDLAR® bag, express all liquid from the ZHE device into the bag, whether for the initial or final liquid/solid separation, and take an aliquot from the liquid in the bag for analysis. The containers listed in Section 4.6 are recommended for use under the conditions stated in Sections 4.6.1 - 4.6.3.

7.3.2 Place the ZHE piston within the body of the ZHE (it may be helpful first to moisten the piston O-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample (based upon sample size requirements determined from Section 7.3, Section 7.1.1 and/or 7.1.2). Secure the gas inlet/outlet flange (bottom flange) onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange (top flange) aside.

7.3.3 If the waste is 100% solid (see Section 7.1.1), weigh out a subsample (25 gram maximum) of the waste, record weight, and proceed to Section 7.3.5.

7.3.4 If the waste contains < 0.5% dry solids (Section 7.1.2), the liquid portion of waste, after filtration, is defined as the TCLP extract. Filter enough of the sample so that the amount of filtered liquid will support all of the volatile analyses required. For wastes containing $\geq$ 0.5% dry solids (Sections 7.1.1 and/or 7.1.2), use the percent solids information obtained in Section 7.1.1 to determine the optimum sample size to charge into the ZHE. The recommended sample size is as follows:

7.3.4.1 For wastes containing < 5% solids (see Section 7.1.1), weigh out a 500 gram subsample of waste and record the weight.

7.3.4.2 For wastes containing $\geq$ 5% solids (see Section 7.1.1), determine the amount of waste to charge into the ZHE as follows:

$$\text{Weight of waste to charge ZHE} = \frac{25}{\text{percent solids (Section 7.1.1)}} \times 100$$

Weigh out a subsample of the waste of the appropriate size and record the weight.

7.3.5 If particle size reduction of the solid portion of the waste was required in Section 7.1.3, proceed to Section 7.3.6. If particle size reduction was not required in Section 7.1.3, proceed to Section 7.3.7.

7.3.6 Prepare the waste for extraction by crushing, cutting, or grinding the solid portion of the waste to a surface area or particle size as described in Section 7.1.3. Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4 °C prior to particle size reduction. The means used to effect particle size reduction must not generate heat in and of itself. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.

NOTE: Sieving of the waste is not recommended due to the possibility that volatiles may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended.

When the surface area or particle size has been appropriately altered, proceed to Section 7.3.7.

7.3.7 Waste slurries need not be allowed to stand to permit the solid phase to settle. Do not centrifuge wastes prior to filtration.

7.3.8 Quantitatively transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens onto the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extract collection device to the top plate.

NOTE: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in Section 7.3.4 to determine the weight of the waste sample that will be filtered.

Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-10 psi (or more if necessary) to force all headspace

slowly out of the ZHE device into a hood. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room tempera- ture, then allow the sample to warm up to room temperature in the device before filtering. If the waste is 100% solid (see Section 7.1.1), slowly increase the pressure to a maximum of 50 psi to force most of the headspace out of the device and proceed to Section 7.3.12.

7.3.9 Attach the evacuated pre-weighed filtrate collection container to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1-10 psi to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate within a 2 minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.3.10 The material in the ZHE is defined as the solid phase of the waste and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the TCLP extraction as a solid.

If the original waste contained <0.5% dry solids (see Section 7.1.2), this filtrate is defined as the TCLP extract and is analyzed directly. Proceed to Section 7.3.15.

7.3.11 The liquid phase may now be either analyzed immediately (See Sections 7.3.13 through 7.3.15) or stored at 4 °C under minimal headspace conditions until time of analysis. Determine the weight of extraction fluid #1 to add to the ZHE as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (Section 7.1.1)} \times \text{weight of waste filtered (Section 7.3.4 or 7.3.8)}}{100}$$

7.3.12 The following Sections detail how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid #1 is used in all cases (See Section 5.7).

7.3.12.1 With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid in- let/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.

7.3.12.2 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5-10 psi (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5-10 psi and check all ZHE fittings to ensure that they are closed.

7.3.12.3 Place the ZHE in the rotary agitation appara- tus (if it is not already there) and rotate at 30 $\pm$ 2 rpm for 18 $\pm$ 2 hours. Ambient temperature (i.e., temperature of room in which extraction occurs) shall be maintained at 23 $\pm$ 2 °C during agita- tion.

7.3.13 Following the 18 $\pm$ 2 hour agitation period, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If the pressure has not been maintained (i.e., no gas release observed), the device is leaking. Check the ZHE for leaking as specified in Section 4.2.1, and perform the extraction again with a new sample of waste. If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases. If the waste contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container (i.e., TEDLAR® bag) holding the initial liquid phase of the waste. A separate filtrate collection container must be used if combining would create multiple phases, or there is not enough volume left within the filtrate collection container. Filter through the glass fiber filter, using the ZHE device as discussed in Section 7.3.9. All extract shall be filtered and collected if the

TEDLAR® bag is used, if the extract is multiphasic, or if the waste contained an initial liquid phase (see Sections 4.6 and 7.3.1).

NOTE: An in-line glass fiber filter may be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured.

7.3.14 If the original waste contained no initial liquid phase, the filtered liquid material obtained from Section 7.3.13 is defined as the TCLP extract. If the waste contained an initial liquid phase, the filtered liquid material obtained from Section 7.3.13 and the initial liquid phase (Section 7.3.9) are collectively defined as the TCLP extract.

7.3.15 Following collection of the TCLP extract, immediately prepare the extract for analysis and store with minimal headspace at 4 °C until analyzed. Analyze the TCLP extract according to the appropriate analytical methods. If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phases (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.3.16 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

8.1 QUALITY ASSURANCE

8.2 A minimum of one blank (using the same extraction fluid as used for the samples) must be analyzed for every 20 extractions that have been conducted in an extraction vessel.

8.3 A matrix spike shall be performed for each waste type (e.g., wastewater treatment sludge, contaminated soil, etc.) unless the result exceeds the regulatory level and the data are being used solely to demonstrate that the waste property exceeds the regulatory level. A minimum of one matrix spike must be analyzed for each analytical batch. As a minimum, follow the matrix spike addition guidance provided in each analytical method.

8.3.1 Matrix spikes are to be added after filtration of the TCLP extract and before preservation. Matrix spikes should not be added prior to TCLP extraction of the sample.

8.3.2 In most cases, matrix spikes should be added at a concentration equivalent to the corresponding regulatory level. If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentra- tion, but may not be not less than five times the method detection limit. In order to avoid differences in matrix effects, the matrix spikes must be added to the same nominal volume of TCLP extract as that which was analyzed for the unspiked sample.

8.3.3 The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to determine whether matrix interferences exist. Use of other internal calibration methods, modification of the analytical methods, or use of alternate analytical methods may be needed to accurately measure the analyte concentration in the TCLP extract when the recovery of the matrix spike is below the expected analytical method performance.

8.3.4 Matrix spike recoveries are calculated by the following formula:

$$\%R\ (\%Recovery) = 100\ (X_s - X_u)/K$$

where:
X_s = measured value for the spiked sample,
X_u = measured value for the unspiked sample, and
K = known value of the spike in the sample.

8.4 All quality control measures described in the appropriate analytical methods shall be followed.

8.5 The use of internal calibration quantitation methods shall be employed for a metallic contaminant if: (1) Recovery of the contaminant from the TCLP extract is not at least 50% and the concentration does not exceed the regulatory level, and (2) The concentration of the contaminant measured in the extract is within 20% of the appropriate regulatory level.

8.4.1. The method of standard additions shall be employed as the internal calibration quantitation method for each metallic contaminant.

8.4.2 The method of standard additions requires preparing calibration standards in the sample matrix rather than reagent water or blank solution. It requires taking four identical aliquots of the solution and adding known amounts of standard to three of these aliquots. The forth aliquot is the unknown. Preferably, the first addition should be prepared so that the resulting concentration is approximately 50% of the expected concentration of the sample. The second and third additions should be prepared so that the concentrations are approximately 100% and

150% of the expected concentration of the sample. All four aliquots are maintained at the same final volume by adding reagent water or a blank solution, and may need dilution adjustment to maintain the signals in the linear range of the instrument technique. All four aliquots are analyzed.

8.4.3 Prepare a plot, or subject data to linear regression, of instrument signals or external-calibration-derived concentrations as the dependant variable (y-axis) versus concentrations of the additions of standard as the independent variable (x-axis). Solve for the intercept of the abscissa (the independent variable, x-axis) which is the concentration in the unknown.

8.4.4 Alternately, subtract the instrumental signal or external- calibration-derived concentration of the unknown (unspiked) sample from the instrumental signals or external-calibration-derived concentrations of the standard additions. Plot or subject to linear regression of the corrected instrument signals or external-calibration-derived concentra- tions as the dependant variable versus the independent variable. Derive concentrations for unknowns using the internal calibration curve as if it were an external calibration curve.

8.5 Samples must undergo TCLP extraction within the following time periods:

SAMPLE MAXIMUM HOLDING TIMES [DAYS]

	From: Field collection To: TCLP extraction	From: TCLP extraction To: Preparative extraction	From: Preparative extraction To: Determinative analysis	Total elapsed time
Volatiles	14	NA	14	28
Semi-volatiles	14	7	40	61
Mercury	28	NA	28	56
Metals, except mercury	180	NA	180	360

NA = Not applicable

If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding the holding time is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory level.

9.1 METHOD PERFORMANCE

9.2 Ruggedness. Two ruggedness studies have been performed to determine the effect of various perturbations on specific elements of the TCLP protocol. Ruggedness testing determines the sensitivity of small procedural variations which might be expected to occur during routine laboratory application.

9.2.1 Metals - The following conditions were used when leaching a waste for metals analysis:

Varying Conditions	
Liquid/Solid ratio	19:1 vs. 21:1
Extraction time	16 hours vs. 18 hours
Headspace	20% vs. 60%
Buffer #2 acidity	190 meq vs. 210 meq
Acid-washed filters	yes vs. no
Filter type	0.7 µm glass fiber vs. 0.45 µm vs. polycarbonate
Bottle type	borosilicate vs. flint glass

Of the seven method variations examined, acidity of the extraction fluid had the greatest impact on the results. Four of 13 metals from an API separator sludge/electroplating waste (API/EW) mixture and two of three metals from an ammonia lime still bottom waste were extracted at higher levels by the more acidic buffer. Because of the sensitivity to pH changes, the method requires that the extraction fluids be prepared so that the final pH is within $\pm$ 0.05 units as specified.

9.2.2 Volatile Organic Compounds - The following conditions were used when leaching a waste for VOC analysis:

Varying Conditions	
Liquid/Solid ratio	19:1 vs. 21:1
Headspace	0% vs. 5%
Buffer #1 acidity	60 meq vs. 80 meq
Method of storing extract	Syringe vs. Tedlar® bag
Aliquotting	yes vs. no
Pressure behind piston	0 psi vs. 20 psi

None of the parameters had a significant effect on the results of the ruggedness test.

9.3 Precision. Many TCLP precision (reproducibility) studies have been performed, and have shown that, in general, the precision of the TCLP is comparable to or exceeds that of the EP toxicity test and that method precision is adequate. One of the more significant contributions to poor precision appears to be related to sample homogeneity and inter-laboratory variation (due to the nature of waste materials).

9.3.1 Metals - The results of a multi-laboratory study are shown in Table 6, and indicate that a single analysis of a waste may not be adequate for waste characterization and identification requirements.

9.3.2 Semi-Volatile Organic Compounds - The results of two studies are shown in Tables 7 and 8. Single laboratory precision was excellent with greater than 90 percent of the results exhibiting an RSD less than 25 percent. Over 85 percent of all individual compounds in the multi-laboratory study fell in the RSD range of 20 - 120 percent. Both studies concluded that the TCLP provides adequate precision. It was also determined that the high acetate content of the extraction fluid did not present problems (i.e., column degradation of the gas chromatograph) for the analytical conditions used.

9.3.3 Volatile Organic Compounds - Eleven laboratories participated in a collaborative study of the use of the ZHE with two waste types which were fortified with a mixture of VOCs. The results of the collaborative study are shown in Table 9. Precision results for VOCs tend to occur over a considerable range. However, the range and mean RSD compared very closely to the same collaborative study metals results in Table 6. Blackburn and Show concluded that at the 95% level of signifi- cance: 1) recoveries among laboratories were statistically similar, 2) recoveries did not vary significantly between the two sample types, and 3) each laboratory showed the same pattern of recovery for each of the two samples.

10.0 REFERENCES

1. Blackburn, W.B. and Show, I. "Collaborative Study of the Toxicity Characteristics Leaching Procedure (TCLP)." Draft Final Report, Contract No. 68- 03-1958, S-Cubed, November 1986.

2. Newcomer, L.R., Blackburn, W.B., Kimmell, T.A. "Performance of the Toxicity Characteristic Leaching Procedure." Wilson Laboratories, S-Cubed, U.S. EPA, December 1986.

3. Williams, L.R., Francis, C.W.; Maskarinec, M.P., Taylor D.R., and Rothman,
N. "Single-Laboratory Evaluation of Mobility Procedure for Solid Waste." EMSL, ORNL, S-Cubed, ENSECO.

Table 1.
Volatile Analytes[1,2]

Compound	CAS No.
Acetone	67-64-1
Benzene	71-43-2
n-Butyl alcohol	71-36-3
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroform	67-66-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethylene	75-35-4
Ethyl acetate	141-78-6
Ethyl benzene	100-41-4
Ethyl ether	60-29-7
Isobutanol	78-83-1
Methanol	67-56-1
Methylene chloride	75-09-2
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-1
Tetrachloroethylene	127-18-4
Toluene	108-88-3
1,1,1,-Trichloroethane	71-55-6
Trichloroethylene	79-01-6
Trichlorofluoromethane	75-69-4
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1
Vinyl chloride	75-01-4
Xylene	1330-20-7

[1] When testing for any or all of these analytes, the zero-headspace extractor vessel shall be used instead of the bottle extractor.

[2] Benzene, carbon tetrachloride, chlorobenzene, chloroform, 1,2-dichloroethane, 1,1-dichloroethylene, methyl ethyl ketone, tetrachloroethylene, and vinyl chloride are toxicity characteristic constituents.

Table 2.
Suitable Rotary Agitation Apparatus[1]

Company	Location	Model No.
Analytical Testing and Services,	Warrington, PA (215) 343-4490	4-vessel extractor (DC20S) Consulting 8-vessel extractor (DC20) Inc. 12-vessel extractor (DC20B) 24-vessel extractor (DC24C)
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	2-vessel (3740-2-BRE) 4-vessel (3740-4-BRE) 6-vessel (3740-6-BRE) 8-vessel (3740-8-BRE) 12-vessel (3740-12-BRE) 24-vessel (3740-24-BRE)
Environmental Machine and Inc.	Lynchburg, VA (804) 845-6424	8-vessel (08-00-00) Design, 4-vessel (04-00-00)
IRA Machine Shop and Laboratory	Santurce, PR (809) 752-4004	8-vessel (011001)
Lars Lande Manufacturing	Whitmore Lake, MI (313) 449-4116	10-vessel (10VRE) 5-vessel (5VRE) 6-vessel (6VRE)
Millipore Corp.	Bedford, MA (800) 225-3384	4-ZHE or 4 2-liter bottle extractor (YT31ORAHW)

[1] Any device that rotates the extraction vessel in an end-over-end fashion at 30 $\pm$ 2 rpm is acceptable.

Table 3.
Suitable Zero-Headspace Extractor Vessels[1]

Company	Location	Model No.
Analytical Testing & Consulting Services, Inc.	Warrington, PA (215) 343-4490	C1O2, Mechanical Pressure Device
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	3745-ZHE, Gas Pressure Device
Lars Lande Manufacturing[2]	Whitmore Lake, MI (313) 449-4116	ZHE-11, Gas Pressure Device
Millipore Corporation	Bedford, MA (800) 225-3384	YT30O9OHW, Gas Pressure Device
Environmental Machine and Design, Inc.	Lynchburg, VA (804) 845-6424	VOLA-TOX1, Gas Pressure Device
Gelman Science	Ann Arbor, MI 521-1520	15400 Gas Pressure (800) Device

[1] Any device that meets the specifications listed in Section 4.2.1 of the method is suitable.

[2] This device uses a 110 mm filter.

Table 4.
Suitable Filter Holders[1]

Company	Location	Model/ Catalogue No.	Size
Nucleopore Corporation	Pleasanton, CA (800) 882-7711	425910 410400	142 mm 47 mm
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	302400 311400	142 mm 47 mm
Millipore Corporation	Bedford, MA (800) 225-3384	YT30142HW XX1004700	142 mm 47 mm

[1] Any device capable of separating the liquid from the solid phase of the waste is suitable, providing that it is chemically compatible with the waste and the constituents to be analyzed. Plastic devices (not listed above) may be used when only inorganic analytes are of concern. The 142 mm size filter holder is recommended.

Table 5.
Suitable Filter Media[1]

Company	Location	Model	Pore Size (µm)
Millipore Corporation	Bedford, MA (800) 225-3384	AP40	0.7
Nucleopore Corporation	Pleasanton, CA (415) 463-2530	211625	0.7
Whatman Laboratory Products, Inc.	Clifton, NJ (201) 773-5800	GFF	0.7
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	GF75	0.7
Gelman Science	Ann Arbor, MI (800) 521-1520	66256 (90mm) 66257 (142mm)	0.7

[1] Any filter that meets the specifications in Section 4.4 of the Method is suitable.

Table 6. Multi-Laboratory TCLP Metals, Precision

Waste	Extraction Fluid	Metal	$\bar{X}$	S	%RSD
Ammonia	#1	Cadmium	0.053	0.031	60
Lime Still	#2		0.023	0.017	76
Bottoms	#1	Chromium	0.015	0.0014	93
	#2		0.0032	0.0037	118
	#1	Lead	0.0030	0.0027	90
	#2		0.0032	0.0028	87
API/EW	#1	Cadmium	0.0046	0.0028	61
Mixture	#2		0.0005	0.0004	77
	#1	Chromium	0.0561	0.0227	40
	#2		0.105	0.018	17
	#1	Lead	0.0031	0.0031	100
	#2		0.0124	0.0136	110
Fossil	#1	Cadmium	0.080	0.069	86
Fuel Fly	#2		0.093	0.067	72
Ash	#1	Chromium	0.017	0.014	85
	#2		0.070	0.040	57
	#1	Lead	0.0087	0.0074	85
	#2		0.0457	0.0083	18
				%RSD Range = 17 - 118 Mean	
				%RSD = 74	

NOTE: $\bar{X}$ = Mean results from 6 - 12 different laboratories Units = mg/L
Extraction Fluid #1 = pH 4.9
#2 = pH 2.9

Table 7. Single-Laboratory Semi-Volatiles, Precision

Waste	Compound	Extraction Fluid	$\overline{X}$	S	%RSD
Ammonia	Phenol	#1	19000	2230	11.6
Lime Still		#2	19400	929	4.8
Bottoms	2-Methylphenol	#1	2000	297	14.9
		#2	1860	52.9	2.8
	4-Methylphenol	#1	7940	1380	17.4
		#2	7490	200	2.7
	2,4-Dimethylphenol	#1	321	46.8	14.6
		#2	307	45.8	14.9
	Naphthalene	#1	3920	413	10.5
		#2	3827	176	4.6
	2-Methylnaphthalene	#1	290	44.8	15.5
		#2	273	19.3	7.1
	Dibenzofuran	#1	187	22.7	12.1
		#2	187	7.2	3.9
	Acenaphthylene	#1	703	89.2	12.7
		#2	663	20.1	3.0
	Fluorene	#1	151	17.6	11.7
		#2	156	2.1	1.3
	Phenanthrene	#1	241	22.7	9.4
		#2	243	7.9	3.3
	Anthracene	#1	33.2	6.19	18.6
		#2	34.6	1.55	4.5
	Fluoranthrene	#1	25.3	1.8	7.1
		#2	26.0	1.8	7.1
API/EW	Phenol	#1	40.7	13.5	33.0
Mixture		#2	19.0	1.76	9.3
	2,4-Dimethylphenol	#1	33.0	9.35	28.3
		#2	43.3	8.61	19.9
	Naphthalene	#1	185	29.4	15.8
		#2	165	24.8	15.0
	2-Methylnaphthalene	#1	265	61.2	23.1
		#2	200	18.9	9.5
				%RSD Range = 1 - 33	
				Mean %RSD = 12	

NOTE: Units = µg/L
Extractions were performed in triplicate
All results were at least 2x the detection limit Extraction Fluid #1 = pH 4.9
#2 = pH 2.9

Table 8. Multi-Laboratory Semi-Volatiles, Precision

Waste	Compound	Extraction Fluid	$\overline{X}$	S	%RSD
Ammonia Lime	BNAs	#1	10043	7680	76.5
Still Bottoms (A)		#2	10376	6552	63.1
API/EW	BNAs	#1	1624	675	41.6
Mixture (B)		#2	2074	1463	70.5
Fossil Fuel	BNAs	#1	750	175	23.4
Fly Ash (C)		#2	739	342	46.3
					Mean %RSD = 54

NOTE: Units = µg/L
X = Mean results from 3 - 10 labs Extraction Fluid #1 = pH 4.9
#2 = pH 2.9

%RSD Range for Individual Compounds

A, #1	0 - 113
A, #2	28 - 108
B, #1	20 - 156
B, #2	49 - 128
C, #1	36 - 143
C, #2	61 - 164

Table 9. Multi-Laboratory (11 Labs) VOCs, Precision

Waste	Compound	$\bar{X}$	S	%RSD
Mine Tailings	Vinyl chloride	6.36	6.36	100
	Methylene chloride	12.1	11.8	98
	Carbon disulfide	5.57	2.83	51
	1,1-Dichloroethene	21.9	27.7	127
	1,1-Dichloroethane	31.4	25.4	81
	Chloroform	46.6	29.2	63
	1,2-Dichloroethane	47.8	33.6	70
	2-Butanone	43.5	36.9	85
	1,1,1-Trichloroethane	20.9	20.9	100
	Carbon tetrachloride	12.0	8.2	68
	Trichloroethene	24.7	21.2	86
	1,1,2-Trichloroethene	19.6	10.9	56
	Benzene	37.9	28.7	76
	1,1,2,2-Tetrachloroethane	34.9	25.6	73
	Toluene	29.3	11.2	38
	Chlorobenzene	35.6	19.3	54
	Ethylbenzene	4.27	2.80	66
	Trichlorofluoromethane	3.82	4.40	115
	Acrylonitrile	76.7	110.8	144
Ammonia Lime Still Bottoms	Vinyl chloride	5.00	4.71	94
	Methylene chloride	14.3	13.1	92
	Carbon disulfide	3.37	2.07	61
	1,1-Dichloroethene	52.1	38.8	75
	1,1-Dichloroethane	52.8	25.6	49
	Chloroform	64.7	28.4	44
	1,2-Dichloroethane	43.1	31.5	73
	2-Butanone	59.0	39.6	67
	1,1,1-Trichloroethane	53.6	40.9	76
	Carbon tetrachloride	7.10	6.1	86
	Trichloroethene	57.3	34.2	60
	1,1,2-Trichloroethene	6.7	4.7	70
	Benzene	61.3	26.8	44
	1,1,2,2-Tetrachloroethane	3.16	2.1	66
	Toluene	69.0	18.5	27
	Chlorobenzene	71.8	12.0	17
	Ethylbenzene	3.70	2.2	58
	Trichlorofluoromethane	4.05	4.8	119
	Acrylonitrile	29.4	34.8	118
				%RSD Range = 17 - 144 Mean %RSD = 75

NOTE: Units = µg/L

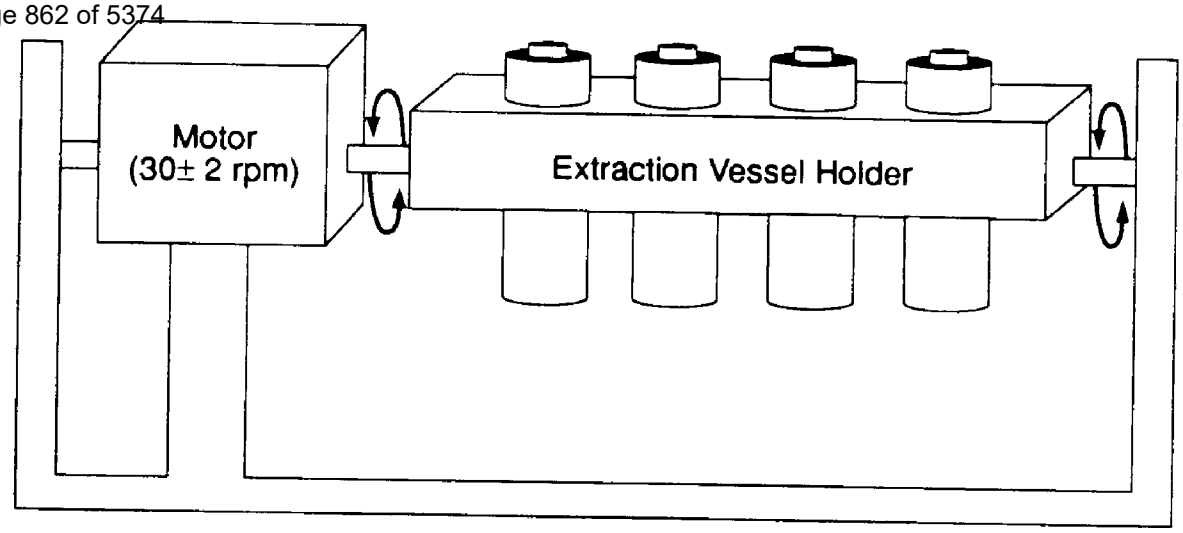


Figure 1. Rotary Agitation Apparatus

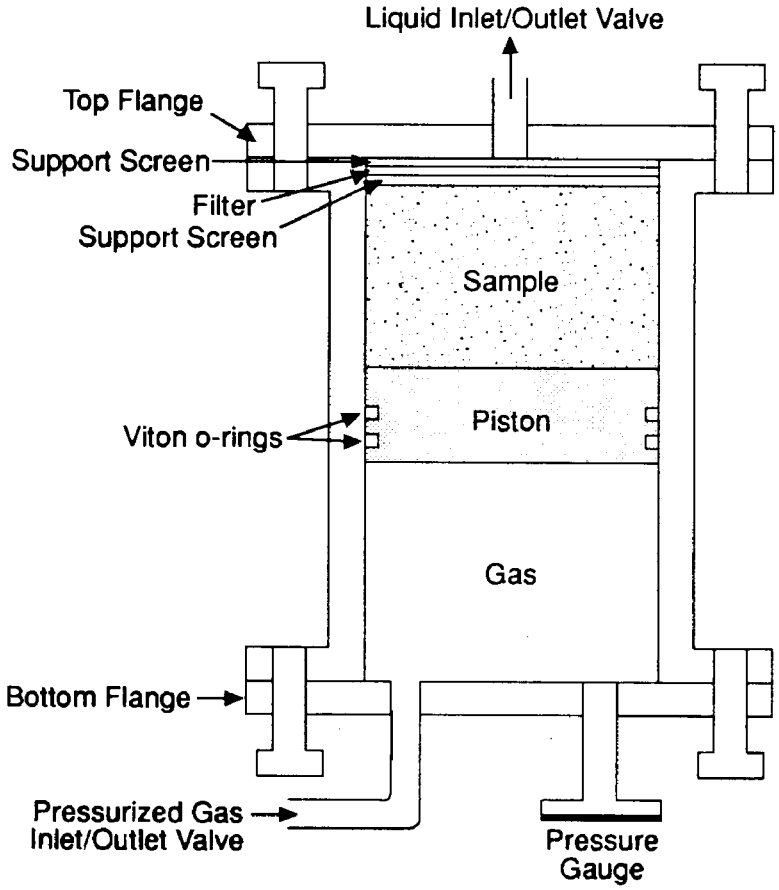
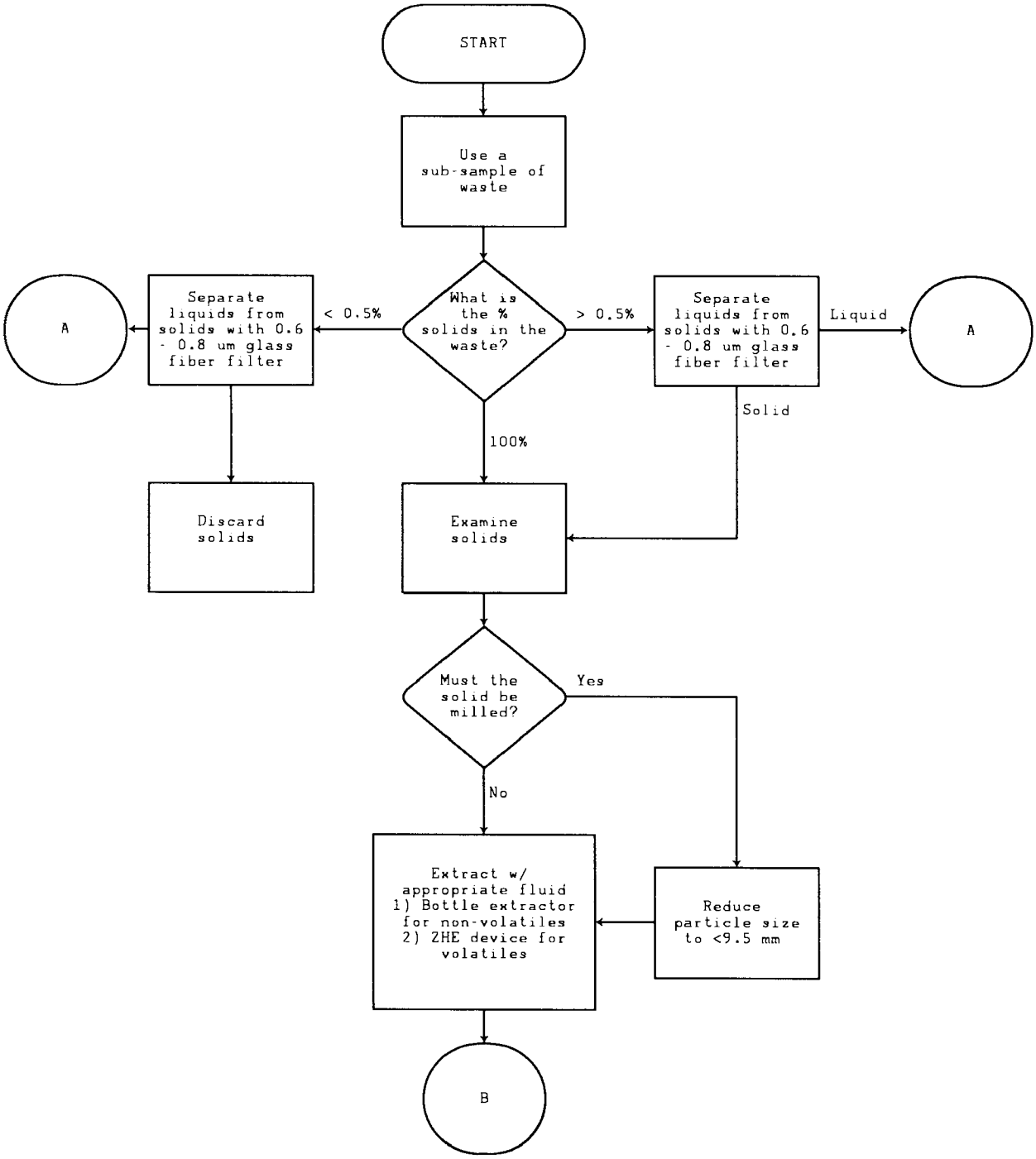
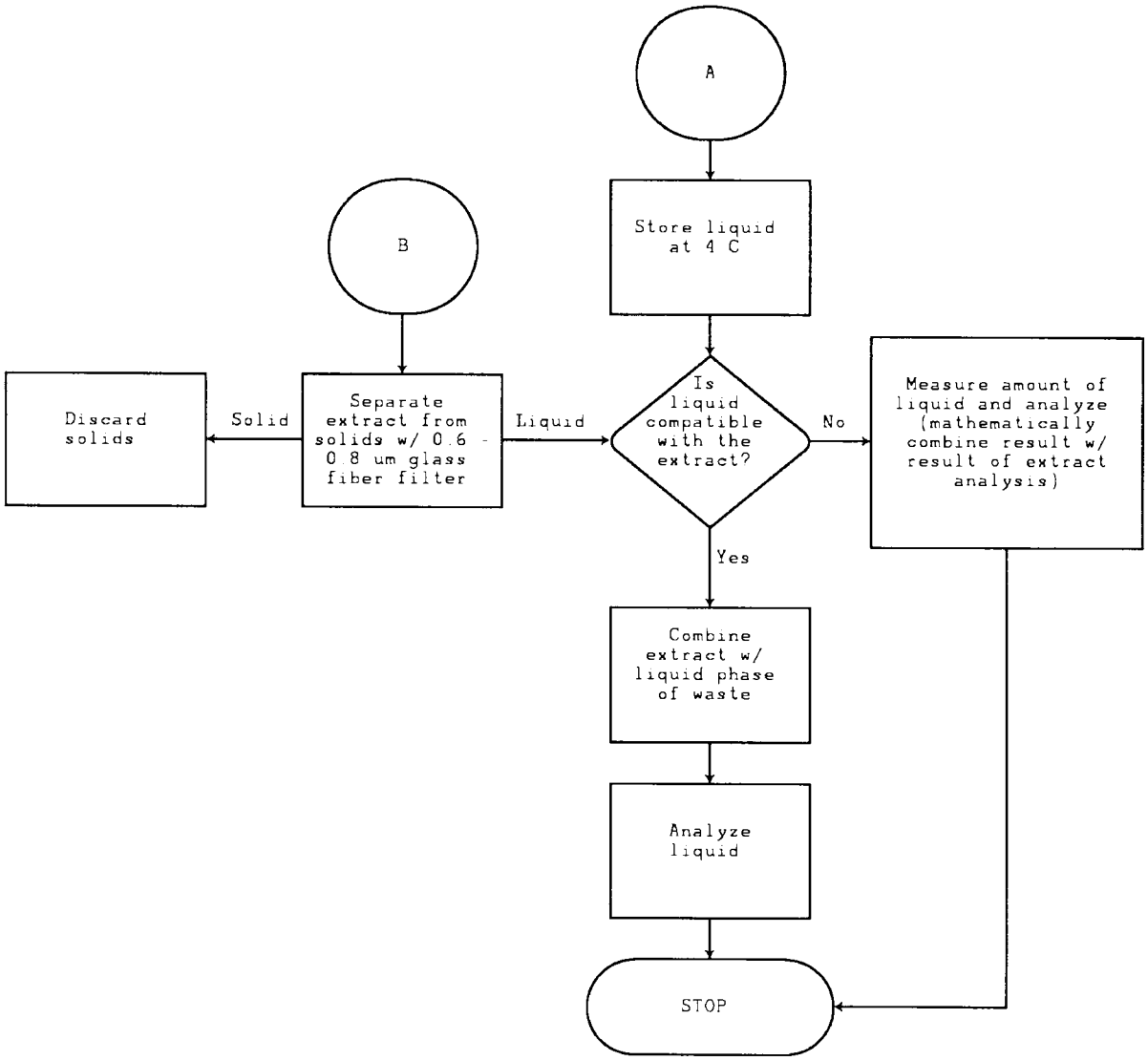


Figure 2. Zero-Headspace Extractor (ZHE)

TOXICITY CHARACTERISTIC LEACHATE PROCEDURE



CHARACTERISTIC LEACHATE PROCEDURE



OAR 340-095-0020

Toxicity Characteristic Leaching Procedure

METHOD 1311

TOXICITY CHARACTERISTIC LEACHING PROCEDURE

1.1 SCOPE AND APPLICATION

1.2 The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes.

1.3 If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the TCLP need not be run.

1.4 If an analysis of any one of the liquid fractions of the TCLP extract indicates that a regulated compound is present at such high concentra- tions that, even after accounting for dilution from the other fractions of the extract, the concentration would be above the regulatory level for that compound, then the waste is hazardous and it is not necessary to analyze the remaining fractions of the extract.

1.5 If an analysis of extract obtained using a bottle extractor shows that the concentration of any regulated volatile analyte exceeds the regulatory level for that compound, then the waste is hazardous and extraction using the ZHE is not necessary. However, extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the regulatory level.

2.1 SUMMARY OF METHOD

2.2 For liquid wastes (i.e., those containing less than 0.5% dry solid material), the waste, after filtration through a 0.6 to 0.8 µm glass fiber filter, is defined as the TCLP extract.

2.3 For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatile analytes (see Table 1 for a list of volatile compounds). Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 µm glass fiber filter.

2.4 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3.1 INTERFERENCES

3.2 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.1 APPARATUS AND MATERIALS

4.2 Agitation apparatus: The agitation apparatus must be capable of rotating the extraction vessel in an end-over-end fashion (see Figure 1) at 30 ± 2 rpm. Suitable devices known to EPA are identified in Table 2.

4.3 Extraction Vessels

4.3.1 Zero-Headspace Extraction Vessel (ZHE). This device is for use only when the waste is being tested for the mobility of volatile analytes (i.e., those listed in Table 1). The ZHE (depicted in Figure 2) allows for liquid/solid separation within the device, and effectively precludes headspace. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel (see Section 4.3.1). The vessels shall have an internal volume of 500-600 mL, and be equipped to accommodate a 90-110 mm filter. The devices contain VITON®[1] O-rings which should be replaced frequently. Suitable ZHE devices known to EPA are identified in Table 3.

For the ZHE to be acceptable for use, the piston within the ZHE should be able to be moved with approximately 15 psi or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for TCLP analyses and the manufacturer should be contacted.

The ZHE should be checked for leaks after every extraction. If the device contains a built-in pressure gauge, pressurize the device to 50 psi, allow it to stand unattended for 1 hour, and recheck the pressure. If the device does not have a built-in pressure gauge, pressurize the device to 50 psi, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted.

Some ZHEs use gas pressure to actuate the ZHE piston, while others use mechanical pressure (see Table 3). Whereas the volatiles procedure (see Section 7.3) refers to pounds per square inch (psi), for the mechanically actuated piston, the pressure applied is measured in torque-inch-pounds. Refer to the manufacturer's instructions as to the proper conversion.

[1] VITON® is a trademark of Du Pont.

4.3.2 Bottle Extraction Vessel. When the waste is being evaluated using the nonvolatile extraction, a jar with sufficient capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel.

The extraction bottles may be constructed from various materials, depending on the analytes to be analyzed and the nature of the waste (see Section 4.3.3). It is recommended that borosilicate glass bottles be used instead of other types of glass, especially when inorganics are of concern. Plastic bottles, other than polytetrafluoroethylene, shall not be used if organics are to be investigated. Bottles are available from a number of laboratory suppliers. When this type of extraction vessel is used, the filtration device discussed in Section 4.3.2 is used for initial liquid/solid separation and final extract filtration.

4.4 Filtration Devices: It is recommended that all filtrations be performed in a hood.

4.4.1 Zero-Headspace Extractor Vessel (ZHE): When the waste is evaluated for volatiles, the zero-headspace extraction vessel described in Section 4.2.1 is used for filtration. The device shall be capable of supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation (50 psi).

NOTE: When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.

4.4.2 Filter Holder: When the waste is evaluated for other than volatile analytes, any filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psi or more. The type of filter holder used depends on the properties of the material to be filtered (see Section 4.3.3). These devices shall have a minimum internal volume of 300 mL and be equipped to accommodate a minimum filter size of 47 mm (filter holders having an internal capacity of 1.5 L or greater, and equipped to accommodate a 142 mm diameter filter, are recommended). Vacuum filtration can only be used for wastes with low solids content (<10%) and for highly granular, liquid-containing wastes. All other types of wastes should be filtered using positive pressure filtration. Suitable filter holders known to EPA are shown in Table 4.

4.4.3 Materials of Construction: Extraction vessels and filtration devices shall be made of inert materials which will not leach or absorb waste components. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride (PVC) may be used only when evaluating the mobility of metals. Borosili-

Outer glass bottles are recommended for use over other types of glass bottles, especially when inorganics are analytes of concern.

4.5 Filters: Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6 to 0.8 µm, or equivalent. Filters known to EPA which meet these specifications are identified in Table 5. Pre-filters must not be used. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 1N nitric acid followed by three consecutive rinses with deionized distilled water (a minimum of 1 L per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

4.5 pH Meters: The meter should be accurate to ± 0.05 units at 25 °C.

4.6 ZHE Extract Collection Devices: TEDLAR®[2] bags or glass, stainless steel or PTFE gas-tight syringes are used to collect the initial liquid phase and the final extract of the waste when using the ZHE device. The devices listed are recommended for use under the following conditions:

4.6.1 If a waste contains an aqueous liquid phase or if a waste does not contain a significant amount of nonaqueous liquid (i.e., <1% of total waste), the TEDLAR® bag or a 600 mL syringe should be used to collect and combine the initial liquid and solid extract.

4.6.2 If a waste contains a significant amount of nonaqueous liquid in the initial liquid phase (i.e., >1% of total waste), the syringe or the TEDLAR® bag may be used for both the initial solid/liquid separation and the final extract filtration. However, analysts should use one or the other, not both.

4.6.3 If the waste contains no initial liquid phase (is 100% solid) or has no significant solid phase (is 100% liquid), either the TEDLAR® bag or the syringe may be used. If the syringe is used, discard the first 5 mL of liquid expressed from the device. The remaining aliquots are used for analysis.

4.7 ZHE Extraction Fluid Transfer Devices: Any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is acceptable (e.g., a positive displacement or peristaltic pump, a gas tight syringe, pressure filtration unit (see Section 4.3.2), or other ZHE device).

4.8 Laboratory Balance: Any laboratory balance accurate to within ± 0.01 grams may be used (all weight measurements are to be within ± 0.1 grams).

4.9 Beaker or Erlenmeyer flask, glass, 500 mL.

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[2] TEDLAR® is a registered trademark of Du Pont.

4.10 Watchglass, appropriate diameter to cover beaker or Erlenmeyer flask.

4.11 Magnetic stirrer.

5.1 REAGENTS

5.2 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.3 Reagent Water. Reagent water is defined as water in which an interferant is not observed at or above the method's detection limit of the analyte(s) of interest. For nonvolatile extractions, ASTM Type II water or equivalent meets the definition of reagent water. For volatile extractions, it is recommended that reagent water be generated by any of the following methods. Reagent water should be monitored periodically for impurities.

5.3.1 Reagent water for volatile extractions may be generated by passing tap water through a carbon filter bed containing about 500 grams of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.3.2 A water purification system (Millipore Super-Q or equivalent) may also be used to generate reagent water for volatile extractions.

5.3.3 Reagent water for volatile extractions may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the water temperature at 90 $\pm$ 5 degrees C, bubble a contaminant-free inert gas (e.g. nitrogen) through the water for 1 hour. While still hot, transfer the water to a narrow mouth screw-cap bottle under zero-headspace and seal with a Teflon-lined septum and cap.

5.4 Hydrochloric acid (1N), HCl, made from ACS reagent grade.

5.5 Nitric acid (1N), HNO_3, made from ACS reagent grade.

5.6 Sodium hydroxide (1N), NaOH, made from ACS reagent grade.

5.7 Glacial acetic acid, CH_3CH_2OOH, ACS reagent grade.

5.8 Extraction fluid.

5.8.1 Extraction fluid # 1: Add 5.7 mL glacial CH_3CH_2OOH to 500 mL of reagent water (See Section 5.2), add 64.3 mL of 1N NaOH, and dilute to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 4.93 $\pm$ 0.05.

5.8.2 Extraction fluid # 2: Dilute 5.7 mL glacial CH_3CH_2OOH with reagent water (See Section 5.2) to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 2.88 $\pm$ 0.05.

NOTE: These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid shall be discarded and fresh extraction fluid prepared.

5.9 Analytical standards shall be prepared according to the appropriate analytical method.

6.1 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.2 All samples shall be collected using an appropriate sampling plan.

6.3 The TCLP may place requirements on the minimal size of the field sample, depending upon the physical state or states of the waste and the analytes of concern. An aliquot is needed for preliminary evaluation of which extraction fluid is to be used for the nonvolatile analyte extraction procedure. Another aliquot may be needed to actually conduct the nonvolatile extraction (see Section 1.4 concerning the use of this extract for volatile organics). If volatile organics are of concern, another aliquot may be needed. Quality control measures may require additional aliquots. Further, it is always wise to collect more sample just in case something goes wrong with the initial attempt to conduct the test.

6.3 Preservatives shall not be added to samples before extraction.

6.4 Samples may be refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

6.5 When the waste is to be evaluated for volatile analytes, care shall be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g., samples should be collected in Teflon-lined septum capped vials and stored at 4 °C. Samples should be opened only immediately prior to extraction).

6.6 TCLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH < 2, unless precipitation occurs (see Section 7.2.14 if precipitation occurs). Extracts should be preserved for other analytes according to the guidance given in the individual analysis methods. Extracts or portions of extracts for organic analyte determinations shall not be allowed to come into contact with the atmosphere (i.e., no headspace) to prevent losses. See Section 8.0 (QA requirements) for acceptable sample and extract holding times.

7.2 Preliminary Evaluations

Perform preliminary TCLP evaluations on a minimum 100 gram aliquot of waste. This aliquot may not actually undergo TCLP extraction. These preliminary evaluations include: (1) determination of the percent solids (Section 7.1.1);
(2) determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration (Section 7.1.2); (3) determination of whether the solid portion of the waste requires particle size reduction (Section 7.1.3); and (4) determination of which of the two extraction fluids are to be used for the nonvolatile TCLP extraction of the waste (Section 7.1.4).

7.1.1 Preliminary determination of percent solids: Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below.

7.1.1.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solids) proceed to Section 7.1.3.

7.1.1.2 If the sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device described in Section 4.3.2 and is outlined in Sections 7.1.1.3 through 7.1.1.9.

7.1.1.3 Pre-weigh the filter and the container that will receive the filtrate.

7.1.1.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

7.1.1.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight.

7.1.1.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.1.1.7 Quantitatively transfer the waste sample to the filter holder (liquid and solid phases). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room temperature then allow the sample to warm up to room temperature in the device before filtering.

NOTE: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Section 7.1.1.5 to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within any 2 minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.1.1.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Section 7.1.1.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.1.1.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (see Section 7.1.1.3) from the total weight of the filtrate-filled container. Determine the weight of the solid phase of the waste sample by subtracting the weight of the liquid phase from the weight of the total waste sample, as determined in Section 7.1.1.5 or 7.1.1.7.

Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\text{Percent solids} = \frac{\text{Weight of solid (Section 7.1.1.9)}}{\text{Total weight of waste (Section 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2 If the percent solids determined in Section 7.1.1.9 is equal to or greater than 0.5%, then proceed either to Section 7.1.3 to

determine whether the solid material requires particle size reduction or to Section 7.1.2.1 if it is noticed that a small amount of the filtrate is entrained in wetting of the filter. If the percent solids determined in Section 7.1.1.9 is less than 0.5%, then proceed to Section 7.2.9 if the nonvolatile TCLP is to be performed and to Section 7.3 with a fresh portion of the waste if the volatile TCLP is to be performed.

7.1.2.1 Remove the solid phase and filter from the filtration apparatus.

7.1.2.2 Dry the filter and solid phase at 100 ± 20 °C until two successive weighing yield the same value within ± 1%. Record the final weight.

NOTE: Caution should be taken to ensure that the subject solid will not flash upon heating. It is recommended that the drying oven be vented to a hood or other appropriate device.

7.1.2.3 Calculate the percent dry solids as follows: (Wt. of dry waste + filter) - tared wt. of filter

$$\text{Percent dry solids} = \frac{\text{(Wt. of dry waste + filter) - tared wt. of filter}}{\text{Initial wt. of waste (Section 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2.4 If the percent dry solids is less than 0.5%, then proceed to Section 7.2.9 if the nonvolatile TCLP is to be performed, and to Section 7.3 if the volatile TCLP is to be performed. If the percent dry solids is greater than or equal to 0.5%, and if the nonvolatile TCLP is to be performed, return to the beginning of this Section (7.1) and, with a fresh portion of waste, determine whether particle size reduction is necessary (Section 7.1.3) and determine the appropriate extraction fluid (Section 7.1.4). If only the volatile TCLP is to be performed, see the note in Section 7.1.4.

7.1.3 Determination of whether the waste requires particle size reduction (particle size is reduced during this step): Using the solid portion of the waste, evaluate the solid for particle size. Particle size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1 cm^2, or is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm (0.375 inch) standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above. If the solids are prepared for organic volatiles extraction, special precautions must be taken (see Section 7.3.6).

NOTE: Surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet

the criteria, sample specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

7.1.4 Determination of appropriate extraction fluid: If the solid content of the waste is greater than or equal to 0.5% and if the sample will be extracted for nonvolatile constituents (Section 7.2), determine the appropriate fluid (Section 5.7) for the nonvolatiles extraction as follows:

NOTE: TCLP extraction for volatile constituents uses only extraction fluid #1 (Section 5.7.1). Therefore, if TCLP extraction for nonvolatiles is not required, proceed to Section 7.3.

7.1.4.1 Weigh out a small subsample of the solid phase of the waste, reduce the solid (if necessary) to a particle size of approximately 1 mm in diameter or less, and transfer 5.0 grams of the solid phase of the waste to a 500 mL beaker or Erlenmeyer flask.

7.1.4.2 Add 96.5 mL of reagent water to the beaker, cover with a watchglass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is <5.0, use extraction fluid #1. Proceed to Section 7.2.

7.1.4.3 If the pH from Section 7.1.4.2 is >5.0, add 3.5 mL 1N HCl, slurry briefly, cover with a watchglass, heat to 50 °C, and hold at 50 °C for 10 minutes.

7.1.4.4 Let the solution cool to room temperature and record the pH. If the pH is <5.0, use extraction fluid #1. If the pH is >5.0, use extraction fluid #2. Proceed to Section 7.2.

7.1.5 If the aliquot of the waste used for the preliminary evaluation (Sections 7.1.1 - 7.1.4) was determined to be 100% solid at Section 7.1.1.1, then it can be used for the Section 7.2 extraction (assuming at least 100 grams remain), and the Section 7.3 extraction (assuming at least 25 grams remain). If the aliquot was subjected to the procedure in Section 7.1.1.7, then another aliquot shall be used for the volatile extraction procedure in Section 7.3. The aliquot of the waste subjected to the procedure in Section 7.1.1.7 might be appropriate for use for the Section 7.2 extraction if an adequate amount of solid (as determined by Section 7.1.1.9) was obtained. The amount of solid necessary is dependent upon whether a sufficient amount of extract will be produced to support the analyses. If an adequate amount of solid remains, proceed to Section 7.2.10 of the nonvolatile TCLP extraction.

7.2 Procedure When Volatiles are not Involved

A minimum sample size of 100 grams (solid and liquid phases) is recommend- ed. In some cases, a larger sample size may be appropriate, depending on the

solids content of the waste sample (percent solids, See Section 7.1.1), whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of TCLP extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single TCLP extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

7.2.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solid, see Section 7.1.1), weigh out a subsample of the waste (100 gram minimum) and proceed to Section 7.2.9.

7.2.2 If the sample is liquid or multiphasic, liquid/solid separation is required. This involves the filtration device described in Section 4.3.2 and is outlined in Sections 7.2.3 to 7.2.8.

7.2.3 Pre-weigh the container that will receive the filtrate.

7.2.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (see Section 4.4).

NOTE: Acid washed filters may be used for all nonvolatile extractions even when metals are not of concern.

7.2.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight. If the waste contains <0.5% dry solids (Section 7.1.2), the liquid portion of the waste, after filtration, is defined as the TCLP extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required of the TCLP extract. For wastes containing >0.5% dry solids (Sections 7.1.1 or 7.1.2), use the percent solids information obtained in Section 7.1.1 to determine the optimum sample size (100 gram minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the TCLP extract.

7.2.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the waste is centrifuged, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.2.7 Quantitatively transfer the waste sample (liquid and solid phases) to the filter holder (see Section 4.3.2). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at

room temperature, then allow the sample to warm up to room temperature in the device before filtering.

NOTE: If waste material (>1% of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Section 7.2.5, to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within a 2 minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.2.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase may now be either analyzed (See Section 7.2.12) or stored at 4 °C until time of analysis.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Section 7.2.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the extraction as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.2.9 If the waste contains <0.5% dry solids (see Section 7.1.2), proceed to Section 7.2.13. If the waste contains >0.5% dry solids (see Section 7.1.1 or 7.1.2), and if particle size reduction of the solid was needed in Section 7.1.3, proceed to Section 7.2.10. If the waste as received passes a 9.5 mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to Section 7.2.11.

7.2.10 Prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described in Section 7.1.3. When the surface area or particle size has been appropriately altered, quantitatively transfer the solid

material into an extractor bottle. Include the filter used to separate the initial liquid from the solid phase.

NOTE: Sieving of the waste is not normally required. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended. If sieving is necessary, a Teflon coated sieve should be used to avoid contamination of the sample.

7.2.11 Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (Section 7.1.1)} \times \text{weight of waste filtered (Section 7.2.5 or 7.2.7)}}{100}$$

Slowly add this amount of appropriate extraction fluid (see Section 7.1.4) to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal), secure in rotary agitation device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at 23 ± 2 °C during the extraction period.

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of wastes (e.g., limed or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

7.2.12 Following the 18 ± 2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in Section 7.2.7. For final filtration of the TCLP extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filter(s) shall be acid-washed (see Section 4.4) if evaluating the mobility of metals.

7.2.13 Prepare the TCLP extract as follows:

7.2.13.1 If the waste contained no initial liquid phase, the filtered liquid material obtained from Section 7.2.12 is defined as the TCLP extract. Proceed to Section 7.2.14.

7.2.13.2 If compatible (e.g., multiple phases will not result on combination), combine the filtered liquid resulting from Section 7.2.12 with the initial liquid phase of the waste obtained in Section 7.2.7. This combined liquid is defined as the TCLP extract. Proceed to Section 7.2.14.

7.2.13.3 If the initial liquid phase of the waste, as obtained from Section 7.2.7, is not or may not be compatible with the filtered liquid resulting from Section 7.2.12, do not combine these liquids. Analyze these liquids, collectively defined as the TCLP extract, and combine the results mathematically, as described in Section 7.2.14.

7.2.14 Following collection of the TCLP extract, the pH of the extract should be recorded. Immediately aliquot and preserve the extract for analysis. Metals aliquots must be acidified with nitric acid to pH <2. If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses shall not be acidified and the extract shall be analyzed as soon as possible. All other aliquots must be stored under refrigeration (4 °C) until analyzed. The TCLP extract shall be prepared and analyzed according to appropriate analytical methods. TCLP extracts to be analyzed for metals shall be acid digested except in those instances where digestion causes loss of metallic analytes. If an analysis of the undigested extract shows that the concentration of any regulated metallic analyte exceeds the regulatory level, then the waste is hazardous and digestion of the extract is not necessary. However, data on undigested extracts alone cannot be used to demonstrate that the waste is not hazardous. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to $\pm$ 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phase (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.2.15 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

7.3 Procedure When Volatiles are Involved

Use the ZHE device to obtain TCLP extract for analysis of volatile compounds only. Extract resulting from the use of the ZHE shall not be used to evaluate the mobility of nonvolatile analytes (e.g., metals, pesticides, etc.).

The ZHE device has approximately a 500 mL internal capacity. The ZHE can thus accommodate a maximum of 25 grams of solid (defined as that fraction of a

sample from which no additional liquid may be forced out by an applied pressure of 50 psi), due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase.

Charge the ZHE with sample only once and do not open the device until the final extract (of the solid) has been collected. Repeated filling of the ZHE to obtain 25 grams of solid is not permitted.

Do not allow the waste, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any manipulation of these materials should be done when cold (4 °C) to minimize loss of volatiles.

7.3.1 Pre-weigh the (evacuated) filtrate collection container (See Section 4.6) and set aside. If using a TEDLAR® bag, express all liquid from the ZHE device into the bag, whether for the initial or final liquid/solid separation, and take an aliquot from the liquid in the bag for analysis. The containers listed in Section 4.6 are recommended for use under the conditions stated in Sections 4.6.1 - 4.6.3.

7.3.2 Place the ZHE piston within the body of the ZHE (it may be helpful first to moisten the piston O-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample (based upon sample size requirements determined from Section 7.3, Section 7.1.1 and/or 7.1.2). Secure the gas inlet/outlet flange (bottom flange) onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange (top flange) aside.

7.3.3 If the waste is 100% solid (see Section 7.1.1), weigh out a subsample (25 gram maximum) of the waste, record weight, and proceed to Section 7.3.5.

7.3.4 If the waste contains < 0.5% dry solids (Section 7.1.2), the liquid portion of waste, after filtration, is defined as the TCLP extract. Filter enough of the sample so that the amount of filtered liquid will support all of the volatile analyses required. For wastes containing $\geq$ 0.5% dry solids (Sections 7.1.1 and/or 7.1.2), use the percent solids information obtained in Section 7.1.1 to determine the optimum sample size to charge into the ZHE. The recommended sample size is as follows:

7.3.4.1 For wastes containing < 5% solids (see Section 7.1.1), weigh out a 500 gram subsample of waste and record the weight.

7.3.4.2 For wastes containing $\geq$ 5% solids (see Section 7.1.1), determine the amount of waste to charge into the ZHE as follows:

$$\text{Weight of waste to charge ZHE} = \frac{25}{\text{percent solids (Section 7.1.1)}} \times 100$$

Weigh out a subsample of the waste of the appropriate size and record the weight.

7.3.5 If particle size reduction of the solid portion of the waste was required in Section 7.1.3, proceed to Section 7.3.6. If particle size reduction was not required in Section 7.1.3, proceed to Section 7.3.7.

7.3.6 Prepare the waste for extraction by crushing, cutting, or grinding the solid portion of the waste to a surface area or particle size as described in Section 7.1.3. Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4 °C prior to particle size reduction. The means used to effect particle size reduction must not generate heat in and of itself. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.

NOTE: Sieving of the waste is not recommended due to the possibility that volatiles may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended.

When the surface area or particle size has been appropriately altered, proceed to Section 7.3.7.

7.3.7 Waste slurries need not be allowed to stand to permit the solid phase to settle. Do not centrifuge wastes prior to filtration.

7.3.8 Quantitatively transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens onto the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extract collection device to the top plate.

NOTE: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in Section 7.3.4 to determine the weight of the waste sample that will be filtered.

Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-10 psi (or more if necessary) to force all headspace

closure of the ZHE device into a hood. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room tempera- ture, then allow the sample to warm up to room temperature in the device before filtering. If the waste is 100% solid (see Section 7.1.1), slowly increase the pressure to a maximum of 50 psi to force most of the headspace out of the device and proceed to Section 7.3.12.

7.3.9 Attach the evacuated pre-weighed filtrate collection container to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1-10 psi to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate within a 2 minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.3.10 The material in the ZHE is defined as the solid phase of the waste and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the TCLP extraction as a solid.

If the original waste contained <0.5% dry solids (see Section 7.1.2), this filtrate is defined as the TCLP extract and is analyzed directly. Proceed to Section 7.3.15.

7.3.11 The liquid phase may now be either analyzed immediately (See Sections 7.3.13 through 7.3.15) or stored at 4 °C under minimal headspace conditions until time of analysis. Determine the weight of extraction fluid #1 to add to the ZHE as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (Section 7.1.1)} \times \text{weight of waste filtered (Section 7.3.4 or 7.3.8)}}{100}$$

7.3.12 The following Sections detail how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid #1 is used in all cases (See Section 5.7).

7.3.12.1 With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid in- let/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.

7.3.12.2 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5-10 psi (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5-10 psi and check all ZHE fittings to ensure that they are closed.

7.3.12.3 Place the ZHE in the rotary agitation appara- tus (if it is not already there) and rotate at 30 $\pm$ 2 rpm for 18 $\pm$ 2 hours. Ambient temperature (i.e., temperature of room in which extraction occurs) shall be maintained at 23 $\pm$ 2 °C during agita- tion.

7.3.13 Following the 18 $\pm$ 2 hour agitation period, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If the pressure has not been maintained (i.e., no gas release observed), the device is leaking. Check the ZHE for leaking as specified in Section 4.2.1, and perform the extraction again with a new sample of waste. If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases. If the waste contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container (i.e., TEDLAR® bag) holding the initial liquid phase of the waste. A separate filtrate collection container must be used if combining would create multiple phases, or there is not enough volume left within the filtrate collection container. Filter through the glass fiber filter, using the ZHE device as discussed in Section 7.3.9. All extract shall be filtered and collected if the

TEDLAR® bag is used, if the extract is multiphasic, or if the waste contained an initial liquid phase (see Sections 4.6 and 7.3.1).

NOTE: An in-line glass fiber filter may be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured.

7.3.14 If the original waste contained no initial liquid phase, the filtered liquid material obtained from Section 7.3.13 is defined as the TCLP extract. If the waste contained an initial liquid phase, the filtered liquid material obtained from Section 7.3.13 and the initial liquid phase (Section 7.3.9) are collectively defined as the TCLP extract.

7.3.15 Following collection of the TCLP extract, immediately prepare the extract for analysis and store with minimal headspace at 4 °C until analyzed. Analyze the TCLP extract according to the appropriate analytical methods. If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phases (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.3.16 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

8.1 QUALITY ASSURANCE

8.2 A minimum of one blank (using the same extraction fluid as used for the samples) must be analyzed for every 20 extractions that have been conducted in an extraction vessel.

8.3 A matrix spike shall be performed for each waste type (e.g., wastewater treatment sludge, contaminated soil, etc.) unless the result exceeds the regulatory level and the data are being used solely to demonstrate that the waste property exceeds the regulatory level. A minimum of one matrix spike must be analyzed for each analytical batch. As a minimum, follow the matrix spike addition guidance provided in each analytical method.

8.3.1 Matrix spikes are to be added after filtration of the TCLP extract and before preservation. Matrix spikes should not be added prior to TCLP extraction of the sample.

8.3.2 In most cases, matrix spikes should be added at a concentration equivalent to the corresponding regulatory level. If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentra- tion, but may not be not less than five times the method detection limit. In order to avoid differences in matrix effects, the matrix spikes must be added to the same nominal volume of TCLP extract as that which was analyzed for the unspiked sample.

8.3.3 The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to determine whether matrix interferences exist. Use of other internal calibration methods, modification of the analytical methods, or use of alternate analytical methods may be needed to accurately measure the analyte concentration in the TCLP extract when the recovery of the matrix spike is below the expected analytical method performance.

8.3.4 Matrix spike recoveries are calculated by the following formula:

$$\%R\ (\%Recovery) = 100\ (X_s - X_u)/K$$

where:
X_s = measured value for the spiked sample,
X_u = measured value for the unspiked sample, and
K = known value of the spike in the sample.

8.4 All quality control measures described in the appropriate analytical methods shall be followed.

8.5 The use of internal calibration quantitation methods shall be employed for a metallic contaminant if: (1) Recovery of the contaminant from the TCLP extract is not at least 50% and the concentration does not exceed the regulatory level, and (2) The concentration of the contaminant measured in the extract is within 20% of the appropriate regulatory level.

8.4.1. The method of standard additions shall be employed as the internal calibration quantitation method for each metallic contaminant.

8.4.2 The method of standard additions requires preparing calibration standards in the sample matrix rather than reagent water or blank solution. It requires taking four identical aliquots of the solution and adding known amounts of standard to three of these aliquots. The forth aliquot is the unknown. Preferably, the first addition should be prepared so that the resulting concentration is approximately 50% of the expected concentration of the sample. The second and third additions should be prepared so that the concentrations are approximately 100% and

150% of the expected concentration of the sample. All four aliquots are maintained at the same final volume by adding reagent water or a blank solution, and may need dilution adjustment to maintain the signals in the linear range of the instrument technique. All four aliquots are analyzed.

8.4.3 Prepare a plot, or subject data to linear regression, of instrument signals or external-calibration-derived concentrations as the dependant variable (y-axis) versus concentrations of the additions of standard as the independent variable (x-axis). Solve for the intercept of the abscissa (the independent variable, x-axis) which is the concentration in the unknown.

8.4.4 Alternately, subtract the instrumental signal or external- calibration-derived concentration of the unknown (unspiked) sample from the instrumental signals or external-calibration-derived concentrations of the standard additions. Plot or subject to linear regression of the corrected instrument signals or external-calibration-derived concentra- tions as the dependant variable versus the independent variable. Derive concentrations for unknowns using the internal calibration curve as if it were an external calibration curve.

8.5 Samples must undergo TCLP extraction within the following time periods:

SAMPLE MAXIMUM HOLDING TIMES [DAYS]

	From: Field collection To: TCLP extraction	From: TCLP extraction To: Preparative extraction	From: Preparative extraction To: Determinative analysis	Total elapsed time
Volatiles	14	NA	14	28
Semi-volatiles	14	7	40	61
Mercury	28	NA	28	56
Metals, except mercury	180	NA	180	360

NA = Not applicable

If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding the holding time is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory level.

9.1 METHOD PERFORMANCE

9.2 Ruggedness. Two ruggedness studies have been performed to determine the effect of various perturbations on specific elements of the TCLP protocol. Ruggedness testing determines the sensitivity of small procedural variations which might be expected to occur during routine laboratory application.

9.2.1 Metals - The following conditions were used when leaching a waste for metals analysis:

Varying Conditions	
Liquid/Solid ratio	19:1 vs. 21:1
Extraction time	16 hours vs. 18 hours
Headspace	20% vs. 60%
Buffer #2 acidity	190 meq vs. 210 meq
Acid-washed filters	yes vs. no
Filter type	0.7 µm glass fiber vs. 0.45 µm vs. polycarbonate
Bottle type	borosilicate vs. flint glass

Of the seven method variations examined, acidity of the extraction fluid had the greatest impact on the results. Four of 13 metals from an API separator sludge/electroplating waste (API/EW) mixture and two of three metals from an ammonia lime still bottom waste were extracted at higher levels by the more acidic buffer. Because of the sensitivity to pH changes, the method requires that the extraction fluids be prepared so that the final pH is within $\pm$ 0.05 units as specified.

9.2.2 Volatile Organic Compounds - The following conditions were used when leaching a waste for VOC analysis:

Varying Conditions	
Liquid/Solid ratio	19:1 vs. 21:1
Headspace	0% vs. 5%
Buffer #1 acidity	60 meq vs. 80 meq
Method of storing extract	Syringe vs. Tedlar® bag
Aliquotting	yes vs. no
Pressure behind piston	0 psi vs. 20 psi

None of the parameters had a significant effect on the results of the ruggedness test.

9.3 Precision. Many TCLP precision (reproducibility) studies have been performed, and have shown that, in general, the precision of the TCLP is comparable to or exceeds that of the EP toxicity test and that method precision is adequate. One of the more significant contributions to poor precision appears to be related to sample homogeneity and inter-laboratory variation (due to the nature of waste materials).

9.3.1 Metals - The results of a multi-laboratory study are shown in Table 6, and indicate that a single analysis of a waste may not be adequate for waste characterization and identification requirements.

9.3.2 Semi-Volatile Organic Compounds - The results of two studies are shown in Tables 7 and 8. Single laboratory precision was excellent with greater than 90 percent of the results exhibiting an RSD less than 25 percent. Over 85 percent of all individual compounds in the multi-laboratory study fell in the RSD range of 20 - 120 percent. Both studies concluded that the TCLP provides adequate precision. It was also determined that the high acetate content of the extraction fluid did not present problems (i.e., column degradation of the gas chromatograph) for the analytical conditions used.

9.3.3 Volatile Organic Compounds - Eleven laboratories participated in a collaborative study of the use of the ZHE with two waste types which were fortified with a mixture of VOCs. The results of the collaborative study are shown in Table 9. Precision results for VOCs tend to occur over a considerable range. However, the range and mean RSD compared very closely to the same collaborative study metals results in Table 6. Blackburn and Show concluded that at the 95% level of signifi- cance: 1) recoveries among laboratories were statistically similar, 2) recoveries did not vary significantly between the two sample types, and 3) each laboratory showed the same pattern of recovery for each of the two samples.

10.0 REFERENCES

1. Blackburn, W.B. and Show, I. "Collaborative Study of the Toxicity Characteristics Leaching Procedure (TCLP)." Draft Final Report, Contract No. 68- 03-1958, S-Cubed, November 1986.

2. Newcomer, L.R., Blackburn, W.B., Kimmell, T.A. "Performance of the Toxicity Characteristic Leaching Procedure." Wilson Laboratories, S-Cubed, U.S. EPA, December 1986.

3. Williams, L.R., Francis, C.W.; Maskarinec, M.P., Taylor D.R., and Rothman, N. "Single-Laboratory Evaluation of Mobility Procedure for Solid Waste." EMSL, ORNL, S-Cubed, ENSECO.

Table 1.
Volatile Analytes[1,2]

Compound	CAS No.
Acetone	67-64-1
Benzene	71-43-2
n-Butyl alcohol	71-36-3
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroform	67-66-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethylene	75-35-4
Ethyl acetate	141-78-6
Ethyl benzene	100-41-4
Ethyl ether	60-29-7
Isobutanol	78-83-1
Methanol	67-56-1
Methylene chloride	75-09-2
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-1
Tetrachloroethylene	127-18-4
Toluene	108-88-3
1,1,1,-Trichloroethane	71-55-6
Trichloroethylene	79-01-6
Trichlorofluoromethane	75-69-4
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1
Vinyl chloride	75-01-4
Xylene	1330-20-7

[1] When testing for any or all of these analytes, the zero-headspace extractor vessel shall be used instead of the bottle extractor.

[2] Benzene, carbon tetrachloride, chlorobenzene, chloroform, 1,2-dichloroethane, 1,1-dichloroethylene, methyl ethyl ketone, tetrachloroethylene, and vinyl chloride are toxicity characteristic constituents.

Table 2.
Suitable Rotary Agitation Apparatus[1]

Company	Location	Model No.
Analytical Testing and Services,	Warrington, PA (215) 343-4490	4-vessel extractor (DC20S) Consulting 8-vessel extractor (DC20) Inc. 12-vessel extractor (DC20B) 24-vessel extractor (DC24C)
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	2-vessel (3740-2-BRE) 4-vessel (3740-4-BRE) 6-vessel (3740-6-BRE) 8-vessel (3740-8-BRE) 12-vessel (3740-12-BRE) 24-vessel (3740-24-BRE)
Environmental Machine and Inc.	Lynchburg, VA (804) 845-6424	8-vessel (08-00-00) Design, 4-vessel (04-00-00)
IRA Machine Shop and Laboratory	Santurce, PR (809) 752-4004	8-vessel (011001)
Lars Lande Manufacturing	Whitmore Lake, MI (313) 449-4116	10-vessel (10VRE) 5-vessel (5VRE) 6-vessel (6VRE)
Millipore Corp.	Bedford, MA (800) 225-3384	4-ZHE or 4 2-liter bottle extractor (YT31ORAHW)

[1] Any device that rotates the extraction vessel in an end-over-end fashion at 30 $\pm$ 2 rpm is acceptable.

Table 3.
Suitable Zero-Headspace Extractor Vessels[1]

Company	Location	Model No.
Analytical Testing & Consulting Services, Inc.	Warrington, PA (215) 343-4490	C1O2, Mechanical Pressure Device
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	3745-ZHE, Gas Pressure Device
Lars Lande Manufacturing[2]	Whitmore Lake, MI (313) 449-4116	ZHE-11, Gas Pressure Device
Millipore Corporation	Bedford, MA (800) 225-3384	YT30O9OHW, Gas Pressure Device
Environmental Machine and Design, Inc.	Lynchburg, VA (804) 845-6424	VOLA-TOX1, Gas Pressure Device
Gelman Science	Ann Arbor, MI 521-1520	15400 Gas Pressure (800) Device

[1] Any device that meets the specifications listed in Section 4.2.1 of the method is suitable.

[2] This device uses a 110 mm filter.

Table 4.
Suitable Filter Holders[1]

Company	Location	Model/ Catalogue No.	Size
Nucleopore Corporation	Pleasanton, CA (800) 882-7711	425910 410400	142 mm 47 mm
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	302400 311400	142 mm 47 mm
Millipore Corporation	Bedford, MA (800) 225-3384	YT30142HW XX1004700	142 mm 47 mm

[1] Any device capable of separating the liquid from the solid phase of the waste is suitable, providing that it is chemically compatible with the waste and the constituents to be analyzed. Plastic devices (not listed above) may be used when only inorganic analytes are of concern. The 142 mm size filter holder is recommended.

Table 5.
Suitable Filter Media[1]

Company	Location	Model	Pore Size (µm)
Millipore Corporation	Bedford, MA (800) 225-3384	AP40	0.7
Nucleopore Corporation	Pleasanton, CA (415) 463-2530	211625	0.7
Whatman Laboratory Products, Inc.	Clifton, NJ (201) 773-5800	GFF	0.7
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	GF75	0.7
Gelman Science	Ann Arbor, MI (800) 521-1520	66256 (90mm) 66257 (142mm)	0.7

[1] Any filter that meets the specifications in Section 4.4 of the Method is suitable.

Table 6. Multi-Laboratory TCLP Metals, Precision

Waste	Extraction Fluid	Metal	$\bar{X}$	S	%RSD
Ammonia	#1	Cadmium	0.053	0.031	60
Lime Still	#2		0.023	0.017	76
Bottoms	#1	Chromium	0.015	0.0014	93
	#2		0.0032	0.0037	118
	#1	Lead	0.0030	0.0027	90
	#2		0.0032	0.0028	87
API/EW	#1	Cadmium	0.0046	0.0028	61
Mixture	#2		0.0005	0.0004	77
	#1	Chromium	0.0561	0.0227	40
	#2		0.105	0.018	17
	#1	Lead	0.0031	0.0031	100
	#2		0.0124	0.0136	110
Fossil	#1	Cadmium	0.080	0.069	86
Fuel Fly	#2		0.093	0.067	72
Ash	#1	Chromium	0.017	0.014	85
	#2		0.070	0.040	57
	#1	Lead	0.0087	0.0074	85
	#2		0.0457	0.0083	18
				%RSD Range = 17 - 118 Mean	
				%RSD = 74	

NOTE: $\bar{X}$ = Mean results from 6 - 12 different laboratories Units = mg/L
Extraction Fluid #1 = pH 4.9
#2 = pH 2.9

Table 7. Single-Laboratory Semi-Volatiles, Precision

Waste	Compound	Extraction Fluid	$\overline{X}$	S	%RSD
Ammonia Lime Still Bottoms	Phenol	#1	19000	2230	11.6
		#2	19400	929	4.8
	2-Methylphenol	#1	2000	297	14.9
		#2	1860	52.9	2.8
	4-Methylphenol	#1	7940	1380	17.4
		#2	7490	200	2.7
	2,4-Dimethylphenol	#1	321	46.8	14.6
		#2	307	45.8	14.9
	Naphthalene	#1	3920	413	10.5
		#2	3827	176	4.6
	2-Methylnaphthalene	#1	290	44.8	15.5
		#2	273	19.3	7.1
	Dibenzofuran	#1	187	22.7	12.1
		#2	187	7.2	3.9
	Acenaphthylene	#1	703	89.2	12.7
		#2	663	20.1	3.0
	Fluorene	#1	151	17.6	11.7
		#2	156	2.1	1.3
	Phenanthrene	#1	241	22.7	9.4
		#2	243	7.9	3.3
	Anthracene	#1	33.2	6.19	18.6
		#2	34.6	1.55	4.5
	Fluoranthrene	#1	25.3	1.8	7.1
		#2	26.0	1.8	7.1
API/EW Mixture	Phenol	#1	40.7	13.5	33.0
		#2	19.0	1.76	9.3
	2,4-Dimethylphenol	#1	33.0	9.35	28.3
		#2	43.3	8.61	19.9
	Naphthalene	#1	185	29.4	15.8
		#2	165	24.8	15.0
	2-Methylnaphthalene	#1	265	61.2	23.1
		#2	200	18.9	9.5
				%RSD Range = 1 - 33	
				Mean %RSD = 12	

NOTE: Units = µg/L
Extractions were performed in triplicate
All results were at least 2x the detection limit Extraction Fluid #1 = pH 4.9
#2 = pH 2.9

Table 8. Multi-Laboratory Semi-Volatiles, Precision

Waste	Compound	Extraction Fluid	$\bar{X}$	S	%RSD
Ammonia Lime	BNAs	#1	10043	7680	76.5
Still Bottoms (A)		#2	10376	6552	63.1
API/EW	BNAs	#1	1624	675	41.6
Mixture (B)		#2	2074	1463	70.5
Fossil Fuel	BNAs	#1	750	175	23.4
Fly Ash (C)		#2	739	342	46.3
					Mean %RSD = 54

NOTE: Units = µg/L
X = Mean results from 3 - 10 labs Extraction Fluid #1 = pH 4.9
#2 = pH 2.9

%RSD Range for Individual Compounds

A, #1	0 - 113
A, #2	28 - 108
B, #1	20 - 156
B, #2	49 - 128
C, #1	36 - 143
C, #2	61 - 164

Table 9. Multi-Laboratory (11 Labs) VOCs, Precision

Waste	Compound	$\bar{X}$	S	%RSD
Mine Tailings	Vinyl chloride	6.36	6.36	100
	Methylene chloride	12.1	11.8	98
	Carbon disulfide	5.57	2.83	51
	1,1-Dichloroethene	21.9	27.7	127
	1,1-Dichloroethane	31.4	25.4	81
	Chloroform	46.6	29.2	63
	1,2-Dichloroethane	47.8	33.6	70
	2-Butanone	43.5	36.9	85
	1,1,1-Trichloroethane	20.9	20.9	100
	Carbon tetrachloride	12.0	8.2	68
	Trichloroethene	24.7	21.2	86
	1,1,2-Trichloroethene	19.6	10.9	56
	Benzene	37.9	28.7	76
	1,1,2,2-Tetrachloroethane	34.9	25.6	73
	Toluene	29.3	11.2	38
	Chlorobenzene	35.6	19.3	54
	Ethylbenzene	4.27	2.80	66
	Trichlorofluoromethane	3.82	4.40	115
	Acrylonitrile	76.7	110.8	144
Ammonia Lime Still Bottoms	Vinyl chloride	5.00	4.71	94
	Methylene chloride	14.3	13.1	92
	Carbon disulfide	3.37	2.07	61
	1,1-Dichloroethene	52.1	38.8	75
	1,1-Dichloroethane	52.8	25.6	49
	Chloroform	64.7	28.4	44
	1,2-Dichloroethane	43.1	31.5	73
	2-Butanone	59.0	39.6	67
	1,1,1-Trichloroethane	53.6	40.9	76
	Carbon tetrachloride	7.10	6.1	86
	Trichloroethene	57.3	34.2	60
	1,1,2-Trichloroethene	6.7	4.7	70
	Benzene	61.3	26.8	44
	1,1,2,2-Tetrachloroethane	3.16	2.1	66
	Toluene	69.0	18.5	27
	Chlorobenzene	71.8	12.0	17
	Ethylbenzene	3.70	2.2	58
	Trichlorofluoromethane	4.05	4.8	119
	Acrylonitrile	29.4	34.8	118
				%RSD Range = 17 - 144 Mean %RSD = 75

NOTE: Units = µg/L

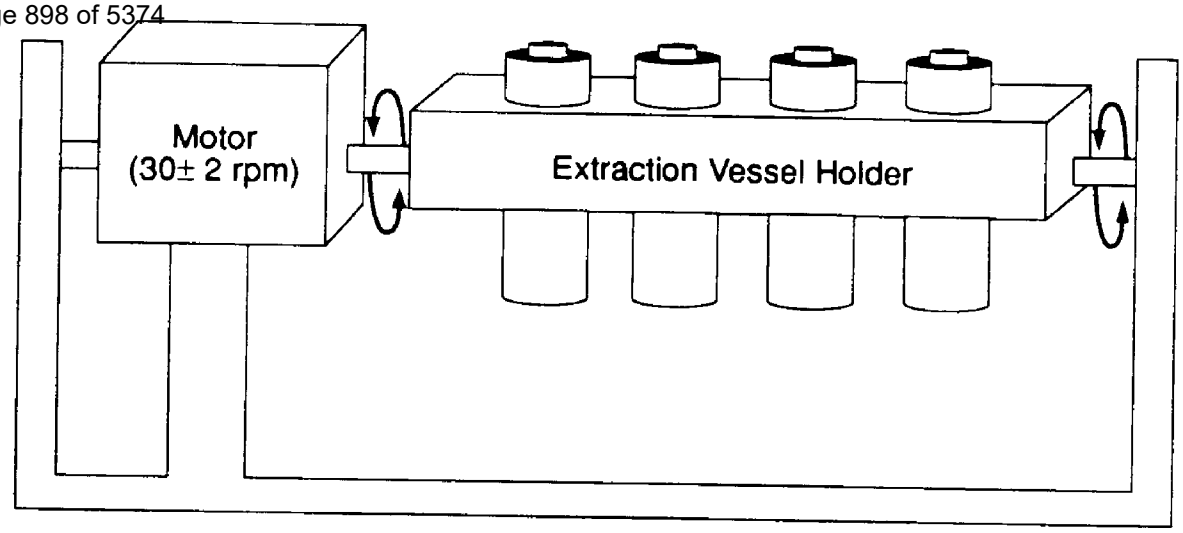


Figure 1. Rotary Agitation Apparatus

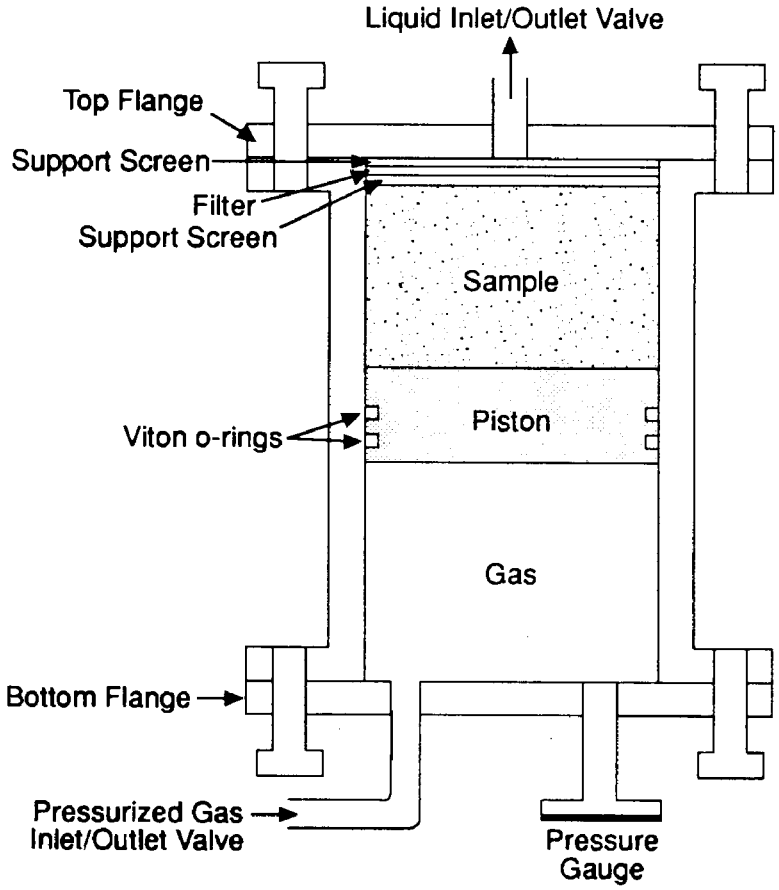
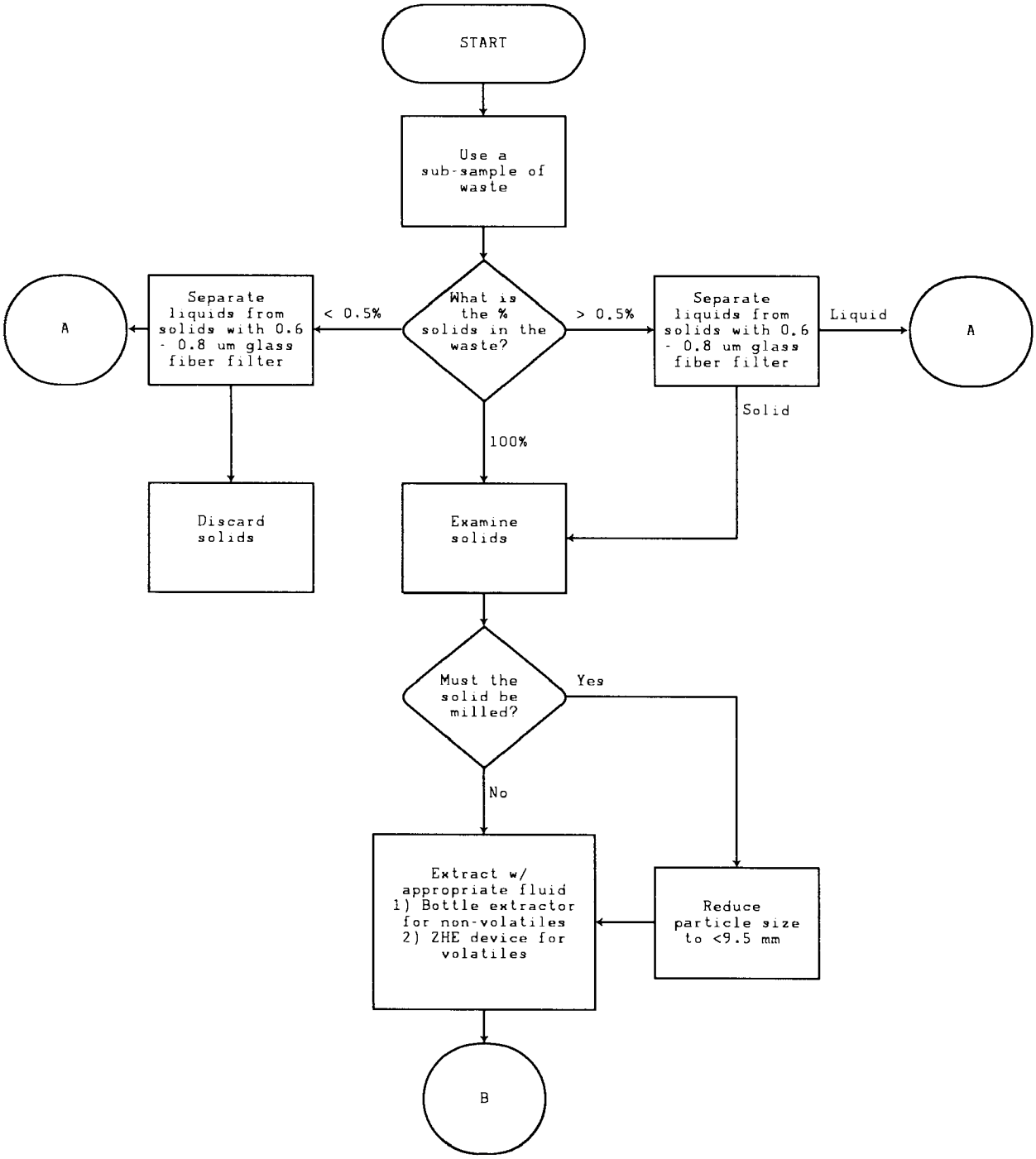
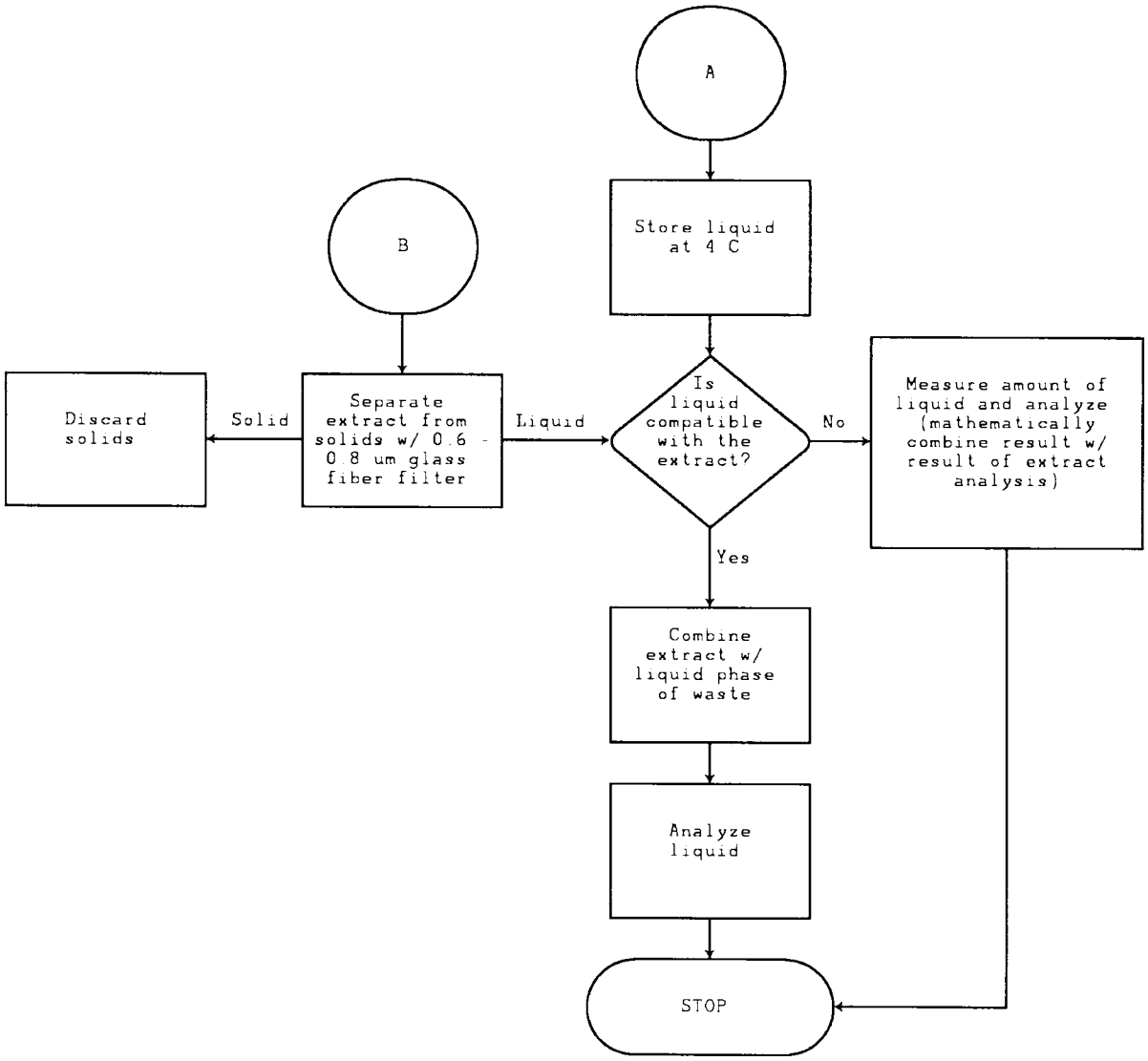


Figure 2. Zero-Headspace Extractor (ZHE)

TOXICITY CHARACTERISTIC LEACHATE PROCEDURE



CHARACTERISTIC LEACHATE PROCEDURE



State of Oregon Department of Environmental Quality

OAR 340-101-0004

Toxicity Characteristic Leaching Procedure

METHOD 1311

TOXICITY CHARACTERISTIC LEACHING PROCEDURE

1.1 SCOPE AND APPLICATION

1.2 The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes.

1.3 If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the TCLP need not be run.

1.4 If an analysis of any one of the liquid fractions of the TCLP extract indicates that a regulated compound is present at such high concentra- tions that, even after accounting for dilution from the other fractions of the extract, the concentration would be above the regulatory level for that compound, then the waste is hazardous and it is not necessary to analyze the remaining fractions of the extract.

1.5 If an analysis of extract obtained using a bottle extractor shows that the concentration of any regulated volatile analyte exceeds the regulatory level for that compound, then the waste is hazardous and extraction using the ZHE is not necessary. However, extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the regulatory level.

2.1 SUMMARY OF METHOD

2.2 For liquid wastes (i.e., those containing less than 0.5% dry solid material), the waste, after filtration through a 0.6 to 0.8 µm glass fiber filter, is defined as the TCLP extract.

2.3 For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatile analytes (see Table 1 for a list of volatile compounds). Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 µm glass fiber filter.

2.4 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3.1 INTERFERENCES

3.2 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.1 APPARATUS AND MATERIALS

4.2 Agitation apparatus: The agitation apparatus must be capable of rotating the extraction vessel in an end-over-end fashion (see Figure 1) at 30 ± 2 rpm. Suitable devices known to EPA are identified in Table 2.

4.3 Extraction Vessels

4.3.1 Zero-Headspace Extraction Vessel (ZHE). This device is for use only when the waste is being tested for the mobility of volatile analytes (i.e., those listed in Table 1). The ZHE (depicted in Figure 2) allows for liquid/solid separation within the device, and effectively precludes headspace. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel (see Section 4.3.1). The vessels shall have an internal volume of 500-600 mL, and be equipped to accommodate a 90-110 mm filter. The devices contain VITON®[1] O-rings which should be replaced frequently. Suitable ZHE devices known to EPA are identified in Table 3.

For the ZHE to be acceptable for use, the piston within the ZHE should be able to be moved with approximately 15 psi or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for TCLP analyses and the manufacturer should be contacted.

The ZHE should be checked for leaks after every extraction. If the device contains a built-in pressure gauge, pressurize the device to 50 psi, allow it to stand unattended for 1 hour, and recheck the pressure. If the device does not have a built-in pressure gauge, pressurize the device to 50 psi, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted.

Some ZHEs use gas pressure to actuate the ZHE piston, while others use mechanical pressure (see Table 3). Whereas the volatiles procedure (see Section 7.3) refers to pounds per square inch (psi), for the mechanically actuated piston, the pressure applied is measured in torque-inch-pounds. Refer to the manufacturer's instructions as to the proper conversion.

[1] VITON® is a trademark of Du Pont.

4.3.2 Bottle Extraction Vessel. When the waste is being evaluated using the nonvolatile extraction, a jar with sufficient capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel.

The extraction bottles may be constructed from various materials, depending on the analytes to be analyzed and the nature of the waste (see Section 4.3.3). It is recommended that borosilicate glass bottles be used instead of other types of glass, especially when inorganics are of concern. Plastic bottles, other than polytetrafluoroethylene, shall not be used if organics are to be investigated. Bottles are available from a number of laboratory suppliers. When this type of extraction vessel is used, the filtration device discussed in Section 4.3.2 is used for initial liquid/solid separation and final extract filtration.

4.4 Filtration Devices: It is recommended that all filtrations be performed in a hood.

4.4.1 Zero-Headspace Extractor Vessel (ZHE): When the waste is evaluated for volatiles, the zero-headspace extraction vessel described in Section 4.2.1 is used for filtration. The device shall be capable of supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation (50 psi).

NOTE: When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.

4.4.2 Filter Holder: When the waste is evaluated for other than volatile analytes, any filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psi or more. The type of filter holder used depends on the properties of the material to be filtered (see Section 4.3.3). These devices shall have a minimum internal volume of 300 mL and be equipped to accommodate a minimum filter size of 47 mm (filter holders having an internal capacity of 1.5 L or greater, and equipped to accommodate a 142 mm diameter filter, are recommended). Vacuum filtration can only be used for wastes with low solids content (<10%) and for highly granular, liquid-containing wastes. All other types of wastes should be filtered using positive pressure filtration. Suitable filter holders known to EPA are shown in Table 4.

4.4.3 Materials of Construction: Extraction vessels and filtration devices shall be made of inert materials which will not leach or absorb waste components. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride (PVC) may be used only when evaluating the mobility of metals. Borosili-

Pyrex glass bottles are recommended for use over other types of glass bottles, especially when inorganics are analytes of concern.

4.5 Filters: Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6 to 0.8 µm, or equivalent. Filters known to EPA which meet these specifications are identified in Table 5. Pre-filters must not be used. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 1N nitric acid followed by three consecutive rinses with deionized distilled water (a minimum of 1 L per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

4.5 pH Meters: The meter should be accurate to ± 0.05 units at 25 °C.

4.6 ZHE Extract Collection Devices: TEDLAR®[2] bags or glass, stainless steel or PTFE gas-tight syringes are used to collect the initial liquid phase and the final extract of the waste when using the ZHE device. The devices listed are recommended for use under the following conditions:

4.6.1 If a waste contains an aqueous liquid phase or if a waste does not contain a significant amount of nonaqueous liquid (i.e., <1% of total waste), the TEDLAR® bag or a 600 mL syringe should be used to collect and combine the initial liquid and solid extract.

4.6.2 If a waste contains a significant amount of nonaqueous liquid in the initial liquid phase (i.e., >1% of total waste), the syringe or the TEDLAR® bag may be used for both the initial solid/liquid separation and the final extract filtration. However, analysts should use one or the other, not both.

4.6.3 If the waste contains no initial liquid phase (is 100% solid) or has no significant solid phase (is 100% liquid), either the TEDLAR® bag or the syringe may be used. If the syringe is used, discard the first 5 mL of liquid expressed from the device. The remaining aliquots are used for analysis.

4.7 ZHE Extraction Fluid Transfer Devices: Any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is acceptable (e.g., a positive displacement or peristaltic pump, a gas tight syringe, pressure filtration unit (see Section 4.3.2), or other ZHE device).

4.8 Laboratory Balance: Any laboratory balance accurate to within ± 0.01 grams may be used (all weight measurements are to be within ± 0.1 grams).

4.9 Beaker or Erlenmeyer flask, glass, 500 mL.

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[2] TEDLAR® is a registered trademark of Du Pont.

4.10 Watchglass, appropriate diameter to cover beaker or Erlenmeyer flask.

4.11 Magnetic stirrer.

5.1 REAGENTS

5.2 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.3 Reagent Water. Reagent water is defined as water in which an interferant is not observed at or above the method's detection limit of the analyte(s) of interest. For nonvolatile extractions, ASTM Type II water or equivalent meets the definition of reagent water. For volatile extractions, it is recommended that reagent water be generated by any of the following methods. Reagent water should be monitored periodically for impurities.

5.3.1 Reagent water for volatile extractions may be generated by passing tap water through a carbon filter bed containing about 500 grams of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.3.2 A water purification system (Millipore Super-Q or equivalent) may also be used to generate reagent water for volatile extractions.

5.3.3 Reagent water for volatile extractions may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the water temperature at 90 $\pm$ 5 degrees C, bubble a contaminant-free inert gas (e.g. nitrogen) through the water for 1 hour. While still hot, transfer the water to a narrow mouth screw-cap bottle under zero-headspace and seal with a Teflon-lined septum and cap.

5.4 Hydrochloric acid (1N), HCl, made from ACS reagent grade.

5.5 Nitric acid (1N), HNO_3, made from ACS reagent grade.

5.6 Sodium hydroxide (1N), NaOH, made from ACS reagent grade.

5.7 Glacial acetic acid, CH_3CH_2OOH, ACS reagent grade.

5.8 Extraction fluid.

5.8.1 Extraction fluid # 1: Add 5.7 mL glacial CH_3CH_2OOH to 500 mL of reagent water (See Section 5.2), add 64.3 mL of 1N NaOH, and dilute to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 4.93 $\pm$ 0.05.

5.8.2 Extraction fluid # 2: Dilute 5.7 mL glacial CH_3CH_2OOH with reagent water (See Section 5.2) to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 2.88 $\pm$ 0.05.

NOTE: These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid shall be discarded and fresh extraction fluid prepared.

5.9 Analytical standards shall be prepared according to the appropriate analytical method.

6.1 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.2 All samples shall be collected using an appropriate sampling plan.

6.3 The TCLP may place requirements on the minimal size of the field sample, depending upon the physical state or states of the waste and the analytes of concern. An aliquot is needed for preliminary evaluation of which extraction fluid is to be used for the nonvolatile analyte extraction procedure. Another aliquot may be needed to actually conduct the nonvolatile extraction (see Section 1.4 concerning the use of this extract for volatile organics). If volatile organics are of concern, another aliquot may be needed. Quality control measures may require additional aliquots. Further, it is always wise to collect more sample just in case something goes wrong with the initial attempt to conduct the test.

6.3 Preservatives shall not be added to samples before extraction.

6.4 Samples may be refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

6.5 When the waste is to be evaluated for volatile analytes, care shall be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g., samples should be collected in Teflon-lined septum capped vials and stored at 4 °C. Samples should be opened only immediately prior to extraction).

6.6 TCLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH < 2, unless precipitation occurs (see Section 7.2.14 if precipitation occurs). Extracts should be preserved for other analytes according to the guidance given in the individual analysis methods. Extracts or portions of extracts for organic analyte determinations shall not be allowed to come into contact with the atmosphere (i.e., no headspace) to prevent losses. See Section 8.0 (QA requirements) for acceptable sample and extract holding times.

7.2 Preliminary Evaluations

Perform preliminary TCLP evaluations on a minimum 100 gram aliquot of waste. This aliquot may not actually undergo TCLP extraction. These preliminary evaluations include: (1) determination of the percent solids (Section 7.1.1);
(2) determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration (Section 7.1.2); (3) determination of whether the solid portion of the waste requires particle size reduction (Section 7.1.3); and (4) determination of which of the two extraction fluids are to be used for the nonvolatile TCLP extraction of the waste (Section 7.1.4).

7.1.1 Preliminary determination of percent solids: Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below.

7.1.1.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solids) proceed to Section 7.1.3.

7.1.1.2 If the sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device described in Section 4.3.2 and is outlined in Sections 7.1.1.3 through 7.1.1.9.

7.1.1.3 Pre-weigh the filter and the container that will receive the filtrate.

7.1.1.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

7.1.1.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight.

7.1.1.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.1.1.7 Quantitatively transfer the waste sample to the filter holder (liquid and solid phases). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room temperature then allow the sample to warm up to room temperature in the device before filtering.

NOTE: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Section 7.1.1.5 to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within any 2 minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.1.1.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Section 7.1.1.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.1.1.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (see Section 7.1.1.3) from the total weight of the filtrate-filled container. Determine the weight of the solid phase of the waste sample by subtracting the weight of the liquid phase from the weight of the total waste sample, as determined in Section 7.1.1.5 or 7.1.1.7.

Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\text{Percent solids} = \frac{\text{Weight of solid (Section 7.1.1.9)}}{\text{Total weight of waste (Section 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2 If the percent solids determined in Section 7.1.1.9 is equal to or greater than 0.5%, then proceed either to Section 7.1.3 to

determine whether the solid material requires particle size reduction or to Section 7.1.2.1 if it is noticed that a small amount of the filtrate is entrained in wetting of the filter. If the percent solids determined in Section 7.1.1.9 is less than 0.5%, then proceed to Section 7.2.9 if the nonvolatile TCLP is to be performed and to Section 7.3 with a fresh portion of the waste if the volatile TCLP is to be performed.

7.1.2.1 Remove the solid phase and filter from the filtration apparatus.

7.1.2.2 Dry the filter and solid phase at 100 ± 20 °C until two successive weighing yield the same value within ± 1%. Record the final weight.

NOTE: Caution should be taken to ensure that the subject solid will not flash upon heating. It is recommended that the drying oven be vented to a hood or other appropriate device.

7.1.2.3 Calculate the percent dry solids as follows: (Wt. of dry waste + filter) - tared wt. of filter

$$\text{Percent dry solids} = \frac{\text{(Wt. of dry waste + filter) - tared wt. of filter}}{\text{Initial wt. of waste (Section 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2.4 If the percent dry solids is less than 0.5%, then proceed to Section 7.2.9 if the nonvolatile TCLP is to be performed, and to Section 7.3 if the volatile TCLP is to be performed. If the percent dry solids is greater than or equal to 0.5%, and if the nonvolatile TCLP is to be performed, return to the beginning of this Section (7.1) and, with a fresh portion of waste, determine whether particle size reduction is necessary (Section 7.1.3) and determine the appropriate extraction fluid (Section 7.1.4). If only the volatile TCLP is to be performed, see the note in Section 7.1.4.

7.1.3 Determination of whether the waste requires particle size reduction (particle size is reduced during this step): Using the solid portion of the waste, evaluate the solid for particle size. Particle size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1 cm^2, or is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm (0.375 inch) standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above. If the solids are prepared for organic volatiles extraction, special precautions must be taken (see Section 7.3.6).

NOTE: Surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet

the criteria, sample specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

7.1.4 Determination of appropriate extraction fluid: If the solid content of the waste is greater than or equal to 0.5% and if the sample will be extracted for nonvolatile constituents (Section 7.2), determine the appropriate fluid (Section 5.7) for the nonvolatiles extraction as follows:

NOTE: TCLP extraction for volatile constituents uses only extraction fluid #1 (Section 5.7.1). Therefore, if TCLP extraction for nonvolatiles is not required, proceed to Section 7.3.

7.1.4.1 Weigh out a small subsample of the solid phase of the waste, reduce the solid (if necessary) to a particle size of approximately 1 mm in diameter or less, and transfer 5.0 grams of the solid phase of the waste to a 500 mL beaker or Erlenmeyer flask.

7.1.4.2 Add 96.5 mL of reagent water to the beaker, cover with a watchglass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is <5.0, use extraction fluid #1. Proceed to Section 7.2.

7.1.4.3 If the pH from Section 7.1.4.2 is >5.0, add 3.5 mL 1N HCl, slurry briefly, cover with a watchglass, heat to 50 °C, and hold at 50 °C for 10 minutes.

7.1.4.4 Let the solution cool to room temperature and record the pH. If the pH is <5.0, use extraction fluid #1. If the pH is >5.0, use extraction fluid #2. Proceed to Section 7.2.

7.1.5 If the aliquot of the waste used for the preliminary evaluation (Sections 7.1.1 - 7.1.4) was determined to be 100% solid at Section 7.1.1.1, then it can be used for the Section 7.2 extraction (assuming at least 100 grams remain), and the Section 7.3 extraction (assuming at least 25 grams remain). If the aliquot was subjected to the procedure in Section 7.1.1.7, then another aliquot shall be used for the volatile extraction procedure in Section 7.3. The aliquot of the waste subjected to the procedure in Section 7.1.1.7 might be appropriate for use for the Section 7.2 extraction if an adequate amount of solid (as determined by Section 7.1.1.9) was obtained. The amount of solid necessary is dependent upon whether a sufficient amount of extract will be produced to support the analyses. If an adequate amount of solid remains, proceed to Section 7.2.10 of the nonvolatile TCLP extraction.

7.2 Procedure When Volatiles are not Involved

A minimum sample size of 100 grams (solid and liquid phases) is recommend- ed. In some cases, a larger sample size may be appropriate, depending on the

solids content of the waste sample (percent solids, See Section 7.1.1), whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of TCLP extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single TCLP extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

7.2.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solid, see Section 7.1.1), weigh out a subsample of the waste (100 gram minimum) and proceed to Section 7.2.9.

7.2.2 If the sample is liquid or multiphasic, liquid/solid separation is required. This involves the filtration device described in Section 4.3.2 and is outlined in Sections 7.2.3 to 7.2.8.

7.2.3 Pre-weigh the container that will receive the filtrate.

7.2.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (see Section 4.4).

NOTE: Acid washed filters may be used for all nonvolatile extractions even when metals are not of concern.

7.2.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight. If the waste contains <0.5% dry solids (Section 7.1.2), the liquid portion of the waste, after filtration, is defined as the TCLP extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required of the TCLP extract. For wastes containing >0.5% dry solids (Sections 7.1.1 or 7.1.2), use the percent solids information obtained in Section 7.1.1 to determine the optimum sample size (100 gram minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the TCLP extract.

7.2.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the waste is centrifuged, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.2.7 Quantitatively transfer the waste sample (liquid and solid phases) to the filter holder (see Section 4.3.2). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at

room temperature, then allow the sample to warm up to room temperature in the device before filtering.

NOTE: If waste material (>1% of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Section 7.2.5, to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within a 2 minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.2.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase may now be either analyzed (See Section 7.2.12) or stored at 4 °C until time of analysis.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Section 7.2.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the extraction as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.2.9 If the waste contains <0.5% dry solids (see Section 7.1.2), proceed to Section 7.2.13. If the waste contains >0.5% dry solids (see Section 7.1.1 or 7.1.2), and if particle size reduction of the solid was needed in Section 7.1.3, proceed to Section 7.2.10. If the waste as received passes a 9.5 mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to Section 7.2.11.

7.2.10 Prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described in Section 7.1.3. When the surface area or particle size has been appropriately altered, quantitatively transfer the solid

material into an extractor bottle. Include the filter used to separate the initial liquid from the solid phase.

NOTE: Sieving of the waste is not normally required. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended. If sieving is necessary, a Teflon coated sieve should be used to avoid contamination of the sample.

7.2.11 Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (Section 7.1.1)} \times \text{weight of waste filtered (Section 7.2.5 or 7.2.7)}}{100}$$

Slowly add this amount of appropriate extraction fluid (see Section 7.1.4) to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal), secure in rotary agitation device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at 23 ± 2 °C during the extraction period.

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of wastes (e.g., limed or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

7.2.12 Following the 18 ± 2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in Section 7.2.7. For final filtration of the TCLP extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filter(s) shall be acid-washed (see Section 4.4) if evaluating the mobility of metals.

7.2.13 Prepare the TCLP extract as follows:

7.2.13.1 If the waste contained no initial liquid phase, the filtered liquid material obtained from Section 7.2.12 is defined as the TCLP extract. Proceed to Section 7.2.14.

7.2.13.2 If compatible (e.g., multiple phases will not result on combination), combine the filtered liquid resulting from Section 7.2.12 with the initial liquid phase of the waste obtained in Section 7.2.7. This combined liquid is defined as the TCLP extract. Proceed to Section 7.2.14.

7.2.13.3 If the initial liquid phase of the waste, as obtained from Section 7.2.7, is not or may not be compatible with the filtered liquid resulting from Section 7.2.12, do not combine these liquids. Analyze these liquids, collectively defined as the TCLP extract, and combine the results mathematically, as described in Section 7.2.14.

7.2.14 Following collection of the TCLP extract, the pH of the extract should be recorded. Immediately aliquot and preserve the extract for analysis. Metals aliquots must be acidified with nitric acid to pH <2. If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses shall not be acidified and the extract shall be analyzed as soon as possible. All other aliquots must be stored under refrigeration (4 °C) until analyzed. The TCLP extract shall be prepared and analyzed according to appropriate analytical methods. TCLP extracts to be analyzed for metals shall be acid digested except in those instances where digestion causes loss of metallic analytes. If an analysis of the undigested extract shows that the concentration of any regulated metallic analyte exceeds the regulatory level, then the waste is hazardous and digestion of the extract is not necessary. However, data on undigested extracts alone cannot be used to demonstrate that the waste is not hazardous. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to $\pm$ 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phase (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.2.15 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

7.3 Procedure When Volatiles are Involved

Use the ZHE device to obtain TCLP extract for analysis of volatile compounds only. Extract resulting from the use of the ZHE shall not be used to evaluate the mobility of nonvolatile analytes (e.g., metals, pesticides, etc.).

The ZHE device has approximately a 500 mL internal capacity. The ZHE can thus accommodate a maximum of 25 grams of solid (defined as that fraction of a

sample from which no additional liquid may be forced out by an applied pressure of 50 psi), due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase.

Charge the ZHE with sample only once and do not open the device until the final extract (of the solid) has been collected. Repeated filling of the ZHE to obtain 25 grams of solid is not permitted.

Do not allow the waste, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any manipulation of these materials should be done when cold (4 °C) to minimize loss of volatiles.

7.3.1 Pre-weigh the (evacuated) filtrate collection container (See Section 4.6) and set aside. If using a TEDLAR® bag, express all liquid from the ZHE device into the bag, whether for the initial or final liquid/solid separation, and take an aliquot from the liquid in the bag for analysis. The containers listed in Section 4.6 are recommended for use under the conditions stated in Sections 4.6.1 - 4.6.3.

7.3.2 Place the ZHE piston within the body of the ZHE (it may be helpful first to moisten the piston O-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample (based upon sample size requirements determined from Section 7.3, Section 7.1.1 and/or 7.1.2). Secure the gas inlet/outlet flange (bottom flange) onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange (top flange) aside.

7.3.3 If the waste is 100% solid (see Section 7.1.1), weigh out a subsample (25 gram maximum) of the waste, record weight, and proceed to Section 7.3.5.

7.3.4 If the waste contains < 0.5% dry solids (Section 7.1.2), the liquid portion of waste, after filtration, is defined as the TCLP extract. Filter enough of the sample so that the amount of filtered liquid will support all of the volatile analyses required. For wastes containing $\geq$ 0.5% dry solids (Sections 7.1.1 and/or 7.1.2), use the percent solids information obtained in Section 7.1.1 to determine the optimum sample size to charge into the ZHE. The recommended sample size is as follows:

7.3.4.1 For wastes containing < 5% solids (see Section 7.1.1), weigh out a 500 gram subsample of waste and record the weight.

7.3.4.2 For wastes containing $\geq$ 5% solids (see Section 7.1.1), determine the amount of waste to charge into the ZHE as follows:

$$\text{Weight of waste to charge ZHE} = \frac{25}{\text{percent solids (Section 7.1.1)}} \times 100$$

Weigh out a subsample of the waste of the appropriate size and record the weight.

7.3.5 If particle size reduction of the solid portion of the waste was required in Section 7.1.3, proceed to Section 7.3.6. If particle size reduction was not required in Section 7.1.3, proceed to Section 7.3.7.

7.3.6 Prepare the waste for extraction by crushing, cutting, or grinding the solid portion of the waste to a surface area or particle size as described in Section 7.1.3. Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4 °C prior to particle size reduction. The means used to effect particle size reduction must not generate heat in and of itself. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.

NOTE: Sieving of the waste is not recommended due to the possibility that volatiles may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended.

When the surface area or particle size has been appropriately altered, proceed to Section 7.3.7.

7.3.7 Waste slurries need not be allowed to stand to permit the solid phase to settle. Do not centrifuge wastes prior to filtration.

7.3.8 Quantitatively transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens onto the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extract collection device to the top plate.

NOTE: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in Section 7.3.4 to determine the weight of the waste sample that will be filtered.

Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-10 psi (or more if necessary) to force all headspace

slowly out of the ZHE device into a hood. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room tempera- ture, then allow the sample to warm up to room temperature in the device before filtering. If the waste is 100% solid (see Section 7.1.1), slowly increase the pressure to a maximum of 50 psi to force most of the headspace out of the device and proceed to Section 7.3.12.

7.3.9 Attach the evacuated pre-weighed filtrate collection container to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1-10 psi to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate within a 2 minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.3.10 The material in the ZHE is defined as the solid phase of the waste and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the TCLP extraction as a solid.

If the original waste contained <0.5% dry solids (see Section 7.1.2), this filtrate is defined as the TCLP extract and is analyzed directly. Proceed to Section 7.3.15.

7.3.11 The liquid phase may now be either analyzed immediately (See Sections 7.3.13 through 7.3.15) or stored at 4 °C under minimal headspace conditions until time of analysis. Determine the weight of extraction fluid #1 to add to the ZHE as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (Section 7.1.1)} \times \text{weight of waste filtered (Section 7.3.4 or 7.3.8)}}{100}$$

7.3.12 The following Sections detail how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid #1 is used in all cases (See Section 5.7).

7.3.12.1 With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid in- let/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.

7.3.12.2 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5-10 psi (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5-10 psi and check all ZHE fittings to ensure that they are closed.

7.3.12.3 Place the ZHE in the rotary agitation appara- tus (if it is not already there) and rotate at 30 $\pm$ 2 rpm for 18 $\pm$ 2 hours. Ambient temperature (i.e., temperature of room in which extraction occurs) shall be maintained at 23 $\pm$ 2 °C during agita- tion.

7.3.13 Following the 18 $\pm$ 2 hour agitation period, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If the pressure has not been maintained (i.e., no gas release observed), the device is leaking. Check the ZHE for leaking as specified in Section 4.2.1, and perform the extraction again with a new sample of waste. If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases. If the waste contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container (i.e., TEDLAR® bag) holding the initial liquid phase of the waste. A separate filtrate collection container must be used if combining would create multiple phases, or there is not enough volume left within the filtrate collection container. Filter through the glass fiber filter, using the ZHE device as discussed in Section 7.3.9. All extract shall be filtered and collected if the

TEDLAR® bag is used, if the extract is multiphasic, or if the waste contained an initial liquid phase (see Sections 4.6 and 7.3.1).

NOTE: An in-line glass fiber filter may be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured.

7.3.14 If the original waste contained no initial liquid phase, the filtered liquid material obtained from Section 7.3.13 is defined as the TCLP extract. If the waste contained an initial liquid phase, the filtered liquid material obtained from Section 7.3.13 and the initial liquid phase (Section 7.3.9) are collectively defined as the TCLP extract.

7.3.15 Following collection of the TCLP extract, immediately prepare the extract for analysis and store with minimal headspace at 4 °C until analyzed. Analyze the TCLP extract according to the appropriate analytical methods. If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phases (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.3.16 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

8.1 QUALITY ASSURANCE

8.2 A minimum of one blank (using the same extraction fluid as used for the samples) must be analyzed for every 20 extractions that have been conducted in an extraction vessel.

8.3 A matrix spike shall be performed for each waste type (e.g., wastewater treatment sludge, contaminated soil, etc.) unless the result exceeds the regulatory level and the data are being used solely to demonstrate that the waste property exceeds the regulatory level. A minimum of one matrix spike must be analyzed for each analytical batch. As a minimum, follow the matrix spike addition guidance provided in each analytical method.

8.3.1 Matrix spikes are to be added after filtration of the TCLP extract and before preservation. Matrix spikes should not be added prior to TCLP extraction of the sample.

8.3.2 In most cases, matrix spikes should be added at a concentration equivalent to the corresponding regulatory level. If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentra- tion, but may not be not less than five times the method detection limit. In order to avoid differences in matrix effects, the matrix spikes must be added to the same nominal volume of TCLP extract as that which was analyzed for the unspiked sample.

8.3.3 The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to determine whether matrix interferences exist. Use of other internal calibration methods, modification of the analytical methods, or use of alternate analytical methods may be needed to accurately measure the analyte concentration in the TCLP extract when the recovery of the matrix spike is below the expected analytical method performance.

8.3.4 Matrix spike recoveries are calculated by the following formula:

$\%R\ (\%Recovery) = 100\ (X_s - X_u)/K$

where:
X_s = measured value for the spiked sample,
X_u = measured value for the unspiked sample, and
K = known value of the spike in the sample.

8.4 All quality control measures described in the appropriate analytical methods shall be followed.

8.5 The use of internal calibration quantitation methods shall be employed for a metallic contaminant if: (1) Recovery of the contaminant from the TCLP extract is not at least 50% and the concentration does not exceed the regulatory level, and (2) The concentration of the contaminant measured in the extract is within 20% of the appropriate regulatory level.

8.4.1. The method of standard additions shall be employed as the internal calibration quantitation method for each metallic contaminant.

8.4.2 The method of standard additions requires preparing calibration standards in the sample matrix rather than reagent water or blank solution. It requires taking four identical aliquots of the solution and adding known amounts of standard to three of these aliquots. The forth aliquot is the unknown. Preferably, the first addition should be prepared so that the resulting concentration is approximately 50% of the expected concentration of the sample. The second and third additions should be prepared so that the concentrations are approximately 100% and

150% of the expected concentration of the sample. All four aliquots are maintained at the same final volume by adding reagent water or a blank solution, and may need dilution adjustment to maintain the signals in the linear range of the instrument technique. All four aliquots are analyzed.

8.4.3 Prepare a plot, or subject data to linear regression, of instrument signals or external-calibration-derived concentrations as the dependant variable (y-axis) versus concentrations of the additions of standard as the independent variable (x-axis). Solve for the intercept of the abscissa (the independent variable, x-axis) which is the concentration in the unknown.

8.4.4 Alternately, subtract the instrumental signal or external- calibration-derived concentration of the unknown (unspiked) sample from the instrumental signals or external-calibration-derived concentrations of the standard additions. Plot or subject to linear regression of the corrected instrument signals or external-calibration-derived concentra- tions as the dependant variable versus the independent variable. Derive concentrations for unknowns using the internal calibration curve as if it were an external calibration curve.

8.5 Samples must undergo TCLP extraction within the following time periods:

SAMPLE MAXIMUM HOLDING TIMES [DAYS]

	From: Field collection To: TCLP extraction	From: TCLP extraction To: Preparative extraction	From: Preparative extraction To: Determinative analysis	Total elapsed time
Volatiles	14	NA	14	28
Semi-volatiles	14	7	40	61
Mercury	28	NA	28	56
Metals, except mercury	180	NA	180	360

NA = Not applicable

If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding the holding time is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory level.

9.1 METHOD PERFORMANCE

9.2 Ruggedness. Two ruggedness studies have been performed to determine the effect of various perturbations on specific elements of the TCLP protocol. Ruggedness testing determines the sensitivity of small procedural variations which might be expected to occur during routine laboratory application.

9.2.1 Metals - The following conditions were used when leaching a waste for metals analysis:

Varying Conditions	
Liquid/Solid ratio	19:1 vs. 21:1
Extraction time	16 hours vs. 18 hours
Headspace	20% vs. 60%
Buffer #2 acidity	190 meq vs. 210 meq
Acid-washed filters	yes vs. no
Filter type	0.7 µm glass fiber vs. 0.45 µm vs. polycarbonate
Bottle type	borosilicate vs. flint glass

Of the seven method variations examined, acidity of the extraction fluid had the greatest impact on the results. Four of 13 metals from an API separator sludge/electroplating waste (API/EW) mixture and two of three metals from an ammonia lime still bottom waste were extracted at higher levels by the more acidic buffer. Because of the sensitivity to pH changes, the method requires that the extraction fluids be prepared so that the final pH is within $\pm$ 0.05 units as specified.

9.2.2 Volatile Organic Compounds - The following conditions were used when leaching a waste for VOC analysis:

Varying Conditions	
Liquid/Solid ratio	19:1 vs. 21:1
Headspace	0% vs. 5%
Buffer #1 acidity	60 meq vs. 80 meq
Method of storing extract	Syringe vs. Tedlar® bag
Aliquotting	yes vs. no
Pressure behind piston	0 psi vs. 20 psi

None of the parameters had a significant effect on the results of the ruggedness test.

9.3 Precision. Many TCLP precision (reproducibility) studies have been performed, and have shown that, in general, the precision of the TCLP is comparable to or exceeds that of the EP toxicity test and that method precision is adequate. One of the more significant contributions to poor precision appears to be related to sample homogeneity and inter-laboratory variation (due to the nature of waste materials).

9.3.1 Metals - The results of a multi-laboratory study are shown in Table 6, and indicate that a single analysis of a waste may not be adequate for waste characterization and identification requirements.

9.3.2 Semi-Volatile Organic Compounds - The results of two studies are shown in Tables 7 and 8. Single laboratory precision was excellent with greater than 90 percent of the results exhibiting an RSD less than 25 percent. Over 85 percent of all individual compounds in the multi-laboratory study fell in the RSD range of 20 - 120 percent. Both studies concluded that the TCLP provides adequate precision. It was also determined that the high acetate content of the extraction fluid did not present problems (i.e., column degradation of the gas chromatograph) for the analytical conditions used.

9.3.3 Volatile Organic Compounds - Eleven laboratories participated in a collaborative study of the use of the ZHE with two waste types which were fortified with a mixture of VOCs. The results of the collaborative study are shown in Table 9. Precision results for VOCs tend to occur over a considerable range. However, the range and mean RSD compared very closely to the same collaborative study metals results in Table 6. Blackburn and Show concluded that at the 95% level of signifi- cance: 1) recoveries among laboratories were statistically similar, 2) recoveries did not vary significantly between the two sample types, and 3) each laboratory showed the same pattern of recovery for each of the two samples.

10.0 REFERENCES

1. Blackburn, W.B. and Show, I. "Collaborative Study of the Toxicity Characteristics Leaching Procedure (TCLP)." Draft Final Report, Contract No. 68- 03-1958, S-Cubed, November 1986.

2. Newcomer, L.R., Blackburn, W.B., Kimmell, T.A. "Performance of the Toxicity Characteristic Leaching Procedure." Wilson Laboratories, S-Cubed, U.S. EPA, December 1986.

3. Williams, L.R., Francis, C.W.; Maskarinec, M.P., Taylor D.R., and Rothman,
N. "Single-Laboratory Evaluation of Mobility Procedure for Solid Waste." EMSL, ORNL, S-Cubed, ENSECO.

Table 1.
Volatile Analytes[1,2]

Compound	CAS No.
Acetone	67-64-1
Benzene	71-43-2
n-Butyl alcohol	71-36-3
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroform	67-66-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethylene	75-35-4
Ethyl acetate	141-78-6
Ethyl benzene	100-41-4
Ethyl ether	60-29-7
Isobutanol	78-83-1
Methanol	67-56-1
Methylene chloride	75-09-2
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-1
Tetrachloroethylene	127-18-4
Toluene	108-88-3
1,1,1,-Trichloroethane	71-55-6
Trichloroethylene	79-01-6
Trichlorofluoromethane	75-69-4
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1
Vinyl chloride	75-01-4
Xylene	1330-20-7

[1] When testing for any or all of these analytes, the zero-headspace extractor vessel shall be used instead of the bottle extractor.

[2] Benzene, carbon tetrachloride, chlorobenzene, chloroform, 1,2-dichloroethane, 1,1-dichloroethylene, methyl ethyl ketone, tetrachloroethylene, and vinyl chloride are toxicity characteristic constituents.

Table 2.
Suitable Rotary Agitation Apparatus[1]

Company	Location	Model No.
Analytical Testing and Services,	Warrington, PA (215) 343-4490	4-vessel extractor (DC20S) Consulting 8-vessel extractor (DC20) Inc. 12-vessel extractor (DC20B) 24-vessel extractor (DC24C)
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	2-vessel (3740-2-BRE) 4-vessel (3740-4-BRE) 6-vessel (3740-6-BRE) 8-vessel (3740-8-BRE) 12-vessel (3740-12-BRE) 24-vessel (3740-24-BRE)
Environmental Machine and Inc.	Lynchburg, VA (804) 845-6424	8-vessel (08-00-00) Design, 4-vessel (04-00-00)
IRA Machine Shop and Laboratory	Santurce, PR (809) 752-4004	8-vessel (011001)
Lars Lande Manufacturing	Whitmore Lake, MI (313) 449-4116	10-vessel (10VRE) 5-vessel (5VRE) 6-vessel (6VRE)
Millipore Corp.	Bedford, MA (800) 225-3384	4-ZHE or 4 2-liter bottle extractor (YT31ORAHW)

[1] Any device that rotates the extraction vessel in an end-over-end fashion at 30 ± 2 rpm is acceptable.

Table 3.
Suitable Zero-Headspace Extractor Vessels[1]

Company	Location	Model No.
Analytical Testing & Consulting Services, Inc.	Warrington, PA (215) 343-4490	C1O2, Mechanical Pressure Device
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	3745-ZHE, Gas Pressure Device
Lars Lande Manufacturing[2]	Whitmore Lake, MI (313) 449-4116	ZHE-11, Gas Pressure Device
Millipore Corporation	Bedford, MA (800) 225-3384	YT30O9OHW, Gas Pressure Device
Environmental Machine and Design, Inc.	Lynchburg, VA (804) 845-6424	VOLA-TOX1, Gas Pressure Device
Gelman Science	Ann Arbor, MI 521-1520	15400 Gas Pressure (800) Device

[1] Any device that meets the specifications listed in Section 4.2.1 of the method is suitable.

[2] This device uses a 110 mm filter.

Table 4.
Suitable Filter Holders[1]

Company	Location	Model/ Catalogue No.	Size
Nucleopore Corporation	Pleasanton, CA (800) 882-7711	425910 410400	142 mm 47 mm
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	302400 311400	142 mm 47 mm
Millipore Corporation	Bedford, MA (800) 225-3384	YT30142HW XX1004700	142 mm 47 mm

[1] Any device capable of separating the liquid from the solid phase of the waste is suitable, providing that it is chemically compatible with the waste and the constituents to be analyzed. Plastic devices (not listed above) may be used when only inorganic analytes are of concern. The 142 mm size filter holder is recommended.

Table 5.
Suitable Filter Media[1]

Company	Location	Model	Pore Size (µm)
Millipore Corporation	Bedford, MA (800) 225-3384	AP40	0.7
Nucleopore Corporation	Pleasanton, CA (415) 463-2530	211625	0.7
Whatman Laboratory Products, Inc.	Clifton, NJ (201) 773-5800	GFF	0.7
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	GF75	0.7
Gelman Science	Ann Arbor, MI (800) 521-1520	66256 (90mm) 66257 (142mm)	0.7

[1] Any filter that meets the specifications in Section 4.4 of the Method is suitable.

Table 6. Multi-Laboratory TCLP Metals, Precision

Waste	Extraction Fluid	Metal	$\bar{X}$	S	%RSD
Ammonia	#1	Cadmium	0.053	0.031	60
Lime Still	#2		0.023	0.017	76
Bottoms	#1	Chromium	0.015	0.0014	93
	#2		0.0032	0.0037	118
	#1	Lead	0.0030	0.0027	90
	#2		0.0032	0.0028	87
API/EW	#1	Cadmium	0.0046	0.0028	61
Mixture	#2		0.0005	0.0004	77
	#1	Chromium	0.0561	0.0227	40
	#2		0.105	0.018	17
	#1	Lead	0.0031	0.0031	100
	#2		0.0124	0.0136	110
Fossil	#1	Cadmium	0.080	0.069	86
Fuel Fly	#2		0.093	0.067	72
Ash	#1	Chromium	0.017	0.014	85
	#2		0.070	0.040	57
	#1	Lead	0.0087	0.0074	85
	#2		0.0457	0.0083	18
				%RSD Range = 17 - 118 Mean	
				%RSD = 74	

NOTE: $\bar{X}$ = Mean results from 6 - 12 different laboratories Units = mg/L
Extraction Fluid #1 = pH 4.9
#2 = pH 2.9

Table 7. Single-Laboratory Semi-Volatiles, Precision

Waste	Compound	Extraction Fluid	$\overline{X}$	S	%RSD
Ammonia	Phenol	#1	19000	2230	11.6
Lime Still		#2	19400	929	4.8
Bottoms	2-Methylphenol	#1	2000	297	14.9
		#2	1860	52.9	2.8
	4-Methylphenol	#1	7940	1380	17.4
		#2	7490	200	2.7
	2,4-Dimethylphenol	#1	321	46.8	14.6
		#2	307	45.8	14.9
	Naphthalene	#1	3920	413	10.5
		#2	3827	176	4.6
	2-Methylnaphthalene	#1	290	44.8	15.5
		#2	273	19.3	7.1
	Dibenzofuran	#1	187	22.7	12.1
		#2	187	7.2	3.9
	Acenaphthylene	#1	703	89.2	12.7
		#2	663	20.1	3.0
	Fluorene	#1	151	17.6	11.7
		#2	156	2.1	1.3
	Phenanthrene	#1	241	22.7	9.4
		#2	243	7.9	3.3
	Anthracene	#1	33.2	6.19	18.6
		#2	34.6	1.55	4.5
	Fluoranthrene	#1	25.3	1.8	7.1
		#2	26.0	1.8	7.1
API/EW	Phenol	#1	40.7	13.5	33.0
Mixture		#2	19.0	1.76	9.3
	2,4-Dimethylphenol	#1	33.0	9.35	28.3
		#2	43.3	8.61	19.9
	Naphthalene	#1	185	29.4	15.8
		#2	165	24.8	15.0
	2-Methylnaphthalene	#1	265	61.2	23.1
		#2	200	18.9	9.5
				%RSD Range = 1 - 33	
				Mean %RSD = 12	

NOTE: Units = µg/L
Extractions were performed in triplicate
All results were at least 2x the detection limit Extraction Fluid #1 = pH 4.9
#2 = pH 2.9

Table 8. Multi-Laboratory Semi-Volatiles, Precision

Waste	Compound	Extraction Fluid	$\overline{X}$	S	%RSD
Ammonia Lime	BNAs	#1	10043	7680	76.5
Still Bottoms (A)		#2	10376	6552	63.1
API/EW	BNAs	#1	1624	675	41.6
Mixture (B)		#2	2074	1463	70.5
Fossil Fuel	BNAs	#1	750	175	23.4
Fly Ash (C)		#2	739	342	46.3
					Mean %RSD = 54

NOTE: Units = µg/L
X = Mean results from 3 - 10 labs Extraction Fluid #1 = pH 4.9
#2 = pH 2.9

%RSD Range for Individual Compounds

A, #1	0 - 113
A, #2	28 - 108
B, #1	20 - 156
B, #2	49 - 128
C, #1	36 - 143
C, #2	61 - 164

Table 9. Multi-Laboratory (11 Labs) VOCs, Precision

Waste	Compound	$\bar{X}$	S	%RSD
Mine Tailings	Vinyl chloride	6.36	6.36	100
	Methylene chloride	12.1	11.8	98
	Carbon disulfide	5.57	2.83	51
	1,1-Dichloroethene	21.9	27.7	127
	1,1-Dichloroethane	31.4	25.4	81
	Chloroform	46.6	29.2	63
	1,2-Dichloroethane	47.8	33.6	70
	2-Butanone	43.5	36.9	85
	1,1,1-Trichloroethane	20.9	20.9	100
	Carbon tetrachloride	12.0	8.2	68
	Trichloroethene	24.7	21.2	86
	1,1,2-Trichloroethene	19.6	10.9	56
	Benzene	37.9	28.7	76
	1,1,2,2-Tetrachloroethane	34.9	25.6	73
	Toluene	29.3	11.2	38
	Chlorobenzene	35.6	19.3	54
	Ethylbenzene	4.27	2.80	66
	Trichlorofluoromethane	3.82	4.40	115
	Acrylonitrile	76.7	110.8	144
Ammonia Lime Still Bottoms	Vinyl chloride	5.00	4.71	94
	Methylene chloride	14.3	13.1	92
	Carbon disulfide	3.37	2.07	61
	1,1-Dichloroethene	52.1	38.8	75
	1,1-Dichloroethane	52.8	25.6	49
	Chloroform	64.7	28.4	44
	1,2-Dichloroethane	43.1	31.5	73
	2-Butanone	59.0	39.6	67
	1,1,1-Trichloroethane	53.6	40.9	76
	Carbon tetrachloride	7.10	6.1	86
	Trichloroethene	57.3	34.2	60
	1,1,2-Trichloroethene	6.7	4.7	70
	Benzene	61.3	26.8	44
	1,1,2,2-Tetrachloroethane	3.16	2.1	66
	Toluene	69.0	18.5	27
	Chlorobenzene	71.8	12.0	17
	Ethylbenzene	3.70	2.2	58
	Trichlorofluoromethane	4.05	4.8	119
	Acrylonitrile	29.4	34.8	118
				%RSD Range = 17 - 144 Mean %RSD = 75

NOTE: Units = µg/L

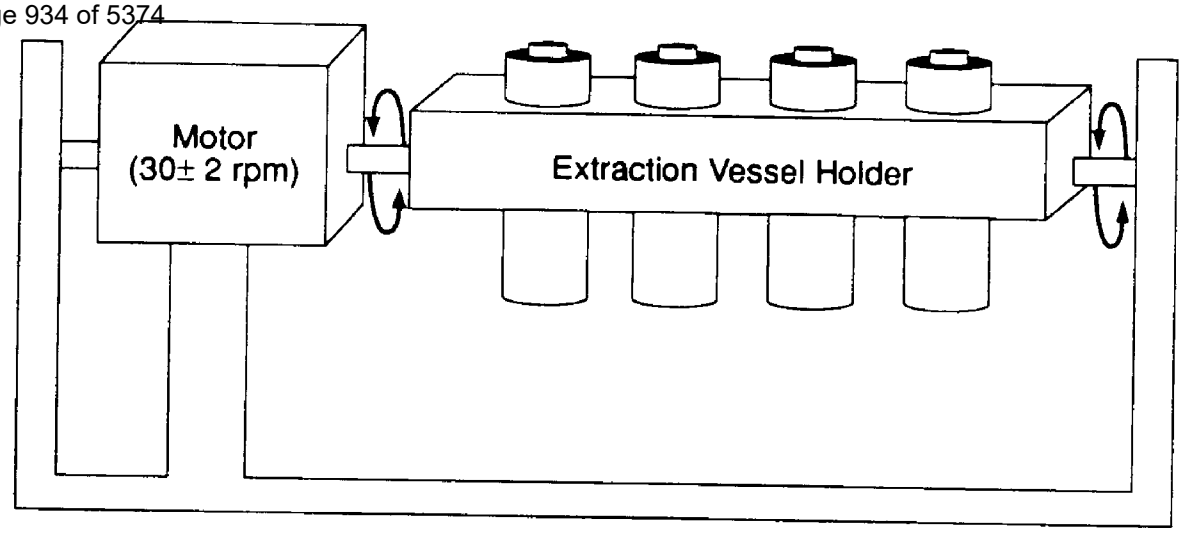


Figure 1. Rotary Agitation Apparatus

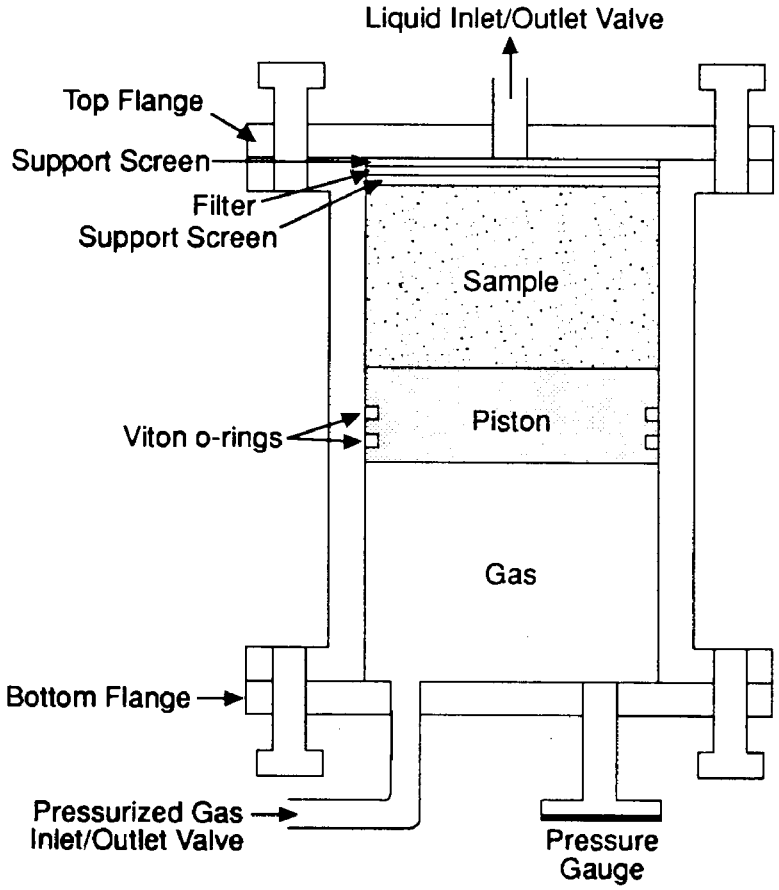
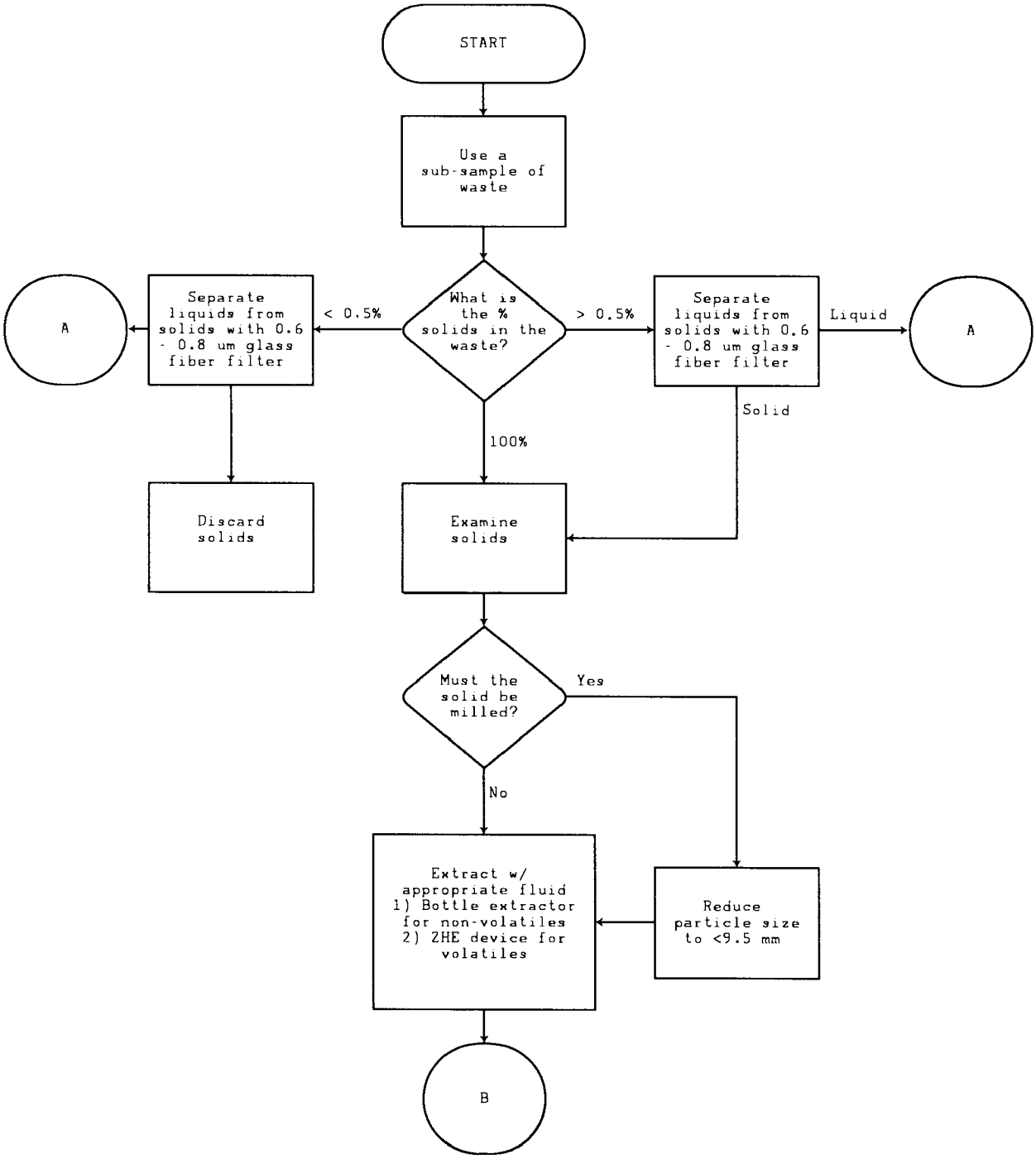
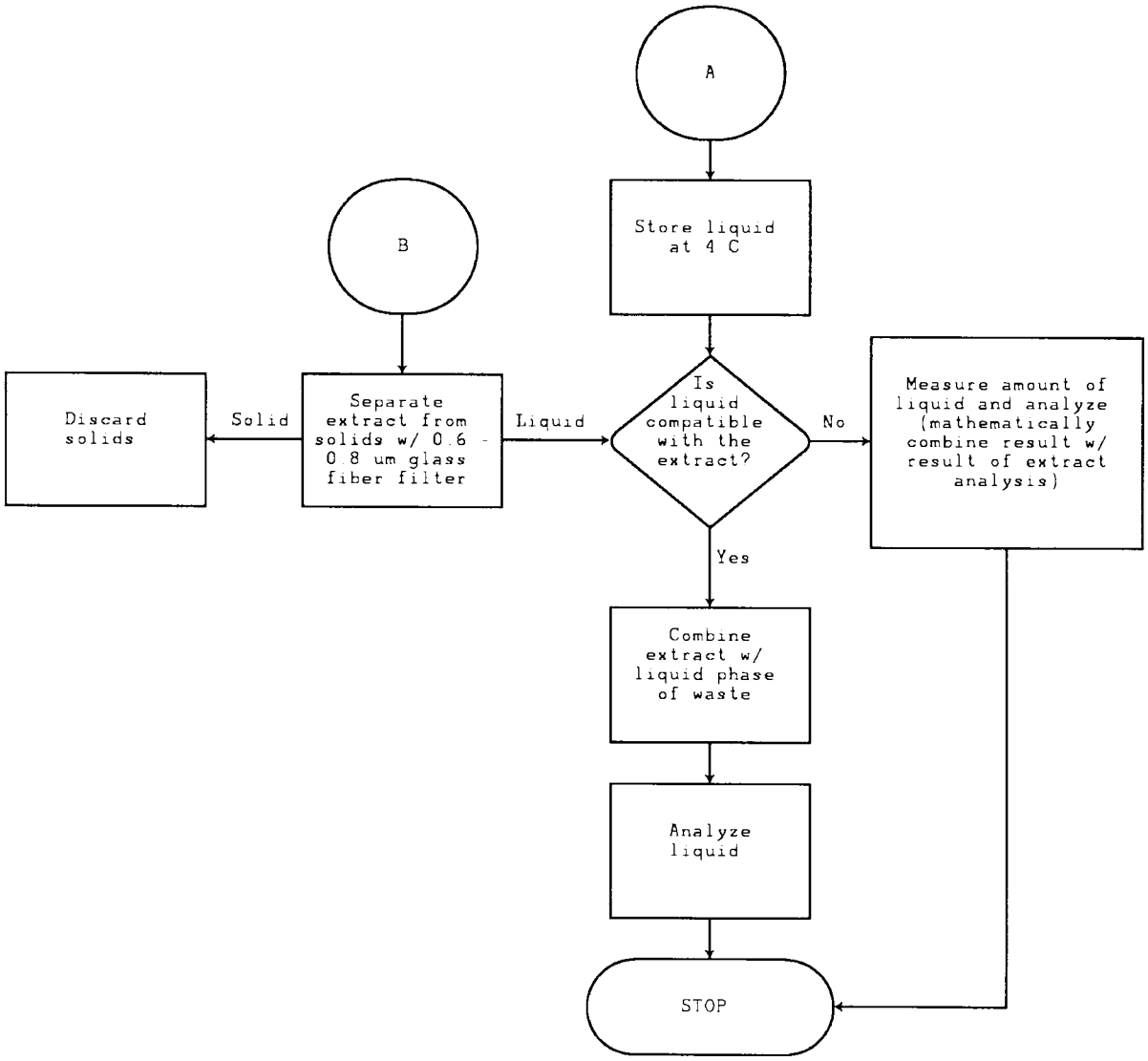


Figure 2. Zero-Headspace Extractor (ZHE)

TOXICITY CHARACTERISTIC LEACHATE PROCEDURE



CHARACTERISTIC LEACHATE PROCEDURE



State of Oregon Department of Environmental Quality

OAR 340-105-0113 Attachments

Modification Types Based on Regulatory Descriptions

1. General Classifications of Permit Modifications and Crosswalk to Applicable Regulations.

2. Classification of Permit Modifications as listed in Appendix I to §270.42

1. General Classifications of Permit Modifications and Crosswalk to Applicable Regulations.

Modifications Category in Appendix I to §270.42	40 CFR Reference
B. General Facility Standards	40 CFR 264 Subpart B
C. Ground-Water Protection	40 CFR 264 Subpart F
D. Closure	40 CFR 264 Subpart G 264.111 – 264.115
E. Post-Closure	40 CFR 264 Subpart G 264.116 – 264.120
F. Containers	40 CFR 264 Subpart I
G. Tanks	40 CFR 264 Subpart J
H. Surface Impoundments	40 CFR 264 Subpart K
I. Enclosed Waste Piles	40 CFR 264 Subpart L
J. Landfills and Unenclosed Waste Piles	40 CFR 264 Subpart N
K. Land Treatment	40 CFR 264 Subpart M
L. Incinerators, Boilers, and Industrial Furnaces	40 CFR 264 Subpart O
M. Containment Buildings	40 CFR 264 Subpart DD
N. Corrective Action	40 CFR 264 Subpart S
O. Burden Reduction	various

40 CFR 270 Subparts

SUBPART O - INCINERATORS - in addition to L above, refer to 40 CFR 270.42(j) and 270.42(k)
SUBPART EE - HAZARDOUS WASTE MUNITIONS AND EXPLOSIVES STORAGE -refer to 40 CFR 270.42(h)

40 CFR 264 Subparts without a specific Permit Modification Category in 40 CFR 270.42 Appendix I

SUBPART C - PREPAREDNESS AND PREVENTION
SUBPART D - CONTINGENCY PLAN AND EMERGENCY PROCEDURES
SUBPART E - MANIFEST SYSTEM, RECORDKEEPING, AND REPORTING
SUBPART H - FINANCIAL REQUIREMENTS
SUBPART W - DRIP PADS
SUBPART X - MISCELLANEOUS UNITS
SUBPART AA - AIR EMISSION STANDARDS FOR PROCESS VENTS
SUBPART BB - AIR EMISSION STANDARDS FOR EQUIPMENT LEAKS
SUBPART CC - AIR EMISSION STANDARDS FOR TANKS, SURFACE IMPOUNDMENTS, AND CONTAINERS
SUBPART EE - HAZARDOUS WASTE MUNITIONS AND EXPLOSIVES STORAGE

2. Classification of Permit Modifications as listed in in Appendix I to §270.42

Modifications	Class	Minor (Mi)
A. ***General Permit Provisions***		
1. Administrative and informational changes	1	Mi*
2. Correction of typographical errors	1	Mi*
3. Equipment replacement or upgrading with functionally equivalent components (e.g., pipes, valves, pumps, conveyors, controls)	1	
4. Changes in the frequency of or procedures for monitoring, reporting, sampling, or maintenance activities by the permittee:		
a. To provide for more frequent monitoring, reporting, sampling, or maintenance	1	Mi*
b. Other changes	2	
5. Schedule of compliance:		
a. Changes in interim compliance dates, with prior approval of the Director	[1]1	Mi*
b. Extension of final compliance date	3	
6. Changes in expiration date of permit to allow earlier permit termination, with prior approval of the Director	[1]1	
7. Changes in ownership or operational control of a facility, provided the procedures of §270.40(b) are followed	[1]1	Mi*
8. Changes to remove permit conditions that are no longer applicable (*i.e.,* because the standards upon which they are based are no longer applicable to the facility).	[1]1	
9. Changes to remove permit conditions applicable to a unit excluded under the provisions of §261.4.	[1]1	
10. Changes in the expiration date of a permit issued to a facility at which all units are excluded under the provisions of §261.4.	[1]1	
B. ***General Facility Standards*** **40 CFR 264 Subpart B**		
1. Changes to waste sampling or analysis methods:		
a. To conform with agency guidance or regulations	1	
b. To incorporate changes associated with F039 (multi-source leachate) sampling or analysis methods	1	
c. To incorporate changes associated with underlying hazardous constituents in ignitable or corrosive wastes	[1]1	
d. Other changes	2	
2. Changes to analytical quality assurance/control plan:		
a. To conform with agency guidance or regulations	1	
b. Other changes	2	
3. Changes in procedures for maintaining the operating record	1	
4. Changes in frequency or content of inspection schedules	2	
5. Changes in the training plan:		
a. That affect the type or decrease the amount of training given to employees	2	
b. Other changes	1	

Modifications	Class	Minor (Mi)
6. Contingency plan:		
a. Changes in emergency procedures (i.e., spill or release response procedures)	2	
b. Replacement with functionally equivalent equipment, upgrade, or relocate emergency equipment listed	1	Mi*
c. Removal of equipment from emergency equipment list	2	
d. Changes in name, address, or phone number of coordinators or other persons or agencies identified in the plan	1	Mi*
7. Construction quality assurance plan:		
a. Changes that the CQA officer certifies in the operating record will provide equivalent or better certainty that the unit components meet the design specifications	1	
b. Other changes	2	
Note: When a permit modification (such as introduction of a new unit) requires a change in facility plans or other general facility standards, that change shall be reviewed under the same procedures as the permit modification.		
C. ***Ground-Water Protection*** **40 CFR 264 Subpart F**		
1. Changes to wells:		
a. Changes in the number, location, depth, or design of upgradient or downgradient wells of permitted ground-water monitoring system	2	
b. Replacement of an existing well that has been damaged or rendered inoperable, without change to location, design, or depth of the well	1	
2. Changes in ground-water sampling or analysis procedures or monitoring schedule, with prior approval of the Director	[1]1	
3. Changes in statistical procedure for determining whether a statistically significant change in ground-water quality between upgradient and downgradient wells has occurred, with prior approval of the Director	[1]1	
4. Changes in point of compliance	2	
5. Changes in indicator parameters, hazardous constituents, or concentration limits (including ACLs):		
a. As specified in the groundwater protection standard	3	
b. As specified in the detection monitoring program	2	
6. Changes to a detection monitoring program as required by §264.98(h), unless otherwise specified in this appendix	2	
7. Compliance monitoring program:		
a. Addition of compliance monitoring program as required by §§264.98(g)(4) and 264.99	3	
b. Changes to a compliance monitoring program as required by §264.99(j), unless otherwise specified in this appendix	2	
8. Corrective action program:		
a. Addition of a corrective action program as required by §§264.99(h)(2) and 264.100	3	
b. Changes to a corrective action program as required by §264.100(h), unless otherwise specified in this appendix	2	

Modifications	Class	Minor (Mi)
D. ***Closure*** **40 CFR 264 Subpart G 264.111 – 264.115**		
1. Changes to the closure plan:		
a. Changes in estimate of maximum extent of operations or maximum inventory of waste on-site at any time during the active life of the facility, with prior approval of the Director	[1]1	Mi*
b. Changes in the closure schedule for any unit, changes in the final closure schedule for the facility, or extension of the closure period, with prior approval of the Director	[1]1	Mi*
c. Changes in the expected year of final closure, where other permit conditions are not changed, with prior approval of the Director	[1]1	Mi*
d. Changes in procedures for decontamination of facility equipment or structures, with prior approval of the Director	[1]1	
e. Changes in approved closure plan resulting from unexpected events occurring during partial or final closure, unless otherwise specified in this appendix	2	
f. Extension of the closure period to allow a landfill, surface impoundment or land treatment unit to receive non-hazardous wastes after final receipt of hazardous wastes under §264.113 (d) and (e)	2	
2. Creation of a new landfill unit as part of closure	3	
3. Addition of the following new units to be used temporarily for closure activities:		
a. Surface impoundments	3	
b. Incinerators	3	
c. Waste piles that do not comply with §264.250(c)	3	
d. Waste piles that comply with §264.250(c)	2	
e. Tanks or containers (other than specified below)	2	
f. Tanks used for neutralization, dewatering, phase separation, or component separation, with prior approval of the Director	[1]1	
g. Staging piles	2	
E. ***Post-Closure*** **40 CFR 264 Subpart G 264.116 – 264.120**		
1. Changes in name, address, or phone number of contact in post-closure plan	1	
2. Extension of post-closure care period	2	
3. Reduction in the post-closure care period	3	
4. Changes to the expected year of final closure, where other permit conditions are not changed	1	
5. Changes in post-closure plan necessitated by events occurring during the active life of the facility, including partial and final closure	2	
F. ***Containers*** **40 CFR 264 Subpart I**		
1. Modification or addition of container units:		
a. Resulting in greater than 25% increase in the facility's container storage capacity, except as provided in F(1)(c) and F(4)(a) below	3	
b. Resulting in up to 25% increase in the facility's container storage capacity, except as provided in F(1)(c) and F(4)(a) below	2	

Modifications	Class	Minor (Mi)
c. Or treatment processes necessary to treat wastes that are restricted from land disposal to meet some or all of the applicable treatment standards or to treat wastes to satisfy (in whole or in part) the standard of "use of practically available technology that yields the greatest environmental benefit" contained in §268.8(a)(2)(ii), with prior approval of the Director. This modification may also involve addition of new waste codes or narrative descriptions of wastes. It is not applicable to dioxin-containing wastes (F020, 021, 022, 023, 026, 027, and 028)	[1]1	
2.		
a. Modification of a container unit without increasing the capacity of the unit	2	
b. Addition of a roof to a container unit without alteration of the containment system	1	
3. Storage of different wastes in containers, except as provided in (F)(4) below:		
a. That require additional or different management practices from those authorized in the permit	3	
b. That do not require additional or different management practices from those authorized in the permit	2	
Note: See §270.42(g) for modification procedures to be used for the management of newly listed or identified wastes.		
4. Storage or treatment of different wastes in containers:		
a. That require addition of units or change in treatment process or management standards, provided that the wastes are restricted from land disposal and are to be treated to meet some or all of the applicable treatment standards, or that are to be treated to satisfy (in whole or in part) the standard of "use of practically available technology that yields the greatest environmental benefit" contained in §268.8(a)(2)(ii). This modification is not applicable to dioxin-containing wastes (F020, 021, 022, 023, 026, 027, and 028)	[1]1	
b. That do not require the addition of units or a change in the treatment process or management standards, and provided that the units have previously received wastes of the same type (e.g., incinerator scrubber water). This modification is not applicable to dioxin-containing wastes (F020, 021, 022, 023, 026, 027, and 028)	[1]1	
G. ***Tanks*** **40 CFR 264 Subpart J**		
1.		
a. Modification or addition of tank units resulting in greater than 25% increase in the facility's tank capacity, except as provided in G(1)(c), G(1)(d), and G(1)(e) below	3	
b. Modification or addition of tank units resulting in up to 25% increase in the facility's tank capacity, except as provided in G(1)(d) and G(1)(e) below	2	
c. Addition of a new tank that will operate for more than 90 days using any of the following physical or chemical treatment technologies: neutralization, dewatering, phase separation, or component separation	2	
d. After prior approval of the Director, addition of a new tank that will operate for up to 90 days using any of the following physical or chemical treatment technologies: neutralization, dewatering, phase separation, or component separation	[1]1	
e. Modification or addition of tank units or treatment processes necessary to treat wastes that are restricted from land disposal to meet some or all of the applicable treatment standards or to treat wastes to satisfy (in whole or in part) the standard of	[1]1	

Modifications	Class	Minor (Mi)
"use of practically available technology that yields the greatest environmental benefit" contained in §268.8(a)(2)(ii), with prior approval of the Director. This modification may also involve addition of new waste codes. It is not applicable to dioxin-containing wastes (F020, 021, 022, 023, 026, 027, and 028)		
2. Modification of a tank unit or secondary containment system without increasing the capacity of the unit	2	
3. Replacement of a tank with a tank that meets the same design standards and has a capacity within ±10% of the replaced tank provided	1	
—The capacity difference is no more than 1500 gallons,		
—The facility's permitted tank capacity is not increased, and		
—The replacement tank meets the same conditions in the permit.		
4. Modification of a tank management practice	2	
5. Management of different wastes in tanks:		
a. That require additional or different management practices, tank design, different fire protection specifications, or significantly different tank treatment process from that authorized in the permit, except as provided in (G)(5)(c) below	3	
b. That do not require additional or different management practices, tank design, different fire protection specifications, or significantly different tank treatment process than authorized in the permit, except as provided in (G)(5)(d)	2	
c. That require addition of units or change in treatment processes or management standards, provided that the wastes are restricted from land disposal and are to be treated to meet some or all of the applicable treatment standards or that are to be treated to satisfy (in whole or in part) the standard of "use of practically available technology that yields the greatest environmental benefit" contained in §268.8(a)(2)(ii). The modification is not applicable to dioxin-containing wastes (F020, 021, 022, 023, 026, 027, and 028)	[1]1	
d. That do not require the addition of units or a change in the treatment process or management standards, and provided that the units have previously received wastes of the same type (e.g., incinerator scrubber water). This modification is not applicable to dioxin-containing wastes (F020, 021, 022, 023, 026, 027, and 028)	1	
Note: See §270.42(g) for modification procedures to be used for the management of newly listed or identified wastes.		
H. ***Surface Impoundments*** **40 CFR Subpart K**		
1. Modification or addition of surface impoundment units that result in increasing the facility's surface impoundment storage or treatment capacity	3	
2. Replacement of a surface impoundment unit	3	
3. Modification of a surface impoundment unit without increasing the facility's surface impoundment storage or treatment capacity and without modifying the unit's liner, leak detection system, or leachate collection system	2	
4. Modification of a surface impoundment management practice	2	
5. Treatment, storage, or disposal of different wastes in surface impoundments:		
a. That require additional or different management practices or different design of the liner or leak detection system than authorized in the permit	3	

Modifications	Class	Minor (Mi)
b. That do not require additional or different management practices or different design of the liner or leak detection system than authorized in the permit	2	
c. That are wastes restricted from land disposal that meet the applicable treatment standards or that are treated to satisfy the standard of "use of practically available technology that yields the greatest environmental benefit" contained in §269.8(a)(2)(ii), and provided that the unit meets the minimum technological requirements stated in §268.5(h)(2). This modification is not applicable to dioxin-containing wastes (F020, 021, 022, 023, 026, 027, and 028)	1	
d. That are residues from wastewater treatment or incineration, provided that disposal occurs in a unit that meets the minimum technological requirements stated in §268.5(h)(2), and provided further that the surface impoundment has previously received wastes of the same type (for example, incinerator scrubber water). This modification is not applicable to dioxin-containing wastes (F020, 021, 022, 023, 026, 027, and 028)	1	
6. Modifications of unconstructed units to comply with §§264.221(c), 264.222, 264.223, and 264.226(d)	[1]1	
7. Changes in response action plan:		
a. Increase in action leakage rate	3	
b. Change in a specific response reducing its frequency or effectiveness	3	
c. Other changes	2	
Note: See §270.42(g) for modification procedures to be used for the management of newly listed or identified wastes		
I. ***Enclosed Waste Piles***. For all waste piles except those complying with §264.250(c), modifications are treated the same as for a landfill. The following modifications are applicable only to waste piles complying with §264.250(c). **40 CFR 264 Subpart L**		
1. Modification or addition of waste pile units:		
a. Resulting in greater than 25% increase in the facility's waste pile storage or treatment capacity	3	
b. Resulting in up to 25% increase in the facility's waste pile storage or treatment capacity	2	
2. Modification of waste pile unit without increasing the capacity of the unit	2	
3. Replacement of a waste pile unit with another waste pile unit of the same design and capacity and meeting all waste pile conditions in the permit	1	
4. Modification of a waste pile management practice	2	
5. Storage or treatment of different wastes in waste piles:		
a. That require additional or different management practices or different design of the unit	3	
b. That do not require additional or different management practices or different design of the unit	2	
6. Conversion of an enclosed waste pile to a containment building unit	2	
Note: See §270.42(g) for modification procedures to be used for the management of newly listed or identified wastes.		

Modifications	Class	Minor (Mi)
J. ***Landfills and Unenclosed Waste Piles*** **40 CFR 264 Subpart N**		
1. Modification or addition of landfill units that result in increasing the facility's disposal capacity	3	
2. Replacement of a landfill	3	
3. Addition or modification of a liner, leachate collection system, leachate detection system, run-off control, or final cover system	3	
4. Modification of a landfill unit without changing a liner, leachate collection system, leachate detection system, run-off control, or final cover system	2	
5. Modification of a landfill management practice	2	
6. Landfill different wastes:		
a. That require additional or different management practices, different design of the liner, leachate collection system, or leachate detection system	3	
b. That do not require additional or different management practices, different design of the liner, leachate collection system, or leachate detection system	2	
c. That are wastes restricted from land disposal that meet the applicable treatment standards or that are treated to satisfy the standard of "use of practically available technology that yields the greatest environmental benefit" contained in §268.8(a)(2)(ii), and provided that the landfill unit meets the minimum technological requirements stated in §268.5(h)(2). This modification is not applicable to dioxin-containing wastes (F020, 021, 022, 023, 026, 027, and 028)	1	
d. That are residues from wastewater treatment or incineration, provided that disposal occurs in a landfill unit that meets the minimum technological requirements stated in §268.5(h)(2), and provided further that the landfill has previously received wastes of the same type (for example, incinerator ash). This modification is not applicable to dioxin-containing wastes (F020, 021, 022, 023, 026, 027, and 028)	1	
7. Modifications of unconstructed units to comply with §§264.251(c), 264.252, 264.253, 264.254(c), 264.301(c), 264.302, 264.303(c), and 264.304	[1]1	
8. Changes in response action plan:		
a. Increase in action leakage rate	3	
b. Change in a specific response reducing its frequency or effectiveness	3	
c. Other changes	2	
Note: See §270.42(g) for modification procedures to be used for the management of newly listed or identified wastes.		
K. ***Land Treatment*** **40 CFR 264 Subpart M**		
1. Lateral expansion of or other modification of a land treatment unit to increase areal extent	3	
2. Modification of run-on control system	2	
3. Modify run-off control system	3	
4. Other modifications of land treatment unit component specifications or standards required in permit	2	
5. Management of different wastes in land treatment units:		

Modifications	Class	Minor (Mi)
a. That require a change in permit operating conditions or unit design specifications	3	
b. That do not require a change in permit operating conditions or unit design specifications	2	
Note: See §270.42(g) for modification procedures to be used for the management of newly listed or identified wastes		
6. Modification of a land treatment unit management practice to:		
a. Increase rate or change method of waste application	3	
b. Decrease rate of waste application	1	
7. Modification of a land treatment unit management practice to change measures of pH or moisture content, or to enhance microbial or chemical reactions	2	
8. Modification of a land treatment unit management practice to grow food chain crops, to add to or replace existing permitted crops with different food chain crops, or to modify operating plans for distribution of animal feeds resulting from such crops	3	
9. Modification of operating practice due to detection of releases from the land treatment unit pursuant to §264.278(g)(2)	3	
10. Changes in the unsaturated zone monitoring system, resulting in a change to the location, depth, number of sampling points, or replace unsaturated zone monitoring devices or components of devices with devices or components that have specifications different from permit requirements	3	
11. Changes in the unsaturated zone monitoring system that do not result in a change to the location, depth, number of sampling points, or that replace unsaturated zone monitoring devices or components of devices with devices or components having specifications different from permit requirements	2	
12. Changes in background values for hazardous constituents in soil and soil-pore liquid	2	
13. Changes in sampling, analysis, or statistical procedure	2	
14. Changes in land treatment demonstration program prior to or during the demonstration	2	
15. Changes in any condition specified in the permit for a land treatment unit to reflect results of the land treatment demonstration, provided performance standards are met, and the Director's prior approval has been received	[1]1	Mi*
16. Changes to allow a second land treatment demonstration to be conducted when the results of the first demonstration have not shown the conditions under which the wastes can be treated completely, provided the conditions for the second demonstration are substantially the same as the conditions for the first demonstration and have received the prior approval of the Director	[1]1	Mi*
17. Changes to allow a second land treatment demonstration to be conducted when the results of the first demonstration have not shown the conditions under which the wastes can be treated completely, where the conditions for the second demonstration are not substantially the same as the conditions for the first demonstration	3	
18. Changes in vegetative cover requirements for closure	2	
L. **Incinerators, Boilers, and Industrial Furnaces**: **40 CFR 264 Subpart O**		
1. Changes to increase by more than 25% any of the following limits authorized in the permit: A thermal feed rate limit, a feedstream feed rate limit, a chlorine/chloride feed rate limit, a metal feed rate limit, or an ash feed rate limit. The Director will require a new trial	3	

Modifications	Class	Minor (Mi)
burn to substantiate compliance with the regulatory performance standards unless this demonstration can be made through other means		
2. Changes to increase by up to 25% any of the following limits authorized in the permit: A thermal feed rate limit, a feedstream feed rate limit, a chlorine/chloride feed rate limit, a metal feed rate limit, or an ash feed rate limit. The Director will require a new trial burn to substantiate compliance with the regulatory performance standards unless this demonstration can be made through other means	2	
3. Modification of an incinerator, boiler, or industrial furnace unit by changing the internal size or geometry of the primary or secondary combustion units, by adding a primary or secondary combustion unit, by substantially changing the design of any component used to remove HCl/Cl_2, metals, or particulate from the combustion gases, or by changing other features of the incinerator, boiler, or industrial furnace that could affect its capability to meet the regulatory performance standards. The Director will require a new trial burn to substantiate compliance with the regulatory performance standards unless this demonstration can be made through other means	3	
4. Modification of an incinerator, boiler, or industrial furnace unit in a manner that would not likely affect the capability of the unit to meet the regulatory performance standards but which would change the operating conditions or monitoring requirements specified in the permit. The Director may require a new trial burn to demonstrate compliance with the regulatory performance standards	2	
5. Operating requirements:		
a. Modification of the limits specified in the permit for minimum or maximum combustion gas temperature, minimum combustion gas residence time, oxygen concentration in the secondary combustion chamber, flue gas carbon monoxide and hydrocarbon concentration, maximum temperature at the inlet to the particulate matter emission control system, or operating parameters for the air pollution control system. The Director will require a new trial burn to substantiate compliance with the regulatory performance standards unless this demonstration can be made through other means	3	
b. Modification of any stack gas emission limits specified in the permit, or modification of any conditions in the permit concerning emergency shutdown or automatic waste feed cutoff procedures or controls	3	
c. Modification of any other operating condition or any inspection or recordkeeping requirement specified in the permit	2	
6. Burning different wastes:		
a. If the waste contains a POHC that is more difficult to burn than authorized by the permit or if burning of the waste requires compliance with different regulatory performance standards than specified in the permit. The Director will require a new trial burn to substantiate compliance with the regulatory performance standards unless this demonstration can be made through other means	3	
b. If the waste does not contain a POHC that is more difficult to burn than authorized by the permit and if burning of the waste does not require compliance with different regulatory performance standards than specified in the permit	2	
Note: See §270.42(g) for modification procedures to be used for the management of newly listed or identified wastes		
7. Shakedown and trial burn:		

Modifications	Class	Minor (Mi)
a. Modification of the trial burn plan or any of the permit conditions applicable during the shakedown period for determining operational readiness after construction, the trial burn period, or the period immediately following the trial burn	2	
b. Authorization of up to an additional 720 hours of waste burning during the shakedown period for determining operational readiness after construction, with the prior approval of the Director	[1]1	Mi*
c. Changes in the operating requirements set in the permit for conducting a trial burn, provided the change is minor and has received the prior approval of the Director	[1]1	Mi*
d. Changes in the ranges of the operating requirements set in the permit to reflect the results of the trial burn, provided the change is minor and has received the prior approval of the Director	[1]1	Mi*
8. Substitution of an alternative type of nonhazardous waste fuel that is not specified in the permit	1	
9. Technology changes needed to meet standards under 40 CFR part 63 (Subpart EEE—National Emission Standards for Hazardous Air Pollutants From Hazardous Waste Combustors), provided the procedures of §270.42(j) are followed.	[1]1	
10. Changes to RCRA permit provisions needed to support transition to 40 CFR part 63 (Subpart EEE—National Emission Standards for Hazardous Air Pollutants From Hazardous Waste Combustors), provided the procedures of §270.42(k) are followed.		
M. ***Containment Buildings***. **40 CFR 264 Subpart DD**		
1. Modification or addition of containment building units:		
a. Resulting in greater than 25% increase in the facility's containment building storage or treatment capacity	3	
b. Resulting in up to 25% increase in the facility's containment building storage or treatment capacity	2	
2. Modification of a containment building unit or secondary containment system without increasing the capacity of the unit	2	
3. Replacement of a containment building with a containment building that meets the same design standards provided:		
a. The unit capacity is not increased	1	
b. The replacement containment building meets the same conditions in the permit	1	
4. Modification of a containment building management practice	2	
5. Storage or treatment of different wastes in containment buildings:		
a. That require additional or different management practices	3	
b. That do not require additional or different management practices	2	
N. ***Corrective Action*** **40 CFR Subpart S**		
1. Approval of a corrective action management unit pursuant to §264.552	3	
2. Approval of a temporary unit or time extension for a temporary unit pursuant to §264.553	2	
3. Approval of a staging pile or staging pile operating term extension pursuant to §264.554	2	
O. ***Burden Reduction***		
1. Approval of reduced inspection frequency for Performance Track member facilities for:		

Modifications	Class	Minor (Mi)
a. Tanks systems pursuant to §264.195	[1]1	
b. Containers pursuant to §264.174	[1]1	
c. Containment buildings pursuant to §264.1101(c)(4)	[1]1	
d. Areas subject to spills pursuant to §264.15(b)(4)	[1]1	
2. Development of one contingency plan based on Integrated Contingency Plan Guidance pursuant to §264.52(b)	1	
3. Changes to recordkeeping and reporting requirements pursuant to: §§264.56(i), 264.343(a)(2), 264.1061(b)(1),(d), 264.1062(a)(2), 264.196(f), 264.100(g), and 264.113(e)(5)	1	
4. Changes to inspection frequency for tank systems pursuant to §264.195(b)	1	
5. Changes to detection and compliance monitoring program pursuant to §§264.98(d), (g)(2), and (g)(3), 264.99(f), and (g)	1	

Class Designations versus Major/Minor Designations for Permit Modifications:
Several states (AL, FL, ME, MN, NY, OH, and SC) use the original "major or minor" permit modification categories, not the three class system introduced in a 1988 rule (53 FR 37912).

[1]Class 1 modifications requiring prior Agency approval.

*Directly referenced as a Minor modification.

State of Oregon Department of Environmental Quality

OAR 340-120-0010 Tables and Figures

Table 1 – Matrix Legend

(03/1991)

Uppermost Aquifer - The first body of saturated rock, alluvium, or other naturally occurring material that contains sufficient permeability to store, transmit, and yield sufficient quantities of water to wells or springs so that the wells can serve as a practical source of water .

Unconfined Aquifer - Unconfined is synonymous with water table. A saturated geologic unit where the hydrostatic pressure at the upper surface of the water body is atmospheric.

Confined Aquifer - Confined is synonymous with artesian. A saturated geologic unit that contains water under sufficient hydrostatic pressure to cause the water level in a well to stand above the bottom of the overlying confining layer.

Aquitard - A saturated geologic unit which yields inappreciable quantities of water compared to an aquifer but through which appreciable leakage of water is possible .

Aquiclude - A saturated geologic unit which yields inappreciable quantities of water compared to an aquifer but through which appreciable leakage of water is riot possible.

Hydraulic Conductivity (K) – The quantity of groundwater flowing through a waterbearing material in one unit of time through a unit cross-sectional area under a driving force of one unit of hydraulic head change per unit length. This is usually expressed as gallons per day per foot squared (gpd/ft^2), or feet per day (ft/day). This is an expression of a geologic unit's ability to transmit a fluid. In the matric, K values refer to both the unsaturated zone above the aquifer and the saturated aquifer. High K's refer to formations that are rapidly draining, such as gravels, sand, karst limestone, permeable basalt, and other fractured igneous and metamorphic rocks. Medium K's refer to formations with some permeability such as clays, glacial tills, shales, and unfractured metamorphic and igneous rocks. General K values would be:

High K	$\geq 1 \times 10^{3}$ gal/day/ft^2
Medium K	Between 1×10^{3} and 1×10^{-3} gal/day/ft^2
Low K	$\leq 1 \times 10^{-4}$ gal/day/ft^2

Sole Source Aquifer - An aquifer that provides the only source of drinking water. No other ground or surface water supplies are available.

Table 2
(*a)
Hazardous Waste and PCB Facility Site Preliminary Groundwater Quality Protection Evaluation Matrix

Aquifer Type	Uppermost Aquifer (*c)				
	Unconfined Aquifer				Confined Aquifer
Beneficial uses within one mile downgradient	1	1	1	1	3
Public/private sole source aquifer *(b)	1	1	2	2	3
Present or potential public/private drinking water and/or livestock water supply and irrigation	1	2	3	2	3
Aquifer discharges to fresh or salt water wetlands or marshes	1	2	3	2	3
Aquifer discharges to surface water body with established uses	1	1	2	1	3
Industrial	1	2	3	3	3
Treatment required for drinking or industrial use	2	2	3	3	3
Total dissolved solid level naturally greater than 10,000 mg\L; no identified uses. Does not meet drinking water standards	3	3	3	3	3

Protection Levels

1. Proposed facility site does not meet groundwater protection criterion.
2. Proposed facility site meets initial groundwater protection screening criterion but the site has limitations that must be addressed in detail in the Part B application.
3. Proposed facility site meets initial groundwater protection screening treatment.

*(a) Table 1 defines the terms of the matrix.
*(b) Unless otherwise noted, groundwater meets drinking water standards without treatment.
*(c) Uppermost aquifer and other aquifers hydraulically connected.

State of Oregon Department of Environmental Quality

OAR 340-122-0210
NW Total Petroleum Hydrocarbon Identification Method

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* The chromatograms are not available in the “electronic” version. They are included in the printed publication.

TOTAL PETROLEUM HYDROCARBONS (TPH)

The following compilation of analytical methods may be used in Oregon and Washington for Underground Storage Tank cleanups and other cleanups of TPH (check with applicable state rules). Each of these Total Petroleum Hydrocarbon (TPH) Methods has its own niche in the overall analytical scheme. The methods are:

NWTPH-HCID.....Hydrocarbon Identification

NWTPH-Gx .....Volatile Petroleum Products (Extended)

NWTPH-Dx .....Semi-volatile Petroleum Products (Extended)

NWTPH-HCID is a qualitative and semi-quantitative screen to determine the presence and type of petroleum products that may exist in water or soil. This method should be used if the type of petroleum contamination is unknown. It should be performed on contaminated soil or water that is representative of the contamination at the site. The results of this method will determine what fully quantitative method/methods, if any, are to be used in determining compliance with the matrix criteria. Should the value of the analysis for gasoline, diesel or heavy oils (or any other identified petroleum product) exceed the reporting limits, then the specific analytical method for that product must be employed.

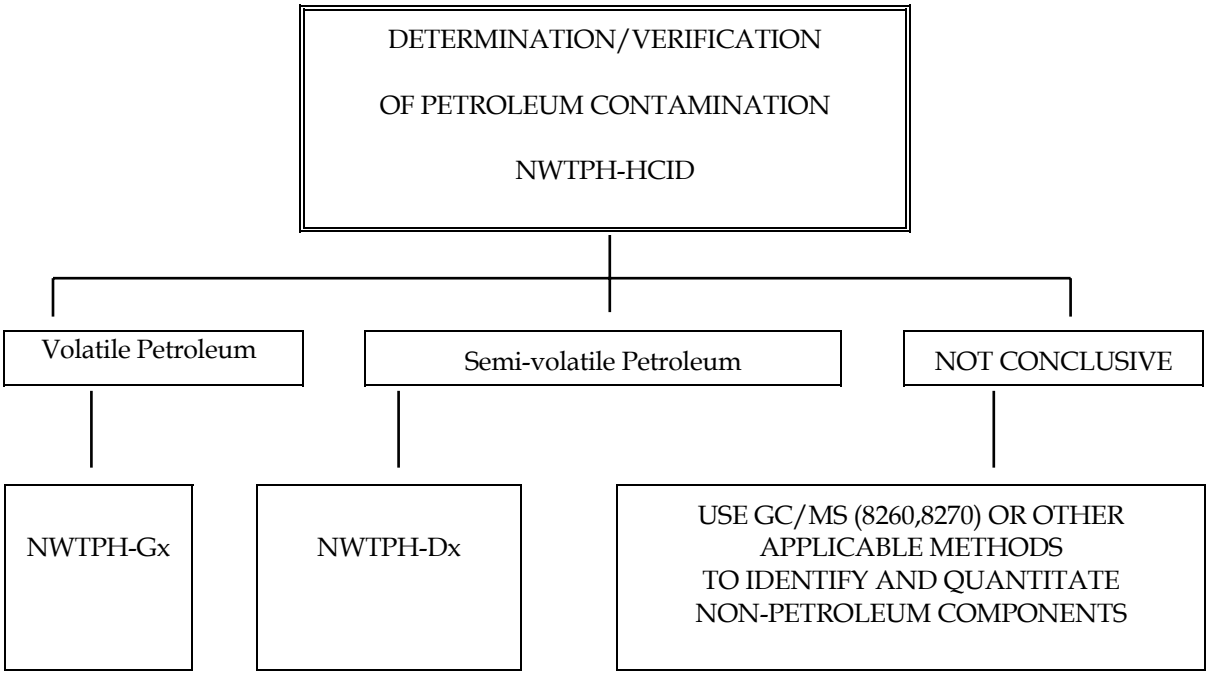
NWTPH-Gx is the qualitative and quantitative method (extended) for volatile ("gasoline") petroleum products in soil and water. Petroleum products applicable for this method include aviation and automotive gasolines, mineral spirits, stoddard solvent and naphtha.

NWTPH-Dx is the qualitative and quantitative method (extended) for semi-volatile ("diesel") petroleum products in soil and water. Petroleum products applicable for this include jet fuels, kerosene, diesel oils, hydaulic fluids, mineral oils, lubricating oils and fuel oils.

NOTE: These "NWTPH" methods result in single TPH values that can be used when compliance with a single cleanup level is desired. When TPH "fractions" are needed, then the VPH and EPH methods must be used.

ANALYTICAL DECISION TREE FOR NWTPH

The following flow chart depicts the laboratory analytical scheme to be used when analyzing samples for single TPH levels. The first step is the qualitative determination of the existence and nature of petroleum contamination and this should be used when the site contamination is unknown. It is required that this first step will be performed on a representative sample from the area that is suspected to be the most contaminated at the site. For those samples containing analytes which, due to their retention times, ratios to each other or their non-hydrocarbon pattern (e.g., creosote), do not suggest petroleum hydrocarbons, then GC/MS methods should be employed to ascertain the components. At those sites where the petroleum contaminants are known or have been identified using the NWTPH-HCID method, the specific product method is to be used.



NWTPH-HCID

Hydrocarbon Identification Method for Soil and Water

Summary

This method is a qualitative and semi-quantitative procedure. It is used for groundwater or surface water, and soil/sediment from sites where the petroleum products are unknown and/or when multiple types of petroleum products are suspected to be present. This method is used to identify petroleum products containing components from C7 to C30 range, as well as heavy oils, with specific product confirmation by pattern matching ("fingerprinting") employing capillary gas chromatography with flame ionization detection (GC/FID). EPA method 3510 has been adapted as the extraction procedure for the water portion of this method.

While this method is intended to be primarily qualitative, it can be used to eliminate the need for further analyses for those samples which demonstrate TPH levels significantly below the regulatory limits. If the sample contains toluene to dodecane (gasoline range), dodecane through tetradecane (diesel range) and/or an unresolved chromatographic envelope greater than tetradecane (e.g. motor oils) above the reporting limits of this method, then the final quantitation must be performed by methods specific for these mixtures. Since the water extraction procedure in this method is identical to that found in the water portion of NWTPH-Dx (semi-volatile petroleum products, i.e. from kerosene through heavy fuel oils), these products may be quantitated using this extract. Because of the possible loss of volatile compounds in the extraction and concentrations steps, gasoline, mineral spirits and other volatile petroleum products that exceed the reporting limits of this method must be quantitated using the NWTPH-Gx method.

The reporting limits for water are 0.25 mg/L for gasoline, 0.63 mg/L for #2 diesel and motor oils. The reporting limits for soil/sediment are 20 mg/Kg for gasoline, 50 mg/Kg for #2 diesel, and 100 mg/Kg for motor oil, all reported on a dry weight basis. These values for soil/sediment assumes 100% solids and will be higher depending on the actual moisture content.

The method relies heavily upon the experience of the analyst for the identification of the specific petroleum product(s) that may be present. Therefore, this method must be run by, or under the direct supervision of, analysts experienced in the use of GC and in the interpretation of gas chromatograms of both fresh and weathered petroleum products.

Equipment and Reagents

Gas Chromatograph, w/wo autosampler
Capillary split/splitless injector
Flame ionization detector
Suggested Capillary Column:
J&W DB-1 or DB-5, 30 M x 0.25 mm or 0.32 mm with 0.25 um film thickness capillary column or equivalent
Chromatography Data System
VOA Vial: 40 mL glass vial with Teflon coated cap septum, Eagle Picher or equivalent
Syringe: Hamilton #701, 10 uL or equivalent
Ultrasonic Bath
Glass Wool: Pyrex or equivalent
Centrifuge tubes: 5 or 15 mL, calibrated in 0.1 mL increments
Analytical Balance: accurate to at least 0.0001 g
Volumetric Flasks: 10 mL, ground glass with ground glass stopper
Separatory funnels: 500 mL, Teflon stopcocks
Kuderna-Danish (KD) Flasks: 250 mL or equivalent
Snyder Columns: 3-ball, 24/40 ground glass joint
Concentrator Tubes: 10 mL
Methylene Chloride: Burdick and Jackson Brand or equivalent
N-Evap Concentrator or equivalent

Standards

Retention Time Standards. Prepare a composite standard, using methylene chloride as the solvent, consisting of toluene, dodecane and tetracosane at 25 ug/mL each. Additional compounds may be added at the discretion of the analyst. The use of this standard is to establish the retention time windows for the quantitation of gasoline #2 diesel and motor oils.

Reference Standards. Prepare individual petroleum product reference standards (i.e. gasoline, mineral spirits, kerosene and #2 diesel oil), using methylene chloride as the solvent, at approximately 50 ug/mL. Prepare a non-synthetic motor oil (pennzoil SAE 30 or equivalent) reference standard at 200 ug/mL. The preparation of reference standards for other types of petroleum products is recommended. The use of these reference standards is to insure the accurate identification of petroleum product contamination by chromatographic pattern matching ("fingerprinting") and establish retention time windows for those petroleum products not determined with the individual compound retention time standard.

Gasoline Stock Standard. A stock standard is prepared by placing approximately 9 mL of methylene chloride in a 10 mL volumetric flask. Tare the flask/methylene chloride and add about five drops of non-oxygenated regular unleaded gasoline, assuring that the liquid falls directly into the methylene chloride without contacting the neck of the flask. Reweigh the flask and dilute to volume with methylene chloride, stopper and mix by inverting the flask several times. It is important that the analyst minimize the amount of time that the flask is left unstoppered, to reduce

the loss of gasoline through volatilization. The use of a commercially prepared gasoline standards is acceptable if it is certified as non-oxygenated gasoline or if the gasoline concentration has been adjusted to reflect the contribution of the oxygenate. Calculate the gasoline concentration as follows:

$$Stock,\ ug / mL = \frac{(final\ wt,\ mg) - (tare\ wt,\ mg)}{10\ mL} \times \frac{1000\ ug}{mg}$$

Note: The use of oxygenated regular unleaded gasoline for the gasoline stock standard is allowed if the weight (mass) of the gasoline used is adjusted for the weight (mass) contribution of the oxygenate to the gasoline. This will necessitate the analysis of the gasoline for the specific oxygenate(s) present to determine the concentration. The analysis for the oxygenates will be conducted by either of the methods published in the Federal Register - Appendix B and C - Testing Procedures - Vol. 57, No. 24, Wednesday, February 5, 1992, Notices.Alternate methods for the analysis of gasoline oxygenates must be approved by the Oregon's Department of Environmental Quality and/or Washington's Department of Ecology prior to use.

Diesel Stock Standard. A stock standard is prepared by adding about five drops of #2 diesel oil stock to tared 10 mL volumetric flask. Reweigh the flask and bring it to volume with methylene chloride, stopper and mix by inverting the flask several times. Calculate the concentration of this standard in the same manner as the gasoline stock standard. The use of a commercially prepared #2 diesel standard is an acceptable alternative to the above procedure.

Motor Oil Stock Standard. A stock standard is prepared by adding about ten drops of a non-synthetic SAE 30 weight motor oil (Pennzoil or equivalent) to a tared 10 mL volumetric flask. Reweigh the flask, bring it to volume with methylene chloride, stopper and mix by inverting the flask several times. Calculate the concentration of this standard in the same manner as the gasoline stock standard. The use of commercially prepared motor oil standards is an acceptable alternative to the above procedure.

Note: The Diesel and Motor Oil Stock Standards required in this method are identical to those required for NWTPH-Dx (extended diesel method including all semi-volatile petroleum products eluting after gasoline, e.g. kerosene, diesels, mineral oils, lubricating oils, heavy fuel oils, etc.).

Surrogate Stock Standard. Suggested surrogates for use in this method are bromofluorobenzene and pentacosane. The use of different or additional surrogates is optional. Prepare the surrogate stock standard by weighing 50 mg of each surrogate compound into a 10 mL volumetric flask, then bring to volume with methylene chloride for a final concentration of 5000 ug/mL for each surrogate compound. The use of a commercially prepared surrogate solution(s) is an acceptable alternative to the above procedure.

Composite Calibration Working Standard. Using serial dilutions of the stock standards, prepare a mixture for water analyses that contains 10 ug/mL of gasoline, 25 ug/mL of #2 diesel oil and the

surrogate standard. For soil/sediment analyses this standard should be prepared to contain 20 ug/mL of gasoline, 50 ug/mL of #2 diesel and the surrogate standard. Add the appropriate volumes, using the equations listed below, and adjusting for the concentration change created by any serial dilutions, of gasoline stock standard, #2 diesel stock standard and the surrogate stock standard to a 10 mL volumetric flask, then dilute to volume with methylene chloride. Stopper and mix by inverting the flask several times. The surrogate standard should be added to a level sufficient to produce a surrogate concentration of between 5 and 50 ug/mL.

$$\textit{Volume Gasoline Stock, uL} = \frac{\textit{20 (soil) / 10 (water) ug / mL x 10 mL}}{\textit{Gasoline Stock Conc, ug / mL}} \; x \; \frac{\textit{1000 uL}}{\textit{mL}}$$

$$\textit{Volume Diesel Stock, uL} = \frac{\textit{50 (soil) / 25 (water) ug / mL x 10 mL}}{\textit{Diesel Stock Conc, ug / mL}} \; x \; \frac{\textit{1000 uL}}{\textit{mL}}$$

This mixture corresponds to 0.25 mg/L gasoline and 0.63 mg/L #2 diesel oil for water and 20 mg/Kg gasoline and 50 mg/Kg diesel in soil following the extraction and analytical procedures of this method.

The motor oil calibration working standard should be made at a concentration of 250 ug/mL for water and 100 ug/mL for soil following the procedure outlined above. This will correspond to a reporting value of 0.63 mg/L for water and 100 mg/kg for soil. If, in the opinion of the analyst, the GC sensitivity to 100 ug/mL of motor oil is insufficient, the analyst is allowed to increase the concentration of this standard and to concentrate a portion of the extract to achieve the reporting limit for soil.

Surrogate Working Standard. Prepare a surrogate working (spiking) standard, using the procedure outlined above, that will yield between 5 ug and 50 ug/mL of the surrogate compounds in the 10 mL sample extract produced in this method.

Note: All samples must be collected in glass jars with Teflon lined lids (Eagle Picher or equivalent) and held at 4 degrees C until extracted. A volume of 400 mL is the minimum sample size to achieve the reporting limits as stated, however, larger volumes are allowed as long as the solvent/sample ratio is maintained. Samples must be extracted within 7 days (for water) or 14 days (for soil/sediment) of the date of collection. The preservation of water samples in the field, to a pH of less than 2 with 1+1 HCL, is recommended.

Extraction Procedures

Water Samples

Mark the water meniscus on the sample jar for later volume determination. Pour the sample into a 500 mL separatory funnel, add the surrogate solution (to achieve the desired concentration in a 10 mL extract). Add 30 mL of methylene chloride to the sample jar, cap and shake the jar vigorously

for a few seconds to wash off any hydrocarbons adhering to the side of the jar. Add this solvent to the separatory funnel, stopper and shake vigorously, venting frequently, for one minute. Allow the two phases to separate, then drain the solvent into a 250 mL K-D flask fitted with a 10 mL concentrator tube. Repeat the extraction twice more using 30 mL of methylene chloride, each time, adding the solvent to the K-D.

Attach a 3-ball Snyder column to the K-D and concentrate the sample extract to 5 - 10 mL on a stream bath. Remove the K-D apparatus and allow it to cool prior to disassembly. During disassembly, rinse the Snyder/K-D joint and K-D/concentrator joint with approximately 1 mL of methylene chloride and add these rinsings to the extract. Adjust the volume of the extract to 10 mL. For those samples which exceed 10 mL, place the concentrator tube into an N-Evap and, under a gentle stream of nitrogen, reduce the volume to 10 mL. Transfer 1 mL of the extract (to be used for the gasoline or gasoline/diesel determination) to an autosampler vial fitted with a screw top and a Teflon coated septum. Concentrate the remainder of the extract (to be used for heavy oils determination) to 0.9 mL, transfer it to an 2 mL autosampler vial equipped with a screw top and a Teflon coated septum. Store both vials in a refrigerator until analysis.

Each extraction set must include one method blank (organic-free water of similar volume to the samples) per 20 samples. The method blank is to receive the surrogate solution and to be extracted and analyzed in the same manner as the samples.

EPA method 3520, Continuous Liquid-Liquid Extraction, may be substituted as an alternate extraction procedure to that outlined above.

Soil Samples

Weigh approximately 10 grams of soil into a 40 mL VOA vial and record the weight to the nearest 0.001 grams. Add 5 grams of anhydrous sodium sulfate, surrogate working solution and 10 mL of methylene chloride to the VOA vial. Cap the vial and place it (no more than 5 at a time) in a sonic bath for 5 minutes. Shake the vials well and return them to the sonic bath for 5 more minutes. A minimum of one method blank per extraction set or 20 samples, whichever is more frequent, must be prepared along with the samples. One sample duplicate must also be extracted for samples set from one to ten samples and two duplicates for sets from eleven to twenty samples.

Determine the moisture content of the samples, for use in the final calculations, by the following procedure. Immediately after weighing the sample for extraction, weigh 5-10 grams of the sample into a tared crucible. Dry the sample/crucible overnight at 105 degrees C. Reweigh the sample/crucible after allowing it to cool to room temperature. Calculate the % solids as follows: [(grams of dry sample/grams of wet sample) x 100].

If the extract contains significant moisture, elute the solvent phase through an anhydrous sodium sulfate micro-column. Place a portion of the extract in a 2 mL autosampler vial (screw cap, Teflon coated septum), taking care to minimize the volume of headspace, and store the vial in a refrigerator until analyzed. Concentration of the extract, when necessary, will be conducted using an N-Evap

with a gentle stream of nitrogen. This concentrate should be stored in the same manner as noted above.

Note: Anhydrous sodium sulfate micro-columns are prepared by plugging a 5 3/4" length disposable Pasteur pipette (pre-rinsed with methylene chloride) with glass wool (precleaned with methylene chloride) and adding approximately 3 cm of anhydrous sodium sulfate (previously muffled at 430 degrees C overnight in a shallow pan and stored in a glass jar with a Teflon lid liner).

For samples containing petroleum products other than gasoline, diesel, or motor oil, the analyst must either prepare calibration standards of them by the methods listed above or analyze the sample by the fully quantitative method, e.g. NWTPH-Gx. Other calibration standards produced for use in this method must be at an equivalent concentration to the previously established standards, e.g. mineral spirits at the gasoline concentration, kerosene at the diesel concentration.

As more information becomes available on new extraction techniques, the Washington State Dept. of Ecology's Manchester Laboratory and Oregon's Department of Environmental Quality will publish descriptions of acceptable alternate extraction methods.

Suggested GC Parameters

Sample injection Volume = 2 uL
Injector Temperature = 290°C
Detector Temperature = 300°C
Hydrogen Flow = 25-35 mL/min
Air Flow = 300-400 mL/min
Make-up Gas Flow = 30 mL/min
GC Temperature Program = Initial temperature of 50°C and hold for 2 minutes; ramp the temperature 10°C/min to 320°C and hold for 5 minutes.

Product Identification

Petroleum products are to be identified by pattern matching with reference product chromatograms generated the same day as the sample analysis. The term "gasoline range" or "diesel range" hydrocarbons, or derivations of them, should only be used when the analyst is unable to identify the petroleum product present. When these terms are used, it is to indicate the presence of compounds eluting from toluene to dodecane, for the former term, and from dodecane through tetracosane, for the latter term. Motor oils, hydraulic fluids and similar petroleum products which present an unresolved chromatographic envelope of compounds, originating or extending beyond tetracosane, may be reported using the collective term, lube oil, unless specific identification is possible. Heavy fuel oils, e.g. fuel oil #6 or Bunker C, which contain a diesel range component as well as a lube oil (and higher) range may be reported using the collective term, heavy fuel oil, unless specific identification is possible. These products should not, however, be confused with mixtures of #2 diesel and motor oils.

Note: The actual identification of the grade or type of lube oil and heavy fuel oil may require equipment and techniques beyond the scope of this method.

Analysis Procedure

The analysis is accomplished by injecting 2 uL of the 10 mL extract, either manually or by autosampler, into the GC using the splitless injection mode. The results from this injection are, for quantitation purposes, compared directly against the single point calibration standard for the product(s) identified. The injection of 2 uL of the concentrated extract (1 mL equivalent) is used primarily for heavy oil determination, because of the reduced sensitivity of the FID to late eluting motor oil-like products. It may be used for the determination of #2 diesel oil and other diesel range petroleum products but it may not be used for the determination of gasoline or gasoline range petroleum products because of the potential for loss of the more volatile components during the concentration step.

Calculations

Gasoline. The area of the components, toluene to dodecane of the calibration standard, is integrated to the baseline as a group. The samples and method blanks are integrated in the same manner and the group areas are compared. If the sample area exceeds the calibration standard area, proceed with method NWTPH-Gx for accurate quantitation using a fresh aliquot of the sample. If the sample area does not exceed the calibration standard area, then report the gasoline concentration as less than 0.25 mg/L for water or 20 mg/kg for soil. This soil value for gasoline, and the subsequent petroleum products, assumes 100% solids and will be higher depending on the actual moisture content.

Other volatile petroleum products, identified as being present (e.g. mineral spirits), must be compared to the appropriate standard produced at the same concentration as gasoline. The requirement for further analyses is determined following the criteria for gasoline as noted above.

Note: For samples containing only #2 diesel oil, kerosene, etc., the portion of these products, that elute within the retention time range of gasoline, should not be identified and/or quantitated as gasoline or gasoline range petroleum.

Diesel. The area of the components, dodecane through tetracosane of the calibration standard, is integrated to the baseline as a group. This integration must include the unresolved envelope of compounds as well as the discrete component peaks. The sample is integrated in the same manner and the group areas are compared. If the sample area exceeds the calibration standard area, then proceed to method NWTPH-Dx. If the sample does not exceed the calibration standards area, then report the #2 diesel concentration as less than 0.63 mg/L for water or 50 mg/Kg for soil.

Other semi-volatile petroleum products, identified as being present (e.g. kerosene), must be compared to the appropriate standard produced at the same concentration as #2 diesel. The requirement for further analyses is determined following the criteria for #2 diesel as noted above.

Lube Oil. For those samples which consist primarily of only an unresolved chromatographic envelope of components eluting after tetracosane, compare their area to the area of the motor oil standard by integrating the unresolved envelope to baseline. If the sample exceeds the standard area, then proceed to method NWTPH-Dx. If the sample area is less than the standard, then report the lube oil concentration as less than 0.63 mg/L for water or 100 mg/Kg for soil. Samples identified as containing heavy fuel oil must be quantitated to the same value as lube oil by utilizing a heavy fuel oil standard and following the procedure outlined for lube oil.

Note: The analyst is expected to adjust the retention time windows used for quantitation of petroleum products, other than gasoline, #2 diesel, or motor oil/lube oils, to incorporate the majority of the chromatographable components associated with those identified products.

If, in the judgement of the analyst, the area of an identified petroleum product other than gasoline, diesel, and motor oil would exceed the reporting limit, the analyst is allowed to report a "greater than" value for that product without performing the quantitative analysis. The analyst must then proceed to the appropriate fully quantitative analytical procedure, e.g. NWTPH-Dx, for the identified petroleum product.

Quality Assurance

The addition of an appropriate extraction surrogate to samples and method blank(s) is required. The surrogate recovery for all samples and blanks should be between 50% and 150% and must be reported with the petroleum results unless the quantity of the petroleum product(s) preclude its determination. The laboratory should analyze one sample from each site in duplicate for sample sets of 10 or less and two samples in duplicate for sets of 11 to 20 samples (i.e. 10% QA). If either of the duplicate results are positive, the sample is to be considered positive. Since this method precludes the preparation of analytical duplicates, the laboratory should recommend that the project manager collect and submit field duplicates for analysis. The laboratory must analyze method blanks prepared identically to the samples. Organic free water must be used in the preparation of water method blank. No "sample" is necessary for use with soil/sediment method blanks.

Author - Bob Carrell, Manchester Environmental Laboratory, Dept. of Ecology, State of Washington. Reviewed and edited by Steve Robb, Toxics Cleanup Program, Department of Ecology, State of Washington. This method is based on Oregon’s Department of Environmental Quality TPH methods and Washington’s Department of Ecology WTPH methods.

NWTPH-Gx Chromatograms

Gasoline
Weathered Gasoline
Naptha
Mineral Spirits #1
Mineral Spirits #2
Mineral Spirits #3

NWTPH-Dx Chromatograms

#2 Diesel
#2 Diesel/Motor Oil
#2 Fuel Oil
Kerosene (Deodorized)
Jet A Fuel
Bunker C #1
Bunker C #2
Motor Oil 30 Wt.
Mineral Oil (USP)
Hydraulic Fluid
Transformer Oil
Gas Oil

See Appendix 6

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NWTPH-Gx

Volatile Petroleum Products Method for Soil and Water

Summary

The NWTPH-Gx method is intended to replace the Oregon's TPH-G and Washington's WTPH-G methods and to present a more comprehensive approach to volatile petroleum product analyses. NWTPH-Gx adapts Oregon's TPH, Washington's WTPH and EPA SW846 Methods 5030 and/or 8020 and covers the quantitative and qualitative analyses of volatile petroleum products, e.g. gasolines, naphtha, mineral spirits, stoddard solvent, and other volatile petroleum products in soil and water. Soil samples are extracted with methanol and analyzed by gas chromatograph with a flame ionization detector (GC/FID). The methanol extracts may be injected directly into the GC or they may be diluted with organic free reagent water and introduced by a purge/trap concentrator. Water samples are introduced directly to the purge/trap concentrator. This method specifies the criteria for the identification and quantitation of volatile petroleum products. When the type of petroleum product is unknown, regular unleaded gasoline will initially be used as the default petroleum standard. The use of GC/PID, GC/MS or GC/AED (Atomic Emission Detector) for the analysis of gasoline may be substituted for GC/FID as long as all other method parameters are met.

The reporting limits for soil are 5 mg/kg by the purge/trap procedure and 20 mg/kg for direct injection. All soil results are reported on a dry weight basis. Since this value assumes 100% solids, the analyst may wish to adjust the amount of soil extracted and/or purge a larger quantity of extract to achieve the reporting limits. For water, the reporting limits are 0.25 mg/L.

The method is applicable for the identification, by pattern matching ("fingerprinting") and quantitation of volatile petroleum products, i.e. those petroleum products for which the majority of the components elute within the gasoline range.

Note: Benzene, Toluene, Ethylbenzene and Xylenes (BTEX) may be determined simultaneously with gasoline if the requirements of EPA Method 8021 or EPA Method 8260 are met (i.e. the use of a PID (Photoionization Detector) for method 8020 or a MS (Mass Spectrometry) for method 8260 and the QA/QC associated with these methods).

This method must be performed by, or under the direct supervision of, analysts experienced in the use of GC and in the interpretation of gas chromatographs of both fresh and weathered volatile petroleum products.

Equipment and Reagents

Gas Chromatograph
Purge/Trap Liquid Concentrator - Tekmar or Equivalent - Autosampler (Optional)
Flame Ionization (FID) or Photo Ionization/Flame Ionization Detectors (PID/FID)
Suggested Capillary Column: Restex RTX-502.2, 60M x 0.53 mm x 3.0 um film thickness or equivalent
Chromatography Data System
Gas tight syringes, various volumes, Hamilton brand or equivalent
Volumetric flasks: 10 mL, ground glass joint with stopper
Methanol: Burdick and Jackson Purge/Trap grade or equivalent
Petroleum Product Standards: Available from commercial sources
Refer to methods 5030 and/or 8020 for the remaining equipment and reagent requirement

Sample Containers/Holding Times

All soil samples for NWTPH-Gx analyses must be collected in soil VOA bottles with Teflon coated septum lined tops. They should be filled to the top to minimize headspace above the soil and stored at 4 degrees C until analyzed. The maximum holding time (the time from the date of collection to the date of analysis) for gasoline and any other volatile petroleum product is 14 days.

All water samples for NWTPH-Gx analyses must be collected in glass VOA vials with Teflon coated septum lined screw tops. They must be filled so that there is no air space (headspace) above the water. Samples should be preserved with 1+1 HCl to a pH <2 and refrigerated at 4 degrees C until analyzed. The maximum holding time (the time from the date of collection to the date of analysis) is 7 days for unpreserved samples and 14 days for preserved samples. The results of any samples which exceed these limits must be qualified as an estimated value.

Standards

Stock Standards. A stock standard is prepared by placing approximately 9 mL of methanol in a 10 mL volumetric flask. Allow the flask to stand, unstoppered, until the methanol wetted surfaces have dried (about ten minutes), then tare the methanol/flask. Add about 5 drops of the petroleum product to the flask while assuring that the liquid falls directly into the methanol without contacting the neck of the flask. Weigh the flask again and dilute to volume with methanol, stopper and mix by inverting the flask several times. The use of commercially prepared standards is acceptable to the above procedure. Commercially prepared gasoline standards must be certified as non-oxygenated gasoline or the gasoline concentration has been adjusted to reflect the contribution of the oxygenate. Calculate the concentration as follows:

$$\textit{Gasoline Stock Standard, ug / mL} = \frac{\textit{(final wt, mg) - (tare wt, mg)}}{\textit{10 mL}} \; x \; \frac{\textit{1000 ug}}{\textit{mg}}$$

The standard for gasoline will be regular unleaded gasoline and this standard is to be used as the default petroleum product for reporting purposes.

Note: The use of oxygenated regular unleaded gasoline for this standard is allowed if the weight (mass) of the gasoline used is adjusted for the weight contribution of the oxygenate to the gasoline. This will necessitate the analysis of the gasoline for the specific oxygenate(s) present to determine their concentration. This analysis must be conducted by either of the methods published in the Federal Register - Appendix B and C - Testing procedures - Vol. 57, No. 24, Wednesday, February 5, 1992, Notices. Alternate methods for the analysis of gasoline oxygenates must be approved by the Oregon's Department of Environmental Quality and/or Washington's Department of Ecology prior to use.

Stock Surrogate Standard

Note: The suggested surrogates are 1,4-difluorobenzene and bromofluorobenzene. The use of additional surrogates is optional. Selected surrogate compounds should be non-polar, purgeable from water and must not coelute with any significant component of gasoline.

Make up a stock standard by accurately weighing the surrogate compound(s) into a 10 mL volumetric flask. Utilize the same procedure as the stock gasoline standard preparation if neat material is used or by adding the appropriate volumes of dilute surrogate if solutions are used. Bring it to volume with methanol. The use of commercially prepared surrogate solutions is an acceptable alternative to the above procedure.

Working Surrogate Spike. Add the appropriate volume of stock surrogate standard to methanol in a partially filled 10 mL volumetric flask and dilute to volume with methanol. The final concentration of the working surrogate solution is left to the discretion of the analyst, however, this solution should produce between 5 ng and 50 ng of surrogate introduced to the GC.

Secondary Dilution Standard. Using serial dilutions of the stock standard, prepare a 50 ug/mL standard by adding the appropriate volumes, as calculated below, to a 10 mL volumetric flask. The appropriate volume of the stock surrogate standard may also be added to this volumetric flask. Dilute to volume with methanol to yield a final working standard concentration of 50 ug/mL for the standard. Surrogate compound(s) may be added automatically during the sampling process by an autosampler. Gasoline is the default petroleum product for reporting purposes.

$$\textit{Stock Std (Gasoline), uL} = \frac{\textit{50 ug / mL x 10 mL}}{\textit{Stock Std Conc, ug / mL}} \; x \; \frac{\textit{1000 uL}}{\textit{mL}}$$

Store all standards in a refrigerator until needed. Allow them to come to room temperature prior to use.

Calibration Standard

The aqueous purge standards are each prepared by adding 5 uL, 10 uL, 20 uL and 50 uL and 100 uL of the secondary dilution standard per 5 mL of organic free water. The five point calibration standard quantities in the purged water are then 250 ng, 500 ng, 1000 ng, 2500 ng and 5000 ng for the volatile petroleum products. At the discretion of the analyst, the concentration of the surrogate can increase with increasing standard concentration or remain at a fixed value for all calibration standards and samples. Extending the calibration range, either up or down, is allowed as long as the standards remain within the linear range of the instrument and a minimum of a five point calibration is produced. In order to be acceptable, the calibration curve must have a linear correlation coefficient of at least 0.990 and none of the standards may vary from their true (known) value by more than plus/minus 15%.

The use of an autosampler may be substituted for this manual method of standards and sample introduction.

Direction Injection. Prepare calibration standards from the stock gasoline standard and surrogate standards at concentrations of 10 ug/mL, 25 ug/mL, 50 ug/mL, 100 ug/mL and 250 ug/mL for gasoline by adding the appropriate volumes to volumetric flasks and diluting to volume with methanol. Increasing the calibration range with higher standards is acceptable as long as the linear range of the instrument is not exceeded.

Purge/Trap and GC Parameters

Follow the procedure outlined in Method 8021 for the set up of the purge and trap operating parameters and for the GC. Adjust the hydrogen/air flow rates to optimize the FID sensitivity.

Soil Extraction Procedure

Weigh approximately 5 grams of soil into a 40 mL VOA vial and record the weight to 0.001 grams. Add 50 uL of the surrogate working standard and 10 mL of methanol. Quickly cap the vial and shake for 1 minute or use an ultrasonic bath for 2 minutes shaking well after 1 minute. Allow the soil methanol mixture to separate, centrifuging if necessary to clarify the methanol extract. For storage, transfer a portion of the extract into a 2 mL glass autosampler vial, with a Teflon-lined cap, minimizing the headspace and store in a freezer for no longer than one week prior to analysis. Along with the samples, prepare at least one method blank and one sample duplicate per ten samples.

Determine the moisture content of the sample, for use in the final calculations, by the following method. Immediately after weighing the sample for extraction, weigh 5-10 grams of the sample into a tared crucible. Dry the sample/crucible overnight at 105 degrees C. Reweigh the sample/crucible after allowing it to cool to room temperature. Calculate the % solids as follows: [(grams of dry sample/grams of wet sample) x 100].

Analysis Procedure

Prior to the analysis of any samples or method blanks, prepare and analyze a mid-range calibration check standard to insure that the instrument is functioning correctly and that the calibration is valid. This standard should be produced daily using the secondary gasoline standard. The value obtained for this analysis must not vary from the true (known) value by more than plus/minus 20%. If the value falls outside this range then a second mid-range calibration standard should be produced and the analysis repeated. If the reanalysis of the fresh standard fails to meet the acceptance criteria, then the instrument must be recalibrated prior to the analysis of any samples. Once the instrument is shown to be in calibration, the analyses of samples may proceed.

After the last sample has been analyzed, a mid-range calibration check sample must be run to demonstrate that the instrument is still operating within the required parameters. Should this standard fail to meet those parameters, then all samples analyzed after the last successful calibration check must either be reanalyzed or the results obtained must be qualified as an estimated value. An increase in the frequency of mid-range calibration check standard analyses beyond the minimum required is recommended.

Significant interferences may be encountered due to the presence of other petroleum products (or non-petroleum products) eluting within the retention time range of the volatile petroleum product being analyzed. If this occurs, the analyst is allowed to adjust the retention time range used for quantitation to exclude the interferences or to subtract the area of the interfering components from the total area prior to the quantity determination. With the former method, the calibration curve must be adjusted in the same manner to reflect the change in retention time range and integration area.

For volatile petroleum products other than gasoline that have a more narrow boiling point range, e.g. mineral spirits, the retention time range used for quantitation should be adjusted to encompass the expected range of the product. Petroleum products which cannot be identified should be quantitated with the gasoline calibration curve. The term "gasoline range" hydrocarbons, or derivations of it, should not be used when reporting the petroleum values unless the analyst is unable to identify the petroleum product present.

Purge/Trap - Soil. A 100 uL aliquot of the methanol extract is transferred via a 100 uL gas tight syringe to 5 mL of organic free water in a 5 mL gas tight syringe and immediately injected into the purging vessel of the purge and trap device. For samples expected to contain concentrations of gasoline range volatiles outside the calibration linear range, or if dilution is required, a smaller aliquot of the methanol extract, or sample, should be used. The analysis then proceeds as in Method 8020. Autosampler techniques may be substituted for this manual method of sample introduction.

Purge/Trap - Water. Sample water (5 mL) is transferred to a 10 mL gas tight syringe and the working surrogate standard spike is added, via a gas tight syringe, into the 5 mL water sample. Immediately inject this water into the purge vessel of the purge/trap device. If necessary, a smaller sample aliquot may be used in order to remain within the linear calibration range of the instrument.

Larger sample volumes may be analyzed, at the discretion of the analyst, if lower quantitation limits are required. Autosampler techniques may be substituted for this manual method of sample introduction.

Direct Injection - For Soil. Allow the extract to come to room temperature, then inject, either manually or by autosampler, 2 uL of the extract into the GC using the splitless injection mode.

Quantitation

The retention time range (window) for gasoline integration must, at a minimum, include toluene through naphthalene. For other volatile petroleum products, the retention time range for integration must be adjusted to incorporate the majority of the components of the petroleum product(s) identified as present in the samples. If specific product identification can not be made, the analyst must quantitate the samples with the calibration curve of the petroleum product that most closely resembles that of the sample.

For those surrogates which elute within the retention time range used for integration, the analyst must subtract the area of the surrogate(s) from the total area to yield the appropriate area of the petroleum product.

The analyst shall use regular unleaded gasoline as the default petroleum product for reporting purposes when no petroleum products were identified in any initial screening or when the type(s) of petroleum products are unknown prior to analysis.

Sample chromatograms of various volatile petroleum products are included at the end of this method to assist the analyst in determining the appropriate integration ranges.

Result Calculation

The area of the components is integrated, as a group, to the baseline and compared to concentrations of the standards which are integrated in the same manner.

For Soil

$$\textit{Soil Sample Conc, mg / kg} = \frac{(A \times R) \times D}{E \times W \times S}$$

where

A = group area of sample

R = Response factor from std curve (ng injected/area count)

D = Extract Volume, mL

W = Weight of sample, grams

E = Volume of extract purged or injected, uL

S = Decimal percent solids of sample

For Water

$$\textit{Water Sample Conc, ug / L} = \frac{(A \times R)}{V}$$

where

A = group area of sample

R = Response factor from std curve (ng purged/area count)

V = Volume of sample purged, mL

The recovery of the surrogate should be between 50% and 150% and must be reported with the results. Report any surrogate recoveries that can not be calculated due to a high level of gasoline contamination.

Author: Bob Carrell, Manchester Environmental Laboratory, Dept. of Ecology, State of Washington. Reviewed and edited by Steve Robb, Toxics Cleanup Program, Department of Ecology, State of Washington. This method is based on Oregon's Department of Environmental Quality TPH-G and Washington's Department of Ecology WTPH-G methods.

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NWTPH-Dx

Semi-Volatile Petroleum Products Method for Soil and Water

Summary

The NWTPH-Dx method is intended to replace the Oregon's Department of Environmental Quality TPH-D and Washington's Department of Ecology WTPH-D methods and to present a more comprehensive approach to semi-volatile petroleum product analyses. NWTPH-Dx adapts Oregon's TPH, Washington's WTPH and EPA SW-846 Methods 3510, 3540/3550 and 8000 and covers the quantitative and qualitative analysis of semi-volatile petroleum products, i.e. jet fuels through heavy fuel oils, in soil and water. The method involves extracting the samples with methylene chloride and injecting a portion of the extract into a gas chromatograph (GC) equipped with a flame ionization detector (FID). This method specifies criteria for the identification and quantitation of semi-volatile petroleum products. A clean-up procedure, which may be used to aid in the removal of non-petroleum based organic interferences, i.e. biogenic interferences, has been included. When the type of petroleum product is unknown, #2 diesel will initially be used as the default petroleum standard.

The reporting limits are 25 mg/kg (soil) and 0.25 mg/L (water) for the petroleum products in the elution range of jet fuels through #2 diesel. For petroleum products eluting after #2 diesel oil, e.g. motor oils, hydraulic fluids, and heavy fuel oils, the reporting limits are 100 mg/kg (soil) and 0.50 mg/L (water). All soil results are reported on a dry weight basis. Since this value assumes 100% solids and therefore will be higher depending on the actual moisture content, the analyst is permitted to concentrate the extract to obtain these reporting limits. When doubt exists as to which reporting limit is applicable for the petroleum product present, the analyst should use the lower value.

The method is applicable for the identification, by pattern matching ("fingerprinting"), and quantitation of semi-volatile petroleum products. These include kerosenes, jet fuels, diesel oils, fuel oils, lubricating oils, hydraulic fluids, mineral oils and insulating oils, e.g. transformer oils. In general, those petroleum products which do not contain a substantial volatile fraction, i.e. the majority of the components eluting outside of the gasoline range, should be analyzed by this method.

Note: The use of GC/MS (Mass Spectrometry) or GC/AED (Atomic Emission Detector) may be substituted for GC/FID as long as all other method parameters are met.

This method is to be used by, or under the direct supervision of, analysts experienced in the use of GC and in the interpretation of gas chromatograms of both fresh and weathered petroleum products.

Equipment and Reagents

Gas Chromatograph, w/wo Autosampler
Flame Ionization Detector
Capillary Split/Splitless Injector
Suggested Column:
J & W Scientific: DB-1 or DB-5, 30 M x 0.25 mm or 0.32 mm I.D. with 0.25 um film thickness capillary column or equivalent
Chromatographic Data System: Capable of group integrations
Analytical Balance, accurate to a least 0.0001 grams
Volumetric Flasks, 10 mL, ground glass stoppered
N-Evap Concentrator or equivalent
Centrifuge tubes, 10 or 15 mL, glass, calibrated in 0.1 mL increments
Centrifuge tubes, 10 or 15 mL, glass, disposable
Kaderna-Danish (K-D) Flasks, 250 mL
Concentrator Tubes, 10 mL
Snyder Columns, 3-ball, 300 mm length
Sodium Sulfate, anhydrous
Methylene Chloride, Burdick and Jackson brand, gas chromatography/pesticide residue grade or equivalent
Sulfuric acid, concentrated
Silica gel, 100/200 mesh, Baker Analyzed Reagent grade or equivalent - Before use, activate for at least 16 hours at 130 degrees C in a shallow tray
Petroleum Product Standards: Available from commercial sources

Note: All samples shall be collected in Eagle Picher, or equivalent, glass jars and held at 4 degrees C until extracted. The holding time, from the date of collection to extraction, is 14 days for soil and preserved water. For unpreserved water, the holding the holding time is 7 days. Preservation is accomplished by adjusting the pH of the water sample to approximately 2 with the addition of 1+1 HCl.

Suggested GC Parameters

Sample Extract Injection Volume = 2 uL
Injector Temperature = 290 degrees C
Detector Temperature = 300 degrees C
Hydrogen Flow = 25-35 cc/min
Air Flow = 300-400 cc/min
Helium Make-up Gas Flow = 30 cc/min
Helium Carrier Gas Head Pressure = 15 psi
GC Temperature Program:
Initial temperature = 50 degrees C, hold 2 minutes
Temperature Ramp Rate = 20 degrees C per minute
Final Temperature = 320 degrees C, hold for 10 minutes

Standards

Reference/Stock Standards. Prepare individual petroleum product reference/stock standards, e.g. kerosene, #2 diesel oil, transformer oil (mineral oil based) and Bunker-C fuel oil.

Add 5 to 10 drops of the pure petroleum product to a zero tared 10 mL flask. Record the weight and bring the flask to volume with methylene chloride, stopper and mix by inverting the flask several times. Calculate the concentration of these standards using the equation shown below. The use of commercially prepared standards is an acceptable alternative to the above procedure. Analysts may not use artificial standards, e.g. diesel range organics mixtures, etc., for quantitation purposes in place of authentic petroleum products.

These standards are to be used to produce calibration working standards which should be used to insure the proper identification of petroleum products by chromatographic pattern matching ("fingerprinting") as well as accurate quantitation.

$$\textit{Stock Conc, ug / mL} = \frac{\textit{(final wt, mg) - (tare wt, mg)}}{\textit{10 mL}} \times \frac{\textit{1000 ug}}{\textit{mg}}$$

Calibration Working Standards. Using the stock standards, prepare calibration working standards for the identified petroleum product(s) to be quantitated. Add the appropriate volume(s), using the equation shown below and adjusting for the concentration change created by any serial dilutions, to a 10 mL volumetric flask(s). Dilute to volume with methylene chloride. Calibration standards must, at a minimum, (1) provide a five point calibration curve, (2) include a sufficiently low standard to provide the necessary reporting limits, and (3) define the linear working range of the instrument.

In order to be acceptable, the calibration curve must have a linear correlation coefficient of at least 0.990 and none of the standards may vary from their true (known) value by more than plus/minus 15%. #2 diesel oil is the default petroleum product for reporting purposes.

Stock Surrogate Standard. Prepare the stock surrogate standard by weighing 50 mg of the surrogate compound(s) into a 10 mL volumetric flask. Bring the flask to volume with methylene chloride for a final concentration of 5000 ug/mL for the surrogate compound. The use of commercially prepared surrogate solutions is an acceptable alternative to the above procedure.

Note: The suggested surrogates are 2-fluorobiphenyl, o, or p-terphenyl or pentacosane. The use of other surrogates is optional. Selected surrogate compounds must be non-polar, unaffected by the cleanup procedure, i.e. the concentrated sulfuric acid/silica gel treatment, and lacking in significant interferences in most standard petroleum products.

Working Surrogate Spike. Using serial dilutions of the stock standard, prepare a surrogate working standard. Add the appropriate volume of the stock surrogate standard, using the equation listed

below, and adjusting for any serial dilutions, to a 10 mL volumetric flask and dilute to volume with methylene chloride. Stopper and mix by inverting the flask several times. The surrogate working standard should be added to a level sufficient to produce a surrogate concentration between 5 and 50 ug/mL.

$$Volume\ Stock,\ uL\ =\ \frac{(Cal\ Std\ Conc,\ ug\ /\ mL)\ x\ 10\ mL}{Stock\ Conc,\ ug\ /\ mL}\ x\ \frac{1000\ uL}{mL}$$

Store all standards in a refrigerator until needed. Allow them to come to room temperature prior to use.

Sample Extraction

Soil Matrix

Weigh approximately 20 grams of soil, recording the weight to the nearest 0.01 grams, and approximately 20 grams of anhydrous sodium sulfate into a 150 mL beaker. Mix completely with a spatula. The mixture should have a grainy texture. If it forms a large clump, add more anhydrous sodium sulfate and grind to grainy texture. Add the appropriate volume of working surrogate standard, 50 mL of methylene chloride and sonicate for 3 minutes utilizing the horn sonicator and power settings in SW-846 Method 3550. Allow the mixture to settle then collect the extract in a 250 mL Kuderna-Danish (KD) flask to which is connected a 10 mL concentrator tube.

Repeat the extraction twice more and add these extracts to the KD. Attach a 3 ball Snyder column and concentrate the extract on a steam bath to a volume of 5-10 mL. Allow the K-D to cool to room temperature. Disassemble the K-D, rinsing the Snyder/K-D and K-D/concentrator tube joints with 1-2 mL of methylene chloride. Add these rinsings to the extract. If necessary, place the concentrator tube in an N-Evap and reduce the volume to 10 mL under a gentle stream of nitrogen. At this point, proceed to the sample cleanup procedure if applicable or transfer a portion of the extract to a 2 mL autosampler vial fitted with a screw top and a Teflon lined septum. Store the extract in a refrigerator until analyzed. If the extract is highly colored or forms a precipitate, a dilution may be necessary to stay within the calibration range. The use of the EPA method 3540 (soxhlet) in place of Method 3550 is optional.

Determine the moisture content of the samples by the following method. Immediately after weighing the sample for extraction, weigh approximately 10 grams of the sample into a tared crucible and record the weight. Dry the sample/crucible overnight at 105 degrees C. Reweigh the sample/crucible after allowing it to cool to room temperature and record the weight. Calculate the % solids as follows: [(grams of dry sample/grams of wet sample) x 100].

Along with each sample set, run at least one duplicate sample per set of 10 or fewer samples (10%) and, for each extraction day, at least one method blank (5%). Spiking of surrogates, extraction and

analyses of the QC samples will be conducted identically to the regular samples with the exception that no soil is added to the method blank.

Water Matrix

Allow the sample to come to room temperature and mark the meniscus for later use in volume determination. Pour the sample into a separartory funnel and adjust the pH to approximately 2 with 1+1 HCl and add the appropriate volume of surrogate working solution. Add 30 mL of methylene chloride to the sample jar and rotate the jar at a sufficient angle to wash the walls. Pour the solvent into the separatory funnel, stopper, and shake it vigorously for one minute, venting frequently. After the two phases have separated, drain the solvent into a 250 mL K-D flask to which is attached a 10 mL concentrator tube.

Note: Due to possible loss of analytes from the water to the sample jar walls, the entire sample must be consumed in the extraction and no aliquots may be used. Since the reporting limits are calculated on a 400 mL sample volume, sample jar size should be appropriate for this volume. For larger sample volume extractions, the analyst must increase the quantity of solvent used to maintain the original solvent/sample ratio.

Repeat the extraction twice more and add these extracts to the K-D. Attach a 3-ball Snyder column to the K-D and concentrate the extract on a steam bath to 5-10 mL. Allow the K-D to cool to room temperature and disassemble it, rinsing the Snyder/K-D and K-D/ concentrator joints with 1-2 mL of methylene chloride. Add these rinsings to the extract. Place the concentrator tube into an N-Evap and reduce the volume to 2 mL under a gentle stream of nitrogen. Transfer the extract to a 2 mL autosampler vial fitted with a screw top and a Teflon lined septum. Store the extract in a refrigerator until analyzed.

Along with each sample set, run at least one duplicate sample per set of 10 or fewer samples (10%) and, for each extraction day, at least one method blank (5%). Spiking of surrogates, extraction and analyses of the QC samples will be conducted identically to the regular samples with the exception that organic free water will be used for the method blank.

As more information becomes available on new extraction techniques, Washington State Dept. of Ecology's Manchester Laboratory and/or Oregon’s Department of Environmental Quality will publish descriptions of acceptable alternative extraction methods.

Sample Cleanup. In those cases where samples contain a significant amount of naturally occurring non-petroleum organics, e.g. leaf litter, bark, etc., which may contribute biogenic interferences, the following cleanup technique may be employed to assist in their reduction or elimination.

Transfer the 10 mL sample extract to a 10 to 15 mL centrifuge tube, add 1 mL of concentrated sulfuric acid to the extract and stopper the tube. Mix thoroughly for 1 minute by either shaking the tube or with the use of a vortex-genie adjusted to the highest setting.

Caution: Since sulfuric acid produces a highly exothermic reaction with water and other polar materials, extreme care should be exercised with its use.

Allow the two phases to separate. Centrifugation can be used to facilitate this process. Using a disposable glass pipet, transfer the methylene chloride (top) phase to another centrifuge tube and add approximately 0.4 grams (roughly equivalent to 1 mL of volume) of silica gel to the tube, stopper and mix as before. Allow the silica gel to settle or centrifuge. Repeat the sulfuric acid/silica gel treatment once more. Transfer a portion of the extract to a 2 mL autosampler vial equipped with a Teflon-lined cap and store the extract in a refrigerator until analyzed. A smaller aliquot of the extract may be used for this cleanup procedure as long as the ratio of extract to acid/silica gel is maintained.

It has been noted that some petroleum products, i.e. heavy fuel oils such as #6 fuel oil or Bunker-C, may experience a concentration loss of between 10 and 20 percent when subjected to this cleanup technique. This loss appears to be primarily associated with the removal of petroleum compounds which contain sulfur. To account for this loss when analyzing samples that have been subjected to the cleanup procedure in preparation for heavy fuel oil determination, the analyst must use utilize standards which have undergone the cleanup technique to calibrate the GC.

Note: The use of EPA method 3611 (Alumina column cleanup) may be substituted for the above cleanup technique if it is demonstrated to provide equivalent results.

Analysis Procedure. Prior to the analysis of any samples or method blanks, the analyst must prepare and analyze a mid-range calibration check standard to insure that the instrument is functioning correctly and that the calibration is still valid. The value obtained for this analysis must not vary from the true (known) value by more than plus/minus 15%. If the value falls outside this range then a second mid-range calibration check standard should be analyzed. If the analysis of the second check standard fails to meet the acceptance criteria, then the instrument must be recalibrated prior to the analysis of any samples. Once the instrument has been shown to be in calibration, the analyses of samples may proceed.

The analyst shall use #2 diesel as the default petroleum product for reporting purposes when no petroleum products were identified in any initial screening or when the type(s) of petroleum products are unknown prior to analysis.

After the last sample has been analyzed, a mid-range calibration check sample must be run to demonstrate that the instrument is still operating within the required parameters. Should this standard fail to meet those parameters, then all samples analyzed after the last successful calibration check standard must be reanalyzed. An increase in the frequency of mid-range calibration check standard analyses beyond the minimum required is recommended.

Qualitative Analysis - Identification

If NWTPH-HCID has not been previously performed on the samples and/or the type of petroleum present is unknown, the analyst should pre-screen the samples to determine the petroleum product.

The observed petroleum product shall be determined by pattern matching with the standard(s) analyzed the same day. Chromatograms used for this "fingerprinting" should be normalized to approximately 90% of full scale for the largest component of the particular petroleum product observed.

When reporting the results, the terms such as "diesel range" or "motor oil range", or derivations of them, should only be used when the analyst is unable to identify the petroleum product(s) present. Motor oils, hydraulic fluids and similar petroleum products which consist primarily of an unresolved chromatographic envelope of compounds originating at, or extending beyond tetracosane, may be reported using the collective term "lube oil" unless specific identification is possible. Heavy fuel oils, e.g. #6 fuel oil or Bunker-C, which contain a diesel range component as well as a lube oil range, may be reported using the collective term "heavy fuel oil" unless specific identification is possible. Heavy fuel oils should not, however, be confused with mixtures of #2 diesel and lube oils.

Note: The actual identification of the grade or type of lube oil and/or heavy fuel oil may require equipment and techniques beyond the scope of this method.

Quantitative Analysis - Integration

The retention time range (window) for integration must be adjusted to incorporate the majority of the components of petroleum product(s) identified as present in the samples. If specific product identification can not be made, the analyst must quantitate the samples with the calibration curve for the petroleum product that most closely resembles that of the sample. In all cases, the selected retention time range (windows) used for quantitation must, at a minimum, include any unresolved envelope of compounds as well as all discrete component peaks with an area greater than or equal to 10% of the largest peak. These components must be integrated to the baseline as a group.

For those surrogates which elute within the retention time range used for integration of a petroleum product, the analyst must subtract the area of the surrogate from the total area to yield the appropriate area of the petroleum product. In this case, the analyst may wish to generate separate calibrations for the petroleum standards and the surrogate(s) to facilitate integration and quantitation.

At the discretion of the analyst, the range of components included in the integration may be adjusted in order to minimize the potential contribution of any co-eluting fractions arising from the presence of multiple petroleum products. Any change in the integration range must be reflected in a concomitant change to the calibration standards integration.

Sample chromatograms of various petroleum products are included at the end of this method to assist the analyst in determining the appropriate integration ranges.

Result Calculation

For Soil

$$Soil\ Sample\ Conc,\ mg / kg = \frac{(A \times R) \times V \times Dilution\ Factor}{E \times W \times S}$$

where

A = Area Count from Sample
R = Response Factor (ng injected/area count)
V = Extract Volume (mL)
W = Weight of Sample (g)
E = Volume injected, (uL)
S = Decimal percent solids of sample

For Water

$$Water\ Sample\ Conc,\ mg / L = \frac{(A \times R) \times V}{E \times S}$$

where

A = Area Count from Sample
R = Response Factor (ng injected/area count)
V = Extract Volume (mL)
S = Volume of Sample (mL)
E = Volume Injected (uL)

The recovery of the surrogate should be between 50% and 150% and must be reported with the results. If the recovery of the surrogate is not able to be obtained due to a high levels of petroleum contamination, then this fact needs to be reported.

Author: Bob Carrell, Manchester Environmental Laboratory, Dept. of Ecology, State of Washington. Reviewed and edited by Steve Robb, Toxics Cleanup Program, Department of Ecology, State of Washington. This method is based on Orgeon's Department of Environmental Quality TPH-D and Washington's Department of Ecology WTPH-D methods.

METHOD FOR THE DETERMINATION

OF

VOLATILE PETROLEUM HYDROCARBONS (VPH) FRACTIONS

Washington State Department of Ecology

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METHOD FOR THE DETERMINATION OF VOLATILE PETROLEUM HYDROCARBONS (VPH)

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DISCLAIMER

Mention of trade names or commercial products does not constitute endorsement by the Washington State Department of Ecology Equipment and materials cited in this method may be replaced by similar products, as long as adequate data exists or has been produced documenting equivalent or superior performance.

METHOD FOR THE DETERMINATION OF VOLATILE PETROLEUM HYDROCARBONS

1.0 SCOPE AND APPLICATION

1.1 This method is designed to measure the collective concentrations of volatile aliphatic and aromatic petroleum hydrocarbons in water and soil. **The carbon ranges used through out this document are given in equivalent carbon (EC) numbers which are related to the boiling point of a chemical normalized to the boiling point of the n-alkanes, and its retention time in a boiling point gas chromatographic (GC) column.** Volatile aliphatic hydrocarbons are collectively quantitated within four ranges: C5 through C6, >C6 through C8, >C8 through C10 and > C10 through C12. Volatile aromatic hydrocarbons are collectively quantitated within the C8 through C10, >C10 through C12 and >C12 through C13 ranges. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 36°C and 220°C.

1.2 This method is also designed to measure the individual concentrations of benzene, toluene, ethylbenzene, xylenes, and methyl tert butylether (MTBE) in water and soil.

1.3 Petroleum products suitable for evaluation by this method include gasoline, mineral spirits, and certain petroleum naphthas. This method, in and of itself, is not suitable for the evaluation of samples contaminated with kerosene, jet fuel, heating oils, lubricating oils, or other petroleum products which contain a significant percentage of hydrocarbons larger than C10. When samples are known or suspected to contain petroleum products containing significant concentration of hydrocarbons >C10, the Extractable Petroleum Hydrocarbon (EPH) method should also be employed to fully evaluate the hydrocarbons present.

1.4 For reporting purposes, the practical quantitation limits (PQL), given the sample volume purged, mass and/or methanol extract volume purged are: 50.0 ug/L for water and 5.0 mg/kg for soil/sediments for the aliphatic and aromatic carbon ranges and 5.0 ug/L and 0.5 mg/kg respectively for the individually targeted compounds. The procedure for Method Detection Limits (MDL) determination in this method and the

Single Laboratory Precision, Accuracy and MDL data (generated by the State of Massachusetts) is added for informational purposes only.

1.5 This method is based on a purge-and-trap, gas chromatography (GC) procedure. This method should be used by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatographs. The analysts should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.

1.6 Like all GC procedures, this method is subject to a "false positive" bias in the reporting of targeted analytes, in that non-petroleum compounds eluting or co-eluting within a specified retention time window may be falsely identified and/or quantitated with the respective carbon ranges. Confirmatory analysis by a GC/MS, EPA Method 8260, or other suitable procedures are recommended in cases where significant concentrations of non-hydrocarbon compounds are known or suspected. If the results of these analyses lead to identification and quantitation of non-petroleum compounds, the analyst may subtract those values from the affected carbon ranges as long as the identities and quantities of subtracted compounds are provided in the analytical report.

2.0 SUMMARY OF METHOD

2.1 Samples are analyzed using purge-and-trap sample concentration. The gas chromatograph is temperature programmed to facilitate separation of organic compounds. Detection is achieved by a photo-ionization detector (PID) and flame ionization detector (FID) in series. Quantitation is based on comparing the PID and FID detector response of a sample to a standard comprised of aromatic and aliphatic hydrocarbons. The PID chromatogram is used to determine the individual concentrations of targeted analytes (BTEX/MTBE) and collective concentration of aromatic hydrocarbons within the C8 through C10, C10 through C12 and C12 through C13 ranges. The FID chromatogram is used to determine the collective concentration of aliphatic hydrocarbons within the C5 through C6, C6 through C8, C8 through C10 and C10 through C12 ranges. To avoid double counting of the aromatic contribution to the aliphatic ranges, the PID concentrations are subtracted from the FID concentrations to yield the aliphatic ranges values.

2.2 This method is suitable for the analysis of waters, soils, and sediments. Water samples may be analyzed directly for volatile petroleum hydrocarbons by purge-and-trap concentration and gas chromatography. Soil samples are either dispersed in methanol to dissolve the volatile organic constituents and a portion of the methanol is analyzed by purge-and-trap GC or combined with water for purging directly from a soil purge vessel (EPA method 5035).

2.3 This method is based on, and constitutes a significant modification of, the “Method for the Determination of Volatile Petroleum Hydrocarbons (VPH)”, Public Comment Draft 1.0, developed by the Massachusetts Department of Environmental Protection and on EPA method 5035. They in turn based their method on (1) USEPA Methods

5030, 8000, 8020, and 8015, SW-846, "Test Methods for Evaluating Solid Wastes", 3rd Edition, 1986; (2) Draft "Method for Determination of Gasoline Range Organics", EPA UST Workgroup, November, 1990; and (3) "Method for Determining Gasoline Range Organics", Wisconsin Department of Natural Resources, PUBL-SW-140, 1992.

3.0 DEFINITIONS

3.1 **Volatile Petroleum Hydrocarbons (VPH)** are defined as all hydrocarbon compounds eluting just prior to n-pentane through 1-methylnaphthalene. VPH is comprised of C5 through C6, >C6 through C8, >C8 through C10 and >C10 through C12 Aliphatic Hydrocarbons, as well as >C8 through C10, >C10 through C12 and >C12 through C13 Aromatic Hydrocarbons as well as benzene and toluene. VPH concentration data are reported as the aggregate concentrations of the aliphatic and aromatic hydrocarbon ranges and as selected targeted analytes.

3.2 **Equivalent Total Petroleum Hydrocarbons (E-TPH)** For samples contaminated ONLY with gasoline or other low molecular weight petroleum products, the E-TPH value is equivalent to the VPH value. For samples contaminated with BOTH light and heavy molecular weight petroleum products (e.g., gasoline and diesel fuel), the E-TPH value is a summation of the VPH value and the Extractable Petroleum Hydrocarbon (EPH) values. In order to avoid double counting of analytes due to the overlap in the carbon ranges existing between the two methods, the analyst will report the highest of the two values determined for the overlapping ranges. In those cases where both the VPH and EPH methods are employed on samples, the analyst may select to quantitate the >C10 through C12 Aliphatic and the >C10 through C12 Aromatic Hydrocarbon ranges only using the EPH method.

3.3 **C5 through C6 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds which elute on the FID chromatogram from (and including) n-pentane through n-hexane.

3.4 **C6 through C8 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbons which elute on the FID chromatogram after n-hexane through n-octane.

3.5 **C8 through C10 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds which elute on the FID chromatogram after n-octane through n-decane.

3.6 **C10 through C12 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbons which elute on the FID chromatogram after n-decane through n-dodecane.

3.7 **C8 through C10 Aromatic Hydrocarbons** are defined as all hydrocarbon compounds which elute on the PID chromatogram after toluene through 1,2,3-trimethylbenzene.

3.8 **C10 through C12 Aromatic Hydrocarbons** are defined as all hydrocarbons which elute on the PID chromatogram after 1,2,3- trimethylbenzene through naphthalene.

3.9 **C12 through C13 Aromatic Hydrocarbons** are defined as all hydrocarbons which elute on the PID chromatogram after naphthalene through 1-methylnaphthalene. This is a hybrid range which is designed to acquire the methylnaphthalenes associated with petroleum products like gasoline and is only used when VPH is run without an accompanying EPH method request.

3.10 **Targeted VPH Analytes** are defined as benzene, toluene, ethylbenzene, p,m,o-xylenes, and MTBE.

3.11 **Volatile Petroleum Hydrocarbon (VPH) Component Standard** is defined as a 15 component mixture of the aliphatic and aromatic compounds, plus surrogate, listed in Table 1. The compounds comprising the VPH Component Standard are used to (a) define the individual retention times and chromatographic response factors for each of the Targeted VPH Analytes, (b) define and establish the windows for the collective aliphatic and aromatic hydrocarbon ranges of interest, and (c) determine average chromatographic response factors that can in turn be used to calculate the collective concentration of hydrocarbons within these ranges.

3.12 **Analytical Batch** is defined as a group of samples with similar matrices which are processed as a unit. For Quality Control purposes, if the number of samples in such a group is greater than 20, then each group of 20 samples or less are defined as separate analytical batches.

3.13 **Laboratory Duplicates** are defined as split samples taken from the same sampling container and analyzed separately with identical procedures. The analysis of laboratory duplicates give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.14 **Field Duplicates** are defined as two separate samples collected at the same time and place under identical circumstances and managed the same throughout field and laboratory procedures. Analyses of field duplicates give a measure of the precision associated with sample collection, preservation, and storage, as well as laboratory procedures.

3.15 **E-TPH Duplicates** are defined as two separate samples collected at the same time and location, for analysis by both EPH and VPH methods. E-TPH duplicates are taken at locations where significant concentrations of petroleum hydrocarbons lighter and heavier than C9 are likely to be present (e.g., locations contaminated by releases of both gasoline and diesel fuel). The resultant EPH and VPH concentrations, adjusted to prevent double counting of overlapping hydrocarbon ranges between the methods, are then summed to determine the Equivalent TPH (E-TPH) concentration.

3.16 **Calibration Standards** are defined as a series of standard solutions prepared from dilutions of a stock standard solution, containing known concentrations of each analyte and surrogate compound of interest.

3.17 **Calibration Check Standard** is defined as a calibration standard used to periodically check the calibration state of an instrument. The calibration check standard is prepared from the same stock solution as calibration standards, and is generally one of the mid-level range calibration standard dilutions.

Table 1. Volatile Petroleum Hydrocarbon (VPH) Component Standard

Compound	Equivalent Carbon Number
n-Pentane	5.0
n-Hexane	6.0
Methyl tert butylether	N/A
Benzene	6.5
Toluene	7.6
n-Octane	8.0
Ethylbenzene	8.5
m- & p- Xylene	8.6
o-Xylene	8.8
1,2,3,-Trimethylbenzene	10.1
n-Decane	10.0
Naphthalene	11.7
n-Dodecane	12.0
1-Methylnaphthalene	13.0
2,5-Dibromotoluene (surrogate)	N/A

3.18 **Matrix Spiking Solution** is defined as a solution which is generally prepared independently from the calibration standards, containing known concentrations of method analytes.

3.19 **Laboratory Method Blank** is defined as, depending on the matrix of the samples, either reagent water or clean sand spiked with a surrogate standard. The laboratory method blank is treated identically as with samples, exposed to all glassware, solvents, reagents, and equipment. A laboratory method blank is analyzed with every batch of samples, to determine if method analytes or other interferences are present in the laboratory environment, reagents, or equipment.

3.20 **Laboratory Fortified Blank (LFB)** is defined as, depending on the matrix of the samples, either reagent water or a clean sand blank fortified with a matrix spiking solution.

The LFB is treated and analyzed identically as with samples and blanks, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements at the required practical quantitation limits..

3.21 **Laboratory Fortified Matrix (LFM) Sample** is defined as an environmental sample which has been spiked with a matrix spiking solution containing known concentrations of method analytes. The LFM sample is treated and analyzed exactly as a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined through the separate analyses of a laboratory or field duplicate, and the measured values in the LFM sample corrected for background concentrations.

3.22 All other terms are as defined in SW-846, "Test Method for Evaluating Solid Waste", USEPA, September, 1986, and as amended.

4.0 INTERFERENCES

4.1 Samples can become contaminated by diffusion of volatile organics through the sample container septum during shipment and storage. Trip blanks prepared from reagent water should be carried through sampling and subsequent storage and handling to serve as a check on such contamination.

4.2 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe and/or purging device must be rinsed between samples with reagent water or solvent. The trap and other parts of the system are also subject to contamination, therefore, frequent bake-out and purging of the entire system may be required. A screening step is recommended to protect analytical instrumentation. Whenever an unusually concentrated sample is encountered, it must be followed by the analysis of a solvent blank to check for cross-contamination.

4.3 Certain organic compounds not associated with releases of petroleum products, including chlorinated solvents, ketones, and ethers, will be quantitated as Volatile Petroleum Hydrocarbons. Some samples may require additional analytical procedures to be employed , e.g. GC/MS, to document the presence and quantity of such compounds.

4.4 The response selectivity of a photo-ionization detector (PID) is used in this method to differentiate aromatic hydrocarbons from aliphatic hydrocarbons. All compounds eluting on the PID chromatogram after toluene are identified by the method as aromatic hydrocarbons. This will lead to an overestimation of aromatic hydrocarbons within samples, as certain aliphatic compounds will elicit a response on the PID, particularly unsaturated compounds such as alkenes. The significance and implications of this overestimation will vary from sample to sample and, where less conservative data are desired, additional actions should be considered to

minimize the detection of non-aromatic compounds, such as the use of a lower energy PID lamp or GC/MS.

5.0 HEALTH AND SAFETY ISSUES

The toxicity and carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis.

6.0 APPARATUS AND MATERIALS

6.1 The following glassware is used in this method:

6.1.1 VOC Vials: Wide mouth 60-mL VOC vials or 40-mL VOC vials with teflon/ silicone septa for soils; 40-mL VOC vials with teflon/silicone septa for waters.

6.1.2 Volumetric flasks: 10-mL, 50-mL, 100-mL, and 1,000-mL with a ground-glass stopper.

6.1.3 Disposal pipets: Pasteur.

6.2 Analytical balance: An analytical balance capable of accurately weighing 0.0001 g must be used for weighing standards. A top-loading balance capable of weighing to the nearest 0.1 g must be used for weighing soil samples.

6.3 **Gas Chromatography**

6.3.1 Gas Chromatograph: An analytical system complete with temperature programmable gas chromatograph and purge-and-trap concentrator. The data station must be capable of storing and reintegrating chromatographic data and must be capable of determining peak areas using a forced baseline projection.

6.3.2 Columns

6.3.2.1 Recommended column: 105M x 0.53 mm I.D. Restek RTX 502.2, 3.0 micron film thickness, or equivalent.

6.3.2.2 Other columns, such as a 60 M x 0.53 mm J&W DB-5, may be used. Capillary columns are required to achieve necessary resolution. The column must be capable of resolving typical gasoline components. It must also resolve ethylbenzene from m/p-xylene. Some columns may require subambient cooling to achieve these criteria.

6.3.3 Detectors: The method utilizes a Photo-ionization Detector (PID) in series with a Flame Ionization Detector (FID); the PID first in the series. The method is based upon the use of a 10.0 eV PID lamp, although lower energy lamps are permissible in order to minimize PID response to aliphatic compounds.

6.3.4 Purge-and-trap device: The purge-and-trap device consists of a sample purger, a trap, and a desorber. Several complete devices are commercially available.

6.3.4.1 The purging chamber must be designed to accept 5 mL samples with a water column at least 3 cm deep. Purging devices larger than 5 mL have a reduced purging efficiency and should not be used. The gaseous headspace between the water column and the top of the vessel should be at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. Fritted glass or needle sparge cells may be used. If needle sparge cells are used, the purge gas must be introduced no more than 5 mm from the base of the water column. Alternate sample purge devices may be used, provided equivalent performance is demonstrated.

6.3.4.2 The trap should be at least 25 cm long and have an inside diameter of at least 0.105 inches. The trap should be packed with 400 mg of Carbopack B (Supelco Cat. No. 209273). Alternative trap packing materials include: Tenax GC (or equivalent); 7.6 cm Carbopack B and 1.3 cm Carbosieve S-III (Supelco Cat No. 2-0321); 7 cm Carbopack C and 1.2 cm Carbopack B (Supelco Cat No. 2-1064); or equal volumes of Tenax, silica gel, and charcoal as described in EPA SW-846 Method 5030. In general, Carbopack trap packing materials are recommended because they have less of a tendency to retain methanol, which could interfere with the elution of pentane and quench the FID flame. The trap length and packing materials may be varied as long as equivalent performance has been verified.

6.3.4.3 Prior to initial use, the Carbopack B trap should be conditioned overnight at 270°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to a hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min. at 260°C with backflushing. The trap may be vented to the analytical column during daily conditioning, however, the column must be run through the temperature program prior to analysis of samples. Devices other than the traps recommended in Section 6.3.4.2 should be conditioned and desorbed according to the manufacturer's guidelines.

6.3.4.4 The desorber should be capable of rapidly heating the trap to 240°C for desorption.

6.4 Ultrasonic bath.

6.5 Syringes: 5-mL Luerlock glass hypodermic and 5-mL gas-tight syringe with shutoff valve.

6.6 Syringe valve: Two-way, with luer ends.

6.7 Microsyringes: 1-µL, 5-µL, 10-µL, 25-µL, 100-µL, 250-µL, 500-µL, and 1,000-µL.

6.8 Spatula: Stainless steel.

7.0 REAGENTS AND STANDARDS

7.1 **Reagents**

7.1.1 Reagent Water: organic free water (ASTM Type I reagent grade water).

7.1.2 Solvent: methanol; purge and trap grade or equivalent. Store away from other solvents.

7.1.3 Ottawa and/or masonry sand: free of volatile petroleum hydrocarbons.

7.2 **Stock Standard Solution**

Prepare a stock standard solution in methanol at approximately 20 µg/µL, or purchase certified solutions. Preparation of stock standards and component standards should be done using volumetric glassware.

7.2.1 The stock standard solution consists of the 15 VPH component standards listed in Table 1 and a surrogate standard. Prepare the stock standard solution by accurately weighing approximately 0.2000 g of each standard component. Dissolve the component in methanol and dilute to volume in a 10-mL volumetric flask. At the discretion of the analyst, the surrogate standard may be made up as a separate solution from the VPH standards.

7.2.1.1 Place about 8 mL of methanol in a 10-mL tared ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min. or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

7.2.1.2 Using a 500-µL syringe, immediately add 100 to 200 µL of each VPH Component Standard to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

7.2.1.3 Dilute to volume, stopper, and then mix by inverting the flask three times. Calculate the concentration in micrograms per microliter (µg/µL) from the net gain in weight. When compound purity is assayed to be 98% or greater, the weight may be used without correction to calculate the

concentration of the stock standard, provided such purities are certified by the manufacturer or by an independent source.

7.2.1.4 Transfer the stock standard solution into a Teflon-lined screw-cap/crimp cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.

7.2.2 Stock standard solutions must be replaced after 6 months, or sooner if comparison with check standards indicates a problem. The use of commercially prepared certified standard solutions is an acceptable alternative to the use of neat compounds in the preparation of standards.

7.3 Primary Dilution Standard

Using the stock standard solution, prepare primary dilution standards in methanol, as needed. The primary dilution standard should be prepared at the concentrations shown in Table 2. These standards should be stored with minimal headspace, at -10°C to -20°, and should be checked frequently for signs of degradation or evaporation. The analyst is allowed to prepare separate surrogate and VPH analyte standards.

The primary dilution standards should be replaced at least monthly.

7.4 VPH Calibration Standards

Prepare VPH Calibration standards in reagent water from the primary dilution standard at a minimum of five concentration levels. One of the concentration levels must be near, but above, the method detection limit and must be at a sufficiently low level to allow the PQL reporting of at least 5.0 ug/L for water and 0.5 mg/kg for soil/sediments for the targeted analytes (BTEX and MTBE) and 50.0 ug/L and 5.0 mg/kg respectively for the aliphatic and aromatic carbon ranges. The other standard concentrations must correspond to the expected range of concentrations found in real samples and/or should define the working range of the detector.

7.4.1 Rapidly inject the methanolic standard into the water in the expanded area of a filled 100-mL volumetric flask. Remove the needle quickly after injection.

7.4.2 Mix aqueous standards by inverting the flask three times.

7.4.3 Discard the solution contained in the neck of the flask, and fill the sample syringe from the standard solution contained in the expanded area of the flask.

7.4.4 Do not use pipets to dilute or transfer samples or aqueous standards.

7.4.5 Do not inject more than 20 µL of methanolic standards into 100 mL of reagent water. Aqueous standards are not stable and should be discarded after one hour.

7.5 Surrogate Control Standard (SCS)

The analyst must monitor both the performance of the analytical system and the effectiveness of the method in dealing with sample matrices by spiking each sample, blank, and matrix spike with a surrogate standard. The surrogate standard is also added to the VPH calibration standard solutions. The recommended surrogate standard is 2,5-dibromotoluene, which elutes after all aliphatic and aromatic compounds of interest. The use of additional surrogates or surrogates other than those listed above may be used, at the discretion of the analyst, as long as their performance in the method is demonstrated as acceptable and does not compromise the quantitation of the various target analytes or carbon ranges.

7.5.1 Surrogate Spiking Solution: From a stock standard solution prepared as in Section 7.2.1, prepare a surrogate spiking solution at 50 µg/mL in methanol. Add 4.0 µL of this surrogate spiking solution directly into the 5-mL syringe with every aqueous sample, blank, and matrix spike. 1.0 mL of the surrogate spiking solution is added to soil samples during the extraction step (See 9.1.2.2).

7.6 **Matrix Spiking Solution**

The recommended matrix spiking solution, consisting of the Targeted VPH Analytes, is prepared in methanol at concentrations of 50 µg/mL.

7.7 **Petroleum Reference Standard**

The use of a Petroleum Reference Standard is recommended for quality control purposes. The Petroleum Reference Standard consists of an API or commercial gasoline standard. Prepare a Petroleum Reference Standard Spiking Solution by accurately weighing approximately 0.0100 g of neat product. Dissolve the neat product in methanol and dilute to volume in a 10-mL volumetric flask.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 **Aqueous Samples**

8.1.1 Aqueous samples should be collected in duplicate (or the number of vials directed by the laboratory) without agitation and without headspace in contaminant-free amber glass VOC vials with Teflon-lined septa screw caps. Samples must be acidified to a pH of 2.0 or less at the time of collection and this can generally be accomplished by adding 3 or 4 drops (0.1 to 0.2 mL) of 1:1 HCl (1 part reagent water and 1 part concentrated HCl) to a 40-mL VOC vial. Samples must be cooled to 4°C immediately after collection.

8.1.2 A chain of custody form should accompany all sampling vials and should document the date and time of sample collection and acid preservation. The pH of all water samples must be determined by the laboratory unless sample vials containing acid for field preservation were supplied by the laboratory (this must be noted on the chain of custody). The pH measurement may be performed on left over sample. Any sample found to contain a pH above 2.0 should be so noted on the laboratory/data report sheet.

8.1.3 Any sample received by the laboratory that is not packed in ice or cooled to 4°C must be so noted on the laboratory/data report sheet.

8.1.4 Acid preserved aqueous samples must be analyzed within 14 days of collection. Aqueous samples which, for whatever reason, have not received acid preservation must be analyzed within 7 days of collection or the data must be reported as an “estimate quantity”.

8.2 **Soil Samples**

8.2.1 Soil samples must be collected in a manner that minimizes sample handling and agitation. All sediment must be removed from the glass threads of the vial to ensure an adequate seal. Samples must be cooled to 4°C immediately after collection.

8.2.3 Samples for VPH analysis should be collected in duplicate 2 or 4 ounce VOC jars with Teflon coated septum lined lids.

8.2.4 Sampling must be accomplished in a manner that ensures a minimum of headspace in the sample vial.

8.2.5 A chain of custody form should accompany all sampling vials and should document the date and time of sample collection.

8.2.6 Soil samples must be analyzed within 14 days of collection.

8.3 A summary of sample collection, preservation and holding times is provided in Table 2 .

Table 2 . Holding Times and Preservatives for VPH Samples

Matrix	Container	Preservation	Holding Time
Aqueous Samples	40-mL VOC vials w/ Teflon-lined septa screw caps	Add 3 to 4 drops of 1:1 HCl; cool to 4°C	14 days 7 days, if not preserved
Soil/Sediments Samples	VOC vials w/ Teflon-lined septa screw caps. 40-mL vials	cool to 4°C	14 days

9.0 PROCEDURE

9.1 **Sample Preparation and Purging**

9.1.1 It is recommended that samples known or suspected to have extremely high levels of volatile petroleum hydrocarbons be screened prior to analysis in order to establish the appropriate volume/mass to be used for analysis. This screening step may be analysis of a soil sample's methanol extract (diluted), the headspace method (SW-846 method 3810), the hexadecane extraction and screening method (SW-846 Method 3820) or other applicable method as determined by the analyst.

9.1.2 Water Samples

Introduce volatile compounds into the gas chromatograph using a purge-and-trap concentrator. The use of autosampling devices for sample introduction is recommended or the analyst may use the manual method outlined below.

9.1.2.1 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and

compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one 40-mL vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 20-mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

9.1.2.2 If necessary, samples should be diluted prior to injection into the purge chamber. In such cases, all steps must be performed without delay until the diluted sample is in a gas-tight syringe.

9.1.2.2.1 Dilutions may be made in volumetric flasks (10 mL to 100 mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for highly concentrated samples.

9.1.2.2.2 Calculate the approximate volume of reagent water to be added to the volumetric flask selected and add slightly less than this volume of reagent water to the flask.

9.1.2.2.3 Inject the proper aliquot of sample from the syringe prepared in Paragraph 9.1.2.1 into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with reagent water. Cap the flask, invert, and shake three times. Repeat the above procedure for additional dilutions. Alternatively the dilutions can be made directly in the glass syringe to avoid further loss of volatiles.

9.1.2.2.4 Fill a 5-mL syringe with diluted sample as in Paragraph 9.1.2.1.

9.1.2.3 Add 4.0 µL of the surrogate spiking solution through the valve bore of the syringe. Close the valves.

9.1.2.4 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

9.1.2.5 Close both valves and purge the sample for 11 min. Recommended purge and trap operating parameters are provided in Table 3.

Table 3. Suggested Purge and Trap Operating Parameters

Purge gas	Helium
Purge gas flow rate (mL/min)	40
Purge time (min)	11.0
Purge temperature	Ambient
Desorb temperature °C	250
Backflush inert gas flow (mL/min)	15-20

9.1.2.6 At the conclusion of the purge time, attach the trap to the chromatograph (if necessary), adjust the device to the desorb mode, and begin the gas chromatographic temperature program (in Section 9.2.1) and GC data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 240°C and backflushing the trap with inert gas between 15 and 20 mL/min for 4 minutes.

9.1.2.7 While the trap is desorbing into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5 mL flushes of reagent water (or methanol followed by reagent water) to avoid carryover of pollutant compounds into subsequent analyses.

9.1.2.8 After desorbing the sample, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 260°C. After approximately 7 to 15 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. After a highly concentrated sample, a longer baking time may be necessary. When cool, the trap is ready for the next sample.

9.1.2.9 If the concentration of an analyte in a sample exceeds the calibration range, a dilution of the sample is required. If a sample analysis results in a saturated detector response for a compound, the analysis must be followed by one or more blank reagent water analyses. If the final blank analysis is not free of significant interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of significant interferences.

9.1.2.10 All dilutions should keep the detector response of the major constituents (previously saturated peaks) in the upper half of the linear range of the calibration curve.

9.1.3 Soil/Sediments

Soil and sediment samples are extracted with methanol. An aliquot of the extract is added to reagent water and introduced into the gas chromatograph using a purge and trap concentrator. Should lower values for the targeted analytes be desired, the analyst may employ direct purging of the soil sample using the method outlined in EPA methods 5030 and 5035. The use of autosampling devices for sample introduction is recommended or the analyst may use the manual method outlined below.

9.1.3.1 Weigh the sample vial to 0.1 g in a top loading balance and add 4 to 5 grams of the sample to the vial, reseal and determine the weight of the soil/sediment sample.

9.1.3.2 Quickly add 9.0 mL of methanol and 1.0 mL of the surrogate spiking solution. Cap and shake the sample vial for 2 minutes.

9.1.3.3 Allow soil/sediment to settle, or centrifuge the vial, until a layer of methanol is apparent.

9.1.3.4 Using a microliter syringe, withdraw an appropriate aliquot of the methanol extract for sparging. Sample screening data can be used to determine the volume of methanol extract to add to the 5 mL of reagent water for analysis. All dilutions must keep the response of the major constituents in the upper half of the linear range of the calibration curve.

9.1.3.5 Remove the plunger from one 5.0-mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to allow for addition of the extract (e.g., for 100 µL of extract adjust to 4.9 mL). Pull the plunger to 5.0 mL for addition of the sample extract. Add the volume of methanol extract determined from screening (100 µL maximum).

9.1.3.6 Attach the syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber. Complete operations as specified in Paragraphs 9.1.2.5 through 9.1.2.8.

9.1.4 Proceed with the analysis as described in Sections 9.2 through 9.5. Analyze all laboratory method blanks and QC samples under the same conditions as that used for samples.

9.1.5 If the responses exceed the calibration or linear range of the system, use a smaller aliquot of methanol or aqueous sample.

9.1.6 Determination of Percent Moisture

9.1.6.1 Soil and sediment results must be reported on a dry-weight basis.

9.1.6.2 Transfer 5 to 10 g of sample into a tared crucible. The amount of material used to determine the percent moisture will depend on the amount of moisture present, thus relatively dry samples require more sample addition in order to achieve a significant weight change than wet samples. Dry the sample overnight in an oven at 105°C. Remove the sample from the oven and allow it to cool in a desiccator before reweighing. Reweigh and calculate the percent moisture of the sample using the equations provided in Section 9.6.2.2.

9.2 GC Conditions

9.2.1 Oven Program: Oven temperature 45°C, hold for 1 min, then to 100°C at 3°C/min, to 160°C at 8°C/min, to 230°C at 20°C/min; hold for 7.5 min. Conditions may be altered to improve resolution of volatile petroleum hydrocarbons.

9.2.2 Gas Flows: The recommended carrier gas is helium.

9.2.2.1 Carrier gas flow: 12.5 mL/min.

9.2.2.2 Air: 350 mL/min

9.2.2.3 Hydrogen: 30 mL/min

9.2.2.4 Make up gas flow: 17.5 mL/min

9.2.3 Miscellaneous:

9.2.3.1 FID temperature: 230°C

9.2.3.2 PID temperature: 230°C

9.2.3.3 Injection port temperature: 250°C

9.2.3.4 Column head pressure: 15 psi

9.3 **Retention Time Windows**

9.3.1 Before establishing retention time windows, make sure the GC system is within optimum operating conditions. Make three injections of the VPH Component Standard throughout the course of a 72-hr period. Serial injections over less than a 72-hr period may result in retention time windows that are too tight.

9.3.2 Calculate the standard deviation of the three absolute retention times for each individual compound in the VPH Component Standard. The retention time window is defined as plus or minus three times the standard deviation of the absolute retention times for each standard. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

9.3.3 In those cases where the standard deviation for a particular standard is zero, the laboratory should substitute the standard deviation of a closely eluting structurally similar compound to develop a valid retention time window.

9.3.4 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. This data must be retained by the laboratory.

9.3.5 VPH retention time (Rt) windows are defined as beginning 0.1 minutes after the Rt of the beginning marker compound and ending 0.1 minutes after the Rt of the ending marker compound. The exception to this is the C5 through C6 aliphatic hydrocarbon range, where its Rt window is defined a beginning 0.1 minutes prior to the beginning marker compound and ending 0.1 minutes after the ending marker compound. VPH marker compounds and windows are summarized in Table 4 .

Table 4 . VPH Marker Compounds

Hydrocarbon Range	Beginning Marker Compound	Ending Marker Compound
C5-C6 Aliphatic Hydrocarbons (FID)	just before n-Pentane	just after n-Hexane
C6-C8 Aliphatic Hydrocarbons (FID)	just after n-Hexane	just after n-Octane
C8-C10 Aliphatic Hydrocarbons (FID)	just after n-Octane	just after n-Decane
C10-C12 Aliphatic Hydrocarbons (FID)	just after n-Decane	just after n-Dodecane
C8-C10 Aromatic Hydrocarbons (PID)	just after Toluene	just after 1,2,3-Trimethylbenzene
C10-C12 Aromatic Hydrocarbons (PID)	just after 1,2,3-Trimethylbenzene	just after Naphthalene
C12-C13 Aromatic Hydrocarbons (PID)	just after Naphthalene	just after 1-Methylnaphthalene

9.4 **Calibration**

9.4.1 External Standard Calibration Procedure

9.4.1.1 Prepare VPH Calibration Standards at a minimum of five concentration levels in accordance with the procedures and specifications contained in Section 7.0.

9.4.1.2 Analyze each VPH Calibration Standard following the procedures outlined in Section 9.5. Tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each targeted analyte. Alternatively, the ratio of the response to the amount injected, defined as the calibration factor (CF), may be calculated for method analytes using Equation 1. If the percent relative standard deviation (%RSD) of the calibration factor is equal to or less than 20 % over the working range for all analytes of interest, as determined using Equation 2, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve.

Equation 1: Calibration Factor

$$Calibration\ Factor\ (CF) = \frac{area\ of\ peak}{mass\ purged\ (ng)}$$

Equation 2: Relative Standard Deviation

$$\%RSD = \frac{Stand\ Dev\ of\ 5\ CFs}{Mean\ of\ 5\ CFs} \times 100$$

9.4.1.3 A collective calibration curve or factor must also be established for each hydrocarbon range of interest. Calculate the collective Calibration Factors (CF) for C5-C6, >C6-C8, >C8-C10 and >C10-C12 Aliphatic Hydrocarbons ranges using the FID chromatogram. Calculate the collective CF for the >C8-C10, >C10-C12 and C12-C13 Aromatic Hydrocarbons ranges using the PID chromatogram. Tabulate the summation of the peak areas of all components, the compounds which define the various ranges, in those fractions (e.g. C6-C8 Aliphatic Hydrocarbons, n-pentane and n-hexane or >C6 - C8, n-octane) against the total mass injected using Equation 3.

Note: Do not include the area of any surrogate standard or internal standard in calculating a Range CF.

Equation 3: Range Calibration Factor

$$Range\ CF = \frac{Total\ area\ of\ peaks}{Total\ mass\ purged\ (ng)}$$

9.4.1.4 At a minimum, the working calibration curve or calibration factor must be verified on each working day, and after every 20 samples, whichever is more frequent, by the injection of a mid-level calibration standard to verify instrument performance and linearity. If the percent difference (%D) for any targeted analyte response varies from the predicted response by more than ± 15 %, as determined using Equation 4, a new calibration curve must be prepared for that analyte. Similarly, if the percent difference of the carbon range compound response varies from the predicted response by more than ± 20 %, a new calibration curve must be prepared.

Equation 4: Percent Difference (%D)

$$\%D = \frac{\overline{CF} - CFv}{\overline{CF}} x\ 100$$

9.4.1.5 Targeted VPH Analytes and Aromatic Hydrocarbons ranges are quantitated on the PID chromatogram.

9.4.1.6 The Aliphatic Hydrocarbons ranges are quantitated on the FID chromatogram after subtraction of the collective concentrations of MTBE, and the BTEX compounds identified on the PID chromatogram from the collective concentration values of the C5 through C6 and C6 through C8 Aliphatic Hydrocarbon concentration values determined using the FID chromatogram. Similarly, the PID concentrations determined for the remaining aromatic ranges are subtracted from the FID concentrations for those ranges to yield the actual FID Aliphatic Hydrocarbon ranges values.

9.4.1.7 The concentration of specific analytes or hydrocarbon ranges in aqueous and non-aqueous samples may also be calculated from a calibration curve by use of linear regression analysis.

9.5 GC Analysis

9.5.1 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by samples interspersed with blanks and QC samples. The analytical sequence ends must end with an acceptable calibration verification. If the final calibration verification is not acceptable, then all samples analyzed after the last acceptable calibration verification must either be reanalyzed or if this is not possible, then the data associated with those samples must be qualified as an "estimate quantity".

9.5.2 Establish daily retention time windows for each analyte. Use the absolute retention time for each analyte as the midpoint of the window for that day. The daily retention time window equals the midpoint ± three times the standard deviation determined in Section 9.3.

9.5.2.1 Tentative identification of an analyte occurs when a peak from a sample falls within the daily retention time window. In cases where interferences are suspected, confirmation on a second dissimilar GC column or by GC/MS analysis may be necessary.

9.5.2.3 Validation of GC system qualitative performance must be accomplished by the analysis of standards, generally mid-level, within the analysis sequence. If any of the standards fall outside their daily retention time window, the system is out of control. In such cases, the cause of the problem must be determined and corrected.

9.5.3 If the response for Targeted VPH Analytes exceeds the linear range of the system, dilute the sample and reanalyze. It is recommended that samples be diluted so that all peaks are on scale. Overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure that all peaks are on scale over a 100-fold range, are acceptable if linearity is demonstrated prior to the analysis of samples. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

9.5.4 If detection of targeted analyte peaks are prevented by the presence of interferences, additional analytical techniques, e.g. GC/MS, are recommended.

9.5.5 Peak area and carbon range area quantification/integration must be from baseline (i.e. forced baseline projection which must include the unresolved complex mixture "hump" areas). The exception to this is the C5 through C6 Aliphatic Hydrocarbon range which, due to the use of capillary columns shorter than 100 meters and/or the purging of methanol volumes greater than 20 uL, may experience a lack of complete resolution between C5 (n-pentane) and methanol. In this event, the analyst is allowed to use tangential skim integration, or other suitable integration techniques, to integrate n-pentane, and subsequent hydrocarbons within the C5-C6 aliphatic range if it/they appear(s) on the trailing edge of the methanol solvent peak.

9.6 External Standard Calculations

The concentration of targeted analytes and hydrocarbon ranges in a sample may be determined by calculating the amount of analyte or hydrocarbon range purged, from the peak response, using the calibration curve or the calibration factor determined in Section 9.4.

9.6.1 Aqueous samples:

The general equation to determine the concentration of a specific analyte or hydrocarbon range in aqueous samples in provided in Equation 5.

Equation 5

$$Concentration\ (\mu g / L) = \frac{(A_x)(A)(D)}{(A_s)(V_s)}$$

where:

A_x = Response for the analyte or hydrocarbon range in the sample, units may be in area counts or peak height.

A = Amount of external standard purged, ng.

D = Dilution factor; if no dilution was made, D = 1, dimensionless.

A_s = Response for the external standard, units same as for A_x.

V_s = Volume of sample purged, mL.

If a Calibration Factor is used, the concentration of a specific analyte or hydrocarbon range in an aqueous sample may be calculated using equations 6 and 7, respectively.

Equation 6

$$Conc\ Analyte\ (\mu g / L) = \frac{(A_x)(D)}{(V_s)(CF)}$$

Equation 7

$$Conc\ HC\ Range\ (\mu g / L) = \frac{(A_x)(D)}{(V_s)(Range\ CF)}$$

where:

A_x = Response for the analyte or hydrocarbon range in the sample, units may be in area counts or peak height.

D = Dilution factor; if no dilution was made, D = 1, dimensionless.

V_s = Volume of sample purged, mL.

CF = Calibration Factor, area counts/ng.

Range CF = Calibration Factor for hydrocarbon range, (collective area count/collective mass), area counts/ng.

9.6.2 **Non-Aqueous Samples (Methanol Extraction):**

9.6.2.1 The general equation to determine the concentration of a specific analyte or hydrocarbon range in a soil or sediment sample is provided in Equation 8.

Equation 8

$$Concentration\ (\mu g / kg) = \frac{(A_x)(A)(V_t)(D)}{(A_s)(V_i)(W_d)}$$

where:

A_x = Response for the analyte or hydrocarbon range in the sample, units may be in area counts or peak height.

A = Amount of external standard purged, ng.

V_t = Volume of total extract, µL (Note: this value must include the 1.0 mL surrogate spiking solution added to soil samples)

D = Dilution factor; if no dilution was made, D = 1, dimensionless.

A_s = Response for the external standard, units same as for A_x.

V_i = Volume of methanol extract added to reagent water for purge and trap analysis, µL.

W_d = Dry weight of sample purged, g (see equations 11 through 13)

If a Calibration Factor is used, the concentration of a specific analyte or hydrocarbon range in a soil or sediment sample may be calculated using Equations 9 and 10, respectively.

Equation 9

$$Conc\ Analyte\ (\mu g / kg) = \frac{(A_x)(V_t)(D)}{(V_i)(W_d)(CF)}$$

Equation 10

$$Conc\ HC\ Range\ (\mu g / kg) = \frac{(A_x)(V_t)(D)}{(V_i)(W_d)(Range\ CF)}$$

where:

V_t = Volume of total extract, µL.

Vi = Volume of extract added for purging, µL

W_d = Dry Weight of sample purged, g (see Equations 11 through 13)

A_x, CF, Range CF and D have the same definition as for aqueous samples.

9.6.2.2 Calculation of Dry Weight of Sample

In order to calculate the dry weight of sample purged (W_d), it is necessary to determine the moisture content of the soil/sediment sample, using the procedure outlined in Section 9.1.6. Using the data obtained from Section 9.1.6, W_d is calculated using Equations 11 through 13.

Equation 11

$$\%\ Moisture = \frac{g\ sample - g\ dry\ sample}{g\ sample}\ X\ 100$$

Equation 12

$$\%\ Dry\ Solids = (1) - (\%\ Moisture)$$

Equation 13

$$W_d\ (g) = (\%\ Dry\ Solids)(g\ of\ extracted\ sample)$$

9.6.3 The concentration of specific analytes or hydrocarbon ranges in aqueous and non-aqueous samples may also be calculated from the calibration curve by linear regression, provided that the correlation coefficient (r) is at least 0.99 and the % D for any targeted analyte must not vary from the predicted response by more than +/- 15%, nor any hydrocarbon range standard from its predicted response by more than +/- 20%.

9.6.4 Peak areas measured from blanks may not be subtracted from sample peak areas.

9.6.5 All integration of collective hydrocarbon ranges must be to baseline.

9.6.6 Required Adjustment of Range Concentration Data: In order to minimize the "double counting" of the same hydrocarbon compounds on both the FID and PID chromatograms, the collective concentrations of MTBE, benzene, toluene, ethylbenzene, and m, p, o-xylene identified on the PID chromatogram must be subtracted from the collective Aliphatic Hydrocarbon concentration values, for the ranges in which they elute, determined using the FID chromatogram. Similarly, the collective concentrations of the remaining aromatic ranges values determined on the PID chromatogram must be subtracted from the corresponding aliphatic ranges values determined on the FID chromatogram.

10.0 QUALITY CONTROL

10.1 **General Requirements and Recommendations**

10.1.1 Each laboratory that uses this method should operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document the quality of data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance standards for the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

10.1.2 A acidified reagent water blank should continually accompany each soil sample or water sample batch, respectively, over the course of sampling, storage, and analysis.

10.1.3 A Laboratory Method Blank should be run after samples suspected of being highly contaminated to determine if sample carryover has occurred.

10.1.4 At a minimum, for each analytical batch (up to 20 samples), a Laboratory Method Blank, Laboratory Fortified Blank, Laboratory Fortified Matrix Spike, and sample

duplicate must be analyzed. For analytical batches with more than 10 samples, the analysis of an additional mid-range calibration check standard is recommended. The blank and spiked samples must be carried through all stages of the sample preparation and measurement process.

10.1.5 The recommended sequence of analysis is as follows:

(1) Calibration Standards (initial) or mid-range Calibration Check Standard (daily check on initial calibration)
(2) Laboratory Method Blank
(3) Samples
(4) QC Samples
(5) Mid-range Calibration Check Standard (also recommended after each 10 samples)

10.1.6 It is recommended that a system of control charts be developed to plot surrogate standard recoveries as a function of time. When surrogate recovery from a sample, blank, or QC sample is less than 60% or more than 140%, check calculations to locate possible errors, the fortifying solution for degradation, and changes in instrument performance. If the cause cannot be determined, the analyst may reanalyze the sample or report the surrogate values as outside acceptance limits.

10.2 **Minimum Instrument QC**

10.2.1 While it is recommended that the n-pentane (C5) peak be adequately resolved from the methanol solvent on the FID chromatogram, the analyst is allowed to follow the guidance as outlined in 9.5.5. Coelution of the m- and p- xylene isomers is permissible. Any surrogates and/or internal standards used must be adequately resolved from individual compounds in the VPH Component Standard.

10.2.2 Retention time windows must be established for each analyte of interest each time a new GC column is installed, and must be verified and/or adjusted on a daily basis. (See Section 9.3)

10.2.3 Calibration curves must be developed based upon the analysis of calibration standards prepared at a minimum of 5 concentration levels. The linearity of calibration or response factors may be assumed if the percent relative standard deviation (%RSD) over the working range of the curve is less than or equal to 20%. Alternatively, if linear regression analysis is used for quantitation, the correlation coefficient (r) must be at least 0.99 and no targeted analyte or carbon range standard may vary from the true value by more than +/- 15% and +/- 20% respectively. (See Section 9.4.)

10.3 **Initial and Periodic Method QC Demonstrations**

The following must be conducted as an initial demonstration of laboratory capability, prior to the analysis of any samples. Subsequent to this initial demonstration, additional evaluations of this nature should be conducted on a periodic basis, in response to changes in instrumentation or operations, and/or in response to confirmed or suspected systems, method, or operational problems.

10.3.1 Accuracy and Precision

To demonstrate initial laboratory capability, analyze a minimum of four replicate reagent water and/or clean sand blanks spiked with each analyte of interest at approximately 20 to 60 µg/L and/or 20 to 60 mg/kg, respectively.

10.3.1.1 Add an appropriate aliquot of the stock or primary dilution standard solution(s) to each of the four replicate reagent water or clean sand blanks. Purge and analyze each replicate according to the procedures described in Section 9.0.

10.3.1.2 Calculate the measured concentrations of each analyte in all replicates, the mean accuracy (as a percentage of true value) for each analyte, and the precision (as %RSD) of the measurements for each analyte.

10.3.1.3 For each analyte, the mean accuracy, expressed as a percentage of the true value, must be between 80% and 120%. For each analyte, the %RSD must be less than or equal to 20%.

10.3.1. If desired, the Accuracy and Precision evaluation may be combined with the MDL evaluation specified in Paragraph 10.3.2.

10.3.2 Method Detection Limits (Optional)

Analyze a minimum of seven replicate reagent water and/or clean sand blanks which have been fortified with all analytes of interest at approximately 0.5 to 5 µg/L and/or 1 to 5 mg/kg, respectively. Calculate the Method Detection Limit (MDL) of each analyte using the procedure described in Section 12.0.

10.3.2.1 Water MDLs are determined by analyzing 7 to 10 replicates of reagent water samples in 100-mL flasks spiked with the VPH Component standard and with 40 µg/L of the surrogate compound 2,5-dibromotoluene.

10.3.2.2 Soil/sediment MDLs are determined by analyzing 7-10 replicates of 5 -g of VPH-free sand blanks spiked with the VPH Component standard and with 2 mg/kg of the surrogate 2,5-dibromotoluene.

10.3.3 Petroleum Reference Standard

As an optional demonstration of the validity and relevance of VPH calibration, analyze a reagent water and/or clean sand blank spiked with a known concentration of a neat gasoline product.

10.3.3.1 Fortify a reagent water and/or clean sand blank with 5 µL and/or 0.5 mL of the Petroleum Standard Spiking Solution, respectively. Purge and analyze in accordance with the procedures outlined in Section 9.0.

10.3.3.2 Calculate the total concentration of all petroleum hydrocarbons within the Aliphatic Hydrocarbon ranges using the FID chromatogram. Add these values together. Do not subtract the concentration of Targeted VPH analytes.

10.3.3.3 The concentration calculated in Paragraph 10.3.3.2 is expected to be within 30% +/- of the known concentration of Petroleum Standard in the reagent water or sand blank.

10.4 **Ongoing Method QC Demonstrations**

10.4.1 Each sample, blank, and matrix spike must be spiked with the surrogate spiking solution. Required surrogate recovery is 60% to 140%.

10.4.2 At a minimum, with every batch of 20 samples or less the laboratory must analyze the following:

10.4.2.1 **Calibration Check Standard** - A mid-range calibration standard, prepared from the same stock standard solution used to develop the calibration curve, must be analyzed prior to sample analysis to verify the calibration state of the instrument. For large analytical batches that contain more than 10 samples, the analysis of an additional mid-range calibration check standard is recommended after the analysis of the tenth sample. If the percent difference (% D) of any analyte within the calibration check standard varies from the predicted response by more than 20 %, a new calibration curve must be prepared for that analyte.

10.4.2.2 **Laboratory Method Blank** - A water or soil laboratory method blank is prepared by fortifying a 5 mL reagent water blank with 4 µL of the surrogate spiking solution, or by fortifying a 5 g sample of clean sand with 1.0 mL of the surrogate spiking solution. Peaks within the retention time windows of any hydrocarbon ranges of interest may not be present at or above the lowest calculated PQL for any sample within its batch. When determining the PQL for soil method blanks, incorporate the lowest percent solids value found for any sample within its batch in the calculation.

10.4.2.3 **Laboratory Fortified Blank (LFB)** - A water or soil component spike is prepared by fortifying a 5 mL reagent water blank with 4 µL of the matrix spiking solution, or by fortifying a 5 g sample of clean sand with 1.0 mL of the matrix spiking solution. The spike recovery must be between 70% and 130% and if these values can not be obtained the analyst must identify and correct the problem before analyses can continue.

10.4.2.4 **Sample duplicates** - Sample duplicates may be laboratory or field duplicates. The RPD of duplicate samples should not exceed +/- 25%. The lack of sample homogeneity may contribute to RPD's for duplicates which exceed this value. Should the values exceed 25%, the analyst must report that occurrence.

10.4.2.5 **Laboratory Fortified Matrix (LFM) Spike** - The water or soil LFM spike is prepared by fortifying an actual 5 mL water sample with 4 µL of the matrix spiking solution, or by fortifying an actual 5 g soil/sediment sample with 1.0 mL of the matrix spiking solution. The purpose

of the LFM is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations. The corrected concentrations of each analyte within the matrix spiking solution must be within 70 - 130% of the true value. Should the values determined exceed this range, the analyst must report that occurrence.

10.4.3 If any of the performance standards specified in Section 10.4 are not met, the problem must be corrected before further samples are analyzed. Exceptions to this are duplicate samples RPD's and high recoveries for LFM spikes which, due to sample non-homogeneity may exceed the allowable limits. Any samples run between the last calibration check standard that meets the criteria and one that does not must be rerun. If this is not possible, that data must be reported as an "estimated concentration".

11.0 DATA PRODUCTION AND REPORTING

11.1 **Sample Analysis**

11.11 PID Chromatogram

11.1.1.1 Determine the peak area count for the Targeted VPH Analytes.

11.1.1.2 Determine the peak area count for the surrogate 2,5-dibromotoluene.

11.1.1.3 Separately determine the total area count for all peaks eluting 0.1 minutes after the Rt's for toluene through 0.1 minutes after the Rt for 1,2,3-trimethylbenzene, for all peaks eluting 0.1 minutes after the retention time (Rt) for 1,2,3-trimethylbenzene and 0.1 minutes after the retention time for naphthalene and for all peaks eluting 0.1 minutes after the Rt for naphthalene through 0.1 minutes after the Rt of 1-methylnaphthalene.

11.1.1.4 Using the equations contained in Section 9.6 or linear regression analysis, calculate the concentrations of the Targeted VPH Analytes, the surrogate standard 2,5-dibromotoluene, and >C8 through C10, >C10 through C12 and >C12 through C13 Aromatic Hydrocarbons.

11.2.1 FID Chromatogram

11.2.1.1 Separately determine the total area count for all peaks eluting 0.1 minutes before the retention time (Rt) for n-pentane to 0.1 minutes after the Rt for n-hexane and for all peaks eluting 0.1 minutes after the Rt for n-hexane to 0.1 minutes after the Rt for n-octane. It is not necessary to identify or quantitate individual aliphatic compounds within these ranges.

11.2.1.2 Determine the total area count for all peaks eluting 0.1 minutes after the Rt for n-octane to 0.1 minutes after the Rt for n-decane and 0.1 minutes after n-decane to 0.1 minutes after n-dodecane. It is not necessary to identify or quantitate individual aliphatic compounds within this range.

11.2.1.3 Determine the peak area count for the surrogate standard 2,5-dibromotoluene.

11.2.1.4 Using the equations contained in Section 9.6 or linear regression analysis, calculate the concentrations of C5 through C6 Aliphatic Hydrocarbons, >C6 through C8 Aliphatic Hydrocarbons, >C8 through C10 Aliphatic Hydrocarbons, >C10 through C12 Aliphatic Hydrocarbons and the surrogate standard 2,5-dibromotoluene.

11.2.1.5 To avoid "double counting" of the same analytes, adjust the concentrations of Aliphatic Hydrocarbons calculated in Paragraph 11.2.1.4 by subtracting the collective concentrations of methyl tert butylether, benzene, toluene, >C8 through C10 and >C10 through C12 Aromatic Hydrocarbons, as determined from the PID chromatogram in Section 11.11, from the Aliphatic Hydrocarbon range values effected.

11.3 **Data Reporting Format**

11.3.1 The following information and data must be reported:

11.3.1.1 The sample matrix (aqueous, soil or sediment);

11.3.1.2 The date(s) the sample was collected, received by the laboratory, and analyzed;

11.3.1.3 A description of the sample(s) received by the laboratory, relative to the physical condition of the containers, the temperature of the samples, and use of appropriate preservatives;

11.3.1.4 Moisture content (for soil/sediment samples);

11.3.1.5 The calculated concentrations of C5 through C6, C6 through C8, C8 through C10 and C10 through C12 Aliphatic Hydrocarbons ranges and C8 through C10, C10 through C12 and C12 through C13 Aromatic Hydrocarbons ranges

11.3.1.6 Surrogate recovery (expressed as percent recovery);

11.3.1.7 The calculated concentrations of Targeted VPH Analytes determined

11.3.1.8 The concentration units for aqueous samples are expressed as ug/L or mg/L and for soil or sediment samples the units are expressed as ug/Kg or mg/Kg on a dry-weight basis.

12.0 METHOD PERFORMANCE

12.1 **Method Detection Limits (Optional)**

12.1.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

12.1.2 The MDL is determined according to the following equation:

Equation 14

$$MDL = (t) \times (SD)$$

where:

t = student t value at the 99% confidence level

SD = standard deviation of the replicate analysis

Student t values are as follows:

Number of replicates	t value
7	3.14
8	3.00
9	2.90
10	2.82

12.1.3 For the purposes of this method, the designated MDL value for a hydrocarbon range of interest shall be the highest value calculated for the individual analytes within that hydrocarbon range.

12.2 **Single Laboratory Accuracy, Precision, and MDL Data**

Single laboratory accuracy, precision and MDL data for method analytes are provided in Tables 1-1 through 1-4 in Appendix 1. Additional investigation will be conducted to further evaluate the low recoveries for naphthalene.

13.0 REFERENCES

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METHOD FOR THE DETERMINATION

OF

EXTRACTABLE PETROLEUM HYDROCARBONS (EPH) FRACTIONS

Washington State Department of Ecology

June 1997

METHOD FOR THE DETERMINATION OF EXTRACTABLE PETROLEUM HYDROCARBONS (EPH)

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DISCLAIMER

Mention of trade names or commercial products does not constitute endorsement by the Washington State Department of Ecology. Equipment and materials cited in this method may be replaced by similar products, as long as adequate data exists or has been produced documenting equivalent or superior performance.

METHOD FOR THE DETERMINATION OF EXTRACTABLE PETROLEUM HYDROCARBONS

1.0 SCOPE AND APPLICATION

1.1 This method is designed to measure the collective concentrations of extractable aliphatic and aromatic petroleum hydrocarbons in water and soil. **The carbon ranges used through out this document are given in equivalent carbon numbers (EC) which are related to the boiling point of a chemical normalized to the boiling point of the n-alkanes and its retention time in a boiling point gas chromatographic column**. Extractable aliphatic hydrocarbons are collectively quantitated within five ranges: C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34. Extractable aromatic hydrocarbons are collectively quantitated within five ranges: C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 150 °C and 500 °C.

1.2 Petroleum products suitable for evaluation by this method include, but are not limited to, kerosene and jet fuels, diesel and fuel oils and hydraulic, insulating and lubricating oils. This method, in and of itself, is not suitable for the evaluation of gasoline, mineral spirits, petroleum naphthas, and other petroleum products which contain a significant percentage of hydrocarbons lighter than C10. When samples are known or suspected to contain petroleum hydrocarbons of these or similar types, the Volatile Petroleum Hydrocarbon (VPH) method must also be employed to fully evaluate the hydrocarbons present.

1.3 For reporting purposes, the practical quantitation limits (PQL), given the sample volume/mass, final extract volume and assuming 100 percent solids for soil/sediments are: 50.0 ug/L for aliphatic and aromatic carbon ranges in water and 5.0 mg/Kg for these components in soil. If lower quantitation limits are desired, the analyst is allowed to extract larger volumes/masses and/or concentrate the extracts to smaller volumes prior to analysis. The procedure for Method Detection Limits

(MDL) determination in this method and the Single Laboratory Precision, Accuracy and MDL data (generated by State of Massachusetts) is added for informational purposes only.

1.4 This method is based on a solvent extraction, silica gel fractionation process and gas chromatography (GC) analysis using a flame ionization detector (FID). This procedure should be used by, or under the supervision of, analysts experienced in extractable organics analysis. Analysts using this method should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.

1.5 Like all GC procedures, this method is subject to a "false positive" bias, in that non-hydrocarbon compounds eluting or co-eluting within a specified retention time window may be falsely identified and/or quantitated with the respective carbon ranges. While the cleanup procedure specified in this method to segregate aliphatic and aromatic fractions will serve to mitigate this concern, confirmatory analyses by gas chromatography/mass spectrometry (GC/MS) analysis, EPA Method 8270, or other suitable techniques are recommended in cases where significant concentrations of non-hydrocarbon compounds are known or suspected. Non-petroleum compounds identified and quantitated by GC/MS may be subtracted from the carbon ranges affected as long as the quantity and identities of the compounds are reported along with the carbon range data.

2.0 SUMMARY OF METHOD

2.1 A sample submitted for EPH analysis is extracted with methylene chloride, dried over sodium sulfate, solvent exchanged into hexane, and concentrated. Sample cleanup and separation into aliphatic and aromatic fractions is conducted using a modification of EPA method 3630 (silica gel cleanup). The use of commercially available silica gel cartridges (Sep-Pak cartridges, Waters, Milford, MA) may be substituted for the silica gel column outlined in method 3630 if they can be shown to achieve comparable results. The two extracts produced are then concentrated to final volumes of 10 mL each (i.e., an aliphatic extract and an aromatic extract) and are then separately analyzed by a gas chromatograph equipped with a capillary column and a flame ionization detector. The resultant chromatogram of aliphatic compounds is collectively integrated within the C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 aliphatic hydrocarbon ranges. The resultant chromatogram of aromatic compounds is collectively integrated within the C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 ranges.

2.2 Average calibration factors or response factors determined using an aliphatic hydrocarbon standard mixture are used to calculate the collective concentrations of the different aliphatic hydrocarbons ranges. An average calibration factor or response factor determined using the aromatic hydrocarbon standard mixture is used to calculate a collective concentrations of the aromatic hydrocarbon ranges.

2.3 This method is suitable for the analysis of waters, soils, and sediments.

2.4 This method is based on, and constitutes a significant modification of, the “Method for the Determination of Extractable Petroleum Hydrocarbons (EPH)” Public Comment Draft 1.0 developed by the Massachusetts Department of Environmental Protection. They in turn based their method on (1) USEPA Methods 8000, 8100, and 3630, SW-846, "Test Methods for Evaluating Solid Waste", 3rd Edition, 1986; (2) Draft "Method for Determination of Diesel Range Organics", EPA UST Workgroup, November, 1990; and (3) "Method for Determining Diesel Range Organics", Wisconsin Department of Natural Resources, PUBL-SW-141, 1992.

Table 1. Aromatic Hydrocarbon Standard

Equivalent Carbon Number	Compound
7. 6	Toluene
10.1	1,2,3-Trimethylbenzene
11.7	Naphthalene
15.5	Acenaphthene
Surrogate	Ortho-Terphenyl
20.8	Pyrene
34.01	Benzo(g,h,i)Perylene

Table 2. Aliphatic Hydrocarbon Standard

Carbon Number	Compound
8	Octane
10	Decane
12	Dodecane
16	Hexadecane
Surrogate	1-Chloro-octadecane
21	Henicosane
34	Tetratriacontane

3.0 DEFINITIONS

3.1 **Extractable Petroleum Hydrocarbons (EPH)** are defined as all hydrocarbon compounds eluting from toluene through benzo(g,h,i)perylene. EPH is comprised of C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 Aliphatic Hydrocarbons and C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 Aromatic Hydrocarbons. EPH concentration data are reported as the aggregate concentration of the aliphatic and aromatic hydrocarbon ranges.

3.2 **Equivalent Total Petroleum Hydrocarbons (E-TPH)** For samples contaminated with petroleum products in the C10 to C34 range, the E-TPH value is equivalent to the EPH value. For samples contaminated with a petroleum product(s) containing significant concentrations of hydrocarbons lighter and heavier than C10, (e.g., contaminated with both gasoline and diesel fuel), the E-TPH value is a summation of the EPH value and the Volatile Petroleum Hydrocarbon (VPH) value. In order to avoid double counting of analytes due to the overlap in the carbon ranges existing between the two methods, the analyst will report the highest of the two values determined for the overlapping ranges. In those cases where both the VPH and EPH methods are employed on samples, the analyst may select to quantitate the >C10 through C12 Aliphatic and the >C10 through C12 Aromatic Hydrocarbon ranges by the EPH method only. Similarly, the analyst may select to quantitate the C8 through C10 Aromatic and C8 through C10 Aliphatic Hydrocarbon ranges by the VPH method only.

3.3 **C8 through C10 Aromatic Hydrocarbons** are defined as all of the aromatic hydrocarbon compounds eluting from (and including) toluene through 1,2,3-trimethylbenzene.

3.4 **>C10 through C12 Aromatic Hydrocarbons** are defined as all aromatic hydrocarbon compounds eluting after 1,2,3-trimethylbenzene through naphthalene.

3.5 **>C12 through C16 Aromatic Hydrocarbons** are defined as all aromatic hydrocarbon compounds eluting after naphthalene through acenaphthene.

3.6 >**C16 through C21 Aromatic Hydrocarbons** are defined as all aromatic hydrocarbons compounds eluting after acenaphthene through pyrene.

3.7 >**C21 through C34 Aromatic Hydrocarbons** are defined as all aromatic hydrocarbons compounds eluting after pyrene through benzo(g,h,i,)perylene.

3.8 **C8 through C10 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds eluting from (and including) n-octane (n-C8) through n-decane (n-C10).

3.9 **>C10 through C12 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds eluting after n-decane through n-dodecane (n-C12).

3.10 **>C12 through C16 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds eluting after n-dodecane through n-hexadecane (nC16)

3.11 >**C16 through C21 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbons eluting after n-hexadecane through n-henicosane (nC21).

3.12 **>C21 through C34 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbons eluting after n-henicosane through tetratriacontane (nC34).

3.13 **Aromatic Hydrocarbon Standard** is defined as a 6 component mixture (plus surrogate) of the aromatic hydrocarbons listed in Table 1. The compounds comprising the Aromatic Hydrocarbon Standard are used to (a) define and establish the windows for the Aromatic Hydrocarbon ranges, and (b) determine chromatographic response factors that can in turn be used to calculate the collective concentration of aromatic hydrocarbons in environmental samples within those hydrocarbon ranges.

3.14 **Aliphatic Hydrocarbon Standard** is defined as a 6 component mixture (plus surrogate) of the normal alkanes listed in Table 2. The compounds comprising the Aliphatic Hydrocarbon Standard are used to (a) define and establish windows for the aliphatic hydrocarbons ranges, and (b) determine chromatographic response factors that can in turn be used to calculate the collective concentration of aliphatic hydrocarbons in environmental samples within those hydrocarbon ranges.

3.15 **Analytical Batch** is defined as a group of samples with similar matrices which are processed as a unit. For Quality Control purposes, if the number of samples in such a group is greater than 20, then each group of 20 samples or less are defined as separate analytical batches.

3.16 **Laboratory Duplicates** are defined as split samples taken from the same sampling container and analyzed separately with identical procedures. The analysis of laboratory duplicates give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.17 **Field Duplicates** are defined as two separate samples collected at the same time and location under identical circumstances and managed the same throughout field and laboratory procedures. Analyses of field duplicates give a measure of the precision associated with sample collection, preservation and storage, as well as laboratory procedures.

3.18 **E-TPH Duplicates** are defined as two separate samples collected at the same time and location, for analysis by both EPH and VPH methods. E-TPH duplicates are taken at locations where significant concentrations of petroleum hydrocarbons lighter and heavier than C10 are likely to be present (e.g., locations contaminated by releases of both gasoline and diesel fuel). The resultant EPH and VPH concentrations are then summed to determine the Equivalent TPH (E-TPH) concentration.

3.19 **Calibration Standards** are defined as a series of standard solutions prepared from dilutions of a stock standard solution, containing known concentrations of each analyte and surrogate compounds of interest.

3.20 **Calibration Check Standard** is defined as a calibration standard used to periodically check the calibration state of an instrument. The calibration check standard is prepared from the same stock standard solution as calibration standards, and is generally one of the mid-level range calibration standard dilutions.

3.21 **Matrix Spiking Solution** is defined as a solution which is generally prepared independently from the calibration standards and which contain known concentrations of method analytes.

3.22 **Laboratory Method Blank** is defined as, depending on the matrix of the samples, either reagent water or clean sand spiked with a surrogate standard. The laboratory method blank is treated identically as with samples, exposed to all glassware, solvents, reagents, and equipment. A laboratory method blank is analyzed with every batch of samples, to determine if method analytes or other interferences are present in the laboratory environment, reagents, or equipment.

3.23 **Laboratory Fortified Blank (LFB)** is defined as, depending on the matrix of the samples, either reagent water or clean sand blank fortified with a matrix spiking solution. The LFB is treated and analyzed identically as with samples and blanks and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements at the required practical quantitation limits.

3.24 **Laboratory Fortified Matrix (LFM) Sample** is defined as an environmental sample which has been spiked with a matrix spiking solution containing known concentrations of method analytes. The LFM sample is treated and analyzed exactly as with samples and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentration of analytes in the sample matrix must be determined through the separate analyses of a laboratory or field duplicate, and the measured values in the LFM sample corrected for background concentrations.

3.25 All other terms are as defined in SW-846, "Test Methods for Evaluating Solid Waste", USEPA, September, 1986, and as amended.

4.0 INTERFERENCES

4.1 Method interferences are reduced by washing all glassware with hot soapy water and then rinsing with warm tap water, acetone, and methylene chloride.

4.2 High purity reagents must be used to minimize interference problems.

4.3 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. Whenever an unusually concentrated sample is analyzed, it should be followed by the analysis of a solvent blank to check for cross-contamination.

4.4 Matrix interferences may be caused by contaminants that are coextracted along with the analytes of interest from the sample. The type and extent of matrix interference will vary considerably from one source to another depending upon the nature and diversity of the site being sampled and may include certain solvents, halogenated hydrocarbons and phthalate esters. A silica gel cleanup procedure is used to overcome many of these interferences however, some samples may require additional cleanup procedures/approaches or analytical techniques, e.g. gel permeation chromatography and/or GC/MS, which are beyond the scope of this method.

5.0 HEALTH AND SAFETY ISSUES

The toxicity and carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDS) should also be made available to all personnel involved in the chemical analysis.

6.0 APPARATUS AND MATERIALS

6.1 The following glassware is used for this method:

6.1.1 1-L amber glass bottles

6.1.2 4 oz. (120 mL) amber glass wide-mouth jars

6.1.3 Vials:

6.1.3.1 autosampler: 2-mL glass vials with Teflon-lined rubber crimp caps

6.1.3.2 10-mL vials with Teflon-lined caps

6.1.4 Glass funnels

6.1.5 2-L Separatory funnels with Teflon stopcock

6.1.6 Kuderna-Danish apparatus including 10-mL concentrator tube, 500-mL Evaporative flask, & 3-ball Snyder column

6.1.7 Chromatographic column: 250 mm long x 10 mm I.D. with teflon stopcock

6.1.8 Disposable pipets: Pasteur

6.1.9 25-mL graduated cylinder

6.1.10 1-Liter graduated cylinder

6.1.11 100-mL beakers

6.1.12 25-mL volumetric flasks

6.2 Analytical balance: An analytical balance capable of accurately weighing 0.0001 g must be used for weighing standards. A top-loading balance capable of weighing to the nearest 0.1 g must be used for weighing soil samples.

6.3 A nitrogen blowdown apparatus for use in concentrating extracts.

6.4 **Gas Chromatography**

6.4.1 Gas Chromatograph: An analytical system complete with temperature programmable gas chromatograph for use with capillary columns is required. The data station must be capable of storing and reintegrating chromatographic data and must be capable of determining peak areas using a forced baseline projection.

6.4.2 Recommended Column: 30-m long x 0.32-mm I.D., 0.25-µm film DB-5 column (J&W Scientific) or equivalent. This column will allow for the adequate resolution of alkanes from n-C8 to n-C34.

6.4.3 Detector: A Flame Ionization Detector (FID).

6.4.4 Autosampler: An autosampler capable of making 1 to 2 µL injections is recommended.

6.5 Water bath: heated with a concentric ring covers, capable of temperature control (± 2°C). The bath should be used in a hood.

6.6 Microsyringes: 10-µL, 100-µL, 250-µL, 500-µL, 1000-µL

6.7 Boiling Chips: glass or teflon, precleaned prior to use

6.8 Soxhlet or Sonication extraction apparatus

6.9 Drying oven

7.0 REAGENTS AND STANDARDS

7.1 **Reagents**

7.1.1 Reagent Water: organic free water

7.1.2 Solvents: hexane, methylene chloride, and acetone; pesticide grade or better. Store away from other solvents.

7.1.3 Sodium sulfate: (ACS) granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray.

7.1.4 Ottawa and/or masonry sand: free of extractable petroleum hydrocarbons.

7.1.5 Silica gel: 100/200 mesh (Davison Chemical grade 923 or equivalent). Heat to 150-160 ^{o}C for several hours before use. Silica Gel Sep-Pak Cartridges: 5 g/20-mL (Waters, Milford, MA) , if it is demonstated to give equivalent separations.

7.2 **Stock Standard Solutions**

Prepare stock standard solutions at approximately 1000 ng/µL, or purchase as certified solutions.

7.2.1 Aromatic Hydrocarbon Standard: The Aromatic Hydrocarbon Standard consists of the 6 aromatic compounds listed in Table 1 and a surrogate compound. Prepare stock standard solutions by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in methylene chloride and dilute to volume in a 10-mL volumetric flask. The use of commercially prepared stock standards solutions is an acceptable alternative to the use of neat material. The analyst is allowed to prepare a separate surrogate solution.

7.2.2 Aliphatic Hydrocarbon Standard: The Aliphatic Hydrocarbon Standard consists of the 6 normal alkanes listed in Table 2 and a surrogate compound. Prepare stock standard solutions by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in hexane and dilute to volume in a 10-mL volumetric flask. The use of commercially prepared stock standard solutions is an acceptable alternative to the use of neat material. The analyst is allowed to prepare a separate surrogate solution.

7.2.3 Petroleum Reference Standard: The use of a Petroleum Reference Standard is recommended for quality control purposes. The Petroleum Reference Standard consists of an API or commercial diesel, fuel oil, kerosene, and/or lubricating oil. Prepare stock standard solutions by accurately weighing approximately 0.0100 g of neat product. Dissolve neat product in hexane and dilute to volume in a 10-mL volumetric flask.

7.3 **Surrogate Standards**

7.3.1 The recommended surrogate standards are chloro-octadecane (COD, available from Restek Corporation, Bellefonte, PA) and ortho-terphenyl (OTP, available from EM Sciences, Gibbstown, NJ). Additional surrogates or surrogates other than those listed above may be used at the discretion of the analyst as long as their performance in the method is demonstrated as acceptable. Preparation and use of those surrogates will be in the same manner as the listed surrogate.

7.3.2 The surrogate standard COD is prepared by accurately weighing approximately 0.0100 g of pure material in a 10-mL volumetric flask. Dissolve the material in hexane. This solution is added to the Aliphatic Hydrocarbon standard.

7.3.3 The surrogate standard OTP is prepared by accurately weighing approximately 0.0100 g of pure material in a 10-mL volumetric flask. Dissolve the material in methylene chloride. This solution is added to the Aromatic Hydrocarbon standard.

7.3.4 Surrogate Spiking Solution: The recommended surrogate spiking solution is comprised of a mixture of the COD and OTP surrogate standards. Prepare a surrogate spiking solution which contains the surrogate standards at a concentration of 20 ng/µL in acetone. Each sample, blank, and matrix spike is fortified with 1.0 mL of the surrogate spiking solution.

7.4 **Internal Standard**

If an internal standard method of calibration is to be used, the recommended internal standard is 5-alpha-androstane (EM Sciences, Gibbstown, NJ).

7.5 **Matrix Spike Standard**

7.5.1 Four or more analytes from each analyte group (i.e., aromatic and aliphatic hydrocarbons) are selected for use in a matrix spiking solution, which is prepared independently from the calibration standards.

7.5.2 The recommended spiking solution, consisting of C10, C12, C16 and C21 normal alkanes and naphthalene, acenaphthene, anthracene, pyrene, benzo(a)pyrene and benzo(g,h,i)perylene, is prepared in acetone at concentrations of 25 ng/µL.

7.5.3 The samples selected as the matrix spike are fortified with 1.0 mL of the matrix spiking solution.

7.6 **Fractionation Check Solution**

7.6.1 The Fractionation Check Solution is used to monitor the fractionation efficiency of different batches (lot numbers) of silica gel used to prepare the silica gel hydrocarbon fractionation columns (and Sep-Pak cartridges if used) as well as check for sample preparation errors (e.g., insufficient/excessive pentane use).

7.6.2 Prepare a Fractionation Check Solution in hexane containing 25 ng/µL each of the n-C8, n-C10, n-C12, n-C16, n-C21, and n-C34 alkanes) and 25 ng/µL each of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene. The final solution will contain 6 alkanes and 16 PAHs at concentrations of 25 ng/µL each. The use of commercially available check solutions containing these compounds is acceptable.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 Aqueous samples are collected in 1 liter amber glass bottles with teflon-lined screw caps.

8.2 Soil and sediment samples are collected in 4 oz. (120 mL) amber wide-mouth glass jars with teflon-lined screw caps.

8.3 Aqueous samples must be preserved at the time of sampling by the addition of an acid to reduce the pH of the sample to less than 2.0. This is accomplished by the addition of approximately 5 mL of 1:1 HCl to a 1 liter sample. Following collection and the addition of acid, the sample must be cooled to 4°C.

8.4 Soil and sediment samples must be cooled to 4°C immediately after collection.

8.5 A chain of custody form must accompany all aqueous, soil and sediment samples, documenting the time and date of sampling and any preservative additions.

8.6 Aqueous, soil and/or sediment samples must be extracted within 14 days of collection. If for whatever reason aqueous samples were not preserved at the time of collection they must be extracted within 7 days of collection. Both aqueous and soil/sediment extracts must be analyzed within 40 days of extraction.

8.7 A summary of sample collection, preservation, and holding times is provided in Table 3.

Table 3. Holding Times and Preservatives for EPH Samples

Matrix	Container	Preservation	Holding Time
Aqueous Samples	1-Liter amber glass bottle with Teflon-lined screw cap	Add 5 mL of 1:1 HCl; cool to 4°C	Samples must be extracted within 14 days and extracts analyzed within 40 days
Soil/Sediments Samples	4-oz. (120 mL) wide mouth amber glass jar with Teflon-lined screw cap	Cool to 4°C	Samples must be extracted within 14 days and extracts analyzed within 40 days

9.0 PROCEDURE

9.1 **Sample Preparation**

9.1.1 Water Extraction

9.1.1.1 Mark the water meniscus on the side of the 1 liter of sample bottle (for later volume determination) and transfer the water to a 2-liter separatory funnel. For blanks and quality control samples, pour 1 liter of reagent water into the separatory funnel. Add 1.0 mL of the surrogate spiking solution to all samples, blanks and matrix spikes. For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking solution.

9.1.1.2 Check the pH of the sample with wide-range pH paper. Note the pH in the laboratory notebook. The pH of the sample need not be adjusted.

9.1.1.3 Add 60 mL methylene chloride to the sample bottle to rinse the inner walls of the container, then add this solvent to the separatory funnel.

9.1.1.4 Seal and shake the separatory funnel vigorously for 1 to 2 minutes with periodic venting to release excess pressure.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, venting should be done immediately after the separatory funnel has been sealed and shaken once.

9.1.1.5 Allow the organic layer to separate from the water phase for a minimum of 5 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.
Collect the solvent extract in an 500ml Kuderna-Danish (K-D) evaporation flask to which is attached a 10 mL concentrator tube..

9.1.1.6 Repeat the extraction two more times using fresh portions of solvent and adding the solvent extracts to the KD flask. (Steps 9.1.1.3 to 9.1.1.5) The use of continuous liquid-liquid extraction (EPA method 3520) is an acceptable alternative to the separatory funnel extraction method described above.

9.1.1.7 For sample volume determination add water to the sample bottle to the level of the meniscus previously marked then transfer this water to a graduated cylinder and record the volume.

9.1.1.8 Add one clean boiling chip to the K-D flask and attach a three ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 4-6 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

9.1.1.9 Solvent exchange the methylene chloride with hexane by adding at least 50 mL of hexane to the top of the Snyder column. and concentrate the extract to less than 10 mL, as described in Paragraph 9.1.1.8, raising the temperature of the water bath, if necessary, to maintain proper distillation.

Note: An alternative solvent exchange method is to use the nitrogen blowdown apparatus to exchange the methylene chloride with hexane. This is accomplished by placing a disposable pipet in the concentrator tube and adding the small amounts of hexane via the pipet to the bottom of the concentrator tube during the concentration process in the apparatus.

9.1.1.10 Remove the Snyder column and evaporation flask from the 10-mL concentrator tube. Place the concentrator tube containing the hexane extract onto a nitrogen blowdown apparatus. Adjust the extract volume to 1-2 mL under a gentle stream of nitrogen . If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume will need to be larger.

9.1.1.11 The extract obtained is now ready to be cleaned and fractionated on a silica gel column. If cleanup will not be performed immediately, transfer the extract to a Teflon-lined screw-cap vial, label, and refrigerate.

9.1.1.12 Record the sample preparation information for the extraction and concentration steps. At a minimum, record the date, sample laboratory number, sample volume, volume and concentration of added surrogate and matrix spike solutions, and any deviations or problems associated with the extraction of the samples.

9.1.1.13 For cleanup and fractionation, refer to Section 9.1.4.

9.1.2 Soil/Sediment Extraction using Ultrasonic Extraction

9.1.2.1 The following steps should be performed rapidly to minimize the loss of the more volatile fractions. In a beaker blend 10 g of the soil/sediment sample with sufficient anhydrous sodium sulfate to form a free flowing powder using a spatula. Add 1.0 mL of the surrogate spiking solution to the samples and blanks. For the samples in each analytical batch selected for matrix spiking, add 1.0 mL of the matrix spiking standard. Immediately add approximately 50 mL of 1:1 methylene chloride:acetone to the beaker. If lower PQL's are desired, the analyst is allowed to increase the sample size extracted. This will necessitate a proportional increase in the volume of extraction solvent used.

9.1.2.2 Place the bottom surface of the tip of the ultrasonic horn about 1/2 inch below the surface of the solvent but above the soil/sediment layer.

9.1.2.3 Sonicate for 3 minutes with the control knob set to the maximum output, pulse mode and 50% duty cycle.

9.1.2.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

9.1.2.5 Decant and filter the extract through Whatman No. 41 filter paper into the K-D concentrator. Repeat the extraction two more times with additional 50 mL portions of the solvent. Decant off and filter the extract into the K-D flask each time. On the last extraction, pour

the entire sample into the funnel and rinse the beaker and sample with additional portions of solvent and add these to the K-D flask. The analyst may find it useful to (1) either add anhydrous sodium sulfate to the filter for drying the extract or (2) to pass the extract through a drying column containing about 10 cm of anhydrous sodium sulfate prior to collecting the extract in the K-D flask.

9.1.2.6 Add one clean boiling chip to the K-D flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10 to 20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1-2 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

9.1.2.7 Exchange the methylene chloride with hexane by adding 50 mL of hexane to the top of the Snyder column and concentrating the extract as described in Paragraph 9.1.2.6, raising the temperature of the water bath, if necessary, to maintain proper distillation. The alternate solvent exchange technique described in note in 9.1.1.9 may also be used.

9.1.2.8 Remove the Snyder column and evaporation flask from the 10-mL concentrator tube. Place the concentrator tube containing the hexane extract onto a nitrogen blowdown apparatus. Adjust the extract volume to 1-2 mL under a gentle stream of nitrogen . If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume will need to be larger.

9.1.2.9 The extract obtained is now ready to be cleaned and fractionated on a silica gel column. If cleanup will not be performed immediately, transfer the extract to a Teflon-lined screw-cap vial, label, and refrigerate.

9.1.2.10 Record the sample preparation information for the extraction and concentration steps, as specified in paragraph 9.1.1.14.

9.1.2.11 For cleanup and fractionation, refer to Section 9.1.4.

9.1.3 <u>Soil/Sediment Extraction by Soxhlet Extraction</u>

9.1.3.1 Blend 10 g of the soil/sediment sample with sufficient anhydrous sodium sulfate to produce a free flowing powder and place this material in an extraction thimble. The extraction thimble must drain freely for the duration

of the extraction period. Add 1.0 mL of the surrogate spiking solution onto the sample. For the samples in each analytical batch selected for matrix spiking, add 1.0 mL of the matrix spiking solution. If lower PQL's are desired, the analyst may increase the quantity of sample extracted.

9.1.3.2 Place approximately 200 mL of methylene chloride into a 250-mL Erlenmeyer or round bottomed flask (depending on the heating source) containing several clean boiling chips. Attach the flask to the extractor and extract the sample for 8-16 hr.

9.1.3.3 Allow the extract to cool after the extraction is completed.

9.1.3.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

9.1.3.5 Dry the extract by passing it through a glass powder funnel containing anhydrous sodium sulfate. Collect the dried extract in the K-D concentrator. Wash the extractor flask and sodium sulfate column with 50 to 75 mL of methylene chloride to complete the quantitative transfer.

9.1.3.6 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10 to 20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1-2 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

9.1.3.7 Exchange the methylene chloride with hexane by adding 50 mL of hexane to the top of the Snyder column and concentrating the extract as described in Paragraph 9.1.3.6, raising the temperature of the water bath, if necessary, to maintain proper distillation. The alternate solvent exchange technique outlined in the note in 9.1.1.9 may also be used.

9.1.3.8 Remove the Snyder column and evaporation flask from the 10 mL concentrator tube. Place the concentrator tube containing the hexane extract onto a nitrogen blowdown apparatus. Adjust the extract volume to 1-2 mL under a gentle stream of nitrogen . If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume will need to be larger.

9.1.3.9 The extract obtained is now ready to be cleaned and fractionated on a silica gel column. If cleanup will not be performed immediately, transfer the extract to a Teflon-lined screw-cap vial, label, and refrigerate.

9.1.3.10 Record the preparation information for the extraction and concentration steps, as specified in 9.1.1.14.

9.1.3.11 For cleanup and fractionation, refer to Section 9.1.4.

9.1.3.12 The use of the Accelerated Solvent Extraction (ASE), EPA Method 3545, is an acceptable alternative to either ultrasonic or soxhlet extraction techniques as long as it is demonstrated to achieve comparable results.

9.1.4 Silica Gel Cleanup and Separation

9.1.4.1 Silica gel is a regenerative adsorbent of amorphous silica with weakly acidic properties. It is produced from sodium silicate and sulfuric acid. Silica gel can be used for column chromatography and is used for separating analytes from interfering compounds of a different chemical polarity. Silica gel is also used to separate petroleum distillates into aliphatic and aromatic fractions. Before the silica gel technique can be utilized, the extract solvent must be exchanged to hexane. This procedure may be performed immediately before the extract concentration step is complete by adding hexane to the K-D (when the volume of remaining methylene chloride is approximately 10 to 15 mL) and reducing the extract volume to 1 to 2 mL. After cooling, disassemble the K-D apparatus, rinsing the joints into the concentrator tube with a minimum of hexane. With a nitrogen blowdown concentrator, further reduce the extract to a final volume of 2 mL.

9.1.4.2 Prepare a slurry of 10g of activated silica gel in methylene chloride and place this into a 10 mm I.D.x 250 mm long chromatographic column. Tap the column to settle the silica gel and elute the methylene chloride. Add 1 to 2 cm of anhydrous sodium sulfate to the top of the silica gel. Note: The activity of each new batch (lot number) of silica gel must be evaluated prior to its use in this procedure. This requires the use of the fractionation check solution to insure that there is an efficient separation of the aromatic fraction from the aliphatic fraction. If necessary, the analyst is allowed to adjust the volumes of the eluants used to facilitate this process.

9.1.4.3 Pre-elute the column with 40 mL of pentane. Let the solvent flow through the column, at a rate of about 2 mL/minute, until the head of the liquid in the

column is just above the sodium sulfate layer. Close the stopcock to stop solvent flow. Discard this pentane.

9.1.4.4 Open the stopcock and immediately transfer the hexane sample extract onto the silica gel column. Rinse the concentrator tube with an additional 1-2 mL of hexane and add this to the column as well.

9.1.4.5 Just prior to exposure of the sodium sulfate layer to the air, add 25 mL of pentane to the column. Collect the eluant in a 250 mL K-D flask to which is attached a 10 mL concentrator tube and label this fraction "aliphatics". Concentrate and solvent exchange this extract into hexane.

9.1.4.6 Following recovery of the aliphatic fraction and just prior to exposure of the sodium sulfate layer, elute the column with 50 mL of methylene chloride/pentane (40:60) (v/v) and collect the eluant in a 250 mL K-D flask equipped with a 10 mL concentrator tube.. Label this fraction "aromatics". Concentrate and solvent exchange this extract into methylene chloride.

9.1.4.7 Concentrate each fraction to a final volume of 10 mL under a gentle stream of nitrogen from a nitrogen blowdown apparatus.

9.1.4.8 Transfer 1 mL of the fractions to a labeled two-mL glass autosampler vials with teflon-rubber crimp caps for analysis and save the remaining extract in a teflon-rubber septum screw topped vial. If lower PQL's are required, the analyst may concentrate the extract to as low as 1 mL prior to analysis

9.1.5 Proceed with the analysis in accordance with Sections 9.2 through 9.5. Analyze all laboratory method blanks and QC samples under the same conditions as that used for samples.

9.1.6 If chromatographic responses exceed the linear range of the system, dilute the extract(s) and re-analyze

9.1.7 <u>Determination of Percent Moisture</u>

9.1.7.1 Soil and sediment sample results must be reported on a dry-weight basis. A portion of sample for moisture determination should be weighed out at the same time as the portion used for hydrocarbon determination.

9.1.7.2 Immediately after weighing a sample for extraction, transfer 5 to 10 g of the sample into a tared crucible. Dry the sample overnight at 105°C in an oven. After drying remove it from the oven allow it to cool in a desiccator before reweighing. Calculate the percent moisture of the sample using the equations provided in Section 9.6.3.

9.2 **GC Conditions**

9.2.1 Suggested Gas Chromatographic Conditions

9.2.1.1 Oven Program: Set oven temperature to 50 °C for 2 minute, then 8°C/min to 320 °C and hold for 10 minutes.

9.2.1.2 Sample/autosampler injection volume is 1 to 2 µL.

9.2.1.3 Gas Flows: The recommended carrier gas is helium.

9.2.1.3.1 Helium carrier gas flow: 1 to 2 mL/min.

9.2.1.3.2 Air: 400 mL/min.

9.2.1.3.3 Hydrogen: 35 mL/min.

9.2.1.3.4 Make up gas flow: 30 mL/min.

9.2.1.4 Miscellaneous:

9.2.1.4.1 FID temperature, 310 to 320 °C

9.2.1.4.2 Injection port temperature, 290 to 300 °C

9.2.1.4.3 GC operated in splitless mode

9.2.1.4.4 Column head pressure 15.0 psi at 50°C

9.2.1.4.5 Linear velocity approximately 50 cm/sec

9.3 **Retention Time Windows**

9.3.1 Before establishing windows, make sure the GC system is within optimum operating conditions. Make three injections of the Aromatic and Aliphatic Hydrocarbon standard mixtures throughout the course of a 72-hr period. Serial injections over less than a 72-hr period may result in retention time windows that are too tight.

9.3.2 Calculate the standard deviation of the three absolute retention times for each standard.

9.3.3 Plus or minus three times the standard deviation of the absolute retention times for each standard should be used to define the retention time window. However, the

experience of the analyst should weigh heavily in the interpretation of chromatograms.

9.3.4 In those cases where the standard deviation for a particular standard is zero, the laboratory should substitute the standard deviation of a closely eluting structurally similar compound to develop a valid retention time window.9.3.5 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed or a portion removed as part of GC maintenance. This data must be retained by the laboratory.

9.3.6 EPH retention time (Rt) windows for all fractions (carbon ranges and hydrocarbon types) except the C8 through C10 are defined as beginning 0.1 minutes after the Rt of the beginning marker compound and ending 0.1 minutes after the Rt of the ending marker compound. Since the first fraction for both the aliphatics and aromatics includes the beginning marker compounds, the Rt windows for them are defined as beginning 0.1 minutes before the Rt of the beginning marker compound and ends 0.1 minutes after the ending marker compound.

EPH marker compounds and windows are summarized in Table 4.

Table 4. EPH Marker Compounds

Range/ Hydrocarbon Standard	Beginning Marker Compound	Ending Marker Compound
C8-C10 Aliphatic Hydrocarbons	just before n-octane	just after n-decane
C10-C12 Aliphatic Hydrocarbons	just after n-decane	just after n-dodecane
C12-C16 Aliphatic Hydrocarbons	just after n-dodecane	just after n-hexadecane
C16-C21 Aliphatic Hydrocarbons	just after n-hexadecane	just after n-henicosane
C21-C34 Aliphatic Hydrocarbons	just after n-henicosane	just after n-tetratriacontane
C8-C10 Aromatic Hydrocarbons	just before toluene	just after 1,2,3-trimethylbenzene
C10-C12 Aromatic Hydrocarbons	just after 1,2,3-trimethylbenzene	just after naphthalene
C12-C16 Aromatic Hydrocarbons	just after naphthalene	just after acenaphthene
C16-C21 Aromatic Hydrocarbons	just after acenaphthene	just after pyrene
C21-C34 Aromatic Hydrocarbons	just after pyrene	just after benzo(g,h,i)perylene

9.4 **Calibration**

Calibrate the GC system using either the external standard procedure (Section 9.4.1) or the internal standard procedure (Section 9.4.2).

9.4.1 External standard calibration procedure

9.4.1.1 Prepare Aromatic and Aliphatic Hydrocarbon calibration standards at a minimum of five concentration levels by adding volumes of one or more stock standard solutions to volumetric flasks and diluting to volume with methylene chloride and hexane, respectively. The surrogate OTP is added to the Aromatic Hydrocarbon Standard; the surrogate COD is added to the Aliphatic Hydrocarbon Standard. One of the calibration

standards must be at a concentration near, but above, the method detection limit and is used to determine the reporting PQL. In order to report the PQL's listed in 1.4, given the volume/mass water or soil extracted of 1 liter or 10 grams and assuming 100% solids on the soil, this standard must be at a 5 ng/uL level. The other concentrations must correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

9.4.1.2 A collective calibration curve or factor must be established for each hydrocarbon range of interest. Inject each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph (e.g., 1 to 2 µL injections). To calculate the collective CF for C8-C10, >C12-C12, >C12-C16, >C16-C21 and C21-C34 Aromatic Hydrocarbons, tabulate the summation of all peak areas of the calibration compounds in that range (e.g. C8-C10, toluene and 1,2,4-trimethylbenzene or >C10-C12, naphthalene) against the total mass injected. Although a forced baseline projection is required for samples and blanks, the analyst is allowed to integrate only the area of the calibration compound(s) to generate the calibration factors. The ratio of the response to the amount injected, defined as the calibration factor (CF), or range CF, may be calculated for hydrocarbon ranges at each standard concentration using Equation 1. If the percent relative standard deviation (%RSD) of the calibration factor is equal to or less than 20 % over the working range for the ranges of interest, as determined using Equation 2, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve. The Aliphatic Hydrocarbon collective CF is calculated in the same manner using the aliphatic standards.

Equation 1: Range Calibration Factor

$$Range\ CF = \frac{total\ area\ of\ peaks}{mass\ injected\ (ng)}$$

Equation 2: Percent Relative Standard Deviation

$$\%RSD = \frac{Stand\ Dev\ of\ 5\ CFs}{Mean\ of\ 5\ CFs} \times 100$$

Note: The area for the surrogates COD and OTP must be subtracted from the area of the range in which they elute (e.g., COD is subtracted from the C16-C21 Aliphatic Hydrocarbon range.

9.4.1.4 At a minimum, the working calibration curve or calibration factor must be verified at the beginning of each working day and after the final analysis of that day, or after every 20 samples, whichever is more frequent, by the injection of a mid-level calibration standard to verify instrument performance and linearity. If the percent difference (%D) for any range varies from the predicted response by more than ± 20 %, as calculated using Equation 4, a new calibration curve must be prepared.

Equation 4: Percent Difference (%D)

$$\%D = \frac{\overline{CF} - CFv}{\overline{CF}} \times 100$$

where:

$\overline{CF}$ = Average Calibration Factor from calibration curve.

CFv = Calibration Factor from verification calibration check.

9.4.1.5 The concentrations of hydrocarbon ranges may also be calculated from a calibration curve by use of linear regression analysis.

9.4.2 Internal standard calibration procedure

9.4.2.1 The suggested internal standard for this method is 5-alpha-androstane (EM Science, Gibbstown, NJ).

9.4.2.2 Prepare Aromatic and Aliphatic Hydrocarbon calibration standards at a minimum of five concentration levels by adding volumes of stock standard solutions to volumetric flasks. The surrogate OTP is added to the Aromatic Hydrocarbon Standard; the surrogate COD is added to the Aliphatic Hydrocarbon Standard. To each calibration standard, add a known constant amount of an internal standard. One of the calibration standards must be at a concentration near, but above, the method detection limit and is used to determine the reporting PQL. The other concentrations must correspond to the expected range of concentration found in real world samples or should define the working range of the detector.

9.4.2.3 Inject each calibration standard using the same technique that will be applied to the samples (e.g., 1 to 2 µL injection). Tabulate the peak area responses against the concentration of each hydrocarbon range and internal standard. Calculate the collective response factors (RF) for each hydrocarbon range using Equation 5.

Note: The area for the surrogates COD and OTP must be subtracted from the area of the range in which they elute (e.g., COD is subtracted from the appropriate Aliphatic Hydrocarbon range).

uation 5: Range Response Factor

$$Range\ RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Summation of peak areas of the fraction (e.g., C10-C12 Aliphatic Hydrocarbons).

C_{is} = Concentration of internal standard, ng/µL.

A_{is} = Response for the internal standard.

C_s = Total mass concentration of injected standards, ng/µL.

9.4.2.4 At a minimum, the working calibration curve or RF must be verified at the beginning of each working day and after the final analysis of that day, or after every 20 samples, whichever is more frequent, by the injection of a mid-level calibration standard to verify instrument performance and linearity. If the percent difference (%D) for any hydrocarbon range varies from the predicted response by more than ± 20 %, as calculated using Equation 4, a new calibration curve must be prepared for that range.

9.4.2.5 The concentrations of hydrocarbon ranges may also be calculated from a calibration curve by the use of linear regression analysis.

9.5 **GC Analysis**

9.5.1 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration, or verification of calibration, followed by sample extracts interspersed with blanks and QC samples. The analytical sequence must end with an acceptable verification calibration standard. If the ending calibration standard is not acceptable, all samples analyzed after the last acceptable calibration verification must be reanalyzed. If, for whatever reason, reanalysis is not possible, then the data for those samples must be qualified as an "estimate".

9.5.2 Aliphatic and aromatic extracts are introduced into the gas chromatograph by slitless injection.

9.5.3 Inject 1 to 2 µL of the sample extract. Record the volume injected and the resulting peak size in area units.

9.5.4 Confirm the established retention time windows for each hydrocarbon range on a daily basis. Use the absolute retention time for each analyte as the midpoint of the window for that day. The daily retention time window equals the midpoint ± three times the standard deviation determined in Section 9.3.

9.5.4.1 Validation of GC system qualitative performance must be accomplished by the analysis of standards within the analysis sequence. If any of the standards fall outside their daily retention time window, the system is out of control. In such cases, the cause of the problem must be determined and corrected.

9.5.5 When quantifying on a peak area basis by internal or external calibration, peak area integration for the aliphatic and aromatic carbon ranges must be <u>from baseline</u> (i.e. must include the unresolved complex mixture "hump" areas).

9.6 **Calculations**

9.6.1 <u>External Standard Calibration</u>

The concentration of each hydrocarbon range in a sample may be determined by calculating the amount of hydrocarbon range compounds injected, from the peak response, using the calibration curve or the calibration factor determined in Section 9.4.

9.6.1.1 **Aqueous samples:**

The general equation to determine the concentration of a hydrocarbon range in aqueous samples in provided in Equation 6.

Equation 6

$$Concentration\ (ug / L) = \frac{(A_x)(A)(V_t)(D)}{(A_s)(V_i)(V_s)}$$

w

here:

A_x = Response for a hydrocarbon range in the sample, units may be in area counts or peak height.

A = Amount of standard injected, ng.

A_s = Response for the external standard, units same as for A_x.

V_i = volume of extract injected, µL.

D = Dilution factor: if no dilution was made, D = 1, dimensionless.

V_t = Volume of total extract, µL.

V_s = Volume of sample extracted, mL.

If a Calibration Factor is used, the concentration of a hydrocarbon range may be calculated using Equation 7.

Equation 7

$$Conc\ HC\ Range\ (ug / L) = \frac{(A_X)(V_t)(D)}{(V_i)(V_s)(Range\ CF)}$$

where:

Range CF = Calibration Factor for hydrocarbon ranges (collective area count/collective mass).

9.6.1.2 **Nonaqueous samples:**

The general equation to determine the concentration of a hydrocarbon range in soil or sediment samples is provided in Equation 8.

Equation 8

$$Concentration\ (ug / kg) = \frac{(A_x)(A)(V_t)(D)}{(A_s)(V_i)(W_d)}$$

where:

W_d = Dry weight of sample extracted, g. (See Equations 12 through 14)

A_x, A_s, A, V_t, D, and V_i have the same definition as for aqueous samples.

If a Calibration Factor is used, the concentration of specific hydrocarbon ranges in a soil or sediment sample may be calculated using Equation 9.

Equation 9

$$Conc\ HC\ Range\ (ug / kg) = \frac{(A_x)(V_t)(D)}{(V_i)(W_d)(Range\ CF)}$$

where:

Range CF = Calibration Factor for a hydrocarbon range (collective area count/collective mass).

9.6.2 Internal Standard Calibration

The concentration of each hydrocarbon range in a sample may be determined by calculating the amount of hydrocarbon range compound(s) injected, from the peak response, based upon the compound/internal-standard response ratio.

9.6.2.1 **Aqueous samples:**

The general equation to determine the concentration of a specific hydrocarbon range in aqueous samples is provided in Equation 10.

Equation 10

$$Concentration\ (ug / L) = \frac{(A_x)(C_{is})(D)}{(A_{is})(RF)(V_s)}$$

where:

A_x = Response of the hydrocarbon range being measured, units may be in area counts or in peak height.

C_{is} = Amount of internal standard added to extract, ng.

D = Dilution factor, if a dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

A_{is} = Response of the internal standard, units same as A_x.

RF = Response factor for the hydrocarbon range, dimensionless.

V_s = Volume of aqueous sample extracted, mL.

9.6.2.2 **Nonaqueous samples:**

The general equation to determine the concentration of a specific or hydrocarbon range in soil or sediment samples is provided in Equation 11.

Equation 11

$$Concentration\ (ug / kg) = \frac{(A_x)(C_{is})(D)}{(A_{is})(RF)(W_d)}$$

where:

W_d = Dry weight of sample extracted, g. (See Equations 12 through 14).

A_x, C_{is}, D, A_{is}, and RF have the same definition as for aqueous samples.

9.6.3 Calculation of Dry Weight of Sample

In order to calculate the dry weight of sample extracted (W_d), it is necessary to determine the moisture content of the soil/sediment sample, using the procedure outlined in Section 9.1.7. Using the data obtained from Section 9.1.7, W_d is calculated using Equations 12 through 14.

Equation 12

$$\% \text{ Moisture} = \frac{g \text{ sample} - g \text{ dry sample}}{g \text{ sample}} X\ 100$$

Equation 13

$$\% \text{ Dry Solids} = (1) - (\% \text{ Moisture})$$

Equation 14

$$W_d\ (g) = (\% \text{ Dry Solids})(g \text{ of extracted sample})$$

10.0 QUALITY CONTROL

10.1 **General Requirements and Recommendations**

10.1.1 Each laboratory that uses this method should operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance standards for the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

10.1.2 Hexane or methylene chloride solvent blanks should be run after samples suspected of being highly contaminated to determine if sample carryover has occurred.

10.1.3 At a minimum, for each analytical batch (up to 20 samples), a Laboratory Method Blank, Laboratory Fortified Blank Spike (Water or Soil), Laboratory Fortified

Matrix Spike, and sample duplicate must be analyzed. For analytical batches with more than 10 samples, the analysis of an additional mid-range calibration check standard is recommended. The blank and spiked samples must be carried through all stages of the sample preparation and measurement process.

10.1.4 The recommended sequence of analysis is as follows:

(1) Calibration Standards (initial) or mid-range Calibration Check (Verification) Standard (i.e. daily check of initial calibration)
(2) Laboratory Method Blank
(3) Samples
(4) QC Samples
(5) Mid-range Calibration Check (Verification) Standard (also recommended after each 10 samples)

10.1.5 It is recommended that a system of control charts be developed to plot surrogate standard recoveries as a function of time. When surrogate recovery from a sample, blank, or QC sample is less than 50% or more than 150%, check calculations to locate possible errors, the fortifying solution for degradation, and changes in instrument performance. If the cause cannot be determined, the analyst may reanalyze the sample extract, report the surrogate values as outside acceptance limits or, if additional sample is available, re-extract and reanalyze the sample.

10.2 **Minimum Instrument QC**

10.2.1 The instrument must be able to achieve adequate separation and resolution of peaks of interest.

10.2.1.1 The n-octane (n-C8) and toluene peaks must be adequately resolved from the solvent front of the chromatographic run.

10.2.1.2 The surrogates COD and OTP and any internal standards used must be adequately resolved from any individual components in the Aliphatic Hydrocarbon and Aromatic Hydrocarbon standards.

10.2.2 Retention time windows must be established for each hydrocarbon range of interest each time a new GC column is installed, and must be verified and/or adjusted on a daily basis. (See Section 9.3)

10.2.3 Calibration curves must be developed based upon the analysis of calibration standards prepared at a minimum of 5 concentration levels. The linearity of calibration or response factors may be assumed if the percent relative standard deviation (%RSD) over the working range of the curve is less than or equal to 20 %. Alternatively, if linear regression analysis is used for

quantitation, the correlation coefficient (r) must be at least 0.99. and the percent difference (% D) of the response for any hydrocarbon range from the predicted response may not vary by more than +/- 20%. (See Section 9.4.)

10.3 **Initial and Periodic Method QC Demonstrations**

The following must be conducted as an initial demonstration of laboratory capability, prior to the analysis of any samples. Subsequent to this initial demonstration, additional evaluations of this nature should be conducted on a periodic basis, in response to changes in instrumentation or operations, and/or in response to confirmed or suspected systems, method, or operational problems.

10.3.1 Accuracy and Precision

To demonstrate initial laboratory capability, analyze a minimum of four replicate reagent water and/or clean sand blanks spiked with the calibration compounds for each range of interest at approximately 50 µg/L and/or 5 mg/kg, respectively.

10.3.1.1 Extract and analyze each replicate according to the procedures described in Section 9.0.

10.3.1.2 Calculate the measured concentrations of each range in all replicates, the mean accuracy (as a percentage of true value) for each compound, and the precision (as %RSD) of the measurements for each compound.

10.3.1.3 For each compound, the mean accuracy, expressed as a percentage of the true value, should be between 70 % and 130 %. For each compound, the %RSD must be less than or equal to 20%.

10.3.2 Method Detection Limits (Optional)

Analyze a minimum of seven replicate reagent water and/or clean sand blanks which have been fortified with all analytes of interest at approximately 0.5 to 2 µg/L and/or 1.0 to 5.0 mg/kg, respectively. Extract and analyze each replicate according to the procedures described in Section 9.0. Calculate the Method Detection Limit (MDL) of each analyte using the procedure described in Section 12.0.

10.3.2.1 Water MDLs are determined by extracting 7 to 10 replicates of 1-L reagent water blanks spiked with OTP, COD and each analyte of interest.

10.3.2.2 Soil/sediment MDLs are determined by extracting 7-10 replicates of 10-g of EPH-free sand blanks spiked with OTP, COD, and each analyte of interest.

10.3.3 Fractionation

To demonstrate the capability of properly fractionating aliphatic and aromatic hydrocarbons in a sample, the analyst must first prepare and analyze the Fractionation Check Solution specified in Section 7.6.

10.3.3.1 Prepare a silica gel column as outlined in 9.1.4

10.3.3.2 Load 1.0 mL of the Fractionation Check Solution onto column and proceed with the elution and collection of the aliphatic and aromatic fractions as outline in 9.1.4.

NOTE: The amount of pentane used during the elution/fractionation is critical. Excessive pentane will cause elution of aromatics into the aliphatic fraction. Insufficient pentane will cause low recoveries of the aliphatic fraction. The volume of pentane and/or methylene chloride/pentane recommended may need to be adjusted to meet QC limits.

10.3.3.3 Solvent exchange the aliphatic fraction to hexane and the aromatic fraction to methylene chloride. Concentrate each solution to a final volume of 1.0 mL under a gentle stream of nitrogen from an nitrogen blowdown apparatus.

10.3.3.4 Transfer the final 1.0 mL extracts to two labeled glass auto sampler vials with teflon-lined rubber crimp caps. Analyze by GC/FID (see Section 9.0).

10.3.3.5 For each analyte within the Fractionation Check Solution, the mean accuracy, expressed as a percentage of the true value, must be between 70 % and 130 %.

10.3.4 Petroleum Reference Standard

As an optional demonstration of the validity and relevance of EPH calibration, analyze a reagent water and/or clean sand blank spiked with a known concentration of a neat petroleum product.

10.3.4.1 Dilute a Petroleum Reference Standard stock standard solution with acetone to a concentration of approximately 250 ng/µL. Spike a 1 Liter reagent water blank or 10 g clean sand blank with 1.0 mL of this spiking solution. Extract and analyze in accordance with the procedures outlined in Section 9.0.

10.3.4.2 Calculate the total concentration of all petroleum hydrocarbons within each range. Add these values together.

10.3.4.3 The concentration calculated in Paragraph 10.3.4.2 is expected to be within +/- 30 % of the known concentration of Petroleum Standard in the reagent water or sand blank.

10.4 **Ongoing Method QC Demonstrations**

10.4.1 Each sample, blank, and matrix spike sample must be spiked with the surrogate spiking solution. Required surrogate recovery is 60% to 140%.

10.4.2 At a minimum, with every batch of 20 samples or less the lab must analyze the following:

10.4.2.1 **Calibration Check Standard** - A mid-range calibration standard, prepared from the same stock standard solution used to develop the calibration curve, must be analyzed prior to sample analysis to verify the calibration state of the instrument. For large analytical batches that contain more than 10 samples, the analysis of an additional mid-range calibration check standard is recommended after the analysis of the tenth sample. If the percent difference (% D) of any compound within a calibration check standard varies from the predicted response by more than 20 %, a new calibration curve must be prepared. (See Section 9.4)

10.4.2.2 **Laboratory Method Blank** - A water or soil laboratory method blank is prepared by fortifying a reagent water or clean sand blank with 1.0 mL of the surrogate spiking solution. Peaks within the retention time windows of any hydrocarbon ranges of interest may not be present at or above the lowest calculated PQL for any sample within its batch. When determining the PQL of soil method blanks, incorporate the lowest percent solids value found for any sample within its batch in the calculation.

10.4.2.3 **Laboratory Fortified Blank Spike** - A water or soil component spike is prepared by fortifying a reagent water or clean sand blank with 1.0 mL of the matrix spiking solution. The spike recovery must be between 70 % and 130 % and, if these values can not be obtained, the analyst must identify and correct the problem before analyses can continue.

10.4.2.4 **Sample duplicates** - Sample duplicates may be laboratory duplicates or field duplicates and the RPD of the duplicate samples should not exceed +/- 25%. The lack of sample homogeneity may contribute to the RPD's values for duplicates which exceed this value. Should the values exceed 25% the analyst must report that occurrence.

10.4.2.5 **Laboratory Fortified Matrix (LFM) Spike** - The water or soil LFM spike is prepared by fortifying an actual water or soil sample with 1.0 mL of the matrix spiking solution. The purpose of the LFM spike is to

determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations. The corrected concentrations of each analyte within the LFM spike sample must be within 70 to 130 % of the true value. Should the values determined exceed this range, the analyst must report that occurrence.

10.4.3 If any of the performance standards specified in Section 10.4 are not met, the problem should be corrected before further samples are analyzed. Exceptions to this are duplicate samples RPD's and high recoveries for LFM spikes which, due to sample non-homogeneity, may exceed the allowable limits. Any samples run between the last calibration check standard that meet the criteria and one that does not must be reanalyzed. If this is not possible, then the data must be reported as an "estimated concentration."

11.0 DATA PRODUCTION AND REPORTING

11.1 **Sample Analysis**

11.1.1 Aliphatic Fraction

11.1.1.1 Determine the total area count for all peaks eluting 0.1 minutes before the retention time (Rt) for C8 to 0.1 minutes after the Rt for C10.

11.1.1.2 Determine the total area count for all peaks eluting 0.1 minutes after the Rt for C10 to 0.1 minutes after the Rt for C12. Determine the total area count of all peaks eluting 0.1 minutes after the Rt for C12 to 0.1 minutes after the Rt for C16, for all peaks eluting 0.1 minutes after the Rt for C16 to 0.1 minutes after the Rt for C21and for all peaks eluting 0.1 minutes after the Rt for C21 to 0.1 minutes after the Rt for C34. It is not necessary to identify or quantitate individual aliphatic compounds within these ranges.

11.1.1.3 Determine the peak area count for the surrogate COD and any internal standard used. Subtract these values from the collective area count value within the appropriate hydrocarbon range(s).

11.1.1.4 Using the equations contained in Section 9.6 or linear regression analysis, calculate the concentrations of C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 Alipiphatic Hydrocarbon ranges and the surrogate standard COD.

11.1.1.5 The term "all peak areas" must include any unresolved envelope of peaks which elute within the Rt windows listed above and below for the aliphatic and aromatic fractions.

11.2.1 Aromatic Fraction

11.2.1.1 Determine the total area count for all peaks eluting 0.1 minutes before the retention time (Rt) for toluene to 0.1 minutes after the Rt for 1,2,3 trimethylbenzene. In the same manner, determine the total area count for all peaks eluting 0.1 minutes after the Rt for 1,2,3-trimethylbenzene to 0.1 minutes after the Rt for naphthalene, from 0.1 minutes after the Rt for naphthalene to 0.1 minutes after the Rt for acenaphthene, from 0.1 minutes after the Rt for acenaphthene to 0.1 minutes after the Rt for pyrene and 0.1 minutes after the Rt for pyrene to 0.1 minutes after the Rt for benzo(g.h.i)perylene.

11.2.1.2 Determine the peak area count for the surrogate OTP and any internal standard used.

11.2.1.3 Subtract the peak area value from 11.2.1.2 from the collective area count value for the range effected determined in 11.2.1.1 to calculate the area count for Aromatic Hydrocarbons ranges.

11.2.1.4 Using the equations contained in Section 9.6 or linear regression analysis, calculate the concentrations of C8 through C10, >C10 through C12, >C12 through C16 , >C16 through C21 and >C21 through C34 Aromatic Hydrocarbons and the surrogate standard COD.

11.3 Data Reporting Format

11.3.1 The following information and data must be reported:

11.3.1.1 The sample matrix (aqueous, soil or sediment);

11.3.1.2 The date(s) the sample was collected, received by the laboratory, extracted, and analyzed;

11.3.1.3 A description of the sample(s) received by the laboratory, relative to the physical condition of the containers, the temperature of the samples, and use of appropriate preservatives;

11.3.1.4 Moisture content (for soil/sediment samples);

11.3.1.5 The calculated concentrations of C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 Aliphatic Hydrocarbons, and C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 Aromatic Hydrocarbons.

11.3.1.6 Surrogate recovery (expressed as percent recovery);

11.3.1.7 The concentration units for aqueous samples are expressed as ug/L or mg/L and soil or sediment samples the units are expressed as µg/Kg or mg/Kg on a dry-weight basis.

12.0 METHOD PERFORMANCE

12.1 **Method Detection Limits (Optional)**

12.1.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

12.1.2 The MDL is determined according to Equation 15.

Equation 15

$$MDL = (t) \times (SD)$$

where:

t = student t value at the 99% confidence level.

SD = standard deviation of the replicate analysis.

Student t values are as follows:

Number of replicates	t value
7	3.14
8	3.00
9	2.90
10	2.82

12.2 **Single Laboratory Accuracy, Precision and MDL Data**

Single laboratory accuracy, precision and MDL data for method analytes are provided in Tables 1-1 through 1-4 in Appendix 1. Tables 1-1 and 1-2 present data collected from spiking reagent water at 5.0 µg/L; Tables 1-3 and 1-4 by spiking sand at 1.0 mg/kg.

13.0 REFERENCES

1. Massachusetts Department of Environmental Protection and ABB Environmental Services, Inc., Wakefield, MA "Interim Petroleum Policy: Development of Health-based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter," August 1994.

2. USEPA, "Measurement of Petroleum Hydrocarbons: Report on Activities to Develop a Manual." Prepared by Midwest Research Institute, Falls Church, VA, under EPA Contract #68-WO-0015, WA No. 4; submitted to USEPA Office of Underground Storage Tanks, Washington, DC; November 20, 1990.

3. USEPA Federal Register 40 CFR Part 136, Appendix B, "Guidelines Establishing Test procedures for the Analysis of Pollutants," July 1992.

4. USEPA Test Methods for Evaluating Solid Waste (SW-846); Method 3510: Separatory Funnel Liquid-Liquid Extraction; September 1986.

5. USEPA Test Methods for Evaluating Solid Waste (SW-846); Method 3540: Soxhlet Extraction; September 1986.

6. USEPA Test Methods for Evaluating Solid Waste (SW-846); Method 3630: Silica Gel Cleanup; September 1986.

7. USEPA Test Methods for Evaluating Solid Waste (SW-846): Method 8000: Gas Chromatography; September 1986.

8. USEPA Test Methods for Evaluating Solid Waste (SW-846); Method 8100: Polynuclear Aromatic Hydrocarbons; September 1986.

9. Wisconsin Department of Natural Resources, "Modified DRO - Method for Determining Diesel Range Organics," PUBL-SW-141, 1992.

APPENDIX 1

SINGLE LABORATORY ACCURACY, PRECISION, AND METHOD DETECTION LIMITS (MDL) DATA FOR VPH

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Table 1-1. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Compounds in Component Standard Spiked Into Reagent Water and Analyzed by the VPH Method

Compound	Spiked Conc. (µg/L)	Method Accuracy[a] (Mean % Recovery[b])		Method Precision[a] (RSD[c] - %)		MDL[a] (µg/L)	
		PID[d]	FID[e]	PID	FID	PID	FID
n-Pentane	6.0		98		7.8		1.4
Methyl tert butylether	1.8	77	79	4.8	15	0.21	0.69
Benzene	0.6	82	97	4.9	10	0.08	0.19
Toluene	0.6	79	104	7.3	6.5	0.11	0.13
n-Nonane	2.0		83		8.0		0.42
Ethylbenzene	0.6	77	94	4.2	9.1	0.06	0.16
m- & p-Xylene	1.2	68	85	4.3	6.4	0.11	0.20
o-Xylene	0.6	79	88	16	6.4	0.23	0.11
1,2,3-Trimethylbenzene	0.6	69	89	8.2	6.4	0.11	0.11
Naphthalene	3.6	58	56	16	18	1.0	1.2
2,5-Dibromotoluene (surrogate)	40	88	92	4.9	13		

[a] Based on analysis of seven samples spiked with component standard.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] PID = photoionization detector.
[e] FID = flame ionization detector.

Table 1-2. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Compounds in Component Standard Spiked Into VPH- Free Sand and Analyzed by the VPH Method

Compound	Spiked Conc. (µg/Kg)	Method Accuracy[a] (Mean % Recovery[b])		Method Precision[a] (RSD[c] - %)		MDL[a] (µg/Kg)	
		PID[d]	FID[e]	PID	FID	PID	FID
n-Pentane	120		124		6.0		28
Methyl tert butylether	120	70	96	3.1	27	8.1	99
Benzene	60	122	128	3.3	5.4	7.6	13
Toluene	60	139	137	4.8	8.6	13	22
n-Nonane	120		119		4.6		21
Ethylbenzene	60	107	103	4.3	5.0	8.6	9.7
m- & p-Xylene	120	109	104	4.1	5.2	17	20
o-Xylene	60	103	111	3.8	6.6	7.4	14
1,2,3-Trimethylbenzene	60	93	102	5.5	5.3	9.6	10
Naphthalene	ND[f]	ND	ND	ND	ND	ND	ND
2,5-Dibromotoluene (surrogate)	2,000	119	117	8.6	9.7		

[a] Based on analysis of seven samples spiked with component standard.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] PID = photoionization detector.
[e] FID = flame ionization detector.
[f] ND = not determined.

Table 1-3. Single Laboratory Accuracy and Precision for Compounds in Component Standard Spiked Into Reagent Water at Concentrations in the Low to Middle End of the Analytical Range and Then Analyzed by the VPH Method

Compound	Spiked Conc. (µg/L)	Method Accuracy[a] (Mean % Recovery[b])		Method Precision[a] (RSD[c] - %)	
		PID[d]	FID[e]	PID	FID
n-Pentane	40		96		7.7
Methyl tert butylether	60	87	88	4.0	3.9
Benzene	20	99	99	4.4	3.7
Toluene	60	99	99	4.1	4.0
n-Nonane	40		104		10
Ethylbenzene	20	99	99	4.2	4.2
m- & p-Xylene	80	99	99	4.3	4.2
o-Xylene	40	99	99	3.7	3.6
1,23-Trimethylbenzene	40	99	99	4.1	4.0
Naphthalene	40	70	81	4.3	3.2
2,5-Dibromotoluene (surrogate)	40	92	94	5.2	4.6

[a] Based on analysis of five samples spiked with component standard.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] PID = photoionization detector.
[e] FID = flame ionization detector.

Table 1-4. Single Laboratory Accuracy and Precision for Compounds in Component Standard Spiked Into VPH-Free Sand at Concentrations in the Low to Middle End of the Analytical Range and Then Analyzed by the VPH Method

Compound	Spiked Conc. (mg/Kg)	Method Accuracy[a] (Mean % Recovery[b])		Method Precision[a] (RSD[c] - %)	
		PID[d]	FID[e]	PID	FID
n-Pentane	2.0		118		1.9
Methyl tert butylether	3.0	100	94	2.4	2.8
Benzene	2.0	119	109	3.0	0.7
Toluene	2.0	118	109	1.7	1.3
n-Nonane	ND	ND	ND	ND	ND
Ethylbenzene	1.0	121	110	1.4	1.2
m- & p-Xylene	3.0	122	110	1.4	1.1
o-Xylene	2.0	118	107	1.3	1.1
1,2,3-Trimethylbenzene	2.0	115	109	1.4	1.3
Naphthalene	2.0	61	57	11	1.8
2,5-Dibromotoluene (surrogate)	2.0	75	64	9.7	3.3

[a] Based on analysis of five samples spiked with component standard.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] PID = photoionization detector.
[e] FID = flame ionization detector.
[f] ND = not determined.

APPENDIX 2

SUGGESTED VPH DATA REPORTING FORMAT

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VOLATILE PETROLEUM HYDROCARBON (VPH) ANALYSIS

Client:
Client Sample ID: Date Received:
Laboratory Sample ID: Date Analyzed:
Matrix: Date Reported:
Percent Moisture:

VPH RESULTS

Parameter	Results	PQL				Units
C5-C6 Aliphatics (FID) *						
C6-C8 Aliphatics (FID) *						
C8-C10 Aliphatics (FID) *						
C10-C12 Aliphatics (FID) *						
C8-C10 Aromatics (PID)						
C10-C12 Aromatics (PID)						
C12-C13 Aromatics (PID)						

*** Excludes any MTBE or BTEX compounds**

SURROGATE RECOVERY

Surrogate	%Recovery	Acceptance Range
2,5-dibromotoluene		80% - 120%

TARGETED VPH ANALYTES

Analyte	**Results**	**PQL**	**Units**
Methyl tert butylether			
Benzene			
Toluene			
Ethylbenzene			
p-Xylene *			
m-Xylene *			
o-Xylene			
Naphthalene			

* p and m-xylenes may not be able to be resolved and may be reported as the total of p and m-xylenes.

APPENDIX 3

SINGLE LABORATORY ACCURACY, PRECISION, AND METHOD DETECTION LIMIT (MDL) DATA FOR EPH

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Table 1-1. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Alkanes Spiked Into Reagent Water and Analyzed by the EPH Method

Compound[a]	Compound Conc. Measured (µg/L)		Mean Accuracy (Mean % Recovery[b])	Method Precision (RSD[c] - %)	MDL (µg/L)
	Mean	Std. Dev.			
C_{10}	4.1	0.040	82	0.98	0.12
C_{12}	4.1	0.021	82	0.51	0.064
C_{16}	4.0	0.062	80	1.6	0.19
COD[d]	44	0.93	88	2.1	-
C21	3.7	0.047	74	1.3	0.14

[a] Compounds were spiked into 7 or 8 samples at a concentration of 5.0 µg/L.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] Surrogate (COD = 1-Chloro-octadecane) was spiked into three samples at a concentration of 50 µg/L.

Table 1-2. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Polynuclear Aromatic Hydrocarbons (PAHs) Spiked Into Reagent Water and Analyzed by the EPH Method

Compound[a]	Compound Conc. Measured (µg/L)		Mean Accuracy (Mean % Recovery[b])	Method Precision (RSD[c] - %)	MDL (µg/L)
	Mean	Std. Dev.			
Naphthalene	5.6	0.088	112	1.6	0.26
2-Methylnaphthalene	6.4	0.096	128	1.5	0.29
Acenaphthylene	5.6	0.085	112	1.5	0.26
Acenaphthene	5.7	0.092	114	1.6	0.28
Fluorene	5.6	0.094	112	1.7	0.28
Phenanthrene	5.5	0.097	110	1.8	0.29
Anthracene	7.0	0.10	140	1.4	0.31
OTP[d]	44	1.6	88	3.6	-
Fluoranthene	5.7	0.090	114	1.6	0.27
Pyrene	6.1	0.098	122	1.6	0.29
Benzo(a)Anthracene	5.9	0.089	118	1.5	0.27
Chrysene	5.8	0.098	116	1.7	0.29
Benzo(b)Fluoranthene	6.3	0.082	126	1.3	0.25
Benzo(k)Fluoranthene	5.6	0.065	112	1.2	0.20
Benzo(a)Pyrene	6.0	0.075	120	1.2	0.22
Indeno(123 cd)Pyrene	5.1	0.17	102	3.3	0.50
Dibenzo(ah)Anthracene	2.8	0.21	56	7.5	0.62
Benzo(ghi)Perylene	3.8	0.18	76	4.7	0.54

[a] Compounds were spiked into 7 or 8 samples at a concentration of 5.0 µg/L.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] Surrogate (OTP = ortho-Terphenyl) was spiked into three samples at a concentration of 50 µg/L.

Table 1-3. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Alkanes Spiked Into EPH-Free Sand and Analyzed by the EPH Method

Compound[a]	Compound Conc. Measured (mg/Kg)		Mean Accuracy (Mean % Recovery[b])	Method Precision (RSD[c] - %)	MDL (mg/Kg)
	Mean	Std. Dev.			
C_{10}	0.72	0.074	72	10	0.22
C_{12}	0.83	0.079	83	9.5	0.24
C_{16}	1.2	0.14	120	12	0.42
COD[d]	4.3	0.48	86	11	-
C21	0.81	0.044	81	5.4	0.13

[a] Compounds were spiked into 8 samples at a concentration of 1.0 mg/Kg.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] Surrogate (COD = 1-Chloro-octadecane) was spiked into three samples at a concentration of 5.0 mg/kg.

Table 1-4. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Polynuclear Aromatic Hydrocarbons (PAHs) Spiked Into EPH-Free Sand and Analyzed by the EPH Method

Compound[a]	Compound Conc. Measured (mg/Kg)		Mean Accuracy (Mean % Recovery[b])	Method Precision (RSD[c] - %)	MDL (mg/Kg)
	Mean	Std. Dev.			
Naphthalene	0.64	0.063	64	9.8	0.19
2-Methylnaphthalene	0.64	0.058	64	9.1	0.17
Acenaphthylene	0.68	0.060	68	8.8	0.18
Acenaphthene	0.70	0.064	70	9.1	0.19
Fluorene	0.79	0.060	79	7.6	0.18
Phenanthrene	0.83	0.041	83	4.9	0.12
Anthracene	1.2	0.082	120	6.8	0.25
OTP[d]	4.8	0.45	96	9.4	-
Fluoranthene	0.92	0.038	92	4.1	0.12
Pyrene	0.91	0.037	91	4.1	0.11
Benzo(a)Anthracene	0.96	0.042	96	4.4	0.12
Chrysene	0.90	0.050	90	5.6	0.15
Benzo(b)Fluoranthene	0.96	0.038	96	4.0	0.11
Benzo(k)Fluoranthene	0.87	0.037	87	4.3	0.11
Benzo(a)Pyrene	0.96	0.036	96	3.8	0.11
Indeno(123 cd)Pyrene	0.90	0.033	90	3.7	0.099
Dibenzo(ah)Anthracene	0.82	0.033	82	4.0	0.099
Benzo(ghi)Perylene	0.82	0.032	82	3.9	0.096

[a] Compounds were spiked into 7 or 8 samples at a concentration of 1.0 mg/Kg.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] Surrogate (OTP = ortho-Terphenyl) was spiked into three samples at a concentration of 5.0 mg/kg.

APPENDIX 4

SUGGESTED EPH DATA REPORTING FORMAT

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EXTRACTABLE PETROLEUM HYDROCARBON (EPH) ANALYSIS

Client:	
Client Sample ID:	Date Received:
Laboratory Sample ID:	Date Extracted:
Matrix:	Date Analyzed:
Percent Moisture:	Date Reported:

EXTRACTABLE PETROLEUM HYDROCARBON (EPH)

Parameter	Results	PQL				Units
C8-C10 Aliphatics						
C10-C12 Aliphatics						
C12-C16 Aliphatics						
C16-C21 Aliphatics						
C21-C34 Aliphatics						
C8-C10 Aromatics						
C10-C12 Aromatics						
C12-C16 Aromatics						
C16-C21 Aromatics						
C21-C34 Aromatics						

SURROGATE RECOVERIES

Surrogate	%Recovery	Acceptance Range
Chloro-octadecane (COD)		50% - 150%
Ortho-terphenyl (OTP)		50% - 150%

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APPENDIX 5

REPORT OF ANALYSIS

SUMMARY SHEET

Client: Client Sample ID Number(s): Laboratory ID Number(s):

SAMPLE INFORMATION

Sample Matrix	¨ Aqueous ¨ Soil ¨ Sediment ¨ Other:	
Analysis Performed	¨ VPH ¨ EPH ¨ VPH and EPH (E-TPH Duplicate samples)	
Condition of Containers	¨ Satisfactory ¨ Broken ¨ Leaking ¨ Other:	
Sample Preservatives	AQUEOUS	¨ N/A ¨ pH ≤ 2 ¨ pH > 2
	SOIL/SEDIMENT	¨ N/A
Sample Temperature	¨ Received on Ice ¨ Received at 4 °C ¨ Other	

ANALYTICAL RESULTS

Parameter	Results	PQL	Units
Volatile Petroleum Hydrocarbons (VPH)			
Extractable Petroleum Hydrocarbons (EPH)			
Equivalent TPH (E-TPH) ** [IF BOTH VPH AND EPH ANALYSES PERFORMED]			

**** Due to overlapping carbon ranges between the VPH and EPH methods and in order to avoid double counting, the analyst must select the higher of the two values to be included for reporting purposes for those ranges effected.**

COMMENTS

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APPENDIX 6*

Petroleum Product Chromatograms

Carburator Cleaner
Automotive Gasoline
Mineral Spirits #1
Mineral Spirits #2
JP-4 Jet Fuel (old)
JP-4 Jet Fuel (new)
JP-5 Jet Fuel
Kerosene
Kerosene (ICP grade)
Gasoline and #2 Diesel Oil
Natural Gas Condensate
#2 Fuel Oil
#2 Fuel Oil (38% aromatic) (See chromatogram in NWTPH-Dx)
#2 Diesel Oil (See chromatogram in NWTPH-Dx)
#2 Diesel Oil and Motor Oil (30w) (See chromatogram in NWTPH-Dx)
2-Cycle Engine Oil #1
2-Cycle Engine Oil #2
2-Cycle Engine Oil #3
Motor Oil (30w) (See chromatogram in NWTPH-Dx)
Automatic Transmission Fluid
Power Steering Fluid
Transformer Oil (used)
Transformer Oil (new)
Hydraulic Fluid #1
Hydraulic Fluid #2
Hydraulic Fluid #3
Mineral Oil #1
Mineral Oil #2
Cutting Oil #1
Cutting Oil #2
Bunker-C #1
Bunker-C #2
CSS-1 (emulsion asphalt)
AR-4000 (asphalt cement)

Non-petroleum Product Chromatograms

Turpentine
Creosote
Synthetic Motor Oil

*** The chromatograms are not available in the "electronic" version. They are included in the printed publication.**

Chromatograms: NWTPH-Gx

Gasoline
Weathered Gasoline
Naphtha
Mineral Spirits #1
Mineral Spirits #2
Mineral Spirits #3

Chromatograms: NWTPH-Dx

#2 Diesel Oil
#2 Diesel Oil/Motor Oil
#2 Fuel Oil (38% Aromatic)
Kerosene (Deodorized)
Jet Fuel A
Bunker C #1
Bunker C #2
Motor Oil 30 Wgt.
Mineral Oil (USP)
Hydraulic Fluid
Transformer Oil
Gas Oil

State of Oregon Department of Environmental Quality

OAR 340-122-0218
NW Total Petroleum Hydrocarbon Identification Method

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* The chromatograms are not available in the “electronic” version. They are included in the printed publication.

TOTAL PETROLEUM HYDROCARBONS (TPH)

The following compilation of analytical methods may be used in Oregon and Washington for Underground Storage Tank cleanups and other cleanups of TPH (check with applicable state rules). Each of these Total Petroleum Hydrocarbon (TPH) Methods has its own niche in the overall analytical scheme. The methods are:

NWTPH-HCID.....Hydrocarbon Identification

NWTPH-Gx .....Volatile Petroleum Products (Extended)

NWTPH-Dx .....Semi-volatile Petroleum Products (Extended)

NWTPH-HCID is a qualitative and semi-quantitative screen to determine the presence and type of petroleum products that may exist in water or soil. This method should be used if the type of petroleum contamination is unknown. It should be performed on contaminated soil or water that is representative of the contamination at the site. The results of this method will determine what fully quantitative method/methods, if any, are to be used in determining compliance with the matrix criteria. Should the value of the analysis for gasoline, diesel or heavy oils (or any other identified petroleum product) exceed the reporting limits, then the specific analytical method for that product must be employed.

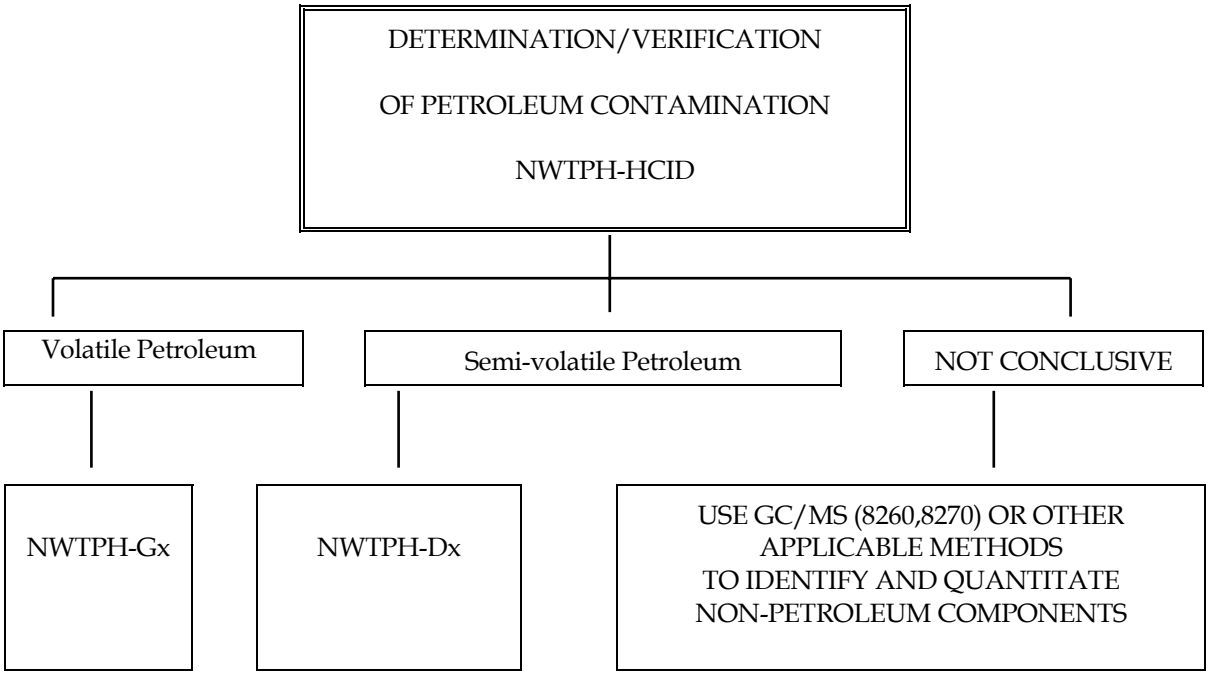
NWTPH-Gx is the qualitative and quantitative method (extended) for volatile ("gasoline") petroleum products in soil and water. Petroleum products applicable for this method include aviation and automotive gasolines, mineral spirits, stoddard solvent and naphtha.

NWTPH-Dx is the qualitative and quantitative method (extended) for semi-volatile ("diesel") petroleum products in soil and water. Petroleum products applicable for this include jet fuels, kerosene, diesel oils, hydaulic fluids, mineral oils, lubricating oils and fuel oils.

NOTE: These "NWTPH" methods result in single TPH values that can be used when compliance with a single cleanup level is desired. When TPH "fractions" are needed, then the VPH and EPH methods must be used.

ANALYTICAL DECISION TREE FOR NWTPH

The following flow chart depicts the laboratory analytical scheme to be used when analyzing samples for single TPH levels. The first step is the qualitative determination of the existence and nature of petroleum contamination and this should be used when the site contamination is unknown. It is required that this first step will be performed on a representative sample from the area that is suspected to be the most contaminated at the site. For those samples containing analytes which, due to their retention times, ratios to each other or their non-hydrocarbon pattern (e.g., creosote), do not suggest petroleum hydrocarbons, then GC/MS methods should be employed to ascertain the components. At those sites where the petroleum contaminants are known or have been identified using the NWTPH-HCID method, the specific product method is to be used.



NWTPH-HCID

Hydrocarbon Identification Method for Soil and Water

Summary

This method is a qualitative and semi-quantitative procedure. It is used for groundwater or surface water, and soil/sediment from sites where the petroleum products are unknown and/or when multiple types of petroleum products are suspected to be present. This method is used to identify petroleum products containing components from C7 to C30 range, as well as heavy oils, with specific product confirmation by pattern matching ("fingerprinting") employing capillary gas chromatography with flame ionization detection (GC/FID). EPA method 3510 has been adapted as the extraction procedure for the water portion of this method.

While this method is intended to be primarily qualitative, it can be used to eliminate the need for further analyses for those samples which demonstrate TPH levels significantly below the regulatory limits. If the sample contains toluene to dodecane (gasoline range), dodecane through tetradecane (diesel range) and/or an unresolved chromatographic envelope greater than tetradecane (e.g. motor oils) above the reporting limits of this method, then the final quantitation must be performed by methods specific for these mixtures. Since the water extraction procedure in this method is identical to that found in the water portion of NWTPH-Dx (semi-volatile petroleum products, i.e. from kerosene through heavy fuel oils), these products may be quantitated using this extract. Because of the possible loss of volatile compounds in the extraction and concentrations steps, gasoline, mineral spirits and other volatile petroleum products that exceed the reporting limits of this method must be quantitated using the NWTPH-Gx method.

The reporting limits for water are 0.25 mg/L for gasoline, 0.63 mg/L for #2 diesel and motor oils. The reporting limits for soil/sediment are 20 mg/Kg for gasoline, 50 mg/Kg for #2 diesel, and 100 mg/Kg for motor oil, all reported on a dry weight basis. These values for soil/sediment assumes 100% solids and will be higher depending on the actual moisture content.

The method relies heavily upon the experience of the analyst for the identification of the specific petroleum product(s) that may be present. Therefore, this method must be run by, or under the direct supervision of, analysts experienced in the use of GC and in the interpretation of gas chromatograms of both fresh and weathered petroleum products.

Equipment and Reagents

Gas Chromatograph, w/wo autosampler
Capillary split/splitless injector
Flame ionization detector
Suggested Capillary Column:
J&W DB-1 or DB-5, 30 M x 0.25 mm or 0.32 mm with 0.25 um film thickness capillary column or equivalent
Chromatography Data System
VOA Vial: 40 mL glass vial with Teflon coated cap septum, Eagle Picher or equivalent
Syringe: Hamilton #701, 10 uL or equivalent
Ultrasonic Bath
Glass Wool: Pyrex or equivalent
Centrifuge tubes: 5 or 15 mL, calibrated in 0.1 mL increments
Analytical Balance: accurate to at least 0.0001 g
Volumetric Flasks: 10 mL, ground glass with ground glass stopper
Separatory funnels: 500 mL, Teflon stopcocks
Kuderna-Danish (KD) Flasks: 250 mL or equivalent
Snyder Columns: 3-ball, 24/40 ground glass joint
Concentrator Tubes: 10 mL
Methylene Chloride: Burdick and Jackson Brand or equivalent
N-Evap Concentrator or equivalent

Standards

Retention Time Standards. Prepare a composite standard, using methylene chloride as the solvent, consisting of toluene, dodecane and tetracosane at 25 ug/mL each. Additional compounds may be added at the discretion of the analyst. The use of this standard is to establish the retention time windows for the quantitation of gasoline #2 diesel and motor oils.

Reference Standards. Prepare individual petroleum product reference standards (i.e. gasoline, mineral spirits, kerosene and #2 diesel oil), using methylene chloride as the solvent, at approximately 50 ug/mL. Prepare a non-synthetic motor oil (pennzoil SAE 30 or equivalent) reference standard at 200 ug/mL. The preparation of reference standards for other types of petroleum products is recommended. The use of these reference standards is to insure the accurate identification of petroleum product contamination by chromatographic pattern matching ("fingerprinting") and establish retention time windows for those petroleum products not determined with the individual compound retention time standard.

Gasoline Stock Standard. A stock standard is prepared by placing approximately 9 mL of methylene chloride in a 10 mL volumetric flask. Tare the flask/methylene chloride and add about five drops of non-oxygenated regular unleaded gasoline, assuring that the liquid falls directly into the methylene chloride without contacting the neck of the flask. Reweigh the flask and dilute to volume with methylene chloride, stopper and mix by inverting the flask several times. It is important that the analyst minimize the amount of time that the flask is left unstoppered, to reduce

the loss of gasoline through volatilization. The use of a commercially prepared gasoline standards is acceptable if it is certified as non-oxygenated gasoline or if the gasoline concentration has been adjusted to reflect the contribution of the oxygenate. Calculate the gasoline concentration as follows:

$$Stock,\ ug / mL = \frac{(final\ wt,\ mg) - (tare\ wt,\ mg)}{10\ mL} \times \frac{1000\ ug}{mg}$$

Note: The use of oxygenated regular unleaded gasoline for the gasoline stock standard is allowed if the weight (mass) of the gasoline used is adjusted for the weight (mass) contribution of the oxygenate to the gasoline. This will necessitate the analysis of the gasoline for the specific oxygenate(s) present to determine the concentration. The analysis for the oxygenates will be conducted by either of the methods published in the Federal Register - Appendix B and C - Testing Procedures - Vol. 57, No. 24, Wednesday, February 5, 1992, Notices.Alternate methods for the analysis of gasoline oxygenates must be approved by the Oregon's Department of Environmental Quality and/or Washington's Department of Ecology prior to use.

Diesel Stock Standard. A stock standard is prepared by adding about five drops of #2 diesel oil stock to tared 10 mL volumetric flask. Reweigh the flask and bring it to volume with methylene chloride, stopper and mix by inverting the flask several times. Calculate the concentration of this standard in the same manner as the gasoline stock standard. The use of a commercially prepared #2 diesel standard is an acceptable alternative to the above procedure.

Motor Oil Stock Standard. A stock standard is prepared by adding about ten drops of a non-synthetic SAE 30 weight motor oil (Pennzoil or equivalent) to a tared 10 mL volumetric flask. Reweigh the flask, bring it to volume with methylene chloride, stopper and mix by inverting the flask several times. Calculate the concentration of this standard in the same manner as the gasoline stock standard. The use of commercially prepared motor oil standards is an acceptable alternative to the above procedure.

Note: The Diesel and Motor Oil Stock Standards required in this method are identical to those required for NWTPH-Dx (extended diesel method including all semi-volatile petroleum products eluting after gasoline, e.g. kerosene, diesels, mineral oils, lubricating oils, heavy fuel oils, etc.).

Surrogate Stock Standard. Suggested surrogates for use in this method are bromofluorobenzene and pentacosane. The use of different or additional surrogates is optional. Prepare the surrogate stock standard by weighing 50 mg of each surrogate compound into a 10 mL volumetric flask, then bring to volume with methylene chloride for a final concentration of 5000 ug/mL for each surrogate compound. The use of a commercially prepared surrogate solution(s) is an acceptable alternative to the above procedure.

Composite Calibration Working Standard. Using serial dilutions of the stock standards, prepare a mixture for water analyses that contains 10 ug/mL of gasoline, 25 ug/mL of #2 diesel oil and the

surrogate standard. For soil/sediment analyses this standard should be prepared to contain 20 ug/mL of gasoline, 50 ug/mL of #2 diesel and the surrogate standard. Add the appropriate volumes, using the equations listed below, and adjusting for the concentration change created by any serial dilutions, of gasoline stock standard, #2 diesel stock standard and the surrogate stock standard to a 10 mL volumetric flask, then dilute to volume with methylene chloride. Stopper and mix by inverting the flask several times. The surrogate standard should be added to a level sufficient to produce a surrogate concentration of between 5 and 50 ug/mL.

$$\textit{Volume Gasoline Stock, uL} = \frac{\textit{20 (soil) / 10 (water) ug / mL x 10 mL}}{\textit{Gasoline Stock Conc, ug / mL}} \; x \; \frac{\textit{1000 uL}}{\textit{mL}}$$

$$\textit{Volume Diesel Stock, uL} = \frac{\textit{50 (soil) / 25 (water) ug / mL x 10 mL}}{\textit{Diesel Stock Conc, ug / mL}} \; x \; \frac{\textit{1000 uL}}{\textit{mL}}$$

This mixture corresponds to 0.25 mg/L gasoline and 0.63 mg/L #2 diesel oil for water and 20 mg/Kg gasoline and 50 mg/Kg diesel in soil following the extraction and analytical procedures of this method.

The motor oil calibration working standard should be made at a concentration of 250 ug/mL for water and 100 ug/mL for soil following the procedure outlined above. This will correspond to a reporting value of 0.63 mg/L for water and 100 mg/kg for soil. If, in the opinion of the analyst, the GC sensitivity to 100 ug/mL of motor oil is insufficient, the analyst is allowed to increase the concentration of this standard and to concentrate a portion of the extract to achieve the reporting limit for soil.

Surrogate Working Standard. Prepare a surrogate working (spiking) standard, using the procedure outlined above, that will yield between 5 ug and 50 ug/mL of the surrogate compounds in the 10 mL sample extract produced in this method.

Note: All samples must be collected in glass jars with Teflon lined lids (Eagle Picher or equivalent) and held at 4 degrees C until extracted. A volume of 400 mL is the minimum sample size to achieve the reporting limits as stated, however, larger volumes are allowed as long as the solvent/sample ratio is maintained. Samples must be extracted within 7 days (for water) or 14 days (for soil/sediment) of the date of collection. The preservation of water samples in the field, to a pH of less than 2 with 1+1 HCL, is recommended.

Extraction Procedures

Water Samples

Mark the water meniscus on the sample jar for later volume determination. Pour the sample into a 500 mL separatory funnel, add the surrogate solution (to achieve the desired concentration in a 10 mL extract). Add 30 mL of methylene chloride to the sample jar, cap and shake the jar vigorously

for a few seconds to wash off any hydrocarbons adhering to the side of the jar. Add this solvent to the separatory funnel, stopper and shake vigorously, venting frequently, for one minute. Allow the two phases to separate, then drain the solvent into a 250 mL K-D flask fitted with a 10 mL concentrator tube. Repeat the extraction twice more using 30 mL of methylene chloride, each time, adding the solvent to the K-D.

Attach a 3-ball Snyder column to the K-D and concentrate the sample extract to 5 - 10 mL on a stream bath. Remove the K-D apparatus and allow it to cool prior to disassembly. During disassembly, rinse the Snyder/K-D joint and K-D/concentrator joint with approximately 1 mL of methylene chloride and add these rinsings to the extract. Adjust the volume of the extract to 10 mL. For those samples which exceed 10 mL, place the concentrator tube into an N-Evap and, under a gentle stream of nitrogen, reduce the volume to 10 mL. Transfer 1 mL of the extract (to be used for the gasoline or gasoline/diesel determination) to an autosampler vial fitted with a screw top and a Teflon coated septum. Concentrate the remainder of the extract (to be used for heavy oils determination) to 0.9 mL, transfer it to an 2 mL autosampler vial equipped with a screw top and a Teflon coated septum. Store both vials in a refrigerator until analysis.

Each extraction set must include one method blank (organic-free water of similar volume to the samples) per 20 samples. The method blank is to receive the surrogate solution and to be extracted and analyzed in the same manner as the samples.

EPA method 3520, Continuous Liquid-Liquid Extraction, may be substituted as an alternate extraction procedure to that outlined above.

Soil Samples

Weigh approximately 10 grams of soil into a 40 mL VOA vial and record the weight to the nearest 0.001 grams. Add 5 grams of anhydrous sodium sulfate, surrogate working solution and 10 mL of methylene chloride to the VOA vial. Cap the vial and place it (no more than 5 at a time) in a sonic bath for 5 minutes. Shake the vials well and return them to the sonic bath for 5 more minutes. A minimum of one method blank per extraction set or 20 samples, whichever is more frequent, must be prepared along with the samples. One sample duplicate must also be extracted for samples set from one to ten samples and two duplicates for sets from eleven to twenty samples.

Determine the moisture content of the samples, for use in the final calculations, by the following procedure. Immediately after weighing the sample for extraction, weigh 5-10 grams of the sample into a tared crucible. Dry the sample/crucible overnight at 105 degrees C. Reweigh the sample/crucible after allowing it to cool to room temperature. Calculate the % solids as follows: [(grams of dry sample/grams of wet sample) x 100].

If the extract contains significant moisture, elute the solvent phase through an anhydrous sodium sulfate micro-column. Place a portion of the extract in a 2 mL autosampler vial (screw cap, Teflon coated septum), taking care to minimize the volume of headspace, and store the vial in a refrigerator until analyzed. Concentration of the extract, when necessary, will be conducted using an N-Evap

with a gentle stream of nitrogen. This concentrate should be stored in the same manner as noted above.

Note: Anhydrous sodium sulfate micro-columns are prepared by plugging a 5 3/4" length disposable Pasteur pipette (pre-rinsed with methylene chloride) with glass wool (precleaned with methylene chloride) and adding approximately 3 cm of anhydrous sodium sulfate (previously muffled at 430 degrees C overnight in a shallow pan and stored in a glass jar with a Teflon lid liner).

For samples containing petroleum products other than gasoline, diesel, or motor oil, the analyst must either prepare calibration standards of them by the methods listed above or analyze the sample by the fully quantitative method, e.g. NWTPH-Gx. Other calibration standards produced for use in this method must be at an equivalent concentration to the previously established standards, e.g. mineral spirits at the gasoline concentration, kerosene at the diesel concentration.

As more information becomes available on new extraction techniques, the Washington State Dept. of Ecology's Manchester Laboratory and Oregon's Department of Environmental Quality will publish descriptions of acceptable alternate extraction methods.

Suggested GC Parameters

Sample injection Volume = 2 uL
Injector Temperature = 290°C
Detector Temperature = 300°C
Hydrogen Flow = 25-35 mL/min
Air Flow = 300-400 mL/min
Make-up Gas Flow = 30 mL/min
GC Temperature Program = Initial temperature of 50°C and hold for 2 minutes; ramp the temperature 10°C/min to 320°C and hold for 5 minutes.

Product Identification

Petroleum products are to be identified by pattern matching with reference product chromatograms generated the same day as the sample analysis. The term "gasoline range" or "diesel range" hydrocarbons, or derivations of them, should only be used when the analyst is unable to identify the petroleum product present. When these terms are used, it is to indicate the presence of compounds eluting from toluene to dodecane, for the former term, and from dodecane through tetracosane, for the latter term. Motor oils, hydraulic fluids and similar petroleum products which present an unresolved chromatographic envelope of compounds, originating or extending beyond tetracosane, may be reported using the collective term, lube oil, unless specific identification is possible. Heavy fuel oils, e.g. fuel oil #6 or Bunker C, which contain a diesel range component as well as a lube oil (and higher) range may be reported using the collective term, heavy fuel oil, unless specific identification is possible. These products should not, however, be confused with mixtures of #2 diesel and motor oils.

Note: The actual identification of the grade or type of lube oil and heavy fuel oil may require equipment and techniques beyond the scope of this method.

Analysis Procedure

The analysis is accomplished by injecting 2 uL of the 10 mL extract, either manually or by autosampler, into the GC using the splitless injection mode. The results from this injection are, for quantitation purposes, compared directly against the single point calibration standard for the product(s) identified. The injection of 2 uL of the concentrated extract (1 mL equivalent) is used primarily for heavy oil determination, because of the reduced sensitivity of the FID to late eluting motor oil-like products. It may be used for the determination of #2 diesel oil and other diesel range petroleum products but it may not be used for the determination of gasoline or gasoline range petroleum products because of the potential for loss of the more volatile components during the concentration step.

Calculations

Gasoline. The area of the components, toluene to dodecane of the calibration standard, is integrated to the baseline as a group. The samples and method blanks are integrated in the same manner and the group areas are compared. If the sample area exceeds the calibration standard area, proceed with method NWTPH-Gx for accurate quantitation using a fresh aliquot of the sample. If the sample area does not exceed the calibration standard area, then report the gasoline concentration as less than 0.25 mg/L for water or 20 mg/kg for soil. This soil value for gasoline, and the subsequent petroleum products, assumes 100% solids and will be higher depending on the actual moisture content.

Other volatile petroleum products, identified as being present (e.g. mineral spirits), must be compared to the appropriate standard produced at the same concentration as gasoline. The requirement for further analyses is determined following the criteria for gasoline as noted above.

Note: For samples containing only #2 diesel oil, kerosene, etc., the portion of these products, that elute within the retention time range of gasoline, should not be identified and/or quantitated as gasoline or gasoline range petroleum.

Diesel. The area of the components, dodecane through tetracosane of the calibration standard, is integrated to the baseline as a group. This integration must include the unresolved envelope of compounds as well as the discrete component peaks. The sample is integrated in the same manner and the group areas are compared. If the sample area exceeds the calibration standard area, then proceed to method NWTPH-Dx. If the sample does not exceed the calibration standards area, then report the #2 diesel concentration as less than 0.63 mg/L for water or 50 mg/Kg for soil.

Other semi-volatile petroleum products, identified as being present (e.g. kerosene), must be compared to the appropriate standard produced at the same concentration as #2 diesel. The requirement for further analyses is determined following the criteria for #2 diesel as noted above.

Lube Oil. For those samples which consist primarily of only an unresolved chromatographic envelope of components eluting after tetracosane, compare their area to the area of the motor oil standard by integrating the unresolved envelope to baseline. If the sample exceeds the standard area, then proceed to method NWTPH-Dx. If the sample area is less than the standard, then report the lube oil concentration as less than 0.63 mg/L for water or 100 mg/Kg for soil. Samples identified as containing heavy fuel oil must be quantitated to the same value as lube oil by utilizing a heavy fuel oil standard and following the procedure outlined for lube oil.

Note: The analyst is expected to adjust the retention time windows used for quantitation of petroleum products, other than gasoline, #2 diesel, or motor oil/lube oils, to incorporate the majority of the chromatographable components associated with those identified products.

If, in the judgement of the analyst, the area of an identified petroleum product other than gasoline, diesel, and motor oil would exceed the reporting limit, the analyst is allowed to report a "greater than" value for that product without performing the quantitative analysis. The analyst must then proceed to the appropriate fully quantitative analytical procedure, e.g. NWTPH-Dx, for the identified petroleum product.

Quality Assurance

The addition of an appropriate extraction surrogate to samples and method blank(s) is required. The surrogate recovery for all samples and blanks should be between 50% and 150% and must be reported with the petroleum results unless the quantity of the petroleum product(s) preclude its determination. The laboratory should analyze one sample from each site in duplicate for sample sets of 10 or less and two samples in duplicate for sets of 11 to 20 samples (i.e. 10% QA). If either of the duplicate results are positive, the sample is to be considered positive. Since this method precludes the preparation of analytical duplicates, the laboratory should recommend that the project manager collect and submit field duplicates for analysis. The laboratory must analyze method blanks prepared identically to the samples. Organic free water must be used in the preparation of water method blank. No "sample" is necessary for use with soil/sediment method blanks.

Author - Bob Carrell, Manchester Environmental Laboratory, Dept. of Ecology, State of Washington. Reviewed and edited by Steve Robb, Toxics Cleanup Program, Department of Ecology, State of Washington. This method is based on Oregon’s Department of Environmental Quality TPH methods and Washington’s Department of Ecology WTPH methods.

NWTPH-Gx Chromatograms

Gasoline
Weathered Gasoline
Naptha
Mineral Spirits #1
Mineral Spirits #2
Mineral Spirits #3

NWTPH-Dx Chromatograms

#2 Diesel
#2 Diesel/Motor Oil
#2 Fuel Oil
Kerosene (Deodorized)
Jet A Fuel
Bunker C #1
Bunker C #2
Motor Oil 30 Wt.
Mineral Oil (USP)
Hydraulic Fluid
Transformer Oil
Gas Oil

See Appendix 6

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NWTPH-Gx

Volatile Petroleum Products Method for Soil and Water

Summary

The NWTPH-Gx method is intended to replace the Oregon's TPH-G and Washington's WTPH-G methods and to present a more comprehensive approach to volatile petroleum product analyses. NWTPH-Gx adapts Oregon's TPH, Washington's WTPH and EPA SW846 Methods 5030 and/or 8020 and covers the quantitative and qualitative analyses of volatile petroleum products, e.g. gasolines, naphtha, mineral spirits, stoddard solvent, and other volatile petroleum products in soil and water. Soil samples are extracted with methanol and analyzed by gas chromatograph with a flame ionization detector (GC/FID). The methanol extracts may be injected directly into the GC or they may be diluted with organic free reagent water and introduced by a purge/trap concentrator. Water samples are introduced directly to the purge/trap concentrator. This method specifies the criteria for the identification and quantitation of volatile petroleum products. When the type of petroleum product is unknown, regular unleaded gasoline will initially be used as the default petroleum standard. The use of GC/PID, GC/MS or GC/AED (Atomic Emission Detector) for the analysis of gasoline may be substituted for GC/FID as long as all other method parameters are met.

The reporting limits for soil are 5 mg/kg by the purge/trap procedure and 20 mg/kg for direct injection. All soil results are reported on a dry weight basis. Since this value assumes 100% solids, the analyst may wish to adjust the amount of soil extracted and/or purge a larger quantity of extract to achieve the reporting limits. For water, the reporting limits are 0.25 mg/L.

The method is applicable for the identification, by pattern matching ("fingerprinting") and quantitation of volatile petroleum products, i.e. those petroleum products for which the majority of the components elute within the gasoline range.

Note: Benzene, Toluene, Ethylbenzene and Xylenes (BTEX) may be determined simultaneously with gasoline if the requirements of EPA Method 8021 or EPA Method 8260 are met (i.e. the use of a PID (Photoionization Detector) for method 8020 or a MS (Mass Spectrometry) for method 8260 and the QA/QC associated with these methods).

This method must be performed by, or under the direct supervision of, analysts experienced in the use of GC and in the interpretation of gas chromatographs of both fresh and weathered volatile petroleum products.

Equipment and Reagents

Gas Chromatograph
Purge/Trap Liquid Concentrator - Tekmar or Equivalent - Autosampler (Optional)
Flame Ionization (FID) or Photo Ionization/Flame Ionization Detectors (PID/FID)
Suggested Capillary Column: Restex RTX-502.2, 60M x 0.53 mm x 3.0 um film thickness or equivalent
Chromatography Data System
Gas tight syringes, various volumes, Hamilton brand or equivalent
Volumetric flasks: 10 mL, ground glass joint with stopper
Methanol: Burdick and Jackson Purge/Trap grade or equivalent
Petroleum Product Standards: Available from commercial sources
Refer to methods 5030 and/or 8020 for the remaining equipment and reagent requirement

Sample Containers/Holding Times

All soil samples for NWTPH-Gx analyses must be collected in soil VOA bottles with Teflon coated septum lined tops. They should be filled to the top to minimize headspace above the soil and stored at 4 degrees C until analyzed. The maximum holding time (the time from the date of collection to the date of analysis) for gasoline and any other volatile petroleum product is 14 days.

All water samples for NWTPH-Gx analyses must be collected in glass VOA vials with Teflon coated septum lined screw tops. They must be filled so that there is no air space (headspace) above the water. Samples should be preserved with 1+1 HCl to a pH <2 and refrigerated at 4 degrees C until analyzed. The maximum holding time (the time from the date of collection to the date of analysis) is 7 days for unpreserved samples and 14 days for preserved samples. The results of any samples which exceed these limits must be qualified as an estimated value.

Standards

Stock Standards. A stock standard is prepared by placing approximately 9 mL of methanol in a 10 mL volumetric flask. Allow the flask to stand, unstoppered, until the methanol wetted surfaces have dried (about ten minutes), then tare the methanol/flask. Add about 5 drops of the petroleum product to the flask while assuring that the liquid falls directly into the methanol without contacting the neck of the flask. Weigh the flask again and dilute to volume with methanol, stopper and mix by inverting the flask several times. The use of commercially prepared standards is acceptable to the above procedure. Commercially prepared gasoline standards must be certified as non-oxygenated gasoline or the gasoline concentration has been adjusted to reflect the contribution of the oxygenate. Calculate the concentration as follows:

$$\textit{Gasoline Stock Standard, ug / mL} = \frac{\textit{(final wt, mg) - (tare wt, mg)}}{\textit{10 mL}} \; x \; \frac{\textit{1000 ug}}{\textit{mg}}$$

The standard for gasoline will be regular unleaded gasoline and this standard is to be used as the default petroleum product for reporting purposes.

Note: The use of oxygenated regular unleaded gasoline for this standard is allowed if the weight (mass) of the gasoline used is adjusted for the weight contribution of the oxygenate to the gasoline. This will necessitate the analysis of the gasoline for the specific oxygenate(s) present to determine their concentration. This analysis must be conducted by either of the methods published in the Federal Register - Appendix B and C - Testing procedures - Vol. 57, No. 24, Wednesday, February 5, 1992, Notices. Alternate methods for the analysis of gasoline oxygenates must be approved by the Oregon's Department of Environmental Quality and/or Washington's Department of Ecology prior to use.

Stock Surrogate Standard

Note: The suggested surrogates are 1,4-difluorobenzene and bromofluorobenzene. The use of additional surrogates is optional. Selected surrogate compounds should be non-polar, purgeable from water and must not coelute with any significant component of gasoline.

Make up a stock standard by accurately weighing the surrogate compound(s) into a 10 mL volumetric flask. Utilize the same procedure as the stock gasoline standard preparation if neat material is used or by adding the appropriate volumes of dilute surrogate if solutions are used. Bring it to volume with methanol. The use of commercially prepared surrogate solutions is an acceptable alternative to the above procedure.

Working Surrogate Spike. Add the appropriate volume of stock surrogate standard to methanol in a partially filled 10 mL volumetric flask and dilute to volume with methanol. The final concentration of the working surrogate solution is left to the discretion of the analyst, however, this solution should produce between 5 ng and 50 ng of surrogate introduced to the GC.

Secondary Dilution Standard. Using serial dilutions of the stock standard, prepare a 50 ug/mL standard by adding the appropriate volumes, as calculated below, to a 10 mL volumetric flask. The appropriate volume of the stock surrogate standard may also be added to this volumetric flask. Dilute to volume with methanol to yield a final working standard concentration of 50 ug/mL for the standard. Surrogate compound(s) may be added automatically during the sampling process by an autosampler. Gasoline is the default petroleum product for reporting purposes.

$$\textit{Stock Std (Gasoline), uL} = \frac{\textit{50 ug / mL x 10 mL}}{\textit{Stock Std Conc, ug / mL}} \; x \; \frac{\textit{1000 uL}}{\textit{mL}}$$

Store all standards in a refrigerator until needed. Allow them to come to room temperature prior to use.

Calibration Standard

The aqueous purge standards are each prepared by adding 5 uL, 10 uL, 20 uL and 50 uL and 100 uL of the secondary dilution standard per 5 mL of organic free water. The five point calibration standard quantities in the purged water are then 250 ng, 500 ng, 1000 ng, 2500 ng and 5000 ng for the volatile petroleum products. At the discretion of the analyst, the concentration of the surrogate can increase with increasing standard concentration or remain at a fixed value for all calibration standards and samples. Extending the calibration range, either up or down, is allowed as long as the standards remain within the linear range of the instrument and a minimum of a five point calibration is produced. In order to be acceptable, the calibration curve must have a linear correlation coefficient of at least 0.990 and none of the standards may vary from their true (known) value by more than plus/minus 15%.

The use of an autosampler may be substituted for this manual method of standards and sample introduction.

Direction Injection. Prepare calibration standards from the stock gasoline standard and surrogate standards at concentrations of 10 ug/mL, 25 ug/mL, 50 ug/mL, 100 ug/mL and 250 ug/mL for gasoline by adding the appropriate volumes to volumetric flasks and diluting to volume with methanol. Increasing the calibration range with higher standards is acceptable as long as the linear range of the instrument is not exceeded.

Purge/Trap and GC Parameters

Follow the procedure outlined in Method 8021 for the set up of the purge and trap operating parameters and for the GC. Adjust the hydrogen/air flow rates to optimize the FID sensitivity.

Soil Extraction Procedure

Weigh approximately 5 grams of soil into a 40 mL VOA vial and record the weight to 0.001 grams. Add 50 uL of the surrogate working standard and 10 mL of methanol. Quickly cap the vial and shake for 1 minute or use an ultrasonic bath for 2 minutes shaking well after 1 minute. Allow the soil methanol mixture to separate, centrifuging if necessary to clarify the methanol extract. For storage, transfer a portion of the extract into a 2 mL glass autosampler vial, with a Teflon-lined cap, minimizing the headspace and store in a freezer for no longer than one week prior to analysis. Along with the samples, prepare at least one method blank and one sample duplicate per ten samples.

Determine the moisture content of the sample, for use in the final calculations, by the following method. Immediately after weighing the sample for extraction, weigh 5-10 grams of the sample into a tared crucible. Dry the sample/crucible overnight at 105 degrees C. Reweigh the sample/crucible after allowing it to cool to room temperature. Calculate the % solids as follows: [(grams of dry sample/grams of wet sample) x 100].

Analysis Procedure

Prior to the analysis of any samples or method blanks, prepare and analyze a mid-range calibration check standard to insure that the instrument is functioning correctly and that the calibration is valid. This standard should be produced daily using the secondary gasoline standard. The value obtained for this analysis must not vary from the true (known) value by more than plus/minus 20%. If the value falls outside this range then a second mid-range calibration standard should be produced and the analysis repeated. If the reanalysis of the fresh standard fails to meet the acceptance criteria, then the instrument must be recalibrated prior to the analysis of any samples. Once the instrument is shown to be in calibration, the analyses of samples may proceed.

After the last sample has been analyzed, a mid-range calibration check sample must be run to demonstrate that the instrument is still operating within the required parameters. Should this standard fail to meet those parameters, then all samples analyzed after the last successful calibration check must either be reanalyzed or the results obtained must be qualified as an estimated value. An increase in the frequency of mid-range calibration check standard analyses beyond the minimum required is recommended.

Significant interferences may be encountered due to the presence of other petroleum products (or non-petroleum products) eluting within the retention time range of the volatile petroleum product being analyzed. If this occurs, the analyst is allowed to adjust the retention time range used for quantitation to exclude the interferences or to subtract the area of the interfering components from the total area prior to the quantity determination. With the former method, the calibration curve must be adjusted in the same manner to reflect the change in retention time range and integration area.

For volatile petroleum products other than gasoline that have a more narrow boiling point range, e.g. mineral spirits, the retention time range used for quantitation should be adjusted to encompass the expected range of the product. Petroleum products which cannot be identified should be quantitated with the gasoline calibration curve. The term "gasoline range" hydrocarbons, or derivations of it, should not be used when reporting the petroleum values unless the analyst is unable to identify the petroleum product present.

Purge/Trap - Soil. A 100 uL aliquot of the methanol extract is transferred via a 100 uL gas tight syringe to 5 mL of organic free water in a 5 mL gas tight syringe and immediately injected into the purging vessel of the purge and trap device. For samples expected to contain concentrations of gasoline range volatiles outside the calibration linear range, or if dilution is required, a smaller aliquot of the methanol extract, or sample, should be used. The analysis then proceeds as in Method 8020. Autosampler techniques may be substituted for this manual method of sample introduction.

Purge/Trap - Water. Sample water (5 mL) is transferred to a 10 mL gas tight syringe and the working surrogate standard spike is added, via a gas tight syringe, into the 5 mL water sample. Immediately inject this water into the purge vessel of the purge/trap device. If necessary, a smaller sample aliquot may be used in order to remain within the linear calibration range of the instrument.

Larger sample volumes may be analyzed, at the discretion of the analyst, if lower quantitation limits are required. Autosampler techniques may be substituted for this manual method of sample introduction.

Direct Injection - For Soil. Allow the extract to come to room temperature, then inject, either manually or by autosampler, 2 uL of the extract into the GC using the splitless injection mode.

Quantitation

The retention time range (window) for gasoline integration must, at a minimum, include toluene through naphthalene. For other volatile petroleum products, the retention time range for integration must be adjusted to incorporate the majority of the components of the petroleum product(s) identified as present in the samples. If specific product identification can not be made, the analyst must quantitate the samples with the calibration curve of the petroleum product that most closely resembles that of the sample.

For those surrogates which elute within the retention time range used for integration, the analyst must subtract the area of the surrogate(s) from the total area to yield the appropriate area of the petroleum product.

The analyst shall use regular unleaded gasoline as the default petroleum product for reporting purposes when no petroleum products were identified in any initial screening or when the type(s) of petroleum products are unknown prior to analysis.

Sample chromatograms of various volatile petroleum products are included at the end of this method to assist the analyst in determining the appropriate integration ranges.

Result Calculation

The area of the components is integrated, as a group, to the baseline and compared to concentrations of the standards which are integrated in the same manner.

For Soil

$$\textit{Soil Sample Conc, mg / kg} = \frac{(A \times R) \times D}{E \times W \times S}$$

where

A = group area of sample

R = Response factor from std curve (ng injected/area count)

D = Extract Volume, mL

W = Weight of sample, grams

E = Volume of extract purged or injected, uL

S = Decimal percent solids of sample

For Water

$$\textit{Water Sample Conc, ug / L} = \frac{(A \times R)}{V}$$

where

A = group area of sample

R = Response factor from std curve (ng purged/area count)

V = Volume of sample purged, mL

The recovery of the surrogate should be between 50% and 150% and must be reported with the results. Report any surrogate recoveries that can not be calculated due to a high level of gasoline contamination.

Author: Bob Carrell, Manchester Environmental Laboratory, Dept. of Ecology, State of Washington. Reviewed and edited by Steve Robb, Toxics Cleanup Program, Department of Ecology, State of Washington. This method is based on Oregon's Department of Environmental Quality TPH-G and Washington's Department of Ecology WTPH-G methods.

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NWTPH-Dx

Semi-Volatile Petroleum Products Method for Soil and Water

Summary

The NWTPH-Dx method is intended to replace the Oregon's Department of Environmental Quality TPH-D and Washington's Department of Ecology WTPH-D methods and to present a more comprehensive approach to semi-volatile petroleum product analyses. NWTPH-Dx adapts Oregon's TPH, Washington's WTPH and EPA SW-846 Methods 3510, 3540/3550 and 8000 and covers the quantitative and qualitative analysis of semi-volatile petroleum products, i.e. jet fuels through heavy fuel oils, in soil and water. The method involves extracting the samples with methylene chloride and injecting a portion of the extract into a gas chromatograph (GC) equipped with a flame ionization detector (FID). This method specifies criteria for the identification and quantitation of semi-volatile petroleum products. A clean-up procedure, which may be used to aid in the removal of non-petroleum based organic interferences, i.e. biogenic interferences, has been included. When the type of petroleum product is unknown, #2 diesel will initially be used as the default petroleum standard.

The reporting limits are 25 mg/kg (soil) and 0.25 mg/L (water) for the petroleum products in the elution range of jet fuels through #2 diesel. For petroleum products eluting after #2 diesel oil, e.g. motor oils, hydraulic fluids, and heavy fuel oils, the reporting limits are 100 mg/kg (soil) and 0.50 mg/L (water). All soil results are reported on a dry weight basis. Since this value assumes 100% solids and therefore will be higher depending on the actual moisture content, the analyst is permitted to concentrate the extract to obtain these reporting limits. When doubt exists as to which reporting limit is applicable for the petroleum product present, the analyst should use the lower value.

The method is applicable for the identification, by pattern matching ("fingerprinting"), and quantitation of semi-volatile petroleum products. These include kerosenes, jet fuels, diesel oils, fuel oils, lubricating oils, hydraulic fluids, mineral oils and insulating oils, e.g. transformer oils. In general, those petroleum products which do not contain a substantial volatile fraction, i.e. the majority of the components eluting outside of the gasoline range, should be analyzed by this method.

Note: The use of GC/MS (Mass Spectrometry) or GC/AED (Atomic Emission Detector) may be substituted for GC/FID as long as all other method parameters are met.

This method is to be used by, or under the direct supervision of, analysts experienced in the use of GC and in the interpretation of gas chromatograms of both fresh and weathered petroleum products.

Equipment and Reagents

Gas Chromatograph, w/wo Autosampler
Flame Ionization Detector
Capillary Split/Splitless Injector
Suggested Column:
J & W Scientific: DB-1 or DB-5, 30 M x 0.25 mm or 0.32 mm I.D. with 0.25 um film thickness capillary column or equivalent
Chromatographic Data System: Capable of group integrations
Analytical Balance, accurate to a least 0.0001 grams
Volumetric Flasks, 10 mL, ground glass stoppered
N-Evap Concentrator or equivalent
Centrifuge tubes, 10 or 15 mL, glass, calibrated in 0.1 mL increments
Centrifuge tubes, 10 or 15 mL, glass, disposable
Kaderna-Danish (K-D) Flasks, 250 mL
Concentrator Tubes, 10 mL
Snyder Columns, 3-ball, 300 mm length
Sodium Sulfate, anhydrous
Methylene Chloride, Burdick and Jackson brand, gas chromatography/pesticide residue grade or equivalent
Sulfuric acid, concentrated
Silica gel, 100/200 mesh, Baker Analyzed Reagent grade or equivalent - Before use, activate for at least 16 hours at 130 degrees C in a shallow tray
Petroleum Product Standards: Available from commercial sources

Note: All samples shall be collected in Eagle Picher, or equivalent, glass jars and held at 4 degrees C until extracted. The holding time, from the date of collection to extraction, is 14 days for soil and preserved water. For unpreserved water, the holding the holding time is 7 days. Preservation is accomplished by adjusting the pH of the water sample to approximately 2 with the addition of 1+1 HCl.

Suggested GC Parameters

Sample Extract Injection Volume = 2 uL
Injector Temperature = 290 degrees C
Detector Temperature = 300 degrees C
Hydrogen Flow = 25-35 cc/min
Air Flow = 300-400 cc/min
Helium Make-up Gas Flow = 30 cc/min
Helium Carrier Gas Head Pressure = 15 psi
GC Temperature Program:
Initial temperature = 50 degrees C, hold 2 minutes
Temperature Ramp Rate = 20 degrees C per minute
Final Temperature = 320 degrees C, hold for 10 minutes

Standards

Reference/Stock Standards. Prepare individual petroleum product reference/stock standards, e.g. kerosene, #2 diesel oil, transformer oil (mineral oil based) and Bunker-C fuel oil.

Add 5 to 10 drops of the pure petroleum product to a zero tared 10 mL flask. Record the weight and bring the flask to volume with methylene chloride, stopper and mix by inverting the flask several times. Calculate the concentration of these standards using the equation shown below. The use of commercially prepared standards is an acceptable alternative to the above procedure. Analysts may not use artificial standards, e.g. diesel range organics mixtures, etc., for quantitation purposes in place of authentic petroleum products.

These standards are to be used to produce calibration working standards which should be used to insure the proper identification of petroleum products by chromatographic pattern matching ("fingerprinting") as well as accurate quantitation.

$$Stock\ Conc,\ ug / mL = \frac{(final\ wt,\ mg) - (tare\ wt,\ mg)}{10\ mL} \times \frac{1000\ ug}{mg}$$

Calibration Working Standards. Using the stock standards, prepare calibration working standards for the identified petroleum product(s) to be quantitated. Add the appropriate volume(s), using the equation shown below and adjusting for the concentration change created by any serial dilutions, to a 10 mL volumetric flask(s). Dilute to volume with methylene chloride. Calibration standards must, at a minimum, (1) provide a five point calibration curve, (2) include a sufficiently low standard to provide the necessary reporting limits, and (3) define the linear working range of the instrument.

In order to be acceptable, the calibration curve must have a linear correlation coefficient of at least 0.990 and none of the standards may vary from their true (known) value by more than plus/minus 15%. #2 diesel oil is the default petroleum product for reporting purposes.

Stock Surrogate Standard. Prepare the stock surrogate standard by weighing 50 mg of the surrogate compound(s) into a 10 mL volumetric flask. Bring the flask to volume with methylene chloride for a final concentration of 5000 ug/mL for the surrogate compound. The use of commercially prepared surrogate solutions is an acceptable alternative to the above procedure.

Note: The suggested surrogates are 2-fluorobiphenyl, o, or p-terphenyl or pentacosane. The use of other surrogates is optional. Selected surrogate compounds must be non-polar, unaffected by the cleanup procedure, i.e. the concentrated sulfuric acid/silica gel treatment, and lacking in significant interferences in most standard petroleum products.

Working Surrogate Spike. Using serial dilutions of the stock standard, prepare a surrogate working standard. Add the appropriate volume of the stock surrogate standard, using the equation listed

below, and adjusting for any serial dilutions, to a 10 mL volumetric flask and dilute to volume with methylene chloride. Stopper and mix by inverting the flask several times. The surrogate working standard should be added to a level sufficient to produce a surrogate concentration between 5 and 50 ug/mL.

$$Volume\ Stock,\ uL\ =\ \frac{(Cal\ Std\ Conc,\ ug\ /\ mL)\ x\ 10\ mL}{Stock\ Conc,\ ug\ /\ mL}\ x\ \frac{1000\ uL}{mL}$$

Store all standards in a refrigerator until needed. Allow them to come to room temperature prior to use.

Sample Extraction

Soil Matrix

Weigh approximately 20 grams of soil, recording the weight to the nearest 0.01 grams, and approximately 20 grams of anhydrous sodium sulfate into a 150 mL beaker. Mix completely with a spatula. The mixture should have a grainy texture. If it forms a large clump, add more anhydrous sodium sulfate and grind to grainy texture. Add the appropriate volume of working surrogate standard, 50 mL of methylene chloride and sonicate for 3 minutes utilizing the horn sonicator and power settings in SW-846 Method 3550. Allow the mixture to settle then collect the extract in a 250 mL Kuderna-Danish (KD) flask to which is connected a 10 mL concentrator tube.

Repeat the extraction twice more and add these extracts to the KD. Attach a 3 ball Snyder column and concentrate the extract on a steam bath to a volume of 5-10 mL. Allow the K-D to cool to room temperature. Disassemble the K-D, rinsing the Snyder/K-D and K-D/concentrator tube joints with 1-2 mL of methylene chloride. Add these rinsings to the extract. If necessary, place the concentrator tube in an N-Evap and reduce the volume to 10 mL under a gentle stream of nitrogen. At this point, proceed to the sample cleanup procedure if applicable or transfer a portion of the extract to a 2 mL autosampler vial fitted with a screw top and a Teflon lined septum. Store the extract in a refrigerator until analyzed. If the extract is highly colored or forms a precipitate, a dilution may be necessary to stay within the calibration range. The use of the EPA method 3540 (soxhlet) in place of Method 3550 is optional.

Determine the moisture content of the samples by the following method. Immediately after weighing the sample for extraction, weigh approximately 10 grams of the sample into a tared crucible and record the weight. Dry the sample/crucible overnight at 105 degrees C. Reweigh the sample/crucible after allowing it to cool to room temperature and record the weight. Calculate the % solids as follows: [(grams of dry sample/grams of wet sample) x 100].

Along with each sample set, run at least one duplicate sample per set of 10 or fewer samples (10%) and, for each extraction day, at least one method blank (5%). Spiking of surrogates, extraction and

analyses of the QC samples will be conducted identically to the regular samples with the exception that no soil is added to the method blank.

Water Matrix

Allow the sample to come to room temperature and mark the meniscus for later use in volume determination. Pour the sample into a separartory funnel and adjust the pH to approximately 2 with 1+1 HCl and add the appropriate volume of surrogate working solution. Add 30 mL of methylene chloride to the sample jar and rotate the jar at a sufficient angle to wash the walls. Pour the solvent into the separatory funnel, stopper, and shake it vigorously for one minute, venting frequently. After the two phases have separated, drain the solvent into a 250 mL K-D flask to which is attached a 10 mL concentrator tube.

Note: Due to possible loss of analytes from the water to the sample jar walls, the entire sample must be consumed in the extraction and no aliquots may be used. Since the reporting limits are calculated on a 400 mL sample volume, sample jar size should be appropriate for this volume. For larger sample volume extractions, the analyst must increase the quantity of solvent used to maintain the original solvent/sample ratio.

Repeat the extraction twice more and add these extracts to the K-D. Attach a 3-ball Snyder column to the K-D and concentrate the extract on a steam bath to 5-10 mL. Allow the K-D to cool to room temperature and disassemble it, rinsing the Snyder/K-D and K-D/ concentrator joints with 1-2 mL of methylene chloride. Add these rinsings to the extract. Place the concentrator tube into an N-Evap and reduce the volume to 2 mL under a gentle stream of nitrogen. Transfer the extract to a 2 mL autosampler vial fitted with a screw top and a Teflon lined septum. Store the extract in a refrigerator until analyzed.

Along with each sample set, run at least one duplicate sample per set of 10 or fewer samples (10%) and, for each extraction day, at least one method blank (5%). Spiking of surrogates, extraction and analyses of the QC samples will be conducted identically to the regular samples with the exception that organic free water will be used for the method blank.

As more information becomes available on new extraction techniques, Washington State Dept. of Ecology's Manchester Laboratory and/or Oregon’s Department of Environmental Quality will publish descriptions of acceptable alternative extraction methods.

Sample Cleanup. In those cases where samples contain a significant amount of naturally occurring non-petroleum organics, e.g. leaf litter, bark, etc., which may contribute biogenic interferences, the following cleanup technique may be employed to assist in their reduction or elimination.

Transfer the 10 mL sample extract to a 10 to 15 mL centrifuge tube, add 1 mL of concentrated sulfuric acid to the extract and stopper the tube. Mix thoroughly for 1 minute by either shaking the tube or with the use of a vortex-genie adjusted to the highest setting.

Caution: Since sulfuric acid produces a highly exothermic reaction with water and other polar materials, extreme care should be exercised with its use.

Allow the two phases to separate. Centrifugation can be used to facilitate this process. Using a disposable glass pipet, transfer the methylene chloride (top) phase to another centrifuge tube and add approximately 0.4 grams (roughly equivalent to 1 mL of volume) of silica gel to the tube, stopper and mix as before. Allow the silica gel to settle or centrifuge. Repeat the sulfuric acid/silica gel treatment once more. Transfer a portion of the extract to a 2 mL autosampler vial equipped with a Teflon-lined cap and store the extract in a refrigerator until analyzed. A smaller aliquot of the extract may be used for this cleanup procedure as long as the ratio of extract to acid/silica gel is maintained.

It has been noted that some petroleum products, i.e. heavy fuel oils such as #6 fuel oil or Bunker-C, may experience a concentration loss of between 10 and 20 percent when subjected to this cleanup technique. This loss appears to be primarily associated with the removal of petroleum compounds which contain sulfur. To account for this loss when analyzing samples that have been subjected to the cleanup procedure in preparation for heavy fuel oil determination, the analyst must use utilize standards which have undergone the cleanup technique to calibrate the GC.

Note: The use of EPA method 3611 (Alumina column cleanup) may be substituted for the above cleanup technique if it is demonstrated to provide equivalent results.

Analysis Procedure. Prior to the analysis of any samples or method blanks, the analyst must prepare and analyze a mid-range calibration check standard to insure that the instrument is functioning correctly and that the calibration is still valid. The value obtained for this analysis must not vary from the true (known) value by more than plus/minus 15%. If the value falls outside this range then a second mid-range calibration check standard should be analyzed. If the analysis of the second check standard fails to meet the acceptance criteria, then the instrument must be recalibrated prior to the analysis of any samples. Once the instrument has been shown to be in calibration, the analyses of samples may proceed.

The analyst shall use #2 diesel as the default petroleum product for reporting purposes when no petroleum products were identified in any initial screening or when the type(s) of petroleum products are unknown prior to analysis.

After the last sample has been analyzed, a mid-range calibration check sample must be run to demonstrate that the instrument is still operating within the required parameters. Should this standard fail to meet those parameters, then all samples analyzed after the last successful calibration check standard must be reanalyzed. An increase in the frequency of mid-range calibration check standard analyses beyond the minimum required is recommended.

Qualitative Analysis - Identification

If NWTPH-HCID has not been previously performed on the samples and/or the type of petroleum present is unknown, the analyst should pre-screen the samples to determine the petroleum product.

The observed petroleum product shall be determined by pattern matching with the standard(s) analyzed the same day. Chromatograms used for this "fingerprinting" should be normalized to approximately 90% of full scale for the largest component of the particular petroleum product observed.

When reporting the results, the terms such as "diesel range" or "motor oil range", or derivations of them, should only be used when the analyst is unable to identify the petroleum product(s) present. Motor oils, hydraulic fluids and similar petroleum products which consist primarily of an unresolved chromatographic envelope of compounds originating at, or extending beyond tetracosane, may be reported using the collective term "lube oil" unless specific identification is possible. Heavy fuel oils, e.g. #6 fuel oil or Bunker-C, which contain a diesel range component as well as a lube oil range, may be reported using the collective term "heavy fuel oil" unless specific identification is possible. Heavy fuel oils should not, however, be confused with mixtures of #2 diesel and lube oils.

Note: The actual identification of the grade or type of lube oil and/or heavy fuel oil may require equipment and techniques beyond the scope of this method.

Quantitative Analysis - Integration

The retention time range (window) for integration must be adjusted to incorporate the majority of the components of petroleum product(s) identified as present in the samples. If specific product identification can not be made, the analyst must quantitate the samples with the calibration curve for the petroleum product that most closely resembles that of the sample. In all cases, the selected retention time range (windows) used for quantitation must, at a minimum, include any unresolved envelope of compounds as well as all discrete component peaks with an area greater than or equal to 10% of the largest peak. These components must be integrated to the baseline as a group.

For those surrogates which elute within the retention time range used for integration of a petroleum product, the analyst must subtract the area of the surrogate from the total area to yield the appropriate area of the petroleum product. In this case, the analyst may wish to generate separate calibrations for the petroleum standards and the surrogate(s) to facilitate integration and quantitation.

At the discretion of the analyst, the range of components included in the integration may be adjusted in order to minimize the potential contribution of any co-eluting fractions arising from the presence of multiple petroleum products. Any change in the integration range must be reflected in a concomitant change to the calibration standards integration.

Sample chromatograms of various petroleum products are included at the end of this method to assist the analyst in determining the appropriate integration ranges.

Result Calculation

For Soil

$$Soil\ Sample\ Conc,\ mg / kg = \frac{(A \times R) \times V \times Dilution\ Factor}{E \times W \times S}$$

where

A = Area Count from Sample
R = Response Factor (ng injected/area count)
V = Extract Volume (mL)
W = Weight of Sample (g)
E = Volume injected, (uL)
S = Decimal percent solids of sample

For Water

$$Water\ Sample\ Conc,\ mg / L = \frac{(A \times R) \times V}{E \times S}$$

where

A = Area Count from Sample
R = Response Factor (ng injected/area count)
V = Extract Volume (mL)
S = Volume of Sample (mL)
E = Volume Injected (uL)

The recovery of the surrogate should be between 50% and 150% and must be reported with the results. If the recovery of the surrogate is not able to be obtained due to a high levels of petroleum contamination, then this fact needs to be reported.

Author: Bob Carrell, Manchester Environmental Laboratory, Dept. of Ecology, State of Washington. Reviewed and edited by Steve Robb, Toxics Cleanup Program, Department of Ecology, State of Washington. This method is based on Orgeon's Department of Environmental Quality TPH-D and Washington's Department of Ecology WTPH-D methods.

METHOD FOR THE DETERMINATION

OF

VOLATILE PETROLEUM HYDROCARBONS (VPH) FRACTIONS

Washington State Department of Ecology

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METHOD FOR THE DETERMINATION OF VOLATILE PETROLEUM HYDROCARBONS (VPH)

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DISCLAIMER

Mention of trade names or commercial products does not constitute endorsement by the Washington State Department of Ecology Equipment and materials cited in this method may be replaced by similar products, as long as adequate data exists or has been produced documenting equivalent or superior performance.

METHOD FOR THE DETERMINATION OF VOLATILE PETROLEUM HYDROCARBONS

1.0 SCOPE AND APPLICATION

1.1 This method is designed to measure the collective concentrations of volatile aliphatic and aromatic petroleum hydrocarbons in water and soil. **The carbon ranges used through out this document are given in equivalent carbon (EC) numbers which are related to the boiling point of a chemical normalized to the boiling point of the n-alkanes, and its retention time in a boiling point gas chromatographic (GC) column.** Volatile aliphatic hydrocarbons are collectively quantitated within four ranges: C5 through C6, >C6 through C8, >C8 through C10 and > C10 through C12. Volatile aromatic hydrocarbons are collectively quantitated within the C8 through C10, >C10 through C12 and >C12 through C13 ranges. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 36°C and 220°C.

1.2 This method is also designed to measure the individual concentrations of benzene, toluene, ethylbenzene, xylenes, and methyl tert butylether (MTBE) in water and soil.

1.3 Petroleum products suitable for evaluation by this method include gasoline, mineral spirits, and certain petroleum naphthas. This method, in and of itself, is not suitable for the evaluation of samples contaminated with kerosene, jet fuel, heating oils, lubricating oils, or other petroleum products which contain a significant percentage of hydrocarbons larger than C10. When samples are known or suspected to contain petroleum products containing significant concentration of hydrocarbons >C10, the Extractable Petroleum Hydrocarbon (EPH) method should also be employed to fully evaluate the hydrocarbons present.

1.4 For reporting purposes, the practical quantitation limits (PQL), given the sample volume purged, mass and/or methanol extract volume purged are: 50.0 ug/L for water and 5.0 mg/kg for soil/sediments for the aliphatic and aromatic carbon ranges and 5.0 ug/L and 0.5 mg/kg respectively for the individually targeted compounds. The procedure for Method Detection Limits (MDL) determination in this method and the

Single Laboratory Precision, Accuracy and MDL data (generated by the State of Massachusetts) is added for informational purposes only.

1.5 This method is based on a purge-and-trap, gas chromatography (GC) procedure. This method should be used by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatographs. The analysts should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.

1.6 Like all GC procedures, this method is subject to a "false positive" bias in the reporting of targeted analytes, in that non-petroleum compounds eluting or co-eluting within a specified retention time window may be falsely identified and/or quantitated with the respective carbon ranges. Confirmatory analysis by a GC/MS, EPA Method 8260, or other suitable procedures are recommended in cases where significant concentrations of non-hydrocarbon compounds are known or suspected. If the results of these analyses lead to identification and quantitation of non-petroleum compounds, the analyst may subtract those values from the affected carbon ranges as long as the identities and quantities of subtracted compounds are provided in the analytical report.

2.0 SUMMARY OF METHOD

2.1 Samples are analyzed using purge-and-trap sample concentration. The gas chromatograph is temperature programmed to facilitate separation of organic compounds. Detection is achieved by a photo-ionization detector (PID) and flame ionization detector (FID) in series. Quantitation is based on comparing the PID and FID detector response of a sample to a standard comprised of aromatic and aliphatic hydrocarbons. The PID chromatogram is used to determine the individual concentrations of targeted analytes (BTEX/MTBE) and collective concentration of aromatic hydrocarbons within the C8 through C10, C10 through C12 and C12 through C13 ranges. The FID chromatogram is used to determine the collective concentration of aliphatic hydrocarbons within the C5 through C6, C6 through C8, C8 through C10 and C10 through C12 ranges. To avoid double counting of the aromatic contribution to the aliphatic ranges, the PID concentrations are subtracted from the FID concentrations to yield the aliphatic ranges values.

2.2 This method is suitable for the analysis of waters, soils, and sediments. Water samples may be analyzed directly for volatile petroleum hydrocarbons by purge-and-trap concentration and gas chromatography. Soil samples are either dispersed in methanol to dissolve the volatile organic constituents and a portion of the methanol is analyzed by purge-and-trap GC or combined with water for purging directly from a soil purge vessel (EPA method 5035).

2.3 This method is based on, and constitutes a significant modification of, the “Method for the Determination of Volatile Petroleum Hydrocarbons (VPH)”, Public Comment Draft 1.0, developed by the Massachusetts Department of Environmental Protection and on EPA method 5035. They in turn based their method on (1) USEPA Methods

5030, 8000, 8020, and 8015, SW-846, "Test Methods for Evaluating Solid Wastes", 3rd Edition, 1986; (2) Draft "Method for Determination of Gasoline Range Organics", EPA UST Workgroup, November, 1990; and (3) "Method for Determining Gasoline Range Organics", Wisconsin Department of Natural Resources, PUBL-SW-140, 1992.

3.0 DEFINITIONS

3.1 **Volatile Petroleum Hydrocarbons (VPH)** are defined as all hydrocarbon compounds eluting just prior to n-pentane through 1-methylnaphthalene. VPH is comprised of C5 through C6, >C6 through C8, >C8 through C10 and >C10 through C12 Aliphatic Hydrocarbons, as well as >C8 through C10, >C10 through C12 and >C12 through C13 Aromatic Hydrocarbons as well as benzene and toluene. VPH concentration data are reported as the aggregate concentrations of the aliphatic and aromatic hydrocarbon ranges and as selected targeted analytes.

3.2 **Equivalent Total Petroleum Hydrocarbons (E-TPH)** For samples contaminated ONLY with gasoline or other low molecular weight petroleum products, the E-TPH value is equivalent to the VPH value. For samples contaminated with BOTH light and heavy molecular weight petroleum products (e.g., gasoline and diesel fuel), the E-TPH value is a summation of the VPH value and the Extractable Petroleum Hydrocarbon (EPH) values. In order to avoid double counting of analytes due to the overlap in the carbon ranges existing between the two methods, the analyst will report the highest of the two values determined for the overlapping ranges. In those cases where both the VPH and EPH methods are employed on samples, the analyst may select to quantitate the >C10 through C12 Aliphatic and the >C10 through C12 Aromatic Hydrocarbon ranges only using the EPH method.

3.3 **C5 through C6 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds which elute on the FID chromatogram from (and including) n-pentane through n-hexane.

3.4 **C6 through C8 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbons which elute on the FID chromatogram after n-hexane through n-octane.

3.5 **C8 through C10 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds which elute on the FID chromatogram after n-octane through n-decane.

3.6 **C10 through C12 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbons which elute on the FID chromatogram after n-decane through n-dodecane.

3.7 **C8 through C10 Aromatic Hydrocarbons** are defined as all hydrocarbon compounds which elute on the PID chromatogram after toluene through 1,2,3-trimethylbenzene.

3.8 **C10 through C12 Aromatic Hydrocarbons** are defined as all hydrocarbons which elute on the PID chromatogram after 1,2,3- trimethylbenzene through naphthalene.

3.9 **C12 through C13 Aromatic Hydrocarbons** are defined as all hydrocarbons which elute on the PID chromatogram after naphthalene through 1-methylnaphthalene. This is a hybrid range which is designed to acquire the methylnaphthalenes associated with petroleum products like gasoline and is only used when VPH is run without an accompanying EPH method request.

3.10 **Targeted VPH Analytes** are defined as benzene, toluene, ethylbenzene, p,m,o-xylenes, and MTBE.

3.11 **Volatile Petroleum Hydrocarbon (VPH) Component Standard** is defined as a 15 component mixture of the aliphatic and aromatic compounds, plus surrogate, listed in Table 1. The compounds comprising the VPH Component Standard are used to (a) define the individual retention times and chromatographic response factors for each of the Targeted VPH Analytes, (b) define and establish the windows for the collective aliphatic and aromatic hydrocarbon ranges of interest, and (c) determine average chromatographic response factors that can in turn be used to calculate the collective concentration of hydrocarbons within these ranges.

3.12 **Analytical Batch** is defined as a group of samples with similar matrices which are processed as a unit. For Quality Control purposes, if the number of samples in such a group is greater than 20, then each group of 20 samples or less are defined as separate analytical batches.

3.13 **Laboratory Duplicates** are defined as split samples taken from the same sampling container and analyzed separately with identical procedures. The analysis of laboratory duplicates give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.14 **Field Duplicates** are defined as two separate samples collected at the same time and place under identical circumstances and managed the same throughout field and laboratory procedures. Analyses of field duplicates give a measure of the precision associated with sample collection, preservation, and storage, as well as laboratory procedures.

3.15 **E-TPH Duplicates** are defined as two separate samples collected at the same time and location, for analysis by both EPH and VPH methods. E-TPH duplicates are taken at locations where significant concentrations of petroleum hydrocarbons lighter and heavier than C9 are likely to be present (e.g., locations contaminated by releases of both gasoline and diesel fuel). The resultant EPH and VPH concentrations, adjusted to prevent double counting of overlapping hydrocarbon ranges between the methods, are then summed to determine the Equivalent TPH (E-TPH) concentration.

3.16 **Calibration Standards** are defined as a series of standard solutions prepared from dilutions of a stock standard solution, containing known concentrations of each analyte and surrogate compound of interest.

3.17 **Calibration Check Standard** is defined as a calibration standard used to periodically check the calibration state of an instrument. The calibration check standard is prepared from the same stock solution as calibration standards, and is generally one of the mid-level range calibration standard dilutions.

Table 1. Volatile Petroleum Hydrocarbon (VPH) Component Standard

Compound	Equivalent Carbon Number
n-Pentane	5.0
n-Hexane	6.0
Methyl tert butylether	N/A
Benzene	6.5
Toluene	7.6
n-Octane	8.0
Ethylbenzene	8.5
m- & p- Xylene	8.6
o-Xylene	8.8
1,2,3,-Trimethylbenzene	10.1
n-Decane	10.0
Naphthalene	11.7
n-Dodecane	12.0
1-Methylnaphthalene	13.0
2,5-Dibromotoluene (surrogate)	N/A

3.18 **Matrix Spiking Solution** is defined as a solution which is generally prepared independently from the calibration standards, containing known concentrations of method analytes.

3.19 **Laboratory Method Blank** is defined as, depending on the matrix of the samples, either reagent water or clean sand spiked with a surrogate standard. The laboratory method blank is treated identically as with samples, exposed to all glassware, solvents, reagents, and equipment. A laboratory method blank is analyzed with every batch of samples, to determine if method analytes or other interferences are present in the laboratory environment, reagents, or equipment.

3.20 **Laboratory Fortified Blank (LFB)** is defined as, depending on the matrix of the samples, either reagent water or a clean sand blank fortified with a matrix spiking solution.

The LFB is treated and analyzed identically as with samples and blanks, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements at the required practical quantitation limits..

3.21 **Laboratory Fortified Matrix (LFM) Sample** is defined as an environmental sample which has been spiked with a matrix spiking solution containing known concentrations of method analytes. The LFM sample is treated and analyzed exactly as a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined through the separate analyses of a laboratory or field duplicate, and the measured values in the LFM sample corrected for background concentrations.

3.22 All other terms are as defined in SW-846, "Test Method for Evaluating Solid Waste", USEPA, September, 1986, and as amended.

4.0 INTERFERENCES

4.1 Samples can become contaminated by diffusion of volatile organics through the sample container septum during shipment and storage. Trip blanks prepared from reagent water should be carried through sampling and subsequent storage and handling to serve as a check on such contamination.

4.2 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe and/or purging device must be rinsed between samples with reagent water or solvent. The trap and other parts of the system are also subject to contamination, therefore, frequent bake-out and purging of the entire system may be required. A screening step is recommended to protect analytical instrumentation. Whenever an unusually concentrated sample is encountered, it must be followed by the analysis of a solvent blank to check for cross-contamination.

4.3 Certain organic compounds not associated with releases of petroleum products, including chlorinated solvents, ketones, and ethers, will be quantitated as Volatile Petroleum Hydrocarbons. Some samples may require additional analytical procedures to be employed , e.g. GC/MS, to document the presence and quantity of such compounds.

4.4 The response selectivity of a photo-ionization detector (PID) is used in this method to differentiate aromatic hydrocarbons from aliphatic hydrocarbons. All compounds eluting on the PID chromatogram after toluene are identified by the method as aromatic hydrocarbons. This will lead to an overestimation of aromatic hydrocarbons within samples, as certain aliphatic compounds will elicit a response on the PID, particularly unsaturated compounds such as alkenes. The significance and implications of this overestimation will vary from sample to sample and, where less conservative data are desired, additional actions should be considered to

minimize the detection of non-aromatic compounds, such as the use of a lower energy PID lamp or GC/MS.

5.0 HEALTH AND SAFETY ISSUES

The toxicity and carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis.

6.0 APPARATUS AND MATERIALS

6.1 The following glassware is used in this method:

6.1.1 VOC Vials: Wide mouth 60-mL VOC vials or 40-mL VOC vials with teflon/ silicone septa for soils; 40-mL VOC vials with teflon/silicone septa for waters.

6.1.2 Volumetric flasks: 10-mL, 50-mL, 100-mL, and 1,000-mL with a ground-glass stopper.

6.1.3 Disposal pipets: Pasteur.

6.2 Analytical balance: An analytical balance capable of accurately weighing 0.0001 g must be used for weighing standards. A top-loading balance capable of weighing to the nearest 0.1 g must be used for weighing soil samples.

6.3 **Gas Chromatography**

6.3.1 Gas Chromatograph: An analytical system complete with temperature programmable gas chromatograph and purge-and-trap concentrator. The data station must be capable of storing and reintegrating chromatographic data and must be capable of determining peak areas using a forced baseline projection.

6.3.2 Columns

6.3.2.1 Recommended column: 105M x 0.53 mm I.D. Restek RTX 502.2, 3.0 micron film thickness, or equivalent.

6.3.2.2 Other columns, such as a 60 M x 0.53 mm J&W DB-5, may be used. Capillary columns are required to achieve necessary resolution. The column must be capable of resolving typical gasoline components. It must also resolve ethylbenzene from m/p-xylene. Some columns may require subambient cooling to achieve these criteria.

6.3.3 Detectors: The method utilizes a Photo-ionization Detector (PID) in series with a Flame Ionization Detector (FID); the PID first in the series. The method is based upon the use of a 10.0 eV PID lamp, although lower energy lamps are permissible in order to minimize PID response to aliphatic compounds.

6.3.4 Purge-and-trap device: The purge-and-trap device consists of a sample purger, a trap, and a desorber. Several complete devices are commercially available.

6.3.4.1 The purging chamber must be designed to accept 5 mL samples with a water column at least 3 cm deep. Purging devices larger than 5 mL have a reduced purging efficiency and should not be used. The gaseous headspace between the water column and the top of the vessel should be at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. Fritted glass or needle sparge cells may be used. If needle sparge cells are used, the purge gas must be introduced no more than 5 mm from the base of the water column. Alternate sample purge devices may be used, provided equivalent performance is demonstrated.

6.3.4.2 The trap should be at least 25 cm long and have an inside diameter of at least 0.105 inches. The trap should be packed with 400 mg of Carbopack B (Supelco Cat. No. 209273). Alternative trap packing materials include: Tenax GC (or equivalent); 7.6 cm Carbopack B and 1.3 cm Carbosieve S-III (Supelco Cat No. 2-0321); 7 cm Carbopack C and 1.2 cm Carbopack B (Supelco Cat No. 2-1064); or equal volumes of Tenax, silica gel, and charcoal as described in EPA SW-846 Method 5030. In general, Carbopack trap packing materials are recommended because they have less of a tendency to retain methanol, which could interfere with the elution of pentane and quench the FID flame. The trap length and packing materials may be varied as long as equivalent performance has been verified.

6.3.4.3 Prior to initial use, the Carbopack B trap should be conditioned overnight at 270°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to a hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min. at 260°C with backflushing. The trap may be vented to the analytical column during daily conditioning, however, the column must be run through the temperature program prior to analysis of samples. Devices other than the traps recommended in Section 6.3.4.2 should be conditioned and desorbed according to the manufacturer's guidelines.

6.3.4.4 The desorber should be capable of rapidly heating the trap to 240°C for desorption.

6.4 Ultrasonic bath.

6.5 Syringes: 5-mL Luerlock glass hypodermic and 5-mL gas-tight syringe with shutoff valve.

6.6 Syringe valve: Two-way, with luer ends.

6.7 Microsyringes: 1-µL, 5-µL, 10-µL, 25-µL, 100-µL, 250-µL, 500-µL, and 1,000-µL.

6.8 Spatula: Stainless steel.

7.0 REAGENTS AND STANDARDS

7.1 **Reagents**

7.1.1 Reagent Water: organic free water (ASTM Type I reagent grade water).

7.1.2 Solvent: methanol; purge and trap grade or equivalent. Store away from other solvents.

7.1.3 Ottawa and/or masonry sand: free of volatile petroleum hydrocarbons.

7.2 **Stock Standard Solution**

Prepare a stock standard solution in methanol at approximately 20 µg/µL, or purchase certified solutions. Preparation of stock standards and component standards should be done using volumetric glassware.

7.2.1 The stock standard solution consists of the 15 VPH component standards listed in Table 1 and a surrogate standard. Prepare the stock standard solution by accurately weighing approximately 0.2000 g of each standard component. Dissolve the component in methanol and dilute to volume in a 10-mL volumetric flask. At the discretion of the analyst, the surrogate standard may be made up as a separate solution from the VPH standards.

7.2.1.1 Place about 8 mL of methanol in a 10-mL tared ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min. or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

7.2.1.2 Using a 500-µL syringe, immediately add 100 to 200 µL of each VPH Component Standard to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

7.2.1.3 Dilute to volume, stopper, and then mix by inverting the flask three times. Calculate the concentration in micrograms per microliter (µg/µL) from the net gain in weight. When compound purity is assayed to be 98% or greater, the weight may be used without correction to calculate the

concentration of the stock standard, provided such purities are certified by the manufacturer or by an independent source.

7.2.1.4 Transfer the stock standard solution into a Teflon-lined screw-cap/crimp cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.

7.2.2 Stock standard solutions must be replaced after 6 months, or sooner if comparison with check standards indicates a problem. The use of commercially prepared certified standard solutions is an acceptable alternative to the use of neat compounds in the preparation of standards.

7.3 Primary Dilution Standard

Using the stock standard solution, prepare primary dilution standards in methanol, as needed. The primary dilution standard should be prepared at the concentrations shown in Table 2. These standards should be stored with minimal headspace, at -10°C to -20°, and should be checked frequently for signs of degradation or evaporation. The analyst is allowed to prepare separate surrogate and VPH analyte standards.

The primary dilution standards should be replaced at least monthly.

7.4 VPH Calibration Standards

Prepare VPH Calibration standards in reagent water from the primary dilution standard at a minimum of five concentration levels. One of the concentration levels must be near, but above, the method detection limit and must be at a sufficiently low level to allow the PQL reporting of at least 5.0 ug/L for water and 0.5 mg/kg for soil/sediments for the targeted analytes (BTEX and MTBE) and 50.0 ug/L and 5.0 mg/kg respectively for the aliphatic and aromatic carbon ranges. The other standard concentrations must correspond to the expected range of concentrations found in real samples and/or should define the working range of the detector.

7.4.1 Rapidly inject the methanolic standard into the water in the expanded area of a filled 100-mL volumetric flask. Remove the needle quickly after injection.

7.4.2 Mix aqueous standards by inverting the flask three times.

7.4.3 Discard the solution contained in the neck of the flask, and fill the sample syringe from the standard solution contained in the expanded area of the flask.

7.4.4 Do not use pipets to dilute or transfer samples or aqueous standards.

7.4.5 Do not inject more than 20 µL of methanolic standards into 100 mL of reagent water. Aqueous standards are not stable and should be discarded after one hour.

7.5 Surrogate Control Standard (SCS)

The analyst must monitor both the performance of the analytical system and the effectiveness of the method in dealing with sample matrices by spiking each sample, blank, and matrix spike with a surrogate standard. The surrogate standard is also added to the VPH calibration standard solutions. The recommended surrogate standard is 2,5-dibromotoluene, which elutes after all aliphatic and aromatic compounds of interest. The use of additional surrogates or surrogates other than those listed above may be used, at the discretion of the analyst, as long as their performance in the method is demonstrated as acceptable and does not compromise the quantitation of the various target analytes or carbon ranges.

7.5.1 Surrogate Spiking Solution: From a stock standard solution prepared as in Section 7.2.1, prepare a surrogate spiking solution at 50 µg/mL in methanol. Add 4.0 µL of this surrogate spiking solution directly into the 5-mL syringe with every aqueous sample, blank, and matrix spike. 1.0 mL of the surrogate spiking solution is added to soil samples during the extraction step (See 9.1.2.2).

7.6 **Matrix Spiking Solution**

The recommended matrix spiking solution, consisting of the Targeted VPH Analytes, is prepared in methanol at concentrations of 50 µg/mL.

7.7 **Petroleum Reference Standard**

The use of a Petroleum Reference Standard is recommended for quality control purposes. The Petroleum Reference Standard consists of an API or commercial gasoline standard. Prepare a Petroleum Reference Standard Spiking Solution by accurately weighing approximately 0.0100 g of neat product. Dissolve the neat product in methanol and dilute to volume in a 10-mL volumetric flask.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 **Aqueous Samples**

8.1.1 Aqueous samples should be collected in duplicate (or the number of vials directed by the laboratory) without agitation and without headspace in contaminant-free amber glass VOC vials with Teflon-lined septa screw caps. Samples must be acidified to a pH of 2.0 or less at the time of collection and this can generally be accomplished by adding 3 or 4 drops (0.1 to 0.2 mL) of 1:1 HCl (1 part reagent water and 1 part concentrated HCl) to a 40-mL VOC vial. Samples must be cooled to 4°C immediately after collection.

8.1.2 A chain of custody form should accompany all sampling vials and should document the date and time of sample collection and acid preservation. The pH of all water samples must be determined by the laboratory unless sample vials containing acid for field preservation were supplied by the laboratory (this must be noted on the chain of custody). The pH measurement may be performed on left over sample. Any sample found to contain a pH above 2.0 should be so noted on the laboratory/data report sheet.

8.1.3 Any sample received by the laboratory that is not packed in ice or cooled to 4°C must be so noted on the laboratory/data report sheet.

8.1.4 Acid preserved aqueous samples must be analyzed within 14 days of collection. Aqueous samples which, for whatever reason, have not received acid preservation must be analyzed within 7 days of collection or the data must be reported as an “estimate quantity”.

8.2 **Soil Samples**

8.2.1 Soil samples must be collected in a manner that minimizes sample handling and agitation. All sediment must be removed from the glass threads of the vial to ensure an adequate seal. Samples must be cooled to 4°C immediately after collection.

8.2.3 Samples for VPH analysis should be collected in duplicate 2 or 4 ounce VOC jars with Teflon coated septum lined lids.

8.2.4 Sampling must be accomplished in a manner that ensures a minimum of headspace in the sample vial.

8.2.5 A chain of custody form should accompany all sampling vials and should document the date and time of sample collection.

8.2.6 Soil samples must be analyzed within 14 days of collection.

8.3 A summary of sample collection, preservation and holding times is provided in Table 2 .

Table 2 . Holding Times and Preservatives for VPH Samples

Matrix	Container	Preservation	Holding Time
Aqueous Samples	40-mL VOC vials w/ Teflon-lined septa screw caps	Add 3 to 4 drops of 1:1 HCl; cool to 4°C	14 days 7 days, if not preserved
Soil/Sediments Samples	VOC vials w/ Teflon-lined septa screw caps. 40-mL vials	cool to 4°C	14 days

9.0 PROCEDURE

9.1 **Sample Preparation and Purging**

9.1.1 It is recommended that samples known or suspected to have extremely high levels of volatile petroleum hydrocarbons be screened prior to analysis in order to establish the appropriate volume/mass to be used for analysis. This screening step may be analysis of a soil sample's methanol extract (diluted), the headspace method (SW-846 method 3810), the hexadecane extraction and screening method (SW-846 Method 3820) or other applicable method as determined by the analyst.

9.1.2 Water Samples

Introduce volatile compounds into the gas chromatograph using a purge-and-trap concentrator. The use of autosampling devices for sample introduction is recommended or the analyst may use the manual method outlined below.

9.1.2.1 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and

compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one 40-mL vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 20-mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

9.1.2.2 If necessary, samples should be diluted prior to injection into the purge chamber. In such cases, all steps must be performed without delay until the diluted sample is in a gas-tight syringe.

9.1.2.2.1 Dilutions may be made in volumetric flasks (10 mL to 100 mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for highly concentrated samples.

9.1.2.2.2 Calculate the approximate volume of reagent water to be added to the volumetric flask selected and add slightly less than this volume of reagent water to the flask.

9.1.2.2.3 Inject the proper aliquot of sample from the syringe prepared in Paragraph 9.1.2.1 into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with reagent water. Cap the flask, invert, and shake three times. Repeat the above procedure for additional dilutions. Alternatively the dilutions can be made directly in the glass syringe to avoid further loss of volatiles.

9.1.2.2.4 Fill a 5-mL syringe with diluted sample as in Paragraph 9.1.2.1.

9.1.2.3 Add 4.0 µL of the surrogate spiking solution through the valve bore of the syringe. Close the valves.

9.1.2.4 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

9.1.2.5 Close both valves and purge the sample for 11 min. Recommended purge and trap operating parameters are provided in Table 3.

Table 3. Suggested Purge and Trap Operating Parameters

Purge gas	Helium
Purge gas flow rate (mL/min)	40
Purge time (min)	11.0
Purge temperature	Ambient
Desorb temperature °C	250
Backflush inert gas flow (mL/min)	15-20

9.1.2.6 At the conclusion of the purge time, attach the trap to the chromatograph (if necessary), adjust the device to the desorb mode, and begin the gas chromatographic temperature program (in Section 9.2.1) and GC data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 240°C and backflushing the trap with inert gas between 15 and 20 mL/min for 4 minutes.

9.1.2.7 While the trap is desorbing into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5 mL flushes of reagent water (or methanol followed by reagent water) to avoid carryover of pollutant compounds into subsequent analyses.

9.1.2.8 After desorbing the sample, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 260°C. After approximately 7 to 15 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. After a highly concentrated sample, a longer baking time may be necessary. When cool, the trap is ready for the next sample.

9.1.2.9 If the concentration of an analyte in a sample exceeds the calibration range, a dilution of the sample is required. If a sample analysis results in a saturated detector response for a compound, the analysis must be followed by one or more blank reagent water analyses. If the final blank analysis is not free of significant interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of significant interferences.

9.1.2.10 All dilutions should keep the detector response of the major constituents (previously saturated peaks) in the upper half of the linear range of the calibration curve.

9.1.3 Soil/Sediments

Soil and sediment samples are extracted with methanol. An aliquot of the extract is added to reagent water and introduced into the gas chromatograph using a purge and trap concentrator. Should lower values for the targeted analytes be desired, the analyst may employ direct purging of the soil sample using the method outlined in EPA methods 5030 and 5035. The use of autosampling devices for sample introduction is recommended or the analyst may use the manual method outlined below.

9.1.3.1 Weigh the sample vial to 0.1 g in a top loading balance and add 4 to 5 grams of the sample to the vial, reseal and determine the weight of the soil/sediment sample.

9.1.3.2 Quickly add 9.0 mL of methanol and 1.0 mL of the surrogate spiking solution. Cap and shake the sample vial for 2 minutes.

9.1.3.3 Allow soil/sediment to settle, or centrifuge the vial, until a layer of methanol is apparent.

9.1.3.4 Using a microliter syringe, withdraw an appropriate aliquot of the methanol extract for sparging. Sample screening data can be used to determine the volume of methanol extract to add to the 5 mL of reagent water for analysis. All dilutions must keep the response of the major constituents in the upper half of the linear range of the calibration curve.

9.1.3.5 Remove the plunger from one 5.0-mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to allow for addition of the extract (e.g., for 100 µL of extract adjust to 4.9 mL). Pull the plunger to 5.0 mL for addition of the sample extract. Add the volume of methanol extract determined from screening (100 µL maximum).

9.1.3.6 Attach the syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber. Complete operations as specified in Paragraphs 9.1.2.5 through 9.1.2.8.

9.1.4 Proceed with the analysis as described in Sections 9.2 through 9.5. Analyze all laboratory method blanks and QC samples under the same conditions as that used for samples.

9.1.5 If the responses exceed the calibration or linear range of the system, use a smaller aliquot of methanol or aqueous sample.

9.1.6 Determination of Percent Moisture

9.1.6.1 Soil and sediment results must be reported on a dry-weight basis.

9.1.6.2 Transfer 5 to 10 g of sample into a tared crucible. The amount of material used to determine the percent moisture will depend on the amount of moisture present, thus relatively dry samples require more sample addition in order to achieve a significant weight change than wet samples. Dry the sample overnight in an oven at 105°C. Remove the sample from the oven and allow it to cool in a desiccator before reweighing. Reweigh and calculate the percent moisture of the sample using the equations provided in Section 9.6.2.2.

9.2 GC Conditions

9.2.1 Oven Program: Oven temperature 45°C, hold for 1 min, then to 100°C at 3°C/min, to 160°C at 8°C/min, to 230°C at 20°C/min; hold for 7.5 min. Conditions may be altered to improve resolution of volatile petroleum hydrocarbons.

9.2.2 Gas Flows: The recommended carrier gas is helium.

9.2.2.1 Carrier gas flow: 12.5 mL/min.

9.2.2.2 Air: 350 mL/min

9.2.2.3 Hydrogen: 30 mL/min

9.2.2.4 Make up gas flow: 17.5 mL/min

9.2.3 Miscellaneous:

9.2.3.1 FID temperature: 230°C

9.2.3.2 PID temperature: 230°C

9.2.3.3 Injection port temperature: 250°C

9.2.3.4 Column head pressure: 15 psi

9.3 **Retention Time Windows**

9.3.1 Before establishing retention time windows, make sure the GC system is within optimum operating conditions. Make three injections of the VPH Component Standard throughout the course of a 72-hr period. Serial injections over less than a 72-hr period may result in retention time windows that are too tight.

9.3.2 Calculate the standard deviation of the three absolute retention times for each individual compound in the VPH Component Standard. The retention time window is defined as plus or minus three times the standard deviation of the absolute retention times for each standard. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

9.3.3 In those cases where the standard deviation for a particular standard is zero, the laboratory should substitute the standard deviation of a closely eluting structurally similar compound to develop a valid retention time window.

9.3.4 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. This data must be retained by the laboratory.

9.3.5 VPH retention time (Rt) windows are defined as beginning 0.1 minutes after the Rt of the beginning marker compound and ending 0.1 minutes after the Rt of the ending marker compound. The exception to this is the C5 through C6 aliphatic hydrocarbon range, where its Rt window is defined a beginning 0.1 minutes prior to the beginning marker compound and ending 0.1 minutes after the ending marker compound. VPH marker compounds and windows are summarized in Table 4 .

Table 4 . VPH Marker Compounds

Hydrocarbon Range	Beginning Marker Compound	Ending Marker Compound
C5-C6 Aliphatic Hydrocarbons (FID)	just before n-Pentane	just after n-Hexane
C6-C8 Aliphatic Hydrocarbons (FID)	just after n-Hexane	just after n-Octane
C8-C10 Aliphatic Hydrocarbons (FID)	just after n-Octane	just after n-Decane
C10-C12 Aliphatic Hydrocarbons (FID)	just after n-Decane	just after n-Dodecane
C8-C10 Aromatic Hydrocarbons (PID)	just after Toluene	just after 1,2,3-Trimethylbenzene
C10-C12 Aromatic Hydrocarbons (PID)	just after 1,2,3-Trimethylbenzene	just after Naphthalene
C12-C13 Aromatic Hydrocarbons (PID)	just after Naphthalene	just after 1-Methylnaphthalene

9.4 **Calibration**

9.4.1 External Standard Calibration Procedure

9.4.1.1 Prepare VPH Calibration Standards at a minimum of five concentration levels in accordance with the procedures and specifications contained in Section 7.0.

9.4.1.2 Analyze each VPH Calibration Standard following the procedures outlined in Section 9.5. Tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each targeted analyte. Alternatively, the ratio of the response to the amount injected, defined as the calibration factor (CF), may be calculated for method analytes using Equation 1. If the percent relative standard deviation (%RSD) of the calibration factor is equal to or less than 20 % over the working range for all analytes of interest, as determined using Equation 2, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve.

Equation 1: Calibration Factor

$$Calibration\ Factor\ (CF) = \frac{area\ of\ peak}{mass\ purged\ (ng)}$$

Equation 2: Relative Standard Deviation

$$\%RSD = \frac{Stand\ Dev\ of\ 5\ CFs}{Mean\ of\ 5\ CFs} \times 100$$

9.4.1.3 A collective calibration curve or factor must also be established for each hydrocarbon range of interest. Calculate the collective Calibration Factors (CF) for C5-C6, >C6-C8, >C8-C10 and >C10-C12 Aliphatic Hydrocarbons ranges using the FID chromatogram. Calculate the collective CF for the >C8-C10, >C10-C12 and C12-C13 Aromatic Hydrocarbons ranges using the PID chromatogram. Tabulate the summation of the peak areas of all components, the compounds which define the various ranges, in those fractions (e.g. C6-C8 Aliphatic Hydrocarbons, n-pentane and n-hexane or >C6 - C8, n-octane) against the total mass injected using Equation 3.

Note: Do not include the area of any surrogate standard or internal standard in calculating a Range CF.

Equation 3: Range Calibration Factor

$$Range\ CF = \frac{Total\ area\ of\ peaks}{Total\ mass\ purged\ (ng)}$$

9.4.1.4 At a minimum, the working calibration curve or calibration factor must be verified on each working day, and after every 20 samples, whichever is more frequent, by the injection of a mid-level calibration standard to verify instrument performance and linearity. If the percent difference (%D) for any targeted analyte response varies from the predicted response by more than ± 15 %, as determined using Equation 4, a new calibration curve must be prepared for that analyte. Similarly, if the percent difference of the carbon range compound response varies from the predicted response by more than ± 20 %, a new calibration curve must be prepared.

Equation 4: Percent Difference (%D)

$$\%D = \frac{\overline{CF} - CFv}{\overline{CF}} x\ 100$$

9.4.1.5 Targeted VPH Analytes and Aromatic Hydrocarbons ranges are quantitated on the PID chromatogram.

9.4.1.6 The Aliphatic Hydrocarbons ranges are quantitated on the FID chromatogram after subtraction of the collective concentrations of MTBE, and the BTEX compounds identified on the PID chromatogram from the collective concentration values of the C5 through C6 and C6 through C8 Aliphatic Hydrocarbon concentration values determined using the FID chromatogram. Similarly, the PID concentrations determined for the remaining aromatic ranges are subtracted from the FID concentrations for those ranges to yield the actual FID Aliphatic Hydrocarbon ranges values.

9.4.1.7 The concentration of specific analytes or hydrocarbon ranges in aqueous and non-aqueous samples may also be calculated from a calibration curve by use of linear regression analysis.

9.5 GC Analysis

9.5.1 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by samples interspersed with blanks and QC samples. The analytical sequence ends must end with an acceptable calibration verification. If the final calibration verification is not acceptable, then all samples analyzed after the last acceptable calibration verification must either be reanalyzed or if this is not possible, then the data associated with those samples must be qualified as an "estimate quantity".

9.5.2 Establish daily retention time windows for each analyte. Use the absolute retention time for each analyte as the midpoint of the window for that day. The daily retention time window equals the midpoint ± three times the standard deviation determined in Section 9.3.

9.5.2.1 Tentative identification of an analyte occurs when a peak from a sample falls within the daily retention time window. In cases where interferences are suspected, confirmation on a second dissimilar GC column or by GC/MS analysis may be necessary.

9.5.2.3 Validation of GC system qualitative performance must be accomplished by the analysis of standards, generally mid-level, within the analysis sequence. If any of the standards fall outside their daily retention time window, the system is out of control. In such cases, the cause of the problem must be determined and corrected.

9.5.3 If the response for Targeted VPH Analytes exceeds the linear range of the system, dilute the sample and reanalyze. It is recommended that samples be diluted so that all peaks are on scale. Overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure that all peaks are on scale over a 100-fold range, are acceptable if linearity is demonstrated prior to the analysis of samples. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

9.5.4 If detection of targeted analyte peaks are prevented by the presence of interferences, additional analytical techniques, e.g. GC/MS, are recommended.

9.5.5 Peak area and carbon range area quantification/integration must be from baseline (i.e. forced baseline projection which must include the unresolved complex mixture "hump" areas). The exception to this is the C5 through C6 Aliphatic Hydrocarbon range which, due to the use of capillary columns shorter than 100 meters and/or the purging of methanol volumes greater than 20 uL, may experience a lack of complete resolution between C5 (n-pentane) and methanol. In this event, the analyst is allowed to use tangential skim integration, or other suitable integration techniques, to integrate n-pentane, and subsequent hydrocarbons within the C5-C6 aliphatic range if it/they appear(s) on the trailing edge of the methanol solvent peak.

9.6 External Standard Calculations

The concentration of targeted analytes and hydrocarbon ranges in a sample may be determined by calculating the amount of analyte or hydrocarbon range purged, from the peak response, using the calibration curve or the calibration factor determined in Section 9.4.

9.6.1 Aqueous samples:

The general equation to determine the concentration of a specific analyte or hydrocarbon range in aqueous samples in provided in Equation 5.

Equation 5

$$Concentration\ (\mu g / L) = \frac{(A_x)(A)(D)}{(A_s)(V_s)}$$

where:

A_x = Response for the analyte or hydrocarbon range in the sample, units may be in area counts or peak height.

A = Amount of external standard purged, ng.

D = Dilution factor; if no dilution was made, D = 1, dimensionless.

A_s = Response for the external standard, units same as for A_x.

V_s = Volume of sample purged, mL.

If a Calibration Factor is used, the concentration of a specific analyte or hydrocarbon range in an aqueous sample may be calculated using equations 6 and 7, respectively.

Equation 6

$$Conc\ Analyte\ (\mu g / L) = \frac{(A_x)(D)}{(V_s)(CF)}$$

Equation 7

$$Conc\ HC\ Range\ (\mu g / L) = \frac{(A_x)(D)}{(V_s)(Range\ CF)}$$

where:

A_x = Response for the analyte or hydrocarbon range in the sample, units may be in area counts or peak height.

D = Dilution factor; if no dilution was made, D = 1, dimensionless.

V_s = Volume of sample purged, mL.

CF = Calibration Factor, area counts/ng.

Range CF = Calibration Factor for hydrocarbon range, (collective area count/collective mass), area counts/ng.

9.6.2 **Non-Aqueous Samples (Methanol Extraction):**

9.6.2.1 The general equation to determine the concentration of a specific analyte or hydrocarbon range in a soil or sediment sample is provided in Equation 8.

Equation 8

$$Concentration\ (\mu g / kg) = \frac{(A_x)(A)(V_t)(D)}{(A_s)(V_i)(W_d)}$$

where:

A_x = Response for the analyte or hydrocarbon range in the sample, units may be in area counts or peak height.

A = Amount of external standard purged, ng.

V_t = Volume of total extract, µL (Note: this value must include the 1.0 mL surrogate spiking solution added to soil samples)

D = Dilution factor; if no dilution was made, D = 1, dimensionless.

A_s = Response for the external standard, units same as for A_x.

V_i = Volume of methanol extract added to reagent water for purge and trap analysis, µL.

W_d = Dry weight of sample purged, g (see equations 11 through 13)

If a Calibration Factor is used, the concentration of a specific analyte or hydrocarbon range in a soil or sediment sample may be calculated using Equations 9 and 10, respectively.

Equation 9

$$Conc\ Analyte\ (\mu g / kg) = \frac{(A_x)(V_t)(D)}{(V_i)(W_d)(CF)}$$

Equation 10

$$Conc\ HC\ Range\ (\mu g / kg) = \frac{(A_x)(V_t)(D)}{(V_i)(W_d)(Range\ CF)}$$

where:

V_t = Volume of total extract, µL.

Vi = Volume of extract added for purging, µL

W_d = Dry Weight of sample purged, g (see Equations 11 through 13)

A_x, CF, Range CF and D have the same definition as for aqueous samples.

9.6.2.2 Calculation of Dry Weight of Sample

In order to calculate the dry weight of sample purged (W_d), it is necessary to determine the moisture content of the soil/sediment sample, using the procedure outlined in Section 9.1.6. Using the data obtained from Section 9.1.6, W_d is calculated using Equations 11 through 13.

Equation 11

$$\%\ Moisture = \frac{g\ sample - g\ dry\ sample}{g\ sample}\ X\ 100$$

Equation 12

$$\%\ Dry\ Solids = (1) - (\%\ Moisture)$$

Equation 13

$$W_d\ (g) = (\%\ Dry\ Solids)(g\ of\ extracted\ sample)$$

9.6.3 The concentration of specific analytes or hydrocarbon ranges in aqueous and non-aqueous samples may also be calculated from the calibration curve by linear regression, provided that the correlation coefficient (r) is at least 0.99 and the % D for any targeted analyte must not vary from the predicted response by more than +/- 15%, nor any hydrocarbon range standard from its predicted response by more than +/- 20%.

9.6.4 Peak areas measured from blanks may not be subtracted from sample peak areas.

9.6.5 All integration of collective hydrocarbon ranges must be to baseline.

9.6.6 Required Adjustment of Range Concentration Data: In order to minimize the "double counting" of the same hydrocarbon compounds on both the FID and PID chromatograms, the collective concentrations of MTBE, benzene, toluene, ethylbenzene, and m, p, o-xylene identified on the PID chromatogram must be subtracted from the collective Aliphatic Hydrocarbon concentration values, for the ranges in which they elute, determined using the FID chromatogram. Similarly, the collective concentrations of the remaining aromatic ranges values determined on the PID chromatogram must be subtracted from the corresponding aliphatic ranges values determined on the FID chromatogram.

10.0 QUALITY CONTROL

10.1 **General Requirements and Recommendations**

10.1.1 Each laboratory that uses this method should operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document the quality of data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance standards for the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

10.1.2 A acidified reagent water blank should continually accompany each soil sample or water sample batch, respectively, over the course of sampling, storage, and analysis.

10.1.3 A Laboratory Method Blank should be run after samples suspected of being highly contaminated to determine if sample carryover has occurred.

10.1.4 At a minimum, for each analytical batch (up to 20 samples), a Laboratory Method Blank, Laboratory Fortified Blank, Laboratory Fortified Matrix Spike, and sample

duplicate must be analyzed. For analytical batches with more than 10 samples, the analysis of an additional mid-range calibration check standard is recommended. The blank and spiked samples must be carried through all stages of the sample preparation and measurement process.

10.1.5 The recommended sequence of analysis is as follows:

(1) Calibration Standards (initial) or mid-range Calibration Check Standard (daily check on initial calibration)
(2) Laboratory Method Blank
(3) Samples
(4) QC Samples
(5) Mid-range Calibration Check Standard (also recommended after each 10 samples)

10.1.6 It is recommended that a system of control charts be developed to plot surrogate standard recoveries as a function of time. When surrogate recovery from a sample, blank, or QC sample is less than 60% or more than 140%, check calculations to locate possible errors, the fortifying solution for degradation, and changes in instrument performance. If the cause cannot be determined, the analyst may reanalyze the sample or report the surrogate values as outside acceptance limits.

10.2 **Minimum Instrument QC**

10.2.1 While it is recommended that the n-pentane (C5) peak be adequately resolved from the methanol solvent on the FID chromatogram, the analyst is allowed to follow the guidance as outlined in 9.5.5. Coelution of the m- and p- xylene isomers is permissible. Any surrogates and/or internal standards used must be adequately resolved from individual compounds in the VPH Component Standard.

10.2.2 Retention time windows must be established for each analyte of interest each time a new GC column is installed, and must be verified and/or adjusted on a daily basis. (See Section 9.3)

10.2.3 Calibration curves must be developed based upon the analysis of calibration standards prepared at a minimum of 5 concentration levels. The linearity of calibration or response factors may be assumed if the percent relative standard deviation (%RSD) over the working range of the curve is less than or equal to 20%. Alternatively, if linear regression analysis is used for quantitation, the correlation coefficient (r) must be at least 0.99 and no targeted analyte or carbon range standard may vary from the true value by more than +/- 15% and +/- 20% respectively. (See Section 9.4.)

10.3 **Initial and Periodic Method QC Demonstrations**

The following must be conducted as an initial demonstration of laboratory capability, prior to the analysis of any samples. Subsequent to this initial demonstration, additional evaluations of this nature should be conducted on a periodic basis, in response to changes in instrumentation or operations, and/or in response to confirmed or suspected systems, method, or operational problems.

10.3.1 Accuracy and Precision

To demonstrate initial laboratory capability, analyze a minimum of four replicate reagent water and/or clean sand blanks spiked with each analyte of interest at approximately 20 to 60 µg/L and/or 20 to 60 mg/kg, respectively.

10.3.1.1 Add an appropriate aliquot of the stock or primary dilution standard solution(s) to each of the four replicate reagent water or clean sand blanks. Purge and analyze each replicate according to the procedures described in Section 9.0.

10.3.1.2 Calculate the measured concentrations of each analyte in all replicates, the mean accuracy (as a percentage of true value) for each analyte, and the precision (as %RSD) of the measurements for each analyte.

10.3.1.3 For each analyte, the mean accuracy, expressed as a percentage of the true value, must be between 80% and 120%. For each analyte, the %RSD must be less than or equal to 20%.

10.3.1. If desired, the Accuracy and Precision evaluation may be combined with the MDL evaluation specified in Paragraph 10.3.2.

10.3.2 Method Detection Limits (Optional)

Analyze a minimum of seven replicate reagent water and/or clean sand blanks which have been fortified with all analytes of interest at approximately 0.5 to 5 µg/L and/or 1 to 5 mg/kg, respectively. Calculate the Method Detection Limit (MDL) of each analyte using the procedure described in Section 12.0.

10.3.2.1 Water MDLs are determined by analyzing 7 to 10 replicates of reagent water samples in 100-mL flasks spiked with the VPH Component standard and with 40 µg/L of the surrogate compound 2,5-dibromotoluene.

10.3.2.2 Soil/sediment MDLs are determined by analyzing 7-10 replicates of 5 -g of VPH-free sand blanks spiked with the VPH Component standard and with 2 mg/kg of the surrogate 2,5-dibromotoluene.

10.3.3 Petroleum Reference Standard

As an optional demonstration of the validity and relevance of VPH calibration, analyze a reagent water and/or clean sand blank spiked with a known concentration of a neat gasoline product.

10.3.3.1 Fortify a reagent water and/or clean sand blank with 5 µL and/or 0.5 mL of the Petroleum Standard Spiking Solution, respectively. Purge and analyze in accordance with the procedures outlined in Section 9.0.

10.3.3.2 Calculate the total concentration of all petroleum hydrocarbons within the Aliphatic Hydrocarbon ranges using the FID chromatogram. Add these values together. Do not subtract the concentration of Targeted VPH analytes.

10.3.3.3 The concentration calculated in Paragraph 10.3.3.2 is expected to be within 30% +/- of the known concentration of Petroleum Standard in the reagent water or sand blank.

10.4 **Ongoing Method QC Demonstrations**

10.4.1 Each sample, blank, and matrix spike must be spiked with the surrogate spiking solution. Required surrogate recovery is 60% to 140%.

10.4.2 At a minimum, with every batch of 20 samples or less the laboratory must analyze the following:

10.4.2.1 **Calibration Check Standard** - A mid-range calibration standard, prepared from the same stock standard solution used to develop the calibration curve, must be analyzed prior to sample analysis to verify the calibration state of the instrument. For large analytical batches that contain more than 10 samples, the analysis of an additional mid-range calibration check standard is recommended after the analysis of the tenth sample. If the percent difference (% D) of any analyte within the calibration check standard varies from the predicted response by more than 20 %, a new calibration curve must be prepared for that analyte.

10.4.2.2 **Laboratory Method Blank** - A water or soil laboratory method blank is prepared by fortifying a 5 mL reagent water blank with 4 µL of the surrogate spiking solution, or by fortifying a 5 g sample of clean sand with 1.0 mL of the surrogate spiking solution. Peaks within the retention time windows of any hydrocarbon ranges of interest may not be present at or above the lowest calculated PQL for any sample within its batch. When determining the PQL for soil method blanks, incorporate the lowest percent solids value found for any sample within its batch in the calculation.

10.4.2.3 **Laboratory Fortified Blank (LFB)** - A water or soil component spike is prepared by fortifying a 5 mL reagent water blank with 4 µL of the matrix spiking solution, or by fortifying a 5 g sample of clean sand with 1.0 mL of the matrix spiking solution. The spike recovery must be between 70% and 130% and if these values can not be obtained the analyst must identify and correct the problem before analyses can continue.

10.4.2.4 **Sample duplicates** - Sample duplicates may be laboratory or field duplicates. The RPD of duplicate samples should not exceed +/- 25%. The lack of sample homogeneity may contribute to RPD's for duplicates which exceed this value. Should the values exceed 25%, the analyst must report that occurrence.

10.4.2.5 **Laboratory Fortified Matrix (LFM) Spike** - The water or soil LFM spike is prepared by fortifying an actual 5 mL water sample with 4 µL of the matrix spiking solution, or by fortifying an actual 5 g soil/sediment sample with 1.0 mL of the matrix spiking solution. The purpose

of the LFM is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations. The corrected concentrations of each analyte within the matrix spiking solution must be within 70 - 130% of the true value. Should the values determined exceed this range, the analyst must report that occurrence.

10.4.3 If any of the performance standards specified in Section 10.4 are not met, the problem must be corrected before further samples are analyzed. Exceptions to this are duplicate samples RPD's and high recoveries for LFM spikes which, due to sample non-homogeneity may exceed the allowable limits. Any samples run between the last calibration check standard that meets the criteria and one that does not must be rerun. If this is not possible, that data must be reported as an "estimated concentration".

11.0 DATA PRODUCTION AND REPORTING

11.1 **Sample Analysis**

11.11 PID Chromatogram

11.1.1.1 Determine the peak area count for the Targeted VPH Analytes.

11.1.1.2 Determine the peak area count for the surrogate 2,5-dibromotoluene.

11.1.1.3 Separately determine the total area count for all peaks eluting 0.1 minutes after the Rt's for toluene through 0.1 minutes after the Rt for 1,2,3-trimethylbenzene, for all peaks eluting 0.1 minutes after the retention time (Rt) for 1,2,3-trimethylbenzene and 0.1 minutes after the retention time for naphthalene and for all peaks eluting 0.1 minutes after the Rt for naphthalene through 0.1 minutes after the Rt of 1-methylnaphthalene.

11.1.1.4 Using the equations contained in Section 9.6 or linear regression analysis, calculate the concentrations of the Targeted VPH Analytes, the surrogate standard 2,5-dibromotoluene, and >C8 through C10, >C10 through C12 and >C12 through C13 Aromatic Hydrocarbons.

11.2.1 FID Chromatogram

11.2.1.1 Separately determine the total area count for all peaks eluting 0.1 minutes before the retention time (Rt) for n-pentane to 0.1 minutes after the Rt for n-hexane and for all peaks eluting 0.1 minutes after the Rt for n-hexane to 0.1 minutes after the Rt for n-octane. It is not necessary to identify or quantitate individual aliphatic compounds within these ranges.

11.2.1.2 Determine the total area count for all peaks eluting 0.1 minutes after the Rt for n-octane to 0.1 minutes after the Rt for n-decane and 0.1 minutes after n-decane to 0.1 minutes after n-dodecane. It is not necessary to identify or quantitate individual aliphatic compounds within this range.

11.2.1.3 Determine the peak area count for the surrogate standard 2,5-dibromotoluene.

11.2.1.4 Using the equations contained in Section 9.6 or linear regression analysis, calculate the concentrations of C5 through C6 Aliphatic Hydrocarbons, >C6 through C8 Aliphatic Hydrocarbons, >C8 through C10 Aliphatic Hydrocarbons, >C10 through C12 Aliphatic Hydrocarbons and the surrogate standard 2,5-dibromotoluene.

11.2.1.5 To avoid "double counting" of the same analytes, adjust the concentrations of Aliphatic Hydrocarbons calculated in Paragraph 11.2.1.4 by subtracting the collective concentrations of methyl tert butylether, benzene, toluene, >C8 through C10 and >C10 through C12 Aromatic Hydrocarbons, as determined from the PID chromatogram in Section 11.11, from the Aliphatic Hydrocarbon range values effected.

11.3 **Data Reporting Format**

11.3.1 The following information and data must be reported:

11.3.1.1 The sample matrix (aqueous, soil or sediment);

11.3.1.2 The date(s) the sample was collected, received by the laboratory, and analyzed;

11.3.1.3 A description of the sample(s) received by the laboratory, relative to the physical condition of the containers, the temperature of the samples, and use of appropriate preservatives;

11.3.1.4 Moisture content (for soil/sediment samples);

11.3.1.5 The calculated concentrations of C5 through C6, C6 through C8, C8 through C10 and C10 through C12 Aliphatic Hydrocarbons ranges and C8 through C10, C10 through C12 and C12 through C13 Aromatic Hydrocarbons ranges

11.3.1.6 Surrogate recovery (expressed as percent recovery);

11.3.1.7 The calculated concentrations of Targeted VPH Analytes determined

11.3.1.8 The concentration units for aqueous samples are expressed as ug/L or mg/L and for soil or sediment samples the units are expressed as ug/Kg or mg/Kg on a dry-weight basis.

12.0 METHOD PERFORMANCE

12.1 **Method Detection Limits (Optional)**

12.1.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

12.1.2 The MDL is determined according to the following equation:

Equation 14

$$MDL = (t) \times (SD)$$

where:

t = student t value at the 99% confidence level

SD = standard deviation of the replicate analysis

Student t values are as follows:

Number of replicates	t value
7	3.14
8	3.00
9	2.90
10	2.82

12.1.3 For the purposes of this method, the designated MDL value for a hydrocarbon range of interest shall be the highest value calculated for the individual analytes within that hydrocarbon range.

12.2 **Single Laboratory Accuracy, Precision, and MDL Data**

Single laboratory accuracy, precision and MDL data for method analytes are provided in Tables 1-1 through 1-4 in Appendix 1. Additional investigation will be conducted to further evaluate the low recoveries for naphthalene.

13.0 REFERENCES

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METHOD FOR THE DETERMINATION

OF

EXTRACTABLE PETROLEUM HYDROCARBONS (EPH) FRACTIONS

Washington State Department of Ecology

June 1997

METHOD FOR THE DETERMINATION OF EXTRACTABLE PETROLEUM HYDROCARBONS (EPH)

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DISCLAIMER

Mention of trade names or commercial products does not constitute endorsement by the Washington State Department of Ecology. Equipment and materials cited in this method may be replaced by similar products, as long as adequate data exists or has been produced documenting equivalent or superior performance.

METHOD FOR THE DETERMINATION OF EXTRACTABLE PETROLEUM HYDROCARBONS

1.0 SCOPE AND APPLICATION

1.1 This method is designed to measure the collective concentrations of extractable aliphatic and aromatic petroleum hydrocarbons in water and soil. **The carbon ranges used through out this document are given in equivalent carbon numbers (EC) which are related to the boiling point of a chemical normalized to the boiling point of the n-alkanes and its retention time in a boiling point gas chromatographic column**. Extractable aliphatic hydrocarbons are collectively quantitated within five ranges: C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34. Extractable aromatic hydrocarbons are collectively quantitated within five ranges: C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 150 °C and 500 °C.

1.2 Petroleum products suitable for evaluation by this method include, but are not limited to, kerosene and jet fuels, diesel and fuel oils and hydraulic, insulating and lubricating oils. This method, in and of itself, is not suitable for the evaluation of gasoline, mineral spirits, petroleum naphthas, and other petroleum products which contain a significant percentage of hydrocarbons lighter than C10. When samples are known or suspected to contain petroleum hydrocarbons of these or similar types, the Volatile Petroleum Hydrocarbon (VPH) method must also be employed to fully evaluate the hydrocarbons present.

1.3 For reporting purposes, the practical quantitation limits (PQL), given the sample volume/mass, final extract volume and assuming 100 percent solids for soil/sediments are: 50.0 ug/L for aliphatic and aromatic carbon ranges in water and 5.0 mg/Kg for these components in soil. If lower quantitation limits are desired, the analyst is allowed to extract larger volumes/masses and/or concentrate the extracts to smaller volumes prior to analysis. The procedure for Method Detection Limits

(MDL) determination in this method and the Single Laboratory Precision, Accuracy and MDL data (generated by State of Massachusetts) is added for informational purposes only.

1.4 This method is based on a solvent extraction, silica gel fractionation process and gas chromatography (GC) analysis using a flame ionization detector (FID). This procedure should be used by, or under the supervision of, analysts experienced in extractable organics analysis. Analysts using this method should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.

1.5 Like all GC procedures, this method is subject to a "false positive" bias, in that non-hydrocarbon compounds eluting or co-eluting within a specified retention time window may be falsely identified and/or quantitated with the respective carbon ranges. While the cleanup procedure specified in this method to segregate aliphatic and aromatic fractions will serve to mitigate this concern, confirmatory analyses by gas chromatography/mass spectrometry (GC/MS) analysis, EPA Method 8270, or other suitable techniques are recommended in cases where significant concentrations of non-hydrocarbon compounds are known or suspected. Non-petroleum compounds identified and quantitated by GC/MS may be subtracted from the carbon ranges affected as long as the quantity and identities of the compounds are reported along with the carbon range data.

2.0 SUMMARY OF METHOD

2.1 A sample submitted for EPH analysis is extracted with methylene chloride, dried over sodium sulfate, solvent exchanged into hexane, and concentrated. Sample cleanup and separation into aliphatic and aromatic fractions is conducted using a modification of EPA method 3630 (silica gel cleanup). The use of commercially available silica gel cartridges (Sep-Pak cartridges, Waters, Milford, MA) may be substituted for the silica gel column outlined in method 3630 if they can be shown to achieve comparable results. The two extracts produced are then concentrated to final volumes of 10 mL each (i.e., an aliphatic extract and an aromatic extract) and are then separately analyzed by a gas chromatograph equipped with a capillary column and a flame ionization detector. The resultant chromatogram of aliphatic compounds is collectively integrated within the C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 aliphatic hydrocarbon ranges. The resultant chromatogram of aromatic compounds is collectively integrated within the C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 ranges.

2.2 Average calibration factors or response factors determined using an aliphatic hydrocarbon standard mixture are used to calculate the collective concentrations of the different aliphatic hydrocarbons ranges. An average calibration factor or response factor determined using the aromatic hydrocarbon standard mixture is used to calculate a collective concentrations of the aromatic hydrocarbon ranges.

2.3 This method is suitable for the analysis of waters, soils, and sediments.

2.4 This method is based on, and constitutes a significant modification of, the "Method for the Determination of Extractable Petroleum Hydrocarbons (EPH)" Public Comment Draft 1.0 developed by the Massachusetts Department of Environmental Protection. They in turn based their method on (1) USEPA Methods 8000, 8100, and 3630, SW-846, "Test Methods for Evaluating Solid Waste", 3rd Edition, 1986; (2) Draft "Method for Determination of Diesel Range Organics", EPA UST Workgroup, November, 1990; and (3) "Method for Determining Diesel Range Organics", Wisconsin Department of Natural Resources, PUBL-SW-141, 1992.

Table 1. Aromatic Hydrocarbon Standard

Equivalent Carbon Number	Compound
7. 6	Toluene
10.1	1,2,3-Trimethylbenzene
11.7	Naphthalene
15.5	Acenaphthene
Surrogate	Ortho-Terphenyl
20.8	Pyrene
34.01	Benzo(g,h,i)Perylene

Table 2. Aliphatic Hydrocarbon Standard

Carbon Number	Compound
8	Octane
10	Decane
12	Dodecane
16	Hexadecane
Surrogate	1-Chloro-octadecane
21	Henicosane
34	Tetratriacontane

3.0 DEFINITIONS

3.1 **Extractable Petroleum Hydrocarbons (EPH)** are defined as all hydrocarbon compounds eluting from toluene through benzo(g,h,i)perylene. EPH is comprised of C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 Aliphatic Hydrocarbons and C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 Aromatic Hydrocarbons. EPH concentration data are reported as the aggregate concentration of the aliphatic and aromatic hydrocarbon ranges.

3.2 **Equivalent Total Petroleum Hydrocarbons (E-TPH)** For samples contaminated with petroleum products in the C10 to C34 range, the E-TPH value is equivalent to the EPH value. For samples contaminated with a petroleum product(s) containing significant concentrations of hydrocarbons lighter and heavier than C10, (e.g., contaminated with both gasoline and diesel fuel), the E-TPH value is a summation of the EPH value and the Volatile Petroleum Hydrocarbon (VPH) value. In order to avoid double counting of analytes due to the overlap in the carbon ranges existing between the two methods, the analyst will report the highest of the two values determined for the overlapping ranges. In those cases where both the VPH and EPH methods are employed on samples, the analyst may select to quantitate the >C10 through C12 Aliphatic and the >C10 through C12 Aromatic Hydrocarbon ranges by the EPH method only. Similarly, the analyst may select to quantitate the C8 through C10 Aromatic and C8 through C10 Aliphatic Hydrocarbon ranges by the VPH method only.

3.3 **C8 through C10 Aromatic Hydrocarbons** are defined as all of the aromatic hydrocarbon compounds eluting from (and including) toluene through 1,2,3-trimethylbenzene.

3.4 **>C10 through C12 Aromatic Hydrocarbons** are defined as all aromatic hydrocarbon compounds eluting after 1,2,3-trimethylbenzene through naphthalene.

3.5 **>C12 through C16 Aromatic Hydrocarbons** are defined as all aromatic hydrocarbon compounds eluting after naphthalene through acenaphthene.

3.6 >**C16 through C21 Aromatic Hydrocarbons** are defined as all aromatic hydrocarbons compounds eluting after acenaphthene through pyrene.

3.7 >**C21 through C34 Aromatic Hydrocarbons** are defined as all aromatic hydrocarbons compounds eluting after pyrene through benzo(g,h,i,)perylene.

3.8 **C8 through C10 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds eluting from (and including) n-octane (n-C8) through n-decane (n-C10).

3.9 **>C10 through C12 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds eluting after n-decane through n-dodecane (n-C12).

3.10 **>C12 through C16 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds eluting after n-dodecane through n-hexadecane (nC16)

3.11 >**C16 through C21 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbons eluting after n-hexadecane through n-henicosane (nC21).

3.12 **>C21 through C34 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbons eluting after n-henicosane through tetratriacontane (nC34).

3.13 **Aromatic Hydrocarbon Standard** is defined as a 6 component mixture (plus surrogate) of the aromatic hydrocarbons listed in Table 1. The compounds comprising the Aromatic Hydrocarbon Standard are used to (a) define and establish the windows for the Aromatic Hydrocarbon ranges, and (b) determine chromatographic response factors that can in turn be used to calculate the collective concentration of aromatic hydrocarbons in environmental samples within those hydrocarbon ranges.

3.14 **Aliphatic Hydrocarbon Standard** is defined as a 6 component mixture (plus surrogate) of the normal alkanes listed in Table 2. The compounds comprising the Aliphatic Hydrocarbon Standard are used to (a) define and establish windows for the aliphatic hydrocarbons ranges, and (b) determine chromatographic response factors that can in turn be used to calculate the collective concentration of aliphatic hydrocarbons in environmental samples within those hydrocarbon ranges.

3.15 **Analytical Batch** is defined as a group of samples with similar matrices which are processed as a unit. For Quality Control purposes, if the number of samples in such a group is greater than 20, then each group of 20 samples or less are defined as separate analytical batches.

3.16 **Laboratory Duplicates** are defined as split samples taken from the same sampling container and analyzed separately with identical procedures. The analysis of laboratory duplicates give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.17 **Field Duplicates** are defined as two separate samples collected at the same time and location under identical circumstances and managed the same throughout field and laboratory procedures. Analyses of field duplicates give a measure of the precision associated with sample collection, preservation and storage, as well as laboratory procedures.

3.18 **E-TPH Duplicates** are defined as two separate samples collected at the same time and location, for analysis by both EPH and VPH methods. E-TPH duplicates are taken at locations where significant concentrations of petroleum hydrocarbons lighter and heavier than C10 are likely to be present (e.g., locations contaminated by releases of both gasoline and diesel fuel). The resultant EPH and VPH concentrations are then summed to determine the Equivalent TPH (E-TPH) concentration.

3.19 **Calibration Standards** are defined as a series of standard solutions prepared from dilutions of a stock standard solution, containing known concentrations of each analyte and surrogate compounds of interest.

3.20 **Calibration Check Standard** is defined as a calibration standard used to periodically check the calibration state of an instrument. The calibration check standard is prepared from the same stock standard solution as calibration standards, and is generally one of the mid-level range calibration standard dilutions.

3.21 **Matrix Spiking Solution** is defined as a solution which is generally prepared independently from the calibration standards and which contain known concentrations of method analytes.

3.22 **Laboratory Method Blank** is defined as, depending on the matrix of the samples, either reagent water or clean sand spiked with a surrogate standard. The laboratory method blank is treated identically as with samples, exposed to all glassware, solvents, reagents, and equipment. A laboratory method blank is analyzed with every batch of samples, to determine if method analytes or other interferences are present in the laboratory environment, reagents, or equipment.

3.23 **Laboratory Fortified Blank (LFB)** is defined as, depending on the matrix of the samples, either reagent water or clean sand blank fortified with a matrix spiking solution. The LFB is treated and analyzed identically as with samples and blanks and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements at the required practical quantitation limits.

3.24 **Laboratory Fortified Matrix (LFM) Sample** is defined as an environmental sample which has been spiked with a matrix spiking solution containing known concentrations of method analytes. The LFM sample is treated and analyzed exactly as with samples and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentration of analytes in the sample matrix must be determined through the separate analyses of a laboratory or field duplicate, and the measured values in the LFM sample corrected for background concentrations.

3.25 All other terms are as defined in SW-846, "Test Methods for Evaluating Solid Waste", USEPA, September, 1986, and as amended.

4.0 INTERFERENCES

4.1 Method interferences are reduced by washing all glassware with hot soapy water and then rinsing with warm tap water, acetone, and methylene chloride.

4.2 High purity reagents must be used to minimize interference problems.

4.3 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. Whenever an unusually concentrated sample is analyzed, it should be followed by the analysis of a solvent blank to check for cross-contamination.

4.4 Matrix interferences may be caused by contaminants that are coextracted along with the analytes of interest from the sample. The type and extent of matrix interference will vary considerably from one source to another depending upon the nature and diversity of the site being sampled and may include certain solvents, halogenated hydrocarbons and phthalate esters. A silica gel cleanup procedure is used to overcome many of these interferences however, some samples may require additional cleanup procedures/approaches or analytical techniques, e.g. gel permeation chromatography and/or GC/MS, which are beyond the scope of this method.

5.0 HEALTH AND SAFETY ISSUES

The toxicity and carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDS) should also be made available to all personnel involved in the chemical analysis.

6.0 APPARATUS AND MATERIALS

6.1 The following glassware is used for this method:

6.1.1 1-L amber glass bottles

6.1.2 4 oz. (120 mL) amber glass wide-mouth jars

6.1.3 Vials:

6.1.3.1 autosampler: 2-mL glass vials with Teflon-lined rubber crimp caps

6.1.3.2 10-mL vials with Teflon-lined caps

6.1.4 Glass funnels

6.1.5 2-L Separatory funnels with Teflon stopcock

6.1.6 Kuderna-Danish apparatus including 10-mL concentrator tube, 500-mL Evaporative flask, & 3-ball Snyder column

6.1.7 Chromatographic column: 250 mm long x 10 mm I.D. with teflon stopcock

6.1.8 Disposable pipets: Pasteur

6.1.9 25-mL graduated cylinder

6.1.10 1-Liter graduated cylinder

6.1.11 100-mL beakers

6.1.12 25-mL volumetric flasks

6.2 Analytical balance: An analytical balance capable of accurately weighing 0.0001 g must be used for weighing standards. A top-loading balance capable of weighing to the nearest 0.1 g must be used for weighing soil samples.

6.3 A nitrogen blowdown apparatus for use in concentrating extracts.

6.4 **Gas Chromatography**

6.4.1 Gas Chromatograph: An analytical system complete with temperature programmable gas chromatograph for use with capillary columns is required. The data station must be capable of storing and reintegrating chromatographic data and must be capable of determining peak areas using a forced baseline projection.

6.4.2 Recommended Column: 30-m long x 0.32-mm I.D., 0.25-µm film DB-5 column (J&W Scientific) or equivalent. This column will allow for the adequate resolution of alkanes from n-C8 to n-C34.

6.4.3 Detector: A Flame Ionization Detector (FID).

6.4.4 Autosampler: An autosampler capable of making 1 to 2 µL injections is recommended.

6.5 Water bath: heated with a concentric ring covers, capable of temperature control (± 2°C). The bath should be used in a hood.

6.6 Microsyringes: 10-µL, 100-µL, 250-µL, 500-µL, 1000-µL

6.7 Boiling Chips: glass or teflon, precleaned prior to use

6.8 Soxhlet or Sonication extraction apparatus

6.9 Drying oven

7.0 REAGENTS AND STANDARDS

7.1 **Reagents**

7.1.1 Reagent Water: organic free water

7.1.2 Solvents: hexane, methylene chloride, and acetone; pesticide grade or better. Store away from other solvents.

7.1.3 Sodium sulfate: (ACS) granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray.

7.1.4 Ottawa and/or masonry sand: free of extractable petroleum hydrocarbons.

7.1.5 Silica gel: 100/200 mesh (Davison Chemical grade 923 or equivalent). Heat to 150-160 ^{o}C for several hours before use. Silica Gel Sep-Pak Cartridges: 5 g/20-mL (Waters, Milford, MA) , if it is demonstated to give equivalent separations.

7.2 **Stock Standard Solutions**

Prepare stock standard solutions at approximately 1000 ng/µL, or purchase as certified solutions.

7.2.1 Aromatic Hydrocarbon Standard: The Aromatic Hydrocarbon Standard consists of the 6 aromatic compounds listed in Table 1 and a surrogate compound. Prepare stock standard solutions by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in methylene chloride and dilute to volume in a 10-mL volumetric flask. The use of commercially prepared stock standards solutions is an acceptable alternative to the use of neat material. The analyst is allowed to prepare a separate surrogate solution.

7.2.2 Aliphatic Hydrocarbon Standard: The Aliphatic Hydrocarbon Standard consists of the 6 normal alkanes listed in Table 2 and a surrogate compound. Prepare stock standard solutions by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in hexane and dilute to volume in a 10-mL volumetric flask. The use of commercially prepared stock standard solutions is an acceptable alternative to the use of neat material. The analyst is allowed to prepare a separate surrogate solution.

7.2.3 Petroleum Reference Standard: The use of a Petroleum Reference Standard is recommended for quality control purposes. The Petroleum Reference Standard consists of an API or commercial diesel, fuel oil, kerosene, and/or lubricating oil. Prepare stock standard solutions by accurately weighing approximately 0.0100 g of neat product. Dissolve neat product in hexane and dilute to volume in a 10-mL volumetric flask.

7.3 Surrogate Standards

7.3.1 The recommended surrogate standards are chloro-octadecane (COD, available from Restek Corporation, Bellefonte, PA) and ortho-terphenyl (OTP, available from EM Sciences, Gibbstown, NJ). Additional surrogates or surrogates other than those listed above may be used at the discretion of the analyst as long as their performance in the method is demonstrated as acceptable. Preparation and use of those surrogates will be in the same manner as the listed surrogate.

7.3.2 The surrogate standard COD is prepared by accurately weighing approximately 0.0100 g of pure material in a 10-mL volumetric flask. Dissolve the material in hexane. This solution is added to the Aliphatic Hydrocarbon standard.

7.3.3 The surrogate standard OTP is prepared by accurately weighing approximately 0.0100 g of pure material in a 10-mL volumetric flask. Dissolve the material in methylene chloride. This solution is added to the Aromatic Hydrocarbon standard.

7.3.4 Surrogate Spiking Solution: The recommended surrogate spiking solution is comprised of a mixture of the COD and OTP surrogate standards. Prepare a surrogate spiking solution which contains the surrogate standards at a concentration of 20 ng/µL in acetone. Each sample, blank, and matrix spike is fortified with 1.0 mL of the surrogate spiking solution.

7.4 Internal Standard

If an internal standard method of calibration is to be used, the recommended internal standard is 5-alpha-androstane (EM Sciences, Gibbstown, NJ).

7.5 Matrix Spike Standard

7.5.1 Four or more analytes from each analyte group (i.e., aromatic and aliphatic hydrocarbons) are selected for use in a matrix spiking solution, which is prepared independently from the calibration standards.

7.5.2 The recommended spiking solution, consisting of C10, C12, C16 and C21 normal alkanes and naphthalene, acenaphthene, anthracene, pyrene, benzo(a)pyrene and benzo(g,h,i)perylene, is prepared in acetone at concentrations of 25 ng/µL.

7.5.3 The samples selected as the matrix spike are fortified with 1.0 mL of the matrix spiking solution.

7.6 Fractionation Check Solution

7.6.1 The Fractionation Check Solution is used to monitor the fractionation efficiency of different batches (lot numbers) of silica gel used to prepare the silica gel hydrocarbon fractionation columns (and Sep-Pak cartridges if used) as well as check for sample preparation errors (e.g., insufficient/excessive pentane use).

7.6.2 Prepare a Fractionation Check Solution in hexane containing 25 ng/µL each of the n-C8, n-C10, n-C12, n-C16, n-C21, and n-C34 alkanes) and 25 ng/µL each of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene. The final solution will contain 6 alkanes and 16 PAHs at concentrations of 25 ng/µL each. The use of commercially available check solutions containing these compounds is acceptable.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 Aqueous samples are collected in 1 liter amber glass bottles with teflon-lined screw caps.

8.2 Soil and sediment samples are collected in 4 oz. (120 mL) amber wide-mouth glass jars with teflon-lined screw caps.

8.3 Aqueous samples must be preserved at the time of sampling by the addition of an acid to reduce the pH of the sample to less than 2.0. This is accomplished by the addition of approximately 5 mL of 1:1 HCl to a 1 liter sample. Following collection and the addition of acid, the sample must be cooled to 4°C.

8.4 Soil and sediment samples must be cooled to 4°C immediately after collection.

8.5 A chain of custody form must accompany all aqueous, soil and sediment samples, documenting the time and date of sampling and any preservative additions.

8.6 Aqueous, soil and/or sediment samples must be extracted within 14 days of collection. If for whatever reason aqueous samples were not preserved at the time of collection they must be extracted within 7 days of collection. Both aqueous and soil/sediment extracts must be analyzed within 40 days of extraction.

8.7 A summary of sample collection, preservation, and holding times is provided in Table 3.

Table 3. Holding Times and Preservatives for EPH Samples

Matrix	Container	Preservation	Holding Time
Aqueous Samples	1-Liter amber glass bottle with Teflon-lined screw cap	Add 5 mL of 1:1 HCl; cool to 4°C	Samples must be extracted within 14 days and extracts analyzed within 40 days
Soil/Sediments Samples	4-oz. (120 mL) wide mouth amber glass jar with Teflon-lined screw cap	Cool to 4°C	Samples must be extracted within 14 days and extracts analyzed within 40 days

9.0 PROCEDURE

9.1 **Sample Preparation**

9.1.1 Water Extraction

9.1.1.1 Mark the water meniscus on the side of the 1 liter of sample bottle (for later volume determination) and transfer the water to a 2-liter separatory funnel. For blanks and quality control samples, pour 1 liter of reagent water into the separatory funnel. Add 1.0 mL of the surrogate spiking solution to all samples, blanks and matrix spikes. For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking solution.

9.1.1.2 Check the pH of the sample with wide-range pH paper. Note the pH in the laboratory notebook. The pH of the sample need not be adjusted.

9.1.1.3 Add 60 mL methylene chloride to the sample bottle to rinse the inner walls of the container, then add this solvent to the separatory funnel.

9.1.1.4 Seal and shake the separatory funnel vigorously for 1 to 2 minutes with periodic venting to release excess pressure.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, venting should be done immediately after the separatory funnel has been sealed and shaken once.

9.1.1.5 Allow the organic layer to separate from the water phase for a minimum of 5 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.
Collect the solvent extract in an 500ml Kuderna-Danish (K-D) evaporation flask to which is attached a 10 mL concentrator tube..

9.1.1.6 Repeat the extraction two more times using fresh portions of solvent and adding the solvent extracts to the KD flask. (Steps 9.1.1.3 to 9.1.1.5) The use of continuous liquid-liquid extraction (EPA method 3520) is an acceptable alternative to the separatory funnel extraction method described above.

9.1.1.7 For sample volume determination add water to the sample bottle to the level of the meniscus previously marked then transfer this water to a graduated cylinder and record the volume.

9.1.1.8 Add one clean boiling chip to the K-D flask and attach a three ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 4-6 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

9.1.1.9 Solvent exchange the methylene chloride with hexane by adding at least 50 mL of hexane to the top of the Snyder column. and concentrate the extract to less than 10 mL, as described in Paragraph 9.1.1.8, raising the temperature of the water bath, if necessary, to maintain proper distillation.

Note: An alternative solvent exchange method is to use the nitrogen blowdown apparatus to exchange the methylene chloride with hexane. This is accomplished by placing a disposable pipet in the concentrator tube and adding the small amounts of hexane via the pipet to the bottom of the concentrator tube during the concentration process in the apparatus.

9.1.1.10 Remove the Snyder column and evaporation flask from the 10-mL concentrator tube. Place the concentrator tube containing the hexane extract onto a nitrogen blowdown apparatus. Adjust the extract volume to 1-2 mL under a gentle stream of nitrogen . If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume will need to be larger.

9.1.1.11 The extract obtained is now ready to be cleaned and fractionated on a silica gel column. If cleanup will not be performed immediately, transfer the extract to a Teflon-lined screw-cap vial, label, and refrigerate.

9.1.1.12 Record the sample preparation information for the extraction and concentration steps. At a minimum, record the date, sample laboratory number, sample volume, volume and concentration of added surrogate and matrix spike solutions, and any deviations or problems associated with the extraction of the samples.

9.1.1.13 For cleanup and fractionation, refer to Section 9.1.4.

9.1.2 Soil/Sediment Extraction using Ultrasonic Extraction

9.1.2.1 The following steps should be performed rapidly to minimize the loss of the more volatile fractions. In a beaker blend 10 g of the soil/sediment sample with sufficient anhydrous sodium sulfate to form a free flowing powder using a spatula. Add 1.0 mL of the surrogate spiking solution to the samples and blanks. For the samples in each analytical batch selected for matrix spiking, add 1.0 mL of the matrix spiking standard. Immediately add approximately 50 mL of 1:1 methylene chloride:acetone to the beaker. If lower PQL's are desired, the analyst is allowed to increase the sample size extracted. This will necessitate a proportional increase in the volume of extraction solvent used.

9.1.2.2 Place the bottom surface of the tip of the ultrasonic horn about 1/2 inch below the surface of the solvent but above the soil/sediment layer.

9.1.2.3 Sonicate for 3 minutes with the control knob set to the maximum output, pulse mode and 50% duty cycle.

9.1.2.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

9.1.2.5 Decant and filter the extract through Whatman No. 41 filter paper into the K-D concentrator. Repeat the extraction two more times with additional 50 mL portions of the solvent. Decant off and filter the extract into the K-D flask each time. On the last extraction, pour

the entire sample into the funnel and rinse the beaker and sample with additional portions of solvent and add these to the K-D flask. The analyst may find it useful to (1) either add anhydrous sodium sulfate to the filter for drying the extract or (2) to pass the extract through a drying column containing about 10 cm of anhydrous sodium sulfate prior to collecting the extract in the K-D flask.

9.1.2.6 Add one clean boiling chip to the K-D flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10 to 20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1-2 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

9.1.2.7 Exchange the methylene chloride with hexane by adding 50 mL of hexane to the top of the Snyder column and concentrating the extract as described in Paragraph 9.1.2.6, raising the temperature of the water bath, if necessary, to maintain proper distillation. The alternate solvent exchange technique described in note in 9.1.1.9 may also be used.

9.1.2.8 Remove the Snyder column and evaporation flask from the 10-mL concentrator tube. Place the concentrator tube containing the hexane extract onto a nitrogen blowdown apparatus. Adjust the extract volume to 1-2 mL under a gentle stream of nitrogen . If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume will need to be larger.

9.1.2.9 The extract obtained is now ready to be cleaned and fractionated on a silica gel column. If cleanup will not be performed immediately, transfer the extract to a Teflon-lined screw-cap vial, label, and refrigerate.

9.1.2.10 Record the sample preparation information for the extraction and concentration steps, as specified in paragraph 9.1.1.14.

9.1.2.11 For cleanup and fractionation, refer to Section 9.1.4.

9.1.3 <u>Soil/Sediment Extraction by Soxhlet Extraction</u>

9.1.3.1 Blend 10 g of the soil/sediment sample with sufficient anhydrous sodium sulfate to produce a free flowing powder and place this material in an extraction thimble. The extraction thimble must drain freely for the duration

of the extraction period. Add 1.0 mL of the surrogate spiking solution onto the sample. For the samples in each analytical batch selected for matrix spiking, add 1.0 mL of the matrix spiking solution. If lower PQL's are desired, the analyst may increase the quantity of sample extracted.

9.1.3.2 Place approximately 200 mL of methylene chloride into a 250-mL Erlenmeyer or round bottomed flask (depending on the heating source) containing several clean boiling chips. Attach the flask to the extractor and extract the sample for 8-16 hr.

9.1.3.3 Allow the extract to cool after the extraction is completed.

9.1.3.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

9.1.3.5 Dry the extract by passing it through a glass powder funnel containing anhydrous sodium sulfate. Collect the dried extract in the K-D concentrator. Wash the extractor flask and sodium sulfate column with 50 to 75 mL of methylene chloride to complete the quantitative transfer.

9.1.3.6 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10 to 20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1-2 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

9.1.3.7 Exchange the methylene chloride with hexane by adding 50 mL of hexane to the top of the Snyder column and concentrating the extract as described in Paragraph 9.1.3.6, raising the temperature of the water bath, if necessary, to maintain proper distillation. The alternate solvent exchange technique outlined in the note in 9.1.1.9 may also be used.

9.1.3.8 Remove the Snyder column and evaporation flask from the 10 mL concentrator tube. Place the concentrator tube containing the hexane extract onto a nitrogen blowdown apparatus. Adjust the extract volume to 1-2 mL under a gentle stream of nitrogen . If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume will need to be larger.

9.1.3.9 The extract obtained is now ready to be cleaned and fractionated on a silica gel column. If cleanup will not be performed immediately, transfer the extract to a Teflon-lined screw-cap vial, label, and refrigerate.

9.1.3.10 Record the preparation information for the extraction and concentration steps, as specified in 9.1.1.14.

9.1.3.11 For cleanup and fractionation, refer to Section 9.1.4.

9.1.3.12 The use of the Accelerated Solvent Extraction (ASE), EPA Method 3545, is an acceptable alternative to either ultrasonic or soxhlet extraction techniques as long as it is demonstrated to achieve comparable results.

9.1.4 Silica Gel Cleanup and Separation

9.1.4.1 Silica gel is a regenerative adsorbent of amorphous silica with weakly acidic properties. It is produced from sodium silicate and sulfuric acid. Silica gel can be used for column chromatography and is used for separating analytes from interfering compounds of a different chemical polarity. Silica gel is also used to separate petroleum distillates into aliphatic and aromatic fractions. Before the silica gel technique can be utilized, the extract solvent must be exchanged to hexane. This procedure may be performed immediately before the extract concentration step is complete by adding hexane to the K-D (when the volume of remaining methylene chloride is approximately 10 to 15 mL) and reducing the extract volume to 1 to 2 mL. After cooling, disassemble the K-D apparatus, rinsing the joints into the concentrator tube with a minimum of hexane. With a nitrogen blowdown concentrator, further reduce the extract to a final volume of 2 mL.

9.1.4.2 Prepare a slurry of 10g of activated silica gel in methylene chloride and place this into a 10 mm I.D.x 250 mm long chromatographic column. Tap the column to settle the silica gel and elute the methylene chloride. Add 1 to 2 cm of anhydrous sodium sulfate to the top of the silica gel. Note: The activity of each new batch (lot number) of silica gel must be evaluated prior to its use in this procedure. This requires the use of the fractionation check solution to insure that there is an efficient separation of the aromatic fraction from the aliphatic fraction. If necessary, the analyst is allowed to adjust the volumes of the eluants used to facilitate this process.

9.1.4.3 Pre-elute the column with 40 mL of pentane. Let the solvent flow through the column, at a rate of about 2 mL/minute, until the head of the liquid in the

column is just above the sodium sulfate layer. Close the stopcock to stop solvent flow. Discard this pentane.

9.1.4.4 Open the stopcock and immediately transfer the hexane sample extract onto the silica gel column. Rinse the concentrator tube with an additional 1-2 mL of hexane and add this to the column as well.

9.1.4.5 Just prior to exposure of the sodium sulfate layer to the air, add 25 mL of pentane to the column. Collect the eluant in a 250 mL K-D flask to which is attached a 10 mL concentrator tube and label this fraction "aliphatics". Concentrate and solvent exchange this extract into hexane.

9.1.4.6 Following recovery of the aliphatic fraction and just prior to exposure of the sodium sulfate layer, elute the column with 50 mL of methylene chloride/pentane (40:60) (v/v) and collect the eluant in a 250 mL K-D flask equipped with a 10 mL concentrator tube.. Label this fraction "aromatics". Concentrate and solvent exchange this extract into methylene chloride.

9.1.4.7 Concentrate each fraction to a final volume of 10 mL under a gentle stream of nitrogen from a nitrogen blowdown apparatus.

9.1.4.8 Transfer 1 mL of the fractions to a labeled two-mL glass autosampler vials with teflon-rubber crimp caps for analysis and save the remaining extract in a teflon-rubber septum screw topped vial. If lower PQL's are required, the analyst may concentrate the extract to as low as 1 mL prior to analysis

9.1.5 Proceed with the analysis in accordance with Sections 9.2 through 9.5. Analyze all laboratory method blanks and QC samples under the same conditions as that used for samples.

9.1.6 If chromatographic responses exceed the linear range of the system, dilute the extract(s) and re-analyze

9.1.7 <u>Determination of Percent Moisture</u>

9.1.7.1 Soil and sediment sample results must be reported on a dry-weight basis. A portion of sample for moisture determination should be weighed out at the same time as the portion used for hydrocarbon determination.

9.1.7.2 Immediately after weighing a sample for extraction, transfer 5 to 10 g of the sample into a tared crucible. Dry the sample overnight at 105°C in an oven. After drying remove it from the oven allow it to cool in a desiccator before reweighing. Calculate the percent moisture of the sample using the equations provided in Section 9.6.3.

9.2 **GC Conditions**

9.2.1 Suggested Gas Chromatographic Conditions

9.2.1.1 Oven Program: Set oven temperature to 50 °C for 2 minute, then 8°C/min to 320 °C and hold for 10 minutes.

9.2.1.2 Sample/autosampler injection volume is 1 to 2 µL.

9.2.1.3 Gas Flows: The recommended carrier gas is helium.

9.2.1.3.1 Helium carrier gas flow: 1 to 2 mL/min.

9.2.1.3.2 Air: 400 mL/min.

9.2.1.3.3 Hydrogen: 35 mL/min.

9.2.1.3.4 Make up gas flow: 30 mL/min.

9.2.1.4 Miscellaneous:

9.2.1.4.1 FID temperature, 310 to 320 °C

9.2.1.4.2 Injection port temperature, 290 to 300 °C

9.2.1.4.3 GC operated in splitless mode

9.2.1.4.4 Column head pressure 15.0 psi at 50°C

9.2.1.4.5 Linear velocity approximately 50 cm/sec

9.3 **Retention Time Windows**

9.3.1 Before establishing windows, make sure the GC system is within optimum operating conditions. Make three injections of the Aromatic and Aliphatic Hydrocarbon standard mixtures throughout the course of a 72-hr period. Serial injections over less than a 72-hr period may result in retention time windows that are too tight.

9.3.2 Calculate the standard deviation of the three absolute retention times for each standard.

9.3.3 Plus or minus three times the standard deviation of the absolute retention times for each standard should be used to define the retention time window. However, the

experience of the analyst should weigh heavily in the interpretation of chromatograms.

9.3.4 In those cases where the standard deviation for a particular standard is zero, the laboratory should substitute the standard deviation of a closely eluting structurally similar compound to develop a valid retention time window.9.3.5 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed or a portion removed as part of GC maintenance. This data must be retained by the laboratory.

9.3.6 EPH retention time (Rt) windows for all fractions (carbon ranges and hydrocarbon types) except the C8 through C10 are defined as beginning 0.1 minutes after the Rt of the beginning marker compound and ending 0.1 minutes after the Rt of the ending marker compound. Since the first fraction for both the aliphatics and aromatics includes the beginning marker compounds, the Rt windows for them are defined as beginning 0.1 minutes before the Rt of the beginning marker compound and ends 0.1 minutes after the ending marker compound.

EPH marker compounds and windows are summarized in Table 4.

Table 4. EPH Marker Compounds

Range/ Hydrocarbon Standard	Beginning Marker Compound	Ending Marker Compound
C8-C10 Aliphatic Hydrocarbons	just before n-octane	just after n-decane
C10-C12 Aliphatic Hydrocarbons	just after n-decane	just after n-dodecane
C12-C16 Aliphatic Hydrocarbons	just after n-dodecane	just after n-hexadecane
C16-C21 Aliphatic Hydrocarbons	just after n-hexadecane	just after n-henicosane
C21-C34 Aliphatic Hydrocarbons	just after n-henicosane	just after n-tetratriacontane
C8-C10 Aromatic Hydrocarbons	just before toluene	just after 1,2,3-trimethylbenzene
C10-C12 Aromatic Hydrocarbons	just after 1,2,3-trimethylbenzene	just after naphthalene
C12-C16 Aromatic Hydrocarbons	just after naphthalene	just after acenaphthene
C16-C21 Aromatic Hydrocarbons	just after acenaphthene	just after pyrene
C21-C34 Aromatic Hydrocarbons	just after pyrene	just after benzo(g,h,i)perylene

9.4 **Calibration**

Calibrate the GC system using either the external standard procedure (Section 9.4.1) or the internal standard procedure (Section 9.4.2).

9.4.1 External standard calibration procedure

9.4.1.1 Prepare Aromatic and Aliphatic Hydrocarbon calibration standards at a minimum of five concentration levels by adding volumes of one or more stock standard solutions to volumetric flasks and diluting to volume with methylene chloride and hexane, respectively. The surrogate OTP is added to the Aromatic Hydrocarbon Standard; the surrogate COD is added to the Aliphatic Hydrocarbon Standard. One of the calibration

standards must be at a concentration near, but above, the method detection limit and is used to determine the reporting PQL. In order to report the PQL's listed in 1.4, given the volume/mass water or soil extracted of 1 liter or 10 grams and assuming 100% solids on the soil, this standard must be at a 5 ng/uL level. The other concentrations must correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

9.4.1.2 A collective calibration curve or factor must be established for each hydrocarbon range of interest. Inject each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph (e.g., 1 to 2 µL injections). To calculate the collective CF for C8-C10, >C12-C12, >C12-C16, >C16-C21 and C21-C34 Aromatic Hydrocarbons, tabulate the summation of all peak areas of the calibration compounds in that range (e.g. C8-C10, toluene and 1,2,4-trimethylbenzene or >C10-C12, naphthalene) against the total mass injected. Although a forced baseline projection is required for samples and blanks, the analyst is allowed to integrate only the area of the calibration compound(s) to generate the calibration factors. The ratio of the response to the amount injected, defined as the calibration factor (CF), or range CF, may be calculated for hydrocarbon ranges at each standard concentration using Equation 1. If the percent relative standard deviation (%RSD) of the calibration factor is equal to or less than 20 % over the working range for the ranges of interest, as determined using Equation 2, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve. The Aliphatic Hydrocarbon collective CF is calculated in the same manner using the aliphatic standards.

Equation 1: Range Calibration Factor

$$Range\ CF = \frac{total\ area\ of\ peaks}{mass\ injected\ (ng)}$$

Equation 2: Percent Relative Standard Deviation

$$\%RSD = \frac{Stand\ Dev\ of\ 5\ CFs}{Mean\ of\ 5\ CFs} \times 100$$

Note: The area for the surrogates COD and OTP must be subtracted from the area of the range in which they elute (e.g., COD is subtracted from the C16-C21 Aliphatic Hydrocarbon range.

9.4.1.4 At a minimum, the working calibration curve or calibration factor must be verified at the beginning of each working day and after the final analysis of that day, or after every 20 samples, whichever is more frequent, by the injection of a mid-level calibration standard to verify instrument performance and linearity. If the percent difference (%D) for any range varies from the predicted response by more than ± 20 %, as calculated using Equation 4, a new calibration curve must be prepared.

Equation 4: Percent Difference (%D)

$$\%D = \frac{\overline{CF} - CFv}{\overline{CF}} \times 100$$

where:

$\overline{CF}$ = Average Calibration Factor from calibration curve.

CFv = Calibration Factor from verification calibration check.

9.4.1.5 The concentrations of hydrocarbon ranges may also be calculated from a calibration curve by use of linear regression analysis.

9.4.2 Internal standard calibration procedure

9.4.2.1 The suggested internal standard for this method is 5-alpha-androstane (EM Science, Gibbstown, NJ).

9.4.2.2 Prepare Aromatic and Aliphatic Hydrocarbon calibration standards at a minimum of five concentration levels by adding volumes of stock standard solutions to volumetric flasks. The surrogate OTP is added to the Aromatic Hydrocarbon Standard; the surrogate COD is added to the Aliphatic Hydrocarbon Standard. To each calibration standard, add a known constant amount of an internal standard. One of the calibration standards must be at a concentration near, but above, the method detection limit and is used to determine the reporting PQL. The other concentrations must correspond to the expected range of concentration found in real world samples or should define the working range of the detector.

9.4.2.3 Inject each calibration standard using the same technique that will be applied to the samples (e.g., 1 to 2 µL injection). Tabulate the peak area responses against the concentration of each hydrocarbon range and internal standard. Calculate the collective response factors (RF) for each hydrocarbon range using Equation 5.

Note: The area for the surrogates COD and OTP must be subtracted from the area of the range in which they elute (e.g., COD is subtracted from the appropriate Aliphatic Hydrocarbon range).

uation 5: Range Response Factor

$$Range\ RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Summation of peak areas of the fraction (e.g., C10-C12 Aliphatic Hydrocarbons).

C_{is} = Concentration of internal standard, ng/µL.

A_{is} = Response for the internal standard.

C_s = Total mass concentration of injected standards, ng/µL.

9.4.2.4 At a minimum, the working calibration curve or RF must be verified at the beginning of each working day and after the final analysis of that day, or after every 20 samples, whichever is more frequent, by the injection of a mid-level calibration standard to verify instrument performance and linearity. If the percent difference (%D) for any hydrocarbon range varies from the predicted response by more than ± 20 %, as calculated using Equation 4, a new calibration curve must be prepared for that range.

9.4.2.5 The concentrations of hydrocarbon ranges may also be calculated from a calibration curve by the use of linear regression analysis.

9.5 **GC Analysis**

9.5.1 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration, or verification of calibration, followed by sample extracts interspersed with blanks and QC samples. The analytical sequence must end with an acceptable verification calibration standard. If the ending calibration standard is not acceptable, all samples analyzed after the last acceptable calibration verification must be reanalyzed. If, for whatever reason, reanalysis is not possible, then the data for those samples must be qualified as an "estimate".

9.5.2 Aliphatic and aromatic extracts are introduced into the gas chromatograph by slitless injection.

9.5.3 Inject 1 to 2 µL of the sample extract. Record the volume injected and the resulting peak size in area units.

9.5.4 Confirm the established retention time windows for each hydrocarbon range on a daily basis. Use the absolute retention time for each analyte as the midpoint of the window for that day. The daily retention time window equals the midpoint ± three times the standard deviation determined in Section 9.3.

9.5.4.1 Validation of GC system qualitative performance must be accomplished by the analysis of standards within the analysis sequence. If any of the standards fall outside their daily retention time window, the system is out of control. In such cases, the cause of the problem must be determined and corrected.

9.5.5 When quantifying on a peak area basis by internal or external calibration, peak area integration for the aliphatic and aromatic carbon ranges must be <u>from baseline</u> (i.e. must include the unresolved complex mixture "hump" areas).

9.6 **Calculations**

9.6.1 <u>External Standard Calibration</u>

The concentration of each hydrocarbon range in a sample may be determined by calculating the amount of hydrocarbon range compounds injected, from the peak response, using the calibration curve or the calibration factor determined in Section 9.4.

9.6.1.1 **Aqueous samples:**

The general equation to determine the concentration of a hydrocarbon range in aqueous samples in provided in Equation 6.

Equation 6

$$Concentration\ (ug / L) = \frac{(A_x)(A)(V_t)(D)}{(A_s)(V_i)(V_s)}$$

w

here:

A_x = Response for a hydrocarbon range in the sample, units may be in area counts or peak height.

A = Amount of standard injected, ng.

A_s = Response for the external standard, units same as for A_x.

V_i = volume of extract injected, µL.

D = Dilution factor: if no dilution was made, D = 1, dimensionless.

V_t = Volume of total extract, µL.

V_s = Volume of sample extracted, mL.

If a Calibration Factor is used, the concentration of a hydrocarbon range may be calculated using Equation 7.

Equation 7

$$Conc\ HC\ Range\ (ug / L) = \frac{(A_X)(V_t)(D)}{(V_i)(V_s)(Range\ CF)}$$

where:

Range CF = Calibration Factor for hydrocarbon ranges (collective area count/collective mass).

9.6.1.2 **Nonaqueous samples:**

The general equation to determine the concentration of a hydrocarbon range in soil or sediment samples is provided in Equation 8.

Equation 8

$$Concentration\ (ug / kg) = \frac{(A_x)(A)(V_t)(D)}{(A_s)(V_i)(W_d)}$$

where:

W_d = Dry weight of sample extracted, g. (See Equations 12 through 14)

A_x, A_s, A, V_t, D, and V_i have the same definition as for aqueous samples.

If a Calibration Factor is used, the concentration of specific hydrocarbon ranges in a soil or sediment sample may be calculated using Equation 9.

Equation 9

$$Conc\ HC\ Range\ (ug / kg) = \frac{(A_x)(V_t)(D)}{(V_i)(W_d)(Range\ CF)}$$

where:

Range CF = Calibration Factor for a hydrocarbon range (collective area count/collective mass).

9.6.2 Internal Standard Calibration

The concentration of each hydrocarbon range in a sample may be determined by calculating the amount of hydrocarbon range compound(s) injected, from the peak response, based upon the compound/internal-standard response ratio.

9.6.2.1 **Aqueous samples:**

The general equation to determine the concentration of a specific hydrocarbon range in aqueous samples is provided in Equation 10.

Equation 10

$$Concentration\ (ug / L) = \frac{(A_x)(C_{is})(D)}{(A_{is})(RF)(V_s)}$$

where:

A_x = Response of the hydrocarbon range being measured, units may be in area counts or in peak height.

C_{is} = Amount of internal standard added to extract, ng.

D = Dilution factor, if a dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

A_{is} = Response of the internal standard, units same as A_x.

RF = Response factor for the hydrocarbon range, dimensionless.

V_s = Volume of aqueous sample extracted, mL.

9.6.2.2 **Nonaqueous samples:**

The general equation to determine the concentration of a specific or hydrocarbon range in soil or sediment samples is provided in Equation 11.

Equation 11

$$Concentration\ (ug / kg) = \frac{(A_x)(C_{is})(D)}{(A_{is})(RF)(W_d)}$$

where:

W_d = Dry weight of sample extracted, g. (See Equations 12 through 14).

A_x, C_{is}, D, A_{is}, and RF have the same definition as for aqueous samples.

9.6.3 Calculation of Dry Weight of Sample

In order to calculate the dry weight of sample extracted (W_d), it is necessary to determine the moisture content of the soil/sediment sample, using the procedure outlined in Section 9.1.7. Using the data obtained from Section 9.1.7, W_d is calculated using Equations 12 through 14.

Equation 12

$$\% \text{ Moisture} = \frac{g \text{ sample} - g \text{ dry sample}}{g \text{ sample}} X\ 100$$

Equation 13

$$\% \text{ Dry Solids} = (1) - (\% \text{ Moisture})$$

Equation 14

$$W_d\ (g) = (\% \text{ Dry Solids})(g \text{ of extracted sample})$$

10.0 QUALITY CONTROL

10.1 **General Requirements and Recommendations**

10.1.1 Each laboratory that uses this method should operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance standards for the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

10.1.2 Hexane or methylene chloride solvent blanks should be run after samples suspected of being highly contaminated to determine if sample carryover has occurred.

10.1.3 At a minimum, for each analytical batch (up to 20 samples), a Laboratory Method Blank, Laboratory Fortified Blank Spike (Water or Soil), Laboratory Fortified

Matrix Spike, and sample duplicate must be analyzed. For analytical batches with more than 10 samples, the analysis of an additional mid-range calibration check standard is recommended. The blank and spiked samples must be carried through all stages of the sample preparation and measurement process.

10.1.4 The recommended sequence of analysis is as follows:

(1) Calibration Standards (initial) or mid-range Calibration Check (Verification) Standard (i.e. daily check of initial calibration)
(2) Laboratory Method Blank
(3) Samples
(4) QC Samples
(5) Mid-range Calibration Check (Verification) Standard (also recommended after each 10 samples)

10.1.5 It is recommended that a system of control charts be developed to plot surrogate standard recoveries as a function of time. When surrogate recovery from a sample, blank, or QC sample is less than 50% or more than 150%, check calculations to locate possible errors, the fortifying solution for degradation, and changes in instrument performance. If the cause cannot be determined, the analyst may reanalyze the sample extract, report the surrogate values as outside acceptance limits or, if additional sample is available, re-extract and reanalyze the sample.

10.2 **Minimum Instrument QC**

10.2.1 The instrument must be able to achieve adequate separation and resolution of peaks of interest.

10.2.1.1 The n-octane (n-C8) and toluene peaks must be adequately resolved from the solvent front of the chromatographic run.

10.2.1.2 The surrogates COD and OTP and any internal standards used must be adequately resolved from any individual components in the Aliphatic Hydrocarbon and Aromatic Hydrocarbon standards.

10.2.2 Retention time windows must be established for each hydrocarbon range of interest each time a new GC column is installed, and must be verified and/or adjusted on a daily basis. (See Section 9.3)

10.2.3 Calibration curves must be developed based upon the analysis of calibration standards prepared at a minimum of 5 concentration levels. The linearity of calibration or response factors may be assumed if the percent relative standard deviation (%RSD) over the working range of the curve is less than or equal to 20 %. Alternatively, if linear regression analysis is used for

quantitation, the correlation coefficient (r) must be at least 0.99. and the percent difference (% D) of the response for any hydrocarbon range from the predicted response may not vary by more than +/- 20%. (See Section 9.4.)

10.3 **Initial and Periodic Method QC Demonstrations**

The following must be conducted as an initial demonstration of laboratory capability, prior to the analysis of any samples. Subsequent to this initial demonstration, additional evaluations of this nature should be conducted on a periodic basis, in response to changes in instrumentation or operations, and/or in response to confirmed or suspected systems, method, or operational problems.

10.3.1 Accuracy and Precision

To demonstrate initial laboratory capability, analyze a minimum of four replicate reagent water and/or clean sand blanks spiked with the calibration compounds for each range of interest at approximately 50 µg/L and/or 5 mg/kg, respectively.

10.3.1.1 Extract and analyze each replicate according to the procedures described in Section 9.0.

10.3.1.2 Calculate the measured concentrations of each range in all replicates, the mean accuracy (as a percentage of true value) for each compound, and the precision (as %RSD) of the measurements for each compound.

10.3.1.3 For each compound, the mean accuracy, expressed as a percentage of the true value, should be between 70 % and 130 %. For each compound, the %RSD must be less than or equal to 20%.

10.3.2 Method Detection Limits (Optional)

Analyze a minimum of seven replicate reagent water and/or clean sand blanks which have been fortified with all analytes of interest at approximately 0.5 to 2 µg/L and/or 1.0 to 5.0 mg/kg, respectively. Extract and analyze each replicate according to the procedures described in Section 9.0. Calculate the Method Detection Limit (MDL) of each analyte using the procedure described in Section 12.0.

10.3.2.1 Water MDLs are determined by extracting 7 to 10 replicates of 1-L reagent water blanks spiked with OTP, COD and each analyte of interest.

10.3.2.2 Soil/sediment MDLs are determined by extracting 7-10 replicates of 10-g of EPH-free sand blanks spiked with OTP, COD, and each analyte of interest.

10.3.3 Fractionation

To demonstrate the capability of properly fractionating aliphatic and aromatic hydrocarbons in a sample, the analyst must first prepare and analyze the Fractionation Check Solution specified in Section 7.6.

10.3.3.1 Prepare a silica gel column as outlined in 9.1.4

10.3.3.2 Load 1.0 mL of the Fractionation Check Solution onto column and proceed with the elution and collection of the aliphatic and aromatic fractions as outline in 9.1.4.

NOTE: The amount of pentane used during the elution/fractionation is critical. Excessive pentane will cause elution of aromatics into the aliphatic fraction. Insufficient pentane will cause low recoveries of the aliphatic fraction. The volume of pentane and/or methylene chloride/pentane recommended may need to be adjusted to meet QC limits.

10.3.3.3 Solvent exchange the aliphatic fraction to hexane and the aromatic fraction to methylene chloride. Concentrate each solution to a final volume of 1.0 mL under a gentle stream of nitrogen from an nitrogen blowdown apparatus.

10.3.3.4 Transfer the final 1.0 mL extracts to two labeled glass auto sampler vials with teflon-lined rubber crimp caps. Analyze by GC/FID (see Section 9.0).

10.3.3.5 For each analyte within the Fractionation Check Solution, the mean accuracy, expressed as a percentage of the true value, must be between 70 % and 130 %.

10.3.4 Petroleum Reference Standard

As an optional demonstration of the validity and relevance of EPH calibration, analyze a reagent water and/or clean sand blank spiked with a known concentration of a neat petroleum product.

10.3.4.1 Dilute a Petroleum Reference Standard stock standard solution with acetone to a concentration of approximately 250 ng/µL. Spike a 1 Liter reagent water blank or 10 g clean sand blank with 1.0 mL of this spiking solution. Extract and analyze in accordance with the procedures outlined in Section 9.0.

10.3.4.2 Calculate the total concentration of all petroleum hydrocarbons within each range. Add these values together.

10.3.4.3 The concentration calculated in Paragraph 10.3.4.2 is expected to be within +/- 30 % of the known concentration of Petroleum Standard in the reagent water or sand blank.

10.4 **Ongoing Method QC Demonstrations**

10.4.1 Each sample, blank, and matrix spike sample must be spiked with the surrogate spiking solution. Required surrogate recovery is 60% to 140%.

10.4.2 At a minimum, with every batch of 20 samples or less the lab must analyze the following:

10.4.2.1 **Calibration Check Standard** - A mid-range calibration standard, prepared from the same stock standard solution used to develop the calibration curve, must be analyzed prior to sample analysis to verify the calibration state of the instrument. For large analytical batches that contain more than 10 samples, the analysis of an additional mid-range calibration check standard is recommended after the analysis of the tenth sample. If the percent difference (% D) of any compound within a calibration check standard varies from the predicted response by more than 20 %, a new calibration curve must be prepared. (See Section 9.4)

10.4.2.2 **Laboratory Method Blank** - A water or soil laboratory method blank is prepared by fortifying a reagent water or clean sand blank with 1.0 mL of the surrogate spiking solution. Peaks within the retention time windows of any hydrocarbon ranges of interest may not be present at or above the lowest calculated PQL for any sample within its batch. When determining the PQL of soil method blanks, incorporate the lowest percent solids value found for any sample within its batch in the calculation.

10.4.2.3 **Laboratory Fortified Blank Spike** - A water or soil component spike is prepared by fortifying a reagent water or clean sand blank with 1.0 mL of the matrix spiking solution. The spike recovery must be between 70 % and 130 % and, if these values can not be obtained, the analyst must identify and correct the problem before analyses can continue.

10.4.2.4 **Sample duplicates** - Sample duplicates may be laboratory duplicates or field duplicates and the RPD of the duplicate samples should not exceed +/- 25%. The lack of sample homogeneity may contribute to the RPD's values for duplicates which exceed this value. Should the values exceed 25% the analyst must report that occurrence.

10.4.2.5 **Laboratory Fortified Matrix (LFM) Spike** - The water or soil LFM spike is prepared by fortifying an actual water or soil sample with 1.0 mL of the matrix spiking solution. The purpose of the LFM spike is to

determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations. The corrected concentrations of each analyte within the LFM spike sample must be within 70 to 130 % of the true value. Should the values determined exceed this range, the analyst must report that occurrence.

10.4.3 If any of the performance standards specified in Section 10.4 are not met, the problem should be corrected before further samples are analyzed. Exceptions to this are duplicate samples RPD's and high recoveries for LFM spikes which, due to sample non-homogeneity, may exceed the allowable limits. Any samples run between the last calibration check standard that meet the criteria and one that does not must be reanalyzed. If this is not possible, then the data must be reported as an "estimated concentration."

11.0 DATA PRODUCTION AND REPORTING

11.1 **Sample Analysis**

11.1.1 Aliphatic Fraction

11.1.1.1 Determine the total area count for all peaks eluting 0.1 minutes before the retention time (Rt) for C8 to 0.1 minutes after the Rt for C10.

11.1.1.2 Determine the total area count for all peaks eluting 0.1 minutes after the Rt for C10 to 0.1 minutes after the Rt for C12. Determine the total area count of all peaks eluting 0.1 minutes after the Rt for C12 to 0.1 minutes after the Rt for C16, for all peaks eluting 0.1 minutes after the Rt for C16 to 0.1 minutes after the Rt for C21and for all peaks eluting 0.1 minutes after the Rt for C21 to 0.1 minutes after the Rt for C34. It is not necessary to identify or quantitate individual aliphatic compounds within these ranges.

11.1.1.3 Determine the peak area count for the surrogate COD and any internal standard used. Subtract these values from the collective area count value within the appropriate hydrocarbon range(s).

11.1.1.4 Using the equations contained in Section 9.6 or linear regression analysis, calculate the concentrations of C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 Alipiphatic Hydrocarbon ranges and the surrogate standard COD.

11.1.1.5 The term "all peak areas" must include any unresolved envelope of peaks which elute within the Rt windows listed above and below for the aliphatic and aromatic fractions.

11.2.1 Aromatic Fraction

11.2.1.1 Determine the total area count for all peaks eluting 0.1 minutes before the retention time (Rt) for toluene to 0.1 minutes after the Rt for 1,2,3 trimethylbenzene. In the same manner, determine the total area count for all peaks eluting 0.1 minutes after the Rt for 1,2,3-trimethylbenzene to 0.1 minutes after the Rt for naphthalene, from 0.1 minutes after the Rt for naphthalene to 0.1 minutes after the Rt for acenaphthene, from 0.1 minutes after the Rt for acenaphthene to 0.1 minutes after the Rt for pyrene and 0.1 minutes after the Rt for pyrene to 0.1 minutes after the Rt for benzo(g.h.i)perylene.

11.2.1.2 Determine the peak area count for the surrogate OTP and any internal standard used.

11.2.1.3 Subtract the peak area value from 11.2.1.2 from the collective area count value for the range effected determined in 11.2.1.1 to calculate the area count for Aromatic Hydrocarbons ranges.

11.2.1.4 Using the equations contained in Section 9.6 or linear regression analysis, calculate the concentrations of C8 through C10, >C10 through C12, >C12 through C16 , >C16 through C21 and >C21 through C34 Aromatic Hydrocarbons and the surrogate standard COD.

11.3 Data Reporting Format

11.3.1 The following information and data must be reported:

11.3.1.1 The sample matrix (aqueous, soil or sediment);

11.3.1.2 The date(s) the sample was collected, received by the laboratory, extracted, and analyzed;

11.3.1.3 A description of the sample(s) received by the laboratory, relative to the physical condition of the containers, the temperature of the samples, and use of appropriate preservatives;

11.3.1.4 Moisture content (for soil/sediment samples);

11.3.1.5 The calculated concentrations of C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 Aliphatic Hydrocarbons, and C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 Aromatic Hydrocarbons.

11.3.1.6 Surrogate recovery (expressed as percent recovery);

11.3.1.7 The concentration units for aqueous samples are expressed as ug/L or mg/L and soil or sediment samples the units are expressed as µg/Kg or mg/Kg on a dry-weight basis.

12.0 METHOD PERFORMANCE

12.1 **Method Detection Limits (Optional)**

12.1.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

12.1.2 The MDL is determined according to Equation 15.

Equation 15

$$MDL = (t) \times (SD)$$

where:

t = student t value at the 99% confidence level.

SD = standard deviation of the replicate analysis.

Student t values are as follows:

Number of replicates	t value
7	3.14
8	3.00
9	2.90
10	2.82

12.2 **Single Laboratory Accuracy, Precision and MDL Data**

Single laboratory accuracy, precision and MDL data for method analytes are provided in Tables 1-1 through 1-4 in Appendix 1. Tables 1-1 and 1-2 present data collected from spiking reagent water at 5.0 µg/L; Tables 1-3 and 1-4 by spiking sand at 1.0 mg/kg.

13.0 REFERENCES

1. Massachusetts Department of Environmental Protection and ABB Environmental Services, Inc., Wakefield, MA "Interim Petroleum Policy: Development of Health-based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter," August 1994.

2. USEPA, "Measurement of Petroleum Hydrocarbons: Report on Activities to Develop a Manual." Prepared by Midwest Research Institute, Falls Church, VA, under EPA Contract #68-WO-0015, WA No. 4; submitted to USEPA Office of Underground Storage Tanks, Washington, DC; November 20, 1990.

3. USEPA Federal Register 40 CFR Part 136, Appendix B, "Guidelines Establishing Test procedures for the Analysis of Pollutants," July 1992.

4. USEPA Test Methods for Evaluating Solid Waste (SW-846); Method 3510: Separatory Funnel Liquid-Liquid Extraction; September 1986.

5. USEPA Test Methods for Evaluating Solid Waste (SW-846); Method 3540: Soxhlet Extraction; September 1986.

6. USEPA Test Methods for Evaluating Solid Waste (SW-846); Method 3630: Silica Gel Cleanup; September 1986.

7. USEPA Test Methods for Evaluating Solid Waste (SW-846): Method 8000: Gas Chromatography; September 1986.

8. USEPA Test Methods for Evaluating Solid Waste (SW-846); Method 8100: Polynuclear Aromatic Hydrocarbons; September 1986.

9. Wisconsin Department of Natural Resources, "Modified DRO - Method for Determining Diesel Range Organics," PUBL-SW-141, 1992.

APPENDIX 1

SINGLE LABORATORY ACCURACY, PRECISION, AND METHOD DETECTION LIMITS (MDL) DATA FOR VPH

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Table 1-1. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Compounds in Component Standard Spiked Into Reagent Water and Analyzed by the VPH Method

Compound	Spiked Conc. (µg/L)	Method Accuracy[a] (Mean % Recovery[b])		Method Precision[a] (RSD[c] - %)		MDL[a] (µg/L)	
		PID[d]	FID[e]	PID	FID	PID	FID
n-Pentane	6.0		98		7.8		1.4
Methyl tert butylether	1.8	77	79	4.8	15	0.21	0.69
Benzene	0.6	82	97	4.9	10	0.08	0.19
Toluene	0.6	79	104	7.3	6.5	0.11	0.13
n-Nonane	2.0		83		8.0		0.42
Ethylbenzene	0.6	77	94	4.2	9.1	0.06	0.16
m- & p-Xylene	1.2	68	85	4.3	6.4	0.11	0.20
o-Xylene	0.6	79	88	16	6.4	0.23	0.11
1,2,3-Trimethylbenzene	0.6	69	89	8.2	6.4	0.11	0.11
Naphthalene	3.6	58	56	16	18	1.0	1.2
2,5-Dibromotoluene (surrogate)	40	88	92	4.9	13		

[a] Based on analysis of seven samples spiked with component standard.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] PID = photoionization detector.
[e] FID = flame ionization detector.

Table 1-2. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Compounds in Component Standard Spiked Into VPH- Free Sand and Analyzed by the VPH Method

Compound	Spiked Conc. (µg/Kg)	Method Accuracy[a] (Mean % Recovery[b])		Method Precision[a] (RSD[c] - %)		MDL[a] (µg/Kg)	
		PID[d]	FID[e]	PID	FID	PID	FID
n-Pentane	120		124		6.0		28
Methyl tert butylether	120	70	96	3.1	27	8.1	99
Benzene	60	122	128	3.3	5.4	7.6	13
Toluene	60	139	137	4.8	8.6	13	22
n-Nonane	120		119		4.6		21
Ethylbenzene	60	107	103	4.3	5.0	8.6	9.7
m- & p-Xylene	120	109	104	4.1	5.2	17	20
o-Xylene	60	103	111	3.8	6.6	7.4	14
1,2,3-Trimethylbenzene	60	93	102	5.5	5.3	9.6	10
Naphthalene	ND[f]	ND	ND	ND	ND	ND	ND
2,5-Dibromotoluene (surrogate)	2,000	119	117	8.6	9.7		

[a] Based on analysis of seven samples spiked with component standard.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] PID = photoionization detector.
[e] FID = flame ionization detector.
[f] ND = not determined.

Table 1-3. Single Laboratory Accuracy and Precision for Compounds in Component Standard Spiked Into Reagent Water at Concentrations in the Low to Middle End of the Analytical Range and Then Analyzed by the VPH Method

Compound	Spiked Conc. (µg/L)	Method Accuracy[a] (Mean % Recovery[b])		Method Precision[a] (RSD[c] - %)	
		PID[d]	FID[e]	PID	FID
n-Pentane	40		96		7.7
Methyl tert butylether	60	87	88	4.0	3.9
Benzene	20	99	99	4.4	3.7
Toluene	60	99	99	4.1	4.0
n-Nonane	40		104		10
Ethylbenzene	20	99	99	4.2	4.2
m- & p-Xylene	80	99	99	4.3	4.2
o-Xylene	40	99	99	3.7	3.6
1,23-Trimethylbenzene	40	99	99	4.1	4.0
Naphthalene	40	70	81	4.3	3.2
2,5-Dibromotoluene (surrogate)	40	92	94	5.2	4.6

[a] Based on analysis of five samples spiked with component standard.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] PID = photoionization detector.
[e] FID = flame ionization detector.

Table 1-4. Single Laboratory Accuracy and Precision for Compounds in Component Standard Spiked Into VPH-Free Sand at Concentrations in the Low to Middle End of the Analytical Range and Then Analyzed by the VPH Method

Compound	Spiked Conc. (mg/Kg)	Method Accuracy[a] (Mean % Recovery[b])		Method Precision[a] (RSD[c] - %)	
		PID[d]	FID[e]	PID	FID
n-Pentane	2.0		118		1.9
Methyl tert butylether	3.0	100	94	2.4	2.8
Benzene	2.0	119	109	3.0	0.7
Toluene	2.0	118	109	1.7	1.3
n-Nonane	ND	ND	ND	ND	ND
Ethylbenzene	1.0	121	110	1.4	1.2
m- & p-Xylene	3.0	122	110	1.4	1.1
o-Xylene	2.0	118	107	1.3	1.1
1,2,3-Trimethylbenzene	2.0	115	109	1.4	1.3
Naphthalene	2.0	61	57	11	1.8
2,5-Dibromotoluene (surrogate)	2.0	75	64	9.7	3.3

[a] Based on analysis of five samples spiked with component standard.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] PID = photoionization detector.
[e] FID = flame ionization detector.
[f] ND = not determined.

APPENDIX 2

SUGGESTED VPH DATA REPORTING FORMAT

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VOLATILE PETROLEUM HYDROCARBON (VPH) ANALYSIS

Client:
Client Sample ID: Date Received:
Laboratory Sample ID: Date Analyzed:
Matrix: Date Reported:
Percent Moisture:

VPH RESULTS

Parameter	Results	PQL				Units
C5-C6 Aliphatics (FID) *						
C6-C8 Aliphatics (FID) *						
C8-C10 Aliphatics (FID) *						
C10-C12 Aliphatics (FID) *						
C8-C10 Aromatics (PID)						
C10-C12 Aromatics (PID)						
C12-C13 Aromatics (PID)						

*** Excludes any MTBE or BTEX compounds**

SURROGATE RECOVERY

Surrogate	%Recovery	Acceptance Range
2,5-dibromotoluene		80% - 120%

TARGETED VPH ANALYTES

Analyte	**Results**	**PQL**	**Units**
Methyl tert butylether			
Benzene			
Toluene			
Ethylbenzene			
p-Xylene *			
m-Xylene *			
o-Xylene			
Naphthalene			

* p and m-xylenes may not be able to be resolved and may be reported as the total of p and m-xylenes.

APPENDIX 3

SINGLE LABORATORY ACCURACY, PRECISION, AND METHOD DETECTION LIMIT (MDL) DATA FOR EPH

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Table 1-1. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Alkanes Spiked Into Reagent Water and Analyzed by the EPH Method

Compound[a]	Compound Conc. Measured (µg/L)		Mean Accuracy (Mean % Recovery[b])	Method Precision (RSD[c] - %)	MDL (µg/L)
	Mean	Std. Dev.			
C_{10}	4.1	0.040	82	0.98	0.12
C_{12}	4.1	0.021	82	0.51	0.064
C_{16}	4.0	0.062	80	1.6	0.19
COD[d]	44	0.93	88	2.1	-
C21	3.7	0.047	74	1.3	0.14

[a] Compounds were spiked into 7 or 8 samples at a concentration of 5.0 µg/L.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] Surrogate (COD = 1-Chloro-octadecane) was spiked into three samples at a concentration of 50 µg/L.

Table 1-2. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Polynuclear Aromatic Hydrocarbons (PAHs) Spiked Into Reagent Water and Analyzed by the EPH Method

Compound[a]	Compound Conc. Measured (µg/L)		Mean Accuracy (Mean % Recovery[b])	Method Precision (RSD[c] - %)	MDL (µg/L)
	Mean	Std. Dev.			
Naphthalene	5.6	0.088	112	1.6	0.26
2-Methylnaphthalene	6.4	0.096	128	1.5	0.29
Acenaphthylene	5.6	0.085	112	1.5	0.26
Acenaphthene	5.7	0.092	114	1.6	0.28
Fluorene	5.6	0.094	112	1.7	0.28
Phenanthrene	5.5	0.097	110	1.8	0.29
Anthracene	7.0	0.10	140	1.4	0.31
OTP[d]	44	1.6	88	3.6	-
Fluoranthene	5.7	0.090	114	1.6	0.27
Pyrene	6.1	0.098	122	1.6	0.29
Benzo(a)Anthracene	5.9	0.089	118	1.5	0.27
Chrysene	5.8	0.098	116	1.7	0.29
Benzo(b)Fluoranthene	6.3	0.082	126	1.3	0.25
Benzo(k)Fluoranthene	5.6	0.065	112	1.2	0.20
Benzo(a)Pyrene	6.0	0.075	120	1.2	0.22
Indeno(123 cd)Pyrene	5.1	0.17	102	3.3	0.50
Dibenzo(ah)Anthracene	2.8	0.21	56	7.5	0.62
Benzo(ghi)Perylene	3.8	0.18	76	4.7	0.54

[a] Compounds were spiked into 7 or 8 samples at a concentration of 5.0 µg/L.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] Surrogate (OTP = ortho-Terphenyl) was spiked into three samples at a concentration of 50 µg/L.

Table 1-3. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Alkanes Spiked Into EPH-Free Sand and Analyzed by the EPH Method

Compound[a]	Compound Conc. Measured (mg/Kg)		Mean Accuracy (Mean % Recovery[b])	Method Precision (RSD[c] - %)	MDL (mg/Kg)
	Mean	Std. Dev.			
C_{10}	0.72	0.074	72	10	0.22
C_{12}	0.83	0.079	83	9.5	0.24
C_{16}	1.2	0.14	120	12	0.42
COD[d]	4.3	0.48	86	11	-
C21	0.81	0.044	81	5.4	0.13

[a] Compounds were spiked into 8 samples at a concentration of 1.0 mg/Kg.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] Surrogate (COD = 1-Chloro-octadecane) was spiked into three samples at a concentration of 5.0 mg/kg.

Table 1-4. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Polynuclear Aromatic Hydrocarbons (PAHs) Spiked Into EPH-Free Sand and Analyzed by the EPH Method

Compound[a]	Compound Conc. Measured (mg/Kg)		Mean Accuracy (Mean % Recovery[b])	Method Precision (RSD[c] - %)	MDL (mg/Kg)
	Mean	Std. Dev.			
Naphthalene	0.64	0.063	64	9.8	0.19
2-Methylnaphthalene	0.64	0.058	64	9.1	0.17
Acenaphthylene	0.68	0.060	68	8.8	0.18
Acenaphthene	0.70	0.064	70	9.1	0.19
Fluorene	0.79	0.060	79	7.6	0.18
Phenanthrene	0.83	0.041	83	4.9	0.12
Anthracene	1.2	0.082	120	6.8	0.25
OTP[d]	4.8	0.45	96	9.4	-
Fluoranthene	0.92	0.038	92	4.1	0.12
Pyrene	0.91	0.037	91	4.1	0.11
Benzo(a)Anthracene	0.96	0.042	96	4.4	0.12
Chrysene	0.90	0.050	90	5.6	0.15
Benzo(b)Fluoranthene	0.96	0.038	96	4.0	0.11
Benzo(k)Fluoranthene	0.87	0.037	87	4.3	0.11
Benzo(a)Pyrene	0.96	0.036	96	3.8	0.11
Indeno(123 cd)Pyrene	0.90	0.033	90	3.7	0.099
Dibenzo(ah)Anthracene	0.82	0.033	82	4.0	0.099
Benzo(ghi)Perylene	0.82	0.032	82	3.9	0.096

[a] Compounds were spiked into 7 or 8 samples at a concentration of 1.0 mg/Kg.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] Surrogate (OTP = ortho-Terphenyl) was spiked into three samples at a concentration of 5.0 mg/kg.

APPENDIX 4

SUGGESTED EPH DATA REPORTING FORMAT

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EXTRACTABLE PETROLEUM HYDROCARBON (EPH) ANALYSIS

Client:	
Client Sample ID:	Date Received:
Laboratory Sample ID:	Date Extracted:
Matrix:	Date Analyzed:
Percent Moisture:	Date Reported:

EXTRACTABLE PETROLEUM HYDROCARBON (EPH)

Parameter	Results	PQL				Units
C8-C10 Aliphatics						
C10-C12 Aliphatics						
C12-C16 Aliphatics						
C16-C21 Aliphatics						
C21-C34 Aliphatics						
C8-C10 Aromatics						
C10-C12 Aromatics						
C12-C16 Aromatics						
C16-C21 Aromatics						
C21-C34 Aromatics						

SURROGATE RECOVERIES

Surrogate	%Recovery	Acceptance Range
Chloro-octadecane (COD)		50% - 150%
Ortho-terphenyl (OTP)		50% - 150%

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APPENDIX 5

REPORT OF ANALYSIS

SUMMARY SHEET

Client: Client Sample ID Number(s): Laboratory ID Number(s):

SAMPLE INFORMATION

Sample Matrix	¨ Aqueous ¨ Soil ¨ Sediment ¨ Other:	
Analysis Performed	¨ VPH ¨ EPH ¨ VPH and EPH (E-TPH Duplicate samples)	
Condition of Containers	¨ Satisfactory ¨ Broken ¨ Leaking ¨ Other:	
Sample Preservatives	AQUEOUS	¨ N/A ¨ pH ≤ 2 ¨ pH > 2
	SOIL/SEDIMENT	¨ N/A
Sample Temperature	¨ Received on Ice ¨ Received at 4 °C ¨ Other	

ANALYTICAL RESULTS

Parameter	Results	PQL	Units
Volatile Petroleum Hydrocarbons (VPH)			
Extractable Petroleum Hydrocarbons (EPH)			
Equivalent TPH (E-TPH) ** [IF BOTH VPH AND EPH ANALYSES PERFORMED]			

**** Due to overlapping carbon ranges between the VPH and EPH methods and in order to avoid double counting, the analyst must select the higher of the two values to be included for reporting purposes for those ranges effected.**

COMMENTS

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APPENDIX 6*

Petroleum Product Chromatograms

Carburator Cleaner
Automotive Gasoline
Mineral Spirits #1
Mineral Spirits #2
JP-4 Jet Fuel (old)
JP-4 Jet Fuel (new)
JP-5 Jet Fuel
Kerosene
Kerosene (ICP grade)
Gasoline and #2 Diesel Oil
Natural Gas Condensate
#2 Fuel Oil
#2 Fuel Oil (38% aromatic) (See chromatogram in NWTPH-Dx)
#2 Diesel Oil (See chromatogram in NWTPH-Dx)
#2 Diesel Oil and Motor Oil (30w) (See chromatogram in NWTPH-Dx)
2-Cycle Engine Oil #1
2-Cycle Engine Oil #2
2-Cycle Engine Oil #3
Motor Oil (30w) (See chromatogram in NWTPH-Dx)
Automatic Transmission Fluid
Power Steering Fluid
Transformer Oil (used)
Transformer Oil (new)
Hydraulic Fluid #1
Hydraulic Fluid #2
Hydraulic Fluid #3
Mineral Oil #1
Mineral Oil #2
Cutting Oil #1
Cutting Oil #2
Bunker-C #1
Bunker-C #2
CSS-1 (emulsion asphalt)
AR-4000 (asphalt cement)

Non-petroleum Product Chromatograms

Turpentine
Creosote
Synthetic Motor Oil

*** The chromatograms are not available in the "electronic" version. They are included in the printed publication.**

Chromatograms: NWTPH-Gx

Gasoline
Weathered Gasoline
Naphtha
Mineral Spirits #1
Mineral Spirits #2
Mineral Spirits #3

Chromatograms: NWTPH-Dx

#2 Diesel Oil
#2 Diesel Oil/Motor Oil
#2 Fuel Oil (38% Aromatic)
Kerosene (Deodorized)
Jet Fuel A
Bunker C #1
Bunker C #2
Motor Oil 30 Wgt.
Mineral Oil (USP)
Hydraulic Fluid
Transformer Oil
Gas Oil

State of Oregon Department of Environmental Quality

OAR 340-122-0330(5)(c)

Evaluation Parameters

(November 1998)

The score for this parameter is taken from the combination of the two descriptors using the following grid:

Distance to Nearest Well	Number of People at Risk		
	Many	Medium	Few
Near	10	10	5
Medium	10	5	1
Far	5	1	1

State of Oregon Department of Environmental Quality

OAR 340-122-0335(2)

Numeric Soil Cleanup Standards

(November 1998)

The following table contains the required numeric soil cleanup standards based on the level of Total Petroleum Hydrocarbons (TPH) as measured by the analytical methods specified in OAR 340-122-0218.

Fuel	Level		
	Level 1	Level 2	Level 3
TPH (Gasoline)	40 ppm	80 ppm	130 ppm
TPH (Diesel)	100 ppm	500 ppm	1000 ppm

OAR 340-124-0040

Toxicity Characteristic Leaching Procedure

METHOD 1311

TOXICITY CHARACTERISTIC LEACHING PROCEDURE

1.1 SCOPE AND APPLICATION

1.2 The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes.

1.3 If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the TCLP need not be run.

1.4 If an analysis of any one of the liquid fractions of the TCLP extract indicates that a regulated compound is present at such high concentra- tions that, even after accounting for dilution from the other fractions of the extract, the concentration would be above the regulatory level for that compound, then the waste is hazardous and it is not necessary to analyze the remaining fractions of the extract.

1.5 If an analysis of extract obtained using a bottle extractor shows that the concentration of any regulated volatile analyte exceeds the regulatory level for that compound, then the waste is hazardous and extraction using the ZHE is not necessary. However, extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the regulatory level.

2.1 SUMMARY OF METHOD

2.2 For liquid wastes (i.e., those containing less than 0.5% dry solid material), the waste, after filtration through a 0.6 to 0.8 µm glass fiber filter, is defined as the TCLP extract.

2.3 For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatile analytes (see Table 1 for a list of volatile compounds). Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 µm glass fiber filter.

2.4 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3.1 INTERFERENCES

3.2 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.1 APPARATUS AND MATERIALS

4.2 Agitation apparatus: The agitation apparatus must be capable of rotating the extraction vessel in an end-over-end fashion (see Figure 1) at 30 ± 2 rpm. Suitable devices known to EPA are identified in Table 2.

4.3 Extraction Vessels

4.3.1 Zero-Headspace Extraction Vessel (ZHE). This device is for use only when the waste is being tested for the mobility of volatile analytes (i.e., those listed in Table 1). The ZHE (depicted in Figure 2) allows for liquid/solid separation within the device, and effectively precludes headspace. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel (see Section 4.3.1). The vessels shall have an internal volume of 500-600 mL, and be equipped to accommodate a 90-110 mm filter. The devices contain VITON®[1] O-rings which should be replaced frequently. Suitable ZHE devices known to EPA are identified in Table 3.

For the ZHE to be acceptable for use, the piston within the ZHE should be able to be moved with approximately 15 psi or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for TCLP analyses and the manufacturer should be contacted.

The ZHE should be checked for leaks after every extraction. If the device contains a built-in pressure gauge, pressurize the device to 50 psi, allow it to stand unattended for 1 hour, and recheck the pressure. If the device does not have a built-in pressure gauge, pressurize the device to 50 psi, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted.

Some ZHEs use gas pressure to actuate the ZHE piston, while others use mechanical pressure (see Table 3). Whereas the volatiles procedure (see Section 7.3) refers to pounds per square inch (psi), for the mechanically actuated piston, the pressure applied is measured in torque-inch-pounds. Refer to the manufacturer's instructions as to the proper conversion.

[1] VITON® is a trademark of Du Pont.

4.3.2 Bottle Extraction Vessel. When the waste is being evaluated using the nonvolatile extraction, a jar with sufficient capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel.

The extraction bottles may be constructed from various materials, depending on the analytes to be analyzed and the nature of the waste (see Section 4.3.3). It is recommended that borosilicate glass bottles be used instead of other types of glass, especially when inorganics are of concern. Plastic bottles, other than polytetrafluoroethylene, shall not be used if organics are to be investigated. Bottles are available from a number of laboratory suppliers. When this type of extraction vessel is used, the filtration device discussed in Section 4.3.2 is used for initial liquid/solid separation and final extract filtration.

4.4 Filtration Devices: It is recommended that all filtrations be performed in a hood.

4.4.1 Zero-Headspace Extractor Vessel (ZHE): When the waste is evaluated for volatiles, the zero-headspace extraction vessel described in Section 4.2.1 is used for filtration. The device shall be capable of supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation (50 psi).

NOTE: When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.

4.4.2 Filter Holder: When the waste is evaluated for other than volatile analytes, any filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psi or more. The type of filter holder used depends on the properties of the material to be filtered (see Section 4.3.3). These devices shall have a minimum internal volume of 300 mL and be equipped to accommodate a minimum filter size of 47 mm (filter holders having an internal capacity of 1.5 L or greater, and equipped to accommodate a 142 mm diameter filter, are recommended). Vacuum filtration can only be used for wastes with low solids content (<10%) and for highly granular, liquid-containing wastes. All other types of wastes should be filtered using positive pressure filtration. Suitable filter holders known to EPA are shown in Table 4.

4.4.3 Materials of Construction: Extraction vessels and filtration devices shall be made of inert materials which will not leach or absorb waste components. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride (PVC) may be used only when evaluating the mobility of metals. Borosili-

One-liter bottles are recommended for use over other types of glass bottles, especially when inorganics are analytes of concern.

4.5 Filters: Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6 to 0.8 µm, or equivalent. Filters known to EPA which meet these specifications are identified in Table 5. Pre-filters must not be used. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 1N nitric acid followed by three consecutive rinses with deionized distilled water (a minimum of 1 L per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

4.5 pH Meters: The meter should be accurate to ± 0.05 units at 25 °C.

4.6 ZHE Extract Collection Devices: TEDLAR®[2] bags or glass, stainless steel or PTFE gas-tight syringes are used to collect the initial liquid phase and the final extract of the waste when using the ZHE device. The devices listed are recommended for use under the following conditions:

4.6.1 If a waste contains an aqueous liquid phase or if a waste does not contain a significant amount of nonaqueous liquid (i.e., <1% of total waste), the TEDLAR® bag or a 600 mL syringe should be used to collect and combine the initial liquid and solid extract.

4.6.2 If a waste contains a significant amount of nonaqueous liquid in the initial liquid phase (i.e., >1% of total waste), the syringe or the TEDLAR® bag may be used for both the initial solid/liquid separation and the final extract filtration. However, analysts should use one or the other, not both.

4.6.3 If the waste contains no initial liquid phase (is 100% solid) or has no significant solid phase (is 100% liquid), either the TEDLAR® bag or the syringe may be used. If the syringe is used, discard the first 5 mL of liquid expressed from the device. The remaining aliquots are used for analysis.

4.7 ZHE Extraction Fluid Transfer Devices: Any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is acceptable (e.g., a positive displacement or peristaltic pump, a gas tight syringe, pressure filtration unit (see Section 4.3.2), or other ZHE device).

4.8 Laboratory Balance: Any laboratory balance accurate to within ± 0.01 grams may be used (all weight measurements are to be within ± 0.1 grams).

4.9 Beaker or Erlenmeyer flask, glass, 500 mL.

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[2] TEDLAR® is a registered trademark of Du Pont.

4.10 Watchglass, appropriate diameter to cover beaker or Erlenmeyer flask.

4.11 Magnetic stirrer.

5.1 REAGENTS

5.2 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.3 Reagent Water. Reagent water is defined as water in which an interferant is not observed at or above the method's detection limit of the analyte(s) of interest. For nonvolatile extractions, ASTM Type II water or equivalent meets the definition of reagent water. For volatile extractions, it is recommended that reagent water be generated by any of the following methods. Reagent water should be monitored periodically for impurities.

5.3.1 Reagent water for volatile extractions may be generated by passing tap water through a carbon filter bed containing about 500 grams of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.3.2 A water purification system (Millipore Super-Q or equivalent) may also be used to generate reagent water for volatile extractions.

5.3.3 Reagent water for volatile extractions may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the water temperature at 90 $\pm$ 5 degrees C, bubble a contaminant-free inert gas (e.g. nitrogen) through the water for 1 hour. While still hot, transfer the water to a narrow mouth screw-cap bottle under zero-headspace and seal with a Teflon-lined septum and cap.

5.4 Hydrochloric acid (1N), HCl, made from ACS reagent grade.

5.5 Nitric acid (1N), HNO_3, made from ACS reagent grade.

5.6 Sodium hydroxide (1N), NaOH, made from ACS reagent grade.

5.7 Glacial acetic acid, CH_3CH_2OOH, ACS reagent grade.

5.8 Extraction fluid.

5.8.1 Extraction fluid # 1: Add 5.7 mL glacial CH_3CH_2OOH to 500 mL of reagent water (See Section 5.2), add 64.3 mL of 1N NaOH, and dilute to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 4.93 $\pm$ 0.05.

5.8.2 Extraction fluid # 2: Dilute 5.7 mL glacial CH_3CH_2OOH with reagent water (See Section 5.2) to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 2.88 $\pm$ 0.05.

NOTE: These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid shall be discarded and fresh extraction fluid prepared.

5.9 Analytical standards shall be prepared according to the appropriate analytical method.

6.1 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.2 All samples shall be collected using an appropriate sampling plan.

6.3 The TCLP may place requirements on the minimal size of the field sample, depending upon the physical state or states of the waste and the analytes of concern. An aliquot is needed for preliminary evaluation of which extraction fluid is to be used for the nonvolatile analyte extraction procedure. Another aliquot may be needed to actually conduct the nonvolatile extraction (see Section 1.4 concerning the use of this extract for volatile organics). If volatile organics are of concern, another aliquot may be needed. Quality control measures may require additional aliquots. Further, it is always wise to collect more sample just in case something goes wrong with the initial attempt to conduct the test.

6.3 Preservatives shall not be added to samples before extraction.

6.4 Samples may be refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

6.5 When the waste is to be evaluated for volatile analytes, care shall be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g., samples should be collected in Teflon-lined septum capped vials and stored at 4 °C. Samples should be opened only immediately prior to extraction).

6.6 TCLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH < 2, unless precipitation occurs (see Section 7.2.14 if precipitation occurs). Extracts should be preserved for other analytes according to the guidance given in the individual analysis methods. Extracts or portions of extracts for organic analyte determinations shall not be allowed to come into contact with the atmosphere (i.e., no headspace) to prevent losses. See Section 8.0 (QA requirements) for acceptable sample and extract holding times.

7.2 Preliminary Evaluations

Perform preliminary TCLP evaluations on a minimum 100 gram aliquot of waste. This aliquot may not actually undergo TCLP extraction. These preliminary evaluations include: (1) determination of the percent solids (Section 7.1.1);
(2) determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration (Section 7.1.2); (3) determination of whether the solid portion of the waste requires particle size reduction (Section 7.1.3); and (4) determination of which of the two extraction fluids are to be used for the nonvolatile TCLP extraction of the waste (Section 7.1.4).

7.1.1 Preliminary determination of percent solids: Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below.

7.1.1.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solids) proceed to Section 7.1.3.

7.1.1.2 If the sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device described in Section 4.3.2 and is outlined in Sections 7.1.1.3 through 7.1.1.9.

7.1.1.3 Pre-weigh the filter and the container that will receive the filtrate.

7.1.1.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

7.1.1.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight.

7.1.1.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.1.1.7 Quantitatively transfer the waste sample to the filter holder (liquid and solid phases). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room temperature then allow the sample to warm up to room temperature in the device before filtering.

NOTE: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Section 7.1.1.5 to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within any 2 minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.1.1.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Section 7.1.1.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.1.1.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (see Section 7.1.1.3) from the total weight of the filtrate-filled container. Determine the weight of the solid phase of the waste sample by subtracting the weight of the liquid phase from the weight of the total waste sample, as determined in Section 7.1.1.5 or 7.1.1.7.

Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\text{Percent solids} = \frac{\text{Weight of solid (Section 7.1.1.9)}}{\text{Total weight of waste (Section 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2 If the percent solids determined in Section 7.1.1.9 is equal to or greater than 0.5%, then proceed either to Section 7.1.3 to

determine whether the solid material requires particle size reduction or to Section 7.1.2.1 if it is noticed that a small amount of the filtrate is entrained in wetting of the filter. If the percent solids determined in Section 7.1.1.9 is less than 0.5%, then proceed to Section 7.2.9 if the nonvolatile TCLP is to be performed and to Section 7.3 with a fresh portion of the waste if the volatile TCLP is to be performed.

7.1.2.1 Remove the solid phase and filter from the filtration apparatus.

7.1.2.2 Dry the filter and solid phase at 100 ± 20 °C until two successive weighing yield the same value within ± 1%. Record the final weight.

NOTE: Caution should be taken to ensure that the subject solid will not flash upon heating. It is recommended that the drying oven be vented to a hood or other appropriate device.

7.1.2.3 Calculate the percent dry solids as follows: (Wt. of dry waste + filter) - tared wt. of filter

$$\text{Percent dry solids} = \frac{\text{(Wt. of dry waste + filter) - tared wt. of filter}}{\text{Initial wt. of waste (Section 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2.4 If the percent dry solids is less than 0.5%, then proceed to Section 7.2.9 if the nonvolatile TCLP is to be performed, and to Section 7.3 if the volatile TCLP is to be performed. If the percent dry solids is greater than or equal to 0.5%, and if the nonvolatile TCLP is to be performed, return to the beginning of this Section (7.1) and, with a fresh portion of waste, determine whether particle size reduction is necessary (Section 7.1.3) and determine the appropriate extraction fluid (Section 7.1.4). If only the volatile TCLP is to be performed, see the note in Section 7.1.4.

7.1.3 Determination of whether the waste requires particle size reduction (particle size is reduced during this step): Using the solid portion of the waste, evaluate the solid for particle size. Particle size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1 cm^2, or is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm (0.375 inch) standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above. If the solids are prepared for organic volatiles extraction, special precautions must be taken (see Section 7.3.6).

NOTE: Surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet

the crushed sample specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

7.1.4 Determination of appropriate extraction fluid: If the solid content of the waste is greater than or equal to 0.5% and if the sample will be extracted for nonvolatile constituents (Section 7.2), determine the appropriate fluid (Section 5.7) for the nonvolatiles extraction as follows:

NOTE: TCLP extraction for volatile constituents uses only extraction fluid #1 (Section 5.7.1). Therefore, if TCLP extraction for nonvolatiles is not required, proceed to Section 7.3.

7.1.4.1 Weigh out a small subsample of the solid phase of the waste, reduce the solid (if necessary) to a particle size of approximately 1 mm in diameter or less, and transfer 5.0 grams of the solid phase of the waste to a 500 mL beaker or Erlenmeyer flask.

7.1.4.2 Add 96.5 mL of reagent water to the beaker, cover with a watchglass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is <5.0, use extraction fluid #1. Proceed to Section 7.2.

7.1.4.3 If the pH from Section 7.1.4.2 is >5.0, add 3.5 mL 1N HCl, slurry briefly, cover with a watchglass, heat to 50 °C, and hold at 50 °C for 10 minutes.

7.1.4.4 Let the solution cool to room temperature and record the pH. If the pH is <5.0, use extraction fluid #1. If the pH is >5.0, use extraction fluid #2. Proceed to Section 7.2.

7.1.5 If the aliquot of the waste used for the preliminary evaluation (Sections 7.1.1 - 7.1.4) was determined to be 100% solid at Section 7.1.1.1, then it can be used for the Section 7.2 extraction (assuming at least 100 grams remain), and the Section 7.3 extraction (assuming at least 25 grams remain). If the aliquot was subjected to the procedure in Section 7.1.1.7, then another aliquot shall be used for the volatile extraction procedure in Section 7.3. The aliquot of the waste subjected to the procedure in Section 7.1.1.7 might be appropriate for use for the Section 7.2 extraction if an adequate amount of solid (as determined by Section 7.1.1.9) was obtained. The amount of solid necessary is dependent upon whether a sufficient amount of extract will be produced to support the analyses. If an adequate amount of solid remains, proceed to Section 7.2.10 of the nonvolatile TCLP extraction.

7.2 Procedure When Volatiles are not Involved

A minimum sample size of 100 grams (solid and liquid phases) is recommend- ed. In some cases, a larger sample size may be appropriate, depending on the

solids content of the waste sample (percent solids, See Section 7.1.1), whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of TCLP extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single TCLP extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

7.2.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solid, see Section 7.1.1), weigh out a subsample of the waste (100 gram minimum) and proceed to Section 7.2.9.

7.2.2 If the sample is liquid or multiphasic, liquid/solid separation is required. This involves the filtration device described in Section 4.3.2 and is outlined in Sections 7.2.3 to 7.2.8.

7.2.3 Pre-weigh the container that will receive the filtrate.

7.2.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (see Section 4.4).

NOTE: Acid washed filters may be used for all nonvolatile extractions even when metals are not of concern.

7.2.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight. If the waste contains <0.5% dry solids (Section 7.1.2), the liquid portion of the waste, after filtration, is defined as the TCLP extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required of the TCLP extract. For wastes containing >0.5% dry solids (Sections 7.1.1 or 7.1.2), use the percent solids information obtained in Section 7.1.1 to determine the optimum sample size (100 gram minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the TCLP extract.

7.2.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the waste is centrifuged, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.2.7 Quantitatively transfer the waste sample (liquid and solid phases) to the filter holder (see Section 4.3.2). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at

room temperature, then allow the sample to warm up to room temperature in the device before filtering.

NOTE: If waste material (>1% of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Section 7.2.5, to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within a 2 minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.2.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase may now be either analyzed (See Section 7.2.12) or stored at 4 °C until time of analysis.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Section 7.2.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the extraction as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.2.9 If the waste contains <0.5% dry solids (see Section 7.1.2), proceed to Section 7.2.13. If the waste contains >0.5% dry solids (see Section 7.1.1 or 7.1.2), and if particle size reduction of the solid was needed in Section 7.1.3, proceed to Section 7.2.10. If the waste as received passes a 9.5 mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to Section 7.2.11.

7.2.10 Prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described in Section 7.1.3. When the surface area or particle size has been appropriately altered, quantitatively transfer the solid

material into an extractor bottle. Include the filter used to separate the initial liquid from the solid phase.

NOTE: Sieving of the waste is not normally required. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended. If sieving is necessary, a Teflon coated sieve should be used to avoid contamination of the sample.

7.2.11 Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (Section 7.1.1)} \times \text{weight of waste filtered (Section 7.2.5 or 7.2.7)}}{100}$$

Slowly add this amount of appropriate extraction fluid (see Section 7.1.4) to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal), secure in rotary agitation device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at 23 ± 2 °C during the extraction period.

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of wastes (e.g., limed or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

7.2.12 Following the 18 ± 2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in Section 7.2.7. For final filtration of the TCLP extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filter(s) shall be acid-washed (see Section 4.4) if evaluating the mobility of metals.

7.2.13 Prepare the TCLP extract as follows:

7.2.13.1 If the waste contained no initial liquid phase, the filtered liquid material obtained from Section 7.2.12 is defined as the TCLP extract. Proceed to Section 7.2.14.

7.2.13.2 If compatible (e.g., multiple phases will not result on combination), combine the filtered liquid resulting from Section 7.2.12 with the initial liquid phase of the waste obtained in Section 7.2.7. This combined liquid is defined as the TCLP extract. Proceed to Section 7.2.14.

7.2.13.3 If the initial liquid phase of the waste, as obtained from Section 7.2.7, is not or may not be compatible with the filtered liquid resulting from Section 7.2.12, do not combine these liquids. Analyze these liquids, collectively defined as the TCLP extract, and combine the results mathematically, as described in Section 7.2.14.

7.2.14 Following collection of the TCLP extract, the pH of the extract should be recorded. Immediately aliquot and preserve the extract for analysis. Metals aliquots must be acidified with nitric acid to pH <2. If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses shall not be acidified and the extract shall be analyzed as soon as possible. All other aliquots must be stored under refrigeration (4 °C) until analyzed. The TCLP extract shall be prepared and analyzed according to appropriate analytical methods. TCLP extracts to be analyzed for metals shall be acid digested except in those instances where digestion causes loss of metallic analytes. If an analysis of the undigested extract shows that the concentration of any regulated metallic analyte exceeds the regulatory level, then the waste is hazardous and digestion of the extract is not necessary. However, data on undigested extracts alone cannot be used to demonstrate that the waste is not hazardous. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to $\pm$ 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phase (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.2.15 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

7.3 Procedure When Volatiles are Involved

Use the ZHE device to obtain TCLP extract for analysis of volatile compounds only. Extract resulting from the use of the ZHE shall not be used to evaluate the mobility of nonvolatile analytes (e.g., metals, pesticides, etc.).

The ZHE device has approximately a 500 mL internal capacity. The ZHE can thus accommodate a maximum of 25 grams of solid (defined as that fraction of a

sample from which no additional liquid may be forced out by an applied pressure of 50 psi), due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase.

Charge the ZHE with sample only once and do not open the device until the final extract (of the solid) has been collected. Repeated filling of the ZHE to obtain 25 grams of solid is not permitted.

Do not allow the waste, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any manipulation of these materials should be done when cold (4 °C) to minimize loss of volatiles.

7.3.1 Pre-weigh the (evacuated) filtrate collection container (See Section 4.6) and set aside. If using a TEDLAR® bag, express all liquid from the ZHE device into the bag, whether for the initial or final liquid/solid separation, and take an aliquot from the liquid in the bag for analysis. The containers listed in Section 4.6 are recommended for use under the conditions stated in Sections 4.6.1 - 4.6.3.

7.3.2 Place the ZHE piston within the body of the ZHE (it may be helpful first to moisten the piston O-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample (based upon sample size requirements determined from Section 7.3, Section 7.1.1 and/or 7.1.2). Secure the gas inlet/outlet flange (bottom flange) onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange (top flange) aside.

7.3.3 If the waste is 100% solid (see Section 7.1.1), weigh out a subsample (25 gram maximum) of the waste, record weight, and proceed to Section 7.3.5.

7.3.4 If the waste contains < 0.5% dry solids (Section 7.1.2), the liquid portion of waste, after filtration, is defined as the TCLP extract. Filter enough of the sample so that the amount of filtered liquid will support all of the volatile analyses required. For wastes containing $\geq$ 0.5% dry solids (Sections 7.1.1 and/or 7.1.2), use the percent solids information obtained in Section 7.1.1 to determine the optimum sample size to charge into the ZHE. The recommended sample size is as follows:

7.3.4.1 For wastes containing < 5% solids (see Section 7.1.1), weigh out a 500 gram subsample of waste and record the weight.

7.3.4.2 For wastes containing $\geq$ 5% solids (see Section 7.1.1), determine the amount of waste to charge into the ZHE as follows:

$$\text{Weight of waste to charge ZHE} = \frac{25}{\text{percent solids (Section 7.1.1)}} \times 100$$

Weigh out a subsample of the waste of the appropriate size and record the weight.

7.3.5 If particle size reduction of the solid portion of the waste was required in Section 7.1.3, proceed to Section 7.3.6. If particle size reduction was not required in Section 7.1.3, proceed to Section 7.3.7.

7.3.6 Prepare the waste for extraction by crushing, cutting, or grinding the solid portion of the waste to a surface area or particle size as described in Section 7.1.3. Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4 °C prior to particle size reduction. The means used to effect particle size reduction must not generate heat in and of itself. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.

NOTE: Sieving of the waste is not recommended due to the possibility that volatiles may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended.

When the surface area or particle size has been appropriately altered, proceed to Section 7.3.7.

7.3.7 Waste slurries need not be allowed to stand to permit the solid phase to settle. Do not centrifuge wastes prior to filtration.

7.3.8 Quantitatively transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens onto the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extract collection device to the top plate.

NOTE: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in Section 7.3.4 to determine the weight of the waste sample that will be filtered.

Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-10 psi (or more if necessary) to force all headspace

slowly out of the ZHE device into a hood. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room tempera- ture, then allow the sample to warm up to room temperature in the device before filtering. If the waste is 100% solid (see Section 7.1.1), slowly increase the pressure to a maximum of 50 psi to force most of the headspace out of the device and proceed to Section 7.3.12.

7.3.9 Attach the evacuated pre-weighed filtrate collection container to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1-10 psi to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate within a 2 minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.3.10 The material in the ZHE is defined as the solid phase of the waste and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the TCLP extraction as a solid.

If the original waste contained <0.5% dry solids (see Section 7.1.2), this filtrate is defined as the TCLP extract and is analyzed directly. Proceed to Section 7.3.15.

7.3.11 The liquid phase may now be either analyzed immediately (See Sections 7.3.13 through 7.3.15) or stored at 4 °C under minimal headspace conditions until time of analysis. Determine the weight of extraction fluid #1 to add to the ZHE as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (Section 7.1.1)} \times \text{weight of waste filtered (Section 7.3.4 or 7.3.8)}}{100}$$

7.3.12 The following Sections detail how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid #1 is used in all cases (See Section 5.7).

7.3.12.1 With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid in- let/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.

7.3.12.2 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5-10 psi (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5-10 psi and check all ZHE fittings to ensure that they are closed.

7.3.12.3 Place the ZHE in the rotary agitation appara- tus (if it is not already there) and rotate at 30 $\pm$ 2 rpm for 18 $\pm$ 2 hours. Ambient temperature (i.e., temperature of room in which extraction occurs) shall be maintained at 23 $\pm$ 2 °C during agita- tion.

7.3.13 Following the 18 $\pm$ 2 hour agitation period, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If the pressure has not been maintained (i.e., no gas release observed), the device is leaking. Check the ZHE for leaking as specified in Section 4.2.1, and perform the extraction again with a new sample of waste. If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases. If the waste contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container (i.e., TEDLAR® bag) holding the initial liquid phase of the waste. A separate filtrate collection container must be used if combining would create multiple phases, or there is not enough volume left within the filtrate collection container. Filter through the glass fiber filter, using the ZHE device as discussed in Section 7.3.9. All extract shall be filtered and collected if the

bag is used, if the extract is multiphasic, or if the waste contained an initial liquid phase (see Sections 4.6 and 7.3.1).

NOTE: An in-line glass fiber filter may be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured.

7.3.14 If the original waste contained no initial liquid phase, the filtered liquid material obtained from Section 7.3.13 is defined as the TCLP extract. If the waste contained an initial liquid phase, the filtered liquid material obtained from Section 7.3.13 and the initial liquid phase (Section 7.3.9) are collectively defined as the TCLP extract.

7.3.15 Following collection of the TCLP extract, immediately prepare the extract for analysis and store with minimal headspace at 4 °C until analyzed. Analyze the TCLP extract according to the appropriate analytical methods. If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phases (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.3.16 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

8.1 QUALITY ASSURANCE

8.2 A minimum of one blank (using the same extraction fluid as used for the samples) must be analyzed for every 20 extractions that have been conducted in an extraction vessel.

8.3 A matrix spike shall be performed for each waste type (e.g., wastewater treatment sludge, contaminated soil, etc.) unless the result exceeds the regulatory level and the data are being used solely to demonstrate that the waste property exceeds the regulatory level. A minimum of one matrix spike must be analyzed for each analytical batch. As a minimum, follow the matrix spike addition guidance provided in each analytical method.

8.3.1 Matrix spikes are to be added after filtration of the TCLP extract and before preservation. Matrix spikes should not be added prior to TCLP extraction of the sample.

8.3.2 In most cases, matrix spikes should be added at a concentration equivalent to the corresponding regulatory level. If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentra- tion, but may not be not less than five times the method detection limit. In order to avoid differences in matrix effects, the matrix spikes must be added to the same nominal volume of TCLP extract as that which was analyzed for the unspiked sample.

8.3.3 The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to determine whether matrix interferences exist. Use of other internal calibration methods, modification of the analytical methods, or use of alternate analytical methods may be needed to accurately measure the analyte concentration in the TCLP extract when the recovery of the matrix spike is below the expected analytical method performance.

8.3.4 Matrix spike recoveries are calculated by the following formula:

$$\%R\ (\%Recovery) = 100\ (X_s - X_u)/K$$

where:
X_s = measured value for the spiked sample,
X_u = measured value for the unspiked sample, and
K = known value of the spike in the sample.

8.4 All quality control measures described in the appropriate analytical methods shall be followed.

8.5 The use of internal calibration quantitation methods shall be employed for a metallic contaminant if: (1) Recovery of the contaminant from the TCLP extract is not at least 50% and the concentration does not exceed the regulatory level, and (2) The concentration of the contaminant measured in the extract is within 20% of the appropriate regulatory level.

8.4.1. The method of standard additions shall be employed as the internal calibration quantitation method for each metallic contaminant.

8.4.2 The method of standard additions requires preparing calibration standards in the sample matrix rather than reagent water or blank solution. It requires taking four identical aliquots of the solution and adding known amounts of standard to three of these aliquots. The forth aliquot is the unknown. Preferably, the first addition should be prepared so that the resulting concentration is approximately 50% of the expected concentration of the sample. The second and third additions should be prepared so that the concentrations are approximately 100% and

150% of the expected concentration of the sample. All four aliquots are maintained at the same final volume by adding reagent water or a blank solution, and may need dilution adjustment to maintain the signals in the linear range of the instrument technique. All four aliquots are analyzed.

8.4.3 Prepare a plot, or subject data to linear regression, of instrument signals or external-calibration-derived concentrations as the dependant variable (y-axis) versus concentrations of the additions of standard as the independent variable (x-axis). Solve for the intercept of the abscissa (the independent variable, x-axis) which is the concentration in the unknown.

8.4.4 Alternately, subtract the instrumental signal or external- calibration-derived concentration of the unknown (unspiked) sample from the instrumental signals or external-calibration-derived concentrations of the standard additions. Plot or subject to linear regression of the corrected instrument signals or external-calibration-derived concentra- tions as the dependant variable versus the independent variable. Derive concentrations for unknowns using the internal calibration curve as if it were an external calibration curve.

8.5 Samples must undergo TCLP extraction within the following time periods:

SAMPLE MAXIMUM HOLDING TIMES [DAYS]

	From: Field collection To: TCLP extraction	From: TCLP extraction To: Preparative extraction	From: Preparative extraction To: Determinative analysis	Total elapsed time
Volatiles	14	NA	14	28
Semi-volatiles	14	7	40	61
Mercury	28	NA	28	56
Metals, except mercury	180	NA	180	360

NA = Not applicable

If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding the holding time is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory level.

9.1 METHOD PERFORMANCE

9.2 Ruggedness. Two ruggedness studies have been performed to determine the effect of various perturbations on specific elements of the TCLP protocol. Ruggedness testing determines the sensitivity of small procedural variations which might be expected to occur during routine laboratory application.

9.2.1 Metals - The following conditions were used when leaching a waste for metals analysis:

Varying Conditions	
Liquid/Solid ratio	19:1 vs. 21:1
Extraction time	16 hours vs. 18 hours
Headspace	20% vs. 60%
Buffer #2 acidity	190 meq vs. 210 meq
Acid-washed filters	yes vs. no
Filter type	0.7 µm glass fiber vs. 0.45 µm vs. polycarbonate
Bottle type	borosilicate vs. flint glass

Of the seven method variations examined, acidity of the extraction fluid had the greatest impact on the results. Four of 13 metals from an API separator sludge/electroplating waste (API/EW) mixture and two of three metals from an ammonia lime still bottom waste were extracted at higher levels by the more acidic buffer. Because of the sensitivity to pH changes, the method requires that the extraction fluids be prepared so that the final pH is within $\pm$ 0.05 units as specified.

9.2.2 Volatile Organic Compounds - The following conditions were used when leaching a waste for VOC analysis:

Varying Conditions	
Liquid/Solid ratio	19:1 vs. 21:1
Headspace	0% vs. 5%
Buffer #1 acidity	60 meq vs. 80 meq
Method of storing extract	Syringe vs. Tedlar® bag
Aliquotting	yes vs. no
Pressure behind piston	0 psi vs. 20 psi

None of the parameters had a significant effect on the results of the ruggedness test.

9.3 Precision. Many TCLP precision (reproducibility) studies have been performed, and have shown that, in general, the precision of the TCLP is comparable to or exceeds that of the EP toxicity test and that method precision is adequate. One of the more significant contributions to poor precision appears to be related to sample homogeneity and inter-laboratory variation (due to the nature of waste materials).

9.3.1 Metals - The results of a multi-laboratory study are shown in Table 6, and indicate that a single analysis of a waste may not be adequate for waste characterization and identification requirements.

9.3.2 Semi-Volatile Organic Compounds - The results of two studies are shown in Tables 7 and 8. Single laboratory precision was excellent with greater than 90 percent of the results exhibiting an RSD less than 25 percent. Over 85 percent of all individual compounds in the multi-laboratory study fell in the RSD range of 20 - 120 percent. Both studies concluded that the TCLP provides adequate precision. It was also determined that the high acetate content of the extraction fluid did not present problems (i.e., column degradation of the gas chromatograph) for the analytical conditions used.

9.3.3 Volatile Organic Compounds - Eleven laboratories participated in a collaborative study of the use of the ZHE with two waste types which were fortified with a mixture of VOCs. The results of the collaborative study are shown in Table 9. Precision results for VOCs tend to occur over a considerable range. However, the range and mean RSD compared very closely to the same collaborative study metals results in Table 6. Blackburn and Show concluded that at the 95% level of signifi- cance: 1) recoveries among laboratories were statistically similar, 2) recoveries did not vary significantly between the two sample types, and 3) each laboratory showed the same pattern of recovery for each of the two samples.

10.0 REFERENCES

1. Blackburn, W.B. and Show, I. "Collaborative Study of the Toxicity Characteristics Leaching Procedure (TCLP)." Draft Final Report, Contract No. 68- 03-1958, S-Cubed, November 1986.

2. Newcomer, L.R., Blackburn, W.B., Kimmell, T.A. "Performance of the Toxicity Characteristic Leaching Procedure." Wilson Laboratories, S-Cubed, U.S. EPA, December 1986.

3. Williams, L.R., Francis, C.W.; Maskarinec, M.P., Taylor D.R., and Rothman, N. "Single-Laboratory Evaluation of Mobility Procedure for Solid Waste." EMSL, ORNL, S-Cubed, ENSECO.

Table 1.
Volatile Analytes[1,2]

Compound	CAS No.
Acetone	67-64-1
Benzene	71-43-2
n-Butyl alcohol	71-36-3
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroform	67-66-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethylene	75-35-4
Ethyl acetate	141-78-6
Ethyl benzene	100-41-4
Ethyl ether	60-29-7
Isobutanol	78-83-1
Methanol	67-56-1
Methylene chloride	75-09-2
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-1
Tetrachloroethylene	127-18-4
Toluene	108-88-3
1,1,1,-Trichloroethane	71-55-6
Trichloroethylene	79-01-6
Trichlorofluoromethane	75-69-4
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1
Vinyl chloride	75-01-4
Xylene	1330-20-7

[1] When testing for any or all of these analytes, the zero-headspace extractor vessel shall be used instead of the bottle extractor.

[2] Benzene, carbon tetrachloride, chlorobenzene, chloroform, 1,2-dichloroethane, 1,1-dichloroethylene, methyl ethyl ketone, tetrachloroethylene, and vinyl chloride are toxicity characteristic constituents.

Table 2.
Suitable Rotary Agitation Apparatus[1]

Company	Location	Model No.
Analytical Testing and Services,	Warrington, PA (215) 343-4490	4-vessel extractor (DC20S) Consulting 8-vessel extractor (DC20) Inc. 12-vessel extractor (DC20B) 24-vessel extractor (DC24C)
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	2-vessel (3740-2-BRE) 4-vessel (3740-4-BRE) 6-vessel (3740-6-BRE) 8-vessel (3740-8-BRE) 12-vessel (3740-12-BRE) 24-vessel (3740-24-BRE)
Environmental Machine and Inc.	Lynchburg, VA (804) 845-6424	8-vessel (08-00-00) Design, 4-vessel (04-00-00)
IRA Machine Shop and Laboratory	Santurce, PR (809) 752-4004	8-vessel (011001)
Lars Lande Manufacturing	Whitmore Lake, MI (313) 449-4116	10-vessel (10VRE) 5-vessel (5VRE) 6-vessel (6VRE)
Millipore Corp.	Bedford, MA (800) 225-3384	4-ZHE or 4 2-liter bottle extractor (YT31ORAHW)

[1] Any device that rotates the extraction vessel in an end-over-end fashion at 30 $\pm$ 2 rpm is acceptable.

Table 3.
Suitable Zero-Headspace Extractor Vessels[1]

Company	Location	Model No.
Analytical Testing & Consulting Services, Inc.	Warrington, PA (215) 343-4490	C1O2, Mechanical Pressure Device
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	3745-ZHE, Gas Pressure Device
Lars Lande Manufacturing[2]	Whitmore Lake, MI (313) 449-4116	ZHE-11, Gas Pressure Device
Millipore Corporation	Bedford, MA (800) 225-3384	YT30O9OHW, Gas Pressure Device
Environmental Machine and Design, Inc.	Lynchburg, VA (804) 845-6424	VOLA-TOX1, Gas Pressure Device
Gelman Science	Ann Arbor, MI 521-1520	15400 Gas Pressure (800) Device

[1] Any device that meets the specifications listed in Section 4.2.1 of the method is suitable.

[2] This device uses a 110 mm filter.

Table 4.
Suitable Filter Holders[1]

Company	Location	Model/ Catalogue No.	Size
Nucleopore Corporation	Pleasanton, CA (800) 882-7711	425910 410400	142 mm 47 mm
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	302400 311400	142 mm 47 mm
Millipore Corporation	Bedford, MA (800) 225-3384	YT30142HW XX1004700	142 mm 47 mm

[1] Any device capable of separating the liquid from the solid phase of the waste is suitable, providing that it is chemically compatible with the waste and the constituents to be analyzed. Plastic devices (not listed above) may be used when only inorganic analytes are of concern. The 142 mm size filter holder is recommended.

Table 5.
Suitable Filter Media[1]

Company	Location	Model	Pore Size (µm)
Millipore Corporation	Bedford, MA (800) 225-3384	AP40	0.7
Nucleopore Corporation	Pleasanton, CA (415) 463-2530	211625	0.7
Whatman Laboratory Products, Inc.	Clifton, NJ (201) 773-5800	GFF	0.7
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	GF75	0.7
Gelman Science	Ann Arbor, MI (800) 521-1520	66256 (90mm) 66257 (142mm)	0.7

[1] Any filter that meets the specifications in Section 4.4 of the Method is suitable.

Table 6. Multi-Laboratory TCLP Metals, Precision

Waste	Extraction Fluid	Metal	$\bar{X}$	S	%RSD
Ammonia	#1	Cadmium	0.053	0.031	60
Lime Still	#2		0.023	0.017	76
Bottoms	#1	Chromium	0.015	0.0014	93
	#2		0.0032	0.0037	118
	#1	Lead	0.0030	0.0027	90
	#2		0.0032	0.0028	87
API/EW	#1	Cadmium	0.0046	0.0028	61
Mixture	#2		0.0005	0.0004	77
	#1	Chromium	0.0561	0.0227	40
	#2		0.105	0.018	17
	#1	Lead	0.0031	0.0031	100
	#2		0.0124	0.0136	110
Fossil	#1	Cadmium	0.080	0.069	86
Fuel Fly	#2		0.093	0.067	72
Ash	#1	Chromium	0.017	0.014	85
	#2		0.070	0.040	57
	#1	Lead	0.0087	0.0074	85
	#2		0.0457	0.0083	18
				%RSD Range = 17 - 118 Mean	
				%RSD = 74	

NOTE: $\bar{X}$ = Mean results from 6 - 12 different laboratories Units = mg/L
Extraction Fluid #1 = pH 4.9
#2 = pH 2.9

Table 7. Single-Laboratory Semi-Volatiles, Precision

Waste	Compound	Extraction Fluid	$\overline{X}$	S	%RSD
Ammonia Lime Still Bottoms	Phenol	#1	19000	2230	11.6
		#2	19400	929	4.8
	2-Methylphenol	#1	2000	297	14.9
		#2	1860	52.9	2.8
	4-Methylphenol	#1	7940	1380	17.4
		#2	7490	200	2.7
	2,4-Dimethylphenol	#1	321	46.8	14.6
		#2	307	45.8	14.9
	Naphthalene	#1	3920	413	10.5
		#2	3827	176	4.6
	2-Methylnaphthalene	#1	290	44.8	15.5
		#2	273	19.3	7.1
	Dibenzofuran	#1	187	22.7	12.1
		#2	187	7.2	3.9
	Acenaphthylene	#1	703	89.2	12.7
		#2	663	20.1	3.0
	Fluorene	#1	151	17.6	11.7
		#2	156	2.1	1.3
	Phenanthrene	#1	241	22.7	9.4
		#2	243	7.9	3.3
	Anthracene	#1	33.2	6.19	18.6
		#2	34.6	1.55	4.5
	Fluoranthrene	#1	25.3	1.8	7.1
		#2	26.0	1.8	7.1
API/EW Mixture	Phenol	#1	40.7	13.5	33.0
		#2	19.0	1.76	9.3
	2,4-Dimethylphenol	#1	33.0	9.35	28.3
		#2	43.3	8.61	19.9
	Naphthalene	#1	185	29.4	15.8
		#2	165	24.8	15.0
	2-Methylnaphthalene	#1	265	61.2	23.1
		#2	200	18.9	9.5
				%RSD Range = 1 - 33	
				Mean %RSD = 12	

NOTE: Units = µg/L
Extractions were performed in triplicate
All results were at least 2x the detection limit Extraction Fluid #1 = pH 4.9
#2 = pH 2.9

Table 8. Multi-Laboratory Semi-Volatiles, Precision

Waste	Compound	Extraction Fluid	$\bar{X}$	S	%RSD
Ammonia Lime	BNAs	#1	10043	7680	76.5
Still Bottoms (A)		#2	10376	6552	63.1
API/EW	BNAs	#1	1624	675	41.6
Mixture (B)		#2	2074	1463	70.5
Fossil Fuel	BNAs	#1	750	175	23.4
Fly Ash (C)		#2	739	342	46.3
					Mean %RSD = 54

NOTE: Units = µg/L
X = Mean results from 3 - 10 labs Extraction Fluid #1 = pH 4.9
#2 = pH 2.9

%RSD Range for Individual Compounds

A, #1	0 - 113
A, #2	28 - 108
B, #1	20 - 156
B, #2	49 - 128
C, #1	36 - 143
C, #2	61 - 164

Table 9. Multi-Laboratory (11 Labs) VOCs, Precision

Waste	Compound	$\bar{X}$	S	%RSD
Mine Tailings	Vinyl chloride	6.36	6.36	100
	Methylene chloride	12.1	11.8	98
	Carbon disulfide	5.57	2.83	51
	1,1-Dichloroethene	21.9	27.7	127
	1,1-Dichloroethane	31.4	25.4	81
	Chloroform	46.6	29.2	63
	1,2-Dichloroethane	47.8	33.6	70
	2-Butanone	43.5	36.9	85
	1,1,1-Trichloroethane	20.9	20.9	100
	Carbon tetrachloride	12.0	8.2	68
	Trichloroethene	24.7	21.2	86
	1,1,2-Trichloroethene	19.6	10.9	56
	Benzene	37.9	28.7	76
	1,1,2,2-Tetrachloroethane	34.9	25.6	73
	Toluene	29.3	11.2	38
	Chlorobenzene	35.6	19.3	54
	Ethylbenzene	4.27	2.80	66
	Trichlorofluoromethane	3.82	4.40	115
	Acrylonitrile	76.7	110.8	144
Ammonia Lime Still Bottoms	Vinyl chloride	5.00	4.71	94
	Methylene chloride	14.3	13.1	92
	Carbon disulfide	3.37	2.07	61
	1,1-Dichloroethene	52.1	38.8	75
	1,1-Dichloroethane	52.8	25.6	49
	Chloroform	64.7	28.4	44
	1,2-Dichloroethane	43.1	31.5	73
	2-Butanone	59.0	39.6	67
	1,1,1-Trichloroethane	53.6	40.9	76
	Carbon tetrachloride	7.10	6.1	86
	Trichloroethene	57.3	34.2	60
	1,1,2-Trichloroethene	6.7	4.7	70
	Benzene	61.3	26.8	44
	1,1,2,2-Tetrachloroethane	3.16	2.1	66
	Toluene	69.0	18.5	27
	Chlorobenzene	71.8	12.0	17
	Ethylbenzene	3.70	2.2	58
	Trichlorofluoromethane	4.05	4.8	119
	Acrylonitrile	29.4	34.8	118
				%RSD Range = 17 - 144 Mean %RSD = 75

NOTE: Units = µg/L

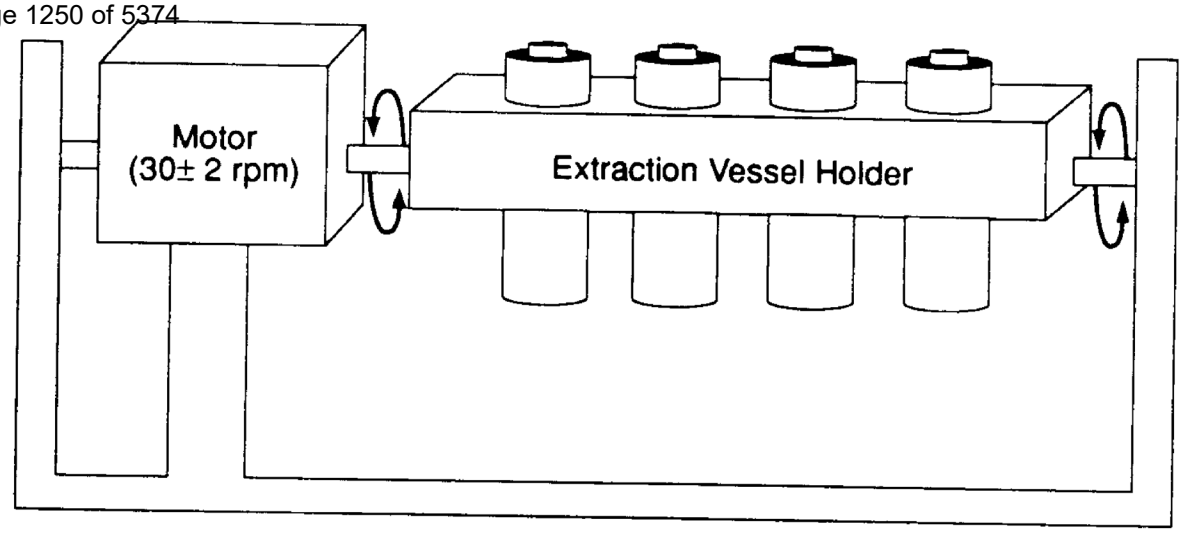


Figure 1. Rotary Agitation Apparatus

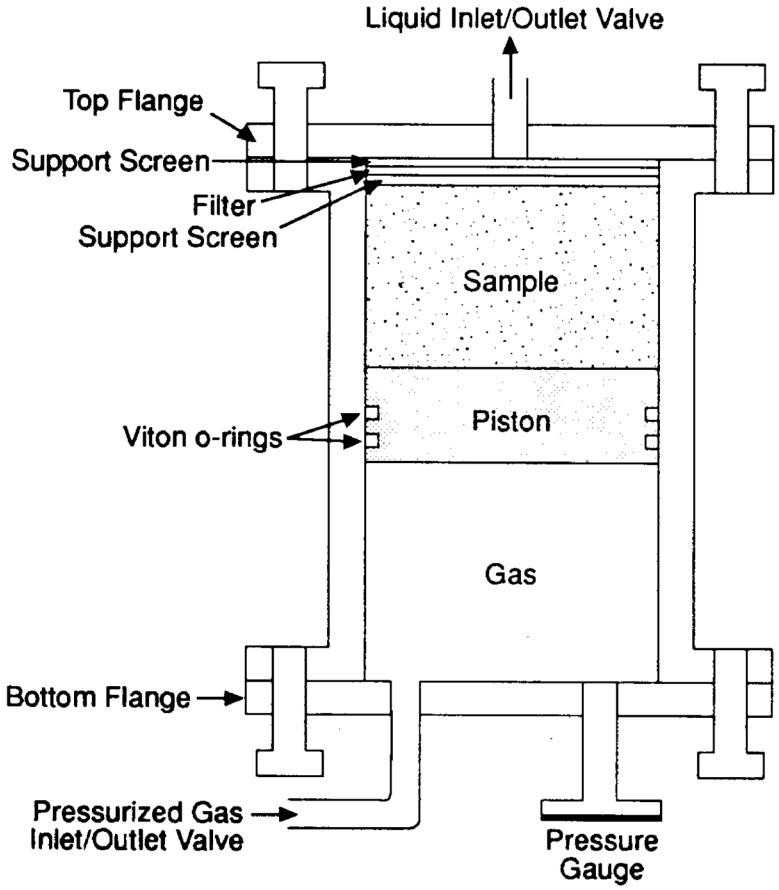
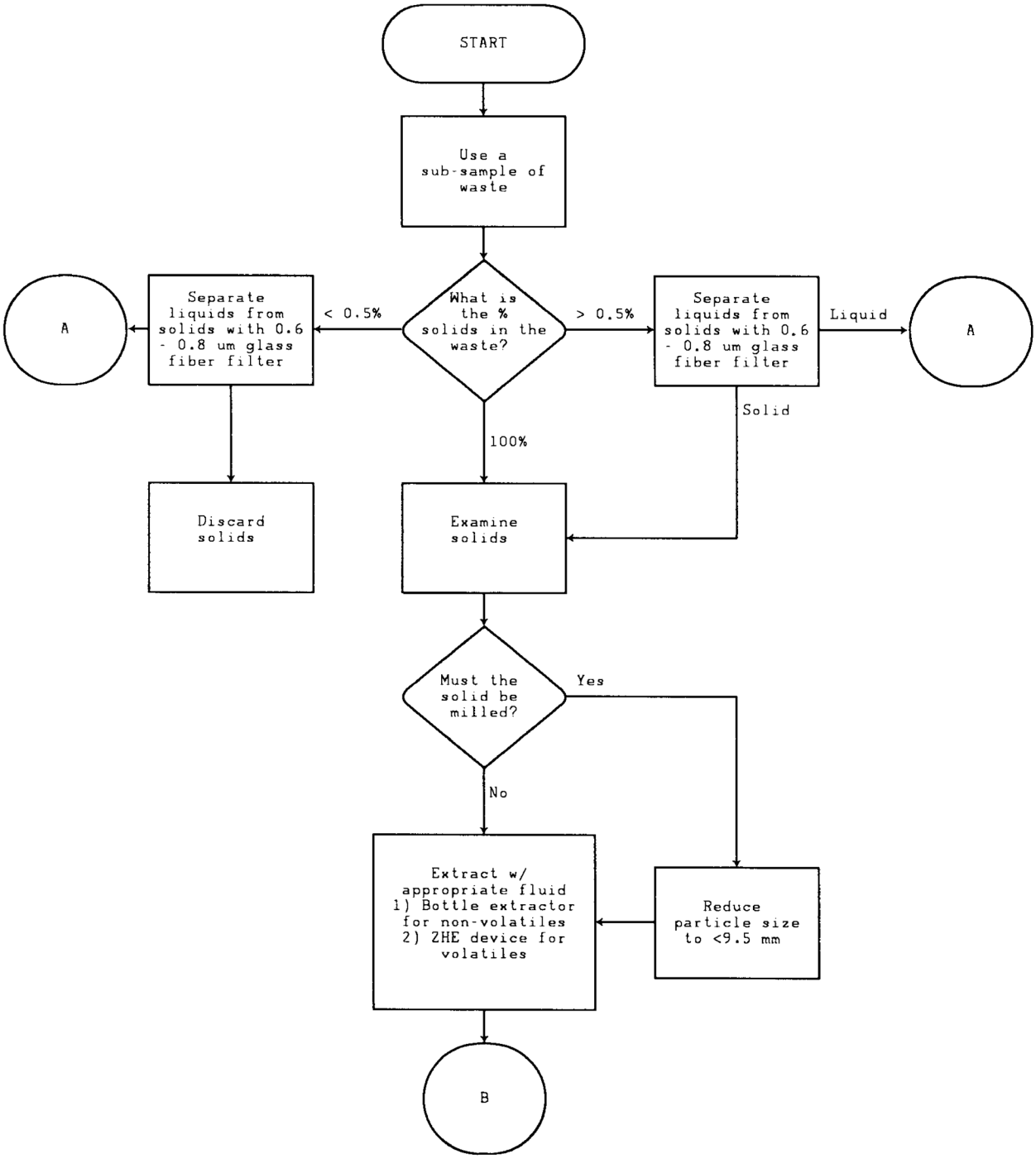
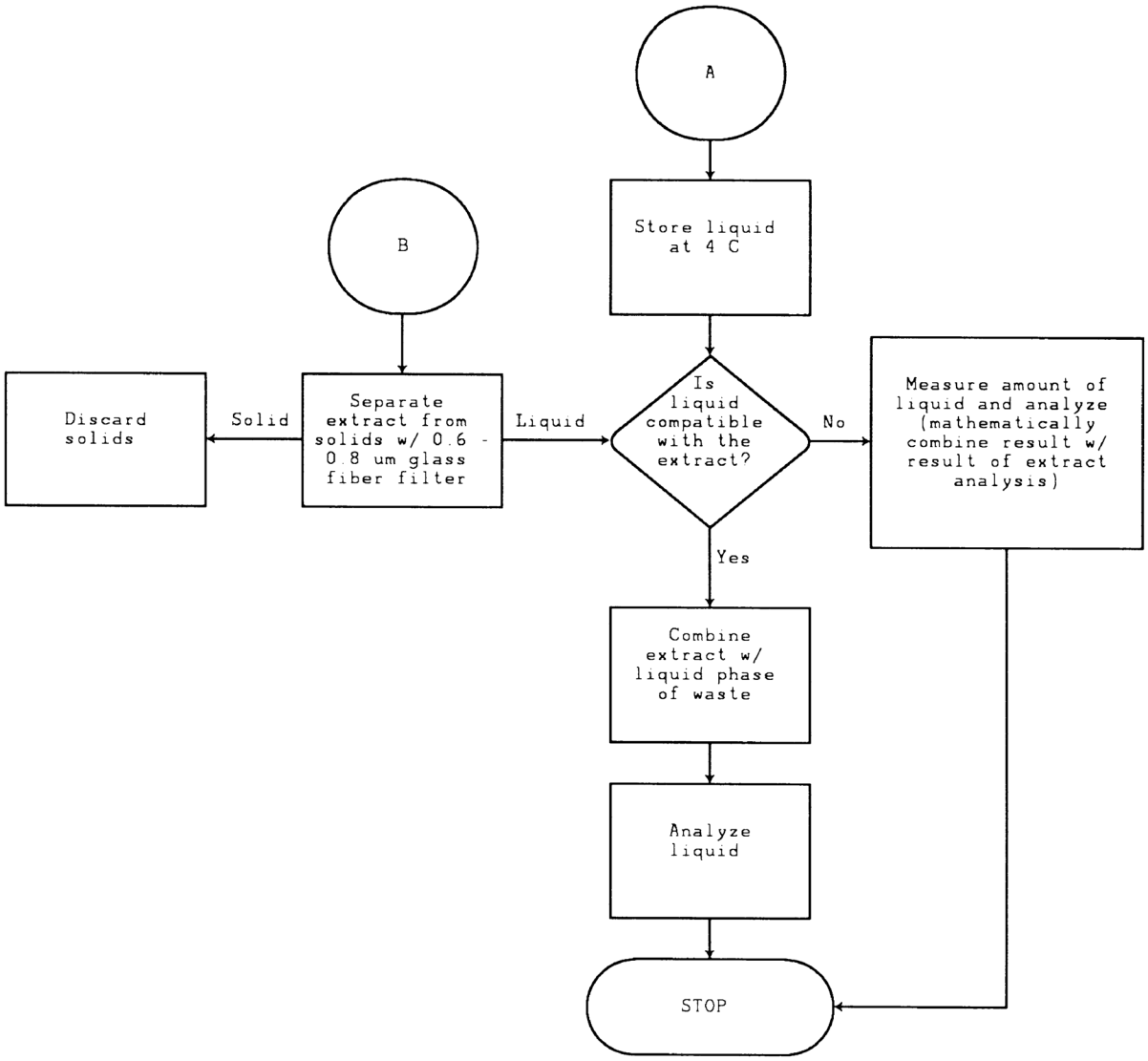


Figure 2. Zero-Headspace Extractor (ZHE)

TOXICITY CHARACTERISTIC LEACHATE PROCEDURE



CHARACTERISTIC LEACHATE PROCEDURE



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40 C.F.R. Part 302 – Table 302.4
List of Hazardous Substances and Reportable Quantities[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
A2213	30558431	4	U394	5000 (2270)
Acenaphthene	83-32-9	2		100 (45.4)
Acenaphthylene	208-96-8	2		5000 (2270)
Acetaldehyde	75-07-0	1,3,4	U001	1000 (454)
Acetaldehyde, chloro-	107-20-0	4	P023	1000 (454)
Acetaldehyde, trichloro-	75-87-6	4	U034	5000 (2270)
Acetamide	60-35-5	3		100 (45.4)
Acetamide, N-(aminothioxomethyl)-	591-08-2	4	P002	1000 (454)
Acetamide, N-(4-ethoxyphenyl)-	62-44-2	4	U187	100 (45.4)
Acetamide, N-9H-fluoren-2-yl-	53-96-3	3,4	U005	1 (0.454)
Acetamide, 2-fluoro-	640-19-7	4	P057	100 (45.4)
Acetic acid	64-19-7	1		5000 (2270)
Acetic acid, (2,4-dichlorophenoxy)-, salts & esters	94-75-7	1,3,4	U240	100 (45.4)
Acetic acid, ethyl ester	141-78-6	4	U112	5000 (2270)
Acetic acid, fluoro-, sodium salt	62-74-8	4	P058	10 (4.54)
Acetic acid, lead(2 +) salt	301-04-2	1,4	U144	10 (4.54)
Acetic acid, thallium(1 +) salt	563-68-8	4	U214	100 (45.4)
Acetic acid, (2,4,5-trichlorophenoxy)-	93-76-5	1,4	See F027	1000 (454)
Acetic anhydride	108-24-7	1		5000 (2270)
Acetone	67-64-1	4	U002	5000 (2270)
Acetone cyanohydrin	75-86-5	1,4	P069	10 (4.54)
Acetonitrile	75-05-8	3,4	U003	5000 (2270)
Acetophenone	98-86-2	3,4	U004	5000 (2270)

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40 C.F.R. Part 302 – Table 302.4
List of Hazardous Substances and Reportable Quantities

[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
2-Acetylaminofluorene	53-96-3	3,4	U005	1 (0.454)
Acetyl bromide	506-96-7	1		5000 (2270)
Acetyl chloride	75-36-5	1,4	U006	5000 (2270)
1-Acetyl-2-thiourea	591-08-2	4	P002	1000 (454)
Acrolein	107-02-8	1,2,3,4	P003	1 (0.454)
Acrylamide	79-06-1	3,4	U007	5000 (2270)
Acrylic acid	79-10-7	3,4	U008	5000 (2270)
Acrylonitrile	107-13-1	1,2,3,4	U009	100 (45.4)
Adipic acid	124-04-9	1		5000 (2270)
Aldicarb	116-06-3	4	P070	1 (0.454)
Aldicarb sulfone	1646884	4	P203	100 (45.4)
Aldrin	309-00-2	1,2,4	P004	1 (0.454)
Allyl alcohol	107-18-6	1,4	P005	100 (45.4)
Allyl chloride	107-05-1	1,3		1000 (454)
Aluminum phosphide	20859-73-8	4	P006	100 (45.4)
Aluminum sulfate	10043-01-3	1		5000 (2270)
4-Aminobiphenyl	92-67-1	3		1 (0.454)
5-(Aminomethyl)-3-isoxazolol	2763-96-4	4	P007	1000 (454)
4-Aminopyridine	504-24-5	4	P008	1000 (454)
Amitrole	61-82-5	4	U011	10 (4.54)
Ammonia	7664-41-7	1		100 (45.4)
Ammonium acetate	631-61-8	1		5000 (2270)
Ammonium benzoate	1863-63-4	1		5000 (2270)
Ammonium bicarbonate	1066-33-7	1		5000 (2270)
Ammonium bichromate	7789-09-5	1		10 (4.54)
Ammonium bifluoride	1341-49-7	1		100 (45.4)

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40 C.F.R. Part 302 – Table 302.4
List of Hazardous Substances and Reportable Quantities[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Ammonium bisulfilte	10192-30-0	1		5000 (2270)
Ammonium carbamate	1111-78-0	1		5000 (2270)
Ammonium carbonate	506-87-6	1		5000 (2270)
Ammonium chloride	12125-02-9	1		5000 (2270)
Ammonium chromate	7788-98-9	1		10 (4.54)
Ammonium citrate, dibasic	3012-65-5	1		5000 (2270)
Ammonium fluoborate	13826-83-0	1		5000 (2270)
Ammonium fluoride	12125-01-8	1		100 (45.4)
Ammonium hydroxide	1336-21-6	1		1000 (454)
Ammonium oxalate	6009-70-7 5972-73-6 14258-49-2	1		5000 (2270)
Ammonium picrate	131-74-8	4	P009	10 (4.54)
Ammonium silicofluoride	16919-19-0	1		1000 (454)
Ammonium sulfamate	7773-06-0	1		5000 (2270)
Ammonium sulfide	12135-76-1	1		100 (45.4)
Ammonium sulfite	10196-04-0	1		5000 (2270)
Ammonium tartrate	14307-43-8 3164-29-2	1		5000 (2270)
Ammonium thiocyanate	1762-95-4	1		5000 (2270)
Ammonium vanadate	7803-55-6	4	P119	1000 (454)
Amyl acetate	628-63-7	1		5000 (2270)
iso-Amyl acetate	123-92-2			
sec-Amyl acetate	626-38-0			
tert-Amyl acetate	625-16-1			

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40 C.F.R. Part 302 – Table 302.4
List of Hazardous Substances and Reportable Quantities[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Aniline	62-53-3	1,3,4	U012	5000 (2270)
o-Anisidine	90-04-0	3		100 (45.4)
Anthracene	120-12-7	2		5000 (2270)
Antimony††	7440-36-0	2		5000 (2270)
ANTIMONY AND COMPOUNDS	N.A.	2,3		**
Antimony Compounds	N.A.	2,3		**
Antimony pentachloride	7647-18-9	1		1000 (454)
Antimony potassium tartrate	28300-74-5	1		100 (45.4)
Antimony tribromide	7789-61-9	1		1000 (454)
Antimony trichloride	10025-91-9	1		1000 (454)
Antimony trifluoride	7783-56-4	1		1000 (454)
Antimony trioxide	1309-64-4	1		1000 (454)
Argentate(1-), bis(cyano-C)-, potassium	506-61-6	4	P099	1 (0.454)
Aroclor 1016	12674-11-2	1,2,3		1 (0.454)
Aroclor 1221	11104-28-2	1,2,3		1 (0.454)
Aroclor 1232	11141-16-5	1,2,3		1 (0.454)
Aroclor 1242	53469-21-9	1,2,3		1 (0.454)
Aroclor 1248	12672-29-6	1,2,3		1 (0.454)
Aroclor 1254	11097-69-1	1,2,3		1 (0.454)
Aroclor 1260	11096-82-5	1,2,3		1 (0.454)
Aroclors	1336-36-3	1,2,3		1 (0.454)
Arsenic††	7440-38-2	2,3		1 (0.454)
Arsenic acid H3AsO4	7778-39-4	4	P010	1 (0.454)
ARSENIC AND COMPOUNDS	N.A.	2,3		**
Arsenic Compounds (inorganic including arsine)	N.A.	2,3		**
Arsenic disulfide	1303-32-8	1		1 (0.454)
Arsenic oxide As2O3	1327-53-3	1,4	P012	1 (0.454)
Arsenic oxide As2O5	1303-28-2	1,4	P011	1 (0.454)
Arsenic pentoxide	1303-28-2	1,4	P011	1 (0.454)
Arsenic trichloride	7784-34-1	1		1 (0.454)
Arsenic trioxide	1327-53-3	1,4	P012	1 (0.454)

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40 C.F.R. Part 302 – Table 302.4
List of Hazardous Substances and Reportable Quantities[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Arsenic trisulfide	1303-33-9	1		1 (0.454)
Arsine, diethyl-	692-42-2	4	P038	1 (0.454)
Arsinic acid, dimethyl-	75-60-5	4	U136	1 (0.454)
Arsonous dichloride, phenyl-	696-28-6	4	P036	1 (0.454)
Asbestos†††	1332-21-4	2,3		1 (0.454)
Auramine	492-80-8	4	U014	100 (45.4)
Azaserine	115-02-6	4	U015	1 (0.454)
Aziridine	151-56-4	3,4	P054	1 (0.454)
Aziridine, 2-methyl-	75-55-8	3,4	P067	1 (0.454)
Azirino[2′,3′:3,4]pyrrolo[1,2-a]indole-4,7-dione, 6-amino-8-[[(aminocarbonyl)oxy]methyl]-1,1a,2,8,8a,8b- hexahydro-8a-methoxy-5- methyl-,[1aS- (1aalpha,8beta,8aalpha, 8balpha)]-	50-07-7	4	U010	10 (4.54)
Barban	101279	4	U280	10 (4.54)
Barium cyanide	542-62-1	1,4	P013	10 (4.54)
Bendiocarb	22781233	4	U278	100 (45.4)
Bendiocarb phenol	22961826	4	U364	1000 (454)
Benomyl	17804352	4	U271	10 (4.54)
Benz[j]aceanthrylene, 1,2-dihydro-3-methyl-	56-49-5	4	U157	10 (4.54)
Benz[c]acridine	225-51-4	4	U016	100 (45.4)
Benzal chloride	98-87-3	4	U017	5000 (2270)
Benzamide, 3,5-dichloro-N-(1,1-dimethyl-2propynyl)-	23950-58-5	4	U192	5000 (2270)
Benz[a]anthracene	56-55-3	2,4	U018	10 (4.54)
1,2-Benzanthracene	56-55-3	2,4	U018	10 (4.54)
Benz[a]anthracene, 7,12-dimethyl-	57-97-6	4	U094	1 (0.454)
Benzenamine	62-53-3	1,3,4	U012	5000 (2270)
Benzenamine, 4,4′-carbonimidoylbis (N,N dimethyl-	492-80-8	4	U014	100 (45.4)
Benzenamine, 4-chloro-	106-47-8	4	P024	1000 (454)
Benzenamine, 4-chloro-2-methyl-, hydrochloride	3165-93-3	4	U049	100 (45.4)
Benzenamine, N,N-dimethyl-4-(phenylazo)-	60-11-7	3,4	U093	10 (4.54)

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40 C.F.R. Part 302 – Table 302.4
List of Hazardous Substances and Reportable Quantities

[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Benzenamine, 2-methyl-	95-53-4	3,4	U328	100 (45.4)
Benzenamine, 4-methyl-	106-49-0	4	U353	100 (45.4)
Benzenamine, 4,4′-methylenebis [2-chloro-	101-14-4	3,4	U158	10 (4.54)
Benzenamine, 2-methyl-,hydrochloride	636-21-5	4	U222	100 (45.4)
Benzenamine, 2-methyl-5-nitro-	99-55-8	4	U181	100 (45.4)
Benzenamine, 4-nitro-	100-01-6	4	P077	5000 (2270)
Benzene[a]	71-43-2	1,2,3,4	U019	10 (4.54)
Benzeneacetic acid, 4-chloro-α-(4-chlorophenyl)-α-hydroxy-, ethyl ester	510-15-6	3,4	U038	10 (4.54)
Benzene, 1-bromo-4-phenoxy-	101-55-3	2,4	U030	100 (45.4)
Benzenebutanoic acid, 4-[bis(2-chloroethyl)amino]-	305-03-3	4	U035	10 (4.54)
Benzene, chloro-	108-90-7	1,2,3,4	U037	100 (45.4)
Benzene, (chloromethyl)-	100-44-7	1,3,4	P028	100 (45.4)
Benzenediamine, ar-methyl-	95-80-7 496-72-0 823-40-5 25376-45-8	3,4	U221	10 (4.54)
1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester	117-81-7	2,3,4	U028	100 (45.4)
1,2-Benzenedicarboxylic acid, dibutyl ester	84-74-2	1,2,3,4	U069	10 (4.54)
1,2-Benzenedicarboxylic acid, diethyl ester	84-66-2	2,4	U088	1000 (454)
1,2-Benzenedicarboxylic acid, dimethyl ester	131-11-3	2,3,4	U102	5000 (2270)
1,2-Benzenedicarboxylic acid, dioctyl ester	117-84-0	2,4	U107	5000 (2270)
Benzene, 1,2-dichloro-	95-50-1	1,2,4	U070	100 (45.4)
Benzene, 1,3-dichloro-	541-73-1	2,4	U071	100 (45.4)
Benzene, 1,4-dichloro-	106-46-7	1,2,3,4	U072	100 (45.4)
Benzene, 1,1′-(2,2-dichloroethylidene) bis[4-chloro-	72-54-8	1,2,4	U060	1 (0.454)
Benzene, (dichloromethyl)-	98-87-3	4	U017	5000 (2270)

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List of Hazardous Substances and Reportable Quantities[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Benzene, 1,3-diisocyanatomethyl-	91-08-7 584-84-9 26471-62-5	3,4	U223	100 (45.4)
Benzene, dimethyl-	1330-20-7	1,3,4	U239	100 (45.4)
1,3-Benzenediol	108-46-3	1,4	U201	5000 (2270)
1,2-Benzenediol,4-[1-hydroxy-2-(methyl amino)ethyl]-	51-43-4	4	P042	1000 (454)
Benzeneethanamine, alpha,alpha-dimethyl-	122-09-8	4	P046	5000 (2270)
Benzene, hexachloro-	118-74-1	2,3,4	U127	10 (4.54)
Benzene, hexahydro-	110-82-7	1,4	U056	1000 (454)
Benzene, methyl-	108-88-3	1,2,3,4	U220	1000 (454)
Benzene, 1-methyl-2,4-dinitro-	121-14-2	1,2,3,4	U105	10 (4.54)
Benzene, 2-methyl-1,3-dinitro-	606-20-2	1,2,4	U106	100 (45.4)
Benzene, (1-methylethyl)-	98-82-8	3,4	U055	5000 (2270)
Benzene, nitro-	98-95-3	1,2,3,4	U169	1000 (454)
Benzene, pentachloro-	608-93-5	4	U183	10 (4.54)
Benzene, pentachloronitro-	82-68-8	3,4	U185	100 (45.4)
Benzenesulfonic acid chloride	98-09-9	4	U020	100 (45.4)
Benzenesulfonyl chloride	98-09-9	4	U020	100 (45.4)
Benzene,1,2,4,5-tetrachloro-	95-94-3	4	U207	5000 (2270)
Benzenethiol	108-98-5	4	P014	100 (45.4)
Benzene,1,1′-(2,2,2-trichloroethylidene) bis[4-chloro-	50-29-3	1,2,4	U061	1 (0.454)
Benzene,1,1′-(2,2,2-trichloroethylidene) bis[4-methoxy-	72-43-5	1,3,4	U247	1 (0.454)
Benzene, (trichloromethyl)-	98-07-7	3,4	U023	10 (4.54)
Benzene, 1,3,5-trinitro-	99-35-4	4	U234	10 (4.54)
Benzidine	92-87-5	2,3,4	U021	1 (0.454)
Benzo[a]anthracene	56-55-3	2,4	U018	10 (4.54)
1,3-Benzodioxole, 5-(1-propenyl)-1	120-58-1	4	U141	100 (45.4)
1,3-Benzodioxole, 5-(2-propenyl)-	94-59-7	4	U203	100 (45.4)

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[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
1,3-Benzodioxole, 5-propyl-	94-58-6	4	U090	10 (4.54)
1,3-Benzodioxol-4-ol, 2,2-dimethyl-	22961826	4	U364	1000 (454)
1,3-Benzodioxol-4-ol, 2,2-dimethyl-, methyl carbamate	22781233	4	U278	100 (45.4)
Benzo[b]fluoranthene	205-99-2	2		1 (0.454)
Benzo(k)fluoranthene	207-08-9	2		5000 (2270)
7-Benzofuranol, 2,3-dihydro-2,2-dimethyl-	1563388	4	U367	10 (4.54)
7-Benzofuranol, 2,3-dihydro-2,2- dimethyl-, methylcarbamate	1563-66-2	1,4	P127	10 (4.54)
Benzoic acid	65-85-0	1		5000 (2270)
Benzoic acid, 2-hydroxy-, compd. with (3aS-cis)-1,2,3,3a,8,8a-hexahydro-1,3a,8-trimethylpyrrolo[2,3-b]indol-5-yl methylcarbamate ester (1:1)	57647	4	P188	100 (45.4)
Benzonitrile	100-47-0	1		5000 (2270)
Benzo[rst]pentaphene	189-55-9	4	U064	10 (4.54)
Benzo[ghi]perylene	191-24-2	2		5000 (2270)
2H-1-Benzopyran-2-one, 4-hydroxy-3-(3-oxo-1-phenylbutyl)-, & salts	81-81-2	4	P001 U248	100 (45.4)
Benzo[a]pyrene	50-32-8	2,4	U022	1 (0.454)
3,4-Benzopyrene	50-32-8	2,4	U022	1 (0.454)
ρ-Benzoquinone	106-51-4	3,4	U197	10 (4.54)
Benzotrichloride	98-07-7	3,4	U023	10 (4.54)
Benzoyl chloride	98-88-4	1		1000 (454)
Benzyl chloride	100-44-7	1,3,4	P028	100 (45.4)
Beryllium ††	7440-41-7	2,3,4	P015	10 (4.54)
BERYLLIUM AND COMPOUNDS	N.A.	2,3		**
Beryllium chloride	7787-47-5	1		1 (0.454)
Beryllium compounds	N.A.	2,3		**
Beryllium fluoride	7787-49-7	1		1 (0.454)

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List of Hazardous Substances and Reportable Quantities[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Beryllium nitrate	13597-99-4 7787-55-5	1		1 (0.454)
Beryllium powder ††	7440-41-7	2,3,4	P015	10 (4.54)
alpha-BHC	319-84-6	2		10 (4.54)
beta-BHC	319-85-7	2		1 (0.454)
delta-BHC	319-86-8	2		1 (0.454)
gamma-BHC	58-89-9	1,2,3,4	U129	1 (0.454)
2,2′-Bioxirane	1464-53-5	4	U085	10 (4.54)
Biphenyl	92-52-4	3		100 (45.4)
[1,1′-Biphenyl]-4,4′-diamine	92-87-5	2,3,4	U021	1 (0.454)
[1,1′-Biphenyl]-4,4′-diamine,3,3′-dichloro-	91-94-1	2,3,4	U073	1 (0.454)
[1,1′-Biphenyl]-4,4′-diamine,3,3′-dimethoxy-	119-90-4	3,4	U091	100 (45.4)
[1,1′-Biphenyl]-4,4′-diamine,3,3′-dimethyl-	119-93-7	3,4	U095	10 (4.54)
Bis(2-chloroethoxy) methane	111-91-1	2,4	U024	1000 (454)
Bis(2-chloroethyl) ether	111-44-4	2,3,4	U025	10 (4.54)
Bis(chloromethyl) ether	542-88-1	2,3,4	P016	10 (4.54)
Bis(2-ethylhexyl) phthalate	117-81-7	3,4	U028	100 (45.4)
Bromoacetone	598-31-2	4	P017	1000 (454)
Bromoform	75-25-2	2,3,4	U225	100 (45.4)
Bromomethane	74-83-9	2,3,4	U029	1000 (454)
4-Bromophenyl phenyl ether	101-55-3	2,4	U030	100 (45.4)
Brucine	357-57-3	4	P018	100 (45.4)
1,3-Butadiene	106-99-0	3		10 (4.54)
1,3-Butadiene, 1,1,2,3,4,4-hexachloro-	87-68-3	2,3,4	U128	1 (0.454)
1-Butanamine, N-butyl-N-nitroso-	924-16-3	4	U172	10 (4.54)
1-Butanol	71-36-3	4	U031	5000 (2270)
2-Butanone	78-93-3	3,4	U159	5000 (2270)
2-Butanone, 3,3-dimethyl-1(methylthio)-, O-[(methylamino)carbonyl] oxime	39196-18-4	4	P045	100 (45.4)
2-Butanone peroxide	1338-23-4	4	U160	10 (4.54)
2-Butenal	123-73-9 4170-30-3	1,4	U053	100 (45.4)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
2-Butene, 1,4-dichloro-	764-41-0	4	U074	1 (0.454)
2-Butenoic acid, 2-methyl-, 7-[[2,3-dihydroxy-2-(1-methoxyethyl)-3- methyl-1-oxobutoxy] methyl]-2,3, 5,7a-tetrahydro- 1H-pyrrolizin-1-yl ester, [1S-[1alpha(Z), 7(2S*,3R*),7aalpha]]-	303-34-4	4	U143	10 (4.54)
Butyl acetate	123-86-4	1		5000 (2270)
iso-Butyl acetate	110-19-0			
sec-Butyl acetate	105-46-4			
tert-Butyl acetate	540-88-5			
n-Butyl alcohol	71-36-3	4	U031	5000 (2270)
Butylamine	109-73-9	1		1000 (454)
iso-Butylamine	78-81-9			
sec-Butylamine	513-49-5 13952-84-6			
tert-Butylamine	75-64-9			
Butyl benzyl phthalate	85-68-7	2		100 (45.4)
n-Butyl phthalate	84-74-2	1,2,3,4	U069	10 (4.54)
Butyric acid	107-92-6	1		5000 (2270)
iso-Butyric acid	79-31-2			
Cacodylic acid	75-60-5	4	U136	1 (0.454)
Cadmium ††	7440-43-9	2		10 (4.54)
Cadmium acetate	543-90-8	1		10 (4.54)
CADMIUM AND COMPOUNDS	N.A.	2,3		**
Cadmium bromide	7789-42-6	1		10 (4.54)
Cadmium chloride	10108-64-2	1		10 (4.54)
Cadmium compounds	N.A.	2,3		**
Calcium arsenate	7778-44-1	1		1 (0.454)
Calcium arsenite	52740-16-6	1		1 (0.454)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Calcium carbide	75-20-7	1		10 (4.54)
Calcium chromate	13765-19-0	1,4	U032	10 (4.54)
Calcium cyanamide	156-62-7	3		1000 (454)
Calcium cyanide Ca(CN)2	592-01-8	1,4	P021	10 (4.54)
Calcium dodecylbenzenesulfonate	26264-06-2	1		1000 (454)
Calcium hypochlorite	7778-54-3	1		10 (4.54)
Captan	133-06-2	1,3		10 (4.54)
Carbamic acid, 1H-benzimidazol-2-yl, methyl ester	10605217	4	U372	10 (4.54)
Carbamic acid, [1-[(butylamino)carbonyl]-1H-benzimidazol-2-yl]-,methyl ester	17804352	4	U271	10 (4.54)
Carbamic acid, (3-chlorophenyl)-, 4-chloro-2-butynyl ester	101279	4	U280	10 (4.54)
Carbamic acid, [(dibutylamino)-thio]methyl-, 2,3-dihydro-2,2-dimethyl-7-benzofuranyl ester	55285148	4	P189	1000 (454)
Carbamic acid, dimethyl-,1-[(dimethyl-amino)carbonyl]-5-methyl-1H-pyrazol-3-yl ester	644644	4	P191	1 (0.454)
Carbamic acid, dimethyl-, 3-methyl-1-(1-methylethyl)-1H-pyrazol-5-yl ester	119380	4	P192	100 (45.4)
Carbamic acid, ethyl ester	51-79-6	3,4	U238	100 (45.4)
Carbamic acid, methyl-, 3-methylphenyl ester	1129415	4	P190	1000 (454)
Carbamic acid, methylnitroso-, ethyl ester	615-53-2	4	U178	1 (0.454)
Carbamic acid, [1,2-phenylenebis(iminocarbonothioyl)]bis-, dimethyl ester	23564058	4	U409	10 (4.54)
Carbamic acid, phenyl-, 1-methylethyl ester	122429	4	U373	1000 (454)
Carbamic chloride, dimethyl-	79-44-7	3,4	U097	1 (0.454)
Carbamodithioic acid, 1,2-ethanediylbis-, salts & esters	111-54-6	4	U114	5000 (2270)
Carbamothioic acid, bis(1-methylethyl)-, S-(2,3-dichloro-2- propenyl) ester	2303-16-4	4	U062	100 (45.4)
Carbamothioic acid, bis(1-methylethyl)-, S-(2,3,3-trichloro-2-propenyl) ester	2303175	4	U389	100 (45.4)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Carbamothioic acid, dipropyl-, S-(phenylmethyl) ester	52888809	4	U387	5000 (2270)
Carbaryl	63-25-2	1,3,4	U279	100 (45.4)
Carbendazim	10605217	4	U372	10 (4.54)
Carbofuran	1563-66-2	1,4	P127	10 (4.54)
Carbofuran phenol	1563388	4	U367	10 (4.54)
Carbon disulfide	75-15-0	1,3,4	P022	100 (45.4)
Carbonic acid, dithallium(1 +) salt	6533-73-9	4	U215	100 (45.4)
Carbonic dichloride	75-44-5	1,3,4	P095	10 (4.54)
Carbonic difluoride	353-50-4	4	U033	1000 (454)
Carbonochloridic acid, methyl ester	79-22-1	4	U156	1000 (454)
Carbon oxyfluoride	353-50-4	4	U033	1000 (454)
Carbon tetrachloride	56-23-5	1,2,3,4	U211	10 (4.54)
Carbonyl sulfide	463-58-1	3		100 (45.4)
Carbosulfan	55285148	4	P189	1000 (454)
Catechol	120-80-9	3		100 (45.4)
Chloral	75-87-6	4	U034	5000 (2270)
Chloramben	133-90-4	3		100 (45.4)
Chlorambucil	305-03-3	4	U035	10 (4.54)
Chlordane	57-74-9	1,2,3,4	U036	1 (0.454)
Chlordane, alpha & gamma isomers	57-74-9	1,2,3,4	U036	1 (0.454)
CHLORDANE (TECHNICAL MIXTURE AND METABOLITES)	57-74-9	1,2,3,4	U036	1 (0.454)
CHLORINATED BENZENES	N.A.	2		**
Chlorinated camphene	8001-35-2	1,2,3,4	P123	1 (0.454)
CHLORINATED ETHANES	N.A.	2		**
CHLORINATED NAPHTHALENE	N.A.	2		**
CHLORINATED PHENOLS	N.A.	2		**
Chlorine	7782-50-5	1,3		10 (4.54)
Chlornaphazine	494-03-1	4	U026	100 (45.4)
Chloroacetaldehyde	107-20-0	4	P023	1000 (454)
Chloroacetic acid	79-11-8	3		100 (45.4)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
2-Chloroacetophenone	532-27-4	3		100 (45.4)
CHLOROALKYL ETHERS	N.A.	2		**
p-Chloroaniline	106-47-8	4	P024	1000 (454)
Chlorobenzene	108-90-7	1,2,3,4	U037	100 (45.4)
Chlorobenzilate	510-15-6	3,4	U038	10 (4.54)
p-Chloro-m-cresol	59-50-7	2,4	U039	5000 (2270)
Chlorodibromomethane	124-48-1	2		100 (45.4)
1-Chloro-2,3-epoxypropane	106-89-8	1,3,4	U041	100 (45.4)
Chloroethane	75-00-3	2,3		100 (45.4)
2-Chloroethyl vinyl ether	110-75-8	2,4	U042	1000 (454)
Chloroform	67-66-3	1,2,3,4	U044	10 (4.54)
Chloromethane	74-87-3	2,3,4	U045	100 (45.4)
Chloromethyl methyl ether	107-30-2	3,4	U046	10 (4.54)
beta-Chloronaphthalene	91-58-7	2,4	U047	5000 (2270)
2-Chloronaphthalene	91-58-7	2,4	U047	5000 (2270)
2-Chlorophenol	95-57-8	2,4	U048	100 (45.4)
o-Chlorophenol	95-57-8	2,4	U048	100 (45.4)
4-Chlorophenyl phenyl ether	7005-72-3	2		5000 (2270)
1-(o-Chlorophenyl)thiourea	5344-82-1	4	P026	100 (45.4)
Chloroprene	126-99-8	3		100 (45.4)
3-Chloropropionitrile	542-76-7	4	P027	1000 (454)
Chlorosulfonic acid	7790-94-5	1		1000 (454)
4-Chloro-o-toluidine, hydrochloride	3165-93-3	4	U049	100 (45.4)
Chlorpyrifos	2921-88-2	1		1 (0.454)
Chromic acetate	1066-30-4	1		1000 (454)
Chromic acid	11115-74-5 7738-94-5	1		10 (4.54)
Chromic acid H2CrO4, calcium salt	13765-19-0	1,4	U032	10 (4.54)
Chromic sulfate	10101-53-8	1		1000 (454)
Chromium††	7440-47-3	2		5000 (2270)

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40 C.F.R. Part 302 – Table 302.4
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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
CHROMIUM AND COMPOUNDS	N.A.	2,3		**
Chromium Compounds	N.A.	2,3		**
Chromous chloride	10049-05-5	1		1000 (454)
Chrysene	218-01-9	2,4	U050	100 (45.4)
Cobalt Compounds	N.A.	3		**
Cobaltous bromide	7789-43-7	1		1000 (454)
Cobaltous formate	544-18-3	1		1000 (454)
Cobaltous sulfamate	14017-41-5	1		1000 (454)
Coke Oven Emissions	N.A.	3		1 (0.454)
Copper††	7440-50-8	2		5000 (2270)
COPPER AND COMPOUNDS	N.A.	2		**
Copper cyanide Cu(CN)	544-92-3	4	P029	10 (4.54)
Coumaphos	56-72-4	1		10 (4.54)
Creosote	N.A.	4	U051	1 (0.454)
Cresol (cresylic acid)	1319-77-3	1,3,4	U052	100 (45.4)
m-Cresol	108-39-4	3		100 (45.4)
o-Cresol	95-48-7	3		100 (45.4)
p-Cresol	106-44-5	3		100 (45.4)
Cresols (isomers and mixture)	1319-77-3	1,3,4	U052	100 (45.4)
Cresylic acid (isomers and mixture)	1319-77-3	1,3,4	U052	100 (45.4)
Crotonaldehyde	123-73-9 4170-30-3	1,4	U053	100 (45.4)
Cumene	98-82-8	3,4	U055	5000 (2270)
m-Cumenyl methylcarbamate	64006	4	P202	10 (4.54)
Cupric acetate	142-71-2	1		100 (45.4)
Cupric acetoarsenite	12002-03-8	1		1 (0.454)
Cupric chloride	7447-39-4	1		10 (4.54)
Cupric nitrate	3251-23-8	1		100 (45.4)
Cupric oxalate	5893-66-3	1		100 (45.4)
Cupric sulfate	7758-98-7	1		10 (4.54)
Cupric sulfate, ammoniated	10380-29-7	1		100 (45.4)
Cupric tartrate	815-82-7	1		100 (45.4)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Cyanide Compounds	N.A.	2,3		**
CYANIDES	N.A.	2,3		**
Cyanides (soluble salts and complexes) not otherwise specified	N.A.	4	P030	10 (4.54)
Cyanogen	460-19-5	4	P031	100 (45.4)
Cyanogen bromide (CN)Br	506-68-3	4	U246	1000 (454)
Cyanogen chloride (CN)Cl	506-77-4	1,4	P033	10 (4.54)
2,5-Cyclohexadiene-1,4-dione	106-51-4	3,4	U197	10 (4.54)
Cyclohexane	110-82-7	1,4	U056	1000 (454)
Cyclohexane, 1,2,3,4,5,6-hexachloro-, (1α, 2α, 3β-, 4α, 5α, 6β)	58-89-9	1,2,3,4	U129	1 (0.454)
Cyclohexanone	108-94-1	4	U057	5000 (2270)
2-Cyclohexyl-4,6-dinitrophenol	131-89-5	4	P034	100 (45.4)
1,3-Cyclopentadiene, 1,2,3,4,5,5-hexachloro-	77-47-4	1,2,3,4	U130	10 (4.54)
Cyclophosphamide	50-18-0	4	U058	10 (4.54)
2,4-D Acid	94-75-7	1,3,4	U240	100 (45.4)
2,4-D Ester	94-11-1 94-79-1 94-80-4 1320-18-9 1928-38-7 1928-61-6 1929-73-3 2971-38-2 25168-26-7 53467-11-1	1		100 (45.4)
2,4-D, salts and esters	94-75-7	1,3,4	U240	100 (45.4)
Daunomycin	20830-81-3	4	U059	10 (4.54)
DDD	72-54-8	1,2,4	U060	1 (0.454)
4,4′-DDD	72-54-8	1,2,4	U060	1 (0.454)
DDE [b]	72-55-9	2		1 (0.454)
DDE [b]	3547-04-4	3		5000 (2270)
4,4′-DDE	72-55-9	2		1 (0.454)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
DDT	50-29-3	1,2,4	U061	1 (0.454)
4,4′-DDT	50-29-3	1,2,4	U061	1 (0.454)
DDT AND METABOLITES	N.A.	2		**
DEHP	117-81-7	2,3,4	U028	100 (45.4)
Diallate	2303-16-4	4	U062	100 (45.4)
Diazinon	333-41-5	1		1 (0.454)
Diazomethane	334-88-3	3		100 (45.4)
Dibenz[a,h]anthracene	53-70-3	2,4	U063	1 (0.454)
1,2:5,6-Dibenzanthracene	53-70-3	2,4	U063	1 (0.454)
Dibenzo[a,h]anthracene	53-70-3	2,4	U063	1 (0.454)
Dibenzofuran	132-64-9	3		100 (45.4)
Dibenzo[a,i]pyrene	189-55-9	4	U064	10 (4.54)
1,2-Dibromo-3-chloropropane	96-12-8	3,4	U066	1 (0.454)
Dibromoethane	106-93-4	1,3,4	U067	1 (0.454)
Dibutyl phthalate	84-74-2	1,2,3,4	U069	10 (4.54)
Di-n-butyl phthalate	84-74-2	1,2,3,4	U069	10 (4.54)
Dicamba	1918-00-9	1		1000 (454)
Dichlobenil	1194-65-6	1		100 (45.4)
Dichlone	117-80-6	1		1 (0.454)
Dichlorobenzene	25321-22-6	1		100 (45.4)
1,2-Dichlorobenzene	95-50-1	1,2,4	U070	100 (45.4)
1,3-Dichlorobenzene	541-73-1	2,4	U071	100 (45.4)
1,4-Dichlorobenzene	106-46-7	1,2,3,4	U072	100 (45.4)
m-Dichlorobenzene	541-73-1	2,4	U071	100 (45.4)
o-Dichlorobenzene	95-50-1	1,2,4	U070	100 (45.4)
p-Dichlorobenzene	106-46-7	1,2,3,4	U072	100 (45.4)
DICHLOROBENZIDINE	N.A.	2		**
3,3′-Dichlorobenzidine	91-94-1	2,3,4	U073	1 (0.454)
Dichlorobromomethane	75-27-4	2		5000 (2270)
1,4-Dichloro-2-butene	764-41-0	4	U074	1 (0.454)
Dichlorodifluoromethane	75-71-8	4	U075	5000 (2270)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
1,1-Dichloroethane	75-34-3	2,3,4	U076	1000 (454)
1,2-Dichloroethane	107-06-2	1,2,3,4	U077	100 (45.4)
1,1-Dichloroethylene	75-35-4	1,2,3,4	U078	100 (45.4)
1,2-Dichloroethylene	156-60-5	2,4	U079	1000 (454)
Dichloroethyl ether	111-44-4	2,3,4	U025	10 (4.54)
Dichloroisopropyl ether	108-60-1	2,4	U027	1000 (454)
Dichloromethane	75-09-2	2,3,4	U080	1000 (454)
Dichloromethoxyethane	111-91-1	2,4	U024	1000 (454)
Dichloromethyl ether	542-88-1	2,3,4	P016	10 (4.54)
2,4-Dichlorophenol	120-83-2	2,4	U081	100 (45.4)
2,6-Dichlorophenol	87-65-0	4	U082	100 (45.4)
Dichlorophenylarsine	696-28-6	4	P036	1 (0.454)
Dichloropropane	26638-19-7	1		1000 (454)
1,1-Dichloropropane	78-99-9			
1,3-Dichloropropane	142-28-9			
1,2-Dichloropropane	78-87-5	1,2,3,4	U083	1000 (454)
Dichloropropane—Dichloropropene (mixture)	8003-19-8	1		100 (45.4)
Dichloropropene	26952-23-8	1		100 (45.4)
2,3-Dichloropropene	78-88-6			
1,3-Dichloropropene	542-75-6	1,2,3,4	U084	100 (45.4)
2,2-Dichloropropionic acid	75-99-0	1		5000 (2270)
Dichlorvos	62-73-7	1,3		10 (4.54)
Dicofol	115-32-2	1		10 (4.54)
Dieldrin	60-57-1	1,2,4	P037	1 (0.454)
1,2:3,4-Diepoxybutane	1464-53-5	4	U085	10 (4.54)
Diethanolamine	111-42-2	3		100 (45.4)
Diethylamine	109-89-7	1		100 (45.4)
N,N-Diethylaniline	91-66-7	3		1000 (454)
Diethylarsine	692-42-2	4	P038	1 (0.454)
1,4-Diethyleneoxide	123-91-1	3,4	U108	100 (45.4)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Diethylene glycol, dicarbamate	5952261	4	U395	5000 (2270)
Diethylhexyl phthalate	117-81-7	2,3,4	U028	100 (45.4)
N,N′-Diethylhydrazine	1615-80-1	4	U086	10 (4.54)
O,O-Diethyl S-methyl dithiophosphate	3288-58-2	4	U087	5000 (2270)
Diethyl-p-nitrophenyl phosphate	311-45-5	4	P041	100 (45.4)
Diethyl phthalate	84-66-2	2,4	U088	1000 (454)
O,O-Diethyl O-pyrazinyl phosphorothioate	297-97-2	4	P040	100 (45.4)
Diethylstilbestrol	56-53-1	4	U089	1 (0.454)
Diethyl sulfate	64-67-5	3		10 (4.54)
Dihydrosafrole	94-58-6	4	U090	10 (4.54)
Diisopropylfluorophosphate (DFP)	55-91-4	4	P043	100 (45.4)
1,4:5,8-Dimethanonaphthalene, 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-, (1alpha,4alpha,4abeta,5alpha, 8alpha,8abeta)-	309-00-2	1,2,4	P004	1 (0.454)
1,4:5,8-Dimethanonaphthalene, 1,2,3,4,10,10-hexachloro- 1,4,4a,5,8,8a-hexahydro-, (1alpha,4alpha,4abeta, 5beta,8beta,8abeta)-	465-73-6	4	P060	1 (0.454)
2,7:3,6-Dimethanonaphth[2,3-b]oxirene,3,4,5,6,9,9- hexachloro-1a,2,2a,3,6,6a,7,7a- octahydro-,(1aalpha,2beta, 2aalpha,3beta,6beta,6aalpha, 7beta,7aalpha)-	60-57-1	1,2,4	P037	1 (0.454)
2,7:3,6-Dimethanonaphth[2, 3-b]oxirene,3,4,5,6,9,9- hexachloro-1a,2,2a,3,6,6a,7,7a- octahydro-,(1aalpha,2beta, 2abeta,3alpha,6alpha, 6abeta,7beta,7aalpha)-, & metabolites	72-20-8	1,2,4	P051	1 (0.454)
Dimethoate	60-51-5	4	P044	10 (4.54)
3,3′-Dimethoxybenzidine	119-90-4	3,4	U091	100 (45.4)
Dimethylamine	124-40-3	1,4	U092	1000 (454)
Dimethyl aminoazobenzene	60-11-7	3,4	U093	10 (4.54)
p-Dimethylaminoazobenzene	60-11-7	3,4	U093	10 (4.54)
N,N-Dimethylaniline	121-69-7	3		100 (45.4)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
7,12-Dimethylbenz[a]anthracene	57-97-6	4	U094	1 (0.454)
3,3′-Dimethylbenzidine	119-93-7	3,4	U095	10 (4.54)
alpha,alpha-Dimethylbenzylhydroperoxide	80-15-9	4	U096	10 (4.54)
Dimethylcarbamoyl chloride	79-44-7	3,4	U097	1 (0.454)
Dimethylformamide	68-12-2	3		100 (45.4)
1,1-Dimethylhydrazine	57-14-7	3,4	U098	10 (4.54)
1,2-Dimethylhydrazine	540-73-8	4	U099	1 (0.454)
alpha,alpha-Dimethylphenethylamine	122-09-8	4	P046	5000 (2270)
2,4-Dimethylphenol	105-67-9	2,4	U101	100 (45.4)
Dimethyl phthalate	131-11-3	2,3,4	U102	5000 (2270)
Dimethyl sulfate	77-78-1	3,4	U103	100 (45.4)
Dimetilan	644644	4	P191	1 (0.454)
Dinitrobenzene (mixed)	25154-54-5	1		100 (45.4)
m-Dinitrobenzene	99-65-0			
o-Dinitrobenzene	528-29-0			
p-Dinitrobenzene	100-25-4			
4,6-Dinitro-o-cresol, and salts	534-52-1	2,3,4	P047	10 (4.54)
Dinitrophenol	25550-58-7	1		10 (4.54)
2,5-Dinitrophenol	329-71-5			
2,6-Dinitrophenol	573-56-8			
2,4-Dinitrophenol	51-28-5	1,2,3,4	P048	10 (4.54)
Dinitrotoluene	25321-14-6	1,2		10 (4.54)
3,4-Dinitrotoluene	610-39-9			
2,4-Dinitrotoluene	121-14-2	1,2,3,4	U105	10 (4.54)
2,6-Dinitrotoluene	606-20-2	1,2,4	U106	100 (45.4)
Dinoseb	88-85-7	4	P020	1000 (454)
Di-n-octyl phthalate	117-84-0	2,4	U107	5000 (2270)
1,4-Dioxane	123-91-1	3,4	U108	100 (45.4)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
DIPHENYLHYDRAZINE	N.A.	2		**
1,2-Diphenylhydrazine	122-66-7	2,3,4	U109	10 (4.54)
Diphosphoramide, octamethyl-	152-16-9	4	P085	100 (45.4)
Diphosphoric acid, tetraethyl ester	107-49-3	1,4	P111	10 (4.54)
Dipropylamine	142-84-7	4	U110	5000 (2270)
Di-n-propylnitrosamine	621-64-7	2,4	U111	10 (4.54)
Diquat	85-00-7 2764-72-9	1		1000 (454)
Disulfoton	298-04-4	1,4	P039	1 (0.454)
Dithiobiuret	541-53-7	4	P049	100 (45.4)
1,3-Dithiolane-2-carboxaldehyde, 2,4-dimethyl-, O-[(methylamino)-carbonyl]oxime	26419738	4	P185	100 (45.4)
Diuron	330-54-1	1		100 (45.4)
Dodecylbenzenesulfonic acid	27176-87-0	1		1000 (454)
Endosulfan	115-29-7	1,2,4	P050	1 (0.454)
alpha-Endosulfan	959-98-8	2		1 (0.454)
beta-Endosulfan	33213-65-9	2		1 (0.454)
ENDOSULFAN AND METABOLITES	N.A.	2		**
Endosulfan sulfate	1031-07-8	2		1 (0.454)
Endothall	145-73-3	4	P088	1000 (454)
Endrin	72-20-8	1,2,4	P051	1 (0.454)
Endrin aldehyde	7421-93-4	2		1 (0.454)
ENDRIN AND METABOLITES	N.A.	2		**
Endrin, & metabolites	72-20-8	1,2,4	P051	1 (0.454)
Epichlorohydrin	106-89-8	1,3,4	U041	100 (45.4)
Epinephrine	51-43-4	4	P042	1000 (454)
1,2-Epoxybutane	106-88-7	3		100 (45.4)
Ethanal	75-07-0	1,3,4	U001	1000 (454)
Ethanamine, N,N-diethyl-	121-44-8	1,3,4	U404	5000 (2270)
Ethanamine, N-ethyl-N-nitroso-	55-18-5	4	U174	1 (0.454)
1,2-Ethanediamine, N,N-dimethyl-N′-2-pyridinyl-N′-(2- thienylmethyl)-	91-80-5	4	U155	5000 (2270)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Ethane, 1,2-dibromo-	106-93-4	1,3,4	U067	1 (0.454)
Ethane, 1,1-dichloro-	75-34-3	2,3,4	U076	1000 (454)
Ethane, 1,2-dichloro-	107-06-2	1,2,3,4	U077	100 (45.4)
Ethanedinitrile	460-19-5	4	P031	100 (45.4)
Ethane, hexachloro-	67-72-1	2,3,4	U131	100 (45.4)
Ethane, 1,1′-[methylenebis(oxy)]bis[2- chloro-	111-91-1	2,4	U024	1000 (454)
Ethane, 1,1′-oxybis-	60-29-7	4	U117	100 (45.4)
Ethane, 1,1′-oxybis[2-chloro-	111-44-4	2,3,4	U025	10 (4.54)
Ethane, pentachloro-	76-01-7	4	U184	10 (4.54)
Ethane, 1,1,1,2-tetrachloro-	630-20-6	4	U208	100 (45.4)
Ethane, 1,1,2,2-tetrachloro-	79-34-5	2,3,4	U209	100 (45.4)
Ethanethioamide	62-55-5	4	U218	10 (4.54)
Ethane, 1,1,1-trichloro-	71-55-6	2,3,4	U226	1000 (454)
Ethane, 1,1,2-trichloro-	79-00-5	2,3,4	U227	100 (45.4)
Ethanimidothioic acid, 2-(dimethylamino)-N-hydroxy-2-oxo-, methyl ester	30558431	4	U394	5000 (2270)
Ethanimidothioic acid, 2-(dimethylamino)-N-[[(methylamino)carbonyl]oxy]-2-oxo-, methyl ester	23135220	4	P194	100 (45.4)
Ethanimidothioic acid, N-[[(methylamino) carbonyl]oxy]-, methyl ester	16752-77-5	4	P066	100 (45.4)
Ethanimidothioic acid, N,N'-[thiobis[(methylimino) carbonyloxy]]bis-, dimethyl ester	59669260	4	U410	100 (45.4)
Ethanol, 2-ethoxy-	110-80-5	4	U359	1000 (454)
Ethanol, 2,2′-(nitrosoimino)bis-	1116-54-7	4	U173	1 (0.454)
Ethanol, 2,2'-oxybis-, dicarbamate	5952261	4	U395	5000 (2270)
Ethanone, 1-phenyl-	98-86-2	3,4	U004	5000 (2270)
Ethene, chloro-	75-01-4	2,3,4	U043	1 (0.454)
Ethene, (2-chloroethoxy)-	110-75-8	2,4	U042	1000 (454)
Ethene, 1,1-dichloro-	75-35-4	1,2,3,4	U078	100 (45.4)
Ethene, 1,2-dichloro-(E)	156-60-5	2,4	U079	1000 (454)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Ethene, tetrachloro-	127-18-4	2,3,4	U210	100 (45.4)
Ethene, trichloro-	79-01-6	1,2,3,4	U228	100 (45.4)
Ethion	563-12-2	1		10 (4.54)
Ethyl acetate	141-78-6	4	U112	5000 (2270)
Ethyl acrylate	140-88-5	3,4	U113	1000 (454)
Ethylbenzene	100-41-4	1,2,3		1000 (454)
Ethyl carbamate	51-79-6	3,4	U238	100 (45.4)
Ethyl chloride	75-00-3	2,3		100 (45.4)
Ethyl cyanide	107-12-0	4	P101	10 (4.54)
Ethylenebisdithiocarbamic acid, salts & esters	111-54-6	4	U114	5000 (2270)
Ethylenediamine	107-15-3	1		5000 (2270)
Ethylenediamine-tetraacetic acid (EDTA)	60-00-4	1		5000 (2270)
Ethylene dibromide	106-93-4	1,3,4	U067	1 (0.454)
Ethylene dichloride	107-06-2	1,2,3,4	U077	100 (45.4)
Ethylene glycol	107-21-1	3		5000 (2270)
Ethylene glycol monoethyl ether	110-80-5	4	U359	1000 (454)
Ethylene oxide	75-21-8	3,4	U115	10 (4.54)
Ethylenethiourea	96-45-7	3,4	U116	10 (4.54)
Ethylenimine	151-56-4	3,4	P054	1 (0.454)
Ethyl ether	60-29-7	4	U117	100 (45.4)
Ethylidene dichloride	75-34-3	2,3,4	U076	1000 (454)
Ethyl methacrylate	97-63-2	4	U118	1000 (454)
Ethyl methanesulfonate	62-50-0	4	U119	1 (0.454)
Famphur	52-85-7	4	P097	1000 (454)
Ferric ammonium citrate	1185-57-5	1		1000 (454)
Ferric ammonium oxalate	2944-67-4 55488-87-4	1		1000 (454)
Ferric chloride	7705-08-0	1		1000 (454)
Ferric fluoride	7783-50-8	1		100 (45.4)
Ferric nitrate	10421-48-4	1		1000 (454)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Ferric sulfate	10028-22-5	1		1000 (454)
Ferrous ammonium sulfate	10045-89-3	1		1000 (454)
Ferrous chloride	7758-94-3	1		100 (45.4)
Ferrous sulfate	7720-78-7 7782-63-0	1		1000 (454)
Fine mineral fibers[c]	N.A.	3		**
Fluoranthene	206-44-0	2,4	U120	100 (45.4)
Fluorene	86-73-7	2		5000 (2270)
Fluorine	7782-41-4	4	P056	10 (4.54)
Fluoroacetamide	640-19-7	4	P057	100 (45.4)
Fluoroacetic acid, sodium salt	62-74-8	4	P058	10 (4.54)
Formaldehyde	50-00-0	1,3,4	U122	100 (45.4)
Formetanate hydrochloride	23422539	4	P198	100 (45.4)
Formic acid	64-18-6	1,4	U123	5000 (2270)
Formparanate	17702577	4	P197	100 (45.4)
Fulminic acid, mercury(2 +)salt	628-86-4	4	P065	10 (4.54)
Fumaric acid	110-17-8	1		5000 (2270)
Furan	110-00-9	4	U124	100 (45.4)
2-Furancarboxaldehyde	98-01-1	1,4	U125	5000 (2270)
2,5-Furandione	108-31-6	1,3,4	U147	5000 (2270)
Furan, tetrahydro-	109-99-9	4	U213	1000 (454)
Furfural	98-01-1	1,4	U125	5000 (2270)
Furfuran	110-00-9	4	U124	100 (45.4)
Glucopyranose, 2-deoxy-2-(3-methyl-3-nitrosoureido)-,D-	18883-66-4	4	U206	1 (0.454)
D-Glucose, 2-deoxy-2-[[(methylnitrosoamino)-carbonyl]amino]-	18883-66-4	4	U206	1 (0.454)
Glycidylaldehyde	765-34-4	4	U126	10 (4.54)
Glycol ethers[d]	N.A.	3		**

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40 C.F.R. Part 302 – Table 302.4
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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Guanidine, N-methyl-N′-nitro-N-nitroso-	70-25-7	4	U163	10 (4.54)
Guthion	86-50-0	1		1 (0.454)
HALOETHERS	N.A.	2		**
HALOMETHANES	N.A.	2		**
Heptachlor	76-44-8	1,2,3,4	P059	1 (0.454)
HEPTACHLOR AND METABOLITES	N.A.	2		**
Heptachlor epoxide	1024-57-3	2		1 (0.454)
Hexachlorobenzene	118-74-1	2,3,4	U127	10 (4.54)
Hexachlorobutadiene	87-68-3	2,3,4	U128	1 (0.454)
HEXACHLOROCYCLOHEXANE (all isomers)	608-73-1	2		**
Hexachlorocyclopentadiene	77-47-4	1,2,3,4	U130	10 (4.54)
Hexachloroethane	67-72-1	2,3,4	U131	100 (45.4)
Hexachlorophene	70-30-4	4	U132	100 (45.4)
Hexachloropropene	1888-71-7	4	U243	1000 (454)
Hexaethyl tetraphosphate	757-58-4	4	P062	100 (45.4)
Hexamethylene-1,6-diisocyanate	822-06-0	3		100 (45.4)
Hexamethylphosphoramide	680-31-9	3		1 (0.454)
Hexane	110-54-3	3		5000 (2270)
Hexone	108-10-1	3,4	U161	5000 (2270)
Hydrazine	302-01-2	3,4	U133	1 (0.454)
Hydrazinecarbothioamide	79-19-6	4	P116	100 (45.4)
Hydrazine, 1,2-diethyl-	1615-80-1	4	U086	10 (4.54)
Hydrazine, 1,1-dimethyl-	57-14-7	3,4	U098	10 (4.54)
Hydrazine, 1,2-dimethyl-	540-73-8	4	U099	1 (0.454)
Hydrazine, 1,2-diphenyl-	122-66-7	2,3,4	U109	10 (4.54)
Hydrazine, methyl-	60-34-4	3,4	P068	10 (4.54)
Hydrochloric acid	7647-01-0	1,3		5000 (2270)
Hydrocyanic acid	74-90-8	1,4	P063	10 (4.54)
Hydrofluoric acid	7664-39-3	1,3,4	U134	100 (45.4)
Hydrogen chloride	7647-01-0	1,3		5000 (2270)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Hydrogen cyanide	74-90-8	1,4	P063	10 (4.54)
Hydrogen fluoride	7664-39-3	1,3,4	U134	100 (45.4)
Hydrogen phosphide	7803-51-2	3,4	P096	100 (45.4)
Hydrogen sulfide H2S	7783-06-4	1,4	U135	100 (45.4)
Hydroperoxide, 1-methyl-1-phenylethyl-	80-15-9	4	U096	10 (4.54)
Hydroquinone	123-31-9	3		100 (45.4)
2-Imidazolidinethione	96-45-7	3,4	U116	10 (4.54)
Indeno(1,2,3-cd)pyrene	193-39-5	2,4	U137	100 (45.4)
Iodomethane	74-88-4	3,4	U138	100 (45.4)
1,3-Isobenzofurandione	85-44-9	3,4	U190	5000 (2270)
Isobutyl alcohol	78-83-1	4	U140	5000 (2270)
Isodrin	465-73-6	4	P060	1 (0.454)
Isolan	119380	4	P192	100 (45.4)
Isophorone	78-59-1	2,3		5000 (2270)
Isoprene	78-79-5	1		100 (45.4)
Isopropanolamine dodecylbenzenesulfonate	42504-46-1	1		1000 (454)
3-Isopropylphenyl N-methylcarbamate	64006	4	P202	10 (4.54)
Isosafrole	120-58-1	4	U141	100 (45.4)
3(2H)-Isoxazolone, 5-(aminomethyl)-	2763-96-4	4	P007	1000 (454)
Kepone	143-50-0	1,4	U142	1 (0.454)
Lasiocarpine	303-34-4	4	U143	10 (4.54)
Lead††	7439-92-1	2		10 (4.54)
Lead acetate	301-04-2	1,4	U144	10 (4.54)
LEAD AND COMPOUNDS	N.A.	2,3		**
Lead arsenate	7784-40-9 7645-25-2 10102-48-4	1		1 (0.454)
Lead, bis(acetato-O)tetrahydroxytri-	1335-32-6	4	U146	10 (4.54)
Lead chloride	7758-95-4	1		10 (4.54)
Lead compounds	N.A.	2,3		**
Lead fluoborate	13814-96-5	1		10 (4.54)

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[Note: All Comments/Notes Are Located at the End of This Table]

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Lead fluoride	7783-46-2	1		10 (4.54)
Lead iodide	10101-63-0	1		10 (4.54)
Lead nitrate	10099-74-8	1		10 (4.54)
Lead phosphate	7446-27-7	4	U145	10 (4.54)
Lead stearate	1072-35-1 7428-48-0 52652-59-2 56189-09-4	1		10 (4.54)
Lead subacetate	1335-32-6	4	U146	10 (4.54)
Lead sulfate	7446-14-2 15739-80-7	1		10 (4.54)
Lead sulfide	1314-87-0	1		10 (4.54)
Lead thiocyanate	592-87-0	1		10 (4.54)
Lindane	58-89-9	1,2,3,4	U129	1 (0.454)
Lindane (all isomers)	58-89-9	1,2,3,4	U129	1 (0.454)
Lithium chromate	14307-35-8	1		10 (4.54)
Malathion	121-75-5	1		100 (45.4)
Maleic acid	110-16-7	1		5000 (2270)
Maleic anhydride	108-31-6	1,3,4	U147	5000 (2270)
Maleic hydrazide	123-33-1	4	U148	5000 (2270)
Malononitrile	109-77-3	4	U149	1000 (454)
Manganese, bis (dimethylcarbamodithioato-S,S')-	15339363	4	P196	10 (4.54)
Manganese Compounds	N.A.	3		**
Manganese dimethyldithiocarbamate	15339363	4	P196	10 (4.54)
MDI	101-68-8	3		5000 (2270)
MEK	78-93-3	3,4	U159	5000 (2270)
Melphalan	148-82-3	4	U150	1 (0.454)
Mercaptodimethur	2032-65-7	1,4	P199	10 (4.54)
Mercuric cyanide	592-04-1	1		1(0.454)
Mercuric nitrate	10045-94-0	1		10 (4.54)
Mercuric sulfate	7783-35-9	1		10 (4.54)

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40 C.F.R. Part 302 – Table 302.4
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Mercuric thiocyanate	592-85-8	1		10 (4.54)
Mercurous nitrate	10415-75-5	1	10 (4.54)	7782-86-7
Mercury	7439-97-6	2,3,4	U151	1 (0.454)
MERCURY AND COMPOUNDS	N.A.	2,3		**
Mercury, (acetato-O)phenyl-	62-38-4	4	P092	100 (45.4)
Mercury Compounds	N.A.	2,3		**
Mercury fulminate	628-86-4	4	P065	10 (4.54)
Methacrylonitrile	126-98-7	4	U152	1000 (454)
Methanamine, N-methyl-	124-40-3	1,4	U092	1000 (454)
Methanamine, N-methyl-N-nitroso-	62-75-9	2,3,4	P082	10 (4.54)
Methane, bromo-	74-83-9	2,3,4	U029	1000 (454)
Methane, chloro-	74-87-3	2,3,4	U045	100 (45.4)
Methane, chloromethoxy-	107-30-2	3,4	U046	10 (4.54)
Methane, dibromo-	74-95-3	4	U068	1000 (454)
Methane, dichloro-	75-09-2	2,3,4	U080	1000 (454)
Methane, dichlorodifluoro-	75-71-8	4	U075	5000 (2270)
Methane, iodo-	74-88-4	3,4	U138	100 (45.4)
Methane, isocyanato-	624-83-9	3,4	P064	10 (4.54)
Methane, oxybis(chloro-	542-88-1	2,3,4	P016	10 (4.54)
Methanesulfenyl chloride, trichloro-	594-42-3	4	P118	100 (45.4)
Methanesulfonic acid, ethyl ester	62-50-0	4	U119	1 (0.454)
Methane, tetrachloro-	56-23-5	1,2,3,4	U211	10 (4.54)
Methane, tetranitro-	509-14-8	4	P112	10 (4.54)
Methanethiol	74-93-1	1,4	U153	100 (45.4)
Methane, tribromo-	75-25-2	2,3,4	U225	100 (45.4)
Methane, trichloro-	67-66-3	1,2,3,4	U044	10 (4.54)
Methane, trichlorofluoro-	75-69-4	4	U121	5000 (2270)
Methanimidamide, N,N-dimethyl-N'-[3-[[(methylamino)-carbonyl]oxy]phenyl]-, monohydrochloride	23422539	4	P198	100 (45.4)

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Methanimidamide, N,N-dimethyl-N'-[2-methyl-4-[[(methylamino) carbonyl]oxy]phenyl]-	17702577	4	P197	100 (45.4)
6,9-Methano-2,4,3-benzodioxathiepin, 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-, 3-oxide	115-29-7	1,2,4	P050	1 (0.454)
4,7-Methano-1H-indene, 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-	76-44-8	1,2,3,4	P059	1 (0.454)
4,7-Methano-1H-indene, 1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-—	57-74-9	1,2,3,4	U036	1 (0.454)
Methanol	67-56-1	3,4	U154	5000 (2270)
Methapyrilene	91-80-5	4	U155	5000 (2270)
1,3,4-Metheno-2H-cyclobuta[cd]pentalen-2-one, 1,1a,3,3a,4,5,5,5a,5b,6-decachlorooctahydro-	143-50-0	1,4	U142	1 (0.454)
Methiocarb	2032-65-7	1,4	P199	10 (4.54)
Methomyl	16752-77-5	4	P066	100 (45.4)
Methoxychlor	72-43-5	1,3,4	U247	1 (0.454)
Methyl alcohol	67-56-1	3,4	U154	5000 (2270)
2-Methyl aziridine	75-55-8	3,4	P067	1 (0.454)
Methyl bromide	74-83-9	2,3,4	U029	1000 (454)
1-Methylbutadiene	504-60-9	4	U186	100 (45.4)
Methyl chloride	74-87-3	2,3,4	U045	100 (45.4)
Methyl chlorocarbonate	79-22-1	4	U156	1000 (454)
Methyl chloroform	71-55-6	2,3,4	U226	1000 (454)
3-Methylcholanthrene	56-49-5	4	U157	10 (4.54)
4,4′-Methylenebis(2-chloroaniline)	101-14-4	3,4	U158	10 (4.54)
Methylene bromide	74-95-3	4	U068	1000 (454)
Methylene chloride	75-09-2	2,3,4	U080	1000 (454)
4,4′-Methylenedianiline	101-77-9	3		10 (4.54)
Methylene diphenyl diisocyanate	101-68-8	3		5000 (2270)
Methyl ethyl ketone	78-93-3	3,4	U159	5000 (2270)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Methyl ethyl ketone peroxide	1338-23-4	4	U160	10 (4.54)
Methyl hydrazine	60-34-4	3,4	P068	10 (4.54)
Methyl iodide	74-88-4	3,4	U138	100 (45.4)
Methyl isobutyl ketone	108-10-1	3,4	U161	5000 (2270)
Methyl isocyanate	624-83-9	3,4	P064	10 (4.54)
2-Methyllactonitrile	75-86-5	1,4	P069	10 (4.54)
Methyl mercaptan	74-93-1	1,4	U153	100 (45.4)
Methyl methacrylate	80-62-6	1,3,4	U162	1000 (454)
Methyl parathion	298-00-0	1,4	P071	100 (45.4)
4-Methyl-2-pentanone	108-10-1	3,4	U161	5000 (2270)
Methyl tert-butyl ether	1634-04-4	3		1000 (454)
Methylthiouracil	56-04-2	4	U164	10 (4.54)
Metolcarb	1129415	4	P190	1000 (454)
Mevinphos	7786-34-7	1		10 (4.54)
Mexacarbate	315-18-4	1,4	P128	1000 (454)
Mitomycin C	50-07-7	4	U010	10 (4.54)
MNNG	70-25-7	4	U163	10 (4.54)
Monoethylamine	75-04-7	1		100 (45.4)
Monomethylamine	74-89-5	1		100 (45.4)
Naled	300-76-5	1		10 (4.54)
5,12-Naphthacenedione, 8-acetyl-10-[(3-amino-2,3,6-trideoxy-alpha-L-lyxo-hexopyranosyl)oxy]-7,8,9,10-tetrahydro-6,8,11-trihydroxy-1-methoxy-, (8S-cis)-	20830-81-3	4	U059	10 (4.54)
1-Naphthalenamine	134-32-7	4	U167	100 (45.4)
2-Naphthalenamine	91-59-8	4	U168	10 (4.54)
Naphthalenamine, N,N′-bis(2-chloroethyl)-	494-03-1	4	U026	100 (45.4)
Naphthalene	91-20-3	1,2,3,4	U165	100 (45.4)
Naphthalene, 2-chloro-	91-58-7	2,4	U047	5000 (2270)
1,4-Naphthalenedione	130-15-4	4	U166	5000 (2270)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
2,7-Naphthalenedisulfonic acid, 3,3′-[(3,3′-dimethyl-(1,1′-biphenyl)-4,4′-diyl)-bis(azo)]bis(5-amino-4-hydroxy)-tetrasodium salt	72-57-1	4	U236	10 (4.54)
1-Naphthalenol, methylcarbamate	63-25-2	1,3,4	U279	100 (45.4)
Naphthenic acid	1338-24-5	1		100 (45.4)
1,4-Naphthoquinone	130-15-4	4	U166	5000 (2270)
alpha-Naphthylamine	134-32-7	4	U167	100 (45.4)
beta-Naphthylamine	91-59-8	4	U168	10 (4.54)
alpha-Naphthylthiourea	86-88-4	4	P072	100 (45.4)
Nickel††	7440-02-0	2		100 (45.4)
Nickel ammonium sulfate	15699-18-0	1		100 (45.4)
NICKEL AND COMPOUNDS	N.A.	2,3		**
Nickel carbonyl Ni(CO)4, (T-4)-	13463-39-3	4	P073	10 (4.54)
Nickel chloride	7718-54-9 37211-05-5	1		100 (45.4)
Nickel compounds	N.A.	2,3		**
Nickel cyanide Ni(CN)2	557-19-7	4	P074	10 (4.54)
Nickel hydroxide	12054-48-7	1		10 (4.54)
Nickel nitrate	14216-75-2	1		100 (45.4)
Nickel sulfate	7786-81-4	1		100 (45.4)
Nicotine, & salts	54-11-5	4	P075	100 (45.4)
Nitric acid	7697-37-2	1		1000 (454)
Nitric acid, thallium (1 +) salt	10102-45-1	4	U217	100 (45.4)
Nitric oxide	10102-43-9	4	P076	10 (4.54)
p-Nitroaniline	100-01-6	4	P077	5000 (2270)
Nitrobenzene	98-95-3	1,2,3,4	U169	1000 (454)
4-Nitrobiphenyl	92-93-3	3		10 (4.54)
Nitrogen dioxide	10102-44-0 10544-72-6	1,4	P078	10 (4.54)
Nitrogen oxide NO	10102-43-9	4	P076	10 (4.54)
Nitrogen oxide NO2	10102-44-0 10544-72-6	1,4	P078	10 (4.54)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Nitroglycerine	55-63-0	4	P081	10 (4.54)
Nitrophenol (mixed)	25154-55-6	1		100 (45.4)
m-Nitrophenol	554-84-7			
o-Nitrophenol	88-75-5	1,2		100 (45.4)
p-Nitrophenol	100-02-7	1,2,3,4	U170	100 (45.4)
2-Nitrophenol	88-75-5	1,2		100 (45.4)
4-Nitrophenol	100-02-7	1,2,3,4	U170	100 (45.4)
NITROPHENOLS	N.A.	2		**
2-Nitropropane	79-46-9	3,4	U171	10 (4.54)
NITROSAMINES	N.A.	2		**
N-Nitrosodi-n-butylamine	924-16-3	4	U172	10 (4.54)
N-Nitrosodiethanolamine	1116-54-7	4	U173	1 (0.454)
N-Nitrosodiethylamine	55-18-5	4	U174	1 (0.454)
N-Nitrosodimethylamine	62-75-9	2,3,4	P082	10 (4.54)
N-Nitrosodiphenylamine	86-30-6	2		100 (45.4)
N-Nitroso-N-ethylurea	759-73-9	4	U176	1 (0.454)
N-Nitroso-N-methylurea	684-93-5	3,4	U177	1 (0.454)
N-Nitroso-N-methylurethane	615-53-2	4	U178	1 (0.454)
N-Nitrosomethylvinylamine	4549-40-0	4	P084	10 (4.54)
N-Nitrosomorpholine	59-89-2	3		1 (0.454)
N-Nitrosopiperidine	100-75-4	4	U179	10 (4.54)
N-Nitrosopyrrolidine	930-55-2	4	U180	1 (0.454)
Nitrotoluene	1321-12-6	1		1000 (454)
m-Nitrotoluene	99-08-1			
o-Nitrotoluene	88-72-2			
p-Nitrotoluene	99-99-0			
5-Nitro-o-toluidine	99-55-8	4	U181	100 (45.4)
Octamethylpyrophosphoramide	152-16-9	4	P085	100 (45.4)
Osmium oxide OsO4, (T-4)-	20816-12-0	4	P087	1000 (454)
Osmium tetroxide	20816-12-0	4	P087	1000 (454)
7-Oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid	145-73-3	4	P088	1000 (454)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Oxamyl	23135220	4	P194	100 (45.4)
1,2-Oxathiolane, 2,2-dioxide	1120-71-4	3,4	U193	10 (4.54)
2H-1,3,2-Oxazaphosphorin-2-amine, N,N- bis(2-chloroethyl)tetrahydro-, 2-oxide	50-18-0	4	U058	10 (4.54)
Oxirane	75-21-8	3,4	U115	10 (4.54)
Oxiranecarboxyaldehyde	765-34-4	4	U126	10 (4.54)
Oxirane, (chloromethyl)-	106-89-8	1,3,4	U041	100 (45.4)
Paraformaldehyde	30525-89-4	1		1000 (454)
Paraldehyde	123-63-7	4	U182	1000 (454)
Parathion	56-38-2	1,3,4	P089	10 (4.54)
PCBs	1336-36-3	1,2,3		1 (0.454)
PCNB	82-68-8	3,4	U185	100 (45.4)
Pentachlorobenzene	608-93-5	4	U183	10 (4.54)
Pentachloroethane	76-01-7	4	U184	10 (4.54)
Pentachloronitrobenzene	82-68-8	3,4	U185	100 (45.4)
Pentachlorophenol	87-86-5	1,2,3,4	See F027	10 (4.54)
1,3-Pentadiene	504-60-9	4	U186	100 (45.4)
Perchloroethylene	127-18-4	2,3,4	U210	100 (45.4)
Phenacetin	62-44-2	4	U187	100 (45.4)
Phenanthrene	85-01-8	2		5000 (2270)
Phenol	108-95-2	1,2,3,4	U188	1000 (454)
Phenol, 2-chloro-	95-57-8	2,4	U048	100 (45.4)
Phenol, 4-chloro-3-methyl-	59-50-7	2,4	U039	5000 (2270)
Phenol, 2-cyclohexyl-4,6-dinitro-	131-89-5	4	P034	100 (45.4)
Phenol, 2,4-dichloro-	120-83-2	2,4	U081	100 (45.4)
Phenol, 2,6-dichloro-	87-65-0	4	U082	100 (45.4)
Phenol, 4,4′-(1,2-diethyl-1,2-ethenediyl)bis-, (E)	56-53-1	4	U089	1 (0.454)
Phenol, 2,4-dimethyl-	105-67-9	2,4	U101	100 (45.4)
Phenol, 4-(dimethylamino)-3,5-dimethyl-, 4 methylcarbamate (ester)	315-18-4	1,4	P128	1000 (454)

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Phenol, (3,5-dimethyl-4-(methylthio)-, methylcarbamate	2032-65-7	1,4	P199	10 (4.54)
Phenol, 2,4-dinitro-	51-28-5	1,2,3,4	P048	10 (4.54)
Phenol, methyl-	1319-77-3	1,3,4	U052	100 (45.4)
Phenol, 2-methyl-4,6-dinitro-, & salts	534-52-1	2,3,4	P047	10 (4.54)
Phenol, 2,2′-methylenebis[3,4,6- trichloro-	70-30-4	4	U132	100 (45.4)
Phenol, 2-(1-methylethoxy)-, methylcarbamate	114-26-1	3,4	U411	100 (45.4)
Phenol, 3-(1-methylethyl)-, methyl carbamate	64006	4	P202	10 (4.54)
Phenol, 3-methyl-5-(1-methylethyl)-, methyl carbamate	2631370	4	P201	1000 (454)
Phenol, 2-(1-methylpropyl)-4,6-dinitro-	88-85-7	4	P020	1000 (454)
Phenol, 4-nitro-	100-02-7	1,2,3,4	U170	100 (45.4)
Phenol, pentachloro-	87-86-5	1,2,3,4	See F027	10 (4.54)
Phenol, 2,3,4,6-tetrachloro-	58-90-2	4	See F027	10 (4.54)
Phenol, 2,4,5-trichloro-	95-95-4	1,3,4	See F027	10 (4.54)
Phenol, 2,4,6-trichloro-	88-06-2	1,2,3,4	See F027	10 (4.54)
Phenol, 2,4,6-trinitro-, ammonium salt	131-74-8	4	P009	10 (4.54)
L-Phenylalanine, 4-[bis(2-chloroethyl)amino]-	148-82-3	4	U150	1 (0.454)
p-Phenylenediamine	106-50-3	3		5000 (2270)
Phenylmercury acetate	62-38-4	4	P092	100 (45.4)
Phenylthiourea	103-85-5	4	P093	100 (45.4)
Phorate	298-02-2	4	P094	10 (4.54)
Phosgene	75-44-5	1,3,4	P095	10 (4.54)
Phosphine	7803-51-2	3,4	P096	100 (45.4)
Phosphoric acid	7664-38-2	1		5000 (2270)
Phosphoric acid, diethyl 4-nitrophenyl ester	311-45-5	4	P041	100 (45.4)
Phosphoric acid, lead(2 +) salt (2:3)	7446-27-7	4	U145	10 (4.54)
Phosphorodithioic acid, O,O-diethyl S-[2-(ethylthio)ethyl] ester	298-04-4	1,4	P039	1 (0.454)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Phosphorodithioic acid, O,O-diethyl S-[(ethylthio)methyl] ester	298-02-2	4	P094	10 (4.54)
Phosphorodithioic acid, O,O-diethyl S-methyl ester	3288-58-2	4	U087	5000 (2270)
Phosphorodithioic acid, O,O-dimethyl S-[2(methylamino)-2-oxoethyl] ester	60-51-5	4	P044	10 (4.54)
Phosphorofluoridic acid, bis(1-methylethyl) ester	55-91-4	4	P043	100 (45.4)
Phosphorothioic acid, O,O-diethyl O-(4-nitrophenyl) ester	56-38-2	1,3,4	P089	10 (4.54)
Phosphorothioic acid, O,O-diethyl O-pyrazinyl ester	297-97-2	4	P040	100 (45.4)
Phosphorothioic acid, O-[4-[(dimethylamino) sulfonyl]phenyl] O,O-dimethyl ester	52-85-7	4	P097	1000 (454)
Phosphorothioic acid, O,O-dimethyl O-(4-nitrophenyl) ester	298-00-0	1,4	P071	100 (45.4)
Phosphorus	7723-14-0	1,3		1 (0.454)
Phosphorus oxychloride	10025-87-3	1		1000 (454)
Phosphorus pentasulfide	1314-80-3	1,4	U189	100 (45.4)
Phosphorus sulfide	1314-80-3	1,4	U189	100 (45.4)
Phosphorus trichloride	7719-12-2	1		1000 (454)
Physostigmine	57476	4	P204	100 (45.4)
Physostigmine salicylate	57647	4	P188	100 (45.4)
PHTHALATE ESTERS	N.A.	2		**
Phthalic anhydride	85-44-9	3,4	U190	5000 (2270)
2-Picoline	109-06-8	4	U191	5000 (2270)
Piperidine, 1-nitroso-	100-75-4	4	U179	10 (4.54)
Plumbane, tetraethyl-	78-00-2	1,4	P110	10 (4.54)
POLYCHLORINATED BIPHENYLS	1336-36-3	1,2,3		1 (0.454)
Polycyclic Organic Matter[e]	N.A.	3		**
POLYNUCLEAR AROMATIC HYDROCARBONS	N.A.	2		**
Potassium arsenate	7784-41-0	1		1 (0.454)

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List of Hazardous Substances and Reportable Quantities

[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Potassium arsenite	10124-50-2	1		1 (0.454)
Potassium bichromate	7778-50-9	1		10 (4.54)
Potassium chromate	7789-00-6	1		10 (4.54)
Potassium cyanide K(CN)	151-50-8	1,4	P098	10 (4.54)
Potassium hydroxide	1310-58-3	1		1000 (454)
Potassium permanganate	7722-64-7	1		100 (45.4)
Potassium silver cyanide	506-61-6	4	P099	1 (0.454)
Promecarb	2631370	4	P201	1000 (454)
Pronamide	23950-58-5	4	U192	5000 (2270)
Propanal, 2-methyl-2-(methyl- sulfonyl)-, O-[(methylamino)carbonyl] oxime	1646884	4	P203	100 (45.4)
Propanal, 2-methyl-2-(methylthio)-, O-[(methylamino)carbonyl]oxime	116-06-3	4	P070	1 (0.454)
1-Propanamine	107-10-8	4	U194	5000 (2270)
1-Propanamine, N-propyl-	142-84-7	4	U110	5000 (2270)
1-Propanamine, N-nitroso-N-propyl-	621-64-7	2,4	U111	10 (4.54)
Propane, 1,2-dibromo-3-chloro-	96-12-8	3,4	U066	1 (0.454)
Propane, 1,2-dichloro-	78-87-5	1,2,3,4	U083	1000 (454)
Propanedinitrile	109-77-3	4	U149	1000 (454)
Propanenitrile	107-12-0	4	P101	10 (4.54)
Propanenitrile, 3-chloro-	542-76-7	4	P027	1000 (454)
Propanenitrile, 2-hydroxy-2-methyl-	75-86-5	1,4	P069	10 (4.54)
Propane, 2-nitro-	79-46-9	3,4	U171	10 (4.54)
Propane, 2,2′-oxybis[2-chloro-	108-60-1	2,4	U027	1000 (454)
1,3-Propane sultone	1120-71-4	3,4	U193	10 (4.54)
1,2,3-Propanetriol, trinitrate	55-63-0	4	P081	10 (4.54)
Propanoic acid, 2-(2,4,5-trichlorophenoxy)-	93-72-1	1,4	See F027	100 (45.4)
1-Propanol, 2,3-dibromo-, phosphate (3:1)	126-72-7	4	U235	10 (4.54)
1-Propanol, 2-methyl-	78-83-1	4	U140	5000 (2270)

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[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
2-Propanone	67-64-1	4	U002	5000 (2270)
2-Propanone, 1-bromo-	598-31-2	4	P017	1000 (454)
Propargite	2312-35-8	1		10 (4.54)
Propargyl alcohol	107-19-7	4	P102	1000 (454)
2-Propenal	107-02-8	1,2,3,4	P003	1 (0.454)
2-Propenamide	79-06-1	3,4	U007	5000 (2270)
1-Propene, 1,3-dichloro-	542-75-6	1,2,3,4	U084	100 (45.4)
1-Propene, 1,1,2,3,3,3-hexachloro-	1888-71-7	4	U243	1000 (454)
2-Propenenitrile	107-13-1	1,2,3,4	U009	100 (45.4)
2-Propenenitrile, 2-methyl-	126-98-7	4	U152	1000 (454)
2-Propenoic acid	79-10-7	3,4	U008	5000 (2270)
2-Propenoic acid, ethyl ester	140-88-5	3,4	U113	1000 (454)
2-Propenoic acid, 2-methyl-, ethyl ester	97-63-2	4	U118	1000 (454)
2-Propenoic acid, 2-methyl-, methyl ester	80-62-6	1,3,4	U162	1000 (454)
2-Propen-1-ol	107-18-6	1,4	P005	100 (45.4)
Propham	122429	4	U373	1000 (454)
beta-Propiolactone	57-57-8	3		10 (4.54)
Propionaldehyde	123-38-6	3	1000 (454)	
Propionic acid	79-09-4	1		5000 (2270)
Propionic anhydride	123-62-6	1		5000 (2270)
Propoxur (Baygon)	114-26-1	3,4	U411	100 (45.4)
n-Propylamine	107-10-8	4	U194	5000 (2270)
Propylene dichloride	78-87-5	1,2,3,4	U083	1000 (454)
Propylene oxide	75-56-9	1,3		100 (45.4)
1,2-Propylenimine	75-55-8	3,4	P067	1 (0.454)
2-Propyn-1-ol	107-19-7	4	P102	1000 (454)
Prosulfocarb	52888809	4	U387	5000 (2270)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Pyrene	129-00-0	2		5000 (2270)
Pyrethrins	121-29-9 121-21-1 8003-34-7	1		1 (0.454)
3,6-Pyridazinedione, 1,2-dihydro-	123-33-1	4	U148	5000 (2270)
4-Pyridinamine	504-24-5	4	P008	1000 (454)
Pyridine	110-86-1	4	U196	1000 (454)
Pyridine, 2-methyl-	109-06-8	4	U191	5000 (2270)
Pyridine, 3-(1-methyl-2-pyrrolidinyl)-, (S)-, & salts	54-11-5	4	P075	100 (45.4)
2,4-(1H,3H)-Pyrimidinedione, 5-[bis(2-chloroethyl)amino]-	66-75-1	4	U237	10 (4.54)
4(1H)-Pyrimidinone, 2,3-dihydro-6-methyl-2-thioxo-	56-04-2	4	U164	10 (4.54)
Pyrrolidine, 1-nitroso-	930-55-2	4	U180	1 (0.454)
Pyrrolo[2,3-b]indol-5-ol, 1,2,3,3a,8,8a-hexahydro-1,3a,8-trimethyl-, methylcarbamate (ester), (3aS-cis)-	57476	4	P204	100 (45.4)
Quinoline	91-22-5	1,3		5000 (2270)
Quinone	106-51-4	3,4	U197	10 (4.54)
Quintobenzene	82-68-8	3,4	U185	100 (45.4)
Radionuclides (including radon)	N.A.	3		§
Reserpine	50-55-5	4	U200	5000 (2270)
Resorcinol	108-46-3	1,4	U201	5000 (2270)
Safrole	94-59-7	4	U203	100 (45.4)
Selenious acid	7783-00-8	4	U204	10 (4.54)
Selenious acid, dithallium (1 +) salt	12039-52-0	4	P114	1000 (454)
Selenium††	7782-49-2	2		100 (45.4)
SELENIUM AND COMPOUNDS	N.A.	2,3		**
Selenium Compounds	N.A.	2,3		**

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Selenium dioxide	7446-08-4	1,4	U204	10 (4.54)
Selenium oxide	7446-08-4	1,4	U204	10 (4.54)
Selenium sulfide SeS2	7488-56-4	4	U205	10 (4.54)
Selenourea	630-10-4	4	P103	1000 (454)
L-Serine, diazoacetate (ester)	115-02-6	4	U015	1 (0.454)
Silver††	7440-22-4	2		1000 (454)
SILVER AND COMPOUNDS	N.A.	2		**
Silver cyanide Ag(CN)	506-64-9	4	P104	1 (0.454)
Silver nitrate	7761-88-8	1		1 (0.454)
Silvex (2,4,5-TP)	93-72-1	1,4	See F027	100 (45.4)
Sodium	7440-23-5	1		10 (4.54)
Sodium arsenate	7631-89-2	1		1 (0.454)
Sodium arsenite	7784-46-5	1		1 (0.454)
Sodium azide	26628-22-8	4	P105	1000 (454)
Sodium bichromate	10588-01-9	1		10 (4.54)
Sodium bifluoride	1333-83-1	1		100 (45.4)
Sodium bisulfite	7631-90-5	1		5000 (2270)
Sodium chromate	7775-11-3	1		10 (4.54)
Sodium cyanide Na(CN)	143-33-9	1,4	P106	10 (4.54)
Sodium dodecylbenzenesulfonate	25155-30-0	1		1000 (454)
Sodium fluoride	7681-49-4	1		1000 (454)
Sodium hydrosulfide	16721-80-5	1		5000 (2270)
Sodium hydroxide	1310-73-2	1		1000 (454)
Sodium hypochlorite	7681-52-9 10022-70-5	1		100 (45.4)
Sodium methylate	124-41-4	1		1000 (454)
Sodium nitrite	7632-00-0	1		100 (45.4)
Sodium phosphate, dibasic	7558-79-4 10039-32-4 10140-65-5	1		5000 (2270)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Sodium phosphate, tribasic	7601-54-9 10101-89-0 10361-89-4	1		5000 (2270)
Sodium selenite	7782-82-3 10102-18-8	1		100 (45.4)
Streptozotocin	18883-66-4	4	U206	1 (0.454)
Strontium chromate	7789-06-2	1		10 (4.54)
Strychnidin-10-one, & salts	57-24-9	1,4	P108	10 (4.54)
Strychnidin-10-one, 2,3-dimethoxy-	357-57-3	4	P018	100 (45.4)
Strychnine, & salts	57-24-9	1,4	P108	10 (4.54)
Styrene	100-42-5	1,3		1000 (454)
Styrene oxide	96-09-3	3		100 (45.4)
Sulfuric acid	7664-93-9 8014-95-7	1		1000 (454)
Sulfuric acid, dimethyl ester	77-78-1	3,4	U103	100 (45.4)
Sulfuric acid, dithallium (1 +) salt	7446-18-6 10031-59-1	1,4	P115	100 (45.4)
Sulfur monochloride	12771-08-3	1		1000 (454)
Sulfur phosphide	1314-80-3	1,4	U189	100 (45.4)
2,4,5-T	93-76-5	1,4	See F027	1000 (454)
2,4,5-T acid	93-76-5	1,4	See F027	1000 (454)
2,4,5-T amines	2008-46-0 1319-72-8 3813-14-7 6369-96-6 6369-97-7	1		5000 (2270)
2,4,5-T esters	93-79-8 1928-47-8 2545-59-7 25168-15-4 61792-07-2	1		1000 (454)
2,4,5-T salts	13560-99-1	1		1000 (454)
TCDD	1746-01-6	2,3		1 (0.454)
TDE	72-54-8	1,2,4	U060	1 (0.454)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
1,2,4,5-Tetrachlorobenzene	95-94-3	4	U207	5000 (2270)
2,3,7,8-Tetrachlorodibenzo-p-dioxin	1746-01-6	2,3		1 (0.454)
1,1,1,2-Tetrachloroethane	630-20-6	4	U208	100 (45.4)
1,1,2,2-Tetrachloroethane	79-34-5	2,3,4	U209	100 (45.4)
Tetrachloroethylene	127-18-4	2,3,4	U210	100 (45.4)
2,3,4,6-Tetrachlorophenol	58-90-2	4	See F027	10 (4.54)
Tetraethyl pyrophosphate	107-49-3	1,4	P111	10 (4.54)
Tetraethyl lead	78-00-2	1,4	P110	10 (4.54)
Tetraethyldithiopyrophosphate	3689-24-5	4	P109	100 (45.4)
Tetrahydrofuran	109-99-9	4	U213	1000 (454)
Tetranitromethane	509-14-8	4	P112	10 (4.54)
Tetraphosphoric acid, hexaethyl ester	757-58-4	4	P062	100 (45.4)
Thallic oxide	1314-32-5	4	P113	100 (45.4)
Thallium††	7440-28-0	2		1000 (454)
THALLIUM AND COMPOUNDS	N.A.	2		**
Thallium (I) acetate	563-68-8	4	U214	100 (45.4)
Thallium (I) carbonate	6533-73-9	4	U215	100 (45.4)
Thallium chloride TlCl	7791-12-0	4	U216	100 (45.4)
Thallium (I) nitrate	10102-45-1	4	U217	100 (45.4)
Thallium oxide Tl2O3	1314-32-5	4	P113	100 (45.4)
Thallium (l) selenite	12039-52-0	4	P114	1000 (454)
Thallium (I) sulfate	7446-18-6 10031-59-1	1,4	P115	100 (45.4)
Thioacetamide	62-55-5	4	U218	10 (4.54)
Thiodicarb	59669260	4	U410	100 (45.4)
Thiodiphosphoric acid, tetraethyl ester	3689-24-5	4	P109	100 (45.4)
Thiofanox	39196-18-4	4	P045	100 (45.4)
Thioimidodicarbonic diamide [(H2N)C(S)] 2NH	541-53-7	4	P049	100 (45.4)
Thiomethanol	74-93-1	1,4	U153	100 (45.4)
Thioperoxydicarbonic diamide [(H2N)C(S)] 2S2, tetramethyl-	137-26-8	4	U244	10 (4.54)
Thiophanate-methyl	23564058	4	U409	10 (4.54)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Thiophenol	108-98-5	4	P014	100 (45.4)
Thiosemicarbazide	79-19-6	4	P116	100 (45.4)
Thiourea	62-56-6	4	U219	10 (4.54)
Thiourea, (2-chlorophenyl)-	5344-82-1	4	P026	100 (45.4)
Thiourea, 1-naphthalenyl-	86-88-4	4	P072	100 (45.4)
Thiourea, phenyl-	103-85-5	4	P093	100 (45.4)
Thiram	137-26-8	4	U244	10 (4.54)
Tirpate	26419738	4	P185	100 (45.4)
Titanium tetrachloride	7550-45-0	3		1,2,41000 (454)
Toluene	108-88-3	1,2,3,4	U220	1000 (454)
Toluenediamine	95-80-7 496-72-0 823-40-5 25376-45-8	3,4	U221	10 (4.54)
2,4-Toluene diamine	95-80-7 496-72-0 823-40-5 25376-45-8	3,4	U221	10 (4.54)
Toluene diisocyanate	91-08-7 584-84-9 26471-62-5	3,4	U223	100 (45.4)
2,4-Toluene diisocyanate	91-08-7 584-84-9 26471-62-5	3,4	U223	100 (45.4)
o-Toluidine	95-53-4	3,4	U328	100 (45.4)
p-Toluidine	106-49-0	4	U353	100 (45.4)
o-Toluidine hydrochloride	636-21-5	4	U222	100 (45.4)
Toxaphene	8001-35-2	1,2,3,4	P123	1 (0.454)
2,4,5-TP acid	93-72-1	1,4	See F027	100 (45.4)
2,4,5-TP esters	32534-95-5	1		100 (45.4)
Triallate	2303175	4	U389	100 (45.4)
1H-1,2,4-Triazol-3-amine	61-82-5	4	U011	10 (4.54)
Trichlorfon	52-68-6	1		100 (45.4)
1,2,4-Trichlorobenzene	120-82-1	2,3		100 (45.4)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
1,1,1-Trichloroethane	71-55-6	2,3,4	U226	1000 (454)
1,1,2-Trichloroethane	79-00-5	2,3,4	U227	100 (45.4)
Trichloroethylene	79-01-6	1,2,3,4	U228	100 (45.4)
Trichloromethanesulfenyl chloride	594-42-3	4	P118	100 (45.4)
Trichloromonofluoromethane	75-69-4	4	U121	5000 (2270)
Trichlorophenol	25167-82-2	1		10 (4.54)
2,3,4-Trichlorophenol	15950-66-0			
2,3,5-Trichlorophenol	933-78-8			
2,3,6-Trichlorophenol	933-75-5			
3,4,5-Trichlorophenol	609-19-8			
2,4,5-Trichlorophenol	95-95-4	1,3,4	See F027	10 (4.54)
2,4,6-Trichlorophenol	88-06-2	1,2,3,4	See F027	10 (4.54)
Triethanolamine dodecylbenzenesulfonate	27323-41-7	1		1000 (454)
Triethylamine	121-44-8	1,3,4	U404	5000 (2270)
Trifluralin	1582-09-8	3		10 (4.54)
Trimethylamine	75-50-3	1		100 (45.4)
2,2,4-Trimethylpentane	540-84-1	3		1000 (454)
1,3,5-Trinitrobenzene	99-35-4	4	U234	10 (4.54)
1,3,5-Trioxane, 2,4,6-trimethyl-	123-63-7	4	U182	1000 (454)
Tris(2,3-dibromopropyl) phosphate	126-72-7	4	U235	10 (4.54)
Trypan blue	72-57-1	4	U236	10 (4.54)
Unlisted Hazardous Wastes Characteristic of Corrosivity	N.A.	4	D002	100 (45.4)
Unlisted Hazardous Wastes Characteristic of Ignitability	N.A.	4	D001	100 (45.4)
Unlisted Hazardous Wastes Characteristic of Reactivity	N.A.	4	D003	100 (45.4)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Unlisted Hazardous Wastes Characteristic of Toxicity:				
Arsenic (D004)	N.A.	4	D004	1 (0.454)
Barium (D005)	N.A.	4	D005	1000 (454)
Benzene (D018)	N.A.	1,2,3,4	D018	10 (4.54)
Cadmium (D006)	N.A.	4	D006	10 (4.54)
Carbon tetrachloride (D019)	N.A.	1,2,4	D019	10 (4.54)
Chlordane (D020)	N.A.	1,2,4	D020	1 (0.454)
Chlorobenzene (D021)	N.A.	1,2,4	D021	100 (45.4)
Chloroform (D022)	N.A.	1,2,4	D022	10 (4.54)
Chromium (D007)	N.A.	4	D007	10 (4.54)
o-Cresol (D023)	N.A.	4	D023	100 (45.4)
m-Cresol (D024)	N.A.	4	D024	100 (45.4)
p-Cresol (D025)	N.A.	4	D025	100 (45.4)
Cresol (D026)	N.A.	4	D026	100 (45.4)
2,4-D (D016)	N.A.	1,4	D016	100 (45.4)
1,4-Dichlorobenzene (D027)	N.A.	1,2,4	D027	100 (45.4)
1,2-Dichloroethane (D028)	N.A.	1,2,4	D028	100 (45.4)
1,1-Dichloroethylene (D029)	N.A.	1,2,4	D029	100 (45.4)
2,4-Dinitrotoluene (D030)	N.A.	1,2,4	D030	10 (4.54)
Endrin (D012)	N.A.	1,4	D012	1 (0.454)
Heptachlor (and epoxide) (D031)	N.A.	1,2,4	D031	1 (0.454)
Hexachlorobenzene (D032)	N.A.	2,4	D032	10 (4.54)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Hexachlorobutadiene (D033)	N.A.	2,4	D033	1 (0.454)
Hexachloroethane (D034)	N.A.	2,4	D034	100 (45.4)
Lead (D008)	N.A.	4	D008	10 (4.54)
Lindane (D013)	N.A.	1,4	D013	1 (0.454)
Mercury (D009)	N.A.	4	D009	1 (0.454)
Methoxychlor (D014)	N.A.	1,4	D014	1 (0.454)
Methyl ethyl ketone (D035)	N.A.	4	D035	5000 (2270)
Nitrobenzene (D036)	N.A.	1,2,4	D036	1000 (454)
Pentachlorophenol (D037)	N.A.	1,2,4	D037	10 (4.54)
Pyridine (D038)	N.A.	4	D038	1000 (454)
Selenium (D010)	N.A.	4	D010	10 (4.54)
Silver (D011)	N.A.	4	D011	1 (0.454)
Tetrachloroethylene (D039)	N.A.	2,4	D039	100 (45.4)
Toxaphene (D015)	N.A.	1,4	D015	1 (0.454)
Trichloroethylene (D040)	N.A.	1,2,4	D040	100 (45.4)
2,4,5-Trichlorophenol (D041)	N.A.	1,4	D041	10 (4.54)
2,4,6-Trichlorophenol (D042)	N.A.	1,2,4	D042	10 (4.54)
2,4,5-TP (D017)	N.A.	1,4	D017	100 (45.4)
Vinyl chloride (D043)	N.A.	2,3,4	D043	1 (0.454)
Uracil mustard	66-75-1	4	U237	10 (4.54)
Uranyl acetate	541-09-3	1		100 (45.4)
Uranyl nitrate	10102-06-4 36478-76-9	1		100 (45.4)
Urea, N-ethyl-N-nitroso-	759-73-9	4	U176	1 (0.454)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Urea, N-methyl-N-nitroso-	684-93-5	3,4	U177	1 (0.454)
Urethane	51-79-6	3,4	U238	100 (45.4)
Vanadic acid, ammonium salt	7803-55-6	4	P119	1000 (454)
Vanadium oxide V2O5	1314-62-1	1,4	P120	1000 (454)
Vanadium pentoxide	1314-62-1	1,4	P120	1000 (454)
Vanadyl sulfate	27774-13-6	1		1000 (454)
Vinyl acetate	108-05-4	1,3		5000 (2270)
Vinyl acetate monomer	108-05-4	1,3		5000 (2270)
Vinylamine, N-methyl-N-nitroso-	4549-40-0	4	P084	10 (4.54)
Vinyl bromide	593-60-2	3		100 (45.4)
Vinyl chloride	75-01-4	2,3,4	U043	1 (0.454)
Vinylidene chloride	75-35-4	1,2,3,4	U078	100 (45.4)
Warfarin, & salts	81-81-2	4	P001, U248	100 (45.4)
Xylene	1330-20-7	1,3,4	U239	100 (45.4)
m-Xylene	108-38-3	3		1000 (454)
o-Xylene	95-47-6	3		1000 (454)
p-Xylene	106-42-3	3		100 (45.4)
Xylene (mixed)	1330-20-7	1,3,4	U239	100 (45.4)
Xylenes (isomers and mixture)	1330-20-7	1,3,4	U239	100 (45.4)
Xylenol	1300-71-6	1		1000 (454)
Yohimban-16-carboxylic acid,11,17-dimethoxy-18-[(3,4,5-trimethoxybenzoyl)oxy]-, methyl ester (3beta,16beta,17alpha, 18beta,20alpha)	50-55-54	4	U200	5000 (2270)
Zinc††	7440-66-6	2		1000 (454)
ZINC AND COMPOUNDS	N.A.	2		**
Zinc acetate	557-34-6	1		1000 (454)
Zinc ammonium chloride	52628-25-8 14639-97-5 14639-98-6	1		1000 (454)
Zinc, bis(dimethylcarbamodithioato-S,S')-	137304	4	P205	10 (4.54)
Zinc borate	1332-07-6	1		1000 (454)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Zinc bromide	7699-45-8	1		1000 (454)
Zinc carbonate	3486-35-9	1		1000 (454)
Zinc chloride	7646-85-7	1		1000 (454)
Zinc cyanide Zn(CN)2	557-21-1	1,4	P121	10 (4.54)
Zinc fluoride	7783-49-5	1		1000 (454)
Zinc formate	557-41-5	1		1000 (454)
Zinc hydrosulfite	7779-86-4	1		1000 (454)
Zinc nitrate	7779-88-6	1		1000 (454)
Zinc phenolsulfonate	127-82-2	1		5000 (2270)
Zinc phosphide Zn3P2	1314-84-7	1,4	P122, U249	100 (45.4)
Zinc silicofluoride	16871-71-9	1		5000 (2270)
Zinc sulfate	7733-02-0	1		1000 (454)
Ziram	137304	4	P205	10 (4.54)
Zirconium nitrate	13746-89-9	1		5000 (2270)
Zirconium potassium fluoride	16923-95-8	1		1000 (454)
Zirconium sulfate	14644-61-2	1		5000 (2270)
Zirconium tetrachloride	10026-11-6	1		5000 (2270)
F001		4	F001	10 (4.54)
The following spent halogenated solvents used in degreasing; all spent solvent mixtures/blends used in degreasing containing, before use, a total of ten percent or more (by volume) of one or more of the halogenated solvents listed below or those solvents listed in F002, F004, and F005; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.				
(a) Tetrachloroethylene	127-18-4	2,3,4	U210	100 (45.4)
(b) Trichloroethylene	79-01-6	1,2,3,4	U228	100 (45.4)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
(c) Methylene chloride	75-09-2	2,3,4	U080	1000 (454)
(d) 1,1,1-Trichloroethane	71-55-6	2,3,4	U226	1000 (454)
(e) Carbon tetrachloride	56-23-5	1,2,3,4	U211	10 (4.54)
(f) Chlorinated fluorocarbons	N.A.			5000 (2270)
F002		4	F002	10 (4.54)
The following spent halogenated solvents; all spent solvent mixtures/blends containing, before use, a total of ten percent or more (by volume) of one or more of the halogenated solvents listed below or those solvents listed in F001, F004, or F005; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.				
(a) Tetrachloroethylene	127-18-4	2,3,4	U210	100 (45.4)
(b) Methylene chloride	75-09-2	2,3,4	U080	1000 (454)
(c) Trichloroethylene	79-01-6	1,2,3,4	U228	100 (45.4)
(d) 1,1,1-Trichloroethane	71-55-6	2,3,4	U226	1000 (454)
(e) Chlorobenzene	108-90-7	1,2,3,4	U037	100 (45.4)
(f) 1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1			5000 (2270)
(g) o-Dichlorobenzene	95-50-1	1,2,4	U070	100 (45.4)
(h) Trichlorofluoromethane	75-69-4	4	U121	5000 (2270)
(i) 1,1,2-Trichloroethane	79-00-5	2,3,4	U227	100 (45.4)
F003		4	F003	100 (45.4)
The following spent non-halogenated solvents and the still bottoms from the recovery of these solvents.				

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
(a) Xylene	1330-20-7			1000 (454)
(b) Acetone	67-64-1			5000 (2270)
(c) Ethyl acetate	141-78-6			5000 (2270)
(d) Ethylbenzene	100-41-4			1000 (454)
(e) Ethyl ether	60-29-7			100 (45.4)
(f) Methyl isobutyl ketone	108-10-1			5000 (2270)
(g) n-Butyl alcohol	71-36-3			5000 (2270)
(h) Cyclohexanone	108-94-1			5000 (2270)
(i) Methanol	67-56-1			5000 (2270)
F004		4	F004	100 (45.4)
The following spent non-halogenated solvents and the still bottoms from the recovery of these solvents:				
(a) Cresols/Cresylic acid	1319-77-3	1,3,4	U052	100 (45.4)
(b) Nitrobenzene	98-95-3	1,2,3,4	U169	1000 (454)
F005		4	F005	100 (45.4)
The following spent non-halogenated solvents and the still bottoms from the recovery of these solvents:				
(a) Toluene	108-88-3	1,2,3,4	U220	1000 (454)
(b) Methyl ethyl ketone	78-93-3	3,4	U159	5000 (2270)
(c) Carbon disulfide	75-15-0	1,3,4	P022	100 (45.4)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
(d) Isobutanol	78-83-1	4	U140	5000 (2270)
(e) Pyridine	110-86-1	4	U196	1000 (454)
F006		4	F006	10 (4.54)
Wastewater treatment sludges from electroplating operations except from the following processes: (1) sulfuric acid anodizing of aluminum, (2) tin plating on carbon steel, (3) zinc plating (segregated basis) on carbon steel, (4) aluminum or zinc-aluminum plating on carbon steel, (5) cleaning/stripping associated with tin, zinc and aluminum plating on carbon steel, and (6) chemical etching and milling of aluminum.				
F007		4	F007	10 (4.54)
Spent cyanide plating bath solutions from electroplating operations.				
F008		4	F008	10 (4.54)
Plating bath residues from the bottom of plating baths from electroplating operations where cyanides are used in the process.				
F009		4	F009	10 (4.54)
Spent stripping and cleaning bath solutions from electroplating operations where cyanides are used in the process.				
F010		4	F010	10 (4.54)
Quenching bath residues from oil baths from metal heat treating operations where cyanides are used in the process.				
F011		4	F011	10 (4.54)
Spent cyanide solutions from salt bath pot cleaning from metal heat treating operations.				
F012		4	F012	10 (4.54)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Quenching wastewater treatment sludges from metal heat treating operations where cyanides are used in the process.				
F019		4	F019	10 (4.54)
Wastewater treatment sludges from the chemical conversion coating of aluminum except from zirconium phosphating in aluminum can washing when such phosphating is an exclusive conversion coating process. Wastewater treatment sludges from the manufacturing of motor vehicles using a zinc phosphating process will not be subject to this listing at the point of generation if the wastes are not placed outside on the land prior to shipment to a landfill for disposal and are either: disposed in a Subtitle D municipal or industrial landfill unit that is equipped with a single clay liner and is permitted, licensed or otherwise authorized by the state; or disposed in a landfill unit subject to, or otherwise meeting, the landfill requirements in §258.40, §264.301 or §265.301. For the purposes of this listing, motor vehicle manufacturing is defined in §261.31(b)(4)(i) and §261.31(b)(4)(ii) describes the recordkeeping requirements for motor vehicle manufacturing facilities				
F020		4	F020	1 (0.454)
Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production or manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tri- or tetrachlorophenol or of intermediates used to produce their pesticide derivatives. (This listing does not include wastes				

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
from the production of hexachlorophene from highly purified 2,4,5-trichlorophenol.)				
F021		4	F021	1 (0.454)
Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production or manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of pentachlorophenol or of intermediates used to produce its derivatives.				
F022		4	F022	1 (0.454)
Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tetra-, penta-, or hexachlorobenzenes under alkaline conditions.				
F023		4	F023	1 (0.454)
Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production of materials on equipment previously used for the production or manufacturing use (as a reactant, chemical intermediate, or a component in a formulating process) of tri- and tetrachlorophenols. (This listing does not include wastes from equipment used only for the production or use of hexachlorophene from highly purified 2,4,5-trichlorophenol.)				
F024		4	F024	1 (0.454)
Process wastes, including but not limited to, distillation residues, heavy ends, tars, and reactor clean-out wastes, from the production of certain chlorinated aliphatic hydrocarbons by free radical catalyzed processes. These chlorinated aliphatic hydrocarbons are those having carbon chain				

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
lengths ranging from one to and including five, with varying amounts and positions of chlorine substitution. (This listing does not include wastewaters, wastewater treatment sludges, spent catalysts, and wastes listed in 40 CFR 261.31 or 261.32.)				
F025		4	F025	1 (0.454)
Condensed light ends, spent filters and filter aids, and spent desiccant wastes from the production of certain chlorinated aliphatic hydrocarbons, by free radical catalyzed processes. These chlorinated aliphatic hydrocarbons are those having carbon chain lengths ranging from one to and including five, with varying amounts and positions of chlorine substitution.				
F026		4	F026	1 (0.454)
Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production of materials on equipment previously used for the manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tetra-, penta-, or hexachlorobenzene under alkaline conditions.				
F027		4	F027	1 (0.454)
Discarded unused formulations containing tri-, tetra-, or pentachlorophenol or discarded unused formulations containing compounds derived from these chlorophenols. (This listing does not include formulations containing hexachlorophene synthesized from prepurified 2,4,5-trichlorophenol as the sole component.)				
F028		4	F028	1 (0.454)
Residues resulting from the incineration or thermal treatment of soil contaminated with EPA				

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Hazardous Waste Nos. F020, F021, F022, F023, F026, and F027.				
F032		4	F032	1 (0.454)
Wastewaters (except those that have not come into contact with process contaminants), process residuals, preservative drippage, and spent formulations from wood preserving processes generated at plants that currently use or have previously used chlorophenolic formulations (except potentially cross-contaminated wastes that have had the F032 waste code deleted in accordance with §261.35 of this chapter or potentially cross-contaminated wastes that are otherwise currently regulated as hazardous wastes (*i.e.*, F034 or F035), and where the generator does not resume or initiate use of chlorophenolic formulations). This listing does not include K001 bottom sediment sludge from the treatment of wastewater from wood preserving processes that use creosote and/or pentachlorophenol.				
F034		4	F034	1 (0.454)
Wastewaters (except those that have not come into contact with process contaminants), process residuals, preservative drippage, and spent formulations from wood preserving processes generated at plants that use creosote formulations. This listing does not include K001 bottom sediment sludge from the treatment of wastewater from wood preserving processes that use creosote and/or pentachlorophenol.				
F035		4	F035	1 (0.454)
Wastewaters (except those that have not come into contact with process contaminants), process residuals, preservative drippage, and spent				

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
formulations from wood preserving processes generated at plants that use inorganic preservatives containing arsenic or chromium. This listing does not include K001 bottom sediment sludge from the treatment of wastewater from wood preserving processes that use creosote and/or pentachlorophenol.				
F037		4	F037	1 (0.454)
Petroleum refinery primary oil/water/solids separation sludge-Any sludge generated from the gravitational separation of oil/water/solids during the storage or treatment of process wastewaters and oily cooling wastewaters from petroleum refineries. Such sludges include, but are not limited to those generated in oil/water/solids separators; tanks and impoundments; ditches and other conveyances; sumps; and stormwater units receiving dry weather flow. Sludges generated in stormwater units that do not receive dry weather flow, sludges generated from non-contact once-through cooling waters segregated for treatment from other process or oily cooling waters, sludges generated in aggressive biological treatment units as defined in §261.31(b)(2) (including sludges generated in one or more additional units after wastewaters have been treated in aggressive biological treatment units) and K051 wastes are not included in this listing. This listing does include residuals generated from processing or recycling oil-bearing hazardous secondary materials excluded under §261.4(a)(12)(i), if those residuals are to be disposed of.				
F038		4	F038	1 (0.454)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Petroleum refinery secondary (emulsified) oil/water/solids separation sludge-Any sludge and/or float generated from the physical and/or chemical separation of oil/water/solids in process wastewaters and oily cooling wastewaters from petroleum refineries. Such wastes include, but are not limited to, all sludges and floats generated in: induced air flotation (IAF) units, tanks and impoundments, and all sludges generated in DAF units. Sludges generated in stormwater units that do not receive dry weather flow, sludges generated from non-contact once-through cooling waters segregated for treatment from other process or oily cooling waters, sludges and floats generated in aggressive biological treatment units as defined in §261.31(b)(2) (including sludges and floats generated in one or more additional units after wastewaters have been treated in aggressive biological treatment units) and F037, K048, and K051 wastes are not included in this listing.				
F039		4	F039	1 (0.454)
Leachate (liquids that have percolated through land disposed wastes) resulting from the disposal of more than one restricted waste classified as hazardous under subpart D of 40 CFR part 261. (Leachate resulting from the disposal of one or more of the following EPA Hazardous Wastes and no other hazardous wastes retains its EPA Hazardous Waste Number(s): F020, F021, F022, F026, F027, and/or F028.)				
K001		4	K001	1 (0.454)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Bottom sediment sludge from the treatment of wastewaters from wood preserving processes that use creosote and/or pentachlorophenol.				
K002		4	K002	10 (4.54)
Wastewater treatment sludge from the production of chrome yellow and orange pigments.				
K003		4	K003	10 (4.54)
Wastewater treatment sludge from the production of molybdate orange pigments.				
K004		4	K004	10 (4.54)
Wastewater treatment sludge from the production of zinc yellow pigments.				
K005		4	K005	10 (4.54)
Wastewater treatment sludge from the production of chrome green pigments.				
K006		4	K006	10 (4.54)
Wastewater treatment sludge from the production of chrome oxide green pigments (anhydrous and hydrated).				
K007		4	K007	10 (4.54)
Wastewater treatment sludge from the production of iron blue pigments.				
K008		4	K008	10 (4.54)
Oven residue from the production of chrome oxide green pigments.				
K009		4	K009	10 (4.54)
Distillation bottoms from the production of acetaldehyde from ethylene.				
K010		4	K010	10 (4.54)
Distillation side cuts from the production of acetaldehyde from ethylene.				
K011		4	K011	10 (4.54)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Bottom stream from the wastewater stripper in the production of acrylonitrile.				
K013		4	K013	10 (4.54)
Bottom stream from the acetonitrile column in the production of acrylonitrile.				
K014		4	K014	5000 (2270)
Bottoms from the acetonitrile purification column in the production of acrylonitrile.				
K015		4	K015	10 (4.54)
Still bottoms from the distillation of benzyl chloride.				
K016		4	K016	1 (0.454)
Heavy ends or distillation residues from the production of carbon tetrachloride.				
K017		4	K017	10 (4.54)
Heavy ends (still bottoms) from the purification column in the production of epichlorohydrin.				
K018		4	K018	1 (0.454)
Heavy ends from the fractionation column in ethyl chloride production.				
K019		4	K019	1 (0.454)
Heavy ends from the distillation of ethylene dichloride in ethylene dichloride production.				
K020		4	K020	1 (0.454)
Heavy ends from the distillation of vinyl chloride in vinyl chloride monomer production.				
K021		4	K021	10 (4.54)
Aqueous spent antimony catalyst waste from fluoromethanes production.				
K022		4	K022	1 (0.454)
Distillation bottom tars from the production of phenol/acetone from cumene.				

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
K023		4	K023	5000 (2270)
Distillation light ends from the production of phthalic anhydride from naphthalene.				
K024		4	K024	5000 (2270)
Distillation bottoms from the production of phthalic anhydride from naphthalene.				
K025		4	K025	10 (4.54)
Distillation bottoms from the production of nitrobenzene by the nitration of benzene.				
K026		4	K026	1000 (454)
Stripping still tails from the production of methyl ethyl pyridines.				
K027		4	K027	10 (4.54)
Centrifuge and distillation residues from toluene diisocyanate production.				
K028		4	K028	1 (0.454)
Spent catalyst from the hydrochlorinator reactor in the production of 1,1,1-trichloroethane.				
K029		4	K029	1 (0.454)
Waste from the product steam stripper in the production of 1,1,1- trichloroethane.				
K030		4	K030	1 (0.454)
Column bottoms or heavy ends from the combined production of trichloroethylene and perchloroethylene.				
K031		4	K031	1 (0.454)
By-product salts generated in the production of MSMA and cacodylic acid.				
K032		4	K032	10 (4.54)
Wastewater treatment sludge from the production of chlordane.				
K033		4	K033	10 (4.54)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Wastewater and scrub water from the chlorination of cyclopentadiene in the production of chlordane.				
K034		4	K034	10 (4.54)
Filter solids from the filtration of hexachlorocyclopentadiene in the production of chlordane.				
K035		4	K035	1 (0.454)
Wastewater treatment sludges generated in the production of creosote.				
K036		4	K036	1 (0.454)
Still bottoms from toluene reclamation distillation in the production of disulfoton.				
K037		4	K037	1 (0.454)
Wastewater treatment sludges from the production of disulfoton.				
K038		4	K038	10 (4.54)
Wastewater from the washing and stripping of phorate production.				
K039		4	K039	10 (4.54)
Filter cake from the filtration of diethylphosphorodithioic acid in the production of phorate.				
K040		4	K040	10 (4.54)
Wastewater treatment sludge from the production of phorate.				
K041		4	K041	1 (0.454)
Wastewater treatment sludge from the production of toxaphene.				
K042		4	K042	10 (4.54)
Heavy ends or distillation residues from the distillation of tetrachlorobenzene in the production of 2,4,5-T.				
K043		4	K043	10 (4.54)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
2,6-Dichlorophenol waste from the production of 2,4-D.				
K044		4	K044	10 (4.54)
Wastewater treatment sludges from the manufacturing and processing of explosives.				
K045		4	K045	10 (4.54)
Spent carbon from the treatment of wastewater containing explosives.				
K046		4	K046	10 (4.54)
Wastewater treatment sludges from the manufacturing, formulation and loading of lead-based initiating compounds.				
K047		4	K047	10 (4.54)
Pink/red water from TNT operations.				
K048		4	K048	10 (4.54)
Dissolved air flotation (DAF) float from the petroleum refining industry.				
K049		4	K049	10 (4.54)
Slop oil emulsion solids from the petroleum refining industry.				
K050		4	K050	10 (4.54)
Heat exchanger bundle cleaning sludge from the petroleum refining industry.				
K051		4	K051	10 (4.54)
API separator sludge from the petroleum refining industry.				
K052		4	K052	10 (4.54)
Tank bottoms (leaded) from the petroleum refining industry.				
K060		4	K060	1 (0.454)
Ammonia still lime sludge from coking operations.				
K061		4	K061	10 (4.54)

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[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Emission control dust/sludge from the primary production of steel in electric furnaces.				
K062		4	K062	10 (4.54)
Spent pickle liquor generated by steel finishing operations of facilities within the iron and steel industry (SIC Codes 331 and 332).				
K064		4	K064	10 (4.54)
Acid plant blowdown slurry/sludge resulting from the thickening of blowdown slurry from primary copper production.				
K065		4	K065	10 (4.54)
Surface impoundment solids contained in and dredged from surface impoundments at primary lead smelting facilities.				
K066		4	K066	10 (4.54)
Sludge from treatment of process wastewater and/or acid plant blowdown from primary zinc production.				
K069		4	K069	10 (4.54)
Emission control dust/sludge from secondary lead smelting. (Note: This listing is stayed administratively for sludge generated from secondary acid scrubber systems. The stay will remain in effect until further administrative action is taken. If EPA takes further action effecting the stay, EPA will publish a notice of the action in the FEDERAL REGISTER.)				
K071		4	K071	1 (0.454)
Brine purification muds from the mercury cell process in chlorine production, where separately prepurified brine is not used.				
K073		4	K073	10 (4.54)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Chlorinated hydrocarbon waste from the purification step of the diaphragm cellprocess using graphite anodes in chlorine production.				
K083		4	K083	100 (45.4)
Distillation bottoms from aniline production.				
K084		4	K084	1 (0.454)
Wastewater treatment sludges generated during the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds.				
K085		4	K085	10 (4.54)
Distillation or fractionation column bottoms from the production of chlorobenzenes.				
K086		4	K086	10 (4.54)
Solvent washes and sludges, caustic washes and sludges, or water washes and sludges from cleaning tubs and equipment used in the formulation of ink from pigments, driers, soaps, and stabilizers containing chromium and lead.				
K087		4	K087	100 (45.4)
Decanter tank tar sludge from coking operations.				
K088		4	K088	10 (4.54)
Spent potliners from primary aluminum reduction.				
K090		4	K090	10 (4.54)
Emission control dust or sludge from ferrochromiumsilicon production.				
K091		4	K091	10 (4.54)
Emission control dust or sludge from ferrochromium production.				
K093		4	K093	5000 (2270)
Distillation light ends from the production of phthalic anhydride from ortho-xylene.				

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
K094		4	K094	5000 (2270)
Distillation bottoms from the production of phthalic anhydride from ortho-xylene.				
K095		4	K095	100 (45.4)
Distillation bottoms from the production of 1,1,1-trichloroethane.				
K096		4	K096	100 (45.4)
Heavy ends from the heavy ends column from the production of 1,1,1-trichloroethane.				
K097		4	K097	1 (0.454)
Vacuum stripper discharge from the chlordane chlorinator in the production of chlordane.				
K098		4	K098	1 (0.454)
Untreated process wastewater from the production of toxaphene.				
K099		4	K099	10 (4.54)
Untreated wastewater from the production of 2,4-D.				
K100		4	K100	10 (4.54)
Waste leaching solution from acid leaching of emission control dust/sludge from secondary lead smelting.				
K101		4	K101	1 (0.454)
Distillation tar residues from the distillation of aniline-based compounds in the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds.				
K102		4	K102	1 (0.454)
Residue from the use of activated carbon for decolorization in the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds.				
K103		4	K103	100 (45.4)

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[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Process residues from aniline extraction from the production of aniline.				
K104		4	K104	10 (4.54)
Combined wastewater streams generated from nitrobenzene/aniline production.				
K105		4	K105	10 (4.54)
Separated aqueous stream from the reactor product washing step in the production of chlorobenzenes.				
K106		4	K106	1 (0.454)
Wastewater treatment sludge from the mercury cell process in chlorine production.				
K107		4	K107	10 (4.54)
Column bottoms from product separation from the production of 1,1- dimethylhydrazine (UDMH) from carboxylic acid hydrazines.				
K108		4	K108	10 (4.54)
Condensed column overheads from product separation and condensed reactor vent gases from the production of 1,1- dimethylhydrazine (UDMH) from carboxylic acid hydrazides.				
K109		4	K109	10 (4.54)
Spent filter cartridges from product purification from the production of 1,1-dimethylhydrazine (UDMH) from carboxylic acid hydrazides.				
K110		4	K110	10 (4.54)
Condensed column overheads from intermediate separation from the production of 1,1-dimethylhydrazine (UDMH) from carboxylic acid hydrazides.				
K111		4	K111	10 (4.54)
Product washwaters from the production of dinitrotoluene via nitration of toluene.				
K112		4	K112	10 (4.54)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Reaction by-product water from the drying column in the production of toluenediamine via hydrogenation of dinitrotoluene.				
K113		4	K113	10 (4.54)
Condensed liquid light ends from the purification of toluenediamine in the production of toluenediamine via hydrogenation of dinitrotoluene.				
K114		4	K114	10 (4.54)
Vicinals from the purification of toluenediamine in the production of toluenediamine via hydrogenation of dinitrotoluene.				
K115		4	K115	10 (4.54)
Heavy ends from the purification of toluenediamine in the production of toluenediamine via hydrogenation of dinitrotoluene.				
K116		4	K116	10 (4.54)
Organic condensate from the solvent recovery column in the production of toluene diisocyanate via phosgenation of toluenediamine.				
K117		4	K117	1 (0.454)
Wastewater from the reactor vent gas scrubber in the production of ethylene dibromide via bromination of ethene.				
K118		4	K118	1 (0.454)
Spent adsorbent solids from purification of ethylene dibromide in the production of ethylene dibromide via bromination of ethene.				
K123		4	K123	10 (4.54)
Process wastewater (including supernates, filtrates, and washwaters) from the production of ethylenebisdithiocarbamic acid and its salts.				
K124		4	K124	10 (4.54)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Reactor vent scrubber water from the production of ethylenebisdithiocarbamic acid and its salts.				
K125		4	K125	10 (4.54)
Filtration, evaporation, and centrifugation solids from the production of ethylenebisdithiocarbamic acid and its salts.				
K126		4	K126	10 (4.54)
Baghouse dust and floor sweepings in milling and packaging operations from the production or formulation of ethylenebisdithiocarbamic acid and its salts.				
K131		4	K131	100 (45.4)
Wastewater from the reactor and spent sulfuric acid from the acid dryer from the production of methyl bromide.				
K132		4	K132	1000 (454)
Spent absorbent and wastewater separator solids from the production of methyl bromide.				
K136		4	K136	1 (0.454)
Still bottoms from the purification of ethylene dibromide in the production of ethylene dibromide via bromination of ethene.				
K141		4	K141	1 (0.454)
Process residues from the recovery of coal tar, including, but not limited to, collecting sump residues from the production of coke from coal or the recovery of coke by-products produced from coal. This listing does not include K087 (decanter tank tar sludges from coking operations).				
K142		4	K142	1 (0.454)
Tar storage tank residues from the production of coke from coal or from the recovery of coke by-products produced from coal.				

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[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
K143		4	K143	1 (0.454)
Process residues from the recovery of light oil, including, but not limited to, those generated in stills, decanters, and wash oil recovery units from the recovery of coke by- products produced from coal.				
K144		4	K144	1 (0.454)
Wastewater sump residues from light oil refining, including, but not limited to, intercepting or contamination sump sludges from the recovery of coke by-products produced from coal.				
K145		4	K145	1 (0.454)
Residues from naphthalene collection and recovery operations from the recovery of coke by-products produced from coal.				
K147		4	K147	1 (0.454)
Tar storage tank residues from coal tar refining.				
K148		4	K148	1 (0.454)
Residues from coal tar distillation, including, but not limited to, still bottoms.				
K149		4	K149	10 (4.54)
Distillation bottoms from the production of alpha- (or methyl-) chlorinated toluenes, ring-chlorinated toluenes, benzoyl chlorides, and compounds with mixtures of these functional groups. [This waste does not include still bottoms from the distillation of benzyl chloride.]				
K150		4	K150	10 (4.54)
Organic residuals, excluding spent carbon adsorbent, from the spent chlorine gas and hydrochloric acid recovery processes associated with the production of alpha- (or methyl-) chlorinated toluenes, ring-chlorinated toluenes,				

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
benzoyl chlorides, and compounds with mixtures of these functional groups.				
K151		4	K151	10 (4.54)
Wastewater treatment sludges, excluding neutralization and biological sludges, generated during the treatment of waste-waters from the production of alpha- (or methyl-) chlorinated toluenes, ring-chlorinated toluenes, benzoyl chlorides, and compounds with mixtures of these functional groups.				
K156		4	K156	10 (4.54)
Organic waste (including heavy ends, still bottoms, light ends, spent solvents, filtrates, and decantates) from the production of carbamates and carbamoyl oximes. (This listing does not apply to wastes generated from the manufacture of 3-iodo-2-propynyl n-butylcarbamate.)				
K157		4	K157	10 (4.54)
Wastewaters (including scrubber waters, condenser waters, washwaters, and separation waters) from the production of carbamates and carbamoyl oximes. (This listing does not apply to wastes generated from the manufacture of 3-iodo-2-propynyl n-butylcarbamate.)				
K158		4	K158	10 (4.54)
Bag house dusts and filter/separation solids from the production of carbamates and carbamoyl oximes. (This listing does not apply to wastes generated from the manufacture of 3-iodo-2-propynyl n-butylcarbamate.)				
K159		4	K159	10 (4.54)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Organics from the treatment of thiocarbamate wastes.				
K161		4	K161	1 (0.454)
Purification solids (including filtration, evaporation, and centrifugation solids), bag-house dust and floor sweepings from the production of dithiocarbamate acids and their salts. (This listing does not include K125 or K126).				
K169[f]		4	K169	10 (4.54)
Crude oil storage tank sediment from petroleum refining operations.				
K170[f]		4	K170	1 (0.454)
Clarified slurry oil tank sediment and/or in-line filter/separation solids from petroleum refining operations.				
K171[f]		4	K171	1 (0.454)
Spent hydrotreating catalyst from petroleum refining operations. (This listing does not include inert support media.)				
K172[f]		4	K172	1 (0.454)
Spent hydrorefining catalyst from petroleum refining operations. (This listing does not include inert support media.)				
K174[f]		4	K174	1 (0.454)
K175[f]		4	K175	1 (0.454)
K176				
Baghouse filters from the production of antimony oxide, including filters from the production of intermediates (e.g., antimony metal or crude antimony oxide)		4	K176	1 (0.454)
K177				

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Slag from the production of antimony oxide that is speculatively accumulated or disposed, including slag from the production of intermediates (e.g., antimony metal or crude antimony oxide)		4	K177	5,000 (2270)
K178		4	K178	1000 (454)
Residues from manufacturing and manufacturing-site storage of ferric chloride from acids formed during the production of titanium dioxide using the chloride-ilmenite process.				
K181		4	K181	##
Nonwastewaters from the production of dyes and/or pigments (including nonwastewaters commingled at the point of generation with nonwastewaters from other processes) that, at the point of generation, contain mass loadings of any of the constituents identified in paragraph (c) of section 261.32 that are equal to or greater than the corresponding paragraph (c) levels, as determined on a calendar year basis				

†Indicates the statutory source defined by 1, 2, 3, and 4, as described in the note preceding Table 302.4.

†Indicates the statutory source defined by 1,2,3, and 4, as described in the note preceding Table 302.4.

††No reporting of releases of this hazardous substance is required if the diameter of the pieces of the solid metal released is larger than 100 micrometers (0.004 inches).

†††The RQ for asbestos is limited to friable forms only.

##The Agency may adjust the statutory RQ for this hazardous substance in a future rulemaking; until then the statutory one-pound RQ applies.

§The adjusted RQs for radionuclides may be found in appendix B to this table.

**Indicates that no RQ is being assigned to the generic or broad class.

[a]Benzene was already a CERCLA hazardous substance prior to the CAA Amendments of 1990 and received an adjusted 10-pound RQ based on potential carcinogenicity in an August 14, 1989, final rule (54 FR 33418). The

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)

CAA Amendments specify that "benzene (including benzene from gasoline)" is a hazardous air pollutant and, thus, a CERCLA hazardous substance.

[b]The CAA Amendments of 1990 list DDE (3547-04-4) as a CAA hazardous air pollutant. The CAS number, 3547-04-4, is for the chemical, p,p′dichlorodiphenylethane. DDE or p,p′-dichlorodiphenyldichloroethylene, CAS number 72-55-9, is already listed in Table 302.4 with a final RQ of 1 pound. The substance identified by the CAS number 3547-04-4 has been evaluated and listed as DDE to be consistent with the CAA section 112 listing, as amended.

[c]Includes mineral fiber emissions from facilities manufacturing or processing glass, rock, or slag fibers (or other mineral derived fibers) of average diameter 1 micrometer or less.

[d]Includes mono- and di-ethers of ethylene glycol, diethylene glycol, and triethylene glycol R-(OCH2CH2)n-OR′ where:
n = 1, 2, or 3;
R = alkyl C7 or less; or
R = phenyl or alkyl substituted phenyl;
R′= H or alkyl C7 or less; or
OR′ consisting of carboxylic acid ester, sulfate, phosphate, nitrate, or sulfonate.

[e]Includes organic compounds with more than one benzene ring, and which have a boiling point greater than or equal to 100 °C.

[f]See 40 CFR 302.6(b)(1) for application of the mixture rule to this hazardous waste.

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
A2213	30558431	4	U394	5000 (2270)
Acenaphthene	83-32-9	2		100 (45.4)
Acenaphthylene	208-96-8	2		5000 (2270)
Acetaldehyde	75-07-0	1,3,4	U001	1000 (454)
Acetaldehyde, chloro-	107-20-0	4	P023	1000 (454)
Acetaldehyde, trichloro-	75-87-6	4	U034	5000 (2270)
Acetamide	60-35-5	3		100 (45.4)
Acetamide, N-(aminothioxomethyl)-	591-08-2	4	P002	1000 (454)
Acetamide, N-(4-ethoxyphenyl)-	62-44-2	4	U187	100 (45.4)
Acetamide, N-9H-fluoren-2-yl-	53-96-3	3,4	U005	1 (0.454)
Acetamide, 2-fluoro-	640-19-7	4	P057	100 (45.4)
Acetic acid	64-19-7	1		5000 (2270)
Acetic acid, (2,4-dichlorophenoxy)-, salts & esters	94-75-7	1,3,4	U240	100 (45.4)
Acetic acid, ethyl ester	141-78-6	4	U112	5000 (2270)
Acetic acid, fluoro-, sodium salt	62-74-8	4	P058	10 (4.54)
Acetic acid, lead(2 +) salt	301-04-2	1,4	U144	10 (4.54)
Acetic acid, thallium(1 +) salt	563-68-8	4	U214	100 (45.4)
Acetic acid, (2,4,5-trichlorophenoxy)-	93-76-5	1,4	See F027	1000 (454)
Acetic anhydride	108-24-7	1		5000 (2270)
Acetone	67-64-1	4	U002	5000 (2270)
Acetone cyanohydrin	75-86-5	1,4	P069	10 (4.54)
Acetonitrile	75-05-8	3,4	U003	5000 (2270)
Acetophenone	98-86-2	3,4	U004	5000 (2270)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
2-Acetylaminofluorene	53-96-3	3,4	U005	1 (0.454)
Acetyl bromide	506-96-7	1		5000 (2270)
Acetyl chloride	75-36-5	1,4	U006	5000 (2270)
1-Acetyl-2-thiourea	591-08-2	4	P002	1000 (454)
Acrolein	107-02-8	1,2,3,4	P003	1 (0.454)
Acrylamide	79-06-1	3,4	U007	5000 (2270)
Acrylic acid	79-10-7	3,4	U008	5000 (2270)
Acrylonitrile	107-13-1	1,2,3,4	U009	100 (45.4)
Adipic acid	124-04-9	1		5000 (2270)
Aldicarb	116-06-3	4	P070	1 (0.454)
Aldicarb sulfone	1646884	4	P203	100 (45.4)
Aldrin	309-00-2	1,2,4	P004	1 (0.454)
Allyl alcohol	107-18-6	1,4	P005	100 (45.4)
Allyl chloride	107-05-1	1,3		1000 (454)
Aluminum phosphide	20859-73-8	4	P006	100 (45.4)
Aluminum sulfate	10043-01-3	1		5000 (2270)
4-Aminobiphenyl	92-67-1	3		1 (0.454)
5-(Aminomethyl)-3-isoxazolol	2763-96-4	4	P007	1000 (454)
4-Aminopyridine	504-24-5	4	P008	1000 (454)
Amitrole	61-82-5	4	U011	10 (4.54)
Ammonia	7664-41-7	1		100 (45.4)
Ammonium acetate	631-61-8	1		5000 (2270)
Ammonium benzoate	1863-63-4	1		5000 (2270)
Ammonium bicarbonate	1066-33-7	1		5000 (2270)
Ammonium bichromate	7789-09-5	1		10 (4.54)
Ammonium bifluoride	1341-49-7	1		100 (45.4)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Ammonium bisulfilte	10192-30-0	1		5000 (2270)
Ammonium carbamate	1111-78-0	1		5000 (2270)
Ammonium carbonate	506-87-6	1		5000 (2270)
Ammonium chloride	12125-02-9	1		5000 (2270)
Ammonium chromate	7788-98-9	1		10 (4.54)
Ammonium citrate, dibasic	3012-65-5	1		5000 (2270)
Ammonium fluoborate	13826-83-0	1		5000 (2270)
Ammonium fluoride	12125-01-8	1		100 (45.4)
Ammonium hydroxide	1336-21-6	1		1000 (454)
Ammonium oxalate	6009-70-7 5972-73-6 14258-49-2	1		5000 (2270)
Ammonium picrate	131-74-8	4	P009	10 (4.54)
Ammonium silicofluoride	16919-19-0	1		1000 (454)
Ammonium sulfamate	7773-06-0	1		5000 (2270)
Ammonium sulfide	12135-76-1	1		100 (45.4)
Ammonium sulfite	10196-04-0	1		5000 (2270)
Ammonium tartrate	14307-43-8 3164-29-2	1		5000 (2270)
Ammonium thiocyanate	1762-95-4	1		5000 (2270)
Ammonium vanadate	7803-55-6	4	P119	1000 (454)
Amyl acetate	628-63-7	1		5000 (2270)
iso-Amyl acetate	123-92-2			
sec-Amyl acetate	626-38-0			
tert-Amyl acetate	625-16-1			

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Aniline	62-53-3	1,3,4	U012	5000 (2270)
o-Anisidine	90-04-0	3		100 (45.4)
Anthracene	120-12-7	2		5000 (2270)
Antimony††	7440-36-0	2		5000 (2270)
ANTIMONY AND COMPOUNDS	N.A.	2,3		**
Antimony Compounds	N.A.	2,3		**
Antimony pentachloride	7647-18-9	1		1000 (454)
Antimony potassium tartrate	28300-74-5	1		100 (45.4)
Antimony tribromide	7789-61-9	1		1000 (454)
Antimony trichloride	10025-91-9	1		1000 (454)
Antimony trifluoride	7783-56-4	1		1000 (454)
Antimony trioxide	1309-64-4	1		1000 (454)
Argentate(1-), bis(cyano-C)-, potassium	506-61-6	4	P099	1 (0.454)
Aroclor 1016	12674-11-2	1,2,3		1 (0.454)
Aroclor 1221	11104-28-2	1,2,3		1 (0.454)
Aroclor 1232	11141-16-5	1,2,3		1 (0.454)
Aroclor 1242	53469-21-9	1,2,3		1 (0.454)
Aroclor 1248	12672-29-6	1,2,3		1 (0.454)
Aroclor 1254	11097-69-1	1,2,3		1 (0.454)
Aroclor 1260	11096-82-5	1,2,3		1 (0.454)
Aroclors	1336-36-3	1,2,3		1 (0.454)
Arsenic††	7440-38-2	2,3		1 (0.454)
Arsenic acid H3AsO4	7778-39-4	4	P010	1 (0.454)
ARSENIC AND COMPOUNDS	N.A.	2,3		**
Arsenic Compounds (inorganic including arsine)	N.A.	2,3		**
Arsenic disulfide	1303-32-8	1		1 (0.454)
Arsenic oxide As2O3	1327-53-3	1,4	P012	1 (0.454)
Arsenic oxide As2O5	1303-28-2	1,4	P011	1 (0.454)
Arsenic pentoxide	1303-28-2	1,4	P011	1 (0.454)
Arsenic trichloride	7784-34-1	1		1 (0.454)
Arsenic trioxide	1327-53-3	1,4	P012	1 (0.454)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Arsenic trisulfide	1303-33-9	1		1 (0.454)
Arsine, diethyl-	692-42-2	4	P038	1 (0.454)
Arsinic acid, dimethyl-	75-60-5	4	U136	1 (0.454)
Arsonous dichloride, phenyl-	696-28-6	4	P036	1 (0.454)
Asbestos†††	1332-21-4	2,3		1 (0.454)
Auramine	492-80-8	4	U014	100 (45.4)
Azaserine	115-02-6	4	U015	1 (0.454)
Aziridine	151-56-4	3,4	P054	1 (0.454)
Aziridine, 2-methyl-	75-55-8	3,4	P067	1 (0.454)
Azirino[2′,3′:3,4]pyrrolo[1,2-a]indole-4,7-dione, 6-amino-8-[[(aminocarbonyl)oxy]methyl]-1,1a,2,8,8a,8b- hexahydro-8a-methoxy-5- methyl-,[1aS- (1aalpha,8beta,8aalpha, 8balpha)]-	50-07-7	4	U010	10 (4.54)
Barban	101279	4	U280	10 (4.54)
Barium cyanide	542-62-1	1,4	P013	10 (4.54)
Bendiocarb	22781233	4	U278	100 (45.4)
Bendiocarb phenol	22961826	4	U364	1000 (454)
Benomyl	17804352	4	U271	10 (4.54)
Benz[j]aceanthrylene, 1,2-dihydro-3-methyl-	56-49-5	4	U157	10 (4.54)
Benz[c]acridine	225-51-4	4	U016	100 (45.4)
Benzal chloride	98-87-3	4	U017	5000 (2270)
Benzamide, 3,5-dichloro-N-(1,1-dimethyl-2propynyl)-	23950-58-5	4	U192	5000 (2270)
Benz[a]anthracene	56-55-3	2,4	U018	10 (4.54)
1,2-Benzanthracene	56-55-3	2,4	U018	10 (4.54)
Benz[a]anthracene, 7,12-dimethyl-	57-97-6	4	U094	1 (0.454)
Benzenamine	62-53-3	1,3,4	U012	5000 (2270)
Benzenamine, 4,4′-carbonimidoylbis (N,N dimethyl-	492-80-8	4	U014	100 (45.4)
Benzenamine, 4-chloro-	106-47-8	4	P024	1000 (454)
Benzenamine, 4-chloro-2-methyl-, hydrochloride	3165-93-3	4	U049	100 (45.4)
Benzenamine, N,N-dimethyl-4-(phenylazo)-	60-11-7	3,4	U093	10 (4.54)

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[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Benzenamine, 2-methyl-	95-53-4	3,4	U328	100 (45.4)
Benzenamine, 4-methyl-	106-49-0	4	U353	100 (45.4)
Benzenamine, 4,4′-methylenebis [2-chloro-	101-14-4	3,4	U158	10 (4.54)
Benzenamine, 2-methyl-,hydrochloride	636-21-5	4	U222	100 (45.4)
Benzenamine, 2-methyl-5-nitro-	99-55-8	4	U181	100 (45.4)
Benzenamine, 4-nitro-	100-01-6	4	P077	5000 (2270)
Benzene[a]	71-43-2	1,2,3,4	U019	10 (4.54)
Benzeneacetic acid, 4-chloro-α-(4-chlorophenyl)-α-hydroxy-, ethyl ester	510-15-6	3,4	U038	10 (4.54)
Benzene, 1-bromo-4-phenoxy-	101-55-3	2,4	U030	100 (45.4)
Benzenebutanoic acid, 4-[bis(2-chloroethyl)amino]-	305-03-3	4	U035	10 (4.54)
Benzene, chloro-	108-90-7	1,2,3,4	U037	100 (45.4)
Benzene, (chloromethyl)-	100-44-7	1,3,4	P028	100 (45.4)
Benzenediamine, ar-methyl-	95-80-7 496-72-0 823-40-5 25376-45-8	3,4	U221	10 (4.54)
1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester	117-81-7	2,3,4	U028	100 (45.4)
1,2-Benzenedicarboxylic acid, dibutyl ester	84-74-2	1,2,3,4	U069	10 (4.54)
1,2-Benzenedicarboxylic acid, diethyl ester	84-66-2	2,4	U088	1000 (454)
1,2-Benzenedicarboxylic acid, dimethyl ester	131-11-3	2,3,4	U102	5000 (2270)
1,2-Benzenedicarboxylic acid, dioctyl ester	117-84-0	2,4	U107	5000 (2270)
Benzene, 1,2-dichloro-	95-50-1	1,2,4	U070	100 (45.4)
Benzene, 1,3-dichloro-	541-73-1	2,4	U071	100 (45.4)
Benzene, 1,4-dichloro-	106-46-7	1,2,3,4	U072	100 (45.4)
Benzene, 1,1′-(2,2-dichloroethylidene) bis[4-chloro-	72-54-8	1,2,4	U060	1 (0.454)
Benzene, (dichloromethyl)-	98-87-3	4	U017	5000 (2270)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Benzene, 1,3-diisocyanatomethyl-	91-08-7 584-84-9 26471-62-5	3,4	U223	100 (45.4)
Benzene, dimethyl-	1330-20-7	1,3,4	U239	100 (45.4)
1,3-Benzenediol	108-46-3	1,4	U201	5000 (2270)
1,2-Benzenediol,4-[1-hydroxy-2-(methyl amino)ethyl]-	51-43-4	4	P042	1000 (454)
Benzeneethanamine, alpha,alpha-dimethyl-	122-09-8	4	P046	5000 (2270)
Benzene, hexachloro-	118-74-1	2,3,4	U127	10 (4.54)
Benzene, hexahydro-	110-82-7	1,4	U056	1000 (454)
Benzene, methyl-	108-88-3	1,2,3,4	U220	1000 (454)
Benzene, 1-methyl-2,4-dinitro-	121-14-2	1,2,3,4	U105	10 (4.54)
Benzene, 2-methyl-1,3-dinitro-	606-20-2	1,2,4	U106	100 (45.4)
Benzene, (1-methylethyl)-	98-82-8	3,4	U055	5000 (2270)
Benzene, nitro-	98-95-3	1,2,3,4	U169	1000 (454)
Benzene, pentachloro-	608-93-5	4	U183	10 (4.54)
Benzene, pentachloronitro-	82-68-8	3,4	U185	100 (45.4)
Benzenesulfonic acid chloride	98-09-9	4	U020	100 (45.4)
Benzenesulfonyl chloride	98-09-9	4	U020	100 (45.4)
Benzene,1,2,4,5-tetrachloro-	95-94-3	4	U207	5000 (2270)
Benzenethiol	108-98-5	4	P014	100 (45.4)
Benzene,1,1′-(2,2,2-trichloroethylidene) bis[4-chloro-	50-29-3	1,2,4	U061	1 (0.454)
Benzene,1,1′-(2,2,2-trichloroethylidene) bis[4-methoxy-	72-43-5	1,3,4	U247	1 (0.454)
Benzene, (trichloromethyl)-	98-07-7	3,4	U023	10 (4.54)
Benzene, 1,3,5-trinitro-	99-35-4	4	U234	10 (4.54)
Benzidine	92-87-5	2,3,4	U021	1 (0.454)
Benzo[a]anthracene	56-55-3	2,4	U018	10 (4.54)
1,3-Benzodioxole, 5-(1-propenyl)-1	120-58-1	4	U141	100 (45.4)
1,3-Benzodioxole, 5-(2-propenyl)-	94-59-7	4	U203	100 (45.4)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
1,3-Benzodioxole, 5-propyl-	94-58-6	4	U090	10 (4.54)
1,3-Benzodioxol-4-ol, 2,2-dimethyl-	22961826	4	U364	1000 (454)
1,3-Benzodioxol-4-ol, 2,2-dimethyl-, methyl carbamate	22781233	4	U278	100 (45.4)
Benzo[b]fluoranthene	205-99-2	2		1 (0.454)
Benzo(k)fluoranthene	207-08-9	2		5000 (2270)
7-Benzofuranol, 2,3-dihydro-2,2-dimethyl-	1563388	4	U367	10 (4.54)
7-Benzofuranol, 2,3-dihydro-2,2- dimethyl-, methylcarbamate	1563-66-2	1,4	P127	10 (4.54)
Benzoic acid	65-85-0	1		5000 (2270)
Benzoic acid, 2-hydroxy-, compd. with (3aS-cis)-1,2,3,3a,8,8a-hexahydro-1,3a,8-trimethylpyrrolo[2,3-b]indol-5-yl methylcarbamate ester (1:1)	57647	4	P188	100 (45.4)
Benzonitrile	100-47-0	1		5000 (2270)
Benzo[rst]pentaphene	189-55-9	4	U064	10 (4.54)
Benzo[ghi]perylene	191-24-2	2		5000 (2270)
2H-1-Benzopyran-2-one, 4-hydroxy-3-(3-oxo-1-phenylbutyl)-, & salts	81-81-2	4	P001 U248	100 (45.4)
Benzo[a]pyrene	50-32-8	2,4	U022	1 (0.454)
3,4-Benzopyrene	50-32-8	2,4	U022	1 (0.454)
ρ-Benzoquinone	106-51-4	3,4	U197	10 (4.54)
Benzotrichloride	98-07-7	3,4	U023	10 (4.54)
Benzoyl chloride	98-88-4	1		1000 (454)
Benzyl chloride	100-44-7	1,3,4	P028	100 (45.4)
Beryllium ††	7440-41-7	2,3,4	P015	10 (4.54)
BERYLLIUM AND COMPOUNDS	N.A.	2,3		**
Beryllium chloride	7787-47-5	1		1 (0.454)
Beryllium compounds	N.A.	2,3		**
Beryllium fluoride	7787-49-7	1		1 (0.454)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Beryllium nitrate	13597-99-4 7787-55-5	1		1 (0.454)
Beryllium powder ††	7440-41-7	2,3,4	P015	10 (4.54)
alpha-BHC	319-84-6	2		10 (4.54)
beta-BHC	319-85-7	2		1 (0.454)
delta-BHC	319-86-8	2		1 (0.454)
gamma-BHC	58-89-9	1,2,3,4	U129	1 (0.454)
2,2′-Bioxirane	1464-53-5	4	U085	10 (4.54)
Biphenyl	92-52-4	3		100 (45.4)
[1,1′-Biphenyl]-4,4′-diamine	92-87-5	2,3,4	U021	1 (0.454)
[1,1′-Biphenyl]-4,4′-diamine,3,3′-dichloro-	91-94-1	2,3,4	U073	1 (0.454)
[1,1′-Biphenyl]-4,4′-diamine,3,3′-dimethoxy-	119-90-4	3,4	U091	100 (45.4)
[1,1′-Biphenyl]-4,4′-diamine,3,3′-dimethyl-	119-93-7	3,4	U095	10 (4.54)
Bis(2-chloroethoxy) methane	111-91-1	2,4	U024	1000 (454)
Bis(2-chloroethyl) ether	111-44-4	2,3,4	U025	10 (4.54)
Bis(chloromethyl) ether	542-88-1	2,3,4	P016	10 (4.54)
Bis(2-ethylhexyl) phthalate	117-81-7	3,4	U028	100 (45.4)
Bromoacetone	598-31-2	4	P017	1000 (454)
Bromoform	75-25-2	2,3,4	U225	100 (45.4)
Bromomethane	74-83-9	2,3,4	U029	1000 (454)
4-Bromophenyl phenyl ether	101-55-3	2,4	U030	100 (45.4)
Brucine	357-57-3	4	P018	100 (45.4)
1,3-Butadiene	106-99-0	3		10 (4.54)
1,3-Butadiene, 1,1,2,3,4,4-hexachloro-	87-68-3	2,3,4	U128	1 (0.454)
1-Butanamine, N-butyl-N-nitroso-	924-16-3	4	U172	10 (4.54)
1-Butanol	71-36-3	4	U031	5000 (2270)
2-Butanone	78-93-3	3,4	U159	5000 (2270)
2-Butanone, 3,3-dimethyl-1(methylthio)-, O-[(methylamino)carbonyl] oxime	39196-18-4	4	P045	100 (45.4)
2-Butanone peroxide	1338-23-4	4	U160	10 (4.54)
2-Butenal	123-73-9 4170-30-3	1,4	U053	100 (45.4)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
2-Butene, 1,4-dichloro-	764-41-0	4	U074	1 (0.454)
2-Butenoic acid, 2-methyl-, 7-[[2,3-dihydroxy-2-(1-methoxyethyl)-3- methyl-1-oxobutoxy] methyl]-2,3, 5,7a-tetrahydro- 1H-pyrrolizin-1-yl ester, [1S-[1alpha(Z), 7(2S*,3R*),7aalpha]]-	303-34-4	4	U143	10 (4.54)
Butyl acetate	123-86-4	1		5000 (2270)
iso-Butyl acetate	110-19-0			
sec-Butyl acetate	105-46-4			
tert-Butyl acetate	540-88-5			
n-Butyl alcohol	71-36-3	4	U031	5000 (2270)
Butylamine	109-73-9	1		1000 (454)
iso-Butylamine	78-81-9			
sec-Butylamine	513-49-5 13952-84-6			
tert-Butylamine	75-64-9			
Butyl benzyl phthalate	85-68-7	2		100 (45.4)
n-Butyl phthalate	84-74-2	1,2,3,4	U069	10 (4.54)
Butyric acid	107-92-6	1		5000 (2270)
iso-Butyric acid	79-31-2			
Cacodylic acid	75-60-5	4	U136	1 (0.454)
Cadmium ††	7440-43-9	2		10 (4.54)
Cadmium acetate	543-90-8	1		10 (4.54)
CADMIUM AND COMPOUNDS	N.A.	2,3		**
Cadmium bromide	7789-42-6	1		10 (4.54)
Cadmium chloride	10108-64-2	1		10 (4.54)
Cadmium compounds	N.A.	2,3		**
Calcium arsenate	7778-44-1	1		1 (0.454)
Calcium arsenite	52740-16-6	1		1 (0.454)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Calcium carbide	75-20-7	1		10 (4.54)
Calcium chromate	13765-19-0	1,4	U032	10 (4.54)
Calcium cyanamide	156-62-7	3		1000 (454)
Calcium cyanide Ca(CN)2	592-01-8	1,4	P021	10 (4.54)
Calcium dodecylbenzenesulfonate	26264-06-2	1		1000 (454)
Calcium hypochlorite	7778-54-3	1		10 (4.54)
Captan	133-06-2	1,3		10 (4.54)
Carbamic acid, 1H-benzimidazol-2-yl, methyl ester	10605217	4	U372	10 (4.54)
Carbamic acid, [1-[(butylamino)carbonyl]-1H-benzimidazol-2-yl]-,methyl ester	17804352	4	U271	10 (4.54)
Carbamic acid, (3-chlorophenyl)-, 4-chloro-2-butynyl ester	101279	4	U280	10 (4.54)
Carbamic acid, [(dibutylamino)-thio]methyl-, 2,3-dihydro-2,2-dimethyl-7-benzofuranyl ester	55285148	4	P189	1000 (454)
Carbamic acid, dimethyl-,1-[(dimethyl-amino)carbonyl]-5-methyl-1H-pyrazol-3-yl ester	644644	4	P191	1 (0.454)
Carbamic acid, dimethyl-, 3-methyl-1-(1-methylethyl)-1H-pyrazol-5-yl ester	119380	4	P192	100 (45.4)
Carbamic acid, ethyl ester	51-79-6	3,4	U238	100 (45.4)
Carbamic acid, methyl-, 3-methylphenyl ester	1129415	4	P190	1000 (454)
Carbamic acid, methylnitroso-, ethyl ester	615-53-2	4	U178	1 (0.454)
Carbamic acid, [1,2-phenylenebis(iminocarbonothioyl)]bis-, dimethyl ester	23564058	4	U409	10 (4.54)
Carbamic acid, phenyl-, 1-methylethyl ester	122429	4	U373	1000 (454)
Carbamic chloride, dimethyl-	79-44-7	3,4	U097	1 (0.454)
Carbamodithioic acid, 1,2-ethanediylbis-, salts & esters	111-54-6	4	U114	5000 (2270)
Carbamothioic acid, bis(1-methylethyl)-, S-(2,3-dichloro-2- propenyl) ester	2303-16-4	4	U062	100 (45.4)
Carbamothioic acid, bis(1-methylethyl)-, S-(2,3,3-trichloro-2-propenyl) ester	2303175	4	U389	100 (45.4)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Carbamothioic acid, dipropyl-, S-(phenylmethyl) ester	52888809	4	U387	5000 (2270)
Carbaryl	63-25-2	1,3,4	U279	100 (45.4)
Carbendazim	10605217	4	U372	10 (4.54)
Carbofuran	1563-66-2	1,4	P127	10 (4.54)
Carbofuran phenol	1563388	4	U367	10 (4.54)
Carbon disulfide	75-15-0	1,3,4	P022	100 (45.4)
Carbonic acid, dithallium(1 +) salt	6533-73-9	4	U215	100 (45.4)
Carbonic dichloride	75-44-5	1,3,4	P095	10 (4.54)
Carbonic difluoride	353-50-4	4	U033	1000 (454)
Carbonochloridic acid, methyl ester	79-22-1	4	U156	1000 (454)
Carbon oxyfluoride	353-50-4	4	U033	1000 (454)
Carbon tetrachloride	56-23-5	1,2,3,4	U211	10 (4.54)
Carbonyl sulfide	463-58-1	3		100 (45.4)
Carbosulfan	55285148	4	P189	1000 (454)
Catechol	120-80-9	3		100 (45.4)
Chloral	75-87-6	4	U034	5000 (2270)
Chloramben	133-90-4	3		100 (45.4)
Chlorambucil	305-03-3	4	U035	10 (4.54)
Chlordane	57-74-9	1,2,3,4	U036	1 (0.454)
Chlordane, alpha & gamma isomers	57-74-9	1,2,3,4	U036	1 (0.454)
CHLORDANE (TECHNICAL MIXTURE AND METABOLITES)	57-74-9	1,2,3,4	U036	1 (0.454)
CHLORINATED BENZENES	N.A.	2		**
Chlorinated camphene	8001-35-2	1,2,3,4	P123	1 (0.454)
CHLORINATED ETHANES	N.A.	2		**
CHLORINATED NAPHTHALENE	N.A.	2		**
CHLORINATED PHENOLS	N.A.	2		**
Chlorine	7782-50-5	1,3		10 (4.54)
Chlornaphazine	494-03-1	4	U026	100 (45.4)
Chloroacetaldehyde	107-20-0	4	P023	1000 (454)
Chloroacetic acid	79-11-8	3		100 (45.4)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
2-Chloroacetophenone	532-27-4	3		100 (45.4)
CHLOROALKYL ETHERS	N.A.	2		**
p-Chloroaniline	106-47-8	4	P024	1000 (454)
Chlorobenzene	108-90-7	1,2,3,4	U037	100 (45.4)
Chlorobenzilate	510-15-6	3,4	U038	10 (4.54)
p-Chloro-m-cresol	59-50-7	2,4	U039	5000 (2270)
Chlorodibromomethane	124-48-1	2		100 (45.4)
1-Chloro-2,3-epoxypropane	106-89-8	1,3,4	U041	100 (45.4)
Chloroethane	75-00-3	2,3		100 (45.4)
2-Chloroethyl vinyl ether	110-75-8	2,4	U042	1000 (454)
Chloroform	67-66-3	1,2,3,4	U044	10 (4.54)
Chloromethane	74-87-3	2,3,4	U045	100 (45.4)
Chloromethyl methyl ether	107-30-2	3,4	U046	10 (4.54)
beta-Chloronaphthalene	91-58-7	2,4	U047	5000 (2270)
2-Chloronaphthalene	91-58-7	2,4	U047	5000 (2270)
2-Chlorophenol	95-57-8	2,4	U048	100 (45.4)
o-Chlorophenol	95-57-8	2,4	U048	100 (45.4)
4-Chlorophenyl phenyl ether	7005-72-3	2		5000 (2270)
1-(o-Chlorophenyl)thiourea	5344-82-1	4	P026	100 (45.4)
Chloroprene	126-99-8	3		100 (45.4)
3-Chloropropionitrile	542-76-7	4	P027	1000 (454)
Chlorosulfonic acid	7790-94-5	1		1000 (454)
4-Chloro-o-toluidine, hydrochloride	3165-93-3	4	U049	100 (45.4)
Chlorpyrifos	2921-88-2	1		1 (0.454)
Chromic acetate	1066-30-4	1		1000 (454)
Chromic acid	11115-74-5 7738-94-5	1		10 (4.54)
Chromic acid H2CrO4, calcium salt	13765-19-0	1,4	U032	10 (4.54)
Chromic sulfate	10101-53-8	1		1000 (454)
Chromium††	7440-47-3	2		5000 (2270)

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40 C.F.R. Part 302 – Table 302.4
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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
CHROMIUM AND COMPOUNDS	N.A.	2,3		**
Chromium Compounds	N.A.	2,3		**
Chromous chloride	10049-05-5	1		1000 (454)
Chrysene	218-01-9	2,4	U050	100 (45.4)
Cobalt Compounds	N.A.	3		**
Cobaltous bromide	7789-43-7	1		1000 (454)
Cobaltous formate	544-18-3	1		1000 (454)
Cobaltous sulfamate	14017-41-5	1		1000 (454)
Coke Oven Emissions	N.A.	3		1 (0.454)
Copper††	7440-50-8	2		5000 (2270)
COPPER AND COMPOUNDS	N.A.	2		**
Copper cyanide Cu(CN)	544-92-3	4	P029	10 (4.54)
Coumaphos	56-72-4	1		10 (4.54)
Creosote	N.A.	4	U051	1 (0.454)
Cresol (cresylic acid)	1319-77-3	1,3,4	U052	100 (45.4)
m-Cresol	108-39-4	3		100 (45.4)
o-Cresol	95-48-7	3		100 (45.4)
p-Cresol	106-44-5	3		100 (45.4)
Cresols (isomers and mixture)	1319-77-3	1,3,4	U052	100 (45.4)
Cresylic acid (isomers and mixture)	1319-77-3	1,3,4	U052	100 (45.4)
Crotonaldehyde	123-73-9 4170-30-3	1,4	U053	100 (45.4)
Cumene	98-82-8	3,4	U055	5000 (2270)
m-Cumenyl methylcarbamate	64006	4	P202	10 (4.54)
Cupric acetate	142-71-2	1		100 (45.4)
Cupric acetoarsenite	12002-03-8	1		1 (0.454)
Cupric chloride	7447-39-4	1		10 (4.54)
Cupric nitrate	3251-23-8	1		100 (45.4)
Cupric oxalate	5893-66-3	1		100 (45.4)
Cupric sulfate	7758-98-7	1		10 (4.54)
Cupric sulfate, ammoniated	10380-29-7	1		100 (45.4)
Cupric tartrate	815-82-7	1		100 (45.4)

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List of Hazardous Substances and Reportable Quantities[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Cyanide Compounds	N.A.	2,3		**
CYANIDES	N.A.	2,3		**
Cyanides (soluble salts and complexes) not otherwise specified	N.A.	4	P030	10 (4.54)
Cyanogen	460-19-5	4	P031	100 (45.4)
Cyanogen bromide (CN)Br	506-68-3	4	U246	1000 (454)
Cyanogen chloride (CN)Cl	506-77-4	1,4	P033	10 (4.54)
2,5-Cyclohexadiene-1,4-dione	106-51-4	3,4	U197	10 (4.54)
Cyclohexane	110-82-7	1,4	U056	1000 (454)
Cyclohexane, 1,2,3,4,5,6-hexachloro-, (1α, 2α, 3β-, 4α, 5α, 6β)	58-89-9	1,2,3,4	U129	1 (0.454)
Cyclohexanone	108-94-1	4	U057	5000 (2270)
2-Cyclohexyl-4,6-dinitrophenol	131-89-5	4	P034	100 (45.4)
1,3-Cyclopentadiene, 1,2,3,4,5,5-hexachloro-	77-47-4	1,2,3,4	U130	10 (4.54)
Cyclophosphamide	50-18-0	4	U058	10 (4.54)
2,4-D Acid	94-75-7	1,3,4	U240	100 (45.4)
2,4-D Ester	94-11-1 94-79-1 94-80-4 1320-18-9 1928-38-7 1928-61-6 1929-73-3 2971-38-2 25168-26-7 53467-11-1	1		100 (45.4)
2,4-D, salts and esters	94-75-7	1,3,4	U240	100 (45.4)
Daunomycin	20830-81-3	4	U059	10 (4.54)
DDD	72-54-8	1,2,4	U060	1 (0.454)
4,4′-DDD	72-54-8	1,2,4	U060	1 (0.454)
DDE [b]	72-55-9	2		1 (0.454)
DDE [b]	3547-04-4	3		5000 (2270)
4,4′-DDE	72-55-9	2		1 (0.454)

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40 C.F.R. Part 302 – Table 302.4
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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
DDT	50-29-3	1,2,4	U061	1 (0.454)
4,4′-DDT	50-29-3	1,2,4	U061	1 (0.454)
DDT AND METABOLITES	N.A.	2		**
DEHP	117-81-7	2,3,4	U028	100 (45.4)
Diallate	2303-16-4	4	U062	100 (45.4)
Diazinon	333-41-5	1		1 (0.454)
Diazomethane	334-88-3	3		100 (45.4)
Dibenz[a,h]anthracene	53-70-3	2,4	U063	1 (0.454)
1,2:5,6-Dibenzanthracene	53-70-3	2,4	U063	1 (0.454)
Dibenzo[a,h]anthracene	53-70-3	2,4	U063	1 (0.454)
Dibenzofuran	132-64-9	3		100 (45.4)
Dibenzo[a,i]pyrene	189-55-9	4	U064	10 (4.54)
1,2-Dibromo-3-chloropropane	96-12-8	3,4	U066	1 (0.454)
Dibromoethane	106-93-4	1,3,4	U067	1 (0.454)
Dibutyl phthalate	84-74-2	1,2,3,4	U069	10 (4.54)
Di-n-butyl phthalate	84-74-2	1,2,3,4	U069	10 (4.54)
Dicamba	1918-00-9	1		1000 (454)
Dichlobenil	1194-65-6	1		100 (45.4)
Dichlone	117-80-6	1		1 (0.454)
Dichlorobenzene	25321-22-6	1		100 (45.4)
1,2-Dichlorobenzene	95-50-1	1,2,4	U070	100 (45.4)
1,3-Dichlorobenzene	541-73-1	2,4	U071	100 (45.4)
1,4-Dichlorobenzene	106-46-7	1,2,3,4	U072	100 (45.4)
m-Dichlorobenzene	541-73-1	2,4	U071	100 (45.4)
o-Dichlorobenzene	95-50-1	1,2,4	U070	100 (45.4)
p-Dichlorobenzene	106-46-7	1,2,3,4	U072	100 (45.4)
DICHLOROBENZIDINE	N.A.	2		**
3,3′-Dichlorobenzidine	91-94-1	2,3,4	U073	1 (0.454)
Dichlorobromomethane	75-27-4	2		5000 (2270)
1,4-Dichloro-2-butene	764-41-0	4	U074	1 (0.454)
Dichlorodifluoromethane	75-71-8	4	U075	5000 (2270)

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40 C.F.R. Part 302 – Table 302.4
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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
1,1-Dichloroethane	75-34-3	2,3,4	U076	1000 (454)
1,2-Dichloroethane	107-06-2	1,2,3,4	U077	100 (45.4)
1,1-Dichloroethylene	75-35-4	1,2,3,4	U078	100 (45.4)
1,2-Dichloroethylene	156-60-5	2,4	U079	1000 (454)
Dichloroethyl ether	111-44-4	2,3,4	U025	10 (4.54)
Dichloroisopropyl ether	108-60-1	2,4	U027	1000 (454)
Dichloromethane	75-09-2	2,3,4	U080	1000 (454)
Dichloromethoxyethane	111-91-1	2,4	U024	1000 (454)
Dichloromethyl ether	542-88-1	2,3,4	P016	10 (4.54)
2,4-Dichlorophenol	120-83-2	2,4	U081	100 (45.4)
2,6-Dichlorophenol	87-65-0	4	U082	100 (45.4)
Dichlorophenylarsine	696-28-6	4	P036	1 (0.454)
Dichloropropane	26638-19-7	1		1000 (454)
1,1-Dichloropropane	78-99-9			
1,3-Dichloropropane	142-28-9			
1,2-Dichloropropane	78-87-5	1,2,3,4	U083	1000 (454)
Dichloropropane—Dichloropropene (mixture)	8003-19-8	1		100 (45.4)
Dichloropropene	26952-23-8	1		100 (45.4)
2,3-Dichloropropene	78-88-6			
1,3-Dichloropropene	542-75-6	1,2,3,4	U084	100 (45.4)
2,2-Dichloropropionic acid	75-99-0	1		5000 (2270)
Dichlorvos	62-73-7	1,3		10 (4.54)
Dicofol	115-32-2	1		10 (4.54)
Dieldrin	60-57-1	1,2,4	P037	1 (0.454)
1,2:3,4-Diepoxybutane	1464-53-5	4	U085	10 (4.54)
Diethanolamine	111-42-2	3		100 (45.4)
Diethylamine	109-89-7	1		100 (45.4)
N,N-Diethylaniline	91-66-7	3		1000 (454)
Diethylarsine	692-42-2	4	P038	1 (0.454)
1,4-Diethyleneoxide	123-91-1	3,4	U108	100 (45.4)

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40 C.F.R. Part 302 – Table 302.4
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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Diethylene glycol, dicarbamate	5952261	4	U395	5000 (2270)
Diethylhexyl phthalate	117-81-7	2,3,4	U028	100 (45.4)
N,N′-Diethylhydrazine	1615-80-1	4	U086	10 (4.54)
O,O-Diethyl S-methyl dithiophosphate	3288-58-2	4	U087	5000 (2270)
Diethyl-p-nitrophenyl phosphate	311-45-5	4	P041	100 (45.4)
Diethyl phthalate	84-66-2	2,4	U088	1000 (454)
O,O-Diethyl O-pyrazinyl phosphorothioate	297-97-2	4	P040	100 (45.4)
Diethylstilbestrol	56-53-1	4	U089	1 (0.454)
Diethyl sulfate	64-67-5	3		10 (4.54)
Dihydrosafrole	94-58-6	4	U090	10 (4.54)
Diisopropylfluorophosphate (DFP)	55-91-4	4	P043	100 (45.4)
1,4:5,8-Dimethanonaphthalene, 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-, (1alpha,4alpha,4abeta,5alpha, 8alpha,8abeta)-	309-00-2	1,2,4	P004	1 (0.454)
1,4:5,8-Dimethanonaphthalene, 1,2,3,4,10,10-hexachloro- 1,4,4a,5,8,8a-hexahydro-, (1alpha,4alpha,4abeta, 5beta,8beta,8abeta)-	465-73-6	4	P060	1 (0.454)
2,7:3,6-Dimethanonaphth[2,3-b]oxirene,3,4,5,6,9,9- hexachloro-1a,2,2a,3,6,6a,7,7a- octahydro-,(1aalpha,2beta, 2aalpha,3beta,6beta,6aalpha, 7beta,7aalpha)-	60-57-1	1,2,4	P037	1 (0.454)
2,7:3,6-Dimethanonaphth[2, 3-b]oxirene,3,4,5,6,9,9- hexachloro-1a,2,2a,3,6,6a,7,7a- octahydro-,(1aalpha,2beta, 2abeta,3alpha,6alpha, 6abeta,7beta,7aalpha)-, & metabolites	72-20-8	1,2,4	P051	1 (0.454)
Dimethoate	60-51-5	4	P044	10 (4.54)
3,3′-Dimethoxybenzidine	119-90-4	3,4	U091	100 (45.4)
Dimethylamine	124-40-3	1,4	U092	1000 (454)
Dimethyl aminoazobenzene	60-11-7	3,4	U093	10 (4.54)
p-Dimethylaminoazobenzene	60-11-7	3,4	U093	10 (4.54)
N,N-Dimethylaniline	121-69-7	3		100 (45.4)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
7,12-Dimethylbenz[a]anthracene	57-97-6	4	U094	1 (0.454)
3,3′-Dimethylbenzidine	119-93-7	3,4	U095	10 (4.54)
alpha,alpha-Dimethylbenzylhydroperoxide	80-15-9	4	U096	10 (4.54)
Dimethylcarbamoyl chloride	79-44-7	3,4	U097	1 (0.454)
Dimethylformamide	68-12-2	3		100 (45.4)
1,1-Dimethylhydrazine	57-14-7	3,4	U098	10 (4.54)
1,2-Dimethylhydrazine	540-73-8	4	U099	1 (0.454)
alpha,alpha-Dimethylphenethylamine	122-09-8	4	P046	5000 (2270)
2,4-Dimethylphenol	105-67-9	2,4	U101	100 (45.4)
Dimethyl phthalate	131-11-3	2,3,4	U102	5000 (2270)
Dimethyl sulfate	77-78-1	3,4	U103	100 (45.4)
Dimetilan	644644	4	P191	1 (0.454)
Dinitrobenzene (mixed)	25154-54-5	1		100 (45.4)
m-Dinitrobenzene	99-65-0			
o-Dinitrobenzene	528-29-0			
p-Dinitrobenzene	100-25-4			
4,6-Dinitro-o-cresol, and salts	534-52-1	2,3,4	P047	10 (4.54)
Dinitrophenol	25550-58-7	1		10 (4.54)
2,5-Dinitrophenol	329-71-5			
2,6-Dinitrophenol	573-56-8			
2,4-Dinitrophenol	51-28-5	1,2,3,4	P048	10 (4.54)
Dinitrotoluene	25321-14-6	1,2		10 (4.54)
3,4-Dinitrotoluene	610-39-9			
2,4-Dinitrotoluene	121-14-2	1,2,3,4	U105	10 (4.54)
2,6-Dinitrotoluene	606-20-2	1,2,4	U106	100 (45.4)
Dinoseb	88-85-7	4	P020	1000 (454)
Di-n-octyl phthalate	117-84-0	2,4	U107	5000 (2270)
1,4-Dioxane	123-91-1	3,4	U108	100 (45.4)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
DIPHENYLHYDRAZINE	N.A.	2		**
1,2-Diphenylhydrazine	122-66-7	2,3,4	U109	10 (4.54)
Diphosphoramide, octamethyl-	152-16-9	4	P085	100 (45.4)
Diphosphoric acid, tetraethyl ester	107-49-3	1,4	P111	10 (4.54)
Dipropylamine	142-84-7	4	U110	5000 (2270)
Di-n-propylnitrosamine	621-64-7	2,4	U111	10 (4.54)
Diquat	85-00-7 2764-72-9	1		1000 (454)
Disulfoton	298-04-4	1,4	P039	1 (0.454)
Dithiobiuret	541-53-7	4	P049	100 (45.4)
1,3-Dithiolane-2-carboxaldehyde, 2,4-dimethyl-, O-[(methylamino)-carbonyl]oxime	26419738	4	P185	100 (45.4)
Diuron	330-54-1	1		100 (45.4)
Dodecylbenzenesulfonic acid	27176-87-0	1		1000 (454)
Endosulfan	115-29-7	1,2,4	P050	1 (0.454)
alpha-Endosulfan	959-98-8	2		1 (0.454)
beta-Endosulfan	33213-65-9	2		1 (0.454)
ENDOSULFAN AND METABOLITES	N.A.	2		**
Endosulfan sulfate	1031-07-8	2		1 (0.454)
Endothall	145-73-3	4	P088	1000 (454)
Endrin	72-20-8	1,2,4	P051	1 (0.454)
Endrin aldehyde	7421-93-4	2		1 (0.454)
ENDRIN AND METABOLITES	N.A.	2		**
Endrin, & metabolites	72-20-8	1,2,4	P051	1 (0.454)
Epichlorohydrin	106-89-8	1,3,4	U041	100 (45.4)
Epinephrine	51-43-4	4	P042	1000 (454)
1,2-Epoxybutane	106-88-7	3		100 (45.4)
Ethanal	75-07-0	1,3,4	U001	1000 (454)
Ethanamine, N,N-diethyl-	121-44-8	1,3,4	U404	5000 (2270)
Ethanamine, N-ethyl-N-nitroso-	55-18-5	4	U174	1 (0.454)
1,2-Ethanediamine, N,N-dimethyl-N′-2-pyridinyl-N′-(2- thienylmethyl)-	91-80-5	4	U155	5000 (2270)

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40 C.F.R. Part 302 – Table 302.4
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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Ethane, 1,2-dibromo-	106-93-4	1,3,4	U067	1 (0.454)
Ethane, 1,1-dichloro-	75-34-3	2,3,4	U076	1000 (454)
Ethane, 1,2-dichloro-	107-06-2	1,2,3,4	U077	100 (45.4)
Ethanedinitrile	460-19-5	4	P031	100 (45.4)
Ethane, hexachloro-	67-72-1	2,3,4	U131	100 (45.4)
Ethane, 1,1′-[methylenebis(oxy)]bis[2- chloro-	111-91-1	2,4	U024	1000 (454)
Ethane, 1,1′-oxybis-	60-29-7	4	U117	100 (45.4)
Ethane, 1,1′-oxybis[2-chloro-	111-44-4	2,3,4	U025	10 (4.54)
Ethane, pentachloro-	76-01-7	4	U184	10 (4.54)
Ethane, 1,1,1,2-tetrachloro-	630-20-6	4	U208	100 (45.4)
Ethane, 1,1,2,2-tetrachloro-	79-34-5	2,3,4	U209	100 (45.4)
Ethanethioamide	62-55-5	4	U218	10 (4.54)
Ethane, 1,1,1-trichloro-	71-55-6	2,3,4	U226	1000 (454)
Ethane, 1,1,2-trichloro-	79-00-5	2,3,4	U227	100 (45.4)
Ethanimidothioic acid, 2-(dimethylamino)-N-hydroxy-2-oxo-, methyl ester	30558431	4	U394	5000 (2270)
Ethanimidothioic acid, 2-(dimethylamino)-N-[[(methylamino)carbonyl]oxy]-2-oxo-, methyl ester	23135220	4	P194	100 (45.4)
Ethanimidothioic acid, N-[[(methylamino) carbonyl]oxy]-, methyl ester	16752-77-5	4	P066	100 (45.4)
Ethanimidothioic acid, N,N'-[thiobis[(methylimino) carbonyloxy]]bis-, dimethyl ester	59669260	4	U410	100 (45.4)
Ethanol, 2-ethoxy-	110-80-5	4	U359	1000 (454)
Ethanol, 2,2′-(nitrosoimino)bis-	1116-54-7	4	U173	1 (0.454)
Ethanol, 2,2'-oxybis-, dicarbamate	5952261	4	U395	5000 (2270)
Ethanone, 1-phenyl-	98-86-2	3,4	U004	5000 (2270)
Ethene, chloro-	75-01-4	2,3,4	U043	1 (0.454)
Ethene, (2-chloroethoxy)-	110-75-8	2,4	U042	1000 (454)
Ethene, 1,1-dichloro-	75-35-4	1,2,3,4	U078	100 (45.4)
Ethene, 1,2-dichloro-(E)	156-60-5	2,4	U079	1000 (454)

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40 C.F.R. Part 302 – Table 302.4
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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Ethene, tetrachloro-	127-18-4	2,3,4	U210	100 (45.4)
Ethene, trichloro-	79-01-6	1,2,3,4	U228	100 (45.4)
Ethion	563-12-2	1		10 (4.54)
Ethyl acetate	141-78-6	4	U112	5000 (2270)
Ethyl acrylate	140-88-5	3,4	U113	1000 (454)
Ethylbenzene	100-41-4	1,2,3		1000 (454)
Ethyl carbamate	51-79-6	3,4	U238	100 (45.4)
Ethyl chloride	75-00-3	2,3		100 (45.4)
Ethyl cyanide	107-12-0	4	P101	10 (4.54)
Ethylenebisdithiocarbamic acid, salts & esters	111-54-6	4	U114	5000 (2270)
Ethylenediamine	107-15-3	1		5000 (2270)
Ethylenediamine-tetraacetic acid (EDTA)	60-00-4	1		5000 (2270)
Ethylene dibromide	106-93-4	1,3,4	U067	1 (0.454)
Ethylene dichloride	107-06-2	1,2,3,4	U077	100 (45.4)
Ethylene glycol	107-21-1	3		5000 (2270)
Ethylene glycol monoethyl ether	110-80-5	4	U359	1000 (454)
Ethylene oxide	75-21-8	3,4	U115	10 (4.54)
Ethylenethiourea	96-45-7	3,4	U116	10 (4.54)
Ethylenimine	151-56-4	3,4	P054	1 (0.454)
Ethyl ether	60-29-7	4	U117	100 (45.4)
Ethylidene dichloride	75-34-3	2,3,4	U076	1000 (454)
Ethyl methacrylate	97-63-2	4	U118	1000 (454)
Ethyl methanesulfonate	62-50-0	4	U119	1 (0.454)
Famphur	52-85-7	4	P097	1000 (454)
Ferric ammonium citrate	1185-57-5	1		1000 (454)
Ferric ammonium oxalate	2944-67-4 55488-87-4	1		1000 (454)
Ferric chloride	7705-08-0	1		1000 (454)
Ferric fluoride	7783-50-8	1		100 (45.4)
Ferric nitrate	10421-48-4	1		1000 (454)

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40 C.F.R. Part 302 – Table 302.4
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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Ferric sulfate	10028-22-5	1		1000 (454)
Ferrous ammonium sulfate	10045-89-3	1		1000 (454)
Ferrous chloride	7758-94-3	1		100 (45.4)
Ferrous sulfate	7720-78-7 7782-63-0	1		1000 (454)
Fine mineral fibers[c]	N.A.	3		**
Fluoranthene	206-44-0	2,4	U120	100 (45.4)
Fluorene	86-73-7	2		5000 (2270)
Fluorine	7782-41-4	4	P056	10 (4.54)
Fluoroacetamide	640-19-7	4	P057	100 (45.4)
Fluoroacetic acid, sodium salt	62-74-8	4	P058	10 (4.54)
Formaldehyde	50-00-0	1,3,4	U122	100 (45.4)
Formetanate hydrochloride	23422539	4	P198	100 (45.4)
Formic acid	64-18-6	1,4	U123	5000 (2270)
Formparanate	17702577	4	P197	100 (45.4)
Fulminic acid, mercury(2 +)salt	628-86-4	4	P065	10 (4.54)
Fumaric acid	110-17-8	1		5000 (2270)
Furan	110-00-9	4	U124	100 (45.4)
2-Furancarboxaldehyde	98-01-1	1,4	U125	5000 (2270)
2,5-Furandione	108-31-6	1,3,4	U147	5000 (2270)
Furan, tetrahydro-	109-99-9	4	U213	1000 (454)
Furfural	98-01-1	1,4	U125	5000 (2270)
Furfuran	110-00-9	4	U124	100 (45.4)
Glucopyranose, 2-deoxy-2-(3-methyl-3-nitrosoureido)-,D-	18883-66-4	4	U206	1 (0.454)
D-Glucose, 2-deoxy-2-[[(methylnitrosoamino)-carbonyl]amino]-	18883-66-4	4	U206	1 (0.454)
Glycidylaldehyde	765-34-4	4	U126	10 (4.54)
Glycol ethers[d]	N.A.	3		**

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40 C.F.R. Part 302 – Table 302.4
List of Hazardous Substances and Reportable Quantities[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Guanidine, N-methyl-N′-nitro-N-nitroso-	70-25-7	4	U163	10 (4.54)
Guthion	86-50-0	1		1 (0.454)
HALOETHERS	N.A.	2		**
HALOMETHANES	N.A.	2		**
Heptachlor	76-44-8	1,2,3,4	P059	1 (0.454)
HEPTACHLOR AND METABOLITES	N.A.	2		**
Heptachlor epoxide	1024-57-3	2		1 (0.454)
Hexachlorobenzene	118-74-1	2,3,4	U127	10 (4.54)
Hexachlorobutadiene	87-68-3	2,3,4	U128	1 (0.454)
HEXACHLOROCYCLOHEXANE (all isomers)	608-73-1	2		**
Hexachlorocyclopentadiene	77-47-4	1,2,3,4	U130	10 (4.54)
Hexachloroethane	67-72-1	2,3,4	U131	100 (45.4)
Hexachlorophene	70-30-4	4	U132	100 (45.4)
Hexachloropropene	1888-71-7	4	U243	1000 (454)
Hexaethyl tetraphosphate	757-58-4	4	P062	100 (45.4)
Hexamethylene-1,6-diisocyanate	822-06-0	3		100 (45.4)
Hexamethylphosphoramide	680-31-9	3		1 (0.454)
Hexane	110-54-3	3		5000 (2270)
Hexone	108-10-1	3,4	U161	5000 (2270)
Hydrazine	302-01-2	3,4	U133	1 (0.454)
Hydrazinecarbothioamide	79-19-6	4	P116	100 (45.4)
Hydrazine, 1,2-diethyl-	1615-80-1	4	U086	10 (4.54)
Hydrazine, 1,1-dimethyl-	57-14-7	3,4	U098	10 (4.54)
Hydrazine, 1,2-dimethyl-	540-73-8	4	U099	1 (0.454)
Hydrazine, 1,2-diphenyl-	122-66-7	2,3,4	U109	10 (4.54)
Hydrazine, methyl-	60-34-4	3,4	P068	10 (4.54)
Hydrochloric acid	7647-01-0	1,3		5000 (2270)
Hydrocyanic acid	74-90-8	1,4	P063	10 (4.54)
Hydrofluoric acid	7664-39-3	1,3,4	U134	100 (45.4)
Hydrogen chloride	7647-01-0	1,3		5000 (2270)

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40 C.F.R. Part 302 – Table 302.4
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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Hydrogen cyanide	74-90-8	1,4	P063	10 (4.54)
Hydrogen fluoride	7664-39-3	1,3,4	U134	100 (45.4)
Hydrogen phosphide	7803-51-2	3,4	P096	100 (45.4)
Hydrogen sulfide H2S	7783-06-4	1,4	U135	100 (45.4)
Hydroperoxide, 1-methyl-1-phenylethyl-	80-15-9	4	U096	10 (4.54)
Hydroquinone	123-31-9	3		100 (45.4)
2-Imidazolidinethione	96-45-7	3,4	U116	10 (4.54)
Indeno(1,2,3-cd)pyrene	193-39-5	2,4	U137	100 (45.4)
Iodomethane	74-88-4	3,4	U138	100 (45.4)
1,3-Isobenzofurandione	85-44-9	3,4	U190	5000 (2270)
Isobutyl alcohol	78-83-1	4	U140	5000 (2270)
Isodrin	465-73-6	4	P060	1 (0.454)
Isolan	119380	4	P192	100 (45.4)
Isophorone	78-59-1	2,3		5000 (2270)
Isoprene	78-79-5	1		100 (45.4)
Isopropanolamine dodecylbenzenesulfonate	42504-46-1	1		1000 (454)
3-Isopropylphenyl N-methylcarbamate	64006	4	P202	10 (4.54)
Isosafrole	120-58-1	4	U141	100 (45.4)
3(2H)-Isoxazolone, 5-(aminomethyl)-	2763-96-4	4	P007	1000 (454)
Kepone	143-50-0	1,4	U142	1 (0.454)
Lasiocarpine	303-34-4	4	U143	10 (4.54)
Lead††	7439-92-1	2		10 (4.54)
Lead acetate	301-04-2	1,4	U144	10 (4.54)
LEAD AND COMPOUNDS	N.A.	2,3		**
Lead arsenate	7784-40-9 7645-25-2 10102-48-4	1		1 (0.454)
Lead, bis(acetato-O)tetrahydroxytri-	1335-32-6	4	U146	10 (4.54)
Lead chloride	7758-95-4	1		10 (4.54)
Lead compounds	N.A.	2,3		**
Lead fluoborate	13814-96-5	1		10 (4.54)

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40 C.F.R. Part 302 – Table 302.4
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[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Lead fluoride	7783-46-2	1		10 (4.54)
Lead iodide	10101-63-0	1		10 (4.54)
Lead nitrate	10099-74-8	1		10 (4.54)
Lead phosphate	7446-27-7	4	U145	10 (4.54)
Lead stearate	1072-35-1 7428-48-0 52652-59-2 56189-09-4	1		10 (4.54)
Lead subacetate	1335-32-6	4	U146	10 (4.54)
Lead sulfate	7446-14-2 15739-80-7	1		10 (4.54)
Lead sulfide	1314-87-0	1		10 (4.54)
Lead thiocyanate	592-87-0	1		10 (4.54)
Lindane	58-89-9	1,2,3,4	U129	1 (0.454)
Lindane (all isomers)	58-89-9	1,2,3,4	U129	1 (0.454)
Lithium chromate	14307-35-8	1		10 (4.54)
Malathion	121-75-5	1		100 (45.4)
Maleic acid	110-16-7	1		5000 (2270)
Maleic anhydride	108-31-6	1,3,4	U147	5000 (2270)
Maleic hydrazide	123-33-1	4	U148	5000 (2270)
Malononitrile	109-77-3	4	U149	1000 (454)
Manganese, bis (dimethylcarbamodithioato-S,S')-	15339363	4	P196	10 (4.54)
Manganese Compounds	N.A.	3		**
Manganese dimethyldithiocarbamate	15339363	4	P196	10 (4.54)
MDI	101-68-8	3		5000 (2270)
MEK	78-93-3	3,4	U159	5000 (2270)
Melphalan	148-82-3	4	U150	1 (0.454)
Mercaptodimethur	2032-65-7	1,4	P199	10 (4.54)
Mercuric cyanide	592-04-1	1		1(0.454)
Mercuric nitrate	10045-94-0	1		10 (4.54)
Mercuric sulfate	7783-35-9	1		10 (4.54)

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40 C.F.R. Part 302 – Table 302.4
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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Mercuric thiocyanate	592-85-8	1		10 (4.54)
Mercurous nitrate	10415-75-5	1	10 (4.54)	7782-86-7
Mercury	7439-97-6	2,3,4	U151	1 (0.454)
MERCURY AND COMPOUNDS	N.A.	2,3		**
Mercury, (acetato-O)phenyl-	62-38-4	4	P092	100 (45.4)
Mercury Compounds	N.A.	2,3		**
Mercury fulminate	628-86-4	4	P065	10 (4.54)
Methacrylonitrile	126-98-7	4	U152	1000 (454)
Methanamine, N-methyl-	124-40-3	1,4	U092	1000 (454)
Methanamine, N-methyl-N-nitroso-	62-75-9	2,3,4	P082	10 (4.54)
Methane, bromo-	74-83-9	2,3,4	U029	1000 (454)
Methane, chloro-	74-87-3	2,3,4	U045	100 (45.4)
Methane, chloromethoxy-	107-30-2	3,4	U046	10 (4.54)
Methane, dibromo-	74-95-3	4	U068	1000 (454)
Methane, dichloro-	75-09-2	2,3,4	U080	1000 (454)
Methane, dichlorodifluoro-	75-71-8	4	U075	5000 (2270)
Methane, iodo-	74-88-4	3,4	U138	100 (45.4)
Methane, isocyanato-	624-83-9	3,4	P064	10 (4.54)
Methane, oxybis(chloro-	542-88-1	2,3,4	P016	10 (4.54)
Methanesulfenyl chloride, trichloro-	594-42-3	4	P118	100 (45.4)
Methanesulfonic acid, ethyl ester	62-50-0	4	U119	1 (0.454)
Methane, tetrachloro-	56-23-5	1,2,3,4	U211	10 (4.54)
Methane, tetranitro-	509-14-8	4	P112	10 (4.54)
Methanethiol	74-93-1	1,4	U153	100 (45.4)
Methane, tribromo-	75-25-2	2,3,4	U225	100 (45.4)
Methane, trichloro-	67-66-3	1,2,3,4	U044	10 (4.54)
Methane, trichlorofluoro-	75-69-4	4	U121	5000 (2270)
Methanimidamide, N,N-dimethyl-N'-[3-[[(methylamino)-carbonyl]oxy]phenyl]-, monohydrochloride	23422539	4	P198	100 (45.4)

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[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Methanimidamide, N,N-dimethyl-N'-[2-methyl-4-[[(methylamino) carbonyl]oxy]phenyl]-	17702577	4	P197	100 (45.4)
6,9-Methano-2,4,3-benzodioxathiepin, 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-, 3-oxide	115-29-7	1,2,4	P050	1 (0.454)
4,7-Methano-1H-indene, 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-	76-44-8	1,2,3,4	P059	1 (0.454)
4,7-Methano-1H-indene, 1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-—	57-74-9	1,2,3,4	U036	1 (0.454)
Methanol	67-56-1	3,4	U154	5000 (2270)
Methapyrilene	91-80-5	4	U155	5000 (2270)
1,3,4-Metheno-2H-cyclobuta[cd]pentalen-2-one, 1,1a,3,3a,4,5,5,5a,5b,6-decachlorooctahydro-	143-50-0	1,4	U142	1 (0.454)
Methiocarb	2032-65-7	1,4	P199	10 (4.54)
Methomyl	16752-77-5	4	P066	100 (45.4)
Methoxychlor	72-43-5	1,3,4	U247	1 (0.454)
Methyl alcohol	67-56-1	3,4	U154	5000 (2270)
2-Methyl aziridine	75-55-8	3,4	P067	1 (0.454)
Methyl bromide	74-83-9	2,3,4	U029	1000 (454)
1-Methylbutadiene	504-60-9	4	U186	100 (45.4)
Methyl chloride	74-87-3	2,3,4	U045	100 (45.4)
Methyl chlorocarbonate	79-22-1	4	U156	1000 (454)
Methyl chloroform	71-55-6	2,3,4	U226	1000 (454)
3-Methylcholanthrene	56-49-5	4	U157	10 (4.54)
4,4′-Methylenebis(2-chloroaniline)	101-14-4	3,4	U158	10 (4.54)
Methylene bromide	74-95-3	4	U068	1000 (454)
Methylene chloride	75-09-2	2,3,4	U080	1000 (454)
4,4′-Methylenedianiline	101-77-9	3		10 (4.54)
Methylene diphenyl diisocyanate	101-68-8	3		5000 (2270)
Methyl ethyl ketone	78-93-3	3,4	U159	5000 (2270)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Methyl ethyl ketone peroxide	1338-23-4	4	U160	10 (4.54)
Methyl hydrazine	60-34-4	3,4	P068	10 (4.54)
Methyl iodide	74-88-4	3,4	U138	100 (45.4)
Methyl isobutyl ketone	108-10-1	3,4	U161	5000 (2270)
Methyl isocyanate	624-83-9	3,4	P064	10 (4.54)
2-Methyllactonitrile	75-86-5	1,4	P069	10 (4.54)
Methyl mercaptan	74-93-1	1,4	U153	100 (45.4)
Methyl methacrylate	80-62-6	1,3,4	U162	1000 (454)
Methyl parathion	298-00-0	1,4	P071	100 (45.4)
4-Methyl-2-pentanone	108-10-1	3,4	U161	5000 (2270)
Methyl tert-butyl ether	1634-04-4	3		1000 (454)
Methylthiouracil	56-04-2	4	U164	10 (4.54)
Metolcarb	1129415	4	P190	1000 (454)
Mevinphos	7786-34-7	1		10 (4.54)
Mexacarbate	315-18-4	1,4	P128	1000 (454)
Mitomycin C	50-07-7	4	U010	10 (4.54)
MNNG	70-25-7	4	U163	10 (4.54)
Monoethylamine	75-04-7	1		100 (45.4)
Monomethylamine	74-89-5	1		100 (45.4)
Naled	300-76-5	1		10 (4.54)
5,12-Naphthacenedione, 8-acetyl-10-[(3-amino-2,3,6-trideoxy-alpha-L-lyxo-hexopyranosyl)oxy]-7,8,9,10-tetrahydro-6,8,11-trihydroxy-1-methoxy-, (8S-cis)-	20830-81-3	4	U059	10 (4.54)
1-Naphthalenamine	134-32-7	4	U167	100 (45.4)
2-Naphthalenamine	91-59-8	4	U168	10 (4.54)
Naphthalenamine, N,N′-bis(2-chloroethyl)-	494-03-1	4	U026	100 (45.4)
Naphthalene	91-20-3	1,2,3,4	U165	100 (45.4)
Naphthalene, 2-chloro-	91-58-7	2,4	U047	5000 (2270)
1,4-Naphthalenedione	130-15-4	4	U166	5000 (2270)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
2,7-Naphthalenedisulfonic acid, 3,3′-[(3,3′-dimethyl-(1,1′-biphenyl)-4,4′-diyl)-bis(azo)]bis(5-amino-4-hydroxy)-tetrasodium salt	72-57-1	4	U236	10 (4.54)
1-Naphthalenol, methylcarbamate	63-25-2	1,3,4	U279	100 (45.4)
Naphthenic acid	1338-24-5	1		100 (45.4)
1,4-Naphthoquinone	130-15-4	4	U166	5000 (2270)
alpha-Naphthylamine	134-32-7	4	U167	100 (45.4)
beta-Naphthylamine	91-59-8	4	U168	10 (4.54)
alpha-Naphthylthiourea	86-88-4	4	P072	100 (45.4)
Nickel††	7440-02-0	2		100 (45.4)
Nickel ammonium sulfate	15699-18-0	1		100 (45.4)
NICKEL AND COMPOUNDS	N.A.	2,3		**
Nickel carbonyl Ni(CO)4, (T-4)-	13463-39-3	4	P073	10 (4.54)
Nickel chloride	7718-54-9 37211-05-5	1		100 (45.4)
Nickel compounds	N.A.	2,3		**
Nickel cyanide Ni(CN)2	557-19-7	4	P074	10 (4.54)
Nickel hydroxide	12054-48-7	1		10 (4.54)
Nickel nitrate	14216-75-2	1		100 (45.4)
Nickel sulfate	7786-81-4	1		100 (45.4)
Nicotine, & salts	54-11-5	4	P075	100 (45.4)
Nitric acid	7697-37-2	1		1000 (454)
Nitric acid, thallium (1 +) salt	10102-45-1	4	U217	100 (45.4)
Nitric oxide	10102-43-9	4	P076	10 (4.54)
p-Nitroaniline	100-01-6	4	P077	5000 (2270)
Nitrobenzene	98-95-3	1,2,3,4	U169	1000 (454)
4-Nitrobiphenyl	92-93-3	3		10 (4.54)
Nitrogen dioxide	10102-44-0 10544-72-6	1,4	P078	10 (4.54)
Nitrogen oxide NO	10102-43-9	4	P076	10 (4.54)
Nitrogen oxide NO2	10102-44-0 10544-72-6	1,4	P078	10 (4.54)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Nitroglycerine	55-63-0	4	P081	10 (4.54)
Nitrophenol (mixed)	25154-55-6	1		100 (45.4)
m-Nitrophenol	554-84-7			
o-Nitrophenol	88-75-5	1,2		100 (45.4)
p-Nitrophenol	100-02-7	1,2,3,4	U170	100 (45.4)
2-Nitrophenol	88-75-5	1,2		100 (45.4)
4-Nitrophenol	100-02-7	1,2,3,4	U170	100 (45.4)
NITROPHENOLS	N.A.	2		**
2-Nitropropane	79-46-9	3,4	U171	10 (4.54)
NITROSAMINES	N.A.	2		**
N-Nitrosodi-n-butylamine	924-16-3	4	U172	10 (4.54)
N-Nitrosodiethanolamine	1116-54-7	4	U173	1 (0.454)
N-Nitrosodiethylamine	55-18-5	4	U174	1 (0.454)
N-Nitrosodimethylamine	62-75-9	2,3,4	P082	10 (4.54)
N-Nitrosodiphenylamine	86-30-6	2		100 (45.4)
N-Nitroso-N-ethylurea	759-73-9	4	U176	1 (0.454)
N-Nitroso-N-methylurea	684-93-5	3,4	U177	1 (0.454)
N-Nitroso-N-methylurethane	615-53-2	4	U178	1 (0.454)
N-Nitrosomethylvinylamine	4549-40-0	4	P084	10 (4.54)
N-Nitrosomorpholine	59-89-2	3		1 (0.454)
N-Nitrosopiperidine	100-75-4	4	U179	10 (4.54)
N-Nitrosopyrrolidine	930-55-2	4	U180	1 (0.454)
Nitrotoluene	1321-12-6	1		1000 (454)
m-Nitrotoluene	99-08-1			
o-Nitrotoluene	88-72-2			
p-Nitrotoluene	99-99-0			
5-Nitro-o-toluidine	99-55-8	4	U181	100 (45.4)
Octamethylpyrophosphoramide	152-16-9	4	P085	100 (45.4)
Osmium oxide OsO4, (T-4)-	20816-12-0	4	P087	1000 (454)
Osmium tetroxide	20816-12-0	4	P087	1000 (454)
7-Oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid	145-73-3	4	P088	1000 (454)

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40 C.F.R. Part 302 – Table 302.4
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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Oxamyl	23135220	4	P194	100 (45.4)
1,2-Oxathiolane, 2,2-dioxide	1120-71-4	3,4	U193	10 (4.54)
2H-1,3,2-Oxazaphosphorin-2-amine, N,N- bis(2-chloroethyl)tetrahydro-, 2-oxide	50-18-0	4	U058	10 (4.54)
Oxirane	75-21-8	3,4	U115	10 (4.54)
Oxiranecarboxyaldehyde	765-34-4	4	U126	10 (4.54)
Oxirane, (chloromethyl)-	106-89-8	1,3,4	U041	100 (45.4)
Paraformaldehyde	30525-89-4	1		1000 (454)
Paraldehyde	123-63-7	4	U182	1000 (454)
Parathion	56-38-2	1,3,4	P089	10 (4.54)
PCBs	1336-36-3	1,2,3		1 (0.454)
PCNB	82-68-8	3,4	U185	100 (45.4)
Pentachlorobenzene	608-93-5	4	U183	10 (4.54)
Pentachloroethane	76-01-7	4	U184	10 (4.54)
Pentachloronitrobenzene	82-68-8	3,4	U185	100 (45.4)
Pentachlorophenol	87-86-5	1,2,3,4	See F027	10 (4.54)
1,3-Pentadiene	504-60-9	4	U186	100 (45.4)
Perchloroethylene	127-18-4	2,3,4	U210	100 (45.4)
Phenacetin	62-44-2	4	U187	100 (45.4)
Phenanthrene	85-01-8	2		5000 (2270)
Phenol	108-95-2	1,2,3,4	U188	1000 (454)
Phenol, 2-chloro-	95-57-8	2,4	U048	100 (45.4)
Phenol, 4-chloro-3-methyl-	59-50-7	2,4	U039	5000 (2270)
Phenol, 2-cyclohexyl-4,6-dinitro-	131-89-5	4	P034	100 (45.4)
Phenol, 2,4-dichloro-	120-83-2	2,4	U081	100 (45.4)
Phenol, 2,6-dichloro-	87-65-0	4	U082	100 (45.4)
Phenol, 4,4′-(1,2-diethyl-1,2-ethenediyl)bis-, (E)	56-53-1	4	U089	1 (0.454)
Phenol, 2,4-dimethyl-	105-67-9	2,4	U101	100 (45.4)
Phenol, 4-(dimethylamino)-3,5-dimethyl-, 4 methylcarbamate (ester)	315-18-4	1,4	P128	1000 (454)

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[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Phenol, (3,5-dimethyl-4-(methylthio)-, methylcarbamate	2032-65-7	1,4	P199	10 (4.54)
Phenol, 2,4-dinitro-	51-28-5	1,2,3,4	P048	10 (4.54)
Phenol, methyl-	1319-77-3	1,3,4	U052	100 (45.4)
Phenol, 2-methyl-4,6-dinitro-, & salts	534-52-1	2,3,4	P047	10 (4.54)
Phenol, 2,2′-methylenebis[3,4,6- trichloro-	70-30-4	4	U132	100 (45.4)
Phenol, 2-(1-methylethoxy)-, methylcarbamate	114-26-1	3,4	U411	100 (45.4)
Phenol, 3-(1-methylethyl)-, methyl carbamate	64006	4	P202	10 (4.54)
Phenol, 3-methyl-5-(1-methylethyl)-, methyl carbamate	2631370	4	P201	1000 (454)
Phenol, 2-(1-methylpropyl)-4,6-dinitro-	88-85-7	4	P020	1000 (454)
Phenol, 4-nitro-	100-02-7	1,2,3,4	U170	100 (45.4)
Phenol, pentachloro-	87-86-5	1,2,3,4	See F027	10 (4.54)
Phenol, 2,3,4,6-tetrachloro-	58-90-2	4	See F027	10 (4.54)
Phenol, 2,4,5-trichloro-	95-95-4	1,3,4	See F027	10 (4.54)
Phenol, 2,4,6-trichloro-	88-06-2	1,2,3,4	See F027	10 (4.54)
Phenol, 2,4,6-trinitro-, ammonium salt	131-74-8	4	P009	10 (4.54)
L-Phenylalanine, 4-[bis(2-chloroethyl)amino]-	148-82-3	4	U150	1 (0.454)
p-Phenylenediamine	106-50-3	3		5000 (2270)
Phenylmercury acetate	62-38-4	4	P092	100 (45.4)
Phenylthiourea	103-85-5	4	P093	100 (45.4)
Phorate	298-02-2	4	P094	10 (4.54)
Phosgene	75-44-5	1,3,4	P095	10 (4.54)
Phosphine	7803-51-2	3,4	P096	100 (45.4)
Phosphoric acid	7664-38-2	1		5000 (2270)
Phosphoric acid, diethyl 4-nitrophenyl ester	311-45-5	4	P041	100 (45.4)
Phosphoric acid, lead(2 +) salt (2:3)	7446-27-7	4	U145	10 (4.54)
Phosphorodithioic acid, O,O-diethyl S-[2-(ethylthio)ethyl] ester	298-04-4	1,4	P039	1 (0.454)

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Phosphorodithioic acid, O,O-diethyl S-[(ethylthio)methyl] ester	298-02-2	4	P094	10 (4.54)
Phosphorodithioic acid, O,O-diethyl S-methyl ester	3288-58-2	4	U087	5000 (2270)
Phosphorodithioic acid, O,O-dimethyl S-[2(methylamino)-2-oxoethyl] ester	60-51-5	4	P044	10 (4.54)
Phosphorofluoridic acid, bis(1-methylethyl) ester	55-91-4	4	P043	100 (45.4)
Phosphorothioic acid, O,O-diethyl O-(4-nitrophenyl) ester	56-38-2	1,3,4	P089	10 (4.54)
Phosphorothioic acid, O,O-diethyl O-pyrazinyl ester	297-97-2	4	P040	100 (45.4)
Phosphorothioic acid, O-[4-[(dimethylamino) sulfonyl]phenyl] O,O-dimethyl ester	52-85-7	4	P097	1000 (454)
Phosphorothioic acid, O,O-dimethyl O-(4-nitrophenyl) ester	298-00-0	1,4	P071	100 (45.4)
Phosphorus	7723-14-0	1,3		1 (0.454)
Phosphorus oxychloride	10025-87-3	1		1000 (454)
Phosphorus pentasulfide	1314-80-3	1,4	U189	100 (45.4)
Phosphorus sulfide	1314-80-3	1,4	U189	100 (45.4)
Phosphorus trichloride	7719-12-2	1		1000 (454)
Physostigmine	57476	4	P204	100 (45.4)
Physostigmine salicylate	57647	4	P188	100 (45.4)
PHTHALATE ESTERS	N.A.	2		**
Phthalic anhydride	85-44-9	3,4	U190	5000 (2270)
2-Picoline	109-06-8	4	U191	5000 (2270)
Piperidine, 1-nitroso-	100-75-4	4	U179	10 (4.54)
Plumbane, tetraethyl-	78-00-2	1,4	P110	10 (4.54)
POLYCHLORINATED BIPHENYLS	1336-36-3	1,2,3		1 (0.454)
Polycyclic Organic Matter[e]	N.A.	3		**
POLYNUCLEAR AROMATIC HYDROCARBONS	N.A.	2		**
Potassium arsenate	7784-41-0	1		1 (0.454)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Potassium arsenite	10124-50-2	1		1 (0.454)
Potassium bichromate	7778-50-9	1		10 (4.54)
Potassium chromate	7789-00-6	1		10 (4.54)
Potassium cyanide K(CN)	151-50-8	1,4	P098	10 (4.54)
Potassium hydroxide	1310-58-3	1		1000 (454)
Potassium permanganate	7722-64-7	1		100 (45.4)
Potassium silver cyanide	506-61-6	4	P099	1 (0.454)
Promecarb	2631370	4	P201	1000 (454)
Pronamide	23950-58-5	4	U192	5000 (2270)
Propanal, 2-methyl-2-(methyl- sulfonyl)-, O-[(methylamino)carbonyl] oxime	1646884	4	P203	100 (45.4)
Propanal, 2-methyl-2-(methylthio)-, O-[(methylamino)carbonyl]oxime	116-06-3	4	P070	1 (0.454)
1-Propanamine	107-10-8	4	U194	5000 (2270)
1-Propanamine, N-propyl-	142-84-7	4	U110	5000 (2270)
1-Propanamine, N-nitroso-N-propyl-	621-64-7	2,4	U111	10 (4.54)
Propane, 1,2-dibromo-3-chloro-	96-12-8	3,4	U066	1 (0.454)
Propane, 1,2-dichloro-	78-87-5	1,2,3,4	U083	1000 (454)
Propanedinitrile	109-77-3	4	U149	1000 (454)
Propanenitrile	107-12-0	4	P101	10 (4.54)
Propanenitrile, 3-chloro-	542-76-7	4	P027	1000 (454)
Propanenitrile, 2-hydroxy-2-methyl-	75-86-5	1,4	P069	10 (4.54)
Propane, 2-nitro-	79-46-9	3,4	U171	10 (4.54)
Propane, 2,2′-oxybis[2-chloro-	108-60-1	2,4	U027	1000 (454)
1,3-Propane sultone	1120-71-4	3,4	U193	10 (4.54)
1,2,3-Propanetriol, trinitrate	55-63-0	4	P081	10 (4.54)
Propanoic acid, 2-(2,4,5-trichlorophenoxy)-	93-72-1	1,4	See F027	100 (45.4)
1-Propanol, 2,3-dibromo-, phosphate (3:1)	126-72-7	4	U235	10 (4.54)
1-Propanol, 2-methyl-	78-83-1	4	U140	5000 (2270)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
2-Propanone	67-64-1	4	U002	5000 (2270)
2-Propanone, 1-bromo-	598-31-2	4	P017	1000 (454)
Propargite	2312-35-8	1		10 (4.54)
Propargyl alcohol	107-19-7	4	P102	1000 (454)
2-Propenal	107-02-8	1,2,3,4	P003	1 (0.454)
2-Propenamide	79-06-1	3,4	U007	5000 (2270)
1-Propene, 1,3-dichloro-	542-75-6	1,2,3,4	U084	100 (45.4)
1-Propene, 1,1,2,3,3,3-hexachloro-	1888-71-7	4	U243	1000 (454)
2-Propenenitrile	107-13-1	1,2,3,4	U009	100 (45.4)
2-Propenenitrile, 2-methyl-	126-98-7	4	U152	1000 (454)
2-Propenoic acid	79-10-7	3,4	U008	5000 (2270)
2-Propenoic acid, ethyl ester	140-88-5	3,4	U113	1000 (454)
2-Propenoic acid, 2-methyl-, ethyl ester	97-63-2	4	U118	1000 (454)
2-Propenoic acid, 2-methyl-, methyl ester	80-62-6	1,3,4	U162	1000 (454)
2-Propen-1-ol	107-18-6	1,4	P005	100 (45.4)
Propham	122429	4	U373	1000 (454)
beta-Propiolactone	57-57-8	3		10 (4.54)
Propionaldehyde	123-38-6	3	1000 (454)	
Propionic acid	79-09-4	1		5000 (2270)
Propionic anhydride	123-62-6	1		5000 (2270)
Propoxur (Baygon)	114-26-1	3,4	U411	100 (45.4)
n-Propylamine	107-10-8	4	U194	5000 (2270)
Propylene dichloride	78-87-5	1,2,3,4	U083	1000 (454)
Propylene oxide	75-56-9	1,3		100 (45.4)
1,2-Propylenimine	75-55-8	3,4	P067	1 (0.454)
2-Propyn-1-ol	107-19-7	4	P102	1000 (454)
Prosulfocarb	52888809	4	U387	5000 (2270)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Pyrene	129-00-0	2		5000 (2270)
Pyrethrins	121-29-9 121-21-1 8003-34-7	1		1 (0.454)
3,6-Pyridazinedione, 1,2-dihydro-	123-33-1	4	U148	5000 (2270)
4-Pyridinamine	504-24-5	4	P008	1000 (454)
Pyridine	110-86-1	4	U196	1000 (454)
Pyridine, 2-methyl-	109-06-8	4	U191	5000 (2270)
Pyridine, 3-(1-methyl-2-pyrrolidinyl)-, (S)-, & salts	54-11-5	4	P075	100 (45.4)
2,4-(1H,3H)-Pyrimidinedione, 5-[bis(2-chloroethyl)amino]-	66-75-1	4	U237	10 (4.54)
4(1H)-Pyrimidinone, 2,3-dihydro-6-methyl-2-thioxo-	56-04-2	4	U164	10 (4.54)
Pyrrolidine, 1-nitroso-	930-55-2	4	U180	1 (0.454)
Pyrrolo[2,3-b]indol-5-ol, 1,2,3,3a,8,8a-hexahydro-1,3a,8-trimethyl-, methylcarbamate (ester), (3aS-cis)-	57476	4	P204	100 (45.4)
Quinoline	91-22-5	1,3		5000 (2270)
Quinone	106-51-4	3,4	U197	10 (4.54)
Quintobenzene	82-68-8	3,4	U185	100 (45.4)
Radionuclides (including radon)	N.A.	3		§
Reserpine	50-55-5	4	U200	5000 (2270)
Resorcinol	108-46-3	1,4	U201	5000 (2270)
Safrole	94-59-7	4	U203	100 (45.4)
Selenious acid	7783-00-8	4	U204	10 (4.54)
Selenious acid, dithallium (1 +) salt	12039-52-0	4	P114	1000 (454)
Selenium††	7782-49-2	2		100 (45.4)
SELENIUM AND COMPOUNDS	N.A.	2,3		**
Selenium Compounds	N.A.	2,3		**

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Selenium dioxide	7446-08-4	1,4	U204	10 (4.54)
Selenium oxide	7446-08-4	1,4	U204	10 (4.54)
Selenium sulfide SeS2	7488-56-4	4	U205	10 (4.54)
Selenourea	630-10-4	4	P103	1000 (454)
L-Serine, diazoacetate (ester)	115-02-6	4	U015	1 (0.454)
Silver††	7440-22-4	2		1000 (454)
SILVER AND COMPOUNDS	N.A.	2		**
Silver cyanide Ag(CN)	506-64-9	4	P104	1 (0.454)
Silver nitrate	7761-88-8	1		1 (0.454)
Silvex (2,4,5-TP)	93-72-1	1,4	See F027	100 (45.4)
Sodium	7440-23-5	1		10 (4.54)
Sodium arsenate	7631-89-2	1		1 (0.454)
Sodium arsenite	7784-46-5	1		1 (0.454)
Sodium azide	26628-22-8	4	P105	1000 (454)
Sodium bichromate	10588-01-9	1		10 (4.54)
Sodium bifluoride	1333-83-1	1		100 (45.4)
Sodium bisulfite	7631-90-5	1		5000 (2270)
Sodium chromate	7775-11-3	1		10 (4.54)
Sodium cyanide Na(CN)	143-33-9	1,4	P106	10 (4.54)
Sodium dodecylbenzenesulfonate	25155-30-0	1		1000 (454)
Sodium fluoride	7681-49-4	1		1000 (454)
Sodium hydrosulfide	16721-80-5	1		5000 (2270)
Sodium hydroxide	1310-73-2	1		1000 (454)
Sodium hypochlorite	7681-52-9 10022-70-5	1		100 (45.4)
Sodium methylate	124-41-4	1		1000 (454)
Sodium nitrite	7632-00-0	1		100 (45.4)
Sodium phosphate, dibasic	7558-79-4 10039-32-4 10140-65-5	1		5000 (2270)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Sodium phosphate, tribasic	7601-54-9 10101-89-0 10361-89-4	1		5000 (2270)
Sodium selenite	7782-82-3 10102-18-8	1		100 (45.4)
Streptozotocin	18883-66-4	4	U206	1 (0.454)
Strontium chromate	7789-06-2	1		10 (4.54)
Strychnidin-10-one, & salts	57-24-9	1,4	P108	10 (4.54)
Strychnidin-10-one, 2,3-dimethoxy-	357-57-3	4	P018	100 (45.4)
Strychnine, & salts	57-24-9	1,4	P108	10 (4.54)
Styrene	100-42-5	1,3		1000 (454)
Styrene oxide	96-09-3	3		100 (45.4)
Sulfuric acid	7664-93-9 8014-95-7	1		1000 (454)
Sulfuric acid, dimethyl ester	77-78-1	3,4	U103	100 (45.4)
Sulfuric acid, dithallium (1 +) salt	7446-18-6 10031-59-1	1,4	P115	100 (45.4)
Sulfur monochloride	12771-08-3	1		1000 (454)
Sulfur phosphide	1314-80-3	1,4	U189	100 (45.4)
2,4,5-T	93-76-5	1,4	See F027	1000 (454)
2,4,5-T acid	93-76-5	1,4	See F027	1000 (454)
2,4,5-T amines	2008-46-0 1319-72-8 3813-14-7 6369-96-6 6369-97-7	1		5000 (2270)
2,4,5-T esters	93-79-8 1928-47-8 2545-59-7 25168-15-4 61792-07-2	1		1000 (454)
2,4,5-T salts	13560-99-1	1		1000 (454)
TCDD	1746-01-6	2,3		1 (0.454)
TDE	72-54-8	1,2,4	U060	1 (0.454)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
1,2,4,5-Tetrachlorobenzene	95-94-3	4	U207	5000 (2270)
2,3,7,8-Tetrachlorodibenzo-p-dioxin	1746-01-6	2,3		1 (0.454)
1,1,1,2-Tetrachloroethane	630-20-6	4	U208	100 (45.4)
1,1,2,2-Tetrachloroethane	79-34-5	2,3,4	U209	100 (45.4)
Tetrachloroethylene	127-18-4	2,3,4	U210	100 (45.4)
2,3,4,6-Tetrachlorophenol	58-90-2	4	See F027	10 (4.54)
Tetraethyl pyrophosphate	107-49-3	1,4	P111	10 (4.54)
Tetraethyl lead	78-00-2	1,4	P110	10 (4.54)
Tetraethyldithiopyrophosphate	3689-24-5	4	P109	100 (45.4)
Tetrahydrofuran	109-99-9	4	U213	1000 (454)
Tetranitromethane	509-14-8	4	P112	10 (4.54)
Tetraphosphoric acid, hexaethyl ester	757-58-4	4	P062	100 (45.4)
Thallic oxide	1314-32-5	4	P113	100 (45.4)
Thallium††	7440-28-0	2		1000 (454)
THALLIUM AND COMPOUNDS	N.A.	2		**
Thallium (I) acetate	563-68-8	4	U214	100 (45.4)
Thallium (I) carbonate	6533-73-9	4	U215	100 (45.4)
Thallium chloride TlCl	7791-12-0	4	U216	100 (45.4)
Thallium (I) nitrate	10102-45-1	4	U217	100 (45.4)
Thallium oxide Tl2O3	1314-32-5	4	P113	100 (45.4)
Thallium (l) selenite	12039-52-0	4	P114	1000 (454)
Thallium (I) sulfate	7446-18-6 10031-59-1	1,4	P115	100 (45.4)
Thioacetamide	62-55-5	4	U218	10 (4.54)
Thiodicarb	59669260	4	U410	100 (45.4)
Thiodiphosphoric acid, tetraethyl ester	3689-24-5	4	P109	100 (45.4)
Thiofanox	39196-18-4	4	P045	100 (45.4)
Thioimidodicarbonic diamide [(H2N)C(S)] 2NH	541-53-7	4	P049	100 (45.4)
Thiomethanol	74-93-1	1,4	U153	100 (45.4)
Thioperoxydicarbonic diamide [(H2N)C(S)] 2S2, tetramethyl-	137-26-8	4	U244	10 (4.54)
Thiophanate-methyl	23564058	4	U409	10 (4.54)

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40 C.F.R. Part 302 – Table 302.4
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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Thiophenol	108-98-5	4	P014	100 (45.4)
Thiosemicarbazide	79-19-6	4	P116	100 (45.4)
Thiourea	62-56-6	4	U219	10 (4.54)
Thiourea, (2-chlorophenyl)-	5344-82-1	4	P026	100 (45.4)
Thiourea, 1-naphthalenyl-	86-88-4	4	P072	100 (45.4)
Thiourea, phenyl-	103-85-5	4	P093	100 (45.4)
Thiram	137-26-8	4	U244	10 (4.54)
Tirpate	26419738	4	P185	100 (45.4)
Titanium tetrachloride	7550-45-0	3		1,2,41000 (454)
Toluene	108-88-3	1,2,3,4	U220	1000 (454)
Toluenediamine	95-80-7 496-72-0 823-40-5 25376-45-8	3,4	U221	10 (4.54)
2,4-Toluene diamine	95-80-7 496-72-0 823-40-5 25376-45-8	3,4	U221	10 (4.54)
Toluene diisocyanate	91-08-7 584-84-9 26471-62-5	3,4	U223	100 (45.4)
2,4-Toluene diisocyanate	91-08-7 584-84-9 26471-62-5	3,4	U223	100 (45.4)
o-Toluidine	95-53-4	3,4	U328	100 (45.4)
p-Toluidine	106-49-0	4	U353	100 (45.4)
o-Toluidine hydrochloride	636-21-5	4	U222	100 (45.4)
Toxaphene	8001-35-2	1,2,3,4	P123	1 (0.454)
2,4,5-TP acid	93-72-1	1,4	See F027	100 (45.4)
2,4,5-TP esters	32534-95-5	1		100 (45.4)
Triallate	2303175	4	U389	100 (45.4)
1H-1,2,4-Triazol-3-amine	61-82-5	4	U011	10 (4.54)
Trichlorfon	52-68-6	1		100 (45.4)
1,2,4-Trichlorobenzene	120-82-1	2,3		100 (45.4)

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40 C.F.R. Part 302 – Table 302.4
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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
1,1,1-Trichloroethane	71-55-6	2,3,4	U226	1000 (454)
1,1,2-Trichloroethane	79-00-5	2,3,4	U227	100 (45.4)
Trichloroethylene	79-01-6	1,2,3,4	U228	100 (45.4)
Trichloromethanesulfenyl chloride	594-42-3	4	P118	100 (45.4)
Trichloromonofluoromethane	75-69-4	4	U121	5000 (2270)
Trichlorophenol	25167-82-2	1		10 (4.54)
2,3,4-Trichlorophenol	15950-66-0			
2,3,5-Trichlorophenol	933-78-8			
2,3,6-Trichlorophenol	933-75-5			
3,4,5-Trichlorophenol	609-19-8			
2,4,5-Trichlorophenol	95-95-4	1,3,4	See F027	10 (4.54)
2,4,6-Trichlorophenol	88-06-2	1,2,3,4	See F027	10 (4.54)
Triethanolamine dodecylbenzenesulfonate	27323-41-7	1		1000 (454)
Triethylamine	121-44-8	1,3,4	U404	5000 (2270)
Trifluralin	1582-09-8	3		10 (4.54)
Trimethylamine	75-50-3	1		100 (45.4)
2,2,4-Trimethylpentane	540-84-1	3		1000 (454)
1,3,5-Trinitrobenzene	99-35-4	4	U234	10 (4.54)
1,3,5-Trioxane, 2,4,6-trimethyl-	123-63-7	4	U182	1000 (454)
Tris(2,3-dibromopropyl) phosphate	126-72-7	4	U235	10 (4.54)
Trypan blue	72-57-1	4	U236	10 (4.54)
Unlisted Hazardous Wastes Characteristic of Corrosivity	N.A.	4	D002	100 (45.4)
Unlisted Hazardous Wastes Characteristic of Ignitability	N.A.	4	D001	100 (45.4)
Unlisted Hazardous Wastes Characteristic of Reactivity	N.A.	4	D003	100 (45.4)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Unlisted Hazardous Wastes Characteristic of Toxicity:				
Arsenic (D004)	N.A.	4	D004	1 (0.454)
Barium (D005)	N.A.	4	D005	1000 (454)
Benzene (D018)	N.A.	1,2,3,4	D018	10 (4.54)
Cadmium (D006)	N.A.	4	D006	10 (4.54)
Carbon tetrachloride (D019)	N.A.	1,2,4	D019	10 (4.54)
Chlordane (D020)	N.A.	1,2,4	D020	1 (0.454)
Chlorobenzene (D021)	N.A.	1,2,4	D021	100 (45.4)
Chloroform (D022)	N.A.	1,2,4	D022	10 (4.54)
Chromium (D007)	N.A.	4	D007	10 (4.54)
o-Cresol (D023)	N.A.	4	D023	100 (45.4)
m-Cresol (D024)	N.A.	4	D024	100 (45.4)
p-Cresol (D025)	N.A.	4	D025	100 (45.4)
Cresol (D026)	N.A.	4	D026	100 (45.4)
2,4-D (D016)	N.A.	1,4	D016	100 (45.4)
1,4-Dichlorobenzene (D027)	N.A.	1,2,4	D027	100 (45.4)
1,2-Dichloroethane (D028)	N.A.	1,2,4	D028	100 (45.4)
1,1-Dichloroethylene (D029)	N.A.	1,2,4	D029	100 (45.4)
2,4-Dinitrotoluene (D030)	N.A.	1,2,4	D030	10 (4.54)
Endrin (D012)	N.A.	1,4	D012	1 (0.454)
Heptachlor (and epoxide) (D031)	N.A.	1,2,4	D031	1 (0.454)
Hexachlorobenzene (D032)	N.A.	2,4	D032	10 (4.54)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Hexachlorobutadiene (D033)	N.A.	2,4	D033	1 (0.454)
Hexachloroethane (D034)	N.A.	2,4	D034	100 (45.4)
Lead (D008)	N.A.	4	D008	10 (4.54)
Lindane (D013)	N.A.	1,4	D013	1 (0.454)
Mercury (D009)	N.A.	4	D009	1 (0.454)
Methoxychlor (D014)	N.A.	1,4	D014	1 (0.454)
Methyl ethyl ketone (D035)	N.A.	4	D035	5000 (2270)
Nitrobenzene (D036)	N.A.	1,2,4	D036	1000 (454)
Pentachlorophenol (D037)	N.A.	1,2,4	D037	10 (4.54)
Pyridine (D038)	N.A.	4	D038	1000 (454)
Selenium (D010)	N.A.	4	D010	10 (4.54)
Silver (D011)	N.A.	4	D011	1 (0.454)
Tetrachloroethylene (D039)	N.A.	2,4	D039	100 (45.4)
Toxaphene (D015)	N.A.	1,4	D015	1 (0.454)
Trichloroethylene (D040)	N.A.	1,2,4	D040	100 (45.4)
2,4,5-Trichlorophenol (D041)	N.A.	1,4	D041	10 (4.54)
2,4,6-Trichlorophenol (D042)	N.A.	1,2,4	D042	10 (4.54)
2,4,5-TP (D017)	N.A.	1,4	D017	100 (45.4)
Vinyl chloride (D043)	N.A.	2,3,4	D043	1 (0.454)
Uracil mustard	66-75-1	4	U237	10 (4.54)
Uranyl acetate	541-09-3	1		100 (45.4)
Uranyl nitrate	10102-06-4 36478-76-9	1		100 (45.4)
Urea, N-ethyl-N-nitroso-	759-73-9	4	U176	1 (0.454)

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Urea, N-methyl-N-nitroso-	684-93-5	3,4	U177	1 (0.454)
Urethane	51-79-6	3,4	U238	100 (45.4)
Vanadic acid, ammonium salt	7803-55-6	4	P119	1000 (454)
Vanadium oxide V2O5	1314-62-1	1,4	P120	1000 (454)
Vanadium pentoxide	1314-62-1	1,4	P120	1000 (454)
Vanadyl sulfate	27774-13-6	1		1000 (454)
Vinyl acetate	108-05-4	1,3		5000 (2270)
Vinyl acetate monomer	108-05-4	1,3		5000 (2270)
Vinylamine, N-methyl-N-nitroso-	4549-40-0	4	P084	10 (4.54)
Vinyl bromide	593-60-2	3		100 (45.4)
Vinyl chloride	75-01-4	2,3,4	U043	1 (0.454)
Vinylidene chloride	75-35-4	1,2,3,4	U078	100 (45.4)
Warfarin, & salts	81-81-2	4	P001, U248	100 (45.4)
Xylene	1330-20-7	1,3,4	U239	100 (45.4)
m-Xylene	108-38-3	3		1000 (454)
o-Xylene	95-47-6	3		1000 (454)
p-Xylene	106-42-3	3		100 (45.4)
Xylene (mixed)	1330-20-7	1,3,4	U239	100 (45.4)
Xylenes (isomers and mixture)	1330-20-7	1,3,4	U239	100 (45.4)
Xylenol	1300-71-6	1		1000 (454)
Yohimban-16-carboxylic acid,11,17-dimethoxy-18-[(3,4,5-trimethoxybenzoyl)oxy]-, methyl ester (3beta,16beta,17alpha, 18beta,20alpha)	50-55-54	4	U200	5000 (2270)
Zinc††	7440-66-6	2		1000 (454)
ZINC AND COMPOUNDS	N.A.	2		**
Zinc acetate	557-34-6	1		1000 (454)
Zinc ammonium chloride	52628-25-8 14639-97-5 14639-98-6	1		1000 (454)
Zinc, bis(dimethylcarbamodithioato-S,S')-	137304	4	P205	10 (4.54)
Zinc borate	1332-07-6	1		1000 (454)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Zinc bromide	7699-45-8	1		1000 (454)
Zinc carbonate	3486-35-9	1		1000 (454)
Zinc chloride	7646-85-7	1		1000 (454)
Zinc cyanide Zn(CN)2	557-21-1	1,4	P121	10 (4.54)
Zinc fluoride	7783-49-5	1		1000 (454)
Zinc formate	557-41-5	1		1000 (454)
Zinc hydrosulfite	7779-86-4	1		1000 (454)
Zinc nitrate	7779-88-6	1		1000 (454)
Zinc phenolsulfonate	127-82-2	1		5000 (2270)
Zinc phosphide Zn3P2	1314-84-7	1,4	P122, U249	100 (45.4)
Zinc silicofluoride	16871-71-9	1		5000 (2270)
Zinc sulfate	7733-02-0	1		1000 (454)
Ziram	137304	4	P205	10 (4.54)
Zirconium nitrate	13746-89-9	1		5000 (2270)
Zirconium potassium fluoride	16923-95-8	1		1000 (454)
Zirconium sulfate	14644-61-2	1		5000 (2270)
Zirconium tetrachloride	10026-11-6	1		5000 (2270)
F001		4	F001	10 (4.54)
The following spent halogenated solvents used in degreasing; all spent solvent mixtures/blends used in degreasing containing, before use, a total of ten percent or more (by volume) of one or more of the halogenated solvents listed below or those solvents listed in F002, F004, and F005; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.				
(a) Tetrachloroethylene	127-18-4	2,3,4	U210	100 (45.4)
(b) Trichloroethylene	79-01-6	1,2,3,4	U228	100 (45.4)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
(c) Methylene chloride	75-09-2	2,3,4	U080	1000 (454)
(d) 1,1,1-Trichloroethane	71-55-6	2,3,4	U226	1000 (454)
(e) Carbon tetrachloride	56-23-5	1,2,3,4	U211	10 (4.54)
(f) Chlorinated fluorocarbons	N.A.			5000 (2270)
F002		4	F002	10 (4.54)
The following spent halogenated solvents; all spent solvent mixtures/blends containing, before use, a total of ten percent or more (by volume) of one or more of the halogenated solvents listed below or those solvents listed in F001, F004, or F005; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.				
(a) Tetrachloroethylene	127-18-4	2,3,4	U210	100 (45.4)
(b) Methylene chloride	75-09-2	2,3,4	U080	1000 (454)
(c) Trichloroethylene	79-01-6	1,2,3,4	U228	100 (45.4)
(d) 1,1,1-Trichloroethane	71-55-6	2,3,4	U226	1000 (454)
(e) Chlorobenzene	108-90-7	1,2,3,4	U037	100 (45.4)
(f) 1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1			5000 (2270)
(g) o-Dichlorobenzene	95-50-1	1,2,4	U070	100 (45.4)
(h) Trichlorofluoromethane	75-69-4	4	U121	5000 (2270)
(i) 1,1,2-Trichloroethane	79-00-5	2,3,4	U227	100 (45.4)
F003		4	F003	100 (45.4)
The following spent non-halogenated solvents and the still bottoms from the recovery of these solvents.				

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
(a) Xylene	1330-20-7			1000 (454)
(b) Acetone	67-64-1			5000 (2270)
(c) Ethyl acetate	141-78-6			5000 (2270)
(d) Ethylbenzene	100-41-4			1000 (454)
(e) Ethyl ether	60-29-7			100 (45.4)
(f) Methyl isobutyl ketone	108-10-1			5000 (2270)
(g) n-Butyl alcohol	71-36-3			5000 (2270)
(h) Cyclohexanone	108-94-1			5000 (2270)
(i) Methanol	67-56-1			5000 (2270)
F004		4	F004	100 (45.4)
The following spent non-halogenated solvents and the still bottoms from the recovery of these solvents:				
(a) Cresols/Cresylic acid	1319-77-3	1,3,4	U052	100 (45.4)
(b) Nitrobenzene	98-95-3	1,2,3,4	U169	1000 (454)
F005		4	F005	100 (45.4)
The following spent non-halogenated solvents and the still bottoms from the recovery of these solvents:				
(a) Toluene	108-88-3	1,2,3,4	U220	1000 (454)
(b) Methyl ethyl ketone	78-93-3	3,4	U159	5000 (2270)
(c) Carbon disulfide	75-15-0	1,3,4	P022	100 (45.4)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
(d) Isobutanol	78-83-1	4	U140	5000 (2270)
(e) Pyridine	110-86-1	4	U196	1000 (454)
F006		4	F006	10 (4.54)
Wastewater treatment sludges from electroplating operations except from the following processes: (1) sulfuric acid anodizing of aluminum, (2) tin plating on carbon steel, (3) zinc plating (segregated basis) on carbon steel, (4) aluminum or zinc-aluminum plating on carbon steel, (5) cleaning/stripping associated with tin, zinc and aluminum plating on carbon steel, and (6) chemical etching and milling of aluminum.				
F007		4	F007	10 (4.54)
Spent cyanide plating bath solutions from electroplating operations.				
F008		4	F008	10 (4.54)
Plating bath residues from the bottom of plating baths from electroplating operations where cyanides are used in the process.				
F009		4	F009	10 (4.54)
Spent stripping and cleaning bath solutions from electroplating operations where cyanides are used in the process.				
F010		4	F010	10 (4.54)
Quenching bath residues from oil baths from metal heat treating operations where cyanides are used in the process.				
F011		4	F011	10 (4.54)
Spent cyanide solutions from salt bath pot cleaning from metal heat treating operations.				
F012		4	F012	10 (4.54)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Quenching wastewater treatment sludges from metal heat treating operations where cyanides are used in the process.				
F019		4	F019	10 (4.54)
Wastewater treatment sludges from the chemical conversion coating of aluminum except from zirconium phosphating in aluminum can washing when such phosphating is an exclusive conversion coating process. Wastewater treatment sludges from the manufacturing of motor vehicles using a zinc phosphating process will not be subject to this listing at the point of generation if the wastes are not placed outside on the land prior to shipment to a landfill for disposal and are either: disposed in a Subtitle D municipal or industrial landfill unit that is equipped with a single clay liner and is permitted, licensed or otherwise authorized by the state; or disposed in a landfill unit subject to, or otherwise meeting, the landfill requirements in §258.40, §264.301 or §265.301. For the purposes of this listing, motor vehicle manufacturing is defined in §261.31(b)(4)(i) and §261.31(b)(4)(ii) describes the recordkeeping requirements for motor vehicle manufacturing facilities				
F020		4	F020	1 (0.454)
Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production or manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tri- or tetrachlorophenol or of intermediates used to produce their pesticide derivatives. (This listing does not include wastes				

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
from the production of hexachlorophene from highly purified 2,4,5-trichlorophenol.)				
F021		4	F021	1 (0.454)
Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production or manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of pentachlorophenol or of intermediates used to produce its derivatives.				
F022		4	F022	1 (0.454)
Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tetra-, penta-, or hexachlorobenzenes under alkaline conditions.				
F023		4	F023	1 (0.454)
Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production of materials on equipment previously used for the production or manufacturing use (as a reactant, chemical intermediate, or a component in a formulating process) of tri- and tetrachlorophenols. (This listing does not include wastes from equipment used only for the production or use of hexachlorophene from highly purified 2,4,5-trichlorophenol.)				
F024		4	F024	1 (0.454)
Process wastes, including but not limited to, distillation residues, heavy ends, tars, and reactor clean-out wastes, from the production of certain chlorinated aliphatic hydrocarbons by free radical catalyzed processes. These chlorinated aliphatic hydrocarbons are those having carbon chain				

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
lengths ranging from one to and including five, with varying amounts and positions of chlorine substitution. (This listing does not include wastewaters, wastewater treatment sludges, spent catalysts, and wastes listed in 40 CFR 261.31 or 261.32.)				
F025		4	F025	1 (0.454)
Condensed light ends, spent filters and filter aids, and spent desiccant wastes from the production of certain chlorinated aliphatic hydrocarbons, by free radical catalyzed processes. These chlorinated aliphatic hydrocarbons are those having carbon chain lengths ranging from one to and including five, with varying amounts and positions of chlorine substitution.				
F026		4	F026	1 (0.454)
Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production of materials on equipment previously used for the manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tetra-, penta-, or hexachlorobenzene under alkaline conditions.				
F027		4	F027	1 (0.454)
Discarded unused formulations containing tri-, tetra-, or pentachlorophenol or discarded unused formulations containing compounds derived from these chlorophenols. (This listing does not include formulations containing hexachlorophene synthesized from prepurified 2,4,5-trichlorophenol as the sole component.)				
F028		4	F028	1 (0.454)
Residues resulting from the incineration or thermal treatment of soil contaminated with EPA				

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Hazardous Waste Nos. F020, F021, F022, F023, F026, and F027.				
F032		4	F032	1 (0.454)
Wastewaters (except those that have not come into contact with process contaminants), process residuals, preservative drippage, and spent formulations from wood preserving processes generated at plants that currently use or have previously used chlorophenolic formulations (except potentially cross-contaminated wastes that have had the F032 waste code deleted in accordance with §261.35 of this chapter or potentially cross-contaminated wastes that are otherwise currently regulated as hazardous wastes (*i.e.*, F034 or F035), and where the generator does not resume or initiate use of chlorophenolic formulations). This listing does not include K001 bottom sediment sludge from the treatment of wastewater from wood preserving processes that use creosote and/or pentachlorophenol.				
F034		4	F034	1 (0.454)
Wastewaters (except those that have not come into contact with process contaminants), process residuals, preservative drippage, and spent formulations from wood preserving processes generated at plants that use creosote formulations. This listing does not include K001 bottom sediment sludge from the treatment of wastewater from wood preserving processes that use creosote and/or pentachlorophenol.				
F035		4	F035	1 (0.454)
Wastewaters (except those that have not come into contact with process contaminants), process residuals, preservative drippage, and spent				

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
formulations from wood preserving processes generated at plants that use inorganic preservatives containing arsenic or chromium. This listing does not include K001 bottom sediment sludge from the treatment of wastewater from wood preserving processes that use creosote and/or pentachlorophenol.				
F037		4	F037	1 (0.454)
Petroleum refinery primary oil/water/solids separation sludge-Any sludge generated from the gravitational separation of oil/water/solids during the storage or treatment of process wastewaters and oily cooling wastewaters from petroleum refineries. Such sludges include, but are not limited to those generated in oil/water/solids separators; tanks and impoundments; ditches and other conveyances; sumps; and stormwater units receiving dry weather flow. Sludges generated in stormwater units that do not receive dry weather flow, sludges generated from non-contact once-through cooling waters segregated for treatment from other process or oily cooling waters, sludges generated in aggressive biological treatment units as defined in §261.31(b)(2) (including sludges generated in one or more additional units after wastewaters have been treated in aggressive biological treatment units) and K051 wastes are not included in this listing. This listing does include residuals generated from processing or recycling oil-bearing hazardous secondary materials excluded under §261.4(a)(12)(i), if those residuals are to be disposed of.				
F038		4	F038	1 (0.454)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Petroleum refinery secondary (emulsified) oil/water/solids separation sludge-Any sludge and/or float generated from the physical and/or chemical separation of oil/water/solids in process wastewaters and oily cooling wastewaters from petroleum refineries. Such wastes include, but are not limited to, all sludges and floats generated in: induced air flotation (IAF) units, tanks and impoundments, and all sludges generated in DAF units. Sludges generated in stormwater units that do not receive dry weather flow, sludges generated from non-contact once-through cooling waters segregated for treatment from other process or oily cooling waters, sludges and floats generated in aggressive biological treatment units as defined in §261.31(b)(2) (including sludges and floats generated in one or more additional units after wastewaters have been treated in aggressive biological treatment units) and F037, K048, and K051 wastes are not included in this listing.				
F039		4	F039	1 (0.454)
Leachate (liquids that have percolated through land disposed wastes) resulting from the disposal of more than one restricted waste classified as hazardous under subpart D of 40 CFR part 261. (Leachate resulting from the disposal of one or more of the following EPA Hazardous Wastes and no other hazardous wastes retains its EPA Hazardous Waste Number(s): F020, F021, F022, F026, F027, and/or F028.)				
K001		4	K001	1 (0.454)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Bottom sediment sludge from the treatment of wastewaters from wood preserving processes that use creosote and/or pentachlorophenol.				
K002		4	K002	10 (4.54)
Wastewater treatment sludge from the production of chrome yellow and orange pigments.				
K003		4	K003	10 (4.54)
Wastewater treatment sludge from the production of molybdate orange pigments.				
K004		4	K004	10 (4.54)
Wastewater treatment sludge from the production of zinc yellow pigments.				
K005		4	K005	10 (4.54)
Wastewater treatment sludge from the production of chrome green pigments.				
K006		4	K006	10 (4.54)
Wastewater treatment sludge from the production of chrome oxide green pigments (anhydrous and hydrated).				
K007		4	K007	10 (4.54)
Wastewater treatment sludge from the production of iron blue pigments.				
K008		4	K008	10 (4.54)
Oven residue from the production of chrome oxide green pigments.				
K009		4	K009	10 (4.54)
Distillation bottoms from the production of acetaldehyde from ethylene.				
K010		4	K010	10 (4.54)
Distillation side cuts from the production of acetaldehyde from ethylene.				
K011		4	K011	10 (4.54)

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List of Hazardous Substances and Reportable Quantities[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Bottom stream from the wastewater stripper in the production of acrylonitrile.				
K013		4	K013	10 (4.54)
Bottom stream from the acetonitrile column in the production of acrylonitrile.				
K014		4	K014	5000 (2270)
Bottoms from the acetonitrile purification column in the production of acrylonitrile.				
K015		4	K015	10 (4.54)
Still bottoms from the distillation of benzyl chloride.				
K016		4	K016	1 (0.454)
Heavy ends or distillation residues from the production of carbon tetrachloride.				
K017		4	K017	10 (4.54)
Heavy ends (still bottoms) from the purification column in the production of epichlorohydrin.				
K018		4	K018	1 (0.454)
Heavy ends from the fractionation column in ethyl chloride production.				
K019		4	K019	1 (0.454)
Heavy ends from the distillation of ethylene dichloride in ethylene dichloride production.				
K020		4	K020	1 (0.454)
Heavy ends from the distillation of vinyl chloride in vinyl chloride monomer production.				
K021		4	K021	10 (4.54)
Aqueous spent antimony catalyst waste from fluoromethanes production.				
K022		4	K022	1 (0.454)
Distillation bottom tars from the production of phenol/acetone from cumene.				

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40 C.F.R. Part 302 – Table 302.4
List of Hazardous Substances and Reportable Quantities[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
K023		4	K023	5000 (2270)
Distillation light ends from the production of phthalic anhydride from naphthalene.				
K024		4	K024	5000 (2270)
Distillation bottoms from the production of phthalic anhydride from naphthalene.				
K025		4	K025	10 (4.54)
Distillation bottoms from the production of nitrobenzene by the nitration of benzene.				
K026		4	K026	1000 (454)
Stripping still tails from the production of methyl ethyl pyridines.				
K027		4	K027	10 (4.54)
Centrifuge and distillation residues from toluene diisocyanate production.				
K028		4	K028	1 (0.454)
Spent catalyst from the hydrochlorinator reactor in the production of 1,1,1-trichloroethane.				
K029		4	K029	1 (0.454)
Waste from the product steam stripper in the production of 1,1,1- trichloroethane.				
K030		4	K030	1 (0.454)
Column bottoms or heavy ends from the combined production of trichloroethylene and perchloroethylene.				
K031		4	K031	1 (0.454)
By-product salts generated in the production of MSMA and cacodylic acid.				
K032		4	K032	10 (4.54)
Wastewater treatment sludge from the production of chlordane.				
K033		4	K033	10 (4.54)

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List of Hazardous Substances and Reportable Quantities[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Wastewater and scrub water from the chlorination of cyclopentadiene in the production of chlordane.				
K034		4	K034	10 (4.54)
Filter solids from the filtration of hexachlorocyclopentadiene in the production of chlordane.				
K035		4	K035	1 (0.454)
Wastewater treatment sludges generated in the production of creosote.				
K036		4	K036	1 (0.454)
Still bottoms from toluene reclamation distillation in the production of disulfoton.				
K037		4	K037	1 (0.454)
Wastewater treatment sludges from the production of disulfoton.				
K038		4	K038	10 (4.54)
Wastewater from the washing and stripping of phorate production.				
K039		4	K039	10 (4.54)
Filter cake from the filtration of diethylphosphorodithioic acid in the production of phorate.				
K040		4	K040	10 (4.54)
Wastewater treatment sludge from the production of phorate.				
K041		4	K041	1 (0.454)
Wastewater treatment sludge from the production of toxaphene.				
K042		4	K042	10 (4.54)
Heavy ends or distillation residues from the distillation of tetrachlorobenzene in the production of 2,4,5-T.				
K043		4	K043	10 (4.54)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
2,6-Dichlorophenol waste from the production of 2,4-D.				
K044		4	K044	10 (4.54)
Wastewater treatment sludges from the manufacturing and processing of explosives.				
K045		4	K045	10 (4.54)
Spent carbon from the treatment of wastewater containing explosives.				
K046		4	K046	10 (4.54)
Wastewater treatment sludges from the manufacturing, formulation and loading of lead-based initiating compounds.				
K047		4	K047	10 (4.54)
Pink/red water from TNT operations.				
K048		4	K048	10 (4.54)
Dissolved air flotation (DAF) float from the petroleum refining industry.				
K049		4	K049	10 (4.54)
Slop oil emulsion solids from the petroleum refining industry.				
K050		4	K050	10 (4.54)
Heat exchanger bundle cleaning sludge from the petroleum refining industry.				
K051		4	K051	10 (4.54)
API separator sludge from the petroleum refining industry.				
K052		4	K052	10 (4.54)
Tank bottoms (leaded) from the petroleum refining industry.				
K060		4	K060	1 (0.454)
Ammonia still lime sludge from coking operations.				
K061		4	K061	10 (4.54)

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[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Emission control dust/sludge from the primary production of steel in electric furnaces.				
K062		4	K062	10 (4.54)
Spent pickle liquor generated by steel finishing operations of facilities within the iron and steel industry (SIC Codes 331 and 332).				
K064		4	K064	10 (4.54)
Acid plant blowdown slurry/sludge resulting from the thickening of blowdown slurry from primary copper production.				
K065		4	K065	10 (4.54)
Surface impoundment solids contained in and dredged from surface impoundments at primary lead smelting facilities.				
K066		4	K066	10 (4.54)
Sludge from treatment of process wastewater and/or acid plant blowdown from primary zinc production.				
K069		4	K069	10 (4.54)
Emission control dust/sludge from secondary lead smelting. (Note: This listing is stayed administratively for sludge generated from secondary acid scrubber systems. The stay will remain in effect until further administrative action is taken. If EPA takes further action effecting the stay, EPA will publish a notice of the action in the FEDERAL REGISTER.)				
K071		4	K071	1 (0.454)
Brine purification muds from the mercury cell process in chlorine production, where separately prepurified brine is not used.				
K073		4	K073	10 (4.54)

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List of Hazardous Substances and Reportable Quantities[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Chlorinated hydrocarbon waste from the purification step of the diaphragm cellprocess using graphite anodes in chlorine production.				
K083		4	K083	100 (45.4)
Distillation bottoms from aniline production.				
K084		4	K084	1 (0.454)
Wastewater treatment sludges generated during the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds.				
K085		4	K085	10 (4.54)
Distillation or fractionation column bottoms from the production of chlorobenzenes.				
K086		4	K086	10 (4.54)
Solvent washes and sludges, caustic washes and sludges, or water washes and sludges from cleaning tubs and equipment used in the formulation of ink from pigments, driers, soaps, and stabilizers containing chromium and lead.				
K087		4	K087	100 (45.4)
Decanter tank tar sludge from coking operations.				
K088		4	K088	10 (4.54)
Spent potliners from primary aluminum reduction.				
K090		4	K090	10 (4.54)
Emission control dust or sludge from ferrochromiumsilicon production.				
K091		4	K091	10 (4.54)
Emission control dust or sludge from ferrochromium production.				
K093		4	K093	5000 (2270)
Distillation light ends from the production of phthalic anhydride from ortho-xylene.				

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List of Hazardous Substances and Reportable Quantities

[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
K094		4	K094	5000 (2270)
Distillation bottoms from the production of phthalic anhydride from ortho-xylene.				
K095		4	K095	100 (45.4)
Distillation bottoms from the production of 1,1,1-trichloroethane.				
K096		4	K096	100 (45.4)
Heavy ends from the heavy ends column from the production of 1,1,1-trichloroethane.				
K097		4	K097	1 (0.454)
Vacuum stripper discharge from the chlordane chlorinator in the production of chlordane.				
K098		4	K098	1 (0.454)
Untreated process wastewater from the production of toxaphene.				
K099		4	K099	10 (4.54)
Untreated wastewater from the production of 2,4-D.				
K100		4	K100	10 (4.54)
Waste leaching solution from acid leaching of emission control dust/sludge from secondary lead smelting.				
K101		4	K101	1 (0.454)
Distillation tar residues from the distillation of aniline-based compounds in the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds.				
K102		4	K102	1 (0.454)
Residue from the use of activated carbon for decolorization in the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds.				
K103		4	K103	100 (45.4)

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List of Hazardous Substances and Reportable Quantities[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Process residues from aniline extraction from the production of aniline.				
K104		4	K104	10 (4.54)
Combined wastewater streams generated from nitrobenzene/aniline production.				
K105		4	K105	10 (4.54)
Separated aqueous stream from the reactor product washing step in the production of chlorobenzenes.				
K106		4	K106	1 (0.454)
Wastewater treatment sludge from the mercury cell process in chlorine production.				
K107		4	K107	10 (4.54)
Column bottoms from product separation from the production of 1,1- dimethylhydrazine (UDMH) from carboxylic acid hydrazines.				
K108		4	K108	10 (4.54)
Condensed column overheads from product separation and condensed reactor vent gases from the production of 1,1- dimethylhydrazine (UDMH) from carboxylic acid hydrazides.				
K109		4	K109	10 (4.54)
Spent filter cartridges from product purification from the production of 1,1-dimethylhydrazine (UDMH) from carboxylic acid hydrazides.				
K110		4	K110	10 (4.54)
Condensed column overheads from intermediate separation from the production of 1,1-dimethylhydrazine (UDMH) from carboxylic acid hydrazides.				
K111		4	K111	10 (4.54)
Product washwaters from the production of dinitrotoluene via nitration of toluene.				
K112		4	K112	10 (4.54)

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List of Hazardous Substances and Reportable Quantities[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Reaction by-product water from the drying column in the production of toluenediamine via hydrogenation of dinitrotoluene.				
K113		4	K113	10 (4.54)
Condensed liquid light ends from the purification of toluenediamine in the production of toluenediamine via hydrogenation of dinitrotoluene.				
K114		4	K114	10 (4.54)
Vicinals from the purification of toluenediamine in the production of toluenediamine via hydrogenation of dinitrotoluene.				
K115		4	K115	10 (4.54)
Heavy ends from the purification of toluenediamine in the production of toluenediamine via hydrogenation of dinitrotoluene.				
K116		4	K116	10 (4.54)
Organic condensate from the solvent recovery column in the production of toluene diisocyanate via phosgenation of toluenediamine.				
K117		4	K117	1 (0.454)
Wastewater from the reactor vent gas scrubber in the production of ethylene dibromide via bromination of ethene.				
K118		4	K118	1 (0.454)
Spent adsorbent solids from purification of ethylene dibromide in the production of ethylene dibromide via bromination of ethene.				
K123		4	K123	10 (4.54)
Process wastewater (including supernates, filtrates, and washwaters) from the production of ethylenebisdithiocarbamic acid and its salts.				
K124		4	K124	10 (4.54)

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List of Hazardous Substances and Reportable Quantities

[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Reactor vent scrubber water from the production of ethylenebisdithiocarbamic acid and its salts.				
K125		4	K125	10 (4.54)
Filtration, evaporation, and centrifugation solids from the production of ethylenebisdithiocarbamic acid and its salts.				
K126		4	K126	10 (4.54)
Baghouse dust and floor sweepings in milling and packaging operations from the production or formulation of ethylenebisdithiocarbamic acid and its salts.				
K131		4	K131	100 (45.4)
Wastewater from the reactor and spent sulfuric acid from the acid dryer from the production of methyl bromide.				
K132		4	K132	1000 (454)
Spent absorbent and wastewater separator solids from the production of methyl bromide.				
K136		4	K136	1 (0.454)
Still bottoms from the purification of ethylene dibromide in the production of ethylene dibromide via bromination of ethene.				
K141		4	K141	1 (0.454)
Process residues from the recovery of coal tar, including, but not limited to, collecting sump residues from the production of coke from coal or the recovery of coke by-products produced from coal. This listing does not include K087 (decanter tank tar sludges from coking operations).				
K142		4	K142	1 (0.454)
Tar storage tank residues from the production of coke from coal or from the recovery of coke by-products produced from coal.				

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List of Hazardous Substances and Reportable Quantities[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
K143		4	K143	1 (0.454)
Process residues from the recovery of light oil, including, but not limited to, those generated in stills, decanters, and wash oil recovery units from the recovery of coke by- products produced from coal.				
K144		4	K144	1 (0.454)
Wastewater sump residues from light oil refining, including, but not limited to, intercepting or contamination sump sludges from the recovery of coke by-products produced from coal.				
K145		4	K145	1 (0.454)
Residues from naphthalene collection and recovery operations from the recovery of coke by-products produced from coal.				
K147		4	K147	1 (0.454)
Tar storage tank residues from coal tar refining.				
K148		4	K148	1 (0.454)
Residues from coal tar distillation, including, but not limited to, still bottoms.				
K149		4	K149	10 (4.54)
Distillation bottoms from the production of alpha- (or methyl-) chlorinated toluenes, ring-chlorinated toluenes, benzoyl chlorides, and compounds with mixtures of these functional groups. [This waste does not include still bottoms from the distillation of benzyl chloride.]				
K150		4	K150	10 (4.54)
Organic residuals, excluding spent carbon adsorbent, from the spent chlorine gas and hydrochloric acid recovery processes associated with the production of alpha- (or methyl-) chlorinated toluenes, ring-chlorinated toluenes,				

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
benzoyl chlorides, and compounds with mixtures of these functional groups.				
K151		4	K151	10 (4.54)
Wastewater treatment sludges, excluding neutralization and biological sludges, generated during the treatment of waste-waters from the production of alpha- (or methyl-) chlorinated toluenes, ring-chlorinated toluenes, benzoyl chlorides, and compounds with mixtures of these functional groups.				
K156		4	K156	10 (4.54)
Organic waste (including heavy ends, still bottoms, light ends, spent solvents, filtrates, and decantates) from the production of carbamates and carbamoyl oximes. (This listing does not apply to wastes generated from the manufacture of 3-iodo-2-propynyl n-butylcarbamate.)				
K157		4	K157	10 (4.54)
Wastewaters (including scrubber waters, condenser waters, washwaters, and separation waters) from the production of carbamates and carbamoyl oximes. (This listing does not apply to wastes generated from the manufacture of 3-iodo-2-propynyl n-butylcarbamate.)				
K158		4	K158	10 (4.54)
Bag house dusts and filter/separation solids from the production of carbamates and carbamoyl oximes. (This listing does not apply to wastes generated from the manufacture of 3-iodo-2-propynyl n-butylcarbamate.)				
K159		4	K159	10 (4.54)

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Organics from the treatment of thiocarbamate wastes.				
K161		4	K161	1 (0.454)
Purification solids (including filtration, evaporation, and centrifugation solids), bag-house dust and floor sweepings from the production of dithiocarbamate acids and their salts. (This listing does not include K125 or K126).				
K169[f]		4	K169	10 (4.54)
Crude oil storage tank sediment from petroleum refining operations.				
K170[f]		4	K170	1 (0.454)
Clarified slurry oil tank sediment and/or in-line filter/separation solids from petroleum refining operations.				
K171[f]		4	K171	1 (0.454)
Spent hydrotreating catalyst from petroleum refining operations. (This listing does not include inert support media.)				
K172[f]		4	K172	1 (0.454)
Spent hydrorefining catalyst from petroleum refining operations. (This listing does not include inert support media.)				
K174[f]		4	K174	1 (0.454)
K175[f]		4	K175	1 (0.454)
K176				
Baghouse filters from the production of antimony oxide, including filters from the production of intermediates (e.g., antimony metal or crude antimony oxide)		4	K176	1 (0.454)
K177				

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List of Hazardous Substances and Reportable Quantities[Note: All Comments/Notes Are Located at the End of This Table]

Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)
Slag from the production of antimony oxide that is speculatively accumulated or disposed, including slag from the production of intermediates (e.g., antimony metal or crude antimony oxide)		4	K177	5,000 (2270)
K178		4	K178	1000 (454)
Residues from manufacturing and manufacturing-site storage of ferric chloride from acids formed during the production of titanium dioxide using the chloride-ilmenite process.				
K181		4	K181	##
Nonwastewaters from the production of dyes and/or pigments (including nonwastewaters commingled at the point of generation with nonwastewaters from other processes) that, at the point of generation, contain mass loadings of any of the constituents identified in paragraph (c) of section 261.32 that are equal to or greater than the corresponding paragraph (c) levels, as determined on a calendar year basis				

†Indicates the statutory source defined by 1, 2, 3, and 4, as described in the note preceding Table 302.4.

†Indicates the statutory source defined by 1,2,3, and 4, as described in the note preceding Table 302.4.

††No reporting of releases of this hazardous substance is required if the diameter of the pieces of the solid metal released is larger than 100 micrometers (0.004 inches).

†††The RQ for asbestos is limited to friable forms only.

##The Agency may adjust the statutory RQ for this hazardous substance in a future rulemaking; until then the statutory one-pound RQ applies.

§The adjusted RQs for radionuclides may be found in appendix B to this table.

**Indicates that no RQ is being assigned to the generic or broad class.

[a]Benzene was already a CERCLA hazardous substance prior to the CAA Amendments of 1990 and received an adjusted 10-pound RQ based on potential carcinogenicity in an August 14, 1989, final rule (54 FR 33418). The

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Hazardous substance	CASRN	Statutory code†	RCRA waste No.	Final RQ pounds (Kg)

CAA Amendments specify that "benzene (including benzene from gasoline)" is a hazardous air pollutant and, thus, a CERCLA hazardous substance.

[b]The CAA Amendments of 1990 list DDE (3547-04-4) as a CAA hazardous air pollutant. The CAS number, 3547-04-4, is for the chemical, p,p′dichlorodiphenylethane. DDE or p,p′-dichlorodiphenyldichloroethylene, CAS number 72-55-9, is already listed in Table 302.4 with a final RQ of 1 pound. The substance identified by the CAS number 3547-04-4 has been evaluated and listed as DDE to be consistent with the CAA section 112 listing, as amended.

[c]Includes mineral fiber emissions from facilities manufacturing or processing glass, rock, or slag fibers (or other mineral derived fibers) of average diameter 1 micrometer or less.

[d]Includes mono- and di-ethers of ethylene glycol, diethylene glycol, and triethylene glycol R-(OCH2CH2)n-OR′ where:
n = 1, 2, or 3;
R = alkyl C7 or less; or
R = phenyl or alkyl substituted phenyl;
R′= H or alkyl C7 or less; or
OR′ consisting of carboxylic acid ester, sulfate, phosphate, nitrate, or sulfonate.

[e]Includes organic compounds with more than one benzene ring, and which have a boiling point greater than or equal to 100 °C.

[f]See 40 CFR 302.6(b)(1) for application of the mixture rule to this hazardous waste.

State of Oregon Department of Environmental Quality

OAR 340-150-0200 Appendix L Training Elements

The following topics must be covered in each UST system operator training session or by an equivalent training or testing method to meet UST system operation and maintenance training requirements:

(1) General overview of department UST program administrative requirements:

(a) Types of registration certificates (i.e., permits) and process for modification of registration certificates;

(b) Notification process and general technical requirements for new UST installation, decommissioning, equipment replacement and retrofits, confirmed releases, suspected releases (including confirmation steps for suspected releases) and other system or test failures;

(c) Annual UST compliance fees and invoicing process;

(d) General requirements for maintaining financial responsibility;

(e) Department process for inspections and technical assistance resources available; and

(f) Enforcement process for violations.

(2) General overview of other regulations pertaining to USTs, including, but not limited to, fire codes, occupational health and safety and any related industry practices pertaining to safety.

(3) Spill prevention and overfill protection:

(a) Rule requirements, including record keeping;

(b) Equipment requirements; and

(c) Operation and maintenance needs.

(4) Release detection: For each type of release detection method listed in OAR 340-150-0400 through 340-150-0470 for both USTs and underground piping:

(a) Rule requirements, including record keeping;

(b) Monitoring and equipment, including third party approval requirements; and

(c) Operation and maintenance requirements.

(5) Corrosion protection, galvanic and impressed current:

(a) UST rule requirements (OAR chapter 340, division 150), including record keeping;

(b) Equipment requirements; and

(c) Operation and maintenance needs, including periodic inspections and testing.

(6) Lined USTs:

(a) Rule requirements, including record keeping; and

(b) Operation and maintenance needs, including periodic inspections and testing.

State of Oregon Department of Environmental Quality

OAR 340-163-0010
NW Total Petroleum Hydrocarbon Identification Method

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TOTAL PETROLEUM HYDROCARBONS (TPH)

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* The chromatograms are not available in the “electronic” version. They are included in the printed publication.

TOTAL PETROLEUM HYDROCARBONS (TPH)

The following compilation of analytical methods may be used in Oregon and Washington for Underground Storage Tank cleanups and other cleanups of TPH (check with applicable state rules). Each of these Total Petroleum Hydrocarbon (TPH) Methods has its own niche in the overall analytical scheme. The methods are:

NWTPH-HCID.....Hydrocarbon Identification

NWTPH-Gx .....Volatile Petroleum Products (Extended)

NWTPH-Dx .....Semi-volatile Petroleum Products (Extended)

NWTPH-HCID is a qualitative and semi-quantitative screen to determine the presence and type of petroleum products that may exist in water or soil. This method should be used if the type of petroleum contamination is unknown. It should be performed on contaminated soil or water that is representative of the contamination at the site. The results of this method will determine what fully quantitative method/methods, if any, are to be used in determining compliance with the matrix criteria. Should the value of the analysis for gasoline, diesel or heavy oils (or any other identified petroleum product) exceed the reporting limits, then the specific analytical method for that product must be employed.

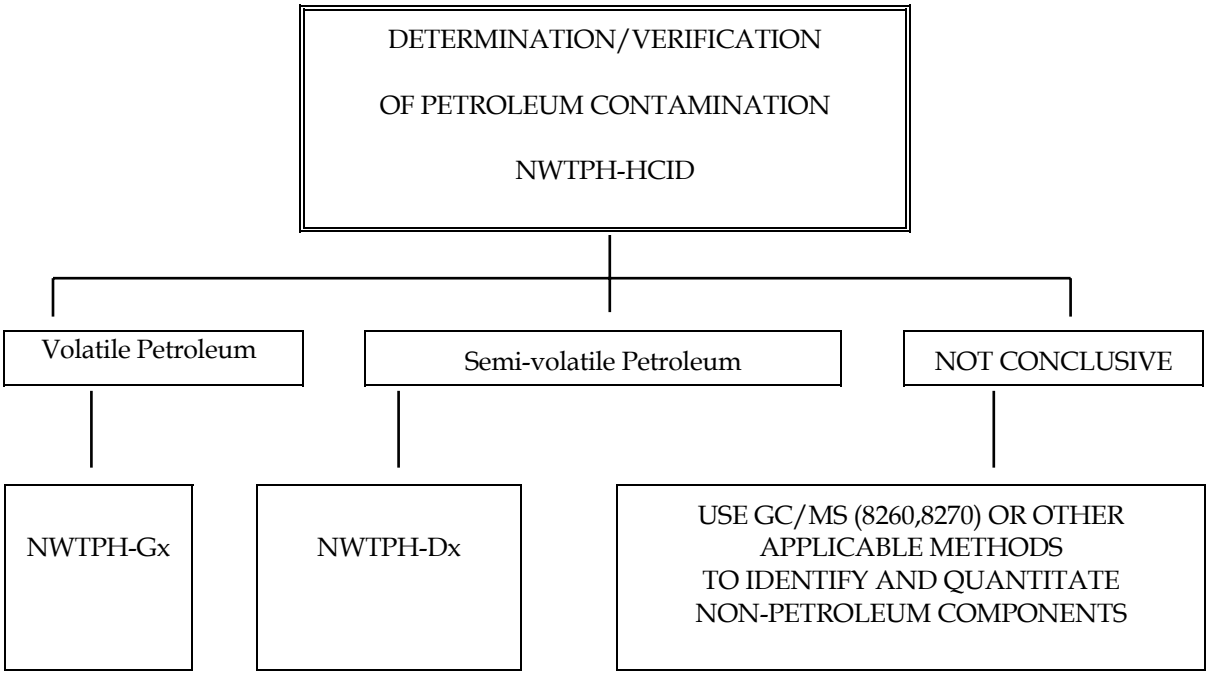
NWTPH-Gx is the qualitative and quantitative method (extended) for volatile ("gasoline") petroleum products in soil and water. Petroleum products applicable for this method include aviation and automotive gasolines, mineral spirits, stoddard solvent and naphtha.

NWTPH-Dx is the qualitative and quantitative method (extended) for semi-volatile ("diesel") petroleum products in soil and water. Petroleum products applicable for this include jet fuels, kerosene, diesel oils, hydaulic fluids, mineral oils, lubricating oils and fuel oils.

NOTE: These "NWTPH" methods result in single TPH values that can be used when compliance with a single cleanup level is desired. When TPH "fractions" are needed, then the VPH and EPH methods must be used.

ANALYTICAL DECISION TREE FOR NWTPH

The following flow chart depicts the laboratory analytical scheme to be used when analyzing samples for single TPH levels. The first step is the qualitative determination of the existence and nature of petroleum contamination and this should be used when the site contamination is unknown. It is required that this first step will be performed on a representative sample from the area that is suspected to be the most contaminated at the site. For those samples containing analytes which, due to their retention times, ratios to each other or their non-hydrocarbon pattern (e.g., creosote), do not suggest petroleum hydrocarbons, then GC/MS methods should be employed to ascertain the components. At those sites where the petroleum contaminants are known or have been identified using the NWTPH-HCID method, the specific product method is to be used.



NWTPH-HCID

Hydrocarbon Identification Method for Soil and Water

Summary

This method is a qualitative and semi-quantitative procedure. It is used for groundwater or surface water, and soil/sediment from sites where the petroleum products are unknown and/or when multiple types of petroleum products are suspected to be present. This method is used to identify petroleum products containing components from C7 to C30 range, as well as heavy oils, with specific product confirmation by pattern matching ("fingerprinting") employing capillary gas chromatography with flame ionization detection (GC/FID). EPA method 3510 has been adapted as the extraction procedure for the water portion of this method.

While this method is intended to be primarily qualitative, it can be used to eliminate the need for further analyses for those samples which demonstrate TPH levels significantly below the regulatory limits. If the sample contains toluene to dodecane (gasoline range), dodecane through tetradecane (diesel range) and/or an unresolved chromatographic envelope greater than tetradecane (e.g. motor oils) above the reporting limits of this method, then the final quantitation must be performed by methods specific for these mixtures. Since the water extraction procedure in this method is identical to that found in the water portion of NWTPH-Dx (semi-volatile petroleum products, i.e. from kerosene through heavy fuel oils), these products may be quantitated using this extract. Because of the possible loss of volatile compounds in the extraction and concentrations steps, gasoline, mineral spirits and other volatile petroleum products that exceed the reporting limits of this method must be quantitated using the NWTPH-Gx method.

The reporting limits for water are 0.25 mg/L for gasoline, 0.63 mg/L for #2 diesel and motor oils. The reporting limits for soil/sediment are 20 mg/Kg for gasoline, 50 mg/Kg for #2 diesel, and 100 mg/Kg for motor oil, all reported on a dry weight basis. These values for soil/sediment assumes 100% solids and will be higher depending on the actual moisture content.

The method relies heavily upon the experience of the analyst for the identification of the specific petroleum product(s) that may be present. Therefore, this method must be run by, or under the direct supervision of, analysts experienced in the use of GC and in the interpretation of gas chromatograms of both fresh and weathered petroleum products.

Equipment and Reagents

Gas Chromatograph, w/wo autosampler
Capillary split/splitless injector
Flame ionization detector
Suggested Capillary Column:
J&W DB-1 or DB-5, 30 M x 0.25 mm or 0.32 mm with 0.25 um film thickness capillary column or equivalent
Chromatography Data System
VOA Vial: 40 mL glass vial with Teflon coated cap septum, Eagle Picher or equivalent
Syringe: Hamilton #701, 10 uL or equivalent
Ultrasonic Bath
Glass Wool: Pyrex or equivalent
Centrifuge tubes: 5 or 15 mL, calibrated in 0.1 mL increments
Analytical Balance: accurate to at least 0.0001 g
Volumetric Flasks: 10 mL, ground glass with ground glass stopper
Separatory funnels: 500 mL, Teflon stopcocks
Kuderna-Danish (KD) Flasks: 250 mL or equivalent
Snyder Columns: 3-ball, 24/40 ground glass joint
Concentrator Tubes: 10 mL
Methylene Chloride: Burdick and Jackson Brand or equivalent
N-Evap Concentrator or equivalent

Standards

Retention Time Standards. Prepare a composite standard, using methylene chloride as the solvent, consisting of toluene, dodecane and tetracosane at 25 ug/mL each. Additional compounds may be added at the discretion of the analyst. The use of this standard is to establish the retention time windows for the quantitation of gasoline #2 diesel and motor oils.

Reference Standards. Prepare individual petroleum product reference standards (i.e. gasoline, mineral spirits, kerosene and #2 diesel oil), using methylene chloride as the solvent, at approximately 50 ug/mL. Prepare a non-synthetic motor oil (pennzoil SAE 30 or equivalent) reference standard at 200 ug/mL. The preparation of reference standards for other types of petroleum products is recommended. The use of these reference standards is to insure the accurate identification of petroleum product contamination by chromatographic pattern matching ("fingerprinting") and establish retention time windows for those petroleum products not determined with the individual compound retention time standard.

Gasoline Stock Standard. A stock standard is prepared by placing approximately 9 mL of methylene chloride in a 10 mL volumetric flask. Tare the flask/methylene chloride and add about five drops of non-oxygenated regular unleaded gasoline, assuring that the liquid falls directly into the methylene chloride without contacting the neck of the flask. Reweigh the flask and dilute to volume with methylene chloride, stopper and mix by inverting the flask several times. It is important that the analyst minimize the amount of time that the flask is left unstoppered, to reduce

the loss of gasoline through volatilization. The use of a commercially prepared gasoline standards is acceptable if it is certified as non-oxygenated gasoline or if the gasoline concentration has been adjusted to reflect the contribution of the oxygenate. Calculate the gasoline concentration as follows:

$$Stock,\ ug / mL = \frac{(final\ wt,\ mg) - (tare\ wt,\ mg)}{10\ mL} \times \frac{1000\ ug}{mg}$$

Note: The use of oxygenated regular unleaded gasoline for the gasoline stock standard is allowed if the weight (mass) of the gasoline used is adjusted for the weight (mass) contribution of the oxygenate to the gasoline. This will necessitate the analysis of the gasoline for the specific oxygenate(s) present to determine the concentration. The analysis for the oxygenates will be conducted by either of the methods published in the Federal Register - Appendix B and C - Testing Procedures - Vol. 57, No. 24, Wednesday, February 5, 1992, Notices.Alternate methods for the analysis of gasoline oxygenates must be approved by the Oregon's Department of Environmental Quality and/or Washington's Department of Ecology prior to use.

Diesel Stock Standard. A stock standard is prepared by adding about five drops of #2 diesel oil stock to tared 10 mL volumetric flask. Reweigh the flask and bring it to volume with methylene chloride, stopper and mix by inverting the flask several times. Calculate the concentration of this standard in the same manner as the gasoline stock standard. The use of a commercially prepared #2 diesel standard is an acceptable alternative to the above procedure.

Motor Oil Stock Standard. A stock standard is prepared by adding about ten drops of a non-synthetic SAE 30 weight motor oil (Pennzoil or equivalent) to a tared 10 mL volumetric flask. Reweigh the flask, bring it to volume with methylene chloride, stopper and mix by inverting the flask several times. Calculate the concentration of this standard in the same manner as the gasoline stock standard. The use of commercially prepared motor oil standards is an acceptable alternative to the above procedure.

Note: The Diesel and Motor Oil Stock Standards required in this method are identical to those required for NWTPH-Dx (extended diesel method including all semi-volatile petroleum products eluting after gasoline, e.g. kerosene, diesels, mineral oils, lubricating oils, heavy fuel oils, etc.).

Surrogate Stock Standard. Suggested surrogates for use in this method are bromofluorobenzene and pentacosane. The use of different or additional surrogates is optional. Prepare the surrogate stock standard by weighing 50 mg of each surrogate compound into a 10 mL volumetric flask, then bring to volume with methylene chloride for a final concentration of 5000 ug/mL for each surrogate compound. The use of a commercially prepared surrogate solution(s) is an acceptable alternative to the above procedure.

Composite Calibration Working Standard. Using serial dilutions of the stock standards, prepare a mixture for water analyses that contains 10 ug/mL of gasoline, 25 ug/mL of #2 diesel oil and the

surrogate standard. For soil/sediment analyses this standard should be prepared to contain 20 ug/mL of gasoline, 50 ug/mL of #2 diesel and the surrogate standard. Add the appropriate volumes, using the equations listed below, and adjusting for the concentration change created by any serial dilutions, of gasoline stock standard, #2 diesel stock standard and the surrogate stock standard to a 10 mL volumetric flask, then dilute to volume with methylene chloride. Stopper and mix by inverting the flask several times. The surrogate standard should be added to a level sufficient to produce a surrogate concentration of between 5 and 50 ug/mL.

$$\textit{Volume Gasoline Stock, uL} = \frac{\textit{20 (soil) / 10 (water) ug / mL x 10 mL}}{\textit{Gasoline Stock Conc, ug / mL}} \; x \; \frac{\textit{1000 uL}}{\textit{mL}}$$

$$\textit{Volume Diesel Stock, uL} = \frac{\textit{50 (soil) / 25 (water) ug / mL x 10 mL}}{\textit{Diesel Stock Conc, ug / mL}} \; x \; \frac{\textit{1000 uL}}{\textit{mL}}$$

This mixture corresponds to 0.25 mg/L gasoline and 0.63 mg/L #2 diesel oil for water and 20 mg/Kg gasoline and 50 mg/Kg diesel in soil following the extraction and analytical procedures of this method.

The motor oil calibration working standard should be made at a concentration of 250 ug/mL for water and 100 ug/mL for soil following the procedure outlined above. This will correspond to a reporting value of 0.63 mg/L for water and 100 mg/kg for soil. If, in the opinion of the analyst, the GC sensitivity to 100 ug/mL of motor oil is insufficient, the analyst is allowed to increase the concentration of this standard and to concentrate a portion of the extract to achieve the reporting limit for soil.

Surrogate Working Standard. Prepare a surrogate working (spiking) standard, using the procedure outlined above, that will yield between 5 ug and 50 ug/mL of the surrogate compounds in the 10 mL sample extract produced in this method.

Note: All samples must be collected in glass jars with Teflon lined lids (Eagle Picher or equivalent) and held at 4 degrees C until extracted. A volume of 400 mL is the minimum sample size to achieve the reporting limits as stated, however, larger volumes are allowed as long as the solvent/sample ratio is maintained. Samples must be extracted within 7 days (for water) or 14 days (for soil/sediment) of the date of collection. The preservation of water samples in the field, to a pH of less than 2 with 1+1 HCL, is recommended.

Extraction Procedures

Water Samples

Mark the water meniscus on the sample jar for later volume determination. Pour the sample into a 500 mL separatory funnel, add the surrogate solution (to achieve the desired concentration in a 10 mL extract). Add 30 mL of methylene chloride to the sample jar, cap and shake the jar vigorously

for a few seconds to wash off any hydrocarbons adhering to the side of the jar. Add this solvent to the separatory funnel, stopper and shake vigorously, venting frequently, for one minute. Allow the two phases to separate, then drain the solvent into a 250 mL K-D flask fitted with a 10 mL concentrator tube. Repeat the extraction twice more using 30 mL of methylene chloride, each time, adding the solvent to the K-D.

Attach a 3-ball Snyder column to the K-D and concentrate the sample extract to 5 - 10 mL on a stream bath. Remove the K-D apparatus and allow it to cool prior to disassembly. During disassembly, rinse the Snyder/K-D joint and K-D/concentrator joint with approximately 1 mL of methylene chloride and add these rinsings to the extract. Adjust the volume of the extract to 10 mL. For those samples which exceed 10 mL, place the concentrator tube into an N-Evap and, under a gentle stream of nitrogen, reduce the volume to 10 mL. Transfer 1 mL of the extract (to be used for the gasoline or gasoline/diesel determination) to an autosampler vial fitted with a screw top and a Teflon coated septum. Concentrate the remainder of the extract (to be used for heavy oils determination) to 0.9 mL, transfer it to an 2 mL autosampler vial equipped with a screw top and a Teflon coated septum. Store both vials in a refrigerator until analysis.

Each extraction set must include one method blank (organic-free water of similar volume to the samples) per 20 samples. The method blank is to receive the surrogate solution and to be extracted and analyzed in the same manner as the samples.

EPA method 3520, Continuous Liquid-Liquid Extraction, may be substituted as an alternate extraction procedure to that outlined above.

Soil Samples

Weigh approximately 10 grams of soil into a 40 mL VOA vial and record the weight to the nearest 0.001 grams. Add 5 grams of anhydrous sodium sulfate, surrogate working solution and 10 mL of methylene chloride to the VOA vial. Cap the vial and place it (no more than 5 at a time) in a sonic bath for 5 minutes. Shake the vials well and return them to the sonic bath for 5 more minutes. A minimum of one method blank per extraction set or 20 samples, whichever is more frequent, must be prepared along with the samples. One sample duplicate must also be extracted for samples set from one to ten samples and two duplicates for sets from eleven to twenty samples.

Determine the moisture content of the samples, for use in the final calculations, by the following procedure. Immediately after weighing the sample for extraction, weigh 5-10 grams of the sample into a tared crucible. Dry the sample/crucible overnight at 105 degrees C. Reweigh the sample/crucible after allowing it to cool to room temperature. Calculate the % solids as follows: [(grams of dry sample/grams of wet sample) x 100].

If the extract contains significant moisture, elute the solvent phase through an anhydrous sodium sulfate micro-column. Place a portion of the extract in a 2 mL autosampler vial (screw cap, Teflon coated septum), taking care to minimize the volume of headspace, and store the vial in a refrigerator until analyzed. Concentration of the extract, when necessary, will be conducted using an N-Evap

with a gentle stream of nitrogen. This concentrate should be stored in the same manner as noted above.

Note: Anhydrous sodium sulfate micro-columns are prepared by plugging a 5 3/4" length disposable Pasteur pipette (pre-rinsed with methylene chloride) with glass wool (precleaned with methylene chloride) and adding approximately 3 cm of anhydrous sodium sulfate (previously muffled at 430 degrees C overnight in a shallow pan and stored in a glass jar with a Teflon lid liner).

For samples containing petroleum products other than gasoline, diesel, or motor oil, the analyst must either prepare calibration standards of them by the methods listed above or analyze the sample by the fully quantitative method, e.g. NWTPH-Gx. Other calibration standards produced for use in this method must be at an equivalent concentration to the previously established standards, e.g. mineral spirits at the gasoline concentration, kerosene at the diesel concentration.

As more information becomes available on new extraction techniques, the Washington State Dept. of Ecology's Manchester Laboratory and Oregon's Department of Environmental Quality will publish descriptions of acceptable alternate extraction methods.

Suggested GC Parameters

Sample injection Volume = 2 uL
Injector Temperature = 290°C
Detector Temperature = 300°C
Hydrogen Flow = 25-35 mL/min
Air Flow = 300-400 mL/min
Make-up Gas Flow = 30 mL/min
GC Temperature Program = Initial temperature of 50°C and hold for 2 minutes; ramp the temperature 10°C/min to 320°C and hold for 5 minutes.

Product Identification

Petroleum products are to be identified by pattern matching with reference product chromatograms generated the same day as the sample analysis. The term "gasoline range" or "diesel range" hydrocarbons, or derivations of them, should only be used when the analyst is unable to identify the petroleum product present. When these terms are used, it is to indicate the presence of compounds eluting from toluene to dodecane, for the former term, and from dodecane through tetracosane, for the latter term. Motor oils, hydraulic fluids and similar petroleum products which present an unresolved chromatographic envelope of compounds, originating or extending beyond tetracosane, may be reported using the collective term, lube oil, unless specific identification is possible. Heavy fuel oils, e.g. fuel oil #6 or Bunker C, which contain a diesel range component as well as a lube oil (and higher) range may be reported using the collective term, heavy fuel oil, unless specific identification is possible. These products should not, however, be confused with mixtures of #2 diesel and motor oils.

Note: The actual identification of the grade or type of lube oil and heavy fuel oil may require equipment and techniques beyond the scope of this method.

Analysis Procedure

The analysis is accomplished by injecting 2 uL of the 10 mL extract, either manually or by autosampler, into the GC using the splitless injection mode. The results from this injection are, for quantitation purposes, compared directly against the single point calibration standard for the product(s) identified. The injection of 2 uL of the concentrated extract (1 mL equivalent) is used primarily for heavy oil determination, because of the reduced sensitivity of the FID to late eluting motor oil-like products. It may be used for the determination of #2 diesel oil and other diesel range petroleum products but it may not be used for the determination of gasoline or gasoline range petroleum products because of the potential for loss of the more volatile components during the concentration step.

Calculations

Gasoline. The area of the components, toluene to dodecane of the calibration standard, is integrated to the baseline as a group. The samples and method blanks are integrated in the same manner and the group areas are compared. If the sample area exceeds the calibration standard area, proceed with method NWTPH-Gx for accurate quantitation using a fresh aliquot of the sample. If the sample area does not exceed the calibration standard area, then report the gasoline concentration as less than 0.25 mg/L for water or 20 mg/kg for soil. This soil value for gasoline, and the subsequent petroleum products, assumes 100% solids and will be higher depending on the actual moisture content.

Other volatile petroleum products, identified as being present (e.g. mineral spirits), must be compared to the appropriate standard produced at the same concentration as gasoline. The requirement for further analyses is determined following the criteria for gasoline as noted above.

Note: For samples containing only #2 diesel oil, kerosene, etc., the portion of these products, that elute within the retention time range of gasoline, should not be identified and/or quantitated as gasoline or gasoline range petroleum.

Diesel. The area of the components, dodecane through tetracosane of the calibration standard, is integrated to the baseline as a group. This integration must include the unresolved envelope of compounds as well as the discrete component peaks. The sample is integrated in the same manner and the group areas are compared. If the sample area exceeds the calibration standard area, then proceed to method NWTPH-Dx. If the sample does not exceed the calibration standards area, then report the #2 diesel concentration as less than 0.63 mg/L for water or 50 mg/Kg for soil.

Other semi-volatile petroleum products, identified as being present (e.g. kerosene), must be compared to the appropriate standard produced at the same concentration as #2 diesel. The requirement for further analyses is determined following the criteria for #2 diesel as noted above.

Lube Oil. For those samples which consist primarily of only an unresolved chromatographic envelope of components eluting after tetracosane, compare their area to the area of the motor oil standard by integrating the unresolved envelope to baseline. If the sample exceeds the standard area, then proceed to method NWTPH-Dx. If the sample area is less than the standard, then report the lube oil concentration as less than 0.63 mg/L for water or 100 mg/Kg for soil. Samples identified as containing heavy fuel oil must be quantitated to the same value as lube oil by utilizing a heavy fuel oil standard and following the procedure outlined for lube oil.

Note: The analyst is expected to adjust the retention time windows used for quantitation of petroleum products, other than gasoline, #2 diesel, or motor oil/lube oils, to incorporate the majority of the chromatographable components associated with those identified products.

If, in the judgement of the analyst, the area of an identified petroleum product other than gasoline, diesel, and motor oil would exceed the reporting limit, the analyst is allowed to report a "greater than" value for that product without performing the quantitative analysis. The analyst must then proceed to the appropriate fully quantitative analytical procedure, e.g. NWTPH-Dx, for the identified petroleum product.

Quality Assurance

The addition of an appropriate extraction surrogate to samples and method blank(s) is required. The surrogate recovery for all samples and blanks should be between 50% and 150% and must be reported with the petroleum results unless the quantity of the petroleum product(s) preclude its determination. The laboratory should analyze one sample from each site in duplicate for sample sets of 10 or less and two samples in duplicate for sets of 11 to 20 samples (i.e. 10% QA). If either of the duplicate results are positive, the sample is to be considered positive. Since this method precludes the preparation of analytical duplicates, the laboratory should recommend that the project manager collect and submit field duplicates for analysis. The laboratory must analyze method blanks prepared identically to the samples. Organic free water must be used in the preparation of water method blank. No "sample" is necessary for use with soil/sediment method blanks.

Author - Bob Carrell, Manchester Environmental Laboratory, Dept. of Ecology, State of Washington. Reviewed and edited by Steve Robb, Toxics Cleanup Program, Department of Ecology, State of Washington. This method is based on Oregon’s Department of Environmental Quality TPH methods and Washington’s Department of Ecology WTPH methods.

NWTPH-Gx Chromatograms

Gasoline
Weathered Gasoline
Naptha
Mineral Spirits #1
Mineral Spirits #2
Mineral Spirits #3

NWTPH-Dx Chromatograms

#2 Diesel
#2 Diesel/Motor Oil
#2 Fuel Oil
Kerosene (Deodorized)
Jet A Fuel
Bunker C #1
Bunker C #2
Motor Oil 30 Wt.
Mineral Oil (USP)
Hydraulic Fluid
Transformer Oil
Gas Oil

See Appendix 6

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NWTPH-Gx

Volatile Petroleum Products Method for Soil and Water

Summary

The NWTPH-Gx method is intended to replace the Oregon's TPH-G and Washington's WTPH-G methods and to present a more comprehensive approach to volatile petroleum product analyses. NWTPH-Gx adapts Oregon's TPH, Washington's WTPH and EPA SW846 Methods 5030 and/or 8020 and covers the quantitative and qualitative analyses of volatile petroleum products, e.g. gasolines, naphtha, mineral spirits, stoddard solvent, and other volatile petroleum products in soil and water. Soil samples are extracted with methanol and analyzed by gas chromatograph with a flame ionization detector (GC/FID). The methanol extracts may be injected directly into the GC or they may be diluted with organic free reagent water and introduced by a purge/trap concentrator. Water samples are introduced directly to the purge/trap concentrator. This method specifies the criteria for the identification and quantitation of volatile petroleum products. When the type of petroleum product is unknown, regular unleaded gasoline will initially be used as the default petroleum standard. The use of GC/PID, GC/MS or GC/AED (Atomic Emission Detector) for the analysis of gasoline may be substituted for GC/FID as long as all other method parameters are met.

The reporting limits for soil are 5 mg/kg by the purge/trap procedure and 20 mg/kg for direct injection. All soil results are reported on a dry weight basis. Since this value assumes 100% solids, the analyst may wish to adjust the amount of soil extracted and/or purge a larger quantity of extract to achieve the reporting limits. For water, the reporting limits are 0.25 mg/L.

The method is applicable for the identification, by pattern matching ("fingerprinting") and quantitation of volatile petroleum products, i.e. those petroleum products for which the majority of the components elute within the gasoline range.

Note: Benzene, Toluene, Ethylbenzene and Xylenes (BTEX) may be determined simultaneously with gasoline if the requirements of EPA Method 8021 or EPA Method 8260 are met (i.e. the use of a PID (Photoionization Detector) for method 8020 or a MS (Mass Spectrometry) for method 8260 and the QA/QC associated with these methods).

This method must be performed by, or under the direct supervision of, analysts experienced in the use of GC and in the interpretation of gas chromatographs of both fresh and weathered volatile petroleum products.

Equipment and Reagents

Gas Chromatograph
Purge/Trap Liquid Concentrator - Tekmar or Equivalent - Autosampler (Optional)
Flame Ionization (FID) or Photo Ionization/Flame Ionization Detectors (PID/FID)
Suggested Capillary Column: Restex RTX-502.2, 60M x 0.53 mm x 3.0 um film thickness or equivalent
Chromatography Data System
Gas tight syringes, various volumes, Hamilton brand or equivalent
Volumetric flasks: 10 mL, ground glass joint with stopper
Methanol: Burdick and Jackson Purge/Trap grade or equivalent
Petroleum Product Standards: Available from commercial sources
Refer to methods 5030 and/or 8020 for the remaining equipment and reagent requirement

Sample Containers/Holding Times

All soil samples for NWTPH-Gx analyses must be collected in soil VOA bottles with Teflon coated septum lined tops. They should be filled to the top to minimize headspace above the soil and stored at 4 degrees C until analyzed. The maximum holding time (the time from the date of collection to the date of analysis) for gasoline and any other volatile petroleum product is 14 days.

All water samples for NWTPH-Gx analyses must be collected in glass VOA vials with Teflon coated septum lined screw tops. They must be filled so that there is no air space (headspace) above the water. Samples should be preserved with 1+1 HCl to a pH <2 and refrigerated at 4 degrees C until analyzed. The maximum holding time (the time from the date of collection to the date of analysis) is 7 days for unpreserved samples and 14 days for preserved samples. The results of any samples which exceed these limits must be qualified as an estimated value.

Standards

Stock Standards. A stock standard is prepared by placing approximately 9 mL of methanol in a 10 mL volumetric flask. Allow the flask to stand, unstoppered, until the methanol wetted surfaces have dried (about ten minutes), then tare the methanol/flask. Add about 5 drops of the petroleum product to the flask while assuring that the liquid falls directly into the methanol without contacting the neck of the flask. Weigh the flask again and dilute to volume with methanol, stopper and mix by inverting the flask several times. The use of commercially prepared standards is acceptable to the above procedure. Commercially prepared gasoline standards must be certified as non-oxygenated gasoline or the gasoline concentration has been adjusted to reflect the contribution of the oxygenate. Calculate the concentration as follows:

$$\textit{Gasoline Stock Standard, ug / mL} = \frac{\textit{(final wt, mg) - (tare wt, mg)}}{\textit{10 mL}} \; x \; \frac{\textit{1000 ug}}{\textit{mg}}$$

The standard for gasoline will be regular unleaded gasoline and this standard is to be used as the default petroleum product for reporting purposes.

Note: The use of oxygenated regular unleaded gasoline for this standard is allowed if the weight (mass) of the gasoline used is adjusted for the weight contribution of the oxygenate to the gasoline. This will necessitate the analysis of the gasoline for the specific oxygenate(s) present to determine their concentration. This analysis must be conducted by either of the methods published in the Federal Register - Appendix B and C - Testing procedures - Vol. 57, No. 24, Wednesday, February 5, 1992, Notices. Alternate methods for the analysis of gasoline oxygenates must be approved by the Oregon's Department of Environmental Quality and/or Washington's Department of Ecology prior to use.

Stock Surrogate Standard

Note: The suggested surrogates are 1,4-difluorobenzene and bromofluorobenzene. The use of additional surrogates is optional. Selected surrogate compounds should be non-polar, purgeable from water and must not coelute with any significant component of gasoline.

Make up a stock standard by accurately weighing the surrogate compound(s) into a 10 mL volumetric flask. Utilize the same procedure as the stock gasoline standard preparation if neat material is used or by adding the appropriate volumes of dilute surrogate if solutions are used. Bring it to volume with methanol. The use of commercially prepared surrogate solutions is an acceptable alternative to the above procedure.

Working Surrogate Spike. Add the appropriate volume of stock surrogate standard to methanol in a partially filled 10 mL volumetric flask and dilute to volume with methanol. The final concentration of the working surrogate solution is left to the discretion of the analyst, however, this solution should produce between 5 ng and 50 ng of surrogate introduced to the GC.

Secondary Dilution Standard. Using serial dilutions of the stock standard, prepare a 50 ug/mL standard by adding the appropriate volumes, as calculated below, to a 10 mL volumetric flask. The appropriate volume of the stock surrogate standard may also be added to this volumetric flask. Dilute to volume with methanol to yield a final working standard concentration of 50 ug/mL for the standard. Surrogate compound(s) may be added automatically during the sampling process by an autosampler. Gasoline is the default petroleum product for reporting purposes.

$$\textit{Stock Std (Gasoline), uL} = \frac{\textit{50 ug / mL x 10 mL}}{\textit{Stock Std Conc, ug / mL}} \; x \; \frac{\textit{1000 uL}}{\textit{mL}}$$

Store all standards in a refrigerator until needed. Allow them to come to room temperature prior to use.

Calibration Standard

The aqueous purge standards are each prepared by adding 5 uL, 10 uL, 20 uL and 50 uL and 100 uL of the secondary dilution standard per 5 mL of organic free water. The five point calibration standard quantities in the purged water are then 250 ng, 500 ng, 1000 ng, 2500 ng and 5000 ng for the volatile petroleum products. At the discretion of the analyst, the concentration of the surrogate can increase with increasing standard concentration or remain at a fixed value for all calibration standards and samples. Extending the calibration range, either up or down, is allowed as long as the standards remain within the linear range of the instrument and a minimum of a five point calibration is produced. In order to be acceptable, the calibration curve must have a linear correlation coefficient of at least 0.990 and none of the standards may vary from their true (known) value by more than plus/minus 15%.

The use of an autosampler may be substituted for this manual method of standards and sample introduction.

Direction Injection. Prepare calibration standards from the stock gasoline standard and surrogate standards at concentrations of 10 ug/mL, 25 ug/mL, 50 ug/mL, 100 ug/mL and 250 ug/mL for gasoline by adding the appropriate volumes to volumetric flasks and diluting to volume with methanol. Increasing the calibration range with higher standards is acceptable as long as the linear range of the instrument is not exceeded.

Purge/Trap and GC Parameters

Follow the procedure outlined in Method 8021 for the set up of the purge and trap operating parameters and for the GC. Adjust the hydrogen/air flow rates to optimize the FID sensitivity.

Soil Extraction Procedure

Weigh approximately 5 grams of soil into a 40 mL VOA vial and record the weight to 0.001 grams. Add 50 uL of the surrogate working standard and 10 mL of methanol. Quickly cap the vial and shake for 1 minute or use an ultrasonic bath for 2 minutes shaking well after 1 minute. Allow the soil methanol mixture to separate, centrifuging if necessary to clarify the methanol extract. For storage, transfer a portion of the extract into a 2 mL glass autosampler vial, with a Teflon-lined cap, minimizing the headspace and store in a freezer for no longer than one week prior to analysis. Along with the samples, prepare at least one method blank and one sample duplicate per ten samples.

Determine the moisture content of the sample, for use in the final calculations, by the following method. Immediately after weighing the sample for extraction, weigh 5-10 grams of the sample into a tared crucible. Dry the sample/crucible overnight at 105 degrees C. Reweigh the sample/crucible after allowing it to cool to room temperature. Calculate the % solids as follows: [(grams of dry sample/grams of wet sample) x 100].

Analysis Procedure

Prior to the analysis of any samples or method blanks, prepare and analyze a mid-range calibration check standard to insure that the instrument is functioning correctly and that the calibration is valid. This standard should be produced daily using the secondary gasoline standard. The value obtained for this analysis must not vary from the true (known) value by more than plus/minus 20%. If the value falls outside this range then a second mid-range calibration standard should be produced and the analysis repeated. If the reanalysis of the fresh standard fails to meet the acceptance criteria, then the instrument must be recalibrated prior to the analysis of any samples. Once the instrument is shown to be in calibration, the analyses of samples may proceed.

After the last sample has been analyzed, a mid-range calibration check sample must be run to demonstrate that the instrument is still operating within the required parameters. Should this standard fail to meet those parameters, then all samples analyzed after the last successful calibration check must either be reanalyzed or the results obtained must be qualified as an estimated value. An increase in the frequency of mid-range calibration check standard analyses beyond the minimum required is recommended.

Significant interferences may be encountered due to the presence of other petroleum products (or non-petroleum products) eluting within the retention time range of the volatile petroleum product being analyzed. If this occurs, the analyst is allowed to adjust the retention time range used for quantitation to exclude the interferences or to subtract the area of the interfering components from the total area prior to the quantity determination. With the former method, the calibration curve must be adjusted in the same manner to reflect the change in retention time range and integration area.

For volatile petroleum products other than gasoline that have a more narrow boiling point range, e.g. mineral spirits, the retention time range used for quantitation should be adjusted to encompass the expected range of the product. Petroleum products which cannot be identified should be quantitated with the gasoline calibration curve. The term "gasoline range" hydrocarbons, or derivations of it, should not be used when reporting the petroleum values unless the analyst is unable to identify the petroleum product present.

Purge/Trap - Soil. A 100 uL aliquot of the methanol extract is transferred via a 100 uL gas tight syringe to 5 mL of organic free water in a 5 mL gas tight syringe and immediately injected into the purging vessel of the purge and trap device. For samples expected to contain concentrations of gasoline range volatiles outside the calibration linear range, or if dilution is required, a smaller aliquot of the methanol extract, or sample, should be used. The analysis then proceeds as in Method 8020. Autosampler techniques may be substituted for this manual method of sample introduction.

Purge/Trap - Water. Sample water (5 mL) is transferred to a 10 mL gas tight syringe and the working surrogate standard spike is added, via a gas tight syringe, into the 5 mL water sample. Immediately inject this water into the purge vessel of the purge/trap device. If necessary, a smaller sample aliquot may be used in order to remain within the linear calibration range of the instrument.

Larger sample volumes may be analyzed, at the discretion of the analyst, if lower quantitation limits are required. Autosampler techniques may be substituted for this manual method of sample introduction.

Direct Injection - For Soil. Allow the extract to come to room temperature, then inject, either manually or by autosampler, 2 uL of the extract into the GC using the splitless injection mode.

Quantitation

The retention time range (window) for gasoline integration must, at a minimum, include toluene through naphthalene. For other volatile petroleum products, the retention time range for integration must be adjusted to incorporate the majority of the components of the petroleum product(s) identified as present in the samples. If specific product identification can not be made, the analyst must quantitate the samples with the calibration curve of the petroleum product that most closely resembles that of the sample.

For those surrogates which elute within the retention time range used for integration, the analyst must subtract the area of the surrogate(s) from the total area to yield the appropriate area of the petroleum product.

The analyst shall use regular unleaded gasoline as the default petroleum product for reporting purposes when no petroleum products were identified in any initial screening or when the type(s) of petroleum products are unknown prior to analysis.

Sample chromatograms of various volatile petroleum products are included at the end of this method to assist the analyst in determining the appropriate integration ranges.

Result Calculation

The area of the components is integrated, as a group, to the baseline and compared to concentrations of the standards which are integrated in the same manner.

For Soil

$$\textit{Soil Sample Conc, mg / kg} = \frac{(A \times R) \times D}{E \times W \times S}$$

where

A = group area of sample

R = Response factor from std curve (ng injected/area count)

D = Extract Volume, mL

W = Weight of sample, grams

E = Volume of extract purged or injected, uL

S = Decimal percent solids of sample

For Water

$$\textit{Water Sample Conc, ug / L} = \frac{(A \times R)}{V}$$

where

A = group area of sample

R = Response factor from std curve (ng purged/area count)

V = Volume of sample purged, mL

The recovery of the surrogate should be between 50% and 150% and must be reported with the results. Report any surrogate recoveries that can not be calculated due to a high level of gasoline contamination.

Author: Bob Carrell, Manchester Environmental Laboratory, Dept. of Ecology, State of Washington. Reviewed and edited by Steve Robb, Toxics Cleanup Program, Department of Ecology, State of Washington. This method is based on Oregon's Department of Environmental Quality TPH-G and Washington's Department of Ecology WTPH-G methods.

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NWTPH-Dx

Semi-Volatile Petroleum Products Method for Soil and Water

Summary

The NWTPH-Dx method is intended to replace the Oregon's Department of Environmental Quality TPH-D and Washington's Department of Ecology WTPH-D methods and to present a more comprehensive approach to semi-volatile petroleum product analyses. NWTPH-Dx adapts Oregon's TPH, Washington's WTPH and EPA SW-846 Methods 3510, 3540/3550 and 8000 and covers the quantitative and qualitative analysis of semi-volatile petroleum products, i.e. jet fuels through heavy fuel oils, in soil and water. The method involves extracting the samples with methylene chloride and injecting a portion of the extract into a gas chromatograph (GC) equipped with a flame ionization detector (FID). This method specifies criteria for the identification and quantitation of semi-volatile petroleum products. A clean-up procedure, which may be used to aid in the removal of non-petroleum based organic interferences, i.e. biogenic interferences, has been included. When the type of petroleum product is unknown, #2 diesel will initially be used as the default petroleum standard.

The reporting limits are 25 mg/kg (soil) and 0.25 mg/L (water) for the petroleum products in the elution range of jet fuels through #2 diesel. For petroleum products eluting after #2 diesel oil, e.g. motor oils, hydraulic fluids, and heavy fuel oils, the reporting limits are 100 mg/kg (soil) and 0.50 mg/L (water). All soil results are reported on a dry weight basis. Since this value assumes 100% solids and therefore will be higher depending on the actual moisture content, the analyst is permitted to concentrate the extract to obtain these reporting limits. When doubt exists as to which reporting limit is applicable for the petroleum product present, the analyst should use the lower value.

The method is applicable for the identification, by pattern matching ("fingerprinting"), and quantitation of semi-volatile petroleum products. These include kerosenes, jet fuels, diesel oils, fuel oils, lubricating oils, hydraulic fluids, mineral oils and insulating oils, e.g. transformer oils. In general, those petroleum products which do not contain a substantial volatile fraction, i.e. the majority of the components eluting outside of the gasoline range, should be analyzed by this method.

Note: The use of GC/MS (Mass Spectrometry) or GC/AED (Atomic Emission Detector) may be substituted for GC/FID as long as all other method parameters are met.

This method is to be used by, or under the direct supervision of, analysts experienced in the use of GC and in the interpretation of gas chromatograms of both fresh and weathered petroleum products.

Equipment and Reagents

Gas Chromatograph, w/wo Autosampler
Flame Ionization Detector
Capillary Split/Splitless Injector
Suggested Column:
J & W Scientific: DB-1 or DB-5, 30 M x 0.25 mm or 0.32 mm I.D. with 0.25 um film thickness capillary column or equivalent
Chromatographic Data System: Capable of group integrations
Analytical Balance, accurate to a least 0.0001 grams
Volumetric Flasks, 10 mL, ground glass stoppered
N-Evap Concentrator or equivalent
Centrifuge tubes, 10 or 15 mL, glass, calibrated in 0.1 mL increments
Centrifuge tubes, 10 or 15 mL, glass, disposable
Kaderna-Danish (K-D) Flasks, 250 mL
Concentrator Tubes, 10 mL
Snyder Columns, 3-ball, 300 mm length
Sodium Sulfate, anhydrous
Methylene Chloride, Burdick and Jackson brand, gas chromatography/pesticide residue grade or equivalent
Sulfuric acid, concentrated
Silica gel, 100/200 mesh, Baker Analyzed Reagent grade or equivalent - Before use, activate for at least 16 hours at 130 degrees C in a shallow tray
Petroleum Product Standards: Available from commercial sources

Note: All samples shall be collected in Eagle Picher, or equivalent, glass jars and held at 4 degrees C until extracted. The holding time, from the date of collection to extraction, is 14 days for soil and preserved water. For unpreserved water, the holding the holding time is 7 days. Preservation is accomplished by adjusting the pH of the water sample to approximately 2 with the addition of 1+1 HCl.

Suggested GC Parameters

Sample Extract Injection Volume = 2 uL
Injector Temperature = 290 degrees C
Detector Temperature = 300 degrees C
Hydrogen Flow = 25-35 cc/min
Air Flow = 300-400 cc/min
Helium Make-up Gas Flow = 30 cc/min
Helium Carrier Gas Head Pressure = 15 psi
GC Temperature Program:
Initial temperature = 50 degrees C, hold 2 minutes
Temperature Ramp Rate = 20 degrees C per minute
Final Temperature = 320 degrees C, hold for 10 minutes

Standards

Reference/Stock Standards. Prepare individual petroleum product reference/stock standards, e.g. kerosene, #2 diesel oil, transformer oil (mineral oil based) and Bunker-C fuel oil.

Add 5 to 10 drops of the pure petroleum product to a zero tared 10 mL flask. Record the weight and bring the flask to volume with methylene chloride, stopper and mix by inverting the flask several times. Calculate the concentration of these standards using the equation shown below. The use of commercially prepared standards is an acceptable alternative to the above procedure. Analysts may not use artificial standards, e.g. diesel range organics mixtures, etc., for quantitation purposes in place of authentic petroleum products.

These standards are to be used to produce calibration working standards which should be used to insure the proper identification of petroleum products by chromatographic pattern matching ("fingerprinting") as well as accurate quantitation.

$$Stock\ Conc,\ ug / mL = \frac{(final\ wt,\ mg) - (tare\ wt,\ mg)}{10\ mL} \times \frac{1000\ ug}{mg}$$

Calibration Working Standards. Using the stock standards, prepare calibration working standards for the identified petroleum product(s) to be quantitated. Add the appropriate volume(s), using the equation shown below and adjusting for the concentration change created by any serial dilutions, to a 10 mL volumetric flask(s). Dilute to volume with methylene chloride. Calibration standards must, at a minimum, (1) provide a five point calibration curve, (2) include a sufficiently low standard to provide the necessary reporting limits, and (3) define the linear working range of the instrument.

In order to be acceptable, the calibration curve must have a linear correlation coefficient of at least 0.990 and none of the standards may vary from their true (known) value by more than plus/minus 15%. #2 diesel oil is the default petroleum product for reporting purposes.

Stock Surrogate Standard. Prepare the stock surrogate standard by weighing 50 mg of the surrogate compound(s) into a 10 mL volumetric flask. Bring the flask to volume with methylene chloride for a final concentration of 5000 ug/mL for the surrogate compound. The use of commercially prepared surrogate solutions is an acceptable alternative to the above procedure.

Note: The suggested surrogates are 2-fluorobiphenyl, o, or p-terphenyl or pentacosane. The use of other surrogates is optional. Selected surrogate compounds must be non-polar, unaffected by the cleanup procedure, i.e. the concentrated sulfuric acid/silica gel treatment, and lacking in significant interferences in most standard petroleum products.

Working Surrogate Spike. Using serial dilutions of the stock standard, prepare a surrogate working standard. Add the appropriate volume of the stock surrogate standard, using the equation listed

below, and adjusting for any serial dilutions, to a 10 mL volumetric flask and dilute to volume with methylene chloride. Stopper and mix by inverting the flask several times. The surrogate working standard should be added to a level sufficient to produce a surrogate concentration between 5 and 50 ug/mL.

$$Volume\ Stock,\ uL\ =\ \frac{(Cal\ Std\ Conc,\ ug\ /\ mL)\ x\ 10\ mL}{Stock\ Conc,\ ug\ /\ mL}\ x\ \frac{1000\ uL}{mL}$$

Store all standards in a refrigerator until needed. Allow them to come to room temperature prior to use.

Sample Extraction

Soil Matrix

Weigh approximately 20 grams of soil, recording the weight to the nearest 0.01 grams, and approximately 20 grams of anhydrous sodium sulfate into a 150 mL beaker. Mix completely with a spatula. The mixture should have a grainy texture. If it forms a large clump, add more anhydrous sodium sulfate and grind to grainy texture. Add the appropriate volume of working surrogate standard, 50 mL of methylene chloride and sonicate for 3 minutes utilizing the horn sonicator and power settings in SW-846 Method 3550. Allow the mixture to settle then collect the extract in a 250 mL Kuderna-Danish (KD) flask to which is connected a 10 mL concentrator tube.

Repeat the extraction twice more and add these extracts to the KD. Attach a 3 ball Snyder column and concentrate the extract on a steam bath to a volume of 5-10 mL. Allow the K-D to cool to room temperature. Disassemble the K-D, rinsing the Snyder/K-D and K-D/concentrator tube joints with 1-2 mL of methylene chloride. Add these rinsings to the extract. If necessary, place the concentrator tube in an N-Evap and reduce the volume to 10 mL under a gentle stream of nitrogen. At this point, proceed to the sample cleanup procedure if applicable or transfer a portion of the extract to a 2 mL autosampler vial fitted with a screw top and a Teflon lined septum. Store the extract in a refrigerator until analyzed. If the extract is highly colored or forms a precipitate, a dilution may be necessary to stay within the calibration range. The use of the EPA method 3540 (soxhlet) in place of Method 3550 is optional.

Determine the moisture content of the samples by the following method. Immediately after weighing the sample for extraction, weigh approximately 10 grams of the sample into a tared crucible and record the weight. Dry the sample/crucible overnight at 105 degrees C. Reweigh the sample/crucible after allowing it to cool to room temperature and record the weight. Calculate the % solids as follows: [(grams of dry sample/grams of wet sample) x 100].

Along with each sample set, run at least one duplicate sample per set of 10 or fewer samples (10%) and, for each extraction day, at least one method blank (5%). Spiking of surrogates, extraction and

analyses of the QC samples will be conducted identically to the regular samples with the exception that no soil is added to the method blank.

Water Matrix

Allow the sample to come to room temperature and mark the meniscus for later use in volume determination. Pour the sample into a separartory funnel and adjust the pH to approximately 2 with 1+1 HCl and add the appropriate volume of surrogate working solution. Add 30 mL of methylene chloride to the sample jar and rotate the jar at a sufficient angle to wash the walls. Pour the solvent into the separatory funnel, stopper, and shake it vigorously for one minute, venting frequently. After the two phases have separated, drain the solvent into a 250 mL K-D flask to which is attached a 10 mL concentrator tube.

Note: Due to possible loss of analytes from the water to the sample jar walls, the entire sample must be consumed in the extraction and no aliquots may be used. Since the reporting limits are calculated on a 400 mL sample volume, sample jar size should be appropriate for this volume. For larger sample volume extractions, the analyst must increase the quantity of solvent used to maintain the original solvent/sample ratio.

Repeat the extraction twice more and add these extracts to the K-D. Attach a 3-ball Snyder column to the K-D and concentrate the extract on a steam bath to 5-10 mL. Allow the K-D to cool to room temperature and disassemble it, rinsing the Snyder/K-D and K-D/ concentrator joints with 1-2 mL of methylene chloride. Add these rinsings to the extract. Place the concentrator tube into an N-Evap and reduce the volume to 2 mL under a gentle stream of nitrogen. Transfer the extract to a 2 mL autosampler vial fitted with a screw top and a Teflon lined septum. Store the extract in a refrigerator until analyzed.

Along with each sample set, run at least one duplicate sample per set of 10 or fewer samples (10%) and, for each extraction day, at least one method blank (5%). Spiking of surrogates, extraction and analyses of the QC samples will be conducted identically to the regular samples with the exception that organic free water will be used for the method blank.

As more information becomes available on new extraction techniques, Washington State Dept. of Ecology's Manchester Laboratory and/or Oregon’s Department of Environmental Quality will publish descriptions of acceptable alternative extraction methods.

Sample Cleanup. In those cases where samples contain a significant amount of naturally occurring non-petroleum organics, e.g. leaf litter, bark, etc., which may contribute biogenic interferences, the following cleanup technique may be employed to assist in their reduction or elimination.

Transfer the 10 mL sample extract to a 10 to 15 mL centrifuge tube, add 1 mL of concentrated sulfuric acid to the extract and stopper the tube. Mix thoroughly for 1 minute by either shaking the tube or with the use of a vortex-genie adjusted to the highest setting.

Caution: Since sulfuric acid produces a highly exothermic reaction with water and other polar materials, extreme care should be exercised with its use.

Allow the two phases to separate. Centrifugation can be used to facilitate this process. Using a disposable glass pipet, transfer the methylene chloride (top) phase to another centrifuge tube and add approximately 0.4 grams (roughly equivalent to 1 mL of volume) of silica gel to the tube, stopper and mix as before. Allow the silica gel to settle or centrifuge. Repeat the sulfuric acid/silica gel treatment once more. Transfer a portion of the extract to a 2 mL autosampler vial equipped with a Teflon-lined cap and store the extract in a refrigerator until analyzed. A smaller aliquot of the extract may be used for this cleanup procedure as long as the ratio of extract to acid/silica gel is maintained.

It has been noted that some petroleum products, i.e. heavy fuel oils such as #6 fuel oil or Bunker-C, may experience a concentration loss of between 10 and 20 percent when subjected to this cleanup technique. This loss appears to be primarily associated with the removal of petroleum compounds which contain sulfur. To account for this loss when analyzing samples that have been subjected to the cleanup procedure in preparation for heavy fuel oil determination, the analyst must use utilize standards which have undergone the cleanup technique to calibrate the GC.

Note: The use of EPA method 3611 (Alumina column cleanup) may be substituted for the above cleanup technique if it is demonstrated to provide equivalent results.

Analysis Procedure. Prior to the analysis of any samples or method blanks, the analyst must prepare and analyze a mid-range calibration check standard to insure that the instrument is functioning correctly and that the calibration is still valid. The value obtained for this analysis must not vary from the true (known) value by more than plus/minus 15%. If the value falls outside this range then a second mid-range calibration check standard should be analyzed. If the analysis of the second check standard fails to meet the acceptance criteria, then the instrument must be recalibrated prior to the analysis of any samples. Once the instrument has been shown to be in calibration, the analyses of samples may proceed.

The analyst shall use #2 diesel as the default petroleum product for reporting purposes when no petroleum products were identified in any initial screening or when the type(s) of petroleum products are unknown prior to analysis.

After the last sample has been analyzed, a mid-range calibration check sample must be run to demonstrate that the instrument is still operating within the required parameters. Should this standard fail to meet those parameters, then all samples analyzed after the last successful calibration check standard must be reanalyzed. An increase in the frequency of mid-range calibration check standard analyses beyond the minimum required is recommended.

Qualitative Analysis - Identification

If NWTPH-HCID has not been previously performed on the samples and/or the type of petroleum present is unknown, the analyst should pre-screen the samples to determine the petroleum product.

The observed petroleum product shall be determined by pattern matching with the standard(s) analyzed the same day. Chromatograms used for this "fingerprinting" should be normalized to approximately 90% of full scale for the largest component of the particular petroleum product observed.

When reporting the results, the terms such as "diesel range" or "motor oil range", or derivations of them, should only be used when the analyst is unable to identify the petroleum product(s) present. Motor oils, hydraulic fluids and similar petroleum products which consist primarily of an unresolved chromatographic envelope of compounds originating at, or extending beyond tetracosane, may be reported using the collective term "lube oil" unless specific identification is possible. Heavy fuel oils, e.g. #6 fuel oil or Bunker-C, which contain a diesel range component as well as a lube oil range, may be reported using the collective term "heavy fuel oil" unless specific identification is possible. Heavy fuel oils should not, however, be confused with mixtures of #2 diesel and lube oils.

Note: The actual identification of the grade or type of lube oil and/or heavy fuel oil may require equipment and techniques beyond the scope of this method.

Quantitative Analysis - Integration

The retention time range (window) for integration must be adjusted to incorporate the majority of the components of petroleum product(s) identified as present in the samples. If specific product identification can not be made, the analyst must quantitate the samples with the calibration curve for the petroleum product that most closely resembles that of the sample. In all cases, the selected retention time range (windows) used for quantitation must, at a minimum, include any unresolved envelope of compounds as well as all discrete component peaks with an area greater than or equal to 10% of the largest peak. These components must be integrated to the baseline as a group.

For those surrogates which elute within the retention time range used for integration of a petroleum product, the analyst must subtract the area of the surrogate from the total area to yield the appropriate area of the petroleum product. In this case, the analyst may wish to generate separate calibrations for the petroleum standards and the surrogate(s) to facilitate integration and quantitation.

At the discretion of the analyst, the range of components included in the integration may be adjusted in order to minimize the potential contribution of any co-eluting fractions arising from the presence of multiple petroleum products. Any change in the integration range must be reflected in a concomitant change to the calibration standards integration.

Sample chromatograms of various petroleum products are included at the end of this method to assist the analyst in determining the appropriate integration ranges.

Result Calculation

For Soil

$$Soil\ Sample\ Conc,\ mg / kg = \frac{(A \times R) \times V \times Dilution\ Factor}{E \times W \times S}$$

where

A = Area Count from Sample
R = Response Factor (ng injected/area count)
V = Extract Volume (mL)
W = Weight of Sample (g)
E = Volume injected, (uL)
S = Decimal percent solids of sample

For Water

$$Water\ Sample\ Conc,\ mg / L = \frac{(A \times R) \times V}{E \times S}$$

where

A = Area Count from Sample
R = Response Factor (ng injected/area count)
V = Extract Volume (mL)
S = Volume of Sample (mL)
E = Volume Injected (uL)

The recovery of the surrogate should be between 50% and 150% and must be reported with the results. If the recovery of the surrogate is not able to be obtained due to a high levels of petroleum contamination, then this fact needs to be reported.

Author: Bob Carrell, Manchester Environmental Laboratory, Dept. of Ecology, State of Washington. Reviewed and edited by Steve Robb, Toxics Cleanup Program, Department of Ecology, State of Washington. This method is based on Orgeon's Department of Environmental Quality TPH-D and Washington's Department of Ecology WTPH-D methods.

METHOD FOR THE DETERMINATION

OF

VOLATILE PETROLEUM HYDROCARBONS (VPH) FRACTIONS

Washington State Department of Ecology

June 1997

METHOD FOR THE DETERMINATION OF VOLATILE PETROLEUM HYDROCARBONS (VPH)

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DISCLAIMER

Mention of trade names or commercial products does not constitute endorsement by the Washington State Department of Ecology Equipment and materials cited in this method may be replaced by similar products, as long as adequate data exists or has been produced documenting equivalent or superior performance.

METHOD FOR THE DETERMINATION OF VOLATILE PETROLEUM HYDROCARBONS

1.0 SCOPE AND APPLICATION

1.1 This method is designed to measure the collective concentrations of volatile aliphatic and aromatic petroleum hydrocarbons in water and soil. **The carbon ranges used through out this document are given in equivalent carbon (EC) numbers which are related to the boiling point of a chemical normalized to the boiling point of the n-alkanes, and its retention time in a boiling point gas chromatographic (GC) column.** Volatile aliphatic hydrocarbons are collectively quantitated within four ranges: C5 through C6, >C6 through C8, >C8 through C10 and > C10 through C12. Volatile aromatic hydrocarbons are collectively quantitated within the C8 through C10, >C10 through C12 and >C12 through C13 ranges. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 36°C and 220°C.

1.2 This method is also designed to measure the individual concentrations of benzene, toluene, ethylbenzene, xylenes, and methyl tert butylether (MTBE) in water and soil.

1.3 Petroleum products suitable for evaluation by this method include gasoline, mineral spirits, and certain petroleum naphthas. This method, in and of itself, is not suitable for the evaluation of samples contaminated with kerosene, jet fuel, heating oils, lubricating oils, or other petroleum products which contain a significant percentage of hydrocarbons larger than C10. When samples are known or suspected to contain petroleum products containing significant concentration of hydrocarbons >C10, the Extractable Petroleum Hydrocarbon (EPH) method should also be employed to fully evaluate the hydrocarbons present.

1.4 For reporting purposes, the practical quantitation limits (PQL), given the sample volume purged, mass and/or methanol extract volume purged are: 50.0 ug/L for water and 5.0 mg/kg for soil/sediments for the aliphatic and aromatic carbon ranges and 5.0 ug/L and 0.5 mg/kg respectively for the individually targeted compounds. The procedure for Method Detection Limits (MDL) determination in this method and the

Single Laboratory Precision, Accuracy and MDL data (generated by the State of Massachusetts) is added for informational purposes only.

1.5 This method is based on a purge-and-trap, gas chromatography (GC) procedure. This method should be used by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatographs. The analysts should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.

1.6 Like all GC procedures, this method is subject to a "false positive" bias in the reporting of targeted analytes, in that non-petroleum compounds eluting or co-eluting within a specified retention time window may be falsely identified and/or quantitated with the respective carbon ranges. Confirmatory analysis by a GC/MS, EPA Method 8260, or other suitable procedures are recommended in cases where significant concentrations of non-hydrocarbon compounds are known or suspected. If the results of these analyses lead to identification and quantitation of non-petroleum compounds, the analyst may subtract those values from the affected carbon ranges as long as the identities and quantities of subtracted compounds are provided in the analytical report.

2.0 SUMMARY OF METHOD

2.1 Samples are analyzed using purge-and-trap sample concentration. The gas chromatograph is temperature programmed to facilitate separation of organic compounds. Detection is achieved by a photo-ionization detector (PID) and flame ionization detector (FID) in series. Quantitation is based on comparing the PID and FID detector response of a sample to a standard comprised of aromatic and aliphatic hydrocarbons. The PID chromatogram is used to determine the individual concentrations of targeted analytes (BTEX/MTBE) and collective concentration of aromatic hydrocarbons within the C8 through C10, C10 through C12 and C12 through C13 ranges. The FID chromatogram is used to determine the collective concentration of aliphatic hydrocarbons within the C5 through C6, C6 through C8, C8 through C10 and C10 through C12 ranges. To avoid double counting of the aromatic contribution to the aliphatic ranges, the PID concentrations are subtracted from the FID concentrations to yield the aliphatic ranges values.

2.2 This method is suitable for the analysis of waters, soils, and sediments. Water samples may be analyzed directly for volatile petroleum hydrocarbons by purge-and-trap concentration and gas chromatography. Soil samples are either dispersed in methanol to dissolve the volatile organic constituents and a portion of the methanol is analyzed by purge-and-trap GC or combined with water for purging directly from a soil purge vessel (EPA method 5035).

2.3 This method is based on, and constitutes a significant modification of, the “Method for the Determination of Volatile Petroleum Hydrocarbons (VPH)”, Public Comment Draft 1.0, developed by the Massachusetts Department of Environmental Protection and on EPA method 5035. They in turn based their method on (1) USEPA Methods

5030, 8000, 8020, and 8015, SW-846, "Test Methods for Evaluating Solid Wastes", 3rd Edition, 1986; (2) Draft "Method for Determination of Gasoline Range Organics", EPA UST Workgroup, November, 1990; and (3) "Method for Determining Gasoline Range Organics", Wisconsin Department of Natural Resources, PUBL-SW-140, 1992.

3.0 DEFINITIONS

3.1 **Volatile Petroleum Hydrocarbons (VPH)** are defined as all hydrocarbon compounds eluting just prior to n-pentane through 1-methylnaphthalene. VPH is comprised of C5 through C6, >C6 through C8, >C8 through C10 and >C10 through C12 Aliphatic Hydrocarbons, as well as >C8 through C10, >C10 through C12 and >C12 through C13 Aromatic Hydrocarbons as well as benzene and toluene. VPH concentration data are reported as the aggregate concentrations of the aliphatic and aromatic hydrocarbon ranges and as selected targeted analytes.

3.2 **Equivalent Total Petroleum Hydrocarbons (E-TPH)** For samples contaminated ONLY with gasoline or other low molecular weight petroleum products, the E-TPH value is equivalent to the VPH value. For samples contaminated with BOTH light and heavy molecular weight petroleum products (e.g., gasoline and diesel fuel), the E-TPH value is a summation of the VPH value and the Extractable Petroleum Hydrocarbon (EPH) values. In order to avoid double counting of analytes due to the overlap in the carbon ranges existing between the two methods, the analyst will report the highest of the two values determined for the overlapping ranges. In those cases where both the VPH and EPH methods are employed on samples, the analyst may select to quantitate the >C10 through C12 Aliphatic and the >C10 through C12 Aromatic Hydrocarbon ranges only using the EPH method.

3.3 **C5 through C6 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds which elute on the FID chromatogram from (and including) n-pentane through n-hexane.

3.4 **C6 through C8 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbons which elute on the FID chromatogram after n-hexane through n-octane.

3.5 **C8 through C10 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds which elute on the FID chromatogram after n-octane through n-decane.

3.6 **C10 through C12 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbons which elute on the FID chromatogram after n-decane through n-dodecane.

3.7 **C8 through C10 Aromatic Hydrocarbons** are defined as all hydrocarbon compounds which elute on the PID chromatogram after toluene through 1,2,3-trimethylbenzene.

3.8 **C10 through C12 Aromatic Hydrocarbons** are defined as all hydrocarbons which elute on the PID chromatogram after 1,2,3- trimethylbenzene through naphthalene.

3.9 **C12 through C13 Aromatic Hydrocarbons** are defined as all hydrocarbons which elute on the PID chromatogram after naphthalene through 1-methylnaphthalene. This is a hybrid range which is designed to acquire the methylnaphthalenes associated with petroleum products like gasoline and is only used when VPH is run without an accompanying EPH method request.

3.10 **Targeted VPH Analytes** are defined as benzene, toluene, ethylbenzene, p,m,o-xylenes, and MTBE.

3.11 **Volatile Petroleum Hydrocarbon (VPH) Component Standard** is defined as a 15 component mixture of the aliphatic and aromatic compounds, plus surrogate, listed in Table 1. The compounds comprising the VPH Component Standard are used to (a) define the individual retention times and chromatographic response factors for each of the Targeted VPH Analytes, (b) define and establish the windows for the collective aliphatic and aromatic hydrocarbon ranges of interest, and (c) determine average chromatographic response factors that can in turn be used to calculate the collective concentration of hydrocarbons within these ranges.

3.12 **Analytical Batch** is defined as a group of samples with similar matrices which are processed as a unit. For Quality Control purposes, if the number of samples in such a group is greater than 20, then each group of 20 samples or less are defined as separate analytical batches.

3.13 **Laboratory Duplicates** are defined as split samples taken from the same sampling container and analyzed separately with identical procedures. The analysis of laboratory duplicates give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.14 **Field Duplicates** are defined as two separate samples collected at the same time and place under identical circumstances and managed the same throughout field and laboratory procedures. Analyses of field duplicates give a measure of the precision associated with sample collection, preservation, and storage, as well as laboratory procedures.

3.15 **E-TPH Duplicates** are defined as two separate samples collected at the same time and location, for analysis by both EPH and VPH methods. E-TPH duplicates are taken at locations where significant concentrations of petroleum hydrocarbons lighter and heavier than C9 are likely to be present (e.g., locations contaminated by releases of both gasoline and diesel fuel). The resultant EPH and VPH concentrations, adjusted to prevent double counting of overlapping hydrocarbon ranges between the methods, are then summed to determine the Equivalent TPH (E-TPH) concentration.

3.16 **Calibration Standards** are defined as a series of standard solutions prepared from dilutions of a stock standard solution, containing known concentrations of each analyte and surrogate compound of interest.

3.17 **Calibration Check Standard** is defined as a calibration standard used to periodically check the calibration state of an instrument. The calibration check standard is prepared from the same stock solution as calibration standards, and is generally one of the mid-level range calibration standard dilutions.

Table 1. Volatile Petroleum Hydrocarbon (VPH) Component Standard

Compound	Equivalent Carbon Number
n-Pentane	5.0
n-Hexane	6.0
Methyl tert butylether	N/A
Benzene	6.5
Toluene	7.6
n-Octane	8.0
Ethylbenzene	8.5
m- & p- Xylene	8.6
o-Xylene	8.8
1,2,3,-Trimethylbenzene	10.1
n-Decane	10.0
Naphthalene	11.7
n-Dodecane	12.0
1-Methylnaphthalene	13.0
2,5-Dibromotoluene (surrogate)	N/A

3.18 **Matrix Spiking Solution** is defined as a solution which is generally prepared independently from the calibration standards, containing known concentrations of method analytes.

3.19 **Laboratory Method Blank** is defined as, depending on the matrix of the samples, either reagent water or clean sand spiked with a surrogate standard. The laboratory method blank is treated identically as with samples, exposed to all glassware, solvents, reagents, and equipment. A laboratory method blank is analyzed with every batch of samples, to determine if method analytes or other interferences are present in the laboratory environment, reagents, or equipment.

3.20 **Laboratory Fortified Blank (LFB)** is defined as, depending on the matrix of the samples, either reagent water or a clean sand blank fortified with a matrix spiking solution.

The LFB is treated and analyzed identically as with samples and blanks, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements at the required practical quantitation limits..

3.21 **Laboratory Fortified Matrix (LFM) Sample** is defined as an environmental sample which has been spiked with a matrix spiking solution containing known concentrations of method analytes. The LFM sample is treated and analyzed exactly as a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined through the separate analyses of a laboratory or field duplicate, and the measured values in the LFM sample corrected for background concentrations.

3.22 All other terms are as defined in SW-846, "Test Method for Evaluating Solid Waste", USEPA, September, 1986, and as amended.

4.0 INTERFERENCES

4.1 Samples can become contaminated by diffusion of volatile organics through the sample container septum during shipment and storage. Trip blanks prepared from reagent water should be carried through sampling and subsequent storage and handling to serve as a check on such contamination.

4.2 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe and/or purging device must be rinsed between samples with reagent water or solvent. The trap and other parts of the system are also subject to contamination, therefore, frequent bake-out and purging of the entire system may be required. A screening step is recommended to protect analytical instrumentation. Whenever an unusually concentrated sample is encountered, it must be followed by the analysis of a solvent blank to check for cross-contamination.

4.3 Certain organic compounds not associated with releases of petroleum products, including chlorinated solvents, ketones, and ethers, will be quantitated as Volatile Petroleum Hydrocarbons. Some samples may require additional analytical procedures to be employed , e.g. GC/MS, to document the presence and quantity of such compounds.

4.4 The response selectivity of a photo-ionization detector (PID) is used in this method to differentiate aromatic hydrocarbons from aliphatic hydrocarbons. All compounds eluting on the PID chromatogram after toluene are identified by the method as aromatic hydrocarbons. This will lead to an overestimation of aromatic hydrocarbons within samples, as certain aliphatic compounds will elicit a response on the PID, particularly unsaturated compounds such as alkenes. The significance and implications of this overestimation will vary from sample to sample and, where less conservative data are desired, additional actions should be considered to

minimize the detection of non-aromatic compounds, such as the use of a lower energy PID lamp or GC/MS.

5.0 HEALTH AND SAFETY ISSUES

The toxicity and carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis.

6.0 APPARATUS AND MATERIALS

6.1 The following glassware is used in this method:

6.1.1 VOC Vials: Wide mouth 60-mL VOC vials or 40-mL VOC vials with teflon/ silicone septa for soils; 40-mL VOC vials with teflon/silicone septa for waters.

6.1.2 Volumetric flasks: 10-mL, 50-mL, 100-mL, and 1,000-mL with a ground-glass stopper.

6.1.3 Disposal pipets: Pasteur.

6.2 Analytical balance: An analytical balance capable of accurately weighing 0.0001 g must be used for weighing standards. A top-loading balance capable of weighing to the nearest 0.1 g must be used for weighing soil samples.

6.3 **Gas Chromatography**

6.3.1 Gas Chromatograph: An analytical system complete with temperature programmable gas chromatograph and purge-and-trap concentrator. The data station must be capable of storing and reintegrating chromatographic data and must be capable of determining peak areas using a forced baseline projection.

6.3.2 Columns

6.3.2.1 Recommended column: 105M x 0.53 mm I.D. Restek RTX 502.2, 3.0 micron film thickness, or equivalent.

6.3.2.2 Other columns, such as a 60 M x 0.53 mm J&W DB-5, may be used. Capillary columns are required to achieve necessary resolution. The column must be capable of resolving typical gasoline components. It must also resolve ethylbenzene from m/p-xylene. Some columns may require subambient cooling to achieve these criteria.

6.3.3 Detectors: The method utilizes a Photo-ionization Detector (PID) in series with a Flame Ionization Detector (FID); the PID first in the series. The method is based upon the use of a 10.0 eV PID lamp, although lower energy lamps are permissible in order to minimize PID response to aliphatic compounds.

6.3.4 Purge-and-trap device: The purge-and-trap device consists of a sample purger, a trap, and a desorber. Several complete devices are commercially available.

6.3.4.1 The purging chamber must be designed to accept 5 mL samples with a water column at least 3 cm deep. Purging devices larger than 5 mL have a reduced purging efficiency and should not be used. The gaseous headspace between the water column and the top of the vessel should be at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. Fritted glass or needle sparge cells may be used. If needle sparge cells are used, the purge gas must be introduced no more than 5 mm from the base of the water column. Alternate sample purge devices may be used, provided equivalent performance is demonstrated.

6.3.4.2 The trap should be at least 25 cm long and have an inside diameter of at least 0.105 inches. The trap should be packed with 400 mg of Carbopack B (Supelco Cat. No. 209273). Alternative trap packing materials include: Tenax GC (or equivalent); 7.6 cm Carbopack B and 1.3 cm Carbosieve S-III (Supelco Cat No. 2-0321); 7 cm Carbopack C and 1.2 cm Carbopack B (Supelco Cat No. 2-1064); or equal volumes of Tenax, silica gel, and charcoal as described in EPA SW-846 Method 5030. In general, Carbopack trap packing materials are recommended because they have less of a tendency to retain methanol, which could interfere with the elution of pentane and quench the FID flame. The trap length and packing materials may be varied as long as equivalent performance has been verified.

6.3.4.3 Prior to initial use, the Carbopack B trap should be conditioned overnight at 270°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to a hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min. at 260°C with backflushing. The trap may be vented to the analytical column during daily conditioning, however, the column must be run through the temperature program prior to analysis of samples. Devices other than the traps recommended in Section 6.3.4.2 should be conditioned and desorbed according to the manufacturer's guidelines.

6.3.4.4 The desorber should be capable of rapidly heating the trap to 240°C for desorption.

6.4 Ultrasonic bath.

6.5 Syringes: 5-mL Luerlock glass hypodermic and 5-mL gas-tight syringe with shutoff valve.

6.6 Syringe valve: Two-way, with luer ends.

6.7 Microsyringes: 1-µL, 5-µL, 10-µL, 25-µL, 100-µL, 250-µL, 500-µL, and 1,000-µL.

6.8 Spatula: Stainless steel.

7.0 REAGENTS AND STANDARDS

7.1 **Reagents**

7.1.1 Reagent Water: organic free water (ASTM Type I reagent grade water).

7.1.2 Solvent: methanol; purge and trap grade or equivalent. Store away from other solvents.

7.1.3 Ottawa and/or masonry sand: free of volatile petroleum hydrocarbons.

7.2 **Stock Standard Solution**

Prepare a stock standard solution in methanol at approximately 20 µg/µL, or purchase certified solutions. Preparation of stock standards and component standards should be done using volumetric glassware.

7.2.1 The stock standard solution consists of the 15 VPH component standards listed in Table 1 and a surrogate standard. Prepare the stock standard solution by accurately weighing approximately 0.2000 g of each standard component. Dissolve the component in methanol and dilute to volume in a 10-mL volumetric flask. At the discretion of the analyst, the surrogate standard may be made up as a separate solution from the VPH standards.

7.2.1.1 Place about 8 mL of methanol in a 10-mL tared ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min. or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

7.2.1.2 Using a 500-µL syringe, immediately add 100 to 200 µL of each VPH Component Standard to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

7.2.1.3 Dilute to volume, stopper, and then mix by inverting the flask three times. Calculate the concentration in micrograms per microliter (µg/µL) from the net gain in weight. When compound purity is assayed to be 98% or greater, the weight may be used without correction to calculate the

concentration of the stock standard, provided such purities are certified by the manufacturer or by an independent source.

7.2.1.4 Transfer the stock standard solution into a Teflon-lined screw-cap/crimp cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.

7.2.2 Stock standard solutions must be replaced after 6 months, or sooner if comparison with check standards indicates a problem. The use of commercially prepared certified standard solutions is an acceptable alternative to the use of neat compounds in the preparation of standards.

7.3 Primary Dilution Standard

Using the stock standard solution, prepare primary dilution standards in methanol, as needed. The primary dilution standard should be prepared at the concentrations shown in Table 2. These standards should be stored with minimal headspace, at -10°C to -20°, and should be checked frequently for signs of degradation or evaporation. The analyst is allowed to prepare separate surrogate and VPH analyte standards.

The primary dilution standards should be replaced at least monthly.

7.4 VPH Calibration Standards

Prepare VPH Calibration standards in reagent water from the primary dilution standard at a minimum of five concentration levels. One of the concentration levels must be near, but above, the method detection limit and must be at a sufficiently low level to allow the PQL reporting of at least 5.0 ug/L for water and 0.5 mg/kg for soil/sediments for the targeted analytes (BTEX and MTBE) and 50.0 ug/L and 5.0 mg/kg respectively for the aliphatic and aromatic carbon ranges. The other standard concentrations must correspond to the expected range of concentrations found in real samples and/or should define the working range of the detector.

7.4.1 Rapidly inject the methanolic standard into the water in the expanded area of a filled 100-mL volumetric flask. Remove the needle quickly after injection.

7.4.2 Mix aqueous standards by inverting the flask three times.

7.4.3 Discard the solution contained in the neck of the flask, and fill the sample syringe from the standard solution contained in the expanded area of the flask.

7.4.4 Do not use pipets to dilute or transfer samples or aqueous standards.

7.4.5 Do not inject more than 20 µL of methanolic standards into 100 mL of reagent water. Aqueous standards are not stable and should be discarded after one hour.

7.5 Surrogate Control Standard (SCS)

The analyst must monitor both the performance of the analytical system and the effectiveness of the method in dealing with sample matrices by spiking each sample, blank, and matrix spike with a surrogate standard. The surrogate standard is also added to the VPH calibration standard solutions. The recommended surrogate standard is 2,5-dibromotoluene, which elutes after all aliphatic and aromatic compounds of interest. The use of additional surrogates or surrogates other than those listed above may be used, at the discretion of the analyst, as long as their performance in the method is demonstrated as acceptable and does not compromise the quantitation of the various target analytes or carbon ranges.

7.5.1 Surrogate Spiking Solution: From a stock standard solution prepared as in Section 7.2.1, prepare a surrogate spiking solution at 50 µg/mL in methanol. Add 4.0 µL of this surrogate spiking solution directly into the 5-mL syringe with every aqueous sample, blank, and matrix spike. 1.0 mL of the surrogate spiking solution is added to soil samples during the extraction step (See 9.1.2.2).

7.6 **Matrix Spiking Solution**

The recommended matrix spiking solution, consisting of the Targeted VPH Analytes, is prepared in methanol at concentrations of 50 µg/mL.

7.7 **Petroleum Reference Standard**

The use of a Petroleum Reference Standard is recommended for quality control purposes. The Petroleum Reference Standard consists of an API or commercial gasoline standard. Prepare a Petroleum Reference Standard Spiking Solution by accurately weighing approximately 0.0100 g of neat product. Dissolve the neat product in methanol and dilute to volume in a 10-mL volumetric flask.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 **Aqueous Samples**

8.1.1 Aqueous samples should be collected in duplicate (or the number of vials directed by the laboratory) without agitation and without headspace in contaminant-free amber glass VOC vials with Teflon-lined septa screw caps. Samples must be acidified to a pH of 2.0 or less at the time of collection and this can generally be accomplished by adding 3 or 4 drops (0.1 to 0.2 mL) of 1:1 HCl (1 part reagent water and 1 part concentrated HCl) to a 40-mL VOC vial. Samples must be cooled to 4°C immediately after collection.

8.1.2 A chain of custody form should accompany all sampling vials and should document the date and time of sample collection and acid preservation. The pH of all water samples must be determined by the laboratory unless sample vials containing acid for field preservation were supplied by the laboratory (this must be noted on the chain of custody). The pH measurement may be performed on left over sample. Any sample found to contain a pH above 2.0 should be so noted on the laboratory/data report sheet.

8.1.3 Any sample received by the laboratory that is not packed in ice or cooled to 4°C must be so noted on the laboratory/data report sheet.

8.1.4 Acid preserved aqueous samples must be analyzed within 14 days of collection. Aqueous samples which, for whatever reason, have not received acid preservation must be analyzed within 7 days of collection or the data must be reported as an “estimate quantity”.

8.2 **Soil Samples**

8.2.1 Soil samples must be collected in a manner that minimizes sample handling and agitation. All sediment must be removed from the glass threads of the vial to ensure an adequate seal. Samples must be cooled to 4°C immediately after collection.

8.2.3 Samples for VPH analysis should be collected in duplicate 2 or 4 ounce VOC jars with Teflon coated septum lined lids.

8.2.4 Sampling must be accomplished in a manner that ensures a minimum of headspace in the sample vial.

8.2.5 A chain of custody form should accompany all sampling vials and should document the date and time of sample collection.

8.2.6 Soil samples must be analyzed within 14 days of collection.

8.3 A summary of sample collection, preservation and holding times is provided in Table 2 .

Table 2 . Holding Times and Preservatives for VPH Samples

Matrix	Container	Preservation	Holding Time
Aqueous Samples	40-mL VOC vials w/ Teflon-lined septa screw caps	Add 3 to 4 drops of 1:1 HCl; cool to 4°C	14 days 7 days, if not preserved
Soil/Sediments Samples	VOC vials w/ Teflon-lined septa screw caps. 40-mL vials	cool to 4°C	14 days

9.0 PROCEDURE

9.1 **Sample Preparation and Purging**

9.1.1 It is recommended that samples known or suspected to have extremely high levels of volatile petroleum hydrocarbons be screened prior to analysis in order to establish the appropriate volume/mass to be used for analysis. This screening step may be analysis of a soil sample's methanol extract (diluted), the headspace method (SW-846 method 3810), the hexadecane extraction and screening method (SW-846 Method 3820) or other applicable method as determined by the analyst.

9.1.2 Water Samples

Introduce volatile compounds into the gas chromatograph using a purge-and-trap concentrator. The use of autosampling devices for sample introduction is recommended or the analyst may use the manual method outlined below.

9.1.2.1 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and

compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one 40-mL vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 20-mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

9.1.2.2 If necessary, samples should be diluted prior to injection into the purge chamber. In such cases, all steps must be performed without delay until the diluted sample is in a gas-tight syringe.

9.1.2.2.1 Dilutions may be made in volumetric flasks (10 mL to 100 mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for highly concentrated samples.

9.1.2.2.2 Calculate the approximate volume of reagent water to be added to the volumetric flask selected and add slightly less than this volume of reagent water to the flask.

9.1.2.2.3 Inject the proper aliquot of sample from the syringe prepared in Paragraph 9.1.2.1 into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with reagent water. Cap the flask, invert, and shake three times. Repeat the above procedure for additional dilutions. Alternatively the dilutions can be made directly in the glass syringe to avoid further loss of volatiles.

9.1.2.2.4 Fill a 5-mL syringe with diluted sample as in Paragraph 9.1.2.1.

9.1.2.3 Add 4.0 µL of the surrogate spiking solution through the valve bore of the syringe. Close the valves.

9.1.2.4 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

9.1.2.5 Close both valves and purge the sample for 11 min. Recommended purge and trap operating parameters are provided in Table 3.

Table 3. Suggested Purge and Trap Operating Parameters

Purge gas	Helium
Purge gas flow rate (mL/min)	40
Purge time (min)	11.0
Purge temperature	Ambient
Desorb temperature °C	250
Backflush inert gas flow (mL/min)	15-20

9.1.2.6 At the conclusion of the purge time, attach the trap to the chromatograph (if necessary), adjust the device to the desorb mode, and begin the gas chromatographic temperature program (in Section 9.2.1) and GC data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 240°C and backflushing the trap with inert gas between 15 and 20 mL/min for 4 minutes.

9.1.2.7 While the trap is desorbing into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5 mL flushes of reagent water (or methanol followed by reagent water) to avoid carryover of pollutant compounds into subsequent analyses.

9.1.2.8 After desorbing the sample, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 260°C. After approximately 7 to 15 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. After a highly concentrated sample, a longer baking time may be necessary. When cool, the trap is ready for the next sample.

9.1.2.9 If the concentration of an analyte in a sample exceeds the calibration range, a dilution of the sample is required. If a sample analysis results in a saturated detector response for a compound, the analysis must be followed by one or more blank reagent water analyses. If the final blank analysis is not free of significant interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of significant interferences.

9.1.2.10 All dilutions should keep the detector response of the major constituents (previously saturated peaks) in the upper half of the linear range of the calibration curve.

9.1.3 Soil/Sediments

Soil and sediment samples are extracted with methanol. An aliquot of the extract is added to reagent water and introduced into the gas chromatograph using a purge and trap concentrator. Should lower values for the targeted analytes be desired, the analyst may employ direct purging of the soil sample using the method outlined in EPA methods 5030 and 5035. The use of autosampling devices for sample introduction is recommended or the analyst may use the manual method outlined below.

9.1.3.1 Weigh the sample vial to 0.1 g in a top loading balance and add 4 to 5 grams of the sample to the vial, reseal and determine the weight of the soil/sediment sample.

9.1.3.2 Quickly add 9.0 mL of methanol and 1.0 mL of the surrogate spiking solution. Cap and shake the sample vial for 2 minutes.

9.1.3.3 Allow soil/sediment to settle, or centrifuge the vial, until a layer of methanol is apparent.

9.1.3.4 Using a microliter syringe, withdraw an appropriate aliquot of the methanol extract for sparging. Sample screening data can be used to determine the volume of methanol extract to add to the 5 mL of reagent water for analysis. All dilutions must keep the response of the major constituents in the upper half of the linear range of the calibration curve.

9.1.3.5 Remove the plunger from one 5.0-mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to allow for addition of the extract (e.g., for 100 µL of extract adjust to 4.9 mL). Pull the plunger to 5.0 mL for addition of the sample extract. Add the volume of methanol extract determined from screening (100 µL maximum).

9.1.3.6 Attach the syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber. Complete operations as specified in Paragraphs 9.1.2.5 through 9.1.2.8.

9.1.4 Proceed with the analysis as described in Sections 9.2 through 9.5. Analyze all laboratory method blanks and QC samples under the same conditions as that used for samples.

9.1.5 If the responses exceed the calibration or linear range of the system, use a smaller aliquot of methanol or aqueous sample.

9.1.6 Determination of Percent Moisture

9.1.6.1 Soil and sediment results must be reported on a dry-weight basis.

9.1.6.2 Transfer 5 to 10 g of sample into a tared crucible. The amount of material used to determine the percent moisture will depend on the amount of moisture present, thus relatively dry samples require more sample addition in order to achieve a significant weight change than wet samples. Dry the sample overnight in an oven at 105°C. Remove the sample from the oven and allow it to cool in a desiccator before reweighing. Reweigh and calculate the percent moisture of the sample using the equations provided in Section 9.6.2.2.

9.2 **GC Conditions**

9.2.1 Oven Program: Oven temperature 45°C, hold for 1 min, then to 100°C at 3°C/min, to 160°C at 8°C/min, to 230°C at 20°C/min; hold for 7.5 min. Conditions may be altered to improve resolution of volatile petroleum hydrocarbons.

9.2.2 Gas Flows: The recommended carrier gas is helium.

9.2.2.1 Carrier gas flow: 12.5 mL/min.

9.2.2.2 Air: 350 mL/min

9.2.2.3 Hydrogen: 30 mL/min

9.2.2.4 Make up gas flow: 17.5 mL/min

9.2.3 Miscellaneous:

9.2.3.1 FID temperature: 230°C

9.2.3.2 PID temperature: 230°C

9.2.3.3 Injection port temperature: 250°C

9.2.3.4 Column head pressure: 15 psi

9.3 **Retention Time Windows**

9.3.1 Before establishing retention time windows, make sure the GC system is within optimum operating conditions. Make three injections of the VPH Component Standard throughout the course of a 72-hr period. Serial injections over less than a 72-hr period may result in retention time windows that are too tight.

9.3.2 Calculate the standard deviation of the three absolute retention times for each individual compound in the VPH Component Standard. The retention time window is defined as plus or minus three times the standard deviation of the absolute retention times for each standard. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

9.3.3 In those cases where the standard deviation for a particular standard is zero, the laboratory should substitute the standard deviation of a closely eluting structurally similar compound to develop a valid retention time window.

9.3.4 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. This data must be retained by the laboratory.

9.3.5 VPH retention time (Rt) windows are defined as beginning 0.1 minutes after the Rt of the beginning marker compound and ending 0.1 minutes after the Rt of the ending marker compound. The exception to this is the C5 through C6 aliphatic hydrocarbon range, where its Rt window is defined a beginning 0.1 minutes prior to the beginning marker compound and ending 0.1 minutes after the ending marker compound. VPH marker compounds and windows are summarized in Table 4 .

Table 4 . VPH Marker Compounds

Hydrocarbon Range	Beginning Marker Compound	Ending Marker Compound
C5-C6 Aliphatic Hydrocarbons (FID)	just before n-Pentane	just after n-Hexane
C6-C8 Aliphatic Hydrocarbons (FID)	just after n-Hexane	just after n-Octane
C8-C10 Aliphatic Hydrocarbons (FID)	just after n-Octane	just after n-Decane
C10-C12 Aliphatic Hydrocarbons (FID)	just after n-Decane	just after n-Dodecane
C8-C10 Aromatic Hydrocarbons (PID)	just after Toluene	just after 1,2,3-Trimethylbenzene
C10-C12 Aromatic Hydrocarbons (PID)	just after 1,2,3-Trimethylbenzene	just after Naphthalene
C12-C13 Aromatic Hydrocarbons (PID)	just after Naphthalene	just after 1-Methylnaphthalene

9.4 **Calibration**

9.4.1 External Standard Calibration Procedure

9.4.1.1 Prepare VPH Calibration Standards at a minimum of five concentration levels in accordance with the procedures and specifications contained in Section 7.0.

9.4.1.2 Analyze each VPH Calibration Standard following the procedures outlined in Section 9.5. Tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each targeted analyte. Alternatively, the ratio of the response to the amount injected, defined as the calibration factor (CF), may be calculated for method analytes using Equation 1. If the percent relative standard deviation (%RSD) of the calibration factor is equal to or less than 20 % over the working range for all analytes of interest, as determined using Equation 2, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve.

Equation 1: Calibration Factor

$$Calibration\ Factor\ (CF) = \frac{area\ of\ peak}{mass\ purged\ (ng)}$$

Equation 2: Relative Standard Deviation

$$\%RSD = \frac{Stand\ Dev\ of\ 5\ CFs}{Mean\ of\ 5\ CFs} \times 100$$

9.4.1.3 A collective calibration curve or factor must also be established for each hydrocarbon range of interest. Calculate the collective Calibration Factors (CF) for C5-C6, >C6-C8, >C8-C10 and >C10-C12 Aliphatic Hydrocarbons ranges using the FID chromatogram. Calculate the collective CF for the >C8-C10, >C10-C12 and C12-C13 Aromatic Hydrocarbons ranges using the PID chromatogram. Tabulate the summation of the peak areas of all components, the compounds which define the various ranges, in those fractions (e.g. C6-C8 Aliphatic Hydrocarbons, n-pentane and n-hexane or >C6 - C8, n-octane) against the total mass injected using Equation 3.

Note: Do not include the area of any surrogate standard or internal standard in calculating a Range CF.

Equation 3: Range Calibration Factor

$$Range\ CF = \frac{Total\ area\ of\ peaks}{Total\ mass\ purged\ (ng)}$$

9.4.1.4 At a minimum, the working calibration curve or calibration factor must be verified on each working day, and after every 20 samples, whichever is more frequent, by the injection of a mid-level calibration standard to verify instrument performance and linearity. If the percent difference (%D) for any targeted analyte response varies from the predicted response by more than ± 15 %, as determined using Equation 4, a new calibration curve must be prepared for that analyte. Similarly, if the percent difference of the carbon range compound response varies from the predicted response by more than ± 20 %, a new calibration curve must be prepared.

Equation 4: Percent Difference (%D)

$$\%D = \frac{\overline{CF} - CFv}{\overline{CF}} x\ 100$$

9.4.1.5 Targeted VPH Analytes and Aromatic Hydrocarbons ranges are quantitated on the PID chromatogram.

9.4.1.6 The Aliphatic Hydrocarbons ranges are quantitated on the FID chromatogram after subtraction of the collective concentrations of MTBE, and the BTEX compounds identified on the PID chromatogram from the collective concentration values of the C5 through C6 and C6 through C8 Aliphatic Hydrocarbon concentration values determined using the FID chromatogram. Similarly, the PID concentrations determined for the remaining aromatic ranges are subtracted from the FID concentrations for those ranges to yield the actual FID Aliphatic Hydrocarbon ranges values.

9.4.1.7 The concentration of specific analytes or hydrocarbon ranges in aqueous and non-aqueous samples may also be calculated from a calibration curve by use of linear regression analysis.

9.5 GC Analysis

9.5.1 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by samples interspersed with blanks and QC samples. The analytical sequence ends must end with an acceptable calibration verification. If the final calibration verification is not acceptable, then all samples analyzed after the last acceptable calibration verification must either be reanalyzed or if this is not possible, then the data associated with those samples must be qualified as an "estimate quantity".

9.5.2 Establish daily retention time windows for each analyte. Use the absolute retention time for each analyte as the midpoint of the window for that day. The daily retention time window equals the midpoint ± three times the standard deviation determined in Section 9.3.

9.5.2.1 Tentative identification of an analyte occurs when a peak from a sample falls within the daily retention time window. In cases where interferences are suspected, confirmation on a second dissimilar GC column or by GC/MS analysis may be necessary.

9.5.2.3 Validation of GC system qualitative performance must be accomplished by the analysis of standards, generally mid-level, within the analysis sequence. If any of the standards fall outside their daily retention time window, the system is out of control. In such cases, the cause of the problem must be determined and corrected.

9.5.3 If the response for Targeted VPH Analytes exceeds the linear range of the system, dilute the sample and reanalyze. It is recommended that samples be diluted so that all peaks are on scale. Overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure that all peaks are on scale over a 100-fold range, are acceptable if linearity is demonstrated prior to the analysis of samples. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

9.5.4 If detection of targeted analyte peaks are prevented by the presence of interferences, additional analytical techniques, e.g. GC/MS, are recommended.

9.5.5 Peak area and carbon range area quantification/integration must be from baseline (i.e. forced baseline projection which must include the unresolved complex mixture "hump" areas). The exception to this is the C5 through C6 Aliphatic Hydrocarbon range which, due to the use of capillary columns shorter than 100 meters and/or the purging of methanol volumes greater than 20 uL, may experience a lack of complete resolution between C5 (n-pentane) and methanol. In this event, the analyst is allowed to use tangential skim integration, or other suitable integration techniques, to integrate n-pentane, and subsequent hydrocarbons within the C5-C6 aliphatic range if it/they appear(s) on the trailing edge of the methanol solvent peak.

9.6 External Standard Calculations

The concentration of targeted analytes and hydrocarbon ranges in a sample may be determined by calculating the amount of analyte or hydrocarbon range purged, from the peak response, using the calibration curve or the calibration factor determined in Section 9.4.

9.6.1 Aqueous samples:

The general equation to determine the concentration of a specific analyte or hydrocarbon range in aqueous samples in provided in Equation 5.

Equation 5

$$Concentration\ (\mu g / L) = \frac{(A_x)(A)(D)}{(A_s)(V_s)}$$

where:

A_x = Response for the analyte or hydrocarbon range in the sample, units may be in area counts or peak height.

A = Amount of external standard purged, ng.

D = Dilution factor; if no dilution was made, D = 1, dimensionless.

A_s = Response for the external standard, units same as for A_x.

V_s = Volume of sample purged, mL.

If a Calibration Factor is used, the concentration of a specific analyte or hydrocarbon range in an aqueous sample may be calculated using equations 6 and 7, respectively.

Equation 6

$$Conc\ Analyte\ (\mu g / L) = \frac{(A_x)(D)}{(V_s)(CF)}$$

Equation 7

$$Conc\ HC\ Range\ (\mu g / L) = \frac{(A_x)(D)}{(V_s)(Range\ CF)}$$

where:

A_x = Response for the analyte or hydrocarbon range in the sample, units may be in area counts or peak height.

D = Dilution factor; if no dilution was made, D = 1, dimensionless.

V_s = Volume of sample purged, mL.

CF = Calibration Factor, area counts/ng.

Range CF = Calibration Factor for hydrocarbon range, (collective area count/collective mass), area counts/ng.

9.6.2 **Non-Aqueous Samples (Methanol Extraction):**

9.6.2.1 The general equation to determine the concentration of a specific analyte or hydrocarbon range in a soil or sediment sample is provided in Equation 8.

Equation 8

$$Concentration\ (\mu g / kg) = \frac{(A_x)(A)(V_t)(D)}{(A_s)(V_i)(W_d)}$$

where:

A_x = Response for the analyte or hydrocarbon range in the sample, units may be in area counts or peak height.

A = Amount of external standard purged, ng.

V_t = Volume of total extract, µL (Note: this value must include the 1.0 mL surrogate spiking solution added to soil samples)

D = Dilution factor; if no dilution was made, D = 1, dimensionless.

A_s = Response for the external standard, units same as for A_x.

V_i = Volume of methanol extract added to reagent water for purge and trap analysis, µL.

W_d = Dry weight of sample purged, g (see equations 11 through 13)

If a Calibration Factor is used, the concentration of a specific analyte or hydrocarbon range in a soil or sediment sample may be calculated using Equations 9 and 10, respectively.

Equation 9

$$Conc\ Analyte\ (\mu g / kg) = \frac{(A_x)(V_t)(D)}{(V_i)(W_d)(CF)}$$

Equation 10

$$Conc\ HC\ Range\ (\mu g / kg) = \frac{(A_x)(V_t)(D)}{(V_i)(W_d)(Range\ CF)}$$

where:

V_t = Volume of total extract, µL.

Vi = Volume of extract added for purging, µL

W_d = Dry Weight of sample purged, g (see Equations 11 through 13)

A_x, CF, Range CF and D have the same definition as for aqueous samples.

9.6.2.2 Calculation of Dry Weight of Sample

In order to calculate the dry weight of sample purged (W_d), it is necessary to determine the moisture content of the soil/sediment sample, using the procedure outlined in Section 9.1.6. Using the data obtained from Section 9.1.6, W_d is calculated using Equations 11 through 13.

Equation 11

$$\%\ Moisture = \frac{g\ sample - g\ dry\ sample}{g\ sample}\ X\ 100$$

Equation 12

$$\%\ Dry\ Solids = (1) - (\%\ Moisture)$$

Equation 13

$$W_d\ (g) = (\%\ Dry\ Solids)(g\ of\ extracted\ sample)$$

9.6.3 The concentration of specific analytes or hydrocarbon ranges in aqueous and non-aqueous samples may also be calculated from the calibration curve by linear regression, provided that the correlation coefficient (r) is at least 0.99 and the % D for any targeted analyte must not vary from the predicted response by more than +/- 15%, nor any hydrocarbon range standard from its predicted response by more than +/- 20%.

9.6.4 Peak areas measured from blanks may not be subtracted from sample peak areas.

9.6.5 All integration of collective hydrocarbon ranges must be to baseline.

9.6.6 Required Adjustment of Range Concentration Data: In order to minimize the "double counting" of the same hydrocarbon compounds on both the FID and PID chromatograms, the collective concentrations of MTBE, benzene, toluene, ethylbenzene, and m, p, o-xylene identified on the PID chromatogram must be subtracted from the collective Aliphatic Hydrocarbon concentration values, for the ranges in which they elute, determined using the FID chromatogram. Similarly, the collective concentrations of the remaining aromatic ranges values determined on the PID chromatogram must be subtracted from the corresponding aliphatic ranges values determined on the FID chromatogram.

10.0 QUALITY CONTROL

10.1 **General Requirements and Recommendations**

10.1.1 Each laboratory that uses this method should operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document the quality of data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance standards for the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

10.1.2 A acidified reagent water blank should continually accompany each soil sample or water sample batch, respectively, over the course of sampling, storage, and analysis.

10.1.3 A Laboratory Method Blank should be run after samples suspected of being highly contaminated to determine if sample carryover has occurred.

10.1.4 At a minimum, for each analytical batch (up to 20 samples), a Laboratory Method Blank, Laboratory Fortified Blank, Laboratory Fortified Matrix Spike, and sample

duplicate must be analyzed. For analytical batches with more than 10 samples, the analysis of an additional mid-range calibration check standard is recommended. The blank and spiked samples must be carried through all stages of the sample preparation and measurement process.

10.1.5 The recommended sequence of analysis is as follows:

(1) Calibration Standards (initial) or mid-range Calibration Check Standard (daily check on initial calibration)
(2) Laboratory Method Blank
(3) Samples
(4) QC Samples
(5) Mid-range Calibration Check Standard (also recommended after each 10 samples)

10.1.6 It is recommended that a system of control charts be developed to plot surrogate standard recoveries as a function of time. When surrogate recovery from a sample, blank, or QC sample is less than 60% or more than 140%, check calculations to locate possible errors, the fortifying solution for degradation, and changes in instrument performance. If the cause cannot be determined, the analyst may reanalyze the sample or report the surrogate values as outside acceptance limits.

10.2 **Minimum Instrument QC**

10.2.1 While it is recommended that the n-pentane (C5) peak be adequately resolved from the methanol solvent on the FID chromatogram, the analyst is allowed to follow the guidance as outlined in 9.5.5. Coelution of the m- and p- xylene isomers is permissible. Any surrogates and/or internal standards used must be adequately resolved from individual compounds in the VPH Component Standard.

10.2.2 Retention time windows must be established for each analyte of interest each time a new GC column is installed, and must be verified and/or adjusted on a daily basis. (See Section 9.3)

10.2.3 Calibration curves must be developed based upon the analysis of calibration standards prepared at a minimum of 5 concentration levels. The linearity of calibration or response factors may be assumed if the percent relative standard deviation (%RSD) over the working range of the curve is less than or equal to 20%. Alternatively, if linear regression analysis is used for quantitation, the correlation coefficient (r) must be at least 0.99 and no targeted analyte or carbon range standard may vary from the true value by more than +/- 15% and +/- 20% respectively. (See Section 9.4.)

10.3 **Initial and Periodic Method QC Demonstrations**

The following must be conducted as an initial demonstration of laboratory capability, prior to the analysis of any samples. Subsequent to this initial demonstration, additional evaluations of this nature should be conducted on a periodic basis, in response to changes in instrumentation or operations, and/or in response to confirmed or suspected systems, method, or operational problems.

10.3.1 Accuracy and Precision

To demonstrate initial laboratory capability, analyze a minimum of four replicate reagent water and/or clean sand blanks spiked with each analyte of interest at approximately 20 to 60 µg/L and/or 20 to 60 mg/kg, respectively.

10.3.1.1 Add an appropriate aliquot of the stock or primary dilution standard solution(s) to each of the four replicate reagent water or clean sand blanks. Purge and analyze each replicate according to the procedures described in Section 9.0.

10.3.1.2 Calculate the measured concentrations of each analyte in all replicates, the mean accuracy (as a percentage of true value) for each analyte, and the precision (as %RSD) of the measurements for each analyte.

10.3.1.3 For each analyte, the mean accuracy, expressed as a percentage of the true value, must be between 80% and 120%. For each analyte, the %RSD must be less than or equal to 20%.

10.3.1. If desired, the Accuracy and Precision evaluation may be combined with the MDL evaluation specified in Paragraph 10.3.2.

10.3.2 Method Detection Limits (Optional)

Analyze a minimum of seven replicate reagent water and/or clean sand blanks which have been fortified with all analytes of interest at approximately 0.5 to 5 µg/L and/or 1 to 5 mg/kg, respectively. Calculate the Method Detection Limit (MDL) of each analyte using the procedure described in Section 12.0.

10.3.2.1 Water MDLs are determined by analyzing 7 to 10 replicates of reagent water samples in 100-mL flasks spiked with the VPH Component standard and with 40 µg/L of the surrogate compound 2,5-dibromotoluene.

10.3.2.2 Soil/sediment MDLs are determined by analyzing 7-10 replicates of 5 -g of VPH-free sand blanks spiked with the VPH Component standard and with 2 mg/kg of the surrogate 2,5-dibromotoluene.

10.3.3 Petroleum Reference Standard

As an optional demonstration of the validity and relevance of VPH calibration, analyze a reagent water and/or clean sand blank spiked with a known concentration of a neat gasoline product.

10.3.3.1 Fortify a reagent water and/or clean sand blank with 5 µL and/or 0.5 mL of the Petroleum Standard Spiking Solution, respectively. Purge and analyze in accordance with the procedures outlined in Section 9.0.

10.3.3.2 Calculate the total concentration of all petroleum hydrocarbons within the Aliphatic Hydrocarbon ranges using the FID chromatogram. Add these values together. Do not subtract the concentration of Targeted VPH analytes.

10.3.3.3 The concentration calculated in Paragraph 10.3.3.2 is expected to be within 30% +/- of the known concentration of Petroleum Standard in the reagent water or sand blank.

10.4 **Ongoing Method QC Demonstrations**

10.4.1 Each sample, blank, and matrix spike must be spiked with the surrogate spiking solution. Required surrogate recovery is 60% to 140%.

10.4.2 At a minimum, with every batch of 20 samples or less the laboratory must analyze the following:

10.4.2.1 **Calibration Check Standard** - A mid-range calibration standard, prepared from the same stock standard solution used to develop the calibration curve, must be analyzed prior to sample analysis to verify the calibration state of the instrument. For large analytical batches that contain more than 10 samples, the analysis of an additional mid-range calibration check standard is recommended after the analysis of the tenth sample. If the percent difference (% D) of any analyte within the calibration check standard varies from the predicted response by more than 20 %, a new calibration curve must be prepared for that analyte.

10.4.2.2 **Laboratory Method Blank** - A water or soil laboratory method blank is prepared by fortifying a 5 mL reagent water blank with 4 µL of the surrogate spiking solution, or by fortifying a 5 g sample of clean sand with 1.0 mL of the surrogate spiking solution. Peaks within the retention time windows of any hydrocarbon ranges of interest may not be present at or above the lowest calculated PQL for any sample within its batch. When determining the PQL for soil method blanks, incorporate the lowest percent solids value found for any sample within its batch in the calculation.

10.4.2.3 **Laboratory Fortified Blank (LFB)** - A water or soil component spike is prepared by fortifying a 5 mL reagent water blank with 4 µL of the matrix spiking solution, or by fortifying a 5 g sample of clean sand with 1.0 mL of the matrix spiking solution. The spike recovery must be between 70% and 130% and if these values can not be obtained the analyst must identify and correct the problem before analyses can continue.

10.4.2.4 **Sample duplicates** - Sample duplicates may be laboratory or field duplicates. The RPD of duplicate samples should not exceed +/- 25%. The lack of sample homogeneity may contribute to RPD's for duplicates which exceed this value. Should the values exceed 25%, the analyst must report that occurrence.

10.4.2.5 **Laboratory Fortified Matrix (LFM) Spike** - The water or soil LFM spike is prepared by fortifying an actual 5 mL water sample with 4 µL of the matrix spiking solution, or by fortifying an actual 5 g soil/sediment sample with 1.0 mL of the matrix spiking solution. The purpose

of the LFM is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations. The corrected concentrations of each analyte within the matrix spiking solution must be within 70 - 130% of the true value. Should the values determined exceed this range, the analyst must report that occurrence.

10.4.3 If any of the performance standards specified in Section 10.4 are not met, the problem must be corrected before further samples are analyzed. Exceptions to this are duplicate samples RPD's and high recoveries for LFM spikes which, due to sample non-homogeneity may exceed the allowable limits. Any samples run between the last calibration check standard that meets the criteria and one that does not must be rerun. If this is not possible, that data must be reported as an "estimated concentration".

11.0 DATA PRODUCTION AND REPORTING

11.1 **Sample Analysis**

11.11 PID Chromatogram

11.1.1.1 Determine the peak area count for the Targeted VPH Analytes.

11.1.1.2 Determine the peak area count for the surrogate 2,5-dibromotoluene.

11.1.1.3 Separately determine the total area count for all peaks eluting 0.1 minutes after the Rt's for toluene through 0.1 minutes after the Rt for 1,2,3-trimethylbenzene, for all peaks eluting 0.1 minutes after the retention time (Rt) for 1,2,3-trimethylbenzene and 0.1 minutes after the retention time for naphthalene and for all peaks eluting 0.1 minutes after the Rt for naphthalene through 0.1 minutes after the Rt of 1-methylnaphthalene.

11.1.1.4 Using the equations contained in Section 9.6 or linear regression analysis, calculate the concentrations of the Targeted VPH Analytes, the surrogate standard 2,5-dibromotoluene, and >C8 through C10, >C10 through C12 and >C12 through C13 Aromatic Hydrocarbons.

11.2.1 FID Chromatogram

11.2.1.1 Separately determine the total area count for all peaks eluting 0.1 minutes before the retention time (Rt) for n-pentane to 0.1 minutes after the Rt for n-hexane and for all peaks eluting 0.1 minutes after the Rt for n-hexane to 0.1 minutes after the Rt for n-octane. It is not necessary to identify or quantitate individual aliphatic compounds within these ranges.

11.2.1.2 Determine the total area count for all peaks eluting 0.1 minutes after the Rt for n-octane to 0.1 minutes after the Rt for n-decane and 0.1 minutes after n-decane to 0.1 minutes after n-dodecane. It is not necessary to identify or quantitate individual aliphatic compounds within this range.

11.2.1.3 Determine the peak area count for the surrogate standard 2,5-dibromotoluene.

11.2.1.4 Using the equations contained in Section 9.6 or linear regression analysis, calculate the concentrations of C5 through C6 Aliphatic Hydrocarbons, >C6 through C8 Aliphatic Hydrocarbons, >C8 through C10 Aliphatic Hydrocarbons, >C10 through C12 Aliphatic Hydrocarbons and the surrogate standard 2,5-dibromotoluene.

11.2.1.5 To avoid "double counting" of the same analytes, adjust the concentrations of Aliphatic Hydrocarbons calculated in Paragraph 11.2.1.4 by subtracting the collective concentrations of methyl tert butylether, benzene, toluene, >C8 through C10 and >C10 through C12 Aromatic Hydrocarbons, as determined from the PID chromatogram in Section 11.11, from the Aliphatic Hydrocarbon range values effected.

11.3 **Data Reporting Format**

11.3.1 The following information and data must be reported:

11.3.1.1 The sample matrix (aqueous, soil or sediment);

11.3.1.2 The date(s) the sample was collected, received by the laboratory, and analyzed;

11.3.1.3 A description of the sample(s) received by the laboratory, relative to the physical condition of the containers, the temperature of the samples, and use of appropriate preservatives;

11.3.1.4 Moisture content (for soil/sediment samples);

11.3.1.5 The calculated concentrations of C5 through C6, C6 through C8, C8 through C10 and C10 through C12 Aliphatic Hydrocarbons ranges and C8 through C10, C10 through C12 and C12 through C13 Aromatic Hydrocarbons ranges

11.3.1.6 Surrogate recovery (expressed as percent recovery);

11.3.1.7 The calculated concentrations of Targeted VPH Analytes determined

11.3.1.8 The concentration units for aqueous samples are expressed as ug/L or mg/L and for soil or sediment samples the units are expressed as ug/Kg or mg/Kg on a dry-weight basis.

12.0 METHOD PERFORMANCE

12.1 **Method Detection Limits (Optional)**

12.1.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

12.1.2 The MDL is determined according to the following equation:

Equation 14

$$MDL = (t) \times (SD)$$

where:

t = student t value at the 99% confidence level

SD = standard deviation of the replicate analysis

Student t values are as follows:

Number of replicates	t value
7	3.14
8	3.00
9	2.90
10	2.82

12.1.3 For the purposes of this method, the designated MDL value for a hydrocarbon range of interest shall be the highest value calculated for the individual analytes within that hydrocarbon range.

12.2 **Single Laboratory Accuracy, Precision, and MDL Data**

Single laboratory accuracy, precision and MDL data for method analytes are provided in Tables 1-1 through 1-4 in Appendix 1. Additional investigation will be conducted to further evaluate the low recoveries for naphthalene.

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METHOD FOR THE DETERMINATION

OF

EXTRACTABLE PETROLEUM HYDROCARBONS (EPH) FRACTIONS

Washington State Department of Ecology

June 1997

METHOD FOR THE DETERMINATION OF EXTRACTABLE PETROLEUM HYDROCARBONS (EPH)

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DISCLAIMER

Mention of trade names or commercial products does not constitute endorsement by the Washington State Department of Ecology. Equipment and materials cited in this method may be replaced by similar products, as long as adequate data exists or has been produced documenting equivalent or superior performance.

METHOD FOR THE DETERMINATION OF EXTRACTABLE PETROLEUM HYDROCARBONS

1.0 SCOPE AND APPLICATION

1.1 This method is designed to measure the collective concentrations of extractable aliphatic and aromatic petroleum hydrocarbons in water and soil. **The carbon ranges used through out this document are given in equivalent carbon numbers (EC) which are related to the boiling point of a chemical normalized to the boiling point of the n-alkanes and its retention time in a boiling point gas chromatographic column**. Extractable aliphatic hydrocarbons are collectively quantitated within five ranges: C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34. Extractable aromatic hydrocarbons are collectively quantitated within five ranges: C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 150 °C and 500 °C.

1.2 Petroleum products suitable for evaluation by this method include, but are not limited to, kerosene and jet fuels, diesel and fuel oils and hydraulic, insulating and lubricating oils. This method, in and of itself, is not suitable for the evaluation of gasoline, mineral spirits, petroleum naphthas, and other petroleum products which contain a significant percentage of hydrocarbons lighter than C10. When samples are known or suspected to contain petroleum hydrocarbons of these or similar types, the Volatile Petroleum Hydrocarbon (VPH) method must also be employed to fully evaluate the hydrocarbons present.

1.3 For reporting purposes, the practical quantitation limits (PQL), given the sample volume/mass, final extract volume and assuming 100 percent solids for soil/sediments are: 50.0 ug/L for aliphatic and aromatic carbon ranges in water and 5.0 mg/Kg for these components in soil. If lower quantitation limits are desired, the analyst is allowed to extract larger volumes/masses and/or concentrate the extracts to smaller volumes prior to analysis. The procedure for Method Detection Limits

(MDL) determination in this method and the Single Laboratory Precision, Accuracy and MDL data (generated by State of Massachusetts) is added for informational purposes only.

1.4 This method is based on a solvent extraction, silica gel fractionation process and gas chromatography (GC) analysis using a flame ionization detector (FID). This procedure should be used by, or under the supervision of, analysts experienced in extractable organics analysis. Analysts using this method should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.

1.5 Like all GC procedures, this method is subject to a "false positive" bias, in that non-hydrocarbon compounds eluting or co-eluting within a specified retention time window may be falsely identified and/or quantitated with the respective carbon ranges. While the cleanup procedure specified in this method to segregate aliphatic and aromatic fractions will serve to mitigate this concern, confirmatory analyses by gas chromatography/mass spectrometry (GC/MS) analysis, EPA Method 8270, or other suitable techniques are recommended in cases where significant concentrations of non-hydrocarbon compounds are known or suspected. Non-petroleum compounds identified and quantitated by GC/MS may be subtracted from the carbon ranges affected as long as the quantity and identities of the compounds are reported along with the carbon range data.

2.0 SUMMARY OF METHOD

2.1 A sample submitted for EPH analysis is extracted with methylene chloride, dried over sodium sulfate, solvent exchanged into hexane, and concentrated. Sample cleanup and separation into aliphatic and aromatic fractions is conducted using a modification of EPA method 3630 (silica gel cleanup). The use of commercially available silica gel cartridges (Sep-Pak cartridges, Waters, Milford, MA) may be substituted for the silica gel column outlined in method 3630 if they can be shown to achieve comparable results. The two extracts produced are then concentrated to final volumes of 10 mL each (i.e., an aliphatic extract and an aromatic extract) and are then separately analyzed by a gas chromatograph equipped with a capillary column and a flame ionization detector. The resultant chromatogram of aliphatic compounds is collectively integrated within the C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 aliphatic hydrocarbon ranges. The resultant chromatogram of aromatic compounds is collectively integrated within the C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 ranges.

2.2 Average calibration factors or response factors determined using an aliphatic hydrocarbon standard mixture are used to calculate the collective concentrations of the different aliphatic hydrocarbons ranges. An average calibration factor or response factor determined using the aromatic hydrocarbon standard mixture is used to calculate a collective concentrations of the aromatic hydrocarbon ranges.

2.3 This method is suitable for the analysis of waters, soils, and sediments.

2.4 This method is based on, and constitutes a significant modification of, the "Method for the Determination of Extractable Petroleum Hydrocarbons (EPH)" Public Comment Draft 1.0 developed by the Massachusetts Department of Environmental Protection. They in turn based their method on (1) USEPA Methods 8000, 8100, and 3630, SW-846, "Test Methods for Evaluating Solid Waste", 3rd Edition, 1986; (2) Draft "Method for Determination of Diesel Range Organics", EPA UST Workgroup, November, 1990; and (3) "Method for Determining Diesel Range Organics", Wisconsin Department of Natural Resources, PUBL-SW-141, 1992.

Table 1. Aromatic Hydrocarbon Standard

Equivalent Carbon Number	Compound
7. 6	Toluene
10.1	1,2,3-Trimethylbenzene
11.7	Naphthalene
15.5	Acenaphthene
Surrogate	Ortho-Terphenyl
20.8	Pyrene
34.01	Benzo(g,h,i)Perylene

Table 2. Aliphatic Hydrocarbon Standard

Carbon Number	Compound
8	Octane
10	Decane
12	Dodecane
16	Hexadecane
Surrogate	1-Chloro-octadecane
21	Henicosane
34	Tetratriacontane

3.0 DEFINITIONS

3.1 **Extractable Petroleum Hydrocarbons (EPH)** are defined as all hydrocarbon compounds eluting from toluene through benzo(g,h,i)perylene. EPH is comprised of C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 Aliphatic Hydrocarbons and C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 Aromatic Hydrocarbons. EPH concentration data are reported as the aggregate concentration of the aliphatic and aromatic hydrocarbon ranges.

3.2 **Equivalent Total Petroleum Hydrocarbons (E-TPH)** For samples contaminated with petroleum products in the C10 to C34 range, the E-TPH value is equivalent to the EPH value. For samples contaminated with a petroleum product(s) containing significant concentrations of hydrocarbons lighter and heavier than C10, (e.g., contaminated with both gasoline and diesel fuel), the E-TPH value is a summation of the EPH value and the Volatile Petroleum Hydrocarbon (VPH) value. In order to avoid double counting of analytes due to the overlap in the carbon ranges existing between the two methods, the analyst will report the highest of the two values determined for the overlapping ranges. In those cases where both the VPH and EPH methods are employed on samples, the analyst may select to quantitate the >C10 through C12 Aliphatic and the >C10 through C12 Aromatic Hydrocarbon ranges by the EPH method only. Similarly, the analyst may select to quantitate the C8 through C10 Aromatic and C8 through C10 Aliphatic Hydrocarbon ranges by the VPH method only.

3.3 **C8 through C10 Aromatic Hydrocarbons** are defined as all of the aromatic hydrocarbon compounds eluting from (and including) toluene through 1,2,3-trimethylbenzene.

3.4 **>C10 through C12 Aromatic Hydrocarbons** are defined as all aromatic hydrocarbon compounds eluting after 1,2,3-trimethylbenzene through naphthalene.

3.5 **>C12 through C16 Aromatic Hydrocarbons** are defined as all aromatic hydrocarbon compounds eluting after naphthalene through acenaphthene.

3.6 >**C16 through C21 Aromatic Hydrocarbons** are defined as all aromatic hydrocarbons compounds eluting after acenaphthene through pyrene.

3.7 >**C21 through C34 Aromatic Hydrocarbons** are defined as all aromatic hydrocarbons compounds eluting after pyrene through benzo(g,h,i,)perylene.

3.8 **C8 through C10 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds eluting from (and including) n-octane (n-C8) through n-decane (n-C10).

3.9 **>C10 through C12 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds eluting after n-decane through n-dodecane (n-C12).

3.10 **>C12 through C16 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds eluting after n-dodecane through n-hexadecane (nC16)

3.11 >**C16 through C21 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbons eluting after n-hexadecane through n-henicosane (nC21).

3.12 **>C21 through C34 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbons eluting after n-henicosane through tetratriacontane (nC34).

3.13 **Aromatic Hydrocarbon Standard** is defined as a 6 component mixture (plus surrogate) of the aromatic hydrocarbons listed in Table 1. The compounds comprising the Aromatic Hydrocarbon Standard are used to (a) define and establish the windows for the Aromatic Hydrocarbon ranges, and (b) determine chromatographic response factors that can in turn be used to calculate the collective concentration of aromatic hydrocarbons in environmental samples within those hydrocarbon ranges.

3.14 **Aliphatic Hydrocarbon Standard** is defined as a 6 component mixture (plus surrogate) of the normal alkanes listed in Table 2. The compounds comprising the Aliphatic Hydrocarbon Standard are used to (a) define and establish windows for the aliphatic hydrocarbons ranges, and (b) determine chromatographic response factors that can in turn be used to calculate the collective concentration of aliphatic hydrocarbons in environmental samples within those hydrocarbon ranges.

3.15 **Analytical Batch** is defined as a group of samples with similar matrices which are processed as a unit. For Quality Control purposes, if the number of samples in such a group is greater than 20, then each group of 20 samples or less are defined as separate analytical batches.

3.16 **Laboratory Duplicates** are defined as split samples taken from the same sampling container and analyzed separately with identical procedures. The analysis of laboratory duplicates give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.17 **Field Duplicates** are defined as two separate samples collected at the same time and location under identical circumstances and managed the same throughout field and laboratory procedures. Analyses of field duplicates give a measure of the precision associated with sample collection, preservation and storage, as well as laboratory procedures.

3.18 **E-TPH Duplicates** are defined as two separate samples collected at the same time and location, for analysis by both EPH and VPH methods. E-TPH duplicates are taken at locations where significant concentrations of petroleum hydrocarbons lighter and heavier than C10 are likely to be present (e.g., locations contaminated by releases of both gasoline and diesel fuel). The resultant EPH and VPH concentrations are then summed to determine the Equivalent TPH (E-TPH) concentration.

3.19 **Calibration Standards** are defined as a series of standard solutions prepared from dilutions of a stock standard solution, containing known concentrations of each analyte and surrogate compounds of interest.

3.20 **Calibration Check Standard** is defined as a calibration standard used to periodically check the calibration state of an instrument. The calibration check standard is prepared from the same stock standard solution as calibration standards, and is generally one of the mid-level range calibration standard dilutions.

3.21 **Matrix Spiking Solution** is defined as a solution which is generally prepared independently from the calibration standards and which contain known concentrations of method analytes.

3.22 **Laboratory Method Blank** is defined as, depending on the matrix of the samples, either reagent water or clean sand spiked with a surrogate standard. The laboratory method blank is treated identically as with samples, exposed to all glassware, solvents, reagents, and equipment. A laboratory method blank is analyzed with every batch of samples, to determine if method analytes or other interferences are present in the laboratory environment, reagents, or equipment.

3.23 **Laboratory Fortified Blank (LFB)** is defined as, depending on the matrix of the samples, either reagent water or clean sand blank fortified with a matrix spiking solution. The LFB is treated and analyzed identically as with samples and blanks and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements at the required practical quantitation limits.

3.24 **Laboratory Fortified Matrix (LFM) Sample** is defined as an environmental sample which has been spiked with a matrix spiking solution containing known concentrations of method analytes. The LFM sample is treated and analyzed exactly as with samples and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentration of analytes in the sample matrix must be determined through the separate analyses of a laboratory or field duplicate, and the measured values in the LFM sample corrected for background concentrations.

3.25 All other terms are as defined in SW-846, "Test Methods for Evaluating Solid Waste", USEPA, September, 1986, and as amended.

4.0 INTERFERENCES

4.1 Method interferences are reduced by washing all glassware with hot soapy water and then rinsing with warm tap water, acetone, and methylene chloride.

4.2 High purity reagents must be used to minimize interference problems.

4.3 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. Whenever an unusually concentrated sample is analyzed, it should be followed by the analysis of a solvent blank to check for cross-contamination.

4.4 Matrix interferences may be caused by contaminants that are coextracted along with the analytes of interest from the sample. The type and extent of matrix interference will vary considerably from one source to another depending upon the nature and diversity of the site being sampled and may include certain solvents, halogenated hydrocarbons and phthalate esters. A silica gel cleanup procedure is used to overcome many of these interferences however, some samples may require additional cleanup procedures/approaches or analytical techniques, e.g. gel permeation chromatography and/or GC/MS, which are beyond the scope of this method.

5.0 HEALTH AND SAFETY ISSUES

The toxicity and carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDS) should also be made available to all personnel involved in the chemical analysis.

6.0 APPARATUS AND MATERIALS

6.1 The following glassware is used for this method:

6.1.1 1-L amber glass bottles

6.1.2 4 oz. (120 mL) amber glass wide-mouth jars

6.1.3 Vials:

6.1.3.1 autosampler: 2-mL glass vials with Teflon-lined rubber crimp caps

6.1.3.2 10-mL vials with Teflon-lined caps

6.1.4 Glass funnels

6.1.5 2-L Separatory funnels with Teflon stopcock

6.1.6 Kuderna-Danish apparatus including 10-mL concentrator tube, 500-mL Evaporative flask, & 3-ball Snyder column

6.1.7 Chromatographic column: 250 mm long x 10 mm I.D. with teflon stopcock

6.1.8 Disposable pipets: Pasteur

6.1.9 25-mL graduated cylinder

6.1.10 1-Liter graduated cylinder

6.1.11 100-mL beakers

6.1.12 25-mL volumetric flasks

6.2 Analytical balance: An analytical balance capable of accurately weighing 0.0001 g must be used for weighing standards. A top-loading balance capable of weighing to the nearest 0.1 g must be used for weighing soil samples.

6.3 A nitrogen blowdown apparatus for use in concentrating extracts.

6.4 **Gas Chromatography**

6.4.1 Gas Chromatograph: An analytical system complete with temperature programmable gas chromatograph for use with capillary columns is required. The data station must be capable of storing and reintegrating chromatographic data and must be capable of determining peak areas using a forced baseline projection.

6.4.2 Recommended Column: 30-m long x 0.32-mm I.D., 0.25-µm film DB-5 column (J&W Scientific) or equivalent. This column will allow for the adequate resolution of alkanes from n-C8 to n-C34.

6.4.3 Detector: A Flame Ionization Detector (FID).

6.4.4 Autosampler: An autosampler capable of making 1 to 2 µL injections is recommended.

6.5 Water bath: heated with a concentric ring covers, capable of temperature control (± 2°C). The bath should be used in a hood.

6.6 Microsyringes: 10-µL, 100-µL, 250-µL, 500-µL, 1000-µL

6.7 Boiling Chips: glass or teflon, precleaned prior to use

6.8 Soxhlet or Sonication extraction apparatus

6.9 Drying oven

7.0 REAGENTS AND STANDARDS

7.1 **Reagents**

7.1.1 Reagent Water: organic free water

7.1.2 Solvents: hexane, methylene chloride, and acetone; pesticide grade or better. Store away from other solvents.

7.1.3 Sodium sulfate: (ACS) granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray.

7.1.4 Ottawa and/or masonry sand: free of extractable petroleum hydrocarbons.

7.1.5 Silica gel: 100/200 mesh (Davison Chemical grade 923 or equivalent). Heat to 150-160 ^{o}C for several hours before use. Silica Gel Sep-Pak Cartridges: 5 g/20-mL (Waters, Milford, MA) , if it is demonstated to give equivalent separations.

7.2 **Stock Standard Solutions**

Prepare stock standard solutions at approximately 1000 ng/µL, or purchase as certified solutions.

7.2.1 Aromatic Hydrocarbon Standard: The Aromatic Hydrocarbon Standard consists of the 6 aromatic compounds listed in Table 1 and a surrogate compound. Prepare stock standard solutions by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in methylene chloride and dilute to volume in a 10-mL volumetric flask. The use of commercially prepared stock standards solutions is an acceptable alternative to the use of neat material. The analyst is allowed to prepare a separate surrogate solution.

7.2.2 Aliphatic Hydrocarbon Standard: The Aliphatic Hydrocarbon Standard consists of the 6 normal alkanes listed in Table 2 and a surrogate compound. Prepare stock standard solutions by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in hexane and dilute to volume in a 10-mL volumetric flask. The use of commercially prepared stock standard solutions is an acceptable alternative to the use of neat material. The analyst is allowed to prepare a separate surrogate solution.

7.2.3 Petroleum Reference Standard: The use of a Petroleum Reference Standard is recommended for quality control purposes. The Petroleum Reference Standard consists of an API or commercial diesel, fuel oil, kerosene, and/or lubricating oil. Prepare stock standard solutions by accurately weighing approximately 0.0100 g of neat product. Dissolve neat product in hexane and dilute to volume in a 10-mL volumetric flask.

7.3 Surrogate Standards

7.3.1 The recommended surrogate standards are chloro-octadecane (COD, available from Restek Corporation, Bellefonte, PA) and ortho-terphenyl (OTP, available from EM Sciences, Gibbstown, NJ). Additional surrogates or surrogates other than those listed above may be used at the discretion of the analyst as long as their performance in the method is demonstrated as acceptable. Preparation and use of those surrogates will be in the same manner as the listed surrogate.

7.3.2 The surrogate standard COD is prepared by accurately weighing approximately 0.0100 g of pure material in a 10-mL volumetric flask. Dissolve the material in hexane. This solution is added to the Aliphatic Hydrocarbon standard.

7.3.3 The surrogate standard OTP is prepared by accurately weighing approximately 0.0100 g of pure material in a 10-mL volumetric flask. Dissolve the material in methylene chloride. This solution is added to the Aromatic Hydrocarbon standard.

7.3.4 Surrogate Spiking Solution: The recommended surrogate spiking solution is comprised of a mixture of the COD and OTP surrogate standards. Prepare a surrogate spiking solution which contains the surrogate standards at a concentration of 20 ng/µL in acetone. Each sample, blank, and matrix spike is fortified with 1.0 mL of the surrogate spiking solution.

7.4 Internal Standard

If an internal standard method of calibration is to be used, the recommended internal standard is 5-alpha-androstane (EM Sciences, Gibbstown, NJ).

7.5 Matrix Spike Standard

7.5.1 Four or more analytes from each analyte group (i.e., aromatic and aliphatic hydrocarbons) are selected for use in a matrix spiking solution, which is prepared independently from the calibration standards.

7.5.2 The recommended spiking solution, consisting of C10, C12, C16 and C21 normal alkanes and naphthalene, acenaphthene, anthracene, pyrene, benzo(a)pyrene and benzo(g,h,i)perylene, is prepared in acetone at concentrations of 25 ng/µL.

7.5.3 The samples selected as the matrix spike are fortified with 1.0 mL of the matrix spiking solution.

7.6 Fractionation Check Solution

7.6.1 The Fractionation Check Solution is used to monitor the fractionation efficiency of different batches (lot numbers) of silica gel used to prepare the silica gel hydrocarbon fractionation columns (and Sep-Pak cartridges if used) as well as check for sample preparation errors (e.g., insufficient/excessive pentane use).

7.6.2 Prepare a Fractionation Check Solution in hexane containing 25 ng/µL each of the n-C8, n-C10, n-C12, n-C16, n-C21, and n-C34 alkanes) and 25 ng/µL each of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene. The final solution will contain 6 alkanes and 16 PAHs at concentrations of 25 ng/µL each. The use of commercially available check solutions containing these compounds is acceptable.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 Aqueous samples are collected in 1 liter amber glass bottles with teflon-lined screw caps.

8.2 Soil and sediment samples are collected in 4 oz. (120 mL) amber wide-mouth glass jars with teflon-lined screw caps.

8.3 Aqueous samples must be preserved at the time of sampling by the addition of an acid to reduce the pH of the sample to less than 2.0. This is accomplished by the addition of approximately 5 mL of 1:1 HCl to a 1 liter sample. Following collection and the addition of acid, the sample must be cooled to 4°C.

8.4 Soil and sediment samples must be cooled to 4°C immediately after collection.

8.5 A chain of custody form must accompany all aqueous, soil and sediment samples, documenting the time and date of sampling and any preservative additions.

8.6 Aqueous, soil and/or sediment samples must be extracted within 14 days of collection. If for whatever reason aqueous samples were not preserved at the time of collection they must be extracted within 7 days of collection. Both aqueous and soil/sediment extracts must be analyzed within 40 days of extraction.

8.7 A summary of sample collection, preservation, and holding times is provided in Table 3.

Table 3. Holding Times and Preservatives for EPH Samples

Matrix	Container	Preservation	Holding Time
Aqueous Samples	1-Liter amber glass bottle with Teflon-lined screw cap	Add 5 mL of 1:1 HCl; cool to 4°C	Samples must be extracted within 14 days and extracts analyzed within 40 days
Soil/Sediments Samples	4-oz. (120 mL) wide mouth amber glass jar with Teflon-lined screw cap	Cool to 4°C	Samples must be extracted within 14 days and extracts analyzed within 40 days

9.0 PROCEDURE

9.1 **Sample Preparation**

9.1.1 Water Extraction

9.1.1.1 Mark the water meniscus on the side of the 1 liter of sample bottle (for later volume determination) and transfer the water to a 2-liter separatory funnel. For blanks and quality control samples, pour 1 liter of reagent water into the separatory funnel. Add 1.0 mL of the surrogate spiking solution to all samples, blanks and matrix spikes. For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking solution.

9.1.1.2 Check the pH of the sample with wide-range pH paper. Note the pH in the laboratory notebook. The pH of the sample need not be adjusted.

9.1.1.3 Add 60 mL methylene chloride to the sample bottle to rinse the inner walls of the container, then add this solvent to the separatory funnel.

9.1.1.4 Seal and shake the separatory funnel vigorously for 1 to 2 minutes with periodic venting to release excess pressure.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, venting should be done immediately after the separatory funnel has been sealed and shaken once.

9.1.1.5 Allow the organic layer to separate from the water phase for a minimum of 5 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.
Collect the solvent extract in an 500ml Kuderna-Danish (K-D) evaporation flask to which is attached a 10 mL concentrator tube..

9.1.1.6 Repeat the extraction two more times using fresh portions of solvent and adding the solvent extracts to the KD flask. (Steps 9.1.1.3 to 9.1.1.5) The use of continuous liquid-liquid extraction (EPA method 3520) is an acceptable alternative to the separatory funnel extraction method described above.

9.1.1.7 For sample volume determination add water to the sample bottle to the level of the meniscus previously marked then transfer this water to a graduated cylinder and record the volume.

9.1.1.8 Add one clean boiling chip to the K-D flask and attach a three ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 4-6 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

9.1.1.9 Solvent exchange the methylene chloride with hexane by adding at least 50 mL of hexane to the top of the Snyder column. and concentrate the extract to less than 10 mL, as described in Paragraph 9.1.1.8, raising the temperature of the water bath, if necessary, to maintain proper distillation.

Note: An alternative solvent exchange method is to use the nitrogen blowdown apparatus to exchange the methylene chloride with hexane. This is accomplished by placing a disposable pipet in the concentrator tube and adding the small amounts of hexane via the pipet to the bottom of the concentrator tube during the concentration process in the apparatus.

9.1.1.10 Remove the Snyder column and evaporation flask from the 10-mL concentrator tube. Place the concentrator tube containing the hexane extract onto a nitrogen blowdown apparatus. Adjust the extract volume to 1-2 mL under a gentle stream of nitrogen . If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume will need to be larger.

9.1.1.11 The extract obtained is now ready to be cleaned and fractionated on a silica gel column. If cleanup will not be performed immediately, transfer the extract to a Teflon-lined screw-cap vial, label, and refrigerate.

9.1.1.12 Record the sample preparation information for the extraction and concentration steps. At a minimum, record the date, sample laboratory number, sample volume, volume and concentration of added surrogate and matrix spike solutions, and any deviations or problems associated with the extraction of the samples.

9.1.1.13 For cleanup and fractionation, refer to Section 9.1.4.

9.1.2 Soil/Sediment Extraction using Ultrasonic Extraction

9.1.2.1 The following steps should be performed rapidly to minimize the loss of the more volatile fractions. In a beaker blend 10 g of the soil/sediment sample with sufficient anhydrous sodium sulfate to form a free flowing powder using a spatula. Add 1.0 mL of the surrogate spiking solution to the samples and blanks. For the samples in each analytical batch selected for matrix spiking, add 1.0 mL of the matrix spiking standard. Immediately add approximately 50 mL of 1:1 methylene chloride:acetone to the beaker. If lower PQL's are desired, the analyst is allowed to increase the sample size extracted. This will necessitate a proportional increase in the volume of extraction solvent used.

9.1.2.2 Place the bottom surface of the tip of the ultrasonic horn about 1/2 inch below the surface of the solvent but above the soil/sediment layer.

9.1.2.3 Sonicate for 3 minutes with the control knob set to the maximum output, pulse mode and 50% duty cycle.

9.1.2.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

9.1.2.5 Decant and filter the extract through Whatman No. 41 filter paper into the K-D concentrator. Repeat the extraction two more times with additional 50 mL portions of the solvent. Decant off and filter the extract into the K-D flask each time. On the last extraction, pour

the entire sample into the funnel and rinse the beaker and sample with additional portions of solvent and add these to the K-D flask. The analyst may find it useful to (1) either add anhydrous sodium sulfate to the filter for drying the extract or (2) to pass the extract through a drying column containing about 10 cm of anhydrous sodium sulfate prior to collecting the extract in the K-D flask.

9.1.2.6 Add one clean boiling chip to the K-D flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10 to 20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1-2 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

9.1.2.7 Exchange the methylene chloride with hexane by adding 50 mL of hexane to the top of the Snyder column and concentrating the extract as described in Paragraph 9.1.2.6, raising the temperature of the water bath, if necessary, to maintain proper distillation. The alternate solvent exchange technique described in note in 9.1.1.9 may also be used.

9.1.2.8 Remove the Snyder column and evaporation flask from the 10-mL concentrator tube. Place the concentrator tube containing the hexane extract onto a nitrogen blowdown apparatus. Adjust the extract volume to 1-2 mL under a gentle stream of nitrogen . If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume will need to be larger.

9.1.2.9 The extract obtained is now ready to be cleaned and fractionated on a silica gel column. If cleanup will not be performed immediately, transfer the extract to a Teflon-lined screw-cap vial, label, and refrigerate.

9.1.2.10 Record the sample preparation information for the extraction and concentration steps, as specified in paragraph 9.1.1.14.

9.1.2.11 For cleanup and fractionation, refer to Section 9.1.4.

9.1.3 <u>Soil/Sediment Extraction by Soxhlet Extraction</u>

9.1.3.1 Blend 10 g of the soil/sediment sample with sufficient anhydrous sodium sulfate to produce a free flowing powder and place this material in an extraction thimble. The extraction thimble must drain freely for the duration

of the extraction period. Add 1.0 mL of the surrogate spiking solution onto the sample. For the samples in each analytical batch selected for matrix spiking, add 1.0 mL of the matrix spiking solution. If lower PQL's are desired, the analyst may increase the quantity of sample extracted.

9.1.3.2 Place approximately 200 mL of methylene chloride into a 250-mL Erlenmeyer or round bottomed flask (depending on the heating source) containing several clean boiling chips. Attach the flask to the extractor and extract the sample for 8-16 hr.

9.1.3.3 Allow the extract to cool after the extraction is completed.

9.1.3.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

9.1.3.5 Dry the extract by passing it through a glass powder funnel containing anhydrous sodium sulfate. Collect the dried extract in the K-D concentrator. Wash the extractor flask and sodium sulfate column with 50 to 75 mL of methylene chloride to complete the quantitative transfer.

9.1.3.6 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10 to 20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1-2 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

9.1.3.7 Exchange the methylene chloride with hexane by adding 50 mL of hexane to the top of the Snyder column and concentrating the extract as described in Paragraph 9.1.3.6, raising the temperature of the water bath, if necessary, to maintain proper distillation. The alternate solvent exchange technique outlined in the note in 9.1.1.9 may also be used.

9.1.3.8 Remove the Snyder column and evaporation flask from the 10 mL concentrator tube. Place the concentrator tube containing the hexane extract onto a nitrogen blowdown apparatus. Adjust the extract volume to 1-2 mL under a gentle stream of nitrogen . If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume will need to be larger.

9.1.3.9 The extract obtained is now ready to be cleaned and fractionated on a silica gel column. If cleanup will not be performed immediately, transfer the extract to a Teflon-lined screw-cap vial, label, and refrigerate.

9.1.3.10 Record the preparation information for the extraction and concentration steps, as specified in 9.1.1.14.

9.1.3.11 For cleanup and fractionation, refer to Section 9.1.4.

9.1.3.12 The use of the Accelerated Solvent Extraction (ASE), EPA Method 3545, is an acceptable alternative to either ultrasonic or soxhlet extraction techniques as long as it is demonstrated to achieve comparable results.

9.1.4 Silica Gel Cleanup and Separation

9.1.4.1 Silica gel is a regenerative adsorbent of amorphous silica with weakly acidic properties. It is produced from sodium silicate and sulfuric acid. Silica gel can be used for column chromatography and is used for separating analytes from interfering compounds of a different chemical polarity. Silica gel is also used to separate petroleum distillates into aliphatic and aromatic fractions. Before the silica gel technique can be utilized, the extract solvent must be exchanged to hexane. This procedure may be performed immediately before the extract concentration step is complete by adding hexane to the K-D (when the volume of remaining methylene chloride is approximately 10 to 15 mL) and reducing the extract volume to 1 to 2 mL. After cooling, disassemble the K-D apparatus, rinsing the joints into the concentrator tube with a minimum of hexane. With a nitrogen blowdown concentrator, further reduce the extract to a final volume of 2 mL.

9.1.4.2 Prepare a slurry of 10g of activated silica gel in methylene chloride and place this into a 10 mm I.D.x 250 mm long chromatographic column. Tap the column to settle the silica gel and elute the methylene chloride. Add 1 to 2 cm of anhydrous sodium sulfate to the top of the silica gel. Note: The activity of each new batch (lot number) of silica gel must be evaluated prior to its use in this procedure. This requires the use of the fractionation check solution to insure that there is an efficient separation of the aromatic fraction from the aliphatic fraction. If necessary, the analyst is allowed to adjust the volumes of the eluants used to facilitate this process.

9.1.4.3 Pre-elute the column with 40 mL of pentane. Let the solvent flow through the column, at a rate of about 2 mL/minute, until the head of the liquid in the

column is just above the sodium sulfate layer. Close the stopcock to stop solvent flow. Discard this pentane.

9.1.4.4 Open the stopcock and immediately transfer the hexane sample extract onto the silica gel column. Rinse the concentrator tube with an additional 1-2 mL of hexane and add this to the column as well.

9.1.4.5 Just prior to exposure of the sodium sulfate layer to the air, add 25 mL of pentane to the column. Collect the eluant in a 250 mL K-D flask to which is attached a 10 mL concentrator tube and label this fraction "aliphatics". Concentrate and solvent exchange this extract into hexane.

9.1.4.6 Following recovery of the aliphatic fraction and just prior to exposure of the sodium sulfate layer, elute the column with 50 mL of methylene chloride/pentane (40:60) (v/v) and collect the eluant in a 250 mL K-D flask equipped with a 10 mL concentrator tube.. Label this fraction "aromatics". Concentrate and solvent exchange this extract into methylene chloride.

9.1.4.7 Concentrate each fraction to a final volume of 10 mL under a gentle stream of nitrogen from a nitrogen blowdown apparatus.

9.1.4.8 Transfer 1 mL of the fractions to a labeled two-mL glass autosampler vials with teflon-rubber crimp caps for analysis and save the remaining extract in a teflon-rubber septum screw topped vial. If lower PQL's are required, the analyst may concentrate the extract to as low as 1 mL prior to analysis

9.1.5 Proceed with the analysis in accordance with Sections 9.2 through 9.5. Analyze all laboratory method blanks and QC samples under the same conditions as that used for samples.

9.1.6 If chromatographic responses exceed the linear range of the system, dilute the extract(s) and re-analyze

9.1.7 <u>Determination of Percent Moisture</u>

9.1.7.1 Soil and sediment sample results must be reported on a dry-weight basis. A portion of sample for moisture determination should be weighed out at the same time as the portion used for hydrocarbon determination.

9.1.7.2 Immediately after weighing a sample for extraction, transfer 5 to 10 g of the sample into a tared crucible. Dry the sample overnight at 105°C in an oven. After drying remove it from the oven allow it to cool in a desiccator before reweighing. Calculate the percent moisture of the sample using the equations provided in Section 9.6.3.

9.2 **GC Conditions**

9.2.1 Suggested Gas Chromatographic Conditions

9.2.1.1 Oven Program: Set oven temperature to 50 °C for 2 minute, then 8°C/min to 320 °C and hold for 10 minutes.

9.2.1.2 Sample/autosampler injection volume is 1 to 2 µL.

9.2.1.3 Gas Flows: The recommended carrier gas is helium.

9.2.1.3.1 Helium carrier gas flow: 1 to 2 mL/min.

9.2.1.3.2 Air: 400 mL/min.

9.2.1.3.3 Hydrogen: 35 mL/min.

9.2.1.3.4 Make up gas flow: 30 mL/min.

9.2.1.4 Miscellaneous:

9.2.1.4.1 FID temperature, 310 to 320 °C

9.2.1.4.2 Injection port temperature, 290 to 300 °C

9.2.1.4.3 GC operated in splitless mode

9.2.1.4.4 Column head pressure 15.0 psi at 50°C

9.2.1.4.5 Linear velocity approximately 50 cm/sec

9.3 **Retention Time Windows**

9.3.1 Before establishing windows, make sure the GC system is within optimum operating conditions. Make three injections of the Aromatic and Aliphatic Hydrocarbon standard mixtures throughout the course of a 72-hr period. Serial injections over less than a 72-hr period may result in retention time windows that are too tight.

9.3.2 Calculate the standard deviation of the three absolute retention times for each standard.

9.3.3 Plus or minus three times the standard deviation of the absolute retention times for each standard should be used to define the retention time window. However, the

experience of the analyst should weigh heavily in the interpretation of chromatograms.

9.3.4 In those cases where the standard deviation for a particular standard is zero, the laboratory should substitute the standard deviation of a closely eluting structurally similar compound to develop a valid retention time window.9.3.5 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed or a portion removed as part of GC maintenance. This data must be retained by the laboratory.

9.3.6 EPH retention time (Rt) windows for all fractions (carbon ranges and hydrocarbon types) except the C8 through C10 are defined as beginning 0.1 minutes after the Rt of the beginning marker compound and ending 0.1 minutes after the Rt of the ending marker compound. Since the first fraction for both the aliphatics and aromatics includes the beginning marker compounds, the Rt windows for them are defined as beginning 0.1 minutes before the Rt of the beginning marker compound and ends 0.1 minutes after the ending marker compound.

EPH marker compounds and windows are summarized in Table 4.

Table 4. EPH Marker Compounds

Range/ Hydrocarbon Standard	Beginning Marker Compound	Ending Marker Compound
C8-C10 Aliphatic Hydrocarbons	just before n-octane	just after n-decane
C10-C12 Aliphatic Hydrocarbons	just after n-decane	just after n-dodecane
C12-C16 Aliphatic Hydrocarbons	just after n-dodecane	just after n-hexadecane
C16-C21 Aliphatic Hydrocarbons	just after n-hexadecane	just after n-henicosane
C21-C34 Aliphatic Hydrocarbons	just after n-henicosane	just after n-tetratriacontane
C8-C10 Aromatic Hydrocarbons	just before toluene	just after 1,2,3-trimethylbenzene
C10-C12 Aromatic Hydrocarbons	just after 1,2,3-trimethylbenzene	just after naphthalene
C12-C16 Aromatic Hydrocarbons	just after naphthalene	just after acenaphthene
C16-C21 Aromatic Hydrocarbons	just after acenaphthene	just after pyrene
C21-C34 Aromatic Hydrocarbons	just after pyrene	just after benzo(g,h,i)perylene

9.4 **Calibration**

Calibrate the GC system using either the external standard procedure (Section 9.4.1) or the internal standard procedure (Section 9.4.2).

9.4.1 External standard calibration procedure

9.4.1.1 Prepare Aromatic and Aliphatic Hydrocarbon calibration standards at a minimum of five concentration levels by adding volumes of one or more stock standard solutions to volumetric flasks and diluting to volume with methylene chloride and hexane, respectively. The surrogate OTP is added to the Aromatic Hydrocarbon Standard; the surrogate COD is added to the Aliphatic Hydrocarbon Standard. One of the calibration

standards must be at a concentration near, but above, the method detection limit and is used to determine the reporting PQL. In order to report the PQL's listed in 1.4, given the volume/mass water or soil extracted of 1 liter or 10 grams and assuming 100% solids on the soil, this standard must be at a 5 ng/uL level. The other concentrations must correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

9.4.1.2 A collective calibration curve or factor must be established for each hydrocarbon range of interest. Inject each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph (e.g., 1 to 2 µL injections). To calculate the collective CF for C8-C10, >C12-C12, >C12-C16, >C16-C21 and C21-C34 Aromatic Hydrocarbons, tabulate the summation of all peak areas of the calibration compounds in that range (e.g. C8-C10, toluene and 1,2,4-trimethylbenzene or >C10-C12, naphthalene) against the total mass injected. Although a forced baseline projection is required for samples and blanks, the analyst is allowed to integrate only the area of the calibration compound(s) to generate the calibration factors. The ratio of the response to the amount injected, defined as the calibration factor (CF), or range CF, may be calculated for hydrocarbon ranges at each standard concentration using Equation 1. If the percent relative standard deviation (%RSD) of the calibration factor is equal to or less than 20 % over the working range for the ranges of interest, as determined using Equation 2, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve. The Aliphatic Hydrocarbon collective CF is calculated in the same manner using the aliphatic standards.

Equation 1: Range Calibration Factor

$$Range\ CF = \frac{total\ area\ of\ peaks}{mass\ injected\ (ng)}$$

Equation 2: Percent Relative Standard Deviation

$$\%RSD = \frac{Stand\ Dev\ of\ 5\ CFs}{Mean\ of\ 5\ CFs} \times 100$$

Note: The area for the surrogates COD and OTP must be subtracted from the area of the range in which they elute (e.g., COD is subtracted from the C16-C21 Aliphatic Hydrocarbon range.

9.4.1.4 At a minimum, the working calibration curve or calibration factor must be verified at the beginning of each working day and after the final analysis of that day, or after every 20 samples, whichever is more frequent, by the injection of a mid-level calibration standard to verify instrument performance and linearity. If the percent difference (%D) for any range varies from the predicted response by more than ± 20 %, as calculated using Equation 4, a new calibration curve must be prepared.

Equation 4: Percent Difference (%D)

$$\%D = \frac{\overline{CF} - CFv}{\overline{CF}} \times 100$$

where:

$\overline{CF}$ = Average Calibration Factor from calibration curve.

CFv = Calibration Factor from verification calibration check.

9.4.1.5 The concentrations of hydrocarbon ranges may also be calculated from a calibration curve by use of linear regression analysis.

9.4.2 Internal standard calibration procedure

9.4.2.1 The suggested internal standard for this method is 5-alpha-androstane (EM Science, Gibbstown, NJ).

9.4.2.2 Prepare Aromatic and Aliphatic Hydrocarbon calibration standards at a minimum of five concentration levels by adding volumes of stock standard solutions to volumetric flasks. The surrogate OTP is added to the Aromatic Hydrocarbon Standard; the surrogate COD is added to the Aliphatic Hydrocarbon Standard. To each calibration standard, add a known constant amount of an internal standard. One of the calibration standards must be at a concentration near, but above, the method detection limit and is used to determine the reporting PQL. The other concentrations must correspond to the expected range of concentration found in real world samples or should define the working range of the detector.

9.4.2.3 Inject each calibration standard using the same technique that will be applied to the samples (e.g., 1 to 2 µL injection). Tabulate the peak area responses against the concentration of each hydrocarbon range and internal standard. Calculate the collective response factors (RF) for each hydrocarbon range using Equation 5.

Note: The area for the surrogates COD and OTP must be subtracted from the area of the range in which they elute (e.g., COD is subtracted from the appropriate Aliphatic Hydrocarbon range).

uation 5: Range Response Factor

$$Range\ RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Summation of peak areas of the fraction (e.g., C10-C12 Aliphatic Hydrocarbons).

C_{is} = Concentration of internal standard, ng/µL.

A_{is} = Response for the internal standard.

C_s = Total mass concentration of injected standards, ng/µL.

9.4.2.4 At a minimum, the working calibration curve or RF must be verified at the beginning of each working day and after the final analysis of that day, or after every 20 samples, whichever is more frequent, by the injection of a mid-level calibration standard to verify instrument performance and linearity. If the percent difference (%D) for any hydrocarbon range varies from the predicted response by more than ± 20 %, as calculated using Equation 4, a new calibration curve must be prepared for that range.

9.4.2.5 The concentrations of hydrocarbon ranges may also be calculated from a calibration curve by the use of linear regression analysis.

9.5 **GC Analysis**

9.5.1 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration, or verification of calibration, followed by sample extracts interspersed with blanks and QC samples. The analytical sequence must end with an acceptable verification calibration standard. If the ending calibration standard is not acceptable, all samples analyzed after the last acceptable calibration verification must be reanalyzed. If, for whatever reason, reanalysis is not possible, then the data for those samples must be qualified as an "estimate".

9.5.2 Aliphatic and aromatic extracts are introduced into the gas chromatograph by slitless injection.

9.5.3 Inject 1 to 2 µL of the sample extract. Record the volume injected and the resulting peak size in area units.

9.5.4 Confirm the established retention time windows for each hydrocarbon range on a daily basis. Use the absolute retention time for each analyte as the midpoint of the window for that day. The daily retention time window equals the midpoint ± three times the standard deviation determined in Section 9.3.

9.5.4.1 Validation of GC system qualitative performance must be accomplished by the analysis of standards within the analysis sequence. If any of the standards fall outside their daily retention time window, the system is out of control. In such cases, the cause of the problem must be determined and corrected.

9.5.5 When quantifying on a peak area basis by internal or external calibration, peak area integration for the aliphatic and aromatic carbon ranges must be <u>from baseline</u> (i.e. must include the unresolved complex mixture "hump" areas).

9.6 **Calculations**

9.6.1 <u>External Standard Calibration</u>

The concentration of each hydrocarbon range in a sample may be determined by calculating the amount of hydrocarbon range compounds injected, from the peak response, using the calibration curve or the calibration factor determined in Section 9.4.

9.6.1.1 **Aqueous samples:**

The general equation to determine the concentration of a hydrocarbon range in aqueous samples in provided in Equation 6.

Equation 6

$$Concentration\ (ug / L) = \frac{(A_x)(A)(V_t)(D)}{(A_s)(V_i)(V_s)}$$

w

here:

A_x = Response for a hydrocarbon range in the sample, units may be in area counts or peak height.

A = Amount of standard injected, ng.

A_s = Response for the external standard, units same as for A_x.

V_i = volume of extract injected, µL.

D = Dilution factor: if no dilution was made, D = 1, dimensionless.

V_t = Volume of total extract, µL.

V_s = Volume of sample extracted, mL.

If a Calibration Factor is used, the concentration of a hydrocarbon range may be calculated using Equation 7.

Equation 7

$$Conc\ HC\ Range\ (ug / L) = \frac{(A_X)(V_t)(D)}{(V_i)(V_s)(Range\ CF)}$$

where:

Range CF = Calibration Factor for hydrocarbon ranges (collective area count/collective mass).

9.6.1.2 **Nonaqueous samples:**

The general equation to determine the concentration of a hydrocarbon range in soil or sediment samples is provided in Equation 8.

Equation 8

$$Concentration\ (ug / kg) = \frac{(A_x)(A)(V_t)(D)}{(A_s)(V_i)(W_d)}$$

where:

W_d = Dry weight of sample extracted, g. (See Equations 12 through 14)

A_x, A_s, A, V_t, D, and V_i have the same definition as for aqueous samples.

If a Calibration Factor is used, the concentration of specific hydrocarbon ranges in a soil or sediment sample may be calculated using Equation 9.

Equation 9

$$Conc\ HC\ Range\ (ug / kg) = \frac{(A_x)(V_t)(D)}{(V_i)(W_d)(Range\ CF)}$$

where:

Range CF = Calibration Factor for a hydrocarbon range (collective area count/collective mass).

9.6.2 Internal Standard Calibration

The concentration of each hydrocarbon range in a sample may be determined by calculating the amount of hydrocarbon range compound(s) injected, from the peak response, based upon the compound/internal-standard response ratio.

9.6.2.1 **Aqueous samples:**

The general equation to determine the concentration of a specific hydrocarbon range in aqueous samples is provided in Equation 10.

Equation 10

$$Concentration\ (ug / L) = \frac{(A_x)(C_{is})(D)}{(A_{is})(RF)(V_s)}$$

where:

A_x = Response of the hydrocarbon range being measured, units may be in area counts or in peak height.

C_{is} = Amount of internal standard added to extract, ng.

D = Dilution factor, if a dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

A_{is} = Response of the internal standard, units same as A_x.

RF = Response factor for the hydrocarbon range, dimensionless.

V_s = Volume of aqueous sample extracted, mL.

9.6.2.2 **Nonaqueous samples:**

The general equation to determine the concentration of a specific or hydrocarbon range in soil or sediment samples is provided in Equation 11.

Equation 11

$$Concentration\ (ug / kg) = \frac{(A_x)(C_{is})(D)}{(A_{is})(RF)(W_d)}$$

where:

W_d = Dry weight of sample extracted, g. (See Equations 12 through 14).

A_x, C_{is}, D, A_{is}, and RF have the same definition as for aqueous samples.

9.6.3 Calculation of Dry Weight of Sample

In order to calculate the dry weight of sample extracted (W_d), it is necessary to determine the moisture content of the soil/sediment sample, using the procedure outlined in Section 9.1.7. Using the data obtained from Section 9.1.7, W_d is calculated using Equations 12 through 14.

Equation 12

$$\% \text{ Moisture} = \frac{g \text{ sample} - g \text{ dry sample}}{g \text{ sample}} X\ 100$$

Equation 13

$$\% \text{ Dry Solids} = (1) - (\% \text{ Moisture})$$

Equation 14

$$W_d\ (g) = (\% \text{ Dry Solids})(g \text{ of extracted sample})$$

10.0 QUALITY CONTROL

10.1 **General Requirements and Recommendations**

10.1.1 Each laboratory that uses this method should operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance standards for the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

10.1.2 Hexane or methylene chloride solvent blanks should be run after samples suspected of being highly contaminated to determine if sample carryover has occurred.

10.1.3 At a minimum, for each analytical batch (up to 20 samples), a Laboratory Method Blank, Laboratory Fortified Blank Spike (Water or Soil), Laboratory Fortified

Matrix Spike, and sample duplicate must be analyzed. For analytical batches with more than 10 samples, the analysis of an additional mid-range calibration check standard is recommended. The blank and spiked samples must be carried through all stages of the sample preparation and measurement process.

10.1.4 The recommended sequence of analysis is as follows:

(1) Calibration Standards (initial) or mid-range Calibration Check (Verification) Standard (i.e. daily check of initial calibration)
(2) Laboratory Method Blank
(3) Samples
(4) QC Samples
(5) Mid-range Calibration Check (Verification) Standard (also recommended after each 10 samples)

10.1.5 It is recommended that a system of control charts be developed to plot surrogate standard recoveries as a function of time. When surrogate recovery from a sample, blank, or QC sample is less than 50% or more than 150%, check calculations to locate possible errors, the fortifying solution for degradation, and changes in instrument performance. If the cause cannot be determined, the analyst may reanalyze the sample extract, report the surrogate values as outside acceptance limits or, if additional sample is available, re-extract and reanalyze the sample.

10.2 **Minimum Instrument QC**

10.2.1 The instrument must be able to achieve adequate separation and resolution of peaks of interest.

10.2.1.1 The n-octane (n-C8) and toluene peaks must be adequately resolved from the solvent front of the chromatographic run.

10.2.1.2 The surrogates COD and OTP and any internal standards used must be adequately resolved from any individual components in the Aliphatic Hydrocarbon and Aromatic Hydrocarbon standards.

10.2.2 Retention time windows must be established for each hydrocarbon range of interest each time a new GC column is installed, and must be verified and/or adjusted on a daily basis. (See Section 9.3)

10.2.3 Calibration curves must be developed based upon the analysis of calibration standards prepared at a minimum of 5 concentration levels. The linearity of calibration or response factors may be assumed if the percent relative standard deviation (%RSD) over the working range of the curve is less than or equal to 20 %. Alternatively, if linear regression analysis is used for

quantitation, the correlation coefficient (r) must be at least 0.99. and the percent difference (% D) of the response for any hydrocarbon range from the predicted response may not vary by more than +/- 20%. (See Section 9.4.)

10.3 **Initial and Periodic Method QC Demonstrations**

The following must be conducted as an initial demonstration of laboratory capability, prior to the analysis of any samples. Subsequent to this initial demonstration, additional evaluations of this nature should be conducted on a periodic basis, in response to changes in instrumentation or operations, and/or in response to confirmed or suspected systems, method, or operational problems.

10.3.1 Accuracy and Precision

To demonstrate initial laboratory capability, analyze a minimum of four replicate reagent water and/or clean sand blanks spiked with the calibration compounds for each range of interest at approximately 50 µg/L and/or 5 mg/kg, respectively.

10.3.1.1 Extract and analyze each replicate according to the procedures described in Section 9.0.

10.3.1.2 Calculate the measured concentrations of each range in all replicates, the mean accuracy (as a percentage of true value) for each compound, and the precision (as %RSD) of the measurements for each compound.

10.3.1.3 For each compound, the mean accuracy, expressed as a percentage of the true value, should be between 70 % and 130 %. For each compound, the %RSD must be less than or equal to 20%.

10.3.2 Method Detection Limits (Optional)

Analyze a minimum of seven replicate reagent water and/or clean sand blanks which have been fortified with all analytes of interest at approximately 0.5 to 2 µg/L and/or 1.0 to 5.0 mg/kg, respectively. Extract and analyze each replicate according to the procedures described in Section 9.0. Calculate the Method Detection Limit (MDL) of each analyte using the procedure described in Section 12.0.

10.3.2.1 Water MDLs are determined by extracting 7 to 10 replicates of 1-L reagent water blanks spiked with OTP, COD and each analyte of interest.

10.3.2.2 Soil/sediment MDLs are determined by extracting 7-10 replicates of 10-g of EPH-free sand blanks spiked with OTP, COD, and each analyte of interest.

10.3.3 Fractionation

To demonstrate the capability of properly fractionating aliphatic and aromatic hydrocarbons in a sample, the analyst must first prepare and analyze the Fractionation Check Solution specified in Section 7.6.

10.3.3.1 Prepare a silica gel column as outlined in 9.1.4

10.3.3.2 Load 1.0 mL of the Fractionation Check Solution onto column and proceed with the elution and collection of the aliphatic and aromatic fractions as outline in 9.1.4.

NOTE: The amount of pentane used during the elution/fractionation is critical. Excessive pentane will cause elution of aromatics into the aliphatic fraction. Insufficient pentane will cause low recoveries of the aliphatic fraction. The volume of pentane and/or methylene chloride/pentane recommended may need to be adjusted to meet QC limits.

10.3.3.3 Solvent exchange the aliphatic fraction to hexane and the aromatic fraction to methylene chloride. Concentrate each solution to a final volume of 1.0 mL under a gentle stream of nitrogen from an nitrogen blowdown apparatus.

10.3.3.4 Transfer the final 1.0 mL extracts to two labeled glass auto sampler vials with teflon-lined rubber crimp caps. Analyze by GC/FID (see Section 9.0).

10.3.3.5 For each analyte within the Fractionation Check Solution, the mean accuracy, expressed as a percentage of the true value, must be between 70 % and 130 %.

10.3.4 Petroleum Reference Standard

As an optional demonstration of the validity and relevance of EPH calibration, analyze a reagent water and/or clean sand blank spiked with a known concentration of a neat petroleum product.

10.3.4.1 Dilute a Petroleum Reference Standard stock standard solution with acetone to a concentration of approximately 250 ng/µL. Spike a 1 Liter reagent water blank or 10 g clean sand blank with 1.0 mL of this spiking solution. Extract and analyze in accordance with the procedures outlined in Section 9.0.

10.3.4.2 Calculate the total concentration of all petroleum hydrocarbons within each range. Add these values together.

10.3.4.3 The concentration calculated in Paragraph 10.3.4.2 is expected to be within +/- 30 % of the known concentration of Petroleum Standard in the reagent water or sand blank.

10.4 **Ongoing Method QC Demonstrations**

10.4.1 Each sample, blank, and matrix spike sample must be spiked with the surrogate spiking solution. Required surrogate recovery is 60% to 140%.

10.4.2 At a minimum, with every batch of 20 samples or less the lab must analyze the following:

10.4.2.1 **Calibration Check Standard** - A mid-range calibration standard, prepared from the same stock standard solution used to develop the calibration curve, must be analyzed prior to sample analysis to verify the calibration state of the instrument. For large analytical batches that contain more than 10 samples, the analysis of an additional mid-range calibration check standard is recommended after the analysis of the tenth sample. If the percent difference (% D) of any compound within a calibration check standard varies from the predicted response by more than 20 %, a new calibration curve must be prepared. (See Section 9.4)

10.4.2.2 **Laboratory Method Blank** - A water or soil laboratory method blank is prepared by fortifying a reagent water or clean sand blank with 1.0 mL of the surrogate spiking solution. Peaks within the retention time windows of any hydrocarbon ranges of interest may not be present at or above the lowest calculated PQL for any sample within its batch. When determining the PQL of soil method blanks, incorporate the lowest percent solids value found for any sample within its batch in the calculation.

10.4.2.3 **Laboratory Fortified Blank Spike** - A water or soil component spike is prepared by fortifying a reagent water or clean sand blank with 1.0 mL of the matrix spiking solution. The spike recovery must be between 70 % and 130 % and, if these values can not be obtained, the analyst must identify and correct the problem before analyses can continue.

10.4.2.4 **Sample duplicates** - Sample duplicates may be laboratory duplicates or field duplicates and the RPD of the duplicate samples should not exceed +/- 25%. The lack of sample homogeneity may contribute to the RPD's values for duplicates which exceed this value. Should the values exceed 25% the analyst must report that occurrence.

10.4.2.5 **Laboratory Fortified Matrix (LFM) Spike** - The water or soil LFM spike is prepared by fortifying an actual water or soil sample with 1.0 mL of the matrix spiking solution. The purpose of the LFM spike is to

determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations. The corrected concentrations of each analyte within the LFM spike sample must be within 70 to 130 % of the true value. Should the values determined exceed this range, the analyst must report that occurrence.

10.4.3 If any of the performance standards specified in Section 10.4 are not met, the problem should be corrected before further samples are analyzed. Exceptions to this are duplicate samples RPD's and high recoveries for LFM spikes which, due to sample non-homogeneity, may exceed the allowable limits. Any samples run between the last calibration check standard that meet the criteria and one that does not must be reanalyzed. If this is not possible, then the data must be reported as an "estimated concentration."

11.0 DATA PRODUCTION AND REPORTING

11.1 **Sample Analysis**

11.1.1 Aliphatic Fraction

11.1.1.1 Determine the total area count for all peaks eluting 0.1 minutes before the retention time (Rt) for C8 to 0.1 minutes after the Rt for C10.

11.1.1.2 Determine the total area count for all peaks eluting 0.1 minutes after the Rt for C10 to 0.1 minutes after the Rt for C12. Determine the total area count of all peaks eluting 0.1 minutes after the Rt for C12 to 0.1 minutes after the Rt for C16, for all peaks eluting 0.1 minutes after the Rt for C16 to 0.1 minutes after the Rt for C21and for all peaks eluting 0.1 minutes after the Rt for C21 to 0.1 minutes after the Rt for C34. It is not necessary to identify or quantitate individual aliphatic compounds within these ranges.

11.1.1.3 Determine the peak area count for the surrogate COD and any internal standard used. Subtract these values from the collective area count value within the appropriate hydrocarbon range(s).

11.1.1.4 Using the equations contained in Section 9.6 or linear regression analysis, calculate the concentrations of C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 Alipiphatic Hydrocarbon ranges and the surrogate standard COD.

11.1.1.5 The term "all peak areas" must include any unresolved envelope of peaks which elute within the Rt windows listed above and below for the aliphatic and aromatic fractions.

11.2.1 Aromatic Fraction

11.2.1.1 Determine the total area count for all peaks eluting 0.1 minutes before the retention time (Rt) for toluene to 0.1 minutes after the Rt for 1,2,3 trimethylbenzene. In the same manner, determine the total area count for all peaks eluting 0.1 minutes after the Rt for 1,2,3-trimethylbenzene to 0.1 minutes after the Rt for naphthalene, from 0.1 minutes after the Rt for naphthalene to 0.1 minutes after the Rt for acenaphthene, from 0.1 minutes after the Rt for acenaphthene to 0.1 minutes after the Rt for pyrene and 0.1 minutes after the Rt for pyrene to 0.1 minutes after the Rt for benzo(g.h.i)perylene.

11.2.1.2 Determine the peak area count for the surrogate OTP and any internal standard used.

11.2.1.3 Subtract the peak area value from 11.2.1.2 from the collective area count value for the range effected determined in 11.2.1.1 to calculate the area count for Aromatic Hydrocarbons ranges.

11.2.1.4 Using the equations contained in Section 9.6 or linear regression analysis, calculate the concentrations of C8 through C10, >C10 through C12, >C12 through C16 , >C16 through C21 and >C21 through C34 Aromatic Hydrocarbons and the surrogate standard COD.

11.3 Data Reporting Format

11.3.1 The following information and data must be reported:

11.3.1.1 The sample matrix (aqueous, soil or sediment);

11.3.1.2 The date(s) the sample was collected, received by the laboratory, extracted, and analyzed;

11.3.1.3 A description of the sample(s) received by the laboratory, relative to the physical condition of the containers, the temperature of the samples, and use of appropriate preservatives;

11.3.1.4 Moisture content (for soil/sediment samples);

11.3.1.5 The calculated concentrations of C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 Aliphatic Hydrocarbons, and C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 Aromatic Hydrocarbons.

11.3.1.6 Surrogate recovery (expressed as percent recovery);

11.3.1.7 The concentration units for aqueous samples are expressed as ug/L or mg/L and soil or sediment samples the units are expressed as µg/Kg or mg/Kg on a dry-weight basis.

12.0 METHOD PERFORMANCE

12.1 **Method Detection Limits (Optional)**

12.1.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

12.1.2 The MDL is determined according to Equation 15.

Equation 15

$$MDL = (t) \times (SD)$$

where:

t = student t value at the 99% confidence level.

SD = standard deviation of the replicate analysis.

Student t values are as follows:

Number of replicates	t value
7	3.14
8	3.00
9	2.90
10	2.82

12.2 **Single Laboratory Accuracy, Precision and MDL Data**

Single laboratory accuracy, precision and MDL data for method analytes are provided in Tables 1-1 through 1-4 in Appendix 1. Tables 1-1 and 1-2 present data collected from spiking reagent water at 5.0 µg/L; Tables 1-3 and 1-4 by spiking sand at 1.0 mg/kg.

13.0 REFERENCES

1. Massachusetts Department of Environmental Protection and ABB Environmental Services, Inc., Wakefield, MA "Interim Petroleum Policy: Development of Health-based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter," August 1994.

2. USEPA, "Measurement of Petroleum Hydrocarbons: Report on Activities to Develop a Manual." Prepared by Midwest Research Institute, Falls Church, VA, under EPA Contract #68-WO-0015, WA No. 4; submitted to USEPA Office of Underground Storage Tanks, Washington, DC; November 20, 1990.

3. USEPA Federal Register 40 CFR Part 136, Appendix B, "Guidelines Establishing Test procedures for the Analysis of Pollutants," July 1992.

4. USEPA Test Methods for Evaluating Solid Waste (SW-846); Method 3510: Separatory Funnel Liquid-Liquid Extraction; September 1986.

5. USEPA Test Methods for Evaluating Solid Waste (SW-846); Method 3540: Soxhlet Extraction; September 1986.

6. USEPA Test Methods for Evaluating Solid Waste (SW-846); Method 3630: Silica Gel Cleanup; September 1986.

7. USEPA Test Methods for Evaluating Solid Waste (SW-846): Method 8000: Gas Chromatography; September 1986.

8. USEPA Test Methods for Evaluating Solid Waste (SW-846); Method 8100: Polynuclear Aromatic Hydrocarbons; September 1986.

9. Wisconsin Department of Natural Resources, "Modified DRO - Method for Determining Diesel Range Organics," PUBL-SW-141, 1992.

APPENDIX 1

SINGLE LABORATORY ACCURACY, PRECISION, AND METHOD DETECTION LIMITS (MDL) DATA FOR VPH

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Table 1-1. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Compounds in Component Standard Spiked Into Reagent Water and Analyzed by the VPH Method

Compound	Spiked Conc. (µg/L)	Method Accuracy[a] (Mean % Recovery[b])		Method Precision[a] (RSD[c] - %)		MDL[a] (µg/L)	
		PID[d]	FID[e]	PID	FID	PID	FID
n-Pentane	6.0		98		7.8		1.4
Methyl tert butylether	1.8	77	79	4.8	15	0.21	0.69
Benzene	0.6	82	97	4.9	10	0.08	0.19
Toluene	0.6	79	104	7.3	6.5	0.11	0.13
n-Nonane	2.0		83		8.0		0.42
Ethylbenzene	0.6	77	94	4.2	9.1	0.06	0.16
m- & p-Xylene	1.2	68	85	4.3	6.4	0.11	0.20
o-Xylene	0.6	79	88	16	6.4	0.23	0.11
1,2,3-Trimethylbenzene	0.6	69	89	8.2	6.4	0.11	0.11
Naphthalene	3.6	58	56	16	18	1.0	1.2
2,5-Dibromotoluene (surrogate)	40	88	92	4.9	13		

[a] Based on analysis of seven samples spiked with component standard.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] PID = photoionization detector.
[e] FID = flame ionization detector.

Table 1-2. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Compounds in Component Standard Spiked Into VPH- Free Sand and Analyzed by the VPH Method

Compound	Spiked Conc. (µg/Kg)	Method Accuracy[a] (Mean % Recovery[b])		Method Precision[a] (RSD[c] - %)		MDL[a] (µg/Kg)	
		PID[d]	FID[e]	PID	FID	PID	FID
n-Pentane	120		124		6.0		28
Methyl tert butylether	120	70	96	3.1	27	8.1	99
Benzene	60	122	128	3.3	5.4	7.6	13
Toluene	60	139	137	4.8	8.6	13	22
n-Nonane	120		119		4.6		21
Ethylbenzene	60	107	103	4.3	5.0	8.6	9.7
m- & p-Xylene	120	109	104	4.1	5.2	17	20
o-Xylene	60	103	111	3.8	6.6	7.4	14
1,2,3-Trimethylbenzene	60	93	102	5.5	5.3	9.6	10
Naphthalene	ND[f]	ND	ND	ND	ND	ND	ND
2,5-Dibromotoluene (surrogate)	2,000	119	117	8.6	9.7		

[a] Based on analysis of seven samples spiked with component standard.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] PID = photoionization detector.
[e] FID = flame ionization detector.
[f] ND = not determined.

Table 1-3. Single Laboratory Accuracy and Precision for Compounds in Component Standard Spiked Into Reagent Water at Concentrations in the Low to Middle End of the Analytical Range and Then Analyzed by the VPH Method

Compound	Spiked Conc. (µg/L)	Method Accuracy[a] (Mean % Recovery[b])		Method Precision[a] (RSD[c] - %)	
		PID[d]	FID[e]	PID	FID
n-Pentane	40		96		7.7
Methyl tert butylether	60	87	88	4.0	3.9
Benzene	20	99	99	4.4	3.7
Toluene	60	99	99	4.1	4.0
n-Nonane	40		104		10
Ethylbenzene	20	99	99	4.2	4.2
m- & p-Xylene	80	99	99	4.3	4.2
o-Xylene	40	99	99	3.7	3.6
1,23-Trimethylbenzene	40	99	99	4.1	4.0
Naphthalene	40	70	81	4.3	3.2
2,5-Dibromotoluene (surrogate)	40	92	94	5.2	4.6

[a] Based on analysis of five samples spiked with component standard.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] PID = photoionization detector.
[e] FID = flame ionization detector.

Table 1-4. Single Laboratory Accuracy and Precision for Compounds in Component Standard Spiked Into VPH-Free Sand at Concentrations in the Low to Middle End of the Analytical Range and Then Analyzed by the VPH Method

Compound	Spiked Conc. (mg/Kg)	Method Accuracy[a] (Mean % Recovery[b])		Method Precision[a] (RSD[c] - %)	
		PID[d]	FID[e]	PID	FID
n-Pentane	2.0		118		1.9
Methyl tert butylether	3.0	100	94	2.4	2.8
Benzene	2.0	119	109	3.0	0.7
Toluene	2.0	118	109	1.7	1.3
n-Nonane	ND	ND	ND	ND	ND
Ethylbenzene	1.0	121	110	1.4	1.2
m- & p-Xylene	3.0	122	110	1.4	1.1
o-Xylene	2.0	118	107	1.3	1.1
1,2,3-Trimethylbenzene	2.0	115	109	1.4	1.3
Naphthalene	2.0	61	57	11	1.8
2,5-Dibromotoluene (surrogate)	2.0	75	64	9.7	3.3

[a] Based on analysis of five samples spiked with component standard.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] PID = photoionization detector.
[e] FID = flame ionization detector.
[f] ND = not determined.

APPENDIX 2

SUGGESTED VPH DATA REPORTING FORMAT

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VOLATILE PETROLEUM HYDROCARBON (VPH) ANALYSIS

Client:
Client Sample ID: Date Received:
Laboratory Sample ID: Date Analyzed:
Matrix: Date Reported:
Percent Moisture:

VPH RESULTS

Parameter	Results	PQL				Units
C5-C6 Aliphatics (FID) *						
C6-C8 Aliphatics (FID) *						
C8-C10 Aliphatics (FID) *						
C10-C12 Aliphatics (FID) *						
C8-C10 Aromatics (PID)						
C10-C12 Aromatics (PID)						
C12-C13 Aromatics (PID)						

*** Excludes any MTBE or BTEX compounds**

SURROGATE RECOVERY

Surrogate	%Recovery	Acceptance Range
2,5-dibromotoluene		80% - 120%

TARGETED VPH ANALYTES

Analyte	**Results**	**PQL**	**Units**
Methyl tert butylether			
Benzene			
Toluene			
Ethylbenzene			
p-Xylene *			
m-Xylene *			
o-Xylene			
Naphthalene			

* p and m-xylenes may not be able to be resolved and may be reported as the total of p and m-xylenes.

APPENDIX 3

SINGLE LABORATORY ACCURACY, PRECISION, AND METHOD DETECTION LIMIT (MDL) DATA FOR EPH

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Table 1-1. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Alkanes Spiked Into Reagent Water and Analyzed by the EPH Method

Compound[a]	Compound Conc. Measured (µg/L)		Mean Accuracy (Mean % Recovery[b])	Method Precision (RSD[c] - %)	MDL (µg/L)
	Mean	Std. Dev.			
C_{10}	4.1	0.040	82	0.98	0.12
C_{12}	4.1	0.021	82	0.51	0.064
C_{16}	4.0	0.062	80	1.6	0.19
COD[d]	44	0.93	88	2.1	-
C21	3.7	0.047	74	1.3	0.14

[a] Compounds were spiked into 7 or 8 samples at a concentration of 5.0 µg/L.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] Surrogate (COD = 1-Chloro-octadecane) was spiked into three samples at a concentration of 50 µg/L.

Table 1-2. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Polynuclear Aromatic Hydrocarbons (PAHs) Spiked Into Reagent Water and Analyzed by the EPH Method

Compound[a]	Compound Conc. Measured (µg/L)		Mean Accuracy (Mean % Recovery[b])	Method Precision (RSD[c] - %)	MDL (µg/L)
	Mean	Std. Dev.			
Naphthalene	5.6	0.088	112	1.6	0.26
2-Methylnaphthalene	6.4	0.096	128	1.5	0.29
Acenaphthylene	5.6	0.085	112	1.5	0.26
Acenaphthene	5.7	0.092	114	1.6	0.28
Fluorene	5.6	0.094	112	1.7	0.28
Phenanthrene	5.5	0.097	110	1.8	0.29
Anthracene	7.0	0.10	140	1.4	0.31
OTP[d]	44	1.6	88	3.6	-
Fluoranthene	5.7	0.090	114	1.6	0.27
Pyrene	6.1	0.098	122	1.6	0.29
Benzo(a)Anthracene	5.9	0.089	118	1.5	0.27
Chrysene	5.8	0.098	116	1.7	0.29
Benzo(b)Fluoranthene	6.3	0.082	126	1.3	0.25
Benzo(k)Fluoranthene	5.6	0.065	112	1.2	0.20
Benzo(a)Pyrene	6.0	0.075	120	1.2	0.22
Indeno(123 cd)Pyrene	5.1	0.17	102	3.3	0.50
Dibenzo(ah)Anthracene	2.8	0.21	56	7.5	0.62
Benzo(ghi)Perylene	3.8	0.18	76	4.7	0.54

[a] Compounds were spiked into 7 or 8 samples at a concentration of 5.0 µg/L.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] Surrogate (OTP = ortho-Terphenyl) was spiked into three samples at a concentration of 50 µg/L.

Table 1-3. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Alkanes Spiked Into EPH-Free Sand and Analyzed by the EPH Method

Compound[a]	Compound Conc. Measured (mg/Kg)		Mean Accuracy (Mean % Recovery[b])	Method Precision (RSD[c] - %)	MDL (mg/Kg)
	Mean	Std. Dev.			
C_{10}	0.72	0.074	72	10	0.22
C_{12}	0.83	0.079	83	9.5	0.24
C_{16}	1.2	0.14	120	12	0.42
COD[d]	4.3	0.48	86	11	-
C21	0.81	0.044	81	5.4	0.13

[a] Compounds were spiked into 8 samples at a concentration of 1.0 mg/Kg.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] Surrogate (COD = 1-Chloro-octadecane) was spiked into three samples at a concentration of 5.0 mg/kg.

Table 1-4. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Polynuclear Aromatic Hydrocarbons (PAHs) Spiked Into EPH-Free Sand and Analyzed by the EPH Method

Compound[a]	Compound Conc. Measured (mg/Kg)		Mean Accuracy (Mean % Recovery[b])	Method Precision (RSD[c] - %)	MDL (mg/Kg)
	Mean	Std. Dev.			
Naphthalene	0.64	0.063	64	9.8	0.19
2-Methylnaphthalene	0.64	0.058	64	9.1	0.17
Acenaphthylene	0.68	0.060	68	8.8	0.18
Acenaphthene	0.70	0.064	70	9.1	0.19
Fluorene	0.79	0.060	79	7.6	0.18
Phenanthrene	0.83	0.041	83	4.9	0.12
Anthracene	1.2	0.082	120	6.8	0.25
OTP[d]	4.8	0.45	96	9.4	-
Fluoranthene	0.92	0.038	92	4.1	0.12
Pyrene	0.91	0.037	91	4.1	0.11
Benzo(a)Anthracene	0.96	0.042	96	4.4	0.12
Chrysene	0.90	0.050	90	5.6	0.15
Benzo(b)Fluoranthene	0.96	0.038	96	4.0	0.11
Benzo(k)Fluoranthene	0.87	0.037	87	4.3	0.11
Benzo(a)Pyrene	0.96	0.036	96	3.8	0.11
Indeno(123 cd)Pyrene	0.90	0.033	90	3.7	0.099
Dibenzo(ah)Anthracene	0.82	0.033	82	4.0	0.099
Benzo(ghi)Perylene	0.82	0.032	82	3.9	0.096

[a] Compounds were spiked into 7 or 8 samples at a concentration of 1.0 mg/Kg.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] Surrogate (OTP = ortho-Terphenyl) was spiked into three samples at a concentration of 5.0 mg/kg.

APPENDIX 4

SUGGESTED EPH DATA REPORTING FORMAT

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EXTRACTABLE PETROLEUM HYDROCARBON (EPH) ANALYSIS

Client:	
Client Sample ID:	Date Received:
Laboratory Sample ID:	Date Extracted:
Matrix:	Date Analyzed:
Percent Moisture:	Date Reported:

EXTRACTABLE PETROLEUM HYDROCARBON (EPH)

Parameter	Results	PQL				Units
C8-C10 Aliphatics						
C10-C12 Aliphatics						
C12-C16 Aliphatics						
C16-C21 Aliphatics						
C21-C34 Aliphatics						
C8-C10 Aromatics						
C10-C12 Aromatics						
C12-C16 Aromatics						
C16-C21 Aromatics						
C21-C34 Aromatics						

SURROGATE RECOVERIES

Surrogate	%Recovery	Acceptance Range
Chloro-octadecane (COD)		50% - 150%
Ortho-terphenyl (OTP)		50% - 150%

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APPENDIX 5

REPORT OF ANALYSIS

SUMMARY SHEET

Client: Client Sample ID Number(s): Laboratory ID Number(s):

SAMPLE INFORMATION

Sample Matrix	¨ Aqueous ¨ Soil ¨ Sediment ¨ Other:	
Analysis Performed	¨ VPH ¨ EPH ¨ VPH and EPH (E-TPH Duplicate samples)	
Condition of Containers	¨ Satisfactory ¨ Broken ¨ Leaking ¨ Other:	
Sample Preservatives	AQUEOUS	¨ N/A ¨ pH ≤ 2 ¨ pH > 2
	SOIL/SEDIMENT	¨ N/A
Sample Temperature	¨ Received on Ice ¨ Received at 4 °C ¨ Other	

ANALYTICAL RESULTS

Parameter	Results	PQL	Units
Volatile Petroleum Hydrocarbons (VPH)			
Extractable Petroleum Hydrocarbons (EPH)			
Equivalent TPH (E-TPH) ** [IF BOTH VPH AND EPH ANALYSES PERFORMED]			

**** Due to overlapping carbon ranges between the VPH and EPH methods and in order to avoid double counting, the analyst must select the higher of the two values to be included for reporting purposes for those ranges effected.**

COMMENTS

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APPENDIX 6*

Petroleum Product Chromatograms

Carburator Cleaner
Automotive Gasoline
Mineral Spirits #1
Mineral Spirits #2
JP-4 Jet Fuel (old)
JP-4 Jet Fuel (new)
JP-5 Jet Fuel
Kerosene
Kerosene (ICP grade)
Gasoline and #2 Diesel Oil
Natural Gas Condensate
#2 Fuel Oil
#2 Fuel Oil (38% aromatic) (See chromatogram in NWTPH-Dx)
#2 Diesel Oil (See chromatogram in NWTPH-Dx)
#2 Diesel Oil and Motor Oil (30w) (See chromatogram in NWTPH-Dx)
2-Cycle Engine Oil #1
2-Cycle Engine Oil #2
2-Cycle Engine Oil #3
Motor Oil (30w) (See chromatogram in NWTPH-Dx)
Automatic Transmission Fluid
Power Steering Fluid
Transformer Oil (used)
Transformer Oil (new)
Hydraulic Fluid #1
Hydraulic Fluid #2
Hydraulic Fluid #3
Mineral Oil #1
Mineral Oil #2
Cutting Oil #1
Cutting Oil #2
Bunker-C #1
Bunker-C #2
CSS-1 (emulsion asphalt)
AR-4000 (asphalt cement)

Non-petroleum Product Chromatograms

Turpentine
Creosote
Synthetic Motor Oil

*** The chromatograms are not available in the "electronic" version. They are included in the printed publication.**

Chromatograms: NWTPH-Gx

Gasoline
Weathered Gasoline
Naphtha
Mineral Spirits #1
Mineral Spirits #2
Mineral Spirits #3

Chromatograms: NWTPH-Dx

#2 Diesel Oil
#2 Diesel Oil/Motor Oil
#2 Fuel Oil (38% Aromatic)
Kerosene (Deodorized)
Jet Fuel A
Bunker C #1
Bunker C #2
Motor Oil 30 Wgt.
Mineral Oil (USP)
Hydraulic Fluid
Transformer Oil
Gas Oil

State of Oregon Department of Environmental Quality

OAR 340-177-0005
NW Total Petroleum Hydrocarbon Identification Method

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* The chromatograms are not available in the "electronic" version. They are included in the printed publication.

TOTAL PETROLEUM HYDROCARBONS (TPH)

The following compilation of analytical methods may be used in Oregon and Washington for Underground Storage Tank cleanups and other cleanups of TPH (check with applicable state rules). Each of these Total Petroleum Hydrocarbon (TPH) Methods has its own niche in the overall analytical scheme. The methods are:

NWTPH-HCID.....Hydrocarbon Identification

NWTPH-Gx .....Volatile Petroleum Products (Extended)

NWTPH-Dx .....Semi-volatile Petroleum Products (Extended)

NWTPH-HCID is a qualitative and semi-quantitative screen to determine the presence and type of petroleum products that may exist in water or soil. This method should be used if the type of petroleum contamination is unknown. It should be performed on contaminated soil or water that is representative of the contamination at the site. The results of this method will determine what fully quantitative method/methods, if any, are to be used in determining compliance with the matrix criteria. Should the value of the analysis for gasoline, diesel or heavy oils (or any other identified petroleum product) exceed the reporting limits, then the specific analytical method for that product must be employed.

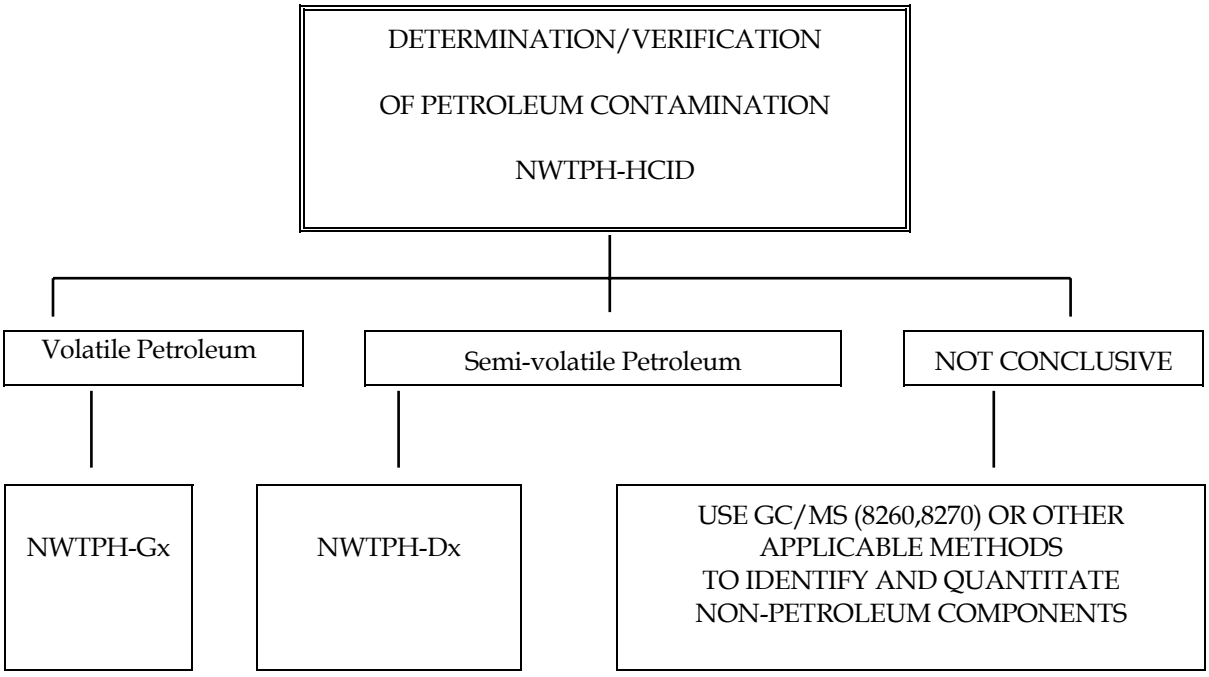
NWTPH-Gx is the qualitative and quantitative method (extended) for volatile ("gasoline") petroleum products in soil and water. Petroleum products applicable for this method include aviation and automotive gasolines, mineral spirits, stoddard solvent and naphtha.

NWTPH-Dx is the qualitative and quantitative method (extended) for semi-volatile ("diesel") petroleum products in soil and water. Petroleum products applicable for this include jet fuels, kerosene, diesel oils, hydaulic fluids, mineral oils, lubricating oils and fuel oils.

NOTE: These "NWTPH" methods result in single TPH values that can be used when compliance with a single cleanup level is desired. When TPH "fractions" are needed, then the VPH and EPH methods must be used.

ANALYTICAL DECISION TREE FOR NWTPH

The following flow chart depicts the laboratory analytical scheme to be used when analyzing samples for single TPH levels. The first step is the qualitative determination of the existence and nature of petroleum contamination and this should be used when the site contamination is unknown. It is required that this first step will be performed on a representative sample from the area that is suspected to be the most contaminated at the site. For those samples containing analytes which, due to their retention times, ratios to each other or their non-hydrocarbon pattern (e.g., creosote), do not suggest petroleum hydrocarbons, then GC/MS methods should be employed to ascertain the components. At those sites where the petroleum contaminants are known or have been identified using the NWTPH-HCID method, the specific product method is to be used.



NWTPH-HCID

Hydrocarbon Identification Method for Soil and Water

Summary

This method is a qualitative and semi-quantitative procedure. It is used for groundwater or surface water, and soil/sediment from sites where the petroleum products are unknown and/or when multiple types of petroleum products are suspected to be present. This method is used to identify petroleum products containing components from C7 to C30 range, as well as heavy oils, with specific product confirmation by pattern matching ("fingerprinting") employing capillary gas chromatography with flame ionization detection (GC/FID). EPA method 3510 has been adapted as the extraction procedure for the water portion of this method.

While this method is intended to be primarily qualitative, it can be used to eliminate the need for further analyses for those samples which demonstrate TPH levels significantly below the regulatory limits. If the sample contains toluene to dodecane (gasoline range), dodecane through tetradecane (diesel range) and/or an unresolved chromatographic envelope greater than tetradecane (e.g. motor oils) above the reporting limits of this method, then the final quantitation must be performed by methods specific for these mixtures. Since the water extraction procedure in this method is identical to that found in the water portion of NWTPH-Dx (semi-volatile petroleum products, i.e. from kerosene through heavy fuel oils), these products may be quantitated using this extract. Because of the possible loss of volatile compounds in the extraction and concentrations steps, gasoline, mineral spirits and other volatile petroleum products that exceed the reporting limits of this method must be quantitated using the NWTPH-Gx method.

The reporting limits for water are 0.25 mg/L for gasoline, 0.63 mg/L for #2 diesel and motor oils. The reporting limits for soil/sediment are 20 mg/Kg for gasoline, 50 mg/Kg for #2 diesel, and 100 mg/Kg for motor oil, all reported on a dry weight basis. These values for soil/sediment assumes 100% solids and will be higher depending on the actual moisture content.

The method relies heavily upon the experience of the analyst for the identification of the specific petroleum product(s) that may be present. Therefore, this method must be run by, or under the direct supervision of, analysts experienced in the use of GC and in the interpretation of gas chromatograms of both fresh and weathered petroleum products.

Equipment and Reagents

Gas Chromatograph, w/wo autosampler
Capillary split/splitless injector
Flame ionization detector
Suggested Capillary Column:
J&W DB-1 or DB-5, 30 M x 0.25 mm or 0.32 mm with 0.25 um film thickness capillary column or equivalent
Chromatography Data System
VOA Vial: 40 mL glass vial with Teflon coated cap septum, Eagle Picher or equivalent
Syringe: Hamilton #701, 10 uL or equivalent
Ultrasonic Bath
Glass Wool: Pyrex or equivalent
Centrifuge tubes: 5 or 15 mL, calibrated in 0.1 mL increments
Analytical Balance: accurate to at least 0.0001 g
Volumetric Flasks: 10 mL, ground glass with ground glass stopper
Separatory funnels: 500 mL, Teflon stopcocks
Kuderna-Danish (KD) Flasks: 250 mL or equivalent
Snyder Columns: 3-ball, 24/40 ground glass joint
Concentrator Tubes: 10 mL
Methylene Chloride: Burdick and Jackson Brand or equivalent
N-Evap Concentrator or equivalent

Standards

Retention Time Standards. Prepare a composite standard, using methylene chloride as the solvent, consisting of toluene, dodecane and tetracosane at 25 ug/mL each. Additional compounds may be added at the discretion of the analyst. The use of this standard is to establish the retention time windows for the quantitation of gasoline #2 diesel and motor oils.

Reference Standards. Prepare individual petroleum product reference standards (i.e. gasoline, mineral spirits, kerosene and #2 diesel oil), using methylene chloride as the solvent, at approximately 50 ug/mL. Prepare a non-synthetic motor oil (pennzoil SAE 30 or equivalent) reference standard at 200 ug/mL. The preparation of reference standards for other types of petroleum products is recommended. The use of these reference standards is to insure the accurate identification of petroleum product contamination by chromatographic pattern matching ("fingerprinting") and establish retention time windows for those petroleum products not determined with the individual compound retention time standard.

Gasoline Stock Standard. A stock standard is prepared by placing approximately 9 mL of methylene chloride in a 10 mL volumetric flask. Tare the flask/methylene chloride and add about five drops of non-oxygenated regular unleaded gasoline, assuring that the liquid falls directly into the methylene chloride without contacting the neck of the flask. Reweigh the flask and dilute to volume with methylene chloride, stopper and mix by inverting the flask several times. It is important that the analyst minimize the amount of time that the flask is left unstoppered, to reduce

the loss of gasoline through volatilization. The use of a commercially prepared gasoline standards is acceptable if it is certified as non-oxygenated gasoline or if the gasoline concentration has been adjusted to reflect the contribution of the oxygenate. Calculate the gasoline concentration as follows:

$$Stock,\ ug / mL = \frac{(final\ wt,\ mg) - (tare\ wt,\ mg)}{10\ mL} \times \frac{1000\ ug}{mg}$$

Note: The use of oxygenated regular unleaded gasoline for the gasoline stock standard is allowed if the weight (mass) of the gasoline used is adjusted for the weight (mass) contribution of the oxygenate to the gasoline. This will necessitate the analysis of the gasoline for the specific oxygenate(s) present to determine the concentration. The analysis for the oxygenates will be conducted by either of the methods published in the Federal Register - Appendix B and C - Testing Procedures - Vol. 57, No. 24, Wednesday, February 5, 1992, Notices.Alternate methods for the analysis of gasoline oxygenates must be approved by the Oregon's Department of Environmental Quality and/or Washington's Department of Ecology prior to use.

Diesel Stock Standard. A stock standard is prepared by adding about five drops of #2 diesel oil stock to tared 10 mL volumetric flask. Reweigh the flask and bring it to volume with methylene chloride, stopper and mix by inverting the flask several times. Calculate the concentration of this standard in the same manner as the gasoline stock standard. The use of a commercially prepared #2 diesel standard is an acceptable alternative to the above procedure.

Motor Oil Stock Standard. A stock standard is prepared by adding about ten drops of a non-synthetic SAE 30 weight motor oil (Pennzoil or equivalent) to a tared 10 mL volumetric flask. Reweigh the flask, bring it to volume with methylene chloride, stopper and mix by inverting the flask several times. Calculate the concentration of this standard in the same manner as the gasoline stock standard. The use of commercially prepared motor oil standards is an acceptable alternative to the above procedure.

Note: The Diesel and Motor Oil Stock Standards required in this method are identical to those required for NWTPH-Dx (extended diesel method including all semi-volatile petroleum products eluting after gasoline, e.g. kerosene, diesels, mineral oils, lubricating oils, heavy fuel oils, etc.).

Surrogate Stock Standard. Suggested surrogates for use in this method are bromofluorobenzene and pentacosane. The use of different or additional surrogates is optional. Prepare the surrogate stock standard by weighing 50 mg of each surrogate compound into a 10 mL volumetric flask, then bring to volume with methylene chloride for a final concentration of 5000 ug/mL for each surrogate compound. The use of a commercially prepared surrogate solution(s) is an acceptable alternative to the above procedure.

Composite Calibration Working Standard. Using serial dilutions of the stock standards, prepare a mixture for water analyses that contains 10 ug/mL of gasoline, 25 ug/mL of #2 diesel oil and the

surrogate standard. For soil/sediment analyses this standard should be prepared to contain 20 ug/mL of gasoline, 50 ug/mL of #2 diesel and the surrogate standard. Add the appropriate volumes, using the equations listed below, and adjusting for the concentration change created by any serial dilutions, of gasoline stock standard, #2 diesel stock standard and the surrogate stock standard to a 10 mL volumetric flask, then dilute to volume with methylene chloride. Stopper and mix by inverting the flask several times. The surrogate standard should be added to a level sufficient to produce a surrogate concentration of between 5 and 50 ug/mL.

$$\textit{Volume Gasoline Stock, uL} = \frac{\textit{20 (soil) / 10 (water) ug / mL x 10 mL}}{\textit{Gasoline Stock Conc, ug / mL}} \; x \; \frac{\textit{1000 uL}}{\textit{mL}}$$

$$\textit{Volume Diesel Stock, uL} = \frac{\textit{50 (soil) / 25 (water) ug / mL x 10 mL}}{\textit{Diesel Stock Conc, ug / mL}} \; x \; \frac{\textit{1000 uL}}{\textit{mL}}$$

This mixture corresponds to 0.25 mg/L gasoline and 0.63 mg/L #2 diesel oil for water and 20 mg/Kg gasoline and 50 mg/Kg diesel in soil following the extraction and analytical procedures of this method.

The motor oil calibration working standard should be made at a concentration of 250 ug/mL for water and 100 ug/mL for soil following the procedure outlined above. This will correspond to a reporting value of 0.63 mg/L for water and 100 mg/kg for soil. If, in the opinion of the analyst, the GC sensitivity to 100 ug/mL of motor oil is insufficient, the analyst is allowed to increase the concentration of this standard and to concentrate a portion of the extract to achieve the reporting limit for soil.

Surrogate Working Standard. Prepare a surrogate working (spiking) standard, using the procedure outlined above, that will yield between 5 ug and 50 ug/mL of the surrogate compounds in the 10 mL sample extract produced in this method.

Note: All samples must be collected in glass jars with Teflon lined lids (Eagle Picher or equivalent) and held at 4 degrees C until extracted. A volume of 400 mL is the minimum sample size to achieve the reporting limits as stated, however, larger volumes are allowed as long as the solvent/sample ratio is maintained. Samples must be extracted within 7 days (for water) or 14 days (for soil/sediment) of the date of collection. The preservation of water samples in the field, to a pH of less than 2 with 1+1 HCL, is recommended.

Extraction Procedures

Water Samples

Mark the water meniscus on the sample jar for later volume determination. Pour the sample into a 500 mL separatory funnel, add the surrogate solution (to achieve the desired concentration in a 10 mL extract). Add 30 mL of methylene chloride to the sample jar, cap and shake the jar vigorously

for a few seconds to wash off any hydrocarbons adhering to the side of the jar. Add this solvent to the separatory funnel, stopper and shake vigorously, venting frequently, for one minute. Allow the two phases to separate, then drain the solvent into a 250 mL K-D flask fitted with a 10 mL concentrator tube. Repeat the extraction twice more using 30 mL of methylene chloride, each time, adding the solvent to the K-D.

Attach a 3-ball Snyder column to the K-D and concentrate the sample extract to 5 - 10 mL on a stream bath. Remove the K-D apparatus and allow it to cool prior to disassembly. During disassembly, rinse the Snyder/K-D joint and K-D/concentrator joint with approximately 1 mL of methylene chloride and add these rinsings to the extract. Adjust the volume of the extract to 10 mL. For those samples which exceed 10 mL, place the concentrator tube into an N-Evap and, under a gentle stream of nitrogen, reduce the volume to 10 mL. Transfer 1 mL of the extract (to be used for the gasoline or gasoline/diesel determination) to an autosampler vial fitted with a screw top and a Teflon coated septum. Concentrate the remainder of the extract (to be used for heavy oils determination) to 0.9 mL, transfer it to an 2 mL autosampler vial equipped with a screw top and a Teflon coated septum. Store both vials in a refrigerator until analysis.

Each extraction set must include one method blank (organic-free water of similar volume to the samples) per 20 samples. The method blank is to receive the surrogate solution and to be extracted and analyzed in the same manner as the samples.

EPA method 3520, Continuous Liquid-Liquid Extraction, may be substituted as an alternate extraction procedure to that outlined above.

Soil Samples

Weigh approximately 10 grams of soil into a 40 mL VOA vial and record the weight to the nearest 0.001 grams. Add 5 grams of anhydrous sodium sulfate, surrogate working solution and 10 mL of methylene chloride to the VOA vial. Cap the vial and place it (no more than 5 at a time) in a sonic bath for 5 minutes. Shake the vials well and return them to the sonic bath for 5 more minutes. A minimum of one method blank per extraction set or 20 samples, whichever is more frequent, must be prepared along with the samples. One sample duplicate must also be extracted for samples set from one to ten samples and two duplicates for sets from eleven to twenty samples.

Determine the moisture content of the samples, for use in the final calculations, by the following procedure. Immediately after weighing the sample for extraction, weigh 5-10 grams of the sample into a tared crucible. Dry the sample/crucible overnight at 105 degrees C. Reweigh the sample/crucible after allowing it to cool to room temperature. Calculate the % solids as follows: [(grams of dry sample/grams of wet sample) x 100].

If the extract contains significant moisture, elute the solvent phase through an anhydrous sodium sulfate micro-column. Place a portion of the extract in a 2 mL autosampler vial (screw cap, Teflon coated septum), taking care to minimize the volume of headspace, and store the vial in a refrigerator until analyzed. Concentration of the extract, when necessary, will be conducted using an N-Evap

with a gentle stream of nitrogen. This concentrate should be stored in the same manner as noted above.

Note: Anhydrous sodium sulfate micro-columns are prepared by plugging a 5 3/4" length disposable Pasteur pipette (pre-rinsed with methylene chloride) with glass wool (precleaned with methylene chloride) and adding approximately 3 cm of anhydrous sodium sulfate (previously muffled at 430 degrees C overnight in a shallow pan and stored in a glass jar with a Teflon lid liner).

For samples containing petroleum products other than gasoline, diesel, or motor oil, the analyst must either prepare calibration standards of them by the methods listed above or analyze the sample by the fully quantitative method, e.g. NWTPH-Gx. Other calibration standards produced for use in this method must be at an equivalent concentration to the previously established standards, e.g. mineral spirits at the gasoline concentration, kerosene at the diesel concentration.

As more information becomes available on new extraction techniques, the Washington State Dept. of Ecology's Manchester Laboratory and Oregon's Department of Environmental Quality will publish descriptions of acceptable alternate extraction methods.

Suggested GC Parameters

Sample injection Volume = 2 uL
Injector Temperature = 290°C
Detector Temperature = 300°C
Hydrogen Flow = 25-35 mL/min
Air Flow = 300-400 mL/min
Make-up Gas Flow = 30 mL/min
GC Temperature Program = Initial temperature of 50°C and hold for 2 minutes; ramp the temperature 10°C/min to 320°C and hold for 5 minutes.

Product Identification

Petroleum products are to be identified by pattern matching with reference product chromatograms generated the same day as the sample analysis. The term "gasoline range" or "diesel range" hydrocarbons, or derivations of them, should only be used when the analyst is unable to identify the petroleum product present. When these terms are used, it is to indicate the presence of compounds eluting from toluene to dodecane, for the former term, and from dodecane through tetracosane, for the latter term. Motor oils, hydraulic fluids and similar petroleum products which present an unresolved chromatographic envelope of compounds, originating or extending beyond tetracosane, may be reported using the collective term, lube oil, unless specific identification is possible. Heavy fuel oils, e.g. fuel oil #6 or Bunker C, which contain a diesel range component as well as a lube oil (and higher) range may be reported using the collective term, heavy fuel oil, unless specific identification is possible. These products should not, however, be confused with mixtures of #2 diesel and motor oils.

Note: The actual identification of the grade or type of lube oil and heavy fuel oil may require equipment and techniques beyond the scope of this method.

Analysis Procedure

The analysis is accomplished by injecting 2 uL of the 10 mL extract, either manually or by autosampler, into the GC using the splitless injection mode. The results from this injection are, for quantitation purposes, compared directly against the single point calibration standard for the product(s) identified. The injection of 2 uL of the concentrated extract (1 mL equivalent) is used primarily for heavy oil determination, because of the reduced sensitivity of the FID to late eluting motor oil-like products. It may be used for the determination of #2 diesel oil and other diesel range petroleum products but it may not be used for the determination of gasoline or gasoline range petroleum products because of the potential for loss of the more volatile components during the concentration step.

Calculations

Gasoline. The area of the components, toluene to dodecane of the calibration standard, is integrated to the baseline as a group. The samples and method blanks are integrated in the same manner and the group areas are compared. If the sample area exceeds the calibration standard area, proceed with method NWTPH-Gx for accurate quantitation using a fresh aliquot of the sample. If the sample area does not exceed the calibration standard area, then report the gasoline concentration as less than 0.25 mg/L for water or 20 mg/kg for soil. This soil value for gasoline, and the subsequent petroleum products, assumes 100% solids and will be higher depending on the actual moisture content.

Other volatile petroleum products, identified as being present (e.g. mineral spirits), must be compared to the appropriate standard produced at the same concentration as gasoline. The requirement for further analyses is determined following the criteria for gasoline as noted above.

Note: For samples containing only #2 diesel oil, kerosene, etc., the portion of these products, that elute within the retention time range of gasoline, should not be identified and/or quantitated as gasoline or gasoline range petroleum.

Diesel. The area of the components, dodecane through tetracosane of the calibration standard, is integrated to the baseline as a group. This integration must include the unresolved envelope of compounds as well as the discrete component peaks. The sample is integrated in the same manner and the group areas are compared. If the sample area exceeds the calibration standard area, then proceed to method NWTPH-Dx. If the sample does not exceed the calibration standards area, then report the #2 diesel concentration as less than 0.63 mg/L for water or 50 mg/Kg for soil.

Other semi-volatile petroleum products, identified as being present (e.g. kerosene), must be compared to the appropriate standard produced at the same concentration as #2 diesel. The requirement for further analyses is determined following the criteria for #2 diesel as noted above.

Lube Oil. For those samples which consist primarily of only an unresolved chromatographic envelope of components eluting after tetracosane, compare their area to the area of the motor oil standard by integrating the unresolved envelope to baseline. If the sample exceeds the standard area, then proceed to method NWTPH-Dx. If the sample area is less than the standard, then report the lube oil concentration as less than 0.63 mg/L for water or 100 mg/Kg for soil. Samples identified as containing heavy fuel oil must be quantitated to the same value as lube oil by utilizing a heavy fuel oil standard and following the procedure outlined for lube oil.

Note: The analyst is expected to adjust the retention time windows used for quantitation of petroleum products, other than gasoline, #2 diesel, or motor oil/lube oils, to incorporate the majority of the chromatographable components associated with those identified products.

If, in the judgement of the analyst, the area of an identified petroleum product other than gasoline, diesel, and motor oil would exceed the reporting limit, the analyst is allowed to report a "greater than" value for that product without performing the quantitative analysis. The analyst must then proceed to the appropriate fully quantitative analytical procedure, e.g. NWTPH-Dx, for the identified petroleum product.

Quality Assurance

The addition of an appropriate extraction surrogate to samples and method blank(s) is required. The surrogate recovery for all samples and blanks should be between 50% and 150% and must be reported with the petroleum results unless the quantity of the petroleum product(s) preclude its determination. The laboratory should analyze one sample from each site in duplicate for sample sets of 10 or less and two samples in duplicate for sets of 11 to 20 samples (i.e. 10% QA). If either of the duplicate results are positive, the sample is to be considered positive. Since this method precludes the preparation of analytical duplicates, the laboratory should recommend that the project manager collect and submit field duplicates for analysis. The laboratory must analyze method blanks prepared identically to the samples. Organic free water must be used in the preparation of water method blank. No "sample" is necessary for use with soil/sediment method blanks.

Author - Bob Carrell, Manchester Environmental Laboratory, Dept. of Ecology, State of Washington. Reviewed and edited by Steve Robb, Toxics Cleanup Program, Department of Ecology, State of Washington. This method is based on Oregon’s Department of Environmental Quality TPH methods and Washington’s Department of Ecology WTPH methods.

NWTPH-Gx Chromatograms

Gasoline
Weathered Gasoline
Naptha
Mineral Spirits #1
Mineral Spirits #2
Mineral Spirits #3

NWTPH-Dx Chromatograms

#2 Diesel
#2 Diesel/Motor Oil
#2 Fuel Oil
Kerosene (Deodorized)
Jet A Fuel
Bunker C #1
Bunker C #2
Motor Oil 30 Wt.
Mineral Oil (USP)
Hydraulic Fluid
Transformer Oil
Gas Oil

See Appendix 6

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NWTPH-Gx

Volatile Petroleum Products Method for Soil and Water

Summary

The NWTPH-Gx method is intended to replace the Oregon's TPH-G and Washington's WTPH-G methods and to present a more comprehensive approach to volatile petroleum product analyses. NWTPH-Gx adapts Oregon's TPH, Washington's WTPH and EPA SW846 Methods 5030 and/or 8020 and covers the quantitative and qualitative analyses of volatile petroleum products, e.g. gasolines, naphtha, mineral spirits, stoddard solvent, and other volatile petroleum products in soil and water. Soil samples are extracted with methanol and analyzed by gas chromatograph with a flame ionization detector (GC/FID). The methanol extracts may be injected directly into the GC or they may be diluted with organic free reagent water and introduced by a purge/trap concentrator. Water samples are introduced directly to the purge/trap concentrator. This method specifies the criteria for the identification and quantitation of volatile petroleum products. When the type of petroleum product is unknown, regular unleaded gasoline will initially be used as the default petroleum standard. The use of GC/PID, GC/MS or GC/AED (Atomic Emission Detector) for the analysis of gasoline may be substituted for GC/FID as long as all other method parameters are met.

The reporting limits for soil are 5 mg/kg by the purge/trap procedure and 20 mg/kg for direct injection. All soil results are reported on a dry weight basis. Since this value assumes 100% solids, the analyst may wish to adjust the amount of soil extracted and/or purge a larger quantity of extract to achieve the reporting limits. For water, the reporting limits are 0.25 mg/L.

The method is applicable for the identification, by pattern matching ("fingerprinting") and quantitation of volatile petroleum products, i.e. those petroleum products for which the majority of the components elute within the gasoline range.

Note: Benzene, Toluene, Ethylbenzene and Xylenes (BTEX) may be determined simultaneously with gasoline if the requirements of EPA Method 8021 or EPA Method 8260 are met (i.e. the use of a PID (Photoionization Detector) for method 8020 or a MS (Mass Spectrometry) for method 8260 and the QA/QC associated with these methods).

This method must be performed by, or under the direct supervision of, analysts experienced in the use of GC and in the interpretation of gas chromatographs of both fresh and weathered volatile petroleum products.

Equipment and Reagents

Gas Chromatograph
Purge/Trap Liquid Concentrator - Tekmar or Equivalent - Autosampler (Optional)
Flame Ionization (FID) or Photo Ionization/Flame Ionization Detectors (PID/FID)
Suggested Capillary Column: Restex RTX-502.2, 60M x 0.53 mm x 3.0 um film thickness or equivalent
Chromatography Data System
Gas tight syringes, various volumes, Hamilton brand or equivalent
Volumetric flasks: 10 mL, ground glass joint with stopper
Methanol: Burdick and Jackson Purge/Trap grade or equivalent
Petroleum Product Standards: Available from commercial sources
Refer to methods 5030 and/or 8020 for the remaining equipment and reagent requirement

Sample Containers/Holding Times

All soil samples for NWTPH-Gx analyses must be collected in soil VOA bottles with Teflon coated septum lined tops. They should be filled to the top to minimize headspace above the soil and stored at 4 degrees C until analyzed. The maximum holding time (the time from the date of collection to the date of analysis) for gasoline and any other volatile petroleum product is 14 days.

All water samples for NWTPH-Gx analyses must be collected in glass VOA vials with Teflon coated septum lined screw tops. They must be filled so that there is no air space (headspace) above the water. Samples should be preserved with 1+1 HCl to a pH <2 and refrigerated at 4 degrees C until analyzed. The maximum holding time (the time from the date of collection to the date of analysis) is 7 days for unpreserved samples and 14 days for preserved samples. The results of any samples which exceed these limits must be qualified as an estimated value.

Standards

Stock Standards. A stock standard is prepared by placing approximately 9 mL of methanol in a 10 mL volumetric flask. Allow the flask to stand, unstoppered, until the methanol wetted surfaces have dried (about ten minutes), then tare the methanol/flask. Add about 5 drops of the petroleum product to the flask while assuring that the liquid falls directly into the methanol without contacting the neck of the flask. Weigh the flask again and dilute to volume with methanol, stopper and mix by inverting the flask several times. The use of commercially prepared standards is acceptable to the above procedure. Commercially prepared gasoline standards must be certified as non-oxygenated gasoline or the gasoline concentration has been adjusted to reflect the contribution of the oxygenate. Calculate the concentration as follows:

$$\textit{Gasoline Stock Standard, ug / mL} = \frac{\textit{(final wt, mg) - (tare wt, mg)}}{\textit{10 mL}} \; x \; \frac{\textit{1000 ug}}{\textit{mg}}$$

The standard for gasoline will be regular unleaded gasoline and this standard is to be used as the default petroleum product for reporting purposes.

Note: The use of oxygenated regular unleaded gasoline for this standard is allowed if the weight (mass) of the gasoline used is adjusted for the weight contribution of the oxygenate to the gasoline. This will necessitate the analysis of the gasoline for the specific oxygenate(s) present to determine their concentration. This analysis must be conducted by either of the methods published in the Federal Register - Appendix B and C - Testing procedures - Vol. 57, No. 24, Wednesday, February 5, 1992, Notices. Alternate methods for the analysis of gasoline oxygenates must be approved by the Oregon's Department of Environmental Quality and/or Washington's Department of Ecology prior to use.

Stock Surrogate Standard

Note: The suggested surrogates are 1,4-difluorobenzene and bromofluorobenzene. The use of additional surrogates is optional. Selected surrogate compounds should be non-polar, purgeable from water and must not coelute with any significant component of gasoline.

Make up a stock standard by accurately weighing the surrogate compound(s) into a 10 mL volumetric flask. Utilize the same procedure as the stock gasoline standard preparation if neat material is used or by adding the appropriate volumes of dilute surrogate if solutions are used. Bring it to volume with methanol. The use of commercially prepared surrogate solutions is an acceptable alternative to the above procedure.

Working Surrogate Spike. Add the appropriate volume of stock surrogate standard to methanol in a partially filled 10 mL volumetric flask and dilute to volume with methanol. The final concentration of the working surrogate solution is left to the discretion of the analyst, however, this solution should produce between 5 ng and 50 ng of surrogate introduced to the GC.

Secondary Dilution Standard. Using serial dilutions of the stock standard, prepare a 50 ug/mL standard by adding the appropriate volumes, as calculated below, to a 10 mL volumetric flask. The appropriate volume of the stock surrogate standard may also be added to this volumetric flask. Dilute to volume with methanol to yield a final working standard concentration of 50 ug/mL for the standard. Surrogate compound(s) may be added automatically during the sampling process by an autosampler. Gasoline is the default petroleum product for reporting purposes.

$$\textit{Stock Std (Gasoline), uL} = \frac{\textit{50 ug / mL x 10 mL}}{\textit{Stock Std Conc, ug / mL}} \; x \; \frac{\textit{1000 uL}}{\textit{mL}}$$

Store all standards in a refrigerator until needed. Allow them to come to room temperature prior to use.

Calibration Standard

The aqueous purge standards are each prepared by adding 5 uL, 10 uL, 20 uL and 50 uL and 100 uL of the secondary dilution standard per 5 mL of organic free water. The five point calibration standard quantities in the purged water are then 250 ng, 500 ng, 1000 ng, 2500 ng and 5000 ng for the volatile petroleum products. At the discretion of the analyst, the concentration of the surrogate can increase with increasing standard concentration or remain at a fixed value for all calibration standards and samples. Extending the calibration range, either up or down, is allowed as long as the standards remain within the linear range of the instrument and a minimum of a five point calibration is produced. In order to be acceptable, the calibration curve must have a linear correlation coefficient of at least 0.990 and none of the standards may vary from their true (known) value by more than plus/minus 15%.

The use of an autosampler may be substituted for this manual method of standards and sample introduction.

Direction Injection. Prepare calibration standards from the stock gasoline standard and surrogate standards at concentrations of 10 ug/mL, 25 ug/mL, 50 ug/mL, 100 ug/mL and 250 ug/mL for gasoline by adding the appropriate volumes to volumetric flasks and diluting to volume with methanol. Increasing the calibration range with higher standards is acceptable as long as the linear range of the instrument is not exceeded.

Purge/Trap and GC Parameters

Follow the procedure outlined in Method 8021 for the set up of the purge and trap operating parameters and for the GC. Adjust the hydrogen/air flow rates to optimize the FID sensitivity.

Soil Extraction Procedure

Weigh approximately 5 grams of soil into a 40 mL VOA vial and record the weight to 0.001 grams. Add 50 uL of the surrogate working standard and 10 mL of methanol. Quickly cap the vial and shake for 1 minute or use an ultrasonic bath for 2 minutes shaking well after 1 minute. Allow the soil methanol mixture to separate, centrifuging if necessary to clarify the methanol extract. For storage, transfer a portion of the extract into a 2 mL glass autosampler vial, with a Teflon-lined cap, minimizing the headspace and store in a freezer for no longer than one week prior to analysis. Along with the samples, prepare at least one method blank and one sample duplicate per ten samples.

Determine the moisture content of the sample, for use in the final calculations, by the following method. Immediately after weighing the sample for extraction, weigh 5-10 grams of the sample into a tared crucible. Dry the sample/crucible overnight at 105 degrees C. Reweigh the sample/crucible after allowing it to cool to room temperature. Calculate the % solids as follows: [(grams of dry sample/grams of wet sample) x 100].

Analysis Procedure

Prior to the analysis of any samples or method blanks, prepare and analyze a mid-range calibration check standard to insure that the instrument is functioning correctly and that the calibration is valid. This standard should be produced daily using the secondary gasoline standard. The value obtained for this analysis must not vary from the true (known) value by more than plus/minus 20%. If the value falls outside this range then a second mid-range calibration standard should be produced and the analysis repeated. If the reanalysis of the fresh standard fails to meet the acceptance criteria, then the instrument must be recalibrated prior to the analysis of any samples. Once the instrument is shown to be in calibration, the analyses of samples may proceed.

After the last sample has been analyzed, a mid-range calibration check sample must be run to demonstrate that the instrument is still operating within the required parameters. Should this standard fail to meet those parameters, then all samples analyzed after the last successful calibration check must either be reanalyzed or the results obtained must be qualified as an estimated value. An increase in the frequency of mid-range calibration check standard analyses beyond the minimum required is recommended.

Significant interferences may be encountered due to the presence of other petroleum products (or non-petroleum products) eluting within the retention time range of the volatile petroleum product being analyzed. If this occurs, the analyst is allowed to adjust the retention time range used for quantitation to exclude the interferences or to subtract the area of the interfering components from the total area prior to the quantity determination. With the former method, the calibration curve must be adjusted in the same manner to reflect the change in retention time range and integration area.

For volatile petroleum products other than gasoline that have a more narrow boiling point range, e.g. mineral spirits, the retention time range used for quantitation should be adjusted to encompass the expected range of the product. Petroleum products which cannot be identified should be quantitated with the gasoline calibration curve. The term "gasoline range" hydrocarbons, or derivations of it, should not be used when reporting the petroleum values unless the analyst is unable to identify the petroleum product present.

Purge/Trap - Soil. A 100 uL aliquot of the methanol extract is transferred via a 100 uL gas tight syringe to 5 mL of organic free water in a 5 mL gas tight syringe and immediately injected into the purging vessel of the purge and trap device. For samples expected to contain concentrations of gasoline range volatiles outside the calibration linear range, or if dilution is required, a smaller aliquot of the methanol extract, or sample, should be used. The analysis then proceeds as in Method 8020. Autosampler techniques may be substituted for this manual method of sample introduction.

Purge/Trap - Water. Sample water (5 mL) is transferred to a 10 mL gas tight syringe and the working surrogate standard spike is added, via a gas tight syringe, into the 5 mL water sample. Immediately inject this water into the purge vessel of the purge/trap device. If necessary, a smaller sample aliquot may be used in order to remain within the linear calibration range of the instrument.

Larger sample volumes may be analyzed, at the discretion of the analyst, if lower quantitation limits are required. Autosampler techniques may be substituted for this manual method of sample introduction.

Direct Injection - For Soil. Allow the extract to come to room temperature, then inject, either manually or by autosampler, 2 uL of the extract into the GC using the splitless injection mode.

Quantitation

The retention time range (window) for gasoline integration must, at a minimum, include toluene through naphthalene. For other volatile petroleum products, the retention time range for integration must be adjusted to incorporate the majority of the components of the petroleum product(s) identified as present in the samples. If specific product identification can not be made, the analyst must quantitate the samples with the calibration curve of the petroleum product that most closely resembles that of the sample.

For those surrogates which elute within the retention time range used for integration, the analyst must subtract the area of the surrogate(s) from the total area to yield the appropriate area of the petroleum product.

The analyst shall use regular unleaded gasoline as the default petroleum product for reporting purposes when no petroleum products were identified in any initial screening or when the type(s) of petroleum products are unknown prior to analysis.

Sample chromatograms of various volatile petroleum products are included at the end of this method to assist the analyst in determining the appropriate integration ranges.

Result Calculation

The area of the components is integrated, as a group, to the baseline and compared to concentrations of the standards which are integrated in the same manner.

For Soil

$$\textit{Soil Sample Conc, mg / kg} = \frac{(A \times R) \times D}{E \times W \times S}$$

where

A = group area of sample

R = Response factor from std curve (ng injected/area count)

D = Extract Volume, mL

W = Weight of sample, grams

E = Volume of extract purged or injected, uL

S = Decimal percent solids of sample

For Water

$$\textit{Water Sample Conc, ug / L} = \frac{(A \times R)}{V}$$

where

A = group area of sample

R = Response factor from std curve (ng purged/area count)

V = Volume of sample purged, mL

The recovery of the surrogate should be between 50% and 150% and must be reported with the results. Report any surrogate recoveries that can not be calculated due to a high level of gasoline contamination.

Author: Bob Carrell, Manchester Environmental Laboratory, Dept. of Ecology, State of Washington. Reviewed and edited by Steve Robb, Toxics Cleanup Program, Department of Ecology, State of Washington. This method is based on Oregon's Department of Environmental Quality TPH-G and Washington's Department of Ecology WTPH-G methods.

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NWTPH-Dx

Semi-Volatile Petroleum Products Method for Soil and Water

Summary

The NWTPH-Dx method is intended to replace the Oregon's Department of Environmental Quality TPH-D and Washington's Department of Ecology WTPH-D methods and to present a more comprehensive approach to semi-volatile petroleum product analyses. NWTPH-Dx adapts Oregon's TPH, Washington's WTPH and EPA SW-846 Methods 3510, 3540/3550 and 8000 and covers the quantitative and qualitative analysis of semi-volatile petroleum products, i.e. jet fuels through heavy fuel oils, in soil and water. The method involves extracting the samples with methylene chloride and injecting a portion of the extract into a gas chromatograph (GC) equipped with a flame ionization detector (FID). This method specifies criteria for the identification and quantitation of semi-volatile petroleum products. A clean-up procedure, which may be used to aid in the removal of non-petroleum based organic interferences, i.e. biogenic interferences, has been included. When the type of petroleum product is unknown, #2 diesel will initially be used as the default petroleum standard.

The reporting limits are 25 mg/kg (soil) and 0.25 mg/L (water) for the petroleum products in the elution range of jet fuels through #2 diesel. For petroleum products eluting after #2 diesel oil, e.g. motor oils, hydraulic fluids, and heavy fuel oils, the reporting limits are 100 mg/kg (soil) and 0.50 mg/L (water). All soil results are reported on a dry weight basis. Since this value assumes 100% solids and therefore will be higher depending on the actual moisture content, the analyst is permitted to concentrate the extract to obtain these reporting limits. When doubt exists as to which reporting limit is applicable for the petroleum product present, the analyst should use the lower value.

The method is applicable for the identification, by pattern matching ("fingerprinting"), and quantitation of semi-volatile petroleum products. These include kerosenes, jet fuels, diesel oils, fuel oils, lubricating oils, hydraulic fluids, mineral oils and insulating oils, e.g. transformer oils. In general, those petroleum products which do not contain a substantial volatile fraction, i.e. the majority of the components eluting outside of the gasoline range, should be analyzed by this method.

Note: The use of GC/MS (Mass Spectrometry) or GC/AED (Atomic Emission Detector) may be substituted for GC/FID as long as all other method parameters are met.

This method is to be used by, or under the direct supervision of, analysts experienced in the use of GC and in the interpretation of gas chromatograms of both fresh and weathered petroleum products.

Equipment and Reagents

Gas Chromatograph, w/wo Autosampler
Flame Ionization Detector
Capillary Split/Splitless Injector
Suggested Column:
J & W Scientific: DB-1 or DB-5, 30 M x 0.25 mm or 0.32 mm I.D. with 0.25 um film thickness capillary column or equivalent
Chromatographic Data System: Capable of group integrations
Analytical Balance, accurate to a least 0.0001 grams
Volumetric Flasks, 10 mL, ground glass stoppered
N-Evap Concentrator or equivalent
Centrifuge tubes, 10 or 15 mL, glass, calibrated in 0.1 mL increments
Centrifuge tubes, 10 or 15 mL, glass, disposable
Kaderna-Danish (K-D) Flasks, 250 mL
Concentrator Tubes, 10 mL
Snyder Columns, 3-ball, 300 mm length
Sodium Sulfate, anhydrous
Methylene Chloride, Burdick and Jackson brand, gas chromatography/pesticide residue grade or equivalent
Sulfuric acid, concentrated
Silica gel, 100/200 mesh, Baker Analyzed Reagent grade or equivalent - Before use, activate for at least 16 hours at 130 degrees C in a shallow tray
Petroleum Product Standards: Available from commercial sources

Note: All samples shall be collected in Eagle Picher, or equivalent, glass jars and held at 4 degrees C until extracted. The holding time, from the date of collection to extraction, is 14 days for soil and preserved water. For unpreserved water, the holding the holding time is 7 days. Preservation is accomplished by adjusting the pH of the water sample to approximately 2 with the addition of 1+1 HCl.

Suggested GC Parameters

Sample Extract Injection Volume = 2 uL
Injector Temperature = 290 degrees C
Detector Temperature = 300 degrees C
Hydrogen Flow = 25-35 cc/min
Air Flow = 300-400 cc/min
Helium Make-up Gas Flow = 30 cc/min
Helium Carrier Gas Head Pressure = 15 psi
GC Temperature Program:
Initial temperature = 50 degrees C, hold 2 minutes
Temperature Ramp Rate = 20 degrees C per minute
Final Temperature = 320 degrees C, hold for 10 minutes

Standards

Reference/Stock Standards. Prepare individual petroleum product reference/stock standards, e.g. kerosene, #2 diesel oil, transformer oil (mineral oil based) and Bunker-C fuel oil.

Add 5 to 10 drops of the pure petroleum product to a zero tared 10 mL flask. Record the weight and bring the flask to volume with methylene chloride, stopper and mix by inverting the flask several times. Calculate the concentration of these standards using the equation shown below. The use of commercially prepared standards is an acceptable alternative to the above procedure. Analysts may not use artificial standards, e.g. diesel range organics mixtures, etc., for quantitation purposes in place of authentic petroleum products.

These standards are to be used to produce calibration working standards which should be used to insure the proper identification of petroleum products by chromatographic pattern matching ("fingerprinting") as well as accurate quantitation.

$$\textit{Stock Conc, ug / mL} = \frac{\textit{(final wt, mg) - (tare wt, mg)}}{\textit{10 mL}} \times \frac{\textit{1000 ug}}{\textit{mg}}$$

Calibration Working Standards. Using the stock standards, prepare calibration working standards for the identified petroleum product(s) to be quantitated. Add the appropriate volume(s), using the equation shown below and adjusting for the concentration change created by any serial dilutions, to a 10 mL volumetric flask(s). Dilute to volume with methylene chloride. Calibration standards must, at a minimum, (1) provide a five point calibration curve, (2) include a sufficiently low standard to provide the necessary reporting limits, and (3) define the linear working range of the instrument.

In order to be acceptable, the calibration curve must have a linear correlation coefficient of at least 0.990 and none of the standards may vary from their true (known) value by more than plus/minus 15%. #2 diesel oil is the default petroleum product for reporting purposes.

Stock Surrogate Standard. Prepare the stock surrogate standard by weighing 50 mg of the surrogate compound(s) into a 10 mL volumetric flask. Bring the flask to volume with methylene chloride for a final concentration of 5000 ug/mL for the surrogate compound. The use of commercially prepared surrogate solutions is an acceptable alternative to the above procedure.

Note: The suggested surrogates are 2-fluorobiphenyl, o, or p-terphenyl or pentacosane. The use of other surrogates is optional. Selected surrogate compounds must be non-polar, unaffected by the cleanup procedure, i.e. the concentrated sulfuric acid/silica gel treatment, and lacking in significant interferences in most standard petroleum products.

Working Surrogate Spike. Using serial dilutions of the stock standard, prepare a surrogate working standard. Add the appropriate volume of the stock surrogate standard, using the equation listed

below, and adjusting for any serial dilutions, to a 10 mL volumetric flask and dilute to volume with methylene chloride. Stopper and mix by inverting the flask several times. The surrogate working standard should be added to a level sufficient to produce a surrogate concentration between 5 and 50 ug/mL.

$$Volume\ Stock,\ uL\ =\ \frac{(Cal\ Std\ Conc,\ ug\ /\ mL)\ x\ 10\ mL}{Stock\ Conc,\ ug\ /\ mL}\ x\ \frac{1000\ uL}{mL}$$

Store all standards in a refrigerator until needed. Allow them to come to room temperature prior to use.

Sample Extraction

Soil Matrix

Weigh approximately 20 grams of soil, recording the weight to the nearest 0.01 grams, and approximately 20 grams of anhydrous sodium sulfate into a 150 mL beaker. Mix completely with a spatula. The mixture should have a grainy texture. If it forms a large clump, add more anhydrous sodium sulfate and grind to grainy texture. Add the appropriate volume of working surrogate standard, 50 mL of methylene chloride and sonicate for 3 minutes utilizing the horn sonicator and power settings in SW-846 Method 3550. Allow the mixture to settle then collect the extract in a 250 mL Kuderna-Danish (KD) flask to which is connected a 10 mL concentrator tube.

Repeat the extraction twice more and add these extracts to the KD. Attach a 3 ball Snyder column and concentrate the extract on a steam bath to a volume of 5-10 mL. Allow the K-D to cool to room temperature. Disassemble the K-D, rinsing the Snyder/K-D and K-D/concentrator tube joints with 1-2 mL of methylene chloride. Add these rinsings to the extract. If necessary, place the concentrator tube in an N-Evap and reduce the volume to 10 mL under a gentle stream of nitrogen. At this point, proceed to the sample cleanup procedure if applicable or transfer a portion of the extract to a 2 mL autosampler vial fitted with a screw top and a Teflon lined septum. Store the extract in a refrigerator until analyzed. If the extract is highly colored or forms a precipitate, a dilution may be necessary to stay within the calibration range. The use of the EPA method 3540 (soxhlet) in place of Method 3550 is optional.

Determine the moisture content of the samples by the following method. Immediately after weighing the sample for extraction, weigh approximately 10 grams of the sample into a tared crucible and record the weight. Dry the sample/crucible overnight at 105 degrees C. Reweigh the sample/crucible after allowing it to cool to room temperature and record the weight. Calculate the % solids as follows: [(grams of dry sample/grams of wet sample) x 100].

Along with each sample set, run at least one duplicate sample per set of 10 or fewer samples (10%) and, for each extraction day, at least one method blank (5%). Spiking of surrogates, extraction and

analyses of the QC samples will be conducted identically to the regular samples with the exception that no soil is added to the method blank.

Water Matrix

Allow the sample to come to room temperature and mark the meniscus for later use in volume determination. Pour the sample into a separartory funnel and adjust the pH to approximately 2 with 1+1 HCl and add the appropriate volume of surrogate working solution. Add 30 mL of methylene chloride to the sample jar and rotate the jar at a sufficient angle to wash the walls. Pour the solvent into the separatory funnel, stopper, and shake it vigorously for one minute, venting frequently. After the two phases have separated, drain the solvent into a 250 mL K-D flask to which is attached a 10 mL concentrator tube.

Note: Due to possible loss of analytes from the water to the sample jar walls, the entire sample must be consumed in the extraction and no aliquots may be used. Since the reporting limits are calculated on a 400 mL sample volume, sample jar size should be appropriate for this volume. For larger sample volume extractions, the analyst must increase the quantity of solvent used to maintain the original solvent/sample ratio.

Repeat the extraction twice more and add these extracts to the K-D. Attach a 3-ball Snyder column to the K-D and concentrate the extract on a steam bath to 5-10 mL. Allow the K-D to cool to room temperature and disassemble it, rinsing the Snyder/K-D and K-D/ concentrator joints with 1-2 mL of methylene chloride. Add these rinsings to the extract. Place the concentrator tube into an N-Evap and reduce the volume to 2 mL under a gentle stream of nitrogen. Transfer the extract to a 2 mL autosampler vial fitted with a screw top and a Teflon lined septum. Store the extract in a refrigerator until analyzed.

Along with each sample set, run at least one duplicate sample per set of 10 or fewer samples (10%) and, for each extraction day, at least one method blank (5%). Spiking of surrogates, extraction and analyses of the QC samples will be conducted identically to the regular samples with the exception that organic free water will be used for the method blank.

As more information becomes available on new extraction techniques, Washington State Dept. of Ecology's Manchester Laboratory and/or Oregon’s Department of Environmental Quality will publish descriptions of acceptable alternative extraction methods.

Sample Cleanup. In those cases where samples contain a significant amount of naturally occurring non-petroleum organics, e.g. leaf litter, bark, etc., which may contribute biogenic interferences, the following cleanup technique may be employed to assist in their reduction or elimination.

Transfer the 10 mL sample extract to a 10 to 15 mL centrifuge tube, add 1 mL of concentrated sulfuric acid to the extract and stopper the tube. Mix thoroughly for 1 minute by either shaking the tube or with the use of a vortex-genie adjusted to the highest setting.

Caution: Since sulfuric acid produces a highly exothermic reaction with water and other polar materials, extreme care should be exercised with its use.

Allow the two phases to separate. Centrifugation can be used to facilitate this process. Using a disposable glass pipet, transfer the methylene chloride (top) phase to another centrifuge tube and add approximately 0.4 grams (roughly equivalent to 1 mL of volume) of silica gel to the tube, stopper and mix as before. Allow the silica gel to settle or centrifuge. Repeat the sulfuric acid/silica gel treatment once more. Transfer a portion of the extract to a 2 mL autosampler vial equipped with a Teflon-lined cap and store the extract in a refrigerator until analyzed. A smaller aliquot of the extract may be used for this cleanup procedure as long as the ratio of extract to acid/silica gel is maintained.

It has been noted that some petroleum products, i.e. heavy fuel oils such as #6 fuel oil or Bunker-C, may experience a concentration loss of between 10 and 20 percent when subjected to this cleanup technique. This loss appears to be primarily associated with the removal of petroleum compounds which contain sulfur. To account for this loss when analyzing samples that have been subjected to the cleanup procedure in preparation for heavy fuel oil determination, the analyst must use utilize standards which have undergone the cleanup technique to calibrate the GC.

Note: The use of EPA method 3611 (Alumina column cleanup) may be substituted for the above cleanup technique if it is demonstrated to provide equivalent results.

Analysis Procedure. Prior to the analysis of any samples or method blanks, the analyst must prepare and analyze a mid-range calibration check standard to insure that the instrument is functioning correctly and that the calibration is still valid. The value obtained for this analysis must not vary from the true (known) value by more than plus/minus 15%. If the value falls outside this range then a second mid-range calibration check standard should be analyzed. If the analysis of the second check standard fails to meet the acceptance criteria, then the instrument must be recalibrated prior to the analysis of any samples. Once the instrument has been shown to be in calibration, the analyses of samples may proceed.

The analyst shall use #2 diesel as the default petroleum product for reporting purposes when no petroleum products were identified in any initial screening or when the type(s) of petroleum products are unknown prior to analysis.

After the last sample has been analyzed, a mid-range calibration check sample must be run to demonstrate that the instrument is still operating within the required parameters. Should this standard fail to meet those parameters, then all samples analyzed after the last successful calibration check standard must be reanalyzed. An increase in the frequency of mid-range calibration check standard analyses beyond the minimum required is recommended.

Qualitative Analysis - Identification

If NWTPH-HCID has not been previously performed on the samples and/or the type of petroleum present is unknown, the analyst should pre-screen the samples to determine the petroleum product.

The observed petroleum product shall be determined by pattern matching with the standard(s) analyzed the same day. Chromatograms used for this "fingerprinting" should be normalized to approximately 90% of full scale for the largest component of the particular petroleum product observed.

When reporting the results, the terms such as "diesel range" or "motor oil range", or derivations of them, should only be used when the analyst is unable to identify the petroleum product(s) present. Motor oils, hydraulic fluids and similar petroleum products which consist primarily of an unresolved chromatographic envelope of compounds originating at, or extending beyond tetracosane, may be reported using the collective term "lube oil" unless specific identification is possible. Heavy fuel oils, e.g. #6 fuel oil or Bunker-C, which contain a diesel range component as well as a lube oil range, may be reported using the collective term "heavy fuel oil" unless specific identification is possible. Heavy fuel oils should not, however, be confused with mixtures of #2 diesel and lube oils.

Note: The actual identification of the grade or type of lube oil and/or heavy fuel oil may require equipment and techniques beyond the scope of this method.

Quantitative Analysis - Integration

The retention time range (window) for integration must be adjusted to incorporate the majority of the components of petroleum product(s) identified as present in the samples. If specific product identification can not be made, the analyst must quantitate the samples with the calibration curve for the petroleum product that most closely resembles that of the sample. In all cases, the selected retention time range (windows) used for quantitation must, at a minimum, include any unresolved envelope of compounds as well as all discrete component peaks with an area greater than or equal to 10% of the largest peak. These components must be integrated to the baseline as a group.

For those surrogates which elute within the retention time range used for integration of a petroleum product, the analyst must subtract the area of the surrogate from the total area to yield the appropriate area of the petroleum product. In this case, the analyst may wish to generate separate calibrations for the petroleum standards and the surrogate(s) to facilitate integration and quantitation.

At the discretion of the analyst, the range of components included in the integration may be adjusted in order to minimize the potential contribution of any co-eluting fractions arising from the presence of multiple petroleum products. Any change in the integration range must be reflected in a concomitant change to the calibration standards integration.

Sample chromatograms of various petroleum products are included at the end of this method to assist the analyst in determining the appropriate integration ranges.

Result Calculation

For Soil

$$Soil\ Sample\ Conc,\ mg / kg = \frac{(A \times R) \times V \times Dilution\ Factor}{E \times W \times S}$$

where

A = Area Count from Sample

R = Response Factor (ng injected/area count)

V = Extract Volume (mL)

W = Weight of Sample (g)

E = Volume injected, (uL)

S = Decimal percent solids of sample

For Water

$$Water\ Sample\ Conc,\ mg / L = \frac{(A \times R) \times V}{E \times S}$$

where

A = Area Count from Sample

R = Response Factor (ng injected/area count)

V = Extract Volume (mL)

S = Volume of Sample (mL)

E = Volume Injected (uL)

The recovery of the surrogate should be between 50% and 150% and must be reported with the results. If the recovery of the surrogate is not able to be obtained due to a high levels of petroleum contamination, then this fact needs to be reported.

Author: Bob Carrell, Manchester Environmental Laboratory, Dept. of Ecology, State of Washington. Reviewed and edited by Steve Robb, Toxics Cleanup Program, Department of Ecology, State of Washington. This method is based on Orgeon's Department of Environmental Quality TPH-D and Washington's Department of Ecology WTPH-D methods.

METHOD FOR THE DETERMINATION

OF

VOLATILE PETROLEUM HYDROCARBONS (VPH) FRACTIONS

Washington State Department of Ecology

June 1997

Item E-001571

METHOD FOR THE DETERMINATION OF VOLATILE PETROLEUM HYDROCARBONS (VPH)

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DISCLAIMER

Mention of trade names or commercial products does not constitute endorsement by the Washington State Department of Ecology Equipment and materials cited in this method may be replaced by similar products, as long as adequate data exists or has been produced documenting equivalent or superior performance.

METHOD FOR THE DETERMINATION OF VOLATILE PETROLEUM HYDROCARBONS

1.0 SCOPE AND APPLICATION

1.1 This method is designed to measure the collective concentrations of volatile aliphatic and aromatic petroleum hydrocarbons in water and soil. **The carbon ranges used through out this document are given in equivalent carbon (EC) numbers which are related to the boiling point of a chemical normalized to the boiling point of the n-alkanes, and its retention time in a boiling point gas chromatographic (GC) column.** Volatile aliphatic hydrocarbons are collectively quantitated within four ranges: C5 through C6, >C6 through C8, >C8 through C10 and > C10 through C12. Volatile aromatic hydrocarbons are collectively quantitated within the C8 through C10, >C10 through C12 and >C12 through C13 ranges. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 36°C and 220°C.

1.2 This method is also designed to measure the individual concentrations of benzene, toluene, ethylbenzene, xylenes, and methyl tert butylether (MTBE) in water and soil.

1.3 Petroleum products suitable for evaluation by this method include gasoline, mineral spirits, and certain petroleum naphthas. This method, in and of itself, is not suitable for the evaluation of samples contaminated with kerosene, jet fuel, heating oils, lubricating oils, or other petroleum products which contain a significant percentage of hydrocarbons larger than C10. When samples are known or suspected to contain petroleum products containing significant concentration of hydrocarbons >C10, the Extractable Petroleum Hydrocarbon (EPH) method should also be employed to fully evaluate the hydrocarbons present.

1.4 For reporting purposes, the practical quantitation limits (PQL), given the sample volume purged, mass and/or methanol extract volume purged are: 50.0 ug/L for water and 5.0 mg/kg for soil/sediments for the aliphatic and aromatic carbon ranges and 5.0 ug/L and 0.5 mg/kg respectively for the individually targeted compounds. The procedure for Method Detection Limits (MDL) determination in this method and the

Single Laboratory Precision, Accuracy and MDL data (generated by the State of Massachusetts) is added for informational purposes only.

1.5 This method is based on a purge-and-trap, gas chromatography (GC) procedure. This method should be used by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatographs. The analysts should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.

1.6 Like all GC procedures, this method is subject to a "false positive" bias in the reporting of targeted analytes, in that non-petroleum compounds eluting or co-eluting within a specified retention time window may be falsely identified and/or quantitated with the respective carbon ranges. Confirmatory analysis by a GC/MS, EPA Method 8260, or other suitable procedures are recommended in cases where significant concentrations of non-hydrocarbon compounds are known or suspected. If the results of these analyses lead to identification and quantitation of non-petroleum compounds, the analyst may subtract those values from the affected carbon ranges as long as the identities and quantities of subtracted compounds are provided in the analytical report.

2.0 SUMMARY OF METHOD

2.1 Samples are analyzed using purge-and-trap sample concentration. The gas chromatograph is temperature programmed to facilitate separation of organic compounds. Detection is achieved by a photo-ionization detector (PID) and flame ionization detector (FID) in series. Quantitation is based on comparing the PID and FID detector response of a sample to a standard comprised of aromatic and aliphatic hydrocarbons. The PID chromatogram is used to determine the individual concentrations of targeted analytes (BTEX/MTBE) and collective concentration of aromatic hydrocarbons within the C8 through C10, C10 through C12 and C12 through C13 ranges. The FID chromatogram is used to determine the collective concentration of aliphatic hydrocarbons within the C5 through C6, C6 through C8, C8 through C10 and C10 through C12 ranges. To avoid double counting of the aromatic contribution to the aliphatic ranges, the PID concentrations are subtracted from the FID concentrations to yield the aliphatic ranges values.

2.2 This method is suitable for the analysis of waters, soils, and sediments. Water samples may be analyzed directly for volatile petroleum hydrocarbons by purge-and-trap concentration and gas chromatography. Soil samples are either dispersed in methanol to dissolve the volatile organic constituents and a portion of the methanol is analyzed by purge-and-trap GC or combined with water for purging directly from a soil purge vessel (EPA method 5035).

2.3 This method is based on, and constitutes a significant modification of, the “Method for the Determination of Volatile Petroleum Hydrocarbons (VPH)”, Public Comment Draft 1.0, developed by the Massachusetts Department of Environmental Protection and on EPA method 5035. They in turn based their method on (1) USEPA Methods

5030, 8000, 8020, and 8015, SW-846, "Test Methods for Evaluating Solid Wastes", 3rd Edition, 1986; (2) Draft "Method for Determination of Gasoline Range Organics", EPA UST Workgroup, November, 1990; and (3) "Method for Determining Gasoline Range Organics", Wisconsin Department of Natural Resources, PUBL-SW-140, 1992.

3.0 DEFINITIONS

3.1 **Volatile Petroleum Hydrocarbons (VPH)** are defined as all hydrocarbon compounds eluting just prior to n-pentane through 1-methylnaphthalene. VPH is comprised of C5 through C6, >C6 through C8, >C8 through C10 and >C10 through C12 Aliphatic Hydrocarbons, as well as >C8 through C10, >C10 through C12 and >C12 through C13 Aromatic Hydrocarbons as well as benzene and toluene. VPH concentration data are reported as the aggregate concentrations of the aliphatic and aromatic hydrocarbon ranges and as selected targeted analytes.

3.2 **Equivalent Total Petroleum Hydrocarbons (E-TPH)** For samples contaminated ONLY with gasoline or other low molecular weight petroleum products, the E-TPH value is equivalent to the VPH value. For samples contaminated with BOTH light and heavy molecular weight petroleum products (e.g., gasoline and diesel fuel), the E-TPH value is a summation of the VPH value and the Extractable Petroleum Hydrocarbon (EPH) values. In order to avoid double counting of analytes due to the overlap in the carbon ranges existing between the two methods, the analyst will report the highest of the two values determined for the overlapping ranges. In those cases where both the VPH and EPH methods are employed on samples, the analyst may select to quantitate the >C10 through C12 Aliphatic and the >C10 through C12 Aromatic Hydrocarbon ranges only using the EPH method.

3.3 **C5 through C6 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds which elute on the FID chromatogram from (and including) n-pentane through n-hexane.

3.4 **C6 through C8 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbons which elute on the FID chromatogram after n-hexane through n-octane.

3.5 **C8 through C10 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds which elute on the FID chromatogram after n-octane through n-decane.

3.6 **C10 through C12 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbons which elute on the FID chromatogram after n-decane through n-dodecane.

3.7 **C8 through C10 Aromatic Hydrocarbons** are defined as all hydrocarbon compounds which elute on the PID chromatogram after toluene through 1,2,3-trimethylbenzene.

3.8 **C10 through C12 Aromatic Hydrocarbons** are defined as all hydrocarbons which elute on the PID chromatogram after 1,2,3- trimethylbenzene through naphthalene.

3.9 **C12 through C13 Aromatic Hydrocarbons** are defined as all hydrocarbons which elute on the PID chromatogram after naphthalene through 1-methylnaphthalene. This is a hybrid range which is designed to acquire the methylnaphthalenes associated with petroleum products like gasoline and is only used when VPH is run without an accompanying EPH method request.

3.10 **Targeted VPH Analytes** are defined as benzene, toluene, ethylbenzene, p,m,o-xylenes, and MTBE.

3.11 **Volatile Petroleum Hydrocarbon (VPH) Component Standard** is defined as a 15 component mixture of the aliphatic and aromatic compounds, plus surrogate, listed in Table 1. The compounds comprising the VPH Component Standard are used to (a) define the individual retention times and chromatographic response factors for each of the Targeted VPH Analytes, (b) define and establish the windows for the collective aliphatic and aromatic hydrocarbon ranges of interest, and (c) determine average chromatographic response factors that can in turn be used to calculate the collective concentration of hydrocarbons within these ranges.

3.12 **Analytical Batch** is defined as a group of samples with similar matrices which are processed as a unit. For Quality Control purposes, if the number of samples in such a group is greater than 20, then each group of 20 samples or less are defined as separate analytical batches.

3.13 **Laboratory Duplicates** are defined as split samples taken from the same sampling container and analyzed separately with identical procedures. The analysis of laboratory duplicates give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.14 **Field Duplicates** are defined as two separate samples collected at the same time and place under identical circumstances and managed the same throughout field and laboratory procedures. Analyses of field duplicates give a measure of the precision associated with sample collection, preservation, and storage, as well as laboratory procedures.

3.15 **E-TPH Duplicates** are defined as two separate samples collected at the same time and location, for analysis by both EPH and VPH methods. E-TPH duplicates are taken at locations where significant concentrations of petroleum hydrocarbons lighter and heavier than C9 are likely to be present (e.g., locations contaminated by releases of both gasoline and diesel fuel). The resultant EPH and VPH concentrations, adjusted to prevent double counting of overlapping hydrocarbon ranges between the methods, are then summed to determine the Equivalent TPH (E-TPH) concentration.

3.16 **Calibration Standards** are defined as a series of standard solutions prepared from dilutions of a stock standard solution, containing known concentrations of each analyte and surrogate compound of interest.

3.17 **Calibration Check Standard** is defined as a calibration standard used to periodically check the calibration state of an instrument. The calibration check standard is prepared from the same stock solution as calibration standards, and is generally one of the mid-level range calibration standard dilutions.

Table 1. Volatile Petroleum Hydrocarbon (VPH) Component Standard

Compound	Equivalent Carbon Number
n-Pentane	5.0
n-Hexane	6.0
Methyl tert butylether	N/A
Benzene	6.5
Toluene	7.6
n-Octane	8.0
Ethylbenzene	8.5
m- & p- Xylene	8.6
o-Xylene	8.8
1,2,3,-Trimethylbenzene	10.1
n-Decane	10.0
Naphthalene	11.7
n-Dodecane	12.0
1-Methylnaphthalene	13.0
2,5-Dibromotoluene (surrogate)	N/A

3.18 **Matrix Spiking Solution** is defined as a solution which is generally prepared independently from the calibration standards, containing known concentrations of method analytes.

3.19 **Laboratory Method Blank** is defined as, depending on the matrix of the samples, either reagent water or clean sand spiked with a surrogate standard. The laboratory method blank is treated identically as with samples, exposed to all glassware, solvents, reagents, and equipment. A laboratory method blank is analyzed with every batch of samples, to determine if method analytes or other interferences are present in the laboratory environment, reagents, or equipment.

3.20 **Laboratory Fortified Blank (LFB)** is defined as, depending on the matrix of the samples, either reagent water or a clean sand blank fortified with a matrix spiking solution.

The LFB is treated and analyzed identically as with samples and blanks, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements at the required practical quantitation limits..

3.21 **Laboratory Fortified Matrix (LFM) Sample** is defined as an environmental sample which has been spiked with a matrix spiking solution containing known concentrations of method analytes. The LFM sample is treated and analyzed exactly as a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined through the separate analyses of a laboratory or field duplicate, and the measured values in the LFM sample corrected for background concentrations.

3.22 All other terms are as defined in SW-846, "Test Method for Evaluating Solid Waste", USEPA, September, 1986, and as amended.

4.0 INTERFERENCES

4.1 Samples can become contaminated by diffusion of volatile organics through the sample container septum during shipment and storage. Trip blanks prepared from reagent water should be carried through sampling and subsequent storage and handling to serve as a check on such contamination.

4.2 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe and/or purging device must be rinsed between samples with reagent water or solvent. The trap and other parts of the system are also subject to contamination, therefore, frequent bake-out and purging of the entire system may be required. A screening step is recommended to protect analytical instrumentation. Whenever an unusually concentrated sample is encountered, it must be followed by the analysis of a solvent blank to check for cross-contamination.

4.3 Certain organic compounds not associated with releases of petroleum products, including chlorinated solvents, ketones, and ethers, will be quantitated as Volatile Petroleum Hydrocarbons. Some samples may require additional analytical procedures to be employed , e.g. GC/MS, to document the presence and quantity of such compounds.

4.4 The response selectivity of a photo-ionization detector (PID) is used in this method to differentiate aromatic hydrocarbons from aliphatic hydrocarbons. All compounds eluting on the PID chromatogram after toluene are identified by the method as aromatic hydrocarbons. This will lead to an overestimation of aromatic hydrocarbons within samples, as certain aliphatic compounds will elicit a response on the PID, particularly unsaturated compounds such as alkenes. The significance and implications of this overestimation will vary from sample to sample and, where less conservative data are desired, additional actions should be considered to

minimize the detection of non-aromatic compounds, such as the use of a lower energy PID lamp or GC/MS.

5.0 HEALTH AND SAFETY ISSUES

The toxicity and carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis.

6.0 APPARATUS AND MATERIALS

6.1 The following glassware is used in this method:

6.1.1 VOC Vials: Wide mouth 60-mL VOC vials or 40-mL VOC vials with teflon/ silicone septa for soils; 40-mL VOC vials with teflon/silicone septa for waters.

6.1.2 Volumetric flasks: 10-mL, 50-mL, 100-mL, and 1,000-mL with a ground-glass stopper.

6.1.3 Disposal pipets: Pasteur.

6.2 Analytical balance: An analytical balance capable of accurately weighing 0.0001 g must be used for weighing standards. A top-loading balance capable of weighing to the nearest 0.1 g must be used for weighing soil samples.

6.3 **Gas Chromatography**

6.3.1 Gas Chromatograph: An analytical system complete with temperature programmable gas chromatograph and purge-and-trap concentrator. The data station must be capable of storing and reintegrating chromatographic data and must be capable of determining peak areas using a forced baseline projection.

6.3.2 Columns

6.3.2.1 Recommended column: 105M x 0.53 mm I.D. Restek RTX 502.2, 3.0 micron film thickness, or equivalent.

6.3.2.2 Other columns, such as a 60 M x 0.53 mm J&W DB-5, may be used. Capillary columns are required to achieve necessary resolution. The column must be capable of resolving typical gasoline components. It must also resolve ethylbenzene from m/p-xylene. Some columns may require subambient cooling to achieve these criteria.

6.3.3 Detectors: The method utilizes a Photo-ionization Detector (PID) in series with a Flame Ionization Detector (FID); the PID first in the series. The method is based upon the use of a 10.0 eV PID lamp, although lower energy lamps are permissible in order to minimize PID response to aliphatic compounds.

6.3.4 Purge-and-trap device: The purge-and-trap device consists of a sample purger, a trap, and a desorber. Several complete devices are commercially available.

6.3.4.1 The purging chamber must be designed to accept 5 mL samples with a water column at least 3 cm deep. Purging devices larger than 5 mL have a reduced purging efficiency and should not be used. The gaseous headspace between the water column and the top of the vessel should be at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. Fritted glass or needle sparge cells may be used. If needle sparge cells are used, the purge gas must be introduced no more than 5 mm from the base of the water column. Alternate sample purge devices may be used, provided equivalent performance is demonstrated.

6.3.4.2 The trap should be at least 25 cm long and have an inside diameter of at least 0.105 inches. The trap should be packed with 400 mg of Carbopack B (Supelco Cat. No. 209273). Alternative trap packing materials include: Tenax GC (or equivalent); 7.6 cm Carbopack B and 1.3 cm Carbosieve S-III (Supelco Cat No. 2-0321); 7 cm Carbopack C and 1.2 cm Carbopack B (Supelco Cat No. 2-1064); or equal volumes of Tenax, silica gel, and charcoal as described in EPA SW-846 Method 5030. In general, Carbopack trap packing materials are recommended because they have less of a tendency to retain methanol, which could interfere with the elution of pentane and quench the FID flame. The trap length and packing materials may be varied as long as equivalent performance has been verified.

6.3.4.3 Prior to initial use, the Carbopack B trap should be conditioned overnight at 270°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to a hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min. at 260°C with backflushing. The trap may be vented to the analytical column during daily conditioning, however, the column must be run through the temperature program prior to analysis of samples. Devices other than the traps recommended in Section 6.3.4.2 should be conditioned and desorbed according to the manufacturer's guidelines.

6.3.4.4 The desorber should be capable of rapidly heating the trap to 240°C for desorption.

6.4 Ultrasonic bath.

6.5 Syringes: 5-mL Luerlock glass hypodermic and 5-mL gas-tight syringe with shutoff valve.

6.6 Syringe valve: Two-way, with luer ends.

6.7 Microsyringes: 1-µL, 5-µL, 10-µL, 25-µL, 100-µL, 250-µL, 500-µL, and 1,000-µL.

6.8 Spatula: Stainless steel.

7.0 REAGENTS AND STANDARDS

7.1 **Reagents**

7.1.1 Reagent Water: organic free water (ASTM Type I reagent grade water).

7.1.2 Solvent: methanol; purge and trap grade or equivalent. Store away from other solvents.

7.1.3 Ottawa and/or masonry sand: free of volatile petroleum hydrocarbons.

7.2 **Stock Standard Solution**

Prepare a stock standard solution in methanol at approximately 20 µg/µL, or purchase certified solutions. Preparation of stock standards and component standards should be done using volumetric glassware.

7.2.1 The stock standard solution consists of the 15 VPH component standards listed in Table 1 and a surrogate standard. Prepare the stock standard solution by accurately weighing approximately 0.2000 g of each standard component. Dissolve the component in methanol and dilute to volume in a 10-mL volumetric flask. At the discretion of the analyst, the surrogate standard may be made up as a separate solution from the VPH standards.

7.2.1.1 Place about 8 mL of methanol in a 10-mL tared ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min. or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

7.2.1.2 Using a 500-µL syringe, immediately add 100 to 200 µL of each VPH Component Standard to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

7.2.1.3 Dilute to volume, stopper, and then mix by inverting the flask three times. Calculate the concentration in micrograms per microliter (µg/µL) from the net gain in weight. When compound purity is assayed to be 98% or greater, the weight may be used without correction to calculate the

concentration of the stock standard, provided such purities are certified by the manufacturer or by an independent source.

7.2.1.4 Transfer the stock standard solution into a Teflon-lined screw-cap/crimp cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.

7.2.2 Stock standard solutions must be replaced after 6 months, or sooner if comparison with check standards indicates a problem. The use of commercially prepared certified standard solutions is an acceptable alternative to the use of neat compounds in the preparation of standards.

7.3 Primary Dilution Standard

Using the stock standard solution, prepare primary dilution standards in methanol, as needed. The primary dilution standard should be prepared at the concentrations shown in Table 2. These standards should be stored with minimal headspace, at -10°C to -20°, and should be checked frequently for signs of degradation or evaporation. The analyst is allowed to prepare separate surrogate and VPH analyte standards.

The primary dilution standards should be replaced at least monthly.

7.4 VPH Calibration Standards

Prepare VPH Calibration standards in reagent water from the primary dilution standard at a minimum of five concentration levels. One of the concentration levels must be near, but above, the method detection limit and must be at a sufficiently low level to allow the PQL reporting of at least 5.0 ug/L for water and 0.5 mg/kg for soil/sediments for the targeted analytes (BTEX and MTBE) and 50.0 ug/L and 5.0 mg/kg respectively for the aliphatic and aromatic carbon ranges. The other standard concentrations must correspond to the expected range of concentrations found in real samples and/or should define the working range of the detector.

7.4.1 Rapidly inject the methanolic standard into the water in the expanded area of a filled 100-mL volumetric flask. Remove the needle quickly after injection.

7.4.2 Mix aqueous standards by inverting the flask three times.

7.4.3 Discard the solution contained in the neck of the flask, and fill the sample syringe from the standard solution contained in the expanded area of the flask.

7.4.4 Do not use pipets to dilute or transfer samples or aqueous standards.

7.4.5 Do not inject more than 20 µL of methanolic standards into 100 mL of reagent water. Aqueous standards are not stable and should be discarded after one hour.

7.5 Surrogate Control Standard (SCS)

The analyst must monitor both the performance of the analytical system and the effectiveness of the method in dealing with sample matrices by spiking each sample, blank, and matrix spike with a surrogate standard. The surrogate standard is also added to the VPH calibration standard solutions. The recommended surrogate standard is 2,5-dibromotoluene, which elutes after all aliphatic and aromatic compounds of interest. The use of additional surrogates or surrogates other than those listed above may be used, at the discretion of the analyst, as long as their performance in the method is demonstrated as acceptable and does not compromise the quantitation of the various target analytes or carbon ranges.

7.5.1 Surrogate Spiking Solution: From a stock standard solution prepared as in Section 7.2.1, prepare a surrogate spiking solution at 50 µg/mL in methanol. Add 4.0 µL of this surrogate spiking solution directly into the 5-mL syringe with every aqueous sample, blank, and matrix spike. 1.0 mL of the surrogate spiking solution is added to soil samples during the extraction step (See 9.1.2.2).

7.6 **Matrix Spiking Solution**

The recommended matrix spiking solution, consisting of the Targeted VPH Analytes, is prepared in methanol at concentrations of 50 µg/mL.

7.7 **Petroleum Reference Standard**

The use of a Petroleum Reference Standard is recommended for quality control purposes. The Petroleum Reference Standard consists of an API or commercial gasoline standard. Prepare a Petroleum Reference Standard Spiking Solution by accurately weighing approximately 0.0100 g of neat product. Dissolve the neat product in methanol and dilute to volume in a 10-mL volumetric flask.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 **Aqueous Samples**

8.1.1 Aqueous samples should be collected in duplicate (or the number of vials directed by the laboratory) without agitation and without headspace in contaminant-free amber glass VOC vials with Teflon-lined septa screw caps. Samples must be acidified to a pH of 2.0 or less at the time of collection and this can generally be accomplished by adding 3 or 4 drops (0.1 to 0.2 mL) of 1:1 HCl (1 part reagent water and 1 part concentrated HCl) to a 40-mL VOC vial. Samples must be cooled to 4°C immediately after collection.

8.1.2 A chain of custody form should accompany all sampling vials and should document the date and time of sample collection and acid preservation. The pH of all water samples must be determined by the laboratory unless sample vials containing acid for field preservation were supplied by the laboratory (this must be noted on the chain of custody). The pH measurement may be performed on left over sample. Any sample found to contain a pH above 2.0 should be so noted on the laboratory/data report sheet.

8.1.3 Any sample received by the laboratory that is not packed in ice or cooled to 4°C must be so noted on the laboratory/data report sheet.

8.1.4 Acid preserved aqueous samples must be analyzed within 14 days of collection. Aqueous samples which, for whatever reason, have not received acid preservation must be analyzed within 7 days of collection or the data must be reported as an “estimate quantity”.

8.2 **Soil Samples**

8.2.1 Soil samples must be collected in a manner that minimizes sample handling and agitation. All sediment must be removed from the glass threads of the vial to ensure an adequate seal. Samples must be cooled to 4°C immediately after collection.

8.2.3 Samples for VPH analysis should be collected in duplicate 2 or 4 ounce VOC jars with Teflon coated septum lined lids.

8.2.4 Sampling must be accomplished in a manner that ensures a minimum of headspace in the sample vial.

8.2.5 A chain of custody form should accompany all sampling vials and should document the date and time of sample collection.

8.2.6 Soil samples must be analyzed within 14 days of collection.

8.3 A summary of sample collection, preservation and holding times is provided in Table 2 .

Table 2 . Holding Times and Preservatives for VPH Samples

Matrix	Container	Preservation	Holding Time
Aqueous Samples	40-mL VOC vials w/ Teflon-lined septa screw caps	Add 3 to 4 drops of 1:1 HCl; cool to 4°C	14 days 7 days, if not preserved
Soil/Sediments Samples	VOC vials w/ Teflon-lined septa screw caps. 40-mL vials	cool to 4°C	14 days

9.0 PROCEDURE

9.1 **Sample Preparation and Purging**

9.1.1 It is recommended that samples known or suspected to have extremely high levels of volatile petroleum hydrocarbons be screened prior to analysis in order to establish the appropriate volume/mass to be used for analysis. This screening step may be analysis of a soil sample's methanol extract (diluted), the headspace method (SW-846 method 3810), the hexadecane extraction and screening method (SW-846 Method 3820) or other applicable method as determined by the analyst.

9.1.2 Water Samples

Introduce volatile compounds into the gas chromatograph using a purge-and-trap concentrator. The use of autosampling devices for sample introduction is recommended or the analyst may use the manual method outlined below.

9.1.2.1 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and

compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one 40-mL vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 20-mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

9.1.2.2 If necessary, samples should be diluted prior to injection into the purge chamber. In such cases, all steps must be performed without delay until the diluted sample is in a gas-tight syringe.

9.1.2.2.1 Dilutions may be made in volumetric flasks (10 mL to 100 mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for highly concentrated samples.

9.1.2.2.2 Calculate the approximate volume of reagent water to be added to the volumetric flask selected and add slightly less than this volume of reagent water to the flask.

9.1.2.2.3 Inject the proper aliquot of sample from the syringe prepared in Paragraph 9.1.2.1 into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with reagent water. Cap the flask, invert, and shake three times. Repeat the above procedure for additional dilutions. Alternatively the dilutions can be made directly in the glass syringe to avoid further loss of volatiles.

9.1.2.2.4 Fill a 5-mL syringe with diluted sample as in Paragraph 9.1.2.1.

9.1.2.3 Add 4.0 µL of the surrogate spiking solution through the valve bore of the syringe. Close the valves.

9.1.2.4 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

9.1.2.5 Close both valves and purge the sample for 11 min. Recommended purge and trap operating parameters are provided in Table 3.

Table 3. Suggested Purge and Trap Operating Parameters

Purge gas	Helium
Purge gas flow rate (mL/min)	40
Purge time (min)	11.0
Purge temperature	Ambient
Desorb temperature °C	250
Backflush inert gas flow (mL/min)	15-20

9.1.2.6 At the conclusion of the purge time, attach the trap to the chromatograph (if necessary), adjust the device to the desorb mode, and begin the gas chromatographic temperature program (in Section 9.2.1) and GC data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 240°C and backflushing the trap with inert gas between 15 and 20 mL/min for 4 minutes.

9.1.2.7 While the trap is desorbing into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5 mL flushes of reagent water (or methanol followed by reagent water) to avoid carryover of pollutant compounds into subsequent analyses.

9.1.2.8 After desorbing the sample, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 260°C. After approximately 7 to 15 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. After a highly concentrated sample, a longer baking time may be necessary. When cool, the trap is ready for the next sample.

9.1.2.9 If the concentration of an analyte in a sample exceeds the calibration range, a dilution of the sample is required. If a sample analysis results in a saturated detector response for a compound, the analysis must be followed by one or more blank reagent water analyses. If the final blank analysis is not free of significant interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of significant interferences.

9.1.2.10 All dilutions should keep the detector response of the major constituents (previously saturated peaks) in the upper half of the linear range of the calibration curve.

9.1.3 Soil/Sediments

Soil and sediment samples are extracted with methanol. An aliquot of the extract is added to reagent water and introduced into the gas chromatograph using a purge and trap concentrator. Should lower values for the targeted analytes be desired, the analyst may employ direct purging of the soil sample using the method outlined in EPA methods 5030 and 5035. The use of autosampling devices for sample introduction is recommended or the analyst may use the manual method outlined below.

9.1.3.1 Weigh the sample vial to 0.1 g in a top loading balance and add 4 to 5 grams of the sample to the vial, reseal and determine the weight of the soil/sediment sample.

9.1.3.2 Quickly add 9.0 mL of methanol and 1.0 mL of the surrogate spiking solution. Cap and shake the sample vial for 2 minutes.

9.1.3.3 Allow soil/sediment to settle, or centrifuge the vial, until a layer of methanol is apparent.

9.1.3.4 Using a microliter syringe, withdraw an appropriate aliquot of the methanol extract for sparging. Sample screening data can be used to determine the volume of methanol extract to add to the 5 mL of reagent water for analysis. All dilutions must keep the response of the major constituents in the upper half of the linear range of the calibration curve.

9.1.3.5 Remove the plunger from one 5.0-mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to allow for addition of the extract (e.g., for 100 µL of extract adjust to 4.9 mL). Pull the plunger to 5.0 mL for addition of the sample extract. Add the volume of methanol extract determined from screening (100 µL maximum).

9.1.3.6 Attach the syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber. Complete operations as specified in Paragraphs 9.1.2.5 through 9.1.2.8.

9.1.4 Proceed with the analysis as described in Sections 9.2 through 9.5. Analyze all laboratory method blanks and QC samples under the same conditions as that used for samples.

9.1.5 If the responses exceed the calibration or linear range of the system, use a smaller aliquot of methanol or aqueous sample.

9.1.6 Determination of Percent Moisture

9.1.6.1 Soil and sediment results must be reported on a dry-weight basis.

9.1.6.2 Transfer 5 to 10 g of sample into a tared crucible. The amount of material used to determine the percent moisture will depend on the amount of moisture present, thus relatively dry samples require more sample addition in order to achieve a significant weight change than wet samples. Dry the sample overnight in an oven at 105°C. Remove the sample from the oven and allow it to cool in a desiccator before reweighing. Reweigh and calculate the percent moisture of the sample using the equations provided in Section 9.6.2.2.

9.2 GC Conditions

9.2.1 Oven Program: Oven temperature 45°C, hold for 1 min, then to 100°C at 3°C/min, to 160°C at 8°C/min, to 230°C at 20°C/min; hold for 7.5 min. Conditions may be altered to improve resolution of volatile petroleum hydrocarbons.

9.2.2 Gas Flows: The recommended carrier gas is helium.

9.2.2.1 Carrier gas flow: 12.5 mL/min.

9.2.2.2 Air: 350 mL/min

9.2.2.3 Hydrogen: 30 mL/min

9.2.2.4 Make up gas flow: 17.5 mL/min

9.2.3 Miscellaneous:

9.2.3.1 FID temperature: 230°C

9.2.3.2 PID temperature: 230°C

9.2.3.3 Injection port temperature: 250°C

9.2.3.4 Column head pressure: 15 psi

9.3 **Retention Time Windows**

9.3.1 Before establishing retention time windows, make sure the GC system is within optimum operating conditions. Make three injections of the VPH Component Standard throughout the course of a 72-hr period. Serial injections over less than a 72-hr period may result in retention time windows that are too tight.

9.3.2 Calculate the standard deviation of the three absolute retention times for each individual compound in the VPH Component Standard. The retention time window is defined as plus or minus three times the standard deviation of the absolute retention times for each standard. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

9.3.3 In those cases where the standard deviation for a particular standard is zero, the laboratory should substitute the standard deviation of a closely eluting structurally similar compound to develop a valid retention time window.

9.3.4 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. This data must be retained by the laboratory.

9.3.5 VPH retention time (Rt) windows are defined as beginning 0.1 minutes after the Rt of the beginning marker compound and ending 0.1 minutes after the Rt of the ending marker compound. The exception to this is the C5 through C6 aliphatic hydrocarbon range, where its Rt window is defined a beginning 0.1 minutes prior to the beginning marker compound and ending 0.1 minutes after the ending marker compound. VPH marker compounds and windows are summarized in Table 4 .

Table 4 . VPH Marker Compounds

Hydrocarbon Range	Beginning Marker Compound	Ending Marker Compound
C5-C6 Aliphatic Hydrocarbons (FID)	just before n-Pentane	just after n-Hexane
C6-C8 Aliphatic Hydrocarbons (FID)	just after n-Hexane	just after n-Octane
C8-C10 Aliphatic Hydrocarbons (FID)	just after n-Octane	just after n-Decane
C10-C12 Aliphatic Hydrocarbons (FID)	just after n-Decane	just after n-Dodecane
C8-C10 Aromatic Hydrocarbons (PID)	just after Toluene	just after 1,2,3-Trimethylbenzene
C10-C12 Aromatic Hydrocarbons (PID)	just after 1,2,3-Trimethylbenzene	just after Naphthalene
C12-C13 Aromatic Hydrocarbons (PID)	just after Naphthalene	just after 1-Methylnaphthalene

9.4 **Calibration**

9.4.1 External Standard Calibration Procedure

9.4.1.1 Prepare VPH Calibration Standards at a minimum of five concentration levels in accordance with the procedures and specifications contained in Section 7.0.

9.4.1.2 Analyze each VPH Calibration Standard following the procedures outlined in Section 9.5. Tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each targeted analyte. Alternatively, the ratio of the response to the amount injected, defined as the calibration factor (CF), may be calculated for method analytes using Equation 1. If the percent relative standard deviation (%RSD) of the calibration factor is equal to or less than 20 % over the working range for all analytes of interest, as determined using Equation 2, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve.

Equation 1: Calibration Factor

$$Calibration\ Factor\ (CF) = \frac{area\ of\ peak}{mass\ purged\ (ng)}$$

Equation 2: Relative Standard Deviation

$$\%RSD = \frac{Stand\ Dev\ of\ 5\ CFs}{Mean\ of\ 5\ CFs} \times 100$$

9.4.1.3 A collective calibration curve or factor must also be established for each hydrocarbon range of interest. Calculate the collective Calibration Factors (CF) for C5-C6, >C6-C8, >C8-C10 and >C10-C12 Aliphatic Hydrocarbons ranges using the FID chromatogram. Calculate the collective CF for the >C8-C10, >C10-C12 and C12-C13 Aromatic Hydrocarbons ranges using the PID chromatogram. Tabulate the summation of the peak areas of all components, the compounds which define the various ranges, in those fractions (e.g. C6-C8 Aliphatic Hydrocarbons, n-pentane and n-hexane or >C6 - C8, n-octane) against the total mass injected using Equation 3.

Note: Do not include the area of any surrogate standard or internal standard in calculating a Range CF.

Equation 3: Range Calibration Factor

$$Range\ CF = \frac{Total\ area\ of\ peaks}{Total\ mass\ purged\ (ng)}$$

9.4.1.4 At a minimum, the working calibration curve or calibration factor must be verified on each working day, and after every 20 samples, whichever is more frequent, by the injection of a mid-level calibration standard to verify instrument performance and linearity. If the percent difference (%D) for any targeted analyte response varies from the predicted response by more than ± 15 %, as determined using Equation 4, a new calibration curve must be prepared for that analyte. Similarly, if the percent difference of the carbon range compound response varies from the predicted response by more than ± 20 %, a new calibration curve must be prepared.

Equation 4: Percent Difference (%D)

$$\%D = \frac{\overline{CF} - CFv}{\overline{CF}} x\ 100$$

9.4.1.5 Targeted VPH Analytes and Aromatic Hydrocarbons ranges are quantitated on the PID chromatogram.

9.4.1.6 The Aliphatic Hydrocarbons ranges are quantitated on the FID chromatogram after subtraction of the collective concentrations of MTBE, and the BTEX compounds identified on the PID chromatogram from the collective concentration values of the C5 through C6 and C6 through C8 Aliphatic Hydrocarbon concentration values determined using the FID chromatogram. Similarly, the PID concentrations determined for the remaining aromatic ranges are subtracted from the FID concentrations for those ranges to yield the actual FID Aliphatic Hydrocarbon ranges values.

9.4.1.7 The concentration of specific analytes or hydrocarbon ranges in aqueous and non-aqueous samples may also be calculated from a calibration curve by use of linear regression analysis.

9.5 GC Analysis

9.5.1 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by samples interspersed with blanks and QC samples. The analytical sequence ends must end with an acceptable calibration verification. If the final calibration verification is not acceptable, then all samples analyzed after the last acceptable calibration verification must either be reanalyzed or if this is not possible, then the data associated with those samples must be qualified as an "estimate quantity".

9.5.2 Establish daily retention time windows for each analyte. Use the absolute retention time for each analyte as the midpoint of the window for that day. The daily retention time window equals the midpoint ± three times the standard deviation determined in Section 9.3.

9.5.2.1 Tentative identification of an analyte occurs when a peak from a sample falls within the daily retention time window. In cases where interferences are suspected, confirmation on a second dissimilar GC column or by GC/MS analysis may be necessary.

9.5.2.3 Validation of GC system qualitative performance must be accomplished by the analysis of standards, generally mid-level, within the analysis sequence. If any of the standards fall outside their daily retention time window, the system is out of control. In such cases, the cause of the problem must be determined and corrected.

9.5.3 If the response for Targeted VPH Analytes exceeds the linear range of the system, dilute the sample and reanalyze. It is recommended that samples be diluted so that all peaks are on scale. Overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure that all peaks are on scale over a 100-fold range, are acceptable if linearity is demonstrated prior to the analysis of samples. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

9.5.4 If detection of targeted analyte peaks are prevented by the presence of interferences, additional analytical techniques, e.g. GC/MS, are recommended.

9.5.5 Peak area and carbon range area quantification/integration must be from baseline (i.e. forced baseline projection which must include the unresolved complex mixture "hump" areas). The exception to this is the C5 through C6 Aliphatic Hydrocarbon range which, due to the use of capillary columns shorter than 100 meters and/or the purging of methanol volumes greater than 20 uL, may experience a lack of complete resolution between C5 (n-pentane) and methanol. In this event, the analyst is allowed to use tangential skim integration, or other suitable integration techniques, to integrate n-pentane, and subsequent hydrocarbons within the C5-C6 aliphatic range if it/they appear(s) on the trailing edge of the methanol solvent peak.

9.6 External Standard Calculations

The concentration of targeted analytes and hydrocarbon ranges in a sample may be determined by calculating the amount of analyte or hydrocarbon range purged, from the peak response, using the calibration curve or the calibration factor determined in Section 9.4.

9.6.1 Aqueous samples:

The general equation to determine the concentration of a specific analyte or hydrocarbon range in aqueous samples in provided in Equation 5.

Equation 5

$$Concentration\ (\mu g / L) = \frac{(A_x)(A)(D)}{(A_s)(V_s)}$$

where:

A_x = Response for the analyte or hydrocarbon range in the sample, units may be in area counts or peak height.

A = Amount of external standard purged, ng.

D = Dilution factor; if no dilution was made, D = 1, dimensionless.

A_s = Response for the external standard, units same as for A_x.

V_s = Volume of sample purged, mL.

If a Calibration Factor is used, the concentration of a specific analyte or hydrocarbon range in an aqueous sample may be calculated using equations 6 and 7, respectively.

Equation 6

$$Conc\ Analyte\ (\mu g / L) = \frac{(A_x)(D)}{(V_s)(CF)}$$

Equation 7

$$Conc\ HC\ Range\ (\mu g / L) = \frac{(A_x)(D)}{(V_s)(Range\ CF)}$$

where:

A_x = Response for the analyte or hydrocarbon range in the sample, units may be in area counts or peak height.

D = Dilution factor; if no dilution was made, D = 1, dimensionless.

V_s = Volume of sample purged, mL.

CF = Calibration Factor, area counts/ng.

Range CF = Calibration Factor for hydrocarbon range, (collective area count/collective mass), area counts/ng.

9.6.2 **Non-Aqueous Samples (Methanol Extraction):**

9.6.2.1 The general equation to determine the concentration of a specific analyte or hydrocarbon range in a soil or sediment sample is provided in Equation 8.

Equation 8

$$Concentration\ (\mu g / kg) = \frac{(A_x)(A)(V_t)(D)}{(A_s)(V_i)(W_d)}$$

where:

A_x = Response for the analyte or hydrocarbon range in the sample, units may be in area counts or peak height.

A = Amount of external standard purged, ng.

V_t = Volume of total extract, µL (Note: this value must include the 1.0 mL surrogate spiking solution added to soil samples)

D = Dilution factor; if no dilution was made, D = 1, dimensionless.

A_s = Response for the external standard, units same as for A_x.

V_i = Volume of methanol extract added to reagent water for purge and trap analysis, µL.

W_d = Dry weight of sample purged, g (see equations 11 through 13)

If a Calibration Factor is used, the concentration of a specific analyte or hydrocarbon range in a soil or sediment sample may be calculated using Equations 9 and 10, respectively.

Equation 9

$$Conc\ Analyte\ (\mu g / kg) = \frac{(A_x)(V_t)(D)}{(V_i)(W_d)(CF)}$$

Equation 10

$$Conc\ HC\ Range\ (\mu g / kg) = \frac{(A_x)(V_t)(D)}{(V_i)(W_d)(Range\ CF)}$$

where:

V_t = Volume of total extract, µL.

Vi = Volume of extract added for purging, µL

W_d = Dry Weight of sample purged, g (see Equations 11 through 13)

A_x, CF, Range CF and D have the same definition as for aqueous samples.

9.6.2.2 Calculation of Dry Weight of Sample

In order to calculate the dry weight of sample purged (W_d), it is necessary to determine the moisture content of the soil/sediment sample, using the procedure outlined in Section 9.1.6. Using the data obtained from Section 9.1.6, W_d is calculated using Equations 11 through 13.

Equation 11

$$\%\ Moisture = \frac{g\ sample - g\ dry\ sample}{g\ sample}\ X\ 100$$

Equation 12

$$\%\ Dry\ Solids = (1) - (\%\ Moisture)$$

Equation 13

$$W_d\ (g) = (\%\ Dry\ Solids)(g\ of\ extracted\ sample)$$

9.6.3 The concentration of specific analytes or hydrocarbon ranges in aqueous and non-aqueous samples may also be calculated from the calibration curve by linear regression, provided that the correlation coefficient (r) is at least 0.99 and the % D for any targeted analyte must not vary from the predicted response by more than +/- 15%, nor any hydrocarbon range standard from its predicted response by more than +/- 20%.

9.6.4 Peak areas measured from blanks may not be subtracted from sample peak areas.

9.6.5 All integration of collective hydrocarbon ranges must be to baseline.

9.6.6 Required Adjustment of Range Concentration Data: In order to minimize the "double counting" of the same hydrocarbon compounds on both the FID and PID chromatograms, the collective concentrations of MTBE, benzene, toluene, ethylbenzene, and m, p, o-xylene identified on the PID chromatogram must be subtracted from the collective Aliphatic Hydrocarbon concentration values, for the ranges in which they elute, determined using the FID chromatogram. Similarly, the collective concentrations of the remaining aromatic ranges values determined on the PID chromatogram must be subtracted from the corresponding aliphatic ranges values determined on the FID chromatogram.

10.0 QUALITY CONTROL

10.1 **General Requirements and Recommendations**

10.1.1 Each laboratory that uses this method should operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document the quality of data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance standards for the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

10.1.2 A acidified reagent water blank should continually accompany each soil sample or water sample batch, respectively, over the course of sampling, storage, and analysis.

10.1.3 A Laboratory Method Blank should be run after samples suspected of being highly contaminated to determine if sample carryover has occurred.

10.1.4 At a minimum, for each analytical batch (up to 20 samples), a Laboratory Method Blank, Laboratory Fortified Blank, Laboratory Fortified Matrix Spike, and sample

duplicate must be analyzed. For analytical batches with more than 10 samples, the analysis of an additional mid-range calibration check standard is recommended. The blank and spiked samples must be carried through all stages of the sample preparation and measurement process.

10.1.5 The recommended sequence of analysis is as follows:

(1) Calibration Standards (initial) or mid-range Calibration Check Standard (daily check on initial calibration)
(2) Laboratory Method Blank
(3) Samples
(4) QC Samples
(5) Mid-range Calibration Check Standard (also recommended after each 10 samples)

10.1.6 It is recommended that a system of control charts be developed to plot surrogate standard recoveries as a function of time. When surrogate recovery from a sample, blank, or QC sample is less than 60% or more than 140%, check calculations to locate possible errors, the fortifying solution for degradation, and changes in instrument performance. If the cause cannot be determined, the analyst may reanalyze the sample or report the surrogate values as outside acceptance limits.

10.2 **Minimum Instrument QC**

10.2.1 While it is recommended that the n-pentane (C5) peak be adequately resolved from the methanol solvent on the FID chromatogram, the analyst is allowed to follow the guidance as outlined in 9.5.5. Coelution of the m- and p- xylene isomers is permissible. Any surrogates and/or internal standards used must be adequately resolved from individual compounds in the VPH Component Standard.

10.2.2 Retention time windows must be established for each analyte of interest each time a new GC column is installed, and must be verified and/or adjusted on a daily basis. (See Section 9.3)

10.2.3 Calibration curves must be developed based upon the analysis of calibration standards prepared at a minimum of 5 concentration levels. The linearity of calibration or response factors may be assumed if the percent relative standard deviation (%RSD) over the working range of the curve is less than or equal to 20%. Alternatively, if linear regression analysis is used for quantitation, the correlation coefficient (r) must be at least 0.99 and no targeted analyte or carbon range standard may vary from the true value by more than +/- 15% and +/- 20% respectively. (See Section 9.4.)

10.3 **Initial and Periodic Method QC Demonstrations**

The following must be conducted as an initial demonstration of laboratory capability, prior to the analysis of any samples. Subsequent to this initial demonstration, additional evaluations of this nature should be conducted on a periodic basis, in response to changes in instrumentation or operations, and/or in response to confirmed or suspected systems, method, or operational problems.

10.3.1 Accuracy and Precision

To demonstrate initial laboratory capability, analyze a minimum of four replicate reagent water and/or clean sand blanks spiked with each analyte of interest at approximately 20 to 60 µg/L and/or 20 to 60 mg/kg, respectively.

10.3.1.1 Add an appropriate aliquot of the stock or primary dilution standard solution(s) to each of the four replicate reagent water or clean sand blanks. Purge and analyze each replicate according to the procedures described in Section 9.0.

10.3.1.2 Calculate the measured concentrations of each analyte in all replicates, the mean accuracy (as a percentage of true value) for each analyte, and the precision (as %RSD) of the measurements for each analyte.

10.3.1.3 For each analyte, the mean accuracy, expressed as a percentage of the true value, must be between 80% and 120%. For each analyte, the %RSD must be less than or equal to 20%.

10.3.1. If desired, the Accuracy and Precision evaluation may be combined with the MDL evaluation specified in Paragraph 10.3.2.

10.3.2 Method Detection Limits (Optional)

Analyze a minimum of seven replicate reagent water and/or clean sand blanks which have been fortified with all analytes of interest at approximately 0.5 to 5 µg/L and/or 1 to 5 mg/kg, respectively. Calculate the Method Detection Limit (MDL) of each analyte using the procedure described in Section 12.0.

10.3.2.1 Water MDLs are determined by analyzing 7 to 10 replicates of reagent water samples in 100-mL flasks spiked with the VPH Component standard and with 40 µg/L of the surrogate compound 2,5-dibromotoluene.

10.3.2.2 Soil/sediment MDLs are determined by analyzing 7-10 replicates of 5 -g of VPH-free sand blanks spiked with the VPH Component standard and with 2 mg/kg of the surrogate 2,5-dibromotoluene.

10.3.3 Petroleum Reference Standard

As an optional demonstration of the validity and relevance of VPH calibration, analyze a reagent water and/or clean sand blank spiked with a known concentration of a neat gasoline product.

10.3.3.1 Fortify a reagent water and/or clean sand blank with 5 µL and/or 0.5 mL of the Petroleum Standard Spiking Solution, respectively. Purge and analyze in accordance with the procedures outlined in Section 9.0.

10.3.3.2 Calculate the total concentration of all petroleum hydrocarbons within the Aliphatic Hydrocarbon ranges using the FID chromatogram. Add these values together. Do not subtract the concentration of Targeted VPH analytes.

10.3.3.3 The concentration calculated in Paragraph 10.3.3.2 is expected to be within 30% +/- of the known concentration of Petroleum Standard in the reagent water or sand blank.

10.4 **Ongoing Method QC Demonstrations**

10.4.1 Each sample, blank, and matrix spike must be spiked with the surrogate spiking solution. Required surrogate recovery is 60% to 140%.

10.4.2 At a minimum, with every batch of 20 samples or less the laboratory must analyze the following:

10.4.2.1 **Calibration Check Standard** - A mid-range calibration standard, prepared from the same stock standard solution used to develop the calibration curve, must be analyzed prior to sample analysis to verify the calibration state of the instrument. For large analytical batches that contain more than 10 samples, the analysis of an additional mid-range calibration check standard is recommended after the analysis of the tenth sample. If the percent difference (% D) of any analyte within the calibration check standard varies from the predicted response by more than 20 %, a new calibration curve must be prepared for that analyte.

10.4.2.2 **Laboratory Method Blank** - A water or soil laboratory method blank is prepared by fortifying a 5 mL reagent water blank with 4 µL of the surrogate spiking solution, or by fortifying a 5 g sample of clean sand with 1.0 mL of the surrogate spiking solution. Peaks within the retention time windows of any hydrocarbon ranges of interest may not be present at or above the lowest calculated PQL for any sample within its batch. When determining the PQL for soil method blanks, incorporate the lowest percent solids value found for any sample within its batch in the calculation.

10.4.2.3 **Laboratory Fortified Blank (LFB)** - A water or soil component spike is prepared by fortifying a 5 mL reagent water blank with 4 µL of the matrix spiking solution, or by fortifying a 5 g sample of clean sand with 1.0 mL of the matrix spiking solution. The spike recovery must be between 70% and 130% and if these values can not be obtained the analyst must identify and correct the problem before analyses can continue.

10.4.2.4 **Sample duplicates** - Sample duplicates may be laboratory or field duplicates. The RPD of duplicate samples should not exceed +/- 25%. The lack of sample homogeneity may contribute to RPD's for duplicates which exceed this value. Should the values exceed 25%, the analyst must report that occurrence.

10.4.2.5 **Laboratory Fortified Matrix (LFM) Spike** - The water or soil LFM spike is prepared by fortifying an actual 5 mL water sample with 4 µL of the matrix spiking solution, or by fortifying an actual 5 g soil/sediment sample with 1.0 mL of the matrix spiking solution. The purpose

of the LFM is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations. The corrected concentrations of each analyte within the matrix spiking solution must be within 70 - 130% of the true value. Should the values determined exceed this range, the analyst must report that occurrence.

10.4.3 If any of the performance standards specified in Section 10.4 are not met, the problem must be corrected before further samples are analyzed. Exceptions to this are duplicate samples RPD's and high recoveries for LFM spikes which, due to sample non-homogeneity may exceed the allowable limits. Any samples run between the last calibration check standard that meets the criteria and one that does not must be rerun. If this is not possible, that data must be reported as an "estimated concentration".

11.0 DATA PRODUCTION AND REPORTING

11.1 **Sample Analysis**

11.11 PID Chromatogram

11.1.1.1 Determine the peak area count for the Targeted VPH Analytes.

11.1.1.2 Determine the peak area count for the surrogate 2,5-dibromotoluene.

11.1.1.3 Separately determine the total area count for all peaks eluting 0.1 minutes after the Rt's for toluene through 0.1 minutes after the Rt for 1,2,3-trimethylbenzene, for all peaks eluting 0.1 minutes after the retention time (Rt) for 1,2,3-trimethylbenzene and 0.1 minutes after the retention time for naphthalene and for all peaks eluting 0.1 minutes after the Rt for naphthalene through 0.1 minutes after the Rt of 1-methylnaphthalene.

11.1.1.4 Using the equations contained in Section 9.6 or linear regression analysis, calculate the concentrations of the Targeted VPH Analytes, the surrogate standard 2,5-dibromotoluene, and >C8 through C10, >C10 through C12 and >C12 through C13 Aromatic Hydrocarbons.

11.2.1 FID Chromatogram

11.2.1.1 Separately determine the total area count for all peaks eluting 0.1 minutes before the retention time (Rt) for n-pentane to 0.1 minutes after the Rt for n-hexane and for all peaks eluting 0.1 minutes after the Rt for n-hexane to 0.1 minutes after the Rt for n-octane. It is not necessary to identify or quantitate individual aliphatic compounds within these ranges.

11.2.1.2 Determine the total area count for all peaks eluting 0.1 minutes after the Rt for n-octane to 0.1 minutes after the Rt for n-decane and 0.1 minutes after n-decane to 0.1 minutes after n-dodecane. It is not necessary to identify or quantitate individual aliphatic compounds within this range.

11.2.1.3 Determine the peak area count for the surrogate standard 2,5-dibromotoluene.

11.2.1.4 Using the equations contained in Section 9.6 or linear regression analysis, calculate the concentrations of C5 through C6 Aliphatic Hydrocarbons, >C6 through C8 Aliphatic Hydrocarbons, >C8 through C10 Aliphatic Hydrocarbons, >C10 through C12 Aliphatic Hydrocarbons and the surrogate standard 2,5-dibromotoluene.

11.2.1.5 To avoid "double counting" of the same analytes, adjust the concentrations of Aliphatic Hydrocarbons calculated in Paragraph 11.2.1.4 by subtracting the collective concentrations of methyl tert butylether, benzene, toluene, >C8 through C10 and >C10 through C12 Aromatic Hydrocarbons, as determined from the PID chromatogram in Section 11.11, from the Aliphatic Hydrocarbon range values effected.

11.3 **Data Reporting Format**

11.3.1 The following information and data must be reported:

11.3.1.1 The sample matrix (aqueous, soil or sediment);

11.3.1.2 The date(s) the sample was collected, received by the laboratory, and analyzed;

11.3.1.3 A description of the sample(s) received by the laboratory, relative to the physical condition of the containers, the temperature of the samples, and use of appropriate preservatives;

11.3.1.4 Moisture content (for soil/sediment samples);

11.3.1.5 The calculated concentrations of C5 through C6, C6 through C8, C8 through C10 and C10 through C12 Aliphatic Hydrocarbons ranges and C8 through C10, C10 through C12 and C12 through C13 Aromatic Hydrocarbons ranges

11.3.1.6 Surrogate recovery (expressed as percent recovery);

11.3.1.7 The calculated concentrations of Targeted VPH Analytes determined

11.3.1.8 The concentration units for aqueous samples are expressed as ug/L or mg/L and for soil or sediment samples the units are expressed as ug/Kg or mg/Kg on a dry-weight basis.

12.0 METHOD PERFORMANCE

12.1 **Method Detection Limits (Optional)**

12.1.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

12.1.2 The MDL is determined according to the following equation:

Equation 14

$$MDL = (t) \times (SD)$$

where:

t = student t value at the 99% confidence level

SD = standard deviation of the replicate analysis

Student t values are as follows:

Number of replicates	t value
7	3.14
8	3.00
9	2.90
10	2.82

12.1.3 For the purposes of this method, the designated MDL value for a hydrocarbon range of interest shall be the highest value calculated for the individual analytes within that hydrocarbon range.

12.2 **Single Laboratory Accuracy, Precision, and MDL Data**

Single laboratory accuracy, precision and MDL data for method analytes are provided in Tables 1-1 through 1-4 in Appendix 1. Additional investigation will be conducted to further evaluate the low recoveries for naphthalene.

13.0 REFERENCES

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METHOD FOR THE DETERMINATION

OF

EXTRACTABLE PETROLEUM HYDROCARBONS (EPH) FRACTIONS

Washington State Department of Ecology

June 1997

METHOD FOR THE DETERMINATION OF EXTRACTABLE PETROLEUM HYDROCARBONS (EPH)

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DISCLAIMER

Mention of trade names or commercial products does not constitute endorsement by the Washington State Department of Ecology. Equipment and materials cited in this method may be replaced by similar products, as long as adequate data exists or has been produced documenting equivalent or superior performance.

METHOD FOR THE DETERMINATION OF EXTRACTABLE PETROLEUM HYDROCARBONS

1.0 SCOPE AND APPLICATION

1.1 This method is designed to measure the collective concentrations of extractable aliphatic and aromatic petroleum hydrocarbons in water and soil. **The carbon ranges used through out this document are given in equivalent carbon numbers (EC) which are related to the boiling point of a chemical normalized to the boiling point of the n-alkanes and its retention time in a boiling point gas chromatographic column**. Extractable aliphatic hydrocarbons are collectively quantitated within five ranges: C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34. Extractable aromatic hydrocarbons are collectively quantitated within five ranges: C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 150 °C and 500 °C.

1.2 Petroleum products suitable for evaluation by this method include, but are not limited to, kerosene and jet fuels, diesel and fuel oils and hydraulic, insulating and lubricating oils. This method, in and of itself, is not suitable for the evaluation of gasoline, mineral spirits, petroleum naphthas, and other petroleum products which contain a significant percentage of hydrocarbons lighter than C10. When samples are known or suspected to contain petroleum hydrocarbons of these or similar types, the Volatile Petroleum Hydrocarbon (VPH) method must also be employed to fully evaluate the hydrocarbons present.

1.3 For reporting purposes, the practical quantitation limits (PQL), given the sample volume/mass, final extract volume and assuming 100 percent solids for soil/sediments are: 50.0 ug/L for aliphatic and aromatic carbon ranges in water and 5.0 mg/Kg for these components in soil. If lower quantitation limits are desired, the analyst is allowed to extract larger volumes/masses and/or concentrate the extracts to smaller volumes prior to analysis. The procedure for Method Detection Limits

(MDL) determination in this method and the Single Laboratory Precision, Accuracy and MDL data (generated by State of Massachusetts) is added for informational purposes only.

1.4 This method is based on a solvent extraction, silica gel fractionation process and gas chromatography (GC) analysis using a flame ionization detector (FID). This procedure should be used by, or under the supervision of, analysts experienced in extractable organics analysis. Analysts using this method should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.

1.5 Like all GC procedures, this method is subject to a "false positive" bias, in that non-hydrocarbon compounds eluting or co-eluting within a specified retention time window may be falsely identified and/or quantitated with the respective carbon ranges. While the cleanup procedure specified in this method to segregate aliphatic and aromatic fractions will serve to mitigate this concern, confirmatory analyses by gas chromatography/mass spectrometry (GC/MS) analysis, EPA Method 8270, or other suitable techniques are recommended in cases where significant concentrations of non-hydrocarbon compounds are known or suspected. Non-petroleum compounds identified and quantitated by GC/MS may be subtracted from the carbon ranges affected as long as the quantity and identities of the compounds are reported along with the carbon range data.

2.0 SUMMARY OF METHOD

2.1 A sample submitted for EPH analysis is extracted with methylene chloride, dried over sodium sulfate, solvent exchanged into hexane, and concentrated. Sample cleanup and separation into aliphatic and aromatic fractions is conducted using a modification of EPA method 3630 (silica gel cleanup). The use of commercially available silica gel cartridges (Sep-Pak cartridges, Waters, Milford, MA) may be substituted for the silica gel column outlined in method 3630 if they can be shown to achieve comparable results. The two extracts produced are then concentrated to final volumes of 10 mL each (i.e., an aliphatic extract and an aromatic extract) and are then separately analyzed by a gas chromatograph equipped with a capillary column and a flame ionization detector. The resultant chromatogram of aliphatic compounds is collectively integrated within the C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 aliphatic hydrocarbon ranges. The resultant chromatogram of aromatic compounds is collectively integrated within the C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 ranges.

2.2 Average calibration factors or response factors determined using an aliphatic hydrocarbon standard mixture are used to calculate the collective concentrations of the different aliphatic hydrocarbons ranges. An average calibration factor or response factor determined using the aromatic hydrocarbon standard mixture is used to calculate a collective concentrations of the aromatic hydrocarbon ranges.

2.3 This method is suitable for the analysis of waters, soils, and sediments.

2.4 This method is based on, and constitutes a significant modification of, the “Method for the Determination of Extractable Petroleum Hydrocarbons (EPH)” Public Comment Draft 1.0 developed by the Massachusetts Department of Environmental Protection. They in turn based their method on (1) USEPA Methods 8000, 8100, and 3630, SW-846, "Test Methods for Evaluating Solid Waste", 3rd Edition, 1986; (2) Draft "Method for Determination of Diesel Range Organics", EPA UST Workgroup, November, 1990; and (3) "Method for Determining Diesel Range Organics", Wisconsin Department of Natural Resources, PUBL-SW-141, 1992.

Table 1. Aromatic Hydrocarbon Standard

Equivalent Carbon Number	Compound
7. 6	Toluene
10.1	1,2,3-Trimethylbenzene
11.7	Naphthalene
15.5	Acenaphthene
Surrogate	Ortho-Terphenyl
20.8	Pyrene
34.01	Benzo(g,h,i)Perylene

Table 2. Aliphatic Hydrocarbon Standard

Carbon Number	Compound
8	Octane
10	Decane
12	Dodecane
16	Hexadecane
Surrogate	1-Chloro-octadecane
21	Henicosane
34	Tetratriacontane

3.0 DEFINITIONS

3.1 **Extractable Petroleum Hydrocarbons (EPH)** are defined as all hydrocarbon compounds eluting from toluene through benzo(g,h,i)perylene. EPH is comprised of C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 Aliphatic Hydrocarbons and C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 Aromatic Hydrocarbons. EPH concentration data are reported as the aggregate concentration of the aliphatic and aromatic hydrocarbon ranges.

3.2 **Equivalent Total Petroleum Hydrocarbons (E-TPH)** For samples contaminated with petroleum products in the C10 to C34 range, the E-TPH value is equivalent to the EPH value. For samples contaminated with a petroleum product(s) containing significant concentrations of hydrocarbons lighter and heavier than C10, (e.g., contaminated with both gasoline and diesel fuel), the E-TPH value is a summation of the EPH value and the Volatile Petroleum Hydrocarbon (VPH) value. In order to avoid double counting of analytes due to the overlap in the carbon ranges existing between the two methods, the analyst will report the highest of the two values determined for the overlapping ranges. In those cases where both the VPH and EPH methods are employed on samples, the analyst may select to quantitate the >C10 through C12 Aliphatic and the >C10 through C12 Aromatic Hydrocarbon ranges by the EPH method only. Similarly, the analyst may select to quantitate the C8 through C10 Aromatic and C8 through C10 Aliphatic Hydrocarbon ranges by the VPH method only.

3.3 **C8 through C10 Aromatic Hydrocarbons** are defined as all of the aromatic hydrocarbon compounds eluting from (and including) toluene through 1,2,3-trimethylbenzene.

3.4 **>C10 through C12 Aromatic Hydrocarbons** are defined as all aromatic hydrocarbon compounds eluting after 1,2,3-trimethylbenzene through naphthalene.

3.5 **>C12 through C16 Aromatic Hydrocarbons** are defined as all aromatic hydrocarbon compounds eluting after naphthalene through acenaphthene.

3.6 >**C16 through C21 Aromatic Hydrocarbons** are defined as all aromatic hydrocarbons compounds eluting after acenaphthene through pyrene.

3.7 >**C21 through C34 Aromatic Hydrocarbons** are defined as all aromatic hydrocarbons compounds eluting after pyrene through benzo(g,h,i,)perylene.

3.8 **C8 through C10 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds eluting from (and including) n-octane (n-C8) through n-decane (n-C10).

3.9 **>C10 through C12 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds eluting after n-decane through n-dodecane (n-C12).

3.10 **>C12 through C16 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds eluting after n-dodecane through n-hexadecane (nC16)

3.11 >**C16 through C21 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbons eluting after n-hexadecane through n-henicosane (nC21).

3.12 **>C21 through C34 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbons eluting after n-henicosane through tetratriacontane (nC34).

3.13 **Aromatic Hydrocarbon Standard** is defined as a 6 component mixture (plus surrogate) of the aromatic hydrocarbons listed in Table 1. The compounds comprising the Aromatic Hydrocarbon Standard are used to (a) define and establish the windows for the Aromatic Hydrocarbon ranges, and (b) determine chromatographic response factors that can in turn be used to calculate the collective concentration of aromatic hydrocarbons in environmental samples within those hydrocarbon ranges.

3.14 **Aliphatic Hydrocarbon Standard** is defined as a 6 component mixture (plus surrogate) of the normal alkanes listed in Table 2. The compounds comprising the Aliphatic Hydrocarbon Standard are used to (a) define and establish windows for the aliphatic hydrocarbons ranges, and (b) determine chromatographic response factors that can in turn be used to calculate the collective concentration of aliphatic hydrocarbons in environmental samples within those hydrocarbon ranges.

3.15 **Analytical Batch** is defined as a group of samples with similar matrices which are processed as a unit. For Quality Control purposes, if the number of samples in such a group is greater than 20, then each group of 20 samples or less are defined as separate analytical batches.

3.16 **Laboratory Duplicates** are defined as split samples taken from the same sampling container and analyzed separately with identical procedures. The analysis of laboratory duplicates give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.17 **Field Duplicates** are defined as two separate samples collected at the same time and location under identical circumstances and managed the same throughout field and laboratory procedures. Analyses of field duplicates give a measure of the precision associated with sample collection, preservation and storage, as well as laboratory procedures.

3.18 **E-TPH Duplicates** are defined as two separate samples collected at the same time and location, for analysis by both EPH and VPH methods. E-TPH duplicates are taken at locations where significant concentrations of petroleum hydrocarbons lighter and heavier than C10 are likely to be present (e.g., locations contaminated by releases of both gasoline and diesel fuel). The resultant EPH and VPH concentrations are then summed to determine the Equivalent TPH (E-TPH) concentration.

3.19 **Calibration Standards** are defined as a series of standard solutions prepared from dilutions of a stock standard solution, containing known concentrations of each analyte and surrogate compounds of interest.

3.20 **Calibration Check Standard** is defined as a calibration standard used to periodically check the calibration state of an instrument. The calibration check standard is prepared from the same stock standard solution as calibration standards, and is generally one of the mid-level range calibration standard dilutions.

3.21 **Matrix Spiking Solution** is defined as a solution which is generally prepared independently from the calibration standards and which contain known concentrations of method analytes.

3.22 **Laboratory Method Blank** is defined as, depending on the matrix of the samples, either reagent water or clean sand spiked with a surrogate standard. The laboratory method blank is treated identically as with samples, exposed to all glassware, solvents, reagents, and equipment. A laboratory method blank is analyzed with every batch of samples, to determine if method analytes or other interferences are present in the laboratory environment, reagents, or equipment.

3.23 **Laboratory Fortified Blank (LFB)** is defined as, depending on the matrix of the samples, either reagent water or clean sand blank fortified with a matrix spiking solution. The LFB is treated and analyzed identically as with samples and blanks and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements at the required practical quantitation limits.

3.24 **Laboratory Fortified Matrix (LFM) Sample** is defined as an environmental sample which has been spiked with a matrix spiking solution containing known concentrations of method analytes. The LFM sample is treated and analyzed exactly as with samples and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentration of analytes in the sample matrix must be determined through the separate analyses of a laboratory or field duplicate, and the measured values in the LFM sample corrected for background concentrations.

3.25 All other terms are as defined in SW-846, "Test Methods for Evaluating Solid Waste", USEPA, September, 1986, and as amended.

4.0 INTERFERENCES

4.1 Method interferences are reduced by washing all glassware with hot soapy water and then rinsing with warm tap water, acetone, and methylene chloride.

4.2 High purity reagents must be used to minimize interference problems.

4.3 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. Whenever an unusually concentrated sample is analyzed, it should be followed by the analysis of a solvent blank to check for cross-contamination.

4.4 Matrix interferences may be caused by contaminants that are coextracted along with the analytes of interest from the sample. The type and extent of matrix interference will vary considerably from one source to another depending upon the nature and diversity of the site being sampled and may include certain solvents, halogenated hydrocarbons and phthalate esters. A silica gel cleanup procedure is used to overcome many of these interferences however, some samples may require additional cleanup procedures/approaches or analytical techniques, e.g. gel permeation chromatography and/or GC/MS, which are beyond the scope of this method.

5.0 HEALTH AND SAFETY ISSUES

The toxicity and carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDS) should also be made available to all personnel involved in the chemical analysis.

6.0 APPARATUS AND MATERIALS

6.1 The following glassware is used for this method:

6.1.1 1-L amber glass bottles

6.1.2 4 oz. (120 mL) amber glass wide-mouth jars

6.1.3 Vials:

6.1.3.1 autosampler: 2-mL glass vials with Teflon-lined rubber crimp caps

6.1.3.2 10-mL vials with Teflon-lined caps

6.1.4 Glass funnels

6.1.5 2-L Separatory funnels with Teflon stopcock

6.1.6 Kuderna-Danish apparatus including 10-mL concentrator tube, 500-mL Evaporative flask, & 3-ball Snyder column

6.1.7 Chromatographic column: 250 mm long x 10 mm I.D. with teflon stopcock

6.1.8 Disposable pipets: Pasteur

6.1.9 25-mL graduated cylinder

6.1.10 1-Liter graduated cylinder

6.1.11 100-mL beakers

6.1.12 25-mL volumetric flasks

6.2 Analytical balance: An analytical balance capable of accurately weighing 0.0001 g must be used for weighing standards. A top-loading balance capable of weighing to the nearest 0.1 g must be used for weighing soil samples.

6.3 A nitrogen blowdown apparatus for use in concentrating extracts.

6.4 **Gas Chromatography**

6.4.1 Gas Chromatograph: An analytical system complete with temperature programmable gas chromatograph for use with capillary columns is required. The data station must be capable of storing and reintegrating chromatographic data and must be capable of determining peak areas using a forced baseline projection.

6.4.2 Recommended Column: 30-m long x 0.32-mm I.D., 0.25-µm film DB-5 column (J&W Scientific) or equivalent. This column will allow for the adequate resolution of alkanes from n-C8 to n-C34.

6.4.3 Detector: A Flame Ionization Detector (FID).

6.4.4 Autosampler: An autosampler capable of making 1 to 2 µL injections is recommended.

6.5 Water bath: heated with a concentric ring covers, capable of temperature control (± 2°C). The bath should be used in a hood.

6.6 Microsyringes: 10-µL, 100-µL, 250-µL, 500-µL, 1000-µL

6.7 Boiling Chips: glass or teflon, precleaned prior to use

6.8 Soxhlet or Sonication extraction apparatus

6.9 Drying oven

7.0 REAGENTS AND STANDARDS

7.1 **Reagents**

7.1.1 Reagent Water: organic free water

7.1.2 Solvents: hexane, methylene chloride, and acetone; pesticide grade or better. Store away from other solvents.

7.1.3 Sodium sulfate: (ACS) granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray.

7.1.4 Ottawa and/or masonry sand: free of extractable petroleum hydrocarbons.

7.1.5 Silica gel: 100/200 mesh (Davison Chemical grade 923 or equivalent). Heat to 150-160 ^{o}C for several hours before use. Silica Gel Sep-Pak Cartridges: 5 g/20-mL (Waters, Milford, MA) , if it is demonstated to give equivalent separations.

7.2 **Stock Standard Solutions**

Prepare stock standard solutions at approximately 1000 ng/µL, or purchase as certified solutions.

7.2.1 Aromatic Hydrocarbon Standard: The Aromatic Hydrocarbon Standard consists of the 6 aromatic compounds listed in Table 1 and a surrogate compound. Prepare stock standard solutions by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in methylene chloride and dilute to volume in a 10-mL volumetric flask. The use of commercially prepared stock standards solutions is an acceptable alternative to the use of neat material. The analyst is allowed to prepare a separate surrogate solution.

7.2.2 Aliphatic Hydrocarbon Standard: The Aliphatic Hydrocarbon Standard consists of the 6 normal alkanes listed in Table 2 and a surrogate compound. Prepare stock standard solutions by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in hexane and dilute to volume in a 10-mL volumetric flask. The use of commercially prepared stock standard solutions is an acceptable alternative to the use of neat material. The analyst is allowed to prepare a separate surrogate solution.

7.2.3 Petroleum Reference Standard: The use of a Petroleum Reference Standard is recommended for quality control purposes. The Petroleum Reference Standard consists of an API or commercial diesel, fuel oil, kerosene, and/or lubricating oil. Prepare stock standard solutions by accurately weighing approximately 0.0100 g of neat product. Dissolve neat product in hexane and dilute to volume in a 10-mL volumetric flask.

7.3 Surrogate Standards

7.3.1 The recommended surrogate standards are chloro-octadecane (COD, available from Restek Corporation, Bellefonte, PA) and ortho-terphenyl (OTP, available from EM Sciences, Gibbstown, NJ). Additional surrogates or surrogates other than those listed above may be used at the discretion of the analyst as long as their performance in the method is demonstrated as acceptable. Preparation and use of those surrogates will be in the same manner as the listed surrogate.

7.3.2 The surrogate standard COD is prepared by accurately weighing approximately 0.0100 g of pure material in a 10-mL volumetric flask. Dissolve the material in hexane. This solution is added to the Aliphatic Hydrocarbon standard.

7.3.3 The surrogate standard OTP is prepared by accurately weighing approximately 0.0100 g of pure material in a 10-mL volumetric flask. Dissolve the material in methylene chloride. This solution is added to the Aromatic Hydrocarbon standard.

7.3.4 Surrogate Spiking Solution: The recommended surrogate spiking solution is comprised of a mixture of the COD and OTP surrogate standards. Prepare a surrogate spiking solution which contains the surrogate standards at a concentration of 20 ng/µL in acetone. Each sample, blank, and matrix spike is fortified with 1.0 mL of the surrogate spiking solution.

7.4 Internal Standard

If an internal standard method of calibration is to be used, the recommended internal standard is 5-alpha-androstane (EM Sciences, Gibbstown, NJ).

7.5 Matrix Spike Standard

7.5.1 Four or more analytes from each analyte group (i.e., aromatic and aliphatic hydrocarbons) are selected for use in a matrix spiking solution, which is prepared independently from the calibration standards.

7.5.2 The recommended spiking solution, consisting of C10, C12, C16 and C21 normal alkanes and naphthalene, acenaphthene, anthracene, pyrene, benzo(a)pyrene and benzo(g,h,i)perylene, is prepared in acetone at concentrations of 25 ng/µL.

7.5.3 The samples selected as the matrix spike are fortified with 1.0 mL of the matrix spiking solution.

7.6 Fractionation Check Solution

7.6.1 The Fractionation Check Solution is used to monitor the fractionation efficiency of different batches (lot numbers) of silica gel used to prepare the silica gel hydrocarbon fractionation columns (and Sep-Pak cartridges if used) as well as check for sample preparation errors (e.g., insufficient/excessive pentane use).

7.6.2 Prepare a Fractionation Check Solution in hexane containing 25 ng/µL each of the n-C8, n-C10, n-C12, n-C16, n-C21, and n-C34 alkanes) and 25 ng/µL each of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene. The final solution will contain 6 alkanes and 16 PAHs at concentrations of 25 ng/µL each. The use of commercially available check solutions containing these compounds is acceptable.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 Aqueous samples are collected in 1 liter amber glass bottles with teflon-lined screw caps.

8.2 Soil and sediment samples are collected in 4 oz. (120 mL) amber wide-mouth glass jars with teflon-lined screw caps.

8.3 Aqueous samples must be preserved at the time of sampling by the addition of an acid to reduce the pH of the sample to less than 2.0. This is accomplished by the addition of approximately 5 mL of 1:1 HCl to a 1 liter sample. Following collection and the addition of acid, the sample must be cooled to 4°C.

8.4 Soil and sediment samples must be cooled to 4°C immediately after collection.

8.5 A chain of custody form must accompany all aqueous, soil and sediment samples, documenting the time and date of sampling and any preservative additions.

8.6 Aqueous, soil and/or sediment samples must be extracted within 14 days of collection. If for whatever reason aqueous samples were not preserved at the time of collection they must be extracted within 7 days of collection. Both aqueous and soil/sediment extracts must be analyzed within 40 days of extraction.

8.7 A summary of sample collection, preservation, and holding times is provided in Table 3.

Table 3. Holding Times and Preservatives for EPH Samples

Matrix	Container	Preservation	Holding Time
Aqueous Samples	1-Liter amber glass bottle with Teflon-lined screw cap	Add 5 mL of 1:1 HCl; cool to 4°C	Samples must be extracted within 14 days and extracts analyzed within 40 days
Soil/Sediments Samples	4-oz. (120 mL) wide mouth amber glass jar with Teflon-lined screw cap	Cool to 4°C	Samples must be extracted within 14 days and extracts analyzed within 40 days

9.0 PROCEDURE

9.1 **Sample Preparation**

9.1.1 Water Extraction

9.1.1.1 Mark the water meniscus on the side of the 1 liter of sample bottle (for later volume determination) and transfer the water to a 2-liter separatory funnel. For blanks and quality control samples, pour 1 liter of reagent water into the separatory funnel. Add 1.0 mL of the surrogate spiking solution to all samples, blanks and matrix spikes. For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking solution.

9.1.1.2 Check the pH of the sample with wide-range pH paper. Note the pH in the laboratory notebook. The pH of the sample need not be adjusted.

9.1.1.3 Add 60 mL methylene chloride to the sample bottle to rinse the inner walls of the container, then add this solvent to the separatory funnel.

9.1.1.4 Seal and shake the separatory funnel vigorously for 1 to 2 minutes with periodic venting to release excess pressure.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, venting should be done immediately after the separatory funnel has been sealed and shaken once.

9.1.1.5 Allow the organic layer to separate from the water phase for a minimum of 5 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.
Collect the solvent extract in an 500ml Kuderna-Danish (K-D) evaporation flask to which is attached a 10 mL concentrator tube..

9.1.1.6 Repeat the extraction two more times using fresh portions of solvent and adding the solvent extracts to the KD flask. (Steps 9.1.1.3 to 9.1.1.5) The use of continuous liquid-liquid extraction (EPA method 3520) is an acceptable alternative to the separatory funnel extraction method described above.

9.1.1.7 For sample volume determination add water to the sample bottle to the level of the meniscus previously marked then transfer this water to a graduated cylinder and record the volume.

9.1.1.8 Add one clean boiling chip to the K-D flask and attach a three ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 4-6 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

9.1.1.9 Solvent exchange the methylene chloride with hexane by adding at least 50 mL of hexane to the top of the Snyder column. and concentrate the extract to less than 10 mL, as described in Paragraph 9.1.1.8, raising the temperature of the water bath, if necessary, to maintain proper distillation.

Note: An alternative solvent exchange method is to use the nitrogen blowdown apparatus to exchange the methylene chloride with hexane. This is accomplished by placing a disposable pipet in the concentrator tube and adding the small amounts of hexane via the pipet to the bottom of the concentrator tube during the concentration process in the apparatus.

9.1.1.10 Remove the Snyder column and evaporation flask from the 10-mL concentrator tube. Place the concentrator tube containing the hexane extract onto a nitrogen blowdown apparatus. Adjust the extract volume to 1-2 mL under a gentle stream of nitrogen . If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume will need to be larger.

9.1.1.11 The extract obtained is now ready to be cleaned and fractionated on a silica gel column. If cleanup will not be performed immediately, transfer the extract to a Teflon-lined screw-cap vial, label, and refrigerate.

9.1.1.12 Record the sample preparation information for the extraction and concentration steps. At a minimum, record the date, sample laboratory number, sample volume, volume and concentration of added surrogate and matrix spike solutions, and any deviations or problems associated with the extraction of the samples.

9.1.1.13 For cleanup and fractionation, refer to Section 9.1.4.

9.1.2 Soil/Sediment Extraction using Ultrasonic Extraction

9.1.2.1 The following steps should be performed rapidly to minimize the loss of the more volatile fractions. In a beaker blend 10 g of the soil/sediment sample with sufficient anhydrous sodium sulfate to form a free flowing powder using a spatula. Add 1.0 mL of the surrogate spiking solution to the samples and blanks. For the samples in each analytical batch selected for matrix spiking, add 1.0 mL of the matrix spiking standard. Immediately add approximately 50 mL of 1:1 methylene chloride:acetone to the beaker. If lower PQL's are desired, the analyst is allowed to increase the sample size extracted. This will necessitate a proportional increase in the volume of extraction solvent used.

9.1.2.2 Place the bottom surface of the tip of the ultrasonic horn about 1/2 inch below the surface of the solvent but above the soil/sediment layer.

9.1.2.3 Sonicate for 3 minutes with the control knob set to the maximum output, pulse mode and 50% duty cycle.

9.1.2.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

9.1.2.5 Decant and filter the extract through Whatman No. 41 filter paper into the K-D concentrator. Repeat the extraction two more times with additional 50 mL portions of the solvent. Decant off and filter the extract into the K-D flask each time. On the last extraction, pour

the entire sample into the funnel and rinse the beaker and sample with additional portions of solvent and add these to the K-D flask. The analyst may find it useful to (1) either add anhydrous sodium sulfate to the filter for drying the extract or (2) to pass the extract through a drying column containing about 10 cm of anhydrous sodium sulfate prior to collecting the extract in the K-D flask.

9.1.2.6 Add one clean boiling chip to the K-D flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10 to 20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1-2 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

9.1.2.7 Exchange the methylene chloride with hexane by adding 50 mL of hexane to the top of the Snyder column and concentrating the extract as described in Paragraph 9.1.2.6, raising the temperature of the water bath, if necessary, to maintain proper distillation. The alternate solvent exchange technique described in note in 9.1.1.9 may also be used.

9.1.2.8 Remove the Snyder column and evaporation flask from the 10-mL concentrator tube. Place the concentrator tube containing the hexane extract onto a nitrogen blowdown apparatus. Adjust the extract volume to 1-2 mL under a gentle stream of nitrogen . If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume will need to be larger.

9.1.2.9 The extract obtained is now ready to be cleaned and fractionated on a silica gel column. If cleanup will not be performed immediately, transfer the extract to a Teflon-lined screw-cap vial, label, and refrigerate.

9.1.2.10 Record the sample preparation information for the extraction and concentration steps, as specified in paragraph 9.1.1.14.

9.1.2.11 For cleanup and fractionation, refer to Section 9.1.4.

9.1.3 <u>Soil/Sediment Extraction by Soxhlet Extraction</u>

9.1.3.1 Blend 10 g of the soil/sediment sample with sufficient anhydrous sodium sulfate to produce a free flowing powder and place this material in an extraction thimble. The extraction thimble must drain freely for the duration

of the extraction period. Add 1.0 mL of the surrogate spiking solution onto the sample. For the samples in each analytical batch selected for matrix spiking, add 1.0 mL of the matrix spiking solution. If lower PQL's are desired, the analyst may increase the quantity of sample extracted.

9.1.3.2 Place approximately 200 mL of methylene chloride into a 250-mL Erlenmeyer or round bottomed flask (depending on the heating source) containing several clean boiling chips. Attach the flask to the extractor and extract the sample for 8-16 hr.

9.1.3.3 Allow the extract to cool after the extraction is completed.

9.1.3.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

9.1.3.5 Dry the extract by passing it through a glass powder funnel containing anhydrous sodium sulfate. Collect the dried extract in the K-D concentrator. Wash the extractor flask and sodium sulfate column with 50 to 75 mL of methylene chloride to complete the quantitative transfer.

9.1.3.6 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10 to 20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1-2 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

9.1.3.7 Exchange the methylene chloride with hexane by adding 50 mL of hexane to the top of the Snyder column and concentrating the extract as described in Paragraph 9.1.3.6, raising the temperature of the water bath, if necessary, to maintain proper distillation. The alternate solvent exchange technique outlined in the note in 9.1.1.9 may also be used.

9.1.3.8 Remove the Snyder column and evaporation flask from the 10 mL concentrator tube. Place the concentrator tube containing the hexane extract onto a nitrogen blowdown apparatus. Adjust the extract volume to 1-2 mL under a gentle stream of nitrogen . If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume will need to be larger.

9.1.3.9 The extract obtained is now ready to be cleaned and fractionated on a silica gel column. If cleanup will not be performed immediately, transfer the extract to a Teflon-lined screw-cap vial, label, and refrigerate.

9.1.3.10 Record the preparation information for the extraction and concentration steps, as specified in 9.1.1.14.

9.1.3.11 For cleanup and fractionation, refer to Section 9.1.4.

9.1.3.12 The use of the Accelerated Solvent Extraction (ASE), EPA Method 3545, is an acceptable alternative to either ultrasonic or soxhlet extraction techniques as long as it is demonstrated to achieve comparable results.

9.1.4 Silica Gel Cleanup and Separation

9.1.4.1 Silica gel is a regenerative adsorbent of amorphous silica with weakly acidic properties. It is produced from sodium silicate and sulfuric acid. Silica gel can be used for column chromatography and is used for separating analytes from interfering compounds of a different chemical polarity. Silica gel is also used to separate petroleum distillates into aliphatic and aromatic fractions. Before the silica gel technique can be utilized, the extract solvent must be exchanged to hexane. This procedure may be performed immediately before the extract concentration step is complete by adding hexane to the K-D (when the volume of remaining methylene chloride is approximately 10 to 15 mL) and reducing the extract volume to 1 to 2 mL. After cooling, disassemble the K-D apparatus, rinsing the joints into the concentrator tube with a minimum of hexane. With a nitrogen blowdown concentrator, further reduce the extract to a final volume of 2 mL.

9.1.4.2 Prepare a slurry of 10g of activated silica gel in methylene chloride and place this into a 10 mm I.D.x 250 mm long chromatographic column. Tap the column to settle the silica gel and elute the methylene chloride. Add 1 to 2 cm of anhydrous sodium sulfate to the top of the silica gel. Note: The activity of each new batch (lot number) of silica gel must be evaluated prior to its use in this procedure. This requires the use of the fractionation check solution to insure that there is an efficient separation of the aromatic fraction from the aliphatic fraction. If necessary, the analyst is allowed to adjust the volumes of the eluants used to facilitate this process.

9.1.4.3 Pre-elute the column with 40 mL of pentane. Let the solvent flow through the column, at a rate of about 2 mL/minute, until the head of the liquid in the

column is just above the sodium sulfate layer. Close the stopcock to stop solvent flow. Discard this pentane.

9.1.4.4 Open the stopcock and immediately transfer the hexane sample extract onto the silica gel column. Rinse the concentrator tube with an additional 1-2 mL of hexane and add this to the column as well.

9.1.4.5 Just prior to exposure of the sodium sulfate layer to the air, add 25 mL of pentane to the column. Collect the eluant in a 250 mL K-D flask to which is attached a 10 mL concentrator tube and label this fraction "aliphatics". Concentrate and solvent exchange this extract into hexane.

9.1.4.6 Following recovery of the aliphatic fraction and just prior to exposure of the sodium sulfate layer, elute the column with 50 mL of methylene chloride/pentane (40:60) (v/v) and collect the eluant in a 250 mL K-D flask equipped with a 10 mL concentrator tube.. Label this fraction "aromatics". Concentrate and solvent exchange this extract into methylene chloride.

9.1.4.7 Concentrate each fraction to a final volume of 10 mL under a gentle stream of nitrogen from a nitrogen blowdown apparatus.

9.1.4.8 Transfer 1 mL of the fractions to a labeled two-mL glass autosampler vials with teflon-rubber crimp caps for analysis and save the remaining extract in a teflon-rubber septum screw topped vial. If lower PQL's are required, the analyst may concentrate the extract to as low as 1 mL prior to analysis

9.1.5 Proceed with the analysis in accordance with Sections 9.2 through 9.5. Analyze all laboratory method blanks and QC samples under the same conditions as that used for samples.

9.1.6 If chromatographic responses exceed the linear range of the system, dilute the extract(s) and re-analyze

9.1.7 <u>Determination of Percent Moisture</u>

9.1.7.1 Soil and sediment sample results must be reported on a dry-weight basis. A portion of sample for moisture determination should be weighed out at the same time as the portion used for hydrocarbon determination.

9.1.7.2 Immediately after weighing a sample for extraction, transfer 5 to 10 g of the sample into a tared crucible. Dry the sample overnight at 105°C in an oven. After drying remove it from the oven allow it to cool in a desiccator before reweighing. Calculate the percent moisture of the sample using the equations provided in Section 9.6.3.

9.2 **GC Conditions**

9.2.1 Suggested Gas Chromatographic Conditions

9.2.1.1 Oven Program: Set oven temperature to 50 °C for 2 minute, then 8°C/min to 320 °C and hold for 10 minutes.

9.2.1.2 Sample/autosampler injection volume is 1 to 2 µL.

9.2.1.3 Gas Flows: The recommended carrier gas is helium.

9.2.1.3.1 Helium carrier gas flow: 1 to 2 mL/min.

9.2.1.3.2 Air: 400 mL/min.

9.2.1.3.3 Hydrogen: 35 mL/min.

9.2.1.3.4 Make up gas flow: 30 mL/min.

9.2.1.4 Miscellaneous:

9.2.1.4.1 FID temperature, 310 to 320 °C

9.2.1.4.2 Injection port temperature, 290 to 300 °C

9.2.1.4.3 GC operated in splitless mode

9.2.1.4.4 Column head pressure 15.0 psi at 50°C

9.2.1.4.5 Linear velocity approximately 50 cm/sec

9.3 **Retention Time Windows**

9.3.1 Before establishing windows, make sure the GC system is within optimum operating conditions. Make three injections of the Aromatic and Aliphatic Hydrocarbon standard mixtures throughout the course of a 72-hr period. Serial injections over less than a 72-hr period may result in retention time windows that are too tight.

9.3.2 Calculate the standard deviation of the three absolute retention times for each standard.

9.3.3 Plus or minus three times the standard deviation of the absolute retention times for each standard should be used to define the retention time window. However, the

experience of the analyst should weigh heavily in the interpretation of chromatograms.

9.3.4 In those cases where the standard deviation for a particular standard is zero, the laboratory should substitute the standard deviation of a closely eluting structurally similar compound to develop a valid retention time window.9.3.5 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed or a portion removed as part of GC maintenance. This data must be retained by the laboratory.

9.3.6 EPH retention time (Rt) windows for all fractions (carbon ranges and hydrocarbon types) except the C8 through C10 are defined as beginning 0.1 minutes after the Rt of the beginning marker compound and ending 0.1 minutes after the Rt of the ending marker compound. Since the first fraction for both the aliphatics and aromatics includes the beginning marker compounds, the Rt windows for them are defined as beginning 0.1 minutes before the Rt of the beginning marker compound and ends 0.1 minutes after the ending marker compound.

EPH marker compounds and windows are summarized in Table 4.

Table 4. EPH Marker Compounds

Range/ Hydrocarbon Standard	Beginning Marker Compound	Ending Marker Compound
C8-C10 Aliphatic Hydrocarbons	just before n-octane	just after n-decane
C10-C12 Aliphatic Hydrocarbons	just after n-decane	just after n-dodecane
C12-C16 Aliphatic Hydrocarbons	just after n-dodecane	just after n-hexadecane
C16-C21 Aliphatic Hydrocarbons	just after n-hexadecane	just after n-henicosane
C21-C34 Aliphatic Hydrocarbons	just after n-henicosane	just after n-tetratriacontane
C8-C10 Aromatic Hydrocarbons	just before toluene	just after 1,2,3-trimethylbenzene
C10-C12 Aromatic Hydrocarbons	just after 1,2,3-trimethylbenzene	just after naphthalene
C12-C16 Aromatic Hydrocarbons	just after naphthalene	just after acenaphthene
C16-C21 Aromatic Hydrocarbons	just after acenaphthene	just after pyrene
C21-C34 Aromatic Hydrocarbons	just after pyrene	just after benzo(g,h,i)perylene

9.4 **Calibration**

Calibrate the GC system using either the external standard procedure (Section 9.4.1) or the internal standard procedure (Section 9.4.2).

9.4.1 External standard calibration procedure

9.4.1.1 Prepare Aromatic and Aliphatic Hydrocarbon calibration standards at a minimum of five concentration levels by adding volumes of one or more stock standard solutions to volumetric flasks and diluting to volume with methylene chloride and hexane, respectively. The surrogate OTP is added to the Aromatic Hydrocarbon Standard; the surrogate COD is added to the Aliphatic Hydrocarbon Standard. One of the calibration

standards must be at a concentration near, but above, the method detection limit and is used to determine the reporting PQL. In order to report the PQL's listed in 1.4, given the volume/mass water or soil extracted of 1 liter or 10 grams and assuming 100% solids on the soil, this standard must be at a 5 ng/uL level. The other concentrations must correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

9.4.1.2 A collective calibration curve or factor must be established for each hydrocarbon range of interest. Inject each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph (e.g., 1 to 2 µL injections). To calculate the collective CF for C8-C10, >C12-C12, >C12-C16, >C16-C21 and C21-C34 Aromatic Hydrocarbons, tabulate the summation of all peak areas of the calibration compounds in that range (e.g. C8-C10, toluene and 1,2,4-trimethylbenzene or >C10-C12, naphthalene) against the total mass injected. Although a forced baseline projection is required for samples and blanks, the analyst is allowed to integrate only the area of the calibration compound(s) to generate the calibration factors. The ratio of the response to the amount injected, defined as the calibration factor (CF), or range CF, may be calculated for hydrocarbon ranges at each standard concentration using Equation 1. If the percent relative standard deviation (%RSD) of the calibration factor is equal to or less than 20 % over the working range for the ranges of interest, as determined using Equation 2, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve. The Aliphatic Hydrocarbon collective CF is calculated in the same manner using the aliphatic standards.

Equation 1: Range Calibration Factor

$$Range\ CF = \frac{total\ area\ of\ peaks}{mass\ injected\ (ng)}$$

Equation 2: Percent Relative Standard Deviation

$$\%RSD = \frac{Stand\ Dev\ of\ 5\ CFs}{Mean\ of\ 5\ CFs} \times 100$$

Note: The area for the surrogates COD and OTP must be subtracted from the area of the range in which they elute (e.g., COD is subtracted from the C16-C21 Aliphatic Hydrocarbon range.

9.4.1.4 At a minimum, the working calibration curve or calibration factor must be verified at the beginning of each working day and after the final analysis of that day, or after every 20 samples, whichever is more frequent, by the injection of a mid-level calibration standard to verify instrument performance and linearity. If the percent difference (%D) for any range varies from the predicted response by more than ± 20 %, as calculated using Equation 4, a new calibration curve must be prepared.

Equation 4: Percent Difference (%D)

$$\%D = \frac{\overline{CF} - CFv}{\overline{CF}} \times 100$$

where:

$\overline{CF}$ = Average Calibration Factor from calibration curve.

CFv = Calibration Factor from verification calibration check.

9.4.1.5 The concentrations of hydrocarbon ranges may also be calculated from a calibration curve by use of linear regression analysis.

9.4.2 Internal standard calibration procedure

9.4.2.1 The suggested internal standard for this method is 5-alpha-androstane (EM Science, Gibbstown, NJ).

9.4.2.2 Prepare Aromatic and Aliphatic Hydrocarbon calibration standards at a minimum of five concentration levels by adding volumes of stock standard solutions to volumetric flasks. The surrogate OTP is added to the Aromatic Hydrocarbon Standard; the surrogate COD is added to the Aliphatic Hydrocarbon Standard. To each calibration standard, add a known constant amount of an internal standard. One of the calibration standards must be at a concentration near, but above, the method detection limit and is used to determine the reporting PQL. The other concentrations must correspond to the expected range of concentration found in real world samples or should define the working range of the detector.

9.4.2.3 Inject each calibration standard using the same technique that will be applied to the samples (e.g., 1 to 2 µL injection). Tabulate the peak area responses against the concentration of each hydrocarbon range and internal standard. Calculate the collective response factors (RF) for each hydrocarbon range using Equation 5.

Note: The area for the surrogates COD and OTP must be subtracted from the area of the range in which they elute (e.g., COD is subtracted from the appropriate Aliphatic Hydrocarbon range).

uation 5: Range Response Factor

$$Range\ RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Summation of peak areas of the fraction (e.g., C10-C12 Aliphatic Hydrocarbons).

C_{is} = Concentration of internal standard, ng/µL.

A_{is} = Response for the internal standard.

C_s = Total mass concentration of injected standards, ng/µL.

9.4.2.4 At a minimum, the working calibration curve or RF must be verified at the beginning of each working day and after the final analysis of that day, or after every 20 samples, whichever is more frequent, by the injection of a mid-level calibration standard to verify instrument performance and linearity. If the percent difference (%D) for any hydrocarbon range varies from the predicted response by more than ± 20 %, as calculated using Equation 4, a new calibration curve must be prepared for that range.

9.4.2.5 The concentrations of hydrocarbon ranges may also be calculated from a calibration curve by the use of linear regression analysis.

9.5 **GC Analysis**

9.5.1 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration, or verification of calibration, followed by sample extracts interspersed with blanks and QC samples. The analytical sequence must end with an acceptable verification calibration standard. If the ending calibration standard is not acceptable, all samples analyzed after the last acceptable calibration verification must be reanalyzed. If, for whatever reason, reanalysis is not possible, then the data for those samples must be qualified as an "estimate".

9.5.2 Aliphatic and aromatic extracts are introduced into the gas chromatograph by slitless injection.

9.5.3 Inject 1 to 2 µL of the sample extract. Record the volume injected and the resulting peak size in area units.

9.5.4 Confirm the established retention time windows for each hydrocarbon range on a daily basis. Use the absolute retention time for each analyte as the midpoint of the window for that day. The daily retention time window equals the midpoint ± three times the standard deviation determined in Section 9.3.

9.5.4.1 Validation of GC system qualitative performance must be accomplished by the analysis of standards within the analysis sequence. If any of the standards fall outside their daily retention time window, the system is out of control. In such cases, the cause of the problem must be determined and corrected.

9.5.5 When quantifying on a peak area basis by internal or external calibration, peak area integration for the aliphatic and aromatic carbon ranges must be <u>from baseline</u> (i.e. must include the unresolved complex mixture "hump" areas).

9.6 **Calculations**

9.6.1 <u>External Standard Calibration</u>

The concentration of each hydrocarbon range in a sample may be determined by calculating the amount of hydrocarbon range compounds injected, from the peak response, using the calibration curve or the calibration factor determined in Section 9.4.

9.6.1.1 **Aqueous samples:**

The general equation to determine the concentration of a hydrocarbon range in aqueous samples in provided in Equation 6.

Equation 6

$$Concentration\ (ug / L) = \frac{(A_x)(A)(V_t)(D)}{(A_s)(V_i)(V_s)}$$

w

here:

A_x = Response for a hydrocarbon range in the sample, units may be in area counts or peak height.

A = Amount of standard injected, ng.

A_s = Response for the external standard, units same as for A_x.

V_i = volume of extract injected, µL.

D = Dilution factor: if no dilution was made, D = 1, dimensionless.

V_t = Volume of total extract, µL.

V_s = Volume of sample extracted, mL.

If a Calibration Factor is used, the concentration of a hydrocarbon range may be calculated using Equation 7.

Equation 7

$$Conc\ HC\ Range\ (ug / L) = \frac{(A_X)(V_t)(D)}{(V_i)(V_s)(Range\ CF)}$$

where:

Range CF = Calibration Factor for hydrocarbon ranges (collective area count/collective mass).

9.6.1.2 **Nonaqueous samples:**

The general equation to determine the concentration of a hydrocarbon range in soil or sediment samples is provided in Equation 8.

Equation 8

$$Concentration\ (ug / kg) = \frac{(A_x)(A)(V_t)(D)}{(A_s)(V_i)(W_d)}$$

where:

W_d = Dry weight of sample extracted, g. (See Equations 12 through 14)

A_x, A_s, A, V_t, D, and V_i have the same definition as for aqueous samples.

If a Calibration Factor is used, the concentration of specific hydrocarbon ranges in a soil or sediment sample may be calculated using Equation 9.

Equation 9

$$Conc\ HC\ Range\ (ug / kg) = \frac{(A_x)(V_t)(D)}{(V_i)(W_d)(Range\ CF)}$$

where:

Range CF = Calibration Factor for a hydrocarbon range (collective area count/collective mass).

9.6.2 Internal Standard Calibration

The concentration of each hydrocarbon range in a sample may be determined by calculating the amount of hydrocarbon range compound(s) injected, from the peak response, based upon the compound/internal-standard response ratio.

9.6.2.1 **Aqueous samples:**

The general equation to determine the concentration of a specific hydrocarbon range in aqueous samples is provided in Equation 10.

Equation 10

$$Concentration\ (ug / L) = \frac{(A_x)(C_{is})(D)}{(A_{is})(RF)(V_s)}$$

where:

A_x = Response of the hydrocarbon range being measured, units may be in area counts or in peak height.

C_{is} = Amount of internal standard added to extract, ng.

D = Dilution factor, if a dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

A_{is} = Response of the internal standard, units same as A_x.

RF = Response factor for the hydrocarbon range, dimensionless.

V_s = Volume of aqueous sample extracted, mL.

9.6.2.2 **Nonaqueous samples:**

The general equation to determine the concentration of a specific or hydrocarbon range in soil or sediment samples is provided in Equation 11.

Equation 11

$$Concentration\ (ug / kg) = \frac{(A_x)(C_{is})(D)}{(A_{is})(RF)(W_d)}$$

where:

W_d = Dry weight of sample extracted, g. (See Equations 12 through 14).

A_x, C_{is}, D, A_{is}, and RF have the same definition as for aqueous samples.

9.6.3 Calculation of Dry Weight of Sample

In order to calculate the dry weight of sample extracted (W_d), it is necessary to determine the moisture content of the soil/sediment sample, using the procedure outlined in Section 9.1.7. Using the data obtained from Section 9.1.7, W_d is calculated using Equations 12 through 14.

Equation 12

$$\% \text{ Moisture} = \frac{g \text{ sample} - g \text{ dry sample}}{g \text{ sample}} X\ 100$$

Equation 13

$$\% \text{ Dry Solids} = (1) - (\% \text{ Moisture})$$

Equation 14

$$W_d\ (g) = (\% \text{ Dry Solids})(g \text{ of extracted sample})$$

10.0 QUALITY CONTROL

10.1 **General Requirements and Recommendations**

10.1.1 Each laboratory that uses this method should operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance standards for the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

10.1.2 Hexane or methylene chloride solvent blanks should be run after samples suspected of being highly contaminated to determine if sample carryover has occurred.

10.1.3 At a minimum, for each analytical batch (up to 20 samples), a Laboratory Method Blank, Laboratory Fortified Blank Spike (Water or Soil), Laboratory Fortified

Matrix Spike, and sample duplicate must be analyzed. For analytical batches with more than 10 samples, the analysis of an additional mid-range calibration check standard is recommended. The blank and spiked samples must be carried through all stages of the sample preparation and measurement process.

10.1.4 The recommended sequence of analysis is as follows:

(1) Calibration Standards (initial) or mid-range Calibration Check (Verification) Standard (i.e. daily check of initial calibration)
(2) Laboratory Method Blank
(3) Samples
(4) QC Samples
(5) Mid-range Calibration Check (Verification) Standard (also recommended after each 10 samples)

10.1.5 It is recommended that a system of control charts be developed to plot surrogate standard recoveries as a function of time. When surrogate recovery from a sample, blank, or QC sample is less than 50% or more than 150%, check calculations to locate possible errors, the fortifying solution for degradation, and changes in instrument performance. If the cause cannot be determined, the analyst may reanalyze the sample extract, report the surrogate values as outside acceptance limits or, if additional sample is available, re-extract and reanalyze the sample.

10.2 **Minimum Instrument QC**

10.2.1 The instrument must be able to achieve adequate separation and resolution of peaks of interest.

10.2.1.1 The n-octane (n-C8) and toluene peaks must be adequately resolved from the solvent front of the chromatographic run.

10.2.1.2 The surrogates COD and OTP and any internal standards used must be adequately resolved from any individual components in the Aliphatic Hydrocarbon and Aromatic Hydrocarbon standards.

10.2.2 Retention time windows must be established for each hydrocarbon range of interest each time a new GC column is installed, and must be verified and/or adjusted on a daily basis. (See Section 9.3)

10.2.3 Calibration curves must be developed based upon the analysis of calibration standards prepared at a minimum of 5 concentration levels. The linearity of calibration or response factors may be assumed if the percent relative standard deviation (%RSD) over the working range of the curve is less than or equal to 20 %. Alternatively, if linear regression analysis is used for

quantitation, the correlation coefficient (r) must be at least 0.99. and the percent difference (% D) of the response for any hydrocarbon range from the predicted response may not vary by more than +/- 20%. (See Section 9.4.)

10.3 **Initial and Periodic Method QC Demonstrations**

The following must be conducted as an initial demonstration of laboratory capability, prior to the analysis of any samples. Subsequent to this initial demonstration, additional evaluations of this nature should be conducted on a periodic basis, in response to changes in instrumentation or operations, and/or in response to confirmed or suspected systems, method, or operational problems.

10.3.1 Accuracy and Precision

To demonstrate initial laboratory capability, analyze a minimum of four replicate reagent water and/or clean sand blanks spiked with the calibration compounds for each range of interest at approximately 50 µg/L and/or 5 mg/kg, respectively.

10.3.1.1 Extract and analyze each replicate according to the procedures described in Section 9.0.

10.3.1.2 Calculate the measured concentrations of each range in all replicates, the mean accuracy (as a percentage of true value) for each compound, and the precision (as %RSD) of the measurements for each compound.

10.3.1.3 For each compound, the mean accuracy, expressed as a percentage of the true value, should be between 70 % and 130 %. For each compound, the %RSD must be less than or equal to 20%.

10.3.2 Method Detection Limits (Optional)

Analyze a minimum of seven replicate reagent water and/or clean sand blanks which have been fortified with all analytes of interest at approximately 0.5 to 2 µg/L and/or 1.0 to 5.0 mg/kg, respectively. Extract and analyze each replicate according to the procedures described in Section 9.0. Calculate the Method Detection Limit (MDL) of each analyte using the procedure described in Section 12.0.

10.3.2.1 Water MDLs are determined by extracting 7 to 10 replicates of 1-L reagent water blanks spiked with OTP, COD and each analyte of interest.

10.3.2.2 Soil/sediment MDLs are determined by extracting 7-10 replicates of 10-g of EPH-free sand blanks spiked with OTP, COD, and each analyte of interest.

10.3.3 Fractionation

To demonstrate the capability of properly fractionating aliphatic and aromatic hydrocarbons in a sample, the analyst must first prepare and analyze the Fractionation Check Solution specified in Section 7.6.

10.3.3.1 Prepare a silica gel column as outlined in 9.1.4

10.3.3.2 Load 1.0 mL of the Fractionation Check Solution onto column and proceed with the elution and collection of the aliphatic and aromatic fractions as outline in 9.1.4.

NOTE: The amount of pentane used during the elution/fractionation is critical. Excessive pentane will cause elution of aromatics into the aliphatic fraction. Insufficient pentane will cause low recoveries of the aliphatic fraction. The volume of pentane and/or methylene chloride/pentane recommended may need to be adjusted to meet QC limits.

10.3.3.3 Solvent exchange the aliphatic fraction to hexane and the aromatic fraction to methylene chloride. Concentrate each solution to a final volume of 1.0 mL under a gentle stream of nitrogen from an nitrogen blowdown apparatus.

10.3.3.4 Transfer the final 1.0 mL extracts to two labeled glass auto sampler vials with teflon-lined rubber crimp caps. Analyze by GC/FID (see Section 9.0).

10.3.3.5 For each analyte within the Fractionation Check Solution, the mean accuracy, expressed as a percentage of the true value, must be between 70 % and 130 %.

10.3.4 Petroleum Reference Standard

As an optional demonstration of the validity and relevance of EPH calibration, analyze a reagent water and/or clean sand blank spiked with a known concentration of a neat petroleum product.

10.3.4.1 Dilute a Petroleum Reference Standard stock standard solution with acetone to a concentration of approximately 250 ng/µL. Spike a 1 Liter reagent water blank or 10 g clean sand blank with 1.0 mL of this spiking solution. Extract and analyze in accordance with the procedures outlined in Section 9.0.

10.3.4.2 Calculate the total concentration of all petroleum hydrocarbons within each range. Add these values together.

10.3.4.3 The concentration calculated in Paragraph 10.3.4.2 is expected to be within +/- 30 % of the known concentration of Petroleum Standard in the reagent water or sand blank.

10.4 **Ongoing Method QC Demonstrations**

10.4.1 Each sample, blank, and matrix spike sample must be spiked with the surrogate spiking solution. Required surrogate recovery is 60% to 140%.

10.4.2 At a minimum, with every batch of 20 samples or less the lab must analyze the following:

10.4.2.1 **Calibration Check Standard** - A mid-range calibration standard, prepared from the same stock standard solution used to develop the calibration curve, must be analyzed prior to sample analysis to verify the calibration state of the instrument. For large analytical batches that contain more than 10 samples, the analysis of an additional mid-range calibration check standard is recommended after the analysis of the tenth sample. If the percent difference (% D) of any compound within a calibration check standard varies from the predicted response by more than 20 %, a new calibration curve must be prepared. (See Section 9.4)

10.4.2.2 **Laboratory Method Blank** - A water or soil laboratory method blank is prepared by fortifying a reagent water or clean sand blank with 1.0 mL of the surrogate spiking solution. Peaks within the retention time windows of any hydrocarbon ranges of interest may not be present at or above the lowest calculated PQL for any sample within its batch. When determining the PQL of soil method blanks, incorporate the lowest percent solids value found for any sample within its batch in the calculation.

10.4.2.3 **Laboratory Fortified Blank Spike** - A water or soil component spike is prepared by fortifying a reagent water or clean sand blank with 1.0 mL of the matrix spiking solution. The spike recovery must be between 70 % and 130 % and, if these values can not be obtained, the analyst must identify and correct the problem before analyses can continue.

10.4.2.4 **Sample duplicates** - Sample duplicates may be laboratory duplicates or field duplicates and the RPD of the duplicate samples should not exceed +/- 25%. The lack of sample homogeneity may contribute to the RPD's values for duplicates which exceed this value. Should the values exceed 25% the analyst must report that occurrence.

10.4.2.5 **Laboratory Fortified Matrix (LFM) Spike** - The water or soil LFM spike is prepared by fortifying an actual water or soil sample with 1.0 mL of the matrix spiking solution. The purpose of the LFM spike is to

determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations. The corrected concentrations of each analyte within the LFM spike sample must be within 70 to 130 % of the true value. Should the values determined exceed this range, the analyst must report that occurrence.

10.4.3 If any of the performance standards specified in Section 10.4 are not met, the problem should be corrected before further samples are analyzed. Exceptions to this are duplicate samples RPD's and high recoveries for LFM spikes which, due to sample non-homogeneity, may exceed the allowable limits. Any samples run between the last calibration check standard that meet the criteria and one that does not must be reanalyzed. If this is not possible, then the data must be reported as an "estimated concentration."

11.0 DATA PRODUCTION AND REPORTING

11.1 **Sample Analysis**

11.1.1 Aliphatic Fraction

11.1.1.1 Determine the total area count for all peaks eluting 0.1 minutes before the retention time (Rt) for C8 to 0.1 minutes after the Rt for C10.

11.1.1.2 Determine the total area count for all peaks eluting 0.1 minutes after the Rt for C10 to 0.1 minutes after the Rt for C12. Determine the total area count of all peaks eluting 0.1 minutes after the Rt for C12 to 0.1 minutes after the Rt for C16, for all peaks eluting 0.1 minutes after the Rt for C16 to 0.1 minutes after the Rt for C21and for all peaks eluting 0.1 minutes after the Rt for C21 to 0.1 minutes after the Rt for C34. It is not necessary to identify or quantitate individual aliphatic compounds within these ranges.

11.1.1.3 Determine the peak area count for the surrogate COD and any internal standard used. Subtract these values from the collective area count value within the appropriate hydrocarbon range(s).

11.1.1.4 Using the equations contained in Section 9.6 or linear regression analysis, calculate the concentrations of C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 Alipiphatic Hydrocarbon ranges and the surrogate standard COD.

11.1.1.5 The term "all peak areas" must include any unresolved envelope of peaks which elute within the Rt windows listed above and below for the aliphatic and aromatic fractions.

11.2.1 Aromatic Fraction

11.2.1.1 Determine the total area count for all peaks eluting 0.1 minutes before the retention time (Rt) for toluene to 0.1 minutes after the Rt for 1,2,3 trimethylbenzene. In the same manner, determine the total area count for all peaks eluting 0.1 minutes after the Rt for 1,2,3-trimethylbenzene to 0.1 minutes after the Rt for naphthalene, from 0.1 minutes after the Rt for naphthalene to 0.1 minutes after the Rt for acenaphthene, from 0.1 minutes after the Rt for acenaphthene to 0.1 minutes after the Rt for pyrene and 0.1 minutes after the Rt for pyrene to 0.1 minutes after the Rt for benzo(g.h.i)perylene.

11.2.1.2 Determine the peak area count for the surrogate OTP and any internal standard used.

11.2.1.3 Subtract the peak area value from 11.2.1.2 from the collective area count value for the range effected determined in 11.2.1.1 to calculate the area count for Aromatic Hydrocarbons ranges.

11.2.1.4 Using the equations contained in Section 9.6 or linear regression analysis, calculate the concentrations of C8 through C10, >C10 through C12, >C12 through C16 , >C16 through C21 and >C21 through C34 Aromatic Hydrocarbons and the surrogate standard COD.

11.3 Data Reporting Format

11.3.1 The following information and data must be reported:

11.3.1.1 The sample matrix (aqueous, soil or sediment);

11.3.1.2 The date(s) the sample was collected, received by the laboratory, extracted, and analyzed;

11.3.1.3 A description of the sample(s) received by the laboratory, relative to the physical condition of the containers, the temperature of the samples, and use of appropriate preservatives;

11.3.1.4 Moisture content (for soil/sediment samples);

11.3.1.5 The calculated concentrations of C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 Aliphatic Hydrocarbons, and C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 Aromatic Hydrocarbons.

11.3.1.6 Surrogate recovery (expressed as percent recovery);

11.3.1.7 The concentration units for aqueous samples are expressed as ug/L or mg/L and soil or sediment samples the units are expressed as µg/Kg or mg/Kg on a dry-weight basis.

12.0 METHOD PERFORMANCE

12.1 **Method Detection Limits (Optional)**

12.1.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

12.1.2 The MDL is determined according to Equation 15.

Equation 15

$$MDL = (t) \times (SD)$$

where:

t = student t value at the 99% confidence level.

SD = standard deviation of the replicate analysis.

Student t values are as follows:

Number of replicates	t value
7	3.14
8	3.00
9	2.90
10	2.82

12.2 **Single Laboratory Accuracy, Precision and MDL Data**

Single laboratory accuracy, precision and MDL data for method analytes are provided in Tables 1-1 through 1-4 in Appendix 1. Tables 1-1 and 1-2 present data collected from spiking reagent water at 5.0 µg/L; Tables 1-3 and 1-4 by spiking sand at 1.0 mg/kg.

13.0 REFERENCES

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2. USEPA, "Measurement of Petroleum Hydrocarbons: Report on Activities to Develop a Manual." Prepared by Midwest Research Institute, Falls Church, VA, under EPA Contract #68-WO-0015, WA No. 4; submitted to USEPA Office of Underground Storage Tanks, Washington, DC; November 20, 1990.

3. USEPA Federal Register 40 CFR Part 136, Appendix B, "Guidelines Establishing Test procedures for the Analysis of Pollutants," July 1992.

4. USEPA Test Methods for Evaluating Solid Waste (SW-846); Method 3510: Separatory Funnel Liquid-Liquid Extraction; September 1986.

5. USEPA Test Methods for Evaluating Solid Waste (SW-846); Method 3540: Soxhlet Extraction; September 1986.

6. USEPA Test Methods for Evaluating Solid Waste (SW-846); Method 3630: Silica Gel Cleanup; September 1986.

7. USEPA Test Methods for Evaluating Solid Waste (SW-846): Method 8000: Gas Chromatography; September 1986.

8. USEPA Test Methods for Evaluating Solid Waste (SW-846); Method 8100: Polynuclear Aromatic Hydrocarbons; September 1986.

9. Wisconsin Department of Natural Resources, "Modified DRO - Method for Determining Diesel Range Organics," PUBL-SW-141, 1992.

APPENDIX 1

SINGLE LABORATORY ACCURACY, PRECISION, AND METHOD DETECTION LIMITS (MDL) DATA FOR VPH

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Table 1-1. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Compounds in Component Standard Spiked Into Reagent Water and Analyzed by the VPH Method

Compound	Spiked Conc. (µg/L)	Method Accuracy[a] (Mean % Recovery[b])		Method Precision[a] (RSD[c] - %)		MDL[a] (µg/L)	
		PID[d]	FID[e]	PID	FID	PID	FID
n-Pentane	6.0		98		7.8		1.4
Methyl tert butylether	1.8	77	79	4.8	15	0.21	0.69
Benzene	0.6	82	97	4.9	10	0.08	0.19
Toluene	0.6	79	104	7.3	6.5	0.11	0.13
n-Nonane	2.0		83		8.0		0.42
Ethylbenzene	0.6	77	94	4.2	9.1	0.06	0.16
m- & p-Xylene	1.2	68	85	4.3	6.4	0.11	0.20
o-Xylene	0.6	79	88	16	6.4	0.23	0.11
1,2,3-Trimethylbenzene	0.6	69	89	8.2	6.4	0.11	0.11
Naphthalene	3.6	58	56	16	18	1.0	1.2
2,5-Dibromotoluene (surrogate)	40	88	92	4.9	13		

[a] Based on analysis of seven samples spiked with component standard.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] PID = photoionization detector.
[e] FID = flame ionization detector.

Table 1-2. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Compounds in Component Standard Spiked Into VPH- Free Sand and Analyzed by the VPH Method

Compound	Spiked Conc. (µg/Kg)	Method Accuracy[a] (Mean % Recovery[b])		Method Precision[a] (RSD[c] - %)		MDL[a] (µg/Kg)	
		PID[d]	FID[e]	PID	FID	PID	FID
n-Pentane	120		124		6.0		28
Methyl tert butylether	120	70	96	3.1	27	8.1	99
Benzene	60	122	128	3.3	5.4	7.6	13
Toluene	60	139	137	4.8	8.6	13	22
n-Nonane	120		119		4.6		21
Ethylbenzene	60	107	103	4.3	5.0	8.6	9.7
m- & p-Xylene	120	109	104	4.1	5.2	17	20
o-Xylene	60	103	111	3.8	6.6	7.4	14
1,2,3-Trimethylbenzene	60	93	102	5.5	5.3	9.6	10
Naphthalene	ND[f]	ND	ND	ND	ND	ND	ND
2,5-Dibromotoluene (surrogate)	2,000	119	117	8.6	9.7		

[a] Based on analysis of seven samples spiked with component standard.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] PID = photoionization detector.
[e] FID = flame ionization detector.
[f] ND = not determined.

Table 1-3. Single Laboratory Accuracy and Precision for Compounds in Component Standard Spiked Into Reagent Water at Concentrations in the Low to Middle End of the Analytical Range and Then Analyzed by the VPH Method

Compound	Spiked Conc. (µg/L)	Method Accuracy[a] (Mean % Recovery[b])		Method Precision[a] (RSD[c] - %)	
		PID[d]	FID[e]	PID	FID
n-Pentane	40		96		7.7
Methyl tert butylether	60	87	88	4.0	3.9
Benzene	20	99	99	4.4	3.7
Toluene	60	99	99	4.1	4.0
n-Nonane	40		104		10
Ethylbenzene	20	99	99	4.2	4.2
m- & p-Xylene	80	99	99	4.3	4.2
o-Xylene	40	99	99	3.7	3.6
1,23-Trimethylbenzene	40	99	99	4.1	4.0
Naphthalene	40	70	81	4.3	3.2
2,5-Dibromotoluene (surrogate)	40	92	94	5.2	4.6

[a] Based on analysis of five samples spiked with component standard.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] PID = photoionization detector.
[e] FID = flame ionization detector.

Table 1-4. Single Laboratory Accuracy and Precision for Compounds in Component Standard Spiked Into VPH-Free Sand at Concentrations in the Low to Middle End of the Analytical Range and Then Analyzed by the VPH Method

Compound	Spiked Conc. (mg/Kg)	Method Accuracy[a] (Mean % Recovery[b])		Method Precision[a] (RSD[c] - %)	
		PID[d]	FID[e]	PID	FID
n-Pentane	2.0		118		1.9
Methyl tert butylether	3.0	100	94	2.4	2.8
Benzene	2.0	119	109	3.0	0.7
Toluene	2.0	118	109	1.7	1.3
n-Nonane	ND	ND	ND	ND	ND
Ethylbenzene	1.0	121	110	1.4	1.2
m- & p-Xylene	3.0	122	110	1.4	1.1
o-Xylene	2.0	118	107	1.3	1.1
1,2,3-Trimethylbenzene	2.0	115	109	1.4	1.3
Naphthalene	2.0	61	57	11	1.8
2,5-Dibromotoluene (surrogate)	2.0	75	64	9.7	3.3

[a] Based on analysis of five samples spiked with component standard.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] PID = photoionization detector.
[e] FID = flame ionization detector.
[f] ND = not determined.

APPENDIX 2

SUGGESTED VPH DATA REPORTING FORMAT

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VOLATILE PETROLEUM HYDROCARBON (VPH) ANALYSIS

Client:
Client Sample ID: Date Received:
Laboratory Sample ID: Date Analyzed:
Matrix: Date Reported:
Percent Moisture:

VPH RESULTS

Parameter	Results	PQL				Units
C5-C6 Aliphatics (FID) *						
C6-C8 Aliphatics (FID) *						
C8-C10 Aliphatics (FID) *						
C10-C12 Aliphatics (FID) *						
C8-C10 Aromatics (PID)						
C10-C12 Aromatics (PID)						
C12-C13 Aromatics (PID)						

*** Excludes any MTBE or BTEX compounds**

SURROGATE RECOVERY

Surrogate	%Recovery	Acceptance Range
2,5-dibromotoluene		80% - 120%

TARGETED VPH ANALYTES

Analyte	**Results**	**PQL**	**Units**
Methyl tert butylether			
Benzene			
Toluene			
Ethylbenzene			
p-Xylene *			
m-Xylene *			
o-Xylene			
Naphthalene			

* p and m-xylenes may not be able to be resolved and may be reported as the total of p and m-xylenes.

APPENDIX 3

SINGLE LABORATORY ACCURACY, PRECISION, AND METHOD DETECTION LIMIT (MDL) DATA FOR EPH

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Table 1-1. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Alkanes Spiked Into Reagent Water and Analyzed by the EPH Method

Compound[a]	Compound Conc. Measured (µg/L)		Mean Accuracy (Mean % Recovery[b])	Method Precision (RSD[c] - %)	MDL (µg/L)
	Mean	Std. Dev.			
C_{10}	4.1	0.040	82	0.98	0.12
C_{12}	4.1	0.021	82	0.51	0.064
C_{16}	4.0	0.062	80	1.6	0.19
COD[d]	44	0.93	88	2.1	-
C21	3.7	0.047	74	1.3	0.14

[a] Compounds were spiked into 7 or 8 samples at a concentration of 5.0 µg/L.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] Surrogate (COD = 1-Chloro-octadecane) was spiked into three samples at a concentration of 50 µg/L.

Table 1-2. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Polynuclear Aromatic Hydrocarbons (PAHs) Spiked Into Reagent Water and Analyzed by the EPH Method

Compound[a]	Compound Conc. Measured (µg/L)		Mean Accuracy (Mean % Recovery[b])	Method Precision (RSD[c] - %)	MDL (µg/L)
	Mean	Std. Dev.			
Naphthalene	5.6	0.088	112	1.6	0.26
2-Methylnaphthalene	6.4	0.096	128	1.5	0.29
Acenaphthylene	5.6	0.085	112	1.5	0.26
Acenaphthene	5.7	0.092	114	1.6	0.28
Fluorene	5.6	0.094	112	1.7	0.28
Phenanthrene	5.5	0.097	110	1.8	0.29
Anthracene	7.0	0.10	140	1.4	0.31
OTP[d]	44	1.6	88	3.6	-
Fluoranthene	5.7	0.090	114	1.6	0.27
Pyrene	6.1	0.098	122	1.6	0.29
Benzo(a)Anthracene	5.9	0.089	118	1.5	0.27
Chrysene	5.8	0.098	116	1.7	0.29
Benzo(b)Fluoranthene	6.3	0.082	126	1.3	0.25
Benzo(k)Fluoranthene	5.6	0.065	112	1.2	0.20
Benzo(a)Pyrene	6.0	0.075	120	1.2	0.22
Indeno(123 cd)Pyrene	5.1	0.17	102	3.3	0.50
Dibenzo(ah)Anthracene	2.8	0.21	56	7.5	0.62
Benzo(ghi)Perylene	3.8	0.18	76	4.7	0.54

[a] Compounds were spiked into 7 or 8 samples at a concentration of 5.0 µg/L.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] Surrogate (OTP = ortho-Terphenyl) was spiked into three samples at a concentration of 50 µg/L.

Table 1-3. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Alkanes Spiked Into EPH-Free Sand and Analyzed by the EPH Method

Compound[a]	Compound Conc. Measured (mg/Kg)		Mean Accuracy (Mean % Recovery[b])	Method Precision (RSD[c] - %)	MDL (mg/Kg)
	Mean	Std. Dev.			
C_{10}	0.72	0.074	72	10	0.22
C_{12}	0.83	0.079	83	9.5	0.24
C_{16}	1.2	0.14	120	12	0.42
COD[d]	4.3	0.48	86	11	-
C21	0.81	0.044	81	5.4	0.13

[a] Compounds were spiked into 8 samples at a concentration of 1.0 mg/Kg.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] Surrogate (COD = 1-Chloro-octadecane) was spiked into three samples at a concentration of 5.0 mg/kg.

Table 1-4. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Polynuclear Aromatic Hydrocarbons (PAHs) Spiked Into EPH-Free Sand and Analyzed by the EPH Method

Compound[a]	Compound Conc. Measured (mg/Kg)		Mean Accuracy (Mean % Recovery[b])	Method Precision (RSD[c] - %)	MDL (mg/Kg)
	Mean	Std. Dev.			
Naphthalene	0.64	0.063	64	9.8	0.19
2-Methylnaphthalene	0.64	0.058	64	9.1	0.17
Acenaphthylene	0.68	0.060	68	8.8	0.18
Acenaphthene	0.70	0.064	70	9.1	0.19
Fluorene	0.79	0.060	79	7.6	0.18
Phenanthrene	0.83	0.041	83	4.9	0.12
Anthracene	1.2	0.082	120	6.8	0.25
OTP[d]	4.8	0.45	96	9.4	-
Fluoranthene	0.92	0.038	92	4.1	0.12
Pyrene	0.91	0.037	91	4.1	0.11
Benzo(a)Anthracene	0.96	0.042	96	4.4	0.12
Chrysene	0.90	0.050	90	5.6	0.15
Benzo(b)Fluoranthene	0.96	0.038	96	4.0	0.11
Benzo(k)Fluoranthene	0.87	0.037	87	4.3	0.11
Benzo(a)Pyrene	0.96	0.036	96	3.8	0.11
Indeno(123 cd)Pyrene	0.90	0.033	90	3.7	0.099
Dibenzo(ah)Anthracene	0.82	0.033	82	4.0	0.099
Benzo(ghi)Perylene	0.82	0.032	82	3.9	0.096

[a] Compounds were spiked into 7 or 8 samples at a concentration of 1.0 mg/Kg.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] Surrogate (OTP = ortho-Terphenyl) was spiked into three samples at a concentration of 5.0 mg/kg.

APPENDIX 4

SUGGESTED EPH DATA REPORTING FORMAT

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EXTRACTABLE PETROLEUM HYDROCARBON (EPH) ANALYSIS

Client:	
Client Sample ID:	Date Received:
Laboratory Sample ID:	Date Extracted:
Matrix:	Date Analyzed:
Percent Moisture:	Date Reported:

EXTRACTABLE PETROLEUM HYDROCARBON (EPH)

Parameter	Results	PQL				Units
C8-C10 Aliphatics						
C10-C12 Aliphatics						
C12-C16 Aliphatics						
C16-C21 Aliphatics						
C21-C34 Aliphatics						
C8-C10 Aromatics						
C10-C12 Aromatics						
C12-C16 Aromatics						
C16-C21 Aromatics						
C21-C34 Aromatics						

SURROGATE RECOVERIES

Surrogate	%Recovery	Acceptance Range
Chloro-octadecane (COD)		50% - 150%
Ortho-terphenyl (OTP)		50% - 150%

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APPENDIX 5

REPORT OF ANALYSIS

SUMMARY SHEET

Client: Client Sample ID Number(s): Laboratory ID Number(s):

SAMPLE INFORMATION

Sample Matrix	¨ Aqueous ¨ Soil ¨ Sediment ¨ Other:	
Analysis Performed	¨ VPH ¨ EPH ¨ VPH and EPH (E-TPH Duplicate samples)	
Condition of Containers	¨ Satisfactory ¨ Broken ¨ Leaking ¨ Other:	
Sample Preservatives	AQUEOUS	¨ N/A ¨ pH ≤ 2 ¨ pH > 2
	SOIL/SEDIMENT	¨ N/A
Sample Temperature	¨ Received on Ice ¨ Received at 4 °C ¨ Other	

ANALYTICAL RESULTS

Parameter	Results	PQL	Units
Volatile Petroleum Hydrocarbons (VPH)			
Extractable Petroleum Hydrocarbons (EPH)			
Equivalent TPH (E-TPH) ** [IF BOTH VPH AND EPH ANALYSES PERFORMED]			

**** Due to overlapping carbon ranges between the VPH and EPH methods and in order to avoid double counting, the analyst must select the higher of the two values to be included for reporting purposes for those ranges effected.**

COMMENTS

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APPENDIX 6*

Petroleum Product Chromatograms

Carburator Cleaner
Automotive Gasoline
Mineral Spirits #1
Mineral Spirits #2
JP-4 Jet Fuel (old)
JP-4 Jet Fuel (new)
JP-5 Jet Fuel
Kerosene
Kerosene (ICP grade)
Gasoline and #2 Diesel Oil
Natural Gas Condensate
#2 Fuel Oil
#2 Fuel Oil (38% aromatic) (See chromatogram in NWTPH-Dx)
#2 Diesel Oil (See chromatogram in NWTPH-Dx)
#2 Diesel Oil and Motor Oil (30w) (See chromatogram in NWTPH-Dx)
2-Cycle Engine Oil #1
2-Cycle Engine Oil #2
2-Cycle Engine Oil #3
Motor Oil (30w) (See chromatogram in NWTPH-Dx)
Automatic Transmission Fluid
Power Steering Fluid
Transformer Oil (used)
Transformer Oil (new)
Hydraulic Fluid #1
Hydraulic Fluid #2
Hydraulic Fluid #3
Mineral Oil #1
Mineral Oil #2
Cutting Oil #1
Cutting Oil #2
Bunker-C #1
Bunker-C #2
CSS-1 (emulsion asphalt)
AR-4000 (asphalt cement)

Non-petroleum Product Chromatograms

Turpentine
Creosote
Synthetic Motor Oil

*** The chromatograms are not available in the "electronic" version. They are included in the printed publication.**

Chromatograms: NWTPH-Gx

Gasoline
Weathered Gasoline
Naphtha
Mineral Spirits #1
Mineral Spirits #2
Mineral Spirits #3

Chromatograms: NWTPH-Dx

#2 Diesel Oil
#2 Diesel Oil/Motor Oil
#2 Fuel Oil (38% Aromatic)
Kerosene (Deodorized)
Jet Fuel A
Bunker C #1
Bunker C #2
Motor Oil 30 Wgt.
Mineral Oil (USP)
Hydraulic Fluid
Transformer Oil
Gas Oil

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OAR 340-177-0025
NW Total Petroleum Hydrocarbon Identification Method

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TOTAL PETROLEUM HYDROCARBONS (TPH)

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* The chromatograms are not available in the “electronic” version. They are included in the printed publication.

TOTAL PETROLEUM HYDROCARBONS (TPH)

The following compilation of analytical methods may be used in Oregon and Washington for Underground Storage Tank cleanups and other cleanups of TPH (check with applicable state rules). Each of these Total Petroleum Hydrocarbon (TPH) Methods has its own niche in the overall analytical scheme. The methods are:

NWTPH-HCID.....Hydrocarbon Identification

NWTPH-Gx .....Volatile Petroleum Products (Extended)

NWTPH-Dx .....Semi-volatile Petroleum Products (Extended)

NWTPH-HCID is a qualitative and semi-quantitative screen to determine the presence and type of petroleum products that may exist in water or soil. This method should be used if the type of petroleum contamination is unknown. It should be performed on contaminated soil or water that is representative of the contamination at the site. The results of this method will determine what fully quantitative method/methods, if any, are to be used in determining compliance with the matrix criteria. Should the value of the analysis for gasoline, diesel or heavy oils (or any other identified petroleum product) exceed the reporting limits, then the specific analytical method for that product must be employed.

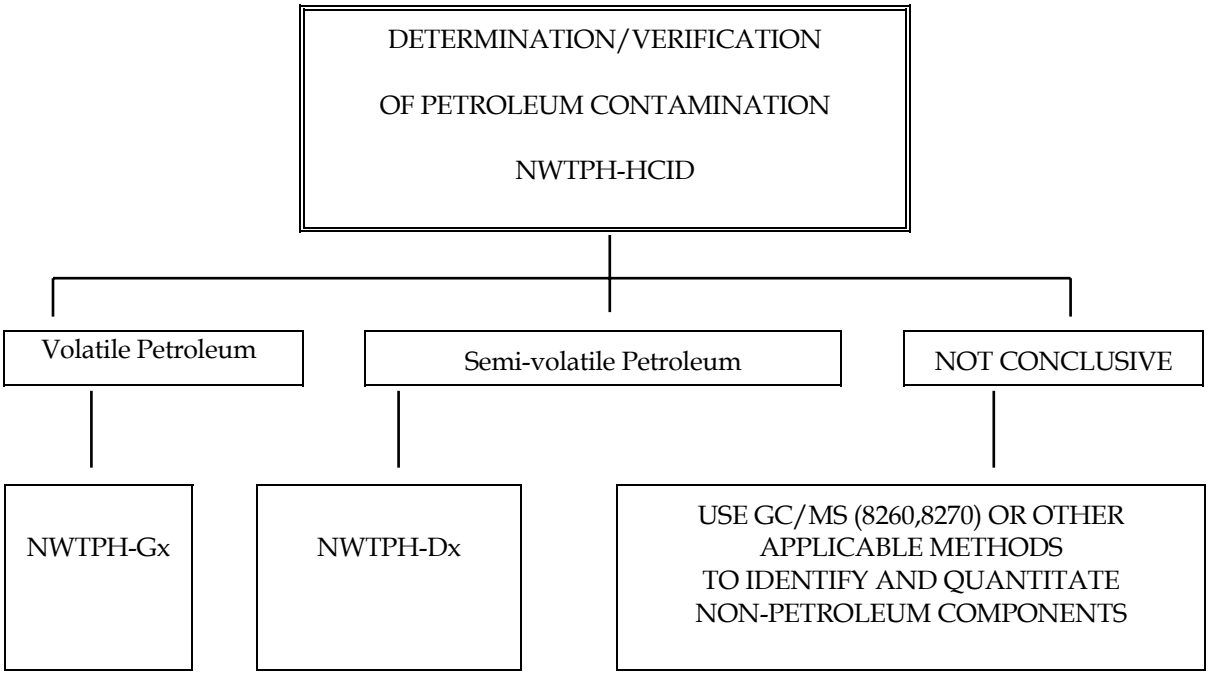
NWTPH-Gx is the qualitative and quantitative method (extended) for volatile ("gasoline") petroleum products in soil and water. Petroleum products applicable for this method include aviation and automotive gasolines, mineral spirits, stoddard solvent and naphtha.

NWTPH-Dx is the qualitative and quantitative method (extended) for semi-volatile ("diesel") petroleum products in soil and water. Petroleum products applicable for this include jet fuels, kerosene, diesel oils, hydaulic fluids, mineral oils, lubricating oils and fuel oils.

NOTE: These "NWTPH" methods result in single TPH values that can be used when compliance with a single cleanup level is desired. When TPH "fractions" are needed, then the VPH and EPH methods must be used.

ANALYTICAL DECISION TREE FOR NWTPH

The following flow chart depicts the laboratory analytical scheme to be used when analyzing samples for single TPH levels. The first step is the qualitative determination of the existence and nature of petroleum contamination and this should be used when the site contamination is unknown. It is required that this first step will be performed on a representative sample from the area that is suspected to be the most contaminated at the site. For those samples containing analytes which, due to their retention times, ratios to each other or their non-hydrocarbon pattern (e.g., creosote), do not suggest petroleum hydrocarbons, then GC/MS methods should be employed to ascertain the components. At those sites where the petroleum contaminants are known or have been identified using the NWTPH-HCID method, the specific product method is to be used.



NWTPH-HCID

Hydrocarbon Identification Method for Soil and Water

Summary

This method is a qualitative and semi-quantitative procedure. It is used for groundwater or surface water, and soil/sediment from sites where the petroleum products are unknown and/or when multiple types of petroleum products are suspected to be present. This method is used to identify petroleum products containing components from C7 to C30 range, as well as heavy oils, with specific product confirmation by pattern matching ("fingerprinting") employing capillary gas chromatography with flame ionization detection (GC/FID). EPA method 3510 has been adapted as the extraction procedure for the water portion of this method.

While this method is intended to be primarily qualitative, it can be used to eliminate the need for further analyses for those samples which demonstrate TPH levels significantly below the regulatory limits. If the sample contains toluene to dodecane (gasoline range), dodecane through tetradecane (diesel range) and/or an unresolved chromatographic envelope greater than tetradecane (e.g. motor oils) above the reporting limits of this method, then the final quantitation must be performed by methods specific for these mixtures. Since the water extraction procedure in this method is identical to that found in the water portion of NWTPH-Dx (semi-volatile petroleum products, i.e. from kerosene through heavy fuel oils), these products may be quantitated using this extract. Because of the possible loss of volatile compounds in the extraction and concentrations steps, gasoline, mineral spirits and other volatile petroleum products that exceed the reporting limits of this method must be quantitated using the NWTPH-Gx method.

The reporting limits for water are 0.25 mg/L for gasoline, 0.63 mg/L for #2 diesel and motor oils. The reporting limits for soil/sediment are 20 mg/Kg for gasoline, 50 mg/Kg for #2 diesel, and 100 mg/Kg for motor oil, all reported on a dry weight basis. These values for soil/sediment assumes 100% solids and will be higher depending on the actual moisture content.

The method relies heavily upon the experience of the analyst for the identification of the specific petroleum product(s) that may be present. Therefore, this method must be run by, or under the direct supervision of, analysts experienced in the use of GC and in the interpretation of gas chromatograms of both fresh and weathered petroleum products.

Equipment and Reagents

Gas Chromatograph, w/wo autosampler
Capillary split/splitless injector
Flame ionization detector
Suggested Capillary Column:
J&W DB-1 or DB-5, 30 M x 0.25 mm or 0.32 mm with 0.25 um film thickness capillary column or equivalent
Chromatography Data System
VOA Vial: 40 mL glass vial with Teflon coated cap septum, Eagle Picher or equivalent
Syringe: Hamilton #701, 10 uL or equivalent
Ultrasonic Bath
Glass Wool: Pyrex or equivalent
Centrifuge tubes: 5 or 15 mL, calibrated in 0.1 mL increments
Analytical Balance: accurate to at least 0.0001 g
Volumetric Flasks: 10 mL, ground glass with ground glass stopper
Separatory funnels: 500 mL, Teflon stopcocks
Kuderna-Danish (KD) Flasks: 250 mL or equivalent
Snyder Columns: 3-ball, 24/40 ground glass joint
Concentrator Tubes: 10 mL
Methylene Chloride: Burdick and Jackson Brand or equivalent
N-Evap Concentrator or equivalent

Standards

Retention Time Standards. Prepare a composite standard, using methylene chloride as the solvent, consisting of toluene, dodecane and tetracosane at 25 ug/mL each. Additional compounds may be added at the discretion of the analyst. The use of this standard is to establish the retention time windows for the quantitation of gasoline #2 diesel and motor oils.

Reference Standards. Prepare individual petroleum product reference standards (i.e. gasoline, mineral spirits, kerosene and #2 diesel oil), using methylene chloride as the solvent, at approximately 50 ug/mL. Prepare a non-synthetic motor oil (pennzoil SAE 30 or equivalent) reference standard at 200 ug/mL. The preparation of reference standards for other types of petroleum products is recommended. The use of these reference standards is to insure the accurate identification of petroleum product contamination by chromatographic pattern matching ("fingerprinting") and establish retention time windows for those petroleum products not determined with the individual compound retention time standard.

Gasoline Stock Standard. A stock standard is prepared by placing approximately 9 mL of methylene chloride in a 10 mL volumetric flask. Tare the flask/methylene chloride and add about five drops of non-oxygenated regular unleaded gasoline, assuring that the liquid falls directly into the methylene chloride without contacting the neck of the flask. Reweigh the flask and dilute to volume with methylene chloride, stopper and mix by inverting the flask several times. It is important that the analyst minimize the amount of time that the flask is left unstoppered, to reduce

the loss of gasoline through volatilization. The use of a commercially prepared gasoline standards is acceptable if it is certified as non-oxygenated gasoline or if the gasoline concentration has been adjusted to reflect the contribution of the oxygenate. Calculate the gasoline concentration as follows:

$$Stock,\ ug / mL = \frac{(final\ wt,\ mg) - (tare\ wt,\ mg)}{10\ mL} \times \frac{1000\ ug}{mg}$$

Note: The use of oxygenated regular unleaded gasoline for the gasoline stock standard is allowed if the weight (mass) of the gasoline used is adjusted for the weight (mass) contribution of the oxygenate to the gasoline. This will necessitate the analysis of the gasoline for the specific oxygenate(s) present to determine the concentration. The analysis for the oxygenates will be conducted by either of the methods published in the Federal Register - Appendix B and C - Testing Procedures - Vol. 57, No. 24, Wednesday, February 5, 1992, Notices.Alternate methods for the analysis of gasoline oxygenates must be approved by the Oregon's Department of Environmental Quality and/or Washington's Department of Ecology prior to use.

Diesel Stock Standard. A stock standard is prepared by adding about five drops of #2 diesel oil stock to tared 10 mL volumetric flask. Reweigh the flask and bring it to volume with methylene chloride, stopper and mix by inverting the flask several times. Calculate the concentration of this standard in the same manner as the gasoline stock standard. The use of a commercially prepared #2 diesel standard is an acceptable alternative to the above procedure.

Motor Oil Stock Standard. A stock standard is prepared by adding about ten drops of a non-synthetic SAE 30 weight motor oil (Pennzoil or equivalent) to a tared 10 mL volumetric flask. Reweigh the flask, bring it to volume with methylene chloride, stopper and mix by inverting the flask several times. Calculate the concentration of this standard in the same manner as the gasoline stock standard. The use of commercially prepared motor oil standards is an acceptable alternative to the above procedure.

Note: The Diesel and Motor Oil Stock Standards required in this method are identical to those required for NWTPH-Dx (extended diesel method including all semi-volatile petroleum products eluting after gasoline, e.g. kerosene, diesels, mineral oils, lubricating oils, heavy fuel oils, etc.).

Surrogate Stock Standard. Suggested surrogates for use in this method are bromofluorobenzene and pentacosane. The use of different or additional surrogates is optional. Prepare the surrogate stock standard by weighing 50 mg of each surrogate compound into a 10 mL volumetric flask, then bring to volume with methylene chloride for a final concentration of 5000 ug/mL for each surrogate compound. The use of a commercially prepared surrogate solution(s) is an acceptable alternative to the above procedure.

Composite Calibration Working Standard. Using serial dilutions of the stock standards, prepare a mixture for water analyses that contains 10 ug/mL of gasoline, 25 ug/mL of #2 diesel oil and the

surrogate standard. For soil/sediment analyses this standard should be prepared to contain 20 ug/mL of gasoline, 50 ug/mL of #2 diesel and the surrogate standard. Add the appropriate volumes, using the equations listed below, and adjusting for the concentration change created by any serial dilutions, of gasoline stock standard, #2 diesel stock standard and the surrogate stock standard to a 10 mL volumetric flask, then dilute to volume with methylene chloride. Stopper and mix by inverting the flask several times. The surrogate standard should be added to a level sufficient to produce a surrogate concentration of between 5 and 50 ug/mL.

$$\textit{Volume Gasoline Stock, uL} = \frac{\textit{20 (soil) / 10 (water) ug / mL x 10 mL}}{\textit{Gasoline Stock Conc, ug / mL}} \; x \; \frac{\textit{1000 uL}}{\textit{mL}}$$

$$\textit{Volume Diesel Stock, uL} = \frac{\textit{50 (soil) / 25 (water) ug / mL x 10 mL}}{\textit{Diesel Stock Conc, ug / mL}} \; x \; \frac{\textit{1000 uL}}{\textit{mL}}$$

This mixture corresponds to 0.25 mg/L gasoline and 0.63 mg/L #2 diesel oil for water and 20 mg/Kg gasoline and 50 mg/Kg diesel in soil following the extraction and analytical procedures of this method.

The motor oil calibration working standard should be made at a concentration of 250 ug/mL for water and 100 ug/mL for soil following the procedure outlined above. This will correspond to a reporting value of 0.63 mg/L for water and 100 mg/kg for soil. If, in the opinion of the analyst, the GC sensitivity to 100 ug/mL of motor oil is insufficient, the analyst is allowed to increase the concentration of this standard and to concentrate a portion of the extract to achieve the reporting limit for soil.

Surrogate Working Standard. Prepare a surrogate working (spiking) standard, using the procedure outlined above, that will yield between 5 ug and 50 ug/mL of the surrogate compounds in the 10 mL sample extract produced in this method.

Note: All samples must be collected in glass jars with Teflon lined lids (Eagle Picher or equivalent) and held at 4 degrees C until extracted. A volume of 400 mL is the minimum sample size to achieve the reporting limits as stated, however, larger volumes are allowed as long as the solvent/sample ratio is maintained. Samples must be extracted within 7 days (for water) or 14 days (for soil/sediment) of the date of collection. The preservation of water samples in the field, to a pH of less than 2 with 1+1 HCL, is recommended.

Extraction Procedures

Water Samples

Mark the water meniscus on the sample jar for later volume determination. Pour the sample into a 500 mL separatory funnel, add the surrogate solution (to achieve the desired concentration in a 10 mL extract). Add 30 mL of methylene chloride to the sample jar, cap and shake the jar vigorously

for a few seconds to wash off any hydrocarbons adhering to the side of the jar. Add this solvent to the separatory funnel, stopper and shake vigorously, venting frequently, for one minute. Allow the two phases to separate, then drain the solvent into a 250 mL K-D flask fitted with a 10 mL concentrator tube. Repeat the extraction twice more using 30 mL of methylene chloride, each time, adding the solvent to the K-D.

Attach a 3-ball Snyder column to the K-D and concentrate the sample extract to 5 - 10 mL on a stream bath. Remove the K-D apparatus and allow it to cool prior to disassembly. During disassembly, rinse the Snyder/K-D joint and K-D/concentrator joint with approximately 1 mL of methylene chloride and add these rinsings to the extract. Adjust the volume of the extract to 10 mL. For those samples which exceed 10 mL, place the concentrator tube into an N-Evap and, under a gentle stream of nitrogen, reduce the volume to 10 mL. Transfer 1 mL of the extract (to be used for the gasoline or gasoline/diesel determination) to an autosampler vial fitted with a screw top and a Teflon coated septum. Concentrate the remainder of the extract (to be used for heavy oils determination) to 0.9 mL, transfer it to an 2 mL autosampler vial equipped with a screw top and a Teflon coated septum. Store both vials in a refrigerator until analysis.

Each extraction set must include one method blank (organic-free water of similar volume to the samples) per 20 samples. The method blank is to receive the surrogate solution and to be extracted and analyzed in the same manner as the samples.

EPA method 3520, Continuous Liquid-Liquid Extraction, may be substituted as an alternate extraction procedure to that outlined above.

Soil Samples

Weigh approximately 10 grams of soil into a 40 mL VOA vial and record the weight to the nearest 0.001 grams. Add 5 grams of anhydrous sodium sulfate, surrogate working solution and 10 mL of methylene chloride to the VOA vial. Cap the vial and place it (no more than 5 at a time) in a sonic bath for 5 minutes. Shake the vials well and return them to the sonic bath for 5 more minutes. A minimum of one method blank per extraction set or 20 samples, whichever is more frequent, must be prepared along with the samples. One sample duplicate must also be extracted for samples set from one to ten samples and two duplicates for sets from eleven to twenty samples.

Determine the moisture content of the samples, for use in the final calculations, by the following procedure. Immediately after weighing the sample for extraction, weigh 5-10 grams of the sample into a tared crucible. Dry the sample/crucible overnight at 105 degrees C. Reweigh the sample/crucible after allowing it to cool to room temperature. Calculate the % solids as follows: [(grams of dry sample/grams of wet sample) x 100].

If the extract contains significant moisture, elute the solvent phase through an anhydrous sodium sulfate micro-column. Place a portion of the extract in a 2 mL autosampler vial (screw cap, Teflon coated septum), taking care to minimize the volume of headspace, and store the vial in a refrigerator until analyzed. Concentration of the extract, when necessary, will be conducted using an N-Evap

with a gentle stream of nitrogen. This concentrate should be stored in the same manner as noted above.

Note: Anhydrous sodium sulfate micro-columns are prepared by plugging a 5 3/4" length disposable Pasteur pipette (pre-rinsed with methylene chloride) with glass wool (precleaned with methylene chloride) and adding approximately 3 cm of anhydrous sodium sulfate (previously muffled at 430 degrees C overnight in a shallow pan and stored in a glass jar with a Teflon lid liner).

For samples containing petroleum products other than gasoline, diesel, or motor oil, the analyst must either prepare calibration standards of them by the methods listed above or analyze the sample by the fully quantitative method, e.g. NWTPH-Gx. Other calibration standards produced for use in this method must be at an equivalent concentration to the previously established standards, e.g. mineral spirits at the gasoline concentration, kerosene at the diesel concentration.

As more information becomes available on new extraction techniques, the Washington State Dept. of Ecology's Manchester Laboratory and Oregon's Department of Environmental Quality will publish descriptions of acceptable alternate extraction methods.

Suggested GC Parameters

Sample injection Volume = 2 uL
Injector Temperature = 290°C
Detector Temperature = 300°C
Hydrogen Flow = 25-35 mL/min
Air Flow = 300-400 mL/min
Make-up Gas Flow = 30 mL/min
GC Temperature Program = Initial temperature of 50°C and hold for 2 minutes; ramp the temperature 10°C/min to 320°C and hold for 5 minutes.

Product Identification

Petroleum products are to be identified by pattern matching with reference product chromatograms generated the same day as the sample analysis. The term "gasoline range" or "diesel range" hydrocarbons, or derivations of them, should only be used when the analyst is unable to identify the petroleum product present. When these terms are used, it is to indicate the presence of compounds eluting from toluene to dodecane, for the former term, and from dodecane through tetracosane, for the latter term. Motor oils, hydraulic fluids and similar petroleum products which present an unresolved chromatographic envelope of compounds, originating or extending beyond tetracosane, may be reported using the collective term, lube oil, unless specific identification is possible. Heavy fuel oils, e.g. fuel oil #6 or Bunker C, which contain a diesel range component as well as a lube oil (and higher) range may be reported using the collective term, heavy fuel oil, unless specific identification is possible. These products should not, however, be confused with mixtures of #2 diesel and motor oils.

Note: The actual identification of the grade or type of lube oil and heavy fuel oil may require equipment and techniques beyond the scope of this method.

Analysis Procedure

The analysis is accomplished by injecting 2 uL of the 10 mL extract, either manually or by autosampler, into the GC using the splitless injection mode. The results from this injection are, for quantitation purposes, compared directly against the single point calibration standard for the product(s) identified. The injection of 2 uL of the concentrated extract (1 mL equivalent) is used primarily for heavy oil determination, because of the reduced sensitivity of the FID to late eluting motor oil-like products. It may be used for the determination of #2 diesel oil and other diesel range petroleum products but it may not be used for the determination of gasoline or gasoline range petroleum products because of the potential for loss of the more volatile components during the concentration step.

Calculations

Gasoline. The area of the components, toluene to dodecane of the calibration standard, is integrated to the baseline as a group. The samples and method blanks are integrated in the same manner and the group areas are compared. If the sample area exceeds the calibration standard area, proceed with method NWTPH-Gx for accurate quantitation using a fresh aliquot of the sample. If the sample area does not exceed the calibration standard area, then report the gasoline concentration as less than 0.25 mg/L for water or 20 mg/kg for soil. This soil value for gasoline, and the subsequent petroleum products, assumes 100% solids and will be higher depending on the actual moisture content.

Other volatile petroleum products, identified as being present (e.g. mineral spirits), must be compared to the appropriate standard produced at the same concentration as gasoline. The requirement for further analyses is determined following the criteria for gasoline as noted above.

Note: For samples containing only #2 diesel oil, kerosene, etc., the portion of these products, that elute within the retention time range of gasoline, should not be identified and/or quantitated as gasoline or gasoline range petroleum.

Diesel. The area of the components, dodecane through tetracosane of the calibration standard, is integrated to the baseline as a group. This integration must include the unresolved envelope of compounds as well as the discrete component peaks. The sample is integrated in the same manner and the group areas are compared. If the sample area exceeds the calibration standard area, then proceed to method NWTPH-Dx. If the sample does not exceed the calibration standards area, then report the #2 diesel concentration as less than 0.63 mg/L for water or 50 mg/Kg for soil.

Other semi-volatile petroleum products, identified as being present (e.g. kerosene), must be compared to the appropriate standard produced at the same concentration as #2 diesel. The requirement for further analyses is determined following the criteria for #2 diesel as noted above.

Lube Oil. For those samples which consist primarily of only an unresolved chromatographic envelope of components eluting after tetracosane, compare their area to the area of the motor oil standard by integrating the unresolved envelope to baseline. If the sample exceeds the standard area, then proceed to method NWTPH-Dx. If the sample area is less than the standard, then report the lube oil concentration as less than 0.63 mg/L for water or 100 mg/Kg for soil. Samples identified as containing heavy fuel oil must be quantitated to the same value as lube oil by utilizing a heavy fuel oil standard and following the procedure outlined for lube oil.

Note: The analyst is expected to adjust the retention time windows used for quantitation of petroleum products, other than gasoline, #2 diesel, or motor oil/lube oils, to incorporate the majority of the chromatographable components associated with those identified products.

If, in the judgement of the analyst, the area of an identified petroleum product other than gasoline, diesel, and motor oil would exceed the reporting limit, the analyst is allowed to report a "greater than" value for that product without performing the quantitative analysis. The analyst must then proceed to the appropriate fully quantitative analytical procedure, e.g. NWTPH-Dx, for the identified petroleum product.

Quality Assurance

The addition of an appropriate extraction surrogate to samples and method blank(s) is required. The surrogate recovery for all samples and blanks should be between 50% and 150% and must be reported with the petroleum results unless the quantity of the petroleum product(s) preclude its determination. The laboratory should analyze one sample from each site in duplicate for sample sets of 10 or less and two samples in duplicate for sets of 11 to 20 samples (i.e. 10% QA). If either of the duplicate results are positive, the sample is to be considered positive. Since this method precludes the preparation of analytical duplicates, the laboratory should recommend that the project manager collect and submit field duplicates for analysis. The laboratory must analyze method blanks prepared identically to the samples. Organic free water must be used in the preparation of water method blank. No "sample" is necessary for use with soil/sediment method blanks.

Author - Bob Carrell, Manchester Environmental Laboratory, Dept. of Ecology, State of Washington. Reviewed and edited by Steve Robb, Toxics Cleanup Program, Department of Ecology, State of Washington. This method is based on Oregon’s Department of Environmental Quality TPH methods and Washington’s Department of Ecology WTPH methods.

NWTPH-Gx Chromatograms

Gasoline
Weathered Gasoline
Naptha
Mineral Spirits #1
Mineral Spirits #2
Mineral Spirits #3

NWTPH-Dx Chromatograms

#2 Diesel
#2 Diesel/Motor Oil
#2 Fuel Oil
Kerosene (Deodorized)
Jet A Fuel
Bunker C #1
Bunker C #2
Motor Oil 30 Wt.
Mineral Oil (USP)
Hydraulic Fluid
Transformer Oil
Gas Oil

See Appendix 6

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NWTPH-Gx

Volatile Petroleum Products Method for Soil and Water

Summary

The NWTPH-Gx method is intended to replace the Oregon's TPH-G and Washington's WTPH-G methods and to present a more comprehensive approach to volatile petroleum product analyses. NWTPH-Gx adapts Oregon's TPH, Washington's WTPH and EPA SW846 Methods 5030 and/or 8020 and covers the quantitative and qualitative analyses of volatile petroleum products, e.g. gasolines, naphtha, mineral spirits, stoddard solvent, and other volatile petroleum products in soil and water. Soil samples are extracted with methanol and analyzed by gas chromatograph with a flame ionization detector (GC/FID). The methanol extracts may be injected directly into the GC or they may be diluted with organic free reagent water and introduced by a purge/trap concentrator. Water samples are introduced directly to the purge/trap concentrator. This method specifies the criteria for the identification and quantitation of volatile petroleum products. When the type of petroleum product is unknown, regular unleaded gasoline will initially be used as the default petroleum standard. The use of GC/PID, GC/MS or GC/AED (Atomic Emission Detector) for the analysis of gasoline may be substituted for GC/FID as long as all other method parameters are met.

The reporting limits for soil are 5 mg/kg by the purge/trap procedure and 20 mg/kg for direct injection. All soil results are reported on a dry weight basis. Since this value assumes 100% solids, the analyst may wish to adjust the amount of soil extracted and/or purge a larger quantity of extract to achieve the reporting limits. For water, the reporting limits are 0.25 mg/L.

The method is applicable for the identification, by pattern matching ("fingerprinting") and quantitation of volatile petroleum products, i.e. those petroleum products for which the majority of the components elute within the gasoline range.

Note: Benzene, Toluene, Ethylbenzene and Xylenes (BTEX) may be determined simultaneously with gasoline if the requirements of EPA Method 8021 or EPA Method 8260 are met (i.e. the use of a PID (Photoionization Detector) for method 8020 or a MS (Mass Spectrometry) for method 8260 and the QA/QC associated with these methods).

This method must be performed by, or under the direct supervision of, analysts experienced in the use of GC and in the interpretation of gas chromatographs of both fresh and weathered volatile petroleum products.

Equipment and Reagents

Gas Chromatograph
Purge/Trap Liquid Concentrator - Tekmar or Equivalent - Autosampler (Optional)
Flame Ionization (FID) or Photo Ionization/Flame Ionization Detectors (PID/FID)
Suggested Capillary Column: Restex RTX-502.2, 60M x 0.53 mm x 3.0 um film thickness or equivalent
Chromatography Data System
Gas tight syringes, various volumes, Hamilton brand or equivalent
Volumetric flasks: 10 mL, ground glass joint with stopper
Methanol: Burdick and Jackson Purge/Trap grade or equivalent
Petroleum Product Standards: Available from commercial sources
Refer to methods 5030 and/or 8020 for the remaining equipment and reagent requirement

Sample Containers/Holding Times

All soil samples for NWTPH-Gx analyses must be collected in soil VOA bottles with Teflon coated septum lined tops. They should be filled to the top to minimize headspace above the soil and stored at 4 degrees C until analyzed. The maximum holding time (the time from the date of collection to the date of analysis) for gasoline and any other volatile petroleum product is 14 days.

All water samples for NWTPH-Gx analyses must be collected in glass VOA vials with Teflon coated septum lined screw tops. They must be filled so that there is no air space (headspace) above the water. Samples should be preserved with 1+1 HCl to a pH <2 and refrigerated at 4 degrees C until analyzed. The maximum holding time (the time from the date of collection to the date of analysis) is 7 days for unpreserved samples and 14 days for preserved samples. The results of any samples which exceed these limits must be qualified as an estimated value.

Standards

Stock Standards. A stock standard is prepared by placing approximately 9 mL of methanol in a 10 mL volumetric flask. Allow the flask to stand, unstoppered, until the methanol wetted surfaces have dried (about ten minutes), then tare the methanol/flask. Add about 5 drops of the petroleum product to the flask while assuring that the liquid falls directly into the methanol without contacting the neck of the flask. Weigh the flask again and dilute to volume with methanol, stopper and mix by inverting the flask several times. The use of commercially prepared standards is acceptable to the above procedure. Commercially prepared gasoline standards must be certified as non-oxygenated gasoline or the gasoline concentration has been adjusted to reflect the contribution of the oxygenate. Calculate the concentration as follows:

$$\textit{Gasoline Stock Standard, ug / mL} = \frac{\textit{(final wt, mg) - (tare wt, mg)}}{\textit{10 mL}} \; x \; \frac{\textit{1000 ug}}{\textit{mg}}$$

The standard for gasoline will be regular unleaded gasoline and this standard is to be used as the default petroleum product for reporting purposes.

Note: The use of oxygenated regular unleaded gasoline for this standard is allowed if the weight (mass) of the gasoline used is adjusted for the weight contribution of the oxygenate to the gasoline. This will necessitate the analysis of the gasoline for the specific oxygenate(s) present to determine their concentration. This analysis must be conducted by either of the methods published in the Federal Register - Appendix B and C - Testing procedures - Vol. 57, No. 24, Wednesday, February 5, 1992, Notices. Alternate methods for the analysis of gasoline oxygenates must be approved by the Oregon's Department of Environmental Quality and/or Washington's Department of Ecology prior to use.

Stock Surrogate Standard

Note: The suggested surrogates are 1,4-difluorobenzene and bromofluorobenzene. The use of additional surrogates is optional. Selected surrogate compounds should be non-polar, purgeable from water and must not coelute with any significant component of gasoline.

Make up a stock standard by accurately weighing the surrogate compound(s) into a 10 mL volumetric flask. Utilize the same procedure as the stock gasoline standard preparation if neat material is used or by adding the appropriate volumes of dilute surrogate if solutions are used. Bring it to volume with methanol. The use of commercially prepared surrogate solutions is an acceptable alternative to the above procedure.

Working Surrogate Spike. Add the appropriate volume of stock surrogate standard to methanol in a partially filled 10 mL volumetric flask and dilute to volume with methanol. The final concentration of the working surrogate solution is left to the discretion of the analyst, however, this solution should produce between 5 ng and 50 ng of surrogate introduced to the GC.

Secondary Dilution Standard. Using serial dilutions of the stock standard, prepare a 50 ug/mL standard by adding the appropriate volumes, as calculated below, to a 10 mL volumetric flask. The appropriate volume of the stock surrogate standard may also be added to this volumetric flask. Dilute to volume with methanol to yield a final working standard concentration of 50 ug/mL for the standard. Surrogate compound(s) may be added automatically during the sampling process by an autosampler. Gasoline is the default petroleum product for reporting purposes.

$$\textit{Stock Std (Gasoline), uL} = \frac{\textit{50 ug / mL x 10 mL}}{\textit{Stock Std Conc, ug / mL}} \; x \; \frac{\textit{1000 uL}}{\textit{mL}}$$

Store all standards in a refrigerator until needed. Allow them to come to room temperature prior to use.

Calibration Standard

The aqueous purge standards are each prepared by adding 5 uL, 10 uL, 20 uL and 50 uL and 100 uL of the secondary dilution standard per 5 mL of organic free water. The five point calibration standard quantities in the purged water are then 250 ng, 500 ng, 1000 ng, 2500 ng and 5000 ng for the volatile petroleum products. At the discretion of the analyst, the concentration of the surrogate can increase with increasing standard concentration or remain at a fixed value for all calibration standards and samples. Extending the calibration range, either up or down, is allowed as long as the standards remain within the linear range of the instrument and a minimum of a five point calibration is produced. In order to be acceptable, the calibration curve must have a linear correlation coefficient of at least 0.990 and none of the standards may vary from their true (known) value by more than plus/minus 15%.

The use of an autosampler may be substituted for this manual method of standards and sample introduction.

Direction Injection. Prepare calibration standards from the stock gasoline standard and surrogate standards at concentrations of 10 ug/mL, 25 ug/mL, 50 ug/mL, 100 ug/mL and 250 ug/mL for gasoline by adding the appropriate volumes to volumetric flasks and diluting to volume with methanol. Increasing the calibration range with higher standards is acceptable as long as the linear range of the instrument is not exceeded.

Purge/Trap and GC Parameters

Follow the procedure outlined in Method 8021 for the set up of the purge and trap operating parameters and for the GC. Adjust the hydrogen/air flow rates to optimize the FID sensitivity.

Soil Extraction Procedure

Weigh approximately 5 grams of soil into a 40 mL VOA vial and record the weight to 0.001 grams. Add 50 uL of the surrogate working standard and 10 mL of methanol. Quickly cap the vial and shake for 1 minute or use an ultrasonic bath for 2 minutes shaking well after 1 minute. Allow the soil methanol mixture to separate, centrifuging if necessary to clarify the methanol extract. For storage, transfer a portion of the extract into a 2 mL glass autosampler vial, with a Teflon-lined cap, minimizing the headspace and store in a freezer for no longer than one week prior to analysis. Along with the samples, prepare at least one method blank and one sample duplicate per ten samples.

Determine the moisture content of the sample, for use in the final calculations, by the following method. Immediately after weighing the sample for extraction, weigh 5-10 grams of the sample into a tared crucible. Dry the sample/crucible overnight at 105 degrees C. Reweigh the sample/crucible after allowing it to cool to room temperature. Calculate the % solids as follows: [(grams of dry sample/grams of wet sample) x 100].

Analysis Procedure

Prior to the analysis of any samples or method blanks, prepare and analyze a mid-range calibration check standard to insure that the instrument is functioning correctly and that the calibration is valid. This standard should be produced daily using the secondary gasoline standard. The value obtained for this analysis must not vary from the true (known) value by more than plus/minus 20%. If the value falls outside this range then a second mid-range calibration standard should be produced and the analysis repeated. If the reanalysis of the fresh standard fails to meet the acceptance criteria, then the instrument must be recalibrated prior to the analysis of any samples. Once the instrument is shown to be in calibration, the analyses of samples may proceed.

After the last sample has been analyzed, a mid-range calibration check sample must be run to demonstrate that the instrument is still operating within the required parameters. Should this standard fail to meet those parameters, then all samples analyzed after the last successful calibration check must either be reanalyzed or the results obtained must be qualified as an estimated value. An increase in the frequency of mid-range calibration check standard analyses beyond the minimum required is recommended.

Significant interferences may be encountered due to the presence of other petroleum products (or non-petroleum products) eluting within the retention time range of the volatile petroleum product being analyzed. If this occurs, the analyst is allowed to adjust the retention time range used for quantitation to exclude the interferences or to subtract the area of the interfering components from the total area prior to the quantity determination. With the former method, the calibration curve must be adjusted in the same manner to reflect the change in retention time range and integration area.

For volatile petroleum products other than gasoline that have a more narrow boiling point range, e.g. mineral spirits, the retention time range used for quantitation should be adjusted to encompass the expected range of the product. Petroleum products which cannot be identified should be quantitated with the gasoline calibration curve. The term "gasoline range" hydrocarbons, or derivations of it, should not be used when reporting the petroleum values unless the analyst is unable to identify the petroleum product present.

Purge/Trap - Soil. A 100 uL aliquot of the methanol extract is transferred via a 100 uL gas tight syringe to 5 mL of organic free water in a 5 mL gas tight syringe and immediately injected into the purging vessel of the purge and trap device. For samples expected to contain concentrations of gasoline range volatiles outside the calibration linear range, or if dilution is required, a smaller aliquot of the methanol extract, or sample, should be used. The analysis then proceeds as in Method 8020. Autosampler techniques may be substituted for this manual method of sample introduction.

Purge/Trap - Water. Sample water (5 mL) is transferred to a 10 mL gas tight syringe and the working surrogate standard spike is added, via a gas tight syringe, into the 5 mL water sample. Immediately inject this water into the purge vessel of the purge/trap device. If necessary, a smaller sample aliquot may be used in order to remain within the linear calibration range of the instrument.

Larger sample volumes may be analyzed, at the discretion of the analyst, if lower quantitation limits are required. Autosampler techniques may be substituted for this manual method of sample introduction.

Direct Injection - For Soil. Allow the extract to come to room temperature, then inject, either manually or by autosampler, 2 uL of the extract into the GC using the splitless injection mode.

Quantitation

The retention time range (window) for gasoline integration must, at a minimum, include toluene through naphthalene. For other volatile petroleum products, the retention time range for integration must be adjusted to incorporate the majority of the components of the petroleum product(s) identified as present in the samples. If specific product identification can not be made, the analyst must quantitate the samples with the calibration curve of the petroleum product that most closely resembles that of the sample.

For those surrogates which elute within the retention time range used for integration, the analyst must subtract the area of the surrogate(s) from the total area to yield the appropriate area of the petroleum product.

The analyst shall use regular unleaded gasoline as the default petroleum product for reporting purposes when no petroleum products were identified in any initial screening or when the type(s) of petroleum products are unknown prior to analysis.

Sample chromatograms of various volatile petroleum products are included at the end of this method to assist the analyst in determining the appropriate integration ranges.

Result Calculation

The area of the components is integrated, as a group, to the baseline and compared to concentrations of the standards which are integrated in the same manner.

For Soil

$$\textit{Soil Sample Conc, mg / kg} = \frac{(A \times R) \times D}{E \times W \times S}$$

where

A = group area of sample

R = Response factor from std curve (ng injected/area count)

D = Extract Volume, mL

W = Weight of sample, grams

E = Volume of extract purged or injected, uL

S = Decimal percent solids of sample

For Water

$$\textit{Water Sample Conc, ug / L} = \frac{(A \times R)}{V}$$

where

A = group area of sample

R = Response factor from std curve (ng purged/area count)

V = Volume of sample purged, mL

The recovery of the surrogate should be between 50% and 150% and must be reported with the results. Report any surrogate recoveries that can not be calculated due to a high level of gasoline contamination.

Author: Bob Carrell, Manchester Environmental Laboratory, Dept. of Ecology, State of Washington. Reviewed and edited by Steve Robb, Toxics Cleanup Program, Department of Ecology, State of Washington. This method is based on Oregon's Department of Environmental Quality TPH-G and Washington's Department of Ecology WTPH-G methods.

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NWTPH-Dx

Semi-Volatile Petroleum Products Method for Soil and Water

Summary

The NWTPH-Dx method is intended to replace the Oregon's Department of Environmental Quality TPH-D and Washington's Department of Ecology WTPH-D methods and to present a more comprehensive approach to semi-volatile petroleum product analyses. NWTPH-Dx adapts Oregon's TPH, Washington's WTPH and EPA SW-846 Methods 3510, 3540/3550 and 8000 and covers the quantitative and qualitative analysis of semi-volatile petroleum products, i.e. jet fuels through heavy fuel oils, in soil and water. The method involves extracting the samples with methylene chloride and injecting a portion of the extract into a gas chromatograph (GC) equipped with a flame ionization detector (FID). This method specifies criteria for the identification and quantitation of semi-volatile petroleum products. A clean-up procedure, which may be used to aid in the removal of non-petroleum based organic interferences, i.e. biogenic interferences, has been included. When the type of petroleum product is unknown, #2 diesel will initially be used as the default petroleum standard.

The reporting limits are 25 mg/kg (soil) and 0.25 mg/L (water) for the petroleum products in the elution range of jet fuels through #2 diesel. For petroleum products eluting after #2 diesel oil, e.g. motor oils, hydraulic fluids, and heavy fuel oils, the reporting limits are 100 mg/kg (soil) and 0.50 mg/L (water). All soil results are reported on a dry weight basis. Since this value assumes 100% solids and therefore will be higher depending on the actual moisture content, the analyst is permitted to concentrate the extract to obtain these reporting limits. When doubt exists as to which reporting limit is applicable for the petroleum product present, the analyst should use the lower value.

The method is applicable for the identification, by pattern matching ("fingerprinting"), and quantitation of semi-volatile petroleum products. These include kerosenes, jet fuels, diesel oils, fuel oils, lubricating oils, hydraulic fluids, mineral oils and insulating oils, e.g. transformer oils. In general, those petroleum products which do not contain a substantial volatile fraction, i.e. the majority of the components eluting outside of the gasoline range, should be analyzed by this method.

Note: The use of GC/MS (Mass Spectrometry) or GC/AED (Atomic Emission Detector) may be substituted for GC/FID as long as all other method parameters are met.

This method is to be used by, or under the direct supervision of, analysts experienced in the use of GC and in the interpretation of gas chromatograms of both fresh and weathered petroleum products.

Equipment and Reagents

Gas Chromatograph, w/wo Autosampler
Flame Ionization Detector
Capillary Split/Splitless Injector
Suggested Column:
J & W Scientific: DB-1 or DB-5, 30 M x 0.25 mm or 0.32 mm I.D. with 0.25 um film thickness capillary column or equivalent
Chromatographic Data System: Capable of group integrations
Analytical Balance, accurate to a least 0.0001 grams
Volumetric Flasks, 10 mL, ground glass stoppered
N-Evap Concentrator or equivalent
Centrifuge tubes, 10 or 15 mL, glass, calibrated in 0.1 mL increments
Centrifuge tubes, 10 or 15 mL, glass, disposable
Kaderna-Danish (K-D) Flasks, 250 mL
Concentrator Tubes, 10 mL
Snyder Columns, 3-ball, 300 mm length
Sodium Sulfate, anhydrous
Methylene Chloride, Burdick and Jackson brand, gas chromatography/pesticide residue grade or equivalent
Sulfuric acid, concentrated
Silica gel, 100/200 mesh, Baker Analyzed Reagent grade or equivalent - Before use, activate for at least 16 hours at 130 degrees C in a shallow tray
Petroleum Product Standards: Available from commercial sources

Note: All samples shall be collected in Eagle Picher, or equivalent, glass jars and held at 4 degrees C until extracted. The holding time, from the date of collection to extraction, is 14 days for soil and preserved water. For unpreserved water, the holding the holding time is 7 days. Preservation is accomplished by adjusting the pH of the water sample to approximately 2 with the addition of 1+1 HCl.

Suggested GC Parameters

Sample Extract Injection Volume = 2 uL
Injector Temperature = 290 degrees C
Detector Temperature = 300 degrees C
Hydrogen Flow = 25-35 cc/min
Air Flow = 300-400 cc/min
Helium Make-up Gas Flow = 30 cc/min
Helium Carrier Gas Head Pressure = 15 psi
GC Temperature Program:
Initial temperature = 50 degrees C, hold 2 minutes
Temperature Ramp Rate = 20 degrees C per minute
Final Temperature = 320 degrees C, hold for 10 minutes

Standards

Reference/Stock Standards. Prepare individual petroleum product reference/stock standards, e.g. kerosene, #2 diesel oil, transformer oil (mineral oil based) and Bunker-C fuel oil.

Add 5 to 10 drops of the pure petroleum product to a zero tared 10 mL flask. Record the weight and bring the flask to volume with methylene chloride, stopper and mix by inverting the flask several times. Calculate the concentration of these standards using the equation shown below. The use of commercially prepared standards is an acceptable alternative to the above procedure. Analysts may not use artificial standards, e.g. diesel range organics mixtures, etc., for quantitation purposes in place of authentic petroleum products.

These standards are to be used to produce calibration working standards which should be used to insure the proper identification of petroleum products by chromatographic pattern matching ("fingerprinting") as well as accurate quantitation.

$$\textit{Stock Conc, ug / mL} = \frac{\textit{(final wt, mg) - (tare wt, mg)}}{\textit{10 mL}} \times \frac{\textit{1000 ug}}{\textit{mg}}$$

Calibration Working Standards. Using the stock standards, prepare calibration working standards for the identified petroleum product(s) to be quantitated. Add the appropriate volume(s), using the equation shown below and adjusting for the concentration change created by any serial dilutions, to a 10 mL volumetric flask(s). Dilute to volume with methylene chloride. Calibration standards must, at a minimum, (1) provide a five point calibration curve, (2) include a sufficiently low standard to provide the necessary reporting limits, and (3) define the linear working range of the instrument.

In order to be acceptable, the calibration curve must have a linear correlation coefficient of at least 0.990 and none of the standards may vary from their true (known) value by more than plus/minus 15%. #2 diesel oil is the default petroleum product for reporting purposes.

Stock Surrogate Standard. Prepare the stock surrogate standard by weighing 50 mg of the surrogate compound(s) into a 10 mL volumetric flask. Bring the flask to volume with methylene chloride for a final concentration of 5000 ug/mL for the surrogate compound. The use of commercially prepared surrogate solutions is an acceptable alternative to the above procedure.

Note: The suggested surrogates are 2-fluorobiphenyl, o, or p-terphenyl or pentacosane. The use of other surrogates is optional. Selected surrogate compounds must be non-polar, unaffected by the cleanup procedure, i.e. the concentrated sulfuric acid/silica gel treatment, and lacking in significant interferences in most standard petroleum products.

Working Surrogate Spike. Using serial dilutions of the stock standard, prepare a surrogate working standard. Add the appropriate volume of the stock surrogate standard, using the equation listed

below, and adjusting for any serial dilutions, to a 10 mL volumetric flask and dilute to volume with methylene chloride. Stopper and mix by inverting the flask several times. The surrogate working standard should be added to a level sufficient to produce a surrogate concentration between 5 and 50 ug/mL.

$$Volume\ Stock,\ uL\ =\ \frac{(Cal\ Std\ Conc,\ ug\ /\ mL)\ x\ 10\ mL}{Stock\ Conc,\ ug\ /\ mL}\ x\ \frac{1000\ uL}{mL}$$

Store all standards in a refrigerator until needed. Allow them to come to room temperature prior to use.

Sample Extraction

Soil Matrix

Weigh approximately 20 grams of soil, recording the weight to the nearest 0.01 grams, and approximately 20 grams of anhydrous sodium sulfate into a 150 mL beaker. Mix completely with a spatula. The mixture should have a grainy texture. If it forms a large clump, add more anhydrous sodium sulfate and grind to grainy texture. Add the appropriate volume of working surrogate standard, 50 mL of methylene chloride and sonicate for 3 minutes utilizing the horn sonicator and power settings in SW-846 Method 3550. Allow the mixture to settle then collect the extract in a 250 mL Kuderna-Danish (KD) flask to which is connected a 10 mL concentrator tube.

Repeat the extraction twice more and add these extracts to the KD. Attach a 3 ball Snyder column and concentrate the extract on a steam bath to a volume of 5-10 mL. Allow the K-D to cool to room temperature. Disassemble the K-D, rinsing the Snyder/K-D and K-D/concentrator tube joints with 1-2 mL of methylene chloride. Add these rinsings to the extract. If necessary, place the concentrator tube in an N-Evap and reduce the volume to 10 mL under a gentle stream of nitrogen. At this point, proceed to the sample cleanup procedure if applicable or transfer a portion of the extract to a 2 mL autosampler vial fitted with a screw top and a Teflon lined septum. Store the extract in a refrigerator until analyzed. If the extract is highly colored or forms a precipitate, a dilution may be necessary to stay within the calibration range. The use of the EPA method 3540 (soxhlet) in place of Method 3550 is optional.

Determine the moisture content of the samples by the following method. Immediately after weighing the sample for extraction, weigh approximately 10 grams of the sample into a tared crucible and record the weight. Dry the sample/crucible overnight at 105 degrees C. Reweigh the sample/crucible after allowing it to cool to room temperature and record the weight. Calculate the % solids as follows: [(grams of dry sample/grams of wet sample) x 100].

Along with each sample set, run at least one duplicate sample per set of 10 or fewer samples (10%) and, for each extraction day, at least one method blank (5%). Spiking of surrogates, extraction and

analyses of the QC samples will be conducted identically to the regular samples with the exception that no soil is added to the method blank.

Water Matrix

Allow the sample to come to room temperature and mark the meniscus for later use in volume determination. Pour the sample into a separartory funnel and adjust the pH to approximately 2 with 1+1 HCl and add the appropriate volume of surrogate working solution. Add 30 mL of methylene chloride to the sample jar and rotate the jar at a sufficient angle to wash the walls. Pour the solvent into the separatory funnel, stopper, and shake it vigorously for one minute, venting frequently. After the two phases have separated, drain the solvent into a 250 mL K-D flask to which is attached a 10 mL concentrator tube.

Note: Due to possible loss of analytes from the water to the sample jar walls, the entire sample must be consumed in the extraction and no aliquots may be used. Since the reporting limits are calculated on a 400 mL sample volume, sample jar size should be appropriate for this volume. For larger sample volume extractions, the analyst must increase the quantity of solvent used to maintain the original solvent/sample ratio.

Repeat the extraction twice more and add these extracts to the K-D. Attach a 3-ball Snyder column to the K-D and concentrate the extract on a steam bath to 5-10 mL. Allow the K-D to cool to room temperature and disassemble it, rinsing the Snyder/K-D and K-D/ concentrator joints with 1-2 mL of methylene chloride. Add these rinsings to the extract. Place the concentrator tube into an N-Evap and reduce the volume to 2 mL under a gentle stream of nitrogen. Transfer the extract to a 2 mL autosampler vial fitted with a screw top and a Teflon lined septum. Store the extract in a refrigerator until analyzed.

Along with each sample set, run at least one duplicate sample per set of 10 or fewer samples (10%) and, for each extraction day, at least one method blank (5%). Spiking of surrogates, extraction and analyses of the QC samples will be conducted identically to the regular samples with the exception that organic free water will be used for the method blank.

As more information becomes available on new extraction techniques, Washington State Dept. of Ecology's Manchester Laboratory and/or Oregon’s Department of Environmental Quality will publish descriptions of acceptable alternative extraction methods.

Sample Cleanup. In those cases where samples contain a significant amount of naturally occurring non-petroleum organics, e.g. leaf litter, bark, etc., which may contribute biogenic interferences, the following cleanup technique may be employed to assist in their reduction or elimination.

Transfer the 10 mL sample extract to a 10 to 15 mL centrifuge tube, add 1 mL of concentrated sulfuric acid to the extract and stopper the tube. Mix thoroughly for 1 minute by either shaking the tube or with the use of a vortex-genie adjusted to the highest setting.

Caution: Since sulfuric acid produces a highly exothermic reaction with water and other polar materials, extreme care should be exercised with its use.

Allow the two phases to separate. Centrifugation can be used to facilitate this process. Using a disposable glass pipet, transfer the methylene chloride (top) phase to another centrifuge tube and add approximately 0.4 grams (roughly equivalent to 1 mL of volume) of silica gel to the tube, stopper and mix as before. Allow the silica gel to settle or centrifuge. Repeat the sulfuric acid/silica gel treatment once more. Transfer a portion of the extract to a 2 mL autosampler vial equipped with a Teflon-lined cap and store the extract in a refrigerator until analyzed. A smaller aliquot of the extract may be used for this cleanup procedure as long as the ratio of extract to acid/silica gel is maintained.

It has been noted that some petroleum products, i.e. heavy fuel oils such as #6 fuel oil or Bunker-C, may experience a concentration loss of between 10 and 20 percent when subjected to this cleanup technique. This loss appears to be primarily associated with the removal of petroleum compounds which contain sulfur. To account for this loss when analyzing samples that have been subjected to the cleanup procedure in preparation for heavy fuel oil determination, the analyst must use utilize standards which have undergone the cleanup technique to calibrate the GC.

Note: The use of EPA method 3611 (Alumina column cleanup) may be substituted for the above cleanup technique if it is demonstrated to provide equivalent results.

Analysis Procedure. Prior to the analysis of any samples or method blanks, the analyst must prepare and analyze a mid-range calibration check standard to insure that the instrument is functioning correctly and that the calibration is still valid. The value obtained for this analysis must not vary from the true (known) value by more than plus/minus 15%. If the value falls outside this range then a second mid-range calibration check standard should be analyzed. If the analysis of the second check standard fails to meet the acceptance criteria, then the instrument must be recalibrated prior to the analysis of any samples. Once the instrument has been shown to be in calibration, the analyses of samples may proceed.

The analyst shall use #2 diesel as the default petroleum product for reporting purposes when no petroleum products were identified in any initial screening or when the type(s) of petroleum products are unknown prior to analysis.

After the last sample has been analyzed, a mid-range calibration check sample must be run to demonstrate that the instrument is still operating within the required parameters. Should this standard fail to meet those parameters, then all samples analyzed after the last successful calibration check standard must be reanalyzed. An increase in the frequency of mid-range calibration check standard analyses beyond the minimum required is recommended.

Qualitative Analysis - Identification

If NWTPH-HCID has not been previously performed on the samples and/or the type of petroleum present is unknown, the analyst should pre-screen the samples to determine the petroleum product.

The observed petroleum product shall be determined by pattern matching with the standard(s) analyzed the same day. Chromatograms used for this "fingerprinting" should be normalized to approximately 90% of full scale for the largest component of the particular petroleum product observed.

When reporting the results, the terms such as "diesel range" or "motor oil range", or derivations of them, should only be used when the analyst is unable to identify the petroleum product(s) present. Motor oils, hydraulic fluids and similar petroleum products which consist primarily of an unresolved chromatographic envelope of compounds originating at, or extending beyond tetracosane, may be reported using the collective term "lube oil" unless specific identification is possible. Heavy fuel oils, e.g. #6 fuel oil or Bunker-C, which contain a diesel range component as well as a lube oil range, may be reported using the collective term "heavy fuel oil" unless specific identification is possible. Heavy fuel oils should not, however, be confused with mixtures of #2 diesel and lube oils.

Note: The actual identification of the grade or type of lube oil and/or heavy fuel oil may require equipment and techniques beyond the scope of this method.

Quantitative Analysis - Integration

The retention time range (window) for integration must be adjusted to incorporate the majority of the components of petroleum product(s) identified as present in the samples. If specific product identification can not be made, the analyst must quantitate the samples with the calibration curve for the petroleum product that most closely resembles that of the sample. In all cases, the selected retention time range (windows) used for quantitation must, at a minimum, include any unresolved envelope of compounds as well as all discrete component peaks with an area greater than or equal to 10% of the largest peak. These components must be integrated to the baseline as a group.

For those surrogates which elute within the retention time range used for integration of a petroleum product, the analyst must subtract the area of the surrogate from the total area to yield the appropriate area of the petroleum product. In this case, the analyst may wish to generate separate calibrations for the petroleum standards and the surrogate(s) to facilitate integration and quantitation.

At the discretion of the analyst, the range of components included in the integration may be adjusted in order to minimize the potential contribution of any co-eluting fractions arising from the presence of multiple petroleum products. Any change in the integration range must be reflected in a concomitant change to the calibration standards integration.

Sample chromatograms of various petroleum products are included at the end of this method to assist the analyst in determining the appropriate integration ranges.

Result Calculation

For Soil

$$Soil\ Sample\ Conc,\ mg / kg = \frac{(A \times R) \times V \times Dilution\ Factor}{E \times W \times S}$$

where

A = Area Count from Sample
R = Response Factor (ng injected/area count)
V = Extract Volume (mL)
W = Weight of Sample (g)
E = Volume injected, (uL)
S = Decimal percent solids of sample

For Water

$$Water\ Sample\ Conc,\ mg / L = \frac{(A \times R) \times V}{E \times S}$$

where

A = Area Count from Sample
R = Response Factor (ng injected/area count)
V = Extract Volume (mL)
S = Volume of Sample (mL)
E = Volume Injected (uL)

The recovery of the surrogate should be between 50% and 150% and must be reported with the results. If the recovery of the surrogate is not able to be obtained due to a high levels of petroleum contamination, then this fact needs to be reported.

Author: Bob Carrell, Manchester Environmental Laboratory, Dept. of Ecology, State of Washington. Reviewed and edited by Steve Robb, Toxics Cleanup Program, Department of Ecology, State of Washington. This method is based on Orgeon's Department of Environmental Quality TPH-D and Washington's Department of Ecology WTPH-D methods.

METHOD FOR THE DETERMINATION

OF

VOLATILE PETROLEUM HYDROCARBONS (VPH) FRACTIONS

Washington State Department of Ecology

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METHOD FOR THE DETERMINATION OF VOLATILE PETROLEUM HYDROCARBONS (VPH)

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DISCLAIMER

Mention of trade names or commercial products does not constitute endorsement by the Washington State Department of Ecology Equipment and materials cited in this method may be replaced by similar products, as long as adequate data exists or has been produced documenting equivalent or superior performance.

METHOD FOR THE DETERMINATION OF VOLATILE PETROLEUM HYDROCARBONS

1.0 SCOPE AND APPLICATION

1.1 This method is designed to measure the collective concentrations of volatile aliphatic and aromatic petroleum hydrocarbons in water and soil. **The carbon ranges used through out this document are given in equivalent carbon (EC) numbers which are related to the boiling point of a chemical normalized to the boiling point of the n-alkanes, and its retention time in a boiling point gas chromatographic (GC) column.** Volatile aliphatic hydrocarbons are collectively quantitated within four ranges: C5 through C6, >C6 through C8, >C8 through C10 and > C10 through C12. Volatile aromatic hydrocarbons are collectively quantitated within the C8 through C10, >C10 through C12 and >C12 through C13 ranges. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 36°C and 220°C.

1.2 This method is also designed to measure the individual concentrations of benzene, toluene, ethylbenzene, xylenes, and methyl tert butylether (MTBE) in water and soil.

1.3 Petroleum products suitable for evaluation by this method include gasoline, mineral spirits, and certain petroleum naphthas. This method, in and of itself, is not suitable for the evaluation of samples contaminated with kerosene, jet fuel, heating oils, lubricating oils, or other petroleum products which contain a significant percentage of hydrocarbons larger than C10. When samples are known or suspected to contain petroleum products containing significant concentration of hydrocarbons >C10, the Extractable Petroleum Hydrocarbon (EPH) method should also be employed to fully evaluate the hydrocarbons present.

1.4 For reporting purposes, the practical quantitation limits (PQL), given the sample volume purged, mass and/or methanol extract volume purged are: 50.0 ug/L for water and 5.0 mg/kg for soil/sediments for the aliphatic and aromatic carbon ranges and 5.0 ug/L and 0.5 mg/kg respectively for the individually targeted compounds. The procedure for Method Detection Limits (MDL) determination in this method and the

Single Laboratory Precision, Accuracy and MDL data (generated by the State of Massachusetts) is added for informational purposes only.

1.5 This method is based on a purge-and-trap, gas chromatography (GC) procedure. This method should be used by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatographs. The analysts should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.

1.6 Like all GC procedures, this method is subject to a "false positive" bias in the reporting of targeted analytes, in that non-petroleum compounds eluting or co-eluting within a specified retention time window may be falsely identified and/or quantitated with the respective carbon ranges. Confirmatory analysis by a GC/MS, EPA Method 8260, or other suitable procedures are recommended in cases where significant concentrations of non-hydrocarbon compounds are known or suspected. If the results of these analyses lead to identification and quantitation of non-petroleum compounds, the analyst may subtract those values from the affected carbon ranges as long as the identities and quantities of subtracted compounds are provided in the analytical report.

2.0 SUMMARY OF METHOD

2.1 Samples are analyzed using purge-and-trap sample concentration. The gas chromatograph is temperature programmed to facilitate separation of organic compounds. Detection is achieved by a photo-ionization detector (PID) and flame ionization detector (FID) in series. Quantitation is based on comparing the PID and FID detector response of a sample to a standard comprised of aromatic and aliphatic hydrocarbons. The PID chromatogram is used to determine the individual concentrations of targeted analytes (BTEX/MTBE) and collective concentration of aromatic hydrocarbons within the C8 through C10, C10 through C12 and C12 through C13 ranges. The FID chromatogram is used to determine the collective concentration of aliphatic hydrocarbons within the C5 through C6, C6 through C8, C8 through C10 and C10 through C12 ranges. To avoid double counting of the aromatic contribution to the aliphatic ranges, the PID concentrations are subtracted from the FID concentrations to yield the aliphatic ranges values.

2.2 This method is suitable for the analysis of waters, soils, and sediments. Water samples may be analyzed directly for volatile petroleum hydrocarbons by purge-and-trap concentration and gas chromatography. Soil samples are either dispersed in methanol to dissolve the volatile organic constituents and a portion of the methanol is analyzed by purge-and-trap GC or combined with water for purging directly from a soil purge vessel (EPA method 5035).

2.3 This method is based on, and constitutes a significant modification of, the “Method for the Determination of Volatile Petroleum Hydrocarbons (VPH)”, Public Comment Draft 1.0, developed by the Massachusetts Department of Environmental Protection and on EPA method 5035. They in turn based their method on (1) USEPA Methods

5030, 8000, 8020, and 8015, SW-846, "Test Methods for Evaluating Solid Wastes", 3rd Edition, 1986; (2) Draft "Method for Determination of Gasoline Range Organics", EPA UST Workgroup, November, 1990; and (3) "Method for Determining Gasoline Range Organics", Wisconsin Department of Natural Resources, PUBL-SW-140, 1992.

3.0 DEFINITIONS

3.1 **Volatile Petroleum Hydrocarbons (VPH)** are defined as all hydrocarbon compounds eluting just prior to n-pentane through 1-methylnaphthalene. VPH is comprised of C5 through C6, >C6 through C8, >C8 through C10 and >C10 through C12 Aliphatic Hydrocarbons, as well as >C8 through C10, >C10 through C12 and >C12 through C13 Aromatic Hydrocarbons as well as benzene and toluene. VPH concentration data are reported as the aggregate concentrations of the aliphatic and aromatic hydrocarbon ranges and as selected targeted analytes.

3.2 **Equivalent Total Petroleum Hydrocarbons (E-TPH)** For samples contaminated ONLY with gasoline or other low molecular weight petroleum products, the E-TPH value is equivalent to the VPH value. For samples contaminated with BOTH light and heavy molecular weight petroleum products (e.g., gasoline and diesel fuel), the E-TPH value is a summation of the VPH value and the Extractable Petroleum Hydrocarbon (EPH) values. In order to avoid double counting of analytes due to the overlap in the carbon ranges existing between the two methods, the analyst will report the highest of the two values determined for the overlapping ranges. In those cases where both the VPH and EPH methods are employed on samples, the analyst may select to quantitate the >C10 through C12 Aliphatic and the >C10 through C12 Aromatic Hydrocarbon ranges only using the EPH method.

3.3 **C5 through C6 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds which elute on the FID chromatogram from (and including) n-pentane through n-hexane.

3.4 **C6 through C8 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbons which elute on the FID chromatogram after n-hexane through n-octane.

3.5 **C8 through C10 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds which elute on the FID chromatogram after n-octane through n-decane.

3.6 **C10 through C12 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbons which elute on the FID chromatogram after n-decane through n-dodecane.

3.7 **C8 through C10 Aromatic Hydrocarbons** are defined as all hydrocarbon compounds which elute on the PID chromatogram after toluene through 1,2,3-trimethylbenzene.

3.8 **C10 through C12 Aromatic Hydrocarbons** are defined as all hydrocarbons which elute on the PID chromatogram after 1,2,3- trimethylbenzene through naphthalene.

3.9 **C12 through C13 Aromatic Hydrocarbons** are defined as all hydrocarbons which elute on the PID chromatogram after naphthalene through 1-methylnaphthalene. This is a hybrid range which is designed to acquire the methylnaphthalenes associated with petroleum products like gasoline and is only used when VPH is run without an accompanying EPH method request.

3.10 **Targeted VPH Analytes** are defined as benzene, toluene, ethylbenzene, p,m,o-xylenes, and MTBE.

3.11 **Volatile Petroleum Hydrocarbon (VPH) Component Standard** is defined as a 15 component mixture of the aliphatic and aromatic compounds, plus surrogate, listed in Table 1. The compounds comprising the VPH Component Standard are used to (a) define the individual retention times and chromatographic response factors for each of the Targeted VPH Analytes, (b) define and establish the windows for the collective aliphatic and aromatic hydrocarbon ranges of interest, and (c) determine average chromatographic response factors that can in turn be used to calculate the collective concentration of hydrocarbons within these ranges.

3.12 **Analytical Batch** is defined as a group of samples with similar matrices which are processed as a unit. For Quality Control purposes, if the number of samples in such a group is greater than 20, then each group of 20 samples or less are defined as separate analytical batches.

3.13 **Laboratory Duplicates** are defined as split samples taken from the same sampling container and analyzed separately with identical procedures. The analysis of laboratory duplicates give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.14 **Field Duplicates** are defined as two separate samples collected at the same time and place under identical circumstances and managed the same throughout field and laboratory procedures. Analyses of field duplicates give a measure of the precision associated with sample collection, preservation, and storage, as well as laboratory procedures.

3.15 **E-TPH Duplicates** are defined as two separate samples collected at the same time and location, for analysis by both EPH and VPH methods. E-TPH duplicates are taken at locations where significant concentrations of petroleum hydrocarbons lighter and heavier than C9 are likely to be present (e.g., locations contaminated by releases of both gasoline and diesel fuel). The resultant EPH and VPH concentrations, adjusted to prevent double counting of overlapping hydrocarbon ranges between the methods, are then summed to determine the Equivalent TPH (E-TPH) concentration.

3.16 **Calibration Standards** are defined as a series of standard solutions prepared from dilutions of a stock standard solution, containing known concentrations of each analyte and surrogate compound of interest.

3.17 **Calibration Check Standard** is defined as a calibration standard used to periodically check the calibration state of an instrument. The calibration check standard is prepared from the same stock solution as calibration standards, and is generally one of the mid-level range calibration standard dilutions.

Table 1. Volatile Petroleum Hydrocarbon (VPH) Component Standard

Compound	Equivalent Carbon Number
n-Pentane	5.0
n-Hexane	6.0
Methyl tert butylether	N/A
Benzene	6.5
Toluene	7.6
n-Octane	8.0
Ethylbenzene	8.5
m- & p- Xylene	8.6
o-Xylene	8.8
1,2,3,-Trimethylbenzene	10.1
n-Decane	10.0
Naphthalene	11.7
n-Dodecane	12.0
1-Methylnaphthalene	13.0
2,5-Dibromotoluene (surrogate)	N/A

3.18 **Matrix Spiking Solution** is defined as a solution which is generally prepared independently from the calibration standards, containing known concentrations of method analytes.

3.19 **Laboratory Method Blank** is defined as, depending on the matrix of the samples, either reagent water or clean sand spiked with a surrogate standard. The laboratory method blank is treated identically as with samples, exposed to all glassware, solvents, reagents, and equipment. A laboratory method blank is analyzed with every batch of samples, to determine if method analytes or other interferences are present in the laboratory environment, reagents, or equipment.

3.20 **Laboratory Fortified Blank (LFB)** is defined as, depending on the matrix of the samples, either reagent water or a clean sand blank fortified with a matrix spiking solution.

The LFB is treated and analyzed identically as with samples and blanks, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements at the required practical quantitation limits..

3.21 **Laboratory Fortified Matrix (LFM) Sample** is defined as an environmental sample which has been spiked with a matrix spiking solution containing known concentrations of method analytes. The LFM sample is treated and analyzed exactly as a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined through the separate analyses of a laboratory or field duplicate, and the measured values in the LFM sample corrected for background concentrations.

3.22 All other terms are as defined in SW-846, "Test Method for Evaluating Solid Waste", USEPA, September, 1986, and as amended.

4.0 INTERFERENCES

4.1 Samples can become contaminated by diffusion of volatile organics through the sample container septum during shipment and storage. Trip blanks prepared from reagent water should be carried through sampling and subsequent storage and handling to serve as a check on such contamination.

4.2 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe and/or purging device must be rinsed between samples with reagent water or solvent. The trap and other parts of the system are also subject to contamination, therefore, frequent bake-out and purging of the entire system may be required. A screening step is recommended to protect analytical instrumentation. Whenever an unusually concentrated sample is encountered, it must be followed by the analysis of a solvent blank to check for cross-contamination.

4.3 Certain organic compounds not associated with releases of petroleum products, including chlorinated solvents, ketones, and ethers, will be quantitated as Volatile Petroleum Hydrocarbons. Some samples may require additional analytical procedures to be employed , e.g. GC/MS, to document the presence and quantity of such compounds.

4.4 The response selectivity of a photo-ionization detector (PID) is used in this method to differentiate aromatic hydrocarbons from aliphatic hydrocarbons. All compounds eluting on the PID chromatogram after toluene are identified by the method as aromatic hydrocarbons. This will lead to an overestimation of aromatic hydrocarbons within samples, as certain aliphatic compounds will elicit a response on the PID, particularly unsaturated compounds such as alkenes. The significance and implications of this overestimation will vary from sample to sample and, where less conservative data are desired, additional actions should be considered to

minimize the detection of non-aromatic compounds, such as the use of a lower energy PID lamp or GC/MS.

5.0 HEALTH AND SAFETY ISSUES

The toxicity and carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis.

6.0 APPARATUS AND MATERIALS

6.1 The following glassware is used in this method:

6.1.1 VOC Vials: Wide mouth 60-mL VOC vials or 40-mL VOC vials with teflon/ silicone septa for soils; 40-mL VOC vials with teflon/silicone septa for waters.

6.1.2 Volumetric flasks: 10-mL, 50-mL, 100-mL, and 1,000-mL with a ground-glass stopper.

6.1.3 Disposal pipets: Pasteur.

6.2 Analytical balance: An analytical balance capable of accurately weighing 0.0001 g must be used for weighing standards. A top-loading balance capable of weighing to the nearest 0.1 g must be used for weighing soil samples.

6.3 **Gas Chromatography**

6.3.1 Gas Chromatograph: An analytical system complete with temperature programmable gas chromatograph and purge-and-trap concentrator. The data station must be capable of storing and reintegrating chromatographic data and must be capable of determining peak areas using a forced baseline projection.

6.3.2 Columns

6.3.2.1 Recommended column: 105M x 0.53 mm I.D. Restek RTX 502.2, 3.0 micron film thickness, or equivalent.

6.3.2.2 Other columns, such as a 60 M x 0.53 mm J&W DB-5, may be used. Capillary columns are required to achieve necessary resolution. The column must be capable of resolving typical gasoline components. It must also resolve ethylbenzene from m/p-xylene. Some columns may require subambient cooling to achieve these criteria.

6.3.3 Detectors: The method utilizes a Photo-ionization Detector (PID) in series with a Flame Ionization Detector (FID); the PID first in the series. The method is based upon the use of a 10.0 eV PID lamp, although lower energy lamps are permissible in order to minimize PID response to aliphatic compounds.

6.3.4 Purge-and-trap device: The purge-and-trap device consists of a sample purger, a trap, and a desorber. Several complete devices are commercially available.

6.3.4.1 The purging chamber must be designed to accept 5 mL samples with a water column at least 3 cm deep. Purging devices larger than 5 mL have a reduced purging efficiency and should not be used. The gaseous headspace between the water column and the top of the vessel should be at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. Fritted glass or needle sparge cells may be used. If needle sparge cells are used, the purge gas must be introduced no more than 5 mm from the base of the water column. Alternate sample purge devices may be used, provided equivalent performance is demonstrated.

6.3.4.2 The trap should be at least 25 cm long and have an inside diameter of at least 0.105 inches. The trap should be packed with 400 mg of Carbopack B (Supelco Cat. No. 209273). Alternative trap packing materials include: Tenax GC (or equivalent); 7.6 cm Carbopack B and 1.3 cm Carbosieve S-III (Supelco Cat No. 2-0321); 7 cm Carbopack C and 1.2 cm Carbopack B (Supelco Cat No. 2-1064); or equal volumes of Tenax, silica gel, and charcoal as described in EPA SW-846 Method 5030. In general, Carbopack trap packing materials are recommended because they have less of a tendency to retain methanol, which could interfere with the elution of pentane and quench the FID flame. The trap length and packing materials may be varied as long as equivalent performance has been verified.

6.3.4.3 Prior to initial use, the Carbopack B trap should be conditioned overnight at 270°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to a hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min. at 260°C with backflushing. The trap may be vented to the analytical column during daily conditioning, however, the column must be run through the temperature program prior to analysis of samples. Devices other than the traps recommended in Section 6.3.4.2 should be conditioned and desorbed according to the manufacturer's guidelines.

6.3.4.4 The desorber should be capable of rapidly heating the trap to 240°C for desorption.

6.4 Ultrasonic bath.

6.5 Syringes: 5-mL Luerlock glass hypodermic and 5-mL gas-tight syringe with shutoff valve.

6.6 Syringe valve: Two-way, with luer ends.

6.7 Microsyringes: 1-µL, 5-µL, 10-µL, 25-µL, 100-µL, 250-µL, 500-µL, and 1,000-µL.

6.8 Spatula: Stainless steel.

7.0 REAGENTS AND STANDARDS

7.1 **Reagents**

7.1.1 Reagent Water: organic free water (ASTM Type I reagent grade water).

7.1.2 Solvent: methanol; purge and trap grade or equivalent. Store away from other solvents.

7.1.3 Ottawa and/or masonry sand: free of volatile petroleum hydrocarbons.

7.2 **Stock Standard Solution**

Prepare a stock standard solution in methanol at approximately 20 µg/µL, or purchase certified solutions. Preparation of stock standards and component standards should be done using volumetric glassware.

7.2.1 The stock standard solution consists of the 15 VPH component standards listed in Table 1 and a surrogate standard. Prepare the stock standard solution by accurately weighing approximately 0.2000 g of each standard component. Dissolve the component in methanol and dilute to volume in a 10-mL volumetric flask. At the discretion of the analyst, the surrogate standard may be made up as a separate solution from the VPH standards.

7.2.1.1 Place about 8 mL of methanol in a 10-mL tared ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min. or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

7.2.1.2 Using a 500-µL syringe, immediately add 100 to 200 µL of each VPH Component Standard to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

7.2.1.3 Dilute to volume, stopper, and then mix by inverting the flask three times. Calculate the concentration in micrograms per microliter (µg/µL) from the net gain in weight. When compound purity is assayed to be 98% or greater, the weight may be used without correction to calculate the

concentration of the stock standard, provided such purities are certified by the manufacturer or by an independent source.

7.2.1.4 Transfer the stock standard solution into a Teflon-lined screw-cap/crimp cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.

7.2.2 Stock standard solutions must be replaced after 6 months, or sooner if comparison with check standards indicates a problem. The use of commercially prepared certified standard solutions is an acceptable alternative to the use of neat compounds in the preparation of standards.

7.3 **Primary Dilution Standard**

Using the stock standard solution, prepare primary dilution standards in methanol, as needed. The primary dilution standard should be prepared at the concentrations shown in Table 2. These standards should be stored with minimal headspace, at -10°C to -20°, and should be checked frequently for signs of degradation or evaporation. The analyst is allowed to prepare separate surrogate and VPH analyte standards.

The primary dilution standards should be replaced at least monthly.

7.4 **VPH Calibration Standards**

Prepare VPH Calibration standards in reagent water from the primary dilution standard at a minimum of five concentration levels. One of the concentration levels must be near, but above, the method detection limit and must be at a sufficiently low level to allow the PQL reporting of at least 5.0 ug/L for water and 0.5 mg/kg for soil/sediments for the targeted analytes (BTEX and MTBE) and 50.0 ug/L and 5.0 mg/kg respectively for the aliphatic and aromatic carbon ranges. The other standard concentrations must correspond to the expected range of concentrations found in real samples and/or should define the working range of the detector.

7.4.1 Rapidly inject the methanolic standard into the water in the expanded area of a filled 100-mL volumetric flask. Remove the needle quickly after injection.

7.4.2 Mix aqueous standards by inverting the flask three times.

7.4.3 Discard the solution contained in the neck of the flask, and fill the sample syringe from the standard solution contained in the expanded area of the flask.

7.4.4 Do not use pipets to dilute or transfer samples or aqueous standards.

7.4.5 Do not inject more than 20 µL of methanolic standards into 100 mL of reagent water. Aqueous standards are not stable and should be discarded after one hour.

7.5 **Surrogate Control Standard (SCS)**

The analyst must monitor both the performance of the analytical system and the effectiveness of the method in dealing with sample matrices by spiking each sample, blank, and matrix spike with a surrogate standard. The surrogate standard is also added to the VPH calibration standard solutions. The recommended surrogate standard is 2,5-dibromotoluene, which elutes after all aliphatic and aromatic compounds of interest. The use of additional surrogates or surrogates other than those listed above may be used, at the discretion of the analyst, as long as their performance in the method is demonstrated as acceptable and does not compromise the quantitation of the various target analytes or carbon ranges.

7.5.1 Surrogate Spiking Solution: From a stock standard solution prepared as in Section 7.2.1, prepare a surrogate spiking solution at 50 µg/mL in methanol. Add 4.0 µL of this surrogate spiking solution directly into the 5-mL syringe with every aqueous sample, blank, and matrix spike. 1.0 mL of the surrogate spiking solution is added to soil samples during the extraction step (See 9.1.2.2).

7.6 **Matrix Spiking Solution**

The recommended matrix spiking solution, consisting of the Targeted VPH Analytes, is prepared in methanol at concentrations of 50 µg/mL.

7.7 **Petroleum Reference Standard**

The use of a Petroleum Reference Standard is recommended for quality control purposes. The Petroleum Reference Standard consists of an API or commercial gasoline standard. Prepare a Petroleum Reference Standard Spiking Solution by accurately weighing approximately 0.0100 g of neat product. Dissolve the neat product in methanol and dilute to volume in a 10-mL volumetric flask.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 **Aqueous Samples**

8.1.1 Aqueous samples should be collected in duplicate (or the number of vials directed by the laboratory) without agitation and without headspace in contaminant-free amber glass VOC vials with Teflon-lined septa screw caps. Samples must be acidified to a pH of 2.0 or less at the time of collection and this can generally be accomplished by adding 3 or 4 drops (0.1 to 0.2 mL) of 1:1 HCl (1 part reagent water and 1 part concentrated HCl) to a 40-mL VOC vial. Samples must be cooled to 4°C immediately after collection.

8.1.2 A chain of custody form should accompany all sampling vials and should document the date and time of sample collection and acid preservation. The pH of all water samples must be determined by the laboratory unless sample vials containing acid for field preservation were supplied by the laboratory (this must be noted on the chain of custody). The pH measurement may be performed on left over sample. Any sample found to contain a pH above 2.0 should be so noted on the laboratory/data report sheet.

8.1.3 Any sample received by the laboratory that is not packed in ice or cooled to 4°C must be so noted on the laboratory/data report sheet.

8.1.4 Acid preserved aqueous samples must be analyzed within 14 days of collection. Aqueous samples which, for whatever reason, have not received acid preservation must be analyzed within 7 days of collection or the data must be reported as an “estimate quantity”.

8.2 **Soil Samples**

8.2.1 Soil samples must be collected in a manner that minimizes sample handling and agitation. All sediment must be removed from the glass threads of the vial to ensure an adequate seal. Samples must be cooled to 4°C immediately after collection.

8.2.3 Samples for VPH analysis should be collected in duplicate 2 or 4 ounce VOC jars with Teflon coated septum lined lids.

8.2.4 Sampling must be accomplished in a manner that ensures a minimum of headspace in the sample vial.

8.2.5 A chain of custody form should accompany all sampling vials and should document the date and time of sample collection.

8.2.6 Soil samples must be analyzed within 14 days of collection.

8.3 A summary of sample collection, preservation and holding times is provided in Table 2 .

Table 2 . Holding Times and Preservatives for VPH Samples

Matrix	Container	Preservation	Holding Time
Aqueous Samples	40-mL VOC vials w/ Teflon-lined septa screw caps	Add 3 to 4 drops of 1:1 HCl; cool to 4°C	14 days 7 days, if not preserved
Soil/Sediments Samples	VOC vials w/ Teflon-lined septa screw caps. 40-mL vials	cool to 4°C	14 days

9.0 PROCEDURE

9.1 **Sample Preparation and Purging**

9.1.1 It is recommended that samples known or suspected to have extremely high levels of volatile petroleum hydrocarbons be screened prior to analysis in order to establish the appropriate volume/mass to be used for analysis. This screening step may be analysis of a soil sample's methanol extract (diluted), the headspace method (SW-846 method 3810), the hexadecane extraction and screening method (SW-846 Method 3820) or other applicable method as determined by the analyst.

9.1.2 Water Samples

Introduce volatile compounds into the gas chromatograph using a purge-and-trap concentrator. The use of autosampling devices for sample introduction is recommended or the analyst may use the manual method outlined below.

9.1.2.1 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and

compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one 40-mL vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 20-mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

9.1.2.2 If necessary, samples should be diluted prior to injection into the purge chamber. In such cases, all steps must be performed without delay until the diluted sample is in a gas-tight syringe.

9.1.2.2.1 Dilutions may be made in volumetric flasks (10 mL to 100 mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for highly concentrated samples.

9.1.2.2.2 Calculate the approximate volume of reagent water to be added to the volumetric flask selected and add slightly less than this volume of reagent water to the flask.

9.1.2.2.3 Inject the proper aliquot of sample from the syringe prepared in Paragraph 9.1.2.1 into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with reagent water. Cap the flask, invert, and shake three times. Repeat the above procedure for additional dilutions. Alternatively the dilutions can be made directly in the glass syringe to avoid further loss of volatiles.

9.1.2.2.4 Fill a 5-mL syringe with diluted sample as in Paragraph 9.1.2.1.

9.1.2.3 Add 4.0 µL of the surrogate spiking solution through the valve bore of the syringe. Close the valves.

9.1.2.4 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

9.1.2.5 Close both valves and purge the sample for 11 min. Recommended purge and trap operating parameters are provided in Table 3.

Table 3. Suggested Purge and Trap Operating Parameters

Purge gas	Helium
Purge gas flow rate (mL/min)	40
Purge time (min)	11.0
Purge temperature	Ambient
Desorb temperature °C	250
Backflush inert gas flow (mL/min)	15-20

9.1.2.6 At the conclusion of the purge time, attach the trap to the chromatograph (if necessary), adjust the device to the desorb mode, and begin the gas chromatographic temperature program (in Section 9.2.1) and GC data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 240°C and backflushing the trap with inert gas between 15 and 20 mL/min for 4 minutes.

9.1.2.7 While the trap is desorbing into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5 mL flushes of reagent water (or methanol followed by reagent water) to avoid carryover of pollutant compounds into subsequent analyses.

9.1.2.8 After desorbing the sample, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 260°C. After approximately 7 to 15 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. After a highly concentrated sample, a longer baking time may be necessary. When cool, the trap is ready for the next sample.

9.1.2.9 If the concentration of an analyte in a sample exceeds the calibration range, a dilution of the sample is required. If a sample analysis results in a saturated detector response for a compound, the analysis must be followed by one or more blank reagent water analyses. If the final blank analysis is not free of significant interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of significant interferences.

9.1.2.10 All dilutions should keep the detector response of the major constituents (previously saturated peaks) in the upper half of the linear range of the calibration curve.

9.1.3 Soil/Sediments

Soil and sediment samples are extracted with methanol. An aliquot of the extract is added to reagent water and introduced into the gas chromatograph using a purge and trap concentrator. Should lower values for the targeted analytes be desired, the analyst may employ direct purging of the soil sample using the method outlined in EPA methods 5030 and 5035. The use of autosampling devices for sample introduction is recommended or the analyst may use the manual method outlined below.

9.1.3.1 Weigh the sample vial to 0.1 g in a top loading balance and add 4 to 5 grams of the sample to the vial, reseal and determine the weight of the soil/sediment sample.

9.1.3.2 Quickly add 9.0 mL of methanol and 1.0 mL of the surrogate spiking solution. Cap and shake the sample vial for 2 minutes.

9.1.3.3 Allow soil/sediment to settle, or centrifuge the vial, until a layer of methanol is apparent.

9.1.3.4 Using a microliter syringe, withdraw an appropriate aliquot of the methanol extract for sparging. Sample screening data can be used to determine the volume of methanol extract to add to the 5 mL of reagent water for analysis. All dilutions must keep the response of the major constituents in the upper half of the linear range of the calibration curve.

9.1.3.5 Remove the plunger from one 5.0-mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to allow for addition of the extract (e.g., for 100 µL of extract adjust to 4.9 mL). Pull the plunger to 5.0 mL for addition of the sample extract. Add the volume of methanol extract determined from screening (100 µL maximum).

9.1.3.6 Attach the syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber. Complete operations as specified in Paragraphs 9.1.2.5 through 9.1.2.8.

9.1.4 Proceed with the analysis as described in Sections 9.2 through 9.5. Analyze all laboratory method blanks and QC samples under the same conditions as that used for samples.

9.1.5 If the responses exceed the calibration or linear range of the system, use a smaller aliquot of methanol or aqueous sample.

9.1.6 Determination of Percent Moisture

9.1.6.1 Soil and sediment results must be reported on a dry-weight basis.

9.1.6.2 Transfer 5 to 10 g of sample into a tared crucible. The amount of material used to determine the percent moisture will depend on the amount of moisture present, thus relatively dry samples require more sample addition in order to achieve a significant weight change than wet samples. Dry the sample overnight in an oven at 105°C. Remove the sample from the oven and allow it to cool in a desiccator before reweighing. Reweigh and calculate the percent moisture of the sample using the equations provided in Section 9.6.2.2.

9.2 GC Conditions

9.2.1 Oven Program: Oven temperature 45°C, hold for 1 min, then to 100°C at 3°C/min, to 160°C at 8°C/min, to 230°C at 20°C/min; hold for 7.5 min. Conditions may be altered to improve resolution of volatile petroleum hydrocarbons.

9.2.2 Gas Flows: The recommended carrier gas is helium.

9.2.2.1 Carrier gas flow: 12.5 mL/min.

9.2.2.2 Air: 350 mL/min

9.2.2.3 Hydrogen: 30 mL/min

9.2.2.4 Make up gas flow: 17.5 mL/min

9.2.3 Miscellaneous:

9.2.3.1 FID temperature: 230°C

9.2.3.2 PID temperature: 230°C

9.2.3.3 Injection port temperature: 250°C

9.2.3.4 Column head pressure: 15 psi

9.3 **Retention Time Windows**

9.3.1 Before establishing retention time windows, make sure the GC system is within optimum operating conditions. Make three injections of the VPH Component Standard throughout the course of a 72-hr period. Serial injections over less than a 72-hr period may result in retention time windows that are too tight.

9.3.2 Calculate the standard deviation of the three absolute retention times for each individual compound in the VPH Component Standard. The retention time window is defined as plus or minus three times the standard deviation of the absolute retention times for each standard. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

9.3.3 In those cases where the standard deviation for a particular standard is zero, the laboratory should substitute the standard deviation of a closely eluting structurally similar compound to develop a valid retention time window.

9.3.4 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. This data must be retained by the laboratory.

9.3.5 VPH retention time (Rt) windows are defined as beginning 0.1 minutes after the Rt of the beginning marker compound and ending 0.1 minutes after the Rt of the ending marker compound. The exception to this is the C5 through C6 aliphatic hydrocarbon range, where its Rt window is defined a beginning 0.1 minutes prior to the beginning marker compound and ending 0.1 minutes after the ending marker compound. VPH marker compounds and windows are summarized in Table 4 .

Table 4 . VPH Marker Compounds

Hydrocarbon Range	Beginning Marker Compound	Ending Marker Compound
C5-C6 Aliphatic Hydrocarbons (FID)	just before n-Pentane	just after n-Hexane
C6-C8 Aliphatic Hydrocarbons (FID)	just after n-Hexane	just after n-Octane
C8-C10 Aliphatic Hydrocarbons (FID)	just after n-Octane	just after n-Decane
C10-C12 Aliphatic Hydrocarbons (FID)	just after n-Decane	just after n-Dodecane
C8-C10 Aromatic Hydrocarbons (PID)	just after Toluene	just after 1,2,3-Trimethylbenzene
C10-C12 Aromatic Hydrocarbons (PID)	just after 1,2,3-Trimethylbenzene	just after Naphthalene
C12-C13 Aromatic Hydrocarbons (PID)	just after Naphthalene	just after 1-Methylnaphthalene

9.4 **Calibration**

9.4.1 External Standard Calibration Procedure

9.4.1.1 Prepare VPH Calibration Standards at a minimum of five concentration levels in accordance with the procedures and specifications contained in Section 7.0.

9.4.1.2 Analyze each VPH Calibration Standard following the procedures outlined in Section 9.5. Tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each targeted analyte. Alternatively, the ratio of the response to the amount injected, defined as the calibration factor (CF), may be calculated for method analytes using Equation 1. If the percent relative standard deviation (%RSD) of the calibration factor is equal to or less than 20 % over the working range for all analytes of interest, as determined using Equation 2, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve.

Equation 1: Calibration Factor

$$Calibration\ Factor\ (CF) = \frac{area\ of\ peak}{mass\ purged\ (ng)}$$

Equation 2: Relative Standard Deviation

$$\%RSD = \frac{Stand\ Dev\ of\ 5\ CFs}{Mean\ of\ 5\ CFs} \times 100$$

9.4.1.3 A collective calibration curve or factor must also be established for each hydrocarbon range of interest. Calculate the collective Calibration Factors (CF) for C5-C6, >C6-C8, >C8-C10 and >C10-C12 Aliphatic Hydrocarbons ranges using the FID chromatogram. Calculate the collective CF for the >C8-C10, >C10-C12 and C12-C13 Aromatic Hydrocarbons ranges using the PID chromatogram. Tabulate the summation of the peak areas of all components, the compounds which define the various ranges, in those fractions (e.g. C6-C8 Aliphatic Hydrocarbons, n-pentane and n-hexane or >C6 - C8, n-octane) against the total mass injected using Equation 3.

Note: Do not include the area of any surrogate standard or internal standard in calculating a Range CF.

Equation 3: Range Calibration Factor

$$Range\ CF = \frac{Total\ area\ of\ peaks}{Total\ mass\ purged\ (ng)}$$

9.4.1.4 At a minimum, the working calibration curve or calibration factor must be verified on each working day, and after every 20 samples, whichever is more frequent, by the injection of a mid-level calibration standard to verify instrument performance and linearity. If the percent difference (%D) for any targeted analyte response varies from the predicted response by more than ± 15 %, as determined using Equation 4, a new calibration curve must be prepared for that analyte. Similarly, if the percent difference of the carbon range compound response varies from the predicted response by more than ± 20 %, a new calibration curve must be prepared.

Equation 4: Percent Difference (%D)

$$\%D = \frac{\overline{CF} - CFv}{\overline{CF}} x\ 100$$

9.4.1.5 Targeted VPH Analytes and Aromatic Hydrocarbons ranges are quantitated on the PID chromatogram.

9.4.1.6 The Aliphatic Hydrocarbons ranges are quantitated on the FID chromatogram after subtraction of the collective concentrations of MTBE, and the BTEX compounds identified on the PID chromatogram from the collective concentration values of the C5 through C6 and C6 through C8 Aliphatic Hydrocarbon concentration values determined using the FID chromatogram. Similarly, the PID concentrations determined for the remaining aromatic ranges are subtracted from the FID concentrations for those ranges to yield the actual FID Aliphatic Hydrocarbon ranges values.

9.4.1.7 The concentration of specific analytes or hydrocarbon ranges in aqueous and non-aqueous samples may also be calculated from a calibration curve by use of linear regression analysis.

9.5 GC Analysis

9.5.1 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by samples interspersed with blanks and QC samples. The analytical sequence ends must end with an acceptable calibration verification. If the final calibration verification is not acceptable, then all samples analyzed after the last acceptable calibration verification must either be reanalyzed or if this is not possible, then the data associated with those samples must be qualified as an "estimate quantity".

9.5.2 Establish daily retention time windows for each analyte. Use the absolute retention time for each analyte as the midpoint of the window for that day. The daily retention time window equals the midpoint ± three times the standard deviation determined in Section 9.3.

9.5.2.1 Tentative identification of an analyte occurs when a peak from a sample falls within the daily retention time window. In cases where interferences are suspected, confirmation on a second dissimilar GC column or by GC/MS analysis may be necessary.

9.5.2.3 Validation of GC system qualitative performance must be accomplished by the analysis of standards, generally mid-level, within the analysis sequence. If any of the standards fall outside their daily retention time window, the system is out of control. In such cases, the cause of the problem must be determined and corrected.

9.5.3 If the response for Targeted VPH Analytes exceeds the linear range of the system, dilute the sample and reanalyze. It is recommended that samples be diluted so that all peaks are on scale. Overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure that all peaks are on scale over a 100-fold range, are acceptable if linearity is demonstrated prior to the analysis of samples. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

9.5.4 If detection of targeted analyte peaks are prevented by the presence of interferences, additional analytical techniques, e.g. GC/MS, are recommended.

9.5.5 Peak area and carbon range area quantification/integration must be from baseline (i.e. forced baseline projection which must include the unresolved complex mixture "hump" areas). The exception to this is the C5 through C6 Aliphatic Hydrocarbon range which, due to the use of capillary columns shorter than 100 meters and/or the purging of methanol volumes greater than 20 uL, may experience a lack of complete resolution between C5 (n-pentane) and methanol. In this event, the analyst is allowed to use tangential skim integration, or other suitable integration techniques, to integrate n-pentane, and subsequent hydrocarbons within the C5-C6 aliphatic range if it/they appear(s) on the trailing edge of the methanol solvent peak.

9.6 External Standard Calculations

The concentration of targeted analytes and hydrocarbon ranges in a sample may be determined by calculating the amount of analyte or hydrocarbon range purged, from the peak response, using the calibration curve or the calibration factor determined in Section 9.4.

9.6.1 Aqueous samples:

The general equation to determine the concentration of a specific analyte or hydrocarbon range in aqueous samples in provided in Equation 5.

Equation 5

$$Concentration\ (\mu g / L) = \frac{(A_x)(A)(D)}{(A_s)(V_s)}$$

where:

A_x = Response for the analyte or hydrocarbon range in the sample, units may be in area counts or peak height.

A = Amount of external standard purged, ng.

D = Dilution factor; if no dilution was made, D = 1, dimensionless.

A_s = Response for the external standard, units same as for A_x.

V_s = Volume of sample purged, mL.

If a Calibration Factor is used, the concentration of a specific analyte or hydrocarbon range in an aqueous sample may be calculated using equations 6 and 7, respectively.

Equation 6

$$Conc\ Analyte\ (\mu g / L) = \frac{(A_x)(D)}{(V_s)(CF)}$$

Equation 7

$$Conc\ HC\ Range\ (\mu g / L) = \frac{(A_x)(D)}{(V_s)(Range\ CF)}$$

where:

A_x = Response for the analyte or hydrocarbon range in the sample, units may be in area counts or peak height.

D = Dilution factor; if no dilution was made, D = 1, dimensionless.

V_s = Volume of sample purged, mL.

CF = Calibration Factor, area counts/ng.

Range CF = Calibration Factor for hydrocarbon range, (collective area count/collective mass), area counts/ng.

9.6.2 **Non-Aqueous Samples (Methanol Extraction):**

9.6.2.1 The general equation to determine the concentration of a specific analyte or hydrocarbon range in a soil or sediment sample is provided in Equation 8.

Equation 8

$$Concentration\ (\mu g / kg) = \frac{(A_x)(A)(V_t)(D)}{(A_s)(V_i)(W_d)}$$

where:

A_x = Response for the analyte or hydrocarbon range in the sample, units may be in area counts or peak height.

A = Amount of external standard purged, ng.

V_t = Volume of total extract, µL (Note: this value must include the 1.0 mL surrogate spiking solution added to soil samples)

D = Dilution factor; if no dilution was made, D = 1, dimensionless.

A_s = Response for the external standard, units same as for A_x.

V_i = Volume of methanol extract added to reagent water for purge and trap analysis, µL.

W_d = Dry weight of sample purged, g (see equations 11 through 13)

If a Calibration Factor is used, the concentration of a specific analyte or hydrocarbon range in a soil or sediment sample may be calculated using Equations 9 and 10, respectively.

Equation 9

$$Conc\ Analyte\ (\mu g / kg) = \frac{(A_x)(V_t)(D)}{(V_i)(W_d)(CF)}$$

Equation 10

$$Conc\ HC\ Range\ (\mu g / kg) = \frac{(A_x)(V_t)(D)}{(V_i)(W_d)(Range\ CF)}$$

where:

V_t = Volume of total extract, µL.

Vi = Volume of extract added for purging, µL

W_d = Dry Weight of sample purged, g (see Equations 11 through 13)

A_x, CF, Range CF and D have the same definition as for aqueous samples.

9.6.2.2 Calculation of Dry Weight of Sample

In order to calculate the dry weight of sample purged (W_d), it is necessary to determine the moisture content of the soil/sediment sample, using the procedure outlined in Section 9.1.6. Using the data obtained from Section 9.1.6, W_d is calculated using Equations 11 through 13.

Equation 11

$$\%\ Moisture = \frac{g\ sample - g\ dry\ sample}{g\ sample}\ X\ 100$$

Equation 12

$$\%\ Dry\ Solids = (1) - (\%\ Moisture)$$

Equation 13

$$W_d\ (g) = (\%\ Dry\ Solids)(g\ of\ extracted\ sample)$$

9.6.3 The concentration of specific analytes or hydrocarbon ranges in aqueous and non-aqueous samples may also be calculated from the calibration curve by linear regression, provided that the correlation coefficient (r) is at least 0.99 and the % D for any targeted analyte must not vary from the predicted response by more than +/- 15%, nor any hydrocarbon range standard from its predicted response by more than +/- 20%.

9.6.4 Peak areas measured from blanks may not be subtracted from sample peak areas.

9.6.5 All integration of collective hydrocarbon ranges must be to baseline.

9.6.6 Required Adjustment of Range Concentration Data: In order to minimize the "double counting" of the same hydrocarbon compounds on both the FID and PID chromatograms, the collective concentrations of MTBE, benzene, toluene, ethylbenzene, and m, p, o-xylene identified on the PID chromatogram must be subtracted from the collective Aliphatic Hydrocarbon concentration values, for the ranges in which they elute, determined using the FID chromatogram. Similarly, the collective concentrations of the remaining aromatic ranges values determined on the PID chromatogram must be subtracted from the corresponding aliphatic ranges values determined on the FID chromatogram.

10.0 QUALITY CONTROL

10.1 **General Requirements and Recommendations**

10.1.1 Each laboratory that uses this method should operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document the quality of data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance standards for the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

10.1.2 A acidified reagent water blank should continually accompany each soil sample or water sample batch, respectively, over the course of sampling, storage, and analysis.

10.1.3 A Laboratory Method Blank should be run after samples suspected of being highly contaminated to determine if sample carryover has occurred.

10.1.4 At a minimum, for each analytical batch (up to 20 samples), a Laboratory Method Blank, Laboratory Fortified Blank, Laboratory Fortified Matrix Spike, and sample

duplicate must be analyzed. For analytical batches with more than 10 samples, the analysis of an additional mid-range calibration check standard is recommended. The blank and spiked samples must be carried through all stages of the sample preparation and measurement process.

10.1.5 The recommended sequence of analysis is as follows:

(1) Calibration Standards (initial) or mid-range Calibration Check Standard (daily check on initial calibration)
(2) Laboratory Method Blank
(3) Samples
(4) QC Samples
(5) Mid-range Calibration Check Standard (also recommended after each 10 samples)

10.1.6 It is recommended that a system of control charts be developed to plot surrogate standard recoveries as a function of time. When surrogate recovery from a sample, blank, or QC sample is less than 60% or more than 140%, check calculations to locate possible errors, the fortifying solution for degradation, and changes in instrument performance. If the cause cannot be determined, the analyst may reanalyze the sample or report the surrogate values as outside acceptance limits.

10.2 **Minimum Instrument QC**

10.2.1 While it is recommended that the n-pentane (C5) peak be adequately resolved from the methanol solvent on the FID chromatogram, the analyst is allowed to follow the guidance as outlined in 9.5.5. Coelution of the m- and p- xylene isomers is permissible. Any surrogates and/or internal standards used must be adequately resolved from individual compounds in the VPH Component Standard.

10.2.2 Retention time windows must be established for each analyte of interest each time a new GC column is installed, and must be verified and/or adjusted on a daily basis. (See Section 9.3)

10.2.3 Calibration curves must be developed based upon the analysis of calibration standards prepared at a minimum of 5 concentration levels. The linearity of calibration or response factors may be assumed if the percent relative standard deviation (%RSD) over the working range of the curve is less than or equal to 20%. Alternatively, if linear regression analysis is used for quantitation, the correlation coefficient (r) must be at least 0.99 and no targeted analyte or carbon range standard may vary from the true value by more than +/- 15% and +/- 20% respectively. (See Section 9.4.)

10.3 **Initial and Periodic Method QC Demonstrations**

The following must be conducted as an initial demonstration of laboratory capability, prior to the analysis of any samples. Subsequent to this initial demonstration, additional evaluations of this nature should be conducted on a periodic basis, in response to changes in instrumentation or operations, and/or in response to confirmed or suspected systems, method, or operational problems.

10.3.1 Accuracy and Precision

To demonstrate initial laboratory capability, analyze a minimum of four replicate reagent water and/or clean sand blanks spiked with each analyte of interest at approximately 20 to 60 µg/L and/or 20 to 60 mg/kg, respectively.

10.3.1.1 Add an appropriate aliquot of the stock or primary dilution standard solution(s) to each of the four replicate reagent water or clean sand blanks. Purge and analyze each replicate according to the procedures described in Section 9.0.

10.3.1.2 Calculate the measured concentrations of each analyte in all replicates, the mean accuracy (as a percentage of true value) for each analyte, and the precision (as %RSD) of the measurements for each analyte.

10.3.1.3 For each analyte, the mean accuracy, expressed as a percentage of the true value, must be between 80% and 120%. For each analyte, the %RSD must be less than or equal to 20%.

10.3.1. If desired, the Accuracy and Precision evaluation may be combined with the MDL evaluation specified in Paragraph 10.3.2.

10.3.2 Method Detection Limits (Optional)

Analyze a minimum of seven replicate reagent water and/or clean sand blanks which have been fortified with all analytes of interest at approximately 0.5 to 5 µg/L and/or 1 to 5 mg/kg, respectively. Calculate the Method Detection Limit (MDL) of each analyte using the procedure described in Section 12.0.

10.3.2.1 Water MDLs are determined by analyzing 7 to 10 replicates of reagent water samples in 100-mL flasks spiked with the VPH Component standard and with 40 µg/L of the surrogate compound 2,5-dibromotoluene.

10.3.2.2 Soil/sediment MDLs are determined by analyzing 7-10 replicates of 5 -g of VPH-free sand blanks spiked with the VPH Component standard and with 2 mg/kg of the surrogate 2,5-dibromotoluene.

10.3.3 Petroleum Reference Standard

As an optional demonstration of the validity and relevance of VPH calibration, analyze a reagent water and/or clean sand blank spiked with a known concentration of a neat gasoline product.

10.3.3.1 Fortify a reagent water and/or clean sand blank with 5 µL and/or 0.5 mL of the Petroleum Standard Spiking Solution, respectively. Purge and analyze in accordance with the procedures outlined in Section 9.0.

10.3.3.2 Calculate the total concentration of all petroleum hydrocarbons within the Aliphatic Hydrocarbon ranges using the FID chromatogram. Add these values together. Do not subtract the concentration of Targeted VPH analytes.

10.3.3.3 The concentration calculated in Paragraph 10.3.3.2 is expected to be within 30% +/- of the known concentration of Petroleum Standard in the reagent water or sand blank.

10.4 **Ongoing Method QC Demonstrations**

10.4.1 Each sample, blank, and matrix spike must be spiked with the surrogate spiking solution. Required surrogate recovery is 60% to 140%.

10.4.2 At a minimum, with every batch of 20 samples or less the laboratory must analyze the following:

10.4.2.1 **Calibration Check Standard** - A mid-range calibration standard, prepared from the same stock standard solution used to develop the calibration curve, must be analyzed prior to sample analysis to verify the calibration state of the instrument. For large analytical batches that contain more than 10 samples, the analysis of an additional mid-range calibration check standard is recommended after the analysis of the tenth sample. If the percent difference (% D) of any analyte within the calibration check standard varies from the predicted response by more than 20 %, a new calibration curve must be prepared for that analyte.

10.4.2.2 **Laboratory Method Blank** - A water or soil laboratory method blank is prepared by fortifying a 5 mL reagent water blank with 4 µL of the surrogate spiking solution, or by fortifying a 5 g sample of clean sand with 1.0 mL of the surrogate spiking solution. Peaks within the retention time windows of any hydrocarbon ranges of interest may not be present at or above the lowest calculated PQL for any sample within its batch. When determining the PQL for soil method blanks, incorporate the lowest percent solids value found for any sample within its batch in the calculation.

10.4.2.3 **Laboratory Fortified Blank (LFB)** - A water or soil component spike is prepared by fortifying a 5 mL reagent water blank with 4 µL of the matrix spiking solution, or by fortifying a 5 g sample of clean sand with 1.0 mL of the matrix spiking solution. The spike recovery must be between 70% and 130% and if these values can not be obtained the analyst must identify and correct the problem before analyses can continue.

10.4.2.4 **Sample duplicates** - Sample duplicates may be laboratory or field duplicates. The RPD of duplicate samples should not exceed +/- 25%. The lack of sample homogeneity may contribute to RPD's for duplicates which exceed this value. Should the values exceed 25%, the analyst must report that occurrence.

10.4.2.5 **Laboratory Fortified Matrix (LFM) Spike** - The water or soil LFM spike is prepared by fortifying an actual 5 mL water sample with 4 µL of the matrix spiking solution, or by fortifying an actual 5 g soil/sediment sample with 1.0 mL of the matrix spiking solution. The purpose

of the LFM is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations. The corrected concentrations of each analyte within the matrix spiking solution must be within 70 - 130% of the true value. Should the values determined exceed this range, the analyst must report that occurrence.

10.4.3 If any of the performance standards specified in Section 10.4 are not met, the problem must be corrected before further samples are analyzed. Exceptions to this are duplicate samples RPD's and high recoveries for LFM spikes which, due to sample non-homogeneity may exceed the allowable limits. Any samples run between the last calibration check standard that meets the criteria and one that does not must be rerun. If this is not possible, that data must be reported as an "estimated concentration".

11.0 DATA PRODUCTION AND REPORTING

11.1 **Sample Analysis**

11.11 PID Chromatogram

11.1.1.1 Determine the peak area count for the Targeted VPH Analytes.

11.1.1.2 Determine the peak area count for the surrogate 2,5-dibromotoluene.

11.1.1.3 Separately determine the total area count for all peaks eluting 0.1 minutes after the Rt's for toluene through 0.1 minutes after the Rt for 1,2,3-trimethylbenzene, for all peaks eluting 0.1 minutes after the retention time (Rt) for 1,2,3-trimethylbenzene and 0.1 minutes after the retention time for naphthalene and for all peaks eluting 0.1 minutes after the Rt for naphthalene through 0.1 minutes after the Rt of 1-methylnaphthalene.

11.1.1.4 Using the equations contained in Section 9.6 or linear regression analysis, calculate the concentrations of the Targeted VPH Analytes, the surrogate standard 2,5-dibromotoluene, and >C8 through C10, >C10 through C12 and >C12 through C13 Aromatic Hydrocarbons.

11.2.1 FID Chromatogram

11.2.1.1 Separately determine the total area count for all peaks eluting 0.1 minutes before the retention time (Rt) for n-pentane to 0.1 minutes after the Rt for n-hexane and for all peaks eluting 0.1 minutes after the Rt for n-hexane to 0.1 minutes after the Rt for n-octane. It is not necessary to identify or quantitate individual aliphatic compounds within these ranges.

11.2.1.2 Determine the total area count for all peaks eluting 0.1 minutes after the Rt for n-octane to 0.1 minutes after the Rt for n-decane and 0.1 minutes after n-decane to 0.1 minutes after n-dodecane. It is not necessary to identify or quantitate individual aliphatic compounds within this range.

11.2.1.3 Determine the peak area count for the surrogate standard 2,5-dibromotoluene.

11.2.1.4 Using the equations contained in Section 9.6 or linear regression analysis, calculate the concentrations of C5 through C6 Aliphatic Hydrocarbons, >C6 through C8 Aliphatic Hydrocarbons, >C8 through C10 Aliphatic Hydrocarbons, >C10 through C12 Aliphatic Hydrocarbons and the surrogate standard 2,5-dibromotoluene.

11.2.1.5 To avoid "double counting" of the same analytes, adjust the concentrations of Aliphatic Hydrocarbons calculated in Paragraph 11.2.1.4 by subtracting the collective concentrations of methyl tert butylether, benzene, toluene, >C8 through C10 and >C10 through C12 Aromatic Hydrocarbons, as determined from the PID chromatogram in Section 11.11, from the Aliphatic Hydrocarbon range values effected.

11.3 **Data Reporting Format**

11.3.1 The following information and data must be reported:

11.3.1.1 The sample matrix (aqueous, soil or sediment);

11.3.1.2 The date(s) the sample was collected, received by the laboratory, and analyzed;

11.3.1.3 A description of the sample(s) received by the laboratory, relative to the physical condition of the containers, the temperature of the samples, and use of appropriate preservatives;

11.3.1.4 Moisture content (for soil/sediment samples);

11.3.1.5 The calculated concentrations of C5 through C6, C6 through C8, C8 through C10 and C10 through C12 Aliphatic Hydrocarbons ranges and C8 through C10, C10 through C12 and C12 through C13 Aromatic Hydrocarbons ranges

11.3.1.6 Surrogate recovery (expressed as percent recovery);

11.3.1.7 The calculated concentrations of Targeted VPH Analytes determined

11.3.1.8 The concentration units for aqueous samples are expressed as ug/L or mg/L and for soil or sediment samples the units are expressed as ug/Kg or mg/Kg on a dry-weight basis.

12.0 METHOD PERFORMANCE

12.1 **Method Detection Limits (Optional)**

12.1.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

12.1.2 The MDL is determined according to the following equation:

Equation 14

$$MDL = (t) \times (SD)$$

where:

t = student t value at the 99% confidence level

SD = standard deviation of the replicate analysis

Student t values are as follows:

Number of replicates	t value
7	3.14
8	3.00
9	2.90
10	2.82

12.1.3 For the purposes of this method, the designated MDL value for a hydrocarbon range of interest shall be the highest value calculated for the individual analytes within that hydrocarbon range.

12.2 **Single Laboratory Accuracy, Precision, and MDL Data**

Single laboratory accuracy, precision and MDL data for method analytes are provided in Tables 1-1 through 1-4 in Appendix 1. Additional investigation will be conducted to further evaluate the low recoveries for naphthalene.

13.0 REFERENCES

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METHOD FOR THE DETERMINATION

OF

EXTRACTABLE PETROLEUM HYDROCARBONS (EPH) FRACTIONS

Washington State Department of Ecology

June 1997

METHOD FOR THE DETERMINATION OF EXTRACTABLE PETROLEUM HYDROCARBONS (EPH)

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DISCLAIMER

Mention of trade names or commercial products does not constitute endorsement by the Washington State Department of Ecology. Equipment and materials cited in this method may be replaced by similar products, as long as adequate data exists or has been produced documenting equivalent or superior performance.

METHOD FOR THE DETERMINATION OF EXTRACTABLE PETROLEUM HYDROCARBONS

1.0 SCOPE AND APPLICATION

1.1 This method is designed to measure the collective concentrations of extractable aliphatic and aromatic petroleum hydrocarbons in water and soil. **The carbon ranges used through out this document are given in equivalent carbon numbers (EC) which are related to the boiling point of a chemical normalized to the boiling point of the n-alkanes and its retention time in a boiling point gas chromatographic column**. Extractable aliphatic hydrocarbons are collectively quantitated within five ranges: C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34. Extractable aromatic hydrocarbons are collectively quantitated within five ranges: C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 150 °C and 500 °C.

1.2 Petroleum products suitable for evaluation by this method include, but are not limited to, kerosene and jet fuels, diesel and fuel oils and hydraulic, insulating and lubricating oils. This method, in and of itself, is not suitable for the evaluation of gasoline, mineral spirits, petroleum naphthas, and other petroleum products which contain a significant percentage of hydrocarbons lighter than C10. When samples are known or suspected to contain petroleum hydrocarbons of these or similar types, the Volatile Petroleum Hydrocarbon (VPH) method must also be employed to fully evaluate the hydrocarbons present.

1.3 For reporting purposes, the practical quantitation limits (PQL), given the sample volume/mass, final extract volume and assuming 100 percent solids for soil/sediments are: 50.0 ug/L for aliphatic and aromatic carbon ranges in water and 5.0 mg/Kg for these components in soil. If lower quantitation limits are desired, the analyst is allowed to extract larger volumes/masses and/or concentrate the extracts to smaller volumes prior to analysis. The procedure for Method Detection Limits

(MDL) determination in this method and the Single Laboratory Precision, Accuracy and MDL data (generated by State of Massachusetts) is added for informational purposes only.

1.4 This method is based on a solvent extraction, silica gel fractionation process and gas chromatography (GC) analysis using a flame ionization detector (FID). This procedure should be used by, or under the supervision of, analysts experienced in extractable organics analysis. Analysts using this method should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.

1.5 Like all GC procedures, this method is subject to a "false positive" bias, in that non-hydrocarbon compounds eluting or co-eluting within a specified retention time window may be falsely identified and/or quantitated with the respective carbon ranges. While the cleanup procedure specified in this method to segregate aliphatic and aromatic fractions will serve to mitigate this concern, confirmatory analyses by gas chromatography/mass spectrometry (GC/MS) analysis, EPA Method 8270, or other suitable techniques are recommended in cases where significant concentrations of non-hydrocarbon compounds are known or suspected. Non-petroleum compounds identified and quantitated by GC/MS may be subtracted from the carbon ranges affected as long as the quantity and identities of the compounds are reported along with the carbon range data.

2.0 SUMMARY OF METHOD

2.1 A sample submitted for EPH analysis is extracted with methylene chloride, dried over sodium sulfate, solvent exchanged into hexane, and concentrated. Sample cleanup and separation into aliphatic and aromatic fractions is conducted using a modification of EPA method 3630 (silica gel cleanup). The use of commercially available silica gel cartridges (Sep-Pak cartridges, Waters, Milford, MA) may be substituted for the silica gel column outlined in method 3630 if they can be shown to achieve comparable results. The two extracts produced are then concentrated to final volumes of 10 mL each (i.e., an aliphatic extract and an aromatic extract) and are then separately analyzed by a gas chromatograph equipped with a capillary column and a flame ionization detector. The resultant chromatogram of aliphatic compounds is collectively integrated within the C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 aliphatic hydrocarbon ranges. The resultant chromatogram of aromatic compounds is collectively integrated within the C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 ranges.

2.2 Average calibration factors or response factors determined using an aliphatic hydrocarbon standard mixture are used to calculate the collective concentrations of the different aliphatic hydrocarbons ranges. An average calibration factor or response factor determined using the aromatic hydrocarbon standard mixture is used to calculate a collective concentrations of the aromatic hydrocarbon ranges.

2.3 This method is suitable for the analysis of waters, soils, and sediments.

2.4 This method is based on, and constitutes a significant modification of, the "Method for the Determination of Extractable Petroleum Hydrocarbons (EPH)" Public Comment Draft 1.0 developed by the Massachusetts Department of Environmental Protection. They in turn based their method on (1) USEPA Methods 8000, 8100, and 3630, SW-846, "Test Methods for Evaluating Solid Waste", 3rd Edition, 1986; (2) Draft "Method for Determination of Diesel Range Organics", EPA UST Workgroup, November, 1990; and (3) "Method for Determining Diesel Range Organics", Wisconsin Department of Natural Resources, PUBL-SW-141, 1992.

Table 1. Aromatic Hydrocarbon Standard

Equivalent Carbon Number	Compound
7. 6	Toluene
10.1	1,2,3-Trimethylbenzene
11.7	Naphthalene
15.5	Acenaphthene
Surrogate	Ortho-Terphenyl
20.8	Pyrene
34.01	Benzo(g,h,i)Perylene

Table 2. Aliphatic Hydrocarbon Standard

Carbon Number	Compound
8	Octane
10	Decane
12	Dodecane
16	Hexadecane
Surrogate	1-Chloro-octadecane
21	Henicosane
34	Tetratriacontane

3.0 DEFINITIONS

3.1 **Extractable Petroleum Hydrocarbons (EPH)** are defined as all hydrocarbon compounds eluting from toluene through benzo(g,h,i)perylene. EPH is comprised of C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 Aliphatic Hydrocarbons and C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 Aromatic Hydrocarbons. EPH concentration data are reported as the aggregate concentration of the aliphatic and aromatic hydrocarbon ranges.

3.2 **Equivalent Total Petroleum Hydrocarbons (E-TPH)** For samples contaminated with petroleum products in the C10 to C34 range, the E-TPH value is equivalent to the EPH value. For samples contaminated with a petroleum product(s) containing significant concentrations of hydrocarbons lighter and heavier than C10, (e.g., contaminated with both gasoline and diesel fuel), the E-TPH value is a summation of the EPH value and the Volatile Petroleum Hydrocarbon (VPH) value. In order to avoid double counting of analytes due to the overlap in the carbon ranges existing between the two methods, the analyst will report the highest of the two values determined for the overlapping ranges. In those cases where both the VPH and EPH methods are employed on samples, the analyst may select to quantitate the >C10 through C12 Aliphatic and the >C10 through C12 Aromatic Hydrocarbon ranges by the EPH method only. Similarly, the analyst may select to quantitate the C8 through C10 Aromatic and C8 through C10 Aliphatic Hydrocarbon ranges by the VPH method only.

3.3 **C8 through C10 Aromatic Hydrocarbons** are defined as all of the aromatic hydrocarbon compounds eluting from (and including) toluene through 1,2,3-trimethylbenzene.

3.4 **>C10 through C12 Aromatic Hydrocarbons** are defined as all aromatic hydrocarbon compounds eluting after 1,2,3-trimethylbenzene through naphthalene.

3.5 **>C12 through C16 Aromatic Hydrocarbons** are defined as all aromatic hydrocarbon compounds eluting after naphthalene through acenaphthene.

3.6 >**C16 through C21 Aromatic Hydrocarbons** are defined as all aromatic hydrocarbons compounds eluting after acenaphthene through pyrene.

3.7 >**C21 through C34 Aromatic Hydrocarbons** are defined as all aromatic hydrocarbons compounds eluting after pyrene through benzo(g,h,i,)perylene.

3.8 **C8 through C10 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds eluting from (and including) n-octane (n-C8) through n-decane (n-C10).

3.9 **>C10 through C12 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds eluting after n-decane through n-dodecane (n-C12).

3.10 **>C12 through C16 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds eluting after n-dodecane through n-hexadecane (nC16)

3.11 >**C16 through C21 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbons eluting after n-hexadecane through n-henicosane (nC21).

3.12 **>C21 through C34 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbons eluting after n-henicosane through tetratriacontane (nC34).

3.13 **Aromatic Hydrocarbon Standard** is defined as a 6 component mixture (plus surrogate) of the aromatic hydrocarbons listed in Table 1. The compounds comprising the Aromatic Hydrocarbon Standard are used to (a) define and establish the windows for the Aromatic Hydrocarbon ranges, and (b) determine chromatographic response factors that can in turn be used to calculate the collective concentration of aromatic hydrocarbons in environmental samples within those hydrocarbon ranges.

3.14 **Aliphatic Hydrocarbon Standard** is defined as a 6 component mixture (plus surrogate) of the normal alkanes listed in Table 2. The compounds comprising the Aliphatic Hydrocarbon Standard are used to (a) define and establish windows for the aliphatic hydrocarbons ranges, and (b) determine chromatographic response factors that can in turn be used to calculate the collective concentration of aliphatic hydrocarbons in environmental samples within those hydrocarbon ranges.

3.15 **Analytical Batch** is defined as a group of samples with similar matrices which are processed as a unit. For Quality Control purposes, if the number of samples in such a group is greater than 20, then each group of 20 samples or less are defined as separate analytical batches.

3.16 **Laboratory Duplicates** are defined as split samples taken from the same sampling container and analyzed separately with identical procedures. The analysis of laboratory duplicates give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.17 **Field Duplicates** are defined as two separate samples collected at the same time and location under identical circumstances and managed the same throughout field and laboratory procedures. Analyses of field duplicates give a measure of the precision associated with sample collection, preservation and storage, as well as laboratory procedures.

3.18 **E-TPH Duplicates** are defined as two separate samples collected at the same time and location, for analysis by both EPH and VPH methods. E-TPH duplicates are taken at locations where significant concentrations of petroleum hydrocarbons lighter and heavier than C10 are likely to be present (e.g., locations contaminated by releases of both gasoline and diesel fuel). The resultant EPH and VPH concentrations are then summed to determine the Equivalent TPH (E-TPH) concentration.

3.19 **Calibration Standards** are defined as a series of standard solutions prepared from dilutions of a stock standard solution, containing known concentrations of each analyte and surrogate compounds of interest.

3.20 **Calibration Check Standard** is defined as a calibration standard used to periodically check the calibration state of an instrument. The calibration check standard is prepared from the same stock standard solution as calibration standards, and is generally one of the mid-level range calibration standard dilutions.

3.21 **Matrix Spiking Solution** is defined as a solution which is generally prepared independently from the calibration standards and which contain known concentrations of method analytes.

3.22 **Laboratory Method Blank** is defined as, depending on the matrix of the samples, either reagent water or clean sand spiked with a surrogate standard. The laboratory method blank is treated identically as with samples, exposed to all glassware, solvents, reagents, and equipment. A laboratory method blank is analyzed with every batch of samples, to determine if method analytes or other interferences are present in the laboratory environment, reagents, or equipment.

3.23 **Laboratory Fortified Blank (LFB)** is defined as, depending on the matrix of the samples, either reagent water or clean sand blank fortified with a matrix spiking solution. The LFB is treated and analyzed identically as with samples and blanks and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements at the required practical quantitation limits.

3.24 **Laboratory Fortified Matrix (LFM) Sample** is defined as an environmental sample which has been spiked with a matrix spiking solution containing known concentrations of method analytes. The LFM sample is treated and analyzed exactly as with samples and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentration of analytes in the sample matrix must be determined through the separate analyses of a laboratory or field duplicate, and the measured values in the LFM sample corrected for background concentrations.

3.25 All other terms are as defined in SW-846, "Test Methods for Evaluating Solid Waste", USEPA, September, 1986, and as amended.

4.0 INTERFERENCES

4.1 Method interferences are reduced by washing all glassware with hot soapy water and then rinsing with warm tap water, acetone, and methylene chloride.

4.2 High purity reagents must be used to minimize interference problems.

4.3 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. Whenever an unusually concentrated sample is analyzed, it should be followed by the analysis of a solvent blank to check for cross-contamination.

4.4 Matrix interferences may be caused by contaminants that are coextracted along with the analytes of interest from the sample. The type and extent of matrix interference will vary considerably from one source to another depending upon the nature and diversity of the site being sampled and may include certain solvents, halogenated hydrocarbons and phthalate esters. A silica gel cleanup procedure is used to overcome many of these interferences however, some samples may require additional cleanup procedures/approaches or analytical techniques, e.g. gel permeation chromatography and/or GC/MS, which are beyond the scope of this method.

5.0 HEALTH AND SAFETY ISSUES

The toxicity and carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDS) should also be made available to all personnel involved in the chemical analysis.

6.0 APPARATUS AND MATERIALS

6.1 The following glassware is used for this method:

6.1.1 1-L amber glass bottles

6.1.2 4 oz. (120 mL) amber glass wide-mouth jars

6.1.3 Vials:

6.1.3.1 autosampler: 2-mL glass vials with Teflon-lined rubber crimp caps

6.1.3.2 10-mL vials with Teflon-lined caps

6.1.4 Glass funnels

6.1.5 2-L Separatory funnels with Teflon stopcock

6.1.6 Kuderna-Danish apparatus including 10-mL concentrator tube, 500-mL Evaporative flask, & 3-ball Snyder column

6.1.7 Chromatographic column: 250 mm long x 10 mm I.D. with teflon stopcock

6.1.8 Disposable pipets: Pasteur

6.1.9 25-mL graduated cylinder

6.1.10 1-Liter graduated cylinder

6.1.11 100-mL beakers

6.1.12 25-mL volumetric flasks

6.2 Analytical balance: An analytical balance capable of accurately weighing 0.0001 g must be used for weighing standards. A top-loading balance capable of weighing to the nearest 0.1 g must be used for weighing soil samples.

6.3 A nitrogen blowdown apparatus for use in concentrating extracts.

6.4 **Gas Chromatography**

6.4.1 Gas Chromatograph: An analytical system complete with temperature programmable gas chromatograph for use with capillary columns is required. The data station must be capable of storing and reintegrating chromatographic data and must be capable of determining peak areas using a forced baseline projection.

6.4.2 Recommended Column: 30-m long x 0.32-mm I.D., 0.25-µm film DB-5 column (J&W Scientific) or equivalent. This column will allow for the adequate resolution of alkanes from n-C8 to n-C34.

6.4.3 Detector: A Flame Ionization Detector (FID).

6.4.4 Autosampler: An autosampler capable of making 1 to 2 µL injections is recommended.

6.5 Water bath: heated with a concentric ring covers, capable of temperature control (± 2°C). The bath should be used in a hood.

6.6 Microsyringes: 10-µL, 100-µL, 250-µL, 500-µL, 1000-µL

6.7 Boiling Chips: glass or teflon, precleaned prior to use

6.8 Soxhlet or Sonication extraction apparatus

6.9 Drying oven

7.0 REAGENTS AND STANDARDS

7.1 **Reagents**

7.1.1 Reagent Water: organic free water

7.1.2 Solvents: hexane, methylene chloride, and acetone; pesticide grade or better. Store away from other solvents.

7.1.3 Sodium sulfate: (ACS) granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray.

7.1.4 Ottawa and/or masonry sand: free of extractable petroleum hydrocarbons.

7.1.5 Silica gel: 100/200 mesh (Davison Chemical grade 923 or equivalent). Heat to 150-160 ^{o}C for several hours before use. Silica Gel Sep-Pak Cartridges: 5 g/20-mL (Waters, Milford, MA) , if it is demonstated to give equivalent separations.

7.2 **Stock Standard Solutions**

Prepare stock standard solutions at approximately 1000 ng/µL, or purchase as certified solutions.

7.2.1 Aromatic Hydrocarbon Standard: The Aromatic Hydrocarbon Standard consists of the 6 aromatic compounds listed in Table 1 and a surrogate compound. Prepare stock standard solutions by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in methylene chloride and dilute to volume in a 10-mL volumetric flask. The use of commercially prepared stock standards solutions is an acceptable alternative to the use of neat material. The analyst is allowed to prepare a separate surrogate solution.

7.2.2 Aliphatic Hydrocarbon Standard: The Aliphatic Hydrocarbon Standard consists of the 6 normal alkanes listed in Table 2 and a surrogate compound. Prepare stock standard solutions by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in hexane and dilute to volume in a 10-mL volumetric flask. The use of commercially prepared stock standard solutions is an acceptable alternative to the use of neat material. The analyst is allowed to prepare a separate surrogate solution.

7.2.3 Petroleum Reference Standard: The use of a Petroleum Reference Standard is recommended for quality control purposes. The Petroleum Reference Standard consists of an API or commercial diesel, fuel oil, kerosene, and/or lubricating oil. Prepare stock standard solutions by accurately weighing approximately 0.0100 g of neat product. Dissolve neat product in hexane and dilute to volume in a 10-mL volumetric flask.

7.3 Surrogate Standards

7.3.1 The recommended surrogate standards are chloro-octadecane (COD, available from Restek Corporation, Bellefonte, PA) and ortho-terphenyl (OTP, available from EM Sciences, Gibbstown, NJ). Additional surrogates or surrogates other than those listed above may be used at the discretion of the analyst as long as their performance in the method is demonstrated as acceptable. Preparation and use of those surrogates will be in the same manner as the listed surrogate.

7.3.2 The surrogate standard COD is prepared by accurately weighing approximately 0.0100 g of pure material in a 10-mL volumetric flask. Dissolve the material in hexane. This solution is added to the Aliphatic Hydrocarbon standard.

7.3.3 The surrogate standard OTP is prepared by accurately weighing approximately 0.0100 g of pure material in a 10-mL volumetric flask. Dissolve the material in methylene chloride. This solution is added to the Aromatic Hydrocarbon standard.

7.3.4 Surrogate Spiking Solution: The recommended surrogate spiking solution is comprised of a mixture of the COD and OTP surrogate standards. Prepare a surrogate spiking solution which contains the surrogate standards at a concentration of 20 ng/µL in acetone. Each sample, blank, and matrix spike is fortified with 1.0 mL of the surrogate spiking solution.

7.4 Internal Standard

If an internal standard method of calibration is to be used, the recommended internal standard is 5-alpha-androstane (EM Sciences, Gibbstown, NJ).

7.5 Matrix Spike Standard

7.5.1 Four or more analytes from each analyte group (i.e., aromatic and aliphatic hydrocarbons) are selected for use in a matrix spiking solution, which is prepared independently from the calibration standards.

7.5.2 The recommended spiking solution, consisting of C10, C12, C16 and C21 normal alkanes and naphthalene, acenaphthene, anthracene, pyrene, benzo(a)pyrene and benzo(g,h,i)perylene, is prepared in acetone at concentrations of 25 ng/µL.

7.5.3 The samples selected as the matrix spike are fortified with 1.0 mL of the matrix spiking solution.

7.6 Fractionation Check Solution

7.6.1 The Fractionation Check Solution is used to monitor the fractionation efficiency of different batches (lot numbers) of silica gel used to prepare the silica gel hydrocarbon fractionation columns (and Sep-Pak cartridges if used) as well as check for sample preparation errors (e.g., insufficient/excessive pentane use).

7.6.2 Prepare a Fractionation Check Solution in hexane containing 25 ng/µL each of the n-C8, n-C10, n-C12, n-C16, n-C21, and n-C34 alkanes) and 25 ng/µL each of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene. The final solution will contain 6 alkanes and 16 PAHs at concentrations of 25 ng/µL each. The use of commercially available check solutions containing these compounds is acceptable.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 Aqueous samples are collected in 1 liter amber glass bottles with teflon-lined screw caps.

8.2 Soil and sediment samples are collected in 4 oz. (120 mL) amber wide-mouth glass jars with teflon-lined screw caps.

8.3 Aqueous samples must be preserved at the time of sampling by the addition of an acid to reduce the pH of the sample to less than 2.0. This is accomplished by the addition of approximately 5 mL of 1:1 HCl to a 1 liter sample. Following collection and the addition of acid, the sample must be cooled to 4°C.

8.4 Soil and sediment samples must be cooled to 4°C immediately after collection.

8.5 A chain of custody form must accompany all aqueous, soil and sediment samples, documenting the time and date of sampling and any preservative additions.

8.6 Aqueous, soil and/or sediment samples must be extracted within 14 days of collection. If for whatever reason aqueous samples were not preserved at the time of collection they must be extracted within 7 days of collection. Both aqueous and soil/sediment extracts must be analyzed within 40 days of extraction.

8.7 A summary of sample collection, preservation, and holding times is provided in Table 3.

Table 3. Holding Times and Preservatives for EPH Samples

Matrix	Container	Preservation	Holding Time
Aqueous Samples	1-Liter amber glass bottle with Teflon-lined screw cap	Add 5 mL of 1:1 HCl; cool to 4°C	Samples must be extracted within 14 days and extracts analyzed within 40 days
Soil/Sediments Samples	4-oz. (120 mL) wide mouth amber glass jar with Teflon-lined screw cap	Cool to 4°C	Samples must be extracted within 14 days and extracts analyzed within 40 days

9.0 PROCEDURE

9.1 **Sample Preparation**

9.1.1 Water Extraction

9.1.1.1 Mark the water meniscus on the side of the 1 liter of sample bottle (for later volume determination) and transfer the water to a 2-liter separatory funnel. For blanks and quality control samples, pour 1 liter of reagent water into the separatory funnel. Add 1.0 mL of the surrogate spiking solution to all samples, blanks and matrix spikes. For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking solution.

9.1.1.2 Check the pH of the sample with wide-range pH paper. Note the pH in the laboratory notebook. The pH of the sample need not be adjusted.

9.1.1.3 Add 60 mL methylene chloride to the sample bottle to rinse the inner walls of the container, then add this solvent to the separatory funnel.

9.1.1.4 Seal and shake the separatory funnel vigorously for 1 to 2 minutes with periodic venting to release excess pressure.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, venting should be done immediately after the separatory funnel has been sealed and shaken once.

9.1.1.5 Allow the organic layer to separate from the water phase for a minimum of 5 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.
Collect the solvent extract in an 500ml Kuderna-Danish (K-D) evaporation flask to which is attached a 10 mL concentrator tube..

9.1.1.6 Repeat the extraction two more times using fresh portions of solvent and adding the solvent extracts to the KD flask. (Steps 9.1.1.3 to 9.1.1.5) The use of continuous liquid-liquid extraction (EPA method 3520) is an acceptable alternative to the separatory funnel extraction method described above.

9.1.1.7 For sample volume determination add water to the sample bottle to the level of the meniscus previously marked then transfer this water to a graduated cylinder and record the volume.

9.1.1.8 Add one clean boiling chip to the K-D flask and attach a three ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 4-6 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

9.1.1.9 Solvent exchange the methylene chloride with hexane by adding at least 50 mL of hexane to the top of the Snyder column. and concentrate the extract to less than 10 mL, as described in Paragraph 9.1.1.8, raising the temperature of the water bath, if necessary, to maintain proper distillation.

Note: An alternative solvent exchange method is to use the nitrogen blowdown apparatus to exchange the methylene chloride with hexane. This is accomplished by placing a disposable pipet in the concentrator tube and adding the small amounts of hexane via the pipet to the bottom of the concentrator tube during the concentration process in the apparatus.

9.1.1.10 Remove the Snyder column and evaporation flask from the 10-mL concentrator tube. Place the concentrator tube containing the hexane extract onto a nitrogen blowdown apparatus. Adjust the extract volume to 1-2 mL under a gentle stream of nitrogen . If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume will need to be larger.

9.1.1.11 The extract obtained is now ready to be cleaned and fractionated on a silica gel column. If cleanup will not be performed immediately, transfer the extract to a Teflon-lined screw-cap vial, label, and refrigerate.

9.1.1.12 Record the sample preparation information for the extraction and concentration steps. At a minimum, record the date, sample laboratory number, sample volume, volume and concentration of added surrogate and matrix spike solutions, and any deviations or problems associated with the extraction of the samples.

9.1.1.13 For cleanup and fractionation, refer to Section 9.1.4.

9.1.2 Soil/Sediment Extraction using Ultrasonic Extraction

9.1.2.1 The following steps should be performed rapidly to minimize the loss of the more volatile fractions. In a beaker blend 10 g of the soil/sediment sample with sufficient anhydrous sodium sulfate to form a free flowing powder using a spatula. Add 1.0 mL of the surrogate spiking solution to the samples and blanks. For the samples in each analytical batch selected for matrix spiking, add 1.0 mL of the matrix spiking standard. Immediately add approximately 50 mL of 1:1 methylene chloride:acetone to the beaker. If lower PQL's are desired, the analyst is allowed to increase the sample size extracted. This will necessitate a proportional increase in the volume of extraction solvent used.

9.1.2.2 Place the bottom surface of the tip of the ultrasonic horn about 1/2 inch below the surface of the solvent but above the soil/sediment layer.

9.1.2.3 Sonicate for 3 minutes with the control knob set to the maximum output, pulse mode and 50% duty cycle.

9.1.2.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

9.1.2.5 Decant and filter the extract through Whatman No. 41 filter paper into the K-D concentrator. Repeat the extraction two more times with additional 50 mL portions of the solvent. Decant off and filter the extract into the K-D flask each time. On the last extraction, pour

the entire sample into the funnel and rinse the beaker and sample with additional portions of solvent and add these to the K-D flask. The analyst may find it useful to (1) either add anhydrous sodium sulfate to the filter for drying the extract or (2) to pass the extract through a drying column containing about 10 cm of anhydrous sodium sulfate prior to collecting the extract in the K-D flask.

9.1.2.6 Add one clean boiling chip to the K-D flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10 to 20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1-2 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

9.1.2.7 Exchange the methylene chloride with hexane by adding 50 mL of hexane to the top of the Snyder column and concentrating the extract as described in Paragraph 9.1.2.6, raising the temperature of the water bath, if necessary, to maintain proper distillation. The alternate solvent exchange technique described in note in 9.1.1.9 may also be used.

9.1.2.8 Remove the Snyder column and evaporation flask from the 10-mL concentrator tube. Place the concentrator tube containing the hexane extract onto a nitrogen blowdown apparatus. Adjust the extract volume to 1-2 mL under a gentle stream of nitrogen . If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume will need to be larger.

9.1.2.9 The extract obtained is now ready to be cleaned and fractionated on a silica gel column. If cleanup will not be performed immediately, transfer the extract to a Teflon-lined screw-cap vial, label, and refrigerate.

9.1.2.10 Record the sample preparation information for the extraction and concentration steps, as specified in paragraph 9.1.1.14.

9.1.2.11 For cleanup and fractionation, refer to Section 9.1.4.

9.1.3 <u>Soil/Sediment Extraction by Soxhlet Extraction</u>

9.1.3.1 Blend 10 g of the soil/sediment sample with sufficient anhydrous sodium sulfate to produce a free flowing powder and place this material in an extraction thimble. The extraction thimble must drain freely for the duration

of the extraction period. Add 1.0 mL of the surrogate spiking solution onto the sample. For the samples in each analytical batch selected for matrix spiking, add 1.0 mL of the matrix spiking solution. If lower PQL's are desired, the analyst may increase the quantity of sample extracted.

9.1.3.2 Place approximately 200 mL of methylene chloride into a 250-mL Erlenmeyer or round bottomed flask (depending on the heating source) containing several clean boiling chips. Attach the flask to the extractor and extract the sample for 8-16 hr.

9.1.3.3 Allow the extract to cool after the extraction is completed.

9.1.3.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

9.1.3.5 Dry the extract by passing it through a glass powder funnel containing anhydrous sodium sulfate. Collect the dried extract in the K-D concentrator. Wash the extractor flask and sodium sulfate column with 50 to 75 mL of methylene chloride to complete the quantitative transfer.

9.1.3.6 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10 to 20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1-2 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

9.1.3.7 Exchange the methylene chloride with hexane by adding 50 mL of hexane to the top of the Snyder column and concentrating the extract as described in Paragraph 9.1.3.6, raising the temperature of the water bath, if necessary, to maintain proper distillation. The alternate solvent exchange technique outlined in the note in 9.1.1.9 may also be used.

9.1.3.8 Remove the Snyder column and evaporation flask from the 10 mL concentrator tube. Place the concentrator tube containing the hexane extract onto a nitrogen blowdown apparatus. Adjust the extract volume to 1-2 mL under a gentle stream of nitrogen . If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume will need to be larger.

9.1.3.9 The extract obtained is now ready to be cleaned and fractionated on a silica gel column. If cleanup will not be performed immediately, transfer the extract to a Teflon-lined screw-cap vial, label, and refrigerate.

9.1.3.10 Record the preparation information for the extraction and concentration steps, as specified in 9.1.1.14.

9.1.3.11 For cleanup and fractionation, refer to Section 9.1.4.

9.1.3.12 The use of the Accelerated Solvent Extraction (ASE), EPA Method 3545, is an acceptable alternative to either ultrasonic or soxhlet extraction techniques as long as it is demonstrated to achieve comparable results.

9.1.4 Silica Gel Cleanup and Separation

9.1.4.1 Silica gel is a regenerative adsorbent of amorphous silica with weakly acidic properties. It is produced from sodium silicate and sulfuric acid. Silica gel can be used for column chromatography and is used for separating analytes from interfering compounds of a different chemical polarity. Silica gel is also used to separate petroleum distillates into aliphatic and aromatic fractions. Before the silica gel technique can be utilized, the extract solvent must be exchanged to hexane. This procedure may be performed immediately before the extract concentration step is complete by adding hexane to the K-D (when the volume of remaining methylene chloride is approximately 10 to 15 mL) and reducing the extract volume to 1 to 2 mL. After cooling, disassemble the K-D apparatus, rinsing the joints into the concentrator tube with a minimum of hexane. With a nitrogen blowdown concentrator, further reduce the extract to a final volume of 2 mL.

9.1.4.2 Prepare a slurry of 10g of activated silica gel in methylene chloride and place this into a 10 mm I.D.x 250 mm long chromatographic column. Tap the column to settle the silica gel and elute the methylene chloride. Add 1 to 2 cm of anhydrous sodium sulfate to the top of the silica gel. Note: The activity of each new batch (lot number) of silica gel must be evaluated prior to its use in this procedure. This requires the use of the fractionation check solution to insure that there is an efficient separation of the aromatic fraction from the aliphatic fraction. If necessary, the analyst is allowed to adjust the volumes of the eluants used to facilitate this process.

9.1.4.3 Pre-elute the column with 40 mL of pentane. Let the solvent flow through the column, at a rate of about 2 mL/minute, until the head of the liquid in the

column is just above the sodium sulfate layer. Close the stopcock to stop solvent flow. Discard this pentane.

9.1.4.4 Open the stopcock and immediately transfer the hexane sample extract onto the silica gel column. Rinse the concentrator tube with an additional 1-2 mL of hexane and add this to the column as well.

9.1.4.5 Just prior to exposure of the sodium sulfate layer to the air, add 25 mL of pentane to the column. Collect the eluant in a 250 mL K-D flask to which is attached a 10 mL concentrator tube and label this fraction "aliphatics". Concentrate and solvent exchange this extract into hexane.

9.1.4.6 Following recovery of the aliphatic fraction and just prior to exposure of the sodium sulfate layer, elute the column with 50 mL of methylene chloride/pentane (40:60) (v/v) and collect the eluant in a 250 mL K-D flask equipped with a 10 mL concentrator tube.. Label this fraction "aromatics". Concentrate and solvent exchange this extract into methylene chloride.

9.1.4.7 Concentrate each fraction to a final volume of 10 mL under a gentle stream of nitrogen from a nitrogen blowdown apparatus.

9.1.4.8 Transfer 1 mL of the fractions to a labeled two-mL glass autosampler vials with teflon-rubber crimp caps for analysis and save the remaining extract in a teflon-rubber septum screw topped vial. If lower PQL's are required, the analyst may concentrate the extract to as low as 1 mL prior to analysis

9.1.5 Proceed with the analysis in accordance with Sections 9.2 through 9.5. Analyze all laboratory method blanks and QC samples under the same conditions as that used for samples.

9.1.6 If chromatographic responses exceed the linear range of the system, dilute the extract(s) and re-analyze

9.1.7 <u>Determination of Percent Moisture</u>

9.1.7.1 Soil and sediment sample results must be reported on a dry-weight basis. A portion of sample for moisture determination should be weighed out at the same time as the portion used for hydrocarbon determination.

9.1.7.2 Immediately after weighing a sample for extraction, transfer 5 to 10 g of the sample into a tared crucible. Dry the sample overnight at 105°C in an oven. After drying remove it from the oven allow it to cool in a desiccator before reweighing. Calculate the percent moisture of the sample using the equations provided in Section 9.6.3.

9.2 **GC Conditions**

9.2.1 Suggested Gas Chromatographic Conditions

9.2.1.1 Oven Program: Set oven temperature to 50 °C for 2 minute, then 8°C/min to 320 °C and hold for 10 minutes.

9.2.1.2 Sample/autosampler injection volume is 1 to 2 µL.

9.2.1.3 Gas Flows: The recommended carrier gas is helium.

9.2.1.3.1 Helium carrier gas flow: 1 to 2 mL/min.

9.2.1.3.2 Air: 400 mL/min.

9.2.1.3.3 Hydrogen: 35 mL/min.

9.2.1.3.4 Make up gas flow: 30 mL/min.

9.2.1.4 Miscellaneous:

9.2.1.4.1 FID temperature, 310 to 320 °C

9.2.1.4.2 Injection port temperature, 290 to 300 °C

9.2.1.4.3 GC operated in splitless mode

9.2.1.4.4 Column head pressure 15.0 psi at 50°C

9.2.1.4.5 Linear velocity approximately 50 cm/sec

9.3 **Retention Time Windows**

9.3.1 Before establishing windows, make sure the GC system is within optimum operating conditions. Make three injections of the Aromatic and Aliphatic Hydrocarbon standard mixtures throughout the course of a 72-hr period. Serial injections over less than a 72-hr period may result in retention time windows that are too tight.

9.3.2 Calculate the standard deviation of the three absolute retention times for each standard.

9.3.3 Plus or minus three times the standard deviation of the absolute retention times for each standard should be used to define the retention time window. However, the

experience of the analyst should weigh heavily in the interpretation of chromatograms.

9.3.4 In those cases where the standard deviation for a particular standard is zero, the laboratory should substitute the standard deviation of a closely eluting structurally similar compound to develop a valid retention time window.9.3.5 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed or a portion removed as part of GC maintenance. This data must be retained by the laboratory.

9.3.6 EPH retention time (Rt) windows for all fractions (carbon ranges and hydrocarbon types) except the C8 through C10 are defined as beginning 0.1 minutes after the Rt of the beginning marker compound and ending 0.1 minutes after the Rt of the ending marker compound. Since the first fraction for both the aliphatics and aromatics includes the beginning marker compounds, the Rt windows for them are defined as beginning 0.1 minutes before the Rt of the beginning marker compound and ends 0.1 minutes after the ending marker compound.

EPH marker compounds and windows are summarized in Table 4.

Table 4. EPH Marker Compounds

Range/ Hydrocarbon Standard	Beginning Marker Compound	Ending Marker Compound
C8-C10 Aliphatic Hydrocarbons	just before n-octane	just after n-decane
C10-C12 Aliphatic Hydrocarbons	just after n-decane	just after n-dodecane
C12-C16 Aliphatic Hydrocarbons	just after n-dodecane	just after n-hexadecane
C16-C21 Aliphatic Hydrocarbons	just after n-hexadecane	just after n-henicosane
C21-C34 Aliphatic Hydrocarbons	just after n-henicosane	just after n-tetratriacontane
C8-C10 Aromatic Hydrocarbons	just before toluene	just after 1,2,3-trimethylbenzene
C10-C12 Aromatic Hydrocarbons	just after 1,2,3-trimethylbenzene	just after naphthalene
C12-C16 Aromatic Hydrocarbons	just after naphthalene	just after acenaphthene
C16-C21 Aromatic Hydrocarbons	just after acenaphthene	just after pyrene
C21-C34 Aromatic Hydrocarbons	just after pyrene	just after benzo(g,h,i)perylene

9.4 **Calibration**

Calibrate the GC system using either the external standard procedure (Section 9.4.1) or the internal standard procedure (Section 9.4.2).

9.4.1 External standard calibration procedure

9.4.1.1 Prepare Aromatic and Aliphatic Hydrocarbon calibration standards at a minimum of five concentration levels by adding volumes of one or more stock standard solutions to volumetric flasks and diluting to volume with methylene chloride and hexane, respectively. The surrogate OTP is added to the Aromatic Hydrocarbon Standard; the surrogate COD is added to the Aliphatic Hydrocarbon Standard. One of the calibration

standards must be at a concentration near, but above, the method detection limit and is used to determine the reporting PQL. In order to report the PQL's listed in 1.4, given the volume/mass water or soil extracted of 1 liter or 10 grams and assuming 100% solids on the soil, this standard must be at a 5 ng/uL level. The other concentrations must correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

9.4.1.2 A collective calibration curve or factor must be established for each hydrocarbon range of interest. Inject each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph (e.g., 1 to 2 µL injections). To calculate the collective CF for C8-C10, >C12-C12, >C12-C16, >C16-C21 and C21-C34 Aromatic Hydrocarbons, tabulate the summation of all peak areas of the calibration compounds in that range (e.g. C8-C10, toluene and 1,2,4-trimethylbenzene or >C10-C12, naphthalene) against the total mass injected. Although a forced baseline projection is required for samples and blanks, the analyst is allowed to integrate only the area of the calibration compound(s) to generate the calibration factors. The ratio of the response to the amount injected, defined as the calibration factor (CF), or range CF, may be calculated for hydrocarbon ranges at each standard concentration using Equation 1. If the percent relative standard deviation (%RSD) of the calibration factor is equal to or less than 20 % over the working range for the ranges of interest, as determined using Equation 2, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve. The Aliphatic Hydrocarbon collective CF is calculated in the same manner using the aliphatic standards.

Equation 1: Range Calibration Factor

$$Range\ CF = \frac{total\ area\ of\ peaks}{mass\ injected\ (ng)}$$

Equation 2: Percent Relative Standard Deviation

$$\%RSD = \frac{Stand\ Dev\ of\ 5\ CFs}{Mean\ of\ 5\ CFs} \times 100$$

Note: The area for the surrogates COD and OTP must be subtracted from the area of the range in which they elute (e.g., COD is subtracted from the C16-C21 Aliphatic Hydrocarbon range.

9.4.1.4 At a minimum, the working calibration curve or calibration factor must be verified at the beginning of each working day and after the final analysis of that day, or after every 20 samples, whichever is more frequent, by the injection of a mid-level calibration standard to verify instrument performance and linearity. If the percent difference (%D) for any range varies from the predicted response by more than ± 20 %, as calculated using Equation 4, a new calibration curve must be prepared.

Equation 4: Percent Difference (%D)

$$\%D = \frac{\overline{CF} - CFv}{\overline{CF}} \times 100$$

where:

$\overline{CF}$ = Average Calibration Factor from calibration curve.

CFv = Calibration Factor from verification calibration check.

9.4.1.5 The concentrations of hydrocarbon ranges may also be calculated from a calibration curve by use of linear regression analysis.

9.4.2 Internal standard calibration procedure

9.4.2.1 The suggested internal standard for this method is 5-alpha-androstane (EM Science, Gibbstown, NJ).

9.4.2.2 Prepare Aromatic and Aliphatic Hydrocarbon calibration standards at a minimum of five concentration levels by adding volumes of stock standard solutions to volumetric flasks. The surrogate OTP is added to the Aromatic Hydrocarbon Standard; the surrogate COD is added to the Aliphatic Hydrocarbon Standard. To each calibration standard, add a known constant amount of an internal standard. One of the calibration standards must be at a concentration near, but above, the method detection limit and is used to determine the reporting PQL. The other concentrations must correspond to the expected range of concentration found in real world samples or should define the working range of the detector.

9.4.2.3 Inject each calibration standard using the same technique that will be applied to the samples (e.g., 1 to 2 µL injection). Tabulate the peak area responses against the concentration of each hydrocarbon range and internal standard. Calculate the collective response factors (RF) for each hydrocarbon range using Equation 5.

Note: The area for the surrogates COD and OTP must be subtracted from the area of the range in which they elute (e.g., COD is subtracted from the appropriate Aliphatic Hydrocarbon range).

uation 5: Range Response Factor

$$Range\ RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Summation of peak areas of the fraction (e.g., C10-C12 Aliphatic Hydrocarbons).

C_{is} = Concentration of internal standard, ng/µL.

A_{is} = Response for the internal standard.

C_s = Total mass concentration of injected standards, ng/µL.

9.4.2.4 At a minimum, the working calibration curve or RF must be verified at the beginning of each working day and after the final analysis of that day, or after every 20 samples, whichever is more frequent, by the injection of a mid-level calibration standard to verify instrument performance and linearity. If the percent difference (%D) for any hydrocarbon range varies from the predicted response by more than ± 20 %, as calculated using Equation 4, a new calibration curve must be prepared for that range.

9.4.2.5 The concentrations of hydrocarbon ranges may also be calculated from a calibration curve by the use of linear regression analysis.

9.5 **GC Analysis**

9.5.1 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration, or verification of calibration, followed by sample extracts interspersed with blanks and QC samples. The analytical sequence must end with an acceptable verification calibration standard. If the ending calibration standard is not acceptable, all samples analyzed after the last acceptable calibration verification must be reanalyzed. If, for whatever reason, reanalysis is not possible, then the data for those samples must be qualified as an "estimate".

9.5.2 Aliphatic and aromatic extracts are introduced into the gas chromatograph by slitless injection.

9.5.3 Inject 1 to 2 µL of the sample extract. Record the volume injected and the resulting peak size in area units.

9.5.4 Confirm the established retention time windows for each hydrocarbon range on a daily basis. Use the absolute retention time for each analyte as the midpoint of the window for that day. The daily retention time window equals the midpoint ± three times the standard deviation determined in Section 9.3.

9.5.4.1 Validation of GC system qualitative performance must be accomplished by the analysis of standards within the analysis sequence. If any of the standards fall outside their daily retention time window, the system is out of control. In such cases, the cause of the problem must be determined and corrected.

9.5.5 When quantifying on a peak area basis by internal or external calibration, peak area integration for the aliphatic and aromatic carbon ranges must be <u>from baseline</u> (i.e. must include the unresolved complex mixture "hump" areas).

9.6 **Calculations**

9.6.1 <u>External Standard Calibration</u>

The concentration of each hydrocarbon range in a sample may be determined by calculating the amount of hydrocarbon range compounds injected, from the peak response, using the calibration curve or the calibration factor determined in Section 9.4.

9.6.1.1 **Aqueous samples:**

The general equation to determine the concentration of a hydrocarbon range in aqueous samples in provided in Equation 6.

Equation 6

$$Concentration\ (ug / L) = \frac{(A_x)(A)(V_t)(D)}{(A_s)(V_i)(V_s)}$$

w

here:

A_x = Response for a hydrocarbon range in the sample, units may be in area counts or peak height.

A = Amount of standard injected, ng.

A_s = Response for the external standard, units same as for A_x.

V_i = volume of extract injected, µL.

D = Dilution factor: if no dilution was made, D = 1, dimensionless.

V_t = Volume of total extract, µL.

V_s = Volume of sample extracted, mL.

If a Calibration Factor is used, the concentration of a hydrocarbon range may be calculated using Equation 7.

Equation 7

$$Conc\ HC\ Range\ (ug / L) = \frac{(A_X)(V_t)(D)}{(V_i)(V_s)(Range\ CF)}$$

where:

Range CF = Calibration Factor for hydrocarbon ranges (collective area count/collective mass).

9.6.1.2 **Nonaqueous samples:**

The general equation to determine the concentration of a hydrocarbon range in soil or sediment samples is provided in Equation 8.

Equation 8

$$Concentration\ (ug / kg) = \frac{(A_x)(A)(V_t)(D)}{(A_s)(V_i)(W_d)}$$

where:

W_d = Dry weight of sample extracted, g. (See Equations 12 through 14)

A_x, A_s, A, V_t, D, and V_i have the same definition as for aqueous samples.

If a Calibration Factor is used, the concentration of specific hydrocarbon ranges in a soil or sediment sample may be calculated using Equation 9.

Equation 9

$$Conc\ HC\ Range\ (ug / kg) = \frac{(A_x)(V_t)(D)}{(V_i)(W_d)(Range\ CF)}$$

where:

Range CF = Calibration Factor for a hydrocarbon range (collective area count/collective mass).

9.6.2 Internal Standard Calibration

The concentration of each hydrocarbon range in a sample may be determined by calculating the amount of hydrocarbon range compound(s) injected, from the peak response, based upon the compound/internal-standard response ratio.

9.6.2.1 **Aqueous samples:**

The general equation to determine the concentration of a specific hydrocarbon range in aqueous samples is provided in Equation 10.

Equation 10

$$Concentration\ (ug / L) = \frac{(A_x)(C_{is})(D)}{(A_{is})(RF)(V_s)}$$

where:

A_x = Response of the hydrocarbon range being measured, units may be in area counts or in peak height.

C_{is} = Amount of internal standard added to extract, ng.

D = Dilution factor, if a dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

A_{is} = Response of the internal standard, units same as A_x.

RF = Response factor for the hydrocarbon range, dimensionless.

V_s = Volume of aqueous sample extracted, mL.

9.6.2.2 **Nonaqueous samples:**

The general equation to determine the concentration of a specific or hydrocarbon range in soil or sediment samples is provided in Equation 11.

Equation 11

$$Concentration\ (ug / kg) = \frac{(A_x)(C_{is})(D)}{(A_{is})(RF)(W_d)}$$

where:

W_d = Dry weight of sample extracted, g. (See Equations 12 through 14).

A_x, C_{is}, D, A_{is}, and RF have the same definition as for aqueous samples.

9.6.3 Calculation of Dry Weight of Sample

In order to calculate the dry weight of sample extracted (W_d), it is necessary to determine the moisture content of the soil/sediment sample, using the procedure outlined in Section 9.1.7. Using the data obtained from Section 9.1.7, W_d is calculated using Equations 12 through 14.

Equation 12

$$\% \text{ Moisture} = \frac{g \text{ sample} - g \text{ dry sample}}{g \text{ sample}} X\ 100$$

Equation 13

$$\% \text{ Dry Solids} = (1) - (\% \text{ Moisture})$$

Equation 14

$$W_d\ (g) = (\% \text{ Dry Solids})(g \text{ of extracted sample})$$

10.0 QUALITY CONTROL

10.1 **General Requirements and Recommendations**

10.1.1 Each laboratory that uses this method should operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance standards for the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

10.1.2 Hexane or methylene chloride solvent blanks should be run after samples suspected of being highly contaminated to determine if sample carryover has occurred.

10.1.3 At a minimum, for each analytical batch (up to 20 samples), a Laboratory Method Blank, Laboratory Fortified Blank Spike (Water or Soil), Laboratory Fortified

Matrix Spike, and sample duplicate must be analyzed. For analytical batches with more than 10 samples, the analysis of an additional mid-range calibration check standard is recommended. The blank and spiked samples must be carried through all stages of the sample preparation and measurement process.

10.1.4 The recommended sequence of analysis is as follows:

(1) Calibration Standards (initial) or mid-range Calibration Check (Verification) Standard (i.e. daily check of initial calibration)
(2) Laboratory Method Blank
(3) Samples
(4) QC Samples
(5) Mid-range Calibration Check (Verification) Standard (also recommended after each 10 samples)

10.1.5 It is recommended that a system of control charts be developed to plot surrogate standard recoveries as a function of time. When surrogate recovery from a sample, blank, or QC sample is less than 50% or more than 150%, check calculations to locate possible errors, the fortifying solution for degradation, and changes in instrument performance. If the cause cannot be determined, the analyst may reanalyze the sample extract, report the surrogate values as outside acceptance limits or, if additional sample is available, re-extract and reanalyze the sample.

10.2 **Minimum Instrument QC**

10.2.1 The instrument must be able to achieve adequate separation and resolution of peaks of interest.

10.2.1.1 The n-octane (n-C8) and toluene peaks must be adequately resolved from the solvent front of the chromatographic run.

10.2.1.2 The surrogates COD and OTP and any internal standards used must be adequately resolved from any individual components in the Aliphatic Hydrocarbon and Aromatic Hydrocarbon standards.

10.2.2 Retention time windows must be established for each hydrocarbon range of interest each time a new GC column is installed, and must be verified and/or adjusted on a daily basis. (See Section 9.3)

10.2.3 Calibration curves must be developed based upon the analysis of calibration standards prepared at a minimum of 5 concentration levels. The linearity of calibration or response factors may be assumed if the percent relative standard deviation (%RSD) over the working range of the curve is less than or equal to 20 %. Alternatively, if linear regression analysis is used for

quantitation, the correlation coefficient (r) must be at least 0.99. and the percent difference (% D) of the response for any hydrocarbon range from the predicted response may not vary by more than +/- 20%. (See Section 9.4.)

10.3 **Initial and Periodic Method QC Demonstrations**

The following must be conducted as an initial demonstration of laboratory capability, prior to the analysis of any samples. Subsequent to this initial demonstration, additional evaluations of this nature should be conducted on a periodic basis, in response to changes in instrumentation or operations, and/or in response to confirmed or suspected systems, method, or operational problems.

10.3.1 Accuracy and Precision

To demonstrate initial laboratory capability, analyze a minimum of four replicate reagent water and/or clean sand blanks spiked with the calibration compounds for each range of interest at approximately 50 µg/L and/or 5 mg/kg, respectively.

10.3.1.1 Extract and analyze each replicate according to the procedures described in Section 9.0.

10.3.1.2 Calculate the measured concentrations of each range in all replicates, the mean accuracy (as a percentage of true value) for each compound, and the precision (as %RSD) of the measurements for each compound.

10.3.1.3 For each compound, the mean accuracy, expressed as a percentage of the true value, should be between 70 % and 130 %. For each compound, the %RSD must be less than or equal to 20%.

10.3.2 Method Detection Limits (Optional)

Analyze a minimum of seven replicate reagent water and/or clean sand blanks which have been fortified with all analytes of interest at approximately 0.5 to 2 µg/L and/or 1.0 to 5.0 mg/kg, respectively. Extract and analyze each replicate according to the procedures described in Section 9.0. Calculate the Method Detection Limit (MDL) of each analyte using the procedure described in Section 12.0.

10.3.2.1 Water MDLs are determined by extracting 7 to 10 replicates of 1-L reagent water blanks spiked with OTP, COD and each analyte of interest.

10.3.2.2 Soil/sediment MDLs are determined by extracting 7-10 replicates of 10-g of EPH-free sand blanks spiked with OTP, COD, and each analyte of interest.

10.3.3 Fractionation

To demonstrate the capability of properly fractionating aliphatic and aromatic hydrocarbons in a sample, the analyst must first prepare and analyze the Fractionation Check Solution specified in Section 7.6.

10.3.3.1 Prepare a silica gel column as outlined in 9.1.4

10.3.3.2 Load 1.0 mL of the Fractionation Check Solution onto column and proceed with the elution and collection of the aliphatic and aromatic fractions as outline in 9.1.4.

NOTE: The amount of pentane used during the elution/fractionation is critical. Excessive pentane will cause elution of aromatics into the aliphatic fraction. Insufficient pentane will cause low recoveries of the aliphatic fraction. The volume of pentane and/or methylene chloride/pentane recommended may need to be adjusted to meet QC limits.

10.3.3.3 Solvent exchange the aliphatic fraction to hexane and the aromatic fraction to methylene chloride. Concentrate each solution to a final volume of 1.0 mL under a gentle stream of nitrogen from an nitrogen blowdown apparatus.

10.3.3.4 Transfer the final 1.0 mL extracts to two labeled glass auto sampler vials with teflon-lined rubber crimp caps. Analyze by GC/FID (see Section 9.0).

10.3.3.5 For each analyte within the Fractionation Check Solution, the mean accuracy, expressed as a percentage of the true value, must be between 70 % and 130 %.

10.3.4 Petroleum Reference Standard

As an optional demonstration of the validity and relevance of EPH calibration, analyze a reagent water and/or clean sand blank spiked with a known concentration of a neat petroleum product.

10.3.4.1 Dilute a Petroleum Reference Standard stock standard solution with acetone to a concentration of approximately 250 ng/µL. Spike a 1 Liter reagent water blank or 10 g clean sand blank with 1.0 mL of this spiking solution. Extract and analyze in accordance with the procedures outlined in Section 9.0.

10.3.4.2 Calculate the total concentration of all petroleum hydrocarbons within each range. Add these values together.

10.3.4.3 The concentration calculated in Paragraph 10.3.4.2 is expected to be within +/- 30 % of the known concentration of Petroleum Standard in the reagent water or sand blank.

10.4 **Ongoing Method QC Demonstrations**

10.4.1 Each sample, blank, and matrix spike sample must be spiked with the surrogate spiking solution. Required surrogate recovery is 60% to 140%.

10.4.2 At a minimum, with every batch of 20 samples or less the lab must analyze the following:

10.4.2.1 **Calibration Check Standard** - A mid-range calibration standard, prepared from the same stock standard solution used to develop the calibration curve, must be analyzed prior to sample analysis to verify the calibration state of the instrument. For large analytical batches that contain more than 10 samples, the analysis of an additional mid-range calibration check standard is recommended after the analysis of the tenth sample. If the percent difference (% D) of any compound within a calibration check standard varies from the predicted response by more than 20 %, a new calibration curve must be prepared. (See Section 9.4)

10.4.2.2 **Laboratory Method Blank** - A water or soil laboratory method blank is prepared by fortifying a reagent water or clean sand blank with 1.0 mL of the surrogate spiking solution. Peaks within the retention time windows of any hydrocarbon ranges of interest may not be present at or above the lowest calculated PQL for any sample within its batch. When determining the PQL of soil method blanks, incorporate the lowest percent solids value found for any sample within its batch in the calculation.

10.4.2.3 **Laboratory Fortified Blank Spike** - A water or soil component spike is prepared by fortifying a reagent water or clean sand blank with 1.0 mL of the matrix spiking solution. The spike recovery must be between 70 % and 130 % and, if these values can not be obtained, the analyst must identify and correct the problem before analyses can continue.

10.4.2.4 **Sample duplicates** - Sample duplicates may be laboratory duplicates or field duplicates and the RPD of the duplicate samples should not exceed +/- 25%. The lack of sample homogeneity may contribute to the RPD's values for duplicates which exceed this value. Should the values exceed 25% the analyst must report that occurrence.

10.4.2.5 **Laboratory Fortified Matrix (LFM) Spike** - The water or soil LFM spike is prepared by fortifying an actual water or soil sample with 1.0 mL of the matrix spiking solution. The purpose of the LFM spike is to

determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations. The corrected concentrations of each analyte within the LFM spike sample must be within 70 to 130 % of the true value. Should the values determined exceed this range, the analyst must report that occurrence.

10.4.3 If any of the performance standards specified in Section 10.4 are not met, the problem should be corrected before further samples are analyzed. Exceptions to this are duplicate samples RPD's and high recoveries for LFM spikes which, due to sample non-homogeneity, may exceed the allowable limits. Any samples run between the last calibration check standard that meet the criteria and one that does not must be reanalyzed. If this is not possible, then the data must be reported as an "estimated concentration."

11.0 DATA PRODUCTION AND REPORTING

11.1 **Sample Analysis**

11.1.1 Aliphatic Fraction

11.1.1.1 Determine the total area count for all peaks eluting 0.1 minutes before the retention time (Rt) for C8 to 0.1 minutes after the Rt for C10.

11.1.1.2 Determine the total area count for all peaks eluting 0.1 minutes after the Rt for C10 to 0.1 minutes after the Rt for C12. Determine the total area count of all peaks eluting 0.1 minutes after the Rt for C12 to 0.1 minutes after the Rt for C16, for all peaks eluting 0.1 minutes after the Rt for C16 to 0.1 minutes after the Rt for C21and for all peaks eluting 0.1 minutes after the Rt for C21 to 0.1 minutes after the Rt for C34. It is not necessary to identify or quantitate individual aliphatic compounds within these ranges.

11.1.1.3 Determine the peak area count for the surrogate COD and any internal standard used. Subtract these values from the collective area count value within the appropriate hydrocarbon range(s).

11.1.1.4 Using the equations contained in Section 9.6 or linear regression analysis, calculate the concentrations of C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 Alipiphatic Hydrocarbon ranges and the surrogate standard COD.

11.1.1.5 The term "all peak areas" must include any unresolved envelope of peaks which elute within the Rt windows listed above and below for the aliphatic and aromatic fractions.

11.2.1 Aromatic Fraction

11.2.1.1 Determine the total area count for all peaks eluting 0.1 minutes before the retention time (Rt) for toluene to 0.1 minutes after the Rt for 1,2,3 trimethylbenzene. In the same manner, determine the total area count for all peaks eluting 0.1 minutes after the Rt for 1,2,3-trimethylbenzene to 0.1 minutes after the Rt for naphthalene, from 0.1 minutes after the Rt for naphthalene to 0.1 minutes after the Rt for acenaphthene, from 0.1 minutes after the Rt for acenaphthene to 0.1 minutes after the Rt for pyrene and 0.1 minutes after the Rt for pyrene to 0.1 minutes after the Rt for benzo(g.h.i)perylene.

11.2.1.2 Determine the peak area count for the surrogate OTP and any internal standard used.

11.2.1.3 Subtract the peak area value from 11.2.1.2 from the collective area count value for the range effected determined in 11.2.1.1 to calculate the area count for Aromatic Hydrocarbons ranges.

11.2.1.4 Using the equations contained in Section 9.6 or linear regression analysis, calculate the concentrations of C8 through C10, >C10 through C12, >C12 through C16 , >C16 through C21 and >C21 through C34 Aromatic Hydrocarbons and the surrogate standard COD.

11.3 Data Reporting Format

11.3.1 The following information and data must be reported:

11.3.1.1 The sample matrix (aqueous, soil or sediment);

11.3.1.2 The date(s) the sample was collected, received by the laboratory, extracted, and analyzed;

11.3.1.3 A description of the sample(s) received by the laboratory, relative to the physical condition of the containers, the temperature of the samples, and use of appropriate preservatives;

11.3.1.4 Moisture content (for soil/sediment samples);

11.3.1.5 The calculated concentrations of C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 Aliphatic Hydrocarbons, and C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 Aromatic Hydrocarbons.

11.3.1.6 Surrogate recovery (expressed as percent recovery);

11.3.1.7 The concentration units for aqueous samples are expressed as ug/L or mg/L and soil or sediment samples the units are expressed as µg/Kg or mg/Kg on a dry-weight basis.

12.0 METHOD PERFORMANCE

12.1 **Method Detection Limits (Optional)**

12.1.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

12.1.2 The MDL is determined according to Equation 15.

Equation 15

$$MDL = (t) \times (SD)$$

where:

t = student t value at the 99% confidence level.

SD = standard deviation of the replicate analysis.

Student t values are as follows:

Number of replicates	t value
7	3.14
8	3.00
9	2.90
10	2.82

12.2 **Single Laboratory Accuracy, Precision and MDL Data**

Single laboratory accuracy, precision and MDL data for method analytes are provided in Tables 1-1 through 1-4 in Appendix 1. Tables 1-1 and 1-2 present data collected from spiking reagent water at 5.0 µg/L; Tables 1-3 and 1-4 by spiking sand at 1.0 mg/kg.

13.0 REFERENCES

1. Massachusetts Department of Environmental Protection and ABB Environmental Services, Inc., Wakefield, MA "Interim Petroleum Policy: Development of Health-based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter," August 1994.

2. USEPA, "Measurement of Petroleum Hydrocarbons: Report on Activities to Develop a Manual." Prepared by Midwest Research Institute, Falls Church, VA, under EPA Contract #68-WO-0015, WA No. 4; submitted to USEPA Office of Underground Storage Tanks, Washington, DC; November 20, 1990.

3. USEPA Federal Register 40 CFR Part 136, Appendix B, "Guidelines Establishing Test procedures for the Analysis of Pollutants," July 1992.

4. USEPA Test Methods for Evaluating Solid Waste (SW-846); Method 3510: Separatory Funnel Liquid-Liquid Extraction; September 1986.

5. USEPA Test Methods for Evaluating Solid Waste (SW-846); Method 3540: Soxhlet Extraction; September 1986.

6. USEPA Test Methods for Evaluating Solid Waste (SW-846); Method 3630: Silica Gel Cleanup; September 1986.

7. USEPA Test Methods for Evaluating Solid Waste (SW-846): Method 8000: Gas Chromatography; September 1986.

8. USEPA Test Methods for Evaluating Solid Waste (SW-846); Method 8100: Polynuclear Aromatic Hydrocarbons; September 1986.

9. Wisconsin Department of Natural Resources, "Modified DRO - Method for Determining Diesel Range Organics," PUBL-SW-141, 1992.

APPENDIX 1

SINGLE LABORATORY ACCURACY, PRECISION, AND METHOD DETECTION LIMITS (MDL) DATA FOR VPH

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Table 1-1. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Compounds in Component Standard Spiked Into Reagent Water and Analyzed by the VPH Method

Compound	Spiked Conc. (µg/L)	Method Accuracy[a] (Mean % Recovery[b])		Method Precision[a] (RSD[c] - %)		MDL[a] (µg/L)	
		PID[d]	FID[e]	PID	FID	PID	FID
n-Pentane	6.0		98		7.8		1.4
Methyl tert butylether	1.8	77	79	4.8	15	0.21	0.69
Benzene	0.6	82	97	4.9	10	0.08	0.19
Toluene	0.6	79	104	7.3	6.5	0.11	0.13
n-Nonane	2.0		83		8.0		0.42
Ethylbenzene	0.6	77	94	4.2	9.1	0.06	0.16
m- & p-Xylene	1.2	68	85	4.3	6.4	0.11	0.20
o-Xylene	0.6	79	88	16	6.4	0.23	0.11
1,2,3-Trimethylbenzene	0.6	69	89	8.2	6.4	0.11	0.11
Naphthalene	3.6	58	56	16	18	1.0	1.2
2,5-Dibromotoluene (surrogate)	40	88	92	4.9	13		

[a] Based on analysis of seven samples spiked with component standard.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] PID = photoionization detector.
[e] FID = flame ionization detector.

Table 1-2. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Compounds in Component Standard Spiked Into VPH- Free Sand and Analyzed by the VPH Method

Compound	Spiked Conc. (µg/Kg)	Method Accuracy[a] (Mean % Recovery[b])		Method Precision[a] (RSD[c] - %)		MDL[a] (µg/Kg)	
		PID[d]	FID[e]	PID	FID	PID	FID
n-Pentane	120		124		6.0		28
Methyl tert butylether	120	70	96	3.1	27	8.1	99
Benzene	60	122	128	3.3	5.4	7.6	13
Toluene	60	139	137	4.8	8.6	13	22
n-Nonane	120		119		4.6		21
Ethylbenzene	60	107	103	4.3	5.0	8.6	9.7
m- & p-Xylene	120	109	104	4.1	5.2	17	20
o-Xylene	60	103	111	3.8	6.6	7.4	14
1,2,3-Trimethylbenzene	60	93	102	5.5	5.3	9.6	10
Naphthalene	ND[f]	ND	ND	ND	ND	ND	ND
2,5-Dibromotoluene (surrogate)	2,000	119	117	8.6	9.7		

[a] Based on analysis of seven samples spiked with component standard.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] PID = photoionization detector.
[e] FID = flame ionization detector.
[f] ND = not determined.

Table 1-3. Single Laboratory Accuracy and Precision for Compounds in Component Standard Spiked Into Reagent Water at Concentrations in the Low to Middle End of the Analytical Range and Then Analyzed by the VPH Method

Compound	Spiked Conc. (µg/L)	Method Accuracy[a] (Mean % Recovery[b])		Method Precision[a] (RSD[c] - %)	
		PID[d]	FID[e]	PID	FID
n-Pentane	40		96		7.7
Methyl tert butylether	60	87	88	4.0	3.9
Benzene	20	99	99	4.4	3.7
Toluene	60	99	99	4.1	4.0
n-Nonane	40		104		10
Ethylbenzene	20	99	99	4.2	4.2
m- & p-Xylene	80	99	99	4.3	4.2
o-Xylene	40	99	99	3.7	3.6
1,23-Trimethylbenzene	40	99	99	4.1	4.0
Naphthalene	40	70	81	4.3	3.2
2,5-Dibromotoluene (surrogate)	40	92	94	5.2	4.6

[a] Based on analysis of five samples spiked with component standard.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] PID = photoionization detector.
[e] FID = flame ionization detector.

Table 1-4. Single Laboratory Accuracy and Precision for Compounds in Component Standard Spiked Into VPH-Free Sand at Concentrations in the Low to Middle End of the Analytical Range and Then Analyzed by the VPH Method

Compound	Spiked Conc. (mg/Kg)	Method Accuracy[a] (Mean % Recovery[b])		Method Precision[a] (RSD[c] - %)	
		PID[d]	FID[e]	PID	FID
n-Pentane	2.0		118		1.9
Methyl tert butylether	3.0	100	94	2.4	2.8
Benzene	2.0	119	109	3.0	0.7
Toluene	2.0	118	109	1.7	1.3
n-Nonane	ND	ND	ND	ND	ND
Ethylbenzene	1.0	121	110	1.4	1.2
m- & p-Xylene	3.0	122	110	1.4	1.1
o-Xylene	2.0	118	107	1.3	1.1
1,2,3-Trimethylbenzene	2.0	115	109	1.4	1.3
Naphthalene	2.0	61	57	11	1.8
2,5-Dibromotoluene (surrogate)	2.0	75	64	9.7	3.3

[a] Based on analysis of five samples spiked with component standard.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] PID = photoionization detector.
[e] FID = flame ionization detector.
[f] ND = not determined.

APPENDIX 2

SUGGESTED VPH DATA REPORTING FORMAT

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VOLATILE PETROLEUM HYDROCARBON (VPH) ANALYSIS

Client:
Client Sample ID: Date Received:
Laboratory Sample ID: Date Analyzed:
Matrix: Date Reported:
Percent Moisture:

VPH RESULTS

Parameter	Results	PQL				Units
C5-C6 Aliphatics (FID) *						
C6-C8 Aliphatics (FID) *						
C8-C10 Aliphatics (FID) *						
C10-C12 Aliphatics (FID) *						
C8-C10 Aromatics (PID)						
C10-C12 Aromatics (PID)						
C12-C13 Aromatics (PID)						

*** Excludes any MTBE or BTEX compounds**

SURROGATE RECOVERY

Surrogate	%Recovery	Acceptance Range
2,5-dibromotoluene		80% - 120%

TARGETED VPH ANALYTES

Analyte	**Results**	**PQL**	**Units**
Methyl tert butylether			
Benzene			
Toluene			
Ethylbenzene			
p-Xylene *			
m-Xylene *			
o-Xylene			
Naphthalene			

* p and m-xylenes may not be able to be resolved and may be reported as the total of p and m-xylenes.

APPENDIX 3

SINGLE LABORATORY ACCURACY, PRECISION, AND METHOD DETECTION LIMIT (MDL) DATA FOR EPH

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Table 1-1. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Alkanes Spiked Into Reagent Water and Analyzed by the EPH Method

Compound[a]	Compound Conc. Measured (µg/L)		Mean Accuracy (Mean % Recovery[b])	Method Precision (RSD[c] - %)	MDL (µg/L)
	Mean	Std. Dev.			
C_{10}	4.1	0.040	82	0.98	0.12
C_{12}	4.1	0.021	82	0.51	0.064
C_{16}	4.0	0.062	80	1.6	0.19
COD[d]	44	0.93	88	2.1	-
C21	3.7	0.047	74	1.3	0.14

[a] Compounds were spiked into 7 or 8 samples at a concentration of 5.0 µg/L.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] Surrogate (COD = 1-Chloro-octadecane) was spiked into three samples at a concentration of 50 µg/L.

Table 1-2. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Polynuclear Aromatic Hydrocarbons (PAHs) Spiked Into Reagent Water and Analyzed by the EPH Method

Compound[a]	Compound Conc. Measured (µg/L)		Mean Accuracy (Mean % Recovery[b])	Method Precision (RSD[c] - %)	MDL (µg/L)
	Mean	Std. Dev.			
Naphthalene	5.6	0.088	112	1.6	0.26
2-Methylnaphthalene	6.4	0.096	128	1.5	0.29
Acenaphthylene	5.6	0.085	112	1.5	0.26
Acenaphthene	5.7	0.092	114	1.6	0.28
Fluorene	5.6	0.094	112	1.7	0.28
Phenanthrene	5.5	0.097	110	1.8	0.29
Anthracene	7.0	0.10	140	1.4	0.31
OTP[d]	44	1.6	88	3.6	-
Fluoranthene	5.7	0.090	114	1.6	0.27
Pyrene	6.1	0.098	122	1.6	0.29
Benzo(a)Anthracene	5.9	0.089	118	1.5	0.27
Chrysene	5.8	0.098	116	1.7	0.29
Benzo(b)Fluoranthene	6.3	0.082	126	1.3	0.25
Benzo(k)Fluoranthene	5.6	0.065	112	1.2	0.20
Benzo(a)Pyrene	6.0	0.075	120	1.2	0.22
Indeno(123 cd)Pyrene	5.1	0.17	102	3.3	0.50
Dibenzo(ah)Anthracene	2.8	0.21	56	7.5	0.62
Benzo(ghi)Perylene	3.8	0.18	76	4.7	0.54

[a] Compounds were spiked into 7 or 8 samples at a concentration of 5.0 µg/L.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] Surrogate (OTP = ortho-Terphenyl) was spiked into three samples at a concentration of 50 µg/L.

Table 1-3. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Alkanes Spiked Into EPH-Free Sand and Analyzed by the EPH Method

Compound[a]	Compound Conc. Measured (mg/Kg)		Mean Accuracy (Mean % Recovery[b])	Method Precision (RSD[c] - %)	MDL (mg/Kg)
	Mean	Std. Dev.			
C_{10}	0.72	0.074	72	10	0.22
C_{12}	0.83	0.079	83	9.5	0.24
C_{16}	1.2	0.14	120	12	0.42
COD[d]	4.3	0.48	86	11	-
C21	0.81	0.044	81	5.4	0.13

[a] Compounds were spiked into 8 samples at a concentration of 1.0 mg/Kg.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] Surrogate (COD = 1-Chloro-octadecane) was spiked into three samples at a concentration of 5.0 mg/kg.

Table 1-4. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Polynuclear Aromatic Hydrocarbons (PAHs) Spiked Into EPH-Free Sand and Analyzed by the EPH Method

Compound[a]	Compound Conc. Measured (mg/Kg)		Mean Accuracy (Mean % Recovery[b])	Method Precision (RSD[c] - %)	MDL (mg/Kg)
	Mean	Std. Dev.			
Naphthalene	0.64	0.063	64	9.8	0.19
2-Methylnaphthalene	0.64	0.058	64	9.1	0.17
Acenaphthylene	0.68	0.060	68	8.8	0.18
Acenaphthene	0.70	0.064	70	9.1	0.19
Fluorene	0.79	0.060	79	7.6	0.18
Phenanthrene	0.83	0.041	83	4.9	0.12
Anthracene	1.2	0.082	120	6.8	0.25
OTP[d]	4.8	0.45	96	9.4	-
Fluoranthene	0.92	0.038	92	4.1	0.12
Pyrene	0.91	0.037	91	4.1	0.11
Benzo(a)Anthracene	0.96	0.042	96	4.4	0.12
Chrysene	0.90	0.050	90	5.6	0.15
Benzo(b)Fluoranthene	0.96	0.038	96	4.0	0.11
Benzo(k)Fluoranthene	0.87	0.037	87	4.3	0.11
Benzo(a)Pyrene	0.96	0.036	96	3.8	0.11
Indeno(123 cd)Pyrene	0.90	0.033	90	3.7	0.099
Dibenzo(ah)Anthracene	0.82	0.033	82	4.0	0.099
Benzo(ghi)Perylene	0.82	0.032	82	3.9	0.096

[a] Compounds were spiked into 7 or 8 samples at a concentration of 1.0 mg/Kg.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] Surrogate (OTP = ortho-Terphenyl) was spiked into three samples at a concentration of 5.0 mg/kg.

APPENDIX 4

SUGGESTED EPH DATA REPORTING FORMAT

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EXTRACTABLE PETROLEUM HYDROCARBON (EPH) ANALYSIS

Client:	
Client Sample ID:	Date Received:
Laboratory Sample ID:	Date Extracted:
Matrix:	Date Analyzed:
Percent Moisture:	Date Reported:

EXTRACTABLE PETROLEUM HYDROCARBON (EPH)

Parameter	Results	PQL				Units
C8-C10 Aliphatics						
C10-C12 Aliphatics						
C12-C16 Aliphatics						
C16-C21 Aliphatics						
C21-C34 Aliphatics						
C8-C10 Aromatics						
C10-C12 Aromatics						
C12-C16 Aromatics						
C16-C21 Aromatics						
C21-C34 Aromatics						

SURROGATE RECOVERIES

Surrogate	%Recovery	Acceptance Range
Chloro-octadecane (COD)		50% - 150%
Ortho-terphenyl (OTP)		50% - 150%

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APPENDIX 5

REPORT OF ANALYSIS

SUMMARY SHEET

Client: Client Sample ID Number(s): Laboratory ID Number(s):

SAMPLE INFORMATION

Sample Matrix	¨ Aqueous ¨ Soil ¨ Sediment ¨ Other:	
Analysis Performed	¨ VPH ¨ EPH ¨ VPH and EPH (E-TPH Duplicate samples)	
Condition of Containers	¨ Satisfactory ¨ Broken ¨ Leaking ¨ Other:	
Sample Preservatives	AQUEOUS	¨ N/A ¨ pH ≤ 2 ¨ pH > 2
	SOIL/SEDIMENT	¨ N/A
Sample Temperature	¨ Received on Ice ¨ Received at 4 °C ¨ Other	

ANALYTICAL RESULTS

Parameter	Results	PQL	Units
Volatile Petroleum Hydrocarbons (VPH)			
Extractable Petroleum Hydrocarbons (EPH)			
Equivalent TPH (E-TPH) ** [IF BOTH VPH AND EPH ANALYSES PERFORMED]			

**** Due to overlapping carbon ranges between the VPH and EPH methods and in order to avoid double counting, the analyst must select the higher of the two values to be included for reporting purposes for those ranges effected.**

COMMENTS

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APPENDIX 6*

Petroleum Product Chromatograms

Carburator Cleaner
Automotive Gasoline
Mineral Spirits #1
Mineral Spirits #2
JP-4 Jet Fuel (old)
JP-4 Jet Fuel (new)
JP-5 Jet Fuel
Kerosene
Kerosene (ICP grade)
Gasoline and #2 Diesel Oil
Natural Gas Condensate
#2 Fuel Oil
#2 Fuel Oil (38% aromatic) (See chromatogram in NWTPH-Dx)
#2 Diesel Oil (See chromatogram in NWTPH-Dx)
#2 Diesel Oil and Motor Oil (30w) (See chromatogram in NWTPH-Dx)
2-Cycle Engine Oil #1
2-Cycle Engine Oil #2
2-Cycle Engine Oil #3
Motor Oil (30w) (See chromatogram in NWTPH-Dx)
Automatic Transmission Fluid
Power Steering Fluid
Transformer Oil (used)
Transformer Oil (new)
Hydraulic Fluid #1
Hydraulic Fluid #2
Hydraulic Fluid #3
Mineral Oil #1
Mineral Oil #2
Cutting Oil #1
Cutting Oil #2
Bunker-C #1
Bunker-C #2
CSS-1 (emulsion asphalt)
AR-4000 (asphalt cement)

Non-petroleum Product Chromatograms

Turpentine
Creosote
Synthetic Motor Oil

*** The chromatograms are not available in the "electronic" version. They are included in the printed publication.**

Chromatograms: NWTPH-Gx

Gasoline
Weathered Gasoline
Naphtha
Mineral Spirits #1
Mineral Spirits #2
Mineral Spirits #3

Chromatograms: NWTPH-Dx

#2 Diesel Oil
#2 Diesel Oil/Motor Oil
#2 Fuel Oil (38% Aromatic)
Kerosene (Deodorized)
Jet Fuel A
Bunker C #1
Bunker C #2
Motor Oil 30 Wgt.
Mineral Oil (USP)
Hydraulic Fluid
Transformer Oil
Gas Oil

State of Oregon Department of Environmental Quality

OAR 340-200-0020 Attachments

OAR 340-200-0020
Table 1 Significant Air Quality Impact

Pollutant	Averaging Time	Air Quality Area Designation		
		Class I	Class II	Class III
SO_2 (µg/m^3)*	Annual	0.10	1.0	1.0
	24-hour	0.20	5.0	5.0
	3-hour	1.0	25.0	25.0
	1-hour	---	8.0	---
PM10 (µg/m3)	Annual	0.20	0.2	0.2
	24-hour	0.30	1.0	1.0
PM2.5 (µg/m3)	Annual	0.06	0.3	0.3
	24-hour	0.07	1.2	1.2
NO2 (µg/m3)	Annual	0.10	1.0	1.0
	1-hour	---	8.0	---
CO (mg/m3)**	8 hour	---	0.5	0.5
	1-hour	---	2.0	2.0

* micrograms/cubic meter
**milligrams/cubic meter

OAR 340-200-0020
Table 2 Significant Emission Rates

Pollutant	Emission Rate
Greenhouse Gases (CO2e)	75,000 tons/year
Carbon Monoxide	100 tons/year
Nitrogen Oxides (NOX)	40 tons/year
Particulate Matter	25 tons/year
PM10	15 tons/year
Direct PM2.5	10 tons/year
PM2.5 precursors (SO2 or NOx)	40 tons/year
Sulfur Dioxide (SO2)	40 tons/year
Volatile Organic Compounds (VOC)	40 tons/year
Ozone precursors (VOC or NOx)	40 tons/year
Lead	0.6 ton/year
Fluorides	3 tons/year
Sulfuric Acid Mist	7 tons/year
Hydrogen Sulfide	10 tons/year
Total Reduced Sulfur (including hydrogen sulfide)	10 tons/year
Reduced sulfur compounds (including hydrogen sulfide)	10 tons/year
Municipal waste combustor organics (measured as total tetra- through octa- chlorinated dibenzo-p- dioxins and dibenzofurans)	0.0000035 ton/year
Municipal waste combustor metals (measured as particulate matter)	15 tons/year
Municipal waste combustor acid gases (measured as sulfur dioxide and hydrogen chloride)	40 tons/year
Municipal solid waste landfill emissions (measured as nonmethane organic compounds)	50 tons/year

OAR 340-200-0020
Table 3 Significant Emission Rates for the Medford-Ashland Air Quality Maintenance Area

Air Contaminant	Emission Rate	
	Annual	Day
PM10	5 tons	50 lbs.

OAR 340-200-0020(33)
Table 4 De Minimis Emission Levels

Pollutant	De Minimis (tons/year, except as noted)
Greenhouse Gases (CO2e)	2,756
CO	1
NOx	1
SO2	1
VOC	1
PM	1
PM10 (except Medford AQMA)	1
PM10/PM2.5 (Medford AQMA)	0.5 [5.0 lbs/day]
Direct PM2.5	1
Lead	0.1
Fluorides	0.3
Sulfuric Acid Mist	0.7
Hydrogen Sulfide	1
Total Reduced Sulfur (including hydrogen sulfide)	1
Reduced Sulfur	1
Municipal waste combustor organics (Dioxin and furans)	0.0000005
Municipal waste combustor metals	1
Municipal waste combustor acid gases	1
Municipal solid waste landfill gases	1
Single HAP	1
Combined HAP (aggregate)	1

OAR 340-200-0020(60)
Table 5 Generic PSELS

Pollutant	Generic PSEL (tons/year, except as noted)
Greenhouse Gases (CO2e)	74,000
CO	99
NOx	39
SO2	39
VOC	39
PM	24
PM10 (except Medford AQMA)	14
PM10/PM2.5 (Medford AQMA)	4.5 [49 lbs/day]
Direct PM2.5	9
Lead	0.5
Fluorides	2
Sulfuric Acid Mist	6
Hydrogen Sulfide	9
Total Reduced Sulfur (including hydrogen sulfide)	9
Reduced Sulfur	9
Municipal waste combustor organics (Dioxin and furans)	0.0000030
Municipal waste combustor metals	14
Municipal waste combustor acid gases	39
Municipal solid waste landfill gases	49
Single HAP	9
Combined HAPs (aggregate)	24

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METHOD 9 - VISUAL DETERMINATION OF THE OPACITY OF EMISSIONS FROM STATIONARY SOURCES

Many stationary sources discharge visible emissions into the atmosphere; these emissions are usually in the shape of a plume. This method involves the determination of plume opacity by qualified observers. The method includes procedures for the training and certification of observers, and procedures to be used in the field for determination of plume opacity. The appearance of a plume as viewed by an observer depends upon a number of variables, some of which may be controllable and some of which may not be controllable in the field. Variables which can be controlled to an extent to which they no longer exert a significant influence upon plume appearance include: Angle of the observer with respect to the plume; angle of the observer with respect to the sun; point of observation of attached and detached steam plume; and angle of the observer with respect to a plume emitted from a rectangular stack with a large length to width ratio. The method includes specific criteria applicable to these variables.

Other variables which may not be controllable in the field are luminescence and color contrast between the plume and the background against which the plume is viewed. These variables exert an influence upon the appearance of a plume as viewed by an observer, and can affect the ability of the observer to accurately assign opacity values to the observed plume. Studies of the theory of plume opacity and field studies have demonstrated that a plume is most visible and presents the greatest apparent opacity when viewed against a contrasting background. It follows from this, and is confirmed by field trials, that the opacity of a plume, viewed under conditions where a contrasting background is present can be assigned with the greatest degree of accuracy. However, the potential for a positive error is also the greatest when a plume is viewed under such contrasting conditions. Under conditions presenting a less contrasting background, the apparent opacity of a plume is less and approaches zero as the color and luminescence contrast decrease toward zero. As a result, significant negative bias and negative errors can be made when a plume is viewed under less contrasting conditions. A negative bias decreases rather than increases the possibility that a plant operator will be cited for a violation of opacity standards due to observer error.

Studies have been undertaken to determine the magnitude of positive errors which can be made by qualified observers while reading plumes under contrasting conditions and using the procedures set forth in this method. The results of these studies (field trials) which involve a total of 769 sets of 25 readings each are as follows:

(1) For black plumes (133 sets at a smoke generator), 100 percent of the sets were read with a positive error[1] of less than 7.5 percent opacity; 99 percent were read with a positive error of less than 5 percent opacity.

(2) For white plumes (170 sets at a smoke generator, 168 sets at a coal-fired power plant, 298 sets at a sulfuric acid plant), 99 percent of the sets were read with a positive error of less than 7.5 percent opacity; 95 percent were read with a positive error of less than 5 percent opacity. The positive observational error associated with an average of twenty-five readings is therefore established. The accuracy of the method must be taken into account when determining possible violations of applicable opacity standards.

[1] For a set, positive error-average opacity determined by observer' s 25 observations-average opacity determined from transmissometer's 25 recordings.

1. Principle and Applicability

1.1 Principle. The opacity of emissions from stationary sources is determined visually by a qualified observer.

1.2 Applicability. This method is applicable for the determination of the opacity of emissions from stationary sources pursuant to §60.11(b) and for qualifying observers for visually determining opacity of emissions.

2. Procedures

The observer qualified in accordance with section 3 of this method shall use the following procedures for visually determining the opacity of emissions:

2.1 Position. The qualified observer shall stand at a distance sufficient to provide a clear view of the emissions with the sun oriented in the 140° sector to his back. Consistent with maintaining the above requirement, the observer shall, as much as possible, make his observations from a position such that his line of vision is approximately perpendicular to the plume direction, and when observing opacity of emissions from rectangular outlets (e.g., roof monitors, open baghouses, noncircular stacks), approximately perpendicular to the longer axis of the outlet. The observer's line of sight should not include more than one plume at a time when multiple stacks are involved, and in any case the observer should make his observations with his line of sight perpendicular to the longer axis of such a set of multiple stacks (e.g., stub stacks on baghouses).

2.2 Field Records. The observer shall record the name of the plant, emission location, type facility, observer's name and affiliation, a sketch of the observer's position relative to the source, and the date on a field data sheet (Figure 9–1). The time, estimated distance to the emission location, approximate wind direction, estimated wind speed, description of the sky condition (presence and color of clouds), and plume background are recorded on a field data sheet at the time opacity readings are initiated and completed.

2.3 Observations. Opacity observations shall be made at the point of greatest opacity in that portion of the plume where condensed water vapor is not present. The observer shall not look continuously at the plume, but instead shall observe the plume momentarily at 15-second intervals.

2.3.1 Attached Steam Plumes. When condensed water vapor is present within the plume as it emerges from the emission outlet, opacity observations shall be made beyond the point in the plume at which condensed water vapor is no longer visible. The observer shall record the approximate distance from the emission outlet to the point in the plume at which the observations are made.

2.3.2 Detached Steam Plume. When water vapor in the plume condenses and becomes visible at a distinct distance from the emission outlet, the opacity of emissions should be evaluated at the emission outlet prior to the condensation of water vapor and the formation of the steam plume.

2.4 Recording Observations. Opacity observations shall be recorded to the nearest 5 percent at 15-second intervals on an observational record sheet. (See Figure 9–2 for an example.) A minimum of 24 observations shall be recorded. Each momentary observation recorded shall be deemed to represent the average opacity of emissions for a 15-second period.

2.5 Data Reduction. Opacity shall be determined as an average of 24 consecutive observations recorded at 15-second intervals. Divide the observations recorded on the record sheet into sets of 24 consecutive observations. A set is composed of any 24 consecutive observations. Sets need not be consecutive in time and in no case shall two sets overlap. For each set of 24 observations, calculate the average by summing the opacity of the 24 observations and dividing this sum by 24. If an applicable standard specifies an averaging time requiring more than 24 observations, calculate the average for all observations made during the specified time period. Record the average opacity on a record sheet. (See Figure 9–1 for an example.)

3. Qualifications and Testing

3.1 Certification Requirements. To receive certification as a qualified observer, a candidate must be tested and demonstrate the ability to assign opacity readings in 5 percent increments to 25 different black plumes and 25 different white plumes, with an error not to exceed 15 percent opacity on any one reading and an average error not to exceed 7.5 percent opacity in each category. Candidates shall be tested according to the procedures described in section 3.2. Smoke generators used pursuant to section 3.2 shall be equipped with a smoke meter which meets the requirements of section 3.3.

The certification shall be valid for a period of 6 months, at which time the qualification procedure must be repeated by any observer in order to retain certification.

3.2 Certification Procedure. The certification test consists of showing the candidate a complete run of 50 plumes—25 black plumes and 25 white plumes—generated by a smoke generator. Plumes within each set of 25 black and 25 white runs shall be presented in random order. The candidate assigns an opacity value to each plume and records his observation on a suitable form. At the completion of each run of 50 readings, the score of the candidate is determined. If a candidate fails to qualify, the complete run of 50 readings must be repeated in any retest. The smoke test may be administered as part of a smoke school or training program, and may be preceded by training or familiarization runs of the smoke generator during which candidates are shown black and white plumes of known opacity.

3.3 Smoke Generator Specifications. Any smoke generator used for the purposes of section 3.2 shall be equipped with a smoke meter installed to measure opacity across the diameter of the smoke generator stack. The smoke meter output shall display instack opacity based upon a pathlength equal to the stack exit diameter, on a full 0 to 100 percent chart recorder scale. The smoke meter optical design and performance shall meet the specifications shown in Table 9–1.
The smoke meter shall be calibrated as prescribed in section 3.3.1 prior to the conduct of each smoke reading test. At the completion of each test, the zero and span drift shall be checked and if the drift exceeds ±1 percent opacity, the condition shall be corrected prior to conducting any subsequent test runs. The smoke meter shall be demonstrated, at the time of installation, to meet the specifications listed in Table 9–1. This demonstration shall be repeated following any subsequent repair or replacement of the photocell or associated electronic circuitry including the chart recorder or output meter, or every 6 months, whichever occurs first.

Table 9–1—Smoke Meter Design and Performance Specifications

Parameter	Specification
a. Light source	Incandescent lamp operated at nominal rated voltage.
b. Spectral response of photocell	Photopic (daylight spectral response of the human eye—Citation 3).
c. Angle of view	15° maximum total angle.

d. Angle of projection	15° maximum total angle.
e. Calibration error	±3% opacity, maximum.
f. Zero and span drift	±1% opacity, 30 minutes.
g. Response time	5 seconds.

3.3.1 Calibration. The smoke meter is calibrated after allowing a minimum of 30 minutes warmup by alternately producing simulated opacity of 0 percent and 100 percent. When stable response at 0 percent or 100 percent is noted, the smoke meter is adjusted to produce an output of 0 percent or 100 percent, as appropriate. This calibration shall be repeated until stable 0 percent and 100 percent readings are produced without adjustment. Simulated 0 percent and 100 percent opacity values may be produced by alternately switching the power to the light source on and off while the smoke generator is not producing smoke.

3.3.2 Smoke Meter Evaluation. The smoke meter design and performance are to be evaluated as follows:

3.3.2.1 Light Source. Verify from manufacturer's data and from voltage measurements made at the lamp, as installed, that the lamp is operated within ±5 percent of the nominal rated voltage.

3.3.2.2 Spectral Response of Photocell. Verify from manufacturer's data that the photocell has a photopic response; i.e., the spectral sensitivity of the cell shall closely approximate the standard spectral-luminosity curve for photopic vision which is referenced in (b) of Table 9–1.

FIGURE 9-1
RECORD OF VISUAL DETERMINATION OF OPACITY

PAGE ___ OF ___

COMPANY _____ HOURS OF OBSERVATION _____
LOCATION _____ OBSERVER _____
TEST NUMBER _____ OBSERVER CERTIFICATION DATE _____
DATE _____ OBSERVER AFFILIATION _____
TYPE FACILITY _____ POINT OF EMISSIONS _____
CONTROL DEVICE _____ HEIGHT OF DISCHARGE POINT _____

CLOCK TIME	Initial			Final
DESCRIBE LOCATION Distance to Discharge				
Direction from Discharge				
Height of Observation Point				
BACKGROUND DESCRIPTION				
WEATHER CONDITIONS Wind Direction				
Wind Speed				
Ambient Temperature				
SKY CONDITIONS (clear, overcast, % clouds, etc.)				
PLUME DESCRIPTION Color				
Distance Visible				
OTHER INFORMATION				

SUMMARY OF AVERAGE OPACITY

Set Number	Time Start--End	Opacity Sum	Opacity Average

Readings ranged from ____ to ____ % opacity

The source was/was not in compliance with ____ at the time evaluation was made.

Figure 9–2—Observation Record

Company	Observer	
Location	Type facility	
Test Number	Point of emissions	
Date		

Hr.	Min.	Seconds				Steam plume (check if applicable)		Comments
		0	15	30	45	Attached	Detached	
	0							
	1							
	2							
	3							
	4							
	5							
	6							
	7							
	8							
	9							
	10							
	11							
	12							
	13							
	14							
	15							
	16							
	17							
	18							
	19							
	20							
	21							
	22							
	23							
	24							
	25							
	26							
	27							
	28							

Company	Observer	
Location	Type facility	
Test Number	Point of emissions	
Date		

Hr.	Min.	Seconds				Steam plume (check if applicable)		Comments
		0	15	30	45	Attached	Detached	
	29							
	30							
	31							
	32							
	33							
	34							
	35							
	36							
	37							
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3.3.2.3 Angle of View. Check construction geometry to ensure that the total angle of view of the smoke plume, as seen by the photocell, does not exceed 15°. The total angle of view may be calculated from: $\Theta = 2 \tan^{-1} d/2L$, where Θ = total angle of view; d = the sum of the photocell diameter+ the diameter of the limiting aperture; and L = the distance from the photocell to the limiting aperture. The limiting aperture is the point in the path between the photocell and the smoke plume where the angle of view is most restricted. In smoke generator smoke meters this is normally an orifice plate.

3.3.2.4 Angle of Projection. Check construction geometry to ensure that the total angle of projection of the lamp on the smoke plume does not exceed 15°. The total angle of projection may be calculated from: $\Theta = 2 \tan^{-1} d/2L$, where Θ = total angle of projection; d=the sum of the length of the lamp filament + the diameter of the limiting aperture; and L = the distance from the lamp to the limiting aperture.

3.3.2.5 Calibration Error. Using neutral-density filters of known opacity, check the error between the actual response and the theoretical linear response of the smoke meter. This check is accomplished by first calibrating the smoke meter according to 3.3.1 and then inserting a series of three neutral-density filters of nominal opacity of 20, 50, and 75 percent in the smoke meter pathlength. Filters calibrated within ±2 percent shall be used. Care should be taken when inserting the filters to prevent stray light from affecting the meter. Make a total of five nonconsecutive readings for each filter. The maximum error on any one reading shall be 3 percent opacity.

3.3.2.6 Zero and Span Drift. Determine the zero and span drift by calibrating and operating the smoke generator in a normal manner over a 1-hour period. The drift is measured by checking the zero and span at the end of this period.

3.3.2.7 Response Time. Determine the response time by producing the series of five simulated 0 percent and 100 percent opacity values and observing the time required to reach stable response. Opacity values of 0 percent and 100 percent may be simulated by alternately switching the power to the light source off and on while the smoke generator is not operating.

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ambient temperature for the sampling site, K;
T_{std} = standard temperature, defined as 298 K;
P_{std} = standard pressure, defined as 101.3 kPa (or 760 mm Hg).

11.2 Calculate the total volume of air sampled as:

$$V_{std} = \bar{Q}_{std} \times t$$

where

V_{std} = total air sampled in standard volume units, std m^3;
t = sampling time, min.

11.3 Calculate the PM_{10} concentration as:

$$PM_{10} = (W_f - W_i) \times 10^6 / V_{std}$$

where

PM_{10} = mass concentration of PM_{10}, µg/std m^3;
W_f, W_i = final and initial weights of filter collecting PM_{1O} particles, g;
10^6 = conversion of g to µg.

NOTE: If more than one size fraction in the PM_{10} size range is collected by the sampler, the sum of the net weight gain by each collection filter $[\Sigma(W_f - W_i)]$ is used to calculate the PM_{10} mass concentration.

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[52 FR 24664, July 1, 1987; 52 FR 29467, Aug. 7, 1987]

APPENDIX K TO PART 50—INTERPRETATION OF THE NATIONAL AMBIENT AIR QUALITY STANDARDS FOR PARTICULATE MATTER

1.0 *General.*

(a) This appendix explains the computations necessary for analyzing particulate matter data to determine attainment of the 24-hour and annual standards specified in 40 CFR 50.6. For the primary and secondary standards, particulate matter is measured in the ambient air as PM_{10} (particles with an aerodynamic diameter less than or equal to a nominal 10 micrometers) by a reference method based on appendix J of this part and designated in accordance with part 53 of this chapter, or by an equivalent method designated in accordance with part 53 of this chapter. The required frequency of measurements is specified in part 58 of this chapter.

(b) The terms used in this appendix are defined as follows:

Average refers to an arithmetic mean. All particulate matter standards are expressed in terms of expected annual values: Expected number of exceedances per year for the 24-hour standards and expected annual arithmetic mean for the annual standards.

Daily value for PM_{10} refers to the 24-hour average concentration of PM_{10} calculated or measured from midnight to midnight (local time).

Exceedance means a daily value that is above the level of the 24-hour standard after

rounding to the nearest 10 μg/m³ (i.e., values ending in 5 or greater are to be rounded up).

Expected annual value is the number approached when the annual values from an increasing number of years are averaged, in the absence of long-term trends in emissions or meteorological conditions.

Year refers to a calendar year.

(c) Although the discussion in this appendix focuses on monitored data, the same principles apply to modeling data, subject to EPA modeling guidelines.

2.0 *Attainment Determinations.*

2.1 *24-Hour Primary and Secondary Standards.*

(a) Under 40 CFR 50.6(a) the 24-hour primary and secondary standards are attained when the expected number of exceedances per year at each monitoring site is less than or equal to one. In the simplest case, the number of expected exceedances at a site is determined by recording the number of exceedances in each calendar year and then averaging them over the past 3 calendar years. Situations in which 3 years of data are not available and possible adjustments for unusual events or trends are discussed in sections 2.3 and 2.4 of this appendix. Further, when data for a year are incomplete, it is necessary to compute an estimated number of exceedances for that year by adjusting the observed number of exceedances. This procedure, performed by calendar quarter, is described in section 3.0 of this appendix. The expected number of exceedances is then estimated by averaging the individual annual estimates for the past 3 years.

(b) The comparison with the allowable expected exceedance rate of one per year is made in terms of a number rounded to the nearest tenth (fractional values equal to or greater than 0.05 are to be rounded up; e.g., an exceedance rate of 1.05 would be rounded to 1.1, which is the lowest rate for nonattainment).

2.2 *Annual Primary and Secondary Standards.* Under 40 CFR 50.6(b), the annual primary and secondary standards are attained when the expected annual arithmetic mean PM_{10} concentration is less than or equal to the level of the standard. In the simplest case, the expected annual arithmetic mean is determined by averaging the annual arithmetic mean PM_{10} concentrations for the past 3 calendar years. Because of the potential for incomplete data and the possible seasonality in PM_{10} concentrations, the annual mean shall be calculated by averaging the four quarterly means of PM_{10} concentrations within the calendar year. The equations for calculating the annual arithmetic mean are given in section 4.0 of this appendix. Situations in which 3 years of data are not available and possible adjustments for unusual events or trends are discussed in sections 2.3 and 2.4 of this appendix. The expected annual arithmetic mean is rounded to the nearest 1 μg/m³ before comparison with the annual standards (fractional values equal to or greater than 0.5 are to be rounded up).

2.3 *Data Requirements.*

(a) 40 CFR 58.13 specifies the required minimum frequency of sampling for PM_{10}. For the purposes of making comparisons with the particulate matter standards, all data produced by National Air Monitoring Stations (NAMS), State and Local Air Monitoring Stations (SLAMS) and other sites submitted to EPA in accordance with the part 58 requirements must be used, and a minimum of 75 percent of the scheduled PM_{10} samples per quarter are required.

(b) To demonstrate attainment of either the annual or 24-hour standards at a monitoring site, the monitor must provide sufficient data to perform the required calculations of sections 3.0 and 4.0 of this appendix. The amount of data required varies with the sampling frequency, data capture rate and the number of years of record. In all cases, 3 years of representative monitoring data that meet the 75 percent criterion of the previous paragraph should be utilized, if available, and would suffice. More than 3 years may be considered, if all additional representative years of data meeting the 75 percent criterion are utilized. Data not meeting these criteria may also suffice to show attainment; however, such exceptions will have to be approved by the appropriate Regional Administrator in accordance with EPA guidance.

(c) There are less stringent data requirements for showing that a monitor has failed an attainment test and thus has recorded a violation of the particulate matter standards. Although it is generally necessary to meet the minimum 75 percent data capture requirement per quarter to use the computational equations described in sections 3.0 and 4.0 of this appendix, this criterion does not apply when less data is sufficient to unambiguously establish nonattainment. The following examples illustrate how nonattainment can be demonstrated when a site fails to meet the completeness criteria. Nonattainment of the 24-hour primary standards can be established by the observed annual number of exceedances (e.g., four observed exceedances in a single year), or by the estimated number of exceedances derived from the observed number of exceedances and the required number of scheduled samples (e.g., two observed exceedances with every other day sampling). Nonattainment of the annual standards can be demonstrated on the basis of quarterly mean concentrations developed from observed data combined with one-half the minimum detectable concentration substituted for missing values. In both cases, expected annual values must exceed the levels allowed by the standards.

2.4 *Adjustment for Exceptional Events and Trends.*

(a) An exceptional event is an uncontrollable event caused by natural sources of particulate matter or an event that is not expected to recur at a given location. Inclusion of such a value in the computation of exceedances or averages could result in inappropriate estimates of their respective expected annual values. To reduce the effect of unusual events, more than 3 years of representative data may be used. Alternatively, other techniques, such as the use of statistical models or the use of historical data could be considered so that the event may be discounted or weighted according to the likelihood that it will recur. The use of such techniques is subject to the approval of the appropriate Regional Administrator in accordance with EPA guidance.

(b) In cases where long–term trends in emissions and air quality are evident, mathematical techniques should be applied to account for the trends to ensure that the expected annual values are not inappropriately biased by unrepresentative data. In the simplest case, if 3 years of data are available under stable emission conditions, this data should be used. In the event of a trend or shift in emission patterns, either the most recent representative year(s) could be used or statistical techniques or models could be used in conjunction with previous years of data to adjust for trends. The use of less than 3 years of data, and any adjustments are subject to the approval of the appropriate Regional Administrator in accordance with EPA guidance.

3.0 *Computational Equations for the 24-hour Standards.*

3.1 *Estimating Exceedances for a Year.*

(a) If PM_{10} sampling is scheduled less frequently than every day, or if some scheduled samples are missed, a PM_{10} value will not be available for each day of the year. To account for the possible effect of incomplete data, an adjustment must be made to the data collected at each monitoring location to estimate the number of exceedances in a calendar year. In this adjustment, the assumption is made that the fraction of missing values that would have exceeded the standard level is identical to the fraction of measured values above this level. This computation is to be made for all sites that are scheduled to monitor throughout the entire year and meet the minimum data requirements of section 2.3 of this appendix. Because of possible seasonal imbalance, this adjustment shall be applied on a quarterly basis. The estimate of the expected number of exceedances for the quarter is equal to the observed number of exceedances plus an increment associated with the missing data. The following equation must be used for these computations:

Equation 1

$$e_q = v_q + \left[\left(v_q/n_q\right)\times\left(N_q - n_q\right)\right] = v_q \times N_q/n_q$$

where:

e_q = the estimated number of exceedances for calendar quarter q;
v_q = the observed number of exceedances for calendar quarter q;
N_q = the number of days in calendar quarter q;
n_q = the number of days in calendar quarter q with PM_{10} data; and
q = the index for calendar quarter, q=1, 2, 3 or 4.

(b) The estimated number of exceedances for a calendar quarter must be rounded to the nearest hundredth (fractional values equal to or greater than 0.005 must be rounded up).

(c) The estimated number of exceedances for the year, e, is the sum of the estimates for each calendar quarter.

Equation 2

$$e = \sum_{q=1}^{4} e_q$$

(d) The estimated number of exceedances for a single year must be rounded to one decimal place (fractional values equal to or greater than 0.05 are to be rounded up). The expected number of exceedances is then estimated by averaging the individual annual estimates for the most recent 3 or more representative years of data. The expected number of exceedances must be rounded to one decimal place (fractional values equal to or greater than 0.05 are to be rounded up).

(e) The adjustment for incomplete data will not be necessary for monitoring or modeling data which constitutes a complete record, i.e., 365 days per year.

(f) To reduce the potential for overestimating the number of expected exceedances, the correction for missing data will not be required for a calendar quarter in which the first observed exceedance has occurred if:

(1) There was only one exceedance in the calendar quarter;

(2) Everyday sampling is subsequently initiated and maintained for 4 calendar quarters in accordance with 40 CFR 58.13; and

(3) Data capture of 75 percent is achieved during the required period of everyday sampling. In addition, if the first exceedance is observed in a calendar quarter in which the monitor is already sampling every day, no adjustment for missing data will be made to the first exceedance if a 75 percent data capture rate was achieved in the quarter in which it was observed.

Example 1

a. During a particular calendar quarter, 39 out of a possible 92 samples were recorded, with one observed exceedance of the 24-hour standard. Using Equation 1, the estimated number of exceedances for the quarter is:

e_q=1×92/39=2.359 or 2.36.

b. If the estimated exceedances for the other 3 calendar quarters in the year were 2.30, 0.0 and 0.0, then, using Equation 2, the estimated number of exceedances for the year is 2.36=2.30=0.0=0.0 which equals 4.66 or 4.7. If no exceedances were observed for the 2 previous years, then the expected number of exceedances is estimated by: (1/3)×(4.7=0=0)=1.57 or 1.6. Since 1.6 exceeds the allowable number of expected exceedances, this monitoring site would fail the attainment test.

Example 2

In this example, everyday sampling was initiated following the first observed exceedance as required by 40 CFR 58.13. Accordingly, the first observed exceedance would not be adjusted for incomplete sampling. During the next three quarters, 1.2 exceedances were estimated. In this case, the estimated exceedances for the year would be 1.0=1.2=0.0=0.0 which equals 2.2. If, as before, no exceedances were observed for the two previous years, then the estimated exceedances for the 3–year period would then be (1/3)×(2.2=0.0=0.0)=0.7, and the monitoring site would *not* fail the attainment test.

3.2 *Adjustments for Non-Scheduled Sampling Days.*

(a) If a systematic sampling schedule is used and sampling is performed on days in addition to the days specified by the systematic sampling schedule, e.g., during episodes of high pollution, then an adjustment must be made in the eqution for the estimation of exceedances. Such an adjustment is needed to eliminate the bias in the estimate of the quarterly and annual number of exceedances that would occur if the chance of an exceedance is different for scheduled than for nonscheduled days, as would be the case with episode sampling.

(b) The required adjustment treats the systematic sampling schedule as a stratified sampling plan. If the period from one scheduled sample until the day preceding the next scheduled sample is defined as a sampling stratum, then there is one stratum for each scheduled sampling day. An average number of observed exceedances is computed for each of these sampling strata. With nonscheduled sampling days, the estimated number of exceedances is defined as:

Equation 3

$$e_q = \left(N_q / m_q\right) \times \sum_{j=1}^{m_q} \left(v_j / k_j\right)$$

where:

e_q = the estimated number of exceedances for the quarter;
N_q = the number of days in the quarter;
m_q = the number of strata with samples during the quarter;
v_j = the number of observed exceedances in stratum j; and
k_j = the number of actual samples in stratum j.

(c) Note that if only one sample value is recorded in each stratum, then Equation 3 reduces to Equation 1.

Example 3

A monitoring site samples according to a systematic sampling schedule of one sample every 6 days, for a total of 15 scheduled samples in a quarter out of a total of 92 possible samples. During one 6-day period, potential episode levels of PM_{10} were suspected, so 5 additional samples were taken. One of the regular scheduled samples was missed, so a total of 19 samples in 14 sampling strata were measured. The one 6-day sampling stratum with 6 samples recorded 2 exceedances. The remainder of the quarter with one sample per stratum recorded zero exceedances. Using Equation 3, the estimated number of exceedances for the quarter is:

e_q=(92/14)×(2/6=0=. . .=0)=2.19.

4.0 *Computational Equations for Annual Standards.*

4.1 *Calculation of the Annual Arithmetic Mean.* (a) An annual arithmetic mean value for PM_{10} is determined by averaging the quarterly means for the 4 calendar quarters of the year. The following equation is to be used for calculation of the mean for a calendar quarter:

Equation 4

$$\bar{x}_q = \left(1/n_q\right) \times \sum_{i=1}^{n_q} x_i$$

where:

$\bar{x}_q$ = the quarterly mean concentration for quarter q, q=1, 2, 3, or 4,
n_q = the number of samples in the quarter, and
x_i = the ith concentration value recorded in the quarter.

(b) The quarterly mean, expressed in μg/m³, must be rounded to the nearest tenth (fractional values of 0.05 should be rounded up).

(c) The annual mean is calculated by using the following equation:

Equation 5

$$\bar{x} = \left(1/4\right) \times \sum_{q=1}^{4} \bar{x}_q$$

where:

$\bar{x}$ = the annual mean; and
$\bar{x}_q$ = the mean for calendar quarter q.

(d) The average of quarterly means must be rounded to the nearest tenth (fractional values of 0.05 should be rounded up).

(e) The use of quarterly averages to compute the annual average will not be necessary for monitoring or modeling data which results in a complete record, i.e., 365 days per year.

(f) The expected annual mean is estimated as the average of three or more annual means. This multi-year estimate, expressed in μg/m³, shall be rounded to the nearest integer for comparison with the annual standard (fractional values of 0.5 should be rounded up).

Example 4

Using Equation 4, the quarterly means are calculated for each calendar quarter. If the quarterly means are 52.4, 75.3, 82.1, and 63.2 μg/m³, then the annual mean is:

$\bar{x}$ = (1/4)×(52.4=75.3=82.1=63.2) = 68.25 or 68.3.

4.2 *Adjustments for Non-scheduled Sampling Days.* (a) An adjustment in the calculation of the annual mean is needed if sampling is performed on days in addition to the days specified by the systematic sampling schedule. For the same reasons given in the discussion of estimated exceedances, under section 3.2 of this appendix, the quarterly averages would be calculated by using the following equation:

Equation 6

$$\bar{x}_q = \left(1/m_q\right) \times \sum_{j=1}^{m_q} \sum_{i=1}^{k_j} \left(x_{ij}/k_j\right)$$

where:

$\bar{x}_q$ = the quarterly mean concentration for quarter q, q=1, 2, 3, or 4;
x_{ij} = the ith concentration value recorded in stratum j;
k_j = the number of actual samples in stratum j; and
m_q = the number of strata with data in the quarter.

(b) If one sample value is recorded in each stratum, Equation 6 reduces to a simple arithmetic average of the observed values as described by Equation 4.

Example 5

a. During one calendar quarter, 9 observations were recorded. These samples were distributed among 7 sampling strata, with 3 observations in one stratum. The concentrations of the 3 observations in the single stratum were 202, 242, and 180 μg/m³. The remaining 6 observed concentrations were 55, 68, 73, 92, 120, and 155 μg/m³. Applying the weighting factors specified in Equation 6, the quarterly mean is:

$\bar{x}_q$ = (1/7) × [(1/3) × (202 = 242 = 180) = 155 = 68 = 73 = 92 = 120 = 155] = 110.1

b. Although 24-hour measurements are rounded to the nearest 10 μg/m³ for determinations of exceedances of the 24-hour standard, note that these values are rounded to the nearest 1 μg/m³ for the calculation of means.

[62 FR 38712, July 18, 1997]

Appendix L to Part 50—Reference Method for the Determination of Fine Particulate Matter as $PM_{2.5}$ in the Atmosphere

1.0 *Applicability.*

1.1 This method provides for the measurement of the mass concentration of fine particulate matter having an aerodynamic diameter less than or equal to a nominal 2.5 micrometers ($PM_{2.5}$) in ambient air over a 24-hour period for purposes of determining whether the primary and secondary national ambient air quality standards for fine particulate matter specified in §50.7 of this part are met. The measurement process is considered to be nondestructive, and the $PM_{2.5}$ sample obtained can be subjected to subsequent physical or chemical analyses. Quality assessment procedures are provided in part 58, appendix A of this chapter, and quality assurance guidance are provided in references 1, 2, and 3 in section 13.0 of this appendix.

1.2 This method will be considered a reference method for purposes of part 58 of this chapter only if:

(a) The associated sampler meets the requirements specified in this appendix and the applicable requirements in part 53 of this chapter, and

(b) The method and associated sampler have been designated as a reference method in accordance with part 53 of this chapter.

1.3 $PM_{2.5}$ samplers that meet nearly all specifications set forth in this method but have minor deviations and/or modifications of the reference method sampler will be designated as ''Class I'' equivalent methods for $PM_{2.5}$ in accordance with part 53 of this chapter.

2.0 *Principle.*

2.1 An electrically powered air sampler draws ambient air at a constant volumetric flow rate into a specially shaped inlet and

APPENDIX M TO PART 50 [RESERVED]

APPENDIX N TO PART 50—INTERPRETATION OF THE NATIONAL AMBIENT AIR QUALITY STANDARDS FOR $PM_{2.5}$

1.0 GENERAL

(a) This appendix explains the data handling conventions and computations necessary for determining when the national ambient air quality standards (NAAQS) for $PM_{2.5}$ are met, specifically the primary and secondary annual and 24-hour $PM_{2.5}$ NAAQS specified in §50.7, 50.13, and 50.18. $PM_{2.5}$ is defined, in general terms, as particles with an aerodynamic diameter less than or equal to a nominal 2.5 micrometers. $PM_{2.5}$ mass concentrations are measured in the ambient air by a Federal Reference Method (FRM) based on appendix L of this part, as applicable, and designated in accordance with part 53 of this chapter; or by a Federal Equivalent Method (FEM) designated in accordance with part 53 of this chapter; or by an Approved Regional Method (ARM) designated in accordance with part 58 of this chapter. Only those FRM, FEM, and ARM measurements that are derived in accordance with part 58 of this chapter (i.e., that are deemed ''suitable'') shall be used in comparisons with the $PM_{2.5}$ NAAQS. The data handling and computation procedures to be used to construct annual and 24-hour NAAQS metrics from reported $PM_{2.5}$ mass concentrations, and the associated instructions for comparing these calculated metrics to the levels of the $PM_{2.5}$ NAAQS, are specified in sections 2.0, 3.0, and 4.0 of this appendix.

(b) Decisions to exclude, retain, or make adjustments to the data affected by exceptional events, including natural events, are made according to the requirements and process deadlines specified in §§50.1, 50.14 and 51.930 of this chapter.

(c) The terms used in this appendix are defined as follows:

Annual mean refers to a weighted arithmetic mean, based on quarterly means, as defined in section 4.4 of this appendix.

The *Air Quality System (AQS)* is EPA's official repository of ambient air data.

Collocated monitors refers to two or more air measurement instruments for the same parameter (e.g., $PM_{2.5}$ mass) operated at the same site location, and whose placement is consistent with §53.1 of this chapter. For purposes of considering a combined site record in this appendix, when two or more monitors are operated at the same site, one monitor is designated as the ''primary'' monitor with any additional monitors designated as ''collocated.'' It is implicit in these appendix procedures that the primary monitor and collocated monitor(s) are all deemed suitable for the applicable NAAQS comparison; however, it is not a requirement that the primary and monitors utilize the same specific sampling and analysis method.

Combined site data record is the data set used for performing calculations in appendix N. It represents data for the primary monitors augmented with data from collocated monitors according to the procedure specified in section 3.0(d) of this appendix.

Creditable samples are daily values in the combined site record that are given credit for data completeness. The number of creditable samples (cn) for a given year also governs which value in the sorted series of daily values represents the 98th percentile for that year. Creditable samples include daily values collected on scheduled sampling days and valid make-up samples taken for missed or invalidated samples on scheduled sampling days.

Daily values refer to the 24-hour average concentrations of $PM_{2.5}$ mass measured (or averaged from hourly measurements in AQS) from midnight to midnight (local standard time) from suitable monitors.

Data substitution tests are diagnostic evaluations performed on an annual $PM_{2.5}$ NAAQS design value (DV) or a 24-hour $PM_{2.5}$ NAAQS DV to determine if those metrics, which are judged to be based on incomplete data in accordance with 4.1(b) or 4.2(b) of this appendix shall nevertheless be deemed valid for NAAQS comparisons, or alternatively, shall still be considered incomplete and not valid for NAAQS comparisons. There are two data substitution tests, the ''minimum quarterly value'' test and the ''maximum quarterly value'' test. *Design values (DVs)* are the 3-year average NAAQS metrics that are compared to the NAAQS levels to determine when a monitoring site meets or does not meet the NAAQS, calculated as shown in section 4. There are two separate DVs specified in this appendix:

(1) The 3-year average of $PM_{2.5}$ annual mean mass concentrations for each eligible monitoring site is referred to as the ''*annual $PM_{2.5}$ NAAQS DV*''.

(2) The 3-year average of annual 98th percentile 24-hour average $PM_{2.5}$ mass concentration values recorded at each eligible monitoring site is referred to as the ''*24-hour (or daily) $PM_{2.5}$ NAAQS DV*''.

Eligible sites are monitoring stations that meet the criteria specified in §58.11 and §58.30 of this chapter, and thus are approved for comparison to the annual $PM_{2.5}$ NAAQS. For the 24-hour $PM_{2.5}$ NAAQS, all site locations that meet the criteria specified in §58.11 are approved (i.e., eligible) for NAAQS comparisons.

Extra samples are non-creditable samples. They are daily values that do not occur on scheduled sampling days and that cannot be used as make-up samples for missed or invalidated scheduled samples. Extra samples

are used in mean calculations and are included in the series of all daily values subject to selection as a 98th percentile value, but are not used to determine which value in the sorted list represents the 98th percentile.

Make-up samples are samples collected to take the place of missed or invalidated required scheduled samples. Make-up samples can be made by either the primary or the collocated monitor. Make-up samples are either taken before the next required sampling day or exactly one week after the missed (or voided) sampling day.

The *maximum quarterly value data substitution test* substitutes actual ''high'' reported daily $PM_{2.5}$ values from the same site (specifically, the highest reported non-excluded quarterly value(s) (year non-specific) contained in the combined site record for the evaluated 3-year period) for missing daily values.

The *minimum quarterly value data substitution test* substitutes actual ''low'' reported daily $PM_{2.5}$ values from the same site (specifically, the lowest reported quarterly value(s) (year non-specific) contained in the combined site record for the evaluated 3-year period) for missing daily values.

98th percentile is the smallest daily value out of a year of $PM_{2.5}$ mass monitoring data below which no more than 98 percent of all daily values fall using the ranking and selection method specified in section 4.5(a) of this appendix.

Primary monitors are suitable monitors designated by a state or local agency in their annual network plan (and in AQS) as the default data source for creating a combined site record for purposes of NAAQS comparisons. If there is only one suitable monitor at a particular site location, then it is presumed to be a primary monitor.

Quarter refers to a calendar quarter (e.g., January through March).

Quarterly data capture rate is the percentage of scheduled samples in a calendar quarter that have corresponding valid reported sample values. Quarterly data capture rates are specifically calculated as the number of creditable samples for the quarter divided by the number of scheduled samples for the quarter, the result then multiplied by 100 and rounded to the nearest integer.

Scheduled $PM_{2.5}$ samples refers to those reported daily values which are consistent with the required sampling frequency (per §58.12 of this chapter) for the primary monitor, or those that meet the special exception noted in section 3.0(e) of this appendix.

Seasonal sampling is the practice of collecting data at a reduced frequency during a season of expected low concentrations.

Suitable monitors are instruments that use sampling and analysis methods approved for NAAQS comparisons. For the annual and 24-hour $PM_{2.5}$ NAAQS, suitable monitors include all FRMs, and all FEMs/ARMs except those specific continuous FEMs/ARMs disqualified by a particular monitoring agency network in accordance with §58.10(b)(13) and approved by the EPA Regional Administrator per §58.11(e) of this chapter.

Test design values (TDV) are numerical values that used in the data substitution tests described in sections 4.1(c)(i), 4.1(c)(ii) and 4.2(c)(i) of this appendix to determine if the $PM_{2.5}$ NAAQS DV with incomplete data are judged to be valid for NAAQS comparisons. There are two TDVs: TDV_{min} to determine if the NAAQS is not met and is used in the ''minimum quarterly value'' data substitution test and TDV_{max} to determine if the NAAQS is met and is used in the ''maximum quarterly value'' data substitution test. These TDV's are derived by substituting historically low or historically high daily concentration values for missing data in an incomplete year(s).

Year refers to a calendar year.

2.0 Monitoring Considerations

(a) Section 58.30 of this chapter provides special considerations for data comparisons to the annual $PM_{2.5}$ NAAQS.

(b) Monitors meeting the network technical requirements detailed in §58.11 of this chapter are suitable for comparison with the NAAQS for $PM_{2.5}$.

(c) Section 58.12 of this chapter specifies the required minimum frequency of sampling for $PM_{2.5}$. Exceptions to the specified sampling frequencies, such as seasonal sampling, are subject to the approval of the EPA Regional Administrator and must be documented in the state or local agency Annual Monitoring Network Plan as required in §58.10 of this chapter and also in AQS.

3.0 Requirements for Data Use and Data Reporting for Comparisons With the NAAQS for $PM_{2.5}$

(a) Except as otherwise provided in this appendix, all valid FRM/FEM/ARM $PM_{2.5}$ mass concentration data produced by suitable monitors that are required to be submitted to AQS, or otherwise available to EPA, meeting the requirements of part 58 of this chapter including appendices A, C, and E shall be used in the DV calculations. Generally, EPA will only use such data if they have been certified by the reporting organization (as prescribed by §58.15 of this chapter); however, data not certified by the reporting organization can nevertheless be used, if the deadline for certification has passed and EPA judges the data to be complete and accurate.

(b) $PM_{2.5}$ mass concentration data (typically collected hourly for continuous instruments and daily for filter-based instruments) shall be reported to AQS in micrograms per cubic meter ($\mu g/m^3$) to at least one decimal place. If concentrations are reported to one

decimal place, additional digits to the right of the tenths decimal place shall be truncated. If concentrations are reported to AQS with more than one decimal place, AQS will truncate the value to one decimal place for NAAQS usage (i.e., for implementing the procedures in this appendix). In situations where suitable $PM_{2.5}$ data are available to EPA but not reported to AQS, the same truncation protocol shall be applied to that data. In situations where $PM_{2.5}$ mass data are submitted to AQS, or are otherwise available, with less precision than specified above, these data shall nevertheless still be deemed appropriate for NAAQS usage.

(c) Twenty-four-hour average concentrations will be computed in AQS from submitted hourly $PM_{2.5}$ concentration data for each corresponding day of the year and the result will be stored in the first, or start, hour (i.e., midnight, hour '0') of the 24-hour period. A 24-hour average concentration shall be considered valid if at least 75 percent of the hourly averages (i.e., 18 hourly values) for the 24-hour period are available. In the event that less than all 24 hourly average concentrations are available (i.e., less than 24, but at least 18), the 24-hour average concentration shall be computed on the basis of the hours available using the number of available hours within the 24-hour period as the divisor (e.g., 19, if 19 hourly values are available). Twenty-four-hour periods with seven or more missing hours shall also be considered valid if, after substituting zero for all missing hourly concentrations, the resulting 24-hour average daily value is greater than the level of the 24-hour $PM_{2.5}$ NAAQS (i.e., greater than or equal to 35.5 $\mu g/m^3$). Twenty-four hour average $PM_{2.5}$ mass concentrations that are averaged in AQS from hourly values will be truncated to one decimal place, consistent with the data handling procedure for the reported hourly (and also 24-hour filter-based) data.

(d) All calculations shown in this appendix shall be implemented on a site-level basis. Site level concentration data shall be processed as follows:

(1) The default dataset for $PM_{2.5}$ mass concentrations for a site shall consist of the measured concentrations recorded from the designated primary monitor(s). All daily values produced by the primary monitor are considered part of the site record; this includes all creditable samples and all extra samples.

(2) Data for the primary monitors shall be augmented as much as possible with data from collocated monitors. If a valid daily value is not produced by the primary monitor for a particular day (scheduled or otherwise), but a value is available from a collocated monitor, then that collocated value shall be considered part of the combined site data record. If more than one collocated daily value is available, the average of those valid collocated values shall be used as the daily value. The data record resulting from this procedure is referred to as the ''combined site data record.''

(e) All daily values in a combined site data record are used in the calculations specified in this appendix; however, not all daily values are given credit towards data completeness requirements. Only creditable samples are given credit for data completeness. Creditable samples include daily values in the combined site record that are collected on scheduled sampling days and valid make-up samples taken for missed or invalidated samples on scheduled sampling days. Days are considered scheduled according to the required sampling frequency of the designated primary monitor with one exception. The exception is, if a collocated continuous FEM/ARM monitor has a more intensive sampling frequency than the primary FRM monitor, then samples contributed to the combined site record from that continuous FEM/ARM monitor are always considered scheduled and, hence, also creditable. Daily values in the combined site data record that are reported for nonscheduled days, but that are not valid make-up samples are referred to as extra samples.

4.0 Comparisons With the Annual and 24-Hour $PM_{2.5}$ NAAQS

4.1 Annual $PM_{2.5}$ NAAQS

(a) The primary annual $PM_{2.5}$ NAAQS is met when the annual $PM_{2.5}$ NAAQS DV is less than or equal to 12.0 $\mu g/m^3$ at each eligible monitoring site. The secondary annual $PM_{2.5}$ NAAQS is met when the annual $PM_{2.5}$ NAAQS DV is less than or equal to 15.0 $\mu g/m^3$ at each eligible monitoring site.

(b) Three years of valid annual means are required to produce a valid annual $PM_{2.5}$ NAAQS DV. A year meets data completeness requirements when quarterly data capture rates for all four quarters are at least 75 percent. However, years with at least 11 creditable samples in each quarter shall also be considered valid if the resulting annual mean or resulting annual $PM_{2.5}$ NAAQS DV (rounded according to the conventions of section 4.3 of this appendix) is greater than the level of the applicable primary or secondary annual $PM_{2.5}$ NAAQS. Furthermore, where the explicit 75 percent data capture and/or 11 sample minimum requirements are not met, the 3-year annual $PM_{2.5}$ NAAQS DV shall still be considered valid if it passes at least one of the two data substitution tests stipulated below.

(c) In the case of one, two, or three years that do not meet the completeness requirements of section 4.1(b) of this appendix and thus would normally not be useable for the calculation of a valid annual $PM_{2.5}$ NAAQS DV, the annual $PM_{2.5}$ NAAQS DV shall nevertheless be considered valid if one of the test

conditions specified in sections 4.1(c)(i) and 4.1(c)(ii) of this appendix is met.

(i) An annual $PM_{2.5}$ NAAQS DV that is above the level of the NAAQS can be validated if it passes the minimum quarterly value data substitution test. This type of data substitution is permitted only if there are at least 30 days across the three quarters of the three years under consideration (e.g., collectively, quarter 1 of year 1, quarter 1 of year 2 and quarter 1 of year 3) from which to select the quarter-specific low value. Data substitution will be performed in all quarter periods that have less than 11 creditable samples.

Procedure: Identify for each deficient quarter (i.e., those with less than 11 creditable samples) the lowest reported daily value for that quarter, looking across those three months of all three years under consideration. If after substituting the lowest reported daily value for a quarter for $(11 - cn)$ daily values in the matching deficient quarter(s) (i.e., to bring the creditable number for those quarters up to 11), the procedure yields a recalculated annual $PM_{2.5}$ NAAQS test DV (TDV_{min}) that is greater than the level of the standard, then the annual $PM_{2.5}$ NAAQS DV is deemed to have passed the diagnostic test and is valid, and the annual $PM_{2.5}$ NAAQS is deemed to have been violated in that 3-year period.

(ii) An annual $PM_{2.5}$ NAAQS DV that is equal to or below the level of the NAAQS can be validated if it passes the maximum quarterly value data substitution test. This type of data substitution is permitted only if there is at least 50 percent data capture in each quarter that is deficient of 75 percent data capture in each of the three years under consideration. Data substitution will be performed in all quarter periods that have less than 75 percent data capture but at least 50 percent data capture. If any quarter has less than 50 percent data capture then this substitution test cannot be used.

Procedure: Identify for each deficient quarter (i.e., those with less than 75 percent but at least 50 percent data capture) the highest reported daily value for that quarter, excluding state-flagged data affected by exceptional events which have been approved for exclusion by the Administrator, looking across those three quarters of all three years under consideration. If after substituting the highest reported daily $PM_{2.5}$ value for a quarter for all missing daily data in the matching deficient quarter(s) (i.e., to make those quarters 100 percent complete), the procedure yields a recalculated annual $PM_{2.5}$ NAAQS test DV (TDV_{max}) that is less than or equal to the level of the standard, then the annual $PM_{2.5}$ NAAQS DV is deemed to have passed the diagnostic test and is valid, and the annual $PM_{2.5}$ NAAQS is deemed to have been met in that 3-year period.

(d) An annual $PM_{2.5}$ NAAQS DV based on data that do not meet the completeness criteria stated in 4(b) and also do not satisfy the test conditions specified in section 4(c), may also be considered valid with the approval of, or at the initiative of, the EPA Administrator, who may consider factors such as monitoring site closures/moves, monitoring diligence, the consistency and levels of the daily values that are available, and nearby concentrations in determining whether to use such data.

(e) The equations for calculating the annual $PM_{2.5}$ NAAQS DVs are given in section 4.4 of this appendix.

4.2 Twenty-four-hour $PM_{2.5}$ NAAQS

(a) The primary and secondary 24-hour $PM_{2.5}$ NAAQS are met when the 24-hour $PM_{2.5}$ NAAQS DV at each eligible monitoring site is less than or equal to 35 $\mu g/m^3$.

(b) Three years of valid annual $PM_{2.5}$ 98th percentile mass concentrations are required to produce a valid 24-hour $PM_{2.5}$ NAAQS DV. A year meets data completeness requirements when quarterly data capture rates for all four quarters are at least 75 percent. However, years shall be considered valid, notwithstanding quarters with less than complete data (even quarters with less than 11 creditable samples, but at least one creditable sample must be present for the year), if the resulting annual 98th percentile value or resulting 24-hour NAAQS DV (rounded according to the conventions of section 4.3 of this appendix) is greater than the level of the standard. Furthermore, where the explicit 75 percent quarterly data capture requirement is not met, the 24-hour $PM_{2.5}$ NAAQS DV shall still be considered valid if it passes the maximum quarterly value data substitution test.

(c) In the case of one, two, or three years that do not meet the completeness requirements of section 4.2(b) of this appendix and thus would normally not be useable for the calculation of a valid 24-hour $PM_{2.5}$ NAAQS DV, the 24-hour $PM_{2.5}$ NAAQS DV shall nevertheless be considered valid if the test conditions specified in section 4.2(c)(i) of this appendix are met.

(i) A $PM_{2.5}$ 24-hour mass NAAQS DV that is equal to or below the level of the NAAQS can be validated if it passes the maximum quarterly value data substitution test. This type of data substitution is permitted only if there is at least 50 percent data capture in each quarter that is deficient of 75 percent data capture in each of the three years under consideration. Data substitution will be performed in all quarters that have less than 75 percent data capture but at least 50 percent data capture. If any quarter has less than 50 percent data capture then this substitution test cannot be used.

Procedure: Identify for each deficient quarter (i.e., those with less than 75 percent but

at least 50 percent data capture) the highest reported daily $PM_{2.5}$ value for that quarter, excluding state-flagged data affected by exceptional events which have been approved for exclusion by the Regional Administrator, looking across those three quarters of all three years under consideration. If, after substituting the highest reported daily maximum $PM_{2.5}$ value for a quarter for all missing daily data in the matching deficient quarter(s) (i.e., to make those quarters 100 percent complete), the procedure yields a recalculated 3-year 24-hour NAAQS test DV (TDV_{max}) less than or equal to the level of the standard, then the 24-hour $PM_{2.5}$ NAAQS DV is deemed to have passed the diagnostic test and is valid, and the 24-hour $PM_{2.5}$ NAAQS is deemed to have been met in that 3-year period.

(d) A 24-hour $PM_{2.5}$ NAAQS DV based on data that do not meet the completeness criteria stated in section 4(b) of this appendix and also do not satisfy the test conditions specified in section 4(c) of this appendix, may also be considered valid with the approval of, or at the initiative of, the EPA Administrator, who may consider factors such as monitoring site closures/moves, monitoring diligence, the consistency and levels of the daily values that are available, and nearby concentrations in determining whether to use such data.

(e) The procedures and equations for calculating the 24-hour $PM_{2.5}$ NAAQS DVs are given in section 4.5 of this appendix.

4.3 Rounding Conventions. For the purposes of comparing calculated $PM_{2.5}$ NAAQS DVs to the applicable level of the standard, it is necessary to round the final results of the calculations described in sections 4.4 and 4.5 of this appendix. Results for all intermediate calculations shall not be rounded.

(a) Annual $PM_{2.5}$ NAAQS DVs shall be rounded to the nearest tenth of a $\mu g/m^3$ (decimals x.x5 and greater are rounded up to the next tenth, and any decimal lower than x.x5 is rounded down to the nearest tenth).

(b) Twenty-four-hour $PM_{2.5}$ NAAQS DVs shall be rounded to the nearest 1 $\mu g/m^3$ (decimals 0.5 and greater are rounded up to the nearest whole number, and any decimal lower than 0.5 is rounded down to the nearest whole number).

4.4 Equations for the Annual $PM_{2.5}$ NAAQS.

(a) An annual mean value for $PM_{2.5}$ is determined by first averaging the daily values of a calendar quarter using equation 1 of this appendix:

Equation 1

$$\overline{X}_{q,y} = \frac{1}{n_q} \sum_{i=1}^{n_q} X_{i,q,y}$$

Where:

$\bar{X}_{q,y}$ = the mean for quarter q of the year y;
n_q = the number of daily values in the quarter; and
$x_{i\ q,y}$ = the i^{th} value in quarter q for year y.

(b) Equation 2 of this appendix is then used to calculate the site annual mean:

Equation 2

$$\overline{X}_{y} = \frac{1}{4} \sum_{q=1}^{4} \overline{X}_{q,y}$$

Where:

$\bar{X}_y$ = the annual mean concentration for year y (y = 1, 2, or 3); and
$\bar{X}_{q,y}$ = the mean for quarter q of year y (result of equation 1).

(c) The annual $PM_{2.5}$ NAAQS DV is calculated using equation 3 of this appendix:

Equation 3

$$\overline{X} = \frac{1}{3}\sum_{y=1}^{3}\overline{X}_y$$

Where:

$\bar{X}$ = the annual $PM_{2.5}$ NAAQS DV; and
$\bar{X}_y$ = the annual mean for year *y* (result of equation 2)

(d) The annual $PM_{2.5}$ NAAQS DV is rounded according to the conventions in section 4.3 of this appendix before comparisons with the levels of the primary and secondary annual $PM_{2.5}$ NAAQS are made.

4.5 Procedures and Equations for the 24-Hour $PM_{2.5}$ NAAQS

(a) When the data for a particular site and year meet the data completeness requirements in section 4.2 of this appendix, calculation of the 98th percentile is accomplished by the steps provided in this subsection. Table 1 of this appendix shall be used to identify annual 98th percentile values.

Identification of annual 98th percentile values using the Table 1 procedure will be based on the creditable number of samples (as described below), rather than on the actual number of samples. Credit will not be granted for extra (non-creditable) samples. Extra samples, however, are candidates for selection as the annual 98th percentile. [The creditable number of samples will determine how deep to go into the data distribution, but all samples (creditable and extra) will be considered when making the percentile assignment.] The annual creditable number of samples is the sum of the four quarterly creditable number of samples.

Procedure: Sort all the daily values from a particular site and year by descending value. (For example: (x[1], x[2], x[3], * * *, x[n]). In this case, x[1] is the largest number and x[n] is the smallest value.) The 98th percentile value is determined from this sorted series of daily values which is ordered from the highest to the lowest number. Using the left column of Table 1, determine the appropriate range for the annual creditable number of samples for year y (cn_y) (e.g., for 120 creditable samples per year, the appropriate range would be 101 to 150). The corresponding ''n'' value in the right column identifies the rank of the annual 98th percentile value in the descending sorted list of site specific daily values for year y (e.g., for the range of 101 to 150, n would be 3). Thus, $P_{0.98,\ y}$ = the n^{th} largest value (e.g., for the range of 101 to 150, the 98th percentile value would be the third highest value in the sorted series of daily values.

TABLE 1

Annual number of creditable samples for year *y* (cn_y)	The 98th percentile for year y ($P_{0.98,y}$), is the n^{th} maximum 24-hour average value for the year where *n* is the listed number
1 to 50	1
51 to 100	2
101 to 150	3
151 to 200	4
201 to 250	5
251 to 300	6
301 to 350	7
351 to 366	8

(b) The 24-hour $PM_{2.5}$ NAAQS DV is then calculated by averaging the annual 98th percentiles using equation 4 of this appendix: $P_{0.98,y}$

Equation 4

$$\overline{P}_{0.98} = \frac{1}{3}\sum_{y=1}^{3}P_{0.98,y}$$

Where:

$\bar{P}_{0.98}$ = the 24-hour $PM_{2.5}$ NAAQS DV; and
$P_{0.98,\ y}$ = the annual 98th percentile for year *y*

(c) The 24-hour $PM_{2.5}$ NAAQS DV is rounded according to the conventions in section 4.3 of this appendix before a comparison with

the level of the primary and secondary 24-hour NAAQS are made.

[78 FR 3277, Jan. 15, 2013]

APPENDIX O TO PART 50—REFERENCE METHOD FOR THE DETERMINATION OF COARSE PARTICULATE MATTER AS $PM_{10-2.5}$ IN THE ATMOSPHERE

1.0 Applicability and Definition

1.1 This method provides for the measurement of the mass concentration of coarse particulate matter ($PM_{10-2.5}$) in ambient air over a 24-hour period. In conjunction with additional analysis, this method may be used to develop speciated data.

1.2 For the purpose of this method, $PM_{10-2.5}$ is defined as particulate matter having an aerodynamic diameter in the nominal range of 2.5 to 10 micrometers, inclusive.

1.3 For this reference method, $PM_{10-2.5}$ concentrations shall be measured as the arithmetic difference between separate but concurrent, collocated measurements of PM_{10} and $PM_{2.5}$, where the PM_{10} measurements are obtained with a specially approved sampler, identified as a ''PM_{10c} sampler,'' that meets more demanding performance requirements than conventional PM_{10} samplers described in appendix J of this part. Measurements obtained with a PM_{10c} sampler are identified as ''PM_{10c} measurements'' to distinguish them from conventional PM_{10} measurements obtained with conventional PM_{10} samplers. Thus, $PM_{10-2.5} = PM_{10c} - PM_{2.5}$.

1.4 The PM_{10c} and $PM_{2.5}$ gravimetric measurement processes are considered to be nondestructive, and the PM_{10c} and $PM_{2.5}$ samples obtained in the $PM_{10-2.5}$ measurement process can be subjected to subsequent physical or chemical analyses.

1.5 Quality assessment procedures are provided in part 58, appendix A of this chapter. The quality assurance procedures and guidance provided in reference 1 in section 13 of this appendix, although written specifically for $PM_{2.5}$, are generally applicable for PM_{10c}, and, hence, $PM_{10-2.5}$ measurements under this method, as well.

1.6 A method based on specific model PM_{10c} and $PM_{2.5}$ samplers will be considered a reference method for purposes of part 58 of this chapter only if:

(a) The PM_{10c} and $PM_{2.5}$ samplers and the associated operational procedures meet the requirements specified in this appendix and all applicable requirements in part 53 of this chapter, and

(b) The method based on the specific samplers and associated operational procedures have been designated as a reference method in accordance with part 53 of this chapter.

1.7 $PM_{10-2.5}$ methods based on samplers that meet nearly all specifications set forth in this method but have one or more significant but minor deviations or modifications from those specifications may be designated as ''Class I'' equivalent methods for $PM_{10-2.5}$ in accordance with part 53 of this chapter.

1.8 $PM_{2.5}$ measurements obtained incidental to the $PM_{10-2.5}$ measurements by this method shall be considered to have been obtained with a reference method for $PM_{2.5}$ in accordance with appendix L of this part.

1.9 PM_{10c} measurements obtained incidental to the $PM_{10-2.5}$ measurements by this method shall be considered to have been obtained with a reference method for PM_{10} in accordance with appendix J of this part, provided that:

(a) The PM_{10c} measurements are adjusted to EPA reference conditions (25 °C and 760 millimeters of mercury), and

(b) Such PM_{10c} measurements are appropriately identified to differentiate them from PM_{10} measurements obtained with other (conventional) methods for PM_{10} designated in accordance with part 53 of this chapter as reference or equivalent methods for PM_{10}.

2.0 Principle

2.1 Separate, collocated, electrically powered air samplers for PM_{10c} and $PM_{2.5}$ concurrently draw ambient air at identical, constant volumetric flow rates into specially shaped inlets and through one or more inertial particle size separators where the suspended particulate matter in the PM_{10} or $PM_{2.5}$ size range, as applicable, is separated for collection on a polytetrafluoroethylene (PTFE) filter over the specified sampling period. The air samplers and other aspects of this $PM_{10-2.5}$ reference method are specified either explicitly in this appendix or by reference to other applicable regulations or quality assurance guidance.

2.2 Each PM_{10c} and $PM_{2.5}$ sample collection filter is weighed (after moisture and temperature conditioning) before and after sample collection to determine the net weight (mass) gain due to collected PM_{10c} or $PM_{2.5}$. The total volume of air sampled by each sampler is determined by the sampler from the measured flow rate at local ambient temperature and pressure and the sampling time. The mass concentrations of both PM_{10c} and $PM_{2.5}$ in the ambient air are computed as the total mass of collected particles in the PM_{10} or $PM_{2.5}$ size range, as appropriate, divided by the total volume of air sampled by the respective samplers, and expressed in micrograms per cubic meter ($\mu g/m^3$)at local temperature and pressure conditions. The mass concentration of $PM_{10-2.5}$ is determined as the PM_{10c} concentration value less the corresponding, concurrently measured $PM_{2.5}$ concentration value.

2.3 Most requirements for $PM_{10-2.5}$ reference methods are similar or identical to the requirements for $PM_{2.5}$ reference methods as set forth in appendix L to this part. To insure uniformity, applicable appendix L

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EPA Reference Methods

Appendix A-1 to Part 50 - Reference Measurement Principle and Calibration Procedure for the Measurement of Sulfur Dioxide in the Atmosphere (Ultraviolet Fluorescence Method)

1.0 Applicability

1.1 This ultraviolet fluorescence (UVF) method provides a measurement of the concentration of sulfur dioxide (SO_2) in ambient air for determining compliance with the national primary and secondary ambient air quality standards for sulfur oxides (sulfur dioxide) as specified in § 50.4, § 50.5, and § 50.17 of this chapter. The method is applicable to the measurement of ambient SO_2 concentrations using continuous (real-time) sampling. Additional quality assurance procedures and guidance are provided in part 58, appendix A, of this chapter and in Reference 3.

2.0 Principle

2.1 This reference method is based on automated measurement of the intensity of the characteristic fluorescence released by SO_2 in an ambient air sample contained in a measurement cell of an analyzer when the air sample is irradiated by ultraviolet (UV) light passed through the cell. The fluorescent light released by the SO_2 is also in the ultraviolet region, but at longer wavelengths than the excitation light. Typically, optimum instrumental measurement of SO_2 concentrations is obtained with an excitation wavelength in a band between approximately 190 to 230 nm, and measurement of the SO_2 fluorescence in a broad band around 320 nm, but these wavelengths are not necessarily constraints of this reference method. Generally, the measurement system (analyzer) also requires means to reduce the effects of aromatic hydrocarbon species, and possibly other compounds, in the air sample to control measurement interferences from these compounds, which may be present in the ambient air. References 1 and 2 describe UVF method.

2.2 The measurement system is calibrated by referencing the instrumental fluorescence measurements to SO_2 standard concentrations traceable to a National Institute of Standards and Technology (NIST) primary standard for SO_2 (*see* Calibration Procedure below).

2.3 An analyzer implementing this measurement principle is shown schematically in Figure 1. Designs should include a measurement cell, a UV light source of appropriate wavelength, a UV detector system with appropriate wave length sensitivity, a pump and flow control system for sampling the ambient air and moving it into the measurement cell, sample air conditioning components as necessary to minimize measurement interferences, suitable control and measurement processing capability, and other apparatus as may be necessary. The analyzer must be designed to provide accurate, repeatable, and continuous measurements of SO_2 concentrations in ambient air, with measurement performance as specified in Subpart B of Part 53 of this chapter.

2.4 *Sampling considerations:* The use of a particle filter on the sample inlet line of a UVF SO_2 analyzer is required to prevent interference, malfunction, or damage due to particles in the sampled air.

3.0 Interferences

3.1 The effects of the principal potential interferences may need to be mitigated to meet the interference equivalent requirements of part 53 of this chapter. Aromatic hydrocarbons such as xylene and naphthalene can fluoresce and act as strong positive interferences. These gases can be removed by using a permeation type scrubber (hydrocarbon “kicker”). Nitrogen oxide (NO) in high concentrations can also fluoresce and cause positive interference. Optical filtering can be employed to improve the rejection of interference from high NO. Ozone can absorb UV light given off by the SO_2 molecule and cause a measurement offset. This effect can be reduced by minimizing the measurement path length between the area where SO_2 fluorescence occurs and the photomultiplier tube detector (e.g., <5 cm). A hydrocarbon scrubber, optical filter and appropriate distancing of the measurement path length may be required method components to reduce interference.

4.0 Calibration Procedure

Atmospheres containing accurately known concentrations of sulfur dioxide are prepared using a compressed gas transfer standard diluted with accurately metered clean air flow rates.

4.1 *Apparatus:* Figure 2 shows a typical generic system suitable for diluting a SO_2 gas cylinder concentration standard with clean air through a mixing chamber to produce the desired calibration concentration standards. A valve may be used to conveniently divert the SO_2 from the sampling manifold to provide clean zero air at the output manifold for zero adjustment. The system may be made up using common laboratory components, or it may be a commercially manufactured system. In either case, the principle components are as follows:

4.1.1 SO_2 standard gas flow control and measurement devices (or a combined device) capable of regulating and maintaining the standard gas flow rate constant to within ±2 percent and measuring the gas flow rate accurate to within ±2, properly calibrated to a NIST-traceable standard.

4.1.2 Dilution air flow control and measurement devices (or a combined device) capable of regulating and maintaining the air flow rate constant to within ±2 percent and measuring the air flow rate accurate to within ±2, properly calibrated to a NIST-traceable standard.

4.1.3 Mixing chamber, of an inert material such as glass and of proper design to provide thorough mixing of pollutant gas and diluent air streams.

4.1.4 Sampling manifold, constructed of glass, polytetrafluoroethylene (PTFE Teflon TM), or other suitably inert material and of sufficient diameter to insure a minimum pressure drop at the analyzer connection, with a vent designed to insure a minimum over-pressure (relative to ambient air pressure) at the analyzer connection and to prevent ambient air from entering the manifold.

4.1.5 Standard gas pressure regulator, of clean stainless steel with a stainless steel diaphragm, suitable for use with a high pressure SO_2 gas cylinder.

4.1.6 Reagents
4.1.6.1 SO_2 gas concentration transfer standard having a certified SO_2 concentration of not less than 10 ppm, in N_2, traceable to a NIST Standard Reference Material (SRM).

4.1.6.2 Clean zero air, free of contaminants that could cause a detectable response or a change in sensitivity of the analyzer. Since ultraviolet fluorescence analyzers may be sensitive to aromatic hydrocarbons and O_2-to-N_2 ratios, it is important that the clean zero air contains less than 0.1 ppm aromatic hydrocarbons and O_2 and N_2 percentages approximately the same as in ambient air. A procedure for generating zero air is given in reference 1.

4.2 Procedure
4.2.1 Obtain a suitable calibration apparatus, such as the one shown schematically in Figure 1, and verify that all materials in contact with the pollutant are of glass, Teflon TM, or other suitably inert material and completely clean.

4.2.2 Purge the SO_2 standard gas lines and pressure regulator to remove any residual air.

4.2.3 Ensure that there are no leaks in the system and that the flow measuring devices are properly and accurately calibrated under the conditions of use against a reliable volume or flow rate standard such as a soap-bubble meter or a wet-test meter traceable to a NIST standard. All volumetric flow rates should be corrected to the same reference temperature and pressure by using the formula below:

$$F_c = F_m \frac{298.15 P_m}{760(T_m + 273.15)}$$

Where:
F_c = corrected flow rate (L/min at 25 °C and 760 mm Hg),
F_m = measured flow rate, (at temperature, T_m and pressure, P_m),

*P*m = measured pressure in mm Hg, (absolute), and
*T*m = measured temperature in degrees Celsius.
4.2.4 Allow the SO_2 analyzer under calibration to sample zero air until a stable response is obtained, then make the proper zero adjustment.

4.2.5 Adjust the airflow to provide an SO_2 concentration of approximately 80 percent of the upper measurement range limit of the SO_2 instrument and verify that the total air flow of the calibration system exceeds the demand of all analyzers sampling from the output manifold (with the excess vented).

4.2.6 Calculate the actual SO_2 calibration concentration standard as:

$$[SO_2] = C\frac{F_p}{F_t}$$

Where:
C = the concentration of the SO_2 gas standard
*F*p = the flow rate of SO_2 gas standard
*F*t = the total air flow rate of pollutant and diluent gases
4.2.7 When the analyzer response has stabilized, adjust the SO_2 span control to obtain the desired response equivalent to the calculated standard concentration. If substantial adjustment of the span control is needed, it may be necessary to re-check the zero and span adjustments by repeating steps 4.2.4 through 4.2.7 until no further adjustments are needed.

4.2.8 Adjust the flow rate(s) to provide several other SO_2 calibration concentrations over the analyzer's measurement range. At least five different concentrations evenly spaced throughout the analyzer's range are suggested.

4.2.9 Plot the analyzer response (vertical or Y-axis) versus SO_2 concentration (horizontal or X-axis). Compute the linear regression slope and intercept and plot the regression line to verify that no point deviates from this line by more than 2 percent of the maximum concentration tested.

NOTE:
Additional information on calibration and pollutant standards is provided in Section 12 of Reference 3.

5.0 FREQUENCY OF CALIBRATION

The frequency of calibration, as well as the number of points necessary to establish the calibration curve and the frequency of other performance checking will vary by analyzer; however, the minimum frequency, acceptance criteria, and subsequent actions are specified in Reference 3, Appendix D: Measurement Quality Objectives and Validation Template for SO_2 (page 9 of 30). The user's quality control program should provide guidelines for initial establishment of these variables and for subsequent alteration as operational experience is accumulated. Manufacturers of analyzers should include in their instruction/operation manuals information and guidance as to these variables and on other matters of operation, calibration, routine maintenance, and quality control.

6.0 REFERENCES FOR SO_2 METHOD

1. H. Okabe, P. L. Splitstone, and J. J. Ball, “Ambient and Source SO_2 Detector Based on a Fluorescence Method”, *Journal of the Air Control Pollution Association,* vol. 23, p. 514-516 (1973).
2. F. P. Schwarz, H. Okabe, and J. K. Whittaker, “Fluorescence Detection of Sulfur Dioxide in Air at the Parts per Billion Level,” *Analytical Chemistry,* vol. 46, pp. 1024-1028 (1974).
3. *QA Handbook for Air Pollution Measurement Systems - Volume II. Ambient Air Quality Monitoring Programs.* U.S.

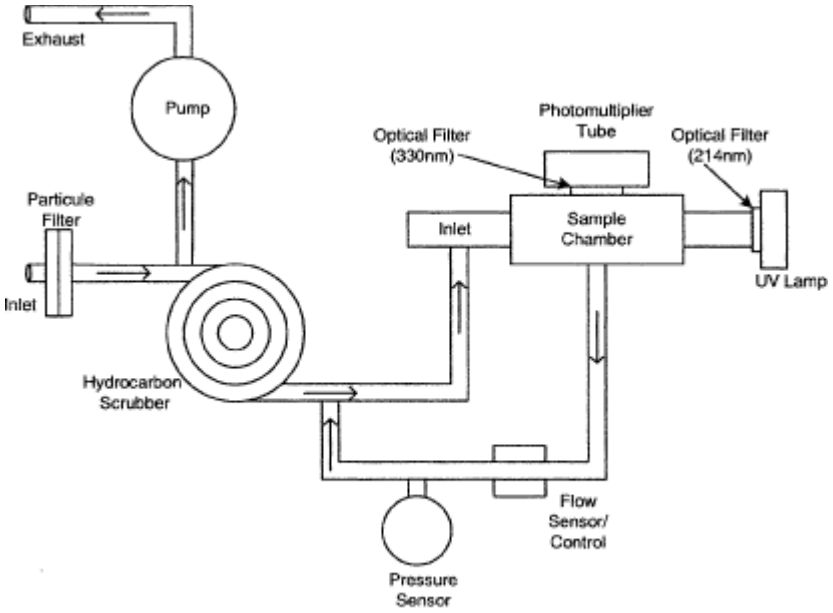

Figure 1. UVF SO_2 analyzer schematic diagram.

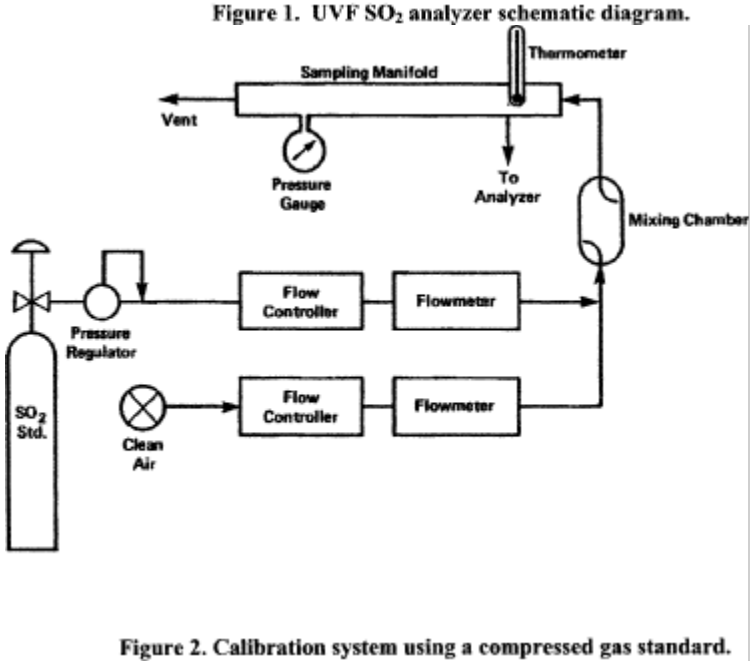

Figure 2. Calibration system using a compressed gas standard.

[75 FR 35593, June 22, 2010]

Appendix A-2 to Part 50 - Reference Method for the Determination of Sulfur Dioxide in the Atmosphere (Pararosaniline Method)

1.0 Applicability.

1.1 This method provides a measurement of the concentration of sulfur dioxide (SO2) in ambient air for determining compliance with the primary and secondary national ambient air quality standards for sulfur oxides (sulfur dioxide) as specified in § 50.4 and § 50.5 of this chapter. The method is applicable to the measurement of ambient SO2 concentrations using sampling periods ranging from 30 minutes to 24 hours. Additional quality assurance procedures and guidance are provided in part 58, appendixes A and B, of this chapter and in references 1 and 2.

2.0 Principle.

2.1 A measured volume of air is bubbled through a solution of 0.04 M potassium tetrachloromercurate (TCM). The SO2 present in the air stream reacts with the TCM solution to form a stable monochlorosulfonatomercurate(3) complex. Once formed, this complex resists air oxidation(4, 5) and is stable in the presence of strong oxidants such as ozone and oxides of nitrogen. During subsequent analysis, the complex is reacted with acid-bleached pararosaniline dye and formaldehyde to form an intensely colored pararosaniline methyl sulfonic acid.

(6) The optical density of this species is determined spectrophotometrically at 548 nm and is directly related to the amount of SO2 collected. The total volume of air sampled, corrected to EPA reference conditions (25 °C, 760 mm Hg [101 kPa]), is determined from the measured flow rate and the sampling time. The concentration of SO2 in the ambient air is computed and expressed in micrograms per standard cubic meter (µg/std m 3).

3.0 Range.

3.1 The lower limit of detection of SO2 in 10 mL of TCM is 0.75 µg (based on collaborative test results).(7) This represents a concentration of 25 µg SO2/m 3 (0.01 ppm) in an air sample of 30 standard liters (short-term sampling) and a concentration of 13 µg SO2/m 3 (0.005 ppm) in an air sample of 288 standard liters (long-term sampling). Concentrations less than 25 µg SO2/m 3 can be measured by sampling larger volumes of ambient air; however, the collection efficiency falls off rapidly at low concentrations.(8, 9) Beer's law is adhered to up to 34 µg of SO2 in 25 mL of final solution. This upper limit of the analysis range represents a concentration of 1,130 µg SO2/m 3 (0.43 ppm) in an air sample of 30 standard liters and a concentration of 590 µg SO2/m 3 (0.23 ppm) in an air sample of 288 standard liters. Higher concentrations can be measured by collecting a smaller volume of air, by increasing the volume of absorbing solution, or by diluting a suitable portion of the collected sample with absorbing solution prior to analysis.

4.0 Interferences.

4.1 The effects of the principal potential interferences have been minimized or eliminated in the following manner: Nitrogen oxides by the addition of sulfamic acid,(10, 11) heavy metals by the addition of ethylenediamine tetracetic acid disodium salt (EDTA) and phosphoric acid,(10, 12) and ozone by time delay.(10) Up to 60 µg Fe (III), 22 µg V (V), 10 µg Cu (II), 10 µg Mn (II),

and 10 µg Cr (III) in 10 mL absorbing reagent can be tolerated in the procedure.(10) No significant interference has been encountered with 2.3 µg NH3.(13)

5.0 Precision and Accuracy.

5.1 The precision of the analysis is 4.6 percent (at the 95 percent confidence level) based on the analysis of standard sulfite samples.(10)

5.2 Collaborative test results (14) based on the analysis of synthetic test atmospheres (SO2 in scrubbed air) using the 24-hour sampling procedure and the sulfite-TCM calibration procedure show that:

• The replication error varies linearly with concentration from ±2.5 µg/m 3 at concentrations of 100 µg/m 3 to ±7 µg/m 3 at concentrations of 400 µg/m 3.

• The day-to-day variability within an individual laboratory (repeatability) varies linearly with concentration from ±18.1 µg/m 3 at levels of 100 µg/m 3 to ±50.9 µg/m 3 at levels of 400 µg/m 3.

• The day-to-day variability between two or more laboratories (reproducibility) varies linearly with concentration from ±36.9 µg/m 3 at levels of 100 µg/m 3 to ±103.5 µ g/m 3 at levels of 400 µg/m 3.

• The method has a concentration-dependent bias, which becomes significant at the 95 percent confidence level at the high concentration level. Observed values tend to be lower than the expected SO2 concentration level.

6.0 Stability.

6.1 By sampling in a controlled temperature environment of 15° ±10 °C, greater than 98.9 percent of the SO2-TCM complex is retained at the completion of sampling. (15) If kept at 5 °C following the completion of sampling, the collected sample has been found to be stable for up to 30 days. (10) The presence of EDTA enhances the stability of SO2 in the TCM solution and the rate of decay is independent of the concentration of SO2. (16)

7.0 Apparatus.

7.1 Sampling.

7.1.1 Sample probe: A sample probe meeting the requirements of section 7 of 40 CFR part 58, appendix E (Teflon ® or glass with residence time less than 20 sec.) is used to transport ambient air to the sampling train location. The end of the probe should be designed or oriented to preclude the sampling of precipitation, large particles, etc. A suitable probe can be constructed from Teflon ® tubing connected to an inverted funnel.

7.1.2 Absorber - short-term sampling: An all glass midget impinger having a solution capacity of 30 mL and a stem clearance of 4 ±1 mm from the bottom of the vessel is used for sampling periods of 30 minutes and 1 hour (or any period considerably less than 24 hours). Such an

impinger is shown in Figure 1. These impingers are commercially available from distributors such as Ace Glass, Incorporated.

7.1.3 Absorber - 24-hour sampling: A polypropylene tube 32 mm in diameter and 164 mm long (available from Bel Art Products, Pequammock, NJ) is used as the absorber. The cap of the absorber must be a polypropylene cap with two ports (rubber stoppers are unacceptable because the absorbing reagent can react with the stopper to yield erroneously high SO2 concentrations). A glass impinger stem, 6 mm in diameter and 158 mm long, is inserted into one port of the absorber cap. The tip of the stem is tapered to a small diameter orifice (0.4 ±0.1 mm) such that a No. 79 jeweler's drill bit will pass through the opening but a No. 78 drill bit will not. Clearance from the bottom of the absorber to the tip of the stem must be 6 ±2 mm. Glass stems can be fabricated by any reputable glass blower or can be obtained from a scientific supply firm. Upon receipt, the orifice test should be performed to verify the orifice size. The 50 mL volume level should be permanently marked on the absorber. The assembled absorber is shown in Figure 2.

7.1.4 Moisture trap: A moisture trap constructed of a glass trap as shown in Figure 1 or a polypropylene tube as shown in Figure 2 is placed between the absorber tube and flow control device to prevent entrained liquid from reaching the flow control device. The tube is packed with indicating silica gel as shown in Figure 2. Glass wool may be substituted for silica gel when collecting short-term samples (1 hour or less) as shown in Figure 1, or for long term (24 hour) samples if flow changes are not routinely encountered.

7.1.5 Cap seals: The absorber and moisture trap caps must seal securely to prevent leaks during use. Heat-shrink material as shown in Figure 2 can be used to retain the cap seals if there is any chance of the caps coming loose during sampling, shipment, or storage.

7.1.6 Flow control device: A calibrated rotameter and needle valve combination capable of maintaining and measuring air flow to within ±2 percent is suitable for short-term sampling but may not be used for long-term sampling. A critical orifice can be used for regulating flow rate for both long-term and short-term sampling. A 22-gauge hypodermic needle 25 mm long may be used as a critical orifice to yield a flow rate of approximately 1 L/min for a 30-minute sampling period. When sampling for 1 hour, a 23-gauge hypodermic needle 16 mm in length will provide a flow rate of approximately 0.5 L/min. Flow control for a 24-hour sample may be provided by a 27-gauge hypodermic needle critical orifice that is 9.5 mm in length. The flow rate should be in the range of 0.18 to 0.22 L/min.

7.1.7 Flow measurement device: Device calibrated as specified in 9.4.1 and used to measure sample flow rate at the monitoring site.

7.1.8 Membrane particle filter: A membrane filter of 0.8 to 2 µm porosity is used to protect the flow controller from particles during long-term sampling. This item is optional for short-term sampling.

7.1.9 Vacuum pump: A vacuum pump equipped with a vacuum gauge and capable of maintaining at least 70 kPa (0.7 atm) vacuum differential across the flow control device at the specified flow rate is required for sampling.

7.1.10 Temperature control device: The temperature of the absorbing solution during sampling must be maintained at 15° ±10 °C. As soon as possible following sampling and until analysis, the temperature of the collected sample must be maintained at 5° ±5 °C. Where an extended period of time may elapse before the collected sample can be moved to the lower storage temperature, a collection temperature near the lower limit of the 15 ±10 °C range should be used to minimize losses during this period. Thermoelectric coolers specifically designed for this temperature control are available commercially and normally operate in the range of 5° to 15 °C. Small refrigerators can be modified to provide the required temperature control; however, inlet lines must be insulated from the lower temperatures to prevent condensation when sampling under humid conditions. A small heating pad may be necessary when sampling at low temperatures (<7 °C) to prevent the absorbing solution from freezing.(17)

7.1.11 Sampling train container: The absorbing solution must be shielded from light during and after sampling. Most commercially available sampler trains are enclosed in a light-proof box.

7.1.12 Timer: A timer is recommended to initiate and to stop sampling for the 24-hour period. The timer is not a required piece of equipment; however, without the timer a technician would be required to start and stop the sampling manually. An elapsed time meter is also recommended to determine the duration of the sampling period.

7.2 Shipping.

7.2.1 Shipping container: A shipping container that can maintain a temperature of 5° ±5 °C is used for transporting the sample from the collection site to the analytical laboratory. Ice coolers or refrigerated shipping containers have been found to be satisfactory. The use of eutectic cold packs instead of ice will give a more stable temperature control. Such equipment is available from Cole-Parmer Company, 7425 North Oak Park Avenue, Chicago, IL 60648.

7.3 Analysis.

7.3.1 Spectrophotometer: A spectrophotometer suitable for measurement of absorbances at 548 nm with an effective spectral bandwidth of less than 15 nm is required for analysis. If the spectrophotometer reads out in transmittance, convert to absorbance as follows:

$$A = \log_{10}(1/T) \qquad (1)$$

where:

A = absorbance, and

T = transmittance ($0 \leq T < 1$).

A standard wavelength filter traceable to the National Bureau of Standards is used to verify the wavelength calibration according to the procedure enclosed with the filter. The wavelength

calibration must be verified upon initial receipt of the instrument and after each 160 hours of normal use or every 6 months, whichever occurs first.

7.3.2 Spectrophotometer cells: A set of 1-cm path length cells suitable for use in the visible region is used during analysis. If the cells are unmatched, a matching correction factor must be determined according to Section 10.1.

7.3.3 Temperature control device: The color development step during analysis must be conducted in an environment that is in the range of 20° to 30 °C and controlled to ±1 °C. Both calibration and sample analysis must be performed under identical conditions (within 1 °C). Adequate temperature control may be obtained by means of constant temperature baths, water baths with manual temperature control, or temperature controlled rooms.

7.3.4 Glassware: Class A volumetric glassware of various capacities is required for preparing and standardizing reagents and standards and for dispensing solutions during analysis. These included pipets, volumetric flasks, and burets.

7.3.5 TCM waste receptacle: A glass waste receptacle is required for the storage of spent TCM solution. This vessel should be stoppered and stored in a hood at all times.

8.0 Reagents.

8.1 Sampling.

8.1.1 Distilled water: Purity of distilled water must be verified by the following procedure:(18)

• Place 0.20 mL of potassium permanganate solution (0.316 g/L), 500 mL of distilled water, and 1mL of concentrated sulfuric acid in a chemically resistant glass bottle, stopper the bottle, and allow to stand.

• If the permanganate color (pink) does not disappear completely after a period of 1 hour at room temperature, the water is suitable for use.

• If the permanganate color does disappear, the water can be purified by redistilling with one crystal each of barium hydroxide and potassium permanganate in an all glass still.

8.1.2 Absorbing reagent (0.04 M potassium tetrachloromercurate [TCM]): Dissolve 10.86 g mercuric chloride, 0.066 g EDTA, and 6.0 g potassium chloride in distilled water and dilute to volume with distilled water in a 1,000-mL volumetric flask. (Caution: Mercuric chloride is highly poisonous. If spilled on skin, flush with water immediately.) The pH of this reagent should be between 3.0 and 5.0 (10) Check the pH of the absorbing solution by using pH indicating paper or a pH meter. If the pH of the solution is not between 3.0 and 5.0, dispose of the solution according to one of the disposal techniques described in Section 13.0. The absorbing reagent is normally stable for 6 months. If a precipitate forms, dispose of the reagent according to one of the procedures described in Section 13.0.

8.2 Analysis.

8.2.1 Sulfamic acid (0.6%): Dissolve 0.6 g sulfamic acid in 100 mL distilled water. Perpare fresh daily.

8.2.2 Formaldehyde (0.2%): Dilute 5 mL formaldehyde solution (36 to 38 percent) to 1,000 mL with distilled water. Prepare fresh daily.

8.2.3 Stock iodine solution (0.1 N): Place 12.7 g resublimed iodine in a 250-mL beaker and add 40 g potassium iodide and 25 mL water. Stir until dissolved, transfer to a 1,000 mL volumetric flask and dilute to volume with distilled water.

8.2.4 Iodine solution (0.01 N): Prepare approximately 0.01 N iodine solution by diluting 50 mL of stock iodine solution (Section 8.2.3) to 500 mL with distilled water.

8.2.5 Starch indicator solution: Triturate 0.4 g soluble starch and 0.002 g mercuric iodide (preservative) with enough distilled water to form a paste. Add the paste slowly to 200 mL of boiling distilled water and continue boiling until clear. Cool and transfer the solution to a glass stopperd bottle.

8.2.6 1 N hydrochloric acid: Slowly and while stirring, add 86 mL of concentrated hydrochloric acid to 500 mL of distilled water. Allow to cool and dilute to 1,000 mL with distilled water.

8.2.7 Potassium iodate solution: Accurately weigh to the nearest 0.1 mg, 1.5 g (record weight) of primary standard grade potassium iodate that has been previously dried at 180 °C for at least 3 hours and cooled in a dessicator. Dissolve, then dilute to volume in a 500-mL volumetric flask with distilled water.

8.2.8 Stock sodium thiosulfate solution (0.1 N): Prepare a stock solution by dissolving 25 g sodium thiosulfate (Na2 S2 O3 ÷ 5H2 O) in 1,000 mL freshly boiled, cooled, distilled water and adding 0.1 g sodium carbonate to the solution. Allow the solution to stand at least 1 day before standardizing. To standardize, accurately pipet 50 mL of potassium iodate solution (Section 8.2.7) into a 500-mL iodine flask and add 2.0 g of potassium iodide and 10 mL of 1 N HCl. Stopper the flask and allow to stand for 5 minutes. Titrate the solution with stock sodium thiosulfate solution (Section 8.2.8) to a pale yellow color. Add 5 mL of starch solution (Section 8.2.5) and titrate until the blue color just disappears. Calculate the normality (Ns) of the stock sodium thiosulfate solution as follows:

$$N_S = \frac{W}{M} \times 2.80 \qquad (2)$$

where:

M = volume of thiosulfate required in mL, and

W = weight of potassium iodate in g (recorded weight in Section 8.2.7).

$$2.80 = \frac{10^3\,(conversion\ of\ g\ to\ mg) \times 0.1\,(fraction\ iodate\ used)}{35.67\,(equivalent\ weight\ of\ potassium iodate)}$$

8.2.9 Working sodium thiosulfate titrant (0.01 N): Accurately pipet 100 mL of stock sodium thiosulfate solution (Section 8.2.8) into a 1,000-mL volumetric flask and dilute to volume with freshly boiled, cooled, distilled water. Calculate the normality of the working sodium thiosulfate titrant (NT) as follows:

$$N_T = N_S \times 0.100 \qquad (3)$$

8.2.10 Standardized sulfite solution for the preparation of working sulfite-TCM solution: Dissolve 0.30 g sodium metabisulfite (Na2 S2 O5) or 0.40 g sodium sulfite (Na2 SO3) in 500 mL of recently boiled, cooled, distilled water. (Sulfite solution is unstable; it is therefore important to use water of the highest purity to minimize this instability.) This solution contains the equivalent of 320 to 400 µg SO2/mL. The actual concentration of the solution is determined by adding excess iodine and back-titrating with standard sodium thiosulfate solution. To back-titrate, pipet 50 mL of the 0.01 N iodine solution (Section 8.2.4) into each of two 500-mL iodine flasks (A and B). To flask A (blank) add 25 mL distilled water, and to flask B (sample) pipet 25 mL sulfite solution. Stopper the flasks and allow to stand for 5 minutes. Prepare the working sulfite-TCM solution (Section 8.2.11) immediately prior to adding the iodine solution to the flasks. Using a buret containing standardized 0.01 N thiosulfate titrant (Section 8.2.9), titrate the solution in each flask to a pale yellow color. Then add 5 mL starch solution (Section 8.2.5) and continue the titration until the blue color just disappears.

8.2.11 Working sulfite-TCM solution: Accurately pipet 5 mL of the standard sulfite solution (Section 8.2.10) into a 250-mL volumetric flask and dilute to volume with 0.04 M TCM. Calculate the concentration of sulfur dioxide in the working solution as follows:

$$C_{TCM/SO2}\left(\mu g\ SO_2/mL\right) = \frac{(A-B)\left(N_T\right)(32,000)}{25} \times 0.02 \qquad (4)$$

where:

A = volume of thiosulfate titrant required for the blank, mL;

B = volume of thiosulfate titrant required for the sample, mL;

NT = normality of the thiosulfate titrant, from equation (3);

32,000 = milliequivalent weight of SO2, µg;

25 = volume of standard sulfite solution, mL; and

0.02 = dilution factor.

This solution is stable for 30 days if kept at 5 °C. (16) If not kept at 5 °C, prepare fresh daily.

8.2.12 Purified pararosaniline (PRA) stock solution (0.2% nominal):

8.2.12.1 Dye specifications -

• The dye must have a maximum absorbance at a wavelength of 540 nm when assayed in a buffered solution of 0.1 M sodium acetate-acetic acid;

• The absorbance of the reagent blank, which is temperature sensitive (0.015 absorbance unit/ °C), must not exceed 0.170 at 22 °C with a 1-cm optical path length when the blank is prepared according to the specified procedure;

• The calibration curve (Section 10.0) must have a slope equal to 0.030 ±0.002 absorbance unit/µg SO_2 with a 1-cm optical path length when the dye is pure and the sulfite solution is properly standardized.

8.2.12.2 Preparation of stock PRA solution - A specially purified (99 to 100 percent pure) solution of pararosaniline, which meets the above specifications, is commercially available in the required 0.20 percent concentration (Harleco Co.). Alternatively, the dye may be purified, a stock solution prepared, and then assayed according to the procedure as described below.(10)

8.2.12.3 Purification procedure for PRA -

1. Place 100 mL each of 1-butanol and 1 N HCl in a large separatory funnel (250-mL) and allow to equilibrate. Note: Certain batches of 1-butanol contain oxidants that create an SO_2 demand. Before using, check by placing 20 mL of 1-butanol and 5 mL of 20 percent potassium iodide (KI) solution in a 50-mL separatory funnel and shake thoroughly. If a yellow color appears in the alcohol phase, redistill the 1-butanol from silver oxide and collect the middle fraction or purchase a new supply of 1-butanol.

2. Weigh 100 mg of pararosaniline hydrochloride dye (PRA) in a small beaker. Add 50 mL of the equilibrated acid (drain in acid from the bottom of the separatory funnel in 1.) to the beaker and let stand for several minutes. Discard the remaining acid phase in the separatory funnel.

3. To a 125-mL separatory funnel, add 50 mL of the equilibrated 1-butanol (draw the 1-butanol from the top of the separatory funnel in 1.). Transfer the acid solution (from 2.) containing the dye to the funnel and shake carefully to extract. The violet impurity will transfer to the organic phase.

4. Transfer the lower aqueous phase into another separatory funnel, add 20 mL of equilibrated 1-butanol, and extract again.

5. Repeat the extraction procedure with three more 10-mL portions of equilibrated 1-butanol.

6. After the final extraction, filter the acid phase through a cotton plug into a 50-mL volumetric flask and bring to volume with 1 N HCl. This stock reagent will be a yellowish red.

7. To check the purity of the PRA, perform the assay and adjustment of concentration (Section 8.2.12.4) and prepare a reagent blank (Section 11.2); the absorbance of this reagent blank at 540 nm should be less than 0.170 at 22 °C. If the absorbance is greater than 0.170 under these conditions, further extractions should be performed.

8.2.12.4 PRA assay procedure - The concentration of pararosaniline hydrochloride (PRA) need be assayed only once after purification. It is also recommended that commercial solutions of pararosaniline be assayed when first purchased. The assay procedure is as follows:(10)

1. Prepare 1 M acetate-acetic acid buffer stock solution with a pH of 4.79 by dissolving 13.61 g of sodium acetate trihydrate in distilled water in a 100-mL volumetric flask. Add 5.70 mL of glacial acetic acid and dilute to volume with distilled water.

2. Pipet 1 mL of the stock PRA solution obtained from the purification process or from a commercial source into a 100-mL volumetric flask and dilute to volume with distilled water.

3. Transfer a 5-mL aliquot of the diluted PRA solution from 2. into a 50-mL volumetric flask. Add 5mL of 1 M acetate-acetic acid buffer solution from 1. and dilute the mixture to volume with distilled water. Let the mixture stand for 1 hour.

4. Measure the absorbance of the above solution at 540 nm with a spectrophotometer against a distilled water reference. Compute the percentage of nominal concentration of PRA by

$$\%PRA = \frac{A \times K}{W} \qquad (5)$$

where:

A = measured absorbance of the final mixture (absorbance units);

W = weight in grams of the PRA dye used in the assay to prepare 50 mL of stock solution (for example, 0.100 g of dye was used to prepare 50 mL of solution in the purification procedure; when obtained from commercial sources, use the stated concentration to compute W; for 98% PRA, W = .098 g.); and

K = 21.3 for spectrophotometers having a spectral bandwidth of less than 15 nm and a path length of 1 cm.

8.2.13 Pararosaniline reagent: To a 250-mL volumetric flask, add 20 mL of stock PRA solution. Add an additional 0.2 mL of stock solution for each percentage that the stock assays below 100 percent. Then add 25 mL of 3 M phosphoric acid and dilute to volume with distilled water. The reagent is stable for at least 9 months. Store away from heat and light.

9.0 Sampling Procedure.

9.1 General Considerations. Procedures are described for short-term sampling (30-minute and 1-hour) and for long-term sampling (24-hour). Different combinations of absorbing reagent volume, sampling rate, and sampling time can be selected to meet special needs. For combinations other than those specifically described, the conditions must be adjusted so that linearity is maintained between absorbance and concentration over the dynamic range. Absorbing reagent volumes less than 10 mL are not recommended. The collection efficiency is above 98 percent for the conditions described; however, the efficiency may be substantially lower when sampling concentrations below 25 μγSO2/m 3.(8,9)

9.2 30-Minute and 1-Hour Sampling. Place 10 mL of TCM absorbing reagent in a midget impinger and seal the impinger with a thin film of silicon stopcock grease (around the ground glass joint). Insert the sealed impinger into the sampling train as shown in Figure 1, making sure that all connections between the various components are leak tight. Greaseless ball joint fittings, heat shrinkable Teflon ® tubing, or Teflon ® tube fittings may be used to attain leakfree conditions for portions of the sampling train that come into contact with air containing SO2. Shield the absorbing reagent from direct sunlight by covering the impinger with aluminum foil or by enclosing the sampling train in a light-proof box. Determine the flow rate according to Section 9.4.2. Collect the sample at 1 ±0.10 L/min for 30-minute sampling or 0.500 ±0.05 L/min for 1-hour sampling. Record the exact sampling time in minutes, as the sample volume will later be determined using the sampling flow rate and the sampling time. Record the atmospheric pressure and temperature.

9.3 24-Hour Sampling. Place 50 mL of TCM absorbing solution in a large absorber, close the cap, and, if needed, apply the heat shrink material as shown in Figure 3. Verify that the reagent level is at the 50 mL mark on the absorber. Insert the sealed absorber into the sampling train as shown in Figure 2. At this time verify that the absorber temperature is controlled to 15 ±10 °C. During sampling, the absorber temperature must be controlled to prevent decomposition of the collected complex. From the onset of sampling until analysis, the absorbing solution must be protected from direct sunlight. Determine the flow rate according to Section 9.4.2. Collect the sample for 24 hours from midnight to midnight at a flow rate of 0.200 ±0.020 L/min. A start/stop timer is helpful for initiating and stopping sampling and an elapsed time meter will be useful for determining the sampling time.

9.4 Flow Measurement.

9.4.1 Calibration: Flow measuring devices used for the on-site flow measurements required in 9.4.2 must be calibrated against a reliable flow or volume standard such as an NBS traceable bubble flowmeter or calibrated wet test meter. Rotameters or critical orifices used in the sampling train may be calibrated, if desired, as a quality control check, but such calibration shall not replace the on-site flow measurements required by 9.4.2. In-line rotameters, if they are to be calibrated, should be calibrated in situ, with the appropriate volume of solution in the absorber.

9.4.2 Determination of flow rate at sampling site: For short-term samples, the standard flow rate is determined at the sampling site at the initiation and completion of sample collection with a calibrated flow measuring device connected to the inlet of the absorber. For 24-hour samples, the standard flow rate is determined at the time the absorber is placed in the sampling train and again when the absorber is removed from the train for shipment to the analytical laboratory with a calibrated flow measuring device connected to the inlet of the sampling train. The flow rate determination must be made with all components of the sampling system in operation (e.g., the absorber temperature controller and any sample box heaters must also be operating). Equation 6 may be used to determine the standard flow rate when a calibrated positive displacement meter is used as the flow measuring device. Other types of calibrated flow measuring devices may also be

used to determine the flow rate at the sampling site provided that the user applies any appropriate corrections to devices for which output is dependent on temperature or pressure.

$$Q_{std} = Q_{act} \times \frac{P_b - (1 - RH)P_{H_2O}}{P_{std}} \times \frac{298.16.}{(T_{meter} + 273.16).} \qquad (6)$$

where:

Qstd = flow rate at standard conditions, std L/min (25 °C and 760 mm Hg);

Qact = flow rate at monitoring site conditions, L/min;

Pb = barometric pressure at monitoring site conditions, mm Hg or kPa;

RH = fractional relative humidity of the air being measured;

PH2O = vapor pressure of water at the temperature of the air in the flow or volume standard, in the same units as Pb, (for wet volume standards only, i.e., bubble flowmeter or wet test meter; for dry standards, i.e., dry test meter, PH2O = 0);

Pstd = standard barometric pressure, in the same units as Pb (760 mm Hg or 101 kPa); and

Tmeter = temperature of the air in the flow or volume standard, °C (e.g., bubble flowmeter).

If a barometer is not available, the following equation may be used to determine the barometric pressure:

$$P_b = 760 - .076(H)\, mm\, Hg, or\, P_b = 101 - .01(H) kPa \qquad (7)$$

where:

H = sampling site elevation above sea level in meters.

If the initial flow rate (Qi) differs from the flow rate of the critical orifice or the flow rate indicated by the flowmeter in the sampling train (Qc) by more than 5 percent as determined by equation (8), check for leaks and redetermine Qi.

$$\%\ Diff = \frac{Q_i - Q_c}{Q_c} \times 100 \qquad (8)$$

Invalidate the sample if the difference between the initial (Qi) and final (Qf) flow rates is more than 5 percent as determined by equation (9):

$$\%\ Diff = \frac{Q_i - Q_f}{Q_f} \times 100 \qquad (9)$$

9.5 Sample Storage and Shipment. Remove the impinger or absorber from the sampling train and stopper immediately. Verify that the temperature of the absorber is not above 25 °C. Mark the level of the solution with a temporary (e.g., grease pencil) mark. If the sample will not be analyzed within 12 hours of sampling, it must be stored at 5° ±5 °C until analysis. Analysis must

occur within 30 days. If the sample is transported or shipped for a period exceeding 12 hours, it is recommended that thermal coolers using eutectic ice packs, refrigerated shipping containers, etc., be used for periods up to 48 hours. (17) Measure the temperature of the absorber solution when the shipment is received. Invalidate the sample if the temperature is above 10 °C. Store the sample at 5° ±5 °C until it is analyzed.

10.0 Analytical Calibration.

10.1 Spectrophotometer Cell Matching. If unmatched spectrophotometer cells are used, an absorbance correction factor must be determined as follows:

1. Fill all cells with distilled water and designate the one that has the lowest absorbance at 548 nm as the reference. (This reference cell should be marked as such and continually used for this purpose throughout all future analyses.)

2. Zero the spectrophotometer with the reference cell.

3. Determine the absorbance of the remaining cells (Ac) in relation to the reference cell and record these values for future use. Mark all cells in a manner that adequately identifies the correction.

The corrected absorbance during future analyses using each cell is determining as follows:

$$A = A_{obs} - A_c \qquad (10)$$

where:

A = corrected absorbance,

Aobs = uncorrected absorbance, and

Ac = cell correction.

10.2 Static Calibration Procedure (Option 1). Prepare a dilute working sulfite-TCM solution by diluting 10 mL of the working sulfite-TCM solution (Section 8.2.11) to 100 mL with TCM absorbing reagent. Following the table below, accurately pipet the indicated volumes of the sulfite-TCM solutions into a series of 25-mL volumetric flasks. Add TCM absorbing reagent as indicated to bring the volume in each flask to 10 mL.

Sulfite-TCM solution	Volume of sulfite-TCM solution	Volume of TCM, mL	Total µg SO2 (approx.*
Working	4.0	6.0	28.8
Working	3.0	7.0	21.6
Working	2.0	8.0	14.4

Dilute working	10.0	0.0	7.2
Dilute working	5.0	5.0	3.6
	0.0	10.0	0.0

*Based on working sulfite-TCM solution concentration of 7.2 µg SO2/mL; the actual total µg SO2 must be calculated using equation 11 below.

To each volumetric flask, add 1 mL 0.6% sulfamic acid (Section 8.2.1), accurately pipet 2 mL 0.2% formaldehyde solution (Section 8.2.2), then add 5 mL pararosaniline solution (Section 8.2.13). Start a laboratory timer that has been set for 30 minutes. Bring all flasks to volume with recently boiled and cooled distilled water and mix thoroughly. The color must be developed (during the 30-minute period) in a temperature environment in the range of 20° to 30 °C, which is controlled to ±1 °C. For increased precision, a constant temperature bath is recommended during the color development step. After 30 minutes, determine the corrected absorbance of each standard at 548 nm against a distilled water reference (Section 10.1). Denote this absorbance as (A). Distilled water is used in the reference cell rather than the reagant blank because of the temperature sensitivity of the reagent blank. Calculate the total micrograms SO2 in each solution:

$$\mu g\ SO_2 = V_{TCM/SO2} \times C_{TCM/SO2} \times D \qquad (11)$$

where:

VTCM/SO2 = volume of sulfite-TCM solution used, mL;

CTCM/SO2 = concentration of sulfur dioxide in the working sulfite-TCM, µg SO2/mL (from equation 4); and

D = dilution factor (D = 1 for the working sulfite-TCM solution; D = 0.1 for the diluted working sulfite-TCM solution).

A calibration equation is determined using the method of linear least squares (Section 12.1). The total micrograms SO2 contained in each solution is the x variable, and the corrected absorbance (eq. 10) associated with each solution is the y variable. For the calibration to be valid, the slope must be in the range of 0.030 ±0.002 absorbance unit/µg SO2, the intercept as determined by the least squares method must be equal to or less than 0.170 absorbance unit when the color is developed at 22 °C (add 0.015 to this 0.170 specification for each °C above 22 °C) and the correlation coefficient must be greater than 0.998. If these criteria are not met, it may be the result of an impure dye and/or an improperly standardized sulfite-TCM solution. A calibration factor (Bs) is determined by calculating the reciprocal of the slope and is subsequently used for calculating the sample concentration (Section 12.3).

10.3 Dynamic Calibration Procedures (Option 2). Atmospheres containing accurately known concentrations of sulfur dioxide are prepared using permeation devices. In the systems for

generating these atmospheres, the permeation device emits gaseous SO2 at a known, low, constant rate, provided the temperature of the device is held constant (±0.1 °C) and the device has been accurately calibrated at the temperature of use. The SO2 permeating from the device is carried by a low flow of dry carrier gas to a mixing chamber where it is diluted with SO2-free air to the desired concentration and supplied to a vented manifold. A typical system is shown schematically in Figure 4 and this system and other similar systems have been described in detail by O'Keeffe and Ortman; (19) Scaringelli, Frey, and Saltzman, (20) and Scaringelli, O'Keeffe, Rosenberg, and Bell. (21) Permeation devices may be prepared or purchased and in both cases must be traceable either to a National Bureau of Standards (NBS) Standard Reference Material (SRM 1625, SRM 1626, SRM 1627) or to an NBS/EPA-approved commercially available Certified Reference Material (CRM). CRM's are described in Reference 22, and a list of CRM sources is available from the address shown for Reference 22. A recommended protocol for certifying a permeation device to an NBS SRM or CRM is given in Section 2.0.7 of Reference 2. Device permeation rates of 0.2 to 0.4 µg/min, inert gas flows of about 50 mL/min, and dilution air flow rates from 1.1 to 15 L/min conveniently yield standard atmospheres in the range of 25 to 600 µg SO2/m 3 (0.010 to 0.230 ppm).

10.3.1 Calibration Option 2A (30-minute and 1-hour samples): Generate a series of six standard atmospheres of SO2 (e.g., 0, 50, 100, 200, 350, 500, 750 µg/m 3) by adjusting the dilution flow rates appropriately. The concentration of SO2 in each atmosphere is calculated as follows:

$$C_a = \frac{P_r \times 10^3}{Q_d + Q_p} \qquad (12)$$

where:

Ca = concentration of SO2 at standard conditions, µg/m 3;

Pr = permeation rate, µg/min;

Qd = flow rate of dilution air, std L/min; and

Qp = flow rate of carrier gas across permeation device, std L/min.

Be sure that the total flow rate of the standard exceeds the flow demand of the sample train, with the excess flow vented at atmospheric pressure. Sample each atmosphere using similar apparatus as shown in Figure 1 and under the same conditions as field sampling (i.e., use same absorbing reagent volume and sample same volume of air at an equivalent flow rate). Due to the length of the sampling periods required, this method is not recommended for 24-hour sampling. At the completion of sampling, quantitatively transfer the contents of each impinger to one of a series of 25-mL volumetric flasks (if 10 mL of absorbing solution was used) using small amounts of distilled water for rinse (<5mL). If >10 mL of absorbing solution was used, bring the absorber solution in each impinger to orginal volume with distilled H2 O and pipet 10-mL portions from each impinger into a series of 25-mL volumetric flasks. If the color development steps are not to

be started within 12 hours of sampling, store the solutions at 5° ±5 °C. Calculate the total micrograms SO2 in each solution as follows:

$$\mu gSO_2 = \frac{C_a \times Q_s \times t \times V_a \times 10^{-3}}{V_b} \qquad (13)$$

where:

Ca = concentration of SO2 in the standard atmosphere, µg/m 3;

Os = sampling flow rate, std L/min;

t = sampling time, min;

Va = volume of absorbing solution used for color development (10 mL); and

Vb = volume of absorbing solution used for sampling, mL.

Add the remaining reagents for color development in the same manner as in Section 10.2 for static solutions. Calculate a calibration equation and a calibration factor (Bg) according to Section 10.2, adhering to all the specified criteria.

10.3.2 Calibration Option 2B (24-hour samples): Generate a standard atmosphere containing approximately 1,050 µg SO2/m 3 and calculate the exact concentration according to equation 12. Set up a series of six absorbers according to Figure 2 and connect to a common manifold for sampling the standard atmosphere. Be sure that the total flow rate of the standard exceeds the flow demand at the sample manifold, with the excess flow vented at atmospheric pressure. The absorbers are then allowed to sample the atmosphere for varying time periods to yield solutions containing 0, 0.2, 0.6, 1.0, 1.4, 1.8, and 2.2 µg SO2/mL solution. The sampling times required to attain these solution concentrations are calculated as follows:

$$t = \frac{V_b \times C_s}{C_a \times Q_s \times 10^{-3}} \qquad (14)$$

where:

t = sampling time, min;

Vb = volume of absorbing solution used for sampling (50 mL);

Cs = desired concentration of SO2 in the absorbing solution, µg/mL;

Ca = concentration of the standard atmosphere calculated according to equation 12, µg/m 3; and

Qs = sampling flow rate, std L/min.

At the completion of sampling, bring the absorber solutions to original volume with distilled water. Pipet a 10-mL portion from each absorber into one of a series of 25-mL volumetric flasks. If the color development steps are not to be started within 12 hours of sampling, store the

solutions at 5° ±5 °C. Add the remaining reagents for color development in the same manner as in Section 10.2 for static solutions. Calculate the total µg SO2 in each standard as follows:

$$\mu gSO_2 = \frac{C_a \times Q_s \times t \times V_a \times 10^{-3}}{V_b} \qquad (15)$$

where:

Va = volume of absorbing solution used for color development (10 mL).

All other parameters are defined in equation 14.

Calculate a calibration equation and a calibration factor (Bt) according to Section 10.2 adhering to all the specified criteria.

11.0 Sample Preparation and Analysis.

11.1 Sample Preparation. Remove the samples from the shipping container. If the shipment period exceeded 12 hours from the completion of sampling, verify that the temperature is below 10 °C. Also, compare the solution level to the temporary level mark on the absorber. If either the temperature is above 10 °C or there was significant loss (more than 10 mL) of the sample during shipping, make an appropriate notation in the record and invalidate the sample. Prepare the samples for analysis as follows:

1. For 30-minute or 1-hour samples: Quantitatively transfer the entire 10 mL amount of absorbing solution to a 25-mL volumetric flask and rinse with a small amount (<5 mL) of distilled water.

2. For 24-hour samples: If the volume of the sample is less than the original 50-mL volume (permanent mark on the absorber), adjust the volume back to the original volume with distilled water to compensate for water lost to evaporation during sampling. If the final volume is greater than the original volume, the volume must be measured using a graduated cylinder. To analyze, pipet 10 mL of the solution into a 25-mL volumetric flask.

11.2 Sample Analysis. For each set of determinations, prepare a reagent blank by adding 10 mL TCM absorbing solution to a 25-mL volumetric flask, and two control standards containing approximately 5 and 15 µg SO2, respectively. The control standards are prepared according to Section 10.2 or 10.3. The analysis is carried out as follows:

1. Allow the sample to stand 20 minutes after the completion of sampling to allow any ozone to decompose (if applicable).

2. To each 25-mL volumetric flask containing reagent blank, sample, or control standard, add 1 mL of 0.6% sulfamic acid (Section 8.2.1) and allow to react for 10 min.

3. Accurately pipet 2 mL of 0.2% formaldehyde solution (Section 8.2.2) and then 5 mL of pararosaniline solution (Section 8.2.13) into each flask. Start a laboratory timer set at 30 minutes.

4. Bring each flask to volume with recently boiled and cooled distilled water and mix thoroughly.

5. During the 30 minutes, the solutions must be in a temperature controlled environment in the range of 20° to 30 °C maintained to ±1 °C. This temperature must also be within 1 °C of that used during calibration.

6. After 30 minutes and before 60 minutes, determine the corrected absorbances (equation 10) of each solution at 548 nm using 1-cm optical path length cells against a distilled water reference (Section 10.1). (Distilled water is used as a reference instead of the reagent blank because of the sensitivity of the reagent blank to temperature.)

7. Do not allow the colored solution to stand in the cells because a film may be deposited. Clean the cells with isopropyl alcohol after use.

8. The reagent blank must be within 0.03 absorbance units of the intercept of the calibration equation determined in Section 10.

11.3 Absorbance range. If the absorbance of the sample solution ranges between 1.0 and 2.0, the sample can be diluted 1:1 with a portion of the reagent blank and the absorbance redetermined within 5 minutes. Solutions with higher absorbances can be diluted up to sixfold with the reagent blank in order to obtain scale readings of less than 1.0 absorbance unit. However, it is recommended that a smaller portion (<10 mL) of the original sample be reanalyzed (if possible) if the sample requires a dilution greater than 1:1.

11.4 Reagent disposal. All reagents containing mercury compounds must be stored and disposed of using one of the procedures contained in Section 13. Until disposal, the discarded solutions can be stored in closed glass containers and should be left in a fume hood.

12.0 Calculations.

12.1 Calibration Slope, Intercept, and Correlation Coefficient. The method of least squares is used to calculate a calibration equation in the form of:

$$y = mx + b \qquad (16)$$

where:

y = corrected absorbance,

m = slope, absorbance unit/µg SO2,

x = micrograms of SO2,

b = y intercept (absorbance units).

The slope (m), intercept (b), and correlation coefficient (r) are calculated as follows:

$$m = \frac{n\sum xy - (\sum x)(\sum y)}{n\sum x^2 - (\sum x)^2} \qquad (17)$$

$$b = \frac{\sum y - m\sum x}{n} \qquad (18)$$

$$r = \sqrt{\frac{m(\sum xy - \sum x \sum y / n)}{\sum y^2 - (\sum y)^2 / n}} \qquad (19)$$

where n is the number of calibration points.

A data form (Figure 5) is supplied for easily organizing calibration data when the slope, intercept, and correlation coefficient are calculated by hand.

12.2 Total Sample Volume. Determine the sampling volume at standard conditions as follows:

$$V_{std} = \frac{Q_i + Q_f}{2} \times t \qquad (20)$$

where:

Vstd = sampling volume in std L,

Qi = standard flow rate determined at the initiation of sampling in std L/min,

Qf = standard flow rate determined at the completion of sampling is std L/min, and

t = total sampling time, min.

12.3 Sulfur Dioxide Concentration. Calculate and report the concentration of each sample as follows:

$$\mu g\ SO_2/m^3 = \frac{(A - A_o)(B_x)(10^3)}{V_{std}} \times \frac{V_b}{V_a} \qquad (21)$$

where:

A = corrected absorbance of the sample solution, from equation (10);

Ao = corrected absorbance of the reagent blank, using equation (10);

BX = calibration factor equal to Bs, Bg, or Bt depending on the calibration procedure used, the reciprocal of the slope of the calibration equation;

Va = volume of absorber solution analyzed, mL;

Vb = total volume of solution in absorber (see 11.1-2), mL; and

Vstd = standard air volume sampled, std L (from Section 12.2).

Data Form

[For hand calculations]

Calibration point no.	Micro- grams So2	Absor- bance units			
	(x)	(y)	x 2	xy	y 2
1					
2					
3					
4					
5					
6					

Σ x=___ Σ y=___ Σ x 2=___ Σxy___ Σy 2___

n=___ (number of pairs of coordinates.)

Figure 5. Data form for hand calculations.

12.4 Control Standards. Calculate the analyzed micrograms of SO2 in each control standard as follows:

$$C_q = (A - A_o) \times B_x \qquad (22)$$

where:

Cq = analyzed µg SO2 in each control standard,

A = corrected absorbance of the control standard, and

Ao = corrected absorbance of the reagent blank.

The difference between the true and analyzed values of the control standards must not be greater than 1 µg. If the difference is greater than 1 µg, the source of the discrepancy must be identified and corrected.

12.5 Conversion of µg/m 3 to ppm (v/v). If desired, the concentration of sulfur dioxide at reference conditions can be converted to ppm SO2 (v/v) as follows:

$$ppm\ SO_2 = \frac{\mu g\ SO_2}{m^3} \times 3.82 \times 10^{-4} \qquad (23)$$

13.0 The TCM absorbing solution and any reagents containing mercury compounds must be treated and disposed of by one of the methods discussed below. Both methods remove greater than 99.99 percent of the mercury.

13.1 Disposal of Mercury-Containing Solutions.

13.2 Method for Forming an Amalgam.

1. Place the waste solution in an uncapped vessel in a hood.

2. For each liter of waste solution, add approximately 10 g of sodium carbonate until neutralization has occurred (NaOH may have to be used).

3. Following neutralization, add 10 g of granular zinc or magnesium.

4. Stir the solution in a hood for 24 hours. Caution must be exercised as hydrogen gas is evolved by this treatment process.

5. After 24 hours, allow the solution to stand without stirring to allow the mercury amalgam (solid black material) to settle to the bottom of the waste receptacle.

6. Upon settling, decant and discard the supernatant liquid.

7. Quantitatively transfer the solid material to a container and allow to dry.

8. The solid material can be sent to a mercury reclaiming plant. It must not be discarded.

13.3 Method Using Aluminum Foil Strips.

1. Place the waste solution in an uncapped vessel in a hood.

2. For each liter of waste solution, add approximately 10 g of aluminum foil strips. If all the aluminum is consumed and no gas is evolved, add an additional 10 g of foil. Repeat until the foil is no longer consumed and allow the gas to evolve for 24 hours.

3. Decant the supernatant liquid and discard.

4. Transfer the elemental mercury that has settled to the bottom of the vessel to a storage container.

5. The mercury can be sent to a mercury reclaiming plant. It must not be discarded.

14.0 References for SO2Method.

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[47 FR 54899, Dec. 6, 1982; 48 FR 17355, Apr. 22, 1983. Redesignated at 75 FR 35595, June 22, 2010]

Appendix T to Part 50 - Interpretation of the Primary National Ambient Air Quality Standards for Oxides of Sulfur (Sulfur Dioxide)

1. General

(a) This appendix explains the data handling conventions and computations necessary for determining when the primary national ambient air quality standards for Oxides of Sulfur as measured by Sulfur Dioxide ("SO_2 NAAQS") specified in § 50.17 are met at an ambient air quality monitoring site. Sulfur Dioxide (SO_2) is measured in the ambient air by a Federal reference method (FRM) based on appendix A or A-1 to this part or by a Federal equivalent method (FEM) designated in accordance with part 53 of this chapter. Data handling and computation procedures to be used in making comparisons between reported SO_2 concentrations and the levels of the SO_2 NAAQS are specified in the following sections.

(b) Decisions to exclude, retain, or make adjustments to the data affected by exceptional events, including natural events, are made according to the requirements and process deadlines specified in §§ 50.1, 50.14 and 51.930 of this chapter.

(c) The terms used in this appendix are defined as follows:

Daily maximum 1-hour values for SO_2 refers to the maximum 1-hour SO_2 concentration values measured from midnight to midnight (local standard time) that are used in NAAQS computations.

Design values are the metrics (*i.e.,* statistics) that are compared to the NAAQS levels to determine compliance, calculated as specified in section 5 of this appendix. The design value for the primary 1-hour NAAQS is the 3-year average of annual 99th percentile daily maximum 1-hour values for a monitoring site (referred to as the "1-hour primary standard design value").

99th percentile daily maximum 1-hour value is the value below which nominally 99 percent of all daily maximum 1-hour concentration values fall, using the ranking and selection method specified in section 5 of this appendix.

Pollutant Occurrence Code (POC) refers to a numerical code (1, 2, 3, *etc.*) used to distinguish the data from two or more monitors for the same parameter at a single monitoring site.

Quarter refers to a calendar quarter.

Year refers to a calendar year.

2. Requirements for Data Used for Comparisons With the SO_2 NAAQS and Data Reporting Considerations

(a) All valid FRM/FEM SO_2 hourly data required to be submitted to EPA's Air Quality System (AQS), or otherwise available to EPA, meeting the requirements of part 58 of this chapter including appendices A, C, and E shall be used in design value calculations. Multi-hour average concentration values collected by wet chemistry methods shall not be used.

(b) Data from two or more monitors from the same year at the same site reported to EPA under distinct Pollutant Occurrence Codes shall not be combined in an attempt to meet data completeness requirements. The Administrator will combine annual 99th percentile daily maximum concentration values from different monitors in different years, selected as described here, for the purpose of developing a valid 1-hour primary standard design value. If more than one of the monitors meets the completeness requirement for all four quarters of a year, the steps specified in section 5(a) of this appendix shall be applied to the data from the monitor with the highest average of the four quarterly completeness values to derive a valid annual 99th percentile daily maximum concentration. If no monitor is complete for all four quarters in a year, the steps specified in section 3(c) and 5(a) of this appendix shall be applied to the data from the monitor with the highest average of the four quarterly

completeness values in an attempt to derive a valid annual 99th percentile daily maximum concentration. This paragraph does not prohibit a monitoring agency from making a local designation of one physical monitor as the primary monitor for a Pollutant Occurrence Code and substituting the 1-hour data from a second physical monitor whenever a valid concentration value is not obtained from the primary monitor; if a monitoring agency substitutes data in this manner, each substituted value must be accompanied by an AQS qualifier code indicating that substitution with a value from a second physical monitor has taken place.

(c) Hourly SO_2 measurement data shall be reported to AQS in units of parts per billion (ppb), to at most one place after the decimal, with additional digits to the right being truncated with no further rounding.

3. COMPARISONS WITH THE 1-HOUR PRIMARY SO_2 NAAQS

(a) The 1-hour primary SO_2 NAAQS is met at an ambient air quality monitoring site when the valid 1-hour primary standard design value is less than or equal to 75 parts per billion (ppb).

(b) An SO_2 1-hour primary standard design value is valid if it encompasses three consecutive calendar years of complete data. A year meets data completeness requirements when all 4 quarters are complete. A quarter is complete when at least 75 percent of the sampling days for each quarter have complete data. A sampling day has complete data if 75 percent of the hourly concentration values, including State-flagged data affected by exceptional events which have been approved for exclusion by the Administrator, are reported.

(c) In the case of one, two, or three years that do not meet the completeness requirements of section 3(b) of this appendix and thus would normally not be useable for the calculation of a valid 3-year 1-hour primary standard design value, the 3-year 1-hour primary standard design value shall nevertheless be considered valid if one of the following conditions is true.

> **(i)** At least 75 percent of the days in each quarter of each of three consecutive years have at least one reported hourly value, and the design value calculated according to the procedures specified in section 5 is above the level of the primary 1-hour standard.
>
> **(ii)**
>
> > **(A)** A 1-hour primary standard design value that is equal to or below the level of the NAAQS can be validated if the substitution test in section 3(c)(ii)(B) results in a “test design value” that is below the level of the NAAQS. The test substitutes actual “high” reported daily maximum 1-hour values from the same site at about the same time of the year (specifically, in the same calendar quarter) for unknown values that were not successfully measured. *Note* that the test is merely diagnostic in nature, intended to confirm that there is a very high likelihood that the original design value (the one with less than 75 percent data capture of hours by day and of days by quarter) reflects the true under-NAAQS-level status for that 3-year period; the result of this data substitution test (the “test design value”, as defined in section 3(c)(ii)(B)) is not considered the actual design value. For this test, substitution is permitted only if there are at least 200 days across the three matching quarters of the three years under consideration (which is about 75 percent of all possible daily values in those three quarters) for which 75 percent of the hours in the day, including State-flagged data affected by exceptional events which have been approved for exclusion by the Administrator, have reported concentrations. However, maximum 1-hour values from days with less than 75 percent of the hours reported shall also be considered in identifying the high value to be used for substitution.
> >
> > **(B)** The substitution test is as follows: Data substitution will be performed in all quarter periods that have less than 75 percent data capture but at least 50 percent data capture, including State-flagged data affected by exceptional events which have been approved for

exclusion by the Administrator; if any quarter has less than 50 percent data capture then this substitution test cannot be used. Identify for each quarter (e.g., January-March) the highest reported daily maximum 1-hour value for that quarter, excluding State-flagged data affected by exceptional events which have been approved for exclusion by the Administrator, looking across those three months of all three years under consideration. All daily maximum 1-hour values from all days in the quarter period shall be considered when identifying this highest value, including days with less than 75 percent data capture. If after substituting the highest reported daily maximum 1-hour value for a quarter for as much of the missing daily data in the matching deficient quarter(s) as is needed to make them 100 percent complete, the procedure in section 5 yields a recalculated 3-year 1-hour standard "test design value" less than or equal to the level of the standard, then the 1-hour primary standard design value is deemed to have passed the diagnostic test and is valid, and the level of the standard is deemed to have been met in that 3-year period. As noted in section 3(c)(i), in such a case, the 3-year design value based on the data actually reported, not the "test design value", shall be used as the valid design value.

(iii)

(A) A 1-hour primary standard design value that is above the level of the NAAQS can be validated if the substitution test in section 3(c)(iii)(B) results in a "test design value" that is above the level of the NAAQS. The test substitutes actual "low" reported daily maximum 1-hour values from the same site at about the same time of the year (specifically, in the same three months of the calendar) for unknown hourly values that were not successfully measured. Note that the test is merely diagnostic in nature, intended to confirm that there is a very high likelihood that the original design value (the one with less than 75 percent data capture of hours by day and of days by quarter) reflects the true above-NAAQS-level status for that 3-year period; the result of this data substitution test (the "test design value", as defined in section 3(c)(iii)(B)) is not considered the actual design value. For this test, substitution is permitted only if there are a minimum number of available daily data points from which to identify the low quarter-specific daily maximum 1-hour values, specifically if there are at least 200 days across the three matching quarters of the three years under consideration (which is about 75 percent of all possible daily values in those three quarters) for which 75 percent of the hours in the day have reported concentrations. Only days with at least 75 percent of the hours reported shall be considered in identifying the low value to be used for substitution.

(B) The substitution test is as follows: Data substitution will be performed in all quarter periods that have less than 75 percent data capture. Identify for each quarter (e.g., January-March) the lowest reported daily maximum 1-hour value for that quarter, looking across those three months of all three years under consideration. All daily maximum 1-hour values from all days with at least 75 percent capture in the quarter period shall be considered when identifying this lowest value. If after substituting the lowest reported daily maximum 1-hour value for a quarter for as much of the missing daily data in the matching deficient quarter(s) as is needed to make them 75 percent complete, the procedure in section 5 yields a recalculated 3-year 1-hour standard "test design value" above the level of the standard, then the 1-hour primary standard design value is deemed to have passed the diagnostic test and is valid, and the level of the standard is deemed to have been exceeded in that 3-year period. As noted in section 3(c)(i), in such a case, the 3-year design value based on the data actually reported, not the "test design value", shall be used as the valid design value.

(d) A 1-hour primary standard design value based on data that do not meet the completeness criteria stated in 3(b) and also do not satisfy section 3(c), may also be considered valid with the approval of, or at the initiative of, the Administrator, who may consider factors such as monitoring site closures/moves, monitoring diligence, the consistency and levels of the valid concentration

measurements that are available, and nearby concentrations in determining whether to use such data.

(e) The procedures for calculating the 1-hour primary standard design values are given in section 5 of this appendix.

4. ROUNDING CONVENTIONS FOR THE 1-HOUR PRIMARY SO_2 NAAQS

(a) Hourly SO_2 measurement data shall be reported to AQS in units of parts per billion (ppb), to at most one place after the decimal, with additional digits to the right being truncated with no further rounding.

(b) Daily maximum 1-hour values and therefore the annual 99th percentile of those daily values are not rounded.

(c) The 1-hour primary standard design value is calculated pursuant to section 5 and then rounded to the nearest whole number or 1 ppb (decimals 0.5 and greater are rounded up to the nearest whole number, and any decimal lower than 0.5 is rounded down to the nearest whole number).

5. CALCULATION PROCEDURES FOR THE 1-HOUR PRIMARY SO_2 NAAQS

(a)*Procedure for identifying annual 99th percentile values.* When the data for a particular ambient air quality monitoring site and year meet the data completeness requirements in section 3(b), or if one of the conditions of section 3(c) is met, or if the Administrator exercises the discretionary authority in section 3(d), identification of annual 99th percentile value is accomplished as follows.

(i) The annual 99th percentile value for a year is the higher of the two values resulting from the following two procedures.

(1)*Procedure 1.* For the year, determine the number of days with at least 75 percent of the hourly values reported.

(A) For the year, determine the number of days with at least 75 percent of the hourly values reported including State-flagged data affected by exceptional events which have been approved for exclusion by the Administrator.

(B) For the year, from only the days with at least 75 percent of the hourly values reported, select from each day the maximum hourly value excluding State-flagged data affected by exceptional events which have been approved for exclusion by the Administrator.

(C) Sort all these daily maximum hourly values from a particular site and year by descending value. (For example: (x[1], x[2], x[3], * * *, x[n]). In this case, x[1] is the largest number and x[n] is the smallest value.) The 99th percentile is determined from this sorted series of daily values which is ordered from the highest to the lowest number. Using the left column of Table 1, determine the appropriate range (*i.e.,* row) for the annual number of days with valid data for year y (cn_y). The corresponding “n” value in the right column identifies the rank of the annual 99th percentile value in the descending sorted list of daily site values for year y. Thus, $P_{0.99, y}$ = the nth largest value.

(2)*Procedure 2.* For the year, determine the number of days with at least one hourly value reported.

(A) For the year, determine the number of days with at least one hourly value reported including State-flagged data affected by exceptional events which have been approved for exclusion by the Administrator.

(B) For the year, from all the days with at least one hourly value reported, select from each day the maximum hourly value excluding State-flagged data affected by exceptional events which have been approved for exclusion by the Administrator.

(C) Sort all these daily maximum values from a particular site and year by descending value. (For example: (x[1], x[2], x[3], * * *, x[n]). In this case, x[1] is the largest number and x[n] is the smallest value.) The 99th percentile is determined from this sorted series of daily values which is ordered from the highest to the lowest number. Using the left column of Table 1, determine the appropriate range (*i.e.,* row) for the annual number of days with valid data for year y (cn_y). The corresponding "n" value in the right column identifies the rank of the annual 99th percentile value in the descending sorted list of daily site values for year y. Thus, $P_{0.99,y}$ = the nth largest value.

(b) The 1-hour primary standard design value for an ambient air quality monitoring site is mean of the three annual 99th percentile values, rounded according to the conventions in section 4.

Table 1

Annual number of days with valid data for year "y" (cn_y)	$P_{0.99,y}$ is the nth maximum value of the year, where n is the listed number
1-100	1
101-200	2
201-300	3
301-366	4

[75 FR 35595, June 23, 2010]

State of Oregon Department of Environmental Quality

OAR 340-202-0090 Attachments

Appendix I to Part 50—Interpretation of the 8-Hour Primary and Secondary National Ambient Air Quality Standards for Ozone

1. *General.*

This appendix explains the data handling conventions and computations necessary for determining whether the national 8-hour primary and secondary ambient air quality standards for ozone specified in §50.10 are met at an ambient ozone air quality monitoring site. Ozone is measured in the ambient air by a reference method based on appendix D of this part. Data reporting, data handling, and computation procedures to be used in making comparisons between reported ozone concentrations and the level of the ozone standard are specified in the following sections. Whether to exclude, retain, or make adjustments to the data affected by stratospheric ozone intrusion or other natural events is subject to the approval of the appropriate Regional Administrator.

2. *Primary and Secondary Ambient Air Quality Standards for Ozone.*

2.1 *Data Reporting and Handling Conventions.*

2.1.1 *Computing 8-hour averages.* Hourly average concentrations shall be reported in parts per million (ppm) to the third decimal place, with additional digits to the right being truncated. Running 8-hour averages shall be computed from the hourly ozone concentration data for each hour of the year and the result shall be stored in the first, or start, hour of the 8-hour period. An 8-hour average shall be considered valid if at least 75% of the hourly averages for the 8-hour period are available. In the event that only 6 (or 7) hourly averages are available, the 8-hour average shall be computed on the basis of the hours available using 6 (or 7) as the divisor. (8-hour periods with three or more missing hours shall not be ignored if, after substituting one-half the minimum detectable limit for the missing hourly concentrations, the 8-hour average concentration is greater than the level of the standard.) The computed 8-hour average ozone concentrations shall be reported to three decimal places (the insignificant digits to the right of the third decimal place are truncated, consistent with the data handling procedures for the reported data.)

2.1.2 *Daily maximum 8-hour average concentrations.* (a) There are 24 possible running 8-hour average ozone concentrations for each calendar day during the ozone monitoring season. (Ozone monitoring seasons vary by geographic location as designated in part 58, appendix D to this chapter.) The daily maximum 8-hour concentration for a given calendar day is the highest of the 24 possible 8-hour average concentrations computed for that day. This process is repeated, yielding a daily maximum 8-hour average ozone concentration for each calendar day with ambient ozone monitoring data. Because the 8-hour averages are recorded in the start hour, the daily maximum 8-hour concentrations from two consecutive days may have some hourly concentrations in common. Generally, overlapping daily maximum 8-hour averages are not likely, except in those non-urban monitoring locations with less pronounced diurnal variation in hourly concentrations.

(b) An ozone monitoring day shall be counted as a valid day if valid 8-hour averages are available for at least 75% of possible hours in the day (*i.e.*, at least 18 of the 24 averages). In the event that less than 75% of the 8-hour averages are available, a day shall also be counted as a valid day if the daily maximum 8-hour average concentration for that day is greater than the level of the ambient standard.

2.2 *Primary and Secondary Standard-related Summary Statistic.* The standard-related summary statistic is the annual fourth-highest daily maximum 8-hour ozone concentration, expressed in parts per million, averaged over three years. The 3-year average shall be computed

using the three most recent, consecutive calendar years of monitoring data meeting the data completeness requirements described in this appendix. The computed 3-year average of the annual fourth-highest daily maximum 8-hour average ozone concentrations shall be expressed to three decimal places (the remaining digits to the right are truncated.)

2.3 *Comparisons with the Primary and Secondary Ozone Standards.* (a) The primary and secondary ozone ambient air quality standards are met at an ambient air quality monitoring site when the 3-year average of the annual fourth-highest daily maximum 8-hour average ozone concentration is less than or equal to 0.08 ppm. The number of significant figures in the level of the standard dictates the rounding convention for comparing the computed 3-year average annual fourth-highest daily maximum 8-hour average ozone concentration with the level of the standard. The third decimal place of the computed value is rounded, with values equal to or greater than 5 rounding up. Thus, a computed 3-year average ozone concentration of 0.085 ppm is the smallest value that is greater than 0.08 ppm.

(b) This comparison shall be based on three consecutive, complete calendar years of air quality monitoring data. This requirement is met for the three year period at a monitoring site if daily maximum 8-hour average concentrations are available for at least 90%, on average, of the days during the designated ozone monitoring season, with a minimum data completeness in any one year of at least 75% of the designated sampling days. When computing whether the minimum data completeness requirements have been met, meteorological or ambient data may be sufficient to demonstrate that meteorological conditions on missing days were not conducive to concentrations above the level of the standard. Missing days assumed less than the level of the standard are counted for the purpose of meeting the data completeness requirement, subject to the approval of the appropriate Regional Administrator.

(c) Years with concentrations greater than the level of the standard shall not be ignored on the ground that they have less than complete data. Thus, in computing the 3-year average fourth maximum concentration, calendar years with less than 75% data completeness shall be included in the computation if the average annual fourth maximum 8-hour concentration is greater than the level of the standard.

(d) Comparisons with the primary and secondary ozone standards are demonstrated by examples 1 and 2 in paragraphs (d)(1) and (d) (2) respectively as follows:

(1) As shown in example 1, the primary and secondary standards are met at this monitoring site because the 3-year average of the annual fourth-highest daily maximum 8-hour average ozone concentrations (*i.e.*, 0.084 ppm) is less than or equal to 0.08 ppm. The data completeness requirement is also met because the average percent of days with valid ambient monitoring data is greater than 90%, and no single year has less than 75% data completeness.

EXAMPLE 1. AMBIENT MONITORING SITE ATTAINING THE PRIMARY AND SECONDARY OZONE STANDARDS

Year	Percent Valid Days	1st Highest Daily Max 8-hour Conc. (ppm)	2nd Highest Daily Max 8-hour Conc. (ppm)	3rd Highest Daily Max 8-hour Conc. (ppm)	4th Highest Daily Max 8-hour Conc. (ppm)	5th Highest Daily Max 8-hour Conc. (ppm)
1993	100%	0.092	0.091	0.090	0.088	0.085

1994	96%	0.090	0.089	0.086	0.084	0.080
1995	98%	0.087	0.085	0.083	0.080	0.075
Average	98%					

(2) As shown in example 2, the primary and secondary standards are not met at this monitoring site because the 3-year average of the fourth-highest daily maximum 8-hour average ozone concentrations (*i.e.*, 0.093 ppm) is greater than 0.08 ppm. Note that the ozone concentration data for 1994 is used in these computations, even though the data capture is less than 75%, because the average fourth-highest daily maximum 8-hour average concentration is greater than 0.08 ppm.

EXAMPLE 2. AMBIENT MONITORING SITE FAILING TO MEET THE PRIMARY AND SECONDARY OZONE STANDARDS

Year	Percent Valid Days	1st Highest Daily Max 8-hour Conc. (ppm)	2nd Highest Daily Max 8-hour Conc. (ppm)	3rd Highest Daily Max 8-hour Conc. (ppm)	4th Highest Daily Max 8-hour Conc. (ppm)	5th Highest Daily Max 8-hour Conc. (ppm)
1993	96%	0.105	0.103	0.103	0.102	0.102
1994	74%	0.090	0.085	0.082	0.080	0.078
1995	98%	0.103	0.101	0.101	0.097	0.095
Average	89%					

3. *Design Values for Primary and Secondary Ambient Air Quality Standards for Ozone.* The air quality design value at a monitoring site is defined as that concentration that when reduced to the level of the standard ensures that the site meets the standard. For a concentration-based standard, the air quality design value is simply the standard-related test statistic. Thus, for the primary and secondary ozone standards, the 3-year average annual fourth-highest daily maximum 8-hour average ozone concentration is also the air quality design value for the site.

[62 FR 38895, July 18, 1997]

State of Oregon Department of Environmental Quality

OAR 340-202-0100 Attachments

APPENDIX E TO PART 50 [RESERVED]

APPENDIX F TO PART 50—MEASUREMENT PRINCIPLE AND CALIBRATION PROCEDURE FOR THE MEASUREMENT OF NITROGEN DIOXIDE IN THE ATMOSPHERE (GAS PHASE CHEMILUMINESCENCE)

PRINCIPLE AND APPLICABILITY

1. Atmospheric concentrations of nitrogen dioxide (NO_2) are measured indirectly by photometrically measuring the light intensity, at wavelengths greater than 600 nanometers, resulting from the chemiluminescent reaction of nitric oxide (NO) with ozone (O_3). (*1,2,3*) NO_2 is first quantitatively reduced to NO(*4,5,6*) by means of a converter. NO, which commonly exists in ambient air together with NO_2, passes through the converter unchanged causing a resultant total NO_X concentration equal to $NO+NO_2$. A sample of the input air is also measured without having passed through the converted. This latter NO measurement is subtracted from the former measurement ($NO+NO_2$) to yield the final NO_2 measurement. The NO and $NO+NO_2$ measurements may be made concurrently with dual systems, or cyclically with the same system provided the cycle time does not exceed 1 minute.

2. *Sampling considerations.*

2.1 Chemiluminescence $NO/NO_X/NO_2$ analyzers will respond to other nitrogen containing compounds, such as peroxyacetyl nitrate (PAN), which might be reduced to NO in the thermal converter. (*7*) Atmospheric concentrations of these potential interferences are generally low relative to NO_2 and valid NO_2 measurements may be obtained. In certain geographical areas, where the concentration of these potential interferences is known or suspected to be high relative to NO_2, the use of an equivalent method for the measurement of NO_2 is recommended.

2.2 The use of integrating flasks on the sample inlet line of chemiluminescence $NO/NO_X/NO_2$ analyzers is optional and left to couraged. The sample residence time between the sampling point and the analyzer should be kept to a minimum to avoid erroneous NO_2 measurements resulting from the reaction of ambient levels of NO and O_3 in the sampling system.

2.3 The use of particulate filters on the sample inlet line of chemiluminescence $NO/NO_X/NO_2$ analyzers is optional and left to the discretion of the user or the manufacturer. Use of the filter should depend on the analyzer's susceptibility to interference, malfunction, or damage due to particulates. Users are cautioned that particulate matter concentrated on a filter may cause erroneous NO_2 measurements and therefore filters should be changed frequently.

3. An analyzer based on this principle will be considered a reference method only if it has been designated as a reference method in accordance with part 53 of this chapter.

CALIBRATION

1. *Alternative A*—Gas phase titration (GPT) of an NO standard with O_3.

Major equipment required: Stable O_3 generator. Chemiluminescence $NO/NO_X/NO_2$ analyzer with strip chart recorder(s). NO concentration standard.

1.1 *Principle.* This calibration technique is based upon the rapid gas phase reaction between NO and O_3 to produce stoichiometric quantities of NO_2 in accordance with the following equation: (*8*)

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (1)$$

The quantitative nature of this reaction is such that when the NO concentration is known, the concentration of NO_2 can be determined. Ozone is added to excess NO in a dynamic calibration system, and the NO channel of the chemiluminescence $NO/NO_X/NO_2$ analyzer is used as an indicator of changes in NO concentration. Upon the addition of O_3, the decrease in NO concentration observed on the calibrated NO channel is equivalent to the concentration of NO_2 produced. The amount of NO_2 generated may be varied by adding variable amounts of O_3 from a stable uncalibrated O_3 generator. (*9*)

1.2 *Apparatus.* Figure 1, a schematic of a typical GPT apparatus, shows the suggested configuration of the components listed below. All connections between components in the calibration system downstream from the O_3 generator should be of glass, Teflon®, or other non-reactive material.

1.2.1 *Air flow controllers.* Devices capable of maintaining constant air flows within ±2% of the required flowrate.

1.2.2 *NO flow controller.* A device capable of maintaining constant NO flows within ±2% of the required flowrate. Component parts in contact with the NO should be of a non-reactive material.

1.2.3 *Air flowmeters.* Calibrated flowmeters capable of measuring and monitoring air flowrates with an accuracy of ±2% of the measured flowrate.

1.2.4 *NO flowmeter.* A calibrated flowmeter capable of measuring and monitoring NO flowrates with an accuracy of ±2% of the measured flowrate. (Rotameters have been reported to operate unreliably when measuring low NO flows and are not recommended.)

1.2.5 *Pressure regulator for standard NO cylinder.* This regulator must have a nonreactive diaphragm and internal parts and a suitable delivery pressure.

1.2.6 *Ozone generator.* The generator must be capable of generating sufficient and stable levels of O_3 for reaction with NO to generate

NO_2 concentrations in the range required. Ozone generators of the electric discharge type may produce NO and NO_2 and are not recommended.

1.2.7 *Valve*. A valve may be used as shown in Figure 1 to divert the NO flow when zero air is required at the manifold. The valve should be constructed of glass, Teflon®, or other nonreactive material.

1.2.8 *Reaction chamber*. A chamber, constructed of glass, Teflon®, or other nonreactive material, for the quantitative reaction of O_3 with excess NO. The chamber should be of sufficient volume (V_{RC}) such that the residence time (t_R) meets the requirements specified in 1.4. For practical reasons, t_R should be less than 2 minutes.

1.2.9 *Mixing chamber*. A chamber constructed of glass, Teflon®, or other nonreactive material and designed to provide thorough mixing of reaction products and diluent air. The residence time is not critical when the dynamic parameter specification given in 1.4 is met.

1.2.10 *Output manifold*. The output manifold should be constructed of glass, Teflon®, or other non-reactive material and should be of sufficient diameter to insure an insignificant pressure drop at the analyzer connection. The system must have a vent designed to insure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

1.3 *Reagents*.

1.3.1 *NO concentration standard*. Gas cylinder standard containing 50 to 100 ppm NO in N_2 with less than 1 ppm NO_2. This standard must be traceable to a National Bureau of Standards (NBS) NO in N_2 Standard Reference Material (SRM 1683 or SRM 1684), an NBS NO_2 Standard Reference Material (SRM 1629), or an NBS/EPA-approved commercially available Certified Reference Material (CRM). CRM's are described in Reference 14, and a list of CRM sources is available from the address shown for Reference 14. A recommended protocol for certifying NO gas cylinders against either an NO SRM or CRM is given in section 2.0.7 of Reference 15. Reference 13 gives procedures for certifying an NO gas cylinder against an NBS NO_2 SRM and for determining the amount of NO_2 impurity in an NO cylinder.

1.3.2 *Zero air*. Air, free of contaminants which will cause a detectable response on the $NO/NO_X/NO_2$ analyzer or which might react with either NO, O_3, or NO_2 in the gas phase titration. A procedure for generating zero air is given in reference 13.

1.4 *Dynamic parameter specification*.

1.4.1 The O_3 generator air flowrate (F_0) and NO flowrate (F_{NO}) (see Figure 1) must be adjusted such that the following relationship holds:

$$P_R = [\mathrm{NO}]_{RC} \times t_R \ 2.75 \text{ ppm-minutes} \quad (2)$$

$$[\mathrm{NO}]_{RC} = [\mathrm{NO}]_{\mathrm{STD}} \left(\frac{F_{\mathrm{NO}}}{F_{\mathrm{O}} + F_{\mathrm{NO}}} \right) \quad (3)$$

$$t_R = \frac{V_{RC}}{F_O + F_{\mathrm{NO}}} < 2 \text{ minutes} \quad (4)$$

where:

P_R = dynamic parameter specification, determined empirically, to insure complete reaction of the available O_3, ppm-minute

$[NO]_{RC}$ = NO concentration in the reaction chamber, ppm

$_R$ = residence time of the reactant gases in the reaction chamber, minute

$[NO]_{STD}$ = concentration of the undiluted NO standard, ppm

F_{NO} = NO flowrate, scm^3/min

F_O = O_3 generator air flowrate, scm^3/min

V_{RC} = volume of the reaction chamber, scm^3

1.4.2 The flow conditions to be used in the GPT system are determined by the following procedure:

(a) Determine F_T, the total flow required at the output manifold (F_T=analyzer demand plus 10 to 50% excess).

(b) Establish $[NO]_{OUT}$ as the highest NO concentration (ppm) which will be required at the output manifold. $[NO]_{OUT}$ should be approximately equivalent to 90% of the upper range limit (*URL*) of the NO_2 concentration range to be covered.

(c) Determine F_{NO} as

$$F_{\mathrm{NO}} = \frac{[NO]_{\mathrm{OUT}} \times F_{\mathrm{T}}}{[NO]_{\mathrm{STD}}} \quad (5)$$

(d) Select a convenient or available reaction chamber volume. Initially, a trial V_{RC} may be selected to be in the range of approximately 200 to 500 scm^3.

(e) Compute FO as

$$F_{\mathrm{O}} = \sqrt{\frac{[\mathrm{NO}]_{\mathrm{STD}} \times F_{\mathrm{NO}} \times V_{\mathrm{RC}}}{2.75}} - F_{\mathrm{NO}} \quad (6)$$

(f) Compute t_R as

$$t_R = \frac{V_{RC}}{F_{\mathrm{O}} + F_{\mathrm{NO}}} \quad (7)$$

Verify that t_R <2 minutes. If not, select a reaction chamber with a smaller V_{RC}.

(g) Compute the diluent air flowrate as

$$F_D = F_T' \, F_O' \, F_{\mathrm{NO}} \quad (8)$$

where:

F_D = diluent air flowrate, scm^3/min

(h) If F_O turns out to be impractical for the desired system, select a reaction chamber

having a different V_{RC} and recompute F_O and F_D.

NOTE: A dynamic parameter lower than 2.75 ppm-minutes may be used if it can be determined empirically that quantitative reaction of O_3 with NO occurs. A procedure for making this determination as well as a more detailed discussion of the above requirements and other related considerations is given in reference 13.

1.5 *Procedure.*

1.5.1 Assemble a dynamic calibration system such as the one shown in Figure 1.

1.5.2 Insure that all flowmeters are calibrated under the conditions of use against a reliable standard such as a soap-bubble meter or wet-test meter. All volumetric flowrates should be corrected to 25 °C and 760 mm Hg. A discussion on the calibration of flowmeters is given in reference 13.

1.5.3 Precautions must be taken to remove O_2 and other contaminants from the NO pressure regulator and delivery system prior to the start of calibration to avoid any conversion of the standard NO to NO_2. Failure to do so can cause significant errors in calibration. This problem may be minimized by (1) carefully evacuating the regulator, when possible, after the regulator has been connected to the cylinder and before opening the cylinder valve; (2) thoroughly flushing the regulator and delivery system with NO after opening the cylinder valve; (3) not removing the regulator from the cylinder between calibrations unless absolutely necessary. Further discussion of these procedures is given in reference 13.

1.5.4 Select the operating range of the NO/NO_X/NO_2 analyzer to be calibrated. In order to obtain maximum precision and accuracy for NO_2 calibration, all three channels of the analyzer should be set to the same range. If operation of the NO and NO_X channels on higher ranges is desired, subsequent recalibration of the NO and NO_X channels on the higher ranges is recommended.

NOTE: Some analyzer designs may require identical ranges for NO, NO_X, and NO_2 during operation of the analyzer.

1.5.5 Connect the recorder output cable(s) of the NO/NO_X/NO_2 analyzer to the input terminals of the strip chart recorder(s). All adjustments to the analyzer should be performed based on the appropriate strip chart readings. References to analyzer responses in the procedures given below refer to recorder responses.

1.5.6 Determine the GPT flow conditions required to meet the dynamic parameter specification as indicated in 1.4.

1.5.7 Adjust the diluent air and O_3 generator air flows to obtain the flows determined in section 1.4.2. The total air flow must exceed the total demand of the analyzer(s) connected to the output manifold to insure that no ambient air is pulled into the manifold vent. Allow the analyzer to sample zero air until stable NO, NO_X, and NO_2 responses are obtained. After the responses have stabilized, adjust the analyzer zero control(s).

NOTE: Some analyzers may have separate zero controls for NO, NO_X, and NO_2. Other analyzers may have separate zero controls only for NO and NO_X, while still others may have only one zero control common to all three channels.

Offsetting the analyzer zero adjustments to +5 percent of scale is recommended to facilitate observing negative zero drift. Record the stable zero air responses as Z_{NO}, ZNOX, and ZNO2.

1.5.8 *Preparation of NO and NO_X calibration curves.*

1.5.8.1 *Adjustment of NO span control.* Adjust the NO flow from the standard NO cylinder to generate an NO concentration of approximately 80 percent of the upper range limit (*URL*) of the NO range. This exact NO concentration is calculated from:

$$[NO]_{OUT} = \frac{F_{NO} \times [NO]_{STD}}{F_{NO} + F_O + F_D} \qquad (9)$$

where:

$[NO]_{OUT}$ = diluted NO concentration at the output manifold, ppm

Sample this NO concentration until the NO and NO_X responses have stabilized. Adjust the NO span control to obtain a recorder response as indicated below:

recorder response (percent scale) =

$$\left(\frac{[NO]_{OUT}}{URL} \times 100 \right) + Z_{NO} \qquad (10)$$

where:

URL = nominal upper range limit of the NO channel, ppm

NOTE: Some analyzers may have separate span controls for NO, NO_X, and NO_2. Other analyzers may have separate span controls only for NO and NO_X, while still others may have only one span control common to all three channels. When only one span control is available, the span adjustment is made on the NO channel of the analyzer.

If substantial adjustment of the NO span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating steps 1.5.7 and 1.5.8.1. Record the NO concentration and the analyzer's NO response.

1.5.8.2 *Adjustment of NO_X span control.* When adjusting the analyzer's NO_X span control, the presence of any NO_2 impurity in the standard NO cylinder must be taken into account. Procedures for determining the amount of NO_2 impurity in the standard NO

cylinder are given in reference 13. The exact NO_X concentration is calculated from:

$$[NO_X]_{OUT} = \frac{F_{NO} \times \left([NO]_{STD} + [NO_2]_{IMP}\right)}{F_{NO} + F_O + F_D} \quad (11)$$

where:

$[NO_X]_{OUT}$ = diluted NO_X concentration at the output manifold, ppm

$[NO_2]_{IMP}$ = concentration of NO_2 impurity in the standard NO cylinder, ppm

Adjust the NO_X span control to obtain a recorder response as indicated below:

recorder response (% scale) =

$$\left(\frac{[NO_X]_{OUT}}{URL} \times 100\right) + Z_{NO_X} \quad (12)$$

NOTE: If the analyzer has only one span control, the span adjustment is made on the NO channel and no further adjustment is made here for NO_X.

If substantial adjustment of the NO_X span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating steps 1.5.7 and 1.5.8.2. Record the NO_X concentration and the analyzer's NO_X response.

1.5.8.3 Generate several additional concentrations (at least five evenly spaced points across the remaining scale are suggested to verify linearity) by decreasing F_{NO} or increasing F_D. For each concentration generated, calculate the exact NO and NO_X concentrations using equations (9) and (11) respectively. Record the analyzer's NO and NO_X responses for each concentration. Plot the analyzer responses versus the respective calculated NO and NO_X concentrations and draw or calculate the NO and NO_X calibration curves. For subsequent calibrations where linearity can be assumed, these curves may be checked with a two-point calibration consisting of a zero air point and NO and NO_X concentrations of approximately 80% of the *URL*.

1.5.9 *Preparation of NO_2 calibration curve.*

1.5.9.1 Assuming the NO_2 zero has been properly adjusted while sampling zero air in step 1.5.7, adjust F_O and F_D as determined in section 1.4.2. Adjust F_{NO} to generate an NO concentration near 90% of the *URL* of the NO range. Sample this NO concentration until the NO and NO_X responses have stabilized. Using the NO calibration curve obtained in section 1.5.8, measure and record the NO concentration as $[NO]_{orig}$. Using the NO_X calibration curve obtained in section 1.5.8, measure and record the NO_X concentration as $[NO_X]_{orig}$.

1.5.9.2 Adjust the O_3 generator to generate sufficient O_3 to produce a decrease in the NO concentration equivalent to approximately 80% of the URL of the NO_2 range. The decrease must not exceed 90% of the NO concentration determined in step 1.5.9.1. After the analyzer responses have stabilized, record the resultant NO and NO_X concentrations as $[NO]_{rem}$ and $[NO_X]_{rem}$.

1.5.9.3 Calculate the resulting NO_2 concentration from:

$$[NO_2]_{OUT} = [NO]_{orig} - [NO]_{rem} + \frac{F_{NO} \times [NO_2]_{IMP}}{F_{NO} + F_O + F_D} \quad (13)$$

where:

$[NO_2]_{OUT}$ = diluted NO_2 concentration at the output manifold, ppm

$[NO]_{orig}$ = original NO concentration, prior to addition of O_3, ppm

$[NO]_{rem}$ = NO concentration remaining after addition of O_3, ppm

Adjust the NO_2 span control to obtain a recorder response as indicated below:

recorder response (% scale) =

$$\left(\frac{[NO_2]_{OUT}}{URL} \times 100\right) + Z_{NO_2} \quad (14)$$

NOTE: If the analyzer has only one or two span controls, the span adjustments are made on the NO channel or NO and NO_X channels and no further adjustment is made here for NO_2.

If substantial adjustment of the NO_2 span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating steps 1.5.7 and 1.5.9.3. Record the NO_2 concentration and the corresponding analyzer NO_2 and NO_X responses.

1.5.9.4 Maintaining the same F_{NO}, F_O, and F_D as in section 1.5.9.1, adjust the ozone generator to obtain several other concentrations of NO_2 over the NO_2 range (at least five evenly spaced points across the remaining scale are suggested). Calculate each NO_2 concentration using equation (13) and record the corresponding analyzer NO_2 and NO_X responses. Plot the analyzer's NO_2 responses versus the corresponding calculated NO_2 concentrations and draw or calculate the NO_2 calibration curve.

1.5.10 *Determination of converter efficiency.*

1.5.10.1 For each NO_2 concentration generated during the preparation of the NO_2 calibration curve (see section 1.5.9) calculate the concentration of NO_2 converted from:

$$[NO_2]_{CONV} = [NO_2]_{OUT} - ([NO_X]_{orig} - [NO_X]_{rem}) \quad (15)$$

where:

$[NO_2]_{CONV}$ = concentration of NO_2 converted, ppm

$[NO_X]_{orig}$ = original NO_X concentration prior to addition of O_3, ppm

$[NO_X]_{rem}$ = NO_X concentration remaining after addition of O_3, ppm

NOTE: Supplemental information on calibration and other procedures in this method are given in reference 13.

Plot $[NO_2]_{CONV}$ (y-axis) versus $[NO_2]_{OUT}$ (x-axis) and draw or calculate the converter efficiency curve. The slope of the curve times 100 is the average converter efficiency, E_C The average converter efficiency must be greater than 96%; if it is less than 96%, replace or service the converter.

2. *Alternative B*—NO_2 permeation device.

Major equipment required:

Stable O_3 generator.

Chemiluminescence $NO/NO_X/NO_2$ analyzer with strip chart recorder(s).

NO concentration standard.

NO_2 concentration standard.

2.1 *Principle.* Atmospheres containing accurately known concentrations of nitrogen dioxide are generated by means of a permeation device. (*10*) The permeation device emits NO_2 at a known constant rate provided the temperature of the device is held constant (±0.1 °C) and the device has been accurately calibrated at the temperature of use. The NO_2 emitted from the device is diluted with zero air to produce NO_2 concentrations suitable for calibration of the NO_2 channel of the $NO/NO_X/NO_2$ analyzer. An NO concentration standard is used for calibration of the NO and NO_X channels of the analyzer.

2.2 *Apparatus.* A typical system suitable for generating the required NO and NO_2 concentrations is shown in Figure 2. All connections between components downstream from the permeation device should be of glass, Teflon®, or other non-reactive material.

2.2.1 *Air flow controllers.* Devices capable of maintaining constant air flows within ±2% of the required flowrate.

2.2.2 *NO flow controller.* A device capable of maintaining constant NO flows within ±2% of the required flowrate. Component parts in contact with the NO must be of a non-reactive material.

2.2.3 *Air flowmeters.* Calibrated flowmeters capable of measuring and monitoring air flowrates with an accuracy of ±2% of the measured flowrate.

2.2.4 *NO flowmeter.* A calibrated flowmeter capable of measuring and monitoring NO flowrates with an accuracy of ±2% of the measured flowrate. (Rotameters have been reported to operate unreliably when measuring low NO flows and are not recommended.)

2.2.5 *Pressure regulator for standard NO cylinder.* This regulator must have a non-reactive diaphragm and internal parts and a suitable delivery pressure.

2.2.6 *Drier.* Scrubber to remove moisture from the permeation device air system. The use of the drier is optional with NO_2 permeation devices not sensitive to moisture. (Refer to the supplier's instructions for use of the permeation device.)

2.2.7 *Constant temperature chamber.* Chamber capable of housing the NO_2 permeation device and maintaining its temperature to within ±0.1 °C.

2.2.8 *Temperature measuring device.* Device capable of measuring and monitoring the temperature of the NO_2 permeation device with an accuracy of ±0.05 °C.

2.2.9 *Valves.* A valve may be used as shown in Figure 2 to divert the NO_2 from the permeation device when zero air or NO is required at the manifold. A second valve may be used to divert the NO flow when zero air or NO_2 is required at the manifold.

The valves should be constructed of glass, Teflon®, or other nonreactive material.

2.2.10 *Mixing chamber.* A chamber constructed of glass, Teflon®, or other nonreactive material and designed to provide thorough mixing of pollutant gas streams and diluent air.

2.2.11 *Output manifold.* The output manifold should be constructed of glass, Teflon®, or other non-reactive material and should be of sufficient diameter to insure an insignificant pressure drop at the analyzer connection. The system must have a vent designed to insure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

2.3 *Reagents.*

2.3.1 *Calibration standards.* Calibration standards are required for both NO and NO_2. The reference standard for the calibration may be either an NO or NO_2 standard, and must be traceable to a National Bureau of Standards (NBS) NO in N_2 Standard Reference Material (SRM 1683 or SRM 1684), and NBS NO_2 Standard Reference Material (SRM 1629), or an NBS/EPA-approved commercially

available Certified Reference Material (CRM). CRM's are described in Reference 14, and a list of CRM sources is available from the address shown for Reference 14. Reference 15 gives recommended procedures for certifying an NO gas cylinder against an NO SRM or CRM and for certifying an NO_2 permeation device against an NO_2 SRM. Reference 13 contains procedures for certifying an NO gas cylinder against an NO_2 SRM and for certifying an NO_2 permeation device against an NO SRM or CRM. A procedure for determining the amount of NO_2 impurity in an NO cylinder is also contained in Reference 13. The NO or NO_2 standard selected as the reference standard must be used to certify the other standard to ensure consistency between the two standards.

2.3.1.1 *NO_2 Concentration standard.* A permeation device suitable for generating NO_2 concentrations at the required flow-rates over the required concentration range. If the permeation device is used as the reference standard, it must be traceable to an SRM or CRM as specified in 2.3.1. If an NO cylinder is used as the reference standard, the NO_2 permeation device must be certified against the NO standard according to the procedure given in Reference 13. The use of the permeation device should be in strict accordance with the instructions supplied with the device. Additional information regarding the use of permeation devices is given by Scaringelli et al. (11) and Rook et al. (12).

2.3.1.2 *NO Concentration standard.* Gas cylinder containing 50 to 100 ppm NO in N_2 with less than 1 ppm NO_2. If this cylinder is used as the reference standard, the cylinder must be traceable to an SRM or CRM as specified in 2.3.1. If an NO_2 permeation device is used as the reference standard, the NO cylinder must be certified against the NO_2 standard according to the procedure given in Reference 13. The cylinder should be recertified on a regular basis as determined by the local quality control program.

2.3.3 *Zero air.* Air, free of contaminants which might react with NO or NO_2 or cause a detectable response on the NO/NO_X/NO_2 analyzer. When using permeation devices that are sensitive to moisture, the zero air passing across the permeation device must be dry to avoid surface reactions on the device. (Refer to the supplier's instructions for use of the permeation device.) A procedure for generating zero air is given in reference 13.

2.4 *Procedure.*

2.4.1 Assemble the calibration apparatus such as the typical one shown in Figure 2.

2.4.2 Insure that all flowmeters are calibrated under the conditions of use against a reliable standard such as a soap bubble meter or wet-test meter. All volumetric flowrates should be corrected to 25 °C and 760 mm Hg. A discussion on the calibration of flowmeters is given in reference 13.

2.4.3 Install the permeation device in the constant temperature chamber. Provide a small fixed air flow (200–400 scm^3/min) across the device. The permeation device should always have a continuous air flow across it to prevent large buildup of NO_2 in the system and a consequent restabilization period. Record the flowrate as FP. Allow the device to stabilize at the calibration temperature for at least 24 hours. The temperature must be adjusted and controlled to within ±0.1 °C or less of the calibration temperature as monitored with the temperature measuring device.

2.4.4 Precautions must be taken to remove O_2 and other contaminants from the NO pressure regulator and delivery system prior to the start of calibration to avoid any conversion of the standard NO to NO_2. Failure to do so can cause significant errors in calibration. This problem may be minimized by

(1) Carefully evacuating the regulator, when possible, after the regulator has been connected to the cylinder and before opening the cylinder valve;

(2) Thoroughly flushing the regulator and delivery system with NO after opening the cylinder valve;

(3) Not removing the regulator from the cylinder between calibrations unless absolutely necessary. Further discussion of these procedures is given in reference 13.

2.4.5 Select the operating range of the NO/NO_X NO_2 analyzer to be calibrated. In order to obtain maximum precision and accuracy for NO_2 calibration, all three channels of the analyzer should be set to the same range. If operation of the NO and NO_X channels on higher ranges is desired, subsequent recalibration of the NO and NO_X channels on the higher ranges is recommended.

NOTE: Some analyzer designs may require identical ranges for NO, NO_X, and NO_2 during operation of the analyzer.

2.4.6 Connect the recorder output cable(s) of the NO/NO_X/NO_2 analyzer to the input terminals of the strip chart recorder(s). All adjustments to the analyzer should be performed based on the appropriate strip chart readings. References to analyzer responses in the procedures given below refer to recorder responses.

2.4.7 Switch the valve to vent the flow from the permeation device and adjust the diluent air flowrate, F_D, to provide zero air at the output manifold. The total air flow must exceed the total demand of the analyzer(s) connected to the output manifold to insure that no ambient air is pulled into the manifold vent. Allow the analyzer to sample zero air until stable NO, NO_X, and NO_2 responses are obtained. After the responses have stabilized, adjust the analyzer zero control(s).

NOTE: Some analyzers may have separate zero controls for NO, NO_X, and NO_2. Other analyzers may have separate zero controls

only for NO and NO_X, while still others may have only one zero common control to all three channels.

Offsetting the analyzer zero adjustments to +5% of scale is recommended to facilitate observing negative zero drift. Record the stable zero air responses as Z_{NO}, Z_{NOX}, and Z_{NO2}.

2.4.8 *Preparation of NO and NO_X calibration curves.*

2.4.8.1 *Adjustment of NO span control.* Adjust the NO flow from the standard NO cylinder to generate an NO concentration of approximately 80% of the upper range limit (URL) of the NO range. The exact NO concentration is calculated from:

$$[NO]_{OUT} = \frac{F_{NO} \times [NO]_{STD}}{F_{NO} + F_D} \quad (16)$$

where:

$[NO]_{OUT}$ = diluted NO concentration at the output manifold, ppm

F_{NO} = NO flowrate, scm^3/min

$[NO]_{STD}$ = concentration of the undiluted NO standard, ppm

F_D = diluent air flowrate, scm^3/min

Sample this NO concentration until the NO and NO_X responses have stabilized. Adjust the NO span control to obtain a recorder response as indicated below:

recorder response (% scale) =

$$= \left(\frac{[NO]_{OUT}}{URL} \times 100 \right) + Z_{NO} \quad (17)$$

$$= \left(\frac{[NO_X]_{OUT}}{URL} \times 100 \right) + Z_{NO_X} \quad (19)$$

where:

URL = nominal upper range limit of the NO channel, ppm

NOTE: Some analyzers may have separate span controls for NO, NO_X, and NO_2. Other analyzers may have separate span controls only for NO and NO_X, while still others may have only one span control common to all three channels. When only one span control is available, the span adjustment is made on the NO channel of the analyzer.

If substantial adjustment of the NO span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating steps 2.4.7 and 2.4.8.1. Record the NO concentration and the analyzer's NO response.

2.4.8.2 *Adjustment of NO_X span control.* When adjusting the analyzer's NO_X span control, the presence of any NO_2 impurity in the standard NO cylinder must be taken into account. Procedures for determining the amount of NO_2 impurity in the standard NO cylinder are given in reference 13. The exact NO_X concentration is calculated from:

$$[NO_X]_{OUT} = \frac{F_{NO} \times \left([NO]_{STD} + [NO_2]_{IMP} \right)}{F_{NO} + F_D} \quad (18)$$

where:

$[NO_X]_{OUT}$ = diluted NO_X cencentration at the output manifold, ppm

$[NO_2]_{IMP}$ = concentration of NO_2 impurity in the standard NO cylinder, ppm

Adjust the NO_X span control to obtain a convenient recorder response as indicated below:

recorder response (% scale)

$$= \left(\frac{[NO_X]_{OUT}}{URL} \times 100 \right) + Z_{NO_X} \quad (19)$$

NOTE: If the analyzer has only one span control, the span adjustment is made on the NO channel and no further adjustment is made here for NO_X.

If substantial adjustment of the NO_X span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating steps 2.4.7 and 2.4.8.2. Record the NO_X concentration and the analyzer's NO_X response.

2.4.8.3 Generate several additional concentrations (at least five evenly spaced points across the remaining scale are suggested to verify linearity) by decreasing F_{NO} or increasing F_D. For each concentration generated, calculate the exact NO and NO_X concentrations using equations (16) and (18) respectively. Record the analyzer's NO and NO_X responses for each concentration. Plot the analyzer responses versus the respective calculated NO and NO_X concentrations and draw or calculate the NO and NO_X calibration curves. For subsequent calibrations where linearity can be assumed, these curves may be checked with a two-point calibration consisting of a zero point and NO and NO_X concentrations of approximately 80 percent of the URL.

2.4.9 *Preparation of NO_2 calibration curve.*

2.4.9.1 Remove the NO flow. Assuming the NO_2 zero has been properly adjusted while sampling zero air in step 2.4.7, switch the valve to provide NO_2 at the output manifold.

2.4.9.2 Adjust F_D to generate an NO_2 concentration of approximately 80 percent of the *URL* of the NO_2 range. The total air flow must exceed the demand of the analyzer(s) under calibration. The actual concentration of NO_2 is calculated from:

$$[NO_2]_{OUT} = \frac{R \times K}{F_P + F_D} \quad (20)$$

where:

$[NO_2]_{OUT}$ = diluted NO_2 concentration at the output manifold, ppm
R = permeation rate, μg/min
K = 0.532 μl NO_2/μg NO_2 (at 25 °C and 760 mm Hg)
F_p = air flowrate across permeation device, scm^3/min
F_D = diluent air flowrate, scm^3/min

Sample this NO_2 concentration until the NO_X and NO_2 responses have stabilized. Adjust the NO_2 span control to obtain a recorder response as indicated below:

recorder response (% scale)

$$= \left(\frac{[NO_2]_{OUT}}{URL} \times 100 \right) + Z_{NO2} \qquad (21)$$

NOTE: If the analyzer has only one or two span controls, the span adjustments are made on the NO channel or NO and NO_X channels and no further adjustment is made here for NO_2.

If substantial adjustment of the NO_2 span control is necessary it may be necessary to recheck the zero and span adjustments by repeating steps 2.4.7 and 2.4.9.2. Record the NO_2 concentration and the analyzer's NO_2 response. Using the NO_X calibration curve obtained in step 2.4.8, measure and record the NO_X concentration as $[NO_X]_M$.

2.4.9.3 Adjust F_D to obtain several other concentrations of NO_2 over the NO_2 range (at least five evenly spaced points across the remaining scale are suggested). Calculate each NO_2 concentration using equation (20) and record the corresponding analyzer NO_2 and NO_X responses. Plot the analyzer's NO_2 responses versus the corresponding calculated NO_2 concentrations and draw or calculate the NO_2 calibration curve.

2.4.10 *Determination of converter efficiency.*

2.4.10.1 Plot $[NO_X]_M$ (y-axis) versus $[NO_2]_{OUT}$ (x-axis) and draw or calculate the converter efficiency curve. The slope of the curve times 100 is the average converter efficiency, E_C. The average converter efficiency must be greater than 96 percent; if it is less than 96 percent, replace or service the converter.

NOTE: Supplemental information on calibration and other procedures in this method are given in reference 13.

3. *Frequency of calibration.* The frequency of calibration, as well as the number of points necessary to establish the calibration curve and the frequency of other performance checks, will vary from one analyzer to another. The user's quality control program should provide guidelines for initial establishment of these variables and for subsequent alteration as operational experience is accumulated. Manufacturers of analyzers should include in their instruction/operation manuals information and guidance as to these variables and on other matters of operation, calibration, and quality control.

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15. *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II, Ambient Air Specific Methods.* The U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC 27711. Publication No. EAP–600/4–77–027a.

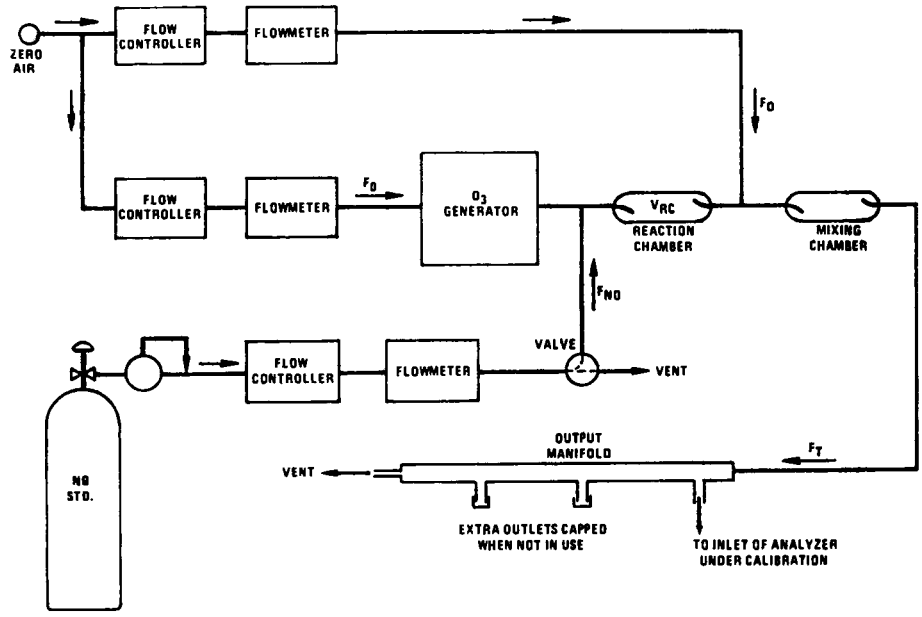

Figure 1. Schematic diagram of a typical GPT calibration system.

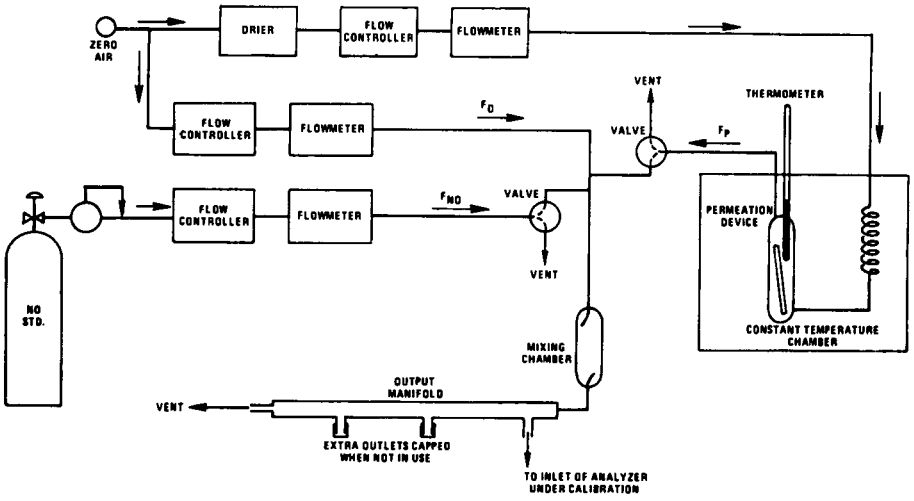

Figure 2. Schematic diagram of a typical calibration apparatus using an NO_2 permeation device.

[41 FR 52688, Dec. 1, 1976, as amended at 48 FR 2529, Jan. 20, 1983]

Appendix G to Part 50—Reference Method for the Determination of Lead in Total Suspended Particulate Matter

1.0 Scope and Applicability

Based on review of the air quality criteria and national ambient air quality standard (NAAQS) for lead (Pb) completed in 2008, the EPA made revisions to the primary and secondary NAAQS for Pb to protect public health and welfare. The EPA revised the level from 1.5 $\mu g/m^3$ to 0.15 $\mu g/m^3$ while retaining the current indicator of Pb in total suspended particulate matter (Pb-TSP).

Pb-TSP is collected for 24 hours on a TSP filter as described in Appendix B of part 50, the Reference Method for the Determination of Suspended Particulate Matter in the Atmosphere (High-Volume Method). This method is for the analysis of Pb from TSP filters by Inductively Coupled Plasma Mass Spectrometry (ICP–MS) using a heated ultrasonic bath with nitric acid (HNO_3) and hydrochloric acid (HCl) or a heated block (hot block) digester with HNO_3 for filter extraction.

This method is based on the EPA's Office of Solid Waste (SW–846) Method 6020A—Inductively Coupled Plasma Mass Spectrometry (U.S. EPA, 2007). Wording in certain sections of this method is paraphrased or taken directly from Method 6020A.

1.1 ICP–MS is applicable for the sub-µg/mL (ppb) determination of Pb in a wide variety of matrices. Results reported for monitoring or compliance purposes are calculated in $\mu g/m^3$ at local conditions (LC). This procedure describes a method for the acid extraction of Pb in particulate matter collected on glass fiber, quartz, or PTFE filters and measurement of the extracted Pb using ICP–MS.

1.2 Due to variations in the isotopic abundance of Pb, the value for total Pb must be based on the sum of the signal intensities for isotopic masses, 206, 207, and 208. Most instrument software packages are able to sum the primary isotope signal intensities automatically.

1.3 ICP–MS requires the use of an internal standard. ^{115}In (Indium), ^{165}Ho (Holmium), and ^{209}Bi (Bismuth) are recommended internal standards for the determination of Pb.

1.4 Use of this method is restricted to use by, or under supervision of, properly trained and experienced laboratory personnel. Requirements include training and experience in inorganic sample preparation, including acid extraction, and also knowledge in the recognition and in the correction of spectral, chemical and physical interference in ICP–MS.

2.0 Summary of Method

2.1 This method describes the acid extraction of Pb in particulate matter collected on glass fiber, quartz, or PTFE ambient air filters with subsequent measurement of Pb by

Equation 2

$$\bar{X}_{m1,m2,m3;s} = \frac{1}{n_m}\sum_{i=1}^{n_m} \bar{X}_{m,y:z,s}$$

Where:

$\bar{X}_{m1,\ m2,\ m3;\ s}$ = the 3-month parameter mean for months m1, m2, and m3 for site s; and

n_m = the number of monthly means available to be averaged (typically 3, sometimes 1 or 2 if one or two months have no valid daily values); and

$X_{m,\ y:\ z,\ s}$ = The mean for month m of the year y (or z) for site s.

(c) Three-month site means are determined from available 3-month parameter means according to the hierarchy established in 2(a) of this appendix.

(d) The site-level Pb design value is the highest valid 3-month site-level mean over the most recent 38-month period (*i.e.*, the most recent 3-year calendar period plus two previous months). Section 4(a) of this appendix explains when the identified design value is itself considered valid for purposes of determining that the NAAQS is met or violated at a site.

[73 FR 67054, Nov. 12, 2008]

Appendix S to Part 50—Interpretation of the Primary National Ambient Air Quality Standards for Oxides of Nitrogen (Nitrogen Dioxide)

1. General

(a) This appendix explains the data handling conventions and computations necessary for determining when the primary national ambient air quality standards for oxides of nitrogen as measured by nitrogen dioxide (''NO_2 NAAQS'') specified in 50.11 are met. Nitrogen dioxide (NO_2) is measured in the ambient air by a Federal reference method (FRM) based on appendix F to this part or by a Federal equivalent method (FEM) designated in accordance with part 53 of this chapter. Data handling and computation procedures to be used in making comparisons between reported NO_2 concentrations and the levels of the NO_2 NAAQS are specified in the following sections.

(b) Whether to exclude, retain, or make adjustments to the data affected by exceptional events, including natural events, is determined by the requirements and process deadlines specified in 50.1, 50.14 and 51.930 of this chapter.

(c) The terms used in this appendix are defined as follows:

Annual mean refers to the annual average of all of the 1-hour concentration values as defined in section 5.1 of this appendix.

Daily maximum 1-hour values for NO_2 refers to the maximum 1-hour NO_2 concentration values measured from midnight to midnight (local standard time) that are used in NAAQS computations.

Design values are the metrics (*i.e.*, statistics) that are compared to the NAAQS levels to determine compliance, calculated as specified in section 5 of this appendix. The design values for the primary NAAQS are:

(1) The annual mean value for a monitoring site for one year (referred to as the ''annual primary standard design value'').

(2) The 3-year average of annual 98th percentile daily maximum 1-hour values for a monitoring site (referred to as the ''1-hour primary standard design value'').

98th percentile daily maximum 1-hour value is the value below which nominally 98 percent of all daily maximum 1-hour concentration values fall, using the ranking and selection method specified in section 5.2 of this appendix.

Quarter refers to a calendar quarter.

Year refers to a calendar year.

2. Requirements for Data Used for Comparisons With the NO_2 NAAQS and Data Reporting Considerations

(a) All valid FRM/FEM NO_2 hourly data required to be submitted to EPA's Air Quality System (AQS), or otherwise available to EPA, meeting the requirements of part 58 of this chapter including appendices A, C, and E shall be used in design value calculations. Multi-hour average concentration values collected by wet chemistry methods shall not be used.

(b) When two or more NO_2 monitors are operated at a site, the State may in advance designate one of them as the primary monitor. If the State has not made this designation, the Administrator will make the designation, either in advance or retrospectively. Design values will be developed using only the data from the primary monitor, if this results in a valid design value. If data from the primary monitor do not allow the development of a valid design value, data solely from the other monitor(s) will be used in turn to develop a valid design value, if this results in a valid design value. If there are three or more monitors, the order for such comparison of the other monitors will be determined by the Administrator. The Administrator may combine data from different monitors in different years for the purpose of developing a valid 1-hour primary standard design value, if a valid design value cannot be developed solely with the data from a single monitor. However, data from two or more monitors in the same year at the same site will not be combined in an attempt to meet data completeness requirements, except if one monitor has physically replaced another instrument permanently, in

which case the two instruments will be considered to be the same monitor, or if the State has switched the designation of the primary monitor from one instrument to another during the year.

(c) Hourly NO_2 measurement data shall be reported to AQS in units of parts per billion (ppb), to at most one place after the decimal, with additional digits to the right being truncated with no further rounding.

3. Comparisons With the NO_2 NAAQS

3.1 The Annual Primary NO_2 NAAQS

(a) The annual primary NO_2 NAAQS is met at a site when the valid annual primary standard design value is less than or equal to 53 parts per billion (ppb).

(b) An annual primary standard design value is valid when at least 75 percent of the hours in the year are reported.

(c) An annual primary standard design value based on data that do not meet the completeness criteria stated in section 3.1(b) may also be considered valid with the approval of, or at the initiative of, the Administrator, who may consider factors such as monitoring site closures/moves, monitoring diligence, the consistency and levels of the valid concentration measurements that are available, and nearby concentrations in determining whether to use such data.

(d) The procedures for calculating the annual primary standard design values are given in section 5.1 of this appendix.

3.2 The 1-hour Primary NO_2 NAAQS

(a) The 1-hour primary NO_2 NAAQS is met at a site when the valid 1-hour primary standard design value is less than or equal to 100 parts per billion (ppb).

(b) An NO_2 1-hour primary standard design value is valid if it encompasses three consecutive calendar years of complete data. A year meets data completeness requirements when all 4 quarters are complete. A quarter is complete when at least 75 percent of the sampling days for each quarter have complete data. A sampling day has complete data if 75 percent of the hourly concentration values, including State-flagged data affected by exceptional events which have been approved for exclusion by the Administrator, are reported.

(c) In the case of one, two, or three years that do not meet the completeness requirements of section 3.2(b) of this appendix and thus would normally not be useable for the calculation of a valid 3-year 1-hour primary standard design value, the 3-year 1-hour primary standard design value shall nevertheless be considered valid if one of the following conditions is true.

(i) At least 75 percent of the days in each quarter of each of three consecutive years have at least one reported hourly value, and the design value calculated according to the procedures specified in section 5.2 is above the level of the primary 1-hour standard.

(ii)(A) A 1-hour primary standard design value that is below the level of the NAAQS can be validated if the substitution test in section 3.2(c)(ii)(B) results in a ''test design value'' that is below the level of the NAAQS. The test substitutes actual ''high'' reported daily maximum 1-hour values from the same site at about the same time of the year (specifically, in the same calendar quarter) for unknown values that were not successfully measured. Note that the test is merely diagnostic in nature, intended to confirm that there is a very high likelihood that the original design value (the one with less than 75 percent data capture of hours by day and of days by quarter) reflects the true under-NAAQS-level status for that 3-year period; the result of this data substitution test (the ''test design value'', as defined in section 3.2(c)(ii)(B)) is not considered the actual design value. For this test, substitution is permitted only if there are at least 200 days across the three matching quarters of the three years under consideration (which is about 75 percent of all possible daily values in those three quarters) for which 75 percent of the hours in the day, including State-flagged data affected by exceptional events which have been approved for exclusion by the Administrator, have reported concentrations. However, maximum 1-hour values from days with less than 75 percent of the hours reported shall also be considered in identifying the high value to be used for substitution.

(B) *The substitution test is as follows:* Data substitution will be performed in all quarter periods that have less than 75 percent data capture but at least 50 percent data capture, including State-flagged data affected by exceptional events which have been approved for exclusion by the Administrator; if any quarter has less than 50 percent data capture then this substitution test cannot be used. Identify for each quarter (e.g., January–March) the highest reported daily maximum 1-hour value for that quarter, excluding State-flagged data affected by exceptional events which have been approved for exclusion by the Administrator, looking across those three months of all three years under consideration. All daily maximum 1-hour values from all days in the quarter period shall be considered when identifying this highest value, including days with less than 75 percent data capture. If after substituting the highest non-excluded reported daily maximum 1-hour value for a quarter for as much of the missing daily data in the matching deficient quarter(s) as is needed to make them 100 percent complete, the procedure in section 5.2 yields a recalculated 3-year 1-hour standard ''test design value'' below the level of the standard, then the 1-hour primary standard design value is deemed to have

passed the diagnostic test and is valid, and the level of the standard is deemed to have been met in that 3-year period. As noted in section 3.2(c)(i), in such a case, the 3-year design value based on the data actually reported, not the ''test design value'', shall be used as the valid design value.

(iii)(A) A 1-hour primary standard design value that is above the level of the NAAQS can be validated if the substitution test in section 3.2(c)(iii)(B) results in a ''test design value'' that is above the level of the NAAQS. The test substitutes actual ''low'' reported daily maximum 1-hour values from the same site at about the same time of the year (specifically, in the same three months of the calendar) for unknown values that were not successfully measured. Note that the test is merely diagnostic in nature, intended to confirm that there is a very high likelihood that the original design value (the one with less than 75 percent data capture of hours by day and of days by quarter) reflects the true above-NAAQS-level status for that 3-year period; the result of this data substitution test (the ''test design value'', as defined in section 3.2(c)(iii)(B)) is not considered the actual design value. For this test, substitution is permitted only if there are a minimum number of available daily data points from which to identify the low quarter-specific daily maximum 1-hour values, specifically if there are at least 200 days across the three matching quarters of the three years under consideration (which is about 75 percent of all possible daily values in those three quarters) for which 75 percent of the hours in the day have reported concentrations. Only days with at least 75 percent of the hours reported shall be considered in identifying the low value to be used for substitution.

(B) The substitution test is as follows: Data substitution will be performed in all quarter periods that have less than 75 percent data capture. Identify for each quarter (e.g., January-March) the lowest reported daily maximum 1-hour value for that quarter, looking across those three months of all three years under consideration. All daily maximum 1-hour values from all days with at least 75 percent capture in the quarter period shall be considered when identifying this lowest value. If after substituting the lowest reported daily maximum 1-hour value for a quarter for as much of the missing daily data in the matching deficient quarter(s) as is needed to make them 75 percent complete, the procedure in section 5.2 yields a recalculated 3-year 1-hour standard ''test design value'' above the level of the standard, then the 1-hour primary standard design value is deemed to have passed the diagnostic test and is valid, and the level of the standard is deemed to have been exceeded in that 3-year period. As noted in section 3.2(c)(i), in such a case, the 3-year design value based on the data actually reported, not the ''test design value'', shall be used as the valid design value.

(d) A 1-hour primary standard design value based on data that do not meet the completeness criteria stated in 3.2(b) and also do not satisfy section 3.2(c), may also be considered valid with the approval of, or at the initiative of, the Administrator, who may consider factors such as monitoring site closures/moves, monitoring diligence, the consistency and levels of the valid concentration measurements that are available, and nearby concentrations in determining whether to use such data.

(e) The procedures for calculating the 1-hour primary standard design values are given in section 5.2 of this appendix.

4. Rounding Conventions

4.1 Rounding Conventions for the Annual Primary NO_2 NAAQS

(a) Hourly NO_2 measurement data shall be reported to AQS in units of parts per billion (ppb), to at most one place after the decimal, with additional digits to the right being truncated with no further rounding.

(b) The annual primary standard design value is calculated pursuant to section 5.1 and then rounded to the nearest whole number or 1 ppb (decimals 0.5 and greater are rounded up to the nearest whole number, and any decimal lower than 0.5 is rounded down to the nearest whole number).

4.2 Rounding Conventions for the 1-hour Primary NO_2 NAAQS

(a) Hourly NO_2 measurement data shall be reported to AQS in units of parts per billion (ppb), to at most one place after the decimal, with additional digits to the right being truncated with no further rounding.

(b) Daily maximum 1-hour values are not rounded.

(c) The 1-hour primary standard design value is calculated pursuant to section 5.2 and then rounded to the nearest whole number or 1 ppb (decimals 0.5 and greater are rounded up to the nearest whole number, and any decimal lower than 0.5 is rounded down to the nearest whole number).

5. Calculation Procedures for the Primary NO_2 NAAQS

5.1 Procedures for the Annual Primary NO_2 NAAQS

(a) When the data for a site and year meet the data completeness requirements in section 3.1(b) of this appendix, or if the Administrator exercises the discretionary authority in section 3.1(c), the annual mean is simply the arithmetic average of all of the reported 1-hour values.

(b) The annual primary standard design value for a site is the valid annual mean

rounded according to the conventions in section 4.1.

5.2 Calculation Procedures for the 1-hour Primary NO_2 NAAQS

(a) *Procedure for identifying annual 98th percentile values.* When the data for a particular site and year meet the data completeness requirements in section 3.2(b), or if one of the conditions of section 3.2(c) is met, or if the Administrator exercises the discretionary authority in section 3.2(d), identification of annual 98th percentile value is accomplished as follows.

(i) The annual 98th percentile value for a year is the higher of the two values resulting from the following two procedures.

(1) Procedure 1.

(A) For the year, determine the number of days with at least 75 percent of the hourly values reported including State-flagged data affected by exceptional events which have been approved for exclusion by the Administrator.

(B) For the year, from only the days with at least 75 percent of the hourly values reported, select from each day the maximum hourly value excluding State-flagged data affected by exceptional events which have been approved for exclusion by the Administrator.

(C) Sort all these daily maximum hourly values from a particular site and year by descending value. (For example: (x[1], x[2], x[3], * * *, x[n]). In this case, x[1] is the largest number and x[n] is the smallest value.) The 98th percentile is determined from this sorted series of daily values which is ordered from the highest to the lowest number. Using the left column of Table 1, determine the appropriate range (*i.e.*, row) for the annual number of days with valid data for year y (cn_y) as determined from step (A). The corresponding ''n'' value in the right column identifies the rank of the annual 98th percentile value in the descending sorted list of daily site values for year y. Thus, $P_{0.98,\ y}$ = the nth largest value.

(2) Procedure 2.

(A) For the year, determine the number of days with at least one hourly value reported including State-flagged data affected by exceptional events which have been approved for exclusion by the Administrator.

(B) For the year, from all the days with at least one hourly value reported, select from each day the maximum hourly value excluding State-flagged data affected by exceptional events which have been approved for exclusion by the Administrator.

(C) Sort all these daily maximum values from a particular site and year by descending value. (For example: (x[1], x[2], x[3], * * *, x[n]). In this case, x[1] is the largest number and x[n] is the smallest value.) The 98th percentile is determined from this sorted series of daily values which is ordered from the highest to the lowest number. Using the left column of Table 1, determine the appropriate range (*i.e.*, row) for the annual number of days with valid data for year y (cn_y) as determined from step (A). The corresponding ''n'' value in the right column identifies the rank of the annual 98th percentile value in the descending sorted list of daily site values for year y. Thus, $P_{0.98,\ y}$ = the nth largest value.

(b) The 1-hour primary standard design value for a site is mean of the three annual 98th percentile values, rounded according to the conventions in section 4.

TABLE 1

Annual number of days with valid data for year ''y'' (cn_y)	$P_{0.98,\ y}$ is the nth maximum value of the year, where n is the listed number
1–50	1
51–100	2
101–150	3
151–200	4
201–250	5
251–300	6
301–350	7
351–366	8

[75 FR 6532, Feb. 9, 2010]

APPENDIX T TO PART 50—INTERPRETATION OF THE PRIMARY NATIONAL AMBIENT AIR QUALITY STANDARDS FOR OXIDES OF SULFUR (SULFUR DIOXIDE)

1. GENERAL

(a) This appendix explains the data handling conventions and computations necessary for determining when the primary national ambient air quality standards for Oxides of Sulfur as measured by Sulfur Dioxide (''SO_2 NAAQS'') specified in §50.17 are met at an ambient air quality monitoring site. Sulfur Dioxide (SO_2) is measured in the ambient air by a Federal reference method (FRM) based on appendix A or A–1 to this part or by a Federal equivalent method (FEM) designated in accordance with part 53 of this chapter. Data handling and computation procedures to be used in making comparisons between reported SO_2 concentrations and the levels of the SO_2 NAAQS are specified in the following sections.

(b) Decisions to exclude, retain, or make adjustments to the data affected by exceptional events, including natural events, are made according to the requirements and process deadlines specified in §§50.1, 50.14 and 51.930 of this chapter.

(c) The terms used in this appendix are defined as follows:

Daily maximum 1-hour values for SO_2 refers to the maximum 1-hour SO_2 concentration

State of Oregon Department of Environmental Quality

OAR 340-202-0130 Attachments

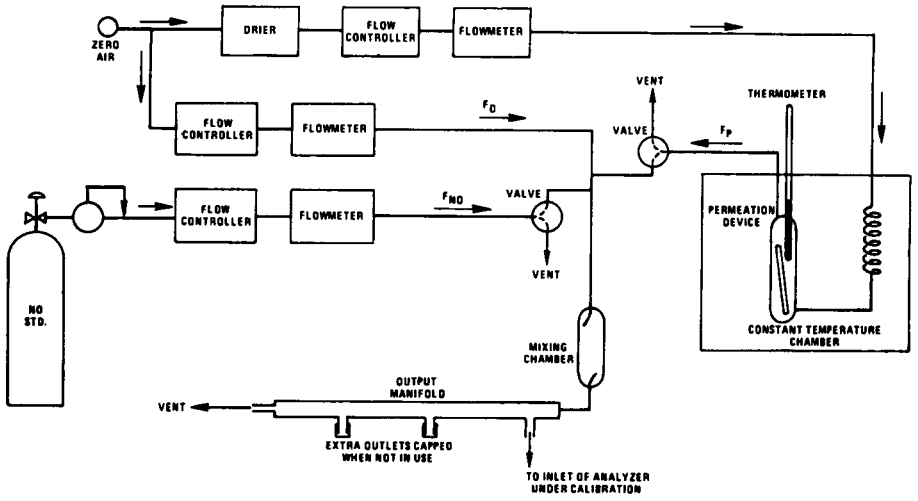

Figure 2. Schematic diagram of a typical calibration apparatus using an NO_2 permeation device.

[41 FR 52688, Dec. 1, 1976, as amended at 48 FR 2529, Jan 20, 1983]

Appendix G to Part 50—Reference Method for the Determination of Lead in Suspended Particulate Matter Collected From Ambient Air

1. *Principle and applicability.*

1.1 Ambient air suspended particulate matter is collected on a glass-fiber filter for 24 hours using a high volume air sampler. The analysis of the 24-hour samples may be performed for either individual samples or composites of the samples collected over a calendar month or quarter, provided that the compositing procedure has been approved in accordance with section 2.8 of appendix C to part 58 of this chapter—*Modifications of methods by users.* (Guidance or assistance in requesting approval under Section 2.8 can be obtained from the address given in section 2.7 of appendix C to part 58 of this chapter.)

1.2 Lead in the particulate matter is solubilized by extraction with nitric acid (HNO_3), facilitated by heat or by a mixture of HNO_3 and hydrochloric acid (HCl) facilitated by ultrasonication.

1.3 The lead content of the sample is analyzed by atomic absorption spectrometry using an air-acetylene flame, the 283.3 or 217.0 nm lead absorption line, and the optimum instrumental conditions recommended by the manufacturer.

1.4 The ultrasonication extraction with HNO_3/HCl will extract metals other than lead from ambient particulate matter.

2. *Range, sensitivity, and lower detectable limit.* The values given below are typical of the methods capabilities. Absolute values will vary for individual situations depending on the type of instrument used, the lead line, and operating conditions.

2.1 *Range.* The typical range of the method is 0.07 to 7.5 μg Pb/m^3 assuming an upper linear range of analysis of 15 μg/ml and an air volume of 2,400 m^3.

2.2 *Sensitivity.* Typical sensitivities for a 1 percent change in absorption (0.0044 absorbance units) are 0.2 and 0.5 μg Pb/ml for the 217.0 and 283.3 nm lines, respectively.

2.3 *Lower detectable limit (LDL).* A typical LDL is 0.07 μg Pb/m^3. The above value was calculated by doubling the between-laboratory standard deviation obtained for the lowest measurable lead concentration in a collaborative test of the method.(*15*) An air volume of 2,400 m^3 was assumed.

3. *Interferences.* Two types of interferences are possible: chemical and light scattering.

3.1 *Chemical.* Reports on the absence (*1, 2, 3, 4, 5*) of chemical interferences far outweigh those reporting their presence, (*6*) therefore, no correction for chemical interferences is given here. If the analyst suspects that the sample matrix is causing a chemical interference, the interference can be verified and corrected for by carrying out the analysis

with and without the method of standard additions.(*7*)

3.2 *Light scattering.* Nonatomic absorption or light scattering, produced by high concentrations of dissolved solids in the sample, can produce a significant interference, especially at low lead concentrations. (*2*) The interference is greater at the 217.0 nm line than at the 283.3 nm line. No interference was observed using the 283.3 nm line with a similar method.(*1*)

Light scattering interferences can, however, be corrected for instrumentally. Since the dissolved solids can vary depending on the origin of the sample, the correction may be necessary, especially when using the 217.0 nm line. Dual beam instruments with a continuum source give the most accurate correction. A less accurate correction can be obtained by using a nonabsorbing lead line that is near the lead analytical line. Information on use of these correction techniques can be obtained from instrument manufacturers' manuals.

If instrumental correction is not feasible, the interference can be eliminated by use of the ammonium pyrrolidinecarbodithioate-methylisobutyl ketone, chelation-solvent extraction technique of sample preparation.(*8*)

4. *Precision and bias.*

4.1 The high-volume sampling procedure used to collect ambient air particulate matter has a between-laboratory relative standard deviation of 3.7 percent over the range 80 to 125 μg/m³.(*9*) The combined extraction-analysis procedure has an average within-laboratory relative standard deviation of 5 to 6 percent over the range 1.5 to 15 μg Pb/ml, and an average between laboratory relative standard deviation of 7 to 9 percent over the same range. These values include use of either extraction procedure.

4.2 Single laboratory experiments and collaborative testing indicate that there is no significant difference in lead recovery between the hot and ultrasonic extraction procedures.(*15*)

5. *Apparatus.*

5.1 *Sampling.*

5.1.1 *High-Volume Sampler.* Use and calibrate the sampler as described in appendix B to this part.

5.2 *Analysis.*

5.2.1 *Atomic absorption spectrophotometer.* Equipped with lead hollow cathode or electrodeless discharge lamp.

5.2.1.1 *Acetylene.* The grade recommended by the instrument manufacturer should be used. Change cylinder when pressure drops below 50–100 psig.

5.2.1.2 *Air.* Filtered to remove particulate, oil, and water.

5.2.2 *Glassware.* Class A borosilicate glassware should be used throughout the analysis.

5.2.2.1 *Beakers.* 30 and 150 ml. graduated, Pyrex.

5.2.2.2 *Volumetric flasks.* 100-ml.

5.2.2.3 *Pipettes.* To deliver 50, 30, 15, 8, 4, 2, 1 ml.

5.2.2.4 *Cleaning.* All glassware should be scrupulously cleaned. The following procedure is suggested. Wash with laboratory detergent, rinse, soak for 4 hours in 20 percent (w/w) HNO_3, rinse 3 times with distilled-deionized water, and dry in a dust free manner.

5.2.3 *Hot plate.*

5.2.4. *Ultrasonication water bath, unheated.* Commercially available laboratory ultrasonic cleaning baths of 450 watts or higher ''cleaning power,'' i.e., actual ultrasonic power output to the bath have been found satisfactory.

5.2.5 *Template.* To aid in sectioning the glass-fiber filter. See figure 1 for dimensions.

5.2.6 *Pizza cutter.* Thin wheel. Thickness 1mm.

5.2.7 *Watch glass.*

5.2.8 *Polyethylene bottles.* For storage of samples. Linear polyethylene gives better storage stability than other polyethylenes and is preferred.

5.2.9 Parafilm ''M''.[1] American Can Co., Marathon Products, Neenah, Wis., or equivalent.

6. *Reagents.*

6.1 *Sampling.*

6.1.1 *Glass fiber filters.* The specifications given below are intended to aid the user in obtaining high quality filters with reproducible properties. These specifications have been met by EPA contractors.

6.1.1.1 *Lead content.* The absolute lead content of filters is not critical, but low values are, of course, desirable. EPA typically obtains filters with a lead content of 75 μg/filter.

It is important that the variation in lead content from filter to filter, within a given batch, be small.

6.1.1.2 *Testing.*

6.1.1.2.1 For large batches of filters (>500 filters) select at random 20 to 30 filters from a given batch. For small batches (>500 filters) a lesser number of filters may be taken. Cut one ¾″×8″ strip from each filter anywhere in the filter. Analyze all strips, separately, according to the directions in sections 7 and 8.

6.1.1.2.2 Calculate the total lead in each filter as

$$F_b = \mu g\ Pb/ml \times \frac{100\ ml}{strip} \times \frac{12\ strips}{filter}$$

where:

F_b = Amount of lead per 72 square inches of filter, μg.

6.1.1.2.3 Calculate the mean, F_b, of the values and the relative standard deviation

[1] Mention of commercial products does not imply endorsement by the U.S. Environmental Protection Agency.

(standard deviation/mean × 100). If the relative standard deviation is high enough so that, in the analysts opinion, subtraction of F_b, (section 10.3) may result in a significant error in the µg Pb/m³, the batch should be rejected.

6.1.1.2.4 For acceptable batches, use the value of F_b to correct all lead analyses (section 10.3) of particulate matter collected using that batch of filters. If the analyses are below the LDL (section 2.3) no correction is necessary.

6.2 *Analysis.*

6.2.1 Concentrated (15.6 *M)* HNO_3. ACS reagent grade HNO_3 and commercially available redistilled HNO_3 has found to have sufficiently low lead concentrations.

6.2.2 Concentrated (11.7 *M*) HCl. ACS reagent grade.

6.2.3 *Distilled-deionized water.* (D.I. water).

6.2.4 3 *M* HNO_3. This solution is used in the hot extraction procedure. To prepare, add 192 ml of concentrated HNO_3 to D.I. water in a 1 *l* volumetric flask. Shake well, cool, and dilute to volume with D.I. water. *Caution:* Nitric acid fumes are toxic. Prepare in a well ventilated fume hood.

6.2.5 0.45 *M* HNO_3. This solution is used as the matrix for calibration standards when using the hot extraction procedure. To prepare, add 29 ml of concentrated HNO_3 to D.I. water in a 1 *l* volumetric flask. Shake well, cool, and dilute to volume with D.I. water.

6.2.6 2.6 *M* HNO_3+0 to 0.9 *M* HCl. This solution is used in the ultrasonic extraction procedure. The concentration of HCl can be varied from 0 to 0.9 *M*. Directions are given for preparation of a 2.6 *M* HNO_3+0.9 *M* HCl solution. Place 167 ml of concentrated HNO_3 into a 1 *l* volumetric flask and add 77 ml of concentrated HCl. Stir 4 to 6 hours, dilute to nearly 1 *l* with D.I. water, cool to room temperature, and dilute to 1 *l*.

6.2.7 0.40 *M* HNO_3 + X *M* HCl. This solution is used as the matrix for calibration standards when using the ultrasonic extraction procedure. To prepare, add 26 ml of concentrated HNO_3, plus the ml of HCl required, to a 1 *l* volumetric flask. Dilute to nearly 1 *l* with D.I. water, cool to room temperature, and dilute to 1 *l*. The amount of HCl required can be determined from the following equation:

$$y = \frac{77\ \text{ml} \times 0.15 \times}{0.9\ \text{M}}$$

where:

y = ml of concentrated HCl required.
x = molarity of HCl in 6.2.6.
0.15 = dilution factor in 7.2.2.

6.2.8 Lead nitrate, $Pb(NO_3)_2$. ACS reagent grade, purity 99.0 percent. Heat for 4 hours at 120 °C and cool in a desiccator.

6.3 *Calibration standards.*

6.3.1 Master standard, 1000 µg Pb/ml in HNO_3. Dissolve 1.598 g of $Pb(NO_3)_2$ in 0.45 *M* HNO_3 contained in a 1 *l* volumetric flask and dilute to volume with 0.45 *M* HNO_3.

6.3.2 Master standard, 1000 µg Pb/ml in HNO_3/HCl. Prepare as in section 6.3.1 except use the HNO_3/HCl solution in section 6.2.7.

Store standards in a polyethylene bottle. Commercially available certified lead standard solutions may also be used.

7. *Procedure.*

7.1 *Sampling.* Collect samples for 24 hours using the procedure described in reference *10* with glass-fiber filters meeting the specifications in section 6.1.1. Transport collected samples to the laboratory taking care to minimize contamination and loss of sample. *(16).*

7.2 *Sample preparation.*

7.2.1 *Hot extraction procedure.*

7.2.1.1 Cut a ¾″×8″ strip from the exposed filter using a template and a pizza cutter as described in Figures 1 and 2. Other cutting procedures may be used.

Lead in ambient particulate matter collected on glass fiber filters has been shown to be uniformly distributed across the filter.[1,3,11] Another study[12] has shown that when sampling near a roadway, strip position contributes significantly to the overall variability associated with lead analyses. Therefore, when sampling near a roadway, additional strips should be analyzed to minimize this variability.

7.2.1.2 Fold the strip in half twice and place in a 150-ml beaker. Add 15 ml of 3 *M* HNO_3 to cover the sample. The acid should completely cover the sample. Cover the beaker with a watch glass.

7.2.1.3 Place beaker on the hot-plate, contained in a fume hood, and boil gently for 30 min. Do not let the sample evaporate to dryness. *Caution:* Nitric acid fumes are toxic.

7.2.1.4 Remove beaker from hot plate and cool to near room temperature.

7.2.1.5 Quantitatively transfer the sample as follows:

7.2.1.5.1 Rinse watch glass and sides of beaker with D.I. water.

7.2.1.5.2 Decant extract and rinsings into a 100-ml volumetric flask.

7.2.1.5.3 Add D.I. water to 40 ml mark on beaker, cover with watch glass, and set aside for a minimum of 30 minutes. This is a critical step and cannot be omitted since it allows the HNO_3 trapped in the filter to diffuse into the rinse water.

7.2.1.5.4 Decant the water from the filter into the volumetric flask.

7.2.1.5.5 Rinse filter and beaker twice with D.I. water and add rinsings to volumetric flask until total volume is 80 to 85 ml.

7.2.1.5.6 Stopper flask and shake vigorously. Set aside for approximately 5 minutes or until foam has dissipated.

7.2.1.5.7 Bring solution to volume with D.I. water. Mix thoroughly.

7.2.1.5.8 Allow solution to settle for one hour before proceeding with analysis.

7.2.1.5.9 If sample is to be stored for subsequent analysis, transfer to a linear polyethylene bottle.

7.2.2 *Ultrasonic extraction procedure.*

7.2.2.1 Cut a ¾″×8″ strip from the exposed filter as described in section 7.2.1.1.

7.2.2.2 Fold the strip in half twice and place in a 30 ml beaker. Add 15 ml of the HNO_3/HCl solution in section 6.2.6. The acid should completely cover the sample. Cover the beaker with parafilm.

The parafilm should be placed over the beaker such that none of the parafilm is in contact with water in the ultrasonic bath. Otherwise, rinsing of the parafilm (section 7.2.2.4.1) may contaminate the sample.

7.2.2.3 Place the beaker in the ultrasonication bath and operate for 30 minutes.

7.2.2.4 Quantitatively transfer the sample as follows:

7.2.2.4.1 Rinse parafilm and sides of beaker with D.I. water.

7.2.2.4.2 Decant extract and rinsings into a 100 ml volumetric flask.

7.2.2.4.3 Add 20 ml D.I. water to cover the filter strip, cover with parafilm, and set aside for a minimum of 30 minutes. This is a critical step and cannot be omitted. The sample is then processed as in sections 7.2.1.5.4 through 7.2.1.5.9.

NOTE: Samples prepared by the hot extraction procedure are now in 0.45 *M* HNO_3. Samples prepared by the ultrasonication procedure are in 0.40 *M* HNO_3 + X *M* HCl.

8. *Analysis.*

8.1 Set the wavelength of the monochromator at 283.3 or 217.0 nm. Set or align other instrumental operating conditions as recommended by the manufacturer.

8.2 The sample can be analyzed directly from the volumetric flask, or an appropriate amount of sample decanted into a sample analysis tube. In either case, care should be taken not to disturb the settled solids.

8.3 Aspirate samples, calibration standards and blanks (section 9.2) into the flame and record the equilibrium absorbance.

8.4 Determine the lead concentration in µg Pb/ml, from the calibration curve, section 9.3.

8.5 Samples that exceed the linear calibration range should be diluted with acid of the same concentration as the calibration standards and reanalyzed.

9. *Calibration.*

9.1 *Working standard*, 20 µg Pb/ml. Prepared by diluting 2.0 ml of the master standard (section 6.3.1 if the hot acid extraction was used or section 6.3.2 if the ultrasonic extraction procedure was used) to 100 ml with acid of the same concentration as used in preparing the master standard.

9.2 *Calibration standards.* Prepare daily by diluting the working standard, with the same acid matrix, as indicated below. Other lead concentrations may be used.

Volume of 20 µg/ml working standard, ml	Final volume, ml	Concentration µg Pb/ml
0	100	0
1.0	200	0.1
2.0	200	0.2
2.0	100	0.4
4.0	100	0.8
8.0	100	1.6
15.0	100	3.0
30.0	100	6.0
50.0	100	10.0
100.0	100	20.0

9.3 *Preparation of calibration curve.* Since the working range of analysis will vary depending on which lead line is used and the type of instrument, no one set of instructions for preparation of a calibration curve can be given. Select standards (plus the reagent blank), in the same acid concentration as the samples, to cover the linear absorption range indicated by the instrument manufacturer. Measure the absorbance of the blank and standards as in section 8.0. Repeat until good agreement is obtained between replicates. Plot absorbance (y-axis) versus concentration in µg Pb/ml (x-axis). Draw (or compute) a straight line through the linear portion of the curve. Do not force the calibration curve through zero. Other calibration procedures may be used.

To determine stability of the calibration curve, remeasure—alternately—one of the following calibration standards for every 10th sample analyzed: Concentration ≤1 µg Pb/ml; concentration ≤10 µg Pb/ml. If either standard deviates by more than 5 percent from the value predicted by the calibration curve, recalibrate and repeat the previous 10 analyses.

10. *Calculation.*

10.1 *Measured air volume.* Calculate the measured air volume at Standard Temperature and Pressure as described in Reference 10.

10.2 *Lead concentration.* Calculate lead concentration in the air sample.

$$C = \frac{(\mu g\ Pb/ml \times 100\ ml/strip \times 12\ strips/filter) - \bar{F}_b}{V_{STP}}$$

where:

C = Concentration, μg Pb/sm³.
μg Pb/ml = Lead concentration determined from section 8.
100 ml/strip = Total sample volume.
12 strips = Total useable filter area, 8″×9″. Exposed area of one strip, ¾″×7″.
Filter = Total area of one strip, ¾″×8″.
F_b = Lead concentration of blank filter, μg, from section 6.1.1.2.3.
V_{STP} = Air volume from section 10.1.

11. *Quality control.*

¾″×8″ glass fiber filter strips containing 80 to 2000 μg Pb/strip (as lead salts) and blank strips with zero Pb content should be used to determine if the method—as being used—has any bias. Quality control charts should be established to monitor differences between measured and true values. The frequency of such checks will depend on the local quality control program.

To minimize the possibility of generating unreliable data, the user should follow practices established for assuring the quality of air pollution data, (*13*) and take part in EPA's semiannual audit program for lead analyses.

12. *Trouble shooting.*

1. During extraction of lead by the hot extraction procedure, it is important to keep the sample covered so that corrosion products—formed on fume hood surfaces which may contain lead—are not deposited in the extract.

2. The sample acid concentration should minimize corrosion of the nebulizer. However, different nebulizers may require lower acid concentrations. Lower concentrations can be used provided samples and standards have the same acid concentration.

3. Ashing of particulate samples has been found, by EPA and contractor laboratories, to be unnecessary in lead analyses by atomic absorption. Therefore, this step was omitted from the method.

4. Filtration of extracted samples, to remove particulate matter, was specifically excluded from sample preparation, because some analysts have observed losses of lead due to filtration.

5. If suspended solids should clog the nebulizer during analysis of samples, centrifuge the sample to remove the solids.

13. *Authority.*

(Secs. 109 and 301(a), Clean Air Act, as amended (42 U.S.C. 7409, 7601(a)))

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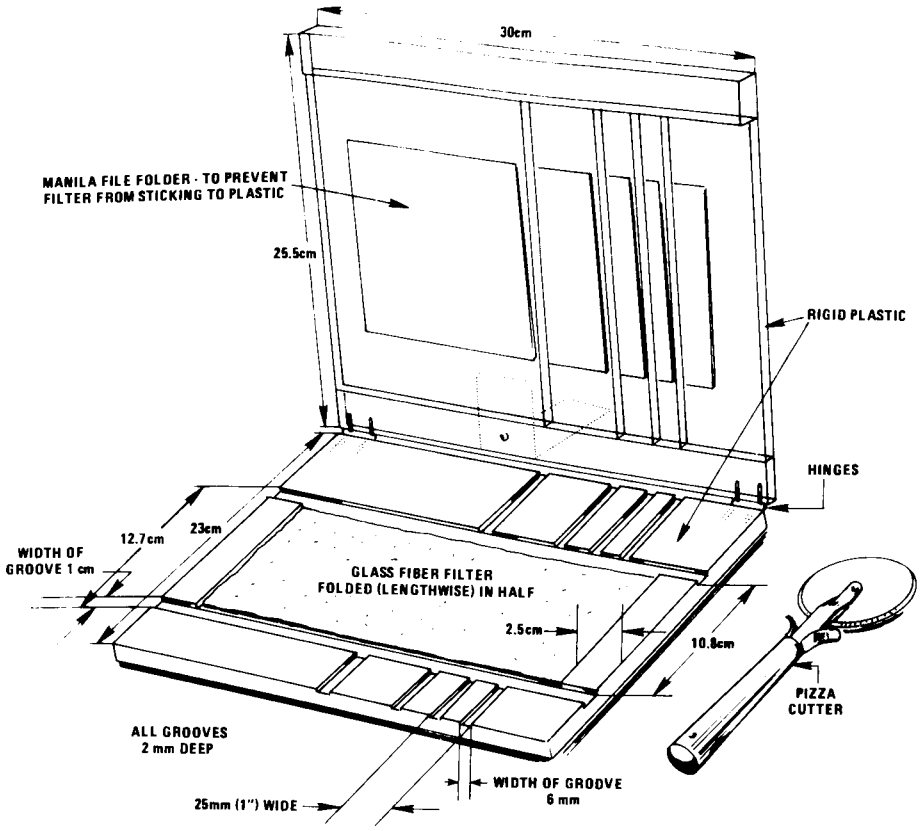

Figure 1

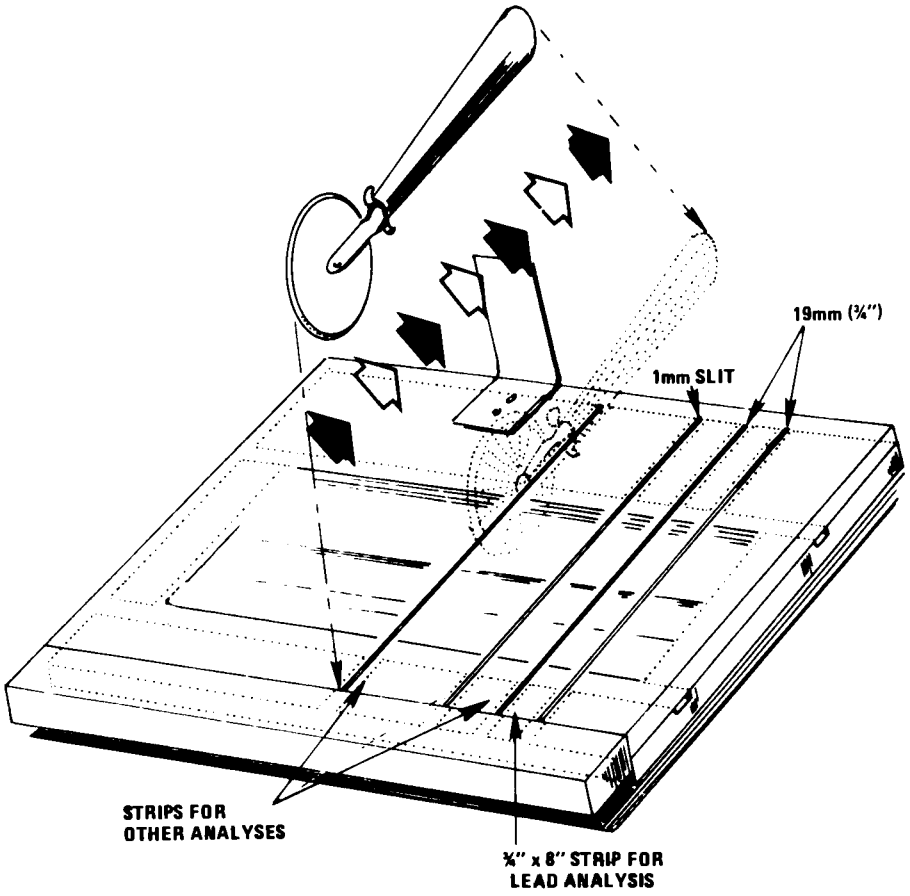

Figure 2

(Secs. 109, 301(a) of the Clean Air Act, as amended (42 U.S.C. 7409, 7601(a)); secs. 110, 301(a) and 319 of the Clean Air Act (42 U.S.C. 7410, 7601(a), 7619))

[43 FR 46258, Oct. 5, 1978; 44 FR 37915, June 29, 1979, as amended at 46 FR 44163, Sept. 3, 1981; 52 FR 24664, July 1, 1987; 73 FR 67052, Nov. 12, 2008]

APPENDIX H TO PART 50—INTERPRETATION OF THE 1-HOUR PRIMARY AND SECONDARY NATIONAL AMBIENT AIR QUALITY STANDARDS FOR OZONE

1. GENERAL

This appendix explains how to determine when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 ppm (235 μg/m³) is equal to or less than 1. An expanded discussion of these procedures and associated examples are contained in the ''Guideline for Interpretation of Ozone Air Quality Standards.'' For purposes of clarity in the following discussion, it is convenient to use the term ''exceedance'' to describe a daily maximum hourly average ozone measurement that is greater than the level of the standard. Therefore, the phrase ''expected number of days with maximum hourly average ozone concentrations above the level of the standard'' may be simply stated as the ''expected number of exceedances.''

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[73 FR 67052, Nov. 12, 2008]

APPENDIX R TO PART 50—INTERPRETATION OF THE NATIONAL AMBIENT AIR QUALITY STANDARDS FOR LEAD

1. General.

(a) This appendix explains the data handling conventions and computations necessary for determining when the primary and secondary national ambient air quality standards (NAAQS) for lead (Pb) specified in §50.16 are met. The NAAQS indicator for Pb is defined as: lead and its compounds, measured as elemental lead in total suspended particulate (Pb-TSP), sampled and analyzed by a Federal reference method (FRM) based on appendix G to this part or by a Federal equivalent method (FEM) designated in accordance with part 53 of this chapter. Although Pb-TSP is the lead NAAQS indicator, surrogate Pb-TSP concentrations shall also be used for NAAQS comparisons; specifically, valid surrogate Pb-TSP data are concentration data for lead and its compounds, measured as elemental lead, in particles with an aerodynamic size of 10 microns or less (Pb-PM_{10}), sampled and analyzed by an FRM based on appendix Q to this part or by an FEM designated in accordance with part 53 of this chapter. Surrogate Pb-TSP data (*i.e.*, Pb-PM_{10} data), however, can only be used to show that the Pb NAAQS were violated (*i.e.*, not met); they can not be used to demonstrate that the Pb NAAQS were met. Pb-PM_{10} data used as surrogate Pb-TSP data shall be processed at face value; that is, without any transformation or scaling. Data handling and computation procedures to be used in making comparisons between reported and/or surrogate Pb-TSP concentrations and the level of the Pb NAAQS are specified in the following sections.

(b) Whether to exclude, retain, or make adjustments to the data affected by exceptional events, including natural events, is determined by the requirements and process deadlines specified in §§50.1, 50.14, and 51.930 of this chapter.

(c) The terms used in this appendix are defined as follows:

Annual monitoring network plan refers to the plan required by section 58.10 of this chapter.

Creditable samples are samples that are given credit for data completeness. They include valid samples collected on required sampling days and valid ''make-up'' samples taken for missed or invalidated samples on required sampling days.

Daily values for Pb refer to the 24-hour mean concentrations of Pb (Pb-TSP or Pb-PM_{10}), measured from midnight to midnight (local standard time), that are used in NAAQS computations.

Design value is the site-level metric (*i.e.*, statistic) that is compared to the NAAQS level to determine compliance; the design value for the Pb NAAQS is selected according to the procedures in this appendix from among the valid three-month Pb-TSP and surrogate Pb-TSP (Pb-PM_{10}) arithmetic mean concentration for the 38-month period consisting of the most recent 3-year calendar period plus two previous months (*i.e.*, 36 3-month periods) using the last month of each 3-month period as the period of report.

Extra samples are non-creditable samples. They are daily values that do not occur on scheduled sampling days and that can not be used as ''make-up samples'' for missed or invalidated scheduled samples. Extra samples are used in mean calculations. For purposes of determining whether a sample must be treated as a make-up sample or an extra sample, Pb-TSP and Pb-PM_{10} data collected before January 1, 2009 will be treated with an assumed scheduled sampling frequency of every sixth day.

Make-up samples are samples taken to replace missed or invalidated required scheduled samples. Make-ups can be made by either the primary or collocated (same size fraction) instruments; to be considered a

valid make-up, the sampling must be conducted with equipment and procedures that meet the requirements for scheduled sampling. Make-up samples are either taken before the next required sampling day or exactly one week after the missed (or voided) sampling day. Make-up samples can not span years; that is, if a scheduled sample for December is missed (or voided), it can not be made up in January. Make-up samples, however, may span months, for example a missed sample on January 31 may be made up on February 1, 2, 3, 4, 5, or 7 (with an assumed sampling frequency of every sixth day). Section 3(e) explains how such month-spanning make-up samples are to be treated for purposes of data completeness and mean calculations. Only two make-up samples are permitted each calendar month; these are counted according to the month in which the miss and not the makeup occurred. For purposes of determining whether a sample must be treated as a make-up sample or an extra sample, Pb-TSP and Pb-PM_{10} data collected before January 1, 2009 will be treated with an assumed scheduled sampling frequency of every sixth day.

Monthly mean refers to an arithmetic mean, calculated as specified in section 6(a) of this appendix. Monthly means are computed at each monitoring site separately for Pb-TSP and Pb-PM_{10} (*i.e.*, by site-parameter-year-month).

Parameter refers either to Pb-TSP or to Pb-PM_{10}.

Pollutant Occurrence Code (POC) refers to a numerical code (1, 2, 3, etc.) used to distinguish the data from two or more monitors for the same parameter at a single monitoring site.

Scheduled sampling day means a day on which sampling is scheduled based on the required sampling frequency for the monitoring site, as provided in section 58.12 of this chapter.

Three-month means are arithmetic averages of three consecutive monthly means. Three-month means are computed on a rolling, overlapping basis. Each distinct monthly mean will be included in three different 3-month means; for example, in a given year, a November mean would be included in: (1) The September-October-November 3-month mean, (2) the October-November-December 3-month mean, and (3) the November-December-January(of the following year) 3-month mean. Three-month means are computed separately for each parameter per section 6(a) (and are referred to as 3-month parameter means) and are validated according to the criteria specified in section 4(c). The parameter-specific 3-month means are then prioritized according to section 2(a) to determine a single 3-month site mean.

Year refers to a calendar year.

2. *Use of Pb-PM_{10} Data as Surrogate Pb-TSP Data.*

(a) As stipulated in section 2.10 of Appendix C to 40 CFR part 58, at some mandatory Pb monitoring locations, monitoring agencies are required to sample for Pb as Pb-TSP, and at other mandatory Pb monitoring sites, monitoring agencies are permitted to monitor for Pb-PM_{10} in lieu of Pb-TSP. In either situation, valid collocated Pb data for the other parameter may be produced. Additionally, there may be non-required monitoring locations that also produce valid Pb-TSP and/or valid Pb-PM_{10} data. Pb-TSP data and Pb-PM_{10} data are always processed separately when computing monthly and 3-month parameter means; monthly and 3-month parameter means are validated according to the criteria stated in section 4 of this appendix. Three-month ''site'' means, which are the final valid 3-month mean from which a design value is identified, are determined from the one or two available valid 3-month parameter means according to the following prioritization which applies to all Pb monitoring locations.

(i) Whenever a valid 3-month Pb-PM_{10} mean shows a violation and either is greater than a corresponding (collocated) 3-month Pb-TSP mean or there is no corresponding valid 3-month Pb-TSP mean present, then that 3-month Pb-PM_{10} mean will be the site-level mean for that (site's) 3-month period.

(ii) Otherwise (*i.e.*, there is no valid violating 3-month Pb-PM_{10} that exceeds a corresponding 3-month Pb-TSP mean),

(A) If a valid 3-month Pb-TSP mean exists, then it will be the site-level mean for that (site's) 3-month period, or

(B) If a valid 3-month Pb-TSP mean does not exist, then there is no valid 3-month site mean for that period (even if a valid non-violating 3-month Pb-PM_{10} mean exists).

(b) As noted in section 1(a) of this appendix, FRM/FEM Pb-PM_{10} data will be processed at face value (*i.e.*, at reported concentrations) without adjustment when computing means and making NAAQS comparisons.

3. *Requirements for Data Used for Comparisons With the Pb NAAQS and Data Reporting Considerations.*

(a) All valid FRM/FEM Pb-TSP data and all valid FRM/FEM Pb-PM_{10} data submitted to EPA's Air Quality System (AQS), or otherwise available to EPA, meeting the requirements of part 58 of this chapter including appendices A, C, and E shall be used in design value calculations. Pb-TSP and Pb-PM_{10} data representing sample collection periods prior to January 1, 2009 (*i.e.*, ''pre-rule'' data) will also be considered valid for NAAQS comparisons and related attainment/nonattainment determinations if the sampling and analysis methods that were utilized to collect that data were consistent with previous or newly designated FRMs or FEMs and with either the provisions of part 58 of this chapter including appendices A, C,

and E that were in effect at the time of original sampling or that are in effect at the time of the attainment/nonattainment determination, and if such data are submitted to AQS prior to September 1, 2009.

(b) Pb-TSP and Pb-PM_{10} measurement data are reported to AQS in units of micrograms per cubic meter ($\mu g/m^3$) at local conditions (local temperature and pressure, LC) to three decimal places; any additional digits to the right of the third decimal place are truncated. Pre-rule Pb-TSP and Pb-PM_{10} concentration data that were reported in standard conditions (standard temperature and standard pressure, STP) will not require a conversion to local conditions but rather, after truncating to three decimal places and processing as stated in this appendix, shall be compared ''as is'' to the NAAQS (*i.e.*, the LC to STP conversion factor will be assumed to be one). However, if the monitoring agency has retroactively resubmitted Pb-TSP or Pb-PM_{10} pre-rule data converted from STP to LC based on suitable meteorological data, only the LC data will be used.

(c) At each monitoring location (site), Pb-TSP and Pb-PM_{10} data are to be processed separately when selecting daily data by day (as specified in section 3(d) of this appendix), when aggregating daily data by month (per section 6(a)), and when forming 3-month means (per section 6(b)). However, when deriving (*i.e.*, identifying) the design value for the 38-month period, 3-month means for the two data types may be considered together; see sections 2(a) and 4(e) of this appendix for details.

(d) Daily values for sites will be selected for a site on a size cut (Pb-TSP or Pb-PM_{10}, i.e., ''parameter'') basis; Pb-TSP concentrations and Pb-PM_{10} concentrations shall not be commingled in these determinations. Site level, parameter-specific daily values will be selected as follows:

(i) The starting dataset for a site-parameter shall consist of the measured daily concentrations recorded from the designated primary FRM/FEM monitor for that parameter. The primary monitor for each parameter shall be designated in the appropriate state or local agency annual Monitoring Network Plan. If no primary monitor is designated, the Administrator will select which monitor to treat as primary. All daily values produced by the primary sampler are considered part of the site-parameter data record (*i.e.*, that site-parameter's set of daily values); this includes all creditable samples and all extra samples. For pre-rule Pb-TSP and Pb-PM_{10} data, valid data records present in AQS for the monitor with the lowest occurring Pollutant Occurrence Code (POC), as selected on a site-parameter-daily basis, will constitute the site-parameter data record. Where pre-rule Pb-TSP data (or subsequent non-required Pb-TSP or Pb-PM_{10} data) are reported in ''composite'' form (*i.e.*, multiple filters for a month of sampling that are analyzed together), the composite concentration will be used as the site-parameter monthly mean concentration if there are no valid daily Pb-TSP data reported for that month with a lower POC.

(ii) Data for the primary monitor for each parameter shall be augmented as much as possible with data from collocated (same parameter) FRM/FEM monitors. If a valid 24-hour measurement is not produced from the primary monitor for a particular day (scheduled or otherwise), but a valid sample is generated by a collocated (same parameter) FRM/FEM instrument, then that collocated value shall be considered part of the site-parameter data record (*i.e.*, that site-parameter's monthly set of daily values). If more than one valid collocated FRM/FEM value is available, the mean of those valid collocated values shall be used as the daily value. Note that this step will not be necessary for pre-rule data given the daily identification presumption for the primary monitor.

(e) All daily values in the composite site-parameter record are used in monthly mean calculations. However, not all daily values are given credit towards data completeness requirements. Only ''creditable'' samples are given credit for data completeness. Creditable samples include valid samples on scheduled sampling days and valid make-up samples. All other types of daily values are referred to as ''extra'' samples. Make-up samples taken in the (first week of the) month after the one in which the miss/void occurred will be credited for data capture in the month of the miss/void but will be included in the month actually taken when computing monthly means. For example, if a make-up sample was taken in February to replace a missed sample scheduled for January, the make-up concentration would be included in the February monthly mean but the sample credited in the January data capture rate.

4. *Comparisons With the Pb NAAQS.*

(a) The Pb NAAQS is met at a monitoring site when the identified design value is valid and less than or equal to 0.15 micrograms per cubic meter ($\mu g/m^3$). A Pb design value that meets the NAAQS (*i.e.*, 0.15 $\mu g/m^3$ or less), is considered valid if it encompasses 36 consecutive valid 3-month site means (specifically for a 3-year calendar period and the two previous months). For sites that begin monitoring Pb after this rule is effective but before January 15, 2010 (or January 15, 2011), a 2010–2012 (or 2011–2013) Pb design value that meets the NAAQS will be considered valid if it encompasses at least 34 consecutive valid 3-month means (specifically encompassing only the 3-year calendar period). See 4(c) of this appendix for the description of a valid 3-month mean and section 6(d) for the definition of the design value.

(b) The Pb NAAQS is violated at a monitoring site when the identified design value is valid and is greater than 0.15 μg/m^3, no matter whether determined from Pb-TSP or Pb-PM_{10} data. A Pb design value greater than 0.15 μg/m^3 is valid no matter how many valid 3-month means in the 3-year period it encompasses; that is, a violating design value is valid even if it (*i.e.*, the highest 3-month mean) is the only valid 3-month mean in the 3-year timeframe. Further, a site does not have to monitor for three full calendar years in order to have a valid violating design value; a site could monitor just three months and still produce a valid (violating) design value.

(c)(i) A 3-month parameter mean is considered valid (*i.e.*, meets data completeness requirements) if the average of the data capture rate of the three constituent monthly means (*i.e.*, the 3-month data capture rate) is greater than or equal to 75 percent. Monthly data capture rates (expressed as a percentage) are specifically calculated as the number of creditable samples for the month (including any make-up samples taken the subsequent month for missed samples in the month in question, and excluding any make-up samples taken in the month in question for missed samples in the previous month) divided by the number of scheduled samples for the month, the result then multiplied by 100 but not rounded. The 3-month data capture rate is the sum of the three corresponding unrounded monthly data capture rates divided by three and the result rounded to the nearest integer (zero decimal places). As noted in section 3(c), Pb-TSP and Pb-PM_{10} daily values are processed separately when calculating monthly means and data capture rates; a Pb-TSP value cannot be used as a make-up for a missing Pb-PM_{10} value or vice versa. For purposes of assessing data capture, Pb-TSP and Pb-PM_{10} data collected before January 1, 2009 will be treated with an assumed scheduled sampling frequency of every sixth day.

(ii) A 3-month parameter mean that does not have at least 75 percent data capture and thus is not considered valid under 4(c)(i) shall be considered valid (and complete) if it passes either of the two following ''data substitution'' tests, one such test for validating an above NAAQS-level (*i.e.*, violating) 3-month Pb-TSP or Pb-PM_{10} mean (using actual ''low'' reported values from the same site at about the same time of the year (*i.e.*, in the same month) looking across three or four years), and the second test for validating a below-NAAQS level 3-month Pb-TSP mean (using actual ''high'' values reported for the same site at about the same time of the year (*i.e.*, in the same month) looking across three or four years). Note that both tests are merely diagnostic in nature intending to confirm that there is a very high likelihood if not certainty that the original mean (the one with less than 75% data capture) reflects the true over/under NAAQS-level status for that 3-month period; the result of one of these data substitution tests (*i.e.*, a ''test mean'', as defined in section 4(c)(ii)(A) or 4(c)(ii)(B)) is not considered the actual 3-month parameter mean and shall not be used in the determination of design values. For both types of data substitution, substitution is permitted only if there are available data points from which to identify the high or low 3-year month-specific values, specifically if there are at least 10 data points total from at least two of the three (or four for November and December) possible year-months. Data substitution may only use data of the same parameter type.

(A) The ''above NAAQS level'' test is as follows: Data substitution will be done in each month of the 3-month period that has less than 75 percent data capture; monthly capture rates are temporarily rounded to integers (zero decimals) for this evaluation. If by substituting the lowest reported daily value for that month (year non-specific; e.g., for January) over the 38-month design value period in question for missing scheduled data in the deficient months (substituting only enough to meet the 75 percent data capture minimum), the computation yields a recalculated test 3-month parameter mean concentration above the level of the standard, then the 3-month period is deemed to have passed the diagnostic test and the level of the standard is deemed to have been exceeded in that 3-month period. As noted in section 4(c)(ii), in such a case, the 3-month parameter mean of the data actually reported, not the recalculated (''test'') result including the low values, shall be used to determine the design value.

(B) The ''below NAAQS level'' test is as follows: Data substitution will be performed for each month of the 3-month period that has less than 75 percent but at least 50 percent data capture; if any month has less than 50% data capture then the 3-month mean can not utilize this substitution test. Also, incomplete 3-month Pb-PM_{10} means can not utilize this test. A 3-month Pb-TSP mean with less than 75% data capture shall still be considered valid (and complete) if, by substituting the highest reported daily value, month-specific, over the 3-year design value period in question, for all missing scheduled data in the deficient months (*i.e.*, bringing the data capture rate up to 100%), the computation yields a recalculated 3-month parameter mean concentration equal or less than the level of the standard (0.15 μg/m^3), then the 3-month mean is deemed to have passed the diagnostic test and the level of the standard is deemed not to have been exceeded in that 3-month period (for that parameter). As noted in section 4(c)(ii), in such a case, the 3-month parameter mean of the data actually reported, not the recalculated (''test'') result

including the high values, shall be used to determine the design value.

(d) Months that do not meet the completeness criteria stated in 4(c)(i) or 4(c)(ii), and design values that do not meet the completeness criteria stated in 4(a) or 4(b), may also be considered valid (and complete) with the approval of, or at the initiative of, the Administrator, who may consider factors such as monitoring site closures/moves, monitoring diligence, the consistency and levels of the valid concentration measurements that are available, and nearby concentrations in determining whether to use such data.

(e) The site-level design value for a 38-month period (three calendar years plus two previous months) is identified from the available (between one and 36) valid 3-month site means. In a situation where there are valid 3-month means for both parameters (Pb-TSP and Pb-PM_{10}), the mean originating from the reported Pb-TSP data will be the one deemed the site-level monthly mean and used in design value identifications unless the Pb-PM_{10} mean shows a violation of the NAAQS and exceeds the Pb-TSP mean; see section 2(a) for details. A monitoring site will have only one site-level 3-month mean per 3-month period; however, the set of site-level 3-month means considered for design value identification (*i.e.*, one to 36 site-level 3-month means) can be a combination of Pb-TSP and Pb-PM_{10} data.

(f) The procedures for calculating monthly means and 3-month means, and identifying Pb design values are given in section 6 of this appendix.

5. *Rounding Conventions.*

(a) Monthly means and monthly data capture rates are not rounded.

(b) Three-month means shall be rounded to the nearest hundredth μg/m^3 (0.xx). Decimals 0.xx5 and greater are rounded up, and any decimal lower than 0.xx5 is rounded down. E.g., a 3-month mean of 0.104925 rounds to 0.10 and a 3-month mean of .10500 rounds to 0.11. Three-month data capture rates, expressed as a percent, are round to zero decimal places.

(c) Because a Pb design value is simply a (highest) 3-month mean and because the NAAQS level is stated to two decimal places, no additional rounding beyond what is specified for 3-month means is required before a design value is compared to the NAAQS.

6. *Procedures and Equations for the Pb NAAQS.*

(a)(i) A monthly mean value for Pb-TSP (or Pb-PM_{10}) is determined by averaging the daily values of a calendar month using equation 1 of this appendix, unless the Administrator chooses to exercise his discretion to use the alternate approach described in 6(a)(ii).

Equation 1

$$\bar{X}_{m,y,s} = \frac{1}{n_m}\sum_{i=1}^{n_m} X_{i,m,y,s}$$

Where:

$X_{m,y,s}$ = the mean for month m of the year y for sites; and

n_m = the number of daily values in the month (creditable plus extra samples); and

$X_{i,m,y,s}$ = the i^{th} value in month m for year y for site s.

(a)(ii) The Administrator may at his discretion use the following alternate approach to calculating the monthly mean concentration if the number of extra sampling days during a month is greater than the number of successfully completed scheduled and make-up sample days in that month. In exercising his discretion, the Administrator will consider whether the approach specified in 6(a)(i) might in the Administrator's judgment result in an unrepresentative value for the monthly mean concentration. This provision is to protect the integrity of the monthly and 3-month mean concentration values in situations in which, by intention or otherwise, extra sampling days are concentrated in a period during which ambient concentrations are particularly high or low. The alternate approach is to average all extra and make-up samples (in the given month) taken after each scheduled sampling day (''Day X'') and before the next scheduled sampling day (e.g., ''Day X + 6'', in the case of one-in-six sampling) with the sample taken on Day X (assuming valid data was obtained on the scheduled sampling day), and then averaging these averages to calculate the monthly mean. This approach has the effect of giving approximately equal weight to periods during a month that have equal number of days, regardless of how many samples were actually obtained during the periods, thus mitigating the potential for the monthly mean to be distorted. The first day of scheduled sampling typically will not fall on the first day of the calendar month, and there may be make-up and/or extra samples (in that same calendar month) preceding the first scheduled day of the month. These samples will not be shifted into the previous month's mean concentration, but rather will stay associated with their actual calendar month as follows. Any extra and make-up samples taken in a month before the first scheduled sampling day of the month will be associated with and averaged with the last scheduled sampling day of that same month.

(b) Three-month parameter means are determined by averaging three consecutive monthly means of the same parameter using Equation 2 of this appendix.

Equation 2

$$\bar{X}_{m1,m2,m3;s} = \frac{1}{n_m}\sum_{i=1}^{n_m} \bar{X}_{m,y:z,s}$$

Where:

$\bar{X}_{m1,\ m2,\ m3;\ s}$ = the 3-month parameter mean for months m1, m2, and m3 for site s; and

n_m = the number of monthly means available to be averaged (typically 3, sometimes 1 or 2 if one or two months have no valid daily values); and

$X_{m,\ y:\ z,\ s}$ = The mean for month m of the year y (or z) for site s.

(c) Three-month site means are determined from available 3-month parameter means according to the hierarchy established in 2(a) of this appendix.

(d) The site-level Pb design value is the highest valid 3-month site-level mean over the most recent 38-month period (*i.e.*, the most recent 3-year calendar period plus two previous months). Section 4(a) of this appendix explains when the identified design value is itself considered valid for purposes of determining that the NAAQS is met or violated at a site.

[73 FR 67054, Nov. 12, 2008]

Appendix S to Part 50—Interpretation of the Primary National Ambient Air Quality Standards for Oxides of Nitrogen (Nitrogen Dioxide)

1. General

(a) This appendix explains the data handling conventions and computations necessary for determining when the primary national ambient air quality standards for oxides of nitrogen as measured by nitrogen dioxide (''NO_2 NAAQS'') specified in 50.11 are met. Nitrogen dioxide (NO_2) is measured in the ambient air by a Federal reference method (FRM) based on appendix F to this part or by a Federal equivalent method (FEM) designated in accordance with part 53 of this chapter. Data handling and computation procedures to be used in making comparisons between reported NO_2 concentrations and the levels of the NO_2 NAAQS are specified in the following sections.

(b) Whether to exclude, retain, or make adjustments to the data affected by exceptional events, including natural events, is determined by the requirements and process deadlines specified in 50.1, 50.14 and 51.930 of this chapter.

(c) The terms used in this appendix are defined as follows:

Annual mean refers to the annual average of all of the 1-hour concentration values as defined in section 5.1 of this appendix.

Daily maximum 1-hour values for NO_2 refers to the maximum 1-hour NO_2 concentration values measured from midnight to midnight (local standard time) that are used in NAAQS computations.

Design values are the metrics (*i.e.*, statistics) that are compared to the NAAQS levels to determine compliance, calculated as specified in section 5 of this appendix. The design values for the primary NAAQS are:

(1) The annual mean value for a monitoring site for one year (referred to as the ''annual primary standard design value'').

(2) The 3-year average of annual 98th percentile daily maximum 1-hour values for a monitoring site (referred to as the ''1-hour primary standard design value'').

98th percentile daily maximum 1-hour value is the value below which nominally 98 percent of all daily maximum 1-hour concentration values fall, using the ranking and selection method specified in section 5.2 of this appendix.

Quarter refers to a calendar quarter.

Year refers to a calendar year.

2. Requirements for Data Used for Comparisons With the NO_2 NAAQS and Data Reporting Considerations

(a) All valid FRM/FEM NO_2 hourly data required to be submitted to EPA's Air Quality System (AQS), or otherwise available to EPA, meeting the requirements of part 58 of this chapter including appendices A, C, and E shall be used in design value calculations. Multi-hour average concentration values collected by wet chemistry methods shall not be used.

(b) When two or more NO_2 monitors are operated at a site, the State may in advance designate one of them as the primary monitor. If the State has not made this designation, the Administrator will make the designation, either in advance or retrospectively. Design values will be developed using only the data from the primary monitor, if this results in a valid design value. If data from the primary monitor do not allow the development of a valid design value, data solely from the other monitor(s) will be used in turn to develop a valid design value, if this results in a valid design value. If there are three or more monitors, the order for such comparison of the other monitors will be determined by the Administrator. The Administrator may combine data from different monitors in different years for the purpose of developing a valid 1-hour primary standard design value, if a valid design value cannot be developed solely with the data from a single monitor. However, data from two or more monitors in the same year at the same site will not be combined in an attempt to meet data completeness requirements, except if one monitor has physically replaced another instrument permanently, in

State of Oregon Department of Environmental Quality

OAR 340-206-8010
Table 1
Air Pollution Emergencies

Table 1 – OAR 340-206-0030

Air Pollution Episode ALERT Conditions Source Emission Reduction Plan Emission Control Actions to be Taken as Appropriate in Alert Episode Area

Part A - Pollution Episode Conditions for Particulate Matter (Except Particulate from Volcanic Activity or Windblown Dust)

a. There shall be no open burning of any material in the designated area.
b. Where appropriate and if air quality maintenance strategies have not already prohibited the use of woodstoves and fireplaces, the public is requested to refrain from using coal or wood in uncertified woodstoves and fireplaces for domestic space heating where other heating methods are available.
c. Sources having Emission Reduction Plans, review plans and assure readiness to put them into effect if conditions worsen.

Part B - Pollution Episode Conditions for Carbon Monoxide, Ozone

a. All persons operating motor vehicles voluntarily reduce or eliminate unnecessary operations within the designated alert area.
b. Where appropriate, the public is requested to refrain from using coal or wood in uncertified woodstoves and fireplaces for domestic space heating where other heating methods are available.
c. Governmental and other agencies, review actions to be taken in the event of an air pollution warning.

OAR 340-206-8020
Air Pollution Episode WARNING Conditions
Emission Reduction Plan

Part A - Pollution Episode Conditions for Particulate Matter (PM10) (Except Particulate from Volcanic Activity or Windblown Dust.)

Source	Emission control action to be taken as appropriate in warning area
a. General (all sources and general public)	a. Continue alert procedures. b. Where legal authority exists, governmental agencies shall prohibit al1 use of woodstoves and fireplaces for domestic space heating except where such woodstoves and fireplaces provide the sole source of heat. c. The use of incinerators for disposal of solid or liquid waste is prohibited. d. Reduce emissions as much as possible consistent with safety to people and prevention of irreparable damage to equipment. e. Prepare for procedures to be followed if an emergency episode develops.
b. Specific additional general requirements for coal, oil or wood- fired electric power or steam generating facility	a. Effect a maximum reduction in emissions by switching to fuels having the lowest available ash and sulfur content. b. Switch to electric power sources located outside the Air Pollution Warning area or to noncombustion sources (hydro, thermonuclear). c. Cease operation of facilities not related to safety or protection of equipment or delivery of priority power.

OAR 340-206-8020
Air Pollution Episode WARNING Conditions
Emission Reduction Plan

Part A - Pollution Episode Conditions for Particulate Matter (PM10) (Except Particulate from Volcanic Activity or Windblown Dust.)

Source	Emission control action to be taken as appropriate in warning area
c. Specific additional general requirements for manufacturing industries including: Petroleum, Refining, Chemical, Primary Metals, Glass, Paper and Allied Products, Mineral Processing, Grain and Wood Processing	a. Reduce process heat load demand to the minimum possible consistent with safety and protection of equipment. b. Reduce emission of air contaminants from manufacturing by closing, postponing or deferring production to the maximum extent possible without causing injury to persons or damage to equipment. In so doing, assume reasonable economic hardships. Do not commence new cooks, batches or furnace changes in batch operation. Reduce continuous operations to minimum operating level where practicable. c. Defer trade waste disposal operations which emit solid particles, gases, vapors or malodorous substances.

(continued)

Air Pollution Episode WARNING Conditions Emission Reduction Plan

Part B - Pollution Episode Conditions for carbon monoxide, ozone: control actions to be taken as appropriate in warning area.

a. All operators of motor vehicles continue alert procedures.
b. Operation of motor vehicles carrying fewer than three persons shall be requested to avoid designated areas from 6 a.m. to 11 a.m., and 2 p.m. to 7 p.m. or other hours as-may be specified by the Department. Exempted from this request are:
    1. Emergency vehicles
    2. Public transportation
    3. Commercial vehicles
    4. Through traffic remaining on Interstate or primary highways

5. Traffic controlled by a preplanned strategy

c. In accordance with a traffic control plan prepared pursuant to OAR 340-206-0050, public transportation operators shall provide the additional service necessary to minimize the public inconvenience resulting from actions taken in accordance with paragraph b above.
d. For ozone episodes there shall be:
    1. No bulk transfer of gasoline without vapor recovery from 2 a.m. to 2 p.m.
    2. No service station pumping sales of gasoline from 2 a.m. to 2 p.m.
    3. No operation of paper coating plants from 2 a.m. to 2 p.m.
    4. No architectural painting or auto refinishing.
    5. No venting of dry cleaning solvents from 2 a.m. to 2 p.m. (except perchloroethylene).

When appropriate for carbon monoxide episodes during the heating season and where legal authority exists, governmental agencies shall prohibit all use of woodstoves and fireplaces for domestic space heating except where such woodstoves and fireplaces provide the sole source of heat.

OAR 340-206-8030
Air Pollution Episode EMERGENCY Conditions Emission Reduction Plan Pollution Episode Conditions for all Pollutants (Except Particulate from Volcanic Activity or Windblown Dust)

Source	Emission control actions to be taken as appropriate in emergency area
a. Requirements for all measures sources and general public.	a. Continue emission reduction taken under warning conditions. b. All places of employment, commerce, trade, public gatherings, government, industry, business, or manufacture shall immediately cease operations. c. Paragraph b. above does not apply to: 1. Police, fire, medical and other emergency services. 2. Utility and communication services. 3. Governmental functioning necessary for civil control and safety. 4. Operations necessary to prevent injury to persons or serious damage to equipment or property. 5. Food stores, drug stores and operations necessary for their supply . 6. Operations necessary for evacuation of persons leaving the area. 7. Operations conducted in accordance with an approved Source Emission Reduction Plan on file with the Department. d. The operation of motor vehicles is prohibited except for the conduct of the functions exempted in paragraph c. above. e. Reduce heat and power loads to a minimum by maintaining heated occupied spaces no higher than 65° F and turning off heat to all other spaces. f. Where legal authority exists, governmental agencies shall prohibit all use of woodstoves and fireplaces for domestic space heating.

OAR 340-206-8030
Air Pollution Episode EMERGENCY Conditions Emission Reduction Plan Pollution Episode Conditions for all Pollutants (Except Particulate from Volcanic Activity or Windblown Dust)

Source	Emission control actions to be taken as appropriate in emergency area
b. Specific additional requirements for coal oil or wood-fired electric power generating facilities operating under an approved source emission reduction plan.	a. Maintain operation at the lowest level possible consistent with prevention of damage to equipment and power production no higher than is required to supply power which is obtained elsewhere for essential services.
c. Specific additional requirements for coal, oil or wood-fired steam generating facilities operating under an approved source emission reduction plan.	a. Reduce operation to lowest level possible consistent with preventing damage to equipment.
d. Specific additional requirements for industries operating under an approved source emission reduction plan including: petroleum refining; chemical; primary metals; glass; paper and allied products; mineral processing; grain; wood processing.	a. Cease all trade waste disposal operations. b. If meteorological conditions are expected to persist for 24 hours or more, cease all operations not required for safety and protection of equipment.

State of Oregon Department of Environmental Quality

OAR 340-206-8040
Table 4

Air pollution episode conditions due to particulate which is primarily fallout from volcanic activity or windblown dust. Ambient Particulate control measures to be taken as appropriate in episode area.

Part A - ALERT Condition Actions

1. Traffic reduction by voluntary route control in contaminated areas.
2. Voluntary motor vehicle speed limits in dusty or fallout areas.
3. Voluntary street sweeping.
4. Voluntary wash down of traffic area

Part B - WARNING Condition Actions

1. Continue and intensify alert procedures.
2. Mandated speed limits and route control in contaminated areas.
3. Mandate wash down of exposed horizontal surfaces where feasible.
4. Request businesses to stagger work hours where possible as a means of avoiding heavy traffic.

Part C - EMERGENCY Condition Actions

1. Continue warning level procedures, expanding applicable area if necessary.
2. Prohibit all except emergency traffic on major roads and thoroughfares until the area has been cleaned. Other measures may be required at the discretion of the Governor.

State of Oregon Department of Environmental Quality

OAR 340-208-0110
EPA Method 9

APPENDIX A–4 TO PART 60—TEST METHODS 6 THROUGH 10B

Method 6—Determination of sulfur dioxide emissions from stationary sources
Method 6A—Determination of sulfur dioxide, moisture, and carbon dioxide emissions from fossil fuel combustion sources
Method 6B—Determination of sulfur dioxide and carbon dioxide daily average emissions from fossil fuel combustion sources
Method 6C—Determination of Sulfur Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure)
Method 7—Determination of nitrogen oxide emissions from stationary sources
Method 7A—Determination of nitrogen oxide emissions from stationary sources—Ion chromatographic method
Method 7B—Determination of nitrogen oxide emissions from stationary sources (Ultraviolet spectrophotometry)
Method 7C—Determination of nitrogen oxide emissions from stationary sources—Alkaline-permanganate/colorimetric method
Method 7D—Determination of nitrogen oxide emissions from stationary sources—Alkaline-permanganate/ion chromatographic method
Method 7E—Determination of Nitrogen Oxides Emissions From Stationary Sources (Instrumental Analyzer Procedure)
Method 8—Determination of sulfuric acid mist and sulfur dioxide emissions from stationary sources
Method 9—Visual determination of the opacity of emissions from stationary sources
Alternate method 1—Determination of the opacity of emissions from stationary sources remotely by lidar
Method 10—Determination of carbon monoxide emissions from stationary sources
Method 10A—Determination of carbon monoxide emissions in certifying continuous emission monitoring systems at petroleum refineries
Method 10B—Determination of carbon monoxide emissions from stationary sources

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that

the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

METHOD 6—DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, and Method 8.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
SO_2	7449–09–5	3.4 mg SO_2/m^3 $(2.12 \times 10)_{-7}$ lb/ft^3

1.2 Applicability. This method applies to the measurement of sulfur dioxide (SO_2) emissions from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the sampling point in the stack. The SO_2 and the sulfur trioxide, including those fractions in any sulfur acid mist, are separated. The SO_2 fraction is measured by the barium-thorin titration method.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Free Ammonia. Free ammonia interferes with this method by reacting with SO_2 to form particulate sulfite and by reacting with the indicator. If free ammonia is present (this can be determined by knowledge of the process and/or noticing white particulate matter in the probe and isopropanol bubbler), alternative methods, subject to the approval of the Administrator are required. One approved alternative is listed in Reference 13 of section 17.0.

4.2 Water-Soluble Cations and Fluorides. The cations and fluorides are removed by a glass wool filter and an isopropanol bubbler; therefore, they do not affect the SO_2 analysis. When samples are collected from a gas stream with high concentrations of metallic fumes (*i.e.*, very fine cation aerosols) a high-efficiency glass fiber filter must be used in place of the glass wool plug (*i.e.*, the one in the probe) to remove the cation interferent.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations before performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs. 30% H_2O_2 is a strong oxidizing agent. Avoid contact with skin, eyes, and combustible material. Wear gloves when handling.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

6.1 Sample Collection. The following items are required for sample collection:

6.1.1 Sampling Train. A schematic of the sampling train is shown in Figure 6–1. The sampling equipment described in Method 8 may be substituted in place of the midget impinger equipment of Method 6. However, the Method 8 train must be modified to include a heated filter between the probe and isopropanol impinger, and the operation of the sampling train and sample analysis must be at the flow rates and solution volumes defined in Method 8. Alternatively, SO_2 may be determined simultaneously with particulate

matter and moisture determinations by either (1) replacing the water in a Method 5 impinger system with a 3 percent H_2O_2 solution, or (2) replacing the Method 5 water impinger system with a Method 8 isopropanol-filter-H_2O_2 system. The analysis for SO_2 must be consistent with the procedure of Method 8. The Method 6 sampling train consists of the following components:

6.1.1.1 Probe. Borosilicate glass or stainless steel (other materials of construction may be used, subject to the approval of the Administrator), approximately 6 mm (0.25 in.) inside diameter, with a heating system to prevent water condensation and a filter (either in-stack or heated out-of-stack) to remove particulate matter, including sulfuric acid mist. A plug of glass wool is a satisfactory filter.

6.1.1.2 Bubbler and Impingers. One midget bubbler with medium-coarse glass frit and borosilicate or quartz glass wool packed in top (see Figure 6–1) to prevent sulfuric acid mist carryover, and three 30-ml midget impingers. The midget bubbler and midget impingers must be connected in series with leak-free glass connectors. Silicone grease may be used, if necessary, to prevent leakage. A midget impinger may be used in place of the midget bubbler.

NOTE: Other collection absorbers and flow rates may be used, subject to the approval of the Administrator, but the collection efficiency must be shown to be at least 99 percent for each test run and must be documented in the report. If the efficiency is found to be acceptable after a series of three tests, further documentation is not required. To conduct the efficiency test, an extra absorber must be added and analyzed separately. This extra absorber must not contain more than 1 percent of the total SO_2.

6.1.1.3 Glass Wool. Borosilicate or quartz.

6.1.1.4 Stopcock Grease. Acetone-insoluble, heat-stable silicone grease may be used, if necessary.

6.1.1.5 Temperature Sensor. Dial thermometer, or equivalent, to measure temperature of gas leaving impinger train to within 1 °C (2 °F).

6.1.1.6 Drying Tube. Tube packed with 6- to 16- mesh indicating-type silica gel, or equivalent, to dry the gas sample and to protect the meter and pump. If silica gel is previously used, dry at 177 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

6.1.1.7 Valve. Needle valve, to regulate sample gas flow rate.

6.1.1.8 Pump. Leak-free diaphragm pump, or equivalent, to pull gas through the train. Install a small surge tank between the pump and rate meter to negate the pulsation effect of the diaphragm pump on the rate meter.

6.1.1.9 Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of the selected flow rate of about 1 liter/min (0.035 cfm).

6.1.1.10 Volume Meter. Dry gas meter (DGM), sufficiently accurate to measure the sample volume to within 2 percent, calibrated at the selected flow rate and conditions actually encountered during sampling, and equipped with a temperature sensor (dial thermometer, or equivalent) capable of measuring temperature accurately to within 3 °C (5.4 °F). A critical orifice may be used in place of the DGM specified in this section provided that it is selected, calibrated, and used as specified in section 16.0.

6.1.2 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). See the note in Method 5, section 6.1.2.

6.1.3 Vacuum Gauge and Rotameter. At least 760-mm Hg (30-in. Hg) gauge and 0- to 40-ml/min rotameter, to be used for leak-check of the sampling train.

6.2 Sample Recovery. The following items are needed for sample recovery:

6.2.1 Wash Bottles. Two polyethylene or glass bottles, 500-ml.

6.2.2 Storage Bottles. Polyethylene bottles, 100-ml, to store impinger samples (one per sample).

6.3 Sample Analysis. The following equipment is needed for sample analysis:

6.3.1 Pipettes. Volumetric type, 5-ml, 20-ml (one needed per sample), and 25-ml sizes.

6.3.2 Volumetric Flasks. 100-ml size (one per sample) and 1000-ml size.

6.3.3 Burettes. 5- and 50-ml sizes.

6.3.4 Erlenmeyer Flasks. 250-ml size (one for each sample, blank, and standard).

6.3.5 Dropping Bottle. 125-ml size, to add indicator.

6.3.6 Graduated Cylinder. 100-ml size.

6.3.7 Spectrophotometer. To measure absorbance at 352 nm.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Water. Deionized distilled to conform to ASTM Specification D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17). The $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.1.2 Isopropanol, 80 Percent by Volume. Mix 80 ml of isopropanol with 20 ml of water.

7.1.2.1 Check each lot of isopropanol for peroxide impurities as follows: Shake 10 ml of isopropanol with 10 ml of freshly prepared 10 percent potassium iodide solution. Prepare a blank by similarly treating 10 ml of water. After 1 minute, read the absorbance at 352 nm on a spectrophotometer using a 1-cm path length. If absorbance exceeds 0.1, reject alcohol for use.

7.1.2.2 Peroxides may be removed from isopropanol by redistilling or by passage through a column of activated alumina; however, reagent grade isopropanol with suitably low peroxide levels may be obtained from commercial sources. Rejection of contaminated lots may, therefore, be a more efficient procedure.

7.1.3 Hydrogen Peroxide (H_2O_2), 3 Percent by Volume. Add 10 ml of 30 percent H_2O_2 to 90 ml of water. Prepare fresh daily.

7.1.4 Potassium Iodide Solution, 10 Percent Weight by Volume (w/v). Dissolve 10.0 g of KI in water, and dilute to 100 ml. Prepare when needed.

7.2 Sample Recovery. The following reagents are required for sample recovery:

7.2.1 Water. Same as in section 7.1.1.

7.2.2 Isopropanol, 80 Percent by Volume. Same as in section 7.1.2.

7.3 Sample Analysis. The following reagents and standards are required for sample analysis:

7.3.1 Water. Same as in section 7.1.1.

7.3.2 Isopropanol, 100 Percent.

7.3.3 Thorin Indicator. 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, disodium salt, or equivalent. Dissolve 0.20 g in 100 ml of water.

7.3.4 Barium Standard Solution, 0.0100 N. Dissolve 1.95 g of barium perchlorate trihydrate [$Ba(ClO_4)_2$ $3H_2O$] in 200 ml water, and dilute to 1 liter with isopropanol. Alternatively, 1.22 g of barium chloride dihydrate [$BaCl_2$ $2H_2O$] may be used instead of the barium perchlorate trihydrate. Standardize as in section 10.5.

7.3.5 Sulfuric Acid Standard, 0.0100 N. Purchase or standardize to ±0.0002 N against 0.0100 N NaOH which has previously been standardized against potassium acid phthalate (primary standard grade).

8.0 Sample Collection, Preservation, Storage and Transport

8.1 Preparation of Sampling Train. Measure 15 ml of 80 percent isopropanol into the midget bubbler and 15 ml of 3 percent H_2O_2 into each of the first two midget impingers. Leave the final midget impinger dry. Assemble the train as shown in Figure 6–1. Adjust the probe heater to a temperature sufficient to prevent water condensation. Place crushed ice and water around the impingers.

8.2 Sampling Train Leak-Check Procedure. A leak-check prior to the sampling run is recommended, but not required. A leak-check after the sampling run is mandatory. The leak-check procedure is as follows:

8.2.1 Temporarily attach a suitable (*e.g.*, 0- to 40- ml/min) rotameter to the outlet of the DGM, and place a vacuum gauge at or near the probe inlet. Plug the probe inlet, pull a vacuum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter. A leakage rate in excess of 2 percent of the average sampling rate is not acceptable.

NOTE: Carefully (*i.e.*, slowly) release the probe inlet plug before turning off the pump.

8.2.2 It is suggested (not mandatory) that the pump be leak-checked separately, either prior to or after the sampling run. To leak-check the pump, proceed as follows: Disconnect the drying tube from the probe-impinger assembly. Place a vacuum gauge at the inlet to either the drying tube or the pump, pull a vacuum of 250 mm Hg (10 in. Hg), plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum should remain stable for at least 30 seconds.

If performed prior to the sampling run, the pump leak-check shall precede the leak-check of the sampling train described immediately above; if performed after the sampling run, the pump leak-check shall follow the sampling train leak-check.

8.2.3 Other leak-check procedures may be used, subject to the approval of the Administrator.

8.3 Sample Collection.

8.3.1 Record the initial DGM reading and barometric pressure. To begin sampling, position the tip of the probe at the sampling point, connect the probe to the bubbler, and start the pump. Adjust the sample flow to a constant rate of approximately 1.0 liter/min as indicated by the rate meter. Maintain this constant rate (±10 percent) during the entire sampling run.

8.3.2 Take readings (DGM volume, temperatures at DGM and at impinger outlet, and rate meter flow rate) at least every 5 minutes. Add more ice during the run to keep the temperature of the gases leaving the last impinger at 20 °C (68 °F) or less.

8.3.3 At the conclusion of each run, turn off the pump, remove the probe from the stack, and record the final readings. Conduct a leak-check as described in section 8.2. (This leak-check is mandatory.) If a leak is detected, void the test run or use procedures acceptable to the Administrator to adjust the sample volume for the leakage.

8.3.4 Drain the ice bath, and purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at the sampling rate. Clean ambient air can be provided by passing air through a charcoal filter or through an extra midget impinger containing 15 ml of 3 percent H_2O_2. Alternatively, ambient air without purification may be used.

8.4 Sample Recovery. Disconnect the impingers after purging. Discard the contents of the midget bubbler. Pour the contents of the midget impingers into a leak-free polyethylene bottle for shipment. Rinse the three midget impingers and the connecting tubes with water, and add the rinse to the same storage container. Mark the fluid level. Seal and identify the sample container.

9.0 Quality Control

Section	Quality control measure	Effect
7.1.2	Isopropanol check	Ensure acceptable level of peroxide impurities in isopropanol.
8.2, 10.1–10.4	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.
10.5	Barium standard solution standardization	Ensure precision of normality determination
11.2.3	Replicate titrations	Ensure precision of titration determinations.

10.0 Calibration and Standardization

10.1 Volume Metering System.

10.1.1 Initial Calibration.

10.1.1.1 Before its initial use in the field, leak-check the metering system (drying tube, needle valve, pump, rate meter, and DGM) as follows: Place a vacuum gauge at the inlet to the drying tube and pull a vacuum of 250 mm Hg (10 in. Hg). Plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum must remain stable for at least 30 seconds. Carefully release the vacuum gauge before releasing the flow meter end.

10.1.1.2 Remove the drying tube, and calibrate the metering system (at the sampling flow rate specified by the method) as follows: Connect an appropriately sized wet-test meter (*e.g.*, 1 liter per revolution) to the inlet of the needle valve. Make three independent calibration runs, using at least five revolutions of the DGM per run. Calculate the calibration factor Y (wet-test meter calibration volume divided by the DGM volume, both volumes adjusted to the same reference temperature and pressure) for each run, and average the results (Y_i). If any Y-value deviates by more than 2 percent from (Y_i), the metering system is unacceptable for use. If the metering system is acceptable, use (Y_i) as the calibration factor for subsequent test runs.

10.1.2 Post-Test Calibration Check. After each field test series, conduct a calibration check using the procedures outlined in section 10.1.1.2, except that three or more revolutions of the DGM may be used, and only two independent runs need be made. If the average of the two post-test calibration factors does not deviate by more than 5 percent from Y_i, then Y_i is accepted as the DGM calibration factor (Y), which is used in Equation 6–1 to calculate collected sample volume (see section 12.2). If the deviation is more than 5 percent, recalibrate the metering system as in section 10.1.1, and determine a post-test calibration factor (Y_f). Compare Y_i and Y_f; the smaller of the two factors is accepted as the DGM calibration factor. If recalibration indicates that the metering system is unacceptable for use, either void the test run or use methods, subject to the approval of the Administrator, to determine an acceptable value for the collected sample volume.

10.1.3 DGM as a Calibration Standard. A DGM may be used as a calibration standard for volume measurements in place of the wet-test meter specified in section 10.1.1.2, provided that it is calibrated initially and recalibrated periodically according to the same procedures outlined in Method 5, section 10.3 with the following exceptions: (a) the DGM is calibrated against a wet-test meter having a capacity of 1 liter/rev (0.035 ft^3/rev) or 3 liters/rev (0.1 ft^3/rev) and having the capability of measuring volume to within 1 percent; (b) the DGM is calibrated at 1 liter/min (0.035 cfm); and (c) the meter box of the Method 6 sampling train is calibrated at the same flow rate.

10.2 Temperature Sensors. Calibrate against mercury-in-glass thermometers. An alternative mercury-free thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

10.3 Rate Meter. The rate meter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instructions.

10.4 Barometer. Calibrate against a mercury barometer or NIST-traceable barometer prior to the field test.

10.5 Barium Standard Solution. Standardize the barium perchlorate or chloride solution against 25 ml of standard sulfuric acid to which 100 ml of 100 percent isopropanol has been added. Run duplicate analyses. Calculate the normality using the average of duplicate analyses where the titrations agree within 1 percent or 0.2 ml, whichever is larger.

11.0 Analytical Procedure

11.1 Sample Loss Check. Note level of liquid in container and confirm whether any sample was lost during shipment; note this

finding on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Analysis.

11.2.1 Transfer the contents of the storage container to a 100-ml volumetric flask, dilute to exactly 100 ml with water, and mix the diluted sample.

11.2.2 Pipette a 20-ml aliquot of the diluted sample into a 250-ml Erlenmeyer flask and add 80 ml of 100 percent isopropanol plus two to four drops of thorin indicator. While stirring the solution, titrate to a pink endpoint using 0.0100 N barium standard solution.

11.2.3 Repeat the procedures in section 11.2.2, and average the titration volumes. Run a blank with each series of samples. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is larger.

NOTE: Protect the 0.0100 N barium standard solution from evaporation at all times.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 NOMENCLATURE

C_{SO2} = Concentration of SO_2, dry basis, corrected to standard conditions, mg/dscm (lb/dscf).
N = Normality of barium standard titrant, meq/ml.
P_{bar} = Barometric pressure, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
T_m = Average DGM absolute temperature, °K (°R).
T_{std} = Standard absolute temperature, 293 °K (528 °R).
V_a = Volume of sample aliquot titrated, ml.
V_m = Dry gas volume as measured by the DGM, dcm (dcf).
$V_{m(std)}$ = Dry gas volume measured by the DGM, corrected to standard conditions, dscm (dscf).
V_{soln} = Total volume of solution in which the SO_2 sample is contained, 100 ml.
V_t = Volume of barium standard titrant used for the sample (average of replicate titration), ml.
V_{tb} = Volume of barium standard titrant used for the blank, ml.
Y = DGM calibration factor.

12.2 Dry Sample Gas Volume, Corrected to Standard Conditions.

$$V_{m(std)} = \frac{\left(V_m Y T_{std} P_{bar}\right)}{\left(T_m P_{std}\right)} = \frac{K_1 Y V_m P_{bar}}{T_m} \quad \text{Eq. 6-1}$$

Where:

K_1 = 0.3855 °K/mm Hg for metric units,
K_1 = 17.65 °R/in. Hg for English units.

12.3 SO_2 Concentration.

$$C_{so_2} = \frac{K_2 N \left(V_t - V_{tb}\right)\left(V_{soln}/V_a\right)}{V_{m(std)}} \quad \text{Eq. 6-2}$$

Where:

K_2 = 32.03 mg SO_2/meq for metric units,
$K_2 = 7.061 \times 10^{-5}$ lb SO_2/meq for English units.

13.0 Method Performance

13.1 Range. The minimum detectable limit of the method has been determined to be 3.4 mg SO_2/m^3 (2.12×10^{-7} lb/ft³). Although no upper limit has been established, tests have shown that concentrations as high as 80,000 mg/m³ (0.005 lb/ft³) of SO_2 can be collected efficiently at a rate of 1.0 liter/min (0.035 cfm) for 20 minutes in two midget impingers, each containing 15 ml of 3 percent H_2O_2. Based on theoretical calculations, the upper concentration limit in a 20 liter (0.7 ft³) sample is about 93,300 mg/m³ (0.00583 lb/ft³).

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Nomenclature. Same as section 12.1, with the following additions:

B_{wa} = Water vapor in ambient air, proportion by volume.
M_a = Molecular weight of the ambient air saturated at impinger temperature, g/g-mole (lb/lb-mole).
M_s = Molecular weight of the sample gas saturated at impinger temperature, g/g-mole (lb/lb-mole).
P_c = Inlet vacuum reading obtained during the calibration run, mm Hg (in. Hg).
P_{sr} = Inlet vacuum reading obtained during the sampling run, mm Hg (in. Hg).

$\bar{Q}_{std}$ = Volumetric flow rate through critical orifice, scm/min (scf/min).
Q_{std} = Average flow rate of pre-test and post-test calibration runs, scm/min (scf/min).
T_{amb} = Ambient absolute temperature of air, °K (°R).
V_{sb} = Volume of gas as measured by the soap bubble meter, m^3 (ft^3).
$V_{sb(std)}$ = Volume of gas as measured by the soap bubble meter, corrected to standard conditions, scm (scf).
θ = Soap bubble travel time, min.
θ_s = Time, min.

16.2 Critical Orifices for Volume and Rate Measurements. A critical orifice may be used in place of the DGM specified in section 6.1.1.10, provided that it is selected, calibrated, and used as follows:

16.2.1 Preparation of Sampling Train. Assemble the sampling train as shown in Figure 6–2. The rate meter and surge tank are optional but are recommended in order to detect changes in the flow rate.

NOTE: The critical orifices can be adapted to a Method 6 type sampling train as follows: Insert sleeve type, serum bottle stoppers into two reducing unions. Insert the needle into the stoppers as shown in Figure 6–3.

16.2.2 Selection of Critical Orifices.

16.2.2.1 The procedure that follows describes the use of hypodermic needles and stainless steel needle tubings, which have been found suitable for use as critical orifices. Other materials and critical orifice designs may be used provided the orifices act as true critical orifices, (*i.e.*, a critical vacuum can be obtained) as described in this section. Select a critical orifice that is sized to operate at the desired flow rate. The needle sizes and tubing lengths shown in Table 6–1 give the following approximate flow rates.

16.2.2.2 Determine the suitability and the appropriate operating vacuum of the critical orifice as follows: If applicable, temporarily attach a rate meter and surge tank to the outlet of the sampling train, if said equipment is not present (see section 16.2.1). Turn on the pump and adjust the valve to give an outlet vacuum reading corresponding to about half of the atmospheric pressure. Observe the rate meter reading. Slowly increase the vacuum until a stable reading is obtained on the rate meter. Record the critical vacuum, which is the outlet vacuum when the rate meter first reaches a stable value. Orifices that do not reach a critical value must not be used.

16.2.3 Field Procedures.

16.2.3.1 Leak-Check Procedure. A leak-check before the sampling run is recommended, but not required. The leak-check procedure is as follows: Temporarily attach a suitable (*e.g.*, 0–40 ml/min) rotameter and surge tank, or a soap bubble meter and surge tank to the outlet of the pump. Plug the probe inlet, pull an outlet vacuum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter or bubble meter. A leakage rate in excess of 2 percent of the average sampling rate ($\bar{Q}_{std}$) is not acceptable. Carefully release the probe inlet plug before turning off the pump.

16.2.3.2 Moisture Determination. At the sampling location, prior to testing, determine the percent moisture of the ambient air using the wet and dry bulb temperatures or, if appropriate, a relative humidity meter.

16.2.3.3 Critical Orifice Calibration. At the sampling location, prior to testing, calibrate the entire sampling train (*i.e.*, determine the flow rate of the sampling train when operated at critical conditions). Attach a 500-ml soap bubble meter to the inlet of the probe, and operate the sampling train at an outlet vacuum of 25 to 50 mm Hg (1 to 2 in. Hg) above the critical vacuum. Record the information listed in Figure 6–4. Calculate the standard volume of air measured by the soap bubble meter and the volumetric flow rate using the equations below:

$$V_{sb(std)} = V_{sb}\left(T_{std}/T_{amb}\right)\left(P_{bar}/P_{std}\right) \qquad \text{Eq. 6-4}$$

$$Q_{std} = \frac{V_{sb(std)}}{\theta} \qquad \text{Eq. 6-5}$$

16.2.3.4 Sampling.

16.2.3.4.1 Operate the sampling train for sample collection at the same vacuum used during the calibration run. Start the watch and pump simultaneously. Take readings (temperature, rate meter, inlet vacuum, and outlet vacuum) at least every 5 minutes. At the end of the sampling run, stop the watch and pump simultaneously.

16.2.3.4.2 Conduct a post-test calibration run using the calibration procedure outlined in section 16.2.3.3. If the Q_{std} obtained before and after the test differ by more than 5 percent, void the test run; if not, calculate the volume of the gas measured with the critical orifice using Equation 6–6 as follows:

$$V_{m(std)} = \frac{\overline{Q}_{std}\ \theta_s\ (1-B_{wa})(P_{bar}+P_{sr})}{(P_{bar}+P_c)} \quad \text{Eq. 6-6}$$

16.2.3.4.3 If the percent difference between the molecular weight of the ambient air at saturated conditions and the sample gas is more that ±3 percent, then the molecular weight of the gas sample must be considered in the calculations using the following equation:

$$_{(std)} = \frac{\overline{Q}_{std}\ \theta_s\ (1-B_{wa})(P_{bar}+P_{sr})(M_a/M_s)^1}{(P_{bar}+P_c)} \quad \text{Eq. 6-7}$$

NOTE: A post-test leak-check is not necessary because the post-test calibration run results will indicate whether there is any leakage.

16.2.3.4.4 Drain the ice bath, and purge the sampling train using the procedure described in section 8.3.4.

16.3 Elimination of Ammonia Interference. The following alternative procedures must be used in addition to those specified in the method when sampling at sources having ammonia emissions.

16.3.1 Sampling. The probe shall be maintained at 275 °C (527 °F) and equipped with a high-efficiency in-stack filter (glass fiber) to remove particulate matter. The filter material shall be unreactive to SO_2. Whatman 934AH (formerly Reeve Angel 934AH) filters treated as described in Reference 10 in section 17.0 of Method 5 is an example of a filter that has been shown to work. Where alkaline particulate matter and condensed moisture are present in the gas stream, the filter shall be heated above the moisture dew point but below 225 °C (437 °F).

16.3.2 Sample Recovery. Recover the sample according to section 8.4 except for discarding the contents of the midget bubbler. Add the bubbler contents, including the rinsings of the bubbler with water, to a separate polyethylene bottle from the rest of the sample. Under normal testing conditions where sulfur trioxide will not be present significantly, the tester may opt to delete the midget bubbler from the sampling train. If an approximation of the sulfur trioxide concentration is desired, transfer the contents of the midget bubbler to a separate polyethylene bottle.

16.3.3 Sample Analysis. Follow the procedures in sections 11.1 and 11.2, except add 0.5 ml of 0.1 N HCl to the Erlenmeyer flask and mix before adding the indicator. The following analysis procedure may be used for an approximation of the sulfur trioxide concentration. The accuracy of the calculated concentration will depend upon the ammonia to SO_2 ratio and the level of oxygen present in the gas stream. A fraction of the SO_2 will be counted as sulfur trioxide as the ammonia to SO_2 ratio and the sample oxygen content increases. Generally, when this ratio is 1 or less and the oxygen content is in the range of 5 percent, less than 10 percent of the SO_2 will be counted as sulfur trioxide. Analyze the peroxide and isopropanol sample portions separately. Analyze the peroxide portion as described above. Sulfur trioxide is determined by difference using sequential titration of the isopropanol portion of the sample. Transfer the contents of the isopropanol storage container to a 100-ml volumetric flask, and dilute to exactly 100 ml with water. Pipette a 20-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 0.5 ml of 0.1 N HCl, 80 ml of 100 percent isopropanol, and two to four drops of thorin indicator. Titrate to a pink endpoint using 0.0100 N barium perchlorate. Repeat and average the titration volumes that agree within 1 percent or 0.2 ml, whichever is larger. Use this volume in Equation 6–2 to determine the sulfur trioxide concentration. From the flask containing the remainder of the isopropanol sample, determine the fraction of SO_2 collected in the bubbler by pipetting 20-ml aliquots into 250-ml Erlenmeyer flasks. Add 5 ml of 3 percent H_2O_2, 100 ml of 100 percent isopropanol, and two to four drips of thorin indicator, and titrate as before. From this titration volume, subtract the titrant volume determined for sulfur trioxide, and add the titrant volume determined for the peroxide portion. This final volume constitutes V_t, the volume of barium perchlorate used for the SO_2 sample.

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18.0 Tables, Diagrams, Flowcharts and Validation Data

TABLE 6–1—APPROXIMATE FLOW RATES FOR VARIOUS NEEDLE SIZES

Needle size (gauge)	Needle length (cm)	Flow rate (ml/min)
21	7.6	1,100
22	2.9	1,000
22	3.8	900
23	3.8	500
23	5.1	450
24	3.2	400

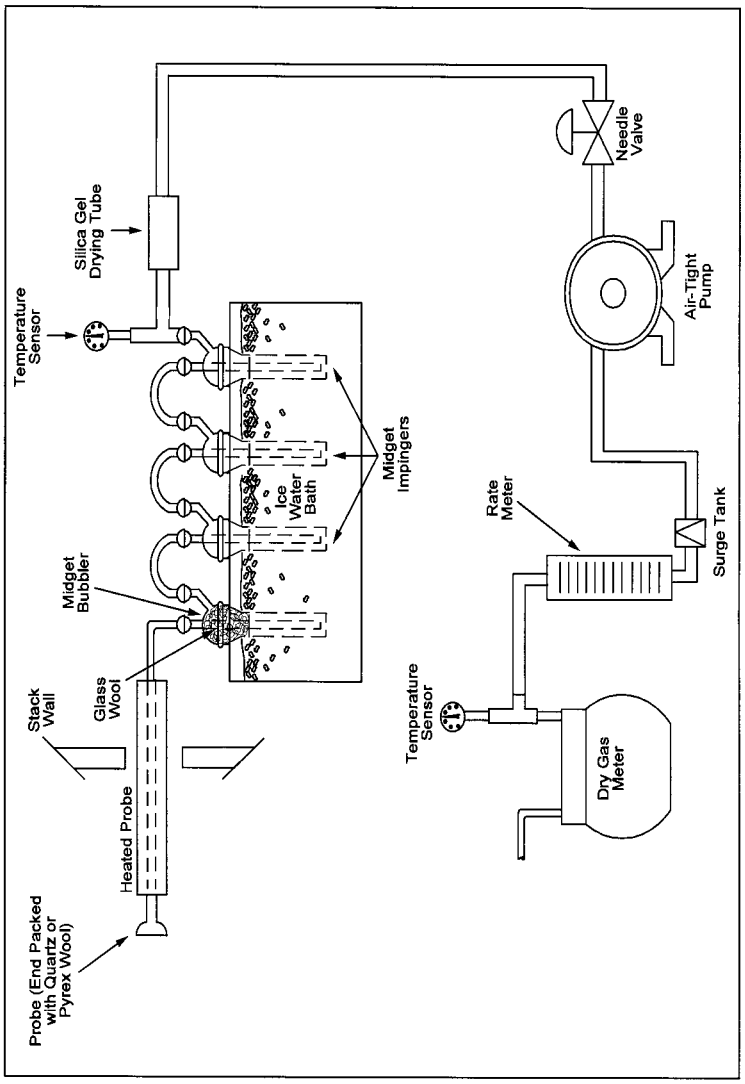

Figure 6-1. Sulfur Dioxide Sampling Train.

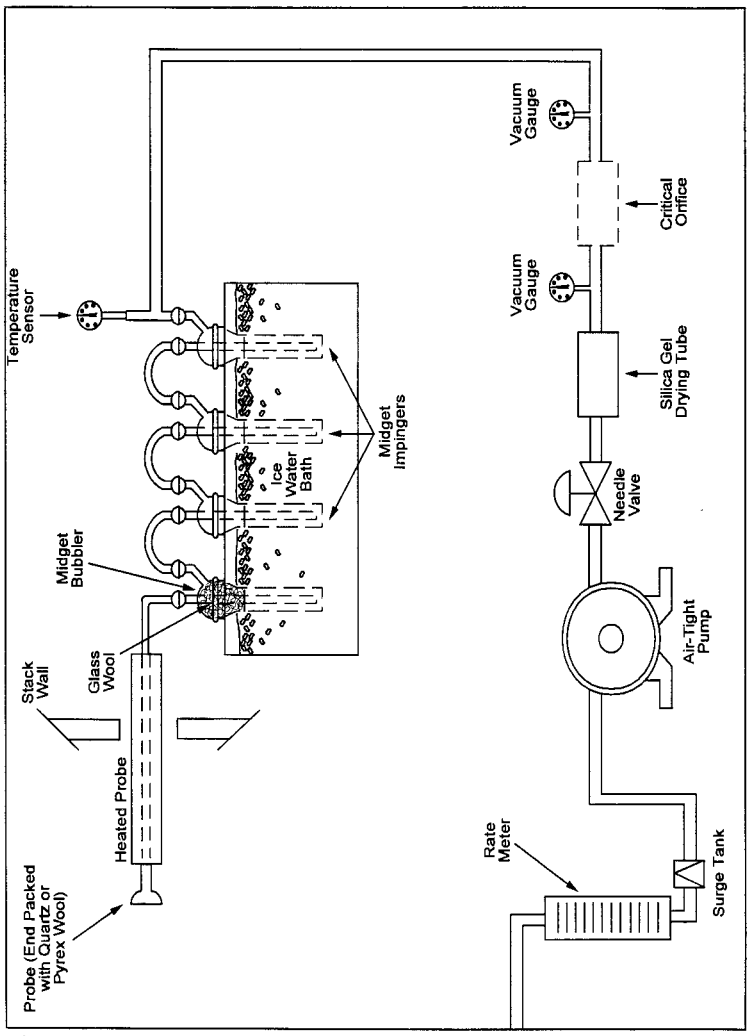

Figure 6-2. Sulfur Dioxide Sampling Train Using a Critical Orifice.

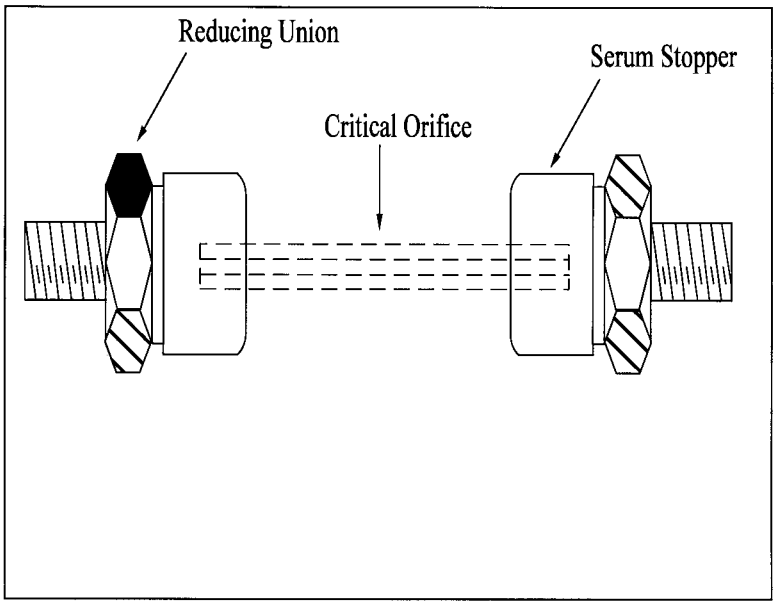

Figure 6-3. Critical Orifice Adaptation for the Method 6 Sampling Train.

Date _____ Train ID _____

Critical orifice size _____ Critical vacuum _____

		Pretest	Post-test
Soap bubble meter volume, V_{sb}	cc		
	m^3 (ft^3)		
Time, θ	sec		
	min		
Barometric pressure, P_{bar}	mm Hg (in. Hg)		
Ambient temperature, t_{amb}	°C (°F)		
Inlet vacuum, P_c	mm Hg (in. Hg)		
Outlet vacuum	mm Hg (in. Hg)		
$V_{sb(std)}$	m^3 (ft^3)		
Flow rate, Q_{std}	$\frac{m^3}{min}\left(\frac{ft^3}{min}\right)$		

Figure 6-4. Critical Orifice Calibration Data Sheet.

METHOD 6A—DETERMINATION OF SULFUR DIOXIDE, MOISTURE, AND CARBON DIOXIDE FROM FOSSIL FUEL COMBUSTION SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, Method 6, and Method 19.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
SO_2	7449–09–05	3.4 mg SO_2/m^3 (2.12×10^{-7} lb/ft^3)
CO_2	124–38–9	N/A
H_2O	7732–18–5	N/A

1.2 Applicability. This method is applicable for the determination of sulfur dioxide (SO_2) emissions from fossil fuel combustion sources in terms of concentration (mg/dscm or lb/dscf) and in terms of emission rate (ng/J or lb/10^6 Btu) and for the determination of carbon dioxide (CO_2) concentration (percent). Moisture content (percent), if desired, may also be determined by this method.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from a sampling point in the stack. The SO_2 and the sulfur trioxide, including those fractions in any sulfur acid mist, are separated. The SO_2 fraction is measured by the barium-thorin titration method. Moisture and CO_2 fractions are collected in the same sampling train, and are determined gravimetrically.

3.0 Definitions [Reserved]

4.0 Interferences

Same as Method 6, section 4.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. Same as Method 6, section 5.2.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 6, section 6.1, with the exception of the following:

6.1.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 6A–1.

6.1.1.1 Impingers and Bubblers. Two 30 = ml midget impingers with a 1 = mm restricted tip and two 30 = ml midget bubblers with unrestricted tips. Other types of impingers and bubblers (*e.g.,* Mae West for SO_2 collection and rigid cylinders containing Drierite for moisture absorbers), may be used with proper attention to reagent volumes and levels, subject to the approval of the Administrator.

6.1.1.2 CO_2 Absorber. A sealable rigid cylinder or bottle with an inside diameter between 30 and 90 mm , a length between 125 and 250 mm, and appropriate connections at both ends. The filter may be a separate heated unit or may be within the heated portion of the probe. If the filter is within the sampling probe, the filter should not be within 15 cm of the probe inlet or any unheated section of the probe, such as the connection to the first bubbler. The probe and filter should be heated to at least 20 °C (68 °F) above the source temperature, but not greater than 120 °C (248 °F). The filter temperature (*i.e.,* the sample gas temperature) should be monitored to assure the desired temperature is maintained. A heated Teflon connector may be used to connect the filter holder or probe to the first impinger.

NOTE: For applications downstream of wet scrubbers, a heated out-of-stack filter (either borosilicate glass wool or glass fiber mat) is necessary.

6.2 Sample Recovery. Same as Method 6, section 6.2.

6.3 Sample Analysis. Same as Method 6, section 6.3, with the addition of a balance to measure within 0.05 g.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

7.1 Sample Collection. Same as Method 6, section 7.1, with the addition of the following:

7.1.1 Drierite. Anhydrous calcium sulfate ($CaSO_4$) desiccant, 8 mesh, indicating type is recommended.

NOTE: Do not use silica gel or similar desiccant in this application.

7.1.2 CO_2 Absorbing Material. Ascarite II. Sodium hydroxide-coated silica, 8- to 20-mesh.

7.2 Sample Recovery and Analysis. Same as Method 6, sections 7.2 and 7.3, respectively.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Preparation of Sampling Train.

8.1.1 Measure 15 ml of 80 percent isopropanol into the first midget bubbler and 15 ml of 3 percent hydrogen peroxide into each of the two midget impingers (the second

and third vessels in the train) as described in Method 6, section 8.1. Insert the glass wool into the top of the isopropanol bubbler as shown in Figure 6A–1. Place about 25 g of Drierite into the second midget bubbler (the fourth vessel in the train). Clean the outside of the bubblers and impingers and allow the vessels to reach room temperature. Weigh the four vessels simultaneously to the nearest 0.1 g, and record this initial weight (m_{wi}).

8.1.2 With one end of the CO_2 absorber sealed, place glass wool into the cylinder to a depth of about 1 cm (0.5 in.). Place about 150 g of CO_2 absorbing material in the cylinder on top of the glass wool, and fill the remaining space in the cylinder with glass wool. Assemble the cylinder as shown in figure 6A–2. With the cylinder in a horizontal position, rotate it around the horizontal axis. The CO_2 absorbing material should remain in position during the rotation, and no open spaces or channels should be formed. If necessary, pack more glass wool into the cylinder to make the CO_2 absorbing material stable. Clean the outside of the cylinder of loose dirt and moisture and allow the cylinder to reach room temperature. Weigh the cylinder to the nearest 0.1 g, and record this initial weight (m_{ai}).

8.1.3 Assemble the train as shown in figure 6A–1. Adjust the probe heater to a temperature sufficient to prevent condensation (see note in section 6.1). Place crushed ice and water around the impingers and bubblers. Mount the CO_2 absorber outside the water bath in a vertical flow position with the sample gas inlet at the bottom. Flexible tubing (*e.g.*, Tygon) may be used to connect the last SO_2 absorbing impinger to the moisture absorber and to connect the moisture absorber to the CO_2 absorber. A second, smaller CO_2 absorber containing Ascarite II may be added in-line downstream of the primary CO_2 absorber as a breakthrough indicator. Ascarite II turns white when CO_2 is absorbed.

8.2 Sampling Train Leak-Check Procedure and Sample Collection. Same as Method 6, sections 8.2 and 8.3, respectively.

8.3 Sample Recovery.

8.3.1 Moisture Measurement. Disconnect the isopropanol bubbler, the SO_2 impingers, and the moisture absorber from the sample train. Allow about 10 minutes for them to reach room temperature, clean the outside of loose dirt and moisture, and weigh them simultaneously in the same manner as in section 8.1. Record this final weight (m_{wf}).

8.3.2 Peroxide Solution. Discard the contents of the isopropanol bubbler and pour the contents of the midget impingers into a leak-free polyethylene bottle for shipping. Rinse the two midget impingers and connecting tubes with water, and add the washing to the same storage container.

8.3.3 CO_2 Absorber. Allow the CO_2 absorber to warm to room temperature (about 10 minutes), clean the outside of loose dirt and moisture, and weigh to the nearest 0.1 g in the same manner as in section 8.1. Record this final weight (m_{af}). Discard used Ascarite II material.

9.0 Quality Control

Same as Method 6, section 9.0.

10.0 Calibration and Standardization

Same as Method 6, section 10.0.

11.0 Analytical Procedure

11.1 Sample Analysis. The sample analysis procedure for SO_2 is the same as that specified in Method 6, section 11.0.

12.0 Data Analysis and Calculations

Same as Method 6, section 12.0, with the addition of the following:

12.1 Nomenclature.

C_w = Concentration of moisture, percent.
C_{CO2} = Concentration of CO_2, dry basis, percent.
E_{SO2} = Emission rate of SO_2, ng/J (lb/10^6 Btu).
F_C = Carbon F-factor from Method 19 for the fuel burned, dscm/J (dscf/10^6 Btu).
m_{wi} = Initial weight of impingers, bubblers, and moisture absorber, g.
m_{wf} = Final weight of impingers, bubblers, and moisture absorber, g.
m_{ai} = Initial weight of CO_2 absorber, g.
m_{af} = Final weight of CO_2 absorber, g.
m_{SO2} = Mass of SO_2 collected, mg.
$V_{CO2(std)}$ = Equivalent volume of CO_2 collected at standard conditions, dscm (dscf).
$V_{w(std)}$ = Equivalent volume of moisture collected at standard conditions, scm (scf).

12.2 CO_2 Volume Collected, Corrected to Standard Conditions.

$$V_{CO_2(std)} = K_3 \left(m_{af} - m_{ai}\right) \qquad \text{Eq. 6A-1}$$

Where:

K_3 = Equivalent volume of gaseous CO_2 at standard conditions, 5.467×10^{-4} dscm/g (1.930×10^{-2} dscf/g).

12.3 Moisture Volume Collected, Corrected to Standard Conditions.

$$V_{w(std)} = K_4 \left(m_{wf} - m_{wi}\right) \qquad \text{Eq. 6A-2}$$

Where:

K_4 = Equivalent volume of water vapor at standard conditions, 1.336×10^{-3} scm/g (4.717×10^{-2} scf/g).

12.4 SO_2 Concentration.

$$C_{so_2} = \frac{K_2 N (V_t - V_{tb})(V_{so\,ln}/V_a)}{V_{m(std)} + V_{co_2(std)}} \qquad \text{Eq. 6A-3}$$

Where:

K_2 = 32.03 mg SO_2/meq. SO_2 (7.061×10^{-5} lb SO_2/meq. SO_2)

12.5 CO_2 Concentration.

$$C_{co_2} = \frac{V_{co_2(std)}}{V_{m(std)} + V_{co_2(std)}} \qquad \text{Eq. 6A-4}$$

12.6 Moisture Concentration.

$$C_w = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)} + V_{co_2(std)}} \qquad \text{Eq. 6A-5}$$

13.0 Method Performance

13.1 Range and Precision. The minimum detectable limit and the upper limit for the measurement of SO_2 are the same as for Method 6. For a 20-liter sample, this method has a precision of ±0.5 percent CO_2 for concentrations between 2.5 and 25 percent CO_2 and ±1.0 percent moisture for moisture concentrations greater than 5 percent.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Methods

If the only emission measurement desired is in terms of emission rate of SO_2 (ng/J or lb/10^6 Btu), an abbreviated procedure may be used. The differences between the above procedure and the abbreviated procedure are described below.

16.1 Sampling Train. The sampling train is the same as that shown in Figure 6A–1 and as described in section 6.1, except that the dry gas meter is not needed.

16.2 Preparation of the Sampling Train. Follow the same procedure as in section 8.1, except do not weigh the isopropanol bubbler, the SO_2 absorbing impingers, or the moisture absorber.

16.3 Sampling Train Leak-Check Procedure and Sample Collection. Leak-check and operate the sampling train as described in section 8.2, except that dry gas meter readings, barometric pressure, and dry gas meter temperatures need not be recorded during sampling.

16.4 Sample Recovery. Follow the procedure in section 8.3, except do not weigh the isopropanol bubbler, the SO_2 absorbing impingers, or the moisture absorber.

16.5 Sample Analysis. Analysis of the peroxide solution is the same as that described in section 11.1.

16.6 Calculations.

16.6.1 SO_2 Collected.

$$m_{SO_2} = K_2 N (V_t - V_{tb})(V_{soln}/V_a) \qquad \text{Eq. 6A-6}$$

Where:

K_2 = 32.03 mg SO_2/meq. SO_2
$K_2 = 7.061 \times 10^{-5}$ lb SO_2/meq. SO_2

16.6.2 Sulfur Dioxide Emission Rate.

$$E_{SO_2} = K_5 F_c m_{so_2} / (m_{af} - m_{ai}) \qquad \text{Eq. 6A-7}$$

Where:

$K_5 = 1.829 \times 10^9$ mg/dscm
$K_2 = 0.1142$ lb/dscf

17.0 References

Same as Method 6, section 17.0, References 1 through 8, with the addition of the following:

1. Stanley, Jon and P.R. Westlin. An Alternate Method for Stack Gas Moisture Determination. Source Evaluation Society Newsletter. *3*(4). November 1978.

2. Whittle, Richard N. and P.R. Westlin. Air Pollution Test Report: Development and Evaluation of an Intermittent Integrated SO_2/CO_2 Emission Sampling Procedure. Environmental Protection Agency, Emission Standard and Engineering Division, Emission Measurement Branch. Research Triangle Park, NC. December 1979. 14 pp.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

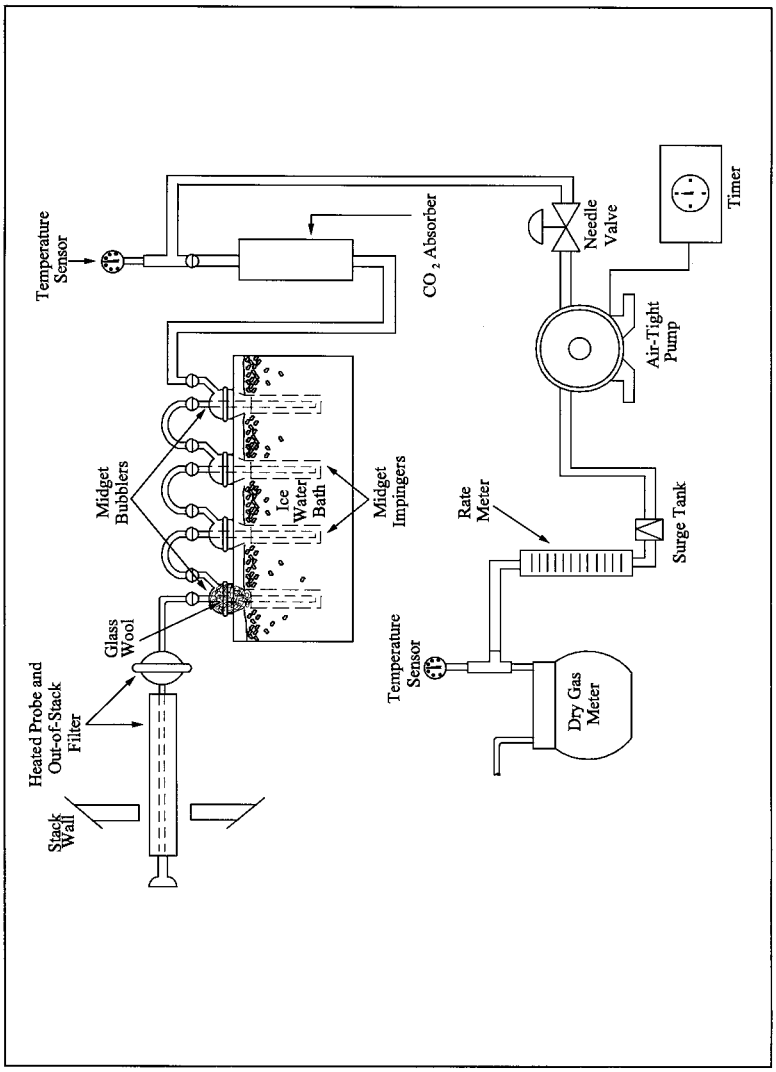

Figure 6A-1. Sampling train.

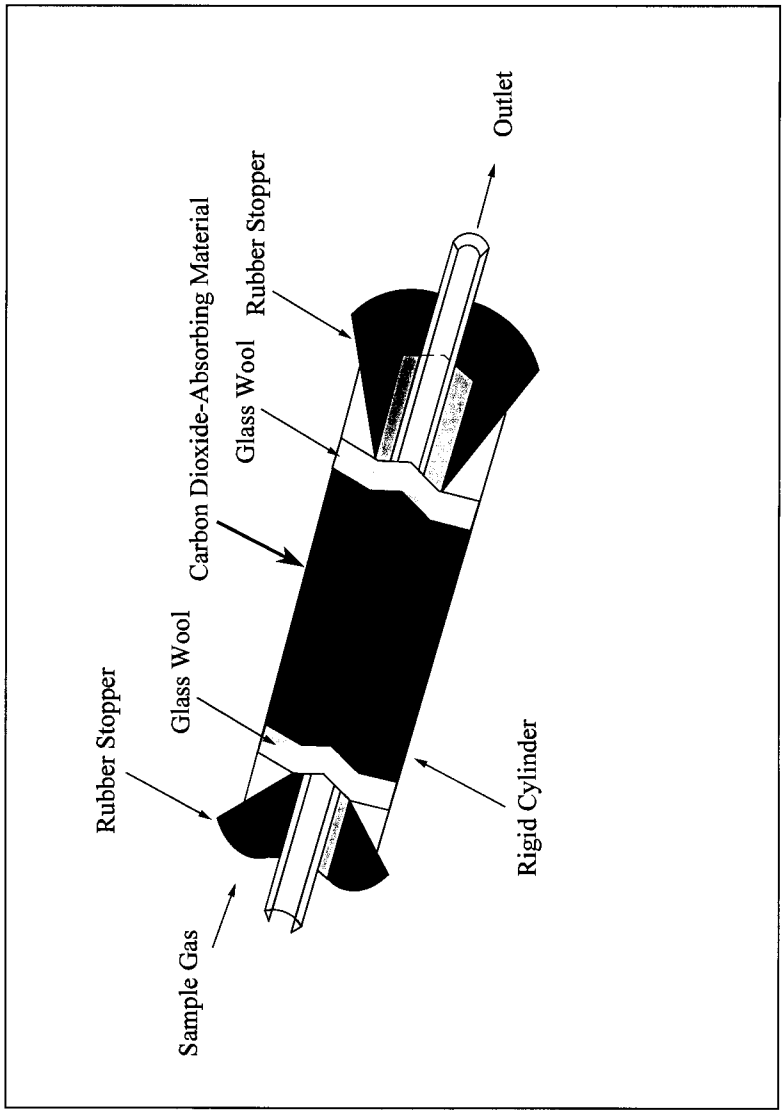

Figure 6A-2. CO_2 Absorber

METHOD 6B—DETERMINATION OF SULFUR DIOXIDE AND CARBON DIOXIDE DAILY AVERAGE EMISSIONS FROM FOSSIL FUEL COMBUSTION SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, Method 6, and Method 6A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Sulfur dioxide (SO_2)	7449–09–05	3.4 mg SO_2/m^3 (2.12×10^{-7} lb/ft^3)
Carbon dioxide (CO_2)	124–38–9	N/A

1.2 Applicability. This method is applicable for the determination of SO_2 emissions from combustion sources in terms of concentration (ng/dscm or lb/dscf) and emission rate (ng/J or lb/10^6 Btu), and for the determination of CO_2 concentration (percent) on a daily (24 hours) basis.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the sampling point in the stack intermittently over a 24-hour or other specified time period. The SO_2 fraction is measured by the barium-thorin titration method. Moisture and CO_2 fractions are collected in the same sampling train, and are determined gravimetrically.

3.0 Definitions [Reserved]

4.0 Interferences

Same as Method 6, section 4.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. Same as Method 6, section 5.2.

6.0 Equipment and Supplies

Same as Method 6A, section 6.0, with the following exceptions and additions:

6.1 The isopropanol bubbler is not used. An empty bubbler for the collection of liquid droplets, that does not allow direct contact between the collected liquid and the gas sample, may be included in the sampling train.

6.2 For intermittent operation, include an industrial timer-switch designed to operate in the ''on'' position at least 2 minutes continuously and ''off'' the remaining period over a repeating cycle. The cycle of operation is designated in the applicable regulation. At a minimum, the sampling operation should include at least 12, equal, evenly-spaced periods per 24 hours.

6.3 Stainless steel sampling probes, type 316, are not recommended for use with Method 6B because of potential sample contamination due to corrosion. Glass probes or other types of stainless steel, *e.g.*, Hasteloy or Carpenter 20, are recommended for long-term use.

NOTE: For applications downstream of wet scrubbers, a heated out-of-stack filter (either borosilicate glass wool or glass fiber mat) is necessary. Probe and filter heating systems capable of maintaining a sample gas temperature of between 20 and 120 °C (68 and 248 °F) at the filter are also required in these cases. The electric supply for these heating systems should be continuous and separate from the timed operation of the sample pump.

7.0 Reagents and Standards

Same as Method 6A, section 7.0, with the following exceptions:

7.1 Isopropanol is not used for sampling.

7.2 The hydrogen peroxide absorbing solution shall be diluted to no less than 6 percent by volume, instead of 3 percent as specified in Methods 6 and 6A.

7.3 If the Method 6B sampling train is to be operated in a low sample flow condition (less than 100 ml/min or 0.21 ft^3/hr), molecular sieve material may be substituted for Ascarite II as the CO_2 absorbing material. The recommended molecular sieve material is Union Carbide 1/16 inch pellets, 5 A°, or equivalent. Molecular sieve material need not be discarded following the sampling run, provided that it is regenerated as per the manufacturer's instruction. Use of molecular sieve material at flow rates higher than 100 ml/min (0.21 ft^3/hr) may cause erroneous CO_2 results.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Preparation of Sampling Train. Same as Method 6A, section 8.1, with the addition of the following:

8.1.1 The sampling train is assembled as shown in Figure 6A–1 of Method 6A, except that the isopropanol bubbler is not included.

8.1.2 Adjust the timer-switch to operate in the ''on'' position from 2 to 4 minutes on a 2-hour repeating cycle or other cycle specified in the applicable regulation. Other timer sequences may be used with the restriction that the total sample volume collected is between 25 and 60 liters (0.9 and 2.1 ft^3) for the amounts of sampling reagents prescribed in this method.

8.1.3 Add cold water to the tank until the impingers and bubblers are covered at least two-thirds of their length. The impingers and bubbler tank must be covered and protected from intense heat and direct sunlight. If freezing conditions exist, the impinger solution and the water bath must be protected.

NOTE: Sampling may be conducted continuously if a low flow-rate sample pump [20

to 40 ml/min (0.04 to 0.08 ft^3/hr) for the reagent volumes described in this method] is used. If sampling is continuous, the timer-switch is not necessary. In addition, if the sample pump is designed for constant rate sampling, the rate meter may be deleted. The total gas volume collected should be between 25 and 60 liters (0.9 and 2.1 ft^3) for the amounts of sampling reagents prescribed in this method.

8.2 Sampling Train Leak-Check Procedure. Same as Method 6, section 8.2.

8.3 Sample Collection.

8.3.1 The probe and filter (either in-stack, out-of-stack, or both) must be heated to a temperature sufficient to prevent water condensation.

8.3.2 Record the initial dry gas meter reading. To begin sampling, position the tip of the probe at the sampling point, connect the probe to the first impinger (or filter), and start the timer and the sample pump. Adjust the sample flow to a constant rate of approximately 1.0 liter/min (0.035 cfm) as indicated by the rotameter. Observe the operation of the timer, and determine that it is operating as intended (*i.e.*, the timer is in the ''on'' position for the desired period, and the cycle repeats as required).

8.3.3 One time between 9 a.m. and 11 a.m. during the 24-hour sampling period, record the dry gas meter temperature (T_m) and the barometric pressure ($P_{(bar)}$).

8.3.4 At the conclusion of the run, turn off the timer and the sample pump, remove the probe from the stack, and record the final gas meter volume reading. Conduct a leak-check as described in section 8.2. If a leak is found, void the test run or use procedures acceptable to the Administrator to adjust the sample volume for leakage. Repeat the steps in sections 8.3.1 to 8.3.4 for successive runs.

8.4 Sample Recovery. The procedures for sample recovery (moisture measurement, peroxide solution, and CO_2 absorber) are the same as those in Method 6A, section 8.3.

9.0 Quality Control

Same as Method 6, section 9.0., with the exception of the isopropanol-check.

10.0 Calibration and Standardization

Same as Method 6, section 10.0, with the addition of the following:

10.1 Periodic Calibration Check. After 30 days of operation of the test train, conduct a calibration check according to the same procedures as the post-test calibration check (Method 6, section 10.1.2). If the deviation between initial and periodic calibration factors exceeds 5 percent, use the smaller of the two factors in calculations for the preceding 30 days of data, but use the most recent calibration factor for succeeding test runs.

11.0 Analytical Procedures

11.1 Sample Loss Check and Analysis. Same as Method 6, sections 11.1 and 11.2, respectively.

12.0 Data Analysis and Calculations

Same as Method 6A, section 12.0, except that P_{bar} and T_m correspond to the values recorded in section 8.3.3 of this method. The values are as follows:

P_{bar} = Initial barometric pressure for the test period, mm Hg.

T_m = Absolute meter temperature for the test period, °K.

13.0 Method Performance

13.1 Range.

13.1.1 Sulfur Dioxide. Same as Method 6.

13.1.2 Carbon Dioxide. Not determined.

13.2 Repeatability and Reproducibility. EPA-sponsored collaborative studies were undertaken to determine the magnitude of repeatability and reproducibility achievable by qualified testers following the procedures in this method. The results of the studies evolve from 145 field tests including comparisons with Methods 3 and 6. For measurements of emission rates from wet, flue gas desulfurization units in (ng/J), the repeatability (intra-laboratory precision) is 8.0 percent and the reproducibility (inter-laboratory precision) is 11.1 percent.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Methods

Same as Method 6A, section 16.0, except that the timer is needed and is operated as outlined in this method.

17.0 References

Same as Method 6A, section 17.0, with the addition of the following:

1. Butler, Frank E., et. al. The Collaborative Test of Method 6B: Twenty-Four-Hour Analysis of SO_2 and CO_2. JAPCA. Vol. 33, No. 10. October 1983.

18.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 6C—DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES (INSTRUMENTAL ANALYZER PROCEDURE)

1.0 Scope and Application

What is Method 6C?

Method 6C is a procedure for measuring sulfur dioxide (SO_2) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that

you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis.

This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 4—Determination of Moisture Content in Stack Gases.

(c) Method 6—Determination of Sulfur Dioxide Emissions from Stationary Sources.

(d) Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure).

1.1 Analytes. What does this method determine? This method measures the concentration of sulfur dioxide.

Analyte	CAS No.	Sensitivity
SO_2	7446–09–5	Typically <2% of Calibration Span.

1.2 Applicability. When is this method required? The use of Method 6C may be required by specific New Source Performance Standards, Clean Air Marketing rules, State Implementation Plans, and permits where SO_2 concentrations in stationary source emissions must be measured, either to determine compliance with an applicable emission standard or to conduct performance testing of a continuous emission monitoring system (CEMS). Other regulations may also require the use of Method 6C.

1.3 Data Quality Objectives. How good must my collected data be? Refer to section 1.3 of Method 7E.

2.0 Summary of Method

In this method, you continuously sample the effluent gas and convey the sample to an analyzer that measures the concentration of SO_2. You must meet the performance requirements of this method to validate your data.

3.0 Definitions

Refer to section 3.0 of Method 7E for the applicable definitions.

4.0 Interferences

Refer to Section 4.0 of Method 7E.

5.0 Safety

Refer to section 5.0 of Method 7E.

6.0 Equipment and Supplies

Figure 7E–1 of Method 7E is a schematic diagram of an acceptable measurement system.

6.1 What do I need for the measurement system? The essential components of the measurement system are the same as those in sections 6.1 and 6.2 of Method 7E, except that the SO_2 analyzer described in section 6.2 of this method must be used instead of the analyzer described in section 6.2 of Method 7E. You must follow the noted specifications in section 6.1 of Method 7E.

6.2 What analyzer must I use? You may use an instrument that uses an ultraviolet, nondispersive infrared, fluorescence, or other detection principle to continuously measure SO_2 in the gas stream and meets the performance specifications in section 13.0. The low-range and dual-range analyzer provisions in sections 6.2.8.1 and 6.2.8.2 of Method 7E apply.

7.0 Reagents and Standards

7.1 Calibration Gas. What calibration gases do I need? Refer to section 7.1 of Method 7E for the calibration gas requirements. Example calibration gas mixtures are listed below.

(a) SO_2 in nitrogen (N_2).

(b) SO_2 in air.

(c) SO_2 and CO_2 in N_2.

(d) SO_2 andO_2 in N_2.

(e) $SO_2/CO_2/O_2$ gas mixture in N_2.

(f) CO_2/NO_X gas mixture in N_2.

(g) $CO_2/SO_2/NO_X$ gas mixture in N_2.

7.2 Interference Check. What additional reagents do I need for the interference check? The test gases for the interference check are listed in Table 7E–3 of Method 7E. For the alternative interference check, you must use the reagents described in section 7.0 of Method 6.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling Site and Sampling Points. You must follow the procedures of section 8.1 of Method 7E.

8.2 Initial Measurement System Performance Tests. You must follow the procedures in section 8.2 of Method 7E. If a dilution-type measurement system is used, the special considerations in section 8.3 of Method 7E also apply.

8.3 Interference Check. You must follow the procedures of section 8.2.7 of Method 7E

to conduct an interference check, substituting SO_2 for NO_X as the method pollutant. For dilution-type measurement systems, you must use the alternative interference check procedure in section 16 and a co-located, unmodified Method 6 sampling train.

8.4 Sample Collection. You must follow the procedures of section 8.4 of Method 7E.

8.5 Post-Run System Bias Check and Drift Assessment. You must follow the procedures of section 8.5 of Method 7E.

9.0 Quality Control

Follow quality control procedures in section 9.0 of Method 7E.

10.0 Calibration and Standardization

Follow the procedures for calibration and standardization in section 10.0 of Method 7E.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the applicable procedures for calculations and data analysis in section 12.0 of Method 7E as applicable, substituting SO_2 for NO_X as appropriate.

13.0 Method Performance

13.1 The specifications for the applicable performance checks are the same as in section 13.0 of Method 7E.

13.2 Alternative Interference Check. The results are acceptable if the difference between the Method 6C result and the modified Method 6 result is less than 7.0 percent of the Method 6 result for each of the three test runs. For the purposes of comparison, the Method 6 and 6C results must be expressed in the same units of measure.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Alternative Interference Check. You may perform an alternative interference check consisting of at least three comparison runs between Method 6C and Method 6. This check validates the Method 6C results at each particular source category (type of facility) where the check is performed. When testing under conditions of low concentrations (<15 ppm), this alternative interference check is not allowed.

NOTE: The procedure described below applies to non-dilution sampling systems only. If this alternative interference check is used for a dilution sampling system, use a standard Method 6 sampling train and extract the sample directly from the exhaust stream at points collocated with the Method 6C sample probe.

a. Build the modified Method 6 sampling train (flow control valve, two midget impingers containing 3 percent hydrogen peroxide, and dry gas meter) shown in Figure 6C–1. Connect the sampling train to the sample bypass discharge vent. Record the dry gas meter reading before you begin sampling. Simultaneously collect modified Method 6 and Method 6C samples. Open the flow control valve in the modified Method 6 train as you begin to sample with Method 6C. Adjust the Method 6 sampling rate to 1 liter per minute (.10 percent). The sampling time per run must be the same as for Method 6 plus twice the average measurement system response time. If your modified Method 6 train does not include a pump, you risk biasing the results high if you over-pressurize the midget impingers and cause a leak. You can reduce this risk by cautiously increasing the flow rate as sampling begins.

b. After completing a run, record the final dry gas meter reading, meter temperature, and barometric pressure. Recover and analyze the contents of the midget impingers using the procedures in Method 6. Determine the average gas concentration reported by Method 6C for the run.

17.0 References

1. ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards'' September 1997 as amended, EPA–600/R–97/121

18.0 Tables, Diagrams, Flowcharts, and Validation Data

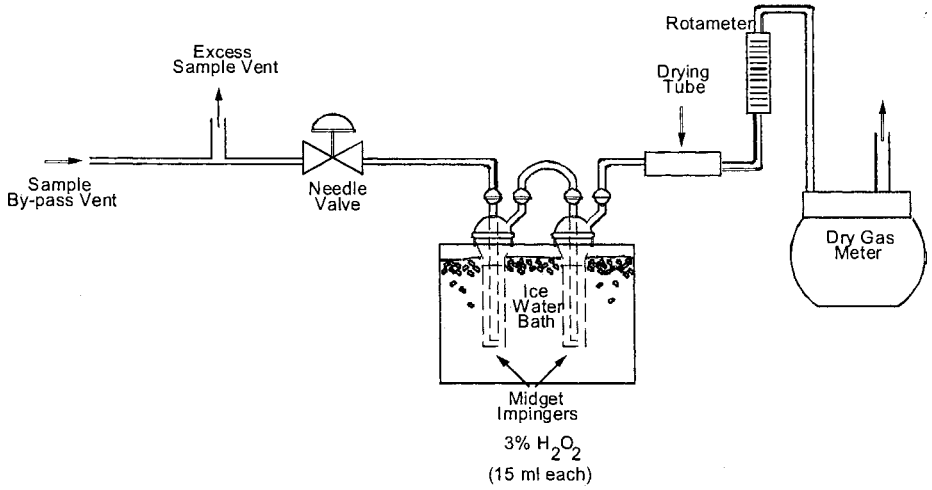

Figure 6C-1. Modified Method 6
Alternative Interference Check Sampling Train

METHOD 7—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1 and Method 5.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–0	2–400 mg/dscm

1.2 Applicability. This method is applicable for the measurement of nitrogen oxides (NO_X) emitted from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sample methods.

2.0 Summary of Method

A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution, and the nitrogen oxides, except nitrous oxide, are measured colorimetrically using the phenoldisulfonic acid (PDS) procedure.

3.0 Definitions [Reserved]

4.0 Interferences

Biased results have been observed when sampling under conditions of high sulfur dioxide concentrations. At or above 2100 ppm SO_2, use five times the H_2O_2 concentration of the Method 7 absorbing solution. Laboratory tests have shown that high concentrations of SO_2 (about 2100 ppm) cause low results in Method 7 and 7A. Increasing the H_2O_2 concentration to five times the original concentration eliminates this bias. However, when no SO_2 is present, increasing the concentration by five times results in a low bias.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs.

5.2.2 Phenoldisulfonic Acid. Irritating to eyes and skin.

5.2.3 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.4 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

5.2.5 Phenol. Poisonous and caustic. Do not handle with bare hands as it is absorbed through the skin.

6.0 Equipment and Supplies

6.1 Sample Collection. A schematic of the sampling train used in performing this method is shown in Figure 7–1. Other grab sampling systems or equipment, capable of measuring sample volume to within 2.0 percent and collecting a sufficient sample volume to allow analytical reproducibility to within 5 percent, will be considered acceptable alternatives, subject to the approval of the Administrator. The following items are required for sample collection:

6.1.1 Probe. Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or heated out-of-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Stainless steel or Teflon tubing may also be used for the probe. Heating is not necessary if the probe remains dry during the purging period.

6.1.2 Collection Flask. Two-liter borosilicate, round bottom flask, with short neck and 24/40 standard taper opening, protected against implosion or breakage.

6.1.3 Flask Valve. T-bore stopcock connected to a 24/40 standard taper joint.

6.1.4 Temperature Gauge. Dial-type thermometer, or other temperature gauge, capable of measuring 1 °C (2 °F) intervals from −5 to 50 °C (23 to 122 °F).

6.1.5 Vacuum Line. Tubing capable of withstanding a vacuum of 75 mm (3 in.) Hg absolute pressure, with ''T'' connection and T-bore stopcock.

6.1.6 Vacuum Gauge. U-tube manometer, 1 meter (39 in.), with 1 mm (0.04 in.) divisions, or other gauge capable of measuring pressure to within 2.5 mm (0.10 in.) Hg.

6.1.7 Pump. Capable of evacuating the collection flask to a pressure equal to or less than 75 mm (3 in.) Hg absolute.

6.1.8 Squeeze Bulb. One-way.

6.1.9 Volumetric Pipette. 25-ml.

6.1.10 Stopcock and Ground Joint Grease. A high-vacuum, high-temperature chlorofluorocarbon grease is required. Halocarbon 25–5S has been found to be effective.

6.1.11 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg. See note in Method 5, section 6.1.2.

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Graduated Cylinder. 50-ml with 1 ml divisions.

6.2.2 Storage Containers. Leak-free polyethylene bottles.

6.2.3 Wash Bottle. Polyethylene or glass.

6.2.4 Glass Stirring Rod.

6.2.5 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

6.3 Analysis. The following items are required for analysis:

6.3.1 Volumetric Pipettes. Two 1-ml, two 2-ml, one 3-ml, one 4-ml, two 10-ml, and one 25-ml for each sample and standard.

6.3.2 Porcelain Evaporating Dishes. 175- to 250-ml capacity with lip for pouring, one for each sample and each standard. The Coors No. 45006 (shallowform, 195-ml) has been found to be satisfactory. Alternatively, polymethyl pentene beakers (Nalge No. 1203, 150-ml), or glass beakers (150-ml) may be used. When glass beakers are used, etching of the beakers may cause solid matter to be present in the analytical step; the solids should be removed by filtration.

6.3.3 Steam Bath. Low-temperature ovens or thermostatically controlled hot plates kept below 70 °C (160 °F) are acceptable alternatives.

6.3.4 Dropping Pipette or Dropper. Three required.

6.3.5 Polyethylene Policeman. One for each sample and each standard.

6.3.6 Graduated Cylinder. 100-ml with 1-ml divisions.

6.3.7 Volumetric Flasks. 50-ml (one for each sample and each standard), 100-ml (one for each sample and each standard, and one for the working standard KNO_3 solution), and 1000-ml (one).

6.3.8 Spectrophotometer. To measure at 410 nm.

6.3.9 Graduated Pipette. 10-ml with 0.1-ml divisions.

6.3.10 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

6.3.11 Analytical Balance. To measure to within 0.1 mg.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. The following reagents are required for sampling:

7.1.1 Water. Deionized distilled to conform to ASTM D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17). The $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.1.2 Absorbing Solution. Cautiously add 2.8 ml concentrated H_2SO_4 to a 1-liter flask partially filled with water. Mix well, and add 6 ml of 3 percent hydrogen peroxide, freshly prepared from 30 percent hydrogen peroxide solution. Dilute to 1 liter of water and mix well. The absorbing solution should be used within 1 week of its preparation. Do not expose to extreme heat or direct sunlight.

7.2 Sample Recovery. The following reagents are required for sample recovery:

7.2.1 Water. Same as in 7.1.1.

7.2.2 Sodium Hydroxide, 1 N. Dissolve 40 g NaOH in water, and dilute to 1 liter.

7.3 Analysis. The following reagents and standards are required for analysis:

7.3.1 Water. Same as in 7.1.1.

7.3.2 Fuming Sulfuric Acid. 15 to 18 percent by weight free sulfur trioxide. HANDLE WITH CAUTION.

7.3.3 Phenol. White solid.

7.3.4 Sulfuric Acid. Concentrated, 95 percent minimum assay.

7.3.5 Potassium Nitrate (KNO_3). Dried at 105 to 110 °C (221 to 230 °F) for a minimum of 2 hours just prior to preparation of standard solution.

7.3.6 Standard KNO_3 Solution. Dissolve exactly 2.198 g of dried KNO_3 in water, and dilute to 1 liter with water in a 1000-ml volumetric flask.

7.3.7 Working Standard KNO_3 Solution. Dilute 10 ml of the standard solution to 100 ml with water. One ml of the working standard solution is equivalent to 100 μg nitrogen dioxide (NO_2).

7.3.8 Phenoldisulfonic Acid Solution. Dissolve 25 g of pure white phenol solid in 150 ml concentrated sulfuric acid on a steam bath. Cool, add 75 ml fuming sulfuric acid (15 to 18 percent by weight free sulfur trioxide—HANDLE WITH CAUTION), and heat at 100 °C (212 °F) for 2 hours. Store in a dark, stoppered bottle.

7.3.9 Concentrated Ammonium Hydroxide.

8.0 Sample Collection, Preservation, Storage and Transport

8.1 Sample Collection.

8.1.1 Flask Volume. The volume of the collection flask and flask valve combination must be known prior to sampling. Assemble the flask and flask valve, and fill with water to the stopcock. Measure the volume of water to ±10 ml. Record this volume on the flask.

8.1.2 Pipette 25 ml of absorbing solution into a sample flask, retaining a sufficient quantity for use in preparing the calibration standards. Insert the flask valve stopper into the flask with the valve in the ''purge'' position. Assemble the sampling train as shown in Figure 7–1, and place the probe at the sampling point. Make sure that all fittings are tight and leak-free, and that all ground glass joints have been greased properly with a high-vacuum, high temperature chlorofluorocarbon-based stopcock grease. Turn the flask valve and the pump valve to their ''evacuate'' positions. Evacuate the flask to 75 mm (3 in.) Hg absolute pressure, or less. Evacuation to a pressure approaching the vapor pressure of water at the existing temperature is desirable. Turn the pump valve to its ''vent'' position, and turn off the pump. Check for leakage by observing the manometer for any pressure fluctuation. (Any variation greater than 10 mm (0.4 in.) Hg over a period of 1 minute is not acceptable, and the flask is not to be used until the leakage problem is corrected. Pressure in the flask is not to exceed 75 mm (3 in.) Hg absolute at the time sampling is commenced.) Record the volume of the flask and valve (V_f), the flask temperature (T_i), and the barometric pressure. Turn the flask valve counterclockwise to its ''purge'' position, and do the same with the pump valve. Purge the probe and the vacuum tube using the squeeze bulb. If condensation occurs in the probe and the flask valve area, heat the probe, and purge until the condensation disappears. Next, turn the pump valve to its ''vent'' position. Turn the flask valve clockwise to its ''evacuate'' position, and record the difference in the mercury levels in the manometer. The absolute internal pressure in the flask (P_i) is equal to the barometric pressure less the manometer reading. Immediately turn the flask valve to the ''sample'' position, and permit the gas to enter the flask until pressures in the flask and sample line (*i.e.*, duct, stack) are equal. This will usually require about 15 seconds; a longer period indicates a plug in the probe, which must be

corrected before sampling is continued. After collecting the sample, turn the flask valve to its ''purge'' position, and disconnect the flask from the sampling train.

8.1.3 Shake the flask for at least 5 minutes.

8.1.4 If the gas being sampled contains insufficient oxygen for the conversion of NO to NO_2 (*e.g.,* an applicable subpart of the standards may require taking a sample of a calibration gas mixture of NO in N_2), then introduce oxygen into the flask to permit this conversion. Oxygen may be introduced into the flask by one of three methods: (1) Before evacuating the sampling flask, flush with pure cylinder oxygen, then evacuate flask to 75 mm (3 in.) Hg absolute pressure or less; or (2) inject oxygen into the flask after sampling; or (3) terminate sampling with a minimum of 50 mm (2 in.) Hg vacuum remaining in the flask, record this final pressure, and then vent the flask to the atmosphere until the flask pressure is almost equal to atmospheric pressure.

8.2 Sample Recovery. Let the flask sit for a minimum of 16 hours, and then shake the contents for 2 minutes.

8.2.1 Connect the flask to a mercury filled U-tube manometer. Open the valve from the flask to the manometer, and record the flask temperature (T_f), the barometric pressure, and the difference between the mercury levels in the manometer. The absolute internal pressure in the flask (P_f) is the barometric pressure less the manometer reading. Transfer the contents of the flask to a leak-free polyethylene bottle. Rinse the flask twice with 5 ml portions of water, and add the rinse water to the bottle. Adjust the pH to between 9 and 12 by adding 1 N NaOH, dropwise (about 25 to 35 drops). Check the pH by dipping a stirring rod into the solution and then touching the rod to the pH test paper. Remove as little material as possible during this step. Mark the height of the liquid level so that the container can be checked for leakage after transport. Label the container to identify clearly its contents. Seal the container for shipping.

9.0 Quality Control

Section	Quality control measure	Effect
10.1	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.

10.0 Calibration and Standardization

10.1 Spectrophotometer.

10.1.1 Optimum Wavelength Determination.

10.1.1.1 Calibrate the wavelength scale of the spectrophotometer every 6 months. The calibration may be accomplished by using an energy source with an intense line emission such as a mercury lamp, or by using a series of glass filters spanning the measuring range of the spectrophotometer. Calibration materials are available commercially and from the National Institute of Standards and Technology. Specific details on the use of such materials should be supplied by the vendor; general information about calibration techniques can be obtained from general reference books on analytical chemistry. The wavelength scale of the spectrophotometer must read correctly within 5 nm at all calibration points; otherwise, repair and recalibrate the spectrophotometer. Once the wavelength scale of the spectrophotometer is in proper calibration, use 410 nm as the optimum wavelength for the measurement of the absorbance of the standards and samples.

10.1.1.2 Alternatively, a scanning procedure may be employed to determine the proper measuring wavelength. If the instrument is a double-beam spectrophotometer, scan the spectrum between 400 and 415 nm using a 200 μg NO_2 standard solution in the sample cell and a blank solution in the reference cell. If a peak does not occur, the spectrophotometer is probably malfunctioning and should be repaired. When a peak is obtained within the 400 to 415 nm range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of absorbance of both the standards and the samples. For a single-beam spectrophotometer, follow the scanning procedure described above, except scan separately the blank and standard solutions. The optimum wavelength shall be the wavelength at which the maximum difference in absorbance between the standard and the blank occurs.

10.1.2 Determination of Spectrophotometer Calibration Factor K_c. Add 0 ml, 2.0 ml, 4.0 ml, 6.0 ml, and 8.0 ml of the KNO_3 working standard solution (1 ml = 100 μg NO_2) to a series of five 50-ml volumetric flasks. To each flask, add 25 ml of absorbing solution and 10 ml water. Add 1 N NaOH to each flask until the pH is between 9 and 12 (about 25 to 35 drops). Dilute to the mark with water. Mix thoroughly, and pipette a 25-ml aliquot of each solution into a separate porcelain evaporating dish. Beginning with the evaporation step, follow the analysis procedure of section 11.2 until the solution has been transferred to the 100-ml volumetric flask and diluted to the mark. Measure the absorbance of each solution at the optimum wavelength as determined in section 10.2.1. This calibration procedure must be repeated on each day that samples are analyzed. Calculate the spectrophotometer calibration factor as shown in section 12.2.

10.1.3 Spectrophotometer Calibration Quality Control. Multiply the absorbance value obtained for each standard by the K_c factor (reciprocal of the least squares slope) to determine the distance each calibration point lies from the theoretical calibration line. The difference between the calculated concentration values and the actual concentrations (*i.e.*, 100, 200, 300, and 400 µg NO_2) should be less than 7 percent for all standards.

10.2 Barometer. Calibrate against a mercury barometer or NIST-traceable barometer prior to the field test.

10.3 Temperature Gauge. Calibrate dial thermometers against mercury-in-glass thermometers. An alternative mercury-free thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

10.4 Vacuum Gauge. Calibrate mechanical gauges, if used, against a mercury manometer such as that specified in section 6.1.6.

10.5 Analytical Balance. Calibrate against standard weights.

11.0 Analytical Procedures

11.1 Sample Loss Check. Note the level of the liquid in the container, and confirm whether any sample was lost during shipment. Note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Preparation. Immediately prior to analysis, transfer the contents of the shipping container to a 50 ml volumetric flask, and rinse the container twice with 5 ml portions of water. Add the rinse water to the flask, and dilute to mark with water; mix thoroughly. Pipette a 25-ml aliquot into the porcelain evaporating dish. Return any unused portion of the sample to the polyethylene storage bottle. Evaporate the 25-ml aliquot to dryness on a steam bath, and allow to cool. Add 2 ml phenoldisulfonic acid solution to the dried residue, and triturate thoroughly with a polyethylene policeman. Make sure the solution contacts all the residue. Add 1 ml water and 4 drops of concentrated sulfuric acid. Heat the solution on a steam bath for 3 minutes with occasional stirring. Allow the solution to cool, add 20 ml water, mix well by stirring, and add concentrated ammonium hydroxide, dropwise, with constant stirring, until the pH is 10 (as determined by pH paper). If the sample contains solids, these must be removed by filtration (centrifugation is an acceptable alternative, subject to the approval of the Administrator) as follows: Filter through Whatman No. 41 filter paper into a 100-ml volumetric flask. Rinse the evaporating dish with three 5-ml portions of water. Filter these three rinses. Wash the filter with at least three 15-ml portions of water. Add the filter washings to the contents of the volumetric flask, and dilute to the mark with water. If solids are absent, the solution can be transferred directly to the 100-ml volumetric flask and diluted to the mark with water.

11.3 Sample Analysis. Mix the contents of the flask thoroughly, and measure the absorbance at the optimum wavelength used for the standards (Section 10.2.1), using the blank solution as a zero reference. Dilute the sample and the blank with equal volumes of water if the absorbance exceeds A_4, the absorbance of the 400-µg NO_2 standard (see section 10.2.2).

12.0 Data Analysis and Calculations

Carry out the calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculations.

12.1 12.1 Nomenclature

A = Absorbance of sample.
A_1 = Absorbance of the 100-µg NO_2 standard.
A_2 = Absorbance of the 200-µg NO_2 standard.
A_3 = Absorbance of the 300-µg NO_2 standard.
A_4 = Absorbance of the 400-µg NO_2 standard.
C = Concentration of NO_X as NO_2, dry basis, corrected to standard conditions, mg/dsm³ (lb/dscf).
F = Dilution factor (*i.e.*, 25/5, 25/10, *etc.*, required only if sample dilution was needed to reduce the absorbance into the range of the calibration).
K_c = Spectrophotometer calibration factor.
M = Mass of NO_X as NO_2 in gas sample, µg.
P_f = Final absolute pressure of flask, mm Hg (in. Hg).
P_i = Initial absolute pressure of flask, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
T_f = Final absolute temperature of flask, °K (°R).
T_i = Initial absolute temperature of flask, °K (°R).
T_{std} = Standard absolute temperature, 293 °K (528°R).
V_{sc} = Sample volume at standard conditions (dry basis), ml.
V_f = Volume of flask and valve, ml.
V_a = Volume of absorbing solution, 25 ml.

12.2 Spectrophotometer Calibration Factor.

$$K_c = 100\frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^{\,2} + A_2^{\,2} + A_3^{\,2} + A_4^{\,2}} \qquad \text{Eq. 7-1}$$

12.3 Sample Volume, Dry Basis, Corrected to Standard Conditions.

$$V_{sc} = \left(V_f - V_a\right)\frac{T_{std}}{P_{std}}\left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right] \qquad \text{Eq. 7-2}$$

$$= K_1\left(V_f - 25\right)\left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right]$$

Where:

K_1 = 0.3858 °K/mm Hg for metric units,
K_1 = 17.65 °R/in. Hg for English units.

12.4 Total µg NO_2 per sample.

$$m = 2K_c AF \qquad \text{Eq. 7-3}$$

Where:

2 = 50/25, the aliquot factor.

NOTE: If other than a 25-ml aliquot is used for analysis, the factor 2 must be replaced by a corresponding factor.

12.5 Sample Concentration, Dry Basis, Corrected to Standard Conditions.

$$C = K_2\left(m/V_{sc}\right) \qquad \text{Eq. 7-4}$$

Where:

K2 = 10^3 (mg/m^3)/(µg/ml) for metric units,
K_2 = 6.242 × 10^{-5} (lb/scf)/(µg/ml) for English units.

13.0 Method Performance

13.1 Range. The analytical range of the method has been determined to be 2 to 400 milligrams NO_X (as NO_2) per dry standard cubic meter, without having to dilute the sample.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Standard Methods of Chemical Analysis. 6th ed. New York, D. Van Nostrand Co., Inc. 1962. Vol. 1, pp. 329–330.

2. Standard Method of Test for Oxides of Nitrogen in Gaseous Combustion Products (Phenoldisulfonic Acid Procedure). In: 1968 Book of ASTM Standards, Part 26. Philadelphia, PA. 1968. ASTM Designation D 1608–60, pp. 725–729.

3. Jacob, M.B. The Chemical Analysis of Air Pollutants. New York. Interscience Publishers, Inc. 1960. Vol. 10, pp. 351–356.

4. Beatty, R.L., L.B. Berger, and H.H. Schrenk. Determination of Oxides of Nitrogen by the Phenoldisulfonic Acid Method. Bureau of Mines, U.S. Dept. of Interior. R.I. 3687. February 1943.

5. Hamil, H.F. and D.E. Camann. Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Fossil Fuel-Fired Steam Generators). Southwest Research Institute Report for Environmental Protection Agency. Research Triangle Park, NC. October 5, 1973.

6. Hamil, H.F. and R.E. Thomas. Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Nitric Acid Plants). Southwest Research Institute Report for Environmental Protection Agency. Research Triangle Park, NC. May 8, 1974.

7. Stack Sampling Safety Manual (Draft). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC. September 1978.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

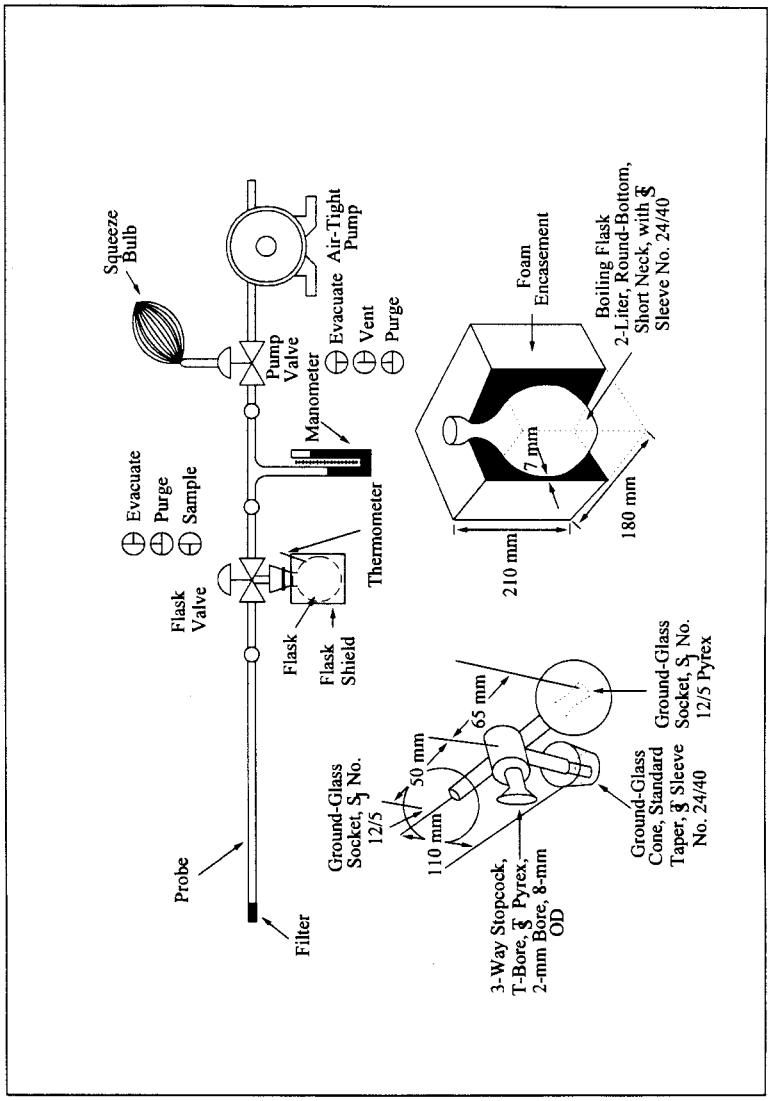

Figure 7-1. Sampling Train, Flask Valve, and Flask.

METHOD 7A—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ION CHROMATOGRAPHIC METHOD)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 3, Method 5, and Method 7.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–0	65–655 ppmv

1.2 Applicability. This method is applicable for the determination of NO_X emissions from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution. The nitrogen oxides, excluding nitrous oxide (N_2O), are oxidized to nitrate and measured by ion chromatography.

3.0 Definitions [Reserved]

4.0 Interferences

Biased results have been observed when sampling under conditions of high sulfur dioxide concentrations. At or above 2100 ppm SO_2, use five times the H_2O_2 concentration of the Method 7 absorbing solution. Laboratory tests have shown that high concentrations of SO_2 (about 2100 ppm) cause low results in Method 7 and 7A. Increasing the H_2O_2 concentration to five times the original concentration eliminates this bias. However, when no SO_2 is present, increasing the concentration by five times results in a low bias.

5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs.

5.2.2 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m^3 will cause lung damage in uninitiated. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as in Method 7, section 6.1.

6.2 Sample Recovery. Same as in Method 7, section 6.2, except the stirring rod and pH paper are not needed.

6.3 Analysis. For the analysis, the following equipment and supplies are required. Alternative instrumentation and procedures will be allowed provided the calibration precision requirement in section 10.1.2 can be met.

6.3.1 Volumetric Pipets. Class A;1-, 2-, 4-, 5-ml (two for the set of standards and one per sample), 6-, 10-, and graduated 5-ml sizes.

6.3.2 Volumetric Flasks. 50-ml (two per sample and one per standard), 200-ml, and 1-liter sizes.

6.3.3 Analytical Balance. To measure to within 0.1 mg.

6.3.4 Ion Chromatograph. The ion chromatograph should have at least the following components:

6.3.4.1 Columns. An anion separation or other column capable of resolving the nitrate ion from sulfate and other species present and a standard anion suppressor column (optional). Suppressor columns are produced as proprietary items; however, one can be produced in the laboratory using the resin available from BioRad Company, 32nd and Griffin Streets, Richmond, California. Peak resolution can be optimized by varying the eluent strength or column flow rate, or by experimenting with alternative columns that may offer more efficient separation. When using guard columns with the stronger reagent to protect the separation column, the analyst should allow rest periods between injection intervals to purge possible sulfate buildup in the guard column.

6.3.4.2 Pump. Capable of maintaining a steady flow as required by the system.

6.3.4.3 Flow Gauges. Capable of measuring the specified system flow rate.

6.3.4.4 Conductivity Detector.

6.3.4.5 Recorder. Compatible with the output voltage range of the detector.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 7, section 7.1.

7.2 Sample Recovery. Same as Method 7, section 7.1.1.

7.3 Analysis. The following reagents and standards are required for analysis:

7.3.1 Water. Same as Method 7, section 7.1.1.

7.3.2 Stock Standard Solution, 1 mg NO_2/ml. Dry an adequate amount of sodium nitrate ($NaNO_3$) at 105 to 110 °C (221 to 230 °F) for a minimum of 2 hours just before preparing the standard solution. Then dissolve exactly 1.847 g of dried $NaNO_3$ in water, and dilute to 1 liter in a volumetric flask. Mix well. This solution is stable for 1 month and should not be used beyond this time.

7.3.3 Working Standard Solution, 25 μg/ml. Dilute 5 ml of the standard solution to 200 ml with water in a volumetric flask, and mix well.

7.3.4 Eluent Solution. Weigh 1.018 g of sodium carbonate (Na_2CO_3) and 1.008 g of sodium bicarbonate ($NaHCO_3$), and dissolve in 4 liters of water. This solution is 0.0024 M Na_2CO_3/0.003 M $NaHCO_3$. Other eluents appropriate to the column type and capable of resolving nitrate ion from sulfate and other species present may be used.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling. Same as in Method 7, section 8.1.

8.2 Sample Recovery. Same as in Method 7, section 8.2, except delete the steps on adjusting and checking the pH of the sample. Do not store the samples more than 4 days between collection and analysis.

9.0 Quality Control

Section	Quality control measure	Effect
10.1	Ion chromatographn calibration	Ensure linearity of ion chromatograph response to standards.

10.0 Calibration and Standardizations

10.1 Ion Chromatograph.

10.1.1 Determination of Ion Chromatograph Calibration Factor S. Prepare a series of five standards by adding 1.0, 2.0, 4.0, 6.0, and 10.0 ml of working standard solution (25 μg/ml) to a series of five 50-ml volumetric flasks. (The standard masses will equal 25, 50, 100, 150, and 250 μg.) Dilute each flask to the mark with water, and mix well. Analyze with the samples as described in section 11.2, and subtract the blank from each value. Prepare or calculate a linear regression plot of the standard masses in μg (x-axis) versus their peak height responses in millimeters (y-axis). (Take peak height measurements with symmetrical peaks; in all other cases, calculate peak areas.) From this curve, or equation, determine the slope, and calculate its reciprocal to denote as the calibration factor, S.

10.1.2 Ion Chromatograph Calibration Quality Control. If any point on the calibration curve deviates from the line by more than 7 percent of the concentration at that point, remake and reanalyze that standard. This deviation can be determined by multiplying S times the peak height response for each standard. The resultant concentrations must not differ by more than 7 percent from each known standard mass (*i.e.*, 25, 50, 100, 150, and 250 μg).

10.2 Conductivity Detector. Calibrate according to manufacturer's specifications prior to initial use.

10.3 Barometer. Calibrate against a mercury barometer.

10.4 Temperature Gauge. Calibrate dial thermometers against mercury-in-glass thermometers. An alternative mercury-free thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

10.5 Vacuum Gauge. Calibrate mechanical gauges, if used, against a mercury manometer such as that specified in section 6.1.6 of Method 7.

10.6 Analytical Balance. Calibrate against standard weights.

11.0 Analytical Procedures

11.1 Sample Preparation.

11.1.1 Note on the analytical data sheet, the level of the liquid in the container, and whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Immediately before analysis, transfer the contents of the shipping container to a 50-ml volumetric flask, and rinse the container twice with 5 ml portions of water. Add the rinse water to the flask, and dilute to the mark with water. Mix thoroughly.

11.1.2 Pipet a 5-ml aliquot of the sample into a 50-ml volumetric flask, and dilute to the mark with water. Mix thoroughly. For each set of determinations, prepare a reagent

blank by diluting 5 ml of absorbing solution to 50 ml with water. (Alternatively, eluent solution may be used instead of water in all sample, standard, and blank dilutions.)

11.2 Analysis.

11.2.1 Prepare a standard calibration curve according to section 10.1.1. Analyze the set of standards followed by the set of samples using the same injection volume for both standards and samples. Repeat this analysis sequence followed by a final analysis of the standard set. Average the results. The two sample values must agree within 5 percent of their mean for the analysis to be valid. Perform this duplicate analysis sequence on the same day. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

11.2.2 Document each sample chromatogram by listing the following analytical parameters: injection point, injection volume, nitrate and sulfate retention times, flow rate, detector sensitivity setting, and recorder chart speed.

12.0 Data Analysis and Calculations

Carry out the calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculations.

12.1 Sample Volume. Calculate the sample volume Vsc (in ml), on a dry basis, corrected to standard conditions, using Equation 7–2 of Method 7.

12.2 Sample Concentration of NO_X as NO_2.

12.2.1 Calculate the sample concentration C (in mg/dscm) as follows:

$$C = (H)(S)(F)\left(10^4\right)/V_{sc} \qquad \text{Eq. 7A-1}$$

Where:

H = Sample peak height, mm.
S = Calibration factor, µg/mm.
F = Dilution factor (required only if sample dilution was needed to reduce the concentration into the range of calibration), dimensionless.
10^4 = 1:10 dilution times conversion factor of: $(mg/10^3\ \mu g)(10^6\ ml/m^3)$.

12.2.2 If desired, the concentration of NO_2 may be calculated as ppm NO_2 at standard conditions as follows:

$$\text{ppm } NO_2 = 0.5228C \qquad \text{Eq. 7A-2}$$

Where:

0.5228 = ml/mg NO_2.

13.0 Method Performance

13.1 Range. The analytical range of the method is from 125 to 1250 mg NO_X/m^3 as NO_2 (65 to 655 ppmv), and higher concentrations may be analyzed by diluting the sample. The lower detection limit is approximately 19 mg/m^3 (10 ppmv), but may vary among instruments.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Mulik, J.D., and E. Sawicki. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor, Ann Arbor Science Publishers, Inc. Vol. 2, 1979.

2. Sawicki, E., J.D. Mulik, and E. Wittgenstein. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor, Ann Arbor Science Publishers, Inc. Vol. 1. 1978.

3. Siemer, D.D. Separation of Chloride and Bromide from Complex Matrices Prior to Ion Chromatographic Determination. Anal. Chem. *52*(12):1874–1877. October 1980.

4. Small, H., T.S. Stevens, and W.C. Bauman. Novel Ion Exchange Chromatographic Method Using Conductimetric Determination. Anal. Chem. *47*(11):1801. 1975.

5. Yu, K.K., and P.R. Westlin. Evaluation of Reference Method 7 Flask Reaction Time. Source Evaluation Society Newsletter. *4*(4). November 1979. 10 pp.

6. Stack Sampling Safety Manual (Draft). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standard, Research Triangle Park, NC. September 1978.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 7B—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ULTRAVIOLET SPECTROPHOTOMETRIC METHOD)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 5, and Method 7.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		

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Analyte	CAS No.	Sensitivity
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–0	30–786 ppmv

1.2 Applicability. This method is applicable for the determination of NO_X emissions from nitric acid plants.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution; the NO_X, excluding nitrous oxide (N_2O), are measured by ultraviolet spectrophotometry.

3.0 Definition [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m^3 will cause lung damage in uninitiated. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 7, section 6.1.

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Wash Bottle. Polyethylene or glass.

6.2.2 Volumetric Flasks. 100-ml (one for each sample).

6.3 Analysis. The following items are required for analysis:

6.3.1 Volumetric Pipettes. 5-, 10-, 15-, and 20-ml to make standards and sample dilutions.

6.3.2 Volumetric Flasks. 1000- and 100-ml for preparing standards and dilution of samples.

6.3.3 Spectrophotometer. To measure ultraviolet absorbance at 210 nm.

6.3.4 Analytical Balance. To measure to within 0.1 mg.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents are to conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 7, section 7.1. It is important that the amount of hydrogen peroxide in the absorbing solution not be increased. Higher concentrations of peroxide may interfere with sample analysis.

7.2 Sample Recovery. Same as Method 7, section 7.2.

7.3 Analysis. Same as Method 7, sections 7.3.1, 7.3.3, and 7.3.4, with the addition of the following:

7.3.1 Working Standard KNO_3 Solution. Dilute 10 ml of the standard solution to 1000 ml with water. One milliliter of the working standard is equivalent to 10 μg NO_2.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sample Collection. Same as Method 7, section 8.1.

8.2 Sample Recovery.

8.2.1 Let the flask sit for a minimum of 16 hours, and then shake the contents for 2 minutes.

8.2.2 Connect the flask to a mercury filled U-tube manometer. Open the valve from the flask to the manometer, and record the flask temperature (T_f), the barometric pressure, and the difference between the mercury levels in the manometer. The absolute internal pressure in the flask (P_f) is the barometric pressure less the manometer reading.

8.2.3 Transfer the contents of the flask to a leak-free wash bottle. Rinse the flask three times with 10-ml portions of water, and add

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to the bottle. Mark the height of the liquid level so that the container can be checked for leakage after transport. Label the container to identify clearly its contents. Seal the container for shipping.

9.0 Quality Control

Section	Quality control measure	Effect
10.1	Spectrophotometer calibration	Ensures linearity of spectrophotometer response to standards.

10.0 Calibration and Standardizations

Same as Method 7, sections 10.2 through 10.5, with the addition of the following:

10.1 Determination of Spectrophotometer Standard Curve. Add 0 ml, 5 ml, 10 ml, 15 ml, and 20 ml of the KNO_3 working standard solution (1 ml = 10 µg NO_2) to a series of five 100-ml volumetric flasks. To each flask, add 5 ml of absorbing solution. Dilute to the mark with water. The resulting solutions contain 0.0, 50, 100, 150, and 200 µg NO_2, respectively. Measure the absorbance by ultraviolet spectrophotometry at 210 nm, using the blank as a zero reference. Prepare a standard curve plotting absorbance vs. µg NO_2.

NOTE: If other than a 20-ml aliquot of sample is used for analysis, then the amount of absorbing solution in the blank and standards must be adjusted such that the same amount of absorbing solution is in the blank and standards as is in the aliquot of sample used.

10.1.1 Calculate the spectrophotometer calibration factor as follows:

$$K_c = \frac{\sum_{i=1}^{n} M_i A_i}{\sum_{i=1}^{n} A_i^2} \qquad \text{Eq. 7B-1}$$

Where:

Mi = Mass of NO_2 in standard i, µg.
Ai = Absorbance of NO_2 standard i.
n = Total number of calibration standards.

10.1.2 For the set of calibration standards specified here, Equation 7B–1 simplifies to the following:

$$K_c = 50\frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2} \qquad \text{Eq. 7B-2}$$

10.2 Spectrophotometer Calibration Quality Control. Multiply the absorbance value obtained for each standard by the K_c factor (reciprocal of the least squares slope) to determine the distance each calibration point lies from the theoretical calibration line. The difference between the calculated concentration values and the actual concentrations (*i.e.*, 50, 100, 150, and 200 µg NO_2) should be less than 7 percent for all standards.

11.0 Analytical Procedures

11.1 Sample Loss Check. Note the level of the liquid in the container, and confirm whether any sample was lost during shipment. Note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Preparation. Immediately prior to analysis, transfer the contents of the shipping container to a 100-ml volumetric flask, and rinse the container twice with 5-ml portions of water. Add the rinse water to the flask, and dilute to mark with water.

11.3 Sample Analysis. Mix the contents of the flask thoroughly and pipette a 20 ml-aliquot of sample into a 100-ml volumetric flask. Dilute to the mark with water. Using the blank as zero reference, read the absorbance of the sample at 210 nm.

11.4 Audit Sample Analysis. Same as Method 7, section 11.4, except that a set of audit samples must be analyzed with each set of compliance samples or once per analysis day, or once per week when averaging continuous samples.

12.0 Data Analysis and Calculations

Same as Method 7, section 12.0, except replace section 12.3 with the following:

12.1 Total µg NO_2 Per Sample.

$$m = 5\,K_c\,A\,F \qquad \text{Eq. 7B-3}$$

Where:

5 = 100/20, the aliquot factor.

NOTE: If other than a 20-ml aliquot is used for analysis, the factor 5 must be replaced by a corresponding factor.

13.0 Method Performance

13.1 Range. The analytical range of the method as outlined has been determined to be 57 to 1500 milligrams NO_X (as NO_2) per dry standard cubic meter, or 30 to 786 parts per million by volume (ppmv) NO_X.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. National Institute for Occupational Safety and Health. Recommendations for Occupational Exposure to Nitric Acid. In: Occupational Safety and Health Reporter. Washington, D.C. Bureau of National Affairs, Inc. 1976. p. 149.

2. Rennie, P.J., A.M. Sumner, and F.B. Basketter. Determination of Nitrate in Raw, Potable, and Waste Waters by Ultraviolet Spectrophotometry. Analyst. *104*:837. September 1979.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 7C—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ALKALINE PERMANGANATE/COLORIMETRIC METHOD)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 3, Method 6 and Method 7.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS no.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–07	ppmv

1.2 Applicability. This method applies to the measurement of NO_X emissions from fossil-fuel fired steam generators, electric utility plants, nitric acid plants, or other sources as specified in the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

An integrated gas sample is extracted from the stack and passed through impingers containing an alkaline potassium permanganate solution; NO_X (NO + NO_2) emissions are oxidized to NO_2 and NO_3. Then NO_3^- is reduced to NO_2^- with cadmium, and the NO_2^- is analyzed colorimetrically.

3.0 Definitions [Reserved]

4.0 Interferences

Possible interferents are sulfur dioxides (SO_2) and ammonia (NH_3).

4.1 High concentrations of SO_2 could interfere because SO_2 consumes MnO_4 (as does NO_X) and, therefore, could reduce the NO_X collection efficiency. However, when sampling emissions from a coal-fired electric utility plant burning 2.1 percent sulfur coal with no control of SO_2 emissions, collection efficiency was not reduced. In fact, calculations show that sampling 3000 ppm SO_2 will reduce the MnO_4 concentration by only 5 percent if all the SO_2 is consumed in the first impinger.

4.2 Ammonia (NH_3) is slowly oxidized to NO_3^- by the absorbing solution. At 100 ppm NH_3 in the gas stream, an interference of 6 ppm NO_X (11 mg NO_2/m^3) was observed when the sample was analyzed 10 days after collection. Therefore, the method may not be applicable to plants using NH_3 injection to control NO_X emissions unless means are taken to correct the results. An equation has been developed to allow quantification of the interference and is discussed in Reference 5 of section 16.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrochloric Acid (HCl). Highly toxic and corrosive. Causes severe damage to skin. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to vapor concentrations of 0.13 to 0.2 percent can be lethal in minutes. Will react with metals, producing hydrogen.

5.2.2 Oxalic Acid $(COOH)_2$. Poisonous. Irritating to eyes, skin, nose, and throat.

5.2.3 Sodium Hydroxide (NaOH). Causes severe damage to eye tissues and to skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with small amounts of water.

5.2.4 Potassium Permanganate ($KMnO_4$). Caustic, strong oxidizer. Avoid bodily contact with.

6.0 Equipment and Supplies

6.1 Sample Collection and Sample Recovery. A schematic of the Method 7C sampling train is shown in Figure 7C–1, and component parts are discussed below. Alternative apparatus and procedures are allowed provided acceptable accuracy and precision can be demonstrated to the satisfaction of the Administrator.

6.1.1 Probe. Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or heated out-of-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Stainless steel or Teflon tubing may also be used for the probe.

6.1.2 Impingers. Three restricted-orifice glass impingers, having the specifications given in Figure 7C–2, are required for each sampling train. The impingers must be connected in series with leak-free glass connectors. Stopcock grease may be used, if necessary, to prevent leakage. (The impingers can be fabricated by a glass blower if not available commercially.)

6.1.3 Glass Wool, Stopcock Grease, Drying Tube, Valve, Pump, Barometer, and Vacuum Gauge and Rotameter. Same as in Method 6, sections 6.1.1.3, 6.1.1.4, 6.1.1.6, 6.1.1.7, 6.1.1.8, 6.1.2, and 6.1.3, respectively.

6.1.4 Rate Meter. Rotameter, or equivalent, accurate to within 2 percent at the selected flow rate of between 400 and 500 ml/min (0.014 to 0.018 cfm). For rotameters, a range of 0 to 1 liter/min (0 to 0.035 cfm) is recommended.

6.1.5 Volume Meter. Dry gas meter (DGM) capable of measuring the sample volume under the sampling conditions of 400 to 500 ml/min (0.014 to 0.018 cfm) for 60 minutes within an accuracy of 2 percent.

6.1.6 Filter. To remove NO_X from ambient air, prepared by adding 20 g of 5-angstrom molecular sieve to a cylindrical tube (*e.g.*, a polyethylene drying tube).

6.1.7 Polyethylene Bottles. 1-liter, for sample recovery.

6.1.8 Funnel and Stirring Rods. For sample recovery.

6.2 Sample Preparation and Analysis.

6.2.1 Hot Plate. Stirring type with 50- by 10-mm Teflon-coated stirring bars.

6.2.2 Beakers. 400-, 600-, and 1000-ml capacities.

6.2.3 Filtering Flask. 500-ml capacity with side arm.

6.2.4 Buchner Funnel. 75-mm ID, with spout equipped with a 13-mm ID by 90-mm long piece of Teflon tubing to minimize possibility of aspirating sample solution during filtration.

6.2.5 Filter Paper. Whatman GF/C, 7.0-cm diameter.

6.2.6 Stirring Rods.

6.2.7 Volumetric Flasks. 100-, 200- or 250-, 500-, and 1000-ml capacity.

6.2.8 Watch Glasses. To cover 600- and 1000-ml beakers.

6.2.9 Graduated Cylinders. 50- and 250-ml capacities.

6.2.10 Pipettes. Class A.

6.2.11 pH Meter. To measure pH from 0.5 to 12.0.

6.2.12 Burette. 50-ml with a micrometer type stopcock. (The stopcock is Catalog No. 8225–t–05, Ace Glass, Inc., Post Office Box 996, Louisville, Kentucky 50201.) Place a glass wool plug in bottom of burette. Cut off burette at a height of 43 cm (17 in.) from the top of plug, and have a blower attach a glass funnel to top of burette such that the diameter of the burette remains essentially unchanged. Other means of attaching the funnel are acceptable.

6.2.13 Glass Funnel. 75-mm ID at the top.

6.2.14 Spectrophotometer. Capable of measuring absorbance at 540 nm; 1-cm cells are adequate.

6.2.15 Metal Thermometers. Bimetallic thermometers, range 0 to 150 °C (32 to 300 °F).

6.2.16 Culture Tubes. 20-by 150-mm, Kimax No. 45048.

6.2.17 Parafilm ''M.'' Obtained from American Can Company, Greenwich, Connecticut 06830.

6.2.18 CO_2 Measurement Equipment. Same as in Method 3, section 6.0.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection.

7.1.1 Water. Deionized distilled to conform to ASTM Specification D 1193–77 or 91 Type 3 (incorporated by reference—see § 60.17).

7.1.2 Potassium Permanganate, 4.0 Percent (w/w), Sodium Hydroxide, 2.0 Percent (w/w) solution ($KMnO_4$/NaOH solution). Dissolve 40.0 g of $KMnO_4$ and 20.0 g of NaOH in 940 ml of water.

7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in section 7.1.1.

7.2.2 Oxalic Acid Solution. Dissolve 48 g of oxalic acid [$(COOH)_2 \cdot 2H_2O$] in water, and dilute to 500 ml. Do not heat the solution.

7.2.3 Sodium Hydroxide, 0.5 N. Dissolve 20 g of NaOH in water, and dilute to 1 liter.

7.2.4 Sodium Hydroxide, 10 N. Dissolve 40 g of NaOH in water, and dilute to 100 ml.

7.2.5 Ethylenediamine Tetraacetic Acid (EDTA) Solution, 6.5 percent (w/v). Dissolve 6.5 g of EDTA (disodium salt) in water, and dilute to 100 ml. Dissolution is best accomplished by using a magnetic stirrer.

7.2.6 Column Rinse Solution. Add 20 ml of 6.5 percent EDTA solution to 960 ml of water, and adjust the pH to between 11.7 and 12.0 with 0.5 N NaOH.

7.2.7 Hydrochloric Acid (HCl), 2 N. Add 86 ml of concentrated HCl to a 500 ml-volumetric flask containing water, dilute to volume, and mix well. Store in a glass-stoppered bottle.

7.2.8 Sulfanilamide Solution. Add 20 g of sulfanilamide (melting point 165 to 167 °C (329 to 333 °F)) to 700 ml of water. Add, with mixing, 50 ml concentrated phosphoric acid (85 percent), and dilute to 1000 ml. This solution is stable for at least 1 month, if refrigerated.

7.2.9 N-(1-Naphthyl)-Ethylenediamine Dihydrochloride (NEDA) Solution. Dissolve 0.5 g of NEDA in 500 ml of water. An aqueous solution should have one absorption peak at 320 nm over the range of 260 to 400 nm. NEDA that shows more than one absorption peak over this range is impure and should not be used. This solution is stable for at least 1 month if protected from light and refrigerated.

7.2.10 Cadmium. Obtained from Matheson Coleman and Bell, 2909 Highland Avenue, Norwood, Ohio 45212, as EM Laboratories Catalog No. 2001. Prepare by rinsing in 2 N HCl for 5 minutes until the color is silver-grey. Then rinse the cadmium with water until the rinsings are neutral when tested with pH paper. CAUTION: H_2 is liberated during preparation. Prepare in an exhaust hood away from any flame or combustion source.

7.2.11 Sodium Sulfite ($NaNO_2$) Standard Solution, Nominal Concentration, 1000 μg NO_2^-/ml. Desiccate NaNO2 overnight. Accurately weigh 1.4 to 1.6 g of $NaNO_2$ (assay of 97 percent $NaNO_2$ or greater), dissolve in water, and dilute to 1 liter. Calculate the exact NO_2^- concentration using Equation 7C–1 in section 12.2. This solution is stable for at least 6 months under laboratory conditions.

7.2.12 Potassium Nitrate (KNO_3) Standard Solution. Dry KNO_3 at 110 °C (230 °F) for 2 hours, and cool in a desiccator. Accurately weigh 9 to 10 g of KNO_3 to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact NO_3^- concentration using Equation 7C–2 in section 12.3. This solution is stable for 2 months without preservative under laboratory conditions.

7.2.13 Spiking Solution. Pipette 7 ml of the KNO_3 standard into a 100-ml volumetric flask, and dilute to volume.

7.2.14 Blank Solution. Dissolve 2.4 g of $KMnO_4$ and 1.2 g of NaOH in 96 ml of water. Alternatively, dilute 60 ml of $KMnO_4$/NaOH solution to 100 ml.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Preparation of Sampling Train. Add 200 ml of $KMnO_4$/NaOH solution (Section 7.1.2) to each of three impingers, and assemble the train as shown in Figure 7C–1. Adjust the probe heater to a temperature sufficient to prevent water condensation.

8.2 Leak-Checks. Same as in Method 6, section 8.2.

8.3 Sample Collection.

8.3.1 Record the initial DGM reading and barometric pressure. Determine the sampling point or points according to the appropriate regulations (*e.g.*, §60.46(b)(5) of 40 CFR Part 60). Position the tip of the probe at the sampling point, connect the probe to the first impinger, and start the pump. Adjust the sample flow to a value between 400 and 500 ml/min (0.014 and 0.018 cfm). CAUTION: DO NOT EXCEED THESE FLOW RATES. Once adjusted, maintain a constant flow rate during the entire sampling run. Sample for 60 minutes. For relative accuracy (RA) testing of continuous emission monitors, the minimum sampling time is 1 hour, sampling 20 minutes at each traverse point.

NOTE: When the SO_2 concentration is greater than 1200 ppm, the sampling time may have to be reduced to 30 minutes to eliminate plugging of the impinger orifice with MnO_2. For RA tests with SO_2 greater than 1200 ppm, sample for 30 minutes (10 minutes at each point).

8.3.2 Record the DGM temperature, and check the flow rate at least every 5 minutes. At the conclusion of each run, turn off the pump, remove the probe from the stack, and record the final readings. Divide the sample volume by the sampling time to determine the average flow rate. Conduct the mandatory post-test leak-check. If a leak is found, void the test run, or use procedures acceptable to the Administrator to adjust the sample volume for the leakage.

8.4 CO_2 Measurement. During sampling, measure the CO_2 content of the stack gas near the sampling point using Method 3. The single-point grab sampling procedure is adequate, provided the measurements are made at least three times (near the start, midway, and before the end of a run), and the average CO_2 concentration is computed. The Orsat or Fyrite analyzer may be used for this analysis.

8.5 Sample Recovery. Disconnect the impingers. Pour the contents of the impingers into a 1-liter polyethylene bottle

using a funnel and a stirring rod (or other means) to prevent spillage. Complete the quantitative transfer by rinsing the impingers and connecting tubes with water until the rinsings are clear to light pink, and add the rinsings to the bottle. Mix the sample, and mark the solution level. Seal and identify the sample container.

9.0 Quality Control

Section	Quality control measure	Effect
8.2, 10.1–10.3	Sampling equipment leak-check and calibration.	Ensure accurate measurement of sample volume.
10.4	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards
11.3	Spiked sample analysis.	Ensure reduction efficiency of column.

10.0 Calibration and Standardizations

10.1 Volume Metering System. Same as Method 6, section 10.1. For detailed instructions on carrying out these calibrations, it is suggested that section 3.5.2 of Reference 4 of section 16.0 be consulted.

10.2 Temperature Sensors and Barometer. Same as in Method 6, sections 10.2 and 10.4, respectively.

10.3 Check of Rate Meter Calibration Accuracy (Optional). Disconnect the probe from the first impinger, and connect the filter. Start the pump, and adjust the rate meter to read between 400 and 500 ml/min (0.014 and 0.018 cfm). After the flow rate has stabilized, start measuring the volume sampled, as recorded by the dry gas meter and the sampling time. Collect enough volume to measure accurately the flow rate. Then calculate the flow rate. This average flow rate must be less than 500 ml/min (0.018 cfm) for the sample to be valid; therefore, it is recommended that the flow rate be checked as above prior to each test.

10.4 Spectrophotometer.

10.4.1 Dilute 5.0 ml of the $NaNO_2$ standard solution to 200 ml with water. This solution nominally contains 25 μg NO_2^-/ml. Use this solution to prepare calibration standards to cover the range of 0.25 to 3.00 μg NO_2^-/ml. Prepare a minimum of three standards each for the linear and slightly nonlinear (described below) range of the curve. Use pipettes for all additions.

10.4.2 Measure the absorbance of the standards and a water blank as instructed in section 11.5. Plot the net absorbance vs. μg NO_2^-/ml. Draw a smooth curve through the points. The curve should be linear up to an absorbance of approximately 1.2 with a slope of approximately 0.53 absorbance units/μg NO_2^-/ml. The curve should pass through the origin. The curve is slightly nonlinear from an absorbance of 1.2 to 1.6.

11.0 Analytical Procedures

11.1 Sample Stability. Collected samples are stable for at least four weeks; thus, analysis must occur within 4 weeks of collection.

11.2 Sample Preparation.

11.2.1 Prepare a cadmium reduction column as follows: Fill the burette with water. Add freshly prepared cadmium slowly, with tapping, until no further settling occurs. The height of the cadmium column should be 39 cm (15 in). When not in use, store the column under rinse solution.

NOTE: The column should not contain any bands of cadmium fines. This may occur if regenerated cadmium is used and will greatly reduce the column lifetime.

11.2.2 Note the level of liquid in the sample container, and determine whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume lost can be determined from the difference between initial and final solution levels, and this value can then be used to correct the analytical result. Quantitatively transfer the contents to a 1-liter volumetric flask, and dilute to volume.

11.2.3 Take a 100-ml aliquot of the sample and blank (unexposed $KMnO_4$/NaOH) solutions, and transfer to 400-ml beakers containing magnetic stirring bars. Using a pH meter, add concentrated H_2SO_4 with stirring until a pH of 0.7 is obtained. Allow the solutions to stand for 15 minutes. Cover the beakers with watch glasses, and bring the temperature of the solutions to 50 °C (122 °F). Keep the temperature below 60 °C (140 °F). Dissolve 4.8 g of oxalic acid in a minimum volume of water, approximately 50 ml, at room temperature. Do not heat the solution. Add this solution slowly, in increments, until the $KMnO_4$ solution becomes colorless. If the color is not completely removed, prepare some more of the above oxalic acid solution, and add until a colorless solution is obtained. Add an excess of oxalic acid by dissolving 1.6 g of oxalic acid in 50 ml of water, and add 6 ml of this solution to the colorless solution. If suspended matter is present, add concentrated H_2SO_4 until a clear solution is obtained.

11.2.4 Allow the samples to cool to near room temperature, being sure that the samples are still clear. Adjust the pH to between 11.7 and 12.0 with 10 N NaOH. Quantitatively transfer the mixture to a Buchner funnel containing GF/C filter paper, and filter the

precipitate. Filter the mixture into a 500-ml filtering flask. Wash the solid material four times with water. When filtration is complete, wash the Teflon tubing, quantitatively transfer the filtrate to a 500-ml volumetric flask, and dilute to volume. The samples are now ready for cadmium reduction. Pipette a 50-ml aliquot of the sample into a 150-ml beaker, and add a magnetic stirring bar. Pipette in 1.0 ml of 6.5 percent EDTA solution, and mix.

11.3 Determine the correct stopcock setting to establish a flow rate of 7 to 9 ml/min of column rinse solution through the cadmium reduction column. Use a 50-ml graduated cylinder to collect and measure the solution volume. After the last of the rinse solution has passed from the funnel into the burette, but before air entrapment can occur, start adding the sample, and collect it in a 250-ml graduated cylinder. Complete the quantitative transfer of the sample to the column as the sample passes through the column. After the last of the sample has passed from the funnel into the burette, start adding 60 ml of column rinse solution, and collect the rinse solution until the solution just disappears from the funnel. Quantitatively transfer the sample to a 200-ml volumetric flask (a 250-ml flask may be required), and dilute to volume. The samples are now ready for NO_2-analysis.

NOTE: Two spiked samples should be run with every group of samples passed through the column. To do this, prepare two additional 50-ml aliquots of the sample suspected to have the highest NO_2-concentration, and add 1 ml of the spiking solution to these aliquots. If the spike recovery or column efficiency (see section 12.2) is below 95 percent, prepare a new column, and repeat the cadmium reduction.

11.5 Sample Analysis. Pipette 10 ml of sample into a culture tube. Pipette in 10 ml of sulfanilamide solution and 1.4 ml of NEDA solution. Cover the culture tube with parafilm, and mix the solution. Prepare a blank in the same manner using the sample from treatment of the unexposed $KMnO_4$/NaOH solution. Also, prepare a calibration standard to check the slope of the calibration curve. After a 10-minute color development interval, measure the absorbance at 540 nm against water. Read μg NO_2^-/ml from the calibration curve. If the absorbance is greater than that of the highest calibration standard, use less than 10 ml of sample, and repeat the analysis. Determine the NO_2^-concentration using the calibration curve obtained in section 10.4.

NOTE: Some test tubes give a high blank NO_2^- value but culture tubes do not.

11.6 Audit Sample Analysis. Same as in Method 7, section 11.4.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature.

B = Analysis of blank, μg NO_2^-/ml.
C = Concentration of NO_X as NO_2, dry basis, mg/dsm³.
E = Column efficiency, dimensionless
$K_2 = 10^{-3}$ mg/μg.
m = Mass of NO_X, as NO_2, in sample, μg.
P_{bar} = Barometric pressure, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
s = Concentration of spiking solution, μg NO_3/ml.
S = Analysis of sample, μg NO_2^-/ml.
T_m = Average dry gas meter absolute temperature, °K.
T_{std} = Standard absolute temperature, 293 °K (528 °R).
$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).
V_m = Dry gas volume as measured by the dry gas meter, scm (scf).
x = Analysis of spiked sample, μg NO_2^-/ml.
X = Correction factor for CO_2 collection = $100/(100 - \%CO_2(V/V))$.
y = Analysis of unspiked sample, μg NO_2^-/ml.
Y = Dry gas meter calibration factor.
1.0 ppm NO = 1.247 mg NO/m³ at STP.
1.0 ppm NO_2 = 1.912 mg NO_2/m³ at STP.
1 ft³ = 2.832×10^{-2} m³.

12.2 NO_2 Concentration. Calculate the NO_2 concentration of the solution (see section 7.2.11) using the following equation:

$$\frac{\mu g\ NO_2^-}{ml} = g\ NaNO_2 \times \frac{purity,\ \%}{100} \times 10^3 \times \frac{46.01}{69.01} \qquad \text{Eq. 7C-1}$$

12.3 NO_3 Concentration. Calculate the NO_3 concentration of the KNO_3 solution (see section 7.2.12) using the following equation:

$$\frac{\mu g\ NO_3^-}{ml} = g\ KNO_3 \times \left(10^3\right) \times \frac{62.01}{101.10} \qquad \text{Eq. 7C-2}$$

12.4 Sample Volume, Dry Basis, Corrected to Standard Conditions.

$$V_{m(std)} = V_m\ X\ Y \frac{T_{std}}{T_m} \frac{P_{bar}}{P_{std}} \qquad \text{Eq. 7C-3}$$

$$= K_1\ X\ Y\ V_m \frac{P_{bar}}{T_m}$$

Where:

K_1 = 0.3855 °K/mm Hg for metric units.
K_1 = 17.65 °R/in. Hg for English units.

12.5 Efficiency of Cadmium Reduction Column. Calculate this value as follows:

$$E = \frac{200\ (x-y)}{1.0\ s\ \frac{46.01}{62.01}} = \frac{269.6\ (x-y)}{s} \qquad \text{Eq. 7C-4}$$

Where:

200 = Final volume of sample and blank after passing through the column, ml.
1.0 = Volume of spiking solution added, ml.
46.01=μg NO_2^-/μmole.
62.01=μg NO_3^-/μmole.

12.6 Total μg NO_2.

$$m = 200\left(\frac{500}{50}\right)\left(\frac{1000}{100}\right)\left(\frac{(S-B)}{E}\right) = \frac{(2\times10^4)(S-B)}{E} \qquad \text{Eq. 7C-5}$$

Where:

500 = Total volume of prepared sample, ml.
50 = Aliquot of prepared sample processed through cadmium column, ml.
100 = Aliquot of $KMnO_4$/NaOH solution, ml.
1000 = Total volume of $KMnO_4$/NaOH solution, ml.

12.7 Sample Concentration.

$$C = K_2 \frac{m}{V_{m(std)}} \qquad \text{Eq. 7C-6}$$

13.0 Method Performance

13.1 Precision. The intra-laboratory relative standard deviation for a single measurement is 2.8 and 2.9 percent at 201 and 268 ppm NO_X, respectively.

13.2 Bias. The method does not exhibit any bias relative to Method 7.

13.3 Range. The lower detectable limit is 13 mg NO_X/m^3, as NO_2 (7 ppm NO_X) when sampling at 500 ml/min for 1 hour. No upper limit has been established; however, when using the recommended sampling conditions, the method has been found to collect NO_X emissions quantitatively up to 1782 mg NO_X/m^3, as NO_2 (932 ppm NO_X).

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Margeson, J.H., W.J. Mitchell, J.C. Suggs, and M.R. Midgett. Integrated Sampling and Analysis Methods for Determining NO_X Emissions at Electric Utility Plants. U.S. Environmental Protection Agency, Research Triangle Park, NC. Journal of the Air Pollution Control Association. *32*:1210–1215. 1982.

2. Memorandum and attachment from J.H. Margeson, Source Branch, Quality Assurance Division, Environmental Monitoring Systems Laboratory, to The Record, EPA. March 30, 1983. NH_3 Interference in Methods 7C and 7D.

3. Margeson, J.H., J.C. Suggs, and M.R. Midgett. Reduction of Nitrate to Nitrite with Cadmium. Anal. Chem. *52*:1955–57. 1980.

4. Quality Assurance Handbook for Air Pollution Measurement Systems. Volume III—Stationary Source Specific Methods. U.S.

Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA–600/4–77–027b. August 1977.

5. Margeson, J.H., *et al.* An Integrated Method for Determining NO_X Emissions at Nitric Acid Plants. Analytical Chemistry. *47* (11):1801. 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

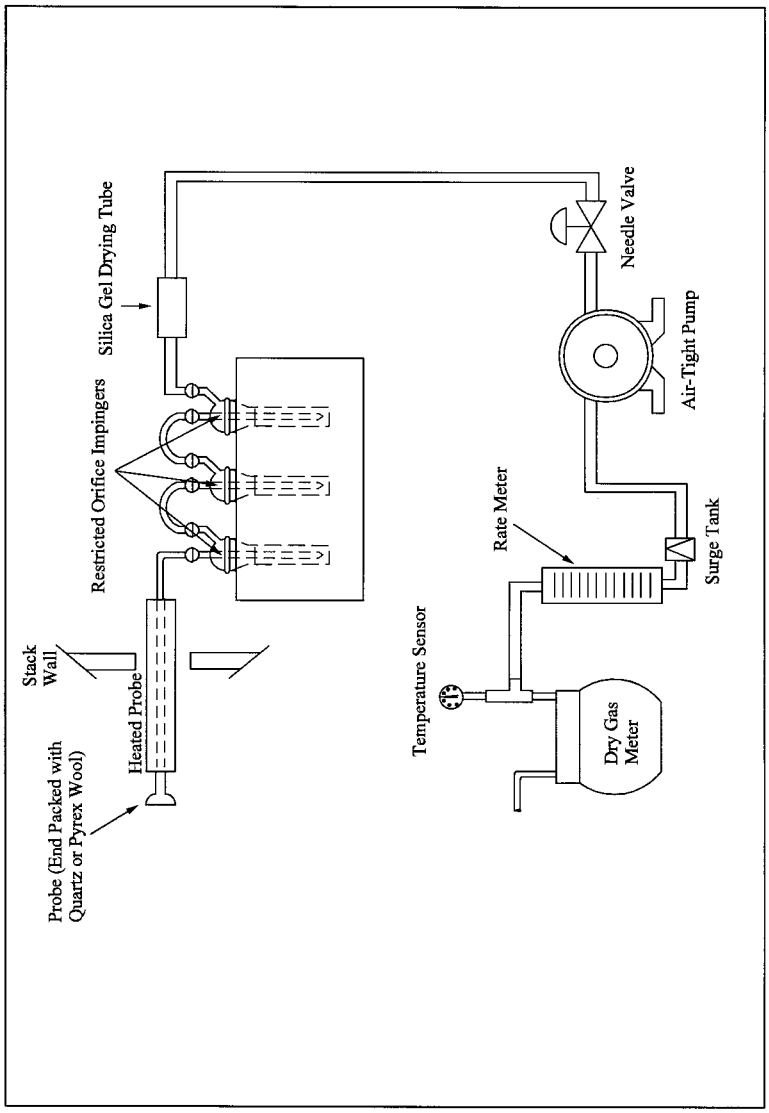

Figure 7C-1. NO_x Sampling Train.

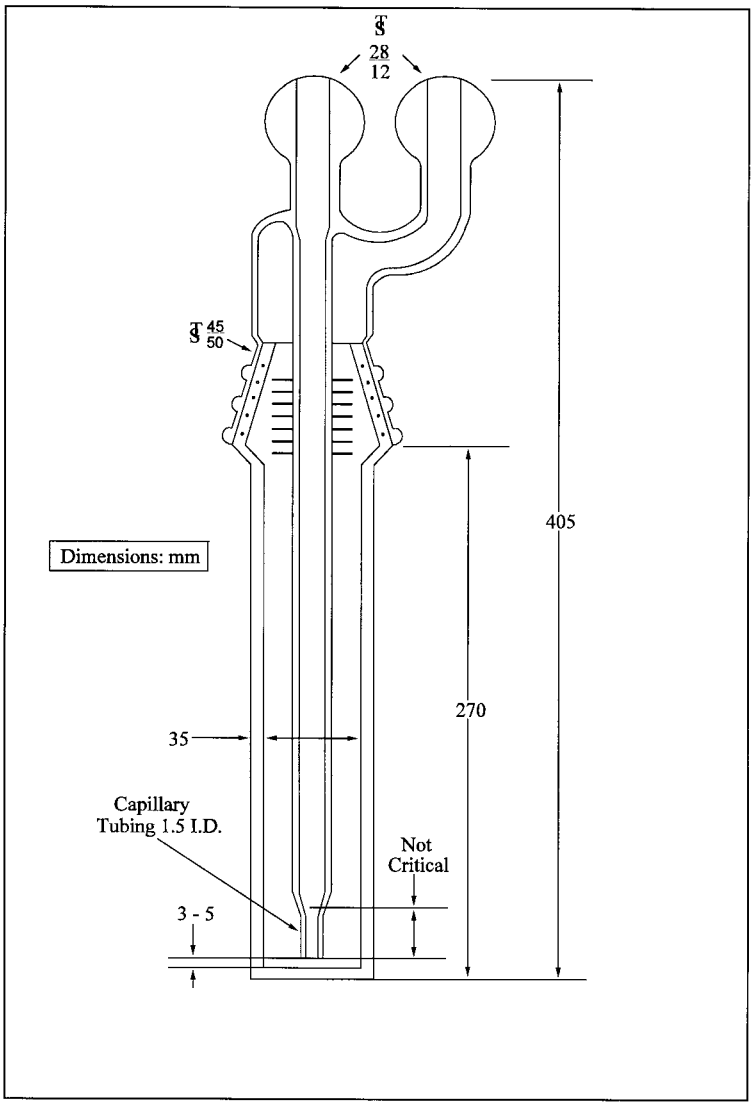

Figure 7C-2. Restricted-Orifice Impinger.

METHOD 7D—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ALKALINE-PERMANGANATE/ION CHROMATOGRAPHIC METHOD)

NOTE: This method is not inclusive with respect to specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 3, Method 6, Method 7, and Method 7C.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–0	7 ppmv

1.2 Applicability. This method applies to the measurement of NO_X emissions from fossil-fuel fired steam generators, electric utility plants, nitric acid plants, or other sources as specified in the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

An integrated gas sample is extracted from the stack and passed through impingers containing an alkaline-potassium permanganate solution; NO_X ($NO + NO_2$) emissions are oxidized to NO_3^-. Then NO_3^- is analyzed by ion chromatography.

3.0 Definitions [Reserved]

4.0 Interferences

Same as in Method 7C, section 4.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs. 30% H_2O_2 is a strong oxidizing agent; avoid contact with skin, eyes, and combustible material. Wear gloves when handling.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eye tissues and to skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Potassium Permanganate ($KMnO_4$). Caustic, strong oxidizer. Avoid bodily contact with.

6.0 Equipment and Supplies

6.1 Sample Collection and Sample Recovery. Same as Method 7C, section 6.1. A schematic of the sampling train used in performing this method is shown in Figure 7C–1 of Method 7C.

6.2 Sample Preparation and Analysis.

6.2.1 Magnetic Stirrer. With 25- by 10-mm Teflon-coated stirring bars.

6.2.2 Filtering Flask. 500-ml capacity with sidearm.

6.2.3 Buchner Funnel. 75-mm ID, with spout equipped with a 13-mm ID by 90-mm long piece of Teflon tubing to minimize possibility of aspirating sample solution during filtration.

6.2.4 Filter Paper. Whatman GF/C, 7.0-cm diameter.

6.2.5 Stirring Rods.

6.2.6 Volumetric Flask. 250-ml.

6.2.7 Pipettes. Class A.

6.2.8 Erlenmeyer Flasks. 250-ml.

6.2.9 Ion Chromatograph. Equipped with an anion separator column to separate NO_3^-, H_3^+ suppressor, and necessary auxiliary equipment. Nonsuppressed and other forms of ion chromatography may also be used provided that adequate resolution of NO_3^- is obtained. The system must also be able to resolve and detect NO_2^-.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection.

7.1.1 Water. Deionized distilled to conform to ASTM specification D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17).

7.1.2 Potassium Permanganate, 4.0 Percent (w/w), Sodium Hydroxide, 2.0 Percent (w/w). Dissolve 40.0 g of $KMnO_4$ and 20.0 g of NaOH in 940 ml of water.

7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in section 7.1.1.

7.2.2 Hydrogen Peroxide (H_2O_2), 5 Percent. Dilute 30 percent H_2O_2 1:5 (v/v) with water.

7.2.3 Blank Solution. Dissolve 2.4 g of $KMnO_4$ and 1.2 g of NaOH in 96 ml of water. Alternatively, dilute 60 ml of $KMnO_4$/NaOH solution to 100 ml.

7.2.4 KNO_3 Standard Solution. Dry KNO_3 at 110 °C for 2 hours, and cool in a desiccator. Accurately weigh 9 to 10 g of KNO_3 to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact NO_3^- concentration using Equation 7D–1 in section 12.2. This

solution is stable for 2 months without preservative under laboratory conditions.

7.2.5 Eluent, 0.003 M $NaHCO_3$/0.0024 M Na_2CO_3. Dissolve 1.008 g $NaHCO_3$ and 1.018 g Na_2CO_3 in water, and dilute to 4 liters. Other eluents capable of resolving nitrate ion from sulfate and other species present may be used.

8.0 Sample Collection, Preservation, Transport, and Storage.

8.1 Sampling. Same as in Method 7C, section 8.1.

8.2 Sample Recovery. Same as in Method 7C, section 8.2.

8.3 Sample Preparation for Analysis.

NOTE: Samples must be analyzed within 28 days of collection.

8.3.1 Note the level of liquid in the sample container, and determine whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume lost can be determined from the difference between initial and final solution levels, and this value can then be used to correct the analytical result. Quantitatively transfer the contents to a 1-liter volumetric flask, and dilute to volume.

8.3.2 Sample preparation can be started 36 hours after collection. This time is necessary to ensure that all NO_2^- is converted to NO_3^- in the collection solution. Take a 50-ml aliquot of the sample and blank, and transfer to 250-ml Erlenmeyer flasks. Add a magnetic stirring bar. Adjust the stirring rate to as fast a rate as possible without loss of solution. Add 5 percent H_2O_2 in increments of approximately 5 ml using a 5-ml pipette. When the $KMnO_4$ color appears to have been removed, allow the precipitate to settle, and examine the supernatant liquid. If the liquid is clear, the H_2O_2 addition is complete. If the $KMnO_4$ color persists, add more H_2O_2, with stirring, until the supernatant liquid is clear.

NOTE: The faster the stirring rate, the less volume of H_2O_2 that will be required to remove the $KMnO_4$.) Quantitatively transfer the mixture to a Buchner funnel containing GF/C filter paper, and filter the precipitate. The spout of the Buchner funnel should be equipped with a 13-mm ID by 90-mm long piece of Teflon tubing. This modification minimizes the possibility of aspirating sample solution during filtration. Filter the mixture into a 500-ml filtering flask. Wash the solid material four times with water. When filtration is complete, wash the Teflon tubing, quantitatively transfer the filtrate to a 250-ml volumetric flask, and dilute to volume. The sample and blank are now ready for NO_3^- analysis.

9.0 Quality Control

Section	Quality control measure	Effect
8.2, 10.1–10.3	Sampling equipment leak-check and calibration.	Ensure accurate measurement of sample volume.
10.4	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.
11.3	Spiked sample analysis	Ensure reduction efficiency of column.

10.0 Calibration and Standardizations

10.1 Dry Gas Meter (DGM) System.

10.1.1 Initial Calibration. Same as in Method 6, section 10.1.1. For detailed instructions on carrying out this calibration, it is suggested that section 3.5.2 of Citation 4 in section 16.0 of Method 7C be consulted.

10.1.2 Post-Test Calibration Check. Same as in Method 6, section 10.1.2.

10.2 Thermometers for DGM and Barometer. Same as in Method 6, sections 10.2 and 10.4, respectively.

10.3 Ion Chromatograph.

10.3.1 Dilute a given volume (1.0 ml or greater) of the KNO_3 standard solution to a convenient volume with water, and use this solution to prepare calibration standards. Prepare at least four standards to cover the range of the samples being analyzed. Use pipettes for all additions. Run standards as instructed in section 11.2. Determine peak height or area, and plot the individual values versus concentration in µg NO_3^-/ml.

10.3.2 Do not force the curve through zero. Draw a smooth curve through the points. The curve should be linear. With the linear curve, use linear regression to determine the calibration equation.

11.0 Analytical Procedures

11.1 The following chromatographic conditions are recommended: 0.003 M $NaHCO_3$/0.0024 Na_2CO_3 eluent solution (Section 7.2.5), full scale range, 3 µMHO; sample loop, 0.5 ml; flow rate, 2.5 ml/min. These conditions should give a NO_3^- retention time of approximately 15 minutes (Figure 7D–1).

11.2 Establish a stable baseline. Inject a sample of water, and determine whether any NO_3^- appears in the chromatogram. If NO_3^- is present, repeat the water load/injection procedure approximately five times; then reinject a water sample and observe the chromatogram. When no NO_3^- is present, the instrument is ready for use. Inject calibration standards. Then inject samples and a blank. Repeat the injection of the calibration

standards (to compensate for any drift in response of the instrument). Measure the NO_3^- peak height or peak area, and determine the sample concentration from the calibration curve.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature. Same as in Method 7C, section 12.1.

12.2 NO_3^- concentration. Calculate the NO_3^- concentration in the KNO_3 standard solution (see section 7.2.4) using the following equation:

$$\frac{\mu g\ NO_3^-}{ml} = g\ of\ KNO_3 \times 10^3 \times \frac{62.01}{101.10} \qquad \text{Eq. 7D-1}$$

12.3 Sample Volume, Dry Basis, Corrected to Standard Conditions. Same as in Method 7C, section 12.4.

12.4 Total μg NO_2 Per Sample.

$$m = 250\left(\frac{1000}{50}\right)\left(\frac{46.01}{62.01}\right)(S-B) \qquad \text{Eq. 7D-2}$$
$$= 3710\ (S-B)$$

Where:

250 = Volume of prepared sample, ml.

1000 = Total volume of $KMnO_4$ solution, ml.

50 = Aliquot of $KMnO_4$/NaOH solution, ml.

46.01 = Molecular weight of NO_3^-.

62.01 = Molecular weight of NO_3^-.

12.5 Sample Concentration. Same as in Method 7C, section 12.7.

13.0 Method Performance

13.1 Precision. The intra-laboratory relative standard deviation for a single measurement is approximately 6 percent at 200 to 270 ppm NO_X.

13.2 Bias. The method does not exhibit any bias relative to Method 7.

13.3 Range. The lower detectable limit is similar to that of Method 7C. No upper limit has been established; however, when using the recommended sampling conditions, the method has been found to collect NO_X emissions quantitatively up to 1782 mg NO_X/m^3, as NO_2 (932 ppm NO_X).

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 7C, section 16.0, References 1, 2, 4, and 5.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

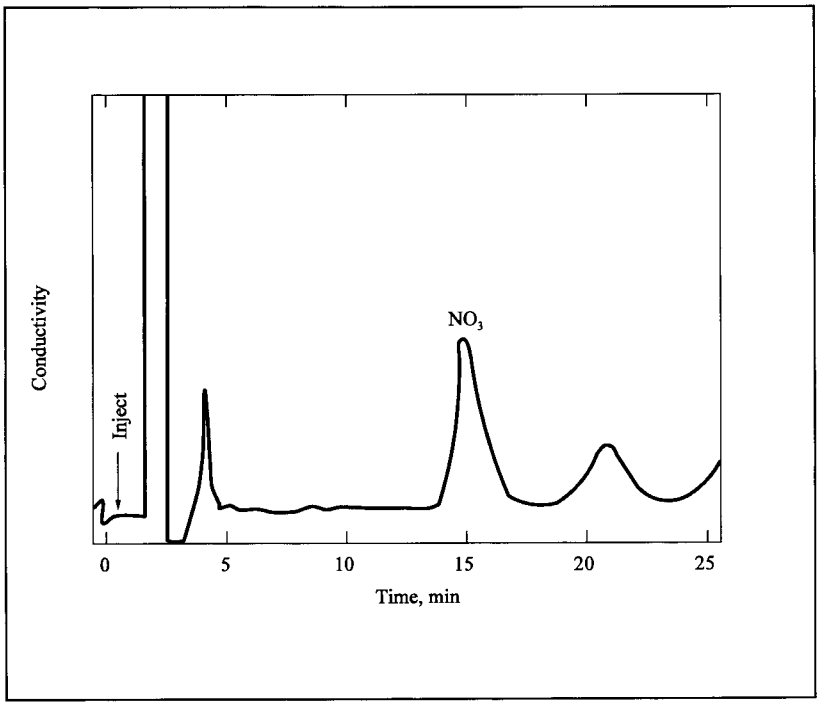

Figure 7D-1. Ion Chromatograph of a Prepared Sample.

METHOD 7E—DETERMINATION OF NITROGEN OXIDES EMISSIONS FROM STATIONARY SOURCES (INSTRUMENTAL ANALYZER PROCEDURE)

1.0 Scope and Application

What is Method 7E?

Method 7E is a procedure for measuring nitrogen oxides (NO_X) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis. This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 4—Determination of Moisture Content in Stack Gases.

1.1 Analytes. What does this method determine? This method measures the concentration of nitrogen oxides as NO_2.

Analyte	CAS No.	Sensitivity
Nitric oxide (NO)	10102–43–9	Typically <2% of
Nitrogen dioxide (NO_2)	10102–44–0	Calibration Span.

1.2 Applicability. When is this method required? The use of Method 7E may be required by specific New Source Performance Standards, Clean Air Marketing rules, State Implementation Plans, and permits where measurement of NO_X concentrations in stationary source emissions is required, either to determine compliance with an applicable

emissions standard or to conduct performance testing of a continuous monitoring system (CEMS). Other regulations may also require the use of Method 7E.

1.3 Data Quality Objectives (DQO). How good must my collected data be? Method 7E is designed to provide high-quality data for determining compliance with Federal and State emission standards and for relative accuracy testing of CEMS. In these and other applications, the principal objective is to ensure the accuracy of the data at the actual emission levels encountered. To meet this objective, the use of EPA traceability protocol calibration gases and measurement system performance tests are required.

1.4 Data Quality Assessment for Low Emitters. Is performance relief granted when testing low-emission units? Yes. For low-emitting sources, there are alternative performance specifications for analyzer calibration error, system bias, drift, and response time. Also, the alternative dynamic spiking procedure in section 16 may provide performance relief for certain low-emitting units.

2.0 Summary of Method

In this method, a sample of the effluent gas is continuously sampled and conveyed to the analyzer for measuring the concentration of NO_X. You may measure NO and NO_2 separately or simultaneously together but, for the purposes of this method, NO_X is the sum of NO and NO_2. You must meet the performance requirements of this method to validate your data.

3.0 Definitions

3.1 Analyzer Calibration Error, for non-dilution systems, means the difference between the manufacturer certified concentration of a calibration gas and the measured concentration of the same gas when it is introduced into the analyzer in direct calibration mode.

3.2 Calibration Curve means the relationship between an analyzer's response to the injection of a series of calibration gases and the actual concentrations of those gases.

3.3 Calibration Gas means the gas mixture containing NO_X at a known concentration and produced and certified in accordance with ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards,'' September 1997, as amended August 25, 1999, EPA–600/R–97/121 or more recent updates. The tests for analyzer calibration error, drift, and system bias require the use of calibration gas prepared according to this protocol. If a zero gas is used for the low-level gas, it must meet the requirements under the definition for ''zero air material'' in 40 CFR 72.2 in place of being prepared by the traceability protocol.

3.3.1 Low-Level Gas means a calibration gas with a concentration that is less than 20 percent of the calibration span and may be a zero gas.

3.3.2 Mid-Level Gas means a calibration gas with a concentration that is 40 to 60 percent of the calibration span.

3.3.3 High-Level Gas means a calibration gas with a concentration that is equal to the calibration span.

3.4 Calibration Span means the upper limit of the analyzer's calibration that is set by the choice of high-level calibration gas. No valid run average concentration may exceed the calibration span. To the extent practicable, the measured emissions should be between 20 to 100 percent of the selected calibration span. This may not be practicable in some cases of low-concentration measurements or testing for compliance with an emission limit when emissions are substantially less than the limit. In such cases, calibration spans that are practicable to achieving the data quality objectives without being excessively high should be chosen.

3.5 Centroidal Area means the central area of the stack or duct that is no greater than 1 percent of the stack or duct cross section. This area has the same geometric shape as the stack or duct.

3.6 Converter Efficiency Gas means a calibration gas with a known NO or NO_2 concentration and of Traceability Protocol quality.

3.7 Data Recorder means the equipment that permanently records the concentrations reported by the analyzer.

3.8 Direct Calibration Mode means introducing the calibration gases directly into the analyzer (or into the assembled measurement system at a point downstream of all sample conditioning equipment) according to manufacturer's recommended calibration procedure. This mode of calibration applies to non-dilution-type measurement systems.

3.9 Drift means the difference between the pre- and post-run system bias (or system calibration error) checks at a specific calibration gas concentration level (*i.e.* low-, mid- or high-).

3.10 Gas Analyzer means the equipment that senses the gas being measured and generates an output proportional to its concentration.

3.11 Interference Check means the test to detect analyzer responses to compounds other than the compound of interest, usually a gas present in the measured gas stream, that is not adequately accounted for in the calibration procedure and may cause measurement bias.

3.12 Low-Concentration Analyzer means any analyzer that operates with a calibration span of 20 ppm NO_X or lower. Each analyzer model used routinely to measure low NO_X concentrations must pass a manufacturer's stability test (MST). An MST subjects the analyzer to a range of line voltages and temperatures that reflect potential field conditions to demonstrate its stability following

procedures similar to those provided in 40 CFR 53.23. Ambient-level analyzers are exempt from the MST requirements of section 16.3. A copy of this information must be included in each test report. Table 7E–5 lists the criteria to be met.

3.13 Measurement System means all of the equipment used to determine the NO_x concentration. The measurement system comprises six major subsystems: Sample acquisition, sample transport, sample conditioning, calibration gas manifold, gas analyzer, and data recorder.

3.14 Response Time means the time it takes the measurement system to respond to a change in gas concentration occurring at the sampling point when the system is operating normally at its target sample flow rate or dilution ratio.

3.15 Run means a series of gas samples taken successively from the stack or duct. A test normally consists of a specific number of runs.

3.16 System Bias means the difference between a calibration gas measured in direct calibration mode and in system calibration mode. System bias is determined before and after each run at the low- and mid- or high-concentration levels. For dilution-type systems, pre- and post-run system calibration error is measured rather than system bias.

3.17 System Calibration Error applies to dilution-type systems and means the difference between the measured concentration of low-, mid-, or high-level calibration gas and the certified concentration for each gas when introduced in system calibration mode. For dilution-type systems, a 3-point system calibration error test is conducted in lieu of the analyzer calibration error test, and 2-point system calibration error tests are conducted in lieu of system bias tests.

3.18 System Calibration Mode means introducing the calibration gases into the measurement system at the probe, upstream of the filter and all sample conditioning components.

3.19 Test refers to the series of runs required by the applicable regulation.

4.0 Interferences

Note that interferences may vary among instruments and that instrument-specific interferences must be evaluated through the interference test.

5.0 Safety

What safety measures should I consider when using this method? This method may require you to work with hazardous materials and in hazardous conditions. We encourage you to establish safety procedures before using the method. Among other precautions, you should become familiar with the safety recommendations in the gas analyzer user's manual. Occupational Safety and Health Administration (OSHA) regulations concerning cylinder and noxious gases may apply. Nitric oxide and NO_2 are toxic and dangerous gases. Nitric oxide is immediately converted to NO_2 upon reaction with air. Nitrogen dioxide is a highly poisonous and insidious gas. Inflammation of the lungs from exposure may cause only slight pain or pass unnoticed, but the resulting edema several days later may cause death. A concentration of 100 ppm is dangerous for even a short exposure, and 200 ppm may be fatal. Calibration gases must be handled with utmost care and with adequate ventilation. Emission-level exposure to these gases should be avoided.

6.0 Equipment and Supplies

The performance criteria in this method will be met or exceeded if you are properly using equipment designed for this application.

6.1 What do I need for the measurement system? You may use any equipment and supplies meeting the following specifications:

(1) Sampling system components that are not evaluated in the system bias or system calibration error test must be glass, Teflon, or stainless steel. Other materials are potentially acceptable, subject to approval by the Administrator.

(2) The interference, calibration error, and system bias criteria must be met.

(3) Sample flow rate must be maintained within 10 percent of the flow rate at which the system response time was measured.

(4) All system components (excluding sample conditioning components, if used) must maintain the sample temperature above the moisture dew point. Ensure minimal contact between any condensate and the sample gas. Section 6.2 provides example equipment specifications for a NO_x measurement system. Figure 7E–1 is a diagram of an example dry-basis measurement system that is likely to meet the method requirements and is provided as guidance. For wet-basis systems, you may use alternative equipment and supplies as needed (some of which are described in Section 6.2), provided that the measurement system meets the applicable performance specifications of this method.

6.2 Measurement System Components

6.2.1 Sample Probe. Glass, stainless steel, or other approved material, of sufficient length to traverse the sample points.

6.2.2 Particulate Filter. An in-stack or out-of-stack filter. The filter must be made of material that is non-reactive to the gas being sampled. The filter media for out-of-stack filters must be included in the system bias test. The particulate filter requirement may be waived in applications where no significant particulate matter is expected (*e.g.*, for emission testing of a combustion turbine firing natural gas).

6.2.3 Sample Line. The sample line from the probe to the conditioning system/sample pump should be made of Teflon or other material that does not absorb or otherwise alter the sample gas. For a dry-basis measurement system (as shown in Figure 7E–1), the temperature of the sample line must be maintained at a sufficiently high level to prevent condensation before the sample conditioning components. For wet-basis measurement systems, the temperature of the sample line must be maintained at a sufficiently high level to prevent condensation before the analyzer.

6.2.4 Conditioning Equipment. For dry basis measurements, a condenser, dryer or other suitable device is required to remove moisture continuously from the sample gas. Any equipment needed to heat the probe or sample line to avoid condensation prior to the sample conditioning component is also required.

For wet basis systems, you must keep the sample above its dew point either by: (1) Heating the sample line and all sample transport components up to the inlet of the analyzer (and, for hot-wet extractive systems, also heating the analyzer) or (2) by diluting the sample prior to analysis using a dilution probe system. The components required to do either of the above are considered to be conditioning equipment.

6.2.5 Sampling Pump. For systems similar to the one shown in Figure 7E–1, a leak-free pump is needed to pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system. The pump may be constructed of any material that is non-reactive to the gas being sampled. For dilution-type measurement systems, an ejector pump (eductor) is used to create a vacuum that draws the sample through a critical orifice at a constant rate.

6.2.6 Calibration Gas Manifold. Prepare a system to allow the introduction of calibration gases either directly to the gas analyzer in direct calibration mode or into the measurement system, at the probe, in system calibration mode, or both, depending upon the type of system used. In system calibration mode, the system should be able to flood the sampling probe and vent excess gas. Alternatively, calibration gases may be introduced at the calibration valve following the probe. Maintain a constant pressure in the gas manifold. For in-stack dilution-type systems, a gas dilution subsystem is required to transport large volumes of purified air to the sample probe and a probe controller is needed to maintain the proper dilution ratio.

6.2.7 Sample Gas Manifold. For the type of system shown in Figure 7E–1, the sample gas manifold diverts a portion of the sample to the analyzer, delivering the remainder to the by-pass discharge vent. The manifold should also be able to introduce calibration gases directly to the analyzer (except for dilution-type systems). The manifold must be made of material that is non-reactive to the gas sampled or the calibration gas and be configured to safely discharge the bypass gas.

6.2.8 NO_X Analyzer. An instrument that continuously measures NO_X in the gas stream and meets the applicable specifications in section 13.0. An analyzer that operates on the principle of chemiluminescence with an NO_2 to NO converter is one example of an analyzer that has been used successfully in the past. Analyzers operating on other principles may also be used provided the performance criteria in section 13.0 are met.

6.2.8.1 Dual Range Analyzers. For certain applications, a wide range of gas concentrations may be encountered, necessitating the use of two measurement ranges. Dual-range analyzers are readily available for these applications. These analyzers are often equipped with automated range-switching capability, so that when readings exceed the full-scale of the low measurement range, they are recorded on the high range. As an alternative to using a dual-range analyzer, you may use two segments of a single, large measurement scale to serve as the low and high ranges. In all cases, when two ranges are used, you must quality-assure both ranges using the proper sets of calibration gases. You must also meet the interference, calibration error, system bias, and drift checks. However, we caution that when you use two segments of a large measurement scale for dual range purposes, it may be difficult to meet the performance specifications on the low range due to signal-to-noise ratio considerations.

6.2.8.2 Low Concentration Analyzer. When an analyzer is routinely calibrated with a calibration span of 20 ppmv or less, the manufacturer's stability test (MST) is required. See Table 7E–5 for test parameters.

6.2.9 Data Recording. A strip chart recorder, computerized data acquisition system, digital recorder, or data logger for recording measurement data may be used.

7.0 Reagents and Standards

7.1 Calibration Gas. What calibration gases do I need? Your calibration gas must be NO in N_2 and certified (or recertified) within an uncertainty of 2.0 percent in accordance with ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards'' September 1997, as amended August 25, 1999, EPA–600/R–97/121. Blended gases meeting the Traceability Protocol are allowed if the additional gas components are shown not to interfere with the analysis. If a zero gas is used for the low-level gas, it must meet the requirements under the definition for ''zero air material'' in 40 CFR 72.2. The calibration gas must not be used after its expiration date. Except for applications under part 75 of

this chapter, it is acceptable to prepare calibration gas mixtures from EPA Traceability Protocol gases in accordance with Method 205 in appendix M to part 51 of this chapter. For part 75 applications, the use of Method 205 is subject to the approval of the Administrator. The goal and recommendation for selecting calibration gases is to bracket the sample concentrations. The following calibration gas concentrations are required:

7.1.1 *High-Level Gas.* This concentration is chosen to set the calibration span as defined in Section 3.4.

7.1.2 Mid-Level Gas. 40 to 60 percent of the calibration span.

7.1.3 Low-Level Gas. Less than 20 percent of the calibration span.

7.1.4 Converter Efficiency Gas. What reagents do I need for the converter efficiency test? The converter efficiency gas is a manufacturer-certified gas with a concentration sufficient to show NO_2 conversion at the concentrations encountered in the source. A test gas concentration in the 40 to 60 ppm range is suggested, but other concentrations may be more appropriate to specific sources. For the test described in section 8.2.4.1, NO_2 is required. For the alternative converter efficiency tests in section 16.2, NO is required.

7.2 Interference Check. What reagents do I need for the interference check? Use the appropriate test gases listed in Table 7E–3 or others not listed that can potentially interfere (as indicated by the test facility type, instrument manufacturer, etc.) to conduct the interference check. These gases should be manufacturer certified but do not have to be prepared by the EPA traceability protocol.

8.0 Sample Collection, Preservation, Storage, and Transport

Emission Test Procedure

Since you are allowed to choose different options to comply with some of the performance criteria, it is your responsibility to identify the specific options you have chosen, to document that the performance criteria for that option have been met, and to identify any deviations from the method.

8.1 What sampling site and sampling points do I select?

8.1.1 Unless otherwise specified in an applicable regulation or by the Administrator, when this method is used to determine compliance with an emission standard, conduct a stratification test as described in section 8.1.2 to determine the sampling traverse points to be used. For performance testing of continuous emission monitoring systems, follow the sampling site selection and traverse point layout procedures described in the appropriate performance specification or applicable regulation (e.g., Performance Specification 2 in appendix B to this part).

8.1.2 Determination of Stratification. Perform a stratification test at each test site to determine the appropriate number of sample traverse points. If testing for multiple pollutants or diluents at the same site, a stratification test using only one pollutant or diluent satisfies this requirement. A stratification test is not required for small stacks that are less than 4 inches in diameter. To test for stratification, use a probe of appropriate length to measure the NO_X (or pollutant of interest) concentration at 12 traverse points located according to Table 1–1 or Table 1–2 of Method 1. Alternatively, you may measure at three points on a line passing through the centroidal area. Space the three points at 16.7, 50.0, and 83.3 percent of the measurement line. Sample for a minimum of twice the system response time (see section 8.2.6) at each traverse point. Calculate the individual point and mean NO_X concentrations. If the concentration at each traverse point differs from the mean concentration for all traverse points by no more than: ±5.0 percent of the mean concentration; or ±0.5 ppm (whichever is less restrictive), the gas stream is considered unstratified, and you may collect samples from a single point that most closely matches the mean. If the 5.0 percent or 0.5 ppm criterion is not met, but the concentration at each traverse point differs from the mean concentration for all traverse points by not more than: ±10.0 percent of the mean concentration; or ±1.0 ppm (whichever is less restrictive), the gas stream is considered to be minimally stratified and you may take samples from three points. Space the three points at 16.7, 50.0, and 83.3 percent of the measurement line. Alternatively, if a 12-point stratification test was performed and the emissions were shown to be minimally stratified (all points within ± 10.0 percent of their mean or within ±1.0 ppm), and if the stack diameter (or equivalent diameter, for a rectangular stack or duct) is greater than 2.4 meters (7.8 ft), then you may use 3-point sampling and locate the three points along the measurement line exhibiting the highest average concentration during the stratification test at 0.4, 1.2 and 2.0 meters from the stack or duct wall. If the gas stream is found to be stratified because the 10.0 percent or 1.0 ppm criterion for a 3-point test is not met, locate 12 traverse points for the test in accordance with Table 1–1 or Table 1–2 of Method 1.

8.2 Initial Measurement System Performance Tests. What initial performance criteria must my system meet before I begin collecting samples? Before measuring emissions, perform the following procedures:

(a) Calibration gas verification,

(b) Measurement system preparation,

(c) Calibration error test,

(d) NO_2 to NO conversion efficiency test, if applicable,

(e) System bias check,

(f) System response time test, and

(g) Interference check

8.2.1 Calibration Gas Verification. How must I verify the concentrations of my calibration gases? Obtain a certificate from the gas manufacturer documenting the quality of the gas. Confirm that the manufacturer certification is complete and current. Ensure that your calibration gas certifications have not expired. This documentation should be available on-site for inspection. To the extent practicable, select a high-level gas concentration that will result in the measured emissions being between 20 and 100 percent of the calibration span.

8.2.2 Measurement System Preparation. How do I prepare my measurement system? Assemble, prepare, and precondition the measurement system according to your standard operating procedure. Adjust the system to achieve the correct sampling rate or dilution ratio (as applicable).

8.2.3 Calibration Error Test. How do I confirm my analyzer calibration is correct? After you have assembled, prepared and calibrated your sampling system and analyzer, you must conduct a 3-point analyzer calibration error test (or a 3-point system calibration error test for dilution systems) before the first run and again after any failed system bias test (or 2-point system calibration error test for dilution systems) or failed drift test. Introduce the low-, mid-, and high-level calibration gases sequentially. For non-dilution-type measurement systems, introduce the gases in direct calibration mode. For dilution-type measurement systems, introduce the gases in system calibration mode.

(1) For non-dilution systems, you may adjust the system to maintain the correct flow rate at the analyzer during the test, but you may not make adjustments for any other purpose. For dilution systems, you must operate the measurement system at the appropriate dilution ratio during all system calibration error checks, and may make only the adjustments necessary to maintain the proper ratio.

(2) Record the analyzer's response to each calibration gas on a form similar to Table 7E–1. For each calibration gas, calculate the analyzer calibration error using Equation 7E–1 in section 12.2 or the system calibration error using Equation 7E–3 in section 12.4 (as applicable). The calibration error specification in section 13.1 must be met for the low-, mid-, and high-level gases. If the calibration error specification is not met, take corrective action and repeat the test until an acceptable 3-point calibration is achieved.

8.2.4 NO_2 to NO Conversion Efficiency Test. Before or after each field test, you must conduct an NO_2 to NO conversion efficiency test if your system converts NO_2 to NO before analyzing for NO_X. You may risk testing multiple facilities before performing this test provided you pass this test at the conclusion of the final facility test. A failed final conversion efficiency test in this case will invalidate all tests performed subsequent to the test in which the converter efficiency test was passed. Follow the procedures in section 8.2.4.1, or 8.2.4.2. If desired, the converter efficiency factor derived from this test may be used to correct the test results for converter efficiency if the NO_2 fraction in the measured test gas is known. Use Equation 7E–8 in section 12.8 for this correction.

8.2.4.1 Introduce NO_2 converter efficiency gas to the analyzer in direct calibration mode and record the NO_X concentration displayed by the analyzer. Calculate the converter efficiency using Equation 7E–7 in section 12.7. The specification for converter efficiency in section 13.5 must be met. The user is cautioned that state-of-the-art NO_2 calibration gases may have limited shelf lives, and this could affect the ability to pass the 90-percent conversion efficiency requirement.

8.2.4.2 Alternatively, either of the procedures for determining conversion efficiency using NO in section 16.2 may be used.

8.2.5 Initial System Bias and System Calibration Error Checks. Before sampling begins, determine whether the high-level or mid-level calibration gas best approximates the emissions and use it as the upscale gas. Introduce the upscale gas at the probe upstream of all sample conditioning components in system calibration mode. Record the time it takes for the measured concentration to increase to a value that is at least 95 percent or within 0.5 ppm (whichever is less restrictive) of a stable response for both the low-level and upscale gases. Continue to observe the gas concentration reading until it has reached a final, stable value. Record this value on a form similar to Table 7E–2.

(1) Next, introduce the low-level gas in system calibration mode and record the time required for the concentration response to decrease to a value that is within 5.0 percent or 0.5 ppm (whichever is less restrictive) of the certified low-range gas concentration. If the low-level gas is a zero gas, use the procedures described above and observe the change in concentration until the response is 0.5 ppm or 5.0 percent of the upscale gas concentration (whichever is less restrictive).

(2) Continue to observe the low-level gas reading until it has reached a final, stable value and record the result on a form similar to Table 7E–2. Operate the measurement system at the normal sampling rate during all system bias checks. Make only the adjustments necessary to achieve proper calibration gas flow rates at the analyzer.

(3) From these data, calculate the measurement system response time (see section 8.2.6) and then calculate the initial system bias using Equation 7E–2 in section 12.3. For dilution systems, calculate the system calibration error in lieu of system bias using

equation 7E–3 in section 12.4. See section 13.2 for acceptable performance criteria for system bias and system calibration error. If the initial system bias (or system calibration error) specification is not met, take corrective action. Then, you must repeat the applicable calibration error test from section 8.2.3 and the initial system bias (or 2-point system calibration error) check until acceptable results are achieved, after which you may begin sampling.

(NOTE: For dilution-type systems, data from the 3-point system calibration error test described in section 8.2.3 may be used to meet the initial 2-point system calibration error test requirement of this section, if the calibration gases were injected as described in this section, and if response time data were recorded).

8.2.6 Measurement System Response Time. As described in section 8.2.5, you must determine the measurement system response time during the initial system bias (or 2-point system calibration error) check. Observe the times required to achieve 95 percent of a stable response for both the low-level and upscale gases. The longer interval is the response time.

8.2.7 Interference Check. Conduct an interference response test of the gas analyzer prior to its initial use in the field. If you have multiple analyzers of the same make and model, you need only perform this alternative interference check on one analyzer. You may also meet the interference check requirement if the instrument manufacturer performs this or a similar check on an analyzer of the same make and model of the analyzer that you use and provides you with documented results.

(1) You may introduce the appropriate interference test gases (that are potentially encountered during a test; see examples in Table 7E–3) into the analyzer separately or as mixtures. Test the analyzer with the interference gas alone at the highest concentration expected at a test source and again with the interference gas and NO_X at a representative NO_X test concentration. For analyzers measuring NO_X greater than 20 ppm, use a calibration gas with a NO_X concentration of 80 to 100 ppm and set this concentration equal to the calibration span. For analyzers measuring less than 20 ppm NO_X, select an NO concentration for the calibration span that reflects the emission levels at the sources to be tested, and perform the interference check at that level. Measure the total interference response of the analyzer to these gases in ppmv. Record the responses and determine the interference using Table 7E–4. The specification in section 13.4 must be met.

(2) A copy of this data, including the date completed and signed certification, must be available for inspection at the test site and included with each test report. This interference test is valid for the life of the instrument unless major analytical components (*e.g.,* the detector) are replaced with different model parts. If major components are replaced with different model parts, the interference gas check must be repeated before returning the analyzer to service. If major components are replaced, the interference gas check must be repeated before returning the analyzer to service. The tester must ensure that any specific technology, equipment, or procedures that are intended to remove interference effects are operating properly during testing.

8.3 Dilution-Type Systems—Special Considerations. When a dilution-type measurement system is used, there are three important considerations that must be taken into account to ensure the quality of the emissions data. First, the critical orifice size and dilution ratio must be selected properly so that the sample dew point will be below the sample line and analyzer temperatures. Second, a high-quality, accurate probe controller must be used to maintain the dilution ratio during the test. The probe controller should be capable of monitoring the dilution air pressure, eductor vacuum, and sample flow rates. Third, differences between the molecular weight of calibration gas mixtures and the stack gas molecular weight must be addressed because these can affect the dilution ratio and introduce measurement bias.

8.4 Sample Collection.

(1) Position the probe at the first sampling point. Purge the system for at least two times the response time before recording any data. Then, traverse all required sampling points, sampling at each point for an equal length of time and maintaining the appropriate sample flow rate or dilution ratio (as applicable). You must record at least one valid data point per minute during the test run.

(2) Each time the probe is removed from the stack and replaced, you must recondition the sampling system for at least two times the system response time prior to your next recording. If the average of any run exceeds the calibration span value, that run is invalid.

(3) You may satisfy the multipoint traverse requirement by sampling sequentially using a single-hole probe or a multi-hole probe designed to sample at the prescribed points with a flow within 10 percent of mean flow rate. Notwithstanding, for applications under part 75 of this chapter, the use of multi-hole probes is subject to the approval of the Administrator.

8.5 Post-Run System Bias Check and Drift Assessment.

How do I confirm that each sample I collect is valid? After each run, repeat the system bias check or 2-point system calibration error check (for dilution systems) to validate

the run. Do not make adjustments to the measurement system (other than to maintain the target sampling rate or dilution ratio) between the end of the run and the completion of the post-run system bias or system calibration error check. Note that for all post-run system bias or 2-point system calibration error checks, you may inject the low-level gas first and the upscale gas last, or vice-versa. You may risk sampling for multiple runs before performing the post-run bias or system calibration error check provided you pass this test at the conclusion of the group of runs. A failed final test in this case will invalidate all runs subsequent to the last passed test.

(1) If you do not pass the post-run system bias (or system calibration error) check, then the run is invalid. You must diagnose and fix the problem and pass another calibration error test (Section 8.2.3) and system bias (or 2-point system calibration error) check (Section 8.2.5) before repeating the run. Record the system bias (or system calibration error) results on a form similar to Table 7E–2.

(2) After each run, calculate the low-level and upscale drift, using Equation 7E–4 in section 12.5. If the post-run low- and upscale bias (or 2-point system calibration error) checks are passed, but the low-or upscale drift exceeds the specification in section 13.3, the run data are valid, but a 3-point calibration error test and a system bias (or 2-point system calibration error) check must be performed and passed before any more test runs are done.

(3) For dilution systems, data from a 3-point system calibration error test may be used to met the pre-run 2-point system calibration error requirement for the first run in a test sequence. Also, the post-run bias (or 2-point calibration error) check data may be used as the pre-run data for the next run in the test sequence at the discretion of the tester.

8.6 Alternative Interference and System Bias Checks (Dynamic Spike Procedure). If I want to use the dynamic spike procedure to validate my data, what procedure should I follow? Except for applications under part 75 of this chapter, you may use the dynamic spiking procedure and requirements provided in section 16.1 during each test as an alternative to the interference check and the pre- and post-run system bias checks. The calibration error test is still required under this option. Use of the dynamic spiking procedure for Part 75 applications is subject to the approval of the Administrator.

8.7 Moisture correction. You must determine the moisture content of the flue gas and correct the measured gas concentrations to a dry basis using Method 4 or other appropriate methods, subject to the approval of the Administrator, when the moisture basis (wet or dry) of the measurements made with this method is different from the moisture basis of either: (1) The applicable emissions limit; or (2) the CEMS being evaluated for relative accuracy. Moisture correction is also required if the applicable limit is in lb/mmBtu and the moisture basis of the Method 7E NO_X analyzer is different from the moisture basis of the Method 3A diluent gas (CO_2 or O_2) analyzer.

9.0 Quality Control

What quality control measures must I take?

The following table is a summary of the mandatory, suggested, and alternative quality assurance and quality control measures and the associated frequency and acceptance criteria. All of the QC data, along with the sample run data, must be documented and included in the test report.

SUMMARY TABLE OF AQ/QC

Status	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
S	Identify Data User		Regulatory Agency or other primary end user of data.	Before designing test.
S	Analyzer Design	Analyzer resolution or sensitivity.	<2.0% of full-scale range	Manufacturer design.
M		Interference gas check.	Sum of responses ≤2.5% of calibration span Alternatively, sum of responses: ≤0.5 ppmv for calibration spans of 5 to 10 ppmv. ≤0.2 ppmv for calibration spans <5 ppmv. See Table 7E-3.	
M	Calibration Gases	Traceability protocol (G1, G2).	Valid certificate required Uncertainty ≤2.0% of tag value.	
M		High-level gas	Equal to the calibration span	Each test.
M		Mid-level gas	40 to 60% of calibration span	Each test.
M		Low-level gas	<20% of calibration span	Each test.
S	Data Recorder Design.	Data resolution	≤0.5% of full-scale range	Manufacturer design.
S	Sample Extraction	Probe material	SS or quartz if stack >500 °F	East test.
M	Sample Extraction	Probe, filter and sample line temperature.	For dry-basis analyzers, keep sample above the dew point by heating, prior to sample conditioning.	Each run.

SUMMARY TABLE OF AQ/QC—Continued

Status	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
			For wet-basis analyzers, keep sample above dew point at all times, by heating or dilution.	
S	Sample Extraction	Calibration valve material.	SS	Each test.
S	Sample Extraction	Sample pump material.	Inert to sample constituents	Each test.
S	Sample Extraction	Manifolding material	Inert to sample constituents	Each test.
S	Moisture Removal	Equipment efficiency	<5% target compound removal	Verified through system bias check.
S	Particulate Removal	Filter inertness	Pass system bias check	Each bias check.
M	Analyzer & Calibration Gas Performance.	Analyzer calibration error (of 3-point system calibration error for dilution systems).	Within ±2.0 percent of the calibration span of the analyzer for the low-, mid-, and high-level calibration gases. Alternative specification: ≤0.5 ppmv absolute difference.	Before initial run and after a failed system bias test or drift test.
M	System Performance	System bias (or pre- and post-run 2-point system calibration error for dilution (Systems).	Within ±5.0% of the analyzer calibration span for low-sacle and upscale calibration gases. Alternative specification: ≤0.5 ppmv absolute difference.	Before and after each run.
M	System Performance	System response time.	Determines minimum sampling time per point.	During initial sampling system bias test.
M	System Performance	Drift	≤3.0% of calibration span for low-level and mid- or high-level gases. Alternative specification: ≤0.5 ppmv absolute difference.	After each test run.
M	System Performance	NO_2-NO conversion efficiency.	≥90% of certified test gas concentration	Before or after each test.
M	System Performance	Purge time	≥2 times system response time	Before starting the first run and when probe is removed from and re-inserted into the stack.
M	System Performance	Minimum sample time at each point.	Two times the system response time	Each sample point.
M	System Performance	Stable sample flow rate (surrogate for maintaining system response time).	Within 10% of flow rate established during system response time check.	Each run.
M	Sample Point Selection.	Stratification test	All points within: ±5% of mean for 1-point sampling. ±10% of mean for 3-point. Alternatively, all points within: ±0.5 ppm of mean for 1-point sampling. ±1.0 ppm of mean for 3-point sampling.	Prior to first run.
A	Multiple sample points simultaneously.	No. of openings in probe.	Multi-hole probe with verifiable constant flow through all holes within 10% of mean flow rate (requires Administrative approval for Part 75).	Each run.
M	Data Recording	Frequency	≤1 minute average	During run.
S	Data Parameters	Sample concentration range.	All 1-minute averages within calibration span.	Each run.
M	Date Parameters	Average concentration for the run.	Run average ≤calibration span	Each run.

S = Suggest.
M = Mandatory.
A = Alternative.
Agency.

10.0 Calibration and Standardization

What measurement system calibrations are required?

(1) The initial 3-point calibration error test as described in section 8.2.3 and the system bias (or system calibration error) checks described in section 8.2.5 are required and must meet the specifications in section 13 before you start the test. Make all necessary adjustments to calibrate the gas analyzer and data recorder. Then, after the test commences, the system bias or system calibration error checks described in section 8.5 are required before and after each run. Your analyzer must be calibrated for all species of NO_X that it detects. Analyzers that measure NO and NO_2 separately without using a converter must be calibrated with both NO and NO_2.

(2) You must include a copy of the manufacturer's certification of the calibration gases used in the testing as part of the test report. This certification must include the 13 documentation requirements in the EPA Traceability Protocol For Assay and Certification of Gaseous Calibration Standards, September 1997, as amended August 25, 1999. When Method 205 is used to produce diluted calibration gases, you must document that the specifications for the gas dilution system are met for the test. You must also include the date of the most recent dilution system calibration against flow standards and the name of the person or manufacturer who carried out the calibration in the test report.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the procedures for calculations and data analysis listed in this section.

12.1 *Nomenclature.* The terms used in the equations are defined as follows:

ACE = Analyzer calibration error, percent of calibration span.

B_{WS} = Moisture content of sample gas as measured by Method 4 or other approved method, percent/100.

C_{Avg} = Average unadjusted gas concentration indicated by data recorder for the test run, ppmv.

C_D = Pollutant concentration adjusted to dry conditions, ppmv.

C_{Dir} = Measured concentration of a calibration gas (low, mid, or high) when introduced in direct calibration mode, ppmv.

C_{Gas} = Average effluent gas concentration adjusted for bias, ppmv.

C_M = Average of initial and final system calibration bias (or 2-point system calibration error) check responses for the upscale calibration gas, ppmv.

C_{MA} = Actual concentration of the upscale calibration gas, ppmv.

C_{Native} = NO_X concentration in the stack gas as calculated in section 12.6, ppmv.

C_O = Average of the initial and final system calibration bias (or 2-point system calibration error) check responses from the low-level (or zero) calibration gas, ppmv.

C_{OA} = Actual concentration of the low-level calibration gas, ppmv.

C_S = Measured concentration of a calibration gas (low, mid, or high) when introduced in system calibration mode, ppmv.

C_{SS} = Concentration of NO_X measured in the spiked sample, ppmv.

C_{Spike} = Concentration of NO_X in the undiluted spike gas, ppmv.

C_{Calc} = Calculated concentration of NO_X in the spike gas diluted in the sample, ppmv.

C_V = Manufacturer certified concentration of a calibration gas (low, mid, or high), ppmv.

C_W = Pollutant concentration measured under moist sample conditions, wet basis, ppmv.

CS = Calibration span, ppmv.

D = Drift assessment, percent of calibration span.

DF = Dilution system dilution factor or spike gas dilution factor, dimensionless.

Eff_{NO2} = NO_2 to NO converter efficiency, percent.

NO_{XCorr} = The NO_X concentration corrected for the converter efficiency, ppmv.

NOX_{Final} = The final NO_X concentration observed during the converter efficiency test in section 16.2.2, ppmv.

NO_{XPeak} = The highest NO_X concentration observed during the converter efficiency test in section 16.2.2, ppmv.

Q_{Spike} = Flow rate of spike gas introduced in system calibration mode, L/min.

Q_{Total} = Total sample flow rate during the spike test, L/min.

R = Spike recovery, percent.

SB = System bias, percent of calibration span.

SB_i = Pre-run system bias, percent of calibration span.

SB_{final} = Post-run system bias, percent of calibration span.

SCE = System calibration error, percent of calibration span.

SCE_i = Pre-run system calibration error, percent of calibration span.

SCE_{Final} = Post-run system calibration error, percent of calibration span.

12.2 Analyzer Calibration Error. For non-dilution systems, use Equation 7E–1 to calculate the analyzer calibration error for the low-, mid-, and high-level calibration gases.

$$ACE = \frac{C_{Dir} - C_v}{CS} \times 100 \qquad \text{Eq. 7E-1}$$

12.3 System Bias. For non-dilution systems, use Equation 7E–2 to calculate the system bias separately for the low-level and upscale calibration gases.

$$SB = \frac{C_S - C_{Dir}}{CS} \times 100 \qquad \text{Eq. 7E-2}$$

12.4 System Calibration Error. Use Equation 7E–3 to calculate the system calibration error for dilution systems. Equation 7E–3 applies to both the initial 3-point system calibration error test and the subsequent 2-point calibration error checks between test runs. In this equation, the term ''C_s'' refers to the diluted calibration gas concentration measured by the analyzer.

$$SCE = \frac{(C_S \quad DF) - C_V}{CS} \times 100 \qquad \text{Eq. 7E-3}$$

12.5 Drift Assessment. Use Equation 7E–4 to separately calculate the low-level and upscale drift over each test run. For dilution systems, replace ''SB_{final}'' and ''SB_i'' with ''SCE_{final}'' and ''SCE_i'', respectively, to calculate and evaluate drift.

$$D = \left|SB_{final} - SB_i\right| \qquad \text{Eq. 7E-4}$$

12.6 Effluent Gas Concentration. For each test run, calculate C_{avg}, the arithmetic average of all valid NO_X concentration values (*e.g.*, 1-minute averages). Then adjust the value of C_{avg} for bias using Equation 7E–5a if you use a non-zero gas as your low-level calibration gas, or Equation 7E–5b if you use a zero gas as your low-level calibration gas.

$$C_{Gas} = \left(C_{Avg} - C_M\right)\frac{C_{MA} - C_{OA}}{C_M - C_O} + C_{MA} \qquad \text{Eq. 7E-5a}$$

$$C_{Gas} = \left(C_{Avg} - C_O\right)\frac{C_{MA}}{C_M - C_O} \qquad \text{Eq. 7E-5b}$$

12.7 NO_2—NO Conversion Efficiency. If the NO_X converter efficiency test described in section 8.2.4.1 is performed, calculate the efficiency using Equation 7E–7.

$$Eff_{NO2} = \frac{C_{Dir}}{C_V} \times 100 \qquad \text{Eq. 7E-7}$$

12.8 NO_2—NO Conversion Efficiency Correction. If desired, calculate the total NO_X concentration with a correction for converter efficiency using Equation 7E–8.

$$NO_{x\,Corr} = NO + \left(\frac{(NO_X - NO)}{Eff_{NO_2}} x\ 100\right) \qquad \text{Eq. 7E-8}$$

12.9 Alternative NO_2 Converter Efficiency. If the alternative procedure of section 16.2.2 is used, determine the NO_X concentration decrease from NO_{XPeak} after the minimum 30-minute test interval using Equation 7E–9.

This decrease from NO_{XPeak} must meet the requirement in section 13.5 for the converter to be acceptable.

$$\%\,Decrease = \frac{NO_{XPeak} - NO_{XFinal}}{NO_{XPeak}} \times 100 \qquad \text{Eq. 7E-9}$$

12.10 Moisture Correction. Use Equation 7E–10 if your measurements need to be corrected to a dry basis.

$$C_D = \frac{C_W}{1 - B_{WS}} \qquad \text{Eq. 7E-10}$$

12.11 Calculated Spike Gas Concentration and Spike Recovery for the Example Alternative Dynamic Spiking Procedure in section 16.1.3. Use Equation 7E–11 to determine the calculated spike gas concentration. Use Equation 7E–12 to calculate the spike recovery.

$$C_{Calc} = \frac{\left(C_{Spike}\right)\left(Q_{Spike}\right)}{Q_{Total}} \qquad \text{Eq. 7E-11}$$

$$R = \frac{DF\left(C_{ss} - C_{native}\right) + C_{native}}{C_{Spike}} \times 100 \qquad \text{Eq. 7E-12}$$

13.0 Method Performance

13.1 Calibration Error. This specification is applicable to both the analyzer calibration error and the 3-point system calibration error tests described in section 8.2.3. At each calibration gas level (low, mid, and high) the calibration error must either be within ±2.0 percent of the calibration span. Alternatively, the results are acceptable if $|C_{dir} - C_v|$ or $|C_s - C_v|$ (as applicable) is ≤0.5 ppmv.

13.2 System Bias. This specification is applicable to both the system bias and 2-point system calibration error tests described in section 8.2.5 and 8.5. The pre- and post-run system bias (or system calibration error) must be within ±5.0 percent of the calibration span for the low-level and upscale calibration gases. Alternatively, the results are acceptable if $|C_s - C_{dir}|$ is ≤0.5 ppmv or if $|C_s - C_v|$ is ≤0.5 ppmv (as applicable).

13.3 Drift. For each run, the low-level and upscale drift must be less than or equal to 3.0 percent of the calibration span. The drift is also acceptable if the pre- and post-run bias (or the pre- and post-run system calibration error) responses do not differ by more than 0.5 ppmv at each gas concentration (i.e. $|C_{s\ post\text{-}run} - C_{s\ pre\text{-}run}| \leq 0.5$ ppmv).

13.4 Interference Check. The total interference response (i.e., the sum of the interference responses of all tested gaseous components) must not be greater than 2.50 percent of the calibration span for the analyzer tested. In summing the interferences, use the larger of the absolute values obtained for the interferent tested with and without the pollutant present. The results are also acceptable if the sum of the responses does not exceed 0.5 ppmv for a calibration span of 5 to 10 ppmv, or 0.2 ppmv for a calibration span <5 ppmv.

13.5 NO_2 to NO Conversion Efficiency Test (as applicable). The NO_2 to NO conversion efficiency, calculated according to Equation 7E–7, must be greater than or equal to 90 percent. The alternative conversion efficiency check, described in section 16.2.2 and calculated according to Equation 7E–9, must not result in a decrease from NO_{XPeak} by more than 2.0 percent.

13.6 Alternative Dynamic Spike Procedure. Recoveries of both pre-test spikes and post-test spikes must be within 100 ±10 percent. If the absolute difference between the calculated spike value and measured spike value is equal to or less than 0.20 ppmv, then the requirements of the ADSC are met.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Dynamic Spike Procedure. Except for applications under part 75 of this chapter, you may use a dynamic spiking procedure to validate your test data for a specific test matrix in place of the interference check and pre- and post-run system bias checks. For part 75 applications, use of this procedure is subject to the approval of the Administrator.

Best results are obtained for this procedure when source emissions are steady and not varying. Fluctuating emissions may render this alternative procedure difficult to pass. To use this alternative, you must meet the following requirements.

16.1.1 Procedure Documentation. You must detail the procedure you followed in the test report, including how the spike was measured, added, verified during the run, and calculated after the test.

16.1.2 Spiking Procedure Requirements. The spikes must be prepared from EPA Traceability Protocol gases. Your procedure must be designed to spike field samples at two target levels both before and after the test. Your target spike levels should bracket the average sample NO_X concentrations. The higher target concentration must be less than the calibration span. You must collect at least 5 data points for each target concentration. The spiking procedure must be performed before the first run and repeated after the last run of the test program.

16.1.3 Example Spiking Procedure. Determine the NO concentration needed to generate concentrations that are 50 and 150 percent of the anticipated NO_X concentration in the stack at the total sampling flow rate while keeping the spike flow rate at or below 10 percent of this total. Use a mass flow meter (accurate within 2.0 percent) to generate these NO spike gas concentrations at a constant flow rate. Use Equation 7E–11 in section 12.11 to determine the calculated spike concentration in the collected sample.

(1) Prepare the measurement system and conduct the analyzer calibration error test as described in sections 8.2.2 and 8.2.3. Following the sampling procedures in section 8.1, determine the stack NO_X concentration and use this concentration as the average stack concentration (C_{avg}) for the first spike level, or if desired, for both pre-test spike levels. Introduce the first level spike gas into the system in system calibration mode and begin sample collection. Wait for at least two times the system response time before measuring the spiked sample concentration. Then record at least five successive 1-minute averages of the spiked sample gas. Monitor the spike gas flow rate and maintain at the determined addition rate. Average the five 1-minute averages and determine the spike recovery using Equation 7E–12. Repeat this procedure for the other pre-test spike level. The recovery at each level must be within the limits in section 13.6 before proceeding with the test.

(2) Conduct the number of runs required for the test. Then repeat the above procedure for the post-test spike evaluation. The last run of the test may serve as the average stack concentration for the post-test spike test calculations. The results of the post-test spikes must meet the limits in section 13.6.

16.2 Alternative NO_2 to NO Conversion Efficiency Procedures. You may use either of the following procedures to determine converter efficiency in place of the procedure in section 8.2.4.1.

16.2.1 The procedure for determining conversion efficiency using NO in 40 CFR 86.123–78.

16.2.2 Bag Procedure. Perform the analyzer calibration error test to document the calibration (both NO and NO_X modes, as applicable). Fill a Tedlar or equivalent bag approximately half full with either ambient air, pure oxygen, or an oxygen standard gas with at least 19.5 percent by volume oxygen content. Fill the remainder of the bag with mid- to high-level NO in N_2 (or other appropriate concentration) calibration gas. (Note that the concentration of the NO standard should be sufficiently high enough for the diluted concentration to be easily and accurately measured on the scale used. The size of the bag should be large enough to accommodate the procedure and time required. Verify through the manufacturer that the Tedlar alternative is suitable for NO and make this verifed information available for inspection.)

(1) Immediately attach the bag to the inlet of the NO_X analyzer (or external converter if used). In the case of a dilution-system, introduce the gas at a point upstream of the dilution assembly. Measure the NO_X concentration for a period of 30 minutes. If the NO_X concentration drops more than 2 percent absolute from the peak value observed, then the NO_2 converter has failed to meet the criteria of this test. Take corrective action. The highest NO_X value observed is considered to be NO_{XPeak}. The final NO_X value observed is considered to be NO_{Xfinal}.

(2) [Reserved]

16.3 Manufacturer's Stability Test. A manufacturer's stability test is required for all analyzers that routinely measure emissions below 20 ppmv and is optional but recommended for other analyzers. This test evaluates each analyzer model by subjecting it to the tests listed in Table 7E–5 following procedures similar to those in 40 CFR 53.23 for thermal stability and insensitivity to supply voltage variations. If the analyzer will be used under temperature conditions that are outside the test conditions in Table B–4 of Part 53.23, alternative test temperatures that better reflect the analyzer field environment should be used. Alternative procedures or documentation that establish the analyzer's stability over the appropriate line voltages and temperatures are acceptable.

17.0 References

1. ''ERA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards'' September 1997 as amended, ERA–600/R–97/121.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

Figure 7E-1. Measurement System

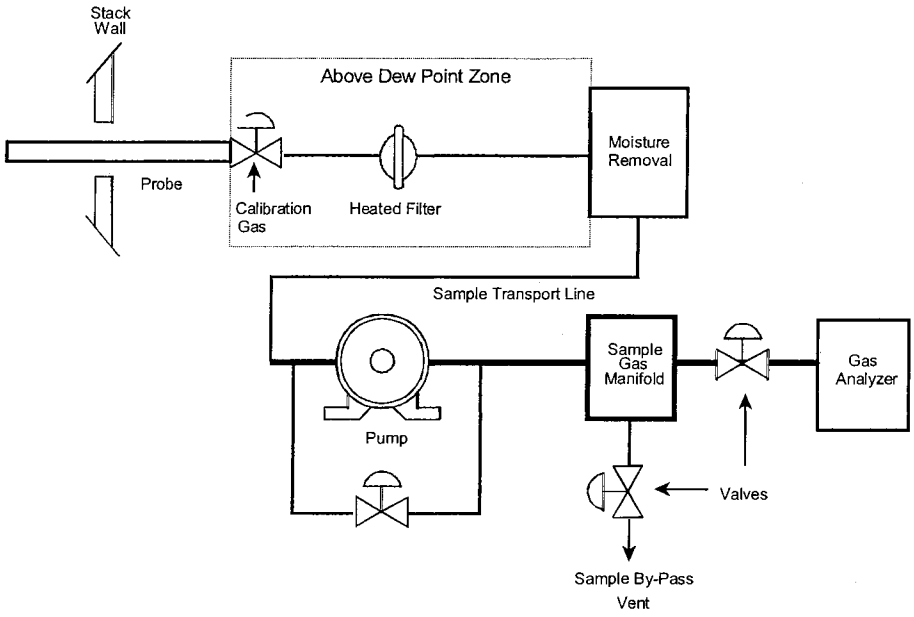

Figure 7E-2. Testing Flow Chart

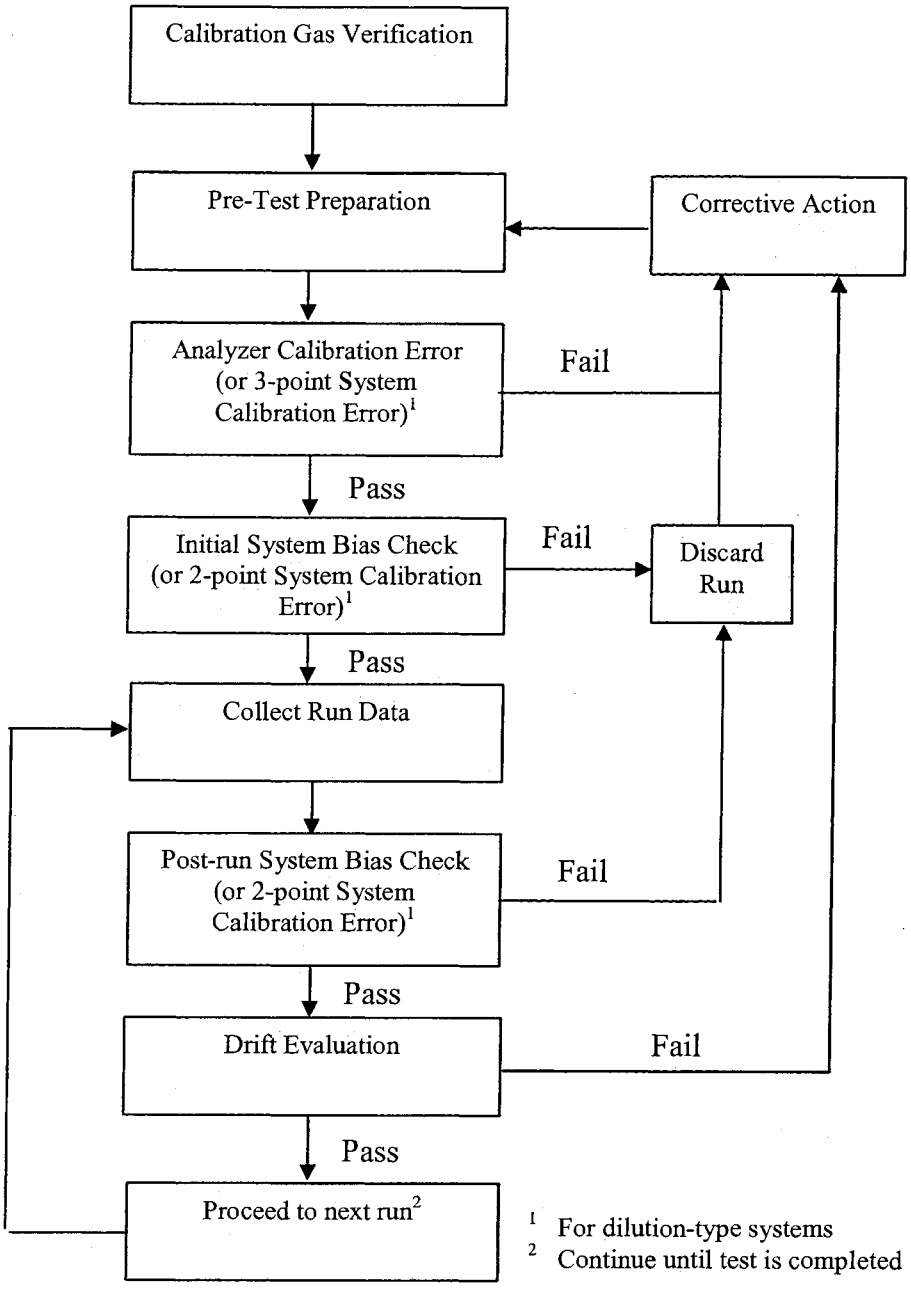

Table 7E-1 - Analyzer (or System) Calibration Error Data

Source Identification: _____ Test personnel: _____ Date: _____ Time: _____		Analyzer[1] or System[2] calibration error data for sampling runs: _____ Analyzer Model No. _____ Serial No. _____ Calibration Span (CS):		
	Manufacturer Certified Cylinder Value (indicate units) A	Analyzer calibration response (indicate units) B	Absolute difference (indicate units) A-B	Calibration Error (percent of calibration span) $\frac{A-B}{CS} \times 100$
Low-level (or zero) calibration gas	.....	.....	.....	.....
Mid-level calibration gas	.....	.....	.....	.....
High-level calibration gas	.....	.....	.....	.....

[1] Refers to data from the analyzer calibration error test of a non-dilution system.
[2] Refers to data from a 3-point system calibration error test of a dilution system.

Table 7E-2 - System Bias (or System Calibration Error) and Drift Data

Source Identification: _____ Run Number: _____
Test personnel: _____ Calibration Span: _____
Date: _____ Response Time: _____
Analyzer Model No. _____ Serial No. _____

	Initial values			Final values		
Calibration Gas Level	Certified Calibration gas value (indicate units)	System Response (indicate units)	System Bias[1] or Calibration Error[2] (% of calibration span)	System response (indicate units)	System Bias[1] or Calibration Error[2] (% of calibration span)	Drift (% of calibration span)
Low-level gas.....	.....	.....	.....	.....	.....	
Upscale (high- or mid-) level gas.....	.....	.....	.....	.....	.....	

[1] Refers to the pre- and post-run system bias checks of a non-dilution system.
[2] Refers to the pre- and post-run system calibration error checks of a dilution system.

TABLE 7E–3—EXAMPLE INTERFERENCE CHECK GAS CONCENTRATIONS

Potential interferent gas[1]	Concentrations[2] sample conditioning type	
	Hot wet	Dried
CO_2	5 and 15%	5 and 15%
H_2O	25%	1%
NO	15 ppmv	15 ppmv
NO_2	15 ppmv	15 ppmv
N_2O	10 ppmv	10 ppmv
CO	50 ppmv	50 ppmv
NH_3	10 ppmv	10 ppmv
CH_4	50 ppmv	50 ppmv
SO_2	20 ppmv	20 ppmv
H_2	50 ppmv	50 ppmv
HCl	10 ppmv	10 ppmv

[1] Any applicable gas may be eliminated or tested at a reduced level if the manufacturer has provided reliable means for limiting or scrubbing that gas to a specified level.
[2] As practicable, gas concentrations should be the highest expected at test sites.

TABLE 7E–4—INTERFERENCE RESPONSE

Date of Test: _____

Analyzer Type: _____
Model No.: _____
Serial No: _____
Calibration Span: _____

Test gas type	Concentration (ppm)	Analyzer response
	Sum of Responses	
	% of Calibration Span	

TABLE 7E–5—MANUFACTURER STABILITY TEST

Test description	Acceptance criteria (note 1)
Thermal Stability	Temperature range when drift does not exceed 3.0% of analyzer range over a 12-hour run when measured with NO_X present @ 80% of calibration span.
Fault Conditions	Identify conditions which, when they occur, result in performance which is not in compliance with the Manufacturer's Stability Test criteria. These are to be indicated visually or electrically to alert the operator of the problem.
Insensitivity to Supply Voltage Variations.	±10.0% (or manufacturers alternative) variation from nominal voltage must produce a drift of ≤2.0% of calibration span for either zero or concentration ≥80% NO_X present.
Analyzer Calibration Error.	For a low-, medium-, and high-calibration gas, the difference between the manufacturer certified value and the analyzer response in direct calibration mode, no more than 2.0% of calibration span.

Note 1: If the instrument is to be used as a Low Range analyzer, all tests must be performed at a calibration span of 20 ppm or less.

METHOD 8—DETERMINATION OF SULFURIC ACID AND SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, and Method 6.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Sulfuric acid, including: Sulfuric acid (H_2SO_4) mist, Sulfur trioxide (SO_3).	7664–93–9, 7449–11–9	0.05 mg/m³ (0.03×10^{-7} lb/ft³).
Sulfur dioxide (SO_2)	7449–09–5	1.2 mg/m³ (3×10^{-9} lb/ft³).

1.2 Applicability. This method is applicable for the determination of H_2SO_4 (including H_2SO_4 mist and SO_3) and gaseous SO_2 emissions from stationary sources.

NOTE: Filterable particulate matter may be determined along with H_2SO_4 and SO_2 (subject to the approval of the Administrator) by inserting a heated glass fiber filter between the probe and isopropanol impinger (see section 6.1.1 of Method 6). If this option is chosen, particulate analysis is gravimetric only; sulfuric acid is not determined separately.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

A gas sample is extracted isokinetically from the stack. The H_2SO_4 and the SO_2 are separated, and both fractions are measured separately by the barium-thorin titration method.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Possible interfering agents of this method are fluorides, free ammonia, and dimethyl aniline. If any of these interfering agents is present (this can be determined by knowledge of the process), alternative methods, subject to the approval of the Administrator, are required.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. Same as Method 6, section 5.2.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 5, section 6.1, with the following additions and exceptions:

6.1.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 8–1; it is similar to the Method 5 sampling train, except that the filter position is different, and the filter holder does not have to be heated. See Method 5, section 6.1.1, for details and guidelines on operation and maintenance.

6.1.1.1 Probe Liner. Borosilicate or quartz glass, with a heating system to prevent visible condensation during sampling. Do not use metal probe liners.

6.1.1.2 Filter Holder. Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other gasket materials (*e.g.*, Teflon or Viton) may be used, subject to the approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The filter holder shall be placed between the first and second impingers. Do not heat the filter holder.

6.1.1.3 Impingers. Four, of the Greenburg-Smith design, as shown in Figure 8–1. The first and third impingers must have standard tips. The second and fourth impingers must be modified by replacing the insert with an approximately 13-mm (½-in.) ID glass tube, having an unconstricted tip located 13 mm (½ in.) from the bottom of the impinger. Similar collection systems, subject to the approval of the Administrator, may be used.

6.1.1.4 Temperature Sensor. Thermometer, or equivalent, to measure the temperature of the gas leaving the impinger train to within 1 °C (2 °F).

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Wash Bottles. Two polyethylene or glass bottles, 500-ml.

6.2.2 Graduated Cylinders. Two graduated cylinders (volumetric flasks may be used), 250-ml, 1-liter.

6.2.3 Storage Bottles. Leak-free polyethylene bottles, 1-liter size (two for each sampling run).

6.2.4 Trip Balance. 500-g capacity, to measure to ±0.5 g (necessary only if a moisture content analysis is to be done).

6.3 Analysis. The following items are required for sample analysis:

6.3.1 Pipettes. Volumetric 10-ml, 100-ml.

6.3.2 Burette. 50-ml.

6.3.3 Erlenmeyer Flask. 250-ml (one for each sample, blank, and standard).

6.3.4 Graduated Cylinder. 100-ml.

6.3.5 Dropping Bottle. To add indicator solution, 125-ml size.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents are to conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Filters and Silica Gel. Same as in Method 5, sections 7.1.1 and 7.1.2, respectively.

7.1.2 Water. Same as in Method 6, section 7.1.1.

7.1.3 Isopropanol, 80 Percent by Volume. Mix 800 ml of isopropanol with 200 ml of water.

NOTE: Check for peroxide impurities using the procedure outlined in Method 6, section 7.1.2.1.

7.1.4 Hydrogen Peroxide (H^2O^2), 3 Percent by Volume. Dilute 100 ml of 30 percent H_2O_2) to 1 liter with water. Prepare fresh daily.

7.1.5 Crushed Ice.

7.2 Sample Recovery. The reagents and standards required for sample recovery are:

7.2.1 Water. Same as in section 7.1.2.

7.2.2 Isopropanol, 80 Percent. Same as in section 7.1.3.

7.3 Sample Analysis. Same as Method 6, section 7.3.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation. Same as Method 5, section 8.1, except that filters should be inspected but need not be desiccated, weighed, or identified. If the effluent gas can be considered dry (i.e., moisture-free), the silica gel need not be weighed.

8.2 Preliminary Determinations. Same as Method 5, section 8.2.

8.3 Preparation of Sampling Train. Same as Method 5, section 8.3, with the following exceptions:

8.3.1 Use Figure 8–1 instead of Figure 5–1.

8.3.2 Replace the second sentence of Method 5, section 8.3.1 with: Place 100 ml of 80 percent isopropanol in the first impinger, 100 ml of 3 percent H_2O_2 in both the second and third impingers; retain a portion of each reagent for use as a blank solution. Place about 200 g of silica gel in the fourth impinger.

8.3.3 Ignore any other statements in section 8.3 of Method 5 that are obviously not applicable to the performance of Method 8.

NOTE: If moisture content is to be determined by impinger analysis, weigh each of the first three impingers (plus absorbing solution) to the nearest 0.5 g, and record these weights. Weigh also the silica gel (or silica gel plus container) to the nearest 0.5 g, and record.)

8.4 Metering System Leak-Check Procedure. Same as Method 5, section 8.4.1.

8.5 Pretest Leak-Check Procedure. Follow the basic procedure in Method 5, section 8.4.2, noting that the probe heater shall be adjusted to the minimum temperature required to prevent condensation, and also that verbage such as ''* * * plugging the inlet to the filter holder * * * '' found in section 8.4.2.2 of Method 5 shall be replaced by '' * * * plugging the inlet to the first impinger * * * ''. The pretest leak-check is recommended, but is not required.

8.6 Sampling Train Operation. Follow the basic procedures in Method 5, section 8.5, in conjunction with the following special instructions:

8.6.1 Record the data on a sheet similar to that shown in Figure 8–2 (alternatively, Figure 5–2 in Method 5 may be used). The sampling rate shall not exceed 0.030 m^3/min (1.0 cfm) during the run. Periodically during the test, observe the connecting line between the probe and first impinger for signs of condensation. If condensation does occur, adjust the probe heater setting upward to the minimum temperature required to prevent condensation. If component changes become necessary during a run, a leak-check shall be performed immediately before each change, according to the procedure outlined in section 8.4.3 of Method 5 (with appropriate modifications, as mentioned in section 8.5 of this method); record all leak rates. If the leakage rate(s) exceeds the specified rate, the tester shall either void the run or plan to correct the sample volume as outlined in section 12.3 of Method 5. Leak-checks immediately after component changes are recommended, but not required. If these leak-checks are performed, the procedure in section 8.4.2 of Method 5 (with appropriate modifications) shall be used.

8.6.2 After turning off the pump and recording the final readings at the conclusion of each run, remove the probe from the stack. Conduct a post-test (mandatory) leak-check as outlined in section 8.4.4 of Method 5 (with appropriate modifications), and record the leak rate. If the post-test leakage rate exceeds the specified acceptable rate, either correct the sample volume, as outlined in section 12.3 of Method 5, or void the run.

8.6.3 Drain the ice bath and, with the probe disconnected, purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at the average flow rate used for sampling.

NOTE: Clean ambient air can be provided by passing air through a charcoal filter. Alternatively, ambient air (without cleaning) may be used.

8.7 Calculation of Percent Isokinetic. Same as Method 5, section 8.6.

8.8 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. Treat the samples as follows:

8.8.1 Container No. 1.

8.8.1.1 If a moisture content analysis is to be performed, clean and weigh the first impinger (plus contents) to the nearest 0.5 g, and record this weight.

8.8.1.2 Transfer the contents of the first impinger to a 250-ml graduated cylinder. Rinse the probe, first impinger, all connecting glassware before the filter, and the front half of the filter holder with 80 percent isopropanol. Add the isopropanol rinse solution to the cylinder. Dilute the contents of the cylinder to 225 ml with 80 percent isopropanol, and transfer the cylinder contents to the storage container. Rinse the cylinder with 25 ml of 80 percent isopropanol, and transfer the rinse to the storage container. Add the filter to the solution in the storage container and mix. Seal the container to protect the solution against evaporation. Mark the level of liquid on the container, and identify the sample container.

8.8.2 Container No. 2.

8.8.2.1 If a moisture content analysis is to be performed, clean and weigh the second and third impingers (plus contents) to the nearest 0.5 g, and record the weights. Also, weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g, and record the weight.

8.8.2.2 Transfer the solutions from the second and third impingers to a 1-liter graduated cylinder. Rinse all connecting glassware (including back half of filter holder) between the filter and silica gel impinger with water, and add this rinse water to the cylinder. Dilute the contents of the cylinder to 950 ml with water. Transfer the solution to a storage container. Rinse the cylinder with 50 ml of water, and transfer the rinse to the storage container. Mark the level of liquid on the container. Seal and identify the sample container.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
7.1.3	Isopropanol check	Ensure acceptable level of peroxide impurities in isopropanol.
8.4, 8.5, 10.1	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.
10.2	Barium standard solution standardization	Ensure normality determination.
11.2	Replicate titrations	Ensure precision of titration determinations.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

10.1 Sampling Equipment. Same as Method 5, section 10.0.

10.2 Barium Standard Solution. Same as Method 6, section 10.5.

11.0 Analytical Procedure

11.1. Sample Loss. Same as Method 6, section 11.1.

11.2. Sample Analysis.

11.2.1 Container No. 1. Shake the container holding the isopropanol solution and the filter. If the filter breaks up, allow the fragments to settle for a few minutes before removing a sample aliquot. Pipette a 100-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 2 to 4 drops of thorin indicator, and titrate to a pink endpoint using 0.0100 N barium standard solution. Repeat the titration with a second aliquot of sample, and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater.

11.2.2 Container No. 2. Thoroughly mix the solution in the container holding the contents of the second and third impingers. Pipette a 10-ml aliquot of sample into a 250-ml Erlenmeyer flask. Add 40 ml of isopropanol, 2 to 4 drops of thorin indicator, and titrate to a pink endpoint using 0.0100 N barium standard solution. Repeat the titration with a second aliquot of sample, and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater.

11.2.3 Blanks. Prepare blanks by adding 2 to 4 drops of thorin indicator to 100 ml of 80 percent isopropanol. Titrate the blanks in the same manner as the samples.

12.0 Data Analysis and Calculations

Carry out calculations retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature. Same as Method 5, section 12.1, with the following additions and exceptions:

$C_{H_2SO_4}$ = Sulfuric acid (including SO_3) concentration, g/dscm (lb/dscf).

C_{SO_2} = Sulfur dioxide concentration, g/dscm (lb/dscf).

N = Normality of barium perchlorate titrant, meq/ml.

V_a = Volume of sample aliquot titrated, 100 ml for H_2SO_4 and 10 ml for SO_2.

V_{soln} = Total volume of solution in which the sample is contained, 1000 ml for the SO_2 sample and 250 ml for the H_2SO_4 sample.

V_t = Volume of barium standard solution titrant used for the sample, ml.

V_{tb} = Volume of barium standard solution titrant used for the blank, ml.

12.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 8–2).

12.3 Dry Gas Volume. Same as Method 5, section 12.3.

12.4 Volume of Water Vapor Condensed and Moisture Content. Calculate the volume of water vapor using Equation 5–2 of Method 5; the weight of water collected in the impingers and silica gel can be converted directly to milliliters (the specific gravity of water is 1 g/ml). Calculate the moisture content of the stack gas (B_{ws}) using Equation 5–3 of Method 5. The note in section 12.5 of Method 5 also applies to this method. Note that if the effluent gas stream can be considered dry, the volume of water vapor and moisture content need not be calculated.

12.5 Sulfuric Acid Mist (Including SO_3) Concentration.

$$C_{H_2SO_4} = K_3\left[N\left(V_t - V_{tb}\right)\left(V_{soln}/V_a\right)\right]/V_{m(std)} \qquad \text{Eq. 8-1}$$

Where:

K_3 = 0.04904 g/meq for metric units,

$K_3 = 1.081 \times 10^{-4}$ lb/meq for English units.

12.6 Sulfur Dioxide Concentration.

$$C_{SO_2} = K_4\left[N\left(V_t - V_{tb}\right)\left(V_{soln}/V_a\right)\right]/V_{m(std)} \qquad \text{Eq. 8-2}$$

Where:

K_4 = 0.03203 g/meq for metric units,

$K_4 = 7.061 \times 10^{-5}$ lb/meq for English units.

12.7 Isokinetic Variation. Same as Method 5, section 12.11.

12.8 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate, if needed, using data obtained in this method and the equations in sections 12.6 and 12.7 of Method 2.

13.0 Method Performance

13.1 Analytical Range. Collaborative tests have shown that the minimum detectable limits of the method are 0.06 mg/m^3 (4×10^{-9} lb/ft^3) for H_2SO_4 and 1.2 mg/m^3 (74×10^{-9} lb/ft^3) for SO_2. No upper limits have been established. Based on theoretical calculations for 200 ml of 3 percent H_2O_2 solution, the upper concentration limit for SO_2 in a 1.0 m^3 (35.3 ft^3) gas sample is about 12,000 mg/m^3 (7.7×10^{-4} lb/ft^3). The upper limit can be extended by increasing the quantity of peroxide solution in the impingers.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as section 17.0 of Methods 5 and 6.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

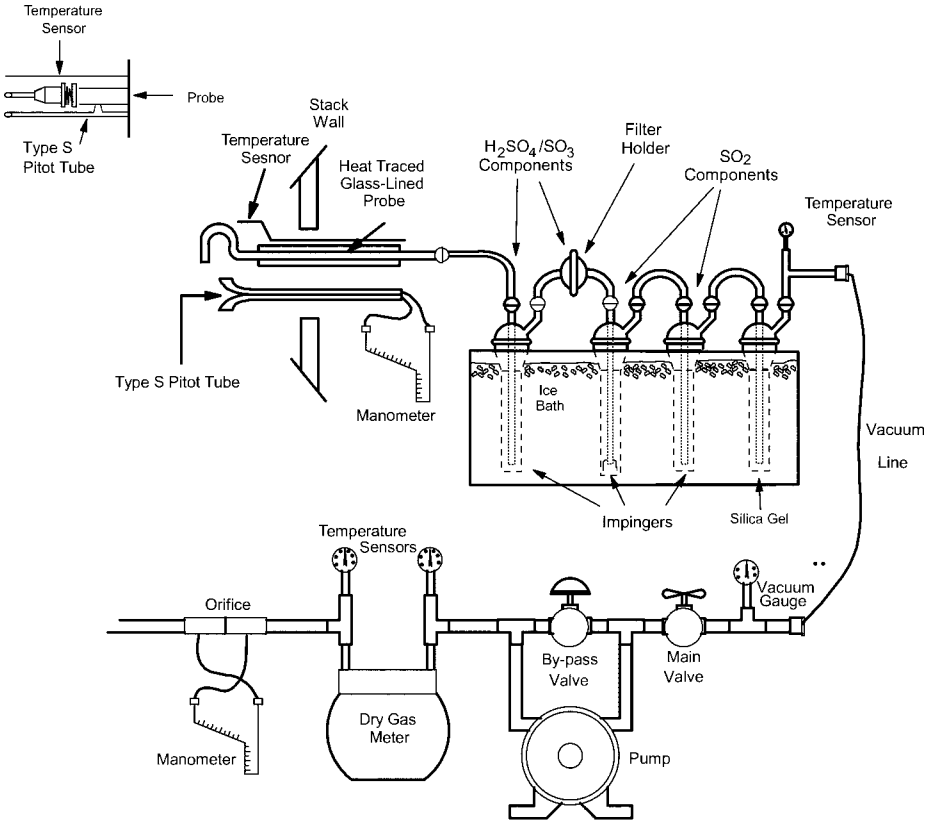

Figure 8-1. Sulfuric Acid Sampling Train

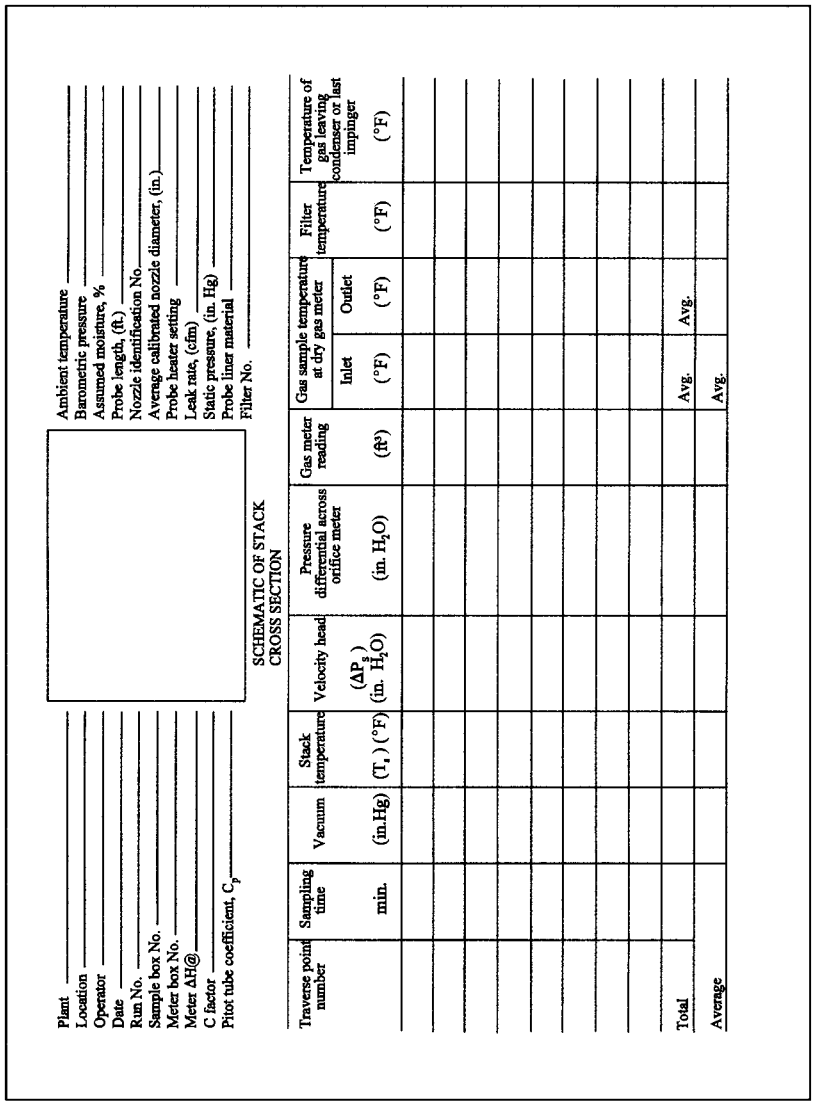

Figure 8-2. Field Data Sheet.

METHOD 9—VISUAL DETERMINATION OF THE OPACITY OF EMISSIONS FROM STATIONARY SOURCES

Many stationary sources discharge visible emissions into the atmosphere; these emissions are usually in the shape of a plume. This method involves the determination of plume opacity by qualified observers. The method includes procedures for the training and certification of observers, and procedures to be used in the field for determination of plume opacity. The appearance of a plume as viewed by an observer depends upon a number of variables, some of which may be controllable and some of which may not be controllable in the field. Variables which can be controlled to an extent to which they no longer exert a significant influence upon

plume appearance include: Angle of the observer with respect to the plume; angle of the observer with respect to the sun; point of observation of attached and detached steam plume; and angle of the observer with respect to a plume emitted from a rectangular stack with a large length to width ratio. The method includes specific criteria applicable to these variables.

Other variables which may not be controllable in the field are luminescence and color contrast between the plume and the background against which the plume is viewed. These variables exert an influence upon the appearance of a plume as viewed by an observer, and can affect the ability of the observer to accurately assign opacity values to the observed plume. Studies of the theory of plume opacity and field studies have demonstrated that a plume is most visible and presents the greatest apparent opacity when viewed against a contrasting background. It follows from this, and is confirmed by field trials, that the opacity of a plume, viewed under conditions where a contrasting background is present can be assigned with the greatest degree of accuracy. However, the potential for a positive error is also the greatest when a plume is viewed under such contrasting conditions. Under conditions presenting a less contrasting background, the apparent opacity of a plume is less and approaches zero as the color and luminescence contrast decrease toward zero. As a result, significant negative bias and negative errors can be made when a plume is viewed under less contrasting conditions. A negative bias decreases rather than increases the possibility that a plant operator will be cited for a violation of opacity standards due to observer error.

Studies have been undertaken to determine the magnitude of positive errors which can be made by qualified observers while reading plumes under contrasting conditions and using the procedures set forth in this method. The results of these studies (field trials) which involve a total of 769 sets of 25 readings each are as follows:

(1) For black plumes (133 sets at a smoke generator), 100 percent of the sets were read with a positive error[1] of less than 7.5 percent opacity; 99 percent were read with a positive error of less than 5 percent opacity.

(2) For white plumes (170 sets at a smoke generator, 168 sets at a coal-fired power plant, 298 sets at a sulfuric acid plant), 99 percent of the sets were read with a positive error of less than 7.5 percent opacity; 95 percent were read with a positive error of less than 5 percent opacity.

[1] For a set, positive error = average opacity determined by observers' 25 observations—average opacity determined from transmissometer's 25 recordings.

The positive observational error associated with an average of twenty-five readings is therefore established. The accuracy of the method must be taken into account when determining possible violations of applicable opacity standards.

1. Principle and Applicability

1.1 Principle. The opacity of emissions from stationary sources is determined visually by a qualified observer.

1.2 Applicability. This method is applicable for the determination of the opacity of emissions from stationary sources pursuant to §60.11(b) and for qualifying observers for visually determining opacity of emissions.

2. Procedures

The observer qualified in accordance with section 3 of this method shall use the following procedures for visually determining the opacity of emissions:

2.1 Position. The qualified observer shall stand at a distance sufficient to provide a clear view of the emissions with the sun oriented in the 140° sector to his back. Consistent with maintaining the above requirement, the observer shall, as much as possible, make his observations from a position such that his line of vision is approximately perpendicular to the plume direction, and when observing opacity of emissions from rectangular outlets (e.g., roof monitors, open baghouses, noncircular stacks), approximately perpendicular to the longer axis of the outlet. The observer's line of sight should not include more than one plume at a time when multiple stacks are involved, and in any case the observer should make his observations with his line of sight perpendicular to the longer axis of such a set of multiple stacks (e.g., stub stacks on baghouses).

2.2 Field Records. The observer shall record the name of the plant, emission location, type facility, observer's name and affiliation, a sketch of the observer's position relative to the source, and the date on a field data sheet (Figure 9–1). The time, estimated distance to the emission location, approximate wind direction, estimated wind speed, description of the sky condition (presence and color of clouds), and plume background are recorded on a field data sheet at the time opacity readings are initiated and completed.

2.3 Observations. Opacity observations shall be made at the point of greatest opacity in that portion of the plume where condensed water vapor is not present. The observer shall not look continuously at the plume, but instead shall observe the plume momentarily at 15-second intervals.

2.3.1 Attached Steam Plumes. When condensed water vapor is present within the

plume as it emerges from the emission outlet, opacity observations shall be made beyond the point in the plume at which condensed water vapor is no longer visible. The observer shall record the approximate distance from the emission outlet to the point in the plume at which the observations are made.

2.3.2 Detached Steam Plume. When water vapor in the plume condenses and becomes visible at a distinct distance from the emission outlet, the opacity of emissions should be evaluated at the emission outlet prior to the condensation of water vapor and the formation of the steam plume.

2.4 Recording Observations. Opacity observations shall be recorded to the nearest 5 percent at 15-second intervals on an observational record sheet. (See Figure 9–2 for an example.) A minimum of 24 observations shall be recorded. Each momentary observation recorded shall be deemed to represent the average opacity of emissions for a 15-second period.

2.5 Data Reduction. Opacity shall be determined as an average of 24 consecutive observations recorded at 15-second intervals. Divide the observations recorded on the record sheet into sets of 24 consecutive observations. A set is composed of any 24 consecutive observations. Sets need not be consecutive in time and in no case shall two sets overlap. For each set of 24 observations, calculate the average by summing the opacity of the 24 observations and dividing this sum by 24. If an applicable standard specifies an averaging time requiring more than 24 observations, calculate the average for all observations made during the specified time period. Record the average opacity on a record sheet. (See Figure 9–1 for an example.)

3. Qualifications and Testing

3.1 Certification Requirements. To receive certification as a qualified observer, a candidate must be tested and demonstrate the ability to assign opacity readings in 5 percent increments to 25 different black plumes and 25 different white plumes, with an error not to exceed 15 percent opacity on any one reading and an average error not to exceed 7.5 percent opacity in each category. Candidates shall be tested according to the procedures described in section 3.2. Smoke generators used pursuant to section 3.2 shall be equipped with a smoke meter which meets the requirements of section 3.3.

The certification shall be valid for a period of 6 months, at which time the qualification procedure must be repeated by any observer in order to retain certification.

3.2 Certification Procedure. The certification test consists of showing the candidate a complete run of 50 plumes—25 black plumes and 25 white plumes—generated by a smoke generator. Plumes within each set of 25 black and 25 white runs shall be presented in random order. The candidate assigns an opacity value to each plume and records his observation on a suitable form. At the completion of each run of 50 readings, the score of the candidate is determined. If a candidate fails to qualify, the complete run of 50 readings must be repeated in any retest. The smoke test may be administered as part of a smoke school or training program, and may be preceded by training or familiarization runs of the smoke generator during which candidates are shown black and white plumes of known opacity.

3.3 Smoke Generator Specifications. Any smoke generator used for the purposes of section 3.2 shall be equipped with a smoke meter installed to measure opacity across the diameter of the smoke generator stack. The smoke meter output shall display instack opacity based upon a pathlength equal to the stack exit diameter, on a full 0 to 100 percent chart recorder scale. The smoke meter optical design and performance shall meet the specifications shown in Table 9–1. The smoke meter shall be calibrated as prescribed in section 3.3.1 prior to the conduct of each smoke reading test. At the completion of each test, the zero and span drift shall be checked and if the drift exceeds ±1 percent opacity, the condition shall be corrected prior to conducting any subsequent test runs. The smoke meter shall be demonstrated, at the time of installation, to meet the specifications listed in Table 9–1. This demonstration shall be repeated following any subsequent repair or replacement of the photocell or associated electronic circuitry including the chart recorder or output meter, or every 6 months, whichever occurs first.

TABLE 9–1—SMOKE METER DESIGN AND PERFORMANCE SPECIFICATIONS

Parameter	Specification
a. Light source	Incandescent lamp operated at nominal rated voltage.
b. Spectral response of photocell.	Photopic (daylight spectral response of the human eye—Citation 3).
c. Angle of view	15° maximum total angle.
d. Angle of projection	15° maximum total angle.
e. Calibration error	±3% opacity, maximum.
f. Zero and span drift	±1% opacity, 30 minutes.
g. Response time	5 seconds.

3.3.1 Calibration. The smoke meter is calibrated after allowing a minimum of 30 minutes warmup by alternately producing simulated opacity of 0 percent and 100 percent. When stable response at 0 percent or 100 percent is noted, the smoke meter is adjusted to produce an output of 0 percent or 100 percent, as appropriate. This calibration shall be repeated until stable 0 percent and 100

percent readings are produced without adjustment. Simulated 0 percent and 100 percent opacity values may be produced by alternately switching the power to the light source on and off while the smoke generator is not producing smoke.

3.3.2 Smoke Meter Evaluation. The smoke meter design and performance are to be evaluated as follows:

3.3.2.1 Light Source. Verify from manufacturer's data and from voltage measurements made at the lamp, as installed, that the lamp is operated within ±5 percent of the nominal rated voltage.

3.3.2.2 Spectral Response of Photocell. Verify from manufacturer's data that the photocell has a photopic response; i.e., the spectral sensitivity of the cell shall closely approximate the standard spectral-luminosity curve for photopic vision which is referenced in (b) of Table 9–1.

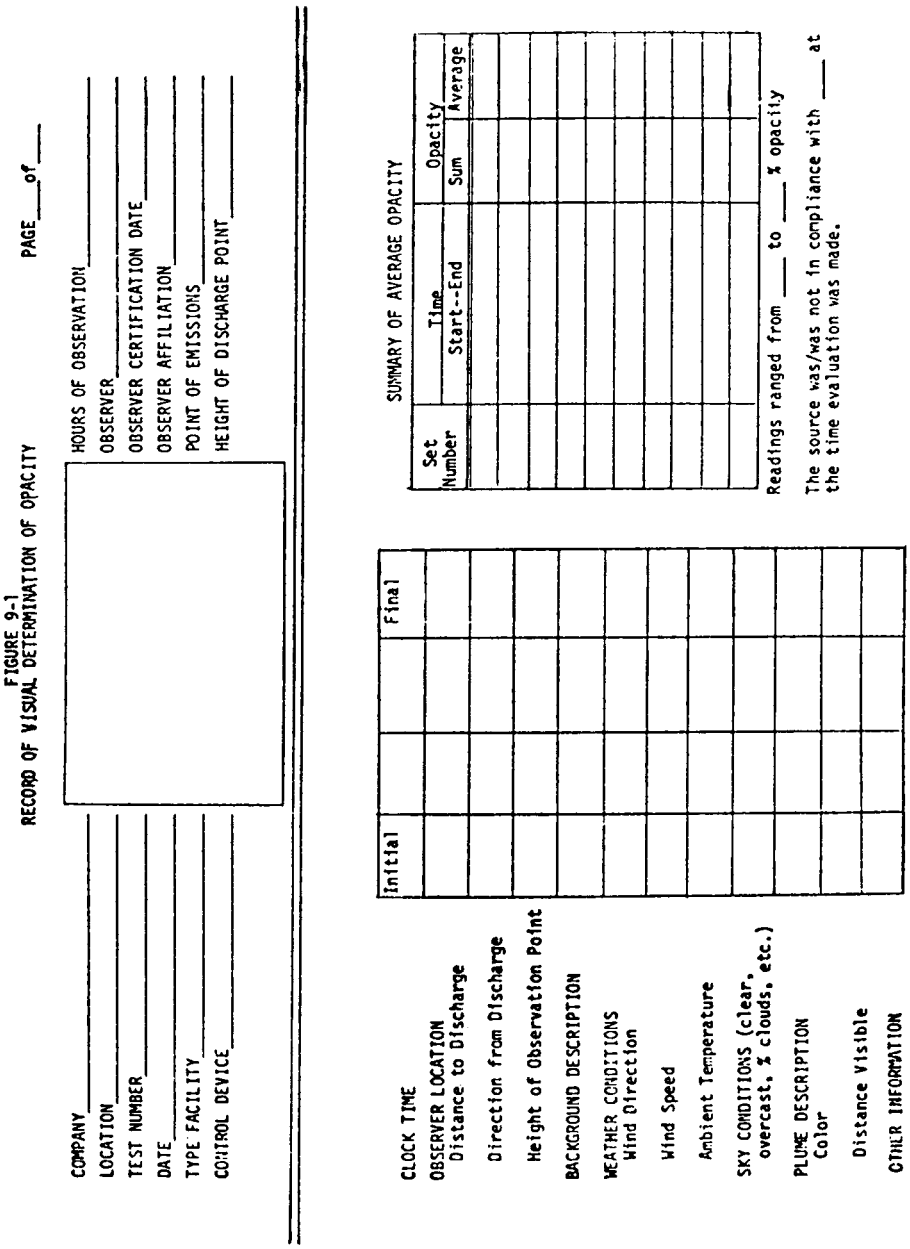

FIGURE 9–2—OBSERVATION RECORD

Page ___ of ___

Company .....
Location .....
Test Number .....
Date.

Observer .....
Type facility .....
Point of emissions .....

Hr.	Min.	Seconds				Steam plume (check if applicable)		Comments
		0	15	30	45	Attached	Detached	
	0							
	1							
	2							
	3							
	4							
	5							
	6							
	7							
	8							
	9							
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FIGURE 9–2—OBSERVATION RECORD (CONTINUED)

Page ____ of ____

Company .....
Location .....
Test Number .....
Date.

Observer .....
Type facility .....
Point of emissions .....

Hr.	Min.	Seconds				Steam plume (check if applicable)		Comments
		0	15	30	45	Attached	Detached	
	30							

Hr.	Min.	Seconds				Steam plume (check if applicable)		Comments
		0	15	30	45	Attached	Detached	
	31							
	32							
	33							
	34							
	35							
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3.3.2.3 Angle of View. Check construction geometry to ensure that the total angle of view of the smoke plume, as seen by the photocell, does not exceed 15°. The total angle of view may be calculated from: $\theta = 2 \tan^{-1} d/2L$, where θ = total angle of view; d = the sum of the photocell diameter + the diameter of the limiting aperture; and L = the distance from the photocell to the limiting aperture. The limiting aperture is the point in the path between the photocell and the smoke plume where the angle of view is most restricted. In smoke generator smoke meters this is normally an orifice plate.

3.3.2.4 Angle of Projection. Check construction geometry to ensure that the total angle of projection of the lamp on the smoke plume does not exceed 15°. The total angle of projection may be calculated from: $\theta = 2 \tan^{-1} d/2L$, where θ = total angle of projection; d = the sum of the length of the lamp

filament + the diameter of the limiting aperture; and L = the distance from the lamp to the limiting aperture.

3.3.2.5 Calibration Error. Using neutral-density filters of known opacity, check the error between the actual response and the theoretical linear response of the smoke meter. This check is accomplished by first calibrating the smoke meter according to 3.3.1 and then inserting a series of three neutral-density filters of nominal opacity of 20, 50, and 75 percent in the smoke meter pathlength. Filters calibrated within ±2 percent shall be used. Care should be taken when inserting the filters to prevent stray light from affecting the meter. Make a total of five nonconsecutive readings for each filter. The maximum error on any one reading shall be 3 percent opacity.

3.3.2.6 Zero and Span Drift. Determine the zero and span drift by calibrating and operating the smoke generator in a normal manner over a 1-hour period. The drift is measured by checking the zero and span at the end of this period.

3.3.2.7 Response Time. Determine the response time by producing the series of five simulated 0 percent and 100 percent opacity values and observing the time required to reach stable response. Opacity values of 0 percent and 100 percent may be simulated by alternately switching the power to the light source off and on while the smoke generator is not operating.

4. Bibliography

1. Air Pollution Control District Rules and Regulations, Los Angeles County Air Pollution Control District, Regulation IV, Prohibitions, Rule 50.

2. Weisburd, Melvin I., Field Operations and Enforcement Manual for Air, U.S. Environmental Protection Agency, Research Triangle Park, NC. APTD–1100, August 1972, pp. 4.1–4.36.

3. Condon, E.U., and Odishaw, H., Handbook of Physics, McGraw-Hill Co., New York, NY, 1958, Table 3.1, p. 6–52.

Alternate Method 1—Determination of the Opacity of Emissions From Stationary Sources Remotely by Lidar

This alternate method provides the quantitative determination of the opacity of an emissions plume remotely by a mobile lidar system (laser radar; Light Detection and Ranging). The method includes procedures for the calibration of the lidar and procedures to be used in the field for the lidar determination of plume opacity. The lidar is used to measure plume opacity during either day or nighttime hours because it contains its own pulsed light source or transmitter. The operation of the lidar is not dependent upon ambient lighting conditions (light, dark, sunny or cloudy).

The lidar mechanism or technique is applicable to measuring plume opacity at numerous wavelengths of laser radiation. However, the performance evaluation and calibration test results given in support of this method apply only to a lidar that employs a ruby (red light) laser [Reference 5.1].

1. Principle and Applicability

1.1 Principle. The opacity of visible emissions from stationary sources (stacks, roof vents, etc.) is measured remotely by a mobile lidar (laser radar).

1.2 Applicability. This method is applicable for the remote measurement of the opacity of visible emissions from stationary sources during both nighttime and daylight conditions, pursuant to 40 CFR §60.11(b). It is also applicable for the calibration and performance verification of the mobile lidar for the measurement of the opacity of emissions. A performance/design specification for a basic lidar system is also incorporated into this method.

1.3 Definitions.

Azimuth angle: The angle in the horizontal plane that designates where the laser beam is pointed. It is measured from an arbitrary fixed reference line in that plane.

Backscatter: The scattering of laser light in a direction opposite to that of the incident laser beam due to reflection from particulates along the beam's atmospheric path which may include a smoke plume.

Backscatter signal: The general term for the lidar return signal which results from laser light being backscattered by atmospheric and smoke plume particulates.

Convergence distance: The distance from the lidar to the point of overlap of the lidar receiver's field-of-view and the laser beam.

Elevation angle: The angle of inclination of the laser beam referenced to the horizontal plane.

Far region: The region of the atmosphere's path along the lidar line-of-sight beyond or behind the plume being measured.

Lidar: Acronym for Light Detection and Ranging.

Lidar range: The range or distance from the lidar to a point of interest along the lidar line-of-sight.

Near region: The region of the atmospheric path along the lidar line-of-sight between the lidar's convergence distance and the plume being measured.

Opacity: One minus the optical transmittance of a smoke plume, screen target, etc.

Pick interval: The time or range intervals in the lidar backscatter signal whose minimum average amplitude is used to calculate opacity. Two pick intervals are required, one in the near region and one in the far region.

Plume: The plume being measured by lidar.

Plume signal: The backscatter signal resulting from the laser light pulse passing through a plume.

$1/R^2$Correction: The correction made for the systematic decrease in lidar backscatter signal amplitude with range.

Reference signal: The backscatter signal resulting from the laser light pulse passing through ambient air.

Sample interval: The time period between successive samples for a digital signal or between successive measurements for an analog signal.

Signal spike: An abrupt, momentary increase and decrease in signal amplitude.

Source: The source being tested by lidar.

Time reference: The time (t_o) when the laser pulse emerges from the laser, used as the reference in all lidar time or range measurements.

2. Procedures

The mobile lidar calibrated in accordance with Paragraph 3 of this method shall use the following procedures for remotely measuring the opacity of stationary source emissions:

2.1 Lidar Position. The lidar shall be positioned at a distance from the plume sufficient to provide an unobstructed view of the source emissions. The plume must be at a range of at least 50 meters or three consecutive pick intervals (whichever is greater) from the lidar's transmitter/receiver convergence distance along the line-of-sight. The maximum effective opacity measurement distance of the lidar is a function of local atmospheric conditions, laser beam diameter, and plume diameter. The test position of the lidar shall be selected so that the diameter of the laser beam at the measurement point within the plume shall be no larger than three-fourths the plume diameter. The beam diameter is calculated by Equation (AM1–1):

$$D(\text{lidar}) = A + R\varphi \leq 0.75\ D(\text{Plume}) \quad \text{(AM1–1)}$$

Where:

D(Plume) = diameter of the plume (cm),
φ = laser beam divergence measured in radians
R = range from the lidar to the source (cm)
D(Lidar) = diameter of the laser beam at range R (cm),
A = diameter of the laser beam or pulse where it leaves the laser.

The lidar range, R, is obtained by aiming and firing the laser at the emissions source structure immediately below the outlet. The range value is then determined from the backscatter signal which consists of a signal spike (return from source structure) and the atmospheric backscatter signal [Reference 5.1]. This backscatter signal should be recorded.

When there is more than one source of emissions in the immediate vicinity of the plume, the lidar shall be positioned so that the laser beam passes through only a single plume, free from any interference of the other plumes for a minimum of 50 meters or three consecutive pick intervals (whichever is greater) in each region before and beyond the plume along the line-of-sight (determined from the backscatter signals). The lidar shall initially be positioned so that its line-of-sight is approximately perpendicular to the plume.

When measuring the opacity of emissions from rectangular outlets (e.g., roof monitors, open baghouses, noncircular stacks, etc.), the lidar shall be placed in a position so that its line-of-sight is approximately perpendicular to the longer (major) axis of the outlet.

2.2 Lidar Operational Restrictions. The lidar receiver shall not be aimed within an angle of ±15° (cone angle) of the sun.

This method shall not be used to make opacity measurements if thunderstorms, snowstorms, hail storms, high wind, high-ambient dust levels, fog or other atmospheric conditions cause the reference signals to consistently exceed the limits specified in section 2.3.

2.3 Reference Signal Requirements. Once placed in its proper position for opacity measurement, the laser is aimed and fired with the line-of-sight near the outlet height and rotated horizontally to a position clear of the source structure and the associated plume. The backscatter signal obtained from this position is called the ambient-air or reference signal. The lidar operator shall inspect this signal [Section V of Reference 5.1] to: (1) determine if the lidar line-of-sight is free from interference from other plumes and from physical obstructions such as cables, power lines, etc., for a minimum of 50 meters or three consecutive pick intervals (whichever is greater) in each region before and beyond the plume, and (2) obtain a qualitative measure of the homogeneity of the ambient air by noting any signal spikes.

Should there be any signal spikes on the reference signal within a minimum of 50 meters or three consecutive pick intervals (whichever is greater) in each region before and beyond the plume, the laser shall be fired three more times and the operator shall inspect the reference signals on the display. If the spike(s) remains, the azimuth angle shall be changed and the above procedures conducted again. If the spike(s) disappears in all three reference signals, the lidar line-of-sight is acceptable if there is shot-to-shot consistency and there is no interference from other plumes.

Shot-to-shot consistency of a series of reference signals over a period of twenty seconds is verified in either of two ways. (1) The lidar operator shall observe the reference signal amplitudes. For shot-to-shot consistency the ratio of R_f to R_n [amplitudes of the near and far region pick intervals (Section 2.6.1)] shall vary by not more than ±6% between shots; or (2) the lidar operator shall accept any one of the reference signals and

treat the other two as plume signals; then the opacity for each of the subsequent reference signals is calculated (Equation AM1–2). For shot-to-shot consistency, the opacity values shall be within ±3% of 0% opacity and the associated S_o values less than or equal to 8% (full scale) [Section 2.6].

If a set of reference signals fails to meet the requirements of this section, then all plume signals [Section 2.4] from the last set of acceptable reference signals to the failed set shall be discarded.

2.3.1 Initial and Final Reference Signals. Three reference signals shall be obtained within a 90-second time period prior to any data run. A final set of three reference signals shall be obtained within three (3) minutes after the completion of the same data run.

2.3.2 Temporal Criterion for Additional Reference Signals. An additional set of reference signals shall be obtained during a data run if there is a change in wind direction or plume drift of 30° or more from the direction that was prevalent when the last set of reference signals was obtained. An additional set of reference signals shall also be obtained if there is an increase in value of S_{In} (near region standard deviation, Equation AM1–5) or S_{If} (far region standard deviation, Equation AM1–6) that is greater than 6% (full scale) over the respective values calculated from the immediately previous plume signal, and this increase in value remains for 30 seconds or longer. An additional set of reference signals shall also be obtained if there is a change in amplitude in either the near or the far region of the plume signal, that is greater than 6% of the near signal amplitude and this change in amplitude remains for 30 seconds or more.

2.4 Plume Signal Requirements. Once properly aimed, the lidar is placed in operation with the nominal pulse or firing rate of six pulses/minute (1 pulse/10 seconds). The lidar operator shall observe the plume backscatter signals to determine the need for additional reference signals as required by section 2.3.2. The plume signals are recorded from lidar start to stop and are called a data run. The length of a data run is determined by operator discretion. Short-term stops of the lidar to record additional reference signals do not constitute the end of a data run if plume signals are resumed within 90 seconds after the reference signals have been recorded, and the total stop or interrupt time does not exceed 3 minutes.

2.4.1 Non-hydrated Plumes. The laser shall be aimed at the region of the plume which displays the greatest opacity. The lidar operator must visually verify that the laser is aimed clearly above the source exit structure.

2.4.2 Hydrated Plumes. The lidar will be used to measure the opacity of hydrated or so-called steam plumes. As listed in the reference method, there are two types, i.e., attached and detached steam plumes.

2.4.2.1 Attached Steam Plumes. When condensed water vapor is present within a plume, lidar opacity measurements shall be made at a point within the residual plume where the condensed water vapor is no longer visible. The laser shall be aimed into the most dense region (region of highest opacity) of the residual plume.

During daylight hours the lidar operator locates the most dense portion of the residual plume visually. During nighttime hours a high-intensity spotlight, night vision scope, or low light level TV, etc., can be used as an aid to locate the residual plume. If visual determination is ineffective, the lidar may be used to locate the most dense region of the residual plume by repeatedly measuring opacity, along the longitudinal axis or center of the plume from the emissions outlet to a point just beyond the steam plume. The lidar operator should also observe color differences and plume reflectivity to ensure that the lidar is aimed completely within the residual plume. If the operator does not obtain a clear indication of the location of the residual plume, this method shall not be used.

Once the region of highest opacity of the residual plume has been located, aiming adjustments shall be made to the laser line-of-sight to correct for the following: movement to the region of highest opacity out of the lidar line-of-sight (away from the laser beam) for more than 15 seconds, expansion of the steam plume (air temperature lowers and/or relative humidity increases) so that it just begins to encroach on the field-of-view of the lidar's optical telescope receiver, or a decrease in the size of the steam plume (air temperature higher and/or relative humidity decreases) so that regions within the residual plume whose opacity is higher than the one being monitored, are present.

2.4.2.2 Detached Steam Plumes. When the water vapor in a hydrated plume condenses and becomes visible at a finite distance from the stack or source emissions outlet, the opacity of the emissions shall be measured in the region of the plume clearly above the emissions outlet and below condensation of the water vapor.

During daylight hours the lidar operators can visually determine if the steam plume is detached from the stack outlet. During nighttime hours a high-intensity spotlight, night vision scope, low light level TV, etc., can be used as an aid in determining if the steam plume is detached. If visual determination is ineffective, the lidar may be used to determine if the steam plume is detached by repeatedly measuring plume opacity from the outlet to the steam plume along the plume's longitudinal axis or center line. The lidar operator should also observe color differences and plume reflectivity to detect a

detached plume. If the operator does not obtain a clear indication of the location of the detached plume, this method shall not be used to make opacity measurements between the outlet and the detached plume.

Once the determination of a detached steam plume has been confirmed, the laser shall be aimed into the region of highest opacity in the plume between the outlet and the formation of the steam plume. Aiming adjustments shall be made to the lidar's line-of-sight within the plume to correct for changes in the location of the most dense region of the plume due to changes in wind direction and speed or if the detached steam plume moves closer to the source outlet encroaching on the most dense region of the plume. If the detached steam plume should move too close to the source outlet for the lidar to make interference-free opacity measurements, this method shall not be used.

2.5 Field Records. In addition to the recording recommendations listed in other sections of this method the following records should be maintained. Each plume measured should be uniquely identified. The name of the facility, type of facility, emission source type, geographic location of the lidar with respect to the plume, and plume characteristics should be recorded. The date of the test, the time period that a source was monitored, the time (to the nearest second) of each opacity measurement, and the sample interval should also be recorded. The wind speed, wind direction, air temperature, relative humidity, visibility (measured at the lidar's position), and cloud cover should be recorded at the beginning and end of each time period for a given source. A small sketch depicting the location of the laser beam within the plume should be recorded.

If a detached or attached steam plume is present at the emissions source, this fact should be recorded. Figures AM1–I and AM1–II are examples of logbook forms that may be used to record this type of data. Magnetic tape or paper tape may also be used to record data.

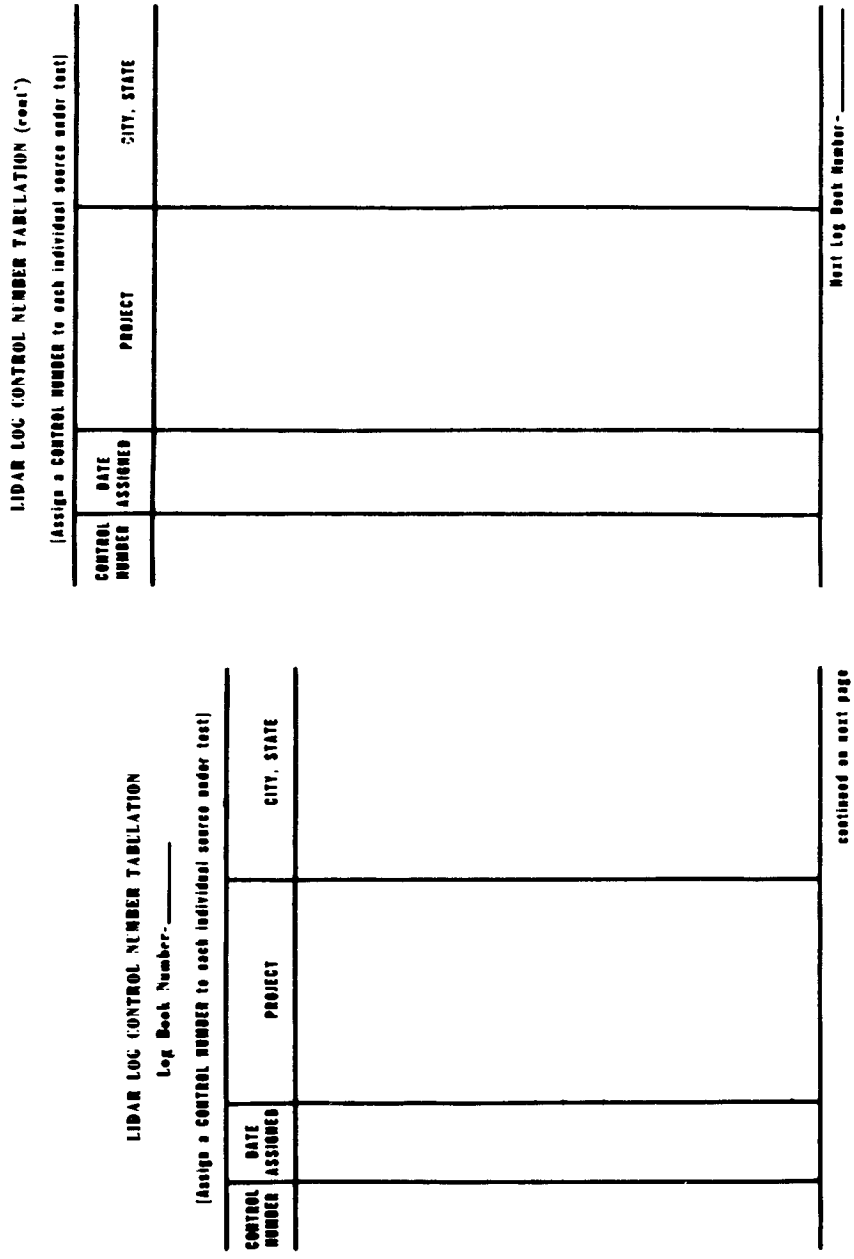


Figure AM1-1 Lidar Log Control Number Tabulation

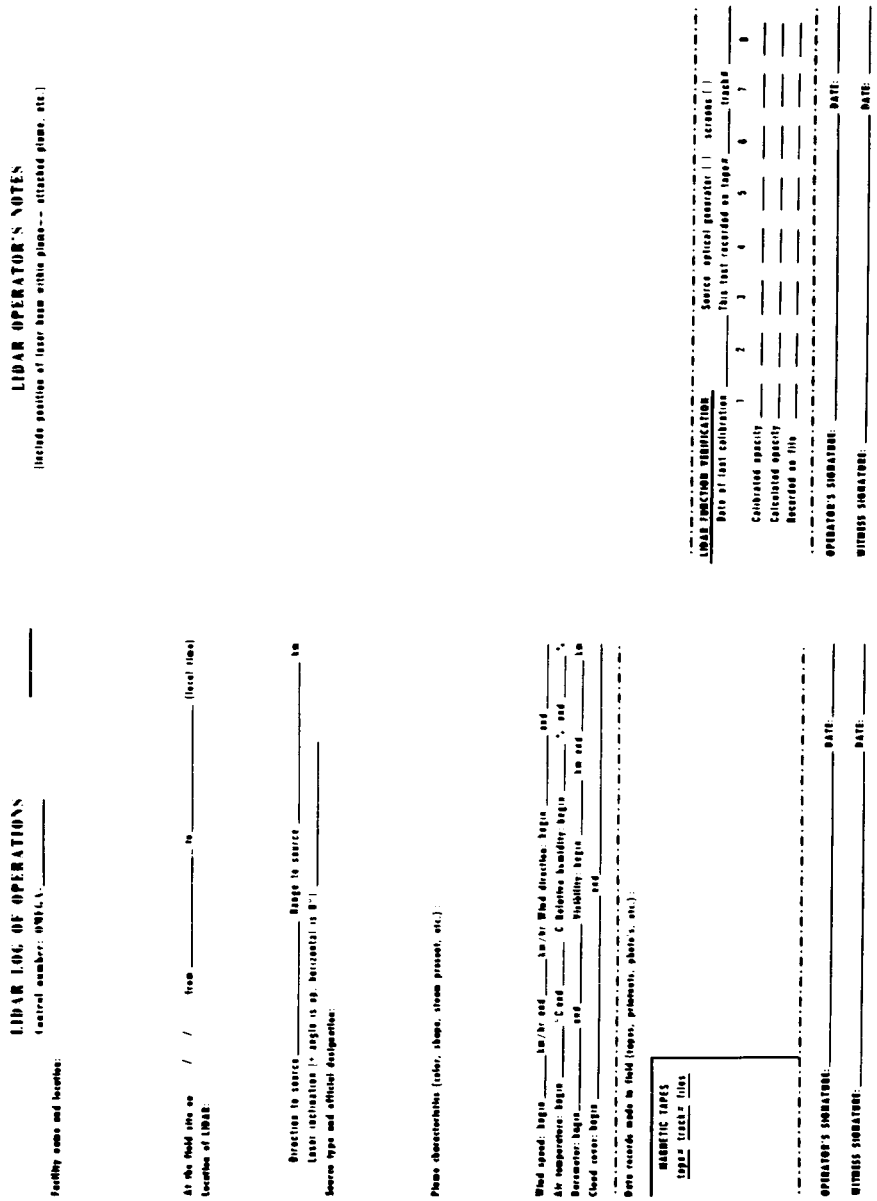
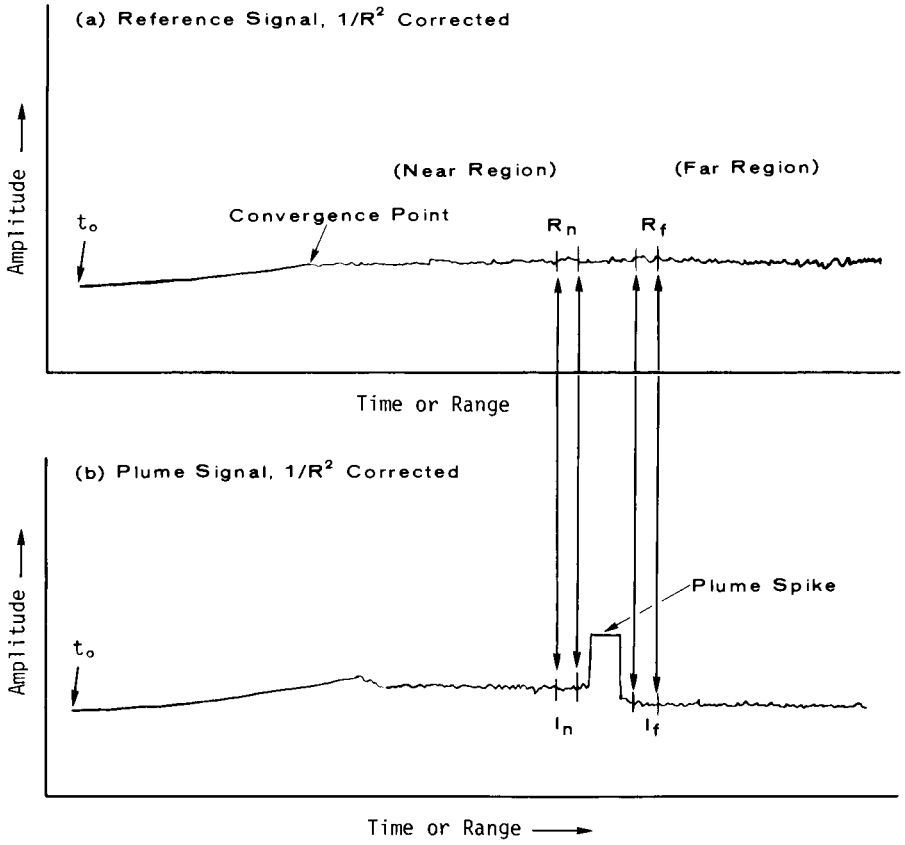


Figure AM1-11 Lidar Log Of Operations



(a) Reference signal, $1/R^2$-corrected. This reference signal is for plume signal (b). R_n, R_f are chosen to coincide with I_n, I_f.

(b) Plume signal, $1/R^2$-corrected. The plume spike and the decrease in the backscatter signal amplitude in the far region are due to the opacity of the plume. I_n, I_f are chosen as indicated in Section 2.6.

Figure AM1-III. Plots of Lidar Backscatter Signals

2.6 Opacity Calculation and Data Analysis. Referring to the reference signal and plume signal in Figure AM1–III, the measured opacity (O_p) in percent for each lidar measurement is calculated using Equation AM1–2. ($O_p = 1 - T_p$; T_p is the plume transmittance.)

$$O_p = (100\%)\left[1 - \left(\frac{I_f}{R_f}\frac{R_n}{I_n}\right)^{\frac{1}{2}}\right], \qquad \text{(AM1-2)}$$

Where:

I_n = near-region pick interval signal amplitude, plume signal, $1/R^2$ corrected,

I_f = far-region pick interval signal amplitude, plume signal, $1/R^2$ corrected,

R_n = near-region pick interval signal amplitude, reference signal, $1/R^2$ corrected, and

R_f = far-region pick interval signal amplitude, reference signal, $1/R^2$ corrected.

The $1/R^2$ correction to the plume and reference signal amplitudes is made by multiplying the amplitude for each successive sample interval from the time reference, by the square of the lidar time (or range) associated with that sample interval [Reference 5.1].

The first step in selecting the pick intervals for Equation AM1–2 is to divide the plume signal amplitude by the reference signal amplitude at the same respective ranges to obtain a ''normalized'' signal. The pick intervals selected using this normalized signal, are a minimum of 15 m (100 nanoseconds) in length and consist of at least 5 contiguous sample intervals. In addition, the following criteria, listed in order of importance, govern pick interval selection. (1) The intervals shall be in a region of the normalized signal where the reference signal meets the requirements of section 2.3 and is everywhere greater than zero. (2) The intervals (near and far) with the minimum average amplitude are chosen. (3) If more than one interval with the same minimum average amplitude is found, the interval closest to the plume is chosen. (4) The standard deviation, S_o, for the calculated opacity shall be 8% or less. (S_o is calculated by Equation AM1–7).

If S_o is greater than 8%, then the far pick interval shall be changed to the next interval of minimal average amplitude. If S_o is still greater than 8%, then this procedure is repeated for the far pick interval. This procedure may be repeated once again for the near pick interval, but if S_o remains greater than 8%, the plume signal shall be discarded.

The reference signal pick intervals, R_n and R_f, must be chosen over the same time interval as the plume signal pick intervals, I_n and I_f, respectively [Figure AM1–III]. Other methods of selecting pick intervals may be used if they give equivalent results. Field-oriented examples of pick interval selection are available in Reference 5.1.

The average amplitudes for each of the pick intervals, I_n, I_f, R_n, R_f, shall be calculated by averaging the respective individual amplitudes of the sample intervals from the plume signal and the associated reference signal each corrected for $1/R^2$. The amplitude of I_n shall be calculated according to Equation (AM–3).

$$I_n = \frac{1}{m}\sum_{i=1}^{m} I_{ni}, \qquad \text{(AM1-3)}$$

Where:

I_{ni} = the amplitude of the ith sample interval (near-region),

Σ = sum of the individual amplitudes for the sample intervals,

m = number of sample intervals in the pick interval, and

I_n = average amplitude of the near-region pick interval.

Similarly, the amplitudes for I_f, R_n, and R_f are calculated with the three expressions in Equation (AM1–4).

$$I_f = \frac{1}{m}\sum_{i=1}^{m} I_{fi}, \quad R_n = \frac{1}{m}\sum_{i=1}^{m} R_{ni}, \quad R_f = \frac{1}{m}\sum_{i=1}^{m} R_{fi}. \qquad \text{(AM1-4)}$$

The standard deviation, S_{In}, of the set of amplitudes for the near-region pick interval, I_n, shall be calculated using Equation (AM1–5).

Similarly, the standard deviations S_{If}, S_{Rn}, and S_{Rf} are calculated with the three expressions in Equation (AM1–6).

$$S_{In} = \left[\sum_{i=1}^{m} \frac{(I_{ni} - I_n)^2}{(m-1)} \right]^{1/2} \quad S_{If} = \left[\sum_{i=1}^{m} \frac{(I_{fi} - I_f)^2}{(m-1)} \right]^{1/2} \quad \text{(AM1-5)}$$

$$S_{Rn} = \left[\sum_{i=1}^{m} \frac{(R_{ni} - R_n)^2}{(m-1)} \right]^{1/2},$$

$$S_{Rf} = \left[\sum_{i=1}^{m} \frac{(R_{fi} - R_f)^2}{(m-1)} \right]^{1/2}. \quad \text{(AM1-6)}$$

The standard deviation, S_o, for each associated opacity value, O_p, shall be calculated using Equation (AM1–7).

$$S_o = \frac{(100\%)}{2} \left(\frac{I_f}{R_f} \frac{R_n}{I_n} \right)^{1/2} \left[\frac{S_{In}^2}{I_n^2} + \frac{S_{If}^2}{I_f^2} + \frac{S_{Rn}^2}{R_n^2} + \frac{S_{Rf}^2}{R_f^2} \right]^{1/2} \quad \text{(AM1-7)}$$

The calculated values of I_n, I_f, R_n, R_f, S_{In}, S_{If}, S_{Rn}, S_{Rf}, O_p, and S_o should be recorded. Any plume signal with an S_o greater than 8% shall be discarded.

2.6.1 Azimuth Angle Correction. If the azimuth angle correction to opacity specified in this section is performed, then the elevation angle correction specified in section 2.6.2 shall not be performed. When opacity is measured in the residual region of an attached steam plume, and the lidar line-of-sight is not perpendicular to the plume, it may be necessary to correct the opacity measured by the lidar to obtain the opacity that would be measured on a path perpendicular to the plume. The following method, or any other method which produces equivalent results, shall be used to determine the need for a correction, to calculate the correction, and to document the point within the plume at which the opacity was measured.

Figure AM1–IV(b) shows the geometry of the opacity correction. L′ is the path through the plume along which the opacity measurement is made. P′ is the path perpendicular to the plume at the same point. The angle ε is the angle between L′ and the plume center line. The angle (π/2-ε), is the angle between the L′ and P′. The measured opacity, O_p, measured along the path L′ shall be corrected to obtain the corrected opacity, O_{pc}, for the path P′, using Equation (AM1–8).

$$O_{pc} = (100\%) \left[1 - (1 - 0.01\, O_p)^{\text{Cos}\,(\pi/2-\varepsilon)} \right]$$

$$= (100\%) \left[1 - (1 - 0.01\, O_p)^{\text{Sin}\,\varepsilon} \right] \quad \text{(AM1-8)}$$

The correction in Equation (AM1–8) shall be performed if the inequality in Equation (AM1–9) is true.

$$\varepsilon \geq \text{Sin}^{-1}\left[\frac{\ln (101 - O_p)}{\ln (100 - O_p)}\right] \qquad \text{(AM1-9)}$$

Figure AM1–IV(a) shows the geometry used to calculate ε and the position in the plume at which the lidar measurement is made. This analysis assumes that for a given lidar measurement, the range from the lidar to the plume, the elevation angle of the lidar from the horizontal plane, and the azimuth angle of the lidar from an arbitrary fixed reference in the horizontal plane can all be obtained directly.

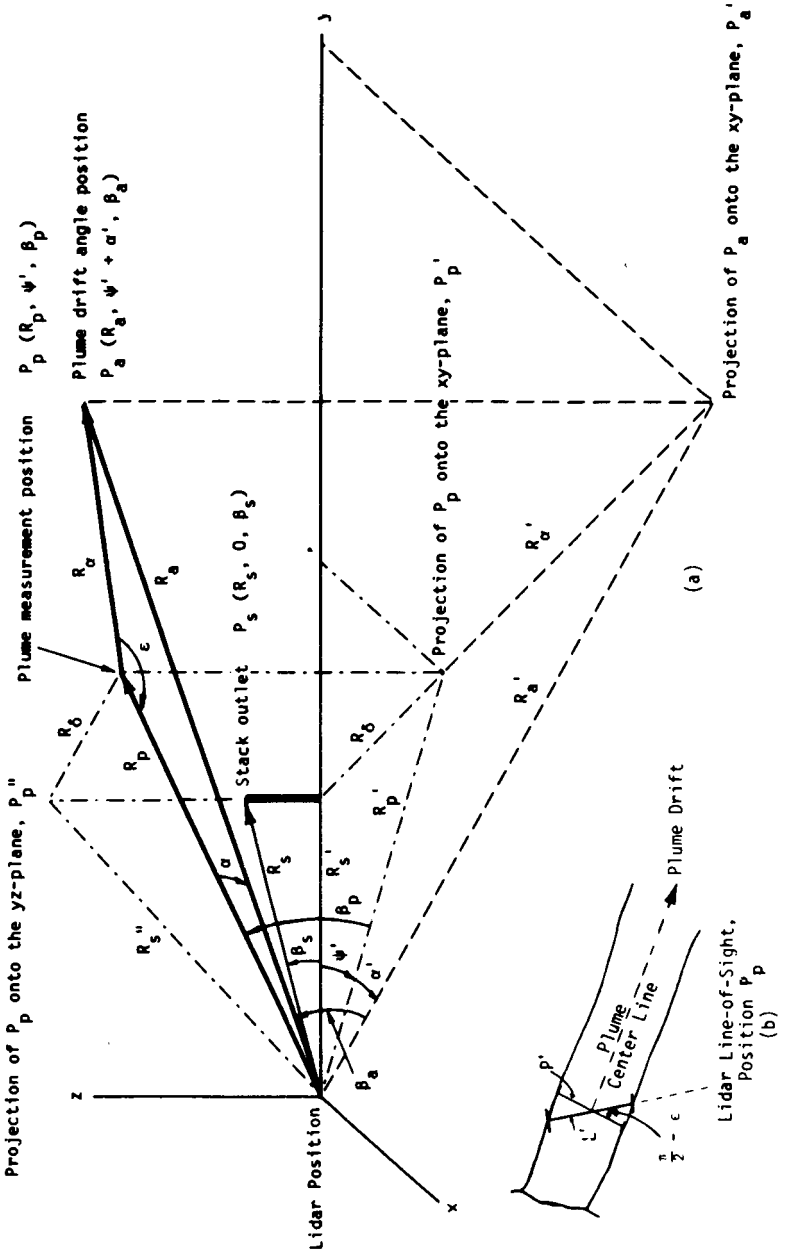


Figure AMI - IV. Correction in Opacity for Drift of the Residual Region of an Attached Steam Plume.

R_s = range from lidar to source*
β_s = elevation angle of R_s*
R_p = range from lidar to plume at the opacity measurement point*
β_p = elevation angle of R_p*
R_a = range from lidar to plume at some arbitrary point, P_a, so the drift angle of the plume can be determined*

β_a = elevation angle of R_a*
α = angle between R_p and R_a
R'_s = projection of R_s in the horizontal plane
R'_p = projection of R_p in the horizontal plane
R'_a = projection of R_a in the horizontal plane
ψ' = angle between R'_s and R'_p*
α' = angle between R'_p and R'_a*
R≤ = distance from the source to the opacity measurement point projected in the horizontal plane
Rθ = distance from opacity measurement point P_p to the point in the plume P_a.

$$O_{pc} = 1 - (1 - O_p)^{\mathrm{Cos}\,(\pi/2-\varepsilon)} = 1 - (1 - O_p)^{\mathrm{Sin}\,\varepsilon} \qquad \text{(AMI-8)}$$

The correction angle ε shall be determined using Equation AM1–10.

Where:

$\alpha = \mathrm{Cos}^{-1}\,(\mathrm{Cos}\beta_p\,\mathrm{Cos}\beta_a\,\mathrm{Cos}\alpha' + \mathrm{Sin}\beta_p\,\mathrm{Sin}\beta_a)$, and

$R\theta = (R_p 2 + R_a 2 - 2\,R_p\,R_a\,\mathrm{Cos}\alpha)^{1/2}$

R≤, the distance from the source to the opacity measurement point projected in the horizontal plane, shall be determined using Equation AM1–11.

$$R_\delta = (R'^2_s + R'^2_p - 2R'_sR'_p\mathrm{Cos}\psi')^{\frac{1}{2}}, \qquad \text{(AM1-11)}$$

Where:

$R'_s = R_s\,\mathrm{Cos}\,\beta_s$, and
$R'_p = R_p\,\mathrm{Cos}\,\beta_p$.

In the special case where the plume centerline at the opacity measurement point is horizontal, parallel to the ground, Equation AM1–12 may be used to determine ε instead of Equation AM1–10.

$$\varepsilon = \mathrm{Cos}^{-1}\left[\frac{R_p^2 + R_\delta^2 - R''^2_s}{2\,R_p\,R_\delta}\right] \qquad \text{(AM1-12)}$$

Where:

$R''_s = (R'^2_s + R_p^2\mathrm{Sin}^2\beta_p)^{1/2}$.

If the angle ε is such that ε≤30° or ε ≥150°, the azimuth angle correction shall not be performed and the associated opacity value shall be discarded.

2.6.2 Elevation Angle Correction. An individual lidar-measured opacity, O_p, shall be corrected for elevation angle if the laser elevation or inclination angle, β_p [Figure AM1–V], is greater than or equal to the value calculated in Equation AM1–13.

$$\beta_p \geq \mathrm{Cos}^{-1}\left[\frac{\ln\,(101 - O_p)}{\ln\,(100 - O_p)}\right] \qquad \text{(AM1-13)}$$

The measured opacity, O_p, along the lidar path L, is adjusted to obtain the corrected opacity, O_{pc}, for the actual plume (horizontal) path, P, by using Equation (AM1–14).

*Obtained directly from lidar. These values should be recorded.

$$O_{pc} = (100\%)\left[1-\left(1-0.01\,O_p\right)^{Cos\beta}p\right], \qquad (AM1\text{-}14)$$

Where:

β_p = lidar elevation or inclination angle,
O_p = measured opacity along path L, and
O_{pc} = corrected opacity for the actual plume thickness P.

The values for β_p, O_p and O_{pc} should be recorded.

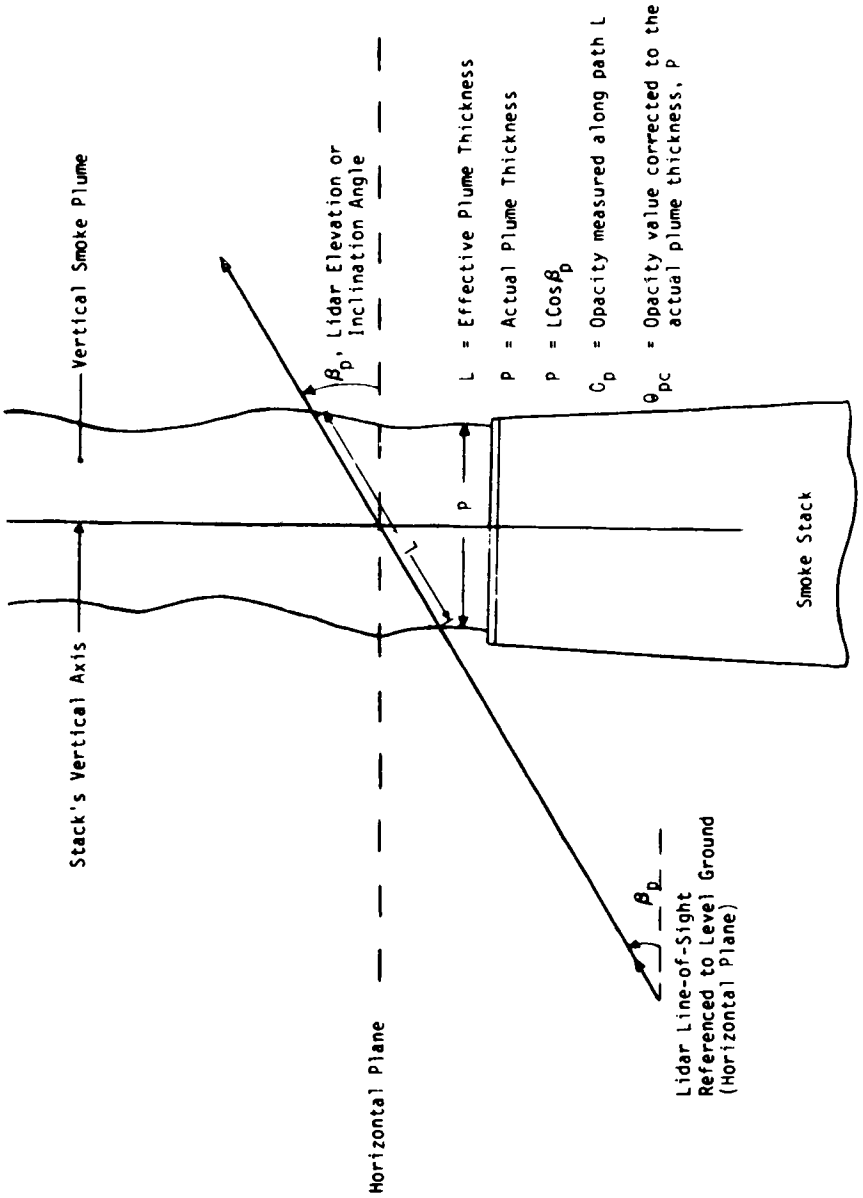


Figure AM1-V. Elevation Angle Correction for Vertical Plumes.

2.6.3 Determination of Actual Plume Opacity. Actual opacity of the plume shall be determined by Equation AM1–15.

$$O_{pa} = O_{pc} - [2\ S_o + 5\%]. \quad \text{(AM1-15)}$$

2.6.4 Calculation of Average Actual Plume Opacity. The average of the actual plume opacity, O_{pa}, shall be calculated as the average of the consecutive individual actual opacity values, O_{pa}, by Equation AM1–16.

$$\bar{O}_{pa} = \frac{1}{n}\sum_{k=1}^{n}(O_{pa})_k \quad , \qquad \text{(AM1-16)}$$

Where:

$(O_{pa})_k$ = the kth actual opacity value in an averaging interval containing n opacity values; k is a summing index.

Σ = the sum of the individual actual opacity values.

n = the number of individual actual opacity values contained in the averaging interval.

O_{pa} = average actual opacity calculated over the averaging interval.

3. Lidar Performance Verification

The lidar shall be subjected to two types of performance verifications that shall be performed in the field. The annual calibration, conducted at least once a year, shall be used to directly verify operation and performance of the entire lidar system. The routine verification, conducted for each emission source measured, shall be used to insure proper performance of the optical receiver and associated electronics.

3.1 Annual Calibration Procedures. Either a plume from a smoke generator or screen targets shall be used to conduct this calibration.

If the screen target method is selected, five screens shall be fabricated by placing an opaque mesh material over a narrow frame (wood, metal extrusion, etc.). The screen shall have a surface area of at least one square meter. The screen material should be chosen for precise optical opacities of about 10, 20, 40, 60, and 80%. Opacity of each target shall be optically determined and should be recorded. If a smoke generator plume is selected, it shall meet the requirements of section 3.3 of Reference Method 9. This calibration shall be performed in the field during calm (as practical) atmospheric conditions. The lidar shall be positioned in accordance with section 2.1.

The screen targets must be placed perpendicular to and coincident with the lidar line-of-sight at sufficient height above the ground (suggest about 30 ft) to avoid ground-level dust contamination. Reference signals shall be obtained just prior to conducting the calibration test.

The lidar shall be aimed through the center of the plume within 1 stack diameter of the exit, or through the geometric center of the screen target selected. The lidar shall be set in operation for a 6-minute data run at a nominal pulse rate of 1 pulse every 10 seconds. Each backscatter return signal and each respective opacity value obtained from the smoke generator transmissometer, shall be obtained in temporal coincidence. The data shall be analyzed and reduced in accordance with section 2.6 of this method. This calibration shall be performed for 0% (clean air), and at least five other opacities (nominally 10, 20, 40, 60, and 80%).

The average of the lidar opacity values obtained during a 6-minute calibration run shall be calculated and should be recorded. Also the average of the opacity values obtained from the smoke generator transmissometer for the same 6-minute run shall be calculated and should be recorded.

Alternate calibration procedures that do not meet the above requirements but produce equivalent results may be used.

3.2 Routine Verification Procedures. Either one of two techniques shall be used to conduct this verification. It shall be performed at least once every 4 hours for each emission source measured. The following parameters shall be directly verified.

1) The opacity value of 0% plus a minimum of 5 (nominally 10, 20, 40, 60, and 80%) opacity values shall be verified through the PMT detector and data processing electronics.

2) The zero-signal level (receiver signal with no optical signal from the source present) shall be inspected to insure that no spurious noise is present in the signal. With the entire lidar receiver and analog/digital electronics turned on and adjusted for normal operating performance, the following procedures shall be used for Techniques 1 and 2, respectively.

3.2.1 Procedure for Technique 1. This test shall be performed with no ambient or stray light reaching the PMT detector. The narrow band filter (694.3 nanometers peak) shall be removed from its position in front of the PMT detector. Neutral density filters of nominal opacities of 10, 20, 40, 60, and 80% shall be used. The recommended test configuration is depicted in Figure AM1–VI.

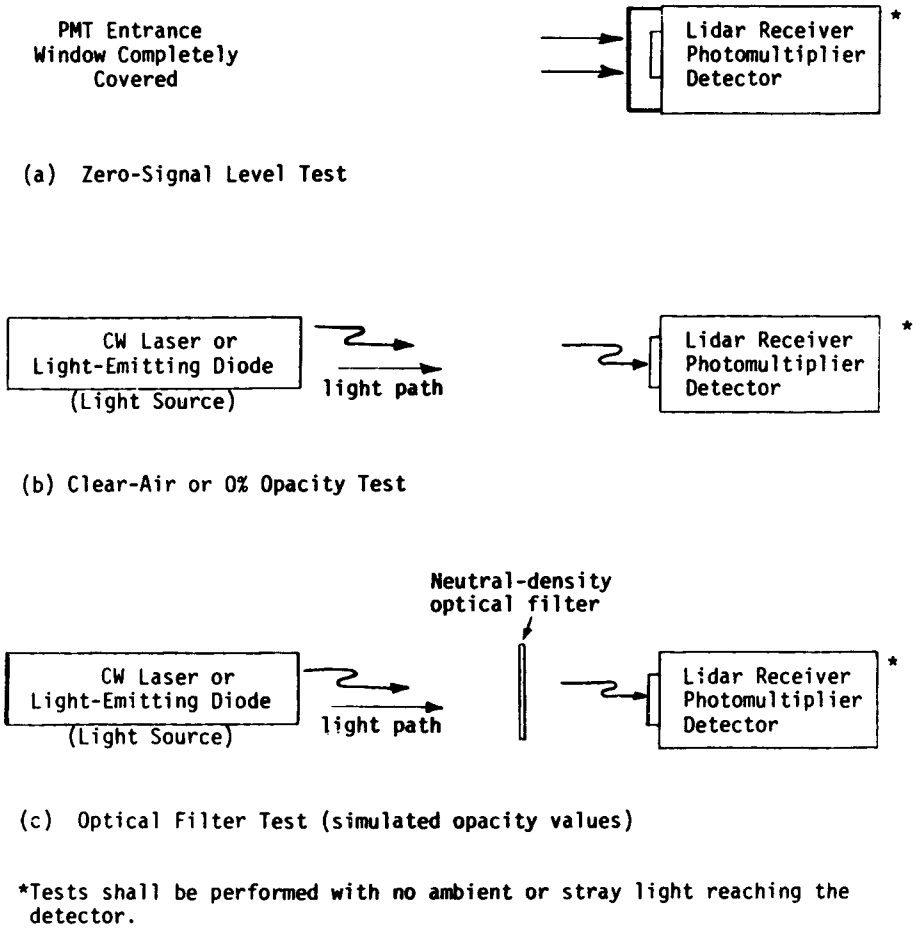


Figure AM1–VI. Test Configuration for Technique 1.

The zero-signal level shall be measured and should be recorded, as indicated in Figure AM1–VI(a). This simulated clear-air or 0% opacity value shall be tested in using the selected light source depicted in Figure AM1–VI(b).

The light source either shall be a continuous wave (CW) laser with the beam mechanically chopped or a light emitting diode controlled with a pulse generator (rectangular pulse). (A laser beam may have to be attenuated so as not to saturate the PMT detector). This signal level shall be measured

and should be recorded. The opacity value is calculated by taking two pick intervals [Section 2.6] about 1 microsecond apart in time and using Equation (AM1–2) setting the ratio $R_n/R_f = 1$. This calculated value should be recorded.

The simulated clear-air signal level is also employed in the optical test using the neutral density filters. Using the test configuration in Figure AM1–VI(c), each neutral density filter shall be separately placed into the light path from the light source to the PMT detector. The signal level shall be measured and should be recorded. The opacity value for each filter is calculated by taking the signal level for that respective filter (I_f), dividing it by the 0% opacity signal level (I_n) and performing the remainder of the calculation by Equation (AM1–2) with $R_n/R_f = 1$. The calculated opacity value for each filter should be recorded.

The neutral density filters used for Technique 1 shall be calibrated for actual opacity with accuracy of ±2% or better. This calibration shall be done monthly while the filters are in use and the calibrated values should be recorded.

3.2.2 Procedure for Technique 2. An optical generator (built-in calibration mechanism) that contains a light-emitting diode (red light for a lidar containing a ruby laser) is used. By injecting an optical signal into the lidar receiver immediately ahead of the PMT detector, a backscatter signal is simulated. With the entire lidar receiver electronics turned on and adjusted for normal operating performance, the optical generator is turned on and the simulation signal (corrected for $1/R^2$) is selected with no plume spike signal and with the opacity value equal to 0%. This simulated clear-air atmospheric return signal is displayed on the system's video display. The lidar operator then makes any fine adjustments that may be necessary to maintain the system's normal operating range.

The opacity values of 0% and the other five values are selected one at a time in any order. The simulated return signal data should be recorded. The opacity value shall be calculated. This measurement/calculation shall be performed at least three times for each selected opacity value. While the order is not important, each of the opacity values from the optical generator shall be verified. The calibrated optical generator opacity value for each selection should be recorded.

The optical generator used for Technique 2 shall be calibrated for actual opacity with an accuracy of ±1% or better. This calibration shall be done monthly while the generator is in use and calibrated value should be recorded.

Alternate verification procedures that do not meet the above requirements but produce equivalent results may be used.

3.3 Deviation. The permissible error for the annual calibration and routine verification are:

3.3.1 Annual Calibration Deviation.

3.3.1.1 Smoke Generator. If the lidar-measured average opacity for each data run is not within ±5% (full scale) of the respective smoke generator's average opacity over the range of 0% through 80%, then the lidar shall be considered out of calibration.

3.3.1.2 Screens. If the lidar-measured average opacity for each data run is not within ±3% (full scale) of the laboratory-determined opacity for each respective simulation screen target over the range of 0% through 80%, then the lidar shall be considered out of calibration.

3.3.2 Routine Verification Error. If the lidar-measured average opacity for each neutral density filter (Technique 1) or optical generator selection (Technique 2) is not within ±3% (full scale) of the respective laboratory calibration value then the lidar shall be considered non-operational.

4. Performance/Design Specification for Basic Lidar System

4.1 Lidar Design Specification. The essential components of the basic lidar system are a pulsed laser (transmitter), optical receiver, detector, signal processor, recorder, and an aiming device that is used in aiming the lidar transmitter and receiver. Figure AM1–VII shows a functional block diagram of a basic lidar system.

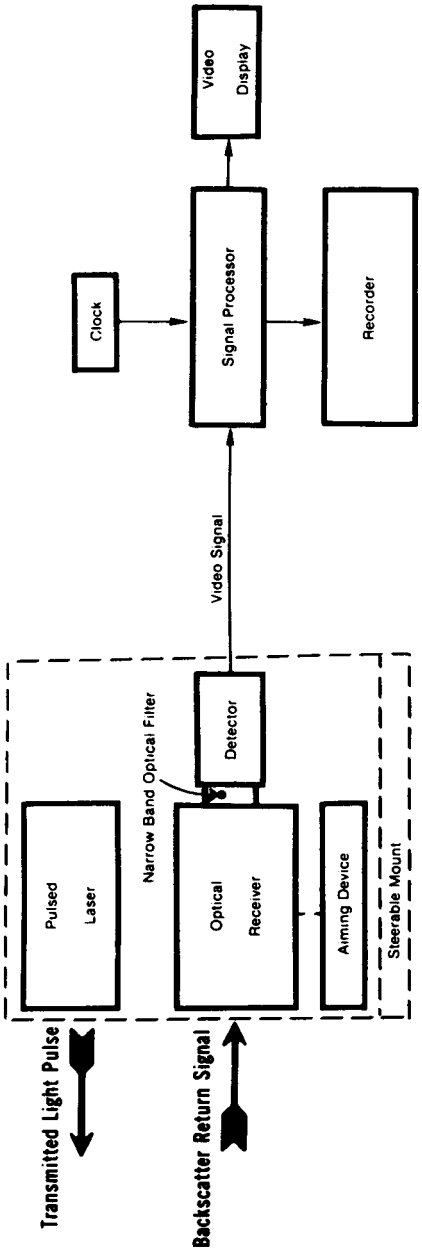


Figure AM1-VII. Functional Block Diagram of a Basic Lidar System

4.2 Performance Evaluation Tests. The owner of a lidar system shall subject such a lidar system to the performance verification tests described in section 3, prior to first use of this method. The annual calibration shall be performed for three separate, complete

runs and the results of each should be recorded. The requirements of section 3.3.1 must be fulfilled for each of the three runs.

Once the conditions of the annual calibration are fulfilled the lidar shall be subjected to the routine verification for three separate complete runs. The requirements of section 3.3.2 must be fulfilled for each of the three runs and the results should be recorded. The Administrator may request that the results of the performance evaluation be submitted for review.

5. References

5.1 The Use of Lidar for Emissions Source Opacity Determination, U.S. Environmental Protection Agency, National Enforcement Investigations Center, Denver, CO. EPA–330/1–79–003–R, Arthur W. Dybdahl, current edition [NTIS No. PB81–246662].

5.2 Field Evaluation of Mobile Lidar for the Measurement of Smoke Plume Opacity, U.S. Environmental Protection Agency, National Enforcement Investigations Center, Denver, CO. EPA/NEIC-TS-128, February 1976.

5.3 Remote Measurement of Smoke Plume Transmittance Using Lidar, C. S. Cook, G. W. Bethke, W. D. Conner (EPA/RTP). Applied Optics 11, pg 1742. August 1972.

5.4 Lidar Studies of Stack Plumes in Rural and Urban Environments, EPA–650/4–73–002, October 1973.

5.5 American National Standard for the Safe Use of Lasers ANSI Z 136.1–176, March 8, 1976.

5.6 U.S. Army Technical Manual TB MED 279, Control of Hazards to Health from Laser Radiation, February 1969.

5.7 Laser Institute of America Laser Safety Manual, 4th Edition.

5.8 U.S. Department of Health, Education and Welfare, Regulations for the Administration and Enforcement of the Radiation Control for Health and Safety Act of 1968, January 1976.

5.9 Laser Safety Handbook, Alex Mallow, Leon Chabot, Van Nostrand Reinhold Co., 1978.

Method 10—Determination of Carbon Monoxide Emissions From Stationary Sources (Instrumental Analyzer Procedure)

1.0 Scope and Application

What is Method 10?

Method 10 is a procedure for measuring carbon monoxide (CO) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis. This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 4—Determination of Moisture Content in Stack Gases.

(c) Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure).

1.1 Analytes. What does this method determine? This method measures the concentration of carbon monoxide.

Analyte	CAS No.	Sensitivity
CO	630–08–0	Typically <2% of Calibration Span.

1.2 Applicability. When is this method required? The use of Method 10 may be required by specific New Source Performance Standards, State Implementation Plans, and permits where CO concentrations in stationary source emissions must be measured, either to determine compliance with an applicable emission standard or to conduct performance testing of a continuous emission monitoring system (CEMS). Other regulations may also require the use of Method 10.

1.3 Data Quality Objectives. Refer to section 1.3 of Method 7E.

2.0 Summary of Method

In this method, you continuously or intermittently sample the effluent gas and convey the sample to an analyzer that measures the concentration of CO. You must meet the performance requirements of this method to validate your data.

3.0 Definitions

Refer to section 3.0 of Method 7E for the applicable definitions.

4.0 Interferences

Substances having a strong absorption of infrared energy may interfere to some extent in some analyzers. Instrumental correction may be used to compensate for the interference. You may also use silica gel and ascarite traps to eliminate the interferences. If this option is used, correct the measured

gas volume for the carbon dioxide (CO_2) removed in the trap.

5.0 Safety

Refer to section 5.0 of Method 7E.

6.0 Equipment and Supplies

What do I need for the measurement system?

6.1 Continuous Sampling. Figure 7E–1 of Method 7E is a schematic diagram of an acceptable measurement system. The components are the same as those in sections 6.1 and 6.2 of Method 7E, except that the CO analyzer described in section 6.2 of this method must be used instead of the analyzer described in section 6.2 of Method 7E. You must follow the noted specifications in section 6.1 of Method 7E except that the requirements to use stainless steel, Teflon, or non-reactive glass filters do not apply. Also, a heated sample line is not required to transport dry gases or for systems that measure the CO concentration on a dry basis.

6.2 Integrated Sampling.

6.2.1 Air-Cooled Condenser or Equivalent. To remove any excess moisture.

6.2.2 Valve. Needle valve, or equivalent, to adjust flow rate.

6.2.3 Pump. Leak-free diaphragm type, or equivalent, to transport gas.

6.2.4 Rate Meter. Rotameter, or equivalent, to measure a flow range from 0 to 1.0 liter per minute (0.035 cfm).

6.2.5 Flexible Bag. Tedlar, or equivalent, with a capacity of 60 to 90 liters (2 to 3 ft^3). (Verify through the manufacturer that the Tedlar alternative is suitable for CO and make this verified information available for inspection.) Leak-test the bag in the laboratory before using by evacuating with a pump followed by a dry gas meter. When the evacuation is complete, there should be no flow through the meter.

6.2.6 Sample Tank. Stainless steel or aluminum tank equipped with a pressure indicator with a minimum volume of 4 liters.

6.3 What analyzer must I use? You must use an instrument that continuously measures CO in the gas stream and meets the specifications in section 13.0. The dual-range analyzer provisions in section 6.2.8.1 of Method 7E apply.

7.0 Reagents and Standards

7.1 Calibration Gas. What calibration gases do I need? Refer to section 7.1 of Method 7E for the calibration gas requirements.

7.2 Interference Check. What additional reagents do I need for the interference check? Use the appropriate test gases listed in Table 7E–3 of Method 7E (i.e., potential interferents, as identified by the instrument manufacturer) to conduct the interference check.

8.0 Sample Collection, Preservation, Storage, and Transport

Emission Test Procedure

8.1 Sampling Site and Sampling Points. You must follow section 8.1 of Method 7E.

8.2 Initial Measurement System Performance Tests. You must follow the procedures in section 8.2 of Method 7E. If a dilution-type measurement system is used, the special considerations in section 8.3 of Method 7E also apply.

8.3 Interference Check. You must follow the procedures of section 8.2.7 of Method 7E.

8.4 Sample Collection.

8.4.1 Continuous Sampling. You must follow the procedures of section 8.4 of Method 7E.

8.4.2 Integrated Sampling. Evacuate the flexible bag or sample tank. Set up the equipment as shown in Figure 10–1 with the bag disconnected. Place the probe in the stack and purge the sampling line. Connect the bag, making sure that all connections are leak-free. Sample at a rate proportional to the stack velocity. If needed, the CO_2 content of the gas may be determined by using the Method 3 integrated sample procedures, or by weighing an ascarite CO_2 removal tube used and computing CO_2 concentration from the gas volume sampled and the weight gain of the tube. Data may be recorded on a form similar to Table 10–1. If a sample tank is used for sample collection, follow procedures similar to those in sections 8.1.2, 8.2.3, 8.3, and 12.4 of Method 25 as appropriate to prepare the tank, conduct the sampling, and correct the measured sample concentration.

8.5 Post-Run System Bias Check, Drift Assessment, and Alternative Dynamic Spike Procedure. You must follow the procedures in sections 8.5 and 8.6 of Method 7E.

9.0 Quality Control

Follow the quality control procedures in section 9.0 of Method 7E.

10.0 Calibration and Standardization

Follow the procedures for calibration and standardization in section 10.0 of Method 7E.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the procedures for calculations and data analysis in section 12.0 of Method 7E, as applicable, substituting CO for NO_X as applicable.

12.1 Concentration Correction for CO_2 Removal. Correct the CO concentration for CO_2 removal (if applicable) using Eq. 10–1.

$$C_{Avg} = C_{CO\ stack}\left(1 - F_{CO2}\right)$$

Where:

C_{Avg} = Average gas concentration for the test run, ppm.

$C_{CO\ stack}$ = Average unadjusted stack gas CO concentration indicated by the data recorder for the test run, ppmv.

F_{CO2} = Volume fraction of CO_2 in the sample, i.e., percent CO_2 from Orsat analysis divided by 100.

13.0 Method Performance

The specifications for analyzer calibration error, system bias, drift, interference check, and alternative dynamic spike procedure are the same as in section 13.0 of Method 7E.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

The dynamic spike procedure and the manufacturer stability test are the same as in sections 16.1 and 16.3 of Method 7E

17.0 References

1. ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards— September 1997 as amended, EPA–600/R–97/121

18.0 Tables, Diagrams, Flowcharts, and Validation Data

Figure 10-1. Integrated Gas Sampling Train.

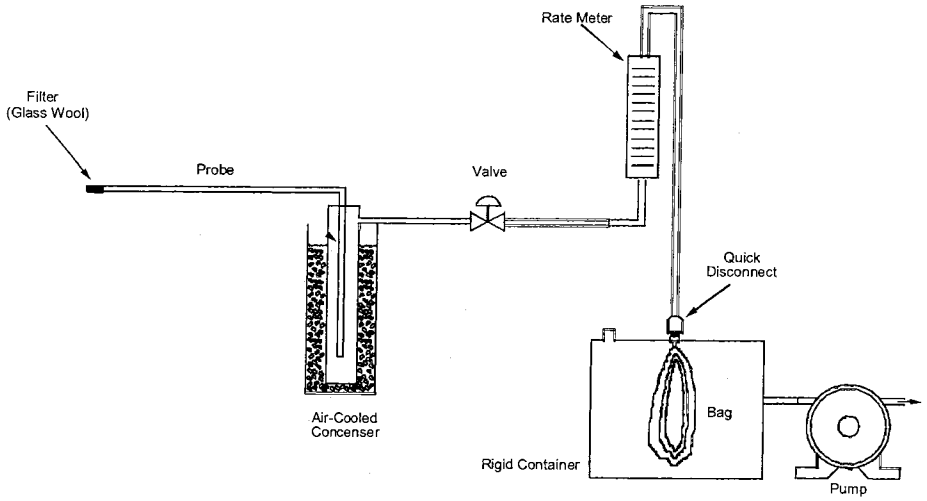


TABLE 10–1—FIELD DATA

[Integrated sampling]

Location:	Date:	
Test:	Operator:	
Clock Time	Rotameter Reading liters/min (cfm)	Comments

TABLE 10–1—FIELD DATA—Continued

[Integrated sampling]

METHOD 10A—DETERMINATION OF CARBON MONOXIDE EMISSIONS IN CERTIFYING CONTINUOUS EMISSION MONITORING SYSTEMS AT PETROLEUM REFINERIES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 4, and Method 5.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Carbon monoxide (CO)	630–08–0	3 ppmv

1.2 Applicability. This method is applicable for the determination of CO emissions at petroleum refineries. This method serves as the reference method in the relative accuracy test for nondispersive infrared (NDIR) CO continuous emission monitoring systems (CEMS) that are required to be installed in petroleum refineries on fluid catalytic cracking unit catalyst regenerators (§60.105(a)(2) of this part).

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

An integrated gas sample is extracted from the stack, passed through an alkaline permanganate solution to remove sulfur oxides and nitrogen oxides, and collected in a Tedlar or equivalent bag. (Verify through the manufacturer that the Tedlar alternative is suitable for NO and make this verified information available for inspection.) The CO concentration in the sample is measured spectrophotometrically using the reaction of CO with *p*-sulfaminobenzoic acid.

3.0 Definitions [Reserved]

4.0 Interferences

Sulfur oxides, nitric oxide, and other acid gases interfere with the colorimetric reaction. They are removed by passing the sampled gas through an alkaline potassium permanganate scrubbing solution. Carbon dioxide (CO_2) does not interfere, but, because it is removed by the scrubbing solution, its concentration must be measured independently and an appropriate volume correction made to the sampled gas.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs.

Reacts exothermically with limited amounts of water.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling train shown in Figure 10A–1 is required for sample collection. Component parts are described below:

6.1.1 Probe. Stainless steel, sheathed Pyrex glass, or equivalent, equipped with a glass wool plug to remove particulate matter.

6.1.2 Sample Conditioning System. Three Greenburg-Smith impingers connected in series with leak-free connections.

6.1.3 Pump. Leak-free pump with stainless steel and Teflon parts to transport sample at a flow rate of 300 ml/min (0.01 ft^3/min) to the flexible bag.

6.1.4 Surge Tank. Installed between the pump and the rate meter to eliminate the pulsation effect of the pump on the rate meter.

6.1.5 Rate Meter. Rotameter, or equivalent, to measure flow rate at 300 ml/min (0.01 ft^3/min). Calibrate according to section 10.2.

6.1.6 Flexible Bag. Tedlar, or equivalent, with a capacity of 10 liters (0.35 ft^3) and equipped with a sealing quick-connect plug. The bag must be leak-free according to section 8.1. For protection, it is recommended that the bag be enclosed within a rigid container.

6.1.7 Sample Tank. Stainless steel or aluminum tank equipped with a pressure indicator with a minimum volume of 10 liters.

6.1.8 Valves. Stainless-steel needle valve to adjust flow rate, and stainless-steel 3-way valve, or equivalent.

6.1.9 CO_2 Analyzer. Fyrite, or equivalent, to measure CO_2 concentration to within 0.5 percent.

6.1.10 Volume Meter. Dry gas meter, capable of measuring the sample volume under calibration conditions of 300 ml/min (0.01 ft^3/min) for 10 minutes.

6.1.11 Pressure Gauge. A water filled U-tube manometer, or equivalent, of about 30 cm (12 in.) to leak-check the flexible bag.

6.2 Sample Analysis.

6.2.1 Spectrophotometer. Single- or double-beam to measure absorbance at 425 and 600 nm. Slit width should not exceed 20 nm.

6.2.2 Spectrophotometer Cells. 1-cm pathlength.

6.2.3 Vacuum Gauge. U-tube mercury manometer, 1 meter (39 in.), with 1-mm divisions, or other gauge capable of measuring pressure to within 1 mm Hg.

6.2.4 Pump. Capable of evacuating the gas reaction bulb to a pressure equal to or less than 40 mm Hg absolute, equipped with coarse and fine flow control valves.

6.2.5 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm Hg.

6.2.6 Reaction Bulbs. Pyrex glass, 100-ml with Teflon stopcock (Figure 10A–2), leak-free at 40 mm Hg, designed so that 10 ml of the colorimetric reagent can be added and removed easily and accurately. Commercially available gas sample bulbs such as Supelco Catalog No. 2–2161 may also be used.

6.2.7 Manifold. Stainless steel, with connections for three reaction bulbs and the appropriate connections for the manometer and sampling bag as shown in Figure 10A–3.

6.2.8 Pipets. Class A, 10–ml size.

6.2.9 Shaker Table. Reciprocating-stroke type such as Eberbach Corporation, Model 6015. A rocking arm or rotary-motion type shaker may also be used. The shaker must be large enough to accommodate at least six gas sample bulbs simultaneously. It may be necessary to construct a table top extension for most commercial shakers to provide sufficient space for the needed bulbs (Figure 10A–4).

6.2.10 Valve. Stainless steel shut-off valve.

6.2.11 Analytical Balance. Capable of weighing to 0.1 mg.

7.0 Reagents and Standards

Unless otherwise indicated, all reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, the best available grade shall be used.

7.1 Sample Collection.

7.1.1 Water. Deionized distilled, to conform to ASTM D 1193–77 or 91, Type 3 (incorporated by reference—see §60.17). If high concentrations of organic matter are not expected to be present, the potassium permanganate test for oxidizable organic matter may be omitted.

7.1.2 Alkaline Permanganate Solution, 0.25 M $KMnO_4$/1.5 M Sodium Hydroxide (NaOH). Dissolve 40 g $KMnO_4$ and 60 g NaOH in approximately 900 ml water, cool, and dilute to 1 liter.

7.2 Sample Analysis.

7.2.1 Water. Same as in section 7.1.1.

7.2.2 1 M Sodium Hydroxide Solution. Dissolve 40 g NaOH in approximately 900 ml of water, cool, and dilute to 1 liter.

7.2.3 0.1 M NaOH Solution. Dilute 50 ml of the 1 M NaOH solution prepared in section 7.2.2 to 500 ml.

7.2.4 0.1 M Silver Nitrate ($AgNO_3$) Solution. Dissolve 8.5 g $AgNO_3$ in water, and dilute to 500 ml.

7.2.5 0.1 M Para-Sulfaminobenzoic Acid (p-SABA) Solution. Dissolve 10.0 g p-SABA in 0.1 M NaOH, and dilute to 500 ml with 0.1 M NaOH.

7.2.6 Colorimetric Solution. To a flask, add 100 ml of 0.1 M p-SABA solution and 100 ml of 0.1 M $AgNO_3$ solution. Mix, and add 50 ml of 1 M NaOH with shaking. The resultant solution should be clear and colorless. This solution is acceptable for use for a period of 2 days.

7.2.7 Standard Gas Mixtures. Traceable to National Institute of Standards and Technology (NIST) standards and containing between 50 and 1000 ppm CO in nitrogen. At least two concentrations are needed to span each calibration range used (Section 10.3). The calibration gases must be certified by the manufacturer to be within 2 percent of the specified concentrations.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sample Bag or Tank Leak-Checks. While a leak-check is required after bag or sample tank use, it should also be done before the bag or sample tank is used for sample collection. The tank should be leak-checked according to the procedure specified in section 8.1.2 of Method 25. The bag should be leak-checked in the inflated and deflated condition according to the following procedure:

8.1.1 Connect the bag to a water manometer, and pressurize the bag to 5 to 10 cm H_2O (2 to 4 in H_2O). Allow the bag to stand for 60 minutes. Any displacement in the water manometer indicates a leak.

8.1.2 Evacuate the bag with a leakless pump that is connected to the downstream side of a flow indicating device such as a 0- to 100-ml/min rotameter or an impinger containing water. When the bag is completely evacuated, no flow should be evident if the bag is leak-free.

8.2 Sample Collection.

8.2.1 Evacuate and leak check the sample bag or tank as specified in section 8.1. Assemble the apparatus as shown in Figure 10A–1. Loosely pack glass wool in the tip of the probe. Place 400 ml of alkaline permanganate solution in the first two impingers and 250 ml in the third. Connect the pump to the third impinger, and follow this with the surge tank, rate meter, and 3-way valve. Do not connect the bag or sample tank to the system at this time.

8.2.2 Leak-check the sampling system by plugging the probe inlet, opening the 3-way valve, and pulling a vacuum of approximately 250 mm Hg on the system while observing the rate meter for flow. If flow is indicated on the rate meter, do not proceed further until the leak is found and corrected.

8.2.3 Purge the system with sample gas by inserting the probe into the stack and drawing the sample gas through the system at 300 ml/min ±10 percent for 5 minutes. Connect the evacuated bag or sample tank to the system, record the starting time, and sample at a rate of 300 ml/min for 30 minutes, or until the bag is nearly full, or the sample tank reaches ambient pressure. Record the sampling time, the barometric pressure, and the ambient temperature. Purge the system as described above immediately before each sample.

8.2.4 The scrubbing solution is adequate for removing sulfur oxides and nitrogen oxides from 50 liters (1.8 ft^3) of stack gas when the concentration of each is less than 1,000 ppm and the CO_2 concentration is less than 15 percent. Replace the scrubber solution after every fifth sample.

8.3 Carbon Dioxide Measurement. Measure the CO_2 content in the stack to the nearest 0.5 percent each time a CO sample is collected. A simultaneous grab sample analyzed by the Fyrite analyzer is acceptable.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.1	Sampling equipment leak-checks and calibration.	Ensure accuracy and precision of sampling measurements.
10.3	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Gas Bulb Calibration. Weigh the empty bulb to the nearest 0.1 g. Fill the bulb to the stopcock with water, and again weigh to the nearest 0.1 g. Subtract the tare weight, and calculate the volume in liters to three significant figures using the density of water at the measurement temperature. Record the volume on the bulb. Alternatively, mark an identification number on the bulb, and record the volume in a notebook.

10.2 Rate Meter Calibration. Assemble the system as shown in Figure 10A–1 (the impingers may be removed), and attach a volume meter to the probe inlet. Set the rotameter at 300 ml/min, record the volume meter reading, start the pump, and pull ambient air through the system for 10 minutes. Record the final volume meter reading. Repeat the procedure and average the results to determine the volume of gas that passed through the system.

10.3 Spectrophotometer Calibration Curve.

10.3.1 Collect the standards as described in section 8.2. Prepare at least two sets of three bulbs as standards to span the 0 to 400 or 400 to 1000 ppm range. If any samples span both

concentration ranges, prepare a calibration curve for each range using separate reagent blanks. Prepare a set of three bulbs containing colorimetric reagent but no CO to serve as a reagent blank. Analyze each standard and blank according to the sample analysis procedure of section 11.0 Reject the standard set where any of the individual bulb absorbances differs from the set mean by more than 10 percent.

10.3.2 Calculate the average absorbance for each set (3 bulbs) of standards using Equation 10A–1 and Table 10A–1. Construct a graph of average absorbance for each standard against its corresponding concentration. Draw a smooth curve through the points. The curve should be linear over the two concentration ranges discussed in section 13.3.

11.0 Analytical Procedure

11.1 Assemble the system shown in Figure 10A–3, and record the information required in Table 10A–1 as it is obtained. Pipet 10.0 ml of the colorimetric reagent into each gas reaction bulb, and attach the bulbs to the system. Open the stopcocks to the reaction bulbs, but leave the valve to the bag closed. Turn on the pump, fully open the coarse-adjust flow valve, and slowly open the fine-adjust valve until the pressure is reduced to at least 40 mm Hg. Now close the coarse adjust valve, and observe the manometer to be certain that the system is leak-free. Wait a minimum of 2 minutes. If the pressure has increased less than 1 mm Hg, proceed as described below. If a leak is present, find and correct it before proceeding further.

11.2 Record the vacuum pressure (P_v) to the nearest 1 mm Hg, and close the reaction bulb stopcocks. Open the bag valve, and allow the system to come to atmospheric pressure. Close the bag valve, open the pump coarse adjust valve, and evacuate the system again. Repeat this fill/evacuation procedure at least twice to flush the manifold completely. Close the pump coarse adjust valve, open the bag valve, and let the system fill to atmospheric pressure. Open the stopcocks to the reaction bulbs, and let the entire system come to atmospheric pressure. Close the bulb stopcocks, remove the bulbs, record the room temperature and barometric pressure (P_{bar}, to nearest mm Hg), and place the bulbs on the shaker table with their main axis either parallel to or perpendicular to the plane of the table top. Purge the bulb-filling system with ambient air for several minutes between samples. Shake the samples for exactly 2 hours.

11.3 Immediately after shaking, measure the absorbance (A) of each bulb sample at 425 nm if the concentration is less than or equal to 400 ppm CO or at 600 nm if the concentration is above 400 ppm.

NOTE: This may be accomplished with multiple bulb sets by sequentially collecting sets and adding to the shaker at staggered intervals, followed by sequentially removing sets from the shaker for absorbance measurement after the two-hour designated intervals have elapsed.

11.4 Use a small portion of the sample to rinse a spectrophotometer cell several times before taking an aliquot for analysis. If one cell is used to analyze multiple samples, rinse the cell with deionized distilled water several times between samples. Prepare and analyze standards and a reagent blank as described in section 10.3. Use water as the reference. Reject the analysis if the blank absorbance is greater than 0.1. All conditions should be the same for analysis of samples and standards. Measure the absorbances as soon as possible after shaking is completed.

11.5 Determine the CO concentration of each bag sample using the calibration curve for the appropriate concentration range as discussed in section 10.3.

12.0 Calculations and Data Analysis

Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature.

A = Sample absorbance, uncorrected for the reagent blank.
A_r = Absorbance of the reagent blank.
A_s = Average sample absorbance per liter, units/liter.
B_w = Moisture content in the bag sample.
C = CO concentration in the stack gas, dry basis, ppm.
C_b = CO concentration of the bag sample, dry basis, ppm.
C_g = CO concentration from the calibration curve, ppm.
F = Volume fraction of CO_2 in the stack.
n = Number of reaction bulbs used per bag sample.
P_b = Barometric pressure, mm Hg.
P_v = Residual pressure in the sample bulb after evacuation, mm Hg.
P_w = Vapor pressure of H_2O in the bag (from Table 10A–2), mm Hg.
V_b = Volume of the sample bulb, liters.
V_r = Volume of reagent added to the sample bulb, 0.0100 liter.

12.2 Average Sample Absorbance per Liter. Calculate A_s for each gas bulb using Equation 10A–1, and record the value in Table 10A–1. Calculate the average A_s for each bag sample, and compare the three values to the average. If any single value differs by more than 10 percent from the average, reject this value, and calculate a new average using the two remaining values.

$$A_s = \frac{(A - A_r)(P_b)}{(V_b - V_r)(P_b - P_v)} \qquad \text{Eq. 10A-1}$$

NOTE: A and A_r must be at the same wavelength.

12.3 CO Concentration in the Bag. Calculate C_b using Equations 10A–2 and 10A–3. If condensate is visible in the bag, calculate B_w using Table 10A–2 and the temperature and barometric pressure in the analysis room. If condensate is not visible, calculate B_w using the temperature and barometric pressure at the sampling site.

$$B_w = \frac{P_w}{P_b} \qquad \text{Eq. 10A-2}$$

$$C_b = \frac{C_g}{(1 - B_w)} \qquad \text{Eq. 10A-3}$$

12.4 CO Concentration in the Stack.

$$C = C_b\,(1 - F) \qquad \text{Eq. 10A-4}$$

13.0 Method Performance

13.1 Precision. The estimated intralaboratory standard deviation of the method is 3 percent of the mean for gas samples analyzed in duplicate in the concentration range of 39 to 412 ppm. The interlaboratory precision has not been established.

13.2 Accuracy. The method contains no significant biases when compared to an NDIR analyzer calibrated with NIST standards.

13.3 Range. Approximately 3 to 1800 ppm CO. Samples having concentrations below 400 ppm are analyzed at 425 nm, and samples having concentrations above 400 ppm are analyzed at 600 nm.

13.4 Sensitivity. The detection limit is 3 ppmv based on a change in concentration equal to three times the standard deviation of the reagent blank solution.

13.5 Stability. The individual components of the colorimetric reagent are stable for at least one month. The colorimetric reagent must be used within two days after preparation to avoid excessive blank correction. The samples in the bag should be stable for at least one week if the bags are leak-free.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Butler, F.E., J.E. Knoll, and M.R. Midgett. Development and Evaluation of Methods for Determining Carbon Monoxide Emissions. U.S. Environmental Protection Agency, Research Triangle Park, N.C. June 1985. 33 pp.

2. Ferguson, B.B., R.E. Lester, and W.J. Mitchell. Field Evaluation of Carbon Monoxide and Hydrogen Sulfide Continuous Emission Monitors at an Oil Refinery. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA–600/4–82–054. August 1982. 100 pp.

3. Lambert, J.L., and R.E. Weins. Induced Colorimetric Method for Carbon Monoxide. Analytical Chemistry. *46*(7):929–930. June 1974.

4. Levaggi, D.A., and M. Feldstein. The Colorimetric Determination of Low Concentrations of Carbon Monoxide. Industrial Hygiene Journal. *25*:64–66. January-February 1964.

5. Repp, M. Evaluation of Continuous Monitors For Carbon Monoxide in Stationary Sources. U.S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA–600/2–77–063. March 1977. 155 pp.

6. Smith, F., D.E. Wagoner, and R.P. Donovan. Guidelines for Development of a Quality Assurance Program: Volume VIII—Determination of CO Emissions from Stationary Sources by NDIR Spectrometry. U.S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA–650/4–74–005–h. February 1975. 96 pp.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 10A–1—DATA RECORDING SHEET FOR SAMPLES ANALYZED IN TRIPLICATE

Sample No./type	Room temp °C	Stack %CO_2	Bulb No.	Bulb vol. liters	Reagent vol. in bulb, liter	Partial pressure of gas in bulb, mm Hg	$P_{b,r}$, mm Hg	Shaking time, min	Abs versus water	A-A_r	A_s	Avg A_s
blank												
Std. 1												
Std. 2												
Sample 1												
Sample 2												
Sample 3												

TABLE 10A–2—MOISTURE CORRECTION

Temperature °C	Vapor pressure of H_2O, mm Hg	Temperature °C	Vapor pressure of H_2, mm Hg
4	6.1	18	15.5
6	7.0	20	17.5
8	8.0	22	19.8
10	9.2	24	22.4
12	10.5	26	25.2
14	12.0	28	28.3
16	13.6	30	31.8

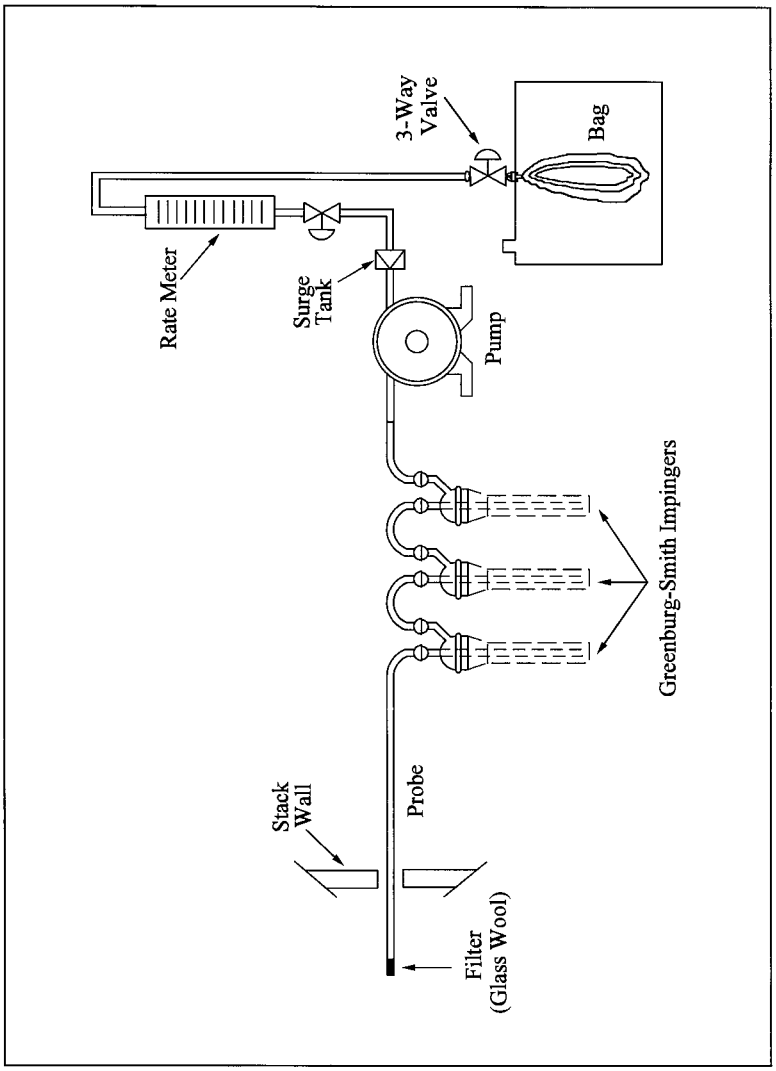


Figure 10A-1. Sampling Train.

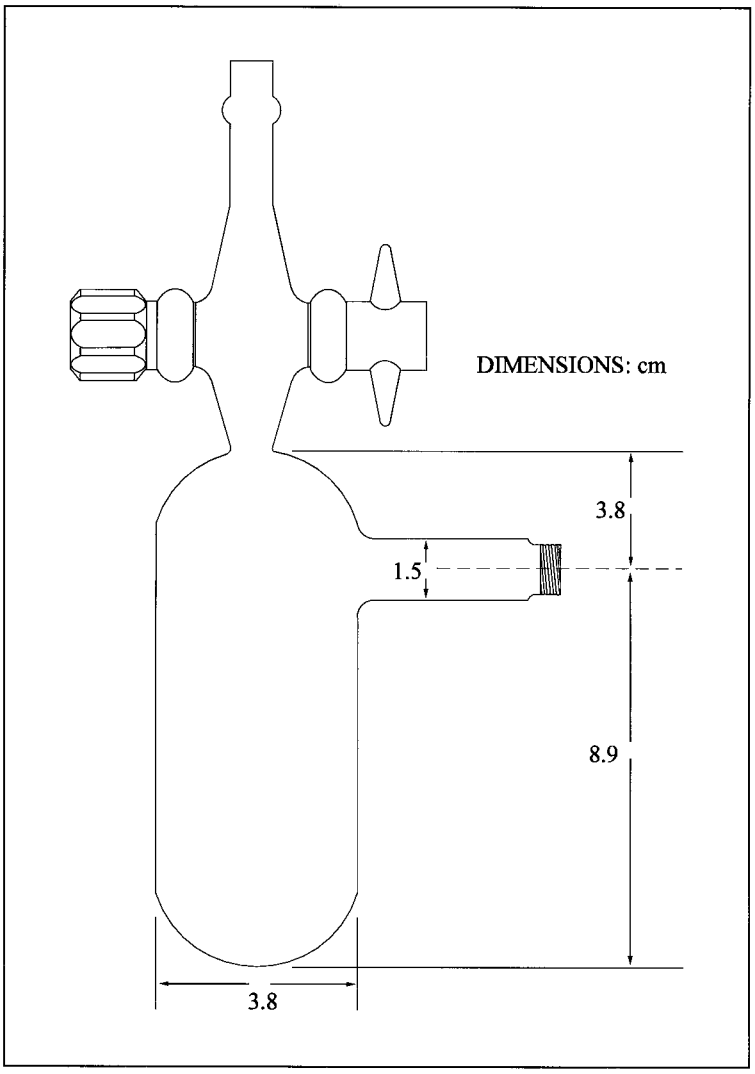


Figure 10A-2. Sample Reaction Bulbs.

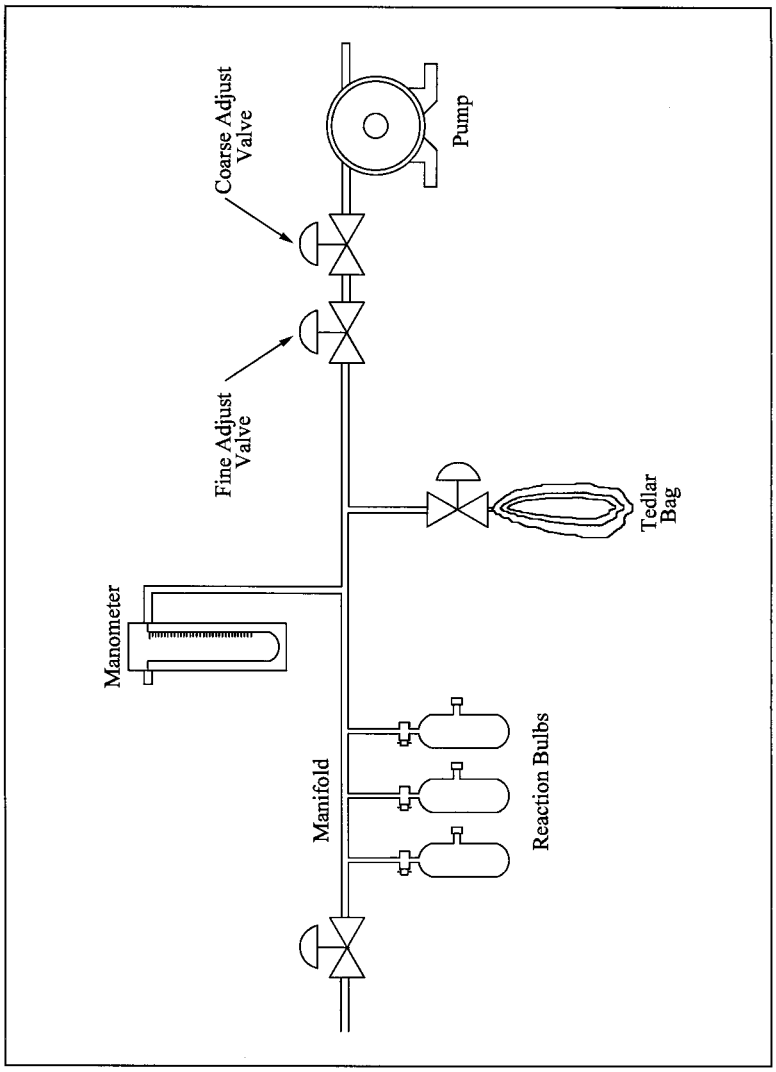


Figure 10A-3. Sample Bulb Filling System.

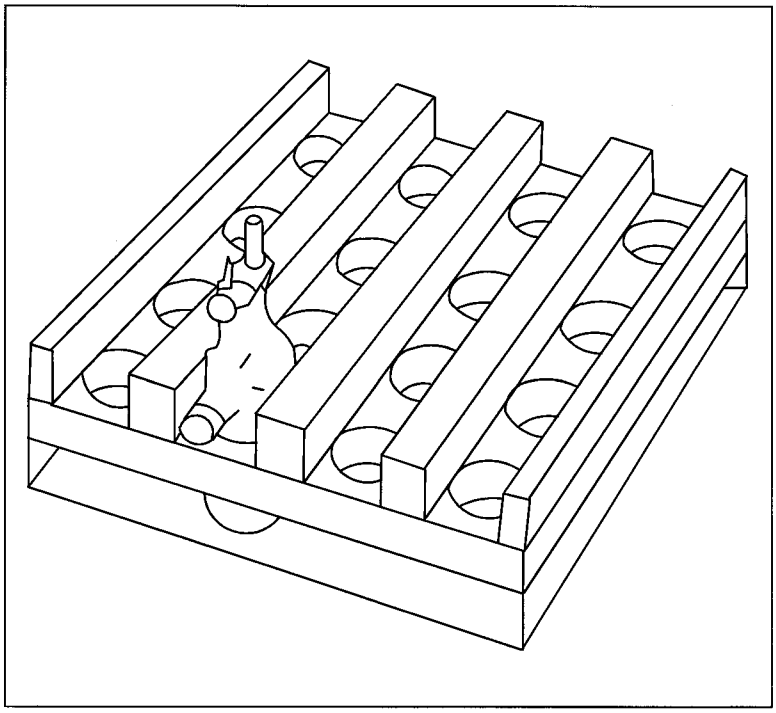


Figure 10A-4. Shaker Table Adapter.

METHOD 10B—DETERMINATION OF CARBON MONOXIDE EMISSIONS FROM STATIONARY SOURCES

NOTE: This method is not inclusive with respect to specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 4, Method 10A, and Method 25.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Carbon monoxide (CO)	630–08–0	Not determined.

1.2 Applicability. This method applies to the measurement of CO emissions at petroleum refineries and from other sources when specified in an applicable subpart of the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 An integrated gas sample is extracted from the sampling point, passed through a conditioning system to remove interferences, and collected in a Tedlar or equivalent bag. (Verify through the manufacturer that the Tedlar alternative is suitable for NO and make this verifying information available for inspection.) The CO is separated from the sample by gas chromatography (GC) and catalytically reduced to methane (CH_4) which is determined by flame ionization detection (FID). The analytical portion of this method is identical to applicable sections in Method 25 detailing CO measurement.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Carbon dioxide (CO_2) and organics potentially can interfere with the analysis. Most of the CO_2 is removed from the sample by the alkaline permanganate conditioning system; any residual CO_2 and organics are separated from the CO by GC.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions concerning the analytical procedure.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as in Method 10A, section 6.1 (paragraphs 6.1.1 through 6.1.11).

6.2 Sample Analysis. A GC/FID analyzer, capable of quantifying CO in the sample and consisting of at least the following major components, is required for sample analysis. [Alternatively, complete Method 25 analytical systems (Method 25, section 6.3) are acceptable alternatives when calibrated for CO and operated in accordance with the Method 25 analytical procedures (Method 25, section 11.0).]

6.2.1 Separation Column. A column capable of separating CO from CO_2 and organic compounds that may be present. A 3.2-mm (⅛-in.) OD stainless steel column packed with 1.7 m (5.5 ft.) of 60/80 mesh Carbosieve S-II (available from Supelco) has been used successfully for this purpose.

6.2.2 Reduction Catalyst. Same as in Method 25, section 6.3.1.2.

6.2.3 Sample Injection System. Same as in Method 25, Section 6.3.1.4, equipped to accept a sample line from the bag.

6.2.4 Flame Ionization Detector. Meeting the linearity specifications of section 10.3 and having a minimal instrument range of 10 to 1,000 ppm CO.

6.2.5 Data Recording System. Analog strip chart recorder or digital integration system, compatible with the FID, for permanently recording the analytical results.

7.0 Reagents and Standards

7.1 Sample Collection. Same as in Method 10A, section 7.1.

7.2 Sample Analysis.

7.2.1 Carrier, Fuel, and Combustion Gases. Same as in Method 25, sections 7.2.1, 7.2.2, and 7.2.3, respectively.

7.2.2 Calibration Gases. Three standard gases with nominal CO concentrations of 20, 200, and 1,000 ppm CO in nitrogen. The calibration gases shall be certified by the manufacturer to be ±2 percent of the specified concentrations.

7.2.3 Reduction Catalyst Efficiency Check Calibration Gas. Standard CH_4 gas with a nominal concentration of 1,000 ppm in air.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as in Method 10A, section 8.0.

9.0 Quality Control

Section	Quality control measure	Effect
8.0	Sample bag/sampling system leak-checks	Ensures that negative bias introduced through leakage is minimized.
10.1	Carrier gas blank check	Ensures that positive bias introduced by contamination of carrier gas is less than 5 ppmv.
10.2	Reduction catalyst efficiency check	Ensures that negative bias introduced by inefficient reduction catalyst is less than 5 percent.
10.3	Analyzer calibration	Ensures linearity of analyzer response to standards.
11.2	Triplicate sample analyses	Ensures precision of analytical results.

10.0 Calibration and Standardization

10.1 Carrier Gas Blank Check. Analyze each new tank of carrier gas with the GC analyzer according to section 11.2 to check for contamination. The corresponding concentration must be less than 5 ppm for the tank to be acceptable for use.

10.2 Reduction Catalyst Efficiency Check. Prior to initial use, the reduction catalyst shall be tested for reduction efficiency. With the heated reduction catalyst bypassed, make triplicate injections of the 1,000 ppm CH_4 gas (Section 7.2.3) to calibrate the analyzer. Repeat the procedure using 1,000 ppm CO gas (Section 7.2.2) with the catalyst in operation. The reduction catalyst operation is acceptable if the CO response is within 5 percent of the certified gas value.

10.3 Analyzer Calibration. Perform this test before the system is first placed into operation. With the reduction catalyst in operation, conduct a linearity check of the analyzer using the standards specified in section 7.2.2. Make triplicate injections of each calibration gas, and then calculate the average

response factor (area/ppm) for each gas, as well as the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within 2.5 percent of the overall mean value and if the relative standard deviation (calculated in section 12.8 of Method 25) for each set of triplicate injections is less than 2 percent. Record the overall mean of the response factor values as the calibration response factor (R).

11.0 Analytical Procedure

11.1 Preparation for Analysis. Before putting the GC analyzer into routine operation, conduct the calibration procedures listed in section 10.0. Establish an appropriate carrier flow rate and detector temperature for the specific instrument used.

11.2 Sample Analysis. Purge the sample loop with sample, and then inject the sample. Analyze each sample in triplicate, and calculate the average sample area (A). Determine the bag CO concentration according to section 12.2.

12.0 Calculations and Data Analysis

Carry out calculations retaining at least one extra significant figure beyond that of the acquired data. Round off results only after the final calculation.

12.1 Nomenclature.

A = Average sample area.
B_w = Moisture content in the bag sample, fraction.
C = CO concentration in the stack gas, dry basis, ppm.
C_b = CO concentration in the bag sample, dry basis, ppm.
F = Volume fraction of CO_2 in the stack, fraction.
P_{bar} = Barometric pressure, mm Hg.
P_w = Vapor pressure of the H_2O in the bag (from Table 10A–2, Method 10A), mm Hg.
R = Mean calibration response factor, area/ppm.

12.2 CO Concentration in the Bag. Calculate C_b using Equations 10B–1 and 10B–2. If condensate is visible in the bag, calculate B_w using Table 10A–2 of Method 10A and the temperature and barometric pressure in the analysis room. If condensate is not visible, calculate B_w using the temperature and barometric pressure at the sampling site.

$$B_w = \frac{P_w}{P_{bar}} \qquad \text{Eq. 10B-1}$$

$$C_b = \frac{A}{R\left(1 - B_w\right)} \qquad \text{Eq. 10B-2}$$

12.3 CO Concentration in the Stack

$$C = C_b\left(1 - F\right) \qquad \text{Eq. 10B-3}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as in Method 25, section 16.0, with the addition of the following:

1. Butler, F.E, J.E. Knoll, and M.R. Midgett. Development and Evaluation of Methods for Determining Carbon Monoxide Emissions. Quality Assurance Division, Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC. June 1985. 33 pp.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–4 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

APPENDIX A–5 TO PART 60—TEST METHODS 11 THROUGH 15A

Method 11—Determination of hydrogen sulfide content of fuel gas streams in petroleum refineries
Method 12—Determination of inorganic lead emissions from stationary sources
Method 13A—Determination of total fluoride emissions from stationary sources—SPADNS zirconium lake method
Method 13B—Determination of total fluoride emissions from stationary sources—Specific ion electrode method
Method 14—Determination of fluoride emissions from potroom roof monitors for primary aluminum plants
Method 14A—Determination of Total Fluoride Emissions from Selected Sources at Primary Aluminum Production Facilities
Method 15—Determination of hydrogen sulfide, carbonyl sulfide, and carbon disulfide emissions from stationary sources
Method 15A—Determination of total reduced sulfur emissions from sulfur recovery plants in petroleum refineries

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods

State of Oregon Department of Environmental Quality

OAR 340-208-0210
EPA Method 22

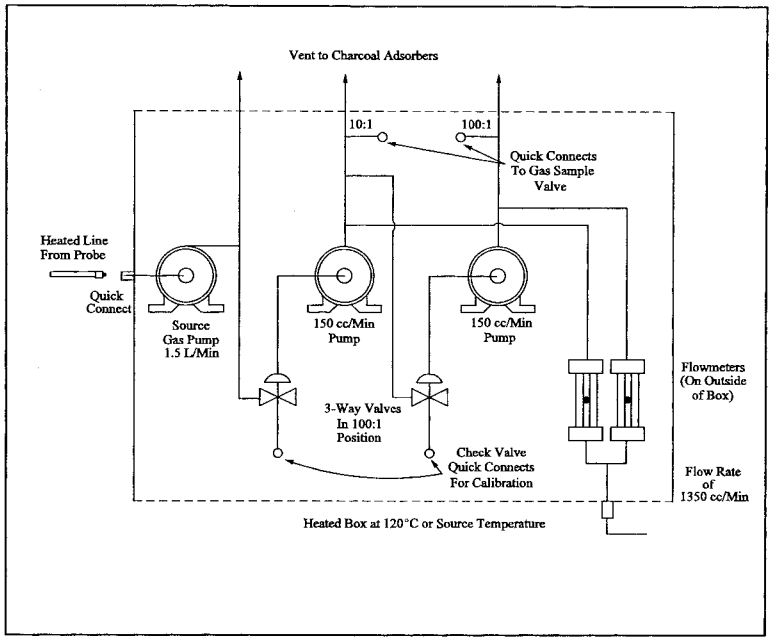


Figure 18-13. Schematic Diagram of the Heated Box Required for Dilution of Sample Gas.

GASEOUS ORGANIC SAMPLING AND ANALYSIS CHECK LIST

[Respond with initials or number as appropriate]

1. Presurvey data:		
A. Grab sample collected	☐	_____
B. Grab sample analyzed for composition	☐	_____
Method GC	☐	_____
GC/MS	☐	_____
Other	☐	_____
C. GC-FID analysis performed	☐	_____
2. Laboratory calibration data:		
A. Calibration curves prepared	☐	_____
Number of components	☐	_____
Number of concentrations/component (3 required).	☐	_____
B. Audit samples (optional):		
Analysis completed	☐	_____
Verified for concentration	☐	_____
OK obtained for field work	☐	_____
3. Sampling procedures:		
A. Method:		
Bag sample	☐	_____
Direct interface	☐	_____
Dilution interface	☐	_____
B. Number of samples collected	☐	_____
4. Field Analysis:		
A. Total hydrocarbon analysis performed	☐	_____
B. Calibration curve prepared	☐	_____
Number of components	☐	_____
Number of concentrations per component (3 required).	☐	_____

Gaseous Organic Sampling and Analysis Data

Date _____
Location _____

Plant _____

GASEOUS ORGANIC SAMPLING AND ANALYSIS CHECK LIST (RESPOND WITH INITIALS OR NUMBER AS APPROPRIATE)

	Date
1. Pre-survey data	
A. Grab sample collected	_____
B. Grab sample analyzed for composition	_____
Method GC	_____
GC/MS	_____
Other_____	_____
C. GC–FID analysis performed	_____
2. Laboratory calibration curves prepared	_____
A. Number of components	_____
B. Number of concentrations per component (3 required)	_____
C. OK obtained for field work	_____
3. Sampling procedures.	
A. Method.	
Bag sample	_____
Direct interface	_____
Dilution interface	_____
B. Number of samples collected	_____
4. Field Analysis.	
A. Total hydrocarbon analysis performed	_____
B. Calibration curve prepared	_____
Number of components	_____
Number of concentrations per component (3 required)	_____

Figure 18–14. Sampling and Analysis Sheet

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–6 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

APPENDIX A–7 TO PART 60—TEST METHODS 19 THROUGH 25E

Method 19—Determination of sulfur dioxide removal efficiency and particulate, sulfur dioxide and nitrogen oxides emission rates
Method 20—Determination of nitrogen oxides, sulfur dioxide, and diluent emissions from stationary gas turbines
Method 21—Determination of volatile organic compound leaks
Method 22—Visual determination of fugitive emissions from material sources and smoke emissions from flares
Method 23—Determination of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans From Stationary Sources
Method 24—Determination of volatile matter content, water content, density, volume solids, and weight solids of surface coatings
Method 24A—Determination of volatile matter content and density of printing inks and related coatings
Method 25—Determination of total gaseous nonmethane organic emissions as carbon
Method 25A—Determination of total gaseous organic concentration using a flame ionization analyzer
Method 25B—Determination of total gaseous organic concentration using a nondispersive infrared analyzer
Method 25C—Determination of nonmethane organic compounds (NMOC) in MSW landfill gases
Method 25D—Determination of the Volatile Organic Concentration of Waste Samples
Method 25E—Determination of Vapor Phase Organic Concentration in Waste Samples

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

Method 19—Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates

1.0 Scope and Application

1.1 Analytes. This method provides data reduction procedures relating to the following pollutants, but does not include any sample collection or analysis procedures.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), including:		
Nitric oxide (NO)	10102–43–9	N/A
Nitrogen dioxide (NO_2)	10102–44–0.	
Particulate matter (PM)	None assigned	N/A
Sulfur dioxide (SO_2)	7499–09–05	N/A

1.2 Applicability. Where specified by an applicable subpart of the regulations, this method is applicable for the determination of (a) PM, SO_2, and NO_X emission rates; (b) sulfur removal efficiencies of fuel pretreatment and SO_2 control devices; and (c) overall reduction of potential SO_2 emissions.

2.0 Summary of Method

2.1 Emission Rates. Oxygen (O_2) or carbon dioxide (CO_2) concentrations and appropriate F factors (ratios of combustion gas volumes to heat inputs) are used to calculate pollutant emission rates from pollutant concentrations.

2.2 Sulfur Reduction Efficiency and SO_2 Removal Efficiency. An overall SO_2 emission reduction efficiency is computed from the efficiency of fuel pretreatment systems, where applicable, and the efficiency of SO_2 control devices.

2.2.1 The sulfur removal efficiency of a fuel pretreatment system is determined by fuel sampling and analysis of the sulfur and heat contents of the fuel before and after the pretreatment system.

2.2.2 The SO_2 removal efficiency of a control device is determined by measuring the SO_2 rates before and after the control device.

2.2.2.1 The inlet rates to SO_2 control systems (or, when SO_2 control systems are not used, SO_2 emission rates to the atmosphere) are determined by fuel sampling and analysis.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety [Reserved]

6.0 Equipment and Supplies [Reserved]

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transport [Reserved]

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedures [Reserved]

12.0 Data Analysis and Calculations

12.1 Nomenclature

B_{wa} = Moisture fraction of ambient air, percent.

B_{ws} = Moisture fraction of effluent gas, percent.

%C = Concentration of carbon from an ultimate analysis of fuel, weight percent.

C_d = Pollutant concentration, dry basis, ng/scm (lb/scf)

$\%CO_{2d}$,$\%CO_{2w}$ = Concentration of carbon dioxide on a dry and wet basis, respectively, percent.

C_w = Pollutant concentration, wet basis, ng/scm (lb/scf).

D = Number of sampling periods during the performance test period.

E = Pollutant emission rate, ng/J (lb/million Btu).

E_a = Average pollutant rate for the specified performance test period, ng/J (lb/million Btu).

E_{ao}, E_{ai} = Average pollutant rate of the control device, outlet and inlet, respectively, for the performance test period, ng/J (lb/million Btu).

E_{bi} = Pollutant rate from the steam generating unit, ng/J (lb/million Btu)

E_{bo} = Pollutant emission rate from the steam generating unit, ng/J (lb/million Btu).

E_{ci} = Pollutant rate in combined effluent, ng/J (lb/million Btu).

E_{co} = Pollutant emission rate in combined effluent, ng/J (lb/million Btu).

E_d = Average pollutant rate for each sampling period (*e.g.*, 24-hr Method 6B sample or 24-hr fuel sample) or for each fuel lot (*e.g.*, amount of fuel bunkered), ng/J (lb/million Btu).

E_{di} = Average inlet SO_2 rate for each sampling period d, ng/J (lb/million Btu)

E_g = Pollutant rate from gas turbine, ng/J (lb/million Btu).

E_{ga} = Daily geometric average pollutant rate, ng/J (lbs/million Btu) or ppm corrected to 7 percent O_2.

E_{jo},E_{ji} = Matched pair hourly arithmetic average pollutant rate, outlet and inlet, respectively, ng/J (lb/million Btu) or ppm corrected to 7 percent O_2.

E_h = Hourly average pollutant, ng/J (lb/million Btu).

E_{hj} = Hourly arithmetic average pollutant rate for hour ''j,'' ng/J (lb/million Btu) or ppm corrected to 7 percent O_2.

EXP = Natural logarithmic base (2.718) raised to the value enclosed by brackets.

F_d, F_w, F_c = Volumes of combustion components per unit of heat content, scm/J (scf/million Btu).

GCV = Gross calorific value of the fuel consistent with the ultimate analysis, kJ/kg (Btu/lb).

GCV_p, GCV_r = Gross calorific value for the product and raw fuel lots, respectively, dry basis, kJ/kg (Btu/lb).

%H = Concentration of hydrogen from an ultimate analysis of fuel, weight percent.

H = Total number of operating hours for which pollutant rates are determined in the performance test period.

H_b = Heat input rate to the steam generating unit from fuels fired in the steam generating unit, J/hr (million Btu/hr).

H_g = Heat input rate to gas turbine from all fuels fired in the gas turbine, J/hr (million Btu/hr).

$\%H_2O$ = Concentration of water from an ultimate analysis of fuel, weight percent.
H_r = Total numbers of hours in the performance test period (*e.g.*, 720 hours for 30-day performance test period).
K = Conversion factor, 10^{-5} (kJ/J)/(%) [10^6 Btu/million Btu].
K_c = (9.57 scm/kg)/% [(1.53 scf/lb)/%].
K_{cc} = (2.0 scm/kg)/% [(0.321 scf/lb)/%].
K_{hd} = (22.7 scm/kg)/% [(3.64 scf/lb)/%].
K_{hw} = (34.74 scm/kg)/% [(5.57 scf/lb)/%].
K_n = (0.86 scm/kg)/% [(0.14 scf/lb)/%].
K_o = (2.85 scm/kg)/% [(0.46 scf/lb)/%].
K_s = (3.54 scm/kg)/% [(0.57 scf/lb)/%].
K_w = (1.30 scm/kg)/% [(0.21 scf/lb)/%].
ln = Natural log of indicated value.
L_p,L_r = Weight of the product and raw fuel lots, respectively, metric ton (ton).
%N = Concentration of nitrogen from an ultimate analysis of fuel, weight percent.
N = Number of fuel lots during the averaging period.
n = Number of fuels being burned in combination.
n_d = Number of operating hours of the affected facility within the performance test period for each E_d determined.
n_t = Total number of hourly averages for which paired inlet and outlet pollutant rates are available within the 24-hr midnight to midnight daily period.
%O = Concentration of oxygen from an ultimate analysis of fuel, weight percent.
$\%O_{2d}$, $\%O_{2w}$ = Concentration of oxygen on a dry and wet basis, respectively, percent.
P_s = Potential SO_2 emissions, percent.
$\%R_f$ = SO_2 removal efficiency from fuel pretreatment, percent.
$\%R_g$ = SO_2 removal efficiency of the control device, percent.
$\%R_{ga}$ = Daily geometric average percent reduction.
$\%R_o$ = Overall SO_2 reduction, percent.
%S = Sulfur content of as-fired fuel lot, dry basis, weight percent.
S_e = Standard deviation of the hourly average pollutant rates for each performance test period, ng/J (lb/million Btu).
$\%S_f$ = Concentration of sulfur from an ultimate analysis of fuel, weight percent.
S_i = Standard deviation of the hourly average inlet pollutant rates for each performance test period, ng/J (lb/million Btu).
S_o = Standard deviation of the hourly average emission rates for each performance test period, ng/J (lb/million Btu).
$\%S_p$, $\%S_r$ = Sulfur content of the product and raw fuel lots respectively, dry basis, weight percent.
$t_{0.95}$ = Values shown in Table 19–3 for the indicated number of data points n.
X_k = Fraction of total heat input from each type of fuel k.

12.2 Emission Rates of PM, SO_2, and NO_X. Select from the following sections the applicable procedure to compute the PM, S_{O2}, or NO_X emission rate (E) in ng/J (lb/million Btu). The pollutant concentration must be in ng/scm (lb/scf) and the F factor must be in scm/J (scf/million Btu). If the pollutant concentration (C) is not in the appropriate units, use Table 19–1 in section 17.0 to make the proper conversion. An F factor is the ratio of the gas volume of the products of combustion to the heat content of the fuel. The dry F factor (F_d) includes all components of combustion less water, the wet F factor (F_w) includes all components of combustion, and the carbon F factor (F_c) includes only carbon dioxide.

NOTE: Since F_w factors include water resulting only from the combustion of hydrogen in the fuel, the procedures using F_w factors are not applicable for computing E from steam generating units with wet scrubbers or with other processes that add water (*e.g.*, steam injection).

12.2.1 Oxygen-Based F Factor, Dry Basis. When measurements are on a dry basis for both O ($\%O_{2d}$) and pollutant (C_d) concentrations, use the following equation:

$$E = C_d F_d \frac{20.9}{(20.9 - \%O_{2d})} \qquad \text{Eq. 19-1}$$

12.2.2 Oxygen-Based F Factor, Wet Basis. When measurements are on a wet basis for both O_2 ($\%O_{2w}$) and pollutant (C_w) concentrations, use either of the following:

12.2.2.1 If the moisture fraction of ambient air (B_{wa}) is measured:

$$E = C_w F_w \frac{20.9}{\left[20.9(1 - B_{wa}) - \%O_{2w}\right]} \qquad \text{Eq. 19-2}$$

Instead of actual measurement, B_{wa} may be estimated according to the procedure below.

NOTE: The estimates are selected to ensure that negative errors will not be larger than −1.5 percent. However, positive errors, or over-estimation of emissions by as much as 5 percent may be introduced depending upon the geographic location of the facility and the associated range of ambient moisture.

12.2.2.1.1 B_{wa} = 0.027. This value may be used at any location at all times.

12.2.2.1.2 B_{wa} = Highest monthly average of B_{wa} that occurred within the previous calendar year at the nearest Weather Service Station. This value shall be determined annually and may be used as an estimate for the entire current calendar year.

12.2.2.1.3 B_{wa} = Highest daily average of Bwa that occurred within a calendar month at the nearest Weather Service Station, calculated from the data from the past 3 years. This value shall be computed for each month and may be used as an estimate for the current respective calendar month.

12.2.2.2 If the moisture fraction (B_{ws}) of the effluent gas is measured:

$$E = C_w F_d \frac{20.9}{\left[20.9\left(1-B_{ws}\right)-\%O_{2w}\right]} \qquad \text{Eq. 19-3}$$

12.2.3 Oxygen-Based F Factor, Dry/Wet Basis.

12.2.3.1 When the pollutant concentration is measured on a wet basis (C_w) and O_2 concentration is measured on a dry basis ($\%O_{2d}$), use the following equation:

$$E = \frac{\left(C_w F_d\right)(20.9)}{\left(1-B_{ws}\right)\left(20.9-\%O_{2d}\right)} \qquad \text{Eq. 19-4}$$

12.2.3.2 When the pollutant concentration is measured on a dry basis (C_d) and the O_2 concentration is measured on a wet basis ($\%O_{2w}$), use the following equation:

$$E = \frac{C_d F_d 20.9}{\frac{\left(20.9-\%O_{2w}\right)}{\left(1-B_{ws}\right)}} \qquad \text{Eq. 19-5}$$

12.2.4 Carbon Dioxide-Based F Factor, Dry Basis. When measurements are on a dry basis for both CO_2 ($\%CO_{2d}$) and pollutant (C_d) concentrations, use the following equation:

$$E = C_d F_c \frac{100}{\%CO_{2d}} \qquad \text{Eq. 19-6}$$

12.2.5 Carbon Dioxide-Based F Factor, Wet Basis. When measurements are on a wet basis for both CO_2 ($\%CO_{2w}$) and pollutant (C_w) concentrations, use the following equation:

$$E = C_w F_c \frac{100}{\%CO_{2w}} \qquad \text{Eq. 19-7}$$

12.2.6 Carbon Dioxide-Based F Factor, Dry/Wet Basis.

12.2.6.1 When the pollutant concentration is measured on a wet basis (C_w) and CO_2 concentration is measured on a dry basis ($\%CO_{2d}$), use the following equation:

$$E = \frac{C_w F_c}{\left(1-B_{ws}\right)} \frac{100}{\%CO_{2d}} \qquad \text{Eq. 19-8}$$

12.2.6.2 When the pollutant concentration is measured on a dry basis (C_d) and CO_2 concentration is measured on a wet basis ($\%CO_{2w}$), use the following equation:

$$E = C_d F_c \left(1-B_{ws}\right) \frac{100}{\%CO_{2w}} \qquad \text{Eq. 19-9}$$

12.2.7 Direct-Fired Reheat Fuel Burning. The effect of direct-fired reheat fuel burning (for the purpose of raising the temperature of the exhaust effluent from wet scrubbers to above the moisture dew-point) on emission rates will be less than 1.0 percent and, therefore, may be ignored.

12.2.8 Combined Cycle-Gas Turbine Systems. For gas turbine-steam generator combined cycle systems, determine the emissions from the steam generating unit or the percent reduction in potential SO_2 emissions as follows:

12.2.8.1 Compute the emission rate from the steam generating unit using the following equation:

$$E_{bo} = E_{co} + \frac{H_g}{H_b}\left(E_{co} - E_g\right) \qquad \text{Eq. 19-10}$$

12.2.8.1.1 Use the test methods and procedures section of 40 CFR Part 60, Subpart GG to obtain E_{co} and E_g. Do not use F_w factors for determining E_g or E_{co}. If an SO_2 control device is used, measure E_{co} after the control device.

12.2.8.1.2 Suitable methods shall be used to determine the heat input rates to the steam generating units (H_b) and the gas turbine (H_g).

12.2.8.2 If a control device is used, compute the percent of potential SO_2 emissions (P_s) using the following equations:

$$E_{bi} = E_{ci} - \frac{H_g}{H_b}\left(E_{ci} - E_g\right) \qquad \text{Eq. 19-11}$$

$$P_s = 100\left(1 - \frac{E_{bo}}{E_{bi}}\right) \qquad \text{Eq. 19-12}$$

NOTE: Use the test methods and procedures section of Subpart GG to obtain E_{ci} and E_g. Do not use F_w factors for determining E_g or E_{ci}.

12.3 F Factors. Use an average F factor according to section 12.3.1 or determine an applicable F factor according to section 12.3.2. If combined fuels are fired, prorate the applicable F factors using the procedure in section 12.3.3.

12.3.1 Average F Factors. Average F factors (F_d, F_w, or F_c) from Table 19–2 in section 17.0 may be used.

12.3.2 Determined F Factors. If the fuel burned is not listed in Table 19–2 or if the owner or operator chooses to determine an F factor rather than use the values in Table 19–2, use the procedure below:

12.3.2.1 Equations. Use the equations below, as appropriate, to compute the F factors:

$$F_d = \frac{K\left(K_{hd}\%H + K_c\%C + K_s\%S + K_n\%N - K_o\%O\right)}{GCV} \qquad \text{Eq. 19-13}$$

$$F_w = \frac{K\left[K_{hw}\%H + K_c\%C + K_s\%S + K_n\%N - K_o\%O + K_w\%H_2O\right]}{GCV_w} \qquad \text{Eq. 19-14}$$

$$F_c = \frac{K\left(K_{cc}\%C\right)}{GCV} \qquad \text{Eq. 19-15}$$

NOTE: Omit the $\%H_2O$ term in the equations for F_w if %H and %O include the unavailable hydrogen and oxygen in the form of H_2O.)

12.3.2.2 Use applicable sampling procedures in section 12.5.2.1 or 12.5.2.2 to obtain samples for analyses.

12.3.2.3 Use ASTM D 3176–74 or 89 (all cited ASTM standards are incorporated by reference—see §60.17) for ultimate analysis of the fuel.

12.3.2.4 Use applicable methods in section 12.5.2.1 or 12.5.2.2 to determine the heat content of solid or liquid fuels. For gaseous fuels, use ASTM D 1826–77 or 94 (incorporated by reference—see §60.17) to determine the heat content.

12.3.3 F Factors for Combination of Fuels. If combinations of fuels are burned, use the following equations, as applicable unless otherwise specified in an applicable subpart:

$$F_d = \sum_{k=1}^{n}\left(X_k F_{dk}\right) \qquad \text{Eq. 19-16}$$

$$F_w = \sum_{k=1}^{n}\left(X_k F_{wk}\right) \qquad \text{Eq. 19-17}$$

$$F_c = \sum_{k=1}^{n}\left(X_k F_{ck}\right) \qquad \text{Eq. 19-18}$$

12.4 Determination of Average Pollutant Rates.

12.4.1 Average Pollutant Rates from Hourly Values. When hourly average pollutant rates (E_h), inlet or outlet, are obtained (*e.g.*, CEMS values), compute the average pollutant rate (E_a) for the performance test period (*e.g.*, 30 days) specified in the applicable regulation using the following equation:

$$E_a = \frac{1}{H}\sum_{j=1}^{n} E_{hj} \qquad \text{Eq. 19-19}$$

12.4.2 Average Pollutant Rates from Other than Hourly Averages. When pollutant rates are determined from measured values representing longer than 1-hour periods (*e.g.*, daily fuel sampling and analyses or Method 6B values), or when pollutant rates are determined from combinations of 1-hour and longer than 1-hour periods (*e.g.*, CEMS and Method 6B values), compute the average pollutant rate (E_a) for the performance test period (*e.g.*, 30 days) specified in the applicable regulation using the following equation:

$$E_a = \frac{\sum_{j=1}^{D}\left(n_d E_d\right)_j}{\sum_{j=1}^{D} n_{dj}} \qquad \text{Eq. 19-20}$$

12.4.3 Daily Geometric Average Pollutant Rates from Hourly Values. The geometric average pollutant rate (E_{ga}) is computed using the following equation:

$$E_{ga} = \exp\left[\frac{1}{n_t}\sum_{j=1}^{n_t}\left[\ln\left(E_{hj}\right)\right]\right] \quad \text{Eq. 19-21}$$

12.5 Determination of Overall Reduction in Potential Sulfur Dioxide Emission.

12.5.1 Overall Percent Reduction. Compute the overall percent SO_2 reduction ($\%R_o$) using the following equation:

$$\%R_o = 100\left[1.0 - \left(1.0 - \frac{\%R_f}{100}\right)\left(1.0 - \frac{\%R_g}{100}\right)\right] \quad \text{Eq. 19-22}$$

12.5.2 Pretreatment Removal Efficiency (Optional). Compute the SO_2 removal efficiency from fuel pretreatment ($\%R_f$) for the averaging period (*e.g.*, 90 days) as specified in the applicable regulation using the following equation:

$$\%R_f = 100\left[1.0 - \frac{\sum_{j=1}^{N}\left(\frac{\%S_{pj}}{GCV_{pj}}\right)L_{pj}}{\sum_{j=1}^{N}\left(\frac{\%S_{rj}}{GCV_{rj}}\right)L_{rj}}\right] \quad \text{Eq. 19-23}$$

NOTE: In calculating $\%R_f$, include %S and GCV values for all fuel lots that are not pretreated and are used during the averaging period.

12.5.2.1 Solid Fossil (Including Waste) Fuel/Sampling and Analysis.

NOTE: For the purposes of this method, raw fuel (coal or oil) is the fuel delivered to the desulfurization (pretreatment) facility. For oil, the input oil to the oil desulfurization process (*e.g.*, hydrotreatment) is considered to be the raw fuel.

12.5.2.1.1 Sample Increment Collection. Use ASTM D 2234–76, 96, 97a, or 98 (incorporated by reference—see §60.17), Type I, Conditions A, B, or C, and systematic spacing. As used in this method, systematic spacing is intended to include evenly spaced increments in time or increments based on equal weights of coal passing the collection area. As a minimum, determine the number and weight of increments required per gross sample representing each coal lot according to Table 2 or Paragraph 7.1.5.2 of ASTM D 2234. Collect one gross sample for each lot of raw coal and one gross sample for each lot of product coal.

12.5.2.1.2 ASTM Lot Size. For the purpose of section 12.5.2 (fuel pretreatment), the lot size of product coal is the weight of product coal from one type of raw coal. The lot size of raw coal is the weight of raw coal used to produce one lot of product coal. Typically, the lot size is the weight of coal processed in a 1-day (24-hour) period. If more than one type of coal is treated and produced in 1 day, then gross samples must be collected and analyzed for each type of coal. A coal lot size equaling the 90-day quarterly fuel quantity for a steam generating unit may be used if representative sampling can be conducted for each raw coal and product coal.

NOTE: Alternative definitions of lot sizes may be used, subject to prior approval of the Administrator.

12.5.2.1.3 Gross Sample Analysis. Use ASTM D 2013–72 or 86 to prepare the sample, ASTM D 3177–75 or 89 or ASTM D 4239–85, 94, or 97 to determine sulfur content (%S), ASTM D 3173–73 or 87 to determine moisture content, and ASTM D 2015–77 (Reapproved 1978) or 96, D 3286–85 or 96, or D 5865–98 or 10 to determine gross calorific value (GCV) (all standards cited are incorporated by reference—see §60.17 for acceptable versions of the standards) on a dry basis for each gross sample.

12.5.2.2 Liquid Fossil Fuel-Sampling and Analysis. See Note under section 12.5.2.1.

12.5.2.2.1 Sample Collection. Follow the procedures for continuous sampling in ASTM D 270 or D 4177–95 (incorporated by reference—see §60.17) for each gross sample from each fuel lot.

12.5.2.2.2 Lot Size. For the purpose of section 12.5.2 (fuel pretreatment), the lot size of a product oil is the weight of product oil from one pretreatment facility and intended as one shipment (ship load, barge load, etc.). The lot size of raw oil is the weight of each crude liquid fuel type used to produce a lot of product oil.

NOTE: Alternative definitions of lot sizes may be used, subject to prior approval of the Administrator.

12.5.2.2.3 Sample Analysis. Use ASTM D 129–64, 78, or 95, ASTM D 1552–83 or 95, or ASTM D 4057–81 or 95 to determine the sulfur content (%S) and ASTM D 240–76 or 92 (all standards cited are incorporated by reference—see §60.17) to determine the GCV of each gross sample. These values may be assumed to be on a dry basis. The owner or operator of an affected facility may elect to determine the GCV by sampling the oil combusted on the first steam generating unit operating day of each calendar month and then using the lowest GCV value of the three GCV values per quarter for the GCV of all oil combusted in that calendar quarter.

12.5.2.3 Use appropriate procedures, subject to the approval of the Administrator, to determine the fraction of total mass input derived from each type of fuel.

12.5.3 Control Device Removal Efficiency. Compute the percent removal efficiency ($\%R_g$) of the control device using the following equation:

$$\%R_g = 100\left(1.0 - \frac{E_{ao}}{E_{ai}}\right) \qquad \text{Eq. 19-24}$$

12.5.3.1 Use continuous emission monitoring systems or test methods, as appropriate, to determine the outlet SO_2 rates and, if appropriate, the inlet SO_2 rates. The rates may be determined as hourly (E_h) or other sampling period averages (E_d). Then, compute the average pollutant rates for the performance test period (E_{ao} and E_{ai}) using the procedures in section 12.4.

12.5.3.2 As an alternative, as-fired fuel sampling and analysis may be used to determine inlet SO_2 rates as follows:

12.5.3.2.1 Compute the average inlet SO_2 rate (E_{di}) for each sampling period using the following equation:

$$E_{di} = K\frac{\%S}{GCV} \qquad \text{Eq. 19-25}$$

Where:

$$K = 2\times10^7\left(\frac{\text{ng SO}_2}{\%S}\right)\left(\frac{(\text{kJ})}{\text{J}}\right)\left(\frac{1}{\text{kg coal}}\right)\left[2\times10^4\left(\frac{\text{lb SO}_2}{\%S}\right)\left(\frac{\text{Btu}}{\text{million Btu}}\right)\left(\frac{1}{\text{lb coal}}\right)\right]$$

After calculating E_{di}, use the procedures in section 12.4 to determine the average inlet SO_2 rate for the performance test period (E_{ai}).

12.5.3.2.2 Collect the fuel samples from a location in the fuel handling system that provides a sample representative of the fuel bunkered or consumed during a steam generating unit operating day. For the purpose of as-fired fuel sampling under section 12.5.3.2 or section 12.6, the lot size for coal is the weight of coal bunkered or consumed during each steam generating unit operating day. The lot size for oil is the weight of oil supplied to the ''day'' tank or consumed during each steam generating unit operating day. For reporting and calculation purposes, the gross sample shall be identified with the calendar day on which sampling began. For steam generating unit operating days when a coal-fired steam generating unit is operated without coal being added to the bunkers, the coal analysis from the previous ''as bunkered'' coal sample shall be used until coal is bunkered again. For steam generating unit operating days when an oil-fired steam generating unit is operated without oil being added to the oil ''day'' tank, the oil analysis from the previous day shall be used until the ''day'' tank is filled again. Alternative definitions of fuel lot size may be used, subject to prior approval of the Administrator.

12.5.3.2.3 Use ASTM procedures specified in section 12.5.2.1 or 12.5.2.2 to determine %S and GCV.

12.5.4 Daily Geometric Average Percent Reduction from Hourly Values. The geometric average percent reduction ($\%R_{ga}$) is computed using the following equation:

$$\%R_{ga} = 100\left[1 - \text{EXP}\left(\frac{1}{n_t}\sum_{j=1}^{n_t}\ln\frac{E_{jo}}{E_{ji}}\right)\right] \qquad \text{Eq. 19-26}$$

NOTE: The calculation includes only paired data sets (hourly average) for the inlet and outlet pollutant measurements.

12.6 Sulfur Retention Credit for Compliance Fuel. If fuel sampling and analysis procedures in section 12.5.2.1 are being used to determine average SO_2 emission rates (E_{as}) to the atmosphere from a coal-fired steam generating unit when there is no SO_2 control device, the following equation may be used to adjust the emission rate for sulfur retention credits (no credits are allowed for oil-fired systems) (E_{di}) for each sampling period using the following equation:

$$E_{di} = 0.97K\ \frac{\%S}{GDV} \qquad \text{Eq. 19-27}$$

Where:

$$K = 2\times10^{7}\left(\frac{\text{ng } SO_2}{\%S}\right)\left(\frac{kJ}{J}\right)\left(\frac{1}{\text{kg coal}}\right)\left[2\times10^{4}\left(\frac{\text{lb } SO_2}{\%S}\right)\left(\frac{\text{Btu}}{\text{million Btu}}\right)\left(\frac{1}{\text{lb coal}}\right)\right]$$

After calculating E_{di}, use the procedures in section 12.4.2 to determine the average SO_2 emission rate to the atmosphere for the performance test period (E_{ao}).

12.7 Determination of Compliance When Minimum Data Requirement Is Not Met.

12.7.1 Adjusted Emission Rates and Control Device Removal Efficiency. When the minimum data requirement is not met, the Administrator may use the following adjusted emission rates or control device removal efficiencies to determine compliance with the applicable standards.

12.7.1.1 Emission Rate. Compliance with the emission rate standard may be determined by using the lower confidence limit of the emission rate (E_{ao}*) as follows:

$$E^{*}_{ao} = E_{ao} - t_{0.95}S_o \qquad \text{Eq. 19-28}$$

12.7.1.2 Control Device Removal Efficiency. Compliance with the overall emission reduction ($\%R_o$) may be determined by using the lower confidence limit of the emission rate (E_{ao}*) and the upper confidence limit of the inlet pollutant rate (E_{ai}*) in calculating the control device removal efficiency ($\%R_g$) as follows:

$$\%R_g = 100\left(1.0 - \frac{E^{*}_{ao}}{E^{*}_{ai}}\right) \qquad \text{Eq. 19-29}$$

$$E^{*}_{ai} = E_{ai} + t_{0.95}S_i \qquad \text{Eq. 19-30}$$

12.7.2 Standard Deviation of Hourly Average Pollutant Rates. Compute the standard deviation (S_e) of the hourly average pollutant rates using the following equation:

$$S_e = \sqrt{\frac{1}{H} - \frac{1}{H_r}}\ \sqrt{\frac{\sum_{j=1}^{H}\left(E_{hj} - E_a\right)^2}{H-1}} \qquad \text{Eq. 19-31}$$

Equation 19–19 through 19–31 may be used to compute the standard deviation for both the outlet (S_o) and, if applicable, inlet (S_i) pollutant rates.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References [Reserved]

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 19–1—CONVERSION FACTORS FOR CONCENTRATION

From	To	Multiply by
g/scm	ng/scm	10^9
mg/scm	ng/scm	10^6
lb/scf	ng/scm	1.602×10^{13}

TABLE 19–1—CONVERSION FACTORS FOR CONCENTRATION—Continued

From	To	Multiply by
ppm SO_2	ng/scm	2.66×10^6
ppm NO_X	ng/scm	1.912×10^6
ppm SO_2	lb/scf	1.660×10^{-7}
ppm NO_X	lb/scf	1.194×10^{-7}

TABLE 19–2—F FACTORS FOR VARIOUS FUELS[1]

Fuel Type	F_d		F_w		F_c	
	dscm/J	dscf/10^6 Btu	wscm/J	wscf/10^6 Btu	scm/J	scf/10^6 Btu
Coal:						
Anthracite[2]	2.71×10^{-7}	10,100	2.83×10^{-7}	10,540	0.530×10^{-7}	1,970
Bituminus[2]	2.63×10^{-7}	9,780	2.86×10^{-7}	10,640	0.484×10^{-7}	1,800
Lignite	2.65×10^{-7}	9,860	3.21×10^{-7}	11,950	0.513×10^{-7}	1,910
Oil[3]	2.47×10^{-7}	9,190	2.77×10^{-7}	10,320	0.383×10^{-7}	1,420
Gas:.						
Natural	2.34×10^{-7}	8,710	2.85×10^{-7}	10,610	0.287×10^{-7}	1,040
Propane	2.34×10^{-7}	8,710	2.74×10^{-7}	10,200	0.321×10^{-7}	1,190
Butane	2.34×10^{-7}	8,710	2.79×10^{-7}	10,390	0.337×10^{-7}	1,250
Wood	2.48×10^{-7}	9,240			0.492×10^{-7}	1,830
Wood Bark	2.58×10^{-7}	9,600			0.516×10^{-7}	1,920
Municipal	2.57×10^{-7}	9,570			0.488×10^{-7}	1,820
Solid Waste						

[1] Determined at standard conditions: 20 °C (68 °F) and 760 mm Hg (29.92 in Hg)
[2] As classified according to ASTM D 388.
[3] Crude, residual, or distillate.

TABLE 19–3—VALUES FOR $T_{0.95*}$

n[1]	$t_{0.95}$	n[1]	$t_{0.95}$	n[1]	$t_{0.95}$
2	6.31	8	1.89	22–26	1.71
3	2.42	9	1.86	27–31	1.70
4	2.35	10	1.83	32–51	1.68
5	2.13	11	1.81	52–91	1.67
6	2.02	12–16	1.77	92–151	1.66
7	1.94	17–21	1.73	152 or more	1.65

[1]The values of this table are corrected for n-1 degrees of freedom. Use n equal to the number (H) of hourly average data points.

METHOD 20—DETERMINATION OF NITROGEN OXIDES, SULFUR DIOXIDE, AND DILUENT EMISSIONS FROM STATIONARY GAS TURBINES

1.0 Scope and Application

What is Method 20?

Method 20 contains the details you must follow when using an instrumental analyzer to determine concentrations of nitrogen oxides, oxygen, carbon dioxide, and sulfur dioxide in the emissions from stationary gas turbines. This method follows the specific instructions for equipment and performance requirements, supplies, sample collection and analysis, calculations, and data analysis in the methods listed in section 2.0.

1.1 Analytes. What does this method determine?

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X) as nitrogen dioxide:	10102–43–9	Typically <2% of Calibration Span.
Nitric oxide (NO)	10102–44–0	
Nitrogen dioxide NO_2.		
Diluent oxygen (O_2) or carbon dioxide (CO_2)		Typically <2% of Calibration Span.
Sulfur dioxide (SO_X)	7446–09–5	Typically <2% of Calibration Span.

1.2 Applicability. When is this method required? The use of Method 20 may be required by specific New Source Performance Standards, Clean Air Marketing rules, and State Implementation Plans and permits where

measuring SO_2, NO_X, CO_2, and/or O_2 concentrations in stationary gas turbines emissions are required. Other regulations may also require its use.

1.3 Data Quality Objectives. How good must my collected data be? Refer to section 1.3 of Method 7E.

2.0 Summary of Method

In this method, NO_X, O_2 (or CO_2), and SO_X are measured using the following methods found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 3A—Determination of Oxygen and Carbon Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(c) Method 6C—Determination of Sulfur Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(d) Method 7E—Determination of Nitrogen Oxides Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(e) Method 19—Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates.

3.0 Definitions

Refer to section 3.0 of Method 7E for the applicable definitions.

4.0 Interferences

Refer to section 4.0 of Methods 3A, 6C, and 7E as applicable.

5.0 Safety

Refer to section 5.0 of Method 7E.

6.0 Equipment and Supplies

The measurement system design is shown in Figure 7E–1 of Method 7E. Refer to the appropriate methods listed in section 2.0 for equipment and supplies.

7.0 Reagents and Standards

Refer to the appropriate methods listed in section 2.0 for reagents and standards.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling Site and Sampling Points. Follow the procedures of section 8.1 of Method 7E. For the stratification test in section 8.1.2, determine the diluent-corrected pollutant concentration at each traverse point.

8.2 Initial Measurement System Performance Tests. You must refer to the appropriate methods listed in section 2.0 for the measurement system performance tests as applicable.

8.3 Interference Check. You must follow the procedures in section 8.3 of Method 3A or 6C, or section 8.2.7 of Method 7E (as appropriate).

8.4 Sample Collection. You must follow the procedures of section 8.4 of the appropriate methods listed in section 2.0. A test run must have a duration of at least 21 minutes.

8.5 Post-Run System Bias Check, Drift Assessment, and Alternative Dynamic Spike Procedure. You must follow the procedures of sections 8.5 and 8.6 of the appropriate methods listed in section 2.0. A test run must have a duration of at least 21 minutes.

9.0 Quality Control

Follow quality control procedures in section 9.0 of Method 7E.

10.0 Calibration and Standardization

Follow the procedures for calibration and standardization in section 10.0 of Method 7E.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the procedures for calculations and data analysis in section 12.0 of the appropriate method listed in section 2.0. Follow the procedures in section 12.0 of Method 19 for calculating fuel-specific F factors, diluent-corrected pollutant concentrations, and emission rates.

13.0 Method Performance

The specifications for the applicable performance checks are the same as in section 13.0 of Method 7E.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

Refer to section 16.0 of the appropriate method listed in section 2.0 for alternative procedures.

17.0 References

Refer to section 17.0 of the appropriate method listed in section 2.0 for references.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

Refer to section 18.0 of the appropriate method listed in section 2.0 for tables, diagrams, flowcharts, and validation data.

METHOD 21—DETERMINATION OF VOLATILE ORGANIC COMPOUND LEAKS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile Organic Compounds (VOC).	No CAS number assigned.

1.2 Scope. This method is applicable for the determination of VOC leaks from process equipment. These sources include, but are not limited to, valves, flanges and other connections, pumps and compressors, pressure relief devices, process drains, open-ended valves, pump and compressor seal system degassing vents, accumulator vessel vents, agitator seals, and access door seals.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A portable instrument is used to detect VOC leaks from individual sources. The instrument detector type is not specified, but it must meet the specifications and performance criteria contained in section 6.0. A leak definition concentration based on a reference compound is specified in each applicable regulation. This method is intended to locate and classify leaks only, and is not to be used as a direct measure of mass emission rate from individual sources.

3.0 Definitions

3.1 *Calibration gas* means the VOC compound used to adjust the instrument meter reading to a known value. The calibration gas is usually the reference compound at a known concentration approximately equal to the leak definition concentration.

3.2 *Calibration precision* means the degree of agreement between measurements of the same known value, expressed as the relative percentage of the average difference between the meter readings and the known concentration to the known concentration.

3.3 *Leak definition concentration* means the local VOC concentration at the surface of a leak source that indicates that a VOC emission (leak) is present. The leak definition is an instrument meter reading based on a reference compound.

3.4 *No detectable emission* means a local VOC concentration at the surface of a leak source, adjusted for local VOC ambient concentration, that is less than 2.5 percent of the specified leak definition concentration. that indicates that a VOC emission (leak) is not present.

3.5 *Reference compound* means the VOC species selected as the instrument calibration basis for specification of the leak definition concentration. (For example, if a leak definition concentration is 10,000 ppm as methane, then any source emission that results in a local concentration that yields a meter reading of 10,000 on an instrument meter calibrated with methane would be classified as a leak. In this example, the leak definition concentration is 10,000 ppm and the reference compound is methane.)

3.6 *Response factor* means the ratio of the known concentration of a VOC compound to the observed meter reading when measured using an instrument calibrated with the reference compound specified in the applicable regulation.

3.7 *Response time* means the time interval from a step change in VOC concentration at the input of the sampling system to the time at which 90 percent of the corresponding final value is reached as displayed on the instrument readout meter.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Pollutants. Several of the compounds, leaks of which may be determined by this method, may be irritating or corrosive to tissues (*e.g.*, heptane) or may be toxic (*e.g.*, benzene, methyl alcohol). Nearly all are fire hazards. Compounds in emissions should be determined through familiarity with the source. Appropriate precautions can be found in reference documents, such as reference No. 4 in section 16.0.

6.0 Equipment and Supplies

A VOC monitoring instrument meeting the following specifications is required:

6.1 The VOC instrument detector shall respond to the compounds being processed. Detector types that may meet this requirement include, but are not limited to, catalytic oxidation, flame ionization, infrared absorption, and photoionization.

6.2 The instrument shall be capable of measuring the leak definition concentration specified in the regulation.

6.3 The scale of the instrument meter shall be readable to ±2.5 percent of the specified leak definition concentration.

6.4 The instrument shall be equipped with an electrically driven pump to ensure that a sample is provided to the detector at a constant flow rate. The nominal sample flow rate, as measured at the sample probe tip, shall be 0.10 to 3.0 l/min (0.004 to 0.1 ft^3/min) when the probe is fitted with a glass wool plug or filter that may be used to prevent plugging of the instrument.

6.5 The instrument shall be equipped with a probe or probe extension or sampling not to exceed 6.4 mm (¼ in) in outside diameter,

with a single end opening for admission of sample.

6.6 The instrument shall be intrinsically safe for operation in explosive atmospheres as defined by the National Electrical Code by the National Fire Prevention Association or other applicable regulatory code for operation in any explosive atmospheres that may be encountered in its use. The instrument shall, at a minimum, be intrinsically safe for Class 1, Division 1 conditions, and/or Class 2, Division 1 conditions, as appropriate, as defined by the example code. The instrument shall not be operated with any safety device, such as an exhaust flame arrestor, removed.

7.0 Reagents and Standards

7.1 Two gas mixtures are required for instrument calibration and performance evaluation:

7.1.1 Zero Gas. Air, less than 10 parts per million by volume (ppmv) VOC.

7.1.2 Calibration Gas. For each organic species that is to be measured during individual source surveys, obtain or prepare a known standard in air at a concentration approximately equal to the applicable leak definition specified in the regulation.

7.2 Cylinder Gases. If cylinder calibration gas mixtures are used, they must be analyzed and certified by the manufacturer to be within 2 percent accuracy, and a shelf life must be specified. Cylinder standards must be either reanalyzed or replaced at the end of the specified shelf life.

7.3 Prepared Gases. Calibration gases may be prepared by the user according to any accepted gaseous preparation procedure that will yield a mixture accurate to within 2 percent. Prepared standards must be replaced each day of use unless it is demonstrated that degradation does not occur during storage.

7.4 Mixtures with non-Reference Compound Gases. Calibrations may be performed using a compound other than the reference compound. In this case, a conversion factor must be determined for the alternative compound such that the resulting meter readings during source surveys can be converted to reference compound results.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Instrument Performance Evaluation. Assemble and start up the instrument according to the manufacturer's instructions for recommended warmup period and preliminary adjustments.

8.1.1 Response Factor. A response factor must be determined for each compound that is to be measured, either by testing or from reference sources. The response factor tests are required before placing the analyzer into service, but do not have to be repeated at subsequent intervals.

8.1.1.1 Calibrate the instrument with the reference compound as specified in the applicable regulation. Introduce the calibration gas mixture to the analyzer and record the observed meter reading. Introduce zero gas until a stable reading is obtained. Make a total of three measurements by alternating between the calibration gas and zero gas. Calculate the response factor for each repetition and the average response factor.

8.1.1.2 The instrument response factors for each of the individual VOC to be measured shall be less than 10 unless otherwise specified in the applicable regulation. When no instrument is available that meets this specification when calibrated with the reference VOC specified in the applicable regulation, the available instrument may be calibrated with one of the VOC to be measured, or any other VOC, so long as the instrument then has a response factor of less than 10 for each of the individual VOC to be measured.

8.1.1.3 Alternatively, if response factors have been published for the compounds of interest for the instrument or detector type, the response factor determination is not required, and existing results may be referenced. Examples of published response factors for flame ionization and catalytic oxidation detectors are included in References 1–3 of section 17.0.

8.1.2 Calibration Precision. The calibration precision test must be completed prior to placing the analyzer into service and at subsequent 3-month intervals or at the next use, whichever is later.

8.1.2.1 Make a total of three measurements by alternately using zero gas and the specified calibration gas. Record the meter readings. Calculate the average algebraic difference between the meter readings and the known value. Divide this average difference by the known calibration value and multiply by 100 to express the resulting calibration precision as a percentage.

8.1.2.2 The calibration precision shall be equal to or less than 10 percent of the calibration gas value.

8.1.3 Response Time. The response time test is required before placing the instrument into service. If a modification to the sample pumping system or flow configuration is made that would change the response time, a new test is required before further use.

8.1.3.1 Introduce zero gas into the instrument sample probe. When the meter reading has stabilized, switch quickly to the specified calibration gas. After switching, measure the time required to attain 90 percent of the final stable reading. Perform this test sequence three times and record the results. Calculate the average response time.

8.1.3.2 The instrument response time shall be equal to or less than 30 seconds. The instrument pump, dilution probe (if any), sample probe, and probe filter that will be used

during testing shall all be in place during the response time determination.

8.2 Instrument Calibration. Calibrate the VOC monitoring instrument according to section 10.0.

8.3 Individual Source Surveys.

8.3.1 Type I—Leak Definition Based on Concentration. Place the probe inlet at the surface of the component interface where leakage could occur. Move the probe along the interface periphery while observing the instrument readout. If an increased meter reading is observed, slowly sample the interface where leakage is indicated until the maximum meter reading is obtained. Leave the probe inlet at this maximum reading location for approximately two times the instrument response time. If the maximum observed meter reading is greater than the leak definition in the applicable regulation, record and report the results as specified in the regulation reporting requirements. Examples of the application of this general technique to specific equipment types are:

8.3.1.1 Valves. The most common source of leaks from valves is the seal between the stem and housing. Place the probe at the interface where the stem exits the packing gland and sample the stem circumference. Also, place the probe at the interface of the packing gland take-up flange seat and sample the periphery. In addition, survey valve housings of multipart assembly at the surface of all interfaces where a leak could occur.

8.3.1.2 Flanges and Other Connections. For welded flanges, place the probe at the outer edge of the flange-gasket interface and sample the circumference of the flange. Sample other types of nonpermanent joints (such as threaded connections) with a similar traverse.

8.3.1.3 Pumps and Compressors. Conduct a circumferential traverse at the outer surface of the pump or compressor shaft and seal interface. If the source is a rotating shaft, position the probe inlet within 1 cm of the shaft-seal interface for the survey. If the housing configuration prevents a complete traverse of the shaft periphery, sample all accessible portions. Sample all other joints on the pump or compressor housing where leakage could occur.

8.3.1.4 Pressure Relief Devices. The configuration of most pressure relief devices prevents sampling at the sealing seat interface. For those devices equipped with an enclosed extension, or horn, place the probe inlet at approximately the center of the exhaust area to the atmosphere.

8.3.1.5 Process Drains. For open drains, place the probe inlet at approximately the center of the area open to the atmosphere. For covered drains, place the probe at the surface of the cover interface and conduct a peripheral traverse.

8.3.1.6 Open-ended Lines or Valves. Place the probe inlet at approximately the center of the opening to the atmosphere.

8.3.1.7 Seal System Degassing Vents and Accumulator Vents. Place the probe inlet at approximately the center of the opening to the atmosphere.

8.3.1.8 Access door seals. Place the probe inlet at the surface of the door seal interface and conduct a peripheral traverse.

8.3.2 Type II—''No Detectable Emission''. Determine the local ambient VOC concentration around the source by moving the probe randomly upwind and downwind at a distance of one to two meters from the source. If an interference exists with this determination due to a nearby emission or leak, the local ambient concentration may be determined at distances closer to the source, but in no case shall the distance be less than 25 centimeters. Then move the probe inlet to the surface of the source and determine the concentration as outlined in section 8.3.1. The difference between these concentrations determines whether there are no detectable emissions. Record and report the results as specified by the regulation. For those cases where the regulation requires a specific device installation, or that specified vents be ducted or piped to a control device, the existence of these conditions shall be visually confirmed. When the regulation also requires that no detectable emissions exist, visual observations and sampling surveys are required. Examples of this technique are:

8.3.2.1 Pump or Compressor Seals. If applicable, determine the type of shaft seal. Perform a survey of the local area ambient VOC concentration and determine if detectable emissions exist as described in section 8.3.2.

8.3.2.2 Seal System Degassing Vents, Accumulator Vessel Vents, Pressure Relief Devices. If applicable, observe whether or not the applicable ducting or piping exists. Also, determine if any sources exist in the ducting or piping where emissions could occur upstream of the control device. If the required ducting or piping exists and there are no sources where the emissions could be vented to the atmosphere upstream of the control device, then it is presumed that no detectable emissions are present. If there are sources in the ducting or piping where emissions could be vented or sources where leaks could occur, the sampling surveys described in section 8.3.2 shall be used to determine if detectable emissions exist.

8.3.3 Alternative Screening Procedure.

8.3.3.1 A screening procedure based on the formation of bubbles in a soap solution that is sprayed on a potential leak source may be used for those sources that do not have continuously moving parts, that do not have surface temperatures greater than the boiling point or less than the freezing point of the soap solution, that do not have open

areas to the atmosphere that the soap solution cannot bridge, or that do not exhibit evidence of liquid leakage. Sources that have these conditions present must be surveyed using the instrument technique of section 8.3.1 or 8.3.2.

8.3.3.2 Spray a soap solution over all potential leak sources. The soap solution may be a commercially available leak detection solution or may be prepared using concentrated detergent and water. A pressure sprayer or squeeze bottle may be used to dispense the solution. Observe the potential leak sites to determine if any bubbles are formed. If no bubbles are observed, the source is presumed to have no detectable emissions or leaks as applicable. If any bubbles are observed, the instrument techniques of section 8.3.1 or 8.3.2 shall be used to determine if a leak exists, or if the source has detectable emissions, as applicable.

9.0 Quality Control

Section	Quality control measure	Effect
8.1.2	Instrument calibration precision check	Ensure precision and accuracy, respectively, of instrument response to standard.
10.0	Instrument calibration.	

10.0 Calibration and Standardization

10.1 Calibrate the VOC monitoring instrument as follows. After the appropriate warmup period and zero internal calibration procedure, introduce the calibration gas into the instrument sample probe. Adjust the instrument meter readout to correspond to the calibration gas value.

NOTE: If the meter readout cannot be adjusted to the proper value, a malfunction of the analyzer is indicated and corrective actions are necessary before use.

11.0 Analytical Procedures [Reserved]

12.0 Data Analyses and Calculations [Reserved]

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Dubose, D.A., and G.E. Harris. Response Factors of VOC Analyzers at a Meter Reading of 10,000 ppmv for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81051. September 1981.

2. Brown, G.E., *et al.* Response Factors of VOC Analyzers Calibrated with Methane for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81–022. May 1981.

3. DuBose, D.A. *et al.* Response of Portable VOC Analyzers to Chemical Mixtures. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81–110. September 1981.

4. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 22—VISUAL DETERMINATION OF FUGITIVE EMISSIONS FROM MATERIAL SOURCES AND SMOKE EMISSIONS FROM FLARES

NOTE: This method is not inclusive with respect to observer certification. Some material is incorporated by reference from Method 9.

1.0 Scope and Application

This method is applicable for the determination of the frequency of fugitive emissions from stationary sources, only as specified in an applicable subpart of the regulations. This method also is applicable for the determination of the frequency of visible smoke emissions from flares.

2.0 Summary of Method

2.1 Fugitive emissions produced during material processing, handling, and transfer operations or smoke emissions from flares are visually determined by an observer without the aid of instruments.

2.2 This method is used also to determine visible smoke emissions from flares used for combustion of waste process materials.

2.3 This method determines the amount of time that visible emissions occur during the observation period (*i.e.*, the accumulated emission time). This method does not require that the opacity of emissions be determined. Since this procedure requires only the determination of whether visible emissions occur and does not require the determination of opacity levels, observer certification according to the procedures of Method 9 is not required. However, it is necessary that the observer is knowledgeable with respect to the general procedures for determining the presence of visible emissions. At a minimum, the observer must be trained and knowledgeable regarding the effects of background contrast, ambient lighting, observer position relative

to lighting, wind, and the presence of uncombined water (condensing water vapor) on the visibility of emissions. This training is to be obtained from written materials found in References 1 and 2 or from the lecture portion of the Method 9 certification course.

3.0 Definitions

3.1 *Emission frequency* means the percentage of time that emissions are visible during the observation period.

3.2 *Emission time* means the accumulated amount of time that emissions are visible during the observation period.

3.3 *Fugitive emissions* means emissions generated by an affected facility which is not collected by a capture system and is released to the atmosphere. This includes emissions that (1) escape capture by process equipment exhaust hoods; (2) are emitted during material transfer; (3) are emitted from buildings housing material processing or handling equipment; or (4) are emitted directly from process equipment.

3.4 *Observation period* means the accumulated time period during which observations are conducted, not to be less than the period specified in the applicable regulation.

3.5 *Smoke emissions* means a pollutant generated by combustion in a flare and occurring immediately downstream of the flame. Smoke occurring within the flame, but not downstream of the flame, is not considered a smoke emission.

4.0 Interferences

4.1 Occasionally, fugitive emissions from sources other than the affected facility (*e.g.*, road dust) may prevent a clear view of the affected facility. This may particularly be a problem during periods of high wind. If the view of the potential emission points is obscured to such a degree that the observer questions the validity of continuing observations, then the observations shall be terminated, and the observer shall clearly note this fact on the data form.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment

6.1 Stopwatches (two). Accumulative type with unit divisions of at least 0.5 seconds.

6.2 Light Meter. Light meter capable of measuring illuminance in the 50 to 200 lux range, required for indoor observations only.

7.0 Reagents and Supplies [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transfer [Reserved]

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

11.1 Selection of Observation Location. Survey the affected facility, or the building or structure housing the process to be observed, and determine the locations of potential emissions. If the affected facility is located inside a building, determine an observation location that is consistent with the requirements of the applicable regulation (*i.e.*, outside observation of emissions escaping the building/structure or inside observation of emissions directly emitted from the affected facility process unit). Then select a position that enables a clear view of the potential emission point(s) of the affected facility or of the building or structure housing the affected facility, as appropriate for the applicable subpart. A position at least 4.6 m (15 feet), but not more than 400 m (0.25 miles), from the emission source is recommended. For outdoor locations, select a position where the sunlight is not shining directly in the observer's eyes.

11.2 Field Records.

11.2.1 Outdoor Location. Record the following information on the field data sheet (Figure 22–1): Company name, industry, process unit, observer's name, observer's affiliation, and date. Record also the estimated wind speed, wind direction, and sky condition. Sketch the process unit being observed, and note the observer location relative to the source and the sun. Indicate the potential and actual emission points on the sketch.

11.2.2 Indoor Location. Record the following information on the field data sheet (Figure 22–2): Company name, industry, process unit, observer's name, observer's affiliation, and date. Record as appropriate the type, location, and intensity of lighting on the data sheet. Sketch the process unit being observed, and note the observer location relative to the source. Indicate the potential and actual fugitive emission points on the sketch.

11.3 Indoor Lighting Requirements. For indoor locations, use a light meter to measure the level of illumination at a location as close to the emission source(s) as is feasible. An illumination of greater than 100 lux (10 foot candles) is considered necessary for proper application of this method.

11.4 Observations.

11.4.1 Procedure. Record the clock time when observations begin. Use one stopwatch to monitor the duration of the observation

period. Start this stopwatch when the observation period begins. If the observation period is divided into two or more segments by process shutdowns or observer rest breaks (see section 11.4.3), stop the stopwatch when a break begins and restart the stopwatch without resetting it when the break ends. Stop the stopwatch at the end of the observation period. The accumulated time indicated by this stopwatch is the duration of observation period. When the observation period is completed, record the clock time. During the observation period, continuously watch the emission source. Upon observing an emission (condensed water vapor is not considered an emission), start the second accumulative stopwatch; stop the watch when the emission stops. Continue this procedure for the entire observation period. The accumulated elapsed time on this stopwatch is the total time emissions were visible during the observation period (*i.e.*, the emission time.)

11.4.2 Observation Period. Choose an observation period of sufficient length to meet the requirements for determining compliance with the emission standard in the applicable subpart of the regulations. When the length of the observation period is specifically stated in the applicable subpart, it may not be necessary to observe the source for this entire period if the emission time required to indicate noncompliance (based on the specified observation period) is observed in a shorter time period. In other words, if the regulation prohibits emissions for more than 6 minutes in any hour, then observations may (optional) be stopped after an emission time of 6 minutes is exceeded. Similarly, when the regulation is expressed as an emission frequency and the regulation prohibits emissions for greater than 10 percent of the time in any hour, then observations may (optional) be terminated after 6 minutes of emission are observed since 6 minutes is 10 percent of an hour. In any case, the observation period shall not be less than 6 minutes in duration. In some cases, the process operation may be intermittent or cyclic. In such cases, it may be convenient for the observation period to coincide with the length of the process cycle.

11.4.3 Observer Rest Breaks. Do not observe emissions continuously for a period of more than 15 to 20 minutes without taking a rest break. For sources requiring observation periods of greater than 20 minutes, the observer shall take a break of not less than 5 minutes and not more than 10 minutes after every 15 to 20 minutes of observation. If continuous observations are desired for extended time periods, two observers can alternate between making observations and taking breaks.

11.5 Recording Observations. Record the accumulated time of the observation period on the data sheet as the observation period duration. Record the accumulated time emissions were observed on the data sheet as the emission time. Record the clock time the observation period began and ended, as well as the clock time any observer breaks began and ended.

12.0 Data Analysis and Calculations

If the applicable subpart requires that the emission rate be expressed as an emission frequency (in percent), determine this value as follows: Divide the accumulated emission time (in seconds) by the duration of the observation period (in seconds) or by any minimum observation period required in the applicable subpart, if the actual observation period is less than the required period, and multiply this quotient by 100.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Missan, R., and A. Stein. Guidelines for Evaluation of Visible Emissions Certification, Field Procedures, Legal Aspects, and Background Material. EPA Publication No. EPA–340/1–75–007. April 1975.

2. Wohlschlegel, P., and D.E. Wagoner. Guideline for Development of a Quality Assurance Program: Volume IX—Visual Determination of Opacity Emissions from Stationary Sources. EPA Publication No. EPA–650/4–74–005i. November 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

FUGITIVE OR SMOKE EMISSION INSPECTION
OUTDOOR LOCATION

Company Location Company Rep.	Observer Affiliation Date
Sky Conditions Precipitation	Wind Direction Wind Speed
Industry	Process Unit

Sketch process unit: indicate observer position relative to source; indicate potential emission points and/or actual emission points.

OBSERVATIONS	Clock Time	Observation period duration, min:sec	Accumulated emission time, min:sec
Begin Observation			
End Observation			

Figure 22-1

FUGITIVE OR SMOKE EMISSION INSPECTION
INDOOR LOCATION

Company Location Company Rep.	Observer Affiliation Date
Industry	Process Unit

Light type (fluorescent, incandescent, natural)
Light location (overhead, behind observer, etc.)
Illuminance (lux or footcandles)
Sketch process unit: indicate observer position relative to source; indicate potential emission points and/or actual emission points.

OBSERVATIONS	Clock Time	Observation period duration, min:sec	Accumulated emission time, min:sec
Begin			
End Observation			

Figure 22-2

METHOD 23—DETERMINATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS FROM STATIONARY SOURCES

1. Applicability and Principle

1.1 Applicability. This method is applicable to the determination of polychlorinated dibenzo-p-dioxins (PCDD's) and polychlorinated dibenzofurans (PCDF's) from stationary sources.

1.2 Principle. A sample is withdrawn from the gas stream isokinetically and collected in the sample probe, on a glass fiber filter, and on a packed column of adsorbent material. The sample cannot be separated into a particle vapor fraction. The PCDD's and

PCDF's are extracted from the sample, separated by high resolution gas chromatography, and measured by high resolution mass spectrometry.

2. Apparatus

2.1 Sampling. A schematic of the sampling train used in this method is shown in Figure 23–1. Sealing greases may not be used in assembling the train. The train is identical to that described in section 2.1 of Method 5 of this appendix with the following additions:

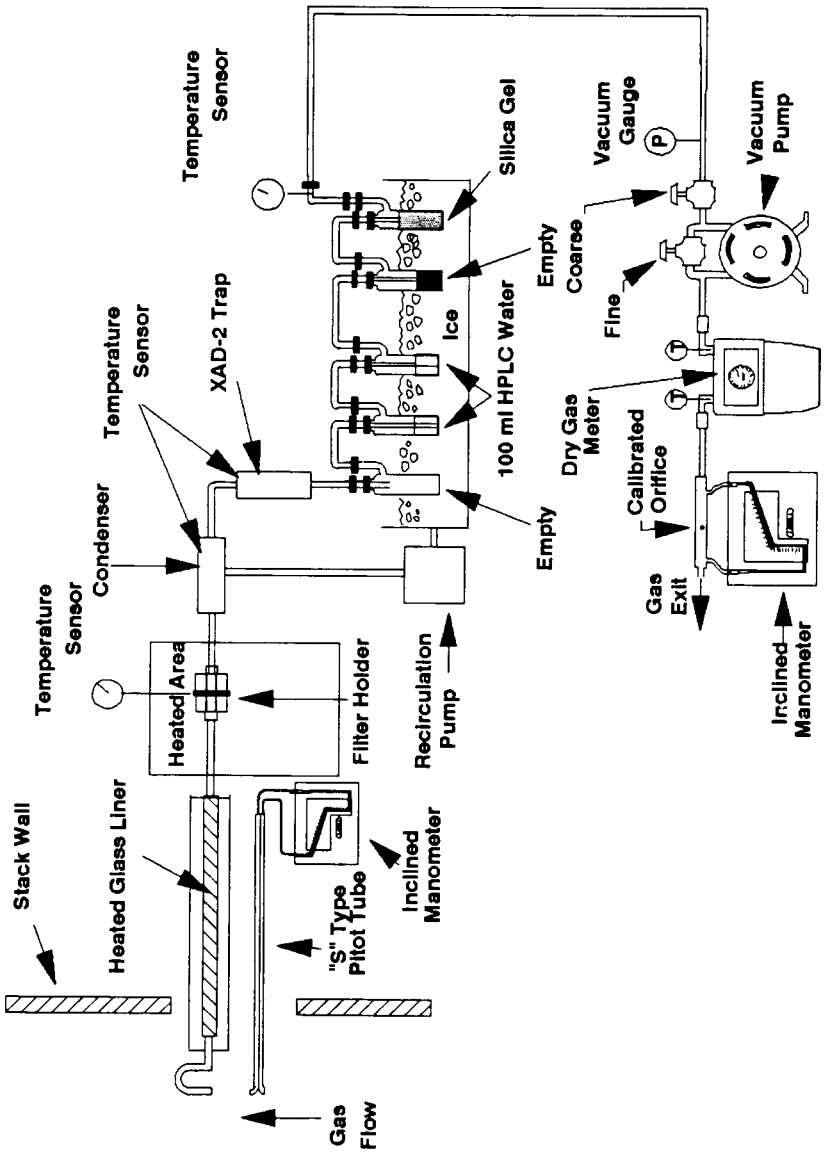


Figure 23.1 Sampling train

2.1.1 Nozzle. The nozzle shall be made of nickel, nickel-plated stainless steel, quartz, or borosilicate glass.

2.1.2 Sample Transfer Lines. The sample transfer lines, if needed, shall be heat traced, heavy walled TFE (½ in. OD with ⅛ in. wall) with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases. The line shall be as short as possible and must be maintained at 120 °C.

2.1.1 Filter Support. Teflon or Teflon-coated wire.

2.1.2 Condenser. Glass, coil type with compatible fittings. A schematic diagram is shown in Figure 23–2.

2.1.3 Water Bath. Thermostatically controlled to maintain the gas temperature exiting the condenser at <20 °C (68 °F).

2.1.4 Adsorbent Module. Glass container to hold the solid adsorbent. A shematic diagram is shown in Figure 23–2. Other physical configurations of the resin trap/condenser assembly are acceptable. The connecting fittings shall form leak-free, vacuum tight seals. No sealant greases shall be used in the sampling train. A coarse glass frit is included to retain the adsorbent.

2.2 Sample Recovery.

2.2.1 Fitting Caps. Ground glass, Teflon tape, or aluminum foil (Section 2.2.6) to cap off the sample exposed sections of the train.

2.2.2 Wash Bottles. Teflon, 500-ml.

2.2.3 Probe-Liner Probe-Nozzle, and Filter-Holder Brushes. Inert bristle brushes with precleaned stainless steel or Teflon handles. The probe brush shall have extensions of stainless steel or Teflon, at least as long as the probe. The brushes shall be properly sized and shaped to brush out the nozzle, probe liner, and transfer line, if used.

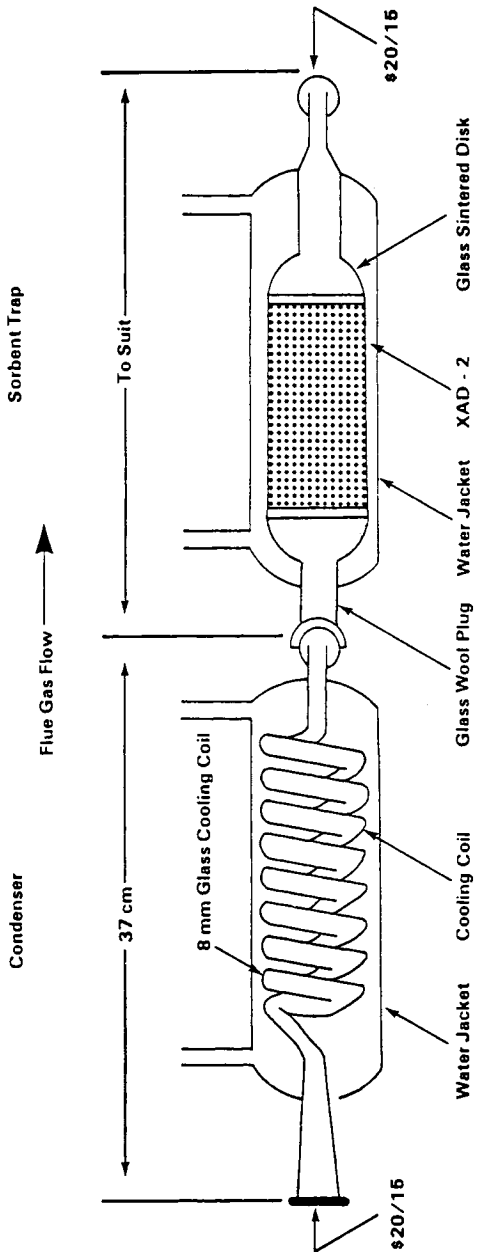


Figure 23.2. Condenser and adsorbent trap

2.2.4 Filter Storage Container. Sealed filter holder, wide-mouth amber glass jar with Teflon-lined cap, or glass petri dish.

2.2.5 Balance. Triple beam.

2.2.6 Aluminum Foil. Heavy duty, hexane-rinsed.

2.2.7 Storage Container. Air-tight container to store silica gel.

2.2.8 Graduated Cylinder. Glass, 250-ml with 2-ml graduation.

2.2.9 Glass Sample Storage Container. Amber glass bottle for sample glassware washes, 500- or 1000-ml, with leak free Teflon-lined caps.

2.3 Analysis.

2.3.1 Sample Container. 125- and 250-ml flint glass bottles with Teflon-lined caps.

2.3.2 Test Tube. Glass.

2.3.3 Soxhlet Extraction Apparatus. Capable of holding 43 × 123 mm extraction thimbles.

2.3.4 Extraction Thimble. Glass, precleaned cellulosic, or glass fiber.

2.3.5 Pasteur Pipettes. For preparing liquid chromatographic columns.

2.3.6 Reacti-vials. Amber glass, 2-ml, silanized prior to use.

2.3.7 Rotary Evaporator. Buchi/Brinkman RF–121 or equivalent.

2.3.8 Nitrogen Evaporative Concentrator. N-Evap Analytical Evaporator Model III or equivalent.

2.3.9 Separatory Funnels. Glass, 2-liter.

2.3.10 Gas Chromatograph. Consisting of the following components:

2.3.10.1 Oven. Capable of maintaining the separation column at the proper operating temperature ±°C and performing programmed increases in temperature at rates of at least 40 °C/min.

2.3.10.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperatures ±1 °C.

2.3.10.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

2.3.10.4 Capillary Columns. A fused silica column, 60 × 0.25 mm inside diameter (ID), coated with DB–5 and a fused silica column, 30 m × 0.25 mm ID coated with DB–225. Other column systems may be used provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of section 6.1.2.2.

2.3.11 Mass Spectrometer. Capable of routine operation at a resolution of 1:10000 with a stability of ±5 ppm.

2.3.12 Data System. Compatible with the mass spectrometer and capable of monitoring at least five groups of 25 ions.

2.3.13 Analytical Balance. To measure within 0.1 mg.

3. Reagents

3.1 Sampling.

3.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D 2986–71 (Reapproved 1978) (incorporated by reference—see §60.17).

3.1.1.1 Precleaning. All filters shall be cleaned before their initial use. Place a glass extraction thimble and 1 g of silica gel and a plug of glass wool into a Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Place no more than 50 filters in the thimble onto the silica gel bed and top with the cleaned glass wool. Charge the Soxhlet with toluene and reflux for 16 hours. After extraction, allow the Soxhlet to cool, remove the filters, and dry them under a clean N_2 stream. Store the filters in a glass petri dish sealed with Teflon tape.

3.1.2 Adsorbent Resin. Amberlite XAD–2 resin. Thoroughly cleaned before initial use.

3.1.2.1 Cleaning Procedure. This procedure may be carried out in a giant Soxhlet extractor. An all-glass filter thimble containing an extra-course frit is used for extraction of XAD–2. The frit is recessed 10–15 mm above a crenelated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass wool plug and a stainless steel ring because it floats on methylene chloride. This process involves sequential extraction in the following order.

Solvent	Procedure
Water	Initial rinse: Place resin in a beaker, rinse once with water, and discard. Fill with water a second time, let stand overnight, and discard.
Water	Extract with water for 8 hours.
Methanol	Extract for 22 hours.
Methylene Chloride	Extract for 22 hours.
Toluene	Extract for 22 hours.

3.1.2.2 Drying.

3.1.2.2.1 Drying Column. Pyrex pipe, 10.2 cm ID by 0.6 m long, with suitable retainers.

3.1.2.2.2 Procedure. The adsorbent must be dried with clean inert gas. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has proven to be a reliable source of large volumes of gas free from organic contaminants. Connect the liquid nitrogen cylinder to the column by a length of cleaned copper tubing, 0.95 cm ID, coiled to pass through a heat source. A convenient heat source is a water-bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40 °C. Continue flowing nitrogen through the adsorbent until all the residual solvent is removed. The flow rate should be sufficient to gently agitate the particles but not so excessive as the cause the particles to fracture.

3.1.2.3 Quality Control Check. The adsorbent must be checked for residual toluene.

3.1.2.3.1 Extraction. Weigh 1.0 g sample of dried resin into a small vial, add 3 ml of toluene, cap the vial, and shake it well.

3.1.2.3.2 Analysis. Inject a 2 µl sample of the extract into a gas chromatograph operated under the following conditions:

Column: 6 ft × ⅛ in stainless steel containing 10 percent OV–101 on 100/120 Supelcoport.
Carrier Gas: Helium at a rate of 30 ml/min.
Detector: Flame ionization detector operated at a sensitivity of 4×10^{-11} A/mV.
Injection Port Temperature: 250 °C.
Detector Temperature: 305 °C.
Oven Temperature: 30 °C for 4 min; programmed to rise at 40 °C/min until it reaches 250 °C; return to 30 °C after 17 minutes.

Compare the results of the analysis to the results from the reference solution. Prepare the reference solution by injection 2.5 µl of methylene chloride into 100 ml of toluene. This corresponds to 100 µg of methylene chloride per g of adsorbent. The maximum acceptable concentration is 1000 µg/g of adsorbent. If the adsorbent exceeds this level, drying must be continued until the excess methylene chloride is removed.

3.1.2.4 Storage. The adsorbent must be used within 4 weeks of cleaning. After cleaning, it may be stored in a wide mouth amber glass container with a Teflon-lined cap or placed in one of the glass adsorbent modules tightly sealed with glass stoppers. If precleaned adsorbent is purchased in sealed containers, it must be used within 4 weeks after the seal is broken.

3.1.3 Glass Wool. Cleaned by sequential immersion in three aliquots of methylene chloride, dried in a 110 °C oven, and stored in a methylene chloride-washed glass jar with a Teflon-lined screw cap.

3.1.4 Water. Deionized distilled and stored in a methylene chloride-rinsed glass container with a Teflon-lined screw cap.

3.1.5 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175 °C (350 °F) for two hours. New silica gel may be used as received. Alternately other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

3.1.6 Chromic Acid Cleaning Solution. Dissolve 20 g of sodium dichromate in 15 ml of water, and then carefully add 400 ml of concentrated sulfuric acid.

3.2 Sample Recovery.

3.2.2 Acetone. Pesticide quality.

3.2.2 Methylene Chloride. Pesticide qualtity.

3.2.3 Toluene. Pesticide quality.

3.3 Analysis.

3.3.1 Potassium Hydroxide. ACS grade, 2-percent (weight/volume) in water.

3.3.2 Sodium Sulfate. Granulated, reagent grade. Purify prior to use by rinsing with methylene chloride and oven drying. Store the cleaned material in a glass container with a Teflon-lined screw cap.

3.3.3 Sulfuric Acid. Reagent grade.

3.3.4 Sodium Hydroxide. 1.0 N. Weigh 40 g of sodium hydroxide into a 1-liter volumetric flask. Dilute to 1 liter with water.

3.3.5 Hexane. Pesticide grade.

3.3.6 Methylene Chloride. Pesticide grade.

3.3.7 Benzene. Pesticide Grade.

3.3.8 Ethyl Acetate.

3.3.9 Methanol. Pesticide Grade.

3.3.10 Toluene. Pesticide Grade.

3.3.11 Nonane. Pesticide Grade.

3.3.12 Cyclohexane. Pesticide Grade.

3.3.13 Basic Alumina. Activity grade 1, 100–200 mesh. Prior to use, activate the alumina by heating for 16 hours at 130 °C before use. Store in a desiccator. Pre-activated alumina may be purchased from a supplier and may be used as received.

3.3.14 Silica Gel. Bio-Sil A, 100–200 mesh. Prior to use, activate the silica gel by heating for at least 30 minutes at 180 °C. After cooling, rinse the silica gel sequentially with methanol and methylene chloride. Heat the rinsed silica gel at 50 °C for 10 minutes, then increase the temperature gradually to 180 °C over 25 minutes and maintain it at this temperature for 90 minutes. Cool at room temperature and store in a glass container with a Teflon-lined screw cap.

3.3.15 Silica Gel Impregnated with Sulfuric Acid. Combine 100 g of silica gel with 44 g of concentrated sulfuric acid in a screw capped glass bottle and agitate thoroughly. Disperse the solids with a stirring rod until a uniform mixture is obtained. Store the mixture in a glass container with a Teflon-lined screw cap.

3.3.16 Silica Gel Impregnated with Sodium Hydroxide. Combine 39 g of 1 N sodium hydroxide with 100 g of silica gel in a screw capped glass bottle and agitate thoroughly. Disperse solids with a stirring rod until a uniform mixture is obtained. Store the mixture in glass container with a Teflon-lined screw cap.

3.3.17 Carbon/Celite. Combine 10.7 g of AX–21 carbon with 124 g of Celite 545 in a 250-ml glass bottle with a Teflon-lined screw cap. Agitate the mixture thoroughly until a uniform mixture is obtained. Store in the glass container.

3.3.18 Nitrogen. Ultra high purity.

3.3.19 Hydrogen. Ultra high purity.

3.3.20 Internal Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Internal Standards'' in 10 ml of nonane.

3.3.21 Surrogate Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Surrogate Standards'' in 10 ml of nonane.

3.3.22 Recovery Standard Solution. Prepare a stock standard solution containing the

isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Recovery Standards'' in 10 ml of nonane.

4. Procedure

4.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, testers should be trained and experienced with the test procedures.

4.1.1 Pretest Preparation.

4.1.1.1 Cleaning Glassware. All glass components of the train upstream of and including the adsorbent module, shall be cleaned as described in section 3A of the ''Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples.'' Special care shall be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. Any residue shall be removed by soaking the glassware for several hours in a chromic acid cleaning solution prior to cleaning as described above.

4.1.1.2 Adsorbent Trap. The traps must be loaded in a clean area to avoid contamination. They may not be loaded in the field. Fill a trap with 20 to 40 g of XAD–2. Follow the XAD–2 with glass wool and tightly cap both ends of the trap. Add 100 μl of the surrogate standard solution (section 3.3.21) to each trap.

4.1.1.3 Sample Train. It is suggested that all components be maintained according to the procedure described in APTD–0576. Alternative mercury-free thermometers may be used if the thermometers are, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

4.1.1.4 Silica Gel. Weigh several 200 to 300 g portions of silica gel in an air tight container to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel may be weighed directly in its impinger or sampling holder just prior to sampling.

4.1.1.5 Filter. Check each filter against light for irregularities and flaws or pinhole leaks. Pack the filters flat in a clean glass container.

4.1.2 Preliminary Determinations. Same as section 4.1.2 of Method 5.

4.1.3 Preparation of Collection Train.

4.1.3.1 During preparation and assembly of the sampling train, keep all train openings where contamination can enter, sealed until just prior to assembly or until sampling is about to begin.

NOTE: Do not use sealant grease in assembling the train.

4.1.3.2 Place approximately 100 ml of water in the second and third impingers, leave the first and fourth impingers empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fifth impinger.

4.1.3.3 Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

4.1.3.4 Assemble the train as shown in Figure 23–1.

4.1.3.5 Turn on the adsorbent module and condenser coil recirculating pump and begin monitoring the adsorbent module gas entry temperature. Ensure proper sorbent temperature gas entry temperature before proceeding and before sampling is initiated. It is extremely important that the XAD–2 adsorbent resin temperature never exceed 50 °C because thermal decomposition will occur. During testing, the XAD–2 temperature must not exceed 20 °C for efficient capture of the PCDD's and PCDF's.

4.1.4 Leak-Check Procedure. Same as Method 5, section 4.1.4.

4.1.5 Sample Train Operation. Same as Method 5, section 4.1.5.

4.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Seal the nozzle end of the sampling probe with Teflon tape or aluminum foil.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe. Remove the probe from the train and close off both ends with aluminum foil. Seal off the inlet to the train with Teflon tape, a ground glass cap, or aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area shall be clean and enclosed so that the chances of losing or contaminating the sample are minimized. Smoking, which could contaminate the sample, shall not be allowed in the cleanup area.

Inspect the train prior to and during disassembly and note any abnormal conditions, e.g., broken filters, colored impinger liquid, etc. Treat the samples as follows:

4.2.1 Container No. 1. Either seal the filter holder or carefully remove the filter from the filter holder and place it in its identified container. Use a pair of cleaned tweezers to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and filter fibers which adhere to the filter holder gasket, by using a dry inert bristle brush and a sharp-edged blade. Seal the container.

4.2.2 Adsorbent Module. Remove the module from the train, tightly cap both ends, label it, cover with aluminum foil, and store it on ice for transport to the laboratory.

4.2.3 Container No. 2. Quantitatively recover material deposited in the nozzle, probe transfer lines, the front half of the filter holder, and the cyclone, if used, first, by

brushing while rinsing three times each with acetone and then, by rinsing the probe three times with methylene chloride. Collect all the rinses in Container No. 2.

Rinse the back half of the filter holder three times with acetone. Rinse the connecting line between the filter and the condenser three times with acetone. Soak the connecting line with three separate portions of methylene chloride for 5 minutes each. If using a separate condenser and adsorbent trap, rinse the condenser in the same manner as the connecting line. Collect all the rinses in Container No. 2 and mark the level of the liquid on the container.

4.2.4 Container No. 3. Repeat the methylene chloride-rinsing described in section 4.2.3 using toluene as the rinse solvent. Collect the rinses in Container No. 3 and mark the level of the liquid on the container.

4.2.5 Impinger Water. Measure the liquid in the first three impingers to within ±1 ml by using a graduated cylinder or by weighing it to within ±0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

Discard the liquid after measuring and recording the volume or weight.

4.2.7 Silica Gel. Note the color of the indicating silica gel to determine if it has been completely spent and make a mention of its condition. Transfer the silica gel from the fifth impinger to its original container and seal. If a moisture determination is made, follow the applicable procedures in sections 8.7.6.3 and 11.2.3 of Method 5 to handle and weigh the silica gel. If moisture is not measured, the silica gel may be disposed.

5. Analysis

All glassware shall be cleaned as described in section 3A of the ''Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples.'' All samples must be extracted within 30 days of collection and analyzed within 45 days of extraction.

5.1 Sample Extraction.

5.1.1 Extraction System. Place an extraction thimble (section 2.3.4), 1 g of silica gel, and a plug of glass wool into the Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Remove the extraction thimble from the extraction system and place it in a glass beaker to catch the solvent rinses.

5.1.2 Container No. 1 (Filter). Transfer the contents directly to the glass thimble of the extraction system and extract them simultaneously with the XAD–2 resin.

5.1.3 Adsorbent Cartridge. Suspend the adsorbent module directly over the extraction thimble in the beaker (See section 5.1.1). The glass frit of the module should be in the up position. Using a Teflon squeeze bottle containing toluene, flush the XAD–2 into the thimble onto the bed of cleaned silica gel. Thoroughly rinse the glass module catching the rinsings in the beaker containing the thimble. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. Add the XAD–2 glass wool plug into the thimble.

5.1.4 Container No. 2 (Acetone and Methylene Chloride). Concentrate the sample to a volume of about 1–5 ml using the rotary evaporator apparatus, at a temperature of less than 37 °C. Rinse the sample container three times with small portions of methylene chloride and add these to the concentrated solution and concentrate further to near dryness. This residue contains particulate matter removed in the rinse of the train probe and nozzle. Add the concentrate to the filter and the XAD–2 resin in the Soxhlet apparatus described in section 5.1.1.

5.1.5 Extraction. Add 100 µl of the internal standard solution (Section 3.3.20) to the extraction thimble containing the contents of the adsorbent cartridge, the contents of Container No. 1, and the concentrate from section 5.1.4. Cover the contents of the extraction thimble with the cleaned glass wool plug to prevent the XAD–2 resin from floating into the solvent reservoir of the extractor. Place the thimble in the extractor, and add the toluene contained in the beaker to the solvent reservoir. Pour additional toluene to fill the reservoir approximately ⅔ full. Add Teflon boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle three times per hour. Extract the sample for 16 hours. After extraction, allow the Soxhlet to cool. Transfer the toluene extract and three 10-ml rinses to the rotary evaporator. Concentrate the extract to approximately 10 ml. At this point the analyst may choose to split the sample in half. If so, split the sample, store one half for future use, and analyze the other according to the procedures in sections 5.2 and 5.3. In either case, use a nitrogen evaporative concentrator to reduce the volume of the sample being analyzed to near dryness. Dissolve the residue in 5 ml of hexane.

5.1.6 Container No. 3 (Toluene Rinse). Add 100 µl of the Internal Standard solution (section 3.3.2) to the contents of the container. Concentrate the sample to a volume of about 1–5 ml using the rotary evaporator apparatus at a temperature of less than 37 °C. Rinse the sample container apparatus at a temperature of less than 37 °C. Rinse the sample container three times with small portions of toluene and add these to the concentrated solution and concentrate further to near dryness. Analyze the extract separately according to the procedures in sections 5.2 and 5.3, but concentrate the solution in a rotary evaporator apparatus rather than a nitrogen evaporative concentrator.

5.2 Sample Cleanup and Fractionation.

5.2.1 Silica Gel Column. Pack one end of a glass column, 20 mm × 230 mm, with glass wool. Add in sequence, 1 g silica gel, 2 g of sodium hydroxide impregnated silica gel, 1 g silica gel, 4 g of acid-modified silica gel, and 1 g of silica gel. Wash the column with 30 ml of hexane and discard it. Add the sample extract, dissolved in 5 ml of hexane to the column with two additional 5-ml rinses. Elute the column with an additional 90 ml of hexane and retain the entire eluate. Concentrate this solution to a volume of about 1 ml using the nitrogen evaporative concentrator (section 2.3.7).

5.2.2 Basic Alumina Column. Shorten a 25-ml disposable Pasteur pipette to about 16 ml. Pack the lower section with glass wool and 12 g of basic alumina. Transfer the concentrated extract from the silica gel column to the top of the basic alumina column and elute the column sequentially with 120 ml of 0.5 percent methylene chloride in hexane followed by 120 ml of 35 percent methylene chloride in hexane. Discard the first 120 ml of eluate. Collect the second 120 ml of eluate and concentrate it to about 0.5 ml using the nitrogen evaporative concentrator.

5.2.3 AX–21 Carbon/Celite 545 Column. Remove the botton 0.5 in. from the tip of a 9-ml disposable Pasteur pipette. Insert a glass fiber filter disk in the top of the pipette 2.5 cm from the constriction. Add sufficient carbon/celite mixture to form a 2 cm column. Top with a glass wool plug. In some cases AX–21 carbon fines may wash through the glass wool plug and enter the sample. This may be prevented by adding a celite plug to the exit end of the column. Rinse the column in sequence with 2 ml of 50 percent benzene in ethyl acetate, 1 ml of 50 percent methylene chloride in cyclohexane, and 2 ml of hexane. Discard these rinses. Transfer the concentrate in 1 ml of hexane from the basic alumina column to the carbon/celite column along with 1 ml of hexane rinse. Elute the column sequentially with 2 ml of 50 percent methylene chloride in hexane and 2 ml of 50 percent benzene in ethyl acetate and discard these eluates. Invert the column and elute in the reverse direction with 13 ml of toluene. Collect this eluate. Concentrate the eluate in a rotary evaporator at 50 °C to about 1 ml. Transfer the concentrate to a Reacti-vial using a toluene rinse and concentrate to a volume of 200 µl using a stream of N_2. Store extracts at room temperature, shielded from light, until the analysis is performed.

5.3 Analysis. Analyze the sample with a gas chromatograph coupled to a mass spectrometer (GC/MS) using the instrumental parameters in sections 5.3.1 and 5.3.2. Immediately prior to analysis, add a 20 µl aliquot of the Recovery Standard solution from Table 1 to each sample. A 2 µl aliquot of the extract is injected into the GC. Sample extracts are first analyzed using the DB–5 capillary column to determine the concentration of each isomer of PCDD's and PCDF's (tetra-through octa-). If tetra-chlorinated dibenzofurans are detected in this analysis, then analyze another aliquot of the sample in a separate run, using the DB–225 column to measure the 2,3,7,8 tetra-chloro dibenzofuran isomer. Other column systems may be used, provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of section 6.1.2.2.

5.3.1 Gas Chromatograph Operating Conditions.

5.3.1.1 Injector. Configured for capillary column, splitless, 250 °C.

5.3.1.2 Carrier Gas. Helium, 1–2 ml/min.

5.3.1.3 Oven. Initially at 150 °C. Raise by at least 40 °C/min to 190 °C and then at 3 °C/min up to 300 °C.

5.3.2 High Resolution Mass Spectrometer.

5.3.2.1 Resolution. 10000 m/e.

5.3.2.2 Ionization Mode. Electron impact.

5.3.2.3 Source Temperature 250 °C.

5.3.2.4 Monitoring Mode. Selected ion monitoring. A list of the various ions to be monitored is summarized in Table 3.

5.3.2.5 Identification Criteria. The following identification criteria shall be used for the characterization of polychlorinated dibenzodioxins and dibenzofurans.

1. The integrated ion-abundance ratio (M/M + 2 or M + 2/M + 4) shall be within 15 percent of the theoretical value. The acceptable ion-abundance ratio ranges for the identification of chlorine-containing compounds are given in Table 4.

2. The retention time for the analytes must be within 3 seconds of the corresponding ^{13}C-labeled internal standard, surrogate or alternate standard.

3. The monitored ions, shown in Table 3 for a given analyte, shall reach their maximum within 2 seconds of each other.

4. The identification of specific isomers that do not have corresponding ^{13}C-labeled standards is done by comparison of the relative retention time (RRT) of the analyte to the nearest internal standard retention time with reference (i.e., within 0.005 RRT units) to the comparable RRT's found in the continuing calibration.

5. The signal to noise ratio for all monitored ions must be greater than 2.5.

6. The confirmation of 2, 3, 7, 8–TCDD and 2, 3, 7, 8–TCDF shall satisfy all of the above identification criteria.

7. For the identification of PCDF's, no signal may be found in the corresponding PCDPE channels.

5.3.2.6 Quantification. The peak areas for the two ions monitored for each analyte are summed to yield the total response for each analyte. Each internal standard is used to quantify the indigenous PCDD's or PCDF's in its homologous series. For example, the $^{13}C_{12}$–2,3,7,8-tetra chlorinated dibenzodioxin is used to calculate the concentrations of all

other tetra chlorinated isomers. Recoveries of the tetra- and penta- internal standards are calculated using the $^{13}C_{12}$–1,2,3,4–TCDD. Recoveries of the hexa- through octa- internal standards are calculated using $^{13}C_{12}$–1,2,3,7,8,9–HxCDD. Recoveries of the surrogate standards are calculated using the corresponding homolog from the internal standard.

6. Calibration

Same as Method 5 with the following additions.

6.1 GC/MS System.

6.1.1 Initial Calibration. Calibrate the GC/MS system using the set of five standards shown in Table 2. The relative standard deviation for the mean response factor from each of the unlabeled analytes (Table 2) and of the internal, surrogate, and alternate standards shall be less than or equal to the values in Table 5. The signal to noise ratio for the GC signal present in every selected ion current profile shall be greater than or equal to 2.5. The ion abundance ratios shall be within the control limits in Table 4.

6.1.2 Daily Performance Check.

6.1.2.1 Calibration Check. Inject on µl of solution Number 3 from Table 2. Calculate the relative response factor (RRF) for each compound and compare each RRF to the corresponding mean RRF obtained during the initial calibration. The analyzer performance is acceptable if the measured RRF's for the labeled and unlabeled compounds for the daily run are within the limits of the mean values shown in Table 5. In addition, the ion-abundance ratios shall be within the allowable control limits shown in Table 4.

6.1.2.2 Column Separation Check. Inject a solution of a mixture of PCDD's and PCDF's that documents resolution between 2,3,7,8–TCDD and other TCDD isomers. Resolution is defined as a valley between peaks that is less than 25 percent of the lower of the two peaks. Identify and record the retention time windows for each homologous series.

Perform a similar resolution check on the confirmation column to document the resolution between 2,3,7,8 TCDF and other TCDF isomers.

6.2 Lock Channels. Set mass spectrometer lock channels as specified in Table 3. Monitor the quality control check channels specified in Table 3 to verify instrument stability during the analysis.

7. Quality Control

7.1 Sampling Train Collection Efficiency Check. Add 100 µl of the surrogate standards in Table 1 to the absorbent cartridge of each train before collecting the field samples.

7.2 Internal Standard Percent Recoveries. A group of nine carbon labeled PCDD's and PCDF's representing, the tetra-through octachlorinated homologues, is added to every sample prior to extraction. The role of the internal standards is to quantify the native PCDD's and PCDF's present in the sample as well as to determine the overall method efficiency. Recoveries of the internal standards must be between 40 to 130 percent for the tetra-through hexachlorinated compounds while the range is 25 to 130 percent for the higher hepta- and octachlorinated homologues.

7.3 Surrogate Recoveries. The five surrogate compounds in Table 2 are added to the resin in the adsorbent sampling cartridge before the sample is collected. The surrogate recoveries are measured relative to the internal standards and are a measure of collection efficiency. They are not used to measure native PCDD's and PCDF's. All recoveries shall be between 70 and 130 percent. Poor recoveries for all the surrogates may be an indication of breakthrough in the sampling train. If the recovery of all standards is below 70 percent, the sampling runs must be repeated. As an alternative, the sampling runs do not have to be repeated if the final results are divided by the fraction of surrogate recovery. Poor recoveries of isolated surrogate compounds should not be grounds for rejecting an entire set of the samples.

7.4 Toluene QA Rinse. Report the results of the toluene QA rinse separately from the total sample catch. Do not add it to the total sample.

8.0 [Reserved]

9. Calculations

Same as Method 5, section 6 with the following additions.

9.1 Nomenclature.

A_{ai} = Integrated ion current of the noise at the retention time of the analyte.

A^*_{ci} = Integrated ion current of the two ions characteristic of the internal standard i in the calibration standard.

A_{cij} = Integrated ion current of the two ions characteristic of compound i in the jth calibration standard.

A^*_{cij} = Integrated ion current of the two ions characteristic of the internal standard i in the jth calibration standard.

A_{csi} = Integrated ion current of the two ions characteristic of surrogate compound i in the calibration standard.

A_i = Integrated ion current of the two ions characteristic of compound i in the sample.

A^*_i = Integrated ion current of the two ions characteristic of internal standard i in the sample.

A_{rs} = Integrated ion current of the two ions characteristic of the recovery standard.

A_{si} = Integrated ion current of the two ions characteristic of surrogate compound i in the sample.

C_i = Concentration of PCDD or PCDF i in the sample, pg/M^3.

C_T = Total concentration of PCDD's or PCDF's in the sample, pg/M^3.
m_{ci} = Mass of compound i in the calibration standard injected into the analyzer, pg.
m_{rs} = Mass of recovery standard in the calibration standard injected into the analyzer, pg.
m_{si} = Mass of surrogate compound in the calibration standard, pg.
RRF_i = Relative response factor.
RRF_{rs} = Recovery standard response factor.
RRF_s = Surrogate compound response factor.

9.2 Average Relative Response Factor.

$$RRF_i = \frac{1}{n}\sum_{j=1}^{n}\frac{A_{cij}\, m^*_{ci}}{A^*_{cij}\, m_{ci}} \qquad \text{Eq. 23-1}$$

9.3 Concentration of the PCDD's and PCDF's.

$$C_i = \frac{m_i^* A_i}{A_i^* RRF_i V_{mstd}} \qquad \text{Eq. 23-2}$$

9.4 Recovery Standard Response Factor.

$$RRF_{rs} = \frac{A_{ci}^* m_{rs}}{A_{rs} m_{ci}^*} \qquad \text{Eq. 23-3}$$

9.5 Recovery of Internal Standards (R*).

$$R^* = \frac{A_i^* m_{rs}}{A_{rs} RF_{rs} m_i^*} \times 100\% \qquad \text{Eq. 23-4}$$

9.6 Surrogate Compound Response Factor.

$$RRF_s = \frac{A_{ci}^* m_s}{A_{cis} m_{ci}^*} \qquad \text{Eq. 23-5}$$

9.7 Recovery of Surrogate Compounds (R_s).

$$R_s = \frac{A_s m_i^*}{A_i^* RRF_s m_s} \times 100\% \qquad \text{Eq. 23-6}$$

9.8 Minimum Detectable Limit (MDL).

$$MDL = \frac{2.5\, A_{ai} m_i^*}{A_{ci}^* RRF_i} \qquad \text{Eq. 23-7}$$

9.9 Total Concentration of PCDD's and PCDF's in the Sample.

$$C_{Tr} = \sum_{i=1}^{n} C_i \qquad \text{Eq. 23-8}$$

Any PCDD's or PCDF's that are reported as nondetected (below the MDL) shall be counted as zero for the purpose of calculating the total concentration of PCDD's and PCDF's in the sample.

10. Bibliography

1. American Society of Mechanical Engineers. Sampling for the Determination of Chlorinated Organic Compounds in Stack Emissions. Prepared for U.S. Department of Energy and U.S. Environmental Protection Agency. Washington DC. December 1984. 25 p.

2. American Society of Mechanical Engineers. Analytical Procedures to Assay Stack Effluent Samples and Residual Combustion Products for Polychlorinated Dibenzo-p-Dioxins (PCDD) and Polychlorinated Dibenzofurans (PCDF). Prepared for the U.S. Department of Energy and U.S. Environmental Protection Agency. Washington, DC. December 1984. 23 p.

3. Thompson, J. R. (ed.). Analysis of Pesticide Residues in Human and Environmental Samples. U.S. Environmental Protection Agency. Research Triangle Park, NC. 1974.

4. Triangle Laboratories. Case Study: Analysis of Samples for the Presence of Tetra Through Octachloro-p-Dibenzodioxins and Dibenzofurans. Research Triangle Park, NC. 1988. 26 p.

5. U.S. Environmental Protection Agency. Method 8290—The Analysis of Polychlorinated Dibenzo-p-dioxin and Polychlorinated Dibenzofurans by High-Resolution Gas Chromotography/High-Resolution Mass Spectrometry. In: Test Methods for Evaluating Solid Waste. Washington, DC. SW–846.

TABLE 1—COMPOSITION OF THE SAMPLE FORTIFICATION AND RECOVERY STANDARDS SOLUTIONS

Analyte	Concentration (pg/µl)
Internal Standards:	
$^{13}C_{12}$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100
$^{13}C_{12}$-OCDD	100
$^{13}C_{12}$-2,3,7,8-TCDF	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100
Surrogate Standards:	
$^{37}Cl_4$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100
Recovery Standards:	
$^{13}C_{12}$-1,2,3,4-TCDD	500
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	500

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS

Compound	Concentrations (pg/µL)				
	Solution No.				
	1	2	3	4	5
Alternate Standard:					
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	2.5	5	25	250	500

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS—Continued

Compound	Concentrations (pg/μL)				
	Solution No.				
	1	2	3	4	5
Recovery Standards:					
$^{13}C_{12}$-1,2,3,4-TCDD ..	100	100	100	100	100

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS—Continued

Compound	Concentrations (pg/μL)				
	Solution No.				
	1	2	3	4	5
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

TABLE 3—ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HIGH RESOLUTION MASS SPECTROMETRY FOR PCDD'S AND PCDF'S

Descriptor No.	Accurate mass	Ion type	Elemental composition	Analyte
2	292.9825	LOCK	C_7F_{11}	PFK
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M + 2	$C_{12}H_4{}^{35}Cl^{37}O$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M + 2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}ClO_2$	TCDD
	321.8936	M + 2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD (S)
	330.9792	QC	C_7F_{13}	PFK
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9339	M + 2	$^{13}C_{12}H_4{}^{35}Cl^{37}ClO_2$	TCDD (S)
	339.8597	M + 2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PECDF
	341.8567	M + 4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M + 2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M + 4	$^{13}C_{12}H_3{}^{35}Cl^{3537}Cl_2O$	PeCDF (S)
	355.8546	M + 2	$C_{12}H_3{}^{35}Cl_3 37ClO_2$	PeCDD
	357.8516	M + 4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M + 2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M + 4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}\ Cl_2O_2$	PeCDD (S)
	375.8364	M + 2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
	409.7974	M + 2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCPDE
3	373.8208	M + 2	$C_{12}H_2 35Cl_5{}^{37}ClO$	HxCDF
	375.8178	M + 4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M + 2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8157	M + 2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M + 4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	392.9760	LOCK	C_9F_{15}	PFK
	401.8559	M + 2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M + 4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDD (S)
	445.7555	M + 4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	430.9729	QC	C_9F_{17}	PFK
4	407.7818	M + 2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M + 4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8253	M	$^{13}C_{12}H^{35}Cl_7O$	HpCDF (S)
	419.8220	M + 2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF (S)
	423.7766	M + 2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M + 4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M + 2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M + 4	$^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S)
	479.7165	M + 4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCPDE
	430.9729	LOCK	C_9F_{17}	PFK
	441.7428	M + 2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M + 4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M + 2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M + 4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M + 2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M + 4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S)
	513.6775	M + 4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O_2$	DCDPE
	442.9728	QC	$C_{10}F_{17}$	PFK

(a) The following nuclidic masses were used:
H = 1.007825
C = 12.000000
^{13}C = 13.003355
F = 18.9984
O = 15.994915
^{35}Cl = 34.968853
^{37}Cl = 36.965903

S = Labeled Standard
QC = Ion selected for monitoring instrument stability during the GC/MS analysis.

TABLE 4—ACCEPTABLE RANGES FOR ION-ABUNDANCE RATIOS OF PCDD'S AND PCDF'S

No. of chlorine atoms	Ion type	Theoretical ratio	Control limits	
			Lower	Upper
4	M/M + 2	0.77	0.65	0.89
5	M + 2/M + 4	1.55	1.32	1.78
6	M + 2/M + 4	1.24	1.05	1.43
6[a]	M/M + 2	0.51	0.43	0.59
7[b]	M/M + 2	0.44	0.37	0.51
7	M + 2/M + 4	1.04	0.88	1.20
8	M + 2/M + 4	0.89	0.76	1.02

[a] Used only for ^{13}C-HxCDF.
[b] Used only for ^{13}C-HpCDF.

TABLE 5—MINIMUM REQUIREMENTS FOR INITIAL AND DAILY CALIBRATION RESPONSE FACTORS

Compound	Relative response factors	
	Initial calibration RSD	Daily calibration % difference
Unlabeled Analytes:		
2,3,7,8-TCDD	25	25
2,3,7,8-TCDF	25	25
1,2,3,7,8-PeCDD	25	25
1,2,3,7,8-PeCDF	25	25
2,3,4,7,8-PeCDF	25	25
1,2,4,5,7,8-HxCDD	25	25
1,2,3,6,7,8-HxCDD	25	25
1,2,3,7,8,9-HxCDD	25	25
1,2,3,4,7,8-HxCDF	25	25
1,2,3,6,7,8-HxCDF	25	25
1,2,3,7,8,9-HxCDF	25	25
2,3,4,6,7,8-HxCDF	25	25
1,2,3,4,6,7,8-HpCDD	25	25
1,2,3,4,6,7,8-HpCDF	25	25
OCDD	25	25
OCDF	30	30
Internal Standards:		
$^{13}C_{12}$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-1,2,3,7,8-PeCDD	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	30	30
$^{13}C_{12}$-OCDD	30	30
$^{13}C_{12}$-2,3,7,8-TCDF	30	30
$^{13}C_{12}$-1,2,3,7,8-PeCDF	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	30	30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	30	30
Surrogate Standards:		
$^{37}Cl_4$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-2,3,4,7,8-PeCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	25	25
Alternate Standard:		
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	25	25

METHOD 24—DETERMINATION OF VOLATILE MATTER CONTENT, WATER CONTENT, DENSITY, VOLUME SOLIDS, AND WEIGHT SOLIDS OF SURFACE COATINGS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile organic compounds	No CAS Number assigned
Water.	7732–18–5

1.2 Applicability. This method is applicable for the determination of volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or other related surface coatings.

1.3 Precision and Bias. Intra-and inter-laboratory analytical precision statements are presented in section 13.1. No bias has been identified.

2.0 Summary of Method

2.1 Standard methods are used to determine the volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or other related surface coatings.

3.0 Definitions

3.1 *Waterborne coating* means any coating which contains more than 5 percent water by weight in its volatile fraction.

3.2 *Multicomponent coatings* are coatings that are packaged in two or more parts, which are combined before application. Upon combination a coreactant from one part of the coating chemically reacts, at ambient conditions, with a coreactant from another part of the coating.

3.3 *Ultraviolet (UV) radiation-cured coatings* are coatings which contain unreacted monomers that are polymerized by exposure to ultraviolet light.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Components. Several of the compounds that may be contained in the coatings analyzed by this method may be irritating or corrosive to tissues (e.g., heptane) or may be toxic (e.g., benzene, methyl alcohol). Nearly all are fire hazards.

Appropriate precautions can be found in reference documents, such as Reference 3 of section 16.0.

6.0 Equipment and Supplies

The equipment and supplies specified in the ASTM methods listed in sections 6.1 through 6.6 (incorporated by reference—see §60.17 for acceptable versions of the methods) are required:

6.1 ASTM D 1475–60, 80, or 90, Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products.

6.2 ASTM D 2369–81, 87, 90, 92, 93, or 95, Standard Test Method for Volatile Content of Coatings.

6.3 ASTM D 3792–79 or 91, Standard Test Method for Water Content of Water Reducible Paints by Direct Injection into a Gas Chromatograph.

6.4 ASTM D 4017–81, 90, or 96a, Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Titration Method.

6.5 ASTM 4457–85 91, Standard Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph.

6.6 ASTM D 5403–93, Standard Test Methods for Volatile Content of Radiation Curable Materials.

6.7 ASTM D 6419–00, Test Method for Volatile Content of Sheet-Fed and Coldset Web Offset Printing Inks.

7.0 Reagents and Standards

7.1 The reagents and standards specified in the ASTM methods listed in sections 6.1 through 6.6 are required.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Follow the sample collection, preservation, storage, and transport procedures described in Reference 1 of section 16.0.

9.0 Quality Control

9.1 Reproducibility

NOTE: Not applicable to UV radiation-cured coatings). The variety of coatings that may be subject to analysis makes it necessary to verify the ability of the analyst and the analytical procedures to obtain reproducible results for the coatings tested. Verification is accomplished by running duplicate analyses on each sample tested (Sections 11.2 through 11.4) and comparing the results with the intra-laboratory precision statements (Section 13.1) for each parameter.

9.2 Confidence Limits for Waterborne Coatings. Because of the inherent increased imprecision in the determination of the VOC content of waterborne coatings as the weight percent of water increases, measured parameters for waterborne coatings are replaced with appropriate confidence limits (Section 12.6). These confidence limits are based on measured parameters and inter-laboratory precision statements.

10.0 Calibration and Standardization

10.1 Perform the calibration and standardization procedures specified in the ASTM methods listed in sections 6.1 through 6.6.

11.0 Analytical Procedure

Additional guidance can be found in Reference 2 of section 16.0.

11.1 Non Thin-film Ultraviolet Radiation-cured (UV radiation-cured) Coatings.

11.1.1 Volatile Content. Use the procedure in ASTM D 5403 to determine the volatile matter content of the coating except the curing test described in NOTE 2 of ASTM D 5403 is required.

11.1.2 Water Content. To determine water content, follow section 11.3.2.

11.1.3 Coating Density. To determine coating density, follow section 11.3.3.

11.1.4 Solids Content. To determine solids content, follow section 11.3.4.

11.1.5 To determine if a coating or ink can be classified as a thin-film UV cured coating or ink, use the equation in section 12.2. If C is less than 0.2 g and A is greater than or equal to 225 cm^2 (35 in^2) then the coating or ink is considered a thin-film UV radiation-cured coating and ASTM D 5403 is not applicable.

NOTE: As noted in section 1.4 of ASTM D 5403, this method may not be applicable to radiation curable materials wherein the volatile material is water.

11.2 Multi-component Coatings.

11.2.1 Sample Preparation.

11.2.1.1 Prepare about 100 ml of sample by mixing the components in a storage container, such as a glass jar with a screw top or a metal can with a cap. The storage container should be just large enough to hold the mixture. Combine the components (by weight or volume) in the ratio recommended by the manufacturer. Tightly close the container between additions and during mixing to prevent loss of volatile materials. However, most manufacturers mixing instructions are by volume. Because of possible error caused by expansion of the liquid when measuring the volume, it is recommended that the components be combined by weight. When weight is used to combine the components and the manufacturer's recommended ratio is by volume, the density must be determined by section 11.3.3.

11.2.1.2 Immediately after mixing, take aliquots from this 100 ml sample for determination of the total volatile content, water content, and density.

11.2.2 Volatile Content. To determine total volatile content, use the apparatus and

reagents described in ASTM D2369 (incorporated by reference; see §60.17 for the approved versions of the standard), respectively, and use the following procedures:

11.2.2.1 Weigh and record the weight of an aluminum foil weighing dish. Add 3 ±1 ml of suitable solvent as specified in ASTM D2369 to the weighing dish. Using a syringe as specified in ASTM D2369, weigh to 1 mg, by difference, a sample of coating into the weighing dish. For coatings believed to have a volatile content less than 40 weight percent, a suitable size is 0.3 + 0.10 g, but for coatings believed to have a volatile content greater than 40 weight percent, a suitable size is 0.5 ±0.1 g.

NOTE: If the volatile content determined pursuant to section 12.4 is not in the range corresponding to the sample size chosen repeat the test with the appropriate sample size. Add the specimen dropwise, shaking (swirling) the dish to disperse the specimen completely in the solvent. If the material forms a lump that cannot be dispersed, discard the specimen and prepare a new one. Similarly, prepare a duplicate. The sample shall stand for a minimum of 1 hour, but no more than 24 hours prior to being oven cured at 110 ±5 °C (230 ±9 °F) for 1 hour.

11.2.2.2 Heat the aluminum foil dishes containing the dispersed specimens in the forced draft oven for 60 min at 110 ±5 °C (230 ±9 °F). Caution—provide adequate ventilation, consistent with accepted laboratory practice, to prevent solvent vapors from accumulating to a dangerous level.

11.2.2.3 Remove the dishes from the oven, place immediately in a desiccator, cool to ambient temperature, and weigh to within 1 mg.

11.2.2.4 Run analyses in pairs (duplicate sets) for each coating mixture until the criterion in section 11.4 is met. Calculate W_v following Equation 24–2 and record the arithmetic average.

11.2.3 Water Content. To determine water content, follow section 11.3.2.

11.2.4 Coating Density. To determine coating density, follow section 11.3.3.

11.2.5 Solids Content. To determine solids content, follow section 11.3.4.

11.2.6 Exempt Solvent Content. To determine the exempt solvent content, follow section 11.3.5.

NOTE: For all other coatings (*i.e.*, water-or solvent-borne coatings) not covered by multicomponent or UV radiation-cured coatings, analyze as shown below:

11.3 Water-or Solvent-borne coatings.

11.3.1 Volatile Content. Use the procedure in ASTM D 2369 to determine the volatile matter content (may include water) of the coating.

11.3.1.1 Record the following information:

W_1 = weight of dish and sample before heating, g

W_2 = weight of dish and sample after heating, g

W_3 = sample weight, g.

11.3.1.2 Calculate the weight fraction of the volatile matter (W_v) for each analysis as shown in section 12.3.

11.3.1.3 Run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement in section 13.1.

11.3.1.4 Record the arithmetic average (W_v).

11.3.2 Water Content. For waterborne coatings only, determine the weight fraction of water (W_w) using either ASTM D 3792 or ASTM D 4017.

11.3.2.1 Run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement in section 13.1.

11.3.2.2 Record the arithmetic average (w_w).

11.3.3 Coating Density. Determine the density (Dc, kg/l) of the surface coating using the procedure in ASTM D 1475.

11.3.3.1 Run duplicate analyses until each value in a set deviates from the mean of the set by no more than the intra-laboratory precision statement in section 13.1.

11.3.3.2 Record the arithmetic average (D_c).

11.3.4 Solids Content. Determine the volume fraction (V_s) solids of the coating by calculation using the manufacturer's formulation.

11.3.5 Exempt Solvent Content. Determine the weight fraction of exempt solvents (W_E) by using ASTM Method D4457. Run a duplicate set of determinations and record the arithmetic average (W_E).

11.4 Sample Analysis Criteria. For W_v and W_w, run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement for that parameter. For D_c, run duplicate analyses until each value in a set deviates from the mean of the set by no more than the intra-laboratory precision statement. If, after several attempts, it is concluded that the ASTM procedures cannot be used for the specific coating with the established intra-laboratory precision (excluding UV radiation-cured coatings), the U.S. Environmental Protection Agency (EPA) will assume responsibility for providing the necessary procedures for revising the method or precision statements upon written request to: Director, Emissions, Monitoring, and Analysis Division, MD–14, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

12.0 Calculations and Data Analysis

12.1 Nomenclature.

A = Area of substrate, cm^2, (in^2).

C = Amount of coating or ink added to the substrate, g.

D_c = Density of coating or ink, g/cm^3 (g/in^3).

F = Manufacturer's recommended film thickness, cm (in).
W_o = Weight fraction of nonaqueous volatile matter, g/g.
W_s = Weight fraction of solids, g/g.
W_v = Weight fraction of the volatile matter, g/g.
W_w = Weight fraction of the water, g/g.

12.2 To determine if a coating or ink can be classified as a thin-film UV cured coating or ink, use the following equation:

$$C = F A D_c \qquad \text{Eq. 24-1}$$

12.3 Calculate W_v for each analysis as shown below:

$$W_v = \frac{W_1 - W_2}{W_3} \qquad \text{Eq. 24-2}$$

12.4 Nonaqueous Volatile Matter.
12.4.1 Solvent-borne Coatings.

$$W_o = W_v \qquad \text{Eq. 24-3}$$

12.4.2 Waterborne Coatings.

$$W_o = W_v - W_w \qquad \text{Eq. 24-4}$$

12.4.3 Coatings Containing Exempt Solvents.

$$W_o = W_v - W_E - W_w \qquad \text{Eq. 24-5}$$

12.5 Weight Fraction Solids.

$$W_s = 1 - W_v \qquad \text{Eq. 24-6}$$

12.6 Confidence Limit Calculations for Waterborne Coatings. To calculate the lower confidence limit, subtract the appropriate inter-laboratory precision value from the measured mean value for that parameter. To calculate the upper confidence limit, add the appropriate inter-laboratory precision value to the measured mean value for that parameter. For W_v and D_c, use the lower confidence limits; for W_w, use the upper confidence limit. Because W_s is calculated, there is no adjustment for this parameter.

13.0 Method Performance

13.1 Analytical Precision Statements. The intra-and inter-laboratory precision statements are given in Table 24–1 in section 17.0.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as specified in section 6.0, with the addition of the following:

1. Standard Procedure for Collection of Coating and Ink Samples for Analysis by Reference Methods 24 and 24A. EPA–340/1–91–010. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

2. Standard Operating Procedure for Analysis of Coating and Ink Samples by Reference Methods 24 and 24A.

EPA–340/1–91–011. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

3. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 24–1—ANALYTICAL PRECISION STATEMENTS

	Intra-laboratory	Inter-laboratory
Volatile matter content, W_v	±0.015 $\overline{W}_v$	±0.047 $\overline{W}_v$
Water content, W_w	±0.029 $\overline{W}_w$	±0.075 $\overline{W}_w$
Density, D_c	±0.001 kg/l	±0.002 kg/l

METHOD 24A—DETERMINATION OF VOLATILE MATTER CONTENT AND DENSITY OF PUBLICATION ROTOGRAVURE INKS AND RELATED PUBLICATION ROTOGRAVURE COATINGS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile organic compounds (VOC).	No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of the VOC content and density of solvent-borne (solvent-reducible) publication rotogravure inks and related publication rotogravure coatings.

2.0 Summary of Method

2.1 Separate procedures are used to determine the VOC weight fraction and density of the ink or related coating and the density of the solvent in the ink or related coating. The VOC weight fraction is determined by measuring the weight loss of a known sample quantity which has been heated for a specified length of time at a specified temperature. The density of both the ink or related coating and solvent are measured by a standard procedure. From this information, the VOC volume fraction is calculated.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Components. Some of the compounds that may be contained in the inks or related coatings analyzed by this method may be irritating or corrosive to tissues or may be toxic. Nearly all are fire hazards. Appropriate precautions can be found in reference documents, such as Reference 6 of section 16.0.

6.0 Equipment and Supplies

The following equipment and supplies are required for sample analysis:

6.1 Weighing Dishes. Aluminum foil, 58 mm (2.3 in.) in diameter by 18 mm (0.7 in.) high, with a flat bottom. There must be at least three weighing dishes per sample.

6.2 Disposable Syringe. 5 ml.

6.3 Analytical Balance. To measure to within 0.1 mg.

6.4 Oven. Vacuum oven capable of maintaining a temperature of 120 ±2 °C (248 ±4 °F) and an absolute pressure of 510 ±51 mm Hg (20 ±2 in. Hg) for 4 hours. Alternatively, a forced draft oven capable of maintaining a temperature of 120 ±2 °C (248 ±4 °F) for 24 hours.

6.5 The equipment and supplies specified in ASTM D 1475–60, 80, or 90 (incorporated by reference—see §60.17).

7.0 Reagents and Standards

7.1 The reagents and standards specified in ASTM D 1475–60, 80, or 90 are required.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Follow the sample collection, preservation, storage, and transport procedures described in Reference 4 of section 16.0.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

Additional guidance can be found in Reference 5 of section 16.0.

11.1 VOC Weight Fraction. Shake or mix the ink or related coating sample thoroughly to assure that all the solids are completely suspended. Label and weigh to the nearest 0.1 mg a weighing dish and record this weight (M_{x1}). Using a 5 ml syringe, without a needle, extract an aliquot from the ink or related coating sample. Weigh the syringe and aliquot to the nearest 0.1 mg and record this weight (M_{cy1}). Transfer 1 to 3 g of the aliquot to the tared weighing dish. Reweigh the syringe and remaining aliquot to the nearest 0.1 mg and record this weight (M_{cy2}). Heat the weighing dish with the transferred aliquot in a vacuum oven at an absolute pressure of 510 ±51 mm Hg (20 ±2 in. Hg) and a temperature of 120 ±2 °C (248 ±4 °F) for 4 hours. Alternatively, heat the weighing dish with the transferred aliquot in a forced draft oven at a temperature of 120 ±2 °C for 24 hours. After the weighing dish has cooled, reweigh it to the nearest 0.1 mg and record the weight (M_{x2}). Repeat this procedure two times for each ink or related coating sample, for a total of three samples.

11.2 Ink or Related Coating Density. Determine the density of the ink or related coating (D_c) according to the procedure outlined in ASTM D 1475. Make a total of three determinations for each ink or related coating sample. Report the ink or related coating density as the arithmetic average (D_c) of the three determinations.

11.3 Solvent Density. Determine the density of the solvent (D_o) according to the procedure outlined in ASTM D 1475. Make a total of three determinations for each ink or related coating sample. Report the solvent density as the arithmetic average (D_o) of the three determinations.

12.0 Calculations and Data Analysis

12.1 VOC Weight Fraction. For each determination, calculate the volatile organic content weight fraction (W_o) using the following equation:

$$W_o = \frac{M_{x1} + M_{cy1} - M_{cy2} - M_{x2}}{M_{cy1} - M_{cy2}} \qquad \text{Eq. 24A-1}$$

Make a total of three determinations. Report the VOC weight fraction as the arithmetic average ($\bar{W}_o$) of the three determinations.

12.2 VOC Volume Fraction. Calculate the volume fraction volatile organic content (V_o) using the following equation:

$$V_o = \frac{\overline{W}_o \overline{D}_c}{\overline{D}_o} \qquad \text{Eq. 24A-2}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products. ASTM Designation D 1475.

2. Teleconversation. Wright, Chuck, Inmont Corporation with Reich, R., A., Radian Corporation. September 25, 1979, Gravure Ink Analysis.

3. Teleconversation. Oppenheimer, Robert, Gravure Research Institute with Burt, Rick, Radian Corporation, November 5, 1979, Gravure Ink Analysis.

4. Standard Procedure for Collection of Coating and Ink Samples for Analysis by Reference Methods 24 and 24A. EPA–340/1–91–010. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

5. Standard Operating Procedure for Analysis of Coating and Ink Samples by Reference Methods 24 and 24A. EPA–340/1–91–011. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

6. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

Method 25—Determination of Total Gaseous Nonmethane Organic Emissions as Carbon

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total gaseous nonmethane organic compounds (TGNMO)	N/A	Dependent upon analytical equipment.

1.2 Applicability.

1.2.1 This method is applicable for the determination of volatile organic compounds (VOC) (measured as total gaseous nonmethane organics (TGNMO) and reported as carbon) in stationary source emissions. This method is not applicable for the determination of organic particulate matter.

1.2.2 This method is not the only method that applies to the measurement of VOC. Costs, logistics, and other practicalities of source testing may make other test methods more desirable for measuring VOC contents of certain effluent streams. Proper judgment is required in determining the most applicable VOC test method. For example, depending upon the molecular composition of the organics in the effluent stream, a totally automated semicontinuous nonmethane organics (NMO) analyzer interfaced directly to the source may yield accurate results. This approach has the advantage of providing emission data semicontinuously over an extended time period.

1.2.3 Direct measurement of an effluent with a flame ionization detector (FID) analyzer may be appropriate with prior characterization of the gas stream and knowledge that the detector responds predictably to the organic compounds in the stream. If present, methane (CH_4) will, of course, also be measured. The FID can be used under any of the following limited conditions: (1) Where only one compound is known to exist; (2) when the organic compounds consist of only hydrogen and carbon; (3) where the relative percentages of the compounds are known or can be determined, and the FID responses to the compounds are known; (4) where a consistent mixture of the compounds exists before and after emission control and only the relative concentrations are to be assessed; or (5) where the FID can be calibrated against mass standards of the compounds emitted (solvent emissions, for example).

1.2.4 Another example of the use of a direct FID is as a screening method. If there is enough information available to provide a rough estimate of the analyzer accuracy, the FID analyzer can be used to determine the VOC content of an uncharacterized gas stream. With a sufficient buffer to account for possible inaccuracies, the direct FID can be a useful tool to obtain the desired results without costly exact determination.

1.2.5 In situations where a qualitative/quantitative analysis of an effluent stream is desired or required, a gas chromatographic FID system may apply. However, for sources emitting numerous organics, the time and expense of this approach will be formidable.

2.0 Summary of Method

2.1 An emission sample is withdrawn from the stack at a constant rate through a heated filter and a chilled condensate trap by means of an evacuated sample tank. After sampling is completed, the TGNMO are determined by independently analyzing the condensate trap and sample tank fractions and combining the analytical results. The organic content of the condensate trap fraction is determined by oxidizing the NMO to carbon dioxide (CO_2) and quantitatively collecting in the effluent in an evacuated vessel; then a portion of the CO_2 is reduced to CH_4 and measured by an FID. The organic content of the sample tank fraction is measured by injecting a portion of the sample into a gas chromatographic column to separate the NMO from carbon monoxide (CO), CO_2, and CH_4; the NMO are oxidized to CO_2, reduced to CH_4, and measured by an FID. In this manner, the variable response of the FID associated with different types of organics is eliminated.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Carbon Dioxide and Water Vapor. When carbon dioxide (CO_2) and water vapor are present together in the stack, they can produce a positive bias in the sample. The magnitude of the bias depends on the concentrations of CO_2 and water vapor. As a guideline, multiply the CO_2 concentration, expressed as volume percent, times the water vapor concentration. If this product does not exceed 100, the bias can be considered insignificant. For example, the bias is not significant for a source having 10 percent CO_2 and 10 percent water vapor, but it might be significant for a source having 10 percent CO_2 and 20 percent water vapor.

4.2. Particulate Matter. Collection of organic particulate matter in the condensate trap would produce a positive bias. A filter is included in the sampling equipment to minimize this bias.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling system consists of a heated probe, heated filter, condensate trap, flow control system, and sample tank (see Figure 25–1). The TGNMO sampling equipment can be constructed from commercially available components and components fabricated in a machine shop. The following equipment is required:

6.1.1 Heated Probe. 6.4-mm (¼-in.) OD stainless steel tubing with a heating system capable of maintaining a gas temperature at the exit end of at least 129 °C (265 °F). The probe shall be equipped with a temperature sensor at the exit end to monitor the gas temperature. A suitable probe is shown in Figure 25–1. The nozzle is an elbow fitting attached to the front end of the probe while the temperature sensor is inserted in the side arm of a tee fitting attached to the rear of the probe. The probe is wrapped with a suitable length of high temperature heating tape, and then covered with two layers of glass cloth insulation and one layer of aluminum foil or an equivalent wrapping.

NOTE: If it is not possible to use a heating system for safety reasons, an unheated system with an in-stack filter is a suitable alternative.

6.1.2 Filter Holder. 25-mm (15/16-in.) ID Gelman filter holder with 303 stainless steel body and 316 stainless steel support screen with the Viton O-ring replaced by a Teflon O-ring.

6.1.3 Filter Heating System.

6.1.3.1 A metal box consisting of an inner and an outer shell separated by insulating material with a heating element in the inner shell capable of maintaining a gas temperature at the filter of 121 ±3 °C (250 ±5 °F). The heating box shall include temperature sensors to monitor the gas temperature immediately upstream and immediately downstream of the filter.

6.1.3.2 A suitable heating box is shown in Figure 25–2. The outer shell is a metal box that measures 102 mm × 280 mm × 292 mm (4 in. × 11 in. × 11½ in.), while the inner shell is a metal box measuring 76 mm × 229 mm × 241 mm (3 in. × 9 in. × 9½ in.). The inner box is supported by 13-mm (½-in.) phenolic rods. The void space between the boxes is filled with ceramic fiber insulation which is sealed in place by means of a silicon rubber bead around the upper sides of the box. A removable lid made in a similar manner, with a 25-mm (1-in.) gap between the parts is used to cover the heating chamber. The inner box is heated with a 250-watt cartridge heater, shielded by a stainless steel shroud. The heater is regulated by a thermostatic temperature controller which is set to maintain a gas temperature of 121 °C (250 °F) as measured by the temperature sensor upstream of the filter.

NOTE: If it is not possible to use a heating system for safety reasons, an unheated system with an in-stack filter is a suitable alternative.

6.1.4 Condensate Trap. 9.5-mm (⅜-in.) OD 316 stainless steel tubing bent into a U-shape. Exact dimensions are shown in Figure

25–3. The tubing shall be packed with coarse quartz wool, to a density of approximately 0.11 g/cm^3 before bending. While the condensate trap is packed with dry ice in the Dewar, an ice bridge may form between the arms of the condensate trap making it difficult to remove the condensate trap. This problem can be prevented by attaching a steel plate between the arms of the condensate trap in the same plane as the arms to completely fill the intervening space.

6.1.5 Valve. Stainless steel control valve for starting and stopping sample flow.

6.1.6 Metering Valve. Stainless steel valve for regulating the sample flow rate through the sample train.

6.1.7 Rate Meter. Rotameter, or equivalent, capable of measuring sample flow in the range of 60 to 100 cm^3/min (0.13 to 0.21 ft^3/hr).

6.1.8 Sample Tank. Stainless steel or aluminum tank with a minimum volume of 4 liters (0.14 ft^3).

NOTE: Sample volumes greater than 4 liters may be required for sources with low organic concentrations.

6.1.9 Mercury Manometer. U-tube manometer or absolute pressure gauge capable of measuring pressure to within 1 mm Hg in the range of 0 to 900 mm.

6.1.10 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

6.2 Condensate Recovery. The system for the recovery of the organics captured in the condensate trap consists of a heat source, an oxidation catalyst, a nondispersive infrared (NDIR) analyzer, and an intermediate collection vessel (ICV). Figure 25–4 is a schematic of a typical system. The system shall be capable of proper oxidation and recovery, as specified in section 10.1.1. The following major components are required:

6.2.1 Heat Source. Sufficient to heat the condensate trap (including probe) to a temperature of 200 °C (390 °F). A system using both a heat gun and an electric tube furnace is recommended.

6.2.2 Heat Tape. Sufficient to heat the connecting tubing between the water trap and the oxidation catalyst to 100 °C (212 °F).

6.2.3 Oxidation Catalyst. A suitable length of 9.5 mm (3/8-in.) OD Inconel 600 tubing packed with 15 cm (6 in.) of 3.2 mm (3/8-in.) diameter 19 percent chromia on alumina pellets. The catalyst material is packed in the center of the catalyst tube with quartz wool packed on either end to hold it in place.

6.2.4 Water Trap. Leak-proof, capable of removing moisture from the gas stream.

6.2.5 Syringe Port. A 6.4-mm (1/4-in.) OD stainless steel tee fitting with a rubber septum placed in the side arm.

6.2.6 NDIR Detector. Capable of indicating CO_2 concentration in the range of zero to 5 percent, to monitor the progress of combustion of the organic compounds from the condensate trap.

6.2.7 Flow-Control Valve. Stainless steel, to maintain the trap conditioning system near atmospheric pressure.

6.2.8 Intermediate Collection Vessel. Stainless steel or aluminum, equipped with a female quick connect. Tanks with nominal volumes of at least 6 liters (0.2 ft^3) are recommended.

6.2.9 Mercury Manometer. Same as described in section 6.1.9.

6.2.10 Syringe. 10-ml gas-tight glass syringe equipped with an appropriate needle.

6.2.11 Syringes. 10-µl and 50-µl liquid injection syringes.

6.2.12 Liquid Sample Injection Unit. 316 Stainless steel U-tube fitted with an injection septum (see Figure 25–7).

6.3 Analysis.

6.3.1 NMO Analyzer. The NMO analyzer is a gas chromatograph (GC) with backflush capability for NMO analysis and is equipped with an oxidation catalyst, reduction catalyst, and FID. Figures 25–5 and 25–6 are schematics of a typical NMO analyzer. This semicontinuous GC/FID analyzer shall be capable of: (1) Separating CO, CO_2, and CH_4 from NMO, (2) reducing the CO_2 to CH_4 and quantifying as CH_4, and (3) oxidizing the NMO to CO_2, reducing the CO_2 to CH_4 and quantifying as CH_4, according to section 10.1.2. The analyzer consists of the following major components:

6.3.1.1 Oxidation Catalyst. A suitable length of 9.5-mm (3/8-in.) OD Inconel 600 tubing packed with 5.1 cm (2 in.) of 19 percent chromia on 3.2-mm (1/8-in.) alumina pellets. The catalyst material is packed in the center of the tube supported on either side by quartz wool. The catalyst tube must be mounted vertically in a 650 °C (1200 °F) furnace. Longer catalysts mounted horizontally may be used, provided they can meet the specifications of section 10.1.2.1.

6.3.1.2 Reduction Catalyst. A 7.6-cm (3-in.) length of 6.4-mm (1/4-in.) OD Inconel tubing fully packed with 100-mesh pure nickel powder. The catalyst tube must be mounted vertically in a 400 °C (750 °F) furnace.

6.3.1.3 Separation Column(s). A 30-cm (1-ft) length of 3.2-mm (1/8-in.) OD stainless steel tubing packed with 60/80 mesh Unibeads 1S followed by a 61-cm (2-ft) length of 3.2-mm (1/8-in.) OD stainless steel tubing packed with 60/80 mesh Carbosieve G. The Carbosieve and Unibeads columns must be baked separately at 200 °C (390 °F) with carrier gas flowing through them for 24 hours before initial use.

6.3.1.4 Sample Injection System. A single 10-port GC sample injection valve or a group of valves with sufficient ports fitted with a sample loop properly sized to interface with the NMO analyzer (1-cc loop recommended).

6.3.1.5 FID. An FID meeting the following specifications is required:

6.3.1.5.1 Linearity. A linear response (±5 percent) over the operating range as demonstrated by the procedures established in section 10.1.2.3.

6.3.1.5.2 Range. A full scale range of 10 to 50,000 ppm CH_4. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.3.1.6 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the analytical results.

6.3.2 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm Hg.

6.3.3 Temperature Sensor. Capable of measuring the laboratory temperature within 1 °C (2 °F).

6.3.4 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

7.0 Reagents and Standards

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Dry Ice. Solid CO2, crushed.

7.1.2 Coarse Quartz Wool. 8 to 15 um.

7.1.3 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Method D2986–71, 78, or 95a (incorporated by reference—see §60.17). Test data from the supplier's quality control program are sufficient for this purpose.

7.2 NMO Analysis. The following gases are required for NMO analysis:

7.2.1 Carrier Gases. Helium (He) and oxygen (O_2) containing less than 1 ppm CO_2 and less than 0.1 ppm hydrocarbon.

7.2.2 Fuel Gas. Hydrogen (H_2), at least 99.999 percent pure.

7.2.3 Combustion Gas. Either air (less than 0.1 ppm total hydrocarbon content) or O_2 (purity 99.99 percent or greater), as required by the detector.

7.3 Condensate Analysis. The following are required for condensate analysis:

7.3.1 Gases. Containing less than 1 ppm carbon.

7.3.1.1 Air.

7.3.1.2 Oxygen.

7.3.2 Liquids. To conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society.

7.3.2.1 Hexane.

7.3.2.2 Decane.

7.4 Calibration. For all calibration gases, the manufacturer must recommend a maximum shelf life for each cylinder (i.e., the length of time the gas concentration is not expected to change more than ±5 percent from its certified value). The date of gas cylinder preparation, certified organic concentration, and recommended maximum shelf life must be affixed to each cylinder before shipment from the gas manufacturer to the buyer. The following calibration gases are required:

7.4.1 Oxidation Catalyst Efficiency Check Calibration Gas. Gas mixture standard with nominal concentration of 1 percent methane in air.

7.4.2 FID Linearity and NMO Calibration Gases. Three gas mixture standards with nominal propane concentrations of 20 ppm, 200 ppm, and 3000 ppm, in air.

7.4.3 CO_2 Calibration Gases. Three gas mixture standards with nominal CO_2 concentrations of 50 ppm, 500 ppm, and 1 percent, in air.

NOTE: Total NMO less than 1 ppm required for 1 percent mixture.

7.4.4 NMO Analyzer System Check Calibration Gases. Four calibration gases are needed as follows:

7.4.4.1 Propane Mixture. Gas mixture standard containing (nominal) 50 ppm CO, 50 ppm CH_4, 1 percent CO_2, and 20 ppm C_3H_8, prepared in air.

7.4.4.2 Hexane. Gas mixture standard containing (nominal) 50 ppm hexane in air.

7.4.4.3 Toluene. Gas mixture standard containing (nominal) 20 ppm toluene in air.

7.4.4.4 Methanol. Gas mixture standard containing (nominal) 100 ppm methanol in air.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Sampling Equipment Preparation.

8.1.1 Condensate Trap Cleaning. Before its initial use and after each use, a condensate trap should be thoroughly cleaned and checked to ensure that it is not contaminated. Both cleaning and checking can be accomplished by installing the trap in the condensate recovery system and treating it as if it were a sample. The trap should be heated as described in section 11.1.3. A trap may be considered clean when the CO_2 concentration in its effluent gas drops below 10 ppm. This check is optional for traps that most recently have been used to collect samples which were then recovered according to the procedure in section 11.1.3.

8.1.2 Sample Tank Evacuation and Leak-Check. Evacuate the sample tank to 10 mm Hg absolute pressure or less. Then close the sample tank valve, and allow the tank to sit for 60 minutes. The tank is acceptable if a change in tank vacuum of less than 1 mm Hg is noted. The evacuation and leak-check may be conducted either in the laboratory or the field.

8.1.3 Sampling Train Assembly. Just before assembly, measure the tank vacuum using a mercury manometer. Record this vacuum, the ambient temperature, and the barometric pressure at this time. Close the sample tank valve and assemble the sampling

system as shown in Figure 25–1. Immerse the condensate trap body in dry ice at least 30 minutes before commencing sampling to improve collection efficiency. The point where the inlet tube joins the trap body should be 2.5 to 5 cm (1 to 2 in.) above the top of the dry ice.

8.1.4 Pretest Leak-Check. A pretest leak-check is required. Calculate or measure the approximate volume of the sampling train from the probe tip to the sample tank valve. After assembling the sampling train, plug the probe tip, and make certain that the sample tank valve is closed. Turn on the vacuum pump, and evacuate the sampling system from the probe tip to the sample tank valve to an absolute pressure of 10 mm Hg or less. Close the purge valve, turn off the pump, wait a minimum period of 10 minutes, and recheck the indicated vacuum. Calculate the maximum allowable pressure change based on a leak rate of 1 percent of the sampling rate using Equation 25–1, section 12.2. If the measured pressure change exceeds the allowable, correct the problem and repeat the leak-check before beginning sampling.

8.2 Sample Collection.

8.2.1 Unplug the probe tip, and place the probe into the stack such that the probe is perpendicular to the duct or stack axis; locate the probe tip at a single preselected point of average velocity facing away from the direction of gas flow. For stacks having a negative static pressure, seal the sample port sufficiently to prevent air in-leakage around the probe. Set the probe temperature controller to 129 °C (265 °F) and the filter temperature controller to 121 °C (250 °F). Allow the probe and filter to heat for about 30 minutes before purging the sample train.

8.2.2 Close the sample valve, open the purge valve, and start the vacuum pump. Set the flow rate between 60 and 100 cm^3/min (0.13 and 0.21 ft^3/hr), and purge the train with stack gas for at least 10 minutes.

8.2.3 When the temperatures at the exit ends of the probe and filter are within the corresponding specified ranges, check the dry ice level around the condensate trap, and add dry ice if necessary. Record the clock time. To begin sampling, close the purge valve and stop the pump. Open the sample valve and the sample tank valve. Using the flow control valve, set the flow through the sample train to the proper rate. Adjust the flow rate as necessary to maintain a constant rate (±10 percent) throughout the duration of the sampling period. Record the sample tank vacuum and flowmeter setting at 5-minute intervals. (See Figure 25–8.) Select a total sample time greater than or equal to the minimum sampling time specified in the applicable subpart of the regulations; end the sampling when this time period is reached or when a constant flow rate can no longer be maintained because of reduced sample tank vacuum.

NOTE: If sampling had to be stopped before obtaining the minimum sampling time (specified in the applicable subpart) because a constant flow rate could not be maintained, proceed as follows: After closing the sample tank valve, remove the used sample tank from the sampling train (without disconnecting other portions of the sampling train). Take another evacuated and leak-checked sample tank, measure and record the tank vacuum, and attach the new tank to the sampling train. After the new tank is attached to the sample train, proceed with the sampling until the required minimum sampling time has been exceeded.

8.3 Sample Recovery. After sampling is completed, close the flow control valve, and record the final tank vacuum; then record the tank temperature and barometric pressure. Close the sample tank valve, and disconnect the sample tank from the sample system. Disconnect the condensate trap at the inlet to the rate meter, and tightly seal both ends of the condensate trap. Do not include the probe from the stack to the filter as part of the condensate sample.

8.4 Sample Storage and Transport. Keep the trap packed in dry ice until the samples are returned to the laboratory for analysis. Ensure that run numbers are identified on the condensate trap and the sample tank(s).

9.0 Quality Control

Section	Quality control measure	Effect
10.1.1	Initial performance check of condensate recovery apparatus.	Ensure acceptable condensate recovery efficiency.
10.1.2, 10.2	NMO analyzer initial and daily performance checks.	Ensure precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Initial Performance Checks.

10.1.1 Condensate Recovery Apparatus. Perform these tests before the system is first placed in operation, after any shutdown of 6 months or more, and after any major modification of the system, or at the frequency recommended by the manufacturer.

10.1.1.1 Carrier Gas and Auxiliary O_2 Blank Check. Analyze each new tank of carrier gas or auxiliary O_2 with the NMO analyzer to

check for contamination. Treat the gas cylinders as noncondensible gas samples, and analyze according to the procedure in section 11.2.3. Add together any measured CH_4, CO, CO_2, or NMO. The total concentration must be less than 5 ppm.

10.1.1.2 Oxidation Catalyst Efficiency Check.

10.1.1.2.1 With a clean condensate trap installed in the recovery system or a ⅛″ stainless steel connector tube, replace the carrier gas cylinder with the high level methane standard gas cylinder (Section 7.4.1). Set the four-port valve to the recovery position, and attach an ICV to the recovery system. With the sample recovery valve in vent position and the flow-control and ICV valves fully open, evacuate the manometer or gauge, the connecting tubing, and the ICV to 10 mm Hg absolute pressure. Close the flow-control and vacuum pump valves.

10.1.1.2.2 After the NDIR response has stabilized, switch the sample recovery valve from vent to collect. When the manometer or pressure gauge begins to register a slight positive pressure, open the flow-control valve. Keep the flow adjusted such that the pressure in the system is maintained within 10 percent of atmospheric pressure. Continue collecting the sample in a normal manner until the ICV is filled to a nominal gauge pressure of 300 mm Hg. Close the ICV valve, and remove the ICV from the system. Place the sample recovery valve in the vent position, and return the recovery system to its normal carrier gas and normal operating conditions. Analyze the ICV for CO_2 using the NMO analyzer; the catalyst efficiency is acceptable if the CO_2 concentration is within 2 percent of the methane standard concentration.

10.1.1.3 System Performance Check. Construct a liquid sample injection unit similar in design to the unit shown in Figure 25–7. Insert this unit into the condensate recovery and conditioning system in place of a condensate trap, and set the carrier gas and auxiliary O_2 flow rates to normal operating levels. Attach an evacuated ICV to the system, and switch from system vent to collect. With the carrier gas routed through the injection unit and the oxidation catalyst, inject a liquid sample (see sections 10.1.1.3.1 to 10.1.1.3.4) into the injection port. Operate the trap recovery system as described in section 11.1.3. Measure the final ICV pressure, and then analyze the vessel to determine the CO_2 concentration. For each injection, calculate the percent recovery according to section 12.7. Calculate the relative standard deviation for each set of triplicate injections according to section 12.8. The performance test is acceptable if the average percent recovery is 100 ±5 percent and the relative standard deviation is less than 2 percent for each set of triplicate injections.

10.1.1.3.1 50 µl hexane.

10.1.1.3.2 10 µl hexane.

10.1.1.3.3 50 µl decane.

10.1.1.3.4 10 µl decane.

10.1.2 NMO Analyzer. Perform these tests before the system is first placed in operation, after any shutdown longer than 6 months, and after any major modification of the system.

10.1.2.1 Oxidation Catalyst Efficiency Check. Turn off or bypass the NMO analyzer reduction catalyst. Make triplicate injections of the high level methane standard (Section 7.4.1). The oxidation catalyst operation is acceptable if the FID response is less than 1 percent of the injected methane concentration.

10.1.2.2 Reduction Catalyst Efficiency Check. With the oxidation catalyst unheated or bypassed and the heated reduction catalyst bypassed, make triplicate injections of the high level methane standard (Section 7.4.1). Repeat this procedure with both catalysts operative. The reduction catalyst operation is acceptable if the responses under both conditions agree within 5 percent of their average.

10.1.2.3 NMO Analyzer Linearity Check Calibration. While operating both the oxidation and reduction catalysts, conduct a linearity check of the analyzer using the propane standards specified in section 7.4.2. Make triplicate injections of each calibration gas. For each gas (*i.e.*, each set of triplicate injections), calculate the average response factor (area/ppm C) for each gas, as well as and the relative standard deviation (according to section 12.8). Then calculate the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within 2.5 percent of the overall mean value and if the relative standard deviation gas is less than 2 percent of the overall mean value. Record the overall mean of the propane response factor values as the NMO calibration response factor (RF_{NMO}). Repeat the linearity check using the CO_2 standards specified in section 7.4.3. Make triplicate injections of each gas, and then calculate the average response factor (area/ppm C) for each gas, as well as the overall mean of the response factor values. Record the overall mean of the response factor values as the CO_2 calibration response factor (RF_{CO2}). The RF_{CO2} must be within 10 percent of the RF_{NMO}.

10.1.2.4 System Performance Check. Check the column separation and overall performance of the analyzer by making triplicate injections of the calibration gases listed in section 7.4.4. The analyzer performance is acceptable if the measured NMO value for each gas (average of triplicate injections) is within 5 percent of the expected value.

10.2 NMO Analyzer Daily Calibration. The following calibration procedures shall be performed before and immediately after the

analysis of each set of samples, or on a daily basis, whichever is more stringent:

10.2.1 CO_2 Response Factor. Inject triplicate samples of the high level CO_2 calibration gas (Section 7.4.3), and calculate the average response factor. The system operation is adequate if the calculated response factor is within 5 percent of the RF_{CO2} calculated during the initial performance test (Section 10.1.2.3). Use the daily response factor (DRF_{CO2}) for analyzer calibration and the calculation of measured CO_2 concentrations in the ICV samples.

10.2.2 NMO Response Factors. Inject triplicate samples of the mixed propane calibration cylinder gas (Section 7.4.4.1), and calculate the average NMO response factor. The system operation is adequate if the calculated response factor is within 10 percent of the RF_{NMO} calculated during the initial performance test (Section 10.1.2.4). Use the daily response factor (DRF_{NMO}) for analyzer calibration and calculation of NMO concentrations in the sample tanks.

10.3 Sample Tank and ICV Volume. The volume of the gas sampling tanks used must be determined. Determine the tank and ICV volumes by weighing them empty and then filled with deionized distilled water; weigh to the nearest 5 g, and record the results. Alternatively, measure the volume of water used to fill them to the nearest 5 ml.

11.0 Analytical Procedure

11.1 Condensate Recovery. See Figure 25–9. Set the carrier gas flow rate, and heat the catalyst to its operating temperature to condition the apparatus.

11.1.1 Daily Performance Checks. Each day before analyzing any samples, perform the following tests:

11.1.1.1 Leak-Check. With the carrier gas inlets and the sample recovery valve closed, install a clean condensate trap in the system, and evacuate the system to 10 mm Hg absolute pressure or less. Monitor the system pressure for 10 minutes. The system is acceptable if the pressure change is less than 2 mm Hg.

11.1.1.2 System Background Test. Adjust the carrier gas and auxiliary oxygen flow rate to their normal values of 100 cc/min and 150 cc/min, respectively, with the sample recovery valve in vent position. Using a 10-ml syringe, withdraw a sample from the system effluent through the syringe port. Inject this sample into the NMO analyzer, and measure the CO_2 content. The system background is acceptable if the CO_2 concentration is less than 10 ppm.

11.1.1.3 Oxidation Catalyst Efficiency Check. Conduct a catalyst efficiency test as specified in section 10.1.1.2. If the criterion of this test cannot be met, make the necessary repairs to the system before proceeding.

11.1.2 Condensate Trap CO_2 Purge and Sample Tank Pressurization.

11.1.2.1 After sampling is completed, the condensate trap will contain condensed water and organics and a small volume of sampled gas. This gas from the stack may contain a significant amount of CO_2 which must be removed from the condensate trap before the sample is recovered. This is accomplished by purging the condensate trap with zero air and collecting the purged gas in the original sample tank.

11.1.2.2 Begin with the sample tank and condensate trap from the test run to be analyzed. Set the four-port valve of the condensate recovery system in the CO_2 purge position as shown in Figure 25–9. With the sample tank valve closed, attach the sample tank to the sample recovery system. With the sample recovery valve in the vent position and the flow control valve fully open, evacuate the manometer or pressure gauge to the vacuum of the sample tank. Next, close the vacuum pump valve, open the sample tank valve, and record the tank pressure.

11.1.2.3 Attach the dry ice-cooled condensate trap to the recovery system, and initiate the purge by switching the sample recovery valve from vent to collect position. Adjust the flow control valve to maintain atmospheric pressure in the recovery system. Continue the purge until the CO_2 concentration of the trap effluent is less than 5 ppm. CO_2 concentration in the trap effluent should be measured by extracting syringe samples from the recovery system and analyzing the samples with the NMO analyzer. This procedure should be used only after the NDIR response has reached a minimum level. Using a 10-ml syringe, extract a sample from the syringe port prior to the NDIR, and inject this sample into the NMO analyzer.

11.1.2.4 After the completion of the CO_2 purge, use the carrier gas bypass valve to pressurize the sample tank to approximately 1,060 mm Hg absolute pressure with zero air.

11.1.3 Recovery of the Condensate Trap Sample (See Figure 25–10).

11.1.3.1 Attach the ICV to the sample recovery system. With the sample recovery valve in a closed position, between vent and collect, and the flow control and ICV valves fully open, evacuate the manometer or gauge, the connecting tubing, and the ICV to 10 mm Hg absolute pressure. Close the flow-control and vacuum pump valves.

11.1.3.2 Begin auxiliary oxygen flow to the oxidation catalyst at a rate of 150 cc/min, then switch the four-way valve to the trap recovery position and the sample recovery valve to collect position. The system should now be set up to operate as indicated in Figure 25–10. After the manometer or pressure gauge begins to register a slight positive pressure, open the flow control valve. Adjust the flow-control valve to maintain atmospheric pressure in the system within 10 percent.

11.1.3.3 Remove the condensate trap from the dry ice, and allow it to warm to ambient temperature while monitoring the NDIR response. If, after 5 minutes, the CO_2 concentration of the catalyst effluent is below 10,000 ppm, discontinue the auxiliary oxygen flow to the oxidation catalyst. Begin heating the trap by placing it in a furnace preheated to 200 °C (390 °F). Once heating has begun, carefully monitor the NDIR response to ensure that the catalyst effluent concentration does not exceed 50,000 ppm. Whenever the CO_2 concentration exceeds 50,000 ppm, supply auxiliary oxygen to the catalyst at the rate of 150 cc/min. Begin heating the tubing that connected the heated sample box to the condensate trap only after the CO_2 concentration falls below 10,000 ppm. This tubing may be heated in the same oven as the condensate trap or with an auxiliary heat source such as a heat gun. Heating temperature must not exceed 200 °C (390 °F). If a heat gun is used, heat the tubing slowly along its entire length from the upstream end to the downstream end, and repeat the pattern for a total of three times. Continue the recovery until the CO_2 concentration drops to less than 10 ppm as determined by syringe injection as described under the condensate trap CO_2 purge procedure (Section 11.1.2).

11.1.3.4 After the sample recovery is completed, use the carrier gas bypass valve to pressurize the ICV to approximately 1060 mm Hg absolute pressure with zero air.

11.2 Analysis. Once the initial performance test of the NMO analyzer has been successfully completed (see section 10.1.2) and the daily CO_2 and NMO response factors have been determined (see section 10.2), proceed with sample analysis as follows:

11.2.1 Operating Conditions. The carrier gas flow rate is 29.5 cc/min He and 2.2 cc/min O_2. The column oven is heated to 85 °C (185 °F). The order of elution for the sample from the column is CO, CH_4, CO_2, and NMO.

11.2.2 Analysis of Recovered Condensate Sample. Purge the sample loop with sample, and then inject the sample. Under the specified operating conditions, the CO_2 in the sample will elute in approximately 100 seconds. As soon as the detector response returns to baseline following the CO_2 peak, switch the carrier gas flow to backflush, and raise the column oven temperature to 195 °C (380 °F) as rapidly as possible. A rate of 30 °C/min (90 °F) has been shown to be adequate. Record the value obtained for the condensible organic material (C_{cm}) measured as CO_2 and any measured NMO. Return the column oven temperature to 85 °C (185 °F) in preparation for the next analysis. Analyze each sample in triplicate, and report the average C_{cm}.

11.2.3 Analysis of Sample Tank. Perform the analysis as described in section 11.2.2, but record only the value measured for NMO (C_{tm}).

12.0 Data Analysis and Calculations

Carry out the calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculations. All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge or manometer pressure.

12.1 Nomenclature.

C = TGNMO concentration of the effluent, ppm C equivalent.
C_c = Calculated condensible organic (condensate trap) concentration of the effluent, ppm C equivalent.
C_{cm} = Measured concentration (NMO analyzer) for the condensate trap ICV, ppm CO_2.
C_t = Calculated noncondensible organic concentration (sample tank) of the effluent, ppm C equivalent.
C_{tm} = Measured concentration (NMO analyzer) for the sample tank, ppm NMO.
F = Sampling flow rate, cc/min.
L = Volume of liquid injected, µl.
M = Molecular weight of the liquid injected, g/g-mole.
M_c = TGNMO mass concentration of the effluent, mg C/dsm³.
N = Carbon number of the liquid compound injected (N = 12 for decane, N = 6 for hexane).
n = Number of data points.
P_f = Final pressure of the intermediate collection vessel, mm Hg absolute.
P_b = Barometric pressure, cm Hg.
P_{ti} = Gas sample tank pressure before sampling, mm Hg absolute.
P_t = Gas sample tank pressure after sampling, but before pressurizing, mm Hg absolute.
P_{tf} = Final gas sample tank pressure after pressurizing, mm Hg absolute.
q = Total number of analyzer injections of intermediate collection vessel during analysis (where k = injection number, 1 * * * q).
r = Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 * * * r).
r = Density of liquid injected, g/cc.
T_f = Final temperature of intermediate collection vessel, °K.
T_{ti} = Sample tank temperature before sampling, °K.
T_t = Sample tank temperature at completion of sampling, °K.
T_{tf} = Sample tank temperature after pressurizing, °K.
V = Sample tank volume, m³.
V_t = Sample train volume, cc.
V_v = Intermediate collection vessel volume, m³.
V_s = Gas volume sampled, dsm³.
x_i = Individual measurements.
$\bar{x}$ = Mean value.

ΔP = Allowable pressure change, cm Hg.
Θ = Leak-check period, min.

12.2 Allowable Pressure Change. For the pretest leak-check, calculate the allowable pressure change using Equation 25–1:

$$\Delta P = 0.01 \frac{F P_b \Theta}{V_t} \qquad \text{Eq. 25-1}$$

12.3 Sample Volume. For each test run, calculate the gas volume sampled using Equation 25–2:

$$V_s = 0.3857\, V \left(\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}} \right) \qquad \text{Eq. 25-2}$$

12.4 Noncondensible Organics. For each sample tank, determine the concentration of nonmethane organics (ppm C) using Equation 25–3:

$$C_t = \left(\frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}} \right) \left(\frac{1}{r} \sum_{j=1}^{r} C_{tm_j} \right) \qquad \text{Eq. 25-3}$$

12.5 Condensible Organics. For each condensate trap determine the concentration of organics (ppm C) using Equation 25–4:

$$C_c = 0.3857 \frac{V_v P_f}{V_s T_f} \left(\frac{1}{q} \sum_{k=1}^{q} C_{cm_k} \right) \qquad \text{Eq. 25-4}$$

12.6 TGNMO Mass Concentration. Determine the TGNMO mass concentration as carbon for each test run, using Equation 25–5:

$$M_c = 0.4993 \left(C_t + C_c \right) \qquad \text{Eq. 25-5}$$

12.7 Percent Recovery. Calculate the percent recovery for the liquid injections to the condensate recovery and conditioning system using Equation 25–6:

$$\text{Percent Recovery} = K \frac{M V_v P_t C_{cm}}{L P T_f N} \qquad \text{Eq. 25-6}$$

where K = 1.604 (°K)(g-mole)(%)/(mm Hg)(ml)(m^3)(ppm).

12.8 Relative Standard Deviation. Use Equation 25–7 to calculate the relative standard deviation (RSD) of percent recovery and analyzer linearity.

$$RSD = \frac{100}{\bar{x}} \left[\frac{\sum_{i=1}^{n} \left(x_i - \bar{x} \right)^2}{n-1} \right]^{\frac{1}{2}} \qquad \text{Eq. 25-7}$$

13.0 Method Performance

13.1 Range. The minimum detectable limit of the method has been determined to be 50 parts per million by volume (ppm). No upper limit has been established.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, A.E., S. Witz, and R.D. MacPhee. Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, MA. June 15–20, 1975.) 14 p.

2. Salo, A.E., W.L. Oaks, and R.D. MacPhee. Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, CO. June 9–13, 1974.) 25 p.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

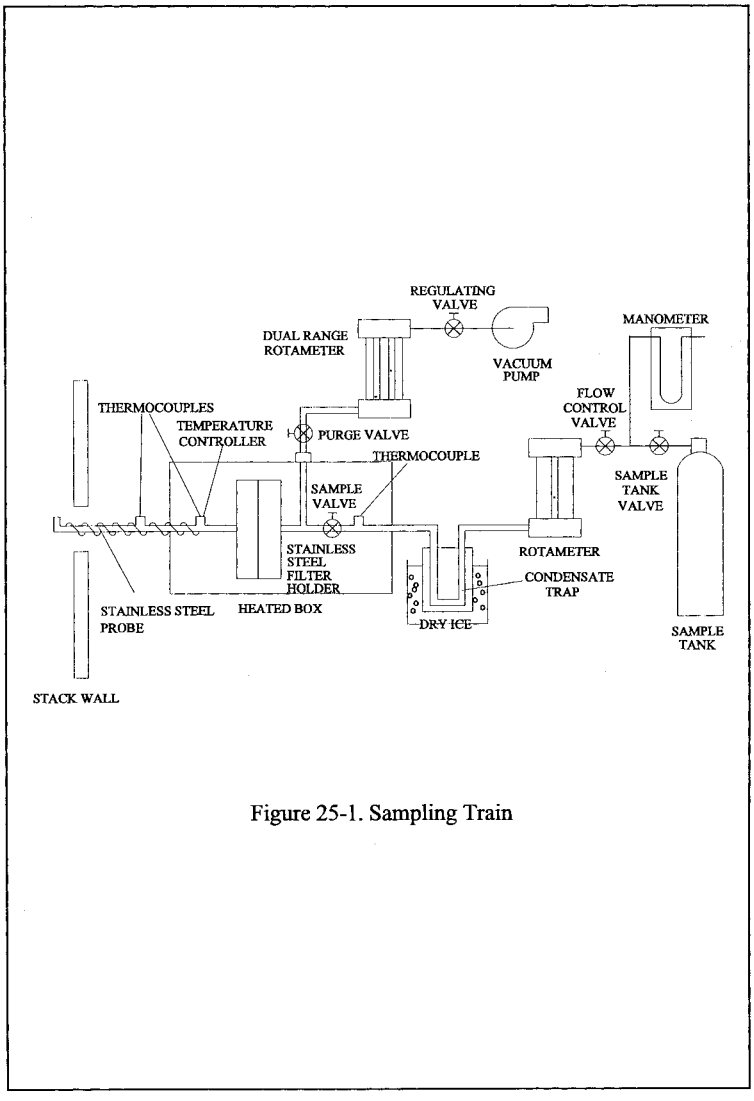


Figure 25-1. Sampling Train

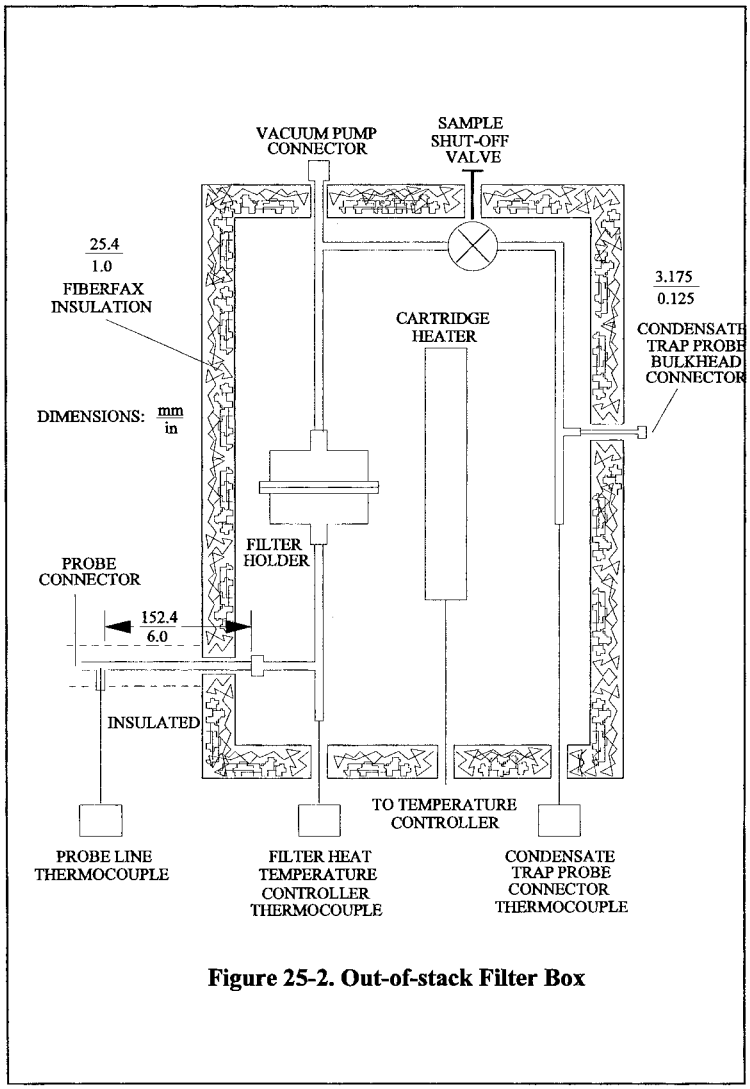


Figure 25-2. Out-of-stack Filter Box

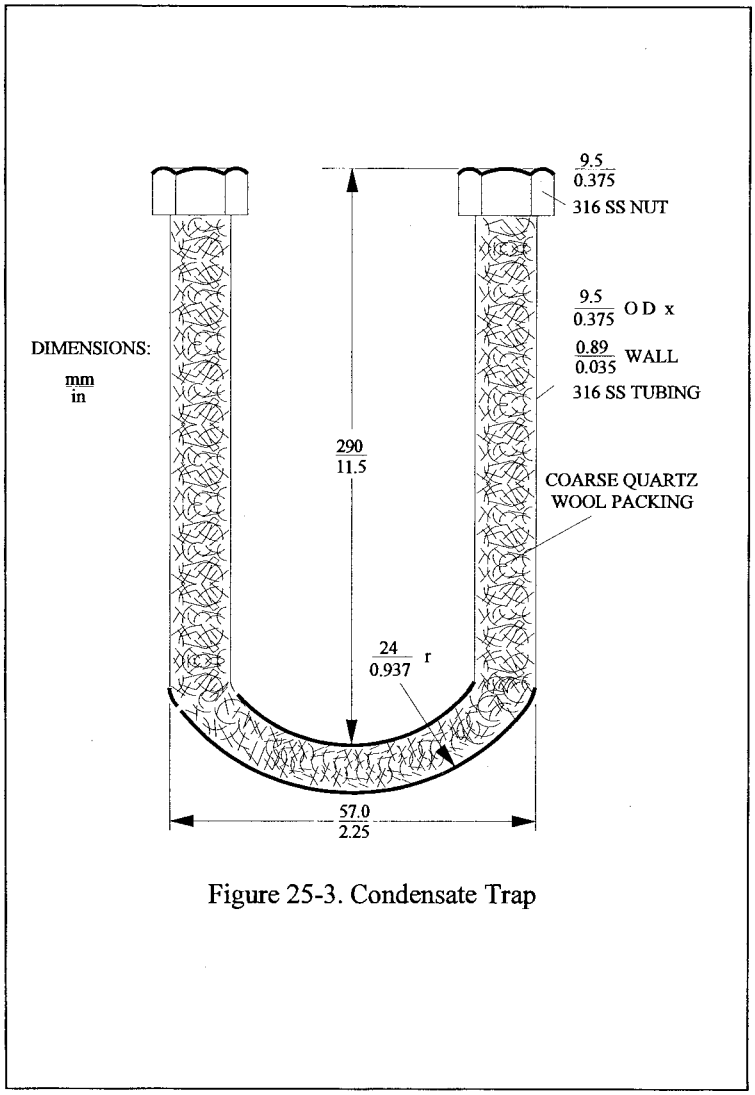


Figure 25-3. Condensate Trap

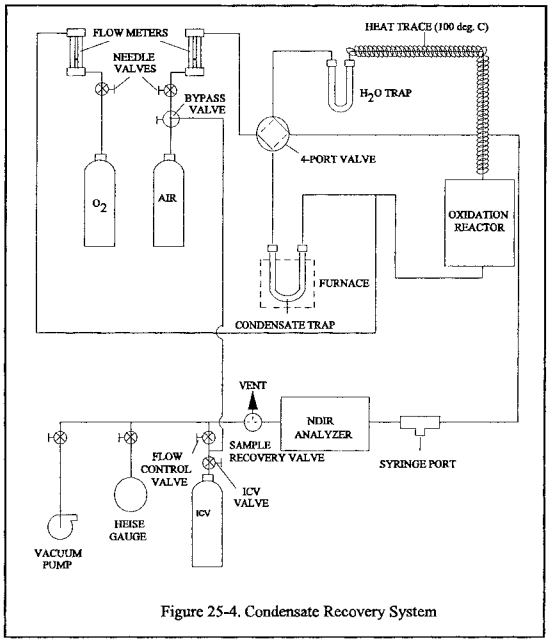


Figure 25-4. Condensate Recovery System

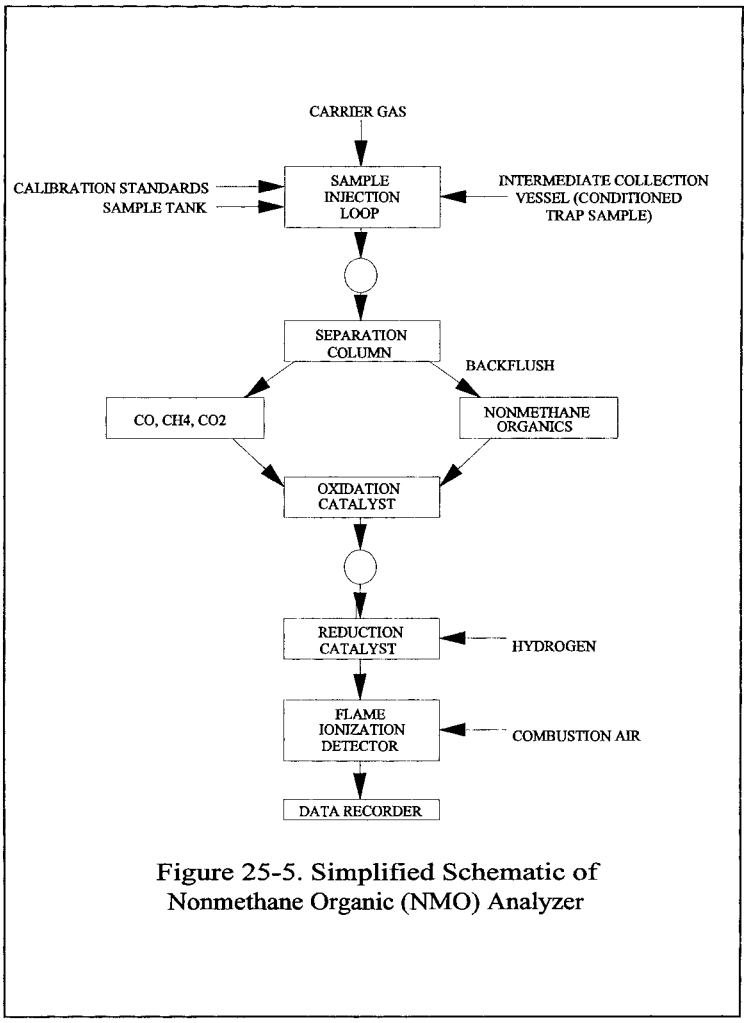


Figure 25-5. Simplified Schematic of Nonmethane Organic (NMO) Analyzer

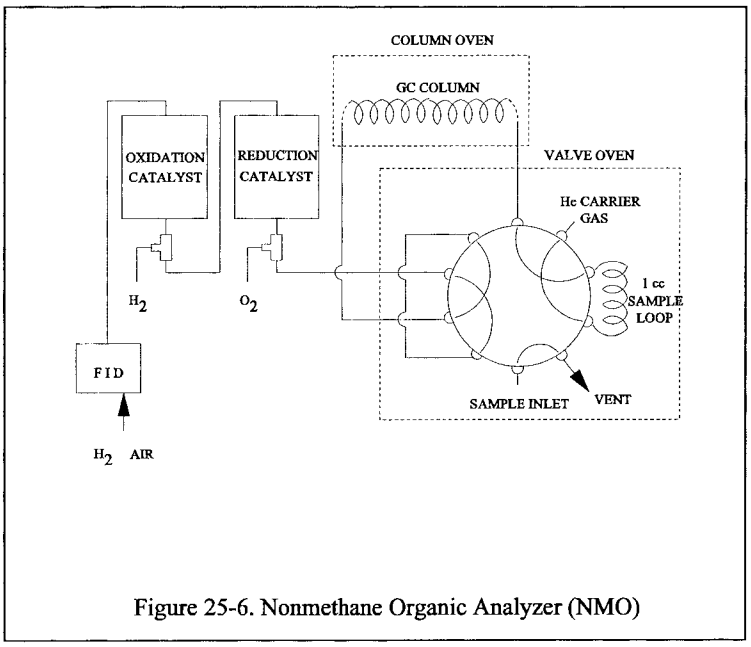


Figure 25-6. Nonmethane Organic Analyzer (NMO)

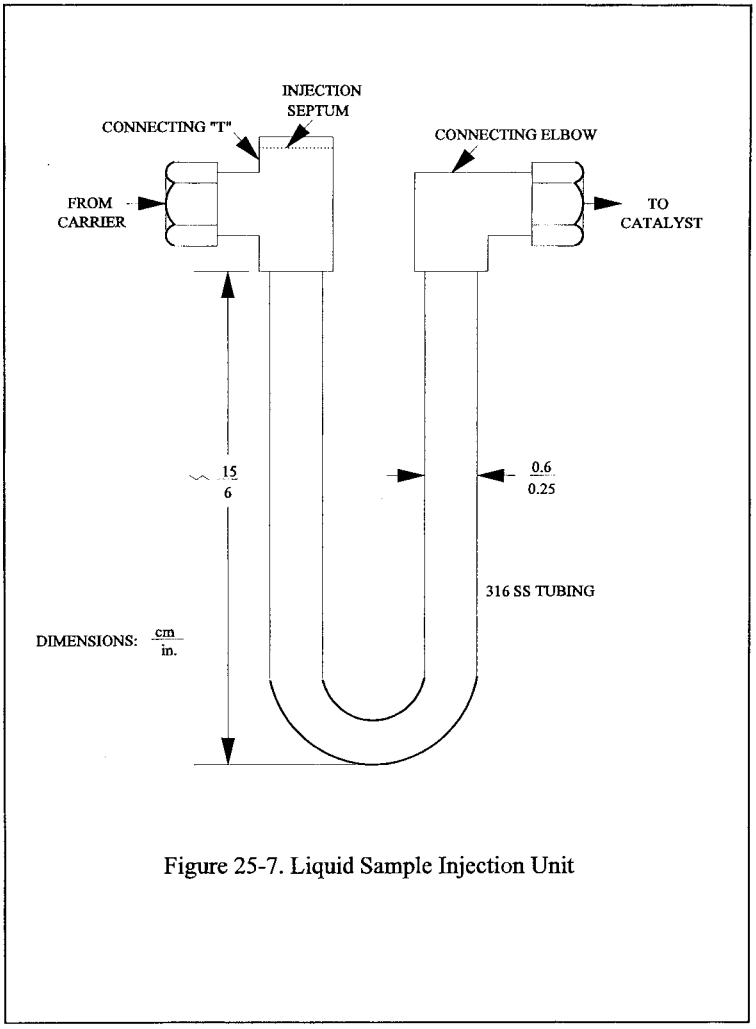


Figure 25-7. Liquid Sample Injection Unit

VOLATILE ORGANIC CARBON

FACILITY _____ SAMPLE LOCATION _____

LOCATION _____ OPERATOR _____

DATE _____ RUN NUMBER _____

TANK NUMBER _____ TRAP NUMBER _____ SAMPLE ID NUMBER _____

TANK VACUUM mm HG	TANK VACUUM cm Hg	BAROMETRIC PRESSURE mm Hg	AMBIENT TEMPERATURE °C
PRETEST (MANOMETER)	(GAUGE)		
POST-TEST (MANOMETER)	(GAUGE)		

LEAK RATE _____ cm Hg / l.0 min

PRETEST _____

TIME CLOCK/SAMPLE	VACUUM cm Hg	FLOWMETER SETTINGS	COMMENTS

Figure 25-8. Example Field Data Form

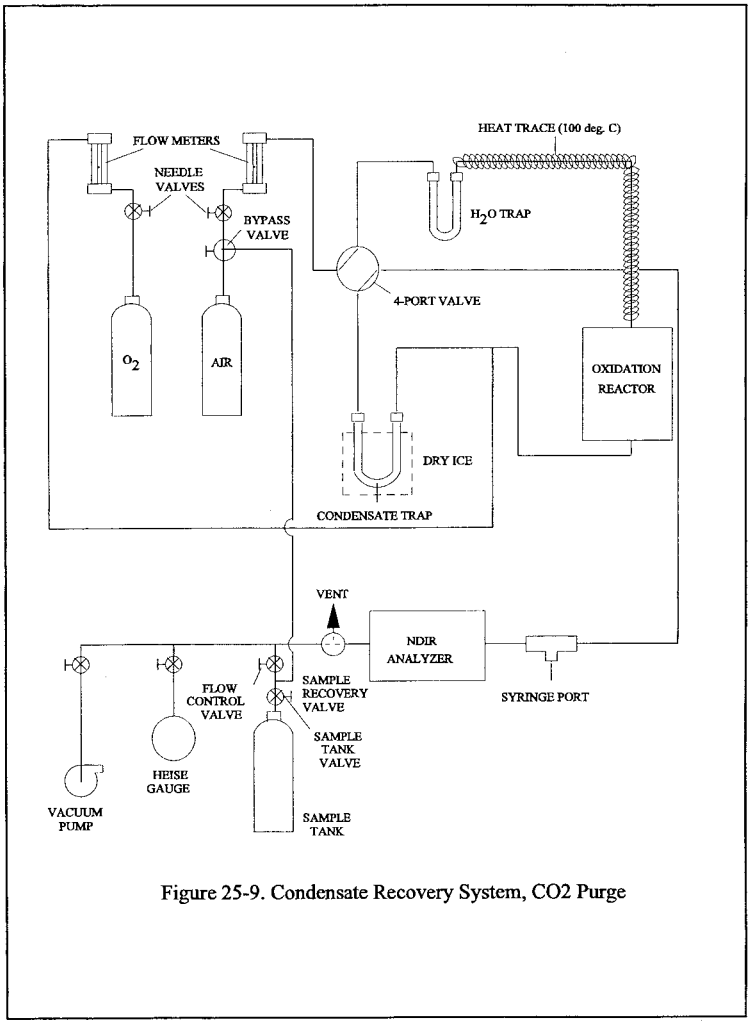


Figure 25-9. Condensate Recovery System, CO2 Purge

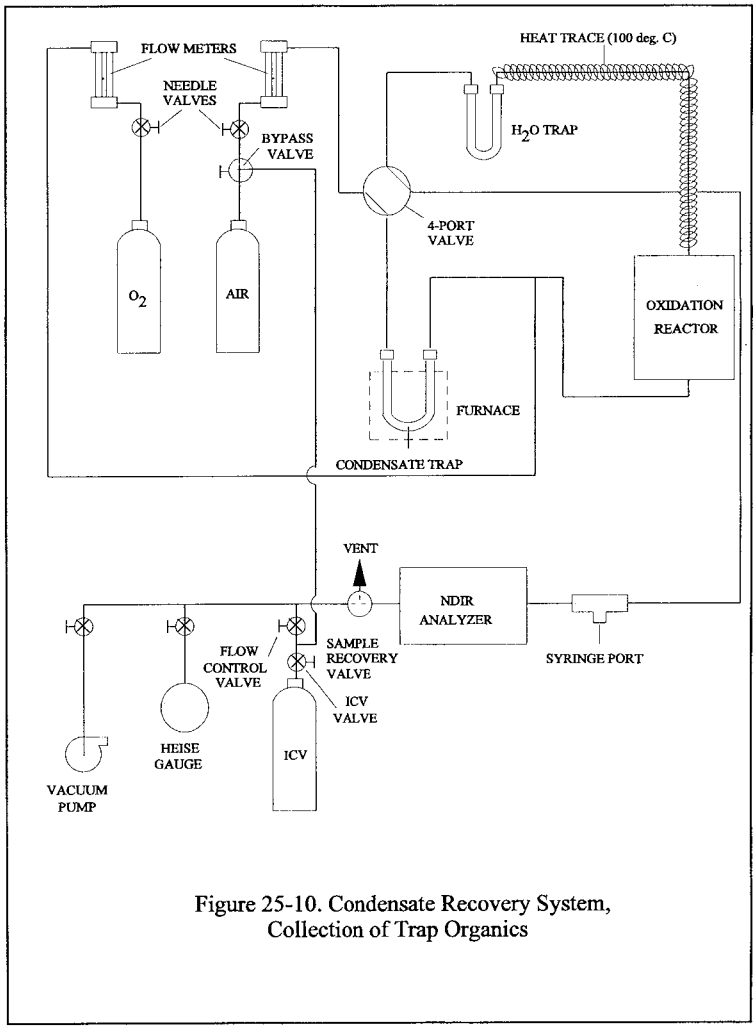


Figure 25-10. Condensate Recovery System, Collection of Trap Organics

METHOD 25A—DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A FLAME IONIZATION ANALYZER

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total Organic Compounds	N/A	<2% of span.

1.2 Applicability. This method is applicable for the determination of total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the source through a heated sample line and glass fiber filter to a flame ionization analyzer (FIA). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

3.0 Definitions

3.1 *Calibration drift* means the difference in the measurement system response to a mid-level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

3.2 *Calibration error* means the difference between the gas concentration indicated by the measurement system and the know concentration of the calibration gas.

3.3 *Calibration gas* means a known concentration of a gas in an appropriate diluent gas.

3.4 *Measurement system* means the total equipment required for the determination of the gas concentration. The system consists of the following major subsystems:

3.4.1 *Sample interface* means that portion of a system used for one or more of the following: sample acquisition, sample transportation, sample conditioning, or protection of the analyzer(s) from the effects of the stack effluent.

3.4.2 *Organic analyzer* means that portion of the measurement system that senses the gas to be measured and generates an output proportional to its concentration.

3.5 *Response time* means the time interval from a step change in pollutant concentration at the inlet to the emission measurement system to the time at which 95 percent of the corresponding final value is reached as displayed on the recorder.

3.6 *Span Value* means the upper limit of a gas concentration measurement range that is specified for affected source categories in the applicable part of the regulations. The span value is established in the applicable regulation and is usually 1.5 to 2.5 times the applicable emission limit. If no span value is provided, use a span value equivalent to 1.5 to 2.5 times the expected concentration. For convenience, the span value should correspond to 100 percent of the recorder scale.

3.7 *Zero drift* means the difference in the measurement system response to a zero level calibration gas before or after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

5.2 Explosive Atmosphere. This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

6.0 Equipment and Supplies

6.1 Measurement System. Any measurement system for total organic concentration that meets the specifications of this method. A schematic of an acceptable measurement system is shown in Figure 25A–1. All sampling components leading to the analyzer shall be heated ≥110 °C (220 °F) throughout the sampling period, unless safety reasons are cited (Section 5.2) The essential components of the measurement system are described below:

6.1.1 Organic Concentration Analyzer. A flame ionization analyzer (FIA) capable of meeting or exceeding the specifications of this method. The flame ionization detector block shall be heated >120 °C (250 °F).

6.1.2 Sample Probe. Stainless steel, or equivalent, three-hole rake type. Sample holes shall be 4 mm (0.16-in.) in diameter or smaller and located at 16.7, 50, and 83.3 percent of the equivalent stack diameter. Alternatively, a single opening probe may be used so that a gas sample is collected from the centrally located 10 percent area of the stack cross-section.

6.1.3 Heated Sample Line. Stainless steel or Teflon'' tubing to transport the sample gas

to the analyzer. The sample line should be heated (≥110 °C) to prevent any condensation.

6.1.4 Calibration Valve Assembly. A three-way valve assembly to direct the zero and calibration gases to the analyzers is recommended. Other methods, such as quick-connect lines, to route calibration gas to the analyzers are applicable.

6.1.5 Particulate Filter. An in-stack or an out-of-stack glass fiber filter is recommended if exhaust gas particulate loading is significant. An out-of-stack filter should be heated to prevent any condensation.

6.1.6 Recorder. A strip-chart recorder, analog computer, or digital recorder for recording measurement data. The minimum data recording requirement is one measurement value per minute.

7.0 Reagents and Standards

7.1 Calibration Gases. The calibration gases for the gas analyzer shall be propane in air or propane in nitrogen. Alternatively, organic compounds other than propane can be used; the appropriate corrections for response factor must be made. Calibration gases shall be prepared in accordance with the procedure listed in Citation 2 of section 16. Additionally, the manufacturer of the cylinder should provide a recommended shelf life for each calibration gas cylinder over which the concentration does not change more than ±2 percent from the certified value. For calibration gas values not generally available (*i.e.*, organics between 1 and 10 percent by volume), alternative methods for preparing calibration gas mixtures, such as dilution systems (Test Method 205, 40 CFR Part 51, Appendix M), may be used with prior approval of the Administrator.

7.1.1 Fuel. A 40 percent H_2/60 percent N_2 gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value.

7.1.2 Zero Gas. High purity air with less than 0.1 part per million by volume (ppmv) of organic material (propane or carbon equivalent) or less than 0.1 percent of the span value, whichever is greater.

7.1.3 Low-level Calibration Gas. An organic calibration gas with a concentration equivalent to 25 to 35 percent of the applicable span value.

7.1.4 Mid-level Calibration Gas. An organic calibration gas with a concentration equivalent to 45 to 55 percent of the applicable span value.

7.1.5 High-level Calibration Gas. An organic calibration gas with a concentration equivalent to 80 to 90 percent of the applicable span value.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Selection of Sampling Site. The location of the sampling site is generally specified by the applicable regulation or purpose of the test (*i.e.*, exhaust stack, inlet line, etc.). The sample port shall be located to meet the testing requirements of Method 1.

8.2 Location of Sample Probe. Install the sample probe so that the probe is centrally located in the stack, pipe, or duct and is sealed tightly at the stack port connection.

8.3 Measurement System Preparation. Prior to the emission test, assemble the measurement system by following the manufacturer's written instructions for preparing sample interface and the organic analyzer. Make the system operable (Section 10.1).

8.4 Calibration Error Test. Immediately prior to the test series (within 2 hours of the start of the test), introduce zero gas and high-level calibration gas at the calibration valve assembly. Adjust the analyzer output to the appropriate levels, if necessary. Calculate the predicted response for the low-level and mid-level gases based on a linear response line between the zero and high-level response. Then introduce low-level and mid-level calibration gases successively to the measurement system. Record the analyzer responses for low-level and mid-level calibration gases and determine the differences between the measurement system responses and the predicted responses. These differences must be less than 5 percent of the respective calibration gas value. If not, the measurement system is not acceptable and must be replaced or repaired prior to testing. No adjustments to the measurement system shall be conducted after the calibration and before the drift check (Section 8.6.2). If adjustments are necessary before the completion of the test series, perform the drift checks prior to the required adjustments and repeat the calibration following the adjustments. If multiple electronic ranges are to be used, each additional range must be checked with a mid-level calibration gas to verify the multiplication factor.

8.5 Response Time Test. Introduce zero gas into the measurement system at the calibration valve assembly. When the system output has stabilized, switch quickly to the high-level calibration gas. Record the time from the concentration change to the measurement system response equivalent to 95 percent of the step change. Repeat the test three times and average the results.

8.6 Emission Measurement Test Procedure.

8.6.1 Organic Measurement. Begin sampling at the start of the test period, recording time and any required process information as appropriate. In particulate, note on the recording chart, periods of process interruption or cyclic operation.

8.6.2 Drift Determination. Immediately following the completion of the test period and hourly during the test period, reintroduce the zero and mid-level calibration gases, one at a time, to the measurement system at the calibration valve assembly. (Make no adjustments to the measurement system until both the zero and calibration drift checks are made.) Record the analyzer response. If the drift values exceed the specified limits, invalidate the test results preceding the check and repeat the test following corrections to the measurement system. Alternatively, recalibrate the test measurement system as in section 8.4 and report the results using both sets of calibration data (i.e., data determined prior to the test period and data determined following the test period).

NOTE: Note on the recording chart periods of process interruption or cyclic operation.

9.0 Quality Control

Method section	Quality control measure	Effect
8.4	Zero and calibration drift tests	Ensures that bias introduced by drift in the measurement system output during the run is no greater than 3 percent of span.

10.0 Calibration and Standardization

10.1 FIA equipment can be calibrated for almost any range of total organic concentrations. For high concentrations of organics (>1.0 percent by volume as propane), modifications to most commonly available analyzers are necessary. One accepted method of equipment modification is to decrease the size of the sample to the analyzer through the use of a smaller diameter sample capillary. Direct and continuous measurement of organic concentration is a necessary consideration when determining any modification design.

11.0 Analytical Procedure

The sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Calculations and Data Analysis

12.1 Determine the average organic concentration in terms of ppmv as propane or other calibration gas. The average shall be determined by integration of the output recording over the period specified in the applicable regulation. If results are required in terms of ppmv as carbon, adjust measured concentrations using Equation 25A–1.

$$C_c = K C_{meas} \qquad \text{Eq. 25A-1}$$

Where:

C_c = Organic concentration as carbon, ppmv.
C_{meas} = Organic concentration as measured, ppmv.
K = Carbon equivalent correction factor.
= 2 for ethane.
= 3 for propane.
= 4 for butane.
= Appropriate response factor for other organic calibration gases.

13.0 Method Performance

13.1 Measurement System Performance Specifications.

13.1.1 Zero Drift. Less than ±3 percent of the span value.

13.1.2 Calibration Drift. Less than ±3 percent of span value.

13.1.3 Calibration Error. Less than ±5 percent of the calibration gas value.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Measurement of Volatile Organic Compounds—Guideline Series. U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA–450/2–78–041. June 1978. p. 46–54.

2. EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards. U.S. Environmental Protection Agency, Quality Assurance and Technical Support Division. Research Triangle Park, N.C. September 1993.

3. Gasoline Vapor Emission Laboratory Evaluation—Part 2. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, NC. EMB Report No. 75–GAS–6. August 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

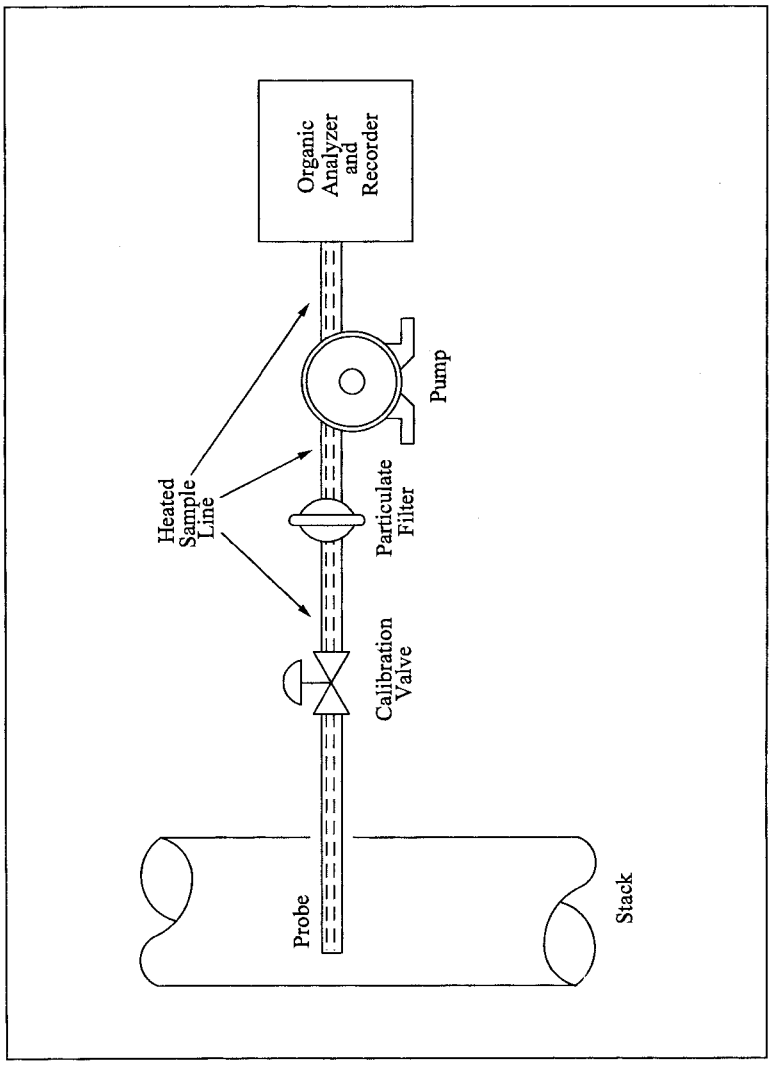


Figure 25A-1. Organic Concentration Measurement System.

METHOD 25B—DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A NONDISPERSIVE INFRARED ANALYZER

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 6C, and Method 25A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total Organic Compounds	N/A	<2% of span.

1.2 Applicability. This method is applicable for the determination of total gaseous organic concentration of vapors consisting primarily of alkanes. Other organic materials may be measured using the general procedure in this method, the appropriate calibration gas, and an analyzer set to the appropriate absorption band.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

A gas sample is extracted from the source through a heated sample line, if necessary, and glass fiber filter to a nondispersive infrared analyzer (NDIR). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

3.0 Definitions

Same as Method 25A, section 3.0.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

5.2 Explosive Atmosphere. This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

6.0 Equipment and Supplies

Same as Method 25A, section 6.0, with the exception of the following:

6.1 Organic Concentration Analyzer. A nondispersive infrared analyzer designed to measure alkane organics and capable of meeting or exceeding the specifications in this method.

7.0 Reagents and Standards

Same as Method 25A, section 7.1. No fuel gas is required for an NDIR.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as Method 25A, section 8.0.

9.0 Quality Control

Same as Method 25A, section 9.0.

10.0 Calibration and Standardization

Same as Method 25A, section 10.0.

11.0 Analytical Procedure

The sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Calculations and Data Analysis

Same as Method 25A, section 12.0.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 25A, section 16.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 25C—DETERMINATION OF NONMETHANE ORGANIC COMPOUNDS (NMOC) IN LANDFILL GASES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should also have a thorough knowledge of EPA Method 25.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Nonmethane organic compounds (NMOC).	No CAS number assigned.

1.2 Applicability. This method is applicable to the sampling and measurement of NMOC as carbon in landfill gases (LFG).

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A sample probe that has been perforated at one end is driven or augured to a depth of 0.9 m (3 ft) below the bottom of the landfill cover. A sample of the landfill gas is extracted with an evacuated cylinder. The NMOC content of the gas is determined by

injecting a portion of the gas into a gas chromatographic column to separate the NMOC from carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4); the NMOC are oxidized to CO_2, reduced to CH_4, and measured by a flame ionization detector (FID). In this manner, the variable response of the FID associated with different types of organics is eliminated.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Since this method is complex, only experienced personnel should perform this test. LFG contains methane, therefore explosive mixtures may exist on or near the landfill. It is advisable to take appropriate safety precautions when testing landfills, such as refraining from smoking and installing explosion-proof equipment.

6.0 Equipment and Supplies

6.1 Sample Probe. Stainless steel, with the bottom third perforated. Teflon probe liners and sampling lines are also allowed. Non-perforated probes are allowed as long as they are withdrawn to create a gap equivalent to having the bottom third perforated. The sample probe must be capped at the bottom and must have a threaded cap with a sampling attachment at the top. The sample probe must be long enough to go through and extend no less than 0.9 m (3 ft) below the landfill cover. If the sample probe is to be driven into the landfill, the bottom cap should be designed to facilitate driving the probe into the landfill.

6.2 Sampling Train.

6.2.1 Rotameter with Flow Control Valve. Capable of measuring a sample flow rate of 100 ±10 ml/min. The control valve must be made of stainless steel.

6.2.2 Sampling Valve. Stainless steel.

6.2.3 Pressure Gauge. U-tube mercury manometer, or equivalent, capable of measuring pressure to within 1 mm Hg (0.5 in H_2O) in the range of 0 to 1,100 mm Hg (0 to 590 in H_2O).

6.2.4 Sample Tank. Stainless steel or aluminum cylinder, equipped with a stainless steel sample tank valve.

6.3 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg (5.4 in H_2O).

6.4 Purging Pump. Portable, explosion proof, and suitable for sampling NMOC.

6.5 Pilot Probe Procedure. The following are needed only if the tester chooses to use the procedure described in section 8.2.1.

6.5.1 Pilot Probe. Tubing of sufficient strength to withstand being driven into the landfill by a post driver and an outside diameter of at least 6 mm (0.25 in.) smaller than the sample probe. The pilot probe shall be capped on both ends and long enough to go through the landfill cover and extend no less than 0.9 m (3 ft) into the landfill.

6.5.2 Post Driver and Compressor. Capable of driving the pilot probe and the sampling probe into the landfill. The Kitty Hawk portable post driver has been found to be acceptable.

6.6 Auger Procedure. The following are needed only if the tester chooses to use the procedure described in section 8.2.2.

6.6.1 Auger. Capable of drilling through the landfill cover and to a depth of no less than 0.9 m (3 ft) into the landfill.

6.6.2 Pea Gravel.

6.6.3 Bentonite.

6.7 NMOC Analyzer, Barometer, Thermometer, and Syringes. Same as in sections 6.3.1, 6.3.2, 6.33, and 6.2.10, respectively, of Method 25.

7.0 Reagents and Standards

7.1 NMOC Analysis. Same as in Method 25, section 7.2.

7.2 Calibration. Same as in Method 25, section 7.4, except omit section 7.4.3.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sample Tank Evacuation and Leak-Check. Conduct the sample tank evacuation and leak-check either in the laboratory or the field. Connect the pressure gauge and sampling valve to the sample tank. Evacuate the sample tank to 10 mm Hg (5.4 in H_2O) absolute pressure or less. Close the sampling valve, and allow the tank to sit for 30 minutes. The tank is acceptable if no change more than ±2 mm is noted. Include the results of the leak-check in the test report.

8.2 Sample Probe Installation. The tester may use the procedure in section 8.2.1 or 8.2.2.

8.2.1 Pilot Probe Procedure. Use the post driver to drive the pilot probe at least 0.9 m (3 ft) below the landfill cover. Alternative procedures to drive the probe into the landfill may be used subject to the approval of the Administrator's designated representative.

8.2.1.1 Remove the pilot probe and drive the sample probe into the hole left by the pilot probe. The sample probe shall extend at least 0.9 m (3 ft) below the landfill cover and shall protrude about 0.3 m (1 ft) above the landfill cover. Seal around the sampling probe with bentonite and cap the sampling probe with the sampling probe cap.

8.2.2 Auger Procedure. Use an auger to drill a hole to at least 0.9 m (3 ft) below the landfill cover. Place the sample probe in the hole and backfill with pea gravel to a level 0.6 m (2 ft) from the surface. The sample probe shall protrude at least 0.3 m (1 ft) above the landfill cover. Seal the remaining area around the probe with bentonite. Allow 24

hours for the landfill gases to equilibrate inside the augured probe before sampling.

8.2.3 Driven Probes. Closed-point probes may be driven directly into the landfill in a single step. This method may not require backfilling if the probe is adequately sealed by its insertion. Unperforated probes that are inserted in this manner and withdrawn at a distance from a detachable tip to create an open space are also acceptable.

8.3 Sample Train Assembly. Just before assembling the sample train, measure the sample tank vacuum using the pressure gauge. Record the vacuum, the ambient temperature, and the barometric pressure at this time. Assemble the sampling probe purging system as shown in Figure 25C–1.

8.4 Sampling Procedure. Open the sampling valve and use the purge pump and the flow control valve to evacuate at least two sample probe volumes from the system at a flow rate of 500 ml/min or less. Close the sampling valve and replace the purge pump with the sample tank apparatus as shown in Figure 25C–2. Open the sampling valve and the sample tank valve and, using the flow control valve, sample at a flow rate of 500 ml/min or less until either a constant flow rate can no longer be maintained because of reduced sample tank vacuum or the appropriate composite volume is attained. Disconnect the sampling tank apparatus and pressurize the sample cylinder to approximately 1,060 mm Hg (567 in. H_2O) absolute pressure with helium, and record the final pressure. Alternatively, the sample tank may be pressurized in the lab.

8.4.1 The following restrictions apply to compositing samples from different probe sites into a single cylinder: (1) Individual composite samples per cylinder must be of equal volume; this must be verified by recording the flow rate, sampling time, vacuum readings, or other appropriate volume measuring data, (2) individual composite samples must have a minimum volume of 1 liter unless data is provided showing smaller volumes can be accurately measured, and (3) composite samples must not be collected using the final cylinder vacuum as it diminishes to ambient pressure.

8.4.2 Use Method 3C to determine the percent N_2 in each cylinder. The presence of N_2 indicates either infiltration of ambient air into the landfill gas sample or an inappropriate testing site has been chosen where anaerobic decomposition has not begun. The landfill gas sample is acceptable if the concentration of N_2 is less than 20 percent. Alternatively, Method 3C may be used to determine the oxygen content of each cylinder as an air infiltration test. With this option, the oxygen content of each cylinder must be less than 5 percent.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4.2	Verify that landfill gas sample contains less than 20 percent N_2 or 5 percent O_2.	Ensures that ambient air was not drawn into the landfill gas sample and gas was sampled from an appropriate location.
10.1, 10.2	NMOC analyzer initial and daily performance checks.	Ensures precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Initial NMOC Analyzer Performance Test. Same as in Method 25, section 10.1, except omit the linearity checks for CO_2 standards.

10.2 NMOC Analyzer Daily Calibration.

10.2.1 NMOC Response Factors. Same as in Method 25, section 10.2.2.

10.3 Sample Tank Volume. The volume of the gas sampling tanks must be determined. Determine the tank volumes by weighing them empty and then filled with deionized water; weigh to the nearest 5 g, and record the results. Alternatively, measure the volume of water used to fill them to the nearest 5 ml.

11.0 Analytical Procedures

11.1 The oxidation, reduction, and measurement of NMOC's is similar to Method 25. Before putting the NMOC analyzer into routine operation, conduct an initial performance test. Start the analyzer, and perform all the necessary functions in order to put the analyzer into proper working order. Conduct the performance test according to the procedures established in section 10.1. Once the performance test has been successfully completed and the NMOC calibration response factor has been determined, proceed with sample analysis as follows:

11.1.1 Daily Operations and Calibration Checks. Before and immediately after the analysis of each set of samples or on a daily basis (whichever occurs first), conduct a calibration test according to the procedures established in section 10.2. If the criteria of the daily calibration test cannot be met, repeat

the NMOC analyzer performance test (Section 10.1) before proceeding.

11.1.2 Operating Conditions. Same as in Method 25, section 11.2.1.

11.1.3 Analysis of Sample Tank. Purge the sample loop with sample, and then inject the sample. Under the specified operating conditions, the CO_2 in the sample will elute in approximately 100 seconds. As soon as the detector response returns to baseline following the CO_2 peak, switch the carrier gas flow to backflush, and raise the column oven temperature to 195 °C (383 °F) as rapidly as possible. A rate of 30 °C/min (54 °F/min) has been shown to be adequate. Record the value obtained for any measured NMOC. Return the column oven temperature to 85 °C (185 °F) in preparation for the next analysis. Analyze each sample in triplicate, and report the average as C_{tm}.

12.0 Data Analysis and Calculations

NOTE: All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge or manometer pressure.

12.1 Nomenclature

B_w = Moisture content in the sample, fraction.

C_{N2} = N_2 concentration in the diluted sample gas.

C_{mN2} = Measured N_2 concentration, fraction in landfill gas.

C_{mOx} = Measured Oxygen concentration, fraction in landfill gas.

C_{Ox} = Oxygen concentration in the diluted sample gas.

C_t = Calculated NMOC concentration, ppmv C equivalent.

C_{tm} = Measured NMOC concentration, ppmv C equivalent.

P_b = Barometric pressure, mm Hg.

P_t = Gas sample tank pressure after sampling, but before pressurizing, mm Hg absolute.

P_{tf} = Final gas sample tank pressure after pressurizing, mm Hg absolute.

P_{ti} = Gas sample tank pressure after evacuation, mm Hg absolute.

P_w = Vapor pressure of H_2O (from Table 25C–1), mm Hg.

r = Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 . . . r).

T_t = Sample tank temperature at completion of sampling, °K.

T_{ti} = Sample tank temperature before sampling, °K.

T_{tf} = Sample tank temperature after pressuring, °K.

12.2 Water Correction. Use Table 25C–1 (Section 17.0), the LFG temperature, and barometric pressure at the sampling site to calculate B_w.

$$B_w = \frac{P_w}{P_b} \qquad \text{Eq. 25C-1}$$

12.3 Nitrogen Concentration in the landfill gas. Use equation 25C–2 to calculate the measured concentration of nitrogen in the original landfill gas.

$$C_{N2} = \left[\frac{\left(\frac{P_{tf}}{T_{tf}}\right)}{\left(\left(\frac{P_t}{T_t}\right)-\left(\frac{P_{ti}}{T_{ti}}\right)\right)}\right] C_{mN2} \qquad \text{Eq.25C-2}$$

12.4 Oxygen Concentration in the landfill gas. Use equation 25C–3 to calculate the measured concentration of oxygen in the original landfill gas.

$$C_{Ox} = \left[\frac{\left(\frac{P_{tf}}{T_{tf}}\right)}{\left(\left(\frac{P_t}{T_t}\right)-\left(\frac{P_{ti}}{T_{ti}}\right)\right)}\right] C_{mOx} \qquad \text{Eq.25C-3}$$

12.5 You must correct the NMOC Concentration for the concentration of nitrogen or oxygen based on which gas or gases passes the requirements in section 9.1.

12.5.1 NMOC Concentration with nitrogen correction. Use Equation 25C–4 to calculate the concentration of NMOC for each sample tank when the nitrogen concentration is less than 20 percent.

$$C_t = \frac{\frac{P_{tf}}{T_{tf}}}{\left(\frac{P_t}{T_t}-\frac{P_{ti}}{T_{ti}}\right)\left(1-\frac{99}{78}C_{N2}\right)-B_w}\frac{1}{r}\sum_{j=1}^{r} C_{tm(j)} \qquad \text{Eq. 25C-4}$$

12.5.2 NMOC Concentration with oxygen correction. Use Equation 25C–5 to calculate the concentration of NMOC for each sample tank if the landfill gas oxygen is less than 5 percent and the landfill gas nitrogen concentration is greater than 20 percent.

$$C_t = \frac{\frac{P_{tf}}{T_{tf}}}{\left(\frac{P_t}{T_t}-\frac{P_{ti}}{T_{ti}}\right)\left(1-\frac{99}{21}C_{Ox}\right)-B_w}\frac{1}{r}\sum_{j=1}^{r} C_{tm(j)} \qquad \text{Eq. 25C-5}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, Albert E., Samuel Witz, and Robert D. MacPhee. Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, Massachusetts. June 15–20, 1975.) 14 p.

2. Salo, Albert E., William L. Oaks, and Robert D. MacPhee. Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, Colorado. June 9–13, 1974.) 25 p.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

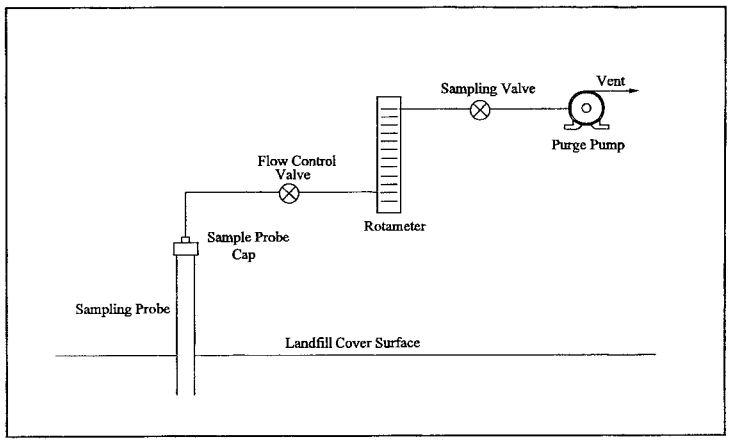


Figure 25C-1. Schematic of Sampling Probe Purging System

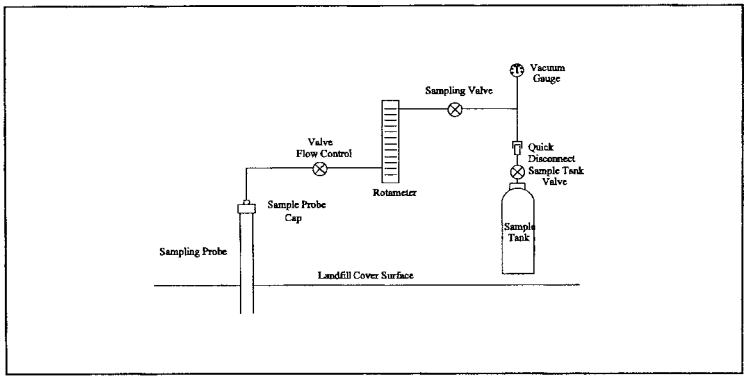


Figure 25C-2. Schematic of Sampling Train.

TABLE 25C–1—MOISTURE CORRECTION

Temperature, °C	Vapor Pressure of H_2O, mm Hg	Temperature, °C	Vapor Pressure of H_2O, mm Hg
4	6.1	18	15.5
6	7.0	20	17.5
8	8.0	22	19.8
10	9.2	24	22.4
12	10.5	26	25.2
14	12.0	28	28.3

TABLE 25C–1—MOISTURE CORRECTION—Continued

Temperature, °C	Vapor Pressure of H_2O, mm Hg	Temperature, °C	Vapor Pressure of H_2O, mm Hg
16	13.6	30	31.8

METHOD 25D—DETERMINATION OF THE VOLATILE ORGANIC CONCENTRATION OF WASTE SAMPLES

NOTE: Performance of this method should not be attempted by persons unfamiliar with the operation of a flame ionization detector (FID) or an electrolytic conductivity detector (ELCD) because knowledge beyond the scope of this presentation is required.

1.0 Scope and Application

1.1 Analyte. Volatile Organic Compounds. No CAS No. assigned.

1.2 Applicability. This method is applicable for determining the volatile organic (VO) concentration of a waste sample.

2.0 Summary of Method

2.1 Principle. A sample of waste is obtained at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to the atmosphere). The sample is suspended in an organic/aqueous matrix, then heated and purged with nitrogen for 30 min. in order to separate certain organic compounds. Part of the sample is analyzed for carbon concentration, as methane, with an FID, and part of the sample is analyzed for chlorine concentration, as chloride, with an ELCD. The VO concentration is the sum of the carbon and chlorine content of the sample.

3.0 Definitions

3.1 *Well-mixed* in the context of this method refers to turbulent flow which results in multiple-phase waste in effect behaving as single-phase waste due to good mixing.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1 Sampling. The following equipment is required:

6.1.1 Sampling Tube. Flexible Teflon, 0.25 in. ID (6.35 mm).

6.1.2 Sample Container. Borosilicate glass, 40-mL, and a Teflon-lined screw cap capable of forming an air tight seal.

6.1.3 Cooling Coil. Fabricated from 0.25 in (6.35 mm). ID 304 stainless steel tubing with a thermocouple at the coil outlet.

6.2 Analysis. The following equipment is required.

6.2.1 Purging Apparatus. For separating the VO from the waste sample. A schematic of the system is shown in Figure 25D–1. The purging apparatus consists of the following major components.

6.2.1.1 Purging Flask. A glass container to hold the sample while it is heated and purged with dry nitrogen. The cap of the purging flask is equipped with three fittings: one for a purging lance (fitting with the #7 Ace-thread), one for the Teflon exit tubing (side fitting, also a #7 Ace-thread), and a third (a 50-mm Ace-thread) to attach the base of the purging flask as shown in Figure 25D–2. The base of the purging flask is a 50-mm ID (2 in) cylindrical glass tube. One end of the tube is open while the other end is sealed. Exact dimensions are shown in Figure 25D–2.

6.2.1.2 Purging Lance. Glass tube, 6-mm OD (0.2 in) by 30 cm (12 in) long. The purging end of the tube is fitted with a four-arm bubbler with each tip drawn to an opening 1 mm (0.04 in) in diameter. Details and exact dimensions are shown in Figure 25D–2.

6.2.1.3 Coalescing Filter. Porous fritted disc incorporated into a container with the same dimensions as the purging flask. The details of the design are shown in Figure 25D–3.

6.2.1.4 Constant Temperature Chamber. A forced draft oven capable of maintaining a uniform temperature around the purging flask and coalescing filter of 75 ±2 °C (167 ±3.6 °F).

6.2.1.5 Three-way Valve. Manually operated, stainless steel. To introduce calibration gas into system.

6.2.1.6 Flow Controllers. Two, adjustable. One capable of maintaining a purge gas flow rate of 6 ±0.06 L/min (0.2 ±0.002 ft^3/min) The other capable of maintaining a calibration gas flow rate of 1–100 mL/min (0.00004–0.004 ft^3/min).

6.2.1.7 Rotameter. For monitoring the air flow through the purging system (0–10 L/min)(0–0.4 ft^3/min).

6.2.1.8 Sample Splitters. Two heated flow restrictors (placed inside oven or heated to 120 ±10 °C (248 ±18 °F)). At a purge rate of 6 L/min (0.2 ft^3/min), one will supply a constant flow to the first detector (the rest of the flow will be directed to the second sample splitter). The second splitter will split the analytical flow between the second detector and the flow restrictor. The approximate flow to the FID will be 40 mL/min (0.0014 ft^3/min) and to the ELCD will be 15 mL/min (0.0005 ft^3/min), but the exact flow must be adjusted to be compatible with the individual detector and to meet its linearity requirement. The two sample splitters will be connected to each other by 1/8″ OD (3.175 mm) stainless steel tubing.

6.2.1.9 Flow Restrictor. Stainless steel tubing, 1/8″ OD (3.175 mm), connecting the second sample splitter to the ice bath. Length is determined by the resulting pressure in the purging flask (as measured by the pressure gauge). The resulting pressure from the use of the flow restrictor shall be 6–7 psig.

6.2.1.10 Filter Flask. With one-hole stopper. Used to hold ice bath. Excess purge gas is vented through the flask to prevent condensation in the flowmeter and to trap volatile organic compounds.

6.2.1.11 Four-way Valve. Manually operated, stainless steel. Placed inside oven, used to bypass purging flask.

6.2.1.12 On/Off Valves. Two, stainless steel. One heat resistant up to 130 °C (266 °F) and placed between oven and ELCD. The other a toggle valve used to control purge gas flow.

6.2.1.13 Pressure Gauge. Range 0–40 psi. To monitor pressure in purging flask and coalescing filter.

6.2.1.14 Sample Lines. Teflon, 1/4″ OD (6.35 mm), used inside the oven to carry purge gas to and from purging chamber and to and from coalescing filter to four-way valve. Also used to carry sample from four-way valve to first sample splitter.

6.2.1.15 Detector Tubing. Stainless steel, 1/8″ OD (3.175 mm), heated to 120 ±10 °C (248 ±18 °F) . Used to carry sample gas from each sample splitter to a detector. Each piece of tubing must be wrapped with heat tape and insulating tape in order to insure that no cold spots exist. The tubing leading to the ELCD will also contain a heat-resistant on-off valve (Section 6.2.1.12) which shall also be wrapped with heat-tape and insulation.

6.2.2 Volatile Organic Measurement System. Consisting of an FID to measure the carbon concentration of the sample and an ELCD to measure the chlorine concentration.

6.2.2.1 FID. A heated FID meeting the following specifications is required.

6.2.2.1.1 Linearity. A linear response (±5 percent) over the operating range as demonstrated by the procedures established in section 10.1.1.

6.2.2.1.2 Range. A full scale range of 50 pg carbon/sec to 50 µg carbon/sec. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.2.2.1.3 Data Recording System. A digital integration system compatible with the FID for permanently recording the output of the detector. The recorder shall have the capability to start and stop integration at points selected by the operator or it shall be capable of the ''integration by slices'' technique (this technique involves breaking down the chromatogram into smaller increments, integrating the area under the curve for each portion, subtracting the background for each portion, and then adding all of the areas together for the final area count).

6.2.2.2 ELCD. An ELCD meeting the following specifications is required. 1-propanol must be used as the electrolyte. The electrolyte flow through the conductivity cell shall be 1 to 2 mL/min (0.00004 to 0.00007 ft^3/min).

NOTE: A ¼-in. ID (6.35 mm) quartz reactor tube is strongly recommended to reduce carbon buildup and the resulting detector maintenance.

6.2.2.2.1 Linearity. A linear response (±10 percent) over the response range as demonstrated by the procedures in section 10.1.2.

6.2.2.2.2 Range. A full scale range of 5.0 pg/sec to 500 ng/sec chloride. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.2.2.2.3 Data Recording System. A digital integration system compatible with the output voltage range of the ELCD. The recorder must have the capability to start and stop integration at points selected by the operator or it shall be capable of performing the ''integration by slices'' technique.

7.0 Reagents and Standards

7.1 Sampling.

7.1.1 Polyethylene Glycol (PEG). Ninety-eight percent pure with an average molecular weight of 400. Before using the PEG, remove any organic compounds that might be detected as volatile organics by heating it to 120 °C (248 °F) and purging it with nitrogen at a flow rate of 1 to 2 L/min (0.04 to 0.07 ft^3/min) for 2 hours. The cleaned PEG must be stored under a 1 to 2 L/min (0.04 to 0.07 ft^3/min) nitrogen purge until use. The purge apparatus is shown in Figure 25D–4.

7.2 Analysis.

7.2.1 Sample Separation. The following are required for the sample purging step.

7.2.1.1 PEG. Same as section 7.1.1.

7.2.1.2 Purge Gas. Zero grade nitrogen (N_2), containing less than 1 ppm carbon.

7.2.2 Volatile Organics Measurement. The following are required for measuring the VO concentration.

7.2.2.1 Hydrogen (H_2). Zero grade H_2, 99.999 percent pure.

7.2.2.2 Combustion Gas. Zero grade air or oxygen as required by the FID.

7.2.2.3 Calibration Gas. Pressurized gas cylinder containing 10 percent propane and 1 percent 1,1-dichloroethylene by volume in nitrogen.

7.2.2.4 Water. Deionized distilled water that conforms to American Society for Testing and Materials Specification D 1193–74, Type 3, is required for analysis. At the option of the analyst, the $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations are not expected to be present.

7.2.2.5 1-Propanol. ACS grade or better. Electrolyte Solution. For use in the ELCD.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling.

8.1.1 Sampling Plan Design and Development. Use the procedures in chapter nine of Reference 1 in section 16 as guidance in developing a sampling plan.

8.1.2 Single Phase or Well-mixed Waste.

8.1.2.1 Install a sampling tap to obtain the sample at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to the atmosphere). Assemble the sampling apparatus as shown in Figure 25D–5.

8.1.2.2 Prepare the sampling containers as follows: Pour 30 mL of clean PEG into the container. PEG will reduce but not eliminate the loss of organics during sample collection. Weigh the sample container with the screw cap, the PEG, and any labels to the nearest 0.01 g and record the weight (m_{st}). Store the containers in an ice bath until 1 hour before sampling (PEG will solidify at ice bath temperatures; allow the containers to reach room temperature before sampling).

8.1.2.3 Begin sampling by purging the sample lines and cooling coil with at least four volumes of waste. Collect the purged material in a separate container and dispose of it properly.

8.1.2.4 After purging, stop the sample flow and direct the sampling tube to a preweighed sample container, prepared as described in section 8.1.2.2. Keep the tip of the tube below the surface of the PEG during sampling to minimize contact with the atmosphere. Sample at a flow rate such that the temperature of the waste is less than 10 °C (50 °F). Fill the sample container and immediately cap it (within 5 seconds) so that a minimum headspace exists in the container. Store immediately in a cooler and cover with ice.

8.1.3 Multiple-phase Waste. Collect a 10 g sample of each phase of waste generated using the procedures described in section 8.1.2 or 8.1.5. Each phase of the waste shall be analyzed as a separate sample. Calculate the weighted average VO concentration of the waste using Equation 25D–13 (Section 12.14).

8.1.4 Solid waste. Add approximately 10 g of the solid waste to a container prepared in the manner described in section 8.1.2.2, minimizing headspace. Cap and chill immediately.

8.1.5 Alternative to Tap Installation. If tap installation is impractical or impossible, fill a large, clean, empty container by submerging the container into the waste below the surface of the waste. Immediately fill a container prepared in the manner described in section 8.1.2.2 with approximately 10 g of the waste collected in the large container. Minimize headspace, cap and chill immediately.

8.1.6 Alternative sampling techniques may be used upon the approval of the Administrator.

8.2 Sample Recovery.

8.2.1 Assemble the purging apparatus as shown in Figures 25D–1 and 25D–2. The oven shall be heated to 75 ±2 °C (167 ±3.6 °F). The sampling lines leading from the oven to the detectors shall be heated to 120 ±10 °C (248 ±18 °F) with no cold spots. The flame ionization detector shall be operated with a heated block. Adjust the purging lance so that it reaches the bottom of the chamber.

8.2.2 Remove the sample container from the cooler, and wipe the exterior of the container to remove any extraneous ice, water, or other debris. Reweigh the sample container to the nearest 0.01 g, and record the weight (m_{sf}). Pour the contents of the sample container into the purging flask, rinse the sample container three times with a total of 20 mL of PEG (since the sample container originally held 30 mL of PEG, the total volume of PEG added to the purging flask will be 50 mL), transferring the rinsings to the purging flask after each rinse. Cap purging flask between rinses. The total volume of PEG in the purging flask shall be 50 mL. Add 50 mL of water to the purging flask.

9.0 Quality Control

9.1 Quality Control Samples. If audit samples are not available, prepare and analyze the two types of quality control samples (QCS) listed in Sections 9.1.1 and 9.1.2. Before placing the system in operation, after a shutdown of greater than six months, and after any major modifications, analyze each QCS in triplicate. For each detector, calculate the percent recovery by dividing measured concentration by theoretical concentration and multiplying by 100. Determine the mean percent recovery for each detector for each QCS triplicate analysis. The RSD for any triplicate analysis shall be ≤10 percent. For QCS 1 (methylene chloride), the percent recovery shall be ≥90 percent for carbon as methane, and ≥55 percent for chlorine as chloride. For QCS 2 (1,3-dichloro-2-propanol), the percent recovery shall be ≤15 percent for carbon as methane, and ≤6 percent for chlorine as chloride. If the analytical system does not meet the above-mentioned criteria for both detectors, check the system parameters (temperature, system pressure, purge rate, etc.), correct the problem, and repeat the triplicate analysis of each QCS.

9.1.1 QCS 1, Methylene Chloride. Prepare a stock solution by weighing, to the nearest 0.1 mg, 55 µL of HPLC grade methylene chloride in a tared 5 mL volumetric flask. Record the weight in milligrams, dilute to 5 mL with cleaned PEG, and inject 100 µL of the stock solution into a sample prepared as a water blank (50 mL of cleaned PEG and 60 mL of water in the purging flask). Analyze

the QCS according to the procedures described in sections 10.2 and 10.3, excluding section 10.2.2. To calculate the theoretical carbon concentration (in mg) in QCS 1, multiply mg of methylene chloride in the stock solution by 3.777×10^{-3}. To calculate the theoretical chlorine concentration (in mg) in QCS 1, multiply mg of methylene chloride in the stock solution by 1.670×10^{-2}.

9.1.2 QCS 2, 1,3-dichloro-2-propanol. Prepare a stock solution by weighing, to the nearest 0.1 mg, 60 μL of high purity grade 1,3-dichloro-2-propanol in a tared 5 mL volumetric flask. Record the weight in milligrams, dilute to 5 mL with cleaned PEG, and inject 100 μL of the stock solution into a sample prepared as a water blank (50 mL of cleaned PEG and 60 mL of water in the purging flask). Analyze the QCS according to the procedures described in sections 10.2 and 10.3, excluding section 10.2.2. To calculate the theoretical carbon concentration (in mg) in QCS 2, multiply mg of 1,3-dichloro-2-propanol in the stock solution by 7.461×10^{-3}. To calculate the theoretical chlorine concentration (in mg) in QCS 2, multiply mg of 1,3-dichloro-2-propanol in the stock solution by 1.099×10^{-2}.

9.1.3 Routine QCS Analysis. For each set of compliance samples (in this context, set is per facility, per compliance test), analyze one QCS 1 and one QCS 2 sample. The percent recovery for each sample for each detector shall be ±13 percent of the mean recovery established for the most recent set of QCS triplicate analysis (Section 9.4). If the sample does not meet this criteria, check the system components and analyze another QCS 1 and 2 until a single set of QCS meet the ±13 percent criteria.

10.0 Calibration and Standardization

10.1 Initial Performance Check of Purging System. Before placing the system in operation, after a shutdown of greater than six months, after any major modifications, and at least once per month during continuous operation, conduct the linearity checks described in sections 10.1.1 and 10.1.2. Install calibration gas at the three-way calibration gas valve. See Figure 25D–1.

10.1.1 Linearity Check Procedure. Using the calibration standard described in section 7.2.2.3 and by varying the injection time, it is possible to calibrate at multiple concentration levels. Use Equation 25D–3 to calculate three sets of calibration gas flow rates and run times needed to introduce a total mass of carbon, as methane, (m_c) of 1, 5, and 10 mg into the system (low, medium and high FID calibration, respectively). Use Equation 25D–4 to calculate three sets of calibration gas flow rates and run times needed to introduce a total chloride mass (m_{ch}) of 1, 5, and 10 mg into the system (low, medium and high ELCD calibration, respectively). With the system operating in standby mode, allow the FID and the ELCD to establish a stable baseline. Set the secondary pressure regulator of the calibration gas cylinder to the same pressure as the purge gas cylinder and set the proper flow rate with the calibration flow controller (see Figure 25D–1). The calibration gas flow rate can be measured with a flowmeter attached to the vent position of the calibration gas valve. Set the four-way bypass valve to standby position so that the calibration gas flows through the coalescing filter only. Inject the calibration gas by turning the calibration gas valve from vent position to inject position. Continue the calibration gas flow for the appropriate period of time before switching the calibration valve to vent position. Continue recording the response of the FID and the ELCD for 5 min after switching off calibration gas flow. Make triplicate injections of all six levels of calibration.

10.1.2 Linearity Criteria. Calculate the average response factor (Equations 25D–5 and 25D–6) and the relative standard deviation (RSD) (Equation 25D–10) at each level of the calibration curve for both detectors. Calculate the overall mean of the three response factor averages for each detector. The FID linearity is acceptable if each response factor is within 5 percent of the overall mean and if the RSD for each set of triplicate injections is less than 5 percent. The ELCD linearity is acceptable if each response factor is within 10 percent of the overall mean and if the RSD for each set of triplicate injections is less than 10 percent. Record the overall mean value of the response factors for the FID and the ELCD. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat sections 10.1.1 and 10.1.2.

10.2 Daily Calibrations.

10.2.1 Daily Linearity Check. Follow the procedures outlined in section 10.1.1 to analyze the medium level calibration for both the FID and the ELCD in duplicate at the start of the day. Calculate the response factors and the RSDs for each detector. For the FID, the calibration is acceptable if the average response factor is within 5 percent of the overall mean response factor (Section 10.1.2) and if the RSD for the duplicate injection is less than 5 percent. For the ELCD, the calibration is acceptable if the average response factor is within 10 percent of the overall mean response factor (Section 10.1.2) and if the RSD for the duplicate injection is less than 10 percent. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat sections 10.1.1 and 10.1.2.

10.2.2 Calibration Range Check.

10.2.2.1 If the waste concentration for either detector falls below the range of calibration for that detector, use the procedure outlined in section 10.1.1 to choose two calibration points that bracket the new target

concentration. Analyze each of these points in triplicate (as outlined in section 10.1.1) and use the criteria in section 10.1.2 to determine the linearity of the detector in this ''mini-calibration'' range.

10.2.2.2 After the initial linearity check of the mini-calibration curve, it is only necessary to test one of the points in duplicate for the daily calibration check (in addition to the points specified in section 10.2.1). The average daily mini-calibration point should fit the linearity criteria specified in section 10.2.1. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat the calibration procedure mentioned in the first paragraph of section 10.2.2. A mini-calibration curve for waste concentrations above the calibration curve for either detector is optional.

10.3 Analytical Balance. Calibrate against standard weights.

11.0 Analysis

11.1 Sample Analysis.

11.1.1 Turn on the constant temperature chamber and allow the temperature to equilibrate at 75 ±2 °C (167 ±3.6 °F). Turn the four-way valve so that the purge gas bypasses the purging flask, the purge gas flowing through the coalescing filter and to the detectors (standby mode). Turn on the purge gas. Allow both the FID and the ELCD to warm up until a stable baseline is achieved on each detector. Pack the filter flask with ice. Replace ice after each run and dispose of the waste water properly. When the temperature of the oven reaches 75 ±2 °C (167 ±3.6 °F), start both integrators and record baseline. After 1 min, turn the four-way valve so that the purge gas flows through the purging flask, to the coalescing filter and to the sample splitters (purge mode). Continue recording the response of the FID and the ELCD. Monitor the readings of the pressure gauge and the rotameter. If the readings fall below established setpoints, stop the purging, determine the source of the leak, and resolve the problem before resuming. Leaks detected during a sampling period invalidate that sample.

11.1.2 As the purging continues, monitor the output of the detectors to make certain that the analysis is proceeding correctly and that the results are being properly recorded. Every 10 minutes read and record the purge flow rate, the pressure and the chamber temperature. Continue the purging for 30 minutes.

11.1.3 For each detector output, integrate over the entire area of the peak starting at 1 minute and continuing until the end of the run. Subtract the established baseline area from the peak area. Record the corrected area of the peak. See Figure 25D–6 for an example integration.

11.2 Water Blank. A water blank shall be analyzed for each batch of cleaned PEG prepared. Transfer about 60 mL of water into the purging flask. Add 50 mL of the cleaned PEG to the purging flask. Treat the blank as described in sections 8.2 and 8.3, excluding section 8.2.2. Calculate the concentration of carbon and chlorine in the blank sample (assume 10 g of waste as the mass). A VO concentration equivalent to ≤10 percent of the applicable standard may be subtracted from the measured VO concentration of the waste samples. Include all blank results and documentation in the test report.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

A_b = Area under the water blank response curve, counts.

A_c = Area under the calibration response curve, counts.

A_s = Area under the sample response curve, counts.

C = Concentration of volatile organics in the sample, ppmw.

C_c = Concentration of carbon, as methane, in the calibration gas, mg/L.

C_{ch} = Concentration of chloride in the calibration gas, mg/L.

C_j = VO concentration of phase j, ppmw.

DR_t = Average daily response factor of the FID, mg CH_4/counts.

Dr_{th} = Average daily response factor of the ELCD, mg Cl^-/counts.

F_j = Weight fraction of phase j present in the waste.

m_c = Mass of carbon, as methane, in a calibration run, mg.

m_{ch} = Mass of chloride in a calibration run, mg.

m_s = Mass of the waste sample, g.

m_{sc} = Mass of carbon, as methane, in the sample, mg.

m_{sf} = Mass of sample container and waste sample, g.

m_{sh} = Mass of chloride in the sample, mg.

m_{st} = Mass of sample container prior to sampling, g.

m_{VO} = Mass of volatile organics in the sample, mg.

n = Total number of phases present in the waste.

P_p = Percent propane in calibration gas (L/L).

P_{vc} = Percent 1,1-dichloroethylene in calibration gas (L/L).

Q_c = Flow rate of calibration gas, L/min.

t_c = Length of time standard gas is delivered to the analyzer, min.

W = Weighted average VO concentration, ppmw.

12.2 Concentration of Carbon, as Methane, in the Calibration Gas.

$$C_c = (19.681 \times P_p) + (13.121 \times P_{vc}) \qquad \text{Eq. 25D-1}$$

12.3 Concentration of Chloride in the Calibration Gas.

$$C_{ch} = 28.998 \times P_{vc} \qquad \text{Eq. 25D-2}$$

12.4 Mass of Carbon, as Methane, in a Calibration Run.

$$M_c = C_c \times Q_c \times t_c \qquad \text{Eq. 25D-3}$$

12.5 Mass of Chloride in a Calibration Run.

$$m_{ch} = C_{ch} \times Q_c \times t_c \qquad \text{Eq. 25D-4}$$

12.6 FID Response Factor, mg/counts.

$$DR_t = \frac{m_c}{A_c} \qquad \text{Eq. 25D-5}$$

12.7 ELCD Response Factor, mg/counts.

$$DR_{th} = \frac{m_{ch}}{A_c} \qquad \text{Eq. 25D-6}$$

12.8 Mass of Carbon in the Sample.

$$m_{sc} = DR_t(A_s - A_b) \qquad \text{Eq. 25D-7}$$

12.9 Mass of Chloride in the Sample.

$$m_{sh} = DR_{th}(A_s - A_b) \qquad \text{Eq. 25D-8}$$

12.10 Mass of Volatile Organics in the Sample.

$$m_{vo} = m_{sc} + m_{sh} \qquad \text{Eq. 25D-9}$$

12.11 Relative Standard Deviation.

$$RSD = \frac{100}{\bar{x}} \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}} \qquad \text{Eq. 25D-10}$$

12.12 Mass of Sample.

$$m_s = m_{sf} - m_{st} \qquad \text{Eq. 25D-11}$$

12.13 Concentration of Volatile Organics in Waste.

$$C = \frac{(m_{vo} \times 1000)}{m_s} \qquad \text{Eq. 25D-12}$$

12.14 Weighted Average VO Concentration of Multi-phase Waste.

$$W = \sum_{j=1}^{n} F_j x \overline{C}_j \qquad \text{Eq. 25D-13}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. ''Test Methods for Evaluating Solid Waste, Physical/Chemistry Methods'', U.S. Environmental Protection Agency. Publication SW–846, 3rd Edition, November 1986 as amended by Update I, November 1990.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

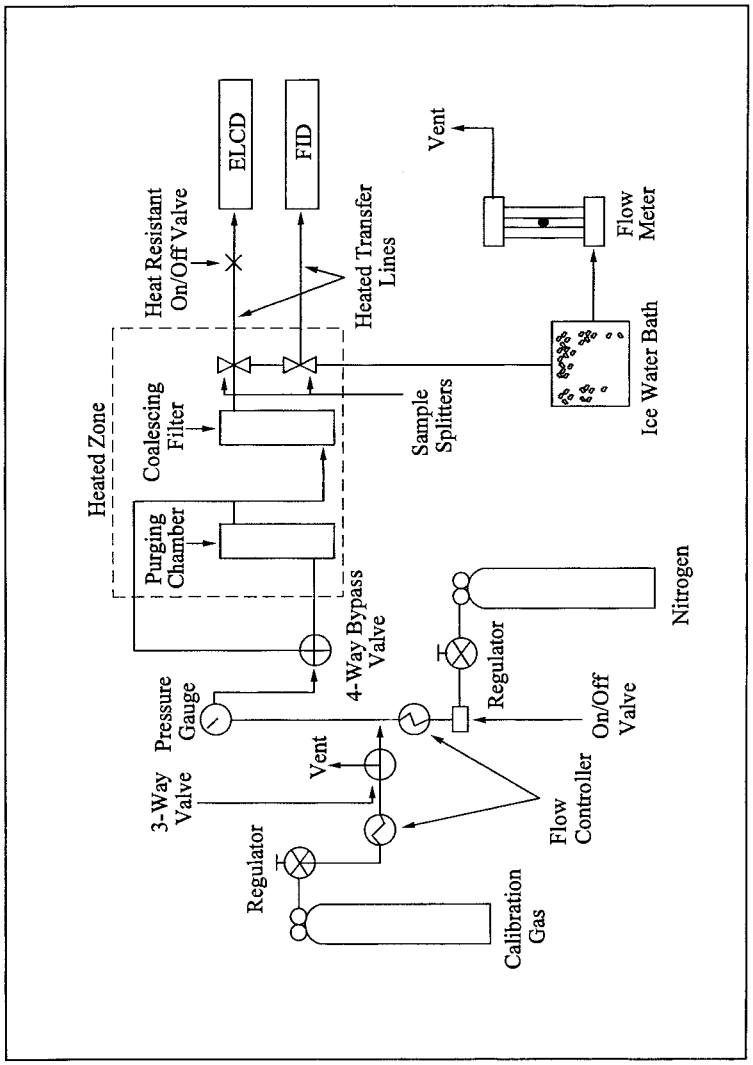


Figure 25D-1. Schematic of Purging Apparatus.

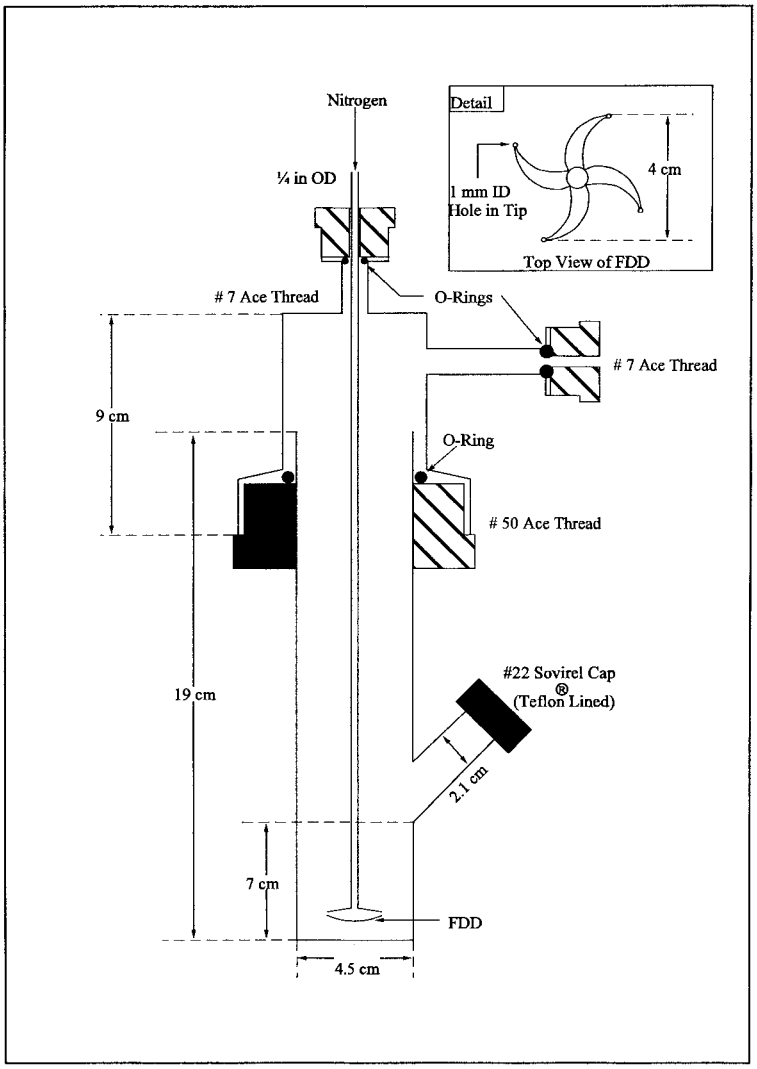
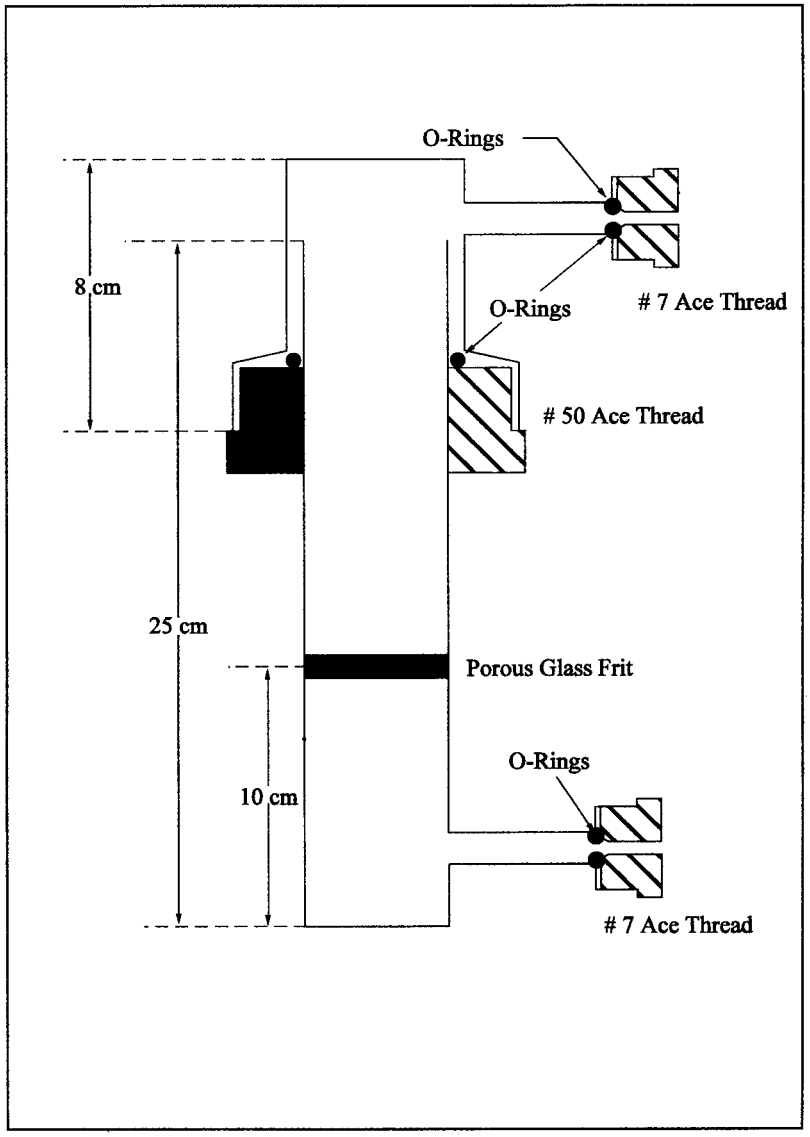


Figure 25D-2. Purging Lance.


O-Rings
8 cm
O-Rings
7 Ace Thread
50 Ace Thread
25 cm
Porous Glass Frit
O-Rings
10 cm
7 Ace Thread

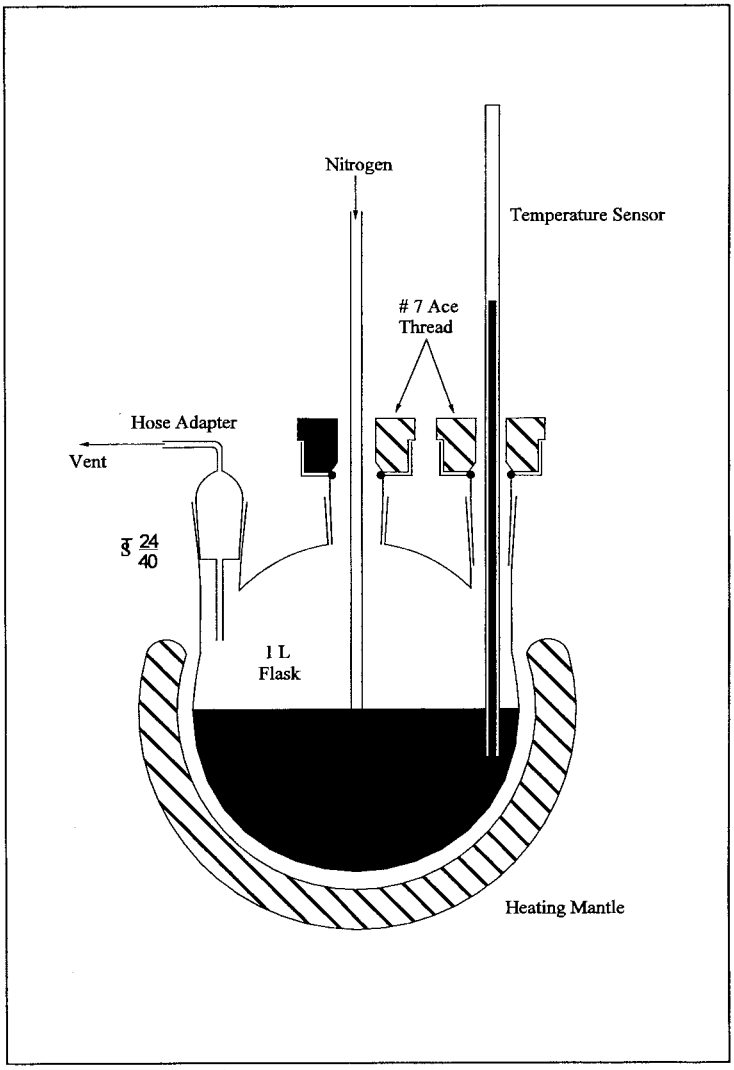


Figure 25D-4. Schematic of PEG Cleaning System.

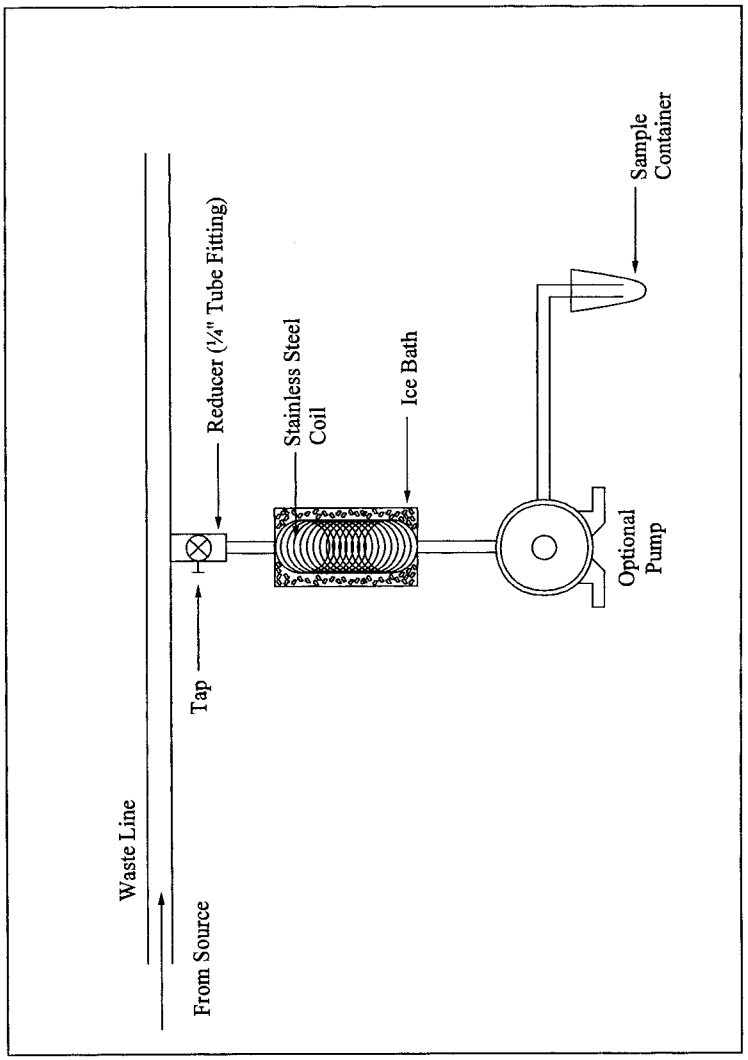


Figure 25D-5. Schematic of Sampling Apparatus.

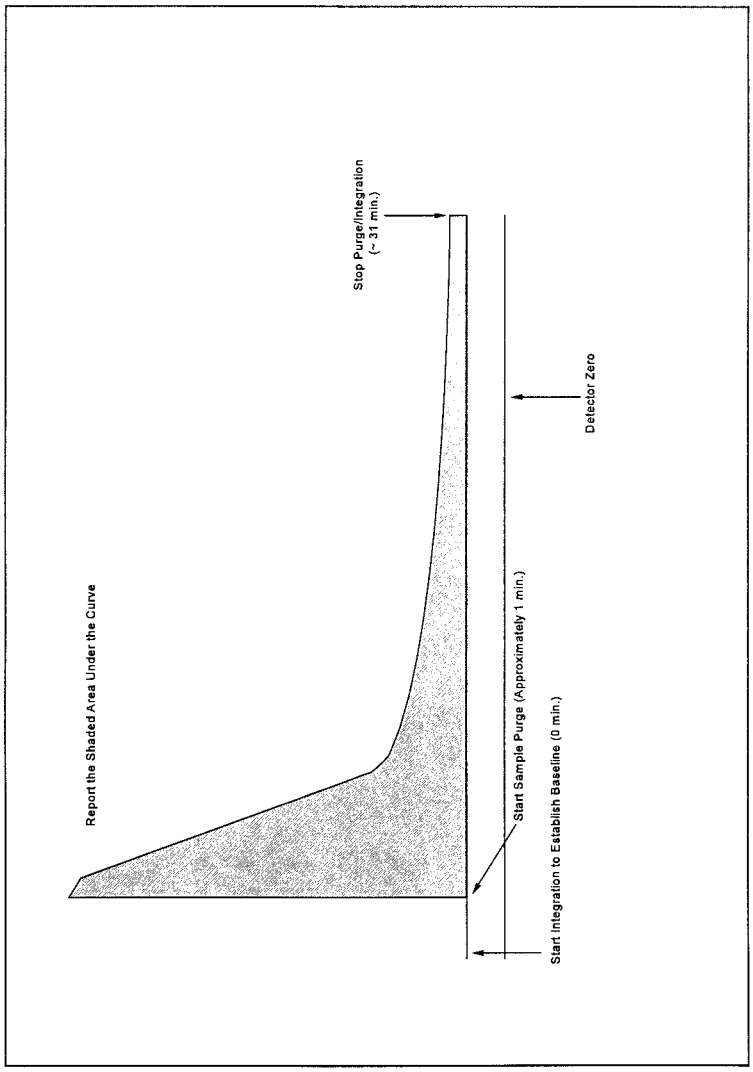


Figure 25D-6. Example Integration of Either Detector.

METHOD 25E—DETERMINATION OF VAPOR PHASE ORGANIC CONCENTRATION IN WASTE SAMPLES

NOTE: Performance of this method should not be attempted by persons unfamiliar with the operation of a flame ionization detector (FID) nor by those who are unfamiliar with source sampling because knowledge beyond the scope of this presentation is required. This method is not inclusive with respect to specifications (*e.g.*, reagents and standards) and calibration procedures. Some material is incorporated by reference from other methods. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 106, part 61, Appendix B, and Method 18, part 60, Appendix A.

1.0 Scope and Application

1.1 Applicability. This method is applicable for determining the vapor pressure of waste cited by an applicable regulation.

1.2 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 The headspace vapor of the sample is analyzed for carbon content by a headspace analyzer, which uses an FID.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 The analyst shall select the operating parameters best suited to the requirements for a particular analysis. The analyst shall produce confirming data through an adequate supplemental analytical technique and have the data available for review by the Administrator.

5.0 Safety [Reserved]

6.0 Equipment and Supplies

6.1 Sampling. The following equipment is required:

6.1.1 Sample Containers. Vials, glass, with butyl rubber septa, Perkin-Elmer Corporation Numbers 0105–0129 (glass vials), B001–0728 (gray butyl rubber septum, plug style), 0105–0131 (butyl rubber septa), or equivalent. The seal must be made from butyl rubber. Silicone rubber seals are not acceptable.

6.1.2 Vial Sealer. Perkin-Elmer Number 105–0106, or equivalent.

6.1.3 Gas-Tight Syringe. Perkin-Elmer Number 00230117, or equivalent.

6.1.4 The following equipment is required for sampling.

6.1.4.1 Tap.

6.1.4.2 Tubing. Teflon, 0.25-in. ID.

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1.4.3 Cooling Coil. Stainless steel (304), 0.25 in.-ID, equipped with a thermocouple at the coil outlet.

6.2 Analysis. The following equipment is required.

6.2.1 Balanced Pressure Headspace Sampler. Perkin-Elmer HS–6, HS–100, or equivalent, equipped with a glass bead column instead of a chromatographic column.

6.2.2 FID. An FID meeting the following specifications is required.

6.2.2.1 Linearity. A linear response (±5 percent) over the operating range as demonstrated by the procedures established in section 10.2.

6.2.2.2 Range. A full scale range of 1 to 10,000 parts per million (ppm) propane (C_3H_8). Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.2.3 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the output of the detector.

6.2.4 Temperature Sensor. Capable of reading temperatures in the range of 30 to 60 °C (86 to 140 °F) with an accuracy of ±0.1 °C (±0.2 °F).

7.0 Reagents and Standards

7.1 Analysis. The following items are required for analysis.

7.1.1 Hydrogen (H_2). Zero grade hydrogen, as required by the FID.

7.1.2 Carrier Gas. Zero grade nitrogen, containing less than 1 ppm carbon (C) and less than 1 ppm carbon dioxide.

7.1.3 Combustion Gas. Zero grade air or oxygen as required by the FID.

7.2 Calibration and Linearity Check.

7.2.1 Stock Cylinder Gas Standard. 100 percent propane. The manufacturer shall: (a) Certify the gas composition to be accurate to ±3 percent or better (see section 7.2.1.1); (b) recommend a maximum shelf life over which the gas concentration does not change by greater than ±5 percent from the certified value; and (c) affix the date of gas cylinder preparation, certified propane concentration, and recommended maximum shelf life to the cylinder before shipment to the buyer.

7.2.1.1 Cylinder Standards Certification. The manufacturer shall certify the concentration of the calibration gas in the cylinder by (a) directly analyzing the cylinder and (b) calibrating his analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use, as a minimum, a three-point calibration curve.

7.2.1.2 Verification of Manufacturer's Calibration Standards. Before using, the manufacturer shall verify each calibration standard by (a) comparing it to gas mixtures prepared in accordance with the procedure described in section 7.1 of Method 106 of Part 61, Appendix B, or by (b) calibrating it against Standard Reference Materials (SRM's) prepared by the National Bureau of Standards, if such SRM's are available. The agreement between the initially determined concentration value and the verification concentration value must be within ±5 percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

8.0 Sampling Collection, Preservation, Storage, and Transport

8.1 Install a sampling tap to obtain a sample at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to

the atmosphere). Assemble the sampling apparatus as shown in Figure 25E–1.

8.2 Begin sampling by purging the sample lines and cooling coil with at least four volumes of waste. Collect the purged material in a separate container and dispose of it properly.

8.3 After purging, stop the sample flow and transfer the Teflon sampling tube to a sample container. Sample at a flow rate such that the temperature of the waste is <10 °C (<50 °F). Fill the sample container halfway (±5 percent) and cap it within 5 seconds. Store immediately in a cooler and cover with ice.

8.4 Alternative sampling techniques may be used upon the approval of the Administrator.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
10.2, 10.3	FID calibration and response check	Ensure precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Use the procedures in sections 10.2 to calibrate the headspace analyzer and FID and check for linearity before the system is first placed in operation, after any shutdown longer than 6 months, and after any modification of the system.

10.2 Calibration and Linearity. Use the procedures in section 10 of Method 18 of Part 60, Appendix A, to prepare the standards and calibrate the flowmeters, using propane as the standard gas. Fill the calibration standard vials halfway (±5 percent) with deionized water. Purge and fill the airspace with calibration standard. Prepare a minimum of three concentrations of calibration standards in triplicate at concentrations that will bracket the applicable cutoff. For a cutoff of 5.2 kPa (0.75 psi), prepare nominal concentrations of 30,000, 50,000, and 70,000 ppm as propane. For a cutoff of 27.6 kPa (4.0 psi), prepare nominal concentrations of 200,000, 300,000, and 400,000 ppm as propane.

10.2.1 Use the procedures in section 11.3 to measure the FID response of each standard. Use a linear regression analysis to calculate the values for the slope (k) and the y-intercept (b). Use the procedures in sections 12.3 and 12.2 to test the calibration and the linearity.

10.3 Daily FID Calibration Check. Check the calibration at the beginning and at the end of the daily runs by using the following procedures. Prepare 2 calibration standards at the nominal cutoff concentration using the procedures in section 10.2. Place one at the beginning and one at the end of the daily run. Measure the FID response of the daily calibration standard and use the values for k and b from the most recent calibration to calculate the concentration of the daily standard. Use an equation similar to 25E–2 to calculate the percent difference between the daily standard and C_s. If the difference is within 5 percent, then the previous values for k and b can be used. Otherwise, use the procedures in section 10.2 to recalibrate the FID.

11.0 Analytical Procedures

11.1 Allow one hour for the headspace vials to equilibrate at the temperature specified in the regulation. Allow the FID to warm up until a stable baseline is achieved on the detector.

11.2 Check the calibration of the FID daily using the procedures in section 10.3.

11.3 Follow the manufacturer's recommended procedures for the normal operation of the headspace sampler and FID.

11.4 Use the procedures in sections 12.4 and 12.5 to calculate the vapor phase organic vapor pressure in the samples.

11.5 Monitor the output of the detector to make certain that the results are being properly recorded.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

A = Measurement of the area under the response curve, counts.
b = y-intercept of the linear regression line.
C_a = Measured vapor phase organic concentration of sample, ppm as propane.
C_{ma} = Average measured vapor phase organic concentration of standard, ppm as propane.
C_m = Measured vapor phase organic concentration of standard, ppm as propane.
C_s = Calculated standard concentration, ppm as propane.
k = Slope of the linear regression line.
P_{bar} = Atmospheric pressure at analysis conditions, mm Hg (in. Hg).
P* = Organic vapor pressure in the sample, kPa (psi).
PD = Percent difference between the average measured vapor phase organic concentration (C_m) and the calculated standard concentration (C_s).
RSD = Relative standard deviation.
$\beta = 1.333 \times 10^{-7}$ kPa/[(mm Hg)(ppm)], $(4.91 \times 10^{-7}$ psi/[(in. Hg)(ppm)])

12.2 Linearity. Use the following equation to calculate the measured standard concentration for each standard vial.

$$C_m = kA + b \qquad \text{Eq. 25E-1}$$

12.2.1 Calculate the average measured standard concentration (C_{ma}) for each set of triplicate standards and use the following equation to calculate PD between C_{ma} and C_s. The instrument linearity is acceptable if the PD is within five for each standard.

$$PD = \frac{C_s - C_{ma}}{C_s} \times 100 \qquad \text{Eq. 25E-2}$$

12.3. Relative Standard Deviation (RSD). Use the following equation to calculate the RSD for each triplicate set of standards.

$$RSD = \frac{100}{C_{ma}} \sqrt{\frac{\sum (C_m - C_{ma})^2}{2}} \qquad \text{Eq. 25E-3}$$

The calibration is acceptable if the RSD is within five for each standard concentration.

12.4 Concentration of organics in the headspace. Use the following equation to calculate the concentration of vapor phase organics in each sample.

$$C_a = kA + b \qquad \text{Eq. 25E-4}$$

12.5 Vapor Pressure of Organics in the Headspace Sample. Use the following equation to calculate the vapor pressure of organics in the sample.

$$P^* = \beta P_{bar} C_a \qquad \text{Eq. 25E-5}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, Albert E., Samuel Witz, and Robert D. MacPhee. ''Determination of Solvent Vapor Concentrations by Total Combustion Analysis: a Comparison of Infared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, Massachusetts.

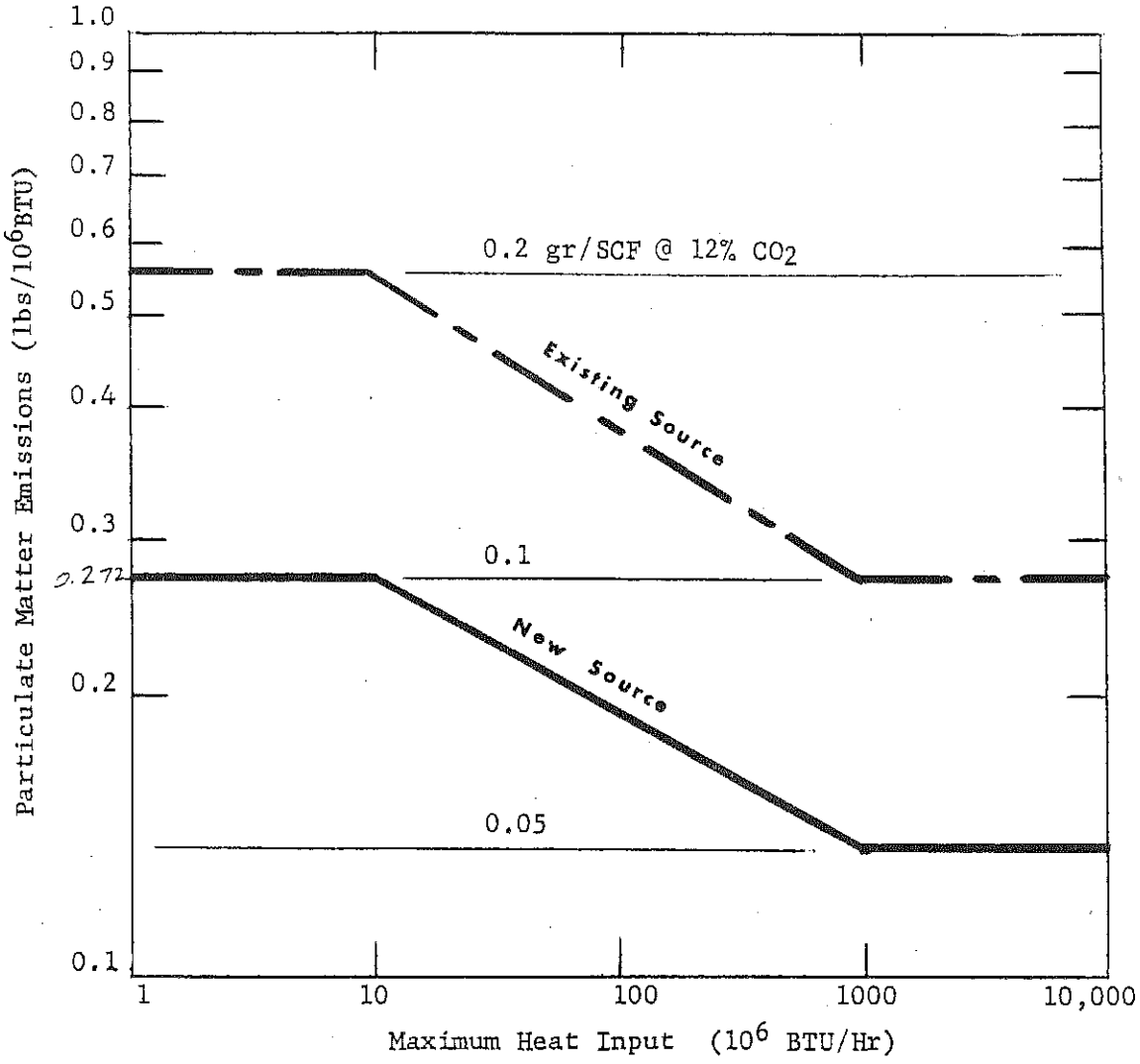
2. Salo, Albert E., William L. Oaks, and Robert D. MacPhee. ''Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, Colorado. June 9–13, 1974.) p. 25.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

State of Oregon Department of Environmental Quality

OAR 340-208-0610
Figure 1
Particulate Matter Emission Standards

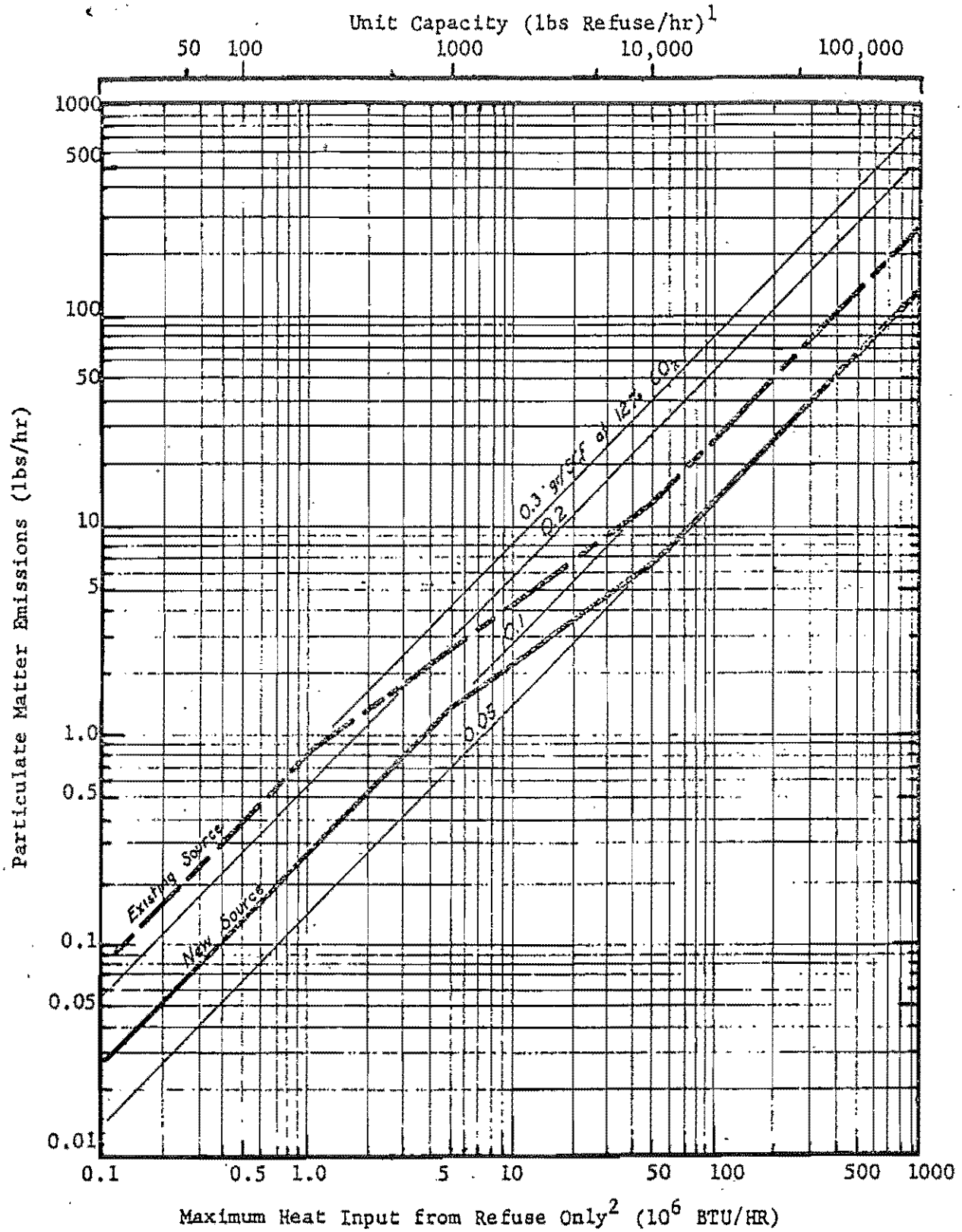
OAR 340-208-0610
Figure 1



PARTICULATE MATTER EMISSION STANDARDS FOR FUEL BURNING EQUIPMENT

Figure 1

PARTICULATE MATTER EMISSION STANDARDS FOR REFUSE BURNING EQUIPMENT



[1] For refuse having heat content of 5000 BTU/lb as fired

[2] Excluding any auxiliary heat

Item E 002095

OAR 340-208-0610
Figure 2

OAR 340-216-8020
Table 2
Air Contaminant Discharge Permits

Part 1. Initial Permitting Application Fees: (in addition to first annual fee)	
Short Term Activity ACDP	$3,600.00
Basic ACDP	$144.00
Assignment to General ACDP [1]	$1,440.00
Simple ACDP	$7,200.00
Construction ACDP	$11,520.00
Standard ACDP	$14,400.00
Standard ACDP (Major NSR or Type A State NSR)	$50,400.00

1. DEQ may waive the assignment fee for an existing source requesting to be assigned to a General ACDP because the source is subject to a newly adopted area source NESHAP as long as the existing source requests assignment within 90 days of notification by DEQ.

Part 2. Annual Fees: (Due date 12/1[1] for 1/1 to 12/31 of the following year)		
Short Term Activity ACDP		$NA
Basic ACDP		$432.00
General ACDP	(A) Fee Class One	$864.00
	(B) Fee Class Two	$1,555.00
	(C) Fee Class Three	$2,246.00
	(D) Fee Class Four	$432.00
	(E) Fee Class Five	$144.00
	(F) Fee Class Six	$288.00
Simple ACDP	(A) Low Fee	$2,304.00
	(B) High Fee	$4,608.00
Standard ACDP		$9,216.00
Greenhouse Gas Reporting, as required by OAR 340, Division 215		12.5% of the applicable annual fee in Part 2

DEQ may extend the payment due date for dry cleaners or gasoline dispensing facilities until March 1st.

Part 3. Cleaner Air Oregon Annual Fees: (Due date 12/1 for 1/1 to 12/31 of the following year)	
Basic ACDP	$106.00

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Table 2
Air Contaminant Discharge Permits

General ACDP	(A) Fee Class One	$213.00
	(B) Fee Class Two	$383.00
	(C) Fee Class Three	$553.00
	(D) Fee Class Four	$106.00
	(E) Fee Class Five	$ 35.00
	(F) Fee Class Six	$ 71.00
Simple ACDP	(A) Low Fee	$568.00
	(B) High Fee	$1,136.00
Standard ACDP		$2,271.00
DEQ may extend the payment due date for dry cleaners or gasoline dispensing facilities until March 1st.		

Part 4. Specific Activity Fees:	
Non-Technical Permit Modification or Air Toxics Permit Attachment Modification [1]	$432.00
Basic Technical Permit Modification or Air Toxics Permit Attachment Modification	$432.00
Simple Technical Permit Modification or Air Toxics Permit Attachment Modification	$1,440.00
Moderate Technical Permit Modification or Air Toxics Permit Attachment Modification	$7,200.00
Complex Technical Permit Modification or Air Toxics Permit Attachment Modification	$14,440.00
Major NSR or Type A State NSR Permit Modification	$50,400.00
Modeling Review (outside Major NSR or Type A State NSR)	$7,200.00
Public Hearing at Source's Request	$2,880.00
State MACT Determination	$7,200.00
Compliance Order Monitoring [2]	$144.00/month
Part 5. Late Fees:	
8-30 days late	5%
31-60 days late	10%
61 or more days late	20%

OAR 340-216-8020
Table 2
Air Contaminant Discharge Permits

1. For gasoline dispensing facilities, a portion of these fees will be used to cover the fees required for changes of ownership in OAR 340-150-0052(4) if DEQ receives both forms at the same time.
2. This is a one-time fee payable when a compliance order is established in a permit or a DEQ order containing a compliance schedule becomes a final order of DEQ and is based on the number of months DEQ will have to oversee the order.

NOTE: See history of this table under OAR 340-216-0020.

OAR 340-216-8030
Table 3
Cleaner Air Oregon Specific Activity Fees

#	ACTIVITY	Permit Type			
		Title V	Standard ACDP	Simple ACDP	General Basic ACDP
1	Existing Source Call-In Fee	$10,000	$10,000	$1,000	$500
2	New Source Consulting Fee	$12,000	$12,000	$1,900	$1,000
3	Reevaluation Fee	$5,000	$5,000	$250	$250
Risk Below Risk Action Levels					
4	Level 1 Risk Assessment - de minimis (no permit attachment required)	$1,500	$1,500	$1,000	$800
5	Level 1 Risk Assessment - permit attachment required	$2,000	$2,000	$1,500	$1,100
6	Level 2 Risk Assessment - de minimis (no permit attachment required)	$2,700	$2,700	$2,000	$1,600
7	Level 2 Risk Assessment - permit attachment required	$3,000	$3,000	$2,200	$1,700
8	Level 3 Risk Assessment - de minimis (no permit attachment required)	$9,000	$8,400	$5,500	$4,700
9	Level 3 Risk Assessment - permit attachment required	$13,300	$10,900	$7,700	$6,800
10	Level 4 Risk Assessment - de minimis (no permit attachment required)	$25,100	$21,500	$13,100	NA
11	Level 4 Risk Assessment - permit attachment required	$31,500	$25,500	$15,800	NA
12	Risk Reduction Plan Application Fee	$47,900	$46,000	$27,300	$27,300
Risk Above Risk Action Levels					
13	Conditional Risk Level Application Fee	$58,900	$58,900	$30,900	$30,900
14	Cleaner Air Oregon Monitoring Plan Application Fee (includes risk assessment)	$59,400	$59,400	NA	NA
16	Director Consultation Fee	$10,000	$10,000	$7,700	$7,700
17	Postponement of Risk Reduction Application Fee	$4,400	$4,400	$2,000	$2,000
Other Fees					
18	Level 2 Modeling review only	$1,300	$1,300	$700	$700
19	Level 3 Modeling review only	$5,300	$5,300	$3,100	$3,100
20	TBACT Analysis (per Toxic Emissions Unit)	$6,000	$6,000	$3,000	$3,000
21	Expedited Permit Attachment Fee	specific activity fee + 20%			

OAR 340-216-8030
Table 3
Cleaner Air Oregon Specific Activity Fees

#	ACTIVITY	Permit Type			
		Title V	Standard ACDP	Simple ACDP	General Basic ACDP
22	DEQ Attendance at New Source Public Meeting (>5 & < 10 in 1 MM)	$2,400	$2,400	$2,400	$2,400
23	Source Test Review Fee (plan and data review)	$5,900	$5,900	$5,900	$5,900

State of Oregon Department of Environmental Quality

OAR 340-220-0150 Attachments

Equations – Determining VOC Emissions Using Material Balance

$VOC_{tot} = VOC_{add} - VOC_{cons}$

Where:

- VOC_{tot} = Total VOC emissions, tons
- VOC_{add} = VOC added to the process, tons
- VOC_{cons} = VOC consumed and/or recovered from the process, tons

APPENDIX A–6 TO PART 60—TEST METHODS 16 THROUGH 18

Method 16—Semicontinuous determination of sulfur emissions from stationary sources
Method 16A—Determination of total reduced sulfur emissions from stationary sources (impinger technique)
Method 16B—Determination of total reduced sulfur emissions from stationary sources
Method 16C—Determination of Total Reduced Sulfur Emissions From Stationary Sources
Method 17—Determination of particulate emissions from stationary sources (in-stack filtration method)
Method 18—Measurement of gaseous organic compound emissions by gas chromatography

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

METHOD 16—SEMICONTINUOUS DETERMINATION OF SULFUR EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of

at least the following additional test methods: Method 1, Method 4, Method 15, and Method 16A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Dimethyl disulfide [$(CH_3)_2S_2$]	62–49–20	50 ppb.
Dimethyl sulfide [$(CH_3)_2S$]	75–18–3	50 ppb.
Hydrogen sulfide [H_2S]	7783–06–4	50 ppb.
Methyl mercaptan [CH_4S]	74–93–1	50 ppb.

1.2 Applicability. This method is applicable for the determination of total reduced sulfur (TRS) compounds from recovery furnaces, lime kilns, and smelt dissolving tanks at kraft pulp mills and fuel gas combustion devices at petroleum refineries.

NOTE: The method described below uses the principle of gas chromatographic (GC) separation and flame photometric detection (FPD). Since there are many systems or sets of operating conditions that represent useable methods of determining sulfur emissions, all systems which employ this principle, but differ only in details of equipment and operation, may be used as alternative methods, provided that the calibration precision and sample line loss criteria are met.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the emission source and an aliquot is analyzed for hydrogen sulfide (H_2S), methyl mercaptan (MeSH), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS) by GC/FPD. These four compounds are known collectively as TRS.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Moisture. Moisture condensation in the sample delivery system, the analytical column, or the FPD burner block can cause losses or interferences. This is prevented by maintaining the probe, filter box, and connections at a temperature of at least 120 °C (248 °F). Moisture is removed in the SO_2 scrubber and heating the sample beyond this point is not necessary when the ambient temperature is above 0 °C (32 °F). Alternatively, moisture may be eliminated by heating the sample line, and by conditioning the sample with dry dilution air to lower its dew point below the operating temperature of the GC/FPD analytical system prior to analysis.

4.2 Carbon Monoxide (CO) and Carbon Dioxide (CO_2). CO and CO_2 have a substantial desensitizing effect on the flame photometric detector even after dilution. Acceptable systems must demonstrate that they have eliminated this interference by some procedure such as eluting these compounds before any of the compounds to be measured. Compliance with this requirement can be demonstrated by submitting chromatograms of calibration gases with and without CO_2 in the diluent gas. The CO_2 level should be approximately 10 percent for the case with CO_2 present. The two chromatograms should show agreement within the precision limits of section 10.2.

4.3 Particulate Matter. Particulate matter in gas samples can cause interference by eventual clogging of the analytical system. This interference is eliminated by using the Teflon filter after the probe.

4.4 Sulfur Dioxide (SO_2). Sulfur dioxide is not a specific interferant but may be present in such large amounts that it cannot effectively be separated from the other compounds of interest. The SO_2 scrubber described in section 6.1.3 will effectively remove SO_2 from the sample.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hydrogen Sulfide. A flammable, poisonous gas with the odor of rotten eggs. H_2S is extremely hazardous and can cause collapse, coma, and death within a few seconds of one or two inhalations at sufficient concentrations. Low concentrations irritate the mucous membranes and may cause nausea, dizziness, and headache after exposure.

6.0 Equipment and Supplies

6.1. Sample Collection. The following items are needed for sample collection.

6.1.1 Probe. Teflon or Teflon-lined stainless steel. The probe must be heated to prevent moisture condensation. It must be designed to allow calibration gas to enter the probe at or near the sample point entry. Any portion of the probe that contacts the stack gas

must be heated to prevent moisture condensation. Figure 16–1 illustrates the probe used in lime kilns and other sources where significant amounts of particulate matter are present. The probe is designed with the deflector shield placed between the sample and the gas inlet holes to reduce clogging of the filter and possible adsorption of sample gas. As an alternative, the probe described in section 6.1.1 of Method 16A having a nozzle directed away from the gas stream may be used at sources having significant amounts of particulate matter.

6.1.2 Particulate Filter. 50–mm Teflon filter holder and a 1- to 2-micron porosity Teflon filter (available through Savillex Corporation, 5325 Highway 101, Minnetonka, Minnesota 55343). The filter holder must be maintained in a hot box at a temperature of at least 120 °C (248 °F).

6.1.3 SO_2 Scrubber. Three 300-ml Teflon segmented impingers connected in series with flexible, thick-walled, Teflon tubing. (Impinger parts and tubing available through Savillex.) The first two impingers contain 100 ml of citrate buffer and the third impinger is initially dry. The tip of the tube inserted into the solution should be constricted to less than 3 mm (⅛ in.) ID and should be immersed to a depth of at least 5 cm (2 in.). Immerse the impingers in an ice water bath and maintain near 0 °C (32 °F). The scrubber solution will normally last for a 3-hour run before needing replacement. This will depend upon the effects of moisture and particulate matter on the solution strength and pH. Connections between the probe, particulate filter, and SO_2 scrubber must be made of Teflon and as short in length as possible. All portions of the probe, particulate filter, and connections prior to the SO_2 scrubber (or alternative point of moisture removal) must be maintained at a temperature of at least 120 °C (248 °F).

6.1.4 Sample Line. Teflon, no greater than 1.3 cm (½ in.) ID. Alternative materials, such as virgin Nylon, may be used provided the line loss test is acceptable.

6.1.5 Sample Pump. The sample pump must be a leakless Teflon-coated diaphragm type or equivalent.

6.2 Analysis. The following items are needed for sample analysis:

6.2.1 Dilution System. Needed only for high sample concentrations. The dilution system must be constructed such that all sample contacts are made of Teflon, glass, or stainless steel.

6.2.2 Gas Chromatograph. The gas chromatograph must have at least the following components:

6.2.2.1 Oven. Capable of maintaining the separation column at the proper operating temperature ±1 °C (2 °F).

6.2.2.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperature ±1 °C (2 °F).

6.2.2.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

6.2.2.4 Flame Photometric Detector.

6.2.2.4.1 Electrometer. Capable of full scale amplification of linear ranges of 10^{-9} to 10^{-4} amperes full scale.

6.2.2.4.2 Power Supply. Capable of delivering up to 750 volts.

6.2.2.4.3 Recorder. Compatible with the output voltage range of the electrometer.

6.2.2.4.4 Rotary Gas Valves. Multiport Teflon-lined valves equipped with sample loop. Sample loop volumes must be chosen to provide the needed analytical range. Teflon tubing and fittings must be used throughout to present an inert surface for sample gas. The gas chromatograph must be calibrated with the sample loop used for sample analysis.

6.2.3 Gas Chromatogram Columns. The column system must be demonstrated to be capable of resolving the four major reduced sulfur compounds: H_2S, MeSH, DMS, and DMDS. It must also demonstrate freedom from known interferences. To demonstrate that adequate resolution has been achieved, submit a chromatogram of a calibration gas containing all four of the TRS compounds in the concentration range of the applicable standard. Adequate resolution will be defined as base line separation of adjacent peaks when the amplifier attenuation is set so that the smaller peak is at least 50 percent of full scale. Baseline separation is defined as a return to zero ±5 percent in the interval between peaks. Systems not meeting this criteria may be considered alternate methods subject to the approval of the Administrator.

6.3 Calibration. A calibration system, containing the following components, is required (see Figure 16–2).

6.3.1 Tube Chamber. Chamber of glass or Teflon of sufficient dimensions to house permeation tubes.

6.3.2 Flow System. To measure air flow over permeation tubes at ±2 percent. Flow over the permeation device may also be determined using a soap bubble flowmeter.

6.3.3 Constant Temperature Bath. Device capable of maintaining the permeation tubes at the calibration temperature within 0.1 °C (0.2 °F).

6.3.4 Temperature Gauge. Thermometer or equivalent to monitor bath temperature within 1 °C (2 °F).

7.0 Reagents and Standards

7.1 Fuel. Hydrogen (H_2), prepurified grade or better.

7.2 Combustion Gas. Oxygen (O_2) or air, research purity or better.

7.3 Carrier Gas. Prepurified grade or better.

7.4 Diluent (if required). Air containing less than 50 ppb total sulfur compounds and less than 10 ppmv each of moisture and total hydrocarbons.

7.5 Calibration Gases

7.5.1 Permeation tubes, one each of H_2S, MeSH, DMS, and DMDS, gravimetrically calibrated and certified at some convenient operating temperature. These tubes consist of hermetically sealed FEP Teflon tubing in which a liquified gaseous substance is enclosed. The enclosed gas permeates through the tubing wall at a constant rate. When the temperature is constant, calibration gases covering a wide range of known concentrations can be generated by varying and accurately measuring the flow rate of diluent gas passing over the tubes. These calibration gases are used to calibrate the GC/FPD system and the dilution system.

7.5.2 Cylinder Gases. Cylinder gases may be used as alternatives to permeation devices. The gases must be traceable to a primary standard (such as permeation tubes) and not used beyond the certification expiration date.

7.6 Citrate Buffer and Sample Line Loss Gas. Same as Method 15, sections 7.6 and 7.7.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as Method 15, section 8.0, except that the references to the dilution system may not be applicable.

9.0 Quality Control

Section	Quality control measure	Effect
8.0	Sample line loss check	Ensures that uncorrected negative bias introduced by sample loss is no greater than 20 percent, and provides for correction of bias of 20 percent or less.
8.0	Calibration drift test	Ensures that bias introduced by drift in the measurement system output during the run is no greater than 5 percent.
10.0	Analytical calibration	Ensures precision of analytical results within 5 percent.

10.0 Calibration and Standardization

Same as Method 15, section 10.0, with the following addition and exceptions:

10.1 Use the four compounds that comprise TRS instead of the three reduced sulfur compounds measured by Method 15.

10.2 Flow Meter. Calibration before each test run is recommended, but not required; calibration following each test series is mandatory. Calibrate each flow meter after each complete test series with a wet-test meter. If the flow measuring device differs from the wet-test meter by 5 percent or more, the completed test runs must be voided. Alternatively, the flow data that yield the lower flow measurement may be used. Flow over the permeation device may also be determined using a soap bubble flowmeter.

11.0 Analytical Procedure

Sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Data Analysis and Calculations

12.1 Concentration of Reduced Sulfur Compounds. Calculate the average concentration of each of the four analytes (*i.e.*, DMDS, DMS, H_2S, and MeSH) over the sample run (specified in section 8.2 of Method 15 as 16 injections).

$$C = \frac{\sum_{i=1}^{N} S_i}{N} \qquad \text{Eq. 16-1}$$

Where:

S_i = Concentration of any reduced sulfur compound from the i^{th} sample injection, ppm.

C = Average concentration of any one of the reduced sulfur compounds for the entire run, ppm.

N = Number of injections in any run period.

12.2 TRS Concentration. Using Equation 16–2, calculate the TRS concentration for each sample run.

$$C_{TRS} = d\sum\left(C_{H_2S} + C_{MeSH} + C_{DMS} + 2C_{DMDS}\right) \qquad \text{Eq. 16-2}$$

Where:

C_{TRS} = TRS concentration, ppmv.

C_{H2S} = Hydrogen sulfide concentration, ppmv.

C_{MeSH} = Methyl mercaptan concentration, ppmv.

C_{DMS} = Dimethyl sulfide concentration, ppmv.

C_{DMDS} = Dimethyl disulfide concentration, ppmv.

d = Dilution factor, dimensionless.

12.3 Average TRS Concentration. Calculate the average TRS concentration for all sample runs performed.

$$\text{Average TRS} = \frac{\sum_{i=1}^{n} TRS_i}{N(1 - B_{wo})} \qquad \text{Eq. 16-3}$$

Where:

Average TRS = Average total reduced sulfur in ppm.

TRS_i = Total reduced sulfur in ppm as determined by Equation 16–2.

N = Number of samples.

B_{wo} = Fraction of volume of water vapor in the gas stream as determined by Method 4—Determination of Moisture in Stack Gases.

13.0 Method Performance

13.1 Analytical Range. The analytical range will vary with the sample loop size. Typically, the analytical range may extend from 0.1 to 100 ppmv using 10- to 0.1-ml sample loop sizes. This eliminates the need for sample dilution in most cases.

13.2 Sensitivity. Using the 10-ml sample size, the minimum detectable concentration is approximately 50 ppb.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. O'Keeffe, A.E., and G.C. Ortman. ''Primary Standards for Trace Gas Analysis.'' Analytical Chemical Journal, 38,76. 1966.

2. Stevens, R.K., A.E. O'Keeffe, and G.C. Ortman. ''Absolute Calibration of a Flame Photometric Detector to Volatile Sulfur Compounds at Sub-Part-Per-Million Levels.'' Environmental Science and Technology, 3:7. July 1969.

3. Mulik, J.D., R.K. Stevens, and R. Baumgardner. ''An Analytical System Designed to Measure Multiple Malodorous Compounds Related to Kraft Mill Activities.'' Presented at the 12th Conference on Methods in Air Pollution and Industrial Hygiene Studies, University of Southern California, Los Angeles, CA. April 6–8, 1971.

4. Devonald, R.H., R.S. Serenius, and A.D. McIntyre. ''Evaluation of the Flame Photometric Detector for Analysis of Sulfur Compounds.'' Pulp and Paper Magazine of Canada, 73,3. March 1972.

5. Grimley, K.W., W.S. Smith, and R.M. Martin. ''The Use of a Dynamic Dilution System in the Conditioning of Stack Gases for Automated Analysis by a Mobile Sampling Van.'' Presented at the 63rd Annual APCA Meeting, St. Louis, MO. June 14–19, 1970.

6. General Reference. Standard Methods of Chemical Analysis, Volumes III-A and III-B Instrumental Methods. Sixth Edition. Van Nostrand Reinhold Co.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

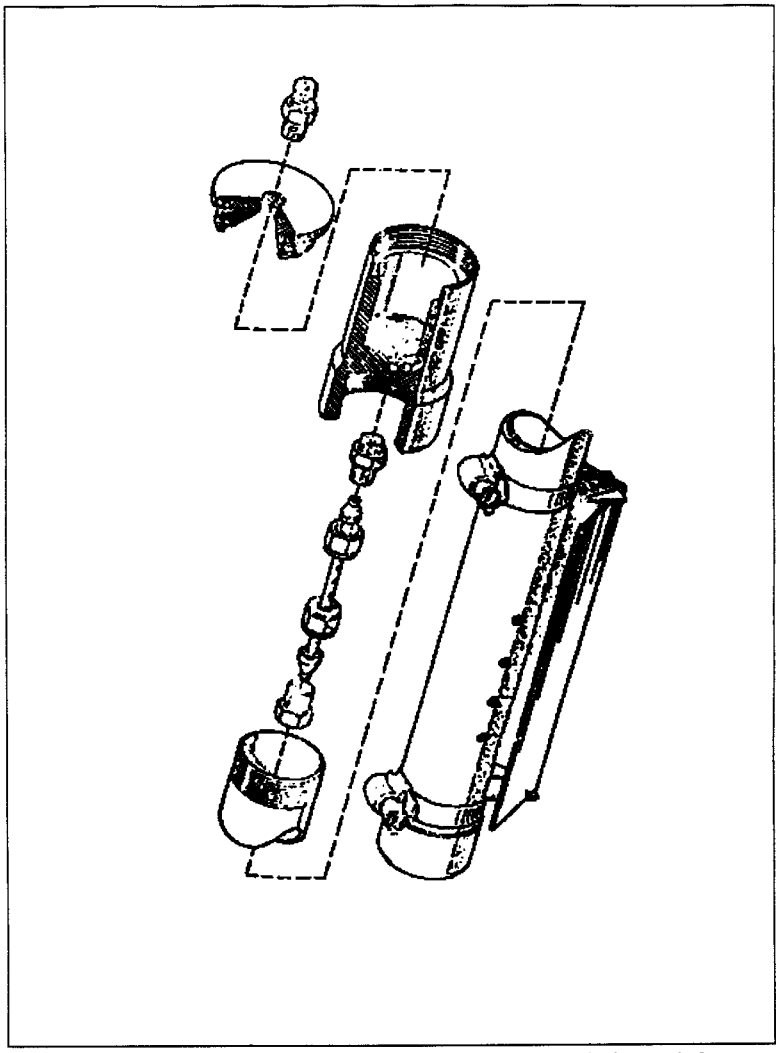

Figure 16-1. Probe used for Sample Gas Containing High Particulate Matter Loading.

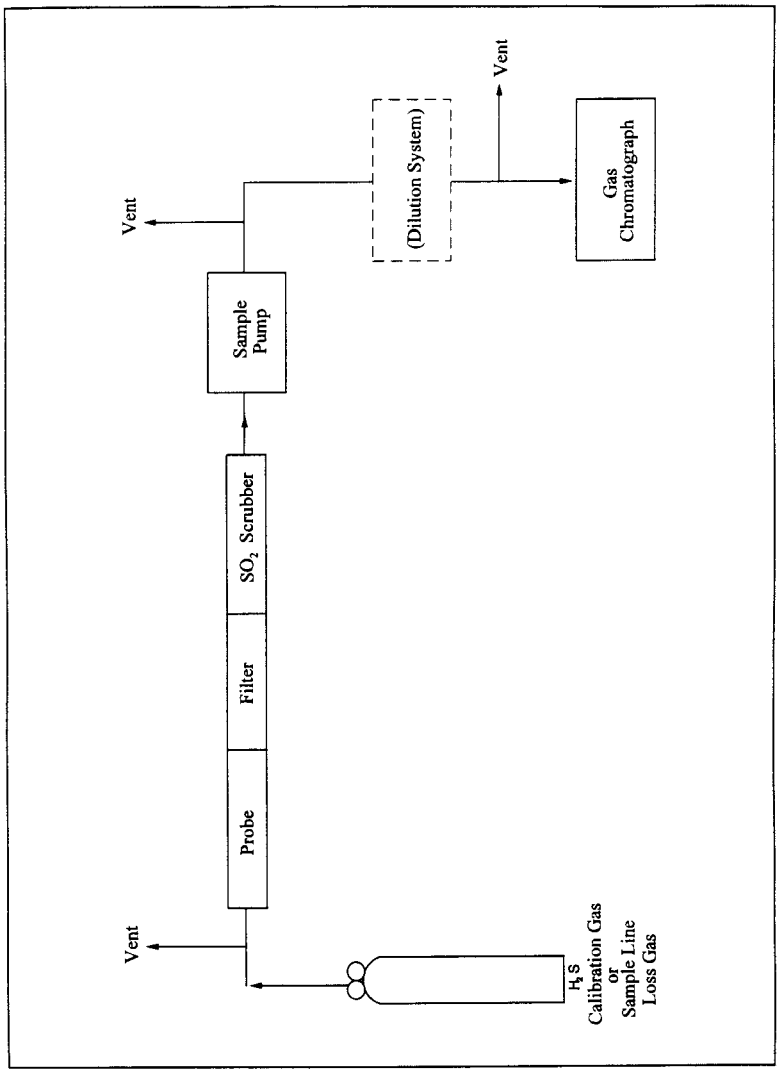

Figure 16-2. Calibration System.

METHOD 16A—DETERMINATION OF TOTAL REDUCED SULFUR EMISSIONS FROM STATIONARY SOURCES (IMPINGER TECHNIQUE)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 6, and Method 16.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total reduced sulfur (TRS) including:	N/A	See section 13.1.
Dimethyl disulfide [$(CH_3)_2S_2$]	62–49–20	
Dimethyl sulfide [$(CH_3)_2S$]	75–18–3	
Hydrogen sulfide [H_2S]	7783–06–4	
Methyl mercaptan [CH_4S]	74–93–1	
Reduced sulfur (RS) including:	N/A	
H_2S	7783–06–4	
Carbonyl sulfide [COS]	463–58–1	
Carbon disulfide [CS_2]	75–15–0	
Reported as: Sulfur dioxide (SO_2)	7449–09–5	

1.2 Applicability. This method is applicable for the determination of TRS emissions from recovery boilers, lime kilns, and smelt dissolving tanks at kraft pulp mills, reduced sulfur compounds (H_2S, carbonyl sulfide, and carbon disulfide) from sulfur recovery units at onshore natural gas processing facilities, and from other sources when specified in an applicable subpart of the regulations. The flue gas must contain at least 1 percent oxygen for complete oxidation of all TRS to SO_2. Note: If sources other than kraft pulp mills experience low oxygen levels in the emissions, the method results may be biased low.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 An integrated gas sample is extracted from the stack. SO_2 is removed selectively from the sample using a citrate buffer solution. TRS compounds are then thermally oxidized to SO_2, collected in hydrogen peroxide as sulfate, and analyzed by the Method 6 barium-thorin titration procedure.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Reduced sulfur compounds other than those regulated by the emission standards, if present, may be measured by this method. Therefore, carbonyl sulfide, which is partially oxidized to SO_2 and may be present in a lime kiln exit stack, would be a positive interferant.

4.2 Particulate matter from the lime kiln stack gas (primarily calcium carbonate) can cause a negative bias if it is allowed to enter the citrate scrubber; the particulate matter will cause the pH to rise and H_2S to be absorbed prior to oxidation. Furthermore, if the calcium carbonate enters the hydrogen peroxide impingers, the calcium will precipitate sulfate ion. Proper use of the particulate filter described in section 6.1.3 will eliminate this interference.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m^3 will cause lung damage in uninitiated. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

5.3 Hydrogen Sulfide (H_2S). A flammable, poisonous gas with the odor of rotten eggs. H_2S is extremely hazardous and can cause collapse, coma, and death within a few seconds of one or two inhalations at sufficient concentrations. Low concentrations irritate the mucous membranes and may cause nausea, dizziness, and headache after exposure.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling train is shown in Figure 16A–1 and component parts are discussed below. Modifications to this sampling train are acceptable provided the system performance check is met (see section 8.5).

6.1.1 Probe. Teflon tubing, 6.4-mm (¼-in.) diameter, sequentially wrapped with heat-resistant fiber strips, a rubberized heat tape

(plug at one end), and heat-resistant adhesive tape. A flexible thermocouple or other suitable temperature measuring device should be placed between the Teflon tubing and the fiber strips so that the temperature can be monitored to prevent softening of the probe. The probe should be sheathed in stainless steel to provide in-stack rigidity. A series of bored-out stainless steel fittings placed at the front of the sheath will prevent moisture and particulate from entering between the probe and sheath. A 6.4-mm (¼-in.) Teflon elbow (bored out) should be attached to the inlet of the probe, and a 2.54 cm (1 in.) piece of Teflon tubing should be attached at the open end of the elbow to permit the opening of the probe to be turned away from the particulate stream; this will reduce the amount of particulate drawn into the sampling train. The probe is depicted in Figure 16A–2.

6.1.2 Probe Brush. Nylon bristle brush with handle inserted into a 3.2-mm (⅛-in.) Teflon tubing. The Teflon tubing should be long enough to pass the brush through the length of the probe.

6.1.3 Particulate Filter. 50-mm Teflon filter holder and a 1- to 2-μm porosity, Teflon filter (available through Savillex Corporation, 5325 Highway 101, Minnetonka, Minnesota 55343). The filter holder must be maintained in a hot box at a temperature sufficient to prevent moisture condensation. A temperature of 121 °C (250 °F) was found to be sufficient when testing a lime kiln under sub-freezing ambient conditions.

6.1.4 SO_2 Scrubber. Three 300-ml Teflon segmented impingers connected in series with flexible, thick-walled, Teflon tubing. (Impinger parts and tubing available through Savillex.) The first two impingers contain 100 ml of citrate buffer and the third impinger is initially dry. The tip of the tube inserted into the solution should be constricted to less than 3 mm (⅛-in.) ID and should be immersed to a depth of at least 5 cm (2 in.).

6.1.5 Combustion Tube. Quartz glass tubing with an expanded combustion chamber 2.54 cm (1 in.) in diameter and at least 30.5 cm (12 in.) long. The tube ends should have an outside diameter of 0.6 cm (¼ in.) and be at least 15.3 cm (6 in.) long. This length is necessary to maintain the quartz-glass connector near ambient temperature and thereby avoid leaks. Alternatively, the outlet may be constructed with a 90-degree glass elbow and socket that would fit directly onto the inlet of the first peroxide impinger.

6.1.6 Furnace. A furnace of sufficient size to enclose the combustion chamber of the combustion tube with a temperature regulator capable of maintaining the temperature at 800 ±100 °C (1472 ±180 °F). The furnace operating temperature should be checked with a thermocouple to ensure accuracy.

6.1.7 Peroxide Impingers, Stopcock Grease, Temperature Sensor, Drying Tube, Valve, Pump, and Barometer. Same as Method 6, sections 6.1.1.2, 6.1.1.4, 6.1.1.5, 6.1.1.6, 6.1.1.7, 6.1.1.8, and 6.1.2, respectively, except that the midget bubbler of Method 6, section 6.1.1.2 is not required.

6.1.8 Vacuum Gauge. At least 760 mm Hg (30 in. Hg) gauge.

6.1.9 Rate Meter. Rotameter, or equivalent, accurate to within 5 percent at the selected flow rate of approximately 2 liters/min (4.2 ft^3/hr).

6.1.10 Volume Meter. Dry gas meter capable of measuring the sample volume under the sampling conditions of 2 liters/min (4.2 ft^3/hr) with an accuracy of 2 percent.

6.2 Sample Recovery. Polyethylene Bottles, 250-ml (one per sample).

6.3 Sample Preparation and Analysis. Same as Method 6, section 6.3, except a 10-ml buret with 0.05-ml graduations is required, and the spectrophotometer is not needed.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. When such specifications are not available, the best available grade must be used.

7.1 Sample Collection. The following reagents are required for sample analysis:

7.1.1 Water. Same as in Method 6, section 7.1.1.

7.1.2 Citrate Buffer. Dissolve 300 g of potassium citrate (or 284 g of sodium citrate) and 41 g of anhydrous citric acid in 1 liter of water (200 ml is needed per test). Adjust the pH to between 5.4 and 5.6 with potassium citrate or citric acid, as required.

7.1.3 Hydrogen Peroxide, 3 percent. Same as in Method 6, section 7.1.3 (40 ml is needed per sample).

7.1.4 Recovery Check Gas. Hydrogen sulfide (100 ppmv or less) in nitrogen, stored in aluminum cylinders. Verify the concentration by Method 11 or by gas chromatography where the instrument is calibrated with an H_2S permeation tube as described below. For Method 11, the relative standard deviation should not exceed 5 percent on at least three 20-minute runs.

NOTE: Alternatively, hydrogen sulfide recovery gas generated from a permeation device gravimetrically calibrated and certified at some convenient operating temperature may be used. The permeation rate of the device must be such that at a dilution gas flow rate of 3 liters/min (6.4 ft^3/hr), an H_2S concentration in the range of the stack gas or within 20 percent of the standard can be generated.

7.1.5 Combustion Gas. Gas containing less than 50 ppb reduced sulfur compounds and less than 10 ppmv total hydrocarbons. The

gas may be generated from a clean-air system that purifies ambient air and consists of the following components: Diaphragm pump, silica gel drying tube, activated charcoal tube, and flow rate measuring device. Flow from a compressed air cylinder is also acceptable.

7.2 Sample Recovery and Analysis. Same as Method 6, sections 7.2.1 and 7.3, respectively.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Preparation of Sampling Train.

8.1.1 For the SO_2 scrubber, measure 100 ml of citrate buffer into the first and second impingers; leave the third impinger empty. Immerse the impingers in an ice bath, and locate them as close as possible to the filter heat box. The connecting tubing should be free of loops. Maintain the probe and filter temperatures sufficiently high to prevent moisture condensation, and monitor with a suitable temperature sensor.

8.1.2 For the Method 6 part of the train, measure 20 ml of 3 percent hydrogen peroxide into the first and second midget impingers. Leave the third midget impinger empty, and place silica gel in the fourth midget impinger. Alternatively, a silica gel drying tube may be used in place of the fourth impinger. Maintain the oxidation furnace at 800 ±100 °C (1472 ±180 °F). Place crushed ice and water around all impingers.

8.2 Citrate Scrubber Conditioning Procedure. Condition the citrate buffer scrubbing solution by pulling stack gas through the Teflon impingers and bypassing all other sampling train components. A purge rate of 2 liters/min for 10 minutes has been found to be sufficient to obtain equilibrium. After the citrate scrubber has been conditioned, assemble the sampling train, and conduct (optional) a leak-check as described in Method 6, section 8.2.

8.3 Sample Collection. Same as in Method 6, section 8.3, except the sampling rate is 2 liters/min (±10 percent) for 1 or 3 hours. After the sample is collected, remove the probe from the stack, and conduct (mandatory) a post-test leak-check as described in Method 6, section 8.2. The 15-minute purge of the train following collection should not be performed. After each 3-hour test run (or after three 1-hour samples), conduct one system performance check (see section 8.5) to determine the reduced sulfur recovery efficiency through the sampling train. After this system performance check and before the next test run, rinse and brush the probe with water, replace the filter, and change the citrate scrubber (optional but recommended).

NOTE: In Method 16, a test run is composed of 16 individual analyses (injects) performed over a period of not less than 3 hours or more than 6 hours. For Method 16A to be consistent with Method 16, the following may be used to obtain a test run: (1) collect three 60-minute samples or (2) collect one 3-hour sample. (Three test runs constitute a test.)

8.4 Sample Recovery. Disconnect the impingers. Quantitatively transfer the contents of the midget impingers of the Method 6 part of the train into a leak-free polyethylene bottle for shipment. Rinse the three midget impingers and the connecting tubes with water and add the washings to the same storage container. Mark the fluid level. Seal and identify the sample container.

8.5 System Performance Check.

8.5.1 A system performance check is done (1) to validate the sampling train components and procedure (prior to testing; optional) and (2) to validate a test run (after a run). Perform a check in the field prior to testing consisting of at least two samples (optional), and perform an additional check after each 3 hour run or after three 1-hour samples (mandatory).

8.5.2 The checks involve sampling a known concentration of H_2S and comparing the analyzed concentration with the known concentration. Mix the H_2S recovery check gas (Section 7.1.4) and combustion gas in a dilution system such as that shown in Figure 16A–3. Adjust the flow rates to generate an H_2S concentration in the range of the stack gas or within 20 percent of the applicable standard and an oxygen concentration greater than 1 percent at a total flow rate of at least 2.5 liters/min (5.3 ft^3/hr). Use Equation 16A–3 to calculate the concentration of recovery gas generated. Calibrate the flow rate from both sources with a soap bubble flow meter so that the diluted concentration of H_2S can be accurately calculated.

8.5.3 Collect 30-minute samples, and analyze in the same manner as the emission samples. Collect the sample through the probe of the sampling train using a manifold or some other suitable device that will ensure extraction of a representative sample.

8.5.4 The recovery check must be performed in the field prior to replacing the SO_2 scrubber and particulate filter and before the probe is cleaned. Use Equation 16A–4 (see section 12.5) to calculate the recovery efficiency. Report the recovery efficiency with the emission data; do not correct the emission data for the recovery efficiency. A sample recovery of 100 ±20 percent must be obtained for the emission data to be valid. However, if the recovery efficiency is not in the 100 ±20 percent range but the results do not affect the compliance or noncompliance status of the affected facility, the Administrator may decide to accept the results of the compliance test.

9.0 Quality Control

Section	Quality control measure	Effect
8.5	System performance check	Ensure validity of sampling train components and analytical procedure.
8.2, 10.0	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.
10.0	Barium standard solution standardization	Ensure precision of normality determination.
11.1	Replicate titrations	Ensure precision of titration determinations.

10.0 Calibration

Same as Method 6, section 10.0.

11.0 Analytical Procedure

11.1 Sample Loss Check and Sample Analysis. Same as Method 6, sections 11.1 and 11.2, respectively, with the following exception: for 1-hour sampling, take a 40-ml aliquot, add 160 ml of 100 percent isopropanol and four drops of thorin.

12.0 Data Analysis and Calculations

In the calculations, at least one extra decimal figure should be retained beyond that of the acquired data. Figures should be rounded off after final calculations.

12.1 Nomenclature.

C_{TRS} = Concentration of TRS as SO_2, dry basis corrected to standard conditions, ppmv.

$C_{RG(act)}$ = Actual concentration of recovery check gas (after dilution), ppm.

$C_{RG(m)}$ = Measured concentration of recovery check gas generated, ppm.

C_{H2S} = Verified concentration of H_2S recovery gas.

N = Normality of barium perchlorate titrant, milliequivalents/ml.

P_{bar} = Barometric pressure at exit orifice of the dry gas meter, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

Q_{H2S} = Calibrated flow rate of H_2S recovery gas, liters/min.

Q_{CG} = Calibrated flow rate of combustion gas, liters/min.

R = Recovery efficiency for the system performance check, percent.

T_m = Average dry gas meter absolute temperature, °K (°R).

T_{std} = Standard absolute temperature, 293 °K (528 °R).

V_a = Volume of sample aliquot titrated, ml.

V_m = Dry gas volume as measured by the dry gas meter, liters (dcf).

$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, liters (dscf).

V_{soln} = Total volume of solution in which the sulfur dioxide sample is contained, 100 ml.

V_t = Volume of barium perchlorate titrant used for the sample, ml (average of replicate titrations).

V_{tb} = Volume of barium perchlorate titrant used for the blank, ml.

Y = Dry gas meter calibration factor.

32.03 = Equivalent weight of sulfur dioxide, mg/meq.

12.2 Dry Sample Gas Volume, Corrected to Standard Conditions.

$$V_{m(std)} = V_m Y \frac{T_{std} P_{bar}}{T_m P_{std}} \qquad \text{Eq. 16A-1}$$

$$= K_1 Y \frac{V_m P_{bar}}{T_m}$$

Where:

K_1 = 0.3855 °K/mm Hg for metric units,
= 17.65 °R/in. Hg for English units.

12.3 Concentration of TRS as ppm SO_2.

$$C_{TRS} = K_2 N \frac{(V_t - V_{tb})(V_{soln}/V_a)}{V_{m(std)}} \qquad \text{Eq. 16A-2}$$

Where:

$$K_2 = 32.03 \frac{mg}{meq} \frac{24.05 L}{mole} \frac{1 mole}{64.06 g} \frac{1 g}{10^3 mg} \frac{10^3 mL}{L} \frac{10^3 \mu L}{lmL}$$
$$= \frac{12025 \mu L}{meq}$$

12.4 Concentration of Recovery Gas Generated in the System Performance Check.

$$C_{RG} = \frac{Q_{H_2S} C_{H_2S}}{Q_{H_2S} + Q_{CG}} \qquad \text{Eq. 16A-3}$$

12.5 Recovery Efficiency for the System Performance Check.

$$R = \frac{C_{RG(m)}}{C_{RG(act)}} \times 100 \qquad \text{Eq. 16A-4}$$

13.0 Method Performance

13.1 Analytical Range. The lower detectable limit is 0.1 ppmv SO_2 when sampling at 2 liters/min (4.2 ft^3/hr) for 3 hours or 0.3 ppmv when sampling at 2 liters/min (4.2 ft^3/hr) for 1 hour. The upper concentration limit of the method exceeds the TRS levels generally encountered at kraft pulp mills.

13.2 Precision. Relative standard deviations of 2.0 and 2.6 percent were obtained when sampling a recovery boiler for 1 and 3 hours, respectively.

13.3 Bias.

13.3.1 No bias was found in Method 16A relative to Method 16 in a separate study at a recovery boiler.

13.3.2 Comparison of Method 16A with Method 16 at a lime kiln indicated that there was no bias in Method 16A. However, instability of the source emissions adversely affected the comparison. The precision of Method 16A at the lime kiln was similar to that obtained at the recovery boiler (Section 13.2.1).

13.3.3 Relative standard deviations of 2.7 and 7.7 percent have been obtained for system performance checks.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

As an alternative to the procedures specified in section 7.1.4, the following procedure may be used to verify the H_2S concentration of the recovery check gas.

16.1 Summary. The H_2S is collected from the calibration gas cylinder and is absorbed in zinc acetate solution to form zinc sulfide. The latter compound is then measured iodometrically.

16.2 Range. The procedure has been examined in the range of 5 to 1500 ppmv.

16.3 Interferences. There are no known interferences to this procedure when used to analyze cylinder gases containing H_2S in nitrogen.

16.4 Precision and Bias. Laboratory tests have shown a relative standard deviation of less than 3 percent. The procedure showed no bias when compared to a gas chromatographic method that used gravimetrically certified permeation tubes for calibration.

16.5 Equipment and Supplies.

16.5.1 Sampling Apparatus. The sampling train is shown in Figure 16A–4. Its component parts are discussed in sections 16.5.1.1 through 16.5.2.

16.5.1.1 Sampling Line. Teflon tubing (¼-in.) to connect the cylinder regulator to the sampling valve.

16.5.1.2 Needle Valve. Stainless steel or Teflon needle valve to control the flow rate of gases to the impingers.

16.5.1.3 Impingers. Three impingers of approximately 100-ml capacity, constructed to permit the addition of reagents through the gas inlet stem. The impingers shall be connected in series with leak-free glass or Teflon connectors. The impinger bottoms have a standard 24/25 ground-glass fitting. The stems are from standard 6.4-mm (¼-in.) ball joint midget impingers, custom lengthened by about 1 in. When fitted together, the stem end should be approximately 1.27 cm (½ in.) from the bottom (Southern Scientific, Inc., Micanopy, Florida: Set Number S6962–048). The third in-line impinger acts as a drop-out bottle.

16.5.1.4 Drying Tube, Rate Meter, and Barometer. Same as Method 11, sections 6.1.5, 6.1.8, and 6.1.10, respectively.

16.5.1.5 Cylinder Gas Regulator. Stainless steel, to reduce the pressure of the gas stream entering the Teflon sampling line to a safe level.

16.5.1.6 Soap Bubble Meter. Calibrated for 100 and 500 ml, or two separate bubble meters.

16.5.1.7 Critical Orifice. For volume and rate measurements. The critical orifice may be fabricated according to section 16.7.3 and must be calibrated as specified in section 16.12.4.

16.5.1.8 Graduated Cylinder. 50-ml size.

16.5.1.9 Volumetric Flask. 1-liter size.

16.5.1.10 Volumetric Pipette. 15-ml size.

16.5.1.11 Vacuum Gauge. Minimum 20 in. Hg capacity.

16.5.1.12 Stopwatch.

16.5.2 Sample Recovery and Analysis.

16.5.2.1 Erlenmeyer Flasks. 125- and 250-ml sizes.

16.5.2.2 Pipettes. 2-, 10-, 20-, and 100-ml volumetric.

16.5.2.3 Burette. 50-ml size.

16.5.2.4 Volumetric Flask. 1-liter size.

16.5.2.5 Graduated Cylinder. 50-ml size.

16.5.2.6 Wash Bottle.

16.5.2.7 Stirring Plate and Bars.

16.6 Reagents and Standards. Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

16.6.1 Water. Same as Method 11, section 7.1.3.

16.6.2 Zinc Acetate Absorbing Solution. Dissolve 20 g zinc acetate in water, and dilute to 1 liter.

16.6.3 Potassium Bi-iodate [$KH(IO_3)_2$] Solution, Standard 0.100 N. Dissolve 3.249 g anhydrous $KH(IO_3)_2$ in water, and dilute to 1 liter.

16.6.4 Sodium Thiosulfate ($Na_2S_2O_3$) Solution, Standard 0.1 N. Same as Method 11, section 7.3.2. Standardize according to section 16.12.2.

16.6.5 $Na_2S_2O_3$ Solution, Standard 0.01 N. Pipette 100.0 ml of 0.1 N $Na_2S_2O_3$ solution into a 1-liter volumetric flask, and dilute to the mark with water.

16.6.6 Iodine Solution, 0.1 N. Same as Method 11, section 7.2.3.

16.6.7 Standard Iodine Solution, 0.01 N. Same as in Method 11, section 7.2.4. Standardize according to section 16.12.3.

16.6.8 Hydrochloric Acid (HCl) Solution, 10 Percent by Weight. Add 230 ml concentrated HCl (specific gravity 1.19) to 770 ml water.

16.6.9 Starch Indicator Solution. To 5 g starch (potato, arrowroot, or soluble), add a little cold water, and grind in a mortar to a thin paste. Pour into 1 liter of boiling water, stir, and let settle overnight. Use the clear supernatant. Preserve with 1.25 g salicylic acid, 4 g zinc chloride, or a combination of 4 g sodium propionate and 2 g sodium azide per liter of starch solution. Some commercial starch substitutes are satisfactory.

16.7 Pre-test Procedures.

16.7.1 Selection of Gas Sample Volumes. This procedure has been validated for estimating the volume of cylinder gas sample needed when the H_2S concentration is in the range of 5 to 1500 ppmv. The sample volume ranges were selected in order to ensure a 35 to 60 percent consumption of the 20 ml of 0.01 N iodine (thus ensuring a 0.01 N $Na_2S_2O_3$ titer of approximately 7 to 12 ml). The sample volumes for various H_2S concentrations can be estimated by dividing the approximate ppm-liters desired for a given concentration range by the H_2S concentration stated by the manufacturer. For example, for analyzing a cylinder gas containing approximately 10 ppmv H_2S, the optimum sample volume is 65 liters (650 ppm-liters/10 ppmv). For analyzing a cylinder gas containing approximately 1000 ppmv H_2S, the optimum sample volume is 1 liter (1000 ppm-liters/1000 ppmv).

Approximate cylinder gas H_2S concentration (ppmv)	Approximate ppm-liters desired
5 to <30	650
30 to <500	800
500 to <1500	1000

16.7.2 Critical Orifice Flow Rate Selection. The following table shows the ranges of sample flow rates that are desirable in order to ensure capture of H_2S in the impinger solution. Slight deviations from these ranges will not have an impact on measured concentrations.

Cylinder gas H_2S concentration (ppmv)	Critical orifice flow rate (ml/min)
5 to 50 ppmv	1500 ±500
50 to 250 ppmv	500 ±250
250 to <1000 ppmv	200 ±50
>1000 ppmv	75 ±25

16.7.3 Critical Orifice Fabrication. Critical orifice of desired flow rates may be fabricated by selecting an orifice tube of desired length and connecting 1/16-in. × 1/4-in. (0.16 cm × 0.64 cm) reducing fittings to both ends. The inside diameters and lengths of orifice tubes needed to obtain specific flow rates are shown below.

Tube (in. OD)	Tube (in. ID)	Length (in.)	Flowrate (ml/min)	Altech Catalog No.
1/16	0.007	1.2	85	301430
1/16	0.01	3.2	215	300530
1/16	0.01	1.2	350	300530
1/16	0.02	1.2	1400	300230

16.7.4 Determination of Critical Orifice Approximate Flow Rate. Connect the critical orifice to the sampling system as shown in Figure 16A–4 but without the H_2S cylinder. Connect a rotameter in the line to the first impinger. Turn on the pump, and adjust the

valve to give a reading of about half atmospheric pressure. Observe the rotameter reading. Slowly increase the vacuum until a stable flow rate is reached, and record this as the critical vacuum. The measured flow rate indicates the expected critical flow rate of the orifice. If this flow rate is in the range shown in section 16.7.2, proceed with the critical orifice calibration according to section 16.12.4.

16.7.5 Determination of Approximate Sampling Time. Determine the approximate sampling time for a cylinder of known concentration. Use the optimum sample volume obtained in section 16.7.1.

$$\text{Approximate sampling time} = \frac{\text{Optimum volume}}{\text{Critical orifice flow rate}}$$

16.8 Sample Collection.

16.8.1 Connect the Teflon tubing, Teflon tee, and rotameter to the flow control needle valve as shown in Figure 16A–4. Vent the rotameter to an exhaust hood. Plug the open end of the tee. Five to 10 minutes prior to sampling, open the cylinder valve while keeping the flow control needle valve closed. Adjust the delivery pressure to 20 psi. Open the needle valve slowly until the rotameter shows a flow rate approximately 50 to 100 ml above the flow rate of the critical orifice being used in the system.

16.8.2 Place 50 ml of zinc acetate solution in two of the impingers, connect them and the empty third impinger (dropout bottle) and the rest of the equipment as shown in Figure 16A–4. Make sure the ground-glass fittings are tight. The impingers can be easily stabilized by using a small cardboard box in which three holes have been cut, to act as a holder. Connect the Teflon sample line to the first impinger. Cover the impingers with a dark cloth or piece of plastic to protect the absorbing solution from light during sampling.

16.8.3 Record the temperature and barometric pressure. Note the gas flow rate through the rotameter. Open the closed end of the tee. Connect the sampling tube to the tee, ensuring a tight connection. Start the sampling pump and stopwatch simultaneously. Note the decrease in flow rate through the excess flow rotameter. This decrease should equal the known flow rate of the critical orifice being used. Continue sampling for the period determined in section 16.7.5.

16.8.4 When sampling is complete, turn off the pump and stopwatch. Disconnect the sampling line from the tee and plug it. Close the needle valve followed by the cylinder valve. Record the sampling time.

16.9 Blank Analysis. While the sample is being collected, run a blank as follows: To a 250-ml Erlenmeyer flask, add 100 ml of zinc acetate solution, 20.0 ml of 0.01 N iodine solution, and 2 ml HCl solution. Titrate, while stirring, with 0.01 N $Na_2S_2O_3$ until the solution is light yellow. Add starch, and continue titrating until the blue color disappears. Analyze a blank with each sample, as the blank titer has been observed to change over the course of a day.

NOTE: Iodine titration of zinc acetate solutions is difficult to perform because the solution turns slightly white in color near the end point, and the disappearance of the blue color is hard to recognize. In addition, a blue color may reappear in the solution about 30 to 45 seconds after the titration endpoint is reached. This should not be taken to mean the original endpoint was in error. It is recommended that persons conducting this test perform several titrations to be able to correctly identify the endpoint. The importance of this should be recognized because the results of this analytical procedure are extremely sensitive to errors in titration.

16.10 Sample Analysis. Sample treatment is similar to the blank treatment. Before detaching the stems from the bottoms of the impingers, add 20.0 ml of 0.01 N iodine solution through the stems of the impingers holding the zinc acetate solution, dividing it between the two (add about 15 ml to the first impinger and the rest to the second). Add 2 ml HCl solution through the stems, dividing it as with the iodine. Disconnect the sampling line, and store the impingers for 30 minutes. At the end of 30 minutes, rinse the impinger stems into the impinger bottoms. Titrate the impinger contents with 0.01 N $Na_2S_2O_3$. Do not transfer the contents of the impinger to a flask because this may result in a loss of iodine and cause a positive bias.

16.11 Post-test Orifice Calibration. Conduct a post-test critical orifice calibration run using the calibration procedures outlined in section 16.12.4. If the Q_{std} obtained before and after the test differs by more than 5 percent, void the sample; if not, proceed to perform the calculations.

16.12 Calibrations and Standardizations.

16.12.1 Rotameter and Barometer. Same as Method 11, sections 10.1.3 and 10.1.4.

16.12.2 $Na_2S_2O_3$ Solution, 0.1 N. Standardize the 0.1 N $Na_2S_2O_3$ solution as follows: To 80 ml water, stirring constantly, add 1 ml concentrated H_2SO_4, 10.0 ml of 0.100 N $KH(IO_3)_2$

and 1 g potassium iodide. Titrate immediately with 0.1 N $Na_2S_2O_3$ until the solution is light yellow. Add 3 ml starch solution, and titrate until the blue color just disappears. Repeat the titration until replicate analyses agree within 0.05 ml. Take the average volume of $Na_2S_2O_3$ consumed to calculate the normality to three decimal figures using Equation 16A–5.

16.12.3 Iodine Solution, 0.01 N. Standardize the 0.01 N iodine solution as follows: Pipet 20.0 ml of 0.01 N iodine solution into a 125-ml Erlenmeyer flask. Titrate with standard 0.01 N $Na_2S_2O_3$ solution until the solution is light yellow. Add 3 ml starch solution, and continue titrating until the blue color just disappears. If the normality of the iodine tested is not 0.010, add a few ml of 0.1 N iodine solution if it is low, or a few ml of water if it is high, and standardize again. Repeat the titration until replicate values agree within 0.05 ml. Take the average volume to calculate the normality to three decimal figures using Equation 16A–6.

16.12.4 Critical Orifice. Calibrate the critical orifice using the sampling train shown in Figure 16A–4 but without the H_2S cylinder and vent rotameter. Connect the soap bubble meter to the Teflon line that is connected to the first impinger. Turn on the pump, and adjust the needle valve until the vacuum is higher than the critical vacuum determined in section 16.7.4. Record the time required for gas flow to equal the soap bubble meter volume (use the 100-ml soap bubble meter for gas flow rates below 100 ml/min, otherwise use the 500-ml soap bubble meter). Make three runs, and record the data listed in Table 16A–1. Use these data to calculate the volumetric flow rate of the orifice.

16.13 Calculations.

16.13.1 Nomenclature.

B_{wa} = Fraction of water vapor in ambient air during orifice calibration.

C_{H_2S} = H_2S concentration in cylinder gas, ppmv.

$$K_2 = 32.03 \frac{\text{mg}}{\text{meq}} \frac{24.05\text{L}}{\text{mole}} \frac{1\text{mole}}{64.06\text{g}} \frac{1\text{g}}{10^3\text{mg}} \frac{10^3\text{mL}}{\text{L}} \frac{10^3\mu\text{L}}{1\text{mL}}$$

$$= \frac{12025\mu\text{L}}{\text{meq}}$$

M_a = Molecular weight of ambient air saturated at impinger temperature, g/g-mole.

M_s = Molecular weight of sample gas (nitrogen) saturated at impinger temperature, g/g-mole.

NOTE: (For tests carried out in a laboratory where the impinger temperature is 25 °C, M_a = 28.5 g/g-mole and M_s = 27.7 g/g-mole.)

N_I = Normality of standard iodine solution (0.01 N), g-eq/liter.

N_T = Normality of standard $Na_2S_2O_3$ solution (0.01 N), g-eq/liter.

P_{bar} = Barometric pressure, mm Hg.

P_{std} = Standard absolute pressure, 760 mm Hg.

Q_{std} = Average volumetric flow rate through critical orifice, liters/min.

T_{amb} = Absolute ambient temperature, °K.

T_{std} = Standard absolute temperature, 293 °K.

θ_s = Sampling time, min.

θ_{sb} = Time for soap bubble meter flow rate measurement, min.

$V_{m(std)}$ = Sample gas volume measured by the critical orifice, corrected to standard conditions, liters.

V_{sb} = Volume of gas as measured by the soap bubble meter, ml.

$V_{sb(std)}$ = Volume of gas as measured by the soap bubble meter, corrected to standard conditions, liters.

V_I = Volume of standard iodine solution (0.01 N) used, ml.

V_T = Volume of standard $Na_2S_2O_3$ solution (0.01 N) used, ml.

V_{TB} = Volume of standard $Na_2S_2O_3$ solution (0.01 N) used for the blank, ml.

16.13.2 Normality of Standard $Na_2S_2O_3$ Solution (0.1 N).

$$N_T = \frac{1}{\text{mL } Na_2S_2O_3 \text{ consumed}} \qquad \text{Eq. 16A-5}$$

16.13.3 Normality of Standard Iodine Solution (0.01 N).

$$N_I = \frac{N_T V_T}{V_I} \qquad \text{Eq. 16A-6}$$

16.13.4 Sample Gas Volume.

$$V_{m(std)} = \overline{Q}_{std}\Theta_s\left(1 - B_{wa}\right)\frac{M_a}{M_b} \qquad \text{Eq. 16A-7}$$

16.13.5 Concentration of H_2S in the Gas Cylinder.

17.0 References

$$C_{H_2S} = \frac{K N_T \left(V_{TB} - V_T\right)}{V_{m(std)}} \qquad \text{Eq. 16A-8}$$

1. American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater. Washington, DC. American Public Health Association. 1975. pp. 316–317.

2. American Society for Testing and Materials. Annual Book of ASTM Standards. Part 31: Water, Atmospheric Analysis. Philadelphia, PA. 1974. pp. 40–42.

3. Blosser, R.O. A Study of TRS Measurement Methods. National Council of the Paper Industry for Air and Stream Improvement, Inc., New York, NY. Technical Bulletin No. 434. May 1984. 14 pp.

4. Blosser, R.O., H.S. Oglesby, and A.K. Jain. A Study of Alternate SO_2 Scrubber Designs Used for TRS Monitoring. A Special Report by the National Council of the Paper Industry for Air and Stream Improvement, Inc., New York, NY. July 1977.

5. Curtis, F., and G.D. McAlister. Development and Evaluation of an Oxidation/Method 6 TRS Emission Sampling Procedure. Emission Measurement Branch, Emission Standards and Engineering Division, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711. February 1980.

6. Gellman, I. A Laboratory and Field Study of Reduced Sulfur Sampling and Monitoring Systems. National Council of the Paper Industry for Air and Stream Improvement, Inc., New York, NY. Atmospheric Quality Improvement Technical Bulletin No. 81. October 1975.

7. Margeson, J.H., J.E. Knoll, and M.R. Midgett. A Manual Method for TRS Determination. Source Branch, Quality Assurance Division, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

8. National Council of the Paper Industry for Air and Stream Improvement. An Investigation of H_2S and SO_2. Calibration Cylinder Gas Stability and Their Standardization Using Wet Chemical Techniques. Special Report 76–06. New York, NY. August 1976.

9. National Council of the Paper Industry for Air and Stream Improvement. Wet Chemical Method for Determining the H_2S Concentration of Calibration Cylinder Gases. Technical Bulletin Number 450. New York, NY. January 1985. 23 pp.

10. National Council of the Paper Industry for Air and Stream Improvement. Modified Wet Chemical Method for Determining the H_2S Concentration of Calibration Cylinder Gases. Draft Report. New York, NY. March 1987. 29 pp.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

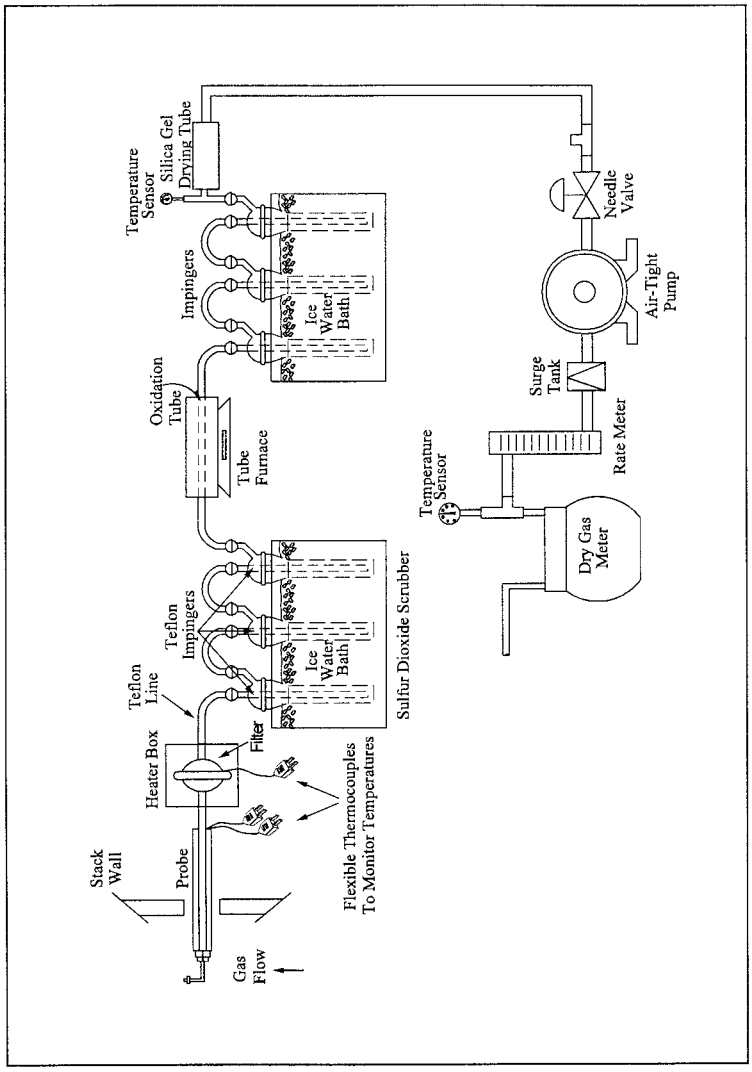

Figure 16A-1. Sampling Train.

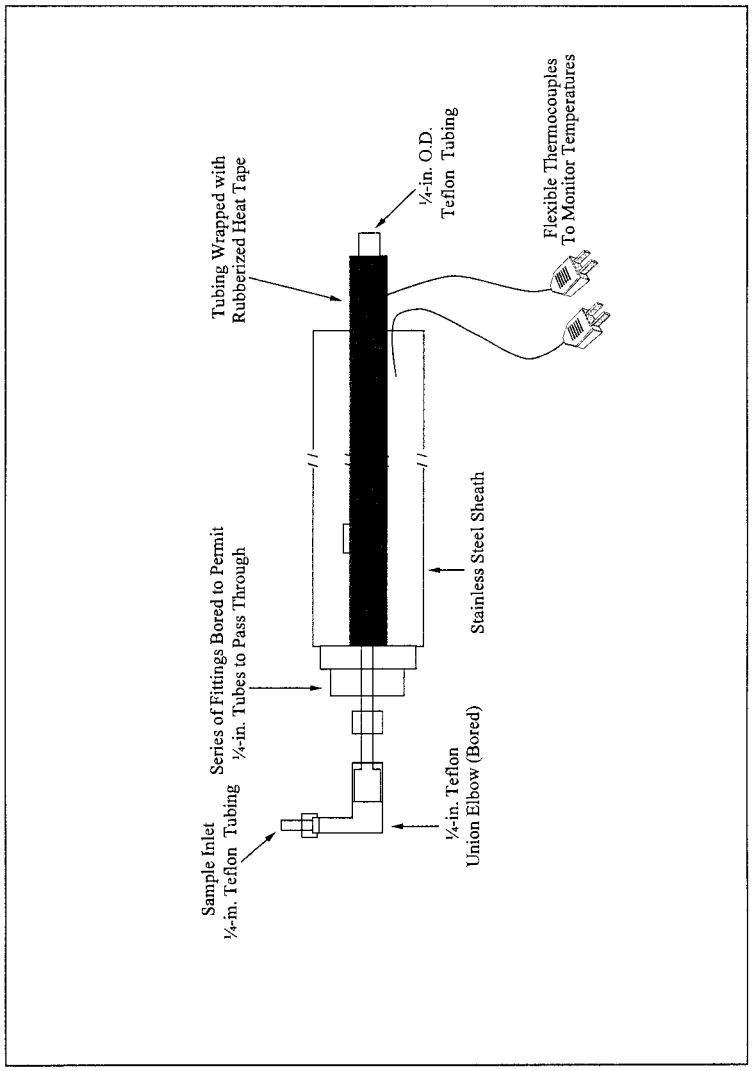

Figure 16A-2. Angled Sampling Probe.

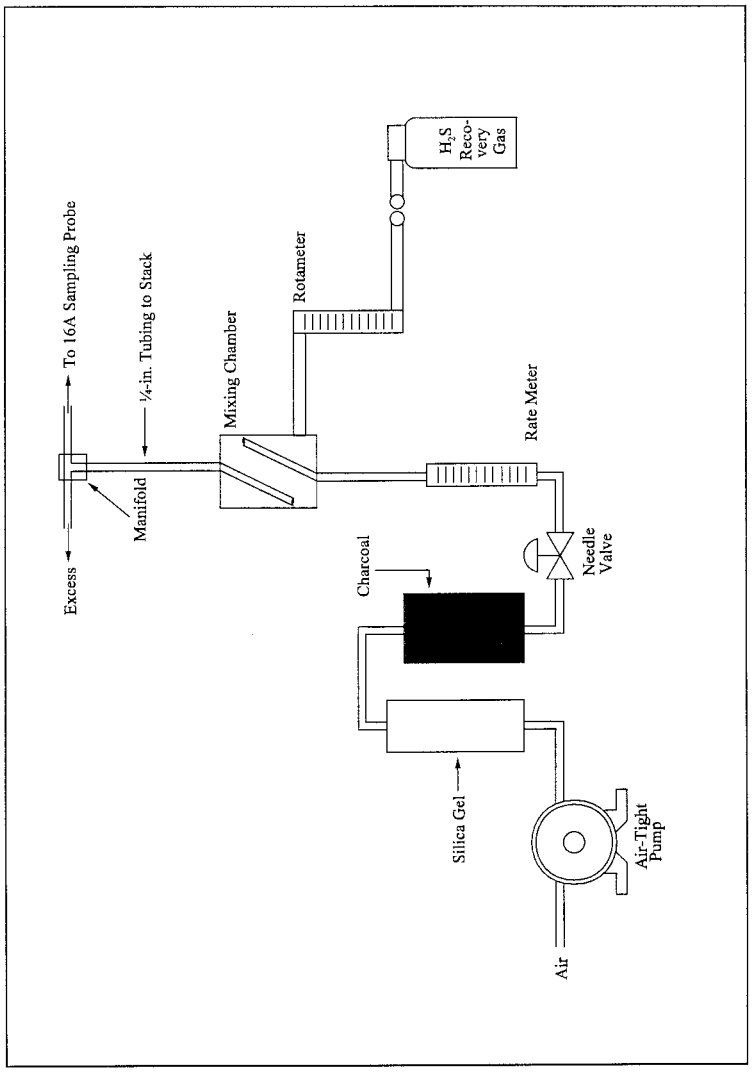

Figure 16A-3. Recovery Gas Dilution System.

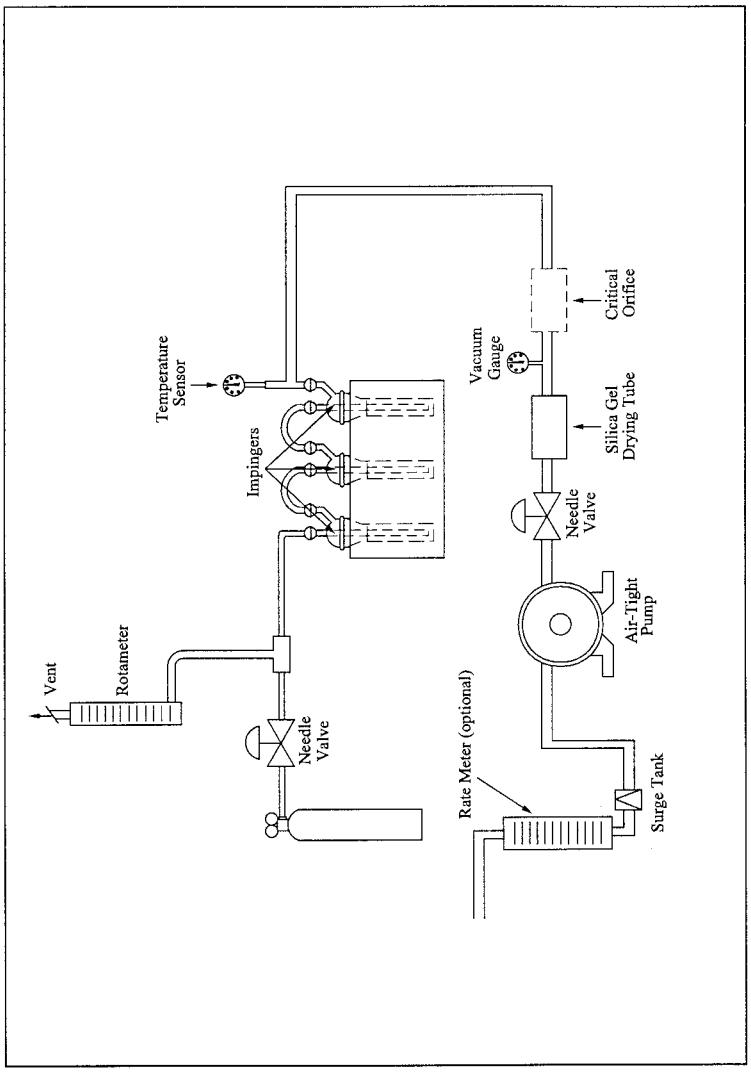

Figure 16A-4. Recovery Check Gas Sampling Train.

Date _____
Critical orifice ID _____
Soap bubble meter volume, Vsb___ liters
Time, θsb
Run no. 1 ___ min ___ sec
Run no. 2 ___ min ___ sec
Run no. 3 ___ min ___ sec
Average ___ min ___ sec
Covert the seconds to fraction of minute:
Time=___ min + ___ Sec/60=___ min

Barometric pressure, P_{bar}=___ mm Hg
Ambient temperature, t_{amb} = 273 + ___ °C=___ °K=___ mm Hg. (This should be approximately 0.4 times barometric pressure.)
Pump vacuum,

$$V_{sb(std)} = \frac{V_{sb} T_{std} P_{bar} (10^{-3})}{T_{amb} P_{std}}$$

$$= ---------- \text{ liters}$$

$$Q_{std} = \frac{V_{sb(std)}}{\Theta_{sb}}$$

$$= ---------- \text{ liters/min}$$

Table 16A–1. Critical Orifice Calibration Data

METHOD 16B—DETERMINATION OF TOTAL REDUCED SULFUR EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a knowledge of at least the following additional test methods: Method 6C, Method 16, and Method 16A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Total reduced sulfur (TRS) including:	N/A
Dimethyl disulfide (DMDS), [$(CH_3)_2S_2$]	62–49–20
Dimethyl sulfide (DMS), [$(CH_3)_2S$]	75–18–3
Hydrogen sulfide (H_2S)	7783–06–4
Methyl mercaptan (MeSH), [CH_4S]	74–93–1
Reported as: Sulfur dioxide (SO_2)	7449–09–5

1.2 Applicability. This method is applicable for determining TRS emissions from recovery furnaces (boilers), lime kilns, and smelt dissolving tanks at kraft pulp mills, and from other sources when specified in an applicable subpart of the regulations. The flue gas must contain at least 1 percent oxygen for complete oxidation of all TRS to SO_2.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 An integrated gas sample is extracted from the stack. The SO_2 is removed selectively from the sample using a citrate buffer solution. The TRS compounds are then thermally oxidized to SO_2 and analyzed as SO_2 by gas chromatography (GC) using flame photometric detection (FPD).

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Reduced sulfur compounds other than those regulated by the emission standards, if present, may be measured by this method. Therefore, carbonyl sulfide, which is partially oxidized to SO_2 and may be present in a lime kiln exit stack, would be a positive interferant.

4.2 Particulate matter from the lime kiln stack gas (primarily calcium carbonate) can cause a negative bias if it is allowed to enter the citrate scrubber; the particulate matter will cause the pH to rise and H_2S to be absorbed before oxidation. Proper use of the particulate filter, described in section 6.1.3 of Method 16A, will eliminate this interference.

4.3 Carbon monoxide (CO) and carbon dioxide (CO_2) have substantial desensitizing effects on the FPD even after dilution. Acceptable systems must demonstrate that they have eliminated this interference by some procedure such as eluting these compounds before the SO_2. Compliance with this requirement can be demonstrated by submitting chromatograms of calibration gases with and without CO_2 in diluent gas. The CO_2 level should be approximately 10 percent for the case with CO_2 present. The two chromatograms should show agreement within the precision limits of section 13.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hydrogen Sulfide (H_2S). A flammable, poisonous gas with the odor of rotten eggs. H_2S is extremely hazardous and can cause collapse, coma, and death within a few seconds of one or two inhalations at sufficient concentrations. Low concentrations irritate the mucous membranes and may cause nausea, dizziness, and headache after exposure.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling train is shown in Figure 16B–1. Modifications to the apparatus are accepted provided the system performance check in section 8.4.1 is met.

6.1.1 Probe, Probe Brush, Particulate Filter, SO_2 Scrubber, Combustion Tube, and Furnace. Same as in Method 16A, sections 6.1.1 to 6.1.6.

6.1.2 Sampling Pump. Leakless Teflon-coated diaphragm type or equivalent.

6.2 Analysis.

6.2.1 Dilution System (optional), Gas Chromatograph, Oven, Temperature Gauges, Flow System, Flame Photometric Detector, Electrometer, Power Supply, Recorder, Calibration System, Tube Chamber, Flow System, and Constant Temperature Bath. Same as in Method 16, sections 6.2.1, 6.2.2, and 6.3.

6.2.2 Gas Chromatograph Columns. Same as in Method 16, section 6.2.3. Other columns with demonstrated ability to resolve SO_2 and be free from known interferences are acceptable alternatives. Single column systems such as a 7-ft Carbsorb B HT 100 column have been found satisfactory in resolving SO_2 from CO_2.

7.0 Reagents and Standards

Same as in Method 16, section 7.0, except for the following:

7.1 Calibration Gas. SO_2 permeation tube gravimetrically calibrated and certified at some convenient operating temperature. These tubes consist of hermetically sealed FEP Teflon tubing in which a liquefied gaseous substance is enclosed. The enclosed gas permeates through the tubing wall at a constant rate. When the temperature is constant, calibration gases covering a wide range of known concentrations can be generated by varying and accurately measuring the flow rate of diluent gas passing over the tubes. In place of SO_2 permeation tubes, cylinder gases containing SO_2 in nitrogen may be used for calibration. The cylinder gas concentration must be verified according to section 8.2.1 of Method 6C. The calibration gas is used to calibrate the GC/FPD system and the dilution system.

7.2 Recovery Check Gas.

7.2.1 Hydrogen sulfide [100 parts per million by volume (ppmv) or less] in nitrogen, stored in aluminum cylinders. Verify the concentration by Method 11, the procedure discussed in section 16.0 of Method 16A, or gas chromatography where the instrument is calibrated with an H_2S permeation tube as described below. For the wet-chemical methods, the standard deviation should not exceed 5 percent on at least three 20-minute runs.

7.2.2 Hydrogen sulfide recovery gas generated from a permeation device gravimetrically calibrated and certified at some convenient operation temperature may be used. The permeation rate of the device must be such that at a dilution gas flow rate of 3 liters/min (64 ft^3/hr), an H_2S concentration in the range of the stack gas or within 20 percent of the emission standard can be generated.

7.3 Combustion Gas. Gas containing less than 50 ppbv reduced sulfur compounds and less than 10 ppmv total hydrocarbons. The gas may be generated from a clean-air system that purifies ambient air and consists of the following components: diaphragm pump, silica gel drying tube, activated charcoal tube, and flow rate measuring device. Gas from a compressed air cylinder is also acceptable.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Procedures. Same as in Method 15, section 8.1.

8.2 Sample Collection. Before any source sampling is performed, conduct a system performance check as detailed in section 8.4.1 to validate the sampling train components and procedures. Although this test is optional, it would significantly reduce the possibility of rejecting tests as a result of failing the post-test performance check. At the completion of the pretest system performance check, insert the sampling probe into the test port making certain that no dilution air enters the stack though the port. Condition the entire system with sample for a minimum of 15 minutes before beginning analysis. If the sample is diluted, determine the dilution factor as in section 10.4 of Method 15.

8.3 Analysis. Inject aliquots of the sample into the GC/FPD analyzer for analysis. Determine the concentration of SO_2 directly from the calibration curves or from the equation for the least-squares line.

8.4. Post-Test Procedures

8.4.1 System Performance Check. Same as in Method 16A, section 8.5. A sufficient number of sample injections should be made so that the precision requirements of section 13.2 are satisfied.

8.4.2 Determination of Calibration Drift. Same as in Method 15, section 8.3.2.

9.0 Quality Control

Section	Quality control measure	Effect
8.2, 8.3	System performance check	Ensure validity of sampling train components and analytical procedure.
8.1	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.
10.0	Analytical calibration	Ensure precision of analytical results within 5 percent.

10.0 Calibration

Same as in Method 16, section 10, except SO_2 is used instead of H_2S.

11.0 Analytical Procedure

11.1 Sample collection and analysis are concurrent for this method (see section 8.3).

12.0 Data Analysis and Calculations

12.1 Nomenclature.

C_{SO2} = Sulfur dioxide concentration, ppmv.
C_{TRS} = Total reduced sulfur concentration as determined by Equation 16B–1, ppmv.
d = Dilution factor, dimensionless.
N = Number of samples.

12.2 SO_2 Concentration. Determine the concentration of SO_2, C_{SO2}, directly from the calibration curves. Alternatively, the concentration may be calculated using the equation for the least-squares line.

12.3 TRS Concentration.

$$C_{TRS} = C_{SO_2} d \qquad \text{Eq. 16B-1}$$

12.4 Average TRS Concentration

$$\text{Avg.}\, C_{TRS} = \frac{\sum_{i=1}^{n} C_{TRS}}{N} \qquad \text{Eq. 16B-2}$$

13.0 Method Performance.

13.1 Range and Sensitivity. Coupled with a GC using a 1-ml sample size, the maximum limit of the FPD for SO_2 is approximately 10 ppmv. This limit is extended by diluting the sample gas before analysis or by reducing the sample aliquot size. For sources with emission levels between 10 and 100 ppm, the measuring range can be best extended by reducing the sample size.

13.2 GC/FPD Calibration and Precision. A series of three consecutive injections of the sample calibration gas, at any dilution, must produce results which do not vary by more than 5 percent from the mean of the three injections.

13.3 Calibration Drift. The calibration drift determined from the mean of the three injections made at the beginning and end of any run or series of runs within a 24-hour period must not exceed 5 percent.

13.4 System Calibration Accuracy. Losses through the sample transport system must be measured and a correction factor developed to adjust the calibration accuracy to 100 percent.

13.5 Field tests between this method and Method 16A showed an average difference of less than 4.0 percent. This difference was not determined to be significant.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Same as in Method 16, section 16.0.

2. National Council of the Paper Industry for Air and Stream Improvement, Inc, A Study of TRS Measurement Methods. Technical Bulletin No. 434. New York, NY. May 1984. 12p.

3. Margeson, J.H., J.E. Knoll, and M.R. Midgett. A Manual Method for TRS Determination. Draft available from the authors. Source Branch, Quality Assurance Division, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

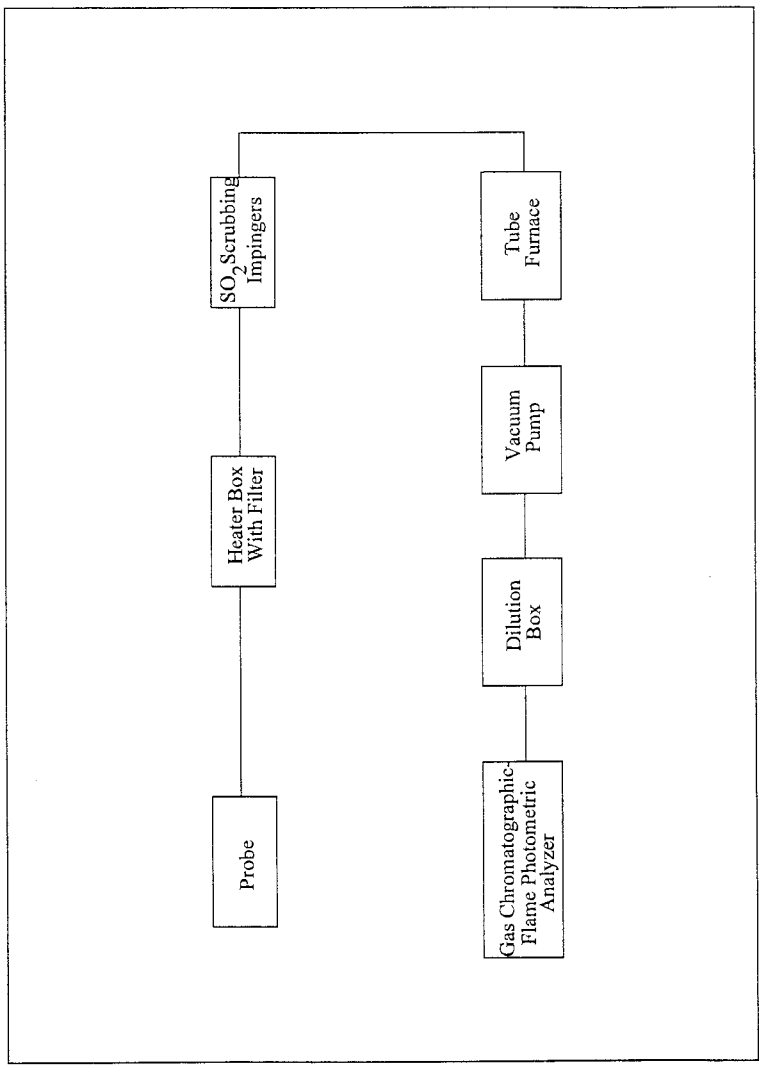

Figure 16B-1. Method 16B Sampling Train.

METHOD 16C—DETERMINATION OF TOTAL REDUCED SULFUR EMISSIONS FROM STATIONARY SOURCES

1.0 Scope and Application

What is Method 16C?

Method 16C is a procedure for measuring total reduced sulfur (TRS) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis. This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to

other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

(a) Method 6C—Determination of Sulfur Dioxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)

(b) Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure)

(c) Method 16A—Determination of Total Reduced Sulfur Emissions from Stationary Sources (Impinger Technique)

1.1 Analytes. What does Method 16C determine?

Analyte	CAS No.
Total reduced sulfur including:	N/A
Dimethyl disulfide (DMDS), [$(CH_3)_2S_2$]	62–49–20
Dimethyl sulfide (DMS), [$(CH_3)_2S$]	75–18–3
Hydrogen sulfide (H_2S)	7783–06–4
Methyl mercaptan (MeSH), (CH_4S)	74–93–1
Reported as: Sulfur dioxide (SO_2)	7449–09–5

1.2 Applicability. This method is applicable for determining TRS emissions from recovery furnaces (boilers), lime kilns, and smelt dissolving tanks at kraft pulp mills, and from other sources when specified in an applicable subpart of the regulations.

1.3 Data Quality Objectives. Adherence to the requirements described in Method 16C will enhance the quality of the data obtained.

2.0 Summary of Method

2.1 An integrated gas sample is extracted from the stack. The SO_2 is removed selectively from the sample using a citrate buffer solution. The TRS compounds are then thermally oxidized to SO_2 and determined as SO_2 by an instrumental analyzer. This method is a combination of the sampling procedures of Method 16A and the analytical procedures of Method 6C (referenced in Method 7E), with minor modifications to facilitate their use together.

3.0 Definitions

Analyzer calibration error, *Calibration curve*, *Calibration gas*, *Low-level gas*, *Mid-level gas*, *High-level gas*, *Calibration drift*, *Calibration span*, *Data recorder*, *Direct calibration mode*, *Gas analyzer*, *Interference check*, *Measurement system*, *Response time*, *Run*, *System calibration mode*, *System performance check*, and *Test* are the same as used in Methods 16A and 6C.

4.0 Interferences

4.1 Reduced sulfur compounds other than those defined as TRS, if present, may be measured by this method. Compounds like carbonyl sulfide, which is partially oxidized to SO_2 and may be present in a lime kiln exit stack, would be a positive interferent. Interferences may vary among instruments, and instrument-specific interferences must be evaluated through the interference check.

4.2 Particulate matter from the lime kiln stack gas (primarily calcium carbonate) can cause a negative bias if it is allowed to enter the citrate scrubber; the particulate matter will cause the pH to rise and H_2S to be absorbed before oxidation. Proper use of the particulate filter, described in section 6.1.3 of Method 16A, will eliminate this interference.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices before performing this test method.

5.2 Hydrogen Sulfide. Hydrogen sulfide is a flammable, poisonous gas with the odor of rotten eggs. Hydrogen sulfide is extremely hazardous and can cause collapse, coma, and death within a few seconds of one or two inhalations at sufficient concentrations. Low concentrations irritate the mucous membranes and may cause nausea, dizziness, and headache after exposure. It is the responsibility of the user of this test method to establish appropriate safety and health practices.

6.0 Equipment and Supplies

What do I need for the measurement system?

The measurement system is similar to those applicable components in Methods 16A and 6C. Modifications to the apparatus are accepted provided the performance criteria in section 13.0 are met.

6.1 Probe. Teflon tubing, 6.4-mm (¼ in.) diameter, sequentially wrapped with heat-resistant fiber strips, a rubberized heat tape (plug at one end), and heat-resistant adhesive tape. A flexible thermocouple or other suitable temperature measuring device must be placed between the Teflon tubing and the fiber strips so that the temperature can be monitored to prevent softening of the probe. The probe must be sheathed in stainless steel to provide in-stack rigidity. A series of bored-out stainless steel fittings placed at the front of the sheath will prevent moisture and particulate from entering between the probe and sheath. A 6.4-mm (¼ in.) Teflon elbow (bored out) must be attached to the inlet of the probe, and a 2.54 cm (1 in.) piece of Teflon tubing must be attached at the open end of the elbow to permit the opening of the probe to be turned away from the particulate stream; this will reduce the amount of particulate drawn into the sampling train. The probe is depicted in Figure 16A–2 of Method 16A.

6.2 Probe Brush. Nylon bristle brush with handle inserted into a 3.2-mm (⅛ in.) Teflon

tubing. The Teflon tubing should be long enough to pass the brush through the length of the probe.

6.3 Particulate Filter. 50-mm Teflon filter holder and a 1- to 2-μm porosity, Teflon filter (may be available through Savillex Corporation, 5325 Highway 101, Minnetonka, Minnesota 55343, or other suppliers of filters). The filter holder must be maintained in a hot box at a temperature sufficient to prevent moisture condensation. A temperature of 121 °C (250 °F) was found to be sufficient when testing a lime kiln under sub-freezing ambient conditions.

6.4 SO_2 Scrubber. Three 300-ml Teflon segmented impingers connected in series with flexible, thick-walled, Teflon tubing. (Impinger parts and tubing may be available through Savillex or other suppliers.) The first two impingers contain 100 ml of citrate buffer, and the third impinger is initially dry. The tip of the tube inserted into the solution should be constricted to less than 3 mm (⅛ in.) ID and should be immersed to a depth of at least 5 cm (2 in.).

6.5 Combustion Tube. Quartz glass tubing with an expanded combustion chamber 2.54 cm (1 in.) in diameter and at least 30.5 cm (12 in.) long. The tube ends should have an outside diameter of 0.6 cm (¼ in.) and be at least 15.3 cm (6 in.) long. This length is necessary to maintain the quartz-glass connector near ambient temperature and thereby avoid leaks. Alternative combustion tubes are acceptable provided they are shown to combust TRS at concentrations encountered during tests.

6.6 Furnace. A furnace of sufficient size to enclose the combustion chamber of the combustion tube with a temperature regulator capable of maintaining the temperature at 800 ±100 °C (1472 ±180 °F). The furnace operating temperature should be checked with a thermocouple to ensure accuracy.

6.7 Sampling Pump. A leak-free pump is required to pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system and must be constructed of material that is non-reactive to the gas it contacts. For dilution-type measurement systems, an eductor pump may be used to create a vacuum that draws the sample through a critical orifice at a constant rate.

6.8 Calibration Gas Manifold. The calibration gas manifold must allow the introduction of calibration gases either directly to the gas analyzer in direct calibration mode or into the measurement system, at the probe, in system calibration mode, or both, depending upon the type of system used. In system calibration mode, the system must be able to flood the sampling probe and vent excess gas. Alternatively, calibration gases may be introduced at the calibration valve following the probe. Maintain a constant pressure in the gas manifold. For in-stack dilution-type systems, a gas dilution subsystem is required to transport large volumes of purified air to the sample probe, and a probe controller is needed to maintain the proper dilution ratio.

6.9 Sample Gas Manifold. The sample gas manifold diverts a portion of the sample to the analyzer, delivering the remainder to the by-pass discharge vent. The manifold should also be able to introduce calibration gases directly to the analyzer. The manifold must be made of material that is non-reactive to SO_2 and be configured to safely discharge the bypass gas.

6.10 SO_2 Analyzer. You must use an instrument that uses an ultraviolet, non-dispersive infrared, fluorescence, or other detection principle to continuously measure SO_2 in the gas stream provided it meets the performance specifications in section 13.0.

6.11 Data Recording. A strip chart recorder, computerized data acquisition system, digital recorder, or data logger for recording measurement data must be used.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. When such specifications are not available, the best available grade must be used.

7.1 Water. Deionized distilled water must conform to ASTM Specification D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17). The $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.2 Citrate Buffer. Dissolve 300 g of potassium citrate (or 284 g of sodium citrate) and 41 g of anhydrous citric acid in 1 liter of water (200 ml is needed per test). Adjust the pH to between 5.4 and 5.6 with potassium citrate or citric acid, as required.

7.3 Calibration Gas. Refer to section 7.1 of Method 7E (as applicable) for the calibration gas requirements. Example calibration gas mixtures are listed below.

(a) SO_2 in nitrogen (N_2).
(b) SO_2 in air.
(c) SO_2 and carbon dioxide (CO_2) in N_2.
(d) SO_2 and oxygen (O_2) in N_2.
(e) $SO_2/CO_2/O_2$ gas mixture in N_2.
(f) CO_2/NO_X gas mixture in N_2.
(g) $CO_2/SO_2/NO_X$ gas mixture in N_2.

For fluorescence-based analyzers, the O_2 and CO_2 concentrations of the calibration gases as introduced to the analyzer must be within 1.0 percent (absolute) O_2 and 1.0 percent (absolute) CO_2 of the O_2 and CO_2 concentrations of the effluent samples as introduced to the analyzer. Alternatively, for fluorescence-based analyzers, use calibration blends of SO_2 in air and the nomographs provided by

the vendor to determine the quenching correction factor (the effluent O_2 and CO_2 concentrations must be known). This requirement does not apply to ambient-level fluorescence analyzers that are used in conjunction with sample dilution systems. Alternatively, H_2S in O_2 or air may be used to calibrate the analyzer through the tube furnace.

7.4 System Performance Check Gas. You must use H_2S (100 ppmv or less) stored in aluminum cylinders with the concentration certified by the manufacturer. Hydrogen sulfide in nitrogen is more stable than H_2S in air, but air may be used as the balance gas.

NOTE: Alternatively, H_2S recovery gas generated from a permeation device gravimetrically calibrated and certified at some convenient operating temperature may be used. The permeation rate of the device must be such that at the appropriate dilution gas flow rate, an H_2S concentration can be generated in the range of the stack gas or within 20 percent of the emission standard.

7.5 Interference Check. Examples of test gases for the interference check are listed in Table 7E–3 of Method 7E.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pre-sampling Tests. Before measuring emissions, perform the following procedures:

(a) Calibration gas verification,

(b) Calibration error test,

(c) System performance check,

(d) Verification that the interference check has been satisfied.

8.1.1 Calibration Gas Verification. Obtain a certificate from the gas manufacturer documenting the quality of the gas. Confirm that the manufacturer certification is complete and current. Ensure that your calibration gas certifications have not expired. This documentation should be available on-site for inspection. To the extent practicable, select a high-level gas concentration that will result in the measured emissions being between 20 and 100 percent of the calibration span.

8.1.2 Analyzer Calibration Error Test. After you have assembled, prepared, and calibrated your sampling system and analyzer, you must conduct a 3-point analyzer calibration error test before the first run and again after any failed system performance check or failed drift test to ensure the calibration is acceptable. Introduce the low-, mid-, and high-level calibration gases sequentially to the analyzer in direct calibration mode. For each calibration gas, calculate the analyzer calibration error using Equation 16C–1 in section 12.2. The calibration error for the low-, mid-, and high-level gases must not exceed 5.0 percent or 0.5 ppmv. If the calibration error specification is not met, take corrective action and repeat the test until an acceptable 3-point calibration is achieved.

8.1.3 System Performance Check. A system performance check is done (1) to validate the sampling train components and procedure (prior to testing), and (2) to validate a test run (after a run). You must conduct a performance check in the field prior to testing, and after each 3-hour run or after three 1-hour runs. A performance check consists of sampling and analyzing a known concentration of H_2S (system performance check gas) and comparing the analyzed concentration to the known concentration. To conduct the system performance check, mix the system performance check gas (Section 7.4) and ambient air, that has been conditioned to remove moisture and sulfur-containing gases, in a dilution system such as that shown in Figure 16A–3 of Method 16A. Alternatively, ultra-high purity (UHP) grade air may be used. Adjust the gas flow rates to generate an H_2S concentration in the range of the stack gas or within 20 percent of the applicable standard and an oxygen concentration greater than 1 percent at a total flow rate of at least 2.5 liters/min (5.3 ft3/hr). Use Equation 16A–3 from Method 16A to calculate the concentration of system performance check gas generated. Calibrate the flow rate from both gas sources with a soap bubble flow meter so that the diluted concentration of H_2S can be accurately calculated. Alternatively, mass flow controllers with documented calibrations may be used if UHP grade air is being used. Sample duration should be sufficiently long to ensure a stable response from the analyzer. Analyze in the same manner as the emission samples. Collect the sample through the probe of the sampling train using a manifold or other suitable device that will ensure extraction of a representative sample. The TRS sample concentration measured between system performance checks is corrected by the average of the pre- and post-system performance checks.

8.1.4 Interference Check. Same as in Method 7E, section 8.2.7.

8.2 Measurement System Preparation.

8.2.1 For the SO_2 scrubber, measure 100 ml of citrate buffer into the first and second impingers; leave the third impinger empty. Immerse the impingers in an ice bath, and locate them as close as possible to the filter heat box. The connecting tubing should be free of loops. Maintain the probe and filter temperatures sufficiently high to prevent moisture condensation, and monitor with a suitable temperature sensor. Prepare the oxidation furnace and maintain at 800 ±100 °C (1472 ±180 °F).

8.2.2 Citrate Scrubber Conditioning Procedure. Condition the citrate buffer scrubbing solution by pulling stack gas through the Teflon impingers as described in section 8.4.1.

8.3 Pretest Procedures. After the complete measurement system has been set up at the site and deemed to be operational, the following procedures must be completed before sampling is initiated.

8.3.1 Leak-Check. Appropriate leak-check procedures must be employed to verify the integrity of all components, sample lines, and connections. For components upstream of the sample pump, attach the probe end of the sample line to a manometer or vacuum gauge, start the pump and pull a vacuum greater than 50 mm (2 in.) Hg, close off the pump outlet, and then stop the pump and ascertain that there is no leak for 1 minute. For components after the pump, apply a slight positive pressure and check for leaks by applying a liquid (detergent in water, for example) at each joint. Bubbling indicates the presence of a leak.

8.3.2 Initial System Performance Check. A system performance check using the test gas (Section 7.4) is performed prior to testing to validate the sampling train components and procedure.

8.4 Sample Collection and Analysis.

8.4.1 After performing the required pretest procedures described in section 8.1, insert the sampling probe into the test port ensuring that no dilution air enters the stack through the port. Condition the sampling system and citrate buffer solution for a minimum of 15 minutes before beginning analysis. Begin sampling and analysis. A source test consists of three test runs. A test run shall consist of a single sample collected over a 3-hour period or three separate 1-hour samples collected over a period not to exceed six hours.

8.5 Post-Run Evaluations.

8.5.1 System Performance Check. Perform a post-run system performance check before replacing the citrate buffer solution and particulate filter and before the probe is cleaned. The check results must not exceed the 100 ±20 percent limit set forth in section 13.2. If this limit is exceeded, the intervening run is considered invalid. However, if the recovery efficiency is not in the 100 ±20 percent range, but the results do not affect the compliance or noncompliance status of the affected facility, the Administrator may decide to accept the results of the compliance test.

8.5.2 Calibration Drift. After a run or series of runs, not to exceed a 24-hour period after initial calibration, perform a calibration drift test using a calibration gas (preferably the level that best approximates the sample concentration) in direct calibration mode. This drift must not differ from the initial calibration error percent by more than 3.0 percent or 0.5 ppm. If the drift exceeds this limit, the intervening run or runs are considered valid, but a new analyzer calibration error test must be performed and passed before continuing sampling.

9.0 Quality Control

Section	Quality control measure	Effect
8.1.2	Analyzer calibration error test	Establishes initial calibration accuracy within 5.0%.
8.1.3, 8.5.1	System performance check	Ensures accuracy of sampling/analytical procedure to 100 ±20%.
8.5.2	Calibration drift test	Ensures calibration drift is within 3.0%.
8.1.4	Interference check	Checks for analytical interferences.
8.3	Sampling equipment leak-check	Ensures accurate measurement of sample gas flow rate, sample volume.

10.0 Calibration

10.1 Calibrate the system using the gases described in section 7.3. Perform the initial 3-point calibration error test as described in section 8.1.2 before you start the test. The specification in section 13 must be met. Conduct an initial system performance test described in section 8.1.3 as well before the test to validate the sampling components and procedures before sampling. After the test commences, a system performance check is required after each run. You must include a copy of the manufacturer's certification of the calibration gases used in the testing as part of the test report. This certification must include the 13 documentation requirements in the EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards, September 1997, as amended August 25, 1999.

11.0 Analytical Procedure

Because sample collection and analysis are performed together (see section 8.0), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

12.1 Nomenclature.

ACE = Analyzer calibration error, percent of calibration span.

CD = Calibration drift, percent.

C_{Dir} = Measured concentration of a calibration gas (low, mid, or high) when introduced in direct calibration mode, ppmv.

C_{H2S} = Concentration of the system performance check gas, ppmv H_2S.

C_S = Measured concentration of the system performance gas when introduced in system calibration mode, ppmv H_2S.
C_V = Manufacturer certified concentration of a calibration gas (low, mid, or high), ppmv SO_2.
C_{SO2} = Unadjusted sample SO_2 concentration, ppmv.
C_{TRS} = Total reduced sulfur concentration corrected for system performance, ppmv.
CS = Calibration span, ppmv.
DF = Dilution system (if used) dilution factor, dimensionless.
SP = System performance, percent.

12.2 Analyzer Calibration Error. For non-dilution systems, use Equation 16C–1 to calculate the analyzer calibration error for the low-, mid-, and high-level calibration gases.

$$ACE = \frac{C_{Dir} - C_v}{CS} X\ 100 \qquad \text{Eq. 16C-1}$$

12.3 System Performance Check. Use Equation 16C–2 to calculate the system performance.

$$SP = \frac{C_S - C_{H2S}}{C_{H2S}} x\ 100 \qquad \text{Eq. 16C-2}$$

12.4 Calibration Drift. Use Equation 16C–3 to calculate the calibration drift at a single concentration level after a run or series of runs (not to exceed a 24-hr period) from initial calibration. Compare the single-level calibration gas error (ACE_n) to the original error obtained for that gas in the initial analyzer calibration error test (ACE_i).

$$CD = \left| ACE_i - ACE_n \right| \qquad \text{Eq. 16C-3}$$

12.5 TRS Concentration as SO_2. For each sample or test run, calculate the arithmetic average of SO_2 concentration values (e.g., 1-minute averages). Then calculate the sample TRS concentration by adjusting the average value of C_{SO2} for system performance using Equation 16C–4.

$$C_{TRS} = \frac{\overline{C_{SO2}}}{1 - \left| \overline{SP} \right|} \qquad \text{Eq. 16C-4}$$

13.0 Method Performance

13.1 Analyzer Calibration Error. At each calibration gas level (low, mid, and high), the calibration error must either not exceed 5.0 percent of the calibration gas concentration or $|C_{Dir} - C_v|$ must be ≤0.5 ppmv.

13.2 System Performance. Each system performance check must not deviate from the system performance gas concentration by more than 20 percent. Alternatively, the results are acceptable if $|C_s - C_{H2S}|$ is ≤0.5 ppmv.

13.3 Calibration Drift. The calibration drift at the end of any run or series of runs within a 24-hour period must not differ by more than 3.0 percent from the original ACE at the test concentration level or $|ACEi - ACE_n|$ must not exceed 0.5 ppmv.

13.4 Interference Check. For the analyzer, the total interference response (i.e., the sum of the interference responses of all tested gaseous components) must not be greater than 2.5 percent of the calibration span. Any interference is also acceptable if the sum of the responses does not exceed 0.5 ppmv for a

calibration span of 5 to 10 ppmv, or 0.2 ppmv for a calibration span <5 ppmv.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. The references are the same as in section 16.0 of Method 16, section 17.0 of Method 16A, and section 17.0 of Method 6C.
2. National Council of the Paper Industry for Air and Stream Improvement, Inc,. A Study of TRS Measurement Methods. Technical Bulletin No. 434. New York, NY. May 1984. 12p.
3. Margeson, J.H., J.E. Knoll, and M.R. Midgett. A Manual Method for TRS Determination. Draft available from the authors. Source Branch, Quality Assurance Division, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 17—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

NOTE: Particulate matter is not an absolute quantity. It is a function of temperature and pressure. Therefore, to prevent variability in PM emission regulations and/or associated test methods, the temperature and pressure at which PM is to be measured must be carefully defined. Of the two variables (*i.e.*, temperature and pressure), temperature has the greater effect upon the amount of PM in an effluent gas stream; in most stationary source categories, the effect of pressure appears to be negligible. In Method 5, 120 °C (248 °F) is established as a nominal reference temperature. Thus, where Method 5 is specified in an applicable subpart of the standard, PM is defined with respect to temperature. In order to maintain a collection temperature of 120 °C (248 °F), Method 5 employs a heated glass sample probe and a heated filter holder. This equipment is somewhat cumbersome and requires care in its operation. Therefore, where PM concentrations (over the normal range of temperature associated with a specified source category) are known to be independent of temperature, it is desirable to eliminate the glass probe and the heating systems, and to sample at stack temperature.

1.2 Applicability. This method is applicable for the determination of PM emissions, where PM concentrations are known to be independent of temperature over the normal range of temperatures characteristic of emissions from a specified source category. It is intended to be used only when specified by an applicable subpart of the standards, and only within the applicable temperature limits (if specified), or when otherwise approved by the Administrator. This method is not applicable to stacks that contain liquid droplets or are saturated with water vapor. In addition, this method shall not be used as written if the projected cross-sectional area of the probe extension-filter holder assembly covers more than 5 percent of the stack cross-sectional area (see section 8.1.2).

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at stack temperature. The PM mass is determined gravimetrically after the removal of uncombined water.

3.0 Definitions

Same as Method 5, section 3.0.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 17–1. The sampling train components and operation and maintenance are very similar to Method 5, which should be consulted for details.

6.1.1 Probe Nozzle, Differential Pressure Gauge, Metering System, Barometer, Gas Density Determination Equipment. Same as in Method 5, sections 6.1.1, 6.1.4, 6.1.8, 6.1.9, and 6.1.10, respectively.

6.1.2 Filter Holder. The in-stack filter holder shall be constructed of borosilicate or

quartz glass, or stainless steel. If a gasket is used, it shall be made of silicone rubber, Teflon, or stainless steel. Other holder and gasket materials may be used, subject to the approval of the Administrator. The filter holder shall be designed to provide a positive seal against leakage from the outside or around the filter.

6.1.3 Probe Extension. Any suitable rigid probe extension may be used after the filter holder.

6.1.4 Pitot Tube. Same as in Method 5, section 6.1.3.

6.1.4.1 It is recommended (1) that the pitot tube have a known baseline coefficient, determined as outlined in section 10 of Method 2; and (2) that this known coefficient be preserved by placing the pitot tube in an interference-free arrangement with respect to the sampling nozzle, filter holder, and temperature sensor (see Figure 17–1). Note that the 1.9 cm (¾-in.) free-space between the nozzle and pitot tube shown in Figure 17–1, is based on a 1.3 cm (½-in.) ID nozzle. If the sampling train is designed for sampling at higher flow rates than that described in APTD-0581, thus necessitating the use of larger sized nozzles, the free-space shall be 1.9 cm (¾-in.) with the largest sized nozzle in place.

6.1.4.2 Source-sampling assemblies that do not meet the minimum spacing requirements of Figure 17–1 (or the equivalent of these requirements, *e.g.*, Figure 2–4 of Method 2) may be used; however, the pitot tube coefficients of such assemblies shall be determined by calibration, using methods subject to the approval of the Administrator.

6.1.5 Condenser. It is recommended that the impinger system or alternatives described in Method 5 be used to determine the moisture content of the stack gas. Flexible tubing may be used between the probe extension and condenser. Long tubing lengths may affect the moisture determination.

6.2 Sample Recovery. Probe-liner and probe-nozzle brushes, wash bottles, glass sample storage containers, petri dishes, graduated cylinder and/or balance, plastic storage containers, funnel and rubber policeman, funnel. Same as in Method 5, sections 6.2.1 through 6.2.8, respectively.

6.3 Sample Analysis. Glass weighing dishes, desiccator, analytical balance, balance, beakers, hygrometer, temperature sensor. Same as in Method 5, sections 6.3.1 through 6.3.7, respectively.

7.0 Reagents and Standards

7.1 Sampling. Filters, silica gel, water, crushed ice, stopcock grease. Same as in Method 5, sections 7.1.1, 7.1.2, 7.1.3, 7.1.4, and 7.1.5, respectively. Thimble glass fiber filters may also be used.

7.2 Sample Recovery. Acetone (reagent grade). Same as in Method 5, section 7.2.

7.3 Sample Analysis. Acetone and Desiccant. Same as in Method 5, sections 7.3.1 and 7.3.2, respectively.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling.

8.1.1 Pretest Preparation. Same as in Method 5, section 8.1.1.

8.1.2 Preliminary Determinations. Same as in Method 5, section 8.1.2, except as follows: Make a projected-area model of the probe extension-filter holder assembly, with the pitot tube face openings positioned along the centerline of the stack, as shown in Figure 17–2. Calculate the estimated cross-section blockage, as shown in Figure 17–2. If the blockage exceeds 5 percent of the duct cross sectional area, the tester has the following options exist: (1) a suitable out-of-stack filtration method may be used instead of in-stack filtration; or (2) a special in-stack arrangement, in which the sampling and velocity measurement sites are separate, may be used; for details concerning this approach, consult with the Administrator (see also Reference 1 in section 17.0). Select a probe extension length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probes.

8.1.3 Preparation of Sampling Train. Same as in Method 5, section 8.1.3, except the following: Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as not to allow the sample gas stream to circumvent the filter. Check filter for tears after assembly is completed. Mark the probe extension with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point. Assemble the train as in Figure 17–1, using a very light coat of silicone grease on all ground glass joints and greasing only the outer portion (see APTD–0576) to avoid possibility of contamination by the silicone grease. Place crushed ice around the impingers.

8.1.4 Leak-Check Procedures. Same as in Method 5, section 8.1.4, except that the filter holder is inserted into the stack during the sampling train leak-check. To do this, plug the inlet to the probe nozzle with a material that will be able to withstand the stack temperature. Insert the filter holder into the stack and wait approximately 5 minutes (or longer, if necessary) to allow the system to come to equilibrium with the temperature of the stack gas stream.

8.1.5 Sampling Train Operation. The operation is the same as in Method 5. Use a data sheet such as the one shown in Figure 5–3 of Method 5, except that the filter holder temperature is not recorded.

8.1.6 Calculation of Percent Isokinetic. Same as in Method 5, section 12.11.

8.2 Sample Recovery.

8.2.1 Proper cleanup procedure begins as soon as the probe extension assembly is removed from the stack at the end of the sampling period. Allow the assembly to cool.

8.2.2 When the assembly can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to prevent losing or gaining particulate matter. Do not cap off the probe tip tightly while the sampling train is cooling down as this would create a vacuum in the filter holder, forcing condenser water backward.

8.2.3 Before moving the sample train to the cleanup site, disconnect the filter holder-probe nozzle assembly from the probe extension; cap the open inlet of the probe extension. Be careful not to lose any condensate, if present. Remove the umbilical cord from the condenser outlet and cap the outlet. If a flexible line is used between the first impinger (or condenser) and the probe extension, disconnect the line at the probe extension and let any condensed water or liquid drain into the impingers or condenser. Disconnect the probe extension from the condenser; cap the probe extension outlet. After wiping off the silicone grease, cap off the condenser inlet. Ground glass stoppers, plastic caps, or serum caps (whichever are appropriate) may be used to close these openings.

8.2.4 Transfer both the filter holder-probe nozzle assembly and the condenser to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

8.2.5 Save a portion of the acetone used for cleanup as a blank. Take 200 ml of this acetone from the wash bottle being used and place it in a glass sample container labeled ''acetone blank.'' Inspect the train prior to and during disassembly and not any abnormal conditions. Treat the sample as discussed in Method 5, section 8.2.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization

The calibrations of the probe nozzle, pitot tube, metering system, temperature sensors, and barometer are the same as in Method 5, sections 10.1 through 10.3, 10.5, and 10.6, respectively.

11.0 Analytical Procedure

Same as in Method 5, section 11.0. Analytical data should be recorded on a form similar to that shown in Figure 5–6 of Method 5.

12.0 Data Analysis and Calculations.

Same as in Method 5, section 12.0.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

Same as in Method 5, section 16.0.

17.0 References

Same as in Method 5, section 17.0, with the addition of the following:

1. Vollaro, R.F. Recommended Procedure for Sample Traverses in Ducts Smaller than 12 Inches in Diameter. U.S. Environmental Protection Agency, Emission Measurement Branch. Research Triangle Park, NC. November 1976.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

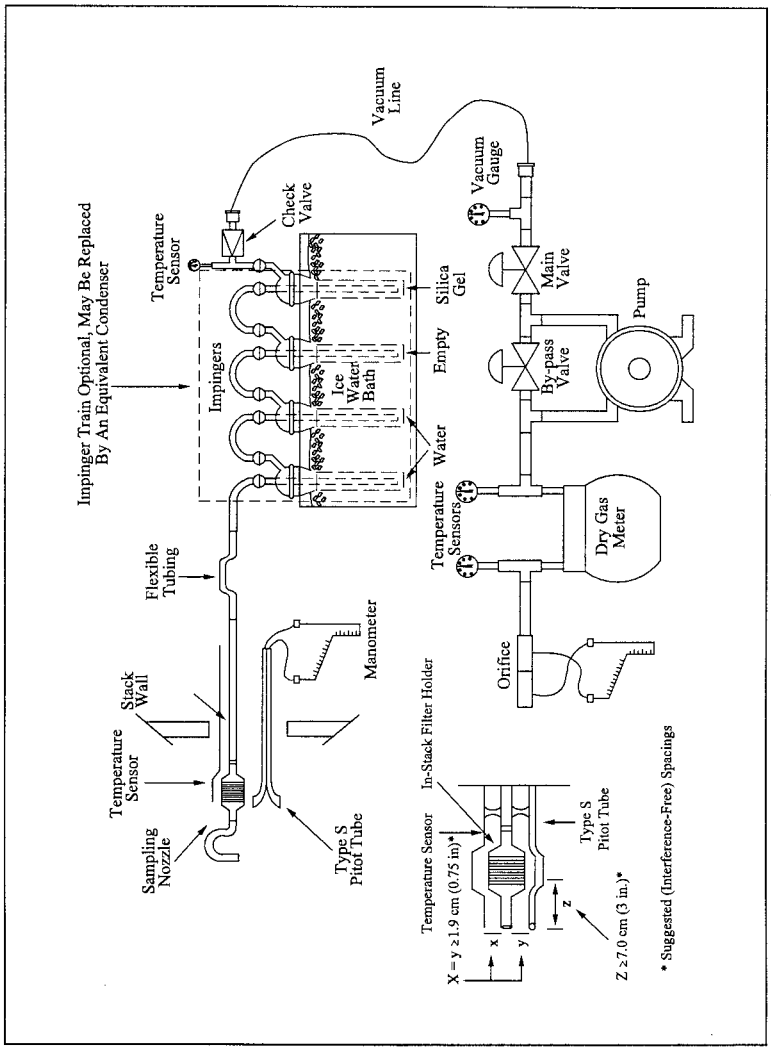

Figure 17-1. Particulate Matter Sampling Train with In-Stack Filter.

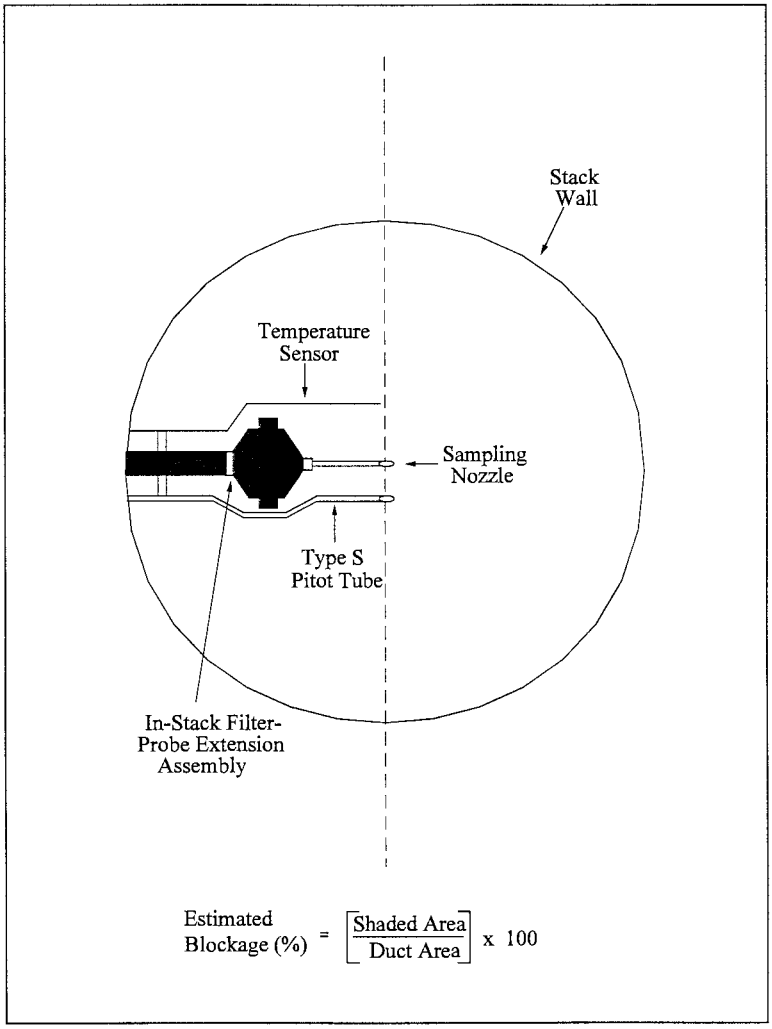

Figure 17-2. Projected-Area Model of Cross-Section Blockage (approximate average for a sample traverse) Caused by an In-Stack Filter Holder-Probe Extension Assembly.

METHOD 18—MEASUREMENT OF GASEOUS ORGANIC COMPOUND EMISSIONS BY GAS CHROMATOGRAPHY

NOTE: This method is not inclusive with respect to specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3.

NOTE: This method should not be attempted by persons unfamiliar with the performance characteristics of gas chromatography, nor by those persons who are unfamiliar with source sampling. Particular care

should be exercised in the area of safety concerning choice of equipment and operation in potentially explosive atmospheres.

1.0 Scope and Application

1.1 Analyte. Total gaseous organic compounds.

1.2 Applicability.

1.2.1 This method is designed to measure gaseous organics emitted from an industrial source. While designed for ppm level sources, some detectors are quite capable of detecting compounds at ambient levels, *e.g.*, ECD, ELCD, and helium ionization detectors. Some other types of detectors are evolving such that the sensitivity and applicability may well be in the ppb range in only a few years.

1.2.2 This method will not determine compounds that (1) are polymeric (high molecular weight), (2) can polymerize before analysis, or (3) have very low vapor pressures at stack or instrument conditions.

1.3 Range. The lower range of this method is determined by the sampling system; adsorbents may be used to concentrate the sample, thus lowering the limit of detection below the 1 part per million (ppm) typically achievable with direct interface or bag sampling. The upper limit is governed by GC detector saturation or column overloading; the upper range can be extended by dilution of sample with an inert gas or by using smaller volume gas sampling loops. The upper limit can also be governed by condensation of higher boiling compounds.

1.4 Sensitivity. The sensitivity limit for a compound is defined as the minimum detectable concentration of that compound, or the concentration that produces a signal-to-noise ratio of three to one. The minimum detectable concentration is determined during the presurvey calibration for each compound.

2.0 Summary of Method

The major organic components of a gas mixture are separated by gas chromatography (GC) and individually quantified by flame ionization, photoionization, electron capture, or other appropriate detection principles. The retention times of each separated component are compared with those of known compounds under identical conditions. Therefore, the analyst confirms the identity and approximate concentrations of the organic emission components beforehand. With this information, the analyst then prepares or purchases commercially available standard mixtures to calibrate the GC under conditions identical to those of the samples. The analyst also determines the need for sample dilution to avoid detector saturation, gas stream filtration to eliminate particulate matter, and prevention of moisture condensation.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Resolution interferences that may occur can be eliminated by appropriate GC column and detector choice or by shifting the retention times through changes in the column flow rate and the use of temperature programming.

4.2 The analytical system is demonstrated to be essentially free from contaminants by periodically analyzing blanks that consist of hydrocarbon-free air or nitrogen.

4.3 Sample cross-contamination that occurs when high-level and low-level samples or standards are analyzed alternately is best dealt with by thorough purging of the GC sample loop between samples.

4.4 To assure consistent detector response, calibration gases are contained in dry air. To adjust gaseous organic concentrations when water vapor is present in the sample, water vapor concentrations are determined for those samples, and a correction factor is applied.

4.5 The gas chromatograph run time must be sufficient to clear all eluting peaks from the column before proceeding to the next run (in order to prevent sample carryover).

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

6.0 Equipment and Supplies

6.1 Equipment needed for the presurvey sampling procedure can be found in section 16.1.1.

6.2 Equipment needed for the integrated bag sampling and analysis procedure can be found in section 8.2.1.1.1.

6.3 Equipment needed for direct interface sampling and analysis can be found in section 8.2.2.1.

6.4 Equipment needed for the dilution interface sampling and analysis can be found in section 8.2.3.1.

6.5 Equipment needed for adsorbent tube sampling and analysis can be found in section 8.2.4.1.

7.0 Reagents and Standards

7.1 Reagents needed for the presurvey sampling procedure can be found in section 16.1.2.

8.0 Sample Collection, Preservation, Storage, and Transport

8.2 Final Sampling and Analysis Procedure. Considering safety (flame hazards) and the source conditions, select an appropriate sampling and analysis procedure (Section 8.2.1, 8.2.2, 8.2.3 or 8.2.4). In situations where a hydrogen flame is a hazard and no intrinsically safe GC is suitable, use the flexible bag collection technique or an adsorption technique.

8.2.1 Integrated Bag Sampling and Analysis.

8.2.1.1 Evacuated Container Sampling Procedure. In this procedure, the bags are filled by evacuating the rigid air-tight container holding the bags. Use a field sample data sheet as shown in Figure 18–10. Collect triplicate samples from each sample location.

8.2.1.1.1 Apparatus.

8.2.1.1.1.1 Probe. Stainless steel, Pyrex glass, or Teflon tubing probe, according to the duct temperature, with Teflon tubing of sufficient length to connect to the sample bag. Use stainless steel or Teflon unions to connect probe and sample line.

8.2.1.1.1.2 Quick Connects. Male (2) and female (2) of stainless steel construction.

8.2.1.1.1.3 Needle Valve. To control gas flow.

8.2.1.1.1.4 Pump. Leakless Teflon-coated diaphragm-type pump or equivalent. To deliver at least 1 liter/min.

8.2.1.1.1.5 Charcoal Adsorption Tube. Tube filled with activated charcoal, with glass wool plugs at each end, to adsorb organic vapors.

8.2.1.1.1.6 Flowmeter. 0 to 500-ml flow range; with manufacturer's calibration curve.

8.2.1.1.2 Sampling Procedure. To obtain a sample, assemble the sample train as shown in Figure 18–9. Leak-check both the bag and the container. Connect the vacuum line from the needle valve to the Teflon sample line from the probe. Place the end of the probe at the centroid of the stack or at a point no closer to the walls than 1 in., and start the pump. Set the flow rate so that the final volume of the sample is approximately 80 percent of the bag capacity. After allowing sufficient time to purge the line several times, connect the vacuum line to the bag, and evacuate until the rotameter indicates no flow. Then position the sample and vacuum lines for sampling, and begin the actual sampling, keeping the rate proportional to the stack velocity. As a precaution, direct the gas exiting the rotameter away from sampling personnel. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Record the source temperature, barometric pressure, ambient temperature, sampling flow rate, and initial and final sampling time on the data sheet shown in Figure 18–10. Protect the bag and its container from sunlight. Record the time lapsed between sample collection and analysis, and then conduct the recovery procedure in Section 8.4.2.

8.2.1.2 Direct Pump Sampling Procedure. Follow 8.2.1.1, except place the pump and needle valve between the probe and the bag. Use a pump and needle valve constructed of inert material not affected by the stack gas. Leak-check the system, and then purge with stack gas before connecting to the previously evacuated bag.

8.2.1.3 Explosion Risk Area Bag Sampling Procedure. Follow 8.2.1.1 except replace the pump with another evacuated can (see Figure 18–9a). Use this method whenever there is a possibility of an explosion due to pumps, heated probes, or other flame producing equipment.

8.2.1.4 Other Modified Bag Sampling Procedures. In the event that condensation is observed in the bag while collecting the sample and a direct interface system cannot be used, heat the bag during collection and maintain it at a suitably elevated temperature during all subsequent operations. (Note: Take care to leak-check the system prior to the dilutions so as not to create a potentially explosive atmosphere.) As an alternative, collect the sample gas, and simultaneously dilute it in the bag.

8.2.1.4.1 First Alternative Procedure. Heat the box containing the sample bag to 120 °C (±5 °C). Then transport the bag as rapidly as possible to the analytical area while maintaining the heating, or cover the box with an insulating blanket. In the analytical area, keep the box heated to 120 °C (±5 °C) until analysis. Be sure that the method of heating the box and the control for the heating circuit are compatible with the safety restrictions required in each area.

8.2.1.4.2 Second Alternative Procedure. Prefill the bag with a known quantity of inert gas. Meter the inert gas into the bag according to the procedure for the preparation of gas concentration standards of volatile liquid materials (Section 10.1.2.2), but eliminate the midget impinger section. Take the partly filled bag to the source, and meter the source gas into the bag through heated sampling lines and a heated flowmeter, or Teflon positive displacement pump. Verify the dilution factors before sampling each bag through dilution and analysis of gases of known concentration.

8.2.1.5 Analysis of Bag Samples.

8.2.1.5.1 Apparatus. Same as section 8.1. A minimum of three gas standards are required.

8.2.1.5.2 Procedure.

8.2.1.5.2.1 Establish proper GC operating conditions as described in section 10.2, and record all data listed in Figure 18–7. Prepare the GC so that gas can be drawn through the sample valve. Flush the sample loop with

calibration gas mixture, and activate the valve (sample pressure at the inlet to the GC introduction valve should be similar during calibration as during actual sample analysis). Obtain at least three chromatograms for the mixture. The results are acceptable when the peak areas for the three injections agree to within 5 percent of their average. If they do not agree, run additional samples or correct the analytical techniques until this requirement is met. Then analyze the other two calibration mixtures in the same manner. Prepare a calibration curve as described in section 10.2.

8.2.1.5.2.2 Analyze the three source gas samples by connecting each bag to the sampling valve with a piece of Teflon tubing identified with that bag. Analyze each bag sample three times. Record the data in Figure 18–11. If certain items do not apply, use the notation ''N.A.'' If the bag has been maintained at an elevated temperature as described in section 8.2.1.4, determine the stack gas water content by Method 4. After all samples have been analyzed, repeat the analysis of the mid-level calibration gas for each compound. Compare the average response factor of the pre- and post-test analysis for each compound. If they differ by >5percent, analyze the other calibration gas levels for that compound, and prepare a calibration curve using all the pre- and post-test calibration gas mixture values. If the two response factor averages (pre-and post-test) differ by less than 5 percent from their mean value, the tester has the option of using only the pre-test calibration curve to generate the concentration values.

8.2.1.6 Determination of Bag Water Vapor Content. Measure the ambient temperature and barometric pressure near the bag. From a water saturation vapor pressure table, determine and record the water vapor content of the bag as a decimal figure. (Assume the relative humidity to be 100 percent unless a lesser value is known.) If the bag has been maintained at an elevated temperature as described in section 8.2.1.4, determine the stack gas water content by Method 4.

8.2.1.8 Emission Calculations. From the calibration curve described in section 8.2.1.5, select the value of C_s that corresponds to the peak area. Calculate the concentration C_c in ppm, dry basis, of each organic in the sample using Equation 18–5 in section 12.6.

8.2.2 Direct Interface Sampling and Analysis Procedure. The direct interface procedure can be used provided that the moisture content of the gas does not interfere with the analysis procedure, the physical requirements of the equipment can be met at the site, and the source gas concentration falls within the linear range of the detector. Adhere to all safety requirements with this method.

8.2.2.1 Apparatus.

8.2.2.1.1 Probe. Constructed of stainless steel, Pyrex glass, or Teflon tubing as dictated by duct temperature and reactivity of target compounds. A filter or glass wool plug may be needed if particulate is present in the stack gas. If necessary, heat the probe with heating tape or a special heating unit capable of maintaining a temperature greater than 110 °C.

8.2.2.1.2 Sample Lines. 6.4-mm OD (or other diameter as needed) Teflon lines, heat-traced to prevent condensation of material (greater than 110 °C).

8.2.2.1.3 Quick Connects. To connect sample line to gas sampling valve on GC instrument and to pump unit used to withdraw source gas. Use a quick connect or equivalent on the cylinder or bag containing calibration gas to allow connection of the calibration gas to the gas sampling valve.

8.2.2.1.4 Thermocouple Readout Device. Potentiometer or digital thermometer, to measure source temperature and probe temperature.

8.2.2.1.5 Heated Gas Sampling Valve. Of two-position, six-port design, to allow sample loop to be purged with source gas or to direct source gas into the GC instrument.

8.2.2.1.6 Needle Valve. To control gas sampling rate from the source.

8.2.2.1.7 Pump. Leakless Teflon-coated diaphragm-type pump or equivalent, capable of at least 1 liter/minute sampling rate.

8.2.2.1.8 Flowmeter. Of suitable range to measure sampling rate.

8.2.2.1.9 Charcoal Adsorber. To adsorb organic vapor vented from the source to prevent exposure of personnel to source gas.

8.2.2.1.10 Gas Cylinders. Carrier gas, oxygen and fuel as needed to run GC and detector.

8.2.2.1.11 Gas Chromatograph. Capable of being moved into the field, with detector, heated gas sampling valve, column required to complete separation of desired components, and option for temperature programming.

8.2.2.1.12 Recorder/Integrator. To record results.

8.2.2.2 Procedure. Calibrate the GC using the procedures in section 8.2.1.5.2.1. To obtain a stack gas sample, assemble the sampling system as shown in Figure 18–12. Make sure all connections are tight. Turn on the probe and sample line heaters. As the temperature of the probe and heated line approaches the target temperature as indicated on the thermocouple readout device, control the heating to maintain a temperature greater than 110 °C. Conduct a 3-point calibration of the GC by analyzing each gas mixture in triplicate. Generate a calibration curve. Place the inlet of the probe at the centroid of the duct, or at a point no closer to the walls than 1 m, and draw source gas into the probe, heated line, and sample loop. After thorough flushing, analyze the stack gas sample using the same conditions as for

the calibration gas mixture. For each run, sample, analyze, and record five consecutive samples. A test consists of three runs (five samples per run times three runs, for a total of fifteen samples). After all samples have been analyzed, repeat the analysis of the mid-level calibration gas for each compound. For each calibration standard, compare the pre- and post-test average response factors (RF) for each compound. If the two calibration RF values (pre- and post-analysis) differ by more than 5 percent from their mean value, then analyze the other calibration gas levels for that compound and determine the stack gas sample concentrations by comparison to both calibration curves (this is done by preparing a calibration curve using all the pre- and post-test calibration gas mixture values.) If the two calibration RF values differ by less than 5 percent from their mean value, the tester has the option of using only the pre-test calibration curve to generate the concentration values. Record this calibration data and the other required data on the data sheet shown in Figure 18–11, deleting the dilution gas information.

NOTE: Take care to draw all samples and calibration mixtures through the sample loop at the same pressure.

8.2.2.3 Determination of Stack Gas Moisture Content. Use Method 4 to measure the stack gas moisture content.

8.2.2.5 Emission Calculations. Same as section 8.2.1.8.

8.2.3 Dilution Interface Sampling and Analysis Procedure. Source samples that contain a high concentration of organic materials may require dilution prior to analysis to prevent saturating the GC detector. The apparatus required for this direct interface procedure is basically the same as that described in the section 8.2.2, except a dilution system is added between the heated sample line and the gas sampling valve. The apparatus is arranged so that either a 10:1 or 100:1 dilution of the source gas can be directed to the chromatograph. A pump of larger capacity is also required, and this pump must be heated and placed in the system between the sample line and the dilution apparatus.

8.2.3.1 Apparatus. The equipment required in addition to that specified for the direct interface system is as follows:

8.2.3.1.1 Sample Pump. Leakless Teflon-coated diaphragm-type that can withstand being heated to 120 °C and deliver 1.5 liters/minute.

8.2.3.1.2 Dilution Pumps. Two Model A–150 Komhyr Teflon positive displacement type delivering 150 cc/minute, or equivalent. As an option, calibrated flowmeters can be used in conjunction with Teflon-coated diaphragm pumps.

8.2.3.1.3 Valves. Two Teflon three-way valves, suitable for connecting to Teflon tubing.

8.2.3.1.4 Flowmeters. Two, for measurement of diluent gas.

8.2.3.1.5 Diluent Gas with Cylinders and Regulators. Gas can be nitrogen or clean dry air, depending on the nature of the source gases.

8.2.3.1.6 Heated Box. Suitable for being heated to 120 °C, to contain the three pumps, three-way valves, and associated connections. The box should be equipped with quick connect fittings to facilitate connection of: (1) the heated sample line from the probe, (2) the gas sampling valve, (3) the calibration gas mixtures, and (4) diluent gas lines. A schematic diagram of the components and connections is shown in Figure 18–13. The heated box shown in Figure 18–13 is designed to receive a heated line from the probe. An optional design is to build a probe unit that attaches directly to the heated box. In this way, the heated box contains the controls for the probe heaters, or, if the box is placed against the duct being sampled, it may be possible to eliminate the probe heaters. In either case, a heated Teflon line is used to connect the heated box to the gas sampling valve on the chromatograph.

NOTE: Care must be taken to leak-check the system prior to the dilutions so as not to create a potentially explosive atmosphere.

8.2.3.2 Procedure.

8.2.3.2.1 Assemble the apparatus by connecting the heated box, shown in Figure 18–13, between the heated sample line from the probe and the gas sampling valve on the chromatograph. Vent the source gas from the gas sampling valve directly to the charcoal filter, eliminating the pump and rotameter. Heat the sample probe, sample line, and heated box. Insert the probe and source thermocouple at the centroid of the duct, or to a point no closer to the walls than 1 m. Measure the source temperature, and adjust all heating units to a temperature 0 to 3 °C above this temperature. If this temperature is above the safe operating temperature of the Teflon components, adjust the heating to maintain a temperature high enough to prevent condensation of water and organic compounds (greater than 110 °C). Calibrate the GC through the dilution system by following the procedures in section 8.2.1.5.2.1. Determine the concentration of the diluted calibration gas using the dilution factor and the certified concentration of the calibration gas. Record the pertinent data on the data sheet shown in Figure 18–11.

8.2.3.2.2 Once the dilution system and GC operations are satisfactory, proceed with the analysis of source gas, maintaining the same dilution settings as used for the standards.

8.2.3.2.3 Analyze the audit samples using either the dilution system, or directly connect to the gas sampling valve as required. Record all data and report the results to the audit supervisor.

8.2.3.3 Determination of Stack Gas Moisture Content. Same as section 8.2.2.3.

8.2.3.4 Quality Assurance. Same as section 8.2.2.4.

8.2.3.5 Emission Calculations. Same as section 8.2.2.5, with the dilution factor applied.

8.2.4 Adsorption Tube Procedure. Any commercially available adsorbent is allowed for the purposes of this method, as long as the recovery study criteria in section 8.4.3 are met. Help in choosing the adsorbent may be found by calling the distributor, or the tester may refer to National Institute for Occupational Safety and Health (NIOSH) methods for the particular organics to be sampled. For some adsorbents, the principal interferent will be water vapor. If water vapor is thought to be a problem, the tester may place a midget impinger in an ice bath before the adsorbent tubes. If this option is chosen, the water catch in the midget impinger shall be analyzed for the target compounds. Also, the spike for the recovery study (in section 8.4.3) shall be conducted in both the midget impinger and the adsorbent tubes. The combined recovery (add the recovered amount in the impinger and the adsorbent tubes to calculate R) shall then meet the criteria in section 8.4.3.

NOTE: Post-test leak-checks are not allowed for this technique since this can result in sample contamination.

8.2.4.1 Additional Apparatus. The following items (or equivalent) are suggested.

8.2.4.1.1 Probe. Borosilicate glass or stainless steel, approximately 6-mm ID, with a heating system if water condensation is a problem, and a filter (either in-stack or out-of-stack, heated to stack temperature) to remove particulate matter. In most instances, a plug of glass wool is a satisfactory filter.

8.2.4.1.2 Flexible Tubing. To connect probe to adsorption tubes. Use a material that exhibits minimal sample adsorption.

8.2.4.1.3 Leakless Sample Pump. Flow controlled, constant rate pump, with a set of limiting (sonic) orifices.

8.2.4.1.4 Bubble-Tube Flowmeter. Volume accuracy within 1 percent, to calibrate pump.

8.2.4.1.5 Stopwatch. To time sampling and pump rate calibration.

8.2.4.1.6 Adsorption Tubes. Precleaned adsorbent, with mass of adsorbent to be determined by calculating breakthrough volume and expected concentration in the stack.

8.2.4.1.7 Barometer. Accurate to 5 mm Hg, to measure atmospheric pressure during sampling and pump calibration.

8.2.4.1.8 Rotameter. O to 100 cc/min, to detect changes in flow rate during sampling.

8.2.4.2 Sampling and Analysis.

8.2.4.2.1 Calibrate the pump and limiting orifice flow rate through adsorption tubes with the bubble tube flowmeter before sampling. The sample system can be operated as a ''recirculating loop'' for this operation. Record the ambient temperature and barometric pressure. Then, during sampling, use the rotameter to verify that the pump and orifice sampling rate remains constant.

8.2.4.2.2 Use a sample probe, if required, to obtain the sample at the centroid of the duct or at a point no closer to the walls than 1 m. Minimize the length of flexible tubing between the probe and adsorption tubes. Several adsorption tubes can be connected in series, if the extra adsorptive capacity is needed. Adsorption tubes should be maintained vertically during the test in order to prevent channeling. Provide the gas sample to the sample system at a pressure sufficient for the limiting orifice to function as a sonic orifice. Record the total time and sample flow rate (or the number of pump strokes), the barometric pressure, and ambient temperature. Obtain a total sample volume commensurate with the expected concentration(s) of the volatile organic(s) present and recommended sample loading factors (weight sample per weight adsorption media). Laboratory tests prior to actual sampling may be necessary to predetermine this volume. If water vapor is present in the sample at concentrations above 2 to 3 percent, the adsorptive capacity may be severely reduced. Operate the gas chromatograph according to the manufacturer's instructions. After establishing optimum conditions, verify and document these conditions during all operations. Calibrate the instrument and then analyze the emission samples.

8.2.4.3 Standards and Calibration. If using thermal desorption, obtain calibration gases using the procedures in section 10.1. If using solvent extraction, prepare liquid standards in the desorption solvent. Use a minimum of three different standards; select the concentrations to bracket the expected average sample concentration. Perform the calibration before and after each day's sample analyses using the procedures in section 8.2.1.5.2.1.

8.2.4.4 Quality Assurance.

8.2.4.4.1 Determine the recovery efficiency of the pollutants of interest according to section 8.4.3.

8.2.4.4.2 Determination of Sample Collection Efficiency (Optional). If sample breakthrough is thought to be a problem, a routine procedure for determining breakthrough is to analyze the primary and backup portions of the adsorption tubes separately. If the backup portion exceeds 10 percent of the total amount (primary and back-up), it is usually a sign of sample breakthrough. For the purposes of this method, only the recovery efficiency value (Section 8.4.3) is used to determine the appropriateness of the sampling and analytical procedure.

8.2.4.4.3 Volume Flow Rate Checks. Perform this check immediately after sampling with all sampling train components in place.

Use the bubble-tube flowmeter to measure the pump volume flow rate with the orifice used in the test sampling, and record the result. If it has changed by more than 5 but less than 20 percent, calculate an average flow rate for the test. If the flow rate has changed by more than 20 percent, recalibrate the pump and repeat the sampling.

8.2.4.4.4 Calculations. Correct all sample volumes to standard conditions. If a sample dilution system has been used, multiply the results by the appropriate dilution ratio. Correct all results according to the applicable procedure in section 8.4.3. Report results as ppm by volume, dry basis.

8.3 Reporting of Results. At the completion of the field analysis portion of the study, ensure that the data sheets shown in Figure 18–11 have been completed. Summarize this data on the data sheets shown in Figure 18–15.

8.4 Recovery Study. After conducting the presurvey and identifying all of the pollutants of interest, conduct the appropriate recovery study during the test based on the sampling system chosen for the compounds of interest.

8.4.1 Recovery Study for Direct Interface or Dilution Interface Sampling. If the procedures in section 8.2.2 or 8.2.3 are to be used to analyze the stack gas, conduct the calibration procedure as stated in section 8.2.2.2 or 8.2.3.2, as appropriate. Upon successful completion of the appropriate calibration procedure, attach the mid-level calibration gas for at least one target compound to the inlet of the probe or as close as possible to the inlet of the probe, but before the filter. Repeat the calibration procedure by sampling and analyzing the mid-level calibration gas through the entire sampling and analytical system in triplicate. The mean of the calibration gas response sampled through the probe shall be within 10 percent of the analyzer response. If the difference in the two means is greater than 10 percent, check for leaks throughout the sampling system and repeat the analysis of the standard through the sampling system until this criterion is met.

8.4.2 Recovery Study for Bag Sampling.

8.4.2.1 Follow the procedures for the bag sampling and analysis in section 8.2.1. After analyzing all three bag samples, choose one of the bag samples and tag this bag as the spiked bag. Spike the chosen bag sample with a known mixture (gaseous or liquid) of all of the target pollutants. The theoretical concentration, in ppm, of each spiked compound in the bag shall be 40 to 60 percent of the average concentration measured in the three bag samples. If a target compound was not detected in the bag samples, the concentration of that compound to be spiked shall be 5 times the limit of detection for that compound. Store the spiked bag for the same period of time as the bag samples collected in the field. After the appropriate storage time has passed, analyze the spiked bag three times. Calculate the average fraction recovered (R) of each spiked target compound with the equation in section 12.7.

8.4.2.2 For the bag sampling technique to be considered valid for a compound, $0.70 \leq R \leq 1.30$. If the R value does not meet this criterion for a target compound, the sampling technique is not acceptable for that compound, and therefore another sampling technique shall be evaluated for acceptance (by repeating the recovery study with another sampling technique). Report the R value in the test report and correct all field measurements with the calculated R value for that compound by using the equation in section 12.8.

8.4.3 Recovery Study for Adsorption Tube Sampling. If following the adsorption tube procedure in section 8.2.4, conduct a recovery study of the compounds of interest during the actual field test. Set up two identical sampling trains. Collocate the two sampling probes in the stack. The probes shall be placed in the same horizontal plane, where the first probe tip is 2.5 cm from the outside edge of the other. One of the sampling trains shall be designated the spiked train and the other the unspiked train. Spike all of the compounds of interest (in gaseous or liquid form) onto the adsorbent tube(s) in the spiked train before sampling. The mass of each spiked compound shall be 40 to 60 percent of the mass expected to be collected with the unspiked train. Sample the stack gas into the two trains simultaneously. Analyze the adsorbents from the two trains utilizing identical analytical procedures and instrumentation. Determine the fraction of spiked compound recovered (R) using the equations in section 12.9.

8.4.3.1 Repeat the procedure in section 8.4.3 twice more, for a total of three runs. In order for the adsorbent tube sampling and analytical procedure to be acceptable for a compound, $0.70 \leq R \leq 1.30$ (R in this case is the average of three runs). If the average R value does not meet this criterion for a target compound, the sampling technique is not acceptable for that compound, and therefore another sampling technique shall be evaluated for acceptance (by repeating the recovery study with another sampling technique). Report the R value in the test report and correct all field measurements with the calculated R value for that compound by using the equation in section 12.8.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures

Section	Quality control measure	Effect
8.4.1	Recovery study for direct interface or dilution interface sampling.	Ensure that there are no significant leaks in the sampling system.
8.4.2	Recovery study for bag sampling	Demonstrate that proper sampling/analysis procedures were selected.
8.4.3	Recovery study for adsorption tube sampling.	Demonstrate that proper sampling/analysis procedures were selected.

10.0 Calibration and Standardization.

10.1 Calibration Standards. Obtain calibration gas standards for each target compound to be analyzed. Commercial cylinder gases certified by the manufacturer to be accurate to within 1 percent of the certified label value are preferable, although cylinder gases certified by the manufacturer to 2 percent accuracy are allowed. Another option allowed by this method is for the tester to obtain high concentration certified cylinder gases and then use a dilution system meeting the requirements of Test Method 205, 40 CFR Part 51, Appendix M to make multilevel calibration gas standards. Prepare or obtain enough calibration standards so that there are three different concentrations of each organic compound expected to be measured in the source sample. For each organic compound, select those concentrations that bracket the concentrations expected in the source samples. A calibration standard may contain more than one organic compound. If samples are collected in adsorbent tubes and extracted using solvent extraction, prepare or obtain standards in the same solvent used for the sample extraction procedure. Verify the stability of all standards for the time periods they are used.

10.2 Preparation of Calibration Curves.

10.2.1 Establish proper GC conditions, then flush the sampling loop for 30 seconds. Allow the sample loop pressure to equilibrate to atmospheric pressure, and activate the injection valve. Record the standard concentration, attenuator factor, injection time, chart speed, retention time, peak area, sample loop temperature, column temperature, and carrier gas flow rate. Analyze each standard in triplicate.

10.2.2 Repeat this procedure for each standard. Prepare a graphical plot of concentration (C_s) versus the calibration area values. Perform a regression analysis, and draw the least square line.

11.0 Analytical Procedures

11.1 Analysis Development

11.1.1 Selection of GC Parameters

11.1.1.1 Column Choice. Based on the initial contact with plant personnel concerning the plant process and the anticipated emissions, choose a column that provides good resolution and rapid analysis time. The choice of an appropriate column can be aided by a literature search, contact with manufacturers of GC columns, and discussion with personnel at the emission source.

NOTE: Most column manufacturers keep excellent records on their products. Their technical service departments may be able to recommend appropriate columns and detector type for separating the anticipated compounds, and they may be able to provide information on interferences, optimum operating conditions, and column limitations. Plants with analytical laboratories may be able to provide information on their analytical procedures.

11.1.1.2 Preliminary GC Adjustment. Using the standards and column obtained in section 11.1.1.1, perform initial tests to determine appropriate GC conditions that provide good resolution and minimum analysis time for the compounds of interest.

11.1.1.3 Preparation of Presurvey Samples. If the samples were collected on an adsorbent, extract the sample as recommended by the manufacturer for removal of the compounds with a solvent suitable to the type of GC analysis. Prepare other samples in an appropriate manner.

11.1.1.4 Presurvey Sample Analysis.

11.1.1.4.1 Before analysis, heat the presurvey sample to the duct temperature to vaporize any condensed material. Analyze the samples by the GC procedure, and compare the retention times against those of the calibration samples that contain the components expected to be in the stream. If any compounds cannot be identified with certainty by this procedure, identify them by other means such as GC/mass spectroscopy (GC/MS) or GC/infrared techniques. A GC/MS system is recommended.

11.1.1.4.2 Use the GC conditions determined by the procedure of section 11.1.1.2 for the first injection. Vary the GC parameters during subsequent injections to determine the optimum settings. Once the optimum settings have been determined, perform repeat injections of the sample to determine the retention time of each compound. To inject a sample, draw sample through the loop at a constant rate (100 ml/min for 30 seconds). Be careful not to pressurize the gas in the loop. Turn off the pump and allow the gas in the sample loop to come to ambient pressure. Activate the sample valve, and record injection time, loop temperature, column temperature, carrier flow rate, chart speed, and attenuator setting. Calculate the retention

time of each peak using the distance from injection to the peak maximum divided by the chart speed. Retention times should be repeatable within 0.5 seconds.

11.1.1.4.3 If the concentrations are too high for appropriate detector response, a smaller sample loop or dilutions may be used for gas samples, and, for liquid samples, dilution with solvent is appropriate. Use the standard curves (Section 10.2) to obtain an estimate of the concentrations.

11.1.1.4.4 Identify all peaks by comparing the known retention times of compounds expected to be in the retention times of peaks in the sample. Identify any remaining unidentified peaks which have areas larger than 5 percent of the total using a GC/MS, or estimation of possible compounds by their retention times compared to known compounds, with confirmation by further GC analysis.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

B_{ws} = Water vapor content of the bag sample or stack gas, proportion by volume.
C_s = Concentration of the organic from the calibration curve, ppm.
G_v = Gas volume or organic compound injected, ml.
L_v = Liquid volume of organic injected, µl.
M = Molecular weight of organic, g/g-mole.
m_s = Total mass of compound measured on adsorbent with spiked train (µg).
m_u = Total mass of compound measured on adsorbent with unspiked train (µg).
m_v = Mass per volume of spiked compound measured (µg/L).
P_i = Barometric or absolute sample loop pressure at time of sample analysis, mm Hg.
P_m = Absolute pressure of dry gas meter, mm Hg.
P_r = Reference pressure, the barometric pressure or absolute sample loop pressure recorded during calibration, mm Hg.
P_s = Absolute pressure of syringe before injection, mm Hg.
q_c = Flow rate of the calibration gas to be diluted.
q_{c1} = Flow rate of the calibration gas to be diluted in stage 1.
q_{c2} = Flow rate of the calibration gas to be diluted in stage 2.
q_d = Diluent gas flow rate.
q_{d1} = Flow rate of diluent gas in stage 1.
q_{d2} = Flow rate of diluent gas in stage 2.
s = Theoretical concentration (ppm) of spiked target compound in the bag.
S = Theoretical mass of compound spiked onto adsorbent in spiked train (µg).
t = Measured average concentration (ppm) of target compound and source sample (analysis results subsequent to bag spiking)
T_i = Sample loop temperature at the time of sample analysis, °K.
T_m = Absolute temperature of dry gas meter, °K.
T_s = Absolute temperature of syringe before injection, °K.
u = Source sample average concentration (ppm) of target compound in the bag (analysis results before bag spiking).
V_m = Gas volume indicated by dry gas meter, liters.
v_s = volume of stack gas sampled with spiked train (L).
v_u = volume of stack gas sampled with unspiked train (L).
X = Mole or volume fraction of the organic in the calibration gas to be diluted.
Y = Dry gas meter calibration factor, dimensionless.
µl = Liquid organic density as determined, g/ml.
24.055 = Ideal gas molar volume at 293 °K and 760 mm Hg, liters/g-mole.
1000 = Conversion factor, ml/liter.
10^6 = Conversion to ppm.

12.2 Calculate the concentration, C_s, in ppm using the following equation:

$$C_s = \frac{10^6\left(\overline{X}q_c\right)}{q_c + q_d} \qquad \text{Eq. 18-1}$$

12.3 Calculate the concentration, C_s, in ppm of the organic in the final gas mixture using the following equation:

$$C_s = 10^6\,\overline{X}\left(\frac{q_{c1}}{q_{c1}+q_{d1}}\right)\left(\frac{q_{c2}}{q_{c2}+q_{d2}}\right) \qquad \text{Eq. 18-2}$$

12.4 Calculate each organic standard concentration, C_s, in ppm using the following equation:

$$C_s = \frac{G_v \times 10^6 \frac{293}{T_s} \frac{P_s}{760}}{V_m Y \frac{293}{T_m} \frac{P_m}{760} 1000} = \frac{G_v \times 10^3 \frac{P_s}{T_s} \frac{T_m}{P_m}}{V_m Y} \quad \text{Eq. 18-3}$$

12.5 Calculate each organic standard concentration, C_s, in ppm using the following equation:

$$C_s = \frac{\frac{L_v}{M}\rho\left(24.055 \times 10^6\right)}{V_m Y \frac{293}{T_m} \frac{P_m}{760} 1000} = 6.24 \times 10^4 \frac{L_v \rho T_m}{M V_m Y P_m} \quad \text{Eq. 18-4}$$

12.6 Calculate the concentration, C_c, in ppm, dry basis, of each organic is the sample using the following equation:

$$C_c = \frac{C_s P_r T_i F_r}{P_i T_r \left(1 - B_{ws}\right)} \quad \text{Eq. 18-5}$$

12.7 Calculate the average fraction recovered (R) of each spiked target compound using the following equation:

$$R = \frac{t - u}{s} \quad \text{Eq. 18-6}$$

12.8 Correct all field measurements with the calculated R value for that compound using the following equation:

$$\text{Reported Result} = \frac{\text{Measured Concentration (ppm)}}{R} \quad \text{Eq. 18-7}$$

12.9 Determine the mass per volume of spiked compound measured using the following equation:

$$m_v = \frac{m_s}{V_s} - \frac{m_u}{V_u} \qquad \text{Eq. 18-8}$$

12.10 Calculate the fraction of spiked compound recovered, R, using the following equation:

$$R = \frac{m_v \times v_s}{S} \qquad \text{Eq. 18-9}$$

13.0 Method Performance

13.1 Since a potential sample may contain a variety of compounds from various sources, a specific precision limit for the analysis of field samples is impractical. Precision in the range of 5 to 10 percent relative standard deviation (RSD) is typical for gas chromatographic techniques, but an experienced GC operator with a reliable instrument can readily achieve 5 percent RSD. For this method, the following combined GC/operator values are required.

(a) Precision. Triplicate analyses of calibration standards fall within 5 percent of their mean value.

(c) Recovery. After developing an appropriate sampling and analytical system for the pollutants of interest, conduct the procedure in section 8.4. Conduct the appropriate recovery study in section 8.4 at each sampling point where the method is being applied. Submit the data and results of the recovery procedure with the reporting of results under section 8.3.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Optional Presurvey and Presurvey Sampling.

NOTE: Presurvey screening is optional. Presurvey sampling should be conducted for sources where the target pollutants are not known from previous tests and/or process knowledge.

Perform a presurvey for each source to be tested. Refer to Figure 18–1. Some of the information can be collected from literature surveys and source personnel. Collect gas samples that can be analyzed to confirm the identities and approximate concentrations of the organic emissions.

16.1.1 Apparatus. This apparatus list also applies to sections 8.2 and 11.

16.1.1.1 Teflon Tubing. (Mention of trade names or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.) Diameter and length determined by connection requirements of cylinder regulators and the GC. Additional tubing is necessary to connect the GC sample loop to the sample.

16.1.1.2 Gas Chromatograph. GC with suitable detector, columns, temperature-controlled sample loop and valve assembly, and temperature programmable oven, if necessary. The GC shall achieve sensitivity requirements for the compounds under study.

16.1.1.3 Pump. Capable of pumping 100 ml/min. For flushing sample loop.

16.1.1.4 Flow Meter. To measure flow rates.

16.1.1.5 Regulators. Used on gas cylinders for GC and for cylinder standards.

16.1.1.6 Recorder. Recorder with linear strip chart is minimum acceptable. Integrator (optional) is recommended.

16.1.1.7 Syringes. 0.5-ml, 1.0- and 10-microliter size, calibrated, maximum accuracy (gas tight) for preparing calibration standards. Other appropriate sizes can be used.

16.1.1.8 Tubing Fittings. To plumb GC and gas cylinders.

16.1.1.9 Septa. For syringe injections.

16.1.1.10 Glass Jars. If necessary, clean, colored glass jars with Teflon-lined lids for condensate sample collection. Size depends on volume of condensate.

16.1.1.11 Soap Film Flowmeter. To determine flow rates.

16.1.1.12 Flexible Bags. Tedlar or equivalent, 10- and 50-liter capacity, for preparation of standards. (Verify through the manufacturer that the Tedlar alternative is suitable for the compound of interest and make this verifying information available for inspection.)

16.1.1.13 Dry Gas Meter with Temperature and Pressure Gauges. Accurate to ±2 percent, for preparation of gas standards.

16.1.1.14 Midget Impinger/Hot Plate Assembly. For preparation of gas standards.

16.1.1.15 Sample Flasks. For presurvey samples, must have gas-tight seals.

16.1.1.16 Adsorption Tubes. If necessary, blank tubes filled with necessary adsorbent (charcoal, Tenax, XAD–2, etc.) for presurvey samples.

16.1.1.17 Personnel Sampling Pump. Calibrated, for collecting adsorbent tube presurvey samples.

16.1.1.18 Dilution System. Calibrated, the dilution system is to be constructed following the specifications of an acceptable method.

16.1.1.19 Sample Probes. Pyrex or stainless steel, of sufficient length to reach centroid of stack, or a point no closer to the walls than 1 m.

16.1.1.20 Barometer. To measure barometric pressure.

16.1.2 Reagents.

16.1.2.1 Water. Deionized distilled.

16.1.2.2 Methylene chloride.

16.1.2.3 Calibration Gases. A series of standards prepared for every compound of interest.

16.1.2.4 Organic Compound Solutions. Pure (99.9 percent), or as pure as can reasonably be obtained, liquid samples of all the organic compounds needed to prepare calibration standards.

16.1.2.5 Extraction Solvents. For extraction of adsorbent tube samples in preparation for analysis.

16.1.2.6 Fuel. As recommended by the manufacturer for operation of the GC.

16.1.2.7 Carrier Gas. Hydrocarbon free, as recommended by the manufacturer for operation of the detector and compatibility with the column.

16.1.2.8 Zero Gas. Hydrocarbon free air or nitrogen, to be used for dilutions, blank preparation, and standard preparation.

16.1.3 Sampling.

16.1.3.1 Collection of Samples with Glass Sampling Flasks. Presurvey samples may be collected in precleaned 250-ml double-ended glass sampling flasks. Teflon stopcocks, without grease, are preferred. Flasks should be cleaned as follows: Remove the stopcocks from both ends of the flasks, and wipe the parts to remove any grease. Clean the stopcocks, barrels, and receivers with methylene chloride (or other non-target pollutant solvent, or heat and humidified air). Clean all glass ports with a soap solution, then rinse with tap and deionized distilled water. Place the flask in a cool glass annealing furnace, and apply heat up to 500 °C. Maintain at this temperature for 1 hour. After this time period, shut off and open the furnace to allow the flask to cool. Return the stopcocks to the flask receivers. Purge the assembly with high-purity nitrogen for 2 to 5 minutes. Close off the stopcocks after purging to maintain a slight positive nitrogen pressure. Secure the stopcocks with tape. Presurvey samples can be obtained either by drawing the gases into the previously evacuated flask or by drawing the gases into and purging the flask with a rubber suction bulb.

16.1.3.1.1 Evacuated Flask Procedure. Use a high-vacuum pump to evacuate the flask to the capacity of the pump; then close off the stopcock leading to the pump. Attach a 6-mm outside diameter (OD) glass tee to the flask inlet with a short piece of Teflon tubing. Select a 6-mm OD borosilicate sampling probe, enlarged at one end to a 12-mm OD and of sufficient length to reach the centroid of the duct to be sampled. Insert a glass wool plug in the enlarged end of the probe to remove particulate matter. Attach the other end of the probe to the tee with a short piece of Teflon tubing. Connect a rubber suction bulb to the third leg of the tee. Place the filter end of the probe at the centroid of the duct, and purge the probe with the rubber suction bulb. After the probe is completely purged and filled with duct gases, open the stopcock to the grab flask until the pressure in the flask reaches duct pressure. Close off the stopcock, and remove the probe from the duct. Remove the tee from the flask and tape the stopcocks to prevent leaks during shipment. Measure and record the duct temperature and pressure.

16.1.3.1.2 Purged Flask Procedure. Attach one end of the sampling flask to a rubber suction bulb. Attach the other end to a 6-mm OD glass probe as described in section 8.3.3.1.1. Place the filter end of the probe at the centroid of the duct, or at a point no closer to the walls than 1 m, and apply suction with the bulb to completely purge the probe and flask. After the flask has been purged, close off the stopcock near the suction bulb, and then close off the stopcock near the probe. Remove the probe from the duct, and disconnect both the probe and suction bulb. Tape the stopcocks to prevent leakage during shipment. Measure and record the duct temperature and pressure.

16.1.3.2 Flexible Bag Procedure. Any leak-free plastic (e.g., Tedlar, Mylar, Teflon) or plastic-coated aluminum (e.g., aluminized Mylar) bag, or equivalent, can be used to obtain the pre-survey sample. Use new bags, and leak-check them before field use. In addition, check the bag before use for contamination by filling it with nitrogen or air and analyzing the gas by GC at high sensitivity. Experience indicates that it is desirable to allow the inert gas to remain in the bag about 24 hours or longer to check for desorption of organics from the bag. Follow the leak-check and sample collection procedures given in Section 8.2.1.

16.1.3.3 Determination of Moisture Content. For combustion or water-controlled processes, obtain the moisture content from plant personnel or by measurement during the presurvey. If the source is below 59 °C, measure the wet bulb and dry bulb temperatures, and calculate the moisture content using a psychrometric chart. At higher temperatures, use Method 4 to determine the moisture content.

16.1.4 Determination of Static Pressure. Obtain the static pressure from the plant personnel or measurement. If a type S pitot tube and an inclined manometer are used, take care to align the pitot tube 90° from the direction of the flow. Disconnect one of the tubes to the manometer, and read the static pressure; note whether the reading is positive or negative.

16.1.5 Collection of Presurvey Samples with Adsorption Tube. Follow section 8.2.4 for presurvey sampling.

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Volume 1—O17–033–00267–3/$13
Volume 2—O17–033–00260–6/$11
Volume 3—O17–033–00261–4/$14
Volume 4—O17–033–00317–3/$7.25
Volume 5—O17–033–00349–1/$10
Volume 6—O17–033–00369–6/$9
Volume 7—O17–033–00396–5/$7

Prices subject to change. Foreign orders add 25 percent.

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18.0 Tables, Diagrams, Flowcharts, and Validation Data

I. Name of company _____
Date _____
Address _____
_____
Contracts _____
Phone _____
Process to be sampled _____
_____
_____
Duct or vent to be sampled _____
_____
II. Process description _____
_____
_____
_____
_____
Raw material _____
_____
_____
Products _____
_____
_____
Operating cycle
Check: Batch _____ Continuous _____
Cyclic _____
Timing of batch or cycle _____
Best time to test _____
III. Sampling site _____
A. Description _____
Site decription _____
Duct shape and size _____

Material _____
Wall thickness _____ inches
Upstream distance _____ inches _____ diameter
Downstream distance _____ inches _____ diameter
Size of port _____
Size of access area _____
Hazards _____ Ambient temp. _____ °F

B. Properties of gas stream
Temperature _____ °C _____ °F, Data source _____
Velocity _____, Data source _____
Static pressure _____ inches H_2O, Data source _____
Moisture content _____%, Data source _____
Particulate content _____, Data source_____

Gaseous components
N_2 _____ % Hydrocarbons _____ ppm
O_2 _____% _____
CO _____ % _____ _____
CO_2 _____ % _____ _____
SO_2 _____ % _____ _____

Hydrocarbon components
_____ _____ ppm
_____ _____ ppm
_____ _____ ppm
_____ _____ ppm
_____ _____ ppm
_____ _____ ppm

C. Sampling considerations
Location to set up GC _____
_____
Special hazards to be considered _____
_____
Power available at duct _____
Power available for GC _____
Plant safety requirements _____
_____
Vehicle traffic rules _____
_____
Plant entry requirements _____
_____
Security agreements _____
_____
Potential problems _____
_____

D. Site diagrams. (Attach additional sheets if required).

Figure 18–1. Preliminary Survey Data Sheet

Components to be analyzed and Expected concentration

_____
_____
_____
_____
_____
_____
Suggested chromatographic column _____
_____
Column flow rate __ ml/min
Head pressure _____ mm Hg
Column temperature: Isothermal _____ °C, Programmed from _____ °C to _____ °C at _____ °C/min
Injection port/sample loop temperature _____ °C
Detector temperature _____ °C
Detector flow rates: Hydrogen _____ ml/min., head pressure _____ mm Hg, Air/Oxygen _____ ml/min., head pressure _____ mm Hg.
Chart speed _____ inches/minute
Compound data:
Compound and Retention time and Attenuation
_____
_____
_____
_____
_____

Figure 18–2. Chromatographic Conditions Data Sheet

FIGURE 18–3. PREPARATION OF STANDARDS IN TEDLAR OR TEDLAR-EQULIVALENT BAGS AND CALIBRATION CURVE

	Standards		
	Mixture #1	Mixture #2	Mixture #3
Standards Preparation Data:			
Organic:			
Bag number or identification.			
Dry gas meter calibration factor.			
Final meter reading (liters).			
Initial meter reading (liters).			
Metered volume (liters).			
Average meter temperature (°K).			
Average meter pressure, gauge (mm Hg).			
Average atmospheric perssure (mm Hg).			
Average meter pressure, absolute (mm Hg).			
Syringe temperature (°K) (see section 10.1.2.1).			
Syringe pressure, absolute (mm Hg) (see section 10.1.2.1).			
Volume of gas in syringe (ml) (Section 10.1.2.1).			
Density of liquid organic (g/ml) (Section 10.1.2.1).			
Volume of liquid in syringe (ml) (Section 10.1.2.1).			

FIGURE 18–3. PREPARATION OF STANDARDS IN TEDLAR OR TEDLAR-EQULIVALENT BAGS AND CALIBRATION CURVE—Continued

	Standards		
	Mixture #1	Mixture #2	Mixture #3
GC Operating Conditions:			
Sample loop volume (ml).			
Sample loop temperature (°C).			
Carrier gas flow rate (ml/min).			
Column temperature:			
Initial (°C).			
Rate change (°C/min).			
Final (°C).			
Organic Peak Identification and Calculated Concentrations:			
Injection time (24 hour clock).			
Distance to peak (cm).			
Chart speed (cm/min).			
Organic retention time (min).			
Attenuation factor.			
Peak height (mm).			
Peak area (mm_2).			
Peak area * attenuation factor (mm_2).			
Calculated concentration (ppm) (Equation 18–3 or 18–4).			

Plot peak area * attenuation factor against calculated concentration to obtain calibration curve.

Flowmeter number or identification _____
Flowmeter Type _____
Method: Bubble meter____ Spirometer____
Wet test meter ____
Readings at laboratory conditions:

Laboratory temperature (T_{lab}) ____ °K
Laboratory barometric pressure (P_{lab})____ mm Hg
Flow data:

FLOWMETER

Reading (as marked)	Temp. (°K)	Pressure (absolute)

CALIBRATION DEVICE

Time (min)	Gas volume [a]	Flow rate [b]

[a] Vol. of gas may be measured in milliliters, liters or cubic feet.
[b] Convert to standard conditions (20 °C and 760 mm Hg). Plot flowmeter reading against flow rate (standard conditions), and draw a smooth curve. If the flowmeter being calibrated is a rotameter or other flow device that is viscosity dependent, it may be necessary to generate a ''family'' of calibration curves that cover the operating pressure and temperature ranges of the flowmeter. While the following technique should be verified before application, it may be possible to calculate flow rate reading for rotameters at standard conditions Q_{std} as follows:

$$Q_{std} = Q_{lab}\left(\frac{760 \times T_{lab}}{P_{lab} \times 293}\right)^{1/2}$$

Flow rate (laboratory conditions)	Flow rate (STD conditions)

Figure 18–4. Flowmeter Calibration

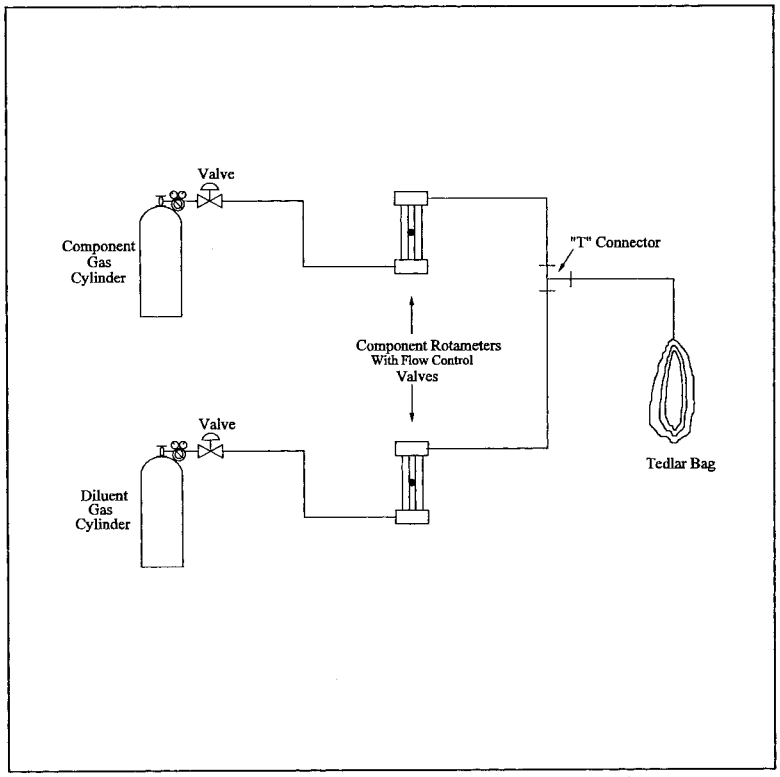

Figure 18-5. Single-Stage Calibration Gas Dilution System.

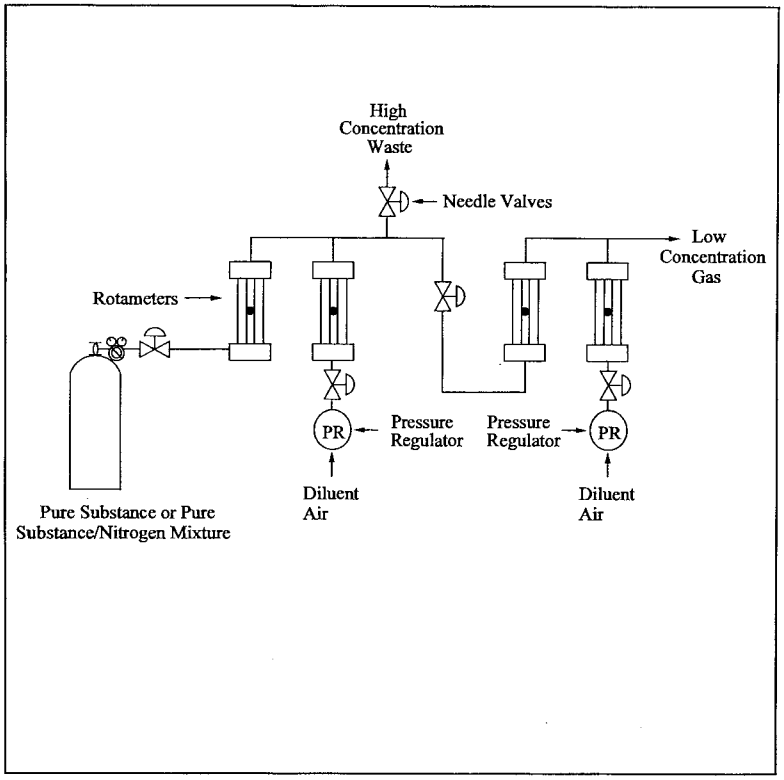

Figure 18-6. Two-Stage Dilution Apparatus.

PREPARATION OF STANDARDS BY DILUTION OF CYLINDER STANDARD

[Cylinder Standard: Organic _____ Certified Concentration _____ ppm]

Standards preparation data:	Date:		
	Mixture 1	Mixture 2	Mixture 3
Stage 1:			
Standard gas flowmeter reading.			
Diluent gas flowmeter reading			
Laboratory temperature (°K)			
Barometric pressure (mm Hg)			
Flowmeter gage pressure (mm Hg)			
Flow rate cylinder gas at standard conditions (ml/min)			
Flow rate diluent gas at standard conditions (ml/min)			
Calculated concentration (ppm)			
Stage 2 (if used):			
Standard gas flowmeter reading			
Diluent gas flowmeter reading			
Flow rate Stage 1 gas at standard conditions (ml/min)			
Flow rate diluent gas at standard conditions			
Calculated concentration (ppm)			
GC Operating Conditions:			
Sample loop volume (ml)			
Sample loop temperature (°C)			
Carrier gas flow rate (ml/min)			
Column temperature:			
Initial (°C)			

PREPARATION OF STANDARDS BY DILUTION OF CYLINDER STANDARD—Continued

[Cylinder Standard: Organic _____ Certified Concentration _____ ppm]

Standards preparation data:	Date:		
	Mixture 1	Mixture 2	Mixture 3
Program rate (°C/min)			
Final (°C)			
Organic Peak Identification and Calculated Concentrations:			
Injection time (24-hour clock)			
Distance to peak (cm)			
Chart speed (cm/min)			
Retention time (min)			
Attenuation factor			
Peak area (mm^2)			
Peak area *attenuation factor			

Plot peak area *attenuation factor against calculated concentration to obtain calibration curve.

Figure 18–7. Standards Prepared by Dilution of Cylinder Standard

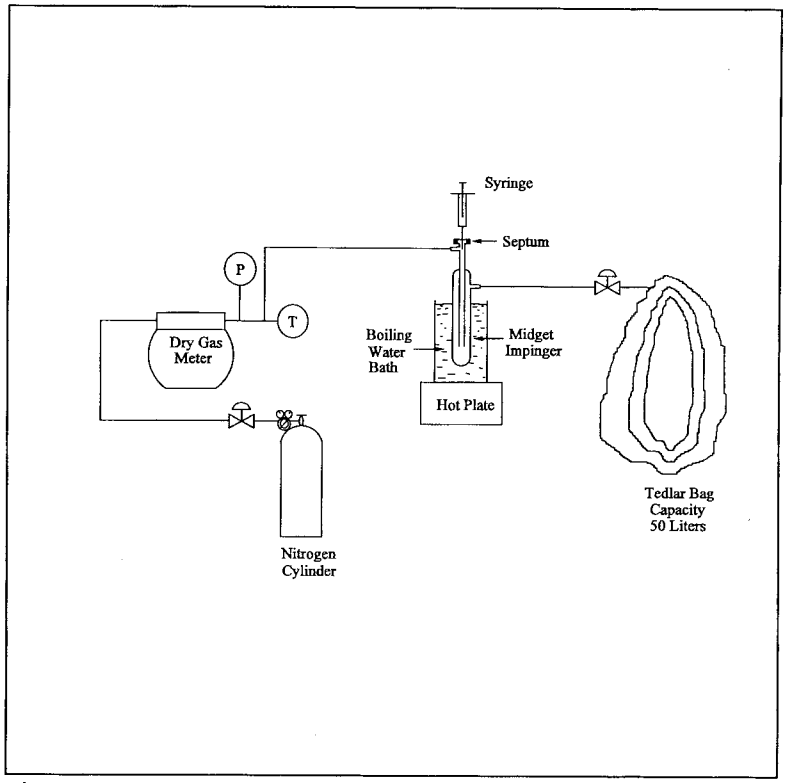

Figure 18-8. Apparatus for Preparation of Liquid Materials.

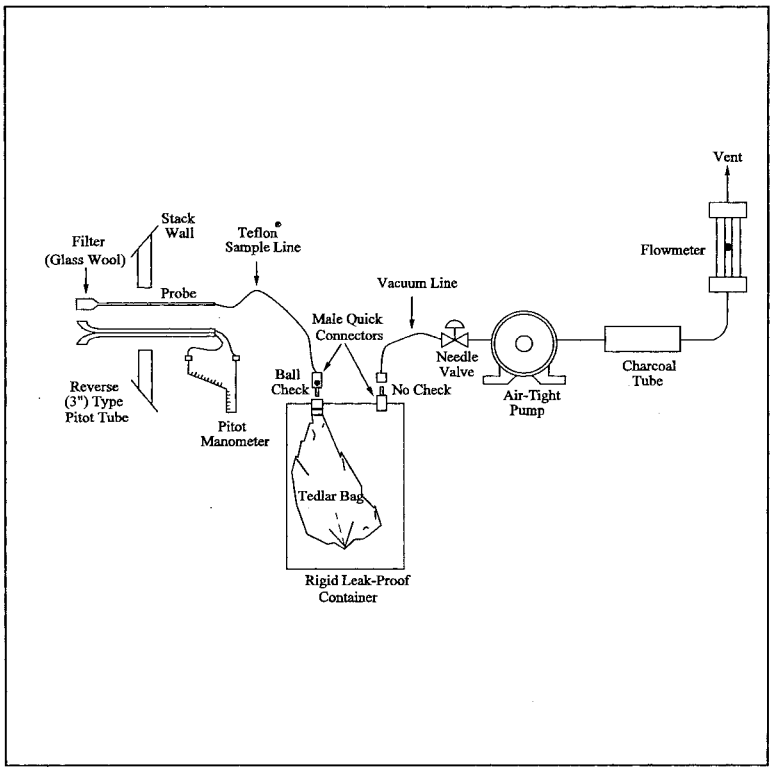

Figure 18-9. Integrated Bag Sampling Train.

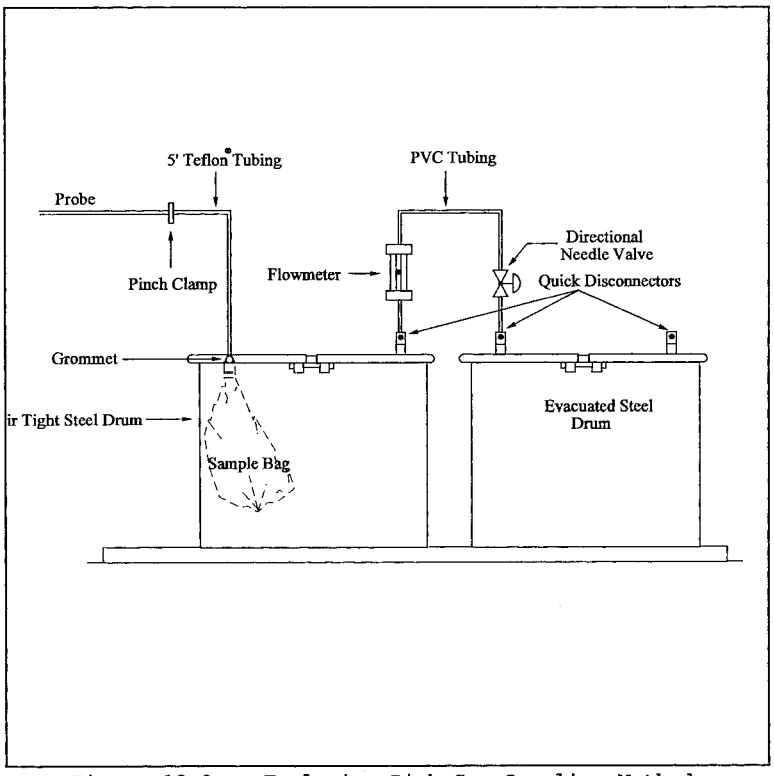

Figure 18-9a. Explosion Risk Gas Sampling Method.

PLANT_____ DATE_____ SITE_____

	Sample 1	Sample 2	Sample 3
Source temperature (°C)			
Barometric pressure (mm Hg)			
Ambient temperature (°C)			
Sample flow rate (appr.)			
Bag number			
Start time			
Finish time			

Figure 18–10. Field Sample Data Sheet—Tedlar or Tedlar-Equivalent Bag Collection Method

PLANT _____ DATE _____ LOCATION _____

1. General information:
- Source temperature (°C) .....
- Probe temperature (°C) .....
- Ambient temperature (°C) .....
- Atmospheric pressure (mm) .....
- Source pressure ('Hg) .....
- Absolute source pressure (mm) .....
- Sampling rate (liter/min) .....
- Sample loop volume (ml) .....
- Sample loop temperature (°C) .....
- Columnar temperature:
  - Initial (°C) time (min) .....
  - Program rate (°C/min) .....
  - Final (°C)/time (min) .....
- Carrier gas flow rate (ml/min) .....

PLANT _____ DATE _____ LOCATION _____—

Continued

Detector temperature (°C) .....
Injection time (24-hour basis) .....
Chart Speed (mm/min) .....
Dilution gas flow rate (ml/min) .....
Dilution gas used (symbol) .....
Dilution ratio .....

2. FIELD ANALYSIS DATA—CALIBRATION GAS

2. [Run No. _____ Time _____]

Components	Area	Attenuation	A × A Factor	Conc.__ (ppm)

Figure 18–11. Field Analysis Data Sheets

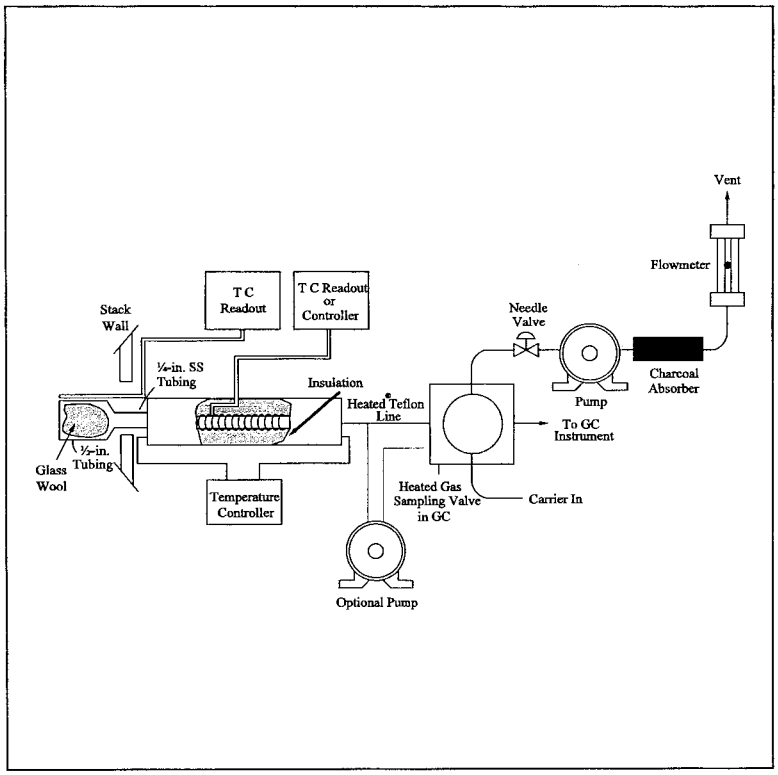

Figure 18-12. Direct Interface Sampling System.

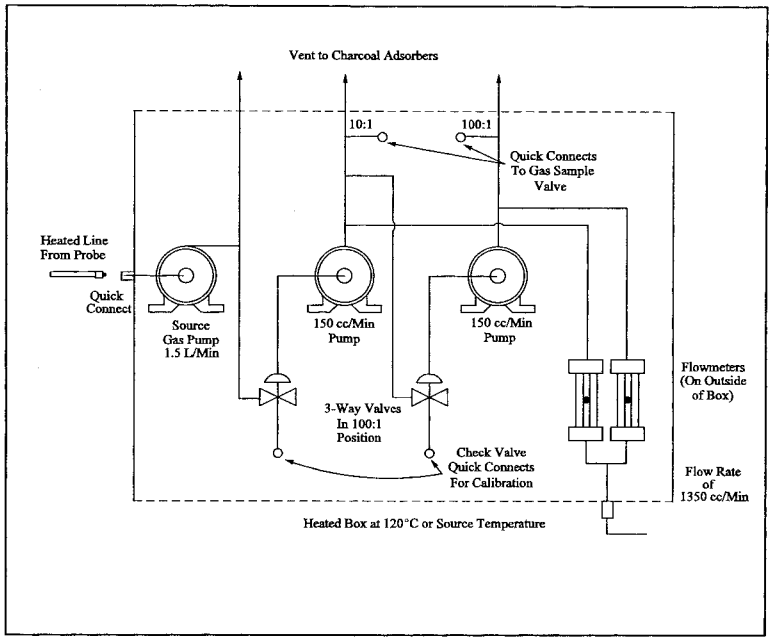

Figure 18-13. Schematic Diagram of the Heated Box Required for Dilution of Sample Gas.

GASEOUS ORGANIC SAMPLING AND ANALYSIS CHECK LIST

[Respond with initials or number as appropriate]

1. Presurvey data:		
A. Grab sample collected	☐	_____
B. Grab sample analyzed for composition	☐	_____
Method GC	☐	_____
GC/MS	☐	_____
Other	☐	_____
C. GC-FID analysis performed	☐	_____
2. Laboratory calibration data:		
A. Calibration curves prepared	☐	_____
Number of components	☐	_____
Number of concentrations/component (3 required).	☐	_____
B. Audit samples (optional):		
Analysis completed	☐	_____
Verified for concentration	☐	_____
OK obtained for field work	☐	_____
3. Sampling procedures:		
A. Method:		
Bag sample	☐	_____
Direct interface	☐	_____
Dilution interface	☐	_____
B. Number of samples collected	☐	_____
4. Field Analysis:		
A. Total hydrocarbon analysis performed	☐	_____
B. Calibration curve prepared	☐	_____
Number of components	☐	_____
Number of concentrations per component (3 required).	☐	_____

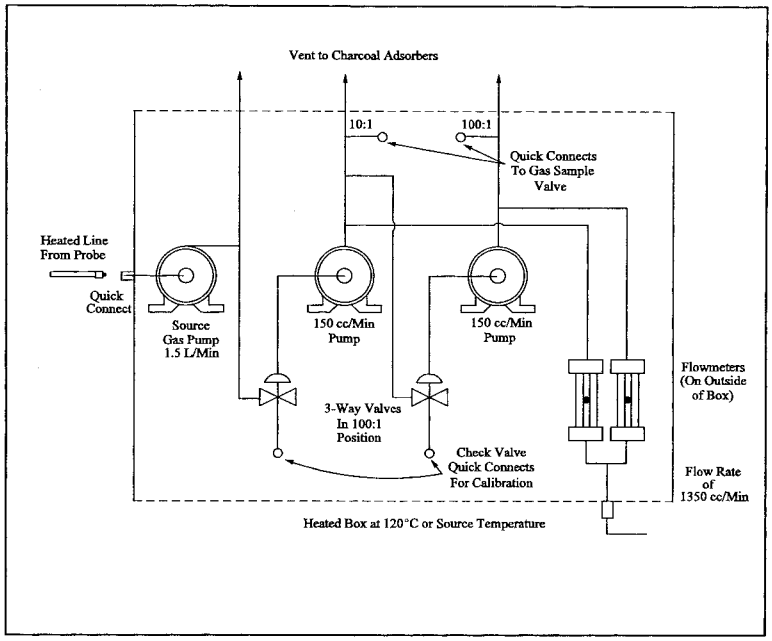

Figure 18-13. Schematic Diagram of the Heated Box Required for Dilution of Sample Gas.

GASEOUS ORGANIC SAMPLING AND ANALYSIS CHECK LIST

[Respond with initials or number as appropriate]

1. Presurvey data:		
A. Grab sample collected	☐	_____
B. Grab sample analyzed for composition	☐	_____
Method GC	☐	_____
GC/MS	☐	_____
Other	☐	_____
C. GC-FID analysis performed	☐	_____
2. Laboratory calibration data:		
A. Calibration curves prepared	☐	_____
Number of components	☐	_____
Number of concentrations/component (3 required).	☐	_____
B. Audit samples (optional):		
Analysis completed	☐	_____
Verified for concentration	☐	_____
OK obtained for field work	☐	_____
3. Sampling procedures:		
A. Method:		
Bag sample	☐	_____
Direct interface	☐	_____
Dilution interface	☐	_____
B. Number of samples collected	☐	_____
4. Field Analysis:		
A. Total hydrocarbon analysis performed	☐	_____
B. Calibration curve prepared	☐	_____
Number of components	☐	_____
Number of concentrations per component (3 required).	☐	_____

Gaseous Organic Sampling and Analysis Data

Date _____
Location _____

Plant _____

GASEOUS ORGANIC SAMPLING AND ANALYSIS CHECK LIST (RESPOND WITH INITIALS OR NUMBER AS APPROPRIATE)

	Date
1. Pre-survey data	
A. Grab sample collected	_____
B. Grab sample analyzed for composition	_____
Method GC	_____
GC/MS	_____
Other_____	_____
C. GC–FID analysis performed	_____
2. Laboratory calibration curves prepared	_____
A. Number of components	_____
B. Number of concentrations per component (3 required)	_____
C. OK obtained for field work	_____
3. Sampling procedures.	
A. Method.	
Bag sample	_____
Direct interface	_____
Dilution interface	_____
B. Number of samples collected	_____
4. Field Analysis.	
A. Total hydrocarbon analysis performed	_____
B. Calibration curve prepared	_____
Number of components	_____
Number of concentrations per component (3 required)	_____

Figure 18–14. Sampling and Analysis Sheet

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–6 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

APPENDIX A–7 TO PART 60—TEST METHODS 19 THROUGH 25E

Method 19—Determination of sulfur dioxide removal efficiency and particulate, sulfur dioxide and nitrogen oxides emission rates

Method 20—Determination of nitrogen oxides, sulfur dioxide, and diluent emissions from stationary gas turbines

Method 21—Determination of volatile organic compound leaks

Method 22—Visual determination of fugitive emissions from material sources and smoke emissions from flares

Method 23—Determination of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans From Stationary Sources

Method 24—Determination of volatile matter content, water content, density, volume solids, and weight solids of surface coatings

Method 24A—Determination of volatile matter content and density of printing inks and related coatings

Method 25—Determination of total gaseous nonmethane organic emissions as carbon

Method 25A—Determination of total gaseous organic concentration using a flame ionization analyzer

Method 25B—Determination of total gaseous organic concentration using a nondispersive infrared analyzer

Method 25C—Determination of nonmethane organic compounds (NMOC) in MSW landfill gases

Method 25D—Determination of the Volatile Organic Concentration of Waste Samples

Method 25E—Determination of Vapor Phase Organic Concentration in Waste Samples

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

Method 19—Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates

1.0 Scope and Application

1.1 Analytes. This method provides data reduction procedures relating to the following pollutants, but does not include any sample collection or analysis procedures.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), including:		
Nitric oxide (NO)	10102–43–9	N/A
Nitrogen dioxide (NO_2)	10102–44–0.	
Particulate matter (PM)	None assigned	N/A
Sulfur dioxide (SO_2)	7499–09–05	N/A

1.2 Applicability. Where specified by an applicable subpart of the regulations, this method is applicable for the determination of (a) PM, SO_2, and NO_X emission rates; (b) sulfur removal efficiencies of fuel pretreatment and SO_2 control devices; and (c) overall reduction of potential SO_2 emissions.

2.0 Summary of Method

2.1 Emission Rates. Oxygen (O_2) or carbon dioxide (CO_2) concentrations and appropriate F factors (ratios of combustion gas volumes to heat inputs) are used to calculate pollutant emission rates from pollutant concentrations.

2.2 Sulfur Reduction Efficiency and SO_2 Removal Efficiency. An overall SO_2 emission reduction efficiency is computed from the efficiency of fuel pretreatment systems, where applicable, and the efficiency of SO_2 control devices.

2.2.1 The sulfur removal efficiency of a fuel pretreatment system is determined by fuel sampling and analysis of the sulfur and heat contents of the fuel before and after the pretreatment system.

2.2.2 The SO_2 removal efficiency of a control device is determined by measuring the SO_2 rates before and after the control device.

2.2.2.1 The inlet rates to SO_2 control systems (or, when SO_2 control systems are not used, SO_2 emission rates to the atmosphere) are determined by fuel sampling and analysis.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety [Reserved]

6.0 Equipment and Supplies [Reserved]

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transport [Reserved]

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedures [Reserved]

12.0 Data Analysis and Calculations

12.1 Nomenclature

B_{wa} = Moisture fraction of ambient air, percent.

B_{ws} = Moisture fraction of effluent gas, percent.

%C = Concentration of carbon from an ultimate analysis of fuel, weight percent.

C_d = Pollutant concentration, dry basis, ng/scm (lb/scf)

$\%CO_{2d}$,$\%CO_{2w}$ = Concentration of carbon dioxide on a dry and wet basis, respectively, percent.

C_w = Pollutant concentration, wet basis, ng/scm (lb/scf).

D = Number of sampling periods during the performance test period.

E = Pollutant emission rate, ng/J (lb/million Btu).

E_a = Average pollutant rate for the specified performance test period, ng/J (lb/million Btu).

E_{ao}, E_{ai} = Average pollutant rate of the control device, outlet and inlet, respectively, for the performance test period, ng/J (lb/million Btu).

E_{bi} = Pollutant rate from the steam generating unit, ng/J (lb/million Btu)

E_{bo} = Pollutant emission rate from the steam generating unit, ng/J (lb/million Btu).

E_{ci} = Pollutant rate in combined effluent, ng/J (lb/million Btu).

E_{co} = Pollutant emission rate in combined effluent, ng/J (lb/million Btu).

E_d = Average pollutant rate for each sampling period (*e.g.*, 24-hr Method 6B sample or 24-hr fuel sample) or for each fuel lot (*e.g.*, amount of fuel bunkered), ng/J (lb/million Btu).

E_{di} = Average inlet SO_2 rate for each sampling period d, ng/J (lb/million Btu)

E_g = Pollutant rate from gas turbine, ng/J (lb/million Btu).

E_{ga} = Daily geometric average pollutant rate, ng/J (lbs/million Btu) or ppm corrected to 7 percent O_2.

E_{jo},E_{ji} = Matched pair hourly arithmetic average pollutant rate, outlet and inlet, respectively, ng/J (lb/million Btu) or ppm corrected to 7 percent O_2.

E_h = Hourly average pollutant, ng/J (lb/million Btu).

E_{hj} = Hourly arithmetic average pollutant rate for hour ''j,'' ng/J (lb/million Btu) or ppm corrected to 7 percent O_2.

EXP = Natural logarithmic base (2.718) raised to the value enclosed by brackets.

F_d, F_w, F_c = Volumes of combustion components per unit of heat content, scm/J (scf/million Btu).

GCV = Gross calorific value of the fuel consistent with the ultimate analysis, kJ/kg (Btu/lb).

GCV_p, GCV_r = Gross calorific value for the product and raw fuel lots, respectively, dry basis, kJ/kg (Btu/lb).

%H = Concentration of hydrogen from an ultimate analysis of fuel, weight percent.

H = Total number of operating hours for which pollutant rates are determined in the performance test period.

H_b = Heat input rate to the steam generating unit from fuels fired in the steam generating unit, J/hr (million Btu/hr).

H_g = Heat input rate to gas turbine from all fuels fired in the gas turbine, J/hr (million Btu/hr).

$\%H_2O$ = Concentration of water from an ultimate analysis of fuel, weight percent.
H_r = Total numbers of hours in the performance test period (*e.g.*, 720 hours for 30-day performance test period).
K = Conversion factor, 10^{-5} (kJ/J)/(%) [10^6 Btu/million Btu].
K_c = (9.57 scm/kg)/% [(1.53 scf/lb)/%].
K_{cc} = (2.0 scm/kg)/% [(0.321 scf/lb)/%].
K_{hd} = (22.7 scm/kg)/% [(3.64 scf/lb)/%].
K_{hw} = (34.74 scm/kg)/% [(5.57 scf/lb)/%].
K_n = (0.86 scm/kg)/% [(0.14 scf/lb)/%].
K_o = (2.85 scm/kg)/% [(0.46 scf/lb)/%].
K_s = (3.54 scm/kg)/% [(0.57 scf/lb)/%].
K_w = (1.30 scm/kg)/% [(0.21 scf/lb)/%].
ln = Natural log of indicated value.
L_p,L_r = Weight of the product and raw fuel lots, respectively, metric ton (ton).
%N = Concentration of nitrogen from an ultimate analysis of fuel, weight percent.
N = Number of fuel lots during the averaging period.
n = Number of fuels being burned in combination.
n_d = Number of operating hours of the affected facility within the performance test period for each E_d determined.
n_t = Total number of hourly averages for which paired inlet and outlet pollutant rates are available within the 24-hr midnight to midnight daily period.
%O = Concentration of oxygen from an ultimate analysis of fuel, weight percent.
$\%O_{2d}$, $\%O_{2w}$ = Concentration of oxygen on a dry and wet basis, respectively, percent.
P_s = Potential SO_2 emissions, percent.
$\%R_f$ = SO_2 removal efficiency from fuel pretreatment, percent.
$\%R_g$ = SO_2 removal efficiency of the control device, percent.
$\%R_{ga}$ = Daily geometric average percent reduction.
$\%R_o$ = Overall SO_2 reduction, percent.
%S = Sulfur content of as-fired fuel lot, dry basis, weight percent.
S_e = Standard deviation of the hourly average pollutant rates for each performance test period, ng/J (lb/million Btu).
$\%S_f$ = Concentration of sulfur from an ultimate analysis of fuel, weight percent.
S_i = Standard deviation of the hourly average inlet pollutant rates for each performance test period, ng/J (lb/million Btu).
S_o = Standard deviation of the hourly average emission rates for each performance test period, ng/J (lb/million Btu).
$\%S_p$, $\%S_r$ = Sulfur content of the product and raw fuel lots respectively, dry basis, weight percent.
$t_{0.95}$ = Values shown in Table 19–3 for the indicated number of data points n.
X_k = Fraction of total heat input from each type of fuel k.

12.2 Emission Rates of PM, SO_2, and NO_X. Select from the following sections the applicable procedure to compute the PM, S_{O2}, or NO_X emission rate (E) in ng/J (lb/million Btu). The pollutant concentration must be in ng/scm (lb/scf) and the F factor must be in scm/J (scf/million Btu). If the pollutant concentration (C) is not in the appropriate units, use Table 19–1 in section 17.0 to make the proper conversion. An F factor is the ratio of the gas volume of the products of combustion to the heat content of the fuel. The dry F factor (F_d) includes all components of combustion less water, the wet F factor (F_w) includes all components of combustion, and the carbon F factor (F_c) includes only carbon dioxide.

NOTE: Since F_w factors include water resulting only from the combustion of hydrogen in the fuel, the procedures using F_w factors are not applicable for computing E from steam generating units with wet scrubbers or with other processes that add water (*e.g.*, steam injection).

12.2.1 Oxygen-Based F Factor, Dry Basis. When measurements are on a dry basis for both O ($\%O_{2d}$) and pollutant (C_d) concentrations, use the following equation:

$$E = C_d F_d \frac{20.9}{(20.9 - \%O_{2d})} \qquad \text{Eq. 19-1}$$

12.2.2 Oxygen-Based F Factor, Wet Basis. When measurements are on a wet basis for both O_2 ($\%O_{2w}$) and pollutant (C_w) concentrations, use either of the following:

12.2.2.1 If the moisture fraction of ambient air (B_{wa}) is measured:

$$E = C_w F_w \frac{20.9}{\left[20.9(1 - B_{wa}) - \%O_{2w}\right]} \qquad \text{Eq. 19-2}$$

Instead of actual measurement, B_{wa} may be estimated according to the procedure below.

NOTE: The estimates are selected to ensure that negative errors will not be larger than −1.5 percent. However, positive errors, or over-estimation of emissions by as much as 5 percent may be introduced depending upon the geographic location of the facility and the associated range of ambient moisture.

12.2.2.1.1 B_{wa} = 0.027. This value may be used at any location at all times.

12.2.2.1.2 B_{wa} = Highest monthly average of B_{wa} that occurred within the previous calendar year at the nearest Weather Service Station. This value shall be determined annually and may be used as an estimate for the entire current calendar year.

12.2.2.1.3 B_{wa} = Highest daily average of Bwa that occurred within a calendar month at the nearest Weather Service Station, calculated from the data from the past 3 years. This value shall be computed for each month and may be used as an estimate for the current respective calendar month.

12.2.2.2 If the moisture fraction (B_{ws}) of the effluent gas is measured:

$$E = C_w F_d \frac{20.9}{\left[20.9\left(1-B_{ws}\right)-\%O_{2w}\right]} \qquad \text{Eq. 19-3}$$

12.2.3 Oxygen-Based F Factor, Dry/Wet Basis.

12.2.3.1 When the pollutant concentration is measured on a wet basis (C_w) and O_2 concentration is measured on a dry basis ($\%O_{2d}$), use the following equation:

$$E = \frac{\left(C_w F_d\right)(20.9)}{\left(1-B_{ws}\right)\left(20.9-\%O_{2d}\right)} \qquad \text{Eq. 19-4}$$

12.2.3.2 When the pollutant concentration is measured on a dry basis (C_d) and the O_2 concentration is measured on a wet basis ($\%O_{2w}$), use the following equation:

$$E = \frac{C_d F_d 20.9}{\frac{\left(20.9-\%O_{2w}\right)}{\left(1-B_{ws}\right)}} \qquad \text{Eq. 19-5}$$

12.2.4 Carbon Dioxide-Based F Factor, Dry Basis. When measurements are on a dry basis for both CO_2 ($\%CO_{2d}$) and pollutant (C_d) concentrations, use the following equation:

$$E = C_d F_c \frac{100}{\%CO_{2d}} \qquad \text{Eq. 19-6}$$

12.2.5 Carbon Dioxide-Based F Factor, Wet Basis. When measurements are on a wet basis for both CO_2 ($\%CO_{2w}$) and pollutant (C_w) concentrations, use the following equation:

$$E = C_w F_c \frac{100}{\%CO_{2w}} \qquad \text{Eq. 19-7}$$

12.2.6 Carbon Dioxide-Based F Factor, Dry/Wet Basis.

12.2.6.1 When the pollutant concentration is measured on a wet basis (C_w) and CO_2 concentration is measured on a dry basis ($\%CO_{2d}$), use the following equation:

$$E = \frac{C_w F_c}{\left(1-B_{ws}\right)} \frac{100}{\%CO_{2d}} \qquad \text{Eq. 19-8}$$

12.2.6.2 When the pollutant concentration is measured on a dry basis (C_d) and CO_2 concentration is measured on a wet basis ($\%CO_{2w}$), use the following equation:

$$E = C_d F_c \left(1-B_{ws}\right) \frac{100}{\%CO_{2w}} \qquad \text{Eq. 19-9}$$

12.2.7 Direct-Fired Reheat Fuel Burning. The effect of direct-fired reheat fuel burning (for the purpose of raising the temperature of the exhaust effluent from wet scrubbers to above the moisture dew-point) on emission rates will be less than 1.0 percent and, therefore, may be ignored.

12.2.8 Combined Cycle-Gas Turbine Systems. For gas turbine-steam generator combined cycle systems, determine the emissions from the steam generating unit or the percent reduction in potential SO_2 emissions as follows:

12.2.8.1 Compute the emission rate from the steam generating unit using the following equation:

$$E_{bo} = E_{co} + \frac{H_g}{H_b}\left(E_{co} - E_g\right) \qquad \text{Eq. 19-10}$$

12.2.8.1.1 Use the test methods and procedures section of 40 CFR Part 60, Subpart GG to obtain E_{co} and E_g. Do not use F_w factors for determining E_g or E_{co}. If an SO_2 control device is used, measure E_{co} after the control device.

12.2.8.1.2 Suitable methods shall be used to determine the heat input rates to the steam generating units (H_b) and the gas turbine (H_g).

12.2.8.2 If a control device is used, compute the percent of potential SO_2 emissions (P_s) using the following equations:

$$E_{bi} = E_{ci} - \frac{H_g}{H_b}\left(E_{ci} - E_g\right) \qquad \text{Eq. 19-11}$$

$$P_s = 100\left(1 - \frac{E_{bo}}{E_{bi}}\right) \qquad \text{Eq. 19-12}$$

NOTE: Use the test methods and procedures section of Subpart GG to obtain E_{ci} and E_g. Do not use F_w factors for determining E_g or E_{ci}.

12.3 F Factors. Use an average F factor according to section 12.3.1 or determine an applicable F factor according to section 12.3.2. If combined fuels are fired, prorate the applicable F factors using the procedure in section 12.3.3.

12.3.1 Average F Factors. Average F factors (F_d, F_w, or F_c) from Table 19–2 in section 17.0 may be used.

12.3.2 Determined F Factors. If the fuel burned is not listed in Table 19–2 or if the owner or operator chooses to determine an F factor rather than use the values in Table 19–2, use the procedure below:

12.3.2.1 Equations. Use the equations below, as appropriate, to compute the F factors:

$$F_d = \frac{K\left(K_{hd}\%H + K_c\%C + K_s\%S + K_n\%N - K_o\%O\right)}{GCV} \qquad \text{Eq. 19-13}$$

$$F_w = \frac{K\left[K_{hw}\%H + K_c\%C + K_s\%S + K_n\%N - K_o\%O + K_w\%H_2O\right]}{GCV_w} \qquad \text{Eq. 19-14}$$

$$F_c = \frac{K\left(K_{cc}\%C\right)}{GCV} \qquad \text{Eq. 19-15}$$

NOTE: Omit the $\%H_2O$ term in the equations for F_w if %H and %O include the unavailable hydrogen and oxygen in the form of H_2O.)

12.3.2.2 Use applicable sampling procedures in section 12.5.2.1 or 12.5.2.2 to obtain samples for analyses.

12.3.2.3 Use ASTM D 3176–74 or 89 (all cited ASTM standards are incorporated by reference—see §60.17) for ultimate analysis of the fuel.

12.3.2.4 Use applicable methods in section 12.5.2.1 or 12.5.2.2 to determine the heat content of solid or liquid fuels. For gaseous fuels, use ASTM D 1826–77 or 94 (incorporated by reference—see §60.17) to determine the heat content.

12.3.3 F Factors for Combination of Fuels. If combinations of fuels are burned, use the following equations, as applicable unless otherwise specified in an applicable subpart:

$$F_d = \sum_{k=1}^{n}\left(X_k F_{dk}\right) \qquad \text{Eq. 19-16}$$

$$F_w = \sum_{k=1}^{n}\left(X_k F_{wk}\right) \qquad \text{Eq. 19-17}$$

$$F_c = \sum_{k=1}^{n}\left(X_k F_{ck}\right) \qquad \text{Eq. 19-18}$$

12.4 Determination of Average Pollutant Rates.

12.4.1 Average Pollutant Rates from Hourly Values. When hourly average pollutant rates (E_h), inlet or outlet, are obtained (*e.g.*, CEMS values), compute the average pollutant rate (E_a) for the performance test period (*e.g.*, 30 days) specified in the applicable regulation using the following equation:

$$E_a = \frac{1}{H}\sum_{j=1}^{n} E_{hj} \qquad \text{Eq. 19-19}$$

12.4.2 Average Pollutant Rates from Other than Hourly Averages. When pollutant rates are determined from measured values representing longer than 1-hour periods (*e.g.*, daily fuel sampling and analyses or Method 6B values), or when pollutant rates are determined from combinations of 1-hour and longer than 1-hour periods (*e.g.*, CEMS and Method 6B values), compute the average pollutant rate (E_a) for the performance test period (*e.g.*, 30 days) specified in the applicable regulation using the following equation:

$$E_a = \frac{\sum_{j=1}^{D}\left(n_d E_d\right)_j}{\sum_{j=1}^{D} n_{dj}} \qquad \text{Eq. 19-20}$$

12.4.3 Daily Geometric Average Pollutant Rates from Hourly Values. The geometric average pollutant rate (E_{ga}) is computed using the following equation:

$$E_{ga} = \exp\left[\frac{1}{n_t}\sum_{j=1}^{n_t}\left[\ln\left(E_{hj}\right)\right]\right] \quad \text{Eq. 19-21}$$

12.5 Determination of Overall Reduction in Potential Sulfur Dioxide Emission.

12.5.1 Overall Percent Reduction. Compute the overall percent SO_2 reduction ($\%R_o$) using the following equation:

$$\%R_o = 100\left[1.0 - \left(1.0 - \frac{\%R_f}{100}\right)\left(1.0 - \frac{\%R_g}{100}\right)\right] \quad \text{Eq. 19-22}$$

12.5.2 Pretreatment Removal Efficiency (Optional). Compute the SO_2 removal efficiency from fuel pretreatment ($\%R_f$) for the averaging period (*e.g.*, 90 days) as specified in the applicable regulation using the following equation:

$$\%R_f = 100\left[1.0 - \frac{\sum_{j=1}^{N}\left(\frac{\%S_{pj}}{GCV_{pj}}\right)L_{pj}}{\sum_{j=1}^{N}\left(\frac{\%S_{rj}}{GCV_{rj}}\right)L_{rj}}\right] \quad \text{Eq. 19-23}$$

NOTE: In calculating $\%R_f$, include %S and GCV values for all fuel lots that are not pretreated and are used during the averaging period.

12.5.2.1 Solid Fossil (Including Waste) Fuel/Sampling and Analysis.

NOTE: For the purposes of this method, raw fuel (coal or oil) is the fuel delivered to the desulfurization (pretreatment) facility. For oil, the input oil to the oil desulfurization process (*e.g.*, hydrotreatment) is considered to be the raw fuel.

12.5.2.1.1 Sample Increment Collection. Use ASTM D 2234–76, 96, 97a, or 98 (incorporated by reference—see §60.17), Type I, Conditions A, B, or C, and systematic spacing. As used in this method, systematic spacing is intended to include evenly spaced increments in time or increments based on equal weights of coal passing the collection area. As a minimum, determine the number and weight of increments required per gross sample representing each coal lot according to Table 2 or Paragraph 7.1.5.2 of ASTM D 2234. Collect one gross sample for each lot of raw coal and one gross sample for each lot of product coal.

12.5.2.1.2 ASTM Lot Size. For the purpose of section 12.5.2 (fuel pretreatment), the lot size of product coal is the weight of product coal from one type of raw coal. The lot size of raw coal is the weight of raw coal used to produce one lot of product coal. Typically, the lot size is the weight of coal processed in a 1-day (24-hour) period. If more than one type of coal is treated and produced in 1 day, then gross samples must be collected and analyzed for each type of coal. A coal lot size equaling the 90-day quarterly fuel quantity for a steam generating unit may be used if representative sampling can be conducted for each raw coal and product coal.

NOTE: Alternative definitions of lot sizes may be used, subject to prior approval of the Administrator.

12.5.2.1.3 Gross Sample Analysis. Use ASTM D 2013–72 or 86 to prepare the sample, ASTM D 3177–75 or 89 or ASTM D 4239–85, 94, or 97 to determine sulfur content (%S), ASTM D 3173–73 or 87 to determine moisture content, and ASTM D 2015–77 (Reapproved 1978) or 96, D 3286–85 or 96, or D 5865–98 or 10 to determine gross calorific value (GCV) (all standards cited are incorporated by reference—see §60.17 for acceptable versions of the standards) on a dry basis for each gross sample.

12.5.2.2 Liquid Fossil Fuel-Sampling and Analysis. See Note under section 12.5.2.1.

12.5.2.2.1 Sample Collection. Follow the procedures for continuous sampling in ASTM D 270 or D 4177–95 (incorporated by reference—see §60.17) for each gross sample from each fuel lot.

12.5.2.2.2 Lot Size. For the purpose of section 12.5.2 (fuel pretreatment), the lot size of a product oil is the weight of product oil from one pretreatment facility and intended as one shipment (ship load, barge load, etc.). The lot size of raw oil is the weight of each crude liquid fuel type used to produce a lot of product oil.

NOTE: Alternative definitions of lot sizes may be used, subject to prior approval of the Administrator.

12.5.2.2.3 Sample Analysis. Use ASTM D 129–64, 78, or 95, ASTM D 1552–83 or 95, or ASTM D 4057–81 or 95 to determine the sulfur content (%S) and ASTM D 240–76 or 92 (all standards cited are incorporated by reference—see §60.17) to determine the GCV of each gross sample. These values may be assumed to be on a dry basis. The owner or operator of an affected facility may elect to determine the GCV by sampling the oil combusted on the first steam generating unit operating day of each calendar month and then using the lowest GCV value of the three GCV values per quarter for the GCV of all oil combusted in that calendar quarter.

12.5.2.3 Use appropriate procedures, subject to the approval of the Administrator, to determine the fraction of total mass input derived from each type of fuel.

12.5.3 Control Device Removal Efficiency. Compute the percent removal efficiency ($\%R_g$) of the control device using the following equation:

$$\%R_g = 100\left(1.0 - \frac{E_{ao}}{E_{ai}}\right) \qquad \text{Eq. 19-24}$$

12.5.3.1 Use continuous emission monitoring systems or test methods, as appropriate, to determine the outlet SO_2 rates and, if appropriate, the inlet SO_2 rates. The rates may be determined as hourly (E_h) or other sampling period averages (E_d). Then, compute the average pollutant rates for the performance test period (E_{ao} and E_{ai}) using the procedures in section 12.4.

12.5.3.2 As an alternative, as-fired fuel sampling and analysis may be used to determine inlet SO_2 rates as follows:

12.5.3.2.1 Compute the average inlet SO_2 rate (E_{di}) for each sampling period using the following equation:

$$E_{di} = K\frac{\%S}{GCV} \qquad \text{Eq. 19-25}$$

Where:

$$K = 2\times10^7\left(\frac{\text{ng SO}_2}{\%S}\right)\left(\frac{(\text{kJ})}{\text{J}}\right)\left(\frac{1}{\text{kg coal}}\right)\left[2\times10^4\left(\frac{\text{lb SO}_2}{\%S}\right)\left(\frac{\text{Btu}}{\text{million Btu}}\right)\left(\frac{1}{\text{lb coal}}\right)\right]$$

After calculating E_{di}, use the procedures in section 12.4 to determine the average inlet SO_2 rate for the performance test period (E_{ai}).

12.5.3.2.2 Collect the fuel samples from a location in the fuel handling system that provides a sample representative of the fuel bunkered or consumed during a steam generating unit operating day. For the purpose of as-fired fuel sampling under section 12.5.3.2 or section 12.6, the lot size for coal is the weight of coal bunkered or consumed during each steam generating unit operating day. The lot size for oil is the weight of oil supplied to the ''day'' tank or consumed during each steam generating unit operating day. For reporting and calculation purposes, the gross sample shall be identified with the calendar day on which sampling began. For steam generating unit operating days when a coal-fired steam generating unit is operated without coal being added to the bunkers, the coal analysis from the previous ''as bunkered'' coal sample shall be used until coal is bunkered again. For steam generating unit operating days when an oil-fired steam generating unit is operated without oil being added to the oil ''day'' tank, the oil analysis from the previous day shall be used until the ''day'' tank is filled again. Alternative definitions of fuel lot size may be used, subject to prior approval of the Administrator.

12.5.3.2.3 Use ASTM procedures specified in section 12.5.2.1 or 12.5.2.2 to determine %S and GCV.

12.5.4 Daily Geometric Average Percent Reduction from Hourly Values. The geometric average percent reduction ($\%R_{ga}$) is computed using the following equation:

$$\%R_{ga} = 100\left[1 - \text{EXP}\left(\frac{1}{n_t}\sum_{j=1}^{n_t} 1n\frac{E_{jo}}{E_{ji}}\right)\right] \qquad \text{Eq. 19-26}$$

NOTE: The calculation includes only paired data sets (hourly average) for the inlet and outlet pollutant measurements.

12.6 Sulfur Retention Credit for Compliance Fuel. If fuel sampling and analysis procedures in section 12.5.2.1 are being used to determine average SO_2 emission rates (E_{as}) to the atmosphere from a coal-fired steam generating unit when there is no SO_2 control device, the following equation may be used to adjust the emission rate for sulfur retention credits (no credits are allowed for oil-fired systems) (E_{di}) for each sampling period using the following equation:

$$E_{di} = 0.97K\ \frac{\%S}{GDV} \qquad \text{Eq. 19-27}$$

Where:

$$K = 2\times10^{7}\left(\frac{\text{ng } SO_2}{\%S}\right)\left(\frac{kJ}{J}\right)\left(\frac{1}{\text{kg coal}}\right)\left[2\times10^{4}\left(\frac{\text{lb } SO_2}{\%S}\right)\left(\frac{\text{Btu}}{\text{million Btu}}\right)\left(\frac{1}{\text{lb coal}}\right)\right]$$

After calculating E_{di}, use the procedures in section 12.4.2 to determine the average SO_2 emission rate to the atmosphere for the performance test period (E_{ao}).

12.7 Determination of Compliance When Minimum Data Requirement Is Not Met.

12.7.1 Adjusted Emission Rates and Control Device Removal Efficiency. When the minimum data requirement is not met, the Administrator may use the following adjusted emission rates or control device removal efficiencies to determine compliance with the applicable standards.

12.7.1.1 Emission Rate. Compliance with the emission rate standard may be determined by using the lower confidence limit of the emission rate (E_{ao}*) as follows:

$$E^{*}_{ao} = E_{ao} - t_{0.95}S_o \qquad \text{Eq. 19-28}$$

12.7.1.2 Control Device Removal Efficiency. Compliance with the overall emission reduction ($\%R_o$) may be determined by using the lower confidence limit of the emission rate (E_{ao}*) and the upper confidence limit of the inlet pollutant rate (E_{ai}*) in calculating the control device removal efficiency ($\%R_g$) as follows:

$$\%R_g = 100\left(1.0 - \frac{E^{*}_{ao}}{E^{*}_{ai}}\right) \qquad \text{Eq. 19-29}$$

$$E^{*}_{ai} = E_{ai} + t_{0.95}S_i \qquad \text{Eq. 19-30}$$

12.7.2 Standard Deviation of Hourly Average Pollutant Rates. Compute the standard deviation (S_e) of the hourly average pollutant rates using the following equation:

$$S_e = \sqrt{\frac{1}{H} - \frac{1}{H_r}}\ \sqrt{\frac{\sum_{j=1}^{H}\left(E_{hj} - E_a\right)^2}{H-1}} \qquad \text{Eq. 19-31}$$

Equation 19–19 through 19–31 may be used to compute the standard deviation for both the outlet (S_o) and, if applicable, inlet (S_i) pollutant rates.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References [Reserved]

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 19–1—CONVERSION FACTORS FOR CONCENTRATION

From	To	Multiply by
g/scm	ng/scm	10^9
mg/scm	ng/scm	10^6
lb/scf	ng/scm	1.602×10^{13}

TABLE 19–1—CONVERSION FACTORS FOR CONCENTRATION—Continued

From	To	Multiply by
ppm SO_2	ng/scm	2.66×10^6
ppm NO_X	ng/scm	1.912×10^6
ppm SO_2	lb/scf	1.660×10^{-7}
ppm NO_X	lb/scf	1.194×10^{-7}

TABLE 19–2—F FACTORS FOR VARIOUS FUELS[1]

Fuel Type	F_d		F_w		F_c	
	dscm/J	dscf/10^6 Btu	wscm/J	wscf/10^6 Btu	scm/J	scf/10^6 Btu
Coal:						
Anthracite[2]	2.71×10^{-7}	10,100	2.83×10^{-7}	10,540	0.530×10^{-7}	1,970
Bituminus[2]	2.63×10^{-7}	9,780	2.86×10^{-7}	10,640	0.484×10^{-7}	1,800
Lignite	2.65×10^{-7}	9,860	3.21×10^{-7}	11,950	0.513×10^{-7}	1,910
Oil[3]	2.47×10^{-7}	9,190	2.77×10^{-7}	10,320	0.383×10^{-7}	1,420
Gas:.						
Natural	2.34×10^{-7}	8,710	2.85×10^{-7}	10,610	0.287×10^{-7}	1,040
Propane	2.34×10^{-7}	8,710	2.74×10^{-7}	10,200	0.321×10^{-7}	1,190
Butane	2.34×10^{-7}	8,710	2.79×10^{-7}	10,390	0.337×10^{-7}	1,250
Wood	2.48×10^{-7}	9,240			0.492×10^{-7}	1,830
Wood Bark	2.58×10^{-7}	9,600			0.516×10^{-7}	1,920
Municipal	2.57×10^{-7}	9,570			0.488×10^{-7}	1,820
Solid Waste						

[1] Determined at standard conditions: 20 °C (68 °F) and 760 mm Hg (29.92 in Hg)
[2] As classified according to ASTM D 388.
[3] Crude, residual, or distillate.

TABLE 19–3—VALUES FOR $T_{0.95*}$

n[1]	$t_{0.95}$	n[1]	$t_{0.95}$	n[1]	$t_{0.95}$
2	6.31	8	1.89	22–26	1.71
3	2.42	9	1.86	27–31	1.70
4	2.35	10	1.83	32–51	1.68
5	2.13	11	1.81	52–91	1.67
6	2.02	12–16	1.77	92–151	1.66
7	1.94	17–21	1.73	152 or more	1.65

[1]The values of this table are corrected for n-1 degrees of freedom. Use n equal to the number (H) of hourly average data points.

METHOD 20—DETERMINATION OF NITROGEN OXIDES, SULFUR DIOXIDE, AND DILUENT EMISSIONS FROM STATIONARY GAS TURBINES

1.0 Scope and Application

What is Method 20?

Method 20 contains the details you must follow when using an instrumental analyzer to determine concentrations of nitrogen oxides, oxygen, carbon dioxide, and sulfur dioxide in the emissions from stationary gas turbines. This method follows the specific instructions for equipment and performance requirements, supplies, sample collection and analysis, calculations, and data analysis in the methods listed in section 2.0.

1.1 Analytes. What does this method determine?

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X) as nitrogen dioxide:	10102–43–9	Typically <2% of Calibration Span.
Nitric oxide (NO)	10102–44–0	
Nitrogen dioxide NO_2.		
Diluent oxygen (O_2) or carbon dioxide (CO_2)		Typically <2% of Calibration Span.
Sulfur dioxide (SO_X)	7446–09–5	Typically <2% of Calibration Span.

1.2 Applicability. When is this method required? The use of Method 20 may be required by specific New Source Performance Standards, Clean Air Marketing rules, and State Implementation Plans and permits where

measuring SO_2, NO_X, CO_2, and/or O_2 concentrations in stationary gas turbines emissions are required. Other regulations may also require its use.

1.3 Data Quality Objectives. How good must my collected data be? Refer to section 1.3 of Method 7E.

2.0 Summary of Method

In this method, NO_X, O_2 (or CO_2), and SO_X are measured using the following methods found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 3A—Determination of Oxygen and Carbon Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(c) Method 6C—Determination of Sulfur Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(d) Method 7E—Determination of Nitrogen Oxides Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(e) Method 19—Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates.

3.0 Definitions

Refer to section 3.0 of Method 7E for the applicable definitions.

4.0 Interferences

Refer to section 4.0 of Methods 3A, 6C, and 7E as applicable.

5.0 Safety

Refer to section 5.0 of Method 7E.

6.0 Equipment and Supplies

The measurement system design is shown in Figure 7E–1 of Method 7E. Refer to the appropriate methods listed in section 2.0 for equipment and supplies.

7.0 Reagents and Standards

Refer to the appropriate methods listed in section 2.0 for reagents and standards.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling Site and Sampling Points. Follow the procedures of section 8.1 of Method 7E. For the stratification test in section 8.1.2, determine the diluent-corrected pollutant concentration at each traverse point.

8.2 Initial Measurement System Performance Tests. You must refer to the appropriate methods listed in section 2.0 for the measurement system performance tests as applicable.

8.3 Interference Check. You must follow the procedures in section 8.3 of Method 3A or 6C, or section 8.2.7 of Method 7E (as appropriate).

8.4 Sample Collection. You must follow the procedures of section 8.4 of the appropriate methods listed in section 2.0. A test run must have a duration of at least 21 minutes.

8.5 Post-Run System Bias Check, Drift Assessment, and Alternative Dynamic Spike Procedure. You must follow the procedures of sections 8.5 and 8.6 of the appropriate methods listed in section 2.0. A test run must have a duration of at least 21 minutes.

9.0 Quality Control

Follow quality control procedures in section 9.0 of Method 7E.

10.0 Calibration and Standardization

Follow the procedures for calibration and standardization in section 10.0 of Method 7E.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the procedures for calculations and data analysis in section 12.0 of the appropriate method listed in section 2.0. Follow the procedures in section 12.0 of Method 19 for calculating fuel-specific F factors, diluent-corrected pollutant concentrations, and emission rates.

13.0 Method Performance

The specifications for the applicable performance checks are the same as in section 13.0 of Method 7E.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

Refer to section 16.0 of the appropriate method listed in section 2.0 for alternative procedures.

17.0 References

Refer to section 17.0 of the appropriate method listed in section 2.0 for references.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

Refer to section 18.0 of the appropriate method listed in section 2.0 for tables, diagrams, flowcharts, and validation data.

METHOD 21—DETERMINATION OF VOLATILE ORGANIC COMPOUND LEAKS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile Organic Compounds (VOC).	No CAS number assigned.

1.2 Scope. This method is applicable for the determination of VOC leaks from process equipment. These sources include, but are not limited to, valves, flanges and other connections, pumps and compressors, pressure relief devices, process drains, open-ended valves, pump and compressor seal system degassing vents, accumulator vessel vents, agitator seals, and access door seals.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A portable instrument is used to detect VOC leaks from individual sources. The instrument detector type is not specified, but it must meet the specifications and performance criteria contained in section 6.0. A leak definition concentration based on a reference compound is specified in each applicable regulation. This method is intended to locate and classify leaks only, and is not to be used as a direct measure of mass emission rate from individual sources.

3.0 Definitions

3.1 *Calibration gas* means the VOC compound used to adjust the instrument meter reading to a known value. The calibration gas is usually the reference compound at a known concentration approximately equal to the leak definition concentration.

3.2 *Calibration precision* means the degree of agreement between measurements of the same known value, expressed as the relative percentage of the average difference between the meter readings and the known concentration to the known concentration.

3.3 *Leak definition concentration* means the local VOC concentration at the surface of a leak source that indicates that a VOC emission (leak) is present. The leak definition is an instrument meter reading based on a reference compound.

3.4 *No detectable emission* means a local VOC concentration at the surface of a leak source, adjusted for local VOC ambient concentration, that is less than 2.5 percent of the specified leak definition concentration. that indicates that a VOC emission (leak) is not present.

3.5 *Reference compound* means the VOC species selected as the instrument calibration basis for specification of the leak definition concentration. (For example, if a leak definition concentration is 10,000 ppm as methane, then any source emission that results in a local concentration that yields a meter reading of 10,000 on an instrument meter calibrated with methane would be classified as a leak. In this example, the leak definition concentration is 10,000 ppm and the reference compound is methane.)

3.6 *Response factor* means the ratio of the known concentration of a VOC compound to the observed meter reading when measured using an instrument calibrated with the reference compound specified in the applicable regulation.

3.7 *Response time* means the time interval from a step change in VOC concentration at the input of the sampling system to the time at which 90 percent of the corresponding final value is reached as displayed on the instrument readout meter.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Pollutants. Several of the compounds, leaks of which may be determined by this method, may be irritating or corrosive to tissues (*e.g.*, heptane) or may be toxic (*e.g.*, benzene, methyl alcohol). Nearly all are fire hazards. Compounds in emissions should be determined through familiarity with the source. Appropriate precautions can be found in reference documents, such as reference No. 4 in section 16.0.

6.0 Equipment and Supplies

A VOC monitoring instrument meeting the following specifications is required:

6.1 The VOC instrument detector shall respond to the compounds being processed. Detector types that may meet this requirement include, but are not limited to, catalytic oxidation, flame ionization, infrared absorption, and photoionization.

6.2 The instrument shall be capable of measuring the leak definition concentration specified in the regulation.

6.3 The scale of the instrument meter shall be readable to ±2.5 percent of the specified leak definition concentration.

6.4 The instrument shall be equipped with an electrically driven pump to ensure that a sample is provided to the detector at a constant flow rate. The nominal sample flow rate, as measured at the sample probe tip, shall be 0.10 to 3.0 l/min (0.004 to 0.1 ft^3/min) when the probe is fitted with a glass wool plug or filter that may be used to prevent plugging of the instrument.

6.5 The instrument shall be equipped with a probe or probe extension or sampling not to exceed 6.4 mm (¼ in) in outside diameter,

with a single end opening for admission of sample.

6.6 The instrument shall be intrinsically safe for operation in explosive atmospheres as defined by the National Electrical Code by the National Fire Prevention Association or other applicable regulatory code for operation in any explosive atmospheres that may be encountered in its use. The instrument shall, at a minimum, be intrinsically safe for Class 1, Division 1 conditions, and/or Class 2, Division 1 conditions, as appropriate, as defined by the example code. The instrument shall not be operated with any safety device, such as an exhaust flame arrestor, removed.

7.0 Reagents and Standards

7.1 Two gas mixtures are required for instrument calibration and performance evaluation:

7.1.1 Zero Gas. Air, less than 10 parts per million by volume (ppmv) VOC.

7.1.2 Calibration Gas. For each organic species that is to be measured during individual source surveys, obtain or prepare a known standard in air at a concentration approximately equal to the applicable leak definition specified in the regulation.

7.2 Cylinder Gases. If cylinder calibration gas mixtures are used, they must be analyzed and certified by the manufacturer to be within 2 percent accuracy, and a shelf life must be specified. Cylinder standards must be either reanalyzed or replaced at the end of the specified shelf life.

7.3 Prepared Gases. Calibration gases may be prepared by the user according to any accepted gaseous preparation procedure that will yield a mixture accurate to within 2 percent. Prepared standards must be replaced each day of use unless it is demonstrated that degradation does not occur during storage.

7.4 Mixtures with non-Reference Compound Gases. Calibrations may be performed using a compound other than the reference compound. In this case, a conversion factor must be determined for the alternative compound such that the resulting meter readings during source surveys can be converted to reference compound results.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Instrument Performance Evaluation. Assemble and start up the instrument according to the manufacturer's instructions for recommended warmup period and preliminary adjustments.

8.1.1 Response Factor. A response factor must be determined for each compound that is to be measured, either by testing or from reference sources. The response factor tests are required before placing the analyzer into service, but do not have to be repeated at subsequent intervals.

8.1.1.1 Calibrate the instrument with the reference compound as specified in the applicable regulation. Introduce the calibration gas mixture to the analyzer and record the observed meter reading. Introduce zero gas until a stable reading is obtained. Make a total of three measurements by alternating between the calibration gas and zero gas. Calculate the response factor for each repetition and the average response factor.

8.1.1.2 The instrument response factors for each of the individual VOC to be measured shall be less than 10 unless otherwise specified in the applicable regulation. When no instrument is available that meets this specification when calibrated with the reference VOC specified in the applicable regulation, the available instrument may be calibrated with one of the VOC to be measured, or any other VOC, so long as the instrument then has a response factor of less than 10 for each of the individual VOC to be measured.

8.1.1.3 Alternatively, if response factors have been published for the compounds of interest for the instrument or detector type, the response factor determination is not required, and existing results may be referenced. Examples of published response factors for flame ionization and catalytic oxidation detectors are included in References 1–3 of section 17.0.

8.1.2 Calibration Precision. The calibration precision test must be completed prior to placing the analyzer into service and at subsequent 3-month intervals or at the next use, whichever is later.

8.1.2.1 Make a total of three measurements by alternately using zero gas and the specified calibration gas. Record the meter readings. Calculate the average algebraic difference between the meter readings and the known value. Divide this average difference by the known calibration value and multiply by 100 to express the resulting calibration precision as a percentage.

8.1.2.2 The calibration precision shall be equal to or less than 10 percent of the calibration gas value.

8.1.3 Response Time. The response time test is required before placing the instrument into service. If a modification to the sample pumping system or flow configuration is made that would change the response time, a new test is required before further use.

8.1.3.1 Introduce zero gas into the instrument sample probe. When the meter reading has stabilized, switch quickly to the specified calibration gas. After switching, measure the time required to attain 90 percent of the final stable reading. Perform this test sequence three times and record the results. Calculate the average response time.

8.1.3.2 The instrument response time shall be equal to or less than 30 seconds. The instrument pump, dilution probe (if any), sample probe, and probe filter that will be used

during testing shall all be in place during the response time determination.

8.2 Instrument Calibration. Calibrate the VOC monitoring instrument according to section 10.0.

8.3 Individual Source Surveys.

8.3.1 Type I—Leak Definition Based on Concentration. Place the probe inlet at the surface of the component interface where leakage could occur. Move the probe along the interface periphery while observing the instrument readout. If an increased meter reading is observed, slowly sample the interface where leakage is indicated until the maximum meter reading is obtained. Leave the probe inlet at this maximum reading location for approximately two times the instrument response time. If the maximum observed meter reading is greater than the leak definition in the applicable regulation, record and report the results as specified in the regulation reporting requirements. Examples of the application of this general technique to specific equipment types are:

8.3.1.1 Valves. The most common source of leaks from valves is the seal between the stem and housing. Place the probe at the interface where the stem exits the packing gland and sample the stem circumference. Also, place the probe at the interface of the packing gland take-up flange seat and sample the periphery. In addition, survey valve housings of multipart assembly at the surface of all interfaces where a leak could occur.

8.3.1.2 Flanges and Other Connections. For welded flanges, place the probe at the outer edge of the flange-gasket interface and sample the circumference of the flange. Sample other types of nonpermanent joints (such as threaded connections) with a similar traverse.

8.3.1.3 Pumps and Compressors. Conduct a circumferential traverse at the outer surface of the pump or compressor shaft and seal interface. If the source is a rotating shaft, position the probe inlet within 1 cm of the shaft-seal interface for the survey. If the housing configuration prevents a complete traverse of the shaft periphery, sample all accessible portions. Sample all other joints on the pump or compressor housing where leakage could occur.

8.3.1.4 Pressure Relief Devices. The configuration of most pressure relief devices prevents sampling at the sealing seat interface. For those devices equipped with an enclosed extension, or horn, place the probe inlet at approximately the center of the exhaust area to the atmosphere.

8.3.1.5 Process Drains. For open drains, place the probe inlet at approximately the center of the area open to the atmosphere. For covered drains, place the probe at the surface of the cover interface and conduct a peripheral traverse.

8.3.1.6 Open-ended Lines or Valves. Place the probe inlet at approximately the center of the opening to the atmosphere.

8.3.1.7 Seal System Degassing Vents and Accumulator Vents. Place the probe inlet at approximately the center of the opening to the atmosphere.

8.3.1.8 Access door seals. Place the probe inlet at the surface of the door seal interface and conduct a peripheral traverse.

8.3.2 Type II—''No Detectable Emission''. Determine the local ambient VOC concentration around the source by moving the probe randomly upwind and downwind at a distance of one to two meters from the source. If an interference exists with this determination due to a nearby emission or leak, the local ambient concentration may be determined at distances closer to the source, but in no case shall the distance be less than 25 centimeters. Then move the probe inlet to the surface of the source and determine the concentration as outlined in section 8.3.1. The difference between these concentrations determines whether there are no detectable emissions. Record and report the results as specified by the regulation. For those cases where the regulation requires a specific device installation, or that specified vents be ducted or piped to a control device, the existence of these conditions shall be visually confirmed. When the regulation also requires that no detectable emissions exist, visual observations and sampling surveys are required. Examples of this technique are:

8.3.2.1 Pump or Compressor Seals. If applicable, determine the type of shaft seal. Perform a survey of the local area ambient VOC concentration and determine if detectable emissions exist as described in section 8.3.2.

8.3.2.2 Seal System Degassing Vents, Accumulator Vessel Vents, Pressure Relief Devices. If applicable, observe whether or not the applicable ducting or piping exists. Also, determine if any sources exist in the ducting or piping where emissions could occur upstream of the control device. If the required ducting or piping exists and there are no sources where the emissions could be vented to the atmosphere upstream of the control device, then it is presumed that no detectable emissions are present. If there are sources in the ducting or piping where emissions could be vented or sources where leaks could occur, the sampling surveys described in section 8.3.2 shall be used to determine if detectable emissions exist.

8.3.3 Alternative Screening Procedure.

8.3.3.1 A screening procedure based on the formation of bubbles in a soap solution that is sprayed on a potential leak source may be used for those sources that do not have continuously moving parts, that do not have surface temperatures greater than the boiling point or less than the freezing point of the soap solution, that do not have open

areas to the atmosphere that the soap solution cannot bridge, or that do not exhibit evidence of liquid leakage. Sources that have these conditions present must be surveyed using the instrument technique of section 8.3.1 or 8.3.2.

8.3.3.2 Spray a soap solution over all potential leak sources. The soap solution may be a commercially available leak detection solution or may be prepared using concentrated detergent and water. A pressure sprayer or squeeze bottle may be used to dispense the solution. Observe the potential leak sites to determine if any bubbles are formed. If no bubbles are observed, the source is presumed to have no detectable emissions or leaks as applicable. If any bubbles are observed, the instrument techniques of section 8.3.1 or 8.3.2 shall be used to determine if a leak exists, or if the source has detectable emissions, as applicable.

9.0 Quality Control

Section	Quality control measure	Effect
8.1.2	Instrument calibration precision check	Ensure precision and accuracy, respectively, of instrument response to standard.
10.0	Instrument calibration.	

10.0 Calibration and Standardization

10.1 Calibrate the VOC monitoring instrument as follows. After the appropriate warmup period and zero internal calibration procedure, introduce the calibration gas into the instrument sample probe. Adjust the instrument meter readout to correspond to the calibration gas value.

NOTE: If the meter readout cannot be adjusted to the proper value, a malfunction of the analyzer is indicated and corrective actions are necessary before use.

11.0 Analytical Procedures [Reserved]

12.0 Data Analyses and Calculations [Reserved]

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Dubose, D.A., and G.E. Harris. Response Factors of VOC Analyzers at a Meter Reading of 10,000 ppmv for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81051. September 1981.

2. Brown, G.E., *et al.* Response Factors of VOC Analyzers Calibrated with Methane for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81–022. May 1981.

3. DuBose, D.A. *et al.* Response of Portable VOC Analyzers to Chemical Mixtures. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81–110. September 1981.

4. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 22—VISUAL DETERMINATION OF FUGITIVE EMISSIONS FROM MATERIAL SOURCES AND SMOKE EMISSIONS FROM FLARES

NOTE: This method is not inclusive with respect to observer certification. Some material is incorporated by reference from Method 9.

1.0 Scope and Application

This method is applicable for the determination of the frequency of fugitive emissions from stationary sources, only as specified in an applicable subpart of the regulations. This method also is applicable for the determination of the frequency of visible smoke emissions from flares.

2.0 Summary of Method

2.1 Fugitive emissions produced during material processing, handling, and transfer operations or smoke emissions from flares are visually determined by an observer without the aid of instruments.

2.2 This method is used also to determine visible smoke emissions from flares used for combustion of waste process materials.

2.3 This method determines the amount of time that visible emissions occur during the observation period (*i.e.*, the accumulated emission time). This method does not require that the opacity of emissions be determined. Since this procedure requires only the determination of whether visible emissions occur and does not require the determination of opacity levels, observer certification according to the procedures of Method 9 is not required. However, it is necessary that the observer is knowledgeable with respect to the general procedures for determining the presence of visible emissions. At a minimum, the observer must be trained and knowledgeable regarding the effects of background contrast, ambient lighting, observer position relative

to lighting, wind, and the presence of uncombined water (condensing water vapor) on the visibility of emissions. This training is to be obtained from written materials found in References 1 and 2 or from the lecture portion of the Method 9 certification course.

3.0 Definitions

3.1 *Emission frequency* means the percentage of time that emissions are visible during the observation period.

3.2 *Emission time* means the accumulated amount of time that emissions are visible during the observation period.

3.3 *Fugitive emissions* means emissions generated by an affected facility which is not collected by a capture system and is released to the atmosphere. This includes emissions that (1) escape capture by process equipment exhaust hoods; (2) are emitted during material transfer; (3) are emitted from buildings housing material processing or handling equipment; or (4) are emitted directly from process equipment.

3.4 *Observation period* means the accumulated time period during which observations are conducted, not to be less than the period specified in the applicable regulation.

3.5 *Smoke emissions* means a pollutant generated by combustion in a flare and occurring immediately downstream of the flame. Smoke occurring within the flame, but not downstream of the flame, is not considered a smoke emission.

4.0 Interferences

4.1 Occasionally, fugitive emissions from sources other than the affected facility (*e.g.*, road dust) may prevent a clear view of the affected facility. This may particularly be a problem during periods of high wind. If the view of the potential emission points is obscured to such a degree that the observer questions the validity of continuing observations, then the observations shall be terminated, and the observer shall clearly note this fact on the data form.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment

6.1 Stopwatches (two). Accumulative type with unit divisions of at least 0.5 seconds.

6.2 Light Meter. Light meter capable of measuring illuminance in the 50 to 200 lux range, required for indoor observations only.

7.0 Reagents and Supplies [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transfer [Reserved]

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

11.1 Selection of Observation Location. Survey the affected facility, or the building or structure housing the process to be observed, and determine the locations of potential emissions. If the affected facility is located inside a building, determine an observation location that is consistent with the requirements of the applicable regulation (*i.e.*, outside observation of emissions escaping the building/structure or inside observation of emissions directly emitted from the affected facility process unit). Then select a position that enables a clear view of the potential emission point(s) of the affected facility or of the building or structure housing the affected facility, as appropriate for the applicable subpart. A position at least 4.6 m (15 feet), but not more than 400 m (0.25 miles), from the emission source is recommended. For outdoor locations, select a position where the sunlight is not shining directly in the observer's eyes.

11.2 Field Records.

11.2.1 Outdoor Location. Record the following information on the field data sheet (Figure 22–1): Company name, industry, process unit, observer's name, observer's affiliation, and date. Record also the estimated wind speed, wind direction, and sky condition. Sketch the process unit being observed, and note the observer location relative to the source and the sun. Indicate the potential and actual emission points on the sketch.

11.2.2 Indoor Location. Record the following information on the field data sheet (Figure 22–2): Company name, industry, process unit, observer's name, observer's affiliation, and date. Record as appropriate the type, location, and intensity of lighting on the data sheet. Sketch the process unit being observed, and note the observer location relative to the source. Indicate the potential and actual fugitive emission points on the sketch.

11.3 Indoor Lighting Requirements. For indoor locations, use a light meter to measure the level of illumination at a location as close to the emission source(s) as is feasible. An illumination of greater than 100 lux (10 foot candles) is considered necessary for proper application of this method.

11.4 Observations.

11.4.1 Procedure. Record the clock time when observations begin. Use one stopwatch to monitor the duration of the observation

period. Start this stopwatch when the observation period begins. If the observation period is divided into two or more segments by process shutdowns or observer rest breaks (see section 11.4.3), stop the stopwatch when a break begins and restart the stopwatch without resetting it when the break ends. Stop the stopwatch at the end of the observation period. The accumulated time indicated by this stopwatch is the duration of observation period. When the observation period is completed, record the clock time. During the observation period, continuously watch the emission source. Upon observing an emission (condensed water vapor is not considered an emission), start the second accumulative stopwatch; stop the watch when the emission stops. Continue this procedure for the entire observation period. The accumulated elapsed time on this stopwatch is the total time emissions were visible during the observation period (*i.e.*, the emission time.)

11.4.2 Observation Period. Choose an observation period of sufficient length to meet the requirements for determining compliance with the emission standard in the applicable subpart of the regulations. When the length of the observation period is specifically stated in the applicable subpart, it may not be necessary to observe the source for this entire period if the emission time required to indicate noncompliance (based on the specified observation period) is observed in a shorter time period. In other words, if the regulation prohibits emissions for more than 6 minutes in any hour, then observations may (optional) be stopped after an emission time of 6 minutes is exceeded. Similarly, when the regulation is expressed as an emission frequency and the regulation prohibits emissions for greater than 10 percent of the time in any hour, then observations may (optional) be terminated after 6 minutes of emission are observed since 6 minutes is 10 percent of an hour. In any case, the observation period shall not be less than 6 minutes in duration. In some cases, the process operation may be intermittent or cyclic. In such cases, it may be convenient for the observation period to coincide with the length of the process cycle.

11.4.3 Observer Rest Breaks. Do not observe emissions continuously for a period of more than 15 to 20 minutes without taking a rest break. For sources requiring observation periods of greater than 20 minutes, the observer shall take a break of not less than 5 minutes and not more than 10 minutes after every 15 to 20 minutes of observation. If continuous observations are desired for extended time periods, two observers can alternate between making observations and taking breaks.

11.5 Recording Observations. Record the accumulated time of the observation period on the data sheet as the observation period duration. Record the accumulated time emissions were observed on the data sheet as the emission time. Record the clock time the observation period began and ended, as well as the clock time any observer breaks began and ended.

12.0 Data Analysis and Calculations

If the applicable subpart requires that the emission rate be expressed as an emission frequency (in percent), determine this value as follows: Divide the accumulated emission time (in seconds) by the duration of the observation period (in seconds) or by any minimum observation period required in the applicable subpart, if the actual observation period is less than the required period, and multiply this quotient by 100.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Missan, R., and A. Stein. Guidelines for Evaluation of Visible Emissions Certification, Field Procedures, Legal Aspects, and Background Material. EPA Publication No. EPA–340/1–75–007. April 1975.

2. Wohlschlegel, P., and D.E. Wagoner. Guideline for Development of a Quality Assurance Program: Volume IX—Visual Determination of Opacity Emissions from Stationary Sources. EPA Publication No. EPA–650/4–74–005i. November 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

FUGITIVE OR SMOKE EMISSION INSPECTION
OUTDOOR LOCATION

Company Location Company Rep.	Observer Affiliation Date
Sky Conditions Precipitation	Wind Direction Wind Speed
Industry	Process Unit

Sketch process unit: indicate observer position relative to source; indicate potential emission points and/or actual emission points.

OBSERVATIONS	Clock Time	Observation period duration, min:sec	Accumulated emission time, min:sec
Begin Observation			
End Observation			

Figure 22-1

FUGITIVE OR SMOKE EMISSION INSPECTION
INDOOR LOCATION

Company Location Company Rep.	Observer Affiliation Date
Industry	Process Unit

Light type (fluorescent, incandescent, natural)
Light location (overhead, behind observer, etc.)
Illuminance (lux or footcandles)
Sketch process unit: indicate observer position relative to source; indicate potential emission points and/or actual emission points.

OBSERVATIONS	Clock Time	Observation period duration, min:sec	Accumulated emission time, min:sec
Begin			
End Observation			

Figure 22-2

METHOD 23—DETERMINATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS FROM STATIONARY SOURCES

1. Applicability and Principle

1.1 Applicability. This method is applicable to the determination of polychlorinated dibenzo-p-dioxins (PCDD's) and polychlorinated dibenzofurans (PCDF's) from stationary sources.

1.2 Principle. A sample is withdrawn from the gas stream isokinetically and collected in the sample probe, on a glass fiber filter, and on a packed column of adsorbent material. The sample cannot be separated into a particle vapor fraction. The PCDD's and

PCDF's are extracted from the sample, separated by high resolution gas chromatography, and measured by high resolution mass spectrometry.

2. Apparatus

2.1 Sampling. A schematic of the sampling train used in this method is shown in Figure 23–1. Sealing greases may not be used in assembling the train. The train is identical to that described in section 2.1 of Method 5 of this appendix with the following additions:

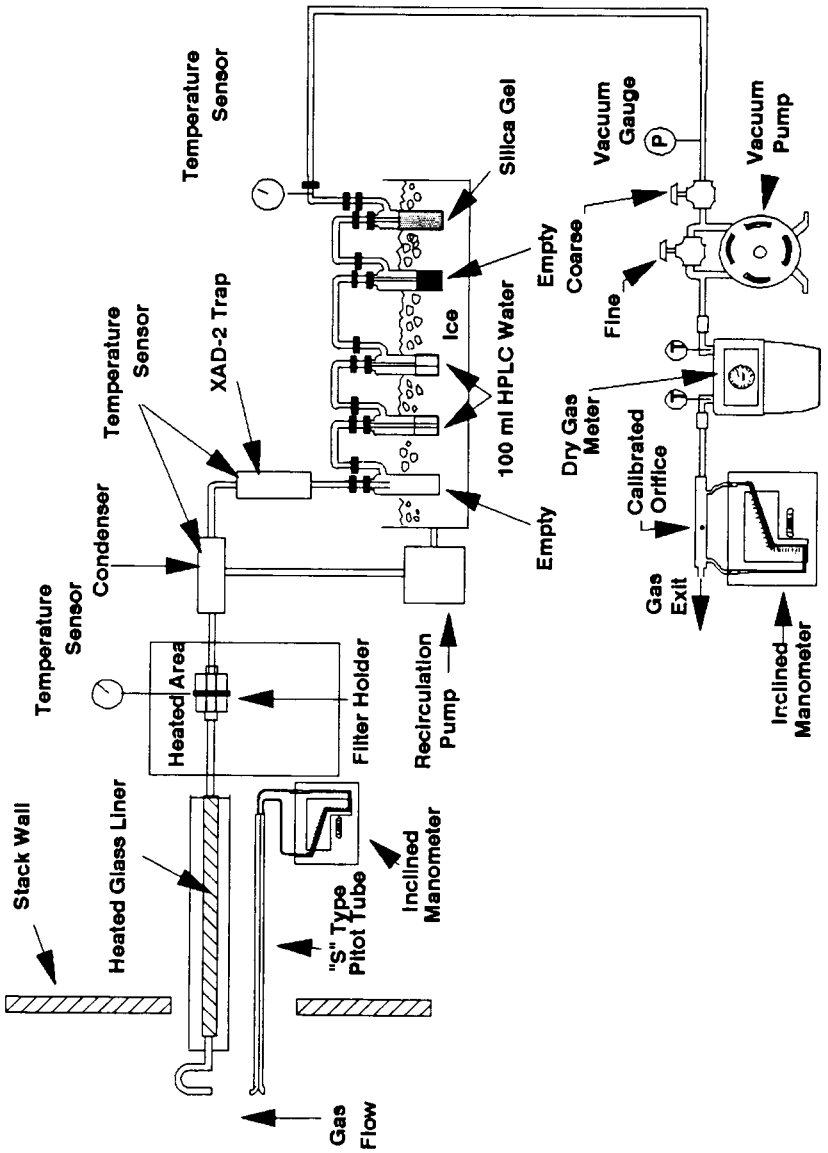

Figure 23.1 Sampling train

2.1.1 Nozzle. The nozzle shall be made of nickel, nickel-plated stainless steel, quartz, or borosilicate glass.

2.1.2 Sample Transfer Lines. The sample transfer lines, if needed, shall be heat traced, heavy walled TFE (½ in. OD with ⅛ in. wall) with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases. The line shall be as short as possible and must be maintained at 120 °C.

2.1.1 Filter Support. Teflon or Teflon-coated wire.

2.1.2 Condenser. Glass, coil type with compatible fittings. A schematic diagram is shown in Figure 23–2.

2.1.3 Water Bath. Thermostatically controlled to maintain the gas temperature exiting the condenser at <20 °C (68 °F).

2.1.4 Adsorbent Module. Glass container to hold the solid adsorbent. A shematic diagram is shown in Figure 23–2. Other physical configurations of the resin trap/condenser assembly are acceptable. The connecting fittings shall form leak-free, vacuum tight seals. No sealant greases shall be used in the sampling train. A coarse glass frit is included to retain the adsorbent.

2.2 Sample Recovery.

2.2.1 Fitting Caps. Ground glass, Teflon tape, or aluminum foil (Section 2.2.6) to cap off the sample exposed sections of the train.

2.2.2 Wash Bottles. Teflon, 500-ml.

2.2.3 Probe-Liner Probe-Nozzle, and Filter-Holder Brushes. Inert bristle brushes with precleaned stainless steel or Teflon handles. The probe brush shall have extensions of stainless steel or Teflon, at least as long as the probe. The brushes shall be properly sized and shaped to brush out the nozzle, probe liner, and transfer line, if used.

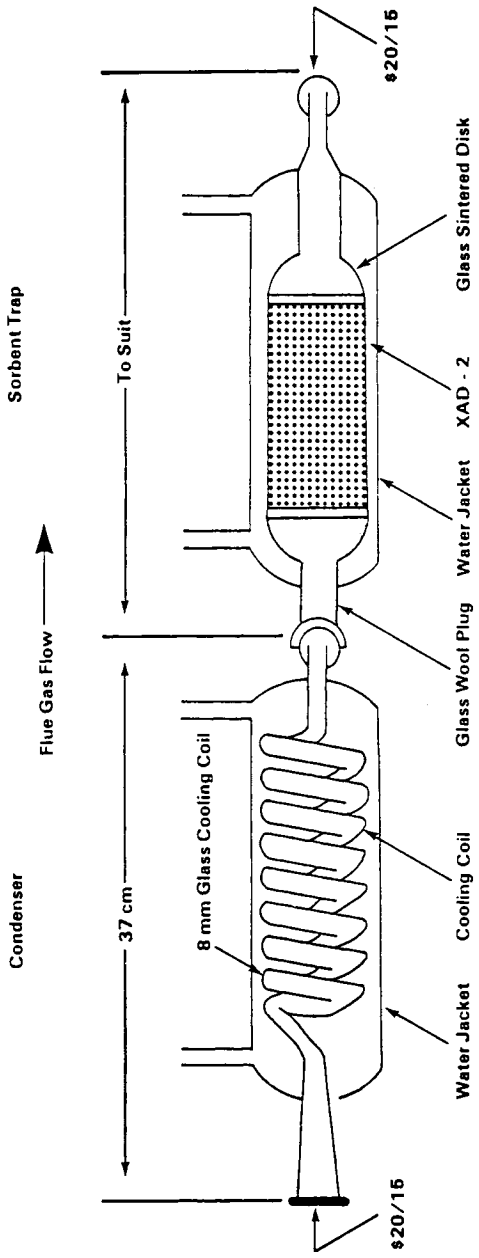

Figure 23.2. Condenser and adsorbent trap

2.2.4 Filter Storage Container. Sealed filter holder, wide-mouth amber glass jar with Teflon-lined cap, or glass petri dish.

2.2.5 Balance. Triple beam.

2.2.6 Aluminum Foil. Heavy duty, hexane-rinsed.

2.2.7 Storage Container. Air-tight container to store silica gel.

2.2.8 Graduated Cylinder. Glass, 250-ml with 2-ml graduation.

2.2.9 Glass Sample Storage Container. Amber glass bottle for sample glassware washes, 500- or 1000-ml, with leak free Teflon-lined caps.

2.3 Analysis.

2.3.1 Sample Container. 125- and 250-ml flint glass bottles with Teflon-lined caps.

2.3.2 Test Tube. Glass.

2.3.3 Soxhlet Extraction Apparatus. Capable of holding 43 × 123 mm extraction thimbles.

2.3.4 Extraction Thimble. Glass, precleaned cellulosic, or glass fiber.

2.3.5 Pasteur Pipettes. For preparing liquid chromatographic columns.

2.3.6 Reacti-vials. Amber glass, 2-ml, silanized prior to use.

2.3.7 Rotary Evaporator. Buchi/Brinkman RF–121 or equivalent.

2.3.8 Nitrogen Evaporative Concentrator. N-Evap Analytical Evaporator Model III or equivalent.

2.3.9 Separatory Funnels. Glass, 2-liter.

2.3.10 Gas Chromatograph. Consisting of the following components:

2.3.10.1 Oven. Capable of maintaining the separation column at the proper operating temperature ±°C and performing programmed increases in temperature at rates of at least 40 °C/min.

2.3.10.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperatures ±1 °C.

2.3.10.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

2.3.10.4 Capillary Columns. A fused silica column, 60 × 0.25 mm inside diameter (ID), coated with DB–5 and a fused silica column, 30 m × 0.25 mm ID coated with DB–225. Other column systems may be used provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of section 6.1.2.2.

2.3.11 Mass Spectrometer. Capable of routine operation at a resolution of 1:10000 with a stability of ±5 ppm.

2.3.12 Data System. Compatible with the mass spectrometer and capable of monitoring at least five groups of 25 ions.

2.3.13 Analytical Balance. To measure within 0.1 mg.

3. Reagents

3.1 Sampling.

3.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D 2986–71 (Reapproved 1978) (incorporated by reference—see §60.17).

3.1.1.1 Precleaning. All filters shall be cleaned before their initial use. Place a glass extraction thimble and 1 g of silica gel and a plug of glass wool into a Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Place no more than 50 filters in the thimble onto the silica gel bed and top with the cleaned glass wool. Charge the Soxhlet with toluene and reflux for 16 hours. After extraction, allow the Soxhlet to cool, remove the filters, and dry them under a clean N_2 stream. Store the filters in a glass petri dish sealed with Teflon tape.

3.1.2 Adsorbent Resin. Amberlite XAD–2 resin. Thoroughly cleaned before initial use.

3.1.2.1 Cleaning Procedure. This procedure may be carried out in a giant Soxhlet extractor. An all-glass filter thimble containing an extra-course frit is used for extraction of XAD–2. The frit is recessed 10–15 mm above a crenelated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass wool plug and a stainless steel ring because it floats on methylene chloride. This process involves sequential extraction in the following order.

Solvent	Procedure
Water	Initial rinse: Place resin in a beaker, rinse once with water, and discard. Fill with water a second time, let stand overnight, and discard.
Water	Extract with water for 8 hours.
Methanol	Extract for 22 hours.
Methylene Chloride	Extract for 22 hours.
Toluene	Extract for 22 hours.

3.1.2.2 Drying.

3.1.2.2.1 Drying Column. Pyrex pipe, 10.2 cm ID by 0.6 m long, with suitable retainers.

3.1.2.2.2 Procedure. The adsorbent must be dried with clean inert gas. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has proven to be a reliable source of large volumes of gas free from organic contaminants. Connect the liquid nitrogen cylinder to the column by a length of cleaned copper tubing, 0.95 cm ID, coiled to pass through a heat source. A convenient heat source is a water-bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40 °C. Continue flowing nitrogen through the adsorbent until all the residual solvent is removed. The flow rate should be sufficient to gently agitate the particles but not so excessive as the cause the particles to fracture.

3.1.2.3 Quality Control Check. The adsorbent must be checked for residual toluene.

3.1.2.3.1 Extraction. Weigh 1.0 g sample of dried resin into a small vial, add 3 ml of toluene, cap the vial, and shake it well.

3.1.2.3.2 Analysis. Inject a 2 µl sample of the extract into a gas chromatograph operated under the following conditions:

Column: 6 ft × ⅛ in stainless steel containing 10 percent OV–101 on 100/120 Supelcoport.
Carrier Gas: Helium at a rate of 30 ml/min.
Detector: Flame ionization detector operated at a sensitivity of 4×10^{-11} A/mV.
Injection Port Temperature: 250 °C.
Detector Temperature: 305 °C.
Oven Temperature: 30 °C for 4 min; programmed to rise at 40 °C/min until it reaches 250 °C; return to 30 °C after 17 minutes.

Compare the results of the analysis to the results from the reference solution. Prepare the reference solution by injection 2.5 µl of methylene chloride into 100 ml of toluene. This corresponds to 100 µg of methylene chloride per g of adsorbent. The maximum acceptable concentration is 1000 µg/g of adsorbent. If the adsorbent exceeds this level, drying must be continued until the excess methylene chloride is removed.

3.1.2.4 Storage. The adsorbent must be used within 4 weeks of cleaning. After cleaning, it may be stored in a wide mouth amber glass container with a Teflon-lined cap or placed in one of the glass adsorbent modules tightly sealed with glass stoppers. If precleaned adsorbent is purchased in sealed containers, it must be used within 4 weeks after the seal is broken.

3.1.3 Glass Wool. Cleaned by sequential immersion in three aliquots of methylene chloride, dried in a 110 °C oven, and stored in a methylene chloride-washed glass jar with a Teflon-lined screw cap.

3.1.4 Water. Deionized distilled and stored in a methylene chloride-rinsed glass container with a Teflon-lined screw cap.

3.1.5 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175 °C (350 °F) for two hours. New silica gel may be used as received. Alternately other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

3.1.6 Chromic Acid Cleaning Solution. Dissolve 20 g of sodium dichromate in 15 ml of water, and then carefully add 400 ml of concentrated sulfuric acid.

3.2 Sample Recovery.

3.2.2 Acetone. Pesticide quality.

3.2.2 Methylene Chloride. Pesticide qualtity.

3.2.3 Toluene. Pesticide quality.

3.3 Analysis.

3.3.1 Potassium Hydroxide. ACS grade, 2-percent (weight/volume) in water.

3.3.2 Sodium Sulfate. Granulated, reagent grade. Purify prior to use by rinsing with methylene chloride and oven drying. Store the cleaned material in a glass container with a Teflon-lined screw cap.

3.3.3 Sulfuric Acid. Reagent grade.

3.3.4 Sodium Hydroxide. 1.0 N. Weigh 40 g of sodium hydroxide into a 1-liter volumetric flask. Dilute to 1 liter with water.

3.3.5 Hexane. Pesticide grade.

3.3.6 Methylene Chloride. Pesticide grade.

3.3.7 Benzene. Pesticide Grade.

3.3.8 Ethyl Acetate.

3.3.9 Methanol. Pesticide Grade.

3.3.10 Toluene. Pesticide Grade.

3.3.11 Nonane. Pesticide Grade.

3.3.12 Cyclohexane. Pesticide Grade.

3.3.13 Basic Alumina. Activity grade 1, 100–200 mesh. Prior to use, activate the alumina by heating for 16 hours at 130 °C before use. Store in a desiccator. Pre-activated alumina may be purchased from a supplier and may be used as received.

3.3.14 Silica Gel. Bio-Sil A, 100–200 mesh. Prior to use, activate the silica gel by heating for at least 30 minutes at 180 °C. After cooling, rinse the silica gel sequentially with methanol and methylene chloride. Heat the rinsed silica gel at 50 °C for 10 minutes, then increase the temperature gradually to 180 °C over 25 minutes and maintain it at this temperature for 90 minutes. Cool at room temperature and store in a glass container with a Teflon-lined screw cap.

3.3.15 Silica Gel Impregnated with Sulfuric Acid. Combine 100 g of silica gel with 44 g of concentrated sulfuric acid in a screw capped glass bottle and agitate thoroughly. Disperse the solids with a stirring rod until a uniform mixture is obtained. Store the mixture in a glass container with a Teflon-lined screw cap.

3.3.16 Silica Gel Impregnated with Sodium Hydroxide. Combine 39 g of 1 N sodium hydroxide with 100 g of silica gel in a screw capped glass bottle and agitate thoroughly. Disperse solids with a stirring rod until a uniform mixture is obtained. Store the mixture in glass container with a Teflon-lined screw cap.

3.3.17 Carbon/Celite. Combine 10.7 g of AX–21 carbon with 124 g of Celite 545 in a 250-ml glass bottle with a Teflon-lined screw cap. Agitate the mixture thoroughly until a uniform mixture is obtained. Store in the glass container.

3.3.18 Nitrogen. Ultra high purity.

3.3.19 Hydrogen. Ultra high purity.

3.3.20 Internal Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Internal Standards'' in 10 ml of nonane.

3.3.21 Surrogate Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Surrogate Standards'' in 10 ml of nonane.

3.3.22 Recovery Standard Solution. Prepare a stock standard solution containing the

isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Recovery Standards'' in 10 ml of nonane.

4. Procedure

4.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, testers should be trained and experienced with the test procedures.

4.1.1 Pretest Preparation.

4.1.1.1 Cleaning Glassware. All glass components of the train upstream of and including the adsorbent module, shall be cleaned as described in section 3A of the ''Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples.'' Special care shall be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. Any residue shall be removed by soaking the glassware for several hours in a chromic acid cleaning solution prior to cleaning as described above.

4.1.1.2 Adsorbent Trap. The traps must be loaded in a clean area to avoid contamination. They may not be loaded in the field. Fill a trap with 20 to 40 g of XAD–2. Follow the XAD–2 with glass wool and tightly cap both ends of the trap. Add 100 μl of the surrogate standard solution (section 3.3.21) to each trap.

4.1.1.3 Sample Train. It is suggested that all components be maintained according to the procedure described in APTD–0576. Alternative mercury-free thermometers may be used if the thermometers are, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

4.1.1.4 Silica Gel. Weigh several 200 to 300 g portions of silica gel in an air tight container to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel may be weighed directly in its impinger or sampling holder just prior to sampling.

4.1.1.5 Filter. Check each filter against light for irregularities and flaws or pinhole leaks. Pack the filters flat in a clean glass container.

4.1.2 Preliminary Determinations. Same as section 4.1.2 of Method 5.

4.1.3 Preparation of Collection Train.

4.1.3.1 During preparation and assembly of the sampling train, keep all train openings where contamination can enter, sealed until just prior to assembly or until sampling is about to begin.

NOTE: Do not use sealant grease in assembling the train.

4.1.3.2 Place approximately 100 ml of water in the second and third impingers, leave the first and fourth impingers empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fifth impinger.

4.1.3.3 Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

4.1.3.4 Assemble the train as shown in Figure 23–1.

4.1.3.5 Turn on the adsorbent module and condenser coil recirculating pump and begin monitoring the adsorbent module gas entry temperature. Ensure proper sorbent temperature gas entry temperature before proceeding and before sampling is initiated. It is extremely important that the XAD–2 adsorbent resin temperature never exceed 50 °C because thermal decomposition will occur. During testing, the XAD–2 temperature must not exceed 20 °C for efficient capture of the PCDD's and PCDF's.

4.1.4 Leak-Check Procedure. Same as Method 5, section 4.1.4.

4.1.5 Sample Train Operation. Same as Method 5, section 4.1.5.

4.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Seal the nozzle end of the sampling probe with Teflon tape or aluminum foil.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe. Remove the probe from the train and close off both ends with aluminum foil. Seal off the inlet to the train with Teflon tape, a ground glass cap, or aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area shall be clean and enclosed so that the chances of losing or contaminating the sample are minimized. Smoking, which could contaminate the sample, shall not be allowed in the cleanup area.

Inspect the train prior to and during disassembly and note any abnormal conditions, e.g., broken filters, colored impinger liquid, etc. Treat the samples as follows:

4.2.1 Container No. 1. Either seal the filter holder or carefully remove the filter from the filter holder and place it in its identified container. Use a pair of cleaned tweezers to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and filter fibers which adhere to the filter holder gasket, by using a dry inert bristle brush and a sharp-edged blade. Seal the container.

4.2.2 Adsorbent Module. Remove the module from the train, tightly cap both ends, label it, cover with aluminum foil, and store it on ice for transport to the laboratory.

4.2.3 Container No. 2. Quantitatively recover material deposited in the nozzle, probe transfer lines, the front half of the filter holder, and the cyclone, if used, first, by

brushing while rinsing three times each with acetone and then, by rinsing the probe three times with methylene chloride. Collect all the rinses in Container No. 2.

Rinse the back half of the filter holder three times with acetone. Rinse the connecting line between the filter and the condenser three times with acetone. Soak the connecting line with three separate portions of methylene chloride for 5 minutes each. If using a separate condenser and adsorbent trap, rinse the condenser in the same manner as the connecting line. Collect all the rinses in Container No. 2 and mark the level of the liquid on the container.

4.2.4 Container No. 3. Repeat the methylene chloride-rinsing described in section 4.2.3 using toluene as the rinse solvent. Collect the rinses in Container No. 3 and mark the level of the liquid on the container.

4.2.5 Impinger Water. Measure the liquid in the first three impingers to within ±1 ml by using a graduated cylinder or by weighing it to within ±0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

Discard the liquid after measuring and recording the volume or weight.

4.2.7 Silica Gel. Note the color of the indicating silica gel to determine if it has been completely spent and make a mention of its condition. Transfer the silica gel from the fifth impinger to its original container and seal. If a moisture determination is made, follow the applicable procedures in sections 8.7.6.3 and 11.2.3 of Method 5 to handle and weigh the silica gel. If moisture is not measured, the silica gel may be disposed.

5. Analysis

All glassware shall be cleaned as described in section 3A of the ''Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples.'' All samples must be extracted within 30 days of collection and analyzed within 45 days of extraction.

5.1 Sample Extraction.

5.1.1 Extraction System. Place an extraction thimble (section 2.3.4), 1 g of silica gel, and a plug of glass wool into the Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Remove the extraction thimble from the extraction system and place it in a glass beaker to catch the solvent rinses.

5.1.2 Container No. 1 (Filter). Transfer the contents directly to the glass thimble of the extraction system and extract them simultaneously with the XAD–2 resin.

5.1.3 Adsorbent Cartridge. Suspend the adsorbent module directly over the extraction thimble in the beaker (See section 5.1.1). The glass frit of the module should be in the up position. Using a Teflon squeeze bottle containing toluene, flush the XAD–2 into the thimble onto the bed of cleaned silica gel. Thoroughly rinse the glass module catching the rinsings in the beaker containing the thimble. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. Add the XAD–2 glass wool plug into the thimble.

5.1.4 Container No. 2 (Acetone and Methylene Chloride). Concentrate the sample to a volume of about 1–5 ml using the rotary evaporator apparatus, at a temperature of less than 37 °C. Rinse the sample container three times with small portions of methylene chloride and add these to the concentrated solution and concentrate further to near dryness. This residue contains particulate matter removed in the rinse of the train probe and nozzle. Add the concentrate to the filter and the XAD–2 resin in the Soxhlet apparatus described in section 5.1.1.

5.1.5 Extraction. Add 100 µl of the internal standard solution (Section 3.3.20) to the extraction thimble containing the contents of the adsorbent cartridge, the contents of Container No. 1, and the concentrate from section 5.1.4. Cover the contents of the extraction thimble with the cleaned glass wool plug to prevent the XAD–2 resin from floating into the solvent reservoir of the extractor. Place the thimble in the extractor, and add the toluene contained in the beaker to the solvent reservoir. Pour additional toluene to fill the reservoir approximately ⅔ full. Add Teflon boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle three times per hour. Extract the sample for 16 hours. After extraction, allow the Soxhlet to cool. Transfer the toluene extract and three 10-ml rinses to the rotary evaporator. Concentrate the extract to approximately 10 ml. At this point the analyst may choose to split the sample in half. If so, split the sample, store one half for future use, and analyze the other according to the procedures in sections 5.2 and 5.3. In either case, use a nitrogen evaporative concentrator to reduce the volume of the sample being analyzed to near dryness. Dissolve the residue in 5 ml of hexane.

5.1.6 Container No. 3 (Toluene Rinse). Add 100 µl of the Internal Standard solution (section 3.3.2) to the contents of the container. Concentrate the sample to a volume of about 1–5 ml using the rotary evaporator apparatus at a temperature of less than 37 °C. Rinse the sample container apparatus at a temperature of less than 37 °C. Rinse the sample container three times with small portions of toluene and add these to the concentrated solution and concentrate further to near dryness. Analyze the extract separately according to the procedures in sections 5.2 and 5.3, but concentrate the solution in a rotary evaporator apparatus rather than a nitrogen evaporative concentrator.

5.2 Sample Cleanup and Fractionation.

5.2.1 Silica Gel Column. Pack one end of a glass column, 20 mm × 230 mm, with glass wool. Add in sequence, 1 g silica gel, 2 g of sodium hydroxide impregnated silica gel, 1 g silica gel, 4 g of acid-modified silica gel, and 1 g of silica gel. Wash the column with 30 ml of hexane and discard it. Add the sample extract, dissolved in 5 ml of hexane to the column with two additional 5-ml rinses. Elute the column with an additional 90 ml of hexane and retain the entire eluate. Concentrate this solution to a volume of about 1 ml using the nitrogen evaporative concentrator (section 2.3.7).

5.2.2 Basic Alumina Column. Shorten a 25-ml disposable Pasteur pipette to about 16 ml. Pack the lower section with glass wool and 12 g of basic alumina. Transfer the concentrated extract from the silica gel column to the top of the basic alumina column and elute the column sequentially with 120 ml of 0.5 percent methylene chloride in hexane followed by 120 ml of 35 percent methylene chloride in hexane. Discard the first 120 ml of eluate. Collect the second 120 ml of eluate and concentrate it to about 0.5 ml using the nitrogen evaporative concentrator.

5.2.3 AX–21 Carbon/Celite 545 Column. Remove the botton 0.5 in. from the tip of a 9-ml disposable Pasteur pipette. Insert a glass fiber filter disk in the top of the pipette 2.5 cm from the constriction. Add sufficient carbon/celite mixture to form a 2 cm column. Top with a glass wool plug. In some cases AX–21 carbon fines may wash through the glass wool plug and enter the sample. This may be prevented by adding a celite plug to the exit end of the column. Rinse the column in sequence with 2 ml of 50 percent benzene in ethyl acetate, 1 ml of 50 percent methylene chloride in cyclohexane, and 2 ml of hexane. Discard these rinses. Transfer the concentrate in 1 ml of hexane from the basic alumina column to the carbon/celite column along with 1 ml of hexane rinse. Elute the column sequentially with 2 ml of 50 percent methylene chloride in hexane and 2 ml of 50 percent benzene in ethyl acetate and discard these eluates. Invert the column and elute in the reverse direction with 13 ml of toluene. Collect this eluate. Concentrate the eluate in a rotary evaporator at 50 °C to about 1 ml. Transfer the concentrate to a Reacti-vial using a toluene rinse and concentrate to a volume of 200 µl using a stream of N_2. Store extracts at room temperature, shielded from light, until the analysis is performed.

5.3 Analysis. Analyze the sample with a gas chromatograph coupled to a mass spectrometer (GC/MS) using the instrumental parameters in sections 5.3.1 and 5.3.2. Immediately prior to analysis, add a 20 µl aliquot of the Recovery Standard solution from Table 1 to each sample. A 2 µl aliquot of the extract is injected into the GC. Sample extracts are first analyzed using the DB–5 capillary column to determine the concentration of each isomer of PCDD's and PCDF's (tetra-through octa-). If tetra-chlorinated dibenzofurans are detected in this analysis, then analyze another aliquot of the sample in a separate run, using the DB–225 column to measure the 2,3,7,8 tetra-chloro dibenzofuran isomer. Other column systems may be used, provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of section 6.1.2.2.

5.3.1 Gas Chromatograph Operating Conditions.

5.3.1.1 Injector. Configured for capillary column, splitless, 250 °C.

5.3.1.2 Carrier Gas. Helium, 1–2 ml/min.

5.3.1.3 Oven. Initially at 150 °C. Raise by at least 40 °C/min to 190 °C and then at 3 °C/min up to 300 °C.

5.3.2 High Resolution Mass Spectrometer.

5.3.2.1 Resolution. 10000 m/e.

5.3.2.2 Ionization Mode. Electron impact.

5.3.2.3 Source Temperature 250 °C.

5.3.2.4 Monitoring Mode. Selected ion monitoring. A list of the various ions to be monitored is summarized in Table 3.

5.3.2.5 Identification Criteria. The following identification criteria shall be used for the characterization of polychlorinated dibenzodioxins and dibenzofurans.

1. The integrated ion-abundance ratio (M/M + 2 or M + 2/M + 4) shall be within 15 percent of the theoretical value. The acceptable ion-abundance ratio ranges for the identification of chlorine-containing compounds are given in Table 4.

2. The retention time for the analytes must be within 3 seconds of the corresponding ^{13}C-labeled internal standard, surrogate or alternate standard.

3. The monitored ions, shown in Table 3 for a given analyte, shall reach their maximum within 2 seconds of each other.

4. The identification of specific isomers that do not have corresponding ^{13}C-labeled standards is done by comparison of the relative retention time (RRT) of the analyte to the nearest internal standard retention time with reference (i.e., within 0.005 RRT units) to the comparable RRT's found in the continuing calibration.

5. The signal to noise ratio for all monitored ions must be greater than 2.5.

6. The confirmation of 2, 3, 7, 8–TCDD and 2, 3, 7, 8–TCDF shall satisfy all of the above identification criteria.

7. For the identification of PCDF's, no signal may be found in the corresponding PCDPE channels.

5.3.2.6 Quantification. The peak areas for the two ions monitored for each analyte are summed to yield the total response for each analyte. Each internal standard is used to quantify the indigenous PCDD's or PCDF's in its homologous series. For example, the $^{13}C_{12}$–2,3,7,8-tetra chlorinated dibenzodioxin is used to calculate the concentrations of all

other tetra chlorinated isomers. Recoveries of the tetra- and penta- internal standards are calculated using the $^{13}C_{12}$–1,2,3,4–TCDD. Recoveries of the hexa- through octa- internal standards are calculated using $^{13}C_{12}$–1,2,3,7,8,9–HxCDD. Recoveries of the surrogate standards are calculated using the corresponding homolog from the internal standard.

6. Calibration

Same as Method 5 with the following additions.

6.1 GC/MS System.

6.1.1 Initial Calibration. Calibrate the GC/MS system using the set of five standards shown in Table 2. The relative standard deviation for the mean response factor from each of the unlabeled analytes (Table 2) and of the internal, surrogate, and alternate standards shall be less than or equal to the values in Table 5. The signal to noise ratio for the GC signal present in every selected ion current profile shall be greater than or equal to 2.5. The ion abundance ratios shall be within the control limits in Table 4.

6.1.2 Daily Performance Check.

6.1.2.1 Calibration Check. Inject on µl of solution Number 3 from Table 2. Calculate the relative response factor (RRF) for each compound and compare each RRF to the corresponding mean RRF obtained during the initial calibration. The analyzer performance is acceptable if the measured RRF's for the labeled and unlabeled compounds for the daily run are within the limits of the mean values shown in Table 5. In addition, the ion-abundance ratios shall be within the allowable control limits shown in Table 4.

6.1.2.2 Column Separation Check. Inject a solution of a mixture of PCDD's and PCDF's that documents resolution between 2,3,7,8–TCDD and other TCDD isomers. Resolution is defined as a valley between peaks that is less than 25 percent of the lower of the two peaks. Identify and record the retention time windows for each homologous series.

Perform a similar resolution check on the confirmation column to document the resolution between 2,3,7,8 TCDF and other TCDF isomers.

6.2 Lock Channels. Set mass spectrometer lock channels as specified in Table 3. Monitor the quality control check channels specified in Table 3 to verify instrument stability during the analysis.

7. Quality Control

7.1 Sampling Train Collection Efficiency Check. Add 100 µl of the surrogate standards in Table 1 to the absorbent cartridge of each train before collecting the field samples.

7.2 Internal Standard Percent Recoveries. A group of nine carbon labeled PCDD's and PCDF's representing, the tetra-through octachlorinated homologues, is added to every sample prior to extraction. The role of the internal standards is to quantify the native PCDD's and PCDF's present in the sample as well as to determine the overall method efficiency. Recoveries of the internal standards must be between 40 to 130 percent for the tetra-through hexachlorinated compounds while the range is 25 to 130 percent for the higher hepta- and octachlorinated homologues.

7.3 Surrogate Recoveries. The five surrogate compounds in Table 2 are added to the resin in the adsorbent sampling cartridge before the sample is collected. The surrogate recoveries are measured relative to the internal standards and are a measure of collection efficiency. They are not used to measure native PCDD's and PCDF's. All recoveries shall be between 70 and 130 percent. Poor recoveries for all the surrogates may be an indication of breakthrough in the sampling train. If the recovery of all standards is below 70 percent, the sampling runs must be repeated. As an alternative, the sampling runs do not have to be repeated if the final results are divided by the fraction of surrogate recovery. Poor recoveries of isolated surrogate compounds should not be grounds for rejecting an entire set of the samples.

7.4 Toluene QA Rinse. Report the results of the toluene QA rinse separately from the total sample catch. Do not add it to the total sample.

8.0 [Reserved]

9. Calculations

Same as Method 5, section 6 with the following additions.

9.1 Nomenclature.

A_{ai} = Integrated ion current of the noise at the retention time of the analyte.

A^*_{ci} = Integrated ion current of the two ions characteristic of the internal standard i in the calibration standard.

A_{cij} = Integrated ion current of the two ions characteristic of compound i in the jth calibration standard.

A^*_{cij} = Integrated ion current of the two ions characteristic of the internal standard i in the jth calibration standard.

A_{csi} = Integrated ion current of the two ions characteristic of surrogate compound i in the calibration standard.

A_i = Integrated ion current of the two ions characteristic of compound i in the sample.

A^*_i = Integrated ion current of the two ions characteristic of internal standard i in the sample.

A_{rs} = Integrated ion current of the two ions characteristic of the recovery standard.

A_{si} = Integrated ion current of the two ions characteristic of surrogate compound i in the sample.

C_i = Concentration of PCDD or PCDF i in the sample, pg/M^3.

C_T = Total concentration of PCDD's or PCDF's in the sample, pg/M^3.
m_{ci} = Mass of compound i in the calibration standard injected into the analyzer, pg.
m_{rs} = Mass of recovery standard in the calibration standard injected into the analyzer, pg.
m_{si} = Mass of surrogate compound in the calibration standard, pg.
RRF_i = Relative response factor.
RRF_{rs} = Recovery standard response factor.
RRF_s = Surrogate compound response factor.

9.2 Average Relative Response Factor.

$$RRF_i = \frac{1}{n}\sum_{j=1}^{n}\frac{A_{cij}\, m^*_{ci}}{A^*_{cij}\, m_{ci}} \qquad \text{Eq. 23-1}$$

9.3 Concentration of the PCDD's and PCDF's.

$$C_i = \frac{m_i^* A_i}{A_i^* RRF_i V_{mstd}} \qquad \text{Eq. 23-2}$$

9.4 Recovery Standard Response Factor.

$$RRF_{rs} = \frac{A_{ci}^* m_{rs}}{A_{rs} m_{ci}^*} \qquad \text{Eq. 23-3}$$

9.5 Recovery of Internal Standards (R*).

$$R^* = \frac{A_i^* m_{rs}}{A_{rs} RF_{rs} m_i^*} \times 100\% \qquad \text{Eq. 23-4}$$

9.6 Surrogate Compound Response Factor.

$$RRF_s = \frac{A_{ci}^* m_s}{A_{cis} m_{ci}^*} \qquad \text{Eq. 23-5}$$

9.7 Recovery of Surrogate Compounds (R_s).

$$R_s = \frac{A_s m_i^*}{A_i^* RRF_s m_s} \times 100\% \qquad \text{Eq. 23-6}$$

9.8 Minimum Detectable Limit (MDL).

$$MDL = \frac{2.5\, A_{ai} m_i^*}{A_{ci}^* RRF_i} \qquad \text{Eq. 23-7}$$

9.9 Total Concentration of PCDD's and PCDF's in the Sample.

$$C_{Tr} = \sum_{i=1}^{n} C_i \qquad \text{Eq. 23-8}$$

Any PCDD's or PCDF's that are reported as nondetected (below the MDL) shall be counted as zero for the purpose of calculating the total concentration of PCDD's and PCDF's in the sample.

10. Bibliography

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TABLE 1—COMPOSITION OF THE SAMPLE FORTIFICATION AND RECOVERY STANDARDS SOLUTIONS

Analyte	Concentration (pg/µl)
Internal Standards:	
$^{13}C_{12}$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100
$^{13}C_{12}$-OCDD	100
$^{13}C_{12}$-2,3,7,8-TCDF	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100
Surrogate Standards:	
$^{37}Cl_4$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100
Recovery Standards:	
$^{13}C_{12}$-1,2,3,4-TCDD	500
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	500

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS

Compound	Concentrations (pg/µL)				
	Solution No.				
	1	2	3	4	5
Alternate Standard:					
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	2.5	5	25	250	500

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS—Continued

Compound	Concentrations (pg/μL)				
	Solution No.				
	1	2	3	4	5
Recovery Standards:					
$^{13}C_{12}$-1,2,3,4-TCDD ..	100	100	100	100	100

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS—Continued

Compound	Concentrations (pg/μL)				
	Solution No.				
	1	2	3	4	5
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

TABLE 3—ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HIGH RESOLUTION MASS SPECTROMETRY FOR PCDD'S AND PCDF'S

Descriptor No.	Accurate mass	Ion type	Elemental composition	Analyte
2	292.9825	LOCK	C_7F_{11}	PFK
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M + 2	$C_{12}H_4{}^{35}Cl^{37}O$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M + 2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}ClO_2$	TCDD
	321.8936	M + 2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD (S)
	330.9792	QC	C_7F_{13}	PFK
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9339	M + 2	$^{13}C_{12}H_4{}^{35}Cl^{37}ClO_2$	TCDD (S)
	339.8597	M + 2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PECDF
	341.8567	M + 4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M + 2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M + 4	$^{13}C_{12}H_3{}^{35}Cl^{3537}Cl_2O$	PeCDF (S)
	355.8546	M + 2	$C_{12}H_3{}^{35}Cl_3{}37ClO_2$	PeCDD
	357.8516	M + 4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M + 2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M + 4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}\ Cl_2O_2$	PeCDD (S)
	375.8364	M + 2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
	409.7974	M + 2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCPDE
3	373.8208	M + 2	$C_{12}H_2{}35Cl_5{}^{37}ClO$	HxCDF
	375.8178	M + 4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M + 2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8157	M + 2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M + 4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	392.9760	LOCK	C_9F_{15}	PFK
	401.8559	M + 2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M + 4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDD (S)
	445.7555	M + 4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	430.9729	QC	C_9F_{17}	PFK
4	407.7818	M + 2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M + 4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8253	M	$^{13}C_{12}H^{35}Cl_7O$	HpCDF (S)
	419.8220	M + 2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF (S)
	423.7766	M + 2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M + 4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M + 2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M + 4	$^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S)
	479.7165	M + 4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCPDE
	430.9729	LOCK	C_9F_{17}	PFK
	441.7428	M + 2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M + 4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M + 2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M + 4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M + 2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M + 4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S)
	513.6775	M + 4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O_2$	DCDPE
	442.9728	QC	$C_{10}F_{17}$	PFK

(a) The following nuclidic masses were used:
H = 1.007825
C = 12.000000
^{13}C = 13.003355
F = 18.9984
O = 15.994915
^{35}Cl = 34.968853
^{37}Cl = 36.965903

S = Labeled Standard
QC = Ion selected for monitoring instrument stability during the GC/MS analysis.

TABLE 4—ACCEPTABLE RANGES FOR ION-ABUNDANCE RATIOS OF PCDD'S AND PCDF'S

No. of chlorine atoms	Ion type	Theoretical ratio	Control limits	
			Lower	Upper
4	M/M + 2	0.77	0.65	0.89
5	M + 2/M + 4	1.55	1.32	1.78
6	M + 2/M + 4	1.24	1.05	1.43
6[a]	M/M + 2	0.51	0.43	0.59
7[b]	M/M + 2	0.44	0.37	0.51
7	M + 2/M + 4	1.04	0.88	1.20
8	M + 2/M + 4	0.89	0.76	1.02

[a] Used only for ^{13}C-HxCDF.
[b] Used only for ^{13}C-HpCDF.

TABLE 5—MINIMUM REQUIREMENTS FOR INITIAL AND DAILY CALIBRATION RESPONSE FACTORS

Compound	Relative response factors	
	Initial calibration RSD	Daily calibration % difference
Unlabeled Analytes:		
2,3,7,8-TCDD	25	25
2,3,7,8-TCDF	25	25
1,2,3,7,8-PeCDD	25	25
1,2,3,7,8-PeCDF	25	25
2,3,4,7,8-PeCDF	25	25
1,2,4,5,7,8-HxCDD	25	25
1,2,3,6,7,8-HxCDD	25	25
1,2,3,7,8,9-HxCDD	25	25
1,2,3,4,7,8-HxCDF	25	25
1,2,3,6,7,8-HxCDF	25	25
1,2,3,7,8,9-HxCDF	25	25
2,3,4,6,7,8-HxCDF	25	25
1,2,3,4,6,7,8-HpCDD	25	25
1,2,3,4,6,7,8-HpCDF	25	25
OCDD	25	25
OCDF	30	30
Internal Standards:		
$^{13}C_{12}$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-1,2,3,7,8-PeCDD	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	30	30
$^{13}C_{12}$-OCDD	30	30
$^{13}C_{12}$-2,3,7,8-TCDF	30	30
$^{13}C_{12}$-1,2,3,7,8-PeCDF	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	30	30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	30	30
Surrogate Standards:		
$^{37}Cl_4$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-2,3,4,7,8-PeCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	25	25
Alternate Standard:		
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	25	25

METHOD 24—DETERMINATION OF VOLATILE MATTER CONTENT, WATER CONTENT, DENSITY, VOLUME SOLIDS, AND WEIGHT SOLIDS OF SURFACE COATINGS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile organic compounds	No CAS Number assigned
Water.	7732–18–5

1.2 Applicability. This method is applicable for the determination of volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or other related surface coatings.

1.3 Precision and Bias. Intra-and inter-laboratory analytical precision statements are presented in section 13.1. No bias has been identified.

2.0 Summary of Method

2.1 Standard methods are used to determine the volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or other related surface coatings.

3.0 Definitions

3.1 *Waterborne coating* means any coating which contains more than 5 percent water by weight in its volatile fraction.

3.2 *Multicomponent coatings* are coatings that are packaged in two or more parts, which are combined before application. Upon combination a coreactant from one part of the coating chemically reacts, at ambient conditions, with a coreactant from another part of the coating.

3.3 *Ultraviolet (UV) radiation-cured coatings* are coatings which contain unreacted monomers that are polymerized by exposure to ultraviolet light.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Components. Several of the compounds that may be contained in the coatings analyzed by this method may be irritating or corrosive to tissues (e.g., heptane) or may be toxic (e.g., benzene, methyl alcohol). Nearly all are fire hazards.

Appropriate precautions can be found in reference documents, such as Reference 3 of section 16.0.

6.0 Equipment and Supplies

The equipment and supplies specified in the ASTM methods listed in sections 6.1 through 6.6 (incorporated by reference—see §60.17 for acceptable versions of the methods) are required:

6.1 ASTM D 1475–60, 80, or 90, Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products.

6.2 ASTM D 2369–81, 87, 90, 92, 93, or 95, Standard Test Method for Volatile Content of Coatings.

6.3 ASTM D 3792–79 or 91, Standard Test Method for Water Content of Water Reducible Paints by Direct Injection into a Gas Chromatograph.

6.4 ASTM D 4017–81, 90, or 96a, Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Titration Method.

6.5 ASTM 4457–85 91, Standard Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph.

6.6 ASTM D 5403–93, Standard Test Methods for Volatile Content of Radiation Curable Materials.

6.7 ASTM D 6419–00, Test Method for Volatile Content of Sheet-Fed and Coldset Web Offset Printing Inks.

7.0 Reagents and Standards

7.1 The reagents and standards specified in the ASTM methods listed in sections 6.1 through 6.6 are required.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Follow the sample collection, preservation, storage, and transport procedures described in Reference 1 of section 16.0.

9.0 Quality Control

9.1 Reproducibility

NOTE: Not applicable to UV radiation-cured coatings). The variety of coatings that may be subject to analysis makes it necessary to verify the ability of the analyst and the analytical procedures to obtain reproducible results for the coatings tested. Verification is accomplished by running duplicate analyses on each sample tested (Sections 11.2 through 11.4) and comparing the results with the intra-laboratory precision statements (Section 13.1) for each parameter.

9.2 Confidence Limits for Waterborne Coatings. Because of the inherent increased imprecision in the determination of the VOC content of waterborne coatings as the weight percent of water increases, measured parameters for waterborne coatings are replaced with appropriate confidence limits (Section 12.6). These confidence limits are based on measured parameters and inter-laboratory precision statements.

10.0 Calibration and Standardization

10.1 Perform the calibration and standardization procedures specified in the ASTM methods listed in sections 6.1 through 6.6.

11.0 Analytical Procedure

Additional guidance can be found in Reference 2 of section 16.0.

11.1 Non Thin-film Ultraviolet Radiation-cured (UV radiation-cured) Coatings.

11.1.1 Volatile Content. Use the procedure in ASTM D 5403 to determine the volatile matter content of the coating except the curing test described in NOTE 2 of ASTM D 5403 is required.

11.1.2 Water Content. To determine water content, follow section 11.3.2.

11.1.3 Coating Density. To determine coating density, follow section 11.3.3.

11.1.4 Solids Content. To determine solids content, follow section 11.3.4.

11.1.5 To determine if a coating or ink can be classified as a thin-film UV cured coating or ink, use the equation in section 12.2. If C is less than 0.2 g and A is greater than or equal to 225 cm^2 (35 in^2) then the coating or ink is considered a thin-film UV radiation-cured coating and ASTM D 5403 is not applicable.

NOTE: As noted in section 1.4 of ASTM D 5403, this method may not be applicable to radiation curable materials wherein the volatile material is water.

11.2 Multi-component Coatings.

11.2.1 Sample Preparation.

11.2.1.1 Prepare about 100 ml of sample by mixing the components in a storage container, such as a glass jar with a screw top or a metal can with a cap. The storage container should be just large enough to hold the mixture. Combine the components (by weight or volume) in the ratio recommended by the manufacturer. Tightly close the container between additions and during mixing to prevent loss of volatile materials. However, most manufacturers mixing instructions are by volume. Because of possible error caused by expansion of the liquid when measuring the volume, it is recommended that the components be combined by weight. When weight is used to combine the components and the manufacturer's recommended ratio is by volume, the density must be determined by section 11.3.3.

11.2.1.2 Immediately after mixing, take aliquots from this 100 ml sample for determination of the total volatile content, water content, and density.

11.2.2 Volatile Content. To determine total volatile content, use the apparatus and

reagents described in ASTM D2369 (incorporated by reference; see §60.17 for the approved versions of the standard), respectively, and use the following procedures:

11.2.2.1 Weigh and record the weight of an aluminum foil weighing dish. Add 3 ±1 ml of suitable solvent as specified in ASTM D2369 to the weighing dish. Using a syringe as specified in ASTM D2369, weigh to 1 mg, by difference, a sample of coating into the weighing dish. For coatings believed to have a volatile content less than 40 weight percent, a suitable size is 0.3 + 0.10 g, but for coatings believed to have a volatile content greater than 40 weight percent, a suitable size is 0.5 ±0.1 g.

NOTE: If the volatile content determined pursuant to section 12.4 is not in the range corresponding to the sample size chosen repeat the test with the appropriate sample size. Add the specimen dropwise, shaking (swirling) the dish to disperse the specimen completely in the solvent. If the material forms a lump that cannot be dispersed, discard the specimen and prepare a new one. Similarly, prepare a duplicate. The sample shall stand for a minimum of 1 hour, but no more than 24 hours prior to being oven cured at 110 ±5 °C (230 ±9 °F) for 1 hour.

11.2.2.2 Heat the aluminum foil dishes containing the dispersed specimens in the forced draft oven for 60 min at 110 ±5 °C (230 ±9 °F). Caution—provide adequate ventilation, consistent with accepted laboratory practice, to prevent solvent vapors from accumulating to a dangerous level.

11.2.2.3 Remove the dishes from the oven, place immediately in a desiccator, cool to ambient temperature, and weigh to within 1 mg.

11.2.2.4 Run analyses in pairs (duplicate sets) for each coating mixture until the criterion in section 11.4 is met. Calculate W_v following Equation 24–2 and record the arithmetic average.

11.2.3 Water Content. To determine water content, follow section 11.3.2.

11.2.4 Coating Density. To determine coating density, follow section 11.3.3.

11.2.5 Solids Content. To determine solids content, follow section 11.3.4.

11.2.6 Exempt Solvent Content. To determine the exempt solvent content, follow section 11.3.5.

NOTE: For all other coatings (*i.e.*, water-or solvent-borne coatings) not covered by multicomponent or UV radiation-cured coatings, analyze as shown below:

11.3 Water-or Solvent-borne coatings.

11.3.1 Volatile Content. Use the procedure in ASTM D 2369 to determine the volatile matter content (may include water) of the coating.

11.3.1.1 Record the following information:

W_1 = weight of dish and sample before heating, g

W_2 = weight of dish and sample after heating, g

W_3 = sample weight, g.

11.3.1.2 Calculate the weight fraction of the volatile matter (W_v) for each analysis as shown in section 12.3.

11.3.1.3 Run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement in section 13.1.

11.3.1.4 Record the arithmetic average (W_v).

11.3.2 Water Content. For waterborne coatings only, determine the weight fraction of water (W_w) using either ASTM D 3792 or ASTM D 4017.

11.3.2.1 Run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement in section 13.1.

11.3.2.2 Record the arithmetic average (w_w).

11.3.3 Coating Density. Determine the density (Dc, kg/l) of the surface coating using the procedure in ASTM D 1475.

11.3.3.1 Run duplicate analyses until each value in a set deviates from the mean of the set by no more than the intra-laboratory precision statement in section 13.1.

11.3.3.2 Record the arithmetic average (D_c).

11.3.4 Solids Content. Determine the volume fraction (V_s) solids of the coating by calculation using the manufacturer's formulation.

11.3.5 Exempt Solvent Content. Determine the weight fraction of exempt solvents (W_E) by using ASTM Method D4457. Run a duplicate set of determinations and record the arithmetic average (W_E).

11.4 Sample Analysis Criteria. For W_v and W_w, run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement for that parameter. For D_c, run duplicate analyses until each value in a set deviates from the mean of the set by no more than the intra-laboratory precision statement. If, after several attempts, it is concluded that the ASTM procedures cannot be used for the specific coating with the established intra-laboratory precision (excluding UV radiation-cured coatings), the U.S. Environmental Protection Agency (EPA) will assume responsibility for providing the necessary procedures for revising the method or precision statements upon written request to: Director, Emissions, Monitoring, and Analysis Division, MD–14, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

12.0 Calculations and Data Analysis

12.1 Nomenclature.

A = Area of substrate, cm^2, (in^2).

C = Amount of coating or ink added to the substrate, g.

D_c = Density of coating or ink, g/cm^3 (g/in^3).

F = Manufacturer's recommended film thickness, cm (in).
W_o = Weight fraction of nonaqueous volatile matter, g/g.
W_s = Weight fraction of solids, g/g.
W_v = Weight fraction of the volatile matter, g/g.
W_w = Weight fraction of the water, g/g.

12.2 To determine if a coating or ink can be classified as a thin-film UV cured coating or ink, use the following equation:

$$C = F A D_c \qquad \text{Eq. 24-1}$$

12.3 Calculate W_v for each analysis as shown below:

$$W_v = \frac{W_1 - W_2}{W_3} \qquad \text{Eq. 24-2}$$

12.4 Nonaqueous Volatile Matter.
12.4.1 Solvent-borne Coatings.

$$W_o = W_v \qquad \text{Eq. 24-3}$$

12.4.2 Waterborne Coatings.

$$W_o = W_v - W_w \qquad \text{Eq. 24-4}$$

12.4.3 Coatings Containing Exempt Solvents.

$$W_o = W_v - W_E - W_w \qquad \text{Eq. 24-5}$$

12.5 Weight Fraction Solids.

$$W_s = 1 - W_v \qquad \text{Eq. 24-6}$$

12.6 Confidence Limit Calculations for Waterborne Coatings. To calculate the lower confidence limit, subtract the appropriate inter-laboratory precision value from the measured mean value for that parameter. To calculate the upper confidence limit, add the appropriate inter-laboratory precision value to the measured mean value for that parameter. For W_v and D_c, use the lower confidence limits; for W_w, use the upper confidence limit. Because W_s is calculated, there is no adjustment for this parameter.

13.0 Method Performance

13.1 Analytical Precision Statements. The intra-and inter-laboratory precision statements are given in Table 24–1 in section 17.0.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as specified in section 6.0, with the addition of the following:

1. Standard Procedure for Collection of Coating and Ink Samples for Analysis by Reference Methods 24 and 24A. EPA–340/1–91–010. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.
2. Standard Operating Procedure for Analysis of Coating and Ink Samples by Reference Methods 24 and 24A.
EPA–340/1–91–011. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.
3. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 24–1—ANALYTICAL PRECISION STATEMENTS

	Intra-laboratory	Inter-laboratory
Volatile matter content, W_v	±0.015 $\overline{W}_v$	±0.047 $\overline{W}_v$
Water content, W_w	±0.029 $\overline{W}_w$	±0.075 $\overline{W}_w$
Density, D_c	±0.001 kg/l	±0.002 kg/l

METHOD 24A—DETERMINATION OF VOLATILE MATTER CONTENT AND DENSITY OF PUBLICATION ROTOGRAVURE INKS AND RELATED PUBLICATION ROTOGRAVURE COATINGS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile organic compounds (VOC).	No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of the VOC content and density of solvent-borne (solvent-reducible) publication rotogravure inks and related publication rotogravure coatings.

2.0 Summary of Method

2.1 Separate procedures are used to determine the VOC weight fraction and density of the ink or related coating and the density of the solvent in the ink or related coating. The VOC weight fraction is determined by measuring the weight loss of a known sample quantity which has been heated for a specified length of time at a specified temperature. The density of both the ink or related coating and solvent are measured by a standard procedure. From this information, the VOC volume fraction is calculated.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Components. Some of the compounds that may be contained in the inks or related coatings analyzed by this method may be irritating or corrosive to tissues or may be toxic. Nearly all are fire hazards. Appropriate precautions can be found in reference documents, such as Reference 6 of section 16.0.

6.0 Equipment and Supplies

The following equipment and supplies are required for sample analysis:

6.1 Weighing Dishes. Aluminum foil, 58 mm (2.3 in.) in diameter by 18 mm (0.7 in.) high, with a flat bottom. There must be at least three weighing dishes per sample.

6.2 Disposable Syringe. 5 ml.

6.3 Analytical Balance. To measure to within 0.1 mg.

6.4 Oven. Vacuum oven capable of maintaining a temperature of 120 ±2 °C (248 ±4 °F) and an absolute pressure of 510 ±51 mm Hg (20 ±2 in. Hg) for 4 hours. Alternatively, a forced draft oven capable of maintaining a temperature of 120 ±2 °C (248 ±4 °F) for 24 hours.

6.5 The equipment and supplies specified in ASTM D 1475–60, 80, or 90 (incorporated by reference—see §60.17).

7.0 Reagents and Standards

7.1 The reagents and standards specified in ASTM D 1475–60, 80, or 90 are required.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Follow the sample collection, preservation, storage, and transport procedures described in Reference 4 of section 16.0.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

Additional guidance can be found in Reference 5 of section 16.0.

11.1 VOC Weight Fraction. Shake or mix the ink or related coating sample thoroughly to assure that all the solids are completely suspended. Label and weigh to the nearest 0.1 mg a weighing dish and record this weight (M_{x1}). Using a 5 ml syringe, without a needle, extract an aliquot from the ink or related coating sample. Weigh the syringe and aliquot to the nearest 0.1 mg and record this weight (M_{cy1}). Transfer 1 to 3 g of the aliquot to the tared weighing dish. Reweigh the syringe and remaining aliquot to the nearest 0.1 mg and record this weight (M_{cy2}). Heat the weighing dish with the transferred aliquot in a vacuum oven at an absolute pressure of 510 ±51 mm Hg (20 ±2 in. Hg) and a temperature of 120 ±2 °C (248 ±4 °F) for 4 hours. Alternatively, heat the weighing dish with the transferred aliquot in a forced draft oven at a temperature of 120 ±2 °C for 24 hours. After the weighing dish has cooled, reweigh it to the nearest 0.1 mg and record the weight (M_{x2}). Repeat this procedure two times for each ink or related coating sample, for a total of three samples.

11.2 Ink or Related Coating Density. Determine the density of the ink or related coating (D_c) according to the procedure outlined in ASTM D 1475. Make a total of three determinations for each ink or related coating sample. Report the ink or related coating density as the arithmetic average (D_c) of the three determinations.

11.3 Solvent Density. Determine the density of the solvent (D_o) according to the procedure outlined in ASTM D 1475. Make a total of three determinations for each ink or related coating sample. Report the solvent density as the arithmetic average (D_o) of the three determinations.

12.0 Calculations and Data Analysis

12.1 VOC Weight Fraction. For each determination, calculate the volatile organic content weight fraction (W_o) using the following equation:

$$W_o = \frac{M_{x1} + M_{cy1} - M_{cy2} - M_{x2}}{M_{cy1} - M_{cy2}} \qquad \text{Eq. 24A-1}$$

Make a total of three determinations. Report the VOC weight fraction as the arithmetic average ($\bar{W}_o$) of the three determinations.

12.2 VOC Volume Fraction. Calculate the volume fraction volatile organic content (V_o) using the following equation:

$$V_o = \frac{\overline{W}_o \overline{D}_c}{\overline{D}_o} \qquad \text{Eq. 24A-2}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products. ASTM Designation D 1475.

2. Teleconversation. Wright, Chuck, Inmont Corporation with Reich, R., A., Radian Corporation. September 25, 1979, Gravure Ink Analysis.

3. Teleconversation. Oppenheimer, Robert, Gravure Research Institute with Burt, Rick, Radian Corporation, November 5, 1979, Gravure Ink Analysis.

4. Standard Procedure for Collection of Coating and Ink Samples for Analysis by Reference Methods 24 and 24A. EPA–340/1–91–010. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

5. Standard Operating Procedure for Analysis of Coating and Ink Samples by Reference Methods 24 and 24A. EPA–340/1–91–011. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

6. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

Method 25—Determination of Total Gaseous Nonmethane Organic Emissions as Carbon

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total gaseous nonmethane organic compounds (TGNMO)	N/A	Dependent upon analytical equipment.

1.2 Applicability.

1.2.1 This method is applicable for the determination of volatile organic compounds (VOC) (measured as total gaseous nonmethane organics (TGNMO) and reported as carbon) in stationary source emissions. This method is not applicable for the determination of organic particulate matter.

1.2.2 This method is not the only method that applies to the measurement of VOC. Costs, logistics, and other practicalities of source testing may make other test methods more desirable for measuring VOC contents of certain effluent streams. Proper judgment is required in determining the most applicable VOC test method. For example, depending upon the molecular composition of the organics in the effluent stream, a totally automated semicontinuous nonmethane organics (NMO) analyzer interfaced directly to the source may yield accurate results. This approach has the advantage of providing emission data semicontinuously over an extended time period.

1.2.3 Direct measurement of an effluent with a flame ionization detector (FID) analyzer may be appropriate with prior characterization of the gas stream and knowledge that the detector responds predictably to the organic compounds in the stream. If present, methane (CH_4) will, of course, also be measured. The FID can be used under any of the following limited conditions: (1) Where only one compound is known to exist; (2) when the organic compounds consist of only hydrogen and carbon; (3) where the relative percentages of the compounds are known or can be determined, and the FID responses to the compounds are known; (4) where a consistent mixture of the compounds exists before and after emission control and only the relative concentrations are to be assessed; or (5) where the FID can be calibrated against mass standards of the compounds emitted (solvent emissions, for example).

1.2.4 Another example of the use of a direct FID is as a screening method. If there is enough information available to provide a rough estimate of the analyzer accuracy, the FID analyzer can be used to determine the VOC content of an uncharacterized gas stream. With a sufficient buffer to account for possible inaccuracies, the direct FID can be a useful tool to obtain the desired results without costly exact determination.

1.2.5 In situations where a qualitative/quantitative analysis of an effluent stream is desired or required, a gas chromatographic FID system may apply. However, for sources emitting numerous organics, the time and expense of this approach will be formidable.

2.0 Summary of Method

2.1 An emission sample is withdrawn from the stack at a constant rate through a heated filter and a chilled condensate trap by means of an evacuated sample tank. After sampling is completed, the TGNMO are determined by independently analyzing the condensate trap and sample tank fractions and combining the analytical results. The organic content of the condensate trap fraction is determined by oxidizing the NMO to carbon dioxide (CO_2) and quantitatively collecting in the effluent in an evacuated vessel; then a portion of the CO_2 is reduced to CH_4 and measured by an FID. The organic content of the sample tank fraction is measured by injecting a portion of the sample into a gas chromatographic column to separate the NMO from carbon monoxide (CO), CO_2, and CH_4; the NMO are oxidized to CO_2, reduced to CH_4, and measured by an FID. In this manner, the variable response of the FID associated with different types of organics is eliminated.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Carbon Dioxide and Water Vapor. When carbon dioxide (CO_2) and water vapor are present together in the stack, they can produce a positive bias in the sample. The magnitude of the bias depends on the concentrations of CO_2 and water vapor. As a guideline, multiply the CO_2 concentration, expressed as volume percent, times the water vapor concentration. If this product does not exceed 100, the bias can be considered insignificant. For example, the bias is not significant for a source having 10 percent CO_2 and 10 percent water vapor, but it might be significant for a source having 10 percent CO_2 and 20 percent water vapor.

4.2. Particulate Matter. Collection of organic particulate matter in the condensate trap would produce a positive bias. A filter is included in the sampling equipment to minimize this bias.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling system consists of a heated probe, heated filter, condensate trap, flow control system, and sample tank (see Figure 25–1). The TGNMO sampling equipment can be constructed from commercially available components and components fabricated in a machine shop. The following equipment is required:

6.1.1 Heated Probe. 6.4-mm (¼-in.) OD stainless steel tubing with a heating system capable of maintaining a gas temperature at the exit end of at least 129 °C (265 °F). The probe shall be equipped with a temperature sensor at the exit end to monitor the gas temperature. A suitable probe is shown in Figure 25–1. The nozzle is an elbow fitting attached to the front end of the probe while the temperature sensor is inserted in the side arm of a tee fitting attached to the rear of the probe. The probe is wrapped with a suitable length of high temperature heating tape, and then covered with two layers of glass cloth insulation and one layer of aluminum foil or an equivalent wrapping.

NOTE: If it is not possible to use a heating system for safety reasons, an unheated system with an in-stack filter is a suitable alternative.

6.1.2 Filter Holder. 25-mm (15/16-in.) ID Gelman filter holder with 303 stainless steel body and 316 stainless steel support screen with the Viton O-ring replaced by a Teflon O-ring.

6.1.3 Filter Heating System.

6.1.3.1 A metal box consisting of an inner and an outer shell separated by insulating material with a heating element in the inner shell capable of maintaining a gas temperature at the filter of 121 ±3 °C (250 ±5 °F). The heating box shall include temperature sensors to monitor the gas temperature immediately upstream and immediately downstream of the filter.

6.1.3.2 A suitable heating box is shown in Figure 25–2. The outer shell is a metal box that measures 102 mm × 280 mm × 292 mm (4 in. × 11 in. × 11½ in.), while the inner shell is a metal box measuring 76 mm × 229 mm × 241 mm (3 in. × 9 in. × 9½ in.). The inner box is supported by 13-mm (½-in.) phenolic rods. The void space between the boxes is filled with ceramic fiber insulation which is sealed in place by means of a silicon rubber bead around the upper sides of the box. A removable lid made in a similar manner, with a 25-mm (1-in.) gap between the parts is used to cover the heating chamber. The inner box is heated with a 250-watt cartridge heater, shielded by a stainless steel shroud. The heater is regulated by a thermostatic temperature controller which is set to maintain a gas temperature of 121 °C (250 °F) as measured by the temperature sensor upstream of the filter.

NOTE: If it is not possible to use a heating system for safety reasons, an unheated system with an in-stack filter is a suitable alternative.

6.1.4 Condensate Trap. 9.5-mm (⅜-in.) OD 316 stainless steel tubing bent into a U-shape. Exact dimensions are shown in Figure

25–3. The tubing shall be packed with coarse quartz wool, to a density of approximately 0.11 g/cm^3 before bending. While the condensate trap is packed with dry ice in the Dewar, an ice bridge may form between the arms of the condensate trap making it difficult to remove the condensate trap. This problem can be prevented by attaching a steel plate between the arms of the condensate trap in the same plane as the arms to completely fill the intervening space.

6.1.5 Valve. Stainless steel control valve for starting and stopping sample flow.

6.1.6 Metering Valve. Stainless steel valve for regulating the sample flow rate through the sample train.

6.1.7 Rate Meter. Rotameter, or equivalent, capable of measuring sample flow in the range of 60 to 100 cm^3/min (0.13 to 0.21 ft^3/hr).

6.1.8 Sample Tank. Stainless steel or aluminum tank with a minimum volume of 4 liters (0.14 ft^3).

NOTE: Sample volumes greater than 4 liters may be required for sources with low organic concentrations.

6.1.9 Mercury Manometer. U-tube manometer or absolute pressure gauge capable of measuring pressure to within 1 mm Hg in the range of 0 to 900 mm.

6.1.10 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

6.2 Condensate Recovery. The system for the recovery of the organics captured in the condensate trap consists of a heat source, an oxidation catalyst, a nondispersive infrared (NDIR) analyzer, and an intermediate collection vessel (ICV). Figure 25–4 is a schematic of a typical system. The system shall be capable of proper oxidation and recovery, as specified in section 10.1.1. The following major components are required:

6.2.1 Heat Source. Sufficient to heat the condensate trap (including probe) to a temperature of 200 °C (390 °F). A system using both a heat gun and an electric tube furnace is recommended.

6.2.2 Heat Tape. Sufficient to heat the connecting tubing between the water trap and the oxidation catalyst to 100 °C (212 °F).

6.2.3 Oxidation Catalyst. A suitable length of 9.5 mm (3/8-in.) OD Inconel 600 tubing packed with 15 cm (6 in.) of 3.2 mm (3/8-in.) diameter 19 percent chromia on alumina pellets. The catalyst material is packed in the center of the catalyst tube with quartz wool packed on either end to hold it in place.

6.2.4 Water Trap. Leak-proof, capable of removing moisture from the gas stream.

6.2.5 Syringe Port. A 6.4-mm (1/4-in.) OD stainless steel tee fitting with a rubber septum placed in the side arm.

6.2.6 NDIR Detector. Capable of indicating CO_2 concentration in the range of zero to 5 percent, to monitor the progress of combustion of the organic compounds from the condensate trap.

6.2.7 Flow-Control Valve. Stainless steel, to maintain the trap conditioning system near atmospheric pressure.

6.2.8 Intermediate Collection Vessel. Stainless steel or aluminum, equipped with a female quick connect. Tanks with nominal volumes of at least 6 liters (0.2 ft^3) are recommended.

6.2.9 Mercury Manometer. Same as described in section 6.1.9.

6.2.10 Syringe. 10-ml gas-tight glass syringe equipped with an appropriate needle.

6.2.11 Syringes. 10-µl and 50-µl liquid injection syringes.

6.2.12 Liquid Sample Injection Unit. 316 Stainless steel U-tube fitted with an injection septum (see Figure 25–7).

6.3 Analysis.

6.3.1 NMO Analyzer. The NMO analyzer is a gas chromatograph (GC) with backflush capability for NMO analysis and is equipped with an oxidation catalyst, reduction catalyst, and FID. Figures 25–5 and 25–6 are schematics of a typical NMO analyzer. This semicontinuous GC/FID analyzer shall be capable of: (1) Separating CO, CO_2, and CH_4 from NMO, (2) reducing the CO_2 to CH_4 and quantifying as CH_4, and (3) oxidizing the NMO to CO_2, reducing the CO_2 to CH_4 and quantifying as CH_4, according to section 10.1.2. The analyzer consists of the following major components:

6.3.1.1 Oxidation Catalyst. A suitable length of 9.5-mm (3/8-in.) OD Inconel 600 tubing packed with 5.1 cm (2 in.) of 19 percent chromia on 3.2-mm (1/8-in.) alumina pellets. The catalyst material is packed in the center of the tube supported on either side by quartz wool. The catalyst tube must be mounted vertically in a 650 °C (1200 °F) furnace. Longer catalysts mounted horizontally may be used, provided they can meet the specifications of section 10.1.2.1.

6.3.1.2 Reduction Catalyst. A 7.6-cm (3-in.) length of 6.4-mm (1/4-in.) OD Inconel tubing fully packed with 100-mesh pure nickel powder. The catalyst tube must be mounted vertically in a 400 °C (750 °F) furnace.

6.3.1.3 Separation Column(s). A 30-cm (1-ft) length of 3.2-mm (1/8-in.) OD stainless steel tubing packed with 60/80 mesh Unibeads 1S followed by a 61-cm (2-ft) length of 3.2-mm (1/8-in.) OD stainless steel tubing packed with 60/80 mesh Carbosieve G. The Carbosieve and Unibeads columns must be baked separately at 200 °C (390 °F) with carrier gas flowing through them for 24 hours before initial use.

6.3.1.4 Sample Injection System. A single 10-port GC sample injection valve or a group of valves with sufficient ports fitted with a sample loop properly sized to interface with the NMO analyzer (1-cc loop recommended).

6.3.1.5 FID. An FID meeting the following specifications is required:

6.3.1.5.1 Linearity. A linear response (±5 percent) over the operating range as demonstrated by the procedures established in section 10.1.2.3.

6.3.1.5.2 Range. A full scale range of 10 to 50,000 ppm CH_4. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.3.1.6 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the analytical results.

6.3.2 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm Hg.

6.3.3 Temperature Sensor. Capable of measuring the laboratory temperature within 1 °C (2 °F).

6.3.4 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

7.0 Reagents and Standards

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Dry Ice. Solid CO2, crushed.

7.1.2 Coarse Quartz Wool. 8 to 15 um.

7.1.3 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Method D2986–71, 78, or 95a (incorporated by reference—see §60.17). Test data from the supplier's quality control program are sufficient for this purpose.

7.2 NMO Analysis. The following gases are required for NMO analysis:

7.2.1 Carrier Gases. Helium (He) and oxygen (O_2) containing less than 1 ppm CO_2 and less than 0.1 ppm hydrocarbon.

7.2.2 Fuel Gas. Hydrogen (H_2), at least 99.999 percent pure.

7.2.3 Combustion Gas. Either air (less than 0.1 ppm total hydrocarbon content) or O_2 (purity 99.99 percent or greater), as required by the detector.

7.3 Condensate Analysis. The following are required for condensate analysis:

7.3.1 Gases. Containing less than 1 ppm carbon.

7.3.1.1 Air.

7.3.1.2 Oxygen.

7.3.2 Liquids. To conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society.

7.3.2.1 Hexane.

7.3.2.2 Decane.

7.4 Calibration. For all calibration gases, the manufacturer must recommend a maximum shelf life for each cylinder (i.e., the length of time the gas concentration is not expected to change more than ±5 percent from its certified value). The date of gas cylinder preparation, certified organic concentration, and recommended maximum shelf life must be affixed to each cylinder before shipment from the gas manufacturer to the buyer. The following calibration gases are required:

7.4.1 Oxidation Catalyst Efficiency Check Calibration Gas. Gas mixture standard with nominal concentration of 1 percent methane in air.

7.4.2 FID Linearity and NMO Calibration Gases. Three gas mixture standards with nominal propane concentrations of 20 ppm, 200 ppm, and 3000 ppm, in air.

7.4.3 CO_2 Calibration Gases. Three gas mixture standards with nominal CO_2 concentrations of 50 ppm, 500 ppm, and 1 percent, in air.

NOTE: Total NMO less than 1 ppm required for 1 percent mixture.

7.4.4 NMO Analyzer System Check Calibration Gases. Four calibration gases are needed as follows:

7.4.4.1 Propane Mixture. Gas mixture standard containing (nominal) 50 ppm CO, 50 ppm CH_4, 1 percent CO_2, and 20 ppm C_3H_8, prepared in air.

7.4.4.2 Hexane. Gas mixture standard containing (nominal) 50 ppm hexane in air.

7.4.4.3 Toluene. Gas mixture standard containing (nominal) 20 ppm toluene in air.

7.4.4.4 Methanol. Gas mixture standard containing (nominal) 100 ppm methanol in air.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Sampling Equipment Preparation.

8.1.1 Condensate Trap Cleaning. Before its initial use and after each use, a condensate trap should be thoroughly cleaned and checked to ensure that it is not contaminated. Both cleaning and checking can be accomplished by installing the trap in the condensate recovery system and treating it as if it were a sample. The trap should be heated as described in section 11.1.3. A trap may be considered clean when the CO_2 concentration in its effluent gas drops below 10 ppm. This check is optional for traps that most recently have been used to collect samples which were then recovered according to the procedure in section 11.1.3.

8.1.2 Sample Tank Evacuation and Leak-Check. Evacuate the sample tank to 10 mm Hg absolute pressure or less. Then close the sample tank valve, and allow the tank to sit for 60 minutes. The tank is acceptable if a change in tank vacuum of less than 1 mm Hg is noted. The evacuation and leak-check may be conducted either in the laboratory or the field.

8.1.3 Sampling Train Assembly. Just before assembly, measure the tank vacuum using a mercury manometer. Record this vacuum, the ambient temperature, and the barometric pressure at this time. Close the sample tank valve and assemble the sampling

system as shown in Figure 25–1. Immerse the condensate trap body in dry ice at least 30 minutes before commencing sampling to improve collection efficiency. The point where the inlet tube joins the trap body should be 2.5 to 5 cm (1 to 2 in.) above the top of the dry ice.

8.1.4 Pretest Leak-Check. A pretest leak-check is required. Calculate or measure the approximate volume of the sampling train from the probe tip to the sample tank valve. After assembling the sampling train, plug the probe tip, and make certain that the sample tank valve is closed. Turn on the vacuum pump, and evacuate the sampling system from the probe tip to the sample tank valve to an absolute pressure of 10 mm Hg or less. Close the purge valve, turn off the pump, wait a minimum period of 10 minutes, and recheck the indicated vacuum. Calculate the maximum allowable pressure change based on a leak rate of 1 percent of the sampling rate using Equation 25–1, section 12.2. If the measured pressure change exceeds the allowable, correct the problem and repeat the leak-check before beginning sampling.

8.2 Sample Collection.

8.2.1 Unplug the probe tip, and place the probe into the stack such that the probe is perpendicular to the duct or stack axis; locate the probe tip at a single preselected point of average velocity facing away from the direction of gas flow. For stacks having a negative static pressure, seal the sample port sufficiently to prevent air in-leakage around the probe. Set the probe temperature controller to 129 °C (265 °F) and the filter temperature controller to 121 °C (250 °F). Allow the probe and filter to heat for about 30 minutes before purging the sample train.

8.2.2 Close the sample valve, open the purge valve, and start the vacuum pump. Set the flow rate between 60 and 100 cm^3/min (0.13 and 0.21 ft^3/hr), and purge the train with stack gas for at least 10 minutes.

8.2.3 When the temperatures at the exit ends of the probe and filter are within the corresponding specified ranges, check the dry ice level around the condensate trap, and add dry ice if necessary. Record the clock time. To begin sampling, close the purge valve and stop the pump. Open the sample valve and the sample tank valve. Using the flow control valve, set the flow through the sample train to the proper rate. Adjust the flow rate as necessary to maintain a constant rate (±10 percent) throughout the duration of the sampling period. Record the sample tank vacuum and flowmeter setting at 5-minute intervals. (See Figure 25–8.) Select a total sample time greater than or equal to the minimum sampling time specified in the applicable subpart of the regulations; end the sampling when this time period is reached or when a constant flow rate can no longer be maintained because of reduced sample tank vacuum.

NOTE: If sampling had to be stopped before obtaining the minimum sampling time (specified in the applicable subpart) because a constant flow rate could not be maintained, proceed as follows: After closing the sample tank valve, remove the used sample tank from the sampling train (without disconnecting other portions of the sampling train). Take another evacuated and leak-checked sample tank, measure and record the tank vacuum, and attach the new tank to the sampling train. After the new tank is attached to the sample train, proceed with the sampling until the required minimum sampling time has been exceeded.

8.3 Sample Recovery. After sampling is completed, close the flow control valve, and record the final tank vacuum; then record the tank temperature and barometric pressure. Close the sample tank valve, and disconnect the sample tank from the sample system. Disconnect the condensate trap at the inlet to the rate meter, and tightly seal both ends of the condensate trap. Do not include the probe from the stack to the filter as part of the condensate sample.

8.4 Sample Storage and Transport. Keep the trap packed in dry ice until the samples are returned to the laboratory for analysis. Ensure that run numbers are identified on the condensate trap and the sample tank(s).

9.0 Quality Control

Section	Quality control measure	Effect
10.1.1	Initial performance check of condensate recovery apparatus.	Ensure acceptable condensate recovery efficiency.
10.1.2, 10.2	NMO analyzer initial and daily performance checks.	Ensure precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Initial Performance Checks.

10.1.1 Condensate Recovery Apparatus. Perform these tests before the system is first placed in operation, after any shutdown of 6 months or more, and after any major modification of the system, or at the frequency recommended by the manufacturer.

10.1.1.1 Carrier Gas and Auxiliary O_2 Blank Check. Analyze each new tank of carrier gas or auxiliary O_2 with the NMO analyzer to

check for contamination. Treat the gas cylinders as noncondensible gas samples, and analyze according to the procedure in section 11.2.3. Add together any measured CH_4, CO, CO_2, or NMO. The total concentration must be less than 5 ppm.

10.1.1.2 Oxidation Catalyst Efficiency Check.

10.1.1.2.1 With a clean condensate trap installed in the recovery system or a ⅛″ stainless steel connector tube, replace the carrier gas cylinder with the high level methane standard gas cylinder (Section 7.4.1). Set the four-port valve to the recovery position, and attach an ICV to the recovery system. With the sample recovery valve in vent position and the flow-control and ICV valves fully open, evacuate the manometer or gauge, the connecting tubing, and the ICV to 10 mm Hg absolute pressure. Close the flow-control and vacuum pump valves.

10.1.1.2.2 After the NDIR response has stabilized, switch the sample recovery valve from vent to collect. When the manometer or pressure gauge begins to register a slight positive pressure, open the flow-control valve. Keep the flow adjusted such that the pressure in the system is maintained within 10 percent of atmospheric pressure. Continue collecting the sample in a normal manner until the ICV is filled to a nominal gauge pressure of 300 mm Hg. Close the ICV valve, and remove the ICV from the system. Place the sample recovery valve in the vent position, and return the recovery system to its normal carrier gas and normal operating conditions. Analyze the ICV for CO_2 using the NMO analyzer; the catalyst efficiency is acceptable if the CO_2 concentration is within 2 percent of the methane standard concentration.

10.1.1.3 System Performance Check. Construct a liquid sample injection unit similar in design to the unit shown in Figure 25–7. Insert this unit into the condensate recovery and conditioning system in place of a condensate trap, and set the carrier gas and auxiliary O_2 flow rates to normal operating levels. Attach an evacuated ICV to the system, and switch from system vent to collect. With the carrier gas routed through the injection unit and the oxidation catalyst, inject a liquid sample (see sections 10.1.1.3.1 to 10.1.1.3.4) into the injection port. Operate the trap recovery system as described in section 11.1.3. Measure the final ICV pressure, and then analyze the vessel to determine the CO_2 concentration. For each injection, calculate the percent recovery according to section 12.7. Calculate the relative standard deviation for each set of triplicate injections according to section 12.8. The performance test is acceptable if the average percent recovery is 100 ±5 percent and the relative standard deviation is less than 2 percent for each set of triplicate injections.

10.1.1.3.1 50 µl hexane.

10.1.1.3.2 10 µl hexane.

10.1.1.3.3 50 µl decane.

10.1.1.3.4 10 µl decane.

10.1.2 NMO Analyzer. Perform these tests before the system is first placed in operation, after any shutdown longer than 6 months, and after any major modification of the system.

10.1.2.1 Oxidation Catalyst Efficiency Check. Turn off or bypass the NMO analyzer reduction catalyst. Make triplicate injections of the high level methane standard (Section 7.4.1). The oxidation catalyst operation is acceptable if the FID response is less than 1 percent of the injected methane concentration.

10.1.2.2 Reduction Catalyst Efficiency Check. With the oxidation catalyst unheated or bypassed and the heated reduction catalyst bypassed, make triplicate injections of the high level methane standard (Section 7.4.1). Repeat this procedure with both catalysts operative. The reduction catalyst operation is acceptable if the responses under both conditions agree within 5 percent of their average.

10.1.2.3 NMO Analyzer Linearity Check Calibration. While operating both the oxidation and reduction catalysts, conduct a linearity check of the analyzer using the propane standards specified in section 7.4.2. Make triplicate injections of each calibration gas. For each gas (*i.e.*, each set of triplicate injections), calculate the average response factor (area/ppm C) for each gas, as well as and the relative standard deviation (according to section 12.8). Then calculate the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within 2.5 percent of the overall mean value and if the relative standard deviation gas is less than 2 percent of the overall mean value. Record the overall mean of the propane response factor values as the NMO calibration response factor (RF_{NMO}). Repeat the linearity check using the CO_2 standards specified in section 7.4.3. Make triplicate injections of each gas, and then calculate the average response factor (area/ppm C) for each gas, as well as the overall mean of the response factor values. Record the overall mean of the response factor values as the CO_2 calibration response factor (RF_{CO2}). The RF_{CO2} must be within 10 percent of the RF_{NMO}.

10.1.2.4 System Performance Check. Check the column separation and overall performance of the analyzer by making triplicate injections of the calibration gases listed in section 7.4.4. The analyzer performance is acceptable if the measured NMO value for each gas (average of triplicate injections) is within 5 percent of the expected value.

10.2 NMO Analyzer Daily Calibration. The following calibration procedures shall be performed before and immediately after the

analysis of each set of samples, or on a daily basis, whichever is more stringent:

10.2.1 CO_2 Response Factor. Inject triplicate samples of the high level CO_2 calibration gas (Section 7.4.3), and calculate the average response factor. The system operation is adequate if the calculated response factor is within 5 percent of the RF_{CO2} calculated during the initial performance test (Section 10.1.2.3). Use the daily response factor (DRF_{CO2}) for analyzer calibration and the calculation of measured CO_2 concentrations in the ICV samples.

10.2.2 NMO Response Factors. Inject triplicate samples of the mixed propane calibration cylinder gas (Section 7.4.4.1), and calculate the average NMO response factor. The system operation is adequate if the calculated response factor is within 10 percent of the RF_{NMO} calculated during the initial performance test (Section 10.1.2.4). Use the daily response factor (DRF_{NMO}) for analyzer calibration and calculation of NMO concentrations in the sample tanks.

10.3 Sample Tank and ICV Volume. The volume of the gas sampling tanks used must be determined. Determine the tank and ICV volumes by weighing them empty and then filled with deionized distilled water; weigh to the nearest 5 g, and record the results. Alternatively, measure the volume of water used to fill them to the nearest 5 ml.

11.0 Analytical Procedure

11.1 Condensate Recovery. See Figure 25–9. Set the carrier gas flow rate, and heat the catalyst to its operating temperature to condition the apparatus.

11.1.1 Daily Performance Checks. Each day before analyzing any samples, perform the following tests:

11.1.1.1 Leak-Check. With the carrier gas inlets and the sample recovery valve closed, install a clean condensate trap in the system, and evacuate the system to 10 mm Hg absolute pressure or less. Monitor the system pressure for 10 minutes. The system is acceptable if the pressure change is less than 2 mm Hg.

11.1.1.2 System Background Test. Adjust the carrier gas and auxiliary oxygen flow rate to their normal values of 100 cc/min and 150 cc/min, respectively, with the sample recovery valve in vent position. Using a 10-ml syringe, withdraw a sample from the system effluent through the syringe port. Inject this sample into the NMO analyzer, and measure the CO_2 content. The system background is acceptable if the CO_2 concentration is less than 10 ppm.

11.1.1.3 Oxidation Catalyst Efficiency Check. Conduct a catalyst efficiency test as specified in section 10.1.1.2. If the criterion of this test cannot be met, make the necessary repairs to the system before proceeding.

11.1.2 Condensate Trap CO_2 Purge and Sample Tank Pressurization.

11.1.2.1 After sampling is completed, the condensate trap will contain condensed water and organics and a small volume of sampled gas. This gas from the stack may contain a significant amount of CO_2 which must be removed from the condensate trap before the sample is recovered. This is accomplished by purging the condensate trap with zero air and collecting the purged gas in the original sample tank.

11.1.2.2 Begin with the sample tank and condensate trap from the test run to be analyzed. Set the four-port valve of the condensate recovery system in the CO_2 purge position as shown in Figure 25–9. With the sample tank valve closed, attach the sample tank to the sample recovery system. With the sample recovery valve in the vent position and the flow control valve fully open, evacuate the manometer or pressure gauge to the vacuum of the sample tank. Next, close the vacuum pump valve, open the sample tank valve, and record the tank pressure.

11.1.2.3 Attach the dry ice-cooled condensate trap to the recovery system, and initiate the purge by switching the sample recovery valve from vent to collect position. Adjust the flow control valve to maintain atmospheric pressure in the recovery system. Continue the purge until the CO_2 concentration of the trap effluent is less than 5 ppm. CO_2 concentration in the trap effluent should be measured by extracting syringe samples from the recovery system and analyzing the samples with the NMO analyzer. This procedure should be used only after the NDIR response has reached a minimum level. Using a 10-ml syringe, extract a sample from the syringe port prior to the NDIR, and inject this sample into the NMO analyzer.

11.1.2.4 After the completion of the CO_2 purge, use the carrier gas bypass valve to pressurize the sample tank to approximately 1,060 mm Hg absolute pressure with zero air.

11.1.3 Recovery of the Condensate Trap Sample (See Figure 25–10).

11.1.3.1 Attach the ICV to the sample recovery system. With the sample recovery valve in a closed position, between vent and collect, and the flow control and ICV valves fully open, evacuate the manometer or gauge, the connecting tubing, and the ICV to 10 mm Hg absolute pressure. Close the flow-control and vacuum pump valves.

11.1.3.2 Begin auxiliary oxygen flow to the oxidation catalyst at a rate of 150 cc/min, then switch the four-way valve to the trap recovery position and the sample recovery valve to collect position. The system should now be set up to operate as indicated in Figure 25–10. After the manometer or pressure gauge begins to register a slight positive pressure, open the flow control valve. Adjust the flow-control valve to maintain atmospheric pressure in the system within 10 percent.

11.1.3.3 Remove the condensate trap from the dry ice, and allow it to warm to ambient temperature while monitoring the NDIR response. If, after 5 minutes, the CO_2 concentration of the catalyst effluent is below 10,000 ppm, discontinue the auxiliary oxygen flow to the oxidation catalyst. Begin heating the trap by placing it in a furnace preheated to 200 °C (390 °F). Once heating has begun, carefully monitor the NDIR response to ensure that the catalyst effluent concentration does not exceed 50,000 ppm. Whenever the CO_2 concentration exceeds 50,000 ppm, supply auxiliary oxygen to the catalyst at the rate of 150 cc/min. Begin heating the tubing that connected the heated sample box to the condensate trap only after the CO_2 concentration falls below 10,000 ppm. This tubing may be heated in the same oven as the condensate trap or with an auxiliary heat source such as a heat gun. Heating temperature must not exceed 200 °C (390 °F). If a heat gun is used, heat the tubing slowly along its entire length from the upstream end to the downstream end, and repeat the pattern for a total of three times. Continue the recovery until the CO_2 concentration drops to less than 10 ppm as determined by syringe injection as described under the condensate trap CO_2 purge procedure (Section 11.1.2).

11.1.3.4 After the sample recovery is completed, use the carrier gas bypass valve to pressurize the ICV to approximately 1060 mm Hg absolute pressure with zero air.

11.2 Analysis. Once the initial performance test of the NMO analyzer has been successfully completed (see section 10.1.2) and the daily CO_2 and NMO response factors have been determined (see section 10.2), proceed with sample analysis as follows:

11.2.1 Operating Conditions. The carrier gas flow rate is 29.5 cc/min He and 2.2 cc/min O_2. The column oven is heated to 85 °C (185 °F). The order of elution for the sample from the column is CO, CH_4, CO_2, and NMO.

11.2.2 Analysis of Recovered Condensate Sample. Purge the sample loop with sample, and then inject the sample. Under the specified operating conditions, the CO_2 in the sample will elute in approximately 100 seconds. As soon as the detector response returns to baseline following the CO_2 peak, switch the carrier gas flow to backflush, and raise the column oven temperature to 195 °C (380 °F) as rapidly as possible. A rate of 30 °C/min (90 °F) has been shown to be adequate. Record the value obtained for the condensible organic material (C_{cm}) measured as CO_2 and any measured NMO. Return the column oven temperature to 85 °C (185 °F) in preparation for the next analysis. Analyze each sample in triplicate, and report the average C_{cm}.

11.2.3 Analysis of Sample Tank. Perform the analysis as described in section 11.2.2, but record only the value measured for NMO (C_{tm}).

12.0 Data Analysis and Calculations

Carry out the calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculations. All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge or manometer pressure.

12.1 Nomenclature.

C = TGNMO concentration of the effluent, ppm C equivalent.
C_c = Calculated condensible organic (condensate trap) concentration of the effluent, ppm C equivalent.
C_{cm} = Measured concentration (NMO analyzer) for the condensate trap ICV, ppm CO_2.
C_t = Calculated noncondensible organic concentration (sample tank) of the effluent, ppm C equivalent.
C_{tm} = Measured concentration (NMO analyzer) for the sample tank, ppm NMO.
F = Sampling flow rate, cc/min.
L = Volume of liquid injected, µl.
M = Molecular weight of the liquid injected, g/g-mole.
M_c = TGNMO mass concentration of the effluent, mg C/dsm³.
N = Carbon number of the liquid compound injected (N = 12 for decane, N = 6 for hexane).
n = Number of data points.
P_f = Final pressure of the intermediate collection vessel, mm Hg absolute.
P_b = Barometric pressure, cm Hg.
P_{ti} = Gas sample tank pressure before sampling, mm Hg absolute.
P_t = Gas sample tank pressure after sampling, but before pressurizing, mm Hg absolute.
P_{tf} = Final gas sample tank pressure after pressurizing, mm Hg absolute.
q = Total number of analyzer injections of intermediate collection vessel during analysis (where k = injection number, 1 * * * q).
r = Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 * * * r).
r = Density of liquid injected, g/cc.
T_f = Final temperature of intermediate collection vessel, °K.
T_{ti} = Sample tank temperature before sampling, °K.
T_t = Sample tank temperature at completion of sampling, °K.
T_{tf} = Sample tank temperature after pressurizing, °K.
V = Sample tank volume, m³.
V_t = Sample train volume, cc.
V_v = Intermediate collection vessel volume, m³.
V_s = Gas volume sampled, dsm³.
x_i = Individual measurements.
$\bar{x}$ = Mean value.

ΔP = Allowable pressure change, cm Hg.
Θ = Leak-check period, min.

12.2 Allowable Pressure Change. For the pretest leak-check, calculate the allowable pressure change using Equation 25–1:

$$\Delta P = 0.01 \frac{F P_b \Theta}{V_t} \qquad \text{Eq. 25-1}$$

12.3 Sample Volume. For each test run, calculate the gas volume sampled using Equation 25–2:

$$V_s = 0.3857\, V \left(\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}} \right) \qquad \text{Eq. 25-2}$$

12.4 Noncondensible Organics. For each sample tank, determine the concentration of nonmethane organics (ppm C) using Equation 25–3:

$$C_t = \left(\frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}} \right) \left(\frac{1}{r} \sum_{j=1}^{r} C_{tm_j} \right) \qquad \text{Eq. 25-3}$$

12.5 Condensible Organics. For each condensate trap determine the concentration of organics (ppm C) using Equation 25–4:

$$C_c = 0.3857 \frac{V_v P_f}{V_s T_f} \left(\frac{1}{q} \sum_{k=1}^{q} C_{cm_k} \right) \qquad \text{Eq. 25-4}$$

12.6 TGNMO Mass Concentration. Determine the TGNMO mass concentration as carbon for each test run, using Equation 25–5:

$$M_c = 0.4993 \left(C_t + C_c \right) \qquad \text{Eq. 25-5}$$

12.7 Percent Recovery. Calculate the percent recovery for the liquid injections to the condensate recovery and conditioning system using Equation 25–6:

$$\text{Percent Recovery} = K \frac{M V_v P_t C_{cm}}{L P T_f N} \qquad \text{Eq. 25-6}$$

where K = 1.604 (°K)(g-mole)(%)/(mm Hg)(ml)(m^3)(ppm).

12.8 Relative Standard Deviation. Use Equation 25–7 to calculate the relative standard deviation (RSD) of percent recovery and analyzer linearity.

$$RSD = \frac{100}{\bar{x}} \left[\frac{\sum_{i=1}^{n} \left(x_i - \bar{x} \right)^2}{n-1} \right]^{\frac{1}{2}} \qquad \text{Eq. 25-7}$$

13.0 Method Performance

13.1 Range. The minimum detectable limit of the method has been determined to be 50 parts per million by volume (ppm). No upper limit has been established.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, A.E., S. Witz, and R.D. MacPhee. Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, MA. June 15–20, 1975.) 14 p.

2. Salo, A.E., W.L. Oaks, and R.D. MacPhee. Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, CO. June 9–13, 1974.) 25 p.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

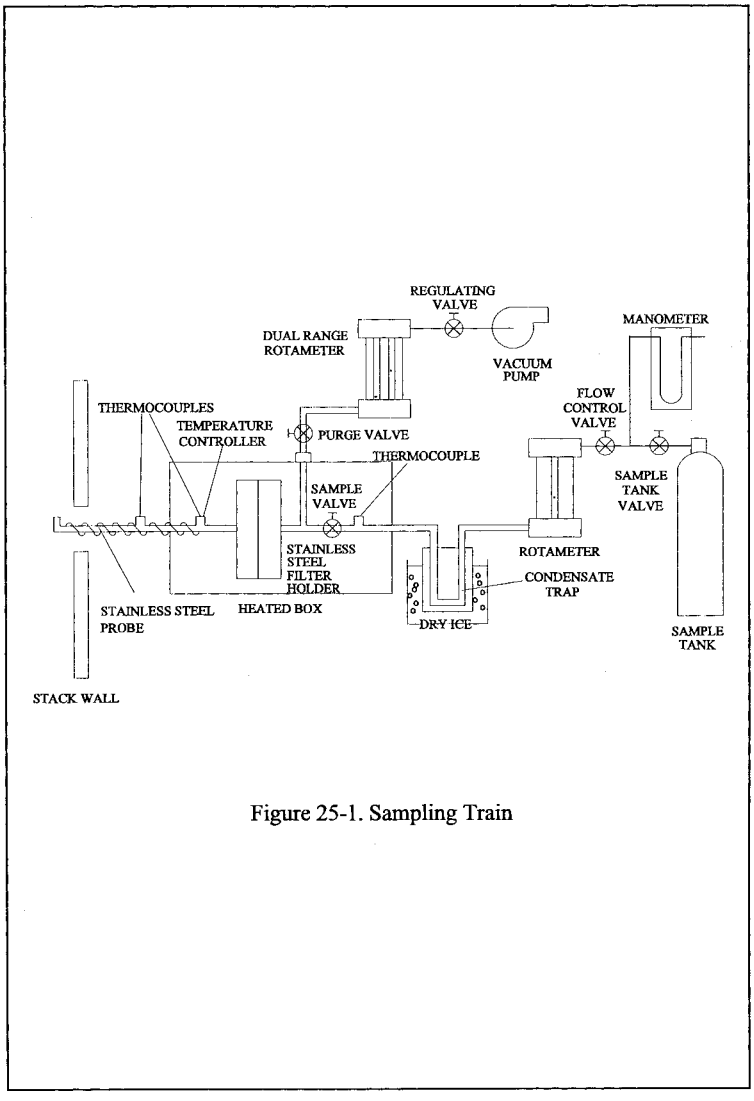


Figure 25-1. Sampling Train

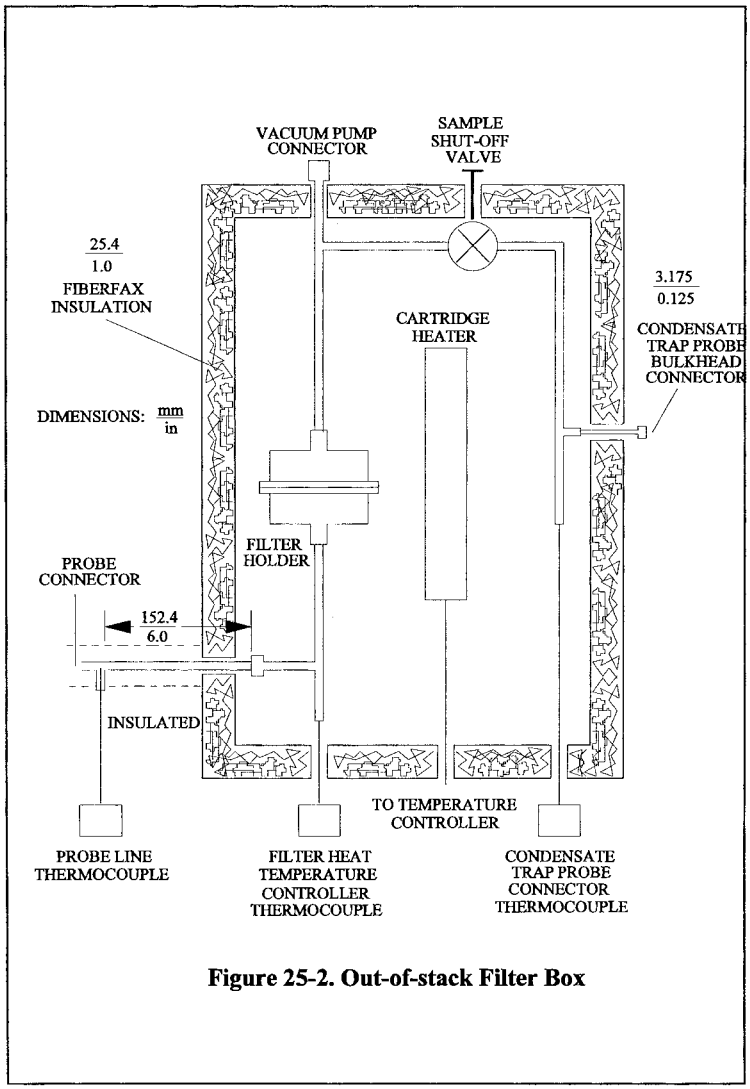


Figure 25-2. Out-of-stack Filter Box

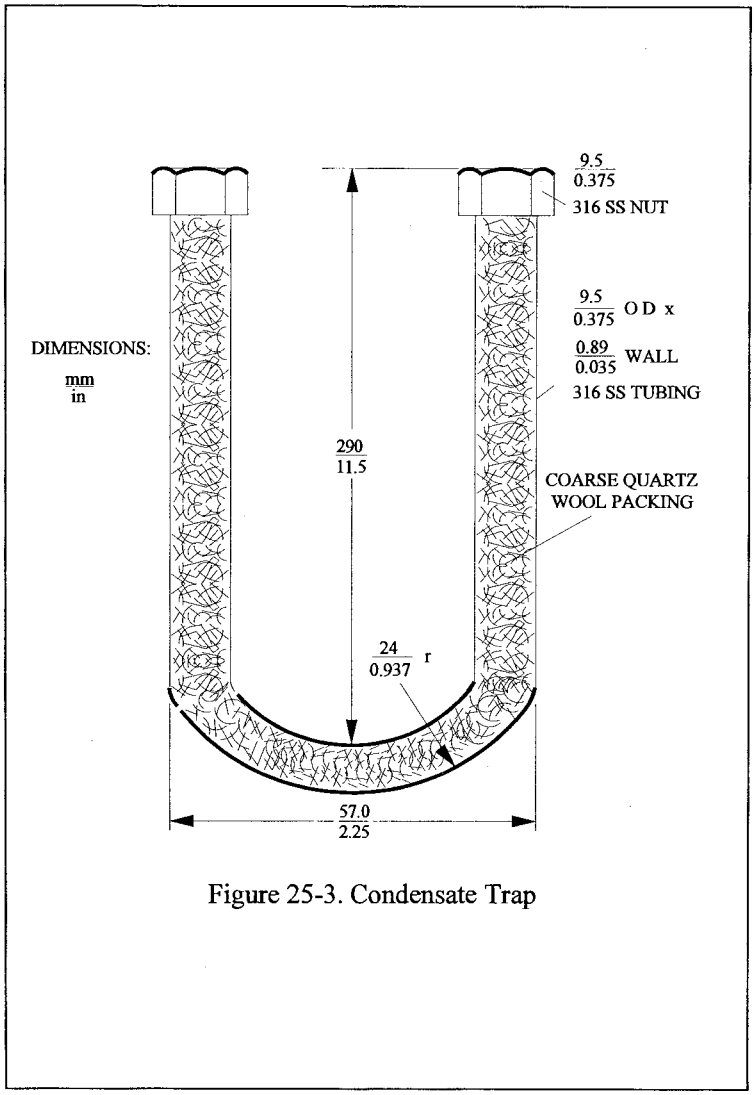


Figure 25-3. Condensate Trap

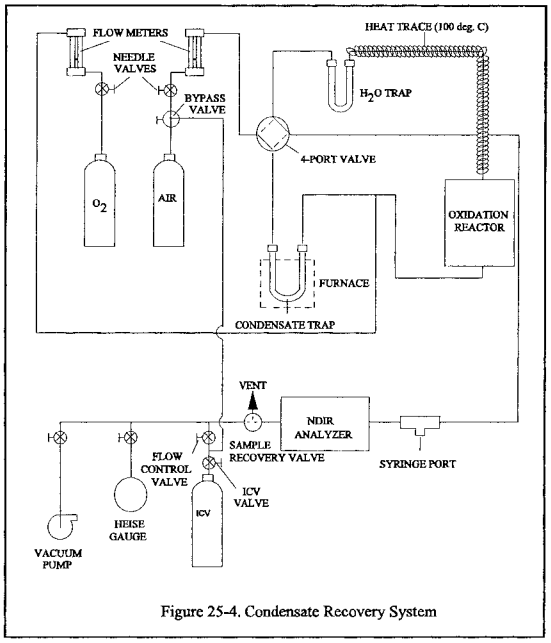


Figure 25-4. Condensate Recovery System

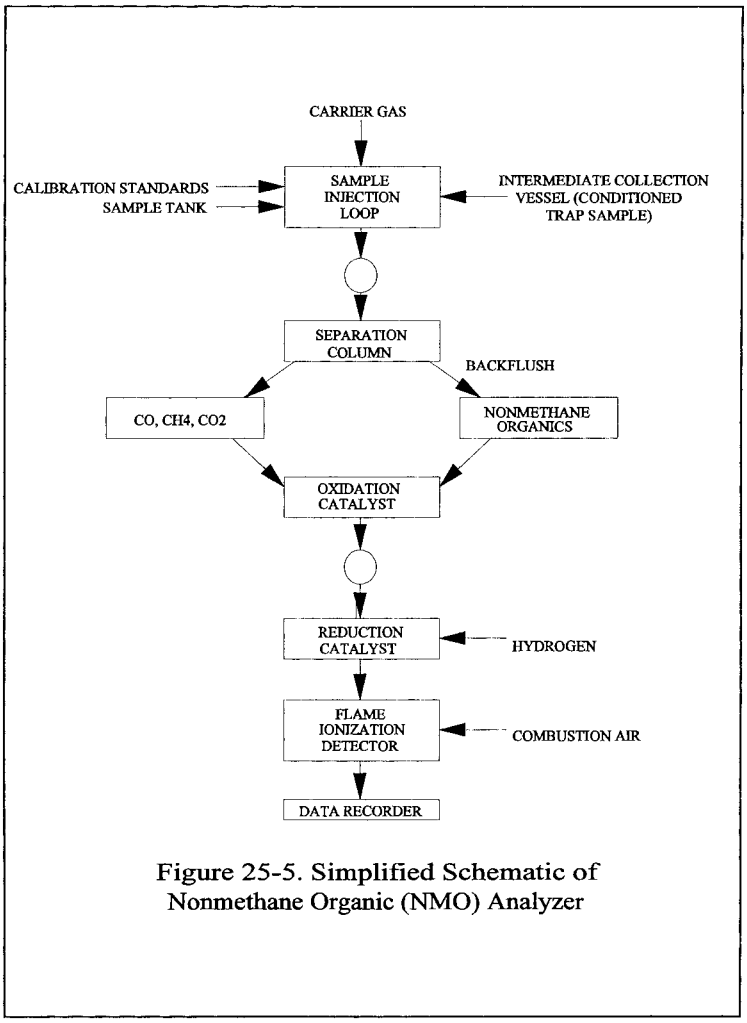


Figure 25-5. Simplified Schematic of Nonmethane Organic (NMO) Analyzer

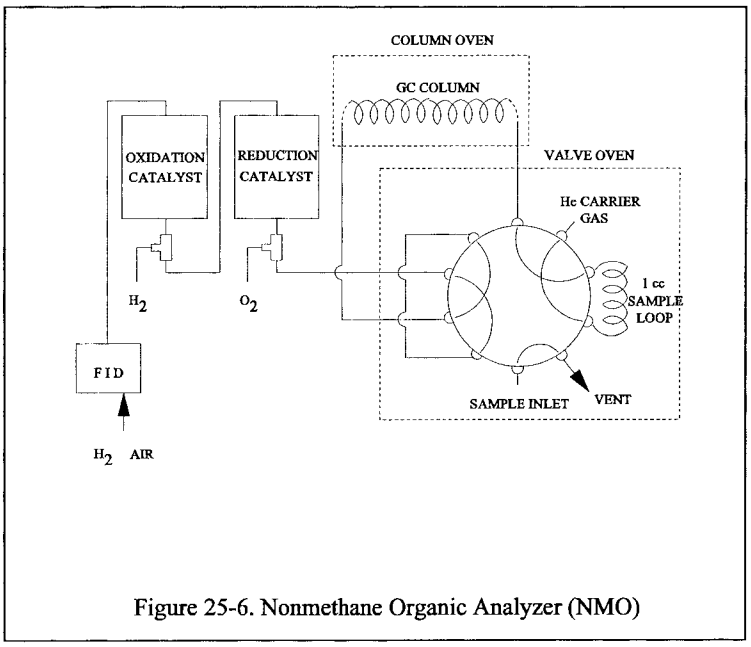


Figure 25-6. Nonmethane Organic Analyzer (NMO)

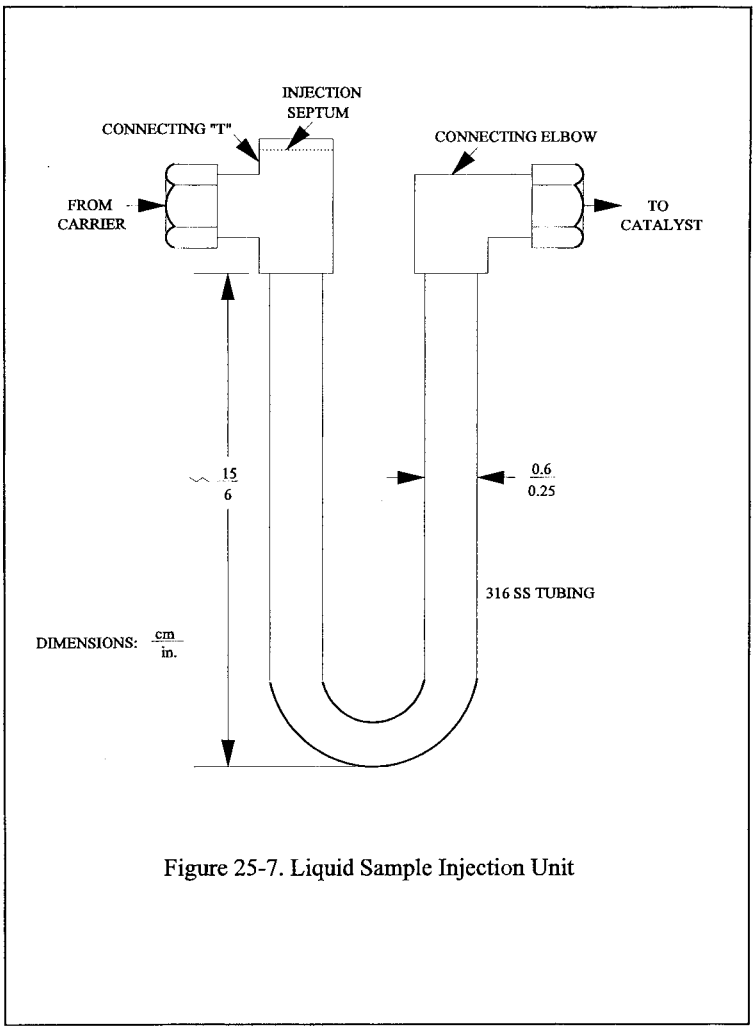


Figure 25-7. Liquid Sample Injection Unit

VOLATILE ORGANIC CARBON

FACILITY _____ SAMPLE LOCATION _____

LOCATION _____ OPERATOR _____

DATE _____ RUN NUMBER _____

TANK NUMBER _____ TRAP NUMBER _____ SAMPLE ID NUMBER _____

TANK VACUUM mm HG	TANK VACUUM cm Hg	BAROMETRIC PRESSURE mm Hg	AMBIENT TEMPERATURE °C
PRETEST (MANOMETER)	(GAUGE)		
POST-TEST (MANOMETER)	(GAUGE)		

LEAK RATE _____ cm Hg / l /l min _____

PRETEST _____

TIME CLOCK/SAMPLE	VACUUM cm Hg	FLOWMETER SETTINGS	COMMENTS

Figure 25-8. Example Field Data Form

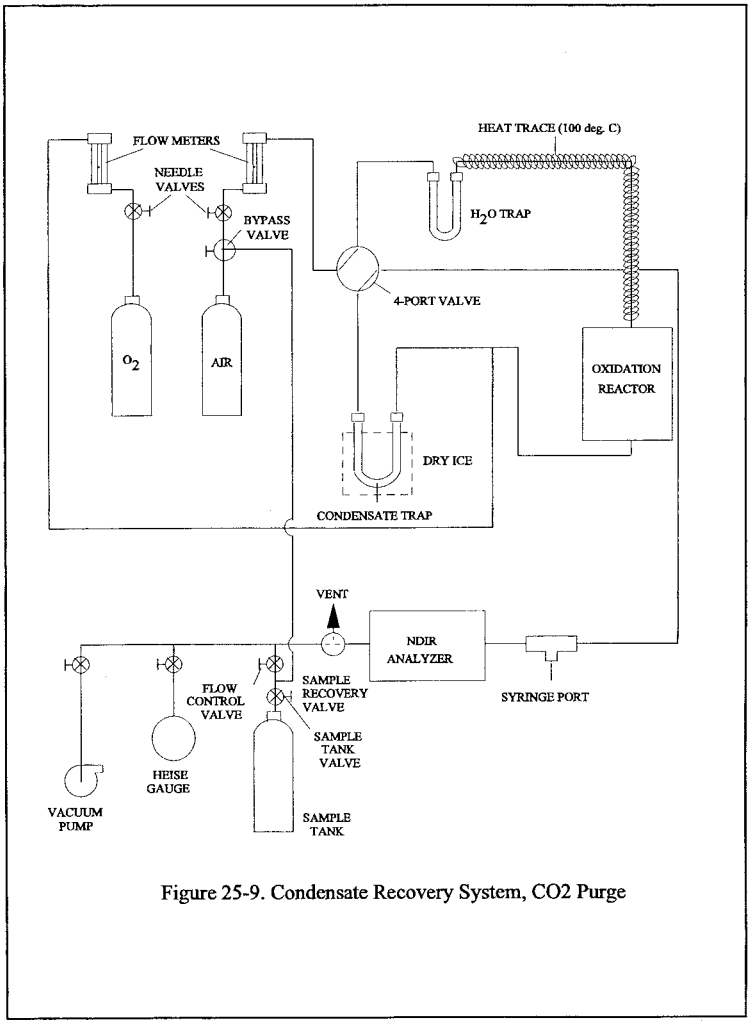


Figure 25-9. Condensate Recovery System, CO2 Purge

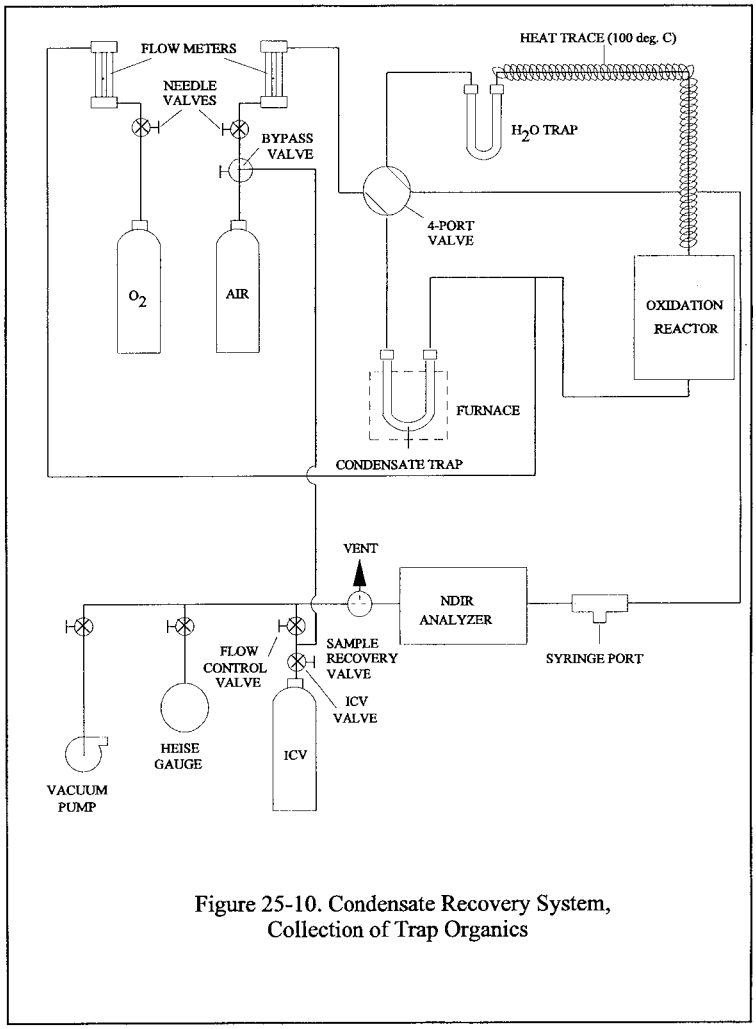


Figure 25-10. Condensate Recovery System, Collection of Trap Organics

METHOD 25A—DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A FLAME IONIZATION ANALYZER

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total Organic Compounds	N/A	<2% of span.

1.2 Applicability. This method is applicable for the determination of total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the source through a heated sample line and glass fiber filter to a flame ionization analyzer (FIA). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

3.0 Definitions

3.1 *Calibration drift* means the difference in the measurement system response to a mid-level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

3.2 *Calibration error* means the difference between the gas concentration indicated by the measurement system and the know concentration of the calibration gas.

3.3 *Calibration gas* means a known concentration of a gas in an appropriate diluent gas.

3.4 *Measurement system* means the total equipment required for the determination of the gas concentration. The system consists of the following major subsystems:

3.4.1 *Sample interface* means that portion of a system used for one or more of the following: sample acquisition, sample transportation, sample conditioning, or protection of the analyzer(s) from the effects of the stack effluent.

3.4.2 *Organic analyzer* means that portion of the measurement system that senses the gas to be measured and generates an output proportional to its concentration.

3.5 *Response time* means the time interval from a step change in pollutant concentration at the inlet to the emission measurement system to the time at which 95 percent of the corresponding final value is reached as displayed on the recorder.

3.6 *Span Value* means the upper limit of a gas concentration measurement range that is specified for affected source categories in the applicable part of the regulations. The span value is established in the applicable regulation and is usually 1.5 to 2.5 times the applicable emission limit. If no span value is provided, use a span value equivalent to 1.5 to 2.5 times the expected concentration. For convenience, the span value should correspond to 100 percent of the recorder scale.

3.7 *Zero drift* means the difference in the measurement system response to a zero level calibration gas before or after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

5.2 Explosive Atmosphere. This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

6.0 Equipment and Supplies

6.1 Measurement System. Any measurement system for total organic concentration that meets the specifications of this method. A schematic of an acceptable measurement system is shown in Figure 25A–1. All sampling components leading to the analyzer shall be heated ≥110 °C (220 °F) throughout the sampling period, unless safety reasons are cited (Section 5.2) The essential components of the measurement system are described below:

6.1.1 Organic Concentration Analyzer. A flame ionization analyzer (FIA) capable of meeting or exceeding the specifications of this method. The flame ionization detector block shall be heated >120 °C (250 °F).

6.1.2 Sample Probe. Stainless steel, or equivalent, three-hole rake type. Sample holes shall be 4 mm (0.16-in.) in diameter or smaller and located at 16.7, 50, and 83.3 percent of the equivalent stack diameter. Alternatively, a single opening probe may be used so that a gas sample is collected from the centrally located 10 percent area of the stack cross-section.

6.1.3 Heated Sample Line. Stainless steel or Teflon'' tubing to transport the sample gas

to the analyzer. The sample line should be heated (≥110 °C) to prevent any condensation.

6.1.4 Calibration Valve Assembly. A three-way valve assembly to direct the zero and calibration gases to the analyzers is recommended. Other methods, such as quick-connect lines, to route calibration gas to the analyzers are applicable.

6.1.5 Particulate Filter. An in-stack or an out-of-stack glass fiber filter is recommended if exhaust gas particulate loading is significant. An out-of-stack filter should be heated to prevent any condensation.

6.1.6 Recorder. A strip-chart recorder, analog computer, or digital recorder for recording measurement data. The minimum data recording requirement is one measurement value per minute.

7.0 Reagents and Standards

7.1 Calibration Gases. The calibration gases for the gas analyzer shall be propane in air or propane in nitrogen. Alternatively, organic compounds other than propane can be used; the appropriate corrections for response factor must be made. Calibration gases shall be prepared in accordance with the procedure listed in Citation 2 of section 16. Additionally, the manufacturer of the cylinder should provide a recommended shelf life for each calibration gas cylinder over which the concentration does not change more than ±2 percent from the certified value. For calibration gas values not generally available (*i.e.*, organics between 1 and 10 percent by volume), alternative methods for preparing calibration gas mixtures, such as dilution systems (Test Method 205, 40 CFR Part 51, Appendix M), may be used with prior approval of the Administrator.

7.1.1 Fuel. A 40 percent H_2/60 percent N_2 gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value.

7.1.2 Zero Gas. High purity air with less than 0.1 part per million by volume (ppmv) of organic material (propane or carbon equivalent) or less than 0.1 percent of the span value, whichever is greater.

7.1.3 Low-level Calibration Gas. An organic calibration gas with a concentration equivalent to 25 to 35 percent of the applicable span value.

7.1.4 Mid-level Calibration Gas. An organic calibration gas with a concentration equivalent to 45 to 55 percent of the applicable span value.

7.1.5 High-level Calibration Gas. An organic calibration gas with a concentration equivalent to 80 to 90 percent of the applicable span value.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Selection of Sampling Site. The location of the sampling site is generally specified by the applicable regulation or purpose of the test (*i.e.*, exhaust stack, inlet line, etc.). The sample port shall be located to meet the testing requirements of Method 1.

8.2 Location of Sample Probe. Install the sample probe so that the probe is centrally located in the stack, pipe, or duct and is sealed tightly at the stack port connection.

8.3 Measurement System Preparation. Prior to the emission test, assemble the measurement system by following the manufacturer's written instructions for preparing sample interface and the organic analyzer. Make the system operable (Section 10.1).

8.4 Calibration Error Test. Immediately prior to the test series (within 2 hours of the start of the test), introduce zero gas and high-level calibration gas at the calibration valve assembly. Adjust the analyzer output to the appropriate levels, if necessary. Calculate the predicted response for the low-level and mid-level gases based on a linear response line between the zero and high-level response. Then introduce low-level and mid-level calibration gases successively to the measurement system. Record the analyzer responses for low-level and mid-level calibration gases and determine the differences between the measurement system responses and the predicted responses. These differences must be less than 5 percent of the respective calibration gas value. If not, the measurement system is not acceptable and must be replaced or repaired prior to testing. No adjustments to the measurement system shall be conducted after the calibration and before the drift check (Section 8.6.2). If adjustments are necessary before the completion of the test series, perform the drift checks prior to the required adjustments and repeat the calibration following the adjustments. If multiple electronic ranges are to be used, each additional range must be checked with a mid-level calibration gas to verify the multiplication factor.

8.5 Response Time Test. Introduce zero gas into the measurement system at the calibration valve assembly. When the system output has stabilized, switch quickly to the high-level calibration gas. Record the time from the concentration change to the measurement system response equivalent to 95 percent of the step change. Repeat the test three times and average the results.

8.6 Emission Measurement Test Procedure.

8.6.1 Organic Measurement. Begin sampling at the start of the test period, recording time and any required process information as appropriate. In particulate, note on the recording chart, periods of process interruption or cyclic operation.

8.6.2 Drift Determination. Immediately following the completion of the test period and hourly during the test period, reintroduce the zero and mid-level calibration gases, one at a time, to the measurement system at the calibration valve assembly. (Make no adjustments to the measurement system until both the zero and calibration drift checks are made.) Record the analyzer response. If the drift values exceed the specified limits, invalidate the test results preceding the check and repeat the test following corrections to the measurement system. Alternatively, recalibrate the test measurement system as in section 8.4 and report the results using both sets of calibration data (i.e., data determined prior to the test period and data determined following the test period).

NOTE: Note on the recording chart periods of process interruption or cyclic operation.

9.0 Quality Control

Method section	Quality control measure	Effect
8.4	Zero and calibration drift tests	Ensures that bias introduced by drift in the measurement system output during the run is no greater than 3 percent of span.

10.0 Calibration and Standardization

10.1 FIA equipment can be calibrated for almost any range of total organic concentrations. For high concentrations of organics (>1.0 percent by volume as propane), modifications to most commonly available analyzers are necessary. One accepted method of equipment modification is to decrease the size of the sample to the analyzer through the use of a smaller diameter sample capillary. Direct and continuous measurement of organic concentration is a necessary consideration when determining any modification design.

11.0 Analytical Procedure

The sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Calculations and Data Analysis

12.1 Determine the average organic concentration in terms of ppmv as propane or other calibration gas. The average shall be determined by integration of the output recording over the period specified in the applicable regulation. If results are required in terms of ppmv as carbon, adjust measured concentrations using Equation 25A–1.

$$C_c = K C_{meas} \qquad \text{Eq. 25A-1}$$

Where:

C_c = Organic concentration as carbon, ppmv.
C_{meas} = Organic concentration as measured, ppmv.
K = Carbon equivalent correction factor.
= 2 for ethane.
= 3 for propane.
= 4 for butane.
= Appropriate response factor for other organic calibration gases.

13.0 Method Performance

13.1 Measurement System Performance Specifications.

13.1.1 Zero Drift. Less than ±3 percent of the span value.

13.1.2 Calibration Drift. Less than ±3 percent of span value.

13.1.3 Calibration Error. Less than ±5 percent of the calibration gas value.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Measurement of Volatile Organic Compounds—Guideline Series. U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA–450/2–78–041. June 1978. p. 46–54.

2. EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards. U.S. Environmental Protection Agency, Quality Assurance and Technical Support Division. Research Triangle Park, N.C. September 1993.

3. Gasoline Vapor Emission Laboratory Evaluation—Part 2. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, NC. EMB Report No. 75–GAS–6. August 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

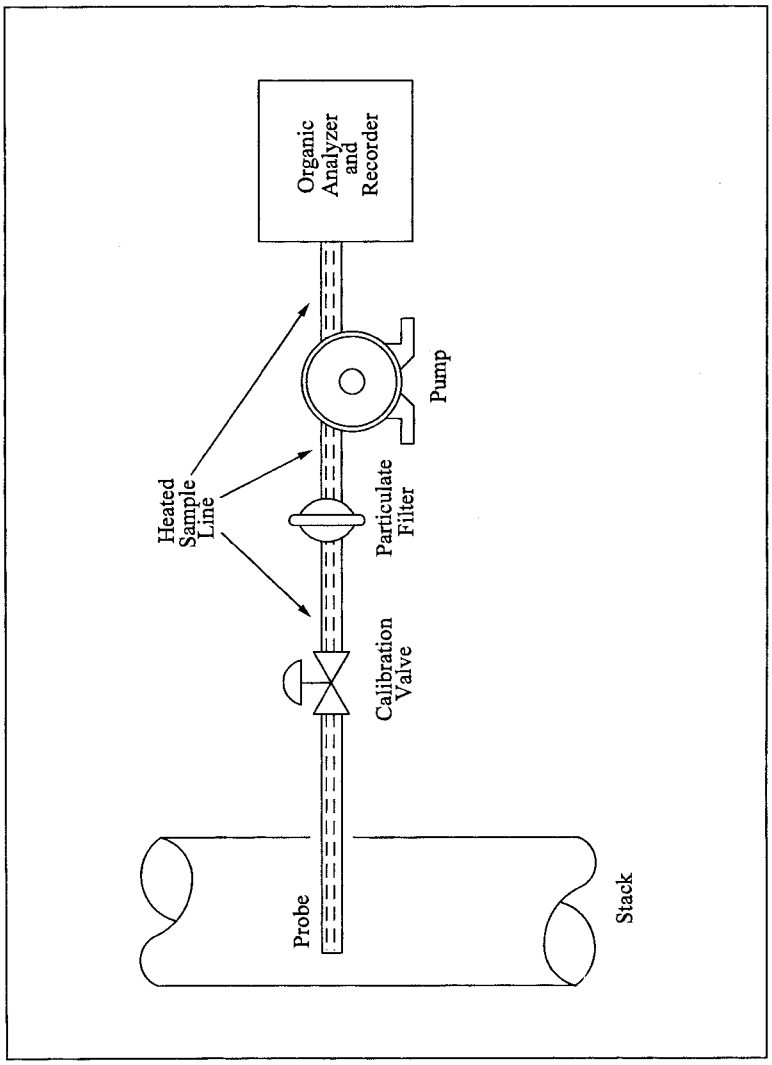


Figure 25A-1. Organic Concentration Measurement System.

METHOD 25B—DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A NONDISPERSIVE INFRARED ANALYZER

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 6C, and Method 25A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total Organic Compounds	N/A	<2% of span.

1.2 Applicability. This method is applicable for the determination of total gaseous organic concentration of vapors consisting primarily of alkanes. Other organic materials may be measured using the general procedure in this method, the appropriate calibration gas, and an analyzer set to the appropriate absorption band.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

A gas sample is extracted from the source through a heated sample line, if necessary, and glass fiber filter to a nondispersive infrared analyzer (NDIR). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

3.0 Definitions

Same as Method 25A, section 3.0.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

5.2 Explosive Atmosphere. This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

6.0 Equipment and Supplies

Same as Method 25A, section 6.0, with the exception of the following:

6.1 Organic Concentration Analyzer. A nondispersive infrared analyzer designed to measure alkane organics and capable of meeting or exceeding the specifications in this method.

7.0 Reagents and Standards

Same as Method 25A, section 7.1. No fuel gas is required for an NDIR.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as Method 25A, section 8.0.

9.0 Quality Control

Same as Method 25A, section 9.0.

10.0 Calibration and Standardization

Same as Method 25A, section 10.0.

11.0 Analytical Procedure

The sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Calculations and Data Analysis

Same as Method 25A, section 12.0.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 25A, section 16.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 25C—DETERMINATION OF NONMETHANE ORGANIC COMPOUNDS (NMOC) IN LANDFILL GASES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should also have a thorough knowledge of EPA Method 25.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Nonmethane organic compounds (NMOC).	No CAS number assigned.

1.2 Applicability. This method is applicable to the sampling and measurement of NMOC as carbon in landfill gases (LFG).

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A sample probe that has been perforated at one end is driven or augured to a depth of 0.9 m (3 ft) below the bottom of the landfill cover. A sample of the landfill gas is extracted with an evacuated cylinder. The NMOC content of the gas is determined by

injecting a portion of the gas into a gas chromatographic column to separate the NMOC from carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4); the NMOC are oxidized to CO_2, reduced to CH_4, and measured by a flame ionization detector (FID). In this manner, the variable response of the FID associated with different types of organics is eliminated.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Since this method is complex, only experienced personnel should perform this test. LFG contains methane, therefore explosive mixtures may exist on or near the landfill. It is advisable to take appropriate safety precautions when testing landfills, such as refraining from smoking and installing explosion-proof equipment.

6.0 Equipment and Supplies

6.1 Sample Probe. Stainless steel, with the bottom third perforated. Teflon probe liners and sampling lines are also allowed. Non-perforated probes are allowed as long as they are withdrawn to create a gap equivalent to having the bottom third perforated. The sample probe must be capped at the bottom and must have a threaded cap with a sampling attachment at the top. The sample probe must be long enough to go through and extend no less than 0.9 m (3 ft) below the landfill cover. If the sample probe is to be driven into the landfill, the bottom cap should be designed to facilitate driving the probe into the landfill.

6.2 Sampling Train.

6.2.1 Rotameter with Flow Control Valve. Capable of measuring a sample flow rate of 100 ±10 ml/min. The control valve must be made of stainless steel.

6.2.2 Sampling Valve. Stainless steel.

6.2.3 Pressure Gauge. U-tube mercury manometer, or equivalent, capable of measuring pressure to within 1 mm Hg (0.5 in H_2O) in the range of 0 to 1,100 mm Hg (0 to 590 in H_2O).

6.2.4 Sample Tank. Stainless steel or aluminum cylinder, equipped with a stainless steel sample tank valve.

6.3 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg (5.4 in H_2O).

6.4 Purging Pump. Portable, explosion proof, and suitable for sampling NMOC.

6.5 Pilot Probe Procedure. The following are needed only if the tester chooses to use the procedure described in section 8.2.1.

6.5.1 Pilot Probe. Tubing of sufficient strength to withstand being driven into the landfill by a post driver and an outside diameter of at least 6 mm (0.25 in.) smaller than the sample probe. The pilot probe shall be capped on both ends and long enough to go through the landfill cover and extend no less than 0.9 m (3 ft) into the landfill.

6.5.2 Post Driver and Compressor. Capable of driving the pilot probe and the sampling probe into the landfill. The Kitty Hawk portable post driver has been found to be acceptable.

6.6 Auger Procedure. The following are needed only if the tester chooses to use the procedure described in section 8.2.2.

6.6.1 Auger. Capable of drilling through the landfill cover and to a depth of no less than 0.9 m (3 ft) into the landfill.

6.6.2 Pea Gravel.

6.6.3 Bentonite.

6.7 NMOC Analyzer, Barometer, Thermometer, and Syringes. Same as in sections 6.3.1, 6.3.2, 6.33, and 6.2.10, respectively, of Method 25.

7.0 Reagents and Standards

7.1 NMOC Analysis. Same as in Method 25, section 7.2.

7.2 Calibration. Same as in Method 25, section 7.4, except omit section 7.4.3.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sample Tank Evacuation and Leak-Check. Conduct the sample tank evacuation and leak-check either in the laboratory or the field. Connect the pressure gauge and sampling valve to the sample tank. Evacuate the sample tank to 10 mm Hg (5.4 in H_2O) absolute pressure or less. Close the sampling valve, and allow the tank to sit for 30 minutes. The tank is acceptable if no change more than ±2 mm is noted. Include the results of the leak-check in the test report.

8.2 Sample Probe Installation. The tester may use the procedure in section 8.2.1 or 8.2.2.

8.2.1 Pilot Probe Procedure. Use the post driver to drive the pilot probe at least 0.9 m (3 ft) below the landfill cover. Alternative procedures to drive the probe into the landfill may be used subject to the approval of the Administrator's designated representative.

8.2.1.1 Remove the pilot probe and drive the sample probe into the hole left by the pilot probe. The sample probe shall extend at least 0.9 m (3 ft) below the landfill cover and shall protrude about 0.3 m (1 ft) above the landfill cover. Seal around the sampling probe with bentonite and cap the sampling probe with the sampling probe cap.

8.2.2 Auger Procedure. Use an auger to drill a hole to at least 0.9 m (3 ft) below the landfill cover. Place the sample probe in the hole and backfill with pea gravel to a level 0.6 m (2 ft) from the surface. The sample probe shall protrude at least 0.3 m (1 ft) above the landfill cover. Seal the remaining area around the probe with bentonite. Allow 24

hours for the landfill gases to equilibrate inside the augured probe before sampling.

8.2.3 Driven Probes. Closed-point probes may be driven directly into the landfill in a single step. This method may not require backfilling if the probe is adequately sealed by its insertion. Unperforated probes that are inserted in this manner and withdrawn at a distance from a detachable tip to create an open space are also acceptable.

8.3 Sample Train Assembly. Just before assembling the sample train, measure the sample tank vacuum using the pressure gauge. Record the vacuum, the ambient temperature, and the barometric pressure at this time. Assemble the sampling probe purging system as shown in Figure 25C–1.

8.4 Sampling Procedure. Open the sampling valve and use the purge pump and the flow control valve to evacuate at least two sample probe volumes from the system at a flow rate of 500 ml/min or less. Close the sampling valve and replace the purge pump with the sample tank apparatus as shown in Figure 25C–2. Open the sampling valve and the sample tank valve and, using the flow control valve, sample at a flow rate of 500 ml/min or less until either a constant flow rate can no longer be maintained because of reduced sample tank vacuum or the appropriate composite volume is attained. Disconnect the sampling tank apparatus and pressurize the sample cylinder to approximately 1,060 mm Hg (567 in. H_2O) absolute pressure with helium, and record the final pressure. Alternatively, the sample tank may be pressurized in the lab.

8.4.1 The following restrictions apply to compositing samples from different probe sites into a single cylinder: (1) Individual composite samples per cylinder must be of equal volume; this must be verified by recording the flow rate, sampling time, vacuum readings, or other appropriate volume measuring data, (2) individual composite samples must have a minimum volume of 1 liter unless data is provided showing smaller volumes can be accurately measured, and (3) composite samples must not be collected using the final cylinder vacuum as it diminishes to ambient pressure.

8.4.2 Use Method 3C to determine the percent N_2 in each cylinder. The presence of N_2 indicates either infiltration of ambient air into the landfill gas sample or an inappropriate testing site has been chosen where anaerobic decomposition has not begun. The landfill gas sample is acceptable if the concentration of N_2 is less than 20 percent. Alternatively, Method 3C may be used to determine the oxygen content of each cylinder as an air infiltration test. With this option, the oxygen content of each cylinder must be less than 5 percent.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4.2	Verify that landfill gas sample contains less than 20 percent N_2 or 5 percent O_2.	Ensures that ambient air was not drawn into the landfill gas sample and gas was sampled from an appropriate location.
10.1, 10.2	NMOC analyzer initial and daily performance checks.	Ensures precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Initial NMOC Analyzer Performance Test. Same as in Method 25, section 10.1, except omit the linearity checks for CO_2 standards.

10.2 NMOC Analyzer Daily Calibration.

10.2.1 NMOC Response Factors. Same as in Method 25, section 10.2.2.

10.3 Sample Tank Volume. The volume of the gas sampling tanks must be determined. Determine the tank volumes by weighing them empty and then filled with deionized water; weigh to the nearest 5 g, and record the results. Alternatively, measure the volume of water used to fill them to the nearest 5 ml.

11.0 Analytical Procedures

11.1 The oxidation, reduction, and measurement of NMOC's is similar to Method 25. Before putting the NMOC analyzer into routine operation, conduct an initial performance test. Start the analyzer, and perform all the necessary functions in order to put the analyzer into proper working order. Conduct the performance test according to the procedures established in section 10.1. Once the performance test has been successfully completed and the NMOC calibration response factor has been determined, proceed with sample analysis as follows:

11.1.1 Daily Operations and Calibration Checks. Before and immediately after the analysis of each set of samples or on a daily basis (whichever occurs first), conduct a calibration test according to the procedures established in section 10.2. If the criteria of the daily calibration test cannot be met, repeat

the NMOC analyzer performance test (Section 10.1) before proceeding.

11.1.2 Operating Conditions. Same as in Method 25, section 11.2.1.

11.1.3 Analysis of Sample Tank. Purge the sample loop with sample, and then inject the sample. Under the specified operating conditions, the CO_2 in the sample will elute in approximately 100 seconds. As soon as the detector response returns to baseline following the CO_2 peak, switch the carrier gas flow to backflush, and raise the column oven temperature to 195 °C (383 °F) as rapidly as possible. A rate of 30 °C/min (54 °F/min) has been shown to be adequate. Record the value obtained for any measured NMOC. Return the column oven temperature to 85 °C (185 °F) in preparation for the next analysis. Analyze each sample in triplicate, and report the average as C_{tm}.

12.0 Data Analysis and Calculations

NOTE: All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge or manometer pressure.

12.1 Nomenclature

B_w = Moisture content in the sample, fraction.
C_{N2} = N_2 concentration in the diluted sample gas.
C_{mN2} = Measured N_2 concentration, fraction in landfill gas.
C_{mOx} = Measured Oxygen concentration, fraction in landfill gas.
C_{Ox} = Oxygen concentration in the diluted sample gas.
C_t = Calculated NMOC concentration, ppmv C equivalent.
C_{tm} = Measured NMOC concentration, ppmv C equivalent.
P_b = Barometric pressure, mm Hg.
P_t = Gas sample tank pressure after sampling, but before pressurizing, mm Hg absolute.
P_{tf} = Final gas sample tank pressure after pressurizing, mm Hg absolute.
P_{ti} = Gas sample tank pressure after evacuation, mm Hg absolute.
P_w = Vapor pressure of H_2O (from Table 25C–1), mm Hg.
r = Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 . . . r).
T_t = Sample tank temperature at completion of sampling, °K.
T_{ti} = Sample tank temperature before sampling, °K.
T_{tf} = Sample tank temperature after pressuring, °K.

12.2 Water Correction. Use Table 25C–1 (Section 17.0), the LFG temperature, and barometric pressure at the sampling site to calculate B_w.

$$B_w = \frac{P_w}{P_b} \qquad \text{Eq. 25C-1}$$

12.3 Nitrogen Concentration in the landfill gas. Use equation 25C–2 to calculate the measured concentration of nitrogen in the original landfill gas.

$$C_{N2} = \left[\frac{\left(\frac{P_{tf}}{T_{tf}}\right)}{\left(\left(\frac{P_t}{T_t}\right)-\left(\frac{P_{ti}}{T_{ti}}\right)\right)}\right] C_{mN2} \qquad \text{Eq.25C-2}$$

12.4 Oxygen Concentration in the landfill gas. Use equation 25C–3 to calculate the measured concentration of oxygen in the original landfill gas.

$$C_{Ox} = \left[\frac{\left(\frac{P_{tf}}{T_{tf}}\right)}{\left(\left(\frac{P_t}{T_t}\right)-\left(\frac{P_{ti}}{T_{ti}}\right)\right)}\right] C_{mOx} \qquad \text{Eq.25C-3}$$

12.5 You must correct the NMOC Concentration for the concentration of nitrogen or oxygen based on which gas or gases passes the requirements in section 9.1.

12.5.1 NMOC Concentration with nitrogen correction. Use Equation 25C–4 to calculate the concentration of NMOC for each sample tank when the nitrogen concentration is less than 20 percent.

$$C_t = \frac{\frac{P_{tf}}{T_{tf}}}{\left(\frac{P_t}{T_t}-\frac{P_{ti}}{T_{ti}}\right)\left(1-\frac{99}{78}C_{N2}\right)-B_w}\frac{1}{r}\sum_{j=1}^{r} C_{tm(j)} \qquad \text{Eq. 25C-4}$$

12.5.2 NMOC Concentration with oxygen correction. Use Equation 25C–5 to calculate the concentration of NMOC for each sample tank if the landfill gas oxygen is less than 5 percent and the landfill gas nitrogen concentration is greater than 20 percent.

$$C_t = \frac{\frac{P_{tf}}{T_{tf}}}{\left(\frac{P_t}{T_t}-\frac{P_{ti}}{T_{ti}}\right)\left(1-\frac{99}{21}C_{Ox}\right)-B_w}\frac{1}{r}\sum_{j=1}^{r} C_{tm(j)} \qquad \text{Eq. 25C-5}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, Albert E., Samuel Witz, and Robert D. MacPhee. Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, Massachusetts. June 15–20, 1975.) 14 p.

2. Salo, Albert E., William L. Oaks, and Robert D. MacPhee. Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, Colorado. June 9–13, 1974.) 25 p.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

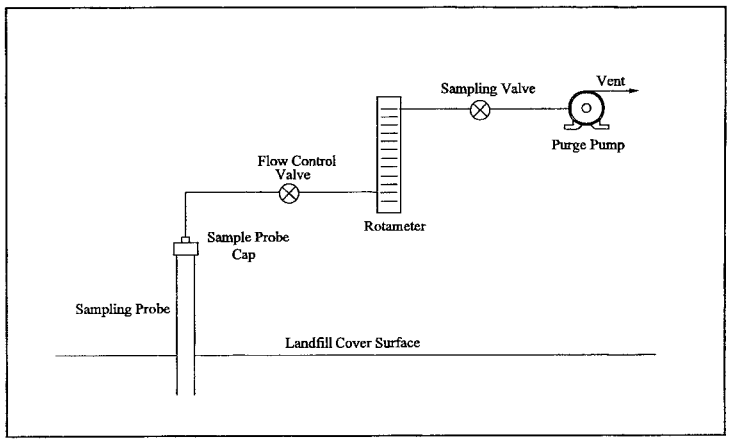


Figure 25C-1. Schematic of Sampling Probe Purging System

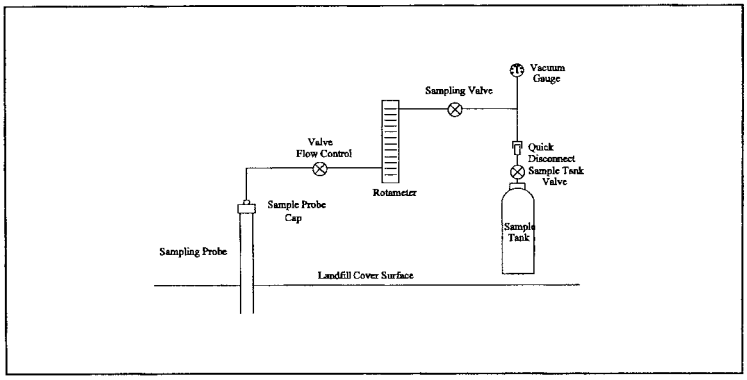


Figure 25C-2. Schematic of Sampling Train.

TABLE 25C–1—MOISTURE CORRECTION

Temperature, °C	Vapor Pressure of H_2O, mm Hg	Temperature, °C	Vapor Pressure of H_2O, mm Hg
4	6.1	18	15.5
6	7.0	20	17.5
8	8.0	22	19.8
10	9.2	24	22.4
12	10.5	26	25.2
14	12.0	28	28.3

TABLE 25C–1—MOISTURE CORRECTION—Continued

Temperature, °C	Vapor Pressure of H_2O, mm Hg	Temperature, °C	Vapor Pressure of H_2O, mm Hg
16	13.6	30	31.8

METHOD 25D—DETERMINATION OF THE VOLATILE ORGANIC CONCENTRATION OF WASTE SAMPLES

NOTE: Performance of this method should not be attempted by persons unfamiliar with the operation of a flame ionization detector (FID) or an electrolytic conductivity detector (ELCD) because knowledge beyond the scope of this presentation is required.

1.0 Scope and Application

1.1 Analyte. Volatile Organic Compounds. No CAS No. assigned.

1.2 Applicability. This method is applicable for determining the volatile organic (VO) concentration of a waste sample.

2.0 Summary of Method

2.1 Principle. A sample of waste is obtained at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to the atmosphere). The sample is suspended in an organic/aqueous matrix, then heated and purged with nitrogen for 30 min. in order to separate certain organic compounds. Part of the sample is analyzed for carbon concentration, as methane, with an FID, and part of the sample is analyzed for chlorine concentration, as chloride, with an ELCD. The VO concentration is the sum of the carbon and chlorine content of the sample.

3.0 Definitions

3.1 *Well-mixed* in the context of this method refers to turbulent flow which results in multiple-phase waste in effect behaving as single-phase waste due to good mixing.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1 Sampling. The following equipment is required:

6.1.1 Sampling Tube. Flexible Teflon, 0.25 in. ID (6.35 mm).

6.1.2 Sample Container. Borosilicate glass, 40-mL, and a Teflon-lined screw cap capable of forming an air tight seal.

6.1.3 Cooling Coil. Fabricated from 0.25 in (6.35 mm). ID 304 stainless steel tubing with a thermocouple at the coil outlet.

6.2 Analysis. The following equipment is required.

6.2.1 Purging Apparatus. For separating the VO from the waste sample. A schematic of the system is shown in Figure 25D–1. The purging apparatus consists of the following major components.

6.2.1.1 Purging Flask. A glass container to hold the sample while it is heated and purged with dry nitrogen. The cap of the purging flask is equipped with three fittings: one for a purging lance (fitting with the #7 Ace-thread), one for the Teflon exit tubing (side fitting, also a #7 Ace-thread), and a third (a 50-mm Ace-thread) to attach the base of the purging flask as shown in Figure 25D–2. The base of the purging flask is a 50-mm ID (2 in) cylindrical glass tube. One end of the tube is open while the other end is sealed. Exact dimensions are shown in Figure 25D–2.

6.2.1.2 Purging Lance. Glass tube, 6-mm OD (0.2 in) by 30 cm (12 in) long. The purging end of the tube is fitted with a four-arm bubbler with each tip drawn to an opening 1 mm (0.04 in) in diameter. Details and exact dimensions are shown in Figure 25D–2.

6.2.1.3 Coalescing Filter. Porous fritted disc incorporated into a container with the same dimensions as the purging flask. The details of the design are shown in Figure 25D–3.

6.2.1.4 Constant Temperature Chamber. A forced draft oven capable of maintaining a uniform temperature around the purging flask and coalescing filter of 75 ±2 °C (167 ±3.6 °F).

6.2.1.5 Three-way Valve. Manually operated, stainless steel. To introduce calibration gas into system.

6.2.1.6 Flow Controllers. Two, adjustable. One capable of maintaining a purge gas flow rate of 6 ±0.06 L/min (0.2 ±0.002 ft^3/min) The other capable of maintaining a calibration gas flow rate of 1–100 mL/min (0.00004–0.004 ft^3/min).

6.2.1.7 Rotameter. For monitoring the air flow through the purging system (0–10 L/min)(0–0.4 ft^3/min).

6.2.1.8 Sample Splitters. Two heated flow restrictors (placed inside oven or heated to 120 ±10 °C (248 ±18 °F)). At a purge rate of 6 L/min (0.2 ft^3/min), one will supply a constant flow to the first detector (the rest of the flow will be directed to the second sample splitter). The second splitter will split the analytical flow between the second detector and the flow restrictor. The approximate flow to the FID will be 40 mL/min (0.0014 ft^3/min) and to the ELCD will be 15 mL/min (0.0005 ft^3/min), but the exact flow must be adjusted to be compatible with the individual detector and to meet its linearity requirement. The two sample splitters will be connected to each other by 1/8′ OD (3.175 mm) stainless steel tubing.

6.2.1.9 Flow Restrictor. Stainless steel tubing, 1/8″ OD (3.175 mm), connecting the second sample splitter to the ice bath. Length is determined by the resulting pressure in the purging flask (as measured by the pressure gauge). The resulting pressure from the use of the flow restrictor shall be 6–7 psig.

6.2.1.10 Filter Flask. With one-hole stopper. Used to hold ice bath. Excess purge gas is vented through the flask to prevent condensation in the flowmeter and to trap volatile organic compounds.

6.2.1.11 Four-way Valve. Manually operated, stainless steel. Placed inside oven, used to bypass purging flask.

6.2.1.12 On/Off Valves. Two, stainless steel. One heat resistant up to 130 °C (266 °F) and placed between oven and ELCD. The other a toggle valve used to control purge gas flow.

6.2.1.13 Pressure Gauge. Range 0–40 psi. To monitor pressure in purging flask and coalescing filter.

6.2.1.14 Sample Lines. Teflon, 1/4″ OD (6.35 mm), used inside the oven to carry purge gas to and from purging chamber and to and from coalescing filter to four-way valve. Also used to carry sample from four-way valve to first sample splitter.

6.2.1.15 Detector Tubing. Stainless steel, 1/8″ OD (3.175 mm), heated to 120 ±10 °C (248 ±18 °F) . Used to carry sample gas from each sample splitter to a detector. Each piece of tubing must be wrapped with heat tape and insulating tape in order to insure that no cold spots exist. The tubing leading to the ELCD will also contain a heat-resistant on-off valve (Section 6.2.1.12) which shall also be wrapped with heat-tape and insulation.

6.2.2 Volatile Organic Measurement System. Consisting of an FID to measure the carbon concentration of the sample and an ELCD to measure the chlorine concentration.

6.2.2.1 FID. A heated FID meeting the following specifications is required.

6.2.2.1.1 Linearity. A linear response (±5 percent) over the operating range as demonstrated by the procedures established in section 10.1.1.

6.2.2.1.2 Range. A full scale range of 50 pg carbon/sec to 50 µg carbon/sec. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.2.2.1.3 Data Recording System. A digital integration system compatible with the FID for permanently recording the output of the detector. The recorder shall have the capability to start and stop integration at points selected by the operator or it shall be capable of the ''integration by slices'' technique (this technique involves breaking down the chromatogram into smaller increments, integrating the area under the curve for each portion, subtracting the background for each portion, and then adding all of the areas together for the final area count).

6.2.2.2 ELCD. An ELCD meeting the following specifications is required. 1-propanol must be used as the electrolyte. The electrolyte flow through the conductivity cell shall be 1 to 2 mL/min (0.00004 to 0.00007 ft^3/min).

NOTE: A ¼-in. ID (6.35 mm) quartz reactor tube is strongly recommended to reduce carbon buildup and the resulting detector maintenance.

6.2.2.2.1 Linearity. A linear response (±10 percent) over the response range as demonstrated by the procedures in section 10.1.2.

6.2.2.2.2 Range. A full scale range of 5.0 pg/sec to 500 ng/sec chloride. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.2.2.2.3 Data Recording System. A digital integration system compatible with the output voltage range of the ELCD. The recorder must have the capability to start and stop integration at points selected by the operator or it shall be capable of performing the ''integration by slices'' technique.

7.0 Reagents and Standards

7.1 Sampling.

7.1.1 Polyethylene Glycol (PEG). Ninety-eight percent pure with an average molecular weight of 400. Before using the PEG, remove any organic compounds that might be detected as volatile organics by heating it to 120 °C (248 °F) and purging it with nitrogen at a flow rate of 1 to 2 L/min (0.04 to 0.07 ft^3/min) for 2 hours. The cleaned PEG must be stored under a 1 to 2 L/min (0.04 to 0.07 ft^3/min) nitrogen purge until use. The purge apparatus is shown in Figure 25D–4.

7.2 Analysis.

7.2.1 Sample Separation. The following are required for the sample purging step.

7.2.1.1 PEG. Same as section 7.1.1.

7.2.1.2 Purge Gas. Zero grade nitrogen (N_2), containing less than 1 ppm carbon.

7.2.2 Volatile Organics Measurement. The following are required for measuring the VO concentration.

7.2.2.1 Hydrogen (H_2). Zero grade H_2, 99.999 percent pure.

7.2.2.2 Combustion Gas. Zero grade air or oxygen as required by the FID.

7.2.2.3 Calibration Gas. Pressurized gas cylinder containing 10 percent propane and 1 percent 1,1-dichloroethylene by volume in nitrogen.

7.2.2.4 Water. Deionized distilled water that conforms to American Society for Testing and Materials Specification D 1193–74, Type 3, is required for analysis. At the option of the analyst, the $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations are not expected to be present.

7.2.2.5 1-Propanol. ACS grade or better. Electrolyte Solution. For use in the ELCD.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling.

8.1.1 Sampling Plan Design and Development. Use the procedures in chapter nine of Reference 1 in section 16 as guidance in developing a sampling plan.

8.1.2 Single Phase or Well-mixed Waste.

8.1.2.1 Install a sampling tap to obtain the sample at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to the atmosphere). Assemble the sampling apparatus as shown in Figure 25D–5.

8.1.2.2 Prepare the sampling containers as follows: Pour 30 mL of clean PEG into the container. PEG will reduce but not eliminate the loss of organics during sample collection. Weigh the sample container with the screw cap, the PEG, and any labels to the nearest 0.01 g and record the weight (m_{st}). Store the containers in an ice bath until 1 hour before sampling (PEG will solidify at ice bath temperatures; allow the containers to reach room temperature before sampling).

8.1.2.3 Begin sampling by purging the sample lines and cooling coil with at least four volumes of waste. Collect the purged material in a separate container and dispose of it properly.

8.1.2.4 After purging, stop the sample flow and direct the sampling tube to a preweighed sample container, prepared as described in section 8.1.2.2. Keep the tip of the tube below the surface of the PEG during sampling to minimize contact with the atmosphere. Sample at a flow rate such that the temperature of the waste is less than 10 °C (50 °F). Fill the sample container and immediately cap it (within 5 seconds) so that a minimum headspace exists in the container. Store immediately in a cooler and cover with ice.

8.1.3 Multiple-phase Waste. Collect a 10 g sample of each phase of waste generated using the procedures described in section 8.1.2 or 8.1.5. Each phase of the waste shall be analyzed as a separate sample. Calculate the weighted average VO concentration of the waste using Equation 25D–13 (Section 12.14).

8.1.4 Solid waste. Add approximately 10 g of the solid waste to a container prepared in the manner described in section 8.1.2.2, minimizing headspace. Cap and chill immediately.

8.1.5 Alternative to Tap Installation. If tap installation is impractical or impossible, fill a large, clean, empty container by submerging the container into the waste below the surface of the waste. Immediately fill a container prepared in the manner described in section 8.1.2.2 with approximately 10 g of the waste collected in the large container. Minimize headspace, cap and chill immediately.

8.1.6 Alternative sampling techniques may be used upon the approval of the Administrator.

8.2 Sample Recovery.

8.2.1 Assemble the purging apparatus as shown in Figures 25D–1 and 25D–2. The oven shall be heated to 75 ±2 °C (167 ±3.6 °F). The sampling lines leading from the oven to the detectors shall be heated to 120 ±10 °C (248 ±18 °F) with no cold spots. The flame ionization detector shall be operated with a heated block. Adjust the purging lance so that it reaches the bottom of the chamber.

8.2.2 Remove the sample container from the cooler, and wipe the exterior of the container to remove any extraneous ice, water, or other debris. Reweigh the sample container to the nearest 0.01 g, and record the weight (m_{sf}). Pour the contents of the sample container into the purging flask, rinse the sample container three times with a total of 20 mL of PEG (since the sample container originally held 30 mL of PEG, the total volume of PEG added to the purging flask will be 50 mL), transferring the rinsings to the purging flask after each rinse. Cap purging flask between rinses. The total volume of PEG in the purging flask shall be 50 mL. Add 50 mL of water to the purging flask.

9.0 Quality Control

9.1 Quality Control Samples. If audit samples are not available, prepare and analyze the two types of quality control samples (QCS) listed in Sections 9.1.1 and 9.1.2. Before placing the system in operation, after a shutdown of greater than six months, and after any major modifications, analyze each QCS in triplicate. For each detector, calculate the percent recovery by dividing measured concentration by theoretical concentration and multiplying by 100. Determine the mean percent recovery for each detector for each QCS triplicate analysis. The RSD for any triplicate analysis shall be ≤10 percent. For QCS 1 (methylene chloride), the percent recovery shall be ≥90 percent for carbon as methane, and ≥55 percent for chlorine as chloride. For QCS 2 (1,3-dichloro-2-propanol), the percent recovery shall be ≤15 percent for carbon as methane, and ≤6 percent for chlorine as chloride. If the analytical system does not meet the above-mentioned criteria for both detectors, check the system parameters (temperature, system pressure, purge rate, etc.), correct the problem, and repeat the triplicate analysis of each QCS.

9.1.1 QCS 1, Methylene Chloride. Prepare a stock solution by weighing, to the nearest 0.1 mg, 55 µL of HPLC grade methylene chloride in a tared 5 mL volumetric flask. Record the weight in milligrams, dilute to 5 mL with cleaned PEG, and inject 100 µL of the stock solution into a sample prepared as a water blank (50 mL of cleaned PEG and 60 mL of water in the purging flask). Analyze

the QCS according to the procedures described in sections 10.2 and 10.3, excluding section 10.2.2. To calculate the theoretical carbon concentration (in mg) in QCS 1, multiply mg of methylene chloride in the stock solution by 3.777×10^{-3}. To calculate the theoretical chlorine concentration (in mg) in QCS 1, multiply mg of methylene chloride in the stock solution by 1.670×10^{-2}.

9.1.2 QCS 2, 1,3-dichloro-2-propanol. Prepare a stock solution by weighing, to the nearest 0.1 mg, 60 μL of high purity grade 1,3-dichloro-2-propanol in a tared 5 mL volumetric flask. Record the weight in milligrams, dilute to 5 mL with cleaned PEG, and inject 100 μL of the stock solution into a sample prepared as a water blank (50 mL of cleaned PEG and 60 mL of water in the purging flask). Analyze the QCS according to the procedures described in sections 10.2 and 10.3, excluding section 10.2.2. To calculate the theoretical carbon concentration (in mg) in QCS 2, multiply mg of 1,3-dichloro-2-propanol in the stock solution by 7.461×10^{-3}. To calculate the theoretical chlorine concentration (in mg) in QCS 2, multiply mg of 1,3-dichloro-2-propanol in the stock solution by 1.099×10^{-2}.

9.1.3 Routine QCS Analysis. For each set of compliance samples (in this context, set is per facility, per compliance test), analyze one QCS 1 and one QCS 2 sample. The percent recovery for each sample for each detector shall be ±13 percent of the mean recovery established for the most recent set of QCS triplicate analysis (Section 9.4). If the sample does not meet this criteria, check the system components and analyze another QCS 1 and 2 until a single set of QCS meet the ±13 percent criteria.

10.0 Calibration and Standardization

10.1 Initial Performance Check of Purging System. Before placing the system in operation, after a shutdown of greater than six months, after any major modifications, and at least once per month during continuous operation, conduct the linearity checks described in sections 10.1.1 and 10.1.2. Install calibration gas at the three-way calibration gas valve. See Figure 25D–1.

10.1.1 Linearity Check Procedure. Using the calibration standard described in section 7.2.2.3 and by varying the injection time, it is possible to calibrate at multiple concentration levels. Use Equation 25D–3 to calculate three sets of calibration gas flow rates and run times needed to introduce a total mass of carbon, as methane, (m_c) of 1, 5, and 10 mg into the system (low, medium and high FID calibration, respectively). Use Equation 25D–4 to calculate three sets of calibration gas flow rates and run times needed to introduce a total chloride mass (m_{ch}) of 1, 5, and 10 mg into the system (low, medium and high ELCD calibration, respectively). With the system operating in standby mode, allow the FID and the ELCD to establish a stable baseline. Set the secondary pressure regulator of the calibration gas cylinder to the same pressure as the purge gas cylinder and set the proper flow rate with the calibration flow controller (see Figure 25D–1). The calibration gas flow rate can be measured with a flowmeter attached to the vent position of the calibration gas valve. Set the four-way bypass valve to standby position so that the calibration gas flows through the coalescing filter only. Inject the calibration gas by turning the calibration gas valve from vent position to inject position. Continue the calibration gas flow for the appropriate period of time before switching the calibration valve to vent position. Continue recording the response of the FID and the ELCD for 5 min after switching off calibration gas flow. Make triplicate injections of all six levels of calibration.

10.1.2 Linearity Criteria. Calculate the average response factor (Equations 25D–5 and 25D–6) and the relative standard deviation (RSD) (Equation 25D–10) at each level of the calibration curve for both detectors. Calculate the overall mean of the three response factor averages for each detector. The FID linearity is acceptable if each response factor is within 5 percent of the overall mean and if the RSD for each set of triplicate injections is less than 5 percent. The ELCD linearity is acceptable if each response factor is within 10 percent of the overall mean and if the RSD for each set of triplicate injections is less than 10 percent. Record the overall mean value of the response factors for the FID and the ELCD. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat sections 10.1.1 and 10.1.2.

10.2 Daily Calibrations.

10.2.1 Daily Linearity Check. Follow the procedures outlined in section 10.1.1 to analyze the medium level calibration for both the FID and the ELCD in duplicate at the start of the day. Calculate the response factors and the RSDs for each detector. For the FID, the calibration is acceptable if the average response factor is within 5 percent of the overall mean response factor (Section 10.1.2) and if the RSD for the duplicate injection is less than 5 percent. For the ELCD, the calibration is acceptable if the average response factor is within 10 percent of the overall mean response factor (Section 10.1.2) and if the RSD for the duplicate injection is less than 10 percent. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat sections 10.1.1 and 10.1.2.

10.2.2 Calibration Range Check.

10.2.2.1 If the waste concentration for either detector falls below the range of calibration for that detector, use the procedure outlined in section 10.1.1 to choose two calibration points that bracket the new target

concentration. Analyze each of these points in triplicate (as outlined in section 10.1.1) and use the criteria in section 10.1.2 to determine the linearity of the detector in this ''mini-calibration'' range.

10.2.2.2 After the initial linearity check of the mini-calibration curve, it is only necessary to test one of the points in duplicate for the daily calibration check (in addition to the points specified in section 10.2.1). The average daily mini-calibration point should fit the linearity criteria specified in section 10.2.1. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat the calibration procedure mentioned in the first paragraph of section 10.2.2. A mini-calibration curve for waste concentrations above the calibration curve for either detector is optional.

10.3 Analytical Balance. Calibrate against standard weights.

11.0 Analysis

11.1 Sample Analysis.

11.1.1 Turn on the constant temperature chamber and allow the temperature to equilibrate at 75 ±2 °C (167 ±3.6 °F). Turn the four-way valve so that the purge gas bypasses the purging flask, the purge gas flowing through the coalescing filter and to the detectors (standby mode). Turn on the purge gas. Allow both the FID and the ELCD to warm up until a stable baseline is achieved on each detector. Pack the filter flask with ice. Replace ice after each run and dispose of the waste water properly. When the temperature of the oven reaches 75 ±2 °C (167 ±3.6 °F), start both integrators and record baseline. After 1 min, turn the four-way valve so that the purge gas flows through the purging flask, to the coalescing filter and to the sample splitters (purge mode). Continue recording the response of the FID and the ELCD. Monitor the readings of the pressure gauge and the rotameter. If the readings fall below established setpoints, stop the purging, determine the source of the leak, and resolve the problem before resuming. Leaks detected during a sampling period invalidate that sample.

11.1.2 As the purging continues, monitor the output of the detectors to make certain that the analysis is proceeding correctly and that the results are being properly recorded. Every 10 minutes read and record the purge flow rate, the pressure and the chamber temperature. Continue the purging for 30 minutes.

11.1.3 For each detector output, integrate over the entire area of the peak starting at 1 minute and continuing until the end of the run. Subtract the established baseline area from the peak area. Record the corrected area of the peak. See Figure 25D–6 for an example integration.

11.2 Water Blank. A water blank shall be analyzed for each batch of cleaned PEG prepared. Transfer about 60 mL of water into the purging flask. Add 50 mL of the cleaned PEG to the purging flask. Treat the blank as described in sections 8.2 and 8.3, excluding section 8.2.2. Calculate the concentration of carbon and chlorine in the blank sample (assume 10 g of waste as the mass). A VO concentration equivalent to ≤10 percent of the applicable standard may be subtracted from the measured VO concentration of the waste samples. Include all blank results and documentation in the test report.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

A_b = Area under the water blank response curve, counts.
A_c = Area under the calibration response curve, counts.
A_s = Area under the sample response curve, counts.
C = Concentration of volatile organics in the sample, ppmw.
C_c = Concentration of carbon, as methane, in the calibration gas, mg/L.
C_{ch} = Concentration of chloride in the calibration gas, mg/L.
C_j = VO concentration of phase j, ppmw.
DR_t = Average daily response factor of the FID, mg CH_4/counts.
Dr_{th} = Average daily response factor of the ELCD, mg Cl^-/counts.
F_j = Weight fraction of phase j present in the waste.
m_c = Mass of carbon, as methane, in a calibration run, mg.
m_{ch} = Mass of chloride in a calibration run, mg.
m_s = Mass of the waste sample, g.
m_{sc} = Mass of carbon, as methane, in the sample, mg.
m_{sf} = Mass of sample container and waste sample, g.
m_{sh} = Mass of chloride in the sample, mg.
m_{st} = Mass of sample container prior to sampling, g.
m_{VO} = Mass of volatile organics in the sample, mg.
n = Total number of phases present in the waste.
P_p = Percent propane in calibration gas (L/L).
P_{vc} = Percent 1,1-dichloroethylene in calibration gas (L/L).
Q_c = Flow rate of calibration gas, L/min.
t_c = Length of time standard gas is delivered to the analyzer, min.
W = Weighted average VO concentration, ppmw.

12.2 Concentration of Carbon, as Methane, in the Calibration Gas.

$$C_c = \left(19.681 \times P_p\right) + \left(13.121 \times P_{vc}\right) \qquad \text{Eq. 25D-1}$$

12.3 Concentration of Chloride in the Calibration Gas.

$$C_{ch} = 28.998 \times P_{vc} \qquad \text{Eq. 25D-2}$$

12.4 Mass of Carbon, as Methane, in a Calibration Run.

$$M_c = C_c \times Q_c \times t_c \qquad \text{Eq. 25D-3}$$

12.5 Mass of Chloride in a Calibration Run.

$$m_{ch} = C_{ch} \times Q_c \times t_c \qquad \text{Eq. 25D-4}$$

12.6 FID Response Factor, mg/counts.

$$DR_t = \frac{m_c}{A_c} \qquad \text{Eq. 25D-5}$$

12.7 ELCD Response Factor, mg/counts.

$$DR_{th} = \frac{m_{ch}}{A_c} \qquad \text{Eq. 25D-6}$$

12.8 Mass of Carbon in the Sample.

$$m_{sc} = DR_t\left(A_s - A_b\right) \qquad \text{Eq. 25D-7}$$

12.9 Mass of Chloride in the Sample.

$$m_{sh} = DR_{th}\left(A_s - A_b\right) \qquad \text{Eq. 25D-8}$$

12.10 Mass of Volatile Organics in the Sample.

$$m_{vo} = m_{sc} + m_{sh} \qquad \text{Eq. 25D-9}$$

12.11 Relative Standard Deviation.

$$RSD = \frac{100}{\bar{x}} \sqrt{\frac{\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2}{n-1}} \qquad \text{Eq. 25D-10}$$

12.12 Mass of Sample.

$$m_s = m_{sf} - m_{st} \qquad \text{Eq. 25D-11}$$

12.13 Concentration of Volatile Organics in Waste.

$$C = \frac{\left(m_{vo} \times 1000\right)}{m_s} \qquad \text{Eq. 25D-12}$$

12.14 Weighted Average VO Concentration of Multi-phase Waste.

$$W = \sum_{j=1}^{n} F_j x \overline{C}_j \qquad \text{Eq. 25D-13}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. ''Test Methods for Evaluating Solid Waste, Physical/Chemistry Methods'', U.S. Environmental Protection Agency. Publication SW–846, 3rd Edition, November 1986 as amended by Update I, November 1990.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

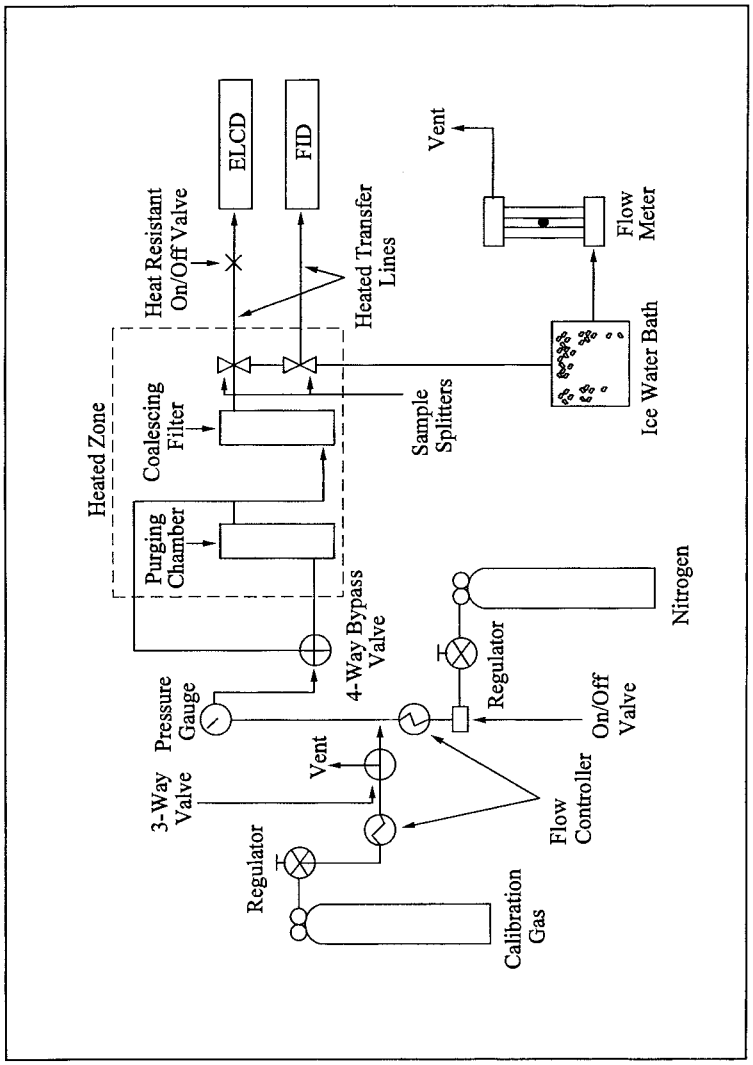


Figure 25D-1. Schematic of Purging Apparatus.

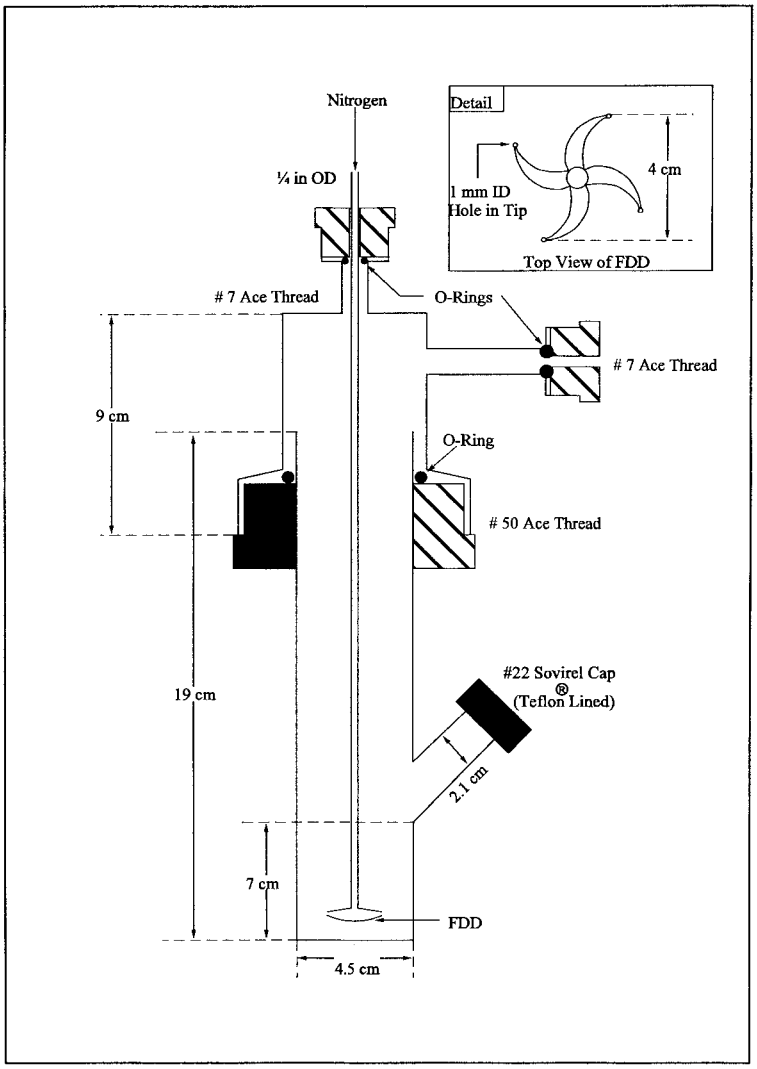
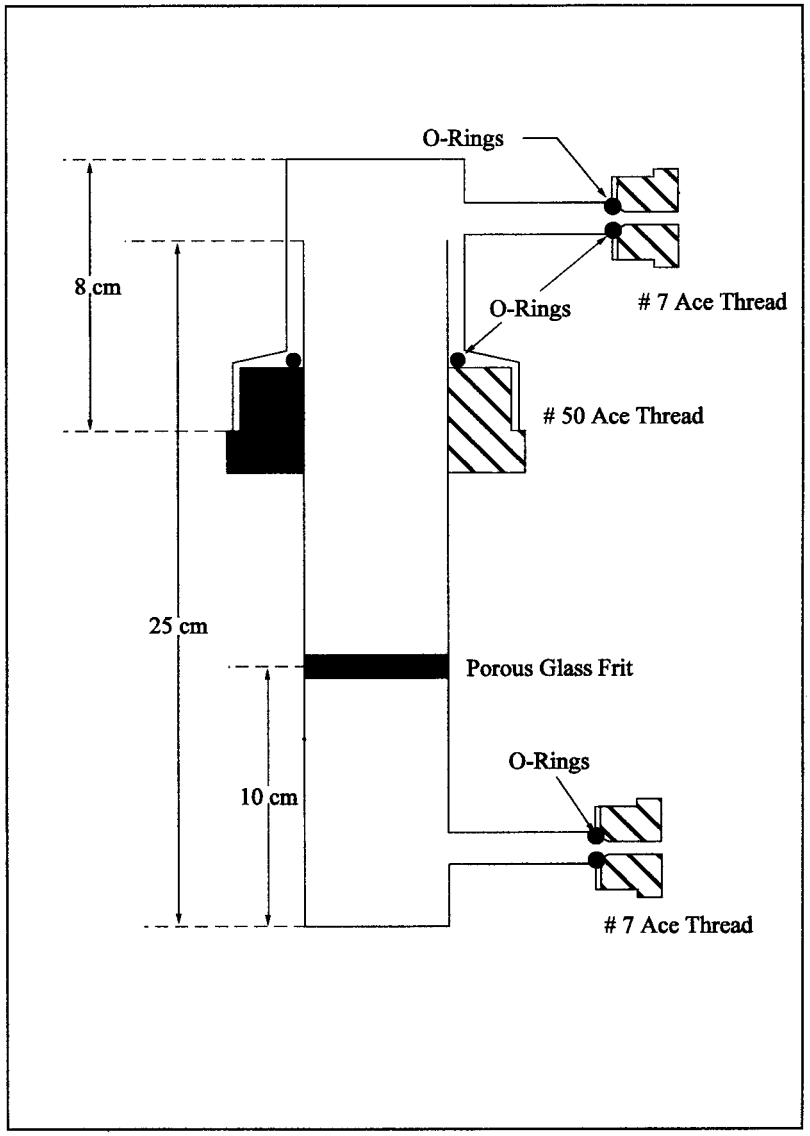


Figure 25D-2. Purging Lance.


O-Rings
8 cm
O-Rings
7 Ace Thread
50 Ace Thread
25 cm
Porous Glass Frit
O-Rings
10 cm
7 Ace Thread

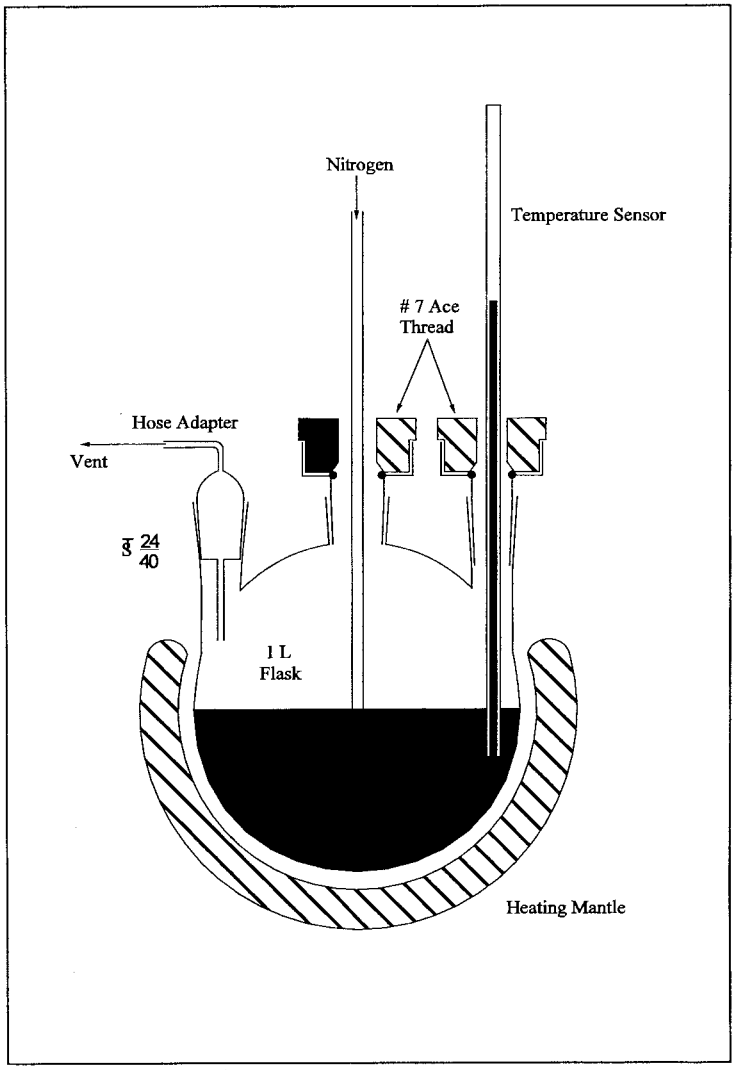


Figure 25D-4. Schematic of PEG Cleaning System.

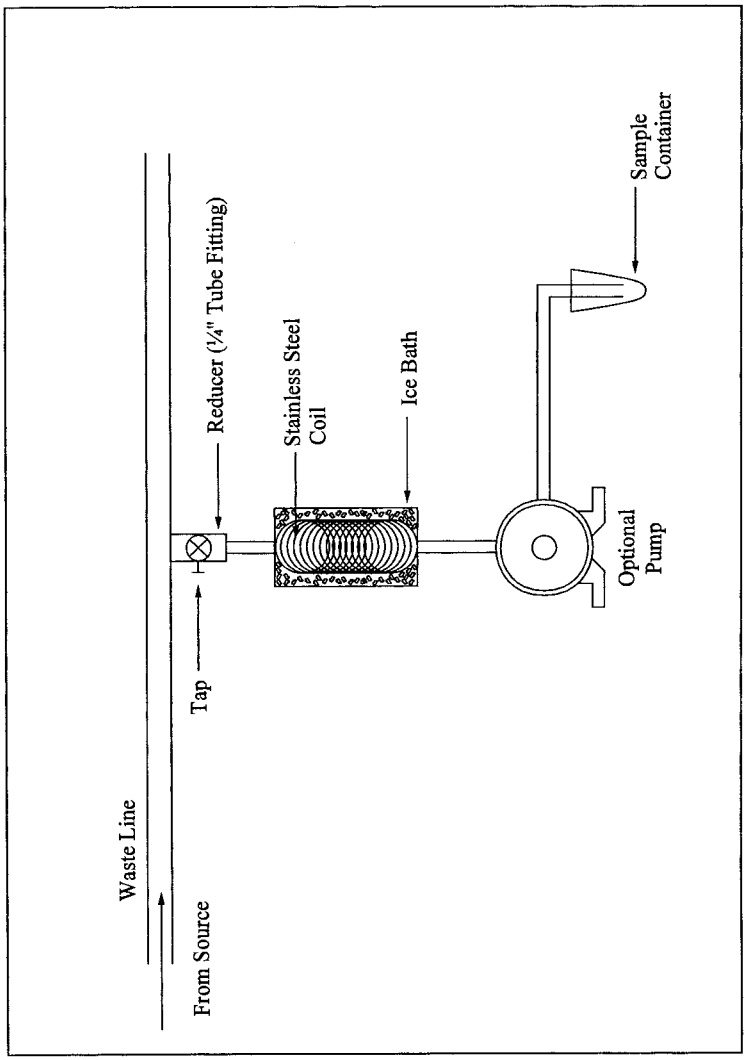


Figure 25D-5. Schematic of Sampling Apparatus.

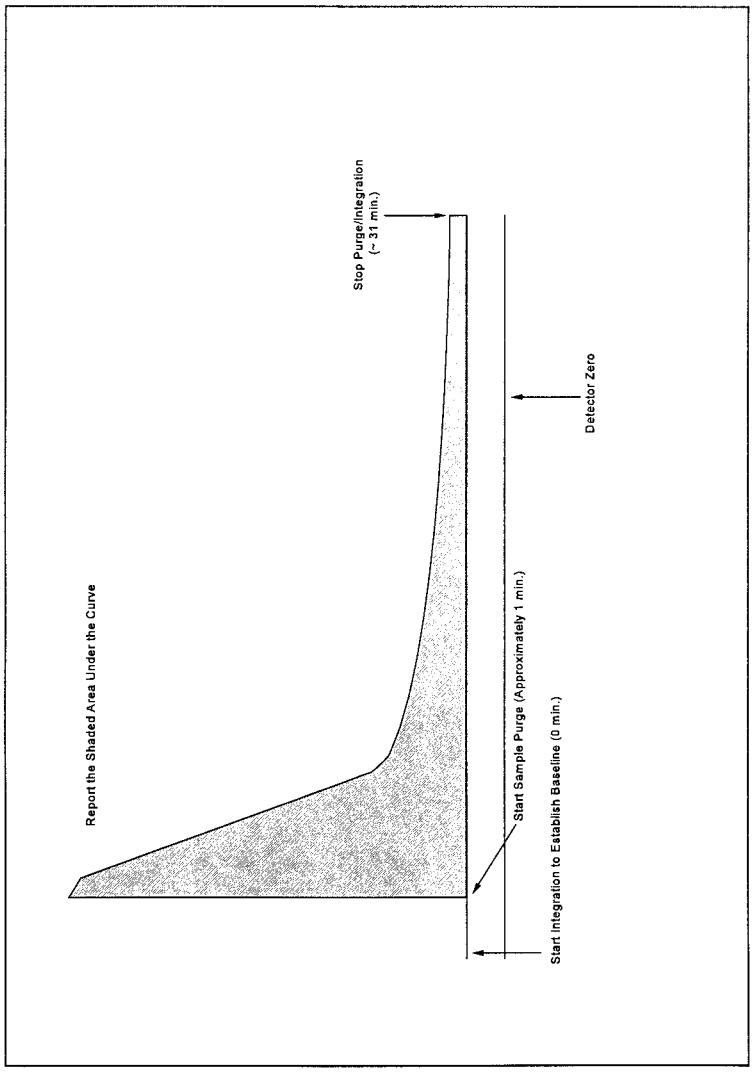


Figure 25D-6. Example Integration of Either Detector.

METHOD 25E—DETERMINATION OF VAPOR PHASE ORGANIC CONCENTRATION IN WASTE SAMPLES

NOTE: Performance of this method should not be attempted by persons unfamiliar with the operation of a flame ionization detector (FID) nor by those who are unfamiliar with source sampling because knowledge beyond the scope of this presentation is required. This method is not inclusive with respect to specifications (*e.g.*, reagents and standards) and calibration procedures. Some material is incorporated by reference from other methods. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 106, part 61, Appendix B, and Method 18, part 60, Appendix A.

1.0 Scope and Application

1.1 Applicability. This method is applicable for determining the vapor pressure of waste cited by an applicable regulation.

1.2 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 The headspace vapor of the sample is analyzed for carbon content by a headspace analyzer, which uses an FID.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 The analyst shall select the operating parameters best suited to the requirements for a particular analysis. The analyst shall produce confirming data through an adequate supplemental analytical technique and have the data available for review by the Administrator.

5.0 Safety [Reserved]

6.0 Equipment and Supplies

6.1 Sampling. The following equipment is required:

6.1.1 Sample Containers. Vials, glass, with butyl rubber septa, Perkin-Elmer Corporation Numbers 0105–0129 (glass vials), B001–0728 (gray butyl rubber septum, plug style), 0105–0131 (butyl rubber septa), or equivalent. The seal must be made from butyl rubber. Silicone rubber seals are not acceptable.

6.1.2 Vial Sealer. Perkin-Elmer Number 105–0106, or equivalent.

6.1.3 Gas-Tight Syringe. Perkin-Elmer Number 00230117, or equivalent.

6.1.4 The following equipment is required for sampling.

6.1.4.1 Tap.

6.1.4.2 Tubing. Teflon, 0.25-in. ID.

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1.4.3 Cooling Coil. Stainless steel (304), 0.25 in.-ID, equipped with a thermocouple at the coil outlet.

6.2 Analysis. The following equipment is required.

6.2.1 Balanced Pressure Headspace Sampler. Perkin-Elmer HS–6, HS–100, or equivalent, equipped with a glass bead column instead of a chromatographic column.

6.2.2 FID. An FID meeting the following specifications is required.

6.2.2.1 Linearity. A linear response (±5 percent) over the operating range as demonstrated by the procedures established in section 10.2.

6.2.2.2 Range. A full scale range of 1 to 10,000 parts per million (ppm) propane (C_3H_8). Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.2.3 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the output of the detector.

6.2.4 Temperature Sensor. Capable of reading temperatures in the range of 30 to 60 °C (86 to 140 °F) with an accuracy of ±0.1 °C (±0.2 °F).

7.0 Reagents and Standards

7.1 Analysis. The following items are required for analysis.

7.1.1 Hydrogen (H_2). Zero grade hydrogen, as required by the FID.

7.1.2 Carrier Gas. Zero grade nitrogen, containing less than 1 ppm carbon (C) and less than 1 ppm carbon dioxide.

7.1.3 Combustion Gas. Zero grade air or oxygen as required by the FID.

7.2 Calibration and Linearity Check.

7.2.1 Stock Cylinder Gas Standard. 100 percent propane. The manufacturer shall: (a) Certify the gas composition to be accurate to ±3 percent or better (see section 7.2.1.1); (b) recommend a maximum shelf life over which the gas concentration does not change by greater than ±5 percent from the certified value; and (c) affix the date of gas cylinder preparation, certified propane concentration, and recommended maximum shelf life to the cylinder before shipment to the buyer.

7.2.1.1 Cylinder Standards Certification. The manufacturer shall certify the concentration of the calibration gas in the cylinder by (a) directly analyzing the cylinder and (b) calibrating his analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use, as a minimum, a three-point calibration curve.

7.2.1.2 Verification of Manufacturer's Calibration Standards. Before using, the manufacturer shall verify each calibration standard by (a) comparing it to gas mixtures prepared in accordance with the procedure described in section 7.1 of Method 106 of Part 61, Appendix B, or by (b) calibrating it against Standard Reference Materials (SRM's) prepared by the National Bureau of Standards, if such SRM's are available. The agreement between the initially determined concentration value and the verification concentration value must be within ±5 percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

8.0 Sampling Collection, Preservation, Storage, and Transport

8.1 Install a sampling tap to obtain a sample at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to

the atmosphere). Assemble the sampling apparatus as shown in Figure 25E–1.

8.2 Begin sampling by purging the sample lines and cooling coil with at least four volumes of waste. Collect the purged material in a separate container and dispose of it properly.

8.3 After purging, stop the sample flow and transfer the Teflon sampling tube to a sample container. Sample at a flow rate such that the temperature of the waste is <10 °C (<50 °F). Fill the sample container halfway (±5 percent) and cap it within 5 seconds. Store immediately in a cooler and cover with ice.

8.4 Alternative sampling techniques may be used upon the approval of the Administrator.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
10.2, 10.3	FID calibration and response check	Ensure precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Use the procedures in sections 10.2 to calibrate the headspace analyzer and FID and check for linearity before the system is first placed in operation, after any shutdown longer than 6 months, and after any modification of the system.

10.2 Calibration and Linearity. Use the procedures in section 10 of Method 18 of Part 60, Appendix A, to prepare the standards and calibrate the flowmeters, using propane as the standard gas. Fill the calibration standard vials halfway (±5 percent) with deionized water. Purge and fill the airspace with calibration standard. Prepare a minimum of three concentrations of calibration standards in triplicate at concentrations that will bracket the applicable cutoff. For a cutoff of 5.2 kPa (0.75 psi), prepare nominal concentrations of 30,000, 50,000, and 70,000 ppm as propane. For a cutoff of 27.6 kPa (4.0 psi), prepare nominal concentrations of 200,000, 300,000, and 400,000 ppm as propane.

10.2.1 Use the procedures in section 11.3 to measure the FID response of each standard. Use a linear regression analysis to calculate the values for the slope (k) and the y-intercept (b). Use the procedures in sections 12.3 and 12.2 to test the calibration and the linearity.

10.3 Daily FID Calibration Check. Check the calibration at the beginning and at the end of the daily runs by using the following procedures. Prepare 2 calibration standards at the nominal cutoff concentration using the procedures in section 10.2. Place one at the beginning and one at the end of the daily run. Measure the FID response of the daily calibration standard and use the values for k and b from the most recent calibration to calculate the concentration of the daily standard. Use an equation similar to 25E–2 to calculate the percent difference between the daily standard and C_s. If the difference is within 5 percent, then the previous values for k and b can be used. Otherwise, use the procedures in section 10.2 to recalibrate the FID.

11.0 Analytical Procedures

11.1 Allow one hour for the headspace vials to equilibrate at the temperature specified in the regulation. Allow the FID to warm up until a stable baseline is achieved on the detector.

11.2 Check the calibration of the FID daily using the procedures in section 10.3.

11.3 Follow the manufacturer's recommended procedures for the normal operation of the headspace sampler and FID.

11.4 Use the procedures in sections 12.4 and 12.5 to calculate the vapor phase organic vapor pressure in the samples.

11.5 Monitor the output of the detector to make certain that the results are being properly recorded.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

A = Measurement of the area under the response curve, counts.
b = y-intercept of the linear regression line.
C_a = Measured vapor phase organic concentration of sample, ppm as propane.
C_{ma} = Average measured vapor phase organic concentration of standard, ppm as propane.
C_m = Measured vapor phase organic concentration of standard, ppm as propane.
C_s = Calculated standard concentration, ppm as propane.
k = Slope of the linear regression line.
P_{bar} = Atmospheric pressure at analysis conditions, mm Hg (in. Hg).
P* = Organic vapor pressure in the sample, kPa (psi).
PD = Percent difference between the average measured vapor phase organic concentration (C_m) and the calculated standard concentration (C_s).
RSD = Relative standard deviation.
$\beta = 1.333 \times 10^{-7}$ kPa/[(mm Hg)(ppm)], $(4.91 \times 10^{-7}$ psi/[(in. Hg)(ppm)])

12.2 Linearity. Use the following equation to calculate the measured standard concentration for each standard vial.

$$C_m = kA + b \qquad \text{Eq. 25E-1}$$

12.2.1 Calculate the average measured standard concentration (C_{ma}) for each set of triplicate standards and use the following equation to calculate PD between C_{ma} and C_s. The instrument linearity is acceptable if the PD is within five for each standard.

$$PD = \frac{C_s - C_{ma}}{C_s} \times 100 \qquad \text{Eq. 25E-2}$$

12.3. Relative Standard Deviation (RSD). Use the following equation to calculate the RSD for each triplicate set of standards.

$$RSD = \frac{100}{C_{ma}} \sqrt{\frac{\sum (C_m - C_{ma})^2}{2}} \qquad \text{Eq. 25E-3}$$

The calibration is acceptable if the RSD is within five for each standard concentration.

12.4 Concentration of organics in the headspace. Use the following equation to calculate the concentration of vapor phase organics in each sample.

$$C_a = kA + b \qquad \text{Eq. 25E-4}$$

12.5 Vapor Pressure of Organics in the Headspace Sample. Use the following equation to calculate the vapor pressure of organics in the sample.

$$P^* = \beta P_{bar} C_a \qquad \text{Eq. 25E-5}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, Albert E., Samuel Witz, and Robert D. MacPhee. ''Determination of Solvent Vapor Concentrations by Total Combustion Analysis: a Comparison of Infared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, Massachusetts.

2. Salo, Albert E., William L. Oaks, and Robert D. MacPhee. ''Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, Colorado. June 9–13, 1974.) p. 25.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

State of Oregon Department of Environmental Quality

OAR 340-220-0160 Attachments

(3) SO_2 = %S/100 x F x 2

Where:

- SO_2 = Sulfur dioxide emissions for each quantity of fuel, tons
- %S = Percent sulfur in the fuel being burned, % (w/w).
- F = Amount of fuel burned, based on a quantity measurement, tons
- 2 = Pounds of sulfur dioxide per pound of sulfur

(4) SO_{2adj} = SO_2 x 0.97

Where:

- SO_{2adj} = Sulfur dioxide adjusted for sulfur retention (40 CFR Part 60, Appendix A, Method 19, Section 5.2)
- SO_2 = Sulfur dioxide emissions from each quantity burned (OAR 340-220-0140(3))

State of Oregon Department of Environmental Quality

OAR 340-220-0170 Verified Emission Factors Using Source Testing

(7)(b) If the correlation coefficient (R^2) is less than 0.50, the EEAF shall be:

$EEAF = 1 + SD/EF_{avg}$

Where:

- SD = Standard Deviation
- EF_{avg} = Average of the Emission Factors

8(a) If the regression analysis correlation coefficient is less than 0.50, the actual emissions shall be the average emission factor determined from at least nine test runs multiplied by the EEAF multiplied by the total production for the entire year; or

$AE = EF_{avg} \times EEAF \times P$

Where:

- AE = Actual Emissions
- EF_{avg} = Average of the Emission Factors
- EEAF = Estimated Emissions Adjustment Factor
- P = Total production for the year

(9)(a) All emissions during startup and shutdown, and emissions greater than normal shall be assumed equivalent to operation without an air pollution control device, unless accurately demonstrated by the owner or operator and approved by the Department in accordance with OAR 340-220-0170(9)(b), (9)(c), (9)(d), and (9)(e). The emission factor plus the EEAF shall be adjusted by the air pollution control device collection efficiency as follows:

Actual emission factor = (EF x EEAF)/(1 - PCDE)

Where:

- EF = Emission Factor
- EEAF = Emission Estimate Adjustment Factor

c. PCDE - Pollution Control Device Collection Efficiency Unless otherwise approved by the Department, the pollution control device collection efficiencies used in this calculation shall be:

Particulate Matter:

ESP or baghouse — 0.90

High energy wet scrubber — 0.80 Low energy wet scrubber — 0.70 Cyclonic separator — 0.50

Acid gases:

Wet or dry scrubber — 0.90 VOCs:

Incinerator — 0.98 Carbon absorber — 0.95

State of Oregon Department of Environmental Quality

OAR 340-223-0020
40 C.F.R. Part 51, Appendix Y

(xvi) Programs to encourage the voluntary removal from use and the marketplace of pre-1980 model year light-duty vehicles and pre-1980 model light-duty trucks.

[59 FR 16715, Apr. 7, 1994]

APPENDIX Y TO PART 51—GUIDELINES FOR BART DETERMINATIONS UNDER THE REGIONAL HAZE RULE

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I. INTRODUCTION AND OVERVIEW

A. What is the purpose of the guidelines?

The Clean Air Act (CAA), in sections 169A and 169B, contains requirements for the protection of visibility in 156 scenic areas across the United States. To meet the CAA's requirements, we published regulations to protect against a particular type of visibility impairment known as ''regional haze.'' The regional haze rule is found in this part at 40 CFR 51.300 through 51.309. These regulations require, in 40 CFR 51.308(e), that certain types of existing stationary sources of air pollutants install best available retrofit technology (BART). The guidelines are designed to help States and others (1) identify those sources that must comply with the BART requirement, and (2) determine the level of control technology that represents BART for each source.

B. What does the CAA require generally for improving visibility?

Section 169A of the CAA, added to the CAA by the 1977 amendments, requires States to protect and improve visibility in certain scenic areas of national importance. The scenic areas protected by section 169A are ''the mandatory Class I Federal Areas * * * where visibility is an important value.'' In these guidelines, we refer to these as ''Class I areas.'' There are 156 Class I areas, including 47 national parks (under the jurisdiction of the Department of Interior—National Park

Service), 108 wilderness areas (under the jurisdiction of the Department of the Interior—Fish and Wildlife Service or the Department of Agriculture—U.S. Forest Service), and one International Park (under the jurisdiction of the Roosevelt-Campobello International Commission). The Federal Agency with jurisdiction over a particular Class I area is referred to in the CAA as the Federal Land Manager. A complete list of the Class I areas is contained in 40 CFR 81.401 through 81.437, and you can find a map of the Class I areas at the following Internet site: *http://www.epa.gov/ttn/oarpg/t1/fr__notices/classimp.gif*.

The CAA establishes a national goal of eliminating man-made visibility impairment from all Class I areas. As part of the plan for achieving this goal, the visibility protection provisions in the CAA mandate that EPA issue regulations requiring that States adopt measures in their State implementation plans (SIPs), including long-term strategies, to provide for reasonable progress towards this national goal. The CAA also requires States to coordinate with the Federal Land Managers as they develop their strategies for addressing visibility.

C. What is the BART requirement in the CAA?

1. Under section 169A(b)(2)(A) of the CAA, States must require certain existing stationary sources to install BART. The BART provision applies to ''major stationary sources'' from 26 identified source categories which have the potential to emit 250 tons per year or more of any air pollutant. The CAA requires only sources which were put in place during a specific 15-year time interval to be subject to BART. The BART provision applies to sources that existed as of the date of the 1977 CAA amendments (that is, August 7, 1977) but which had not been in operation for more than 15 years (that is, not in operation as of August 7, 1962).

2. The CAA requires BART review when any source meeting the above description ''emits any air pollutant which may reasonably be anticipated to cause or contribute to any impairment of visibility'' in any Class I area. In identifying a level of control as BART, States are required by section 169A(g) of the CAA to consider:

(a) The costs of compliance,

(b) The energy and non-air quality environmental impacts of compliance,

(c) Any existing pollution control technology in use at the source,

(d) The remaining useful life of the source, and

(e) The degree of visibility improvement which may reasonably be anticipated from the use of BART.

3. The CAA further requires States to make BART emission limitations part of their SIPs. As with any SIP revision, States must provide an opportunity for public comment on the BART determinations, and EPA's action on any SIP revision will be subject to judicial review.

D. What types of visibility problems does EPA address in its regulations?

1. We addressed the problem of visibility in two phases. In 1980, we published regulations addressing what we termed ''reasonably attributable'' visibility impairment. Reasonably attributable visibility impairment is the result of emissions from one or a few sources that are generally located in close proximity to a specific Class I area. The regulations addressing reasonably attributable visibility impairment are published in 40 CFR 51.300 through 51.307.

2. On July 1, 1999, we amended these regulations to address the second, more common, type of visibility impairment known as ''regional haze.'' Regional haze is the result of the collective contribution of many sources over a broad region. The regional haze rule slightly modified 40 CFR 51.300 through 51.307, including the addition of a few definitions in §51.301, and added new §§51.308 and 51.309.

E. What are the BART requirements in EPA's regional haze regulations?

1. In the July 1, 1999 rulemaking, we added a BART requirement for regional haze. We amended the BART requirements in 2005. You will find the BART requirements in 40 CFR 51.308(e). Definitions of terms used in 40 CFR 51.308(e)(1) are found in 40 CFR 51.301.

2. As we discuss in detail in these guidelines, the regional haze rule codifies and clarifies the BART provisions in the CAA. The rule requires that States identify and list ''BART-eligible sources,'' that is, that States identify and list those sources that fall within the 26 source categories, were put in place during the 15-year window of time from 1962 to 1977, and have potential emissions greater than 250 tons per year. Once the State has identified the BART-eligible sources, the next step is to identify those BART-eligible sources that may ''emit any air pollutant which may reasonably be anticipated to cause or contribute to any impairment of visibility.'' Under the rule, a source which fits this description is ''subject to BART.'' For each source subject to BART, 40 CFR 51.308(e)(1)(ii)(A) requires that States identify the level of control representing BART after considering the factors set out in CAA section 169A(g), as follows:

—States must identify the best system of continuous emission control technology for each source subject to BART taking into account the technology available, the costs of compliance, the energy and non-air quality environmental impacts of compliance, any pollution control equipment in use at the source, the remaining useful

life of the source, and the degree of visibility improvement that may be expected from available control technology.

3. After a State has identified the level of control representing BART (if any), it must establish an emission limit representing BART and must ensure compliance with that requirement no later than 5 years after EPA approves the SIP. States may establish design, equipment, work practice or other operational standards when limitations on measurement technologies make emission standards infeasible.

F. What is included in the guidelines?

1. The guidelines provide a process for making BART determinations that States can use in implementing the regional haze BART requirements on a source-by-source basis, as provided in 40 CFR 51.308(e)(1). States must follow the guidelines in making BART determinations on a source-by-source basis for 750 megawatt (MW) power plants but are not required to use the process in the guidelines when making BART determinations for other types of sources.

2. The BART analysis process, and the contents of these guidelines, are as follows:

(a) *Identification of all BART-eligible sources.* Section II of these guidelines outlines a step-by-step process for identifying BART-eligible sources.

(b) *Identification of sources subject to BART.* As noted above, sources ''subject to BART'' are those BART-eligible sources which ''emit a pollutant which may reasonably be anticipated to cause or contribute to any impairment of visibility in any Class I area.'' We discuss considerations for identifying sources subject to BART in section III of the guidance.

(c) *The BART determination process.* For each source subject to BART, the next step is to conduct an analysis of emissions control alternatives. This step includes the identification of available, technically feasible retrofit technologies, and for each technology identified, an analysis of the cost of compliance, the energy and non-air quality environmental impacts, and the degree of visibility improvement in affected Class I areas resulting from the use of the control technology. As part of the BART analysis, the State should also take into account the remaining useful life of the source and any existing control technology present at the source. For each source, the State will determine a ''best system of continuous emission reduction'' based upon its evaluation of these factors. Procedures for the BART determination step are described in section IV of these guidelines.

(d) *Emissions limits.* States must establish emission limits, including a deadline for compliance, consistent with the BART determination process for each source subject to BART. Considerations related to these limits are discussed in section V of these guidelines.

G. Who is the target audience for the guidelines?

1. The guidelines are written primarily for the benefit of State, local and Tribal agencies, and describe a process for making the BART determinations and establishing the emission limitations that must be included in their SIPs or Tribal implementation plans (TIPs). Throughout the guidelines, which are written in a question and answer format, we ask questions ''How do I * * *?'' and answer with phrases ''you should * * *, you must * * *'' The ''you'' means a State, local or Tribal agency conducting the analysis. We have used this format to make the guidelines simpler to understand, but we recognize that States have the authority to require source owners to assume part of the analytical burden, and that there will be differences in how the supporting information is collected and documented. We also recognize that data collection, analysis, and rule development may be performed by Regional Planning Organizations, for adoption within each SIP or TIP.

2. The preamble to the 1999 regional haze rule discussed at length the issue of Tribal implementation of the requirements to submit a plan to address visibility. As explained there, requirements related to visibility are among the programs for which Tribes may be determined eligible and receive authorization to implement under the ''Tribal Authority Rule'' (''TAR'') (40 CFR 49.1 through 49.11). Tribes are not subject to the deadlines for submitting visibility implementation plans and may use a modular approach to CAA implementation. We believe there are very few BART-eligible sources located on Tribal lands. Where such sources exist, the affected Tribe may apply for delegation of implementation authority for this rule, following the process set forth in the TAR.

H. Do EPA regulations require the use of these guidelines?

Section 169A(b) requires us to issue guidelines for States to follow in establishing BART emission limitations for fossil-fuel fired power plants having a capacity in excess of 750 megawatts. This document fulfills that requirement, which is codified in 40 CFR 51.308(e)(1)(ii)(B). The guidelines establish an approach to implementing the requirements of the BART provisions of the regional haze rule; we believe that these procedures and the discussion of the requirements of the regional haze rule and the CAA should be useful to the States. For sources other than 750 MW power plants, however, States retain the discretion to adopt approaches that differ from the guidelines.

II. How To Identify BART-Eligible Sources

This section provides guidelines on how to identify BART-eligible sources. A BART-eligible source is an existing stationary source in any of 26 listed categories which meets criteria for startup dates and potential emissions.

A. What are the steps in identifying BART-eligible sources?

Figure 1 shows the steps for identifying whether the source is a ''BART-eligible source:''

Step 1: Identify the emission units in the BART categories,

Step 2: Identify the start-up dates of those emission units, and

Step 3: Compare the potential emissions to the 250 ton/yr cutoff.

Figure 1. How to determine whether a source is BART-eligible:

Step 1: Identify emission units in the BART categories

Does the plant contain emissions units in one or more of the 26 source categories?
➜ No ➜ Stop
➜ Yes ➜ Proceed to Step 2

Step 2: Identify the start-up dates of these emission units

Do any of these emissions units meet the following two tests?
In existence on August 7, 1977
AND
Began operation after August 7, 1962
➜ No ➜ Stop
➜ Yes ➜ Proceed to Step 3

Step 3: Compare the potential emissions from these emission units to the 250 ton/yr cutoff

Identify the ''stationary source'' that includes the emission units you identified in Step 2.

Add the current potential emissions from all the emission units identified in Steps 1 and 2 that are included within the ''stationary source'' boundary.

Are the potential emissions from these units 250 tons per year or more for any visibility-impairing pollutant?
➜ No ➜ Stop
➜ Yes ➜ These emissions units comprise the ''BART-eligible source.''

1. Step 1: Identify Emission Units in the BART Categories

1. The BART requirement only applies to sources in specific categories listed in the CAA. The BART requirement does not apply to sources in other source categories, regardless of their emissions. The listed categories are:

(1) Fossil-fuel fired steam electric plants of more than 250 million British thermal units (BTU) per hour heat input,

(2) Coal cleaning plants (thermal dryers),

(3) Kraft pulp mills,

(4) Portland cement plants,

(5) Primary zinc smelters,

(6) Iron and steel mill plants,

(7) Primary aluminum ore reduction plants,

(8) Primary copper smelters,

(9) Municipal incinerators capable of charging more than 250 tons of refuse per day,

(10) Hydrofluoric, sulfuric, and nitric acid plants,

(11) Petroleum refineries,

(12) Lime plants,

(13) Phosphate rock processing plants,

(14) Coke oven batteries,

(15) Sulfur recovery plants,

(16) Carbon black plants (furnace process),

(17) Primary lead smelters,

(18) Fuel conversion plants,

(19) Sintering plants,

(20) Secondary metal production facilities,

(21) Chemical process plants,

(22) Fossil-fuel boilers of more than 250 million BTUs per hour heat input,

(23) Petroleum storage and transfer facilities with a capacity exceeding 300,000 barrels,

(24) Taconite ore processing facilities,

(25) Glass fiber processing plants, and

(26) Charcoal production facilities.

2. Some plants may have emission units from more than one category, and some emitting equipment may fit into more than one category. Examples of this situation are sulfur recovery plants at petroleum refineries, coke oven batteries and sintering plants at steel mills, and chemical process plants at refineries. For Step 1, you identify all of the emissions units at the plant that fit into one or more of the listed categories. You do not identify emission units in other categories.

Example: A mine is collocated with an electric steam generating plant and a coal cleaning plant. You would identify emission units associated with the electric steam generating plant and the coal cleaning plant, because they are listed categories, but not the mine, because coal mining is not a listed category.

3. The category titles are generally clear in describing the types of equipment to be listed. Most of the category titles are very broad descriptions that encompass all emission units associated with a plant site (for example, ''petroleum refining'' and ''kraft pulp mills''). This same list of categories appears in the PSD regulations. States and source owners need not revisit any interpretations of the list made previously for purposes of the PSD program. We provide the following clarifications for a few of the category titles:

(1) ''*Steam electric plants of more than 250 million BTU/hr heat input.*'' Because the category refers to ''plants,'' we interpret this

category title to mean that boiler capacities should be aggregated to determine whether the 250 million BTU/hr threshold is reached. This definition includes only those plants that generate electricity for sale. Plants that cogenerate steam and electricity also fall within the definition of ''steam electric plants''. Similarly, combined cycle turbines are also considered ''steam electric plants'' because such facilities incorporate heat recovery steam generators. Simple cycle turbines, in contrast, are not ''steam electric plants'' because these turbines typically do not generate steam.

Example: A stationary source includes a steam electric plant with three 100 million BTU/hr boilers. Because the aggregate capacity exceeds 250 million BTU/hr for the ''plant,'' these boilers would be identified in Step 2.

(2) ''*Fossil-fuel boilers of more than 250 million BTU/hr heat input.*'' We interpret this category title to cover only those boilers that are individually greater than 250 million BTU/hr. However, an individual boiler smaller than 250 million BTU/hr should be subject to BART if it is an integral part of a process description at a plant that is in a different BART category—for example, a boiler at a Kraft pulp mill that, in addition to providing steam or mechanical power, uses the waste liquor from the process as a fuel. In general, if the process uses any by-product of the boiler and the boiler's function is to serve the process, then the boiler is integral to the process and should be considered to be part of the process description.

Also, you should consider a multi-fuel boiler to be a ''fossil-fuel boiler'' if it burns any amount of fossil fuel. You may take federally and State enforceable operational limits into account in determining whether a multi-fuel boiler's fossil fuel capacity exceeds 250 million Btu/hr.

(3) ''*Petroleum storage and transfer facilities with a capacity exceeding 300,000 barrels.*'' The 300,000 barrel cutoff refers to total facility-wide tank capacity for tanks that were put in place within the 1962–1977 time period, and includes gasoline and other petroleum-derived liquids.

(4) ''*Phosphate rock processing plants.*'' This category descriptor is broad, and includes all types of phosphate rock processing facilities, including elemental phosphorous plants as well as fertilizer production plants.

(5) ''*Charcoal production facilities.*'' We interpret this category to include charcoal briquet manufacturing and activated carbon production.

(6) ''*Chemical process plants.*'' and pharmaceutical manufacturing. Consistent with past policy, we interpret the category ''chemical process plants'' to include those facilities within the 2-digit Standard Industrial Classification (SIC) code 28. Accordingly, we interpret the term ''chemical process plants'' to include pharmaceutical manufacturing facilities.

(7) ''*Secondary metal production.*'' We interpret this category to include nonferrous metal facilities included within SIC code 3341, and secondary ferrous metal facilities that we also consider to be included within the category ''iron and steel mill plants.''

(8) ''*Primary aluminum ore reduction.*'' We interpret this category to include those facilities covered by 40 CFR 60.190, the new source performance standard (NSPS) for primary aluminum ore reduction plants. This definition is also consistent with the definition at 40 CFR 63.840.

2. Step 2: Identify the Start-Up Dates of the Emission Units

1. Emissions units listed under Step 1 are BART-eligible only if they were ''in existence'' on August 7, 1977 but were not ''in operation'' before August 7, 1962.

What does ''in existence on August 7, 1977'' mean?

2. The regional haze rule defines ''in existence'' to mean that:

''the owner or operator has obtained all necessary preconstruction approvals or permits required by Federal, State, or local air pollution emissions and air quality laws or regulations and either has (1) begun, or caused to begin, a continuous program of physical on-site construction of the facility or (2) entered into binding agreements or contractual obligations, which cannot be canceled or modified without substantial loss to the owner or operator, to undertake a program of construction of the facility to be completed in a reasonable time.'' 40 CFR 51.301.

As this definition is essentially identical to the definition of ''commence construction'' as that term is used in the PSD regulations, the two terms mean the same thing. *See* 40 CFR 51.165(a)(1)(xvi) and 40 CFR 52.21(b)(9). Under this definition, an emissions unit could be ''in existence'' even if it did not begin operating until several years after 1977.

Example: The owner of a source obtained all necessary permits in early 1977 and entered into binding construction agreements in June 1977. Actual on-site construction began in late 1978, and construction was completed in mid-1979. The source began operating in September 1979. The emissions unit was ''in existence'' as of August 7, 1977.

Major stationary sources which commenced construction AFTER August 7, 1977 (*i.e.*, major stationary sources which were not ''in existence'' on August 7, 1977) were subject to new source review (NSR) under the PSD program. Thus, the August 7, 1977 ''in existence'' test is essentially the same

thing as the identification of emissions units that were grandfathered from the NSR review requirements of the 1977 CAA amendments.

3. Sources are not BART-eligible if the only change at the plant during the relevant time period was the addition of pollution controls. For example, if the only change at a copper smelter during the 1962 through 1977 time period was the addition of acid plants for the reduction of SO_2 emissions, these emission controls would not by themselves trigger a BART review.

What does ''in operation before August 7, 1962'' mean?

An emissions unit that meets the August 7, 1977 ''in existence'' test is not BART-eligible if it was in operation before August 7, 1962. ''In operation'' is defined as ''engaged in activity related to the primary design function of the source.'' This means that a source must have begun actual operations by August 7, 1962 to satisfy this test.

Example: The owner or operator entered into binding agreements in 1960. Actual onsite construction began in 1961, and construction was complete in mid-1962. The source began operating in September 1962. The emissions unit *was not* ''in operation'' before August 7, 1962 and is therefore subject to BART.

What is a ''reconstructed source?'

1. Under a number of CAA programs, an existing source which is completely or substantially rebuilt is treated as a new source. Such ''reconstructed'' sources are treated as new sources as of the time of the reconstruction. Consistent with this overall approach to reconstructions, the definition of BART-eligible facility (reflected in detail in the definition of ''existing stationary facility'') includes consideration of sources that were in operation before August 7, 1962, but were reconstructed during the August 7, 1962 to August 7, 1977 time period.

2. Under the regional haze regulations at 40 CFR 51.301, a reconstruction has taken place if ''the fixed capital cost of the new component exceeds 50 percent of the fixed capital cost of a comparable entirely new source.'' The rule also states that ''[a]ny final decision as to whether reconstruction has occurred must be made in accordance with the provisions of §§ 60.15 (f)(1) through (3) of this title.'' ''[T]he provisions of §§ 60.15(f)(1) through (3)'' refers to the general provisions for New Source Performance Standards (NSPS). Thus, the same policies and procedures for identifying reconstructed ''affected facilities'' under the NSPS program must also be used to identify reconstructed ''stationary sources'' for purposes of the BART requirement.

3. You should identify reconstructions on an emissions unit basis, rather than on a plantwide basis. That is, you need to identify only the reconstructed emission units meeting the 50 percent cost criterion. You should include reconstructed emission units in the list of emission units you identified in Step 1. You need consider as possible reconstructions only those emissions units with the potential to emit more than 250 tons per year of any visibility-impairing pollutant.

4. The ''in operation'' and ''in existence'' tests apply to reconstructed sources. If an emissions unit was reconstructed and began actual operation before August 7, 1962, it is not BART-eligible. Similarly, any emissions unit for which a reconstruction ''commenced'' after August 7, 1977, is not BART-eligible.

How are modifications treated under the BART provision?

1. The NSPS program and the major source NSR program both contain the concept of modifications. In general, the term ''modification'' refers to any physical change or change in the method of operation of an emissions unit that results in an increase in emissions.

2. The BART provision in the regional haze rule contains no explicit treatment of modifications or how modified emissions units, previously subject to the requirement to install best available control technology (BACT), lowest achievable emission rate (LAER) controls, and/or NSPS are treated under the rule. As the BART requirements in the CAA do not appear to provide any exemption for sources which have been modified since 1977, the best interpretation of the CAA visibility provisions is that a subsequent modification does not change a unit's construction date for the purpose of BART applicability. Accordingly, if an emissions unit began operation before 1962, it is not BART-eligible if it was modified between 1962 and 1977, so long as the modification is not also a ''reconstruction.'' On the other hand, an emissions unit which began operation within the 1962–1977 time window, but was modified after August 7, 1977, is BART-eligible. We note, however, that if such a modification was a major modification that resulted in the installation of controls, the State will take this into account during the review process and may find that the level of controls already in place are consistent with BART.

3. Step 3: Compare the Potential Emissions to the 250 Ton/Yr Cutoff

The result of Steps 1 and 2 will be a list of emissions units at a given plant site, including reconstructed emissions units, that are within one or more of the BART categories and that were placed into operation within

the 1962–1977 time window. The third step is to determine whether the total emissions represent a current potential to emit that is greater than 250 tons per year of any single visibility impairing pollutant. Fugitive emissions, to the extent quantifiable, must be counted. In most cases, you will add the potential emissions from all emission units on the list resulting from Steps 1 and 2. In a few cases, you may need to determine whether the plant contains more than one ''stationary source'' as the regional haze rule defines that term, and as we explain further below.

What pollutants should I address?

Visibility-impairing pollutants include the following:

(1) Sulfur dioxide (SO_2),

(2) Nitrogen oxides (NO_X), and

(3) Particulate matter.

You may use PM_{10} as an indicator for particulate matter in this intial step. [Note that we do not recommend use of total suspended particulates (TSP) as in indicator for particulate matter.] As emissions of PM_{10} include the components of $PM_{2.5}$ as a subset, there is no need to have separate 250 ton thresholds for PM_{10} and $PM_{2.5}$; 250 tons of PM_{10} represents at most 250 tons of $PM_{2.5}$, and at most 250 tons of any individual particulate species such as elemental carbon, crustal material, etc.

However, if you determine that a source of particulate matter is BART-eligible, it will be important to distinguish between the fine and coarse particle components of direct particulate emissions in the remainder of the BART analysis, including for the purpose of modeling the source's impact on visibility. This is because although both fine and coarse particulate matter contribute to visibility impairment, the long-range transport of fine particles is of particular concern in the formation of regional haze. Thus, for example, air quality modeling results used in the BART determination will provide a more accurate prediction of a source's impact on visibility if the inputs into the model account for the relative particle size of any directly emitted particulate matter (*i.e.* PM_{10} vs. $PM_{2.5}$).

You should exercise judgment in deciding whether the following pollutants impair visibility in an area:

(4) Volatile organic compounds (VOC), and

(5) Ammonia and ammonia compounds.

You should use your best judgment in deciding whether VOC or ammonia emissions from a source are likely to have an impact on visibility in an area. Certain types of VOC emissions, for example, are more likely to form secondary organic aerosols than others.[1] Similarly, controlling ammonia emissions in some areas may not have a significant impact on visibility. You need not provide a formal showing of an individual decision that a source of VOC or ammonia emissions is not subject to BART review. Because air quality modeling may not be feasible for individual sources of VOC or ammonia, you should also exercise your judgement in assessing the degree of visibility impacts due to emissions of VOC and emissions of ammonia or ammonia compounds. You should fully document the basis for judging that a VOC or ammonia source merits BART review, including your assessment of the source's contribution to visibility impairment.

What does the term ''potential'' emissions mean?

The regional haze rule defines potential to emit as follows:

''Potential to emit'' means the maximum capacity of a stationary source to emit a pollutant under its physical and operational design. Any physical or operational limitation on the capacity of the source to emit a pollutant including air pollution control equipment and restrictions on hours of operation or on the type or amount of material combusted, stored, or processed, shall be treated as part of its design if the limitation or the effect it would have on emissions is federally enforceable. Secondary emissions do not count in determining the potential to emit of a stationary source.

The definition of ''potential to emit'' means that a source which actually emits less than 250 tons per year of a visibility-impairing pollutant is BART-eligible if its emissions would exceed 250 tons per year when operating at its maximum capacity given its physical and operational design (and considering all federally enforceable and State enforceable permit limits.)

Example: A source, while operating at one-fourth of its capacity, emits 75 tons per year of SO_2. If it were operating at 100 percent of its maximum capacity, the source would emit 300 tons per year. Because under the above definition such a source would have ''potential'' emissions that exceed 250 tons per year, the source (if in a listed category and built during the 1962–1977 time window) would be BART-eligible.

How do I identify whether a plant has more than one ''stationary source?''

1. The regional haze rule, in 40 CFR 51.301, defines a stationary source as a ''building, structure, facility or installation which

[1] *Fine particles: Overview of Atmospheric Chemistry, Sources of Emissions, and Ambient Monitoring Data,* Memorandum to Docket OAR 2002–006, April 1, 2005.

emits or may emit any air pollutant.''[2] The rule further defines ''building, structure or facility'' as:

all of the pollutant-emitting activities which belong to the same industrial grouping, are located on one or more contiguous or adjacent properties, and are under the control of the same person (or persons under common control). Pollutant-emitting activities must be considered as part of the same industrial grouping if they belong to the same Major Group (*i.e.*, which have the same two-digit code) as described in the Standard Industrial Classification Manual, 1972 as amended by the 1977 Supplement (U.S. Government Printing Office stock numbers 4101–0066 and 003–005–00176–0, respectively).

2. In applying this definition, it is necessary to determine which facilities are located on ''contiguous or adjacent properties.'' Within this contiguous and adjacent area, it is also necessary to group those emission units that are under ''common control.'' We note that these plant boundary issues and ''common control'' issues are very similar to those already addressed in implementation of the title V operating permits program and in NSR.

3. For emission units within the ''contiguous or adjacent'' boundary and under common control, you must group emission units that are within the same industrial grouping (that is, associated with the same 2-digit SIC code) in order to define the stationary source.[3] For most plants on the BART source category list, there will only be one 2-digit SIC that applies to the entire plant. For example, all emission units associated with kraft pulp mills are within SIC code 26, and chemical process plants will generally include emission units that are all within SIC code 28. The ''2-digit SIC test'' applies in the same way as the test is applied in the major source NSR programs.[4]

4. For purposes of the regional haze rule, you must group emissions from all emission units put in place within the 1962–1977 time period that are within the 2-digit SIC code, even if those emission units are in different categories on the BART category list.

Examples: A chemical plant which started operations within the 1962 to 1977 time period manufactures hydrochloric acid (within the category title ''Hydrochloric, sulfuric, and nitric acid plants'') and various organic chemicals (within the category title ''chemical process plants''). All of the emission units are within SIC code 28 and, therefore, all the emission units are considered in determining BART eligibility of the plant. You sum the emissions over all of these emission units to see whether there are more than 250 tons per year of potential emissions.

A steel mill which started operations within the 1962 to 1977 time period includes a sintering plant, a coke oven battery, and various other emission units. All of the emission units are within SIC code 33. You sum the emissions over all of these emission units to see whether there are more than 250 tons per year of potential emissions.

4. Final Step: Identify the Emissions Units and Pollutants That Constitute the BART-Eligible Source

If the emissions from the list of emissions units at a stationary source exceed a potential to emit of 250 tons per year for any visibility-impairing pollutant, then that collection of emissions units is a BART-eligible source.

Example: A stationary source comprises the following two emissions units, with the following potential emissions:

Emissions unit A
200 tons/yr SO_2
150 tons/yr NO_X
25 tons/yr PM
Emissions unit B
100 tons/yr SO_2
75 tons/yr NO_X
10 tons/yr PM

For this example, potential emissions of SO_2 are 300 tons/yr, which exceeds the 250 tons/yr threshold. Accordingly, the entire ''stationary source'', that is, emissions units A and B, may be subject to a BART review for SO_2, NO_X, and PM, even though the potential emissions of PM and NO_X at each emissions unit are less than 250 tons/yr each.

Example: The total potential emissions, obtained by adding the potential emissions of

[2] NOTE: Most of these terms and definitions are the same for regional haze and the 1980 visibility regulations. For the regional haze rule we use the term ''BART-eligible source'' rather than ''existing stationary facility'' to clarify that only a limited subset of existing stationary sources are subject to BART.

[3] We recognize that we are in a transition period from the use of the SIC system to a new system called the North American Industry Classification System (NAICS). For purposes of identifying BART-eligible sources, you may use either 2-digit SICS or the equivalent in the NAICS system.

[4] NOTE: The concept of support facility used for the NSR program applies here as well. Support facilities, that is facilities that convey, store or otherwise assist in the production of the principal product, must be grouped with primary facilities even when the facilities fall wihin separate SIC codes. For purposes of BART reviews, however, such support facilities (a) must be within one of the 26 listed source categories and (b) must have been in existence as of August 7, 1977, and (c) must not have been in operation as of August 7, 1962.

all emission units in a listed category at a plant site, are as follows:

200 tons/yr SO_2
150 tons/yr NO_X
25 tons/yr PM

Even though total emissions exceed 250 tons/yr, no individual regulated pollutant exceeds 250 tons/yr and this source is not BART-eligible.

Can States establish de minimis levels of emissions for pollutants at BART-eligible sources?

In order to simplify BART determinations, States may choose to identify de minimis levels of pollutants at BART-eligible sources (but are not required to do so). De minimis values should be identified with the purpose of excluding only those emissions so minimal that they are unlikely to contribute to regional haze. Any de minimis values that you adopt must not be higher than the PSD applicability levels: 40 tons/yr for SO_2 and NO_X and 15 tons/yr for PM_{10}. These de minimis levels may only be applied on a plant-wide basis.

III. How To Identify Sources ''Subject to BART''

Once you have compiled your list of BART-eligible sources, you need to determine whether (1) to make BART determinations for all of them or (2) to consider exempting some of them from BART because they may not reasonably be anticipated to cause or contribute to any visibility impairment in a Class I area. If you decide to make BART determinations for all the BART-eligible sources on your list, you should work with your regional planning organization (RPO) to show that, collectively, they cause or contribute to visibility impairment in at least one Class I area. You should then make individual BART determinations by applying the five statutory factors discussed in Section IV below.

On the other hand, you also may choose to perform an initial examination to determine whether a particular BART-eligible source or group of sources causes or contributes to visibility impairment in nearby Class I areas. If your analysis, or information submitted by the source, shows that an individual source or group of sources (or certain pollutants from those sources) is not reasonably anticipated to cause or contribute to any visibility impairment in a Class I area, then you do not need to make BART determinations for that source or group of sources (or for certain pollutants from those sources). In such a case, the source is not ''subject to BART'' and you do not need to apply the five statutory factors to make a BART determination. This section of the Guideline discusses several approaches that you can use to exempt sources from the BART determination process.

A. What Steps Do I Follow To Determine Whether a Source or Group of Sources Cause or Contribute to Visibility Impairment for Purposes of BART?

1. How Do I Establish a Threshold?

One of the first steps in determining whether sources cause or contribute to visibility impairment for purposes of BART is to establish a threshold (measured in deciviews) against which to measure the visibility impact of one or more sources. A single source that is responsible for a 1.0 deciview change or more should be considered to ''cause'' visibility impairment; a source that causes less than a 1.0 deciview change may still contribute to visibility impairment and thus be subject to BART.

Because of varying circumstances affecting different Class I areas, the appropriate threshold for determining whether a source ''contributes to any visibility impairment'' for the purposes of BART may reasonably differ across States. As a general matter, any threshold that you use for determining whether a source ''contributes'' to visibility impairment should not be higher than 0.5 deciviews.

In setting a threshold for ''contribution,'' you should consider the number of emissions sources affecting the Class I areas at issue and the magnitude of the individual sources' impacts.[5] In general, a larger number of sources causing impacts in a Class I area may warrant a lower contribution threshold. States remain free to use a threshold lower than 0.5 deciviews if they conclude that the location of a large number of BART-eligible sources within the State and in proximity to a Class I area justify this approach.[6]

2. What Pollutants Do I Need To Consider?

You must look at SO_2, NO_X, and direct particulate matter (PM) emissions in determining whether sources cause or contribute to visibility impairment, including both PM_{10} and $PM_{2.5}$. Consistent with the approach for identifying your BART-eligible sources, you do not need to consider less

[5] We expect that regional planning organizations will have modeling information that identifies sources affecting visibility in individual class I areas.

[6] Note that the contribution threshold should be used to determine whether an individual source is reasonably anticipated to contribute to visibility impairment. You should not aggregate the visibility effects of multiple sources and compare their collective effects against your contribution threshold because this would inappropriately create a ''contribute to contribution'' test.

than de minimis emissions of these pollutants from a source.

As explained in section II, you must use your best judgement to determine whether VOC or ammonia emissions are likely to have an impact on visibility in an area. In addition, although as explained in Section II, you may use PM_{10} an indicator for particulate matter in determining whether a source is BART-eligible, in determining whether a source contributes to visibility impairment, you should distinguish between the fine and coarse particle components of direct particulate emissions. Although both fine and coarse particulate matter contribute to visibility impairment, the long-range transport of fine particles is of particular concern in the formation of regional haze. Air quality modeling results used in the BART determination will provide a more accurate prediction of a source's impact on visibility if the inputs into the model account for the relative particle size of any directly emitted particulate matter (*i.e.*, PM_{10} vs. $PM_{2.5}$).

3. What Kind of Modeling Should I Use To Determine Which Sources and Pollutants Need Not Be Subject to BART?

This section presents several options for determining that certain sources need not be subject to BART. These options rely on different modeling and/or emissions analysis approaches. They are provided for your guidance. You may also use other reasonable approaches for analyzing the visibility impacts of an individual source or group of sources.

Option 1: Individual Source Attribution Approach (Dispersion Modeling)

You can use dispersion modeling to determine that an individual source cannot reasonably be anticipated to cause or contribute to visibility impairment in a Class I area and thus is not subject to BART. Under this option, you can analyze an individual source's impact on visibility as a result of its emissions of SO_2, NO_X and direct PM emissions. Dispersion modeling cannot currently be used to estimate the predicted impacts on visibility from an individual source's emissions of VOC or ammonia. You may use a more qualitative assessment to determine on a case-by-case basis which sources of VOC or ammonia emissions may be likely to impair visibility and should therefore be subject to BART review, as explained in section II.A.3. above.

You can use CALPUFF[7] or other appropriate model to predict the visibility impacts from a single source at a Class I area. CALPUFF is the best regulatory modeling application currently available for predicting a single source's contribution to visibility impairment and is currently the only EPA-approved model for use in estimating single source pollutant concentrations resulting from the long range transport of primary pollutants.[8] It can also be used for some other purposes, such as the visibility assessments addressed in today's rule, to account for the chemical transformation of SO_2 and NO_X.

There are several steps for making an individual source attribution using a dispersion model:

1. *Develop a modeling protocol.* Some critical items to include in the protocol are the meteorological and terrain data that will be used, as well as the source-specific information (stack height, temperature, exit velocity, elevation, and emission rates of applicable pollutants) and receptor data from appropriate Class I areas. We recommend following EPA's *Interagency Workgroup on Air Quality Modeling (IWAQM) Phase 2 Summary Report and Recommendations for Modeling Long Range Transport Impacts*[9] for parameter settings and meteorological data inputs. You may use other settings from those in IWAQM, but you should identify these settings and explain your selection of these settings.

One important element of the protocol is in establishing the receptors that will be used in the model. The receptors that you use should be located in the nearest Class I area with sufficient density to identify the likely visibility effects of the source. For other Class I areas in relatively close proximity to a BART-eligible source, you may model a few strategic receptors to determine whether effects at those areas may be greater than at the nearest Class I area. For example, you might chose to locate receptors at these areas at the closest point to the source, at the highest and lowest elevation in the Class I area, at the IMPROVE monitor, and at the approximate expected plume release height. If the highest modeled effects are observed at the nearest Class I area, you may choose not to analyze the other Class I areas any further as additional analyses might be unwarranted.

[7] The model code and its documentation are available at no cost for download from *http://www.epa.gov/scram001/tt22.htm#calpuff*.

[8] The Guideline on Air Quality Models, 40 CFR part 51, appendix W, addresses the regulatory application of air quality models for assessing criteria pollutants under the CAA, and describes further the procedures for using the CALPUFF model, as well as for obtaining approval for the use of other, non-guideline models.

[9] *Interagency Workgroup on Air Quality Modeling (IWAQM) Phase 2 Summary Report and Recommendations for Modeling Long Range Transport Impacts*, U.S. Environmental Protection Agency, EPA–454/R–98–019, December 1998.

You should bear in mind that some receptors within the relevant Class I area may be less than 50 km from the source while other receptors within that same Class I area may be greater than 50 km from the same source. As indicated by the Guideline on Air Quality Models, 40 CFR part 51, appendix W, this situation may call for the use of two different modeling approaches for the same Class I area and source, depending upon the State's chosen method for modeling sources less than 50 km. In situations where you are assessing visibility impacts for source-receptor distances less than 50 km, you should use expert modeling judgment in determining visibility impacts, giving consideration to both CALPUFF and other appropriate methods.

In developing your modeling protocol, you may want to consult with EPA and your regional planning organization (RPO). Up-front consultation will ensure that key technical issues are addressed before you conduct your modeling.

2. *With the accepted protocol and compare the predicted visibility impacts with your threshold for ''contribution.''* You should calculate daily visibility values for each receptor as the change in deciviews compared against natural visibility conditions. You can use EPA's ''Guidance for Estimating Natural Visibility Conditions Under the Regional Haze Rule,'' EPA–454/B–03–005 (September 2003) in making this calculation. To determine whether a source may reasonably be anticipated to cause or contribute to visibility impairment at Class I area, you then compare the impacts predicted by the model against the threshold that you have selected.

The emissions estimates used in the models are intended to reflect steady-state operating conditions during periods of high capacity utilization. We do not generally recommend that emissions reflecting periods of start-up, shutdown, and malfunction be used, as such emission rates could produce higher than normal effects than would be typical of most facilities. We recommend that States use the 24 hour average actual emission rate from the highest emitting day of the meteorological period modeled, unless this rate reflects periods start-up, shutdown, or malfunction. In addition, the monthly average relative humidity is used, rather than the daily average humidity—an approach that effectively lowers the peak values in daily model averages.

For these reasons, if you use the modeling approach we recommend, you should compare your ''contribution'' threshold against the 98th percentile of values. If the 98th percentile value from your modeling is less than your contribution threshold, then you may conclude that the source does not contribute to visibility impairment and is not subject to BART.

Option 2: Use of Model Plants To Exempt Individual Sources With Common Characteristics

Under this option, analyses of model plants could be used to exempt certain BART-eligible sources that share specific characteristics. It may be most useful to use this type of analysis to identify the types of small sources that do not cause or contribute to visibility impairment for purposes of BART, and thus should not be subject to a BART review. Different Class I areas may have different characteristics, however, so you should use care to ensure that the criteria you develop are appropriate for the applicable cases.

In carrying out this approach, you could use modeling analyses of representative plants to reflect groupings of specific sources with important common characteristics. Based on these analyses, you may find that certain types of sources are clearly anticipated to cause or contribute to visibility impairment. You could then choose to categorically require those types of sources to undergo a BART determination. Conversely, you may find based on representative plant analyses that certain types of sources are not reasonably anticipated to cause or contribute to visibility impairment. To do this, you may conduct your own modeling to establish emission levels and distances from Class I areas on which you can rely to exempt sources with those characteristics. For example, based on your modeling you might choose to exempt all NO_X-only sources that emit less than a certain amount per year and are located a certain distance from a Class I area. You could then choose to categorically exempt such sources from the BART determination process.

Our analyses of visibility impacts from model plants provide a useful example of the type of analyses that can be used to exempt categories of sources from BART.[10] In our analyses, we developed model plants (EGUs and non-EGUs), with representative plume and stack characteristics, for use in considering the visibility impact from emission sources of different sizes and compositions at distances of 50, 100 and 200 kilometers from two hypothetical Class I areas (one in the East and one in the West). As the plume and stack characteristics of these model plants were developed considering the broad range of sources within the EGU and non-EGU categories, they do not necessarily represent any specific plant. However, the results of these analyses are instructive in the development of an exemption process for any Class I area.

[10] CALPUFF Analysis in Support of the June 2005 Changes to the Regional Haze Rule, U.S. Environmental Protection Agency, June 15, 2005, Docket No. OAR–2002–0076.

In preparing our analyses, we have made a number of assumptions and exercised certain modeling choices; some of these have a tendency to lend conservatism to the results, overstating the likely effects, while others may understate the likely effects. On balance, when all of these factors are considered, we believe that our examples reflect realistic treatments of the situations being modeled. Based on our analyses, we believe that a State that has established 0.5 deciviews as a contribution threshold could reasonably exempt from the BART review process sources that emit less than 500 tons per year of NO_X or SO_2 (or combined NO_X and SO_2), as long as these sources are located more than 50 kilometers from any Class I area; and sources that emit less than 1000 tons per year of NO_X or SO_2 (or combined NO_X and SO_2) that are located more than 100 kilometers from any Class I area. You do, however, have the option of showing other thresholds might also be appropriate given your specific circumstances.

Option 3: Cumulative Modeling To Show That No Sources in a State Are Subject to BART

You may also submit to EPA a demonstration based on an analysis of overall visibility impacts that emissions from BART-eligible sources in your State, considered together, are not reasonably anticipated to cause or contribute to any visibility impairment in a Class I area, and thus no source should be subject to BART. You may do this on a pollutant by pollutant basis or for all visibility-impairing pollutants to determine if emissions from these sources contribute to visibility impairment.

For example, emissions of SO_2 from your BART-eligible sources may clearly cause or contribute to visibility impairment while direct emissions of $PM_{2.5}$ from these sources may not contribute to impairment. If you can make such a demonstration, then you may reasonably conclude that none of your BART-eligible sources are subject to BART for a particular pollutant or pollutants. As noted above, your demonstration should take into account the interactions among pollutants and their resulting impacts on visibility before making any pollutant-specific determinations.

Analyses may be conducted using several alternative modeling approaches. First, you may use the CALPUFF or other appropriate model as described in Option 1 to evaluate the impacts of individual sources on downwind Class I areas, aggregating those impacts to determine the collective contribution of all BART-eligible sources to visibility impairment. You may also use a photochemical grid model. As a general matter, the larger the number of sources being modeled, the more appropriate it may be to use a photochemical grid model. However, because such models are significantly less sensitive than dispersion models to the contributions of one or a few sources, as well as to the interactions among sources that are widely distributed geographically, if you wish to use a grid model, you should consult with the appropriate EPA Regional Office to develop an appropriate modeling protocol.

IV. The BART Determination: Analysis of BART Options

This section describes the process for the analysis of control options for sources subject to BART.

A. What factors must I address in the BART review?

The visibility regulations define BART as follows:

Best Available Retrofit Technology (BART) means an emission limitation based on the degree of reduction achievable through the application of the best system of continuous emission reduction for each pollutant which is emitted by . . . [a BART-eligible source]. The emission limitation must be established, on a case-by-case basis, taking into consideration the technology available, the costs of compliance, the energy and non-air quality environmental impacts of compliance, any pollution control equipment in use or in existence at the source, the remaining useful life of the source, and the degree of improvement in visibility which may reasonably be anticipated to result from the use of such technology.

The BART analysis identifies the best system of continuous emission reduction taking into account:

(1) The available retrofit control options,

(2) Any pollution control equipment in use at the source (which affects the availability of options and their impacts),

(3) The costs of compliance with control options,

(4) The remaining useful life of the facility,

(5) The energy and non-air quality environmental impacts of control options

(6) The visibility impacts analysis.

B. What is the scope of the BART review?

Once you determine that a source is subject to BART for a particular pollutant, then for each affected emission unit, you must establish BART for that pollutant. The BART determination must address air pollution control measures for each emissions unit or pollutant emitting activity subject to review.

Example: Plantwide emissions from emission units within the listed categories that began operation within the ''time window''

for BART[11] are 300 tons/yr of NO_X, 200 tons/yr of SO_2, and 150 tons/yr of primary particulate. Emissions unit A emits 200 tons/yr of NO_X, 100 tons/yr of SO_2, and 100 tons/yr of primary particulate. Other emission units, units B through H, which began operating in 1966, contribute lesser amounts of each pollutant. For this example, a BART review is required for NO_X, SO_2, and primary particulate, and control options must be analyzed for units B through H as well as unit A.

C. How does a BART review relate to Maximum Achievable Control Technology (MACT) Standards under CAA section 112, or to other emission limitations required under the CAA?

For VOC and PM sources subject to MACT standards, States may streamline the analysis by including a discussion of the MACT controls and whether any major new technologies have been developed subsequent to the MACT standards. We believe that there are many VOC and PM sources that are well controlled because they are regulated by the MACT standards, which EPA developed under CAA section 112. For a few MACT standards, this may also be true for SO_2. Any source subject to MACT standards must meet a level that is as stringent as the best-controlled 12 percent of sources in the industry. Examples of these hazardous air pollutant sources which effectively control VOC and PM emissions include (among others) secondary lead facilities, organic chemical plants subject to the hazardous organic NESHAP (HON), pharmaceutical production facilities, and equipment leaks and wastewater operations at petroleum refineries. We believe that, in many cases, it will be unlikely that States will identify emission controls more stringent than the MACT standards without identifying control options that would cost many thousands of dollars per ton. Unless there are new technologies subsequent to the MACT standards which would lead to cost-effective increases in the level of control, you may rely on the MACT standards for purposes of BART.

We believe that the same rationale also holds true for emissions standards developed for municipal waste incinerators under CAA section 111(d), and for many NSR/PSD determinations and NSR/PSD settlement agreements. However, we do not believe that technology determinations from the 1970s or early 1980s, including new source performance standards (NSPS), should be considered to represent best control for existing sources, as best control levels for recent plant retrofits are more stringent than these older levels.

[11] That is, emission units that were in existence on August 7, 1977 and which began actual operation on or after August 7, 1962.

Where you are relying on these standards to represent a BART level of control, you should provide the public with a discussion of whether any new technologies have subsequently become available.

D. What Are the Five Basic Steps of a Case-by-Case BART Analysis?

The five steps are:

STEP 1—Identify All[12] Available Retrofit Control Technologies,

STEP 2—Eliminate Technically Infeasible Options,

STEP 3—Evaluate Control Effectiveness of Remaining Control Technologies,

STEP 4—Evaluate Impacts and Document the Results, and

STEP 5—Evaluate Visibility Impacts.

1. STEP 1: How do I identify all available retrofit emission control techniques?

1. Available retrofit control options are those air pollution control technologies with a practical potential for application to the emissions unit and the regulated pollutant under evaluation. Air pollution control technologies can include a wide variety of available methods, systems, and techniques for control of the affected pollutant. Technologies required as BACT or LAER are available for BART purposes and must be included as control alternatives. The control alternatives can include not only existing controls for the source category in question but also take into account technology transfer of controls that have been applied to similar source categories and gas streams. Technologies which have not yet been applied to (or permitted for) full scale operations need not be considered as available; we do not expect the source owner to purchase or construct a process or control device that has not already been demonstrated in practice.

2. Where a NSPS exists for a source category (which is the case for most of the categories affected by BART), you should include a level of control equivalent to the NSPS as one of the control options.[13] The

[12] In identifying ''all'' options, you must identify the most stringent option and a reasonable set of options for analysis that reflects a comprehensive list of available technologies. It is not necessary to list all permutations of available control levels that exist for a given technology—the list is complete if it includes the maximum level of control each technology is capable of achieving.

[13] In EPA's 1980 BART guidelines for reasonably attributable visibility impairment, we concluded that NSPS standards generally, at that time, represented the best level sources could install as BART. In the 20

Continued

NSPS standards are codified in 40 CFR part 60. We note that there are situations where NSPS standards do not require the most stringent level of available control for all sources within a category. For example, post-combustion NO_X controls (the most stringent controls for stationary gas turbines) are not required under subpart GG of the NSPS for Stationary Gas Turbines. However, such controls must still be considered available technologies for the BART selection process.

3. Potentially applicable retrofit control alternatives can be categorized in three ways.

• Pollution prevention: use of inherently lower-emitting processes/practices, including the use of control techniques (e.g., low-NO_X burners) and work practices that prevent emissions and result in lower ''production-specific'' emissions (note that it is not our intent to direct States to switch fuel forms, e.g., from coal to gas),

• Use of (and where already in place, improvement in the performance of) add-on controls, such as scrubbers, fabric filters, thermal oxidizers and other devices that control and reduce emissions after they are produced, and

• Combinations of inherently lower-emitting processes and add-on controls.

4. In the course of the BART review, one or more of the available control options may be eliminated from consideration because they are demonstrated to be technically infeasible or to have unacceptable energy, cost, or non-air quality environmental impacts on a case-by-case (or site-specific) basis. However, at the outset, you should initially identify all control options with potential application to the emissions unit under review.

5. We do not consider BART as a requirement to redesign the source when considering available control alternatives. For example, where the source subject to BART is a coal-fired electric generator, we do not require the BART analysis to consider building a natural gas-fired electric turbine although the turbine may be inherently less polluting on a per unit basis.

6. For emission units subject to a BART review, there will often be control measures or devices already in place. For such emission units, it is important to include control options that involve improvements to existing controls and not to limit the control options only to those measures that involve a complete replacement of control devices.

Example: For a power plant with an existing wet scrubber, the current control efficiency is 66 percent. Part of the reason for the relatively low control efficiency is that 22 percent of the gas stream bypasses the scrubber. A BART review identifies options for improving the performance of the wet scrubber by redesigning the internal components of the scrubber and by eliminating or reducing the percentage of the gas stream that bypasses the scrubber. Four control options are identified: (1) 78 percent control based upon improved scrubber performance while maintaining the 22 percent bypass, (2) 83 percent control based upon improved scrubber performance while reducing the bypass to 15 percent, (3) 93 percent control based upon improving the scrubber performance while eliminating the bypass entirely, (this option results in a ''wet stack'' operation in which the gas leaving the stack is saturated with water) and (4) 93 percent as in option 3, with the addition of an indirect reheat system to reheat the stack gas above the saturation temperature. You must consider each of these four options in a BART analysis for this source.

7. You are expected to identify potentially applicable retrofit control technologies that represent the full range of demonstrated alternatives. Examples of general information sources to consider include:

• The EPA's Clean Air Technology Center, which includes the RACT/BACT/LAER Clearinghouse (RBLC);

• State and Local Best Available Control Technology Guidelines—many agencies have online information—for example South Coast Air Quality Management District, Bay Area Air Quality Management District, and Texas Natural Resources Conservation Commission;

• Control technology vendors;

• Federal/State/Local NSR permits and associated inspection/performance test reports;

• Environmental consultants;

• Technical journals, reports and newsletters, air pollution control seminars; and

• The EPA's NSR bulletin board—*http://www.epa.gov/ttn/nsr;*

• Department of Energy's Clean Coal Program—technical reports;

• The NO_X Control Technology ''Cost Tool''—Clean Air Markets Division Web page—*http://www.epa.gov/airmarkets/arp/nox/controltech.html;*

• Performance of selective catalytic reduction on coal-fired steam generating units—

year period since this guidance was developed, there have been advances in SO_2 control technologies as well as technologies for the control of other pollutants, confirmed by a number of recent retrofits at Western power plants. Accordingly, EPA no longer concludes that the NSPS level of controls automatically represents ''the best these sources can install.'' Analysis of the BART factors could result in the selection of a NSPS level of control, but you should reach this conclusion only after considering the full range of control options.

final report. OAR/ARD, June 1997 (also available at *http://www.epa.gov/airmarkets/arp/nox/controltech.html*);

• Cost estimates for selected applications of NO_X control technologies on stationary combustion boilers. OAR/ARD June 1997. (Docket for NO_X SIP Call, A–96–56, item II–A–03);

• Investigation of performance and cost of NO_X controls as applied to group 2 boilers. OAR/ARD, August 1996. (Docket for Phase II NO_X rule, A–95–28, item IV–A–4);

• Controlling SO_2 Emissions: A Review of Technologies. EPA–600/R–00–093, USEPA/ORD/NRMRL, October 2000; and

• The OAQPS Control Cost Manual.

You are expected to compile appropriate information from these information sources.

8. There may be situations where a specific set of units within a fenceline constitutes the logical set to which controls would apply and that set of units may or may not all be BART-eligible. (For example, some units in that set may not have been constructed between 1962 and 1977.)

9. If you find that a BART source has controls already in place which are the most stringent controls available (note that this means that all possible improvements to any control devices have been made), then it is not necessary to comprehensively complete each following step of the BART analysis in this section. As long these most stringent controls available are made federally enforceable for the purpose of implementing BART for that source, you may skip the remaining analyses in this section, including the visibility analysis in step 5. Likewise, if a source commits to a BART determination that consists of the most stringent controls available, then there is no need to complete the remaining analyses in this section.

2. STEP 2: How do I determine whether the options identified in Step 1 are technically feasible?

In Step 2, you evaluate the technical feasibility of the control options you identified in Step 1. You should document a demonstration of technical infeasibility and should explain, based on physical, chemical, or engineering principles, why technical difficulties would preclude the successful use of the control option on the emissions unit under review. You may then eliminate such technically infeasible control options from further consideration in the BART analysis.

In general, what do we mean by technical feasibility?

Control technologies are technically feasible if either (1) they have been installed and operated successfully for the type of source under review under similar conditions, or (2) the technology could be applied to the source under review. Two key concepts are important in determining whether a technology could be applied: ''availability'' and ''applicability.'' As explained in more detail below, a technology is considered ''available'' if the source owner may obtain it through commercial channels, or it is otherwise available within the common sense meaning of the term. An available technology is ''applicable'' if it can reasonably be installed and operated on the source type under consideration. A technology that is available and applicable is technically feasible.

What do we mean by ''available'' technology?

1. The typical stages for bringing a control technology concept to reality as a commercial product are:

• Concept stage;
• Research and patenting;
• Bench scale or laboratory testing;
• Pilot scale testing;
• Licensing and commercial demonstration; and
• Commercial sales.

2. A control technique is considered available, within the context presented above, if it has reached the stage of licensing and commercial availability. Similarly, we do not expect a source owner to conduct extended trials to learn how to apply a technology on a totally new and dissimilar source type. Consequently, you would not consider technologies in the pilot scale testing stages of development as ''available'' for purposes of BART review.

3. Commercial availability by itself, however, is not necessarily a sufficient basis for concluding a technology to be applicable and therefore technically feasible. Technical feasibility, as determined in Step 2, also means a control option may reasonably be deployed on or ''applicable'' to the source type under consideration.

Because a new technology may become available at various points in time during the BART analysis process, we believe that guidelines are needed on when a technology must be considered. For example, a technology may become available during the public comment period on the State's rule development process. Likewise, it is possible that new technologies may become available after the close of the State's public comment period and before submittal of the SIP to EPA, or during EPA's review process on the SIP submittal. In order to provide certainty in the process, all technologies should be considered if available before the close of the State's public comment period. You need not consider technologies that become available after this date. As part of your analysis, you should consider any technologies brought to your attention in public comments. If you disagree with public comments asserting that the technology is available, you should

provide an explanation for the public record as to the basis for your conclusion.

What do we mean by ''applicable'' technology?

You need to exercise technical judgment in determining whether a control alternative is applicable to the source type under consideration. In general, a commercially available control option will be presumed applicable if it has been used on the same or a similar source type. Absent a showing of this type, you evaluate technical feasibility by examining the physical and chemical characteristics of the pollutant-bearing gas stream, and comparing them to the gas stream characteristics of the source types to which the technology had been applied previously. Deployment of the control technology on a new or existing source with similar gas stream characteristics is generally a sufficient basis for concluding the technology is technically feasible barring a demonstration to the contrary as described below.

What type of demonstration is required if I conclude that an option is not technically feasible?

1. Where you conclude that a control option identified in Step 1 is technically infeasible, you should demonstrate that the option is either commercially unavailable, or that specific circumstances preclude its application to a particular emission unit. Generally, such a demonstration involves an evaluation of the characteristics of the pollutant-bearing gas stream and the capabilities of the technology. Alternatively, a demonstration of technical infeasibility may involve a showing that there are unresolvable technical difficulties with applying the control to the source (e.g., size of the unit, location of the proposed site, operating problems related to specific circumstances of the source, space constraints, reliability, and adverse side effects on the rest of the facility). Where the resolution of technical difficulties is merely a matter of increased cost, you should consider the technology to be technically feasible. The cost of a control alternative is considered later in the process.

2. The determination of technical feasibility is sometimes influenced by recent air quality permits. In some cases, an air quality permit may require a certain level of control, but the level of control in a permit is not expected to be achieved in practice (e.g., a source has received a permit but the project was canceled, or every operating source at that permitted level has been physically unable to achieve compliance with the limit). Where this is the case, you should provide supporting documentation showing why such limits are not technically feasible, and, therefore, why the level of control (but not necessarily the technology) may be eliminated from further consideration. However, if there is a permit requiring the application of a certain technology or emission limit to be achieved for such technology, this usually is sufficient justification for you to assume the technical feasibility of that technology or emission limit.

3. Physical modifications needed to resolve technical obstacles do not, in and of themselves, provide a justification for eliminating the control technique on the basis of technical infeasibility. However, you may consider the cost of such modifications in estimating costs. This, in turn, may form the basis for eliminating a control technology (see later discussion).

4. Vendor guarantees may provide an indication of commercial availability and the technical feasibility of a control technique and could contribute to a determination of technical feasibility or technical infeasibility, depending on circumstances. However, we do not consider a vendor guarantee alone to be sufficient justification that a control option will work. Conversely, lack of a vendor guarantee by itself does not present sufficient justification that a control option or an emissions limit is technically infeasible. Generally, you should make decisions about technical feasibility based on chemical, and engineering analyses (as discussed above), in conjunction with information about vendor guarantees.

5. A possible outcome of the BART procedures discussed in these guidelines is the evaluation of multiple control technology alternatives which result in essentially equivalent emissions. It is not our intent to encourage evaluation of unnecessarily large numbers of control alternatives for every emissions unit. Consequently, you should use judgment in deciding on those alternatives for which you will conduct the detailed impacts analysis (Step 4 below). For example, if two or more control techniques result in control levels that are essentially identical, considering the uncertainties of emissions factors and other parameters pertinent to estimating performance, you may evaluate only the less costly of these options. You should narrow the scope of the BART analysis in this way only if there is a negligible difference in emissions and energy and nonair quality environmental impacts between control alternatives.

3. STEP 3: How do I evaluate technically feasible alternatives?

Step 3 involves evaluating the control effectiveness of all the technically feasible control alternatives identified in Step 2 for the pollutant and emissions unit under review.

Two key issues in this process include:

(1) Making sure that you express the degree of control using a metric that ensures

an ''apples to apples'' comparison of emissions performance levels among options, and

(2) Giving appropriate treatment and consideration of control techniques that can operate over a wide range of emission performance levels.

What are the appropriate metrics for comparison?

This issue is especially important when you compare inherently lower-polluting processes to one another or to add-on controls. In such cases, it is generally most effective to express emissions performance as an average steady state emissions level per unit of product produced or processed.

Examples of common metrics:

• Pounds of SO_2 emissions per million Btu heat input, and

• Pounds of NO_X emissions per ton of cement produced.

How do I evaluate control techniques with a wide range of emission performance levels?

1. Many control techniques, including both add-on controls and inherently lower polluting processes, can perform at a wide range of levels. Scrubbers and high and low efficiency electrostatic precipitators (ESPs) are two of the many examples of such control techniques that can perform at a wide range of levels. It is not our intent to require analysis of each possible level of efficiency for a control technique as such an analysis would result in a large number of options. It is important, however, that in analyzing the technology you take into account the most stringent emission control level that the technology is capable of achieving. You should consider recent regulatory decisions and performance data (e.g., manufacturer's data, engineering estimates and the experience of other sources) when identifying an emissions performance level or levels to evaluate.

2. In assessing the capability of the control alternative, latitude exists to consider special circumstances pertinent to the specific source under review, or regarding the prior application of the control alternative. However, you should explain the basis for choosing the alternate level (or range) of control in the BART analysis. Without a showing of differences between the source and other sources that have achieved more stringent emissions limits, you should conclude that the level being achieved by those other sources is representative of the achievable level for the source being analyzed.

3. You may encounter cases where you may wish to evaluate other levels of control in addition to the most stringent level for a given device. While you must consider the most stringent level as one of the control options, you may consider less stringent levels of control as additional options. This would be useful, particularly in cases where the selection of additional options would have widely varying costs and other impacts.

4. Finally, we note that for retrofitting existing sources in addressing BART, you should consider ways to improve the performance of existing control devices, particularly when a control device is not achieving the level of control that other similar sources are achieving in practice with the same device. For example, you should consider requiring those sources with electrostatic precipitators (ESPs) performing below currently achievable levels to improve their performance.

4. STEP 4: For a BART review, what impacts am I expected to calculate and report? What methods does EPA recommend for the impacts analysis?

After you identify the available and technically feasible control technology options, you are expected to conduct the following analyses when you make a BART determination:

Impact analysis part 1: Costs of compliance,

Impact analysis part 2: Energy impacts, and

Impact analysis part 3: Non-air quality environmental impacts.

Impact analysis part 4: Remaining useful life.

In this section, we describe how to conduct each of these three analyses. You are responsible for presenting an evaluation of each impact along with appropriate supporting information. You should discuss and, where possible, quantify both beneficial and adverse impacts. In general, the analysis should focus on the direct impact of the control alternative.

a. Impact analysis part 1: how do I estimate the costs of control?

1. To conduct a cost analysis, you:

(1) Identify the emissions units being controlled,

(2) Identify design parameters for emission controls, and

(3) Develop cost estimates based upon those design parameters.

2. It is important to identify clearly the emission units being controlled, that is, to specify a well-defined area or process segment within the plant. In some cases, multiple emission units can be controlled jointly. However, in other cases, it may be appropriate in the cost analysis to consider whether multiple units will be required to install separate and/or different control devices. The analysis should provide a clear summary list of equipment and the associated control costs. Inadequate documentation of the equipment whose emissions are being controlled is a potential cause for confusion in

comparison of costs of the same controls applied to similar sources.

3. You then specify the control system design parameters. Potential sources of these design parameters include equipment vendors, background information documents used to support NSPS development, control technique guidelines documents, cost manuals developed by EPA, control data in trade publications, and engineering and performance test data. The following are a few examples of design parameters for two example control measures:

Control device	Examples of design parameters
Wet Scrubbers	Type of sorbent used (lime, limestone, etc.). Gas pressure drop. Liquid/gas ratio.
Selective Catalytic Reduction.	Ammonia to NO_X molar ratio. Pressure drop. Catalyst life.

4. The value selected for the design parameter should ensure that the control option will achieve the level of emission control being evaluated. You should include in your analysis documentation of your assumptions regarding design parameters. Examples of supporting references would include the EPA OAQPS *Control Cost Manual* (see below) and background information documents used for NSPS and hazardous pollutant emission standards. If the design parameters you specified differ from typical designs, you should document the difference by supplying performance test data for the control technology in question applied to the same source or a similar source.

5. Once the control technology alternatives and achievable emissions performance levels have been identified, you then develop estimates of capital and annual costs. The basis for equipment cost estimates also should be documented, either with data supplied by an equipment vendor (*i.e.*, budget estimates or bids) or by a referenced source (such as the *OAQPS Control Cost Manual*, Fifth Edition, February 1996, EPA 453/B–96–001).[14] In order to maintain and improve consistency, cost estimates should be based on the *OAQPS Control Cost Manual,* where possible.[15] The *Control Cost Manual* addresses most control technologies in sufficient detail for a BART analysis. The cost analysis should also take into account any site-specific design or other conditions identified above that affect the cost of a particular BART technology option.

b. What do we mean by cost effectiveness?

Cost effectiveness, in general, is a criterion used to assess the potential for achieving an objective in the most economical way. For purposes of air pollutant analysis, ''effectiveness'' is measured in terms of tons of pollutant emissions removed, and ''cost'' is measured in terms of annualized control costs. We recommend two types of cost-effectiveness calculations—average cost effectiveness, and incremental cost effectiveness.

c. How do I calculate average cost effectiveness?

Average cost effectiveness means the total annualized costs of control divided by annual emissions reductions (the difference between baseline annual emissions and the estimate of emissions after controls), using the following formula:

Average cost effectiveness (dollars per ton removed) =*Control option annualized cost*[16]

Baseline annual emissions—Annual emissions with Control option

Because you calculate costs in (annualized) dollars per year ($/yr) and because you calculate emissions rates in tons per year (tons/yr), the result is an average cost-effectiveness number in (annualized) dollars per ton ($/ton) of pollutant removed.

d. How do I calculate baseline emissions?

1. The baseline emissions rate should represent a realistic depiction of anticipated annual emissions for the source. In general, for the existing sources subject to BART, you will estimate the anticipated annual emissions based upon actual emissions from a baseline period.

2. When you project that future operating parameters (e.g., limited hours of operation or capacity utilization, type of fuel, raw materials or product mix or type) will differ from past practice, and if this projection has a deciding effect in the BART determination,

[14] The *OAQPS Control Cost Manual* is updated periodically. While this citation refers to the latest version at the time this guidance was written, you should use the version that is current as of when you conduct your impact analysis. This document is available at the following Web site: *http://www.epa.gov/ttn/catc/dir1/cs1ch2.pdf*.

[15] You should include documentation for any additional information you used for the cost calculations, including any information supplied by vendors that affects your assumptions regarding purchased equipment costs, equipment life, replacement of major components, and any other element of the calculation that differs from the *Control Cost Manual*.

[16] Whenever you calculate or report annual costs, you should indicate the year for which the costs are estimated. For example, if you use the year 2000 as the basis for cost comparisons, you would report that an annualized cost of $20 million would be: $20 million (year 2000 dollars).

then you must make these parameters or assumptions into enforceable limitations. In the absence of enforceable limitations, you calculate baseline emissions based upon continuation of past practice.

3. For example, the baseline emissions calculation for an emergency standby generator may consider the fact that the source owner would not operate more than past practice of 2 weeks a year. On the other hand, baseline emissions associated with a base-loaded turbine should be based on its past practice which would indicate a large number of hours of operation. This produces a significantly higher level of baseline emissions than in the case of the emergency/standby unit and results in more cost-effective controls. As a consequence of the dissimilar baseline emissions, BART for the two cases could be very different.

e. How do I calculate incremental cost effectiveness?

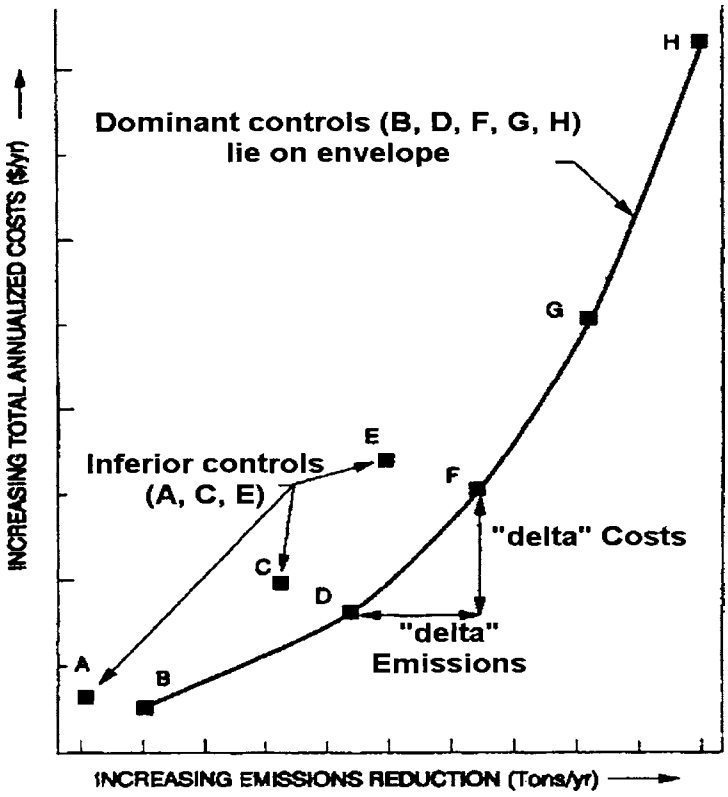
1. In addition to the average cost effectiveness of a control option, you should also calculate incremental cost effectiveness. You should consider the incremental cost effectiveness in combination with the average cost effectiveness when considering whether to eliminate a control option. The incremental cost effectiveness calculation compares the costs and performance level of a control option to those of the next most stringent option, as shown in the following formula (with respect to cost per emissions reduction):

Incremental Cost Effectiveness (dollars per incremental ton removed) = (Total annualized costs of control option) − (Total annualized costs of next control option) ÷ (Control option annual emissions) − (Next control option annual emissions)

Example 1: Assume that Option F on Figure 2 has total annualized costs of $1 million to reduce 2000 tons of a pollutant, and that Option D on Figure 2 has total annualized costs of $500,000 to reduce 1000 tons of the same pollutant. The incremental cost effectiveness of Option F relative to Option D is ($1 million − $500,000) divided by (2000 tons − 1000 tons), or $500,000 divided by 1000 tons, which is $500/ton.

Example 2: Assume that two control options exist: Option 1 and Option 2. Option 1 achieves a 1,000 ton/yr reduction at an annualized cost of $1,900,000. This represents an average cost of ($1,900,000/1,000 tons) = $1,900/ton. Option 2 achieves a 980 tons/yr reduction at an annualized cost of $1,500,000. This represents an average cost of ($1,500,000/980 tons) = $1,531/ton. The incremental cost effectiveness of Option 1 relative to Option 2 is ($1,900,000 − $1,500,000) divided by (1,000 tons − 980 tons). The adoption of Option 1 instead of Option 2 results in an incremental emission reduction of 20 tons per year at an additional cost of $400,000 per year. The incremental cost of Option 1, then, is $20,000 per ton − 11 times the average cost of $1,900 per ton. While $1,900 per ton may still be deemed reasonable, it is useful to consider both the average and incremental cost in making an overall cost-effectiveness finding. Of course, there may be other differences between these options, such as, energy or water use, or non-air environmental effects, which also should be considered in selecting a BART technology.

2. You should exercise care in deriving incremental costs of candidate control options. Incremental cost-effectiveness comparisons should focus on annualized cost and emission reduction differences between ''dominant'' alternatives. To identify dominant alternatives, you generate a graphical plot of total annualized costs for total emissions reductions for all control alternatives identified in the BART analysis, and by identifying a ''least-cost envelope'' as shown in Figure 2. (A ''least-cost envelope'' represents the set of options that should be dominant in the choice of a specific option.)



Example: Eight technically feasible control options for analysis are listed. These are represented as A through H in Figure 2. The dominant set of control options, B, D, F, G, and H, represent the least-cost envelope, as we depict by the cost curve connecting them. Points A, C and E are inferior options, and you should not use them in calculating incremental cost effectiveness. Points A, C and E represent inferior controls because B will buy more emissions reductions for less money than A; and similarly, D and F will buy more reductions for less money than C and E, respectively.

3. In calculating incremental costs, you:

(1) Array the control options in ascending order of annualized total costs,

(2) Develop a graph of the most reasonable smooth curve of the control options, as shown in Figure 2. This is to show the ''least-cost envelope'' discussed above; and

(3) Calculate the incremental cost effectiveness for each dominant option, which is the difference in total annual costs between that option and the next most stringent option, divided by the difference in emissions, after controls have been applied, between those two control options. For example, using Figure 2, you would calculate incremental cost effectiveness for the difference between options B and D, options D and F, options F and G, and options G and H.

4. A comparison of incremental costs can also be useful in evaluating the viability of a specific control option over a range of efficiencies. For example, depending on the capital and operational cost of a control device, total and incremental cost may vary significantly (either increasing or decreasing) over the operational range of a control device. Also, the greater the number of possible control options that exist, the more weight should be given to the incremental costs vs. average costs. It should be noted that average and incremental cost effectiveness are identical when only one candidate control option is known to exist.

5. You should exercise caution not to misuse these techniques. For example, you may be faced with a choice between two available control devices at a source, control A and control B, where control B achieves slightly

greater emission reductions. The average cost (total annual cost/total annual emission reductions) for each may be deemed to be reasonable. However, the incremental cost (total annual $cost_{A-B}$/total annual emission $reductions_{A-B}$) of the additional emission reductions to be achieved by control B may be very great. In such an instance, it may be inappropriate to choose control B, based on its high incremental costs, even though its average cost may be considered reasonable.

6. In addition, when you evaluate the average or incremental cost effectiveness of a control alternative, you should make reasonable and supportable assumptions regarding control efficiencies. An unrealistically low assessment of the emission reduction potential of a certain technology could result in inflated cost-effectiveness figures.

f. What other information should I provide in the cost impacts analysis?

You should provide documentation of any unusual circumstances that exist for the source that would lead to cost-effectiveness estimates that would exceed that for recent retrofits. This is especially important in cases where recent retrofits have cost-effectiveness values that are within what has been considered a reasonable range, but your analysis concludes that costs for the source being analyzed are not considered reasonable. (A reasonable range would be a range that is consistent with the range of cost effectiveness values used in other similar permit decisions over a period of time.)

Example: In an arid region, large amounts of water are needed for a scrubbing system. Acquiring water from a distant location could greatly increase the cost per ton of emissions reduced of wet scrubbing as a control option.

g. What other things are important to consider in the cost impacts analysis?

In the cost analysis, you should take care not to focus on incomplete results or partial calculations. For example, large capital costs for a control option alone would not preclude selection of a control measure if large emissions reductions are projected. In such a case, low or reasonable cost effectiveness numbers may validate the option as an appropriate BART alternative irrespective of the large capital costs. Similarly, projects with relatively low capital costs may not be cost effective if there are few emissions reduced.

h. Impact analysis part 2: How should I analyze and report energy impacts?

1. You should examine the energy requirements of the control technology and determine whether the use of that technology results in energy penalties or benefits. A source owner may, for example, benefit from the combustion of a concentrated gas stream rich in volatile organic compounds; on the other hand, more often extra fuel or electricity is required to power a control device or incinerate a dilute gas stream. If such benefits or penalties exist, they should be quantified to the extent practicable. Because energy penalties or benefits can usually be quantified in terms of additional cost or income to the source, the energy impacts analysis can, in most cases, simply be factored into the cost impacts analysis. The fact of energy use in and of itself does not disqualify a technology.

2. Your energy impact analysis should consider only direct energy consumption and not indirect energy impacts. For example, you could estimate the direct energy impacts of the control alternative in units of energy consumption at the source (e.g., BTU, kWh, barrels of oil, tons of coal). The energy requirements of the control options should be shown in terms of total (and in certain cases, also incremental) energy costs per ton of pollutant removed. You can then convert these units into dollar costs and, where appropriate, factor these costs into the control cost analysis.

3. You generally do not consider indirect energy impacts (such as energy to produce raw materials for construction of control equipment). However, if you determine, either independently or based on a showing by the source owner, that the indirect energy impact is unusual or significant and that the impact can be well quantified, you may consider the indirect impact.

4. The energy impact analysis may also address concerns over the use of locally scarce fuels. The designation of a scarce fuel may vary from region to region. However, in general, a scarce fuel is one which is in short supply locally and can be better used for alternative purposes, or one which may not be reasonably available to the source either at the present time or in the near future.

5. Finally, the energy impacts analysis may consider whether there are relative differences between alternatives regarding the use of locally or regionally available coal, and whether a given alternative would result in significant economic disruption or unemployment. For example, where two options are equally cost effective and achieve equivalent or similar emissions reductions, one option may be preferred if the other alternative results in significant disruption or unemployment.

i. Impact analysis part 3: How do I analyze ''non-air quality environmental impacts?''

1. In the non-air quality related environmental impacts portion of the BART analysis, you address environmental impacts other than air quality due to emissions of the pollutant in question. Such environmental impacts include solid or hazardous

waste generation and discharges of polluted water from a control device.

2. You should identify any significant or unusual environmental impacts associated with a control alternative that have the potential to affect the selection or elimination of a control alternative. Some control technologies may have potentially significant secondary environmental impacts. Scrubber effluent, for example, may affect water quality and land use. Alternatively, water availability may affect the feasibility and costs of wet scrubbers. Other examples of secondary environmental impacts could include hazardous waste discharges, such as spent catalysts or contaminated carbon. Generally, these types of environmental concerns become important when sensitive site-specific receptors exist or when the incremental emissions reductions potential of the more stringent control is only marginally greater than the next most-effective option. However, the fact that a control device creates liquid and solid waste that must be disposed of does not necessarily argue against selection of that technology as BART, particularly if the control device has been applied to similar facilities elsewhere and the solid or liquid waste is similar to those other applications. On the other hand, where you or the source owner can show that unusual circumstances at the proposed facility create greater problems than experienced elsewhere, this may provide a basis for the elimination of that control alternative as BART.

3. The procedure for conducting an analysis of non-air quality environmental impacts should be made based on a consideration of site-specific circumstances. If you propose to adopt the most stringent alternative, then it is not necessary to perform this analysis of environmental impacts for the entire list of technologies you ranked in Step 3. In general, the analysis need only address those control alternatives with any significant or unusual environmental impacts that have the potential to affect the selection of a control alternative, or elimination of a more stringent control alternative. Thus, any important relative environmental impacts (both positive and negative) of alternatives can be compared with each other.

4. In general, the analysis of impacts starts with the identification and quantification of the solid, liquid, and gaseous discharges from the control device or devices under review. Initially, you should perform a qualitative or semi-quantitative screening to narrow the analysis to discharges with potential for causing adverse environmental effects. Next, you should assess the mass and composition of any such discharges and quantify them to the extent possible, based on readily available information. You should also assemble pertinent information about the public or environmental consequences of releasing these materials.

j. Impact analysis part 4: What are examples of non-air quality environmental impacts?

The following are examples of how to conduct non-air quality environmental impacts:

(1) *Water Impact*

You should identify the relative quantities of water used and water pollutants produced and discharged as a result of the use of each alternative emission control system. Where possible, you should assess the effect on ground water and such local surface water quality parameters as ph, turbidity, dissolved oxygen, salinity, toxic chemical levels, temperature, and any other important considerations. The analysis could consider whether applicable water quality standards will be met and the availability and effectiveness of various techniques to reduce potential adverse effects.

(2) *Solid Waste Disposal Impact*

You could also compare the quality and quantity of solid waste (e.g., sludges, solids) that must be stored and disposed of or recycled as a result of the application of each alternative emission control system. You should consider the composition and various other characteristics of the solid waste (such as permeability, water retention, rewatering of dried material, compression strength, leachability of dissolved ions, bulk density, ability to support vegetation growth and hazardous characteristics) which are significant with regard to potential surface water pollution or transport into and contamination of subsurface waters or aquifers.

(3) *Irreversible or Irretrievable Commitment of Resources*

You may consider the extent to which the alternative emission control systems may involve a trade-off between short-term environmental gains at the expense of long-term environmental losses and the extent to which the alternative systems may result in irreversible or irretrievable commitment of resources (for example, use of scarce water resources).

(4) *Other Adverse Environmental Impacts*

You may consider significant differences in noise levels, radiant heat, or dissipated static electrical energy of pollution control alternatives. Other examples of non-air quality environmental impacts would include hazardous waste discharges such as spent catalysts or contaminated carbon.

k. How do I take into account a project's ''remaining useful life'' in calculating control costs?

1. You may decide to treat the requirement to consider the source's ''remaining useful life'' of the source for BART determinations as one element of the overall cost analysis. The ''remaining useful life'' of a source, if it

represents a relatively short time period, may affect the annualized costs of retrofit controls. For example, the methods for calculating annualized costs in EPA's *OAQPS Control Cost Manual* require the use of a specified time period for amortization that varies based upon the type of control. If the remaining useful life will clearly exceed this time period, the remaining useful life has essentially no effect on control costs and on the BART determination process. Where the remaining useful life is less than the time period for amortizing costs, you should use this shorter time period in your cost calculations.

2. For purposes of these guidelines, the remaining useful life is the difference between:

(1) The date that controls will be put in place (capital and other construction costs incurred before controls are put in place can be rolled into the first year, as suggested in EPA's *OAQPS Control Cost Manual*); you are conducting the BART analysis; and

(2) The date the facility permanently stops operations. Where this affects the BART determination, this date should be assured by a federally- or State-enforceable restriction preventing further operation.

3. We recognize that there may be situations where a source operator intends to shut down a source by a given date, but wishes to retain the flexibility to continue operating beyond that date in the event, for example, that market conditions change. Where this is the case, your BART analysis may account for this, but it must maintain consistency with the statutory requirement to install BART within 5 years. Where the source chooses not to accept a federally enforceable condition requiring the source to shut down by a given date, it is necessary to determine whether a reduced time period for the remaining useful life changes the level of controls that would have been required as BART.

If the reduced time period does change the level of BART controls, you may identify, and include as part of the BART emission limitation, the more stringent level of control that would be required as BART if there were no assumption that reduced the remaining useful life. You may incorporate into the BART emission limit this more stringent level, which would serve as a contingency should the source continue operating more than 5 years after the date EPA approves the relevant SIP. The source would not be allowed to operate after the 5-year mark without such controls. If a source does operate after the 5-year mark without BART in place, the source is considered to be in violation of the BART emissions limit for each day of operation.

5. Step 5: How should I determine visibility impacts in the BART determination?

The following is an approach you may use to determine visibility impacts (the degree of visibility improvement for each source subject to BART) for the BART determination. Once you have determined that your source or sources are subject to BART, you must conduct a visibility improvement determination for the source(s) as part of the BART determination. When making this determination, we believe you have flexibility in setting absolute thresholds, target levels of improvement, or *de minimis* levels since the deciview improvement must be weighed among the five factors, and you are free to determine the weight and significance to be assigned to each factor. For example, a 0.3 deciview improvement may merit a stronger weighting in one case versus another, so one ''bright line'' may not be appropriate. [Note that if sources have elected to apply the most stringent controls available, consistent with the discussion in section E. step 1. below, you need not conduct, or require the source to conduct, an air quality modeling analysis for the purpose of determining its visibility impacts.]

Use CALPUFF,[17] or other appropriate dispersion model to determine the visibility improvement expected at a Class I area from the potential BART control technology applied to the source. Modeling should be conducted for SO_2, NO_X, and direct PM emissions ($PM_{2.5}$ and/or PM_{10}). If the source is making the visibility determination, you should review and approve or disapprove of the source's analysis before making the expected improvement determination. There are several steps for determining the visibility impacts from an individual source using a dispersion model:

- Develop a modeling protocol.

Some critical items to include in a modeling protocol are meteorological and terrain data, as well as source-specific information (stack height, temperature, exit velocity, elevation, and allowable and actual emission rates of applicable pollutants), and receptor data from appropriate Class I areas. We recommend following EPA's *Interagency Workgroup on Air Quality Modeling (IWAQM) Phase 2 Summary Report and Recommendations for Modeling Long Range Transport Impacts*[18] for parameter settings and meteorological data inputs; the use of other settings from

[17] The model code and its documentation are available at no cost for download from *http://www.epa.gov/scram001/tt22.htm#calpuff*.

[18] *Interagency Workgroup on Air Quality Modeling (IWAQM) Phase 2 Summary Report and Recommendations for Modeling Long Range Transport Impacts*, U.S. Environmental Protection Agency, EPA–454/R–98–019, December 1998.

those in IWAQM should be identified and explained in the protocol.

One important element of the protocol is in establishing the receptors that will be used in the model. The receptors that you use should be located in the nearest Class I area with sufficient density to identify the likely visibility effects of the source. For other Class I areas in relatively close proximity to a BART-eligible source, you may model a few strategic receptors to determine whether effects at those areas may be greater than at the nearest Class I area. For example, you might chose to locate receptors at these areas at the closest point to the source, at the highest and lowest elevation in the Class I area, at the IMPROVE monitor, and at the approximate expected plume release height. If the highest modeled effects are observed at the nearest Class I area, you may choose not to analyze the other Class I areas any further as additional analyses might be unwarranted.

You should bear in mind that some receptors within the relevant Class I area may be less than 50 km from the source while other receptors within that same Class I area may be greater than 50 km from the same source. As indicated by the *Guideline on Air Quality Models,* this situation may call for the use of two different modeling approaches for the same Class I area and source, depending upon the State's chosen method for modeling sources less than 50 km. In situations where you are assessing visibility impacts for source-receptor distances less than 50 km, you should use expert modeling judgment in determining visibility impacts, giving consideration to both CALPUFF and other EPA-approved methods.

In developing your modeling protocol, you may want to consult with EPA and your regional planning organization (RPO). Up-front consultation will ensure that key technical issues are addressed before you conduct your modeling.

• For each source, run the model, at pre-control and post-control emission rates according to the accepted methodology in the protocol.

Use the 24-hour average actual emission rate from the highest emitting day of the meteorological period modeled (for the pre-control scenario). Calculate the model results for each receptor as the change in deciviews compared against natural visibility conditions. Post-control emission rates are calculated as a percentage of pre-control emission rates. For example, if the 24-hr pre-control emission rate is 100 lb/hr of SO_2, then the post control rate is 5 lb/hr if the control efficiency being evaluated is 95 percent.

• Make the net visibility improvement determination.

Assess the visibility improvement based on the modeled change in visibility impacts for the pre-control and post-control emission scenarios. You have flexibility to assess visibility improvements due to BART controls by one or more methods. You may consider the frequency, magnitude, and duration components of impairment. Suggestions for making the determination are:

• Use of a comparison threshold, as is done for determining if BART-eligible sources should be subject to a BART determination. Comparison thresholds can be used in a number of ways in evaluating visibility improvement (e.g., the number of days or hours that the threshold was exceeded, a single threshold for determining whether a change in impacts is significant, or a threshold representing an x percent change in improvement).

• Compare the 98th percent days for the pre- and post-control runs.

Note that each of the modeling options may be supplemented with source apportionment data or source apportionment modeling.

E. How do I select the ''best'' alternative, using the results of Steps 1 through 5?

1. Summary of the Impacts Analysis

From the alternatives you evaluated in Step 3, we recommend you develop a chart (or charts) displaying for each of the alternatives:

(1) Expected emission rate (tons per year, pounds per hour);

(2) Emissions performance level (e.g., percent pollutant removed, emissions per unit product, lb/MMBtu, ppm);

(3) Expected emissions reductions (tons per year);

(4) Costs of compliance—total annualized costs ($), cost effectiveness ($/ton), and incremental cost effectiveness ($/ton), and/or any other cost-effectiveness measures (such as $/deciview);

(5) Energy impacts;

(6) Non-air quality environmental impacts; and

(7) Modeled visibility impacts.

2. Selecting a ''best'' alternative

1. You have discretion to determine the order in which you should evaluate control options for BART. Whatever the order in which you choose to evaluate options, you should always (1) display the options evaluated; (2) identify the average and incremental costs of each option; (3) consider the energy and non-air quality environmental impacts of each option; (4) consider the remaining useful life; and (5) consider the modeled visibility impacts. You should provide a justification for adopting the technology that you select as the ''best'' level of control, including an explanation of the CAA factors that led you to choose that option over other control levels.

2. In the case where you are conducting a BART determination for two regulated pollutants on the same source, if the result is two different BART technologies that do not work well together, you could then substitute a different technology or combination of technologies.

3. In selecting a ''best'' alternative, should I consider the affordability of controls?

1. Even if the control technology is cost effective, there may be cases where the installation of controls would affect the viability of continued plant operations.

2. There may be unusual circumstances that justify taking into consideration the conditions of the plant and the economic effects of requiring the use of a given control technology. These effects would include effects on product prices, the market share, and profitability of the source. Where there are such unusual circumstances that are judged to affect plant operations, you may take into consideration the conditions of the plant and the economic effects of requiring the use of a control technology. Where these effects are judged to have a severe impact on plant operations you may consider them in the selection process, but you may wish to provide an economic analysis that demonstrates, in sufficient detail for public review, the specific economic effects, parameters, and reasoning. (We recognize that this review process must preserve the confidentiality of sensitive business information). Any analysis may also consider whether other competing plants in the same industry have been required to install BART controls if this information is available.

4. Sulfur dioxide limits for utility boilers

You must require 750 MW power plants to meet specific control levels for SO_2 of either 95 percent control or 0.15 lbs/MMBtu, for each EGU greater than 200 MW that is currently uncontrolled unless you determine that an alternative control level is justified based on a careful consideration of the statutory factors. Thus, for example, if the source demonstrates circumstances affecting its ability to cost-effectively reduce its emissions, you should take that into account in determining whether the presumptive levels of control are appropriate for that facility. For a currently uncontrolled EGU greater than 200 MW in size, but located at a power plant smaller than 750 MW in size, such controls are generally cost-effective and could be used in your BART determination considering the five factors specified in CAA section 169A(g)(2). While these levels may represent current control capabilities, we expect that scrubber technology will continue to improve and control costs continue to decline. You should be sure to consider the level of control that is currently best achievable at the time that you are conducting your BART analysis.

For coal-fired EGUs with existing post-combustion SO_2 controls achieving less than 50 percent removal efficiencies, we recommend that you evaluate constructing a new FGD system to meet the same emission limits as above (95 percent removal or 0.15 lb/mmBtu), in addition to the evaluation of scrubber upgrades discussed below. For oil-fired units, regardless of size, you should evaluate limiting the sulfur content of the fuel oil burned to 1 percent or less by weight.

For those BART-eligible EGUs with pre-existing post-combustion SO_2 controls achieving removal efficiencies of at least 50 percent, your BART determination should consider cost effective scrubber upgrades designed to improve the system's overall SO_2 removal efficiency. There are numerous scrubber enhancements available to upgrade the average removal efficiencies of all types of existing scrubber systems. We recommend that as you evaluate the definition of ''upgrade,'' you evaluate options that not only improve the design removal efficiency of the scrubber vessel itself, but also consider upgrades that can improve the overall SO_2 removal efficiency of the scrubber system. Increasing a scrubber system's reliability, and conversely decreasing its downtime, by way of optimizing operation procedures, improving maintenance practices, adjusting scrubber chemistry, and increasing auxiliary equipment redundancy, are all ways to improve average SO_2 removal efficiencies.

We recommend that as you evaluate the performance of existing wet scrubber systems, you consider some of the following upgrades, in no particular order, as potential scrubber upgrades that have been proven in the industry as cost effective means to increase overall SO_2 removal of wet systems:

(a) Elimination of Bypass Reheat;

(b) Installation of Liquid Distribution Rings;

(c) Installation of Perforated Trays;

(d) Use of Organic Acid Additives;

(e) Improve or Upgrade Scrubber Auxiliary System Equipment;

(f) Redesign Spray Header or Nozzle Configuration.

We recommend that as you evaluate upgrade options for dry scrubber systems, you should consider the following cost effective upgrades, in no particular order:

(a) Use of Performance Additives;

(b) Use of more Reactive Sorbent;

(c) Increase the Pulverization Level of Sorbent;

(d) Engineering redesign of atomizer or slurry injection system.

You should evaluate scrubber upgrade options based on the 5 step BART analysis process.

5. Nitrogen oxide limits for utility boilers

You should establish specific numerical limits for NO_X control for each BART determination. For power plants with a generating capacity in excess of 750 MW currently using selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) for part of the year, you should presume that use of those same controls year-round is BART. For other sources currently using SCR or SNCR to reduce NO_X emissions during part of the year, you should carefully consider requiring the use of these controls year-round as the additional costs of operating the equipment throughout the year would be relatively modest.

For coal-fired EGUs greater than 200 MW located at greater than 750 MW power plants and operating without post-combustion controls (*i.e.* SCR or SNCR), we have provided presumptive NO_X limits, differentiated by boiler design and type of coal burned. You may determine that an alternative control level is appropriate based on a careful consideration of the statutory factors. For coal-fired EGUs greater than 200 MW located at power plants 750 MW or less in size and operating without post-combustion controls, you should likewise presume that these same levels are cost-effective. You should require such utility boilers to meet the following NO_X emission limits, unless you determine that an alternative control level is justified based on consideration of the statutory factors. The following NO_X emission rates were determined based on a number of assumptions, including that the EGU boiler has enough volume to allow for installation and effective operation of separated overfire air ports. For boilers where these assumptions are incorrect, these emission limits may not be cost-effective.

TABLE 1—PRESUMPTIVE NO_X EMISSION LIMITS FOR BART-ELIGIBLE COAL-FIRED UNITS. [19]

Unit type	Coal type	NO_X presumptive limit (lb/mmbtu) [20]
Dry-bottom wall-fired	Bituminous	0.39
	Sub-bituminous	0.23
	Lignite	0.29
Tangential-fired	Bituminous	0.28
	Sub-bituminous	0.15
	Lignite	0.17
Cell Burners	Bituminous	0.40
	Sub-bituminous	0.45
Dry-turbo-fired	Bituminous	0.32
	Sub-bituminous	0.23
Wet-bottom tangential-fired	Bituminous	0.62

[19] No Cell burners, dry-turbo-fired units, nor wet-bottom tangential-fired units burning lignite were identified as BART-eligible, thus no presumptive limit was determined. Similarly, no wet-bottom tangential-fired units burning sub-bituminous were identified as BART-eligible.

[20] These limits reflect the design and technological assumptions discussed in the technical support document for NO_X limits for these guidelines. See *Technical Support Document for BART NO_X Limits for Electric Generating Units and Technical Support Document for BART NO_X* Limits for Electric Generating Units Excel Spreadsheet, Memorandum to Docket OAR 2002–0076, April 15, 2005.

Most EGUs can meet these presumptive NO_X limits through the use of current combustion control technology, *i.e.* the careful control of combustion air and low-NO_X burners. For units that cannot meet these limits using such technologies, you should consider whether advanced combustion control technologies such as rotating opposed fire air should be used to meet these limits.

Because of the relatively high NO_X emission rates of cyclone units, SCR is more cost-effective than the use of current combustion control technology for these units. The use of SCRs at cyclone units burning bituminous coal, sub-bituminous coal, and lignite should enable the units to cost-effectively meet NO_X rates of 0.10 lbs/mmbtu. As a result, we are establishing a presumptive NO_X limit of 0.10 lbs/mmbtu based on the use of SCR for coal-fired cyclone units greater than 200 MW located at 750 MW power plants. As with the other presumptive limits established in this guideline, you may determine that an alternative level of control is appropriate based on your consideration of the relevant statutory factors. For other cyclone units, you should review the use of SCR and consider whether these post-combustion controls should be required as BART.

For oil-fired and gas-fired EGUs larger than 200MW, we believe that installation of current combustion control technology to control NO_X is generally highly cost-effective and should be considered in your determination of BART for these sources. Many such units can make significant reductions

in NO_X emissions which are highly cost-effective through the application of current combustion control technology.[21]

V. ENFORCEABLE LIMITS/COMPLIANCE DATE

To complete the BART process, you must establish enforceable emission limits that reflect the BART requirements and require compliance within a given period of time. In particular, you must establish an enforceable emission limit for each subject emission unit at the source and for each pollutant subject to review that is emitted from the source. In addition, you must require compliance with the BART emission limitations no later than 5 years after EPA approves your regional haze SIP. If technological or economic limitations in the application of a measurement methodology to a particular emission unit make a conventional emissions limit infeasible, you may instead prescribe a design, equipment, work practice, operation standard, or combination of these types of standards. You should consider allowing sources to ''average'' emissions across any set of BART-eligible emission units within a fenceline, so long as the emission reductions from each pollutant being controlled for BART would be equal to those reductions that would be obtained by simply controlling each of the BART-eligible units that constitute BART-eligible source.

You should ensure that any BART requirements are written in a way that clearly specifies the individual emission unit(s) subject to BART regulation. Because the BART requirements themselves are ''applicable'' requirements of the CAA, they must be included as title V permit conditions according to the procedures established in 40 CFR part 70 or 40 CFR part 71.

Section 302(k) of the CAA requires emissions limits such as BART to be met on a continuous basis. Although this provision does not necessarily require the use of continuous emissions monitoring (CEMs), it is important that sources employ techniques that ensure compliance on a continuous basis. Monitoring requirements generally applicable to sources, including those that are subject to BART, are governed by other regulations. See, e.g., 40 CFR part 64 (compliance assurance monitoring); 40 CFR 70.6(a)(3) (periodic monitoring); 40 CFR 70.6(c)(1) (sufficiency monitoring). Note also that while we do not believe that CEMs would necessarily be required for all BART sources, the vast majority of electric generating units potentially subject to BART already employ CEM technology for other programs, such as the acid rain program. In addition, emissions limits must be enforceable as a practical matter (contain appropriate averaging times, compliance verification procedures and recordkeeping requirements). In light of the above, the permit must:

- Be sufficient to show compliance or noncompliance (*i.e.*, through monitoring times of operation, fuel input, or other indices of operating conditions and practices); and
- Specify a reasonable averaging time consistent with established reference methods, contain reference methods for determining compliance, and provide for adequate reporting and recordkeeping so that air quality agency personnel can determine the compliance status of the source; and
- For EGUS, specify an averaging time of a 30-day rolling average, and contain a definition of ''boiler operating day'' that is consistent with the definition in the proposed revisions to the NSPS for utility boilers in 40 CFR Part 60, subpart Da.[22] You should consider a boiler operating day to be any 24-hour period between 12:00 midnight and the following midnight during which any fuel is combusted at any time at the steam generating unit. This would allow 30-day rolling average emission rates to be calculated consistently across sources.

[70 FR 39156, July 6, 2005]

[21] See *Technical Support Document for BART NO_X Limits for Electric Generating Units* and *Technical Support Document for BART NO_X Limits for Electric Generating Units Excel Spreadsheet*, Memorandum to Docket OAR 2002–0076, April 15, 2005.

[22] 70 FR 9705, February 28, 2005.

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$$B_w = \frac{P_w}{P_{bar}} \qquad 3C\text{-}1$$

$$C = \frac{A}{R\left(1 - B_w\right)} \qquad 3C\text{-}2$$

$$C = \frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}} \qquad \frac{A}{R\left(1 - B_w\right)} \qquad 3C\text{-}3$$

7.3 Measured N_2 Concentration Correction. Calculate the reported N_2 correction for Method 25–C using Eq. 3C–4. If oxygen is determined in place of N_2, substitute the oxygen concentration for the nitrogen concentration in the equation.

$$C_{N_2 Corr} = \frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}}\left(C_{N_2}\right) \quad Eq.\ 3C-4$$

8. Bibliography

1. McNair, H.M., and E.J. Bonnelli. Basic Gas Chromatography. Consolidated Printers, Berkeley, CA. 1969.

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–2 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

APPENDIX A–3 TO PART 60—TEST METHODS 4 THROUGH 5I

Method 4—Determination of moisture content in stack gases
Method 5—Determination of particulate matter emissions from stationary sources
Method 5A—Determination of particulate matter emissions from the asphalt processing and asphalt roofing industry
Method 5B—Determination of nonsulfuric acid particulate matter emissions from stationary sources
Method 5C [Reserved]
Method 5D—Determination of particulate matter emissions from positive pressure fabric filters
Method 5E—Determination of particulate matter emissions from the wool fiberglass insulation manufacturing industry
Method 5F—Determination of nonsulfate particulate matter emissions from stationary sources
Method 5G—Determination of particulate matter emissions from wood heaters (dilution tunnel sampling location)
Method 5H—Determination of particulate emissions from wood heaters from a stack location
Method 5I—Determination of Low Level Particulate Matter Emissions From Stationary Sources

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference

method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

METHOD 4—DETERMINATION OF MOISTURE CONTENT IN STACK GASES

NOTE: This method does not include all the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 5, and Method 6.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Water vapor (H_2O) ...	7732–18–5	N/A

1.2 Applicability. This method is applicable for the determination of the moisture content of stack gas.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted at a constant rate from the source; moisture is removed from the sample stream and determined either volumetrically or gravimetrically.

2.2 The method contains two possible procedures: a reference method and an approximation method.

2.2.1 The reference method is used for accurate determinations of moisture content (such as are needed to calculate emission data). The approximation method, provides estimates of percent moisture to aid in setting isokinetic sampling rates prior to a pollutant emission measurement run. The approximation method described herein is only a suggested approach; alternative means for approximating the moisture content (*e.g.*, drying tubes, wet bulb-dry bulb techniques, condensation techniques, stoichiometric calculations, previous experience, etc.) are also acceptable.

2.2.2 The reference method is often conducted simultaneously with a pollutant emission measurement run. When it is, calculation of percent isokinetic, pollutant emission rate, etc., for the run shall be based upon the results of the reference method or its equivalent. These calculations shall not

be based upon the results of the approximation method, unless the approximation method is shown, to the satisfaction of the Administrator, to be capable of yielding results within one percent H_2O of the reference method.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 The moisture content of saturated gas streams or streams that contain water droplets, as measured by the reference method, may be positively biased. Therefore, when these conditions exist or are suspected, a second determination of the moisture content shall be made simultaneously with the reference method, as follows: Assume that the gas stream is saturated. Attach a temperature sensor [capable of measuring to ±1 °C (2 °F)] to the reference method probe. Measure the stack gas temperature at each traverse point (see section 8.1.1.1) during the reference method traverse, and calculate the average stack gas temperature. Next, determine the moisture percentage, either by: (1) Using a psychrometric chart and making appropriate corrections if the stack pressure is different from that of the chart, or (2) using saturation vapor pressure tables. In cases where the psychrometric chart or the saturation vapor pressure tables are not applicable (based on evaluation of the process), alternative methods, subject to the approval of the Administrator, shall be used.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Reference Method. A schematic of the sampling train used in this reference method is shown in Figure 4–1.

6.1.1 Probe. Stainless steel or glass tubing, sufficiently heated to prevent water condensation, and equipped with a filter, either in-stack (*e.g.*, a plug of glass wool inserted into the end of the probe) or heated out-of-stack (*e.g.*, as described in Method 5), to remove particulate matter. When stack conditions permit, other metals or plastic tubing may be used for the probe, subject to the approval of the Administrator.

6.1.2 Condenser. Same as Method 5, section 6.1.1.8.

6.1.3 Cooling System. An ice bath container, crushed ice, and water (or equivalent), to aid in condensing moisture.

6.1.4 Metering System. Same as in Method 5, section 6.1.1.9, except do not use sampling systems designed for flow rates higher than 0.0283 m^3/min (1.0 cfm). Other metering systems, capable of maintaining a constant sampling rate to within 10 percent and determining sample gas volume to within 2 percent, may be used, subject to the approval of the Administrator.

6.1.5 Barometer and Graduated Cylinder and/or Balance. Same as Method 5, sections 6.1.2 and 6.2.5, respectively.

6.2. Approximation Method. A schematic of the sampling train used in this approximation method is shown in Figure 4–2.

6.2.1 Probe. Same as section 6.1.1.

6.2.2 Condenser. Two midget impingers, each with 30-ml capacity, or equivalent.

6.2.3 Cooling System. Ice bath container, crushed ice, and water, to aid in condensing moisture in impingers.

6.2.4 Drying Tube. Tube packed with new or regenerated 6- to 16-mesh indicating-type silica gel (or equivalent desiccant), to dry the sample gas and to protect the meter and pump.

6.2.5 Valve. Needle valve, to regulate the sample gas flow rate.

6.2.6 Pump. Leak-free, diaphragm type, or equivalent, to pull the gas sample through the train.

6.2.7 Volume Meter. Dry gas meter, sufficiently accurate to measure the sample volume to within 2 percent, and calibrated over the range of flow rates and conditions actually encountered during sampling.

6.2.8 Rate Meter. Rotameter, or equivalent, to measure the flow range from 0 to 3 liters/min (0 to 0.11 cfm).

6.2.9 Graduated Cylinder. 25-ml.

6.2.10 Barometer. Same as Method 5, section 6.1.2.

6.2.11 Vacuum Gauge. At least 760-mm (30-in.) Hg gauge, to be used for the sampling leak check.

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Reference Method. The following procedure is intended for a condenser system (such as the impinger system described in section 6.1.1.8 of Method 5) incorporating volumetric analysis to measure the condensed moisture, and silica gel and gravimetric analysis to measure the moisture leaving the condenser.

8.1.1 Preliminary Determinations.

8.1.1.1 Unless otherwise specified by the Administrator, a minimum of eight traverse points shall be used for circular stacks having diameters less than 0.61 m (24 in.), a minimum of nine points shall be used for rectangular stacks having equivalent diameters less than 0.61 m (24 in.), and a minimum of twelve traverse points shall be used in all

other cases. The traverse points shall be located according to Method 1. The use of fewer points is subject to the approval of the Administrator. Select a suitable probe and probe length such that all traverse points can be sampled. Consider sampling from opposite sides of the stack (four total sampling ports) for large stacks, to permit use of shorter probe lengths. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

8.1.1.2 Select a total sampling time such that a minimum total gas volume of 0.60 scm (21 scf) will be collected, at a rate no greater than 0.021 m^3/min (0.75 cfm). When both moisture content and pollutant emission rate are to be determined, the moisture determination shall be simultaneous with, and for the same total length of time as, the pollutant emission rate run, unless otherwise specified in an applicable subpart of the standards.

8.1.2 Preparation of Sampling Train.

8.1.2.1 Place known volumes of water in the first two impingers; alternatively, transfer water into the first two impingers and record the weight of each impinger (plus water) to the nearest 0.5 g. Weigh and record the weight of the silica gel to the nearest 0.5 g, and transfer the silica gel to the fourth impinger; alternatively, the silica gel may first be transferred to the impinger, and the weight of the silica gel plus impinger recorded.

8.1.2.2 Set up the sampling train as shown in Figure 4–1. Turn on the probe heater and (if applicable) the filter heating system to temperatures of approximately 120 °C (248 °F), to prevent water condensation ahead of the condenser. Allow time for the temperatures to stabilize. Place crushed ice and water in the ice bath container.

8.1.3 Leak Check Procedures. It is recommended, but not required, that the volume metering system and sampling train be leak-checked as follows:

8.1.3.1 Metering System. Same as Method 5, section 8.4.1.

8.1.3.2 Sampling Train. Disconnect the probe from the first impinger or (if applicable) from the filter holder. Plug the inlet to the first impinger (or filter holder), and pull a 380 mm (15 in.) Hg vacuum. A lower vacuum may be used, provided that it is not exceeded during the test. A leakage rate in excess of 4 percent of the average sampling rate or 0.00057 m^3/min (0.020 cfm), whichever is less, is unacceptable. Following the leak check, reconnect the probe to the sampling train.

8.1.4 Sampling Train Operation. During the sampling run, maintain a sampling rate within 10 percent of constant rate, or as specified by the Administrator. For each run, record the data required on a data sheet similar to that shown in Figure 4–3. Be sure to record the dry gas meter reading at the beginning and end of each sampling time increment and whenever sampling is halted. Take other appropriate readings at each sample point at least once during each time increment.

NOTE: When Method 4 is used concurrently with an isokinetic method (*e.g.*, Method 5) the sampling rate should be maintained at isokinetic conditions rather than 10 percent of constant rate.

8.1.4.1 To begin sampling, position the probe tip at the first traverse point. Immediately start the pump, and adjust the flow to the desired rate. Traverse the cross section, sampling at each traverse point for an equal length of time. Add more ice and, if necessary, salt to maintain a temperature of less than 20 °C (68 °F) at the silica gel outlet.

8.1.4.2 After collecting the sample, disconnect the probe from the first impinger (or from the filter holder), and conduct a leak check (mandatory) of the sampling train as described in section 8.1.3.2. Record the leak rate. If the leakage rate exceeds the allowable rate, either reject the test results or correct the sample volume as in section 12.3 of Method 5.

8.2 Approximation Method.

NOTE: The approximation method described below is presented only as a suggested method (see section 2.0).

8.2.1 Place exactly 5 ml water in each impinger. Leak check the sampling train as follows: Temporarily insert a vacuum gauge at or near the probe inlet. Then, plug the probe inlet and pull a vacuum of at least 250 mm (10 in.) Hg. Note the time rate of change of the dry gas meter dial; alternatively, a rotameter (0 to 40 ml/min) may be temporarily attached to the dry gas meter outlet to determine the leakage rate. A leak rate not in excess of 2 percent of the average sampling rate is acceptable.

NOTE: Release the probe inlet plug slowly before turning off the pump.

8.2.2 Connect the probe, insert it into the stack, and sample at a constant rate of 2 liters/min (0.071 cfm). Continue sampling until the dry gas meter registers about 30 liters (1.1 ft^3) or until visible liquid droplets are carried over from the first impinger to the second. Record temperature, pressure, and dry gas meter readings as indicated by Figure 4–4.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
Section 8.1.1.4	Leak rate of the sampling system cannot exceed four percent of the average sampling rate or 0.00057 m^3/min (0.020 cfm).	Ensures the accuracy of the volume of gas sampled. (Reference Method).
Section 8.2.1	Leak rate of the sampling system cannot exceed two percent of the average sampling rate.	Ensures the accuracy of the volume of gas sampled. (Approximation Method).

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Reference Method. Calibrate the metering system, temperature sensors, and barometer according to Method 5, sections 10.3, 10.5, and 10.6, respectively.

10.2 Approximation Method. Calibrate the metering system and the barometer according to Method 6, section 10.1 and Method 5, section 10.6, respectively.

10.3 Field Balance Calibration Check. Check the calibration of the balance used to weigh impingers with a weight that is at least 500g or within 50g of a loaded impinger. The weight must be ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference-see 40 CFR 60.17) Class 6 (or better). Daily, before use, the field balance must measure the weight within ± 0.5g of the certified mass. If the daily balance calibration check fails, perform corrective measures and repeat the check before using balance.

11.0 Analytical Procedure

11.1 Reference Method. Measure the volume of the moisture condensed in each of the impingers to the nearest ml. Alternatively, if the impingers were weighed prior to sampling, weigh the impingers after sampling and record the difference in weight to the nearest 0.5 g. Determine the increase in weight of the silica gel (or silica gel plus impinger) to the nearest 0.5 g. Record this information (see example data sheet, Figure 4–5), and calculate the moisture content, as described in section 12.0.

11.2 Approximation Method. Combine the contents of the two impingers, and measure the volume to the nearest 0.5 ml.

12.0 Data Analysis and Calculations

Carry out the following calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Reference Method.

12.1.1 Nomenclature.

B_{ws} = Proportion of water vapor, by volume, in the gas stream.

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P_m = Absolute pressure (for this method, same as barometric pressure) at the dry gas meter, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 (mm Hg)(m^3)/(g-mole)(°K) for metric units and 21.85 (in. Hg)(ft^3)/(lb-mole)(°R) for English units.

T_m = Absolute temperature at meter, °K (°R).

T_{std} = Standard absolute temperature, 293 °K (528 °R).

V_f = Final volume of condenser water, ml.

V_i = Initial volume, if any, of condenser water, ml.

V_m = Dry gas volume measured by dry gas meter, dcm (dcf).

$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

$V_{wc(std)}$ = Volume of water vapor condensed, corrected to standard conditions, scm (scf).

$V_{wsg(std)}$ = Volume of water vapor collected in silica gel, corrected to standard conditions, scm (scf).

W_f = Final weight of silica gel or silica gel plus impinger, g.

W_i = Initial weight of silica gel or silica gel plus impinger, g.

Y = Dry gas meter calibration factor.

ΔV_m = Incremental dry gas volume measured by dry gas meter at each traverse point, dcm (dcf).

ρ_w = Density of water, 0.9982 g/ml (0.002201 lb/ml).

12.1.2 Volume of Water Vapor Condensed.

$$V_{wc(std)} = \frac{(V_f - V_i)\,\rho_w R\,T_{std}}{P_{std} M_W} = K_1 (V_f - V_i) \qquad \text{Eq. 4-1}$$

Where:

K_1 = 0.001333 m^3/ml for metric units,
= 0.04706 ft^3/ml for English units.

12.1.3 Volume of Water Collected in Silica Gel.

$$V_{wsg(std)} = \frac{(W_f - W_i)\,R\,T_{std}}{P_{std} M_W K_2} = K_3 (W_f - W_i) \qquad \text{Eq. 4-2}$$

Where:

K_2 = 1.0 g/g for metric units,
= 453.6 g/lb for English units.
K_3 = 0.001335 m^3/g for metric units,
= 0.04715 ft^3/g for English units.

12.1.4 Sample Gas Volume.

$$V_{m(std)} = \frac{V_m\ Y\ P_m T_{std}}{P_{std} T_m} = K_4 Y \frac{V_m P_m}{T_m} \qquad \text{Eq. 4-3}$$

Where:

K_4 = 0.3855 °K/mm Hg for metric units,
= 17.64 °R/in. Hg for English units.

NOTE: If the post-test leak rate (Section 8.1.4.2) exceeds the allowable rate, correct the value of Vm in Equation 4–3, as described in section 12.3 of Method 5.

12.1.5 Moisture Content.

$$B_{ws} = \frac{V_{wc(std)} + V_{wsg(std)}}{V_{wc(std)} + V_{wsg(std)} + V_{m(std)}} \qquad \text{Eq. 4-4}$$

12.1.6 Verification of Constant Sampling Rate. For each time increment, determine the ΔV_m. Calculate the average. If the value for any time increment differs from the average by more than 10 percent, reject the results, and repeat the run.

12.1.7 In saturated or moisture droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one using a value based upon the saturated conditions (see section 4.1), and another based upon the results of the impinger analysis. The lower of these two values of B_{ws} shall be considered correct.

12.2 Approximation Method. The approximation method presented is designed to estimate the moisture in the stack gas; therefore, other data, which are only necessary for accurate moisture determinations, are not collected. The following equations adequately estimate the moisture content for the purpose of determining isokinetic sampling rate settings.

12.2.1 Nomenclature.

B_{wm} = Approximate proportion by volume of water vapor in the gas stream leaving the second impinger, 0.025.
B_{ws} = Water vapor in the gas stream, proportion by volume.
M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
P_m = Absolute pressure (for this method, same as barometric pressure) at the dry gas meter, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
R = Ideal gas constant, 0.06236 [(mm Hg)(m^3)]/[(g-mole)(K)] for metric units and 21.85 [(in. Hg)(ft^3)]/[(lb-mole)(°R)] for English units.
T_m = Absolute temperature at meter, °K (°R).
T_{std} = Standard absolute temperature, 293 °K (528 °R).
V_f = Final volume of impinger contents, ml.
V_i = Initial volume of impinger contents, ml.
V_m = Dry gas volume measured by dry gas meter, dcm (dcf).
$V_{m(std)}$ = Dry gas volume measured by dry gas meter, corrected to standard conditions, dscm (dscf).
$V_{wc(std)}$ = Volume of water vapor condensed, corrected to standard conditions, scm (scf).
Y = Dry gas meter calibration factor.
ρ_w = Density of water, 0.09982 g/ml (0.002201 lb/ml).

12.2.2 Volume of Water Vapor Collected.

$$V_{wc(std)} = \frac{(V_f - V_i)\,\rho_w R\, T_{std}}{P_{std} M_W} = K_5 (V_f - V_i) \qquad \text{Eq. 4-5}$$

Where:

K_5 = 0.001333 m^3/ml for metric units,
= 0.04706 ft^3/ml for English units.

12.2.3 Sample Gas Volume.

$$V_{m(std)} = \frac{V_m\ Y\ P_m T_{std}}{P_{std} T_m} = K_6 Y \frac{V_m P_m}{T_m} \qquad \text{Eq. 4-6}$$

Where:

K_6 = 0.3855 °K/mm Hg for metric units,
= 17.64 °R/in. Hg for English units.

12.2.4 Approximate Moisture Content.

$$B_{ws} = \frac{V_{wc(std)}}{V_{wc(std)} + V_{m(std)}} + B_{wm} = \frac{V_{wc(std)}}{V_{wc(std)} + V_{m(std)}} + (0.025) \qquad \text{Eq. 4-7}$$

12.2.5 Using F-factors to determine approximate moisture for estimating moisture content where no wet scrubber is being used, for the purpose of determining isokinetic sampling rate settings with no fuel sample, is acceptable using the average F_c or F_d factor from Method 19 (see Method 19, section 12.3.1). If this option is selected, calculate the approximate moisture as follows:

$B_{ws} = B_H + B_A + B_F$

Where:

B_A = Mole Fraction of moisture in the ambient air.

$$B_A = \frac{\%RH}{100 * P_{Bar}} * 10^{\left[6.6912 - \left(\frac{3144}{T+390.86}\right)\right]}$$

B_F = Mole fraction of moisture from free water in the fuel.

$$B_F = \left[\frac{0.0036W^2 + 0.075W}{100}\right]\left[\frac{20.9 - O_2}{20.9}\right]$$

B_H = Mole fraction of moisture from the hydrogen in the fuel.

$$B_H = \left[1 - \frac{F_d}{F_w}\right]\frac{(20.9 - O_2)}{20.9}$$

B_{ws} = Mole fraction of moisture in the stack gas.

F_d = Volume of dry combustion components per unit of heat content at 0 percent oxygen, dscf/10^6.

Btu (scm/J). See Table 19–2 in Method 19.

F_w = Volume of wet combustion components per unit of heat content at 0 percent oxygen, wet.

scf/10^6 Btu (scm/J). See Table 19–2 in Method 19.

%RH = Percent relative humidity (calibrated hygrometer acceptable), percent.

P_{Bar} = Barometric pressure, in. Hg.

T = Ambient temperature, °F.

W = Percent free water by weight, percent.

O_2 = Percent oxygen in stack gas, dry basis, percent.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 The procedure described in Method 5 for determining moisture content is an acceptable alternative to Method 4.

16.2 The procedures in Method 6A for determining moisture is an acceptable alternative to Method 4.

16.3 Method 320 is an acceptable alternative to Method 4 for determining moisture.

16.4 Using F-factors to determine moisture is an acceptable alternative to Method 4 for a combustion stack not using a scrubber, and where a fuel sample is taken during the test run and analyzed for development of an F_d factor (see Method 19, section 12.3.2), and where stack O_2 content is measured by Method 3A or 3B during each test run. If this option is selected, calculate the moisture content as follows:

$B_{ws} = B_H + B_A + B_F$

Where:

B_A = Mole fraction of moisture in the ambient air.

$$B_A = \frac{\%RH}{100\ P_{Bar}}\left[10^{\left[6.6912-\left(\frac{3144}{T+390.86}\right)\right]}\right]$$

NOTE: Values of B_A should be between 0.00 and 0.06 with common values being about 0.015.

B_F = Mole fraction of moisture from free water in the fuel.

$$B_F = \left[\frac{0.0036\ W^2 + 0.075\ W}{100}\right]\left[\frac{20.9 - O_2}{20.9}\right]$$

NOTE: Free water in fuel is minimal for distillate oil and gases, such as propane and natural gas, so this step may be omitted for those fuels.

B_H = Mole fraction of moisture from the hydrogen in the fuel.

$$B_H = \left(1 - \frac{F_d}{F_w}\right)\frac{(20.9 - O_2)}{20.9}$$

B_{ws} = Mole fraction of moisture in the stack gas.
F_d = Volume of dry combustion components per unit of heat content at 0 percent oxygen, dscf/10^6 Btu (scm/J). Develop a test specific F_d value using an integrated fuel sample from each test run and Equation 19–13 in section 12.3.2 of Method 19.
F_w = Volume of wet combustion components per unit of heat content at 0 percent oxygen, wet scf/10^6 Btu (scm/J). Develop a test specific F_w value using an integrated fuel sample from each test run and Equation 19–14 in section 12.3.2 of Method 19.
%RH = Percent relative humidity (calibrated hygrometer acceptable), percent.
P_{Bar} = Barometric pressure, in. Hg.
T = Ambient temperature, °F.
W = Percent free water by weight, percent.
O_2 = Percent oxygen in stack gas, dry basis, percent.

17.0 References

1. Air Pollution Engineering Manual (Second Edition). Danielson, J.A. (ed.). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, NC. Publication No. AP–40. 1973.

2. Devorkin, Howard, et al. Air Pollution Source Testing Manual. Air Pollution Control District, Los Angeles, CA. November 1963.

3. Methods for Determination of Velocity, Volume, Dust and Mist Content of Gases. Western Precipitation Division of Joy Manufacturing Co. Los Angeles, CA. Bulletin WP–50. 1968.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

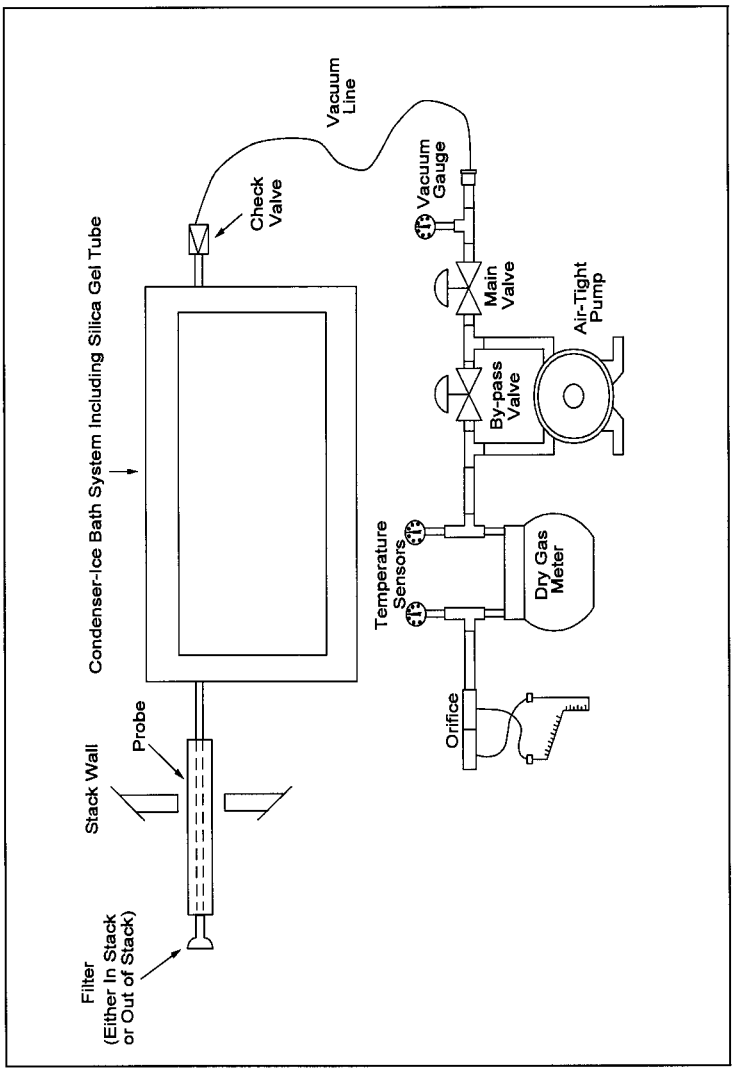

Figure 4-1. Moisture Sampling Train-Reference Method

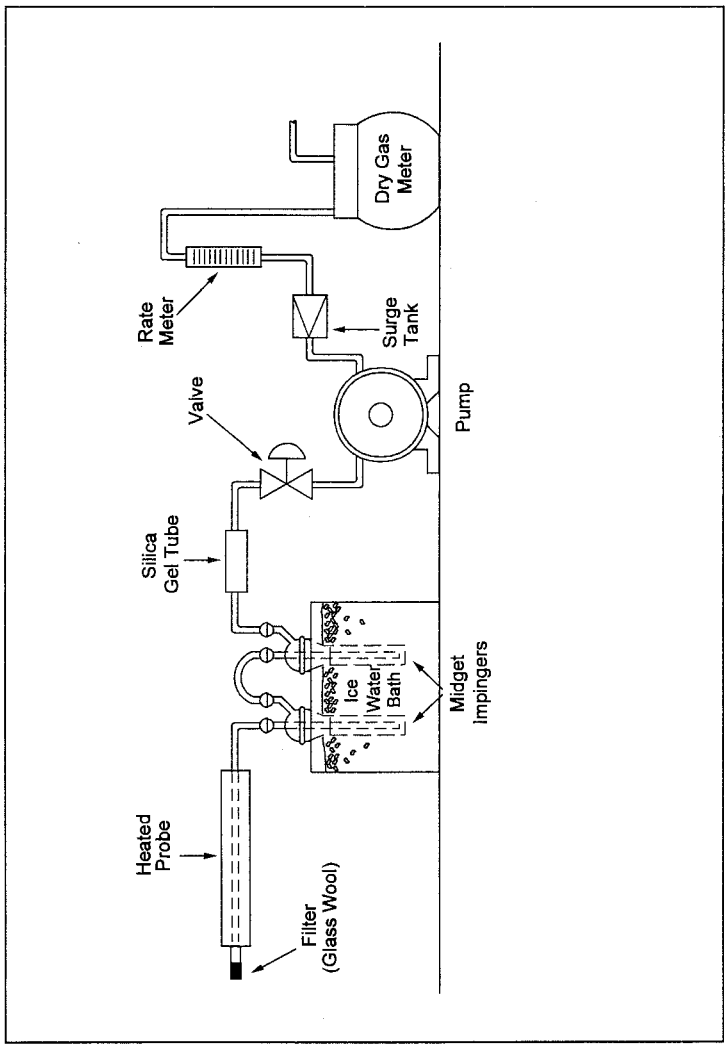

Figure 4-2. Moisture Sampling Train - Approximation Method.

Plant		Run No.	
Location		Ambient temperature	
Operator		Barometric pressure	
Date		Probe Length	

Traverse Pt. No.	Sampling time (Δ), min	Stack temperature °C (°F)	Pressure differential across orifice meter ΔH mm (in.) H_2O	Meter reading gas sample volume m^3 (ft^3)	ΔV_m m^3 (ft^3)	Gas sample temperature at dry gas meter		Temperature of gas leaving condenser or last impinger °C (°F)
						Inlet Tm_{in} °C (°F)	Outlet Tm_{out} °C (°F)	
Average								

Location _____ Barometric pressure _____
Test _____ Comments: _____
Date _____
Operator _____

Figure 4–3. Moisture Determination—Reference Method

Clock time	Gas Volume through meter, (V_m), m^3 (ft^3)	Rate meter setting m^3/min (ft^3/min)	Meter temperature °C (°F)

Figure 4–4. Example Moisture Determination Field Data Sheet—Approximation Method

	Impinger volume, ml	Silica gel weight, g
Final Initial Difference		

Figure 4–5. Analytical Data—Reference Method

METHOD 5—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of PM emissions from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature of 120 ±14 °C (248 ±25 °F) or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. The PM mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after the removal of uncombined water.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. The following items are required for sample collection:

6.1.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 5–1 in section 18.0. Complete construction details are given in APTD–0581 (Reference 2 in section 17.0); commercial models of this train are also available. For

changes from APTD–0581 and for allowable modifications of the train shown in Figure 5–1, see the following subsections.

NOTE: The operating and maintenance procedures for the sampling train are described in APTD–0576 (Reference 3 in section 17.0). Since correct usage is important in obtaining valid results, all users should read APTD–0576 and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein.

6.1.1.1 Probe Nozzle. Stainless steel (316) or glass with a sharp, tapered leading edge. The angle of taper shall be ≤30°, and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. If made of stainless steel, the nozzle shall be constructed from seamless tubing. Other materials of construction may be used, subject to the approval of the Administrator. A range of nozzle sizes suitable for isokinetic sampling should be available. Typical nozzle sizes range from 0.32 to 1.27 cm (⅛ to ½ in) inside diameter (ID) in increments of 0.16 cm (1⁄16 in). Larger nozzles sizes are also available if higher volume sampling trains are used. Each nozzle shall be calibrated, according to the procedures outlined in section 10.1.

6.1.1.2 Probe Liner. Borosilicate or quartz glass tubing with a heating system capable of maintaining a probe gas temperature during sampling of 120 ±14 °C (248 ±25 °F), or such other temperature as specified by an applicable subpart of the standards or as approved by the Administrator for a particular application. Since the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to APTD–0581 and utilizing the calibration curves of APTD–0576 (or calibrated according to the procedure outlined in APTD–0576) will be considered acceptable. Either borosilicate or quartz glass probe liners may be used for stack temperatures up to about 480 °C (900 °F); quartz glass liners shall be used for temperatures between 480 and 900 °C (900 and 1,650 °F). Both types of liners may be used at higher temperatures than specified for short periods of time, subject to the approval of the Administrator. The softening temperature for borosilicate glass is 820 °C (1500 °F), and for quartz glass it is 1500 °C (2700 °F). Whenever practical, every effort should be made to use borosilicate or quartz glass probe liners. Alternatively, metal liners (e.g., 316 stainless steel, Incoloy 825 or other corrosion resistant metals) made of seamless tubing may be used, subject to the approval of the Administrator.

6.1.1.3 Pitot Tube. Type S, as described in section 6.1 of Method 2, or other device approved by the Administrator. The pitot tube shall be attached to the probe (as shown in Figure 5–1) to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see Method 2, Figure 2–7) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in section 10.0 of Method 2.

6.1.1.4 Differential Pressure Gauge. Inclined manometer or equivalent device (two), as described in section 6.2 of Method 2. One manometer shall be used for velocity head (Δp) readings, and the other, for orifice differential pressure readings.

6.1.1.5 Filter Holder. Borosilicate glass, with a glass or Teflon frit filter support and a silicone rubber gasket. Other materials of construction (e.g., stainless steel or Viton) may be used, subject to the approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe (or cyclone, if used).

6.1.1.6 Filter Heating System. Any heating system capable of monitoring and maintaining temperature around the filter shall be used to ensure the sample gas temperature exiting the filter of 120 ±14 °C (248 ±25 °F) during sampling or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. The monitoring and regulation of the temperature around the filter may be done with the filter temperature sensor or another temperature sensor.

6.1.1.7 Filter Temperature Sensor. A temperature sensor capable of measuring temperature to within ±3 °C (5.4 °F) shall be installed so that the sensing tip of the temperature sensor is in direct contact with the sample gas exiting the filter. The sensing tip of the sensor may be encased in glass, Teflon, or metal and must protrude at least ½ in. into the sample gas exiting the filter. The filter temperature sensor must be monitored and recorded during sampling to ensure a sample gas temperature exiting the filter of 120 ±14 °C (248 ±25 °F), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application.

6.1.1.8 Condenser. The following system shall be used to determine the stack gas moisture content: Four impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with a 1.3 cm (½ in.) ID glass tube extending to about 1.3 cm (½ in.) from the bottom of the flask. The second impinger shall be of the Greenburg-Smith design with the standard

tip. Modifications (e.g., using flexible connections between the impingers, using materials other than glass, or using flexible vacuum lines to connect the filter holder to the condenser) may be used, subject to the approval of the Administrator. The first and second impingers shall contain known quantities of water (Section 8.3.1), the third shall be empty, and the fourth shall contain a known weight of silica gel, or equivalent desiccant. A temperature sensor, capable of measuring temperature to within 1 °C (2 °F) shall be placed at the outlet of the fourth impinger for monitoring purposes. Alternatively, any system that cools the sample gas stream and allows measurement of the water condensed and moisture leaving the condenser, each to within 1 ml or 1 g may be used, subject to the approval of the Administrator. An acceptable technique involves the measurement of condensed water either gravimetrically or volumetrically and the determination of the moisture leaving the condenser by: (1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's law of partial pressures; or (2) passing the sample gas stream through a tared silica gel (or equivalent desiccant) trap with exit gases kept below 20 °C (68 °F) and determining the weight gain. If means other than silica gel are used to determine the amount of moisture leaving the condenser, it is recommended that silica gel (or equivalent) still be used between the condenser system and pump to prevent moisture condensation in the pump and metering devices and to avoid the need to make corrections for moisture in the metered volume.

NOTE: If a determination of the PM collected in the impingers is desired in addition to moisture content, the impinger system described above shall be used, without modification. Individual States or control agencies requiring this information shall be contacted as to the sample recovery and analysis of the impinger contents.

6.1.1.9 Metering System. Vacuum gauge, leak-free pump, calibrated temperature sensors, dry gas meter (DGM) capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 5–1. Other metering systems capable of maintaining sampling rates within 10 percent of isokinetic and of determining sample volumes to within 2 percent may be used, subject to the approval of the Administrator. When the metering system is used in conjunction with a pitot tube, the system shall allow periodic checks of isokinetic rates.

6.1.1.10 Sampling trains utilizing metering systems designed for higher flow rates than that described in APTD–0581 or APTD–0576 may be used provided that the specifications of this method are met.

6.1.2 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in.).

NOTE: The barometric pressure reading may be obtained from a nearby National Weather Service station. In this case, the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be made at a rate of minus 2.5 mm Hg (0.1 in.) per 30 m (100 ft) elevation increase or plus 2.5 mm Hg (0.1 in) per 30 m (100 ft) elevation decrease.

6.1.3 Gas Density Determination Equipment. Temperature sensor and pressure gauge, as described in sections 6.3 and 6.4 of Method 2, and gas analyzer, if necessary, as described in Method 3. The temperature sensor shall, preferably, be permanently attached to the pitot tube or sampling probe in a fixed configuration, such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see Method 2, Figure 2–4). As a second alternative, if a difference of not more than 1 percent in the average velocity measurement is to be introduced, the temperature sensor need not be attached to the probe or pitot tube. (This alternative is subject to the approval of the Administrator.)

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Probe-Liner and Probe-Nozzle Brushes. Nylon bristle brushes with stainless steel wire handles. The probe brush shall have extensions (at least as long as the probe) constructed of stainless steel, Nylon, Teflon, or similarly inert material. The brushes shall be properly sized and shaped to brush out the probe liner and nozzle.

6.2.2 Wash Bottles. Two Glass wash bottles are recommended. Alternatively, polyethylene wash bottles may be used. It is recommended that acetone not be stored in polyethylene bottles for longer than a month.

6.2.3 Glass Sample Storage Containers. Chemically resistant, borosilicate glass bottles, for acetone washes, 500 ml or 1000 ml. Screw cap liners shall either be rubber-backed Teflon or shall be constructed so as to be leak-free and resistant to chemical attack by acetone. (Narrow mouth glass bottles have been found to be less prone to leakage.) Alternatively, polyethylene bottles may be used.

6.2.4 Petri Dishes. For filter samples; glass or polyethylene, unless otherwise specified by the Administrator.

6.2.5 Graduated Cylinder and/or Balance. To measure condensed water to within 1 ml or 0.5 g. Graduated cylinders shall have subdivisions no greater than 2 ml.

6.2.6 Plastic Storage Containers. Air-tight containers to store silica gel.

6.2.7 Funnel and Rubber Policeman. To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

6.2.8 Funnel. Glass or polyethylene, to aid in sample recovery.

6.3 Sample Analysis. The following equipment is required for sample analysis:

6.3.1 Glass Weighing Dishes.

6.3.2 Desiccator.

6.3.3 Analytical Balance. To measure to within 0.1 mg.

6.3.4 Balance. To measure to within 0.5 g.

6.3.5 Beakers. 250 ml.

6.3.6 Hygrometer. To measure the relative humidity of the laboratory environment.

6.3.7 Temperature Sensor. To measure the temperature of the laboratory environment.

7.0 Reagents and Standards

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Method D 2986–71, 78, or 95a (incorporated by reference—see §60.17). Test data from the supplier's quality control program are sufficient for this purpose. In sources containing SO_2 or SO_3, the filter material must be of a type that is unreactive to SO_2 or SO_3. Reference 10 in section 17.0 may be used to select the appropriate filter.

7.1.2 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

7.1.3 Water. When analysis of the material caught in the impingers is required, deionized distilled water [to conform to ASTM D1193–77 or 91 Type 3 (incorporated by reference—see §60.17)] with at least <0.001 percent residue shall be used or as specified in the applicable method requiring analysis of the water. Run reagent blanks prior to field use to eliminate a high blank on test samples.

7.1.4 Crushed Ice.

7.2 Sample Recovery. Acetone, reagent grade, ≤0.001 percent residue, in glass bottles, is required. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers; thus, acetone blanks shall be run prior to field use and only acetone with low blank values (≤0.001 percent) shall be used. In no case shall a blank value of greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight.

7.3 Sample Analysis. The following reagents are required for sample analysis:

7.3.1 Acetone. Same as in section 7.2.

7.3.2 Desiccant. Anhydrous calcium sulfate, indicating type. Alternatively, other types of desiccants may be used, subject to the approval of the Administrator.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation. It is suggested that sampling equipment be maintained according to the procedures described in APTD–0576. Alternative mercury-free thermometers may be used if the thermometers are at a minimum equivalent in terms of performance or suitably effective for the specific temperature measurement application.

8.1.1 Place 200 to 300 g of silica gel in each of several air-tight containers. Weigh each container, including silica gel, to the nearest 0.5 g, and record this weight. As an alternative, the silica gel need not be preweighed, but may be weighed directly in its impinger or sampling holder just prior to train assembly.

8.1.2 Check filters visually against light for irregularities, flaws, or pinhole leaks. Label filters of the proper diameter on the back side near the edge using numbering machine ink. As an alternative, label the shipping containers (glass or polyethylene petri dishes), and keep each filter in its identified container at all times except during sampling.

8.1.3 Desiccate the filters at 20 ±5.6 °C (68 ±10 °F) and ambient pressure for at least 24 hours. Weigh each filter (or filter and shipping container) at intervals of at least 6 hours to a constant weight (*i.e.*, ≤0.5 mg change from previous weighing). Record results to the nearest 0.1 mg. During each weighing, the period for which the filter is exposed to the laboratory atmosphere shall be less than 2 minutes. Alternatively (unless otherwise specified by the Administrator), the filters may be oven dried at 105 °C (220 °F) for 2 to 3 hours, desiccated for 2 hours, and weighed. Procedures other than those described, which account for relative humidity effects, may be used, subject to the approval of the Administrator.

8.2 Preliminary Determinations.

8.2.1 Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and the range of velocity heads using Method 2; it is recommended that a leak check of the pitot lines (see Method 2, section 8.1) be performed. Determine the moisture content using Approximation Method 4 or its alternatives for the purpose

of making isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in Method 2, section 8.6; if integrated Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the particulate sample run.

8.2.2 Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see section 8.3 of Method 2).

8.2.3 Select a suitable probe liner and probe length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the required probe length.

8.2.4 Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that (1) the sampling time per point is not less than 2 minutes (or some greater time interval as specified by the Administrator), and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume. The latter is based on an approximate average sampling rate.

8.2.5 The sampling time at each point shall be the same. It is recommended that the number of minutes sampled at each point be an integer or an integer plus one-half minute, in order to avoid timekeeping errors.

8.2.6 In some circumstances (*e.g.*, batch cycles) it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the Administrator's approval must first be obtained.

8.3 Preparation of Sampling Train.

8.3.1 During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin. Place 100 ml of water in each of the first two impingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

8.3.2 Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly is completed.

8.3.3 When glass probe liners are used, install the selected nozzle using a Viton A O-ring when stack temperatures are less than 260 °C (500 °F) or a heat-resistant string gasket when temperatures are higher. See APTD–0576 for details. Other connecting systems using either 316 stainless steel or Teflon ferrules may be used. When metal liners are used, install the nozzle as discussed above or by a leak-free direct mechanical connection. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

8.3.4 Set up the train as shown in Figure 5–1 ensuring that the connections are leaktight. Subject to the approval of the Administrator, a glass cyclone may be used between the probe and filter holder when the total particulate catch is expected to exceed 100 mg or when water droplets are present in the stack gas.

8.3.5 Place crushed ice around the impingers.

8.4 Leak-Check Procedures.

8.4.1 Leak Check of Metering System Shown in Figure 5–1. That portion of the sampling train from the pump to the orifice meter should be leak-checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The following procedure is suggested (see Figure 5–2): Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 to 18 cm (5 to 7 in.) water column by blowing into the rubber tubing. Pinch off the tubing, and observe the manometer for one minute. A loss of pressure on the manometer indicates a leak in the meter box; leaks, if present, must be corrected.

8.4.2 Pretest Leak Check. A pretest leak check of the sampling train is recommended, but not required. If the pretest leak check is conducted, the following procedure should be used.

8.4.2.1 After the sampling train has been assembled, turn on and set the filter and probe heating systems to the desired operating temperatures. Allow time for the temperatures to stabilize. If a Viton A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 380 mm (15 in.) Hg vacuum.

NOTE: A lower vacuum may be used, provided that it is not exceeded during the test.

8.4.2.2 If a heat-resistant string is used, do not connect the probe to the train during the leak check. Instead, leak-check the train by first plugging the inlet to the filter holder (cyclone, if applicable) and pulling a 380 mm (15 in.) Hg vacuum (see note in section 8.4.2.1). Then connect the probe to the train, and leak-check at approximately 25 mm (1 in.) Hg vacuum; alternatively, the probe may be leak-checked with the rest of the sampling train, in one step, at 380 mm (15 in.) Hg vacuum. Leakage rates in excess of 4 percent of the average sampling rate or 0.00057 m^3/min (0.020 cfm), whichever is less, are unacceptable.

8.4.2.3 The following leak-check instructions for the sampling train described in APTD–0576 and APTD–0581 may be helpful. Start the pump with the bypass valve fully open and the coarse adjust valve completely closed. Partially open the coarse adjust valve, and slowly close the bypass valve until the desired vacuum is reached. Do not reverse the direction of the bypass valve, as this will cause water to back up into the filter holder. If the desired vacuum is exceeded, either leak-check at this higher vacuum, or end the leak check and start over.

8.4.2.4 When the leak check is completed, first slowly remove the plug from the inlet to the probe, filter holder, or cyclone (if applicable), and immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the filter holder and the silica gel from being entrained backward into the third impinger.

8.4.3 Leak Checks During Sample Run. If, during the sampling run, a component (*e.g.*, filter assembly or impinger) change becomes necessary, a leak check shall be conducted immediately before the change is made. The leak check shall be done according to the procedure outlined in section 8.4.2 above, except that it shall be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.020 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered; if, however, a higher leakage rate is obtained, either record the leakage rate and plan to correct the sample volume as shown in section 12.3 of this method, or void the sample run.

NOTE: Immediately after component changes, leak checks are optional. If such leak checks are done, the procedure outlined in section 8.4.2 above should be used.

8.4.4 Post-Test Leak Check. A leak check of the sampling train is mandatory at the conclusion of each sampling run. The leak check shall be performed in accordance with the procedures outlined in section 8.4.2, except that it shall be conducted at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m^3 min (0.020 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, either record the leakage rate and correct the sample volume as shown in section 12.3 of this method, or void the sampling run.

8.5 Sampling Train Operation. During the sampling run, maintain an isokinetic sampling rate (within 10 percent of true isokinetic unless otherwise specified by the Administrator) and a sample gas temperature through the filter of 120 ±14 °C (248 ±25 °F) or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator.

8.5.1 For each run, record the data required on a data sheet such as the one shown in Figure 5–3. Be sure to record the initial DGM reading. Record the DGM readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak check, and when sampling is halted. Take other readings indicated by Figure 5–3 at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

8.5.2 Clean the portholes prior to the test run to minimize the chance of collecting deposited material. To begin sampling, verify that the filter and probe heating systems are up to temperature, remove the nozzle cap, verify that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump, and adjust the flow to isokinetic conditions. Nomographs are available which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pitot tube coefficient (C_p) is 0.85 ±0.02, and the stack gas equivalent density [dry molecular weight (M_d)] is equal to 29 ±4. APTD–0576 details the procedure for using the nomographs. If C_p and M_d are outside the above stated ranges, do not use the nomographs unless appropriate steps (see Reference 7 in section 17.0) are taken to compensate for the deviations.

8.5.3 When the stack is under significant negative pressure (*i.e.*, height of impinger stem), take care to close the coarse adjust valve before inserting the probe into the stack to prevent water from backing into the

filter holder. If necessary, the pump may be turned on with the coarse adjust valve closed.

8.5.4 When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

8.5.5 Traverse the stack cross-section, as required by Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the portholes; this minimizes the chance of extracting deposited material.

8.5.6 During the test run, make periodic adjustments to keep the temperature around the filter holder at the proper level to maintain the sample gas temperature exiting the filter; add more ice and, if necessary, salt to maintain a temperature of less than 20 °C (68 °F) at the condenser/silica gel outlet. Also, periodically check the level and zero of the manometer.

8.5.7 If the pressure drop across the filter becomes too high, making isokinetic sampling difficult to maintain, the filter may be replaced in the midst of the sample run. It is recommended that another complete filter assembly be used rather than attempting to change the filter itself. Before a new filter assembly is installed, conduct a leak check (see section 8.4.3). The total PM weight shall include the summation of the filter assembly catches.

8.5.8 A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator.

NOTE: When two or more trains are used, separate analyses of the front-half and (if applicable) impinger catches from each train shall be performed, unless identical nozzle sizes were used on all trains, in which case, the front-half catches from the individual trains may be combined (as may the impinger catches) and one analysis of front-half catch and one analysis of impinger catch may be performed. Consult with the Administrator for details concerning the calculation of results when two or more trains are used.

8.5.9 At the end of the sample run, close the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final DGM meter reading, and conduct a post-test leak check, as outlined in section 8.4.4. Also, leak-check the pitot lines as described in Method 2, section 8.1. The lines must pass this leak check, in order to validate the velocity head data.

8.6 Calculation of Percent Isokinetic. Calculate percent isokinetic (see Calculations, section 12.11) to determine whether the run was valid or another test run should be made. If there was difficulty in maintaining isokinetic rates because of source conditions, consult with the Administrator for possible variance on the isokinetic rates.

8.7 Sample Recovery.

8.7.1 Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

8.7.2 When the probe can be safely handled, wipe off all external PM near the tip of the probe nozzle, and place a cap over it to prevent losing or gaining PM. Do not cap off the probe tip tightly while the sampling train is cooling down. This would create a vacuum in the filter holder, thereby drawing water from the impingers into the filter holder.

8.7.3 Before moving the sample train to the cleanup site, remove the probe from the sample train and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Cap the filter inlet where the probe was fastened. Remove the umbilical cord from the last impinger, and cap the impinger. If a flexible line is used between the first impinger or condenser and the filter holder, disconnect the line at the filter holder, and let any condensed water or liquid drain into the impingers or condenser. Cap off the filter holder outlet and impinger inlet. Either ground-glass stoppers, plastic caps, or serum caps may be used to close these openings.

8.7.4 Transfer the probe and filter-impinger assembly to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

8.7.5 Save a portion of the acetone used for cleanup as a blank. From each storage container of acetone used for cleanup, save 200 ml and place in a glass sample container labeled ''acetone blank.'' To minimize any particulate contamination, rinse the wash bottle prior to filling from the tested container.

8.7.6 Inspect the train prior to and during disassembly, and note any abnormal conditions. Treat the samples as follows:

8.7.6.1 Container No. 1. Carefully remove the filter from the filter holder, and place it in its identified petri dish container. Use a pair of tweezers and/or clean disposable surgical gloves to handle the filter. If it is necessary to fold the filter, do so such that the PM cake is inside the fold. Using a dry Nylon bristle brush and/or a sharp-edged blade, carefully transfer to the petri dish any PM and/or filter fibers that adhere to the filter holder gasket. Seal the container.

8.7.6.2 Container No. 2. Taking care to see that dust on the outside of the probe or other

exterior surfaces does not get into the sample, quantitatively recover PM or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with acetone and placing the wash in a glass container. Deionized distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator. In these cases, save a water blank, and follow the Administrator's directions on analysis. Perform the acetone rinse as follows:

8.7.6.2.1 Carefully remove the probe nozzle. Clean the inside surface by rinsing with acetone from a wash bottle and brushing with a Nylon bristle brush. Brush until the acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

8.7.6.2.2 Brush and rinse the inside parts of the fitting with acetone in a similar way until no visible particles remain.

8.7.6.2.3 Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Let the acetone drain from the lower end into the sample container. A funnel (glass or polyethylene) may be used to aid in transferring liquid washes to the container. Follow the acetone rinse with a probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action through the probe; hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter that is brushed from the probe. Run the brush through the probe three times or more until no visible PM is carried out with the acetone or until none remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times since metal probes have small crevices in which particulate matter can be entrapped. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe.

8.7.6.2.4 It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

8.7.6.2.5 Clean the inside of the front half of the filter holder by rubbing the surfaces with a Nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone, also (if applicable). After all acetone washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to allow determination of whether leakage occurred during transport. Label the container to clearly identify its contents.

8.7.6.3 Container No. 3. Note the color of the indicating silica gel to determine whether it has been completely spent, and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container, and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, follow the procedure for Container No. 3 in section 11.2.3.

8.7.6.4 Impinger Water. Treat the impingers as follows: Make a notation of any color or film in the liquid catch. Measure the liquid that is in the first three impingers to within 1 ml by using a graduated cylinder or by weighing it to within 0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas. Discard the liquid after measuring and recording the volume or weight, unless analysis of the impinger catch is required (see NOTE, section 6.1.1.8). If a different type of condenser is used, measure the amount of moisture condensed either volumetrically or gravimetrically.

8.8 Sample Transport. Whenever possible, containers should be shipped in such a way that they remain upright at all times.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4, 10.1–10.6	Sampling equipment leak check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.

9.2 Volume Metering System Checks. The following procedures are suggested to check the volume metering system calibration values at the field test site prior to sample collection. These procedures are optional.

9.2.1 Meter Orifice Check. Using the calibration data obtained during the calibration procedure described in section 10.3, determine the ΔH@ for the metering system orifice. The ΔH@ is the orifice pressure differential in units of in. H_2O that correlates to 0.75 cfm of air at 528 °R and 29.92 in. Hg. The ΔH@ is calculated as follows:

$$\Delta H@ = 0.0319\ \Delta H \frac{T_M \theta^2}{P_{bar} Y^2 V_m^2}$$

Where:

ΔH = Average pressure differential across the orifice meter, in. H_2O.
T_m = Absolute average DGM temperature, °R.
P_{bar} = Barometric pressure, in. Hg.
θ = Total sampling time, min.
Y = DGM calibration factor, dimensionless.
V_m = Volume of gas sample as measured by DGM, dcf.
0.0319 = (0.0567 in. Hg/°R) (0.75 cfm)^2

9.2.1.1 Before beginning the field test (a set of three runs usually constitutes a field test), operate the metering system (*i.e.*, pump, volume meter, and orifice) at the ΔH@ pressure differential for 10 minutes. Record the volume collected, the DGM temperature, and the barometric pressure. Calculate a DGM calibration check value, Y_c, as follows:

$$Y_c = \frac{10}{V_m}\left[\frac{0.0319\ T_m}{P_{bar}}\right]^{\frac{1}{2}}$$

where:

Y_c = DGM calibration check value, dimensionless.
10 = Run time, min.

9.2.1.2 Compare the Y_c value with the dry gas meter calibration factor Y to determine that: $0.97Y < Y_c < 1.03Y$. If the Y_c value is not within this range, the volume metering system should be investigated before beginning the test.

9.2.2 Calibrated Critical Orifice. A critical orifice, calibrated against a wet test meter or spirometer and designed to be inserted at the inlet of the sampling meter box, may be used as a check by following the procedure of section 16.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Probe Nozzle. Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the ID of the nozzle to the nearest 0.025 mm (0.001 in.). Make three separate measurements using different diameters each time, and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

10.2 Pitot Tube Assembly. The Type S pitot tube assembly shall be calibrated according to the procedure outlined in section 10.1 of Method 2.

10.3 Metering System.

10.3.1 Calibration Prior to Use. Before its initial use in the field, the metering system shall be calibrated as follows: Connect the metering system inlet to the outlet of a wet test meter that is accurate to within 1 percent. Refer to Figure 5–4. The wet test meter should have a capacity of 30 liters/rev (1 ft^3/rev). A spirometer of 400 liters (14 ft^3) or more capacity, or equivalent, may be used for this calibration, although a wet test meter is usually more practical. The wet test meter should be periodically calibrated with a spirometer or a liquid displacement meter to ensure the accuracy of the wet test meter. Spirometers or wet test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained. Run the metering system pump for about 15 minutes with the orifice manometer indicating a median reading as expected in field use to allow the pump to warm up and to permit the interior surface of the wet test meter to be thoroughly wetted. Then, at each of a minimum of three orifice manometer settings, pass an exact quantity of gas through the wet test meter and note the gas volume indicated by the DGM. Also note the barometric pressure and the temperatures of the wet test meter, the inlet of the DGM, and the outlet of the DGM. Select the highest and lowest orifice settings to bracket the expected field operating range of the orifice. Use a minimum volume of 0.14 m^3 (5 ft^3) at all orifice settings. Record all the data on a form similar to Figure 5–5 and calculate Y, the DGM calibration factor, and ΔH , the orifice calibration factor, at each orifice setting as shown on Figure 5–5. Allowable tolerances for individual Y and ΔH values are given in Figure 5–5. Use the average of the Y values in the calculations in section 12.0.

10.3.1.1 Before calibrating the metering system, it is suggested that a leak check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. For these cases the following leak-check procedure is suggested: make a 10-minute calibration run at 0.00057 m^3/min (0.020 cfm). At the end of the run, take the difference of the measured wet test meter and DGM volumes. Divide the difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 m^3/min (0.020 cfm).

10.3.2 Calibration After Use. After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single, intermediate

orifice setting (based on the previous field test), with the vacuum set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet test meter and the inlet of the metering system. Calculate the average value of the DGM calibration factor. If the value has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as detailed in section 10.3.1.

NOTE: Alternative procedures (*e.g.*, rechecking the orifice meter coefficient) may be used, subject to the approval of the Administrator.

10.3.3 Acceptable Variation in Calibration Check. If the DGM coefficient values obtained before and after a test series differ by more than 5 percent, the test series shall either be voided, or calculations for the test series shall be performed using whichever meter coefficient value (*i.e.*, before or after) gives the lower value of total sample volume.

10.4 Probe Heater Calibration. Use a heat source to generate air heated to selected temperatures that approximate those expected to occur in the sources to be sampled. Pass this air through the probe at a typical sample flow rate while measuring the probe inlet and outlet temperatures at various probe heater settings. For each air temperature generated, construct a graph of probe heating system setting versus probe outlet temperature. The procedure outlined in APTD–0576 can also be used. Probes constructed according to APTD–0581 need not be calibrated if the calibration curves in APTD–0576 are used. Also, probes with outlet temperature monitoring capabilities do not require calibration.

NOTE: The probe heating system shall be calibrated before its initial use in the field.

10.5 Temperature Sensors. Use the procedure in Section 10.3 of Method 2 to calibrate in-stack temperature sensors. Dial thermometers, such as are used for the DGM and condenser outlet, shall be calibrated against mercury-in-glass thermometers. An alternative mercury-free NIST-traceable thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application. As an alternative, the following single-point calibration procedure may be used. After each test run series, check the accuracy (and, hence, the calibration) of each thermocouple system at ambient temperature, or any other temperature, within the range specified by the manufacturer, using a reference thermometer (either ASTM reference thermometer or a thermometer that has been calibrated against an ASTM reference thermometer). The temperatures of the thermocouple and reference thermometers shall agree to within ±2 °F.

10.6 Barometer. Calibrate against a mercury barometer or NIST-traceable barometer prior to the field test. Alternatively, barometric pressure may be obtained from a weather report that has been adjusted for the test point (on the stack) elevation.

10.7 Field Balance Calibration Check. Check the calibration of the balance used to weigh impingers with a weight that is at least 500g or within 50g of a loaded impinger. The weight must be ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 6 (or better). Daily before use, the field balance must measure the weight within ±0.5g of the certified mass. If the daily balance calibration check fails, perform corrective measures and repeat the check before using balance.

10.8 Analytical Balance Calibration. Perform a multipoint calibration (at least five points spanning the operational range) of the analytical balance before the first use, and semiannually thereafter. The calibration of the analytical balance must be conducted using ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 2 (or better) tolerance weights. Audit the balance each day it is used for gravimetric measurements by weighing at least one ASTM E617–13 Class 2 tolerance (or better) calibration weight that corresponds to 50 to 150 percent of the weight of one filter or between 1g and 5g. If the scale cannot reproduce the value of the calibration weight to within 0.5 mg of the certified mass, perform corrective measures, and conduct the multipoint calibration before use.

11.0 Analytical Procedure

11.1 Record the data required on a sheet such as the one shown in Figure 5–6.

11.2 Handle each sample container as follows:

11.2.1 Container No. 1. Leave the contents in the shipping container or transfer the filter and any loose PM from the sample container to a tared glass weighing dish. Desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh to a constant weight, and report the results to the nearest 0.1 mg. For the purposes of this section, the term ''constant weight'' means a difference of no more than 0.5 mg or 1 percent of total weight less tare weight, whichever is greater, between two consecutive weighings, with no less than 6 hours of desiccation time between weighings. Alternatively, the sample may be oven dried at 104 °C (220 °F) for 2 to 3 hours, cooled in the desiccator, and weighed to a constant weight, unless otherwise specified by the Administrator. The sample may be oven dried at 104 °C (220 °F) for 2 to 3 hours. Once the

sample has cooled, weigh the sample, and use this weight as a final weight.

11.2.2 Container No. 2. Note the level of liquid in the container, and confirm on the analysis sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to ±1 ml or gravimetrically to ±0.5 g. Transfer the contents to a tared 250 ml beaker, and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours, and weigh to a constant weight. Report the results to the nearest 0.1 mg.

11.2.3 Container No. 3. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. This step may be conducted in the field.

11.2.4 Acetone Blank Container. Measure the acetone in this container either volumetrically or gravimetrically. Transfer the acetone to a tared 250 ml beaker, and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours, and weigh to a constant weight. Report the results to the nearest 0.1 mg.

NOTE: The contents of Container No. 2 as well as the acetone blank container may be evaporated at temperatures higher than ambient. If evaporation is done at an elevated temperature, the temperature must be below the boiling point of the solvent; also, to prevent ''bumping,'' the evaporation process must be closely supervised, and the contents of the beaker must be swirled occasionally to maintain an even temperature. Use extreme care, as acetone is highly flammable and has a low flash point.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used, provided that they give equivalent results.

12.1 Nomenclature.

A_n = Cross-sectional area of nozzle, m^2 (ft^2).
B_{ws} = Water vapor in the gas stream, proportion by volume.
C_a = Acetone blank residue concentration, mg/mg.
c_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (gr/dscf).
I = Percent of isokinetic sampling.
L_1 = Individual leakage rate observed during the leak-check conducted prior to the first component change, m^3/min (ft^3/min)
L_a = Maximum acceptable leakage rate for either a pretest leak-check or for a leak-check following a component change; equal to 0.00057 m^3/min (0.020 cfm) or 4 percent of the average sampling rate, whichever is less.
L_i = Individual leakage rate observed during the leak-check conducted prior to the ''i^{th}'' component change (i = 1, 2, 3 . . . n), m^3/min (cfm).
L_p = Leakage rate observed during the post-test leak-check, m^3/min (cfm).
m_a = Mass of residue of acetone after evaporation, mg.
m_n = Total amount of particulate matter collected, mg.
M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).
P_s = Absolute stack gas pressure, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
R = Ideal gas constant, 0.06236 ((mm Hg)(m^3))/((K)(g-mole)) {21.85 ((in. Hg) (ft^3))/((°R)(lb-mole))}.
T_m = Absolute average DGM temperature (see Figure 5–3), K (°R).
T_s = Absolute average stack gas temperature (see Figure 5–3), K (°R).
T_{std} = Standard absolute temperature, 293 K (528 °R).
V_a = Volume of acetone blank, ml.
V_{aw} = Volume of acetone used in wash, ml.
V_{1c} = Total volume of liquid collected in impingers and silica gel (see Figure 5–6), ml.
V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).
$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).
$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).
V_s = Stack gas velocity, calculated by Method 2, Equation 2–7, using data obtained from Method 5, m/sec (ft/sec).
W_a = Weight of residue in acetone wash, mg.
Y = Dry gas meter calibration factor.
ΔH = Average pressure differential across the orifice meter (see Figure 5–4), mm H_2O (in. H_2O).
ρ_a = Density of acetone, mg/ml (see label on bottle).
ρ_w = Density of water, 0.9982 g/ml. (0.002201 lb/ml).
θ = Total sampling time, min.
θ_1 = Sampling time interval, from the beginning of a run until the first component change, min.
θ_i = Sampling time interval, between two successive component changes, beginning with the interval between the first and second changes, min.
θ_p = Sampling time interval, from the final (n^{th}) component change until the end of the sampling run, min.
13.6 = Specific gravity of mercury.
60 = Sec/min.

100 = Conversion to percent.

12.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 5–3).

12.3 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (20 °C, 760 mm Hg or 68 °F, 29.92 in. Hg) by using Equation 5–1.

$$V_{m(std)} = V_m Y \frac{T_{std}\left(P_{bar} + \frac{\Delta H}{13.6}\right)}{T_m P_{std}} \qquad \text{Eq. 5-1}$$

$$= K_1 V_m Y \frac{P_{bar} + \left(\frac{\Delta H}{13.6}\right)}{T_m}$$

Where:

K_1 = 0.3858 °K/mm Hg for metric units, = 17.64 °R/in. Hg for English units.

NOTE: Equation 5–1 can be used as written unless the leakage rate observed during any of the mandatory leak checks (*i.e.*, the post-test leak check or leak checks conducted prior to component changes) exceeds L_a. If L_p or L_i exceeds L_a, Equation 5–1 must be modified as follows:

(a) Case I. No component changes made during sampling run. In this case, replace V_m in Equation 5–1 with the expression:

$$\left(V_m - \left(L_p - L_a\right)\theta\right)$$

(b) Case II. One or more component changes made during the sampling run. In this case, replace V_m in Equation 5–1 by the expression:

$$\left[V_m - \left(L_1 - L_a\right)\theta_1 - \sum_{i=2}^{n}\left(L_1 - L_a\right)\theta_i - \left(L_p - L_a\right)\theta_p\right]$$

and substitute only for those leakage rates (L_i or L_p) which exceed L_a.

12.4 Volume of Water Vapor Condensed.

$$V_{w(std)} = V_{1c}\frac{\rho_w R T_{std}}{M_w P_{std}} \qquad \text{Eq. 5-2}$$

$$= K_2 V_{1c}$$

Where:

K_2 = 0.001333 m^3/ml for metric units, = 0.04706 ft^3/ml for English units.

12.5 Moisture Content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad \text{Eq. 5-3}$$

NOTE: In saturated or water droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation 5–3), and a second from the assumption of saturated conditions. The lower of the two values of B_{ws} shall be considered correct. The procedure for determining the moisture content based upon the assumption of saturated conditions is given in section 4.0 of Method 4. For the purposes of this method, the average stack gas temperature from Figure 5–3 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is ±1 °C (2 °F).

12.6 Acetone Blank Concentration.

$$C_a = \frac{m_a}{V_a \rho_a} \qquad \text{Eq. 5-4}$$

12.7 Acetone Wash Blank.

$$W_a = C_a V_{aw} \rho_a \qquad \text{Eq. 5-5}$$

12.8 Total Particulate Weight. Determine the total particulate matter catch from the sum of the weights obtained from Containers 1 and 2 less the acetone blank (see Figure 5–6).

NOTE: In no case shall a blank value of greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight. Refer to section 8.5.8 to assist in calculation of results involving two or more filter assemblies or two or more sampling trains.

12.9 Particulate Concentration.

$$C_s = \frac{K_3 m_n}{V_{m(std)}} \qquad \text{Eq. 5-6}$$

Where:

K_3 = 0.001 g/mg for metric units.
= 0.0154 gr/mg for English units.

12.10 Conversion Factors:

From	To	Multiply by
ft^3	m^3	0.02832
gr	mg	64.80004
gr/ft^3	mg/m^3	2288.4
mg	g	0.001
gr	lb	1.429×10^{-4}

12.11 Isokinetic Variation.

12.11.1 Calculation from Raw Data.

$$I = \frac{100\,T_s\left[K_4 V_{1c} + \frac{(V_m Y)}{T_m}\left(P_{bar} + \frac{\Delta H}{13.6}\right)\right]}{60\,\theta\,v_s\,P_s\,A_n} \qquad \text{Eq. 5-7}$$

Where:

K_4 = 0.003454 ((mm Hg)(m^3))/((ml)(°K)) for metric units,
= 0.002669 ((in. Hg)(ft^3))/((ml)(°R)) for English units.

12.11.2 Calculation from Intermediate Values.

$$I = \frac{T_s V_{m(std)} P_{std} 100}{T_{std} v_s \theta A_n P_s 60\left(1 - B_{ws}\right)} \qquad \text{Eq. 5-8}$$

$$= K_5 \frac{T_s V_{m(std)}}{P_s v_s A_n \theta\left(1 - B_{ws}\right)}$$

Where:

K_5 = 4.320 for metric units,
= 0.09450 for English units.

12.11.3 Acceptable Results. If 90 percent ≤I ≤110 percent, the results are acceptable. If the PM results are low in comparison to the standard, and ''I'' is over 110 percent or less than 90 percent, the Administrator may opt to accept the results. Reference 4 in section 17.0 may be used to make acceptability judgments. If ''I'' is judged to be unacceptable, reject the results, and repeat the sampling run.

12.12 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate, if needed, using data obtained in this method and the equations in sections 12.3 and 12.4 of Method 2.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Dry Gas Meter as a Calibration Standard. A DGM may be used as a calibration standard for volume measurements in place of the wet test meter specified in section 10.3, provided that it is calibrated initially and recalibrated periodically as follows:

16.1.1 Standard Dry Gas Meter Calibration.

16.1.1.1. The DGM to be calibrated and used as a secondary reference meter should be of high quality and have an appropriately sized capacity (*e.g.*, 3 liters/rev (0.1 ft^3/rev)). A spirometer (400 liters (14 ft^3) or more capacity), or equivalent, may be used for this calibration, although a wet test meter is usually more practical. The wet test meter should have a capacity of 30 liters/rev (1 ft^3/rev) and capable of measuring volume to within 1.0 percent. Wet test meters should be checked against a spirometer or a liquid displacement meter to ensure the accuracy of the wet test meter. Spirometers or wet test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained.

16.1.1.2 Set up the components as shown in Figure 5–7. A spirometer, or equivalent, may be used in place of the wet test meter in the system. Run the pump for at least 5 minutes at a flow rate of about 10 liters/min (0.35 cfm) to condition the interior surface of the wet test meter. The pressure drop indicated by the manometer at the inlet side of the DGM should be minimized (no greater than 100 mm

H_2O (4 in. H_2O) at a flow rate of 30 liters/min (1 cfm)). This can be accomplished by using large diameter tubing connections and straight pipe fittings.

16.1.1.3 Collect the data as shown in the example data sheet (see Figure 5–8). Make triplicate runs at each of the flow rates and at no less than five different flow rates. The range of flow rates should be between 10 and 34 liters/min (0.35 and 1.2 cfm) or over the expected operating range.

16.1.1.4 Calculate flow rate, Q, for each run using the wet test meter volume, V_w, and the run time, θ. Calculate the DGM coefficient, Y_{ds}, for each run. These calculations are as follows:

$$Q = K_1 \frac{P_{bar} V_w}{(T_w + T_{std})\theta} \qquad \text{Eq. 5-9}$$

$$Y_{ds} = \frac{V_w (T_{ds} + T_{std}) P_{bar}}{V_{ds} (T_w + T_{std}) \left(P_{bar} + \frac{\Delta p}{13.6} \right)} \qquad \text{Eq. 5-10}$$

Where:

K_1 = 0.3858 °C/mm Hg for metric units = 17.64 °F/in. Hg for English units.
V_W = Wet test meter volume, liter (ft^3).
V_{ds} = Dry gas meter volume, liter (ft^3).
T_{ds} = Average dry gas meter temperature, °C (°F).
T_{adj} = 273 °C for metric units = 460 °F for English units.
T_W = Average wet test meter temperature, °C (°F)
P_{bar} = Barometric pressure, mm Hg (in. Hg).
Δp = Dry gas meter inlet differential pressure, mm H_2O (in. H_2O).
θ = Run time, min.

16.1.1.5 Compare the three Y_{ds} values at each of the flow rates and determine the maximum and minimum values. The difference between the maximum and minimum values at each flow rate should be no greater than 0.030. Extra sets of triplicate runs may be made in order to complete this requirement. In addition, the meter coefficients should be between 0.95 and 1.05. If these specifications cannot be met in three sets of successive triplicate runs, the meter is not suitable as a calibration standard and should not be used as such. If these specifications are met, average the three Y_{ds} values at each flow rate resulting in no less than five average meter coefficients, Y_{ds}.

16.1.1.6 Prepare a curve of meter coefficient, Y_{ds}, versus flow rate, Q, for the DGM. This curve shall be used as a reference when the meter is used to calibrate other DGMs and to determine whether recalibration is required.

16.1.2 Standard Dry Gas Meter Recalibration.

16.1.2.1 Recalibrate the standard DGM against a wet test meter or spirometer annually or after every 200 hours of operation, whichever comes first. This requirement is valid provided the standard DGM is kept in a laboratory and, if transported, cared for as any other laboratory instrument. Abuse to the standard meter may cause a change in the calibration and will require more frequent recalibrations.

16.1.2.2 As an alternative to full recalibration, a two-point calibration check may be made. Follow the same procedure and equipment arrangement as for a full recalibration, but run the meter at only two flow rates [suggested rates are 14 and 30 liters/min (0.5 and 1.0 cfm)]. Calculate the meter coefficients for these two points, and compare the values with the meter calibration curve. If the two coefficients are within 1.5 percent of the calibration curve values at the same flow rates, the meter need not be recalibrated until the next date for a recalibration check.

16.2 Critical Orifices As Calibration Standards. Critical orifices may be used as calibration standards in place of the wet test meter specified in section 16.1, provided that they are selected, calibrated, and used as follows:

16.2.1 Selection of Critical Orifices.

16.2.1.1 The procedure that follows describes the use of hypodermic needles or stainless steel needle tubings which have been found suitable for use as critical orifices. Other materials and critical orifice designs may be used provided the orifices act as true critical orifices (*i.e.,* a critical vacuum can be obtained, as described in section 16.2.2.2.3). Select five critical orifices that are appropriately sized to cover the range of flow rates between 10 and 34 liters/min (0.35 and 1.2 cfm) or the expected operating range. Two of the critical orifices should bracket the expected operating range. A minimum of three critical orifices will be needed to calibrate a Method 5 DGM; the other two critical

orifices can serve as spares and provide better selection for bracketing the range of operating flow rates. The needle sizes and tubing lengths shown in Table 5–1 in section 18.0 give the approximate flow rates.

16.2.1.2 These needles can be adapted to a Method 5 type sampling train as follows: Insert a serum bottle stopper, 13 by 20 mm sleeve type, into a ½-inch Swagelok (or equivalent) quick connect. Insert the needle into the stopper as shown in Figure 5–9.

16.2.2 Critical Orifice Calibration. The procedure described in this section uses the Method 5 meter box configuration with a DGM as described in section 6.1.1.9 to calibrate the critical orifices. Other schemes may be used, subject to the approval of the Administrator.

16.2.2.1 Calibration of Meter Box. The critical orifices must be calibrated in the same configuration as they will be used (*i.e.*, there should be no connections to the inlet of the orifice).

16.2.2.1.1 Before calibrating the meter box, leak check the system as follows: Fully open the coarse adjust valve, and completely close the by-pass valve. Plug the inlet. Then turn on the pump, and determine whether there is any leakage. The leakage rate shall be zero (*i.e.*, no detectable movement of the DGM dial shall be seen for 1 minute).

16.2.2.1.2 Check also for leakages in that portion of the sampling train between the pump and the orifice meter. See section 8.4.1 for the procedure; make any corrections, if necessary. If leakage is detected, check for cracked gaskets, loose fittings, worn O-rings, etc., and make the necessary repairs.

16.2.2.1.3 After determining that the meter box is leakless, calibrate the meter box according to the procedure given in section 10.3. Make sure that the wet test meter meets the requirements stated in section 16.1.1.1. Check the water level in the wet test meter. Record the DGM calibration factor, Y.

16.2.2.2 Calibration of Critical Orifices. Set up the apparatus as shown in Figure 5–10.

16.2.2.2.1 Allow a warm-up time of 15 minutes. This step is important to equilibrate the temperature conditions through the DGM.

16.2.2.2.2 Leak check the system as in section 16.2.2.1.1. The leakage rate shall be zero.

16.2.2.2.3 Before calibrating the critical orifice, determine its suitability and the appropriate operating vacuum as follows: Turn on the pump, fully open the coarse adjust valve, and adjust the by-pass valve to give a vacuum reading corresponding to about half of atmospheric pressure. Observe the meter box orifice manometer reading, ΔH. Slowly increase the vacuum reading until a stable reading is obtained on the meter box orifice manometer. Record the critical vacuum for each orifice. Orifices that do not reach a critical value shall not be used.

16.2.2.2.4 Obtain the barometric pressure using a barometer as described in section 6.1.2. Record the barometric pressure, P_{bar}, in mm Hg (in. Hg).

16.2.2.2.5 Conduct duplicate runs at a vacuum of 25 to 50 mm Hg (1 to 2 in. Hg) above the critical vacuum. The runs shall be at least 5 minutes each. The DGM volume readings shall be in increments of complete revolutions of the DGM. As a guideline, the times should not differ by more than 3.0 seconds (this includes allowance for changes in the DGM temperatures) to achieve ±0.5 percent in K′ (see Eq. 5–11). Record the information listed in Figure 5–11.

16.2.2.2.6 Calculate K′ using Equation 5–11.

$$K' = \frac{K_1 V_m Y \left(P_{bar} + \frac{\Delta H}{13.6} \right) T_{amb}^{1/2}}{P_{bar} T_m \theta} \qquad \text{Eq. 5-11}$$

Where:

K′ = Critical orifice coefficient,
$[m^3)(°K)^{1/2}]/$
$[(mm\ Hg)(min)]\ \{[(ft^3)(°R)^{1/2})]\ [(in.\ Hg)(min)]$.

T_{amb} = Absolute ambient temperature, °K (°R).

Calculate the arithmetic mean of the K′ values. The individual K' values should not differ by more than ±0.5 percent from the mean value.

16.2.3 Using the Critical Orifices as Calibration Standards.

16.2.3.1 Record the barometric pressure.

16.2.3.2 Calibrate the metering system according to the procedure outlined in section 16.2.2. Record the information listed in Figure 5–12.

16.2.3.3 Calculate the standard volumes of air passed through the DGM and the critical orifices, and calculate the DGM calibration factor, Y, using the equations below:

$$V_{m(std)} = \frac{K_1 V_m \left[P_{bar} + \left(\frac{\Delta H}{13.6} \right) \right]}{T_m} \qquad \text{Eq. 5-12}$$

$$V_{cr(std)} = K' \frac{P_{bar}\theta}{\sqrt{T_{amb}}} \qquad \text{Eq. 5-13}$$

$$Y = \frac{V_{cr\ (std)}}{V_{m(std)}} \qquad \text{Eq. 5-14}$$

Where:

$V_{cr(std)}$ = Volume of gas sample passed through the critical orifice, corrected to standard conditions, dscm (dscf).

K_1 = 0.3858 K/mm Hg for metric units
= 17.64 °R/in. Hg for English units.

16.2.3.4 Average the DGM calibration values for each of the flow rates. The calibration factor, Y, at each of the flow rates should not differ by more than ±2 percent from the average.

16.2.3.5 To determine the need for recalibrating the critical orifices, compare the DGM Y factors obtained from two adjacent orifices each time a DGM is calibrated; for example, when checking orifice 13/2.5, use orifices 12/10.2 and 13/5.1. If any critical orifice yields a DGM Y factor differing by more than 2 percent from the others, recalibrate the critical orifice according to section 16.2.2.

16.3 Alternative Post-Test Metering System Calibration. The following procedure may be used as an alternative to the post-test calibration described in Section 10.3.2. This alternative procedure does not detect leakages between the inlet of the metering system and the dry gas meter. Therefore, two steps must be included to make it an equivalent alternative:

(1) The metering system must pass the post-test leak-check from either the inlet of the sampling train or the inlet of the metering system. Therefore, if the train fails the former leak-check, another leak-check from the inlet of the metering system must be conducted;

(2) The metering system must pass the leak-check of that portion of the train from the pump to the orifice meter as described in Section 8.4.1.

16.3.1 After each test run, do the following:

16.3.1.1 Ensure that the metering system has passed the post-test leak-check. If not, conduct a leak-check of the metering system from its inlet.

16.3.1.2 Conduct the leak-check of that portion of the train from the pump to the orifice meter as described in Section 10.3.1.1.

16.3.1.3 Calculate Y_{qa} for each test run using the following equation:

$$Y_{qa} = \frac{\theta}{V_m} \sqrt{\frac{0.0319 T_m}{\Delta H@ \left(P_{bar} + \frac{\Delta H_{avg}}{13.6} \right)} \left(\frac{29}{M_d} \right)} \left(\sqrt{\Delta H} \right)_{avg} \qquad \text{Eq. 5-15}$$

Where:

Y_{qa} = Dry gas meter calibration check value, dimensionless.

0.0319 = (29.92/528) (0.75)^2 (in. Hg/°R) cfm^2.

$\Delta H@$ = Orifice meter calibration coefficient, in. H_2O.

M_d = Dry molecular weight of stack gas, lb/lb-mole.

29 = Dry molecular weight of air, lb/lb-mole.

16.3.2 After each test run series, do the following:

16.3.2.1 Average the three or more Y_{qa}'s obtained from the test run series and compare this average Y_{qa} with the dry gas meter calibration factor Y. The average Y_{qa} must be within 5 percent of Y.

16.3.2.2 If the average Y_{qa} does not meet the 5 percent criterion, recalibrate the meter

over the full range of orifice settings as detailed in Section 10.3.1. Then follow the procedure in Section 10.3.3.

17.0 References.

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13. Shigehara, Roger T., P.G. Royals, and E.W. Steward. ''Alternative Method 5 Post-Test Calibration.'' Entropy Incorporated, Research Triangle Park, NC 27709.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 5–1 FLOR RATES FOR VARIOUS NEEDLE SIZES AND TUBE LENGTHS

Gauge/cm	Flow rate liters/min.	Gauge/cm	Flow rate liters/min.
12/7.6	32.56	14/2.5	19.54
12/10.2	30.02	14/5.1	17.27
13/2.5	25.77	14/7.6	16.14
13/5.1	23.50	15/3.2	14.16
13/7.6	22.37	15/7.6	11.61
13/10.2	20.67	15/10.2	10.48

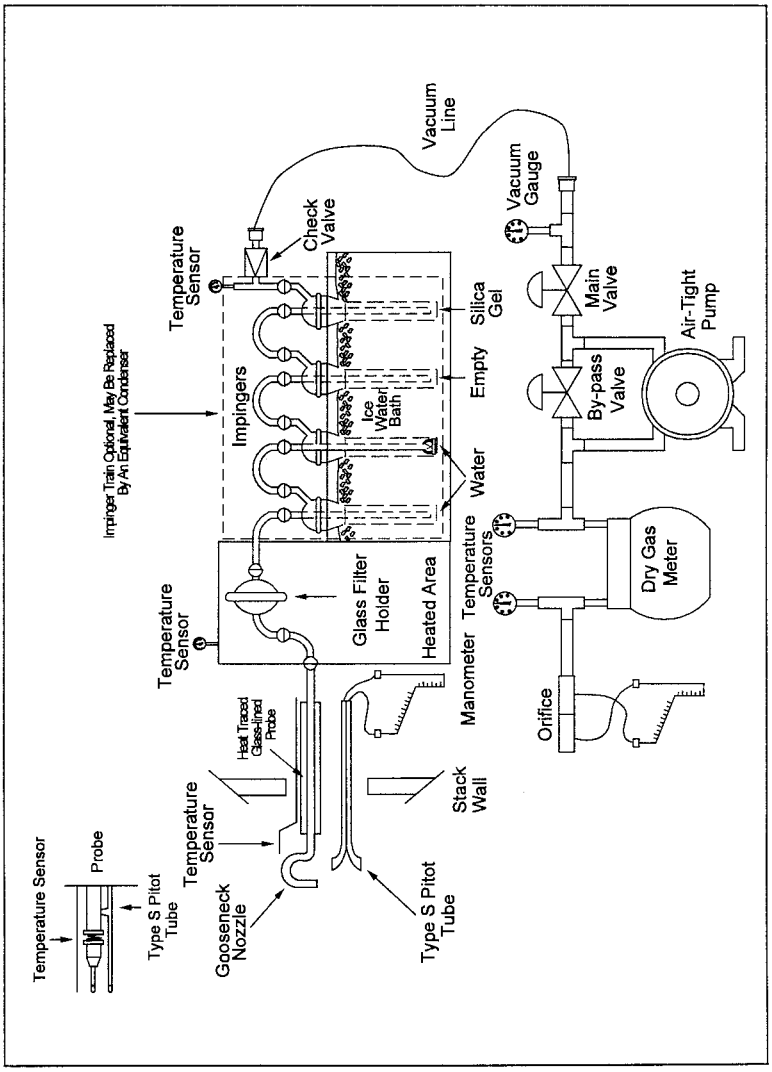


Figure 5-1. Particulate Sampling Train.

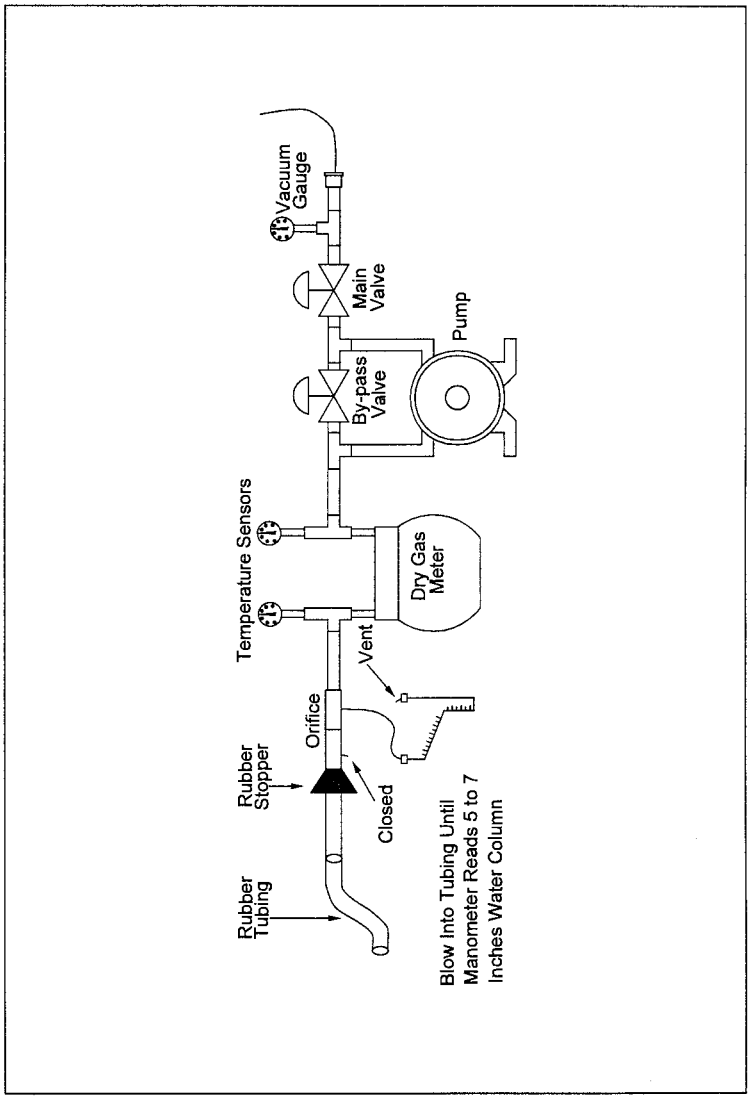


Figure 5-2. Leak Check of Meter Box.

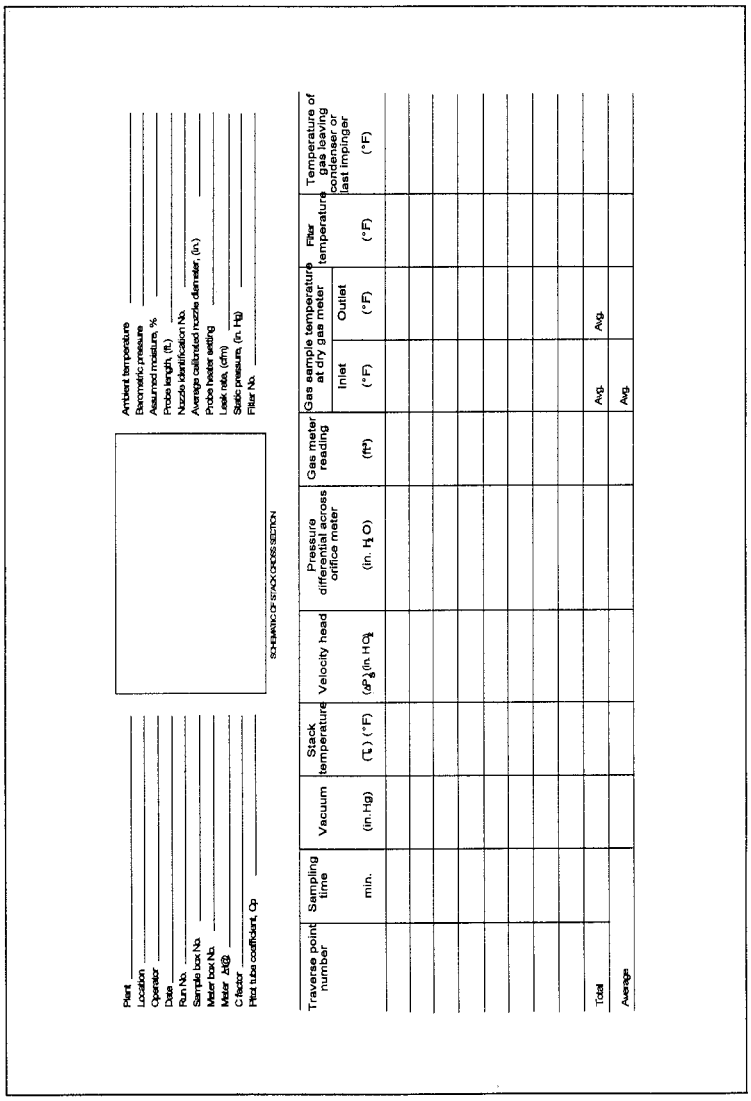


Figure 5-3. Particulate Field Data.

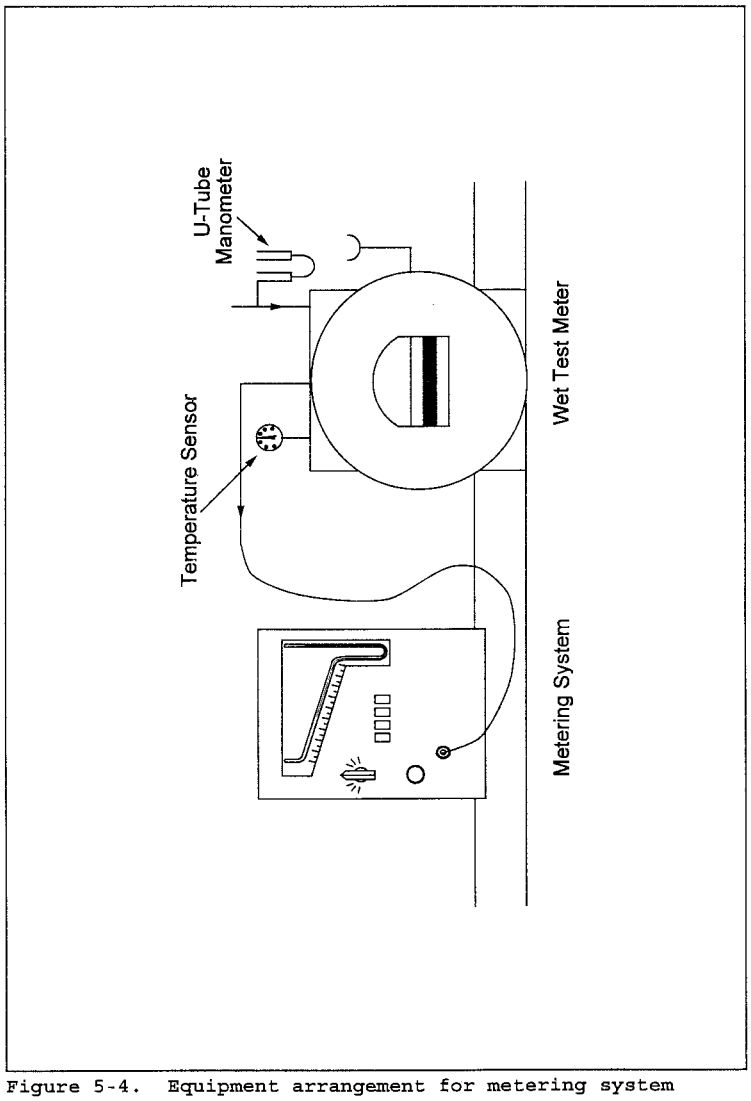
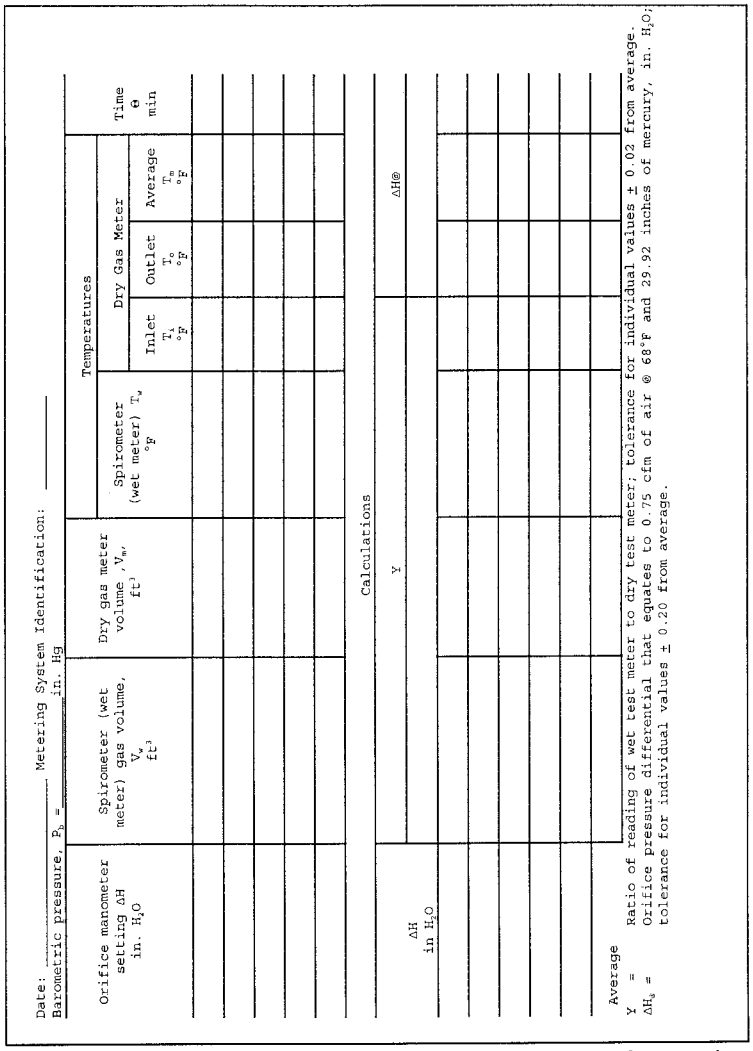


Figure 5-4. Equipment arrangement for metering system calibration.



Date: _____ Metering System Identification: _____
Barometric pressure, P_b = _____ in. Hg

Orifice manometer setting ΔH in. H_2O	Spirometer (wet meter) gas volume, V_w, ft^3	Dry gas meter volume, V_m, ft^3	Temperatures: Spirometer (wet meter) T_w °F	Temperatures: Dry Gas Meter Inlet T_i °F	Temperatures: Dry Gas Meter Outlet T_o °F	Temperatures: Dry Gas Meter Average T_m °F	Time θ min
Average							

Calculations

ΔH in H_2O	Y	ΔH@

Y = Ratio of reading of wet test meter to dry test meter; tolerance for individual values ± 0.02 from average.
$\Delta H_@$ = Orifice pressure differential that equates to 0.75 cfm of air @ 68°F and 29.92 inches of mercury, in. H_2O; tolerance for individual values ± 0.20 from average.

Figure 5-5. Example Data Sheet for Calibration of Metering System (English Units).

Plant _____
Date _____
Run No. _____
Filter No. _____
Amount liquid lost during transport _____

Acetone blank volume, m1 _____
Acetone blank concentration, mg/mg (Equation 5–4) _____
Acetone wash blank, mg (Equation 5–5) ____

Container number	Weight of particulate collected, mg		
	Final weight	Tare weight	Weight gain
1.			
2.			
Total: Less acetone blank. Weight of particulate matter.			

	Volume of liquid water collected	
	Impinger volume, ml	Silica gel weight, g
Final Initial Liquid collected Total volume collected	.....	g* ml

*Convert weight of water to volume by dividing total weight increase by density of water (1 g/ml).

Figure 5–6. Analytical Data Sheet

$$\frac{\text{Increase, g}}{(1\text{g/ml})} = \text{Volume water, ml}$$

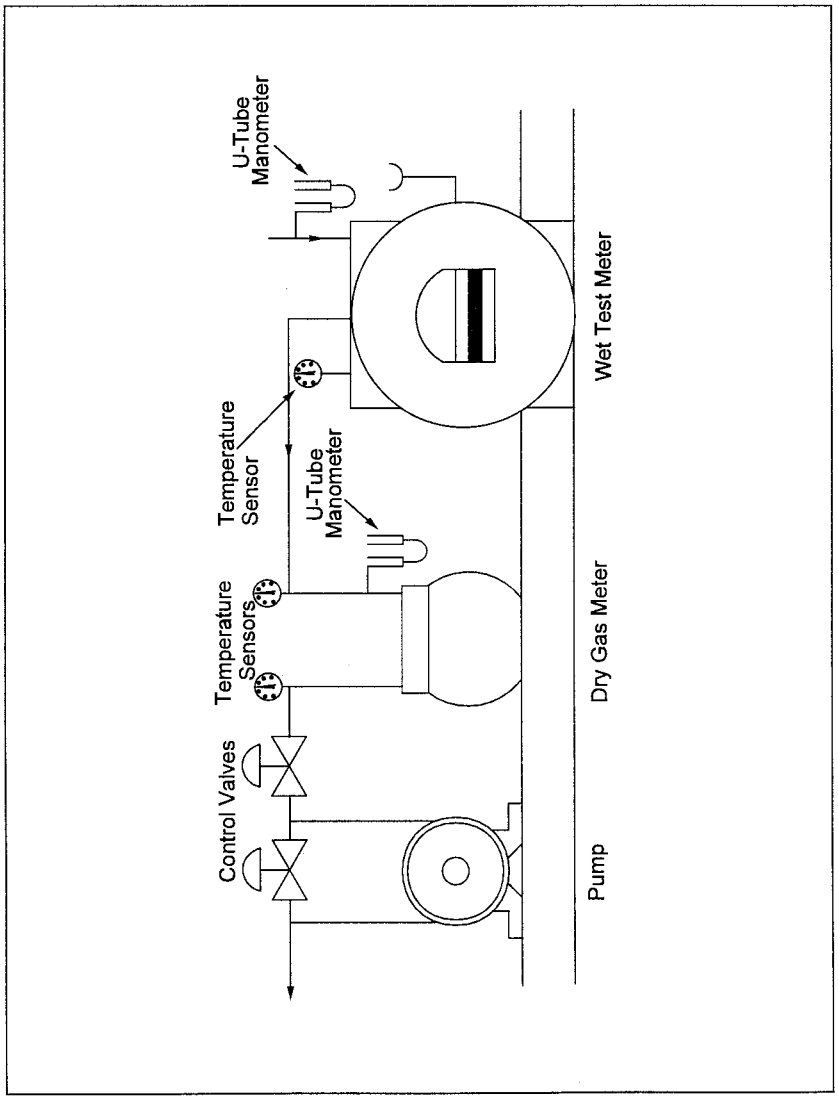


Figure 5-7. Equipment Arrangement for Dry Gas Meter Calibration.

Date: _____

Dry Gas Meter Identification: _____

Barometric Pressure (P): _____ in. Hg

Approximate Flow Rate (Q) cfm	Spirometer (Wet Meter) Gas Volume (V_s) ft³	Dry Gas Meter Volume (V_{dg}) ft³	Temperatures: Spirometer (Wet Meter) (t_g) °F	Temperatures: Dry Gas Meter Inlet (t_i) °F	Temperatures: Dry Gas Meter Outlet (t_o) °F	Temperatures: Dry Gas Meter Average (t_d) °F	Dry Gas Meter Pressure (Δp) in. H_2O	Time (θ) ft³	Flow Rate (Q) cfm	Meter Coefficient (Y_{ds})	Average Meter Coefficient ($\overline{Y}_{ds}$)
0.40											
0.60											
0.80											
1.00											
1.20											

$$Q = K_1 \frac{P_{bar} V_w}{(T_w + T_{std}) Q}$$

$$Y_{ds} = \frac{V_w (T_{ds} + T_{std}) P_{bar}}{V_{ds} (T_w + T_{std}) (P_{bar} + \Delta P/13.6)}$$

Figure 5-8. Example Data Sheet for Calibration of a Standard Dry Gas Meter for Method 5 Sampling Equipment (English units).

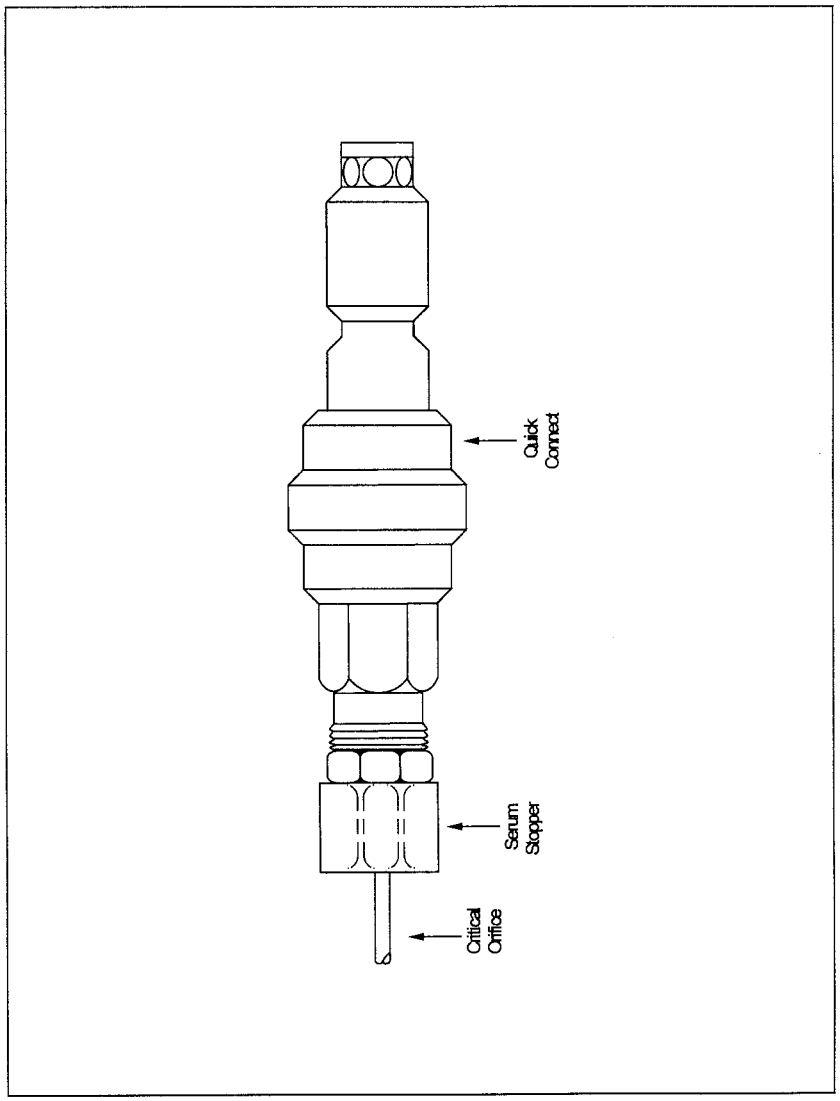


Figure 5-9. Critical Orifice Adaptation to Method 5 Metering System.

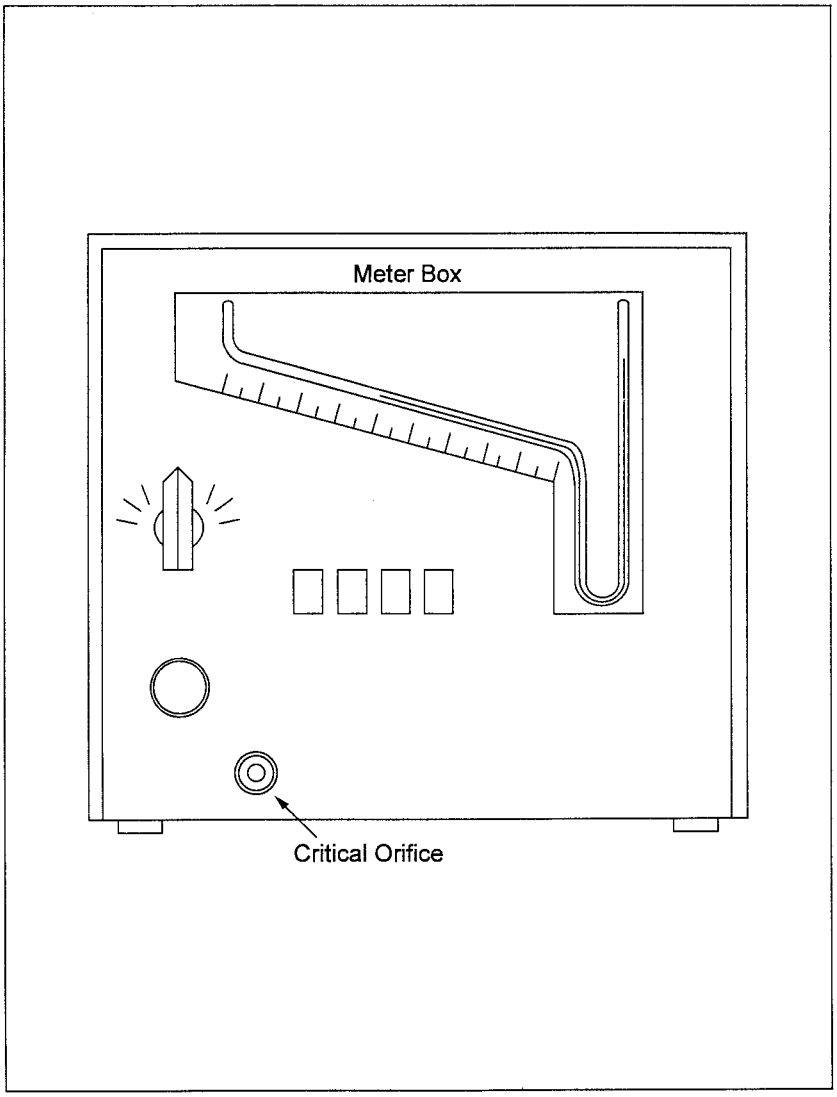


Figure 5-10. Apparatus Setup.

Date _____ DGM cal. factor _____
Train ID _____ Critical orifice ID _____

Dry gas meter		Run No.	
		1	2
Final reading	m^3 (ft^3)		
Initial reading	m^3 (ft^3)		
Difference, V_m	m^3 (ft^3)		
Inlet/Outlet			

Dry gas meter		Run No.	
		1	2
Temperatures:	°C (°F)	/	/
Initial	°C (°F)	/	/
Final	min/sec	/	/
Av. Temeperature, t_m	min		
Time, θ			
Orifice man. rdg., ΔH	mm (in.) H_2		
Bar. pressure, P^{bar}	mm (in.) Hg		
Ambient temperature, t_{amb}	mm (in.) Hg		
Pump vacuum			
K′ factor			
Average			

Figure 5–11. Data sheet of determining K′ factor.

Train ID _____
Critical orifice ID _____
Critical orifice K' factor _____

Date _____

Dry gas meter		Run No.	
		1	2
Final reading	m^3 (ft^3)		
Initial reading	m^3 (ft^3)		
Difference, V_m	m^3 (ft^3)		
Inlet/outlet temperatures	°C (°F)	/	/
Initial	°C (°F)	/	/
Final	°C (°F)		
Avg. Temperature, t_m	min/sec	/	/
Time, θ	min		
Orifice man. rdg., ΔH	min		
Bar. pressure, P_{bar}	mm (in.) H_2O		
Ambient temperature, t_{amb}	mm (in.) Hg		
Pump vacuum	°C (°F)		
$V_{m(std)}$	mm (in.) Hg		
$V_{cr(std)}$	m^3 (ft^3)		
DGM cal. factor, Y	m^3 (ft^3)		

Figure 5–12. Data Sheet for Determining DGM Y Factor

Method 5A—Determination of Particulate Matter Emissions From the Asphalt Processing and Asphalt Roofing Industry

Note: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5.

1.0 Scope and Applications

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of PM emissions from asphalt roofing industry process saturators, blowing stills, and other sources as specified in the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature of 42 ±10 °C (108 ±18 °F). The PM mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after the removal of uncombined water.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the

applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 5, section 6.1, with the following exceptions and additions:

6.1.1 Probe Liner. Same as Method 5, section 6.1.1.2, with the note that at high stack gas temperatures greater than 250 °C (480 °F), water-cooled probes may be required to control the probe exit temperature to 42 ±10 °C (108 ±18 °F).

6.1.2 Precollector Cyclone. Borosilicate glass following the construction details shown in Air Pollution Technical Document (APTD)–0581, ''Construction Details of Isokinetic Source-Sampling Equipment'' (Reference 2 in Method 5, section 17.0).

NOTE: The cyclone shall be used when the stack gas moisture is greater than 10 percent, and shall not be used otherwise.

6.1.3 Filter Heating System. Any heating (or cooling) system capable of maintaining a sample gas temperature at the exit end of the filter holder during sampling at 42 ±10 °C (108 ±18 °F).

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Probe-Liner and Probe-Nozzle Brushes, Graduated Cylinder and/or Balance, Plastic Storage Containers, and Funnel and Rubber Policeman. Same as in Method 5, sections 6.2.1, 6.2.5, 6.2.6, and 6.2.7, respectively.

6.2.2 Wash Bottles. Glass.

6.2.3 Sample Storage Containers. Chemically resistant 500-ml or 1,000-ml borosilicate glass bottles, with rubber-backed Teflon screw cap liners or caps that are constructed so as to be leak-free, and resistant to chemical attack by 1,1,1-trichloroethane (TCE). (Narrow-mouth glass bottles have been found to be less prone to leakage.)

6.2.4 Petri Dishes. Glass, unless otherwise specified by the Administrator.

6.2.5 Funnel. Glass.

6.3 Sample Analysis. Same as Method 5, section 6.3, with the following additions:

6.3.1 Beakers. Glass, 250-ml and 500-ml.

6.3.2 Separatory Funnel. 100-ml or greater.

7.0. Reagents and Standards

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Filters, Silica Gel, Water, and Crushed Ice. Same as in Method 5, sections 7.1.1, 7.1.2, 7.1.3, and 7.1.4, respectively.

7.1.2 Stopcock Grease. TCE-insoluble, heat-stable grease (if needed). This is not necessary if screw-on connectors with Teflon sleeves, or similar, are used.

7.2 Sample Recovery. Reagent grade TCE, ≤0.001 percent residue and stored in glass bottles. Run TCE blanks before field use, and use only TCE with low blank values (≤0.001 percent). In no case shall a blank value of greater than 0.001 percent of the weight of TCE used be subtracted from the sample weight.

7.3 Analysis. Two reagents are required for the analysis:

7.3.1 TCE. Same as in section 7.2.

7.3.2 Desiccant. Same as in Method 5, section 7.3.2.

8.0. Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation. Unless otherwise specified, maintain and calibrate all components according to the procedure described in APTD–0576, ''Maintenance, Calibration, and Operation of Isokinetic Source-Sampling Equipment'' (Reference 3 in Method 5, Section 17.0). Alternative mercury-free thermometers may be used if the thermometers are, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

8.1.1 Prepare probe liners and sampling nozzles as needed for use. Thoroughly clean each component with soap and water followed by a minimum of three TCE rinses. Use the probe and nozzle brushes during at least one of the TCE rinses (refer to section 8.7 for rinsing techniques). Cap or seal the open ends of the probe liners and nozzles to prevent contamination during shipping.

8.1.2 Prepare silica gel portions and glass filters as specified in Method 5, section 8.1.

8.2 Preliminary Determinations. Select the sampling site, probe nozzle, and probe length as specified in Method 5, section 8.2. Select a total sampling time greater than or equal to the minimum total sampling time specified in the ''Test Methods and Procedures'' section of the applicable subpart of the regulations. Follow the guidelines outlined in Method 5, section 8.2 for sampling time per point and total sample volume collected.

8.3 Preparation of Sampling Train. Prepare the sampling train as specified in Method 5, section 8.3, with the addition of the precollector cyclone, if used, between the probe and filter holder. The temperature of the precollector cyclone, if used, should be maintained in the same range as that of the filter, *i.e.*, 42 ±10 °C (108 ±18 °F). Use no stopcock grease on ground glass joints unless grease is insoluble in TCE.

8.4 Leak-Check Procedures. Same as Method 5, section 8.4.

8.5 Sampling Train Operation. Operate the sampling train as described in Method 5, section 8.5, except maintain the temperature of the gas exiting the filter holder at 42 ±10 °C (108 ±18 °F).

8.6 Calculation of Percent Isokinetic. Same as Method 5, section 8.6.

8.7 Sample Recovery. Same as Method 5, section 8.7.1 through 8.7.6.1, with the addition of the following:

8.7.1 Container No. 2 (Probe to Filter Holder).

8.7.1.1 Taking care to see that material on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover PM or any condensate from the probe nozzle, probe fitting, probe liner, precollector cyclone and collector flask (if used), and front half of the filter holder by washing these components with TCE and placing the wash in a glass container. Carefully measure the total amount of TCE used in the rinses. Perform the TCE rinses as described in Method 5, section 8.7.6.2, using TCE instead of acetone.

8.7.1.2 Brush and rinse the inside of the cyclone, cyclone collection flask, and the front half of the filter holder. Brush and rinse each surface three times or more, if necessary, to remove visible PM.

8.7.2 Container No. 3 (Silica Gel). Same as in Method 5, section 8.7.6.3.

8.7.3 Impinger Water. Same as Method 5, section 8.7.6.4.

8.8 Blank. Save a portion of the TCE used for cleanup as a blank. Take 200 ml of this TCE directly from the wash bottle being used, and place it in a glass sample container labeled ''TCE Blank.''

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4, 10.0	Sampling equipment leak check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.

9.2 A quality control (QC) check of the volume metering system at the field site is suggested before collecting the sample. Use the procedure outlined in Method 5, section 9.2.

10.0 Calibration and Standardization

Same as Method 5, section 10.0.

11.0 Analytical Procedures

11.1 Analysis. Record the data required on a sheet such as the one shown in Figure 5A–1. Handle each sample container as follows:

11.1.1 Container No. 1 (Filter). Transfer the filter from the sample container to a tared glass weighing dish, and desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Rinse Container No. 1 with a measured amount of TCE, and analyze this rinse with the contents of Container No. 2. Weigh the filter to a constant weight. For the purpose of this analysis, the term ''constant weight'' means a difference of no more than 10 percent of the net filter weight or 2 mg (whichever is greater) between two consecutive weighings made 24 hours apart. Report the ''final weight'' to the nearest 0.1 mg as the average of these two values.

11.1.2 Container No. 2 (Probe to Filter Holder).

11.1.2.1 Before adding the rinse from Container No. 1 to Container No. 2, note the level of liquid in Container No. 2, and confirm on the analysis sheet whether leakage occurred during transport. If noticeable leakage occurred, either void the sample or take steps, subject to the approval of the Administrator, to correct the final results.

11.1.2.2 Add the rinse from Container No. 1 to Container No. 2 and measure the liquid in this container either volumetrically to ±1 ml or gravimetrically to ±0.5 g. Check to see whether there is any appreciable quantity of condensed water present in the TCE rinse (look for a boundary layer or phase separation). If the volume of condensed water appears larger than 5 ml, separate the oil-TCE fraction from the water fraction using a separatory funnel. Measure the volume of the water phase to the nearest ml; adjust the stack gas moisture content, if necessary (see sections 12.3 and 12.4). Next, extract the water phase with several 25-ml portions of TCE until, by visual observation, the TCE does not remove any additional organic material. Transfer the remaining water fraction to a tared beaker and evaporate to dryness at 93 °C (200 °F), desiccate for 24 hours, and weigh to the nearest 0.1 mg.

11.1.2.3 Treat the total TCE fraction (including TCE from the filter container rinse and water phase extractions) as follows: Transfer the TCE and oil to a tared beaker, and evaporate at ambient temperature and pressure. The evaporation of TCE from the solution may take several days. Do not desiccate the sample until the solution reaches an apparent constant volume or until the odor of TCE is not detected. When it appears that the TCE has evaporated, desiccate the sample, and weigh it at 24-hour intervals to obtain a ''constant weight'' (as defined for Container No. 1 above). The ''total weight'' for Container No. 2 is the sum of the evaporated PM weight of the TCE-oil and water phase fractions. Report the results to the nearest 0.1 mg.

11.1.3 Container No. 3 (Silica Gel). This step may be conducted in the field. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance.

11.1.4 ''TCE Blank'' Container. Measure TCE in this container either volumetrically or gravimetrically. Transfer the TCE to a tared 250-ml beaker, and evaporate to dryness at ambient temperature and pressure.

Desiccate for 24 hours, and weigh to a constant weight. Report the results to the nearest 0.1 mg.

NOTE: In order to facilitate the evaporation of TCE liquid samples, these samples may be dried in a controlled temperature oven at temperatures up to 38 °C (100 °F) until the liquid is evaporated.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

12.1 Nomenclature. Same as Method 5, section 12.1, with the following additions:

C_t = TCE blank residue concentration, mg/g.
m_t = Mass of residue of TCE blank after evaporation, mg.
V_{pc} = Volume of water collected in precollector, ml.
V_t = Volume of TCE blank, ml.
V_{tw} = Volume of TCE used in wash, ml.
W_t = Weight of residue in TCE wash, mg.
ρ_t = Density of TCE (see label on bottle), g/ml.

12.2 Dry Gas Meter Temperature, Orifice Pressure Drop, and Dry Gas Volume. Same as Method 5, sections 12.2 and 12.3, except use data obtained in performing this test.

12.3 Volume of Water Vapor.

$$V_{w(std)} = K_2\left(V_{1c} + V_{pc}\right) \qquad \text{Eq. 5A-1}$$

Where:

K_2 = 0.001333 m^3/ml for metric units.
= 0.04706 ft^3/ml for English units.

12.4 Moisture Content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad \text{Eq. 5A-2}$$

NOTE: In saturated or water droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger and precollector analysis (Equations 5A–1 and 5A–2) and a second from the assumption of saturated conditions. The lower of the two values of moisture content shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in section 4.0 of Method 4. For the purpose of this method, the average stack gas temperature from Figure 5–3 of Method 5 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is within 1 °C (2 °F).

12.5 TCE Blank Concentration.

$$C_t = \frac{m_t}{V_t \rho_t} \qquad \text{Eq. 5A-3}$$

NOTE: In no case shall a blank value of greater than 0.001 percent of the weight of TCE used be subtracted from the sample weight.

12.6 TCE Wash Blank.

$$W_t = C_t V_{tw} \rho_t \qquad \text{Eq. 5A-4}$$

12.7 Total PM Weight. Determine the total PM catch from the sum of the weights obtained from Containers 1 and 2, less the TCE blank.

12.8 PM Concentration.

$$c_s = K_3 \frac{m_n}{V_{m(std)}} \qquad \text{Eq. 5A-5}$$

Where:

K_3 = 0.001 g/mg for metric units
= 0.0154 gr/mg for English units

12.9 Isokinetic Variation. Same as in Method 5, section 12.11.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 5, section 17.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

Plant _____
Date _____
Run No. _____
Filter No. _____
Amount liquid lost during transport _____
Acetone blank volume, ml _____
Acetone blank concentration, mg/mg (Equation 5–4) _____
Acetone wash blank, mg (Equation 5–5) _____

Container number	Weight of particulate collected, mg		
	Final weight	Tare weight	Weight gain
1.			
2.			
Total: Less acetone blank.			

Container number	Weight of particulate collected, mg		
	Final weight	Tare weight	Weight gain
Weight of particulate matter.			

	Volume of liquid water collected	
	Impinger volume, ml	Silica gel weight, g
Final		
Initial		
Liquid collected		
Total volume collected		g* ml

*Convert weight of water to volume by dividing total weight increase by density of water (1 g/ml).

$$\frac{\text{Increase, g}}{(1\text{g/ml})} = \text{Volume water, ml}$$

METHOD 5B—DETERMINATION OF NONSULFURIC ACID PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5.

1.0 Scope and Application

1.1 Analyte. Nonsulfuric acid particulate matter. No CAS number assigned.

1.2 Applicability. This method is determining applicable for the determination of nonsulfuric acid particulate matter from stationary sources, only where specified by an applicable subpart of the regulations or where approved by the Administrator for a particular application.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature of 160 ±14 °C (320 ±25 °F). The collected sample is then heated in an oven at 160 °C (320 °F) for 6 hours to volatilize any condensed sulfuric acid that may have been collected, and the nonsulfuric acid particulate mass is determined gravimetrically.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

Same as Method 5, section 6.0, with the following addition and exceptions:

6.1 Sample Collection. The probe liner heating system and filter heating system must be capable of maintaining a sample gas temperature of 160 ±14 °C (320 ±25 °F).

6.2 Sample Preparation. An oven is required for drying the sample.

7.0 Reagents and Standards

Same as Method 5, section 7.0.

8.0 Sample Collection, Preservation, Storage, and Transport.

Same as Method 5, with the exception of the following:

8.1 Initial Filter Tare. Oven dry the filter at 160 ±5 °C (320 ±10 °F) for 2 to 3 hours, cool in a desiccator for 2 hours, and weigh. Desiccate to constant weight to obtain the initial tare weight. Use the applicable specifications and techniques of section 8.1.3 of Method 5 for this determination.

8.2 Probe and Filter Temperatures. Maintain the probe outlet and filter temperatures at 160 ±14 °C (320 ±25 °F).

9.0 Quality Control

Same as Method 5, section 9.0.

10.0 Calibration and Standardization

Same as Method 5, section 10.0.

11.0 Analytical Procedure

Same as Method 5, section 11.0, except replace section

11.2.2 With the following:

11.1 Container No. 2. Note the level of liquid in the container, and confirm on the analysis sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to ±1 ml or gravimetrically to ±0.5 g. Transfer the contents to a tared 250 ml beaker, and evaporate to dryness at ambient temperature and pressure. Then oven dry the probe and filter samples at a temperature of 160 ±5 °C (320 ±10 °F) for 6 hours. Cool in a desiccator for 2 hours, and weigh to constant weight. Report the results to the nearest 0.1 mg.

12.0 Data Analysis and Calculations

Same as in Method 5, section 12.0.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 5, section 17.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 5C [RESERVED]

METHOD 5D—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM POSITIVE PRESSURE FABRIC FILTERS

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, Method 17.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability.

1.2.1 This method is applicable for the determination of PM emissions from positive pressure fabric filters. Emissions are determined in terms of concentration (mg/m^3 or gr/ft^3) and emission rate (kg/hr or lb/hr).

1.2.2 The General Provisions of 40 CFR part 60, §60.8(e), require that the owner or operator of an affected facility shall provide performance testing facilities. Such performance testing facilities include sampling ports, safe sampling platforms, safe access to sampling sites, and utilities for testing. It is intended that affected facilities also provide sampling locations that meet the specification for adequate stack length and minimal flow disturbances as described in Method 1. Provisions for testing are often overlooked factors in designing fabric filters or are extremely costly. The purpose of this procedure is to identify appropriate alternative locations and procedures for sampling the emissions from positive pressure fabric filters. The requirements that the affected facility owner or operator provide adequate access to performance testing facilities remain in effect.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature at or above the exhaust gas temperature up to a nominal 120 °C (248 ±25 °F). The particulate mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after the removal of uncombined water.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

Same as section 6.0 of either Method 5 or Method 17.

7.0 Reagents and Standards

Same as section 7.0 of either Method 5 or Method 17.

8.0 Sample Collection, Preservation, Storage, and Transport

Same section 8.0 of either Method 5 or Method 17, except replace section 8.2.1 of Method 5 with the following:

8.1 Determination of Measurement Site. The configuration of positive pressure fabric filter structures frequently are not amenable

to emission testing according to the requirements of Method 1. Following are several alternatives for determining measurement sites for positive pressure fabric filters.

8.1.1 Stacks Meeting Method 1 Criteria. Use a measurement site as specified in Method 1, section 11.1.

8.1.2 Short Stacks Not Meeting Method 1 Criteria. Use stack extensions and the procedures in Method 1. Alternatively, use flow straightening vanes of the ''egg-crate'' type (see Figure 5D–1). Locate the measurement site downstream of the straightening vanes at a distance equal to or greater than two times the average equivalent diameter of the vane openings and at least one-half of the overall stack diameter upstream of the stack outlet.

8.1.3 Roof Monitor or Monovent. (See Figure 5D–2). For a positive pressure fabric filter equipped with a peaked roof monitor, ridge vent, or other type of monovent, use a measurement site at the base of the monovent. Examples of such locations are shown in Figure 5D–2. The measurement site must be upstream of any exhaust point (*e.g.*, louvered vent).

8.1.4 Compartment Housing. Sample immediately downstream of the filter bags directly above the tops of the bags as shown in the examples in Figure 5D–2. Depending on the housing design, use sampling ports in the housing walls or locate the sampling equipment within the compartment housing.

8.2 Determination of Number and Location of Traverse Points. Locate the traverse points according to Method 1, section 11.3. Because a performance test consists of at least three test runs and because of the varied configurations of positive pressure fabric filters, there are several schemes by which the number of traverse points can be determined and the three test runs can be conducted.

8.2.1 Single Stacks Meeting Method 1 Criteria. Select the number of traverse points according to Method 1. Sample all traverse points for each test run.

8.2.2 Other Single Measurement Sites. For a roof monitor or monovent, single compartment housing, or other stack not meeting Method 1 criteria, use at least 24 traverse points. For example, for a rectangular measurement site, such as a monovent, use a balanced 5×5 traverse point matrix. Sample all traverse points for each test run.

8.2.3 Multiple Measurement Sites. Sampling from two or more stacks or measurement sites may be combined for a test run, provided the following guidelines are met:

8.2.3.1 All measurement sites up to 12 must be sampled. For more than 12 measurement sites, conduct sampling on at least 12 sites or 50 percent of the sites, whichever is greater. The measurement sites sampled should be evenly, or nearly evenly, distributed among the available sites; if not, all sites are to be sampled.

8.2.3.2 The same number of measurement sites must be sampled for each test run.

8.2.3.3 The minimum number of traverse points per test run is 24. An exception to the 24-point minimum would be a test combining the sampling from two stacks meeting Method 1 criteria for acceptable stack length, and Method 1 specifies fewer than 12 points per site.

8.2.3.4 As long as the 24 traverse points per test run criterion is met, the number of traverse points per measurement site may be reduced to eight.

8.2.3.5 Alternatively, conduct a test run for each measurement site individually using the criteria in section 8.2.1 or 8.2.2 to determine the number of traverse points. Each test run shall count toward the total of three required for a performance test. If more than three measurement sites are sampled, the number of traverse points per measurement site may be reduced to eight as long as at least 72 traverse points are sampled for all the tests.

8.2.3.6 The following examples demonstrate the procedures for sampling multiple measurement sites.

8.2.3.6.1 Example 1: A source with nine circular measurement sites of equal areas may be tested as follows: For each test run, traverse three measurement sites using four points per diameter (eight points per measurement site). In this manner, test run number 1 will include sampling from sites 1,2, and 3; run 2 will include samples from sites 4, 5, and 6; and run 3 will include sites 7, 8, and 9. Each test area may consist of a separate test of each measurement site using eight points. Use the results from all nine tests in determining the emission average.

8.2.3.6.2 Example 2: A source with 30 rectangular measurement sites of equal areas may be tested as follows: For each of the three test runs, traverse five measurement sites using a 3×3 matrix of traverse points for each site. In order to distribute the sampling evenly over all the available measurement sites while sampling only 50 percent of the sites, number the sites consecutively from 1 to 30 and sample all the even numbered (or odd numbered) sites. Alternatively, conduct a separate test of each of 15 measurement sites using section 8.2.1 or 8.2.2 to determine the number and location of traverse points, as appropriate.

8.2.3.6.3 Example 3: A source with two measurement sites of equal areas may be tested as follows: For each test of three test runs, traverse both measurement sites, using section 8.2.3 in determining the number of traverse points. Alternatively, conduct two full emission test runs for each measurement site using the criteria in section 8.2.1 or 8.2.2 to determine the number of traverse points.

8.2.3.7 Other test schemes, such as random determination of traverse points for a large number of measurement sites, may be used with prior approval from the Administrator.

8.3 Velocity Determination.

8.3.1 The velocities of exhaust gases from positive pressure baghouses are often too low to measure accurately with the type S pitot tube specified in Method 2 (*i.e.*, velocity head <1.3 mm H_2O (0.05 in. H_2O)). For these conditions, measure the gas flow rate at the fabric filter inlet following the procedures outlined in Method 2. Calculate the average gas velocity at the measurement site as shown in section 12.2 and use this average velocity in determining and maintaining isokinetic sampling rates.

8.3.2 Velocity determinations to determine and maintain isokinetic rates at measurement sites with gas velocities within the range measurable with the type S pitot tube (*i.e.*, velocity head greater than 1.3 mm H_2O (0.05 in. H_2O)) shall be conducted according to the procedures outlined in Method 2.

8.4 Sampling. Follow the procedures specified in sections 8.1 through 8.6 of Method 5 or sections 8.1 through 8.25 in Method 17 with the exceptions as noted above.

8.5 Sample Recovery. Follow the procedures specified in section 8.7 of Method 5 or section 8.2 of Method 17.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.0, 10.0	Sampling equipment leak check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

Same as section 10.0 of either Method 5 or Method 17.

11.0 Analytical Procedure

Same as section 11.0 of either Method 5 or Method 17.

12.0 Data Analysis and Calculations

Same as section 12.0 of either Method 5 or Method 17 with the following exceptions:

12.1 Nomenclature.

A_o = Measurement site(s) total cross-sectional area, m^2 (ft^2).

$\bar{C}$ or C_{avg} = Average concentration of PM for all n runs, mg/scm (gr/scf).

Q_i = Inlet gas volume flow rate, m^3/sec (ft^3/sec).

m_i = Mass collected for run i of n, mg (gr).

T_o = Average temperature of gas at measurement site, °K (°R).

T_i = Average temperature of gas at inlet, °K (°R).

Vol_i = Sample volume collected for run i of n, scm (scf).

$\bar{v}$ = Average gas velocity at the measurement site(s), m/s (ft/s)

Q_o = Total baghouse exhaust volumetric flow rate, m^3/sec (ft^3/sec).

Q_d = Dilution air flow rate, m^3/sec (ft^3/sec).

Tamb = Ambient Temperature, (°K).

12.2 Average Gas Velocity. When following section 8.3.1, calculate the average gas velocity at the measurement site as follows:

$$\bar{v} = \frac{Q_o}{A_o} \qquad \text{Eq. 5D-1}$$

12.3 Volumetric Flow Rate. Total volumetric flow rate may be determined as follows:

$$Q_o = Q_i + Q_d \qquad \text{Eq. 5D-2}$$

12.4 Dilution Air Flow Rate.

$$Q_d = \frac{Q_i\left(T_i - T_o\right)}{T_o - T_{amb}} \qquad \text{Eq. 5D-3}$$

12.5 Average PM Concentration. For multiple measurement sites, calculate the average PM concentration as follows:

$$C_{avg} \text{ or } \bar{C} = \frac{\sum_{i=1}^{n} m_i}{\sum_{i=1}^{n} Vol_i} \qquad \text{Eq. 5D-4}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 5, section 17.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

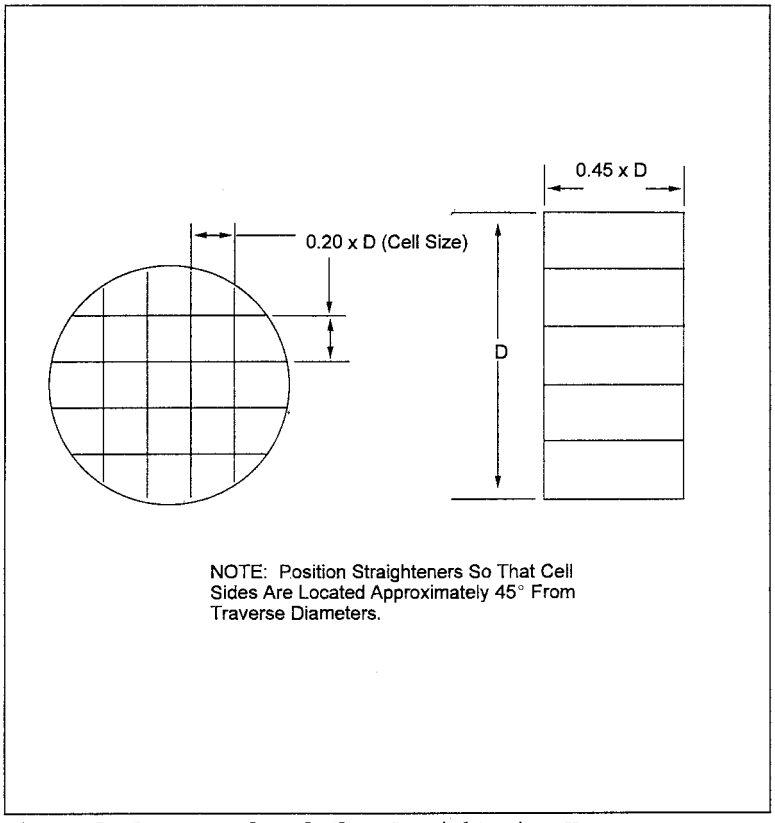


Figure 5D-1. Example of Flow Straightening Vanes.

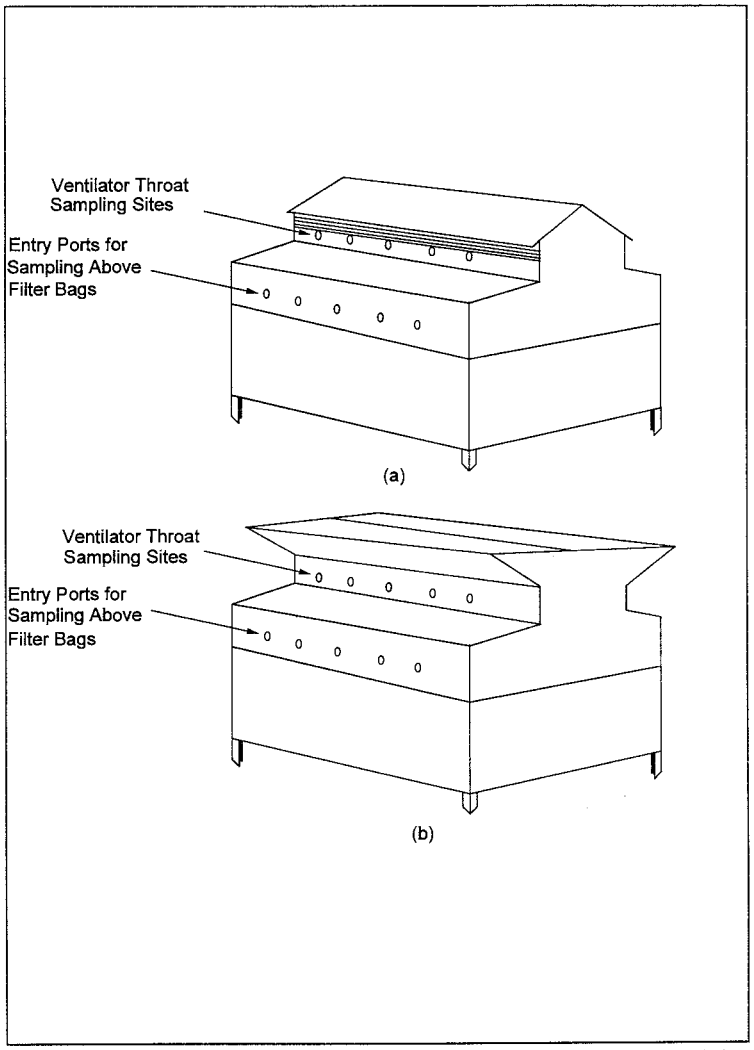


Figure 5D-2. Acceptable Sampling Site Locations for: (a) Peaked Roof; and (b) Ridge Vent Type Fabric Filters

METHOD 5E—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM THE WOOL FIBERGLASS INSULATION MANUFACTURING INDUSTRY

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5.

1.0 Scope and Applications

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of PM emissions from wool fiberglass insulation manufacturing sources.

2.0 Summary of Method

Particulate matter is withdrawn isokinetically from the source and is collected either on a glass fiber filter maintained at a temperature in the range of 120 ±14 °C (248 ±25 °F) and in impingers in solutions of 0.1 N sodium hydroxide (NaOH). The filtered particulate mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after the removal of uncombined water. The condensed PM collected in the impinger solutions is determined as total organic carbon (TOC) using a nondispersive infrared type of analyzer. The sum of the filtered PM mass and the condensed PM is reported as the total PM mass.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Hydrochloric Acid (HCl). Highly toxic. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent in air can be lethal in minutes. Will react with metals, producing hydrogen.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eye tissues and to skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 5, section 6.1, with the exception of the following:

6.1.1 Probe Liner. Same as described in section 6.1.1.2 of Method 5 except use only borosilicate or quartz glass liners.

6.1.2 Filter Holder. Same as described in section 6.1.1.5 of Method 5 with the addition of a leak-tight connection in the rear half of the filter holder designed for insertion of a temperature sensor used for measuring the sample gas exit temperature.

6.2 Sample Recovery. Same as Method 5, section 6.2, except three wash bottles are needed instead of two and only glass storage bottles and funnels may be used.

6.3 Sample Analysis. Same as Method 5, section 6.3, with the additional equipment for TOC analysis as described below:

6.3.1 Sample Blender or Homogenizer. Waring type or ultrasonic.

6.3.2 Magnetic Stirrer.

6.3.3 Hypodermic Syringe. 0- to 100-µl capacity.

6.3.4 Total Organic Carbon Analyzer. Rosemount Model 2100A analyzer or equivalent and a recorder.

6.3.5 Beaker. 30-ml.

6.3.6 Water Bath. Temperature controlled.

6.3.7 Volumetric Flasks. 1000-ml and 500-ml.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 5, section 7.1, with the addition of 0.1 N NaOH (Dissolve 4 g of NaOH in water and dilute to 1 liter).

7.2 Sample Recovery. Same as Method 5, section 7.2, with the addition of the following:

7.2.1 Water. Deionized distilled to conform to ASTM Specification D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17). The potassium permanganate ($KMnO_4$) test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.2.2 Sodium Hydroxide. Same as described in section 7.1.

7.3 Sample Analysis. Same as Method 5, section 7.3, with the addition of the following:

7.3.1 Carbon Dioxide-Free Water. Distilled or deionized water that has been freshly boiled for 15 minutes and cooled to room temperature while preventing exposure to ambient air by using a cover vented with an Ascarite tube.

7.3.2 Hydrochloric Acid. HCl, concentrated, with a dropper.

7.3.3 Organic Carbon Stock Solution. Dissolve 2.1254 g of dried potassium biphthalate ($HOOCC_6H_4COOK$) in CO_2-free water, and dilute to 1 liter in a volumetric flask. This solution contains 1000 mg/L organic carbon.

7.3.4 Inorganic Carbon Stock Solution. Dissolve 4.404 g anhydrous sodium carbonate

(Na_2CO_3.) in about 500 ml of CO_2-free water in a 1-liter volumetric flask. Add 3.497 g anhydrous sodium bicarbonate ($NaHCO_3$) to the flask, and dilute to 1 liter with CO_2 -free water. This solution contains 1000 mg/L inorganic carbon.

7.3.5 Oxygen Gas. CO_2 -free.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation and Preliminary Determinations. Same as Method 5, sections 8.1 and 8.2, respectively.

8.2 Preparation of Sampling Train. Same as Method 5, section 8.3, except that 0.1 N NaOH is used in place of water in the impingers. The volumes of the solutions are the same as in Method 5.

8.3 Leak-Check Procedures, Sampling Train Operation, Calculation of Percent Isokinetic. Same as Method 5, sections 8.4 through 8.6, respectively.

8.4 Sample Recovery. Same as Method 5, sections 8.7.1 through 8.7.4, with the addition of the following:

8.4.1 Save portions of the water, acetone, and 0.1 N NaOH used for cleanup as blanks. Take 200 ml of each liquid directly from the wash bottles being used, and place in glass sample containers labeled ''water blank,'' ''acetone blank,'' and ''NaOH blank,'' respectively.

8.4.2 Inspect the train prior to and during disassembly, and note any abnormal conditions. Treat the samples as follows:

8.4.2.1 Container No. 1. Same as Method 5, section 8.7.6.1.

8.4.2.2 Container No. 2. Use water to rinse the sample nozzle, probe, and front half of the filter holder three times in the manner described in section 8.7.6.2 of Method 5 except that no brushing is done. Put all the water wash in one container, seal, and label.

8.4.2.3 Container No. 3. Rinse and brush the sample nozzle, probe, and front half of the filter holder with acetone as described for Container No. 2 in section 8.7.6.2 of Method 5.

8.4.2.4 Container No. 4. Place the contents of the silica gel impinger in its original container as described for Container No. 3 in section 8.7.6.3 of Method 5.

8.4.2.5 Container No. 5. Measure the liquid in the first three impingers and record the volume or weight as described for the Impinger Water in section 8.7.6.4 of Method 5. Do not discard this liquid, but place it in a sample container using a glass funnel to aid in the transfer from the impingers or graduated cylinder (if used) to the sample container. Rinse each impinger thoroughly with 0.1 N NaOH three times, as well as the graduated cylinder (if used) and the funnel, and put these rinsings in the same sample container. Seal the container and label to clearly identify its contents.

8.5 Sample Transport. Whenever possible, containers should be shipped in such a way that they remain upright at all times.

9.0 Quality Control.

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.3, 10.0	Sampling equipment leak-check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.
10.1.2, 11.2.5.3	Repetitive analyses	Ensures precise measurement of total carbon and inorganic carbon concentration of samples, blank, and standards.
10.1.4	TOC analyzer calibration	Ensures linearity of analyzer response to standards.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

Same as Method 5, section 10.0, with the addition of the following procedures for calibrating the total organic carbon analyzer:

10.1 Preparation of Organic Carbon Standard Curve.

10.1.1 Add 10 ml, 20 ml, 30 ml, 40 ml, and 50 ml of the organic carbon stock solution to a series of five 1000-ml volumetric flasks. Add 30 ml, 40 ml, and 50 ml of the same solution to a series of three 500-ml volumetric flasks. Dilute the contents of each flask to the mark using CO_2-free water. These flasks contain 10, 20, 30, 40, 50, 60, 80, and 100 mg/L organic carbon, respectively.

10.1.2 Use a hypodermic syringe to withdraw a 20- to 50-µl aliquot from the 10 mg/L standard solution and inject it into the total carbon port of the analyzer. Measure the peak height. Repeat the injections until three consecutive peaks are obtained within 10 percent of their arithmetic mean. Repeat this procedure for the remaining organic carbon standard solutions.

10.1.3 Calculate the corrected peak height for each standard by deducting the blank correction (see section 11.2.5.3) as follows:

$$\text{Corrected Peak Height} = A - B \qquad \text{Eq. 5E-1}$$

Where:

A = Peak height of standard or sample, mm or other appropriate unit.

B = Peak height of blank, mm or other appropriate unit.

10.1.4 Prepare a linear regression plot of the arithmetic mean of the three consecutive peak heights obtained for each standard solution against the concentration of that solution. Calculate the calibration factor as the inverse of the slope of this curve. If the product of the arithmetic mean peak height for any standard solution and the calibration factor differs from the actual concentration by more than 5 percent, remake and reanalyze that standard.

10.2 Preparation of Inorganic Carbon Standard Curve. Repeat the procedures outlined in sections 10.1.1 through 10.1.4, substituting the inorganic carbon stock solution for the organic carbon stock solution, and the inorganic carbon port of the analyzer for the total carbon port.

11.0 Analytical Procedure

11.1 Record the data required on a sheet such as the one shown in Figure 5–6 of Method 5.

11.2 Handle each sample container as follows:

11.2.1 Container No. 1. Same as Method 5, section 11.2.1, except that the filters must be dried at 20 ±6 °C (68 ±10 °F) and ambient pressure.

11.2.2 Containers No. 2 and No. 3. Same as Method 5, section 11.2.2, except that evaporation of the samples must be at 20 ±6 °C (68 ±10 °F) and ambient pressure.

11.2.3 Container No. 4. Same as Method 5, section 11.2.3.

11.2.4 ''Water Blank'' and ''Acetone Blank'' Containers. Determine the water and acetone blank values following the procedures for the ''Acetone Blank'' container in section 11.2.4 of Method 5. Evaporate the samples at ambient temperature (20 ±6 °C (68 ±10 °F)) and pressure.

11.2.5 Container No. 5. For the determination of total organic carbon, perform two analyses on successive identical samples, *i.e.*, total carbon and inorganic carbon. The desired quantity is the difference between the two values obtained. Both analyses are based on conversion of sample carbon into carbon dioxide for measurement by a nondispersive infrared analyzer. Results of analyses register as peaks on a strip chart recorder.

11.2.5.1 The principal differences between the operating parameters for the two channels involve the combustion tube packing material and temperature. In the total carbon channel, a high temperature (950 °C (1740 °F)) furnace heats a Hastelloy combustion tube packed with cobalt oxide-impregnated asbestos fiber. The oxygen in the carrier gas, the elevated temperature, and the catalytic effect of the packing result in oxidation of both organic and inorganic carbonaceous material to CO_2, and steam. In the inorganic carbon channel, a low temperature (150 °C (300 °F)) furnace heats a glass tube containing quartz chips wetted with 85 percent phosphoric acid. The acid liberates CO_2 and steam from inorganic carbonates. The operating temperature is below that required to oxidize organic matter. Follow the manufacturer's instructions for assembly, testing, calibration, and operation of the analyzer.

11.2.5.2 As samples collected in 0.1 N NaOH often contain a high measure of inorganic carbon that inhibits repeatable determinations of TOC, sample pretreatment is necessary. Measure and record the liquid volume of each sample (or impinger contents). If the sample contains solids or immiscible liquid matter, homogenize the sample with a blender or ultrasonics until satisfactory repeatability is obtained. Transfer a representative portion of 10 to 15 ml to a 30-ml beaker, and acidify with about 2 drops of concentrated HCl to a pH of 2 or less. Warm the acidified sample at 50 °C (120 °F) in a water bath for 15 minutes.

11.2.5.3 While stirring the sample with a magnetic stirrer, use a hypodermic syringe to withdraw a 20-to 50-µl aliquot from the beaker. Analyze the sample for total carbon and calculate its corrected mean peak height according to the procedures outlined in sections 10.1.2 and 10.1.3. Similarly analyze an aliquot of the sample for inorganic carbon. Repeat the analyses for all the samples and for the 0.1 N NaOH blank.

11.2.5.4 Ascertain the total carbon and inorganic carbon concentrations (C_{TC} and C_{IC}, respectively) of each sample and blank by comparing the corrected mean peak heights for each sample and blank to the appropriate standard curve.

NOTE: If samples must be diluted for analysis, apply an appropriate dilution factor.

12.0 Data Analysis and Calculations

Same as Method 5, section 12.0, with the addition of the following:

12.1 Nomenclature.

C_c = Concentration of condensed particulate matter in stack gas, gas dry basis, corrected to standard conditions, g/dscm (gr/dscf).

C_{IC} = Concentration of condensed TOC in the liquid sample, from section 11.2.5, mg/L.

C_t = Total particulate concentration, dry basis, corrected to standard conditions, g/dscm (gr/dscf).
C_{TC} = Concentration of condensed TOC in the liquid sample, from section 11.2.5, mg/L.
C_{TOC} = Concentration of condensed TOC in the liquid sample, mg/L.
m_{TOC} = Mass of condensed TOC collected in the impingers, mg.
$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, from section 12.3 of Method 5, dscm (dscf).
V_s = Total volume of liquid sample, ml.

12.2 Concentration of Condensed TOC in Liquid Sample.

$$C_{TOC} = C_{TC} - C_{IC} \qquad \text{Eq. 5E-2}$$

12.3 Mass of Condensed TOC Collected.

$$m_{TOC} = 0.001\, C_{TOC} V_s \qquad \text{Eq. 5E-3}$$

Where:

0.001 = Liters per milliliter.

12.4 Concentration of Condensed Particulate Material.

$$C_c = K_4 m_{TOC} / V_{m(std)} \qquad \text{Eq. 5E-4}$$

Where:

K_4 = 0.001 g/mg for metric units.
= 0.0154 gr/mg for English units.

12.5 Total Particulate Concentration.

$$C_t = C_s + C_c \qquad \text{Eq. 5E-4}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Total Organic Carbon Analyzer. Tekmar-Dohrmann analyzers using the single injection technique may be used as an alternative to Rosemount Model 2100A analyzers.

17.0 References.

Same as section 17.0 of Method 5, with the addition of the following:

1. American Public Health Association, American Water Works Association, Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater. Fifteenth Edition. Washington, D.C. 1980.

18.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

Method 5F—Determination of Nonsulfate Particulate Matter Emissions From Stationary Sources

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5.

1.0 Scope and Applications

1.1 Analyte. Nonsulfate particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of nonsulfate PM emissions from stationary sources. Use of this method must be specified by an applicable subpart of the standards, or approved by the Administrator for a particular application.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

Particulate matter is withdrawn isokinetically from the source and collected on a filter maintained at a temperature in the range 160 ±14 °C (320 ±25 °F). The collected sample is extracted with water. A portion of the extract is analyzed for sulfate content by ion chromatography. The remainder is neutralized with ammonium hydroxide (NH_4OH), dried, and weighed. The weight of sulfate in the sample is calculated as ammonium sulfate ($(NH_4)_2SO_4$), and is subtracted from the total particulate weight; the result is reported as nonsulfate particulate matter.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection and Recovery. Same as Method 5, sections 6.1 and 6.2, respectively.

6.2 Sample Analysis. Same as Method 5, section 6.3, with the addition of the following:

6.2.1 Erlenmeyer Flasks. 125-ml, with ground glass joints.

6.2.2 Air Condenser. With ground glass joint compatible with the Erlenmeyer flasks.

6.2.3 Beakers. 600-ml.

6.2.4 Volumetric Flasks. 1-liter, 500-ml (one for each sample), 200-ml, and 50-ml (one for each sample and standard).

6.2.5 Pipet. 5-ml (one for each sample and standard).

6.2.6 Ion Chromatograph. The ion chromatograph should have at least the following components.

6.2.6.1 Columns. An anion separation column or other column capable of resolving the sulfate ion from other species present and a standard anion suppressor column. Suppressor columns are produced as proprietary items; however, one can be produced in the laboratory using the resin available from BioRad Company, 32nd and Griffin Streets, Richmond, California. Other systems which do not use suppressor columns may also be used.

6.2.6.2 Pump. Capable of maintaining a steady flow as required by the system.

6.2.6.3 Flow Gauges. Capable of measuring the specified system flow rate.

6.2.6.4 Conductivity Detector.

6.2.6.5 Recorder. Compatible with the output voltage range of the detector.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 5, section 7.1.

7.2 Sample Recovery. Same as Method 5, section 7.2, with the addition of the following:

7.2.1 Water. Deionized distilled, to conform to ASTM D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17). The potassium permanganate ($KMnO_4$) test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.3 Analysis. Same as Method 5, section 7.3, with the addition of the following:

7.3.1 Water. Same as in section 7.2.1.

7.3.2 Stock Standard Solution, 1 mg $(NH_4)_2SO_4$/ml. Dry an adequate amount of primary standard grade ammonium sulfate ($(NH_4)_2SO_4$) at 105 to 110 °C (220 to 230 °F) for a minimum of 2 hours before preparing the standard solution. Then dissolve exactly 1.000 g of dried $(NH_4)_2SO_4$ in water in a 1-liter volumetric flask, and dilute to 1 liter. Mix well.

7.3.3 Working Standard Solution, 25 µg $(NH_4)_2SO_4$/ml. Pipet 5 ml of the stock standard solution into a 200-ml volumetric flask. Dilute to 200 ml with water.

7.3.4 Eluent Solution. Weigh 1.018 g of sodium carbonate (Na_2CO_3) and 1.008 g of sodium bicarbonate ($NaHCO_3$), and dissolve in 4 liters of water. This solution is 0.0024 M Na_2CO_3/0.003 M $NaHCO_3$. Other eluents appropriate to the column type and capable of resolving sulfate ion from other species present may be used.

7.3.5 Ammonium Hydroxide. Concentrated, 14.8 M.

7.3.6 Phenolphthalein Indicator. 3,3-Bis(4-hydroxyphenyl)-1-(3H)-isobenzo-furanone. Dissolve 0.05 g in 50 ml of ethanol and 50 ml of water.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as Method 5, section 8.0, with the exception of the following:

8.1 Sampling Train Operation. Same as Method 5, section 8.5, except that the probe outlet and filter temperatures shall be maintained at 160 ±14 °C (320 ±25 °F).

8.2 Sample Recovery. Same as Method 5, section 8.7, except that the recovery solvent shall be water instead of acetone, and a clean filter from the same lot as those used during testing shall be saved for analysis as a blank.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures

Section	Quality control measure	Effect
8.3, 10.0	Sampling equipment leak check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.
10.1.2, 11.2.5.3	Repetitive analyses	Ensures precise measurement of total carbon and inorganic carbon concentration of samples, blank, and standards.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

Same as Method 5, section 10.0, with the addition of the following:

10.1 Determination of Ion Chromatograph Calibration Factor S. Prepare a series of five standards by adding 1.0, 2.0, 4.0, 6.0, and 10.0 ml of working standard solution (25 μg/ml) to a series of five 50-ml volumetric flasks. (The standard masses will equal 25, 50, 100, 150, and 250 μg.) Dilute each flask to the mark with water, and mix well. Analyze each standard according to the chromatograph manufacturer's instructions. Take peak height measurements with symmetrical peaks; in all other cases, calculate peak areas. Prepare or calculate a linear regression plot of the standard masses in μg (x-axis) versus their responses (y-axis). From this line, or equation, determine the slope and calculate its reciprocal which is the calibration factor, S. If any point deviates from the line by more than 7 percent of the concentration at that point, remake and reanalyze that standard. This deviation can be determined by multiplying S times the response for each standard. The resultant concentrations must not differ by more than 7 percent from each known standard mass (*i.e.*, 25, 50, 100, 150, and 250 μg).

10.2 Conductivity Detector. Calibrate according to manufacturer's specifications prior to initial use.

11.0 Analytical Procedure

11.1 Sample Extraction.

11.1.1 Note on the analytical data sheet, the level of the liquid in the container, and whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.1.2 Cut the filter into small pieces, and place it in a 125-ml Erlenmeyer flask with a ground glass joint equipped with an air condenser. Rinse the shipping container with water, and pour the rinse into the flask. Add additional water to the flask until it contains about 75 ml, and place the flask on a hot plate. Gently reflux the contents for 6 to 8 hours. Cool the solution, and transfer it to a 500-ml volumetric flask. Rinse the Erlenmeyer flask with water, and transfer the rinsings to the volumetric flask including the pieces of filter.

11.1.3 Transfer the probe rinse to the same 500-ml volumetric flask with the filter sample. Rinse the sample bottle with water, and add the rinsings to the volumetric flask. Dilute the contents of the flask to the mark with water.

11.1.4 Allow the contents of the flask to settle until all solid material is at the bottom of the flask. If necessary, remove and centrifuge a portion of the sample.

11.1.5 Repeat the procedures outlined in sections 11.1.1 through 11.1.4 for each sample and for the filter blank.

11.2 Sulfate (SO_4) Analysis.

11.2.1 Prepare a standard calibration curve according to the procedures outlined in section 10.1.

11.2.2 Pipet 5 ml of the sample into a 50-ml volumetric flask, and dilute to 50 ml with water. (Alternatively, eluent solution may be used instead of water in all sample, standard, and blank dilutions.) Analyze the set of standards followed by the set of samples, including the filter blank, using the same injection volume used for the standards.

11.2.3 Repeat the analyses of the standards and the samples, with the standard set being done last. The two peak height or peak area responses for each sample must agree within 5 percent of their arithmetic mean for the analysis to be valid. Perform this analysis sequence on the same day. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

11.2.4 Document each sample chromatogram by listing the following analytical parameters: injection point, injection volume, sulfate retention time, flow rate, detector sensitivity setting, and recorder chart speed.

11.3 Sample Residue.

11.3.1 Transfer the remaining contents of the volumetric flask to a tared 600-ml beaker or similar container. Rinse the volumetric flask with water, and add the rinsings to the tared beaker. Make certain that all particulate matter is transferred to the beaker. Evaporate the water in an oven at 105 °C (220 °F) until only about 100 ml of water remains. Remove the beakers from the oven, and allow them to cool.

11.3.2 After the beakers have cooled, add five drops of phenolphthalein indicator, and then add concentrated ammonium hydroxide until the solution turns pink. Return the samples to the oven at 105 °C (220 °F), and evaporate the samples to dryness. Cool the samples in a desiccator, and weigh the samples to constant weight.

12.0 Data Analysis and Calculations

Same as Method 5, section 12.0, with the addition of the following:

12.1 Nomenclature.

C_W = Water blank residue concentration, mg/ml.

F = Dilution factor (required only if sample dilution was needed to reduce the concentration into the range of calibration).

H_S = Arithmetic mean response of duplicate sample analyses, mm for height or mm2 for area.

H_b = Arithmetic mean response of duplicate filter blank analyses, mm for height or mm2 for area.
m_b = Mass of beaker used to dry sample, mg.
m_f = Mass of sample filter, mg.
m_n = Mass of nonsulfate particulate matter in the sample as collected, mg.
m_s = Mass of ammonium sulfate in the sample as collected, mg.
m_t = Mass of beaker, filter, and dried sample, mg.
m_w = Mass of residue after evaporation of water blank, mg.
S = Calibration factor, µg/mm.
V_b = Volume of water blank, ml.
V_S = Volume of sample collected, 500 ml.

12.2 Water Blank Concentration.

$$C_w = \frac{m_w}{V_b} \qquad \text{Eq. 5F-1}$$

12.3 Mass of Ammonium Sulfate.

$$m_s = \frac{(99)\, S\, (H_s - H_b)}{(1000)} F \qquad \text{Eq. 5F-2}$$

Where:
100 = Aliquot factor, 495 ml/5 ml
1000 = Constant, µg/mg

12.4 Mass of Nonsulfate Particulate Matter.

$$m_n = m_t - m_b - m_s - m_f - V_s C_w \qquad \text{Eq. 5F-3}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 The following procedure may be used as an alternative to the procedure in section 11.0

16.1.1 Apparatus. Same as for Method 6, sections 6.3.3 to 6.3.6 with the following additions.

16.1.1.1 Beakers. 250-ml, one for each sample, and 600-ml.

16.1.1.2 Oven. Capable of maintaining temperatures of 75 ±5 °C (167 ±9 °F) and 105 ±5 °C (221 ±9 °F).

16.1.1.3 Buchner Funnel.

16.1.1.4 Glass Columns. 25-mm × 305-mm (1-in. × 12-in.) with Teflon stopcock.

16.1.1.5 Volumetric Flasks. 50-ml and 500-ml, one set for each sample, and 100-ml, 200-ml, and 1000-ml.

16.1.1.6 Pipettes. Two 20-ml and one 200-ml, one set for each sample, and 5-ml.

16.1.1.7 Filter Flasks. 500-ml.

16.1.1.8 Polyethylene Bottle. 500-ml, one for each sample.

16.1.2 Reagents. Same as Method 6, sections 7.3.2 to 7.3.5 with the following additions:

16.1.2.1 Water, Ammonium Hydroxide, and Phenolphthalein. Same as sections 7.2.1, 7.3.5, and 7.3.6 of this method, respectively.

16.1.2.2 Filter. Glass fiber to fit Buchner funnel.

16.1.2.3 Hydrochloric Acid (HCl), 1 m. Add 8.3 ml of concentrated HCl (12 M) to 50 ml of water in a 100-ml volumetric flask. Dilute to 100 ml with water.

16.1.2.4 Glass Wool.

16.1.2.5 Ion Exchange Resin. Strong cation exchange resin, hydrogen form, analytical grade.

16.1.2.6 pH Paper. Range of 1 to 7.

16.1.3 Analysis.

16.1.3.1 Ion Exchange Column Preparation. Slurry the resin with 1 M HCl in a 250-ml beaker, and allow to stand overnight. Place 2.5 cm (1 in.) of glass wool in the bottom of the glass column. Rinse the slurried resin twice with water. Resuspend the resin in water, and pour sufficient resin into the column to make a bed 5.1 cm (2 in.) deep. Do not allow air bubbles to become entrapped in the resin or glass wool to avoid channeling, which may produce erratic results. If necessary, stir the resin with a glass rod to remove air bubbles, after the column has been prepared, never let the liquid level fall below the top of the upper glass wool plug. Place a 2.5-cm (1-in.) plug of glass wool on top of the resin. Rinse the column with water until the eluate gives a pH of 5 or greater as measured with pH paper.

16.1.3.2 Sample Extraction. Followup the procedure given in section 11.1.3 except do not dilute the sample to 500 ml.

16.1.3.3 Sample Residue.

16.1.3.3.1 Place at least one clean glass filter for each sample in a Buchner funnel, and rinse the filters with water. Remove the filters from the funnel, and dry them in an oven at 105 ±5 °C (221 ±9 °F); then cool in a desiccator. Weigh each filter to constant weight according to the procedure in Method 5, section 11.0. Record the weight of each filter to the nearest 0.1 mg.

16.1.3.3.2 Assemble the vacuum filter apparatus, and place one of the clean, tared glass fiber filters in the Buchner funnel. Decant the liquid portion of the extracted sample (Section 16.1.3.2) through the tared glass fiber filter into a clean, dry, 500-ml filter flask. Rinse all the particulate matter remaining in the volumetric flask onto the glass fiber filter with water. Rinse the particulate matter with additional water.

Transfer the filtrate to a 500-ml volumetric flask, and dilute to 500 ml with water. Dry the filter overnight at 105 ±5 °C (221 ±9 °F), cool in a desiccator, and weigh to the nearest 0.1 mg.

16.1.3.3.3 Dry a 250-ml beaker at 75 ±5 °C (167 ±9 °F), and cool in a desiccator; then weigh to constant weight to the nearest 0.1 mg. Pipette 200 ml of the filtrate that was saved into a tared 250-ml beaker; add five drops of phenolphthalein indicator and sufficient concentrated ammonium hydroxide to turn the solution pink. Carefully evaporate the contents of the beaker to dryness at 75 ±5 °C (167 ±9 °F). Check for dryness every 30 minutes. Do not continue to bake the sample once it has dried. Cool the sample in a desiccator, and weigh to constant weight to the nearest 0.1 mg.

16.1.3.4 Sulfate Analysis. Adjust the flow rate through the ion exchange column to 3 ml/min. Pipette a 20-ml aliquot of the filtrate onto the top of the ion exchange column, and collect the eluate in a 50-ml volumetric flask. Rinse the column with two 15-ml portions of water. Stop collection of the eluate when the volume in the flask reaches 50-ml. Pipette a 20-ml aliquot of the eluate into a 250-ml Erlenmeyer flask, add 80 ml of 100 percent isopropanol and two to four drops of thorin indicator, and titrate to a pink end point using 0.0100 N barium perchlorate. Repeat and average the titration volumes. Run a blank with each series of samples. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is larger. Perform the ion exchange and titration procedures on duplicate portions of the filtrate. Results should agree within 5 percent. Regenerate or replace the ion exchange resin after 20 sample aliquots have been analyzed or if the end point of the titration becomes unclear.

NOTE: Protect the 0.0100 N barium perchlorate solution from evaporation at all times.

16.1.3.5 Blank Determination. Begin with a sample of water of the same volume as the samples being processed and carry it through the analysis steps described in sections 16.1.3.3 and 16.1.3.4. A blank value larger than 5 mg should not be subtracted from the final particulate matter mass. Causes for large blank values should be investigated and any problems resolved before proceeding with further analyses.

16.1.4 Calibration. Calibrate the barium perchlorate solutions as in Method 6, section 10.5.

16.1.5 Calculations.

16.1.5.1 Nomenclature. Same as section 12.1 with the following additions:

m_a = Mass of clean analytical filter, mg.
m_d = Mass of dissolved particulate matter, mg.
m_e = Mass of beaker and dissolved particulate matter after evaporation of filtrate, mg.
m_p = Mass of insoluble particulate matter, mg.
m_r = Mass of analytical filter, sample filter, and insoluble particulate matter, mg.
m_{bk} = Mass of nonsulfate particulate matter in blank sample, mg.
m_n = Mass of nonsulfate particulate matter, mg.
m_s = Mass of Ammonium sulfate, mg.
N = Normality of $Ba(ClO_4)$ titrant, meq/ml.
V_a = Volume of aliquot taken for titration, 20 ml.
V_c = Volume of titrant used for titration blank, ml.
V_d = Volume of filtrate evaporated, 200 ml.
V_e = Volume of eluate collected, 50 ml.
V_f = Volume of extracted sample, 500 ml.
V_i = Volume of filtrate added to ion exchange column, 20 ml.
V_t = Volume of $Ba(C10_4)_2$ titrant, ml.
W = Equivalent weight of ammonium sulfate, 66.07 mg/meq.

16.1.5.2 Mass of Insoluble Particulate Matter.

$$m_p = m_r - m_a - m_f \qquad \text{Eq. 5F-4}$$

16.1.5.3 Mass of Dissolved Particulate Matter.

$$m_d = \left(m_e - \left(V_f / V_d\right) m_b\right) \qquad \text{Eq. 5F-5}$$

16.1.5.4 Mass of Ammonium Sulfate.

$$m_s = \frac{\left(V_t - V_c\right) N\, W\, V_e V_f}{V_a V_i} \qquad \text{Eq. 5F-6}$$

16.1.5.5 Mass of Nonsulfate Particulate Matter.

$$m_n = m_p + m_d - m_s - m_{bk} \qquad \text{Eq. 5F-7}$$

17.0 References

Same as Method 5, section 17.0, with the addition of the following:

1. Mulik, J.D. and E. Sawicki. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor, Ann Arbor Science Publishers, Inc. Vol. 2, 1979.

2. Sawicki, E., J.D. Mulik, and E. Wittgenstein. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor, Ann Arbor Science Publishers, Inc. Vol. 1. 1978.

3. Siemer, D.D. Separation of Chloride and Bromide from Complex Matrices Prior to Ion Chromatographic Determination. Analytical Chemistry 52(12): 1874–1877. October 1980.

4. Small, H., T.S. Stevens, and W.C. Bauman. Novel Ion Exchange Chromatographic Method Using

Conductimetric Determination. Analytical Chemistry. *47*(11):1801. 1975.

18.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 5G—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM WOOD HEATERS (DILUTION TUNNEL SAMPLING LOCATION)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 4, Method 5, Method 5H, and Method 28.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of PM emissions from wood heaters.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 The exhaust from a wood heater is collected with a total collection hood, and is combined with ambient dilution air. Particulate matter is withdrawn proportionally from a single point in a sampling tunnel, and is collected on two glass fiber filters in series. The filters are maintained at a temperature of no greater than 32 °C (90 °F). The particulate mass is determined gravimetrically after the removal of uncombined water.

2.2 There are three sampling train approaches described in this method: (1) One dual-filter dry sampling train operated at about 0.015 m^3/min (0.5 cfm), (2) One dual-filter plus impingers sampling train operated at about 0.015 m^3/min (0.5 cfm), and (3) two dual-filter dry sampling trains operated simultaneously at any flow rate. Options (2) and (3) are referenced in section 16.0 of this method. The dual-filter dry sampling train equipment and operation, option (1), are described in detail in this method.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. The following items are required for sample collection:

6.1.1 Sampling Train. The sampling train configuration is shown in Figure 5G–1 and consists of the following components:

6.1.1.1 Probe. Stainless steel (*e.g.*, 316 or grade more corrosion resistant) or glass about 9.5 mm (3⁄8 in.) I.D., 0.6 m (24 in.) in length. If made of stainless steel, the probe shall be constructed from seamless tubing.

6.1.1.2 Pitot Tube. Type S, as described in section 6.1 of Method 2. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Method 2, section 10. Alternatively, a standard pitot may be used as described in Method 2, section 6.1.2.

6.1.1.3 Differential Pressure Gauge. Inclined manometer or equivalent device, as described in Method 2, section 6.2. One manometer shall be used for velocity head (Δp) readings and another (optional) for orifice differential pressure readings (ΔH).

6.1.1.4 Filter Holders. Two each made of borosilicate glass, stainless steel, or Teflon, with a glass frit or stainless steel filter support and a silicone rubber, Teflon, or Viton gasket. The holder design shall provide a positive seal against leakage from the outside or around the filters. The filter holders shall be placed in series with the backup filter holder located 25 to 100 mm (1 to 4 in.) downstream from the primary filter holder. The filter holder shall be capable of holding a filter with a 100 mm (4 in.) diameter, except as noted in section 16.

6.1.1.5 Filter Temperature Monitoring System. A temperature sensor capable of measuring temperature to within ±3 °C (±5 °F). The sensor shall be installed at the exit side of the front filter holder so that the sensing tip of the temperature sensor is in direct contact with the sample gas or in a thermowell as shown in Figure 5G–1. The temperature sensor shall comply with the calibration specifications in Method 2, section 10.3. Alternatively, the sensing tip of the temperature sensor may be installed at the inlet side of the front filter holder.

6.1.1.6 Dryer. Any system capable of removing water from the sample gas to less than 1.5 percent moisture (volume percent) prior to the metering system. The system shall include a temperature sensor for demonstrating that sample gas temperature exiting the dryer is less than 20 °C (68 °F).

6.1.1.7 Metering System. Same as Method 5, section 6.1.1.9.

6.1.2 Barometer. Same as Method 5, section 6.1.2.

6.1.3 Dilution Tunnel Gas Temperature Measurement. A temperature sensor capable

of measuring temperature to within ±3 °C (±5 °F).

6.1.4 Dilution Tunnel. The dilution tunnel apparatus is shown in Figure 5G–2 and consists of the following components:

6.1.4.1 Hood. Constructed of steel with a minimum diameter of 0.3 m (1 ft) on the large end and a standard 0.15 to 0.3 m (0.5 to 1 ft) coupling capable of connecting to standard 0.15 to 0.3 m (0.5 to 1 ft) stove pipe on the small end.

6.1.4.2 90° Elbows. Steel 90° elbows, 0.15 to 0.3 m (0.5 to 1 ft) in diameter for connecting mixing duct, straight duct and optional damper assembly. There shall be at least two 90° elbows upstream of the sampling section (see Figure 5G–2).

6.1.4.3 Straight Duct. Steel, 0.15 to 0.3 m (0.5 to 1 ft) in diameter to provide the ducting for the dilution apparatus upstream of the sampling section. Steel duct, 0.15 m (0.5 ft) in diameter shall be used for the sampling section. In the sampling section, at least 1.2 m (4 ft) downstream of the elbow, shall be two holes (velocity traverse ports) at 90° to each other of sufficient size to allow entry of the pitot for traverse measurements. At least 1.2 m (4 ft) downstream of the velocity traverse ports, shall be one hole (sampling port) of sufficient size to allow entry of the sampling probe. Ducts of larger diameter may be used for the sampling section, provided the specifications for minimum gas velocity and the dilution rate range shown in section 8 are maintained. The length of duct from the hood inlet to the sampling ports shall not exceed 9.1 m (30 ft).

6.1.4.4 Mixing Baffles. Steel semicircles (two) attached at 90° to the duct axis on opposite sides of the duct midway between the two elbows upstream of sampling section. The space between the baffles shall be about 0.3 m (1 ft).

6.1.4.5 Blower. Squirrel cage or other fan capable of extracting gas from the dilution tunnel of sufficient flow to maintain the velocity and dilution rate specifications in section 8 and exhausting the gas to the atmosphere.

6.2 Sample Recovery. The following items are required for sample recovery: probe brushes, wash bottles, sample storage containers, petri dishes, and funnel. Same as Method 5, sections 6.2.1 through 6.2.4, and 6.2.8, respectively.

6.3 Sample Analysis. The following items are required for sample analysis: glass weighing dishes, desiccator, analytical balance, beakers (250-ml or smaller), hygrometer, and temperature sensor. Same as Method 5, sections 6.3.1 through 6.3.3 and 6.3.5 through 6.3.7, respectively.

7.0 Reagents and Standards

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Filters. Glass fiber filters with a minimum diameter of 100 mm (4 in.), without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. Gelman A/E 61631 has been found acceptable for this purpose.

7.1.2 Stopcock Grease. Same as Method 5, section 7.1.5. 7.2 Sample Recovery. Acetone-reagent grade, same as Method 5, section 7.2.

7.3 Sample Analysis. Two reagents are required for the sample analysis:

7.3.1 Acetone. Same as in section 7.2.

7.3.2 Desiccant. Anhydrous calcium sulfate, calcium chloride, or silica gel, indicating type.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Dilution Tunnel Assembly and Cleaning. A schematic of a dilution tunnel is shown in Figure 5G–2. The dilution tunnel dimensions and other features are described in section 6.1.4. Assemble the dilution tunnel, sealing joints and seams to prevent air leakage. Clean the dilution tunnel with an appropriately sized wire chimney brush before each certification test.

8.2 Draft Determination. Prepare the wood heater as in Method 28, section 6.2.1. Locate the dilution tunnel hood centrally over the wood heater stack exhaust. Operate the dilution tunnel blower at the flow rate to be used during the test run. Measure the draft imposed on the wood heater by the dilution tunnel (*i.e.*, the difference in draft measured with and without the dilution tunnel operating) as described in Method 28, section 6.2.3. Adjust the distance between the top of the wood heater stack exhaust and the dilution tunnel hood so that the dilution tunnel induced draft is less than 1.25 Pa (0.005 in. H_2O). Have no fire in the wood heater, close the wood heater doors, and open fully the air supply controls during this check and adjustment.

8.3 Pretest Ignition. Same as Method 28, section 8.7.

8.4 Smoke Capture. During the pretest ignition period, operate the dilution tunnel and visually monitor the wood heater stack exhaust. Operate the wood heater with the doors closed and determine that 100 percent of the exhaust gas is collected by the dilution tunnel hood. If less than 100 percent of the wood heater exhaust gas is collected, adjust the distance between the wood heater stack and the dilution tunnel hood until no visible exhaust gas is escaping. Stop the pretest ignition period, and repeat the draft determination procedure described in section 8.2.

8.5 Velocity Measurements. During the pretest ignition period, conduct a velocity traverse to identify the point of average velocity. This single point shall be used for measuring velocity during the test run.

8.5.1 Velocity Traverse. Measure the diameter of the duct at the velocity traverse port location through both ports. Calculate the duct area using the average of the two diameters. A pretest leak-check of pitot lines as in Method 2, section 8.1, is recommended. Place the calibrated pitot tube at the centroid of the stack in either of the velocity traverse ports. Adjust the damper or similar device on the blower inlet until the velocity indicated by the pitot is approximately 220 m/min (720 ft/min). Continue to read the Δp and temperature until the velocity has remained constant (less than 5 percent change) for 1 minute. Once a constant velocity is obtained at the centroid of the duct, perform a velocity traverse as outlined in Method 2, section 8.3 using four points per traverse as outlined in Method 1. Measure the Δp and tunnel temperature at each traverse point and record the readings. Calculate the total gas flow rate using calculations contained in Method 2, section 12. Verify that the flow rate is 4 ±0.40 dscm/min (140 ±14 dscf/min); if not, readjust the damper, and repeat the velocity traverse. The moisture may be assumed to be 4 percent (100 percent relative humidity at 85 °F). Direct moisture measurements (*e.g.*, according to Method 4) are also permissible.

NOTE: If burn rates exceed 3 kg/hr (6.6 lb/hr), dilution tunnel duct flow rates greater than 4 dscm/min (140 dscfm) and sampling section duct diameters larger than 150 mm (6 in.) are allowed. If larger ducts or flow rates are used, the sampling section velocity shall be at least 220 m/min (720 fpm). In order to ensure measurable particulate mass catch, it is recommended that the ratio of the average mass flow rate in the dilution tunnel to the average fuel burn rate be less than 150:1 if larger duct sizes or flow rates are used.

8.5.2 Testing Velocity Measurements. After obtaining velocity traverse results that meet the flow rate requirements, choose a point of average velocity and place the pitot and temperature sensor at that location in the duct. Alternatively, locate the pitot and the temperature sensor at the duct centroid and calculate a velocity correction factor for the centroidal position. Mount the pitot to ensure no movement during the test run and seal the port holes to prevent any air leakage. Align the pitot opening to be parallel with the duct axis at the measurement point. Check that this condition is maintained during the test run (about 30-minute intervals). Monitor the temperature and velocity during the pretest ignition period to ensure that the proper flow rate is maintained. Make adjustments to the dilution tunnel flow rate as necessary.

8.6 Pretest Preparation. Same as Method 5, section 8.1.

8.7 Preparation of Sampling Train. During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin.

Using a tweezer or clean disposable surgical gloves, place one labeled (identified) and weighed filter in each of the filter holders. Be sure that each filter is properly centered and that the gasket is properly placed so as to prevent the sample gas stream from circumventing the filter. Check each filter for tears after assembly is completed.

Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct. Set up the train as shown in Figure 5G–1.

8.8 Leak-Check Procedures.

8.8.1 Leak-Check of Metering System Shown in Figure 5G–1. That portion of the sampling train from the pump to the orifice meter shall be leak-checked prior to initial use and after each certification or audit test. Leakage after the pump will result in less volume being recorded than is actually sampled. Use the procedure described in Method 5, section 8.4.1. Similar leak-checks shall be conducted for other types of metering systems (*i.e.*, without orifice meters).

8.8.2 Pretest Leak-Check. A pretest leak-check of the sampling train is recommended, but not required. If the pretest leak check is conducted, the procedures outlined in Method 5, section 8.4.2 should be used. A vacuum of 130 mm Hg (5 in. Hg) may be used instead of 380 mm Hg (15 in. Hg).

8.8.3 Post-Test Leak-Check. A leak-check of the sampling train is mandatory at the conclusion of each test run. The leak-check shall be performed in accordance with the procedures outlined in Method 5, section 8.4.2. A vacuum of 130 mm Hg (5 in. Hg) or the highest vacuum measured during the test run, whichever is greater, may be used instead of 380 mm Hg (15 in. Hg).

8.9 Preliminary Determinations. Determine the pressure, temperature and the average velocity of the tunnel gases as in section 8.5. Moisture content of diluted tunnel gases is assumed to be 4 percent for making flow rate calculations; the moisture content may be measured directly as in Method 4.

8.10 Sampling Train Operation. Position the probe inlet at the stack centroid, and block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream. Be careful not to bump the probe into the stack wall when removing or inserting the probe through the porthole; this minimizes the chance of extracting deposited material.

8.10.1 Begin sampling at the start of the test run as defined in Method 28, section 8.8.1. During the test run, maintain a sample flow rate proportional to the dilution tunnel flow rate (within 10 percent of the initial proportionality ratio) and a filter holder temperature of no greater than 32 °C (90 °F).

The initial sample flow rate shall be approximately 0.015 m^3/min (0.5 cfm).

8.10.2 For each test run, record the data required on a data sheet such as the one shown in Figure 5G–3. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment and when sampling is halted. Take other readings as indicated on Figure 5G–3 at least once each 10 minutes during the test run. Since the manometer level and zero may drift because of vibrations and temperature changes, make periodic checks during the test run.

8.10.3 For the purposes of proportional sampling rate determinations, data from calibrated flow rate devices, such as glass rotameters, may be used in lieu of incremental dry gas meter readings. Proportional rate calculation procedures must be revised, but acceptability limits remain the same.

8.10.4 During the test run, make periodic adjustments to keep the temperature between (or upstream of) the filters at the proper level. Do not change sampling trains during the test run.

8.10.5 At the end of the test run (see Method 28, section 6.4.6), turn off the coarse adjust valve, remove the probe from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak-check, as outlined in section 8.8.2. Also, leak-check the pitot lines as described in Method 2, section 8.1; the lines must pass this leak-check in order to validate the velocity head data.

8.11 Calculation of Proportional Sampling Rate. Calculate percent proportionality (see section 12.7) to determine whether the run was valid or another test run should be made.

8.12 Sample Recovery. Same as Method 5, section 8.7, with the exception of the following:

8.12.1 An acetone blank volume of about 50-ml or more may be used.

8.12.2 Treat the samples as follows:

8.12.2.1 Container Nos. 1 and 1A. Treat the two filters according to the procedures outlined in Method 5, section 8.7.6.1. The filters may be stored either in a single container or in separate containers. Use the sum of the filter tare weights to determine the sample mass collected.

8.12.2.3 Container No. 2.

8.12.2.3.1 Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe and filter holders by washing and brushing these components with acetone and placing the wash in a labeled glass container. At least three cycles of brushing and rinsing are required.

8.12.2.3.2 Between sampling runs, keep brushes clean and protected from contamination.

8.12.2.3.3 After all acetone washings and particulate matter have been collected in the sample containers, tighten the lids on the sample containers so that the acetone will not leak out when transferred to the laboratory weighing area. Mark the height of the fluid levels to determine whether leakage occurs during transport. Label the containers clearly to identify contents.

8.13 Sample Transport. Whenever possible, containers should be shipped in such a way that they remain upright at all times.

NOTE: Requirements for capping and transport of sample containers are not applicable if sample recovery and analysis occur in the same room.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.8, 10.1–10.4	Sampling equipment leak check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.
10.5	Analytical balance calibration	Ensure accurate and precise measurement of collected particulate.
16.2.5	Simultaneous, dual-train sample collection.	Ensure precision of measured particulate concentration.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory record of all calibrations.

10.1 Pitot Tube. The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Method 2, section 10.1, prior to the first certification test and checked semiannually, thereafter. A standard pitot need not be calibrated but shall be inspected and cleaned, if necessary, prior to each certification test.

10.2 Volume Metering System.

10.2.1 Initial and Periodic Calibration. Before its initial use and at least semiannually thereafter, calibrate the volume metering system as described in Method 5, section 10.3.1, except that the wet test meter with a capacity of 3.0 liters/rev (0.1 ft^3/rev) may be used. Other liquid displacement systems accurate to within ±1 percent, may be used as calibration standards.

NOTE: Procedures and equipment specified in Method 5, section 16.0, for alternative calibration standards, including calibrated dry gas meters and critical orifices, are allowed for calibrating the dry gas meter in the sampling train. A dry gas meter used as a calibration standard shall be recalibrated at least once annually.

10.2.2 Calibration After Use. After each certification or audit test (four or more test runs conducted on a wood heater at the four burn rates specified in Method 28), check calibration of the metering system by performing three calibration runs at a single, intermediate flow rate as described in Method 5, section 10.3.2.

NOTE: Procedures and equipment specified in Method 5, section 16.0, for alternative calibration standards are allowed for the post-test dry gas meter calibration check.

10.2.3 Acceptable Variation in Calibration. If the dry gas meter coefficient values obtained before and after a certification test differ by more than 5 percent, the certification test shall either be voided and repeated, or calculations for the certification test shall be performed using whichever meter coefficient value (*i.e.*, before or after) gives the lower value of total sample volume.

10.3 Temperature Sensors. Use the procedure in Method 2, section 10.3, to calibrate temperature sensors before the first certification or audit test and at least semiannually, thereafter.

10.4 Barometer. Calibrate against a mercury barometer before the first certification test and at least semiannually, thereafter. If a mercury barometer is used, no calibration is necessary. Follow the manufacturer's instructions for operation.

10.5 Analytical Balance. Perform a multipoint calibration (at least five points spanning the operational range) of the analytical balance before the first certification test and semiannually, thereafter. Before each certification test, audit the balance by weighing at least one calibration weight (class F) that corresponds to 50 to 150 percent of the weight of one filter. If the scale cannot reproduce the value of the calibration weight to within 0.1 mg, conduct the multipoint calibration before use.

11.0 Analytical Procedure

11.1 Record the data required on a sheet such as the one shown in Figure 5G–4. Use the same analytical balance for determining tare weights and final sample weights.

11.2 Handle each sample container as follows:

11.2.1 Container Nos. 1 and 1A. Treat the two filters according to the procedures outlined in Method 5, section 11.2.1.

11.2.2 Container No. 2. Same as Method 5, section 11.2.2, except that the beaker may be smaller than 250 ml.

11.2.3 Acetone Blank Container. Same as Method 5, section 11.2.4, except that the beaker may be smaller than 250 ml.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

12.1 Nomenclature.

B_{ws} = Water vapor in the gas stream, proportion by volume (assumed to be 0.04).
c_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (gr/dscf).
E = Particulate emission rate, g/hr (lb/hr).
E_{adj} = Adjusted particulate emission rate, g/hr (lb/hr).
L_a = Maximum acceptable leakage rate for either a pretest or post-test leak-check, equal to 0.00057 m^3/min (0.020 cfm) or 4 percent of the average sampling rate, whichever is less.
L_p = Leakage rate observed during the post-test leak-check, m^3/min (cfm).
m_a = Mass of residue of acetone blank after evaporation, mg.
m_{aw} = Mass of residue from acetone wash after evaporation, mg.
m_n = Total amount of particulate matter collected, mg.
M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).
PR = Percent of proportional sampling rate.
P_s = Absolute gas pressure in dilution tunnel, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
Q_{sd} = Average gas flow rate in dilution tunnel, calculated as in Method 2, Equation 2–8, dscm/hr (dscf/hr).
T_m = Absolute average dry gas meter temperature (see Figure 5G–3), °K (°R).
T_{mi} = Absolute average dry gas meter temperature during each 10-minute interval, i, of the test run, °K (°R).
T_s = Absolute average gas temperature in the dilution tunnel (see Figure 5G–3), °K (°R).
T_{si} = Absolute average gas temperature in the dilution tunnel during each 10 minute interval, i, of the test run, °K (°R).
T_{std} = Standard absolute temperature, 293 °K (528 °R).
V_a = Volume of acetone blank, ml.
V_{aw} = Volume of acetone used in wash, ml.
V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).

V_{mi} = Volume of gas sample as measured by dry gas meter during each 10-minute interval, i, of the test run, dcm.
$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).
V_s = Average gas velocity in the dilution tunnel, calculated by Method 2, Equation 2–7, m/sec (ft/sec). The dilution tunnel dry gas molecular weight may be assumed to be 29 g/g mole (lb/lb mole).
V_{si} = Average gas velocity in dilution tunnel during each 10-minute interval, i, of the test run, calculated by Method 2, Equation 2–7, m/sec (ft/sec).
Y = Dry gas meter calibration factor.
ΔH = Average pressure differential across the orifice meter, if used (see Figure 5G–2), mm H^2O (in. H^2O).
U = Total sampling time, min.
10 = 10 minutes, length of first sampling period.
13.6 = Specific gravity of mercury.
100 = Conversion to percent.

12.2 Dry Gas Volume. Same as Method 5, section 12.2, except that component changes are not allowable.

12.3 Solvent Wash Blank.

$$m_{aw} = \frac{m_a V_{aw}}{V_a} \qquad \text{Eq. 5G-1}$$

12.4 Total Particulate Weight. Determine the total particulate catch, mn, from the sum of the weights obtained from Container Nos. 1, 1A, and 2, less the acetone blank (see Figure 5G–4).

12.5 Particulate Concentration.

$$c_s = K_2 \frac{m_n}{V_{m(std)}} \qquad \text{Eq. 5G-2}$$

Where:
K_2 = 0.001 g/mg for metric units.
= 0.0154 gr/mg for English units.

12.6 Particulate Emission Rate.

$$E = C_s Q_{sd} \qquad \text{Eq. 5G-3}$$

NOTE: Particulate emission rate results produced using the sampling train described in section 6 and shown in Figure 5G–1 shall be adjusted for reporting purposes by the following method adjustment factor:

$$E_{adj} = K_3 E^{0.83} \qquad \text{Eq. 5G-4}$$

Where:
K_3 = constant, 1.82 for metric units.
= constant, 0.643 for English units.

12.7 Proportional Rate Variation. Calculate PR for each 10-minute interval, i, of the test run.

$$PR = \left(\frac{\theta \left(V_{mi} V_s T_m T_{si} \right)}{10 \left(V_m V_{si} T_s T_{mi} \right)} \right) \times 100 \qquad \text{Eq. 5G-5}$$

Alternate calculation procedures for proportional rate variation may be used if other sample flow rate data (e.g., orifice flow meters or rotameters) are monitored to maintain proportional sampling rates. The proportional rate variations shall be calculated for each 10-minute interval by comparing the stack to nozzle velocity ratio for each 10-minute interval to the average stack to nozzle velocity ratio for the test run. Proportional rate variation may be calculated for intervals shorter than 10 minutes with appropriate revisions to Equation 5G–5. If no more than 10 percent of the PR values for all the intervals exceed 90 percent ≤PR ≤110 percent, and if no PR value for any interval exceeds 80 percent ≤PR ≤120 percent, the results are acceptable. If the PR values for the test run are judged to be unacceptable, report the test run emission results, but do not include the results in calculating the weighted average emission rate, and repeat the test run.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Method 5H Sampling Train. The sampling train and sample collection, recovery, and analysis procedures described in Method 5H, sections 6.1.1, 7.1, 7.2, 8.1, 8.10, 8.11, and 11.0, respectively, may be used in lieu of similar sections in Method 5G. Operation of the Method 5H sampling train in the dilution tunnel is as described in section 8.10 of this method. Filter temperatures and condenser conditions are as described in Method 5H. No adjustment to the measured particulate matter emission rate (Equation 5G–4, section 12.6) is to be applied to the particulate emission rate measured by this alternative method.

16.2 Dual Sampling Trains. Two sampling trains may be operated simultaneously at sample flow rates other than that specified

in section 8.10, provided that the following specifications are met.

16.2.1 Sampling Train. The sampling train configuration shall be the same as specified in section 6.1.1, except the probe, filter, and filter holder need not be the same sizes as specified in the applicable sections. Filter holders of plastic materials such as Nalgene or polycarbonate materials may be used (the Gelman 1119 filter holder has been found suitable for this purpose). With such materials, it is recommended that solvents not be used in sample recovery. The filter face velocity shall not exceed 150 mm/sec (30 ft/min) during the test run. The dry gas meter shall be calibrated for the same flow rate range as encountered during the test runs. Two separate, complete sampling trains are required for each test run.

16.2.2 Probe Location. Locate the two probes in the dilution tunnel at the same level (see section 6.1.4.3). Two sample ports are necessary. Locate the probe inlets within the 50 mm (2 in.) diameter centroidal area of the dilution tunnel no closer than 25 mm (1 in.) apart.

16.2.3 Sampling Train Operation. Operate the sampling trains as specified in section 8.10, maintaining proportional sampling rates and starting and stopping the two sampling trains simultaneously. The pitot values as described in section 8.5.2 shall be used to adjust sampling rates in both sampling trains.

16.2.4 Recovery and Analysis of Sample. Recover and analyze the samples from the two sampling trains separately, as specified in sections 8.12 and 11.0, respectively.

16.2.4.1 For this alternative procedure, the probe and filter holder assembly may be weighed without sample recovery (use no solvents) described above in order to determine the sample weight gains. For this approach, weigh the clean, dry probe and filter holder assembly upstream of the front filter (without filters) to the nearest 0.1 mg to establish the tare weights. The filter holder section between the front and second filter need not be weighed. At the end of the test run, carefully clean the outside of the probe, cap the ends, and identify the sample (label). Remove the filters from the filter holder assemblies as described for container Nos. 1 and 1A in section 8.12.2.1. Reassemble the filter holder assembly, cap the ends, identify the sample (label), and transfer all the samples to the laboratory weighing area for final weighing. Requirements for capping and transport of sample containers are not applicable if sample recovery and analysis occur in the same room.

16.2.4.2 For this alternative procedure, filters may be weighed directly without a petri dish. If the probe and filter holder assembly are to be weighed to determine the sample weight, rinse the probe with acetone to remove moisture before desiccating prior to the test run. Following the test run, transport the probe and filter holder to the desiccator, and uncap the openings of the probe and the filter holder assembly. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

16.2.5 Calculations. Calculate an emission rate (Section 12.6) for the sample from each sampling train separately and determine the average emission rate for the two values. The two emission rates shall not differ by more than 7.5 percent from the average emission rate, or 7.5 percent of the weighted average emission rate limit in the applicable subpart of the regulations, whichever is greater. If this specification is not met, the results are unacceptable. Report the results, but do not include the results in calculating the weighted average emission rate. Repeat the test run until acceptable results are achieved, report the average emission rate for the acceptable test run, and use the average in calculating the weighted average emission rate.

17.0 References

Same as Method 5, section 17.0, References 1 through 11, with the addition of the following:

1. Oregon Department of Environmental Quality. Standard Method for Measuring the Emissions and Efficiencies of Woodstoves. June 8, 1984. Pursuant to Oregon Administrative Rules Chapter 340, Division 21.

2. American Society for Testing and Materials. Proposed Test Methods for Heating Performance and Emissions of Residential Wood-fired Closed Combustion-Chamber Heating Appliances. E–6 Proposal P 180. August 1986.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

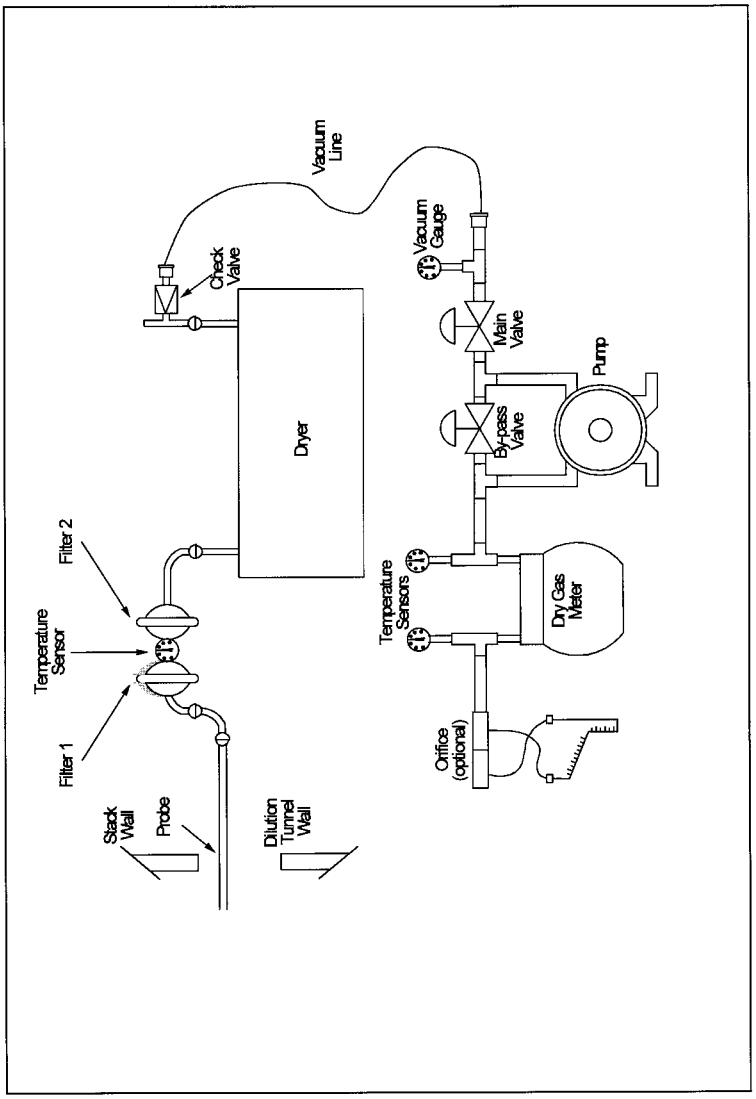


Figure 5G-1. Method 5G Sampling Train.

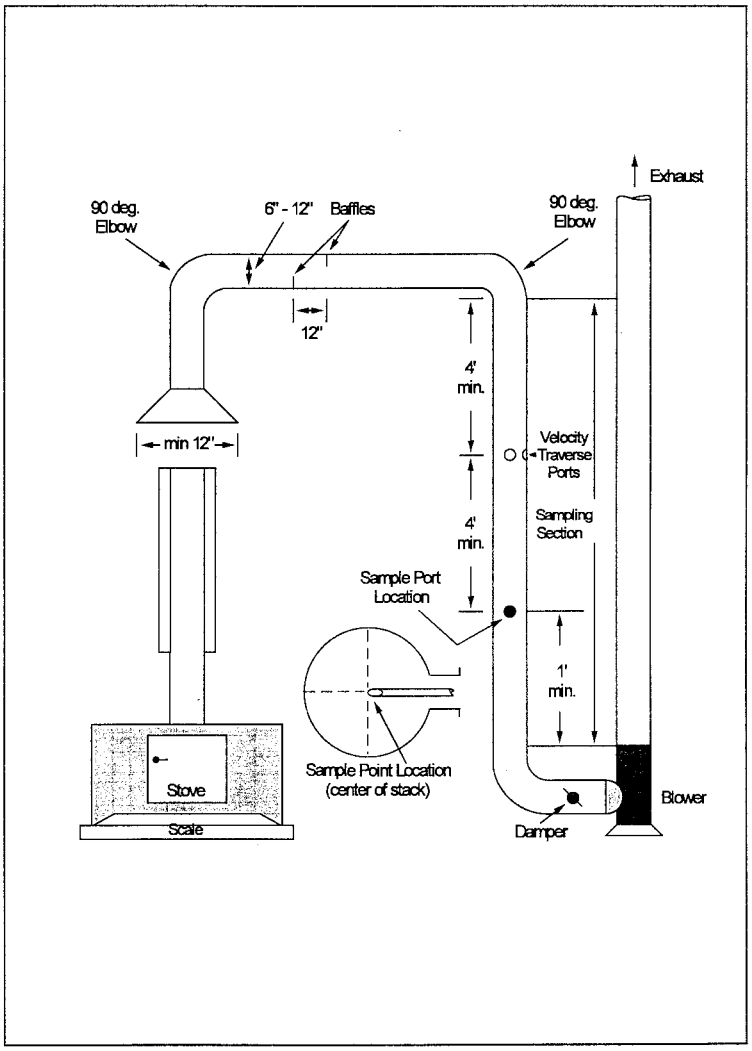


Figure 5G-2. Suggested Construction Details of the Dilution Tunnel.

Stove _____ Pitot tube coefficient, C_p _____
Test Method _____ Room temperature, °C (°F) _____
Operator _____ Barometric pressure mb (in. Hg) _____
Date _____ Measured or assumed moisture, % _____
Run No. _____ Final leak rate, m^3/min, (cfm) _____
Start Time _____ Probe liner material _____
Stop Time _____ Draft or static pressure, mm H_2O (in. H_2O) _____
Sample Box No. _____ Filter No. _____
Meter Box No. _____
Meter ΔH @ (optional) _____

Clock time	Test run time (e) min.	Vacuum mm Hg (in. Hg)	Tunnel temp (T_s) °C (°F)	Velocity head (ΔP_s) mm (in. H_2O)	Sample flow rate indicator (orifice meter optional) mm H_2O (in. H_2O)	Gas meter volume m^3 (ft^3)	Gas sample temp at dry gas meter Inlet °C (°F)	Gas sample temp at dry gas meter Outlet °C (°F)	Filter holder temp °C (°F)	Temperature of gas leaving dryer or last impinger °C (°F)
Total							Avg.	Avg.		
Average							Avg.			

Figure 5G-3. Sampling Data Sheet.

Stove _____
Date _____
Run No. _____
Filter Nos. _____
Liquid lost during transport, ml _____
Acetone blank volume, ml _____
Acetone wash volume, ml _____
Acetone blank concentration, mg/mg _____
Acetone wash blank, mg _____

Container number	Weight of particulate collected, mg	
	Final weight	Tare weight
1		
2		
3		
Total		
Less acetone blank		
Weight of particulate matter		

Stack Moisture Measurement Data
(Optional)

	Volume of liquid water collected	
	Implinger volume, ml	Silica gel weight, g
Final		
Initial		
Liquid collected		
Total volume collected		g[1] or ml

[1]Convert weight of water to volume by dividing total weight increase by density of water (1 g/ml).

$$\frac{\text{Increase, g}}{\text{(1 g/ml)}} = \text{Volume water, ml}$$

Figure 5G-4. Analysis Data Sheet.

METHOD 5H—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM WOOD HEATERS FROM A STACK LOCATION

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 2, Method 3, Method 5, Method 5G, Method 6, Method 6C, Method 16A, and Method 28.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of PM and condensible emissions from wood heaters.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Particulate matter is withdrawn proportionally from the wood heater exhaust and is collected on two glass fiber filters separated by impingers immersed in an ice water bath. The first filter is maintained at a temperature of no greater than 120 °C (248 °F). The second filter and the impinger system are cooled such that the temperature of the gas exiting the second filter is no greater than 20 °C (68 °F). The particulate mass collected in the probe, on the filters, and in the impingers is determined gravimetrically after the removal of uncombined water.

3.0 Definitions

Same as in Method 6C, section 3.0.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. The following items are required for sample collection:

6.1.1 Sampling Train. The sampling train configuration is shown in Figure 5H–1. Same as Method 5, section 6.1.1, with the exception of the following:

6.1.1.1 Probe Nozzle. The nozzle is optional; a straight sampling probe without a nozzle is an acceptable alternative.

6.1.1.2 Probe Liner. Same as Method 5, section 6.1.1.2, except that the maximum length of the sample probe shall be 0.6 m (2 ft) and probe heating is optional.

6.1.1.3 Filter Holders. Two each of borosilicate glass, with a glass frit or stainless steel filter support and a silicone rubber, Teflon, or Viton gasket. The holder design shall provide a positive seal against leakage from the outside or around the filter. The front filter holder shall be attached immediately at the outlet of the probe and prior to the first impinger. The second filter holder shall be attached on the outlet of the third impinger and prior to the inlet of the fourth (silica gel) impinger.

6.1.2 Barometer. Same as Method 5, section 6.2.

6.1.3 Stack Gas Flow Rate Measurement System. A schematic of an example test system is shown in Figure 5H–2. The flow rate measurement system consists of the following components:

6.1.3.1 Sample Probe. A glass or stainless steel sampling probe.

6.1.3.2 Gas Conditioning System. A high density filter to remove particulate matter and a condenser capable of lowering the dew point of the gas to less than 5 °C (40 °F). Desiccant, such as Drierite, may be used to dry the sample gas. Do not use silica gel.

6.1.3.3 Pump. An inert (*e.g.*, Teflon or stainless steel heads) sampling pump capable of delivering more than the total amount of sample required in the manufacturer's instructions for the individual instruments. A means of controlling the analyzer flow rate and a device for determining proper sample flow rate (*e.g.*, precision rotameter, pressure gauge downstream of all flow controls) shall be provided at the analyzer. The requirements for measuring and controlling the analyzer flow rate are not applicable if data are presented that demonstrate that the analyzer is insensitive to flow variations over the range encountered during the test.

6.1.3.4 Carbon Monoxide (CO) Analyzer. Any analyzer capable of providing a measure of CO in the range of 0 to 10 percent by volume at least once every 10 minutes.

6.1.3.5 Carbon Dioxide (CO_2) Analyzer. Any analyzer capable of providing a measure of CO_2 in the range of 0 to 25 percent by volume at least once every 10 minutes.

NOTE: Analyzers with ranges less than those specified above may be used provided actual concentrations do not exceed the range of the analyzer.

6.1.3.6 Manifold. A sampling tube capable of delivering the sample gas to two analyzers and handling an excess of the total amount used by the analyzers. The excess gas is exhausted through a separate port.

6.1.3.7 Recorders (optional). To provide a permanent record of the analyzer outputs.

6.1.4 Proportional Gas Flow Rate System. To monitor stack flow rate changes and provide a measurement that can be used to adjust and maintain particulate sampling flow rates proportional to the stack gas flow rate. A schematic of the proportional flow rate system is shown in Figure 5H–2 and consists of the following components:

6.1.4.1 Tracer Gas Injection System. To inject a known concentration of sulfur dioxide (SO_2) into the flue. The tracer gas injection system consists of a cylinder of SO_2, a gas cylinder regulator, a stainless steel needle valve or flow controller, a nonreactive (stainless steel and glass) rotameter, and an injection loop to disperse the SO_2 evenly in the flue.

6.1.4.2 Sample Probe. A glass or stainless steel sampling probe.

6.1.4.3 Gas Conditioning System. A combustor as described in Method 16A, sections 6.1.5 and 6.1.6, followed by a high density filter to remove particulate matter, and a condenser capable of lowering the dew point of the gas to less than 5 °C (40 °F). Desiccant, such as Drierite, may be used to dry the sample gas. Do not use silica gel.

6.1.4.4 Pump. Same as described in section 6.1.3.3.

6.1.4.5 SO_2 Analyzer. Any analyzer capable of providing a measure of the SO_2 concentration in the range of 0 to 1,000 ppm by volume (or other range necessary to measure the SO_2 concentration) at least once every 10 minutes.

6.1.4.6 Recorder (optional). To provide a permanent record of the analyzer outputs.

NOTE: Other tracer gas systems, including helium gas systems, are acceptable for determination of instantaneous proportional sampling rates.

6.2 Sample Recovery. Same as Method 5, section 6.2.

6.3 Sample Analysis. Same as Method 5, section 6.3, with the addition of the following:

6.3.1 Separatory Funnel. Glass or Teflon, 500-ml or greater.

7.0 Reagents and Standards

7.1 Sample Collection. Same as Method 5, section 7.1, including deionized distilled water.

7.2 Sample Recovery. Same as Method 5, section 7.2.

7.3 Sample Analysis. The following reagents and standards are required for sample analysis:

7.3.1 Acetone. Same as Method 5 section 7.2.

7.3.2 Dichloromethane (Methylene Chloride). Reagent grade, <0.001 percent residue in glass bottles.

7.3.3 Desiccant. Anhydrous calcium sulfate, calcium chloride, or silica gel, indicating type.

7.3.4 Cylinder Gases. For the purposes of this procedure, span value is defined as the upper limit of the range specified for each analyzer as described in section 6.1.3.4 or 6.1.3.5. If an analyzer with a range different from that specified in this method is used, the span value shall be equal to the upper limit of the range for the analyzer used (see note in section 6.1.3.5).

7.3.4.1 Calibration Gases. The calibration gases for the CO_2, CO, and SO_2 analyzers shall be CO_2 in nitrogen (N_2), CO in N_2, and SO_2 in N_2, respectively. CO_2 and CO calibration gases may be combined in a single cylinder. Use three calibration gases as specified in Method 6C, sections 7.2.1 through 7.2.3.

7.3.4.2 SO_2 Injection Gas. A known concentration of SO_2 in N_2. The concentration must be at least 2 percent SO_2 with a maximum of 100 percent SO_2.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Pretest Preparation. Same as Method 5, section 8.1.

8.2 Calibration Gas and SO_2 Injection Gas Concentration Verification, Sampling System Bias Check, Response Time Test, and Zero and Calibration Drift Tests. Same as Method 6C, sections 8.2.1, 8.2.3, 8.2.4, and 8.5, respectively, except that for verification of CO and CO_2 gas concentrations, substitute Method 3 for Method 6.

8.3 Preliminary Determinations.

8.3.1 Sampling Location. The sampling location for the particulate sampling probe shall be 2.45 ±0.15 m (8 ±0.5 ft) above the platform upon which the wood heater is placed (*i.e.*, the top of the scale).

8.3.2 Sampling Probe and Nozzle. Select a nozzle, if used, sized for the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain proportional sampling rates. During the run, do not change the nozzle size. Select a suitable probe liner and probe length to effect minimum blockage.

8.4 Preparation of Particulate Sampling Train. Same as Method 5, section 8.3, with the exception of the following:

8.4.1 The train should be assembled as shown in Figure 5H–1.

8.4.2 A glass cyclone may not be used between the probe and filter holder.

8.5 Leak-Check Procedures.

8.5.1 Leak-Check of Metering System Shown in Figure 5H–1. That portion of the sampling train from the pump to the orifice meter shall be leak-checked after each certification or audit test. Use the procedure described in Method 5, section 8.4.1.

8.5.2 Pretest Leak-Check. A pretest leak-check of the sampling train is recommended, but not required. If the pretest leak-check is conducted, the procedures outlined in Method 5, section 8.5.2 should be used. A vacuum of 130 mm Hg (5 in. Hg) may be used instead of 380 mm Hg (15 in. Hg).

8.5.2 Leak-Checks During Sample Run. If, during the sampling run, a component (*e.g.*, filter assembly or impinger) change becomes necessary, conduct a leak-check as described in Method 5, section 8.4.3.

8.5.3 Post-Test Leak-Check. A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be performed in accordance with the procedures outlined in Method 5, section 8.4.4, except that a vacuum of 130 mm Hg (5 in. Hg) or the greatest vacuum measured during the test run, whichever is greater, may be used instead of 380 mm Hg (15 in. Hg).

8.6 Tracer Gas Procedure. A schematic of the tracer gas injection and sampling systems is shown in Figure 5H–2.

8.6.1 SO_2 Injection Probe. Install the SO_2 injection probe and dispersion loop in the stack at a location 2.9 ±0.15 m (9.5 ±0.5 ft) above the sampling platform.

8.6.2 SO_2 Sampling Probe. Install the SO_2 sampling probe at the centroid of the stack at a location 4.1 ±0.15 m (13.5 ±0.5 ft) above the sampling platform.

8.7 Flow Rate Measurement System. A schematic of the flow rate measurement system is shown in Figure 5H–2. Locate the flow rate measurement sampling probe at the centroid of the stack at a location 2.3 ±0.3 m (7.5 ±1 ft) above the sampling platform.

8.8 Tracer Gas Procedure. Within 1 minute after closing the wood heater door at the start of the test run (as defined in Method 28, section 8.8.1), meter a known concentration of SO_2 tracer gas at a constant flow rate into the wood heater stack. Monitor the SO_2 concentration in the stack, and record the SO_2 concentrations at 10-minute intervals or more often. Adjust the particulate sampling flow rate proportionally to the SO_2 concentration changes using Equation 5H–6 (*e.g.*, the SO_2 concentration at the first 10-minute reading is measured to be 100 ppm; the next 10 minute SO_2 concentration is measured to be 75 ppm: the particulate sample flow rate is adjusted from the initial 0.15 cfm to 0.20 cfm). A check for proportional rate variation shall be made at the completion of the test run using Equation 5H–10.

8.9 Volumetric Flow Rate Procedure. Apply stoichiometric relationships to the wood combustion process in determining the exhaust gas flow rate as follows:

8.9.1 Test Fuel Charge Weight. Record the test fuel charge weight (wet) as specified in Method 28, section 8.8.2. The wood is assumed to have the following weight percent composition: 51 percent carbon, 7.3 percent hydrogen, 41 percent oxygen. Record the wood moisture for each fuel charge as described in Method 28, section 8.6.5. The ash is assumed to have negligible effect on associated C, H, and O concentrations after the test burn.

8.9.2 Measured Values. Record the CO and CO_2 concentrations in the stack on a dry basis every 10 minutes during the test run or more often. Average these values for the test run. Use as a mole fraction (*e.g.*, 10 percent CO_2 is recorded as 0.10) in the calculations to express total flow (see Equation 5H–6).

8.10 Sampling Train Operation.

8.10.1 For each run, record the data required on a data sheet such as the one shown in Figure 5H–3. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak-check, and when sampling is halted. Take other readings as indicated on Figure 5H–3 at least once each 10 minutes during the test run.

8.10.2 Remove the nozzle cap, verify that the filter and probe heating systems are up to temperature, and that the probe is properly positioned. Position the nozzle, if used, facing into gas stream, or the probe tip in the 50 mm (2 in.) centroidal area of the stack.

8.10.3 Be careful not to bump the probe tip into the stack wall when removing or inserting the probe through the porthole; this minimizes the chance of extracting deposited material.

8.10.4 When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

8.10.5 Begin sampling at the start of the test run as defined in Method 28, section 8.8.1, start the sample pump, and adjust the sample flow rate to between 0.003 and 0.014 m^3/min (0.1 and 0.5 cfm). Adjust the sample flow rate proportionally to the stack gas flow during the test run according to the procedures outlined in section 8. Maintain a proportional sampling rate (within 10 percent of the desired value) and a filter holder temperature no greater than 120 °C (248 °F).

8.10.6 During the test run, make periodic adjustments to keep the temperature around the filter holder at the proper level. Add more ice to the impinger box and, if necessary, salt to maintain a temperature of less than 20 °C (68 °F) at the condenser/silica gel outlet.

8.10.7 If the pressure drop across the filter becomes too high, making proportional sampling difficult to maintain, either filter may be replaced during a sample run. It is recommended that another complete filter assembly be used rather than attempting to change the filter itself. Before a new filter assembly is installed, conduct a leak-check (see section 8.5.2). The total particulate weight shall include the summation of all filter assembly catches. The total time for changing sample train components shall not exceed 10 minutes. No more than one component change is allowed for any test run.

8.10.8 At the end of the test run, turn off the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak-check, as outlined in section 8.5.3.

8.11 Sample Recovery. Same as Method 5, section 8.7, with the exception of the following:

8.11.1 Blanks. The volume of the acetone blank may be about 50-ml, rather than 200-ml; a 200-ml water blank shall also be saved for analysis.

8.11.2 Samples.

8.11.2.1 Container Nos. 1 and 1A. Treat the two filters according to the procedures outlined in Method 5, section 8.7.6.1. The filters

may be stored either in a single container or in separate containers.

8.11.2.2 Container No. 2. Same as Method 5, section 8.7.6.2, except that the container should not be sealed until the impinger rinse solution is added (see section 8.10.2.4).

8.11.2.3 Container No. 3. Treat the impingers as follows: Measure the liquid which is in the first three impingers to within 1-ml by using a graduated cylinder or by weighing it to within 0.5 g by using a balance (if one is available). Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas. Transfer the water from the first, second, and third impingers to a glass container. Tighten the lid on the sample container so that water will not leak out.

8.11.2.4 Rinse impingers and graduated cylinder, if used, with acetone three times or more. Avoid direct contact between the acetone and any stopcock grease or collection of any stopcock grease in the rinse solutions. Add these rinse solutions to sample Container No. 2.

8.11.2.5 Container No. 4. Same as Method 5, section 8.7.6.3

8.12 Sample Transport. Whenever possible, containers should be transferred in such a way that they remain upright at all times.

NOTE: Requirements for capping and transport of sample containers are not applicable if sample recovery and analysis occur in the same room.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.2	Sampling system bias check	Ensures that bias introduced by measurement system, minus analyzer, is no greater than 3 percent of span.
8.2	Analyzer zero and calibration drift tests	Ensures that bias introduced by drift in the measurement system output during the run is no greater than 3 percent of span.
8.5, 10.1, 12.13	Sampling equipment leak-check and calibration; proportional sampling rate verification.	Ensures accurate measurement of stack gas flow rate, sample volume.
10.1	Analytical balance calibration	Ensure accurate and precise measurement of collected particulate.
10.3	Analyzer calibration error check	Ensures that bias introduced by analyzer calibration error is no greater than 2 percent of span.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory record of all calibrations.

10.1 Volume Metering System, Temperature Sensors, Barometer, and Analytical Balance. Same as Method 5G, sections 10.2 through 10.5, respectively.

10.2 SO_2 Injection Rotameter. Calibrate the SO_2 injection rotameter system with a soap film flowmeter or similar direct volume measuring device with an accuracy of 2 percent. Operate the rotameter at a single reading for at least three calibration runs for 10 minutes each. When three consecutive calibration flow rates agree within 5 percent, average the three flow rates, mark the rotameter at the calibrated setting, and use the calibration flow rate as the SO_2 injection flow rate during the test run. Repeat the rotameter calibration before the first certification test and semiannually thereafter.

10.3. Gas Analyzers. Same as Method 6C, section 10.0.

10.4 Field Balance Calibration Check. Check the calibration of the balance used to weigh impingers with a weight that is at least 500g or within 50g of a loaded impinger. The weight must be ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 6 (or better). Daily before use, the field balance must measure the weight within ± 0.5g of the certified mass. If the daily balance calibration check fails, perform corrective measures and repeat the check before using balance.

10.5 Analytical Balance Calibration. Perform a multipoint calibration (at least five points spanning the operational range) of the analytical balance before the first use, and semiannually thereafter. The calibration of the analytical balance must be conducted using ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 2 (or better) tolerance weights. Audit the balance each day it is used for gravimetric measurements by weighing at least one ASTM E617–13 Class 2 tolerance (or better) calibration weight that corresponds to 50 to 150 percent of the weight of one filter or between 1g and 5g. If the scale cannot reproduce the value of the calibration weight to within 0.5 mg of the certified mass, perform corrective measures, and conduct the multipoint calibration before use.

11.0 Analytical Procedure

11.1 Record the data required on a sheet such as the one shown in Figure 5H–4.

11.2 Handle each sample container as follows:

11.2.1 Container Nos. 1 and 1A. Treat the two filters according to the procedures outlined in Method 5, section 11.2.1.

11.2.2 Container No. 2. Same as Method 5, section 11.2.2, except that the beaker may be smaller than 250-ml.

11.2.3 Container No. 3. Note the level of liquid in the container and confirm on the analysis sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Determination of sample leakage is not applicable if sample recovery and analysis occur in the same room. Measure the liquid in this container either volumetrically to within 1-ml or gravimetrically to within 0.5 g. Transfer the contents to a 500-ml or larger separatory funnel. Rinse the container with water, and add to the separatory funnel. Add 25-ml of dichloromethane to the separatory funnel, stopper and vigorously shake 1 minute, let separate and transfer the dichloromethane (lower layer) into a tared beaker or evaporating dish. Repeat twice more. It is necessary to rinse Container No. 3 with dichloromethane. This rinse is added to the impinger extract container. Transfer the remaining water from the separatory funnel to a tared beaker or evaporating dish and evaporate to dryness at 104 °C (220 °F). Desiccate and weigh to a constant weight. Evaporate the combined impinger water extracts at ambient temperature and pressure. Desiccate and weigh to a constant weight. Report both results to the nearest 0.1 mg.

11.2.4 Container No. 4. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance.

11.2.5 Acetone Blank Container. Same as Method 5, section 11.2.4, except that the beaker may be smaller than 250 ml.

11.2.6 Dichloromethane Blank Container. Treat the same as the acetone blank.

11.2.7 Water Blank Container. Transfer the water to a tared 250 ml beaker and evaporate to dryness at 104 °C (220 °F). Desiccate and weigh to a constant weight.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

12.1 Nomenclature.

A = Sample flow rate adjustment factor.
BR = Dry wood burn rate, kg/hr (lb/hr), from Method 28, Section 8.3.
B_{ws} = Water vapor in the gas stream, proportion by volume.
C_i = Tracer gas concentration at inlet, ppmv.
C_o = Tracer gas concentration at outlet, ppmv.
C_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (g/dscf).
E = Particulate emission rate, g/hr (lb/hr).
ΔH = Average pressure differential across the orifice meter (see Figure 5H–1), mm H_2O (in. H_2O).
L_a = Maximum acceptable leakage rate for either a post-test leak-check or for a leak-check following a component change; equal to 0.00057 cmm (0.020 cfm) or 4 percent of the average sampling rate, whichever is less.
L_1 = Individual leakage rate observed during the leak-check conducted before a component change, cmm (cfm).
L_p = Leakage rate observed during the post-test leak-check, cmm (cfm).
m_n = Total amount of particulate matter collected, mg.
M_a = Mass of residue of solvent after evaporation, mg.
N_C = Grams of carbon/gram of dry fuel (lb/lb), equal to 0.0425.
N_T = Total dry moles of exhaust gas/kg of dry wood burned, g-moles/kg (lb-moles/lb).
PR = Percent of proportional sampling rate.
P_{bar} = Barometric pressure at the sampling site, mm Hg (in.Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in.Hg).
Q_i = Gas volumetric flow rate at inlet, cfm (l/min).
Q_o = Gas volumetric flow rate at outlet, cfm (l/min).

12.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 5H–3).

12.3 Dry Gas Volume. Same as Method 5, section 12.3.

12.4 Volume of Water Vapor.

$$V_{w(std)} = K_2 V_{1c} \qquad \text{Eq. 5H-1}$$

Where:

K_2 = 0.001333 m^3/ml for metric units.
K_2 = 0.04707 ft^3/ml for English units.

12.5 Moisture Content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad \text{Eq. 5H-2}$$

12.6 Solvent Wash Blank.

$$W_a = \frac{M_a V_{aw}}{V_a} \qquad \text{Eq. 5H-3}$$

12.7 Total Particulate Weight. Determine the total particulate catch from the sum of the weights obtained from containers 1, 2, 3,

and 4 less the appropriate solvent blanks (see Figure 5H–4).

NOTE: Refer to Method 5, section 8.5 to assist in calculation of results involving two filter assemblies.

12.8 Particulate Concentration.

$$C_s = \frac{0.001g}{mg}\ \frac{m_n}{V_{m(std)}} \qquad \text{Eq. 5H-4}$$

12.9 Sample Flow Rate Adjustment.

$$a = \frac{S_1}{S_i} \qquad \text{Eq. 5H-5}$$

12.10 Carbon Balance for Total Moles of Exhaust Gas (dry)/kg of Wood Burned in the Exhaust Gas.

$$N_T = \frac{K_3 N_C}{Y_{CO_2} + Y_{CO} + Y_{HC}} \qquad \text{Eq. 5H-6}$$

Where:

K_3 = 1000 g/kg for metric units.
K_3 = 1.0 lb/lb for English units.

NOTE: The NO_X/SO_X portion of the gas is assumed to be negligible.

12.11 Total Stack Gas Flow Rate.

$$Q_{sd} = K_4\ N_T\ BR \qquad \text{Eq. 5H-7}$$

Where:

K_4 = 0.02406 dscm/g-mole for metric units.
K_4 = 384.8 dscf/lb-mole for English units.

12.12 Particulate Emission Rate.

$$E = C_s\ Q_{sd} \qquad \text{Eq. 5H-8}$$

12.13 Proportional Rate Variation. Calculate PR for each 10-minute interval, i, of the test run.

$$PR = \frac{\theta\ S_i V_{mi(std)}}{10\sum_{i=1}^{N}\left[S_i V_{mi(std)}\right]} \times 100 \qquad \text{Eq. 5H-9}$$

12.14 Acceptable Results. If no more than 15 percent of the PR values for all the intervals fall outside the range 90 percent ≤PR ≤110 percent, and if no PR value for any interval falls outside the range 75 ≤PR ≤125 percent, the results are acceptable. If the PR values for the test runs are judged to be unacceptable, report the test run emission results, but do not include the test run results in calculating the weighted average emission rate, and repeat the test.

12.15 Alternative Tracer Gas Flow Rate Determination.

$$Q_o = \frac{Q_i \times C_i}{C_o} \qquad Eq.\ 5H-10$$

NOTE: This gives Q for a single instance only. Repeated multiple determinations are needed to track temporal variations. Very small variations in Q_i, C_i, or C_o may give very large variations in Q_o.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Alternative Stack Gas Volumetric Flow Rate Determination (Tracer Gas).

16.1.1 Apparatus.

16.1.1.1 Tracer Gas Injector System. This is to inject a known concentration of tracer gas into the stack. This system consists of a cylinder of tracer gas, a gas cylinder regulator, a stainless steel needle valve or a flow controller, a nonreactive (stainless steel or glass) rotameter, and an injection loop to disperse the tracer gas evenly in the stack.

16.1.1.2 Tracer Gas Probe. A glass or stainless steel sampling probe.

16.1.1.3 Gas Conditioning System. A gas conditioning system is suitable for delivering a cleaned sample to the analyzer consisting of a filter to remove particulate and a condenser capable of lowering the dew point of the sample gas to less than 5 °C (40 °F). A desiccant such as anhydrous calcium sulfate may be used to dry the sample gas. Desiccants which react or absorb tracer gas or stack gas may not be used, e.g. silica gel absorbs CO_2.

16.1.1.4 Pump. An inert (*i.e.*, stainless steel or Teflon head) pump to deliver more than the total sample required by the manufacturer's specifications for the analyzer used to measure the downstream tracer gas concentration.

16.1.1.5 Gas Analyzer. A gas analyzer is any analyzer capable of measuring the tracer gas concentration in the range necessary at least every 10 minutes. A means of controlling the analyzer flow rate and a device for determining proper sample flow rate shall be provided unless data is provided to show that the analyzer is insensitive to flow variations over the range encountered during the test.

The gas analyzer needs to meet or exceed the following performance specifications:

Linearity	±1 percent of full scale.
Calibration Error	≤2 percent of span.
Response Time	≤10 seconds.
Zero Drift (24 hour)	≤2 percent of full scale.
Span Drift (24 hour)	≤2 percent of full scale.
Resolution	≤0.5 percent of span.

16.1.1.6 Recorder (optional). To provide a permanent record of the analyzer output.

16.1.2 Reagents.

16.1.2.1 Tracer Gas. The tracer gas is sulfur hexafluoride in an appropriate concentration for accurate analyzer measurement or pure sulfur dioxide. The gas used must be nonreactive with the stack effluent and give minimal (<3 percent) interference to measurement by the gas analyzer.

16.1.3 Procedure. Select upstream and downstream locations in the stack or duct for introducing the tracer gas and delivering the sampled gas to the analyzer. The inlet location should be 8 or more duct diameters beyond any upstream flow disturbance. The outlet should be 8 or more undisturbed duct diameters from the inlet and 2 or more duct diameters from the duct exit. After installing the apparatus, meter a known concentration of the tracer gas into the stack at the inlet location. Use the gas sample probe and analyzer to show that no stratification of the tracer gas is found in the stack at the measurement locations. Monitor the tracer gas concentration from the outlet location and record the concentration at 10-minute intervals or more often at the option of the tester. A minimum of three measured intervals is recommended to determine the stack gas volumetric flow rate. Other statistical procedures may be applied for complete flow characterization and additional QA/QC.

17.0 References

Same as Method 5G, section 17.0.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

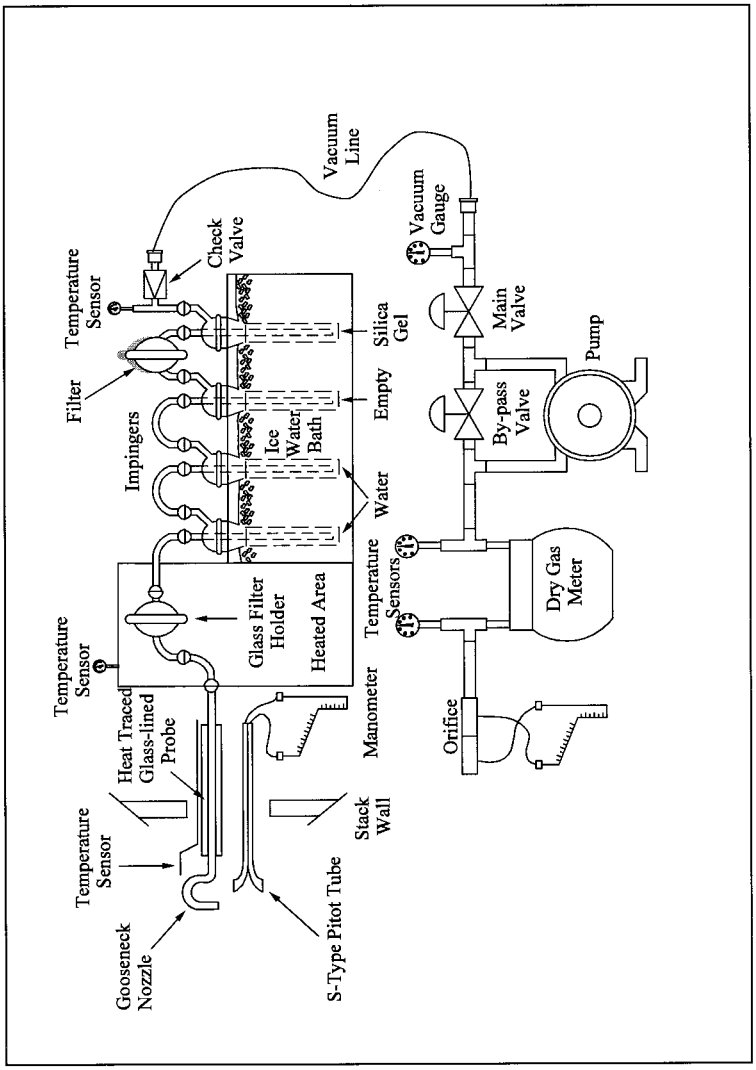


Figure 5H-1. Sampling Train.

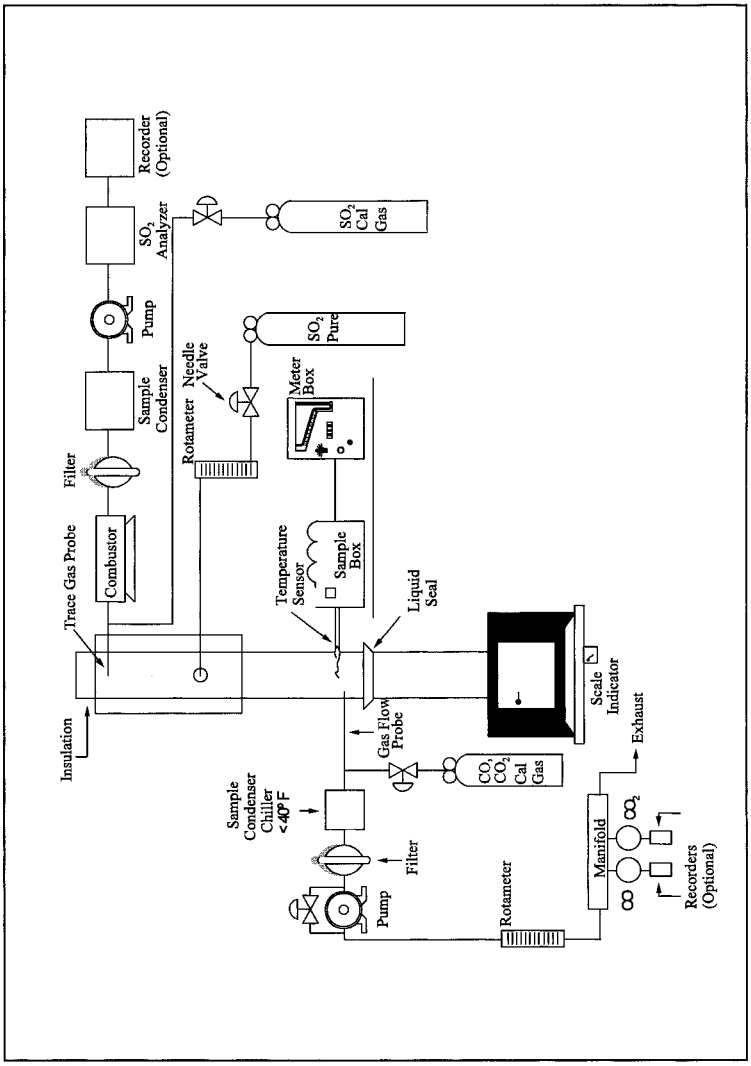
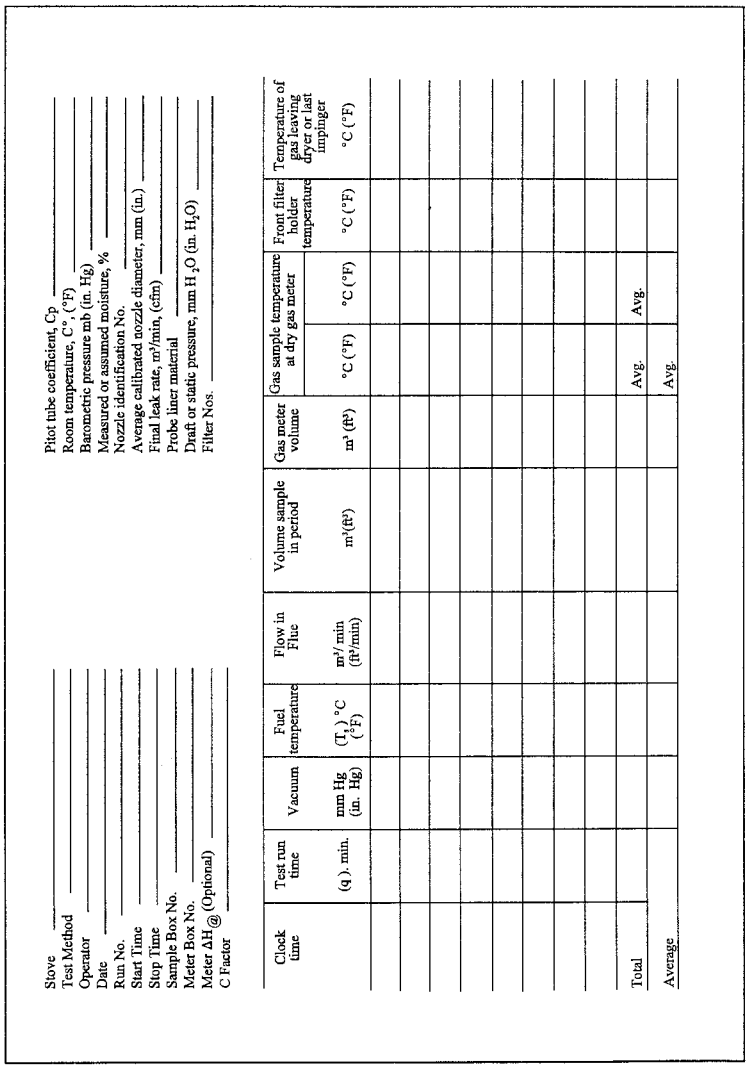


Figure 5H-2. Test System Schematic.



Stove _____
Test Method _____
Operator _____
Date _____
Run No. _____
Start Time _____
Stop Time _____
Sample Box No. _____
Meter Box No. _____
Meter ΔH@ (Optional) _____
C Factor _____

Pitot tube coefficient, Cp _____
Room temperature, C°, (°F) _____
Barometric pressure mb (in. Hg) _____
Measured or assumed moisture, % _____
Nozzle identification No. _____
Average calibrated nozzle diameter, mm (in.) _____
Final leak rate, m³/min, (cfm) _____
Probe liner material _____
Draft or static pressure, mm H_2O (in. H_2O) _____
Filter Nos. _____

Clock time	Test run time (q), min.	Vacuum mm Hg (in. Hg)	Fuel temperature (T_s) °C (°F)	Flow in Flue m³/ min (ft³/min)	Volume sample in period m³(ft³)	Gas meter volume m³ (ft³)	Gas sample temperature at dry gas meter °C (°F)	Gas sample temperature at dry gas meter °C (°F)	Front filter holder temperature °C (°F)	Temperature of gas leaving dryer or last impinger °C (°F)
Total							Avg.	Avg.		
Average							Avg.			

Figure 5H-3. Sampling Data Sheet.

Stove _____
Date _____
Run No. _____
Filter Nos. _____
Amount liquid lost during transport, ml _____
Acetone blank volume, ml _____
Acetone wash volume, ml _____
Acetone blank concentration, mg/ml _____
Acetone wash blank, mg _____

Dichloromethane blank volume, ml _____
Dichloromethane wash volume, ml _____
Dichloromethane blank concentration, mg/ml _____
Dichloromethane wash blank, mg _____
Water blank volume, ml _____
Waster wash volume, ml _____
Water blank concentration, mg/ml _____
Water wash blank, mg _____

Container number	Weight of particulate collected, mg		
	Final weight	Tare weight	Weight gain
1 _____			
2 _____			
3 _____			
4 _____			
5 _____			
Total			
Less acetone blank			
Less dichloromethane blank			
Less water blank			
Weight of particulate matter			

	Volume of liquid water collected	
	Impinger volume, ml	Silica gel weight, g
Final _____		
Initial _____		
Liquid collected _____		
Total volume collected _____		g or ml

* Convert weight of water to volume by dividing total weight increase by density of water (1 g/ml).

$$\frac{\text{Increase, g}}{\text{(1 g/ml)}} = \text{Volume water, ml}$$

Figure 5H-4. Analysis data sheet.

Figure 5H-4. Analysis Data Sheet.

METHOD 5I—DETERMINATION OF LOW LEVEL PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Certain information is contained in other EPA procedures found in this part. Therefore, to obtain reliable results, persons using this method should have experience with and a thorough knowledge of the following Methods: Methods 1, 2, 3, 4 and 5.

1. Scope and Application.

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of low level particulate matter (PM) emissions from stationary sources. The method is most effective for total PM catches of 50 mg or less. This method was initially developed for performing correlation of manual PM measurements to PM continuous emission monitoring systems (CEMS), however it is also useful for other low particulate concentration applications.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods. Method 5I requires the use of paired trains. Acceptance criteria for the identification of data quality outliers from the paired trains are provided in section 12.2 of this Method.

2. Summary of Method.

2.1. Description. The system setup and operation is essentially identical to Method 5. Particulate is withdrawn isokinetically from the source and collected on a 47 mm glass fiber filter maintained at a temperature of 120 ±14 °C (248 ±25 °F). The PM mass is determined by gravimetric analysis after the removal of uncombined water. Specific measures in this procedure designed to improve system performance at low particulate levels include:

1. Improved sample handling procedures
2 Light weight sample filter assembly
3. Use of low residue grade acetone

Accuracy is improved through the minimization of systemic errors associated with sample handling and weighing procedures. High purity reagents, all glass, grease free, sample train components, and light weight filter assemblies and beakers, each contribute to the overall objective of improved precision and accuracy at low particulate concentrations.

2.2 Paired Trains. This method must be performed using a paired train configuration. These trains may be operated as co-located trains (to trains operating collecting from one port) or as simultaneous trains (separate trains operating from different ports at the same time). Procedures for calculating precision of the paired trains are provided in section 12.

2.3 Detection Limit. a. Typical detection limit for manual particulate testing is 0.5 mg. This mass is also cited as the accepted weight variability limit in determination of ''constant weight'' as cited in section 8.1.2 of this Method. EPA has performed studies to provide guidance on minimum PM catch. The minimum detection limit (MDL) is the minimum concentration or amount of an analyte that can be determined with a specified degree of confidence to be different from zero. We have defined the minimum or target catch as a concentration or amount sufficiently larger than the MDL to ensure that the results are reliable and repeatable. The particulate matter catch is the product of the average particulate matter concentration on a mass per volume basis and the volume of gas collected by the sample train. The tester can generally control the volume of gas collected by increasing the sampling time or to a lesser extent by increasing the rate at which sample is collected. If the tester has a reasonable estimate of the PM concentration from the source, the tester can ensure that the target catch is collected by sampling the appropriate gas volume.

b. However, if the source has a very low particulate matter concentration in the stack, the volume of gas sampled may need to be very large which leads to unacceptably long sampling times. When determining compliance with an emission limit, EPA guidance has been that the tester does not always have to collect the target catch. Instead, we have suggested that the tester sample enough stack gas, that if the source were exactly at the level of the emission standard, the sample catch would equal the target catch. Thus, if at the end of the test the catch were smaller than the target, we could still conclude that the source is in compliance though we might not know the exact emission level. This volume of gas becomes a target volume that can be translated into a target sampling time by assuming an average sampling rate. Because the MDL forms the basis for our guidance on target sampling times, EPA has conducted a systematic laboratory study to define what is the MDL for Method 5 and determined the Method to have a calculated practical quantitation limit (PQL) of 3 mg of PM and an MDL of 1 mg.

c. Based on these results, the EPA has concluded that for PM testing, the target catch must be no less than 3 mg. Those sample catches between 1 mg and 3 mg are between the detection limit and the limit of quantitation. If a tester uses the target catch to estimate a target sampling time that results in sample catches that are less than 3 mg, you should not automatically reject the results. If the tester calculated the target sampling time as described above by assuming that the source was at the level of the emission limit, the results would still be valid for determining that the source was in compliance. For purposes other than determining compliance, results should be divided into two categories—those that fall between 3 mg and 1 mg and those that are below 1 mg. A sample catch between 1 and 3 mg may be used for such purposes as calculating emission rates with the understanding that the resulting emission rates can have a high degree of uncertainty. Results of less than 1 mg should not be used for calculating emission rates or pollutant concentrations.

d. When collecting small catches such as 3 mg, bias becomes an important issue. Source testers must use extreme caution to reach the PQL of 3 mg by assuring that sampling

probes are very clean (perhaps confirmed by low blank weights) before use in the field. They should also use low tare weight sample containers, and establish a well-controlled balance room to weigh the samples.

3. Definitions.

3.1 *Light Weight Filter Housing.* A smaller housing that allows the entire filtering system to be weighed before and after sample collection. (See. 6.1.3)

3.2 *Paired Train.* Sample systems trains may be operated as co-located trains (two sample probes attached to each other in the same port) or as simultaneous trains (two separate trains operating from different ports at the same time).

4. Interferences.

a. There are numerous potential interferents that may be encountered during performance of Method 5I sampling and analyses. This Method should be considered more sensitive to the normal interferents typically encountered during particulate testing because of the low level concentrations of the flue gas stream being sampled.

b. Care must be taken to minimize field contamination, especially to the filter housing since the entire unit is weighed (not just the filter media). Care must also be taken to ensure that no sample is lost during the sampling process (such as during port changes, removal of the filter assemblies from the probes, etc.).

c. Balance room conditions are a source of concern for analysis of the low level samples. Relative humidity, ambient temperatures variations, air draft, vibrations and even barometric pressure can affect consistent reproducible measurements of the sample media. Ideally, the same analyst who performs the tare weights should perform the final weights to minimize the effects of procedural differences specific to the analysts.

d. Attention must also be provided to weighing artifacts caused by electrostatic charges which may have to be discharged or neutralized prior to sample analysis. Static charge can affect consistent and reliable gravimetric readings in low humidity environments. Method 5I recommends a relative humidity of less than 50 percent in the weighing room environment used for sample analyses. However, lower humidity may be encountered or required to address sample precision problems. Low humidity conditions can increase the effects of static charge.

e. Other interferences associated with typical Method 5 testing (sulfates, acid gases, etc.) are also applicable to Method 5I.

5. Safety.

Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety concerns associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability and observe all regulatory limitations before using this method.

6. Equipment and Supplies.

6.1 Sample Collection Equipment and Supplies. The sample train is nearly identical in configuration to the train depicted in Figure 5–1 of Method 5. The primary difference in the sample trains is the lightweight Method 5I filter assembly that attaches directly to the exit to the probe. Other exceptions and additions specific to Method 5I include:

6.1.1 Probe Nozzle. Same as Method 5, with the exception that it must be constructed of borosilicate or quartz glass tubing.

6.1.2 Probe Liner. Same as Method 5, with the exception that it must be constructed of borosilicate or quartz glass tubing.

6.1.3 Filter Holder. The filter holder is constructed of borosilicate or quartz glass front cover designed to hold a 47-mm glass fiber filter, with a wafer thin stainless steel (SS) filter support, a silicone rubber or Viton O-ring, and Teflon tape seal. This holder design will provide a positive seal against leakage from the outside or around the filter. The filter holder assembly fits into a SS filter holder and attaches directly to the outlet of the probe. The tare weight of the filter, borosilicate or quartz glass holder, SS filter support, O-ring and Teflon tape seal generally will not exceed approximately 35 grams. The filter holder is designed to use a 47-mm glass fiber filter meeting the quality criteria in of Method 5. These units are commercially available from several source testing equipment vendors. Once the filter holder has been assembled, desiccated and tared, protect it from external sources of contamination by covering the front socket with a ground glass plug. Secure the plug with an impinger clamp or other item that will ensure a leak-free fitting.

6.2 Sample Recovery Equipment and Supplies. Same as Method 5, with the following exceptions:

6.2.1 Probe-Liner and Probe-Nozzle Brushes. Teflon or nylon bristle brushes with stainless steel wire handles, should be used to clean the probe. The probe brush must have extensions (at least as long as the probe) of Teflon, nylon or similarly inert material. The brushes must be properly sized and shaped for brushing out the probe liner and nozzle.

6.2.2 Wash Bottles. Two Teflon wash bottles are recommended however, polyethylene wash bottles may be used at the option of the tester. Acetone should not be stored in polyethylene bottles for longer than one month.

6.2.3 Filter Assembly Transport. A system should be employed to minimize contamination of the filter assemblies during transport to and from the field test location. A carrying case or packet with clean compartments of sufficient size to accommodate each filter assembly can be used. This system should have an air tight seal to further minimize contamination during transport to and from the field.

6.3 Analysis Equipment and Supplies. Same as Method 5, with the following exception:

6.3.1 Lightweight Beaker Liner. Teflon or other lightweight beaker liners are used for the analysis of the probe and nozzle rinses. These light weight liners are used in place of the borosilicate glass beakers typically used for the Method 5 weighings in order to improve sample analytical precision.

6.3.2 Anti-static Treatment. Commercially available gaseous anti-static rinses are recommended for low humidity situations that contribute to static charge problems.

7. Reagents and Standards.

7.1 Sampling Reagents. The reagents used in sampling are the same as Method 5 with the following exceptions:

7.1.1 Filters. The quality specifications for the filters are identical to those cited for Method 5. The only difference is the filter diameter of 47 millimeters.

7.1.2 Stopcock Grease. Stopcock grease cannot be used with this sampling train. We recommend that the sampling train be assembled with glass joints containing O-ring seals or screw-on connectors, or similar.

7.1.3 Acetone. Low residue type acetone, ≤0.001 percent residue, purchased in glass bottles is used for the recovery of particulate matter from the probe and nozzle. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers; thus, acetone blanks must be run prior to field use and only acetone with low blank values (≤0.001 percent residue, as specified by the manufacturer) must be used. Acetone blank correction is not allowed for this method; therefore, it is critical that high purity reagents be purchased and verified prior to use.

7.1.4 Gloves. Disposable, powder-free, latex surgical gloves, or their equivalent are used at all times when handling the filter housings or performing sample recovery.

7.2 Standards. There are no applicable standards commercially available for Method 5I analyses.

8. Sample Collection, Preservation, Storage, and Transport.

8.1 Pretest Preparation. Same as Method 5 with several exceptions specific to filter assembly and weighing.

8.1.1 Filter Assembly. Uniquely identify each filter support before loading filters into the holder assembly. This can be done with an engraving tool or a permanent marker. Use powder free latex surgical gloves whenever handling the filter holder assemblies. Place the O-ring on the back of the filter housing in the O-ring groove. Place a 47 mm glass fiber filter on the O-ring with the face down. Place a stainless steel filter holder against the back of the filter. Carefully wrap 5 mm (¼ inch) wide Teflon'' tape one timearound the outside of the filter holder overlapping the stainless steel filter support by approximately 2.5 mm (⅛ inch). Gently brush the Teflon tape down on the back of the stainless steel filter support. Store the filter assemblies in their transport case until time for weighing or field use.

8.1.2 Filter Weighing Procedures. a. Desiccate the entire filter holder assemblies at 20 ±5.6 °C (68 ±10 °F) and ambient pressure for at least 24 hours. Weigh at intervals of at least 6 hours to a constant weight, *i.e.,* 0.5 mg change from previous weighing. Record the results to the nearest 0.1 mg. During each weighing, the filter holder assemblies must not be exposed to the laboratory atmosphere for a period greater than 2 minutes and a relative humidity above 50 percent. Lower relative humidity may be required in order to improve analytical precision. However, low humidity conditions increase static charge to the sample media.

b. Alternatively (unless otherwise specified by the Administrator), the filters holder assemblies may be oven dried at 105 °C (220 °F) for a minimum of 2 hours, desiccated for 2 hours, and weighed. The procedure used for the tare weigh must also be used for the final weight determination.

c. Experience has shown that weighing uncertainties are not only related to the balance performance but to the entire weighing procedure. Therefore, before performing any measurement, establish and follow standard operating procedures, taking into account the sampling equipment and filters to be used.

8.2 Preliminary Determinations. Select the sampling site, traverse points, probe nozzle, and probe length as specified in Method 5.

8.3 Preparation of Sampling Train. Same as Method 5, section 8.3, with the following exception: During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until justbefore assembly or until sampling is about to begin. Using gloves, place a labeled (identified) and weighed filter holder assembly into the stainless steel holder. Then place this whole unit in the Method 5 hot box, and attach it to the probe. Do not use stopcock grease.

8.4 Leak-Check Procedures. Same as Method 5.

8.5 Sampling Train Operation.

8.5.1. Operation. Operate the sampling train in a manner consistent with those described in Methods 1, 2, 4 and 5 in terms of the number of sample points and minimum time per point. The sample rate and total gas volume should be adjusted based on estimated grain loading of the source being characterized. The total sampling time must be a function of the estimated mass of particulate to be collected for the run. Targeted mass to be collected in a typical Method 5I sample train should be on the order of 10 to 20 mg. Method 5I is most appropriate for total collected masses of less than 50 milligrams, however, there is not an exact particulate loading cutoff, and it is likely that some runs may exceed 50 mg. Exceeding 50 mg (or less than 10 mg) for the sample mass does not necessarily justify invalidating a sample run if all other Method criteria are met.

8.5.2 Paired Train. This Method requires PM samples be collected with paired trains.

8.5.2.1 It is important that the systems be operated truly simultaneously. This implies that both sample systems start and stop at the same times. This also means that if one sample system is stopped during the run, the other sample systems must also be stopped until the cause has been corrected.

8.5.2.2 Care should be taken to maintain the filter box temperature of the paired trains as close as possible to the Method required temperature of 120 ±14 °C (248 ±25 °F). If separate ovens are being used for simultaneously operated trains, it is recommended that the oven temperature of each train be maintained within ±14 °C (±25 °F) of each other.

8.5.2.3 The nozzles for paired trains need not be identically sized.

8.5.2.4 Co-located sample nozzles must be within the same plane perpendicular to the gas flow. Co-located nozzles and pitot assemblies should be within a 6.0 cm × 6.0 cm square (as cited for a quadruple train in Reference Method 301).

8.5.3 Duplicate gas samples for molecular weight determination need not be collected.

8.6 Sample Recovery. Same as Method 5 with several exceptions specific to the filter housing.

8.6.1 Before moving the sampling train to the cleanup site, remove the probe from the train and seal the nozzle inlet and outlet of the probe. Be careful not to lose any condensate that might be present. Cap the filter inlet using a standard ground glass plug and secure the cap with an impinger clamp. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger condenser and the filter holder, disconnect the line at the filter holder and let any condensed water or liquid drain into the impingers or condenser.

8.6.2 Transfer the probe and filter-impinger assembly to the cleanup area. This area must be clean and protected from the wind so that the possibility of losing any of the sample will be minimized.

8.6.3 Inspect the train prior to and during disassembly and note any abnormal conditions such as particulate color, filter loading, impinger liquid color, etc.

8.6.4 Container No. 1, Filter Assembly. Carefully remove the cooled filter holder assembly from the Method 5 hot box and place it in the transport case. Use a pair of clean gloves to handle the filter holder assembly.

8.6.5 Container No. 2, Probe Nozzle and Probe Liner Rinse. Rinse the probe and nozzle components with acetone. Be certain that the probe and nozzle brushes have been thoroughly rinsed prior to use as they can be a source of contamination.

8.6.6 All Other Train Components. (Impingers) Same as Method 5.

8.7 Sample Storage and Transport. Whenever possible, containers should be shipped in such a way that they remain upright at all times. All appropriate dangerous goods shipping requirements must be observed since acetone is a flammable liquid.

9. Quality Control.

9.1 Miscellaneous Field Quality Control Measures.

9.1.1 A quality control (QC) check of the volume metering system at the field site is suggested before collecting the sample using the procedures in Method 5, section 4.4.1.

9.1.2 All other quality control checks outlined in Methods 1, 2, 4 and 5 also apply to Method 5I. This includes procedures such as leak-checks, equipment calibration checks, and independent checks of field data sheets for reasonableness and completeness.

9.2 Quality Control Samples.

9.2.1 Required QC Sample. A laboratory reagent blank must be collected and analyzed for each lot of acetone used for a field program to confirm that it is of suitable purity. The particulate samples cannot be blank corrected.

9.2.2 Recommended QC Samples. These samples may be collected and archived for future analyses.

9.2.2.1 A field reagent blank is a recommended QC sample collected from a portion of the acetone used for cleanup of the probe and nozzle. Take 100 ml of this acetone directly from the wash bottle being used and place it in a glass sample container labeled ''field acetone reagent blank.'' At least one field reagent blank is recommended for every five runs completed. The field reagent blank samples demonstrate the purity of the acetone was maintained throughout the program.

9.2.2.2 A field bias blank train is a recommended QC sample. This sample is collected by recovering a probe and filter assembly that has been assembled, taken to the sample location, leak checked, heated, allowed to sit at the sample location for a similar duration of time as a regular sample run, leak-checked again, and then recovered in the same manner as a regular sample. Field bias blanks are not a Method requirement, however, they are recommended and are very useful for identifying sources of contamination in emission testing samples. Field bias blank train results greater than 5 times the method detection limit may be considered problematic.

10. Calibration and Standardization Same as Method 5, section 5.

10.1 Field Balance Calibration Check. Check the calibration of the balance used to weigh impingers with a weight that is at least 500g or within 50g of a loaded impinger. The weight must be ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 6 (or better). Daily, before use, the field balance must measure the weight within ±0.5g of the certified mass. If the daily balance calibration check fails, perform corrective measures and repeat the check before using balance.

10.2 Analytical Balance Calibration. Perform a multipoint calibration (at least five points spanning the operational range) of the analytical balance before the first use, and semiannually thereafter. The calibration of the analytical balance must be conducted using ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 2 (or better) tolerance weights. Audit the balance each day it is used for gravimetric measurements by weighing at least one ASTM E617–13 Class 2 tolerance (or better) calibration weight that corresponds to 50 to 150 percent of the weight of one filter or between 1g and 5g. If the scale cannot reproduce the value of the calibration weight to within 0.5 mg of the certified mass, perform corrective measures and conduct the multipoint calibration before use.

11. Analytical Procedures.

11.1 Analysis. Same as Method 5, sections 11.1–11.2.4, with the following exceptions:

11.1.1 Container No. 1. Same as Method 5, section 11.2.1, with the following exception: Use disposable gloves to remove each of the filter holder assemblies from the desiccator, transport container, or sample oven (after appropriate cooling).

11.1.2 Container No. 2. Same as Method 5, section 11.2.2, with the following exception: It is recommended that the contents of Container No. 2 be transferred to a 250 ml beaker with a Teflon liner or similar container that has a minimal tare weight before bringing to dryness.

12. Data Analysis and Calculations.

12.1 Particulate Emissions. The analytical results cannot be blank corrected for residual acetone found in any of the blanks. All other sample calculations are identical to Method 5.

12.2 Paired Trains Outliers. a. Outliers are identified through the determination of precision and any systemic bias of the paired trains. Data that do not meet this criteria should be flagged as a data quality problem. The primary reason for performing dual train sampling is to generate information to quantify the precision of the Reference Method data. The relative standard deviation (RSD) of paired data is the parameter used to quantify data precision. RSD for two simultaneously gathered data points is determined according to:

$$RSD = 100\% * \left|\left(C_a - C_b\right)\right| / \left(C_a + C_b\right)$$

where, Ca and Cb are concentration values determined from trains A and B respectively. For RSD calculation, the concentration units are unimportant so long as they are consistent.

b. A minimum precision criteria for Reference Method PM data is that RSD for any data pair must be less than 10% as long as the mean PM concentration is greater than 10 mg/dscm. If the mean PM concentration is less than 10 mg/dscm higher RSD values are acceptable. At mean PM concentration of 1 mg/dscm acceptable RSD for paired trains is 25%. Between 1 and 10 mg/dscm acceptable RSD criteria should be linearly scaled from 25% to 10%. Pairs of manual method data exceeding these RSD criteria should be eliminated from the data set used to develop a PM CEMS correlation or to assess RCA. If the mean PM concentration is less than 1 mg/dscm, RSD does not apply and the mean result is acceptable.

13. Method Performance [Reserved]

14. Pollution Prevention [Reserved]

15. Waste Management [Reserved]

16. Alternative Procedures. Same as Method 5.

17. Bibliography. Same as Method 5.

18. Tables, Diagrams, Flowcharts and Validation Data. Figure 5I–1 is a schematic of the sample train.

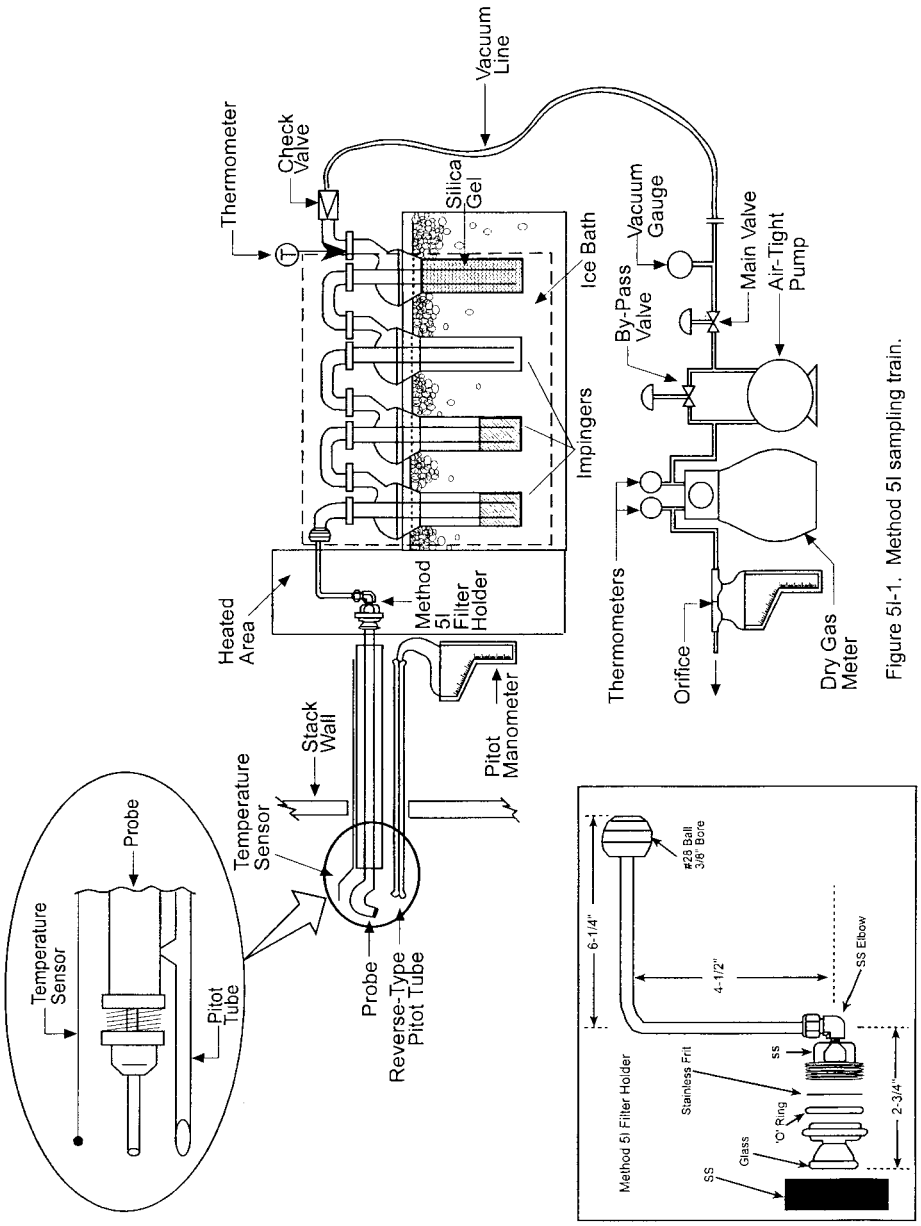


Figure 5I-1. Method 5I sampling train.

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–3 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

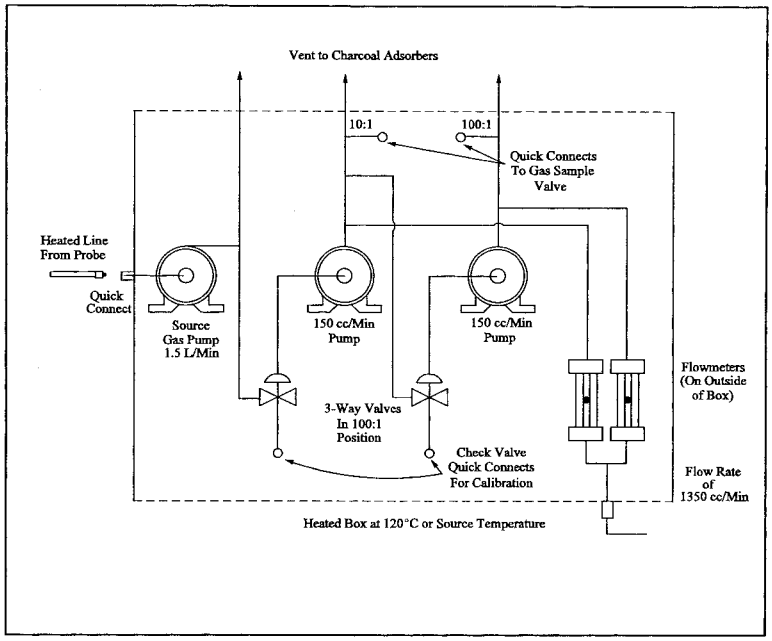


Figure 18-13. Schematic Diagram of the Heated Box Required for Dilution of Sample Gas.

GASEOUS ORGANIC SAMPLING AND ANALYSIS CHECK LIST

[Respond with initials or number as appropriate]

1. Presurvey data:		
A. Grab sample collected	☐	_____
B. Grab sample analyzed for composition	☐	_____
Method GC	☐	_____
GC/MS	☐	_____
Other	☐	_____
C. GC-FID analysis performed	☐	_____
2. Laboratory calibration data:		
A. Calibration curves prepared	☐	_____
Number of components	☐	_____
Number of concentrations/component (3 required).	☐	_____
B. Audit samples (optional):		
Analysis completed	☐	_____
Verified for concentration	☐	_____
OK obtained for field work	☐	_____
3. Sampling procedures:		
A. Method:		
Bag sample	☐	_____
Direct interface	☐	_____
Dilution interface	☐	_____
B. Number of samples collected	☐	_____
4. Field Analysis:		
A. Total hydrocarbon analysis performed	☐	_____
B. Calibration curve prepared	☐	_____
Number of components	☐	_____
Number of concentrations per component (3 required).	☐	_____

Gaseous Organic Sampling and Analysis Data

Date _____
Location _____

Plant _____

GASEOUS ORGANIC SAMPLING AND ANALYSIS CHECK LIST (RESPOND WITH INITIALS OR NUMBER AS APPROPRIATE)

	Date
1. Pre-survey data	
A. Grab sample collected	_____
B. Grab sample analyzed for composition	_____
Method GC	_____
GC/MS	_____
Other_____	_____
C. GC–FID analysis performed	_____
2. Laboratory calibration curves prepared	_____
A. Number of components	_____
B. Number of concentrations per component (3 required)	_____
C. OK obtained for field work	_____
3. Sampling procedures.	
A. Method.	
Bag sample	_____
Direct interface	_____
Dilution interface	_____
B. Number of samples collected	_____
4. Field Analysis.	
A. Total hydrocarbon analysis performed	_____
B. Calibration curve prepared	_____
Number of components	_____
Number of concentrations per component (3 required)	_____

Figure 18–14. Sampling and Analysis Sheet

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–6 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

APPENDIX A–7 TO PART 60—TEST METHODS 19 THROUGH 25E

Method 19—Determination of sulfur dioxide removal efficiency and particulate, sulfur dioxide and nitrogen oxides emission rates

Method 20—Determination of nitrogen oxides, sulfur dioxide, and diluent emissions from stationary gas turbines

Method 21—Determination of volatile organic compound leaks

Method 22—Visual determination of fugitive emissions from material sources and smoke emissions from flares

Method 23—Determination of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans From Stationary Sources

Method 24—Determination of volatile matter content, water content, density, volume solids, and weight solids of surface coatings

Method 24A—Determination of volatile matter content and density of printing inks and related coatings

Method 25—Determination of total gaseous nonmethane organic emissions as carbon

Method 25A—Determination of total gaseous organic concentration using a flame ionization analyzer

Method 25B—Determination of total gaseous organic concentration using a nondispersive infrared analyzer

Method 25C—Determination of nonmethane organic compounds (NMOC) in MSW landfill gases

Method 25D—Determination of the Volatile Organic Concentration of Waste Samples

Method 25E—Determination of Vapor Phase Organic Concentration in Waste Samples

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

Method 19—Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates

1.0 Scope and Application

1.1 Analytes. This method provides data reduction procedures relating to the following pollutants, but does not include any sample collection or analysis procedures.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), including:		
Nitric oxide (NO)	10102–43–9	N/A
Nitrogen dioxide (NO_2)	10102–44–0.	
Particulate matter (PM)	None assigned	N/A
Sulfur dioxide (SO_2)	7499–09–05	N/A

1.2 Applicability. Where specified by an applicable subpart of the regulations, this method is applicable for the determination of (a) PM, SO_2, and NO_X emission rates; (b) sulfur removal efficiencies of fuel pretreatment and SO_2 control devices; and (c) overall reduction of potential SO_2 emissions.

2.0 Summary of Method

2.1 Emission Rates. Oxygen (O_2) or carbon dioxide (CO_2) concentrations and appropriate F factors (ratios of combustion gas volumes to heat inputs) are used to calculate pollutant emission rates from pollutant concentrations.

2.2 Sulfur Reduction Efficiency and SO_2 Removal Efficiency. An overall SO_2 emission reduction efficiency is computed from the efficiency of fuel pretreatment systems, where applicable, and the efficiency of SO_2 control devices.

2.2.1 The sulfur removal efficiency of a fuel pretreatment system is determined by fuel sampling and analysis of the sulfur and heat contents of the fuel before and after the pretreatment system.

2.2.2 The SO_2 removal efficiency of a control device is determined by measuring the SO_2 rates before and after the control device.

2.2.2.1 The inlet rates to SO_2 control systems (or, when SO_2 control systems are not used, SO_2 emission rates to the atmosphere) are determined by fuel sampling and analysis.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety [Reserved]

6.0 Equipment and Supplies [Reserved]

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transport [Reserved]

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedures [Reserved]

12.0 Data Analysis and Calculations

12.1 Nomenclature

B_{wa} = Moisture fraction of ambient air, percent.

B_{ws} = Moisture fraction of effluent gas, percent.

%C = Concentration of carbon from an ultimate analysis of fuel, weight percent.

C_d = Pollutant concentration, dry basis, ng/scm (lb/scf)

$\%CO_{2d}$,$\%CO_{2w}$ = Concentration of carbon dioxide on a dry and wet basis, respectively, percent.

C_w = Pollutant concentration, wet basis, ng/scm (lb/scf).

D = Number of sampling periods during the performance test period.

E = Pollutant emission rate, ng/J (lb/million Btu).

E_a = Average pollutant rate for the specified performance test period, ng/J (lb/million Btu).

E_{ao}, E_{ai} = Average pollutant rate of the control device, outlet and inlet, respectively, for the performance test period, ng/J (lb/million Btu).

E_{bi} = Pollutant rate from the steam generating unit, ng/J (lb/million Btu)

E_{bo} = Pollutant emission rate from the steam generating unit, ng/J (lb/million Btu).

E_{ci} = Pollutant rate in combined effluent, ng/J (lb/million Btu).

E_{co} = Pollutant emission rate in combined effluent, ng/J (lb/million Btu).

E_d = Average pollutant rate for each sampling period (*e.g.*, 24-hr Method 6B sample or 24-hr fuel sample) or for each fuel lot (*e.g.*, amount of fuel bunkered), ng/J (lb/million Btu).

E_{di} = Average inlet SO_2 rate for each sampling period d, ng/J (lb/million Btu)

E_g = Pollutant rate from gas turbine, ng/J (lb/million Btu).

E_{ga} = Daily geometric average pollutant rate, ng/J (lbs/million Btu) or ppm corrected to 7 percent O_2.

E_{jo},E_{ji} = Matched pair hourly arithmetic average pollutant rate, outlet and inlet, respectively, ng/J (lb/million Btu) or ppm corrected to 7 percent O_2.

E_h = Hourly average pollutant, ng/J (lb/million Btu).

E_{hj} = Hourly arithmetic average pollutant rate for hour ''j,'' ng/J (lb/million Btu) or ppm corrected to 7 percent O_2.

EXP = Natural logarithmic base (2.718) raised to the value enclosed by brackets.

F_d, F_w, F_c = Volumes of combustion components per unit of heat content, scm/J (scf/million Btu).

GCV = Gross calorific value of the fuel consistent with the ultimate analysis, kJ/kg (Btu/lb).

GCV_p, GCV_r = Gross calorific value for the product and raw fuel lots, respectively, dry basis, kJ/kg (Btu/lb).

%H = Concentration of hydrogen from an ultimate analysis of fuel, weight percent.

H = Total number of operating hours for which pollutant rates are determined in the performance test period.

H_b = Heat input rate to the steam generating unit from fuels fired in the steam generating unit, J/hr (million Btu/hr).

H_g = Heat input rate to gas turbine from all fuels fired in the gas turbine, J/hr (million Btu/hr).

$\%H_2O$ = Concentration of water from an ultimate analysis of fuel, weight percent.
H_r = Total numbers of hours in the performance test period (*e.g.*, 720 hours for 30-day performance test period).
K = Conversion factor, 10^{-5} (kJ/J)/(%) [10^6 Btu/million Btu].
K_c = (9.57 scm/kg)/% [(1.53 scf/lb)/%].
K_{cc} = (2.0 scm/kg)/% [(0.321 scf/lb)/%].
K_{hd} = (22.7 scm/kg)/% [(3.64 scf/lb)/%].
K_{hw} = (34.74 scm/kg)/% [(5.57 scf/lb)/%].
K_n = (0.86 scm/kg)/% [(0.14 scf/lb)/%].
K_o = (2.85 scm/kg)/% [(0.46 scf/lb)/%].
K_s = (3.54 scm/kg)/% [(0.57 scf/lb)/%].
K_w = (1.30 scm/kg)/% [(0.21 scf/lb)/%].
ln = Natural log of indicated value.
L_p,L_r = Weight of the product and raw fuel lots, respectively, metric ton (ton).
%N = Concentration of nitrogen from an ultimate analysis of fuel, weight percent.
N = Number of fuel lots during the averaging period.
n = Number of fuels being burned in combination.
n_d = Number of operating hours of the affected facility within the performance test period for each E_d determined.
n_t = Total number of hourly averages for which paired inlet and outlet pollutant rates are available within the 24-hr midnight to midnight daily period.
%O = Concentration of oxygen from an ultimate analysis of fuel, weight percent.
$\%O_{2d}$, $\%O_{2w}$ = Concentration of oxygen on a dry and wet basis, respectively, percent.
P_s = Potential SO_2 emissions, percent.
$\%R_f$ = SO_2 removal efficiency from fuel pretreatment, percent.
$\%R_g$ = SO_2 removal efficiency of the control device, percent.
$\%R_{ga}$ = Daily geometric average percent reduction.
$\%R_o$ = Overall SO_2 reduction, percent.
%S = Sulfur content of as-fired fuel lot, dry basis, weight percent.
S_e = Standard deviation of the hourly average pollutant rates for each performance test period, ng/J (lb/million Btu).
$\%S_f$ = Concentration of sulfur from an ultimate analysis of fuel, weight percent.
S_i = Standard deviation of the hourly average inlet pollutant rates for each performance test period, ng/J (lb/million Btu).
S_o = Standard deviation of the hourly average emission rates for each performance test period, ng/J (lb/million Btu).
$\%S_p$, $\%S_r$ = Sulfur content of the product and raw fuel lots respectively, dry basis, weight percent.
$t_{0.95}$ = Values shown in Table 19–3 for the indicated number of data points n.
X_k = Fraction of total heat input from each type of fuel k.

12.2 Emission Rates of PM, SO_2, and NO_X. Select from the following sections the applicable procedure to compute the PM, S_{O2}, or NO_X emission rate (E) in ng/J (lb/million Btu). The pollutant concentration must be in ng/scm (lb/scf) and the F factor must be in scm/J (scf/million Btu). If the pollutant concentration (C) is not in the appropriate units, use Table 19–1 in section 17.0 to make the proper conversion. An F factor is the ratio of the gas volume of the products of combustion to the heat content of the fuel. The dry F factor (F_d) includes all components of combustion less water, the wet F factor (F_w) includes all components of combustion, and the carbon F factor (F_c) includes only carbon dioxide.

NOTE: Since F_w factors include water resulting only from the combustion of hydrogen in the fuel, the procedures using F_w factors are not applicable for computing E from steam generating units with wet scrubbers or with other processes that add water (*e.g.*, steam injection).

12.2.1 Oxygen-Based F Factor, Dry Basis. When measurements are on a dry basis for both O ($\%O_{2d}$) and pollutant (C_d) concentrations, use the following equation:

$$E = C_d F_d \frac{20.9}{(20.9 - \%O_{2d})} \qquad \text{Eq. 19-1}$$

12.2.2 Oxygen-Based F Factor, Wet Basis. When measurements are on a wet basis for both O_2 ($\%O_{2w}$) and pollutant (C_w) concentrations, use either of the following:

12.2.2.1 If the moisture fraction of ambient air (B_{wa}) is measured:

$$E = C_w F_w \frac{20.9}{\left[20.9(1 - B_{wa}) - \%O_{2w}\right]} \qquad \text{Eq. 19-2}$$

Instead of actual measurement, B_{wa} may be estimated according to the procedure below.

NOTE: The estimates are selected to ensure that negative errors will not be larger than −1.5 percent. However, positive errors, or over-estimation of emissions by as much as 5 percent may be introduced depending upon the geographic location of the facility and the associated range of ambient moisture.

12.2.2.1.1 B_{wa} = 0.027. This value may be used at any location at all times.

12.2.2.1.2 B_{wa} = Highest monthly average of B_{wa} that occurred within the previous calendar year at the nearest Weather Service Station. This value shall be determined annually and may be used as an estimate for the entire current calendar year.

12.2.2.1.3 B_{wa} = Highest daily average of Bwa that occurred within a calendar month at the nearest Weather Service Station, calculated from the data from the past 3 years. This value shall be computed for each month and may be used as an estimate for the current respective calendar month.

12.2.2.2 If the moisture fraction (B_{ws}) of the effluent gas is measured:

$$E = C_w F_d \frac{20.9}{\left[20.9\left(1-B_{ws}\right)-\%O_{2w}\right]} \qquad \text{Eq. 19-3}$$

12.2.3 Oxygen-Based F Factor, Dry/Wet Basis.

12.2.3.1 When the pollutant concentration is measured on a wet basis (C_w) and O_2 concentration is measured on a dry basis ($\%O_{2d}$), use the following equation:

$$E = \frac{\left(C_w F_d\right)(20.9)}{\left(1-B_{ws}\right)\left(20.9-\%O_{2d}\right)} \qquad \text{Eq. 19-4}$$

12.2.3.2 When the pollutant concentration is measured on a dry basis (C_d) and the O_2 concentration is measured on a wet basis ($\%O_{2w}$), use the following equation:

$$E = \frac{C_d F_d 20.9}{\frac{\left(20.9-\%O_{2w}\right)}{\left(1-B_{ws}\right)}} \qquad \text{Eq. 19-5}$$

12.2.4 Carbon Dioxide-Based F Factor, Dry Basis. When measurements are on a dry basis for both CO_2 ($\%CO_{2d}$) and pollutant (C_d) concentrations, use the following equation:

$$E = C_d F_c \frac{100}{\%CO_{2d}} \qquad \text{Eq. 19-6}$$

12.2.5 Carbon Dioxide-Based F Factor, Wet Basis. When measurements are on a wet basis for both CO_2 ($\%CO_{2w}$) and pollutant (C_w) concentrations, use the following equation:

$$E = C_w F_c \frac{100}{\%CO_{2w}} \qquad \text{Eq. 19-7}$$

12.2.6 Carbon Dioxide-Based F Factor, Dry/Wet Basis.

12.2.6.1 When the pollutant concentration is measured on a wet basis (C_w) and CO_2 concentration is measured on a dry basis ($\%CO_{2d}$), use the following equation:

$$E = \frac{C_w F_c}{\left(1-B_{ws}\right)} \frac{100}{\%CO_{2d}} \qquad \text{Eq. 19-8}$$

12.2.6.2 When the pollutant concentration is measured on a dry basis (C_d) and CO_2 concentration is measured on a wet basis ($\%CO_{2w}$), use the following equation:

$$E = C_d F_c \left(1-B_{ws}\right) \frac{100}{\%CO_{2w}} \qquad \text{Eq. 19-9}$$

12.2.7 Direct-Fired Reheat Fuel Burning. The effect of direct-fired reheat fuel burning (for the purpose of raising the temperature of the exhaust effluent from wet scrubbers to above the moisture dew-point) on emission rates will be less than 1.0 percent and, therefore, may be ignored.

12.2.8 Combined Cycle-Gas Turbine Systems. For gas turbine-steam generator combined cycle systems, determine the emissions from the steam generating unit or the percent reduction in potential SO_2 emissions as follows:

12.2.8.1 Compute the emission rate from the steam generating unit using the following equation:

$$E_{bo} = E_{co} + \frac{H_g}{H_b}\left(E_{co} - E_g\right) \qquad \text{Eq. 19-10}$$

12.2.8.1.1 Use the test methods and procedures section of 40 CFR Part 60, Subpart GG to obtain E_{co} and E_g. Do not use F_w factors for determining E_g or E_{co}. If an SO_2 control device is used, measure E_{co} after the control device.

12.2.8.1.2 Suitable methods shall be used to determine the heat input rates to the steam generating units (H_b) and the gas turbine (H_g).

12.2.8.2 If a control device is used, compute the percent of potential SO_2 emissions (P_s) using the following equations:

$$E_{bi} = E_{ci} - \frac{H_g}{H_b}\left(E_{ci} - E_g\right) \qquad \text{Eq. 19-11}$$

$$P_s = 100\left(1 - \frac{E_{bo}}{E_{bi}}\right) \qquad \text{Eq. 19-12}$$

NOTE: Use the test methods and procedures section of Subpart GG to obtain E_{ci} and E_g. Do not use F_w factors for determining E_g or E_{ci}.

12.3 F Factors. Use an average F factor according to section 12.3.1 or determine an applicable F factor according to section 12.3.2. If combined fuels are fired, prorate the applicable F factors using the procedure in section 12.3.3.

12.3.1 Average F Factors. Average F factors (F_d, F_w, or F_c) from Table 19–2 in section 17.0 may be used.

12.3.2 Determined F Factors. If the fuel burned is not listed in Table 19–2 or if the owner or operator chooses to determine an F factor rather than use the values in Table 19–2, use the procedure below:

12.3.2.1 Equations. Use the equations below, as appropriate, to compute the F factors:

$$F_d = \frac{K\left(K_{hd}\%H + K_c\%C + K_s\%S + K_n\%N - K_o\%O\right)}{GCV} \qquad \text{Eq. 19-13}$$

$$F_w = \frac{K\left[K_{hw}\%H + K_c\%C + K_s\%S + K_n\%N - K_o\%O + K_w\%H_2O\right]}{GCV_w} \qquad \text{Eq. 19-14}$$

$$F_c = \frac{K\left(K_{cc}\%C\right)}{GCV} \qquad \text{Eq. 19-15}$$

NOTE: Omit the $\%H_2O$ term in the equations for F_w if %H and %O include the unavailable hydrogen and oxygen in the form of H_2O.)

12.3.2.2 Use applicable sampling procedures in section 12.5.2.1 or 12.5.2.2 to obtain samples for analyses.

12.3.2.3 Use ASTM D 3176–74 or 89 (all cited ASTM standards are incorporated by reference—see §60.17) for ultimate analysis of the fuel.

12.3.2.4 Use applicable methods in section 12.5.2.1 or 12.5.2.2 to determine the heat content of solid or liquid fuels. For gaseous fuels, use ASTM D 1826–77 or 94 (incorporated by reference—see §60.17) to determine the heat content.

12.3.3 F Factors for Combination of Fuels. If combinations of fuels are burned, use the following equations, as applicable unless otherwise specified in an applicable subpart:

$$F_d = \sum_{k=1}^{n}\left(X_k F_{dk}\right) \qquad \text{Eq. 19-16}$$

$$F_w = \sum_{k=1}^{n}\left(X_k F_{wk}\right) \qquad \text{Eq. 19-17}$$

$$F_c = \sum_{k=1}^{n}\left(X_k F_{ck}\right) \qquad \text{Eq. 19-18}$$

12.4 Determination of Average Pollutant Rates.

12.4.1 Average Pollutant Rates from Hourly Values. When hourly average pollutant rates (E_h), inlet or outlet, are obtained (*e.g.*, CEMS values), compute the average pollutant rate (E_a) for the performance test period (*e.g.*, 30 days) specified in the applicable regulation using the following equation:

$$E_a = \frac{1}{H}\sum_{j=1}^{n} E_{hj} \qquad \text{Eq. 19-19}$$

12.4.2 Average Pollutant Rates from Other than Hourly Averages. When pollutant rates are determined from measured values representing longer than 1-hour periods (*e.g.*, daily fuel sampling and analyses or Method 6B values), or when pollutant rates are determined from combinations of 1-hour and longer than 1-hour periods (*e.g.*, CEMS and Method 6B values), compute the average pollutant rate (E_a) for the performance test period (*e.g.*, 30 days) specified in the applicable regulation using the following equation:

$$E_a = \frac{\sum_{j=1}^{D}\left(n_d E_d\right)_j}{\sum_{j=1}^{D} n_{dj}} \qquad \text{Eq. 19-20}$$

12.4.3 Daily Geometric Average Pollutant Rates from Hourly Values. The geometric average pollutant rate (E_{ga}) is computed using the following equation:

$$E_{ga} = \exp\left[\frac{1}{n_t}\sum_{j=1}^{n_t}\left[\ln\left(E_{hj}\right)\right]\right] \quad \text{Eq. 19-21}$$

12.5 Determination of Overall Reduction in Potential Sulfur Dioxide Emission.

12.5.1 Overall Percent Reduction. Compute the overall percent SO_2 reduction ($\%R_o$) using the following equation:

$$\%R_o = 100\left[1.0 - \left(1.0 - \frac{\%R_f}{100}\right)\left(1.0 - \frac{\%R_g}{100}\right)\right] \quad \text{Eq. 19-22}$$

12.5.2 Pretreatment Removal Efficiency (Optional). Compute the SO_2 removal efficiency from fuel pretreatment ($\%R_f$) for the averaging period (*e.g.*, 90 days) as specified in the applicable regulation using the following equation:

$$\%R_f = 100\left[1.0 - \frac{\sum_{j=1}^{N}\left(\frac{\%S_{pj}}{GCV_{pj}}\right)L_{pj}}{\sum_{j=1}^{N}\left(\frac{\%S_{rj}}{GCV_{rj}}\right)L_{rj}}\right] \quad \text{Eq. 19-23}$$

NOTE: In calculating $\%R_f$, include %S and GCV values for all fuel lots that are not pretreated and are used during the averaging period.

12.5.2.1 Solid Fossil (Including Waste) Fuel/Sampling and Analysis.

NOTE: For the purposes of this method, raw fuel (coal or oil) is the fuel delivered to the desulfurization (pretreatment) facility. For oil, the input oil to the oil desulfurization process (*e.g.*, hydrotreatment) is considered to be the raw fuel.

12.5.2.1.1 Sample Increment Collection. Use ASTM D 2234–76, 96, 97a, or 98 (incorporated by reference—see §60.17), Type I, Conditions A, B, or C, and systematic spacing. As used in this method, systematic spacing is intended to include evenly spaced increments in time or increments based on equal weights of coal passing the collection area. As a minimum, determine the number and weight of increments required per gross sample representing each coal lot according to Table 2 or Paragraph 7.1.5.2 of ASTM D 2234. Collect one gross sample for each lot of raw coal and one gross sample for each lot of product coal.

12.5.2.1.2 ASTM Lot Size. For the purpose of section 12.5.2 (fuel pretreatment), the lot size of product coal is the weight of product coal from one type of raw coal. The lot size of raw coal is the weight of raw coal used to produce one lot of product coal. Typically, the lot size is the weight of coal processed in a 1-day (24-hour) period. If more than one type of coal is treated and produced in 1 day, then gross samples must be collected and analyzed for each type of coal. A coal lot size equaling the 90-day quarterly fuel quantity for a steam generating unit may be used if representative sampling can be conducted for each raw coal and product coal.

NOTE: Alternative definitions of lot sizes may be used, subject to prior approval of the Administrator.

12.5.2.1.3 Gross Sample Analysis. Use ASTM D 2013–72 or 86 to prepare the sample, ASTM D 3177–75 or 89 or ASTM D 4239–85, 94, or 97 to determine sulfur content (%S), ASTM D 3173–73 or 87 to determine moisture content, and ASTM D 2015–77 (Reapproved 1978) or 96, D 3286–85 or 96, or D 5865–98 or 10 to determine gross calorific value (GCV) (all standards cited are incorporated by reference—see §60.17 for acceptable versions of the standards) on a dry basis for each gross sample.

12.5.2.2 Liquid Fossil Fuel-Sampling and Analysis. See Note under section 12.5.2.1.

12.5.2.2.1 Sample Collection. Follow the procedures for continuous sampling in ASTM D 270 or D 4177–95 (incorporated by reference—see §60.17) for each gross sample from each fuel lot.

12.5.2.2.2 Lot Size. For the purpose of section 12.5.2 (fuel pretreatment), the lot size of a product oil is the weight of product oil from one pretreatment facility and intended as one shipment (ship load, barge load, etc.). The lot size of raw oil is the weight of each crude liquid fuel type used to produce a lot of product oil.

NOTE: Alternative definitions of lot sizes may be used, subject to prior approval of the Administrator.

12.5.2.2.3 Sample Analysis. Use ASTM D 129–64, 78, or 95, ASTM D 1552–83 or 95, or ASTM D 4057–81 or 95 to determine the sulfur content (%S) and ASTM D 240–76 or 92 (all standards cited are incorporated by reference—see §60.17) to determine the GCV of each gross sample. These values may be assumed to be on a dry basis. The owner or operator of an affected facility may elect to determine the GCV by sampling the oil combusted on the first steam generating unit operating day of each calendar month and then using the lowest GCV value of the three GCV values per quarter for the GCV of all oil combusted in that calendar quarter.

12.5.2.3 Use appropriate procedures, subject to the approval of the Administrator, to determine the fraction of total mass input derived from each type of fuel.

12.5.3 Control Device Removal Efficiency. Compute the percent removal efficiency ($\%R_g$) of the control device using the following equation:

$$\%R_g = 100\left(1.0 - \frac{E_{ao}}{E_{ai}}\right) \qquad \text{Eq. 19-24}$$

12.5.3.1 Use continuous emission monitoring systems or test methods, as appropriate, to determine the outlet SO_2 rates and, if appropriate, the inlet SO_2 rates. The rates may be determined as hourly (E_h) or other sampling period averages (E_d). Then, compute the average pollutant rates for the performance test period (E_{ao} and E_{ai}) using the procedures in section 12.4.

12.5.3.2 As an alternative, as-fired fuel sampling and analysis may be used to determine inlet SO_2 rates as follows:

12.5.3.2.1 Compute the average inlet SO_2 rate (E_{di}) for each sampling period using the following equation:

$$E_{di} = K\frac{\%S}{GCV} \qquad \text{Eq. 19-25}$$

Where:

$$K = 2\times10^7\left(\frac{\text{ng SO}_2}{\%S}\right)\left(\frac{(\text{kJ})}{\text{J}}\right)\left(\frac{1}{\text{kg coal}}\right)\left[2\times10^4\left(\frac{\text{lb SO}_2}{\%S}\right)\left(\frac{\text{Btu}}{\text{million Btu}}\right)\left(\frac{1}{\text{lb coal}}\right)\right]$$

After calculating E_{di}, use the procedures in section 12.4 to determine the average inlet SO_2 rate for the performance test period (E_{ai}).

12.5.3.2.2 Collect the fuel samples from a location in the fuel handling system that provides a sample representative of the fuel bunkered or consumed during a steam generating unit operating day. For the purpose of as-fired fuel sampling under section 12.5.3.2 or section 12.6, the lot size for coal is the weight of coal bunkered or consumed during each steam generating unit operating day. The lot size for oil is the weight of oil supplied to the ''day'' tank or consumed during each steam generating unit operating day. For reporting and calculation purposes, the gross sample shall be identified with the calendar day on which sampling began. For steam generating unit operating days when a coal-fired steam generating unit is operated without coal being added to the bunkers, the coal analysis from the previous ''as bunkered'' coal sample shall be used until coal is bunkered again. For steam generating unit operating days when an oil-fired steam generating unit is operated without oil being added to the oil ''day'' tank, the oil analysis from the previous day shall be used until the ''day'' tank is filled again. Alternative definitions of fuel lot size may be used, subject to prior approval of the Administrator.

12.5.3.2.3 Use ASTM procedures specified in section 12.5.2.1 or 12.5.2.2 to determine %S and GCV.

12.5.4 Daily Geometric Average Percent Reduction from Hourly Values. The geometric average percent reduction ($\%R_{ga}$) is computed using the following equation:

$$\%R_{ga} = 100\left[1 - EXP\left(\frac{1}{n_t}\sum_{j=1}^{n_t} 1n\frac{E_{jo}}{E_{ji}}\right)\right] \qquad \text{Eq. 19-26}$$

NOTE: The calculation includes only paired data sets (hourly average) for the inlet and outlet pollutant measurements.

12.6 Sulfur Retention Credit for Compliance Fuel. If fuel sampling and analysis procedures in section 12.5.2.1 are being used to determine average SO_2 emission rates (E_{as}) to the atmosphere from a coal-fired steam generating unit when there is no SO_2 control device, the following equation may be used to adjust the emission rate for sulfur retention credits (no credits are allowed for oil-fired systems) (E_{di}) for each sampling period using the following equation:

$$E_{di} = 0.97K\ \frac{\%S}{GDV} \qquad \text{Eq. 19-27}$$

Where:

$$K = 2\times10^{7}\left(\frac{\text{ng } SO_2}{\%S}\right)\left(\frac{kJ}{J}\right)\left(\frac{1}{\text{kg coal}}\right)\left[2\times10^{4}\left(\frac{\text{lb } SO_2}{\%S}\right)\left(\frac{Btu}{\text{million Btu}}\right)\left(\frac{1}{\text{lb coal}}\right)\right]$$

After calculating E_{di}, use the procedures in section 12.4.2 to determine the average SO_2 emission rate to the atmosphere for the performance test period (E_{ao}).

12.7 Determination of Compliance When Minimum Data Requirement Is Not Met.

12.7.1 Adjusted Emission Rates and Control Device Removal Efficiency. When the minimum data requirement is not met, the Administrator may use the following adjusted emission rates or control device removal efficiencies to determine compliance with the applicable standards.

12.7.1.1 Emission Rate. Compliance with the emission rate standard may be determined by using the lower confidence limit of the emission rate (E_{ao}*) as follows:

$$E^{*}_{ao} = E_{ao} - t_{0.95}S_o \qquad \text{Eq. 19-28}$$

12.7.1.2 Control Device Removal Efficiency. Compliance with the overall emission reduction ($\%R_o$) may be determined by using the lower confidence limit of the emission rate (E_{ao}*) and the upper confidence limit of the inlet pollutant rate (E_{ai}*) in calculating the control device removal efficiency ($\%R_g$) as follows:

$$\%R_g = 100\left(1.0 - \frac{E^{*}_{ao}}{E^{*}_{ai}}\right) \qquad \text{Eq. 19-29}$$

$$E^{*}_{ai} = E_{ai} + t_{0.95}S_i \qquad \text{Eq. 19-30}$$

12.7.2 Standard Deviation of Hourly Average Pollutant Rates. Compute the standard deviation (S_e) of the hourly average pollutant rates using the following equation:

$$S_e = \sqrt{\frac{1}{H} - \frac{1}{H_r}}\ \sqrt{\frac{\sum_{j=1}^{H}\left(E_{hj} - E_a\right)^2}{H-1}} \qquad \text{Eq. 19-31}$$

Equation 19–19 through 19–31 may be used to compute the standard deviation for both the outlet (S_o) and, if applicable, inlet (S_i) pollutant rates.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References [Reserved]

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 19–1—CONVERSION FACTORS FOR CONCENTRATION

From	To	Multiply by
g/scm	ng/scm	10^9
mg/scm	ng/scm	10^6
lb/scf	ng/scm	1.602×10^{13}

TABLE 19–1—CONVERSION FACTORS FOR CONCENTRATION—Continued

From	To	Multiply by
ppm SO_2	ng/scm	2.66×10^6
ppm NO_X	ng/scm	1.912×10^6
ppm SO_2	lb/scf	1.660×10^{-7}
ppm NO_X	lb/scf	1.194×10^{-7}

TABLE 19–2—F FACTORS FOR VARIOUS FUELS[1]

Fuel Type	F_d		F_w		F_c	
	dscm/J	dscf/10^6 Btu	wscm/J	wscf/10^6 Btu	scm/J	scf/10^6 Btu
Coal:						
Anthracite[2]	2.71×10^{-7}	10,100	2.83×10^{-7}	10,540	0.530×10^{-7}	1,970
Bituminus[2]	2.63×10^{-7}	9,780	2.86×10^{-7}	10,640	0.484×10^{-7}	1,800
Lignite	2.65×10^{-7}	9,860	3.21×10^{-7}	11,950	0.513×10^{-7}	1,910
Oil[3]	2.47×10^{-7}	9,190	2.77×10^{-7}	10,320	0.383×10^{-7}	1,420
Gas:.						
Natural	2.34×10^{-7}	8,710	2.85×10^{-7}	10,610	0.287×10^{-7}	1,040
Propane	2.34×10^{-7}	8,710	2.74×10^{-7}	10,200	0.321×10^{-7}	1,190
Butane	2.34×10^{-7}	8,710	2.79×10^{-7}	10,390	0.337×10^{-7}	1,250
Wood	2.48×10^{-7}	9,240			0.492×10^{-7}	1,830
Wood Bark	2.58×10^{-7}	9,600			0.516×10^{-7}	1,920
Municipal	2.57×10^{-7}	9,570			0.488×10^{-7}	1,820
Solid Waste						

[1] Determined at standard conditions: 20 °C (68 °F) and 760 mm Hg (29.92 in Hg)
[2] As classified according to ASTM D 388.
[3] Crude, residual, or distillate.

TABLE 19–3—VALUES FOR $T_{0.95*}$

n[1]	$t_{0.95}$	n[1]	$t_{0.95}$	n[1]	$t_{0.95}$
2	6.31	8	1.89	22–26	1.71
3	2.42	9	1.86	27–31	1.70
4	2.35	10	1.83	32–51	1.68
5	2.13	11	1.81	52–91	1.67
6	2.02	12–16	1.77	92–151	1.66
7	1.94	17–21	1.73	152 or more	1.65

[1] The values of this table are corrected for n-1 degrees of freedom. Use n equal to the number (H) of hourly average data points.

METHOD 20—DETERMINATION OF NITROGEN OXIDES, SULFUR DIOXIDE, AND DILUENT EMISSIONS FROM STATIONARY GAS TURBINES

1.0 Scope and Application

What is Method 20?

Method 20 contains the details you must follow when using an instrumental analyzer to determine concentrations of nitrogen oxides, oxygen, carbon dioxide, and sulfur dioxide in the emissions from stationary gas turbines. This method follows the specific instructions for equipment and performance requirements, supplies, sample collection and analysis, calculations, and data analysis in the methods listed in section 2.0.

1.1 Analytes. What does this method determine?

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X) as nitrogen dioxide:	10102–43–9	Typically <2% of Calibration Span.
Nitric oxide (NO)	10102–44–0	
Nitrogen dioxide NO_2.		
Diluent oxygen (O_2) or carbon dioxide (CO_2)		Typically <2% of Calibration Span.
Sulfur dioxide (SO_X)	7446–09–5	Typically <2% of Calibration Span.

1.2 Applicability. When is this method required? The use of Method 20 may be required by specific New Source Performance Standards, Clean Air Marketing rules, and State Implementation Plans and permits where

measuring SO_2, NO_X, CO_2, and/or O_2 concentrations in stationary gas turbines emissions are required. Other regulations may also require its use.

1.3 Data Quality Objectives. How good must my collected data be? Refer to section 1.3 of Method 7E.

2.0 Summary of Method

In this method, NO_X, O_2 (or CO_2), and SO_X are measured using the following methods found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 3A—Determination of Oxygen and Carbon Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(c) Method 6C—Determination of Sulfur Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(d) Method 7E—Determination of Nitrogen Oxides Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(e) Method 19—Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates.

3.0 Definitions

Refer to section 3.0 of Method 7E for the applicable definitions.

4.0 Interferences

Refer to section 4.0 of Methods 3A, 6C, and 7E as applicable.

5.0 Safety

Refer to section 5.0 of Method 7E.

6.0 Equipment and Supplies

The measurement system design is shown in Figure 7E–1 of Method 7E. Refer to the appropriate methods listed in section 2.0 for equipment and supplies.

7.0 Reagents and Standards

Refer to the appropriate methods listed in section 2.0 for reagents and standards.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling Site and Sampling Points. Follow the procedures of section 8.1 of Method 7E. For the stratification test in section 8.1.2, determine the diluent-corrected pollutant concentration at each traverse point.

8.2 Initial Measurement System Performance Tests. You must refer to the appropriate methods listed in section 2.0 for the measurement system performance tests as applicable.

8.3 Interference Check. You must follow the procedures in section 8.3 of Method 3A or 6C, or section 8.2.7 of Method 7E (as appropriate).

8.4 Sample Collection. You must follow the procedures of section 8.4 of the appropriate methods listed in section 2.0. A test run must have a duration of at least 21 minutes.

8.5 Post-Run System Bias Check, Drift Assessment, and Alternative Dynamic Spike Procedure. You must follow the procedures of sections 8.5 and 8.6 of the appropriate methods listed in section 2.0. A test run must have a duration of at least 21 minutes.

9.0 Quality Control

Follow quality control procedures in section 9.0 of Method 7E.

10.0 Calibration and Standardization

Follow the procedures for calibration and standardization in section 10.0 of Method 7E.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the procedures for calculations and data analysis in section 12.0 of the appropriate method listed in section 2.0. Follow the procedures in section 12.0 of Method 19 for calculating fuel-specific F factors, diluent-corrected pollutant concentrations, and emission rates.

13.0 Method Performance

The specifications for the applicable performance checks are the same as in section 13.0 of Method 7E.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

Refer to section 16.0 of the appropriate method listed in section 2.0 for alternative procedures.

17.0 References

Refer to section 17.0 of the appropriate method listed in section 2.0 for references.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

Refer to section 18.0 of the appropriate method listed in section 2.0 for tables, diagrams, flowcharts, and validation data.

METHOD 21—DETERMINATION OF VOLATILE ORGANIC COMPOUND LEAKS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile Organic Compounds (VOC).	No CAS number assigned.

1.2 Scope. This method is applicable for the determination of VOC leaks from process equipment. These sources include, but are not limited to, valves, flanges and other connections, pumps and compressors, pressure relief devices, process drains, open-ended valves, pump and compressor seal system degassing vents, accumulator vessel vents, agitator seals, and access door seals.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A portable instrument is used to detect VOC leaks from individual sources. The instrument detector type is not specified, but it must meet the specifications and performance criteria contained in section 6.0. A leak definition concentration based on a reference compound is specified in each applicable regulation. This method is intended to locate and classify leaks only, and is not to be used as a direct measure of mass emission rate from individual sources.

3.0 Definitions

3.1 *Calibration gas* means the VOC compound used to adjust the instrument meter reading to a known value. The calibration gas is usually the reference compound at a known concentration approximately equal to the leak definition concentration.

3.2 *Calibration precision* means the degree of agreement between measurements of the same known value, expressed as the relative percentage of the average difference between the meter readings and the known concentration to the known concentration.

3.3 *Leak definition concentration* means the local VOC concentration at the surface of a leak source that indicates that a VOC emission (leak) is present. The leak definition is an instrument meter reading based on a reference compound.

3.4 *No detectable emission* means a local VOC concentration at the surface of a leak source, adjusted for local VOC ambient concentration, that is less than 2.5 percent of the specified leak definition concentration. that indicates that a VOC emission (leak) is not present.

3.5 *Reference compound* means the VOC species selected as the instrument calibration basis for specification of the leak definition concentration. (For example, if a leak definition concentration is 10,000 ppm as methane, then any source emission that results in a local concentration that yields a meter reading of 10,000 on an instrument meter calibrated with methane would be classified as a leak. In this example, the leak definition concentration is 10,000 ppm and the reference compound is methane.)

3.6 *Response factor* means the ratio of the known concentration of a VOC compound to the observed meter reading when measured using an instrument calibrated with the reference compound specified in the applicable regulation.

3.7 *Response time* means the time interval from a step change in VOC concentration at the input of the sampling system to the time at which 90 percent of the corresponding final value is reached as displayed on the instrument readout meter.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Pollutants. Several of the compounds, leaks of which may be determined by this method, may be irritating or corrosive to tissues (*e.g.*, heptane) or may be toxic (*e.g.*, benzene, methyl alcohol). Nearly all are fire hazards. Compounds in emissions should be determined through familiarity with the source. Appropriate precautions can be found in reference documents, such as reference No. 4 in section 16.0.

6.0 Equipment and Supplies

A VOC monitoring instrument meeting the following specifications is required:

6.1 The VOC instrument detector shall respond to the compounds being processed. Detector types that may meet this requirement include, but are not limited to, catalytic oxidation, flame ionization, infrared absorption, and photoionization.

6.2 The instrument shall be capable of measuring the leak definition concentration specified in the regulation.

6.3 The scale of the instrument meter shall be readable to ±2.5 percent of the specified leak definition concentration.

6.4 The instrument shall be equipped with an electrically driven pump to ensure that a sample is provided to the detector at a constant flow rate. The nominal sample flow rate, as measured at the sample probe tip, shall be 0.10 to 3.0 l/min (0.004 to 0.1 ft^3/min) when the probe is fitted with a glass wool plug or filter that may be used to prevent plugging of the instrument.

6.5 The instrument shall be equipped with a probe or probe extension or sampling not to exceed 6.4 mm (¼ in) in outside diameter,

with a single end opening for admission of sample.

6.6 The instrument shall be intrinsically safe for operation in explosive atmospheres as defined by the National Electrical Code by the National Fire Prevention Association or other applicable regulatory code for operation in any explosive atmospheres that may be encountered in its use. The instrument shall, at a minimum, be intrinsically safe for Class 1, Division 1 conditions, and/or Class 2, Division 1 conditions, as appropriate, as defined by the example code. The instrument shall not be operated with any safety device, such as an exhaust flame arrestor, removed.

7.0 Reagents and Standards

7.1 Two gas mixtures are required for instrument calibration and performance evaluation:

7.1.1 Zero Gas. Air, less than 10 parts per million by volume (ppmv) VOC.

7.1.2 Calibration Gas. For each organic species that is to be measured during individual source surveys, obtain or prepare a known standard in air at a concentration approximately equal to the applicable leak definition specified in the regulation.

7.2 Cylinder Gases. If cylinder calibration gas mixtures are used, they must be analyzed and certified by the manufacturer to be within 2 percent accuracy, and a shelf life must be specified. Cylinder standards must be either reanalyzed or replaced at the end of the specified shelf life.

7.3 Prepared Gases. Calibration gases may be prepared by the user according to any accepted gaseous preparation procedure that will yield a mixture accurate to within 2 percent. Prepared standards must be replaced each day of use unless it is demonstrated that degradation does not occur during storage.

7.4 Mixtures with non-Reference Compound Gases. Calibrations may be performed using a compound other than the reference compound. In this case, a conversion factor must be determined for the alternative compound such that the resulting meter readings during source surveys can be converted to reference compound results.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Instrument Performance Evaluation. Assemble and start up the instrument according to the manufacturer's instructions for recommended warmup period and preliminary adjustments.

8.1.1 Response Factor. A response factor must be determined for each compound that is to be measured, either by testing or from reference sources. The response factor tests are required before placing the analyzer into service, but do not have to be repeated at subsequent intervals.

8.1.1.1 Calibrate the instrument with the reference compound as specified in the applicable regulation. Introduce the calibration gas mixture to the analyzer and record the observed meter reading. Introduce zero gas until a stable reading is obtained. Make a total of three measurements by alternating between the calibration gas and zero gas. Calculate the response factor for each repetition and the average response factor.

8.1.1.2 The instrument response factors for each of the individual VOC to be measured shall be less than 10 unless otherwise specified in the applicable regulation. When no instrument is available that meets this specification when calibrated with the reference VOC specified in the applicable regulation, the available instrument may be calibrated with one of the VOC to be measured, or any other VOC, so long as the instrument then has a response factor of less than 10 for each of the individual VOC to be measured.

8.1.1.3 Alternatively, if response factors have been published for the compounds of interest for the instrument or detector type, the response factor determination is not required, and existing results may be referenced. Examples of published response factors for flame ionization and catalytic oxidation detectors are included in References 1–3 of section 17.0.

8.1.2 Calibration Precision. The calibration precision test must be completed prior to placing the analyzer into service and at subsequent 3-month intervals or at the next use, whichever is later.

8.1.2.1 Make a total of three measurements by alternately using zero gas and the specified calibration gas. Record the meter readings. Calculate the average algebraic difference between the meter readings and the known value. Divide this average difference by the known calibration value and multiply by 100 to express the resulting calibration precision as a percentage.

8.1.2.2 The calibration precision shall be equal to or less than 10 percent of the calibration gas value.

8.1.3 Response Time. The response time test is required before placing the instrument into service. If a modification to the sample pumping system or flow configuration is made that would change the response time, a new test is required before further use.

8.1.3.1 Introduce zero gas into the instrument sample probe. When the meter reading has stabilized, switch quickly to the specified calibration gas. After switching, measure the time required to attain 90 percent of the final stable reading. Perform this test sequence three times and record the results. Calculate the average response time.

8.1.3.2 The instrument response time shall be equal to or less than 30 seconds. The instrument pump, dilution probe (if any), sample probe, and probe filter that will be used

during testing shall all be in place during the response time determination.

8.2 Instrument Calibration. Calibrate the VOC monitoring instrument according to section 10.0.

8.3 Individual Source Surveys.

8.3.1 Type I—Leak Definition Based on Concentration. Place the probe inlet at the surface of the component interface where leakage could occur. Move the probe along the interface periphery while observing the instrument readout. If an increased meter reading is observed, slowly sample the interface where leakage is indicated until the maximum meter reading is obtained. Leave the probe inlet at this maximum reading location for approximately two times the instrument response time. If the maximum observed meter reading is greater than the leak definition in the applicable regulation, record and report the results as specified in the regulation reporting requirements. Examples of the application of this general technique to specific equipment types are:

8.3.1.1 Valves. The most common source of leaks from valves is the seal between the stem and housing. Place the probe at the interface where the stem exits the packing gland and sample the stem circumference. Also, place the probe at the interface of the packing gland take-up flange seat and sample the periphery. In addition, survey valve housings of multipart assembly at the surface of all interfaces where a leak could occur.

8.3.1.2 Flanges and Other Connections. For welded flanges, place the probe at the outer edge of the flange-gasket interface and sample the circumference of the flange. Sample other types of nonpermanent joints (such as threaded connections) with a similar traverse.

8.3.1.3 Pumps and Compressors. Conduct a circumferential traverse at the outer surface of the pump or compressor shaft and seal interface. If the source is a rotating shaft, position the probe inlet within 1 cm of the shaft-seal interface for the survey. If the housing configuration prevents a complete traverse of the shaft periphery, sample all accessible portions. Sample all other joints on the pump or compressor housing where leakage could occur.

8.3.1.4 Pressure Relief Devices. The configuration of most pressure relief devices prevents sampling at the sealing seat interface. For those devices equipped with an enclosed extension, or horn, place the probe inlet at approximately the center of the exhaust area to the atmosphere.

8.3.1.5 Process Drains. For open drains, place the probe inlet at approximately the center of the area open to the atmosphere. For covered drains, place the probe at the surface of the cover interface and conduct a peripheral traverse.

8.3.1.6 Open-ended Lines or Valves. Place the probe inlet at approximately the center of the opening to the atmosphere.

8.3.1.7 Seal System Degassing Vents and Accumulator Vents. Place the probe inlet at approximately the center of the opening to the atmosphere.

8.3.1.8 Access door seals. Place the probe inlet at the surface of the door seal interface and conduct a peripheral traverse.

8.3.2 Type II—''No Detectable Emission''. Determine the local ambient VOC concentration around the source by moving the probe randomly upwind and downwind at a distance of one to two meters from the source. If an interference exists with this determination due to a nearby emission or leak, the local ambient concentration may be determined at distances closer to the source, but in no case shall the distance be less than 25 centimeters. Then move the probe inlet to the surface of the source and determine the concentration as outlined in section 8.3.1. The difference between these concentrations determines whether there are no detectable emissions. Record and report the results as specified by the regulation. For those cases where the regulation requires a specific device installation, or that specified vents be ducted or piped to a control device, the existence of these conditions shall be visually confirmed. When the regulation also requires that no detectable emissions exist, visual observations and sampling surveys are required. Examples of this technique are:

8.3.2.1 Pump or Compressor Seals. If applicable, determine the type of shaft seal. Perform a survey of the local area ambient VOC concentration and determine if detectable emissions exist as described in section 8.3.2.

8.3.2.2 Seal System Degassing Vents, Accumulator Vessel Vents, Pressure Relief Devices. If applicable, observe whether or not the applicable ducting or piping exists. Also, determine if any sources exist in the ducting or piping where emissions could occur upstream of the control device. If the required ducting or piping exists and there are no sources where the emissions could be vented to the atmosphere upstream of the control device, then it is presumed that no detectable emissions are present. If there are sources in the ducting or piping where emissions could be vented or sources where leaks could occur, the sampling surveys described in section 8.3.2 shall be used to determine if detectable emissions exist.

8.3.3 Alternative Screening Procedure.

8.3.3.1 A screening procedure based on the formation of bubbles in a soap solution that is sprayed on a potential leak source may be used for those sources that do not have continuously moving parts, that do not have surface temperatures greater than the boiling point or less than the freezing point of the soap solution, that do not have open

areas to the atmosphere that the soap solution cannot bridge, or that do not exhibit evidence of liquid leakage. Sources that have these conditions present must be surveyed using the instrument technique of section 8.3.1 or 8.3.2.

8.3.3.2 Spray a soap solution over all potential leak sources. The soap solution may be a commercially available leak detection solution or may be prepared using concentrated detergent and water. A pressure sprayer or squeeze bottle may be used to dispense the solution. Observe the potential leak sites to determine if any bubbles are formed. If no bubbles are observed, the source is presumed to have no detectable emissions or leaks as applicable. If any bubbles are observed, the instrument techniques of section 8.3.1 or 8.3.2 shall be used to determine if a leak exists, or if the source has detectable emissions, as applicable.

9.0 Quality Control

Section	Quality control measure	Effect
8.1.2	Instrument calibration precision check	Ensure precision and accuracy, respectively, of instrument response to standard.
10.0	Instrument calibration.	

10.0 Calibration and Standardization

10.1 Calibrate the VOC monitoring instrument as follows. After the appropriate warmup period and zero internal calibration procedure, introduce the calibration gas into the instrument sample probe. Adjust the instrument meter readout to correspond to the calibration gas value.

NOTE: If the meter readout cannot be adjusted to the proper value, a malfunction of the analyzer is indicated and corrective actions are necessary before use.

11.0 Analytical Procedures [Reserved]

12.0 Data Analyses and Calculations [Reserved]

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Dubose, D.A., and G.E. Harris. Response Factors of VOC Analyzers at a Meter Reading of 10,000 ppmv for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81051. September 1981.

2. Brown, G.E., *et al.* Response Factors of VOC Analyzers Calibrated with Methane for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81–022. May 1981.

3. DuBose, D.A. *et al.* Response of Portable VOC Analyzers to Chemical Mixtures. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81–110. September 1981.

4. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 22—VISUAL DETERMINATION OF FUGITIVE EMISSIONS FROM MATERIAL SOURCES AND SMOKE EMISSIONS FROM FLARES

NOTE: This method is not inclusive with respect to observer certification. Some material is incorporated by reference from Method 9.

1.0 Scope and Application

This method is applicable for the determination of the frequency of fugitive emissions from stationary sources, only as specified in an applicable subpart of the regulations. This method also is applicable for the determination of the frequency of visible smoke emissions from flares.

2.0 Summary of Method

2.1 Fugitive emissions produced during material processing, handling, and transfer operations or smoke emissions from flares are visually determined by an observer without the aid of instruments.

2.2 This method is used also to determine visible smoke emissions from flares used for combustion of waste process materials.

2.3 This method determines the amount of time that visible emissions occur during the observation period (*i.e.*, the accumulated emission time). This method does not require that the opacity of emissions be determined. Since this procedure requires only the determination of whether visible emissions occur and does not require the determination of opacity levels, observer certification according to the procedures of Method 9 is not required. However, it is necessary that the observer is knowledgeable with respect to the general procedures for determining the presence of visible emissions. At a minimum, the observer must be trained and knowledgeable regarding the effects of background contrast, ambient lighting, observer position relative

to lighting, wind, and the presence of uncombined water (condensing water vapor) on the visibility of emissions. This training is to be obtained from written materials found in References 1 and 2 or from the lecture portion of the Method 9 certification course.

3.0 Definitions

3.1 *Emission frequency* means the percentage of time that emissions are visible during the observation period.

3.2 *Emission time* means the accumulated amount of time that emissions are visible during the observation period.

3.3 *Fugitive emissions* means emissions generated by an affected facility which is not collected by a capture system and is released to the atmosphere. This includes emissions that (1) escape capture by process equipment exhaust hoods; (2) are emitted during material transfer; (3) are emitted from buildings housing material processing or handling equipment; or (4) are emitted directly from process equipment.

3.4 *Observation period* means the accumulated time period during which observations are conducted, not to be less than the period specified in the applicable regulation.

3.5 *Smoke emissions* means a pollutant generated by combustion in a flare and occurring immediately downstream of the flame. Smoke occurring within the flame, but not downstream of the flame, is not considered a smoke emission.

4.0 Interferences

4.1 Occasionally, fugitive emissions from sources other than the affected facility (*e.g.*, road dust) may prevent a clear view of the affected facility. This may particularly be a problem during periods of high wind. If the view of the potential emission points is obscured to such a degree that the observer questions the validity of continuing observations, then the observations shall be terminated, and the observer shall clearly note this fact on the data form.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment

6.1 Stopwatches (two). Accumulative type with unit divisions of at least 0.5 seconds.

6.2 Light Meter. Light meter capable of measuring illuminance in the 50 to 200 lux range, required for indoor observations only.

7.0 Reagents and Supplies [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transfer [Reserved]

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

11.1 Selection of Observation Location. Survey the affected facility, or the building or structure housing the process to be observed, and determine the locations of potential emissions. If the affected facility is located inside a building, determine an observation location that is consistent with the requirements of the applicable regulation (*i.e.*, outside observation of emissions escaping the building/structure or inside observation of emissions directly emitted from the affected facility process unit). Then select a position that enables a clear view of the potential emission point(s) of the affected facility or of the building or structure housing the affected facility, as appropriate for the applicable subpart. A position at least 4.6 m (15 feet), but not more than 400 m (0.25 miles), from the emission source is recommended. For outdoor locations, select a position where the sunlight is not shining directly in the observer's eyes.

11.2 Field Records.

11.2.1 Outdoor Location. Record the following information on the field data sheet (Figure 22–1): Company name, industry, process unit, observer's name, observer's affiliation, and date. Record also the estimated wind speed, wind direction, and sky condition. Sketch the process unit being observed, and note the observer location relative to the source and the sun. Indicate the potential and actual emission points on the sketch.

11.2.2 Indoor Location. Record the following information on the field data sheet (Figure 22–2): Company name, industry, process unit, observer's name, observer's affiliation, and date. Record as appropriate the type, location, and intensity of lighting on the data sheet. Sketch the process unit being observed, and note the observer location relative to the source. Indicate the potential and actual fugitive emission points on the sketch.

11.3 Indoor Lighting Requirements. For indoor locations, use a light meter to measure the level of illumination at a location as close to the emission source(s) as is feasible. An illumination of greater than 100 lux (10 foot candles) is considered necessary for proper application of this method.

11.4 Observations.

11.4.1 Procedure. Record the clock time when observations begin. Use one stopwatch to monitor the duration of the observation

period. Start this stopwatch when the observation period begins. If the observation period is divided into two or more segments by process shutdowns or observer rest breaks (see section 11.4.3), stop the stopwatch when a break begins and restart the stopwatch without resetting it when the break ends. Stop the stopwatch at the end of the observation period. The accumulated time indicated by this stopwatch is the duration of observation period. When the observation period is completed, record the clock time. During the observation period, continuously watch the emission source. Upon observing an emission (condensed water vapor is not considered an emission), start the second accumulative stopwatch; stop the watch when the emission stops. Continue this procedure for the entire observation period. The accumulated elapsed time on this stopwatch is the total time emissions were visible during the observation period (*i.e.*, the emission time.)

11.4.2 Observation Period. Choose an observation period of sufficient length to meet the requirements for determining compliance with the emission standard in the applicable subpart of the regulations. When the length of the observation period is specifically stated in the applicable subpart, it may not be necessary to observe the source for this entire period if the emission time required to indicate noncompliance (based on the specified observation period) is observed in a shorter time period. In other words, if the regulation prohibits emissions for more than 6 minutes in any hour, then observations may (optional) be stopped after an emission time of 6 minutes is exceeded. Similarly, when the regulation is expressed as an emission frequency and the regulation prohibits emissions for greater than 10 percent of the time in any hour, then observations may (optional) be terminated after 6 minutes of emission are observed since 6 minutes is 10 percent of an hour. In any case, the observation period shall not be less than 6 minutes in duration. In some cases, the process operation may be intermittent or cyclic. In such cases, it may be convenient for the observation period to coincide with the length of the process cycle.

11.4.3 Observer Rest Breaks. Do not observe emissions continuously for a period of more than 15 to 20 minutes without taking a rest break. For sources requiring observation periods of greater than 20 minutes, the observer shall take a break of not less than 5 minutes and not more than 10 minutes after every 15 to 20 minutes of observation. If continuous observations are desired for extended time periods, two observers can alternate between making observations and taking breaks.

11.5 Recording Observations. Record the accumulated time of the observation period on the data sheet as the observation period duration. Record the accumulated time emissions were observed on the data sheet as the emission time. Record the clock time the observation period began and ended, as well as the clock time any observer breaks began and ended.

12.0 Data Analysis and Calculations

If the applicable subpart requires that the emission rate be expressed as an emission frequency (in percent), determine this value as follows: Divide the accumulated emission time (in seconds) by the duration of the observation period (in seconds) or by any minimum observation period required in the applicable subpart, if the actual observation period is less than the required period, and multiply this quotient by 100.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Missan, R., and A. Stein. Guidelines for Evaluation of Visible Emissions Certification, Field Procedures, Legal Aspects, and Background Material. EPA Publication No. EPA–340/1–75–007. April 1975.

2. Wohlschlegel, P., and D.E. Wagoner. Guideline for Development of a Quality Assurance Program: Volume IX—Visual Determination of Opacity Emissions from Stationary Sources. EPA Publication No. EPA–650/4–74–005i. November 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

FUGITIVE OR SMOKE EMISSION INSPECTION
OUTDOOR LOCATION

Company Location Company Rep.	Observer Affiliation Date
Sky Conditions Precipitation	Wind Direction Wind Speed
Industry	Process Unit

Sketch process unit: indicate observer position relative to source; indicate potential emission points and/or actual emission points.

OBSERVATIONS	Clock Time	Observation period duration, min:sec	Accumulated emission time, min:sec
Begin Observation			
End Observation			

Figure 22-1

FUGITIVE OR SMOKE EMISSION INSPECTION
INDOOR LOCATION

Company Location Company Rep.	Observer Affiliation Date
Industry	Process Unit

Light type (fluorescent, incandescent, natural)
Light location (overhead, behind observer, etc.)
Illuminance (lux or footcandles)
Sketch process unit: indicate observer position relative to source; indicate potential emission points and/or actual emission points.

OBSERVATIONS	Clock Time	Observation period duration, min:sec	Accumulated emission time, min:sec
Begin			
End Observation			

Figure 22-2

METHOD 23—DETERMINATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS FROM STATIONARY SOURCES

1. Applicability and Principle

1.1 Applicability. This method is applicable to the determination of polychlorinated dibenzo-p-dioxins (PCDD's) and polychlorinated dibenzofurans (PCDF's) from stationary sources.

1.2 Principle. A sample is withdrawn from the gas stream isokinetically and collected in the sample probe, on a glass fiber filter, and on a packed column of adsorbent material. The sample cannot be separated into a particle vapor fraction. The PCDD's and

PCDF's are extracted from the sample, separated by high resolution gas chromatography, and measured by high resolution mass spectrometry.

2. Apparatus

2.1 Sampling. A schematic of the sampling train used in this method is shown in Figure 23–1. Sealing greases may not be used in assembling the train. The train is identical to that described in section 2.1 of Method 5 of this appendix with the following additions:

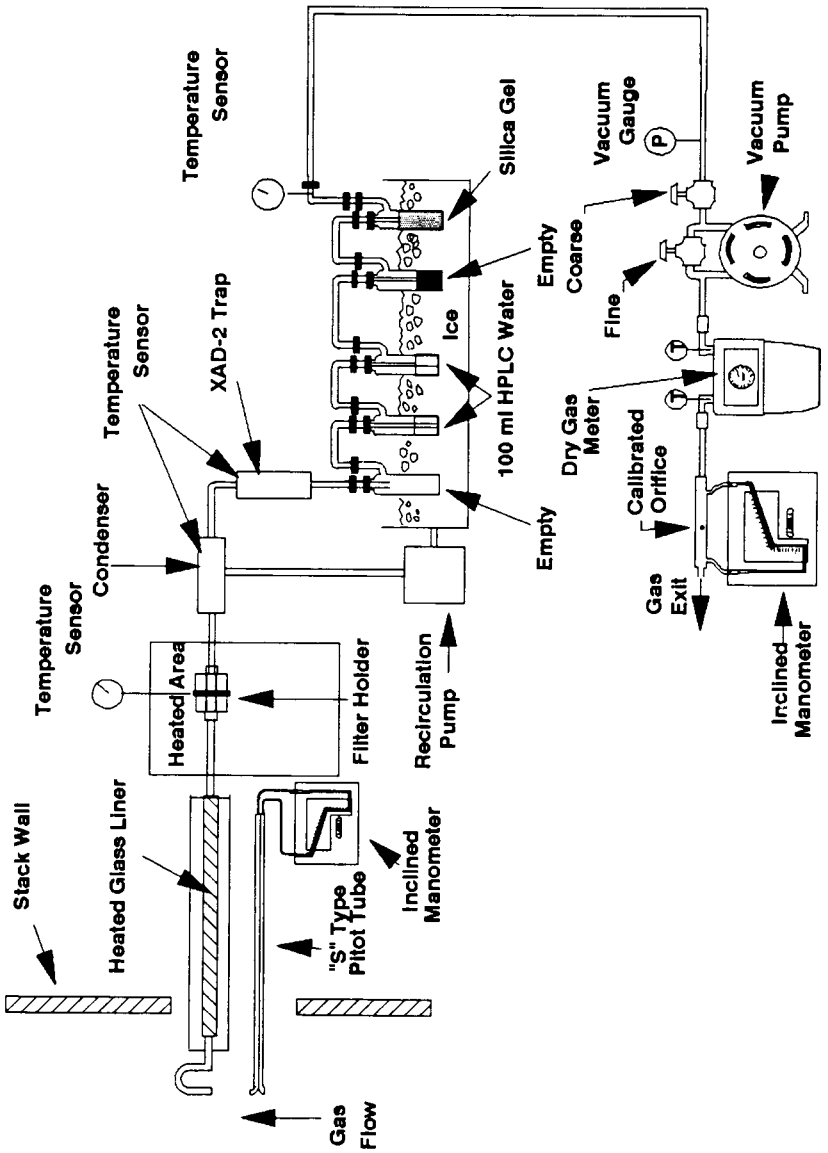


Figure 23.1 Sampling train

2.1.1 Nozzle. The nozzle shall be made of nickel, nickel-plated stainless steel, quartz, or borosilicate glass.

2.1.2 Sample Transfer Lines. The sample transfer lines, if needed, shall be heat traced, heavy walled TFE (½ in. OD with ⅛ in. wall) with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases. The line shall be as short as possible and must be maintained at 120 °C.

2.1.1 Filter Support. Teflon or Teflon-coated wire.

2.1.2 Condenser. Glass, coil type with compatible fittings. A schematic diagram is shown in Figure 23–2.

2.1.3 Water Bath. Thermostatically controlled to maintain the gas temperature exiting the condenser at <20 °C (68 °F).

2.1.4 Adsorbent Module. Glass container to hold the solid adsorbent. A shematic diagram is shown in Figure 23–2. Other physical configurations of the resin trap/condenser assembly are acceptable. The connecting fittings shall form leak-free, vacuum tight seals. No sealant greases shall be used in the sampling train. A coarse glass frit is included to retain the adsorbent.

2.2 Sample Recovery.

2.2.1 Fitting Caps. Ground glass, Teflon tape, or aluminum foil (Section 2.2.6) to cap off the sample exposed sections of the train.

2.2.2 Wash Bottles. Teflon, 500-ml.

2.2.3 Probe-Liner Probe-Nozzle, and Filter-Holder Brushes. Inert bristle brushes with precleaned stainless steel or Teflon handles. The probe brush shall have extensions of stainless steel or Teflon, at least as long as the probe. The brushes shall be properly sized and shaped to brush out the nozzle, probe liner, and transfer line, if used.

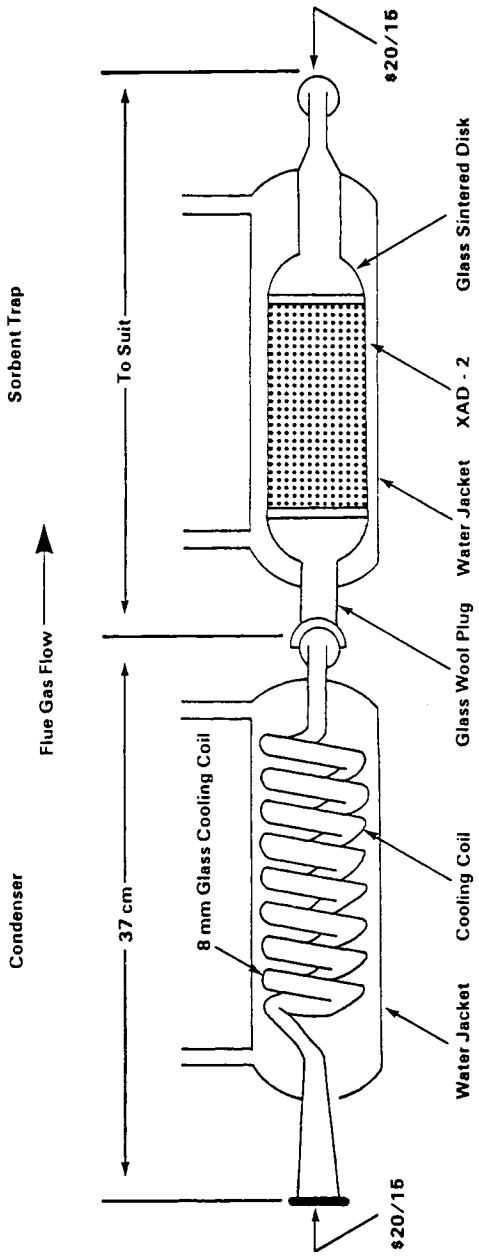


Figure 23.2. Condenser and adsorbent trap

2.2.4 Filter Storage Container. Sealed filter holder, wide-mouth amber glass jar with Teflon-lined cap, or glass petri dish.

2.2.5 Balance. Triple beam.

2.2.6 Aluminum Foil. Heavy duty, hexane-rinsed.

2.2.7 Storage Container. Air-tight container to store silica gel.

2.2.8 Graduated Cylinder. Glass, 250-ml with 2-ml graduation.

2.2.9 Glass Sample Storage Container. Amber glass bottle for sample glassware washes, 500- or 1000-ml, with leak free Teflon-lined caps.

2.3 Analysis.

2.3.1 Sample Container. 125- and 250-ml flint glass bottles with Teflon-lined caps.

2.3.2 Test Tube. Glass.

2.3.3 Soxhlet Extraction Apparatus. Capable of holding 43 × 123 mm extraction thimbles.

2.3.4 Extraction Thimble. Glass, precleaned cellulosic, or glass fiber.

2.3.5 Pasteur Pipettes. For preparing liquid chromatographic columns.

2.3.6 Reacti-vials. Amber glass, 2-ml, silanized prior to use.

2.3.7 Rotary Evaporator. Buchi/Brinkman RF–121 or equivalent.

2.3.8 Nitrogen Evaporative Concentrator. N-Evap Analytical Evaporator Model III or equivalent.

2.3.9 Separatory Funnels. Glass, 2-liter.

2.3.10 Gas Chromatograph. Consisting of the following components:

2.3.10.1 Oven. Capable of maintaining the separation column at the proper operating temperature ±°C and performing programmed increases in temperature at rates of at least 40 °C/min.

2.3.10.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperatures ±1 °C.

2.3.10.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

2.3.10.4 Capillary Columns. A fused silica column, 60 × 0.25 mm inside diameter (ID), coated with DB–5 and a fused silica column, 30 m × 0.25 mm ID coated with DB–225. Other column systems may be used provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of section 6.1.2.2.

2.3.11 Mass Spectrometer. Capable of routine operation at a resolution of 1:10000 with a stability of ±5 ppm.

2.3.12 Data System. Compatible with the mass spectrometer and capable of monitoring at least five groups of 25 ions.

2.3.13 Analytical Balance. To measure within 0.1 mg.

3. Reagents

3.1 Sampling.

3.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D 2986–71 (Reapproved 1978) (incorporated by reference—see §60.17).

3.1.1.1 Precleaning. All filters shall be cleaned before their initial use. Place a glass extraction thimble and 1 g of silica gel and a plug of glass wool into a Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Place no more than 50 filters in the thimble onto the silica gel bed and top with the cleaned glass wool. Charge the Soxhlet with toluene and reflux for 16 hours. After extraction, allow the Soxhlet to cool, remove the filters, and dry them under a clean N_2 stream. Store the filters in a glass petri dish sealed with Teflon tape.

3.1.2 Adsorbent Resin. Amberlite XAD–2 resin. Thoroughly cleaned before initial use.

3.1.2.1 Cleaning Procedure. This procedure may be carried out in a giant Soxhlet extractor. An all-glass filter thimble containing an extra-course frit is used for extraction of XAD–2. The frit is recessed 10–15 mm above a crenelated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass wool plug and a stainless steel ring because it floats on methylene chloride. This process involves sequential extraction in the following order.

Solvent	Procedure
Water	Initial rinse: Place resin in a beaker, rinse once with water, and discard. Fill with water a second time, let stand overnight, and discard.
Water	Extract with water for 8 hours.
Methanol	Extract for 22 hours.
Methylene Chloride	Extract for 22 hours.
Toluene	Extract for 22 hours.

3.1.2.2 Drying.

3.1.2.2.1 Drying Column. Pyrex pipe, 10.2 cm ID by 0.6 m long, with suitable retainers.

3.1.2.2.2 Procedure. The adsorbent must be dried with clean inert gas. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has proven to be a reliable source of large volumes of gas free from organic contaminants. Connect the liquid nitrogen cylinder to the column by a length of cleaned copper tubing, 0.95 cm ID, coiled to pass through a heat source. A convenient heat source is a water-bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40 °C. Continue flowing nitrogen through the adsorbent until all the residual solvent is removed. The flow rate should be sufficient to gently agitate the particles but not so excessive as the cause the particles to fracture.

3.1.2.3 Quality Control Check. The adsorbent must be checked for residual toluene.

3.1.2.3.1 Extraction. Weigh 1.0 g sample of dried resin into a small vial, add 3 ml of toluene, cap the vial, and shake it well.

3.1.2.3.2 Analysis. Inject a 2 µl sample of the extract into a gas chromatograph operated under the following conditions:

Column: 6 ft × ⅛ in stainless steel containing 10 percent OV–101 on 100/120 Supelcoport.
Carrier Gas: Helium at a rate of 30 ml/min.
Detector: Flame ionization detector operated at a sensitivity of 4×10^{-11} A/mV.
Injection Port Temperature: 250 °C.
Detector Temperature: 305 °C.
Oven Temperature: 30 °C for 4 min; programmed to rise at 40 °C/min until it reaches 250 °C; return to 30 °C after 17 minutes.

Compare the results of the analysis to the results from the reference solution. Prepare the reference solution by injection 2.5 µl of methylene chloride into 100 ml of toluene. This corresponds to 100 µg of methylene chloride per g of adsorbent. The maximum acceptable concentration is 1000 µg/g of adsorbent. If the adsorbent exceeds this level, drying must be continued until the excess methylene chloride is removed.

3.1.2.4 Storage. The adsorbent must be used within 4 weeks of cleaning. After cleaning, it may be stored in a wide mouth amber glass container with a Teflon-lined cap or placed in one of the glass adsorbent modules tightly sealed with glass stoppers. If precleaned adsorbent is purchased in sealed containers, it must be used within 4 weeks after the seal is broken.

3.1.3 Glass Wool. Cleaned by sequential immersion in three aliquots of methylene chloride, dried in a 110 °C oven, and stored in a methylene chloride-washed glass jar with a Teflon-lined screw cap.

3.1.4 Water. Deionized distilled and stored in a methylene chloride-rinsed glass container with a Teflon-lined screw cap.

3.1.5 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175 °C (350 °F) for two hours. New silica gel may be used as received. Alternately other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

3.1.6 Chromic Acid Cleaning Solution. Dissolve 20 g of sodium dichromate in 15 ml of water, and then carefully add 400 ml of concentrated sulfuric acid.

3.2 Sample Recovery.

3.2.2 Acetone. Pesticide quality.

3.2.2 Methylene Chloride. Pesticide qualtity.

3.2.3 Toluene. Pesticide quality.

3.3 Analysis.

3.3.1 Potassium Hydroxide. ACS grade, 2-percent (weight/volume) in water.

3.3.2 Sodium Sulfate. Granulated, reagent grade. Purify prior to use by rinsing with methylene chloride and oven drying. Store the cleaned material in a glass container with a Teflon-lined screw cap.

3.3.3 Sulfuric Acid. Reagent grade.

3.3.4 Sodium Hydroxide. 1.0 N. Weigh 40 g of sodium hydroxide into a 1-liter volumetric flask. Dilute to 1 liter with water.

3.3.5 Hexane. Pesticide grade.

3.3.6 Methylene Chloride. Pesticide grade.

3.3.7 Benzene. Pesticide Grade.

3.3.8 Ethyl Acetate.

3.3.9 Methanol. Pesticide Grade.

3.3.10 Toluene. Pesticide Grade.

3.3.11 Nonane. Pesticide Grade.

3.3.12 Cyclohexane. Pesticide Grade.

3.3.13 Basic Alumina. Activity grade 1, 100–200 mesh. Prior to use, activate the alumina by heating for 16 hours at 130 °C before use. Store in a desiccator. Pre-activated alumina may be purchased from a supplier and may be used as received.

3.3.14 Silica Gel. Bio-Sil A, 100–200 mesh. Prior to use, activate the silica gel by heating for at least 30 minutes at 180 °C. After cooling, rinse the silica gel sequentially with methanol and methylene chloride. Heat the rinsed silica gel at 50 °C for 10 minutes, then increase the temperature gradually to 180 °C over 25 minutes and maintain it at this temperature for 90 minutes. Cool at room temperature and store in a glass container with a Teflon-lined screw cap.

3.3.15 Silica Gel Impregnated with Sulfuric Acid. Combine 100 g of silica gel with 44 g of concentrated sulfuric acid in a screw capped glass bottle and agitate thoroughly. Disperse the solids with a stirring rod until a uniform mixture is obtained. Store the mixture in a glass container with a Teflon-lined screw cap.

3.3.16 Silica Gel Impregnated with Sodium Hydroxide. Combine 39 g of 1 N sodium hydroxide with 100 g of silica gel in a screw capped glass bottle and agitate thoroughly. Disperse solids with a stirring rod until a uniform mixture is obtained. Store the mixture in glass container with a Teflon-lined screw cap.

3.3.17 Carbon/Celite. Combine 10.7 g of AX–21 carbon with 124 g of Celite 545 in a 250-ml glass bottle with a Teflon-lined screw cap. Agitate the mixture thoroughly until a uniform mixture is obtained. Store in the glass container.

3.3.18 Nitrogen. Ultra high purity.

3.3.19 Hydrogen. Ultra high purity.

3.3.20 Internal Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Internal Standards'' in 10 ml of nonane.

3.3.21 Surrogate Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Surrogate Standards'' in 10 ml of nonane.

3.3.22 Recovery Standard Solution. Prepare a stock standard solution containing the

isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Recovery Standards'' in 10 ml of nonane.

4. Procedure

4.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, testers should be trained and experienced with the test procedures.

4.1.1 Pretest Preparation.

4.1.1.1 Cleaning Glassware. All glass components of the train upstream of and including the adsorbent module, shall be cleaned as described in section 3A of the ''Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples.'' Special care shall be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. Any residue shall be removed by soaking the glassware for several hours in a chromic acid cleaning solution prior to cleaning as described above.

4.1.1.2 Adsorbent Trap. The traps must be loaded in a clean area to avoid contamination. They may not be loaded in the field. Fill a trap with 20 to 40 g of XAD–2. Follow the XAD–2 with glass wool and tightly cap both ends of the trap. Add 100 μl of the surrogate standard solution (section 3.3.21) to each trap.

4.1.1.3 Sample Train. It is suggested that all components be maintained according to the procedure described in APTD–0576. Alternative mercury-free thermometers may be used if the thermometers are, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

4.1.1.4 Silica Gel. Weigh several 200 to 300 g portions of silica gel in an air tight container to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel may be weighed directly in its impinger or sampling holder just prior to sampling.

4.1.1.5 Filter. Check each filter against light for irregularities and flaws or pinhole leaks. Pack the filters flat in a clean glass container.

4.1.2 Preliminary Determinations. Same as section 4.1.2 of Method 5.

4.1.3 Preparation of Collection Train.

4.1.3.1 During preparation and assembly of the sampling train, keep all train openings where contamination can enter, sealed until just prior to assembly or until sampling is about to begin.

NOTE: Do not use sealant grease in assembling the train.

4.1.3.2 Place approximately 100 ml of water in the second and third impingers, leave the first and fourth impingers empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fifth impinger.

4.1.3.3 Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

4.1.3.4 Assemble the train as shown in Figure 23–1.

4.1.3.5 Turn on the adsorbent module and condenser coil recirculating pump and begin monitoring the adsorbent module gas entry temperature. Ensure proper sorbent temperature gas entry temperature before proceeding and before sampling is initiated. It is extremely important that the XAD–2 adsorbent resin temperature never exceed 50 °C because thermal decomposition will occur. During testing, the XAD–2 temperature must not exceed 20 °C for efficient capture of the PCDD's and PCDF's.

4.1.4 Leak-Check Procedure. Same as Method 5, section 4.1.4.

4.1.5 Sample Train Operation. Same as Method 5, section 4.1.5.

4.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Seal the nozzle end of the sampling probe with Teflon tape or aluminum foil.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe. Remove the probe from the train and close off both ends with aluminum foil. Seal off the inlet to the train with Teflon tape, a ground glass cap, or aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area shall be clean and enclosed so that the chances of losing or contaminating the sample are minimized. Smoking, which could contaminate the sample, shall not be allowed in the cleanup area.

Inspect the train prior to and during disassembly and note any abnormal conditions, e.g., broken filters, colored impinger liquid, etc. Treat the samples as follows:

4.2.1 Container No. 1. Either seal the filter holder or carefully remove the filter from the filter holder and place it in its identified container. Use a pair of cleaned tweezers to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and filter fibers which adhere to the filter holder gasket, by using a dry inert bristle brush and a sharp-edged blade. Seal the container.

4.2.2 Adsorbent Module. Remove the module from the train, tightly cap both ends, label it, cover with aluminum foil, and store it on ice for transport to the laboratory.

4.2.3 Container No. 2. Quantitatively recover material deposited in the nozzle, probe transfer lines, the front half of the filter holder, and the cyclone, if used, first, by

brushing while rinsing three times each with acetone and then, by rinsing the probe three times with methylene chloride. Collect all the rinses in Container No. 2.

Rinse the back half of the filter holder three times with acetone. Rinse the connecting line between the filter and the condenser three times with acetone. Soak the connecting line with three separate portions of methylene chloride for 5 minutes each. If using a separate condenser and adsorbent trap, rinse the condenser in the same manner as the connecting line. Collect all the rinses in Container No. 2 and mark the level of the liquid on the container.

4.2.4 Container No. 3. Repeat the methylene chloride-rinsing described in section 4.2.3 using toluene as the rinse solvent. Collect the rinses in Container No. 3 and mark the level of the liquid on the container.

4.2.5 Impinger Water. Measure the liquid in the first three impingers to within ±1 ml by using a graduated cylinder or by weighing it to within ±0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

Discard the liquid after measuring and recording the volume or weight.

4.2.7 Silica Gel. Note the color of the indicating silica gel to determine if it has been completely spent and make a mention of its condition. Transfer the silica gel from the fifth impinger to its original container and seal. If a moisture determination is made, follow the applicable procedures in sections 8.7.6.3 and 11.2.3 of Method 5 to handle and weigh the silica gel. If moisture is not measured, the silica gel may be disposed.

5. Analysis

All glassware shall be cleaned as described in section 3A of the ''Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples.'' All samples must be extracted within 30 days of collection and analyzed within 45 days of extraction.

5.1 Sample Extraction.

5.1.1 Extraction System. Place an extraction thimble (section 2.3.4), 1 g of silica gel, and a plug of glass wool into the Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Remove the extraction thimble from the extraction system and place it in a glass beaker to catch the solvent rinses.

5.1.2 Container No. 1 (Filter). Transfer the contents directly to the glass thimble of the extraction system and extract them simultaneously with the XAD–2 resin.

5.1.3 Adsorbent Cartridge. Suspend the adsorbent module directly over the extraction thimble in the beaker (See section 5.1.1). The glass frit of the module should be in the up position. Using a Teflon squeeze bottle containing toluene, flush the XAD–2 into the thimble onto the bed of cleaned silica gel. Thoroughly rinse the glass module catching the rinsings in the beaker containing the thimble. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. Add the XAD–2 glass wool plug into the thimble.

5.1.4 Container No. 2 (Acetone and Methylene Chloride). Concentrate the sample to a volume of about 1–5 ml using the rotary evaporator apparatus, at a temperature of less than 37 °C. Rinse the sample container three times with small portions of methylene chloride and add these to the concentrated solution and concentrate further to near dryness. This residue contains particulate matter removed in the rinse of the train probe and nozzle. Add the concentrate to the filter and the XAD–2 resin in the Soxhlet apparatus described in section 5.1.1.

5.1.5 Extraction. Add 100 µl of the internal standard solution (Section 3.3.20) to the extraction thimble containing the contents of the adsorbent cartridge, the contents of Container No. 1, and the concentrate from section 5.1.4. Cover the contents of the extraction thimble with the cleaned glass wool plug to prevent the XAD–2 resin from floating into the solvent reservoir of the extractor. Place the thimble in the extractor, and add the toluene contained in the beaker to the solvent reservoir. Pour additional toluene to fill the reservoir approximately ⅔ full. Add Teflon boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle three times per hour. Extract the sample for 16 hours. After extraction, allow the Soxhlet to cool. Transfer the toluene extract and three 10-ml rinses to the rotary evaporator. Concentrate the extract to approximately 10 ml. At this point the analyst may choose to split the sample in half. If so, split the sample, store one half for future use, and analyze the other according to the procedures in sections 5.2 and 5.3. In either case, use a nitrogen evaporative concentrator to reduce the volume of the sample being analyzed to near dryness. Dissolve the residue in 5 ml of hexane.

5.1.6 Container No. 3 (Toluene Rinse). Add 100 µl of the Internal Standard solution (section 3.3.2) to the contents of the container. Concentrate the sample to a volume of about 1–5 ml using the rotary evaporator apparatus at a temperature of less than 37 °C. Rinse the sample container apparatus at a temperature of less than 37 °C. Rinse the sample container three times with small portions of toluene and add these to the concentrated solution and concentrate further to near dryness. Analyze the extract separately according to the procedures in sections 5.2 and 5.3, but concentrate the solution in a rotary evaporator apparatus rather than a nitrogen evaporative concentrator.

5.2 Sample Cleanup and Fractionation.

5.2.1 Silica Gel Column. Pack one end of a glass column, 20 mm × 230 mm, with glass wool. Add in sequence, 1 g silica gel, 2 g of sodium hydroxide impregnated silica gel, 1 g silica gel, 4 g of acid-modified silica gel, and 1 g of silica gel. Wash the column with 30 ml of hexane and discard it. Add the sample extract, dissolved in 5 ml of hexane to the column with two additional 5-ml rinses. Elute the column with an additional 90 ml of hexane and retain the entire eluate. Concentrate this solution to a volume of about 1 ml using the nitrogen evaporative concentrator (section 2.3.7).

5.2.2 Basic Alumina Column. Shorten a 25-ml disposable Pasteur pipette to about 16 ml. Pack the lower section with glass wool and 12 g of basic alumina. Transfer the concentrated extract from the silica gel column to the top of the basic alumina column and elute the column sequentially with 120 ml of 0.5 percent methylene chloride in hexane followed by 120 ml of 35 percent methylene chloride in hexane. Discard the first 120 ml of eluate. Collect the second 120 ml of eluate and concentrate it to about 0.5 ml using the nitrogen evaporative concentrator.

5.2.3 AX–21 Carbon/Celite 545 Column. Remove the botton 0.5 in. from the tip of a 9-ml disposable Pasteur pipette. Insert a glass fiber filter disk in the top of the pipette 2.5 cm from the constriction. Add sufficient carbon/celite mixture to form a 2 cm column. Top with a glass wool plug. In some cases AX–21 carbon fines may wash through the glass wool plug and enter the sample. This may be prevented by adding a celite plug to the exit end of the column. Rinse the column in sequence with 2 ml of 50 percent benzene in ethyl acetate, 1 ml of 50 percent methylene chloride in cyclohexane, and 2 ml of hexane. Discard these rinses. Transfer the concentrate in 1 ml of hexane from the basic alumina column to the carbon/celite column along with 1 ml of hexane rinse. Elute the column sequentially with 2 ml of 50 percent methylene chloride in hexane and 2 ml of 50 percent benzene in ethyl acetate and discard these eluates. Invert the column and elute in the reverse direction with 13 ml of toluene. Collect this eluate. Concentrate the eluate in a rotary evaporator at 50 °C to about 1 ml. Transfer the concentrate to a Reacti-vial using a toluene rinse and concentrate to a volume of 200 µl using a stream of N_2. Store extracts at room temperature, shielded from light, until the analysis is performed.

5.3 Analysis. Analyze the sample with a gas chromatograph coupled to a mass spectrometer (GC/MS) using the instrumental parameters in sections 5.3.1 and 5.3.2. Immediately prior to analysis, add a 20 µl aliquot of the Recovery Standard solution from Table 1 to each sample. A 2 µl aliquot of the extract is injected into the GC. Sample extracts are first analyzed using the DB–5 capillary column to determine the concentration of each isomer of PCDD's and PCDF's (tetra-through octa-). If tetra-chlorinated dibenzofurans are detected in this analysis, then analyze another aliquot of the sample in a separate run, using the DB–225 column to measure the 2,3,7,8 tetra-chloro dibenzofuran isomer. Other column systems may be used, provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of section 6.1.2.2.

5.3.1 Gas Chromatograph Operating Conditions.

5.3.1.1 Injector. Configured for capillary column, splitless, 250 °C.

5.3.1.2 Carrier Gas. Helium, 1–2 ml/min.

5.3.1.3 Oven. Initially at 150 °C. Raise by at least 40 °C/min to 190 °C and then at 3 °C/min up to 300 °C.

5.3.2 High Resolution Mass Spectrometer.

5.3.2.1 Resolution. 10000 m/e.

5.3.2.2 Ionization Mode. Electron impact.

5.3.2.3 Source Temperature 250 °C.

5.3.2.4 Monitoring Mode. Selected ion monitoring. A list of the various ions to be monitored is summarized in Table 3.

5.3.2.5 Identification Criteria. The following identification criteria shall be used for the characterization of polychlorinated dibenzodioxins and dibenzofurans.

1. The integrated ion-abundance ratio (M/M + 2 or M + 2/M + 4) shall be within 15 percent of the theoretical value. The acceptable ion-abundance ratio ranges for the identification of chlorine-containing compounds are given in Table 4.

2. The retention time for the analytes must be within 3 seconds of the corresponding ^{13}C-labeled internal standard, surrogate or alternate standard.

3. The monitored ions, shown in Table 3 for a given analyte, shall reach their maximum within 2 seconds of each other.

4. The identification of specific isomers that do not have corresponding ^{13}C-labeled standards is done by comparison of the relative retention time (RRT) of the analyte to the nearest internal standard retention time with reference (i.e., within 0.005 RRT units) to the comparable RRT's found in the continuing calibration.

5. The signal to noise ratio for all monitored ions must be greater than 2.5.

6. The confirmation of 2, 3, 7, 8–TCDD and 2, 3, 7, 8–TCDF shall satisfy all of the above identification criteria.

7. For the identification of PCDF's, no signal may be found in the corresponding PCDPE channels.

5.3.2.6 Quantification. The peak areas for the two ions monitored for each analyte are summed to yield the total response for each analyte. Each internal standard is used to quantify the indigenous PCDD's or PCDF's in its homologous series. For example, the $^{13}C_{12}$–2,3,7,8-tetra chlorinated dibenzodioxin is used to calculate the concentrations of all

other tetra chlorinated isomers. Recoveries of the tetra- and penta- internal standards are calculated using the $^{13}C_{12}$–1,2,3,4–TCDD. Recoveries of the hexa- through octa- internal standards are calculated using $^{13}C_{12}$–1,2,3,7,8,9–HxCDD. Recoveries of the surrogate standards are calculated using the corresponding homolog from the internal standard.

6. Calibration

Same as Method 5 with the following additions.

6.1 GC/MS System.

6.1.1 Initial Calibration. Calibrate the GC/MS system using the set of five standards shown in Table 2. The relative standard deviation for the mean response factor from each of the unlabeled analytes (Table 2) and of the internal, surrogate, and alternate standards shall be less than or equal to the values in Table 5. The signal to noise ratio for the GC signal present in every selected ion current profile shall be greater than or equal to 2.5. The ion abundance ratios shall be within the control limits in Table 4.

6.1.2 Daily Performance Check.

6.1.2.1 Calibration Check. Inject on µl of solution Number 3 from Table 2. Calculate the relative response factor (RRF) for each compound and compare each RRF to the corresponding mean RRF obtained during the initial calibration. The analyzer performance is acceptable if the measured RRF's for the labeled and unlabeled compounds for the daily run are within the limits of the mean values shown in Table 5. In addition, the ion-abundance ratios shall be within the allowable control limits shown in Table 4.

6.1.2.2 Column Separation Check. Inject a solution of a mixture of PCDD's and PCDF's that documents resolution between 2,3,7,8–TCDD and other TCDD isomers. Resolution is defined as a valley between peaks that is less than 25 percent of the lower of the two peaks. Identify and record the retention time windows for each homologous series.

Perform a similar resolution check on the confirmation column to document the resolution between 2,3,7,8 TCDF and other TCDF isomers.

6.2 Lock Channels. Set mass spectrometer lock channels as specified in Table 3. Monitor the quality control check channels specified in Table 3 to verify instrument stability during the analysis.

7. Quality Control

7.1 Sampling Train Collection Efficiency Check. Add 100 µl of the surrogate standards in Table 1 to the absorbent cartridge of each train before collecting the field samples.

7.2 Internal Standard Percent Recoveries. A group of nine carbon labeled PCDD's and PCDF's representing, the tetra-through octachlorinated homologues, is added to every sample prior to extraction. The role of the internal standards is to quantify the native PCDD's and PCDF's present in the sample as well as to determine the overall method efficiency. Recoveries of the internal standards must be between 40 to 130 percent for the tetra-through hexachlorinated compounds while the range is 25 to 130 percent for the higher hepta- and octachlorinated homologues.

7.3 Surrogate Recoveries. The five surrogate compounds in Table 2 are added to the resin in the adsorbent sampling cartridge before the sample is collected. The surrogate recoveries are measured relative to the internal standards and are a measure of collection efficiency. They are not used to measure native PCDD's and PCDF's. All recoveries shall be between 70 and 130 percent. Poor recoveries for all the surrogates may be an indication of breakthrough in the sampling train. If the recovery of all standards is below 70 percent, the sampling runs must be repeated. As an alternative, the sampling runs do not have to be repeated if the final results are divided by the fraction of surrogate recovery. Poor recoveries of isolated surrogate compounds should not be grounds for rejecting an entire set of the samples.

7.4 Toluene QA Rinse. Report the results of the toluene QA rinse separately from the total sample catch. Do not add it to the total sample.

8.0 [Reserved]

9. Calculations

Same as Method 5, section 6 with the following additions.

9.1 Nomenclature.

A_{ai} = Integrated ion current of the noise at the retention time of the analyte.

A^*_{ci} = Integrated ion current of the two ions characteristic of the internal standard i in the calibration standard.

A_{cij} = Integrated ion current of the two ions characteristic of compound i in the jth calibration standard.

A^*_{cij} = Integrated ion current of the two ions characteristic of the internal standard i in the jth calibration standard.

A_{csi} = Integrated ion current of the two ions characteristic of surrogate compound i in the calibration standard.

A_i = Integrated ion current of the two ions characteristic of compound i in the sample.

A^*_i = Integrated ion current of the two ions characteristic of internal standard i in the sample.

A_{rs} = Integrated ion current of the two ions characteristic of the recovery standard.

A_{si} = Integrated ion current of the two ions characteristic of surrogate compound i in the sample.

C_i = Concentration of PCDD or PCDF i in the sample, pg/M^3.

C_T = Total concentration of PCDD's or PCDF's in the sample, pg/M^3.
m_{ci} = Mass of compound i in the calibration standard injected into the analyzer, pg.
m_{rs} = Mass of recovery standard in the calibration standard injected into the analyzer, pg.
m_{si} = Mass of surrogate compound in the calibration standard, pg.
RRF_i = Relative response factor.
RRF_{rs} = Recovery standard response factor.
RRF_s = Surrogate compound response factor.

9.2 Average Relative Response Factor.

$$RRF_i = \frac{1}{n}\sum_{j=1}^{n}\frac{A_{cij}\, m^*_{ci}}{A^*_{cij}\, m_{ci}} \qquad \text{Eq. 23-1}$$

9.3 Concentration of the PCDD's and PCDF's.

$$C_i = \frac{m_i^* A_i}{A_i^* RRF_i V_{mstd}} \qquad \text{Eq. 23-2}$$

9.4 Recovery Standard Response Factor.

$$RRF_{rs} = \frac{A_{ci}^* m_{rs}}{A_{rs} m_{ci}^*} \qquad \text{Eq. 23-3}$$

9.5 Recovery of Internal Standards (R*).

$$R^* = \frac{A_i^* m_{rs}}{A_{rs} RF_{rs} m_i^*} \times 100\% \qquad \text{Eq. 23-4}$$

9.6 Surrogate Compound Response Factor.

$$RRF_s = \frac{A_{ci}^* m_s}{A_{cis} m_{ci}^*} \qquad \text{Eq. 23-5}$$

9.7 Recovery of Surrogate Compounds (R_s).

$$R_s = \frac{A_s m_i^*}{A_i^* RRF_s m_s} \times 100\% \qquad \text{Eq. 23-6}$$

9.8 Minimum Detectable Limit (MDL).

$$MDL = \frac{2.5\, A_{ai} m_i^*}{A_{ci}^* RRF_i} \qquad \text{Eq. 23-7}$$

9.9 Total Concentration of PCDD's and PCDF's in the Sample.

$$C_{Tr} = \sum_{i=1}^{n} C_i \qquad \text{Eq. 23-8}$$

Any PCDD's or PCDF's that are reported as nondetected (below the MDL) shall be counted as zero for the purpose of calculating the total concentration of PCDD's and PCDF's in the sample.

10. Bibliography

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TABLE 1—COMPOSITION OF THE SAMPLE FORTIFICATION AND RECOVERY STANDARDS SOLUTIONS

Analyte	Concentration (pg/µl)
Internal Standards:	
$^{13}C_{12}$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100
$^{13}C_{12}$-OCDD	100
$^{13}C_{12}$-2,3,7,8-TCDF	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100
Surrogate Standards:	
$^{37}Cl_4$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100
Recovery Standards:	
$^{13}C_{12}$-1,2,3,4-TCDD	500
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	500

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS

Compound	Concentrations (pg/µL)				
	Solution No.				
	1	2	3	4	5
Alternate Standard:					
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	2.5	5	25	250	500

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS—Continued

Compound	Concentrations (pg/μL)				
	Solution No.				
	1	2	3	4	5
Recovery Standards:					
$^{13}C_{12}$-1,2,3,4-TCDD ..	100	100	100	100	100

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS—Continued

Compound	Concentrations (pg/μL)				
	Solution No.				
	1	2	3	4	5
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

TABLE 3—ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HIGH RESOLUTION MASS SPECTROMETRY FOR PCDD'S AND PCDF'S

Descriptor No.	Accurate mass	Ion type	Elemental composition	Analyte
2	292.9825	LOCK	C_7F_{11}	PFK
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M + 2	$C_{12}H_4{}^{35}Cl^{37}O$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M + 2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}ClO_2$	TCDD
	321.8936	M + 2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD (S)
	330.9792	QC	C_7F_{13}	PFK
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9339	M + 2	$^{13}C_{12}H_4{}^{35}Cl^{37}ClO_2$	TCDD (S)
	339.8597	M + 2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PECDF
	341.8567	M + 4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M + 2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M + 4	$^{13}C_{12}H_3{}^{35}Cl^{3537}Cl_2O$	PeCDF (S)
	355.8546	M + 2	$C_{12}H_3{}^{35}Cl_3 37ClO_2$	PeCDD
	357.8516	M + 4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M + 2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M + 4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}\ Cl_2O_2$	PeCDD (S)
	375.8364	M + 2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
	409.7974	M + 2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCPDE
3	373.8208	M + 2	$C_{12}H_2 35Cl_5{}^{37}ClO$	HxCDF
	375.8178	M + 4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M + 2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8157	M + 2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M + 4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	392.9760	LOCK	C_9F_{15}	PFK
	401.8559	M + 2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M + 4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDD (S)
	445.7555	M + 4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	430.9729	QC	C_9F_{17}	PFK
4	407.7818	M + 2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M + 4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8253	M	$^{13}C_{12}H^{35}Cl_7O$	HpCDF (S)
	419.8220	M + 2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF (S)
	423.7766	M + 2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M + 4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M + 2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M + 4	$^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S)
	479.7165	M + 4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCPDE
	430.9729	LOCK	C_9F_{17}	PFK
	441.7428	M + 2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M + 4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M + 2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M + 4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M + 2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M + 4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S)
	513.6775	M + 4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O_2$	DCDPE
	442.9728	QC	$C_{10}F_{17}$	PFK

(a) The following nuclidic masses were used:
H = 1.007825
C = 12.000000
^{13}C = 13.003355
F = 18.9984
O = 15.994915
^{35}Cl = 34.968853
^{37}Cl = 36.965903

S = Labeled Standard
QC = Ion selected for monitoring instrument stability during the GC/MS analysis.

TABLE 4—ACCEPTABLE RANGES FOR ION-ABUNDANCE RATIOS OF PCDD'S AND PCDF'S

No. of chlorine atoms	Ion type	Theoretical ratio	Control limits	
			Lower	Upper
4	M/M + 2	0.77	0.65	0.89
5	M + 2/M + 4	1.55	1.32	1.78
6	M + 2/M + 4	1.24	1.05	1.43
6[a]	M/M + 2	0.51	0.43	0.59
7[b]	M/M + 2	0.44	0.37	0.51
7	M + 2/M + 4	1.04	0.88	1.20
8	M + 2/M + 4	0.89	0.76	1.02

[a] Used only for ^{13}C-HxCDF.
[b] Used only for ^{13}C-HpCDF.

TABLE 5—MINIMUM REQUIREMENTS FOR INITIAL AND DAILY CALIBRATION RESPONSE FACTORS

Compound	Relative response factors	
	Initial calibration RSD	Daily calibration % difference
Unlabeled Analytes:		
2,3,7,8-TCDD	25	25
2,3,7,8-TCDF	25	25
1,2,3,7,8-PeCDD	25	25
1,2,3,7,8-PeCDF	25	25
2,3,4,7,8-PeCDF	25	25
1,2,4,5,7,8-HxCDD	25	25
1,2,3,6,7,8-HxCDD	25	25
1,2,3,7,8,9-HxCDD	25	25
1,2,3,4,7,8-HxCDF	25	25
1,2,3,6,7,8-HxCDF	25	25
1,2,3,7,8,9-HxCDF	25	25
2,3,4,6,7,8-HxCDF	25	25
1,2,3,4,6,7,8-HpCDD	25	25
1,2,3,4,6,7,8-HpCDF	25	25
OCDD	25	25
OCDF	30	30
Internal Standards:		
$^{13}C_{12}$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-1,2,3,7,8-PeCDD	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	30	30
$^{13}C_{12}$-OCDD	30	30
$^{13}C_{12}$-2,3,7,8-TCDF	30	30
$^{13}C_{12}$-1,2,3,7,8-PeCDF	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	30	30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	30	30
Surrogate Standards:		
$^{37}Cl_4$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-2,3,4,7,8-PeCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	25	25
Alternate Standard:		
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	25	25

METHOD 24—DETERMINATION OF VOLATILE MATTER CONTENT, WATER CONTENT, DENSITY, VOLUME SOLIDS, AND WEIGHT SOLIDS OF SURFACE COATINGS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile organic compounds	No CAS Number assigned
Water.	7732–18–5

1.2 Applicability. This method is applicable for the determination of volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or other related surface coatings.

1.3 Precision and Bias. Intra-and inter-laboratory analytical precision statements are presented in section 13.1. No bias has been identified.

2.0 Summary of Method

2.1 Standard methods are used to determine the volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or other related surface coatings.

3.0 Definitions

3.1 *Waterborne coating* means any coating which contains more than 5 percent water by weight in its volatile fraction.

3.2 *Multicomponent coatings* are coatings that are packaged in two or more parts, which are combined before application. Upon combination a coreactant from one part of the coating chemically reacts, at ambient conditions, with a coreactant from another part of the coating.

3.3 *Ultraviolet (UV) radiation-cured coatings* are coatings which contain unreacted monomers that are polymerized by exposure to ultraviolet light.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Components. Several of the compounds that may be contained in the coatings analyzed by this method may be irritating or corrosive to tissues (e.g., heptane) or may be toxic (e.g., benzene, methyl alcohol). Nearly all are fire hazards.

Appropriate precautions can be found in reference documents, such as Reference 3 of section 16.0.

6.0 Equipment and Supplies

The equipment and supplies specified in the ASTM methods listed in sections 6.1 through 6.6 (incorporated by reference—see §60.17 for acceptable versions of the methods) are required:

6.1 ASTM D 1475–60, 80, or 90, Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products.

6.2 ASTM D 2369–81, 87, 90, 92, 93, or 95, Standard Test Method for Volatile Content of Coatings.

6.3 ASTM D 3792–79 or 91, Standard Test Method for Water Content of Water Reducible Paints by Direct Injection into a Gas Chromatograph.

6.4 ASTM D 4017–81, 90, or 96a, Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Titration Method.

6.5 ASTM 4457–85 91, Standard Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph.

6.6 ASTM D 5403–93, Standard Test Methods for Volatile Content of Radiation Curable Materials.

6.7 ASTM D 6419–00, Test Method for Volatile Content of Sheet-Fed and Coldset Web Offset Printing Inks.

7.0 Reagents and Standards

7.1 The reagents and standards specified in the ASTM methods listed in sections 6.1 through 6.6 are required.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Follow the sample collection, preservation, storage, and transport procedures described in Reference 1 of section 16.0.

9.0 Quality Control

9.1 Reproducibility

NOTE: Not applicable to UV radiation-cured coatings). The variety of coatings that may be subject to analysis makes it necessary to verify the ability of the analyst and the analytical procedures to obtain reproducible results for the coatings tested. Verification is accomplished by running duplicate analyses on each sample tested (Sections 11.2 through 11.4) and comparing the results with the intra-laboratory precision statements (Section 13.1) for each parameter.

9.2 Confidence Limits for Waterborne Coatings. Because of the inherent increased imprecision in the determination of the VOC content of waterborne coatings as the weight percent of water increases, measured parameters for waterborne coatings are replaced with appropriate confidence limits (Section 12.6). These confidence limits are based on measured parameters and inter-laboratory precision statements.

10.0 Calibration and Standardization

10.1 Perform the calibration and standardization procedures specified in the ASTM methods listed in sections 6.1 through 6.6.

11.0 Analytical Procedure

Additional guidance can be found in Reference 2 of section 16.0.

11.1 Non Thin-film Ultraviolet Radiation-cured (UV radiation-cured) Coatings.

11.1.1 Volatile Content. Use the procedure in ASTM D 5403 to determine the volatile matter content of the coating except the curing test described in NOTE 2 of ASTM D 5403 is required.

11.1.2 Water Content. To determine water content, follow section 11.3.2.

11.1.3 Coating Density. To determine coating density, follow section 11.3.3.

11.1.4 Solids Content. To determine solids content, follow section 11.3.4.

11.1.5 To determine if a coating or ink can be classified as a thin-film UV cured coating or ink, use the equation in section 12.2. If C is less than 0.2 g and A is greater than or equal to 225 cm^2 (35 in^2) then the coating or ink is considered a thin-film UV radiation-cured coating and ASTM D 5403 is not applicable.

NOTE: As noted in section 1.4 of ASTM D 5403, this method may not be applicable to radiation curable materials wherein the volatile material is water.

11.2 Multi-component Coatings.

11.2.1 Sample Preparation.

11.2.1.1 Prepare about 100 ml of sample by mixing the components in a storage container, such as a glass jar with a screw top or a metal can with a cap. The storage container should be just large enough to hold the mixture. Combine the components (by weight or volume) in the ratio recommended by the manufacturer. Tightly close the container between additions and during mixing to prevent loss of volatile materials. However, most manufacturers mixing instructions are by volume. Because of possible error caused by expansion of the liquid when measuring the volume, it is recommended that the components be combined by weight. When weight is used to combine the components and the manufacturer's recommended ratio is by volume, the density must be determined by section 11.3.3.

11.2.1.2 Immediately after mixing, take aliquots from this 100 ml sample for determination of the total volatile content, water content, and density.

11.2.2 Volatile Content. To determine total volatile content, use the apparatus and

reagents described in ASTM D2369 (incorporated by reference; see §60.17 for the approved versions of the standard), respectively, and use the following procedures:

11.2.2.1 Weigh and record the weight of an aluminum foil weighing dish. Add 3 ±1 ml of suitable solvent as specified in ASTM D2369 to the weighing dish. Using a syringe as specified in ASTM D2369, weigh to 1 mg, by difference, a sample of coating into the weighing dish. For coatings believed to have a volatile content less than 40 weight percent, a suitable size is 0.3 + 0.10 g, but for coatings believed to have a volatile content greater than 40 weight percent, a suitable size is 0.5 ±0.1 g.

NOTE: If the volatile content determined pursuant to section 12.4 is not in the range corresponding to the sample size chosen repeat the test with the appropriate sample size. Add the specimen dropwise, shaking (swirling) the dish to disperse the specimen completely in the solvent. If the material forms a lump that cannot be dispersed, discard the specimen and prepare a new one. Similarly, prepare a duplicate. The sample shall stand for a minimum of 1 hour, but no more than 24 hours prior to being oven cured at 110 ±5 °C (230 ±9 °F) for 1 hour.

11.2.2.2 Heat the aluminum foil dishes containing the dispersed specimens in the forced draft oven for 60 min at 110 ±5 °C (230 ±9 °F). Caution—provide adequate ventilation, consistent with accepted laboratory practice, to prevent solvent vapors from accumulating to a dangerous level.

11.2.2.3 Remove the dishes from the oven, place immediately in a desiccator, cool to ambient temperature, and weigh to within 1 mg.

11.2.2.4 Run analyses in pairs (duplicate sets) for each coating mixture until the criterion in section 11.4 is met. Calculate W_v following Equation 24–2 and record the arithmetic average.

11.2.3 Water Content. To determine water content, follow section 11.3.2.

11.2.4 Coating Density. To determine coating density, follow section 11.3.3.

11.2.5 Solids Content. To determine solids content, follow section 11.3.4.

11.2.6 Exempt Solvent Content. To determine the exempt solvent content, follow section 11.3.5.

NOTE: For all other coatings (*i.e.*, water-or solvent-borne coatings) not covered by multicomponent or UV radiation-cured coatings, analyze as shown below:

11.3 Water-or Solvent-borne coatings.

11.3.1 Volatile Content. Use the procedure in ASTM D 2369 to determine the volatile matter content (may include water) of the coating.

11.3.1.1 Record the following information:

W_1 = weight of dish and sample before heating, g

W_2 = weight of dish and sample after heating, g

W_3 = sample weight, g.

11.3.1.2 Calculate the weight fraction of the volatile matter (W_v) for each analysis as shown in section 12.3.

11.3.1.3 Run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement in section 13.1.

11.3.1.4 Record the arithmetic average (W_v).

11.3.2 Water Content. For waterborne coatings only, determine the weight fraction of water (W_w) using either ASTM D 3792 or ASTM D 4017.

11.3.2.1 Run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement in section 13.1.

11.3.2.2 Record the arithmetic average (w_w).

11.3.3 Coating Density. Determine the density (Dc, kg/l) of the surface coating using the procedure in ASTM D 1475.

11.3.3.1 Run duplicate analyses until each value in a set deviates from the mean of the set by no more than the intra-laboratory precision statement in section 13.1.

11.3.3.2 Record the arithmetic average (D_c).

11.3.4 Solids Content. Determine the volume fraction (V_s) solids of the coating by calculation using the manufacturer's formulation.

11.3.5 Exempt Solvent Content. Determine the weight fraction of exempt solvents (W_E) by using ASTM Method D4457. Run a duplicate set of determinations and record the arithmetic average (W_E).

11.4 Sample Analysis Criteria. For W_v and W_w, run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement for that parameter. For D_c, run duplicate analyses until each value in a set deviates from the mean of the set by no more than the intra-laboratory precision statement. If, after several attempts, it is concluded that the ASTM procedures cannot be used for the specific coating with the established intra-laboratory precision (excluding UV radiation-cured coatings), the U.S. Environmental Protection Agency (EPA) will assume responsibility for providing the necessary procedures for revising the method or precision statements upon written request to: Director, Emissions, Monitoring, and Analysis Division, MD–14, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

12.0 Calculations and Data Analysis

12.1 Nomenclature.

A = Area of substrate, cm^2, (in^2).

C = Amount of coating or ink added to the substrate, g.

D_c = Density of coating or ink, g/cm^3 (g/in^3).

F = Manufacturer's recommended film thickness, cm (in).
W_o = Weight fraction of nonaqueous volatile matter, g/g.
W_s = Weight fraction of solids, g/g.
W_v = Weight fraction of the volatile matter, g/g.
W_w = Weight fraction of the water, g/g.

12.2 To determine if a coating or ink can be classified as a thin-film UV cured coating or ink, use the following equation:

$$C = F A D_c \qquad \text{Eq. 24-1}$$

12.3 Calculate W_v for each analysis as shown below:

$$W_v = \frac{W_1 - W_2}{W_3} \qquad \text{Eq. 24-2}$$

12.4 Nonaqueous Volatile Matter.
12.4.1 Solvent-borne Coatings.

$$W_o = W_v \qquad \text{Eq. 24-3}$$

12.4.2 Waterborne Coatings.

$$W_o = W_v - W_w \qquad \text{Eq. 24-4}$$

12.4.3 Coatings Containing Exempt Solvents.

$$W_o = W_v - W_E - W_w \qquad \text{Eq. 24-5}$$

12.5 Weight Fraction Solids.

$$W_s = 1 - W_v \qquad \text{Eq. 24-6}$$

12.6 Confidence Limit Calculations for Waterborne Coatings. To calculate the lower confidence limit, subtract the appropriate inter-laboratory precision value from the measured mean value for that parameter. To calculate the upper confidence limit, add the appropriate inter-laboratory precision value to the measured mean value for that parameter. For W_v and D_c, use the lower confidence limits; for W_w, use the upper confidence limit. Because W_s is calculated, there is no adjustment for this parameter.

13.0 Method Performance

13.1 Analytical Precision Statements. The intra-and inter-laboratory precision statements are given in Table 24–1 in section 17.0.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as specified in section 6.0, with the addition of the following:

1. Standard Procedure for Collection of Coating and Ink Samples for Analysis by Reference Methods 24 and 24A. EPA–340/1–91–010. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

2. Standard Operating Procedure for Analysis of Coating and Ink Samples by Reference Methods 24 and 24A.

EPA–340/1–91–011. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

3. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 24–1—ANALYTICAL PRECISION STATEMENTS

	Intra-laboratory	Inter-laboratory
Volatile matter content, W_v	±0.015 $\overline{W}_v$	±0.047 $\overline{W}_v$
Water content, W_w	±0.029 $\overline{W}_w$	±0.075 $\overline{W}_w$
Density, D_c	±0.001 kg/l	±0.002 kg/l

METHOD 24A—DETERMINATION OF VOLATILE MATTER CONTENT AND DENSITY OF PUBLICATION ROTOGRAVURE INKS AND RELATED PUBLICATION ROTOGRAVURE COATINGS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile organic compounds (VOC).	No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of the VOC content and density of solvent-borne (solvent-reducible) publication rotogravure inks and related publication rotogravure coatings.

2.0 Summary of Method

2.1 Separate procedures are used to determine the VOC weight fraction and density of the ink or related coating and the density of the solvent in the ink or related coating. The VOC weight fraction is determined by measuring the weight loss of a known sample quantity which has been heated for a specified length of time at a specified temperature. The density of both the ink or related coating and solvent are measured by a standard procedure. From this information, the VOC volume fraction is calculated.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Components. Some of the compounds that may be contained in the inks or related coatings analyzed by this method may be irritating or corrosive to tissues or may be toxic. Nearly all are fire hazards. Appropriate precautions can be found in reference documents, such as Reference 6 of section 16.0.

6.0 Equipment and Supplies

The following equipment and supplies are required for sample analysis:

6.1 Weighing Dishes. Aluminum foil, 58 mm (2.3 in.) in diameter by 18 mm (0.7 in.) high, with a flat bottom. There must be at least three weighing dishes per sample.

6.2 Disposable Syringe. 5 ml.

6.3 Analytical Balance. To measure to within 0.1 mg.

6.4 Oven. Vacuum oven capable of maintaining a temperature of 120 ±2 °C (248 ±4 °F) and an absolute pressure of 510 ±51 mm Hg (20 ±2 in. Hg) for 4 hours. Alternatively, a forced draft oven capable of maintaining a temperature of 120 ±2 °C (248 ±4 °F) for 24 hours.

6.5 The equipment and supplies specified in ASTM D 1475–60, 80, or 90 (incorporated by reference—see §60.17).

7.0 Reagents and Standards

7.1 The reagents and standards specified in ASTM D 1475–60, 80, or 90 are required.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Follow the sample collection, preservation, storage, and transport procedures described in Reference 4 of section 16.0.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

Additional guidance can be found in Reference 5 of section 16.0.

11.1 VOC Weight Fraction. Shake or mix the ink or related coating sample thoroughly to assure that all the solids are completely suspended. Label and weigh to the nearest 0.1 mg a weighing dish and record this weight (M_{x1}). Using a 5 ml syringe, without a needle, extract an aliquot from the ink or related coating sample. Weigh the syringe and aliquot to the nearest 0.1 mg and record this weight (M_{cy1}). Transfer 1 to 3 g of the aliquot to the tared weighing dish. Reweigh the syringe and remaining aliquot to the nearest 0.1 mg and record this weight (M_{cy2}). Heat the weighing dish with the transferred aliquot in a vacuum oven at an absolute pressure of 510 ±51 mm Hg (20 ±2 in. Hg) and a temperature of 120 ±2 °C (248 ±4 °F) for 4 hours. Alternatively, heat the weighing dish with the transferred aliquot in a forced draft oven at a temperature of 120 ±2 °C for 24 hours. After the weighing dish has cooled, reweigh it to the nearest 0.1 mg and record the weight (M_{x2}). Repeat this procedure two times for each ink or related coating sample, for a total of three samples.

11.2 Ink or Related Coating Density. Determine the density of the ink or related coating (D_c) according to the procedure outlined in ASTM D 1475. Make a total of three determinations for each ink or related coating sample. Report the ink or related coating density as the arithmetic average (D_c) of the three determinations.

11.3 Solvent Density. Determine the density of the solvent (D_o) according to the procedure outlined in ASTM D 1475. Make a total of three determinations for each ink or related coating sample. Report the solvent density as the arithmetic average (D_o) of the three determinations.

12.0 Calculations and Data Analysis

12.1 VOC Weight Fraction. For each determination, calculate the volatile organic content weight fraction (W_o) using the following equation:

$$W_o = \frac{M_{x1} + M_{cy1} - M_{cy2} - M_{x2}}{M_{cy1} - M_{cy2}} \qquad \text{Eq. 24A-1}$$

Make a total of three determinations. Report the VOC weight fraction as the arithmetic average ($\bar{W}_o$) of the three determinations.

12.2 VOC Volume Fraction. Calculate the volume fraction volatile organic content (V_o) using the following equation:

$$V_o = \frac{\overline{W}_o \overline{D}_c}{\overline{D}_o} \qquad \text{Eq. 24A-2}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products. ASTM Designation D 1475.

2. Teleconversation. Wright, Chuck, Inmont Corporation with Reich, R., A., Radian Corporation. September 25, 1979, Gravure Ink Analysis.

3. Teleconversation. Oppenheimer, Robert, Gravure Research Institute with Burt, Rick, Radian Corporation, November 5, 1979, Gravure Ink Analysis.

4. Standard Procedure for Collection of Coating and Ink Samples for Analysis by Reference Methods 24 and 24A. EPA–340/1–91–010. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

5. Standard Operating Procedure for Analysis of Coating and Ink Samples by Reference Methods 24 and 24A. EPA–340/1–91–011. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

6. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

Method 25—Determination of Total Gaseous Nonmethane Organic Emissions as Carbon

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total gaseous nonmethane organic compounds (TGNMO)	N/A	Dependent upon analytical equipment.

1.2 Applicability.

1.2.1 This method is applicable for the determination of volatile organic compounds (VOC) (measured as total gaseous nonmethane organics (TGNMO) and reported as carbon) in stationary source emissions. This method is not applicable for the determination of organic particulate matter.

1.2.2 This method is not the only method that applies to the measurement of VOC. Costs, logistics, and other practicalities of source testing may make other test methods more desirable for measuring VOC contents of certain effluent streams. Proper judgment is required in determining the most applicable VOC test method. For example, depending upon the molecular composition of the organics in the effluent stream, a totally automated semicontinuous nonmethane organics (NMO) analyzer interfaced directly to the source may yield accurate results. This approach has the advantage of providing emission data semicontinuously over an extended time period.

1.2.3 Direct measurement of an effluent with a flame ionization detector (FID) analyzer may be appropriate with prior characterization of the gas stream and knowledge that the detector responds predictably to the organic compounds in the stream. If present, methane (CH_4) will, of course, also be measured. The FID can be used under any of the following limited conditions: (1) Where only one compound is known to exist; (2) when the organic compounds consist of only hydrogen and carbon; (3) where the relative percentages of the compounds are known or can be determined, and the FID responses to the compounds are known; (4) where a consistent mixture of the compounds exists before and after emission control and only the relative concentrations are to be assessed; or (5) where the FID can be calibrated against mass standards of the compounds emitted (solvent emissions, for example).

1.2.4 Another example of the use of a direct FID is as a screening method. If there is enough information available to provide a rough estimate of the analyzer accuracy, the FID analyzer can be used to determine the VOC content of an uncharacterized gas stream. With a sufficient buffer to account for possible inaccuracies, the direct FID can be a useful tool to obtain the desired results without costly exact determination.

1.2.5 In situations where a qualitative/quantitative analysis of an effluent stream is desired or required, a gas chromatographic FID system may apply. However, for sources emitting numerous organics, the time and expense of this approach will be formidable.

2.0 Summary of Method

2.1 An emission sample is withdrawn from the stack at a constant rate through a heated filter and a chilled condensate trap by means of an evacuated sample tank. After sampling is completed, the TGNMO are determined by independently analyzing the condensate trap and sample tank fractions and combining the analytical results. The organic content of the condensate trap fraction is determined by oxidizing the NMO to carbon dioxide (CO_2) and quantitatively collecting in the effluent in an evacuated vessel; then a portion of the CO_2 is reduced to CH_4 and measured by an FID. The organic content of the sample tank fraction is measured by injecting a portion of the sample into a gas chromatographic column to separate the NMO from carbon monoxide (CO), CO_2, and CH_4; the NMO are oxidized to CO_2, reduced to CH_4, and measured by an FID. In this manner, the variable response of the FID associated with different types of organics is eliminated.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Carbon Dioxide and Water Vapor. When carbon dioxide (CO_2) and water vapor are present together in the stack, they can produce a positive bias in the sample. The magnitude of the bias depends on the concentrations of CO_2 and water vapor. As a guideline, multiply the CO_2 concentration, expressed as volume percent, times the water vapor concentration. If this product does not exceed 100, the bias can be considered insignificant. For example, the bias is not significant for a source having 10 percent CO_2 and 10 percent water vapor, but it might be significant for a source having 10 percent CO_2 and 20 percent water vapor.

4.2. Particulate Matter. Collection of organic particulate matter in the condensate trap would produce a positive bias. A filter is included in the sampling equipment to minimize this bias.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling system consists of a heated probe, heated filter, condensate trap, flow control system, and sample tank (see Figure 25–1). The TGNMO sampling equipment can be constructed from commercially available components and components fabricated in a machine shop. The following equipment is required:

6.1.1 Heated Probe. 6.4-mm (¼-in.) OD stainless steel tubing with a heating system capable of maintaining a gas temperature at the exit end of at least 129 °C (265 °F). The probe shall be equipped with a temperature sensor at the exit end to monitor the gas temperature. A suitable probe is shown in Figure 25–1. The nozzle is an elbow fitting attached to the front end of the probe while the temperature sensor is inserted in the side arm of a tee fitting attached to the rear of the probe. The probe is wrapped with a suitable length of high temperature heating tape, and then covered with two layers of glass cloth insulation and one layer of aluminum foil or an equivalent wrapping.

NOTE: If it is not possible to use a heating system for safety reasons, an unheated system with an in-stack filter is a suitable alternative.

6.1.2 Filter Holder. 25-mm (15/16-in.) ID Gelman filter holder with 303 stainless steel body and 316 stainless steel support screen with the Viton O-ring replaced by a Teflon O-ring.

6.1.3 Filter Heating System.

6.1.3.1 A metal box consisting of an inner and an outer shell separated by insulating material with a heating element in the inner shell capable of maintaining a gas temperature at the filter of 121 ±3 °C (250 ±5 °F). The heating box shall include temperature sensors to monitor the gas temperature immediately upstream and immediately downstream of the filter.

6.1.3.2 A suitable heating box is shown in Figure 25–2. The outer shell is a metal box that measures 102 mm × 280 mm × 292 mm (4 in. × 11 in. × 11½ in.), while the inner shell is a metal box measuring 76 mm × 229 mm × 241 mm (3 in. × 9 in. × 9½ in.). The inner box is supported by 13-mm (½-in.) phenolic rods. The void space between the boxes is filled with ceramic fiber insulation which is sealed in place by means of a silicon rubber bead around the upper sides of the box. A removable lid made in a similar manner, with a 25-mm (1-in.) gap between the parts is used to cover the heating chamber. The inner box is heated with a 250-watt cartridge heater, shielded by a stainless steel shroud. The heater is regulated by a thermostatic temperature controller which is set to maintain a gas temperature of 121 °C (250 °F) as measured by the temperature sensor upstream of the filter.

NOTE: If it is not possible to use a heating system for safety reasons, an unheated system with an in-stack filter is a suitable alternative.

6.1.4 Condensate Trap. 9.5-mm (⅜-in.) OD 316 stainless steel tubing bent into a U-shape. Exact dimensions are shown in Figure

25–3. The tubing shall be packed with coarse quartz wool, to a density of approximately 0.11 g/cm^3 before bending. While the condensate trap is packed with dry ice in the Dewar, an ice bridge may form between the arms of the condensate trap making it difficult to remove the condensate trap. This problem can be prevented by attaching a steel plate between the arms of the condensate trap in the same plane as the arms to completely fill the intervening space.

6.1.5 Valve. Stainless steel control valve for starting and stopping sample flow.

6.1.6 Metering Valve. Stainless steel valve for regulating the sample flow rate through the sample train.

6.1.7 Rate Meter. Rotameter, or equivalent, capable of measuring sample flow in the range of 60 to 100 cm^3/min (0.13 to 0.21 ft^3/hr).

6.1.8 Sample Tank. Stainless steel or aluminum tank with a minimum volume of 4 liters (0.14 ft^3).

NOTE: Sample volumes greater than 4 liters may be required for sources with low organic concentrations.

6.1.9 Mercury Manometer. U-tube manometer or absolute pressure gauge capable of measuring pressure to within 1 mm Hg in the range of 0 to 900 mm.

6.1.10 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

6.2 Condensate Recovery. The system for the recovery of the organics captured in the condensate trap consists of a heat source, an oxidation catalyst, a nondispersive infrared (NDIR) analyzer, and an intermediate collection vessel (ICV). Figure 25–4 is a schematic of a typical system. The system shall be capable of proper oxidation and recovery, as specified in section 10.1.1. The following major components are required:

6.2.1 Heat Source. Sufficient to heat the condensate trap (including probe) to a temperature of 200 °C (390 °F). A system using both a heat gun and an electric tube furnace is recommended.

6.2.2 Heat Tape. Sufficient to heat the connecting tubing between the water trap and the oxidation catalyst to 100 °C (212 °F).

6.2.3 Oxidation Catalyst. A suitable length of 9.5 mm (3/8-in.) OD Inconel 600 tubing packed with 15 cm (6 in.) of 3.2 mm (3/8-in.) diameter 19 percent chromia on alumina pellets. The catalyst material is packed in the center of the catalyst tube with quartz wool packed on either end to hold it in place.

6.2.4 Water Trap. Leak-proof, capable of removing moisture from the gas stream.

6.2.5 Syringe Port. A 6.4-mm (1/4-in.) OD stainless steel tee fitting with a rubber septum placed in the side arm.

6.2.6 NDIR Detector. Capable of indicating CO_2 concentration in the range of zero to 5 percent, to monitor the progress of combustion of the organic compounds from the condensate trap.

6.2.7 Flow-Control Valve. Stainless steel, to maintain the trap conditioning system near atmospheric pressure.

6.2.8 Intermediate Collection Vessel. Stainless steel or aluminum, equipped with a female quick connect. Tanks with nominal volumes of at least 6 liters (0.2 ft^3) are recommended.

6.2.9 Mercury Manometer. Same as described in section 6.1.9.

6.2.10 Syringe. 10-ml gas-tight glass syringe equipped with an appropriate needle.

6.2.11 Syringes. 10-µl and 50-µl liquid injection syringes.

6.2.12 Liquid Sample Injection Unit. 316 Stainless steel U-tube fitted with an injection septum (see Figure 25–7).

6.3 Analysis.

6.3.1 NMO Analyzer. The NMO analyzer is a gas chromatograph (GC) with backflush capability for NMO analysis and is equipped with an oxidation catalyst, reduction catalyst, and FID. Figures 25–5 and 25–6 are schematics of a typical NMO analyzer. This semicontinuous GC/FID analyzer shall be capable of: (1) Separating CO, CO_2, and CH_4 from NMO, (2) reducing the CO_2 to CH_4 and quantifying as CH_4, and (3) oxidizing the NMO to CO_2, reducing the CO_2 to CH_4 and quantifying as CH_4, according to section 10.1.2. The analyzer consists of the following major components:

6.3.1.1 Oxidation Catalyst. A suitable length of 9.5-mm (3/8-in.) OD Inconel 600 tubing packed with 5.1 cm (2 in.) of 19 percent chromia on 3.2-mm (1/8-in.) alumina pellets. The catalyst material is packed in the center of the tube supported on either side by quartz wool. The catalyst tube must be mounted vertically in a 650 °C (1200 °F) furnace. Longer catalysts mounted horizontally may be used, provided they can meet the specifications of section 10.1.2.1.

6.3.1.2 Reduction Catalyst. A 7.6-cm (3-in.) length of 6.4-mm (1/4-in.) OD Inconel tubing fully packed with 100-mesh pure nickel powder. The catalyst tube must be mounted vertically in a 400 °C (750 °F) furnace.

6.3.1.3 Separation Column(s). A 30-cm (1-ft) length of 3.2-mm (1/8-in.) OD stainless steel tubing packed with 60/80 mesh Unibeads 1S followed by a 61-cm (2-ft) length of 3.2-mm (1/8-in.) OD stainless steel tubing packed with 60/80 mesh Carbosieve G. The Carbosieve and Unibeads columns must be baked separately at 200 °C (390 °F) with carrier gas flowing through them for 24 hours before initial use.

6.3.1.4 Sample Injection System. A single 10-port GC sample injection valve or a group of valves with sufficient ports fitted with a sample loop properly sized to interface with the NMO analyzer (1-cc loop recommended).

6.3.1.5 FID. An FID meeting the following specifications is required:

6.3.1.5.1 Linearity. A linear response (±5 percent) over the operating range as demonstrated by the procedures established in section 10.1.2.3.

6.3.1.5.2 Range. A full scale range of 10 to 50,000 ppm CH_4. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.3.1.6 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the analytical results.

6.3.2 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm Hg.

6.3.3 Temperature Sensor. Capable of measuring the laboratory temperature within 1 °C (2 °F).

6.3.4 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

7.0 Reagents and Standards

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Dry Ice. Solid CO2, crushed.

7.1.2 Coarse Quartz Wool. 8 to 15 um.

7.1.3 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Method D2986–71, 78, or 95a (incorporated by reference—see §60.17). Test data from the supplier's quality control program are sufficient for this purpose.

7.2 NMO Analysis. The following gases are required for NMO analysis:

7.2.1 Carrier Gases. Helium (He) and oxygen (O_2) containing less than 1 ppm CO_2 and less than 0.1 ppm hydrocarbon.

7.2.2 Fuel Gas. Hydrogen (H_2), at least 99.999 percent pure.

7.2.3 Combustion Gas. Either air (less than 0.1 ppm total hydrocarbon content) or O_2 (purity 99.99 percent or greater), as required by the detector.

7.3 Condensate Analysis. The following are required for condensate analysis:

7.3.1 Gases. Containing less than 1 ppm carbon.

7.3.1.1 Air.

7.3.1.2 Oxygen.

7.3.2 Liquids. To conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society.

7.3.2.1 Hexane.

7.3.2.2 Decane.

7.4 Calibration. For all calibration gases, the manufacturer must recommend a maximum shelf life for each cylinder (i.e., the length of time the gas concentration is not expected to change more than ±5 percent from its certified value). The date of gas cylinder preparation, certified organic concentration, and recommended maximum shelf life must be affixed to each cylinder before shipment from the gas manufacturer to the buyer. The following calibration gases are required:

7.4.1 Oxidation Catalyst Efficiency Check Calibration Gas. Gas mixture standard with nominal concentration of 1 percent methane in air.

7.4.2 FID Linearity and NMO Calibration Gases. Three gas mixture standards with nominal propane concentrations of 20 ppm, 200 ppm, and 3000 ppm, in air.

7.4.3 CO_2 Calibration Gases. Three gas mixture standards with nominal CO_2 concentrations of 50 ppm, 500 ppm, and 1 percent, in air.

NOTE: Total NMO less than 1 ppm required for 1 percent mixture.

7.4.4 NMO Analyzer System Check Calibration Gases. Four calibration gases are needed as follows:

7.4.4.1 Propane Mixture. Gas mixture standard containing (nominal) 50 ppm CO, 50 ppm CH_4, 1 percent CO_2, and 20 ppm C_3H_8, prepared in air.

7.4.4.2 Hexane. Gas mixture standard containing (nominal) 50 ppm hexane in air.

7.4.4.3 Toluene. Gas mixture standard containing (nominal) 20 ppm toluene in air.

7.4.4.4 Methanol. Gas mixture standard containing (nominal) 100 ppm methanol in air.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Sampling Equipment Preparation.

8.1.1 Condensate Trap Cleaning. Before its initial use and after each use, a condensate trap should be thoroughly cleaned and checked to ensure that it is not contaminated. Both cleaning and checking can be accomplished by installing the trap in the condensate recovery system and treating it as if it were a sample. The trap should be heated as described in section 11.1.3. A trap may be considered clean when the CO_2 concentration in its effluent gas drops below 10 ppm. This check is optional for traps that most recently have been used to collect samples which were then recovered according to the procedure in section 11.1.3.

8.1.2 Sample Tank Evacuation and Leak-Check. Evacuate the sample tank to 10 mm Hg absolute pressure or less. Then close the sample tank valve, and allow the tank to sit for 60 minutes. The tank is acceptable if a change in tank vacuum of less than 1 mm Hg is noted. The evacuation and leak-check may be conducted either in the laboratory or the field.

8.1.3 Sampling Train Assembly. Just before assembly, measure the tank vacuum using a mercury manometer. Record this vacuum, the ambient temperature, and the barometric pressure at this time. Close the sample tank valve and assemble the sampling

system as shown in Figure 25–1. Immerse the condensate trap body in dry ice at least 30 minutes before commencing sampling to improve collection efficiency. The point where the inlet tube joins the trap body should be 2.5 to 5 cm (1 to 2 in.) above the top of the dry ice.

8.1.4 Pretest Leak-Check. A pretest leak-check is required. Calculate or measure the approximate volume of the sampling train from the probe tip to the sample tank valve. After assembling the sampling train, plug the probe tip, and make certain that the sample tank valve is closed. Turn on the vacuum pump, and evacuate the sampling system from the probe tip to the sample tank valve to an absolute pressure of 10 mm Hg or less. Close the purge valve, turn off the pump, wait a minimum period of 10 minutes, and recheck the indicated vacuum. Calculate the maximum allowable pressure change based on a leak rate of 1 percent of the sampling rate using Equation 25–1, section 12.2. If the measured pressure change exceeds the allowable, correct the problem and repeat the leak-check before beginning sampling.

8.2 Sample Collection.

8.2.1 Unplug the probe tip, and place the probe into the stack such that the probe is perpendicular to the duct or stack axis; locate the probe tip at a single preselected point of average velocity facing away from the direction of gas flow. For stacks having a negative static pressure, seal the sample port sufficiently to prevent air in-leakage around the probe. Set the probe temperature controller to 129 °C (265 °F) and the filter temperature controller to 121 °C (250 °F). Allow the probe and filter to heat for about 30 minutes before purging the sample train.

8.2.2 Close the sample valve, open the purge valve, and start the vacuum pump. Set the flow rate between 60 and 100 cm^3/min (0.13 and 0.21 ft^3/hr), and purge the train with stack gas for at least 10 minutes.

8.2.3 When the temperatures at the exit ends of the probe and filter are within the corresponding specified ranges, check the dry ice level around the condensate trap, and add dry ice if necessary. Record the clock time. To begin sampling, close the purge valve and stop the pump. Open the sample valve and the sample tank valve. Using the flow control valve, set the flow through the sample train to the proper rate. Adjust the flow rate as necessary to maintain a constant rate (±10 percent) throughout the duration of the sampling period. Record the sample tank vacuum and flowmeter setting at 5-minute intervals. (See Figure 25–8.) Select a total sample time greater than or equal to the minimum sampling time specified in the applicable subpart of the regulations; end the sampling when this time period is reached or when a constant flow rate can no longer be maintained because of reduced sample tank vacuum.

NOTE: If sampling had to be stopped before obtaining the minimum sampling time (specified in the applicable subpart) because a constant flow rate could not be maintained, proceed as follows: After closing the sample tank valve, remove the used sample tank from the sampling train (without disconnecting other portions of the sampling train). Take another evacuated and leak-checked sample tank, measure and record the tank vacuum, and attach the new tank to the sampling train. After the new tank is attached to the sample train, proceed with the sampling until the required minimum sampling time has been exceeded.

8.3 Sample Recovery. After sampling is completed, close the flow control valve, and record the final tank vacuum; then record the tank temperature and barometric pressure. Close the sample tank valve, and disconnect the sample tank from the sample system. Disconnect the condensate trap at the inlet to the rate meter, and tightly seal both ends of the condensate trap. Do not include the probe from the stack to the filter as part of the condensate sample.

8.4 Sample Storage and Transport. Keep the trap packed in dry ice until the samples are returned to the laboratory for analysis. Ensure that run numbers are identified on the condensate trap and the sample tank(s).

9.0 Quality Control

Section	Quality control measure	Effect
10.1.1	Initial performance check of condensate recovery apparatus.	Ensure acceptable condensate recovery efficiency.
10.1.2, 10.2	NMO analyzer initial and daily performance checks.	Ensure precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Initial Performance Checks.

10.1.1 Condensate Recovery Apparatus. Perform these tests before the system is first placed in operation, after any shutdown of 6 months or more, and after any major modification of the system, or at the frequency recommended by the manufacturer.

10.1.1.1 Carrier Gas and Auxiliary O_2 Blank Check. Analyze each new tank of carrier gas or auxiliary O_2 with the NMO analyzer to

check for contamination. Treat the gas cylinders as noncondensible gas samples, and analyze according to the procedure in section 11.2.3. Add together any measured CH_4, CO, CO_2, or NMO. The total concentration must be less than 5 ppm.

10.1.1.2 Oxidation Catalyst Efficiency Check.

10.1.1.2.1 With a clean condensate trap installed in the recovery system or a ⅛″ stainless steel connector tube, replace the carrier gas cylinder with the high level methane standard gas cylinder (Section 7.4.1). Set the four-port valve to the recovery position, and attach an ICV to the recovery system. With the sample recovery valve in vent position and the flow-control and ICV valves fully open, evacuate the manometer or gauge, the connecting tubing, and the ICV to 10 mm Hg absolute pressure. Close the flow-control and vacuum pump valves.

10.1.1.2.2 After the NDIR response has stabilized, switch the sample recovery valve from vent to collect. When the manometer or pressure gauge begins to register a slight positive pressure, open the flow-control valve. Keep the flow adjusted such that the pressure in the system is maintained within 10 percent of atmospheric pressure. Continue collecting the sample in a normal manner until the ICV is filled to a nominal gauge pressure of 300 mm Hg. Close the ICV valve, and remove the ICV from the system. Place the sample recovery valve in the vent position, and return the recovery system to its normal carrier gas and normal operating conditions. Analyze the ICV for CO_2 using the NMO analyzer; the catalyst efficiency is acceptable if the CO_2 concentration is within 2 percent of the methane standard concentration.

10.1.1.3 System Performance Check. Construct a liquid sample injection unit similar in design to the unit shown in Figure 25–7. Insert this unit into the condensate recovery and conditioning system in place of a condensate trap, and set the carrier gas and auxiliary O_2 flow rates to normal operating levels. Attach an evacuated ICV to the system, and switch from system vent to collect. With the carrier gas routed through the injection unit and the oxidation catalyst, inject a liquid sample (see sections 10.1.1.3.1 to 10.1.1.3.4) into the injection port. Operate the trap recovery system as described in section 11.1.3. Measure the final ICV pressure, and then analyze the vessel to determine the CO_2 concentration. For each injection, calculate the percent recovery according to section 12.7. Calculate the relative standard deviation for each set of triplicate injections according to section 12.8. The performance test is acceptable if the average percent recovery is 100 ±5 percent and the relative standard deviation is less than 2 percent for each set of triplicate injections.

10.1.1.3.1 50 µl hexane.

10.1.1.3.2 10 µl hexane.

10.1.1.3.3 50 µl decane.

10.1.1.3.4 10 µl decane.

10.1.2 NMO Analyzer. Perform these tests before the system is first placed in operation, after any shutdown longer than 6 months, and after any major modification of the system.

10.1.2.1 Oxidation Catalyst Efficiency Check. Turn off or bypass the NMO analyzer reduction catalyst. Make triplicate injections of the high level methane standard (Section 7.4.1). The oxidation catalyst operation is acceptable if the FID response is less than 1 percent of the injected methane concentration.

10.1.2.2 Reduction Catalyst Efficiency Check. With the oxidation catalyst unheated or bypassed and the heated reduction catalyst bypassed, make triplicate injections of the high level methane standard (Section 7.4.1). Repeat this procedure with both catalysts operative. The reduction catalyst operation is acceptable if the responses under both conditions agree within 5 percent of their average.

10.1.2.3 NMO Analyzer Linearity Check Calibration. While operating both the oxidation and reduction catalysts, conduct a linearity check of the analyzer using the propane standards specified in section 7.4.2. Make triplicate injections of each calibration gas. For each gas (*i.e.*, each set of triplicate injections), calculate the average response factor (area/ppm C) for each gas, as well as and the relative standard deviation (according to section 12.8). Then calculate the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within 2.5 percent of the overall mean value and if the relative standard deviation gas is less than 2 percent of the overall mean value. Record the overall mean of the propane response factor values as the NMO calibration response factor (RF_{NMO}). Repeat the linearity check using the CO_2 standards specified in section 7.4.3. Make triplicate injections of each gas, and then calculate the average response factor (area/ppm C) for each gas, as well as the overall mean of the response factor values. Record the overall mean of the response factor values as the CO_2 calibration response factor (RF_{CO2}). The RF_{CO2} must be within 10 percent of the RF_{NMO}.

10.1.2.4 System Performance Check. Check the column separation and overall performance of the analyzer by making triplicate injections of the calibration gases listed in section 7.4.4. The analyzer performance is acceptable if the measured NMO value for each gas (average of triplicate injections) is within 5 percent of the expected value.

10.2 NMO Analyzer Daily Calibration. The following calibration procedures shall be performed before and immediately after the

analysis of each set of samples, or on a daily basis, whichever is more stringent:

10.2.1 CO_2 Response Factor. Inject triplicate samples of the high level CO_2 calibration gas (Section 7.4.3), and calculate the average response factor. The system operation is adequate if the calculated response factor is within 5 percent of the RF_{CO2} calculated during the initial performance test (Section 10.1.2.3). Use the daily response factor (DRF_{CO2}) for analyzer calibration and the calculation of measured CO_2 concentrations in the ICV samples.

10.2.2 NMO Response Factors. Inject triplicate samples of the mixed propane calibration cylinder gas (Section 7.4.4.1), and calculate the average NMO response factor. The system operation is adequate if the calculated response factor is within 10 percent of the RF_{NMO} calculated during the initial performance test (Section 10.1.2.4). Use the daily response factor (DRF_{NMO}) for analyzer calibration and calculation of NMO concentrations in the sample tanks.

10.3 Sample Tank and ICV Volume. The volume of the gas sampling tanks used must be determined. Determine the tank and ICV volumes by weighing them empty and then filled with deionized distilled water; weigh to the nearest 5 g, and record the results. Alternatively, measure the volume of water used to fill them to the nearest 5 ml.

11.0 Analytical Procedure

11.1 Condensate Recovery. See Figure 25–9. Set the carrier gas flow rate, and heat the catalyst to its operating temperature to condition the apparatus.

11.1.1 Daily Performance Checks. Each day before analyzing any samples, perform the following tests:

11.1.1.1 Leak-Check. With the carrier gas inlets and the sample recovery valve closed, install a clean condensate trap in the system, and evacuate the system to 10 mm Hg absolute pressure or less. Monitor the system pressure for 10 minutes. The system is acceptable if the pressure change is less than 2 mm Hg.

11.1.1.2 System Background Test. Adjust the carrier gas and auxiliary oxygen flow rate to their normal values of 100 cc/min and 150 cc/min, respectively, with the sample recovery valve in vent position. Using a 10-ml syringe, withdraw a sample from the system effluent through the syringe port. Inject this sample into the NMO analyzer, and measure the CO_2 content. The system background is acceptable if the CO_2 concentration is less than 10 ppm.

11.1.1.3 Oxidation Catalyst Efficiency Check. Conduct a catalyst efficiency test as specified in section 10.1.1.2. If the criterion of this test cannot be met, make the necessary repairs to the system before proceeding.

11.1.2 Condensate Trap CO_2 Purge and Sample Tank Pressurization.

11.1.2.1 After sampling is completed, the condensate trap will contain condensed water and organics and a small volume of sampled gas. This gas from the stack may contain a significant amount of CO_2 which must be removed from the condensate trap before the sample is recovered. This is accomplished by purging the condensate trap with zero air and collecting the purged gas in the original sample tank.

11.1.2.2 Begin with the sample tank and condensate trap from the test run to be analyzed. Set the four-port valve of the condensate recovery system in the CO_2 purge position as shown in Figure 25–9. With the sample tank valve closed, attach the sample tank to the sample recovery system. With the sample recovery valve in the vent position and the flow control valve fully open, evacuate the manometer or pressure gauge to the vacuum of the sample tank. Next, close the vacuum pump valve, open the sample tank valve, and record the tank pressure.

11.1.2.3 Attach the dry ice-cooled condensate trap to the recovery system, and initiate the purge by switching the sample recovery valve from vent to collect position. Adjust the flow control valve to maintain atmospheric pressure in the recovery system. Continue the purge until the CO_2 concentration of the trap effluent is less than 5 ppm. CO_2 concentration in the trap effluent should be measured by extracting syringe samples from the recovery system and analyzing the samples with the NMO analyzer. This procedure should be used only after the NDIR response has reached a minimum level. Using a 10-ml syringe, extract a sample from the syringe port prior to the NDIR, and inject this sample into the NMO analyzer.

11.1.2.4 After the completion of the CO_2 purge, use the carrier gas bypass valve to pressurize the sample tank to approximately 1,060 mm Hg absolute pressure with zero air.

11.1.3 Recovery of the Condensate Trap Sample (See Figure 25–10).

11.1.3.1 Attach the ICV to the sample recovery system. With the sample recovery valve in a closed position, between vent and collect, and the flow control and ICV valves fully open, evacuate the manometer or gauge, the connecting tubing, and the ICV to 10 mm Hg absolute pressure. Close the flow-control and vacuum pump valves.

11.1.3.2 Begin auxiliary oxygen flow to the oxidation catalyst at a rate of 150 cc/min, then switch the four-way valve to the trap recovery position and the sample recovery valve to collect position. The system should now be set up to operate as indicated in Figure 25–10. After the manometer or pressure gauge begins to register a slight positive pressure, open the flow control valve. Adjust the flow-control valve to maintain atmospheric pressure in the system within 10 percent.

11.1.3.3 Remove the condensate trap from the dry ice, and allow it to warm to ambient temperature while monitoring the NDIR response. If, after 5 minutes, the CO_2 concentration of the catalyst effluent is below 10,000 ppm, discontinue the auxiliary oxygen flow to the oxidation catalyst. Begin heating the trap by placing it in a furnace preheated to 200 °C (390 °F). Once heating has begun, carefully monitor the NDIR response to ensure that the catalyst effluent concentration does not exceed 50,000 ppm. Whenever the CO_2 concentration exceeds 50,000 ppm, supply auxiliary oxygen to the catalyst at the rate of 150 cc/min. Begin heating the tubing that connected the heated sample box to the condensate trap only after the CO_2 concentration falls below 10,000 ppm. This tubing may be heated in the same oven as the condensate trap or with an auxiliary heat source such as a heat gun. Heating temperature must not exceed 200 °C (390 °F). If a heat gun is used, heat the tubing slowly along its entire length from the upstream end to the downstream end, and repeat the pattern for a total of three times. Continue the recovery until the CO_2 concentration drops to less than 10 ppm as determined by syringe injection as described under the condensate trap CO_2 purge procedure (Section 11.1.2).

11.1.3.4 After the sample recovery is completed, use the carrier gas bypass valve to pressurize the ICV to approximately 1060 mm Hg absolute pressure with zero air.

11.2 Analysis. Once the initial performance test of the NMO analyzer has been successfully completed (see section 10.1.2) and the daily CO_2 and NMO response factors have been determined (see section 10.2), proceed with sample analysis as follows:

11.2.1 Operating Conditions. The carrier gas flow rate is 29.5 cc/min He and 2.2 cc/min O_2. The column oven is heated to 85 °C (185 °F). The order of elution for the sample from the column is CO, CH_4, CO_2, and NMO.

11.2.2 Analysis of Recovered Condensate Sample. Purge the sample loop with sample, and then inject the sample. Under the specified operating conditions, the CO_2 in the sample will elute in approximately 100 seconds. As soon as the detector response returns to baseline following the CO_2 peak, switch the carrier gas flow to backflush, and raise the column oven temperature to 195 °C (380 °F) as rapidly as possible. A rate of 30 °C/min (90 °F) has been shown to be adequate. Record the value obtained for the condensible organic material (C_{cm}) measured as CO_2 and any measured NMO. Return the column oven temperature to 85 °C (185 °F) in preparation for the next analysis. Analyze each sample in triplicate, and report the average C_{cm}.

11.2.3 Analysis of Sample Tank. Perform the analysis as described in section 11.2.2, but record only the value measured for NMO (C_{tm}).

12.0 Data Analysis and Calculations

Carry out the calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculations. All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge or manometer pressure.

12.1 Nomenclature.

C = TGNMO concentration of the effluent, ppm C equivalent.
C_c = Calculated condensible organic (condensate trap) concentration of the effluent, ppm C equivalent.
C_{cm} = Measured concentration (NMO analyzer) for the condensate trap ICV, ppm CO_2.
C_t = Calculated noncondensible organic concentration (sample tank) of the effluent, ppm C equivalent.
C_{tm} = Measured concentration (NMO analyzer) for the sample tank, ppm NMO.
F = Sampling flow rate, cc/min.
L = Volume of liquid injected, µl.
M = Molecular weight of the liquid injected, g/g-mole.
M_c = TGNMO mass concentration of the effluent, mg C/dsm³.
N = Carbon number of the liquid compound injected (N = 12 for decane, N = 6 for hexane).
n = Number of data points.
P_f = Final pressure of the intermediate collection vessel, mm Hg absolute.
P_b = Barometric pressure, cm Hg.
P_{ti} = Gas sample tank pressure before sampling, mm Hg absolute.
P_t = Gas sample tank pressure after sampling, but before pressurizing, mm Hg absolute.
P_{tf} = Final gas sample tank pressure after pressurizing, mm Hg absolute.
q = Total number of analyzer injections of intermediate collection vessel during analysis (where k = injection number, 1 * * * q).
r = Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 * * * r).
r = Density of liquid injected, g/cc.
T_f = Final temperature of intermediate collection vessel, °K.
T_{ti} = Sample tank temperature before sampling, °K.
T_t = Sample tank temperature at completion of sampling, °K.
T_{tf} = Sample tank temperature after pressurizing, °K.
V = Sample tank volume, m³.
V_t = Sample train volume, cc.
V_v = Intermediate collection vessel volume, m³.
V_s = Gas volume sampled, dsm³.
x_i = Individual measurements.
$\bar{x}$ = Mean value.

ΔP = Allowable pressure change, cm Hg.
Θ = Leak-check period, min.

12.2 Allowable Pressure Change. For the pretest leak-check, calculate the allowable pressure change using Equation 25–1:

$$\Delta P = 0.01 \frac{F P_b \Theta}{V_t} \qquad \text{Eq. 25-1}$$

12.3 Sample Volume. For each test run, calculate the gas volume sampled using Equation 25–2:

$$V_s = 0.3857\, V \left(\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}} \right) \qquad \text{Eq. 25-2}$$

12.4 Noncondensible Organics. For each sample tank, determine the concentration of nonmethane organics (ppm C) using Equation 25–3:

$$C_t = \left(\frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}} \right) \left(\frac{1}{r} \sum_{j=1}^{r} C_{tm_j} \right) \qquad \text{Eq. 25-3}$$

12.5 Condensible Organics. For each condensate trap determine the concentration of organics (ppm C) using Equation 25–4:

$$C_c = 0.3857 \frac{V_v P_f}{V_s T_f} \left(\frac{1}{q} \sum_{k=1}^{q} C_{cm_k} \right) \qquad \text{Eq. 25-4}$$

12.6 TGNMO Mass Concentration. Determine the TGNMO mass concentration as carbon for each test run, using Equation 25–5:

$$M_c = 0.4993 \left(C_t + C_c \right) \qquad \text{Eq. 25-5}$$

12.7 Percent Recovery. Calculate the percent recovery for the liquid injections to the condensate recovery and conditioning system using Equation 25–6:

$$\text{Percent Recovery} = K \frac{M V_v P_t C_{cm}}{L P T_f N} \qquad \text{Eq. 25-6}$$

where K = 1.604 (°K)(g-mole)(%)/(mm Hg)(ml)(m^3)(ppm).

12.8 Relative Standard Deviation. Use Equation 25–7 to calculate the relative standard deviation (RSD) of percent recovery and analyzer linearity.

$$RSD = \frac{100}{\bar{x}} \left[\frac{\sum_{i=1}^{n} \left(x_i - \bar{x} \right)^2}{n-1} \right]^{\frac{1}{2}} \qquad \text{Eq. 25-7}$$

13.0 Method Performance

13.1 Range. The minimum detectable limit of the method has been determined to be 50 parts per million by volume (ppm). No upper limit has been established.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, A.E., S. Witz, and R.D. MacPhee. Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, MA. June 15–20, 1975.) 14 p.

2. Salo, A.E., W.L. Oaks, and R.D. MacPhee. Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, CO. June 9–13, 1974.) 25 p.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

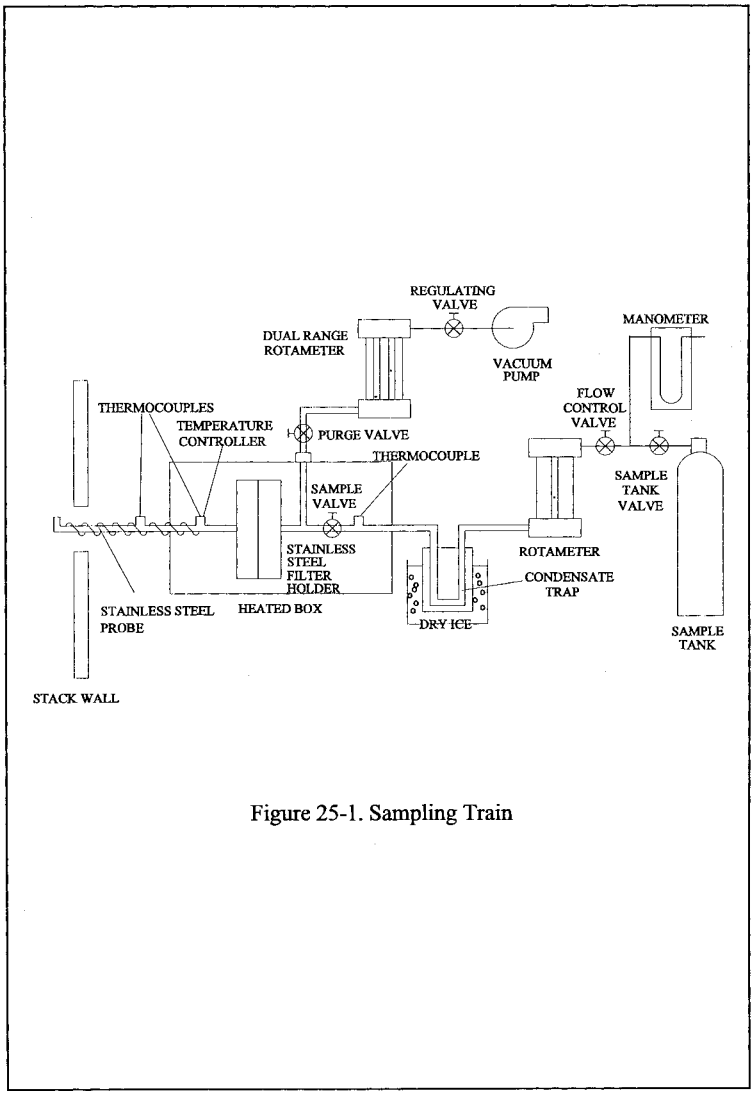


Figure 25-1. Sampling Train

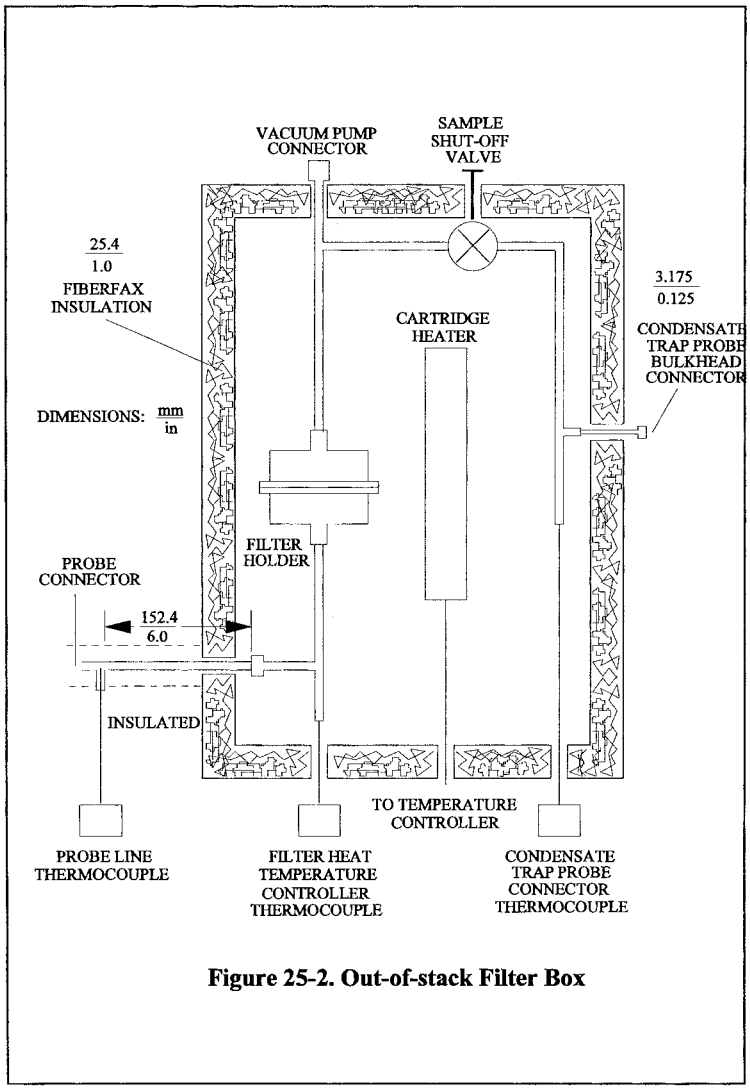


Figure 25-2. Out-of-stack Filter Box

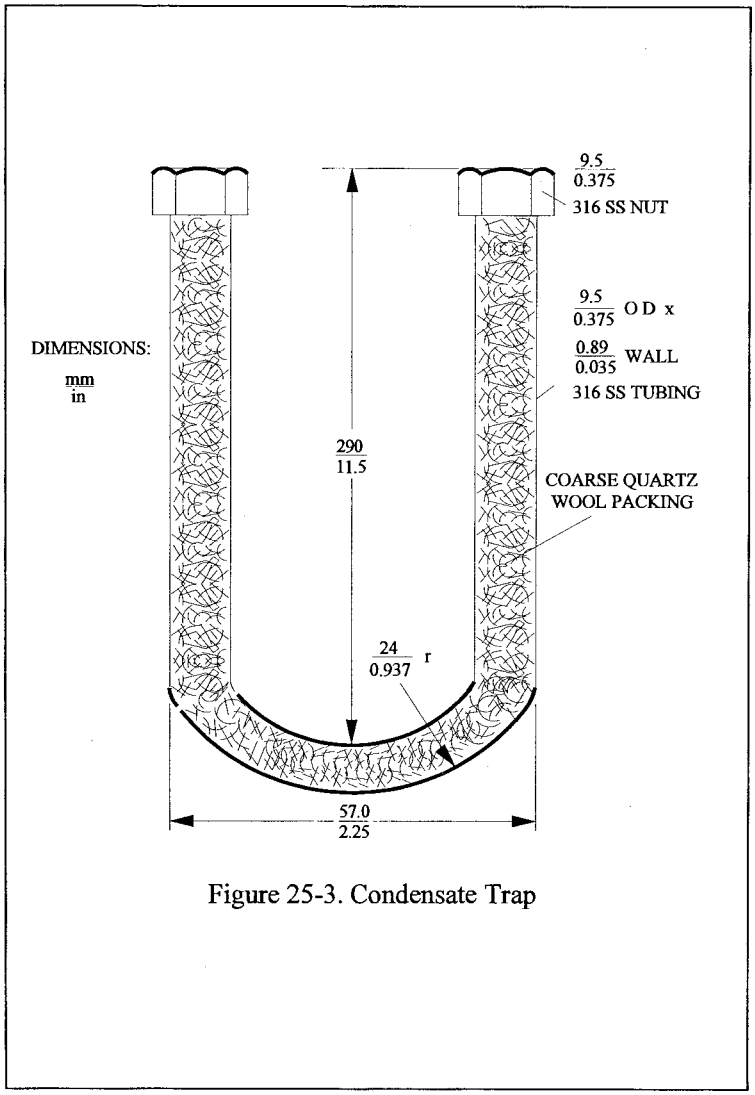


Figure 25-3. Condensate Trap

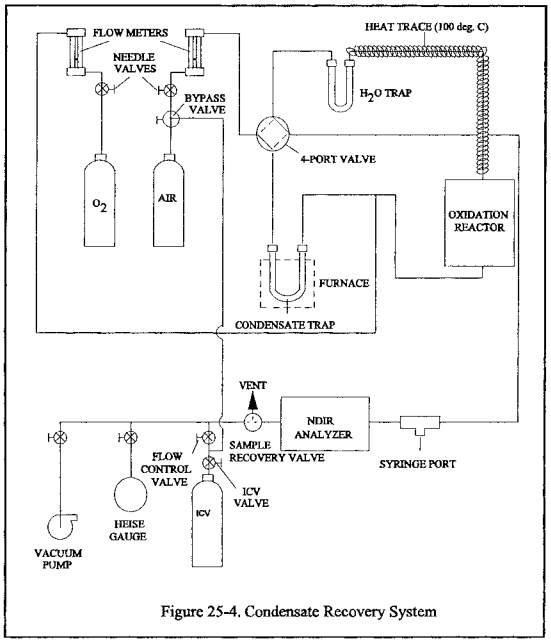


Figure 25-4. Condensate Recovery System

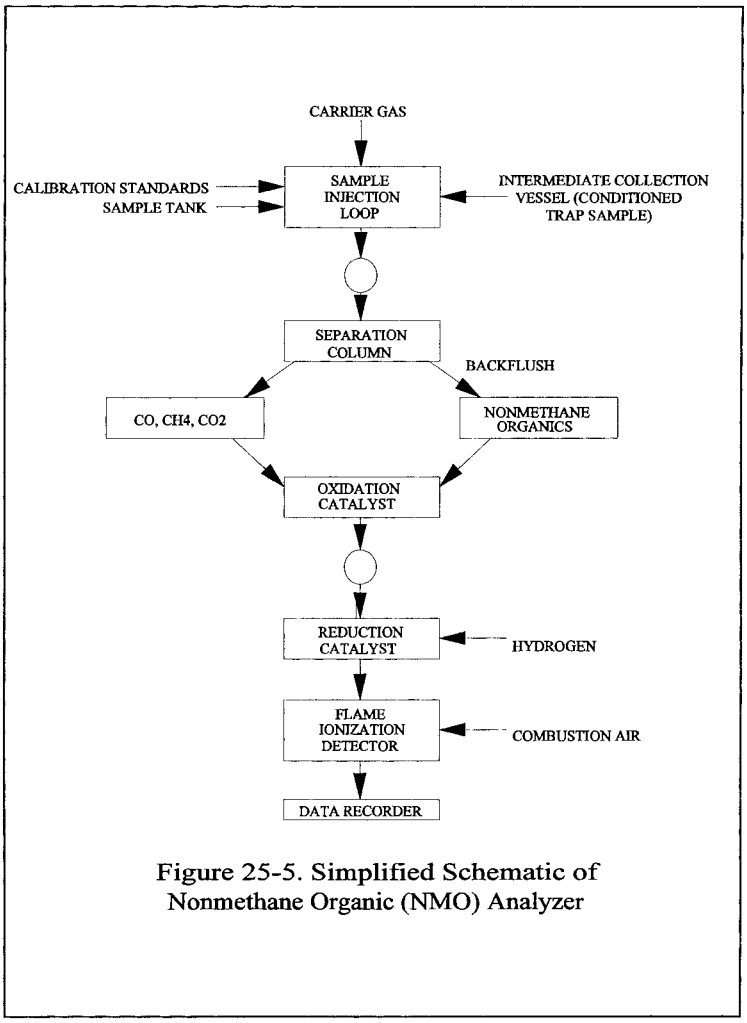


Figure 25-5. Simplified Schematic of Nonmethane Organic (NMO) Analyzer

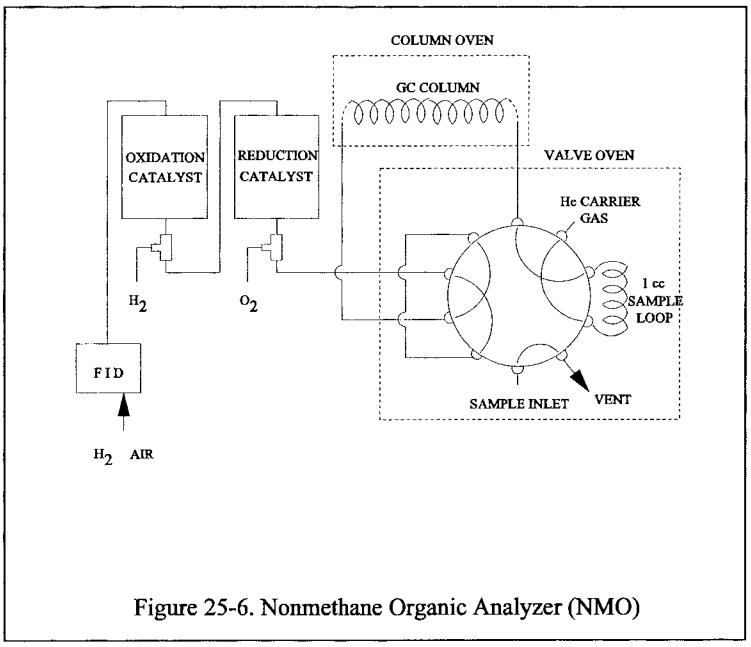


Figure 25-6. Nonmethane Organic Analyzer (NMO)

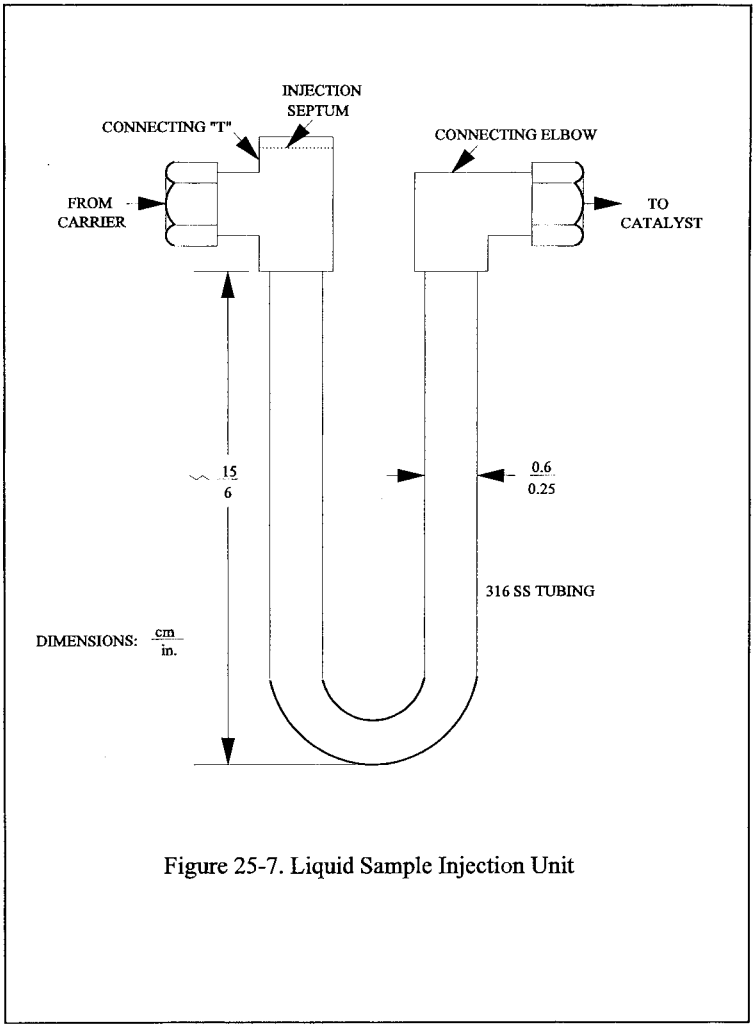


Figure 25-7. Liquid Sample Injection Unit

VOLATILE ORGANIC CARBON

FACILITY _____ SAMPLE LOCATION _____

LOCATION _____ OPERATOR _____

DATE _____ RUN NUMBER _____

TANK NUMBER _____ TRAP NUMBER _____ SAMPLE ID NUMBER _____

TANK VACUUM mm HG	TANK VACUUM cm Hg	BAROMETRIC PRESSURE mm Hg	AMBIENT TEMPERATURE °C
PRETEST (MANOMETER)	(GAUGE)		
POST-TEST (MANOMETER)	(GAUGE)		

LEAK RATE _____ cm Hg / 1 ft min _____

PRETEST _____

TIME CLOCK/SAMPLE	VACUUM cm Hg	FLOWMETER SETTINGS	COMMENTS

Figure 25-8. Example Field Data Form

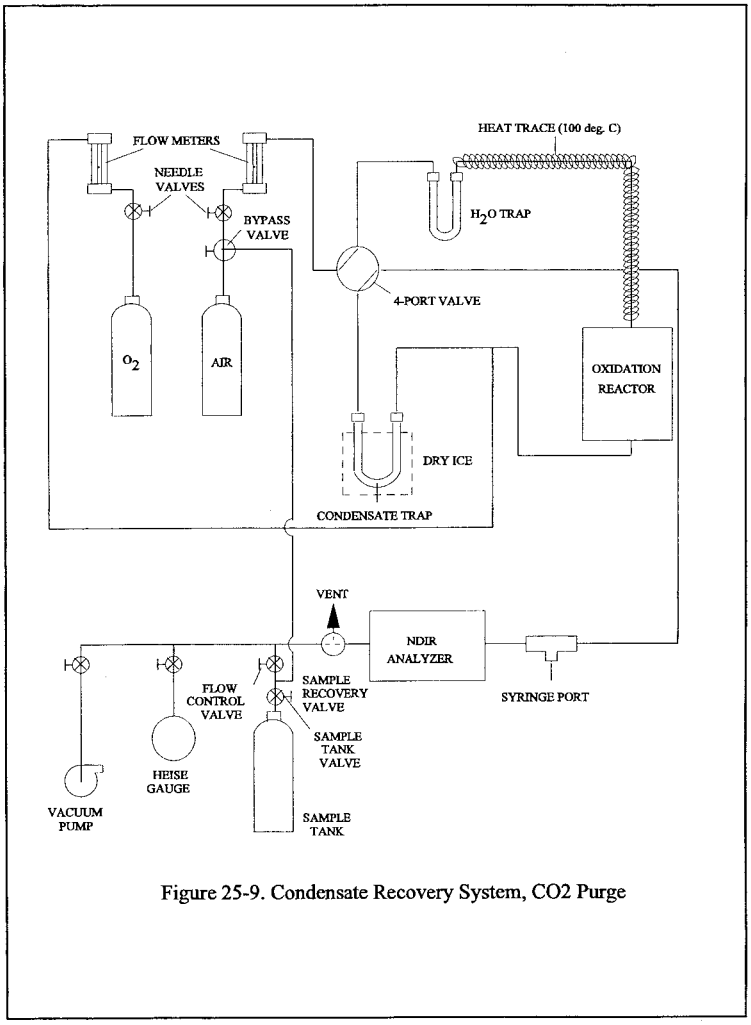


Figure 25-9. Condensate Recovery System, CO2 Purge

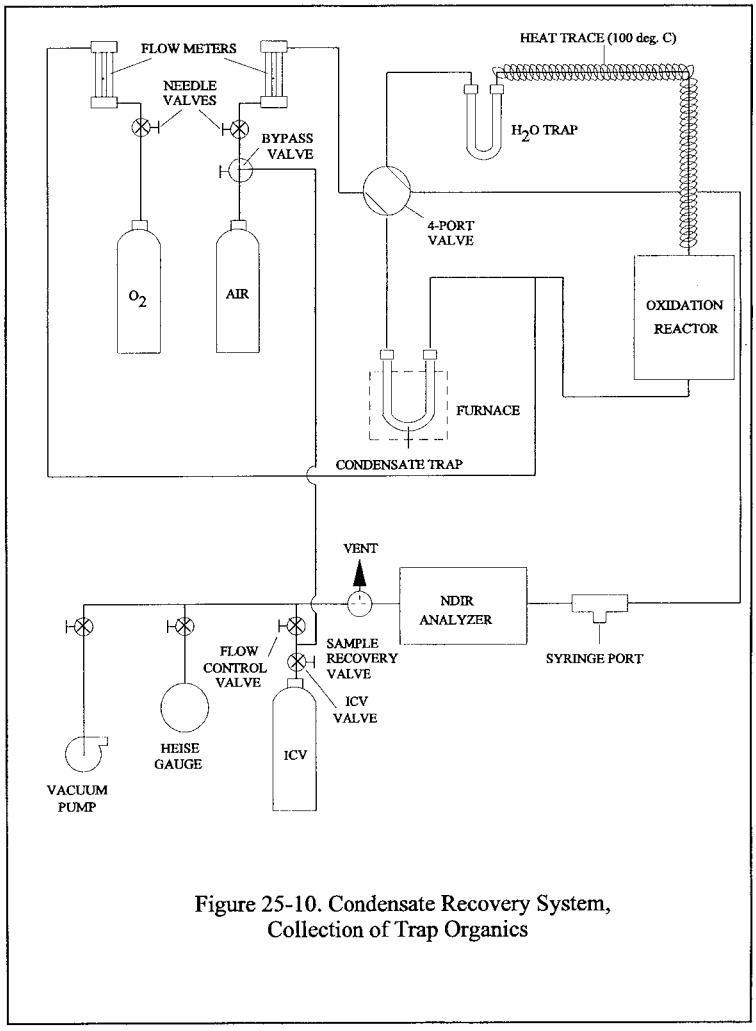


Figure 25-10. Condensate Recovery System, Collection of Trap Organics

METHOD 25A—DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A FLAME IONIZATION ANALYZER

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total Organic Compounds	N/A	<2% of span.

1.2 Applicability. This method is applicable for the determination of total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the source through a heated sample line and glass fiber filter to a flame ionization analyzer (FIA). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

3.0 Definitions

3.1 *Calibration drift* means the difference in the measurement system response to a mid-level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

3.2 *Calibration error* means the difference between the gas concentration indicated by the measurement system and the know concentration of the calibration gas.

3.3 *Calibration gas* means a known concentration of a gas in an appropriate diluent gas.

3.4 *Measurement system* means the total equipment required for the determination of the gas concentration. The system consists of the following major subsystems:

3.4.1 *Sample interface* means that portion of a system used for one or more of the following: sample acquisition, sample transportation, sample conditioning, or protection of the analyzer(s) from the effects of the stack effluent.

3.4.2 *Organic analyzer* means that portion of the measurement system that senses the gas to be measured and generates an output proportional to its concentration.

3.5 *Response time* means the time interval from a step change in pollutant concentration at the inlet to the emission measurement system to the time at which 95 percent of the corresponding final value is reached as displayed on the recorder.

3.6 *Span Value* means the upper limit of a gas concentration measurement range that is specified for affected source categories in the applicable part of the regulations. The span value is established in the applicable regulation and is usually 1.5 to 2.5 times the applicable emission limit. If no span value is provided, use a span value equivalent to 1.5 to 2.5 times the expected concentration. For convenience, the span value should correspond to 100 percent of the recorder scale.

3.7 *Zero drift* means the difference in the measurement system response to a zero level calibration gas before or after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

5.2 Explosive Atmosphere. This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

6.0 Equipment and Supplies

6.1 Measurement System. Any measurement system for total organic concentration that meets the specifications of this method. A schematic of an acceptable measurement system is shown in Figure 25A–1. All sampling components leading to the analyzer shall be heated ≥110 °C (220 °F) throughout the sampling period, unless safety reasons are cited (Section 5.2) The essential components of the measurement system are described below:

6.1.1 Organic Concentration Analyzer. A flame ionization analyzer (FIA) capable of meeting or exceeding the specifications of this method. The flame ionization detector block shall be heated >120 °C (250 °F).

6.1.2 Sample Probe. Stainless steel, or equivalent, three-hole rake type. Sample holes shall be 4 mm (0.16-in.) in diameter or smaller and located at 16.7, 50, and 83.3 percent of the equivalent stack diameter. Alternatively, a single opening probe may be used so that a gas sample is collected from the centrally located 10 percent area of the stack cross-section.

6.1.3 Heated Sample Line. Stainless steel or Teflon'' tubing to transport the sample gas

to the analyzer. The sample line should be heated (≥110 °C) to prevent any condensation.

6.1.4 Calibration Valve Assembly. A three-way valve assembly to direct the zero and calibration gases to the analyzers is recommended. Other methods, such as quick-connect lines, to route calibration gas to the analyzers are applicable.

6.1.5 Particulate Filter. An in-stack or an out-of-stack glass fiber filter is recommended if exhaust gas particulate loading is significant. An out-of-stack filter should be heated to prevent any condensation.

6.1.6 Recorder. A strip-chart recorder, analog computer, or digital recorder for recording measurement data. The minimum data recording requirement is one measurement value per minute.

7.0 Reagents and Standards

7.1 Calibration Gases. The calibration gases for the gas analyzer shall be propane in air or propane in nitrogen. Alternatively, organic compounds other than propane can be used; the appropriate corrections for response factor must be made. Calibration gases shall be prepared in accordance with the procedure listed in Citation 2 of section 16. Additionally, the manufacturer of the cylinder should provide a recommended shelf life for each calibration gas cylinder over which the concentration does not change more than ±2 percent from the certified value. For calibration gas values not generally available (*i.e.*, organics between 1 and 10 percent by volume), alternative methods for preparing calibration gas mixtures, such as dilution systems (Test Method 205, 40 CFR Part 51, Appendix M), may be used with prior approval of the Administrator.

7.1.1 Fuel. A 40 percent H_2/60 percent N_2 gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value.

7.1.2 Zero Gas. High purity air with less than 0.1 part per million by volume (ppmv) of organic material (propane or carbon equivalent) or less than 0.1 percent of the span value, whichever is greater.

7.1.3 Low-level Calibration Gas. An organic calibration gas with a concentration equivalent to 25 to 35 percent of the applicable span value.

7.1.4 Mid-level Calibration Gas. An organic calibration gas with a concentration equivalent to 45 to 55 percent of the applicable span value.

7.1.5 High-level Calibration Gas. An organic calibration gas with a concentration equivalent to 80 to 90 percent of the applicable span value.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Selection of Sampling Site. The location of the sampling site is generally specified by the applicable regulation or purpose of the test (*i.e.*, exhaust stack, inlet line, etc.). The sample port shall be located to meet the testing requirements of Method 1.

8.2 Location of Sample Probe. Install the sample probe so that the probe is centrally located in the stack, pipe, or duct and is sealed tightly at the stack port connection.

8.3 Measurement System Preparation. Prior to the emission test, assemble the measurement system by following the manufacturer's written instructions for preparing sample interface and the organic analyzer. Make the system operable (Section 10.1).

8.4 Calibration Error Test. Immediately prior to the test series (within 2 hours of the start of the test), introduce zero gas and high-level calibration gas at the calibration valve assembly. Adjust the analyzer output to the appropriate levels, if necessary. Calculate the predicted response for the low-level and mid-level gases based on a linear response line between the zero and high-level response. Then introduce low-level and mid-level calibration gases successively to the measurement system. Record the analyzer responses for low-level and mid-level calibration gases and determine the differences between the measurement system responses and the predicted responses. These differences must be less than 5 percent of the respective calibration gas value. If not, the measurement system is not acceptable and must be replaced or repaired prior to testing. No adjustments to the measurement system shall be conducted after the calibration and before the drift check (Section 8.6.2). If adjustments are necessary before the completion of the test series, perform the drift checks prior to the required adjustments and repeat the calibration following the adjustments. If multiple electronic ranges are to be used, each additional range must be checked with a mid-level calibration gas to verify the multiplication factor.

8.5 Response Time Test. Introduce zero gas into the measurement system at the calibration valve assembly. When the system output has stabilized, switch quickly to the high-level calibration gas. Record the time from the concentration change to the measurement system response equivalent to 95 percent of the step change. Repeat the test three times and average the results.

8.6 Emission Measurement Test Procedure.

8.6.1 Organic Measurement. Begin sampling at the start of the test period, recording time and any required process information as appropriate. In particulate, note on the recording chart, periods of process interruption or cyclic operation.

8.6.2 Drift Determination. Immediately following the completion of the test period and hourly during the test period, reintroduce the zero and mid-level calibration gases, one at a time, to the measurement system at the calibration valve assembly. (Make no adjustments to the measurement system until both the zero and calibration drift checks are made.) Record the analyzer response. If the drift values exceed the specified limits, invalidate the test results preceding the check and repeat the test following corrections to the measurement system. Alternatively, recalibrate the test measurement system as in section 8.4 and report the results using both sets of calibration data (i.e., data determined prior to the test period and data determined following the test period).

NOTE: Note on the recording chart periods of process interruption or cyclic operation.

9.0 Quality Control

Method section	Quality control measure	Effect
8.4	Zero and calibration drift tests	Ensures that bias introduced by drift in the measurement system output during the run is no greater than 3 percent of span.

10.0 Calibration and Standardization

10.1 FIA equipment can be calibrated for almost any range of total organic concentrations. For high concentrations of organics (>1.0 percent by volume as propane), modifications to most commonly available analyzers are necessary. One accepted method of equipment modification is to decrease the size of the sample to the analyzer through the use of a smaller diameter sample capillary. Direct and continuous measurement of organic concentration is a necessary consideration when determining any modification design.

11.0 Analytical Procedure

The sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Calculations and Data Analysis

12.1 Determine the average organic concentration in terms of ppmv as propane or other calibration gas. The average shall be determined by integration of the output recording over the period specified in the applicable regulation. If results are required in terms of ppmv as carbon, adjust measured concentrations using Equation 25A–1.

$$C_c = K C_{meas} \qquad \text{Eq. 25A-1}$$

Where:

C_c = Organic concentration as carbon, ppmv.
C_{meas} = Organic concentration as measured, ppmv.
K = Carbon equivalent correction factor.
= 2 for ethane.
= 3 for propane.
= 4 for butane.
= Appropriate response factor for other organic calibration gases.

13.0 Method Performance

13.1 Measurement System Performance Specifications.

13.1.1 Zero Drift. Less than ±3 percent of the span value.

13.1.2 Calibration Drift. Less than ±3 percent of span value.

13.1.3 Calibration Error. Less than ±5 percent of the calibration gas value.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Measurement of Volatile Organic Compounds—Guideline Series. U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA–450/2–78–041. June 1978. p. 46–54.

2. EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards. U.S. Environmental Protection Agency, Quality Assurance and Technical Support Division. Research Triangle Park, N.C. September 1993.

3. Gasoline Vapor Emission Laboratory Evaluation—Part 2. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, NC. EMB Report No. 75–GAS–6. August 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

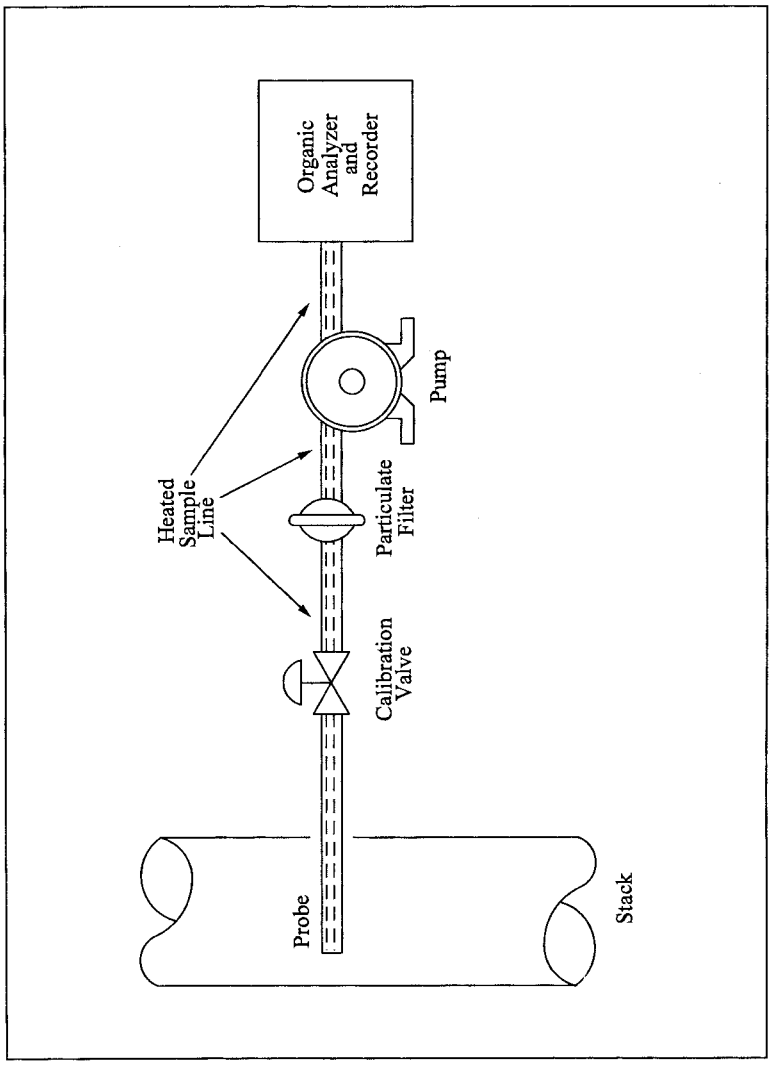


Figure 25A-1. Organic Concentration Measurement System.

METHOD 25B—DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A NONDISPERSIVE INFRARED ANALYZER

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 6C, and Method 25A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total Organic Compounds	N/A	<2% of span.

1.2 Applicability. This method is applicable for the determination of total gaseous organic concentration of vapors consisting primarily of alkanes. Other organic materials may be measured using the general procedure in this method, the appropriate calibration gas, and an analyzer set to the appropriate absorption band.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

A gas sample is extracted from the source through a heated sample line, if necessary, and glass fiber filter to a nondispersive infrared analyzer (NDIR). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

3.0 Definitions

Same as Method 25A, section 3.0.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

5.2 Explosive Atmosphere. This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

6.0 Equipment and Supplies

Same as Method 25A, section 6.0, with the exception of the following:

6.1 Organic Concentration Analyzer. A nondispersive infrared analyzer designed to measure alkane organics and capable of meeting or exceeding the specifications in this method.

7.0 Reagents and Standards

Same as Method 25A, section 7.1. No fuel gas is required for an NDIR.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as Method 25A, section 8.0.

9.0 Quality Control

Same as Method 25A, section 9.0.

10.0 Calibration and Standardization

Same as Method 25A, section 10.0.

11.0 Analytical Procedure

The sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Calculations and Data Analysis

Same as Method 25A, section 12.0.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 25A, section 16.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 25C—DETERMINATION OF NONMETHANE ORGANIC COMPOUNDS (NMOC) IN LANDFILL GASES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should also have a thorough knowledge of EPA Method 25.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Nonmethane organic compounds (NMOC).	No CAS number assigned.

1.2 Applicability. This method is applicable to the sampling and measurement of NMOC as carbon in landfill gases (LFG).

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A sample probe that has been perforated at one end is driven or augured to a depth of 0.9 m (3 ft) below the bottom of the landfill cover. A sample of the landfill gas is extracted with an evacuated cylinder. The NMOC content of the gas is determined by

injecting a portion of the gas into a gas chromatographic column to separate the NMOC from carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4); the NMOC are oxidized to CO_2, reduced to CH_4, and measured by a flame ionization detector (FID). In this manner, the variable response of the FID associated with different types of organics is eliminated.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Since this method is complex, only experienced personnel should perform this test. LFG contains methane, therefore explosive mixtures may exist on or near the landfill. It is advisable to take appropriate safety precautions when testing landfills, such as refraining from smoking and installing explosion-proof equipment.

6.0 Equipment and Supplies

6.1 Sample Probe. Stainless steel, with the bottom third perforated. Teflon probe liners and sampling lines are also allowed. Non-perforated probes are allowed as long as they are withdrawn to create a gap equivalent to having the bottom third perforated. The sample probe must be capped at the bottom and must have a threaded cap with a sampling attachment at the top. The sample probe must be long enough to go through and extend no less than 0.9 m (3 ft) below the landfill cover. If the sample probe is to be driven into the landfill, the bottom cap should be designed to facilitate driving the probe into the landfill.

6.2 Sampling Train.

6.2.1 Rotameter with Flow Control Valve. Capable of measuring a sample flow rate of 100 ±10 ml/min. The control valve must be made of stainless steel.

6.2.2 Sampling Valve. Stainless steel.

6.2.3 Pressure Gauge. U-tube mercury manometer, or equivalent, capable of measuring pressure to within 1 mm Hg (0.5 in H_2O) in the range of 0 to 1,100 mm Hg (0 to 590 in H_2O).

6.2.4 Sample Tank. Stainless steel or aluminum cylinder, equipped with a stainless steel sample tank valve.

6.3 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg (5.4 in H_2O).

6.4 Purging Pump. Portable, explosion proof, and suitable for sampling NMOC.

6.5 Pilot Probe Procedure. The following are needed only if the tester chooses to use the procedure described in section 8.2.1.

6.5.1 Pilot Probe. Tubing of sufficient strength to withstand being driven into the landfill by a post driver and an outside diameter of at least 6 mm (0.25 in.) smaller than the sample probe. The pilot probe shall be capped on both ends and long enough to go through the landfill cover and extend no less than 0.9 m (3 ft) into the landfill.

6.5.2 Post Driver and Compressor. Capable of driving the pilot probe and the sampling probe into the landfill. The Kitty Hawk portable post driver has been found to be acceptable.

6.6 Auger Procedure. The following are needed only if the tester chooses to use the procedure described in section 8.2.2.

6.6.1 Auger. Capable of drilling through the landfill cover and to a depth of no less than 0.9 m (3 ft) into the landfill.

6.6.2 Pea Gravel.

6.6.3 Bentonite.

6.7 NMOC Analyzer, Barometer, Thermometer, and Syringes. Same as in sections 6.3.1, 6.3.2, 6.33, and 6.2.10, respectively, of Method 25.

7.0 Reagents and Standards

7.1 NMOC Analysis. Same as in Method 25, section 7.2.

7.2 Calibration. Same as in Method 25, section 7.4, except omit section 7.4.3.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sample Tank Evacuation and Leak-Check. Conduct the sample tank evacuation and leak-check either in the laboratory or the field. Connect the pressure gauge and sampling valve to the sample tank. Evacuate the sample tank to 10 mm Hg (5.4 in H_2O) absolute pressure or less. Close the sampling valve, and allow the tank to sit for 30 minutes. The tank is acceptable if no change more than ±2 mm is noted. Include the results of the leak-check in the test report.

8.2 Sample Probe Installation. The tester may use the procedure in section 8.2.1 or 8.2.2.

8.2.1 Pilot Probe Procedure. Use the post driver to drive the pilot probe at least 0.9 m (3 ft) below the landfill cover. Alternative procedures to drive the probe into the landfill may be used subject to the approval of the Administrator's designated representative.

8.2.1.1 Remove the pilot probe and drive the sample probe into the hole left by the pilot probe. The sample probe shall extend at least 0.9 m (3 ft) below the landfill cover and shall protrude about 0.3 m (1 ft) above the landfill cover. Seal around the sampling probe with bentonite and cap the sampling probe with the sampling probe cap.

8.2.2 Auger Procedure. Use an auger to drill a hole to at least 0.9 m (3 ft) below the landfill cover. Place the sample probe in the hole and backfill with pea gravel to a level 0.6 m (2 ft) from the surface. The sample probe shall protrude at least 0.3 m (1 ft) above the landfill cover. Seal the remaining area around the probe with bentonite. Allow 24

hours for the landfill gases to equilibrate inside the augured probe before sampling.

8.2.3 Driven Probes. Closed-point probes may be driven directly into the landfill in a single step. This method may not require backfilling if the probe is adequately sealed by its insertion. Unperforated probes that are inserted in this manner and withdrawn at a distance from a detachable tip to create an open space are also acceptable.

8.3 Sample Train Assembly. Just before assembling the sample train, measure the sample tank vacuum using the pressure gauge. Record the vacuum, the ambient temperature, and the barometric pressure at this time. Assemble the sampling probe purging system as shown in Figure 25C–1.

8.4 Sampling Procedure. Open the sampling valve and use the purge pump and the flow control valve to evacuate at least two sample probe volumes from the system at a flow rate of 500 ml/min or less. Close the sampling valve and replace the purge pump with the sample tank apparatus as shown in Figure 25C–2. Open the sampling valve and the sample tank valve and, using the flow control valve, sample at a flow rate of 500 ml/min or less until either a constant flow rate can no longer be maintained because of reduced sample tank vacuum or the appropriate composite volume is attained. Disconnect the sampling tank apparatus and pressurize the sample cylinder to approximately 1,060 mm Hg (567 in. H_2O) absolute pressure with helium, and record the final pressure. Alternatively, the sample tank may be pressurized in the lab.

8.4.1 The following restrictions apply to compositing samples from different probe sites into a single cylinder: (1) Individual composite samples per cylinder must be of equal volume; this must be verified by recording the flow rate, sampling time, vacuum readings, or other appropriate volume measuring data, (2) individual composite samples must have a minimum volume of 1 liter unless data is provided showing smaller volumes can be accurately measured, and (3) composite samples must not be collected using the final cylinder vacuum as it diminishes to ambient pressure.

8.4.2 Use Method 3C to determine the percent N_2 in each cylinder. The presence of N_2 indicates either infiltration of ambient air into the landfill gas sample or an inappropriate testing site has been chosen where anaerobic decomposition has not begun. The landfill gas sample is acceptable if the concentration of N_2 is less than 20 percent. Alternatively, Method 3C may be used to determine the oxygen content of each cylinder as an air infiltration test. With this option, the oxygen content of each cylinder must be less than 5 percent.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4.2	Verify that landfill gas sample contains less than 20 percent N_2 or 5 percent O_2.	Ensures that ambient air was not drawn into the landfill gas sample and gas was sampled from an appropriate location.
10.1, 10.2	NMOC analyzer initial and daily performance checks.	Ensures precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Initial NMOC Analyzer Performance Test. Same as in Method 25, section 10.1, except omit the linearity checks for CO_2 standards.

10.2 NMOC Analyzer Daily Calibration.

10.2.1 NMOC Response Factors. Same as in Method 25, section 10.2.2.

10.3 Sample Tank Volume. The volume of the gas sampling tanks must be determined. Determine the tank volumes by weighing them empty and then filled with deionized water; weigh to the nearest 5 g, and record the results. Alternatively, measure the volume of water used to fill them to the nearest 5 ml.

11.0 Analytical Procedures

11.1 The oxidation, reduction, and measurement of NMOC's is similar to Method 25. Before putting the NMOC analyzer into routine operation, conduct an initial performance test. Start the analyzer, and perform all the necessary functions in order to put the analyzer into proper working order. Conduct the performance test according to the procedures established in section 10.1. Once the performance test has been successfully completed and the NMOC calibration response factor has been determined, proceed with sample analysis as follows:

11.1.1 Daily Operations and Calibration Checks. Before and immediately after the analysis of each set of samples or on a daily basis (whichever occurs first), conduct a calibration test according to the procedures established in section 10.2. If the criteria of the daily calibration test cannot be met, repeat

the NMOC analyzer performance test (Section 10.1) before proceeding.

11.1.2 Operating Conditions. Same as in Method 25, section 11.2.1.

11.1.3 Analysis of Sample Tank. Purge the sample loop with sample, and then inject the sample. Under the specified operating conditions, the CO_2 in the sample will elute in approximately 100 seconds. As soon as the detector response returns to baseline following the CO_2 peak, switch the carrier gas flow to backflush, and raise the column oven temperature to 195 °C (383 °F) as rapidly as possible. A rate of 30 °C/min (54 °F/min) has been shown to be adequate. Record the value obtained for any measured NMOC. Return the column oven temperature to 85 °C (185 °F) in preparation for the next analysis. Analyze each sample in triplicate, and report the average as C_{tm}.

12.0 Data Analysis and Calculations

NOTE: All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge or manometer pressure.

12.1 Nomenclature

B_w = Moisture content in the sample, fraction.
C_{N2} = N_2 concentration in the diluted sample gas.
C_{mN2} = Measured N_2 concentration, fraction in landfill gas.
C_{mOx} = Measured Oxygen concentration, fraction in landfill gas.
C_{Ox} = Oxygen concentration in the diluted sample gas.
C_t = Calculated NMOC concentration, ppmv C equivalent.
C_{tm} = Measured NMOC concentration, ppmv C equivalent.
P_b = Barometric pressure, mm Hg.
P_t = Gas sample tank pressure after sampling, but before pressurizing, mm Hg absolute.
P_{tf} = Final gas sample tank pressure after pressurizing, mm Hg absolute.
P_{ti} = Gas sample tank pressure after evacuation, mm Hg absolute.
P_w = Vapor pressure of H_2O (from Table 25C–1), mm Hg.
r = Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 . . . r).
T_t = Sample tank temperature at completion of sampling, °K.
T_{ti} = Sample tank temperature before sampling, °K.
T_{tf} = Sample tank temperature after pressuring, °K.

12.2 Water Correction. Use Table 25C–1 (Section 17.0), the LFG temperature, and barometric pressure at the sampling site to calculate B_w.

$$B_w = \frac{P_w}{P_b} \qquad \text{Eq. 25C-1}$$

12.3 Nitrogen Concentration in the landfill gas. Use equation 25C–2 to calculate the measured concentration of nitrogen in the original landfill gas.

$$C_{N2} = \left[\frac{\left(\frac{P_{tf}}{T_{tf}}\right)}{\left(\left(\frac{P_t}{T_t}\right)-\left(\frac{P_{ti}}{T_{ti}}\right)\right)}\right] C_{mN2} \qquad \text{Eq.25C-2}$$

12.4 Oxygen Concentration in the landfill gas. Use equation 25C–3 to calculate the measured concentration of oxygen in the original landfill gas.

$$C_{Ox} = \left[\frac{\left(\frac{P_{tf}}{T_{tf}}\right)}{\left(\left(\frac{P_t}{T_t}\right)-\left(\frac{P_{ti}}{T_{ti}}\right)\right)}\right] C_{mOx} \qquad \text{Eq.25C-3}$$

12.5 You must correct the NMOC Concentration for the concentration of nitrogen or oxygen based on which gas or gases passes the requirements in section 9.1.

12.5.1 NMOC Concentration with nitrogen correction. Use Equation 25C–4 to calculate the concentration of NMOC for each sample tank when the nitrogen concentration is less than 20 percent.

$$C_t = \frac{\frac{P_{tf}}{T_{tf}}}{\left(\frac{P_t}{T_t}-\frac{P_{ti}}{T_{ti}}\right)\left(1-\frac{99}{78}C_{N2}\right)-B_w}\frac{1}{r}\sum_{j=1}^{r} C_{tm(j)} \qquad \text{Eq. 25C-4}$$

12.5.2 NMOC Concentration with oxygen correction. Use Equation 25C–5 to calculate the concentration of NMOC for each sample tank if the landfill gas oxygen is less than 5 percent and the landfill gas nitrogen concentration is greater than 20 percent.

$$C_t = \frac{\frac{P_{tf}}{T_{tf}}}{\left(\frac{P_t}{T_t}-\frac{P_{ti}}{T_{ti}}\right)\left(1-\frac{99}{21}C_{Ox}\right)-B_w}\frac{1}{r}\sum_{j=1}^{r} C_{tm(j)} \qquad \text{Eq. 25C-5}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, Albert E., Samuel Witz, and Robert D. MacPhee. Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, Massachusetts. June 15–20, 1975.) 14 p.

2. Salo, Albert E., William L. Oaks, and Robert D. MacPhee. Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, Colorado. June 9–13, 1974.) 25 p.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

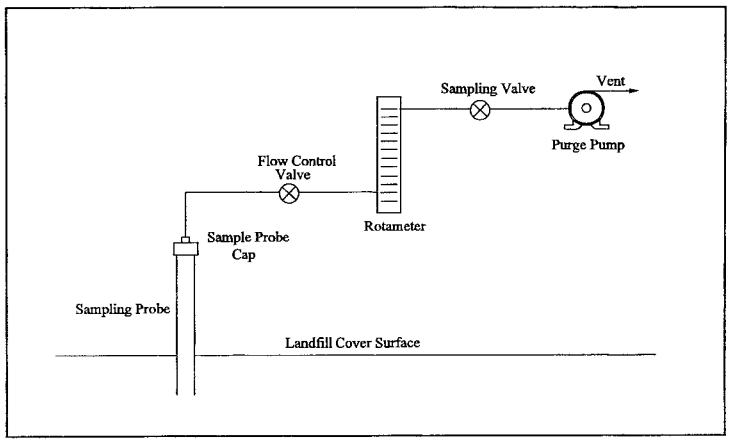


Figure 25C-1. Schematic of Sampling Probe Purging System

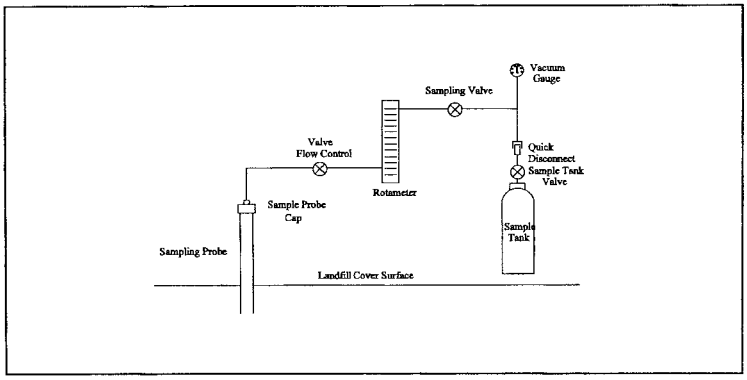


Figure 25C-2. Schematic of Sampling Train.

TABLE 25C–1—MOISTURE CORRECTION

Temperature, °C	Vapor Pressure of H_2O, mm Hg	Temperature, °C	Vapor Pressure of H_2O, mm Hg
4	6.1	18	15.5
6	7.0	20	17.5
8	8.0	22	19.8
10	9.2	24	22.4
12	10.5	26	25.2
14	12.0	28	28.3

TABLE 25C–1—MOISTURE CORRECTION—Continued

Temperature, °C	Vapor Pressure of H_2O, mm Hg	Temperature, °C	Vapor Pressure of H_2O, mm Hg
16	13.6	30	31.8

METHOD 25D—DETERMINATION OF THE VOLATILE ORGANIC CONCENTRATION OF WASTE SAMPLES

NOTE: Performance of this method should not be attempted by persons unfamiliar with the operation of a flame ionization detector (FID) or an electrolytic conductivity detector (ELCD) because knowledge beyond the scope of this presentation is required.

1.0 Scope and Application

1.1 Analyte. Volatile Organic Compounds. No CAS No. assigned.

1.2 Applicability. This method is applicable for determining the volatile organic (VO) concentration of a waste sample.

2.0 Summary of Method

2.1 Principle. A sample of waste is obtained at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to the atmosphere). The sample is suspended in an organic/aqueous matrix, then heated and purged with nitrogen for 30 min. in order to separate certain organic compounds. Part of the sample is analyzed for carbon concentration, as methane, with an FID, and part of the sample is analyzed for chlorine concentration, as chloride, with an ELCD. The VO concentration is the sum of the carbon and chlorine content of the sample.

3.0 Definitions

3.1 *Well-mixed* in the context of this method refers to turbulent flow which results in multiple-phase waste in effect behaving as single-phase waste due to good mixing.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1 Sampling. The following equipment is required:

6.1.1 Sampling Tube. Flexible Teflon, 0.25 in. ID (6.35 mm).

6.1.2 Sample Container. Borosilicate glass, 40-mL, and a Teflon-lined screw cap capable of forming an air tight seal.

6.1.3 Cooling Coil. Fabricated from 0.25 in (6.35 mm). ID 304 stainless steel tubing with a thermocouple at the coil outlet.

6.2 Analysis. The following equipment is required.

6.2.1 Purging Apparatus. For separating the VO from the waste sample. A schematic of the system is shown in Figure 25D–1. The purging apparatus consists of the following major components.

6.2.1.1 Purging Flask. A glass container to hold the sample while it is heated and purged with dry nitrogen. The cap of the purging flask is equipped with three fittings: one for a purging lance (fitting with the #7 Ace-thread), one for the Teflon exit tubing (side fitting, also a #7 Ace-thread), and a third (a 50-mm Ace-thread) to attach the base of the purging flask as shown in Figure 25D–2. The base of the purging flask is a 50-mm ID (2 in) cylindrical glass tube. One end of the tube is open while the other end is sealed. Exact dimensions are shown in Figure 25D–2.

6.2.1.2 Purging Lance. Glass tube, 6-mm OD (0.2 in) by 30 cm (12 in) long. The purging end of the tube is fitted with a four-arm bubbler with each tip drawn to an opening 1 mm (0.04 in) in diameter. Details and exact dimensions are shown in Figure 25D–2.

6.2.1.3 Coalescing Filter. Porous fritted disc incorporated into a container with the same dimensions as the purging flask. The details of the design are shown in Figure 25D–3.

6.2.1.4 Constant Temperature Chamber. A forced draft oven capable of maintaining a uniform temperature around the purging flask and coalescing filter of 75 ±2 °C (167 ±3.6 °F).

6.2.1.5 Three-way Valve. Manually operated, stainless steel. To introduce calibration gas into system.

6.2.1.6 Flow Controllers. Two, adjustable. One capable of maintaining a purge gas flow rate of 6 ±0.06 L/min (0.2 ±0.002 ft^3/min) The other capable of maintaining a calibration gas flow rate of 1–100 mL/min (0.00004–0.004 ft^3/min).

6.2.1.7 Rotameter. For monitoring the air flow through the purging system (0–10 L/min)(0–0.4 ft^3/min).

6.2.1.8 Sample Splitters. Two heated flow restrictors (placed inside oven or heated to 120 ±10 °C (248 ±18 °F)). At a purge rate of 6 L/min (0.2 ft^3/min), one will supply a constant flow to the first detector (the rest of the flow will be directed to the second sample splitter). The second splitter will split the analytical flow between the second detector and the flow restrictor. The approximate flow to the FID will be 40 mL/min (0.0014 ft^3/min) and to the ELCD will be 15 mL/min (0.0005 ft^3/min), but the exact flow must be adjusted to be compatible with the individual detector and to meet its linearity requirement. The two sample splitters will be connected to each other by 1/8″ OD (3.175 mm) stainless steel tubing.

6.2.1.9 Flow Restrictor. Stainless steel tubing, 1/8″ OD (3.175 mm), connecting the second sample splitter to the ice bath. Length is determined by the resulting pressure in the purging flask (as measured by the pressure gauge). The resulting pressure from the use of the flow restrictor shall be 6–7 psig.

6.2.1.10 Filter Flask. With one-hole stopper. Used to hold ice bath. Excess purge gas is vented through the flask to prevent condensation in the flowmeter and to trap volatile organic compounds.

6.2.1.11 Four-way Valve. Manually operated, stainless steel. Placed inside oven, used to bypass purging flask.

6.2.1.12 On/Off Valves. Two, stainless steel. One heat resistant up to 130 °C (266 °F) and placed between oven and ELCD. The other a toggle valve used to control purge gas flow.

6.2.1.13 Pressure Gauge. Range 0–40 psi. To monitor pressure in purging flask and coalescing filter.

6.2.1.14 Sample Lines. Teflon, 1/4″ OD (6.35 mm), used inside the oven to carry purge gas to and from purging chamber and to and from coalescing filter to four-way valve. Also used to carry sample from four-way valve to first sample splitter.

6.2.1.15 Detector Tubing. Stainless steel, 1/8″ OD (3.175 mm), heated to 120 ±10 °C (248 ±18 °F) . Used to carry sample gas from each sample splitter to a detector. Each piece of tubing must be wrapped with heat tape and insulating tape in order to insure that no cold spots exist. The tubing leading to the ELCD will also contain a heat-resistant on-off valve (Section 6.2.1.12) which shall also be wrapped with heat-tape and insulation.

6.2.2 Volatile Organic Measurement System. Consisting of an FID to measure the carbon concentration of the sample and an ELCD to measure the chlorine concentration.

6.2.2.1 FID. A heated FID meeting the following specifications is required.

6.2.2.1.1 Linearity. A linear response (±5 percent) over the operating range as demonstrated by the procedures established in section 10.1.1.

6.2.2.1.2 Range. A full scale range of 50 pg carbon/sec to 50 µg carbon/sec. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.2.2.1.3 Data Recording System. A digital integration system compatible with the FID for permanently recording the output of the detector. The recorder shall have the capability to start and stop integration at points selected by the operator or it shall be capable of the ''integration by slices'' technique (this technique involves breaking down the chromatogram into smaller increments, integrating the area under the curve for each portion, subtracting the background for each portion, and then adding all of the areas together for the final area count).

6.2.2.2 ELCD. An ELCD meeting the following specifications is required. 1-propanol must be used as the electrolyte. The electrolyte flow through the conductivity cell shall be 1 to 2 mL/min (0.00004 to 0.00007 ft^3/min).

NOTE: A ¼-in. ID (6.35 mm) quartz reactor tube is strongly recommended to reduce carbon buildup and the resulting detector maintenance.

6.2.2.2.1 Linearity. A linear response (±10 percent) over the response range as demonstrated by the procedures in section 10.1.2.

6.2.2.2.2 Range. A full scale range of 5.0 pg/sec to 500 ng/sec chloride. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.2.2.2.3 Data Recording System. A digital integration system compatible with the output voltage range of the ELCD. The recorder must have the capability to start and stop integration at points selected by the operator or it shall be capable of performing the ''integration by slices'' technique.

7.0 Reagents and Standards

7.1 Sampling.

7.1.1 Polyethylene Glycol (PEG). Ninety-eight percent pure with an average molecular weight of 400. Before using the PEG, remove any organic compounds that might be detected as volatile organics by heating it to 120 °C (248 °F) and purging it with nitrogen at a flow rate of 1 to 2 L/min (0.04 to 0.07 ft^3/min) for 2 hours. The cleaned PEG must be stored under a 1 to 2 L/min (0.04 to 0.07 ft^3/min) nitrogen purge until use. The purge apparatus is shown in Figure 25D–4.

7.2 Analysis.

7.2.1 Sample Separation. The following are required for the sample purging step.

7.2.1.1 PEG. Same as section 7.1.1.

7.2.1.2 Purge Gas. Zero grade nitrogen (N_2), containing less than 1 ppm carbon.

7.2.2 Volatile Organics Measurement. The following are required for measuring the VO concentration.

7.2.2.1 Hydrogen (H_2). Zero grade H_2, 99.999 percent pure.

7.2.2.2 Combustion Gas. Zero grade air or oxygen as required by the FID.

7.2.2.3 Calibration Gas. Pressurized gas cylinder containing 10 percent propane and 1 percent 1,1-dichloroethylene by volume in nitrogen.

7.2.2.4 Water. Deionized distilled water that conforms to American Society for Testing and Materials Specification D 1193–74, Type 3, is required for analysis. At the option of the analyst, the $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations are not expected to be present.

7.2.2.5 1-Propanol. ACS grade or better. Electrolyte Solution. For use in the ELCD.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling.

8.1.1 Sampling Plan Design and Development. Use the procedures in chapter nine of Reference 1 in section 16 as guidance in developing a sampling plan.

8.1.2 Single Phase or Well-mixed Waste.

8.1.2.1 Install a sampling tap to obtain the sample at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to the atmosphere). Assemble the sampling apparatus as shown in Figure 25D–5.

8.1.2.2 Prepare the sampling containers as follows: Pour 30 mL of clean PEG into the container. PEG will reduce but not eliminate the loss of organics during sample collection. Weigh the sample container with the screw cap, the PEG, and any labels to the nearest 0.01 g and record the weight (m_{st}). Store the containers in an ice bath until 1 hour before sampling (PEG will solidify at ice bath temperatures; allow the containers to reach room temperature before sampling).

8.1.2.3 Begin sampling by purging the sample lines and cooling coil with at least four volumes of waste. Collect the purged material in a separate container and dispose of it properly.

8.1.2.4 After purging, stop the sample flow and direct the sampling tube to a preweighed sample container, prepared as described in section 8.1.2.2. Keep the tip of the tube below the surface of the PEG during sampling to minimize contact with the atmosphere. Sample at a flow rate such that the temperature of the waste is less than 10 °C (50 °F). Fill the sample container and immediately cap it (within 5 seconds) so that a minimum headspace exists in the container. Store immediately in a cooler and cover with ice.

8.1.3 Multiple-phase Waste. Collect a 10 g sample of each phase of waste generated using the procedures described in section 8.1.2 or 8.1.5. Each phase of the waste shall be analyzed as a separate sample. Calculate the weighted average VO concentration of the waste using Equation 25D–13 (Section 12.14).

8.1.4 Solid waste. Add approximately 10 g of the solid waste to a container prepared in the manner described in section 8.1.2.2, minimizing headspace. Cap and chill immediately.

8.1.5 Alternative to Tap Installation. If tap installation is impractical or impossible, fill a large, clean, empty container by submerging the container into the waste below the surface of the waste. Immediately fill a container prepared in the manner described in section 8.1.2.2 with approximately 10 g of the waste collected in the large container. Minimize headspace, cap and chill immediately.

8.1.6 Alternative sampling techniques may be used upon the approval of the Administrator.

8.2 Sample Recovery.

8.2.1 Assemble the purging apparatus as shown in Figures 25D–1 and 25D–2. The oven shall be heated to 75 ±2 °C (167 ±3.6 °F). The sampling lines leading from the oven to the detectors shall be heated to 120 ±10 °C (248 ±18 °F) with no cold spots. The flame ionization detector shall be operated with a heated block. Adjust the purging lance so that it reaches the bottom of the chamber.

8.2.2 Remove the sample container from the cooler, and wipe the exterior of the container to remove any extraneous ice, water, or other debris. Reweigh the sample container to the nearest 0.01 g, and record the weight (m_{sf}). Pour the contents of the sample container into the purging flask, rinse the sample container three times with a total of 20 mL of PEG (since the sample container originally held 30 mL of PEG, the total volume of PEG added to the purging flask will be 50 mL), transferring the rinsings to the purging flask after each rinse. Cap purging flask between rinses. The total volume of PEG in the purging flask shall be 50 mL. Add 50 mL of water to the purging flask.

9.0 Quality Control

9.1 Quality Control Samples. If audit samples are not available, prepare and analyze the two types of quality control samples (QCS) listed in Sections 9.1.1 and 9.1.2. Before placing the system in operation, after a shutdown of greater than six months, and after any major modifications, analyze each QCS in triplicate. For each detector, calculate the percent recovery by dividing measured concentration by theoretical concentration and multiplying by 100. Determine the mean percent recovery for each detector for each QCS triplicate analysis. The RSD for any triplicate analysis shall be ≤10 percent. For QCS 1 (methylene chloride), the percent recovery shall be ≥90 percent for carbon as methane, and ≥55 percent for chlorine as chloride. For QCS 2 (1,3-dichloro-2-propanol), the percent recovery shall be ≤15 percent for carbon as methane, and ≤6 percent for chlorine as chloride. If the analytical system does not meet the above-mentioned criteria for both detectors, check the system parameters (temperature, system pressure, purge rate, etc.), correct the problem, and repeat the triplicate analysis of each QCS.

9.1.1 QCS 1, Methylene Chloride. Prepare a stock solution by weighing, to the nearest 0.1 mg, 55 µL of HPLC grade methylene chloride in a tared 5 mL volumetric flask. Record the weight in milligrams, dilute to 5 mL with cleaned PEG, and inject 100 µL of the stock solution into a sample prepared as a water blank (50 mL of cleaned PEG and 60 mL of water in the purging flask). Analyze

the QCS according to the procedures described in sections 10.2 and 10.3, excluding section 10.2.2. To calculate the theoretical carbon concentration (in mg) in QCS 1, multiply mg of methylene chloride in the stock solution by 3.777×10^{-3}. To calculate the theoretical chlorine concentration (in mg) in QCS 1, multiply mg of methylene chloride in the stock solution by 1.670×10^{-2}.

9.1.2 QCS 2, 1,3-dichloro-2-propanol. Prepare a stock solution by weighing, to the nearest 0.1 mg, 60 μL of high purity grade 1,3-dichloro-2-propanol in a tared 5 mL volumetric flask. Record the weight in milligrams, dilute to 5 mL with cleaned PEG, and inject 100 μL of the stock solution into a sample prepared as a water blank (50 mL of cleaned PEG and 60 mL of water in the purging flask). Analyze the QCS according to the procedures described in sections 10.2 and 10.3, excluding section 10.2.2. To calculate the theoretical carbon concentration (in mg) in QCS 2, multiply mg of 1,3-dichloro-2-propanol in the stock solution by 7.461×10^{-3}. To calculate the theoretical chlorine concentration (in mg) in QCS 2, multiply mg of 1,3-dichloro-2-propanol in the stock solution by 1.099×10^{-2}.

9.1.3 Routine QCS Analysis. For each set of compliance samples (in this context, set is per facility, per compliance test), analyze one QCS 1 and one QCS 2 sample. The percent recovery for each sample for each detector shall be ±13 percent of the mean recovery established for the most recent set of QCS triplicate analysis (Section 9.4). If the sample does not meet this criteria, check the system components and analyze another QCS 1 and 2 until a single set of QCS meet the ±13 percent criteria.

10.0 Calibration and Standardization

10.1 Initial Performance Check of Purging System. Before placing the system in operation, after a shutdown of greater than six months, after any major modifications, and at least once per month during continuous operation, conduct the linearity checks described in sections 10.1.1 and 10.1.2. Install calibration gas at the three-way calibration gas valve. See Figure 25D–1.

10.1.1 Linearity Check Procedure. Using the calibration standard described in section 7.2.2.3 and by varying the injection time, it is possible to calibrate at multiple concentration levels. Use Equation 25D–3 to calculate three sets of calibration gas flow rates and run times needed to introduce a total mass of carbon, as methane, (m_c) of 1, 5, and 10 mg into the system (low, medium and high FID calibration, respectively). Use Equation 25D–4 to calculate three sets of calibration gas flow rates and run times needed to introduce a total chloride mass (m_{ch}) of 1, 5, and 10 mg into the system (low, medium and high ELCD calibration, respectively). With the system operating in standby mode, allow the FID and the ELCD to establish a stable baseline. Set the secondary pressure regulator of the calibration gas cylinder to the same pressure as the purge gas cylinder and set the proper flow rate with the calibration flow controller (see Figure 25D–1). The calibration gas flow rate can be measured with a flowmeter attached to the vent position of the calibration gas valve. Set the four-way bypass valve to standby position so that the calibration gas flows through the coalescing filter only. Inject the calibration gas by turning the calibration gas valve from vent position to inject position. Continue the calibration gas flow for the appropriate period of time before switching the calibration valve to vent position. Continue recording the response of the FID and the ELCD for 5 min after switching off calibration gas flow. Make triplicate injections of all six levels of calibration.

10.1.2 Linearity Criteria. Calculate the average response factor (Equations 25D–5 and 25D–6) and the relative standard deviation (RSD) (Equation 25D–10) at each level of the calibration curve for both detectors. Calculate the overall mean of the three response factor averages for each detector. The FID linearity is acceptable if each response factor is within 5 percent of the overall mean and if the RSD for each set of triplicate injections is less than 5 percent. The ELCD linearity is acceptable if each response factor is within 10 percent of the overall mean and if the RSD for each set of triplicate injections is less than 10 percent. Record the overall mean value of the response factors for the FID and the ELCD. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat sections 10.1.1 and 10.1.2.

10.2 Daily Calibrations.

10.2.1 Daily Linearity Check. Follow the procedures outlined in section 10.1.1 to analyze the medium level calibration for both the FID and the ELCD in duplicate at the start of the day. Calculate the response factors and the RSDs for each detector. For the FID, the calibration is acceptable if the average response factor is within 5 percent of the overall mean response factor (Section 10.1.2) and if the RSD for the duplicate injection is less than 5 percent. For the ELCD, the calibration is acceptable if the average response factor is within 10 percent of the overall mean response factor (Section 10.1.2) and if the RSD for the duplicate injection is less than 10 percent. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat sections 10.1.1 and 10.1.2.

10.2.2 Calibration Range Check.

10.2.2.1 If the waste concentration for either detector falls below the range of calibration for that detector, use the procedure outlined in section 10.1.1 to choose two calibration points that bracket the new target

concentration. Analyze each of these points in triplicate (as outlined in section 10.1.1) and use the criteria in section 10.1.2 to determine the linearity of the detector in this ''mini-calibration'' range.

10.2.2.2 After the initial linearity check of the mini-calibration curve, it is only necessary to test one of the points in duplicate for the daily calibration check (in addition to the points specified in section 10.2.1). The average daily mini-calibration point should fit the linearity criteria specified in section 10.2.1. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat the calibration procedure mentioned in the first paragraph of section 10.2.2. A mini-calibration curve for waste concentrations above the calibration curve for either detector is optional.

10.3 Analytical Balance. Calibrate against standard weights.

11.0 Analysis

11.1 Sample Analysis.

11.1.1 Turn on the constant temperature chamber and allow the temperature to equilibrate at 75 ±2 °C (167 ±3.6 °F). Turn the four-way valve so that the purge gas bypasses the purging flask, the purge gas flowing through the coalescing filter and to the detectors (standby mode). Turn on the purge gas. Allow both the FID and the ELCD to warm up until a stable baseline is achieved on each detector. Pack the filter flask with ice. Replace ice after each run and dispose of the waste water properly. When the temperature of the oven reaches 75 ±2 °C (167 ±3.6 °F), start both integrators and record baseline. After 1 min, turn the four-way valve so that the purge gas flows through the purging flask, to the coalescing filter and to the sample splitters (purge mode). Continue recording the response of the FID and the ELCD. Monitor the readings of the pressure gauge and the rotameter. If the readings fall below established setpoints, stop the purging, determine the source of the leak, and resolve the problem before resuming. Leaks detected during a sampling period invalidate that sample.

11.1.2 As the purging continues, monitor the output of the detectors to make certain that the analysis is proceeding correctly and that the results are being properly recorded. Every 10 minutes read and record the purge flow rate, the pressure and the chamber temperature. Continue the purging for 30 minutes.

11.1.3 For each detector output, integrate over the entire area of the peak starting at 1 minute and continuing until the end of the run. Subtract the established baseline area from the peak area. Record the corrected area of the peak. See Figure 25D–6 for an example integration.

11.2 Water Blank. A water blank shall be analyzed for each batch of cleaned PEG prepared. Transfer about 60 mL of water into the purging flask. Add 50 mL of the cleaned PEG to the purging flask. Treat the blank as described in sections 8.2 and 8.3, excluding section 8.2.2. Calculate the concentration of carbon and chlorine in the blank sample (assume 10 g of waste as the mass). A VO concentration equivalent to ≤10 percent of the applicable standard may be subtracted from the measured VO concentration of the waste samples. Include all blank results and documentation in the test report.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

A_b = Area under the water blank response curve, counts.

A_c = Area under the calibration response curve, counts.

A_s = Area under the sample response curve, counts.

C = Concentration of volatile organics in the sample, ppmw.

C_c = Concentration of carbon, as methane, in the calibration gas, mg/L.

C_{ch} = Concentration of chloride in the calibration gas, mg/L.

C_j = VO concentration of phase j, ppmw.

DR_f = Average daily response factor of the FID, mg CH_4/counts.

Dr_{th} = Average daily response factor of the ELCD, mg Cl^-/counts.

F_j = Weight fraction of phase j present in the waste.

m_c = Mass of carbon, as methane, in a calibration run, mg.

m_{ch} = Mass of chloride in a calibration run, mg.

m_s = Mass of the waste sample, g.

m_{sc} = Mass of carbon, as methane, in the sample, mg.

m_{sf} = Mass of sample container and waste sample, g.

m_{sh} = Mass of chloride in the sample, mg.

m_{st} = Mass of sample container prior to sampling, g.

m_{VO} = Mass of volatile organics in the sample, mg.

n = Total number of phases present in the waste.

P_p = Percent propane in calibration gas (L/L).

P_{vc} = Percent 1,1-dichloroethylene in calibration gas (L/L).

Q_c = Flow rate of calibration gas, L/min.

t_c = Length of time standard gas is delivered to the analyzer, min.

W = Weighted average VO concentration, ppmw.

12.2 Concentration of Carbon, as Methane, in the Calibration Gas.

$$C_c = (19.681 \times P_p) + (13.121 \times P_{vc}) \qquad \text{Eq. 25D-1}$$

12.3 Concentration of Chloride in the Calibration Gas.

$$C_{ch} = 28.998 \times P_{vc} \qquad \text{Eq. 25D-2}$$

12.4 Mass of Carbon, as Methane, in a Calibration Run.

$$M_c = C_c \times Q_c \times t_c \qquad \text{Eq. 25D-3}$$

12.5 Mass of Chloride in a Calibration Run.

$$m_{ch} = C_{ch} \times Q_c \times t_c \qquad \text{Eq. 25D-4}$$

12.6 FID Response Factor, mg/counts.

$$DR_t = \frac{m_c}{A_c} \qquad \text{Eq. 25D-5}$$

12.7 ELCD Response Factor, mg/counts.

$$DR_{th} = \frac{m_{ch}}{A_c} \qquad \text{Eq. 25D-6}$$

12.8 Mass of Carbon in the Sample.

$$m_{sc} = DR_t(A_s - A_b) \qquad \text{Eq. 25D-7}$$

12.9 Mass of Chloride in the Sample.

$$m_{sh} = DR_{th}(A_s - A_b) \qquad \text{Eq. 25D-8}$$

12.10 Mass of Volatile Organics in the Sample.

$$m_{vo} = m_{sc} + m_{sh} \qquad \text{Eq. 25D-9}$$

12.11 Relative Standard Deviation.

$$RSD = \frac{100}{\bar{x}} \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}} \qquad \text{Eq. 25D-10}$$

12.12 Mass of Sample.

$$m_s = m_{sf} - m_{st} \qquad \text{Eq. 25D-11}$$

12.13 Concentration of Volatile Organics in Waste.

$$C = \frac{(m_{vo} \times 1000)}{m_s} \qquad \text{Eq. 25D-12}$$

12.14 Weighted Average VO Concentration of Multi-phase Waste.

$$W = \sum_{j=1}^{n} F_j x \overline{C}_j \qquad \text{Eq. 25D-13}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. ''Test Methods for Evaluating Solid Waste, Physical/Chemistry Methods'', U.S. Environmental Protection Agency. Publication SW–846, 3rd Edition, November 1986 as amended by Update I, November 1990.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

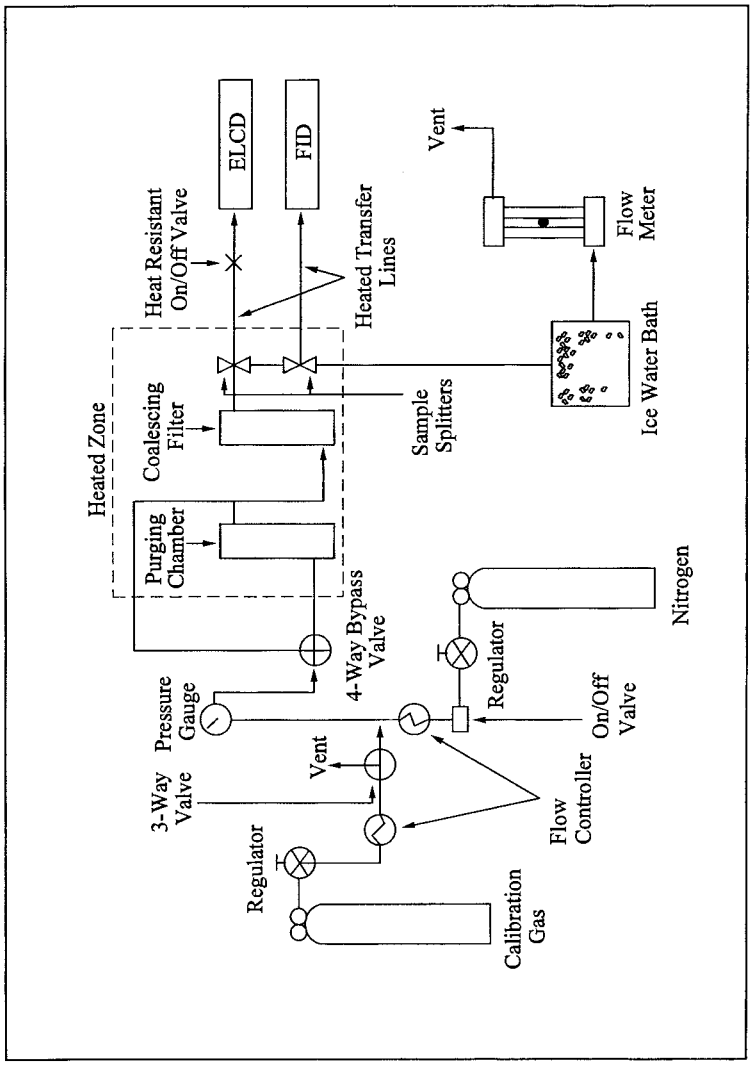


Figure 25D-1. Schematic of Purging Apparatus.

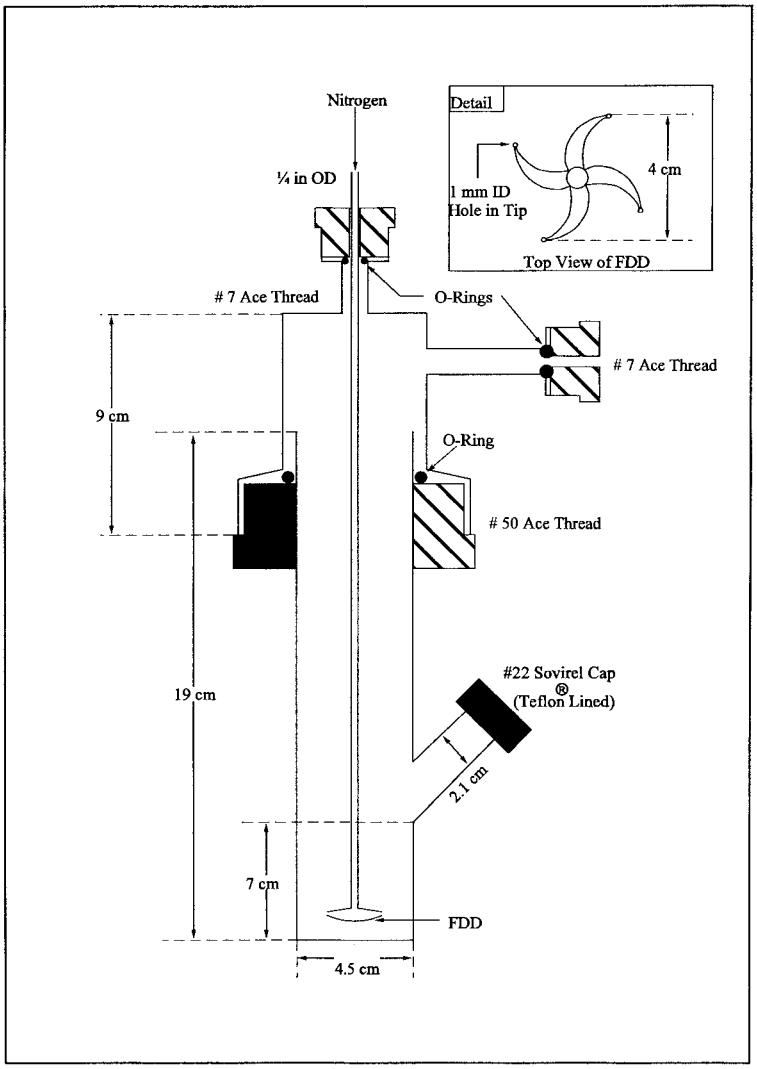
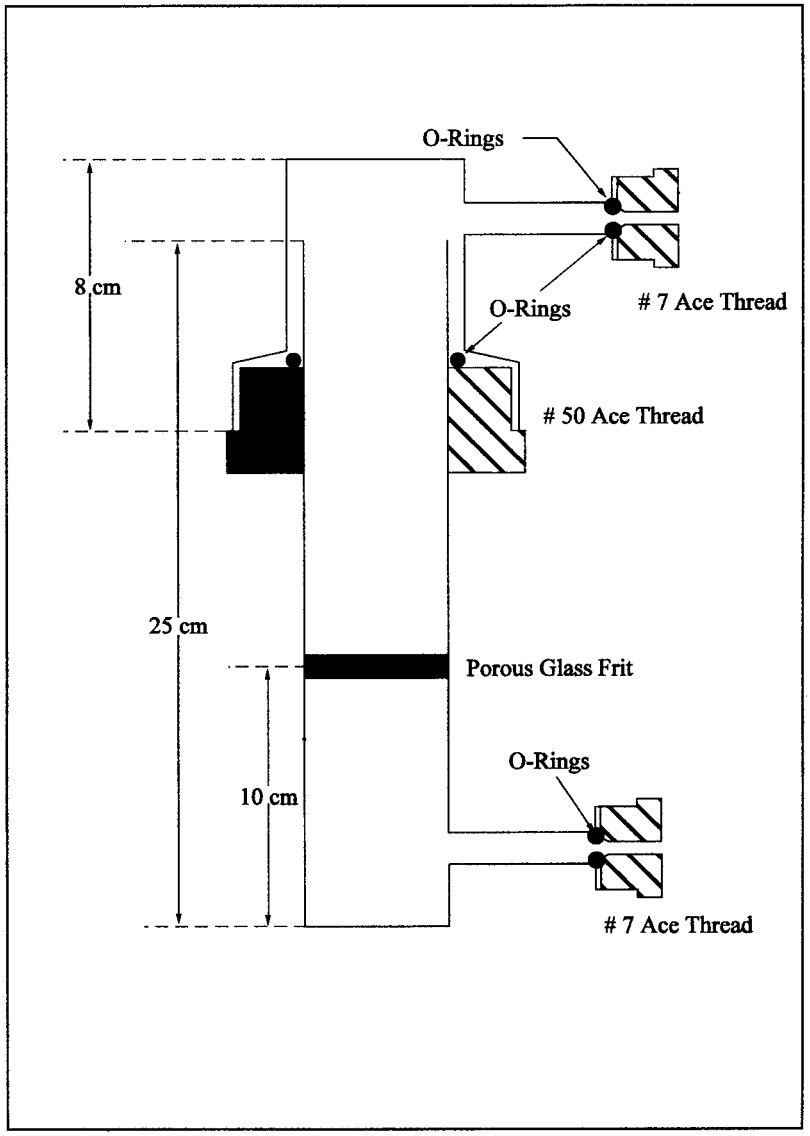


Figure 25D-2. Purging Lance.


O-Rings
8 cm
O-Rings
7 Ace Thread
50 Ace Thread
25 cm
Porous Glass Frit
O-Rings
10 cm
7 Ace Thread

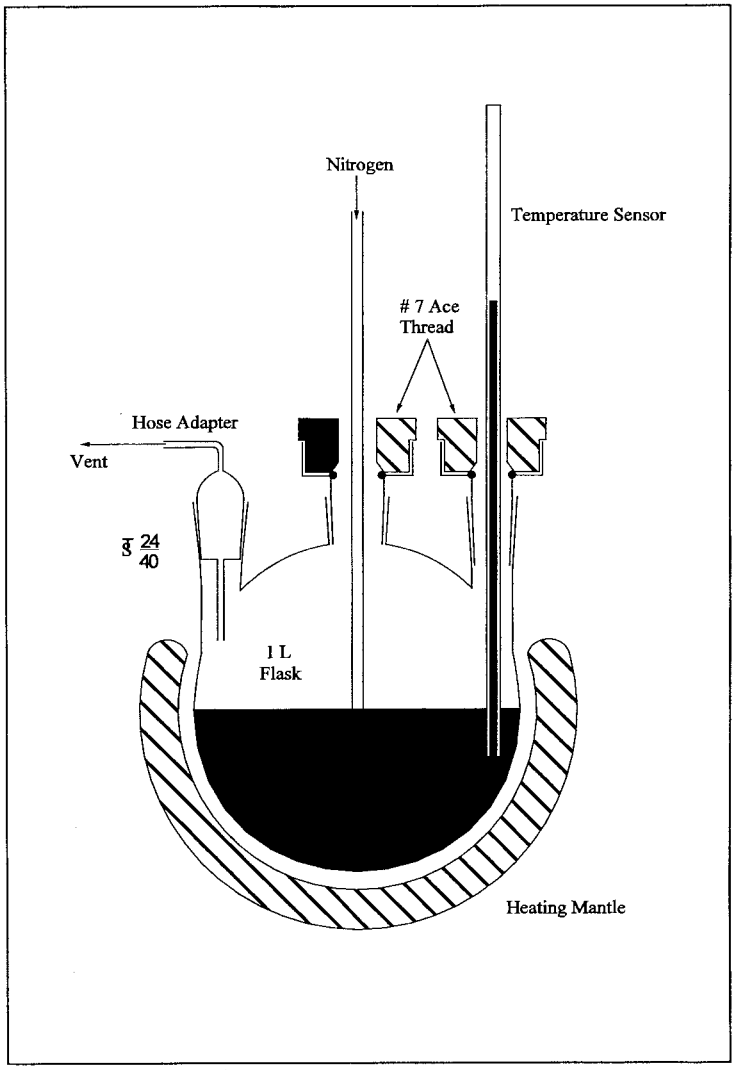


Figure 25D-4. Schematic of PEG Cleaning System.

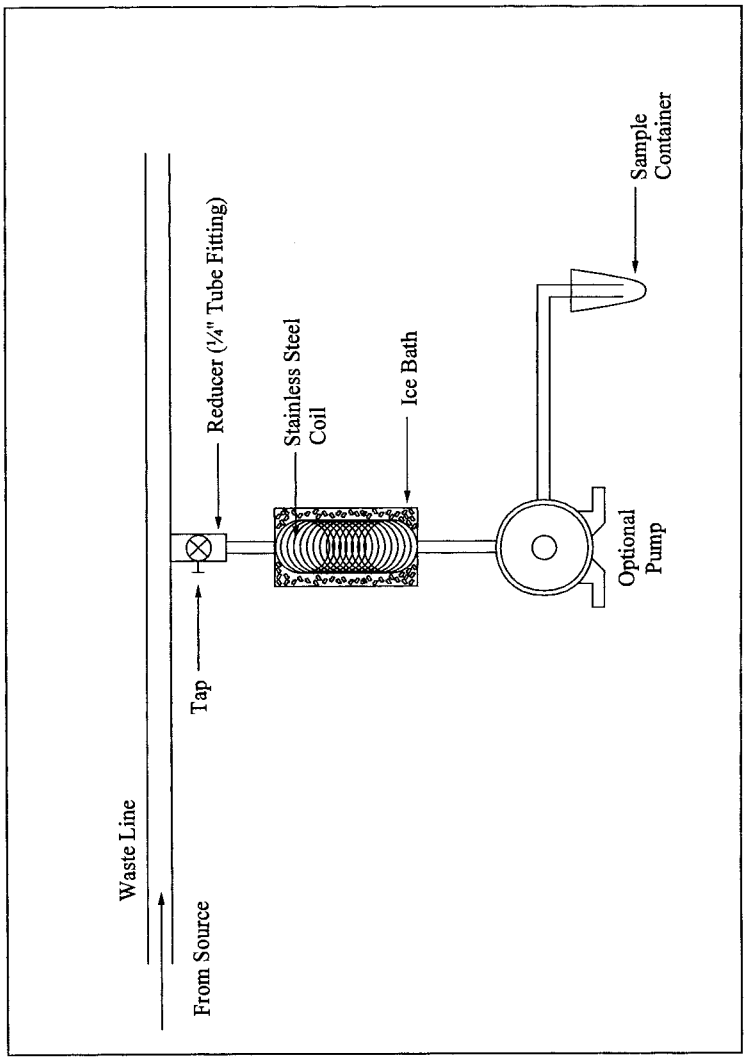


Figure 25D-5. Schematic of Sampling Apparatus.

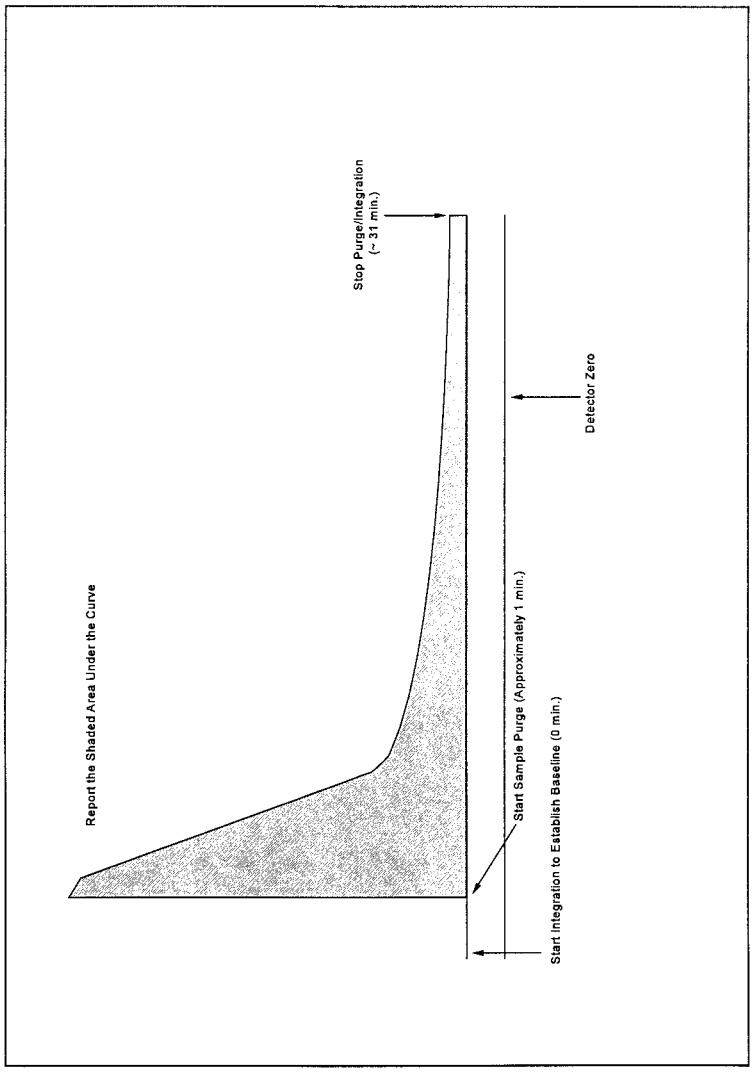


Figure 25D-6. Example Integration of Either Detector.

METHOD 25E—DETERMINATION OF VAPOR PHASE ORGANIC CONCENTRATION IN WASTE SAMPLES

NOTE: Performance of this method should not be attempted by persons unfamiliar with the operation of a flame ionization detector (FID) nor by those who are unfamiliar with source sampling because knowledge beyond the scope of this presentation is required. This method is not inclusive with respect to specifications (*e.g.*, reagents and standards) and calibration procedures. Some material is incorporated by reference from other methods. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 106, part 61, Appendix B, and Method 18, part 60, Appendix A.

1.0 Scope and Application

1.1 Applicability. This method is applicable for determining the vapor pressure of waste cited by an applicable regulation.

1.2 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 The headspace vapor of the sample is analyzed for carbon content by a headspace analyzer, which uses an FID.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 The analyst shall select the operating parameters best suited to the requirements for a particular analysis. The analyst shall produce confirming data through an adequate supplemental analytical technique and have the data available for review by the Administrator.

5.0 Safety [Reserved]

6.0 Equipment and Supplies

6.1 Sampling. The following equipment is required:

6.1.1 Sample Containers. Vials, glass, with butyl rubber septa, Perkin-Elmer Corporation Numbers 0105–0129 (glass vials), B001–0728 (gray butyl rubber septum, plug style), 0105–0131 (butyl rubber septa), or equivalent. The seal must be made from butyl rubber. Silicone rubber seals are not acceptable.

6.1.2 Vial Sealer. Perkin-Elmer Number 105–0106, or equivalent.

6.1.3 Gas-Tight Syringe. Perkin-Elmer Number 00230117, or equivalent.

6.1.4 The following equipment is required for sampling.

6.1.4.1 Tap.

6.1.4.2 Tubing. Teflon, 0.25-in. ID.

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1.4.3 Cooling Coil. Stainless steel (304), 0.25 in.-ID, equipped with a thermocouple at the coil outlet.

6.2 Analysis. The following equipment is required.

6.2.1 Balanced Pressure Headspace Sampler. Perkin-Elmer HS–6, HS–100, or equivalent, equipped with a glass bead column instead of a chromatographic column.

6.2.2 FID. An FID meeting the following specifications is required.

6.2.2.1 Linearity. A linear response (±5 percent) over the operating range as demonstrated by the procedures established in section 10.2.

6.2.2.2 Range. A full scale range of 1 to 10,000 parts per million (ppm) propane (C_3H_8). Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.2.3 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the output of the detector.

6.2.4 Temperature Sensor. Capable of reading temperatures in the range of 30 to 60 °C (86 to 140 °F) with an accuracy of ±0.1 °C (±0.2 °F).

7.0 Reagents and Standards

7.1 Analysis. The following items are required for analysis.

7.1.1 Hydrogen (H_2). Zero grade hydrogen, as required by the FID.

7.1.2 Carrier Gas. Zero grade nitrogen, containing less than 1 ppm carbon (C) and less than 1 ppm carbon dioxide.

7.1.3 Combustion Gas. Zero grade air or oxygen as required by the FID.

7.2 Calibration and Linearity Check.

7.2.1 Stock Cylinder Gas Standard. 100 percent propane. The manufacturer shall: (a) Certify the gas composition to be accurate to ±3 percent or better (see section 7.2.1.1); (b) recommend a maximum shelf life over which the gas concentration does not change by greater than ±5 percent from the certified value; and (c) affix the date of gas cylinder preparation, certified propane concentration, and recommended maximum shelf life to the cylinder before shipment to the buyer.

7.2.1.1 Cylinder Standards Certification. The manufacturer shall certify the concentration of the calibration gas in the cylinder by (a) directly analyzing the cylinder and (b) calibrating his analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use, as a minimum, a three-point calibration curve.

7.2.1.2 Verification of Manufacturer's Calibration Standards. Before using, the manufacturer shall verify each calibration standard by (a) comparing it to gas mixtures prepared in accordance with the procedure described in section 7.1 of Method 106 of Part 61, Appendix B, or by (b) calibrating it against Standard Reference Materials (SRM's) prepared by the National Bureau of Standards, if such SRM's are available. The agreement between the initially determined concentration value and the verification concentration value must be within ±5 percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

8.0 Sampling Collection, Preservation, Storage, and Transport

8.1 Install a sampling tap to obtain a sample at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to

the atmosphere). Assemble the sampling apparatus as shown in Figure 25E–1.

8.2 Begin sampling by purging the sample lines and cooling coil with at least four volumes of waste. Collect the purged material in a separate container and dispose of it properly.

8.3 After purging, stop the sample flow and transfer the Teflon sampling tube to a sample container. Sample at a flow rate such that the temperature of the waste is <10 °C (<50 °F). Fill the sample container halfway (±5 percent) and cap it within 5 seconds. Store immediately in a cooler and cover with ice.

8.4 Alternative sampling techniques may be used upon the approval of the Administrator.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
10.2, 10.3	FID calibration and response check	Ensure precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Use the procedures in sections 10.2 to calibrate the headspace analyzer and FID and check for linearity before the system is first placed in operation, after any shutdown longer than 6 months, and after any modification of the system.

10.2 Calibration and Linearity. Use the procedures in section 10 of Method 18 of Part 60, Appendix A, to prepare the standards and calibrate the flowmeters, using propane as the standard gas. Fill the calibration standard vials halfway (±5 percent) with deionized water. Purge and fill the airspace with calibration standard. Prepare a minimum of three concentrations of calibration standards in triplicate at concentrations that will bracket the applicable cutoff. For a cutoff of 5.2 kPa (0.75 psi), prepare nominal concentrations of 30,000, 50,000, and 70,000 ppm as propane. For a cutoff of 27.6 kPa (4.0 psi), prepare nominal concentrations of 200,000, 300,000, and 400,000 ppm as propane.

10.2.1 Use the procedures in section 11.3 to measure the FID response of each standard. Use a linear regression analysis to calculate the values for the slope (k) and the y-intercept (b). Use the procedures in sections 12.3 and 12.2 to test the calibration and the linearity.

10.3 Daily FID Calibration Check. Check the calibration at the beginning and at the end of the daily runs by using the following procedures. Prepare 2 calibration standards at the nominal cutoff concentration using the procedures in section 10.2. Place one at the beginning and one at the end of the daily run. Measure the FID response of the daily calibration standard and use the values for k and b from the most recent calibration to calculate the concentration of the daily standard. Use an equation similar to 25E–2 to calculate the percent difference between the daily standard and C_s. If the difference is within 5 percent, then the previous values for k and b can be used. Otherwise, use the procedures in section 10.2 to recalibrate the FID.

11.0 Analytical Procedures

11.1 Allow one hour for the headspace vials to equilibrate at the temperature specified in the regulation. Allow the FID to warm up until a stable baseline is achieved on the detector.

11.2 Check the calibration of the FID daily using the procedures in section 10.3.

11.3 Follow the manufacturer's recommended procedures for the normal operation of the headspace sampler and FID.

11.4 Use the procedures in sections 12.4 and 12.5 to calculate the vapor phase organic vapor pressure in the samples.

11.5 Monitor the output of the detector to make certain that the results are being properly recorded.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

A = Measurement of the area under the response curve, counts.
b = y-intercept of the linear regression line.
C_a = Measured vapor phase organic concentration of sample, ppm as propane.
C_{ma} = Average measured vapor phase organic concentration of standard, ppm as propane.
C_m = Measured vapor phase organic concentration of standard, ppm as propane.
C_s = Calculated standard concentration, ppm as propane.
k = Slope of the linear regression line.
P_{bar} = Atmospheric pressure at analysis conditions, mm Hg (in. Hg).
P* = Organic vapor pressure in the sample, kPa (psi).
PD = Percent difference between the average measured vapor phase organic concentration (C_m) and the calculated standard concentration (C_s).
RSD = Relative standard deviation.
$\beta = 1.333 \times 10^{-7}$ kPa/[(mm Hg)(ppm)], $(4.91 \times 10^{-7}$ psi/[(in. Hg)(ppm)])

12.2 Linearity. Use the following equation to calculate the measured standard concentration for each standard vial.

$$C_m = kA + b \qquad \text{Eq. 25E-1}$$

12.2.1 Calculate the average measured standard concentration (C_{ma}) for each set of triplicate standards and use the following equation to calculate PD between C_{ma} and C_s. The instrument linearity is acceptable if the PD is within five for each standard.

$$PD = \frac{C_s - C_{ma}}{C_s} \times 100 \qquad \text{Eq. 25E-2}$$

12.3. Relative Standard Deviation (RSD). Use the following equation to calculate the RSD for each triplicate set of standards.

$$RSD = \frac{100}{C_{ma}} \sqrt{\frac{\sum (C_m - C_{ma})^2}{2}} \qquad \text{Eq. 25E-3}$$

The calibration is acceptable if the RSD is within five for each standard concentration.

12.4 Concentration of organics in the headspace. Use the following equation to calculate the concentration of vapor phase organics in each sample.

$$C_a = kA + b \qquad \text{Eq. 25E-4}$$

12.5 Vapor Pressure of Organics in the Headspace Sample. Use the following equation to calculate the vapor pressure of organics in the sample.

$$P^* = \beta P_{bar} C_a \qquad \text{Eq. 25E-5}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, Albert E., Samuel Witz, and Robert D. MacPhee. ''Determination of Solvent Vapor Concentrations by Total Combustion Analysis: a Comparison of Infared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, Massachusetts.

2. Salo, Albert E., William L. Oaks, and Robert D. MacPhee. ''Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, Colorado. June 9–13, 1974.) p. 25.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

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EPA Reference Methods

$$B_w = \frac{P_w}{P_{bar}} \qquad 3C\text{-}1$$

$$C = \frac{A}{R(1-B_w)} \qquad 3C\text{-}2$$

$$C = \frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}} \quad \frac{A}{R(1-B_w)} \qquad 3C\text{-}3$$

7.3 Measured N_2 Concentration Correction. Calculate the reported N_2 correction for Method 25–C using Eq. 3C–4. If oxygen is determined in place of N_2, substitute the oxygen concentration for the nitrogen concentration in the equation.

$$C_{N_2 Corr} = \frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}}(C_{N_2}) \quad Eq.\ 3C-4$$

8. Bibliography

1. McNair, H.M., and E.J. Bonnelli. Basic Gas Chromatography. Consolidated Printers, Berkeley, CA. 1969.

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–2 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

APPENDIX A–3 TO PART 60—TEST METHODS 4 THROUGH 5I

Method 4—Determination of moisture content in stack gases
Method 5—Determination of particulate matter emissions from stationary sources
Method 5A—Determination of particulate matter emissions from the asphalt processing and asphalt roofing industry
Method 5B—Determination of nonsulfuric acid particulate matter emissions from stationary sources
Method 5C [Reserved]
Method 5D—Determination of particulate matter emissions from positive pressure fabric filters
Method 5E—Determination of particulate matter emissions from the wool fiberglass insulation manufacturing industry
Method 5F—Determination of nonsulfate particulate matter emissions from stationary sources
Method 5G—Determination of particulate matter emissions from wood heaters (dilution tunnel sampling location)
Method 5H—Determination of particulate emissions from wood heaters from a stack location
Method 5I—Determination of Low Level Particulate Matter Emissions From Stationary Sources

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference

method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

METHOD 4—DETERMINATION OF MOISTURE CONTENT IN STACK GASES

NOTE: This method does not include all the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 5, and Method 6.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Water vapor (H_2O) ...	7732–18–5	N/A

1.2 Applicability. This method is applicable for the determination of the moisture content of stack gas.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted at a constant rate from the source; moisture is removed from the sample stream and determined either volumetrically or gravimetrically.

2.2 The method contains two possible procedures: a reference method and an approximation method.

2.2.1 The reference method is used for accurate determinations of moisture content (such as are needed to calculate emission data). The approximation method, provides estimates of percent moisture to aid in setting isokinetic sampling rates prior to a pollutant emission measurement run. The approximation method described herein is only a suggested approach; alternative means for approximating the moisture content (*e.g.*, drying tubes, wet bulb-dry bulb techniques, condensation techniques, stoichiometric calculations, previous experience, etc.) are also acceptable.

2.2.2 The reference method is often conducted simultaneously with a pollutant emission measurement run. When it is, calculation of percent isokinetic, pollutant emission rate, etc., for the run shall be based upon the results of the reference method or its equivalent. These calculations shall not

be based upon the results of the approximation method, unless the approximation method is shown, to the satisfaction of the Administrator, to be capable of yielding results within one percent H_2O of the reference method.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 The moisture content of saturated gas streams or streams that contain water droplets, as measured by the reference method, may be positively biased. Therefore, when these conditions exist or are suspected, a second determination of the moisture content shall be made simultaneously with the reference method, as follows: Assume that the gas stream is saturated. Attach a temperature sensor [capable of measuring to ±1 °C (2 °F)] to the reference method probe. Measure the stack gas temperature at each traverse point (see section 8.1.1.1) during the reference method traverse, and calculate the average stack gas temperature. Next, determine the moisture percentage, either by: (1) Using a psychrometric chart and making appropriate corrections if the stack pressure is different from that of the chart, or (2) using saturation vapor pressure tables. In cases where the psychrometric chart or the saturation vapor pressure tables are not applicable (based on evaluation of the process), alternative methods, subject to the approval of the Administrator, shall be used.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Reference Method. A schematic of the sampling train used in this reference method is shown in Figure 4–1.

6.1.1 Probe. Stainless steel or glass tubing, sufficiently heated to prevent water condensation, and equipped with a filter, either in-stack (*e.g.*, a plug of glass wool inserted into the end of the probe) or heated out-of-stack (*e.g.*, as described in Method 5), to remove particulate matter. When stack conditions permit, other metals or plastic tubing may be used for the probe, subject to the approval of the Administrator.

6.1.2 Condenser. Same as Method 5, section 6.1.1.8.

6.1.3 Cooling System. An ice bath container, crushed ice, and water (or equivalent), to aid in condensing moisture.

6.1.4 Metering System. Same as in Method 5, section 6.1.1.9, except do not use sampling systems designed for flow rates higher than 0.0283 m^3/min (1.0 cfm). Other metering systems, capable of maintaining a constant sampling rate to within 10 percent and determining sample gas volume to within 2 percent, may be used, subject to the approval of the Administrator.

6.1.5 Barometer and Graduated Cylinder and/or Balance. Same as Method 5, sections 6.1.2 and 6.2.5, respectively.

6.2. Approximation Method. A schematic of the sampling train used in this approximation method is shown in Figure 4–2.

6.2.1 Probe. Same as section 6.1.1.

6.2.2 Condenser. Two midget impingers, each with 30-ml capacity, or equivalent.

6.2.3 Cooling System. Ice bath container, crushed ice, and water, to aid in condensing moisture in impingers.

6.2.4 Drying Tube. Tube packed with new or regenerated 6- to 16-mesh indicating-type silica gel (or equivalent desiccant), to dry the sample gas and to protect the meter and pump.

6.2.5 Valve. Needle valve, to regulate the sample gas flow rate.

6.2.6 Pump. Leak-free, diaphragm type, or equivalent, to pull the gas sample through the train.

6.2.7 Volume Meter. Dry gas meter, sufficiently accurate to measure the sample volume to within 2 percent, and calibrated over the range of flow rates and conditions actually encountered during sampling.

6.2.8 Rate Meter. Rotameter, or equivalent, to measure the flow range from 0 to 3 liters/min (0 to 0.11 cfm).

6.2.9 Graduated Cylinder. 25-ml.

6.2.10 Barometer. Same as Method 5, section 6.1.2.

6.2.11 Vacuum Gauge. At least 760-mm (30-in.) Hg gauge, to be used for the sampling leak check.

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Reference Method. The following procedure is intended for a condenser system (such as the impinger system described in section 6.1.1.8 of Method 5) incorporating volumetric analysis to measure the condensed moisture, and silica gel and gravimetric analysis to measure the moisture leaving the condenser.

8.1.1 Preliminary Determinations.

8.1.1.1 Unless otherwise specified by the Administrator, a minimum of eight traverse points shall be used for circular stacks having diameters less than 0.61 m (24 in.), a minimum of nine points shall be used for rectangular stacks having equivalent diameters less than 0.61 m (24 in.), and a minimum of twelve traverse points shall be used in all

other cases. The traverse points shall be located according to Method 1. The use of fewer points is subject to the approval of the Administrator. Select a suitable probe and probe length such that all traverse points can be sampled. Consider sampling from opposite sides of the stack (four total sampling ports) for large stacks, to permit use of shorter probe lengths. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

8.1.1.2 Select a total sampling time such that a minimum total gas volume of 0.60 scm (21 scf) will be collected, at a rate no greater than 0.021 m^3/min (0.75 cfm). When both moisture content and pollutant emission rate are to be determined, the moisture determination shall be simultaneous with, and for the same total length of time as, the pollutant emission rate run, unless otherwise specified in an applicable subpart of the standards.

8.1.2 Preparation of Sampling Train.

8.1.2.1 Place known volumes of water in the first two impingers; alternatively, transfer water into the first two impingers and record the weight of each impinger (plus water) to the nearest 0.5 g. Weigh and record the weight of the silica gel to the nearest 0.5 g, and transfer the silica gel to the fourth impinger; alternatively, the silica gel may first be transferred to the impinger, and the weight of the silica gel plus impinger recorded.

8.1.2.2 Set up the sampling train as shown in Figure 4–1. Turn on the probe heater and (if applicable) the filter heating system to temperatures of approximately 120 °C (248 °F), to prevent water condensation ahead of the condenser. Allow time for the temperatures to stabilize. Place crushed ice and water in the ice bath container.

8.1.3 Leak Check Procedures. It is recommended, but not required, that the volume metering system and sampling train be leak-checked as follows:

8.1.3.1 Metering System. Same as Method 5, section 8.4.1.

8.1.3.2 Sampling Train. Disconnect the probe from the first impinger or (if applicable) from the filter holder. Plug the inlet to the first impinger (or filter holder), and pull a 380 mm (15 in.) Hg vacuum. A lower vacuum may be used, provided that it is not exceeded during the test. A leakage rate in excess of 4 percent of the average sampling rate or 0.00057 m^3/min (0.020 cfm), whichever is less, is unacceptable. Following the leak check, reconnect the probe to the sampling train.

8.1.4 Sampling Train Operation. During the sampling run, maintain a sampling rate within 10 percent of constant rate, or as specified by the Administrator. For each run, record the data required on a data sheet similar to that shown in Figure 4–3. Be sure to record the dry gas meter reading at the beginning and end of each sampling time increment and whenever sampling is halted. Take other appropriate readings at each sample point at least once during each time increment.

NOTE: When Method 4 is used concurrently with an isokinetic method (*e.g.*, Method 5) the sampling rate should be maintained at isokinetic conditions rather than 10 percent of constant rate.

8.1.4.1 To begin sampling, position the probe tip at the first traverse point. Immediately start the pump, and adjust the flow to the desired rate. Traverse the cross section, sampling at each traverse point for an equal length of time. Add more ice and, if necessary, salt to maintain a temperature of less than 20 °C (68 °F) at the silica gel outlet.

8.1.4.2 After collecting the sample, disconnect the probe from the first impinger (or from the filter holder), and conduct a leak check (mandatory) of the sampling train as described in section 8.1.3.2. Record the leak rate. If the leakage rate exceeds the allowable rate, either reject the test results or correct the sample volume as in section 12.3 of Method 5.

8.2 Approximation Method.

NOTE: The approximation method described below is presented only as a suggested method (see section 2.0).

8.2.1 Place exactly 5 ml water in each impinger. Leak check the sampling train as follows: Temporarily insert a vacuum gauge at or near the probe inlet. Then, plug the probe inlet and pull a vacuum of at least 250 mm (10 in.) Hg. Note the time rate of change of the dry gas meter dial; alternatively, a rotameter (0 to 40 ml/min) may be temporarily attached to the dry gas meter outlet to determine the leakage rate. A leak rate not in excess of 2 percent of the average sampling rate is acceptable.

NOTE: Release the probe inlet plug slowly before turning off the pump.

8.2.2 Connect the probe, insert it into the stack, and sample at a constant rate of 2 liters/min (0.071 cfm). Continue sampling until the dry gas meter registers about 30 liters (1.1 ft^3) or until visible liquid droplets are carried over from the first impinger to the second. Record temperature, pressure, and dry gas meter readings as indicated by Figure 4–4.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
Section 8.1.1.4	Leak rate of the sampling system cannot exceed four percent of the average sampling rate or 0.00057 m^3/min (0.020 cfm).	Ensures the accuracy of the volume of gas sampled. (Reference Method).
Section 8.2.1	Leak rate of the sampling system cannot exceed two percent of the average sampling rate.	Ensures the accuracy of the volume of gas sampled. (Approximation Method).

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Reference Method. Calibrate the metering system, temperature sensors, and barometer according to Method 5, sections 10.3, 10.5, and 10.6, respectively.

10.2 Approximation Method. Calibrate the metering system and the barometer according to Method 6, section 10.1 and Method 5, section 10.6, respectively.

10.3 Field Balance Calibration Check. Check the calibration of the balance used to weigh impingers with a weight that is at least 500g or within 50g of a loaded impinger. The weight must be ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference-see 40 CFR 60.17) Class 6 (or better). Daily, before use, the field balance must measure the weight within ± 0.5g of the certified mass. If the daily balance calibration check fails, perform corrective measures and repeat the check before using balance.

11.0 Analytical Procedure

11.1 Reference Method. Measure the volume of the moisture condensed in each of the impingers to the nearest ml. Alternatively, if the impingers were weighed prior to sampling, weigh the impingers after sampling and record the difference in weight to the nearest 0.5 g. Determine the increase in weight of the silica gel (or silica gel plus impinger) to the nearest 0.5 g. Record this information (see example data sheet, Figure 4–5), and calculate the moisture content, as described in section 12.0.

11.2 Approximation Method. Combine the contents of the two impingers, and measure the volume to the nearest 0.5 ml.

12.0 Data Analysis and Calculations

Carry out the following calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Reference Method.

12.1.1 Nomenclature.

B_{ws} = Proportion of water vapor, by volume, in the gas stream.

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P_m = Absolute pressure (for this method, same as barometric pressure) at the dry gas meter, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 (mm Hg)(m^3)/(g-mole)(°K) for metric units and 21.85 (in. Hg)(ft^3)/(lb-mole)(°R) for English units.

T_m = Absolute temperature at meter, °K (°R).

T_{std} = Standard absolute temperature, 293 °K (528 °R).

V_f = Final volume of condenser water, ml.

V_i = Initial volume, if any, of condenser water, ml.

V_m = Dry gas volume measured by dry gas meter, dcm (dcf).

$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

$V_{wc(std)}$ = Volume of water vapor condensed, corrected to standard conditions, scm (scf).

$V_{wsg(std)}$ = Volume of water vapor collected in silica gel, corrected to standard conditions, scm (scf).

W_f = Final weight of silica gel or silica gel plus impinger, g.

W_i = Initial weight of silica gel or silica gel plus impinger, g.

Y = Dry gas meter calibration factor.

ΔV_m = Incremental dry gas volume measured by dry gas meter at each traverse point, dcm (dcf).

ρ_w = Density of water, 0.9982 g/ml (0.002201 lb/ml).

12.1.2 Volume of Water Vapor Condensed.

$$V_{wc(std)} = \frac{(V_f - V_i)\,\rho_w R\,T_{std}}{P_{std} M_W} = K_1 (V_f - V_i) \qquad \text{Eq. 4-1}$$

Where:

K_1 = 0.001333 m^3/ml for metric units,
= 0.04706 ft^3/ml for English units.

12.1.3 Volume of Water Collected in Silica Gel.

$$V_{wsg(std)} = \frac{(W_f - W_i)\,R\,T_{std}}{P_{std} M_W K_2} = K_3 (W_f - W_i) \qquad \text{Eq. 4-2}$$

Where:

K_2 = 1.0 g/g for metric units,
= 453.6 g/lb for English units.
K_3 = 0.001335 m^3/g for metric units,
= 0.04715 ft^3/g for English units.

12.1.4 Sample Gas Volume.

$$V_{m(std)} = \frac{V_m\ Y\ P_m T_{std}}{P_{std} T_m} \qquad \text{Eq. 4-3}$$

$$= K_4 Y \frac{V_m P_m}{T_m}$$

Where:

K_4 = 0.3855 °K/mm Hg for metric units,
= 17.64 °R/in. Hg for English units.

NOTE: If the post-test leak rate (Section 8.1.4.2) exceeds the allowable rate, correct the value of Vm in Equation 4–3, as described in section 12.3 of Method 5.

12.1.5 Moisture Content.

$$B_{ws} = \frac{V_{wc(std)} + V_{wsg(std)}}{V_{wc(std)} + V_{wsg(std)} + V_{m(std)}} \qquad \text{Eq. 4-4}$$

12.1.6 Verification of Constant Sampling Rate. For each time increment, determine the ΔV_m. Calculate the average. If the value for any time increment differs from the average by more than 10 percent, reject the results, and repeat the run.

12.1.7 In saturated or moisture droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one using a value based upon the saturated conditions (see section 4.1), and another based upon the results of the impinger analysis. The lower of these two values of B_{ws} shall be considered correct.

12.2 Approximation Method. The approximation method presented is designed to estimate the moisture in the stack gas; therefore, other data, which are only necessary for accurate moisture determinations, are not collected. The following equations adequately estimate the moisture content for the purpose of determining isokinetic sampling rate settings.

12.2.1 Nomenclature.

B_{wm} = Approximate proportion by volume of water vapor in the gas stream leaving the second impinger, 0.025.
B_{ws} = Water vapor in the gas stream, proportion by volume.
M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
P_m = Absolute pressure (for this method, same as barometric pressure) at the dry gas meter, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
R = Ideal gas constant, 0.06236 [(mm Hg)(m^3)]/[(g-mole)(K)] for metric units and 21.85 [(in. Hg)(ft^3)]/[(lb-mole)(°R)] for English units.
T_m = Absolute temperature at meter, °K (°R).
T_{std} = Standard absolute temperature, 293 °K (528 °R).
V_f = Final volume of impinger contents, ml.
V_i = Initial volume of impinger contents, ml.
V_m = Dry gas volume measured by dry gas meter, dcm (dcf).
$V_{m(std)}$ = Dry gas volume measured by dry gas meter, corrected to standard conditions, dscm (dscf).
$V_{wc(std)}$ = Volume of water vapor condensed, corrected to standard conditions, scm (scf).
Y = Dry gas meter calibration factor.
ρ_w = Density of water, 0.09982 g/ml (0.002201 lb/ml).

12.2.2 Volume of Water Vapor Collected.

$$V_{wc(std)} = \frac{\left(V_f - V_i\right) \rho_w R\ T_{std}}{P_{std} M_W} \qquad \text{Eq. 4-5}$$

$$= K_5\left(V_f - V_i\right)$$

Where:

K_5 = 0.001333 m^3/ml for metric units,
= 0.04706 ft^3/ml for English units.

12.2.3 Sample Gas Volume.

$$V_{m(std)} = \frac{V_m\ Y\ P_m T_{std}}{P_{std} T_m} \qquad \text{Eq. 4-6}$$

$$= K_6 Y \frac{V_m P_m}{T_m}$$

Where:

K_6 = 0.3855 °K/mm Hg for metric units,
= 17.64 °R/in. Hg for English units.

12.2.4 Approximate Moisture Content.

$$B_{ws} = \frac{V_{wc(std)}}{V_{wc(std)} + V_{m(std)}} + B_{wm} \qquad \text{Eq. 4-7}$$

$$= \frac{V_{wc(std)}}{V_{wc(std)} + V_{m(std)}} + (0.025)$$

12.2.5 Using F-factors to determine approximate moisture for estimating moisture content where no wet scrubber is being used, for the purpose of determining isokinetic sampling rate settings with no fuel sample, is acceptable using the average F_c or F_d factor from Method 19 (see Method 19, section 12.3.1). If this option is selected, calculate the approximate moisture as follows:

$B_{ws} = B_H + B_A + B_F$

Where:

B_A = Mole Fraction of moisture in the ambient air.

$$B_A = \frac{\%RH}{100 * P_{Bar}} * 10^{\left[6.6912 - \left(\frac{3144}{T+390.86}\right)\right]}$$

B_F = Mole fraction of moisture from free water in the fuel.

$$B_F = \left[\frac{0.0036W^2 + 0.075W}{100}\right]\left[\frac{20.9 - O_2}{20.9}\right]$$

B_H = Mole fraction of moisture from the hydrogen in the fuel.

$$B_H = \left[1 - \frac{F_d}{F_w}\right]\frac{(20.9 - O_2)}{20.9}$$

B_{ws} = Mole fraction of moisture in the stack gas.

F_d = Volume of dry combustion components per unit of heat content at 0 percent oxygen, dscf/10^6.

Btu (scm/J). See Table 19–2 in Method 19.

F_w = Volume of wet combustion components per unit of heat content at 0 percent oxygen, wet.

scf/10^6 Btu (scm/J). See Table 19–2 in Method 19.

%RH = Percent relative humidity (calibrated hygrometer acceptable), percent.

P_{Bar} = Barometric pressure, in. Hg.

T = Ambient temperature, °F.

W = Percent free water by weight, percent.

O_2 = Percent oxygen in stack gas, dry basis, percent.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 The procedure described in Method 5 for determining moisture content is an acceptable alternative to Method 4.

16.2 The procedures in Method 6A for determining moisture is an acceptable alternative to Method 4.

16.3 Method 320 is an acceptable alternative to Method 4 for determining moisture.

16.4 Using F-factors to determine moisture is an acceptable alternative to Method 4 for a combustion stack not using a scrubber, and where a fuel sample is taken during the test run and analyzed for development of an F_d factor (see Method 19, section 12.3.2), and where stack O_2 content is measured by Method 3A or 3B during each test run. If this option is selected, calculate the moisture content as follows:

$B_{ws} = B_H + B_A + B_F$

Where:

B_A = Mole fraction of moisture in the ambient air.

$$B_A = \frac{\%RH}{100\ P_{Bar}}\left[10^{\left[6.6912-\left(\frac{3144}{T+390.86}\right)\right]}\right]$$

NOTE: Values of B_A should be between 0.00 and 0.06 with common values being about 0.015.

B_F = Mole fraction of moisture from free water in the fuel.

$$B_F = \left[\frac{0.0036\ W^2 + 0.075\ W}{100}\right]\left[\frac{20.9 - O_2}{20.9}\right]$$

NOTE: Free water in fuel is minimal for distillate oil and gases, such as propane and natural gas, so this step may be omitted for those fuels.

B_H = Mole fraction of moisture from the hydrogen in the fuel.

$$B_H = \left(1 - \frac{F_d}{F_w}\right)\frac{(20.9 - O_2)}{20.9}$$

B_{ws} = Mole fraction of moisture in the stack gas.
F_d = Volume of dry combustion components per unit of heat content at 0 percent oxygen, dscf/10^6 Btu (scm/J). Develop a test specific F_d value using an integrated fuel sample from each test run and Equation 19–13 in section 12.3.2 of Method 19.
F_w = Volume of wet combustion components per unit of heat content at 0 percent oxygen, wet scf/10^6 Btu (scm/J). Develop a test specific F_w value using an integrated fuel sample from each test run and Equation 19–14 in section 12.3.2 of Method 19.
%RH = Percent relative humidity (calibrated hygrometer acceptable), percent.
P_{Bar} = Barometric pressure, in. Hg.
T = Ambient temperature, °F.
W = Percent free water by weight, percent.
O_2 = Percent oxygen in stack gas, dry basis, percent.

17.0 References

1. Air Pollution Engineering Manual (Second Edition). Danielson, J.A. (ed.). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, NC. Publication No. AP–40. 1973.

2. Devorkin, Howard, et al. Air Pollution Source Testing Manual. Air Pollution Control District, Los Angeles, CA. November 1963.

3. Methods for Determination of Velocity, Volume, Dust and Mist Content of Gases. Western Precipitation Division of Joy Manufacturing Co. Los Angeles, CA. Bulletin WP–50. 1968.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

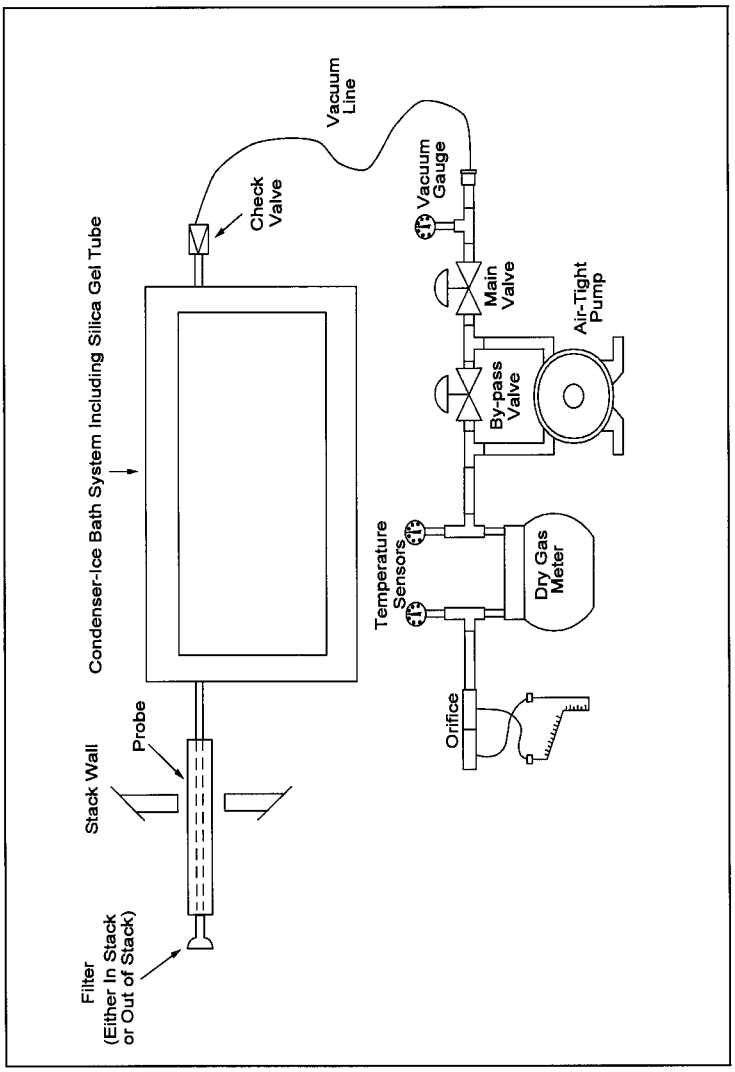

Figure 4-1. Moisture Sampling Train-Reference Method

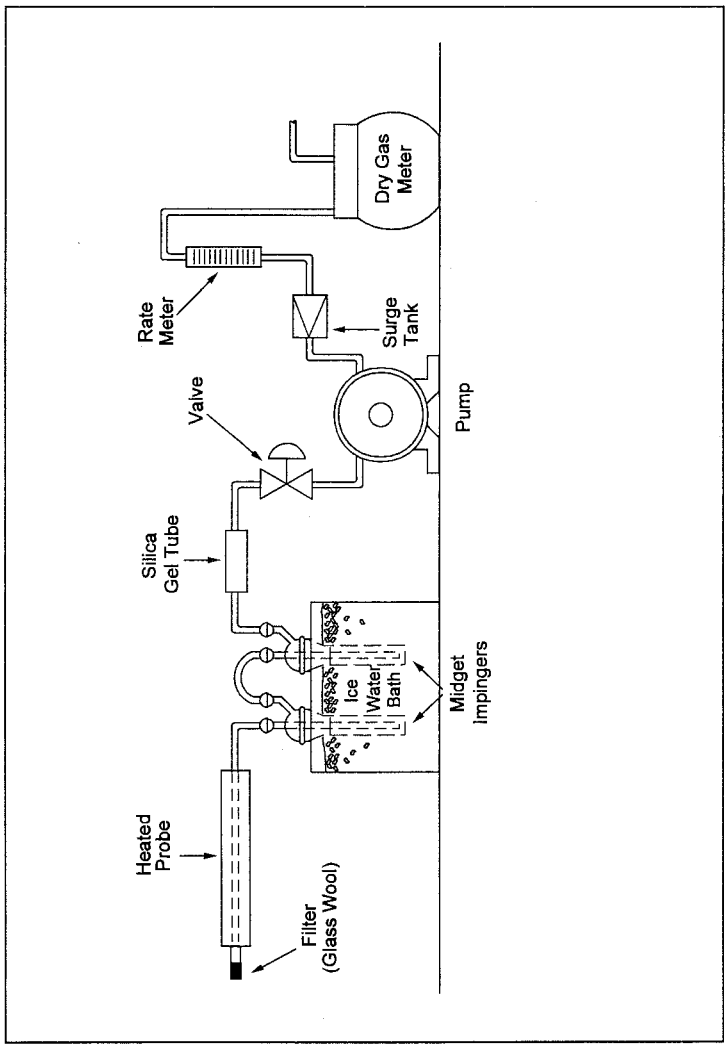

Figure 4-2. Moisture Sampling Train - Approximation Method.

Plant		Run No.	
Location		Ambient temperature	
Operator		Barometric pressure	
Date		Probe Length	

Traverse Pt. No.	Sampling time (Δ), min	Stack temperature °C (°F)	Pressure differential across orifice meter ΔH mm (in.) H_2O	Meter reading gas sample volume m^3 (ft^3)	ΔV_m m^3 (ft^3)	Gas sample temperature at dry gas meter		Temperature of gas leaving condenser or last impinger °C (°F)
						Inlet Tm_{in} °C (°F)	Outlet Tm_{out} °C (°F)	
Average								

Location _____ Barometric pressure _____
Test _____ Comments: _____
Date _____
Operator _____

Figure 4–3. Moisture Determination—Reference Method

Clock time	Gas Volume through meter, (V_m), m^3 (ft^3)	Rate meter setting m^3/min (ft^3/min)	Meter temperature °C (°F)

Figure 4–4. Example Moisture Determination Field Data Sheet—Approximation Method

	Impinger volume, ml	Silica gel weight, g
Final Initial Difference		

Figure 4–5. Analytical Data—Reference Method

METHOD 5—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of PM emissions from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature of 120 ±14 °C (248 ±25 °F) or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. The PM mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after the removal of uncombined water.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. The following items are required for sample collection:

6.1.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 5–1 in section 18.0. Complete construction details are given in APTD–0581 (Reference 2 in section 17.0); commercial models of this train are also available. For

changes from APTD–0581 and for allowable modifications of the train shown in Figure 5–1, see the following subsections.

NOTE: The operating and maintenance procedures for the sampling train are described in APTD–0576 (Reference 3 in section 17.0). Since correct usage is important in obtaining valid results, all users should read APTD–0576 and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein.

6.1.1.1 Probe Nozzle. Stainless steel (316) or glass with a sharp, tapered leading edge. The angle of taper shall be ≤30°, and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. If made of stainless steel, the nozzle shall be constructed from seamless tubing. Other materials of construction may be used, subject to the approval of the Administrator. A range of nozzle sizes suitable for isokinetic sampling should be available. Typical nozzle sizes range from 0.32 to 1.27 cm (⅛ to ½ in) inside diameter (ID) in increments of 0.16 cm (1⁄16 in). Larger nozzles sizes are also available if higher volume sampling trains are used. Each nozzle shall be calibrated, according to the procedures outlined in section 10.1.

6.1.1.2 Probe Liner. Borosilicate or quartz glass tubing with a heating system capable of maintaining a probe gas temperature during sampling of 120 ±14 °C (248 ±25 °F), or such other temperature as specified by an applicable subpart of the standards or as approved by the Administrator for a particular application. Since the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to APTD–0581 and utilizing the calibration curves of APTD–0576 (or calibrated according to the procedure outlined in APTD–0576) will be considered acceptable. Either borosilicate or quartz glass probe liners may be used for stack temperatures up to about 480 °C (900 °F); quartz glass liners shall be used for temperatures between 480 and 900 °C (900 and 1,650 °F). Both types of liners may be used at higher temperatures than specified for short periods of time, subject to the approval of the Administrator. The softening temperature for borosilicate glass is 820 °C (1500 °F), and for quartz glass it is 1500 °C (2700 °F). Whenever practical, every effort should be made to use borosilicate or quartz glass probe liners. Alternatively, metal liners (e.g., 316 stainless steel, Incoloy 825 or other corrosion resistant metals) made of seamless tubing may be used, subject to the approval of the Administrator.

6.1.1.3 Pitot Tube. Type S, as described in section 6.1 of Method 2, or other device approved by the Administrator. The pitot tube shall be attached to the probe (as shown in Figure 5–1) to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see Method 2, Figure 2–7) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in section 10.0 of Method 2.

6.1.1.4 Differential Pressure Gauge. Inclined manometer or equivalent device (two), as described in section 6.2 of Method 2. One manometer shall be used for velocity head (Δp) readings, and the other, for orifice differential pressure readings.

6.1.1.5 Filter Holder. Borosilicate glass, with a glass or Teflon frit filter support and a silicone rubber gasket. Other materials of construction (e.g., stainless steel or Viton) may be used, subject to the approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe (or cyclone, if used).

6.1.1.6 Filter Heating System. Any heating system capable of monitoring and maintaining temperature around the filter shall be used to ensure the sample gas temperature exiting the filter of 120 ±14 °C (248 ±25 °F) during sampling or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. The monitoring and regulation of the temperature around the filter may be done with the filter temperature sensor or another temperature sensor.

6.1.1.7 Filter Temperature Sensor. A temperature sensor capable of measuring temperature to within ±3 °C (5.4 °F) shall be installed so that the sensing tip of the temperature sensor is in direct contact with the sample gas exiting the filter. The sensing tip of the sensor may be encased in glass, Teflon, or metal and must protrude at least ½ in. into the sample gas exiting the filter. The filter temperature sensor must be monitored and recorded during sampling to ensure a sample gas temperature exiting the filter of 120 ±14 °C (248 ±25 °F), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application.

6.1.1.8 Condenser. The following system shall be used to determine the stack gas moisture content: Four impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with a 1.3 cm (½ in.) ID glass tube extending to about 1.3 cm (½ in.) from the bottom of the flask. The second impinger shall be of the Greenburg-Smith design with the standard

tip. Modifications (e.g., using flexible connections between the impingers, using materials other than glass, or using flexible vacuum lines to connect the filter holder to the condenser) may be used, subject to the approval of the Administrator. The first and second impingers shall contain known quantities of water (Section 8.3.1), the third shall be empty, and the fourth shall contain a known weight of silica gel, or equivalent desiccant. A temperature sensor, capable of measuring temperature to within 1 °C (2 °F) shall be placed at the outlet of the fourth impinger for monitoring purposes. Alternatively, any system that cools the sample gas stream and allows measurement of the water condensed and moisture leaving the condenser, each to within 1 ml or 1 g may be used, subject to the approval of the Administrator. An acceptable technique involves the measurement of condensed water either gravimetrically or volumetrically and the determination of the moisture leaving the condenser by: (1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's law of partial pressures; or (2) passing the sample gas stream through a tared silica gel (or equivalent desiccant) trap with exit gases kept below 20 °C (68 °F) and determining the weight gain. If means other than silica gel are used to determine the amount of moisture leaving the condenser, it is recommended that silica gel (or equivalent) still be used between the condenser system and pump to prevent moisture condensation in the pump and metering devices and to avoid the need to make corrections for moisture in the metered volume.

NOTE: If a determination of the PM collected in the impingers is desired in addition to moisture content, the impinger system described above shall be used, without modification. Individual States or control agencies requiring this information shall be contacted as to the sample recovery and analysis of the impinger contents.

6.1.1.9 Metering System. Vacuum gauge, leak-free pump, calibrated temperature sensors, dry gas meter (DGM) capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 5–1. Other metering systems capable of maintaining sampling rates within 10 percent of isokinetic and of determining sample volumes to within 2 percent may be used, subject to the approval of the Administrator. When the metering system is used in conjunction with a pitot tube, the system shall allow periodic checks of isokinetic rates.

6.1.1.10 Sampling trains utilizing metering systems designed for higher flow rates than that described in APTD–0581 or APTD–0576 may be used provided that the specifications of this method are met.

6.1.2 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in.).

NOTE: The barometric pressure reading may be obtained from a nearby National Weather Service station. In this case, the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be made at a rate of minus 2.5 mm Hg (0.1 in.) per 30 m (100 ft) elevation increase or plus 2.5 mm Hg (0.1 in) per 30 m (100 ft) elevation decrease.

6.1.3 Gas Density Determination Equipment. Temperature sensor and pressure gauge, as described in sections 6.3 and 6.4 of Method 2, and gas analyzer, if necessary, as described in Method 3. The temperature sensor shall, preferably, be permanently attached to the pitot tube or sampling probe in a fixed configuration, such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see Method 2, Figure 2–4). As a second alternative, if a difference of not more than 1 percent in the average velocity measurement is to be introduced, the temperature sensor need not be attached to the probe or pitot tube. (This alternative is subject to the approval of the Administrator.)

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Probe-Liner and Probe-Nozzle Brushes. Nylon bristle brushes with stainless steel wire handles. The probe brush shall have extensions (at least as long as the probe) constructed of stainless steel, Nylon, Teflon, or similarly inert material. The brushes shall be properly sized and shaped to brush out the probe liner and nozzle.

6.2.2 Wash Bottles. Two Glass wash bottles are recommended. Alternatively, polyethylene wash bottles may be used. It is recommended that acetone not be stored in polyethylene bottles for longer than a month.

6.2.3 Glass Sample Storage Containers. Chemically resistant, borosilicate glass bottles, for acetone washes, 500 ml or 1000 ml. Screw cap liners shall either be rubber-backed Teflon or shall be constructed so as to be leak-free and resistant to chemical attack by acetone. (Narrow mouth glass bottles have been found to be less prone to leakage.) Alternatively, polyethylene bottles may be used.

6.2.4 Petri Dishes. For filter samples; glass or polyethylene, unless otherwise specified by the Administrator.

6.2.5 Graduated Cylinder and/or Balance. To measure condensed water to within 1 ml or 0.5 g. Graduated cylinders shall have subdivisions no greater than 2 ml.

6.2.6 Plastic Storage Containers. Air-tight containers to store silica gel.

6.2.7 Funnel and Rubber Policeman. To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

6.2.8 Funnel. Glass or polyethylene, to aid in sample recovery.

6.3 Sample Analysis. The following equipment is required for sample analysis:

6.3.1 Glass Weighing Dishes.

6.3.2 Desiccator.

6.3.3 Analytical Balance. To measure to within 0.1 mg.

6.3.4 Balance. To measure to within 0.5 g.

6.3.5 Beakers. 250 ml.

6.3.6 Hygrometer. To measure the relative humidity of the laboratory environment.

6.3.7 Temperature Sensor. To measure the temperature of the laboratory environment.

7.0 Reagents and Standards

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Method D 2986–71, 78, or 95a (incorporated by reference—see §60.17). Test data from the supplier's quality control program are sufficient for this purpose. In sources containing SO_2 or SO_3, the filter material must be of a type that is unreactive to SO_2 or SO_3. Reference 10 in section 17.0 may be used to select the appropriate filter.

7.1.2 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

7.1.3 Water. When analysis of the material caught in the impingers is required, deionized distilled water [to conform to ASTM D1193–77 or 91 Type 3 (incorporated by reference—see §60.17)] with at least <0.001 percent residue shall be used or as specified in the applicable method requiring analysis of the water. Run reagent blanks prior to field use to eliminate a high blank on test samples.

7.1.4 Crushed Ice.

7.2 Sample Recovery. Acetone, reagent grade, ≤0.001 percent residue, in glass bottles, is required. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers; thus, acetone blanks shall be run prior to field use and only acetone with low blank values (≤0.001 percent) shall be used. In no case shall a blank value of greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight.

7.3 Sample Analysis. The following reagents are required for sample analysis:

7.3.1 Acetone. Same as in section 7.2.

7.3.2 Desiccant. Anhydrous calcium sulfate, indicating type. Alternatively, other types of desiccants may be used, subject to the approval of the Administrator.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation. It is suggested that sampling equipment be maintained according to the procedures described in APTD–0576. Alternative mercury-free thermometers may be used if the thermometers are at a minimum equivalent in terms of performance or suitably effective for the specific temperature measurement application.

8.1.1 Place 200 to 300 g of silica gel in each of several air-tight containers. Weigh each container, including silica gel, to the nearest 0.5 g, and record this weight. As an alternative, the silica gel need not be preweighed, but may be weighed directly in its impinger or sampling holder just prior to train assembly.

8.1.2 Check filters visually against light for irregularities, flaws, or pinhole leaks. Label filters of the proper diameter on the back side near the edge using numbering machine ink. As an alternative, label the shipping containers (glass or polyethylene petri dishes), and keep each filter in its identified container at all times except during sampling.

8.1.3 Desiccate the filters at 20 ±5.6 °C (68 ±10 °F) and ambient pressure for at least 24 hours. Weigh each filter (or filter and shipping container) at intervals of at least 6 hours to a constant weight (*i.e.*, ≤0.5 mg change from previous weighing). Record results to the nearest 0.1 mg. During each weighing, the period for which the filter is exposed to the laboratory atmosphere shall be less than 2 minutes. Alternatively (unless otherwise specified by the Administrator), the filters may be oven dried at 105 °C (220 °F) for 2 to 3 hours, desiccated for 2 hours, and weighed. Procedures other than those described, which account for relative humidity effects, may be used, subject to the approval of the Administrator.

8.2 Preliminary Determinations.

8.2.1 Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and the range of velocity heads using Method 2; it is recommended that a leak check of the pitot lines (see Method 2, section 8.1) be performed. Determine the moisture content using Approximation Method 4 or its alternatives for the purpose

of making isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in Method 2, section 8.6; if integrated Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the particulate sample run.

8.2.2 Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see section 8.3 of Method 2).

8.2.3 Select a suitable probe liner and probe length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the required probe length.

8.2.4 Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that (1) the sampling time per point is not less than 2 minutes (or some greater time interval as specified by the Administrator), and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume. The latter is based on an approximate average sampling rate.

8.2.5 The sampling time at each point shall be the same. It is recommended that the number of minutes sampled at each point be an integer or an integer plus one-half minute, in order to avoid timekeeping errors.

8.2.6 In some circumstances (*e.g.*, batch cycles) it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the Administrator's approval must first be obtained.

8.3 Preparation of Sampling Train.

8.3.1 During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin. Place 100 ml of water in each of the first two impingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

8.3.2 Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly is completed.

8.3.3 When glass probe liners are used, install the selected nozzle using a Viton A O-ring when stack temperatures are less than 260 °C (500 °F) or a heat-resistant string gasket when temperatures are higher. See APTD–0576 for details. Other connecting systems using either 316 stainless steel or Teflon ferrules may be used. When metal liners are used, install the nozzle as discussed above or by a leak-free direct mechanical connection. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

8.3.4 Set up the train as shown in Figure 5–1 ensuring that the connections are leaktight. Subject to the approval of the Administrator, a glass cyclone may be used between the probe and filter holder when the total particulate catch is expected to exceed 100 mg or when water droplets are present in the stack gas.

8.3.5 Place crushed ice around the impingers.

8.4 Leak-Check Procedures.

8.4.1 Leak Check of Metering System Shown in Figure 5–1. That portion of the sampling train from the pump to the orifice meter should be leak-checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The following procedure is suggested (see Figure 5–2): Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 to 18 cm (5 to 7 in.) water column by blowing into the rubber tubing. Pinch off the tubing, and observe the manometer for one minute. A loss of pressure on the manometer indicates a leak in the meter box; leaks, if present, must be corrected.

8.4.2 Pretest Leak Check. A pretest leak check of the sampling train is recommended, but not required. If the pretest leak check is conducted, the following procedure should be used.

8.4.2.1 After the sampling train has been assembled, turn on and set the filter and probe heating systems to the desired operating temperatures. Allow time for the temperatures to stabilize. If a Viton A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 380 mm (15 in.) Hg vacuum.

NOTE: A lower vacuum may be used, provided that it is not exceeded during the test.

8.4.2.2 If a heat-resistant string is used, do not connect the probe to the train during the leak check. Instead, leak-check the train by first plugging the inlet to the filter holder (cyclone, if applicable) and pulling a 380 mm (15 in.) Hg vacuum (see note in section 8.4.2.1). Then connect the probe to the train, and leak-check at approximately 25 mm (1 in.) Hg vacuum; alternatively, the probe may be leak-checked with the rest of the sampling train, in one step, at 380 mm (15 in.) Hg vacuum. Leakage rates in excess of 4 percent of the average sampling rate or 0.00057 m^3/min (0.020 cfm), whichever is less, are unacceptable.

8.4.2.3 The following leak-check instructions for the sampling train described in APTD–0576 and APTD–0581 may be helpful. Start the pump with the bypass valve fully open and the coarse adjust valve completely closed. Partially open the coarse adjust valve, and slowly close the bypass valve until the desired vacuum is reached. Do not reverse the direction of the bypass valve, as this will cause water to back up into the filter holder. If the desired vacuum is exceeded, either leak-check at this higher vacuum, or end the leak check and start over.

8.4.2.4 When the leak check is completed, first slowly remove the plug from the inlet to the probe, filter holder, or cyclone (if applicable), and immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the filter holder and the silica gel from being entrained backward into the third impinger.

8.4.3 Leak Checks During Sample Run. If, during the sampling run, a component (*e.g.*, filter assembly or impinger) change becomes necessary, a leak check shall be conducted immediately before the change is made. The leak check shall be done according to the procedure outlined in section 8.4.2 above, except that it shall be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.020 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered; if, however, a higher leakage rate is obtained, either record the leakage rate and plan to correct the sample volume as shown in section 12.3 of this method, or void the sample run.

NOTE: Immediately after component changes, leak checks are optional. If such leak checks are done, the procedure outlined in section 8.4.2 above should be used.

8.4.4 Post-Test Leak Check. A leak check of the sampling train is mandatory at the conclusion of each sampling run. The leak check shall be performed in accordance with the procedures outlined in section 8.4.2, except that it shall be conducted at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m^3 min (0.020 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, either record the leakage rate and correct the sample volume as shown in section 12.3 of this method, or void the sampling run.

8.5 Sampling Train Operation. During the sampling run, maintain an isokinetic sampling rate (within 10 percent of true isokinetic unless otherwise specified by the Administrator) and a sample gas temperature through the filter of 120 ±14 °C (248 ±25 °F) or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator.

8.5.1 For each run, record the data required on a data sheet such as the one shown in Figure 5–3. Be sure to record the initial DGM reading. Record the DGM readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak check, and when sampling is halted. Take other readings indicated by Figure 5–3 at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

8.5.2 Clean the portholes prior to the test run to minimize the chance of collecting deposited material. To begin sampling, verify that the filter and probe heating systems are up to temperature, remove the nozzle cap, verify that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump, and adjust the flow to isokinetic conditions. Nomographs are available which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pitot tube coefficient (C_p) is 0.85 ±0.02, and the stack gas equivalent density [dry molecular weight (M_d)] is equal to 29 ±4. APTD–0576 details the procedure for using the nomographs. If C_p and M_d are outside the above stated ranges, do not use the nomographs unless appropriate steps (see Reference 7 in section 17.0) are taken to compensate for the deviations.

8.5.3 When the stack is under significant negative pressure (*i.e.*, height of impinger stem), take care to close the coarse adjust valve before inserting the probe into the stack to prevent water from backing into the

filter holder. If necessary, the pump may be turned on with the coarse adjust valve closed.

8.5.4 When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

8.5.5 Traverse the stack cross-section, as required by Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the portholes; this minimizes the chance of extracting deposited material.

8.5.6 During the test run, make periodic adjustments to keep the temperature around the filter holder at the proper level to maintain the sample gas temperature exiting the filter; add more ice and, if necessary, salt to maintain a temperature of less than 20 °C (68 °F) at the condenser/silica gel outlet. Also, periodically check the level and zero of the manometer.

8.5.7 If the pressure drop across the filter becomes too high, making isokinetic sampling difficult to maintain, the filter may be replaced in the midst of the sample run. It is recommended that another complete filter assembly be used rather than attempting to change the filter itself. Before a new filter assembly is installed, conduct a leak check (see section 8.4.3). The total PM weight shall include the summation of the filter assembly catches.

8.5.8 A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator.

NOTE: When two or more trains are used, separate analyses of the front-half and (if applicable) impinger catches from each train shall be performed, unless identical nozzle sizes were used on all trains, in which case, the front-half catches from the individual trains may be combined (as may the impinger catches) and one analysis of front-half catch and one analysis of impinger catch may be performed. Consult with the Administrator for details concerning the calculation of results when two or more trains are used.

8.5.9 At the end of the sample run, close the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final DGM meter reading, and conduct a post-test leak check, as outlined in section 8.4.4. Also, leak-check the pitot lines as described in Method 2, section 8.1. The lines must pass this leak check, in order to validate the velocity head data.

8.6 Calculation of Percent Isokinetic. Calculate percent isokinetic (see Calculations, section 12.11) to determine whether the run was valid or another test run should be made. If there was difficulty in maintaining isokinetic rates because of source conditions, consult with the Administrator for possible variance on the isokinetic rates.

8.7 Sample Recovery.

8.7.1 Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

8.7.2 When the probe can be safely handled, wipe off all external PM near the tip of the probe nozzle, and place a cap over it to prevent losing or gaining PM. Do not cap off the probe tip tightly while the sampling train is cooling down. This would create a vacuum in the filter holder, thereby drawing water from the impingers into the filter holder.

8.7.3 Before moving the sample train to the cleanup site, remove the probe from the sample train and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Cap the filter inlet where the probe was fastened. Remove the umbilical cord from the last impinger, and cap the impinger. If a flexible line is used between the first impinger or condenser and the filter holder, disconnect the line at the filter holder, and let any condensed water or liquid drain into the impingers or condenser. Cap off the filter holder outlet and impinger inlet. Either ground-glass stoppers, plastic caps, or serum caps may be used to close these openings.

8.7.4 Transfer the probe and filter-impinger assembly to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

8.7.5 Save a portion of the acetone used for cleanup as a blank. From each storage container of acetone used for cleanup, save 200 ml and place in a glass sample container labeled ''acetone blank.'' To minimize any particulate contamination, rinse the wash bottle prior to filling from the tested container.

8.7.6 Inspect the train prior to and during disassembly, and note any abnormal conditions. Treat the samples as follows:

8.7.6.1 Container No. 1. Carefully remove the filter from the filter holder, and place it in its identified petri dish container. Use a pair of tweezers and/or clean disposable surgical gloves to handle the filter. If it is necessary to fold the filter, do so such that the PM cake is inside the fold. Using a dry Nylon bristle brush and/or a sharp-edged blade, carefully transfer to the petri dish any PM and/or filter fibers that adhere to the filter holder gasket. Seal the container.

8.7.6.2 Container No. 2. Taking care to see that dust on the outside of the probe or other

exterior surfaces does not get into the sample, quantitatively recover PM or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with acetone and placing the wash in a glass container. Deionized distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator. In these cases, save a water blank, and follow the Administrator's directions on analysis. Perform the acetone rinse as follows:

8.7.6.2.1 Carefully remove the probe nozzle. Clean the inside surface by rinsing with acetone from a wash bottle and brushing with a Nylon bristle brush. Brush until the acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

8.7.6.2.2 Brush and rinse the inside parts of the fitting with acetone in a similar way until no visible particles remain.

8.7.6.2.3 Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Let the acetone drain from the lower end into the sample container. A funnel (glass or polyethylene) may be used to aid in transferring liquid washes to the container. Follow the acetone rinse with a probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action through the probe; hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter that is brushed from the probe. Run the brush through the probe three times or more until no visible PM is carried out with the acetone or until none remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times since metal probes have small crevices in which particulate matter can be entrapped. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe.

8.7.6.2.4 It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

8.7.6.2.5 Clean the inside of the front half of the filter holder by rubbing the surfaces with a Nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone, also (if applicable). After all acetone washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to allow determination of whether leakage occurred during transport. Label the container to clearly identify its contents.

8.7.6.3 Container No. 3. Note the color of the indicating silica gel to determine whether it has been completely spent, and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container, and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, follow the procedure for Container No. 3 in section 11.2.3.

8.7.6.4 Impinger Water. Treat the impingers as follows: Make a notation of any color or film in the liquid catch. Measure the liquid that is in the first three impingers to within 1 ml by using a graduated cylinder or by weighing it to within 0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas. Discard the liquid after measuring and recording the volume or weight, unless analysis of the impinger catch is required (see NOTE, section 6.1.1.8). If a different type of condenser is used, measure the amount of moisture condensed either volumetrically or gravimetrically.

8.8 Sample Transport. Whenever possible, containers should be shipped in such a way that they remain upright at all times.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4, 10.1–10.6	Sampling equipment leak check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.

9.2 Volume Metering System Checks. The following procedures are suggested to check the volume metering system calibration values at the field test site prior to sample collection. These procedures are optional.

9.2.1 Meter Orifice Check. Using the calibration data obtained during the calibration procedure described in section 10.3, determine the ΔH@ for the metering system orifice. The ΔH@ is the orifice pressure differential in units of in. H_2O that correlates to 0.75 cfm of air at 528 °R and 29.92 in. Hg. The ΔH@ is calculated as follows:

$$\Delta H@ = 0.0319\ \Delta H \frac{T_M \theta^2}{P_{bar} Y^2 V_m^2}$$

Where:

ΔH = Average pressure differential across the orifice meter, in. H_2O.
T_m = Absolute average DGM temperature, °R.
P_{bar} = Barometric pressure, in. Hg.
θ = Total sampling time, min.
Y = DGM calibration factor, dimensionless.
V_m = Volume of gas sample as measured by DGM, dcf.
0.0319 = (0.0567 in. Hg/°R) (0.75 cfm)^2

9.2.1.1 Before beginning the field test (a set of three runs usually constitutes a field test), operate the metering system (*i.e.*, pump, volume meter, and orifice) at the ΔH@ pressure differential for 10 minutes. Record the volume collected, the DGM temperature, and the barometric pressure. Calculate a DGM calibration check value, Y_c, as follows:

$$Y_c = \frac{10}{V_m}\left[\frac{0.0319\ T_m}{P_{bar}}\right]^{\frac{1}{2}}$$

where:

Y_c = DGM calibration check value, dimensionless.
10 = Run time, min.

9.2.1.2 Compare the Y_c value with the dry gas meter calibration factor Y to determine that: $0.97Y < Y_c < 1.03Y$. If the Y_c value is not within this range, the volume metering system should be investigated before beginning the test.

9.2.2 Calibrated Critical Orifice. A critical orifice, calibrated against a wet test meter or spirometer and designed to be inserted at the inlet of the sampling meter box, may be used as a check by following the procedure of section 16.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Probe Nozzle. Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the ID of the nozzle to the nearest 0.025 mm (0.001 in.). Make three separate measurements using different diameters each time, and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

10.2 Pitot Tube Assembly. The Type S pitot tube assembly shall be calibrated according to the procedure outlined in section 10.1 of Method 2.

10.3 Metering System.

10.3.1 Calibration Prior to Use. Before its initial use in the field, the metering system shall be calibrated as follows: Connect the metering system inlet to the outlet of a wet test meter that is accurate to within 1 percent. Refer to Figure 5–4. The wet test meter should have a capacity of 30 liters/rev (1 ft^3/rev). A spirometer of 400 liters (14 ft^3) or more capacity, or equivalent, may be used for this calibration, although a wet test meter is usually more practical. The wet test meter should be periodically calibrated with a spirometer or a liquid displacement meter to ensure the accuracy of the wet test meter. Spirometers or wet test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained. Run the metering system pump for about 15 minutes with the orifice manometer indicating a median reading as expected in field use to allow the pump to warm up and to permit the interior surface of the wet test meter to be thoroughly wetted. Then, at each of a minimum of three orifice manometer settings, pass an exact quantity of gas through the wet test meter and note the gas volume indicated by the DGM. Also note the barometric pressure and the temperatures of the wet test meter, the inlet of the DGM, and the outlet of the DGM. Select the highest and lowest orifice settings to bracket the expected field operating range of the orifice. Use a minimum volume of 0.14 m^3 (5 ft^3) at all orifice settings. Record all the data on a form similar to Figure 5–5 and calculate Y, the DGM calibration factor, and ΔH , the orifice calibration factor, at each orifice setting as shown on Figure 5–5. Allowable tolerances for individual Y and ΔH values are given in Figure 5–5. Use the average of the Y values in the calculations in section 12.0.

10.3.1.1 Before calibrating the metering system, it is suggested that a leak check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. For these cases the following leak-check procedure is suggested: make a 10-minute calibration run at 0.00057 m^3/min (0.020 cfm). At the end of the run, take the difference of the measured wet test meter and DGM volumes. Divide the difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 m^3/min (0.020 cfm).

10.3.2 Calibration After Use. After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single, intermediate

orifice setting (based on the previous field test), with the vacuum set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet test meter and the inlet of the metering system. Calculate the average value of the DGM calibration factor. If the value has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as detailed in section 10.3.1.

NOTE: Alternative procedures (*e.g.*, rechecking the orifice meter coefficient) may be used, subject to the approval of the Administrator.

10.3.3 Acceptable Variation in Calibration Check. If the DGM coefficient values obtained before and after a test series differ by more than 5 percent, the test series shall either be voided, or calculations for the test series shall be performed using whichever meter coefficient value (*i.e.*, before or after) gives the lower value of total sample volume.

10.4 Probe Heater Calibration. Use a heat source to generate air heated to selected temperatures that approximate those expected to occur in the sources to be sampled. Pass this air through the probe at a typical sample flow rate while measuring the probe inlet and outlet temperatures at various probe heater settings. For each air temperature generated, construct a graph of probe heating system setting versus probe outlet temperature. The procedure outlined in APTD–0576 can also be used. Probes constructed according to APTD–0581 need not be calibrated if the calibration curves in APTD–0576 are used. Also, probes with outlet temperature monitoring capabilities do not require calibration.

NOTE: The probe heating system shall be calibrated before its initial use in the field.

10.5 Temperature Sensors. Use the procedure in Section 10.3 of Method 2 to calibrate in-stack temperature sensors. Dial thermometers, such as are used for the DGM and condenser outlet, shall be calibrated against mercury-in-glass thermometers. An alternative mercury-free NIST-traceable thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application. As an alternative, the following single-point calibration procedure may be used. After each test run series, check the accuracy (and, hence, the calibration) of each thermocouple system at ambient temperature, or any other temperature, within the range specified by the manufacturer, using a reference thermometer (either ASTM reference thermometer or a thermometer that has been calibrated against an ASTM reference thermometer). The temperatures of the thermocouple and reference thermometers shall agree to within ±2 °F.

10.6 Barometer. Calibrate against a mercury barometer or NIST-traceable barometer prior to the field test. Alternatively, barometric pressure may be obtained from a weather report that has been adjusted for the test point (on the stack) elevation.

10.7 Field Balance Calibration Check. Check the calibration of the balance used to weigh impingers with a weight that is at least 500g or within 50g of a loaded impinger. The weight must be ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 6 (or better). Daily before use, the field balance must measure the weight within ±0.5g of the certified mass. If the daily balance calibration check fails, perform corrective measures and repeat the check before using balance.

10.8 Analytical Balance Calibration. Perform a multipoint calibration (at least five points spanning the operational range) of the analytical balance before the first use, and semiannually thereafter. The calibration of the analytical balance must be conducted using ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 2 (or better) tolerance weights. Audit the balance each day it is used for gravimetric measurements by weighing at least one ASTM E617–13 Class 2 tolerance (or better) calibration weight that corresponds to 50 to 150 percent of the weight of one filter or between 1g and 5g. If the scale cannot reproduce the value of the calibration weight to within 0.5 mg of the certified mass, perform corrective measures, and conduct the multipoint calibration before use.

11.0 Analytical Procedure

11.1 Record the data required on a sheet such as the one shown in Figure 5–6.

11.2 Handle each sample container as follows:

11.2.1 Container No. 1. Leave the contents in the shipping container or transfer the filter and any loose PM from the sample container to a tared glass weighing dish. Desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh to a constant weight, and report the results to the nearest 0.1 mg. For the purposes of this section, the term ''constant weight'' means a difference of no more than 0.5 mg or 1 percent of total weight less tare weight, whichever is greater, between two consecutive weighings, with no less than 6 hours of desiccation time between weighings. Alternatively, the sample may be oven dried at 104 °C (220 °F) for 2 to 3 hours, cooled in the desiccator, and weighed to a constant weight, unless otherwise specified by the Administrator. The sample may be oven dried at 104 °C (220 °F) for 2 to 3 hours. Once the

sample has cooled, weigh the sample, and use this weight as a final weight.

11.2.2 Container No. 2. Note the level of liquid in the container, and confirm on the analysis sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to ±1 ml or gravimetrically to ±0.5 g. Transfer the contents to a tared 250 ml beaker, and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours, and weigh to a constant weight. Report the results to the nearest 0.1 mg.

11.2.3 Container No. 3. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. This step may be conducted in the field.

11.2.4 Acetone Blank Container. Measure the acetone in this container either volumetrically or gravimetrically. Transfer the acetone to a tared 250 ml beaker, and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours, and weigh to a constant weight. Report the results to the nearest 0.1 mg.

NOTE: The contents of Container No. 2 as well as the acetone blank container may be evaporated at temperatures higher than ambient. If evaporation is done at an elevated temperature, the temperature must be below the boiling point of the solvent; also, to prevent ''bumping,'' the evaporation process must be closely supervised, and the contents of the beaker must be swirled occasionally to maintain an even temperature. Use extreme care, as acetone is highly flammable and has a low flash point.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used, provided that they give equivalent results.

12.1 Nomenclature.

A_n = Cross-sectional area of nozzle, m^2 (ft^2).
B_{ws} = Water vapor in the gas stream, proportion by volume.
C_a = Acetone blank residue concentration, mg/mg.
c_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (gr/dscf).
I = Percent of isokinetic sampling.
L_1 = Individual leakage rate observed during the leak-check conducted prior to the first component change, m^3/min (ft^3/min)
L_a = Maximum acceptable leakage rate for either a pretest leak-check or for a leak-check following a component change; equal to 0.00057 m^3/min (0.020 cfm) or 4 percent of the average sampling rate, whichever is less.
L_i = Individual leakage rate observed during the leak-check conducted prior to the ''i^{th}'' component change (i = 1, 2, 3 . . . n), m^3/min (cfm).
L_p = Leakage rate observed during the post-test leak-check, m^3/min (cfm).
m_a = Mass of residue of acetone after evaporation, mg.
m_n = Total amount of particulate matter collected, mg.
M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).
P_s = Absolute stack gas pressure, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
R = Ideal gas constant, 0.06236 ((mm Hg)(m^3))/((K)(g-mole)) {21.85 ((in. Hg) (ft^3))/((°R)(lb-mole))}.
T_m = Absolute average DGM temperature (see Figure 5–3), K (°R).
T_s = Absolute average stack gas temperature (see Figure 5–3), K (°R).
T_{std} = Standard absolute temperature, 293 K (528 °R).
V_a = Volume of acetone blank, ml.
V_{aw} = Volume of acetone used in wash, ml.
V_{1c} = Total volume of liquid collected in impingers and silica gel (see Figure 5–6), ml.
V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).
$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).
$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).
V_s = Stack gas velocity, calculated by Method 2, Equation 2–7, using data obtained from Method 5, m/sec (ft/sec).
W_a = Weight of residue in acetone wash, mg.
Y = Dry gas meter calibration factor.
ΔH = Average pressure differential across the orifice meter (see Figure 5–4), mm H_2O (in. H_2O).
ρ_a = Density of acetone, mg/ml (see label on bottle).
ρ_w = Density of water, 0.9982 g/ml. (0.002201 lb/ml).
θ = Total sampling time, min.
θ_1 = Sampling time interval, from the beginning of a run until the first component change, min.
θ_i = Sampling time interval, between two successive component changes, beginning with the interval between the first and second changes, min.
θ_p = Sampling time interval, from the final (n^{th}) component change until the end of the sampling run, min.
13.6 = Specific gravity of mercury.
60 = Sec/min.

100 = Conversion to percent.

12.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 5–3).

12.3 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (20 °C, 760 mm Hg or 68 °F, 29.92 in. Hg) by using Equation 5–1.

$$V_{m(std)} = V_m Y \frac{T_{std}\left(P_{bar} + \frac{\Delta H}{13.6}\right)}{T_m P_{std}} \qquad \text{Eq. 5-1}$$

$$= K_1 V_m Y \frac{P_{bar} + \left(\frac{\Delta H}{13.6}\right)}{T_m}$$

Where:

K_1 = 0.3858 °K/mm Hg for metric units, = 17.64 °R/in. Hg for English units.

NOTE: Equation 5–1 can be used as written unless the leakage rate observed during any of the mandatory leak checks (*i.e.*, the post-test leak check or leak checks conducted prior to component changes) exceeds L_a. If L_p or L_i exceeds L_a, Equation 5–1 must be modified as follows:

(a) Case I. No component changes made during sampling run. In this case, replace V_m in Equation 5–1 with the expression:

$$\left(V_m - \left(L_p - L_a\right)\theta\right)$$

(b) Case II. One or more component changes made during the sampling run. In this case, replace V_m in Equation 5–1 by the expression:

$$\left[V_m - \left(L_1 - L_a\right)\theta_1 - \sum_{i=2}^{n}\left(L_1 - L_a\right)\theta_i - \left(L_p - L_a\right)\theta_p\right]$$

and substitute only for those leakage rates (L_i or L_p) which exceed L_a.

12.4 Volume of Water Vapor Condensed.

$$V_{w(std)} = V_{1c}\frac{\rho_w R T_{std}}{M_w P_{std}} \qquad \text{Eq. 5-2}$$

$$= K_2 V_{1c}$$

Where:

K_2 = 0.001333 m^3/ml for metric units, = 0.04706 ft^3/ml for English units.

12.5 Moisture Content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad \text{Eq. 5-3}$$

NOTE: In saturated or water droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation 5–3), and a second from the assumption of saturated conditions. The lower of the two values of B_{ws} shall be considered correct. The procedure for determining the moisture content based upon the assumption of saturated conditions is given in section 4.0 of Method 4. For the purposes of this method, the average stack gas temperature from Figure 5–3 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is ±1 °C (2 °F).

12.6 Acetone Blank Concentration.

$$C_a = \frac{m_a}{V_a \rho_a} \qquad \text{Eq. 5-4}$$

12.7 Acetone Wash Blank.

$$W_a = C_a V_{aw} \rho_a \qquad \text{Eq. 5-5}$$

12.8 Total Particulate Weight. Determine the total particulate matter catch from the sum of the weights obtained from Containers 1 and 2 less the acetone blank (see Figure 5–6).

NOTE: In no case shall a blank value of greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight. Refer to section 8.5.8 to assist in calculation of results involving two or more filter assemblies or two or more sampling trains.

12.9 Particulate Concentration.

$$C_s = \frac{K_3 m_n}{V_{m(std)}} \qquad \text{Eq. 5-6}$$

Where:

K_3 = 0.001 g/mg for metric units.
= 0.0154 gr/mg for English units.

12.10 Conversion Factors:

From	To	Multiply by
ft^3	m^3	0.02832
gr	mg	64.80004
gr/ft^3	mg/m^3	2288.4
mg	g	0.001
gr	lb	1.429×10^{-4}

12.11 Isokinetic Variation.

12.11.1 Calculation from Raw Data.

$$I = \frac{100\,T_s\left[K_4 V_{1c} + \frac{(V_m Y)}{T_m}\left(P_{bar} + \frac{\Delta H}{13.6}\right)\right]}{60\,\theta\,v_s\,P_s\,A_n} \qquad \text{Eq. 5-7}$$

Where:

K_4 = 0.003454 ((mm Hg)(m^3))/((ml)(°K)) for metric units,
= 0.002669 ((in. Hg)(ft^3))/((ml)(°R)) for English units.

12.11.2 Calculation from Intermediate Values.

$$I = \frac{T_s V_{m(std)} P_{std} 100}{T_{std} v_s \theta A_n P_s 60(1 - B_{ws})} \qquad \text{Eq. 5-8}$$

$$= K_5 \frac{T_s V_{m(std)}}{P_s v_s A_n \theta (1 - B_{ws})}$$

Where:

K_5 = 4.320 for metric units,
= 0.09450 for English units.

12.11.3 Acceptable Results. If 90 percent ≤I ≤110 percent, the results are acceptable. If the PM results are low in comparison to the standard, and ''I'' is over 110 percent or less than 90 percent, the Administrator may opt to accept the results. Reference 4 in section 17.0 may be used to make acceptability judgments. If ''I'' is judged to be unacceptable, reject the results, and repeat the sampling run.

12.12 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate, if needed, using data obtained in this method and the equations in sections 12.3 and 12.4 of Method 2.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Dry Gas Meter as a Calibration Standard. A DGM may be used as a calibration standard for volume measurements in place of the wet test meter specified in section 10.3, provided that it is calibrated initially and recalibrated periodically as follows:

16.1.1 Standard Dry Gas Meter Calibration.

16.1.1.1. The DGM to be calibrated and used as a secondary reference meter should be of high quality and have an appropriately sized capacity (*e.g.*, 3 liters/rev (0.1 ft^3/rev)). A spirometer (400 liters (14 ft^3) or more capacity), or equivalent, may be used for this calibration, although a wet test meter is usually more practical. The wet test meter should have a capacity of 30 liters/rev (1 ft^3/rev) and capable of measuring volume to within 1.0 percent. Wet test meters should be checked against a spirometer or a liquid displacement meter to ensure the accuracy of the wet test meter. Spirometers or wet test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained.

16.1.1.2 Set up the components as shown in Figure 5–7. A spirometer, or equivalent, may be used in place of the wet test meter in the system. Run the pump for at least 5 minutes at a flow rate of about 10 liters/min (0.35 cfm) to condition the interior surface of the wet test meter. The pressure drop indicated by the manometer at the inlet side of the DGM should be minimized (no greater than 100 mm

H_2O (4 in. H_2O) at a flow rate of 30 liters/min (1 cfm)). This can be accomplished by using large diameter tubing connections and straight pipe fittings.

16.1.1.3 Collect the data as shown in the example data sheet (see Figure 5–8). Make triplicate runs at each of the flow rates and at no less than five different flow rates. The range of flow rates should be between 10 and 34 liters/min (0.35 and 1.2 cfm) or over the expected operating range.

16.1.1.4 Calculate flow rate, Q, for each run using the wet test meter volume, V_w, and the run time, θ. Calculate the DGM coefficient, Y_{ds}, for each run. These calculations are as follows:

$$Q = K_1 \frac{P_{bar} V_w}{(T_w + T_{std})\theta} \qquad \text{Eq. 5-9}$$

$$Y_{ds} = \frac{V_w (T_{ds} + T_{std}) P_{bar}}{V_{ds} (T_w + T_{std}) \left(P_{bar} + \frac{\Delta p}{13.6} \right)} \qquad \text{Eq. 5-10}$$

Where:

K_1 = 0.3858 °C/mm Hg for metric units = 17.64 °F/in. Hg for English units.
V_W = Wet test meter volume, liter (ft^3).
V_{ds} = Dry gas meter volume, liter (ft^3).
T_{ds} = Average dry gas meter temperature, °C (°F).
T_{adj} = 273 °C for metric units = 460 °F for English units.
T_W = Average wet test meter temperature, °C (°F)
P_{bar} = Barometric pressure, mm Hg (in. Hg).
Δp = Dry gas meter inlet differential pressure, mm H_2O (in. H_2O).
θ = Run time, min.

16.1.1.5 Compare the three Y_{ds} values at each of the flow rates and determine the maximum and minimum values. The difference between the maximum and minimum values at each flow rate should be no greater than 0.030. Extra sets of triplicate runs may be made in order to complete this requirement. In addition, the meter coefficients should be between 0.95 and 1.05. If these specifications cannot be met in three sets of successive triplicate runs, the meter is not suitable as a calibration standard and should not be used as such. If these specifications are met, average the three Y_{ds} values at each flow rate resulting in no less than five average meter coefficients, Y_{ds}.

16.1.1.6 Prepare a curve of meter coefficient, Y_{ds}, versus flow rate, Q, for the DGM. This curve shall be used as a reference when the meter is used to calibrate other DGMs and to determine whether recalibration is required.

16.1.2 Standard Dry Gas Meter Recalibration.

16.1.2.1 Recalibrate the standard DGM against a wet test meter or spirometer annually or after every 200 hours of operation, whichever comes first. This requirement is valid provided the standard DGM is kept in a laboratory and, if transported, cared for as any other laboratory instrument. Abuse to the standard meter may cause a change in the calibration and will require more frequent recalibrations.

16.1.2.2 As an alternative to full recalibration, a two-point calibration check may be made. Follow the same procedure and equipment arrangement as for a full recalibration, but run the meter at only two flow rates [suggested rates are 14 and 30 liters/min (0.5 and 1.0 cfm)]. Calculate the meter coefficients for these two points, and compare the values with the meter calibration curve. If the two coefficients are within 1.5 percent of the calibration curve values at the same flow rates, the meter need not be recalibrated until the next date for a recalibration check.

16.2 Critical Orifices As Calibration Standards. Critical orifices may be used as calibration standards in place of the wet test meter specified in section 16.1, provided that they are selected, calibrated, and used as follows:

16.2.1 Selection of Critical Orifices.

16.2.1.1 The procedure that follows describes the use of hypodermic needles or stainless steel needle tubings which have been found suitable for use as critical orifices. Other materials and critical orifice designs may be used provided the orifices act as true critical orifices (*i.e.,* a critical vacuum can be obtained, as described in section 16.2.2.2.3). Select five critical orifices that are appropriately sized to cover the range of flow rates between 10 and 34 liters/min (0.35 and 1.2 cfm) or the expected operating range. Two of the critical orifices should bracket the expected operating range. A minimum of three critical orifices will be needed to calibrate a Method 5 DGM; the other two critical

orifices can serve as spares and provide better selection for bracketing the range of operating flow rates. The needle sizes and tubing lengths shown in Table 5–1 in section 18.0 give the approximate flow rates.

16.2.1.2 These needles can be adapted to a Method 5 type sampling train as follows: Insert a serum bottle stopper, 13 by 20 mm sleeve type, into a ½-inch Swagelok (or equivalent) quick connect. Insert the needle into the stopper as shown in Figure 5–9.

16.2.2 Critical Orifice Calibration. The procedure described in this section uses the Method 5 meter box configuration with a DGM as described in section 6.1.1.9 to calibrate the critical orifices. Other schemes may be used, subject to the approval of the Administrator.

16.2.2.1 Calibration of Meter Box. The critical orifices must be calibrated in the same configuration as they will be used (*i.e.*, there should be no connections to the inlet of the orifice).

16.2.2.1.1 Before calibrating the meter box, leak check the system as follows: Fully open the coarse adjust valve, and completely close the by-pass valve. Plug the inlet. Then turn on the pump, and determine whether there is any leakage. The leakage rate shall be zero (*i.e.*, no detectable movement of the DGM dial shall be seen for 1 minute).

16.2.2.1.2 Check also for leakages in that portion of the sampling train between the pump and the orifice meter. See section 8.4.1 for the procedure; make any corrections, if necessary. If leakage is detected, check for cracked gaskets, loose fittings, worn O-rings, etc., and make the necessary repairs.

16.2.2.1.3 After determining that the meter box is leakless, calibrate the meter box according to the procedure given in section 10.3. Make sure that the wet test meter meets the requirements stated in section 16.1.1.1. Check the water level in the wet test meter. Record the DGM calibration factor, Y.

16.2.2.2 Calibration of Critical Orifices. Set up the apparatus as shown in Figure 5–10.

16.2.2.2.1 Allow a warm-up time of 15 minutes. This step is important to equilibrate the temperature conditions through the DGM.

16.2.2.2.2 Leak check the system as in section 16.2.2.1.1. The leakage rate shall be zero.

16.2.2.2.3 Before calibrating the critical orifice, determine its suitability and the appropriate operating vacuum as follows: Turn on the pump, fully open the coarse adjust valve, and adjust the by-pass valve to give a vacuum reading corresponding to about half of atmospheric pressure. Observe the meter box orifice manometer reading, ΔH. Slowly increase the vacuum reading until a stable reading is obtained on the meter box orifice manometer. Record the critical vacuum for each orifice. Orifices that do not reach a critical value shall not be used.

16.2.2.2.4 Obtain the barometric pressure using a barometer as described in section 6.1.2. Record the barometric pressure, P_{bar}, in mm Hg (in. Hg).

16.2.2.2.5 Conduct duplicate runs at a vacuum of 25 to 50 mm Hg (1 to 2 in. Hg) above the critical vacuum. The runs shall be at least 5 minutes each. The DGM volume readings shall be in increments of complete revolutions of the DGM. As a guideline, the times should not differ by more than 3.0 seconds (this includes allowance for changes in the DGM temperatures) to achieve ±0.5 percent in K′ (see Eq. 5–11). Record the information listed in Figure 5–11.

16.2.2.2.6 Calculate K′ using Equation 5–11.

$$K' = \frac{K_1 V_m Y \left(P_{bar} + \frac{\Delta H}{13.6} \right) T_{amb}^{1/2}}{P_{bar} T_m \theta} \qquad \text{Eq. 5-11}$$

Where:

K′ = Critical orifice coefficient,
$[m^3)(°K)^{1/2}]/$
$[(mm\ Hg)(min)]\ \{[(ft^3)(°R)^{1/2})]\ [(in.\ Hg)(min)]$.
T_{amb} = Absolute ambient temperature, °K (°R).

Calculate the arithmetic mean of the K′ values. The individual K' values should not differ by more than ±0.5 percent from the mean value.

16.2.3 Using the Critical Orifices as Calibration Standards.

16.2.3.1 Record the barometric pressure.

16.2.3.2 Calibrate the metering system according to the procedure outlined in section 16.2.2. Record the information listed in Figure 5–12.

16.2.3.3 Calculate the standard volumes of air passed through the DGM and the critical orifices, and calculate the DGM calibration factor, Y, using the equations below:

$$V_{m(std)} = \frac{K_1 V_m \left[P_{bar} + \left(\frac{\Delta H}{13.6} \right) \right]}{T_m} \qquad \text{Eq. 5-12}$$

$$V_{cr(std)} = K' \frac{P_{bar}\theta}{\sqrt{T_{amb}}} \qquad \text{Eq. 5-13}$$

$$Y = \frac{V_{cr\ (std)}}{V_{m(std)}} \qquad \text{Eq. 5-14}$$

Where:

$V_{cr(std)}$ = Volume of gas sample passed through the critical orifice, corrected to standard conditions, dscm (dscf).

K_1 = 0.3858 K/mm Hg for metric units
= 17.64 °R/in. Hg for English units.

16.2.3.4 Average the DGM calibration values for each of the flow rates. The calibration factor, Y, at each of the flow rates should not differ by more than ±2 percent from the average.

16.2.3.5 To determine the need for recalibrating the critical orifices, compare the DGM Y factors obtained from two adjacent orifices each time a DGM is calibrated; for example, when checking orifice 13/2.5, use orifices 12/10.2 and 13/5.1. If any critical orifice yields a DGM Y factor differing by more than 2 percent from the others, recalibrate the critical orifice according to section 16.2.2.

16.3 Alternative Post-Test Metering System Calibration. The following procedure may be used as an alternative to the post-test calibration described in Section 10.3.2. This alternative procedure does not detect leakages between the inlet of the metering system and the dry gas meter. Therefore, two steps must be included to make it an equivalent alternative:

(1) The metering system must pass the post-test leak-check from either the inlet of the sampling train or the inlet of the metering system. Therefore, if the train fails the former leak-check, another leak-check from the inlet of the metering system must be conducted;

(2) The metering system must pass the leak-check of that portion of the train from the pump to the orifice meter as described in Section 8.4.1.

16.3.1 After each test run, do the following:

16.3.1.1 Ensure that the metering system has passed the post-test leak-check. If not, conduct a leak-check of the metering system from its inlet.

16.3.1.2 Conduct the leak-check of that portion of the train from the pump to the orifice meter as described in Section 10.3.1.1.

16.3.1.3 Calculate Y_{qa} for each test run using the following equation:

$$Y_{qa} = \frac{\theta}{V_m} \sqrt{\frac{0.0319 T_m}{\Delta H@ \left(P_{bar} + \frac{\Delta H_{avg}}{13.6} \right)} \left(\frac{29}{M_d} \right)} \left(\sqrt{\Delta H} \right)_{avg} \qquad \text{Eq. 5-15}$$

Where:

Y_{qa} = Dry gas meter calibration check value, dimensionless.

0.0319 = (29.92/528) (0.75)^2 (in. Hg/°R) cfm^2.

$\Delta H@$ = Orifice meter calibration coefficient, in. H_2O.

M_d = Dry molecular weight of stack gas, lb/lb-mole.

29 = Dry molecular weight of air, lb/lb-mole.

16.3.2 After each test run series, do the following:

16.3.2.1 Average the three or more Y_{qa}'s obtained from the test run series and compare this average Y_{qa} with the dry gas meter calibration factor Y. The average Y_{qa} must be within 5 percent of Y.

16.3.2.2 If the average Y_{qa} does not meet the 5 percent criterion, recalibrate the meter

over the full range of orifice settings as detailed in Section 10.3.1. Then follow the procedure in Section 10.3.3.

17.0 References.

1. Addendum to Specifications for Incinerator Testing at Federal Facilities. PHS, NCAPC. December 6, 1967.

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18.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 5–1 FLOR RATES FOR VARIOUS NEEDLE SIZES AND TUBE LENGTHS

Gauge/cm	Flow rate liters/min.	Gauge/cm	Flow rate liters/min.
12/7.6	32.56	14/2.5	19.54
12/10.2	30.02	14/5.1	17.27
13/2.5	25.77	14/7.6	16.14
13/5.1	23.50	15/3.2	14.16
13/7.6	22.37	15/7.6	11.61
13/10.2	20.67	15/10.2	10.48

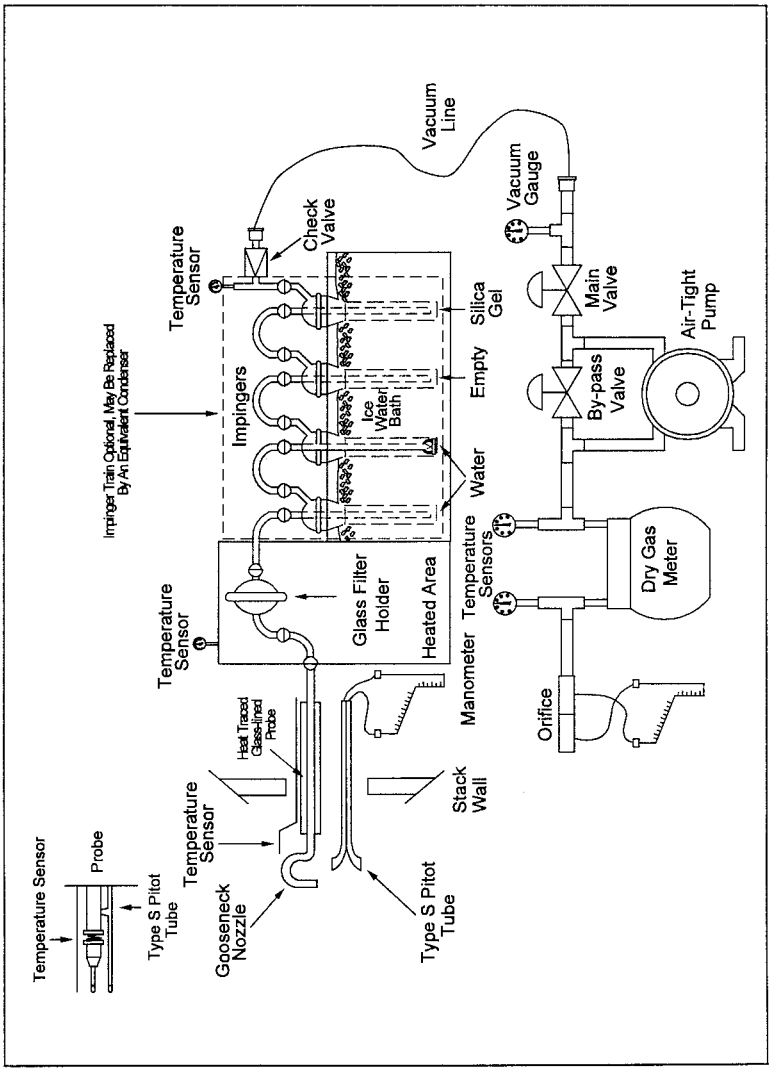

Figure 5-1. Particulate Sampling Train.

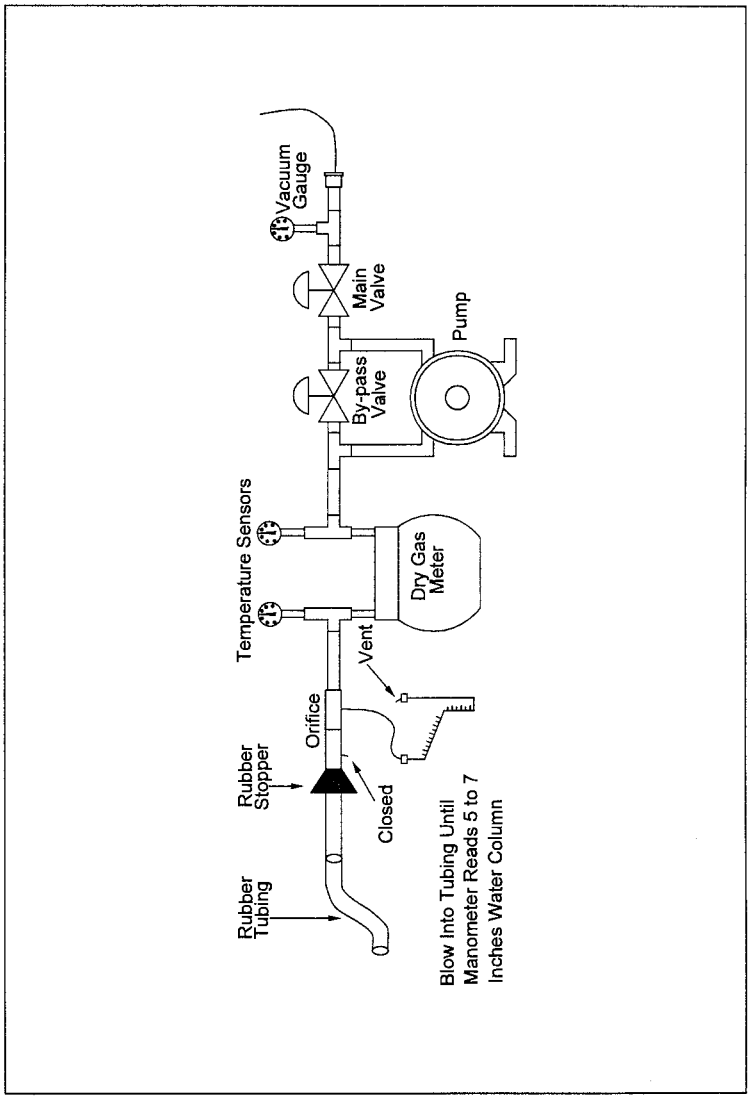

Figure 5-2. Leak Check of Meter Box.

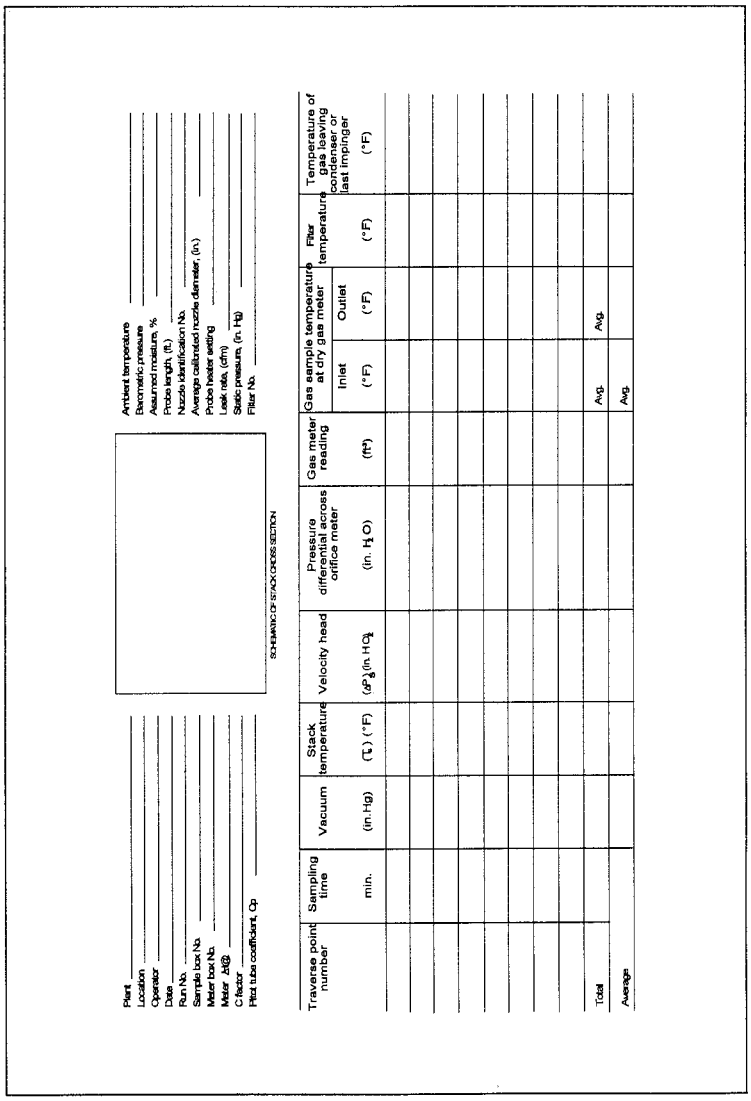

Figure 5-3. Particulate Field Data.

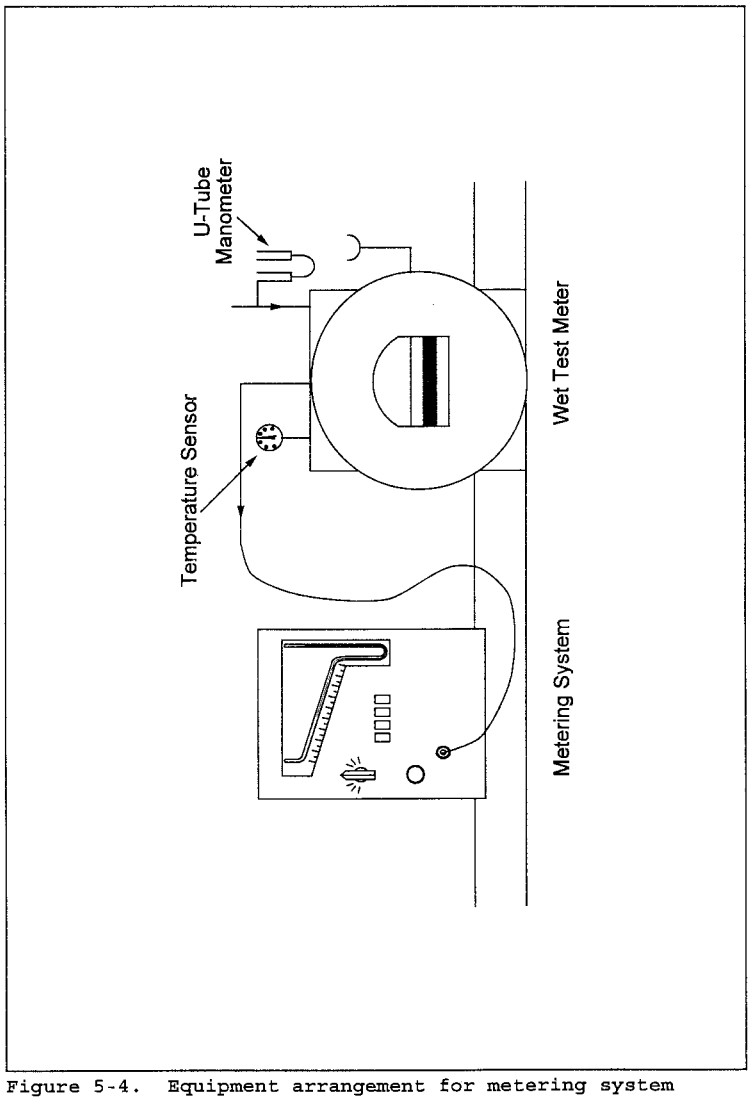

Figure 5-4. Equipment arrangement for metering system calibration.

Date: _____ Metering System Identification: _____
Barometric pressure, P_b = _____ in. Hg

Orifice manometer setting ΔH in. H_2O	Spirometer (wet meter) gas volume, V_w, ft^3	Dry gas meter volume, V_m, ft^3	Temperatures: Spirometer (wet meter) T_w °F	Temperatures: Dry Gas Meter Inlet T_i °F	Temperatures: Dry Gas Meter Outlet T_o °F	Temperatures: Dry Gas Meter Average T_m °F	Time θ min	Calculations: ΔH in H_2O	Calculations: Y	Calculations: ΔH@
Average										

Y = Ratio of reading of wet test meter to dry test meter; tolerance for individual values ± 0.02 from average.
$\Delta H_@$ = Orifice pressure differential that equates to 0.75 cfm of air @ 68°F and 29.92 inches of mercury, in. H_2O; tolerance for individual values ± 0.20 from average.

Figure 5-5. Example Data Sheet for Calibration of Metering System (English Units).

Plant _____
Date _____
Run No. _____
Filter No. _____
Amount liquid lost during transport _____

Acetone blank volume, m1 _____
Acetone blank concentration, mg/mg (Equation 5–4) _____
Acetone wash blank, mg (Equation 5–5) ____

Container number	Weight of particulate collected, mg		
	Final weight	Tare weight	Weight gain
1.			
2.			
Total: Less acetone blank. Weight of particulate matter.			

	Volume of liquid water collected	
	Impinger volume, ml	Silica gel weight, g
Final Initial Liquid collected Total volume collected	.....	g* ml

*Convert weight of water to volume by dividing total weight increase by density of water (1 g/ml).

Figure 5–6. Analytical Data Sheet

$$\frac{\text{Increase, g}}{(1\text{g/ml})} = \text{Volume water, ml}$$

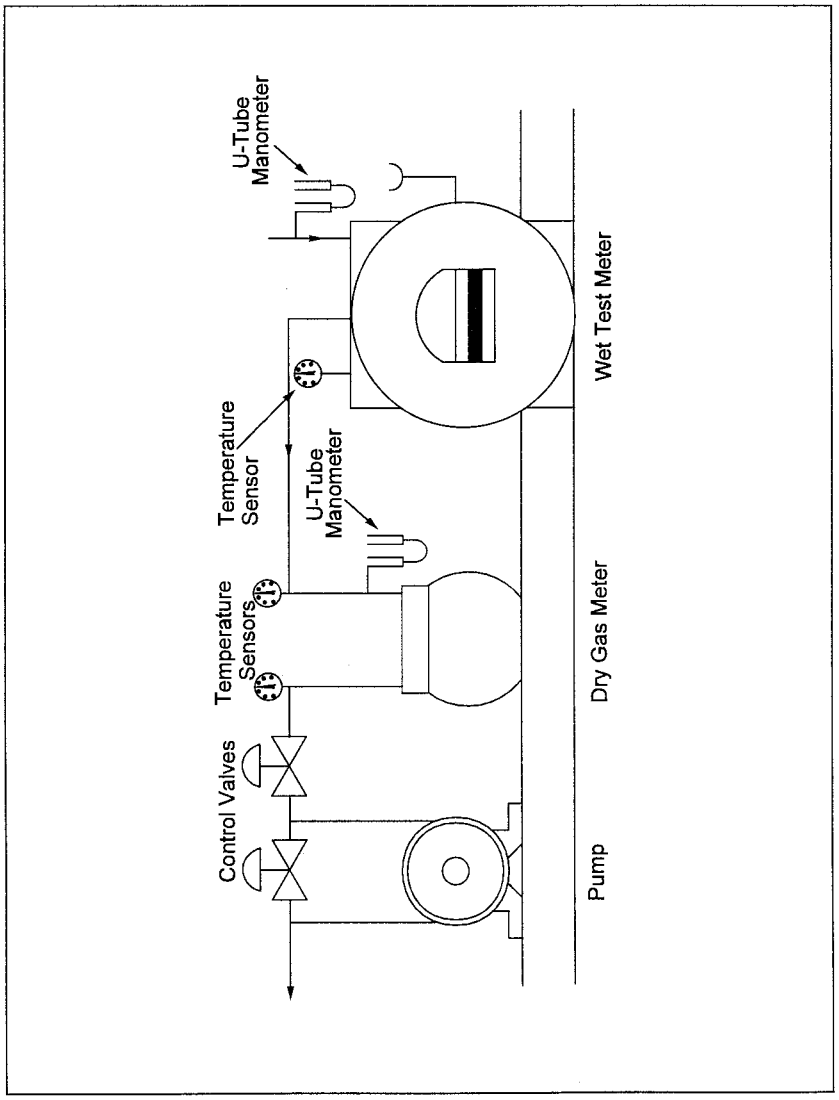

Figure 5-7. Equipment Arrangement for Dry Gas Meter Calibration.

Date: _____

Dry Gas Meter Identification: _____

Barometric Pressure (P): _____ in. Hg

Approximate Flow Rate (Q) cfm	Spirometer (Wet Meter) Gas Volume (V_s) ft³	Dry Gas Meter Volume (V_{dg}) ft³	Temperatures: Spirometer (Wet Meter) (t_g) °F	Temperatures: Dry Gas Meter Inlet (t_i) °F	Temperatures: Dry Gas Meter Outlet (t_o) °F	Temperatures: Dry Gas Meter Average (t_d) °F	Dry Gas Meter Pressure (Δp) in. H_2O	Time (θ) ft³	Flow Rate (Q) cfm	Meter Coefficient (Y_{ds})	Average Meter Coefficient ($\overline{Y}_{ds}$)
0.40											
0.60											
0.80											
1.00											
1.20											

$$Q = K_1 \frac{P_{bar} V_w}{(T_w + T_{std}) \theta}$$

$$Y_{ds} = \frac{V_w (T_{ds} + T_{std}) P_{bar}}{V_{ds} (T_w + T_{std}) (P_{bar} + \Delta P/13.6)}$$

Figure 5-8. Example Data Sheet for Calibration of a Standard Dry Gas Meter for Method 5 Sampling Equipment (English units).

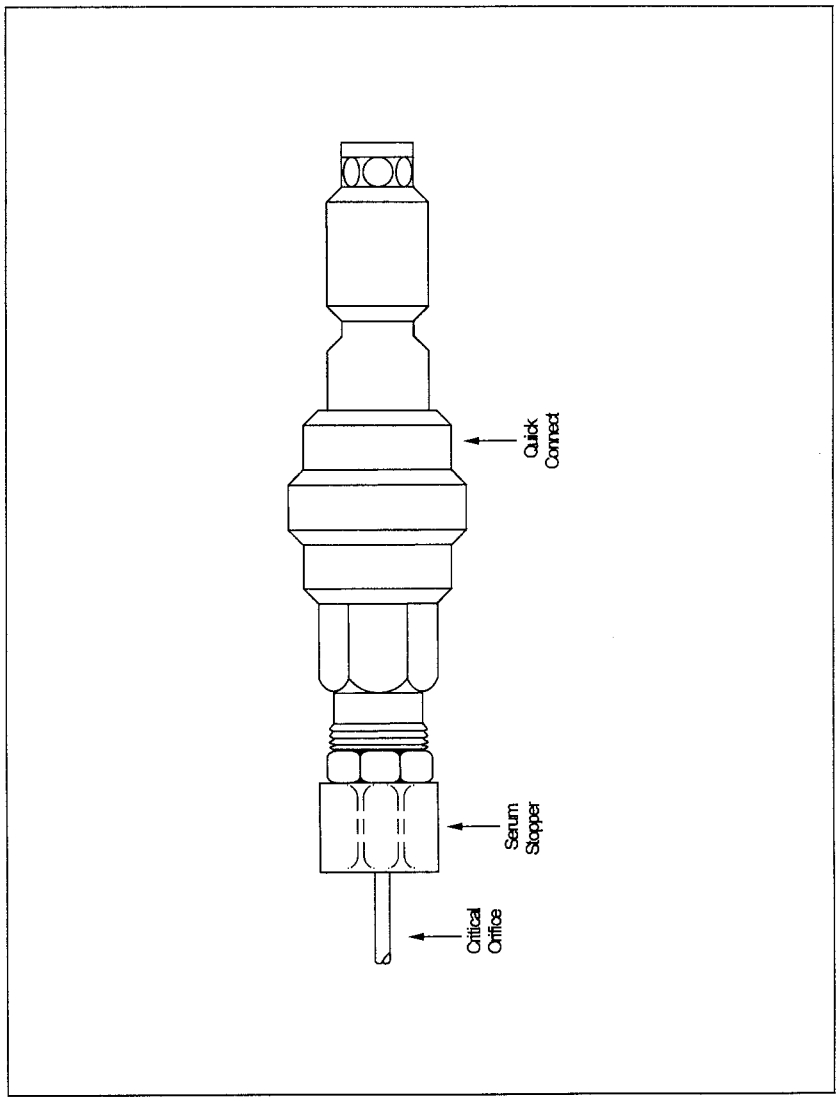

Figure 5-9. Critical Orifice Adaptation to Method 5 Metering System.

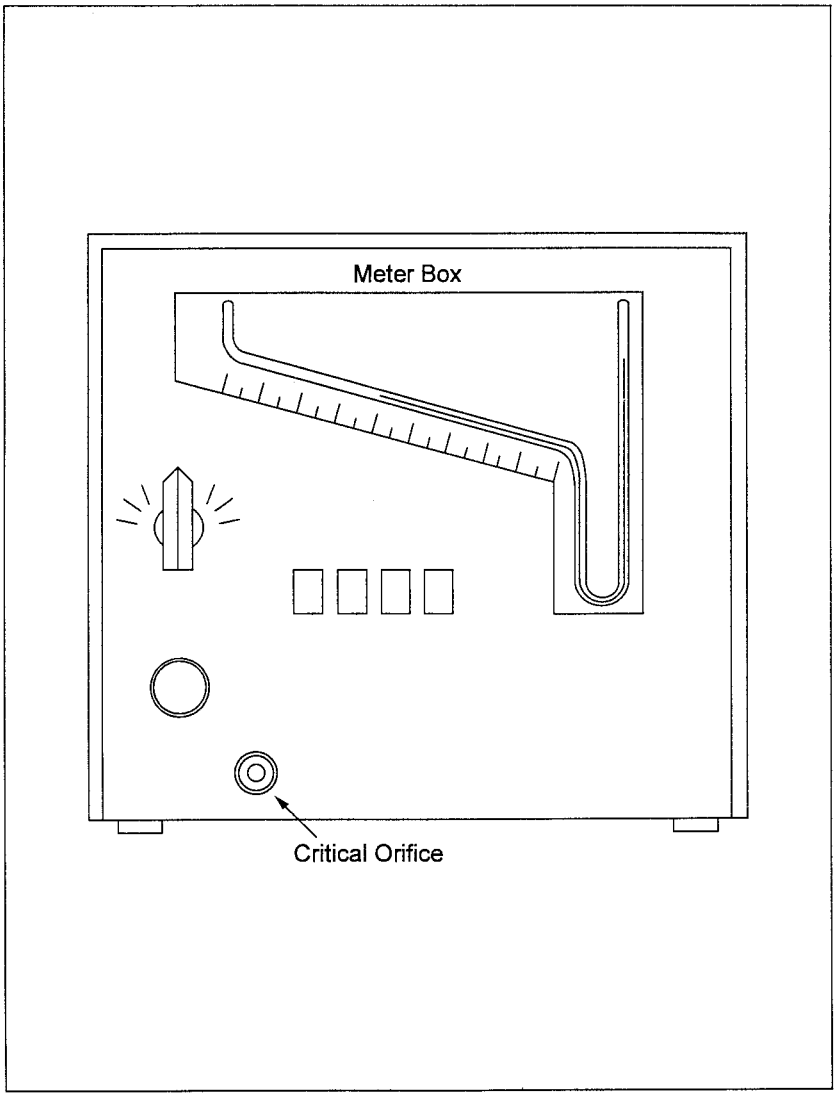

Figure 5-10. Apparatus Setup.

Date _____ DGM cal. factor _____
Train ID _____ Critical orifice ID _____

Dry gas meter		Run No.	
		1	2
Final reading	m^3 (ft^3)		
Initial reading	m^3 (ft^3)		
Difference, V_m	m^3 (ft^3)		
Inlet/Outlet			

Dry gas meter		Run No.	
		1	2
Temperatures:	°C (°F)	/	/
Initial	°C (°F)	/	/
Final	min/sec	/	/
Av. Temeperature, t_m	min		
Time, θ			
Orifice man. rdg., ΔH	mm (in.) H_2		
Bar. pressure, P^{bar}	mm (in.) Hg		
Ambient temperature, t_{amb}	mm (in.) Hg		
Pump vacuum			
K′ factor			
Average			

Figure 5–11. Data sheet of determining K′ factor.

Train ID _____
Critical orifice ID _____
Critical orifice K' factor _____

Date _____

Dry gas meter		Run No.	
		1	2
Final reading	m^3 (ft^3)		
Initial reading	m^3 (ft^3)		
Difference, V_m	m^3 (ft^3)		
Inlet/outlet temperatures	°C (°F)	/	/
Initial	°C (°F)	/	/
Final	°C (°F)		
Avg. Temperature, t_m	min/sec	/	/
Time, θ	min		
Orifice man. rdg., ΔH	min		
Bar. pressure, P_{bar}	mm (in.) H_2O		
Ambient temperature, t_{amb}	mm (in.) Hg		
Pump vacuum	°C (°F)		
$V_{m(std)}$	mm (in.) Hg		
$V_{cr(std)}$	m^3 (ft^3)		
DGM cal. factor, Y	m^3 (ft^3)		

Figure 5–12. Data Sheet for Determining DGM Y Factor

Method 5A—Determination of Particulate Matter Emissions From the Asphalt Processing and Asphalt Roofing Industry

Note: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5.

1.0 Scope and Applications

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of PM emissions from asphalt roofing industry process saturators, blowing stills, and other sources as specified in the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature of 42 ±10 °C (108 ±18 °F). The PM mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after the removal of uncombined water.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the

applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 5, section 6.1, with the following exceptions and additions:

6.1.1 Probe Liner. Same as Method 5, section 6.1.1.2, with the note that at high stack gas temperatures greater than 250 °C (480 °F), water-cooled probes may be required to control the probe exit temperature to 42 ±10 °C (108 ±18 °F).

6.1.2 Precollector Cyclone. Borosilicate glass following the construction details shown in Air Pollution Technical Document (APTD)–0581, ''Construction Details of Isokinetic Source-Sampling Equipment'' (Reference 2 in Method 5, section 17.0).

NOTE: The cyclone shall be used when the stack gas moisture is greater than 10 percent, and shall not be used otherwise.

6.1.3 Filter Heating System. Any heating (or cooling) system capable of maintaining a sample gas temperature at the exit end of the filter holder during sampling at 42 ±10 °C (108 ±18 °F).

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Probe-Liner and Probe-Nozzle Brushes, Graduated Cylinder and/or Balance, Plastic Storage Containers, and Funnel and Rubber Policeman. Same as in Method 5, sections 6.2.1, 6.2.5, 6.2.6, and 6.2.7, respectively.

6.2.2 Wash Bottles. Glass.

6.2.3 Sample Storage Containers. Chemically resistant 500-ml or 1,000-ml borosilicate glass bottles, with rubber-backed Teflon screw cap liners or caps that are constructed so as to be leak-free, and resistant to chemical attack by 1,1,1-trichloroethane (TCE). (Narrow-mouth glass bottles have been found to be less prone to leakage.)

6.2.4 Petri Dishes. Glass, unless otherwise specified by the Administrator.

6.2.5 Funnel. Glass.

6.3 Sample Analysis. Same as Method 5, section 6.3, with the following additions:

6.3.1 Beakers. Glass, 250-ml and 500-ml.

6.3.2 Separatory Funnel. 100-ml or greater.

7.0. Reagents and Standards

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Filters, Silica Gel, Water, and Crushed Ice. Same as in Method 5, sections 7.1.1, 7.1.2, 7.1.3, and 7.1.4, respectively.

7.1.2 Stopcock Grease. TCE-insoluble, heat-stable grease (if needed). This is not necessary if screw-on connectors with Teflon sleeves, or similar, are used.

7.2 Sample Recovery. Reagent grade TCE, ≤0.001 percent residue and stored in glass bottles. Run TCE blanks before field use, and use only TCE with low blank values (≤0.001 percent). In no case shall a blank value of greater than 0.001 percent of the weight of TCE used be subtracted from the sample weight.

7.3 Analysis. Two reagents are required for the analysis:

7.3.1 TCE. Same as in section 7.2.

7.3.2 Desiccant. Same as in Method 5, section 7.3.2.

8.0. Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation. Unless otherwise specified, maintain and calibrate all components according to the procedure described in APTD–0576, ''Maintenance, Calibration, and Operation of Isokinetic Source-Sampling Equipment'' (Reference 3 in Method 5, Section 17.0). Alternative mercury-free thermometers may be used if the thermometers are, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

8.1.1 Prepare probe liners and sampling nozzles as needed for use. Thoroughly clean each component with soap and water followed by a minimum of three TCE rinses. Use the probe and nozzle brushes during at least one of the TCE rinses (refer to section 8.7 for rinsing techniques). Cap or seal the open ends of the probe liners and nozzles to prevent contamination during shipping.

8.1.2 Prepare silica gel portions and glass filters as specified in Method 5, section 8.1.

8.2 Preliminary Determinations. Select the sampling site, probe nozzle, and probe length as specified in Method 5, section 8.2. Select a total sampling time greater than or equal to the minimum total sampling time specified in the ''Test Methods and Procedures'' section of the applicable subpart of the regulations. Follow the guidelines outlined in Method 5, section 8.2 for sampling time per point and total sample volume collected.

8.3 Preparation of Sampling Train. Prepare the sampling train as specified in Method 5, section 8.3, with the addition of the precollector cyclone, if used, between the probe and filter holder. The temperature of the precollector cyclone, if used, should be maintained in the same range as that of the filter, *i.e.*, 42 ±10 °C (108 ±18 °F). Use no stopcock grease on ground glass joints unless grease is insoluble in TCE.

8.4 Leak-Check Procedures. Same as Method 5, section 8.4.

8.5 Sampling Train Operation. Operate the sampling train as described in Method 5, section 8.5, except maintain the temperature of the gas exiting the filter holder at 42 ±10 °C (108 ±18 °F).

8.6 Calculation of Percent Isokinetic. Same as Method 5, section 8.6.

8.7 Sample Recovery. Same as Method 5, section 8.7.1 through 8.7.6.1, with the addition of the following:

8.7.1 Container No. 2 (Probe to Filter Holder).

8.7.1.1 Taking care to see that material on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover PM or any condensate from the probe nozzle, probe fitting, probe liner, precollector cyclone and collector flask (if used), and front half of the filter holder by washing these components with TCE and placing the wash in a glass container. Carefully measure the total amount of TCE used in the rinses. Perform the TCE rinses as described in Method 5, section 8.7.6.2, using TCE instead of acetone.

8.7.1.2 Brush and rinse the inside of the cyclone, cyclone collection flask, and the front half of the filter holder. Brush and rinse each surface three times or more, if necessary, to remove visible PM.

8.7.2 Container No. 3 (Silica Gel). Same as in Method 5, section 8.7.6.3.

8.7.3 Impinger Water. Same as Method 5, section 8.7.6.4.

8.8 Blank. Save a portion of the TCE used for cleanup as a blank. Take 200 ml of this TCE directly from the wash bottle being used, and place it in a glass sample container labeled ''TCE Blank.''

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4, 10.0	Sampling equipment leak check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.

9.2 A quality control (QC) check of the volume metering system at the field site is suggested before collecting the sample. Use the procedure outlined in Method 5, section 9.2.

10.0 Calibration and Standardization

Same as Method 5, section 10.0.

11.0 Analytical Procedures

11.1 Analysis. Record the data required on a sheet such as the one shown in Figure 5A–1. Handle each sample container as follows:

11.1.1 Container No. 1 (Filter). Transfer the filter from the sample container to a tared glass weighing dish, and desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Rinse Container No. 1 with a measured amount of TCE, and analyze this rinse with the contents of Container No. 2. Weigh the filter to a constant weight. For the purpose of this analysis, the term ''constant weight'' means a difference of no more than 10 percent of the net filter weight or 2 mg (whichever is greater) between two consecutive weighings made 24 hours apart. Report the ''final weight'' to the nearest 0.1 mg as the average of these two values.

11.1.2 Container No. 2 (Probe to Filter Holder).

11.1.2.1 Before adding the rinse from Container No. 1 to Container No. 2, note the level of liquid in Container No. 2, and confirm on the analysis sheet whether leakage occurred during transport. If noticeable leakage occurred, either void the sample or take steps, subject to the approval of the Administrator, to correct the final results.

11.1.2.2 Add the rinse from Container No. 1 to Container No. 2 and measure the liquid in this container either volumetrically to ±1 ml or gravimetrically to ±0.5 g. Check to see whether there is any appreciable quantity of condensed water present in the TCE rinse (look for a boundary layer or phase separation). If the volume of condensed water appears larger than 5 ml, separate the oil-TCE fraction from the water fraction using a separatory funnel. Measure the volume of the water phase to the nearest ml; adjust the stack gas moisture content, if necessary (see sections 12.3 and 12.4). Next, extract the water phase with several 25-ml portions of TCE until, by visual observation, the TCE does not remove any additional organic material. Transfer the remaining water fraction to a tared beaker and evaporate to dryness at 93 °C (200 °F), desiccate for 24 hours, and weigh to the nearest 0.1 mg.

11.1.2.3 Treat the total TCE fraction (including TCE from the filter container rinse and water phase extractions) as follows: Transfer the TCE and oil to a tared beaker, and evaporate at ambient temperature and pressure. The evaporation of TCE from the solution may take several days. Do not desiccate the sample until the solution reaches an apparent constant volume or until the odor of TCE is not detected. When it appears that the TCE has evaporated, desiccate the sample, and weigh it at 24-hour intervals to obtain a ''constant weight'' (as defined for Container No. 1 above). The ''total weight'' for Container No. 2 is the sum of the evaporated PM weight of the TCE-oil and water phase fractions. Report the results to the nearest 0.1 mg.

11.1.3 Container No. 3 (Silica Gel). This step may be conducted in the field. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance.

11.1.4 ''TCE Blank'' Container. Measure TCE in this container either volumetrically or gravimetrically. Transfer the TCE to a tared 250-ml beaker, and evaporate to dryness at ambient temperature and pressure.

Desiccate for 24 hours, and weigh to a constant weight. Report the results to the nearest 0.1 mg.

NOTE: In order to facilitate the evaporation of TCE liquid samples, these samples may be dried in a controlled temperature oven at temperatures up to 38 °C (100 °F) until the liquid is evaporated.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

12.1 Nomenclature. Same as Method 5, section 12.1, with the following additions:

C_t = TCE blank residue concentration, mg/g.
m_t = Mass of residue of TCE blank after evaporation, mg.
V_{pc} = Volume of water collected in precollector, ml.
V_t = Volume of TCE blank, ml.
V_{tw} = Volume of TCE used in wash, ml.
W_t = Weight of residue in TCE wash, mg.
ρ_t = Density of TCE (see label on bottle), g/ml.

12.2 Dry Gas Meter Temperature, Orifice Pressure Drop, and Dry Gas Volume. Same as Method 5, sections 12.2 and 12.3, except use data obtained in performing this test.

12.3 Volume of Water Vapor.

$$V_{w(std)} = K_2\left(V_{1c} + V_{pc}\right) \qquad \text{Eq. 5A-1}$$

Where:

K_2 = 0.001333 m^3/ml for metric units.
= 0.04706 ft^3/ml for English units.

12.4 Moisture Content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad \text{Eq. 5A-2}$$

NOTE: In saturated or water droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger and precollector analysis (Equations 5A–1 and 5A–2) and a second from the assumption of saturated conditions. The lower of the two values of moisture content shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in section 4.0 of Method 4. For the purpose of this method, the average stack gas temperature from Figure 5–3 of Method 5 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is within 1 °C (2 °F).

12.5 TCE Blank Concentration.

$$C_t = \frac{m_t}{V_t \rho_t} \qquad \text{Eq. 5A-3}$$

NOTE: In no case shall a blank value of greater than 0.001 percent of the weight of TCE used be subtracted from the sample weight.

12.6 TCE Wash Blank.

$$W_t = C_t V_{tw} \rho_t \qquad \text{Eq. 5A-4}$$

12.7 Total PM Weight. Determine the total PM catch from the sum of the weights obtained from Containers 1 and 2, less the TCE blank.

12.8 PM Concentration.

$$c_s = K_3 \frac{m_n}{V_{m(std)}} \qquad \text{Eq. 5A-5}$$

Where:

K_3 = 0.001 g/mg for metric units
= 0.0154 gr/mg for English units

12.9 Isokinetic Variation. Same as in Method 5, section 12.11.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 5, section 17.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

Plant _____
Date _____
Run No. _____
Filter No. _____
Amount liquid lost during transport _____
Acetone blank volume, ml _____
Acetone blank concentration, mg/mg (Equation 5–4) _____
Acetone wash blank, mg (Equation 5–5) _____

Container number	Weight of particulate collected, mg		
	Final weight	Tare weight	Weight gain
1.			
2.			
Total: Less acetone blank.			

Container number	Weight of particulate collected, mg		
	Final weight	Tare weight	Weight gain
Weight of particulate matter.			

	Volume of liquid water collected	
	Impinger volume, ml	Silica gel weight, g
Final		
Initial		
Liquid collected		
Total volume collected		g* ml

*Convert weight of water to volume by dividing total weight increase by density of water (1 g/ml).

$$\frac{\text{Increase, g}}{(1\text{g/ml})} = \text{Volume water, ml}$$

METHOD 5B—DETERMINATION OF NONSULFURIC ACID PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5.

1.0 Scope and Application

1.1 Analyte. Nonsulfuric acid particulate matter. No CAS number assigned.

1.2 Applicability. This method is determining applicable for the determination of nonsulfuric acid particulate matter from stationary sources, only where specified by an applicable subpart of the regulations or where approved by the Administrator for a particular application.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature of 160 ±14 °C (320 ±25 °F). The collected sample is then heated in an oven at 160 °C (320 °F) for 6 hours to volatilize any condensed sulfuric acid that may have been collected, and the nonsulfuric acid particulate mass is determined gravimetrically.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

Same as Method 5, section 6.0, with the following addition and exceptions:

6.1 Sample Collection. The probe liner heating system and filter heating system must be capable of maintaining a sample gas temperature of 160 ±14 °C (320 ±25 °F).

6.2 Sample Preparation. An oven is required for drying the sample.

7.0 Reagents and Standards

Same as Method 5, section 7.0.

8.0 Sample Collection, Preservation, Storage, and Transport.

Same as Method 5, with the exception of the following:

8.1 Initial Filter Tare. Oven dry the filter at 160 ±5 °C (320 ±10 °F) for 2 to 3 hours, cool in a desiccator for 2 hours, and weigh. Desiccate to constant weight to obtain the initial tare weight. Use the applicable specifications and techniques of section 8.1.3 of Method 5 for this determination.

8.2 Probe and Filter Temperatures. Maintain the probe outlet and filter temperatures at 160 ±14 °C (320 ±25 °F).

9.0 Quality Control

Same as Method 5, section 9.0.

10.0 Calibration and Standardization

Same as Method 5, section 10.0.

11.0 Analytical Procedure

Same as Method 5, section 11.0, except replace section

11.2.2 With the following:

11.1 Container No. 2. Note the level of liquid in the container, and confirm on the analysis sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to ±1 ml or gravimetrically to ±0.5 g. Transfer the contents to a tared 250 ml beaker, and evaporate to dryness at ambient temperature and pressure. Then oven dry the probe and filter samples at a temperature of 160 ±5 °C (320 ±10 °F) for 6 hours. Cool in a desiccator for 2 hours, and weigh to constant weight. Report the results to the nearest 0.1 mg.

12.0 Data Analysis and Calculations

Same as in Method 5, section 12.0.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 5, section 17.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 5C [RESERVED]

METHOD 5D—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM POSITIVE PRESSURE FABRIC FILTERS

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, Method 17.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability.

1.2.1 This method is applicable for the determination of PM emissions from positive pressure fabric filters. Emissions are determined in terms of concentration (mg/m^3 or gr/ft^3) and emission rate (kg/hr or lb/hr).

1.2.2 The General Provisions of 40 CFR part 60, §60.8(e), require that the owner or operator of an affected facility shall provide performance testing facilities. Such performance testing facilities include sampling ports, safe sampling platforms, safe access to sampling sites, and utilities for testing. It is intended that affected facilities also provide sampling locations that meet the specification for adequate stack length and minimal flow disturbances as described in Method 1. Provisions for testing are often overlooked factors in designing fabric filters or are extremely costly. The purpose of this procedure is to identify appropriate alternative locations and procedures for sampling the emissions from positive pressure fabric filters. The requirements that the affected facility owner or operator provide adequate access to performance testing facilities remain in effect.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature at or above the exhaust gas temperature up to a nominal 120 °C (248 ±25 °F). The particulate mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after the removal of uncombined water.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

Same as section 6.0 of either Method 5 or Method 17.

7.0 Reagents and Standards

Same as section 7.0 of either Method 5 or Method 17.

8.0 Sample Collection, Preservation, Storage, and Transport

Same section 8.0 of either Method 5 or Method 17, except replace section 8.2.1 of Method 5 with the following:

8.1 Determination of Measurement Site. The configuration of positive pressure fabric filter structures frequently are not amenable

to emission testing according to the requirements of Method 1. Following are several alternatives for determining measurement sites for positive pressure fabric filters.

8.1.1 Stacks Meeting Method 1 Criteria. Use a measurement site as specified in Method 1, section 11.1.

8.1.2 Short Stacks Not Meeting Method 1 Criteria. Use stack extensions and the procedures in Method 1. Alternatively, use flow straightening vanes of the ''egg-crate'' type (see Figure 5D–1). Locate the measurement site downstream of the straightening vanes at a distance equal to or greater than two times the average equivalent diameter of the vane openings and at least one-half of the overall stack diameter upstream of the stack outlet.

8.1.3 Roof Monitor or Monovent. (See Figure 5D–2). For a positive pressure fabric filter equipped with a peaked roof monitor, ridge vent, or other type of monovent, use a measurement site at the base of the monovent. Examples of such locations are shown in Figure 5D–2. The measurement site must be upstream of any exhaust point (*e.g.*, louvered vent).

8.1.4 Compartment Housing. Sample immediately downstream of the filter bags directly above the tops of the bags as shown in the examples in Figure 5D–2. Depending on the housing design, use sampling ports in the housing walls or locate the sampling equipment within the compartment housing.

8.2 Determination of Number and Location of Traverse Points. Locate the traverse points according to Method 1, section 11.3. Because a performance test consists of at least three test runs and because of the varied configurations of positive pressure fabric filters, there are several schemes by which the number of traverse points can be determined and the three test runs can be conducted.

8.2.1 Single Stacks Meeting Method 1 Criteria. Select the number of traverse points according to Method 1. Sample all traverse points for each test run.

8.2.2 Other Single Measurement Sites. For a roof monitor or monovent, single compartment housing, or other stack not meeting Method 1 criteria, use at least 24 traverse points. For example, for a rectangular measurement site, such as a monovent, use a balanced 5×5 traverse point matrix. Sample all traverse points for each test run.

8.2.3 Multiple Measurement Sites. Sampling from two or more stacks or measurement sites may be combined for a test run, provided the following guidelines are met:

8.2.3.1 All measurement sites up to 12 must be sampled. For more than 12 measurement sites, conduct sampling on at least 12 sites or 50 percent of the sites, whichever is greater. The measurement sites sampled should be evenly, or nearly evenly, distributed among the available sites; if not, all sites are to be sampled.

8.2.3.2 The same number of measurement sites must be sampled for each test run.

8.2.3.3 The minimum number of traverse points per test run is 24. An exception to the 24-point minimum would be a test combining the sampling from two stacks meeting Method 1 criteria for acceptable stack length, and Method 1 specifies fewer than 12 points per site.

8.2.3.4 As long as the 24 traverse points per test run criterion is met, the number of traverse points per measurement site may be reduced to eight.

8.2.3.5 Alternatively, conduct a test run for each measurement site individually using the criteria in section 8.2.1 or 8.2.2 to determine the number of traverse points. Each test run shall count toward the total of three required for a performance test. If more than three measurement sites are sampled, the number of traverse points per measurement site may be reduced to eight as long as at least 72 traverse points are sampled for all the tests.

8.2.3.6 The following examples demonstrate the procedures for sampling multiple measurement sites.

8.2.3.6.1 Example 1: A source with nine circular measurement sites of equal areas may be tested as follows: For each test run, traverse three measurement sites using four points per diameter (eight points per measurement site). In this manner, test run number 1 will include sampling from sites 1,2, and 3; run 2 will include samples from sites 4, 5, and 6; and run 3 will include sites 7, 8, and 9. Each test area may consist of a separate test of each measurement site using eight points. Use the results from all nine tests in determining the emission average.

8.2.3.6.2 Example 2: A source with 30 rectangular measurement sites of equal areas may be tested as follows: For each of the three test runs, traverse five measurement sites using a 3×3 matrix of traverse points for each site. In order to distribute the sampling evenly over all the available measurement sites while sampling only 50 percent of the sites, number the sites consecutively from 1 to 30 and sample all the even numbered (or odd numbered) sites. Alternatively, conduct a separate test of each of 15 measurement sites using section 8.2.1 or 8.2.2 to determine the number and location of traverse points, as appropriate.

8.2.3.6.3 Example 3: A source with two measurement sites of equal areas may be tested as follows: For each test of three test runs, traverse both measurement sites, using section 8.2.3 in determining the number of traverse points. Alternatively, conduct two full emission test runs for each measurement site using the criteria in section 8.2.1 or 8.2.2 to determine the number of traverse points.

8.2.3.7 Other test schemes, such as random determination of traverse points for a large number of measurement sites, may be used with prior approval from the Administrator.

8.3 Velocity Determination.

8.3.1 The velocities of exhaust gases from positive pressure baghouses are often too low to measure accurately with the type S pitot tube specified in Method 2 (*i.e.*, velocity head <1.3 mm H_2O (0.05 in. H_2O)). For these conditions, measure the gas flow rate at the fabric filter inlet following the procedures outlined in Method 2. Calculate the average gas velocity at the measurement site as shown in section 12.2 and use this average velocity in determining and maintaining isokinetic sampling rates.

8.3.2 Velocity determinations to determine and maintain isokinetic rates at measurement sites with gas velocities within the range measurable with the type S pitot tube (*i.e.*, velocity head greater than 1.3 mm H_2O (0.05 in. H_2O)) shall be conducted according to the procedures outlined in Method 2.

8.4 Sampling. Follow the procedures specified in sections 8.1 through 8.6 of Method 5 or sections 8.1 through 8.25 in Method 17 with the exceptions as noted above.

8.5 Sample Recovery. Follow the procedures specified in section 8.7 of Method 5 or section 8.2 of Method 17.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.0, 10.0	Sampling equipment leak check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

Same as section 10.0 of either Method 5 or Method 17.

11.0 Analytical Procedure

Same as section 11.0 of either Method 5 or Method 17.

12.0 Data Analysis and Calculations

Same as section 12.0 of either Method 5 or Method 17 with the following exceptions:

12.1 Nomenclature.

A_o = Measurement site(s) total cross-sectional area, m^2 (ft^2).

$\bar{C}$ or C_{avg} = Average concentration of PM for all n runs, mg/scm (gr/scf).

Q_i = Inlet gas volume flow rate, m^3/sec (ft^3/sec).

m_i = Mass collected for run i of n, mg (gr).

T_o = Average temperature of gas at measurement site, °K (°R).

T_i = Average temperature of gas at inlet, °K (°R).

Vol_i = Sample volume collected for run i of n, scm (scf).

$\bar{v}$ = Average gas velocity at the measurement site(s), m/s (ft/s)

Q_o = Total baghouse exhaust volumetric flow rate, m^3/sec (ft^3/sec).

Q_d = Dilution air flow rate, m^3/sec (ft^3/sec).

Tamb = Ambient Temperature, (°K).

12.2 Average Gas Velocity. When following section 8.3.1, calculate the average gas velocity at the measurement site as follows:

$$\bar{v} = \frac{Q_o}{A_o} \qquad \text{Eq. 5D-1}$$

12.3 Volumetric Flow Rate. Total volumetric flow rate may be determined as follows:

$$Q_o = Q_i + Q_d \qquad \text{Eq. 5D-2}$$

12.4 Dilution Air Flow Rate.

$$Q_d = \frac{Q_i\left(T_i - T_o\right)}{T_o - T_{amb}} \qquad \text{Eq. 5D-3}$$

12.5 Average PM Concentration. For multiple measurement sites, calculate the average PM concentration as follows:

$$C_{avg} \text{ or } \overline{C} = \frac{\sum_{i=1}^{n} m_i}{\sum_{i=1}^{n} Vol_i} \qquad \text{Eq. 5D-4}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 5, section 17.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

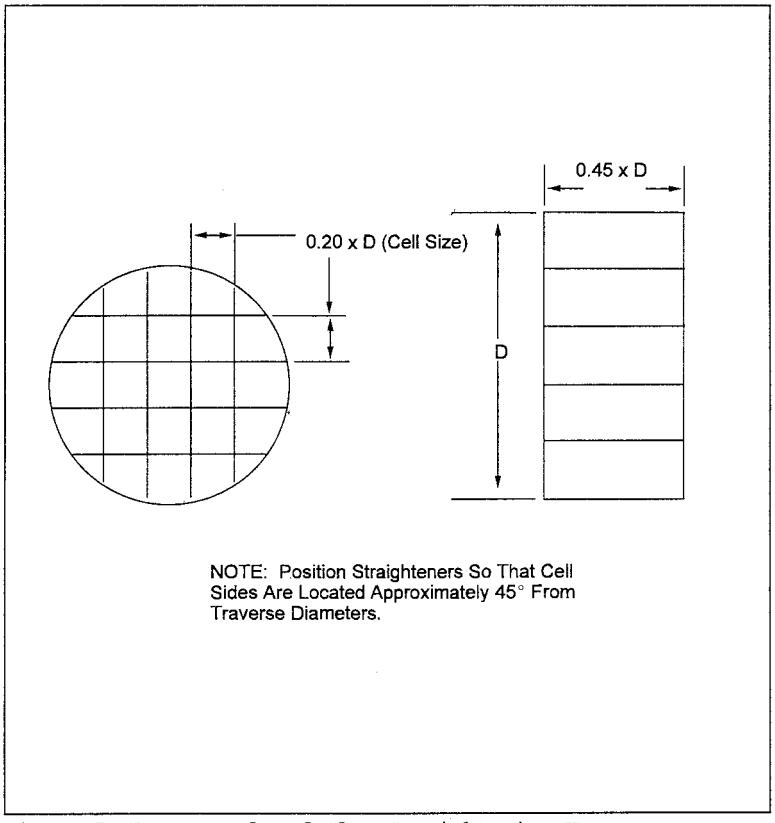

Figure 5D-1. Example of Flow Straightening Vanes.

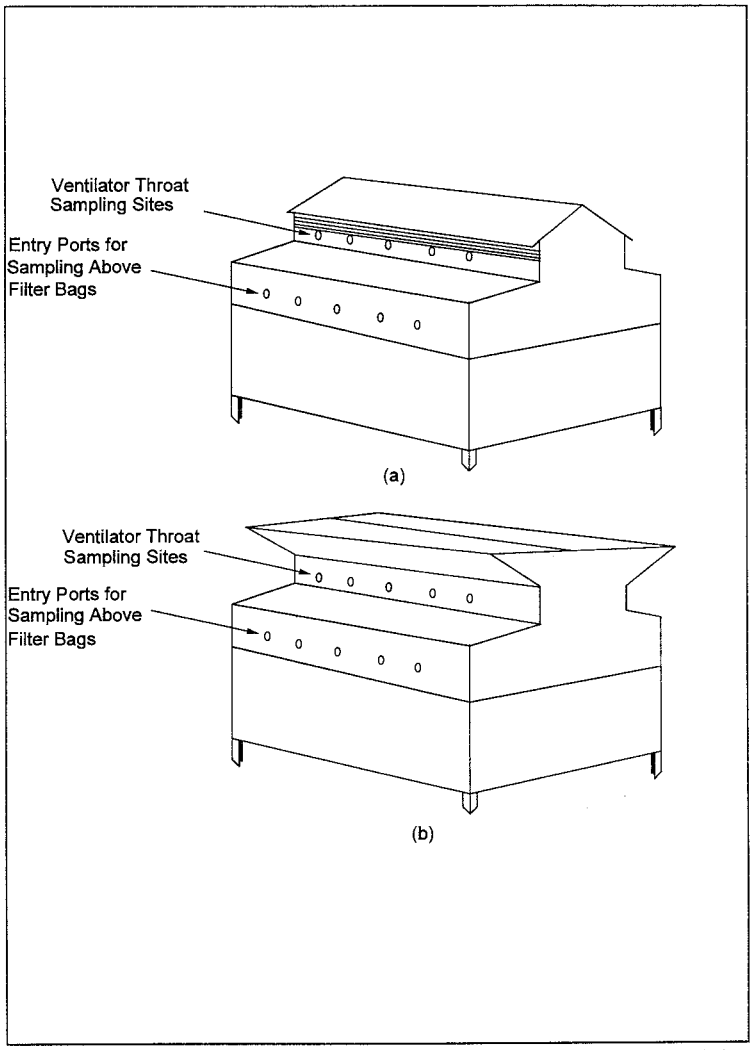

Figure 5D-2. Acceptable Sampling Site Locations for: (a) Peaked Roof; and (b) Ridge Vent Type Fabric Filters

METHOD 5E—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM THE WOOL FIBERGLASS INSULATION MANUFACTURING INDUSTRY

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5.

1.0 Scope and Applications

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of PM emissions from wool fiberglass insulation manufacturing sources.

2.0 Summary of Method

Particulate matter is withdrawn isokinetically from the source and is collected either on a glass fiber filter maintained at a temperature in the range of 120 ±14 °C (248 ±25 °F) and in impingers in solutions of 0.1 N sodium hydroxide (NaOH). The filtered particulate mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after the removal of uncombined water. The condensed PM collected in the impinger solutions is determined as total organic carbon (TOC) using a nondispersive infrared type of analyzer. The sum of the filtered PM mass and the condensed PM is reported as the total PM mass.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Hydrochloric Acid (HCl). Highly toxic. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent in air can be lethal in minutes. Will react with metals, producing hydrogen.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eye tissues and to skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 5, section 6.1, with the exception of the following:

6.1.1 Probe Liner. Same as described in section 6.1.1.2 of Method 5 except use only borosilicate or quartz glass liners.

6.1.2 Filter Holder. Same as described in section 6.1.1.5 of Method 5 with the addition of a leak-tight connection in the rear half of the filter holder designed for insertion of a temperature sensor used for measuring the sample gas exit temperature.

6.2 Sample Recovery. Same as Method 5, section 6.2, except three wash bottles are needed instead of two and only glass storage bottles and funnels may be used.

6.3 Sample Analysis. Same as Method 5, section 6.3, with the additional equipment for TOC analysis as described below:

6.3.1 Sample Blender or Homogenizer. Waring type or ultrasonic.

6.3.2 Magnetic Stirrer.

6.3.3 Hypodermic Syringe. 0- to 100-µl capacity.

6.3.4 Total Organic Carbon Analyzer. Rosemount Model 2100A analyzer or equivalent and a recorder.

6.3.5 Beaker. 30-ml.

6.3.6 Water Bath. Temperature controlled.

6.3.7 Volumetric Flasks. 1000-ml and 500-ml.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 5, section 7.1, with the addition of 0.1 N NaOH (Dissolve 4 g of NaOH in water and dilute to 1 liter).

7.2 Sample Recovery. Same as Method 5, section 7.2, with the addition of the following:

7.2.1 Water. Deionized distilled to conform to ASTM Specification D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17). The potassium permanganate ($KMnO_4$) test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.2.2 Sodium Hydroxide. Same as described in section 7.1.

7.3 Sample Analysis. Same as Method 5, section 7.3, with the addition of the following:

7.3.1 Carbon Dioxide-Free Water. Distilled or deionized water that has been freshly boiled for 15 minutes and cooled to room temperature while preventing exposure to ambient air by using a cover vented with an Ascarite tube.

7.3.2 Hydrochloric Acid. HCl, concentrated, with a dropper.

7.3.3 Organic Carbon Stock Solution. Dissolve 2.1254 g of dried potassium biphthalate ($HOOCC_6H_4COOK$) in CO_2-free water, and dilute to 1 liter in a volumetric flask. This solution contains 1000 mg/L organic carbon.

7.3.4 Inorganic Carbon Stock Solution. Dissolve 4.404 g anhydrous sodium carbonate

(Na_2CO_3.) in about 500 ml of CO_2-free water in a 1-liter volumetric flask. Add 3.497 g anhydrous sodium bicarbonate ($NaHCO_3$) to the flask, and dilute to 1 liter with CO_2 -free water. This solution contains 1000 mg/L inorganic carbon.

7.3.5 Oxygen Gas. CO_2 -free.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation and Preliminary Determinations. Same as Method 5, sections 8.1 and 8.2, respectively.

8.2 Preparation of Sampling Train. Same as Method 5, section 8.3, except that 0.1 N NaOH is used in place of water in the impingers. The volumes of the solutions are the same as in Method 5.

8.3 Leak-Check Procedures, Sampling Train Operation, Calculation of Percent Isokinetic. Same as Method 5, sections 8.4 through 8.6, respectively.

8.4 Sample Recovery. Same as Method 5, sections 8.7.1 through 8.7.4, with the addition of the following:

8.4.1 Save portions of the water, acetone, and 0.1 N NaOH used for cleanup as blanks. Take 200 ml of each liquid directly from the wash bottles being used, and place in glass sample containers labeled ''water blank,'' ''acetone blank,'' and ''NaOH blank,'' respectively.

8.4.2 Inspect the train prior to and during disassembly, and note any abnormal conditions. Treat the samples as follows:

8.4.2.1 Container No. 1. Same as Method 5, section 8.7.6.1.

8.4.2.2 Container No. 2. Use water to rinse the sample nozzle, probe, and front half of the filter holder three times in the manner described in section 8.7.6.2 of Method 5 except that no brushing is done. Put all the water wash in one container, seal, and label.

8.4.2.3 Container No. 3. Rinse and brush the sample nozzle, probe, and front half of the filter holder with acetone as described for Container No. 2 in section 8.7.6.2 of Method 5.

8.4.2.4 Container No. 4. Place the contents of the silica gel impinger in its original container as described for Container No. 3 in section 8.7.6.3 of Method 5.

8.4.2.5 Container No. 5. Measure the liquid in the first three impingers and record the volume or weight as described for the Impinger Water in section 8.7.6.4 of Method 5. Do not discard this liquid, but place it in a sample container using a glass funnel to aid in the transfer from the impingers or graduated cylinder (if used) to the sample container. Rinse each impinger thoroughly with 0.1 N NaOH three times, as well as the graduated cylinder (if used) and the funnel, and put these rinsings in the same sample container. Seal the container and label to clearly identify its contents.

8.5 Sample Transport. Whenever possible, containers should be shipped in such a way that they remain upright at all times.

9.0 Quality Control.

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.3, 10.0	Sampling equipment leak-check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.
10.1.2, 11.2.5.3	Repetitive analyses	Ensures precise measurement of total carbon and inorganic carbon concentration of samples, blank, and standards.
10.1.4	TOC analyzer calibration	Ensures linearity of analyzer response to standards.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

Same as Method 5, section 10.0, with the addition of the following procedures for calibrating the total organic carbon analyzer:

10.1 Preparation of Organic Carbon Standard Curve.

10.1.1 Add 10 ml, 20 ml, 30 ml, 40 ml, and 50 ml of the organic carbon stock solution to a series of five 1000-ml volumetric flasks. Add 30 ml, 40 ml, and 50 ml of the same solution to a series of three 500-ml volumetric flasks. Dilute the contents of each flask to the mark using CO_2-free water. These flasks contain 10, 20, 30, 40, 50, 60, 80, and 100 mg/L organic carbon, respectively.

10.1.2 Use a hypodermic syringe to withdraw a 20- to 50-µl aliquot from the 10 mg/L standard solution and inject it into the total carbon port of the analyzer. Measure the peak height. Repeat the injections until three consecutive peaks are obtained within 10 percent of their arithmetic mean. Repeat this procedure for the remaining organic carbon standard solutions.

10.1.3 Calculate the corrected peak height for each standard by deducting the blank correction (see section 11.2.5.3) as follows:

$$\text{Corrected Peak Height} = A - B \qquad \text{Eq. 5E-1}$$

Where:

A = Peak height of standard or sample, mm or other appropriate unit.

B = Peak height of blank, mm or other appropriate unit.

10.1.4 Prepare a linear regression plot of the arithmetic mean of the three consecutive peak heights obtained for each standard solution against the concentration of that solution. Calculate the calibration factor as the inverse of the slope of this curve. If the product of the arithmetic mean peak height for any standard solution and the calibration factor differs from the actual concentration by more than 5 percent, remake and reanalyze that standard.

10.2 Preparation of Inorganic Carbon Standard Curve. Repeat the procedures outlined in sections 10.1.1 through 10.1.4, substituting the inorganic carbon stock solution for the organic carbon stock solution, and the inorganic carbon port of the analyzer for the total carbon port.

11.0 Analytical Procedure

11.1 Record the data required on a sheet such as the one shown in Figure 5–6 of Method 5.

11.2 Handle each sample container as follows:

11.2.1 Container No. 1. Same as Method 5, section 11.2.1, except that the filters must be dried at 20 ±6 °C (68 ±10 °F) and ambient pressure.

11.2.2 Containers No. 2 and No. 3. Same as Method 5, section 11.2.2, except that evaporation of the samples must be at 20 ±6 °C (68 ±10 °F) and ambient pressure.

11.2.3 Container No. 4. Same as Method 5, section 11.2.3.

11.2.4 ''Water Blank'' and ''Acetone Blank'' Containers. Determine the water and acetone blank values following the procedures for the ''Acetone Blank'' container in section 11.2.4 of Method 5. Evaporate the samples at ambient temperature (20 ±6 °C (68 ±10 °F)) and pressure.

11.2.5 Container No. 5. For the determination of total organic carbon, perform two analyses on successive identical samples, *i.e.*, total carbon and inorganic carbon. The desired quantity is the difference between the two values obtained. Both analyses are based on conversion of sample carbon into carbon dioxide for measurement by a nondispersive infrared analyzer. Results of analyses register as peaks on a strip chart recorder.

11.2.5.1 The principal differences between the operating parameters for the two channels involve the combustion tube packing material and temperature. In the total carbon channel, a high temperature (950 °C (1740 °F)) furnace heats a Hastelloy combustion tube packed with cobalt oxide-impregnated asbestos fiber. The oxygen in the carrier gas, the elevated temperature, and the catalytic effect of the packing result in oxidation of both organic and inorganic carbonaceous material to CO_2, and steam. In the inorganic carbon channel, a low temperature (150 °C (300 °F)) furnace heats a glass tube containing quartz chips wetted with 85 percent phosphoric acid. The acid liberates CO_2 and steam from inorganic carbonates. The operating temperature is below that required to oxidize organic matter. Follow the manufacturer's instructions for assembly, testing, calibration, and operation of the analyzer.

11.2.5.2 As samples collected in 0.1 N NaOH often contain a high measure of inorganic carbon that inhibits repeatable determinations of TOC, sample pretreatment is necessary. Measure and record the liquid volume of each sample (or impinger contents). If the sample contains solids or immiscible liquid matter, homogenize the sample with a blender or ultrasonics until satisfactory repeatability is obtained. Transfer a representative portion of 10 to 15 ml to a 30-ml beaker, and acidify with about 2 drops of concentrated HCl to a pH of 2 or less. Warm the acidified sample at 50 °C (120 °F) in a water bath for 15 minutes.

11.2.5.3 While stirring the sample with a magnetic stirrer, use a hypodermic syringe to withdraw a 20-to 50-µl aliquot from the beaker. Analyze the sample for total carbon and calculate its corrected mean peak height according to the procedures outlined in sections 10.1.2 and 10.1.3. Similarly analyze an aliquot of the sample for inorganic carbon. Repeat the analyses for all the samples and for the 0.1 N NaOH blank.

11.2.5.4 Ascertain the total carbon and inorganic carbon concentrations (C_{TC} and C_{IC}, respectively) of each sample and blank by comparing the corrected mean peak heights for each sample and blank to the appropriate standard curve.

NOTE: If samples must be diluted for analysis, apply an appropriate dilution factor.

12.0 Data Analysis and Calculations

Same as Method 5, section 12.0, with the addition of the following:

12.1 Nomenclature.

C_c = Concentration of condensed particulate matter in stack gas, gas dry basis, corrected to standard conditions, g/dscm (gr/dscf).

C_{IC} = Concentration of condensed TOC in the liquid sample, from section 11.2.5, mg/L.

C_t = Total particulate concentration, dry basis, corrected to standard conditions, g/dscm (gr/dscf).
C_{TC} = Concentration of condensed TOC in the liquid sample, from section 11.2.5, mg/L.
C_{TOC} = Concentration of condensed TOC in the liquid sample, mg/L.
m_{TOC} = Mass of condensed TOC collected in the impingers, mg.
$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, from section 12.3 of Method 5, dscm (dscf).
V_s = Total volume of liquid sample, ml.

12.2 Concentration of Condensed TOC in Liquid Sample.

$$C_{TOC} = C_{TC} - C_{IC} \qquad \text{Eq. 5E-2}$$

12.3 Mass of Condensed TOC Collected.

$$m_{TOC} = 0.001\, C_{TOC} V_s \qquad \text{Eq. 5E-3}$$

Where:

0.001 = Liters per milliliter.

12.4 Concentration of Condensed Particulate Material.

$$C_c = K_4 m_{TOC} / V_{m(std)} \qquad \text{Eq. 5E-4}$$

Where:

K_4 = 0.001 g/mg for metric units.
= 0.0154 gr/mg for English units.

12.5 Total Particulate Concentration.

$$C_t = C_s + C_c \qquad \text{Eq. 5E-4}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Total Organic Carbon Analyzer. Tekmar-Dohrmann analyzers using the single injection technique may be used as an alternative to Rosemount Model 2100A analyzers.

17.0 References.

Same as section 17.0 of Method 5, with the addition of the following:

1. American Public Health Association, American Water Works Association, Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater. Fifteenth Edition. Washington, D.C. 1980.

18.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

Method 5F—Determination of Nonsulfate Particulate Matter Emissions From Stationary Sources

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5.

1.0 Scope and Applications

1.1 Analyte. Nonsulfate particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of nonsulfate PM emissions from stationary sources. Use of this method must be specified by an applicable subpart of the standards, or approved by the Administrator for a particular application.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

Particulate matter is withdrawn isokinetically from the source and collected on a filter maintained at a temperature in the range 160 ±14 °C (320 ±25 °F). The collected sample is extracted with water. A portion of the extract is analyzed for sulfate content by ion chromatography. The remainder is neutralized with ammonium hydroxide (NH_4OH), dried, and weighed. The weight of sulfate in the sample is calculated as ammonium sulfate ($(NH_4)_2SO_4$), and is subtracted from the total particulate weight; the result is reported as nonsulfate particulate matter.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection and Recovery. Same as Method 5, sections 6.1 and 6.2, respectively.

6.2 Sample Analysis. Same as Method 5, section 6.3, with the addition of the following:

6.2.1 Erlenmeyer Flasks. 125-ml, with ground glass joints.

6.2.2 Air Condenser. With ground glass joint compatible with the Erlenmeyer flasks.

6.2.3 Beakers. 600-ml.

6.2.4 Volumetric Flasks. 1-liter, 500-ml (one for each sample), 200-ml, and 50-ml (one for each sample and standard).

6.2.5 Pipet. 5-ml (one for each sample and standard).

6.2.6 Ion Chromatograph. The ion chromatograph should have at least the following components.

6.2.6.1 Columns. An anion separation column or other column capable of resolving the sulfate ion from other species present and a standard anion suppressor column. Suppressor columns are produced as proprietary items; however, one can be produced in the laboratory using the resin available from BioRad Company, 32nd and Griffin Streets, Richmond, California. Other systems which do not use suppressor columns may also be used.

6.2.6.2 Pump. Capable of maintaining a steady flow as required by the system.

6.2.6.3 Flow Gauges. Capable of measuring the specified system flow rate.

6.2.6.4 Conductivity Detector.

6.2.6.5 Recorder. Compatible with the output voltage range of the detector.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 5, section 7.1.

7.2 Sample Recovery. Same as Method 5, section 7.2, with the addition of the following:

7.2.1 Water. Deionized distilled, to conform to ASTM D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17). The potassium permanganate ($KMnO_4$) test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.3 Analysis. Same as Method 5, section 7.3, with the addition of the following:

7.3.1 Water. Same as in section 7.2.1.

7.3.2 Stock Standard Solution, 1 mg $(NH_4)_2SO_4$/ml. Dry an adequate amount of primary standard grade ammonium sulfate ($(NH_4)_2SO_4$) at 105 to 110 °C (220 to 230 °F) for a minimum of 2 hours before preparing the standard solution. Then dissolve exactly 1.000 g of dried $(NH_4)_2SO_4$ in water in a 1-liter volumetric flask, and dilute to 1 liter. Mix well.

7.3.3 Working Standard Solution, 25 µg $(NH_4)_2SO_4$/ml. Pipet 5 ml of the stock standard solution into a 200-ml volumetric flask. Dilute to 200 ml with water.

7.3.4 Eluent Solution. Weigh 1.018 g of sodium carbonate (Na_2CO_3) and 1.008 g of sodium bicarbonate ($NaHCO_3$), and dissolve in 4 liters of water. This solution is 0.0024 M Na_2CO_3/0.003 M $NaHCO_3$. Other eluents appropriate to the column type and capable of resolving sulfate ion from other species present may be used.

7.3.5 Ammonium Hydroxide. Concentrated, 14.8 M.

7.3.6 Phenolphthalein Indicator. 3,3-Bis(4-hydroxyphenyl)-1-(3H)-isobenzo-furanone. Dissolve 0.05 g in 50 ml of ethanol and 50 ml of water.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as Method 5, section 8.0, with the exception of the following:

8.1 Sampling Train Operation. Same as Method 5, section 8.5, except that the probe outlet and filter temperatures shall be maintained at 160 ±14 °C (320 ±25 °F).

8.2 Sample Recovery. Same as Method 5, section 8.7, except that the recovery solvent shall be water instead of acetone, and a clean filter from the same lot as those used during testing shall be saved for analysis as a blank.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures

Section	Quality control measure	Effect
8.3, 10.0	Sampling equipment leak check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.
10.1.2, 11.2.5.3	Repetitive analyses	Ensures precise measurement of total carbon and inorganic carbon concentration of samples, blank, and standards.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

Same as Method 5, section 10.0, with the addition of the following:

10.1 Determination of Ion Chromatograph Calibration Factor S. Prepare a series of five standards by adding 1.0, 2.0, 4.0, 6.0, and 10.0 ml of working standard solution (25 µg/ml) to a series of five 50-ml volumetric flasks. (The standard masses will equal 25, 50, 100, 150, and 250 µg.) Dilute each flask to the mark with water, and mix well. Analyze each standard according to the chromatograph manufacturer's instructions. Take peak height measurements with symmetrical peaks; in all other cases, calculate peak areas. Prepare or calculate a linear regression plot of the standard masses in µg (x-axis) versus their responses (y-axis). From this line, or equation, determine the slope and calculate its reciprocal which is the calibration factor, S. If any point deviates from the line by more than 7 percent of the concentration at that point, remake and reanalyze that standard. This deviation can be determined by multiplying S times the response for each standard. The resultant concentrations must not differ by more than 7 percent from each known standard mass (*i.e.*, 25, 50, 100, 150, and 250 µg).

10.2 Conductivity Detector. Calibrate according to manufacturer's specifications prior to initial use.

11.0 Analytical Procedure

11.1 Sample Extraction.

11.1.1 Note on the analytical data sheet, the level of the liquid in the container, and whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.1.2 Cut the filter into small pieces, and place it in a 125-ml Erlenmeyer flask with a ground glass joint equipped with an air condenser. Rinse the shipping container with water, and pour the rinse into the flask. Add additional water to the flask until it contains about 75 ml, and place the flask on a hot plate. Gently reflux the contents for 6 to 8 hours. Cool the solution, and transfer it to a 500-ml volumetric flask. Rinse the Erlenmeyer flask with water, and transfer the rinsings to the volumetric flask including the pieces of filter.

11.1.3 Transfer the probe rinse to the same 500-ml volumetric flask with the filter sample. Rinse the sample bottle with water, and add the rinsings to the volumetric flask. Dilute the contents of the flask to the mark with water.

11.1.4 Allow the contents of the flask to settle until all solid material is at the bottom of the flask. If necessary, remove and centrifuge a portion of the sample.

11.1.5 Repeat the procedures outlined in sections 11.1.1 through 11.1.4 for each sample and for the filter blank.

11.2 Sulfate (SO_4) Analysis.

11.2.1 Prepare a standard calibration curve according to the procedures outlined in section 10.1.

11.2.2 Pipet 5 ml of the sample into a 50-ml volumetric flask, and dilute to 50 ml with water. (Alternatively, eluent solution may be used instead of water in all sample, standard, and blank dilutions.) Analyze the set of standards followed by the set of samples, including the filter blank, using the same injection volume used for the standards.

11.2.3 Repeat the analyses of the standards and the samples, with the standard set being done last. The two peak height or peak area responses for each sample must agree within 5 percent of their arithmetic mean for the analysis to be valid. Perform this analysis sequence on the same day. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

11.2.4 Document each sample chromatogram by listing the following analytical parameters: injection point, injection volume, sulfate retention time, flow rate, detector sensitivity setting, and recorder chart speed.

11.3 Sample Residue.

11.3.1 Transfer the remaining contents of the volumetric flask to a tared 600-ml beaker or similar container. Rinse the volumetric flask with water, and add the rinsings to the tared beaker. Make certain that all particulate matter is transferred to the beaker. Evaporate the water in an oven at 105 °C (220 °F) until only about 100 ml of water remains. Remove the beakers from the oven, and allow them to cool.

11.3.2 After the beakers have cooled, add five drops of phenolphthalein indicator, and then add concentrated ammonium hydroxide until the solution turns pink. Return the samples to the oven at 105 °C (220 °F), and evaporate the samples to dryness. Cool the samples in a desiccator, and weigh the samples to constant weight.

12.0 Data Analysis and Calculations

Same as Method 5, section 12.0, with the addition of the following:

12.1 Nomenclature.

C_W = Water blank residue concentration, mg/ml.

F = Dilution factor (required only if sample dilution was needed to reduce the concentration into the range of calibration).

H_S = Arithmetic mean response of duplicate sample analyses, mm for height or mm2 for area.

H_b = Arithmetic mean response of duplicate filter blank analyses, mm for height or mm2 for area.
m_b = Mass of beaker used to dry sample, mg.
m_f = Mass of sample filter, mg.
m_n = Mass of nonsulfate particulate matter in the sample as collected, mg.
m_s = Mass of ammonium sulfate in the sample as collected, mg.
m_t = Mass of beaker, filter, and dried sample, mg.
m_w = Mass of residue after evaporation of water blank, mg.
S = Calibration factor, µg/mm.
V_b = Volume of water blank, ml.
V_S = Volume of sample collected, 500 ml.

12.2 Water Blank Concentration.

$$C_w = \frac{m_w}{V_b} \qquad \text{Eq. 5F-1}$$

12.3 Mass of Ammonium Sulfate.

$$m_s = \frac{(99)\, S\, (H_s - H_b)}{(1000)} F \qquad \text{Eq. 5F-2}$$

Where:
100 = Aliquot factor, 495 ml/5 ml
1000 = Constant, µg/mg

12.4 Mass of Nonsulfate Particulate Matter.

$$m_n = m_t - m_b - m_s - m_f - V_s C_w \qquad \text{Eq. 5F-3}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 The following procedure may be used as an alternative to the procedure in section 11.0

16.1.1 Apparatus. Same as for Method 6, sections 6.3.3 to 6.3.6 with the following additions.

16.1.1.1 Beakers. 250-ml, one for each sample, and 600-ml.

16.1.1.2 Oven. Capable of maintaining temperatures of 75 ±5 °C (167 ±9 °F) and 105 ±5 °C (221 ±9 °F).

16.1.1.3 Buchner Funnel.

16.1.1.4 Glass Columns. 25-mm × 305-mm (1-in. × 12-in.) with Teflon stopcock.

16.1.1.5 Volumetric Flasks. 50-ml and 500-ml, one set for each sample, and 100-ml, 200-ml, and 1000-ml.

16.1.1.6 Pipettes. Two 20-ml and one 200-ml, one set for each sample, and 5-ml.

16.1.1.7 Filter Flasks. 500-ml.

16.1.1.8 Polyethylene Bottle. 500-ml, one for each sample.

16.1.2 Reagents. Same as Method 6, sections 7.3.2 to 7.3.5 with the following additions:

16.1.2.1 Water, Ammonium Hydroxide, and Phenolphthalein. Same as sections 7.2.1, 7.3.5, and 7.3.6 of this method, respectively.

16.1.2.2 Filter. Glass fiber to fit Buchner funnel.

16.1.2.3 Hydrochloric Acid (HCl), 1 m. Add 8.3 ml of concentrated HCl (12 M) to 50 ml of water in a 100-ml volumetric flask. Dilute to 100 ml with water.

16.1.2.4 Glass Wool.

16.1.2.5 Ion Exchange Resin. Strong cation exchange resin, hydrogen form, analytical grade.

16.1.2.6 pH Paper. Range of 1 to 7.

16.1.3 Analysis.

16.1.3.1 Ion Exchange Column Preparation. Slurry the resin with 1 M HCl in a 250-ml beaker, and allow to stand overnight. Place 2.5 cm (1 in.) of glass wool in the bottom of the glass column. Rinse the slurried resin twice with water. Resuspend the resin in water, and pour sufficient resin into the column to make a bed 5.1 cm (2 in.) deep. Do not allow air bubbles to become entrapped in the resin or glass wool to avoid channeling, which may produce erratic results. If necessary, stir the resin with a glass rod to remove air bubbles, after the column has been prepared, never let the liquid level fall below the top of the upper glass wool plug. Place a 2.5-cm (1-in.) plug of glass wool on top of the resin. Rinse the column with water until the eluate gives a pH of 5 or greater as measured with pH paper.

16.1.3.2 Sample Extraction. Followup the procedure given in section 11.1.3 except do not dilute the sample to 500 ml.

16.1.3.3 Sample Residue.

16.1.3.3.1 Place at least one clean glass filter for each sample in a Buchner funnel, and rinse the filters with water. Remove the filters from the funnel, and dry them in an oven at 105 ±5 °C (221 ±9 °F); then cool in a desiccator. Weigh each filter to constant weight according to the procedure in Method 5, section 11.0. Record the weight of each filter to the nearest 0.1 mg.

16.1.3.3.2 Assemble the vacuum filter apparatus, and place one of the clean, tared glass fiber filters in the Buchner funnel. Decant the liquid portion of the extracted sample (Section 16.1.3.2) through the tared glass fiber filter into a clean, dry, 500-ml filter flask. Rinse all the particulate matter remaining in the volumetric flask onto the glass fiber filter with water. Rinse the particulate matter with additional water.

Transfer the filtrate to a 500-ml volumetric flask, and dilute to 500 ml with water. Dry the filter overnight at 105 ±5 °C (221 ±9 °F), cool in a desiccator, and weigh to the nearest 0.1 mg.

16.1.3.3.3 Dry a 250-ml beaker at 75 ±5 °C (167 ±9 °F), and cool in a desiccator; then weigh to constant weight to the nearest 0.1 mg. Pipette 200 ml of the filtrate that was saved into a tared 250-ml beaker; add five drops of phenolphthalein indicator and sufficient concentrated ammonium hydroxide to turn the solution pink. Carefully evaporate the contents of the beaker to dryness at 75 ±5 °C (167 ±9 °F). Check for dryness every 30 minutes. Do not continue to bake the sample once it has dried. Cool the sample in a desiccator, and weigh to constant weight to the nearest 0.1 mg.

16.1.3.4 Sulfate Analysis. Adjust the flow rate through the ion exchange column to 3 ml/min. Pipette a 20-ml aliquot of the filtrate onto the top of the ion exchange column, and collect the eluate in a 50-ml volumetric flask. Rinse the column with two 15-ml portions of water. Stop collection of the eluate when the volume in the flask reaches 50-ml. Pipette a 20-ml aliquot of the eluate into a 250-ml Erlenmeyer flask, add 80 ml of 100 percent isopropanol and two to four drops of thorin indicator, and titrate to a pink end point using 0.0100 N barium perchlorate. Repeat and average the titration volumes. Run a blank with each series of samples. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is larger. Perform the ion exchange and titration procedures on duplicate portions of the filtrate. Results should agree within 5 percent. Regenerate or replace the ion exchange resin after 20 sample aliquots have been analyzed or if the end point of the titration becomes unclear.

NOTE: Protect the 0.0100 N barium perchlorate solution from evaporation at all times.

16.1.3.5 Blank Determination. Begin with a sample of water of the same volume as the samples being processed and carry it through the analysis steps described in sections 16.1.3.3 and 16.1.3.4. A blank value larger than 5 mg should not be subtracted from the final particulate matter mass. Causes for large blank values should be investigated and any problems resolved before proceeding with further analyses.

16.1.4 Calibration. Calibrate the barium perchlorate solutions as in Method 6, section 10.5.

16.1.5 Calculations.

16.1.5.1 Nomenclature. Same as section 12.1 with the following additions:

m_a = Mass of clean analytical filter, mg.
m_d = Mass of dissolved particulate matter, mg.
m_e = Mass of beaker and dissolved particulate matter after evaporation of filtrate, mg.
m_p = Mass of insoluble particulate matter, mg.
m_r = Mass of analytical filter, sample filter, and insoluble particulate matter, mg.
m_{bk} = Mass of nonsulfate particulate matter in blank sample, mg.
m_n = Mass of nonsulfate particulate matter, mg.
m_s = Mass of Ammonium sulfate, mg.
N = Normality of $Ba(ClO_4)$ titrant, meq/ml.
V_a = Volume of aliquot taken for titration, 20 ml.
V_c = Volume of titrant used for titration blank, ml.
V_d = Volume of filtrate evaporated, 200 ml.
V_e = Volume of eluate collected, 50 ml.
V_f = Volume of extracted sample, 500 ml.
V_i = Volume of filtrate added to ion exchange column, 20 ml.
V_t = Volume of $Ba(C10_4)_2$ titrant, ml.
W = Equivalent weight of ammonium sulfate, 66.07 mg/meq.

16.1.5.2 Mass of Insoluble Particulate Matter.

$$m_p = m_r - m_a - m_f \qquad \text{Eq. 5F-4}$$

16.1.5.3 Mass of Dissolved Particulate Matter.

$$m_d = \left(m_e - \left(V_f / V_d\right) m_b\right) \qquad \text{Eq. 5F-5}$$

16.1.5.4 Mass of Ammonium Sulfate.

$$m_s = \frac{\left(V_t - V_c\right) N\, W\, V_e V_f}{V_a V_i} \qquad \text{Eq. 5F-6}$$

16.1.5.5 Mass of Nonsulfate Particulate Matter.

$$m_n = m_p + m_d - m_s - m_{bk} \qquad \text{Eq. 5F-7}$$

17.0 References

Same as Method 5, section 17.0, with the addition of the following:

1. Mulik, J.D. and E. Sawicki. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor, Ann Arbor Science Publishers, Inc. Vol. 2, 1979.

2. Sawicki, E., J.D. Mulik, and E. Wittgenstein. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor, Ann Arbor Science Publishers, Inc. Vol. 1. 1978.

3. Siemer, D.D. Separation of Chloride and Bromide from Complex Matrices Prior to Ion Chromatographic Determination. Analytical Chemistry 52(12): 1874–1877. October 1980.

4. Small, H., T.S. Stevens, and W.C. Bauman. Novel Ion Exchange Chromatographic Method Using

Conductimetric Determination. Analytical Chemistry. *47*(11):1801. 1975.

18.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 5G—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM WOOD HEATERS (DILUTION TUNNEL SAMPLING LOCATION)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 4, Method 5, Method 5H, and Method 28.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of PM emissions from wood heaters.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 The exhaust from a wood heater is collected with a total collection hood, and is combined with ambient dilution air. Particulate matter is withdrawn proportionally from a single point in a sampling tunnel, and is collected on two glass fiber filters in series. The filters are maintained at a temperature of no greater than 32 °C (90 °F). The particulate mass is determined gravimetrically after the removal of uncombined water.

2.2 There are three sampling train approaches described in this method: (1) One dual-filter dry sampling train operated at about 0.015 m^3/min (0.5 cfm), (2) One dual-filter plus impingers sampling train operated at about 0.015 m^3/min (0.5 cfm), and (3) two dual-filter dry sampling trains operated simultaneously at any flow rate. Options (2) and (3) are referenced in section 16.0 of this method. The dual-filter dry sampling train equipment and operation, option (1), are described in detail in this method.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. The following items are required for sample collection:

6.1.1 Sampling Train. The sampling train configuration is shown in Figure 5G–1 and consists of the following components:

6.1.1.1 Probe. Stainless steel (*e.g.*, 316 or grade more corrosion resistant) or glass about 9.5 mm (⅜ in.) I.D., 0.6 m (24 in.) in length. If made of stainless steel, the probe shall be constructed from seamless tubing.

6.1.1.2 Pitot Tube. Type S, as described in section 6.1 of Method 2. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Method 2, section 10. Alternatively, a standard pitot may be used as described in Method 2, section 6.1.2.

6.1.1.3 Differential Pressure Gauge. Inclined manometer or equivalent device, as described in Method 2, section 6.2. One manometer shall be used for velocity head (Δp) readings and another (optional) for orifice differential pressure readings (ΔH).

6.1.1.4 Filter Holders. Two each made of borosilicate glass, stainless steel, or Teflon, with a glass frit or stainless steel filter support and a silicone rubber, Teflon, or Viton gasket. The holder design shall provide a positive seal against leakage from the outside or around the filters. The filter holders shall be placed in series with the backup filter holder located 25 to 100 mm (1 to 4 in.) downstream from the primary filter holder. The filter holder shall be capable of holding a filter with a 100 mm (4 in.) diameter, except as noted in section 16.

6.1.1.5 Filter Temperature Monitoring System. A temperature sensor capable of measuring temperature to within ±3 °C (±5 °F). The sensor shall be installed at the exit side of the front filter holder so that the sensing tip of the temperature sensor is in direct contact with the sample gas or in a thermowell as shown in Figure 5G–1. The temperature sensor shall comply with the calibration specifications in Method 2, section 10.3. Alternatively, the sensing tip of the temperature sensor may be installed at the inlet side of the front filter holder.

6.1.1.6 Dryer. Any system capable of removing water from the sample gas to less than 1.5 percent moisture (volume percent) prior to the metering system. The system shall include a temperature sensor for demonstrating that sample gas temperature exiting the dryer is less than 20 °C (68 °F).

6.1.1.7 Metering System. Same as Method 5, section 6.1.1.9.

6.1.2 Barometer. Same as Method 5, section 6.1.2.

6.1.3 Dilution Tunnel Gas Temperature Measurement. A temperature sensor capable

of measuring temperature to within ±3 °C (±5 °F).

6.1.4 Dilution Tunnel. The dilution tunnel apparatus is shown in Figure 5G–2 and consists of the following components:

6.1.4.1 Hood. Constructed of steel with a minimum diameter of 0.3 m (1 ft) on the large end and a standard 0.15 to 0.3 m (0.5 to 1 ft) coupling capable of connecting to standard 0.15 to 0.3 m (0.5 to 1 ft) stove pipe on the small end.

6.1.4.2 90° Elbows. Steel 90° elbows, 0.15 to 0.3 m (0.5 to 1 ft) in diameter for connecting mixing duct, straight duct and optional damper assembly. There shall be at least two 90° elbows upstream of the sampling section (see Figure 5G–2).

6.1.4.3 Straight Duct. Steel, 0.15 to 0.3 m (0.5 to 1 ft) in diameter to provide the ducting for the dilution apparatus upstream of the sampling section. Steel duct, 0.15 m (0.5 ft) in diameter shall be used for the sampling section. In the sampling section, at least 1.2 m (4 ft) downstream of the elbow, shall be two holes (velocity traverse ports) at 90° to each other of sufficient size to allow entry of the pitot for traverse measurements. At least 1.2 m (4 ft) downstream of the velocity traverse ports, shall be one hole (sampling port) of sufficient size to allow entry of the sampling probe. Ducts of larger diameter may be used for the sampling section, provided the specifications for minimum gas velocity and the dilution rate range shown in section 8 are maintained. The length of duct from the hood inlet to the sampling ports shall not exceed 9.1 m (30 ft).

6.1.4.4 Mixing Baffles. Steel semicircles (two) attached at 90° to the duct axis on opposite sides of the duct midway between the two elbows upstream of sampling section. The space between the baffles shall be about 0.3 m (1 ft).

6.1.4.5 Blower. Squirrel cage or other fan capable of extracting gas from the dilution tunnel of sufficient flow to maintain the velocity and dilution rate specifications in section 8 and exhausting the gas to the atmosphere.

6.2 Sample Recovery. The following items are required for sample recovery: probe brushes, wash bottles, sample storage containers, petri dishes, and funnel. Same as Method 5, sections 6.2.1 through 6.2.4, and 6.2.8, respectively.

6.3 Sample Analysis. The following items are required for sample analysis: glass weighing dishes, desiccator, analytical balance, beakers (250-ml or smaller), hygrometer, and temperature sensor. Same as Method 5, sections 6.3.1 through 6.3.3 and 6.3.5 through 6.3.7, respectively.

7.0 Reagents and Standards

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Filters. Glass fiber filters with a minimum diameter of 100 mm (4 in.), without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. Gelman A/E 61631 has been found acceptable for this purpose.

7.1.2 Stopcock Grease. Same as Method 5, section 7.1.5. 7.2 Sample Recovery. Acetone-reagent grade, same as Method 5, section 7.2.

7.3 Sample Analysis. Two reagents are required for the sample analysis:

7.3.1 Acetone. Same as in section 7.2.

7.3.2 Desiccant. Anhydrous calcium sulfate, calcium chloride, or silica gel, indicating type.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Dilution Tunnel Assembly and Cleaning. A schematic of a dilution tunnel is shown in Figure 5G–2. The dilution tunnel dimensions and other features are described in section 6.1.4. Assemble the dilution tunnel, sealing joints and seams to prevent air leakage. Clean the dilution tunnel with an appropriately sized wire chimney brush before each certification test.

8.2 Draft Determination. Prepare the wood heater as in Method 28, section 6.2.1. Locate the dilution tunnel hood centrally over the wood heater stack exhaust. Operate the dilution tunnel blower at the flow rate to be used during the test run. Measure the draft imposed on the wood heater by the dilution tunnel (*i.e.*, the difference in draft measured with and without the dilution tunnel operating) as described in Method 28, section 6.2.3. Adjust the distance between the top of the wood heater stack exhaust and the dilution tunnel hood so that the dilution tunnel induced draft is less than 1.25 Pa (0.005 in. H_2O). Have no fire in the wood heater, close the wood heater doors, and open fully the air supply controls during this check and adjustment.

8.3 Pretest Ignition. Same as Method 28, section 8.7.

8.4 Smoke Capture. During the pretest ignition period, operate the dilution tunnel and visually monitor the wood heater stack exhaust. Operate the wood heater with the doors closed and determine that 100 percent of the exhaust gas is collected by the dilution tunnel hood. If less than 100 percent of the wood heater exhaust gas is collected, adjust the distance between the wood heater stack and the dilution tunnel hood until no visible exhaust gas is escaping. Stop the pretest ignition period, and repeat the draft determination procedure described in section 8.2.

8.5 Velocity Measurements. During the pretest ignition period, conduct a velocity traverse to identify the point of average velocity. This single point shall be used for measuring velocity during the test run.

8.5.1 Velocity Traverse. Measure the diameter of the duct at the velocity traverse port location through both ports. Calculate the duct area using the average of the two diameters. A pretest leak-check of pitot lines as in Method 2, section 8.1, is recommended. Place the calibrated pitot tube at the centroid of the stack in either of the velocity traverse ports. Adjust the damper or similar device on the blower inlet until the velocity indicated by the pitot is approximately 220 m/min (720 ft/min). Continue to read the Δp and temperature until the velocity has remained constant (less than 5 percent change) for 1 minute. Once a constant velocity is obtained at the centroid of the duct, perform a velocity traverse as outlined in Method 2, section 8.3 using four points per traverse as outlined in Method 1. Measure the Δp and tunnel temperature at each traverse point and record the readings. Calculate the total gas flow rate using calculations contained in Method 2, section 12. Verify that the flow rate is 4 ±0.40 dscm/min (140 ±14 dscf/min); if not, readjust the damper, and repeat the velocity traverse. The moisture may be assumed to be 4 percent (100 percent relative humidity at 85 °F). Direct moisture measurements (*e.g.*, according to Method 4) are also permissible.

NOTE: If burn rates exceed 3 kg/hr (6.6 lb/hr), dilution tunnel duct flow rates greater than 4 dscm/min (140 dscfm) and sampling section duct diameters larger than 150 mm (6 in.) are allowed. If larger ducts or flow rates are used, the sampling section velocity shall be at least 220 m/min (720 fpm). In order to ensure measurable particulate mass catch, it is recommended that the ratio of the average mass flow rate in the dilution tunnel to the average fuel burn rate be less than 150:1 if larger duct sizes or flow rates are used.

8.5.2 Testing Velocity Measurements. After obtaining velocity traverse results that meet the flow rate requirements, choose a point of average velocity and place the pitot and temperature sensor at that location in the duct. Alternatively, locate the pitot and the temperature sensor at the duct centroid and calculate a velocity correction factor for the centroidal position. Mount the pitot to ensure no movement during the test run and seal the port holes to prevent any air leakage. Align the pitot opening to be parallel with the duct axis at the measurement point. Check that this condition is maintained during the test run (about 30-minute intervals). Monitor the temperature and velocity during the pretest ignition period to ensure that the proper flow rate is maintained. Make adjustments to the dilution tunnel flow rate as necessary.

8.6 Pretest Preparation. Same as Method 5, section 8.1.

8.7 Preparation of Sampling Train. During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin.

Using a tweezer or clean disposable surgical gloves, place one labeled (identified) and weighed filter in each of the filter holders. Be sure that each filter is properly centered and that the gasket is properly placed so as to prevent the sample gas stream from circumventing the filter. Check each filter for tears after assembly is completed.

Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct. Set up the train as shown in Figure 5G–1.

8.8 Leak-Check Procedures.

8.8.1 Leak-Check of Metering System Shown in Figure 5G–1. That portion of the sampling train from the pump to the orifice meter shall be leak-checked prior to initial use and after each certification or audit test. Leakage after the pump will result in less volume being recorded than is actually sampled. Use the procedure described in Method 5, section 8.4.1. Similar leak-checks shall be conducted for other types of metering systems (*i.e.*, without orifice meters).

8.8.2 Pretest Leak-Check. A pretest leak-check of the sampling train is recommended, but not required. If the pretest leak check is conducted, the procedures outlined in Method 5, section 8.4.2 should be used. A vacuum of 130 mm Hg (5 in. Hg) may be used instead of 380 mm Hg (15 in. Hg).

8.8.3 Post-Test Leak-Check. A leak-check of the sampling train is mandatory at the conclusion of each test run. The leak-check shall be performed in accordance with the procedures outlined in Method 5, section 8.4.2. A vacuum of 130 mm Hg (5 in. Hg) or the highest vacuum measured during the test run, whichever is greater, may be used instead of 380 mm Hg (15 in. Hg).

8.9 Preliminary Determinations. Determine the pressure, temperature and the average velocity of the tunnel gases as in section 8.5. Moisture content of diluted tunnel gases is assumed to be 4 percent for making flow rate calculations; the moisture content may be measured directly as in Method 4.

8.10 Sampling Train Operation. Position the probe inlet at the stack centroid, and block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream. Be careful not to bump the probe into the stack wall when removing or inserting the probe through the porthole; this minimizes the chance of extracting deposited material.

8.10.1 Begin sampling at the start of the test run as defined in Method 28, section 8.8.1. During the test run, maintain a sample flow rate proportional to the dilution tunnel flow rate (within 10 percent of the initial proportionality ratio) and a filter holder temperature of no greater than 32 °C (90 °F).

The initial sample flow rate shall be approximately 0.015 m^3/min (0.5 cfm).

8.10.2 For each test run, record the data required on a data sheet such as the one shown in Figure 5G–3. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment and when sampling is halted. Take other readings as indicated on Figure 5G–3 at least once each 10 minutes during the test run. Since the manometer level and zero may drift because of vibrations and temperature changes, make periodic checks during the test run.

8.10.3 For the purposes of proportional sampling rate determinations, data from calibrated flow rate devices, such as glass rotameters, may be used in lieu of incremental dry gas meter readings. Proportional rate calculation procedures must be revised, but acceptability limits remain the same.

8.10.4 During the test run, make periodic adjustments to keep the temperature between (or upstream of) the filters at the proper level. Do not change sampling trains during the test run.

8.10.5 At the end of the test run (see Method 28, section 6.4.6), turn off the coarse adjust valve, remove the probe from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak-check, as outlined in section 8.8.2. Also, leak-check the pitot lines as described in Method 2, section 8.1; the lines must pass this leak-check in order to validate the velocity head data.

8.11 Calculation of Proportional Sampling Rate. Calculate percent proportionality (see section 12.7) to determine whether the run was valid or another test run should be made.

8.12 Sample Recovery. Same as Method 5, section 8.7, with the exception of the following:

8.12.1 An acetone blank volume of about 50-ml or more may be used.

8.12.2 Treat the samples as follows:

8.12.2.1 Container Nos. 1 and 1A. Treat the two filters according to the procedures outlined in Method 5, section 8.7.6.1. The filters may be stored either in a single container or in separate containers. Use the sum of the filter tare weights to determine the sample mass collected.

8.12.2.3 Container No. 2.

8.12.2.3.1 Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe and filter holders by washing and brushing these components with acetone and placing the wash in a labeled glass container. At least three cycles of brushing and rinsing are required.

8.12.2.3.2 Between sampling runs, keep brushes clean and protected from contamination.

8.12.2.3.3 After all acetone washings and particulate matter have been collected in the sample containers, tighten the lids on the sample containers so that the acetone will not leak out when transferred to the laboratory weighing area. Mark the height of the fluid levels to determine whether leakage occurs during transport. Label the containers clearly to identify contents.

8.13 Sample Transport. Whenever possible, containers should be shipped in such a way that they remain upright at all times.

NOTE: Requirements for capping and transport of sample containers are not applicable if sample recovery and analysis occur in the same room.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.8, 10.1–10.4	Sampling equipment leak check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.
10.5	Analytical balance calibration	Ensure accurate and precise measurement of collected particulate.
16.2.5	Simultaneous, dual-train sample collection.	Ensure precision of measured particulate concentration.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory record of all calibrations.

10.1 Pitot Tube. The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Method 2, section 10.1, prior to the first certification test and checked semiannually, thereafter. A standard pitot need not be calibrated but shall be inspected and cleaned, if necessary, prior to each certification test.

10.2 Volume Metering System.

10.2.1 Initial and Periodic Calibration. Before its initial use and at least semiannually thereafter, calibrate the volume metering system as described in Method 5, section 10.3.1, except that the wet test meter with a capacity of 3.0 liters/rev (0.1 ft^3/rev) may be used. Other liquid displacement systems accurate to within ±1 percent, may be used as calibration standards.

NOTE: Procedures and equipment specified in Method 5, section 16.0, for alternative calibration standards, including calibrated dry gas meters and critical orifices, are allowed for calibrating the dry gas meter in the sampling train. A dry gas meter used as a calibration standard shall be recalibrated at least once annually.

10.2.2 Calibration After Use. After each certification or audit test (four or more test runs conducted on a wood heater at the four burn rates specified in Method 28), check calibration of the metering system by performing three calibration runs at a single, intermediate flow rate as described in Method 5, section 10.3.2.

NOTE: Procedures and equipment specified in Method 5, section 16.0, for alternative calibration standards are allowed for the post-test dry gas meter calibration check.

10.2.3 Acceptable Variation in Calibration. If the dry gas meter coefficient values obtained before and after a certification test differ by more than 5 percent, the certification test shall either be voided and repeated, or calculations for the certification test shall be performed using whichever meter coefficient value (*i.e.*, before or after) gives the lower value of total sample volume.

10.3 Temperature Sensors. Use the procedure in Method 2, section 10.3, to calibrate temperature sensors before the first certification or audit test and at least semiannually, thereafter.

10.4 Barometer. Calibrate against a mercury barometer before the first certification test and at least semiannually, thereafter. If a mercury barometer is used, no calibration is necessary. Follow the manufacturer's instructions for operation.

10.5 Analytical Balance. Perform a multipoint calibration (at least five points spanning the operational range) of the analytical balance before the first certification test and semiannually, thereafter. Before each certification test, audit the balance by weighing at least one calibration weight (class F) that corresponds to 50 to 150 percent of the weight of one filter. If the scale cannot reproduce the value of the calibration weight to within 0.1 mg, conduct the multipoint calibration before use.

11.0 Analytical Procedure

11.1 Record the data required on a sheet such as the one shown in Figure 5G–4. Use the same analytical balance for determining tare weights and final sample weights.

11.2 Handle each sample container as follows:

11.2.1 Container Nos. 1 and 1A. Treat the two filters according to the procedures outlined in Method 5, section 11.2.1.

11.2.2 Container No. 2. Same as Method 5, section 11.2.2, except that the beaker may be smaller than 250 ml.

11.2.3 Acetone Blank Container. Same as Method 5, section 11.2.4, except that the beaker may be smaller than 250 ml.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

12.1 Nomenclature.

B_{ws} = Water vapor in the gas stream, proportion by volume (assumed to be 0.04).
c_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (gr/dscf).
E = Particulate emission rate, g/hr (lb/hr).
E_{adj} = Adjusted particulate emission rate, g/hr (lb/hr).
L_a = Maximum acceptable leakage rate for either a pretest or post-test leak-check, equal to 0.00057 m^3/min (0.020 cfm) or 4 percent of the average sampling rate, whichever is less.
L_p = Leakage rate observed during the post-test leak-check, m^3/min (cfm).
m_a = Mass of residue of acetone blank after evaporation, mg.
m_{aw} = Mass of residue from acetone wash after evaporation, mg.
m_n = Total amount of particulate matter collected, mg.
M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).
PR = Percent of proportional sampling rate.
P_s = Absolute gas pressure in dilution tunnel, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
Q_{sd} = Average gas flow rate in dilution tunnel, calculated as in Method 2, Equation 2–8, dscm/hr (dscf/hr).
T_m = Absolute average dry gas meter temperature (see Figure 5G–3), °K (°R).
T_{mi} = Absolute average dry gas meter temperature during each 10-minute interval, i, of the test run, °K (°R).
T_s = Absolute average gas temperature in the dilution tunnel (see Figure 5G–3), °K (°R).
T_{si} = Absolute average gas temperature in the dilution tunnel during each 10 minute interval, i, of the test run, °K (°R).
T_{std} = Standard absolute temperature, 293 °K (528 °R).
V_a = Volume of acetone blank, ml.
V_{aw} = Volume of acetone used in wash, ml.
V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).

V_{mi} = Volume of gas sample as measured by dry gas meter during each 10-minute interval, i, of the test run, dcm.
$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).
V_s = Average gas velocity in the dilution tunnel, calculated by Method 2, Equation 2–7, m/sec (ft/sec). The dilution tunnel dry gas molecular weight may be assumed to be 29 g/g mole (lb/lb mole).
V_{si} = Average gas velocity in dilution tunnel during each 10-minute interval, i, of the test run, calculated by Method 2, Equation 2–7, m/sec (ft/sec).
Y = Dry gas meter calibration factor.
ΔH = Average pressure differential across the orifice meter, if used (see Figure 5G–2), mm H^2O (in. H^2O).
U = Total sampling time, min.
10 = 10 minutes, length of first sampling period.
13.6 = Specific gravity of mercury.
100 = Conversion to percent.

12.2 Dry Gas Volume. Same as Method 5, section 12.2, except that component changes are not allowable.

12.3 Solvent Wash Blank.

$$m_{aw} = \frac{m_a V_{aw}}{V_a} \qquad \text{Eq. 5G-1}$$

12.4 Total Particulate Weight. Determine the total particulate catch, mn, from the sum of the weights obtained from Container Nos. 1, 1A, and 2, less the acetone blank (see Figure 5G–4).

12.5 Particulate Concentration.

$$c_s = K_2 \frac{m_n}{V_{m(std)}} \qquad \text{Eq. 5G-2}$$

Where:
K_2 = 0.001 g/mg for metric units.
= 0.0154 gr/mg for English units.

12.6 Particulate Emission Rate.

$$E = C_s Q_{sd} \qquad \text{Eq. 5G-3}$$

NOTE: Particulate emission rate results produced using the sampling train described in section 6 and shown in Figure 5G–1 shall be adjusted for reporting purposes by the following method adjustment factor:

$$E_{adj} = K_3 E^{0.83} \qquad \text{Eq. 5G-4}$$

Where:
K_3 = constant, 1.82 for metric units.
= constant, 0.643 for English units.

12.7 Proportional Rate Variation. Calculate PR for each 10-minute interval, i, of the test run.

$$PR = \left(\frac{\theta \left(V_{mi} V_s T_m T_{si} \right)}{10 \left(V_m V_{si} T_s T_{mi} \right)} \right) \times 100 \qquad \text{Eq. 5G-5}$$

Alternate calculation procedures for proportional rate variation may be used if other sample flow rate data (e.g., orifice flow meters or rotameters) are monitored to maintain proportional sampling rates. The proportional rate variations shall be calculated for each 10-minute interval by comparing the stack to nozzle velocity ratio for each 10-minute interval to the average stack to nozzle velocity ratio for the test run. Proportional rate variation may be calculated for intervals shorter than 10 minutes with appropriate revisions to Equation 5G–5. If no more than 10 percent of the PR values for all the intervals exceed 90 percent ≤PR ≤110 percent, and if no PR value for any interval exceeds 80 percent ≤PR ≤120 percent, the results are acceptable. If the PR values for the test run are judged to be unacceptable, report the test run emission results, but do not include the results in calculating the weighted average emission rate, and repeat the test run.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Method 5H Sampling Train. The sampling train and sample collection, recovery, and analysis procedures described in Method 5H, sections 6.1.1, 7.1, 7.2, 8.1, 8.10, 8.11, and 11.0, respectively, may be used in lieu of similar sections in Method 5G. Operation of the Method 5H sampling train in the dilution tunnel is as described in section 8.10 of this method. Filter temperatures and condenser conditions are as described in Method 5H. No adjustment to the measured particulate matter emission rate (Equation 5G–4, section 12.6) is to be applied to the particulate emission rate measured by this alternative method.

16.2 Dual Sampling Trains. Two sampling trains may be operated simultaneously at sample flow rates other than that specified

in section 8.10, provided that the following specifications are met.

16.2.1 Sampling Train. The sampling train configuration shall be the same as specified in section 6.1.1, except the probe, filter, and filter holder need not be the same sizes as specified in the applicable sections. Filter holders of plastic materials such as Nalgene or polycarbonate materials may be used (the Gelman 1119 filter holder has been found suitable for this purpose). With such materials, it is recommended that solvents not be used in sample recovery. The filter face velocity shall not exceed 150 mm/sec (30 ft/min) during the test run. The dry gas meter shall be calibrated for the same flow rate range as encountered during the test runs. Two separate, complete sampling trains are required for each test run.

16.2.2 Probe Location. Locate the two probes in the dilution tunnel at the same level (see section 6.1.4.3). Two sample ports are necessary. Locate the probe inlets within the 50 mm (2 in.) diameter centroidal area of the dilution tunnel no closer than 25 mm (1 in.) apart.

16.2.3 Sampling Train Operation. Operate the sampling trains as specified in section 8.10, maintaining proportional sampling rates and starting and stopping the two sampling trains simultaneously. The pitot values as described in section 8.5.2 shall be used to adjust sampling rates in both sampling trains.

16.2.4 Recovery and Analysis of Sample. Recover and analyze the samples from the two sampling trains separately, as specified in sections 8.12 and 11.0, respectively.

16.2.4.1 For this alternative procedure, the probe and filter holder assembly may be weighed without sample recovery (use no solvents) described above in order to determine the sample weight gains. For this approach, weigh the clean, dry probe and filter holder assembly upstream of the front filter (without filters) to the nearest 0.1 mg to establish the tare weights. The filter holder section between the front and second filter need not be weighed. At the end of the test run, carefully clean the outside of the probe, cap the ends, and identify the sample (label). Remove the filters from the filter holder assemblies as described for container Nos. 1 and 1A in section 8.12.2.1. Reassemble the filter holder assembly, cap the ends, identify the sample (label), and transfer all the samples to the laboratory weighing area for final weighing. Requirements for capping and transport of sample containers are not applicable if sample recovery and analysis occur in the same room.

16.2.4.2 For this alternative procedure, filters may be weighed directly without a petri dish. If the probe and filter holder assembly are to be weighed to determine the sample weight, rinse the probe with acetone to remove moisture before desiccating prior to the test run. Following the test run, transport the probe and filter holder to the desiccator, and uncap the openings of the probe and the filter holder assembly. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

16.2.5 Calculations. Calculate an emission rate (Section 12.6) for the sample from each sampling train separately and determine the average emission rate for the two values. The two emission rates shall not differ by more than 7.5 percent from the average emission rate, or 7.5 percent of the weighted average emission rate limit in the applicable subpart of the regulations, whichever is greater. If this specification is not met, the results are unacceptable. Report the results, but do not include the results in calculating the weighted average emission rate. Repeat the test run until acceptable results are achieved, report the average emission rate for the acceptable test run, and use the average in calculating the weighted average emission rate.

17.0 References

Same as Method 5, section 17.0, References 1 through 11, with the addition of the following:

1. Oregon Department of Environmental Quality. Standard Method for Measuring the Emissions and Efficiencies of Woodstoves. June 8, 1984. Pursuant to Oregon Administrative Rules Chapter 340, Division 21.

2. American Society for Testing and Materials. Proposed Test Methods for Heating Performance and Emissions of Residential Wood-fired Closed Combustion-Chamber Heating Appliances. E–6 Proposal P 180. August 1986.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

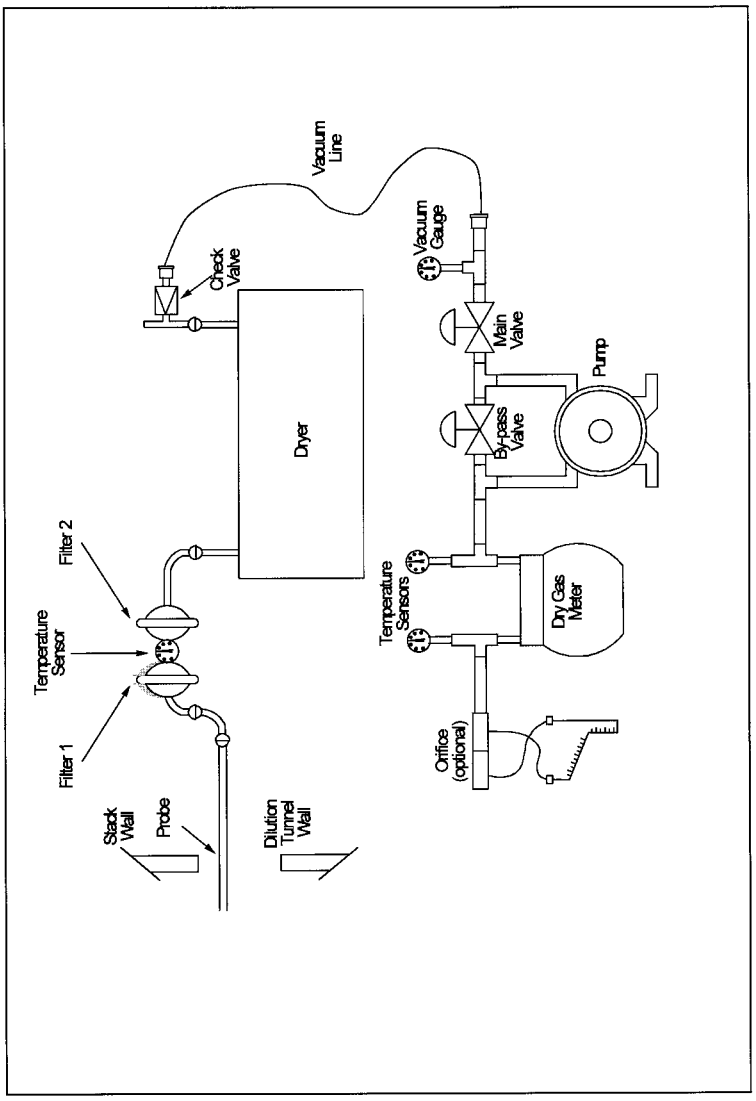

Figure 5G-1. Method 5G Sampling Train.

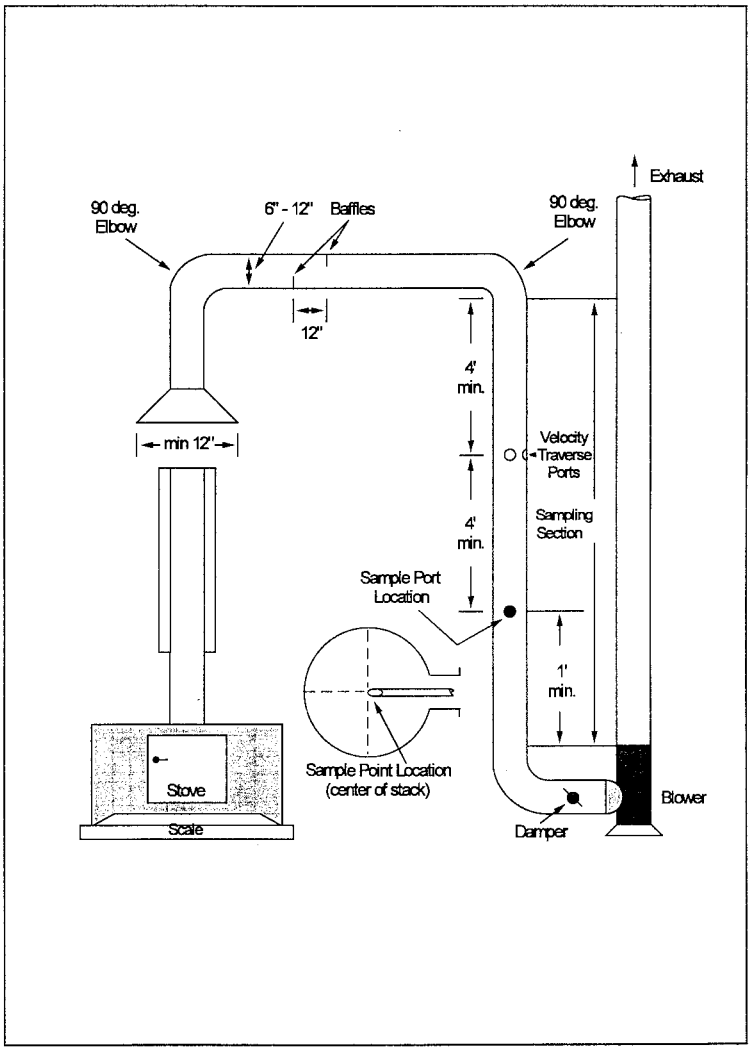

Figure 5G-2. Suggested Construction Details of the Dilution Tunnel.

Stove _____ Pitot tube coefficient, C_p _____
Test Method _____ Room temperature, °C (°F) _____
Operator _____ Barometric pressure mb (in. Hg) _____
Date _____ Measured or assumed moisture, % _____
Run No. _____ Final leak rate, m^3/min, (cfm) _____
Start Time _____ Probe liner material _____
Stop Time _____ Draft or static pressure, mm H_2O (in. H_2O) _____
Sample Box No. _____ Filter No. _____
Meter Box No. _____
Meter ΔH @ (optional) _____

Clock time	Test run time (e) min.	Vacuum mm Hg (in. Hg)	Tunnel temp (T_s) °C (°F)	Velocity head (ΔP_s) mm (in. H_2O)	Sample flow rate indicator (orifice meter optional) mm H_2O (in. H_2O)	Gas meter volume m^3 (ft^3)	Gas sample temp at dry gas meter Inlet °C (°F)	Gas sample temp at dry gas meter Outlet °C (°F)	Filter holder temp °C (°F)	Temperature of gas leaving dryer or last impinger °C (°F)
Total							Avg.	Avg.		
Average							Avg.			

Figure 5G-3. Sampling Data Sheet.

Stove _____
Date _____
Run No. _____
Filter Nos. _____
Liquid lost during transport, ml _____
Acetone blank volume, ml _____
Acetone wash volume, ml _____
Acetone blank concentration, mg/mg _____
Acetone wash blank, mg _____

Container number	Weight of particulate collected, mg	
	Final weight	Tare weight
1		
2		
3		
Total		
Less acetone blank		
Weight of particulate matter		

Stack Moisture Measurement Data
(Optional)

	Volume of liquid water collected	
	Implinger volume, ml	Silica gel weight, g
Final		
Initial		
Liquid collected		
Total volume collected		g[1] or ml

[1]Convert weight of water to volume by dividing total weight increase by density of water (1 g/ml).

$$\frac{\text{Increase, g}}{\text{(1 g/ml)}} = \text{Volume water, ml}$$

Figure 5G-4. Analysis Data Sheet.

METHOD 5H—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM WOOD HEATERS FROM A STACK LOCATION

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 2, Method 3, Method 5, Method 5G, Method 6, Method 6C, Method 16A, and Method 28.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of PM and condensible emissions from wood heaters.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Particulate matter is withdrawn proportionally from the wood heater exhaust and is collected on two glass fiber filters separated by impingers immersed in an ice water bath. The first filter is maintained at a temperature of no greater than 120 °C (248 °F). The second filter and the impinger system are cooled such that the temperature of the gas exiting the second filter is no greater than 20 °C (68 °F). The particulate mass collected in the probe, on the filters, and in the impingers is determined gravimetrically after the removal of uncombined water.

3.0 Definitions

Same as in Method 6C, section 3.0.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. The following items are required for sample collection:

6.1.1 Sampling Train. The sampling train configuration is shown in Figure 5H–1. Same as Method 5, section 6.1.1, with the exception of the following:

6.1.1.1 Probe Nozzle. The nozzle is optional; a straight sampling probe without a nozzle is an acceptable alternative.

6.1.1.2 Probe Liner. Same as Method 5, section 6.1.1.2, except that the maximum length of the sample probe shall be 0.6 m (2 ft) and probe heating is optional.

6.1.1.3 Filter Holders. Two each of borosilicate glass, with a glass frit or stainless steel filter support and a silicone rubber, Teflon, or Viton gasket. The holder design shall provide a positive seal against leakage from the outside or around the filter. The front filter holder shall be attached immediately at the outlet of the probe and prior to the first impinger. The second filter holder shall be attached on the outlet of the third impinger and prior to the inlet of the fourth (silica gel) impinger.

6.1.2 Barometer. Same as Method 5, section 6.2.

6.1.3 Stack Gas Flow Rate Measurement System. A schematic of an example test system is shown in Figure 5H–2. The flow rate measurement system consists of the following components:

6.1.3.1 Sample Probe. A glass or stainless steel sampling probe.

6.1.3.2 Gas Conditioning System. A high density filter to remove particulate matter and a condenser capable of lowering the dew point of the gas to less than 5 °C (40 °F). Desiccant, such as Drierite, may be used to dry the sample gas. Do not use silica gel.

6.1.3.3 Pump. An inert (*e.g.*, Teflon or stainless steel heads) sampling pump capable of delivering more than the total amount of sample required in the manufacturer's instructions for the individual instruments. A means of controlling the analyzer flow rate and a device for determining proper sample flow rate (*e.g.*, precision rotameter, pressure gauge downstream of all flow controls) shall be provided at the analyzer. The requirements for measuring and controlling the analyzer flow rate are not applicable if data are presented that demonstrate that the analyzer is insensitive to flow variations over the range encountered during the test.

6.1.3.4 Carbon Monoxide (CO) Analyzer. Any analyzer capable of providing a measure of CO in the range of 0 to 10 percent by volume at least once every 10 minutes.

6.1.3.5 Carbon Dioxide (CO_2) Analyzer. Any analyzer capable of providing a measure of CO_2 in the range of 0 to 25 percent by volume at least once every 10 minutes.

NOTE: Analyzers with ranges less than those specified above may be used provided actual concentrations do not exceed the range of the analyzer.

6.1.3.6 Manifold. A sampling tube capable of delivering the sample gas to two analyzers and handling an excess of the total amount used by the analyzers. The excess gas is exhausted through a separate port.

6.1.3.7 Recorders (optional). To provide a permanent record of the analyzer outputs.

6.1.4 Proportional Gas Flow Rate System. To monitor stack flow rate changes and provide a measurement that can be used to adjust and maintain particulate sampling flow rates proportional to the stack gas flow rate. A schematic of the proportional flow rate system is shown in Figure 5H–2 and consists of the following components:

6.1.4.1 Tracer Gas Injection System. To inject a known concentration of sulfur dioxide (SO_2) into the flue. The tracer gas injection system consists of a cylinder of SO_2, a gas cylinder regulator, a stainless steel needle valve or flow controller, a nonreactive (stainless steel and glass) rotameter, and an injection loop to disperse the SO_2 evenly in the flue.

6.1.4.2 Sample Probe. A glass or stainless steel sampling probe.

6.1.4.3 Gas Conditioning System. A combustor as described in Method 16A, sections 6.1.5 and 6.1.6, followed by a high density filter to remove particulate matter, and a condenser capable of lowering the dew point of the gas to less than 5 °C (40 °F). Desiccant, such as Drierite, may be used to dry the sample gas. Do not use silica gel.

6.1.4.4 Pump. Same as described in section 6.1.3.3.

6.1.4.5 SO_2 Analyzer. Any analyzer capable of providing a measure of the SO_2 concentration in the range of 0 to 1,000 ppm by volume (or other range necessary to measure the SO_2 concentration) at least once every 10 minutes.

6.1.4.6 Recorder (optional). To provide a permanent record of the analyzer outputs.

NOTE: Other tracer gas systems, including helium gas systems, are acceptable for determination of instantaneous proportional sampling rates.

6.2 Sample Recovery. Same as Method 5, section 6.2.

6.3 Sample Analysis. Same as Method 5, section 6.3, with the addition of the following:

6.3.1 Separatory Funnel. Glass or Teflon, 500-ml or greater.

7.0 Reagents and Standards

7.1 Sample Collection. Same as Method 5, section 7.1, including deionized distilled water.

7.2 Sample Recovery. Same as Method 5, section 7.2.

7.3 Sample Analysis. The following reagents and standards are required for sample analysis:

7.3.1 Acetone. Same as Method 5 section 7.2.

7.3.2 Dichloromethane (Methylene Chloride). Reagent grade, <0.001 percent residue in glass bottles.

7.3.3 Desiccant. Anhydrous calcium sulfate, calcium chloride, or silica gel, indicating type.

7.3.4 Cylinder Gases. For the purposes of this procedure, span value is defined as the upper limit of the range specified for each analyzer as described in section 6.1.3.4 or 6.1.3.5. If an analyzer with a range different from that specified in this method is used, the span value shall be equal to the upper limit of the range for the analyzer used (see note in section 6.1.3.5).

7.3.4.1 Calibration Gases. The calibration gases for the CO_2, CO, and SO_2 analyzers shall be CO_2 in nitrogen (N_2), CO in N_2, and SO_2 in N_2, respectively. CO_2 and CO calibration gases may be combined in a single cylinder. Use three calibration gases as specified in Method 6C, sections 7.2.1 through 7.2.3.

7.3.4.2 SO_2 Injection Gas. A known concentration of SO_2 in N_2. The concentration must be at least 2 percent SO_2 with a maximum of 100 percent SO_2.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Pretest Preparation. Same as Method 5, section 8.1.

8.2 Calibration Gas and SO_2 Injection Gas Concentration Verification, Sampling System Bias Check, Response Time Test, and Zero and Calibration Drift Tests. Same as Method 6C, sections 8.2.1, 8.2.3, 8.2.4, and 8.5, respectively, except that for verification of CO and CO_2 gas concentrations, substitute Method 3 for Method 6.

8.3 Preliminary Determinations.

8.3.1 Sampling Location. The sampling location for the particulate sampling probe shall be 2.45 ±0.15 m (8 ±0.5 ft) above the platform upon which the wood heater is placed (*i.e.*, the top of the scale).

8.3.2 Sampling Probe and Nozzle. Select a nozzle, if used, sized for the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain proportional sampling rates. During the run, do not change the nozzle size. Select a suitable probe liner and probe length to effect minimum blockage.

8.4 Preparation of Particulate Sampling Train. Same as Method 5, section 8.3, with the exception of the following:

8.4.1 The train should be assembled as shown in Figure 5H–1.

8.4.2 A glass cyclone may not be used between the probe and filter holder.

8.5 Leak-Check Procedures.

8.5.1 Leak-Check of Metering System Shown in Figure 5H–1. That portion of the sampling train from the pump to the orifice meter shall be leak-checked after each certification or audit test. Use the procedure described in Method 5, section 8.4.1.

8.5.2 Pretest Leak-Check. A pretest leak-check of the sampling train is recommended, but not required. If the pretest leak-check is conducted, the procedures outlined in Method 5, section 8.5.2 should be used. A vacuum of 130 mm Hg (5 in. Hg) may be used instead of 380 mm Hg (15 in. Hg).

8.5.2 Leak-Checks During Sample Run. If, during the sampling run, a component (*e.g.*, filter assembly or impinger) change becomes necessary, conduct a leak-check as described in Method 5, section 8.4.3.

8.5.3 Post-Test Leak-Check. A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be performed in accordance with the procedures outlined in Method 5, section 8.4.4, except that a vacuum of 130 mm Hg (5 in. Hg) or the greatest vacuum measured during the test run, whichever is greater, may be used instead of 380 mm Hg (15 in. Hg).

8.6 Tracer Gas Procedure. A schematic of the tracer gas injection and sampling systems is shown in Figure 5H–2.

8.6.1 SO_2 Injection Probe. Install the SO_2 injection probe and dispersion loop in the stack at a location 2.9 ±0.15 m (9.5 ±0.5 ft) above the sampling platform.

8.6.2 SO_2 Sampling Probe. Install the SO_2 sampling probe at the centroid of the stack at a location 4.1 ±0.15 m (13.5 ±0.5 ft) above the sampling platform.

8.7 Flow Rate Measurement System. A schematic of the flow rate measurement system is shown in Figure 5H–2. Locate the flow rate measurement sampling probe at the centroid of the stack at a location 2.3 ±0.3 m (7.5 ±1 ft) above the sampling platform.

8.8 Tracer Gas Procedure. Within 1 minute after closing the wood heater door at the start of the test run (as defined in Method 28, section 8.8.1), meter a known concentration of SO_2 tracer gas at a constant flow rate into the wood heater stack. Monitor the SO_2 concentration in the stack, and record the SO_2 concentrations at 10-minute intervals or more often. Adjust the particulate sampling flow rate proportionally to the SO_2 concentration changes using Equation 5H–6 (*e.g.*, the SO_2 concentration at the first 10-minute reading is measured to be 100 ppm; the next 10 minute SO_2 concentration is measured to be 75 ppm: the particulate sample flow rate is adjusted from the initial 0.15 cfm to 0.20 cfm). A check for proportional rate variation shall be made at the completion of the test run using Equation 5H–10.

8.9 Volumetric Flow Rate Procedure. Apply stoichiometric relationships to the wood combustion process in determining the exhaust gas flow rate as follows:

8.9.1 Test Fuel Charge Weight. Record the test fuel charge weight (wet) as specified in Method 28, section 8.8.2. The wood is assumed to have the following weight percent composition: 51 percent carbon, 7.3 percent hydrogen, 41 percent oxygen. Record the wood moisture for each fuel charge as described in Method 28, section 8.6.5. The ash is assumed to have negligible effect on associated C, H, and O concentrations after the test burn.

8.9.2 Measured Values. Record the CO and CO_2 concentrations in the stack on a dry basis every 10 minutes during the test run or more often. Average these values for the test run. Use as a mole fraction (*e.g.*, 10 percent CO_2 is recorded as 0.10) in the calculations to express total flow (see Equation 5H–6).

8.10 Sampling Train Operation.

8.10.1 For each run, record the data required on a data sheet such as the one shown in Figure 5H–3. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak-check, and when sampling is halted. Take other readings as indicated on Figure 5H–3 at least once each 10 minutes during the test run.

8.10.2 Remove the nozzle cap, verify that the filter and probe heating systems are up to temperature, and that the probe is properly positioned. Position the nozzle, if used, facing into gas stream, or the probe tip in the 50 mm (2 in.) centroidal area of the stack.

8.10.3 Be careful not to bump the probe tip into the stack wall when removing or inserting the probe through the porthole; this minimizes the chance of extracting deposited material.

8.10.4 When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

8.10.5 Begin sampling at the start of the test run as defined in Method 28, section 8.8.1, start the sample pump, and adjust the sample flow rate to between 0.003 and 0.014 m^3/min (0.1 and 0.5 cfm). Adjust the sample flow rate proportionally to the stack gas flow during the test run according to the procedures outlined in section 8. Maintain a proportional sampling rate (within 10 percent of the desired value) and a filter holder temperature no greater than 120 °C (248 °F).

8.10.6 During the test run, make periodic adjustments to keep the temperature around the filter holder at the proper level. Add more ice to the impinger box and, if necessary, salt to maintain a temperature of less than 20 °C (68 °F) at the condenser/silica gel outlet.

8.10.7 If the pressure drop across the filter becomes too high, making proportional sampling difficult to maintain, either filter may be replaced during a sample run. It is recommended that another complete filter assembly be used rather than attempting to change the filter itself. Before a new filter assembly is installed, conduct a leak-check (see section 8.5.2). The total particulate weight shall include the summation of all filter assembly catches. The total time for changing sample train components shall not exceed 10 minutes. No more than one component change is allowed for any test run.

8.10.8 At the end of the test run, turn off the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak-check, as outlined in section 8.5.3.

8.11 Sample Recovery. Same as Method 5, section 8.7, with the exception of the following:

8.11.1 Blanks. The volume of the acetone blank may be about 50-ml, rather than 200-ml; a 200-ml water blank shall also be saved for analysis.

8.11.2 Samples.

8.11.2.1 Container Nos. 1 and 1A. Treat the two filters according to the procedures outlined in Method 5, section 8.7.6.1. The filters

may be stored either in a single container or in separate containers.

8.11.2.2 Container No. 2. Same as Method 5, section 8.7.6.2, except that the container should not be sealed until the impinger rinse solution is added (see section 8.10.2.4).

8.11.2.3 Container No. 3. Treat the impingers as follows: Measure the liquid which is in the first three impingers to within 1-ml by using a graduated cylinder or by weighing it to within 0.5 g by using a balance (if one is available). Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas. Transfer the water from the first, second, and third impingers to a glass container. Tighten the lid on the sample container so that water will not leak out.

8.11.2.4 Rinse impingers and graduated cylinder, if used, with acetone three times or more. Avoid direct contact between the acetone and any stopcock grease or collection of any stopcock grease in the rinse solutions. Add these rinse solutions to sample Container No. 2.

8.11.2.5 Container No. 4. Same as Method 5, section 8.7.6.3

8.12 Sample Transport. Whenever possible, containers should be transferred in such a way that they remain upright at all times.

NOTE: Requirements for capping and transport of sample containers are not applicable if sample recovery and analysis occur in the same room.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.2	Sampling system bias check	Ensures that bias introduced by measurement system, minus analyzer, is no greater than 3 percent of span.
8.2	Analyzer zero and calibration drift tests	Ensures that bias introduced by drift in the measurement system output during the run is no greater than 3 percent of span.
8.5, 10.1, 12.13	Sampling equipment leak-check and calibration; proportional sampling rate verification.	Ensures accurate measurement of stack gas flow rate, sample volume.
10.1	Analytical balance calibration	Ensure accurate and precise measurement of collected particulate.
10.3	Analyzer calibration error check	Ensures that bias introduced by analyzer calibration error is no greater than 2 percent of span.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory record of all calibrations.

10.1 Volume Metering System, Temperature Sensors, Barometer, and Analytical Balance. Same as Method 5G, sections 10.2 through 10.5, respectively.

10.2 SO_2 Injection Rotameter. Calibrate the SO_2 injection rotameter system with a soap film flowmeter or similar direct volume measuring device with an accuracy of 2 percent. Operate the rotameter at a single reading for at least three calibration runs for 10 minutes each. When three consecutive calibration flow rates agree within 5 percent, average the three flow rates, mark the rotameter at the calibrated setting, and use the calibration flow rate as the SO_2 injection flow rate during the test run. Repeat the rotameter calibration before the first certification test and semiannually thereafter.

10.3. Gas Analyzers. Same as Method 6C, section 10.0.

10.4 Field Balance Calibration Check. Check the calibration of the balance used to weigh impingers with a weight that is at least 500g or within 50g of a loaded impinger. The weight must be ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 6 (or better). Daily before use, the field balance must measure the weight within ± 0.5g of the certified mass. If the daily balance calibration check fails, perform corrective measures and repeat the check before using balance.

10.5 Analytical Balance Calibration. Perform a multipoint calibration (at least five points spanning the operational range) of the analytical balance before the first use, and semiannually thereafter. The calibration of the analytical balance must be conducted using ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 2 (or better) tolerance weights. Audit the balance each day it is used for gravimetric measurements by weighing at least one ASTM E617–13 Class 2 tolerance (or better) calibration weight that corresponds to 50 to 150 percent of the weight of one filter or between 1g and 5g. If the scale cannot reproduce the value of the calibration weight to within 0.5 mg of the certified mass, perform corrective measures, and conduct the multipoint calibration before use.

11.0 Analytical Procedure

11.1 Record the data required on a sheet such as the one shown in Figure 5H–4.

11.2 Handle each sample container as follows:

11.2.1 Container Nos. 1 and 1A. Treat the two filters according to the procedures outlined in Method 5, section 11.2.1.

11.2.2 Container No. 2. Same as Method 5, section 11.2.2, except that the beaker may be smaller than 250-ml.

11.2.3 Container No. 3. Note the level of liquid in the container and confirm on the analysis sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Determination of sample leakage is not applicable if sample recovery and analysis occur in the same room. Measure the liquid in this container either volumetrically to within 1-ml or gravimetrically to within 0.5 g. Transfer the contents to a 500-ml or larger separatory funnel. Rinse the container with water, and add to the separatory funnel. Add 25-ml of dichloromethane to the separatory funnel, stopper and vigorously shake 1 minute, let separate and transfer the dichloromethane (lower layer) into a tared beaker or evaporating dish. Repeat twice more. It is necessary to rinse Container No. 3 with dichloromethane. This rinse is added to the impinger extract container. Transfer the remaining water from the separatory funnel to a tared beaker or evaporating dish and evaporate to dryness at 104 °C (220 °F). Desiccate and weigh to a constant weight. Evaporate the combined impinger water extracts at ambient temperature and pressure. Desiccate and weigh to a constant weight. Report both results to the nearest 0.1 mg.

11.2.4 Container No. 4. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance.

11.2.5 Acetone Blank Container. Same as Method 5, section 11.2.4, except that the beaker may be smaller than 250 ml.

11.2.6 Dichloromethane Blank Container. Treat the same as the acetone blank.

11.2.7 Water Blank Container. Transfer the water to a tared 250 ml beaker and evaporate to dryness at 104 °C (220 °F). Desiccate and weigh to a constant weight.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

12.1 Nomenclature.

A = Sample flow rate adjustment factor.
BR = Dry wood burn rate, kg/hr (lb/hr), from Method 28, Section 8.3.
B_{ws} = Water vapor in the gas stream, proportion by volume.
C_i = Tracer gas concentration at inlet, ppmv.
C_o = Tracer gas concentration at outlet, ppmv.
C_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (g/dscf).
E = Particulate emission rate, g/hr (lb/hr).
ΔH = Average pressure differential across the orifice meter (see Figure 5H–1), mm H_2O (in. H_2O).
L_a = Maximum acceptable leakage rate for either a post-test leak-check or for a leak-check following a component change; equal to 0.00057 cmm (0.020 cfm) or 4 percent of the average sampling rate, whichever is less.
L_1 = Individual leakage rate observed during the leak-check conducted before a component change, cmm (cfm).
L_p = Leakage rate observed during the post-test leak-check, cmm (cfm).
m_n = Total amount of particulate matter collected, mg.
M_a = Mass of residue of solvent after evaporation, mg.
N_C = Grams of carbon/gram of dry fuel (lb/lb), equal to 0.0425.
N_T = Total dry moles of exhaust gas/kg of dry wood burned, g-moles/kg (lb-moles/lb).
PR = Percent of proportional sampling rate.
P_{bar} = Barometric pressure at the sampling site, mm Hg (in.Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in.Hg).
Q_i = Gas volumetric flow rate at inlet, cfm (l/min).
Q_o = Gas volumetric flow rate at outlet, cfm (l/min).

12.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 5H–3).

12.3 Dry Gas Volume. Same as Method 5, section 12.3.

12.4 Volume of Water Vapor.

$$V_{w(std)} = K_2 V_{1c} \qquad \text{Eq. 5H-1}$$

Where:

K_2 = 0.001333 m^3/ml for metric units.
K_2 = 0.04707 ft^3/ml for English units.

12.5 Moisture Content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad \text{Eq. 5H-2}$$

12.6 Solvent Wash Blank.

$$W_a = \frac{M_a V_{aw}}{V_a} \qquad \text{Eq. 5H-3}$$

12.7 Total Particulate Weight. Determine the total particulate catch from the sum of the weights obtained from containers 1, 2, 3,

and 4 less the appropriate solvent blanks (see Figure 5H–4).

NOTE: Refer to Method 5, section 8.5 to assist in calculation of results involving two filter assemblies.

12.8 Particulate Concentration.

$$C_s = \frac{0.001g}{mg}\ \frac{m_n}{V_{m(std)}} \qquad \text{Eq. 5H-4}$$

12.9 Sample Flow Rate Adjustment.

$$a = \frac{S_1}{S_i} \qquad \text{Eq. 5H-5}$$

12.10 Carbon Balance for Total Moles of Exhaust Gas (dry)/kg of Wood Burned in the Exhaust Gas.

$$N_T = \frac{K_3 N_C}{Y_{CO_2} + Y_{CO} + Y_{HC}} \qquad \text{Eq. 5H-6}$$

Where:

K_3 = 1000 g/kg for metric units.
K_3 = 1.0 lb/lb for English units.

NOTE: The NO_X/SO_X portion of the gas is assumed to be negligible.

12.11 Total Stack Gas Flow Rate.

$$Q_{sd} = K_4\ N_T\ BR \qquad \text{Eq. 5H-7}$$

Where:

K_4 = 0.02406 dscm/g-mole for metric units.
K_4 = 384.8 dscf/lb-mole for English units.

12.12 Particulate Emission Rate.

$$E = C_s\ Q_{sd} \qquad \text{Eq. 5H-8}$$

12.13 Proportional Rate Variation. Calculate PR for each 10-minute interval, i, of the test run.

$$PR = \frac{\theta\ S_i V_{mi(std)}}{10\sum_{i=1}^{N}\left[S_i V_{mi(std)}\right]} \times 100 \qquad \text{Eq. 5H-9}$$

12.14 Acceptable Results. If no more than 15 percent of the PR values for all the intervals fall outside the range 90 percent ≤PR ≤110 percent, and if no PR value for any interval falls outside the range 75 ≤PR ≤125 percent, the results are acceptable. If the PR values for the test runs are judged to be unacceptable, report the test run emission results, but do not include the test run results in calculating the weighted average emission rate, and repeat the test.

12.15 Alternative Tracer Gas Flow Rate Determination.

$$Q_o = \frac{Q_i \times C_i}{C_o} \qquad Eq.\ 5H-10$$

NOTE: This gives Q for a single instance only. Repeated multiple determinations are needed to track temporal variations. Very small variations in Q_i, C_i, or C_o may give very large variations in Q_o.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Alternative Stack Gas Volumetric Flow Rate Determination (Tracer Gas).

16.1.1 Apparatus.

16.1.1.1 Tracer Gas Injector System. This is to inject a known concentration of tracer gas into the stack. This system consists of a cylinder of tracer gas, a gas cylinder regulator, a stainless steel needle valve or a flow controller, a nonreactive (stainless steel or glass) rotameter, and an injection loop to disperse the tracer gas evenly in the stack.

16.1.1.2 Tracer Gas Probe. A glass or stainless steel sampling probe.

16.1.1.3 Gas Conditioning System. A gas conditioning system is suitable for delivering a cleaned sample to the analyzer consisting of a filter to remove particulate and a condenser capable of lowering the dew point of the sample gas to less than 5 °C (40 °F). A desiccant such as anhydrous calcium sulfate may be used to dry the sample gas. Desiccants which react or absorb tracer gas or stack gas may not be used, e.g. silica gel absorbs CO_2.

16.1.1.4 Pump. An inert (*i.e.*, stainless steel or Teflon head) pump to deliver more than the total sample required by the manufacturer's specifications for the analyzer used to measure the downstream tracer gas concentration.

16.1.1.5 Gas Analyzer. A gas analyzer is any analyzer capable of measuring the tracer gas concentration in the range necessary at least every 10 minutes. A means of controlling the analyzer flow rate and a device for determining proper sample flow rate shall be provided unless data is provided to show that the analyzer is insensitive to flow variations over the range encountered during the test.

The gas analyzer needs to meet or exceed the following performance specifications:

Linearity	±1 percent of full scale.
Calibration Error	≤2 percent of span.
Response Time	≤10 seconds.
Zero Drift (24 hour)	≤2 percent of full scale.
Span Drift (24 hour)	≤2 percent of full scale.
Resolution	≤0.5 percent of span.

16.1.1.6 Recorder (optional). To provide a permanent record of the analyzer output.

16.1.2 Reagents.

16.1.2.1 Tracer Gas. The tracer gas is sulfur hexafluoride in an appropriate concentration for accurate analyzer measurement or pure sulfur dioxide. The gas used must be nonreactive with the stack effluent and give minimal (<3 percent) interference to measurement by the gas analyzer.

16.1.3 Procedure. Select upstream and downstream locations in the stack or duct for introducing the tracer gas and delivering the sampled gas to the analyzer. The inlet location should be 8 or more duct diameters beyond any upstream flow disturbance. The outlet should be 8 or more undisturbed duct diameters from the inlet and 2 or more duct diameters from the duct exit. After installing the apparatus, meter a known concentration of the tracer gas into the stack at the inlet location. Use the gas sample probe and analyzer to show that no stratification of the tracer gas is found in the stack at the measurement locations. Monitor the tracer gas concentration from the outlet location and record the concentration at 10-minute intervals or more often at the option of the tester. A minimum of three measured intervals is recommended to determine the stack gas volumetric flow rate. Other statistical procedures may be applied for complete flow characterization and additional QA/QC.

17.0 References

Same as Method 5G, section 17.0.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

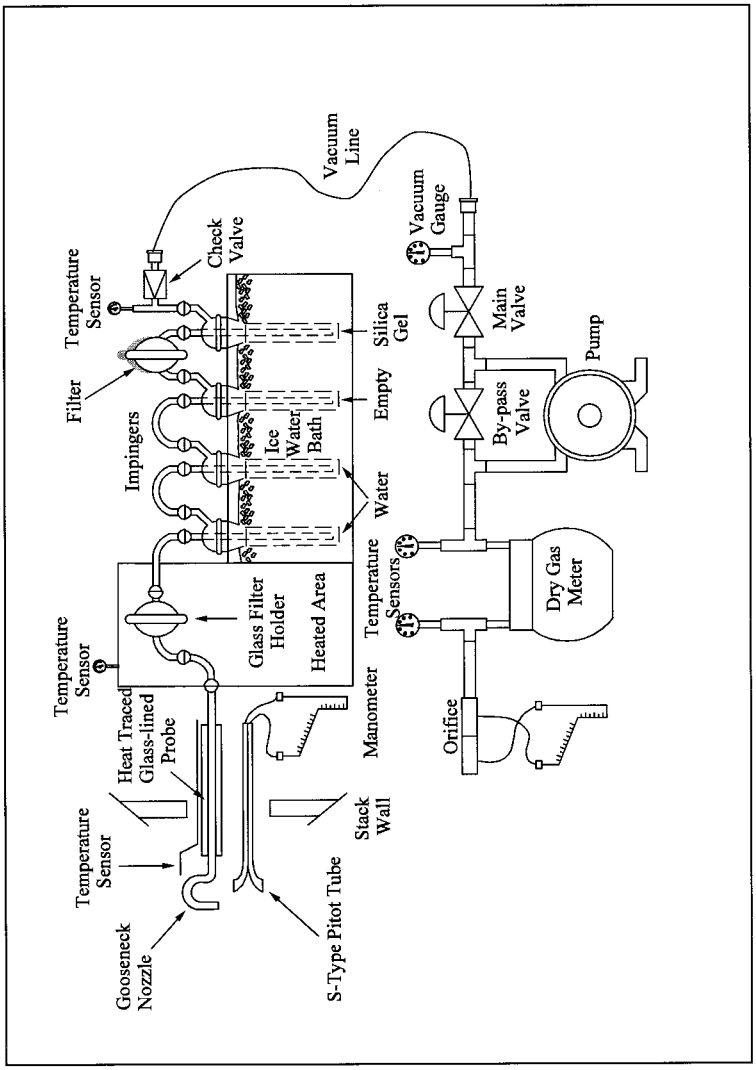

Figure 5H-1. Sampling Train.

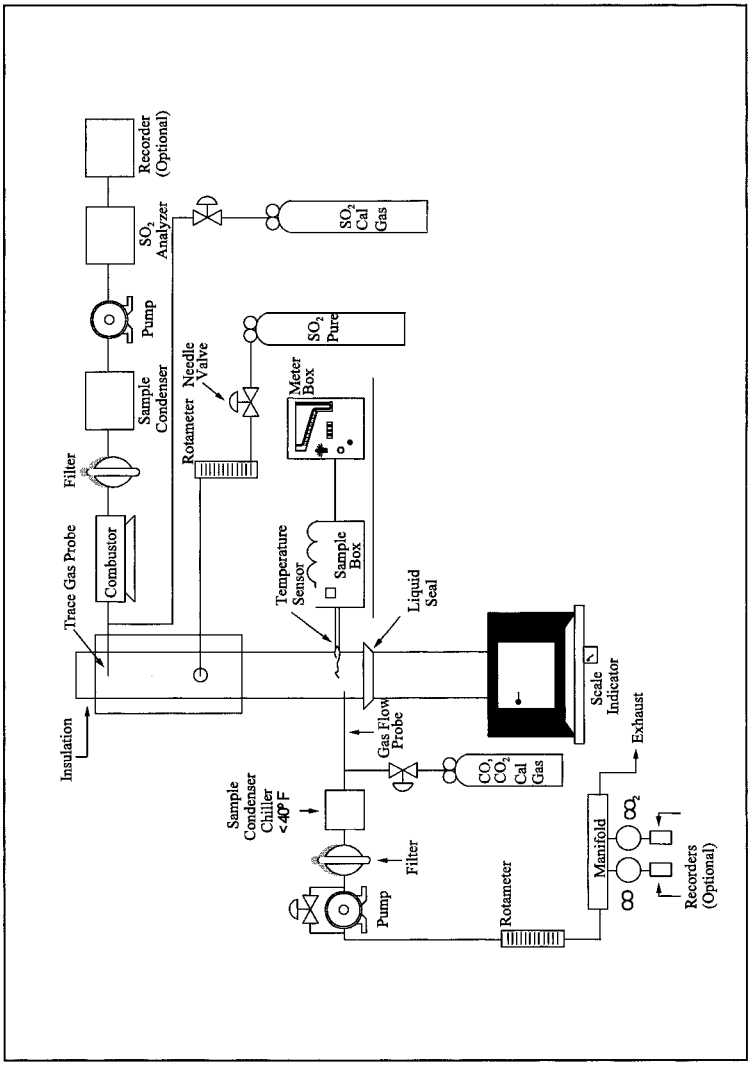

Figure 5H-2. Test System Schematic.

Stove _____ Pitot tube coefficient, Cp _____
Test Method _____ Room temperature, C°, (°F) _____
Operator _____ Barometric pressure mb (in. Hg) _____
Date _____ Measured or assumed moisture, % _____
Run No. _____ Nozzle identification No. _____
Start Time _____ Average calibrated nozzle diameter, mm (in.) _____
Stop Time _____ Final leak rate, m³/min, (cfm) _____
Sample Box No. _____ Probe liner material _____
Meter Box No. _____ Draft or static pressure, mm H_2O (in. H_2O) _____
Meter ΔH @ (Optional) _____ Filter Nos. _____
C Factor _____

Clock time	Test run time (q), min.	Vacuum mm Hg (in. Hg)	Fuel temperature (T_s) °C (°F)	Flow in Flue m³/ min (ft³/min)	Volume sample in period m³(ft³)	Gas meter volume m³ (ft³)	Gas sample temperature at dry gas meter °C (°F)		Front filter holder temperature °C (°F)	Temperature of gas leaving dryer or last impinger °C (°F)
								°C (°F)		
Total							Avg.	Avg.		
Average							Avg.			

Figure 5H-3. Sampling Data Sheet.

Stove _____
Date _____
Run No. _____
Filter Nos. _____
Amount liquid lost during transport, ml _____
Acetone blank volume, ml _____
Acetone wash volume, ml _____
Acetone blank concentration, mg/ml _____
Acetone wash blank, mg _____

Dichloromethane blank volume, ml _____
Dichloromethane wash volume, ml _____
Dichloromethane blank concentration, mg/ml _____
Dichloromethane wash blank, mg _____
Water blank volume, ml _____
Waster wash volume, ml _____
Water blank concentration, mg/ml _____
Water wash blank, mg _____

Container number	Weight of particulate collected, mg		
	Final weight	Tare weight	Weight gain
1 _____			
2 _____			
3 _____			
4 _____			
5 _____			
Total			
Less acetone blank			
Less dichloromethane blank			
Less water blank			
Weight of particulate matter			

	Volume of liquid water collected	
	Impinger volume, ml	Silica gel weight, g
Final _____		
Initial _____		
Liquid collected _____		
Total volume collected _____		g or ml

* Convert weight of water to volume by dividing total weight increase by density of water (1 g/ml).

$$\frac{\text{Increase, g}}{\text{(1 g/ml)}} = \text{Volume water, ml}$$

Figure 5H-4. Analysis data sheet.

Figure 5H-4. Analysis Data Sheet.

METHOD 5I—DETERMINATION OF LOW LEVEL PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Certain information is contained in other EPA procedures found in this part. Therefore, to obtain reliable results, persons using this method should have experience with and a thorough knowledge of the following Methods: Methods 1, 2, 3, 4 and 5.

1. Scope and Application.

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of low level particulate matter (PM) emissions from stationary sources. The method is most effective for total PM catches of 50 mg or less. This method was initially developed for performing correlation of manual PM measurements to PM continuous emission monitoring systems (CEMS), however it is also useful for other low particulate concentration applications.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods. Method 5I requires the use of paired trains. Acceptance criteria for the identification of data quality outliers from the paired trains are provided in section 12.2 of this Method.

2. Summary of Method.

2.1. Description. The system setup and operation is essentially identical to Method 5. Particulate is withdrawn isokinetically from the source and collected on a 47 mm glass fiber filter maintained at a temperature of 120 ±14 °C (248 ±25 °F). The PM mass is determined by gravimetric analysis after the removal of uncombined water. Specific measures in this procedure designed to improve system performance at low particulate levels include:

1. Improved sample handling procedures
2 Light weight sample filter assembly
3. Use of low residue grade acetone

Accuracy is improved through the minimization of systemic errors associated with sample handling and weighing procedures. High purity reagents, all glass, grease free, sample train components, and light weight filter assemblies and beakers, each contribute to the overall objective of improved precision and accuracy at low particulate concentrations.

2.2 Paired Trains. This method must be performed using a paired train configuration. These trains may be operated as co-located trains (to trains operating collecting from one port) or as simultaneous trains (separate trains operating from different ports at the same time). Procedures for calculating precision of the paired trains are provided in section 12.

2.3 Detection Limit. a. Typical detection limit for manual particulate testing is 0.5 mg. This mass is also cited as the accepted weight variability limit in determination of ''constant weight'' as cited in section 8.1.2 of this Method. EPA has performed studies to provide guidance on minimum PM catch. The minimum detection limit (MDL) is the minimum concentration or amount of an analyte that can be determined with a specified degree of confidence to be different from zero. We have defined the minimum or target catch as a concentration or amount sufficiently larger than the MDL to ensure that the results are reliable and repeatable. The particulate matter catch is the product of the average particulate matter concentration on a mass per volume basis and the volume of gas collected by the sample train. The tester can generally control the volume of gas collected by increasing the sampling time or to a lesser extent by increasing the rate at which sample is collected. If the tester has a reasonable estimate of the PM concentration from the source, the tester can ensure that the target catch is collected by sampling the appropriate gas volume.

b. However, if the source has a very low particulate matter concentration in the stack, the volume of gas sampled may need to be very large which leads to unacceptably long sampling times. When determining compliance with an emission limit, EPA guidance has been that the tester does not always have to collect the target catch. Instead, we have suggested that the tester sample enough stack gas, that if the source were exactly at the level of the emission standard, the sample catch would equal the target catch. Thus, if at the end of the test the catch were smaller than the target, we could still conclude that the source is in compliance though we might not know the exact emission level. This volume of gas becomes a target volume that can be translated into a target sampling time by assuming an average sampling rate. Because the MDL forms the basis for our guidance on target sampling times, EPA has conducted a systematic laboratory study to define what is the MDL for Method 5 and determined the Method to have a calculated practical quantitation limit (PQL) of 3 mg of PM and an MDL of 1 mg.

c. Based on these results, the EPA has concluded that for PM testing, the target catch must be no less than 3 mg. Those sample catches between 1 mg and 3 mg are between the detection limit and the limit of quantitation. If a tester uses the target catch to estimate a target sampling time that results in sample catches that are less than 3 mg, you should not automatically reject the results. If the tester calculated the target sampling time as described above by assuming that the source was at the level of the emission limit, the results would still be valid for determining that the source was in compliance. For purposes other than determining compliance, results should be divided into two categories—those that fall between 3 mg and 1 mg and those that are below 1 mg. A sample catch between 1 and 3 mg may be used for such purposes as calculating emission rates with the understanding that the resulting emission rates can have a high degree of uncertainty. Results of less than 1 mg should not be used for calculating emission rates or pollutant concentrations.

d. When collecting small catches such as 3 mg, bias becomes an important issue. Source testers must use extreme caution to reach the PQL of 3 mg by assuring that sampling

probes are very clean (perhaps confirmed by low blank weights) before use in the field. They should also use low tare weight sample containers, and establish a well-controlled balance room to weigh the samples.

3. Definitions.

3.1 *Light Weight Filter Housing.* A smaller housing that allows the entire filtering system to be weighed before and after sample collection. (See. 6.1.3)

3.2 *Paired Train.* Sample systems trains may be operated as co-located trains (two sample probes attached to each other in the same port) or as simultaneous trains (two separate trains operating from different ports at the same time).

4. Interferences.

a. There are numerous potential interferents that may be encountered during performance of Method 5I sampling and analyses. This Method should be considered more sensitive to the normal interferents typically encountered during particulate testing because of the low level concentrations of the flue gas stream being sampled.

b. Care must be taken to minimize field contamination, especially to the filter housing since the entire unit is weighed (not just the filter media). Care must also be taken to ensure that no sample is lost during the sampling process (such as during port changes, removal of the filter assemblies from the probes, etc.).

c. Balance room conditions are a source of concern for analysis of the low level samples. Relative humidity, ambient temperatures variations, air draft, vibrations and even barometric pressure can affect consistent reproducible measurements of the sample media. Ideally, the same analyst who performs the tare weights should perform the final weights to minimize the effects of procedural differences specific to the analysts.

d. Attention must also be provided to weighing artifacts caused by electrostatic charges which may have to be discharged or neutralized prior to sample analysis. Static charge can affect consistent and reliable gravimetric readings in low humidity environments. Method 5I recommends a relative humidity of less than 50 percent in the weighing room environment used for sample analyses. However, lower humidity may be encountered or required to address sample precision problems. Low humidity conditions can increase the effects of static charge.

e. Other interferences associated with typical Method 5 testing (sulfates, acid gases, etc.) are also applicable to Method 5I.

5. Safety.

Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety concerns associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability and observe all regulatory limitations before using this method.

6. Equipment and Supplies.

6.1 Sample Collection Equipment and Supplies. The sample train is nearly identical in configuration to the train depicted in Figure 5–1 of Method 5. The primary difference in the sample trains is the lightweight Method 5I filter assembly that attaches directly to the exit to the probe. Other exceptions and additions specific to Method 5I include:

6.1.1 Probe Nozzle. Same as Method 5, with the exception that it must be constructed of borosilicate or quartz glass tubing.

6.1.2 Probe Liner. Same as Method 5, with the exception that it must be constructed of borosilicate or quartz glass tubing.

6.1.3 Filter Holder. The filter holder is constructed of borosilicate or quartz glass front cover designed to hold a 47-mm glass fiber filter, with a wafer thin stainless steel (SS) filter support, a silicone rubber or Viton O-ring, and Teflon tape seal. This holder design will provide a positive seal against leakage from the outside or around the filter. The filter holder assembly fits into a SS filter holder and attaches directly to the outlet of the probe. The tare weight of the filter, borosilicate or quartz glass holder, SS filter support, O-ring and Teflon tape seal generally will not exceed approximately 35 grams. The filter holder is designed to use a 47-mm glass fiber filter meeting the quality criteria in of Method 5. These units are commercially available from several source testing equipment vendors. Once the filter holder has been assembled, desiccated and tared, protect it from external sources of contamination by covering the front socket with a ground glass plug. Secure the plug with an impinger clamp or other item that will ensure a leak-free fitting.

6.2 Sample Recovery Equipment and Supplies. Same as Method 5, with the following exceptions:

6.2.1 Probe-Liner and Probe-Nozzle Brushes. Teflon or nylon bristle brushes with stainless steel wire handles, should be used to clean the probe. The probe brush must have extensions (at least as long as the probe) of Teflon, nylon or similarly inert material. The brushes must be properly sized and shaped for brushing out the probe liner and nozzle.

6.2.2 Wash Bottles. Two Teflon wash bottles are recommended however, polyethylene wash bottles may be used at the option of the tester. Acetone should not be stored in polyethylene bottles for longer than one month.

6.2.3 Filter Assembly Transport. A system should be employed to minimize contamination of the filter assemblies during transport to and from the field test location. A carrying case or packet with clean compartments of sufficient size to accommodate each filter assembly can be used. This system should have an air tight seal to further minimize contamination during transport to and from the field.

6.3 Analysis Equipment and Supplies. Same as Method 5, with the following exception:

6.3.1 Lightweight Beaker Liner. Teflon or other lightweight beaker liners are used for the analysis of the probe and nozzle rinses. These light weight liners are used in place of the borosilicate glass beakers typically used for the Method 5 weighings in order to improve sample analytical precision.

6.3.2 Anti-static Treatment. Commercially available gaseous anti-static rinses are recommended for low humidity situations that contribute to static charge problems.

7. Reagents and Standards.

7.1 Sampling Reagents. The reagents used in sampling are the same as Method 5 with the following exceptions:

7.1.1 Filters. The quality specifications for the filters are identical to those cited for Method 5. The only difference is the filter diameter of 47 millimeters.

7.1.2 Stopcock Grease. Stopcock grease cannot be used with this sampling train. We recommend that the sampling train be assembled with glass joints containing O-ring seals or screw-on connectors, or similar.

7.1.3 Acetone. Low residue type acetone, ≤0.001 percent residue, purchased in glass bottles is used for the recovery of particulate matter from the probe and nozzle. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers; thus, acetone blanks must be run prior to field use and only acetone with low blank values (≤0.001 percent residue, as specified by the manufacturer) must be used. Acetone blank correction is not allowed for this method; therefore, it is critical that high purity reagents be purchased and verified prior to use.

7.1.4 Gloves. Disposable, powder-free, latex surgical gloves, or their equivalent are used at all times when handling the filter housings or performing sample recovery.

7.2 Standards. There are no applicable standards commercially available for Method 5I analyses.

8. Sample Collection, Preservation, Storage, and Transport.

8.1 Pretest Preparation. Same as Method 5 with several exceptions specific to filter assembly and weighing.

8.1.1 Filter Assembly. Uniquely identify each filter support before loading filters into the holder assembly. This can be done with an engraving tool or a permanent marker. Use powder free latex surgical gloves whenever handling the filter holder assemblies. Place the O-ring on the back of the filter housing in the O-ring groove. Place a 47 mm glass fiber filter on the O-ring with the face down. Place a stainless steel filter holder against the back of the filter. Carefully wrap 5 mm (¼ inch) wide Teflon'' tape one timearound the outside of the filter holder overlapping the stainless steel filter support by approximately 2.5 mm (⅛ inch). Gently brush the Teflon tape down on the back of the stainless steel filter support. Store the filter assemblies in their transport case until time for weighing or field use.

8.1.2 Filter Weighing Procedures. a. Desiccate the entire filter holder assemblies at 20 ±5.6 °C (68 ±10 °F) and ambient pressure for at least 24 hours. Weigh at intervals of at least 6 hours to a constant weight, *i.e.,* 0.5 mg change from previous weighing. Record the results to the nearest 0.1 mg. During each weighing, the filter holder assemblies must not be exposed to the laboratory atmosphere for a period greater than 2 minutes and a relative humidity above 50 percent. Lower relative humidity may be required in order to improve analytical precision. However, low humidity conditions increase static charge to the sample media.

b. Alternatively (unless otherwise specified by the Administrator), the filters holder assemblies may be oven dried at 105 °C (220 °F) for a minimum of 2 hours, desiccated for 2 hours, and weighed. The procedure used for the tare weigh must also be used for the final weight determination.

c. Experience has shown that weighing uncertainties are not only related to the balance performance but to the entire weighing procedure. Therefore, before performing any measurement, establish and follow standard operating procedures, taking into account the sampling equipment and filters to be used.

8.2 Preliminary Determinations. Select the sampling site, traverse points, probe nozzle, and probe length as specified in Method 5.

8.3 Preparation of Sampling Train. Same as Method 5, section 8.3, with the following exception: During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until justbefore assembly or until sampling is about to begin. Using gloves, place a labeled (identified) and weighed filter holder assembly into the stainless steel holder. Then place this whole unit in the Method 5 hot box, and attach it to the probe. Do not use stopcock grease.

8.4 Leak-Check Procedures. Same as Method 5.

8.5 Sampling Train Operation.

8.5.1. Operation. Operate the sampling train in a manner consistent with those described in Methods 1, 2, 4 and 5 in terms of the number of sample points and minimum time per point. The sample rate and total gas volume should be adjusted based on estimated grain loading of the source being characterized. The total sampling time must be a function of the estimated mass of particulate to be collected for the run. Targeted mass to be collected in a typical Method 5I sample train should be on the order of 10 to 20 mg. Method 5I is most appropriate for total collected masses of less than 50 milligrams, however, there is not an exact particulate loading cutoff, and it is likely that some runs may exceed 50 mg. Exceeding 50 mg (or less than 10 mg) for the sample mass does not necessarily justify invalidating a sample run if all other Method criteria are met.

8.5.2 Paired Train. This Method requires PM samples be collected with paired trains.

8.5.2.1 It is important that the systems be operated truly simultaneously. This implies that both sample systems start and stop at the same times. This also means that if one sample system is stopped during the run, the other sample systems must also be stopped until the cause has been corrected.

8.5.2.2 Care should be taken to maintain the filter box temperature of the paired trains as close as possible to the Method required temperature of 120 ±14 °C (248 ±25 °F). If separate ovens are being used for simultaneously operated trains, it is recommended that the oven temperature of each train be maintained within ±14 °C (±25 °F) of each other.

8.5.2.3 The nozzles for paired trains need not be identically sized.

8.5.2.4 Co-located sample nozzles must be within the same plane perpendicular to the gas flow. Co-located nozzles and pitot assemblies should be within a 6.0 cm × 6.0 cm square (as cited for a quadruple train in Reference Method 301).

8.5.3 Duplicate gas samples for molecular weight determination need not be collected.

8.6 Sample Recovery. Same as Method 5 with several exceptions specific to the filter housing.

8.6.1 Before moving the sampling train to the cleanup site, remove the probe from the train and seal the nozzle inlet and outlet of the probe. Be careful not to lose any condensate that might be present. Cap the filter inlet using a standard ground glass plug and secure the cap with an impinger clamp. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger condenser and the filter holder, disconnect the line at the filter holder and let any condensed water or liquid drain into the impingers or condenser.

8.6.2 Transfer the probe and filter-impinger assembly to the cleanup area. This area must be clean and protected from the wind so that the possibility of losing any of the sample will be minimized.

8.6.3 Inspect the train prior to and during disassembly and note any abnormal conditions such as particulate color, filter loading, impinger liquid color, etc.

8.6.4 Container No. 1, Filter Assembly. Carefully remove the cooled filter holder assembly from the Method 5 hot box and place it in the transport case. Use a pair of clean gloves to handle the filter holder assembly.

8.6.5 Container No. 2, Probe Nozzle and Probe Liner Rinse. Rinse the probe and nozzle components with acetone. Be certain that the probe and nozzle brushes have been thoroughly rinsed prior to use as they can be a source of contamination.

8.6.6 All Other Train Components. (Impingers) Same as Method 5.

8.7 Sample Storage and Transport. Whenever possible, containers should be shipped in such a way that they remain upright at all times. All appropriate dangerous goods shipping requirements must be observed since acetone is a flammable liquid.

9. Quality Control.

9.1 Miscellaneous Field Quality Control Measures.

9.1.1 A quality control (QC) check of the volume metering system at the field site is suggested before collecting the sample using the procedures in Method 5, section 4.4.1.

9.1.2 All other quality control checks outlined in Methods 1, 2, 4 and 5 also apply to Method 5I. This includes procedures such as leak-checks, equipment calibration checks, and independent checks of field data sheets for reasonableness and completeness.

9.2 Quality Control Samples.

9.2.1 Required QC Sample. A laboratory reagent blank must be collected and analyzed for each lot of acetone used for a field program to confirm that it is of suitable purity. The particulate samples cannot be blank corrected.

9.2.2 Recommended QC Samples. These samples may be collected and archived for future analyses.

9.2.2.1 A field reagent blank is a recommended QC sample collected from a portion of the acetone used for cleanup of the probe and nozzle. Take 100 ml of this acetone directly from the wash bottle being used and place it in a glass sample container labeled ''field acetone reagent blank.'' At least one field reagent blank is recommended for every five runs completed. The field reagent blank samples demonstrate the purity of the acetone was maintained throughout the program.

9.2.2.2 A field bias blank train is a recommended QC sample. This sample is collected by recovering a probe and filter assembly that has been assembled, taken to the sample location, leak checked, heated, allowed to sit at the sample location for a similar duration of time as a regular sample run, leak-checked again, and then recovered in the same manner as a regular sample. Field bias blanks are not a Method requirement, however, they are recommended and are very useful for identifying sources of contamination in emission testing samples. Field bias blank train results greater than 5 times the method detection limit may be considered problematic.

10. Calibration and Standardization Same as Method 5, section 5.

10.1 Field Balance Calibration Check. Check the calibration of the balance used to weigh impingers with a weight that is at least 500g or within 50g of a loaded impinger. The weight must be ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 6 (or better). Daily, before use, the field balance must measure the weight within ±0.5g of the certified mass. If the daily balance calibration check fails, perform corrective measures and repeat the check before using balance.

10.2 Analytical Balance Calibration. Perform a multipoint calibration (at least five points spanning the operational range) of the analytical balance before the first use, and semiannually thereafter. The calibration of the analytical balance must be conducted using ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 2 (or better) tolerance weights. Audit the balance each day it is used for gravimetric measurements by weighing at least one ASTM E617–13 Class 2 tolerance (or better) calibration weight that corresponds to 50 to 150 percent of the weight of one filter or between 1g and 5g. If the scale cannot reproduce the value of the calibration weight to within 0.5 mg of the certified mass, perform corrective measures and conduct the multipoint calibration before use.

11. Analytical Procedures.

11.1 Analysis. Same as Method 5, sections 11.1–11.2.4, with the following exceptions:

11.1.1 Container No. 1. Same as Method 5, section 11.2.1, with the following exception: Use disposable gloves to remove each of the filter holder assemblies from the desiccator, transport container, or sample oven (after appropriate cooling).

11.1.2 Container No. 2. Same as Method 5, section 11.2.2, with the following exception: It is recommended that the contents of Container No. 2 be transferred to a 250 ml beaker with a Teflon liner or similar container that has a minimal tare weight before bringing to dryness.

12. Data Analysis and Calculations.

12.1 Particulate Emissions. The analytical results cannot be blank corrected for residual acetone found in any of the blanks. All other sample calculations are identical to Method 5.

12.2 Paired Trains Outliers. a. Outliers are identified through the determination of precision and any systemic bias of the paired trains. Data that do not meet this criteria should be flagged as a data quality problem. The primary reason for performing dual train sampling is to generate information to quantify the precision of the Reference Method data. The relative standard deviation (RSD) of paired data is the parameter used to quantify data precision. RSD for two simultaneously gathered data points is determined according to:

$$RSD = 100\% * \left|\left(C_a - C_b\right)\right| / \left(C_a + C_b\right)$$

where, Ca and Cb are concentration values determined from trains A and B respectively. For RSD calculation, the concentration units are unimportant so long as they are consistent.

b. A minimum precision criteria for Reference Method PM data is that RSD for any data pair must be less than 10% as long as the mean PM concentration is greater than 10 mg/dscm. If the mean PM concentration is less than 10 mg/dscm higher RSD values are acceptable. At mean PM concentration of 1 mg/dscm acceptable RSD for paired trains is 25%. Between 1 and 10 mg/dscm acceptable RSD criteria should be linearly scaled from 25% to 10%. Pairs of manual method data exceeding these RSD criteria should be eliminated from the data set used to develop a PM CEMS correlation or to assess RCA. If the mean PM concentration is less than 1 mg/dscm, RSD does not apply and the mean result is acceptable.

13. Method Performance [Reserved]

14. Pollution Prevention [Reserved]

15. Waste Management [Reserved]

16. Alternative Procedures. Same as Method 5.

17. Bibliography. Same as Method 5.

18. Tables, Diagrams, Flowcharts and Validation Data. Figure 5I–1 is a schematic of the sample train.

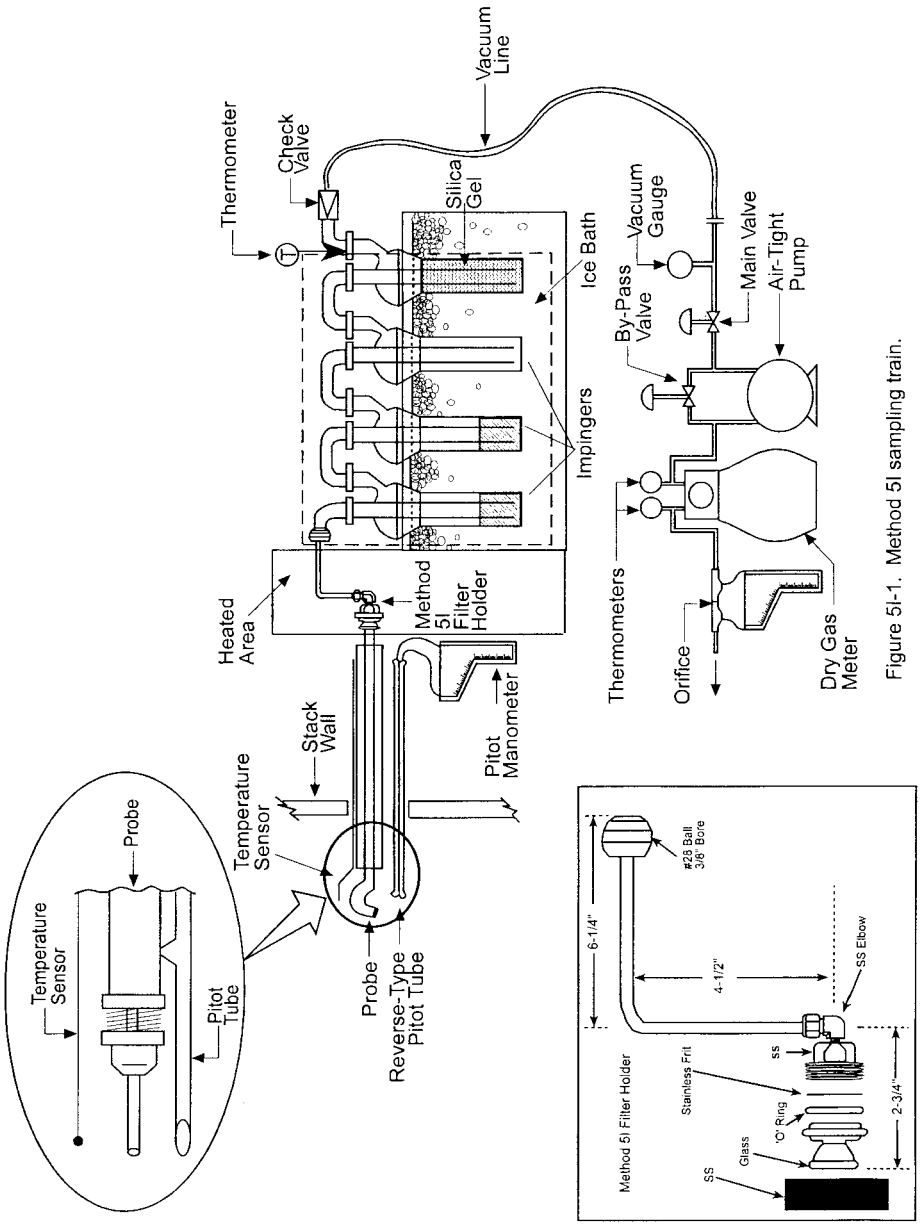

Figure 5I-1. Method 5I sampling train.

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–3 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

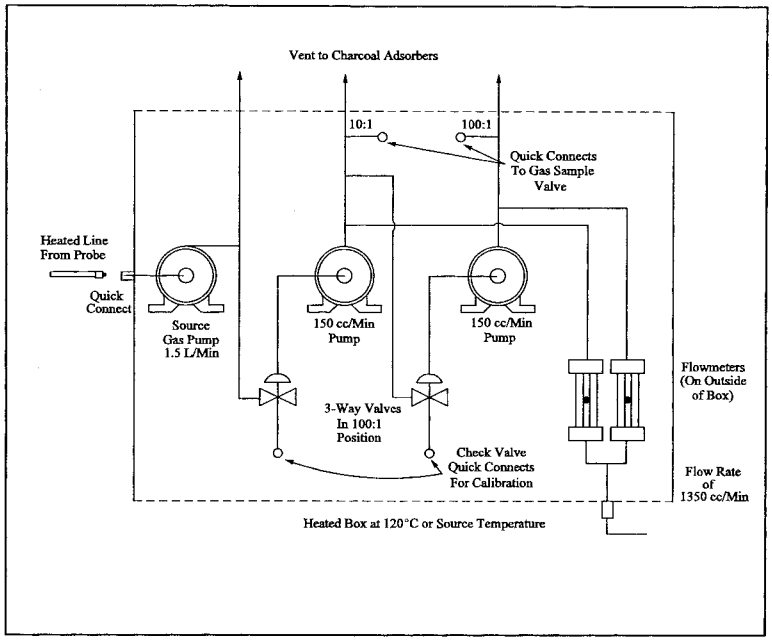

Figure 18-13. Schematic Diagram of the Heated Box Required for Dilution of Sample Gas.

GASEOUS ORGANIC SAMPLING AND ANALYSIS CHECK LIST

[Respond with initials or number as appropriate]

1. Presurvey data:		
A. Grab sample collected	☐	_____
B. Grab sample analyzed for composition	☐	_____
Method GC	☐	_____
GC/MS	☐	_____
Other	☐	_____
C. GC-FID analysis performed	☐	_____
2. Laboratory calibration data:		
A. Calibration curves prepared	☐	_____
Number of components	☐	_____
Number of concentrations/component (3 required).	☐	_____
B. Audit samples (optional):		
Analysis completed	☐	_____
Verified for concentration	☐	_____
OK obtained for field work	☐	_____
3. Sampling procedures:		
A. Method:		
Bag sample	☐	_____
Direct interface	☐	_____
Dilution interface	☐	_____
B. Number of samples collected	☐	_____
4. Field Analysis:		
A. Total hydrocarbon analysis performed	☐	_____
B. Calibration curve prepared	☐	_____
Number of components	☐	_____
Number of concentrations per component (3 required).	☐	_____

Gaseous Organic Sampling and Analysis Data

Date _____
Location _____

Plant _____

GASEOUS ORGANIC SAMPLING AND ANALYSIS CHECK LIST (RESPOND WITH INITIALS OR NUMBER AS APPROPRIATE)

	Date
1. Pre-survey data	
A. Grab sample collected	_____
B. Grab sample analyzed for composition	_____
Method GC	_____
GC/MS	_____
Other_____	_____
C. GC–FID analysis performed	_____
2. Laboratory calibration curves prepared	_____
A. Number of components	_____
B. Number of concentrations per component (3 required)	_____
C. OK obtained for field work	_____
3. Sampling procedures.	
A. Method.	
Bag sample	_____
Direct interface	_____
Dilution interface	_____
B. Number of samples collected	_____
4. Field Analysis.	
A. Total hydrocarbon analysis performed	_____
B. Calibration curve prepared	_____
Number of components	_____
Number of concentrations per component (3 required)	_____

Figure 18–14. Sampling and Analysis Sheet

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–6 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

APPENDIX A–7 TO PART 60—TEST METHODS 19 THROUGH 25E

Method 19—Determination of sulfur dioxide removal efficiency and particulate, sulfur dioxide and nitrogen oxides emission rates
Method 20—Determination of nitrogen oxides, sulfur dioxide, and diluent emissions from stationary gas turbines
Method 21—Determination of volatile organic compound leaks
Method 22—Visual determination of fugitive emissions from material sources and smoke emissions from flares
Method 23—Determination of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans From Stationary Sources
Method 24—Determination of volatile matter content, water content, density, volume solids, and weight solids of surface coatings
Method 24A—Determination of volatile matter content and density of printing inks and related coatings
Method 25—Determination of total gaseous nonmethane organic emissions as carbon
Method 25A—Determination of total gaseous organic concentration using a flame ionization analyzer
Method 25B—Determination of total gaseous organic concentration using a nondispersive infrared analyzer
Method 25C—Determination of nonmethane organic compounds (NMOC) in MSW landfill gases
Method 25D—Determination of the Volatile Organic Concentration of Waste Samples
Method 25E—Determination of Vapor Phase Organic Concentration in Waste Samples

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

Method 19—Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates

1.0 Scope and Application

1.1 Analytes. This method provides data reduction procedures relating to the following pollutants, but does not include any sample collection or analysis procedures.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), including:		
Nitric oxide (NO)	10102–43–9	N/A
Nitrogen dioxide (NO_2)	10102–44–0.	
Particulate matter (PM)	None assigned	N/A
Sulfur dioxide (SO_2)	7499–09–05	N/A

1.2 Applicability. Where specified by an applicable subpart of the regulations, this method is applicable for the determination of (a) PM, SO_2, and NO_X emission rates; (b) sulfur removal efficiencies of fuel pretreatment and SO_2 control devices; and (c) overall reduction of potential SO_2 emissions.

2.0 Summary of Method

2.1 Emission Rates. Oxygen (O_2) or carbon dioxide (CO_2) concentrations and appropriate F factors (ratios of combustion gas volumes to heat inputs) are used to calculate pollutant emission rates from pollutant concentrations.

2.2 Sulfur Reduction Efficiency and SO_2 Removal Efficiency. An overall SO_2 emission reduction efficiency is computed from the efficiency of fuel pretreatment systems, where applicable, and the efficiency of SO_2 control devices.

2.2.1 The sulfur removal efficiency of a fuel pretreatment system is determined by fuel sampling and analysis of the sulfur and heat contents of the fuel before and after the pretreatment system.

2.2.2 The SO_2 removal efficiency of a control device is determined by measuring the SO_2 rates before and after the control device.

2.2.2.1 The inlet rates to SO_2 control systems (or, when SO_2 control systems are not used, SO_2 emission rates to the atmosphere) are determined by fuel sampling and analysis.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety [Reserved]

6.0 Equipment and Supplies [Reserved]

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transport [Reserved]

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedures [Reserved]

12.0 Data Analysis and Calculations

12.1 Nomenclature

B_{wa} = Moisture fraction of ambient air, percent.

B_{ws} = Moisture fraction of effluent gas, percent.

%C = Concentration of carbon from an ultimate analysis of fuel, weight percent.

C_d = Pollutant concentration, dry basis, ng/scm (lb/scf)

$\%CO_{2d}$,$\%CO_{2w}$ = Concentration of carbon dioxide on a dry and wet basis, respectively, percent.

C_w = Pollutant concentration, wet basis, ng/scm (lb/scf).

D = Number of sampling periods during the performance test period.

E = Pollutant emission rate, ng/J (lb/million Btu).

E_a = Average pollutant rate for the specified performance test period, ng/J (lb/million Btu).

E_{ao}, E_{ai} = Average pollutant rate of the control device, outlet and inlet, respectively, for the performance test period, ng/J (lb/million Btu).

E_{bi} = Pollutant rate from the steam generating unit, ng/J (lb/million Btu)

E_{bo} = Pollutant emission rate from the steam generating unit, ng/J (lb/million Btu).

E_{ci} = Pollutant rate in combined effluent, ng/J (lb/million Btu).

E_{co} = Pollutant emission rate in combined effluent, ng/J (lb/million Btu).

E_d = Average pollutant rate for each sampling period (*e.g.*, 24-hr Method 6B sample or 24-hr fuel sample) or for each fuel lot (*e.g.*, amount of fuel bunkered), ng/J (lb/million Btu).

E_{di} = Average inlet SO_2 rate for each sampling period d, ng/J (lb/million Btu)

E_g = Pollutant rate from gas turbine, ng/J (lb/million Btu).

E_{ga} = Daily geometric average pollutant rate, ng/J (lbs/million Btu) or ppm corrected to 7 percent O_2.

E_{jo},E_{ji} = Matched pair hourly arithmetic average pollutant rate, outlet and inlet, respectively, ng/J (lb/million Btu) or ppm corrected to 7 percent O_2.

E_h = Hourly average pollutant, ng/J (lb/million Btu).

E_{hj} = Hourly arithmetic average pollutant rate for hour ''j,'' ng/J (lb/million Btu) or ppm corrected to 7 percent O_2.

EXP = Natural logarithmic base (2.718) raised to the value enclosed by brackets.

F_d, F_w, F_c = Volumes of combustion components per unit of heat content, scm/J (scf/million Btu).

GCV = Gross calorific value of the fuel consistent with the ultimate analysis, kJ/kg (Btu/lb).

GCV_p, GCV_r = Gross calorific value for the product and raw fuel lots, respectively, dry basis, kJ/kg (Btu/lb).

%H = Concentration of hydrogen from an ultimate analysis of fuel, weight percent.

H = Total number of operating hours for which pollutant rates are determined in the performance test period.

H_b = Heat input rate to the steam generating unit from fuels fired in the steam generating unit, J/hr (million Btu/hr).

H_g = Heat input rate to gas turbine from all fuels fired in the gas turbine, J/hr (million Btu/hr).

$\%H_2O$ = Concentration of water from an ultimate analysis of fuel, weight percent.
H_r = Total numbers of hours in the performance test period (*e.g.*, 720 hours for 30-day performance test period).
K = Conversion factor, 10^{-5} (kJ/J)/(%) [10^6 Btu/million Btu].
K_c = (9.57 scm/kg)/% [(1.53 scf/lb)/%].
K_{cc} = (2.0 scm/kg)/% [(0.321 scf/lb)/%].
K_{hd} = (22.7 scm/kg)/% [(3.64 scf/lb)/%].
K_{hw} = (34.74 scm/kg)/% [(5.57 scf/lb)/%].
K_n = (0.86 scm/kg)/% [(0.14 scf/lb)/%].
K_o = (2.85 scm/kg)/% [(0.46 scf/lb)/%].
K_s = (3.54 scm/kg)/% [(0.57 scf/lb)/%].
K_w = (1.30 scm/kg)/% [(0.21 scf/lb)/%].
ln = Natural log of indicated value.
L_p,L_r = Weight of the product and raw fuel lots, respectively, metric ton (ton).
%N = Concentration of nitrogen from an ultimate analysis of fuel, weight percent.
N = Number of fuel lots during the averaging period.
n = Number of fuels being burned in combination.
n_d = Number of operating hours of the affected facility within the performance test period for each E_d determined.
n_t = Total number of hourly averages for which paired inlet and outlet pollutant rates are available within the 24-hr midnight to midnight daily period.
%O = Concentration of oxygen from an ultimate analysis of fuel, weight percent.
$\%O_{2d}$, $\%O_{2w}$ = Concentration of oxygen on a dry and wet basis, respectively, percent.
P_s = Potential SO_2 emissions, percent.
$\%R_f$ = SO_2 removal efficiency from fuel pretreatment, percent.
$\%R_g$ = SO_2 removal efficiency of the control device, percent.
$\%R_{ga}$ = Daily geometric average percent reduction.
$\%R_o$ = Overall SO_2 reduction, percent.
%S = Sulfur content of as-fired fuel lot, dry basis, weight percent.
S_e = Standard deviation of the hourly average pollutant rates for each performance test period, ng/J (lb/million Btu).
$\%S_f$ = Concentration of sulfur from an ultimate analysis of fuel, weight percent.
S_i = Standard deviation of the hourly average inlet pollutant rates for each performance test period, ng/J (lb/million Btu).
S_o = Standard deviation of the hourly average emission rates for each performance test period, ng/J (lb/million Btu).
$\%S_p$, $\%S_r$ = Sulfur content of the product and raw fuel lots respectively, dry basis, weight percent.
$t_{0.95}$ = Values shown in Table 19–3 for the indicated number of data points n.
X_k = Fraction of total heat input from each type of fuel k.

12.2 Emission Rates of PM, SO_2, and NO_X. Select from the following sections the applicable procedure to compute the PM, S_{O2}, or NO_X emission rate (E) in ng/J (lb/million Btu). The pollutant concentration must be in ng/scm (lb/scf) and the F factor must be in scm/J (scf/million Btu). If the pollutant concentration (C) is not in the appropriate units, use Table 19–1 in section 17.0 to make the proper conversion. An F factor is the ratio of the gas volume of the products of combustion to the heat content of the fuel. The dry F factor (F_d) includes all components of combustion less water, the wet F factor (F_w) includes all components of combustion, and the carbon F factor (F_c) includes only carbon dioxide.

NOTE: Since F_w factors include water resulting only from the combustion of hydrogen in the fuel, the procedures using F_w factors are not applicable for computing E from steam generating units with wet scrubbers or with other processes that add water (*e.g.*, steam injection).

12.2.1 Oxygen-Based F Factor, Dry Basis. When measurements are on a dry basis for both O ($\%O_{2d}$) and pollutant (C_d) concentrations, use the following equation:

$$E = C_d F_d \frac{20.9}{(20.9 - \%O_{2d})} \qquad \text{Eq. 19-1}$$

12.2.2 Oxygen-Based F Factor, Wet Basis. When measurements are on a wet basis for both O_2 ($\%O_{2w}$) and pollutant (C_w) concentrations, use either of the following:

12.2.2.1 If the moisture fraction of ambient air (B_{wa}) is measured:

$$E = C_w F_w \frac{20.9}{\left[20.9(1 - B_{wa}) - \%O_{2w}\right]} \qquad \text{Eq. 19-2}$$

Instead of actual measurement, B_{wa} may be estimated according to the procedure below.

NOTE: The estimates are selected to ensure that negative errors will not be larger than −1.5 percent. However, positive errors, or over-estimation of emissions by as much as 5 percent may be introduced depending upon the geographic location of the facility and the associated range of ambient moisture.

12.2.2.1.1 B_{wa} = 0.027. This value may be used at any location at all times.

12.2.2.1.2 B_{wa} = Highest monthly average of B_{wa} that occurred within the previous calendar year at the nearest Weather Service Station. This value shall be determined annually and may be used as an estimate for the entire current calendar year.

12.2.2.1.3 B_{wa} = Highest daily average of Bwa that occurred within a calendar month at the nearest Weather Service Station, calculated from the data from the past 3 years. This value shall be computed for each month and may be used as an estimate for the current respective calendar month.

12.2.2.2 If the moisture fraction (B_{ws}) of the effluent gas is measured:

$$E = C_w F_d \frac{20.9}{\left[20.9\left(1-B_{ws}\right)-\%O_{2w}\right]} \qquad \text{Eq. 19-3}$$

12.2.3 Oxygen-Based F Factor, Dry/Wet Basis.

12.2.3.1 When the pollutant concentration is measured on a wet basis (C_w) and O_2 concentration is measured on a dry basis ($\%O_{2d}$), use the following equation:

$$E = \frac{\left(C_w F_d\right)(20.9)}{\left(1-B_{ws}\right)\left(20.9-\%O_{2d}\right)} \qquad \text{Eq. 19-4}$$

12.2.3.2 When the pollutant concentration is measured on a dry basis (C_d) and the O_2 concentration is measured on a wet basis ($\%O_{2w}$), use the following equation:

$$E = \frac{C_d F_d 20.9}{\frac{\left(20.9-\%O_{2w}\right)}{\left(1-B_{ws}\right)}} \qquad \text{Eq. 19-5}$$

12.2.4 Carbon Dioxide-Based F Factor, Dry Basis. When measurements are on a dry basis for both CO_2 ($\%CO_{2d}$) and pollutant (C_d) concentrations, use the following equation:

$$E = C_d F_c \frac{100}{\%CO_{2d}} \qquad \text{Eq. 19-6}$$

12.2.5 Carbon Dioxide-Based F Factor, Wet Basis. When measurements are on a wet basis for both CO_2 ($\%CO_{2w}$) and pollutant (C_w) concentrations, use the following equation:

$$E = C_w F_c \frac{100}{\%CO_{2w}} \qquad \text{Eq. 19-7}$$

12.2.6 Carbon Dioxide-Based F Factor, Dry/Wet Basis.

12.2.6.1 When the pollutant concentration is measured on a wet basis (C_w) and CO_2 concentration is measured on a dry basis ($\%CO_{2d}$), use the following equation:

$$E = \frac{C_w F_c}{\left(1-B_{ws}\right)} \frac{100}{\%CO_{2d}} \qquad \text{Eq. 19-8}$$

12.2.6.2 When the pollutant concentration is measured on a dry basis (C_d) and CO_2 concentration is measured on a wet basis ($\%CO_{2w}$), use the following equation:

$$E = C_d F_c \left(1-B_{ws}\right) \frac{100}{\%CO_{2w}} \qquad \text{Eq. 19-9}$$

12.2.7 Direct-Fired Reheat Fuel Burning. The effect of direct-fired reheat fuel burning (for the purpose of raising the temperature of the exhaust effluent from wet scrubbers to above the moisture dew-point) on emission rates will be less than 1.0 percent and, therefore, may be ignored.

12.2.8 Combined Cycle-Gas Turbine Systems. For gas turbine-steam generator combined cycle systems, determine the emissions from the steam generating unit or the percent reduction in potential SO_2 emissions as follows:

12.2.8.1 Compute the emission rate from the steam generating unit using the following equation:

$$E_{bo} = E_{co} + \frac{H_g}{H_b}\left(E_{co} - E_g\right) \qquad \text{Eq. 19-10}$$

12.2.8.1.1 Use the test methods and procedures section of 40 CFR Part 60, Subpart GG to obtain E_{co} and E_g. Do not use F_w factors for determining E_g or E_{co}. If an SO_2 control device is used, measure E_{co} after the control device.

12.2.8.1.2 Suitable methods shall be used to determine the heat input rates to the steam generating units (H_b) and the gas turbine (H_g).

12.2.8.2 If a control device is used, compute the percent of potential SO_2 emissions (P_s) using the following equations:

$$E_{bi} = E_{ci} - \frac{H_g}{H_b}\left(E_{ci} - E_g\right) \qquad \text{Eq. 19-11}$$

$$P_s = 100\left(1 - \frac{E_{bo}}{E_{bi}}\right) \qquad \text{Eq. 19-12}$$

NOTE: Use the test methods and procedures section of Subpart GG to obtain E_{ci} and E_g. Do not use F_w factors for determining E_g or E_{ci}.

12.3 F Factors. Use an average F factor according to section 12.3.1 or determine an applicable F factor according to section 12.3.2. If combined fuels are fired, prorate the applicable F factors using the procedure in section 12.3.3.

12.3.1 Average F Factors. Average F factors (F_d, F_w, or F_c) from Table 19–2 in section 17.0 may be used.

12.3.2 Determined F Factors. If the fuel burned is not listed in Table 19–2 or if the owner or operator chooses to determine an F factor rather than use the values in Table 19–2, use the procedure below:

12.3.2.1 Equations. Use the equations below, as appropriate, to compute the F factors:

$$F_d = \frac{K\left(K_{hd}\%H + K_c\%C + K_s\%S + K_n\%N - K_o\%O\right)}{GCV} \qquad \text{Eq. 19-13}$$

$$F_w = \frac{K\left[K_{hw}\%H + K_c\%C + K_s\%S + K_n\%N - K_o\%O + K_w\%H_2O\right]}{GCV_w} \qquad \text{Eq. 19-14}$$

$$F_c = \frac{K\left(K_{cc}\%C\right)}{GCV} \qquad \text{Eq. 19-15}$$

NOTE: Omit the $\%H_2O$ term in the equations for F_w if %H and %O include the unavailable hydrogen and oxygen in the form of H_2O.)

12.3.2.2 Use applicable sampling procedures in section 12.5.2.1 or 12.5.2.2 to obtain samples for analyses.

12.3.2.3 Use ASTM D 3176–74 or 89 (all cited ASTM standards are incorporated by reference—see §60.17) for ultimate analysis of the fuel.

12.3.2.4 Use applicable methods in section 12.5.2.1 or 12.5.2.2 to determine the heat content of solid or liquid fuels. For gaseous fuels, use ASTM D 1826–77 or 94 (incorporated by reference—see §60.17) to determine the heat content.

12.3.3 F Factors for Combination of Fuels. If combinations of fuels are burned, use the following equations, as applicable unless otherwise specified in an applicable subpart:

$$F_d = \sum_{k=1}^{n}\left(X_k F_{dk}\right) \qquad \text{Eq. 19-16}$$

$$F_w = \sum_{k=1}^{n}\left(X_k F_{wk}\right) \qquad \text{Eq. 19-17}$$

$$F_c = \sum_{k=1}^{n}\left(X_k F_{ck}\right) \qquad \text{Eq. 19-18}$$

12.4 Determination of Average Pollutant Rates.

12.4.1 Average Pollutant Rates from Hourly Values. When hourly average pollutant rates (E_h), inlet or outlet, are obtained (*e.g.*, CEMS values), compute the average pollutant rate (E_a) for the performance test period (*e.g.*, 30 days) specified in the applicable regulation using the following equation:

$$E_a = \frac{1}{H}\sum_{j=1}^{n} E_{hj} \qquad \text{Eq. 19-19}$$

12.4.2 Average Pollutant Rates from Other than Hourly Averages. When pollutant rates are determined from measured values representing longer than 1-hour periods (*e.g.*, daily fuel sampling and analyses or Method 6B values), or when pollutant rates are determined from combinations of 1-hour and longer than 1-hour periods (*e.g.*, CEMS and Method 6B values), compute the average pollutant rate (E_a) for the performance test period (*e.g.*, 30 days) specified in the applicable regulation using the following equation:

$$E_a = \frac{\sum_{j=1}^{D}\left(n_d E_d\right)_j}{\sum_{j=1}^{D} n_{dj}} \qquad \text{Eq. 19-20}$$

12.4.3 Daily Geometric Average Pollutant Rates from Hourly Values. The geometric average pollutant rate (E_{ga}) is computed using the following equation:

$$E_{ga} = \exp\left[\frac{1}{n_t}\sum_{j=1}^{n_t}\left[\ln\left(E_{hj}\right)\right]\right] \quad \text{Eq. 19-21}$$

12.5 Determination of Overall Reduction in Potential Sulfur Dioxide Emission.

12.5.1 Overall Percent Reduction. Compute the overall percent SO_2 reduction ($\%R_o$) using the following equation:

$$\%R_o = 100\left[1.0 - \left(1.0 - \frac{\%R_f}{100}\right)\left(1.0 - \frac{\%R_g}{100}\right)\right] \quad \text{Eq. 19-22}$$

12.5.2 Pretreatment Removal Efficiency (Optional). Compute the SO_2 removal efficiency from fuel pretreatment ($\%R_f$) for the averaging period (*e.g.*, 90 days) as specified in the applicable regulation using the following equation:

$$\%R_f = 100\left[1.0 - \frac{\sum_{j=1}^{N}\left(\frac{\%S_{pj}}{GCV_{pj}}\right)L_{pj}}{\sum_{j=1}^{N}\left(\frac{\%S_{rj}}{GCV_{rj}}\right)L_{rj}}\right] \quad \text{Eq. 19-23}$$

NOTE: In calculating $\%R_f$, include %S and GCV values for all fuel lots that are not pretreated and are used during the averaging period.

12.5.2.1 Solid Fossil (Including Waste) Fuel/Sampling and Analysis.

NOTE: For the purposes of this method, raw fuel (coal or oil) is the fuel delivered to the desulfurization (pretreatment) facility. For oil, the input oil to the oil desulfurization process (*e.g.*, hydrotreatment) is considered to be the raw fuel.

12.5.2.1.1 Sample Increment Collection. Use ASTM D 2234–76, 96, 97a, or 98 (incorporated by reference—see §60.17), Type I, Conditions A, B, or C, and systematic spacing. As used in this method, systematic spacing is intended to include evenly spaced increments in time or increments based on equal weights of coal passing the collection area. As a minimum, determine the number and weight of increments required per gross sample representing each coal lot according to Table 2 or Paragraph 7.1.5.2 of ASTM D 2234. Collect one gross sample for each lot of raw coal and one gross sample for each lot of product coal.

12.5.2.1.2 ASTM Lot Size. For the purpose of section 12.5.2 (fuel pretreatment), the lot size of product coal is the weight of product coal from one type of raw coal. The lot size of raw coal is the weight of raw coal used to produce one lot of product coal. Typically, the lot size is the weight of coal processed in a 1-day (24-hour) period. If more than one type of coal is treated and produced in 1 day, then gross samples must be collected and analyzed for each type of coal. A coal lot size equaling the 90-day quarterly fuel quantity for a steam generating unit may be used if representative sampling can be conducted for each raw coal and product coal.

NOTE: Alternative definitions of lot sizes may be used, subject to prior approval of the Administrator.

12.5.2.1.3 Gross Sample Analysis. Use ASTM D 2013–72 or 86 to prepare the sample, ASTM D 3177–75 or 89 or ASTM D 4239–85, 94, or 97 to determine sulfur content (%S), ASTM D 3173–73 or 87 to determine moisture content, and ASTM D 2015–77 (Reapproved 1978) or 96, D 3286–85 or 96, or D 5865–98 or 10 to determine gross calorific value (GCV) (all standards cited are incorporated by reference—see §60.17 for acceptable versions of the standards) on a dry basis for each gross sample.

12.5.2.2 Liquid Fossil Fuel-Sampling and Analysis. See Note under section 12.5.2.1.

12.5.2.2.1 Sample Collection. Follow the procedures for continuous sampling in ASTM D 270 or D 4177–95 (incorporated by reference—see §60.17) for each gross sample from each fuel lot.

12.5.2.2.2 Lot Size. For the purpose of section 12.5.2 (fuel pretreatment), the lot size of a product oil is the weight of product oil from one pretreatment facility and intended as one shipment (ship load, barge load, etc.). The lot size of raw oil is the weight of each crude liquid fuel type used to produce a lot of product oil.

NOTE: Alternative definitions of lot sizes may be used, subject to prior approval of the Administrator.

12.5.2.2.3 Sample Analysis. Use ASTM D 129–64, 78, or 95, ASTM D 1552–83 or 95, or ASTM D 4057–81 or 95 to determine the sulfur content (%S) and ASTM D 240–76 or 92 (all standards cited are incorporated by reference—see §60.17) to determine the GCV of each gross sample. These values may be assumed to be on a dry basis. The owner or operator of an affected facility may elect to determine the GCV by sampling the oil combusted on the first steam generating unit operating day of each calendar month and then using the lowest GCV value of the three GCV values per quarter for the GCV of all oil combusted in that calendar quarter.

12.5.2.3 Use appropriate procedures, subject to the approval of the Administrator, to determine the fraction of total mass input derived from each type of fuel.

12.5.3 Control Device Removal Efficiency. Compute the percent removal efficiency ($\%R_g$) of the control device using the following equation:

$$\%R_g = 100\left(1.0 - \frac{E_{ao}}{E_{ai}}\right) \qquad \text{Eq. 19-24}$$

12.5.3.1 Use continuous emission monitoring systems or test methods, as appropriate, to determine the outlet SO_2 rates and, if appropriate, the inlet SO_2 rates. The rates may be determined as hourly (E_h) or other sampling period averages (E_d). Then, compute the average pollutant rates for the performance test period (E_{ao} and E_{ai}) using the procedures in section 12.4.

12.5.3.2 As an alternative, as-fired fuel sampling and analysis may be used to determine inlet SO_2 rates as follows:

12.5.3.2.1 Compute the average inlet SO_2 rate (E_{di}) for each sampling period using the following equation:

$$E_{di} = K\frac{\%S}{GCV} \qquad \text{Eq. 19-25}$$

Where:

$$K = 2\times10^7\left(\frac{\text{ng SO}_2}{\%S}\right)\left(\frac{(\text{kJ})}{\text{J}}\right)\left(\frac{1}{\text{kg coal}}\right)\left[2\times10^4\left(\frac{\text{lb SO}_2}{\%S}\right)\left(\frac{\text{Btu}}{\text{million Btu}}\right)\left(\frac{1}{\text{lb coal}}\right)\right]$$

After calculating E_{di}, use the procedures in section 12.4 to determine the average inlet SO_2 rate for the performance test period (E_{ai}).

12.5.3.2.2 Collect the fuel samples from a location in the fuel handling system that provides a sample representative of the fuel bunkered or consumed during a steam generating unit operating day. For the purpose of as-fired fuel sampling under section 12.5.3.2 or section 12.6, the lot size for coal is the weight of coal bunkered or consumed during each steam generating unit operating day. The lot size for oil is the weight of oil supplied to the ''day'' tank or consumed during each steam generating unit operating day. For reporting and calculation purposes, the gross sample shall be identified with the calendar day on which sampling began. For steam generating unit operating days when a coal-fired steam generating unit is operated without coal being added to the bunkers, the coal analysis from the previous ''as bunkered'' coal sample shall be used until coal is bunkered again. For steam generating unit operating days when an oil-fired steam generating unit is operated without oil being added to the oil ''day'' tank, the oil analysis from the previous day shall be used until the ''day'' tank is filled again. Alternative definitions of fuel lot size may be used, subject to prior approval of the Administrator.

12.5.3.2.3 Use ASTM procedures specified in section 12.5.2.1 or 12.5.2.2 to determine %S and GCV.

12.5.4 Daily Geometric Average Percent Reduction from Hourly Values. The geometric average percent reduction ($\%R_{ga}$) is computed using the following equation:

$$\%R_{ga} = 100\left[1 - \text{EXP}\left(\frac{1}{n_t}\sum_{j=1}^{n_t} 1n\frac{E_{jo}}{E_{ji}}\right)\right] \qquad \text{Eq. 19-26}$$

NOTE: The calculation includes only paired data sets (hourly average) for the inlet and outlet pollutant measurements.

12.6 Sulfur Retention Credit for Compliance Fuel. If fuel sampling and analysis procedures in section 12.5.2.1 are being used to determine average SO_2 emission rates (E_{as}) to the atmosphere from a coal-fired steam generating unit when there is no SO_2 control device, the following equation may be used to adjust the emission rate for sulfur retention credits (no credits are allowed for oil-fired systems) (E_{di}) for each sampling period using the following equation:

$$E_{di} = 0.97K\ \frac{\%S}{GDV} \qquad \text{Eq. 19-27}$$

Where:

$$K = 2\times10^{7}\left(\frac{\text{ng } SO_2}{\%S}\right)\left(\frac{kJ}{J}\right)\left(\frac{1}{\text{kg coal}}\right)\left[2\times10^{4}\left(\frac{\text{lb } SO_2}{\%S}\right)\left(\frac{\text{Btu}}{\text{million Btu}}\right)\left(\frac{1}{\text{lb coal}}\right)\right]$$

After calculating E_{di}, use the procedures in section 12.4.2 to determine the average SO_2 emission rate to the atmosphere for the performance test period (E_{ao}).

12.7 Determination of Compliance When Minimum Data Requirement Is Not Met.

12.7.1 Adjusted Emission Rates and Control Device Removal Efficiency. When the minimum data requirement is not met, the Administrator may use the following adjusted emission rates or control device removal efficiencies to determine compliance with the applicable standards.

12.7.1.1 Emission Rate. Compliance with the emission rate standard may be determined by using the lower confidence limit of the emission rate (E_{ao}*) as follows:

$$E^{*}_{ao} = E_{ao} - t_{0.95}S_o \qquad \text{Eq. 19-28}$$

12.7.1.2 Control Device Removal Efficiency. Compliance with the overall emission reduction ($\%R_o$) may be determined by using the lower confidence limit of the emission rate (E_{ao}*) and the upper confidence limit of the inlet pollutant rate (E_{ai}*) in calculating the control device removal efficiency ($\%R_g$) as follows:

$$\%R_g = 100\left(1.0 - \frac{E^{*}_{ao}}{E^{*}_{ai}}\right) \qquad \text{Eq. 19-29}$$

$$E^{*}_{ai} = E_{ai} + t_{0.95}S_i \qquad \text{Eq. 19-30}$$

12.7.2 Standard Deviation of Hourly Average Pollutant Rates. Compute the standard deviation (S_e) of the hourly average pollutant rates using the following equation:

$$S_e = \sqrt{\frac{1}{H} - \frac{1}{H_r}}\ \sqrt{\frac{\sum_{j=1}^{H}\left(E_{hj} - E_a\right)^2}{H-1}} \qquad \text{Eq. 19-31}$$

Equation 19–19 through 19–31 may be used to compute the standard deviation for both the outlet (S_o) and, if applicable, inlet (S_i) pollutant rates.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References [Reserved]

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 19–1—CONVERSION FACTORS FOR CONCENTRATION

From	To	Multiply by
g/scm	ng/scm	10^9
mg/scm	ng/scm	10^6
lb/scf	ng/scm	1.602×10^{13}

TABLE 19–1—CONVERSION FACTORS FOR CONCENTRATION—Continued

From	To	Multiply by
ppm SO_2	ng/scm	2.66×10^6
ppm NO_X	ng/scm	1.912×10^6
ppm SO_2	lb/scf	1.660×10^{-7}
ppm NO_X	lb/scf	1.194×10^{-7}

TABLE 19–2—F FACTORS FOR VARIOUS FUELS[1]

Fuel Type	F_d		F_w		F_c	
	dscm/J	dscf/10^6 Btu	wscm/J	wscf/10^6 Btu	scm/J	scf/10^6 Btu
Coal:						
Anthracite[2]	2.71×10^{-7}	10,100	2.83×10^{-7}	10,540	0.530×10^{-7}	1,970
Bituminus[2]	2.63×10^{-7}	9,780	2.86×10^{-7}	10,640	0.484×10^{-7}	1,800
Lignite	2.65×10^{-7}	9,860	3.21×10^{-7}	11,950	0.513×10^{-7}	1,910
Oil[3]	2.47×10^{-7}	9,190	2.77×10^{-7}	10,320	0.383×10^{-7}	1,420
Gas:.						
Natural	2.34×10^{-7}	8,710	2.85×10^{-7}	10,610	0.287×10^{-7}	1,040
Propane	2.34×10^{-7}	8,710	2.74×10^{-7}	10,200	0.321×10^{-7}	1,190
Butane	2.34×10^{-7}	8,710	2.79×10^{-7}	10,390	0.337×10^{-7}	1,250
Wood	2.48×10^{-7}	9,240			0.492×10^{-7}	1,830
Wood Bark	2.58×10^{-7}	9,600			0.516×10^{-7}	1,920
Municipal	2.57×10^{-7}	9,570			0.488×10^{-7}	1,820
Solid Waste						

[1] Determined at standard conditions: 20 °C (68 °F) and 760 mm Hg (29.92 in Hg)
[2] As classified according to ASTM D 388.
[3] Crude, residual, or distillate.

TABLE 19–3—VALUES FOR $T_{0.95*}$

n[1]	$t_{0.95}$	n[1]	$t_{0.95}$	n[1]	$t_{0.95}$
2	6.31	8	1.89	22–26	1.71
3	2.42	9	1.86	27–31	1.70
4	2.35	10	1.83	32–51	1.68
5	2.13	11	1.81	52–91	1.67
6	2.02	12–16	1.77	92–151	1.66
7	1.94	17–21	1.73	152 or more	1.65

[1]The values of this table are corrected for n-1 degrees of freedom. Use n equal to the number (H) of hourly average data points.

METHOD 20—DETERMINATION OF NITROGEN OXIDES, SULFUR DIOXIDE, AND DILUENT EMISSIONS FROM STATIONARY GAS TURBINES

1.0 Scope and Application

What is Method 20?

Method 20 contains the details you must follow when using an instrumental analyzer to determine concentrations of nitrogen oxides, oxygen, carbon dioxide, and sulfur dioxide in the emissions from stationary gas turbines. This method follows the specific instructions for equipment and performance requirements, supplies, sample collection and analysis, calculations, and data analysis in the methods listed in section 2.0.

1.1 Analytes. What does this method determine?

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X) as nitrogen dioxide:	10102–43–9	Typically <2% of Calibration Span.
Nitric oxide (NO)	10102–44–0	
Nitrogen dioxide NO_2.		
Diluent oxygen (O_2) or carbon dioxide (CO_2)		Typically <2% of Calibration Span.
Sulfur dioxide (SO_X)	7446–09–5	Typically <2% of Calibration Span.

1.2 Applicability. When is this method required? The use of Method 20 may be required by specific New Source Performance Standards, Clean Air Marketing rules, and State Implementation Plans and permits where

measuring SO_2, NO_X, CO_2, and/or O_2 concentrations in stationary gas turbines emissions are required. Other regulations may also require its use.

1.3 Data Quality Objectives. How good must my collected data be? Refer to section 1.3 of Method 7E.

2.0 Summary of Method

In this method, NO_X, O_2 (or CO_2), and SO_X are measured using the following methods found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 3A—Determination of Oxygen and Carbon Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(c) Method 6C—Determination of Sulfur Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(d) Method 7E—Determination of Nitrogen Oxides Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(e) Method 19—Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates.

3.0 Definitions

Refer to section 3.0 of Method 7E for the applicable definitions.

4.0 Interferences

Refer to section 4.0 of Methods 3A, 6C, and 7E as applicable.

5.0 Safety

Refer to section 5.0 of Method 7E.

6.0 Equipment and Supplies

The measurement system design is shown in Figure 7E–1 of Method 7E. Refer to the appropriate methods listed in section 2.0 for equipment and supplies.

7.0 Reagents and Standards

Refer to the appropriate methods listed in section 2.0 for reagents and standards.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling Site and Sampling Points. Follow the procedures of section 8.1 of Method 7E. For the stratification test in section 8.1.2, determine the diluent-corrected pollutant concentration at each traverse point.

8.2 Initial Measurement System Performance Tests. You must refer to the appropriate methods listed in section 2.0 for the measurement system performance tests as applicable.

8.3 Interference Check. You must follow the procedures in section 8.3 of Method 3A or 6C, or section 8.2.7 of Method 7E (as appropriate).

8.4 Sample Collection. You must follow the procedures of section 8.4 of the appropriate methods listed in section 2.0. A test run must have a duration of at least 21 minutes.

8.5 Post-Run System Bias Check, Drift Assessment, and Alternative Dynamic Spike Procedure. You must follow the procedures of sections 8.5 and 8.6 of the appropriate methods listed in section 2.0. A test run must have a duration of at least 21 minutes.

9.0 Quality Control

Follow quality control procedures in section 9.0 of Method 7E.

10.0 Calibration and Standardization

Follow the procedures for calibration and standardization in section 10.0 of Method 7E.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the procedures for calculations and data analysis in section 12.0 of the appropriate method listed in section 2.0. Follow the procedures in section 12.0 of Method 19 for calculating fuel-specific F factors, diluent-corrected pollutant concentrations, and emission rates.

13.0 Method Performance

The specifications for the applicable performance checks are the same as in section 13.0 of Method 7E.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

Refer to section 16.0 of the appropriate method listed in section 2.0 for alternative procedures.

17.0 References

Refer to section 17.0 of the appropriate method listed in section 2.0 for references.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

Refer to section 18.0 of the appropriate method listed in section 2.0 for tables, diagrams, flowcharts, and validation data.

METHOD 21—DETERMINATION OF VOLATILE ORGANIC COMPOUND LEAKS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile Organic Compounds (VOC).	No CAS number assigned.

1.2 Scope. This method is applicable for the determination of VOC leaks from process equipment. These sources include, but are not limited to, valves, flanges and other connections, pumps and compressors, pressure relief devices, process drains, open-ended valves, pump and compressor seal system degassing vents, accumulator vessel vents, agitator seals, and access door seals.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A portable instrument is used to detect VOC leaks from individual sources. The instrument detector type is not specified, but it must meet the specifications and performance criteria contained in section 6.0. A leak definition concentration based on a reference compound is specified in each applicable regulation. This method is intended to locate and classify leaks only, and is not to be used as a direct measure of mass emission rate from individual sources.

3.0 Definitions

3.1 *Calibration gas* means the VOC compound used to adjust the instrument meter reading to a known value. The calibration gas is usually the reference compound at a known concentration approximately equal to the leak definition concentration.

3.2 *Calibration precision* means the degree of agreement between measurements of the same known value, expressed as the relative percentage of the average difference between the meter readings and the known concentration to the known concentration.

3.3 *Leak definition concentration* means the local VOC concentration at the surface of a leak source that indicates that a VOC emission (leak) is present. The leak definition is an instrument meter reading based on a reference compound.

3.4 *No detectable emission* means a local VOC concentration at the surface of a leak source, adjusted for local VOC ambient concentration, that is less than 2.5 percent of the specified leak definition concentration. that indicates that a VOC emission (leak) is not present.

3.5 *Reference compound* means the VOC species selected as the instrument calibration basis for specification of the leak definition concentration. (For example, if a leak definition concentration is 10,000 ppm as methane, then any source emission that results in a local concentration that yields a meter reading of 10,000 on an instrument meter calibrated with methane would be classified as a leak. In this example, the leak definition concentration is 10,000 ppm and the reference compound is methane.)

3.6 *Response factor* means the ratio of the known concentration of a VOC compound to the observed meter reading when measured using an instrument calibrated with the reference compound specified in the applicable regulation.

3.7 *Response time* means the time interval from a step change in VOC concentration at the input of the sampling system to the time at which 90 percent of the corresponding final value is reached as displayed on the instrument readout meter.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Pollutants. Several of the compounds, leaks of which may be determined by this method, may be irritating or corrosive to tissues (*e.g.*, heptane) or may be toxic (*e.g.*, benzene, methyl alcohol). Nearly all are fire hazards. Compounds in emissions should be determined through familiarity with the source. Appropriate precautions can be found in reference documents, such as reference No. 4 in section 16.0.

6.0 Equipment and Supplies

A VOC monitoring instrument meeting the following specifications is required:

6.1 The VOC instrument detector shall respond to the compounds being processed. Detector types that may meet this requirement include, but are not limited to, catalytic oxidation, flame ionization, infrared absorption, and photoionization.

6.2 The instrument shall be capable of measuring the leak definition concentration specified in the regulation.

6.3 The scale of the instrument meter shall be readable to ±2.5 percent of the specified leak definition concentration.

6.4 The instrument shall be equipped with an electrically driven pump to ensure that a sample is provided to the detector at a constant flow rate. The nominal sample flow rate, as measured at the sample probe tip, shall be 0.10 to 3.0 l/min (0.004 to 0.1 ft^3/min) when the probe is fitted with a glass wool plug or filter that may be used to prevent plugging of the instrument.

6.5 The instrument shall be equipped with a probe or probe extension or sampling not to exceed 6.4 mm (¼ in) in outside diameter,

with a single end opening for admission of sample.

6.6 The instrument shall be intrinsically safe for operation in explosive atmospheres as defined by the National Electrical Code by the National Fire Prevention Association or other applicable regulatory code for operation in any explosive atmospheres that may be encountered in its use. The instrument shall, at a minimum, be intrinsically safe for Class 1, Division 1 conditions, and/or Class 2, Division 1 conditions, as appropriate, as defined by the example code. The instrument shall not be operated with any safety device, such as an exhaust flame arrestor, removed.

7.0 Reagents and Standards

7.1 Two gas mixtures are required for instrument calibration and performance evaluation:

7.1.1 Zero Gas. Air, less than 10 parts per million by volume (ppmv) VOC.

7.1.2 Calibration Gas. For each organic species that is to be measured during individual source surveys, obtain or prepare a known standard in air at a concentration approximately equal to the applicable leak definition specified in the regulation.

7.2 Cylinder Gases. If cylinder calibration gas mixtures are used, they must be analyzed and certified by the manufacturer to be within 2 percent accuracy, and a shelf life must be specified. Cylinder standards must be either reanalyzed or replaced at the end of the specified shelf life.

7.3 Prepared Gases. Calibration gases may be prepared by the user according to any accepted gaseous preparation procedure that will yield a mixture accurate to within 2 percent. Prepared standards must be replaced each day of use unless it is demonstrated that degradation does not occur during storage.

7.4 Mixtures with non-Reference Compound Gases. Calibrations may be performed using a compound other than the reference compound. In this case, a conversion factor must be determined for the alternative compound such that the resulting meter readings during source surveys can be converted to reference compound results.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Instrument Performance Evaluation. Assemble and start up the instrument according to the manufacturer's instructions for recommended warmup period and preliminary adjustments.

8.1.1 Response Factor. A response factor must be determined for each compound that is to be measured, either by testing or from reference sources. The response factor tests are required before placing the analyzer into service, but do not have to be repeated at subsequent intervals.

8.1.1.1 Calibrate the instrument with the reference compound as specified in the applicable regulation. Introduce the calibration gas mixture to the analyzer and record the observed meter reading. Introduce zero gas until a stable reading is obtained. Make a total of three measurements by alternating between the calibration gas and zero gas. Calculate the response factor for each repetition and the average response factor.

8.1.1.2 The instrument response factors for each of the individual VOC to be measured shall be less than 10 unless otherwise specified in the applicable regulation. When no instrument is available that meets this specification when calibrated with the reference VOC specified in the applicable regulation, the available instrument may be calibrated with one of the VOC to be measured, or any other VOC, so long as the instrument then has a response factor of less than 10 for each of the individual VOC to be measured.

8.1.1.3 Alternatively, if response factors have been published for the compounds of interest for the instrument or detector type, the response factor determination is not required, and existing results may be referenced. Examples of published response factors for flame ionization and catalytic oxidation detectors are included in References 1–3 of section 17.0.

8.1.2 Calibration Precision. The calibration precision test must be completed prior to placing the analyzer into service and at subsequent 3-month intervals or at the next use, whichever is later.

8.1.2.1 Make a total of three measurements by alternately using zero gas and the specified calibration gas. Record the meter readings. Calculate the average algebraic difference between the meter readings and the known value. Divide this average difference by the known calibration value and multiply by 100 to express the resulting calibration precision as a percentage.

8.1.2.2 The calibration precision shall be equal to or less than 10 percent of the calibration gas value.

8.1.3 Response Time. The response time test is required before placing the instrument into service. If a modification to the sample pumping system or flow configuration is made that would change the response time, a new test is required before further use.

8.1.3.1 Introduce zero gas into the instrument sample probe. When the meter reading has stabilized, switch quickly to the specified calibration gas. After switching, measure the time required to attain 90 percent of the final stable reading. Perform this test sequence three times and record the results. Calculate the average response time.

8.1.3.2 The instrument response time shall be equal to or less than 30 seconds. The instrument pump, dilution probe (if any), sample probe, and probe filter that will be used

during testing shall all be in place during the response time determination.

8.2 Instrument Calibration. Calibrate the VOC monitoring instrument according to section 10.0.

8.3 Individual Source Surveys.

8.3.1 Type I—Leak Definition Based on Concentration. Place the probe inlet at the surface of the component interface where leakage could occur. Move the probe along the interface periphery while observing the instrument readout. If an increased meter reading is observed, slowly sample the interface where leakage is indicated until the maximum meter reading is obtained. Leave the probe inlet at this maximum reading location for approximately two times the instrument response time. If the maximum observed meter reading is greater than the leak definition in the applicable regulation, record and report the results as specified in the regulation reporting requirements. Examples of the application of this general technique to specific equipment types are:

8.3.1.1 Valves. The most common source of leaks from valves is the seal between the stem and housing. Place the probe at the interface where the stem exits the packing gland and sample the stem circumference. Also, place the probe at the interface of the packing gland take-up flange seat and sample the periphery. In addition, survey valve housings of multipart assembly at the surface of all interfaces where a leak could occur.

8.3.1.2 Flanges and Other Connections. For welded flanges, place the probe at the outer edge of the flange-gasket interface and sample the circumference of the flange. Sample other types of nonpermanent joints (such as threaded connections) with a similar traverse.

8.3.1.3 Pumps and Compressors. Conduct a circumferential traverse at the outer surface of the pump or compressor shaft and seal interface. If the source is a rotating shaft, position the probe inlet within 1 cm of the shaft-seal interface for the survey. If the housing configuration prevents a complete traverse of the shaft periphery, sample all accessible portions. Sample all other joints on the pump or compressor housing where leakage could occur.

8.3.1.4 Pressure Relief Devices. The configuration of most pressure relief devices prevents sampling at the sealing seat interface. For those devices equipped with an enclosed extension, or horn, place the probe inlet at approximately the center of the exhaust area to the atmosphere.

8.3.1.5 Process Drains. For open drains, place the probe inlet at approximately the center of the area open to the atmosphere. For covered drains, place the probe at the surface of the cover interface and conduct a peripheral traverse.

8.3.1.6 Open-ended Lines or Valves. Place the probe inlet at approximately the center of the opening to the atmosphere.

8.3.1.7 Seal System Degassing Vents and Accumulator Vents. Place the probe inlet at approximately the center of the opening to the atmosphere.

8.3.1.8 Access door seals. Place the probe inlet at the surface of the door seal interface and conduct a peripheral traverse.

8.3.2 Type II—''No Detectable Emission''. Determine the local ambient VOC concentration around the source by moving the probe randomly upwind and downwind at a distance of one to two meters from the source. If an interference exists with this determination due to a nearby emission or leak, the local ambient concentration may be determined at distances closer to the source, but in no case shall the distance be less than 25 centimeters. Then move the probe inlet to the surface of the source and determine the concentration as outlined in section 8.3.1. The difference between these concentrations determines whether there are no detectable emissions. Record and report the results as specified by the regulation. For those cases where the regulation requires a specific device installation, or that specified vents be ducted or piped to a control device, the existence of these conditions shall be visually confirmed. When the regulation also requires that no detectable emissions exist, visual observations and sampling surveys are required. Examples of this technique are:

8.3.2.1 Pump or Compressor Seals. If applicable, determine the type of shaft seal. Perform a survey of the local area ambient VOC concentration and determine if detectable emissions exist as described in section 8.3.2.

8.3.2.2 Seal System Degassing Vents, Accumulator Vessel Vents, Pressure Relief Devices. If applicable, observe whether or not the applicable ducting or piping exists. Also, determine if any sources exist in the ducting or piping where emissions could occur upstream of the control device. If the required ducting or piping exists and there are no sources where the emissions could be vented to the atmosphere upstream of the control device, then it is presumed that no detectable emissions are present. If there are sources in the ducting or piping where emissions could be vented or sources where leaks could occur, the sampling surveys described in section 8.3.2 shall be used to determine if detectable emissions exist.

8.3.3 Alternative Screening Procedure.

8.3.3.1 A screening procedure based on the formation of bubbles in a soap solution that is sprayed on a potential leak source may be used for those sources that do not have continuously moving parts, that do not have surface temperatures greater than the boiling point or less than the freezing point of the soap solution, that do not have open

areas to the atmosphere that the soap solution cannot bridge, or that do not exhibit evidence of liquid leakage. Sources that have these conditions present must be surveyed using the instrument technique of section 8.3.1 or 8.3.2.

8.3.3.2 Spray a soap solution over all potential leak sources. The soap solution may be a commercially available leak detection solution or may be prepared using concentrated detergent and water. A pressure sprayer or squeeze bottle may be used to dispense the solution. Observe the potential leak sites to determine if any bubbles are formed. If no bubbles are observed, the source is presumed to have no detectable emissions or leaks as applicable. If any bubbles are observed, the instrument techniques of section 8.3.1 or 8.3.2 shall be used to determine if a leak exists, or if the source has detectable emissions, as applicable.

9.0 Quality Control

Section	Quality control measure	Effect
8.1.2	Instrument calibration precision check	Ensure precision and accuracy, respectively, of instrument response to standard.
10.0	Instrument calibration.	

10.0 Calibration and Standardization

10.1 Calibrate the VOC monitoring instrument as follows. After the appropriate warmup period and zero internal calibration procedure, introduce the calibration gas into the instrument sample probe. Adjust the instrument meter readout to correspond to the calibration gas value.

NOTE: If the meter readout cannot be adjusted to the proper value, a malfunction of the analyzer is indicated and corrective actions are necessary before use.

11.0 Analytical Procedures [Reserved]

12.0 Data Analyses and Calculations [Reserved]

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Dubose, D.A., and G.E. Harris. Response Factors of VOC Analyzers at a Meter Reading of 10,000 ppmv for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81051. September 1981.

2. Brown, G.E., *et al.* Response Factors of VOC Analyzers Calibrated with Methane for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81–022. May 1981.

3. DuBose, D.A. *et al.* Response of Portable VOC Analyzers to Chemical Mixtures. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81–110. September 1981.

4. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 22—VISUAL DETERMINATION OF FUGITIVE EMISSIONS FROM MATERIAL SOURCES AND SMOKE EMISSIONS FROM FLARES

NOTE: This method is not inclusive with respect to observer certification. Some material is incorporated by reference from Method 9.

1.0 Scope and Application

This method is applicable for the determination of the frequency of fugitive emissions from stationary sources, only as specified in an applicable subpart of the regulations. This method also is applicable for the determination of the frequency of visible smoke emissions from flares.

2.0 Summary of Method

2.1 Fugitive emissions produced during material processing, handling, and transfer operations or smoke emissions from flares are visually determined by an observer without the aid of instruments.

2.2 This method is used also to determine visible smoke emissions from flares used for combustion of waste process materials.

2.3 This method determines the amount of time that visible emissions occur during the observation period (*i.e.*, the accumulated emission time). This method does not require that the opacity of emissions be determined. Since this procedure requires only the determination of whether visible emissions occur and does not require the determination of opacity levels, observer certification according to the procedures of Method 9 is not required. However, it is necessary that the observer is knowledgeable with respect to the general procedures for determining the presence of visible emissions. At a minimum, the observer must be trained and knowledgeable regarding the effects of background contrast, ambient lighting, observer position relative

to lighting, wind, and the presence of uncombined water (condensing water vapor) on the visibility of emissions. This training is to be obtained from written materials found in References 1 and 2 or from the lecture portion of the Method 9 certification course.

3.0 Definitions

3.1 *Emission frequency* means the percentage of time that emissions are visible during the observation period.

3.2 *Emission time* means the accumulated amount of time that emissions are visible during the observation period.

3.3 *Fugitive emissions* means emissions generated by an affected facility which is not collected by a capture system and is released to the atmosphere. This includes emissions that (1) escape capture by process equipment exhaust hoods; (2) are emitted during material transfer; (3) are emitted from buildings housing material processing or handling equipment; or (4) are emitted directly from process equipment.

3.4 *Observation period* means the accumulated time period during which observations are conducted, not to be less than the period specified in the applicable regulation.

3.5 *Smoke emissions* means a pollutant generated by combustion in a flare and occurring immediately downstream of the flame. Smoke occurring within the flame, but not downstream of the flame, is not considered a smoke emission.

4.0 Interferences

4.1 Occasionally, fugitive emissions from sources other than the affected facility (*e.g.*, road dust) may prevent a clear view of the affected facility. This may particularly be a problem during periods of high wind. If the view of the potential emission points is obscured to such a degree that the observer questions the validity of continuing observations, then the observations shall be terminated, and the observer shall clearly note this fact on the data form.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment

6.1 Stopwatches (two). Accumulative type with unit divisions of at least 0.5 seconds.

6.2 Light Meter. Light meter capable of measuring illuminance in the 50 to 200 lux range, required for indoor observations only.

7.0 Reagents and Supplies [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transfer [Reserved]

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

11.1 Selection of Observation Location. Survey the affected facility, or the building or structure housing the process to be observed, and determine the locations of potential emissions. If the affected facility is located inside a building, determine an observation location that is consistent with the requirements of the applicable regulation (*i.e.*, outside observation of emissions escaping the building/structure or inside observation of emissions directly emitted from the affected facility process unit). Then select a position that enables a clear view of the potential emission point(s) of the affected facility or of the building or structure housing the affected facility, as appropriate for the applicable subpart. A position at least 4.6 m (15 feet), but not more than 400 m (0.25 miles), from the emission source is recommended. For outdoor locations, select a position where the sunlight is not shining directly in the observer's eyes.

11.2 Field Records.

11.2.1 Outdoor Location. Record the following information on the field data sheet (Figure 22–1): Company name, industry, process unit, observer's name, observer's affiliation, and date. Record also the estimated wind speed, wind direction, and sky condition. Sketch the process unit being observed, and note the observer location relative to the source and the sun. Indicate the potential and actual emission points on the sketch.

11.2.2 Indoor Location. Record the following information on the field data sheet (Figure 22–2): Company name, industry, process unit, observer's name, observer's affiliation, and date. Record as appropriate the type, location, and intensity of lighting on the data sheet. Sketch the process unit being observed, and note the observer location relative to the source. Indicate the potential and actual fugitive emission points on the sketch.

11.3 Indoor Lighting Requirements. For indoor locations, use a light meter to measure the level of illumination at a location as close to the emission source(s) as is feasible. An illumination of greater than 100 lux (10 foot candles) is considered necessary for proper application of this method.

11.4 Observations.

11.4.1 Procedure. Record the clock time when observations begin. Use one stopwatch to monitor the duration of the observation

period. Start this stopwatch when the observation period begins. If the observation period is divided into two or more segments by process shutdowns or observer rest breaks (see section 11.4.3), stop the stopwatch when a break begins and restart the stopwatch without resetting it when the break ends. Stop the stopwatch at the end of the observation period. The accumulated time indicated by this stopwatch is the duration of observation period. When the observation period is completed, record the clock time. During the observation period, continuously watch the emission source. Upon observing an emission (condensed water vapor is not considered an emission), start the second accumulative stopwatch; stop the watch when the emission stops. Continue this procedure for the entire observation period. The accumulated elapsed time on this stopwatch is the total time emissions were visible during the observation period (*i.e.*, the emission time.)

11.4.2 Observation Period. Choose an observation period of sufficient length to meet the requirements for determining compliance with the emission standard in the applicable subpart of the regulations. When the length of the observation period is specifically stated in the applicable subpart, it may not be necessary to observe the source for this entire period if the emission time required to indicate noncompliance (based on the specified observation period) is observed in a shorter time period. In other words, if the regulation prohibits emissions for more than 6 minutes in any hour, then observations may (optional) be stopped after an emission time of 6 minutes is exceeded. Similarly, when the regulation is expressed as an emission frequency and the regulation prohibits emissions for greater than 10 percent of the time in any hour, then observations may (optional) be terminated after 6 minutes of emission are observed since 6 minutes is 10 percent of an hour. In any case, the observation period shall not be less than 6 minutes in duration. In some cases, the process operation may be intermittent or cyclic. In such cases, it may be convenient for the observation period to coincide with the length of the process cycle.

11.4.3 Observer Rest Breaks. Do not observe emissions continuously for a period of more than 15 to 20 minutes without taking a rest break. For sources requiring observation periods of greater than 20 minutes, the observer shall take a break of not less than 5 minutes and not more than 10 minutes after every 15 to 20 minutes of observation. If continuous observations are desired for extended time periods, two observers can alternate between making observations and taking breaks.

11.5 Recording Observations. Record the accumulated time of the observation period on the data sheet as the observation period duration. Record the accumulated time emissions were observed on the data sheet as the emission time. Record the clock time the observation period began and ended, as well as the clock time any observer breaks began and ended.

12.0 Data Analysis and Calculations

If the applicable subpart requires that the emission rate be expressed as an emission frequency (in percent), determine this value as follows: Divide the accumulated emission time (in seconds) by the duration of the observation period (in seconds) or by any minimum observation period required in the applicable subpart, if the actual observation period is less than the required period, and multiply this quotient by 100.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Missan, R., and A. Stein. Guidelines for Evaluation of Visible Emissions Certification, Field Procedures, Legal Aspects, and Background Material. EPA Publication No. EPA–340/1–75–007. April 1975.

2. Wohlschlegel, P., and D.E. Wagoner. Guideline for Development of a Quality Assurance Program: Volume IX—Visual Determination of Opacity Emissions from Stationary Sources. EPA Publication No. EPA–650/4–74–005i. November 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

FUGITIVE OR SMOKE EMISSION INSPECTION
OUTDOOR LOCATION

Company Location Company Rep.	Observer Affiliation Date
Sky Conditions Precipitation	Wind Direction Wind Speed
Industry	Process Unit

Sketch process unit: indicate observer position relative to source; indicate potential emission points and/or actual emission points.

OBSERVATIONS	Clock Time	Observation period duration, min:sec	Accumulated emission time, min:sec
Begin Observation			
End Observation			

Figure 22-1

FUGITIVE OR SMOKE EMISSION INSPECTION
INDOOR LOCATION

Company Location Company Rep.	Observer Affiliation Date
Industry	Process Unit

Light type (fluorescent, incandescent, natural)
Light location (overhead, behind observer, etc.)
Illuminance (lux or footcandles)
Sketch process unit: indicate observer position relative to source; indicate potential emission points and/or actual emission points.

OBSERVATIONS	Clock Time	Observation period duration, min:sec	Accumulated emission time, min:sec
Begin			
End Observation			

Figure 22-2

METHOD 23—DETERMINATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS FROM STATIONARY SOURCES

1. Applicability and Principle

1.1 Applicability. This method is applicable to the determination of polychlorinated dibenzo-p-dioxins (PCDD's) and polychlorinated dibenzofurans (PCDF's) from stationary sources.

1.2 Principle. A sample is withdrawn from the gas stream isokinetically and collected in the sample probe, on a glass fiber filter, and on a packed column of adsorbent material. The sample cannot be separated into a particle vapor fraction. The PCDD's and

PCDF's are extracted from the sample, separated by high resolution gas chromatography, and measured by high resolution mass spectrometry.

2. Apparatus

2.1 Sampling. A schematic of the sampling train used in this method is shown in Figure 23–1. Sealing greases may not be used in assembling the train. The train is identical to that described in section 2.1 of Method 5 of this appendix with the following additions:

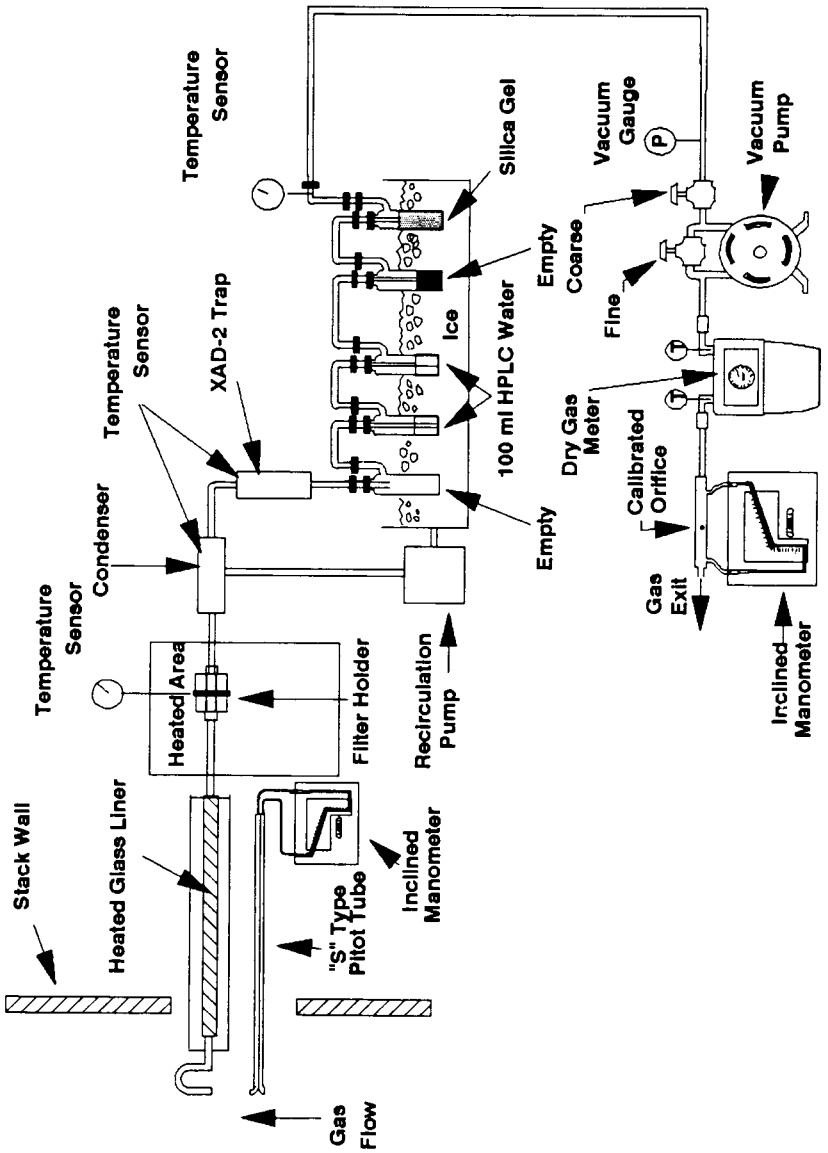

Figure 23.1 Sampling train

2.1.1 Nozzle. The nozzle shall be made of nickel, nickel-plated stainless steel, quartz, or borosilicate glass.

2.1.2 Sample Transfer Lines. The sample transfer lines, if needed, shall be heat traced, heavy walled TFE (½ in. OD with ⅛ in. wall) with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases. The line shall be as short as possible and must be maintained at 120 °C.

2.1.1 Filter Support. Teflon or Teflon-coated wire.

2.1.2 Condenser. Glass, coil type with compatible fittings. A schematic diagram is shown in Figure 23–2.

2.1.3 Water Bath. Thermostatically controlled to maintain the gas temperature exiting the condenser at <20 °C (68 °F).

2.1.4 Adsorbent Module. Glass container to hold the solid adsorbent. A shematic diagram is shown in Figure 23–2. Other physical configurations of the resin trap/condenser assembly are acceptable. The connecting fittings shall form leak-free, vacuum tight seals. No sealant greases shall be used in the sampling train. A coarse glass frit is included to retain the adsorbent.

2.2 Sample Recovery.

2.2.1 Fitting Caps. Ground glass, Teflon tape, or aluminum foil (Section 2.2.6) to cap off the sample exposed sections of the train.

2.2.2 Wash Bottles. Teflon, 500-ml.

2.2.3 Probe-Liner Probe-Nozzle, and Filter-Holder Brushes. Inert bristle brushes with precleaned stainless steel or Teflon handles. The probe brush shall have extensions of stainless steel or Teflon, at least as long as the probe. The brushes shall be properly sized and shaped to brush out the nozzle, probe liner, and transfer line, if used.

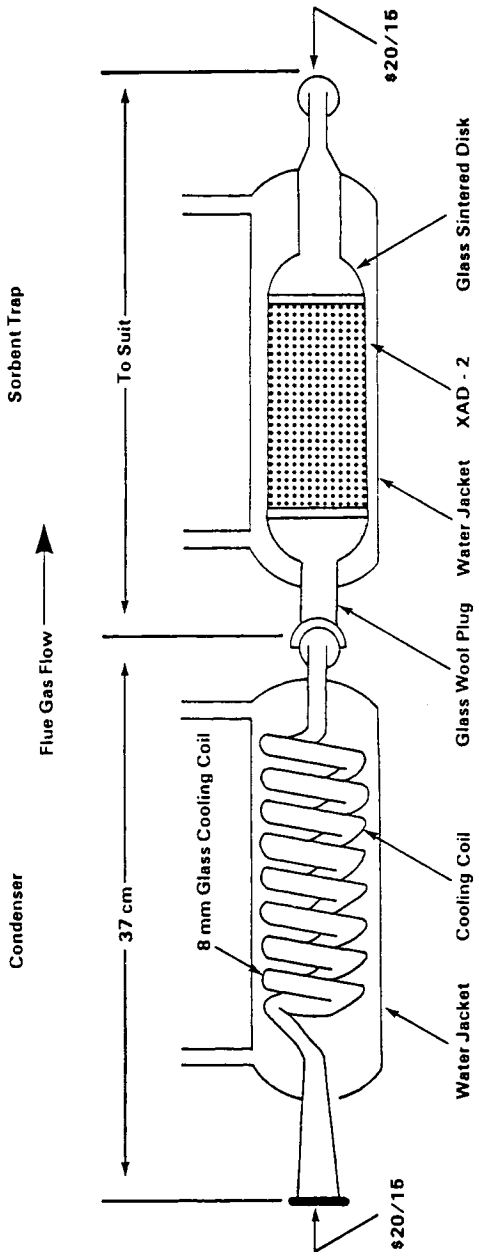

Figure 23.2. Condenser and adsorbent trap

2.2.4 Filter Storage Container. Sealed filter holder, wide-mouth amber glass jar with Teflon-lined cap, or glass petri dish.

2.2.5 Balance. Triple beam.

2.2.6 Aluminum Foil. Heavy duty, hexane-rinsed.

2.2.7 Storage Container. Air-tight container to store silica gel.

2.2.8 Graduated Cylinder. Glass, 250-ml with 2-ml graduation.

2.2.9 Glass Sample Storage Container. Amber glass bottle for sample glassware washes, 500- or 1000-ml, with leak free Teflon-lined caps.

2.3 Analysis.

2.3.1 Sample Container. 125- and 250-ml flint glass bottles with Teflon-lined caps.

2.3.2 Test Tube. Glass.

2.3.3 Soxhlet Extraction Apparatus. Capable of holding 43 × 123 mm extraction thimbles.

2.3.4 Extraction Thimble. Glass, precleaned cellulosic, or glass fiber.

2.3.5 Pasteur Pipettes. For preparing liquid chromatographic columns.

2.3.6 Reacti-vials. Amber glass, 2-ml, silanized prior to use.

2.3.7 Rotary Evaporator. Buchi/Brinkman RF–121 or equivalent.

2.3.8 Nitrogen Evaporative Concentrator. N-Evap Analytical Evaporator Model III or equivalent.

2.3.9 Separatory Funnels. Glass, 2-liter.

2.3.10 Gas Chromatograph. Consisting of the following components:

2.3.10.1 Oven. Capable of maintaining the separation column at the proper operating temperature ±°C and performing programmed increases in temperature at rates of at least 40 °C/min.

2.3.10.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperatures ±1 °C.

2.3.10.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

2.3.10.4 Capillary Columns. A fused silica column, 60 × 0.25 mm inside diameter (ID), coated with DB–5 and a fused silica column, 30 m × 0.25 mm ID coated with DB–225. Other column systems may be used provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of section 6.1.2.2.

2.3.11 Mass Spectrometer. Capable of routine operation at a resolution of 1:10000 with a stability of ±5 ppm.

2.3.12 Data System. Compatible with the mass spectrometer and capable of monitoring at least five groups of 25 ions.

2.3.13 Analytical Balance. To measure within 0.1 mg.

3. Reagents

3.1 Sampling.

3.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D 2986–71 (Reapproved 1978) (incorporated by reference—see §60.17).

3.1.1.1 Precleaning. All filters shall be cleaned before their initial use. Place a glass extraction thimble and 1 g of silica gel and a plug of glass wool into a Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Place no more than 50 filters in the thimble onto the silica gel bed and top with the cleaned glass wool. Charge the Soxhlet with toluene and reflux for 16 hours. After extraction, allow the Soxhlet to cool, remove the filters, and dry them under a clean N_2 stream. Store the filters in a glass petri dish sealed with Teflon tape.

3.1.2 Adsorbent Resin. Amberlite XAD–2 resin. Thoroughly cleaned before initial use.

3.1.2.1 Cleaning Procedure. This procedure may be carried out in a giant Soxhlet extractor. An all-glass filter thimble containing an extra-course frit is used for extraction of XAD–2. The frit is recessed 10–15 mm above a crenelated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass wool plug and a stainless steel ring because it floats on methylene chloride. This process involves sequential extraction in the following order.

Solvent	Procedure
Water	Initial rinse: Place resin in a beaker, rinse once with water, and discard. Fill with water a second time, let stand overnight, and discard.
Water	Extract with water for 8 hours.
Methanol	Extract for 22 hours.
Methylene Chloride	Extract for 22 hours.
Toluene	Extract for 22 hours.

3.1.2.2 Drying.

3.1.2.2.1 Drying Column. Pyrex pipe, 10.2 cm ID by 0.6 m long, with suitable retainers.

3.1.2.2.2 Procedure. The adsorbent must be dried with clean inert gas. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has proven to be a reliable source of large volumes of gas free from organic contaminants. Connect the liquid nitrogen cylinder to the column by a length of cleaned copper tubing, 0.95 cm ID, coiled to pass through a heat source. A convenient heat source is a water-bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40 °C. Continue flowing nitrogen through the adsorbent until all the residual solvent is removed. The flow rate should be sufficient to gently agitate the particles but not so excessive as the cause the particles to fracture.

3.1.2.3 Quality Control Check. The adsorbent must be checked for residual toluene.

3.1.2.3.1 Extraction. Weigh 1.0 g sample of dried resin into a small vial, add 3 ml of toluene, cap the vial, and shake it well.

3.1.2.3.2 Analysis. Inject a 2 µl sample of the extract into a gas chromatograph operated under the following conditions:

Column: 6 ft × ⅛ in stainless steel containing 10 percent OV–101 on 100/120 Supelcoport.
Carrier Gas: Helium at a rate of 30 ml/min.
Detector: Flame ionization detector operated at a sensitivity of 4×10^{-11} A/mV.
Injection Port Temperature: 250 °C.
Detector Temperature: 305 °C.
Oven Temperature: 30 °C for 4 min; programmed to rise at 40 °C/min until it reaches 250 °C; return to 30 °C after 17 minutes.

Compare the results of the analysis to the results from the reference solution. Prepare the reference solution by injection 2.5 µl of methylene chloride into 100 ml of toluene. This corresponds to 100 µg of methylene chloride per g of adsorbent. The maximum acceptable concentration is 1000 µg/g of adsorbent. If the adsorbent exceeds this level, drying must be continued until the excess methylene chloride is removed.

3.1.2.4 Storage. The adsorbent must be used within 4 weeks of cleaning. After cleaning, it may be stored in a wide mouth amber glass container with a Teflon-lined cap or placed in one of the glass adsorbent modules tightly sealed with glass stoppers. If precleaned adsorbent is purchased in sealed containers, it must be used within 4 weeks after the seal is broken.

3.1.3 Glass Wool. Cleaned by sequential immersion in three aliquots of methylene chloride, dried in a 110 °C oven, and stored in a methylene chloride-washed glass jar with a Teflon-lined screw cap.

3.1.4 Water. Deionized distilled and stored in a methylene chloride-rinsed glass container with a Teflon-lined screw cap.

3.1.5 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175 °C (350 °F) for two hours. New silica gel may be used as received. Alternately other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

3.1.6 Chromic Acid Cleaning Solution. Dissolve 20 g of sodium dichromate in 15 ml of water, and then carefully add 400 ml of concentrated sulfuric acid.

3.2 Sample Recovery.

3.2.2 Acetone. Pesticide quality.

3.2.2 Methylene Chloride. Pesticide qualtity.

3.2.3 Toluene. Pesticide quality.

3.3 Analysis.

3.3.1 Potassium Hydroxide. ACS grade, 2-percent (weight/volume) in water.

3.3.2 Sodium Sulfate. Granulated, reagent grade. Purify prior to use by rinsing with methylene chloride and oven drying. Store the cleaned material in a glass container with a Teflon-lined screw cap.

3.3.3 Sulfuric Acid. Reagent grade.

3.3.4 Sodium Hydroxide. 1.0 N. Weigh 40 g of sodium hydroxide into a 1-liter volumetric flask. Dilute to 1 liter with water.

3.3.5 Hexane. Pesticide grade.

3.3.6 Methylene Chloride. Pesticide grade.

3.3.7 Benzene. Pesticide Grade.

3.3.8 Ethyl Acetate.

3.3.9 Methanol. Pesticide Grade.

3.3.10 Toluene. Pesticide Grade.

3.3.11 Nonane. Pesticide Grade.

3.3.12 Cyclohexane. Pesticide Grade.

3.3.13 Basic Alumina. Activity grade 1, 100–200 mesh. Prior to use, activate the alumina by heating for 16 hours at 130 °C before use. Store in a desiccator. Pre-activated alumina may be purchased from a supplier and may be used as received.

3.3.14 Silica Gel. Bio-Sil A, 100–200 mesh. Prior to use, activate the silica gel by heating for at least 30 minutes at 180 °C. After cooling, rinse the silica gel sequentially with methanol and methylene chloride. Heat the rinsed silica gel at 50 °C for 10 minutes, then increase the temperature gradually to 180 °C over 25 minutes and maintain it at this temperature for 90 minutes. Cool at room temperature and store in a glass container with a Teflon-lined screw cap.

3.3.15 Silica Gel Impregnated with Sulfuric Acid. Combine 100 g of silica gel with 44 g of concentrated sulfuric acid in a screw capped glass bottle and agitate thoroughly. Disperse the solids with a stirring rod until a uniform mixture is obtained. Store the mixture in a glass container with a Teflon-lined screw cap.

3.3.16 Silica Gel Impregnated with Sodium Hydroxide. Combine 39 g of 1 N sodium hydroxide with 100 g of silica gel in a screw capped glass bottle and agitate thoroughly. Disperse solids with a stirring rod until a uniform mixture is obtained. Store the mixture in glass container with a Teflon-lined screw cap.

3.3.17 Carbon/Celite. Combine 10.7 g of AX–21 carbon with 124 g of Celite 545 in a 250-ml glass bottle with a Teflon-lined screw cap. Agitate the mixture thoroughly until a uniform mixture is obtained. Store in the glass container.

3.3.18 Nitrogen. Ultra high purity.

3.3.19 Hydrogen. Ultra high purity.

3.3.20 Internal Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Internal Standards'' in 10 ml of nonane.

3.3.21 Surrogate Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Surrogate Standards'' in 10 ml of nonane.

3.3.22 Recovery Standard Solution. Prepare a stock standard solution containing the

isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Recovery Standards'' in 10 ml of nonane.

4. Procedure

4.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, testers should be trained and experienced with the test procedures.

4.1.1 Pretest Preparation.

4.1.1.1 Cleaning Glassware. All glass components of the train upstream of and including the adsorbent module, shall be cleaned as described in section 3A of the ''Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples.'' Special care shall be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. Any residue shall be removed by soaking the glassware for several hours in a chromic acid cleaning solution prior to cleaning as described above.

4.1.1.2 Adsorbent Trap. The traps must be loaded in a clean area to avoid contamination. They may not be loaded in the field. Fill a trap with 20 to 40 g of XAD–2. Follow the XAD–2 with glass wool and tightly cap both ends of the trap. Add 100 μl of the surrogate standard solution (section 3.3.21) to each trap.

4.1.1.3 Sample Train. It is suggested that all components be maintained according to the procedure described in APTD–0576. Alternative mercury-free thermometers may be used if the thermometers are, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

4.1.1.4 Silica Gel. Weigh several 200 to 300 g portions of silica gel in an air tight container to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel may be weighed directly in its impinger or sampling holder just prior to sampling.

4.1.1.5 Filter. Check each filter against light for irregularities and flaws or pinhole leaks. Pack the filters flat in a clean glass container.

4.1.2 Preliminary Determinations. Same as section 4.1.2 of Method 5.

4.1.3 Preparation of Collection Train.

4.1.3.1 During preparation and assembly of the sampling train, keep all train openings where contamination can enter, sealed until just prior to assembly or until sampling is about to begin.

NOTE: Do not use sealant grease in assembling the train.

4.1.3.2 Place approximately 100 ml of water in the second and third impingers, leave the first and fourth impingers empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fifth impinger.

4.1.3.3 Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

4.1.3.4 Assemble the train as shown in Figure 23–1.

4.1.3.5 Turn on the adsorbent module and condenser coil recirculating pump and begin monitoring the adsorbent module gas entry temperature. Ensure proper sorbent temperature gas entry temperature before proceeding and before sampling is initiated. It is extremely important that the XAD–2 adsorbent resin temperature never exceed 50 °C because thermal decomposition will occur. During testing, the XAD–2 temperature must not exceed 20 °C for efficient capture of the PCDD's and PCDF's.

4.1.4 Leak-Check Procedure. Same as Method 5, section 4.1.4.

4.1.5 Sample Train Operation. Same as Method 5, section 4.1.5.

4.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Seal the nozzle end of the sampling probe with Teflon tape or aluminum foil.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe. Remove the probe from the train and close off both ends with aluminum foil. Seal off the inlet to the train with Teflon tape, a ground glass cap, or aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area shall be clean and enclosed so that the chances of losing or contaminating the sample are minimized. Smoking, which could contaminate the sample, shall not be allowed in the cleanup area.

Inspect the train prior to and during disassembly and note any abnormal conditions, e.g., broken filters, colored impinger liquid, etc. Treat the samples as follows:

4.2.1 Container No. 1. Either seal the filter holder or carefully remove the filter from the filter holder and place it in its identified container. Use a pair of cleaned tweezers to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and filter fibers which adhere to the filter holder gasket, by using a dry inert bristle brush and a sharp-edged blade. Seal the container.

4.2.2 Adsorbent Module. Remove the module from the train, tightly cap both ends, label it, cover with aluminum foil, and store it on ice for transport to the laboratory.

4.2.3 Container No. 2. Quantitatively recover material deposited in the nozzle, probe transfer lines, the front half of the filter holder, and the cyclone, if used, first, by

brushing while rinsing three times each with acetone and then, by rinsing the probe three times with methylene chloride. Collect all the rinses in Container No. 2.

Rinse the back half of the filter holder three times with acetone. Rinse the connecting line between the filter and the condenser three times with acetone. Soak the connecting line with three separate portions of methylene chloride for 5 minutes each. If using a separate condenser and adsorbent trap, rinse the condenser in the same manner as the connecting line. Collect all the rinses in Container No. 2 and mark the level of the liquid on the container.

4.2.4 Container No. 3. Repeat the methylene chloride-rinsing described in section 4.2.3 using toluene as the rinse solvent. Collect the rinses in Container No. 3 and mark the level of the liquid on the container.

4.2.5 Impinger Water. Measure the liquid in the first three impingers to within ±1 ml by using a graduated cylinder or by weighing it to within ±0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

Discard the liquid after measuring and recording the volume or weight.

4.2.7 Silica Gel. Note the color of the indicating silica gel to determine if it has been completely spent and make a mention of its condition. Transfer the silica gel from the fifth impinger to its original container and seal. If a moisture determination is made, follow the applicable procedures in sections 8.7.6.3 and 11.2.3 of Method 5 to handle and weigh the silica gel. If moisture is not measured, the silica gel may be disposed.

5. Analysis

All glassware shall be cleaned as described in section 3A of the ''Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples.'' All samples must be extracted within 30 days of collection and analyzed within 45 days of extraction.

5.1 Sample Extraction.

5.1.1 Extraction System. Place an extraction thimble (section 2.3.4), 1 g of silica gel, and a plug of glass wool into the Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Remove the extraction thimble from the extraction system and place it in a glass beaker to catch the solvent rinses.

5.1.2 Container No. 1 (Filter). Transfer the contents directly to the glass thimble of the extraction system and extract them simultaneously with the XAD–2 resin.

5.1.3 Adsorbent Cartridge. Suspend the adsorbent module directly over the extraction thimble in the beaker (See section 5.1.1). The glass frit of the module should be in the up position. Using a Teflon squeeze bottle containing toluene, flush the XAD–2 into the thimble onto the bed of cleaned silica gel. Thoroughly rinse the glass module catching the rinsings in the beaker containing the thimble. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. Add the XAD–2 glass wool plug into the thimble.

5.1.4 Container No. 2 (Acetone and Methylene Chloride). Concentrate the sample to a volume of about 1–5 ml using the rotary evaporator apparatus, at a temperature of less than 37 °C. Rinse the sample container three times with small portions of methylene chloride and add these to the concentrated solution and concentrate further to near dryness. This residue contains particulate matter removed in the rinse of the train probe and nozzle. Add the concentrate to the filter and the XAD–2 resin in the Soxhlet apparatus described in section 5.1.1.

5.1.5 Extraction. Add 100 µl of the internal standard solution (Section 3.3.20) to the extraction thimble containing the contents of the adsorbent cartridge, the contents of Container No. 1, and the concentrate from section 5.1.4. Cover the contents of the extraction thimble with the cleaned glass wool plug to prevent the XAD–2 resin from floating into the solvent reservoir of the extractor. Place the thimble in the extractor, and add the toluene contained in the beaker to the solvent reservoir. Pour additional toluene to fill the reservoir approximately ⅔ full. Add Teflon boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle three times per hour. Extract the sample for 16 hours. After extraction, allow the Soxhlet to cool. Transfer the toluene extract and three 10-ml rinses to the rotary evaporator. Concentrate the extract to approximately 10 ml. At this point the analyst may choose to split the sample in half. If so, split the sample, store one half for future use, and analyze the other according to the procedures in sections 5.2 and 5.3. In either case, use a nitrogen evaporative concentrator to reduce the volume of the sample being analyzed to near dryness. Dissolve the residue in 5 ml of hexane.

5.1.6 Container No. 3 (Toluene Rinse). Add 100 µl of the Internal Standard solution (section 3.3.2) to the contents of the container. Concentrate the sample to a volume of about 1–5 ml using the rotary evaporator apparatus at a temperature of less than 37 °C. Rinse the sample container apparatus at a temperature of less than 37 °C. Rinse the sample container three times with small portions of toluene and add these to the concentrated solution and concentrate further to near dryness. Analyze the extract separately according to the procedures in sections 5.2 and 5.3, but concentrate the solution in a rotary evaporator apparatus rather than a nitrogen evaporative concentrator.

5.2 Sample Cleanup and Fractionation.

5.2.1 Silica Gel Column. Pack one end of a glass column, 20 mm × 230 mm, with glass wool. Add in sequence, 1 g silica gel, 2 g of sodium hydroxide impregnated silica gel, 1 g silica gel, 4 g of acid-modified silica gel, and 1 g of silica gel. Wash the column with 30 ml of hexane and discard it. Add the sample extract, dissolved in 5 ml of hexane to the column with two additional 5-ml rinses. Elute the column with an additional 90 ml of hexane and retain the entire eluate. Concentrate this solution to a volume of about 1 ml using the nitrogen evaporative concentrator (section 2.3.7).

5.2.2 Basic Alumina Column. Shorten a 25-ml disposable Pasteur pipette to about 16 ml. Pack the lower section with glass wool and 12 g of basic alumina. Transfer the concentrated extract from the silica gel column to the top of the basic alumina column and elute the column sequentially with 120 ml of 0.5 percent methylene chloride in hexane followed by 120 ml of 35 percent methylene chloride in hexane. Discard the first 120 ml of eluate. Collect the second 120 ml of eluate and concentrate it to about 0.5 ml using the nitrogen evaporative concentrator.

5.2.3 AX–21 Carbon/Celite 545 Column. Remove the botton 0.5 in. from the tip of a 9-ml disposable Pasteur pipette. Insert a glass fiber filter disk in the top of the pipette 2.5 cm from the constriction. Add sufficient carbon/celite mixture to form a 2 cm column. Top with a glass wool plug. In some cases AX–21 carbon fines may wash through the glass wool plug and enter the sample. This may be prevented by adding a celite plug to the exit end of the column. Rinse the column in sequence with 2 ml of 50 percent benzene in ethyl acetate, 1 ml of 50 percent methylene chloride in cyclohexane, and 2 ml of hexane. Discard these rinses. Transfer the concentrate in 1 ml of hexane from the basic alumina column to the carbon/celite column along with 1 ml of hexane rinse. Elute the column sequentially with 2 ml of 50 percent methylene chloride in hexane and 2 ml of 50 percent benzene in ethyl acetate and discard these eluates. Invert the column and elute in the reverse direction with 13 ml of toluene. Collect this eluate. Concentrate the eluate in a rotary evaporator at 50 °C to about 1 ml. Transfer the concentrate to a Reacti-vial using a toluene rinse and concentrate to a volume of 200 µl using a stream of N_2. Store extracts at room temperature, shielded from light, until the analysis is performed.

5.3 Analysis. Analyze the sample with a gas chromatograph coupled to a mass spectrometer (GC/MS) using the instrumental parameters in sections 5.3.1 and 5.3.2. Immediately prior to analysis, add a 20 µl aliquot of the Recovery Standard solution from Table 1 to each sample. A 2 µl aliquot of the extract is injected into the GC. Sample extracts are first analyzed using the DB–5 capillary column to determine the concentration of each isomer of PCDD's and PCDF's (tetra-through octa-). If tetra-chlorinated dibenzofurans are detected in this analysis, then analyze another aliquot of the sample in a separate run, using the DB–225 column to measure the 2,3,7,8 tetra-chloro dibenzofuran isomer. Other column systems may be used, provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of section 6.1.2.2.

5.3.1 Gas Chromatograph Operating Conditions.

5.3.1.1 Injector. Configured for capillary column, splitless, 250 °C.

5.3.1.2 Carrier Gas. Helium, 1–2 ml/min.

5.3.1.3 Oven. Initially at 150 °C. Raise by at least 40 °C/min to 190 °C and then at 3 °C/min up to 300 °C.

5.3.2 High Resolution Mass Spectrometer.

5.3.2.1 Resolution. 10000 m/e.

5.3.2.2 Ionization Mode. Electron impact.

5.3.2.3 Source Temperature 250 °C.

5.3.2.4 Monitoring Mode. Selected ion monitoring. A list of the various ions to be monitored is summarized in Table 3.

5.3.2.5 Identification Criteria. The following identification criteria shall be used for the characterization of polychlorinated dibenzodioxins and dibenzofurans.

1. The integrated ion-abundance ratio (M/M + 2 or M + 2/M + 4) shall be within 15 percent of the theoretical value. The acceptable ion-abundance ratio ranges for the identification of chlorine-containing compounds are given in Table 4.

2. The retention time for the analytes must be within 3 seconds of the corresponding ^{13}C-labeled internal standard, surrogate or alternate standard.

3. The monitored ions, shown in Table 3 for a given analyte, shall reach their maximum within 2 seconds of each other.

4. The identification of specific isomers that do not have corresponding ^{13}C-labeled standards is done by comparison of the relative retention time (RRT) of the analyte to the nearest internal standard retention time with reference (i.e., within 0.005 RRT units) to the comparable RRT's found in the continuing calibration.

5. The signal to noise ratio for all monitored ions must be greater than 2.5.

6. The confirmation of 2, 3, 7, 8–TCDD and 2, 3, 7, 8–TCDF shall satisfy all of the above identification criteria.

7. For the identification of PCDF's, no signal may be found in the corresponding PCDPE channels.

5.3.2.6 Quantification. The peak areas for the two ions monitored for each analyte are summed to yield the total response for each analyte. Each internal standard is used to quantify the indigenous PCDD's or PCDF's in its homologous series. For example, the $^{13}C_{12}$–2,3,7,8-tetra chlorinated dibenzodioxin is used to calculate the concentrations of all

other tetra chlorinated isomers. Recoveries of the tetra- and penta- internal standards are calculated using the $^{13}C_{12}$–1,2,3,4–TCDD. Recoveries of the hexa- through octa- internal standards are calculated using $^{13}C_{12}$–1,2,3,7,8,9–HxCDD. Recoveries of the surrogate standards are calculated using the corresponding homolog from the internal standard.

6. Calibration

Same as Method 5 with the following additions.

6.1 GC/MS System.

6.1.1 Initial Calibration. Calibrate the GC/MS system using the set of five standards shown in Table 2. The relative standard deviation for the mean response factor from each of the unlabeled analytes (Table 2) and of the internal, surrogate, and alternate standards shall be less than or equal to the values in Table 5. The signal to noise ratio for the GC signal present in every selected ion current profile shall be greater than or equal to 2.5. The ion abundance ratios shall be within the control limits in Table 4.

6.1.2 Daily Performance Check.

6.1.2.1 Calibration Check. Inject on µl of solution Number 3 from Table 2. Calculate the relative response factor (RRF) for each compound and compare each RRF to the corresponding mean RRF obtained during the initial calibration. The analyzer performance is acceptable if the measured RRF's for the labeled and unlabeled compounds for the daily run are within the limits of the mean values shown in Table 5. In addition, the ion-abundance ratios shall be within the allowable control limits shown in Table 4.

6.1.2.2 Column Separation Check. Inject a solution of a mixture of PCDD's and PCDF's that documents resolution between 2,3,7,8–TCDD and other TCDD isomers. Resolution is defined as a valley between peaks that is less than 25 percent of the lower of the two peaks. Identify and record the retention time windows for each homologous series.

Perform a similar resolution check on the confirmation column to document the resolution between 2,3,7,8 TCDF and other TCDF isomers.

6.2 Lock Channels. Set mass spectrometer lock channels as specified in Table 3. Monitor the quality control check channels specified in Table 3 to verify instrument stability during the analysis.

7. Quality Control

7.1 Sampling Train Collection Efficiency Check. Add 100 µl of the surrogate standards in Table 1 to the absorbent cartridge of each train before collecting the field samples.

7.2 Internal Standard Percent Recoveries. A group of nine carbon labeled PCDD's and PCDF's representing, the tetra-through octachlorinated homologues, is added to every sample prior to extraction. The role of the internal standards is to quantify the native PCDD's and PCDF's present in the sample as well as to determine the overall method efficiency. Recoveries of the internal standards must be between 40 to 130 percent for the tetra-through hexachlorinated compounds while the range is 25 to 130 percent for the higher hepta- and octachlorinated homologues.

7.3 Surrogate Recoveries. The five surrogate compounds in Table 2 are added to the resin in the adsorbent sampling cartridge before the sample is collected. The surrogate recoveries are measured relative to the internal standards and are a measure of collection efficiency. They are not used to measure native PCDD's and PCDF's. All recoveries shall be between 70 and 130 percent. Poor recoveries for all the surrogates may be an indication of breakthrough in the sampling train. If the recovery of all standards is below 70 percent, the sampling runs must be repeated. As an alternative, the sampling runs do not have to be repeated if the final results are divided by the fraction of surrogate recovery. Poor recoveries of isolated surrogate compounds should not be grounds for rejecting an entire set of the samples.

7.4 Toluene QA Rinse. Report the results of the toluene QA rinse separately from the total sample catch. Do not add it to the total sample.

8.0 [Reserved]

9. Calculations

Same as Method 5, section 6 with the following additions.

9.1 Nomenclature.

A_{ai} = Integrated ion current of the noise at the retention time of the analyte.

A^*_{ci} = Integrated ion current of the two ions characteristic of the internal standard i in the calibration standard.

A_{cij} = Integrated ion current of the two ions characteristic of compound i in the jth calibration standard.

A^*_{cij} = Integrated ion current of the two ions characteristic of the internal standard i in the jth calibration standard.

A_{csi} = Integrated ion current of the two ions characteristic of surrogate compound i in the calibration standard.

A_i = Integrated ion current of the two ions characteristic of compound i in the sample.

A^*_i = Integrated ion current of the two ions characteristic of internal standard i in the sample.

A_{rs} = Integrated ion current of the two ions characteristic of the recovery standard.

A_{si} = Integrated ion current of the two ions characteristic of surrogate compound i in the sample.

C_i = Concentration of PCDD or PCDF i in the sample, pg/M^3.

C_T = Total concentration of PCDD's or PCDF's in the sample, pg/M^3.
m_{ci} = Mass of compound i in the calibration standard injected into the analyzer, pg.
m_{rs} = Mass of recovery standard in the calibration standard injected into the analyzer, pg.
m_{si} = Mass of surrogate compound in the calibration standard, pg.
RRF_i = Relative response factor.
RRF_{rs} = Recovery standard response factor.
RRF_s = Surrogate compound response factor.

9.2 Average Relative Response Factor.

$$RRF_i = \frac{1}{n}\sum_{j=1}^{n}\frac{A_{cij}\, m^*_{ci}}{A^*_{cij}\, m_{ci}} \qquad \text{Eq. 23-1}$$

9.3 Concentration of the PCDD's and PCDF's.

$$C_i = \frac{m_i^* A_i}{A_i^* RRF_i V_{mstd}} \qquad \text{Eq. 23-2}$$

9.4 Recovery Standard Response Factor.

$$RRF_{rs} = \frac{A_{ci}^* m_{rs}}{A_{rs} m_{ci}^*} \qquad \text{Eq. 23-3}$$

9.5 Recovery of Internal Standards (R*).

$$R^* = \frac{A_i^* m_{rs}}{A_{rs} RF_{rs} m_i^*} \times 100\% \qquad \text{Eq. 23-4}$$

9.6 Surrogate Compound Response Factor.

$$RRF_s = \frac{A_{ci}^* m_s}{A_{cis} m_{ci}^*} \qquad \text{Eq. 23-5}$$

9.7 Recovery of Surrogate Compounds (R_s).

$$R_s = \frac{A_s m_i^*}{A_i^* RRF_s m_s} \times 100\% \qquad \text{Eq. 23-6}$$

9.8 Minimum Detectable Limit (MDL).

$$MDL = \frac{2.5\, A_{ai} m_i^*}{A_{ci}^* RRF_i} \qquad \text{Eq. 23-7}$$

9.9 Total Concentration of PCDD's and PCDF's in the Sample.

$$C_{Tr} = \sum_{i=1}^{n} C_i \qquad \text{Eq. 23-8}$$

Any PCDD's or PCDF's that are reported as nondetected (below the MDL) shall be counted as zero for the purpose of calculating the total concentration of PCDD's and PCDF's in the sample.

10. Bibliography

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TABLE 1—COMPOSITION OF THE SAMPLE FORTIFICATION AND RECOVERY STANDARDS SOLUTIONS

Analyte	Concentration (pg/µl)
Internal Standards:	
$^{13}C_{12}$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100
$^{13}C_{12}$-OCDD	100
$^{13}C_{12}$-2,3,7,8-TCDF	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100
Surrogate Standards:	
$^{37}Cl_4$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100
Recovery Standards:	
$^{13}C_{12}$-1,2,3,4-TCDD	500
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	500

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS

Compound	Concentrations (pg/µL)				
	Solution No.				
	1	2	3	4	5
Alternate Standard:					
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	2.5	5	25	250	500

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS—Continued

Compound	Concentrations (pg/μL)				
	Solution No.				
	1	2	3	4	5
Recovery Standards:					
$^{13}C_{12}$-1,2,3,4-TCDD ..	100	100	100	100	100

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS—Continued

Compound	Concentrations (pg/μL)				
	Solution No.				
	1	2	3	4	5
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

TABLE 3—ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HIGH RESOLUTION MASS SPECTROMETRY FOR PCDD'S AND PCDF'S

Descriptor No.	Accurate mass	Ion type	Elemental composition	Analyte
2	292.9825	LOCK	C_7F_{11}	PFK
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M + 2	$C_{12}H_4{}^{35}Cl^{37}O$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M + 2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}ClO_2$	TCDD
	321.8936	M + 2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD (S)
	330.9792	QC	C_7F_{13}	PFK
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9339	M + 2	$^{13}C_{12}H_4{}^{35}Cl^{37}ClO_2$	TCDD (S)
	339.8597	M + 2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PECDF
	341.8567	M + 4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M + 2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M + 4	$^{13}C_{12}H_3{}^{35}Cl^{3537}Cl_2O$	PeCDF (S)
	355.8546	M + 2	$C_{12}H_3{}^{35}Cl_3 37ClO_2$	PeCDD
	357.8516	M + 4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M + 2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M + 4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}\ Cl_2O_2$	PeCDD (S)
	375.8364	M + 2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
	409.7974	M + 2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCPDE
3	373.8208	M + 2	$C_{12}H_2 35Cl_5{}^{37}ClO$	HxCDF
	375.8178	M + 4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M + 2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8157	M + 2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M + 4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	392.9760	LOCK	C_9F_{15}	PFK
	401.8559	M + 2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M + 4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDD (S)
	445.7555	M + 4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	430.9729	QC	C_9F_{17}	PFK
4	407.7818	M + 2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M + 4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8253	M	$^{13}C_{12}H^{35}Cl_7O$	HpCDF (S)
	419.8220	M + 2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF (S)
	423.7766	M + 2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M + 4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M + 2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M + 4	$^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S)
	479.7165	M + 4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCPDE
	430.9729	LOCK	C_9F_{17}	PFK
	441.7428	M + 2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M + 4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M + 2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M + 4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M + 2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M + 4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S)
	513.6775	M + 4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O_2$	DCDPE
	442.9728	QC	$C_{10}F_{17}$	PFK

(a) The following nuclidic masses were used:
H = 1.007825
C = 12.000000
^{13}C = 13.003355
F = 18.9984
O = 15.994915
^{35}Cl = 34.968853
^{37}Cl = 36.965903

S = Labeled Standard
QC = Ion selected for monitoring instrument stability during the GC/MS analysis.

TABLE 4—ACCEPTABLE RANGES FOR ION-ABUNDANCE RATIOS OF PCDD'S AND PCDF'S

No. of chlorine atoms	Ion type	Theoretical ratio	Control limits	
			Lower	Upper
4	M/M + 2	0.77	0.65	0.89
5	M + 2/M + 4	1.55	1.32	1.78
6	M + 2/M + 4	1.24	1.05	1.43
6[a]	M/M + 2	0.51	0.43	0.59
7[b]	M/M + 2	0.44	0.37	0.51
7	M + 2/M + 4	1.04	0.88	1.20
8	M + 2/M + 4	0.89	0.76	1.02

[a] Used only for ^{13}C-HxCDF.
[b] Used only for ^{13}C-HpCDF.

TABLE 5—MINIMUM REQUIREMENTS FOR INITIAL AND DAILY CALIBRATION RESPONSE FACTORS

Compound	Relative response factors	
	Initial calibration RSD	Daily calibration % difference
Unlabeled Analytes:		
2,3,7,8-TCDD	25	25
2,3,7,8-TCDF	25	25
1,2,3,7,8-PeCDD	25	25
1,2,3,7,8-PeCDF	25	25
2,3,4,7,8-PeCDF	25	25
1,2,4,5,7,8-HxCDD	25	25
1,2,3,6,7,8-HxCDD	25	25
1,2,3,7,8,9-HxCDD	25	25
1,2,3,4,7,8-HxCDF	25	25
1,2,3,6,7,8-HxCDF	25	25
1,2,3,7,8,9-HxCDF	25	25
2,3,4,6,7,8-HxCDF	25	25
1,2,3,4,6,7,8-HpCDD	25	25
1,2,3,4,6,7,8-HpCDF	25	25
OCDD	25	25
OCDF	30	30
Internal Standards:		
$^{13}C_{12}$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-1,2,3,7,8-PeCDD	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	30	30
$^{13}C_{12}$-OCDD	30	30
$^{13}C_{12}$-2,3,7,8-TCDF	30	30
$^{13}C_{12}$-1,2,3,7,8-PeCDF	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	30	30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	30	30
Surrogate Standards:		
$^{37}Cl_4$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-2,3,4,7,8-PeCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	25	25
Alternate Standard:		
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	25	25

METHOD 24—DETERMINATION OF VOLATILE MATTER CONTENT, WATER CONTENT, DENSITY, VOLUME SOLIDS, AND WEIGHT SOLIDS OF SURFACE COATINGS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile organic compounds	No CAS Number assigned
Water.	7732–18–5

1.2 Applicability. This method is applicable for the determination of volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or other related surface coatings.

1.3 Precision and Bias. Intra-and inter-laboratory analytical precision statements are presented in section 13.1. No bias has been identified.

2.0 Summary of Method

2.1 Standard methods are used to determine the volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or other related surface coatings.

3.0 Definitions

3.1 *Waterborne coating* means any coating which contains more than 5 percent water by weight in its volatile fraction.

3.2 *Multicomponent coatings* are coatings that are packaged in two or more parts, which are combined before application. Upon combination a coreactant from one part of the coating chemically reacts, at ambient conditions, with a coreactant from another part of the coating.

3.3 *Ultraviolet (UV) radiation-cured coatings* are coatings which contain unreacted monomers that are polymerized by exposure to ultraviolet light.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Components. Several of the compounds that may be contained in the coatings analyzed by this method may be irritating or corrosive to tissues (e.g., heptane) or may be toxic (e.g., benzene, methyl alcohol). Nearly all are fire hazards.

Appropriate precautions can be found in reference documents, such as Reference 3 of section 16.0.

6.0 Equipment and Supplies

The equipment and supplies specified in the ASTM methods listed in sections 6.1 through 6.6 (incorporated by reference—see §60.17 for acceptable versions of the methods) are required:

6.1 ASTM D 1475–60, 80, or 90, Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products.

6.2 ASTM D 2369–81, 87, 90, 92, 93, or 95, Standard Test Method for Volatile Content of Coatings.

6.3 ASTM D 3792–79 or 91, Standard Test Method for Water Content of Water Reducible Paints by Direct Injection into a Gas Chromatograph.

6.4 ASTM D 4017–81, 90, or 96a, Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Titration Method.

6.5 ASTM 4457–85 91, Standard Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph.

6.6 ASTM D 5403–93, Standard Test Methods for Volatile Content of Radiation Curable Materials.

6.7 ASTM D 6419–00, Test Method for Volatile Content of Sheet-Fed and Coldset Web Offset Printing Inks.

7.0 Reagents and Standards

7.1 The reagents and standards specified in the ASTM methods listed in sections 6.1 through 6.6 are required.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Follow the sample collection, preservation, storage, and transport procedures described in Reference 1 of section 16.0.

9.0 Quality Control

9.1 Reproducibility

NOTE: Not applicable to UV radiation-cured coatings). The variety of coatings that may be subject to analysis makes it necessary to verify the ability of the analyst and the analytical procedures to obtain reproducible results for the coatings tested. Verification is accomplished by running duplicate analyses on each sample tested (Sections 11.2 through 11.4) and comparing the results with the intra-laboratory precision statements (Section 13.1) for each parameter.

9.2 Confidence Limits for Waterborne Coatings. Because of the inherent increased imprecision in the determination of the VOC content of waterborne coatings as the weight percent of water increases, measured parameters for waterborne coatings are replaced with appropriate confidence limits (Section 12.6). These confidence limits are based on measured parameters and inter-laboratory precision statements.

10.0 Calibration and Standardization

10.1 Perform the calibration and standardization procedures specified in the ASTM methods listed in sections 6.1 through 6.6.

11.0 Analytical Procedure

Additional guidance can be found in Reference 2 of section 16.0.

11.1 Non Thin-film Ultraviolet Radiation-cured (UV radiation-cured) Coatings.

11.1.1 Volatile Content. Use the procedure in ASTM D 5403 to determine the volatile matter content of the coating except the curing test described in NOTE 2 of ASTM D 5403 is required.

11.1.2 Water Content. To determine water content, follow section 11.3.2.

11.1.3 Coating Density. To determine coating density, follow section 11.3.3.

11.1.4 Solids Content. To determine solids content, follow section 11.3.4.

11.1.5 To determine if a coating or ink can be classified as a thin-film UV cured coating or ink, use the equation in section 12.2. If C is less than 0.2 g and A is greater than or equal to 225 cm^2 (35 in^2) then the coating or ink is considered a thin-film UV radiation-cured coating and ASTM D 5403 is not applicable.

NOTE: As noted in section 1.4 of ASTM D 5403, this method may not be applicable to radiation curable materials wherein the volatile material is water.

11.2 Multi-component Coatings.

11.2.1 Sample Preparation.

11.2.1.1 Prepare about 100 ml of sample by mixing the components in a storage container, such as a glass jar with a screw top or a metal can with a cap. The storage container should be just large enough to hold the mixture. Combine the components (by weight or volume) in the ratio recommended by the manufacturer. Tightly close the container between additions and during mixing to prevent loss of volatile materials. However, most manufacturers mixing instructions are by volume. Because of possible error caused by expansion of the liquid when measuring the volume, it is recommended that the components be combined by weight. When weight is used to combine the components and the manufacturer's recommended ratio is by volume, the density must be determined by section 11.3.3.

11.2.1.2 Immediately after mixing, take aliquots from this 100 ml sample for determination of the total volatile content, water content, and density.

11.2.2 Volatile Content. To determine total volatile content, use the apparatus and

reagents described in ASTM D2369 (incorporated by reference; see §60.17 for the approved versions of the standard), respectively, and use the following procedures:

11.2.2.1 Weigh and record the weight of an aluminum foil weighing dish. Add 3 ±1 ml of suitable solvent as specified in ASTM D2369 to the weighing dish. Using a syringe as specified in ASTM D2369, weigh to 1 mg, by difference, a sample of coating into the weighing dish. For coatings believed to have a volatile content less than 40 weight percent, a suitable size is 0.3 + 0.10 g, but for coatings believed to have a volatile content greater than 40 weight percent, a suitable size is 0.5 ±0.1 g.

NOTE: If the volatile content determined pursuant to section 12.4 is not in the range corresponding to the sample size chosen repeat the test with the appropriate sample size. Add the specimen dropwise, shaking (swirling) the dish to disperse the specimen completely in the solvent. If the material forms a lump that cannot be dispersed, discard the specimen and prepare a new one. Similarly, prepare a duplicate. The sample shall stand for a minimum of 1 hour, but no more than 24 hours prior to being oven cured at 110 ±5 °C (230 ±9 °F) for 1 hour.

11.2.2.2 Heat the aluminum foil dishes containing the dispersed specimens in the forced draft oven for 60 min at 110 ±5 °C (230 ±9 °F). Caution—provide adequate ventilation, consistent with accepted laboratory practice, to prevent solvent vapors from accumulating to a dangerous level.

11.2.2.3 Remove the dishes from the oven, place immediately in a desiccator, cool to ambient temperature, and weigh to within 1 mg.

11.2.2.4 Run analyses in pairs (duplicate sets) for each coating mixture until the criterion in section 11.4 is met. Calculate W_v following Equation 24–2 and record the arithmetic average.

11.2.3 Water Content. To determine water content, follow section 11.3.2.

11.2.4 Coating Density. To determine coating density, follow section 11.3.3.

11.2.5 Solids Content. To determine solids content, follow section 11.3.4.

11.2.6 Exempt Solvent Content. To determine the exempt solvent content, follow section 11.3.5.

NOTE: For all other coatings (*i.e.*, water-or solvent-borne coatings) not covered by multicomponent or UV radiation-cured coatings, analyze as shown below:

11.3 Water-or Solvent-borne coatings.

11.3.1 Volatile Content. Use the procedure in ASTM D 2369 to determine the volatile matter content (may include water) of the coating.

11.3.1.1 Record the following information:

W_1 = weight of dish and sample before heating, g

W_2 = weight of dish and sample after heating, g

W_3 = sample weight, g.

11.3.1.2 Calculate the weight fraction of the volatile matter (W_v) for each analysis as shown in section 12.3.

11.3.1.3 Run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement in section 13.1.

11.3.1.4 Record the arithmetic average (W_v).

11.3.2 Water Content. For waterborne coatings only, determine the weight fraction of water (W_w) using either ASTM D 3792 or ASTM D 4017.

11.3.2.1 Run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement in section 13.1.

11.3.2.2 Record the arithmetic average (w_w).

11.3.3 Coating Density. Determine the density (Dc, kg/l) of the surface coating using the procedure in ASTM D 1475.

11.3.3.1 Run duplicate analyses until each value in a set deviates from the mean of the set by no more than the intra-laboratory precision statement in section 13.1.

11.3.3.2 Record the arithmetic average (D_c).

11.3.4 Solids Content. Determine the volume fraction (V_s) solids of the coating by calculation using the manufacturer's formulation.

11.3.5 Exempt Solvent Content. Determine the weight fraction of exempt solvents (W_E) by using ASTM Method D4457. Run a duplicate set of determinations and record the arithmetic average (W_E).

11.4 Sample Analysis Criteria. For W_v and W_w, run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement for that parameter. For D_c, run duplicate analyses until each value in a set deviates from the mean of the set by no more than the intra-laboratory precision statement. If, after several attempts, it is concluded that the ASTM procedures cannot be used for the specific coating with the established intra-laboratory precision (excluding UV radiation-cured coatings), the U.S. Environmental Protection Agency (EPA) will assume responsibility for providing the necessary procedures for revising the method or precision statements upon written request to: Director, Emissions, Monitoring, and Analysis Division, MD–14, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

12.0 Calculations and Data Analysis

12.1 Nomenclature.

A = Area of substrate, cm^2, (in^2).

C = Amount of coating or ink added to the substrate, g.

D_c = Density of coating or ink, g/cm^3 (g/in^3).

F = Manufacturer's recommended film thickness, cm (in).
W_o = Weight fraction of nonaqueous volatile matter, g/g.
W_s = Weight fraction of solids, g/g.
W_v = Weight fraction of the volatile matter, g/g.
W_w = Weight fraction of the water, g/g.

12.2 To determine if a coating or ink can be classified as a thin-film UV cured coating or ink, use the following equation:

$$C = F A D_c \qquad \text{Eq. 24-1}$$

12.3 Calculate W_v for each analysis as shown below:

$$W_v = \frac{W_1 - W_2}{W_3} \qquad \text{Eq. 24-2}$$

12.4 Nonaqueous Volatile Matter.
12.4.1 Solvent-borne Coatings.

$$W_o = W_v \qquad \text{Eq. 24-3}$$

12.4.2 Waterborne Coatings.

$$W_o = W_v - W_w \qquad \text{Eq. 24-4}$$

12.4.3 Coatings Containing Exempt Solvents.

$$W_o = W_v - W_E - W_w \qquad \text{Eq. 24-5}$$

12.5 Weight Fraction Solids.

$$W_s = 1 - W_v \qquad \text{Eq. 24-6}$$

12.6 Confidence Limit Calculations for Waterborne Coatings. To calculate the lower confidence limit, subtract the appropriate inter-laboratory precision value from the measured mean value for that parameter. To calculate the upper confidence limit, add the appropriate inter-laboratory precision value to the measured mean value for that parameter. For W_v and D_c, use the lower confidence limits; for W_w, use the upper confidence limit. Because W_s is calculated, there is no adjustment for this parameter.

13.0 Method Performance

13.1 Analytical Precision Statements. The intra-and inter-laboratory precision statements are given in Table 24–1 in section 17.0.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as specified in section 6.0, with the addition of the following:

1. Standard Procedure for Collection of Coating and Ink Samples for Analysis by Reference Methods 24 and 24A. EPA–340/1–91–010. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

2. Standard Operating Procedure for Analysis of Coating and Ink Samples by Reference Methods 24 and 24A.

EPA–340/1–91–011. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

3. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 24–1—ANALYTICAL PRECISION STATEMENTS

	Intra-laboratory	Inter-laboratory
Volatile matter content, W_v	±0.015 $\overline{W}_v$	±0.047 $\overline{W}_v$
Water content, W_w	±0.029 $\overline{W}_w$	±0.075 $\overline{W}_w$
Density, D_c	±0.001 kg/l	±0.002 kg/l

METHOD 24A—DETERMINATION OF VOLATILE MATTER CONTENT AND DENSITY OF PUBLICATION ROTOGRAVURE INKS AND RELATED PUBLICATION ROTOGRAVURE COATINGS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile organic compounds (VOC).	No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of the VOC content and density of solvent-borne (solvent-reducible) publication rotogravure inks and related publication rotogravure coatings.

2.0 Summary of Method

2.1 Separate procedures are used to determine the VOC weight fraction and density of the ink or related coating and the density of the solvent in the ink or related coating. The VOC weight fraction is determined by measuring the weight loss of a known sample quantity which has been heated for a specified length of time at a specified temperature. The density of both the ink or related coating and solvent are measured by a standard procedure. From this information, the VOC volume fraction is calculated.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Components. Some of the compounds that may be contained in the inks or related coatings analyzed by this method may be irritating or corrosive to tissues or may be toxic. Nearly all are fire hazards. Appropriate precautions can be found in reference documents, such as Reference 6 of section 16.0.

6.0 Equipment and Supplies

The following equipment and supplies are required for sample analysis:

6.1 Weighing Dishes. Aluminum foil, 58 mm (2.3 in.) in diameter by 18 mm (0.7 in.) high, with a flat bottom. There must be at least three weighing dishes per sample.

6.2 Disposable Syringe. 5 ml.

6.3 Analytical Balance. To measure to within 0.1 mg.

6.4 Oven. Vacuum oven capable of maintaining a temperature of 120 ±2 °C (248 ±4 °F) and an absolute pressure of 510 ±51 mm Hg (20 ±2 in. Hg) for 4 hours. Alternatively, a forced draft oven capable of maintaining a temperature of 120 ±2 °C (248 ±4 °F) for 24 hours.

6.5 The equipment and supplies specified in ASTM D 1475–60, 80, or 90 (incorporated by reference—see §60.17).

7.0 Reagents and Standards

7.1 The reagents and standards specified in ASTM D 1475–60, 80, or 90 are required.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Follow the sample collection, preservation, storage, and transport procedures described in Reference 4 of section 16.0.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

Additional guidance can be found in Reference 5 of section 16.0.

11.1 VOC Weight Fraction. Shake or mix the ink or related coating sample thoroughly to assure that all the solids are completely suspended. Label and weigh to the nearest 0.1 mg a weighing dish and record this weight (M_{x1}). Using a 5 ml syringe, without a needle, extract an aliquot from the ink or related coating sample. Weigh the syringe and aliquot to the nearest 0.1 mg and record this weight (M_{cy1}). Transfer 1 to 3 g of the aliquot to the tared weighing dish. Reweigh the syringe and remaining aliquot to the nearest 0.1 mg and record this weight (M_{cy2}). Heat the weighing dish with the transferred aliquot in a vacuum oven at an absolute pressure of 510 ±51 mm Hg (20 ±2 in. Hg) and a temperature of 120 ±2 °C (248 ±4 °F) for 4 hours. Alternatively, heat the weighing dish with the transferred aliquot in a forced draft oven at a temperature of 120 ±2 °C for 24 hours. After the weighing dish has cooled, reweigh it to the nearest 0.1 mg and record the weight (M_{x2}). Repeat this procedure two times for each ink or related coating sample, for a total of three samples.

11.2 Ink or Related Coating Density. Determine the density of the ink or related coating (D_c) according to the procedure outlined in ASTM D 1475. Make a total of three determinations for each ink or related coating sample. Report the ink or related coating density as the arithmetic average (D_c) of the three determinations.

11.3 Solvent Density. Determine the density of the solvent (D_o) according to the procedure outlined in ASTM D 1475. Make a total of three determinations for each ink or related coating sample. Report the solvent density as the arithmetic average (D_o) of the three determinations.

12.0 Calculations and Data Analysis

12.1 VOC Weight Fraction. For each determination, calculate the volatile organic content weight fraction (W_o) using the following equation:

$$W_o = \frac{M_{x1} + M_{cy1} - M_{cy2} - M_{x2}}{M_{cy1} - M_{cy2}} \qquad \text{Eq. 24A-1}$$

Make a total of three determinations. Report the VOC weight fraction as the arithmetic average ($\bar{W}_o$) of the three determinations.

12.2 VOC Volume Fraction. Calculate the volume fraction volatile organic content (V_o) using the following equation:

$$V_o = \frac{\overline{W}_o \overline{D}_c}{\overline{D}_o} \qquad \text{Eq. 24A-2}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products. ASTM Designation D 1475.

2. Teleconversation. Wright, Chuck, Inmont Corporation with Reich, R., A., Radian Corporation. September 25, 1979, Gravure Ink Analysis.

3. Teleconversation. Oppenheimer, Robert, Gravure Research Institute with Burt, Rick, Radian Corporation, November 5, 1979, Gravure Ink Analysis.

4. Standard Procedure for Collection of Coating and Ink Samples for Analysis by Reference Methods 24 and 24A. EPA–340/1–91–010. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

5. Standard Operating Procedure for Analysis of Coating and Ink Samples by Reference Methods 24 and 24A. EPA–340/1–91–011. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

6. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

Method 25—Determination of Total Gaseous Nonmethane Organic Emissions as Carbon

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total gaseous nonmethane organic compounds (TGNMO)	N/A	Dependent upon analytical equipment.

1.2 Applicability.

1.2.1 This method is applicable for the determination of volatile organic compounds (VOC) (measured as total gaseous nonmethane organics (TGNMO) and reported as carbon) in stationary source emissions. This method is not applicable for the determination of organic particulate matter.

1.2.2 This method is not the only method that applies to the measurement of VOC. Costs, logistics, and other practicalities of source testing may make other test methods more desirable for measuring VOC contents of certain effluent streams. Proper judgment is required in determining the most applicable VOC test method. For example, depending upon the molecular composition of the organics in the effluent stream, a totally automated semicontinuous nonmethane organics (NMO) analyzer interfaced directly to the source may yield accurate results. This approach has the advantage of providing emission data semicontinuously over an extended time period.

1.2.3 Direct measurement of an effluent with a flame ionization detector (FID) analyzer may be appropriate with prior characterization of the gas stream and knowledge that the detector responds predictably to the organic compounds in the stream. If present, methane (CH_4) will, of course, also be measured. The FID can be used under any of the following limited conditions: (1) Where only one compound is known to exist; (2) when the organic compounds consist of only hydrogen and carbon; (3) where the relative percentages of the compounds are known or can be determined, and the FID responses to the compounds are known; (4) where a consistent mixture of the compounds exists before and after emission control and only the relative concentrations are to be assessed; or (5) where the FID can be calibrated against mass standards of the compounds emitted (solvent emissions, for example).

1.2.4 Another example of the use of a direct FID is as a screening method. If there is enough information available to provide a rough estimate of the analyzer accuracy, the FID analyzer can be used to determine the VOC content of an uncharacterized gas stream. With a sufficient buffer to account for possible inaccuracies, the direct FID can be a useful tool to obtain the desired results without costly exact determination.

1.2.5 In situations where a qualitative/quantitative analysis of an effluent stream is desired or required, a gas chromatographic FID system may apply. However, for sources emitting numerous organics, the time and expense of this approach will be formidable.

2.0 Summary of Method

2.1 An emission sample is withdrawn from the stack at a constant rate through a heated filter and a chilled condensate trap by means of an evacuated sample tank. After sampling is completed, the TGNMO are determined by independently analyzing the condensate trap and sample tank fractions and combining the analytical results. The organic content of the condensate trap fraction is determined by oxidizing the NMO to carbon dioxide (CO_2) and quantitatively collecting in the effluent in an evacuated vessel; then a portion of the CO_2 is reduced to CH_4 and measured by an FID. The organic content of the sample tank fraction is measured by injecting a portion of the sample into a gas chromatographic column to separate the NMO from carbon monoxide (CO), CO_2, and CH_4; the NMO are oxidized to CO_2, reduced to CH_4, and measured by an FID. In this manner, the variable response of the FID associated with different types of organics is eliminated.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Carbon Dioxide and Water Vapor. When carbon dioxide (CO_2) and water vapor are present together in the stack, they can produce a positive bias in the sample. The magnitude of the bias depends on the concentrations of CO_2 and water vapor. As a guideline, multiply the CO_2 concentration, expressed as volume percent, times the water vapor concentration. If this product does not exceed 100, the bias can be considered insignificant. For example, the bias is not significant for a source having 10 percent CO_2 and 10 percent water vapor, but it might be significant for a source having 10 percent CO_2 and 20 percent water vapor.

4.2. Particulate Matter. Collection of organic particulate matter in the condensate trap would produce a positive bias. A filter is included in the sampling equipment to minimize this bias.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling system consists of a heated probe, heated filter, condensate trap, flow control system, and sample tank (see Figure 25–1). The TGNMO sampling equipment can be constructed from commercially available components and components fabricated in a machine shop. The following equipment is required:

6.1.1 Heated Probe. 6.4-mm (¼-in.) OD stainless steel tubing with a heating system capable of maintaining a gas temperature at the exit end of at least 129 °C (265 °F). The probe shall be equipped with a temperature sensor at the exit end to monitor the gas temperature. A suitable probe is shown in Figure 25–1. The nozzle is an elbow fitting attached to the front end of the probe while the temperature sensor is inserted in the side arm of a tee fitting attached to the rear of the probe. The probe is wrapped with a suitable length of high temperature heating tape, and then covered with two layers of glass cloth insulation and one layer of aluminum foil or an equivalent wrapping.

NOTE: If it is not possible to use a heating system for safety reasons, an unheated system with an in-stack filter is a suitable alternative.

6.1.2 Filter Holder. 25-mm (15/16-in.) ID Gelman filter holder with 303 stainless steel body and 316 stainless steel support screen with the Viton O-ring replaced by a Teflon O-ring.

6.1.3 Filter Heating System.

6.1.3.1 A metal box consisting of an inner and an outer shell separated by insulating material with a heating element in the inner shell capable of maintaining a gas temperature at the filter of 121 ±3 °C (250 ±5 °F). The heating box shall include temperature sensors to monitor the gas temperature immediately upstream and immediately downstream of the filter.

6.1.3.2 A suitable heating box is shown in Figure 25–2. The outer shell is a metal box that measures 102 mm × 280 mm × 292 mm (4 in. × 11 in. × 11½ in.), while the inner shell is a metal box measuring 76 mm × 229 mm × 241 mm (3 in. × 9 in. × 9½ in.). The inner box is supported by 13-mm (½-in.) phenolic rods. The void space between the boxes is filled with ceramic fiber insulation which is sealed in place by means of a silicon rubber bead around the upper sides of the box. A removable lid made in a similar manner, with a 25-mm (1-in.) gap between the parts is used to cover the heating chamber. The inner box is heated with a 250-watt cartridge heater, shielded by a stainless steel shroud. The heater is regulated by a thermostatic temperature controller which is set to maintain a gas temperature of 121 °C (250 °F) as measured by the temperature sensor upstream of the filter.

NOTE: If it is not possible to use a heating system for safety reasons, an unheated system with an in-stack filter is a suitable alternative.

6.1.4 Condensate Trap. 9.5-mm (⅜-in.) OD 316 stainless steel tubing bent into a U-shape. Exact dimensions are shown in Figure

25–3. The tubing shall be packed with coarse quartz wool, to a density of approximately 0.11 g/cm^3 before bending. While the condensate trap is packed with dry ice in the Dewar, an ice bridge may form between the arms of the condensate trap making it difficult to remove the condensate trap. This problem can be prevented by attaching a steel plate between the arms of the condensate trap in the same plane as the arms to completely fill the intervening space.

6.1.5 Valve. Stainless steel control valve for starting and stopping sample flow.

6.1.6 Metering Valve. Stainless steel valve for regulating the sample flow rate through the sample train.

6.1.7 Rate Meter. Rotameter, or equivalent, capable of measuring sample flow in the range of 60 to 100 cm^3/min (0.13 to 0.21 ft^3/hr).

6.1.8 Sample Tank. Stainless steel or aluminum tank with a minimum volume of 4 liters (0.14 ft^3).

NOTE: Sample volumes greater than 4 liters may be required for sources with low organic concentrations.

6.1.9 Mercury Manometer. U-tube manometer or absolute pressure gauge capable of measuring pressure to within 1 mm Hg in the range of 0 to 900 mm.

6.1.10 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

6.2 Condensate Recovery. The system for the recovery of the organics captured in the condensate trap consists of a heat source, an oxidation catalyst, a nondispersive infrared (NDIR) analyzer, and an intermediate collection vessel (ICV). Figure 25–4 is a schematic of a typical system. The system shall be capable of proper oxidation and recovery, as specified in section 10.1.1. The following major components are required:

6.2.1 Heat Source. Sufficient to heat the condensate trap (including probe) to a temperature of 200 °C (390 °F). A system using both a heat gun and an electric tube furnace is recommended.

6.2.2 Heat Tape. Sufficient to heat the connecting tubing between the water trap and the oxidation catalyst to 100 °C (212 °F).

6.2.3 Oxidation Catalyst. A suitable length of 9.5 mm (3/8-in.) OD Inconel 600 tubing packed with 15 cm (6 in.) of 3.2 mm (3/8-in.) diameter 19 percent chromia on alumina pellets. The catalyst material is packed in the center of the catalyst tube with quartz wool packed on either end to hold it in place.

6.2.4 Water Trap. Leak-proof, capable of removing moisture from the gas stream.

6.2.5 Syringe Port. A 6.4-mm (1/4-in.) OD stainless steel tee fitting with a rubber septum placed in the side arm.

6.2.6 NDIR Detector. Capable of indicating CO_2 concentration in the range of zero to 5 percent, to monitor the progress of combustion of the organic compounds from the condensate trap.

6.2.7 Flow-Control Valve. Stainless steel, to maintain the trap conditioning system near atmospheric pressure.

6.2.8 Intermediate Collection Vessel. Stainless steel or aluminum, equipped with a female quick connect. Tanks with nominal volumes of at least 6 liters (0.2 ft^3) are recommended.

6.2.9 Mercury Manometer. Same as described in section 6.1.9.

6.2.10 Syringe. 10-ml gas-tight glass syringe equipped with an appropriate needle.

6.2.11 Syringes. 10-µl and 50-µl liquid injection syringes.

6.2.12 Liquid Sample Injection Unit. 316 Stainless steel U-tube fitted with an injection septum (see Figure 25–7).

6.3 Analysis.

6.3.1 NMO Analyzer. The NMO analyzer is a gas chromatograph (GC) with backflush capability for NMO analysis and is equipped with an oxidation catalyst, reduction catalyst, and FID. Figures 25–5 and 25–6 are schematics of a typical NMO analyzer. This semicontinuous GC/FID analyzer shall be capable of: (1) Separating CO, CO_2, and CH_4 from NMO, (2) reducing the CO_2 to CH_4 and quantifying as CH_4, and (3) oxidizing the NMO to CO_2, reducing the CO_2 to CH_4 and quantifying as CH_4, according to section 10.1.2. The analyzer consists of the following major components:

6.3.1.1 Oxidation Catalyst. A suitable length of 9.5-mm (3/8-in.) OD Inconel 600 tubing packed with 5.1 cm (2 in.) of 19 percent chromia on 3.2-mm (1/8-in.) alumina pellets. The catalyst material is packed in the center of the tube supported on either side by quartz wool. The catalyst tube must be mounted vertically in a 650 °C (1200 °F) furnace. Longer catalysts mounted horizontally may be used, provided they can meet the specifications of section 10.1.2.1.

6.3.1.2 Reduction Catalyst. A 7.6-cm (3-in.) length of 6.4-mm (1/4-in.) OD Inconel tubing fully packed with 100-mesh pure nickel powder. The catalyst tube must be mounted vertically in a 400 °C (750 °F) furnace.

6.3.1.3 Separation Column(s). A 30-cm (1-ft) length of 3.2-mm (1/8-in.) OD stainless steel tubing packed with 60/80 mesh Unibeads 1S followed by a 61-cm (2-ft) length of 3.2-mm (1/8-in.) OD stainless steel tubing packed with 60/80 mesh Carbosieve G. The Carbosieve and Unibeads columns must be baked separately at 200 °C (390 °F) with carrier gas flowing through them for 24 hours before initial use.

6.3.1.4 Sample Injection System. A single 10-port GC sample injection valve or a group of valves with sufficient ports fitted with a sample loop properly sized to interface with the NMO analyzer (1-cc loop recommended).

6.3.1.5 FID. An FID meeting the following specifications is required:

6.3.1.5.1 Linearity. A linear response (±5 percent) over the operating range as demonstrated by the procedures established in section 10.1.2.3.

6.3.1.5.2 Range. A full scale range of 10 to 50,000 ppm CH_4. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.3.1.6 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the analytical results.

6.3.2 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm Hg.

6.3.3 Temperature Sensor. Capable of measuring the laboratory temperature within 1 °C (2 °F).

6.3.4 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

7.0 Reagents and Standards

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Dry Ice. Solid CO2, crushed.

7.1.2 Coarse Quartz Wool. 8 to 15 um.

7.1.3 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Method D2986–71, 78, or 95a (incorporated by reference—see §60.17). Test data from the supplier's quality control program are sufficient for this purpose.

7.2 NMO Analysis. The following gases are required for NMO analysis:

7.2.1 Carrier Gases. Helium (He) and oxygen (O_2) containing less than 1 ppm CO_2 and less than 0.1 ppm hydrocarbon.

7.2.2 Fuel Gas. Hydrogen (H_2), at least 99.999 percent pure.

7.2.3 Combustion Gas. Either air (less than 0.1 ppm total hydrocarbon content) or O_2 (purity 99.99 percent or greater), as required by the detector.

7.3 Condensate Analysis. The following are required for condensate analysis:

7.3.1 Gases. Containing less than 1 ppm carbon.

7.3.1.1 Air.

7.3.1.2 Oxygen.

7.3.2 Liquids. To conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society.

7.3.2.1 Hexane.

7.3.2.2 Decane.

7.4 Calibration. For all calibration gases, the manufacturer must recommend a maximum shelf life for each cylinder (i.e., the length of time the gas concentration is not expected to change more than ±5 percent from its certified value). The date of gas cylinder preparation, certified organic concentration, and recommended maximum shelf life must be affixed to each cylinder before shipment from the gas manufacturer to the buyer. The following calibration gases are required:

7.4.1 Oxidation Catalyst Efficiency Check Calibration Gas. Gas mixture standard with nominal concentration of 1 percent methane in air.

7.4.2 FID Linearity and NMO Calibration Gases. Three gas mixture standards with nominal propane concentrations of 20 ppm, 200 ppm, and 3000 ppm, in air.

7.4.3 CO_2 Calibration Gases. Three gas mixture standards with nominal CO_2 concentrations of 50 ppm, 500 ppm, and 1 percent, in air.

NOTE: Total NMO less than 1 ppm required for 1 percent mixture.

7.4.4 NMO Analyzer System Check Calibration Gases. Four calibration gases are needed as follows:

7.4.4.1 Propane Mixture. Gas mixture standard containing (nominal) 50 ppm CO, 50 ppm CH_4, 1 percent CO_2, and 20 ppm C_3H_8, prepared in air.

7.4.4.2 Hexane. Gas mixture standard containing (nominal) 50 ppm hexane in air.

7.4.4.3 Toluene. Gas mixture standard containing (nominal) 20 ppm toluene in air.

7.4.4.4 Methanol. Gas mixture standard containing (nominal) 100 ppm methanol in air.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Sampling Equipment Preparation.

8.1.1 Condensate Trap Cleaning. Before its initial use and after each use, a condensate trap should be thoroughly cleaned and checked to ensure that it is not contaminated. Both cleaning and checking can be accomplished by installing the trap in the condensate recovery system and treating it as if it were a sample. The trap should be heated as described in section 11.1.3. A trap may be considered clean when the CO_2 concentration in its effluent gas drops below 10 ppm. This check is optional for traps that most recently have been used to collect samples which were then recovered according to the procedure in section 11.1.3.

8.1.2 Sample Tank Evacuation and Leak-Check. Evacuate the sample tank to 10 mm Hg absolute pressure or less. Then close the sample tank valve, and allow the tank to sit for 60 minutes. The tank is acceptable if a change in tank vacuum of less than 1 mm Hg is noted. The evacuation and leak-check may be conducted either in the laboratory or the field.

8.1.3 Sampling Train Assembly. Just before assembly, measure the tank vacuum using a mercury manometer. Record this vacuum, the ambient temperature, and the barometric pressure at this time. Close the sample tank valve and assemble the sampling

system as shown in Figure 25–1. Immerse the condensate trap body in dry ice at least 30 minutes before commencing sampling to improve collection efficiency. The point where the inlet tube joins the trap body should be 2.5 to 5 cm (1 to 2 in.) above the top of the dry ice.

8.1.4 Pretest Leak-Check. A pretest leak-check is required. Calculate or measure the approximate volume of the sampling train from the probe tip to the sample tank valve. After assembling the sampling train, plug the probe tip, and make certain that the sample tank valve is closed. Turn on the vacuum pump, and evacuate the sampling system from the probe tip to the sample tank valve to an absolute pressure of 10 mm Hg or less. Close the purge valve, turn off the pump, wait a minimum period of 10 minutes, and recheck the indicated vacuum. Calculate the maximum allowable pressure change based on a leak rate of 1 percent of the sampling rate using Equation 25–1, section 12.2. If the measured pressure change exceeds the allowable, correct the problem and repeat the leak-check before beginning sampling.

8.2 Sample Collection.

8.2.1 Unplug the probe tip, and place the probe into the stack such that the probe is perpendicular to the duct or stack axis; locate the probe tip at a single preselected point of average velocity facing away from the direction of gas flow. For stacks having a negative static pressure, seal the sample port sufficiently to prevent air in-leakage around the probe. Set the probe temperature controller to 129 °C (265 °F) and the filter temperature controller to 121 °C (250 °F). Allow the probe and filter to heat for about 30 minutes before purging the sample train.

8.2.2 Close the sample valve, open the purge valve, and start the vacuum pump. Set the flow rate between 60 and 100 cm^3/min (0.13 and 0.21 ft^3/hr), and purge the train with stack gas for at least 10 minutes.

8.2.3 When the temperatures at the exit ends of the probe and filter are within the corresponding specified ranges, check the dry ice level around the condensate trap, and add dry ice if necessary. Record the clock time. To begin sampling, close the purge valve and stop the pump. Open the sample valve and the sample tank valve. Using the flow control valve, set the flow through the sample train to the proper rate. Adjust the flow rate as necessary to maintain a constant rate (±10 percent) throughout the duration of the sampling period. Record the sample tank vacuum and flowmeter setting at 5-minute intervals. (See Figure 25–8.) Select a total sample time greater than or equal to the minimum sampling time specified in the applicable subpart of the regulations; end the sampling when this time period is reached or when a constant flow rate can no longer be maintained because of reduced sample tank vacuum.

NOTE: If sampling had to be stopped before obtaining the minimum sampling time (specified in the applicable subpart) because a constant flow rate could not be maintained, proceed as follows: After closing the sample tank valve, remove the used sample tank from the sampling train (without disconnecting other portions of the sampling train). Take another evacuated and leak-checked sample tank, measure and record the tank vacuum, and attach the new tank to the sampling train. After the new tank is attached to the sample train, proceed with the sampling until the required minimum sampling time has been exceeded.

8.3 Sample Recovery. After sampling is completed, close the flow control valve, and record the final tank vacuum; then record the tank temperature and barometric pressure. Close the sample tank valve, and disconnect the sample tank from the sample system. Disconnect the condensate trap at the inlet to the rate meter, and tightly seal both ends of the condensate trap. Do not include the probe from the stack to the filter as part of the condensate sample.

8.4 Sample Storage and Transport. Keep the trap packed in dry ice until the samples are returned to the laboratory for analysis. Ensure that run numbers are identified on the condensate trap and the sample tank(s).

9.0 Quality Control

Section	Quality control measure	Effect
10.1.1	Initial performance check of condensate recovery apparatus.	Ensure acceptable condensate recovery efficiency.
10.1.2, 10.2	NMO analyzer initial and daily performance checks.	Ensure precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Initial Performance Checks.

10.1.1 Condensate Recovery Apparatus. Perform these tests before the system is first placed in operation, after any shutdown of 6 months or more, and after any major modification of the system, or at the frequency recommended by the manufacturer.

10.1.1.1 Carrier Gas and Auxiliary O_2 Blank Check. Analyze each new tank of carrier gas or auxiliary O_2 with the NMO analyzer to

check for contamination. Treat the gas cylinders as noncondensible gas samples, and analyze according to the procedure in section 11.2.3. Add together any measured CH_4, CO, CO_2, or NMO. The total concentration must be less than 5 ppm.

10.1.1.2 Oxidation Catalyst Efficiency Check.

10.1.1.2.1 With a clean condensate trap installed in the recovery system or a ⅛″ stainless steel connector tube, replace the carrier gas cylinder with the high level methane standard gas cylinder (Section 7.4.1). Set the four-port valve to the recovery position, and attach an ICV to the recovery system. With the sample recovery valve in vent position and the flow-control and ICV valves fully open, evacuate the manometer or gauge, the connecting tubing, and the ICV to 10 mm Hg absolute pressure. Close the flow-control and vacuum pump valves.

10.1.1.2.2 After the NDIR response has stabilized, switch the sample recovery valve from vent to collect. When the manometer or pressure gauge begins to register a slight positive pressure, open the flow-control valve. Keep the flow adjusted such that the pressure in the system is maintained within 10 percent of atmospheric pressure. Continue collecting the sample in a normal manner until the ICV is filled to a nominal gauge pressure of 300 mm Hg. Close the ICV valve, and remove the ICV from the system. Place the sample recovery valve in the vent position, and return the recovery system to its normal carrier gas and normal operating conditions. Analyze the ICV for CO_2 using the NMO analyzer; the catalyst efficiency is acceptable if the CO_2 concentration is within 2 percent of the methane standard concentration.

10.1.1.3 System Performance Check. Construct a liquid sample injection unit similar in design to the unit shown in Figure 25–7. Insert this unit into the condensate recovery and conditioning system in place of a condensate trap, and set the carrier gas and auxiliary O_2 flow rates to normal operating levels. Attach an evacuated ICV to the system, and switch from system vent to collect. With the carrier gas routed through the injection unit and the oxidation catalyst, inject a liquid sample (see sections 10.1.1.3.1 to 10.1.1.3.4) into the injection port. Operate the trap recovery system as described in section 11.1.3. Measure the final ICV pressure, and then analyze the vessel to determine the CO_2 concentration. For each injection, calculate the percent recovery according to section 12.7. Calculate the relative standard deviation for each set of triplicate injections according to section 12.8. The performance test is acceptable if the average percent recovery is 100 ±5 percent and the relative standard deviation is less than 2 percent for each set of triplicate injections.

10.1.1.3.1 50 µl hexane.

10.1.1.3.2 10 µl hexane.

10.1.1.3.3 50 µl decane.

10.1.1.3.4 10 µl decane.

10.1.2 NMO Analyzer. Perform these tests before the system is first placed in operation, after any shutdown longer than 6 months, and after any major modification of the system.

10.1.2.1 Oxidation Catalyst Efficiency Check. Turn off or bypass the NMO analyzer reduction catalyst. Make triplicate injections of the high level methane standard (Section 7.4.1). The oxidation catalyst operation is acceptable if the FID response is less than 1 percent of the injected methane concentration.

10.1.2.2 Reduction Catalyst Efficiency Check. With the oxidation catalyst unheated or bypassed and the heated reduction catalyst bypassed, make triplicate injections of the high level methane standard (Section 7.4.1). Repeat this procedure with both catalysts operative. The reduction catalyst operation is acceptable if the responses under both conditions agree within 5 percent of their average.

10.1.2.3 NMO Analyzer Linearity Check Calibration. While operating both the oxidation and reduction catalysts, conduct a linearity check of the analyzer using the propane standards specified in section 7.4.2. Make triplicate injections of each calibration gas. For each gas (*i.e.*, each set of triplicate injections), calculate the average response factor (area/ppm C) for each gas, as well as and the relative standard deviation (according to section 12.8). Then calculate the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within 2.5 percent of the overall mean value and if the relative standard deviation gas is less than 2 percent of the overall mean value. Record the overall mean of the propane response factor values as the NMO calibration response factor (RF_{NMO}). Repeat the linearity check using the CO_2 standards specified in section 7.4.3. Make triplicate injections of each gas, and then calculate the average response factor (area/ppm C) for each gas, as well as the overall mean of the response factor values. Record the overall mean of the response factor values as the CO_2 calibration response factor (RF_{CO2}). The RF_{CO2} must be within 10 percent of the RF_{NMO}.

10.1.2.4 System Performance Check. Check the column separation and overall performance of the analyzer by making triplicate injections of the calibration gases listed in section 7.4.4. The analyzer performance is acceptable if the measured NMO value for each gas (average of triplicate injections) is within 5 percent of the expected value.

10.2 NMO Analyzer Daily Calibration. The following calibration procedures shall be performed before and immediately after the

analysis of each set of samples, or on a daily basis, whichever is more stringent:

10.2.1 CO_2 Response Factor. Inject triplicate samples of the high level CO_2 calibration gas (Section 7.4.3), and calculate the average response factor. The system operation is adequate if the calculated response factor is within 5 percent of the RF_{CO2} calculated during the initial performance test (Section 10.1.2.3). Use the daily response factor (DRF_{CO2}) for analyzer calibration and the calculation of measured CO_2 concentrations in the ICV samples.

10.2.2 NMO Response Factors. Inject triplicate samples of the mixed propane calibration cylinder gas (Section 7.4.4.1), and calculate the average NMO response factor. The system operation is adequate if the calculated response factor is within 10 percent of the RF_{NMO} calculated during the initial performance test (Section 10.1.2.4). Use the daily response factor (DRF_{NMO}) for analyzer calibration and calculation of NMO concentrations in the sample tanks.

10.3 Sample Tank and ICV Volume. The volume of the gas sampling tanks used must be determined. Determine the tank and ICV volumes by weighing them empty and then filled with deionized distilled water; weigh to the nearest 5 g, and record the results. Alternatively, measure the volume of water used to fill them to the nearest 5 ml.

11.0 Analytical Procedure

11.1 Condensate Recovery. See Figure 25–9. Set the carrier gas flow rate, and heat the catalyst to its operating temperature to condition the apparatus.

11.1.1 Daily Performance Checks. Each day before analyzing any samples, perform the following tests:

11.1.1.1 Leak-Check. With the carrier gas inlets and the sample recovery valve closed, install a clean condensate trap in the system, and evacuate the system to 10 mm Hg absolute pressure or less. Monitor the system pressure for 10 minutes. The system is acceptable if the pressure change is less than 2 mm Hg.

11.1.1.2 System Background Test. Adjust the carrier gas and auxiliary oxygen flow rate to their normal values of 100 cc/min and 150 cc/min, respectively, with the sample recovery valve in vent position. Using a 10-ml syringe, withdraw a sample from the system effluent through the syringe port. Inject this sample into the NMO analyzer, and measure the CO_2 content. The system background is acceptable if the CO_2 concentration is less than 10 ppm.

11.1.1.3 Oxidation Catalyst Efficiency Check. Conduct a catalyst efficiency test as specified in section 10.1.1.2. If the criterion of this test cannot be met, make the necessary repairs to the system before proceeding.

11.1.2 Condensate Trap CO_2 Purge and Sample Tank Pressurization.

11.1.2.1 After sampling is completed, the condensate trap will contain condensed water and organics and a small volume of sampled gas. This gas from the stack may contain a significant amount of CO_2 which must be removed from the condensate trap before the sample is recovered. This is accomplished by purging the condensate trap with zero air and collecting the purged gas in the original sample tank.

11.1.2.2 Begin with the sample tank and condensate trap from the test run to be analyzed. Set the four-port valve of the condensate recovery system in the CO_2 purge position as shown in Figure 25–9. With the sample tank valve closed, attach the sample tank to the sample recovery system. With the sample recovery valve in the vent position and the flow control valve fully open, evacuate the manometer or pressure gauge to the vacuum of the sample tank. Next, close the vacuum pump valve, open the sample tank valve, and record the tank pressure.

11.1.2.3 Attach the dry ice-cooled condensate trap to the recovery system, and initiate the purge by switching the sample recovery valve from vent to collect position. Adjust the flow control valve to maintain atmospheric pressure in the recovery system. Continue the purge until the CO_2 concentration of the trap effluent is less than 5 ppm. CO_2 concentration in the trap effluent should be measured by extracting syringe samples from the recovery system and analyzing the samples with the NMO analyzer. This procedure should be used only after the NDIR response has reached a minimum level. Using a 10-ml syringe, extract a sample from the syringe port prior to the NDIR, and inject this sample into the NMO analyzer.

11.1.2.4 After the completion of the CO_2 purge, use the carrier gas bypass valve to pressurize the sample tank to approximately 1,060 mm Hg absolute pressure with zero air.

11.1.3 Recovery of the Condensate Trap Sample (See Figure 25–10).

11.1.3.1 Attach the ICV to the sample recovery system. With the sample recovery valve in a closed position, between vent and collect, and the flow control and ICV valves fully open, evacuate the manometer or gauge, the connecting tubing, and the ICV to 10 mm Hg absolute pressure. Close the flow-control and vacuum pump valves.

11.1.3.2 Begin auxiliary oxygen flow to the oxidation catalyst at a rate of 150 cc/min, then switch the four-way valve to the trap recovery position and the sample recovery valve to collect position. The system should now be set up to operate as indicated in Figure 25–10. After the manometer or pressure gauge begins to register a slight positive pressure, open the flow control valve. Adjust the flow-control valve to maintain atmospheric pressure in the system within 10 percent.

11.1.3.3 Remove the condensate trap from the dry ice, and allow it to warm to ambient temperature while monitoring the NDIR response. If, after 5 minutes, the CO_2 concentration of the catalyst effluent is below 10,000 ppm, discontinue the auxiliary oxygen flow to the oxidation catalyst. Begin heating the trap by placing it in a furnace preheated to 200 °C (390 °F). Once heating has begun, carefully monitor the NDIR response to ensure that the catalyst effluent concentration does not exceed 50,000 ppm. Whenever the CO_2 concentration exceeds 50,000 ppm, supply auxiliary oxygen to the catalyst at the rate of 150 cc/min. Begin heating the tubing that connected the heated sample box to the condensate trap only after the CO_2 concentration falls below 10,000 ppm. This tubing may be heated in the same oven as the condensate trap or with an auxiliary heat source such as a heat gun. Heating temperature must not exceed 200 °C (390 °F). If a heat gun is used, heat the tubing slowly along its entire length from the upstream end to the downstream end, and repeat the pattern for a total of three times. Continue the recovery until the CO_2 concentration drops to less than 10 ppm as determined by syringe injection as described under the condensate trap CO_2 purge procedure (Section 11.1.2).

11.1.3.4 After the sample recovery is completed, use the carrier gas bypass valve to pressurize the ICV to approximately 1060 mm Hg absolute pressure with zero air.

11.2 Analysis. Once the initial performance test of the NMO analyzer has been successfully completed (see section 10.1.2) and the daily CO_2 and NMO response factors have been determined (see section 10.2), proceed with sample analysis as follows:

11.2.1 Operating Conditions. The carrier gas flow rate is 29.5 cc/min He and 2.2 cc/min O_2. The column oven is heated to 85 °C (185 °F). The order of elution for the sample from the column is CO, CH_4, CO_2, and NMO.

11.2.2 Analysis of Recovered Condensate Sample. Purge the sample loop with sample, and then inject the sample. Under the specified operating conditions, the CO_2 in the sample will elute in approximately 100 seconds. As soon as the detector response returns to baseline following the CO_2 peak, switch the carrier gas flow to backflush, and raise the column oven temperature to 195 °C (380 °F) as rapidly as possible. A rate of 30 °C/min (90 °F) has been shown to be adequate. Record the value obtained for the condensible organic material (C_{cm}) measured as CO_2 and any measured NMO. Return the column oven temperature to 85 °C (185 °F) in preparation for the next analysis. Analyze each sample in triplicate, and report the average C_{cm}.

11.2.3 Analysis of Sample Tank. Perform the analysis as described in section 11.2.2, but record only the value measured for NMO (C_{tm}).

12.0 Data Analysis and Calculations

Carry out the calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculations. All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge or manometer pressure.

12.1 Nomenclature.

C = TGNMO concentration of the effluent, ppm C equivalent.
C_c = Calculated condensible organic (condensate trap) concentration of the effluent, ppm C equivalent.
C_{cm} = Measured concentration (NMO analyzer) for the condensate trap ICV, ppm CO_2.
C_t = Calculated noncondensible organic concentration (sample tank) of the effluent, ppm C equivalent.
C_{tm} = Measured concentration (NMO analyzer) for the sample tank, ppm NMO.
F = Sampling flow rate, cc/min.
L = Volume of liquid injected, µl.
M = Molecular weight of the liquid injected, g/g-mole.
M_c = TGNMO mass concentration of the effluent, mg C/dsm³.
N = Carbon number of the liquid compound injected (N = 12 for decane, N = 6 for hexane).
n = Number of data points.
P_f = Final pressure of the intermediate collection vessel, mm Hg absolute.
P_b = Barometric pressure, cm Hg.
P_{ti} = Gas sample tank pressure before sampling, mm Hg absolute.
P_t = Gas sample tank pressure after sampling, but before pressurizing, mm Hg absolute.
P_{tf} = Final gas sample tank pressure after pressurizing, mm Hg absolute.
q = Total number of analyzer injections of intermediate collection vessel during analysis (where k = injection number, 1 * * * q).
r = Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 * * * r).
r = Density of liquid injected, g/cc.
T_f = Final temperature of intermediate collection vessel, °K.
T_{ti} = Sample tank temperature before sampling, °K.
T_t = Sample tank temperature at completion of sampling, °K.
T_{tf} = Sample tank temperature after pressurizing, °K.
V = Sample tank volume, m³.
V_t = Sample train volume, cc.
V_v = Intermediate collection vessel volume, m³.
V_s = Gas volume sampled, dsm³.
x_i = Individual measurements.
$\bar{x}$ = Mean value.

ΔP = Allowable pressure change, cm Hg.
Θ = Leak-check period, min.

12.2 Allowable Pressure Change. For the pretest leak-check, calculate the allowable pressure change using Equation 25–1:

$$\Delta P = 0.01 \frac{F P_b \Theta}{V_t} \qquad \text{Eq. 25-1}$$

12.3 Sample Volume. For each test run, calculate the gas volume sampled using Equation 25–2:

$$V_s = 0.3857\, V \left(\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}} \right) \qquad \text{Eq. 25-2}$$

12.4 Noncondensible Organics. For each sample tank, determine the concentration of nonmethane organics (ppm C) using Equation 25–3:

$$C_t = \left(\frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}} \right) \left(\frac{1}{r} \sum_{j=1}^{r} C_{tm_j} \right) \qquad \text{Eq. 25-3}$$

12.5 Condensible Organics. For each condensate trap determine the concentration of organics (ppm C) using Equation 25–4:

$$C_c = 0.3857 \frac{V_v P_f}{V_s T_f} \left(\frac{1}{q} \sum_{k=1}^{q} C_{cm_k} \right) \qquad \text{Eq. 25-4}$$

12.6 TGNMO Mass Concentration. Determine the TGNMO mass concentration as carbon for each test run, using Equation 25–5:

$$M_c = 0.4993 \left(C_t + C_c \right) \qquad \text{Eq. 25-5}$$

12.7 Percent Recovery. Calculate the percent recovery for the liquid injections to the condensate recovery and conditioning system using Equation 25–6:

$$\text{Percent Recovery} = K \frac{M V_v P_t C_{cm}}{L P T_f N} \qquad \text{Eq. 25-6}$$

where K = 1.604 (°K)(g-mole)(%)/(mm Hg)(ml)(m^3)(ppm).

12.8 Relative Standard Deviation. Use Equation 25–7 to calculate the relative standard deviation (RSD) of percent recovery and analyzer linearity.

$$RSD = \frac{100}{\bar{x}} \left[\frac{\sum_{i=1}^{n} \left(x_i - \bar{x} \right)^2}{n - 1} \right]^{\frac{1}{2}} \qquad \text{Eq. 25-7}$$

13.0 Method Performance

13.1 Range. The minimum detectable limit of the method has been determined to be 50 parts per million by volume (ppm). No upper limit has been established.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, A.E., S. Witz, and R.D. MacPhee. Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, MA. June 15–20, 1975.) 14 p.

2. Salo, A.E., W.L. Oaks, and R.D. MacPhee. Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, CO. June 9–13, 1974.) 25 p.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

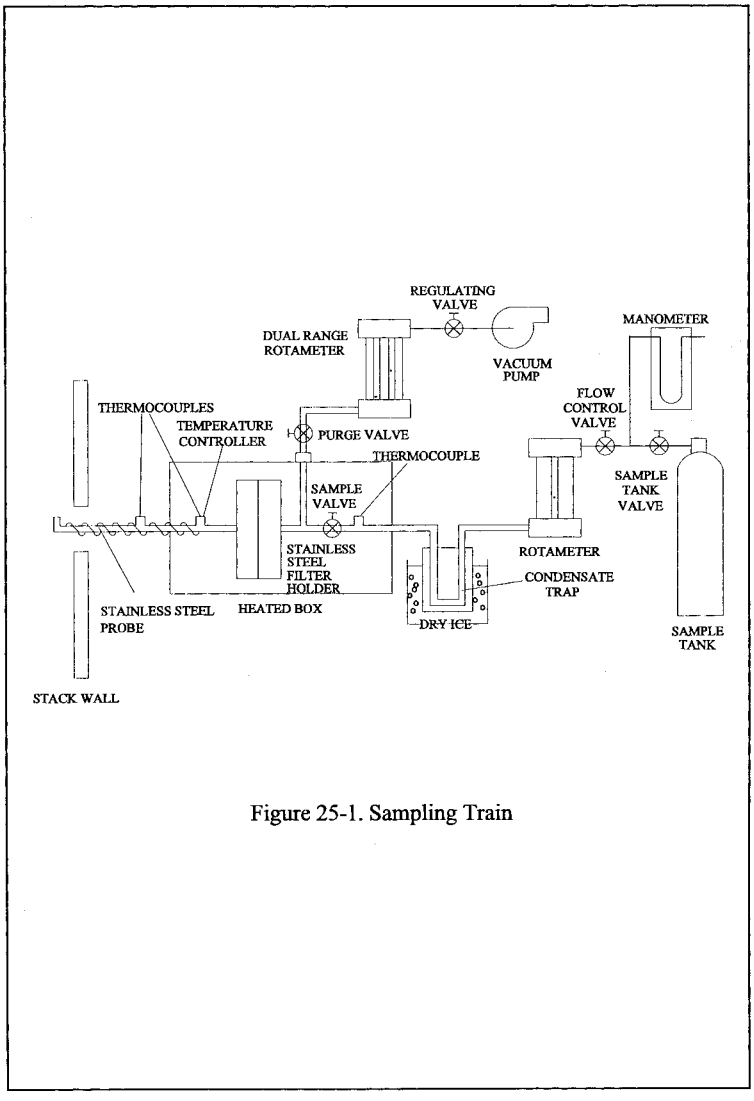


Figure 25-1. Sampling Train

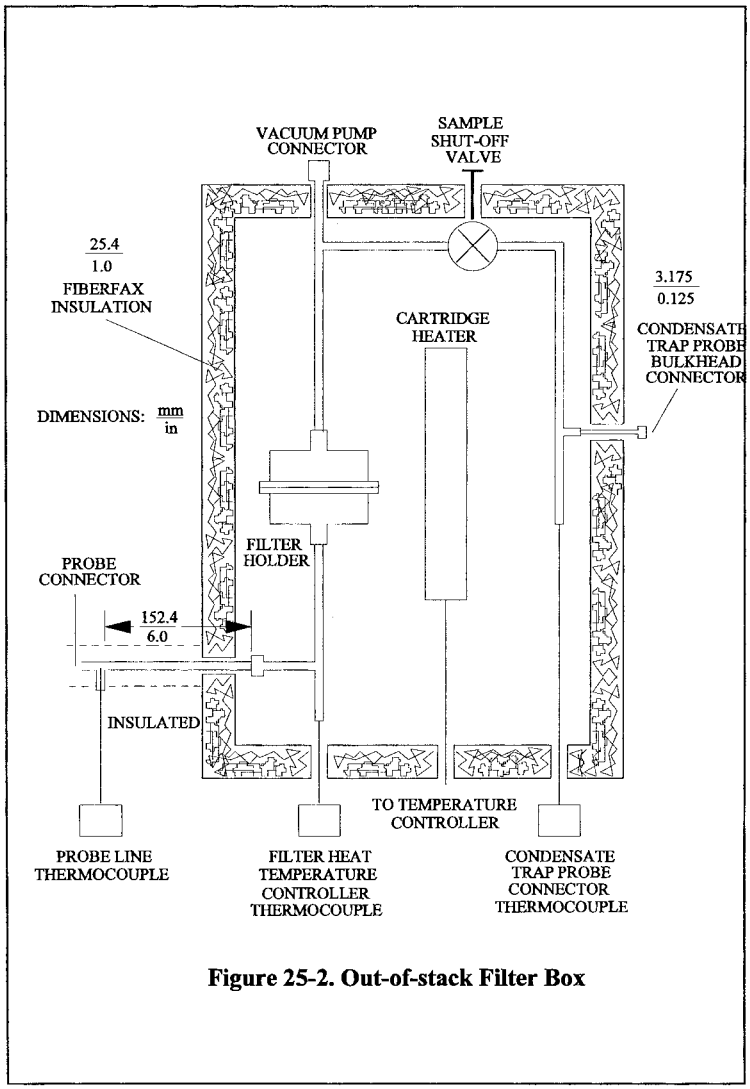


Figure 25-2. Out-of-stack Filter Box

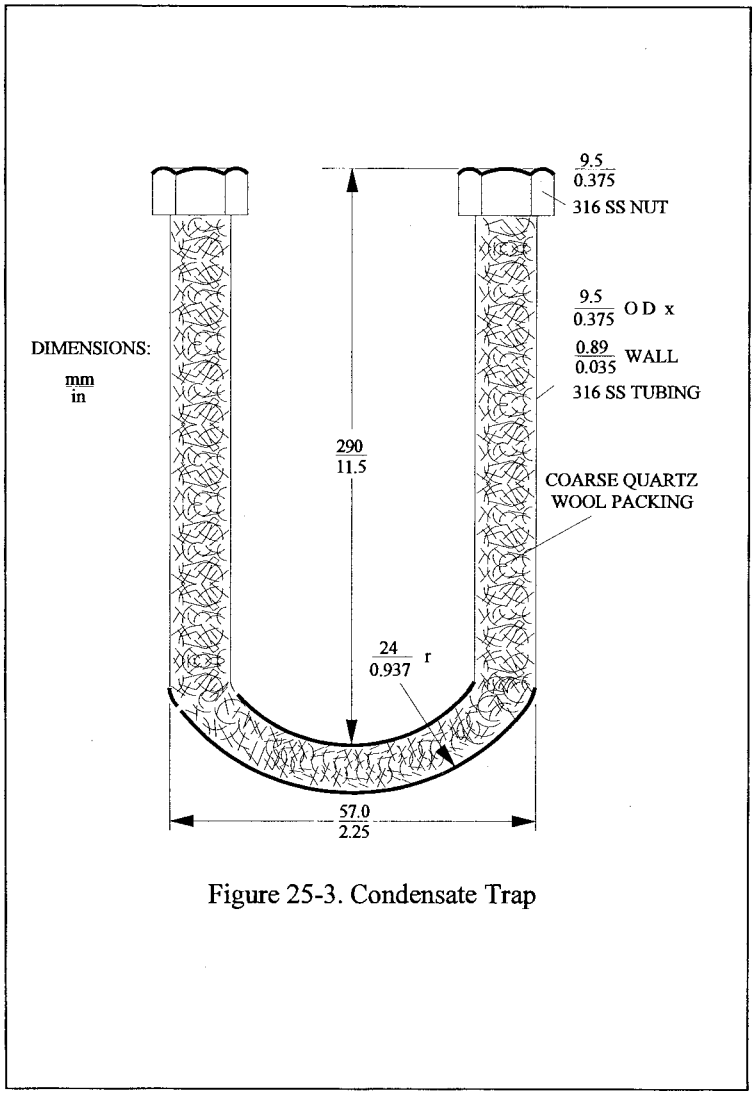


Figure 25-3. Condensate Trap

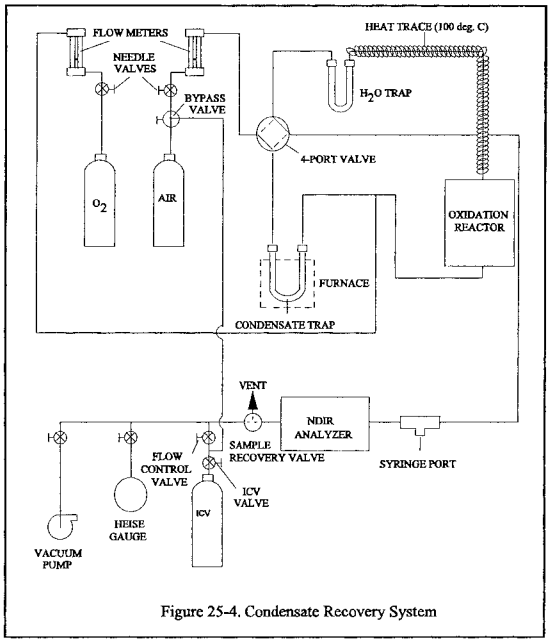


Figure 25-4. Condensate Recovery System

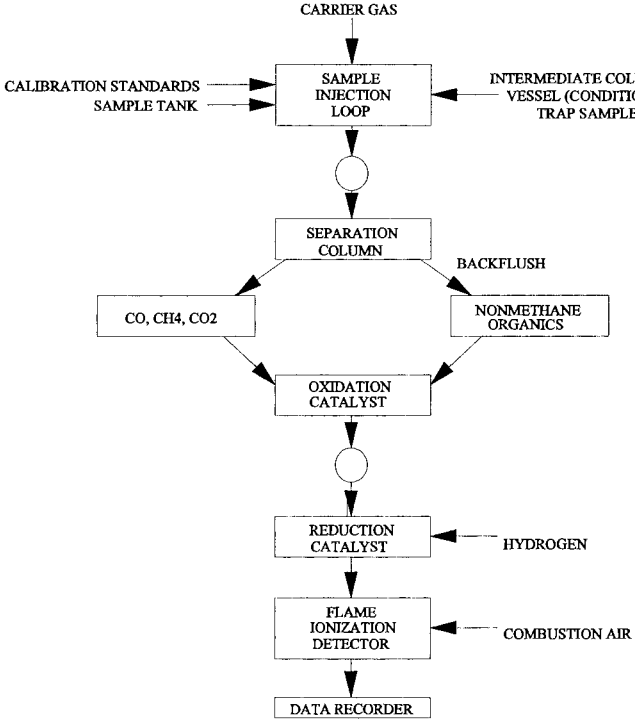


Figure 25-5. Simplified Schematic of Nonmethane Organic (NMO) Analyzer

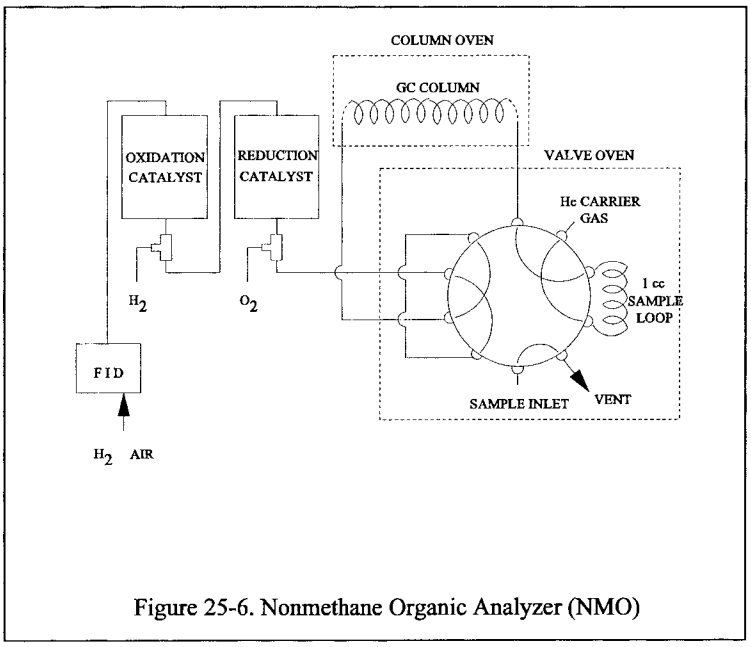


Figure 25-6. Nonmethane Organic Analyzer (NMO)

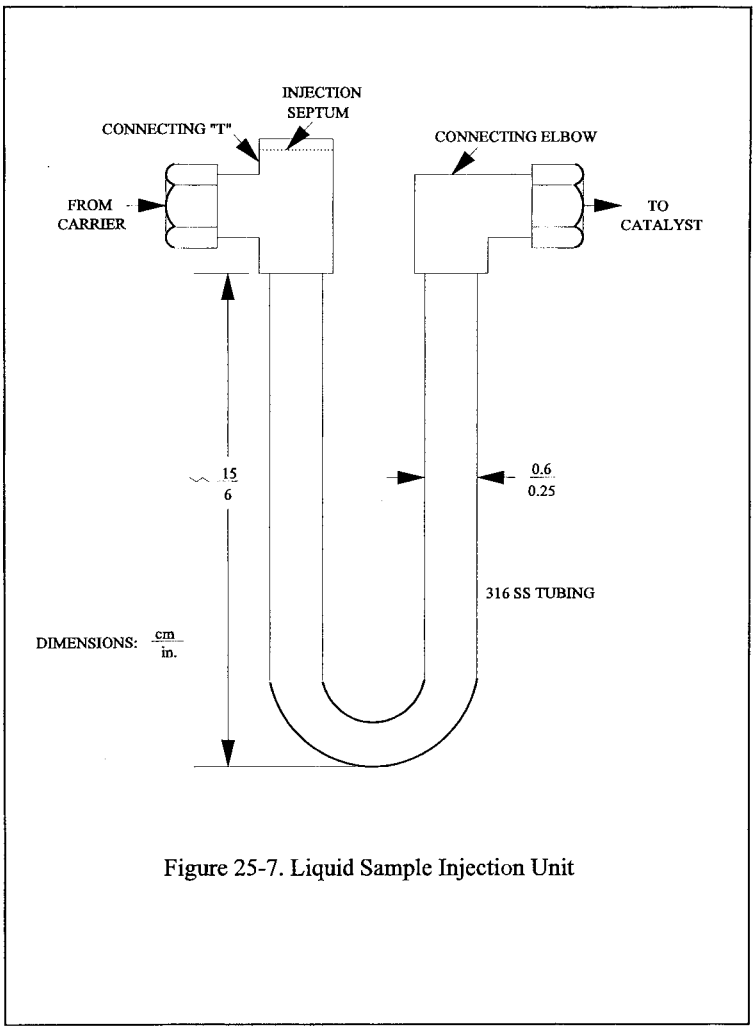


Figure 25-7. Liquid Sample Injection Unit

VOLATILE ORGANIC CARBON

FACILITY _____ SAMPLE LOCATION _____

LOCATION _____ OPERATOR _____

DATE _____ RUN NUMBER _____

TANK NUMBER _____ TRAP NUMBER _____ SAMPLE ID NUMBER _____

TANK VACUUM mm HG	TANK VACUUM cm Hg	BAROMETRIC PRESSURE mm Hg	AMBIENT TEMPERATURE °C
PRETEST (MANOMETER)	(GAUGE)		
POST-TEST (MANOMETER)	(GAUGE)		

LEAK RATE _____ cm Hg / l.0 min

PRETEST _____

TIME CLOCK/SAMPLE	VACUUM cm Hg	FLOWMETER SETTINGS	COMMENTS

Figure 25-8. Example Field Data Form

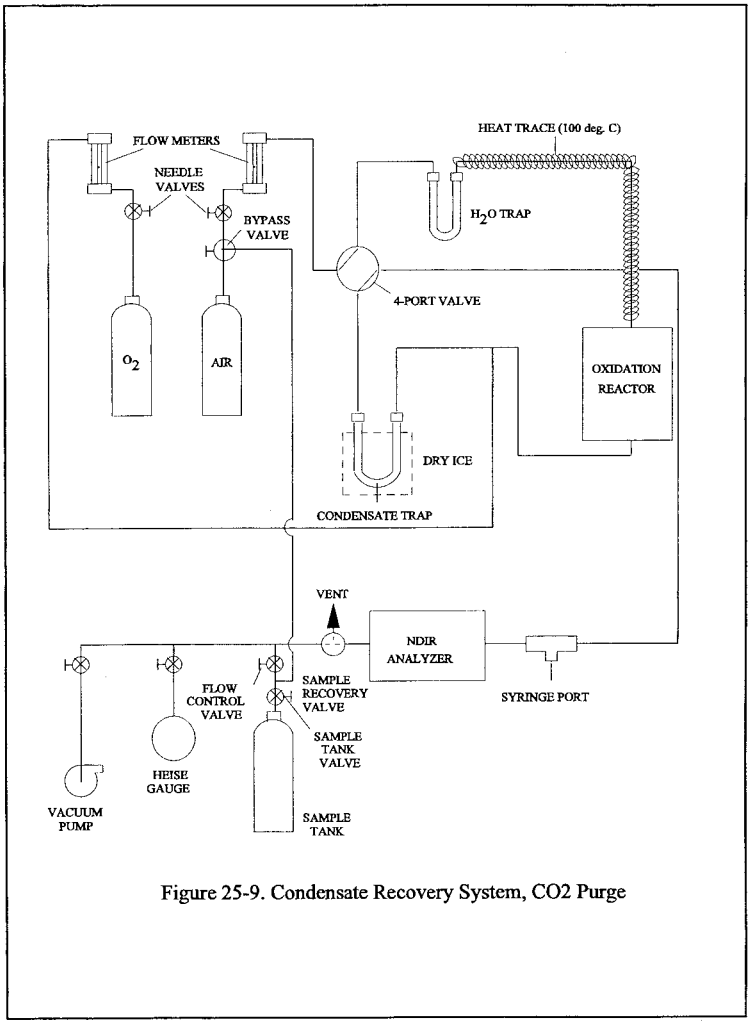


Figure 25-9. Condensate Recovery System, CO2 Purge

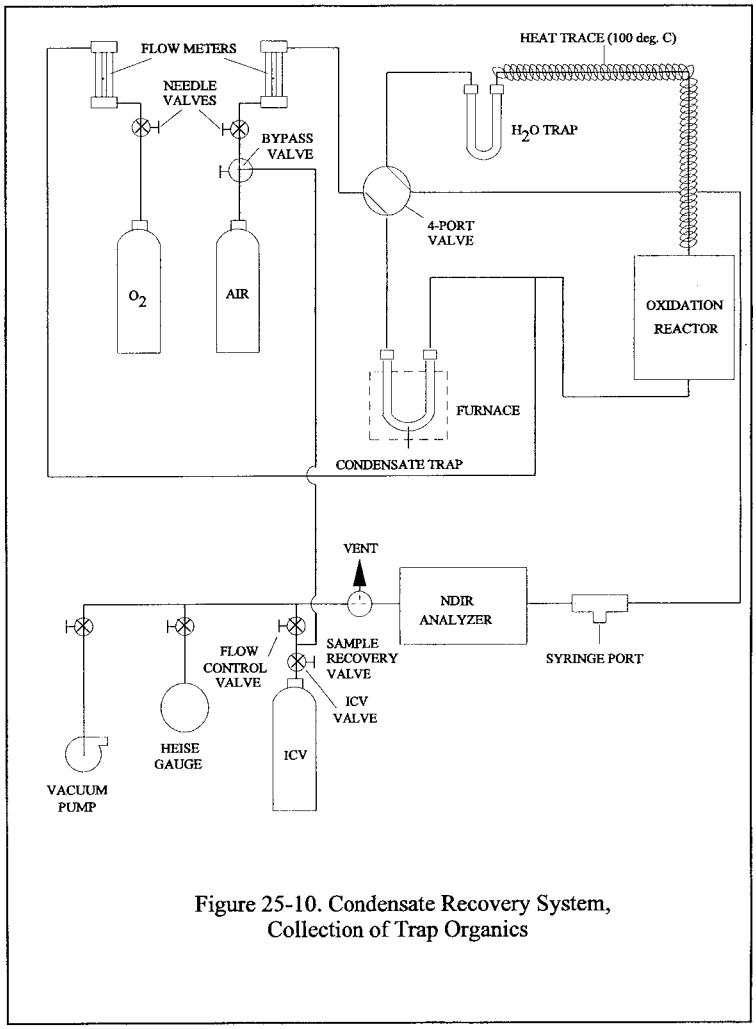


Figure 25-10. Condensate Recovery System, Collection of Trap Organics

METHOD 25A—DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A FLAME IONIZATION ANALYZER

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total Organic Compounds	N/A	<2% of span.

1.2 Applicability. This method is applicable for the determination of total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the source through a heated sample line and glass fiber filter to a flame ionization analyzer (FIA). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

3.0 Definitions

3.1 *Calibration drift* means the difference in the measurement system response to a mid-level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

3.2 *Calibration error* means the difference between the gas concentration indicated by the measurement system and the know concentration of the calibration gas.

3.3 *Calibration gas* means a known concentration of a gas in an appropriate diluent gas.

3.4 *Measurement system* means the total equipment required for the determination of the gas concentration. The system consists of the following major subsystems:

3.4.1 *Sample interface* means that portion of a system used for one or more of the following: sample acquisition, sample transportation, sample conditioning, or protection of the analyzer(s) from the effects of the stack effluent.

3.4.2 *Organic analyzer* means that portion of the measurement system that senses the gas to be measured and generates an output proportional to its concentration.

3.5 *Response time* means the time interval from a step change in pollutant concentration at the inlet to the emission measurement system to the time at which 95 percent of the corresponding final value is reached as displayed on the recorder.

3.6 *Span Value* means the upper limit of a gas concentration measurement range that is specified for affected source categories in the applicable part of the regulations. The span value is established in the applicable regulation and is usually 1.5 to 2.5 times the applicable emission limit. If no span value is provided, use a span value equivalent to 1.5 to 2.5 times the expected concentration. For convenience, the span value should correspond to 100 percent of the recorder scale.

3.7 *Zero drift* means the difference in the measurement system response to a zero level calibration gas before or after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

5.2 Explosive Atmosphere. This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

6.0 Equipment and Supplies

6.1 Measurement System. Any measurement system for total organic concentration that meets the specifications of this method. A schematic of an acceptable measurement system is shown in Figure 25A–1. All sampling components leading to the analyzer shall be heated ≥110 °C (220 °F) throughout the sampling period, unless safety reasons are cited (Section 5.2) The essential components of the measurement system are described below:

6.1.1 Organic Concentration Analyzer. A flame ionization analyzer (FIA) capable of meeting or exceeding the specifications of this method. The flame ionization detector block shall be heated >120 °C (250 °F).

6.1.2 Sample Probe. Stainless steel, or equivalent, three-hole rake type. Sample holes shall be 4 mm (0.16-in.) in diameter or smaller and located at 16.7, 50, and 83.3 percent of the equivalent stack diameter. Alternatively, a single opening probe may be used so that a gas sample is collected from the centrally located 10 percent area of the stack cross-section.

6.1.3 Heated Sample Line. Stainless steel or Teflon'' tubing to transport the sample gas

to the analyzer. The sample line should be heated (≥110 °C) to prevent any condensation.

6.1.4 Calibration Valve Assembly. A three-way valve assembly to direct the zero and calibration gases to the analyzers is recommended. Other methods, such as quick-connect lines, to route calibration gas to the analyzers are applicable.

6.1.5 Particulate Filter. An in-stack or an out-of-stack glass fiber filter is recommended if exhaust gas particulate loading is significant. An out-of-stack filter should be heated to prevent any condensation.

6.1.6 Recorder. A strip-chart recorder, analog computer, or digital recorder for recording measurement data. The minimum data recording requirement is one measurement value per minute.

7.0 Reagents and Standards

7.1 Calibration Gases. The calibration gases for the gas analyzer shall be propane in air or propane in nitrogen. Alternatively, organic compounds other than propane can be used; the appropriate corrections for response factor must be made. Calibration gases shall be prepared in accordance with the procedure listed in Citation 2 of section 16. Additionally, the manufacturer of the cylinder should provide a recommended shelf life for each calibration gas cylinder over which the concentration does not change more than ±2 percent from the certified value. For calibration gas values not generally available (*i.e.*, organics between 1 and 10 percent by volume), alternative methods for preparing calibration gas mixtures, such as dilution systems (Test Method 205, 40 CFR Part 51, Appendix M), may be used with prior approval of the Administrator.

7.1.1 Fuel. A 40 percent H_2/60 percent N_2 gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value.

7.1.2 Zero Gas. High purity air with less than 0.1 part per million by volume (ppmv) of organic material (propane or carbon equivalent) or less than 0.1 percent of the span value, whichever is greater.

7.1.3 Low-level Calibration Gas. An organic calibration gas with a concentration equivalent to 25 to 35 percent of the applicable span value.

7.1.4 Mid-level Calibration Gas. An organic calibration gas with a concentration equivalent to 45 to 55 percent of the applicable span value.

7.1.5 High-level Calibration Gas. An organic calibration gas with a concentration equivalent to 80 to 90 percent of the applicable span value.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Selection of Sampling Site. The location of the sampling site is generally specified by the applicable regulation or purpose of the test (*i.e.*, exhaust stack, inlet line, etc.). The sample port shall be located to meet the testing requirements of Method 1.

8.2 Location of Sample Probe. Install the sample probe so that the probe is centrally located in the stack, pipe, or duct and is sealed tightly at the stack port connection.

8.3 Measurement System Preparation. Prior to the emission test, assemble the measurement system by following the manufacturer's written instructions for preparing sample interface and the organic analyzer. Make the system operable (Section 10.1).

8.4 Calibration Error Test. Immediately prior to the test series (within 2 hours of the start of the test), introduce zero gas and high-level calibration gas at the calibration valve assembly. Adjust the analyzer output to the appropriate levels, if necessary. Calculate the predicted response for the low-level and mid-level gases based on a linear response line between the zero and high-level response. Then introduce low-level and mid-level calibration gases successively to the measurement system. Record the analyzer responses for low-level and mid-level calibration gases and determine the differences between the measurement system responses and the predicted responses. These differences must be less than 5 percent of the respective calibration gas value. If not, the measurement system is not acceptable and must be replaced or repaired prior to testing. No adjustments to the measurement system shall be conducted after the calibration and before the drift check (Section 8.6.2). If adjustments are necessary before the completion of the test series, perform the drift checks prior to the required adjustments and repeat the calibration following the adjustments. If multiple electronic ranges are to be used, each additional range must be checked with a mid-level calibration gas to verify the multiplication factor.

8.5 Response Time Test. Introduce zero gas into the measurement system at the calibration valve assembly. When the system output has stabilized, switch quickly to the high-level calibration gas. Record the time from the concentration change to the measurement system response equivalent to 95 percent of the step change. Repeat the test three times and average the results.

8.6 Emission Measurement Test Procedure.

8.6.1 Organic Measurement. Begin sampling at the start of the test period, recording time and any required process information as appropriate. In particulate, note on the recording chart, periods of process interruption or cyclic operation.

8.6.2 Drift Determination. Immediately following the completion of the test period and hourly during the test period, reintroduce the zero and mid-level calibration gases, one at a time, to the measurement system at the calibration valve assembly. (Make no adjustments to the measurement system until both the zero and calibration drift checks are made.) Record the analyzer response. If the drift values exceed the specified limits, invalidate the test results preceding the check and repeat the test following corrections to the measurement system. Alternatively, recalibrate the test measurement system as in section 8.4 and report the results using both sets of calibration data (i.e., data determined prior to the test period and data determined following the test period).

NOTE: Note on the recording chart periods of process interruption or cyclic operation.

9.0 Quality Control

Method section	Quality control measure	Effect
8.4	Zero and calibration drift tests	Ensures that bias introduced by drift in the measurement system output during the run is no greater than 3 percent of span.

10.0 Calibration and Standardization

10.1 FIA equipment can be calibrated for almost any range of total organic concentrations. For high concentrations of organics (>1.0 percent by volume as propane), modifications to most commonly available analyzers are necessary. One accepted method of equipment modification is to decrease the size of the sample to the analyzer through the use of a smaller diameter sample capillary. Direct and continuous measurement of organic concentration is a necessary consideration when determining any modification design.

11.0 Analytical Procedure

The sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Calculations and Data Analysis

12.1 Determine the average organic concentration in terms of ppmv as propane or other calibration gas. The average shall be determined by integration of the output recording over the period specified in the applicable regulation. If results are required in terms of ppmv as carbon, adjust measured concentrations using Equation 25A–1.

$$C_c = K C_{meas} \qquad \text{Eq. 25A-1}$$

Where:

C_c = Organic concentration as carbon, ppmv.
C_{meas} = Organic concentration as measured, ppmv.
K = Carbon equivalent correction factor.
= 2 for ethane.
= 3 for propane.
= 4 for butane.
= Appropriate response factor for other organic calibration gases.

13.0 Method Performance

13.1 Measurement System Performance Specifications.

13.1.1 Zero Drift. Less than ±3 percent of the span value.

13.1.2 Calibration Drift. Less than ±3 percent of span value.

13.1.3 Calibration Error. Less than ±5 percent of the calibration gas value.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Measurement of Volatile Organic Compounds—Guideline Series. U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA–450/2–78–041. June 1978. p. 46–54.

2. EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards. U.S. Environmental Protection Agency, Quality Assurance and Technical Support Division. Research Triangle Park, N.C. September 1993.

3. Gasoline Vapor Emission Laboratory Evaluation—Part 2. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, NC. EMB Report No. 75–GAS–6. August 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

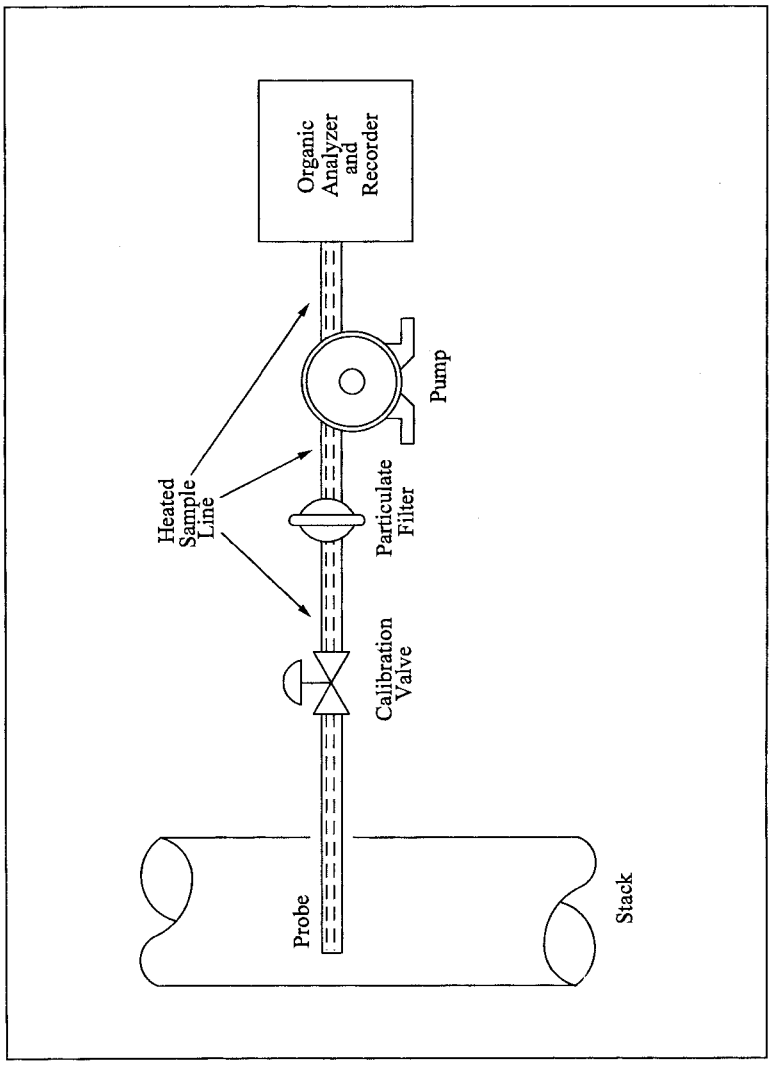


Figure 25A-1. Organic Concentration Measurement System.

METHOD 25B—DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A NONDISPERSIVE INFRARED ANALYZER

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 6C, and Method 25A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total Organic Compounds	N/A	<2% of span.

1.2 Applicability. This method is applicable for the determination of total gaseous organic concentration of vapors consisting primarily of alkanes. Other organic materials may be measured using the general procedure in this method, the appropriate calibration gas, and an analyzer set to the appropriate absorption band.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

A gas sample is extracted from the source through a heated sample line, if necessary, and glass fiber filter to a nondispersive infrared analyzer (NDIR). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

3.0 Definitions

Same as Method 25A, section 3.0.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

5.2 Explosive Atmosphere. This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

6.0 Equipment and Supplies

Same as Method 25A, section 6.0, with the exception of the following:

6.1 Organic Concentration Analyzer. A nondispersive infrared analyzer designed to measure alkane organics and capable of meeting or exceeding the specifications in this method.

7.0 Reagents and Standards

Same as Method 25A, section 7.1. No fuel gas is required for an NDIR.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as Method 25A, section 8.0.

9.0 Quality Control

Same as Method 25A, section 9.0.

10.0 Calibration and Standardization

Same as Method 25A, section 10.0.

11.0 Analytical Procedure

The sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Calculations and Data Analysis

Same as Method 25A, section 12.0.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 25A, section 16.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 25C—DETERMINATION OF NONMETHANE ORGANIC COMPOUNDS (NMOC) IN LANDFILL GASES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should also have a thorough knowledge of EPA Method 25.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Nonmethane organic compounds (NMOC).	No CAS number assigned.

1.2 Applicability. This method is applicable to the sampling and measurement of NMOC as carbon in landfill gases (LFG).

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A sample probe that has been perforated at one end is driven or augured to a depth of 0.9 m (3 ft) below the bottom of the landfill cover. A sample of the landfill gas is extracted with an evacuated cylinder. The NMOC content of the gas is determined by

injecting a portion of the gas into a gas chromatographic column to separate the NMOC from carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4); the NMOC are oxidized to CO_2, reduced to CH_4, and measured by a flame ionization detector (FID). In this manner, the variable response of the FID associated with different types of organics is eliminated.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Since this method is complex, only experienced personnel should perform this test. LFG contains methane, therefore explosive mixtures may exist on or near the landfill. It is advisable to take appropriate safety precautions when testing landfills, such as refraining from smoking and installing explosion-proof equipment.

6.0 Equipment and Supplies

6.1 Sample Probe. Stainless steel, with the bottom third perforated. Teflon probe liners and sampling lines are also allowed. Non-perforated probes are allowed as long as they are withdrawn to create a gap equivalent to having the bottom third perforated. The sample probe must be capped at the bottom and must have a threaded cap with a sampling attachment at the top. The sample probe must be long enough to go through and extend no less than 0.9 m (3 ft) below the landfill cover. If the sample probe is to be driven into the landfill, the bottom cap should be designed to facilitate driving the probe into the landfill.

6.2 Sampling Train.

6.2.1 Rotameter with Flow Control Valve. Capable of measuring a sample flow rate of 100 ±10 ml/min. The control valve must be made of stainless steel.

6.2.2 Sampling Valve. Stainless steel.

6.2.3 Pressure Gauge. U-tube mercury manometer, or equivalent, capable of measuring pressure to within 1 mm Hg (0.5 in H_2O) in the range of 0 to 1,100 mm Hg (0 to 590 in H_2O).

6.2.4 Sample Tank. Stainless steel or aluminum cylinder, equipped with a stainless steel sample tank valve.

6.3 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg (5.4 in H_2O).

6.4 Purging Pump. Portable, explosion proof, and suitable for sampling NMOC.

6.5 Pilot Probe Procedure. The following are needed only if the tester chooses to use the procedure described in section 8.2.1.

6.5.1 Pilot Probe. Tubing of sufficient strength to withstand being driven into the landfill by a post driver and an outside diameter of at least 6 mm (0.25 in.) smaller than the sample probe. The pilot probe shall be capped on both ends and long enough to go through the landfill cover and extend no less than 0.9 m (3 ft) into the landfill.

6.5.2 Post Driver and Compressor. Capable of driving the pilot probe and the sampling probe into the landfill. The Kitty Hawk portable post driver has been found to be acceptable.

6.6 Auger Procedure. The following are needed only if the tester chooses to use the procedure described in section 8.2.2.

6.6.1 Auger. Capable of drilling through the landfill cover and to a depth of no less than 0.9 m (3 ft) into the landfill.

6.6.2 Pea Gravel.

6.6.3 Bentonite.

6.7 NMOC Analyzer, Barometer, Thermometer, and Syringes. Same as in sections 6.3.1, 6.3.2, 6.33, and 6.2.10, respectively, of Method 25.

7.0 Reagents and Standards

7.1 NMOC Analysis. Same as in Method 25, section 7.2.

7.2 Calibration. Same as in Method 25, section 7.4, except omit section 7.4.3.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sample Tank Evacuation and Leak-Check. Conduct the sample tank evacuation and leak-check either in the laboratory or the field. Connect the pressure gauge and sampling valve to the sample tank. Evacuate the sample tank to 10 mm Hg (5.4 in H_2O) absolute pressure or less. Close the sampling valve, and allow the tank to sit for 30 minutes. The tank is acceptable if no change more than ±2 mm is noted. Include the results of the leak-check in the test report.

8.2 Sample Probe Installation. The tester may use the procedure in section 8.2.1 or 8.2.2.

8.2.1 Pilot Probe Procedure. Use the post driver to drive the pilot probe at least 0.9 m (3 ft) below the landfill cover. Alternative procedures to drive the probe into the landfill may be used subject to the approval of the Administrator's designated representative.

8.2.1.1 Remove the pilot probe and drive the sample probe into the hole left by the pilot probe. The sample probe shall extend at least 0.9 m (3 ft) below the landfill cover and shall protrude about 0.3 m (1 ft) above the landfill cover. Seal around the sampling probe with bentonite and cap the sampling probe with the sampling probe cap.

8.2.2 Auger Procedure. Use an auger to drill a hole to at least 0.9 m (3 ft) below the landfill cover. Place the sample probe in the hole and backfill with pea gravel to a level 0.6 m (2 ft) from the surface. The sample probe shall protrude at least 0.3 m (1 ft) above the landfill cover. Seal the remaining area around the probe with bentonite. Allow 24

hours for the landfill gases to equilibrate inside the augured probe before sampling.

8.2.3 Driven Probes. Closed-point probes may be driven directly into the landfill in a single step. This method may not require backfilling if the probe is adequately sealed by its insertion. Unperforated probes that are inserted in this manner and withdrawn at a distance from a detachable tip to create an open space are also acceptable.

8.3 Sample Train Assembly. Just before assembling the sample train, measure the sample tank vacuum using the pressure gauge. Record the vacuum, the ambient temperature, and the barometric pressure at this time. Assemble the sampling probe purging system as shown in Figure 25C–1.

8.4 Sampling Procedure. Open the sampling valve and use the purge pump and the flow control valve to evacuate at least two sample probe volumes from the system at a flow rate of 500 ml/min or less. Close the sampling valve and replace the purge pump with the sample tank apparatus as shown in Figure 25C–2. Open the sampling valve and the sample tank valve and, using the flow control valve, sample at a flow rate of 500 ml/min or less until either a constant flow rate can no longer be maintained because of reduced sample tank vacuum or the appropriate composite volume is attained. Disconnect the sampling tank apparatus and pressurize the sample cylinder to approximately 1,060 mm Hg (567 in. H_2O) absolute pressure with helium, and record the final pressure. Alternatively, the sample tank may be pressurized in the lab.

8.4.1 The following restrictions apply to compositing samples from different probe sites into a single cylinder: (1) Individual composite samples per cylinder must be of equal volume; this must be verified by recording the flow rate, sampling time, vacuum readings, or other appropriate volume measuring data, (2) individual composite samples must have a minimum volume of 1 liter unless data is provided showing smaller volumes can be accurately measured, and (3) composite samples must not be collected using the final cylinder vacuum as it diminishes to ambient pressure.

8.4.2 Use Method 3C to determine the percent N_2 in each cylinder. The presence of N_2 indicates either infiltration of ambient air into the landfill gas sample or an inappropriate testing site has been chosen where anaerobic decomposition has not begun. The landfill gas sample is acceptable if the concentration of N_2 is less than 20 percent. Alternatively, Method 3C may be used to determine the oxygen content of each cylinder as an air infiltration test. With this option, the oxygen content of each cylinder must be less than 5 percent.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4.2	Verify that landfill gas sample contains less than 20 percent N_2 or 5 percent O_2.	Ensures that ambient air was not drawn into the landfill gas sample and gas was sampled from an appropriate location.
10.1, 10.2	NMOC analyzer initial and daily performance checks.	Ensures precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Initial NMOC Analyzer Performance Test. Same as in Method 25, section 10.1, except omit the linearity checks for CO_2 standards.

10.2 NMOC Analyzer Daily Calibration.

10.2.1 NMOC Response Factors. Same as in Method 25, section 10.2.2.

10.3 Sample Tank Volume. The volume of the gas sampling tanks must be determined. Determine the tank volumes by weighing them empty and then filled with deionized water; weigh to the nearest 5 g, and record the results. Alternatively, measure the volume of water used to fill them to the nearest 5 ml.

11.0 Analytical Procedures

11.1 The oxidation, reduction, and measurement of NMOC's is similar to Method 25. Before putting the NMOC analyzer into routine operation, conduct an initial performance test. Start the analyzer, and perform all the necessary functions in order to put the analyzer into proper working order. Conduct the performance test according to the procedures established in section 10.1. Once the performance test has been successfully completed and the NMOC calibration response factor has been determined, proceed with sample analysis as follows:

11.1.1 Daily Operations and Calibration Checks. Before and immediately after the analysis of each set of samples or on a daily basis (whichever occurs first), conduct a calibration test according to the procedures established in section 10.2. If the criteria of the daily calibration test cannot be met, repeat

the NMOC analyzer performance test (Section 10.1) before proceeding.

11.1.2 Operating Conditions. Same as in Method 25, section 11.2.1.

11.1.3 Analysis of Sample Tank. Purge the sample loop with sample, and then inject the sample. Under the specified operating conditions, the CO_2 in the sample will elute in approximately 100 seconds. As soon as the detector response returns to baseline following the CO_2 peak, switch the carrier gas flow to backflush, and raise the column oven temperature to 195 °C (383 °F) as rapidly as possible. A rate of 30 °C/min (54 °F/min) has been shown to be adequate. Record the value obtained for any measured NMOC. Return the column oven temperature to 85 °C (185 °F) in preparation for the next analysis. Analyze each sample in triplicate, and report the average as C_{tm}.

12.0 Data Analysis and Calculations

NOTE: All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge or manometer pressure.

12.1 Nomenclature

B_w = Moisture content in the sample, fraction.
C_{N2} = N_2 concentration in the diluted sample gas.
C_{mN2} = Measured N_2 concentration, fraction in landfill gas.
C_{mOx} = Measured Oxygen concentration, fraction in landfill gas.
C_{Ox} = Oxygen concentration in the diluted sample gas.
C_t = Calculated NMOC concentration, ppmv C equivalent.
C_{tm} = Measured NMOC concentration, ppmv C equivalent.
P_b = Barometric pressure, mm Hg.
P_t = Gas sample tank pressure after sampling, but before pressurizing, mm Hg absolute.
P_{tf} = Final gas sample tank pressure after pressurizing, mm Hg absolute.
P_{ti} = Gas sample tank pressure after evacuation, mm Hg absolute.
P_w = Vapor pressure of H_2O (from Table 25C–1), mm Hg.
r = Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 . . . r).
T_t = Sample tank temperature at completion of sampling, °K.
T_{ti} = Sample tank temperature before sampling, °K.
T_{tf} = Sample tank temperature after pressuring, °K.

12.2 Water Correction. Use Table 25C–1 (Section 17.0), the LFG temperature, and barometric pressure at the sampling site to calculate B_w.

$$B_w = \frac{P_w}{P_b} \qquad \text{Eq. 25C-1}$$

12.3 Nitrogen Concentration in the landfill gas. Use equation 25C–2 to calculate the measured concentration of nitrogen in the original landfill gas.

$$C_{N2} = \left[\frac{\left(\frac{P_{tf}}{T_{tf}}\right)}{\left(\left(\frac{P_t}{T_t}\right)-\left(\frac{P_{ti}}{T_{ti}}\right)\right)}\right] C_{mN2} \qquad \text{Eq.25C-2}$$

12.4 Oxygen Concentration in the landfill gas. Use equation 25C–3 to calculate the measured concentration of oxygen in the original landfill gas.

$$C_{Ox} = \left[\frac{\left(\frac{P_{tf}}{T_{tf}}\right)}{\left(\left(\frac{P_t}{T_t}\right)-\left(\frac{P_{ti}}{T_{ti}}\right)\right)}\right] C_{mOx} \qquad \text{Eq.25C-3}$$

12.5 You must correct the NMOC Concentration for the concentration of nitrogen or oxygen based on which gas or gases passes the requirements in section 9.1.

12.5.1 NMOC Concentration with nitrogen correction. Use Equation 25C–4 to calculate the concentration of NMOC for each sample tank when the nitrogen concentration is less than 20 percent.

$$C_t = \frac{\frac{P_{tf}}{T_{tf}}}{\left(\frac{P_t}{T_t}-\frac{P_{ti}}{T_{ti}}\right)\left(1-\frac{99}{78}C_{N2}\right)-B_w}\frac{1}{r}\sum_{j=1}^{r} C_{tm(j)} \qquad \text{Eq. 25C-4}$$

12.5.2 NMOC Concentration with oxygen correction. Use Equation 25C–5 to calculate the concentration of NMOC for each sample tank if the landfill gas oxygen is less than 5 percent and the landfill gas nitrogen concentration is greater than 20 percent.

$$C_t = \frac{\frac{P_{tf}}{T_{tf}}}{\left(\frac{P_t}{T_t}-\frac{P_{ti}}{T_{ti}}\right)\left(1-\frac{99}{21}C_{Ox}\right)-B_w}\frac{1}{r}\sum_{j=1}^{r} C_{tm(j)} \qquad \text{Eq. 25C-5}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, Albert E., Samuel Witz, and Robert D. MacPhee. Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, Massachusetts. June 15–20, 1975.) 14 p.

2. Salo, Albert E., William L. Oaks, and Robert D. MacPhee. Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, Colorado. June 9–13, 1974.) 25 p.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

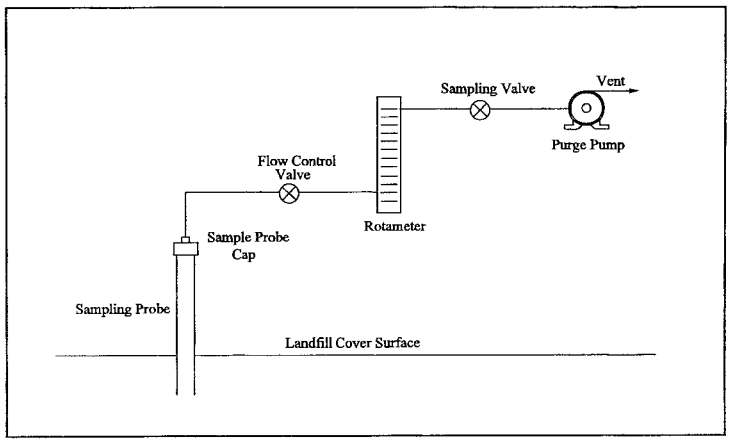


Figure 25C-1. Schematic of Sampling Probe Purging System

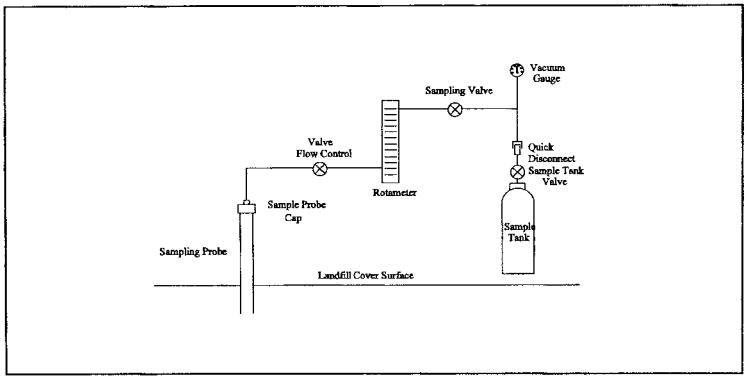


Figure 25C-2. Schematic of Sampling Train.

TABLE 25C–1—MOISTURE CORRECTION

Temperature, °C	Vapor Pressure of H_2O, mm Hg	Temperature, °C	Vapor Pressure of H_2O, mm Hg
4	6.1	18	15.5
6	7.0	20	17.5
8	8.0	22	19.8
10	9.2	24	22.4
12	10.5	26	25.2
14	12.0	28	28.3

TABLE 25C–1—MOISTURE CORRECTION—Continued

Temperature, °C	Vapor Pressure of H_2O, mm Hg	Temperature, °C	Vapor Pressure of H_2O, mm Hg
16	13.6	30	31.8

METHOD 25D—DETERMINATION OF THE VOLATILE ORGANIC CONCENTRATION OF WASTE SAMPLES

NOTE: Performance of this method should not be attempted by persons unfamiliar with the operation of a flame ionization detector (FID) or an electrolytic conductivity detector (ELCD) because knowledge beyond the scope of this presentation is required.

1.0 Scope and Application

1.1 Analyte. Volatile Organic Compounds. No CAS No. assigned.

1.2 Applicability. This method is applicable for determining the volatile organic (VO) concentration of a waste sample.

2.0 Summary of Method

2.1 Principle. A sample of waste is obtained at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to the atmosphere). The sample is suspended in an organic/aqueous matrix, then heated and purged with nitrogen for 30 min. in order to separate certain organic compounds. Part of the sample is analyzed for carbon concentration, as methane, with an FID, and part of the sample is analyzed for chlorine concentration, as chloride, with an ELCD. The VO concentration is the sum of the carbon and chlorine content of the sample.

3.0 Definitions

3.1 *Well-mixed* in the context of this method refers to turbulent flow which results in multiple-phase waste in effect behaving as single-phase waste due to good mixing.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1 Sampling. The following equipment is required:

6.1.1 Sampling Tube. Flexible Teflon, 0.25 in. ID (6.35 mm).

6.1.2 Sample Container. Borosilicate glass, 40-mL, and a Teflon-lined screw cap capable of forming an air tight seal.

6.1.3 Cooling Coil. Fabricated from 0.25 in (6.35 mm). ID 304 stainless steel tubing with a thermocouple at the coil outlet.

6.2 Analysis. The following equipment is required.

6.2.1 Purging Apparatus. For separating the VO from the waste sample. A schematic of the system is shown in Figure 25D–1. The purging apparatus consists of the following major components.

6.2.1.1 Purging Flask. A glass container to hold the sample while it is heated and purged with dry nitrogen. The cap of the purging flask is equipped with three fittings: one for a purging lance (fitting with the #7 Ace-thread), one for the Teflon exit tubing (side fitting, also a #7 Ace-thread), and a third (a 50-mm Ace-thread) to attach the base of the purging flask as shown in Figure 25D–2. The base of the purging flask is a 50-mm ID (2 in) cylindrical glass tube. One end of the tube is open while the other end is sealed. Exact dimensions are shown in Figure 25D–2.

6.2.1.2 Purging Lance. Glass tube, 6-mm OD (0.2 in) by 30 cm (12 in) long. The purging end of the tube is fitted with a four-arm bubbler with each tip drawn to an opening 1 mm (0.04 in) in diameter. Details and exact dimensions are shown in Figure 25D–2.

6.2.1.3 Coalescing Filter. Porous fritted disc incorporated into a container with the same dimensions as the purging flask. The details of the design are shown in Figure 25D–3.

6.2.1.4 Constant Temperature Chamber. A forced draft oven capable of maintaining a uniform temperature around the purging flask and coalescing filter of 75 ±2 °C (167 ±3.6 °F).

6.2.1.5 Three-way Valve. Manually operated, stainless steel. To introduce calibration gas into system.

6.2.1.6 Flow Controllers. Two, adjustable. One capable of maintaining a purge gas flow rate of 6 ±0.06 L/min (0.2 ±0.002 ft^3/min) The other capable of maintaining a calibration gas flow rate of 1–100 mL/min (0.00004–0.004 ft^3/min).

6.2.1.7 Rotameter. For monitoring the air flow through the purging system (0–10 L/min)(0–0.4 ft^3/min).

6.2.1.8 Sample Splitters. Two heated flow restrictors (placed inside oven or heated to 120 ±10 °C (248 ±18 °F)). At a purge rate of 6 L/min (0.2 ft^3/min), one will supply a constant flow to the first detector (the rest of the flow will be directed to the second sample splitter). The second splitter will split the analytical flow between the second detector and the flow restrictor. The approximate flow to the FID will be 40 mL/min (0.0014 ft^3/min) and to the ELCD will be 15 mL/min (0.0005 ft^3/min), but the exact flow must be adjusted to be compatible with the individual detector and to meet its linearity requirement. The two sample splitters will be connected to each other by 1/8″ OD (3.175 mm) stainless steel tubing.

6.2.1.9 Flow Restrictor. Stainless steel tubing, 1/8″ OD (3.175 mm), connecting the second sample splitter to the ice bath. Length is determined by the resulting pressure in the purging flask (as measured by the pressure gauge). The resulting pressure from the use of the flow restrictor shall be 6–7 psig.

6.2.1.10 Filter Flask. With one-hole stopper. Used to hold ice bath. Excess purge gas is vented through the flask to prevent condensation in the flowmeter and to trap volatile organic compounds.

6.2.1.11 Four-way Valve. Manually operated, stainless steel. Placed inside oven, used to bypass purging flask.

6.2.1.12 On/Off Valves. Two, stainless steel. One heat resistant up to 130 °C (266 °F) and placed between oven and ELCD. The other a toggle valve used to control purge gas flow.

6.2.1.13 Pressure Gauge. Range 0–40 psi. To monitor pressure in purging flask and coalescing filter.

6.2.1.14 Sample Lines. Teflon, 1/4″ OD (6.35 mm), used inside the oven to carry purge gas to and from purging chamber and to and from coalescing filter to four-way valve. Also used to carry sample from four-way valve to first sample splitter.

6.2.1.15 Detector Tubing. Stainless steel, 1/8″ OD (3.175 mm), heated to 120 ±10 °C (248 ±18 °F) . Used to carry sample gas from each sample splitter to a detector. Each piece of tubing must be wrapped with heat tape and insulating tape in order to insure that no cold spots exist. The tubing leading to the ELCD will also contain a heat-resistant on-off valve (Section 6.2.1.12) which shall also be wrapped with heat-tape and insulation.

6.2.2 Volatile Organic Measurement System. Consisting of an FID to measure the carbon concentration of the sample and an ELCD to measure the chlorine concentration.

6.2.2.1 FID. A heated FID meeting the following specifications is required.

6.2.2.1.1 Linearity. A linear response (±5 percent) over the operating range as demonstrated by the procedures established in section 10.1.1.

6.2.2.1.2 Range. A full scale range of 50 pg carbon/sec to 50 µg carbon/sec. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.2.2.1.3 Data Recording System. A digital integration system compatible with the FID for permanently recording the output of the detector. The recorder shall have the capability to start and stop integration at points selected by the operator or it shall be capable of the ''integration by slices'' technique (this technique involves breaking down the chromatogram into smaller increments, integrating the area under the curve for each portion, subtracting the background for each portion, and then adding all of the areas together for the final area count).

6.2.2.2 ELCD. An ELCD meeting the following specifications is required. 1-propanol must be used as the electrolyte. The electrolyte flow through the conductivity cell shall be 1 to 2 mL/min (0.00004 to 0.00007 ft^3/min).

NOTE: A ¼-in. ID (6.35 mm) quartz reactor tube is strongly recommended to reduce carbon buildup and the resulting detector maintenance.

6.2.2.2.1 Linearity. A linear response (±10 percent) over the response range as demonstrated by the procedures in section 10.1.2.

6.2.2.2.2 Range. A full scale range of 5.0 pg/sec to 500 ng/sec chloride. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.2.2.2.3 Data Recording System. A digital integration system compatible with the output voltage range of the ELCD. The recorder must have the capability to start and stop integration at points selected by the operator or it shall be capable of performing the ''integration by slices'' technique.

7.0 Reagents and Standards

7.1 Sampling.

7.1.1 Polyethylene Glycol (PEG). Ninety-eight percent pure with an average molecular weight of 400. Before using the PEG, remove any organic compounds that might be detected as volatile organics by heating it to 120 °C (248 °F) and purging it with nitrogen at a flow rate of 1 to 2 L/min (0.04 to 0.07 ft^3/min) for 2 hours. The cleaned PEG must be stored under a 1 to 2 L/min (0.04 to 0.07 ft^3/min) nitrogen purge until use. The purge apparatus is shown in Figure 25D–4.

7.2 Analysis.

7.2.1 Sample Separation. The following are required for the sample purging step.

7.2.1.1 PEG. Same as section 7.1.1.

7.2.1.2 Purge Gas. Zero grade nitrogen (N_2), containing less than 1 ppm carbon.

7.2.2 Volatile Organics Measurement. The following are required for measuring the VO concentration.

7.2.2.1 Hydrogen (H_2). Zero grade H_2, 99.999 percent pure.

7.2.2.2 Combustion Gas. Zero grade air or oxygen as required by the FID.

7.2.2.3 Calibration Gas. Pressurized gas cylinder containing 10 percent propane and 1 percent 1,1-dichloroethylene by volume in nitrogen.

7.2.2.4 Water. Deionized distilled water that conforms to American Society for Testing and Materials Specification D 1193–74, Type 3, is required for analysis. At the option of the analyst, the $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations are not expected to be present.

7.2.2.5 1-Propanol. ACS grade or better. Electrolyte Solution. For use in the ELCD.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling.

8.1.1 Sampling Plan Design and Development. Use the procedures in chapter nine of Reference 1 in section 16 as guidance in developing a sampling plan.

8.1.2 Single Phase or Well-mixed Waste.

8.1.2.1 Install a sampling tap to obtain the sample at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to the atmosphere). Assemble the sampling apparatus as shown in Figure 25D–5.

8.1.2.2 Prepare the sampling containers as follows: Pour 30 mL of clean PEG into the container. PEG will reduce but not eliminate the loss of organics during sample collection. Weigh the sample container with the screw cap, the PEG, and any labels to the nearest 0.01 g and record the weight (m_{st}). Store the containers in an ice bath until 1 hour before sampling (PEG will solidify at ice bath temperatures; allow the containers to reach room temperature before sampling).

8.1.2.3 Begin sampling by purging the sample lines and cooling coil with at least four volumes of waste. Collect the purged material in a separate container and dispose of it properly.

8.1.2.4 After purging, stop the sample flow and direct the sampling tube to a preweighed sample container, prepared as described in section 8.1.2.2. Keep the tip of the tube below the surface of the PEG during sampling to minimize contact with the atmosphere. Sample at a flow rate such that the temperature of the waste is less than 10 °C (50 °F). Fill the sample container and immediately cap it (within 5 seconds) so that a minimum headspace exists in the container. Store immediately in a cooler and cover with ice.

8.1.3 Multiple-phase Waste. Collect a 10 g sample of each phase of waste generated using the procedures described in section 8.1.2 or 8.1.5. Each phase of the waste shall be analyzed as a separate sample. Calculate the weighted average VO concentration of the waste using Equation 25D–13 (Section 12.14).

8.1.4 Solid waste. Add approximately 10 g of the solid waste to a container prepared in the manner described in section 8.1.2.2, minimizing headspace. Cap and chill immediately.

8.1.5 Alternative to Tap Installation. If tap installation is impractical or impossible, fill a large, clean, empty container by submerging the container into the waste below the surface of the waste. Immediately fill a container prepared in the manner described in section 8.1.2.2 with approximately 10 g of the waste collected in the large container. Minimize headspace, cap and chill immediately.

8.1.6 Alternative sampling techniques may be used upon the approval of the Administrator.

8.2 Sample Recovery.

8.2.1 Assemble the purging apparatus as shown in Figures 25D–1 and 25D–2. The oven shall be heated to 75 ±2 °C (167 ±3.6 °F). The sampling lines leading from the oven to the detectors shall be heated to 120 ±10 °C (248 ±18 °F) with no cold spots. The flame ionization detector shall be operated with a heated block. Adjust the purging lance so that it reaches the bottom of the chamber.

8.2.2 Remove the sample container from the cooler, and wipe the exterior of the container to remove any extraneous ice, water, or other debris. Reweigh the sample container to the nearest 0.01 g, and record the weight (m_{sf}). Pour the contents of the sample container into the purging flask, rinse the sample container three times with a total of 20 mL of PEG (since the sample container originally held 30 mL of PEG, the total volume of PEG added to the purging flask will be 50 mL), transferring the rinsings to the purging flask after each rinse. Cap purging flask between rinses. The total volume of PEG in the purging flask shall be 50 mL. Add 50 mL of water to the purging flask.

9.0 Quality Control

9.1 Quality Control Samples. If audit samples are not available, prepare and analyze the two types of quality control samples (QCS) listed in Sections 9.1.1 and 9.1.2. Before placing the system in operation, after a shutdown of greater than six months, and after any major modifications, analyze each QCS in triplicate. For each detector, calculate the percent recovery by dividing measured concentration by theoretical concentration and multiplying by 100. Determine the mean percent recovery for each detector for each QCS triplicate analysis. The RSD for any triplicate analysis shall be ≤10 percent. For QCS 1 (methylene chloride), the percent recovery shall be ≥90 percent for carbon as methane, and ≥55 percent for chlorine as chloride. For QCS 2 (1,3-dichloro-2-propanol), the percent recovery shall be ≤15 percent for carbon as methane, and ≤6 percent for chlorine as chloride. If the analytical system does not meet the above-mentioned criteria for both detectors, check the system parameters (temperature, system pressure, purge rate, etc.), correct the problem, and repeat the triplicate analysis of each QCS.

9.1.1 QCS 1, Methylene Chloride. Prepare a stock solution by weighing, to the nearest 0.1 mg, 55 µL of HPLC grade methylene chloride in a tared 5 mL volumetric flask. Record the weight in milligrams, dilute to 5 mL with cleaned PEG, and inject 100 µL of the stock solution into a sample prepared as a water blank (50 mL of cleaned PEG and 60 mL of water in the purging flask). Analyze

the QCS according to the procedures described in sections 10.2 and 10.3, excluding section 10.2.2. To calculate the theoretical carbon concentration (in mg) in QCS 1, multiply mg of methylene chloride in the stock solution by 3.777×10^{-3}. To calculate the theoretical chlorine concentration (in mg) in QCS 1, multiply mg of methylene chloride in the stock solution by 1.670×10^{-2}.

9.1.2 QCS 2, 1,3-dichloro-2-propanol. Prepare a stock solution by weighing, to the nearest 0.1 mg, 60 μL of high purity grade 1,3-dichloro-2-propanol in a tared 5 mL volumetric flask. Record the weight in milligrams, dilute to 5 mL with cleaned PEG, and inject 100 μL of the stock solution into a sample prepared as a water blank (50 mL of cleaned PEG and 60 mL of water in the purging flask). Analyze the QCS according to the procedures described in sections 10.2 and 10.3, excluding section 10.2.2. To calculate the theoretical carbon concentration (in mg) in QCS 2, multiply mg of 1,3-dichloro-2-propanol in the stock solution by 7.461×10^{-3}. To calculate the theoretical chlorine concentration (in mg) in QCS 2, multiply mg of 1,3-dichloro-2-propanol in the stock solution by 1.099×10^{-2}.

9.1.3 Routine QCS Analysis. For each set of compliance samples (in this context, set is per facility, per compliance test), analyze one QCS 1 and one QCS 2 sample. The percent recovery for each sample for each detector shall be ±13 percent of the mean recovery established for the most recent set of QCS triplicate analysis (Section 9.4). If the sample does not meet this criteria, check the system components and analyze another QCS 1 and 2 until a single set of QCS meet the ±13 percent criteria.

10.0 Calibration and Standardization

10.1 Initial Performance Check of Purging System. Before placing the system in operation, after a shutdown of greater than six months, after any major modifications, and at least once per month during continuous operation, conduct the linearity checks described in sections 10.1.1 and 10.1.2. Install calibration gas at the three-way calibration gas valve. See Figure 25D–1.

10.1.1 Linearity Check Procedure. Using the calibration standard described in section 7.2.2.3 and by varying the injection time, it is possible to calibrate at multiple concentration levels. Use Equation 25D–3 to calculate three sets of calibration gas flow rates and run times needed to introduce a total mass of carbon, as methane, (m_c) of 1, 5, and 10 mg into the system (low, medium and high FID calibration, respectively). Use Equation 25D–4 to calculate three sets of calibration gas flow rates and run times needed to introduce a total chloride mass (m_{ch}) of 1, 5, and 10 mg into the system (low, medium and high ELCD calibration, respectively). With the system operating in standby mode, allow the FID and the ELCD to establish a stable baseline. Set the secondary pressure regulator of the calibration gas cylinder to the same pressure as the purge gas cylinder and set the proper flow rate with the calibration flow controller (see Figure 25D–1). The calibration gas flow rate can be measured with a flowmeter attached to the vent position of the calibration gas valve. Set the four-way bypass valve to standby position so that the calibration gas flows through the coalescing filter only. Inject the calibration gas by turning the calibration gas valve from vent position to inject position. Continue the calibration gas flow for the appropriate period of time before switching the calibration valve to vent position. Continue recording the response of the FID and the ELCD for 5 min after switching off calibration gas flow. Make triplicate injections of all six levels of calibration.

10.1.2 Linearity Criteria. Calculate the average response factor (Equations 25D–5 and 25D–6) and the relative standard deviation (RSD) (Equation 25D–10) at each level of the calibration curve for both detectors. Calculate the overall mean of the three response factor averages for each detector. The FID linearity is acceptable if each response factor is within 5 percent of the overall mean and if the RSD for each set of triplicate injections is less than 5 percent. The ELCD linearity is acceptable if each response factor is within 10 percent of the overall mean and if the RSD for each set of triplicate injections is less than 10 percent. Record the overall mean value of the response factors for the FID and the ELCD. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat sections 10.1.1 and 10.1.2.

10.2 Daily Calibrations.

10.2.1 Daily Linearity Check. Follow the procedures outlined in section 10.1.1 to analyze the medium level calibration for both the FID and the ELCD in duplicate at the start of the day. Calculate the response factors and the RSDs for each detector. For the FID, the calibration is acceptable if the average response factor is within 5 percent of the overall mean response factor (Section 10.1.2) and if the RSD for the duplicate injection is less than 5 percent. For the ELCD, the calibration is acceptable if the average response factor is within 10 percent of the overall mean response factor (Section 10.1.2) and if the RSD for the duplicate injection is less than 10 percent. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat sections 10.1.1 and 10.1.2.

10.2.2 Calibration Range Check.

10.2.2.1 If the waste concentration for either detector falls below the range of calibration for that detector, use the procedure outlined in section 10.1.1 to choose two calibration points that bracket the new target

concentration. Analyze each of these points in triplicate (as outlined in section 10.1.1) and use the criteria in section 10.1.2 to determine the linearity of the detector in this ''mini-calibration'' range.

10.2.2.2 After the initial linearity check of the mini-calibration curve, it is only necessary to test one of the points in duplicate for the daily calibration check (in addition to the points specified in section 10.2.1). The average daily mini-calibration point should fit the linearity criteria specified in section 10.2.1. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat the calibration procedure mentioned in the first paragraph of section 10.2.2. A mini-calibration curve for waste concentrations above the calibration curve for either detector is optional.

10.3 Analytical Balance. Calibrate against standard weights.

11.0 Analysis

11.1 Sample Analysis.

11.1.1 Turn on the constant temperature chamber and allow the temperature to equilibrate at 75 ±2 °C (167 ±3.6 °F). Turn the four-way valve so that the purge gas bypasses the purging flask, the purge gas flowing through the coalescing filter and to the detectors (standby mode). Turn on the purge gas. Allow both the FID and the ELCD to warm up until a stable baseline is achieved on each detector. Pack the filter flask with ice. Replace ice after each run and dispose of the waste water properly. When the temperature of the oven reaches 75 ±2 °C (167 ±3.6 °F), start both integrators and record baseline. After 1 min, turn the four-way valve so that the purge gas flows through the purging flask, to the coalescing filter and to the sample splitters (purge mode). Continue recording the response of the FID and the ELCD. Monitor the readings of the pressure gauge and the rotameter. If the readings fall below established setpoints, stop the purging, determine the source of the leak, and resolve the problem before resuming. Leaks detected during a sampling period invalidate that sample.

11.1.2 As the purging continues, monitor the output of the detectors to make certain that the analysis is proceeding correctly and that the results are being properly recorded. Every 10 minutes read and record the purge flow rate, the pressure and the chamber temperature. Continue the purging for 30 minutes.

11.1.3 For each detector output, integrate over the entire area of the peak starting at 1 minute and continuing until the end of the run. Subtract the established baseline area from the peak area. Record the corrected area of the peak. See Figure 25D–6 for an example integration.

11.2 Water Blank. A water blank shall be analyzed for each batch of cleaned PEG prepared. Transfer about 60 mL of water into the purging flask. Add 50 mL of the cleaned PEG to the purging flask. Treat the blank as described in sections 8.2 and 8.3, excluding section 8.2.2. Calculate the concentration of carbon and chlorine in the blank sample (assume 10 g of waste as the mass). A VO concentration equivalent to ≤10 percent of the applicable standard may be subtracted from the measured VO concentration of the waste samples. Include all blank results and documentation in the test report.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

A_b = Area under the water blank response curve, counts.

A_c = Area under the calibration response curve, counts.

A_s = Area under the sample response curve, counts.

C = Concentration of volatile organics in the sample, ppmw.

C_c = Concentration of carbon, as methane, in the calibration gas, mg/L.

C_{ch} = Concentration of chloride in the calibration gas, mg/L.

C_j = VO concentration of phase j, ppmw.

DR_t = Average daily response factor of the FID, mg CH_4/counts.

Dr_{th} = Average daily response factor of the ELCD, mg Cl^-/counts.

F_j = Weight fraction of phase j present in the waste.

m_c = Mass of carbon, as methane, in a calibration run, mg.

m_{ch} = Mass of chloride in a calibration run, mg.

m_s = Mass of the waste sample, g.

m_{sc} = Mass of carbon, as methane, in the sample, mg.

m_{sf} = Mass of sample container and waste sample, g.

m_{sh} = Mass of chloride in the sample, mg.

m_{st} = Mass of sample container prior to sampling, g.

m_{VO} = Mass of volatile organics in the sample, mg.

n = Total number of phases present in the waste.

P_p = Percent propane in calibration gas (L/L).

P_{vc} = Percent 1,1-dichloroethylene in calibration gas (L/L).

Q_c = Flow rate of calibration gas, L/min.

t_c = Length of time standard gas is delivered to the analyzer, min.

W = Weighted average VO concentration, ppmw.

12.2 Concentration of Carbon, as Methane, in the Calibration Gas.

$$C_c = (19.681 \times P_p) + (13.121 \times P_{vc}) \qquad \text{Eq. 25D-1}$$

12.3 Concentration of Chloride in the Calibration Gas.

$$C_{ch} = 28.998 \times P_{vc} \qquad \text{Eq. 25D-2}$$

12.4 Mass of Carbon, as Methane, in a Calibration Run.

$$M_c = C_c \times Q_c \times t_c \qquad \text{Eq. 25D-3}$$

12.5 Mass of Chloride in a Calibration Run.

$$m_{ch} = C_{ch} \times Q_c \times t_c \qquad \text{Eq. 25D-4}$$

12.6 FID Response Factor, mg/counts.

$$DR_t = \frac{m_c}{A_c} \qquad \text{Eq. 25D-5}$$

12.7 ELCD Response Factor, mg/counts.

$$DR_{th} = \frac{m_{ch}}{A_c} \qquad \text{Eq. 25D-6}$$

12.8 Mass of Carbon in the Sample.

$$m_{sc} = DR_t(A_s - A_b) \qquad \text{Eq. 25D-7}$$

12.9 Mass of Chloride in the Sample.

$$m_{sh} = DR_{th}(A_s - A_b) \qquad \text{Eq. 25D-8}$$

12.10 Mass of Volatile Organics in the Sample.

$$m_{vo} = m_{sc} + m_{sh} \qquad \text{Eq. 25D-9}$$

12.11 Relative Standard Deviation.

$$RSD = \frac{100}{\bar{x}} \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}} \qquad \text{Eq. 25D-10}$$

12.12 Mass of Sample.

$$m_s = m_{sf} - m_{st} \qquad \text{Eq. 25D-11}$$

12.13 Concentration of Volatile Organics in Waste.

$$C = \frac{(m_{vo} \times 1000)}{m_s} \qquad \text{Eq. 25D-12}$$

12.14 Weighted Average VO Concentration of Multi-phase Waste.

$$W = \sum_{j=1}^{n} F_j x \overline{C}_j \qquad \text{Eq. 25D-13}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. ''Test Methods for Evaluating Solid Waste, Physical/Chemistry Methods'', U.S. Environmental Protection Agency. Publication SW–846, 3rd Edition, November 1986 as amended by Update I, November 1990.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

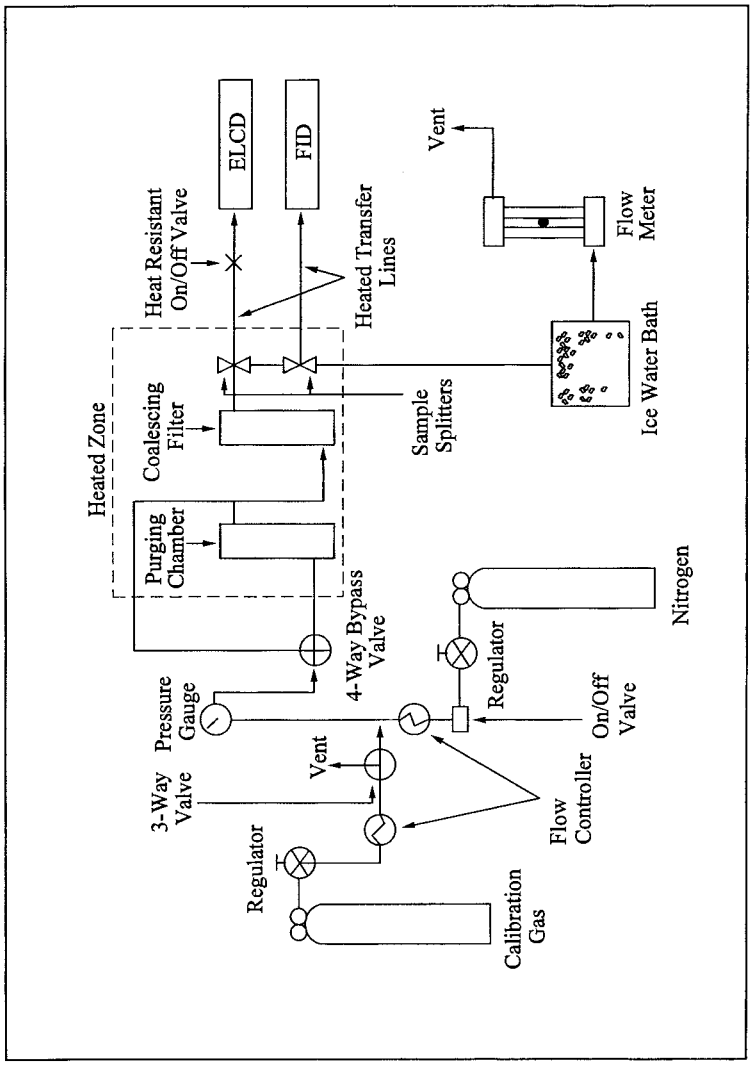


Figure 25D-1. Schematic of Purging Apparatus.

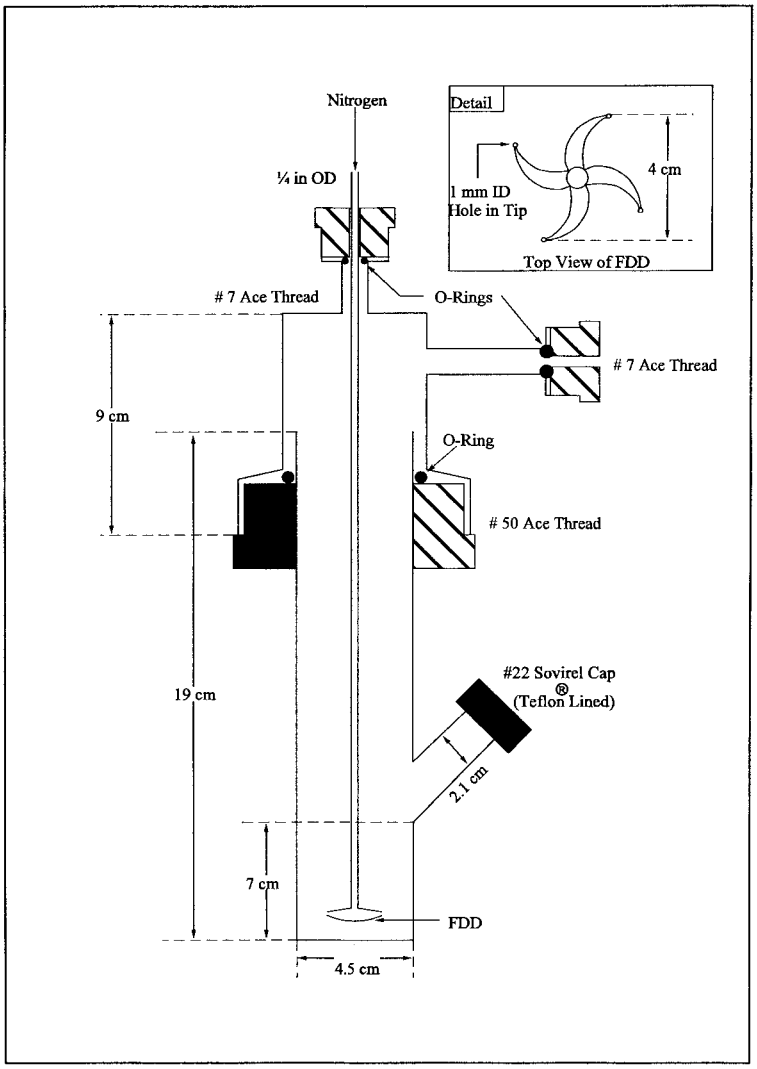
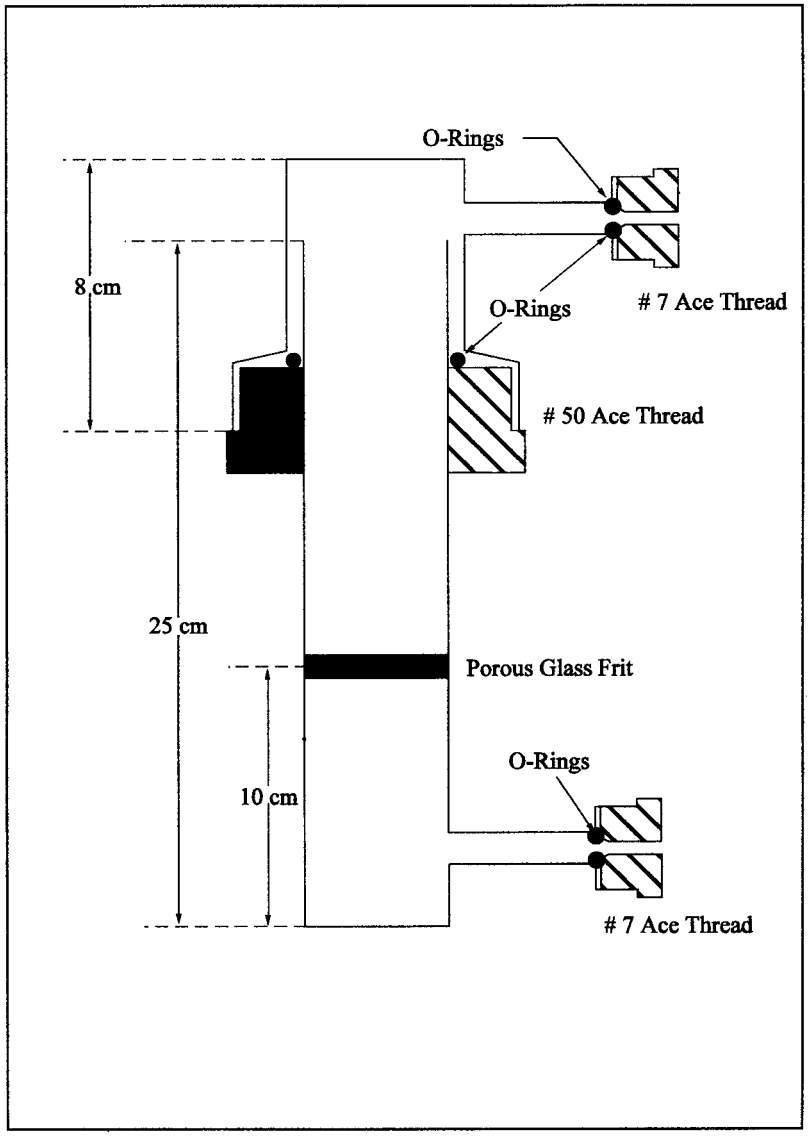


Figure 25D-2. Purging Lance.


O-Rings
8 cm
O-Rings
7 Ace Thread
50 Ace Thread
25 cm
Porous Glass Frit
O-Rings
10 cm
7 Ace Thread

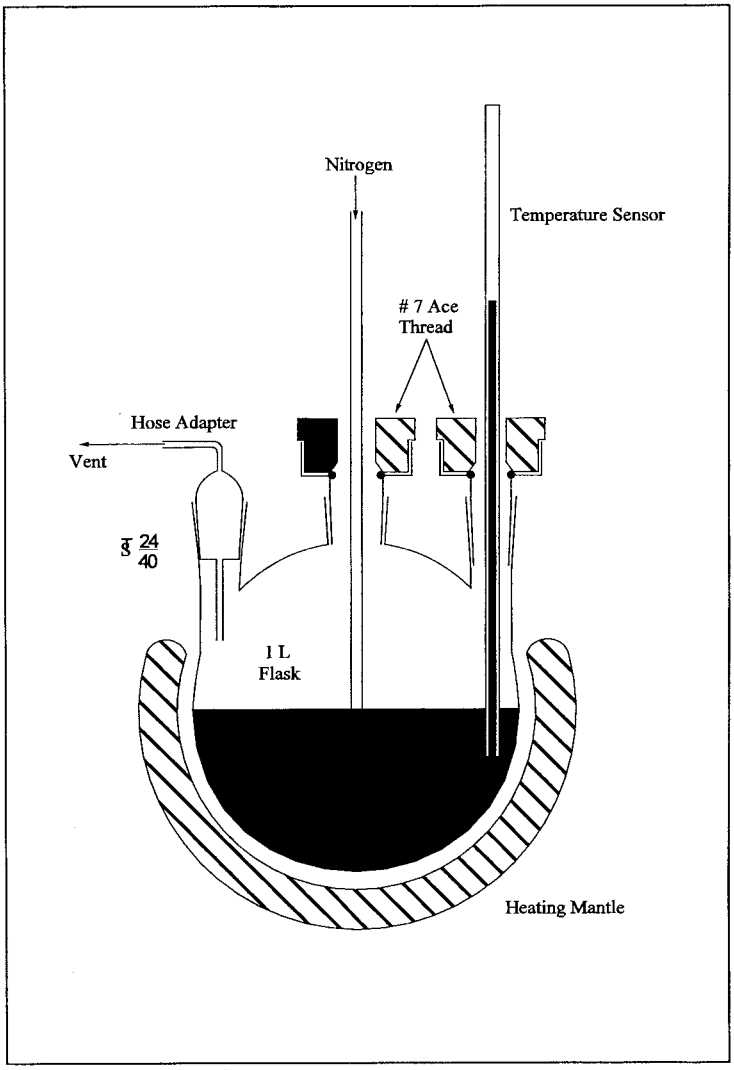


Figure 25D-4. Schematic of PEG Cleaning System.

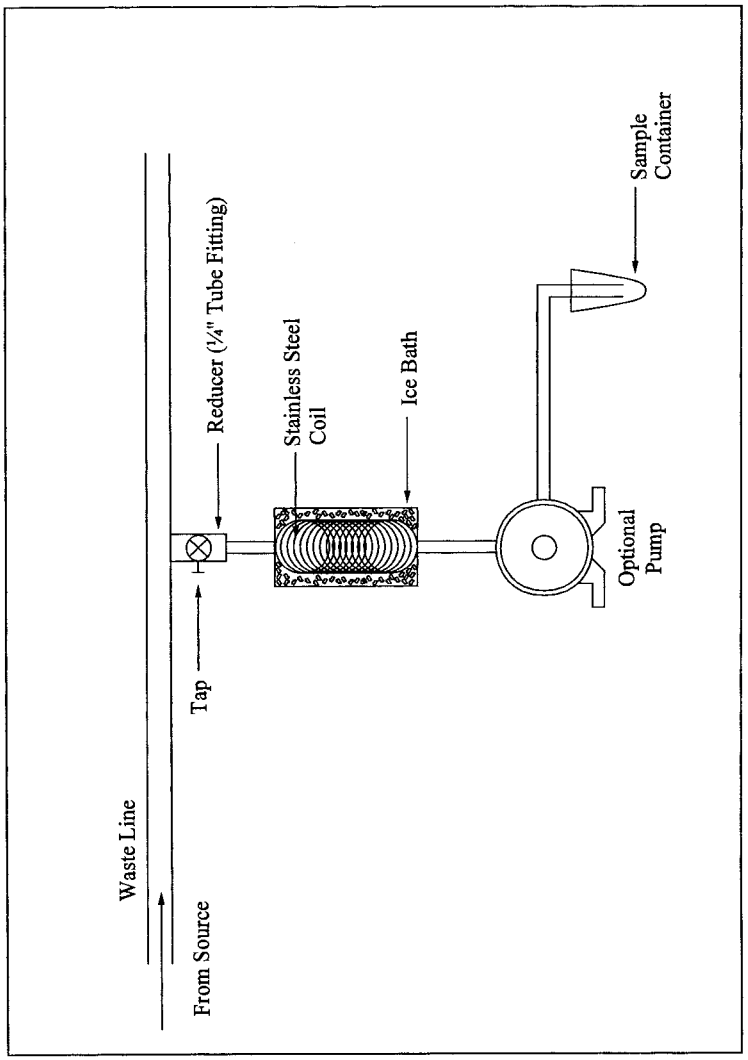


Figure 25D-5. Schematic of Sampling Apparatus.

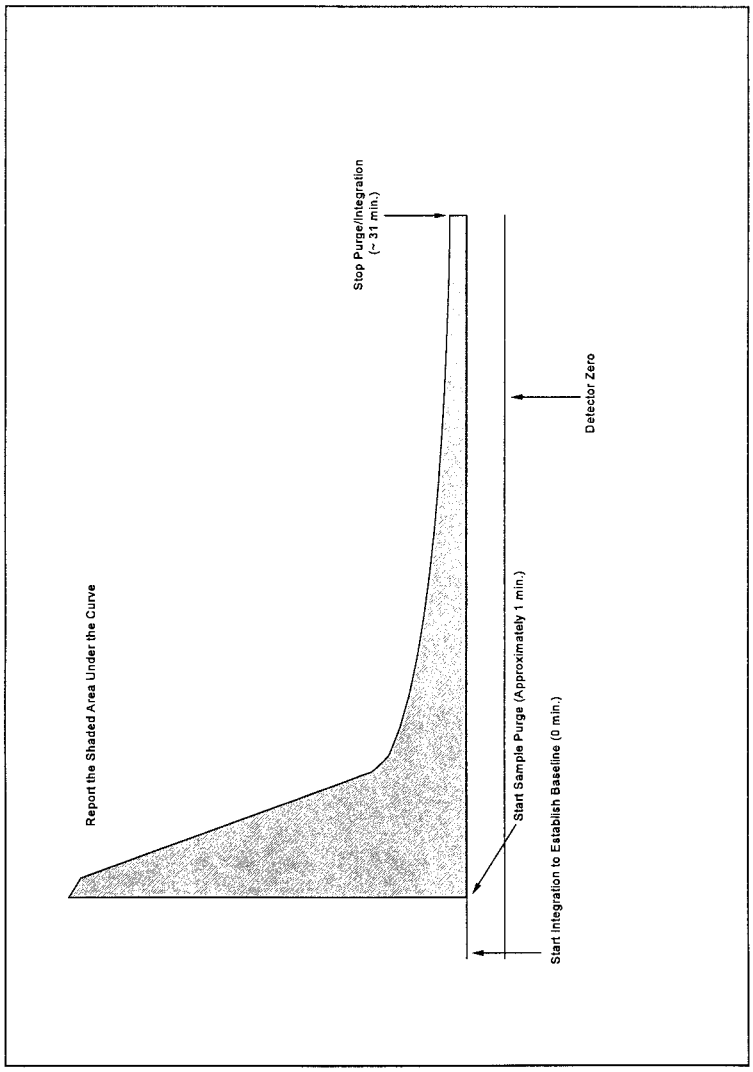


Figure 25D-6. Example Integration of Either Detector.

METHOD 25E—DETERMINATION OF VAPOR PHASE ORGANIC CONCENTRATION IN WASTE SAMPLES

NOTE: Performance of this method should not be attempted by persons unfamiliar with the operation of a flame ionization detector (FID) nor by those who are unfamiliar with source sampling because knowledge beyond the scope of this presentation is required. This method is not inclusive with respect to specifications (*e.g.*, reagents and standards) and calibration procedures. Some material is incorporated by reference from other methods. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 106, part 61, Appendix B, and Method 18, part 60, Appendix A.

1.0 Scope and Application

1.1 Applicability. This method is applicable for determining the vapor pressure of waste cited by an applicable regulation.

1.2 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 The headspace vapor of the sample is analyzed for carbon content by a headspace analyzer, which uses an FID.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 The analyst shall select the operating parameters best suited to the requirements for a particular analysis. The analyst shall produce confirming data through an adequate supplemental analytical technique and have the data available for review by the Administrator.

5.0 Safety [Reserved]

6.0 Equipment and Supplies

6.1 Sampling. The following equipment is required:

6.1.1 Sample Containers. Vials, glass, with butyl rubber septa, Perkin-Elmer Corporation Numbers 0105–0129 (glass vials), B001–0728 (gray butyl rubber septum, plug style), 0105–0131 (butyl rubber septa), or equivalent. The seal must be made from butyl rubber. Silicone rubber seals are not acceptable.

6.1.2 Vial Sealer. Perkin-Elmer Number 105–0106, or equivalent.

6.1.3 Gas-Tight Syringe. Perkin-Elmer Number 00230117, or equivalent.

6.1.4 The following equipment is required for sampling.

6.1.4.1 Tap.

6.1.4.2 Tubing. Teflon, 0.25-in. ID.

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1.4.3 Cooling Coil. Stainless steel (304), 0.25 in.-ID, equipped with a thermocouple at the coil outlet.

6.2 Analysis. The following equipment is required.

6.2.1 Balanced Pressure Headspace Sampler. Perkin-Elmer HS–6, HS–100, or equivalent, equipped with a glass bead column instead of a chromatographic column.

6.2.2 FID. An FID meeting the following specifications is required.

6.2.2.1 Linearity. A linear response (±5 percent) over the operating range as demonstrated by the procedures established in section 10.2.

6.2.2.2 Range. A full scale range of 1 to 10,000 parts per million (ppm) propane (C_3H_8). Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.2.3 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the output of the detector.

6.2.4 Temperature Sensor. Capable of reading temperatures in the range of 30 to 60 °C (86 to 140 °F) with an accuracy of ±0.1 °C (±0.2 °F).

7.0 Reagents and Standards

7.1 Analysis. The following items are required for analysis.

7.1.1 Hydrogen (H_2). Zero grade hydrogen, as required by the FID.

7.1.2 Carrier Gas. Zero grade nitrogen, containing less than 1 ppm carbon (C) and less than 1 ppm carbon dioxide.

7.1.3 Combustion Gas. Zero grade air or oxygen as required by the FID.

7.2 Calibration and Linearity Check.

7.2.1 Stock Cylinder Gas Standard. 100 percent propane. The manufacturer shall: (a) Certify the gas composition to be accurate to ±3 percent or better (see section 7.2.1.1); (b) recommend a maximum shelf life over which the gas concentration does not change by greater than ±5 percent from the certified value; and (c) affix the date of gas cylinder preparation, certified propane concentration, and recommended maximum shelf life to the cylinder before shipment to the buyer.

7.2.1.1 Cylinder Standards Certification. The manufacturer shall certify the concentration of the calibration gas in the cylinder by (a) directly analyzing the cylinder and (b) calibrating his analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use, as a minimum, a three-point calibration curve.

7.2.1.2 Verification of Manufacturer's Calibration Standards. Before using, the manufacturer shall verify each calibration standard by (a) comparing it to gas mixtures prepared in accordance with the procedure described in section 7.1 of Method 106 of Part 61, Appendix B, or by (b) calibrating it against Standard Reference Materials (SRM's) prepared by the National Bureau of Standards, if such SRM's are available. The agreement between the initially determined concentration value and the verification concentration value must be within ±5 percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

8.0 Sampling Collection, Preservation, Storage, and Transport

8.1 Install a sampling tap to obtain a sample at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to

the atmosphere). Assemble the sampling apparatus as shown in Figure 25E–1.

8.2 Begin sampling by purging the sample lines and cooling coil with at least four volumes of waste. Collect the purged material in a separate container and dispose of it properly.

8.3 After purging, stop the sample flow and transfer the Teflon sampling tube to a sample container. Sample at a flow rate such that the temperature of the waste is <10 °C (<50 °F). Fill the sample container halfway (±5 percent) and cap it within 5 seconds. Store immediately in a cooler and cover with ice.

8.4 Alternative sampling techniques may be used upon the approval of the Administrator.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
10.2, 10.3	FID calibration and response check	Ensure precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Use the procedures in sections 10.2 to calibrate the headspace analyzer and FID and check for linearity before the system is first placed in operation, after any shutdown longer than 6 months, and after any modification of the system.

10.2 Calibration and Linearity. Use the procedures in section 10 of Method 18 of Part 60, Appendix A, to prepare the standards and calibrate the flowmeters, using propane as the standard gas. Fill the calibration standard vials halfway (±5 percent) with deionized water. Purge and fill the airspace with calibration standard. Prepare a minimum of three concentrations of calibration standards in triplicate at concentrations that will bracket the applicable cutoff. For a cutoff of 5.2 kPa (0.75 psi), prepare nominal concentrations of 30,000, 50,000, and 70,000 ppm as propane. For a cutoff of 27.6 kPa (4.0 psi), prepare nominal concentrations of 200,000, 300,000, and 400,000 ppm as propane.

10.2.1 Use the procedures in section 11.3 to measure the FID response of each standard. Use a linear regression analysis to calculate the values for the slope (k) and the y-intercept (b). Use the procedures in sections 12.3 and 12.2 to test the calibration and the linearity.

10.3 Daily FID Calibration Check. Check the calibration at the beginning and at the end of the daily runs by using the following procedures. Prepare 2 calibration standards at the nominal cutoff concentration using the procedures in section 10.2. Place one at the beginning and one at the end of the daily run. Measure the FID response of the daily calibration standard and use the values for k and b from the most recent calibration to calculate the concentration of the daily standard. Use an equation similar to 25E–2 to calculate the percent difference between the daily standard and C_s. If the difference is within 5 percent, then the previous values for k and b can be used. Otherwise, use the procedures in section 10.2 to recalibrate the FID.

11.0 Analytical Procedures

11.1 Allow one hour for the headspace vials to equilibrate at the temperature specified in the regulation. Allow the FID to warm up until a stable baseline is achieved on the detector.

11.2 Check the calibration of the FID daily using the procedures in section 10.3.

11.3 Follow the manufacturer's recommended procedures for the normal operation of the headspace sampler and FID.

11.4 Use the procedures in sections 12.4 and 12.5 to calculate the vapor phase organic vapor pressure in the samples.

11.5 Monitor the output of the detector to make certain that the results are being properly recorded.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

A = Measurement of the area under the response curve, counts.
b = y-intercept of the linear regression line.
C_a = Measured vapor phase organic concentration of sample, ppm as propane.
C_{ma} = Average measured vapor phase organic concentration of standard, ppm as propane.
C_m = Measured vapor phase organic concentration of standard, ppm as propane.
C_s = Calculated standard concentration, ppm as propane.
k = Slope of the linear regression line.
P_{bar} = Atmospheric pressure at analysis conditions, mm Hg (in. Hg).
P* = Organic vapor pressure in the sample, kPa (psi).
PD = Percent difference between the average measured vapor phase organic concentration (C_m) and the calculated standard concentration (C_s).
RSD = Relative standard deviation.
$\beta = 1.333 \times 10^{-7}$ kPa/[(mm Hg)(ppm)], $(4.91 \times 10^{-7}$ psi/[(in. Hg)(ppm)])

12.2 Linearity. Use the following equation to calculate the measured standard concentration for each standard vial.

$$C_m = kA + b \qquad \text{Eq. 25E-1}$$

12.2.1 Calculate the average measured standard concentration (C_{ma}) for each set of triplicate standards and use the following equation to calculate PD between C_{ma} and C_s. The instrument linearity is acceptable if the PD is within five for each standard.

$$PD = \frac{C_s - C_{ma}}{C_s} \times 100 \qquad \text{Eq. 25E-2}$$

12.3. Relative Standard Deviation (RSD). Use the following equation to calculate the RSD for each triplicate set of standards.

$$RSD = \frac{100}{C_{ma}} \sqrt{\frac{\sum (C_m - C_{ma})^2}{2}} \qquad \text{Eq. 25E-3}$$

The calibration is acceptable if the RSD is within five for each standard concentration.

12.4 Concentration of organics in the headspace. Use the following equation to calculate the concentration of vapor phase organics in each sample.

$$C_a = kA + b \qquad \text{Eq. 25E-4}$$

12.5 Vapor Pressure of Organics in the Headspace Sample. Use the following equation to calculate the vapor pressure of organics in the sample.

$$P^* = \beta P_{bar} C_a \qquad \text{Eq. 25E-5}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, Albert E., Samuel Witz, and Robert D. MacPhee. ''Determination of Solvent Vapor Concentrations by Total Combustion Analysis: a Comparison of Infared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, Massachusetts.

2. Salo, Albert E., William L. Oaks, and Robert D. MacPhee. ''Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, Colorado. June 9–13, 1974.) p. 25.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

State of Oregon Department of Environmental Quality

OAR 340-224-0070
40 C.F.R. Part 50, Appendices J, L
40 C.F.R. Part 58, Appendix A

3. *Design Values for Primary and Secondary Ambient Air Quality Standards for Ozone.* The air quality design value at a monitoring site is defined as that concentration that when reduced to the level of the standard ensures that the site meets the standard. For a concentration-based standard, the air quality design value is simply the standard-related test statistic. Thus, for the primary and secondary ozone standards, the 3-year average annual fourth-highest daily maximum 8-hour average ozone concentration is also the air quality design value for the site.

[62 FR 38895, July 18, 1997]

Appendix J to Part 50—Reference Method for the Determination of Particulate Matter as PM_{10} in the Atmosphere

1.0 *Applicability.*

1.1 This method provides for the measurement of the mass concentration of particulate matter with an aerodynamic diameter less than or equal to a nominal 10 micrometers (PM_{10}) in ambient air over a 24-hour period for purposes of determining attainment and maintenance of the primary and secondary national ambient air quality standards for particulate matter specified in §50.6 of this chapter. The measurement process is nondestructive, and the PM_{10} sample can be subjected to subsequent physical or chemical analyses. Quality assurance procedures and guidance are provided in part 58, appendices A and B, of this chapter and in References 1 and 2.

2.0 *Principle.*

2.1 An air sampler draws ambient air at a constant flow rate into a specially shaped inlet where the suspended particulate matter is inertially separated into one or more size fractions within the PM_{10} size range. Each size fraction in the PM_{10} size range is then collected on a separate filter over the specified sampling period. The particle size discrimination characteristics (sampling effectiveness and 50 percent cutpoint) of the sampler inlet are prescribed as performance specifications in part 53 of this chapter.

2.2 Each filter is weighed (after moisture equilibration) before and after use to determine the net weight (mass) gain due to collected PM_{10}. The total volume of air sampled, corrected to EPA reference conditions (25 C, 101.3 kPa), is determined from the measured flow rate and the sampling time. The mass concentration of PM_{10} in the ambient air is computed as the total mass of collected particles in the PM_{10} size range divided by the volume of air sampled, and is expressed in micrograms per standard cubic meter (μg/std m^3). For PM_{10} samples collected at temperatures and pressures significantly different from EPA reference conditions, these corrected concentrations sometimes differ substantially from actual concentrations (in micrograms per actual cubic meter), particularly at high elevations. Although not required, the actual PM_{10} concentration can be calculated from the corrected concentration, using the average ambient temperature and barometric pressure during the sampling period.

2.3 A method based on this principle will be considered a reference method only if (a) the associated sampler meets the requirements specified in this appendix and the requirements in part 53 of this chapter, and (b) the method has been designated as a reference method in accordance with part 53 of this chapter.

3.0 *Range.*

3.1 The lower limit of the mass concentration range is determined by the repeatability of filter tare weights, assuming the nominal air sample volume for the sampler. For samplers having an automatic filter-changing mechanism, there may be no upper limit. For samplers that do not have an automatic filter-changing mechanism, the upper limit is determined by the filter mass loading beyond which the sampler no longer maintains the operating flow rate within specified limits due to increased pressure drop across the loaded filter. This upper limit cannot be specified precisely because it is a complex function of the ambient particle size distribution and type, humidity, filter type, and perhaps other factors. Nevertheless, all samplers should be capable of measuring 24-hour PM_{10} mass concentrations of at least 300 μg/std m^3 while maintaining the operating flow rate within the specified limits.

4.0 *Precision.*

4.1 The precision of PM_{10} samplers must be 5 μg/m^3 for PM_{10} concentrations below 80 μg/m^3 and 7 percent for PM_{10} concentrations above 80 μg/m^3, as required by part 53 of this chapter, which prescribes a test procedure that determines the variation in the PM_{10} concentration measurements of identical samplers under typical sampling conditions. Continual assessment of precision via collocated samplers is required by part 58 of this chapter for PM_{10} samplers used in certain monitoring networks.

5.0 *Accuracy.*

5.1 Because the size of the particles making up ambient particulate matter varies over a wide range and the concentration of particles varies with particle size, it is difficult to define the absolute accuracy of PM_{10} samplers. Part 53 of this chapter provides a specification for the sampling effectiveness of PM_{10} samplers. This specification requires that the expected mass concentration calculated for a candidate PM_{10} sampler, when sampling a specified particle size distribution, be within ±10 percent of that calculated

for an ideal sampler whose sampling effectiveness is explicitly specified. Also, the particle size for 50 percent sampling effectiveness is required to be 10 ±0.5 micrometers. Other specifications related to accuracy apply to flow measurement and calibration, filter media, analytical (weighing) procedures, and artifact. The flow rate accuracy of PM_{10} samplers used in certain monitoring networks is required by part 58 of this chapter to be assessed periodically via flow rate audits.

6.0 *Potential Sources of Error*.

6.1 *Volatile Particles*. Volatile particles collected on filters are often lost during shipment and/or storage of the filters prior to the post-sampling weighing[3]. Although shipment or storage of loaded filters is sometimes unavoidable, filters should be reweighed as soon as practical to minimize these losses.

6.2 *Artifacts*. Positive errors in PM_{10} concentration measurements may result from retention of gaseous species on filters.[4 5] Such errors include the retention of sulfur dioxide and nitric acid. Retention of sulfur dioxide on filters, followed by oxidation to sulfate, is referred to as artifact sulfate formation, a phenomenon which increases with increasing filter alkalinity.[6] Little or no artifact sulfate formation should occur using filters that meet the alkalinity specification in section 7.2.4. Artifact nitrate formation, resulting primarily from retention of nitric acid, occurs to varying degrees on many filter types, including glass fiber, cellulose ester, and many quartz fiber filters.[5 7 8 9 10] Loss of true atmospheric particulate nitrate during or following sampling may also occur due to dissociation or chemical reaction. This phenomenon has been observed on Teflon® filters[8] and inferred for quartz fiber filters.[11 12] The magnitude of nitrate artifact errors in PM_{10} mass concentration measurements will vary with location and ambient temperature; however, for most sampling locations, these errors are expected to be small.

6.3 *Humidity*. The effects of ambient humidity on the sample are unavoidable. The filter equilibration procedure in section 9.0 is designed to minimize the effects of moisture on the filter medium.

6.4 *Filter Handling*. Careful handling of filters between presampling and postsampling weighings is necessary to avoid errors due to damaged filters or loss of collected particles from the filters. Use of a filter cartridge or cassette may reduce the magnitude of these errors. Filters must also meet the integrity specification in section 7.2.3.

6.5 *Flow Rate Variation*. Variations in the sampler's operating flow rate may alter the particle size discrimination characteristics of the sampler inlet. The magnitude of this error will depend on the sensitivity of the inlet to variations in flow rate and on the particle distribution in the atmosphere during the sampling period. The use of a flow control device (section 7.1.3) is required to minimize this error.

6.6 *Air Volume Determination*. Errors in the air volume determination may result from errors in the flow rate and/or sampling time measurements. The flow control device serves to minimize errors in the flow rate determination, and an elapsed time meter (section 7.1.5) is required to minimize the error in the sampling time measurement.

7.0 *Apparatus*.

7.1 *PM_{10} Sampler*.

7.1.1 The sampler shall be designed to:

a. Draw the air sample into the sampler inlet and through the particle collection filter at a uniform face velocity.

b. Hold and seal the filter in a horizontal position so that sample air is drawn downward through the filter.

c. Allow the filter to be installed and removed conveniently.

d. Protect the filter and sampler from precipitation and prevent insects and other debris from being sampled.

e. Minimize air leaks that would cause error in the measurement of the air volume passing through the filter.

f. Discharge exhaust air at a sufficient distance from the sampler inlet to minimize the sampling of exhaust air.

g. Minimize the collection of dust from the supporting surface.

7.1.2 The sampler shall have a sample air inlet system that, when operated within a specified flow rate range, provides particle size discrimination characteristics meeting all of the applicable performance specifications prescribed in part 53 of this chapter. The sampler inlet shall show no significant wind direction dependence. The latter requirement can generally be satisfied by an inlet shape that is circularly symmetrical about a vertical axis.

7.1.3 The sampler shall have a flow control device capable of maintaining the sampler's operating flow rate within the flow rate limits specified for the sampler inlet over normal variations in line voltage and filter pressure drop.

7.1.4 The sampler shall provide a means to measure the total flow rate during the sampling period. A continuous flow recorder is recommended but not required. The flow measurement device shall be accurate to ±2 percent.

7.1.5 A timing/control device capable of starting and stopping the sampler shall be used to obtain a sample collection period of 24 ±1 hr (1,440 ±60 min). An elapsed time meter, accurate to within ±15 minutes, shall be used to measure sampling time. This meter is optional for samplers with continuous flow recorders if the sampling time

measurement obtained by means of the recorder meets the ±15 minute accuracy specification.

7.1.6 The sampler shall have an associated operation or instruction manual as required by part 53 of this chapter which includes detailed instructions on the calibration, operation, and maintenance of the sampler.

7.2 *Filters.*

7.2.1 *Filter Medium.* No commercially available filter medium is ideal in all respects for all samplers. The user's goals in sampling determine the relative importance of various filter characteristics (e.g., cost, ease of handling, physical and chemical characteristics, etc.) and, consequently, determine the choice among acceptable filters. Furthermore, certain types of filters may not be suitable for use with some samplers, particularly under heavy loading conditions (high mass concentrations), because of high or rapid increase in the filter flow resistance that would exceed the capability of the sampler's flow control device. However, samplers equipped with automatic filter-changing mechanisms may allow use of these types of filters. The specifications given below are minimum requirements to ensure acceptability of the filter medium for measurement of PM_{10} mass concentrations. Other filter evaluation criteria should be considered to meet individual sampling and analysis objectives.

7.2.2 *Collection Efficiency.* ≥99 percent, as measured by the DOP test (ASTM–2986) with 0.3 μm particles at the sampler's operating face velocity.

7.2.3 *Integrity.* ±5 μg/m³ (assuming sampler's nominal 24-hour air sample volume). Integrity is measured as the PM_{10} concentration equivalent corresponding to the average difference between the initial and the final weights of a random sample of test filters that are weighed and handled under actual or simulated sampling conditions, but have no air sample passed through them (*i.e.*, filter blanks). As a minimum, the test procedure must include initial equilibration and weighing, installation on an inoperative sampler, removal from the sampler, and final equilibration and weighing.

7.2.4 *Alkalinity.* <25 microequivalents/gram of filter, as measured by the procedure given in Reference 13 following at least two months storage in a clean environment (free from contamination by acidic gases) at room temperature and humidity.

7.3 *Flow Rate Transfer Standard.* The flow rate transfer standard must be suitable for the sampler's operating flow rate and must be calibrated against a primary flow or volume standard that is traceable to the National Bureau of Standards (NBS). The flow rate transfer standard must be capable of measuring the sampler's operating flow rate with an accuracy of ±2 percent.

7.4 *Filter Conditioning Environment.*

7.4.1 Temperature range: 15 to 30 C.

7.4.2 Temperature control: ±3 C.

7.4.3 Humidity range: 20% to 45% RH.

7.4.4 Humidity control: ±5% RH.

7.5 *Analytical Balance.* The analytical balance must be suitable for weighing the type and size of filters required by the sampler. The range and sensitivity required will depend on the filter tare weights and mass loadings. Typically, an analytical balance with a sensitivity of 0.1 mg is required for high volume samplers (flow rates >0.5 m^3/min). Lower volume samplers (flow rates <0.5 m^3/min) will require a more sensitive balance.

8.0 *Calibration.*

8.1 *General Requirements.*

8.1.1 Calibration of the sampler's flow measurement device is required to establish traceability of subsequent flow measurements to a primary standard. A flow rate transfer standard calibrated against a primary flow or volume standard shall be used to calibrate or verify the accuracy of the sampler's flow measurement device.

8.1.2 Particle size discrimination by inertial separation requires that specific air velocities be maintained in the sampler's air inlet system. Therefore, the flow rate through the sampler's inlet must be maintained throughout the sampling period within the design flow rate range specified by the manufacturer. Design flow rates are specified as actual volumetric flow rates, measured at existing conditions of temperature and pressure (Q_a). In contrast, mass concentrations of PM_{10} are computed using flow rates corrected to EPA reference conditions of temperature and pressure (Q_{std}).

8.2 *Flow Rate Calibration Procedure.*

8.2.1 PM_{10} samplers employ various types of flow control and flow measurement devices. The specific procedure used for flow rate calibration or verification will vary depending on the type of flow controller and flow indicator employed. Calibration in terms of actual volumetric flow rates (Q_a) is generally recommended, but other measures of flow rate (e.g., Q_{std}) may be used provided the requirements of section 8.1 are met. The general procedure given here is based on actual volumetric flow units (Q_a) and serves to illustrate the steps involved in the calibration of a PM_{10} sampler. Consult the sampler manufacturer's instruction manual and Reference 2 for specific guidance on calibration. Reference 14 provides additional information on the use of the commonly used measures of flow rate and their interrelationships.

8.2.2 Calibrate the flow rate transfer standard against a primary flow or volume standard traceable to NBS. Establish a calibration relationship (e.g., an equation or family of curves) such that traceability to the primary standard is accurate to within 2 percent over the expected range of ambient conditions (*i.e.*, temperatures and pressures) under

which the transfer standard will be used. Recalibrate the transfer standard periodically.

8.2.3 Following the sampler manufacturer's instruction manual, remove the sampler inlet and connect the flow rate transfer standard to the sampler such that the transfer standard accurately measures the sampler's flow rate. Make sure there are no leaks between the transfer standard and the sampler.

8.2.4 Choose a minimum of three flow rates (actual m^3/min), spaced over the acceptable flow rate range specified for the inlet (see 7.1.2) that can be obtained by suitable adjustment of the sampler flow rate. In accordance with the sampler manufacturer's instruction manual, obtain or verify the calibration relationship between the flow rate (actual m^3/min) as indicated by the transfer standard and the sampler's flow indicator response. Record the ambient temperature and barometric pressure. Temperature and pressure corrections to subsequent flow indicator readings may be required for certain types of flow measurement devices. When such corrections are necessary, correction on an individual or daily basis is preferable. However, seasonal average temperature and average barometric pressure for the sampling site may be incorporated into the sampler calibration to avoid daily corrections. Consult the sampler manufacturer's instruction manual and Reference 2 for additional guidance.

8.2.5 Following calibration, verify that the sampler is operating at its design flow rate (actual m^3/min) with a clean filter in place.

8.2.6 Replace the sampler inlet.

9.0 *Procedure.*

9.1 The sampler shall be operated in accordance with the specific guidance provided in the sampler manufacturer's instruction manual and in Reference 2. The general procedure given here assumes that the sampler's flow rate calibration is based on flow rates at ambient conditions (Q_a) and serves to illustrate the steps involved in the operation of a PM_{10} sampler.

9.2 Inspect each filter for pinholes, particles, and other imperfections. Establish a filter information record and assign an identification number to each filter.

9.3 Equilibrate each filter in the conditioning environment (see 7.4) for at least 24 hours.

9.4 Following equilibration, weigh each filter and record the presampling weight with the filter identification number.

9.5 Install a preweighed filter in the sampler following the instructions provided in the sampler manufacturer's instruction manual.

9.6 Turn on the sampler and allow it to establish run-temperature conditions. Record the flow indicator reading and, if needed, the ambient temperature and barometric pressure. Determine the sampler flow rate (actual m^3/min) in accordance with the instructions provided in the sampler manufacturer's instruction manual. NOTE.—No onsite temperature or pressure measurements are necessary if the sampler's flow indicator does not require temperature or pressure corrections or if seasonal average temperature and average barometric pressure for the sampling site are incorporated into the sampler calibration (see step 8.2.4). If individual or daily temperature and pressure corrections are required, ambient temperature and barometric pressure can be obtained by on-site measurements or from a nearby weather station. Barometric pressure readings obtained from airports must be station pressure, not corrected to sea level, and may need to be corrected for differences in elevation between the sampling site and the airport.

9.7 If the flow rate is outside the acceptable range specified by the manufacturer, check for leaks, and if necessary, adjust the flow rate to the specified setpoint. Stop the sampler.

9.8 Set the timer to start and stop the sampler at appropriate times. Set the elapsed time meter to zero or record the initial meter reading.

9.9 Record the sample information (site location or identification number, sample date, filter identification number, and sampler model and serial number).

9.10 Sample for 24 ±1 hours.

9.11 Determine and record the average flow rate ($\bar{Q}_a$) in actual m^3/min for the sampling period in accordance with the instructions provided in the sampler manufacturer's instruction manual. Record the elapsed time meter final reading and, if needed, the average ambient temperature and barometric pressure for the sampling period (see note following step 9.6).

9.12 Carefully remove the filter from the sampler, following the sampler manufacturer's instruction manual. Touch only the outer edges of the filter.

9.13 Place the filter in a protective holder or container (e.g., petri dish, glassine envelope, or manila folder).

9.14 Record any factors such as meteorological conditions, construction activity, fires or dust storms, etc., that might be pertinent to the measurement on the filter information record.

9.15 Transport the exposed sample filter to the filter conditioning environment as soon as possible for equilibration and subsequent weighing.

9.16 Equilibrate the exposed filter in the conditioning environment for at least 24 hours under the same temperature and humidity conditions used for presampling filter equilibration (see 9.3).

9.17 Immediately after equilibration, reweigh the filter and record the postsampling weight with the filter identification number.

10.0 *Sampler Maintenance.*

10.1 The PM_{10} sampler shall be maintained in strict accordance with the maintenance procedures specified in the sampler manufacturer's instruction manual.

11.0 *Calculations.*

11.1 Calculate the average flow rate over the sampling period corrected to EPA reference conditions as $\bar{Q}_{std}$. When the sampler's flow indicator is calibrated in actual volumetric units (Q_a), $\bar{Q}_{std}$ is calculated as:

$$\bar{Q}_{std} = \bar{Q}_a \times (P_{av}/T_{av})(T_{std}/P_{std})$$

where

$\bar{Q}_{std}$ = average flow rate at EPA reference conditions, std m^3/min;
$\bar{Q}_a$ = average flow rate at ambient conditions, m^3/min;
P_{av} = average barometric pressure during the sampling period or average barometric pressure for the sampling site, kPa (or mm Hg);
T_{av} = average ambient temperature during the sampling period or seasonal average ambient temperature for the sampling site, K;
T_{std} = standard temperature, defined as 298 K;
P_{std} = standard pressure, defined as 101.3 kPa (or 760 mm Hg).

11.2 Calculate the total volume of air sampled as:

$$V_{std} = \bar{Q}_{std} \times t$$

where

V_{std} = total air sampled in standard volume units, std m^3;
t = sampling time, min.

11.3 Calculate the PM_{10} concentration as:

$$PM_{10} = (W_f - W_i) \times 10^6/V_{std}$$

where

PM_{10} = mass concentration of PM_{10}, µg/std m^3;
W_f, W_i = final and initial weights of filter collecting PM_{1O} particles, g;
10^6 = conversion of g to µg.

NOTE: If more than one size fraction in the PM_{10} size range is collected by the sampler, the sum of the net weight gain by each collection filter $[\Sigma(W_f - W_i)]$ is used to calculate the PM_{10} mass concentration.

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[52 FR 24664, July 1, 1987; 52 FR 29467, Aug. 7, 1987]

APPENDIX K TO PART 50—INTERPRETATION OF THE NATIONAL AMBIENT AIR QUALITY STANDARDS FOR PARTICULATE MATTER

1.0 General

(a) This appendix explains the computations necessary for analyzing particulate matter data to determine attainment of the 24-hour standards specified in 40 CFR 50.6. For the primary and secondary standards, particulate matter is measured in the ambient air as PM_{10} (particles with an aerodynamic diameter less than or equal to a

Example 1

a. During a particular calendar quarter, 39 out of a possible 92 samples were recorded, with one observed exceedance of the 24-hour standard. Using Equation 1, the estimated number of exceedances for the quarter is:

$e_q = 1 \times 92/39 = 2.359$ or 2.36.

b. If the estimated exceedances for the other 3 calendar quarters in the year were 2.30, 0.0 and 0.0, then, using Equation 2, the estimated number of exceedances for the year is 2.36 + 2.30 + 0.0 + 0.0 which equals 4.66 or 4.7. If no exceedances were observed for the 2 previous years, then the expected number of exceedances is estimated by: (⅓) × (4.7 + 0 + 0) = 1.57 or 1.6. Since 1.6 exceeds the allowable number of expected exceedances, this monitoring site would fail the attainment test.

Example 2

In this example, everyday sampling was initiated following the first observed exceedance as required by 40 CFR 58.12. Accordingly, the first observed exceedance would not be adjusted for incomplete sampling. During the next three quarters, 1.2 exceedances were estimated. In this case, the estimated exceedances for the year would be 1.0 + 1.2 + 0.0 + 0.0 which equals 2.2. If, as before, no exceedances were observed for the two previous years, then the estimated exceedances for the 3-year period would then be (⅓) × (2.2 + 0.0 + 0.0) = 0.7, and the monitoring site would not fail the attainment test.

3.2 Adjustments for Non-Scheduled Sampling Days

(a) If a systematic sampling schedule is used and sampling is performed on days in addition to the days specified by the systematic sampling schedule, e.g., during episodes of high pollution, then an adjustment must be made in the equation for the estimation of exceedances. Such an adjustment is needed to eliminate the bias in the estimate of the quarterly and annual number of exceedances that would occur if the chance of an exceedance is different for scheduled than for non-scheduled days, as would be the case with episode sampling.

(b) The required adjustment treats the systematic sampling schedule as a stratified sampling plan. If the period from one scheduled sample until the day preceding the next scheduled sample is defined as a sampling stratum, then there is one stratum for each scheduled sampling day. An average number of observed exceedances is computed for each of these sampling strata. With nonscheduled sampling days, the estimated number of exceedances is defined as:

Equation 3

$$e_q = \left(\frac{N_q}{m_q}\right) \times \sum_{j=1}^{m_q} \left(\frac{v_j}{k_j}\right)$$

Where:

e_q = the estimated number of exceedances for the quarter;
N_q = the number of days in the quarter;
m_q = the number of strata with samples during the quarter;
v_j = the number of observed exceedances in stratum j; and
k_j = the number of actual samples in stratum j.

(c) Note that if only one sample value is recorded in each stratum, then Equation 3 reduces to Equation 1.

Example 3

A monitoring site samples according to a systematic sampling schedule of one sample every 6 days, for a total of 15 scheduled samples in a quarter out of a total of 92 possible samples. During one 6-day period, potential episode levels of PM_{10} were suspected, so 5 additional samples were taken. One of the regular scheduled samples was missed, so a total of 19 samples in 14 sampling strata were measured. The one 6-day sampling stratum with 6 samples recorded 2 exceedances. The remainder of the quarter with one sample per stratum recorded zero exceedances. Using Equation 3, the estimated number of exceedances for the quarter is:

Eq = (92/14) × (2/6 + 0 + . . . + 0) = 2.19.

[71 FR 61224, Oct. 17, 2006]

Appendix L to Part 50—Reference Method for the Determination of Fine Particulate Matter as $PM_{2.5}$ in the Atmosphere

1.0 *Applicability.*

1.1 This method provides for the measurement of the mass concentration of fine particulate matter having an aerodynamic diameter less than or equal to a nominal 2.5 micrometers ($PM_{2.5}$) in ambient air over a 24-hour period for purposes of determining whether the primary and secondary national ambient air quality standards for fine particulate matter specified in §50.7 and §50.13 of this part are met. The measurement process is considered to be nondestructive, and the $PM_{2.5}$ sample obtained can be subjected to subsequent physical or chemical analyses. Quality assessment procedures are provided in part 58, appendix A of this chapter, and quality assurance guidance are provided in references 1, 2, and 3 in section 13.0 of this appendix.

1.2 This method will be considered a reference method for purposes of part 58 of this chapter only if:

(a) The associated sampler meets the requirements specified in this appendix and the applicable requirements in part 53 of this chapter, and

(b) The method and associated sampler have been designated as a reference method in accordance with part 53 of this chapter.

1.3 $PM_{2.5}$ samplers that meet nearly all specifications set forth in this method but have minor deviations and/or modifications of the reference method sampler will be designated as ''Class I'' equivalent methods for $PM_{2.5}$ in accordance with part 53 of this chapter.

2.0 *Principle.*

2.1 An electrically powered air sampler draws ambient air at a constant volumetric flow rate into a specially shaped inlet and through an inertial particle size separator (impactor) where the suspended particulate matter in the $PM_{2.5}$ size range is separated for collection on a polytetrafluoroethylene (PTFE) filter over the specified sampling period. The air sampler and other aspects of this reference method are specified either explicitly in this appendix or generally with reference to other applicable regulations or quality assurance guidance.

2.2 Each filter is weighed (after moisture and temperature conditioning) before and after sample collection to determine the net gain due to collected $PM_{2.5}$. The total volume of air sampled is determined by the sampler from the measured flow rate at actual ambient temperature and pressure and the sampling time. The mass concentration of $PM_{2.5}$ in the ambient air is computed as the total mass of collected particles in the $PM_{2.5}$ size range divided by the actual volume of air sampled, and is expressed in micrograms per cubic meter of air ($\mu g/m^3$).

3.0 *$PM_{2.5}$ Measurement Range.*

3.1 *Lower concentration limit.* The lower detection limit of the mass concentration measurement range is estimated to be approximately 2 $\mu g/m^3$, based on noted mass changes in field blanks in conjunction with the 24 m^3 nominal total air sample volume specified for the 24-hour sample.

3.2 *Upper concentration limit.* The upper limit of the mass concentration range is determined by the filter mass loading beyond which the sampler can no longer maintain the operating flow rate within specified limits due to increased pressure drop across the loaded filter. This upper limit cannot be specified precisely because it is a complex function of the ambient particle size distribution and type, humidity, the individual filter used, the capacity of the sampler flow rate control system, and perhaps other factors. Nevertheless, all samplers are estimated to be capable of measuring 24-hour $PM_{2.5}$ mass concentrations of at least 200 $\mu g/m^3$ while maintaining the operating flow rate within the specified limits.

3.3 *Sample period.* The required sample period for $PM_{2.5}$ concentration measurements by this method shall be 1,380 to 1500 minutes (23 to 25 hours). However, when a sample period is less than 1,380 minutes, the measured concentration (as determined by the collected $PM_{2.5}$ mass divided by the actual sampled air volume), multiplied by the actual number of minutes in the sample period and divided by 1,440, may be used as if it were a valid concentration measurement for the specific purpose of determining a violation of the NAAQS. This value assumes that the $PM_{2.5}$ concentration is zero for the remaining portion of the sample period and therefore represents the minimum concentration that could have been measured for the full 24-hour sample period. Accordingly, if the value thus calculated is high enough to be an exceedance, such an exceedance would be a valid exceedance for the sample period. When reported to AIRS, this data value should receive a special code to identify it as not to be commingled with normal concentration measurements or used for other purposes.

4.0 *Accuracy.*

4.1 Because the size and volatility of the particles making up ambient particulate matter vary over a wide range and the mass concentration of particles varies with particle size, it is difficult to define the accuracy of $PM_{2.5}$ measurements in an absolute sense. The accuracy of $PM_{2.5}$ measurements is therefore defined in a relative sense, referenced to measurements provided by this reference method. Accordingly, accuracy shall be defined as the degree of agreement between a subject field $PM_{2.5}$ sampler and a collocated $PM_{2.5}$ reference method audit sampler operating simultaneously at the monitoring site location of the subject sampler and includes both random (precision) and systematic (bias) errors. The requirements for this field sampler audit procedure are set forth in part 58, appendix A of this chapter.

4.2 *Measurement system bias.* Results of collocated measurements where the duplicate sampler is a reference method sampler are used to assess a portion of the measurement system bias according to the schedule and procedure specified in part 58, appendix A of this chapter.

4.3 *Audits with reference method samplers to determine system accuracy and bias.* According to the schedule and procedure specified in part 58, appendix A of this chapter, a reference method sampler is required to be located at each of selected $PM_{2.5}$ SLAMS sites as a duplicate sampler. The results from the primary sampler and the duplicate reference method sampler are used to calculate accuracy of the primary sampler on a quarterly

basis, bias of the primary sampler on an annual basis, and bias of a single reporting organization on an annual basis. Reference 2 in section 13.0 of this appendix provides additional information and guidance on these reference method audits.

4.4 *Flow rate accuracy and bias.* Part 58, appendix A of this chapter requires that the flow rate accuracy and bias of individual $PM_{2.5}$ samplers used in SLAMS monitoring networks be assessed periodically via audits of each sampler's operational flow rate. In addition, part 58, appendix A of this chapter requires that flow rate bias for each reference and equivalent method operated by each reporting organization be assessed quarterly and annually. Reference 2 in section 13.0 of this appendix provides additional information and guidance on flow rate accuracy audits and calculations for accuracy and bias.

5.0 *Precision.* A data quality objective of 10 percent coefficient of variation or better has been established for the operational precision of $PM_{2.5}$ monitoring data.

5.1 Tests to establish initial operational precision for each reference method sampler are specified as a part of the requirements for designation as a reference method under §53.58 of this chapter.

5.2 *Measurement System Precision.* Collocated sampler results, where the duplicate sampler is not a reference method sampler but is a sampler of the same designated method as the primary sampler, are used to assess measurement system precision according to the schedule and procedure specified in part 58, appendix A of this chapter. Part 58, appendix A of this chapter requires that these collocated sampler measurements be used to calculate quarterly and annual precision estimates for each primary sampler and for each designated method employed by each reporting organization. Reference 2 in section 13.0 of this appendix provides additional information and guidance on this requirement.

6.0 *Filter for $PM_{2.5}$ Sample Collection.* Any filter manufacturer or vendor who sells or offers to sell filters specifically identified for use with this $PM_{2.5}$ reference method shall certify that the required number of filters from each lot of filters offered for sale as such have been tested as specified in this section 6.0 and meet all of the following design and performance specifications.

6.1 *Size.* Circular, 46.2 mm diameter ±0.25 mm.

6.2 *Medium.* Polytetrafluoroethylene (PTFE Teflon), with integral support ring.

6.3 *Support ring.* Polymethylpentene (PMP) or equivalent inert material, 0.38 ±0.04 mm thick, outer diameter 46.2 mm ±0.25 mm, and width of 3.68 mm (±0.00, −0.51 mm).

6.4 *Pore size.* 2 μm as measured by ASTM F 316–94.

6.5 *Filter thickness.* 30 to 50 μm.

6.6 *Maximum pressure drop (clean filter).* 30 cm H_2O column @ 16.67 L/min clean air flow.

6.7 *Maximum moisture pickup.* Not more than 10 μg weight increase after 24-hour exposure to air of 40 percent relative humidity, relative to weight after 24-hour exposure to air of 35 percent relative humidity.

6.8 *Collection efficiency.* Greater than 99.7 percent, as measured by the DOP test (ASTM D 2986–91) with 0.3 μm particles at the sampler's operating face velocity.

6.9 *Filter weight stability.* Filter weight loss shall be less than 20 μg, as measured in each of the following two tests specified in sections 6.9.1 and 6.9.2 of this appendix. The following conditions apply to both of these tests: Filter weight loss shall be the average difference between the initial and the final filter weights of a random sample of test filters selected from each lot prior to sale. The number of filters tested shall be not less than 0.1 percent of the filters of each manufacturing lot, or 10 filters, whichever is greater. The filters shall be weighed under laboratory conditions and shall have had no air sample passed through them, i.e., filter blanks. Each test procedure must include initial conditioning and weighing, the test, and final conditioning and weighing. Conditioning and weighing shall be in accordance with sections 8.0 through 8.2 of this appendix and general guidance provided in reference 2 of section 13.0 of this appendix.

6.9.1 *Test for loose, surface particle contamination.* After the initial weighing, install each test filter, in turn, in a filter cassette (Figures L–27, L–28, and L–29 of this appendix) and drop the cassette from a height of 25 cm to a flat hard surface, such as a particle-free wood bench. Repeat two times, for a total of three drop tests for each test filter. Remove the test filter from the cassette and weigh the filter. The average change in weight must be less than 20 μg.

6.9.2 *Test for temperature stability.* After weighing each filter, place the test filters in a drying oven set at 40 °C ±2 °C for not less than 48 hours. Remove, condition, and reweigh each test filter. The average change in weight must be less than 20 μg.

6.10 *Alkalinity.* Less than 25 microequivalents/gram of filter, as measured by the guidance given in reference 2 in section 13.0 of this appendix.

6.11 *Supplemental requirements.* Although not required for determination of $PM_{2.5}$ mass concentration under this reference method, additional specifications for the filter must be developed by users who intend to subject $PM_{2.5}$ filter samples to subsequent chemical analysis. These supplemental specifications include background chemical contamination of the filter and any other filter parameters that may be required by the method of chemical analysis. All such supplemental filter specifications must be compatible with and

secondary to the primary filter specifications given in this section 6.0 of this appendix.

7.0 *$PM_{2.5}$ Sampler*.

7.1 *Configuration*. The sampler shall consist of a sample air inlet, downtube, particle size separator (impactor), filter holder assembly, air pump and flow rate control system, flow rate measurement device, ambient and filter temperature monitoring system, barometric pressure measurement system, timer, outdoor environmental enclosure, and suitable mechanical, electrical, or electronic control capability to meet or exceed the design and functional performance as specified in this section 7.0 of this appendix. The performance specifications require that the sampler:

(a) Provide automatic control of sample volumetric flow rate and other operational parameters.

(b) Monitor these operational parameters as well as ambient temperature and pressure.

(c) Provide this information to the sampler operator at the end of each sample period in digital form, as specified in table L–1 of section 7.4.19 of this appendix.

7.2 *Nature of specifications*. The $PM_{2.5}$ sampler is specified by a combination of design and performance requirements. The sample inlet, downtube, particle size discriminator, filter cassette, and the internal configuration of the filter holder assembly are specified explicitly by design figures and associated mechanical dimensions, tolerances, materials, surface finishes, assembly instructions, and other necessary specifications. All other aspects of the sampler are specified by required operational function and performance, and the design of these other aspects (including the design of the lower portion of the filter holder assembly) is optional, subject to acceptable operational performance. Test procedures to demonstrate compliance with both the design and performance requirements are set forth in subpart E of part 53 of this chapter.

7.3 *Design specifications*. Except as indicated in this section 7.3 of this appendix, these components must be manufactured or reproduced exactly as specified, in an ISO 9001-registered facility, with registration initially approved and subsequently maintained during the period of manufacture. See §53.1(t) of this chapter for the definition of an ISO-registered facility. Minor modifications or variances to one or more components that clearly would not affect the aerodynamic performance of the inlet, downtube, impactor, or filter cassette will be considered for specific approval. Any such proposed modifications shall be described and submitted to the EPA for specific individual acceptability either as part of a reference or equivalent method application under part 53 of this chapter or in writing in advance of such an intended application under part 53 of this chapter.

7.3.1 *Sample inlet assembly*. The sample inlet assembly, consisting of the inlet, downtube, and impactor shall be configured and assembled as indicated in Figure L–1 of this appendix and shall meet all associated requirements. A portion of this assembly shall also be subject to the maximum overall sampler leak rate specification under section 7.4.6 of this appendix.

7.3.2 *Inlet*. The sample inlet shall be fabricated as indicated in Figures L–2 through L–18 of this appendix and shall meet all associated requirements.

7.3.3 *Downtube*. The downtube shall be fabricated as indicated in Figure L–19 of this appendix and shall meet all associated requirements.

7.3.4 *Particle size separator*. The sampler shall be configured with either one of the two alternative particle size separators described in this section 7.3.4. One separator is an impactor-type separator (WINS impactor) described in sections 7.3.4.1, 7.3.4.2, and 7.3.4.3 of this appendix. The alternative separator is a cyclone-type separator (VSCC™) described in section 7.3.4.4 of this appendix.

7.3.4.1 The impactor (particle size separator) shall be fabricated as indicated in Figures L–20 through L–24 of this appendix and shall meet all associated requirements. Following the manufacture and finishing of each upper impactor housing (Figure L–21 of this appendix), the dimension of the impaction jet must be verified by the manufacturer using Class ZZ go/no-go plug gauges that are traceable to NIST.

7.3.4.2 Impactor filter specifications:

(a) Size. Circular, 35 to 37 mm diameter.

(b) Medium. Borosilicate glass fiber, without binder.

(c) Pore size. 1 to 1.5 micrometer, as measured by ASTM F 316–80.

(d) Thickness. 300 to 500 micrometers.

7.3.4.3 Impactor oil specifications:

(a) Composition. Dioctyl sebacate (DOS), single-compound diffusion oil.

(b) Vapor pressure. Maximum 2×10^{-8} mm Hg at 25 °C.

(c) Viscosity. 36 to 40 centistokes at 25 °C.

(d) Density. 1.06 to 1.07 g/cm^3 at 25 °C.

(e) Quantity. 1 mL ±0.1 mL.

7.3.4.4 The cyclone-type separator is identified as a BGI VSCC™ Very Sharp Cut Cyclone particle size separator specified as part of EPA-designated equivalent method EQPM–0202–142 (67 FR 15567, April 2, 2002) and as manufactured by BGI Incorporated, 58 Guinan Street, Waltham, Massachusetts 20451.

7.3.5 *Filter holder assembly*. The sampler shall have a sample filter holder assembly to adapt and seal to the down tube and to hold and seal the specified filter, under section 6.0 of this appendix, in the sample air stream in a horizontal position below the downtube such that the sample air passes downward through the filter at a uniform face velocity.

The upper portion of this assembly shall be fabricated as indicated in Figures L–25 and L–26 of this appendix and shall accept and seal with the filter cassette, which shall be fabricated as indicated in Figures L–27 through L–29 of this appendix.

(a) The lower portion of the filter holder assembly shall be of a design and construction that:

(1) Mates with the upper portion of the assembly to complete the filter holder assembly,

(2) Completes both the external air seal and the internal filter cassette seal such that all seals are reliable over repeated filter changings, and

(3) Facilitates repeated changing of the filter cassette by the sampler operator.

(b) Leak-test performance requirements for the filter holder assembly are included in section 7.4.6 of this appendix.

(c) If additional or multiple filters are stored in the sampler as part of an automatic sequential sample capability, all such filters, unless they are currently and directly installed in a sampling channel or sampling configuration (either active or inactive), shall be covered or (preferably) sealed in such a way as to:

(1) Preclude significant exposure of the filter to possible contamination or accumulation of dust, insects, or other material that may be present in the ambient air, sampler, or sampler ventilation air during storage periods either before or after sampling; and

(2) To minimize loss of volatile or semivolatile PM sample components during storage of the filter following the sample period.

7.3.6 *Flow rate measurement adapter.* A flow rate measurement adapter as specified in Figure L–30 of this appendix shall be furnished with each sampler.

7.3.7 *Surface finish.* All internal surfaces exposed to sample air prior to the filter shall be treated electrolytically in a sulfuric acid bath to produce a clear, uniform anodized surface finish of not less than 1000 mg/ft^2 (1.08 mg/cm^2) in accordance with military standard specification (mil. spec.) 8625F, Type II, Class 1 in reference 4 of section 13.0 of this appendix. This anodic surface coating shall not be dyed or pigmented. Following anodization, the surfaces shall be sealed by immersion in boiling deionized water for not less than 15 minutes. Section 53.51(d)(2) of this chapter should also be consulted.

7.3.8 *Sampling height.* The sampler shall be equipped with legs, a stand, or other means to maintain the sampler in a stable, upright position and such that the center of the sample air entrance to the inlet, during sample collection, is maintained in a horizontal plane and is 2.0 ±0.2 meters above the floor or other horizontal supporting surface. Suitable bolt holes, brackets, tie-downs, or other means should be provided to facilitate mechanically securing the sample to the supporting surface to prevent toppling of the sampler due to wind.

7.4 *Performance specifications.*

7.4.1 *Sample flow rate.* Proper operation of the impactor requires that specific air velocities be maintained through the device. Therefore, the design sample air flow rate through the inlet shall be 16.67 L/min (1.000 m^3/hour) measured as actual volumetric flow rate at the temperature and pressure of the sample air entering the inlet.

7.4.2 *Sample air flow rate control system.* The sampler shall have a sample air flow rate control system which shall be capable of providing a sample air volumetric flow rate within the specified range, under section 7.4.1 of this appendix, for the specified filter, under section 6.0 of this appendix, at any atmospheric conditions specified, under section 7.4.7 of this appendix, at a filter pressure drop equal to that of a clean filter plus up to 75 cm water column (55 mm Hg), and over the specified range of supply line voltage, under section 7.4.15.1 of this appendix. This flow control system shall allow for operator adjustment of the operational flow rate of the sampler over a range of at least ±15 percent of the flow rate specified in section 7.4.1 of this appendix.

7.4.3 *Sample flow rate regulation.* The sample flow rate shall be regulated such that for the specified filter, under section 6.0 of this appendix, at any atmospheric conditions specified, under section 7.4.7 of this appendix, at a filter pressure drop equal to that of a clean filter plus up to 75 cm water column (55 mm Hg), and over the specified range of supply line voltage, under section 7.4.15.1 of this appendix, the flow rate is regulated as follows:

7.4.3.1 The volumetric flow rate, measured or averaged over intervals of not more than 5 minutes over a 24-hour period, shall not vary more than ±5 percent from the specified 16.67 L/min flow rate over the entire sample period.

7.4.3.2 The coefficient of variation (sample standard deviation divided by the mean) of the flow rate, measured over a 24-hour period, shall not be greater than 2 percent.

7.4.3.3 The amplitude of short-term flow rate pulsations, such as may originate from some types of vacuum pumps, shall be attenuated such that they do not cause significant flow measurement error or affect the collection of particles on the particle collection filter.

7.4.4 *Flow rate cut off.* The sampler's sample air flow rate control system shall terminate sample collection and stop all sample flow for the remainder of the sample period in the event that the sample flow rate deviates by more than 10 percent from the sampler design flow rate specified in section 7.4.1 of this appendix for more than 60 seconds. However, this sampler cut-off provision shall not apply during periods when the sampler is inoperative due to a temporary power interruption,

and the elapsed time of the inoperative period shall not be included in the total sample time measured and reported by the sampler, under section 7.4.13 of this appendix.

7.4.5 *Flow rate measurement.*

7.4.5.1 The sampler shall provide a means to measure and indicate the instantaneous sample air flow rate, which shall be measured as volumetric flow rate at the temperature and pressure of the sample air entering the inlet, with an accuracy of ±2 percent. The measured flow rate shall be available for display to the sampler operator at any time in either sampling or standby modes, and the measurement shall be updated at least every 30 seconds. The sampler shall also provide a simple means by which the sampler operator can manually start the sample flow temporarily during non-sampling modes of operation, for the purpose of checking the sample flow rate or the flow rate measurement system.

7.4.5.2 During each sample period, the sampler's flow rate measurement system shall automatically monitor the sample volumetric flow rate, obtaining flow rate measurements at intervals of not greater than 30 seconds.

(a) Using these interval flow rate measurements, the sampler shall determine or calculate the following flow-related parameters, scaled in the specified engineering units:

(1) The instantaneous or interval-average flow rate, in L/min.

(2) The value of the average sample flow rate for the sample period, in L/min.

(3) The value of the coefficient of variation (sample standard deviation divided by the average) of the sample flow rate for the sample period, in percent.

(4) The occurrence of any time interval during the sample period in which the measured sample flow rate exceeds a range of ±5 percent of the average flow rate for the sample period for more than 5 minutes, in which case a warning flag indicator shall be set.

(5) The value of the integrated total sample volume for the sample period, in m^3.

(b) Determination or calculation of these values shall properly exclude periods when the sampler is inoperative due to temporary interruption of electrical power, under section 7.4.13 of this appendix, or flow rate cut off, under section 7.4.4 of this appendix.

(c) These parameters shall be accessible to the sampler operator as specified in table L–1 of section 7.4.19 of this appendix. In addition, it is strongly encouraged that the flow rate for each 5-minute interval during the sample period be available to the operator following the end of the sample period.

7.4.6 *Leak test capability.*

7.4.6.1 *External leakage.* The sampler shall include an external air leak-test capability consisting of components, accessory hardware, operator interface controls, a written procedure in the associated Operation/Instruction Manual, under section 7.4.18 of this appendix, and all other necessary functional capability to permit and facilitate the sampler operator to conveniently carry out a leak test of the sampler at a field monitoring site without additional equipment. The sampler components to be subjected to this leak test include all components and their interconnections in which external air leakage would or could cause an error in the sampler's measurement of the total volume of sample air that passes through the sample filter.

(a) The suggested technique for the operator to use for this leak test is as follows:

(1) Remove the sampler inlet and installs the flow rate measurement adapter supplied with the sampler, under section 7.3.6 of this appendix.

(2) Close the valve on the flow rate measurement adapter and use the sampler air pump to draw a partial vacuum in the sampler, including (at least) the impactor, filter holder assembly (filter in place), flow measurement device, and interconnections between these devices, of at least 55 mm Hg (75 cm water column), measured at a location downstream of the filter holder assembly.

(3) Plug the flow system downstream of these components to isolate the components under vacuum from the pump, such as with a built-in valve.

(4) Stop the pump.

(5) Measure the trapped vacuum in the sampler with a built-in pressure measuring device.

(6) (i) Measure the vacuum in the sampler with the built-in pressure measuring device again at a later time at least 10 minutes after the first pressure measurement.

(ii) CAUTION: Following completion of the test, the adaptor valve should be opened slowly to limit the flow rate of air into the sampler. Excessive air flow rate may blow oil out of the impactor.

(7) Upon completion of the test, open the adaptor valve, remove the adaptor and plugs, and restore the sampler to the normal operating configuration.

(b) The associated leak test procedure shall require that for successful passage of this test, the difference between the two pressure measurements shall not be greater than the number of mm of Hg specified for the sampler by the manufacturer, based on the actual internal volume of the sampler, that indicates a leak of less than 80 mL/min.

(c) Variations of the suggested technique or an alternative external leak test technique may be required for samplers whose design or configuration would make the suggested technique impossible or impractical. The specific proposed external leak test procedure, or particularly an alternative leak

test technique, proposed for a particular candidate sampler may be described and submitted to the EPA for specific individual acceptability either as part of a reference or equivalent method application under part 53 of this chapter or in writing in advance of such an intended application under part 53 of this chapter.

7.4.6.2 *Internal, filter bypass leakage.* The sampler shall include an internal, filter bypass leak-check capability consisting of components, accessory hardware, operator interface controls, a written procedure in the Operation/Instruction Manual, and all other necessary functional capability to permit and facilitate the sampler operator to conveniently carry out a test for internal filter bypass leakage in the sampler at a field monitoring site without additional equipment. The purpose of the test is to determine that any portion of the sample flow rate that leaks past the sample filter without passing through the filter is insignificant relative to the design flow rate for the sampler.

(a) The suggested technique for the operator to use for this leak test is as follows:

(1) Carry out an external leak test as provided under section 7.4.6.1 of this appendix which indicates successful passage of the prescribed external leak test.

(2) Install a flow-impervious membrane material in the filter cassette, either with or without a filter, as appropriate, which effectively prevents air flow through the filter.

(3) Use the sampler air pump to draw a partial vacuum in the sampler, downstream of the filter holder assembly, of at least 55 mm Hg (75 cm water column).

(4) Plug the flow system downstream of the filter holder to isolate the components under vacuum from the pump, such as with a built-in valve.

(5) Stop the pump.

(6) Measure the trapped vacuum in the sampler with a built-in pressure measuring device.

(7) Measure the vacuum in the sampler with the built-in pressure measuring device again at a later time at least 10 minutes after the first pressure measurement.

(8) Remove the flow plug and membrane and restore the sampler to the normal operating configuration.

(b) The associated leak test procedure shall require that for successful passage of this test, the difference between the two pressure measurements shall not be greater than the number of mm of Hg specified for the sampler by the manufacturer, based on the actual internal volume of the portion of the sampler under vacuum, that indicates a leak of less than 80 mL/min.

(c) Variations of the suggested technique or an alternative internal, filter bypass leak test technique may be required for samplers whose design or configuration would make the suggested technique impossible or impractical. The specific proposed internal leak test procedure, or particularly an alternative internal leak test technique proposed for a particular candidate sampler may be described and submitted to the EPA for specific individual acceptability either as part of a reference or equivalent method application under part 53 of this chapter or in writing in advance of such intended application under part 53 of this chapter.

7.4.7 *Range of operational conditions.* The sampler is required to operate properly and meet all requirements specified in this appendix over the following operational ranges.

7.4.7.1 *Ambient temperature.* −30 to = 45 °C (Note: Although for practical reasons, the temperature range over which samplers are required to be tested under part 53 of this chapter is −20 to = 40 °C, the sampler shall be designed to operate properly over this wider temperature range.).

7.4.7.2 *Ambient relative humidity.* 0 to 100 percent.

7.4.7.3 *Barometric pressure range.* 600 to 800 mm Hg.

7.4.8 *Ambient temperature sensor.* The sampler shall have capability to measure the temperature of the ambient air surrounding the sampler over the range of −30 to = 45 °C, with a resolution of 0.1 °C and accuracy of ±2.0 °C, referenced as described in reference 3 in section 13.0 of this appendix, with and without maximum solar insolation.

7.4.8.1 The ambient temperature sensor shall be mounted external to the sampler enclosure and shall have a passive, naturally ventilated sun shield. The sensor shall be located such that the entire sun shield is at least 5 cm above the horizontal plane of the sampler case or enclosure (disregarding the inlet and downtube) and external to the vertical plane of the nearest side or protuberance of the sampler case or enclosure. The maximum temperature measurement error of the ambient temperature measurement system shall be less than 1.6 °C at 1 m/s wind speed and 1000 W/m2 solar radiation intensity.

7.4.8.2 The ambient temperature sensor shall be of such a design and mounted in such a way as to facilitate its convenient dismounting and immersion in a liquid for calibration and comparison to the filter temperature sensor, under section 7.4.11 of this appendix.

7.4.8.3 This ambient temperature measurement shall be updated at least every 30 seconds during both sampling and standby (non-sampling) modes of operation. A visual indication of the current (most recent) value of the ambient temperature measurement, updated at least every 30 seconds, shall be available to the sampler operator during both sampling and standby (non-sampling) modes of operation, as specified in table L–1 of section 7.4.19 of this appendix.

7.4.8.4 This ambient temperature measurement shall be used for the purpose of monitoring filter temperature deviation from ambient temperature, as required by section 7.4.11 of this appendix, and may be used for purposes of effecting filter temperature control, under section 7.4.10 of this appendix, or computation of volumetric flow rate, under sections 7.4.1 to 7.4.5 of this appendix, if appropriate.

7.4.8.5 Following the end of each sample period, the sampler shall report the maximum, minimum, and average temperature for the sample period, as specified in table L–1 of section 7.4.19 of this appendix.

7.4.9 *Ambient barometric sensor*. The sampler shall have capability to measure the barometric pressure of the air surrounding the sampler over a range of 600 to 800 mm Hg referenced as described in reference 3 in section 13.0 of this appendix; also see part 53, subpart E of this chapter. This barometric pressure measurement shall have a resolution of 5 mm Hg and an accuracy of ±10 mm Hg and shall be updated at least every 30 seconds. A visual indication of the value of the current (most recent) barometric pressure measurement, updated at least every 30 seconds, shall be available to the sampler operator during both sampling and standby (non-sampling) modes of operation, as specified in table L–1 of section 7.4.19 of this appendix. This barometric pressure measurement may be used for purposes of computation of volumetric flow rate, under sections 7.4.1 to 7.4.5 of this appendix, if appropriate. Following the end of a sample period, the sampler shall report the maximum, minimum, and mean barometric pressures for the sample period, as specified in table L–1 of section 7.4.19 of this appendix.

7.4.10 *Filter temperature control (sampling and post-sampling)*. The sampler shall provide a means to limit the temperature rise of the sample filter (all sample filters for sequential samplers), from insolation and other sources, to no more 5 °C above the temperature of the ambient air surrounding the sampler, during both sampling and post-sampling periods of operation. The post-sampling period is the non-sampling period between the end of the active sampling period and the time of retrieval of the sample filter by the sampler operator.

7.4.11 *Filter temperature sensor(s)*.

7.4.11.1 The sampler shall have the capability to monitor the temperature of the sample filter (all sample filters for sequential samplers) over the range of −30 to = 45 °C during both sampling and non-sampling periods. While the exact location of this temperature sensor is not explicitly specified, the filter temperature measurement system must demonstrate agreement, within 1 °C, with a test temperature sensor located within 1 cm of the center of the filter downstream of the filter during both sampling and non-sampling modes, as specified in the filter temperature measurement test described in part 53, subpart E of this chapter. This filter temperature measurement shall have a resolution of 0.1 °C and accuracy of ±1.0 °C, referenced as described in reference 3 in section 13.0 of this appendix. This temperature sensor shall be of such a design and mounted in such a way as to facilitate its reasonably convenient dismounting and immersion in a liquid for calibration and comparison to the ambient temperature sensor under section 7.4.8 of this appendix.

7.4.11.2 The filter temperature measurement shall be updated at least every 30 seconds during both sampling and standby (non-sampling) modes of operation. A visual indication of the current (most recent) value of the filter temperature measurement, updated at least every 30 seconds, shall be available to the sampler operator during both sampling and standby (non-sampling) modes of operation, as specified in table L–1 of section 7.4.19 of this appendix.

7.4.11.3 For sequential samplers, the temperature of each filter shall be measured individually unless it can be shown, as specified in the filter temperature measurement test described in §53.57 of this chapter, that the temperature of each filter can be represented by fewer temperature sensors.

7.4.11.4 The sampler shall also provide a warning flag indicator following any occurrence in which the filter temperature (any filter temperature for sequential samplers) exceeds the ambient temperature by more than 5 °C for more than 30 consecutive minutes during either the sampling or post-sampling periods of operation, as specified in table L–1 of section 7.4.19 of this appendix, under section 10.12 of this appendix, regarding sample validity when a warning flag occurs. It is further recommended (not required) that the sampler be capable of recording the maximum differential between the measured filter temperature and the ambient temperature and its time and date of occurrence during both sampling and post-sampling (non-sampling) modes of operation and providing for those data to be accessible to the sampler operator following the end of the sample period, as suggested in table L–1 of section 7.4.19 of this appendix.

7.4.12 *Clock/timer system*.

(a) The sampler shall have a programmable real-time clock timing/control system that:

(1) Is capable of maintaining local time and date, including year, month, day-of-month, hour, minute, and second to an accuracy of ±1.0 minute per month.

(2) Provides a visual indication of the current system time, including year, month, day-of-month, hour, and minute, updated at least each minute, for operator verification.

(3) Provides appropriate operator controls for setting the correct local time and date.

(4) Is capable of starting the sample collection period and sample air flow at a specific, operator-settable time and date, and stopping the sample air flow and terminating the sampler collection period 24 hours (1440 minutes) later, or at a specific, operator-settable time and date.

(b) These start and stop times shall be readily settable by the sampler operator to within ±1.0 minute. The system shall provide a visual indication of the current start and stop time settings, readable to ±1.0 minute, for verification by the operator, and the start and stop times shall also be available via the data output port, as specified in table L–1 of section 7.4.19 of this appendix. Upon execution of a programmed sample period start, the sampler shall automatically reset all sample period information and warning flag indications pertaining to a previous sample period. Refer also to section 7.4.15.4 of this appendix regarding retention of current date and time and programmed start and stop times during a temporary electrical power interruption.

7.4.13 *Sample time determination*. The sampler shall be capable of determining the elapsed sample collection time for each $PM_{2.5}$ sample, accurate to within ±1.0 minute, measured as the time between the start of the sampling period, under section 7.4.12 of this appendix and the termination of the sample period, under section 7.4.12 of this appendix or section 7.4.4 of this appendix. This elapsed sample time shall not include periods when the sampler is inoperative due to a temporary interruption of electrical power, under section 7.4.15.4 of this appendix. In the event that the elapsed sample time determined for the sample period is not within the range specified for the required sample period in section 3.3 of this appendix, the sampler shall set a warning flag indicator. The date and time of the start of the sample period, the value of the elapsed sample time for the sample period, and the flag indicator status shall be available to the sampler operator following the end of the sample period, as specified in table L–1 of section 7.4.19 of this appendix.

7.4.14 *Outdoor environmental enclosure*. The sampler shall have an outdoor enclosure (or enclosures) suitable to protect the filter and other non-weatherproof components of the sampler from precipitation, wind, dust, extremes of temperature and humidity; to help maintain temperature control of the filter (or filters, for sequential samplers); and to provide reasonable security for sampler components and settings.

7.4.15 *Electrical power supply*.

7.4.15.1 The sampler shall be operable and function as specified herein when operated on an electrical power supply voltage of 105 to 125 volts AC (RMS) at a frequency of 59 to 61 Hz. Optional operation as specified at additional power supply voltages and/or frequencies shall not be precluded by this requirement.

7.4.15.2 The design and construction of the sampler shall comply with all applicable National Electrical Code and Underwriters Laboratories electrical safety requirements.

7.4.15.3 The design of all electrical and electronic controls shall be such as to provide reasonable resistance to interference or malfunction from ordinary or typical levels of stray electromagnetic fields (EMF) as may be found at various monitoring sites and from typical levels of electrical transients or electronic noise as may often or occasionally be present on various electrical power lines.

7.4.15.4 In the event of temporary loss of electrical supply power to the sampler, the sampler shall not be required to sample or provide other specified functions during such loss of power, except that the internal clock/timer system shall maintain its local time and date setting within ±1 minute per week, and the sampler shall retain all other time and programmable settings and all data required to be available to the sampler operator following each sample period for at least 7 days without electrical supply power. When electrical power is absent at the operator-set time for starting a sample period or is interrupted during a sample period, the sampler shall automatically start or resume sampling when electrical power is restored, if such restoration of power occurs before the operator-set stop time for the sample period.

7.4.15.5 The sampler shall have the capability to record and retain a record of the year, month, day-of-month, hour, and minute of the start of each power interruption of more than 1 minute duration, up to 10 such power interruptions per sample period. (More than 10 such power interruptions shall invalidate the sample, except where an exceedance is measured, under section 3.3 of this appendix.) The sampler shall provide for these power interruption data to be available to the sampler operator following the end of the sample period, as specified in table L–1 of section 7.4.19 of this appendix.

7.4.16 *Control devices and operator interface*. The sampler shall have mechanical, electrical, or electronic controls, control devices, electrical or electronic circuits as necessary to provide the timing, flow rate measurement and control, temperature control, data storage and computation, operator interface, and other functions specified. Operator-accessible controls, data displays, and interface devices shall be designed to be simple, straightforward, reliable, and easy to learn, read, and operate under field conditions. The sampler shall have provision for operator input and storage of up to 64 characters of numeric (or alphanumeric) data for purposes of site, sampler, and sample identification. This information shall be available to the sampler operator for verification and

change and for output via the data output port along with other data following the end of a sample period, as specified in table L–1 of section 7.4.19 of this appendix. All data required to be available to the operator following a sample collection period or obtained during standby mode in a post-sampling period shall be retained by the sampler until reset, either manually by the operator or automatically by the sampler upon initiation of a new sample collection period.

7.4.17 *Data output port requirement.* The sampler shall have a standard RS–232C data output connection through which digital data may be exported to an external data storage or transmission device. All information which is required to be available at the end of each sample period shall be accessible through this data output connection. The information that shall be accessible though this output port is summarized in table L–1 of section 7.4.19 of this appendix. Since no specific format for the output data is provided, the sampler manufacturer or vendor shall make available to sampler purchasers appropriate computer software capable of receiving exported sampler data and correctly translating the data into a standard spreadsheet format and optionally any other formats as may be useful to sampler users. This requirement shall not preclude the sampler from offering other types of output connections in addition to the required RS–232C port.

7.4.18 *Operation/instruction manual.* The sampler shall include an associated comprehensive operation or instruction manual, as required by part 53 of this chapter, which includes detailed operating instructions on the setup, operation, calibration, and maintenance of the sampler. This manual shall provide complete and detailed descriptions of the operational and calibration procedures prescribed for field use of the sampler and all instruments utilized as part of this reference method. The manual shall include adequate warning of potential safety hazards that may result from normal use or malfunction of the method and a description of necessary safety precautions. The manual shall also include a clear description of all procedures pertaining to installation, operation, periodic and corrective maintenance, and troubleshooting, and shall include parts identification diagrams.

7.4.19 *Data reporting requirements.* The various information that the sampler is required to provide and how it is to be provided is summarized in the following table L–1.

TABLE L–1 TO APPENDIX L OF PART 50—SUMMARY OF INFORMATION TO BE PROVIDED BY THE SAMPLER

Information to be provided	Appendix L section reference	Availability			Format		
		Anytime [1]	End of period [2]	Visual display [3]	Data output [4]	Digital reading [5]	Units
Flow rate, 30-second maximum interval.	7.4.5.1	✓	.....	✓	*	XX.X	L/min
Flow rate, average for the sample period.	7.4.5.2	*	✓	*	✓	XX.X	L/min
Flow rate, CV, for sample period.	7.4.5.2	*	✓	*	✓	XX.X	%
Flow rate, 5-min. average out of spec. (FLAG [6]).	7.4.5.2	✓	✓	✓	✓■	On/Off	
Sample volume, total.	7.4.5.2	*	✓	✓	✓	XX.X	m^3
Temperature, ambient, 30-second interval.	7.4.8	✓	.....	✓	.....	XX.X	°C
Temperature, ambient, min., max., average for the sample period.	7.4.8	*	✓	✓	✓■	XX.X	°C
Baro. pressure, ambient, 30-second interval.	7.4.9	✓	.....	✓	.....	XXX	mm Hg
Baro. pressure, ambient, min., max., average for the sample period.	7.4.9	*	✓	✓	✓■	XXX	mm Hg
Filter temperature, 30-second interval.	7.4.11 ..	✓	.....	✓	.....	XX.X	°C

TABLE L–1 TO APPENDIX L OF PART 50—SUMMARY OF INFORMATION TO BE PROVIDED BY THE SAMPLER—Continued

Information to be provided	Appendix L section reference	Availability			Format		
		Anytime [1]	End of period [2]	Visual display [3]	Data output [4]	Digital reading [5]	Units
Filter temp. differential, 30-second interval, out of spec. (FLAG [6]).	7.4.11 ..	*	✓	✓	✓■	On/Off	
Filter temp., maximum differential from ambient, date, time of occurrence.	7.4.11 ..	*	*	*	*	X.X, YY/MM/DD HH.mm.	°C, Yr/Mon/Day Hrs. min
Date and Time	7.4.12 ..	✓	.....	✓	.....	YY/MM/DD HH.mm.	Yr/Mon/Day Hrs. min
Sample start and stop time settings.	7.4.12 ..	✓	✓	✓	✓	YY/MM/DD HH.mm.	Yr/Mon/Day Hrs. min
Sample period start time.	7.4.12 ..	.....	✓	✓	✓	YY/MM/DD HH.mm.	Yr/Mon/Day Hrs. min
Elapsed sample time.	7.4.13 ..	*	✓	✓	✓	HH.mm	Hrs. min
Elapsed sample time, out of spec. (FLAG [6]).	7.4.13 ..	.....	✓	✓	✓■	On/Off	
Power interruptions ≤1 min., start time of first 10.	7.4.15.5	*	✓	*	✓	1HH.mm, 2HH.mm, etc..	Hrs. min
User-entered information, such as sampler and site identification.	7.4.16 ..	✓	✓	✓	✓■	As entered.	

✓ Provision of this information is required.
* Provision of this information is optional. If information related to the entire sample period is optionally provided prior to the end of the sample period, the value provided should be the value calculated for the portion of the sampler period completed up to the time the information is provided.
■ Indicates that this information is also required to be provided to the Air Quality System (AQS) data bank; see §58.16 of this chapter. For ambient temperature and barometric pressure, only the average for the sample period must be reported.
1. Information is required to be available to the operator at any time the sampler is operating, whether sampling or not.
2. Information relates to the entire sampler period and must be provided following the end of the sample period until reset manually by the operator or automatically by the sampler upon the start of a new sample period.
3. Information shall be available to the operator visually.
4. Information is to be available as digital data at the sampler's data output port specified in section 7.4.16 of this appendix following the end of the sample period until reset manually by the operator or automatically by the sampler upon the start of a new sample period.
5. Digital readings, both visual and data output, shall have not less than the number of significant digits and resolution specified.
6. Flag warnings may be displayed to the operator by a single flag indicator or each flag may be displayed individually. Only a set (on) flag warning must be indicated; an off (unset) flag may be indicated by the absence of a flag warning. Sampler users should refer to section 10.12 of this appendix regarding the validity of samples for which the sampler provided an associated flag warning.

8.0 *Filter Weighing*. See reference 2 in section 13.0 of this appendix, for additional, more detailed guidance.

8.1 *Analytical balance*. The analytical balance used to weigh filters must be suitable for weighing the type and size of filters specified, under section 6.0 of this appendix, and have a readability of ±1 µg. The balance shall be calibrated as specified by the manufacturer at installation and recalibrated immediately prior to each weighing session. See reference 2 in section 13.0 of this appendix for additional guidance.

8.2 *Filter conditioning*. All sample filters used shall be conditioned immediately before both the pre- and post-sampling weighings as specified below. See reference 2 in section 13.0 of this appendix for additional guidance.

8.2.1 *Mean temperature*. 20 - 23 °C.

8.2.2 *Temperature control*. ±2 °C over 24 hours.

8.2.3 *Mean humidity*. Generally, 30–40 percent relative humidity; however, where it can be shown that the mean ambient relative humidity during sampling is less than 30 percent, conditioning is permissible at a mean

relative humidity within ±5 relative humidity percent of the mean ambient relative humidity during sampling, but not less than 20 percent.

8.2.4 *Humidity control.* ±5 relative humidity percent over 24 hours.

8.2.5 *Conditioning time.* Not less than 24 hours.

8.3 *Weighing procedure.*

8.3.1 New filters should be placed in the conditioning environment immediately upon arrival and stored there until the pre-sampling weighing. See reference 2 in section 13.0 of this appendix for additional guidance.

8.3.2 The analytical balance shall be located in the same controlled environment in which the filters are conditioned. The filters shall be weighed immediately following the conditioning period without intermediate or transient exposure to other conditions or environments.

8.3.3 Filters must be conditioned at the same conditions (humidity within ±5 relative humidity percent) before both the pre- and post-sampling weighings.

8.3.4 Both the pre- and post-sampling weighings should be carried out on the same analytical balance, using an effective technique to neutralize static charges on the filter, under reference 2 in section 13.0 of this appendix. If possible, both weighings should be carried out by the same analyst.

8.3.5 The pre-sampling (tare) weighing shall be within 30 days of the sampling period.

8.3.6 The post-sampling conditioning and weighing shall be completed within 240 hours (10 days) after the end of the sample period, unless the filter sample is maintained at temperatures below the average ambient temperature during sampling (or 4 °C or below for average sampling temperatures less than 4 °C) during the time between retrieval from the sampler and the start of the conditioning, in which case the period shall not exceed 30 days. Reference 2 in section 13.0 of this appendix has additional guidance on transport of cooled filters.

8.3.7 *Filter blanks.*

8.3.7.1 New field blank filters shall be weighed along with the pre-sampling (tare) weighing of each lot of $PM_{2.5}$ filters. These blank filters shall be transported to the sampling site, installed in the sampler, retrieved from the sampler without sampling, and reweighed as a quality control check.

8.3.7.2 New laboratory blank filters shall be weighed along with the pre-sampling (tare) weighing of each set of $PM_{2.5}$ filters. These laboratory blank filters should remain in the laboratory in protective containers during the field sampling and should be reweighed as a quality control check.

8.3.8 Additional guidance for proper filter weighing and related quality assurance activities is provided in reference 2 in section 13.0 of this appendix.

9.0 *Calibration.* Reference 2 in section 13.0 of this appendix contains additional guidance.

9.1 *General requirements.*

9.1.1 Multipoint calibration and single-point verification of the sampler's flow rate measurement device must be performed periodically to establish and maintain traceability of subsequent flow measurements to a flow rate standard.

9.1.2 An authoritative flow rate standard shall be used for calibrating or verifying the sampler's flow rate measurement device with an accuracy of ±2 percent. The flow rate standard shall be a separate, stand-alone device designed to connect to the flow rate measurement adapter, Figure L–30 of this appendix. This flow rate standard must have its own certification and be traceable to a National Institute of Standards and Technology (NIST) primary standard for volume or flow rate. If adjustments to the sampler's flow rate measurement system calibration are to be made in conjunction with an audit of the sampler's flow measurement system, such adjustments shall be made following the audit. Reference 2 in section 13.0 of this appendix contains additional guidance.

9.1.3 The sampler's flow rate measurement device shall be re-calibrated after electromechanical maintenance or transport of the sampler.

9.2 *Flow rate calibration/verification procedure.*

9.2.1 $PM_{2.5}$ samplers may employ various types of flow control and flow measurement devices. The specific procedure used for calibration or verification of the flow rate measurement device will vary depending on the type of flow rate controller and flow rate measurement employed. Calibration shall be in terms of actual ambient volumetric flow rates (Q^a), measured at the sampler's inlet downtube. The generic procedure given here serves to illustrate the general steps involved in the calibration of a $PM_{2.5}$ sampler. The sampler operation/instruction manual required under section 7.4.18 of this appendix and the Quality Assurance Handbook in reference 2 in section 13.0 of this appendix provide more specific and detailed guidance for calibration.

9.2.2 The flow rate standard used for flow rate calibration shall have its own certification and be traceable to a NIST primary standard for volume or flow rate. A calibration relationship for the flow rate standard, e.g., an equation, curve, or family of curves relating actual flow rate (Q_a) to the flow rate indicator reading, shall be established that is accurate to within 2 percent over the expected range of ambient temperatures and pressures at which the flow rate standard may be used. The flow rate standard must be re-calibrated or re-verified at least annually.

9.2.3 The sampler flow rate measurement device shall be calibrated or verified by removing the sampler inlet and connecting the

flow rate standard to the sampler's downtube in accordance with the operation/instruction manual, such that the flow rate standard accurately measures the sampler's flow rate. The sampler operator shall first carry out a sampler leak check and confirm that the sampler passes the leak test and then verify that no leaks exist between the flow rate standard and the sampler.

9.2.4 The calibration relationship between the flow rate (in actual L/min) indicated by the flow rate standard and by the sampler's flow rate measurement device shall be established or verified in accordance with the sampler operation/instruction manual. Temperature and pressure corrections to the flow rate indicated by the flow rate standard may be required for certain types of flow rate standards. Calibration of the sampler's flow rate measurement device shall consist of at least three separate flow rate measurements (multipoint calibration) evenly spaced within the range of −10 percent to = 10 percent of the sampler's operational flow rate, section 7.4.1 of this appendix. Verification of the sampler's flow rate shall consist of one flow rate measurement at the sampler's operational flow rate. The sampler operation/instruction manual and reference 2 in section 13.0 of this appendix provide additional guidance.

9.2.5 If during a flow rate verification the reading of the sampler's flow rate indicator or measurement device differs by ±4 percent or more from the flow rate measured by the flow rate standard, a new multipoint calibration shall be performed and the flow rate verification must then be repeated.

9.2.6 Following the calibration or verification, the flow rate standard shall be removed from the sampler and the sampler inlet shall be reinstalled. Then the sampler's normal operating flow rate (in L/min) shall be determined with a clean filter in place. If the flow rate indicated by the sampler differs by ±2 percent or more from the required sampler flow rate, the sampler flow rate must be adjusted to the required flow rate, under section 7.4.1 of this appendix.

9.3 Periodic calibration or verification of the calibration of the sampler's ambient temperature, filter temperature, and barometric pressure measurement systems is also required. Reference 3 of section 13.0 of this appendix contains additional guidance.

10.0 *$PM_{2.5}$ Measurement Procedure.* The detailed procedure for obtaining valid $PM_{2.5}$ measurements with each specific sampler designated as part of a reference method for $PM_{2.5}$ under part 53 of this chapter shall be provided in the sampler-specific operation or instruction manual required by section 7.4.18 of this appendix. Supplemental guidance is provided in section 2.12 of the Quality Assurance Handbook listed in reference 2 in section 13.0 of this appendix. The generic procedure given here serves to illustrate the general steps involved in the $PM_{2.5}$ sample collection and measurement, using a $PM_{2.5}$ reference method sampler.

10.1 The sampler shall be set up, calibrated, and operated in accordance with the specific, detailed guidance provided in the specific sampler's operation or instruction manual and in accordance with a specific quality assurance program developed and established by the user, based on applicable supplementary guidance provided in reference 2 in section 13.0 of this appendix.

10.2 Each new sample filter shall be inspected for correct type and size and for pinholes, particles, and other imperfections. Unacceptable filters should be discarded. A unique identification number shall be assigned to each filter, and an information record shall be established for each filter. If the filter identification number is not or cannot be marked directly on the filter, alternative means, such as a number-identified storage container, must be established to maintain positive filter identification.

10.3 Each filter shall be conditioned in the conditioning environment in accordance with the requirements specified in section 8.2 of this appendix.

10.4 Following conditioning, each filter shall be weighed in accordance with the requirements specified in section 8.0 of this appendix and the presampling weight recorded with the filter identification number.

10.5 A numbered and preweighed filter shall be installed in the sampler following the instructions provided in the sampler operation or instruction manual.

10.6 The sampler shall be checked and prepared for sample collection in accordance with instructions provided in the sampler operation or instruction manual and with the specific quality assurance program established for the sampler by the user.

10.7 The sampler's timer shall be set to start the sample collection at the beginning of the desired sample period and stop the sample collection 24 hours later.

10.8 Information related to the sample collection (site location or identification number, sample date, filter identification number, and sampler model and serial number) shall be recorded and, if appropriate, entered into the sampler.

10.9 The sampler shall be allowed to collect the $PM_{2.5}$ sample during the set 24-hour time period.

10.10 Within 177 hours (7 days, 9 hours) of the end of the sample collection period, the filter, while still contained in the filter cassette, shall be carefully removed from the sampler, following the procedure provided in the sampler operation or instruction manual and the quality assurance program, and placed in a protective container. The protective container shall contain no loose material that could be transferred to the filter. The protective container shall hold the filter

cassette securely such that the cover shall not come in contact with the filter's surfaces. Reference 2 in section 13.0 of this appendix contains additional information.

10.11 The total sample volume in actual m^3 for the sampling period and the elapsed sample time shall be obtained from the sampler and recorded in accordance with the instructions provided in the sampler operation or instruction manual. All sampler warning flag indications and other information required by the local quality assurance program shall also be recorded.

10.12 All factors related to the validity or representativeness of the sample, such as sampler tampering or malfunctions, unusual meteorological conditions, construction activity, fires or dust storms, etc. shall be recorded as required by the local quality assurance program. The occurrence of a flag warning during a sample period shall not necessarily indicate an invalid sample but rather shall indicate the need for specific review of the QC data by a quality assurance officer to determine sample validity.

10.13 After retrieval from the sampler, the exposed filter containing the $PM_{2.5}$ sample should be transported to the filter conditioning environment as soon as possible, ideally to arrive at the conditioning environment within 24 hours for conditioning and subsequent weighing. During the period between filter retrieval from the sampler and the start of the conditioning, the filter shall be maintained as cool as practical and continuously protected from exposure to temperatures over 25 °C to protect the integrity of the sample and minimize loss of volatile components during transport and storage. See section 8.3.6 of this appendix regarding time limits for completing the post-sampling weighing. See reference 2 in section 13.0 of this appendix for additional guidance on transporting filter samplers to the conditioning and weighing laboratory.

10.14. The exposed filter containing the $PM_{2.5}$ sample shall be re-conditioned in the conditioning environment in accordance with the requirements specified in section 8.2 of this appendix.

10.15. The filter shall be reweighed immediately after conditioning in accordance with the requirements specified in section 8.0 of this appendix, and the postsampling weight shall be recorded with the filter identification number.

10.16 The $PM_{2.5}$ concentration shall be calculated as specified in section 12.0 of this appendix.

11.0 *Sampler Maintenance.* The sampler shall be maintained as described by the sampler's manufacturer in the sampler-specific operation or instruction manual required under section 7.4.18 of this appendix and in accordance with the specific quality assurance program developed and established by the user based on applicable supplementary guidance provided in reference 2 in section 13.0 of this appendix.

12.0 *Calculations*

12.1 (a) The $PM_{2.5}$ concentration is calculated as:

$$PM_{2.5} = (W_f - W_i)/V_a$$

where:

$PM_{2.5}$ = mass concentration of $PM_{2.5}$, $\mu g/m^3$;

W_f, W_i = final and initial weights, respectively, of the filter used to collect the $PM_{2.5}$ particle sample, µg;

V_a = total air volume sampled in actual volume units, as provided by the sampler, m^3.

NOTE: Total sample time must be between 1,380 and 1,500 minutes (23 and 25 hrs) for a fully valid $PM_{2.5}$ sample; however, see also section 3.3 of this appendix.

13.0 *References.*

1. Quality Assurance Handbook for Air Pollution Measurement Systems, Volume I, Principles. EPA/600/R–94/038a, April 1994. Available from CERI, ORD Publications, U.S. Environmental Protection Agency, 26 West Martin Luther King Drive, Cincinnati, Ohio 45268.

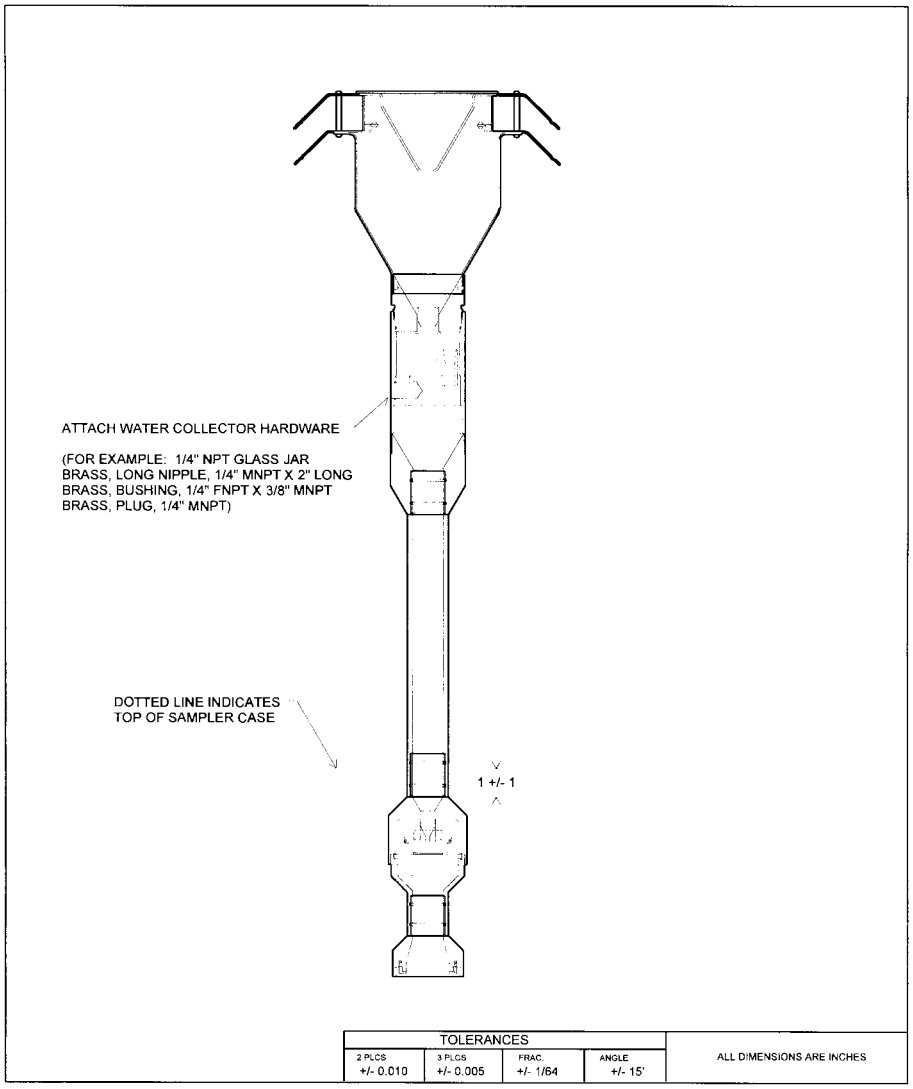
2. Quality Assurance Guidance Document 2.12. Monitoring $PM_{2.5}$ in Ambient Air Using Designated Reference or Class I Equivalent Methods. U.S. EPA, National Exposure Research Laboratory. Research Triangle Park, NC, November 1988 or later edition. Currently available at: *http://www.epa.gov/ttn/amtic/pmqainf.html*.

3. Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV: Meteorological Measurements, (Revised Edition) EPA/600/R–94/038d, March, 1995. Available from CERI, ORD Publications, U.S. Environmental Protection Agency, 26 West Martin Luther King Drive, Cincinnati, Ohio 45268.

4. Military standard specification (mil. spec.) 8625F, Type II, Class 1 as listed in Department of Defense Index of Specifications and Standards (DODISS), available from DODSSP-Customer Service, Standardization Documents Order Desk, 700 Robbins Avenue, Building 4D, Philadelphia, PA 1911–5094.

14.0 *Figures L–1 through L–30 to Appendix L.*

FIGURE L-1. PM2.5 SAMPLER, ASSEMBLY



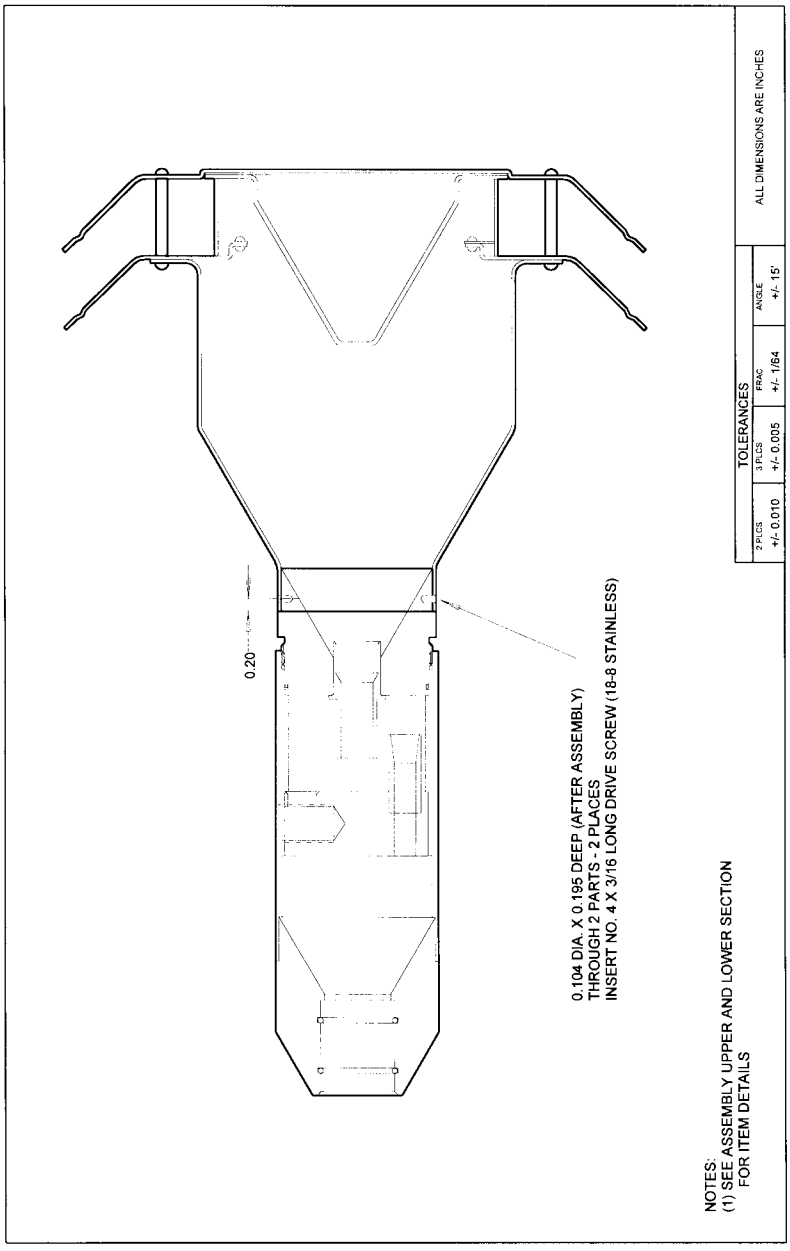


FIGURE L-2. 10-MICRON INLET, ASSEMBLY

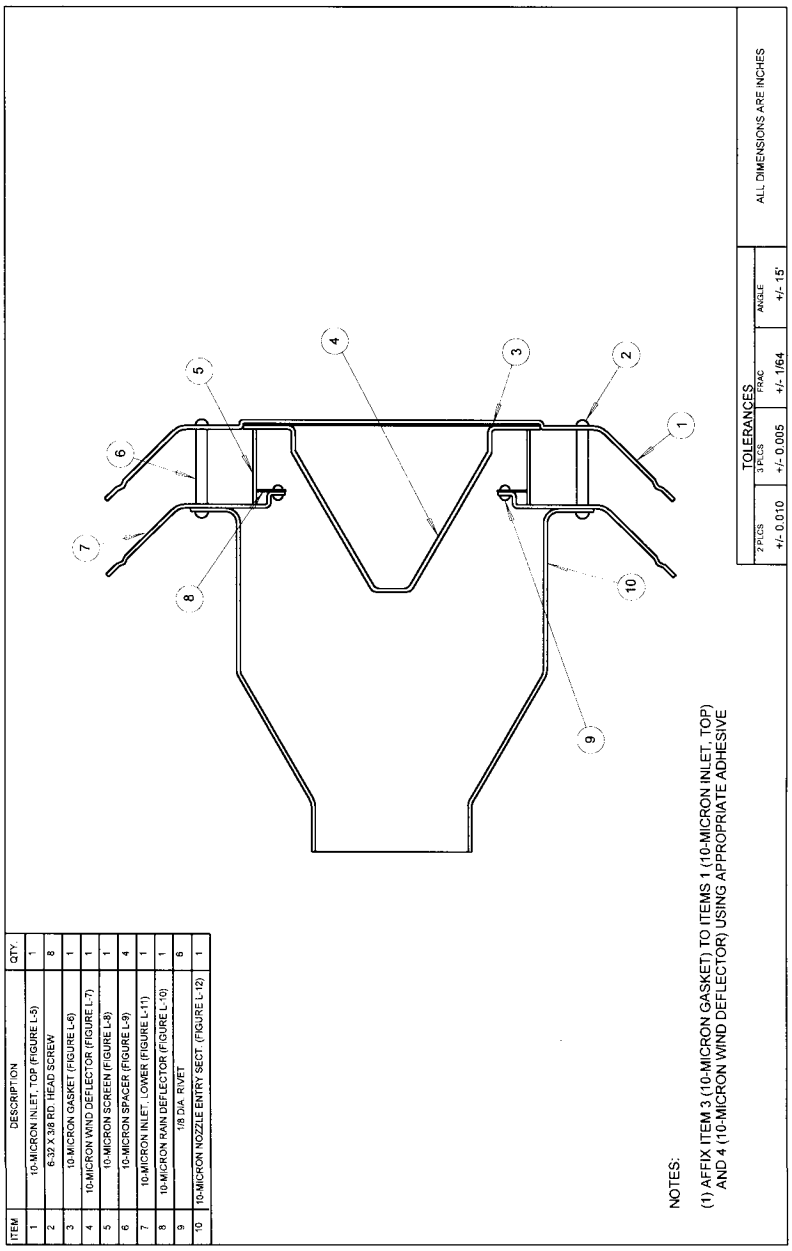
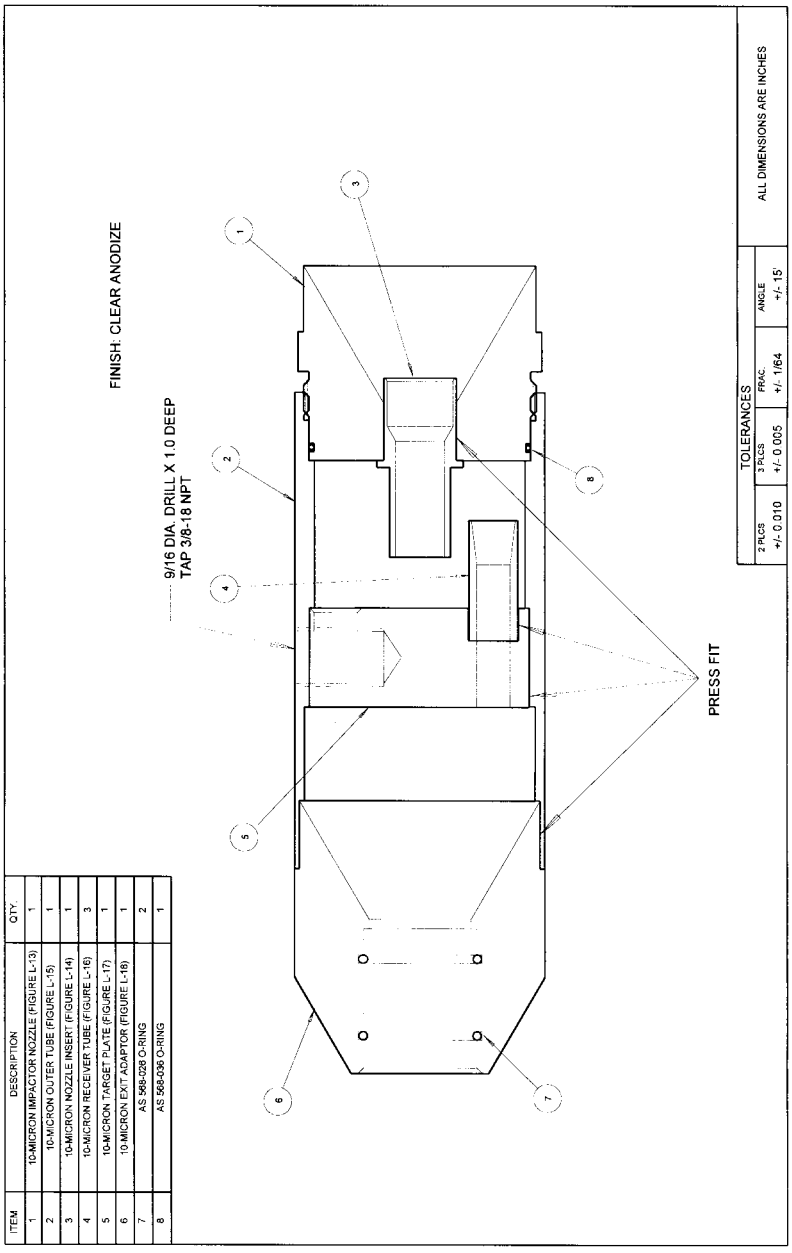


FIGURE L-3. 10-MICRON ASSEMBLY, UPPER SECTION



ITEM	DESCRIPTION	QTY.
1	10-MICRON IMPACTOR NOZZLE (FIGURE L-13)	1
2	10-MICRON OUTER TUBE (FIGURE L-15)	1
3	10-MICRON NOZZLE INSERT (FIGURE L-14)	1
4	10-MICRON RECEIVER TUBE (FIGURE L-16)	3
5	10-MICRON TARGET PLATE (FIGURE L-17)	1
6	10-MICRON EXIT ADAPTOR (FIGURE L-18)	1
7	AS 568-028 O-RING	2
8	AS 568-036 O-RING	1

FIGURE L-4. 10-MICRON ASSEMBLY, LOWER SECTION

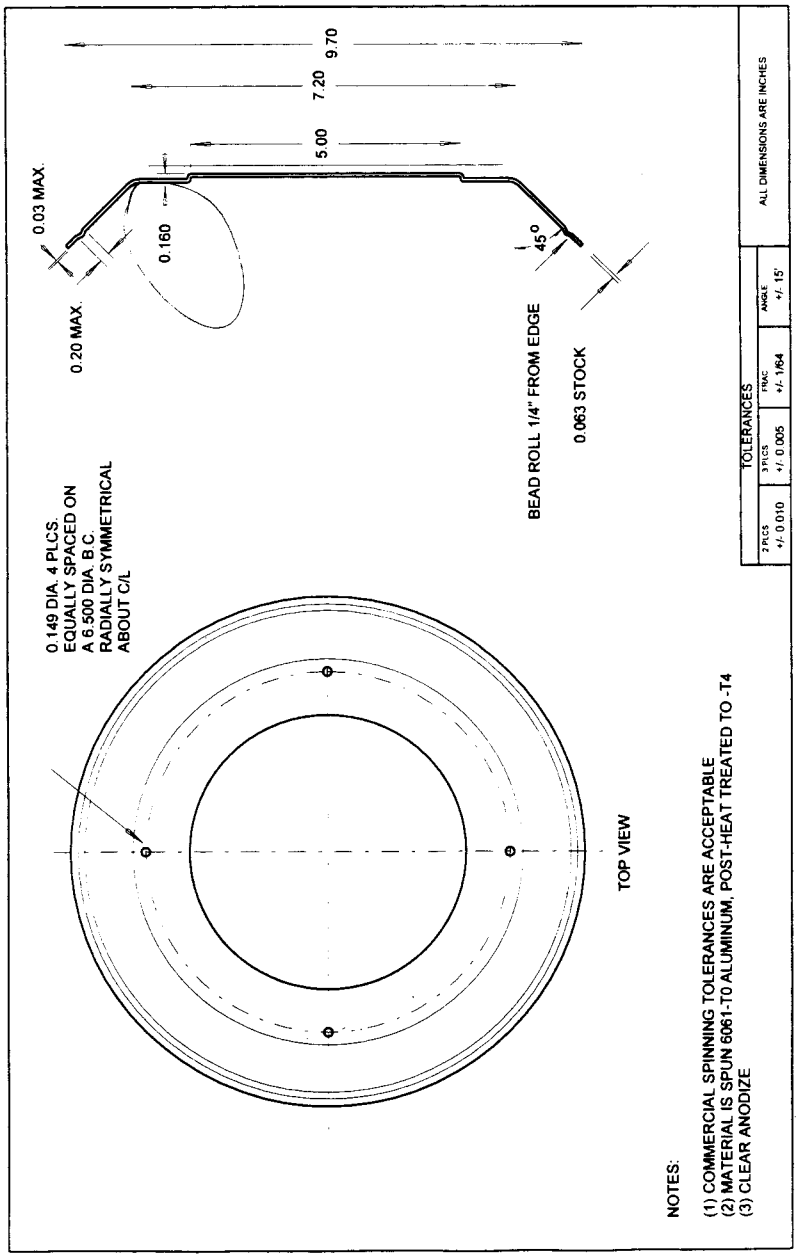


FIGURE L-5. 10-MICRON INLET, TOP

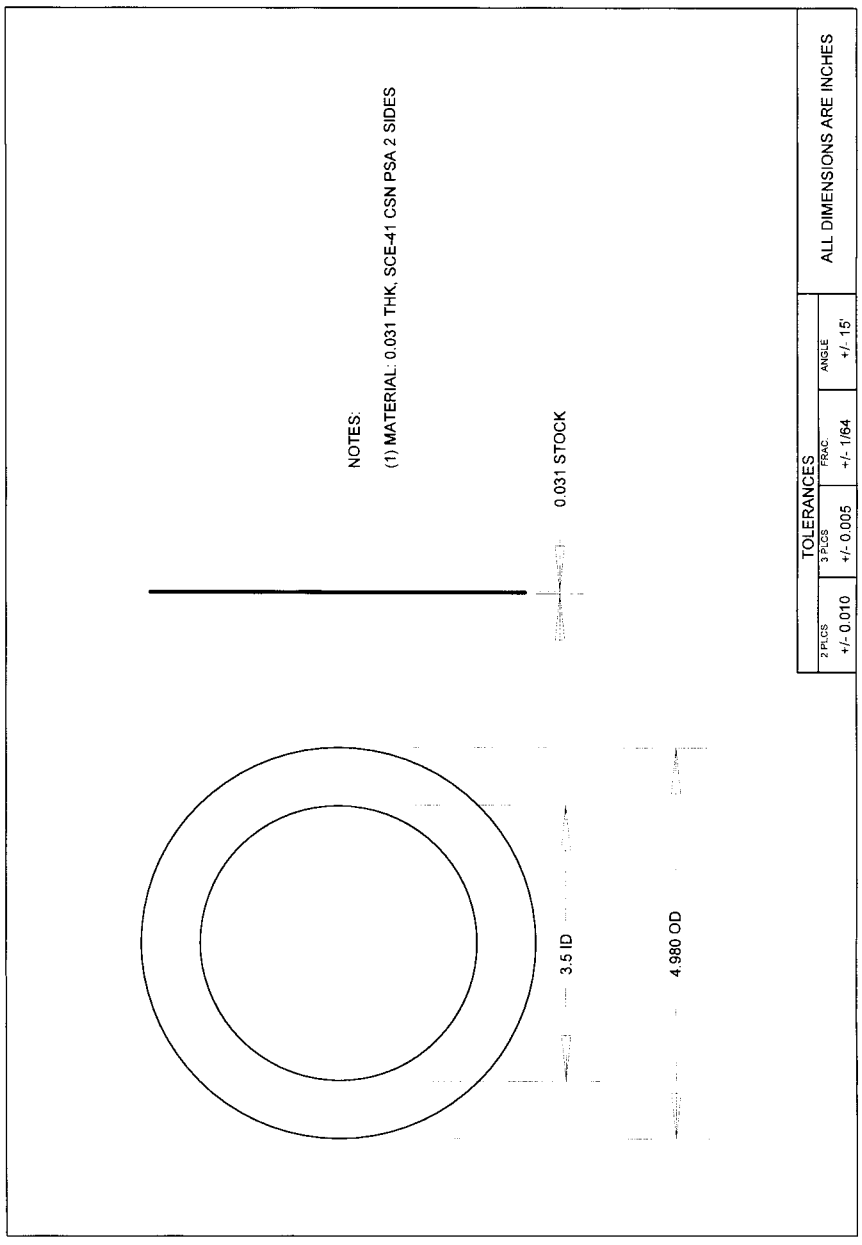


FIGURE L-6. 10-MICRON GASKET

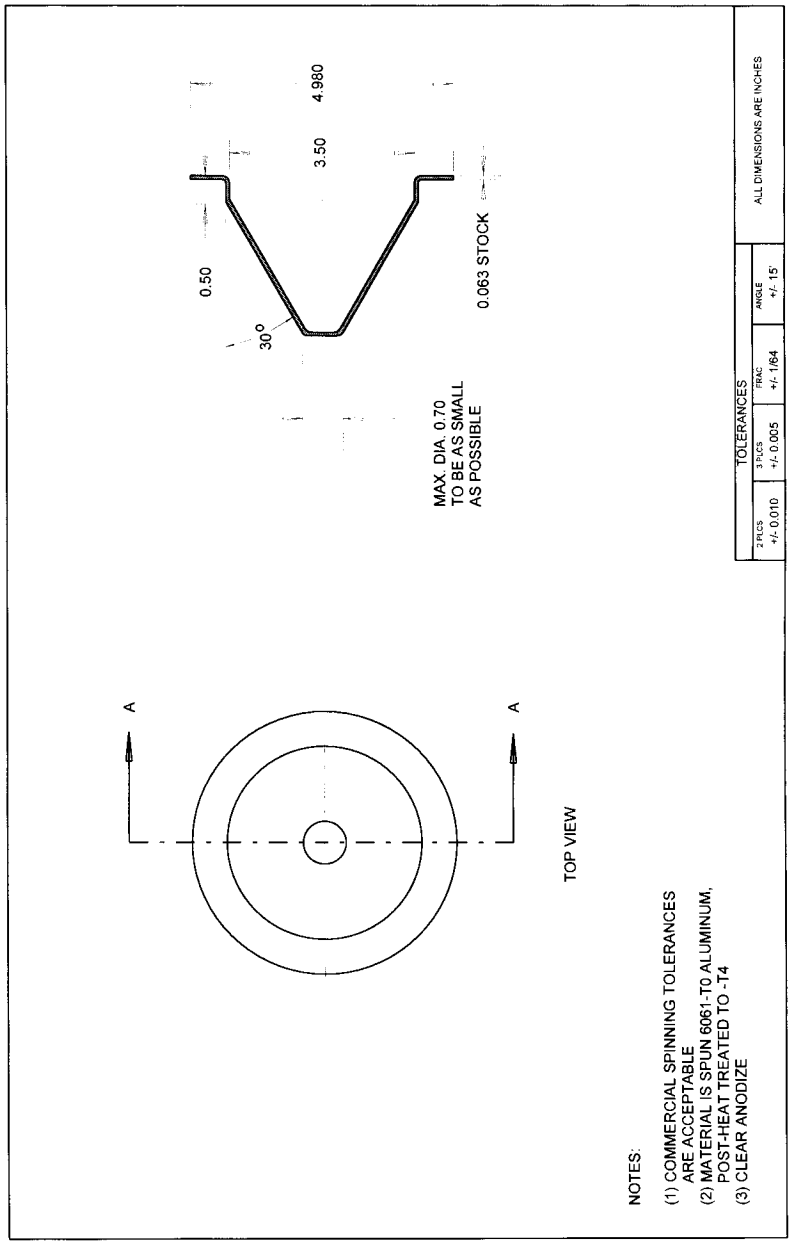


FIGURE L-7. 10-MICRON WIND DEFLECTOR

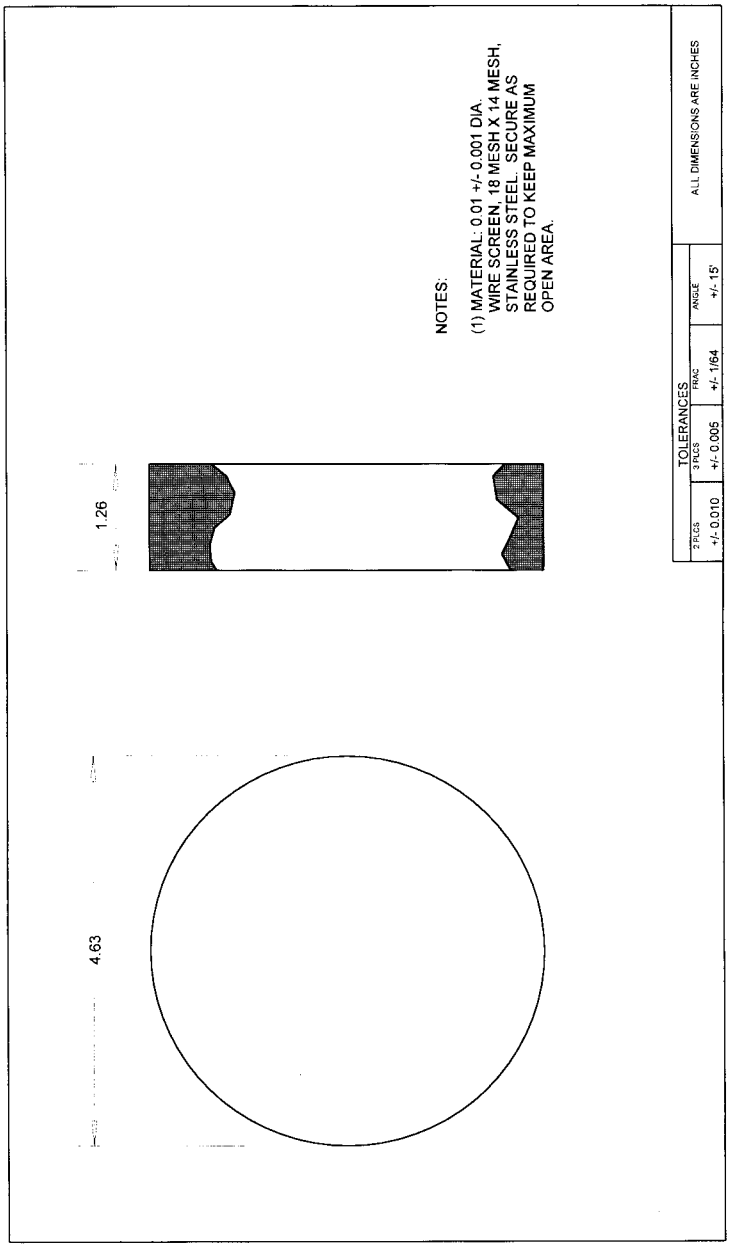


FIGURE L-8. 10-MICRON SCREEN

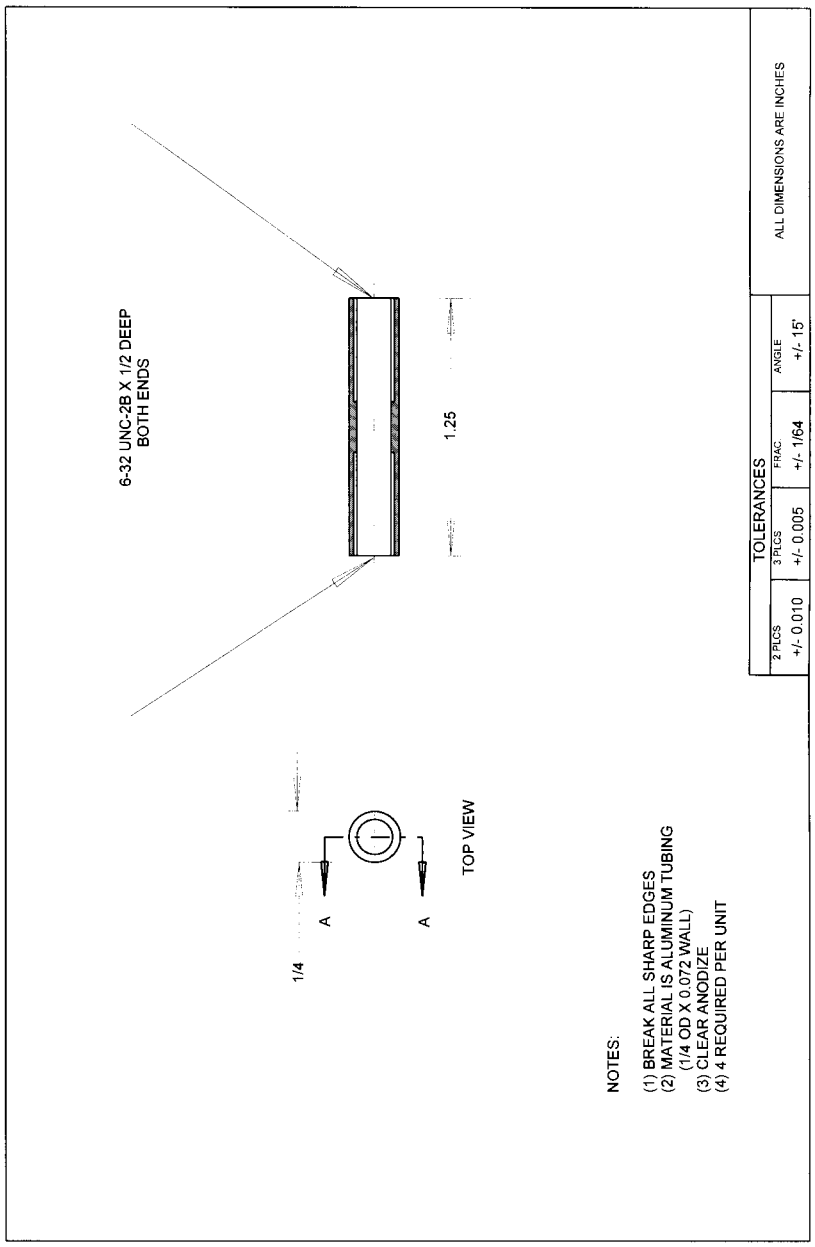


FIGURE L-9. 10-MICRON SPACER

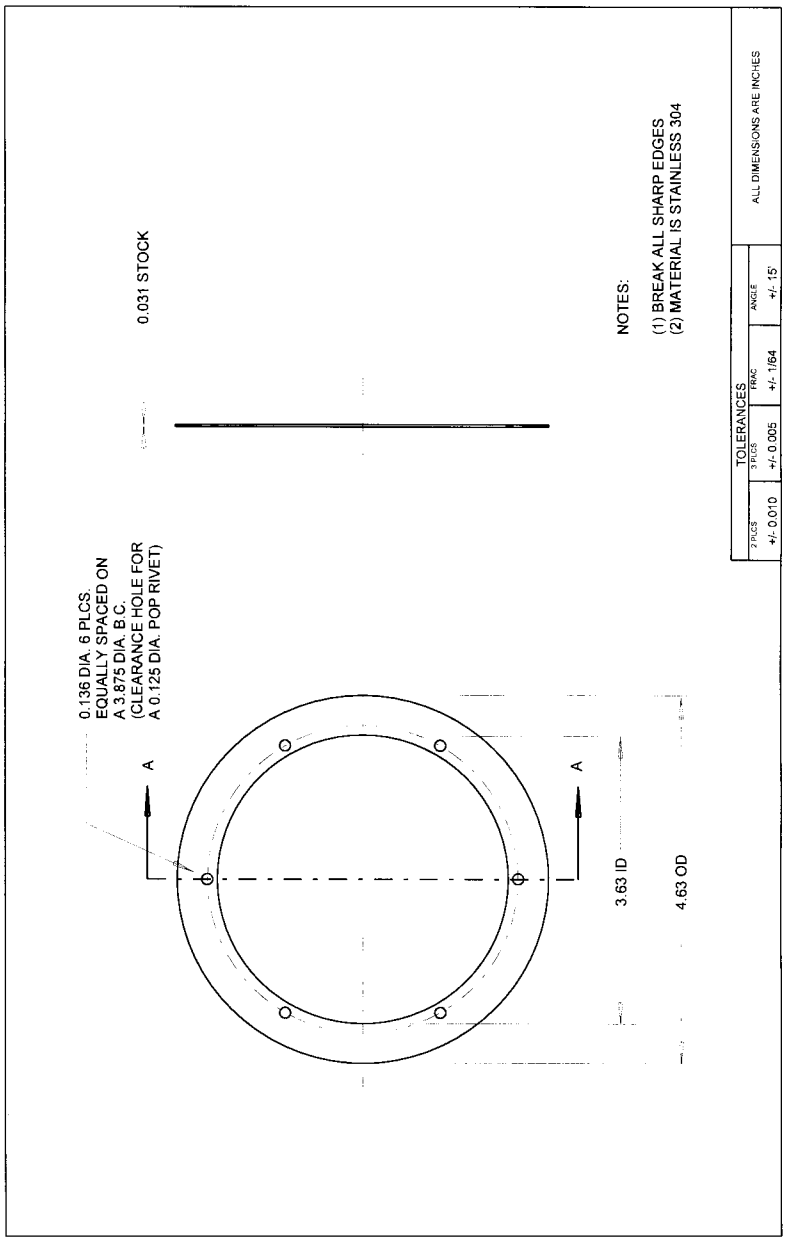


FIGURE L-10. 10-MICRON RAIN DEFLECTOR

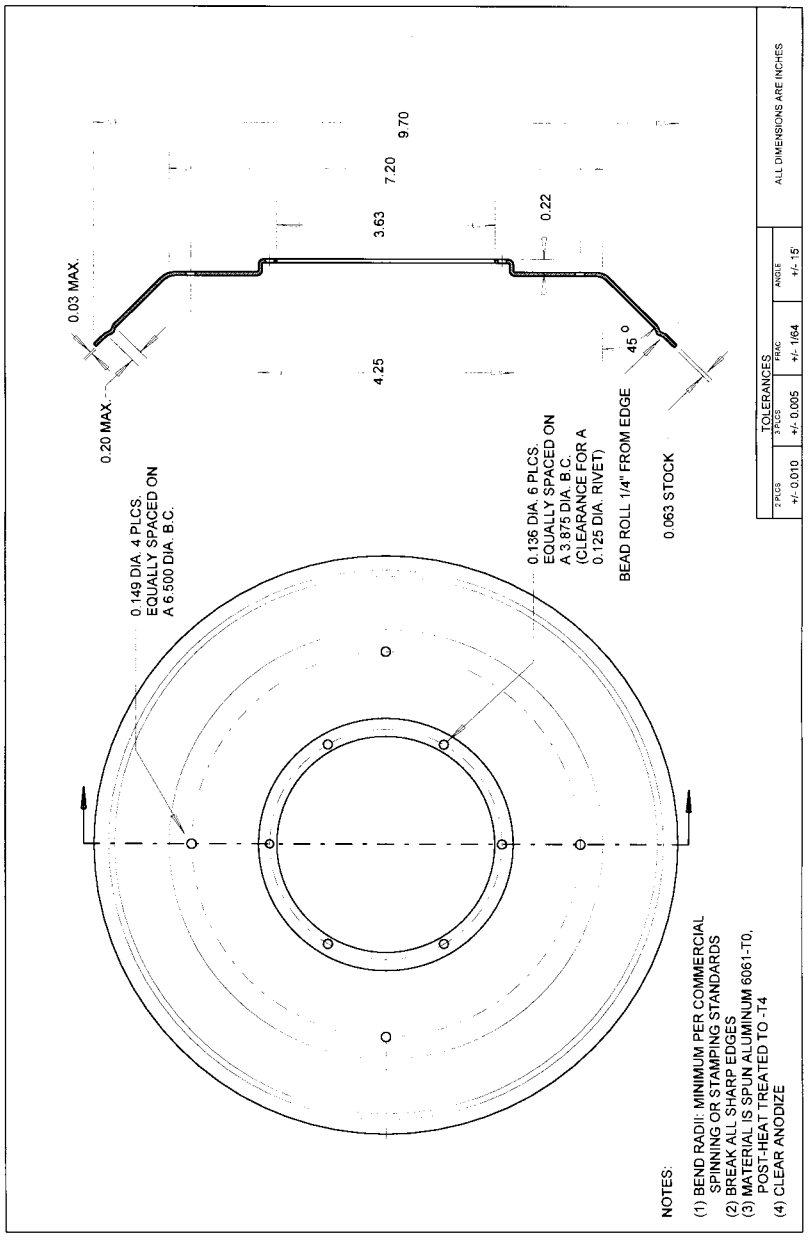


FIGURE L-11. 10-MICRON INLET, LOWER

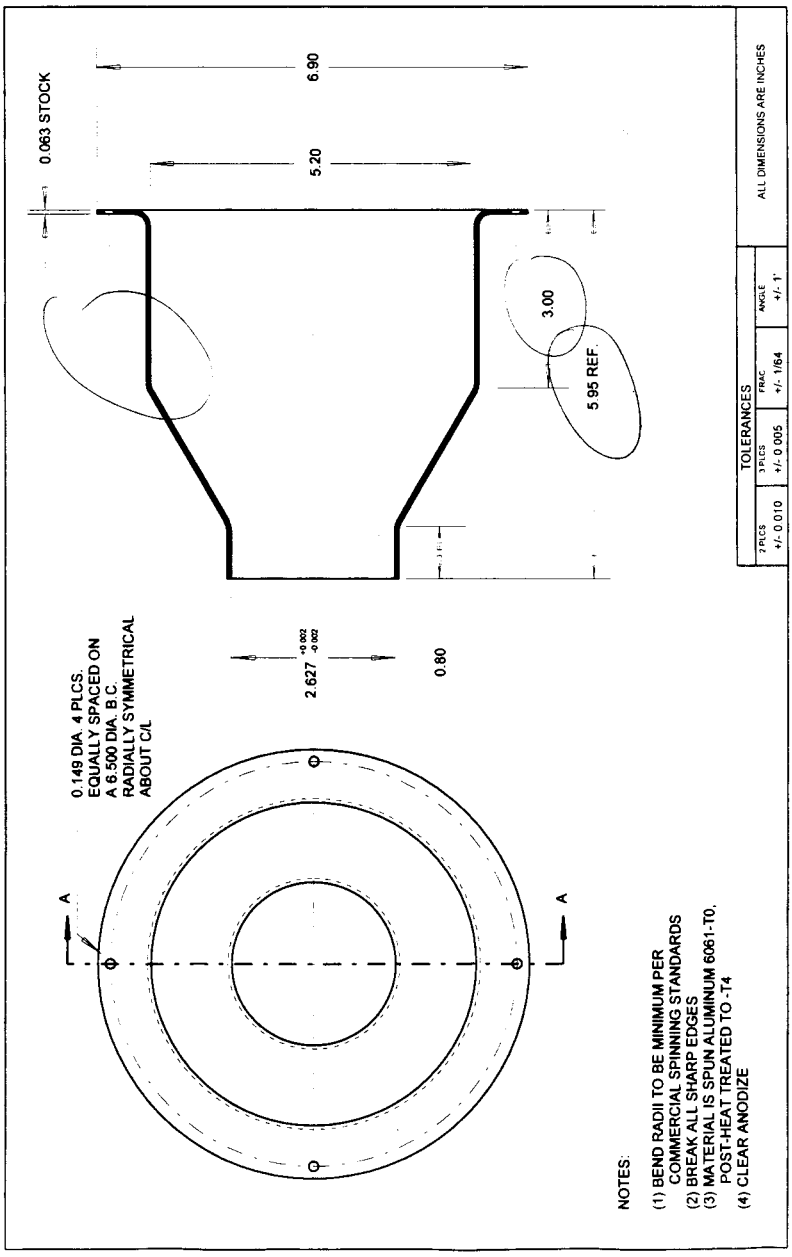


FIGURE L-12. 10-MICRON NOZZLE ENTRY SECTION

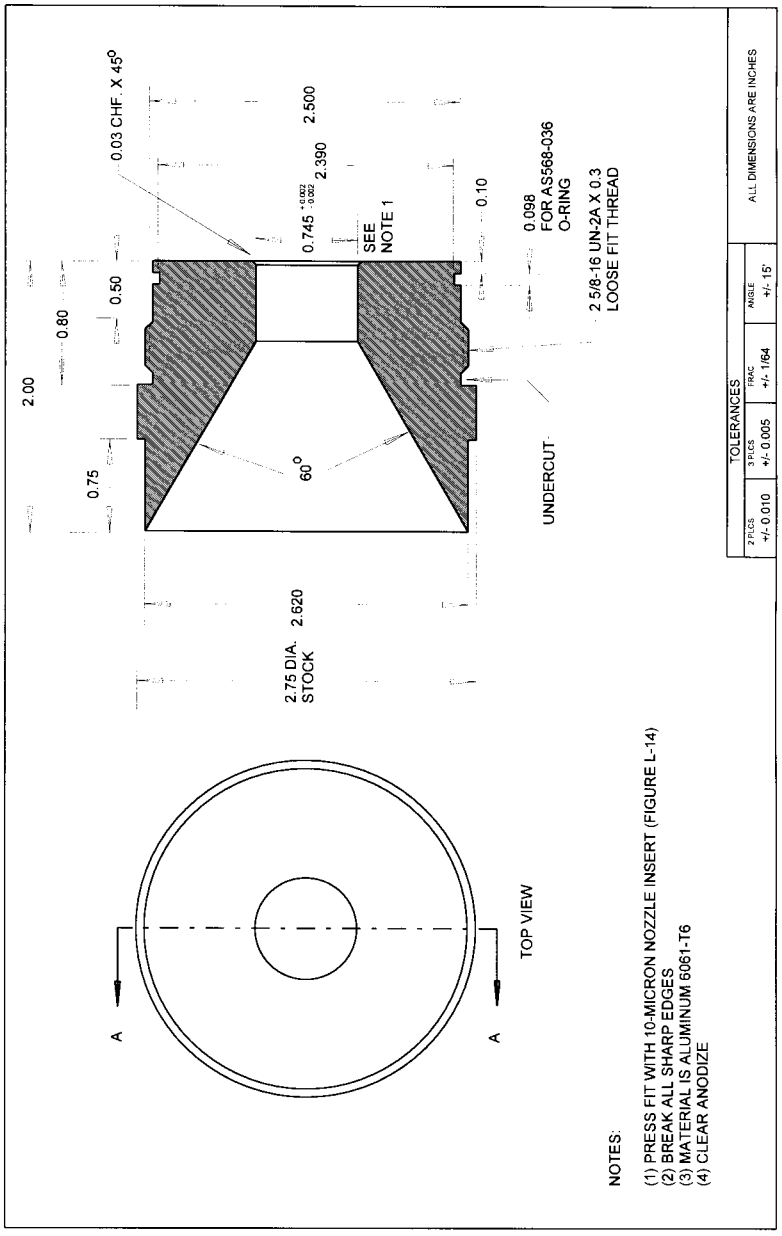


FIGURE L-13. 10-MICRON IMPACTOR NOZZLE

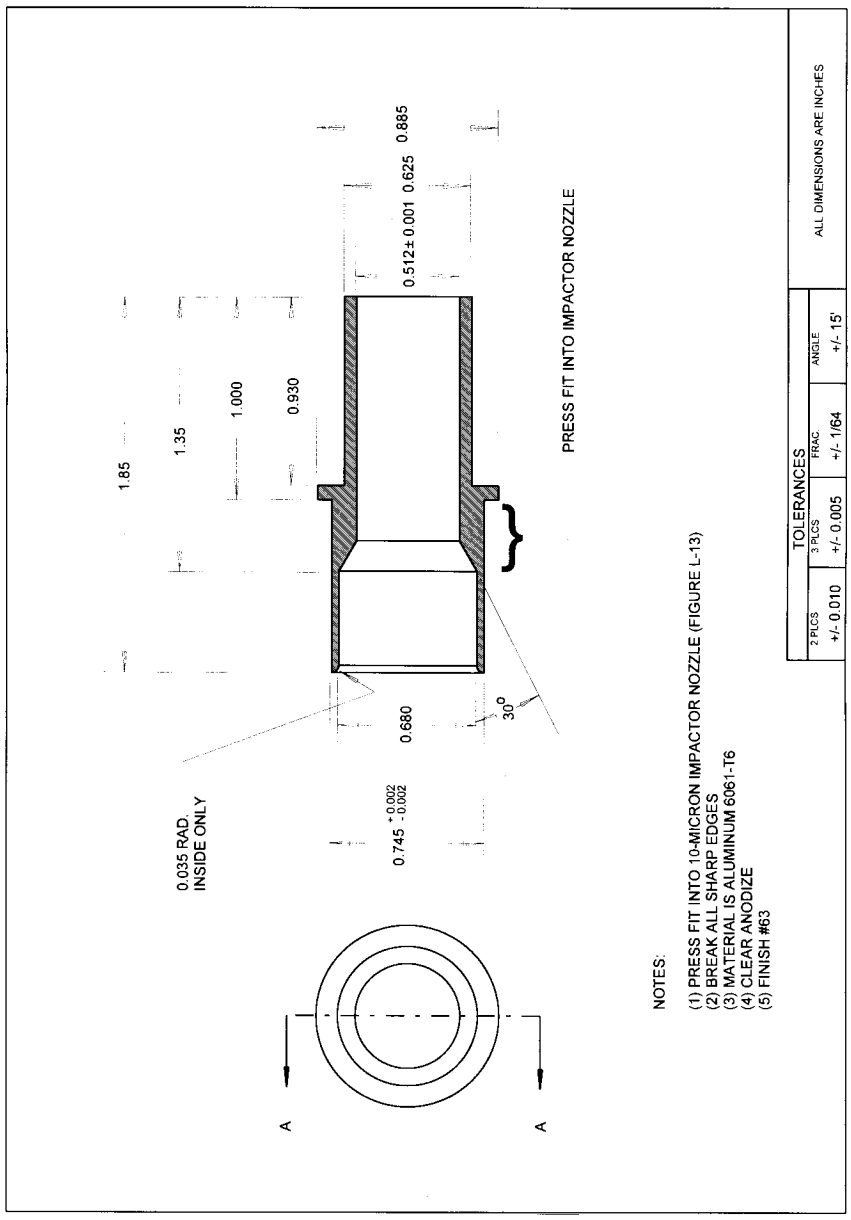


FIGURE L-14. 10-MICRON NOZZLE INSERT

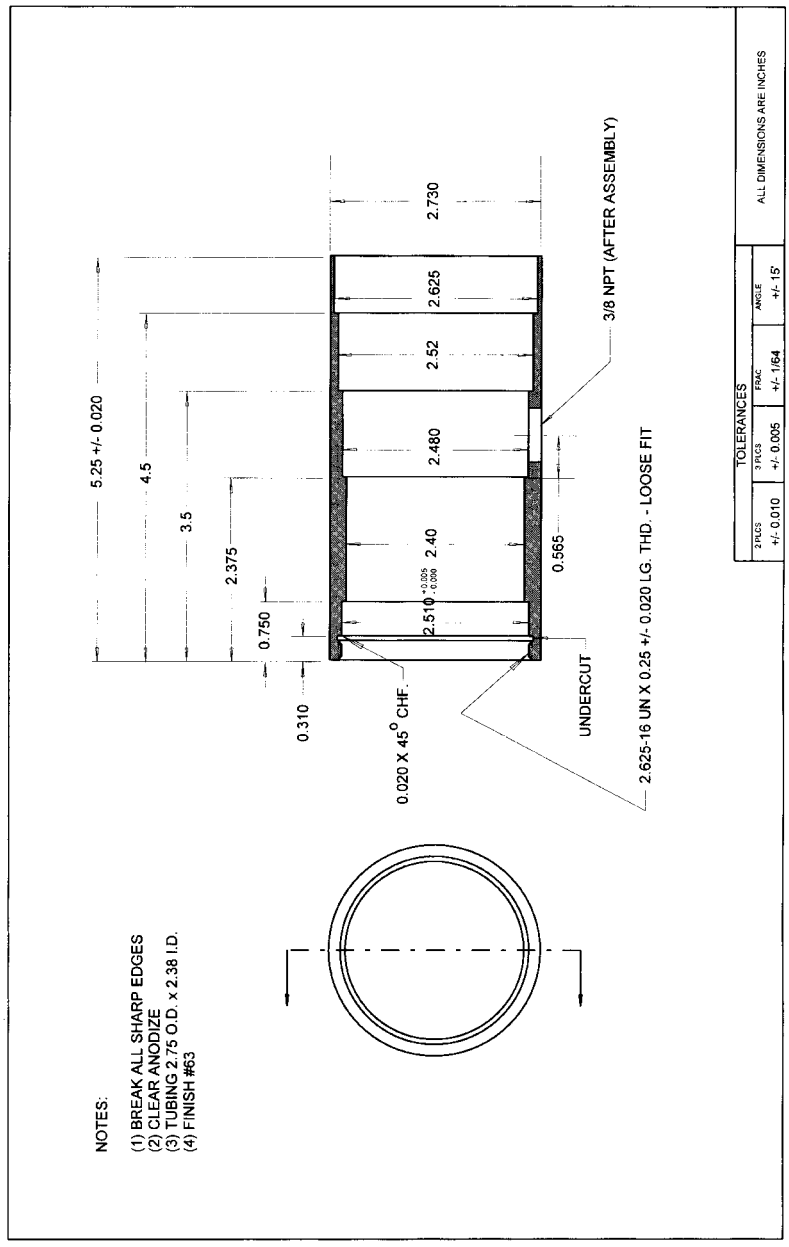


FIGURE L–15. 10-MICRON OUTER TUBE

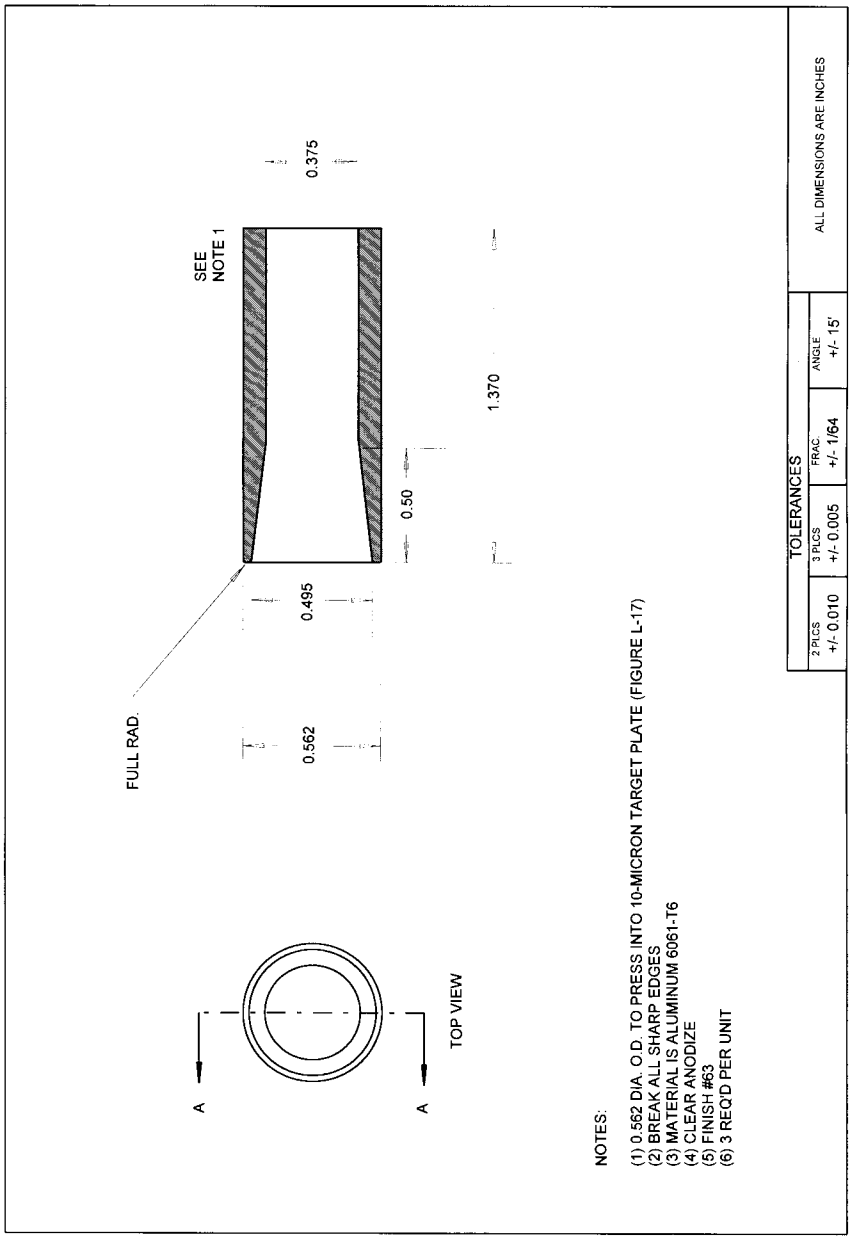


FIGURE L-16. 10-MICRON RECEIVER TUBE

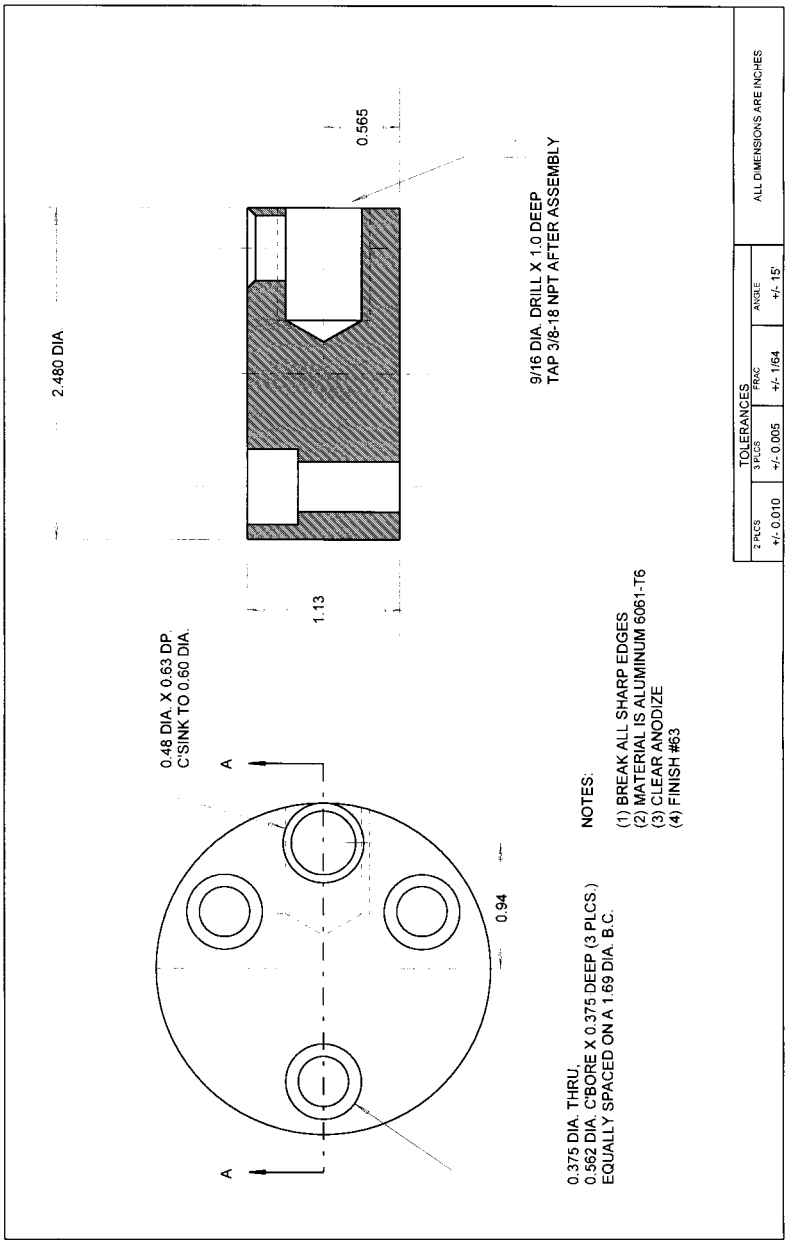


FIGURE L-17. 10-MICRON TARGET PLATE

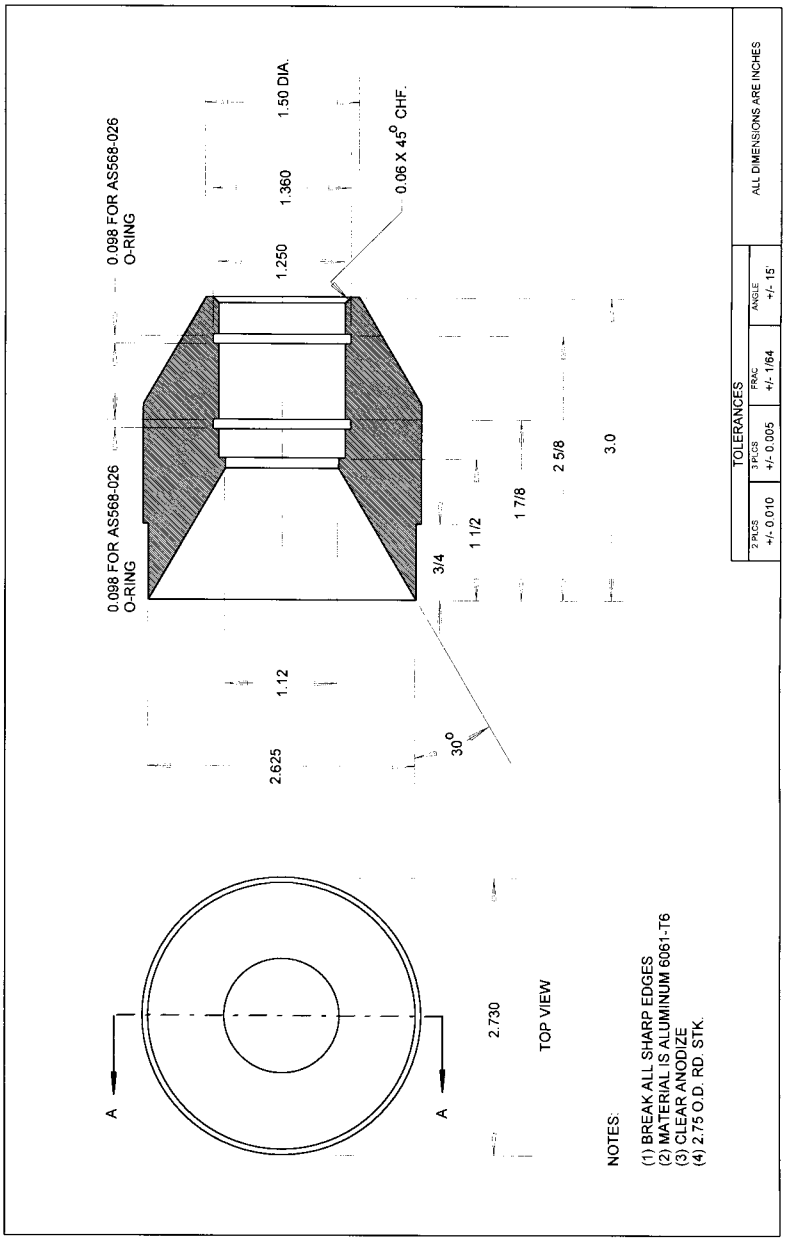


FIGURE L-18. 10-MICRON EXIT ADAPTOR

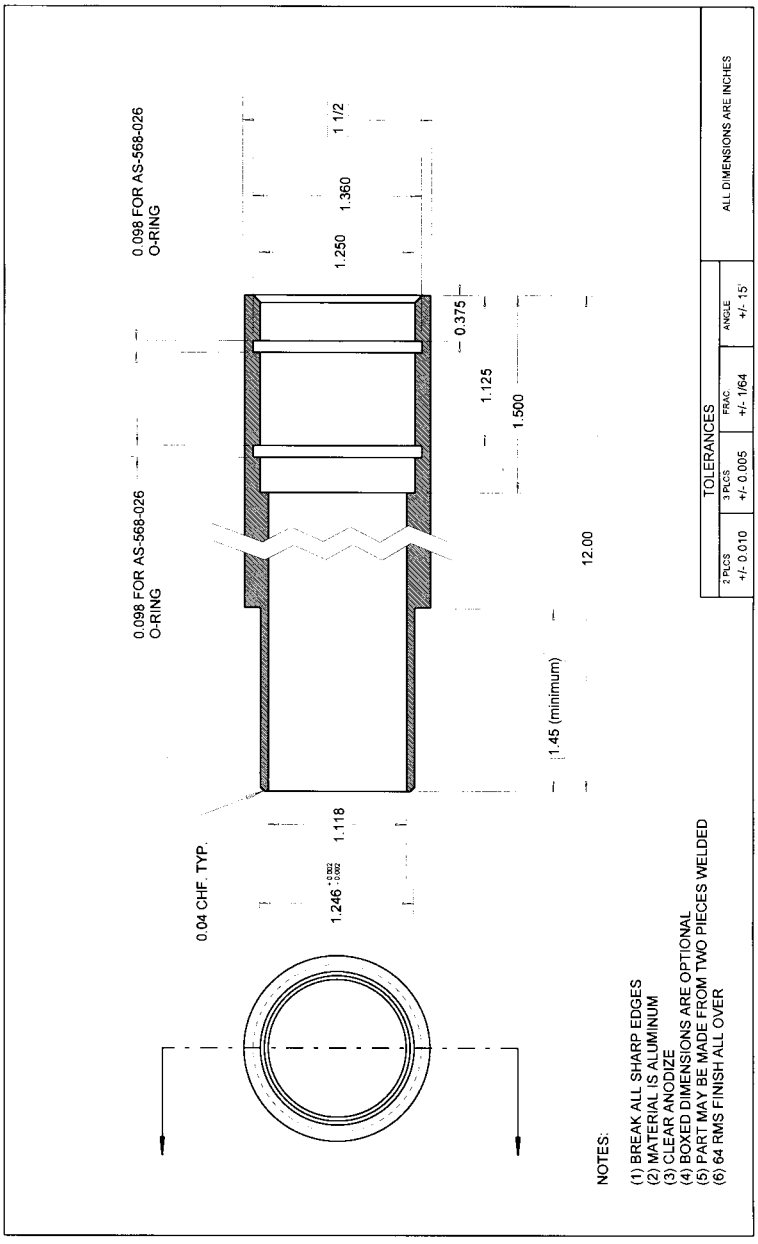


FIGURE L-19. 10-MICRON DOWN TUBE

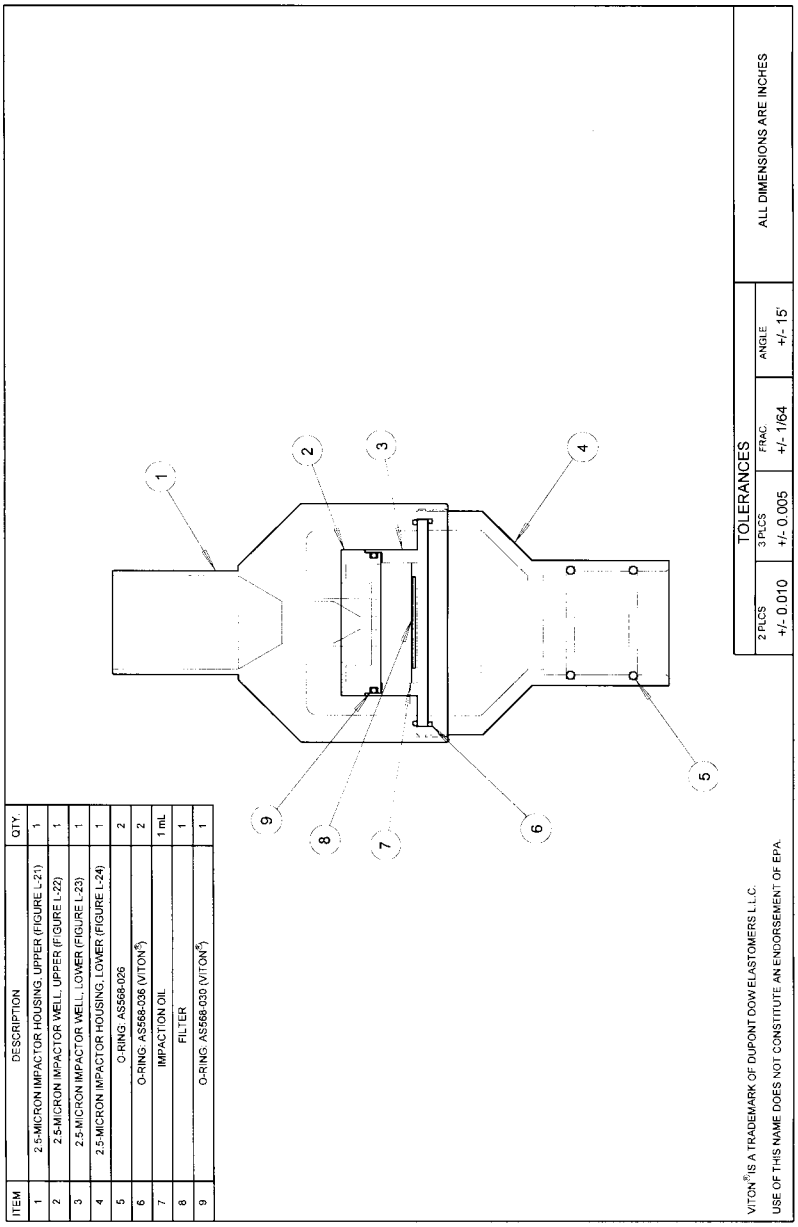


FIGURE L-20. 2.5-MICRON IMPACTOR ASSEMBLY

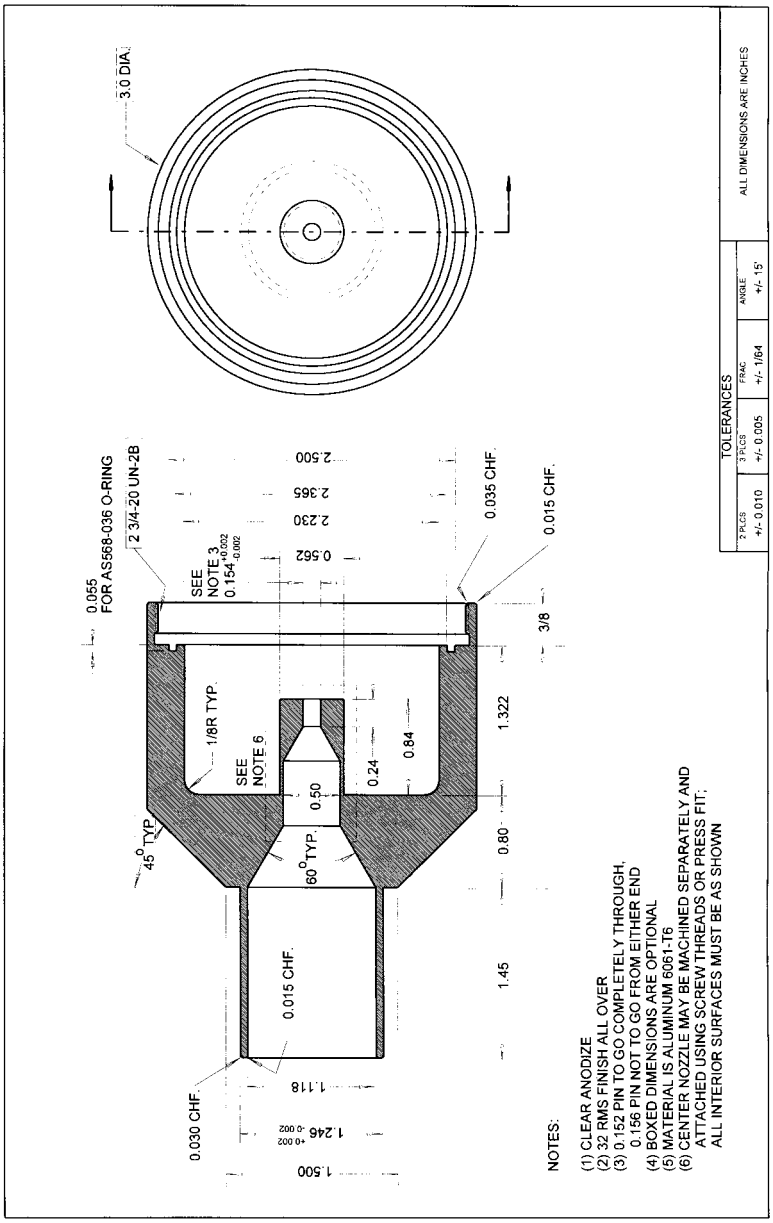


FIGURE L-21. 2.5-MICRON IMPACTOR HOUSING, UPPER

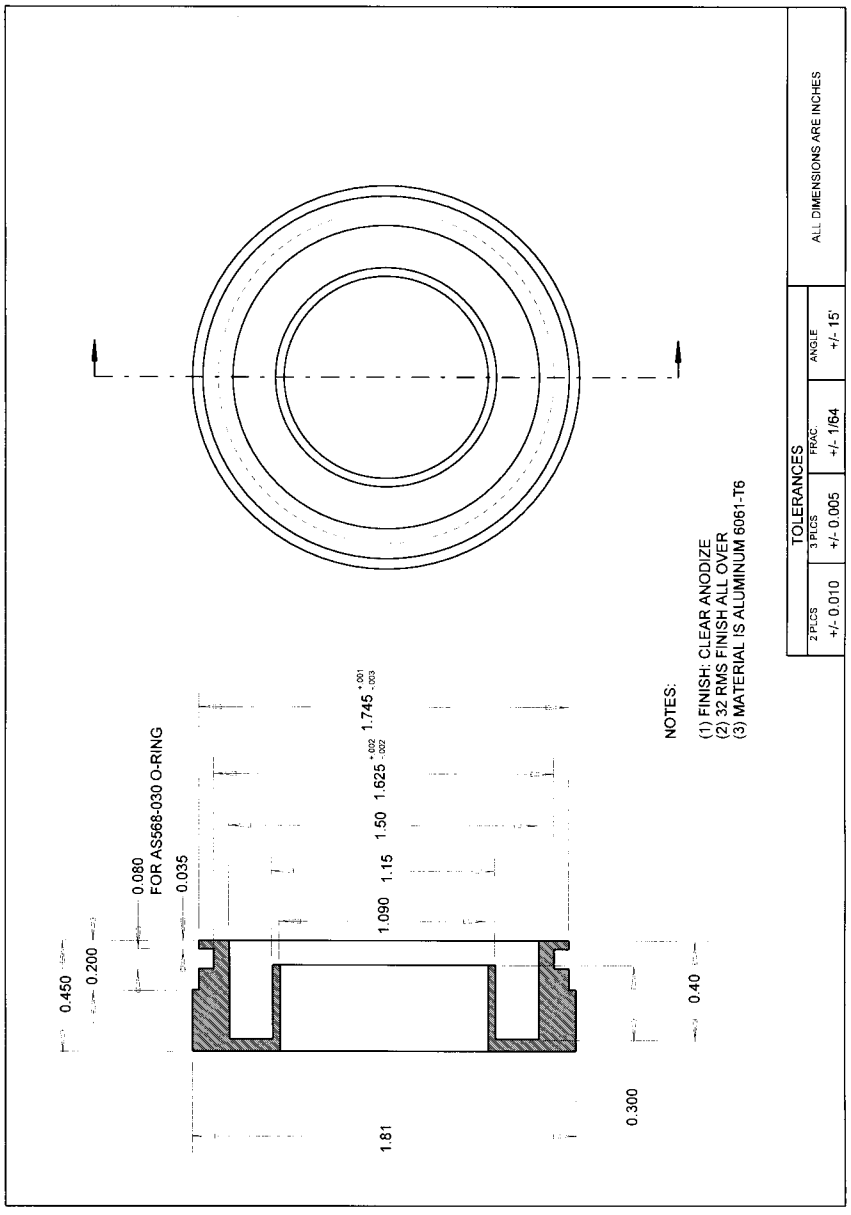


FIGURE L-22. 2.5-MICRON IMPACTOR WELL, UPPER SECTION

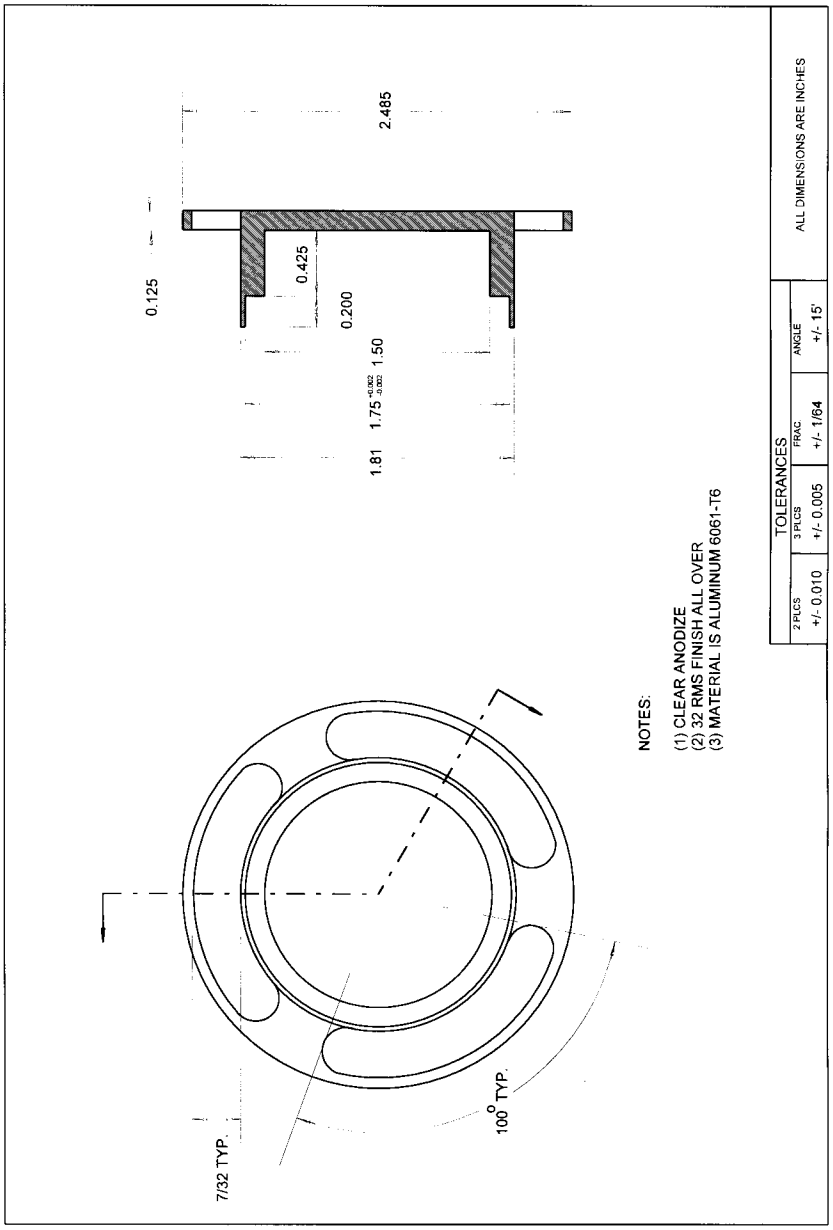


FIGURE L-23. 2.5-MICRON IMPACTOR WELL, LOWER SECTION

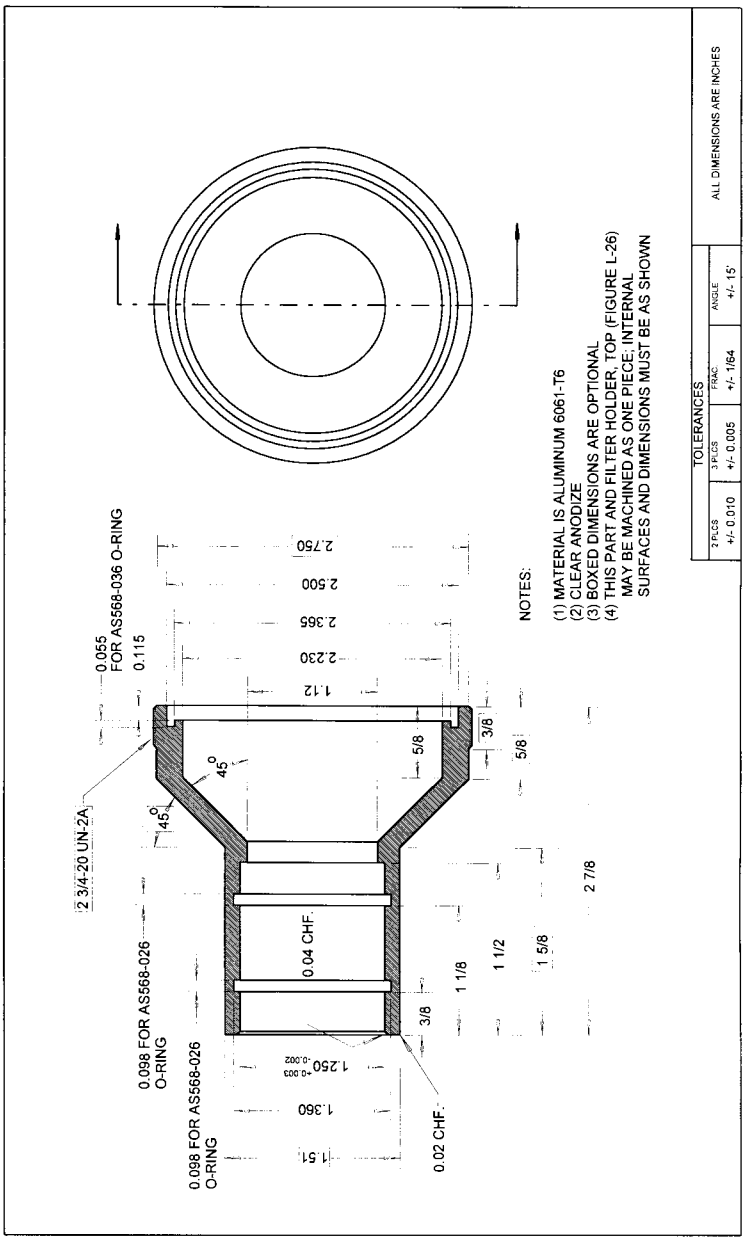


FIGURE L-24. 2.5-MICRON IMPACTOR HOUSING, LOWER

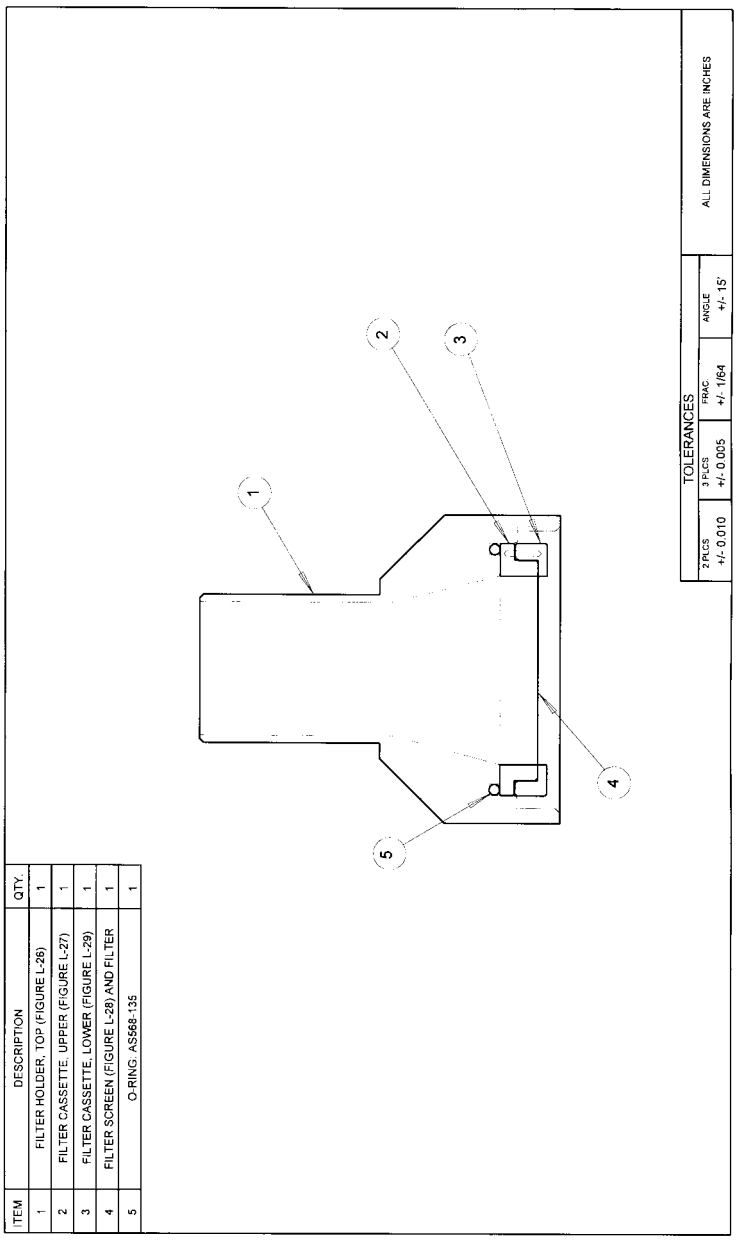


FIGURE L-25. FILTER HOLDER, ASSEMBLY

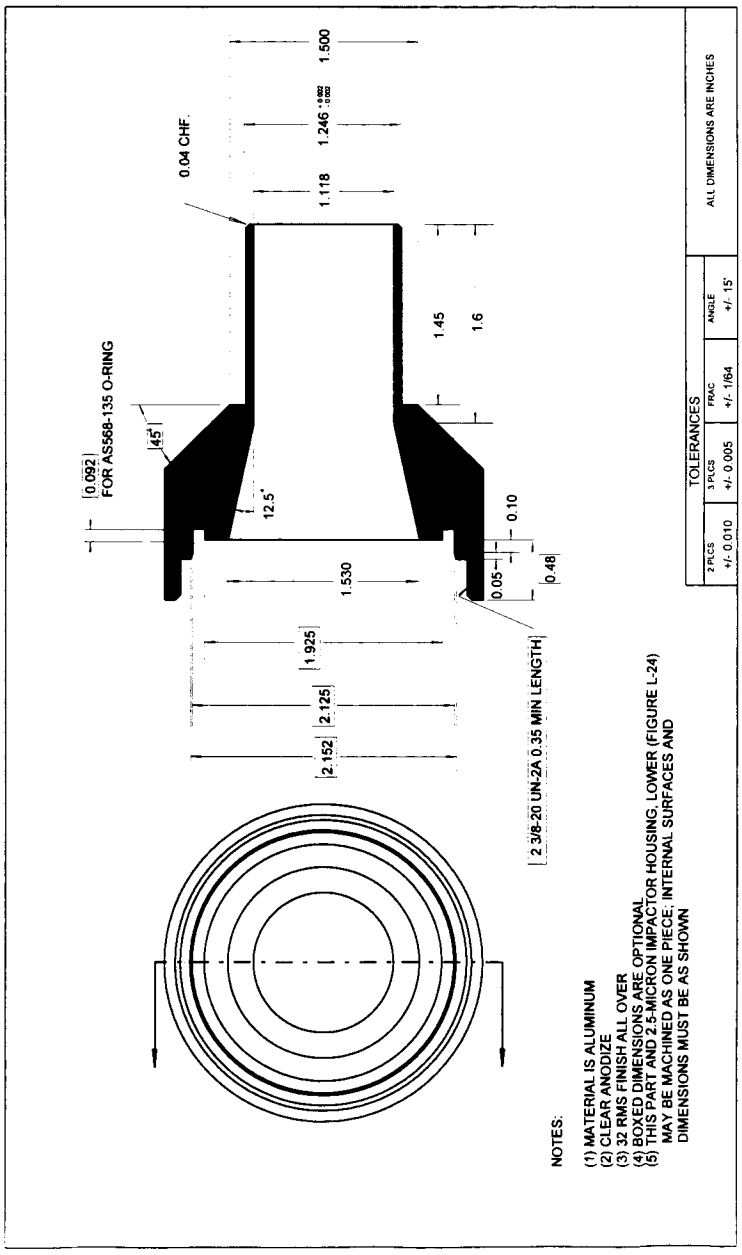


FIGURE L-26. FILTER HOLDER, TOP

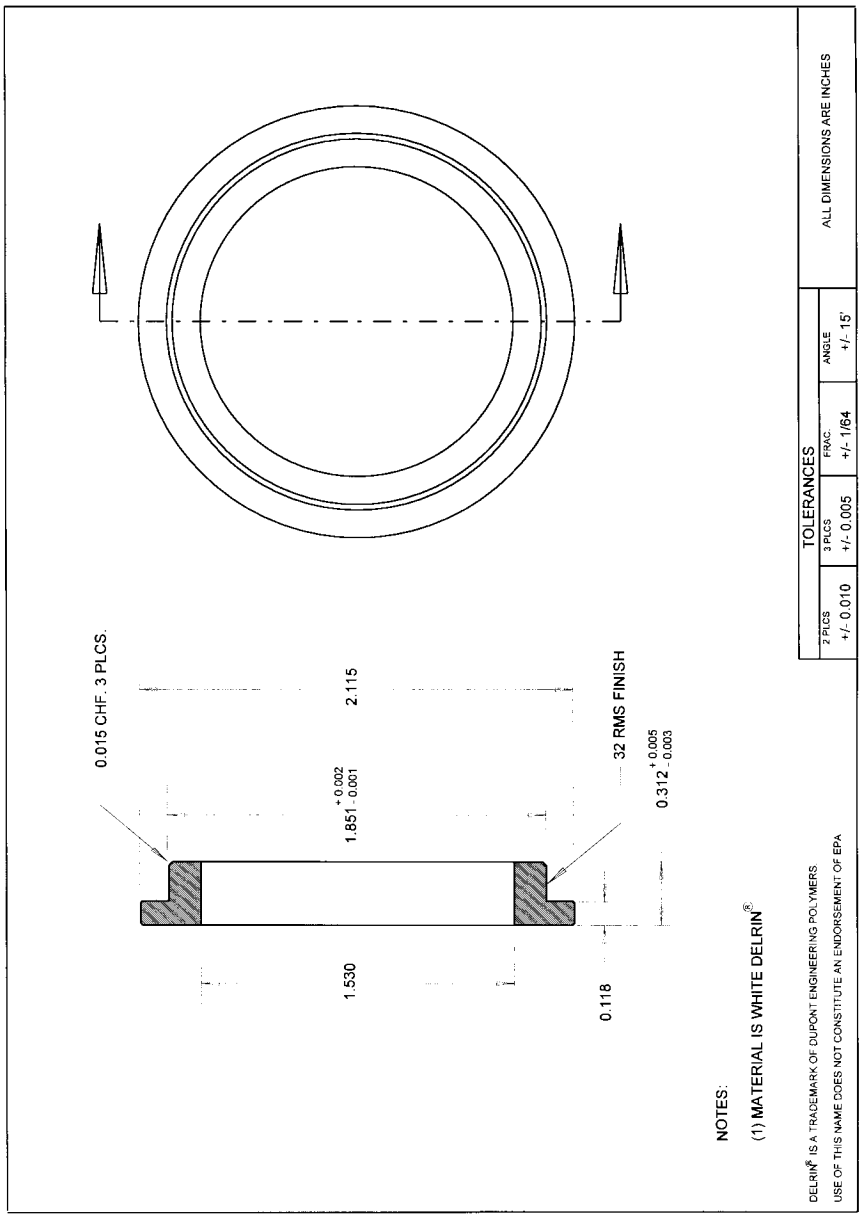


FIGURE L-27. FILTER CASSETTE, UPPER SECTION

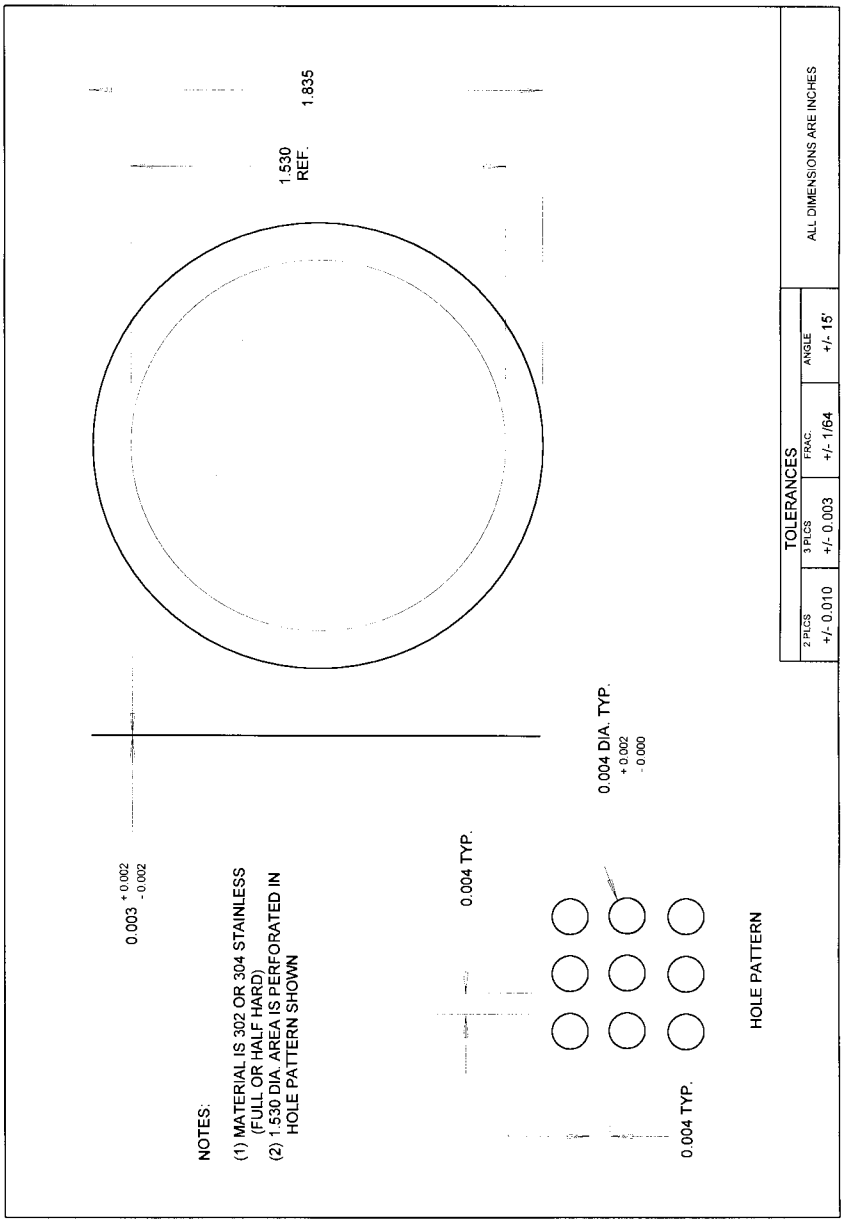


FIGURE L-28. FILTER SCREEN

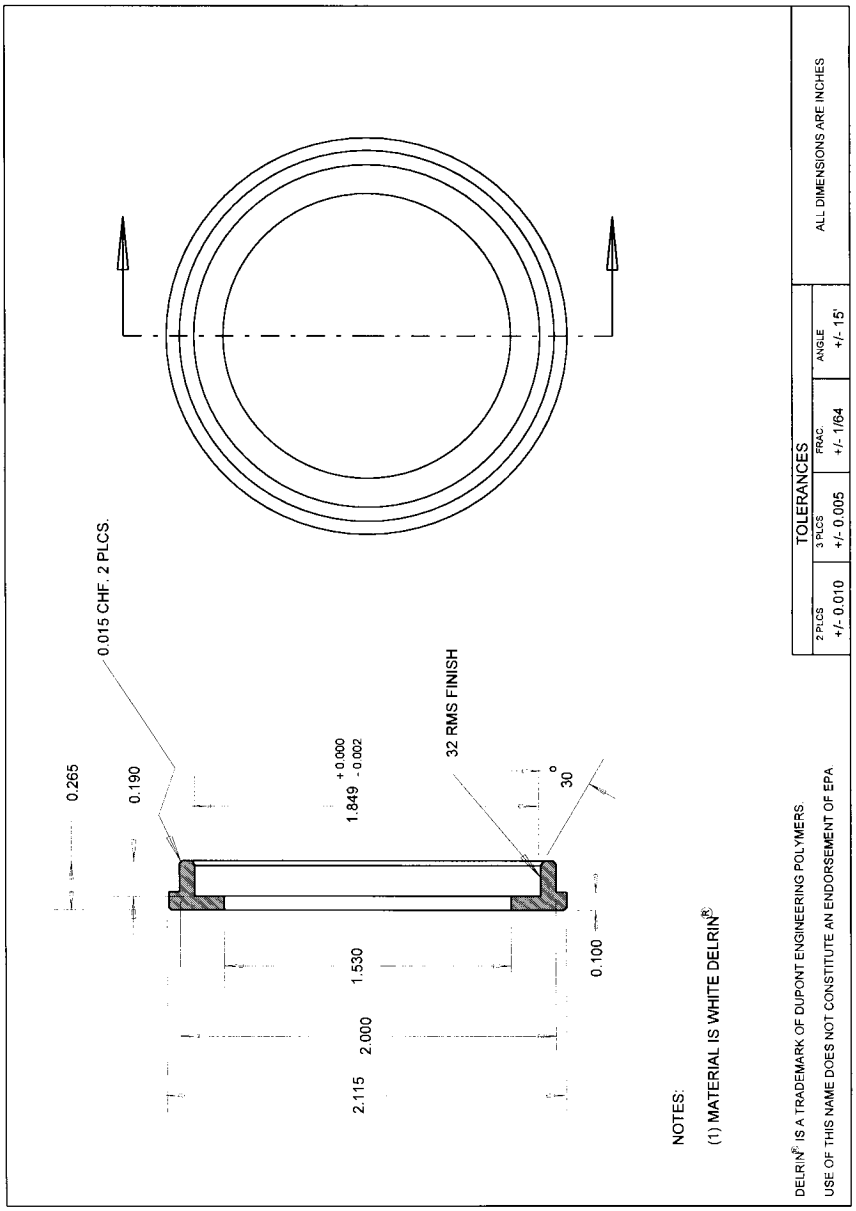


FIGURE L-29. FILTER CASSETTE, LOWER SECTION

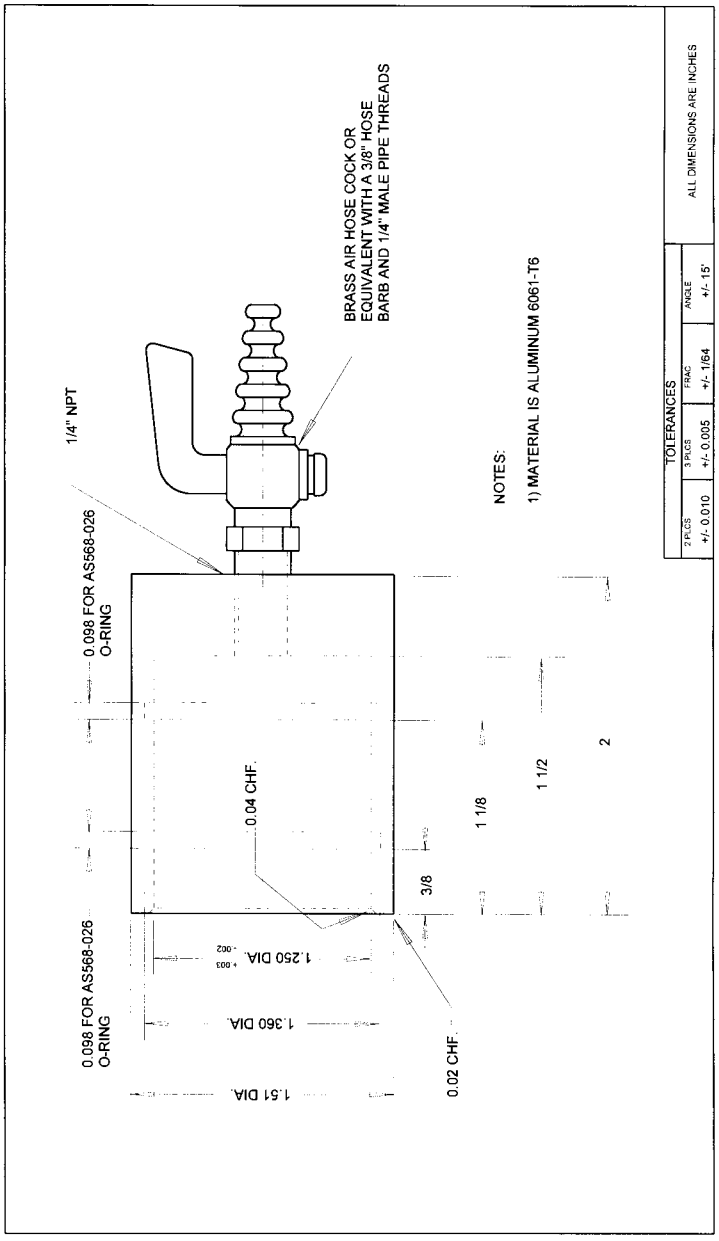


FIGURE L-30. FLOW RATE MEASUREMENT ADAPTER

[62 FR 38714, July 18, 1997, as amended at 64 FR 19719, Apr. 22, 1999; 71 FR 61226, Oct. 17, 2006]

$PM_{2.5}$ concentrations, such sites would be considered representative of an area-wide location and, therefore, eligible for comparison to the annual $PM_{2.5}$ NAAQS. $PM_{2.5}$ measurement data from monitors that are not representative of area-wide air quality but rather of relatively unique micro-scale, or localized hot spot, or unique middle-scale impact sites are not eligible for comparison to the annual $PM_{2.5}$ NAAQS. $PM_{2.5}$ measurement data from these monitors are eligible for comparison to the 24-hour $PM_{2.5}$ NAAQS. For example, if a micro- or middle-scale $PM_{2.5}$ monitoring site is adjacent to a unique dominating local $PM_{2.5}$ source, then the $PM_{2.5}$ measurement data from such a site would only be eligible for comparison to the 24-hour $PM_{2.5}$ NAAQS. Approval of sites that are suitable and sites that are not suitable for comparison with the annual $PM_{2.5}$ NAAQS is provided for as part of the annual monitoring network plan described in §58.10.

(b) [Reserved]

[71 FR 61302, Oct. 17, 2006, as amended at 78 FR 3283, Jan. 15, 2013]

Subpart E [Reserved]

Subpart F—Air Quality Index Reporting

§58.50 Index reporting.

(a) The State or where applicable, local agency shall report to the general public on a daily basis through prominent notice an air quality index that complies with the requirements of appendix G to this part.

(b) Reporting is required for all individual MSA with a population exceeding 350,000.

(c) The population of a metropolitan statistical area for purposes of index reporting is the latest available U.S. census population.

[71 FR 61302, Oct. 17, 2006, as amended at 80 FR 65466, Oct. 26, 2015]

Subpart G—Federal Monitoring

SOURCE: 44 FR 27571, May 10, 1979, unless otherwise noted. Redesignated at 58 FR 8467, Feb. 12, 1993.

§58.60 Federal monitoring.

The Administrator may locate and operate an ambient air monitoring site if the State or local agency fails to locate, or schedule to be located, during the initial network design process, or as a result of the 5-year network assessments required in §58.10, a SLAMS station at a site which is necessary in the judgment of the Regional Administrator to meet the objectives defined in appendix D to this part.

[71 FR 61303, Oct. 17, 2006]

§58.61 Monitoring other pollutants.

The Administrator may promulgate criteria similar to that referenced in subpart B of this part for monitoring a pollutant for which an NAAQS does not exist. Such an action would be taken whenever the Administrator determines that a nationwide monitoring program is necessary to monitor such a pollutant.

[71 FR 61303, Oct. 17, 2006]

APPENDIX A TO PART 58—QUALITY ASSURANCE REQUIREMENTS FOR MONITORS USED IN EVALUATIONS OF NATIONAL AMBIENT AIR QUALITY STANDARDS

1. General Information
2. Quality System Requirements
3. Measurement Quality Check Requirements
4. Calculations for Data Quality Assessments
5. Reporting Requirements
6. References

1. General Information

1.1 *Applicability*. (a) This appendix specifies the minimum quality system requirements applicable to SLAMS and other monitor types whose data are intended to be used to determine compliance with the NAAQS (*e.g.*, SPMs, tribal, CASTNET, NCore, industrial, etc.), unless the EPA Regional Administrator has reviewed and approved the monitor for exclusion from NAAQS use and these quality assurance requirements.

(b) Primary quality assurance organizations are encouraged to develop and maintain quality systems more extensive than the required minimums. Additional guidance for the requirements reflected in this appendix can be found in the ''Quality Assurance Handbook for Air Pollution Measurement Systems,'' Volume II (see reference 10 of this appendix) and at a national level in references 1, 2, and 3 of this appendix.

1.2 *Primary Quality Assurance Organization (PQAO)*. A PQAO is defined as a monitoring

organization or a group of monitoring organizations or other organization that is responsible for a set of stations that monitors the same pollutant and for which data quality assessments will be pooled. Each criteria pollutant sampler/monitor must be associated with only one PQAO. In some cases, data quality is assessed at the PQAO level.

1.2.1 Each PQAO shall be defined such that measurement uncertainty among all stations in the organization can be expected to be reasonably homogeneous as a result of common factors. Common factors that should be considered in defining PQAOs include:

(a) Operation by a common team of field operators according to a common set of procedures;

(b) Use of a common quality assurance project plan (QAPP) or standard operating procedures;

(c) Common calibration facilities and standards;

(d) Oversight by a common quality assurance organization; and

(e) Support by a common management organization (*i.e.*, state agency) or laboratory.

Since data quality assessments are made and data certified at the PQAO level, the monitoring organization identified as the PQAO will be responsible for the oversight of the quality of data of all monitoring organizations within the PQAO.

1.2.2 Monitoring organizations having difficulty describing its PQAO or in assigning specific monitors to primary quality assurance organizations should consult with the appropriate EPA Regional Office. Any consolidation of monitoring organizations to PQAOs shall be subject to final approval by the appropriate EPA Regional Office.

1.2.3 Each PQAO is required to implement a quality system that provides sufficient information to assess the quality of the monitoring data. The quality system must, at a minimum, include the specific requirements described in this appendix. Failure to conduct or pass a required check or procedure, or a series of required checks or procedures, does not by itself invalidate data for regulatory decision making. Rather, PQAOs and the EPA shall use the checks and procedures required in this appendix in combination with other data quality information, reports, and similar documentation that demonstrate overall compliance with Part 58. Accordingly, the EPA and PQAOs shall use a ''weight of evidence'' approach when determining the suitability of data for regulatory decisions. The EPA reserves the authority to use or not use monitoring data submitted by a monitoring organization when making regulatory decisions based on the EPA's assessment of the quality of the data. Consensus built validation templates or validation criteria already approved in QAPPs should be used as the basis for the weight of evidence approach.

1.3 *Definitions.*

(a) *Measurement Uncertainty*. A term used to describe deviations from a true concentration or estimate that are related to the measurement process and not to spatial or temporal population attributes of the air being measured.

(b) *Precision*. A measurement of mutual agreement among individual measurements of the same property usually under prescribed similar conditions, expressed generally in terms of the standard deviation.

(c) *Bias*. The systematic or persistent distortion of a measurement process which causes errors in one direction.

(d) *Accuracy*. The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (imprecision) and systematic error (bias) components which are due to sampling and analytical operations.

(e) *Completeness*. A measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under correct, normal conditions.

(f) *Detection Limit*. The lowest concentration or amount of target analyte that can be determined to be different from zero by a single measurement at a stated level of probability.

1.4 *Measurement Quality Checks*. The measurement quality checks described in section 3 of this appendix shall be reported to AQS and are included in the data required for certification.

1.5 *Assessments and Reports*. Periodic assessments and documentation of data quality are required to be reported to the EPA. To provide national uniformity in this assessment and reporting of data quality for all networks, specific assessment and reporting procedures are prescribed in detail in sections 3, 4, and 5 of this appendix. On the other hand, the selection and extent of the quality assurance and quality control activities used by a monitoring organization depend on a number of local factors such as field and laboratory conditions, the objectives for monitoring, the level of data quality needed, the expertise of assigned personnel, the cost of control procedures, pollutant concentration levels, etc. Therefore, quality system requirements in section 2 of this appendix are specified in general terms to allow each monitoring organization to develop a quality system that is most efficient and effective for its own circumstances while achieving the data quality objectives described in this appendix.

2. Quality System Requirements

A quality system (reference 1 of this appendix) is the means by which an organization manages the quality of the monitoring

information it produces in a systematic, organized manner. It provides a framework for planning, implementing, assessing and reporting work performed by an organization and for carrying out required quality assurance and quality control activities.

2.1 *Quality Management Plans and Quality Assurance Project Plans.* All PQAOs must develop a quality system that is described and approved in quality management plans (QMP) and QAPPs to ensure that the monitoring results:

(a) Meet a well-defined need, use, or purpose (reference 5 of this appendix);

(b) Provide data of adequate quality for the intended monitoring objectives;

(c) Satisfy stakeholder expectations;

(d) Comply with applicable standards specifications;

(e) Comply with statutory (and other legal) requirements; and

(f) Reflect consideration of cost and economics.

2.1.1 The QMP describes the quality system in terms of the organizational structure, functional responsibilities of management and staff, lines of authority, and required interfaces for those planning, implementing, assessing and reporting activities involving environmental data operations (EDO). The QMP must be suitably documented in accordance with EPA requirements (reference 2 of this appendix), and approved by the appropriate Regional Administrator, or his or her representative. The quality system described in the QMP will be reviewed during the systems audits described in section 2.5 of this appendix. Organizations that implement long-term monitoring programs with EPA funds should have a separate QMP document. Smaller organizations, organizations that do infrequent work with the EPA or have monitoring programs of limited size or scope may combine the QMP with the QAPP if approved by, and subject to any conditions of the EPA. Additional guidance on this process can be found in reference 10 of this appendix. Approval of the recipient's QMP by the appropriate Regional Administrator or his or her representative may allow delegation of authority to the PQAOs independent quality assurance function to review and approve environmental data collection activities adequately described and covered under the scope of the QMP and documented in appropriate planning documents (QAPP). Where a PQAO or monitoring organization has been delegated authority to review and approve their QAPP, an electronic copy must be submitted to the EPA region at the time it is submitted to the PQAO/monitoring organization's QAPP approving authority. The QAPP will be reviewed by the EPA during systems audits or circumstances related to data quality. The QMP submission and approval dates for PQAOs/monitoring organizations must be reported to AQS either by the monitoring organization or the EPA Region.

2.1.2 The QAPP is a formal document describing, in sufficient detail, the quality system that must be implemented to ensure that the results of work performed will satisfy the stated objectives. PQAOs must develop QAPPs that describe how the organization intends to control measurement uncertainty to an appropriate level in order to achieve the data quality objectives for the EDO. The quality assurance policy of the EPA requires every EDO to have a written and approved QAPP prior to the start of the EDO. It is the responsibility of the PQAO/monitoring organization to adhere to this policy. The QAPP must be suitably documented in accordance with EPA requirements (reference 3 of this appendix) and include standard operating procedures for all EDOs either within the document or by appropriate reference. The QAPP must identify each PQAO operating monitors under the QAPP as well as generally identify the sites and monitors to which it is applicable either within the document or by appropriate reference. The QAPP submission and approval dates must be reported to AQS either by the monitoring organization or the EPA Region.

2.1.3 The PQAO/monitoring organization's quality system must have adequate resources both in personnel and funding to plan, implement, assess and report on the achievement of the requirements of this appendix and it's approved QAPP.

2.2 *Independence of Quality Assurance.* The PQAO must provide for a quality assurance management function, that aspect of the overall management system of the organization that determines and implements the quality policy defined in a PQAO's QMP. Quality management includes strategic planning, allocation of resources and other systematic planning activities (*e.g.*, planning, implementation, assessing and reporting) pertaining to the quality system. The quality assurance management function must have sufficient technical expertise and management authority to conduct independent oversight and assure the implementation of the organization's quality system relative to the ambient air quality monitoring program and should be organizationally independent of environmental data generation activities.

2.3. *Data Quality Performance Requirements.*

2.3.1 *Data Quality Objectives.* The DQOs, or the results of other systematic planning processes, are statements that define the appropriate type of data to collect and specify the tolerable levels of potential decision errors that will be used as a basis for establishing the quality and quantity of data needed to support the monitoring objectives (reference 5 of this appendix). The DQOs will be developed by the EPA to support the primary regulatory objectives for each criteria

pollutant. As they are developed, they will be added to the regulation. The quality of the conclusions derived from data interpretation can be affected by population uncertainty (spatial or temporal uncertainty) and measurement uncertainty (uncertainty associated with collecting, analyzing, reducing and reporting concentration data). This appendix focuses on assessing and controlling measurement uncertainty.

2.3.1.1 *Measurement Uncertainty for Automated and Manual $PM_{2.5}$ Methods.* The goal for acceptable measurement uncertainty is defined for precision as an upper 90 percent confidence limit for the coefficient of variation (CV) of 10 percent and ±10 percent for total bias.

2.3.1.2 *Measurement Uncertainty for Automated O_3 Methods.* The goal for acceptable measurement uncertainty is defined for precision as an upper 90 percent confidence limit for the CV of 7 percent and for bias as an upper 95 percent confidence limit for the absolute bias of 7 percent.

2.3.1.3 *Measurement Uncertainty for Pb Methods.* The goal for acceptable measurement uncertainty is defined for precision as an upper 90 percent confidence limit for the CV of 20 percent and for bias as an upper 95 percent confidence limit for the absolute bias of 15 percent.

2.3.1.4 *Measurement Uncertainty for NO_2.* The goal for acceptable measurement uncertainty is defined for precision as an upper 90 percent confidence limit for the CV of 15 percent and for bias as an upper 95 percent confidence limit for the absolute bias of 15 percent.

2.3.1.5 *Measurement Uncertainty for SO_2.* The goal for acceptable measurement uncertainty for precision is defined as an upper 90 percent confidence limit for the CV of 10 percent and for bias as an upper 95 percent confidence limit for the absolute bias of 10 percent.

2.4 *National Performance Evaluation Programs.* The PQAO shall provide for the implementation of a program of independent and adequate audits of all monitors providing data for NAAQS compliance purposes including the provision of adequate resources for such audit programs. A monitoring plan (or QAPP) which provides for PQAO participation in the EPA's National Performance Audit Program (NPAP), the $PM_{2.5}$ Performance Evaluation Program ($PM_{2.5}$-PEP) program and the Pb Performance Evaluation Program (Pb-PEP) and indicates the consent of the PQAO for the EPA to apply an appropriate portion of the grant funds, which the EPA would otherwise award to the PQAO for these QA activities, will be deemed by the EPA to meet this requirement. For clarification and to participate, PQAOs should contact either the appropriate EPA regional quality assurance (QA) coordinator at the appropriate EPA Regional Office location, or the NPAP coordinator at the EPA Air Quality Assessment Division, Office of Air Quality Planning and Standards, in Research Triangle Park, North Carolina. The PQAOs that plan to implement these programs (self-implement) rather than use the federal programs must meet the adequacy requirements found in the appropriate sections that follow, as well as meet the definition of independent assessment that follows.

2.4.1 *Independent assessment.* An assessment performed by a qualified individual, group, or organization that is not part of the organization directly performing and accountable for the work being assessed. This auditing organization must not be involved with the generation of the ambient air monitoring data. An organization can conduct the performance evaluation (PE) if it can meet this definition and has a management structure that, at a minimum, will allow for the separation of its routine sampling personnel from its auditing personnel by two levels of management. In addition, the sample analysis of audit filters must be performed by a laboratory facility and laboratory equipment separate from the facilities used for routine sample analysis. Field and laboratory personnel will be required to meet PE field and laboratory training and certification requirements to establish comparability to federally implemented programs.

2.5 *Technical Systems Audit Program.* Technical systems audits of each PQAO shall be conducted at least every 3 years by the appropriate EPA Regional Office and reported to the AQS. If a PQAO is made up of more than one monitoring organization, all monitoring organizations in the PQAO should be audited within 6 years (two TSA cycles of the PQAO). As an example, if a state has five local monitoring organizations that are consolidated under one PQAO, all five local monitoring organizations should receive a technical systems audit within a 6-year period. Systems audit programs are described in reference 10 of this appendix.

2.6 *Gaseous and Flow Rate Audit Standards.*

2.6.1 Gaseous pollutant concentration standards (permeation devices or cylinders of compressed gas) used to obtain test concentrations for CO, SO_2, NO, and NO_2 must be traceable to either a National Institute of Standards and Technology (NIST) Traceable Reference Material (NTRM) or a NIST-certified Gas Manufacturer's Internal Standard (GMIS), certified in accordance with one of the procedures given in reference 4 of this appendix. Vendors advertising certification with the procedures provided in reference 4 of this appendix and distributing gases as ''EPA Protocol Gas'' for ambient air monitoring purposes must participate in the EPA

Ambient Air Protocol Gas Verification Program or not use ''EPA'' in any form of advertising. Monitoring organizations must provide information to the EPA on the gas producers they use on an annual basis and those PQAOs purchasing standards will be obligated, at the request of the EPA, to participate in the program at least once every 5 years by sending a new unused standard to a designated verification laboratory.

2.6.2 Test concentrations for O_3 must be obtained in accordance with the ultraviolet photometric calibration procedure specified in appendix D to Part 50 of this chapter and by means of a certified NIST-traceable O_3 transfer standard. Consult references 7 and 8 of this appendix for guidance on transfer standards for O_3.

2.6.3 Flow rate measurements must be made by a flow measuring instrument that is NIST-traceable to an authoritative volume or other applicable standard. Guidance for certifying some types of flowmeters is provided in reference 10 of this appendix.

2.7 *Primary Requirements and Guidance.* Requirements and guidance documents for developing the quality system are contained in references 1 through 11 of this appendix, which also contain many suggested procedures, checks, and control specifications. Reference 10 describes specific guidance for the development of a quality system for data collected for comparison to the NAAQS. Many specific quality control checks and specifications for methods are included in the respective reference methods described in Part 50 of this chapter or in the respective equivalent method descriptions available from the EPA (reference 6 of this appendix). Similarly, quality control procedures related to specifically designated reference and equivalent method monitors are contained in the respective operation or instruction manuals associated with those monitors.

3. Measurement Quality Check Requirements

This section provides the requirements for PQAOs to perform the measurement quality checks that can be used to assess data quality. Data from these checks are required to be submitted to the AQS within the same time frame as routinely-collected ambient concentration data as described in 40 CFR 58.16. Table A–1 of this appendix provides a summary of the types and frequency of the measurement quality checks that will be described in this section.

3.1. *Gaseous Monitors of SO_2, NO_2, O_3, and CO.*

3.1.1 *One-Point Quality Control (QC) Check for SO_2,* NO_2, O_3, and CO. (a) A one-point QC check must be performed at least once every 2 weeks on each automated monitor used to measure SO_2, NO_2, O_3 and CO. With the advent of automated calibration systems, more frequent checking is strongly encouraged. See Reference 10 of this appendix for guidance on the review procedure. The QC check is made by challenging the monitor with a QC check gas of known concentration (effective concentration for open path monitors) between the prescribed range of 0.005 and 0.08 parts per million (ppm) for SO_2, NO_2, and O_3, and between the prescribed range of 0.5 and 5 ppm for CO monitors. The QC check gas concentration selected within the prescribed range should be related to the monitoring objectives for the monitor. If monitoring at an NCore site or for trace level monitoring, the QC check concentration should be selected to represent the mean or median concentrations at the site. If the mean or median concentrations at trace gas sites are below the MDL of the instrument the agency can select the lowest concentration in the prescribed range that can be practically achieved. If the mean or median concentrations at trace gas sites are above the prescribed range the agency can select the highest concentration in the prescribed range. An additional QC check point is encouraged for those organizations that may have occasional high values or would like to confirm the monitors' linearity at the higher end of the operational range or around NAAQS concentrations. If monitoring for NAAQS decisions, the QC concentration can be selected at a higher concentration within the prescribed range but should also consider precision points around mean or median monitor concentrations.

(b) Point analyzers must operate in their normal sampling mode during the QC check and the test atmosphere must pass through all filters, scrubbers, conditioners and other components used during normal ambient sampling and as much of the ambient air inlet system as is practicable. The QC check must be conducted before any calibration or adjustment to the monitor.

(c) Open path monitors are tested by inserting a test cell containing a QC check gas concentration into the optical measurement beam of the instrument. If possible, the normally used transmitter, receiver, and as appropriate, reflecting devices should be used during the test, and the normal monitoring configuration of the instrument should be altered as little as possible to accommodate the test cell for the test. However, if permitted by the associated operation or instruction manual, an alternate local light source or an alternate optical path that does not include the normal atmospheric monitoring path may be used. The actual concentration of the QC check gas in the test cell must be selected to produce an effective concentration in the range specified earlier in this section. Generally, the QC test concentration measurement will be the sum of the atmospheric pollutant concentration and

the QC test concentration. As such, the result must be corrected to remove the atmospheric concentration contribution. The corrected concentration is obtained by subtracting the average of the atmospheric concentrations measured by the open path instrument under test immediately before and immediately after the QC test from the QC check gas concentration measurement. If the difference between these before and after measurements is greater than 20 percent of the effective concentration of the test gas, discard the test result and repeat the test. If possible, open path monitors should be tested during periods when the atmospheric pollutant concentrations are relatively low and steady.

(d) Report the audit concentration of the QC gas and the corresponding measured concentration indicated by the monitor to AQS. The percent differences between these concentrations are used to assess the precision and bias of the monitoring data as described in sections 4.1.2 (precision) and 4.1.3 (bias) of this appendix.

3.1.2 *Annual performance evaluation for SO_2, NO_2, O_3, or CO.* A performance evaluation must be conducted on each primary monitor once a year. This can be accomplished by evaluating 25 percent of the primary monitors each quarter. The evaluation should be conducted by a trained experienced technician other than the routine site operator.

3.1.2.1 The evaluation is made by challenging the monitor with audit gas standards of known concentration from at least three audit levels. One point must be within two to three times the method detection limit of the instruments within the PQAOs network, the second point will be less than or equal to the 99th percentile of the data at the site or the network of sites in the PQAO or the next highest audit concentration level. The third point can be around the primary NAAQS or the highest 3-year concentration at the site or the network of sites in the PQAO. An additional 4th level is encouraged for those agencies that would like to confirm the monitors' linearity at the higher end of the operational range. In rare circumstances, there may be sites measuring concentrations above audit level 10. Notify the appropriate EPA region and the AQS program in order to make accommodations for auditing at levels above level 10.

Audit level	Concentration Range, ppm			
	O_3	SO_2	NO_2	CO
1	0.004–0.0059	0.0003–0.0029	0.0003–0.0029	0.020–0.059
2	0.006–0.019	0.0030–0.0049	0.0030–0.0049	0.060–0.199
3	0.020–0.039	0.0050–0.0079	0.0050–0.0079	0.200–0.899
4	0.040–0.069	0.0080–0.0199	0.0080–0.0199	0.900–2.999
5	0.070–0.089	0.0200–0.0499	0.0200–0.0499	3.000–7.999
6	0.090–0.119	0.0500–0.0999	0.0500–0.0999	8.000–15.999
7	0.120–0.139	0.1000–0.1499	0.1000–0.2999	16.000–30.999
8	0.140–0.169	0.1500–0.2599	0.3000–0.4999	31.000–39.999
9	0.170–0.189	0.2600–0.7999	0.5000–0.7999	40.000–49.999
10	0.190–0.259	0.8000–1.000	0.8000–1.000	50.000–60.000

3.1.2.2 The NO_2 audit techniques may vary depending on the ambient monitoring method. For chemiluminescence-type NO_2 analyzers, gas phase titration (GPT) techniques should be based on EPA guidance documents and monitoring agency experience. The NO_2 gas standards may be more appropriate than GPT for direct NO_2 methods that do not employ converters. Care should be taken to ensure the stability of such gas standards prior to use.

3.1.2.3 The standards from which audit gas test concentrations are obtained must meet the specifications of section 2.6.1 of this appendix. The gas standards and equipment used for the performance evaluation must not be the same as the standards and equipment used for one-point QC, calibrations, span evaluations or NPAP.

3.1.2.4 For point analyzers, the evaluation shall be carried out by allowing the monitor to analyze the audit gas test atmosphere in its normal sampling mode such that the test atmosphere passes through all filters, scrubbers, conditioners, and other sample inlet components used during normal ambient sampling and as much of the ambient air inlet system as is practicable.

3.1.2.5 Open-path monitors are evaluated by inserting a test cell containing the various audit gas concentrations into the optical measurement beam of the instrument. If possible, the normally used transmitter, receiver, and, as appropriate, reflecting devices should be used during the evaluation, and the normal monitoring configuration of the instrument should be modified as little as possible to accommodate the test cell for the evaluation. However, if permitted by the associated operation or instruction manual, an alternate local light source or an alternate optical path that does not include the normal atmospheric monitoring path may be used. The actual concentrations of the audit gas in the test cell must be selected to

produce effective concentrations in the evaluation level ranges specified in this section of this appendix. Generally, each evaluation concentration measurement result will be the sum of the atmospheric pollutant concentration and the evaluation test concentration. As such, the result must be corrected to remove the atmospheric concentration contribution. The corrected concentration is obtained by subtracting the average of the atmospheric concentrations measured by the open path instrument under test immediately before and immediately after the evaluation test (or preferably before and after each evaluation concentration level) from the evaluation concentration measurement. If the difference between the before and after measurements is greater than 20 percent of the effective concentration of the test gas standard, discard the test result for that concentration level and repeat the test for that level. If possible, open path monitors should be evaluated during periods when the atmospheric pollutant concentrations are relatively low and steady. Also, if the open-path instrument is not installed in a permanent manner, the monitoring path length must be reverified to be within ±3 percent to validate the evaluation since the monitoring path length is critical to the determination of the effective concentration.

3.1.2.6 Report both the evaluation concentrations (effective concentrations for open-path monitors) of the audit gases and the corresponding measured concentration (corrected concentrations, if applicable, for open path monitors) indicated or produced by the monitor being tested to AQS. The percent differences between these concentrations are used to assess the quality of the monitoring data as described in section 4.1.1 of this appendix.

3.1.3 *National Performance Audit Program (NPAP).*

The NPAP is a performance evaluation which is a type of audit where quantitative data are collected independently in order to evaluate the proficiency of an analyst, monitoring instrument or laboratory. Due to the implementation approach used in the program, NPAP provides a national independent assessment of performance while maintaining a consistent level of data quality. Details of the program can be found in reference 11 of this appendix. The program requirements include:

3.1.3.1 Performing audits of the primary monitors at 20 percent of monitoring sites per year, and 100 percent of the sites every 6 years. High-priority sites may be audited more frequently. Since not all gaseous criteria pollutants are monitored at every site within a PQAO, it is not required that 20 percent of the primary monitors for each pollutant receive an NPAP audit each year only that 20 percent of the PQAOs monitoring sites receive an NPAP audit. It is expected that over the 6-year period all primary monitors for all gaseous pollutants will receive an NPAP audit.

3.1.3.2 Developing a delivery system that will allow for the audit concentration gasses to be introduced to the probe inlet where logistically feasible.

3.1.3.3 Using audit gases that are verified against the NIST standard reference methods or special review procedures and validated annually for CO, SO_2 and NO_2, and at the beginning of each quarter of audits for O_3.

3.1.3.4 As described in section 2.4 of this appendix, the PQAO may elect, on an annual basis, to utilize the federally implemented NPAP program. If the PQAO plans to self-implement NPAP, the EPA will establish training and other technical requirements for PQAOs to establish comparability to federally implemented programs. In addition to meeting the requirements in sections 3.1.3.1 through 3.1.3.3 of this appendix, the PQAO must:

(a) Utilize an audit system equivalent to the federally implemented NPAP audit system and is separate from equipment used in annual performance evaluations.

(b) Perform a whole system check by having the NPAP system tested against an independent and qualified EPA lab, or equivalent.

(c) Evaluate the system with the EPA NPAP program through collocated auditing at an acceptable number of sites each year (at least one for an agency network of five or less sites; at least two for a network with more than five sites).

(d) Incorporate the NPAP in the PQAO's quality assurance project plan.

(e) Be subject to review by independent, EPA-trained personnel.

(f) Participate in initial and update training/certification sessions.

3.1.3.5 OAQPS, in consultation with the relevant EPA Regional Office, may approve the PQAO's plan to self-implement NPAP if the OAQPS determines that the PQAO's self-implementation plan is equivalent to the federal programs and adequate to meet the objectives of national consistency and data quality.

3.2 *$PM_{2.5}$.*

3.2.1 *Flow Rate Verification for $PM_{2.5}$.* A one-point flow rate verification check must be performed at least once every month (each verification minimally separated by 14 days) on each monitor used to measure $PM_{2.5}$. The verification is made by checking the operational flow rate of the monitor. If the verification is made in conjunction with a flow rate adjustment, it must be made prior to such flow rate adjustment. For the standard procedure, use a flow rate transfer standard certified in accordance with section 2.6 of this appendix to check the monitor's

normal flow rate. Care should be used in selecting and using the flow rate measurement device such that it does not alter the normal operating flow rate of the monitor. Report the flow rate of the transfer standard and the corresponding flow rate measured by the monitor to AQS. The percent differences between the audit and measured flow rates are used to assess the bias of the monitoring data as described in section 4.2.2 of this appendix (using flow rates in lieu of concentrations).

3.2.2 *Semi-Annual Flow Rate Audit for $PM_{2.5}$.* Audit the flow rate of the particulate monitor twice a year. The two audits should ideally be spaced between 5 and 7 months apart. The EPA strongly encourages more frequent auditing. The audit should (preferably) be conducted by a trained experienced technician other than the routine site operator. The audit is made by measuring the monitor's normal operating flow rate(s) using a flow rate transfer standard certified in accordance with section 2.6 of this appendix. The flow rate standard used for auditing must not be the same flow rate standard used for verifications or to calibrate the monitor. However, both the calibration standard and the audit standard may be referenced to the same primary flow rate or volume standard. Care must be taken in auditing the flow rate to be certain that the flow measurement device does not alter the normal operating flow rate of the monitor. Report the audit flow rate of the transfer standard and the corresponding flow rate measured by the monitor to AQS. The percent differences between these flow rates are used to evaluate monitor performance.

3.2.3 *Collocated Quality Control Sampling Procedures for $PM_{2.5}$.* For each pair of collocated monitors, designate one sampler as the primary monitor whose concentrations will be used to report air quality for the site, and designate the other as the quality control monitor. There can be only one primary monitor at a monitoring site for a given time period.

3.2.3.1 For each distinct monitoring method designation (FRM or FEM) that a PQAO is using for a primary monitor, the PQAO must have 15 percent of the primary monitors of each method designation collocated (values of 0.5 and greater round up); and have at least one collocated quality control monitor (if the total number of monitors is less than three). The first collocated monitor must be a designated FRM monitor.

3.2.3.2 In addition, monitors selected for collocation must also meet the following requirements:

(a) A primary monitor designated as an EPA FRM shall be collocated with a quality control monitor having the same EPA FRM method designation.

(b) For each primary monitor designated as an EPA FEM used by the PQAO, 50 percent of the monitors designated for collocation, or the first if only one collocation is necessary, shall be collocated with a FRM quality control monitor and 50 percent of the monitors shall be collocated with a monitor having the same method designation as the FEM primary monitor. If an odd number of collocated monitors is required, the additional monitor shall be a FRM quality control monitor. An example of the distribution of collocated monitors for each unique FEM is provided below. Table A–2 of this appendix demonstrates the collocation procedure with a PQAO having one type of primary FRM and multiple primary FEMs.

#Primary FEMS of a unique method designation	#Collocated	#Collocated with an FRM	#Collocated with same method designation
1–9	1	1	0
10–16	2	1	1
17–23	3	2	1
24–29	4	2	2
30–36	5	3	2
37–43	6	3	3

3.2.3.3 Since the collocation requirements are used to assess precision of the primary monitors and there can only be one primary monitor at a monitoring site, a site can only count for the collocation of the method designation of the primary monitor at that site.

3.2.3.4 The collocated monitors should be deployed according to the following protocol:

(a) Fifty percent of the collocated quality control monitors should be deployed at sites with annual average or daily concentrations estimated to be within plus or minus 20 percent of either the annual or 24-hour NAAQS and the remainder at the PQAOs discretion;

(b) If an organization has no sites with annual average or daily concentrations within ±20 percent of the annual NAAQS or 24-hour NAAQS, 50 percent of the collocated quality control monitors should be deployed at those sites with the annual mean concentrations or 24-hour concentrations among the highest for all sites in the network and the remainder at the PQAOs discretion.

(c) The two collocated monitors must be within 4 meters (inlet to inlet) of each other and at least 2 meters apart for flow rates greater than 200 liters/min or at least 1 meter apart for samplers having flow rates less than 200 liters/min to preclude airflow interference. A waiver allowing up to 10 meters horizontal distance and up to 3 meters vertical distance (inlet to inlet) between a primary and collocated sampler may be approved by the Regional Administrator for sites at a neighborhood or larger scale of representation during the annual network plan approval process. Sampling and analytical methodologies must be the consistently implemented for both primary and collocated quality control samplers and for all other samplers in the network.

(d) Sample the collocated quality control monitor on a 1-in-12 day schedule. Report the measurements from both primary and collocated quality control monitors at each collocated sampling site to AQS. The calculations for evaluating precision between the two collocated monitors are described in section 4.2.1 of this appendix.

3.2.4 *$PM_{2.5}$ Performance Evaluation Program (PEP) Procedures.* The PEP is an independent assessment used to estimate total measurement system bias. These evaluations will be performed under the NPEP as described in section 2.4 of this appendix or a comparable program. Performance evaluations will be performed annually within each PQAO. For PQAOs with less than or equal to five monitoring sites, five valid performance evaluation audits must be collected and reported each year. For PQAOs with greater than five monitoring sites, eight valid performance evaluation audits must be collected and reported each year. A valid performance evaluation audit means that both the primary monitor and PEP audit concentrations are valid and above 3 $\mu g/m^3$. Siting of the PEP monitor must be consistent with section 3.2.3.4(c). However, any horizontal distance greater than 4 meters and any vertical distance greater than one meter must be reported to the EPA regional PEP coordinator. Additionally for every monitor designated as a primary monitor, a primary quality assurance organization must:

3.2.4.1 Have each method designation evaluated each year; and,

3.2.4.2 Have all FRM, FEM or ARM samplers subject to a PEP audit at least once every 6 years, which equates to approximately 15 percent of the monitoring sites audited each year.

3.2.4.3. Additional information concerning the PEP is contained in reference 10 of this appendix. The calculations for evaluating bias between the primary monitor and the performance evaluation monitor for $PM_{2.5}$ are described in section 4.2.5 of this appendix.

3.3*PM_{10}.*

3.3.1 *Flow Rate Verification for PM_{10} Low Volume Samplers (less than 200 liter/minute).* A one-point flow rate verification check must be performed at least once every month (each verification minimally separated by 14 days) on each monitor used to measure PM_{10}. The verification is made by checking the operational flow rate of the monitor. If the verification is made in conjunction with a flow rate adjustment, it must be made prior to such flow rate adjustment. For the standard procedure, use a flow rate transfer standard certified in accordance with section 2.6 of this appendix to check the monitor's normal flow rate. Care should be taken in selecting and using the flow rate measurement device such that it does not alter the normal operating flow rate of the monitor. The percent differences between the audit and measured flow rates are reported to AQS and used to assess the bias of the monitoring data as described in section 4.2.2 of this appendix (using flow rates in lieu of concentrations).

3.3.2 *Flow Rate Verification for PM_{10} High Volume Samplers (greater than 200 liters/minute).* For PM_{10} high volume samplers, the verification frequency is one verification every 90 days (quarter) with 4 in a year. Other than verification frequency, follow the same technical procedure as described in section 3.3.1 of this appendix.

3.3.3 *Semi-Annual Flow Rate Audit for PM_{10}.* Audit the flow rate of the particulate monitor twice a year. The two audits should ideally be spaced between 5 and 7 months apart. The EPA strongly encourages more frequent auditing. The audit should (preferably) be conducted by a trained experienced technician other than the routine site operator. The audit is made by measuring the monitor's normal operating flow rate using a flow rate transfer standard certified in accordance with section 2.6 of this appendix. The flow rate standard used for auditing must not be the same flow rate standard used for verifications or to calibrate the monitor. However, both the calibration standard and the audit standard may be referenced to the same primary flow rate or volume standard. Care must be taken in auditing the flow rate to be certain that the flow measurement device does not alter the normal operating flow rate of the monitor. Report the audit flow rate of the transfer standard and the corresponding flow rate measured by the monitor to AQS. The percent differences between these flow rates are used to evaluate monitor performance.

3.3.4 *Collocated Quality Control Sampling Procedures for Manual PM_{10}.* Collocated sampling for PM_{10} is only required for manual samplers. For each pair of collocated monitors, designate one sampler as the primary monitor whose concentrations will be used to report air quality for the site and designate the other as the quality control monitor.

3.3.4.1 For manual PM_{10} samplers, a PQAO must:

(a) Have 15 percent of the primary monitors collocated (values of 0.5 and greater round up); and

(b) Have at least one collocated quality control monitor (if the total number of monitors is less than three).

3.3.4.2 The collocated quality control monitors should be deployed according to the following protocol:

(a) Fifty percent of the collocated quality control monitors should be deployed at sites with daily concentrations estimated to be within plus or minus 20 percent of the applicable NAAQS and the remainder at the PQAOs discretion;

(b) If an organization has no sites with daily concentrations within plus or minus 20 percent of the NAAQS, 50 percent of the collocated quality control monitors should be deployed at those sites with the daily mean concentrations among the highest for all sites in the network and the remainder at the PQAOs discretion.

(c) The two collocated monitors must be within 4 meters (inlet to inlet) of each other and at least 2 meters apart for flow rates greater than 200 liters/min or at least 1 meter apart for samplers having flow rates less than 200 liters/min to preclude airflow interference. A waiver allowing up to 10 meters horizontal distance and up to 3 meters vertical distance (inlet to inlet) between a primary and collocated sampler may be approved by the Regional Administrator for sites at a neighborhood or larger scale of representation. This waiver may be approved during the annual network plan approval process. Sampling and analytical methodologies must be the consistently implemented for both collocated samplers and for all other samplers in the network.

(d) Sample the collocated quality control monitor on a 1-in-12 day schedule. Report the measurements from both primary and collocated quality control monitors at each collocated sampling site to AQS. The calculations for evaluating precision between the two collocated monitors are described in section 4.2.1 of this appendix.

(e) In determining the number of collocated quality control sites required for PM_{10}, monitoring networks for lead ($Pb–PM_{10}$) should be treated independently from networks for particulate matter (PM), even though the separate networks may share one or more common samplers. However, a single quality control monitor that meets the collocation requirements for $Pb\text{-}PM_{10}$ and PM_{10} may serve as a collocated quality control monitor for both networks. Extreme care must be taken when using the filter from a quality control monitor for both PM_{10} and Pb analysis. A PM_{10} filter weighing should occur prior to any Pb analysis.

3.4 *Pb*.

3.4.1 *Flow Rate Verification for $Pb–PM_{10}$ Low Volume Samplers (less than 200 liter/minute)*. A one-point flow rate verification check must be performed at least once every month (each verification minimally separated by 14 days) on each monitor used to measure Pb. The verification is made by checking the operational flow rate of the monitor. If the verification is made in conjunction with a flow rate adjustment, it must be made prior to such flow rate adjustment. For the standard procedure, use a flow rate transfer standard certified in accordance with section 2.6 of this appendix to check the monitor's normal flow rate. Care should be taken in selecting and using the flow rate measurement device such that it does not alter the normal operating flow rate of the monitor. The percent differences between the audit and measured flow rates are reported to AQS and used to assess the bias of the monitoring data as described in section 4.2.2 of this appendix (using flow rates in lieu of concentrations).

3.4.2 *Flow Rate Verification for Pb High Volume Samplers (greater than 200 liters/minute)*. For high volume samplers, the verification frequency is one verification every 90 days (quarter) with four in a year. Other than verification frequency, follow the same technical procedure as described in section 3.4.1 of this appendix.

3.4.3 *Semi-Annual Flow Rate Audit for Pb*. Audit the flow rate of the particulate monitor twice a year. The two audits should ideally be spaced between 5 and 7 months apart. The EPA strongly encourages more frequent auditing. The audit should (preferably) be conducted by a trained experienced technician other than the routine site operator. The audit is made by measuring the monitor's normal operating flow rate using a flow rate transfer standard certified in accordance with section 2.6 of this appendix. The flow rate standard used for auditing must not be the same flow rate standard used for verifications or to calibrate the monitor. However, both the calibration standard and the audit standard may be referenced to the same primary flow rate or volume standard. Care must be taken in auditing the flow rate to be certain that the flow measurement device does not alter the normal operating flow rate of the monitor. Report the audit flow rate of the transfer standard and the corresponding flow rate measured by the monitor to AQS. The percent differences between these flow rates are used to evaluate monitor performance.

3.4.4 Collocated Quality Control Sampling for TSP Pb for monitoring sites other than non-source oriented NCore. For each pair of collocated monitors for manual TSP Pb samplers, designate one sampler as the primary monitor whose concentrations will be used to report air quality for the site, and designate the other as the quality control monitor.

3.4.4.1 A PQAO must:

(a) Have 15 percent of the primary monitors (not counting non-source oriented NCore sites in PQAO) collocated. Values of 0.5 and greater round up; and

(b) Have at least one collocated quality control monitor (if the total number of monitors is less than three).

3.4.4.2 The collocated quality control monitors should be deployed according to the following protocol:

(a) The first collocated Pb site selected must be the site measuring the highest Pb concentrations in the network. If the site is impractical, alternative sites, approved by

the EPA Regional Administrator, may be selected. If additional collocated sites are necessary, collocated sites may be chosen that reflect average ambient air Pb concentrations in the network.

(b) The two collocated monitors must be within 4 meters (inlet to inlet) of each other and at least 2 meters apart for flow rates greater than 200 liters/min or at least 1 meter apart for samplers having flow rates less than 200 liters/min to preclude airflow interference.

(c) Sample the collocated quality control monitor on a 1-in-12 day schedule. Report the measurements from both primary and collocated quality control monitors at each collocated sampling site to AQS. The calculations for evaluating precision between the two collocated monitors are described in section 4.2.1 of this appendix.

3.4.5 Collocated Quality Control Sampling for Pb–PM_{10} at monitoring sites other than non-source oriented NCore. If a PQAO is monitoring for Pb–PM_{10} at sites other than at a non-source oriented NCore site then the PQAO must:

3.4.5.1 Have 15 percent of the primary monitors (not counting non-source oriented NCore sites in PQAO) collocated. Values of 0.5 and greater round up; and

3.4.5.2 Have at least one collocated quality control monitor (if the total number of monitors is less than three).

3.4.5.3 The collocated monitors should be deployed according to the following protocol:

(a) Fifty percent of the collocated quality control monitors should be deployed at sites with the highest 3-month average concentrations and the remainder at the PQAOs discretion.

(b) The two collocated monitors must be within 4 meters (inlet to inlet) of each other and at least 2 meters apart for flow rates greater than 200 liters/min or at least 1 meter apart for samplers having flow rates less than 200 liters/min to preclude airflow interference. A waiver allowing up to 10 meters horizontal distance and up to 3 meters vertical distance (inlet to inlet) between a primary and collocated sampler may be approved by the Regional Administrator for sites at a neighborhood or larger scale of representation. This waiver may be approved during the annual network plan approval process. Sampling and analytical methodologies must be the consistently implemented for both collocated samplers and for all other samplers in the network.

(c) Sample the collocated quality control monitor on a 1-in-12 day schedule. Report the measurements from both primary and collocated quality control monitors at each collocated sampling site to AQS. The calculations for evaluating precision between the two collocated monitors are described in section 4.2.1 of this appendix.

(d) In determining the number of collocated quality control sites required for Pb–PM_{10}, monitoring networks for PM_{10} should be treated independently from networks for Pb–PM_{10}, even though the separate networks may share one or more common samplers. However, a single quality control monitor that meets the collocation requirements for Pb–PM_{10} and PM_{10} may serve as a collocated quality control monitor for both networks. Extreme care must be taken when using a using the filter from a quality control monitor for both PM_{10} and Pb analysis. A PM_{10} filter weighing should occur prior to any Pb analysis.

3.4.6 *Pb Analysis Audits.* Each calendar quarter, audit the Pb reference or equivalent method analytical procedure using filters containing a known quantity of Pb. These audit filters are prepared by depositing a Pb standard on unexposed filters and allowing them to dry thoroughly. The audit samples must be prepared using batches of reagents different from those used to calibrate the Pb analytical equipment being audited. Prepare audit samples in the following concentration ranges:

Range	Equivalent ambient Pb concentration, $\mu g/m^3$
1	30–100% of Pb NAAQS.
2	200–300% of Pb NAAQS.

(a) Extract the audit samples using the same extraction procedure used for exposed filters.

(b) Analyze three audit samples in each of the two ranges each quarter samples are analyzed. The audit sample analyses shall be distributed as much as possible over the entire calendar quarter.

(c) Report the audit concentrations (in µg Pb/filter or strip) and the corresponding measured concentrations (in µg Pb/filter or strip) to AQS using AQS unit code 077. The percent differences between the concentrations are used to calculate analytical accuracy as described in section 4.2.6 of this appendix.

3.4.7 Pb PEP Procedures for monitoring sites other than non-source oriented NCore. The PEP is an independent assessment used to estimate total measurement system bias. These evaluations will be performed under the NPEP described in section 2.4 of this appendix or a comparable program. Each year, one performance evaluation audit must be performed at one Pb site in each primary quality assurance organization that has less than or equal to five sites and two audits at PQAOs with greater than five sites. Non-source oriented NCore sites are not counted. Siting of the PEP monitor must be consistent with section 3.4.5.3(b). However, any horizontal distance greater than 4 meters and any vertical distance greater than 1 meter must be reported to the EPA regional

PEP coordinator. In addition, each year, four collocated samples from PQAOs with less than or equal to five sites and six collocated samples at PQAOs with greater than five sites must be sent to an independent laboratory, the same laboratory as the performance evaluation audit, for analysis. The calculations for evaluating bias between the primary monitor and the performance evaluation monitor for Pb are described in section 4.2.4 of this appendix.

4. Calculations for Data Quality Assessments

(a) Calculations of measurement uncertainty are carried out by the EPA according to the following procedures. The PQAOs must report the data to AQS for all measurement quality checks as specified in this appendix even though they may elect to perform some or all of the calculations in this section on their own.

(b) The EPA will provide annual assessments of data quality aggregated by site and PQAO for SO_2, NO_2, O_3 and CO and by PQAO for PM_{10}, $PM_{2.5}$, and Pb.

(c) At low concentrations, agreement between the measurements of collocated quality control samplers, expressed as relative percent difference or percent difference, may be relatively poor. For this reason, collocated measurement pairs are selected for use in the precision and bias calculations only when both measurements are equal to or above the following limits:

(1) Pb: 0.002 μg/m³ (Methods approved after 3/04/2010, with exception of manual equivalent method EQLA–0813–803).

(2) Pb: 0.02 μg/m³ (Methods approved before 3/04/2010, and manual equivalent method EQLA–0813–803).

(3) PM_{10} (Hi-Vol): 15 μg/m³.

(4) PM_{10} (Lo-Vol): 3 μg/m³.

(5) $PM_{2.5}$: 3 μg/m³.

4.1 *Statistics for the Assessment of QC Checks for* SO_2, NO_2, O_3 and CO.

4.1.1 *Percent Difference.* Many of the measurement quality checks start with a comparison of an audit concentration or value (flow rate) to the concentration/value measured by the monitor and use percent difference as the comparison statistic as described in equation 1 of this section. For each single point check, calculate the percent difference, d_i, as follows:

Equation 1

$$d_i = \frac{meas - audit}{audit} \cdot 100$$

where *meas* is the concentration indicated by the PQAO's instrument and *audit* is the audit concentration of the standard used in the QC check being measured.

4.1.2 *Precision Estimate.* The precision estimate is used to assess the one-point QC checks for SO_2, NO_2, O_3, or CO described in section 3.1.1 of this appendix. The precision estimator is the coefficient of variation upper bound and is calculated using equation 2 of this section:

Equation 2

$$CV = \sqrt{\frac{n \cdot \sum_{i=1}^{n} d_i^2 - \left(\sum_{i=1}^{n} d_i\right)^2}{n(n-1)}} \cdot \sqrt{\frac{n-1}{\chi^2_{0.1,n-1}}}$$

where n is the number of single point checks being aggregated; $X^2_{0.1,n-1}$ is the 10th percentile of a chi-squared distribution with n–1 degrees of freedom.

4.1.3 *Bias Estimate.* The bias estimate is calculated using the one-point QC checks for SO_2, NO_2, O_3, or CO described in section 3.1.1 of this appendix. The bias estimator is an upper bound on the mean absolute value of the percent differences as described in equation 3 of this section:

Equation 3

$$|bias| = AB + t_{0.95,n-1} \cdot \frac{AS}{\sqrt{n}}$$

where n is the number of single point checks being aggregated; $t_{0.95,n-1}$ is the 95th quantile of a t-distribution with n–1 degrees of freedom; the quantity AB is the mean of the absolute values of the $d_{i's}$ and is calculated using equation 4 of this section:

Equation 4

$$AB = \frac{1}{n} \cdot \sum_{i=1}^{n} |d_i|$$

and the quantity AS is the standard deviation of the absolute value of the $d_{i's}$ and is calculated using equation 5 of this section:

Equation 5

$$AS = \sqrt{\frac{n \cdot \sum_{i=1}^{n} |d_i|^2 - \left(\sum_{i=1}^{n} |d_i|\right)^2}{n(n-1)}}$$

4.1.3.1 *Assigning a sign (positive/negative) to the bias estimate.* Since the bias statistic as calculated in equation 3 of this appendix uses absolute values, it does not have a tendency (negative or positive bias) associated with it. A sign will be designated by rank ordering the percent differences of the QC check samples from a given site for a particular assessment interval.

4.1.3.2 Calculate the 25th and 75th percentiles of the percent differences for each site. The absolute bias upper bound should be flagged as positive if both percentiles are positive and negative if both percentiles are negative. The absolute bias upper bound would not be flagged if the 25th and 75th percentiles are of different signs.

4.2 *Statistics for the Assessment of* PM_{10}, $PM_{2.5}$, and Pb.

4.2.1 *Collocated Quality Control Sampler Precision Estimate for PM_{10}, $PM_{2.5}$ and Pb.* Precision is estimated via duplicate measurements from collocated samplers. It is recommended that the precision be aggregated at the PQAO level quarterly, annually, and at the 3-year level. The data pair would only be considered valid if both concentrations are greater than or equal to the minimum values specified in section 4(c) of this appendix. For each collocated data pair, calculate the relative percent difference, d_i, using equation 6 of this appendix:

Equation 6

$$d_i = \frac{X_i - Y_i}{(X_i + Y_i)/2} \cdot 100$$

where X_i is the concentration from the primary sampler and Y_i is the concentration value from the audit sampler. The coefficient of variation upper bound is calculated using equation 7 of this appendix:

Equation 7

$$CV = \sqrt{\frac{n \cdot \sum_{i=1}^{n} d_i^2 - \left(\sum_{i=1}^{n} d_i\right)^2}{2n(n-1)}} \cdot \sqrt{\frac{n-1}{X^2_{0.1,n-1}}}$$

where n is the number of valid data pairs being aggregated, and $X^2_{0.1,n-1}$ is the 10th percentile of a chi-squared distribution with n–1 degrees of freedom. The factor of 2 in the denominator adjusts for the fact that each d_i is calculated from two values with error.

4.2.2 *One-Point Flow Rate Verification Bias Estimate for PM_{10}, $PM_{2.5}$ and Pb.* For each one-point flow rate verification, calculate the percent difference in volume using equation 1 of this appendix where *meas* is the value indicated by the sampler's volume measurement and *audit* is the actual volume indicated by the auditing flow meter. The absolute volume bias upper bound is then calculated using equation 3, where n is the number of flow rate audits being aggregated; $t_{0.95,n-1}$ is the 95th quantile of a t-distribution with n-1 degrees of freedom, the quantity *AB* is the mean of the absolute values of the d_i's and is calculated using equation 4 of this appendix, and the quantity *AS* in equation 3 of this appendix is the standard deviation of the absolute values if the d_i's and is calculated using equation 5 of this appendix.

4.2.3 *Semi-Annual Flow Rate Audit Bias Estimate for PM_{10}, $PM_{2.5}$ and Pb.* Use the same procedure described in section 4.2.2 for the evaluation of flow rate audits.

4.2.4 *Performance Evaluation Programs Bias Estimate for Pb.* The Pb bias estimate is calculated using the paired routine and the PEP monitor as described in section 3.4.7. Use the same procedures as described in section 4.1.3 of this appendix.

4.2.5 *Performance Evaluation Programs Bias Estimate for $PM_{2.5}$.* The bias estimate is calculated using the PEP audits described in section 4.1.3 of this appendix. The bias estimator is based on the mean percent differences (Equation 1). The mean percent difference, D, is calculated by Equation 8 below.

Equation 8

$$D = \frac{1}{n_j} \cdot \sum_{i=1}^{n_j} d_i$$

where n_j is the number of pairs and $d_1, d_2, \ldots d_{nj}$ are the biases for each pair to be averaged.

4.2.6 *Pb Analysis Audit Bias Estimate.* The bias estimate is calculated using the analysis audit data described in section 3.4.6. Use the same bias estimate procedure as described in section 4.1.3 of this appendix.

5. Reporting Requirements

5.1 *Reporting Requirements.* For each pollutant, prepare a list of all monitoring sites and their AQS site identification codes in each PQAO and submit the list to the appropriate EPA Regional Office, with a copy to AQS. Whenever there is a change in this list of monitoring sites in a PQAO, report this change to the EPA Regional Office and to AQS.

5.1.1 *Quarterly Reports.* For each quarter, each PQAO shall report to AQS directly (or via the appropriate EPA Regional Office for organizations not direct users of AQS) the results of all valid measurement quality checks it has carried out during the quarter. The quarterly reports must be submitted consistent with the data reporting requirements specified for air quality data as set forth in 40 CFR 58.16. The EPA strongly encourages early submission of the quality assurance data in order to assist the PQAOs ability to control and evaluate the quality of the ambient air data.

5.1.2 *Annual Reports.*

5.1.2.1 When the PQAO has certified relevant data for the calendar year, the EPA will calculate and report the measurement uncertainty for the entire calendar year.

6. REFERENCES

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(11) National Performance Evaluation Program Standard Operating Procedures. *http://www3.epa.gov/ttn/amtic/npapsop.html*.

TABLE A–1 OF APPENDIX A TO PART 58—MINIMUM DATA ASSESSMENT REQUIREMENTS FOR NAAQS RELATED CRITERIA POLLUTANT MONITORS

Method	Assessment method	Coverage	Minimum frequency	Parameters reported	AQS assessment type
Gaseous Methods (CO, NO_2, SO_2, O_3)					
One-Point QC for SO_2, NO_2, O3, CO.	Response check at concentration 0.005–0.08 ppm SO_2, NO_2, O3, and. 0.5 and 5 ppm CO	Each analyzer	Once per 2 weeks.	Audit concentration [1] and measured concentration. [2]	One-Point QC.
Annual performance evaluation for SO_2, NO_2, O3, CO.	See section 3.1.2 of this appendix.	Each analyzer	Once per year.	Audit concentration [1] and measured concentration [2] for each level.	Annual PE.
NPAP for SO_2, NO_2, O3, CO.	Independent Audit	20% of sites each year.	Once per year.	Audit concentration [1] and measured concentration [2] for each level.	NPAP.
Particulate Methods					
Continuous [4] method—collocated quality control sampling $PM_{2.5}$.	Collocated samplers ..	15%	1-in-12 days	Primary sampler concentration and duplicate sampler concentration. [3]	No Transaction reported as raw data.

TABLE A–1 OF APPENDIX A TO PART 58—MINIMUM DATA ASSESSMENT REQUIREMENTS FOR NAAQS RELATED CRITERIA POLLUTANT MONITORS—Continued

Method	Assessment method	Coverage	Minimum frequency	Parameters reported	AQS assessment type
Manual method—collocated quality control sampling PM_{10}, $PM_{2.5}$, Pb–TSP, Pb–PM_{10}.	Collocated samplers ..	15%	1-in-12 days	Primary sampler concentration and duplicate sampler concentration. [3]	No Transaction reported as raw data.
Flow rate verification PM_{10} (low Vol) $PM_{2.5}$, Pb–PM_{10}.	Check of sampler flow rate.	Each sampler	Once every month.	Audit flow rate and measured flow rate indicated by the sampler.	Flow Rate Verification.
Flow rate verification PM_{10} (High-Vol), Pb–TSP.	Check of sampler flow rate.	Each sampler	Once every quarter.	Audit flow rate and measured flow rate indicated by the sampler.	Flow Rate Verification.
Semi-annual flow rate audit PM_{10}, TSP, PM_{10}–2.5, $PM_{2.5}$, Pb–TSP, Pb–PM_{10}.	Check of sampler flow rate using independent standard.	Each sampler, ...	Once every 6 months.	Audit flow rate and measured flow rate indicated by the sampler.	Semi Annual Flow Rate Audit.
Pb analysis audits Pb–TSP, Pb–PM_{10}.	Check of analytical system with Pb audit strips/filters.	Analytical	Once each quarter.	Measured value and audit value (ug Pb/filter) using AQS unit code 077.	Pb Analysis Audits.
Performance Evaluation Program $PM_{2.5}$.	Collocated samplers ..	(1) 5 valid audits for primary QA orgs, with ≤5 sites.. (2) 8 valid audits for primary QA orgs, with >5 sites.. (3) All samplers in 6 years.	Distributed over all 4 quarters.	Primary sampler concentration and performance evaluation sampler concentration.	PEP.
Performance Evaluation Program Pb–TSP, Pb–PM_{10}.	Collocated samplers ..	(1) 1 valid audit and 4 collocated samples for primary QA orgs, with ≤5 sites.. (2) 2 valid audits and 6 collocated samples for primary QA orgs with >5 sites.	Distributed over all 4 quarters.	Primary sampler concentration and performance evaluation sampler concentration. Primary sampler concentration and duplicate sampler concentration.	PEP.

[1] Effective concentration for open path analyzers.
[2] Corrected concentration, if applicable for open path analyzers.
[3] Both primary and collocated sampler values are reported as raw data.
[4] $PM_{2.5}$ is the only particulate criteria pollutant requiring collocation of continuous and manual primary monitors.

TABLE A–2 OF APPENDIX A TO PART 58—SUMMARY OF $PM_{2.5}$ NUMBER AND TYPE OF COLLOCATION (15% COLLOCATION REQUIREMENT) REQUIRED USING AN EXAMPLE OF A PQAO THAT HAS 54 PRIMARY MONITORS (54 SITES) WITH ONE FEDERAL REFERENCE METHOD TYPE AND THREE TYPES OF APPROVED FEDERAL EQUIVALENT METHODS

Primary sampler method designation	Total No. of monitors	Total No. of collocated	No. of collocated with FRM	No. of collocated with same method designation as primary
FRM	20	3	3	3
FEM (A)	20	3	2	1
FEM (B)	2	1	1	0
FEM (C)	12	2	1	1

[81 FR 17280, Mar. 28, 2016]

State of Oregon Department of Environmental Quality

OAR 340-225-0020 Federal Land Managers' Air Quality Related Values Work Group Phase I Report - Revised

National Park Service
U.S. Department of the Interior

Natural Resource Program Center

Federal Land Managers' Air Quality Related Values Work Group (FLAG)

Phase I Report—Revised (2010)

Natural Resource Report NPS/NRPC/NRR—2010/232

Item E 002669

ON THE COVER

Courthouse Towers, Arches National Park, Utah.
Photo by Debbie Miller.

THIS PAGE:

Jumping Cholla, Superstition Wilderness, Arizona.
Photo by Steve Boutcher

Federal Land Managers' Air Quality Related Values Work Group (FLAG)

Phase I Report—Revised (2010)

Natural Resource Report NPS/NRPC/NRR—2010/232

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October 2010

The National Park Service, Natural Resource Program Center publishes a range of reports that address natural resource topics of interest and applicability to a broad audience in the National Park Service and others in natural resource management, including scientists, conservation and environmental constituencies, and the public.

The Natural Resource Report Series is used to disseminate high-priority, current natural resource management information with managerial application. The series targets a general, diverse audience, and may contain NPS policy considerations or address sensitive issues of management applicability.

All manuscripts in the series receive the appropriate level of peer review to ensure that the information is scientifically credible, technically accurate, appropriately written for the intended audience, and designed and published in a professional manner.

This guidance document was jointly prepared by the National Park Service, U.S. Forest Service, and the U.S. Fish and Wildlife Service, in collaboration with the Environmental Protection Agency. Guidance contained herein has been reviewed by subject matter experts and the general public through formal public review and comment period. This guidance document provides information for Federal Land Managers, permitting authorities, and permit applicants to use when assessing air quality impacts to air quality related values. Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. Government.

This report is available from the Air Resources Division of the NPS (http://www.nature.nps.gov/air) and the Natural Resource Publications Management Web site (http://www.nature.nps.gov/publications/NRPM) on the Internet.

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NPS 999/105412, October 2010

United States Department of the Interior

OFFICE OF THE SECRETARY
Washington, D.C. 20240

OCT -7 2010

Dear FLAG User:

We are pleased to provide the final revised FLAG report (FLAG 2010). FLAG was formed at the request of permit applicants and State permit review authorities to develop a more consistent and objective approach for the Federal Land Managers (FLMs), *i.e.*, National Park Service, U.S. Fish and Wildlife Service, and U.S. Department of Agriculture Forest Service, to evaluate air pollution effects on their Air Quality Related Values (AQRVs). The FLAG effort focused on how air pollutants – primarily particulate matter, nitrogen dioxide, sulfur dioxide, nitrates, sulfates, ozone – affect the health and status of resources in areas managed by the three agencies. FLAG subgroups concentrated on four key issues: (1) visibility; (2) aquatic and terrestrial effects of wet and dry pollutant deposition; (3) terrestrial effects of ozone; and (4) process and policy issues. In December 2000, the FLMs published a final Phase I report (FLAG 2000). Based on knowledge gained and regulatory developments since FLAG 2000, the FLMs believe certain revisions to FLAG 2000 are now appropriate. The final revised FLAG 2010 report reflects those changes.

The FLAG 2010 report contains a wealth of information and should continue to be a very useful tool; we support its recommendations. The FLAG report is guidance and reflects agency direction, but it is not a rule. Nevertheless, we encourage all FLMs, permitting authorities, permit applicants, and other interested parties to take advantage of the helpful information contained in the FLAG report when assessing air pollution impacts on AQRVs.

We want to thank the many people who contributed to this important and worthwhile project.

Sincerely,

Thomas L. Strickland
Assistant Secretary for Fish and Wildlife and Parks
Department of the Interior

Sincerely,

Harris Sherman, Under Secretary
Natural Resources and the Environment
Department of Agriculture

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Item E 002678

Preface to this Edition of the FLAG Phase I Report (New)

Under the Clean Air Act, the Federal Land Manager (FLM) and the Federal official with direct responsibility for management of Federal Class I parks and wilderness areas (i.e., Park Superintendent, Refuge Manager, Forest Supervisor) have an affirmative responsibility to protect the air quality related values (AQRVs) (including visibility) of such lands, and to consider whether a proposed major emitting facility will have an adverse impact on such values. The FLM's decision regarding whether there is an adverse impact is then conveyed to the permitting authority – usually a State agency – for consideration in its determinations regarding the permit. The permitting authority's determinations generally consider a wide range of factors, including the potential impact of the new source or major modification on the AQRVs of Class I areas, if applicable.

Both State permitting agencies and permit applicants requested that the FLMs provide better consistency pertaining to their role in the review of new source permit applications near Federal Class I areas. To address this concern, the FLMs formed the Federal Land Managers' Air Quality Related Values Work Group (FLAG). The official "FLM" is the Secretary of the department with authority over the Federal Class I areas (or the Secretary's designee). For the Department of the Interior, the Secretary has designated the Assistant Secretary for Fish and Wildlife and Parks as the FLM, whereas the Secretary of Agriculture has delegated the FLM responsibilities to the Regional Forester, and in some cases, the Forest Supervisor.

The purpose of FLAG is twofold: (1) to develop a more consistent and objective approach for the FLMs to evaluate air pollution effects on public AQRVs in Class I areas, including a process to identify those resources and any potential adverse impacts, and (2) to provide State permitting authorities and potential permit applicants consistency on how to assess the impacts of new and existing sources on AQRVs in Class I areas, especially in the review of Prevention of Significant Deterioration (PSD) of air quality permit applications. Under the Clean Air Act, the FLM formal "affirmative responsibility" role in the permitting process is limited to the extent a proposed new or modified source may affect AQRVs in a Class I area.[1]

Adult Brown Pelicans on Breton Island National Wildlife Refuge, Louisiana.
Credit: USFWS

FLAG members include representatives from three of the federal land management agencies that administer Federal Class I areas: the U.S. Forest Service (USFS), under the Department of Agriculture, and the National Park Service (NPS) and U.S. Fish and Wildlife Service (FWS) under the Department of the Interior, hereafter referred to as "the Agencies" or the "FLMs." In addition, five Tribal governments each administer their redesignated Class I areas, and the Bureau of Land Management (BLM) jointly administers four mandatory Federal Class I areas with the USFS. BLM is not a member of FLAG. However, because BLM does manage federal PSD Class I lands, as well as large amounts of acres in the vicinity of many FLAG Agencies' Class I areas, they may apply, when appropriate, the assessment methodologies outlined in the FLAG report. Applicants with the potential to adversely impact visibility or other AQRVs at PSD Class I areas administered by the BLM should contact that agency directly to discuss their considerations. The Agencies review permit applications for projects that may impact their areas, and make recommendations to their respective FLM as to whether or not those impacts might be considered adverse. The FLM will then make the final decision regarding the nature of the potential impacts to AQRVs, which is then conveyed to the permitting authority for its consideration.

In December 2000, after undergoing a public review and comment process that included a 90 day public comment period announced in the *Federal Register* and a public meeting, the FLMs published a *FLAG Phase I Report* (FLAG 2000), along with an accompanying "Response to Public Comments" document. The FLAG 2000 report described the work accomplished in Phase I of the FLAG effort. FLAG 2000 provided State permitting authorities and potential permit applicants a consistent methodology for conducting Class I area impact analyses. At that time, the Agencies envisioned a FLAG Phase II to address unresolved issues

1. Nevertheless, the FLMs are also concerned about resources in Class II parks and wilderness areas because they have other mandates to protect those areas as well. The information and procedures outlined in this document are generally applicable to evaluating the effect of new or modified sources on the AQRVs in both Class I and Class II areas, including the evaluation of effects as part of Environmental Assessments and/or Environmental Impact Statements under the National Environmental Policy Act (NEPA). However, FLAG does not preclude more refined or regional analyses being performed under NEPA or other programs.

including those that will require research and the collection of new data. However, resource constraints have prevented the Agencies from embarking on a formal FLAG Phase II process, but the Agencies have made significant progress in obtaining effects-based information as part of their resource-protection responsibilities. This information is included in this revised report.

The Agencies formed three separate subgroups to deal with area specific technical and policy issues associated with visibility impairment, ozone effects on vegetation, and effects of pollutant deposition on soils and surface waters. FLAG 2000 consolidated the results of those three subgroups.

FLAG 2000 included recommendations for completing and evaluating New Source Review (NSR) projects that may affect federally protected areas. It was intended to be a screening tool to help the Agencies and permit applicants determine whether impacts would be negligible. It was not intended to provide a bright-line test that would allow one to determine whether or not a proposed source of air pollution would cause or contribute to an adverse impact on AQRVs. That determination remains a project-specific management decision of the FLM. Among other factors, the FLMs' assessment of whether or not an adverse impact would occur is based on the sensitivity of the AQRVs at the particular federally protected area under consideration, and the magnitude, frequency, duration, timing, and geographic extent of the estimated new source impacts. This report (FLAG 2010) reaffirms these intentions.

FLAG 2000 has been a useful tool to the Agencies, State permitting authorities, and permit applicants. It was intended to be a working document that would be revised as necessary as the Agencies learn more about how to better assess the health and status of AQRVs. Based on knowledge gained and regulatory developments since FLAG 2000, the Agencies believe certain revisions to FLAG 2000 are now appropriate. This revised report (FLAG 2010) reflects those changes. However, it is important to emphasize that in this revision the Agencies have made certain changes to update specific information and data, but retain intact much of the background and general information contained in FLAG 2000 (e.g., Appendices A through H). Therefore, while this version replaces FLAG 2000, FLAG 2010 does not constitute a comprehensive update of all the information and material contained in FLAG 2000. Instead, the Agencies have focused their efforts on those areas of FLAG 2000 that have received the most attention and concern from permit applicants and permitting authorities. In that regard, the Agencies have included substantial changes to the visibility analysis sections, as well as included a more detailed discussion of the factors that the FLMs will use in the decision making process for an adverse impact determination. The Agencies have also taken this opportunity to discuss some key regulatory developments since FLAG 2000, as well as update some information in the FLAG 2000 deposition and ozone sections. To aid the FLAG user wanting to focus on the most recent changes, the Agencies have identified those new and revised sections throughout the FLAG 2010 report.

The most significant changes in this FLAG 2010 revision are summarized as follows:

- Adopts similar criteria derived from EPA's 2005 Best Available Retrofit Technology (BART) guidelines for the Regional Haze Rule to screen out from AQRV review those sources with relatively small amounts of emissions located a large distance from a Class I area (i.e., Q/D ≤ 10, for sources located greater than 50 km away).
- Utilizes the most recent EPA estimates to determine annual average or 20% best natural visibility conditions for Class I areas, using the new EPA-approved visibility algorithm.
- Adopts criteria derived from the 2005 BART guidelines that utilizes monthly average relative humidity adjustment factors to minimize the effects of weather events (i.e., short-term meteorological phenomena) on modeled visibility impacts.
- Adopts criteria derived from the 2005 BART guidelines that sets a 98th percentile value to screen out roughly seven days of haze-type visibility impairment per year.
- Includes deposition analysis thresholds and concern thresholds for nitrogen and sulfur deposition impacts on vegetation, soils, and water.
- Increases transparency and consistency of factors considered for adverse impact determinations.

A comparison of these FLAG 2010 changes to information contained in FLAG 2000 is provided in Table 1:

Other changes of note included in FLAG 2010 are:

- Clarifies the near field visibility analysis techniques for analyzing plumes or layers viewed against a background;
- Expands discussion of "Critical Loads" to reflect some significant developments in this area since FLAG 2000;
- Updates ozone sensitive species lists contained in Appendix 3.A of the FLAG 2000 report, but now includes that information on individual agency web sites rather than in the FLAG 2010 report;
- Replaces Appendix 3.B of FLAG 2000 (W126 and N100 ozone values) with current information on the individual agency web sites;
- Updates the information contained in Table D-2 of FLAG 2000 to reflect current information, but now includes that information on individual agency web sites rather than in the FLAG 2010 report;
- Replaces the dated sulfate, nitrate, and ammonium ion concentration maps (Figures D-2, D-3, and D-4 of FLAG 2000), with a reference to the NADP site for current trends data.

Table 1. FLAG 2000 vs. FLAG 2010 Analyses

	FLAG 2000	FLAG 2010
Annual emissions/Distance (Q/D) screening criteria. (Not applicable for Class I increment analyses).	None	≤10 (sum of certain pollutant emissions (TPY) divided by distance (km) from Class I area; applies to all AQRVs, not just visibility. See section 3.2.
Background Visibility Conditions.	Based on annual average natural, using NAPAP estimates.	Based on annual average natural, or 20% best natural, using EPA data from Regional Haze Rule development. See section 3.3.3.
Relative Humidity Adjustment Factor (f(RH)).	Hour-by-hour (with RH capped at 98%).	Monthly average (with RH capped at 95%). See section 3.3.3.
First Level Screening Model.	CALPUFF or CALPUFF-lite.	CALPUFF only. See section 3.3.3.
Visibility Assessment Criteria.	Maximum modeled value.	98th percentile modeled value at any receptor. See section 3.3.3.
Deposition Analysis Thresholds/ Concern Thresholds	None	Provided for nitrogen and sulfur deposition. See section 3.5.6.
Adverse Impact Determination Criteria.	"Likely to Object" if 10% threshold exceeded; regulatory factors implicitly considered.	Adverse impact determination process more explicit; considers regulatory and other factors. See sections 4.2-4.4

Executive Summary (Revised)

The Federal Land Managers' Air Quality Related Values Work Group (FLAG) formed to develop a more consistent approach for the Federal Land Managers (FLMs) to evaluate air pollution effects on resources. As discussed in the Preface, the *FLAG Phase I Report* (FLAG 2000) is being revised in part at this time. The primary—but not sole—focus of FLAG is the New Source Review (NSR) program, especially in the review of Prevention of Significant Deterioration (PSD) of air quality permit applications. The goals of FLAG have been to provide consistent policies and processes both for identifying air quality related values (AQRVs) and for evaluating the effects of air pollution on AQRVs, primarily in Federal Class I air quality areas, but also in some instances, in other national parks, national forests, national wildlife refuges, wilderness areas, and national monuments. Federal Class I areas are defined in the Clean Air Act as national parks over 6,000 acres and wilderness areas and memorial parks over 5,000 acres, established as of 1977. All other FLM areas are designated Class II. Maps of the Agencies' Federal Class I areas are provided in Appendix E.

FLMs have an "affirmative responsibility" to protect AQRVs. In this respect, the FLM role consists of considering whether emissions from a new or modified source may have an adverse impact on AQRVs and providing comments to permitting authorities (States or EPA). FLMs have no permitting authority under the Clean Air Act, and they have no authority under the Clean Air Act to establish air quality-related rules or standards. It is important to emphasize that the FLAG report only explains factors and information the FLMs expect to use when carrying out their consultative role. It is separate from Federal regulatory programs.

FLAG members include representatives from the three primary agencies that administer the nation's Federal Class I areas: the U.S. Forest Service (USFS), the National Park Service (NPS), and the U.S. Fish and Wildlife Service (FWS). (Subsequently in this report, these three agencies collectively will be referred to as "the Agencies" or the "FLMs." Class I and Class II air quality areas are called "FLM areas" in this report.) Appendix F contains a list of participants that worked on the original FLAG 2000 report.

This report describes the work accomplished in Phase I of the FLAG effort as revised to reflect current developments. That work includes identifying policies and processes common to the FLMs (herein called "commonalities") and developing new policies and processes using readily available information. This report provides State permitting authorities and potential permit applicants a consistent and predictable process for assessing the impacts of new and existing sources on AQRVs, including a process to identify those AQRVs and potential adverse impacts. The report also discusses considerations unrelated to new source review and managing emissions in Federal areas. If and when the Agencies embark on Phase II, FLAG will address unresolved issues including those that will require research and the collection of new data.

Marble Mountain Wilderness, California.
Credit: Steve Boutcher

This revised *FLAG Phase I Report* consolidates the results of the FLAG Visibility, Ozone, and Deposition subgroups. The chapters prepared by these subgroups contain issue-specific technical and policy analyses, recommendations for evaluating AQRVs, and information for completing and evaluating NSR permit applications. This information and the associated recommendations are intended for use by the FLMs, permitting authorities, NSR permit applicants, and other interested parties. The report includes background information on the roles and responsibilities of the FLMs under the NSR program.

This document includes recommendations for completing and evaluating NSR applications that may affect Class I FLM areas. This information can also be used to evaluate impacts on Class II parks and wilderness areas. It does not provide a universal formula that would, in all situations, allow one to determine whether or not a source of air pollution causes or contributes to an adverse impact. That determination remains a project-specific management decision, the responsibility for which remains with the FLM, as delegated by Congress. The FLM's assessment of whether or not an adverse impact would occur is based on the sensitivity of the AQRVs at the particular FLM area under consideration, as well as the consideration of several other factors, including the magnitude, frequency, duration, timing, and geographic extent of the new source's impacts.

To provide information for the FLM's assessment of adverse impacts on AQRVs, the permit applicant should identify the potential impacts of the source on all applicable AQRVs of that area. An FLM may ask that an applicant address any or all of the areas of concern. The primary areas of concern to the FLMs with respect to air pollution emissions are

visibility impairment, ozone effects on vegetation, and effects of pollutant deposition on soils and surface waters.

The *FLAG Phase I Report* also describes the FLAG effort, including the FLAG approach, organization, and plans for future FLAG work. Appendix A of the report contains a glossary of technical terms, abbreviations, and acronyms used in the report along with associated definitions. Appendix G provides a list of all references cited in the FLAG report.

The key recommendations developed by the Visibility, Ozone, and Deposition subgroups are summarized below, and updated in part in this FLAG 2010 revision. However, for all three subject matter areas, FLAG recommends that the permit applicant consult with the appropriate permitting authority and with the FLM for the affected area(s) for confirmation of preferred procedures. This consultation should take place in the early stages of the permit application process.

Recommendations for Evaluating Visibility Impacts (Revised)

FLAG provides recommendations, specific procedures, and interpretation of results for assessing visibility impacts of new or modified sources on Class I area resources.[2]

FLAG addresses assessments for sources proposed for locations near (generally within 50 km) and at large distances (greater than 50 km) from these areas. The key components of the recommendations are highlighted below.

In general, FLAG recommends that an applicant:

- Apply the Q/D test (see "INITIAL SCREENING TEST" below) for proposed sources greater than 50 km from a Class I area to determine whether or not any further visibility analysis is necessary.
- Consult with the appropriate regulatory agency and with the FLM for the affected Class I area(s) or other affected area for confirmation of preferred visibility analysis procedures.
- Obtain FLM recommendation for the specified reference levels (estimate of natural conditions) and, if applicable, FLM recommended plume/observer geometries and model receptor locations.
- Apply the applicable EPA Guideline, steady-state models for regions within the Class I area that are affected by plumes or layers that are viewed against a background (generally within 50 km of the source).
  - Calculate hourly estimates of changes in visibility, as characterized by the change in the color difference index (ΔE) and plume contrast (C), with respect to natural conditions, and compare these estimates with the thresholds given in section 3.3.3.
- For regions of the Class I area where visibility impairment from the source would cause a general alteration of the appearance of the scene (generally 50 km or more away from the source or from the interaction of the emissions from multiple sources), apply a non-steady-state air quality model with chemical transformation capabilities (refer to EPA's *Guideline on Air Quality Models*), which yields ambient concentrations of visibility-impairing pollutants. At each Class I receptor:
  - Calculate the change in extinction due to the source being analyzed, compare these changes with the reference conditions, and then compare these results with the thresholds given in section 3.3.3.
  - Utilize estimates of annual average natural visibility conditions for each Class I area as presented in Table 6, unless otherwise recommended by the FLM or permitting authority. Alternative estimates of visibility conditions are provided in Table 5 for consistency with State agencies that elected to use 20% best visibility for regional haze or BART implementations, or when FLMs recommend using the 20% best visibility as natural background.
- If first-level modeling results are above levels of concern, continue to consult with the Agencies to discuss other considerations (e.g., possible impact mitigation, more refined analyses).

This review process for distant/multi-source applications is portrayed schematically in Figure 1.

Recommendations for Evaluating Ozone Impacts (Revised)

- FLM actions or specific requests on a permit application will be based on the existing air pollution situation at the area they manage. These conditions include (1) whether or not actual ozone damage has occurred in the area, and (2) whether or not ozone exposure levels occurring in the area are high enough to cause damage to vegetation (i.e., phytotoxic O_3 exposures). Figure 2 shows the FLM review process to assess ozone impacts for a project that exceeds the initial annual emissions over distance (Q/D) screening criteria. As noted in Figure 2, ambient ozone concentrations are considered along with data from exposure response studies (EPA 2007a) to determine whether a source will cause or contribute to phytotoxic

2. Nevertheless, the FLMs are also concerned about resources in Class II parks and wilderness areas because they have other mandates to protect those areas as well. The information and procedures outlined in this document are generally applicable to evaluating the effect of new or modified sources on the AQRVs in both Class I and Class II areas, including the evaluation of effects as part of Environmental Assessments and/or Environmental Impact Statements under the National Environmental Policy Act (NEPA). However, FLAG does not preclude more refined or regional analyses being performed under NEPA or other programs.

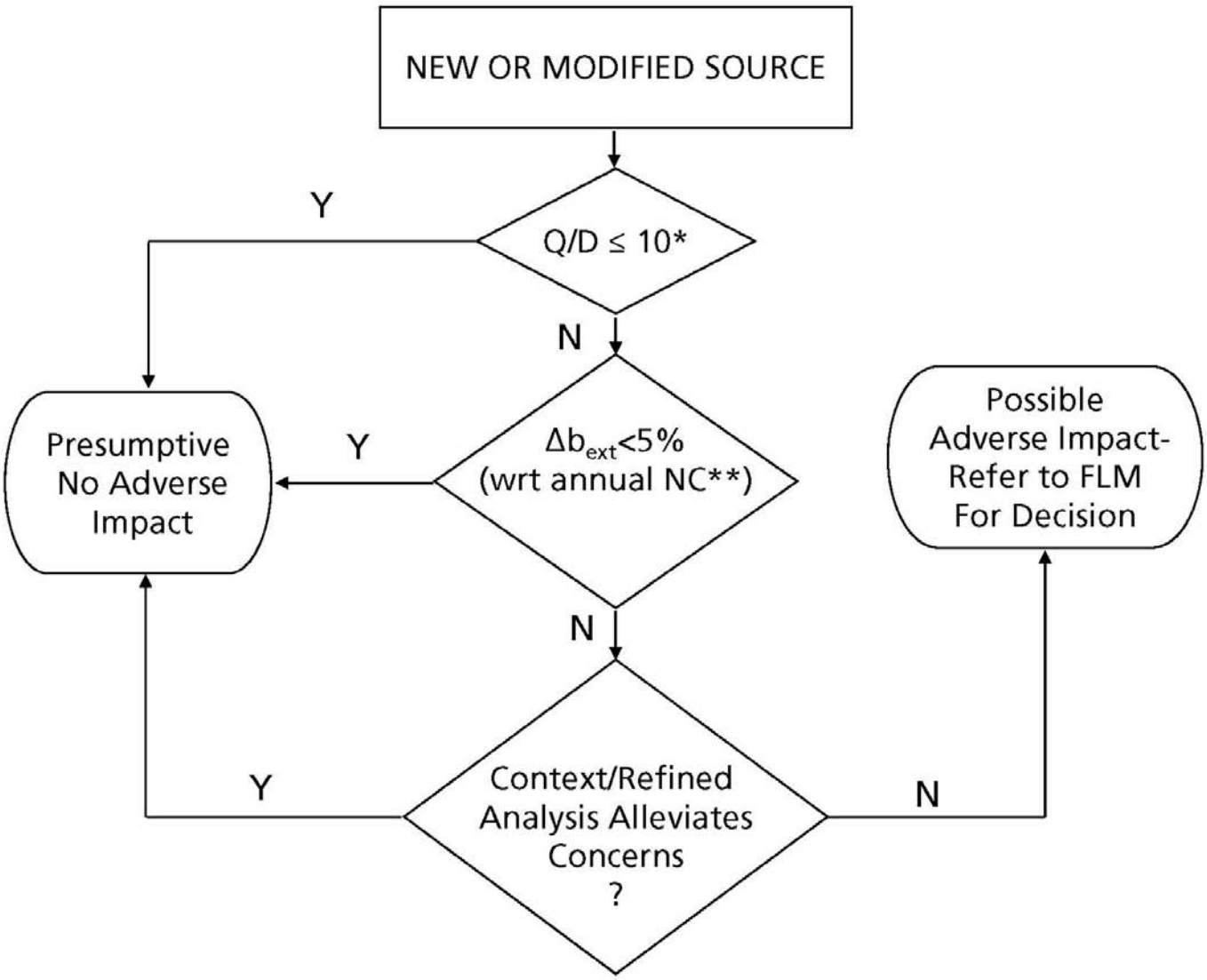

Figure 1. Procedure for Visibility Assessment for Distant/Multi-Source Applications (Revised)
*Q/D test only applies to sources located greater that 50 km from a Class I area.
**Difference Change in the 98th percentile with respect to (wrt) the annual average Natural Condition (NC). Applicant should use the 20th percentile best natural condition background if recommended by the FLM or permitting authority.

ozone levels (i.e., levels toxic to plants) at the affected site. The FLM may ask the applicant to calculate the ozone exposure values if these data are not already available. Ozone damage to vegetation is determined from field observations at the impacted site.

- Oxidant stipple necrosis on plant foliage and ozone-induced senescence infer adverse physiological or ecological effects, and are considered to be damage if they are determined to have a negative impact on aesthetic value.
- Established ozone metrics to describe ozone exposure are referenced.
- NO_x and VOC emissions are of concern because they are precursors of ozone. Current information indicates most FLM areas are NO_x limited. Until we determine the VOC or NO_x status of each area, we will focus on NO_x emission sources.

Recommendations for Evaluating Deposition Impacts (Revised)

For a project that exceeds the initial annual emissions over distance (Q/D) screening criteria, the permit applicant should consult with the appropriate regulatory agency and FLM for the affected area(s) to determine if a deposition impact analysis should be done (i.e., expected sulfur and/

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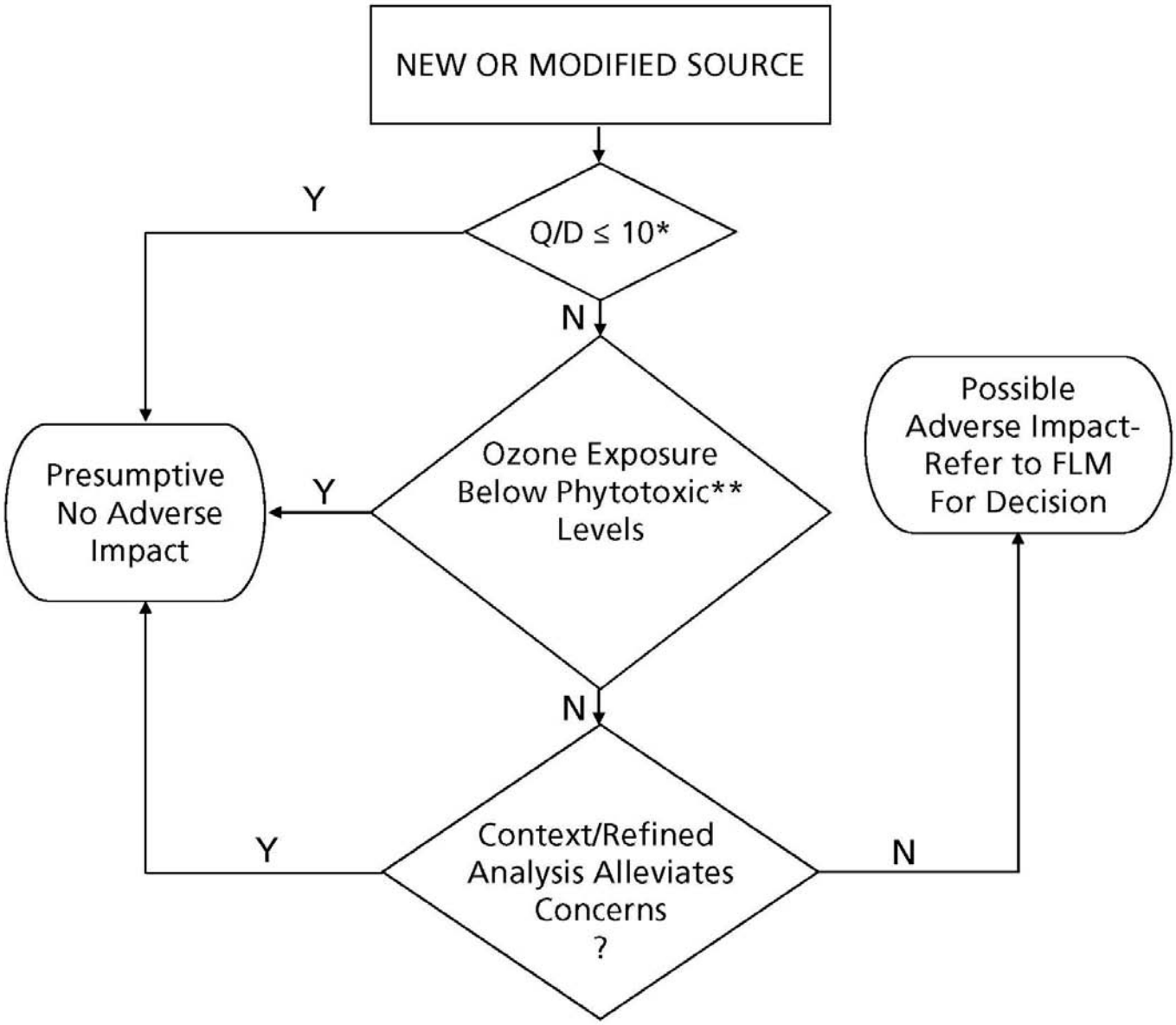

Figure 2. FLM Assessment of Potential Ozone Effects from New Emissions Source (Revised)
*Q/D test only applies to sources located greater that 50 km from a Class I area.
**Note: Ambient ozone concentrations are considered along with data from exposure response studies (EPA 2007b) to determine whether a source will cause or contribute to phytotoxic ozone levels (i.e., levels toxic to plants) at the affected site.

or nitrogen deposition impacts are above the Deposition Analysis Threshold (DAT) or concern threshold (see section 3.5.6). Please note that although mercury and other toxic emissions are of interest to the FLM, the deposition impact analyses discussed here applies only to nitrogen and sulfur emissions. If an analysis is advised, the permit applicant should obtain available information on Class I AQRVs, critical loads, and concern thresholds from the FLM. In addition, the applicant should refer to section 3.5.6 'Recommendations for Evaluating Potential Effects from Proposed Increases in Deposition to an FLM Area' section of the Deposition Chapter. The following steps summarize that process.

- From the respective Agency web sites, identify available on-site or representative wet and dry deposition data for the FLM area.
- Estimate the future deposition rate by adding the existing rate, the new emissions' contribution to deposition, and the contribution of sources permitted but not yet operating, while subtracting emission reductions that will occur before the proposed source begins operation. Modeling of new, reduced, and permitted but not yet operating emissions' contribution to deposition should be conducted following EPA recommendations.
- Compare the future deposition rate with the recommended screening criteria (e.g., critical load,

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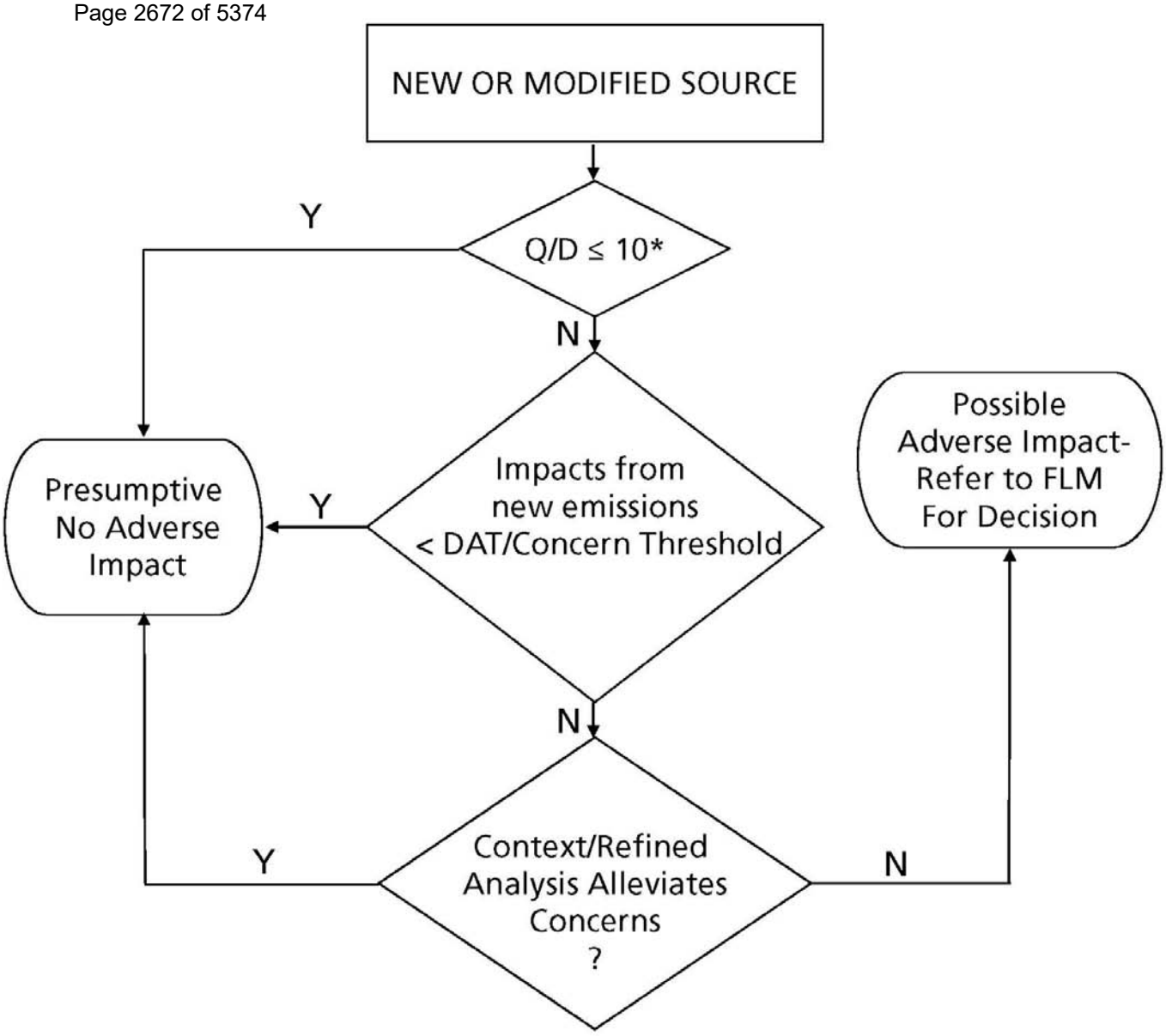

Figure 3. FLM Assessment of Potential Deposition Effects from New Emissions Sources (Revised)
*Q/D test only applies to sources located greater that 50 km from a Class I area.

concern threshold, or screening level value) for the affected FLM area. A list of documents summarizing these screening criteria, where available, can be found in Appendix G.

- Information for USFS Class I areas is also available at: http://www.fs.fed.us/air
- NPS and FWS Class I area information is available at: http://www.nature.nps.gov/air

- Figure 3 shows the FLM review process to assess deposition impacts from new emission sources.

1. Background

1.1. History (Revised)

The Clean Air Act Amendments of 1977 give Federal Land Managers (FLMs) an "affirmative responsibility" to protect the natural and cultural resources of Class I areas from the adverse impacts of air pollution (see Appendix B: 'Legal Framework for Managing Air Quality and Air Quality Effects on Federal Lands'). FLM responsibilities include the review of air quality permit applications from proposed new or modified major pollution sources near these Class I areas. If, in its permit review, an FLM demonstrates that emissions from a proposed source will cause or contribute to adverse impacts on the air quality related values (AQRVs) of a Class I area, the permitting authority, typically the State, can deny the permit.

The FLMs' role in the reviewing of permit applications focuses on impacts to Class I areas.[3] Individually, FLMs have developed different approaches to identifying AQRVs and defining adverse impacts on AQRVs in Class I areas. For example, in 1988, the U.S. Department of Agriculture Forest Service (USFS) conducted a national screening process to identify the AQRVs for each of its Class I areas. Using this national process as a starting point, each USFS Region refined the screening parameters and identified sensitive AQRVs for many Class I areas. However, this resulted in differences in the approaches and levels used by USFS Regions. The U.S. Department of the Interior National Park Service (NPS) and the U.S. Fish and Wildlife Service (FWS) have adopted a case-by-case approach to permit review, considering the most recent information available for each area. NPS and FWS have included lists of sensitive AQRVs for their Class I areas in their Air Resources Information System (ARIS) database.

1.1.1. FLAG Approach (Revised)

Air resource managers from the USFS, NPS, and FWS recognized the need for a more consistent approach among their agencies with respect to their efforts to protect AQRVs. In April 1997, an interagency Work Group was formed whose objective was "to achieve greater consistency in the procedures each agency uses in identifying and evaluating AQRVs." The Work Group named itself the

UL Bend National Wildlife Refuge, Montana.
Credit: Maribeth Oaks/The Wilderness Society

Federal Land Managers' Air Quality Related Values Work Group, or FLAG. Although FLAG membership comprises air resource managers and subject matter experts from the three agencies, representatives from the Bureau of Land Management, the U.S. Environmental Protection Agency (EPA), U.S. Geological Survey, and State air agencies have also participated in FLAG efforts.

FLAG participants have collaborated to:

- define sensitive AQRVs,
- identify the critical loads (or pollutant levels) that would protect an area and identify the criteria that define adverse impacts, and
- standardize the methods and procedures for conducting AQRV analyses.

To accomplish its objective, FLAG started with (and will continue to build on) the procedures, terms, definitions, and screening levels common to the three agencies. Many such "commonalities" were identified early in the FLAG planning sessions (see section 1.4, 'Commonalities Among Federal Land Managers').

FLAG's "Action Plan" stipulates a phased approach. Phase I addressed issues that could be resolved without research or the collection of new data. When the Agencies embark on FLAG Phase II, they will address the more complex and unresolved issues from Phase I that may require additional data collection (see section 5, 'Future FLAG Work').

The FLAG effort focuses on the effects of the air pollutants that could affect the health of resources in Class I areas, primarily pollutants such as ozone, particulate matter, nitrogen dioxide, sulfur dioxide, nitrates, and sulfates. In Phase I, FLAG concentrated on four issues: (1) terrestrial effects of ozone; (2) aquatic and terrestrial effects of wet and dry pollutant deposition; (3) visibility impairment; and (4) process and policy issues. Four subgroups, one for each of

3. Nevertheless, the FLMs are also concerned about resources in Class II parks and wilderness areas because they have other mandates to protect those areas as well. The information and procedures outlined in this document are generally applicable to evaluating the effect of new or modified sources on the AQRVs in both Class I and Class II areas, including the evaluation of effects as part of Environmental Assessments and/or Environmental Impact Statements under the National Environmental Policy Act (NEPA). However, FLAG does not preclude more refined or regional analyses being performed under NEPA or other programs.

these issues, were formed and charged with developing a set of recommendations for consistent policies and processes.

FLAG 2000's findings and technical recommendations underwent scientific peer review, as well as review by agency decision-makers such as Class I area Park Superintendents, Refuge Managers, and Forest Supervisors; Regional Foresters; and the Assistant Secretary for Fish and Wildlife and Parks. (Note: USFS has designated the FLM as the Regional Foresters and, in some cases, Forest Supervisors.) FLAG products have also undergone public review and comment. A "notice of availability" of the draft FLAG 2000 report was published in the *Federal Register*, and the FLMs conducted a public meeting to discuss the draft FLAG report and provided a 90 day public comment period. For the FLAG 2010 revisions, the FLMs announced the availability of the draft report in the *Federal Register* and provided a 60 day public comment period. There was not sufficient public interest to conduct a public meeting to discuss the proposed revisions to the FLAG report.

1.1.2. FLAG Organization

In addition to the four subgroups (policy, deposition, ozone, and visibility), the FLAG organization included Leadership and Coordinating Committees and a Project Manager. The Leadership Committee, which includes the air quality program chiefs from the three FLM agencies, was responsible for providing direction to the Work Group and the resources necessary for FLAG to accomplish its objective. The Coordinating Committee, which also includes representatives from each agency, was responsible for communications within the Work Group, including coordination among the agencies and subgroups. The FLAG Project Manager coordinated FLAG activities, served as a single point-of-contact for the subgroups, and performed other administrative functions.

1.2. Overview of Resource Issues (Revised)

Research conducted on Federal lands by FLMs and others has characterized natural resource effects associated with air pollution, and has helped identify those particular resources that are vulnerable to pollution in different areas. This effort does not address the impacts from air pollution on cultural resources. Documented effects include impairment of visibility, injury and reduced growth of vegetation, and acidification and fertilization of soils and surface waters. Air pollution effects on resources have been identified in a number of FLM areas; a few examples are provided below. It is important to note that similar, or even more serious, air pollution effects may be occurring on all Federal lands, but FLMs have not had the financial resources to perform the inventorying, monitoring, and/or research necessary to document such effects. Furthermore, the sensitivity of resources may vary from area to area because the nature of the resource, as well as geological, meteorological, biological, and other factors, vary from place to place.

1.2.1. Visibility

Visitors to national parks and wildernesses list the ability to view unobscured scenic vistas as a significant part of a satisfying experience. Unfortunately, visibility impairment has been documented in all Class I areas with visibility monitoring. Most visibility impairment is in the form of regional haze. The greatest visibility impairment due to regional haze occurs in the eastern United States and in southern California, while the least impairment occurs in the Colorado Plateau and Nevada Great Basin areas, and in Alaska. Ammonium sulfate contributes at least 50% to visibility impairment at most Class I areas in the eastern United States. The contribution to visibility impairment from ammonium nitrate is highest in central and southern California and in the Midwest. The largest region of high rural organic carbon visibility impairment is in the southeastern United States; impairment in this range is also present in the Sierra Nevada region of California and in the northern Rockies of Montana. The highest contribution to visibility impairment from fine soil is found in the arid Southwest. The highest coarse particle contribution to impairment is also in the arid Southwest and southern California. (DeBell et al. 2006) Visibility impairment on Federal lands can also result from plume intrusion and has been documented in Mount Zirkel Wilderness, Moosehorn National Wildlife Refuge, and Grand Canyon National Park.

1.2.2. Vegetation

While several components of air pollution (e.g., sulfur dioxide, nitrogen dioxide, and peroxyacyl nitrates) can affect vegetation, ozone is generally acknowledged as the air pollutant causing the greatest amount of injury and damage to vegetation. The most common visible effects are stipple (dark colored lesions on leaves resulting from pigmentation of injured cells), fleck (collapse of a few cells in isolated areas of the upper layers of the leaf, resulting in tiny light-colored lesions), mottle (degeneration of the chlorophyll in certain areas of the leaf giving the leaf a blotchy appearance), necrosis (death of tissue), and in extreme cases, mortality. Aside from visible injury, ozone exposure can result in less obvious physiological impairment such as decreased growth or altered carbon allocation.

Ozone fumigation experiments have identified a number of plant species that are sensitive to ozone. For example, fumigations were conducted in Great Smoky Mountains National Park (Tennessee and North Carolina) from 1987 to 1992. On the basis of foliar injury, thirty species were rated as sensitive to ozone levels that occurred in the park. The species with foliar injury included black cherry (*Prunus serotina*) and American sycamore (*Platanus occidentalis*). Additional observations and physiological measurements

indicated elevated ozone concentrations reduced leaf, root, and total dry weights, and increased the severity of leaf stipple and premature leaf abscission in these two species (Neufeld and Renfro 1993a,b). Field observations have documented foliar injury of these species in other eastern United States areas such as Brigantine Wilderness (New Jersey) and Cape Romain Wilderness (South Carolina).

Ponderosa pine (*Pinus ponderosa*) and Jeffrey pine (*Pinus jeffreyi*) are recognized as good candidates for ozone-injury surveys in the western United States, based on their documented sensitivity. For example, these species were examined for ozone injury in national parks and national forests in the California Sierra Nevada from 1991 to 1995. The sites surveyed included Lassen Volcanic, Yosemite, and Sequoia/Kings Canyon National Parks and the Tahoe, Eldorado, Stanislaus, Sierra, and Sequoia National Forests. Foliar injury attributable to ozone was found at all areas, and the extent of injury generally increased in a southward direction along the Sierra Nevada (Miller 1995).

1.2.3. Soils and Surface Waters

Acidity in rain, snow, cloud water, and dry deposition can affect soil fertility and nutrient cycling processes in watersheds and can result in acidification of lakes and streams with low buffering capacity. Deposition of sulfate to sensitive watersheds results in leaching of base cations, soil acidification, and surface-water acidification. In some soils, sulfate adsorption results in "delayed" acidification of surface waters. Deposition of excess nitrogen species (nitrate and ammonium) to both terrestrial and aquatic systems can result in acidifying streams, lakes, and soils. There is also evidence that nitrogen deposition can cause shifts in phytoplankton composition in lakes in which biological activity is limited by nitrogen availability, i.e., increased nitrogen deposition can cause phytoplankton species that use nitrogen more efficiently to eventually dominate the lake.

Water chemistry surveys and on-going monitoring show that many high elevation lakes on Federal lands in the Sierra Nevada, Cascades, and Rocky Mountains are sensitive to acid deposition. In general, these lakes are on bedrock that provides them with very little buffering capacity. Some of these lakes, for example, Loch Vale in Rocky Mountain National Park (Colorado) experience episodic acidification during Spring snow melt (Baron and Campbell 1997).

Through funding provided by the Southern Appalachian Mountains Initiative, Herlihy et al. (1996) compiled information on surface water sensitivity of streams in nine of the eleven Class I areas in the Southern Appalachians. The nine Class I areas were grouped according to geology, physiography, and stream chemistry, then the groupings were ranked in terms of effects. Class I areas in the West Virginia Plateau (Otter Creek and Dolly Sods Wildernesses) had the highest percentage of acidic stream length and lowest pH values. Class I areas in the Northern and Southern Blue Ridge (e.g., Shenandoah National Park in Virginia and Joyce Kilmer/Slickrock Wilderness in North Carolina) had a lower percentage of acidic stream length, however, streams with low buffering capacity were common. The Alabama Plateau Class I area (Sipsey Wilderness) had streams with the highest buffering capacity. (Note that the authors based their report on surveys conducted by others and did not account for potential differences in methods of data collection.)

A number of Federal areas contain estuarine and coastal areas that may experience eutrophication as a result of excess nitrogen deposition resulting from air pollution and other sources of nitrogen. For example, symptoms of eutrophication, including nutrient enrichment and algal blooms, have been observed in Everglades National Park and Chassahowitzka Wilderness (Florida).

1.3. Legal Responsibilities (Revised)

The specific legal responsibilities that Congress has given FLMs to protect natural, cultural, and scenic resources on the public lands from air pollution are identified in Appendix B. Statutes described in Appendix B include agency organic acts, the Wilderness Act, and the Clean Air Act (CAA).

The fundamental Congressional direction for managing public lands arises out of respective organic acts. Each of these laws is essentially a charter from Congress to the Executive Branch providing a purpose for parks, wildernesses, and refuges, respectively, and establishing broad management objectives for these areas. The Wilderness Act sets aside a subset of these public lands where natural processes are allowed to dominate. The agency stewards develop specific management objectives building on the organic acts using public involvement, regulations, best available science, and additional direction provided by Congress.

Among this additional Congressional direction is the Clean Air Act (CAA). It further characterizes some of the public lands as "Class I" areas and bestows on the land managers an affirmative responsibility to protect these areas from air pollution. The CAA directs that the FLMs identify and protect air quality related values, including visibility. This direction is consistent with the underlying charters provided by the organic acts and the Wilderness Act. The similarities of management objectives, and of the policies and procedures necessary for protecting Class I areas, are at the core of the FLAG process. Please note that although all wilderness is not Class I, and the FLMs have not proposed that non-Class I wilderness be classified as Class I, management actions (e.g., limiting human activities) that satisfy wilderness management objectives for Class II areas, are often substantially the same as those used in Class I area management.

In implementing laws, it is essential to understand the intent of Congress. In the case of the CAA, the FLM gleans additional insight from a passage in Senate Report No. 95-127, 95th Congress, 1st Session, 1977 which states:

> The Federal Land Manager holds a powerful tool. He is required to protect Federal lands from deterioration of an established value, even when Class I [increments] are not exceeded. . . . While the general scope of the Federal Government's activities in preventing significant deterioration has been carefully limited, the FLM should assume an aggressive role in protecting the air quality values of land areas under their jurisdiction. In cases of doubt the land manager should err on the side of protecting the air quality-related values for future generations.

Although the FLMs have an "affirmative responsibility" to protect AQRVs, they have no permitting authority under the CAA, and they have no authority under the CAA to establish air quality-related rules or standards. The FLM role within the regulatory context consists of considering whether emissions from a new source, or emission increases from a modified source, may have an adverse impact on AQRVs and providing comments to permitting authorities (States or EPA). It is important to emphasize that the FLAG report only explains factors and information the FLMs expect to use when carrying out their consultative role. It is not a rule or standard.

The FLAG report describes the steps and process that the FLMs intend to go through in order to perform their statutory duties. Consequently, the scope of the FLAG report is to provide a more consistent approach for the three FLM agencies to evaluate air pollution effects on resources, and to provide guidance to permitting authorities and permit applicants regarding necessary AQRV analyses. Although FLAG strives to be consistent with regulatory programs and initiatives such as the Regional Haze Rule and New Source Review Reform, no direct ties exist between FLAG and these regulatory requirements.

1.4. Commonalities Among Federal Land Managers

If a new source is proposed near two or more areas managed by different FLMs, the FLMs generally try to coordinate in their interactions with the permitting authority and with the applicant. For example, two or more FLMs involved in pre-application meetings typically try to minimize the workload for the applicant by reaching agreement on the types of analyses the application should contain. Beyond coordinating during permit review, FLMs currently base requests and decisions on similar principles regarding resource protection and FLM responsibilities. Listed below are the common principles in five areas of air resource management. In addition, Appendix C provides the FLM's 'General Policy for Managing Air Quality Related Values in Class I Areas.'

1.4.1. Identifying AQRVs (Revised)

FLMs agree on the following definition of an AQRV:

> A resource, as identified by the FLM for one or more Federal areas that may be adversely affected by a change in air quality. The resource may include visibility or a specific scenic, cultural, physical, biological, ecological, or recreational resource identified by the FLM for a particular area.

This definition is compatible with the general definition of AQRV that appears in the *Federal Register* (45 FR 43003, June 25, 1980). That definition includes visibility, flora, fauna, odor, water, soils, geologic features, and cultural resources. FLMs have the responsibility to identify specific AQRVs of areas they manage. To this end, FLMs further refine AQRVs beyond the above definition to be more site-specific (i.e., area specific) by using on-site information. To the extent possible, the FLMs have identified specific AQRVs for many Class I areas. Site-specific AQRV lists are available on the respective Agency web sites, or by contacting the Agencies directly. The FLMs also recognize that, ideally, inventories should be developed for all Class I areas. The FLMs may identify additional AQRVs in the future as more is learned through science about the sensitivity of resources to air pollution. A public process involving the regulated community and other interested members of the public is necessary and will be accomplished through participation in the land management planning process or reply to an announcement in the *Federal Register*. Finally, FLMs agree on the need for continued inventory, research, and monitoring to improve their ability to determine which AQRVs are most sensitive to air pollution and the sensitivity of these AQRVs.

1.4.2. Determining the Levels of Pollution that Trigger Concern for the Well-Being of AQRVs (Revised)

FLMs acknowledge the importance of being able to agree among themselves on the levels of pollution that trigger concerns for AQRVs. FLMs recognize the need to assess cumulative impacts and the difficulties associated with this process. Difficulties arise when a large number of minor source impacts eventually lead to an unacceptable cumulative impact or when a new source applies for a PSD permit in an area that has a high background concentration of pollution from existing sources. The agencies will evaluate a proposed new source within the context of the total impacts that are occurring or that potentially could occur from permitted/existing sources on the AQRVs of the area and should consider the effects of both emission increases and decreases.

1.4.3. Visibility

FLMs use EPA-approved models [Appendix W of Part 51 (EPA's *Guideline on Air Quality Models*, revised November 2005), as required under the PSD regulations at 40 CFR 51.166(1) and 52.21(1)] and the recommendations of the Interagency Work Group on Air Quality Modeling (IWAQM) to evaluate visibility impacts. The models use thresholds of visibility degradation measured in light extinction to evaluate source impacts to haze (far-field/multi-source impacts), and EPA established criteria for coherent plume impacts (near-field impacts). Currently all FLMs use Interagency Monitoring of Protected Visual Environments (IMPROVE) monitoring data to determine current conditions for visibility in FLM areas.

1.4.4. Biological and Physical Effects

All FLMs rely on research, monitoring, models, and effects experts to identify and understand physical, biological, and chemical changes resulting from air pollution and relating them to changes in AQRVs. Further, they focus on sensitive AQRVs (defined as either species or processes) to assess this biological/physical/chemical change.

1.4.5. Determining Pollution Levels of Concern (Revised)

FLMs rely on the best scientific information available in the published literature and best available data to make informed decisions regarding levels of pollution likely to cause adverse impacts. FLMs re-evaluate, update, and assess this information as appropriate. They consider specific Agency and Class I area legislative mandates in their decisions and, in cases of doubt, "err on the side of protecting the AQRVs for future generations." (Senate Report No. 95-127, 95th Congress, 1st Session, 1977)

For air quality dispersion modeling analyses, FLMs follow Appendix W of Part 51 (EPA's *Guideline on Air Quality Models*, revised November 2005), as required under the PSD regulations at 40 CFR 51.166(1) and 52.21(1), and the recommendations of the Interagency Work Group on Air Quality Modeling (IWAQM). FLMs recommend protocols for modeling analyses to permit applicants on a case-by-case basis considering types and amount of emissions, location of source, and meteorology. When reviewing modeling and impact analysis results, all FLMs consider frequency, magnitude, duration, location of impacts, and other factors, in determining whether impacts are adverse.

1.4.6. FLM Databases (Revised)

Air Resources Information System (ARIS) (Formerly Air Synthesis) (Revised)

ARIS provides information on air quality related values in NPS and FWS Class I areas, as well as in many NPS Class II areas. ARIS identifies specific AQRVs, and provides information on air quality and its effects in parks and wildernesses.

Natural Resource Information System – Air Module (NRIS-AIR) (Revised)

Publicly available USDA Forest Service Class I and II area information and related resource data can be linked to or found at http://www.fs.fed.us/air. If desired information and data cannot be found, contact any air program manager or specialist at national or regional offices for assistance.

1.5. Regulatory Developments Since FLAG 2000 (New)

Several regulatory developments have occurred since the FLMs published the FLAG report in December 2000. Some of these regulatory developments may have a significant effect on air resource management in mandatory Class I areas, or how these effects are assessed. First, on April 15, 2003, the Environmental Protection Agency (EPA) promulgated revisions to Appendix W of 40 C.F.R. §51 (*Guideline on Air Quality Models*). EPA revised the Guideline to adopt the CALPUFF model as a preferred long-range transport model for inclusion in Appendix A of that document. Prior to that date, FLAG 2000 relied on CALPUFF as the suggested model of choice for long-range transport assessments in accordance with recommendations of the Interagency Work Group on Air Quality Models (IWAQM). EPA's adoption of CALPUFF substantiates the Agencies' model choice. In addition, EPA's action, combined with improved computer technology, has resulted in the availability of more meteorological data. These improvements have enhanced the ability of permitting authorities and applicants to perform the types of modeling analyses suggested in FLAG. However, the FLMs will continue to work with the EPA on recommendations for future long-range transport model development.

On May 12, 2005, the EPA published the Clean Air Interstate Rule (CAIR) to reduce interstate transport of fine particulate matter and ozone. The CAIR applied to 28 eastern states and the District of Columbia, and required those areas to significantly reduce emissions of sulfur dioxide (SO_2) and/or nitrogen oxides (NO_x) from utilities. Although EPA developed the CAIR to address violations of the National Ambient Air Quality Standards (NAAQS) for fine particulates ($PM_{2.5}$) and ozone, the associated SO_2 and NO_x emission reductions would also benefit visibility and other AQRVs at many eastern Class I areas. The Agencies supported the CAIR, however, because it did not apply to western states, the majority of the Class I areas would not have directly benefited from the rule. Please note that at the time of this writing CAIR has been remanded to the EPA for revision to address various court challenges, and EPA has proposed a new transport rule as a replacement (EPA 2010a).

On July 6, 2005, the EPA published a final rule and associated guidelines that detail the Best Available Retrofit Technology (BART) requirements of the Regional Haze Rule. Among other things, the BART guidelines advise States to rely on the CALPUFF model for long-range visibility impairment assessments, provide thresholds for what constitutes causing or contributing to regional haze visibility impairment, and includes screening level values that exempt certain sources from further analysis. As discussed in more detail below, the Agencies believe the assumptions and methodology included in the BART guidelines also have merit with respect to evaluating haze-like visibility impairment for New Source Review under the PSD and other programs. Consequently, the Agencies are paralleling some of those BART guidelines in this FLAG revision.

Please note that FLAG 2000 acknowledges the EPA's July 1999 Regional Haze Rule, and discusses possible changes to FLAG that may be necessary as States implement the Regional Haze Rule. Although the EPA promulgated the Regional Haze Rule before the FLMs published FLAG 2000, there were several improvements and differences in the associated EPA guidance documents (e.g., those related to Natural Conditions and Tracking Progress) that were not finalized until December 2003. Therefore, these documents were not reflected in FLAG 2000, but have been considered in this revision. Currently, State Implementation Plans (SIPs) under the Regional Haze Rule are being developed, and submitted to the EPA for approval. If the new visibility SIPs adequately account for new source growth, the Agencies may need to make further revisions to the FLAG recommendations to reflect progress made through the SIP process that could minimize the focus the FLMs place on individual sources.

EPA has also developed other regulations, standards, and policies that will help reduce air pollution and resulting impacts at FLM areas (e.g., revised ozone, sulfur dioxide, nitrogen dioxide, and particulate matter standards; mobile source controls).

2. Federal Land Managers' Approach to AQRV Protection

FLM responsibilities for resource protection on Federal lands are clear and there should be no misunderstanding regarding the tools the FLM uses to fulfill these responsibilities. Opportunities to influence decisions regarding pollution sources external to the park or wilderness are limited. However, FLMs strive to minimize emissions from internal sources and their effects. Approaches for minimizing air pollution from external and internal sources are discussed in detail below.

2.1. AQRV Protection and Identification (Revised)

Congress assigned the FLMs an affirmative responsibility to protect AQRVs in Federal Class I areas. The FLMs interpret this assignment as a responsibility to:

- Identify AQRVs in each of the Class I areas.
- Establish inventorying and monitoring protocols for AQRVs.
- Prioritize AQRV inventorying and monitoring.
- Specify a process for evaluating air pollution effects on AQRVs, including the use of sensitive indicators.
- Specify adverse effects for each AQRV.

To the extent possible, AQRVs have been identified for each Class I area. As noted above, the FLMs may identify additional AQRVs in the future as more is learned about the sensitivity of resources to air pollution. The FLMs will provide a public process involving the regulated community and other interested members of the public in order to seek public input regarding AQRV-identification issues. This desired public involvement will be accomplished through participation in the land management planning process or reply to an announcement in the *Federal Register*.

While the sensitivity of an AQRV to air pollution may be known, long-term monitoring of the health or status of the AQRV may not have been accomplished. The expense of monitoring all AQRVs simultaneously is prohibitive. Consequently, FLMs seek opportunities through the permitting process and through partnerships to gather more information about condition of AQRVs.

Because AQRVs themselves are often difficult to measure, surrogates are used as indicators, or sensitive indicators, of the health or status of the AQRV. A working process for Class I area management and AQRV protection is outlined ahead in this document.

An adverse impact is determined for each AQRV. An adverse impact from air pollution results in a diminishment of

Sipsey Wilderness, Alabama.
Credit: Steve Boutcher

the Class I area's national significance, that is, the reason the Class I area was created. Adverse impacts can also be an impairment of the structure or functioning of the ecosystem, as well as an impairment of the quality of the visitor experience. The FLMs make an adverse impact determination on a case-by-case basis, based on technical and other information, which is then conveyed to the permitting authority.[4] The permitting authority then considers this, along with other factors, in its determination regarding the permit application.

2.2. New Source Review (Revised)

Section 165 of the CAA spells out the roles and responsibilities for FLMs in New Source Review, including the Prevention of Significant Deterioration (PSD) permitting program. Other laws, such as the respective agency organic acts and the Wilderness Act, provide the fundamental underpinning of land management direction to land managers. The following discussion merges this complex labyrinth of legal responsibilities as it relates to air resource management.

2.2.1. Roles and Responsibilities of FLMs (Revised)

The federal officials directly responsible for the national parks, national wildlife refuges, and national forests (e.g., park superintendents, refuge managers, and forest supervisors, respectively) derive their responsibility from the respective agency organic acts. Furthermore, these officials, and the FLM for the respective agencies, have an affirmative responsibility under Section 165 of the CAA to protect and

4. As discussed elsewhere in this report, if a proposed source's impacts on AQRVs exceed established significance criteria, the FLMs will consider the magnitude, frequency, geographic extent, etc. of the impacts, and other relevant factors, in determining whether or not the impacts are adverse.

enhance the AQRVs of Class I areas from the adverse effects of air pollution. The FLM for the USFS is the Regional Forester or the Forest Supervisor depending on the specific location. The FLM for the NPS and FWS is the Department of the Interior's Assistant Secretary for Fish and Wildlife and Parks.

The FLMs have visibility protection responsibility under 40 CFR §51.307 (New source review), which spells out the requirements for State Implementation Plan (SIP) visibility protection programs, as well as 40 CFR §52.27 (Protection of visibility from sources in attainment areas) and 40 CFR §52.28 (Protection of visibility from sources in non-attainment areas). These three provisions, taken together along with the SIP-approved rules, establish the visibility protection program for new and modified sources throughout the country.

Notification

Section 165 (42 USC 7475) of the CAA requires the EPA, or the State/local permitting authority, to notify the FLM if emissions from a proposed project may impact a Class I area. The permitting authority should forward PSD applications to the FLM for review and analysis as soon as possible after receipt, giving the FLM an opportunity to review the application concurrently with the permitting authority.

Generally, the permitting authority should notify the FLM of all new or modified major facilities proposing to locate within 100 km (62 miles) of a Class I area. In addition, the permitting authority should notify the FLM of "very large sources" with the potential to affect Class I areas proposing to locate at distances greater than 100 km. (Reference March 19, 1979, memorandum from EPA Assistant Administrator for Air, Noise, and Radiation to Regional Administrators, Regions I - X). Given the multitude of possible size/distance combinations, the FLMs can not precisely define in advance what constitutes a "very large source" located more than 100 km away that may impact a particular Class I area. However, as discussed elsewhere in this report, the Agencies have adopted a size (Q)/distance (D) criteria to screen out from AQRV review those sources with relatively small amounts of emissions located a large distance from a Class I area. Consequently, as a minimum, the permitting authority should notify the FLM of all sources that exceed this Q/D criteria. Nevertheless, the FLM and permitting authority should still work together to determine which other PSD applications the FLM is to be made aware of in excess of 100 km. In making this determination, the FLM and permitting authority should consider, on a case-by-case basis, such factors as:

- Current conditions of sensitive AQRVs;
- Magnitude of emissions;
- Distance from the Class I area;
- Potential for source growth in an area/region;
- Existing/prevailing meteorological conditions;
- Cumulative effects of several sources to AQRVs, as well as changes in their emissions.

Additionally, such dialogue facilitates coordination between permitting authorities and the FLMs. The significance of the impact to AQRVs is more important than the distance of the source. Not all PSD permit applications that the FLM is notified of will be analyzed in-depth by the FLM. FLM notification of a PSD permit application for a project located greater than 100 km does not mean that the permit application will be reviewed by the FLM in detail. Notification of PSD permit applications in excess of 100 km by the permitting authority allows the FLM to gauge the level of potential cumulative effects. As indicated above, the FLM decides which PSD permit applications to review on a case-by-case basis depending on the potential impacts to AQRVs.

Pre-Application Meetings

To expedite the PSD permit review process, the FLM encourages pre-application meetings with permitting authorities and permit applicants to discuss air quality concerns for a specific Class I area in question. Given preliminary information, such as the source's location and the types and quantity of projected air emissions, the FLM can discuss specific AQRVs for an area and advise the applicant of the analyses needed to assess potential impacts on these resources.

Completeness Determination

To further minimize delays, the FLMs encourage the permitting authority to use comments provided by the FLM concerning the completeness of the application, and to not deem the application complete until the applicant performs all necessary air quality impact analyses, including all relevant AQRV impact information. The permitting authority should then notify the FLM when they deem the application to be complete.

Visibility Protection Procedures

Additional procedural requirements apply when a proposed source has the potential to impair visibility in a Class I area (40 CFR §52.27(d)(2007); 40 CFR §51.307(a)(2007)). Specifically, the permitting authority must, upon receiving a permit application for a source that may affect visibility in any Class I area, notify the FLM in writing. Such notification shall include a copy of all information relevant to the permit application, including the proposed source's anticipated impacts on visibility in a Class I area. The permitting authority shall notify the FLM within 30 days of receipt and at least 60 days prior to the close of the comment period.

If the FLM notifies the permitting authority that the proposed source may adversely impact visibility in a Class I area, or may adversely impact visibility in a previously identified integral (scenic) vista, then the permitting

authority is to work with the FLM to address their concerns. If the permitting authority agrees with the FLM's finding that visibility in a Class I area may be adversely affected, the permit may not be issued. Even though the permitting authority may agree with the FLM's adverse impact finding regarding integral vistas, the permitting authority may still issue a permit if the emissions from the source are consistent with reasonable progress toward the national goal of preventing or remedying visibility impairment. In making this decision, the permitting authority may take into account the costs of compliance, the time needed for compliance, the energy and non-air quality environmental impacts of compliance, and the useful life of the source.

The FLM will make a preliminary determination regarding possible adverse visibility impacts upon receipt of all relevant information, including the draft permit and any associated staff analysis.

2.2.2. Elements of Permit Review

The FLM review of a PSD application for a proposed project that may impact a Class I area generally consists of three main analyses:

1. Air quality impact analysis to ensure that predicted pollutant levels in Class I areas do not exceed National Ambient Air Quality Standards (NAAQS) and PSD increments, and to provide sufficient information for the FLM to conduct an AQRV impact analysis. Ensuring that permit applicants meet these requirements is the direct responsibility of the permitting authority (see discussion below);
2. AQRV impact analysis to ensure that the Class I area resources (i.e., visibility, flora, fauna, etc.) are not adversely affected by the proposed emissions. The AQRV impact analysis includes interpreting the significance of the results from the applicant's air quality impact analysis and is the responsibility of the FLM (see discussion below); and
3. Best Available Control Technology (BACT) analysis to help ensure that the source installs the best control technology to minimize emission increases from the proposed project (See Appendix D for a summary of this analysis). The final BACT determination is a direct responsibility of the permitting authority.

Air Quality Impact Analysis

The permit applicant must perform an air quality impact analysis for each pollutant subject to PSD review (40 CFR §51.166). This analysis must show the contribution of the proposed emissions to increment consumption and to the existing ambient pollution levels in a Class I park or wilderness area. The applicant must perform a cumulative increment analysis for each pollutant and averaging time for which the proposed source will have a significant impact.

Because proposed sources are not yet operating, the air quality analysis should rely on mathematical dispersion models to estimate the air quality impact of the proposed emissions. The FLMs provide the applicants with guidance on where to place model receptors within the Class I area. The applicant is responsible to provide sufficient information for the FLM to make a decision about the acceptability of potential AQRV impacts as a consequence of the new source.

The applicant must perform the air quality impact analysis using approved models and procedures as specified in Appendix W of Part 51 (EPA's *Guideline on Air Quality Models*, revised November 2005), as required under the PSD regulations at 40 CFR 51.166(1) and 52.21(1). The applicant should explicitly state all assumptions for the analysis, and furnish sufficient information on modeling input so that the FLM can validate and duplicate the model results. FLMs encourage the permit applicant to submit a modeling protocol for review before performing the Class I modeling analyses. This protocol should include the proposed air quality analysis methodology and model input (i.e., emissions, stack data, meteorological data, etc.), and the proposed location of the receptors in the FLM area.

AQRV Impact Analysis

According to the CAA's legislative history and current EPA regulations and guidance, the air quality impact analysis that provides sufficient information to enable the FLM to conduct the AQRV impact analysis is one part of a permit application just as are the BACT analysis and the air quality impact analysis relative to the increments and NAAQS. The applicant bears the entire cost of preparing the permit application including the complete air quality impact analysis.

It is important to highlight the distinction between the air quality impact analyses that the applicant performs and the AQRV impact analyses that FLMs perform. Whereas the permit applicant calculates changes in pollutant concentrations, deposition rates, or visibility extinction, the FLM assesses the extent to which these impacts affect sensitive visual, aquatic, or terrestrial resources. Given the FLM's statutory responsibilities and expertise, the FLM must have responsibility to consider whether the amount of pollution dispersed into the air or deposited on the ground (or in water) would have an adverse impact on any AQRV, and if so, to demonstrate that claim to the permitting authority. In making an adverse impact finding, FLMs consider such factors as magnitude, frequency, duration, location, geographic extent, and timing of impacts, as well as current and projected conditions of AQRVs based on cumulative impacts.

The FLM uses the results from the applicant's air quality impact analysis and other information to conduct the

AQRV impact analysis and make an informed decision about whether or not AQRVs will be adversely affected. If the FLM concludes that AQRVs will be adversely affected, the FLM will so demonstrate to the permitting authority. The following sections of this document give guidance to applicants on how to conduct an air quality impact analysis and how the FLM uses this information to make an AQRV impact decision.

Cumulative Impact Analysis

The FLM will evaluate on a case-by-case basis both the permit applicant's contribution to the AQRV impacts, as well as the cumulative source impacts on AQRVs, taking into account expected emission reductions. A cumulative air quality analysis in which the proposed source and any recently permitted (but not yet operating) sources in the area are modeled is an important part of any AQRV impact analysis. This cumulative modeled impact is then added to measured ambient levels (to the extent that such monitoring data are available) so that the FLM can assess the total effect of the anticipated ambient concentrations on AQRVs. If no representative monitoring data are available, the total pollutant concentrations should be estimated by modeling emissions from all contributing sources in the area.

Information Provided by the FLM to the Applicant

To assist the permit applicant in performing air quality impact analyses, the FLMs will provide all available information about AQRVs for a particular Class I area that may be adversely affected by emissions from the proposed source. FLMs will recommend available methods the applicant should use to analyze the potential effects (i.e., pollutant concentration, deposition rates, and visibility extinction) in the Class I area. In addition to identifying AQRVs, FLMs will, to the extent possible:

- identify inventories, surveys, monitoring data, scientific studies, or other published reports that are the basis for identification of AQRVs;
- identify specific receptors known to be most sensitive to air pollution and the pollutant or pollutants that individually or in combination can cause or contribute to an adverse effect on each receptor;
- identify the critical pollutant concentrations above which adverse effects are known or suspected to occur;
- recommend methods the applicant should use for predicting ambient pollutant concentrations and other related impacts (e.g., deposition, visibility) which may cause or contribute to an adverse effect on each receptor; and
- suggest screening level values or criteria that would be used to assess whether a proposed emissions increase would have a *de minimis* impact on AQRVs.

2.2.3. FLM Permit Review Process

The FLM's current permit review process for any application that may impact a FLM area is described below.

1. **Pre-application.** If possible, participate in any pre-application meeting to learn specifics of the proposed project (size, emissions, location, etc.) and to provide information regarding recommended Class I analyses.
2. **Modeling Protocol.** The FLMs encourage the permit applicant to submit a modeling protocol for review before performing the Class I modeling analyses. This protocol should include the proposed air quality analysis methodology and model input (i.e., emissions, stack data, meteorological data, etc.), and the proposed location of the receptors in the FLM area.
3. **Completeness Determination.** Upon receipt, the FLM will review the application and provide comments to the permitting authority regarding the completeness of the application and the need for additional information regarding the BACT, Air Quality Impacts, and AQRV Impacts analyses. The FLM will coordinate with the permitting authority and the permit applicant to ensure that all the necessary information to enable the FLM to make an impact determination is included.
4. **Public Comment Period.** After review of all relevant information, the FLM will provide pertinent comments to the permitting authority, before or during the official public comment period, and/or at scheduled public hearings.
5. **No Class I Increment Violated and No Adverse Impacts.** If no Class I increment is violated and no adverse impacts to AQRVs are expected, the FLM will inform the permitting authority of this determination and no further FLM action is necessary. The FLM may still provide BACT comments.
6. **No Class I Increment Violated but AQRV Impacts Uncertain.** If no Class I increment is violated but uncertainty exists regarding potential adverse impacts to AQRVs, the FLM may request that the permitting authority include a permit condition that requires the permittee to conduct relevant post-construction AQRV or air quality monitoring. The FLM may also request certain control technologies or methods to reduce impacts.
7. **Class I Increment Violated, but No Adverse AQRV Impacts.** If the Class I increment is violated, but no adverse AQRV impacts are anticipated, the applicant requests the FLM to "certify" no adverse impact under Section 165(d)(2)C)(iii) of the Clean Air Act [42 USC 7475(d)(2)(C)(iii)(1998)]. If the FLM concurs, (s)he makes a preliminary determination that no adverse impacts will occur.

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- The FLM will inform the applicant, the State/local permitting authority, and EPA of the preliminary no adverse impact determination.
- The FLM will notify the public of its preliminary no adverse impact determination either through the permitting authority's notice procedures, or through separate notice in the *Federal Register*. Such notice should include a statement as to the availability of supporting documentation for inspection and copying, and an announcement of at least a 30 day public comment period on issues directly relevant to the determination in question.
- The FLM will review and prepare response to public comments.
- The FLM will make a final determination regarding no adverse impacts, with a clear and concise statement of reasons supporting that determination.
- The FLM will inform the permit applicant, the permitting authority, and EPA of its final determination and if the final determination is "no adverse impact," the FLM shall so "certify" in a letter to the affected parties.
- Simultaneous with above, the FLM will publish a final determination in the 'Notice' section of the *Federal Register*, including a clear and concise statement of reasons supporting that determination, statement as to availability of supporting documentation for inspection and copying, and statement as to immediate effective date (date signed) of final determination.
- The FLM will contact the permitting authority and request a revision to the State Implementation Plan (SIP) to eliminate the Class I increment violations.

8. **Adverse Impact Determination**. Regardless of increment status, the FLM may make a preliminary determination that the proposed project will cause, or contribute to, an adverse impact on AQRVs. Before officially declaring an adverse impact, the FLM will inform the proposed new source and the permitting authority that an adverse impact determination is imminent and suggest that the draft permit be modified. If the draft permit is modified to satisfy the concerns of the FLM, then an adverse determination is avoided.
   - The FLM will inform the applicant, the permitting authority, and EPA of a preliminary adverse impact determination.
   - The FLM will notify the public of the preliminary adverse impact determination either through the permitting authority's notice procedures, or through separate notice in the *Federal Register*. Such notice should include a statement as to the availability of supporting documentation for inspection and copying, and an announcement of at least a 30 day public comment period on issues directly relevant to the determination in question.
   - The FLM will review and prepare response to public comments.
   - The FLM will make a final determination regarding adverse impacts, with a clear and concise statement of reasons supporting that determination.
   - The FLM will inform the permit applicant, the permitting authority, and EPA of its final determination.
   - Simultaneous with above, the FLM will publish a final determination in the 'Notice' section of the *Federal Register*, including a clear and concise statement of reasons supporting that determination, statement as to availability of supporting documentation for inspection and copying, and statement as to immediate effective date (date signed) of final determination.
   - If the FLM makes a final determination that a source will have an adverse impact, the FLM will oppose the permit. However, the permit applicant may propose to mitigate any adverse impacts (via reducing emissions, obtaining emission offsets, etc.). If the applicant adequately mitigates the adverse impacts to the satisfaction of the FLM, the FLM will withdraw his objection to the permit. If the adverse impacts are not adequately mitigated and the permitting authority nevertheless issues the permit, the FLM may appeal the permit.

Note: If the permitting authority's SIP makes execution of the above listed steps impossible (e.g., inadequate time allotments for the FLM's determination or lack of timely FLM notice) the procedures shall be adjusted as appropriate. In addition, the above procedures (6 and 7) could also be modified to accommodate those situations when the FLM chooses to certify that existing impacts are adverse, absent a proposed new source. Such an action would alert potential permit applicants that adverse impacts exist and any new source would need to mitigate its potential impacts. Although each FLM may implement the above procedures somewhat differently, the FLAG goal is to reduce the differences in implementing the above steps.

Furthermore, FLMs intend to coordinate on air permit modeling requirements for new or modified sources that are geographically near more than one FLM area. For example, a proposed source in eastern Tennessee that lies equidistant from NPS-administered Great Smoky Mountains National Park and the FS-administered Joyce Kilmer/ Slickrock Wilderness would receive coordinated guidance on modeling requirements from the FLMs. The FLMs may or may not have common AQRVs and Class I areas, making coordination beneficial. The FLMs may also

coordinate on potential permit conditions and mitigation strategies.

2.2.4. Criteria for Decision Making (Adverse Impact Considerations) (Revised)

As previously mentioned, the legislative history of the CAA provides direction to the FLM on how to comply with the affirmative responsibility to protect AQRVs in Class I areas, and in cases of doubt, the land manager should err on the side of protecting air quality-related values for future generations.

The FLMs define adverse impact on AQRVs as:

> An unacceptable effect, as identified by an FLM that results from current, or would result from predicted, deterioration of air quality in a Federal Class I or Class II area. A determination of unacceptable effect shall be made on a case-by-case basis for each area taking into account existing air quality conditions. It should be based on a demonstration that the current or predicted deterioration of air quality will cause or contribute to a diminishment of the area's national significance, impairment of the structure and functioning of the area's ecosystem, or impairment of the quality of the visitor experience in the area.

Also, the Federal visibility protection regulations (40 CFR §51.300, et seq., §52.27) define adverse impact on visibility as:

> [V]isibility impairment which interferes with the management, protection, preservation or enjoyment of the visitor's visual experience of the Federal class I area. This determination must be made on a case-by-case basis taking into account the geographic extent, intensity, duration, frequency, and time of visibility impairment, and how these factors correlate with: (1) times of visitor use of the Federal class I area, and (2) the frequency and timing of natural conditions that reduce visibility. (Id. §51.301(a))

FLMs typically address adverse impacts on a case-by-case basis in response to PSD permit applications. The factors the FLMs will consider in making an adverse impact determination are discussed in more detail below (see section 4.3). When an adverse impact is predicted, FLMs recommend that permits either be modified to protect AQRVs or be denied. FLMs can also address adverse conditions outside of the PSD process. They do so through a variety of mechanisms: certify visibility impairment; participate in regional assessments; informally collaborate with States and EPA; review lease permits, SIP revisions, National Environmental Policy Act (NEPA) analyses, Park/Refuge/Forest management plans, CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act) reviews, and other documents.

In some States, FLMs use screening procedures or thresholds that indicate when the condition of an AQRV is acceptable or unacceptable. The pollutant concentration or loading rate that will adversely impact an AQRV can vary among Class I areas, and depends on current conditions. After a threshold is reached, an increase in pollutant concentrations is likely to be unacceptable. A concern threshold can be an adverse impact threshold or other quantifiable level in resource condition or pollutant exposure identified by the FLM.

2.2.5. Air Pollution Permit Conditions that Benefit Class I Areas

The FLM does not determine what permit conditions will be required or administer permit conditions; that is the responsibility of the permitting authority. However, the FLMs may request permit conditions or agree to withdraw objections to permit issuance if requested conditions are included. The FLMs view the inclusion of certain PSD permit conditions by the permitting authority as a means to help protect or enhance the condition of AQRVs when:

1. Air pollution source(s) may cause impacts that exceed protection thresholds for AQRVs;
2. Terrestrial resources, aquatic resources, and/or visibility are currently adversely impacted by air pollution and proposed emissions will exacerbate these adverse conditions;
3. FLM policies require improvement or restoration of AQRVs in parks and wildernesses; and
4. There is uncertainty on the extent and magnitude of air pollution effects on AQRVs.

Recommended permit conditions may include requiring emission offsets, AQRV and/or air quality monitoring, inventories, post-construction reassessment, LAER (or other improved control technologies), or other measures to protect, enhance, or restore resources and values of parks and wildernesses. Permit conditions may:

1. Result in net air quality benefits at a protected area or within a region;
2. Contribute to a reduction of air pollution within a region;
3. Promote ecosystem inventories and/or monitoring to evaluate physical and biological resource damage caused by air pollution emissions; and
4. Promote ecosystem restoration or improve the condition of resources that have been damaged by air pollution emissions.

The basis of an air permit condition should be identified in the public notice for the draft permit. To be effective, permit conditions must be federally enforceable and guaranteed. Air permit provisions may be temporary or permanent depending on the nature of the permit requirements.

Procedures to implement an air permit condition must be acceptable to the FLM (e.g., an agreement between parties [memorandum of understanding, interagency agreement] is an option to accomplish inventory, monitoring, or other requirements).

2.2.6. Reducing Pollution in Nonattainment Areas (Nonattainment Permit Process)

The PSD program does not apply with respect to a particular pollutant when the source locates in an area designated non-attainment for that pollutant. Instead, pollution sources are regulated by Non-attainment Area New Source Review (NNSR). NNSR includes air quality planning and regulation of stationary sources. Air quality planning addresses issues such as lowest achievable emission rate (LAER), offsets, reasonably available control technology (RACT), and mobile and stationary source control strategies. New major stationary sources and major modifications of sources in designated non-attainment areas must satisfy NNSR before construction begins. For visibility protection, SIPs must include either EPA-approved provisions to comply with 40 CFR §51.307 for the non-attainment pollutant, otherwise, the federally promulgated visibility provisions at 40 CFR §52.28 would apply to all sources located in non-attainment areas. Therefore, FLMs can provide suggestions to the permitting authority regarding these conditions during the permitting and planning processes.

SIPs provide a mechanism to address AQRV impacts when the source or the Class I area is located in a non-attainment area. FLMs may recommend that States adopt policies, rules, or regulations in their SIPs requiring a demonstration that offsets will result in a net air quality benefit within any Class I area likely to be impacted by emissions from the source to be permitted. FLMs may also request emissions reductions greater than 1:1, perhaps offset rates of 1.5 or 2.0 to 1, or higher, depending on the nature and magnitude of impacts to be offset. Such recommendations can be developed jointly in a meeting with the regulatory authority or in a letter from the FLM.

Mitigation measures recommended by FLMs may include stringent control technologies to minimize the increase in emissions and the impact on AQRVs. Monitoring can determine whether predicted resource conditions are observed. Offsets ensure that net emissions reductions from all sources will occur within a geographic area and their resulting air quality impacts at the Class I area will be mitigated.

2.3. Other Air Quality Review Considerations (Revised)

At all Class I areas where visibility has been monitored, visibility conditions have been found to be impaired by human-caused pollution. The impairment comes primarily from older sources, not new sources. From a regional perspective, new or modified sources (using new/cleaner technologies) contribute far less to impaired AQRV conditions than old sources. EPA has implemented a call for reducing NO_x emissions from older sources in the eastern U.S. to meet existing ozone standards. In addition to complying with national ambient standards, States are now developing plans to implement EPA's Regional Haze Regulations. If these requirements are implemented, then progress toward remedying impaired AQRVs is likely. However, given the sensitivity of some AQRVs to low levels of pollution, programs focused on reaching national goals, such as the NAAQS or visibility, may not fully remedy impacts on AQRVs in all locations. It is for this reason that the FLM does pursue other strategies to protect AQRVs. The following sections discuss FLM issues that go beyond NSR.

2.3.1. Remedying Existing Adverse Impacts

Allowing the existence of adverse impacts would be inconsistent with the mandates of the FLM agencies. Consequently, FLMs may request or participate in regional assessments to protect AQRVs, and remedy any existing adverse impacts on AQRVs, as appropriate. Regional assessments often use a multi-faceted approach to remedy impairment. For example, categories addressed by the Grand Canyon Visibility Transport Commission (GCVTC) include air pollution prevention; clean air corridors; stationary sources; sources in and near Class I areas; mobile sources; road dust; fire; and future regional coordination.

Clean Air Act requirements for remedying existing visibility impairment provide a mechanism for addressing impacts from specific sources or groups of sources [42 USC 7491). Negotiations at the Centralia Power Plant in the state of Washington provide an example of how to build partnerships and work collaboratively to obtain retrofit controls or more stringent control technologies for sources that affect a FLM area. Through a collaborative decision making process, owners of the Centralia plant agreed to reduce sulfur dioxide emissions at the plant by 90%. In another case, the FWS identified plume impacts from a pulp and paper mill located seven miles upwind of the Moosehorn Wilderness Area. Using cameras provided by the IMPROVE monitoring network, plumes from the mill were documented entering the Moosehorn Wilderness Area. In collaboration with the State of Maine, additional controls for nitrogen oxides and updated particulate controls were incorporated into the mill's PSD permit to address the plume impacts.

FLMs may also coordinate with others to ensure that emission reductions in nonattainment areas will improve air quality in FLM areas. Recommendations on urban planning were developed with FLM involvement to address nonattainment areas in California. Data documenting ozone effects on vegetation were provided to the planning authority.

2.3.2. Requesting State Implementation Plan (SIP) Revisions to Address AQRV Adverse Impacts (Revised)

A SIP is the mechanism that states use to develop the pollution control programs that will be used to achieve and maintain the NAAQS, as well as prevent significant deterioration of air quality. It is important for FLMs to be involved in SIP development, as participation provides an opportunity to influence planning of pollution control programs that can benefit air quality in FLM areas. Once a SIP is fully approved by EPA, it is legally enforceable under both State and Federal law. FLMs assist in the development of SIPs by providing analysis and comment to address existing impacts of concern. This approach is particularly useful for addressing impacts on AQRVs other than visibility, since the Clean Air Act does not provide specific requirements for other AQRVs.

SIP revisions could be used to address multiple sources and regional pollution that adversely affect AQRVs in all Class I areas. For example, in South Coast and San Diego, California, SIP revisions included FLM recommendations to reduce the impact of minor sources on AQRVs. South Coast recommendations addressed visibility while the San Diego recommendations addressed all AQRVs. EPA's NO_x SIP Call in the east is another example of obtaining emission reductions through the SIP revision process. The NO_x SIP Call was directed at 20 eastern States and the District of Columbia to address NO_x emissions from existing large sources. Significant reductions in ozone formation and nitrogen deposition have occurred as a result of these efforts.

2.3.3. Periodic Increment Consumption Review (Revised)

EPA has indicated its intention to establish a SIP revision requirement to address existing adverse impacts on AQRVs. The FLMs strongly support EPA exercising its authority in this way. In the interim, however, there are existing SIP revision requirements that are not being fully utilized. EPA's current regulations require States to conduct a periodic review of the adequacy of their PSD plan and program. [40 CFR §51.166(a)(4)] This would include an assessment of increment consumption in Class I and Class II areas. Few States have ever conducted a comprehensive, cumulative increment consumption analysis for one or more Class I areas. In addition, many PSD sources have not exceeded the significant impact levels for increment consumption; thus, few PSD permit applicants have had to perform a cumulative increment consumption analysis for Class I areas. Such a periodic increment consumption review would be beneficial given that the burden of proof for AQRV adverse impact determinations shifts from the FLM to the applicant when the increment has been consumed.

In its 1990 report, *Air Pollution: Protecting Parks and Wilderness From Nearby Pollution Sources,* the U.S. General Accounting Office (GAO) found that only 1 percent of the sources within 100 kilometers of five Class I areas it investigated were required to have permits under the PSD program, with 99 percent of the sources being minor or grandfathered sources. It also found that "non-PSD sources contribute from 53 to 90 percent of five of the six criteria pollutants emitted within a 100-kilometer radius of each of the five Class I areas." As part of its investigation, GAO noted that "a significant portion of total emissions of volatile organic compounds generally comes from small sources...and suggested that as part of the overall control strategy, States may want to consider lowering thresholds for regulating new sources to 25 tons of volatile organic compounds a year." According to the investigation, 55 percent of anthropogenic VOC emissions come from new sources or modifications totaling five tons per year or less. In a review of PSD permit applications near Mesa Verde National Park (a Class I area in Colorado), a cumulative modeling analysis of increment-consuming sources found that approximately 80 percent of the NO_2 Class I increment at the park had been consumed, but much of it by minor sources.

The FLMs have encouraged EPA to provide clearer direction on how often these periodic reviews should occur as the lack of a prescribed time-frame for conducting such analyses has clearly led to noncompliance with this requirement over the past twenty years by States.

2.4. Managing Emissions Generated in and Near FLM Areas (Revised)

Specific strategies need to be developed and implemented for reducing and preventing pollution from the many diverse sources and activities in communities surrounding FLM areas, including "gateway" communities (i.e., those adjacent to FLM areas). Accountability mechanisms are needed to ensure that appropriate actions are taken, reported and incorporated into SIPs, visibility protection plans, and Federal land management plans. Various forums (e.g., the Western Regional Air Partnership, and the Southern Appalachian Mountains Initiative) addressed some of the emissions sources of concern and developed regional strategies. In addition, EPA has formed other "regional planning organizations" for implementing its regional haze rule. FLMs participate in these forums, consistent with Federal law (e.g., Federal Advisory Committee Act), to the

maximum extent possible and coordinate their activities within those forums to ensure that comprehensive strategies are developed and implemented to address all the key emissions sources near FLM areas.

A systematic assessment of emission sources in and near FLM areas would be extremely helpful for formulating strategies aimed at mitigating or eliminating adverse impacts on area resources, and the NPS has performed micro-emission inventories for several of its Class I areas. However, without this assessment for all areas it is not possible to accurately quantify the extent to which these emissions contribute to the overall problem. Nevertheless, FLMs can, and should, take steps to minimize emissions generated on FLM lands even without an accurate inventory of emissions sources.

2.4.1. Prescribed Fire

Prescribed fire is a land management tool used for multiple landscape objectives. Prescribed fire allows the FLM to mimic natural fire return intervals under controlled conditions where smoke management can minimize air quality impacts. The alternative is wildfires, which can be very difficult to control and may cause much more severe air quality impacts. A modeling assessment suggests that using prescribed fire to minimize wildfires can result in a net reduction in fine particle ($PM_{2.5}$) emissions in the long-term. In the Pacific Northwest wildfire emissions were found to be greater than prescribed fire emissions in the same airshed (Ottmar 1996).

Since the early 1900s, wildfire has been aggressively suppressed on most of the nation's public lands to protect public safety, property, and to prevent what was thought to be the destruction of our natural and cultural resources. Fire-exclusion practices have resulted in forests, shrub lands, and grasslands plagued with a variety of problems, including overcrowding, resulting from the encroachment of species normally suppressed by fire; vulnerability of trees to insects and disease; and inadequate reproduction of certain species. In addition, heavy accumulation of fuels (such as dead vegetation on the forest floor) can cause fires to be catastrophic, which threatens firefighter and public safety, impairs forest and ecosystem health, destroys property and natural and cultural resources, and degrades air quality. The intense or extended periods of smoke associated with wildfires can also cause serious health effects and significantly decrease visibility.

FLMs recognize prescribed fire as a valuable tool; they also recognize that emissions from prescribed fire can be a significant source of air pollution. Smoke particles are also in the size range (< 2.5 μm) that they play a significant role in visibility impairment. Particulate matter is the main pollutant of concern from smoke because it can cause serious health problems, especially for people with respiratory illness.

The FLMs are committed to minimizing the impacts from smoke by following sound smoke management practices, and if practical, using non-burning alternatives (i.e., mechanical clearing, chipping, mulching) to achieve land management objectives. Each prescribed burn site will have unique characteristics, but in general, smoke impacts can be minimized by burning during weather conditions that provide optimal humidity levels and dispersion conditions for the type of materials being burned, in addition to limiting the amount of materials and acreage burned at one time.

EPA has worked in partnership with land management agencies in the U.S. Departments of Agriculture, Defense, and the Interior; State Foresters; State air regulators; Tribes; and others to obtain recommendations and develop a national policy that addresses how best to improve the quality of wildland ecosystems (including forests and grasslands) and reduce threats of catastrophic wildfires through the increased use of managed fire, while achieving national clean air goals (EPA 1998b). EPA's interim air quality policy on fire describes criteria for wildland managers (federal, state, tribal, and private), and state and tribal air pollution agencies, to use in planning for and implementing prescribed fires, and recommends a variety of smoke management techniques that land managers can use to help reduce smoke impacts from prescribed fires. The policy is available at EPA's web site: http://www.epa.gov/ttn/faca/fa08.html. In addition, on March 22, 2007, EPA promulgated its Exceptional Events Rule that clarifies how ambient air quality standard exceedances from wildland fire will be treated in determining attainment and nonattainment status. In that rule, EPA committed to revising its 1998 wildland fire policy (72 FR 13560, March 22, 2007).

2.4.2. Strategies to Minimize Emissions from Sources In and Near FLM Areas (Revised)

Aside from prescribed fire, other activities in and near FLM areas that generate air pollution include vehicle emissions, road building, operation of generators, oil and gas development, etc. Developing strategies for addressing natural resource impacts in or near an FLM area should not only take into consideration the type of activities generating the emissions and their amount, but also the existing condition of the resources of that area. More stringent measures should be recommended for sources in and near FLM areas that are already experiencing adverse effects from air pollution.

Examples of potential air pollution prevention practices that FLM agencies may encourage or develop and use are categorized under the following three strategies:

Pollution Prevention Strategies

- Review land management plans for affected FLM areas to assess whether they include strategies to limit and reduce air pollution emissions and incorporate protective measures into planning and decision documents.
- Place priority on pollution prevention.
- Encourage zero and near-zero emitting technologies.
- Promote energy conservation and the use of renewable energy sources.
- Promote use of clean fuels.

Mobile Source Strategies

- Promote the adoption of Low Emission Vehicle standards or the conversion of Federal fleets to alternative fuels.
- Improve control of evaporative emissions.
- Promote more stringent emission standards for the tour bus industry and other high-emitting vehicles used in federal areas (e.g., park shuttle vehicles).
- Considering restricting access of high emitting vehicles to sensitive areas.
- Retire high-emitting vehicles from Federal fleets as quickly as practicable and/or relocate high-emitting vehicles to less sensitive areas until they can be retired.
- Establish emission budgets from the transportation sector for selected FLM areas.
- Develop mass transit systems in some NPS units (e.g., light rail in Grand Canyon NP and a bus system in Zion NP).

Minor Source Strategies (Revised)

- Apply RACT, BACT, LAER, best and reasonably available control measures, etc., to existing federal sources, as appropriate.
- Recommend going beyond conformity requirements to include the protection of AQRVs in FLM areas, and ensure all actions FLMs can practicably control in and near FLM areas will not cause, or contribute to, an adverse impact on any AQRV.

Improved involvement with interested parties in gateway communities will likely be required to ensure growth in these communities occurs in a manner that mitigates the impact on natural resources. These communities may need to enhance their participation in the planning processes of FLMs. Similarly, FLMs should participate in planning activities for public lands located in the FLM area and communities adjacent to FLM areas to ensure air quality concerns are adequately addressed. Mechanisms should be identified and developed for community involvement in developing, implementing, and enforcing emission management strategies for sources near and in FLM areas.

Implementing strategies to achieve emission reductions in and near FLM areas will require efforts in at least three specific areas:

1. FLMs should ensure that sufficient emphasis is placed in agency planning documents requiring the minimization of air pollution emissions from new activities or practices.
2. FLMs should inventory air pollution emissions within FLM areas. After emissions have been quantified, FLMs, States, and adjacent communities will be able to assess the impact of these emissions through the use of appropriate models. Knowledge of Class I area emissions will also improve FLM ability to consult with States during the development and review of their SIPs (especially visibility SIPs). The NPS has developed an emissions inventory tool, the Climate Leadership in Parks (CLIP) Tool, that can be utilized by FLMs to inventory both greenhouse gases and all criteria air pollutants.
3. FLMs should cooperate with States and local communities in assessing the need for, and the development of, appropriate emission reduction strategies in and near FLM areas that address non-PSD sources. For Class I areas, the Regional Planning Organizations have completed analyses of emissions from nearby communities and activities that will serve as the basis for identifying strategies to reduce emissions. Without an acknowledgment from States and local communities that these sources may pose a threat to FLM areas and a systematic assessment of these potential impacts, current efforts to protect FLM area resources may be insufficient.

2.4.3. Conformity Requirements in Nonattainment Areas

Conformity criteria and procedures ensure that actions on lands administered by Federal agencies do not cause a violation of the NAAQS, increase the frequency of any standards violations, or delay attainment of a standard. Conformity to SIPs is only required for activities within nonattainment areas for non-transportation related sources if emissions are above de minimis levels and regionally significant. Any activity that represents 10 percent, or more, of the emission inventory for that pollutant in the non-attainment or maintenance area is regionally significant. Examples of actions that may require a conformity determination include road paving projects, ski area development, or mining. Activities such as prescribed fire, that are included in a conforming land management plan, are exempt from conformity requirements. Please note that conformity determinations must be made in accordance with applicable EPA regulations, are typically done before a project is approved, and are part of the NEPA process.

The FLM should define the process to be used in conformity determinations and perform the conformity analysis before

a project is implemented. A conformity analysis typically includes emission calculations, public participation, mitigation measures/implementation schedules, and reporting methods. The Pacific Southwest Region of the USFS has published a *Conformity Handbook for FLMs* to assist in conformity compliance. In an approved Plan of Operation, FLMs can require monitoring. For example, in the case of Carlota Mine, located on National Forest land in Arizona, the USFS requested additional mitigation measures to protect AQRVs in the Superstition Wilderness.

Transportation projects in FLM areas classified as nonattainment are subject to a more complicated transportation conformity process. Consultation with State and local air quality and transportation agencies will be required to comply with applicable regulations.

3. Subgroup Reports: Technical Analyses and Recommendations

3.1. Subgroup Objectives and Tasks

Subgroups were formed to address the four key issues relevant to AQRV identification and evaluation issues: policy (and procedures), visibility, ozone, and deposition. Each of these subgroups reviewed the commonalities among the FLMs then addressed the tasks assigned to them by FLAG. One of their first tasks was to differentiate between Phase I tasks, those which could be resolved in the short term without significant additional resources, and Phase II issues, those that would require a longer period or greater effort.

Subgroups were asked to reach common ground among the FLMs on the issues. The intent was to develop, to the extent possible, consistent policies, processes, and terminology that could be used when identifying AQRVs and evaluating impacts on AQRVs. This involves recommending consistent approaches for identifying air pollution effects on AQRVs, for determining adverse impacts, and for attributing adverse impacts to specific pollution sources. In addition, the FLMs consider that AQRV protection from visibility, ozone, and deposition impacts are equally important. However, we also recognize that given the current state of the science, attributing adverse impacts to specific sources are easier to document for visibility than for deposition and ozone, and easier for deposition than ozone.

The individual subgroup reports document the common policies, procedures, and definitions identified or developed during Phase I activities. The Visibility, Ozone, and Deposition subgroup reports are included below. The FLAG Policy Subgroup Report was used as the basis for much of the rest of this *FLAG Phase I Report*, including much of section 1 'Background' and section 2 'Federal Land Managers' Approach to AQRV Protection'.

3.2. Initial Screening Criteria (New)

Experience with the FLAG 2000 recommendations in dealing with many new source review applications led the Agencies to believe that an initial screen that would exempt a source from AQRV impact review based on its annual emissions and distance from a Class I area may be appropriate in most situations. As part of its Regional Haze Regulation, the EPA has introduced a screening criteria in its BART guidelines based on a source's annual emission strength and distance from a Class I area. The EPA stated that it would be reasonable to conclude that the following sources would not be considered to cause or contribute to visibility impairment:

Acadia National Park, Maine.
Credit: National Park Service

- those located more than 50 km from any Class I area that emit less than 500 tons per year of NO_x or SO_2 (or combined NO_x and SO_2), and
- those located more than 100 km from any Class I area that emit less than 1,000 tons per year of NO_x or SO_2 (or combined NO_x and SO_2).

In both cases, the annual emissions over distance factor equates to 10.

The Agencies have concluded that a similar approach has merit with respect to new source impacts at Class I areas, for air pollution sources with relatively steady emissions throughout each year. However, the Agencies are modifying the size criteria to also include Particulate Matter less than 10 microns in size (PM_{10}) and sulfuric acid mist (H_2SO_4) emissions because those pollutants also impair visibility and contribute to other resource impacts. In addition, rather than the two-step BART test, the Agencies are using a fixed Q/D factor of 10 as a screening criteria for sources locating/located greater than 50 km from a Class I area. Furthermore, the Agencies are expanding the screening criteria to include all AQRVs, not just visibility. Therefore, the Agencies will consider a source locating greater than 50 km from a Class I area to have negligible impacts with respect to Class I AQRVs if its total SO_2, NO_x, PM_{10}, and H_2SO_4 annual emissions (in tons per year, based on 24-hour maximum allowable emissions), divided by the distance (in km) from the Class I

area (Q/D) is 10 or less. The Agencies would not request any further Class I AQRV impact analyses from such sources.

In cases where a source's operations which generate visibility-affecting emissions are limited to time periods shorter than a year, the short-term potential to impact visibility may not be adequately expressed by the Q/D concept. For example, a source that is operated either seasonally or intermittently, and has zero emissions for substantial portions of a year, would have a total annual emission rate that under-represents its potential emission strength over a shorter time frame, such as a day or week. Because visibility is an air quality related value that is sensitive to immediate and short-term conditions, in order to apply the Q/D≤10 screening tool, these types of sources need to first adjust the tons-per-year emissions to reflect what the emissions would be if the source operated year-round. For instance, if operations are restricted to 3,000 hours per year, then the annual steady-state-equivalent emission rate (Q) is found by multiplying the permitted total tons per year for SO_2, NO_x, PM_{10} , and H_2SO_4 by the ratio of hours: 8,760 hours per year/3,000 hours operation.[5] Then, using this annual equivalent Q in the Q/D test, the Agencies will consider a source locating greater than 50 km and showing that its ratio of annual equivalent Q (tons per year) divided by distance from the Class I area (km) of 10 or less, as having negligible impacts with respect to Class I visibility impacts, and would not request any further Class I visibility impact analyses from such sources.

3.3. Visibility

3.3.1. Introduction (Revised)

This chapter describes methods for analyzing the impacts on visibility from new or modified air pollution sources. This includes sources that fall under the purview of the Prevention of Significant Deterioration (PSD) regulations and sources that are being analyzed for Environmental Assessments and/or Environmental Impact Statements under the National Environmental Policy Act (NEPA). The basis for some of the decisions outlined in this chapter is Section 169A of the Clean Air Act. The opening statement of this section states: "Congress hereby declares as a national goal the prevention of any future, and the remedying of any existing, impairment of visibility in mandatory class I Federal areas which impairment results from man made air pollution." Under the regulations promulgated for visibility protection (40 CFR §51.301 (x)) visibility impairment is defined as "…any humanly perceptible change in visibility (visual range, contrast, coloration) from that which would have existed under natural conditions." The remainder of this chapter describes methods that allow for new source growth to be analyzed against the constraint of preventing visibility impairment as defined in 40 CFR §51.301 (x), that is, new source growth should not allow any humanly perceptible change in visibility as compared against natural conditions.

Visibility Impairment

Before proceeding with the discussion, it is useful to identify the ways that visibility impairment can manifest itself. First, the pollutant loading of a section of the atmosphere can become visible, by the contrast or color difference between a layer or plume and a viewed background, such as a landscape feature or the sky. The second way that visibility is impaired is a general alteration in the appearance of landscape features or the sky, changing the color or the contrast between landscape features or causing features of a view to disappear. The first phenomenon is commonly referred to as plume impairment, whereas the second phenomenon is sometimes referred to as uniform haze impairment. As plumes are transported within a stable atmospheric layer, they may become a layered haze. As plumes and other more diffuse emission sources are transported and become well mixed in the atmosphere, they may develop into a uniform haze.

Visibility Parameters (Revised)

The analysis methods for new source growth, described in this chapter, deal with the visibility effects of discrete plumes and the aggregation of discrete plumes into a uniform haze. The difference in these phenomena, as treated in this chapter, is whether the visibility effect is primarily seen as a section of the atmosphere which exhibits a change in contrast or color as compared with a viewed background, or whether the effect is due to an alteration of the appearance of the background features themselves. For the first situation, the contrast (C) and color difference index (ΔE) of the plume and the viewing background are calculated. For the second situation, the change in atmospheric light extinction (Δb_{ext}), relative to natural conditions, is calculated. The light extinction is inversely proportional to "visual range." An approximation for which situation applies is the distance from the point of emission. (Distance serves as an indicator of where steady state conditions may apply.) The visibility impairment from sources within 50 kilometers of a view is usually calculated using contrast and color difference, whereas visibility impairment from sources greater than 50 kilometers from a view, or the aggregation of a number of plumes, regardless of distance, is usually calculated using the change in light extinction. The distance approximation is useful for distinguishing these two phenomena; the terms "near field" and "distant/multi-source" are sometimes used in the remainder of this document to make this distinction.

5. Or, an intermittent hourly emission limit could be annualized by multiplying by 8,760 hours per year/2,000 lb/ton (= 4.38).

3.3.2. Recommendations for Evaluating Visibility Impacts (Revised)

There are two fundamentally different approaches one could adopt to determine visibility impairment. One is a technically rigorous, complex, and situation-specific method, while the other is a more generalized approach. The more rigorous approach requires determination of particle concentrations and size distributions, calculation of particle growth dynamics, and application of elaborate physics (e.g., Mie Theory) to determine the optical characteristics of the aerosol distribution. Sophisticated radiative transfer models are then applied, using aerosol optical characteristics, lighting and scene characteristics, and spatial distribution of the pollutants to calculate the path and wavelength of image-forming and non-image-forming light that reaches a specific observer from all points in the scene being viewed.

While such a detailed analysis may be useful for assessing specific cases, it is usually impractical for situations in which visibility could be experienced in a nearly infinite variety of circumstances. Practical limitations frequently dictate that it is more reasonable to use a generalized approach to determine the change in extinction by using bulk-averaged aerosol-specific extinction efficiencies rather than trying to reproduce the complex optical phenomena that may occur in the atmosphere.

Consequently, as a first-level analysis, FLAG recommends the generalized approach for determining the effects on visibility from a proposed new source's emissions. The procedure is to estimate the atmospheric concentrations of visibility impairing pollutants, apply representative visibility parameters, calculate the change from specified reference levels, and compare this change with prescribed threshold values. The more detailed analysis described above may be appropriate as a refined analysis in the event the source fails the first-level analysis.

FLAG is using EPA's estimates of natural visibility conditions under its Regional Haze Rule as reference levels for Class I visibility analyses. Comparison with natural conditions will help ensure that those conditions will not be impaired in keeping with Section 169A of the CAA. Because of the different requirements of the two modeling approaches discussed below, natural conditions should be expressed using two different metrics:

- Standard visual range (visual range adjusted to a Rayleigh condition of 10 Mm^{-1}), for near field modeling. Present EPA guideline visibility models traditionally accept visibility conditions expressed in these terms.
- Extinction, for distant/multi-source modeling. Visibility conditions should be expressed in terms of the averaged extinction efficiencies of the individual atmospheric constituents that comprise the total extinction. The relative humidity effects of the hygroscopic particles should be accounted for when the change in extinction is calculated.

Information needed to calculate the above indices for all 156 Class I areas for which visibility is an important attribute is provided in Tables 5 through 10 at the end of this chapter. If estimates are needed for Class II areas, the FLM can provide them.

3.3.3. Air Quality Models and Visibility Assessment Procedures (Revised)

The modeling discussion will be divided into two parts to address the very different requirements for 1) near field modeling where plumes or layers are compared against a viewing background, and 2) distant/multi-source modeling for plumes and aggregations of plumes that affect the general appearance of a scene. Note that both of the above analyses might apply depending on the source's proximity to all portions of the Class I area or multiple Class I areas.

FLAG 2000 provided information in the form of recommendations, specific processes, and interpretations of results for assessing visibility impacts of sources affecting Class I areas (although some of this information is generally applicable to Class II areas, as well). The information separately addressed assessments for sources proposing to locate relatively near (within 50 km) and at farther distances (greater than 50 km) from these areas. It also recommended impairment thresholds and identified the conditions for which cumulative analyses could be warranted. This revision (FLAG 2010) updates the Distant/Multi-source analysis discussed in FLAG 2000, and clarifies the recommendations regarding the near-field (within 50 km)/steady-state analysis.

Near Field Analysis Technique for Analyzing Plumes or Layers Viewed Against a Background (Revised)

The Model (Near Field – Steady State Conditions Applicable) (Revised)

EPA has recommended a methodology to assess impacts due to coherent plumes. A guideline for when these steady state conditions apply is the distance from the source to the view of concern. This technique is usually applied for sources locating within 50 km of a Class I area. Applicants should first model their potential plume impacts using the screening model, VISCREEN (EPA 1992a), or, if the next level of analysis is called for, PLUVUE II (EPA 1992b and 1996a). Both of these models use steady-state, gaussian-based plume dispersion techniques to calculate one-hour concentrations within an elevated plume. These two models calculate the change in the color difference index (ΔE) and contrast between the plume and the viewing background. Values of ΔE and plume contrast are based on the concentrations of fine primary particulates (including sulfates), nitrogen dioxide (NO_2), and the geometry of the observer, target, plume, and the position of the sun. PLUVUE II also allows

consideration of the effects of secondarily formed sulfates. Plume contrast results from an increase or decrease in light transmitted from the viewing background through the plume to the observer. The specifics of the emission scenarios and plume/observer geometries for modeling should be selected in consultation with the appropriate Agency representatives. At the present time there is no recommended procedure for conducting analyses of multiple sources with these modeling tools, so multiple coherent plumes should be treated individually, or combined into a representative single source if appropriate. Alternatively, the techniques outlined in the Distant/Multi-Source section below may be used on a case-by-case basis.

The Recommended Procedures (Near Field – Steady State Conditions) (Revised)

Until better modeling tools are available, FLAG recommends using the present EPA techniques for plume visual impact screening analyses (EPA 1992c). However, unlike those procedures, which suggest the use of current average annual visibility conditions, FLAG recommends that for Class I areas the visual range corresponding to natural conditions be used to generate the hourly estimates of ΔE and plume contrast. FLAG recommends this change in order for the analysis technique to be consistent with the national visibility goal. For plume analyses, FLAG recommends using the monthly average natural visual range conditions provided for each area in Table 10.

If a screening analysis of a new or modified source can demonstrate that its emissions will not cause a plume with any hourly estimates of ΔE greater than or equal to 2.0, or the absolute value of the contrast values ($|C|$) greater than or equal to 0.05, the FLM is likely not to object to the issuance of the PSD permit based on near field visibility impacts and no further near field visibility analyses will be requested. More refined analyses (i.e., PLUVUE II) would be undertaken if the above conditions are not met and would be compared against lower levels of concern. For PLUVUE II analyses, the FLM would likely not object if $\Delta E < 1.0$ and $|C| < 0.02$.

All analysis for Class I visibility impacts should include all visibility impairing emissions. This means that even if a facility is only considered a significant emitter of one pollutant, all pollutants that may contribute to impairment should be modeled together. Furthermore, since visibility is an instantaneous value, short-term (24-hour) maximum allowable emissions should be used.

- Level-1 Near Field Screening. Conducting a complete refined plume blight analysis can become rather complex, so three levels of evaluation are available to an applicant. The first, Level-1 screening, is the simplest and most conservative method. As described in the EPA's Workbook for Estimating Visibility Impairment (EPA-450/4-80-031):

  > Level-1 Screening: Level-1 screening is designed to provide a conservative estimate of plume visual impacts (i.e., impacts that would be larger than those calculated with more realistic input and modeling assumptions). This conservatism is achieved by the use within the screening model VISCREEN of worst-case meteorological conditions: extremely stable (F) atmospheric condition, coupled with a very low wind speed (1 m/s) persisting for 12 hours, with a wind that would transport the plume directly adjacent to the observer (as shown schematically in Figure 7).

  Since little project specific information is used for a Level-1 screening analysis, documentation requirements are minimal. Basic information of emissions, meteorological parameters, and model results should be provided. Applicants are encouraged to supply electronic copies of all files necessary to reproduce the results. If an application shows estimated impact values within the thresholds, it is unlikely that additional evaluation will be necessary.

- Level-2 Near Field Screening. If Level-2 screening is necessary, more project specific information is now incorporated. Actual meteorology from the area and emission characteristics of the facility are used. Again, as described in the EPA's Workbook for Estimating Visibility Impairment:

  > Level-2 Screening: As shown in Figure 1, Level-2 plume visual impact screening is done if the Level-1 results exceed the screening criteria. The objective of Level-2 screening is identical to that of Level-1—the estimation of worst-day plume visual impacts—but in Level-2 screening more realistic (less conservative) input, representative of the given source and the Class I area, is provided. This situation-specific input may include particle size distributions for plume and background that are different from those used in the default Level-1 analysis. Median background visual range based on on-site measurements rather than the map shown in Figure 9 might be used. However, the most important potential difference in input between Level-1 and Level-2 analysis centers on meteorology and plume transport and dispersion patterns. While the Level-1 analysis assumes F stability, a 1 m/s wind speed, and a wind direction that would carry plume material very close to the observer, in the Level-2 analysis, meteorological data and topography representative of the source area and Class I area may suggest that worst-case plume dispersion conditions are different.

  It is important to note that the Agencies have maintained the recommendation that all applicants compare

estimated modeled impacts from a facility against natural conditions. This is true for all analysis levels. The use of five years of site-representative meteorology and facility-specific emission characteristics is what makes this analysis different.

As a result of the increased project-specific information, documentation also should include summaries and/or tables describing the additional data sets and evaluation steps taken to conduct the analysis.

Once again, meeting screening thresholds means that it is likely that the Agencies' Class I air quality modeling procedures will have been satisfied.

- Level-3 Near Field Refined Analysis. A Level-3 analysis is the final assessment. An applicant can conduct a full refined analysis demonstrating estimates of frequency, magnitude, and spatial extent of a proposed project's visibility impacts. The EPA's Workbook for Estimating Visibility Impairment says:

  > Level-3 Analysis: In Level-3 analysis, the objective is broadened from conservative analysis of worst-case conditions to a realistic analysis of all conditions that would be expected to occur in a typical year in the region that includes both the emission source and the observer. Level-3 analysis is no longer considered screening because it is a comprehensive analysis of the magnitude and frequency of occurrence of plume visual impacts as observed at a sensitive Class I area vista.
  >
  > It is important to determine the frequency of occurrence of visual impact because the adversity or significance of impact is dependent on how frequently an impact of a given magnitude occurs. For example, if a plume is perceptible from a Class I area a third of the time, the impact would be considered much more significant than if it were perceptible only one day per year. The assessment of frequency of occurrence of impact should be an integral part of Level-3 visual impact analysis.

  As mentioned above, the threshold values for this analysis step changed. For this step, EPA's PLUVUE II model is currently recommended. One main difference with PLUVUE II is its inability to evaluate more than one hour of impact per run. Because it is customary to evaluate five years of site-specific meteorology, it can become an extensive process. Applicants may want to develop and utilize tools to group hourly meteorological and post processing scenarios. The analysis identifies specific locations for plume/observer relationships. These observation points should be established within each potentially impacted Class I area. With each observer, potential impacts are calculated for all possible views. As with the meteorology, PLUVUE II is only able to assess one observer location per model run. Specific information on setup methods can be found in EPA's Workbook for Estimating Visibility Impairment and PLUVUE II manual.

  Substantial documentation is needed for this more refined analysis. The discussion should summarize data sources, processing methods, and modeling utilities used, and information regarding all assumptions or consolidation criteria. In short, sufficient information and electronic files should be provided to the Agencies that will allow reviewers to reproduce the results. Due to the complexity of this refined analysis, the Agencies suggest that consultation occur between the applicant and the Agencies before working on the impact analysis begins. Furthermore, selection of model parameters and input data should be documented in a written protocol and agreed upon by the affected Agencies in advance of any modeling being conducted.

If the estimated plume parameters exceed the aforementioned values, the FLM would rely on a case-by-case effects-based test (NPS 1993), taking into account magnitude, frequency, duration, and other factors, to decide whether to make an adverse impact determination.

Distant/Multi-Source Techniques for Analyzing Whether a Plume or an Aggregation of Plumes Alters the General Appearance of a Scene (Revised)

This analysis is generally more complex than the near field, coherent plume modeling analyses and the guidance from EPA is less definitive, though it is evolving. The modeling system should include the capability to assess single and multiple sources in a temporally and spatially varying meteorological domain, accommodate modeling domains measuring hundreds of kilometers, include rough and complex terrain, provide pollutant concentration estimates for averaging times from one-hour to annual, and address inert and secondarily formed pollutants and dry and wet deposition. In the early 1990s the FLMs and the EPA recognized the need for a consistent, technically credible technique to estimate contributions to air quality of multiple new sources locating more than 50 km from Class I areas. Towards that end, on April 15, 2003, the EPA promulgated revisions to Appendix W of 40 C.F.R. §51 (*Guideline on Air Quality Models*). The EPA revised the Guideline to adopt the CALPUFF model as the preferred long-range transport model for inclusion in Appendix A of that document. This technique is usually applied when sources are located more than 50 kilometers from portions of a Class I area, when an aggregation of plumes may impact an area, or when the assumptions inherent in steady state visibility models do not apply.

The first-level analysis procedures discussed in this revision differ from FLAG 2000 in several discrete areas, but

generally remain the same. The primary differences are in the areas of the reference natural conditions that are used in the comparisons for thresholds of concern and using the average monthly relative humidity adjustment factors rather than the hour-by-hour factors identified in FLAG 2000. CALPUFF is still the preferred first-level air quality model for calculating pollutant concentrations, however, using "CALPUFF Lite" with single station meteorology is no longer recommended. We wish to emphasize that the first-level procedures defined herein are to be taken as a whole; any deviations from these procedures or ostensible refinements compromise the integrity of the analysis, and may warrant an hourly analysis for all hours in the analysis. Furthermore, the metric used for the first-level analysis (relative change in light extinction) is not necessarily the appropriate metric for a refined analysis. The procedures and metrics for refined analyses will need to be agreed upon by the affected Agencies.

The initial step in conducting the first-level analysis is to run CALPUFF using a minimum of three years of mesoscale meteorological model output, and preferably five years, consistent with current EPA guidance. Selection of model parameters and input data should be documented in a written protocol and agreed upon by the affected Agencies in advance of any modeling being conducted. Please note emissions input considerations and model receptor grid data are discussed below. The indices for comparison with the Agencies' levels of concern are calculated in CALPOST. The remainder of this discussion is focused on CALPOST.

After CALPUFF is run, CALPOST is used to evaluate whether the proposed source or modification will be below the Agencies' threshold for concern (i.e., 5% change in light extinction). The CALPOST parameter MVISBK is set to eight (8), sub-mode five (M8_MODE = 5), and the background hygroscopic and non-hygroscopic aerosol levels are derived from the annual average natural conditions provided in Table 6. The monthly relative humidity adjustment factors for the Class I area are input to the RHFAC array (Tables 7-9) in CALPOST. The 98th percentile test applies to the number of days that any model receptor in the Class I area exceeds the threshold. The visibility threshold for concern is not exceeded if the 98th percentile change in light extinction is less than 5% for each year modeled, when compared to the annual average natural condition value for that Class I area.

If this analysis indicates that the 98th percentile values for change in light extinction are equal to or greater than 5% for any year, then the Agencies will further scrutinize the applicant's proposal. The Agencies will consider the full range of factors discussed below (in the "Expansion of Discussion of Process for Adverse Impact Determination" chapter) and any refined analyses provided by the applicant before making a recommendation to the FLM regarding potential adverse impacts. As noted above, these refined analyses should account for the relevant physicochemical processes that produce visibility impairing pollutants and accurately treat the relevant radiative transfer properties affecting visibility. This will likely entail using different meteorological and air quality models capable of producing hourly concentrations, or less, and using a three dimensional radiative transfer model (see refined analysis discussion below).

For consistency with implementation of BART or the regional haze rule to specific Class I areas, the FLM or permitting authority may recommend use of the 20% best natural background values provided in Table 5 in lieu of annual averages on a case-by-case basis.

Background Information on Thresholds

In its BART guidelines, EPA indicated that for regional haze, a source whose 98th percentile value of the haze index is greater than 0.5 deciview (dv) (approximately a 5% change in light extinction) is considered to contribute to regional haze visibility impairment. Similarly, a source that exceeds 1.0 dv (approximately a 10% change in light extinction) causes visibility impairment. The 0.5 dv and 1.0 dv thresholds are similar to what the Agencies used in FLAG 2000. Therefore, for consistency between visibility protection programs and to address similar concerns, the Agencies will also use the 98th percentile value as a threshold in the first-level visibility analyses for new source impacts.

In its 2005 BART guidelines, the EPA also concluded that by using the 98th percentile of CALPUFF modeled impacts the sources that contribute 0.5 deciview to regional haze visibility impairment in a Class I area would effectively be captured, while minimizing the likelihood that the highest modeled visibility impacts might be caused by conservative assumptions in the model. Similarly, using the monthly average relative humidity adjustment factors, rather than the hour-by-hour factors, reduces some of the higher (e.g., weather –related) values seen in FLAG 2000.

Using the 98th percentile of modeled visibility values to compare to the 5% change in extinction threshold would exclude roughly seven days per year from consideration for each Class I area. However, consistent with the BART guidelines, the 98th percentile test applies to the number of days that any model receptor in the Class I area exceeds the threshold. Also, this test is limited to haze-like, first-level analyses. Therefore, all applicable sources locating within 50 km of a Class I area would still need to assess coherent plume impacts in accordance with the procedure described above. Furthermore, applicable sources would need to assess sulfur and nitrogen deposition impacts at the Class I area.

Natural Conditions

FLAG 2000 discussed assessing the change in visibility due to a proposed new source relative to annual average natural conditions. Therefore, it is important to define

natural conditions for each Class I area. At the time of FLAG 2000, the Agencies acknowledged that the EPA was working on defining natural conditions in support of their visibility regulations. In the absence of more specific data, the FLMs at that time adopted the appropriate aerosol concentrations developed by the National Acid Precipitation Assessment Program (NAPAP) as estimates of natural conditions for each Class I area. The EPA has since published natural condition estimates for each Class I area. The natural condition values provided in FLAG 2000 and those developed by the EPA are based on similar underlying assumptions; consequently, the estimates are similar. Regardless, the EPA estimates should be used by applicants in future visibility impact assessments. Please note that Tables 5 and 6 contain estimates for the 20% best natural visibility and annual average natural visibility conditions for each Class I area, respectively.

Relative Humidity Adjustment Factor

FLAG 2000 discussed the importance of the relative humidity adjustment factor (f(RH)) when calculating the sulfate and nitrate components of the visibility extinction coefficient. These aerosols are hygroscopic and the addition of water enhances their scattering efficiencies. FLAG 2000 recommended using hour-by-hour f(RH) for the analysis. The EPA, in its 2005 BART guidelines, concluded that by using a monthly average f(RH) the likelihood that the highest modeled visibility impacts were caused by short-term and geographically different meteorological phenomena (e.g., weather events) would be minimized. The Agencies agree with the EPA that using the monthly f(RH) effectively neutralizes short-term weather events and are adopting a similar approach for Class I visibility impact analyses for new sources. Therefore, new sources performing Class I visibility analyses should use monthly average f(RH) values developed by EPA for large hygroscopic particles (Table 7), small hygroscopic particles (Table 8), and sea salt (Table 9), rather than the hourly values discussed in FLAG 2000.

Emissions Input

There are two other aspects of the visibility impact analysis that the Agencies would like to clarify at this time: (1) emissions input, and (2) the model receptor grid. Regarding the emission inputs, because applicants are assessing a 24-hour average regional haze visibility impact, it is important that they model a corresponding maximum allowable 24-hour mass emission rate, as opposed to monthly or annual average emissions. Using a 30 day average emission rate as input to the visibility modeling analyses does not restrict the facility from emitting pollution at a higher rate for shorter time periods (e.g., 24-hour average). A 30 day average emission rate smooths out days with high emissions, and therefore, would underestimate the predicted 24-hour visibility impacts. Because the emission rates and the corresponding averaging times influence the outcome of the analyses, it is critical that appropriate emissions are matched to the averaging time being assessed, and that these emission rates ultimately are included as enforceable permit conditions. This approach is consistent with the *Guideline on Air Quality Models* (Appendix W of 40 C.F.R. §51) and the EPA BART guidelines. Furthermore, if an applicant chooses to conduct any refined analyses, where visibility impairment is assessed at no more than an hourly basis, maximum hourly emissions should be analyzed.

Please note that all visibility impairing pollutants should be modeled from all modified or affected emission unit(s), regardless of which pollutants actually triggered NSR. Particulate Matter (PM) should also be speciated into filterable PM (coarse, fine, elemental carbon) and Condensable PM (organic carbon and sulfates) based on the best available information. Particulate speciation data for several source types can be found on the NPS Air Resources Division's web site at:

- http://www.nature.nps.gov/air/permits/ect/index.cfm

Applicants should calculate the 24-hour average net emission increase for each pollutant from modified facilities as the maximum allowable 24-hour average minus the actual hourly rate averaged over the past two years (annual emissions over past two years/hours of operation over last two years).[6]

Model Receptor Grid

Since FLAG 2000 was published, the NPS Air Resources Division has developed a database of modeling receptors for all of the Class I areas in the contiguous United States. A file conversion program to convert the data from latitude/longitude to other common mapping coordinates (currently Lambert Conformal and Universal Transverse Mercator (UTM)) has also been developed. Alaska and Hawaii are not yet complete, but will be included in the data sets when they are available.

Permit applicants can download the Class I Receptor Data files, as well as the Conversion program, from the link below. For modeling consistency, the Agencies ask that permit applicants use the uniform receptor grids provided. Also available are the Class I boundary shape files that were used to create the receptor data files.

- http://www.nature.nps.gov/air/Maps/Receptors/index.cfm

Receptor grids for FLM Class II areas should be dense enough to determine Class II increment consumption and

6. Note that this is different from the emission change calculation used for short-term increment, which is calculated as the maximum allowable 24-hour average minus the highest occurrence over the past two years.

to perform any required "secondary impacts" (i.e., soils, vegetation and visibility) analyses.

Refined Analysis

It is important to reiterate that the FLAG distant/multi-source visibility analysis is only a first-level screening technique, primarily designed to identify those sources that are unlikely to significantly affect visibility and warrant no further analysis, and those that may adversely impact visibility and warrant further scrutiny. Visibility is experienced instantaneously, not on a 24-hour average basis. The 24-hour average visibility calculation in FLAG is acceptable because of a number of simplifying assumptions in the prescribed technique. Accepting certain EPA BART guideline procedures as an update to the FLAG techniques does not alter the first-level nature of the procedure. Modifying those simplifying assumptions negates the acceptability of using a 24-hour average. Consequently, any applicant whose visibility analysis deviates from the recommended FLAG screening procedures warrants performing an hour-by-hour analysis.

Deviations from the first-level screening procedure should lead to refinements in the modeling and visibility analyses, not arbitrary adjustments to the prescribed first-level technique. This is especially important in dealing with weather-related events. The Agencies believe that by paralleling the BART guideline procedures they have adequately taken into account the effects of meteorological extremes, and model uncertainty. Therefore, given the Agencies' desire to balance the positive and negative biases of the FLAG screening methodology, any modifications to the screening technique invalidate the Level 1 model results. Consequently, the Agencies do not expect permit applicants that exceed the visibility effects thresholds to scrutinize the data and attempt to disregard specific impact days due to weather. Under those circumstances, the permit applicant can accept the modeling results at face value, and then the FLM will decide whether or not those impacts are adverse. Alternatively, the applicant could conduct an hour-by-hour analysis (as opposed to using a 24-hour average) by performing a refined analysis using a more sophisticated approach that requires determining particle concentrations and size distributions, calculation of particle growth dynamics, and application of Mie Theory to determine the optical characteristics of the aerosol distribution. Sophisticated radiative transfer models can then be applied, using aerosol optical characteristics, lighting and scene characteristics, and spatial distribution of the pollutants to calculate the path and wavelength of image-forming and non-image-forming light that reaches a specific observer from all points in the scene being viewed. The concept of this more refined approach is discussed in FLAG 2000, and one possible approach is included in "*Proposed FLAG Level II and III Visibility Assessment*" (Schichtel et al. 2006). However, if this situation arises, permit applicants are encouraged to consult with the Agencies and discuss the specifics of this refined analysis.

3.3.4. Summary (Revised)

FLAG provides recommendations, specific procedures, and interpretation of results for assessing visibility impacts of new or modified sources on Class I area resources. Although FLMs only have a formal role in the permitting process for applications that affect Class I areas, this information can be used for Class II areas as well. FLAG addresses assessments for sources proposed for locations near (generally within 50 km) and at large distances (greater than 50 km) from these areas. The key components of the recommendations are highlighted below.

In general, FLAG recommends that an applicant:

- Apply the Q/D test (see section 3.2, 'Initial Screening Criteria') for proposed sources greater than 50 km from a Class I area to determine whether or not any further visibility analysis is necessary.
- Consult with the appropriate regulatory agency and with the FLM for the affected Class I area(s) or other affected area for confirmation of preferred visibility analysis procedures.
- Obtain FLM recommendation for the specified reference levels (estimate of natural conditions) and, if applicable, FLM recommended plume/observer geometries and model receptor locations.
- Apply the applicable EPA Guideline, steady-state models for regions within the Class I area that are affected by plumes or layers that are viewed against a background (generally within 50 km of the source).
    - Calculate hourly estimates of changes in visibility, as characterized by the change in the color difference index (ΔE) and plume contrast (C), with respect to natural conditions, and compare these estimates with the thresholds given in section 3.3.3.
- For regions of the Class I area where visibility impairment from the source would cause a general alteration of the appearance of the scene (generally 50 km or more away from the source or from the interaction of the emissions from multiple sources), apply a non-steady-state air quality model with chemical transformation capabilities (refer to EPA guidance documents), which yields ambient concentrations of visibility-impairing pollutants. At each Class I receptor:
    - Calculate the change in extinction due to the source being analyzed, compare these changes with the reference conditions, and then compare these results with the thresholds given in section 3.3.3.
    - Utilize estimates of annual average natural visibility conditions for each Class I area as presented in Table 6, unless otherwise recommended by the

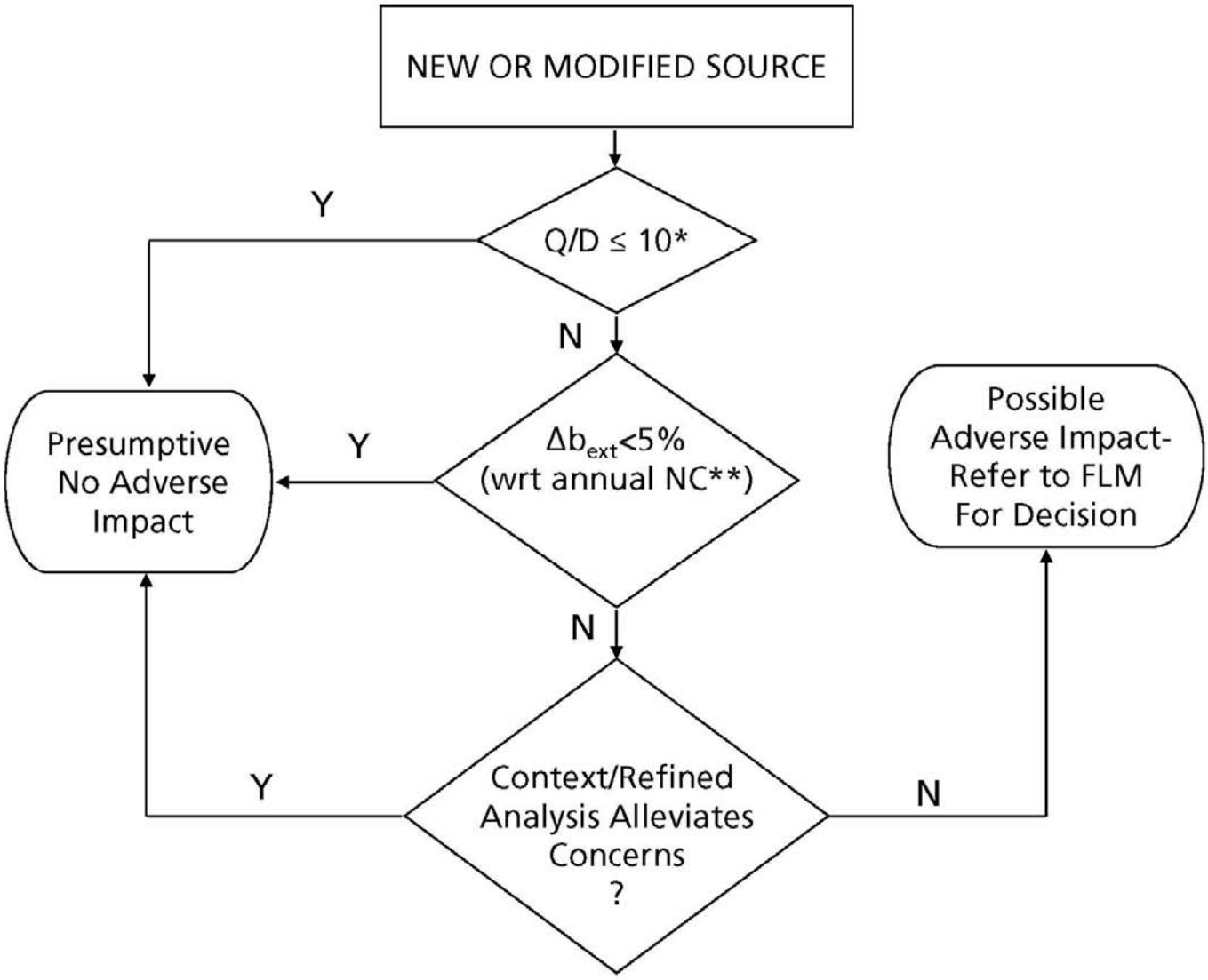

Figure 4. Procedure for Visibility Assessment for Distant/Multi-Source Applications (Revised)
*Q/D test only applies to sources located greater that 50 km from a Class I area.
**Difference Change in the 98th percentile with respect to (wrt) the annual average Natural Condition (NC). Applicant should use the 20th percentile best natural condition background if recommended by the FLM or permitting authority.

FLM or permitting authority. Alternative estimates of visibility conditions are provided in Table 5 for consistency with State agencies that elected to use 20% best visibility for regional haze or BART implementations.

- If first-level modeling results are above levels of concern, continue to consult with the Agencies to discuss other considerations (e.g., possible impact mitigation, more refined analyses).

This review process for distant/multi-source applications is portrayed schematically in Figure 4.

3.3.5. Natural Visibility Conditions and Analysis Methods (New)

Both distant/multi-source applications and near-field analyses require an estimate of natural visibility conditions. The effects of visibility impairing emissions from a source are compared to the natural visibility conditions to determine the potential for unacceptable visibility impacts. The methods and data for calculating natural visibility conditions in FLAG are presented in this section. The calculation of visibility metrics under the distant/multi-source application is also described. For the distant/multi-source application, aerosol species components are provided for input to the CALPUFF modeling system, which is the suggested model

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for most of these applications. For near-field analyses, visual ranges under natural conditions are provided for input to the VISCREEN and PLUVUE-II models.

Natural visibility conditions

Distant/Multi-source: Natural visibility conditions are affected by the light scattering of air molecules (Rayleigh scattering) and by naturally occurring aerosols. The majority of aerosols, both natural and anthropogenic, that affect light extinction can be categorized as sulfates ($(NH_4)_2SO_4$), nitrates (NH_4NO_3), organic mass (OM), elemental carbon (EC), soil, sea salt, and coarse mass (CM). The light scattering efficiency of aerosols is affected by the size of the aerosol relative to the wavelength of light. Sulfates, nitrates, and sea salt are all hygroscopic, which affects their size and their light scattering efficiency as they acquire or shed water molecules. The relationship between the aerosol components and light extinction is shown through the equations in Figure 5. The hygroscopic effects are accounted for through the relative humidity adjustment factors (f(RH)) terms in the equations in Figure 5. The aerosol concentrations and monthly relative humidity adjustment factors for calculating natural visibility conditions are found in Tables 5 through 10.

Table 2. Section of Table 6 Used for Step 1 Calculations of the Alpine Lakes Wilderness Example

Class I Area	$(NH_4)_2SO_4$ µg/m³	NH_4NO_3 µg/m³	OM µg/m³	EC µg/m³	Soil µg/m³	CM µg/m³	Sea Salt µg/m³	Rayleigh Mm^{-1}
Acadia NP	0.23	0.10	1.67	0.02	0.24	2.14	0.14	12
Agua Tibia Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.14	11
Alpine Lakes Wilderness	0.12	0.10	0.60	0.02	0.23	1.30	0.06	11
…	…	…	…	…	…	…	…	…

The aerosol concentrations for the 20% best natural conditions are found in Table 5 and the annual average natural concentrations are found in Table 6.

Near-field: The near-field visibility analysis is generally performed using either VISCREEN or PLUVUE-II. For calculating the effect of a plume on visibility, a background visibility, expressed as a visual range, must be input to these models. Appropriate average natural conditions, by month and Class I area are listed in Table 10. The values in Table 10 were determined by calculating the month by month light extinction values and calculating the visual range (VR) ($VR=3912/b_{ext}$).

Example Calculation of Natural Conditions and Change in Light Extinction

The annual average concentration and the relative humidity adjustment factors ($f_{\{L,S,SS\}}(RH)$) for the Alpine Lakes Wilderness for January will be used for illustration of the calculations.

1. Look up the Alpine Lakes Wilderness annual average concentration values in Table 6 for sulfate ($(NH_4)_2SO_4$), nitrate (NH_4NO_3), organic mass (OM), Elemental Carbon (EC), soil, coarse mass (CM), sea salt, and Rayleigh scattering.
2. Look up the f(RH) factors for large sulfate/nitrate (table 7), small sulfate/nitrate (table 8), and sea salt (table 9); January in this example.
   a. $f_L(RH) = 3.86$
   b. $f_S(RH) = 5.87$
   c. $f_{SS}(RH) = 5.35$
3. Calculate the large and small sulfate, nitrate, and organic mass, as defined in Figure 5.

Table 3. Step 3 Calculation Results for the Alpine Lakes Wilderness Example

	Total	Large	Small
Sulfate	0.12	0.00072	0.11928
Nitrate	0.10	0.0005	0.0995
Organic Mass	0.60	0.018	0.582

4. Apply to b_{ext} equation in Figure 5:

b_{ext}=

$2.2 \times 5.87 \times 0.11928 + 4.8 \times 3.86 \times 0.00072$	{Sulfate}
$+ 2.4 \times 5.87 \times 0.0995 + 5.1 \times 3.86 \times 0.0005$	{Nitrate}
$+ 2.8 \times 0.582 + 6.1 \times 0.018$	{Organic Mass}
$+ 10 \times 0.02$	{Elemental Carbon}
$+ 1 \times 0.23$	{Soil}
$+ 0.6 \times 1.30$	{Coarse Mass}
$+ 1.7 \times 5.35 \times 0.06\}$	{Sea Salt
$+ 11$	{Rayleigh}
$+ 0.33 \times 0$	{NO_2}

b_{ext} $=17.46\ Mm^{-1}$

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To calculate the change in light extinction from the impacts from an air pollution source, the species concentrations from the source are added to the total species concentrations in steps 3 and 4 above and the new total light extinction is calculated. Therefore, if a source contributed 0.05 µg/m^3 of sulfate ($(NH_4)_2SO_4$) and 0.01 µg/m^3 of nitrate (NH_4NO_3) at a receptor, the total, large and small sulfate and nitrate values would be:

Table 4. Step 4 Calculation Results for the Alpine Lakes Wilderness Example

	Total	Large	Small
Sulfate	0.17 (0.12+0.05)	0.001445	0.168555
Nitrate	0.11 (0.10+0.01)	0.000605	0.109395

The other concentrations and the relative humidity adjustment factors would remain as in step 4 of the natural condition example. After recalculating the light extinction accounting for the effect of the source ($b_{ext(source+nat\ cond)}$), the new light extinction would be 18.25 Mm^{-1}.

The change in light extinction (Δb_{ext}) would simply be:

$$\Delta b_{ext} = (b_{ext(source+nat\ cond)} - b_{ext(nat\ cond)}) / b_{ext(nat\ cond)} \text{ or:}$$

$$\Delta b_{ext} = (18.25 - 17.46) / 17.46$$

$$\Delta b_{ext} = 0.045\ (4.5\%)$$

The example provided here is to illustrate the process. Usually the concentrations and relative humidity adjustment factors would be extracted from the appropriate tables and input to one of the air quality model post processing programs.

$$b_{ext} = 2.2 \times f_S(RH) \times [\text{Small Sulfate}] + 4.8 \times f_L(RH) \times [\text{Large Sulfate}]$$
$$+ 2.4 \times f_S(RH) \times [\text{Small Nitrate}] + 5.1 \times f_L(RH) \times [\text{Large Nitrate}]$$
$$+ 2.8 \times [\text{Small Organic Mass}] + 6.1 \times [\text{Large Organic Mass}]$$
$$+ 10 \times [\text{Elemental Carbon}]$$
$$+ 1 \times [\text{Fine Soil}]$$
$$+ 0.6 \times [\text{Coarse Mass}]$$
$$+ 1.7 \times f_{SS}(RH) \times [\text{Sea Salt}]$$
$$+ \text{Rayleigh Scattering (Site Specific)}$$
$$+ 0.33 \times [NO_2 \text{ (ppb)}] \quad \{\text{or as: } 0.1755 \times [NO_2 \text{ (}\mu g/m^3\text{)}]\}$$

Where:

[ ] indicates concentrations in $\mu g/m^3$

$f_S(RH)$ = Relative humidity adjustment factor for small sulfate and nitrate

$f_L(RH)$ = Relative humidity adjustment factor for large sulfate and nitrate

$f_{SS}(RH)$ = Relative humidity adjustment factor for sea salt

For Total Sulfate $< 20\ \mu g/m^3$:

[Large Sulfate] = ([Total Sulfate] / $20\ \mu g/m^3$) × [Total Sulfate]

For Total Sulfate $\geq 20\ \mu g/m^3$:

[Large Sulfate] = [Total Sulfate]

And:

[Small Sulfate] = [Total Sulfate] – [Large Sulfate]

To calculate large and small nitrate and organic mass, substitute ({Large, Small, Total} {Nitrate, Organic Mass}) for Sulfate.

Figure 5. IMPROVE Equation for Calculating Light Extinction
http://vista.cira.colostate.edu/improve/Publications/GrayLit/019_RevisedIMPROVEeq/RevisedIMPROVEAlgorithm3.doc

Table 5. Page Best/Natural Conditions – Concentrations and Rayleigh Scattering By Class I Area

Class I Area	$(NH_4)_2SO_4$ µg/m3	NH_4NO_3 µg/m3	OM µg/m³	EC µg/m³	Soil µg/m³	CM µg/m³	Sea Salt µg/m³	Rayleigh Mm^{-1}	Type
Acadia NP	0.09	0.03	0.68	0.01	0.10	0.94	0.03	12	B20%
Agua Tibia Wilderness	0.03	0.04	0.26	0.01	0.26	1.20	0.04	11	B20%
Alpine Lakes Wilderness	0.04	0.03	0.15	0.01	0.05	0.30	0.02	11	B20%
Anaconda Pintler Wilderness	0.04	0.03	0.12	0.01	0.07	0.31	0.00	10	B20%
Ansel Adams Wilderness	0.02	0.01	0.12	0.01	0.07	0.44	0.01	9	B20%
Arches NP	0.07	0.06	0.23	0.01	0.14	0.89	0.01	9	B20%
Badlands NP	0.05	0.05	0.23	0.01	0.22	0.99	0.00	11	B20%
Bandelier NM	0.07	0.06	0.31	0.01	0.16	0.91	0.00	9	B20%
Bering Sea Wilderness									B20%
Big Bend NP	0.05	0.04	0.24	0.01	0.11	0.80	0.00	10	B20%
Black Canyon of the Gunnison NP	0.06	0.04	0.24	0.01	0.13	0.88	0.00	9	B20%
Bob Marshall Wilderness	0.05	0.04	0.19	0.01	0.08	0.37	0.00	10	B20%
Bosque del Apache Wilderness	0.08	0.06	0.30	0.01	0.15	0.97	0.02	10	B20%
Boundary Waters Canoe Area Wilderness	0.11	0.02	0.50	0.01	0.13	0.86	0.01	11	B20%
Breton Wilderness	0.14	0.05	0.73	0.01	0.27	2.26	0.07	11	B20%
Bridger Wilderness	0.05	0.04	0.14	0.01	0.07	0.33	0.00	9	B20%
Brigantine Wilderness	0.12	0.04	0.86	0.01	0.24	1.73	0.04	12	B20%
Bryce Canyon NP	0.04	0.05	0.18	0.01	0.10	0.60	0.00	9	B20%
Cabinet Mountains Wilderness	0.05	0.05	0.13	0.01	0.09	0.42	0.01	10	B20%
Caney Creek Wilderness	0.07	0.06	0.68	0.01	0.14	1.51	0.02	11	B20%
Canyonlands NP	0.07	0.06	0.23	0.01	0.14	0.89	0.01	9	B20%
Cape Romain Wilderness	0.14	0.06	0.88	0.01	0.24	1.99	0.04	12	B20%
Capitol Reef NP	0.06	0.07	0.26	0.01	0.15	0.79	0.01	9	B20%
Caribou Wilderness	0.03	0.02	0.12	0.01	0.08	0.24	0.01	10	B20%
Carlsbad Caverns NP	0.06	0.05	0.26	0.01	0.12	0.82	0.00	9	B20%
Chassahowitzka Wilderness	0.14	0.08	1.02	0.01	0.28	2.46	0.02	11	B20%
Chiricahua NM	0.06	0.05	0.27	0.01	0.13	0.81	0.00	10	B20%
Chiricahua Wilderness	0.06	0.05	0.27	0.01	0.13	0.81	0.00	10	B20%
Cohutta Wilderness	0.09	0.08	0.69	0.01	0.15	1.06	0.01	11	B20%
Crater Lake NP	0.02	0.02	0.08	0.01	0.07	0.23	0.01	9	B20%
Craters of the Moon NM	0.06	0.05	0.19	0.01	0.12	0.69	0.01	10	B20%
Cucamonga Wilderness	0.03	0.03	0.15	0.01	0.14	0.67	0.01	9	B20%
Denali NP & Pres	0.04	0.02	0.08	0.01	0.05	0.31	0.01	11	B20%
Desolation Wilderness	0.04	0.03	0.15	0.01	0.09	0.51	0.01	9	B20%
Diamond Peak Wilderness	0.02	0.02	0.08	0.01	0.07	0.23	0.01	9	B20%
Dolly Sods Wilderness	0.10	0.05	0.80	0.01	0.17	0.96	0.01	10	B20%
Dome Land Wilderness	0.03	0.02	0.18	0.01	0.08	0.43	0.01	10	B20%
Eagle Cap Wilderness	0.05	0.02	0.17	0.01	0.10	0.50	0.01	10	B20%
Eagles Nest Wilderness	0.04	0.03	0.14	0.01	0.08	0.36	0.00	8	B20%
Emigrant Wilderness	0.03	0.02	0.10	0.00	0.08	0.50	0.01	10	B20%
Everglades NP	0.16	0.07	0.77	0.01	0.16	1.86	0.12	11	B20%
Fitzpatrick Wilderness	0.05	0.04	0.14	0.01	0.07	0.33	0.00	9	B20%
Flat Tops Wilderness	0.04	0.03	0.14	0.01	0.08	0.36	0.00	8	B20%
Galiuro Wilderness	0.06	0.05	0.27	0.01	0.13	0.81	0.00	10	B20%

Table 9. 20% Best Natural Conditions – Concentrations and Rayleigh Scattering By Class I Area

Class I Area	$(NH_4)_2SO_4$ µg/m3	NH_4NO_3 µg/m3	OM µg/m³	EC µg/m³	Soil µg/m³	CM µg/m³	Sea Salt µg/m³	Rayleigh Mm^{-1}	Type
Gates of the Mountains Wilderness	0.04	0.04	0.13	0.01	0.07	0.49	0.00	9	B20%
Gearhart Mountain Wilderness	0.02	0.02	0.08	0.01	0.07	0.23	0.01	9	B20%
Gila Wilderness	0.06	0.04	0.22	0.01	0.09	0.45	0.00	9	B20%
Glacier NP	0.05	0.03	0.17	0.01	0.11	0.57	0.00	11	B20%
Glacier Peak Wilderness	0.02	0.03	0.09	0.00	0.04	0.28	0.01	11	B20%
Goat Rocks Wilderness	0.02	0.01	0.06	0.00	0.04	0.21	0.01	10	B20%
Grand Canyon NP	0.04	0.03	0.12	0.01	0.10	0.59	0.00	9	B20%
Grand Teton NP	0.06	0.05	0.17	0.01	0.08	0.33	0.00	9	B20%
Great Gulf Wilderness	0.09	0.04	0.56	0.01	0.10	1.05	0.02	11	B20%
Great Sand Dunes NP & Pres	0.06	0.05	0.29	0.01	0.15	0.90	0.00	9	B20%
Great Smoky Mountains NP	0.09	0.06	0.78	0.01	0.16	1.47	0.01	11	B20%
Guadalupe Mountains NP	0.06	0.05	0.26	0.01	0.12	0.82	0.00	9	B20%
Haleakala NP	0.05	0.04	0.24	0.01	0.11	1.59	0.13	10	B20%
Hawaii Volcanoes NP	0.03	0.04	0.27	0.01	0.06	0.64	0.11	10	B20%
Hells Canyon Wilderness	0.06	0.02	0.19	0.01	0.14	0.81	0.01	11	B20%
Hercules-Glades Wilderness	0.09	0.06	0.78	0.01	0.16	1.86	0.02	11	B20%
Hoover Wilderness	0.03	0.02	0.08	0.01	0.06	0.55	0.00	9	B20%
Isle Royale NP	0.10	0.02	0.34	0.01	0.09	0.79	0.01	12	B20%
James River Face Wilderness	0.11	0.06	0.71	0.01	0.20	1.39	0.01	11	B20%
Jarbidge Wilderness	0.05	0.03	0.14	0.01	0.05	0.33	0.00	10	B20%
John Muir Wilderness	0.02	0.01	0.12	0.01	0.07	0.44	0.01	9	B20%
Joshua Tree NP	0.04	0.02	0.20	0.01	0.17	0.94	0.02	10	B20%
Joyce Kilmer-Slickrock Wilderness	0.09	0.06	0.78	0.01	0.16	1.47	0.01	11	B20%
Kaiser Wilderness	0.02	0.01	0.12	0.01	0.07	0.44	0.01	9	B20%
Kalmiopsis Wilderness	0.03	0.02	0.31	0.01	0.05	0.99	0.04	12	B20%
Kings Canyon	0.03	0.03	0.18	0.01	0.08	0.73	0.02	11	B20%
La Garita Wilderness	0.06	0.04	0.24	0.01	0.13	0.88	0.00	9	B20%
Lassen Volcanic NP	0.03	0.02	0.12	0.01	0.08	0.24	0.01	10	B20%
Lava Beds NM	0.03	0.03	0.14	0.01	0.06	0.46	0.00	10	B20%
Linville Gorge Wilderness	0.08	0.06	0.67	0.01	0.14	1.04	0.01	11	B20%
Lostwood Wilderness	0.06	0.04	0.23	0.01	0.22	1.05	0.01	11	B20%
Lye Brook Wilderness	0.05	0.03	0.36	0.01	0.09	0.63	0.01	11	B20%
Mammoth Cave NP	0.11	0.08	0.86	0.01	0.24	1.54	0.01	11	B20%
Marble Mountain Wilderness	0.03	0.02	0.12	0.01	0.06	0.36	0.01	10	B20%
Maroon Bells-Snowmass Wilderness	0.04	0.03	0.14	0.01	0.08	0.36	0.00	8	B20%
Mazatzal Wilderness	0.06	0.05	0.30	0.01	0.14	0.80	0.00	10	B20%
Medicine Lake Wilderness	0.06	0.05	0.24	0.01	0.20	1.13	0.00	11	B20%
Mesa Verde NP	0.06	0.05	0.24	0.01	0.17	0.67	0.00	9	B20%
Mingo Wilderness	0.12	0.04	0.88	0.01	0.21	1.49	0.01	12	B20%
Mission Mountains Wilderness	0.05	0.04	0.19	0.01	0.08	0.37	0.00	10	B20%
Mokelumne Wilderness	0.04	0.03	0.15	0.01	0.09	0.51	0.01	9	B20%
Moosehorn Wilderness	0.11	0.04	0.76	0.01	0.12	1.25	0.02	12	B20%
Mount Adams Wilderness	0.02	0.01	0.06	0.00	0.04	0.21	0.01	10	B20%
Mount Baldy Wilderness	0.05	0.04	0.19	0.01	0.11	0.53	0.00	9	B20%
Mount Hood Wilderness	0.02	0.02	0.06	0.00	0.05	0.15	0.01	10	B20%

Table 5. Page Best Natural Conditions – Concentrations and Rayleigh Scattering By Class I Area

Class I Area	$(NH_4)_2SO_4$ µg/m3	NH_4NO_3 µg/m3	OM µg/m³	EC µg/m³	Soil µg/m³	CM µg/m³	Sea Salt µg/m³	Rayleigh Mm^{-1}	Type
Mount Jefferson Wilderness	0.02	0.02	0.08	0.00	0.03	0.31	0.01	11	B20%
Mount Rainier NP	0.03	0.02	0.18	0.01	0.06	0.83	0.02	11	B20%
Mount Washington Wilderness	0.02	0.02	0.08	0.00	0.03	0.31	0.01	11	B20%
Mount Zirkel Wilderness	0.06	0.04	0.16	0.01	0.09	0.60	0.00	8	B20%
Mountain Lakes Wilderness	0.02	0.02	0.08	0.01	0.07	0.23	0.01	9	B20%
North Absaroka Wilderness	0.05	0.04	0.16	0.00	0.11	0.82	0.00	9	B20%
North Cascades NP	0.02	0.03	0.09	0.00	0.04	0.28	0.01	11	B20%
Okefenokee Wilderness	0.13	0.07	0.92	0.01	0.22	1.69	0.03	11	B20%
Olympic NP	0.04	0.03	0.23	0.01	0.03	0.50	0.04	11	B20%
Otter Creek Wilderness	0.10	0.05	0.80	0.01	0.17	0.96	0.01	10	B20%
Pasayten Wilderness	0.04	0.03	0.07	0.00	0.07	0.24	0.01	10	B20%
Pecos Wilderness	0.04	0.03	0.16	0.01	0.08	0.67	0.00	8	B20%
Petrified Forest NP	0.06	0.06	0.28	0.01	0.15	0.75	0.00	9	B20%
Pine Mountain Wilderness	0.06	0.05	0.30	0.01	0.14	0.80	0.00	10	B20%
Pinnacles NM	0.06	0.04	0.31	0.01	0.16	1.50	0.06	11	B20%
Point Reyes NS	0.12	0.04	0.33	0.01	0.13	1.08	0.25	12	B20%
Presidential Range-Dry River Wilderness	0.09	0.04	0.56	0.01	0.10	1.05	0.02	11	B20%
Rawah Wilderness	0.06	0.04	0.16	0.01	0.09	0.60	0.00	8	B20%
Red Rock Lakes Wilderness	0.06	0.05	0.17	0.01	0.08	0.33	0.00	9	B20%
Redwood NP	0.05	0.03	0.28	0.01	0.06	1.02	0.10	11	B20%
Rocky Mountain NP	0.04	0.02	0.15	0.01	0.09	0.68	0.00	9	B20%
Roosevelt Campobello International Park	0.11	0.04	0.76	0.01	0.12	1.25	0.02	12	B20%
Saguaro NP	0.07	0.05	0.32	0.01	0.22	1.15	0.03	10	B20%
Saint Marks Wilderness	0.14	0.06	0.81	0.01	0.24	2.17	0.04	11	B20%
Salt Creek Wilderness	0.05	0.06	0.31	0.01	0.17	1.00	0.02	10	B20%
San Gabriel Wilderness	0.03	0.03	0.15	0.01	0.14	0.67	0.01	9	B20%
San Gorgonio Wilderness	0.03	0.02	0.15	0.01	0.10	0.62	0.02	10	B20%
San Jacinto Wilderness	0.03	0.02	0.15	0.01	0.10	0.62	0.02	10	B20%
San Pedro Parks Wilderness	0.05	0.04	0.14	0.01	0.09	0.34	0.01	8	B20%
San Rafael Wilderness	0.03	0.04	0.22	0.01	0.11	0.79	0.02	10	B20%
Sawtooth Wilderness	0.05	0.04	0.23	0.01	0.10	0.37	0.00	10	B20%
Scapegoat Wilderness	0.05	0.04	0.19	0.01	0.08	0.37	0.00	10	B20%
Selway-Bitterroot Wilderness	0.04	0.03	0.12	0.01	0.07	0.31	0.00	10	B20%
Seney Wilderness	0.08	0.01	0.38	0.01	0.09	0.80	0.01	12	B20%
Sequoia NP	0.03	0.03	0.18	0.01	0.08	0.73	0.02	11	B20%
Shenandoah NP	0.08	0.07	0.56	0.01	0.14	1.20	0.01	10	B20%
Shining Rock Wilderness	0.05	0.05	0.51	0.01	0.13	0.56	0.01	10	B20%
Sierra Ancha Wilderness	0.06	0.05	0.33	0.02	0.14	0.73	0.01	10	B20%
Simeonof Wilderness	0.06	0.05	0.25	0.02	0.04	1.18	0.25	12	B20%
Sipsey Wilderness	0.11	0.10	0.81	0.01	0.25	1.66	0.01	11	B20%
South Warner Wilderness	0.03	0.03	0.14	0.01	0.06	0.46	0.00	10	B20%
Strawberry Mountain Wilderness	0.05	0.02	0.17	0.01	0.10	0.50	0.01	10	B20%
Superstition Wilderness	0.07	0.05	0.31	0.01	0.16	0.84	0.00	10	B20%

Table 9. 20% Best Natural Conditions – Concentrations and Rayleigh Scattering By Class I Area

Class I Area	$(NH_4)_2SO_4$ µg/m3	NH_4NO_3 µg/m3	OM µg/m³	EC µg/m³	Soil µg/m³	CM µg/m³	Sea Salt µg/m³	Rayleigh Mm^{-1}	Type
Swanquarter Wilderness	0.12	0.06	0.65	0.01	0.23	2.38	0.05	12	B20%
Sycamore Canyon Wilderness	0.06	0.05	0.28	0.01	0.12	0.62	0.00	9	B20%
Teton Wilderness	0.06	0.05	0.17	0.01	0.08	0.33	0.00	9	B20%
Theodore Roosevelt NP	0.07	0.04	0.26	0.01	0.21	1.20	0.01	11	B20%
Thousand Lakes Wilderness	0.03	0.02	0.12	0.01	0.08	0.24	0.01	10	B20%
Three Sisters Wilderness	0.02	0.02	0.08	0.00	0.03	0.31	0.01	11	B20%
Tuxedni Wilderness	0.03	0.04	0.09	0.01	0.03	0.52	0.05	12	B20%
UL Bend Wilderness	0.05	0.03	0.18	0.01	0.15	0.93	0.01	11	B20%
Upper Buffalo Wilderness	0.08	0.06	0.68	0.01	0.16	1.33	0.01	11	B20%
Ventana Wilderness	0.06	0.04	0.31	0.01	0.16	1.50	0.06	11	B20%
Virgin Islands NP	0.18	0.07	0.21	0.01	0.12	1.53	0.26	11	B20%
Voyageurs NP	0.12	0.02	0.56	0.01	0.10	0.86	0.01	12	B20%
Washakie Wilderness	0.05	0.04	0.16	0.00	0.11	0.82	0.00	9	B20%
Weminuche Wilderness	0.06	0.04	0.24	0.01	0.13	0.88	0.00	9	B20%
West Elk Wilderness	0.04	0.03	0.14	0.01	0.08	0.36	0.00	8	B20%
Wheeler Peak Wilderness	0.04	0.03	0.16	0.01	0.08	0.67	0.00	8	B20%
White Mountain Wilderness	0.05	0.03	0.24	0.01	0.08	0.67	0.01	9	B20%
Wichita Mountains Wilderness	0.03	0.04	0.28	0.01	0.15	1.52	0.01	11	B20%
Wind Cave NP	0.05	0.04	0.20	0.01	0.19	1.05	0.00	10	B20%
Wolf Island Wilderness	0.13	0.07	0.92	0.01	0.22	1.69	0.03	11	B20%
Yellowstone NP	0.06	0.05	0.17	0.01	0.08	0.33	0.00	9	B20%
Yolla Bolly-Middle Eel Wilderness	0.03	0.02	0.12	0.01	0.06	0.36	0.01	10	B20%
Yosemite NP	0.03	0.02	0.10	0.00	0.08	0.50	0.01	10	B20%
Zion NP	0.05	0.06	0.28	0.01	0.10	0.60	0.01	10	B20%

Table 6. Page 1 Average Natural Conditions - Concentrations and Rayleigh Scattering By Class I Area

Class I Area	$(NH_4)_2SO_4$ µg/m3	NH_4NO_3 µg/m3	OM µg/m³	EC µg/m³	Soil µg/m³	CM µg/m³	Sea Salt µg/m³	Rayleigh Mm^{-1}	Type
Acadia NP	0.23	0.10	1.67	0.02	0.25	2.14	0.14	12	Annual
Agua Tibia Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.14	11	Annual
Alpine Lakes Wilderness	0.12	0.10	0.60	0.02	0.23	1.30	0.06	11	Annual
Anaconda Pintler Wilderness	0.12	0.10	0.60	0.02	0.39	1.79	0.02	10	Annual
Ansel Adams Wilderness	0.12	0.10	0.58	0.02	0.46	2.88	0.03	9	Annual
Arches NP	0.12	0.10	0.60	0.02	0.50	2.92	0.01	9	Annual
Badlands NP	0.12	0.10	0.60	0.02	0.50	3.00	0.01	11	Annual
Bandelier NM	0.12	0.10	0.60	0.02	0.50	2.86	0.02	9	Annual
Bering Sea Wilderness									Annual
Big Bend NP	0.12	0.10	0.60	0.02	0.50	3.00	0.03	10	Annual
Black Canyon of the Gunnison NP	0.12	0.10	0.60	0.02	0.49	2.59	0.01	9	Annual
Bob Marshall Wilderness	0.12	0.10	0.60	0.02	0.44	2.34	0.01	10	Annual
Bosque del Apache Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.04	10	Annual
Boundary Waters Canoe Area Wilderness	0.23	0.10	1.71	0.02	0.31	2.53	0.02	11	Annual
Breton Wilderness	0.23	0.10	1.78	0.02	0.48	3.01	0.19	11	Annual
Bridger Wilderness	0.12	0.10	0.60	0.02	0.44	1.88	0.01	9	Annual
Brigantine Wilderness	0.23	0.10	1.80	0.02	0.47	3.00	0.22	12	Annual
Bryce Canyon NP	0.12	0.10	0.60	0.02	0.50	2.87	0.01	9	Annual
Cabinet Mountains Wilderness	0.12	0.10	0.60	0.02	0.41	2.31	0.02	10	Annual
Caney Creek Wilderness	0.23	0.10	1.80	0.02	0.50	3.00	0.03	11	Annual
Canyonlands NP	0.12	0.10	0.60	0.02	0.50	2.92	0.01	9	Annual
Cape Romain Wilderness	0.23	0.10	1.80	0.02	0.45	3.00	0.20	12	Annual
Capitol Reef NP	0.11	0.10	0.58	0.02	0.50	2.78	0.00	9	Annual
Caribou Wilderness	0.12	0.10	0.60	0.02	0.44	1.82	0.01	10	Annual
Carlsbad Caverns NP	0.12	0.10	0.60	0.02	0.50	3.00	0.02	9	Annual
Chassahowitzka Wilderness	0.23	0.10	1.81	0.02	0.50	3.00	0.08	11	Annual
Chiricahua NM	0.12	0.10	0.60	0.02	0.50	3.00	0.02	10	Annual
Chiricahua Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.02	10	Annual
Cohutta Wilderness	0.23	0.10	1.71	0.02	0.50	2.45	0.02	11	Annual
Crater Lake NP	0.12	0.10	0.60	0.02	0.39	1.67	0.02	9	Annual
Craters of the Moon NM	0.12	0.10	0.60	0.02	0.50	2.92	0.01	10	Annual
Cucamonga Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.04	9	Annual
Denali NP & Pres	0.12	0.05	0.60	0.02	0.14	1.12	0.04	11	Annual
Desolation Wilderness	0.12	0.10	0.60	0.02	0.43	1.92	0.01	9	Annual
Diamond Peak Wilderness	0.12	0.10	0.60	0.02	0.39	1.67	0.02	9	Annual
Dolly Sods Wilderness	0.23	0.10	1.80	0.02	0.43	2.19	0.02	10	Annual
Dome Land Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.03	10	Annual
Eagle Cap Wilderness	0.12	0.10	0.60	0.02	0.50	2.99	0.04	10	Annual
Eagles Nest Wilderness	0.12	0.10	0.60	0.02	0.48	2.12	0.00	8	Annual
Emigrant Wilderness	0.12	0.10	0.60	0.02	0.44	3.00	0.02	10	Annual
Everglades NP	0.23	0.10	1.79	0.02	0.50	3.00	0.31	11	Annual
Fitzpatrick Wilderness	0.12	0.10	0.60	0.02	0.44	1.88	0.01	9	Annual
Flat Tops Wilderness	0.12	0.10	0.60	0.02	0.48	2.12	0.00	8	Annual
Galiuro Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.02	10	Annual

Table 9. Annual Average Natural Conditions - Concentrations and Rayleigh Scattering By Class I Area

Class I Area	$(NH_4)_2SO_4$ µg/m3	NH_4NO_3 µg/m3	OM µg/m³	EC µg/m³	Soil µg/m³	CM µg/m³	Sea Salt µg/m³	Rayleigh Mm^{-1}	Type
Gates of the Mountains Wilderness	0.12	0.10	0.60	0.02	0.35	1.55	0.01	9	Annual
Gearhart Mountain Wilderness	0.12	0.10	0.60	0.02	0.39	1.67	0.02	9	Annual
Gila Wilderness	0.12	0.10	0.60	0.02	0.50	2.54	0.01	9	Annual
Glacier NP	0.11	0.10	0.59	0.02	0.50	3.00	0.01	11	Annual
Glacier Peak Wilderness	0.11	0.10	0.60	0.02	0.19	1.32	0.02	11	Annual
Goat Rocks Wilderness	0.12	0.10	0.60	0.02	0.23	1.23	0.03	10	Annual
Grand Canyon NP	0.12	0.10	0.60	0.02	0.50	2.88	0.02	9	Annual
Grand Teton NP	0.12	0.10	0.60	0.02	0.41	1.92	0.01	9	Annual
Great Gulf Wilderness	0.23	0.10	1.70	0.02	0.25	2.65	0.03	11	Annual
Great Sand Dunes NP & Pres	0.12	0.10	0.60	0.02	0.50	2.99	0.01	9	Annual
Great Smoky Mountains NP	0.23	0.10	1.80	0.02	0.48	2.92	0.02	11	Annual
Guadalupe Mountains NP	0.12	0.10	0.60	0.02	0.50	3.00	0.02	9	Annual
Haleakala NP	0.12	0.10	0.57	0.02	0.23	2.93	0.25	10	Annual
Hawaii Volcanoes NP	0.12	0.10	0.45	0.02	0.16	1.42	0.29	10	Annual
Hells Canyon Wilderness	0.12	0.10	0.60	0.02	0.48	2.97	0.01	11	Annual
Hercules-Glades Wilderness	0.23	0.10	1.80	0.02	0.50	3.00	0.02	11	Annual
Hoover Wilderness	0.12	0.10	0.60	0.02	0.50	2.97	0.01	9	Annual
Isle Royale NP	0.23	0.10	1.55	0.02	0.24	2.89	0.03	12	Annual
James River Face Wilderness	0.23	0.10	1.80	0.02	0.48	3.00	0.02	11	Annual
Jarbidge Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.02	10	Annual
John Muir Wilderness	0.12	0.10	0.58	0.02	0.46	2.88	0.03	9	Annual
Joshua Tree NP	0.12	0.10	0.60	0.02	0.50	3.00	0.03	10	Annual
Joyce Kilmer-Slickrock Wilderness	0.23	0.10	1.80	0.02	0.48	2.92	0.02	11	Annual
Kaiser Wilderness	0.12	0.10	0.58	0.02	0.46	2.88	0.03	9	Annual
Kalmiopsis Wilderness	0.12	0.10	0.60	0.02	0.20	2.24	0.23	12	Annual
Kings Canyon	0.11	0.10	0.60	0.02	0.50	3.00	0.04	11	Annual
La Garita Wilderness	0.12	0.10	0.60	0.02	0.49	2.59	0.01	9	Annual
Lassen Volcanic NP	0.12	0.10	0.60	0.02	0.44	1.82	0.01	10	Annual
Lava Beds NM	0.12	0.10	0.60	0.02	0.44	2.36	0.01	10	Annual
Linville Gorge Wilderness	0.23	0.10	1.80	0.02	0.45	2.60	0.02	11	Annual
Lostwood Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.03	11	Annual
Lye Brook Wilderness	0.23	0.10	1.59	0.02	0.28	1.79	0.02	11	Annual
Mammoth Cave NP	0.23	0.10	1.80	0.02	0.50	2.73	0.02	11	Annual
Marble Mountain Wilderness	0.12	0.10	0.52	0.02	0.42	2.08	0.04	10	Annual
Maroon Bells-Snowmass Wilderness	0.12	0.10	0.60	0.02	0.48	2.12	0.00	8	Annual
Mazatzal Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.02	10	Annual
Medicine Lake Wilderness	0.12	0.10	0.60	0.02	0.48	3.00	0.01	11	Annual
Mesa Verde NP	0.12	0.10	0.60	0.02	0.50	2.88	0.00	9	Annual
Mingo Wilderness	0.23	0.10	1.83	0.02	0.51	3.05	0.04	12	Annual
Mission Mountains Wilderness	0.12	0.10	0.60	0.02	0.44	2.34	0.01	10	Annual
Mokelumne Wilderness	0.12	0.10	0.60	0.02	0.43	1.92	0.01	9	Annual
Moosehorn Wilderness	0.23	0.10	1.79	0.02	0.23	2.56	0.11	12	Annual
Mount Adams Wilderness	0.12	0.10	0.60	0.02	0.23	1.23	0.03	10	Annual

Table 6. Annual Average Natural Conditions - Concentrations and Rayleigh Scattering By Class I Area

Class I Area	$(NH_4)_2SO_4$ µg/m3	NH_4NO_3 µg/m3	OM µg/m³	EC µg/m³	Soil µg/m³	CM µg/m³	Sea Salt µg/m³	Rayleigh Mm^{-1}	Type
Mount Baldy Wilderness	0.12	0.10	0.57	0.02	0.50	2.82	0.01	9	Annual
Mount Hood Wilderness	0.12	0.10	0.60	0.02	0.29	1.58	0.05	10	Annual
Mount Jefferson Wilderness	0.12	0.10	0.60	0.02	0.26	1.98	0.05	11	Annual
Mount Rainier NP	0.12	0.10	0.60	0.02	0.24	2.27	0.07	11	Annual
Mount Washington Wilderness	0.12	0.10	0.60	0.02	0.26	1.98	0.05	11	Annual
Mount Zirkel Wilderness	0.12	0.10	0.60	0.02	0.45	2.69	0.00	8	Annual
Mountain Lakes Wilderness	0.12	0.10	0.60	0.02	0.39	1.67	0.02	9	Annual
North Absaroka Wilderness	0.12	0.10	0.60	0.02	0.43	2.84	0.01	9	Annual
North Cascades NP	0.11	0.10	0.60	0.02	0.19	1.32	0.02	11	Annual
Okefenokee Wilderness	0.23	0.10	1.80	0.02	0.50	3.00	0.08	11	Annual
Olympic NP	0.12	0.10	0.60	0.02	0.15	1.88	0.14	11	Annual
Otter Creek Wilderness	0.23	0.10	1.80	0.02	0.43	2.19	0.02	10	Annual
Pasayten Wilderness	0.12	0.10	0.60	0.02	0.33	1.50	0.01	10	Annual
Pecos Wilderness	0.12	0.10	0.60	0.02	0.50	2.29	0.03	8	Annual
Petrified Forest NP	0.12	0.10	0.60	0.02	0.50	3.00	0.01	9	Annual
Pine Mountain Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.02	10	Annual
Pinnacles NM	0.12	0.10	0.60	0.02	0.35	3.00	0.19	11	Annual
Point Reyes NS	0.12	0.10	0.60	0.02	0.24	3.00	2.11	12	Annual
Presidential Range-Dry River Wilderness	0.23	0.10	1.70	0.02	0.25	2.65	0.03	11	Annual
Rawah Wilderness	0.12	0.10	0.60	0.02	0.45	2.69	0.00	8	Annual
Red Rock Lakes Wilderness	0.12	0.10	0.60	0.02	0.41	1.92	0.01	9	Annual
Redwood NP	0.12	0.10	0.60	0.02	0.16	3.00	0.96	11	Annual
Rocky Mountain NP	0.12	0.10	0.60	0.02	0.50	2.90	0.00	9	Annual
Roosevelt Campobello International Park	0.23	0.10	1.79	0.02	0.23	2.56	0.11	12	Annual
Saguaro NP	0.12	0.10	0.60	0.02	0.50	3.00	0.06	10	Annual
Saint Marks Wilderness	0.23	0.10	1.80	0.02	0.50	3.00	0.10	11	Annual
Salt Creek Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.04	10	Annual
San Gabriel Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.04	9	Annual
San Gorgonio Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.05	10	Annual
San Jacinto Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.05	10	Annual
San Pedro Parks Wilderness	0.12	0.10	0.60	0.02	0.50	2.19	0.01	8	Annual
San Rafael Wilderness	0.11	0.10	0.60	0.02	0.50	3.00	0.11	10	Annual
Sawtooth Wilderness	0.12	0.08	0.60	0.02	0.41	1.64	0.01	10	Annual
Scapegoat Wilderness	0.12	0.10	0.60	0.02	0.44	2.34	0.01	10	Annual
Selway-Bitterroot Wilderness	0.12	0.10	0.60	0.02	0.39	1.79	0.02	10	Annual
Seney Wilderness	0.23	0.10	1.74	0.02	0.26	1.95	0.02	12	Annual
Sequoia NP	0.11	0.10	0.60	0.02	0.50	3.00	0.04	11	Annual
Shenandoah NP	0.23	0.10	1.80	0.02	0.41	2.88	0.02	10	Annual
Shining Rock Wilderness	0.23	0.10	1.76	0.02	0.50	1.76	0.02	10	Annual
Sierra Ancha Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.02	10	Annual
Simeonof Wilderness	0.12	0.10	0.46	0.02	0.13	3.00	1.26	12	Annual
Sipsey Wilderness	0.23	0.10	1.80	0.02	0.50	3.00	0.04	11	Annual
South Warner Wilderness	0.12	0.10	0.60	0.02	0.44	2.36	0.01	10	Annual

Table 9. Annual Average Natural Conditions - Concentrations and Rayleigh Scattering By Class I Area

Class I Area	$(NH_4)_2SO_4$ µg/m3	NH_4NO_3 µg/m3	OM µg/m³	EC µg/m³	Soil µg/m³	CM µg/m³	Sea Salt µg/m³	Rayleigh Mm^{-1}	Type
Strawberry Mountain Wilderness	0.12	0.10	0.60	0.02	0.50	2.99	0.04	10	Annual
Superstition Wilderness	0.11	0.10	0.59	0.02	0.50	3.00	0.02	10	Annual
Swanquarter Wilderness	0.23	0.10	1.63	0.02	0.41	3.00	0.14	12	Annual
Sycamore Canyon Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.03	9	Annual
Teton Wilderness	0.12	0.10	0.60	0.02	0.41	1.92	0.01	9	Annual
Theodore Roosevelt NP	0.12	0.10	0.60	0.02	0.50	3.00	0.01	11	Annual
Thousand Lakes Wilderness	0.12	0.10	0.60	0.02	0.44	1.82	0.01	10	Annual
Three Sisters Wilderness	0.12	0.10	0.60	0.02	0.26	1.98	0.05	11	Annual
Tuxedni Wilderness	0.12	0.09	0.60	0.02	0.10	2.06	0.38	12	Annual
UL Bend Wilderness	0.12	0.10	0.60	0.02	0.45	3.00	0.00	11	Annual
Upper Buffalo Wilderness	0.23	0.10	1.80	0.02	0.50	3.00	0.03	11	Annual
Ventana Wilderness	0.12	0.10	0.60	0.02	0.35	3.00	0.19	11	Annual
Virgin Islands NP	0.23	0.10	0.35	0.02	0.50	3.00	0.84	11	Annual
Voyageurs NP	0.23	0.10	1.75	0.02	0.26	2.73	0.04	12	Annual
Washakie Wilderness	0.12	0.10	0.60	0.02	0.43	2.84	0.01	9	Annual
Weminuche Wilderness	0.12	0.10	0.60	0.02	0.49	2.59	0.01	9	Annual
West Elk Wilderness	0.12	0.10	0.60	0.02	0.48	2.12	0.00	8	Annual
Wheeler Peak Wilderness	0.12	0.10	0.60	0.02	0.50	2.29	0.03	8	Annual
White Mountain Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.03	9	Annual
Wichita Mountains Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.03	11	Annual
Wind Cave NP	0.12	0.10	0.60	0.02	0.49	2.98	0.01	10	Annual
Wolf Island Wilderness	0.23	0.10	1.80	0.02	0.50	3.00	0.08	11	Annual
Yellowstone NP	0.12	0.10	0.60	0.02	0.41	1.92	0.01	9	Annual
Yolla Bolly-Middle Eel Wilderness	0.12	0.10	0.52	0.02	0.42	2.08	0.04	10	Annual
Yosemite NP	0.12	0.10	0.60	0.02	0.44	3.00	0.02	10	Annual
Zion NP	0.12	0.10	0.60	0.02	0.50	3.00	0.01	10	Annual

Table 7. Monthly $f_L(RH)$ - Large $(NH_4)_2SO_4$ and NH_4NO_3 Relative Humidity Adjustment Factor

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Acadia NP	2.74	2.46	2.45	2.66	2.67	2.73	2.99	3.03	3.16	2.91	2.89	2.96
Agua Tibia Wilderness	2.10	2.08	2.11	1.98	1.98	1.93	1.93	2.01	2.02	1.99	1.87	1.95
Alpine Lakes Wilderness	3.86	3.58	3.04	2.92	2.99	2.58	2.62	2.67	2.97	3.60	4.00	3.99
Anaconda Pintler Wilderness	2.75	2.46	2.24	2.08	2.06	2.01	1.76	1.72	1.88	2.22	2.66	2.74
Ansel Adams Wilderness	2.56	2.34	2.20	1.88	1.79	1.59	1.52	1.52	1.59	1.70	2.01	2.34
Arches NP	2.28	2.12	1.73	1.57	1.50	1.28	1.34	1.47	1.51	1.56	1.90	2.13
Badlands NP	2.31	2.31	2.31	2.21	2.34	2.25	2.08	2.05	2.02	2.05	2.38	2.33
Bandelier NM	2.10	1.90	1.72	1.51	1.53	1.38	1.63	1.87	1.80	1.59	1.87	2.04
Bering Sea Wilderness	3.02	3.17	3.20	3.19	3.23	3.34	3.78	4.16	3.64	3.19	3.12	3.13
Big Bend NP	1.72	1.61	1.44	1.38	1.47	1.48	1.58	1.74	1.83	1.63	1.63	1.70
Black Canyon of the Gunnison NP	2.15	2.05	1.83	1.75	1.74	1.51	1.59	1.78	1.80	1.68	1.96	2.06
Bob Marshall Wilderness	2.82	2.54	2.35	2.22	2.21	2.19	1.98	1.92	2.15	2.43	2.78	2.81
Bosque del Apache Wilderness	2.03	1.82	1.55	1.37	1.36	1.27	1.61	1.79	1.73	1.54	1.73	2.00
Boundary Waters Canoe Area Wilderness	2.50	2.25	2.28	2.09	2.20	2.43	2.57	2.71	2.78	2.38	2.64	2.64
Breton Wilderness	2.91	2.76	2.74	2.72	2.83	2.94	3.10	3.07	2.97	2.82	2.83	2.90
Bridger Wilderness	2.22	2.10	2.04	1.95	1.95	1.67	1.46	1.44	1.68	1.83	2.19	2.16
Brigantine Wilderness	2.49	2.32	2.38	2.28	2.50	2.56	2.69	2.81	2.82	2.71	2.45	2.50
Bryce Canyon NP	2.31	2.16	1.82	1.56	1.47	1.26	1.30	1.46	1.46	1.55	1.87	2.15
Cabinet Mountains Wilderness	3.07	2.73	2.45	2.26	2.24	2.21	1.98	1.92	2.19	2.53	3.03	3.11
Caney Creek Wilderness	2.77	2.53	2.37	2.43	2.68	2.71	2.59	2.60	2.71	2.69	2.67	2.79
Canyonlands NP	2.32	2.16	1.78	1.58	1.51	1.28	1.36	1.53	1.55	1.58	1.93	2.17
Cape Romain Wilderness	2.66	2.47	2.42	2.32	2.56	2.80	2.82	3.04	3.03	2.86	2.65	2.70
Capitol Reef NP	2.36	2.22	1.84	1.63	1.54	1.31	1.36	1.52	1.55	1.61	1.95	2.22
Caribou Wilderness	2.96	2.58	2.35	2.10	2.01	1.85	1.79	1.82	1.88	2.03	2.50	2.82
Carlsbad Caverns NP	2.07	1.81	1.50	1.42	1.51	1.48	1.72	1.90	2.03	1.64	1.76	2.00
Chassahowitzka Wilderness	3.03	2.82	2.74	2.65	2.63	3.00	3.02	3.15	3.14	3.03	2.97	3.09
Chiricahua NM	1.87	1.79	1.52	1.24	1.22	1.13	1.64	1.87	1.66	1.45	1.55	1.89
Chiricahua Wilderness	1.84	1.76	1.49	1.22	1.20	1.12	1.64	1.86	1.64	1.43	1.53	1.87
Cohutta Wilderness	2.84	2.61	2.49	2.36	2.72	2.97	3.00	3.07	3.08	2.89	2.72	2.85
Crater Lake NP	3.71	3.25	3.07	2.91	2.70	2.50	2.31	2.33	2.49	2.99	3.67	3.74
Craters of the Moon NM	2.58	2.34	2.03	1.84	1.83	1.65	1.40	1.39	1.52	1.80	2.35	2.54
Cucamonga Wilderness	2.21	2.14	2.13	1.96	1.95	1.90	1.91	1.96	1.98	1.96	1.90	2.02
Denali NP & Pres	2.48	2.44	2.15	1.96	1.98	2.13	2.47	2.90	2.95	2.84	2.69	2.68
Desolation Wilderness	2.73	2.42	2.18	1.84	1.74	1.56	1.47	1.49	1.58	1.73	2.12	2.54
Diamond Peak Wilderness	3.82	3.38	3.18	3.04	2.79	2.60	2.33	2.35	2.58	3.18	3.80	3.86
Dolly Sods Wilderness	2.53	2.39	2.38	2.20	2.63	2.65	2.74	2.90	2.94	2.65	2.45	2.61
Dome Land Wilderness	2.26	2.07	2.00	1.79	1.73	1.63	1.61	1.64	1.68	1.71	1.81	2.01
Eagle Cap Wilderness	3.44	3.02	2.54	2.31	2.28	2.01	1.78	1.75	1.97	2.61	3.34	3.56
Eagles Nest Wilderness	2.02	2.01	1.87	1.87	1.92	1.69	1.68	1.83	1.86	1.73	1.96	1.97
Emigrant Wilderness	2.67	2.42	2.26	1.92	1.81	1.59	1.49	1.50	1.58	1.72	2.08	2.45
Everglades NP	2.43	2.31	2.26	2.16	2.15	2.38	2.32	2.49	2.55	2.42	2.34	2.39
Fitzpatrick Wilderness	2.22	2.10	2.04	1.95	1.94	1.68	1.47	1.44	1.68	1.83	2.18	2.16
Flat Tops Wilderness	2.09	2.04	1.87	1.84	1.86	1.62	1.59	1.70	1.79	1.72	1.97	2.03
Galiuro Wilderness	1.80	1.67	1.47	1.21	1.18	1.10	1.43	1.66	1.53	1.42	1.57	1.87
Gates of the Mountains Wilderness	2.46	2.25	2.15	2.05	2.02	2.00	1.81	1.77	1.91	2.15	2.37	2.41

Table 3. Monthly $f_L(RH)$ – Large $(NH_4)_2SO_4$ and NH_4NO_3 Relative Humidity Adjustment Factor

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Gearhart Mountain Wilderness	3.30	2.89	2.62	2.45	2.29	2.13	1.88	1.90	2.03	2.47	3.09	3.27
Gila Wilderness	1.93	1.78	1.52	1.31	1.28	1.23	1.72	1.76	1.68	1.50	1.67	1.96
Glacier NP	3.21	2.84	2.69	2.55	2.58	2.56	2.24	2.22	2.57	2.81	3.08	3.13
Glacier Peak Wilderness	3.69	3.39	2.97	2.85	2.79	2.54	2.49	2.59	2.91	3.45	3.83	3.84
Goat Rocks Wilderness	3.83	3.44	3.10	2.97	2.82	2.60	2.48	2.55	2.88	3.49	3.91	3.98
Grand Canyon NP	2.13	2.01	1.74	1.46	1.36	1.19	1.29	1.49	1.47	1.50	1.75	1.98
Grand Teton NP	2.27	2.14	2.01	1.91	1.90	1.68	1.48	1.44	1.64	1.84	2.16	2.24
Great Gulf Wilderness	2.51	2.32	2.36	2.41	2.45	2.55	2.72	2.87	2.98	2.80	2.67	2.60
Great Sand Dunes NP & Pres	2.11	2.04	1.85	1.77	1.80	1.62	1.70	1.97	1.92	1.72	2.04	2.09
Great Smoky Mountains NP	2.85	2.57	2.51	2.35	2.72	2.98	2.98	3.08	3.10	2.87	2.71	2.85
Guadalupe Mountains NP	2.14	1.82	1.49	1.38	1.48	1.47	1.78	1.98	2.10	1.60	1.78	2.08
Haleakala NP	2.34	2.27	2.25	2.20	2.13	2.09	2.16	2.14	2.10	2.19	2.33	2.30
Hawaii Volcanoes NP	2.56	2.45	2.47	2.47	2.47	2.45	2.53	2.59	2.55	2.57	2.78	2.55
Hells Canyon Wilderness	3.05	2.65	2.22	1.97	1.91	1.81	1.55	1.52	1.68	2.15	2.90	3.15
Hercules-Glades Wilderness	2.70	2.48	2.30	2.30	2.57	2.59	2.56	2.60	2.69	2.54	2.57	2.72
Hoover Wilderness	2.63	2.38	2.21	1.88	1.77	1.56	1.46	1.47	1.55	1.69	2.05	2.42
Isle Royale NP	2.53	2.21	2.26	2.07	1.99	2.32	2.65	2.69	2.82	2.28	2.76	2.74
James River Face Wilderness	2.44	2.30	2.29	2.12	2.47	2.58	2.65	2.78	2.82	2.57	2.36	2.51
Jarbidge Wilderness	2.51	2.28	1.90	1.92	1.97	1.82	1.51	1.37	1.34	1.56	2.14	2.42
John Muir Wilderness	2.51	2.29	2.20	1.95	1.86	1.65	1.60	1.61	1.69	1.78	2.03	2.28
Joshua Tree NP	2.06	1.99	1.97	1.82	1.81	1.74	1.68	1.82	1.83	1.81	1.75	1.87
Joyce Kilmer-Slickrock Wilderness	2.86	2.58	2.51	2.36	2.71	2.97	2.98	3.06	3.08	2.87	2.72	2.85
Kaiser Wilderness	2.58	2.35	2.22	1.90	1.80	1.62	1.56	1.57	1.64	1.75	2.03	2.36
Kalmiopsis Wilderness	3.57	3.17	3.03	2.88	2.75	2.60	2.52	2.53	2.60	2.92	3.51	3.55
Kings Canyon	2.47	2.26	2.18	1.94	1.85	1.65	1.59	1.60	1.68	1.77	2.01	2.24
La Garita Wilderness	2.14	2.03	1.81	1.70	1.69	1.49	1.63	1.87	1.83	1.67	1.98	2.08
Lassen Volcanic NP	2.99	2.61	2.38	2.13	2.03	1.86	1.81	1.84	1.90	2.06	2.54	2.86
Lava Beds NM	3.31	2.88	2.64	2.44	2.29	2.13	1.98	1.99	2.10	2.43	3.03	3.26
Linville Gorge Wilderness	2.71	2.54	2.48	2.31	2.70	2.96	3.00	3.20	3.19	2.84	2.62	2.74
Lostwood Wilderness	2.51	2.45	2.54	2.06	2.03	2.21	2.23	2.05	2.02	2.13	2.69	2.67
Lye Brook Wilderness	2.46	2.30	2.34	2.31	2.42	2.47	2.60	2.76	2.84	2.70	2.54	2.51
Mammoth Cave NP	2.79	2.57	2.47	2.56	3.29	3.76	3.67	2.92	2.95	2.71	2.61	2.82
Marble Mountain Wilderness	3.48	3.08	2.95	2.78	2.67	2.53	2.50	2.52	2.55	2.78	3.32	3.42
Maroon Bells-Snowmass Wilderness	2.02	1.99	1.84	1.84	1.83	1.59	1.69	1.90	1.89	1.71	1.94	1.96
Mazatzal Wilderness	1.91	1.80	1.59	1.32	1.25	1.13	1.38	1.61	1.51	1.45	1.63	1.89
Medicine Lake Wilderness	2.53	2.46	2.46	2.02	2.00	2.13	2.12	1.95	1.98	2.10	2.63	2.65
Mesa Verde NP	2.45	2.25	1.98	1.57	1.61	1.31	1.62	1.87	1.75	1.66	2.01	2.30
Mingo Wilderness	2.73	2.52	2.34	2.28	2.53	2.60	2.64	2.67	2.71	2.56	2.56	2.73
Mission Mountains Wilderness	2.93	2.62	2.37	2.20	2.21	2.19	1.98	1.92	2.15	2.46	2.91	2.96
Mokelumne Wilderness	2.72	2.42	2.20	1.86	1.75	1.57	1.48	1.50	1.58	1.73	2.11	2.52
Moosehorn Wilderness	2.65	2.39	2.38	2.52	2.49	2.57	2.83	2.95	3.07	2.83	2.77	2.78
Mount Adams Wilderness	3.78	3.40	3.10	2.98	2.78	2.60	2.43	2.52	2.84	3.45	3.87	3.92
Mount Baldy Wilderness	2.00	1.86	1.62	1.34	1.29	1.18	1.50	1.73	1.60	1.51	1.73	2.01
Mount Hood Wilderness	3.71	3.33	3.08	2.96	2.74	2.55	2.34	2.42	2.72	3.35	3.81	3.84
Mount Jefferson Wilderness	3.89	3.48	3.27	3.16	2.89	2.66	2.35	2.35	2.63	3.34	3.92	3.95

Table 7. Hygroscopic ($f(RH)$) Large $(NH_4)_2SO_4$ and NH_4NO_3 Relative Humidity Adjustment Factor

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Mount Rainier NP	3.93	3.54	3.23	3.12	2.96	2.75	2.61	2.69	3.04	3.66	4.04	4.07
Mount Washington Wilderness	4.09	3.63	3.49	3.41	3.06	2.80	2.37	2.34	2.62	3.41	4.07	4.10
Mount Zirkel Wilderness	2.00	1.99	1.89	1.92	1.98	1.72	1.63	1.70	1.81	1.75	1.97	1.95
Mountain Lakes Wilderness	3.51	3.03	2.80	2.62	2.44	2.25	2.08	2.09	2.23	2.65	3.37	3.52
North Absaroka Wilderness	2.16	2.05	2.01	1.95	1.94	1.77	1.58	1.50	1.67	1.87	2.12	2.14
North Cascades NP	3.60	3.32	2.99	2.88	2.74	2.59	2.49	2.63	2.97	3.43	3.77	3.76
Okefenokee Wilderness	2.94	2.73	2.73	2.65	2.74	3.11	3.00	3.17	3.16	3.05	2.96	3.03
Olympic NP	3.80	3.50	3.30	3.21	2.76	2.89	2.61	2.94	3.23	3.73	3.99	3.95
Otter Creek Wilderness	2.55	2.41	2.40	2.23	2.64	2.69	2.80	2.96	3.00	2.69	2.48	2.63
Pasayten Wilderness	3.65	3.34	2.97	2.84	2.72	2.53	2.45	2.56	2.88	3.39	3.78	3.81
Pecos Wilderness	2.09	1.93	1.73	1.57	1.58	1.44	1.65	1.90	1.84	1.63	1.90	2.05
Petrified Forest NP	2.11	1.95	1.64	1.40	1.32	1.18	1.46	1.72	1.58	1.53	1.81	2.09
Pine Mountain Wilderness	1.96	1.86	1.64	1.35	1.28	1.15	1.38	1.62	1.53	1.48	1.66	1.93
Pinnacles NM	2.84	2.86	2.87	2.27	2.15	1.99	1.91	1.97	1.98	2.10	2.16	2.46
Point Reyes NS	2.96	2.73	2.61	2.28	2.20	2.04	2.12	2.16	2.18	2.23	2.47	2.75
Presidential Range-Dry River Wilderness	2.52	2.32	2.37	2.42	2.49	2.61	2.78	2.93	3.03	2.83	2.68	2.59
Rawah Wilderness	1.91	1.96	1.89	1.96	2.04	1.79	1.71	1.78	1.86	1.75	1.94	1.90
Red Rock Lakes Wilderness	2.39	2.20	2.06	1.95	1.92	1.80	1.60	1.54	1.69	1.93	2.30	2.37
Redwood NP	3.31	3.10	3.16	3.04	3.11	3.08	3.26	3.28	3.11	2.99	3.20	3.12
Rocky Mountain NP	1.77	1.85	1.84	1.95	2.04	1.80	1.73	1.77	1.84	1.70	1.84	1.76
Roosevelt Campobello International Park	2.66	2.39	2.38	2.53	2.49	2.57	2.82	2.93	3.05	2.83	2.78	2.79
Saguaro NP	1.69	1.56	1.40	1.13	1.12	1.05	1.37	1.62	1.47	1.38	1.50	1.83
Saint Marks Wilderness	2.98	2.78	2.73	2.69	2.74	3.04	3.17	3.21	3.10	2.96	2.94	3.06
Salt Creek Wilderness	2.01	1.79	1.51	1.45	1.55	1.48	1.64	1.80	1.91	1.64	1.72	1.91
San Gabriel Wilderness	2.25	2.17	2.14	1.96	1.95	1.90	1.91	1.95	1.98	1.97	1.91	2.04
San Gorgonio Wilderness	2.21	2.23	2.13	1.90	1.90	1.69	1.62	1.71	1.72	1.70	1.73	1.92
San Jacinto Wilderness	2.12	2.09	2.06	1.90	1.90	1.81	1.71	1.88	1.89	1.87	1.80	1.92
San Pedro Parks Wilderness	2.14	1.97	1.73	1.55	1.53	1.38	1.59	1.83	1.77	1.61	1.91	2.08
San Rafael Wilderness	2.50	2.37	2.34	2.12	2.10	2.05	2.10	2.15	2.20	2.15	2.07	2.25
Sawtooth Wilderness	2.79	2.44	2.05	1.83	1.80	1.66	1.37	1.35	1.43	1.77	2.47	2.75
Scapegoat Wilderness	2.74	2.47	2.30	2.18	2.16	2.14	1.93	1.87	2.07	2.35	2.70	2.72
Selway-Bitterroot Wilderness	2.90	2.57	2.26	2.05	2.03	1.95	1.67	1.63	1.81	2.19	2.76	2.91
Seney Wilderness	2.75	2.42	2.49	2.35	2.30	2.55	2.75	3.01	3.03	2.78	2.88	2.85
Sequoia NP	2.40	2.22	2.21	2.05	1.95	1.67	1.60	1.59	1.69	1.78	2.04	2.17
Shenandoah NP	2.44	2.28	2.29	2.12	2.45	2.56	2.65	2.79	2.81	2.53	2.34	2.55
Shining Rock Wilderness	2.78	2.56	2.48	2.33	2.72	2.98	3.02	3.17	3.18	2.91	2.68	2.79
Sierra Ancha Wilderness	1.92	1.81	1.59	1.32	1.25	1.13	1.42	1.65	1.54	1.47	1.66	1.93
Simeonof Wilderness	3.39	3.40	3.15	3.26	3.40	3.69	4.00	4.14	3.61	3.09	3.21	3.44
Sipsey Wilderness	2.79	2.58	2.42	2.36	2.64	2.86	2.94	2.92	2.93	2.78	2.64	2.80
South Warner Wilderness	3.06	2.67	2.39	2.16	2.05	1.90	1.68	1.69	1.79	2.11	2.67	2.97
Strawberry Mountain Wilderness	3.55	3.10	2.69	2.47	2.37	2.10	1.82	1.81	2.05	2.73	3.45	3.65
Superstition Wilderness	1.84	1.72	1.53	1.26	1.20	1.11	1.36	1.56	1.46	1.40	1.58	1.85
Swanquarter Wilderness	2.48	2.35	2.31	2.18	2.38	2.55	2.67	2.72	2.64	2.55	2.40	2.49
Sycamore Canyon Wilderness	2.01	1.93	1.70	1.40	1.33	1.17	1.38	1.67	1.58	1.52	1.70	1.97
Teton Wilderness	2.22	2.09	2.01	1.92	1.91	1.72	1.52	1.47	1.65	1.86	2.15	2.19

Table 9. Monthly $f_L(RH)$ – Large $(NH_4)_2SO_4$ and NH_4NO_3 Relative Humidity Adjustment Factor

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Theodore Roosevelt NP	2.47	2.42	2.45	2.12	2.14	2.21	2.14	1.99	1.99	2.10	2.58	2.57
Thousand Lakes Wilderness	3.04	2.63	2.42	2.17	2.06	1.88	1.82	1.85	1.91	2.08	2.61	2.91
Three Sisters Wilderness	4.03	3.59	3.43	3.34	3.02	2.78	2.40	2.38	2.65	3.39	4.02	4.04
Tuxedni Wilderness	2.97	2.83	2.47	2.40	2.38	2.50	2.96	3.19	3.18	2.91	2.91	3.03
UL Bend Wilderness	2.33	2.20	2.19	2.03	1.96	1.95	1.80	1.66	1.76	2.00	2.31	2.32
Upper Buffalo Wilderness	2.71	2.48	2.31	2.33	2.61	2.64	2.57	2.59	2.71	2.58	2.59	2.72
Ventana Wilderness	2.80	2.67	2.63	2.20	2.10	1.96	1.97	2.01	2.05	2.11	2.21	2.51
Virgin Islands NP	2.04	2.00	1.94	2.03	2.06	2.04	2.05	2.14	2.14	2.18	2.20	2.12
Voyageurs NP	2.46	2.22	2.22	2.07	2.09	2.46	2.46	2.59	2.70	2.35	2.58	2.55
Washakie Wilderness	2.16	2.05	2.01	1.94	1.93	1.74	1.54	1.48	1.66	1.86	2.12	2.14
Weminuche Wilderness	2.19	2.05	1.81	1.65	1.64	1.44	1.60	1.85	1.79	1.65	1.97	2.11
West Elk Wilderness	2.11	2.04	1.84	1.77	1.77	1.54	1.63	1.83	1.83	1.69	1.96	2.04
Wheeler Peak Wilderness	2.14	2.00	1.78	1.65	1.67	1.52	1.66	1.94	1.89	1.68	1.98	2.10
White Mountain Wilderness	2.00	1.79	1.51	1.40	1.44	1.37	1.64	1.82	1.85	1.59	1.72	1.95
Wichita Mountains Wilderness	2.39	2.25	2.10	2.11	2.39	2.24	2.02	2.13	2.35	2.22	2.28	2.41
Wind Cave NP	2.23	2.22	2.22	2.18	2.32	2.18	2.00	1.97	1.95	2.00	2.30	2.24
Wolf Island Wilderness	2.86	2.67	2.61	2.54	2.63	2.96	2.94	3.13	3.12	2.99	2.88	2.95
Yellowstone NP	2.24	2.11	2.03	1.95	1.94	1.78	1.59	1.53	1.69	1.91	2.19	2.22
Yolla Bolly-Middle Eel Wilderness	3.12	2.76	2.60	2.37	2.29	2.13	2.14	2.18	2.21	2.33	2.75	2.98
Yosemite NP	2.61	2.45	2.34	1.99	1.88	1.61	1.48	1.46	1.54	1.69	2.06	2.38
Zion NP	2.32	2.18	1.83	1.56	1.45	1.26	1.24	1.38	1.40	1.51	1.84	2.14

Table 8. Hygroscopic (dry) Small $(NH_4)_2SO_4$ and NH_4NO_3 Relative Humidity Adjustment Factor

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Acadia NP	3.80	3.28	3.30	3.71	3.72	3.81	4.28	4.34	4.58	4.10	4.06	4.19
Agua Tibia Wilderness	2.68	2.61	2.63	2.42	2.40	2.33	2.33	2.45	2.49	2.46	2.29	2.42
Alpine Lakes Wilderness	5.87	5.35	4.34	4.13	4.30	3.50	3.61	3.69	4.27	5.43	6.15	6.08
Anaconda Pintler Wilderness	3.72	3.23	2.87	2.62	2.60	2.52	2.14	2.07	2.33	2.87	3.60	3.71
Ansel Adams Wilderness	3.51	3.11	2.87	2.34	2.18	1.86	1.75	1.76	1.88	2.05	2.55	3.12
Arches NP	2.96	2.70	2.09	1.84	1.75	1.40	1.49	1.69	1.76	1.83	2.33	2.69
Badlands NP	2.94	2.96	3.01	2.87	3.10	2.91	2.64	2.59	2.56	2.58	3.11	2.98
Bandelier NM	2.66	2.36	2.10	1.77	1.80	1.55	1.93	2.30	2.21	1.87	2.32	2.60
Bering Sea Wilderness	4.16	4.48	4.52	4.50	4.64	4.86	5.71	6.43	5.40	4.52	4.36	4.37
Big Bend NP	2.11	1.92	1.65	1.56	1.67	1.67	1.83	2.07	2.22	1.92	1.92	2.04
Black Canyon of the Gunnison NP	2.71	2.56	2.23	2.12	2.12	1.75	1.87	2.17	2.21	2.00	2.42	2.57
Bob Marshall Wilderness	3.84	3.35	3.06	2.86	2.86	2.84	2.49	2.39	2.77	3.22	3.81	3.83
Bosque del Apache Wilderness	2.56	2.23	1.83	1.54	1.54	1.39	1.90	2.16	2.09	1.79	2.09	2.53
Boundary Waters Canoe Area Wilderness	3.23	2.81	2.93	2.63	2.89	3.22	3.44	3.71	3.83	3.08	3.49	3.49
Breton Wilderness	4.08	3.82	3.79	3.74	3.94	4.12	4.41	4.37	4.18	3.92	3.93	4.06
Bridger Wilderness	2.78	2.60	2.55	2.43	2.45	1.99	1.65	1.63	2.03	2.25	2.78	2.68
Brigantine Wilderness	3.34	3.07	3.17	2.99	3.37	3.45	3.68	3.90	3.91	3.73	3.27	3.36
Bryce Canyon NP	3.02	2.77	2.23	1.84	1.70	1.38	1.42	1.67	1.67	1.81	2.30	2.75
Cabinet Mountains Wilderness	4.30	3.69	3.23	2.91	2.91	2.87	2.50	2.40	2.84	3.40	4.26	4.37
Caney Creek Wilderness	3.85	3.44	3.14	3.24	3.66	3.71	3.49	3.51	3.73	3.72	3.68	3.88
Canyonlands NP	3.03	2.77	2.17	1.86	1.76	1.40	1.52	1.78	1.81	1.87	2.38	2.77
Cape Romain Wilderness	3.66	3.33	3.24	3.07	3.46	3.88	3.91	4.31	4.30	4.00	3.62	3.73
Capitol Reef NP	3.10	2.86	2.27	1.94	1.81	1.45	1.52	1.77	1.81	1.91	2.43	2.86
Caribou Wilderness	4.17	3.50	3.11	2.68	2.54	2.28	2.21	2.26	2.36	2.60	3.39	3.93
Carlsbad Caverns NP	2.70	2.25	1.75	1.63	1.77	1.70	2.06	2.34	2.59	1.95	2.16	2.57
Chassahowitzka Wilderness	4.31	3.92	3.79	3.62	3.57	4.22	4.26	4.50	4.49	4.29	4.18	4.43
Chiricahua NM	2.29	2.19	1.75	1.34	1.31	1.18	1.94	2.28	1.95	1.64	1.79	2.34
Chiricahua Wilderness	2.25	2.14	1.71	1.30	1.28	1.17	1.95	2.26	1.93	1.61	1.75	2.31
Cohutta Wilderness	3.99	3.59	3.38	3.16	3.76	4.19	4.24	4.37	4.41	4.09	3.77	4.00
Crater Lake NP	5.58	4.73	4.37	4.09	3.70	3.37	3.05	3.08	3.38	4.26	5.52	5.64
Craters of the Moon NM	3.40	3.00	2.52	2.22	2.23	1.94	1.56	1.55	1.76	2.17	3.04	3.32
Cucamonga Wilderness	2.87	2.73	2.68	2.40	2.37	2.29	2.31	2.38	2.43	2.42	2.34	2.54
Denali NP & Pres	3.21	3.19	2.71	2.39	2.46	2.69	3.27	4.05	4.17	3.90	3.59	3.58
Desolation Wilderness	3.77	3.22	2.82	2.26	2.09	1.80	1.67	1.71	1.84	2.08	2.72	3.44
Diamond Peak Wilderness	5.79	4.97	4.61	4.35	3.90	3.55	3.08	3.12	3.55	4.63	5.75	5.88
Dolly Sods Wilderness	3.39	3.16	3.17	2.87	3.63	3.62	3.78	4.06	4.15	3.63	3.27	3.53
Dome Land Wilderness	2.97	2.64	2.51	2.17	2.08	1.91	1.89	1.93	2.01	2.06	2.23	2.56
Eagle Cap Wilderness	5.05	4.28	3.45	3.05	3.02	2.56	2.20	2.15	2.53	3.62	4.89	5.26
Eagles Nest Wilderness	2.48	2.48	2.29	2.32	2.42	2.03	2.02	2.24	2.31	2.09	2.42	2.42
Emigrant Wilderness	3.69	3.25	2.98	2.39	2.21	1.86	1.71	1.73	1.85	2.07	2.68	3.32
Everglades NP	3.14	2.93	2.83	2.67	2.63	3.03	2.91	3.22	3.33	3.12	2.95	3.08
Fitzpatrick Wilderness	2.78	2.60	2.54	2.43	2.44	1.99	1.66	1.63	2.02	2.25	2.77	2.68
Flat Tops Wilderness	2.61	2.53	2.28	2.26	2.31	1.91	1.86	2.04	2.19	2.06	2.42	2.51
Galiuro Wilderness	2.17	1.99	1.68	1.30	1.26	1.14	1.62	1.96	1.75	1.60	1.82	2.31
Gates of the Mountains Wilderness	3.20	2.85	2.71	2.57	2.53	2.50	2.21	2.14	2.37	2.74	3.09	3.12

Table 3. Monthly $f_S(RH)$ – Small $(NH_4)_2SO_4$ and NH_4NO_3 Relative Humidity Adjustment Factor

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Gearhart Mountain Wilderness	4.80	4.05	3.60	3.30	3.04	2.76	2.37	2.39	2.62	3.36	4.45	4.76
Gila Wilderness	2.40	2.16	1.77	1.45	1.41	1.33	2.11	2.12	2.00	1.73	1.99	2.45
Glacier NP	4.53	3.87	3.63	3.39	3.51	3.48	2.91	2.87	3.47	3.86	4.29	4.37
Glacier Peak Wilderness	5.53	4.98	4.21	3.99	3.90	3.43	3.35	3.54	4.14	5.12	5.80	5.80
Goat Rocks Wilderness	5.81	5.08	4.46	4.23	3.97	3.57	3.35	3.48	4.11	5.22	5.98	6.09
Grand Canyon NP	2.73	2.53	2.12	1.69	1.52	1.27	1.42	1.72	1.69	1.74	2.11	2.49
Grand Teton NP	2.88	2.66	2.48	2.35	2.34	2.00	1.68	1.62	1.94	2.25	2.73	2.82
Great Gulf Wilderness	3.34	3.02	3.12	3.23	3.31	3.46	3.76	4.03	4.22	3.90	3.64	3.50
Great Sand Dunes NP & Pres	2.66	2.55	2.27	2.16	2.22	1.92	2.04	2.47	2.41	2.07	2.57	2.63
Great Smoky Mountains NP	4.01	3.52	3.43	3.14	3.76	4.20	4.21	4.39	4.45	4.05	3.76	3.99
Guadalupe Mountains NP	2.85	2.28	1.74	1.57	1.73	1.69	2.16	2.48	2.74	1.90	2.20	2.71
Haleakala NP	2.98	2.85	2.81	2.72	2.60	2.53	2.65	2.63	2.56	2.69	2.95	2.89
Hawaii Volcanoes NP	3.35	3.10	3.14	3.13	3.14	3.11	3.24	3.42	3.34	3.38	3.76	3.34
Hells Canyon Wilderness	4.28	3.56	2.83	2.42	2.34	2.19	1.80	1.75	2.01	2.75	4.03	4.45
Hercules-Glades Wilderness	3.70	3.33	3.01	3.01	3.47	3.48	3.41	3.51	3.67	3.43	3.46	3.73
Hoover Wilderness	3.63	3.18	2.89	2.33	2.16	1.82	1.66	1.68	1.81	2.02	2.62	3.25
Isle Royale NP	3.26	2.74	2.87	2.58	2.46	3.00	3.59	3.68	3.92	2.88	3.72	3.67
James River Face Wilderness	3.25	3.03	3.02	2.72	3.31	3.48	3.59	3.83	3.91	3.48	3.11	3.38
Jarbidge Wilderness	3.29	2.92	2.31	2.34	2.44	2.22	1.73	1.51	1.48	1.80	2.70	3.13
John Muir Wilderness	3.42	3.02	2.86	2.44	2.29	1.94	1.86	1.87	2.01	2.16	2.60	3.03
Joshua Tree NP	2.62	2.49	2.44	2.19	2.16	2.05	1.97	2.18	2.21	2.19	2.11	2.31
Joyce Kilmer-Slickrock Wilderness	4.02	3.54	3.42	3.15	3.74	4.19	4.21	4.35	4.41	4.04	3.77	4.00
Kaiser Wilderness	3.55	3.13	2.89	2.36	2.21	1.90	1.81	1.83	1.95	2.12	2.59	3.16
Kalmiopsis Wilderness	5.32	4.56	4.30	4.02	3.79	3.54	3.43	3.44	3.56	4.12	5.21	5.28
Kings Canyon	3.35	2.97	2.82	2.42	2.28	1.93	1.85	1.87	2.01	2.15	2.56	2.96
La Garita Wilderness	2.71	2.54	2.21	2.04	2.05	1.72	1.93	2.31	2.26	2.00	2.46	2.62
Lassen Volcanic NP	4.24	3.55	3.16	2.73	2.58	2.31	2.24	2.29	2.39	2.64	3.46	4.00
Lava Beds NM	4.84	4.05	3.63	3.28	3.04	2.76	2.53	2.55	2.75	3.29	4.35	4.75
Linville Gorge Wilderness	3.76	3.46	3.37	3.07	3.74	4.18	4.24	4.62	4.61	4.00	3.59	3.80
Lostwood Wilderness	3.21	3.15	3.36	2.60	2.54	2.86	2.89	2.60	2.53	2.72	3.60	3.52
Lye Brook Wilderness	3.25	2.99	3.10	3.06	3.24	3.30	3.52	3.80	3.95	3.71	3.42	3.35
Mammoth Cave NP	3.86	3.47	3.32	3.54	4.90	5.77	5.58	4.09	4.15	3.73	3.54	3.91
Marble Mountain Wilderness	5.15	4.40	4.15	3.84	3.67	3.44	3.41	3.44	3.50	3.89	4.87	5.04
Maroon Bells-Snowmass Wilderness	2.48	2.44	2.23	2.25	2.25	1.87	2.02	2.35	2.35	2.04	2.36	2.38
Mazatzal Wilderness	2.36	2.20	1.88	1.46	1.36	1.18	1.54	1.89	1.74	1.66	1.91	2.33
Medicine Lake Wilderness	3.25	3.15	3.21	2.52	2.49	2.71	2.71	2.42	2.46	2.65	3.48	3.48
Mesa Verde NP	3.32	2.96	2.55	1.88	1.96	1.46	1.94	2.35	2.13	2.04	2.57	3.06
Mingo Wilderness	3.74	3.38	3.07	2.97	3.39	3.52	3.57	3.64	3.72	3.47	3.43	3.74
Mission Mountains Wilderness	4.03	3.51	3.08	2.82	2.84	2.83	2.49	2.40	2.78	3.28	4.04	4.08
Mokelumne Wilderness	3.75	3.23	2.86	2.29	2.12	1.81	1.68	1.72	1.84	2.08	2.71	3.41
Moosehorn Wilderness	3.59	3.14	3.16	3.44	3.38	3.49	3.98	4.18	4.40	3.94	3.82	3.82
Mount Adams Wilderness	5.71	5.00	4.46	4.23	3.89	3.55	3.26	3.41	4.02	5.13	5.89	5.98
Mount Baldy Wilderness	2.51	2.30	1.92	1.51	1.43	1.25	1.73	2.08	1.88	1.76	2.08	2.54
Mount Hood Wilderness	5.56	4.87	4.40	4.19	3.79	3.44	3.07	3.22	3.79	4.93	5.76	5.81
Mount Jefferson Wilderness	5.95	5.16	4.78	4.57	4.09	3.65	3.10	3.11	3.63	4.91	5.88	6.05

Table 8. Hygroscopicity ($f(RH)$) for Small $(NH_4)_2SO_4$ and NH_4NO_3 Relative Humidity Adjustment Factor

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Mount Rainier NP	6.01	5.29	4.71	4.51	4.23	3.82	3.59	3.73	4.39	5.55	6.23	6.27
Mount Washington Wilderness	6.35	5.47	5.22	5.07	4.42	3.93	3.16	3.09	3.63	5.07	6.31	6.35
Mount Zirkel Wilderness	2.43	2.44	2.31	2.37	2.51	2.07	1.92	2.02	2.23	2.12	2.41	2.37
Mountain Lakes Wilderness	5.20	4.32	3.90	3.58	3.26	2.96	2.69	2.70	2.94	3.67	4.96	5.24
North Absaroka Wilderness	2.68	2.51	2.50	2.42	2.40	2.13	1.83	1.72	1.98	2.31	2.65	2.65
North Cascades NP	5.37	4.86	4.24	4.04	3.80	3.51	3.34	3.61	4.23	5.08	5.68	5.66
Okefenokee Wilderness	4.16	3.79	3.80	3.65	3.79	4.46	4.24	4.55	4.55	4.35	4.18	4.33
Olympic NP	5.76	5.20	4.81	4.64	3.81	4.04	3.52	4.16	4.70	5.63	6.11	6.02
Otter Creek Wilderness	3.41	3.20	3.20	2.91	3.64	3.70	3.88	4.18	4.26	3.72	3.32	3.56
Pasayten Wilderness	5.46	4.89	4.20	3.96	3.77	3.42	3.28	3.49	4.08	5.00	5.72	5.74
Pecos Wilderness	2.65	2.40	2.10	1.85	1.88	1.65	1.96	2.34	2.27	1.94	2.36	2.60
Petrified Forest NP	2.67	2.43	1.96	1.59	1.46	1.26	1.67	2.06	1.85	1.79	2.20	2.66
Pine Mountain Wilderness	2.44	2.29	1.95	1.51	1.41	1.20	1.54	1.91	1.77	1.70	1.96	2.39
Pinnacles NM	4.02	4.05	4.09	3.01	2.81	2.54	2.40	2.52	2.54	2.74	2.82	3.36
Point Reyes NS	4.16	3.74	3.53	2.96	2.80	2.55	2.69	2.77	2.80	2.90	3.30	3.80
Presidential Range-Dry River Wilderness	3.36	3.02	3.15	3.26	3.37	3.56	3.86	4.14	4.33	3.96	3.68	3.50
Rawah Wilderness	2.31	2.39	2.32	2.44	2.61	2.19	2.05	2.16	2.31	2.12	2.37	2.29
Red Rock Lakes Wilderness	3.09	2.76	2.57	2.41	2.38	2.17	1.86	1.77	2.01	2.39	2.96	3.05
Redwood NP	4.81	4.41	4.51	4.27	4.40	4.37	4.73	4.76	4.46	4.24	4.62	4.45
Rocky Mountain NP	2.09	2.24	2.24	2.45	2.62	2.22	2.09	2.15	2.29	2.04	2.23	2.08
Roosevelt Campobello International Park	3.61	3.14	3.16	3.45	3.37	3.49	3.95	4.15	4.36	3.93	3.84	3.85
Saguaro NP	1.99	1.80	1.56	1.18	1.16	1.07	1.51	1.89	1.66	1.54	1.72	2.25
Saint Marks Wilderness	4.24	3.89	3.79	3.72	3.79	4.32	4.56	4.63	4.43	4.19	4.16	4.39
Salt Creek Wilderness	2.57	2.19	1.75	1.67	1.82	1.69	1.93	2.16	2.37	1.94	2.07	2.38
San Gabriel Wilderness	2.94	2.78	2.72	2.41	2.37	2.29	2.32	2.39	2.44	2.44	2.36	2.58
San Gorgonio Wilderness	2.94	2.94	2.74	2.36	2.34	2.00	1.88	2.02	2.05	2.04	2.10	2.43
San Jacinto Wilderness	2.73	2.65	2.59	2.33	2.30	2.16	2.02	2.26	2.30	2.28	2.19	2.38
San Pedro Parks Wilderness	2.73	2.45	2.10	1.81	1.80	1.55	1.87	2.24	2.16	1.91	2.36	2.65
San Rafael Wilderness	3.38	3.13	3.07	2.68	2.64	2.57	2.66	2.74	2.84	2.77	2.63	2.94
Sawtooth Wilderness	3.78	3.18	2.55	2.20	2.17	1.95	1.51	1.50	1.61	2.11	3.26	3.70
Scapegoat Wilderness	3.70	3.24	2.97	2.79	2.78	2.75	2.41	2.31	2.65	3.09	3.67	3.68
Selway-Bitterroot Wilderness	3.99	3.41	2.90	2.56	2.54	2.43	2.00	1.93	2.21	2.82	3.78	4.01
Seney Wilderness	3.69	3.10	3.30	3.10	3.03	3.45	3.80	4.27	4.31	3.82	3.97	3.87
Sequoia NP	3.25	2.91	2.87	2.59	2.46	1.97	1.85	1.84	2.02	2.18	2.64	2.85
Shenandoah NP	3.26	2.99	3.02	2.72	3.28	3.46	3.59	3.85	3.91	3.41	3.08	3.44
Shining Rock Wilderness	3.89	3.51	3.37	3.11	3.77	4.22	4.29	4.58	4.60	4.12	3.69	3.88
Sierra Ancha Wilderness	2.38	2.21	1.87	1.46	1.36	1.19	1.60	1.95	1.78	1.69	1.96	2.41
Simeonof Wilderness	4.86	4.88	4.44	4.64	4.92	5.46	6.08	6.35	5.30	4.29	4.52	4.98
Sipsey Wilderness	3.89	3.52	3.23	3.13	3.60	3.99	4.13	4.09	4.12	3.87	3.61	3.89
South Warner Wilderness	4.36	3.67	3.20	2.81	2.64	2.39	2.04	2.07	2.24	2.76	3.71	4.20
Strawberry Mountain Wilderness	5.26	4.45	3.71	3.32	3.18	2.70	2.26	2.24	2.66	3.84	5.11	5.44
Superstition Wilderness	2.25	2.06	1.77	1.38	1.29	1.15	1.52	1.81	1.66	1.58	1.83	2.28
Swanquarter Wilderness	3.31	3.09	3.01	2.78	3.09	3.39	3.57	3.68	3.55	3.40	3.14	3.33
Sycamore Canyon Wilderness	2.52	2.41	2.05	1.59	1.47	1.23	1.53	1.98	1.85	1.77	2.03	2.45
Teton Wilderness	2.78	2.59	2.49	2.37	2.36	2.06	1.75	1.67	1.96	2.28	2.70	2.73

Table 8. Monthly $f_{(RH)}$ – Small $(NH_4)_2SO_4$ and NH_4NO_3 Relative Humidity Adjustment Factor

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Theodore Roosevelt NP	3.17	3.11	3.22	2.71	2.74	2.85	2.73	2.49	2.48	2.66	3.42	3.37
Thousand Lakes Wilderness	4.34	3.60	3.22	2.79	2.62	2.34	2.26	2.31	2.41	2.69	3.58	4.11
Three Sisters Wilderness	6.22	5.38	5.09	4.92	4.35	3.89	3.21	3.17	3.68	5.02	6.20	6.24
Tuxedni Wilderness	4.11	3.89	3.26	3.14	3.11	3.31	4.13	4.57	4.57	4.04	4.04	4.23
UL Bend Wilderness	2.94	2.75	2.77	2.55	2.44	2.41	2.19	1.97	2.12	2.50	2.96	2.95
Upper Buffalo Wilderness	3.73	3.33	3.03	3.07	3.54	3.57	3.43	3.50	3.71	3.51	3.52	3.74
Ventana Wilderness	3.92	3.69	3.61	2.86	2.69	2.46	2.46	2.55	2.61	2.72	2.89	3.43
Virgin Islands NP	2.41	2.36	2.27	2.39	2.44	2.40	2.43	2.57	2.58	2.63	2.68	2.54
Voyageurs NP	3.16	2.77	2.82	2.59	2.65	3.28	3.25	3.48	3.66	3.02	3.37	3.32
Washakie Wilderness	2.68	2.52	2.49	2.40	2.40	2.09	1.77	1.68	1.98	2.29	2.66	2.65
Weminuche Wilderness	2.80	2.58	2.22	1.97	1.97	1.64	1.89	2.28	2.20	1.97	2.45	2.69
West Elk Wilderness	2.64	2.53	2.24	2.15	2.16	1.79	1.92	2.24	2.26	2.02	2.41	2.53
Wheeler Peak Wilderness	2.72	2.50	2.17	1.97	2.02	1.76	1.98	2.42	2.36	2.01	2.48	2.66
White Mountain Wilderness	2.54	2.19	1.76	1.58	1.65	1.53	1.94	2.20	2.29	1.87	2.07	2.45
Wichita Mountains Wilderness	3.17	2.94	2.69	2.68	3.15	2.86	2.49	2.70	3.07	2.87	2.97	3.20
Wind Cave NP	2.81	2.81	2.86	2.82	3.06	2.81	2.50	2.46	2.44	2.52	2.97	2.83
Wolf Island Wilderness	4.02	3.68	3.58	3.45	3.59	4.17	4.13	4.47	4.46	4.23	4.05	4.18
Yellowstone NP	2.82	2.61	2.53	2.42	2.41	2.16	1.86	1.76	2.02	2.36	2.78	2.80
Yolla Bolly-Middle Eel Wilderness	4.48	3.82	3.53	3.13	3.00	2.75	2.81	2.87	2.93	3.11	3.84	4.24
Yosemite NP	3.62	3.32	3.13	2.52	2.34	1.89	1.69	1.67	1.78	2.04	2.65	3.22
Zion NP	3.05	2.81	2.26	1.84	1.67	1.37	1.33	1.54	1.58	1.75	2.25	2.72

Table 9. Hygroscopic ($f(RH)$) Sea Salt Relative Humidity Adjustment Factor

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Acadia NP	3.90	3.48	3.40	3.66	3.71	3.81	4.19	4.27	4.44	4.13	4.10	4.19
Agua Tibia Wilderness	2.94	2.95	3.02	2.85	2.88	2.81	2.78	2.90	2.90	2.83	2.56	2.69
Alpine Lakes Wilderness	5.35	4.96	4.27	4.11	4.18	3.64	3.68	3.73	4.12	4.98	5.51	5.53
Anaconda Pintler Wilderness	4.00	3.56	3.18	2.90	2.85	2.75	2.33	2.25	2.52	3.10	3.81	3.97
Ansel Adams Wilderness	3.55	3.25	3.04	2.54	2.38	2.05	1.91	1.91	2.03	2.21	2.72	3.21
Arches NP	3.25	2.99	2.26	1.97	1.86	1.48	1.59	1.82	1.88	1.96	2.60	3.02
Badlands NP	3.37	3.33	3.27	3.05	3.25	3.15	2.89	2.81	2.74	2.82	3.41	3.38
Bandelier NM	2.91	2.59	2.22	1.87	1.90	1.67	2.11	2.54	2.37	2.00	2.49	2.78
Bering Sea Wilderness	4.39	4.57	4.60	4.58	4.57	4.70	5.26	5.73	5.11	4.59	4.52	4.54
Big Bend NP	2.20	2.03	1.75	1.67	1.84	1.87	2.03	2.34	2.47	2.09	2.10	2.22
Black Canyon of the Gunnison NP	3.05	2.89	2.47	2.31	2.28	1.89	2.04	2.36	2.37	2.18	2.71	2.92
Bob Marshall Wilderness	4.08	3.66	3.35	3.11	3.08	3.04	2.68	2.59	2.94	3.42	3.98	4.05
Bosque del Apache Wilderness	2.77	2.43	1.95	1.62	1.62	1.47	2.06	2.40	2.29	1.92	2.27	2.71
Boundary Waters Canoe Area Wilderness	3.73	3.35	3.29	2.91	3.00	3.44	3.68	3.88	3.98	3.45	3.89	3.91
Breton Wilderness	4.10	3.89	3.87	3.85	4.02	4.21	4.44	4.38	4.23	3.99	4.01	4.11
Bridger Wilderness	3.25	3.05	2.90	2.67	2.62	2.17	1.81	1.79	2.17	2.43	3.15	3.17
Brigantine Wilderness	3.53	3.24	3.30	3.15	3.49	3.63	3.84	4.02	4.02	3.82	3.48	3.55
Bryce Canyon NP	3.24	3.00	2.40	1.96	1.80	1.45	1.52	1.80	1.78	1.93	2.52	2.99
Cabinet Mountains Wilderness	4.42	3.93	3.50	3.18	3.13	3.06	2.67	2.59	3.01	3.58	4.33	4.46
Caney Creek Wilderness	3.90	3.52	3.31	3.41	3.83	3.88	3.69	3.68	3.82	3.76	3.77	3.93
Canyonlands NP	3.30	3.04	2.33	1.99	1.87	1.48	1.63	1.90	1.94	2.00	2.64	3.07
Cape Romain Wilderness	3.74	3.44	3.37	3.23	3.62	3.99	4.04	4.32	4.29	4.03	3.74	3.81
Capitol Reef NP	3.35	3.11	2.45	2.08	1.93	1.54	1.62	1.90	1.94	2.05	2.68	3.13
Caribou Wilderness	4.16	3.63	3.28	2.89	2.75	2.47	2.33	2.37	2.49	2.74	3.48	3.97
Carlsbad Caverns NP	2.75	2.36	1.86	1.72	1.89	1.86	2.27	2.59	2.75	2.09	2.29	2.68
Chassahowitzka Wilderness	4.29	3.99	3.89	3.76	3.77	4.29	4.34	4.51	4.49	4.33	4.23	4.38
Chiricahua NM	2.53	2.38	1.91	1.41	1.38	1.21	2.12	2.55	2.18	1.78	1.99	2.56
Chiricahua Wilderness	2.48	2.33	1.86	1.37	1.35	1.20	2.12	2.54	2.16	1.75	1.94	2.52
Cohutta Wilderness	3.97	3.62	3.44	3.26	3.82	4.20	4.24	4.35	4.35	4.05	3.82	4.02
Crater Lake NP	5.15	4.56	4.31	4.12	3.80	3.52	3.20	3.23	3.44	4.17	5.10	5.19
Craters of the Moon NM	3.78	3.41	2.86	2.51	2.48	2.16	1.72	1.69	1.93	2.43	3.38	3.72
Cucamonga Wilderness	3.07	3.01	3.03	2.79	2.80	2.72	2.72	2.80	2.81	2.76	2.58	2.77
Denali NP & Pres	3.68	3.57	3.07	2.74	2.74	3.01	3.53	4.13	4.19	4.09	3.92	3.94
Desolation Wilderness	3.85	3.39	3.02	2.48	2.32	2.01	1.84	1.87	2.02	2.28	2.94	3.58
Diamond Peak Wilderness	5.29	4.72	4.45	4.27	3.92	3.65	3.23	3.26	3.56	4.43	5.26	5.34
Dolly Sods Wilderness	3.60	3.35	3.31	3.03	3.66	3.76	3.91	4.12	4.16	3.72	3.47	3.72
Dome Land Wilderness	3.10	2.86	2.75	2.42	2.33	2.15	2.11	2.16	2.22	2.26	2.40	2.71
Eagle Cap Wilderness	4.84	4.27	3.57	3.22	3.14	2.74	2.33	2.27	2.60	3.61	4.68	4.99
Eagles Nest Wilderness	2.86	2.82	2.54	2.52	2.57	2.20	2.20	2.44	2.46	2.27	2.73	2.79
Emigrant Wilderness	3.70	3.37	3.13	2.60	2.42	2.05	1.88	1.88	2.01	2.24	2.84	3.39
Everglades NP	3.60	3.44	3.37	3.22	3.21	3.58	3.50	3.72	3.78	3.61	3.50	3.55
Fitzpatrick Wilderness	3.25	3.05	2.88	2.66	2.62	2.18	1.82	1.79	2.16	2.43	3.13	3.18
Flat Tops Wilderness	2.99	2.88	2.54	2.47	2.47	2.07	2.03	2.23	2.35	2.25	2.75	2.89
Galiuro Wilderness	2.42	2.19	1.82	1.35	1.31	1.16	1.76	2.18	1.94	1.73	2.00	2.52
Gates of the Mountains Wilderness	3.62	3.27	3.05	2.85	2.80	2.74	2.43	2.35	2.58	2.99	3.41	3.52

Table 9. Monthly $f_{ss}(RH)$ – Sea Salt Relative Humidity Adjustment Factor

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Gearhart Mountain Wilderness	4.63	4.06	3.67	3.40	3.16	2.90	2.49	2.50	2.70	3.39	4.31	4.60
Gila Wilderness	2.63	2.35	1.91	1.52	1.48	1.36	2.22	2.36	2.19	1.87	2.17	2.65
Glacier NP	4.61	4.12	3.87	3.64	3.63	3.59	3.11	3.11	3.63	4.03	4.43	4.51
Glacier Peak Wilderness	5.14	4.73	4.19	4.03	3.93	3.60	3.51	3.63	4.04	4.79	5.31	5.34
Goat Rocks Wilderness	5.30	4.79	4.32	4.15	3.94	3.65	3.46	3.55	3.99	4.83	5.40	5.51
Grand Canyon NP	2.93	2.73	2.26	1.78	1.61	1.32	1.50	1.85	1.79	1.84	2.29	2.70
Grand Teton NP	3.34	3.10	2.82	2.59	2.56	2.21	1.85	1.78	2.12	2.48	3.10	3.29
Great Gulf Wilderness	3.60	3.29	3.29	3.34	3.41	3.58	3.85	4.07	4.20	3.96	3.81	3.73
Great Sand Dunes NP & Pres	2.98	2.84	2.48	2.33	2.36	2.08	2.24	2.66	2.56	2.26	2.82	2.94
Great Smoky Mountains NP	4.01	3.57	3.47	3.22	3.82	4.23	4.24	4.37	4.38	4.03	3.81	4.02
Guadalupe Mountains NP	2.82	2.35	1.84	1.64	1.82	1.83	2.36	2.72	2.85	2.01	2.28	2.76
Haleakala NP	3.52	3.43	3.40	3.35	3.25	3.18	3.29	3.27	3.22	3.33	3.52	3.47
Hawaii Volcanoes NP	3.80	3.68	3.71	3.72	3.72	3.69	3.79	3.83	3.79	3.83	4.08	3.80
Hells Canyon Wilderness	4.39	3.81	3.15	2.75	2.63	2.44	1.97	1.90	2.19	3.00	4.13	4.51
Hercules-Glades Wilderness	3.86	3.51	3.23	3.22	3.66	3.72	3.69	3.73	3.81	3.57	3.65	3.88
Hoover Wilderness	3.66	3.31	3.05	2.53	2.36	2.00	1.82	1.82	1.96	2.18	2.79	3.34
Isle Royale NP	3.78	3.34	3.28	2.93	2.78	3.31	3.83	3.87	4.06	3.40	4.05	4.04
James River Face Wilderness	3.43	3.19	3.16	2.90	3.46	3.69	3.79	3.97	4.00	3.61	3.31	3.56
Jarbidge Wilderness	3.65	3.28	2.62	2.69	2.71	2.44	1.95	1.67	1.60	2.01	3.03	3.51
John Muir Wilderness	3.46	3.18	3.07	2.68	2.51	2.17	2.06	2.08	2.20	2.35	2.75	3.12
Joshua Tree NP	2.83	2.76	2.75	2.52	2.53	2.41	2.28	2.53	2.53	2.48	2.32	2.54
Joyce Kilmer-Slickrock Wilderness	4.01	3.58	3.46	3.24	3.81	4.22	4.23	4.35	4.35	4.03	3.82	4.02
Kaiser Wilderness	3.58	3.27	3.08	2.58	2.42	2.10	1.99	2.00	2.12	2.29	2.75	3.24
Kalmiopsis Wilderness	4.98	4.45	4.28	4.09	3.89	3.66	3.49	3.51	3.60	4.08	4.90	4.96
Kings Canyon	3.40	3.13	3.03	2.66	2.50	2.16	2.05	2.07	2.20	2.33	2.71	3.05
La Garita Wilderness	3.03	2.83	2.41	2.21	2.19	1.86	2.10	2.50	2.42	2.16	2.72	2.93
Lassen Volcanic NP	4.21	3.66	3.33	2.93	2.78	2.50	2.36	2.40	2.51	2.78	3.54	4.02
Lava Beds NM	4.64	4.04	3.68	3.37	3.15	2.89	2.62	2.65	2.82	3.32	4.21	4.56
Linville Gorge Wilderness	3.80	3.52	3.43	3.18	3.80	4.20	4.25	4.51	4.48	3.97	3.67	3.86
Lostwood Wilderness	3.77	3.66	3.67	2.86	2.79	3.07	3.11	2.82	2.80	2.99	3.93	3.95
Lye Brook Wilderness	3.53	3.26	3.27	3.20	3.36	3.48	3.70	3.93	4.04	3.82	3.63	3.61
Mammoth Cave NP	3.99	3.63	3.45	3.50	4.52	5.19	5.08	4.16	4.17	3.81	3.73	4.03
Marble Mountain Wilderness	4.85	4.32	4.16	3.92	3.76	3.53	3.44	3.46	3.51	3.86	4.63	4.78
Maroon Bells-Snowmass Wilderness	2.89	2.82	2.52	2.49	2.45	2.04	2.22	2.57	2.54	2.26	2.71	2.80
Mazatzal Wilderness	2.60	2.40	2.03	1.53	1.42	1.21	1.66	2.06	1.90	1.77	2.10	2.55
Medicine Lake Wilderness	3.79	3.66	3.56	2.80	2.75	2.94	2.93	2.66	2.73	2.95	3.85	3.92
Mesa Verde NP	3.40	3.10	2.61	1.95	2.00	1.53	2.04	2.45	2.28	2.05	2.69	3.15
Mingo Wilderness	3.92	3.58	3.30	3.19	3.58	3.72	3.80	3.82	3.85	3.61	3.66	3.90
Mission Mountains Wilderness	4.24	3.79	3.38	3.10	3.08	3.04	2.68	2.59	2.96	3.48	4.17	4.26
Mokelumne Wilderness	3.81	3.38	3.04	2.51	2.34	2.02	1.86	1.88	2.02	2.27	2.91	3.52
Moosehorn Wilderness	3.80	3.42	3.32	3.50	3.47	3.60	3.98	4.15	4.31	4.02	3.97	3.99
Mount Adams Wilderness	5.24	4.74	4.34	4.18	3.91	3.66	3.41	3.51	3.93	4.78	5.36	5.44
Mount Baldy Wilderness	2.74	2.50	2.05	1.58	1.50	1.29	1.87	2.28	2.06	1.87	2.26	2.74
Mount Hood Wilderness	5.16	4.67	4.33	4.18	3.87	3.61	3.29	3.38	3.78	4.67	5.29	5.33
Mount Jefferson Wilderness	5.38	4.84	4.55	4.42	4.05	3.74	3.27	3.28	3.63	4.64	5.41	5.46
Mount Rainier NP	5.42	4.92	4.50	4.36	4.13	3.86	3.67	3.76	4.20	5.05	5.56	5.62

Table 9.1 Hygroscopic (f_{RH}) Sea Salt Relative Humidity Adjustment Factor

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Mount Washington Wilderness	5.61	5.03	4.81	4.71	4.24	3.91	3.31	3.25	3.60	4.73	5.59	5.62
Mount Zirkel Wilderness	2.85	2.83	2.61	2.61	2.67	2.24	2.10	2.23	2.38	2.31	2.75	2.78
Mountain Lakes Wilderness	4.89	4.26	3.93	3.67	3.40	3.11	2.82	2.83	3.04	3.67	4.68	4.91
North Absaroka Wilderness	3.18	2.97	2.83	2.66	2.64	2.35	2.02	1.89	2.16	2.53	3.03	3.13
North Cascades NP	5.03	4.65	4.22	4.08	3.88	3.68	3.53	3.70	4.13	4.78	5.24	5.25
Okefenokee Wilderness	4.13	3.83	3.82	3.69	3.85	4.38	4.28	4.51	4.48	4.31	4.18	4.27
Olympic NP	5.27	4.87	4.61	4.51	3.94	4.12	3.76	4.16	4.51	5.17	5.51	5.46
Otter Creek Wilderness	3.63	3.40	3.34	3.06	3.67	3.82	3.98	4.19	4.23	3.78	3.51	3.76
Pasayten Wilderness	5.09	4.67	4.18	4.00	3.84	3.58	3.45	3.58	3.99	4.71	5.25	5.30
Pecos Wilderness	2.91	2.64	2.25	1.97	2.00	1.78	2.15	2.57	2.44	2.09	2.56	2.83
Petrified Forest NP	2.93	2.66	2.11	1.66	1.53	1.30	1.81	2.26	2.03	1.91	2.40	2.88
Pine Mountain Wilderness	2.69	2.50	2.11	1.60	1.47	1.24	1.67	2.09	1.92	1.82	2.16	2.62
Pinnacles NM	3.94	3.97	3.99	3.12	2.94	2.67	2.54	2.63	2.65	2.80	2.96	3.36
Point Reyes NS	4.20	3.88	3.72	3.25	3.12	2.88	2.96	3.01	3.05	3.12	3.48	3.90
Presidential Range-Dry River Wilderness	3.60	3.28	3.31	3.36	3.45	3.66	3.92	4.14	4.27	3.99	3.83	3.72
Rawah Wilderness	2.70	2.74	2.58	2.65	2.76	2.36	2.23	2.37	2.45	2.31	2.69	2.66
Red Rock Lakes Wilderness	3.51	3.18	2.91	2.67	2.63	2.41	2.06	1.94	2.20	2.63	3.29	3.46
Redwood NP	4.66	4.38	4.48	4.34	4.41	4.35	4.56	4.59	4.34	4.19	4.51	4.44
Rocky Mountain NP	2.44	2.56	2.47	2.64	2.75	2.37	2.26	2.36	2.41	2.20	2.51	2.41
Roosevelt Campobello International Park	3.82	3.43	3.32	3.52	3.47	3.61	3.96	4.13	4.29	4.02	3.99	4.01
Saguaro NP	2.24	2.00	1.69	1.21	1.20	1.08	1.67	2.13	1.86	1.65	1.89	2.44
Saint Marks Wilderness	4.18	3.89	3.82	3.76	3.85	4.30	4.49	4.54	4.39	4.19	4.15	4.30
Salt Creek Wilderness	2.72	2.37	1.88	1.77	1.96	1.87	2.15	2.44	2.59	2.12	2.26	2.56
San Gabriel Wilderness	3.12	3.04	3.04	2.77	2.78	2.69	2.69	2.77	2.79	2.74	2.59	2.79
San Gorgonio Wilderness	2.97	3.06	2.93	2.60	2.63	2.28	2.13	2.30	2.31	2.24	2.25	2.55
San Jacinto Wilderness	2.92	2.91	2.91	2.67	2.69	2.55	2.33	2.64	2.64	2.57	2.40	2.60
San Pedro Parks Wilderness	3.00	2.71	2.25	1.94	1.91	1.66	2.04	2.45	2.33	2.05	2.57	2.88
San Rafael Wilderness	3.49	3.35	3.34	3.00	2.99	2.90	2.97	3.04	3.09	3.00	2.86	3.12
Sawtooth Wilderness	4.05	3.53	2.89	2.53	2.44	2.18	1.66	1.61	1.76	2.38	3.55	4.00
Scapegoat Wilderness	3.97	3.57	3.27	3.04	3.01	2.96	2.60	2.51	2.83	3.30	3.86	3.93
Selway-Bitterroot Wilderness	4.20	3.71	3.21	2.86	2.80	2.66	2.18	2.09	2.39	3.06	3.96	4.20
Seney Wilderness	4.05	3.60	3.60	3.30	3.20	3.58	3.91	4.28	4.30	4.00	4.19	4.16
Sequoia NP	3.27	3.07	3.10	2.84	2.66	2.21	2.06	2.05	2.21	2.35	2.75	2.93
Shenandoah NP	3.44	3.17	3.17	2.90	3.42	3.66	3.78	3.97	3.98	3.56	3.28	3.62
Shining Rock Wilderness	3.90	3.55	3.43	3.21	3.82	4.22	4.28	4.48	4.48	4.06	3.76	3.92
Sierra Ancha Wilderness	2.62	2.42	2.02	1.53	1.42	1.22	1.73	2.14	1.95	1.81	2.15	2.62
Simeonof Wilderness	4.83	4.85	4.54	4.68	4.83	5.20	5.57	5.72	5.11	4.48	4.62	4.89
Sipsey Wilderness	3.94	3.60	3.36	3.28	3.72	4.06	4.18	4.14	4.13	3.91	3.74	3.96
South Warner Wilderness	4.32	3.75	3.31	2.94	2.77	2.51	2.13	2.15	2.31	2.83	3.71	4.19
Strawberry Mountain Wilderness	4.97	4.37	3.77	3.44	3.28	2.88	2.41	2.38	2.73	3.77	4.82	5.10
Superstition Wilderness	2.49	2.27	1.92	1.44	1.34	1.17	1.64	1.98	1.82	1.69	2.01	2.49
Swanquarter Wilderness	3.52	3.30	3.25	3.09	3.42	3.71	3.88	3.96	3.83	3.67	3.43	3.55
Sycamore Canyon Wilderness	2.78	2.62	2.22	1.68	1.55	1.27	1.67	2.17	2.00	1.90	2.25	2.69
Teton Wilderness	3.26	3.04	2.83	2.61	2.59	2.27	1.93	1.83	2.14	2.50	3.07	3.21
Theodore Roosevelt NP	3.67	3.56	3.51	2.93	2.97	3.09	2.96	2.72	2.72	2.93	3.75	3.78

Table 9. Monthly $f_{ss(RH)}$ – Sea Salt Relative Humidity Adjustment Factor

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Thousand Lakes Wilderness	4.27	3.70	3.38	2.99	2.82	2.52	2.37	2.42	2.53	2.82	3.62	4.08
Three Sisters Wilderness	5.53	4.97	4.74	4.63	4.20	3.89	3.35	3.31	3.65	4.70	5.53	5.56
Tuxedni Wilderness	4.28	4.06	3.53	3.46	3.44	3.64	4.26	4.56	4.51	4.17	4.17	4.37
UL Bend Wilderness	3.44	3.22	3.12	2.79	2.70	2.67	2.42	2.18	2.35	2.77	3.34	3.40
Upper Buffalo Wilderness	3.85	3.47	3.23	3.27	3.72	3.78	3.69	3.70	3.84	3.64	3.67	3.86
Ventana Wilderness	3.91	3.76	3.70	3.08	2.93	2.69	2.69	2.75	2.80	2.87	3.06	3.48
Virgin Islands NP	3.17	3.12	3.04	3.15	3.19	3.17	3.18	3.31	3.30	3.36	3.39	3.28
Voyageurs NP	3.69	3.31	3.20	2.90	2.89	3.46	3.55	3.71	3.87	3.42	3.83	3.80
Washakie Wilderness	3.18	2.98	2.83	2.64	2.62	2.31	1.96	1.85	2.15	2.50	3.04	3.14
Weminuche Wilderness	3.08	2.85	2.39	2.11	2.09	1.77	2.05	2.46	2.36	2.12	2.69	2.95
West Elk Wilderness	3.00	2.87	2.49	2.36	2.33	1.94	2.10	2.44	2.43	2.20	2.72	2.89
Wheeler Peak Wilderness	3.00	2.76	2.35	2.11	2.15	1.92	2.17	2.63	2.52	2.18	2.71	2.93
White Mountain Wilderness	2.71	2.37	1.89	1.68	1.76	1.66	2.14	2.46	2.49	2.02	2.25	2.63
Wichita Mountains Wilderness	3.35	3.12	2.91	2.94	3.40	3.21	2.84	3.01	3.32	3.10	3.20	3.40
Wind Cave NP	3.25	3.20	3.13	3.01	3.22	3.06	2.75	2.68	2.63	2.75	3.28	3.24
Wolf Island Wilderness	4.03	3.74	3.66	3.55	3.72	4.20	4.20	4.46	4.42	4.22	4.08	4.15
Yellowstone NP	3.29	3.05	2.87	2.66	2.65	2.39	2.05	1.93	2.21	2.59	3.14	3.25
Yolla Bolly-Middle Eel Wilderness	4.38	3.89	3.66	3.31	3.18	2.92	2.89	2.94	3.00	3.20	3.84	4.19
Yosemite NP	3.58	3.38	3.23	2.71	2.54	2.08	1.84	1.79	1.93	2.18	2.78	3.25
Zion NP	3.26	3.03	2.44	1.96	1.78	1.44	1.41	1.66	1.67	1.88	2.48	2.98

Table 10. Agency Average Natural Conditions Visual Range In Kilometers

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Acadia NP	173	177	177	174	174	173	170	169	167	171	171	170
Agua Tibia Wilderness	226	227	226	228	228	229	229	228	228	228	230	229
Alpine Lakes Wilderness	224	228	236	238	236	243	242	242	237	227	222	222
Anaconda Pintler Wilderness	256	259	262	267	268	271	273	272	271	269	265	259
Ansel Adams Wilderness	258	263	266	269	269	270	274	275	272	267	259	258
Arches NP	265	268	274	276	277	281	280	278	277	276	271	268
Badlands NP	233	233	233	234	232	233	235	236	236	236	232	233
Bandelier NM	269	272	276	280	281	283	278	274	276	277	274	269
Bering Sea Wilderness												
Big Bend NP	236	234	233	234	233	231	225	220	227	233	235	235
Black Canyon of the Gunnison NP	278	280	282	283	282	282	281	278	276	280	280	278
Bob Marshall Wilderness	257	259	262	263	263	266	265	262	262	264	260	258
Bosque del Apache Wilderness	249	252	256	259	259	260	255	252	253	256	253	249
Boundary Waters Canoe Area Wilderness	184	187	189	190	190	191	193	194	191	188	184	184
Breton Wilderness	173	176	176	179	177	174	172	170	169	174	171	171
Bridger Wilderness	278	280	286	290	292	296	295	292	292	291	285	280
Brigantine Wilderness	159	161	161	161	160	158	156	157	158	160	160	159
Bryce Canyon NP	268	269	270	271	271	275	279	279	275	273	268	268
Cabinet Mountains Wilderness	252	254	253	255	251	251	249	247	247	248	252	251
Caney Creek Wilderness	174	177	180	183	183	183	186	186	183	179	174	173
Canyonlands NP	257	261	264	263	259	259	260	260	258	258	259	257
Cape Romain Wilderness	167	169	174	177	178	181	180	178	177	177	172	169
Capitol Reef NP	269	271	277	280	281	285	284	281	281	280	275	271
Caribou Wilderness	250	256	259	263	264	267	267	267	266	264	257	252
Carlsbad Caverns NP	266	271	276	277	275	276	272	270	267	274	271	267
Chassahowitzka Wilderness	171	173	174	175	175	171	171	169	169	171	171	170
Chiricahua NM	253	254	258	261	262	263	256	253	256	259	257	252
Chiricahua Wilderness	253	254	258	262	262	263	256	253	256	259	258	252
Cohutta Wilderness	181	184	185	187	183	180	180	179	179	181	183	181
Crater Lake NP	255	263	266	269	273	276	280	279	276	267	256	255
Craters of the Moon NM	245	248	252	255	255	257	261	261	259	255	248	246
Cucamonga Wilderness	263	264	264	267	267	268	268	267	267	267	268	266
Denali NP & Pres	257	257	261	263	263	261	257	251	250	252	254	254
Desolation Wilderness	270	275	279	285	287	290	292	292	290	287	280	273
Diamond Peak Wilderness	253	261	264	267	271	275	279	279	275	264	254	253
Dolly Sods Wilderness	197	200	201	203	204	206	206	205	205	204	203	200
Dome Land Wilderness	242	244	244	247	241	241	239	237	236	241	243	241
Eagle Cap Wilderness	229	234	241	245	245	249	252	253	249	240	230	227
Eagles Nest Wilderness	302	302	304	304	303	308	308	305	304	307	303	303
Emigrant Wilderness	242	245	248	253	254	258	259	259	258	256	250	245
Everglades NP	168	170	171	172	172	169	170	167	166	168	169	168
Fitzpatrick Wilderness	280	282	283	284	284	289	292	293	288	286	280	281
Flat Tops Wilderness	301	302	305	305	304	309	310	307	306	307	303	302
Galiuro Wilderness	254	255	258	262	262	263	259	256	258	259	257	252
Gates of the Mountains Wilderness	281	285	287	288	289	289	292	293	291	286	283	282

Table 9a. Monthly Average Natural Conditions Visual Range In Kilometers

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Gearhart Mountain Wilderness	262	269	274	277	280	283	287	287	285	277	266	263
Gila Wilderness	275	278	282	285	285	286	278	278	279	282	279	275
Glacier NP	224	228	230	231	231	231	235	235	231	228	225	225
Glacier Peak Wilderness	233	237	243	245	245	249	250	248	244	236	231	231
Goat Rocks Wilderness	243	249	254	256	259	263	265	263	258	248	241	241
Grand Canyon NP	267	269	273	278	280	282	281	277	278	277	273	269
Grand Teton NP	274	278	277	276	275	273	270	268	266	269	272	273
Great Gulf Wilderness	192	192	195	195	195	197	196	193	193	196	192	192
Great Sand Dunes NP & Pres	255	260	260	263	257	254	253	252	251	255	257	255
Great Smoky Mountains NP	184	185	187	188	188	190	192	193	190	188	185	184
Guadalupe Mountains NP	265	270	276	278	276	276	271	268	266	274	271	266
Haleakala NP	232	234	234	235	237	238	236	236	237	235	232	233
Hawaii Volcanoes NP	243	246	246	246	246	246	244	243	244	243	238	243
Hells Canyon Wilderness	224	229	234	237	238	239	242	243	241	235	226	223
Hercules-Glades Wilderness	178	180	182	182	179	179	180	179	178	180	179	178
Hoover Wilderness	259	263	265	271	273	276	278	277	276	274	268	262
Isle Royale NP	182	185	184	186	187	183	179	179	177	184	179	179
James River Face Wilderness	181	183	187	187	186	188	192	193	193	191	185	182
Jarbidge Wilderness	245	246	246	249	244	243	242	240	239	243	246	243
John Muir Wilderness	256	260	261	264	258	254	254	253	252	255	258	256
Joshua Tree NP	242	246	247	251	252	255	256	256	255	253	249	246
Joyce Kilmer-Slickrock Wilderness	186	187	187	189	189	190	190	189	188	189	189	188
Kaiser Wilderness	260	264	266	272	273	277	278	278	276	274	269	264
Kalmiopsis Wilderness	194	200	202	205	207	209	211	210	209	204	195	195
Kings Canyon	229	232	233	236	237	240	240	240	239	238	235	232
La Garita Wilderness	252	259	263	266	268	271	273	273	271	266	256	253
Lassen Volcanic NP	263	264	267	269	269	272	270	266	267	269	265	263
Lava Beds NM	244	250	253	257	258	261	261	261	260	258	251	246
Linville Gorge Wilderness	180	182	183	185	180	177	177	175	175	178	181	180
Lostwood Wilderness	229	230	228	234	235	232	232	234	235	233	227	227
Lye Brook Wilderness	196	198	197	197	196	195	194	192	191	192	195	195
Mammoth Cave NP	187	188	189	189	189	192	191	188	188	191	188	188
Marble Mountain Wilderness	251	255	256	254	242	235	237	249	248	252	254	250
Maroon Bells-Snowmass Wilderness	274	281	284	287	289	291	292	291	291	286	276	275
Mazatzal Wilderness	252	253	256	260	261	263	259	256	258	258	256	252
Medicine Lake Wilderness	231	232	231	236	237	235	235	237	237	236	230	229
Mesa Verde NP	264	267	271	277	276	281	276	272	275	275	270	266
Mingo Wilderness	166	169	172	174	173	173	176	176	174	171	166	166
Mission Mountains Wilderness	249	252	254	255	251	250	250	249	249	251	251	249
Mokelumne Wilderness	252	259	263	266	269	272	275	273	268	257	251	250
Moosehorn Wilderness	159	163	166	167	170	172	174	173	170	162	158	157
Mount Adams Wilderness	242	248	251	253	258	262	267	267	262	250	241	241
Mount Baldy Wilderness	261	266	269	275	276	280	281	281	279	277	271	264
Mount Hood Wilderness	241	249	253	256	259	262	265	265	262	255	243	241
Mount Jefferson Wilderness	237	240	240	238	239	238	234	232	230	234	235	235

Table 10. Monthly Average Natural Conditions Visual Range In Kilometers

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Mount Rainier NP	215	220	224	226	228	231	233	232	227	218	213	213
Mount Washington Wilderness	216	223	224	225	230	234	240	241	237	225	217	216
Mount Zirkel Wilderness	296	296	297	296	295	300	301	300	298	299	296	296
Mountain Lakes Wilderness	284	285	286	287	287	290	294	295	292	288	284	284
North Absaroka Wilderness	246	251	256	258	260	262	264	261	256	249	244	244
North Cascades NP	243	246	246	247	246	241	243	240	240	242	243	242
Okefenokee Wilderness	162	166	168	169	174	173	176	172	169	163	160	161
Olympic NP	233	235	235	238	231	230	228	226	225	230	234	231
Otter Creek Wilderness	180	183	188	190	191	194	195	193	189	183	178	178
Pasayten Wilderness	269	271	274	277	276	279	276	272	272	276	272	269
Pecos Wilderness	294	297	303	308	310	313	307	302	304	305	300	294
Petrified Forest NP	269	271	274	279	280	282	278	275	276	277	274	270
Pine Mountain Wilderness	238	238	238	247	248	251	252	251	251	249	248	244
Pinnacles NM	211	215	216	222	223	226	225	224	224	223	219	214
Point Reyes NS	128	134	133	132	130	127	122	119	117	121	124	126
Presidential Range-Dry River Wilderness	186	188	189	191	192	192	192	191	190	191	192	190
Rawah Wilderness	297	296	297	296	294	298	300	299	297	299	296	297
Red Rock Lakes Wilderness	261	264	263	266	264	265	261	261	264	266	262	264
Redwood NP	176	182	187	191	192	196	204	206	201	192	180	177
Rocky Mountain NP	261	265	265	262	263	262	258	256	254	258	259	259
Roosevelt Campobello Int Pk	170	173	173	175	172	169	169	166	166	168	171	170
Saguaro NP	252	250	250	248	247	251	252	251	250	252	250	252
Saint Marks Wilderness	182	185	189	190	188	189	187	185	184	187	186	184
Salt Creek Wilderness	245	247	247	250	250	251	251	250	250	250	251	249
San Gabriel Wilderness	262	262	264	268	268	272	273	271	271	271	271	267
San Gorgonio Wilderness	253	255	258	262	262	263	258	254	257	258	256	251
San Jacinto Wilderness	247	247	248	250	250	252	253	251	250	251	252	250
San Pedro Parks Wilderness	280	284	285	286	285	279	277	276	278	281	281	279
San Rafael Wilderness	243	246	250	253	253	256	252	248	249	252	247	244
Sawtooth Wilderness	259	263	269	272	272	274	278	278	277	273	263	259
Scapegoat Wilderness	249	253	255	257	257	257	260	261	258	254	249	249
Selway-Bitterroot Wilderness	251	256	261	264	265	266	270	271	268	262	253	251
Seney Wilderness	179	182	181	182	183	180	178	175	175	178	177	177
Sequoia NP	230	232	232	234	236	239	240	240	239	238	234	233
Shenandoah NP	191	193	193	195	191	190	189	187	186	190	192	190
Shining Rock Wilderness	193	196	197	199	194	191	190	188	188	192	195	193
Sierra Ancha Wilderness	252	253	256	260	261	263	259	256	257	258	256	252
Simeonof Wilderness	138	138	143	141	138	133	128	127	135	144	142	138
Sipsey Wilderness	176	178	180	181	178	175	174	174	174	176	178	176
South Warner Wilderness	243	249	253	256	258	260	263	263	261	257	249	245
Strawberry Mountain Wilderness	227	233	239	242	244	248	252	252	248	238	228	226
Superstition Wilderness	254	256	259	262	263	264	261	258	259	260	258	254
Swanquarter Wilderness	172	174	174	176	174	171	170	169	170	171	173	172
Sycamore Canyon Wilderness	267	268	272	277	278	281	277	273	274	275	272	268
Teton Wilderness	280	282	283	285	285	288	291	292	289	286	281	281

Table 6. Monthly Average Natural Conditions Visual Range In Kilometers

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Theodore Roosevelt NP	223	228	231	234	235	238	238	238	237	235	229	225
Thousand Lakes Wilderness	258	259	258	263	262	261	262	265	265	263	256	257
Three Sisters Wilderness	217	223	225	227	231	234	240	240	236	226	217	217
Tuxedni Wilderness	195	198	205	206	206	204	195	192	192	196	196	194
UL Bend Wilderness	235	236	236	237	238	238	240	242	241	238	234	235
Upper Buffalo Wilderness	177	180	182	182	178	178	179	179	177	179	179	177
Ventana Wilderness	213	215	216	223	225	227	227	227	226	225	223	218
Virgin Islands NP	188	189	190	188	187	188	187	185	185	184	183	185
Voyageurs NP	177	179	179	181	180	176	176	175	174	178	175	176
Washakie Wilderness	270	272	272	273	273	276	279	280	277	274	270	270
Weminuche Wilderness	272	273	276	277	277	281	280	276	276	279	275	273
West Elk Wilderness	298	301	305	308	308	312	309	305	306	308	303	300
Wheeler Peak Wilderness	296	300	306	308	307	309	303	300	299	304	301	297
White Mountain Wilderness	265	267	271	273	272	275	273	268	269	272	267	265
Wichita Mountains Wilderness	232	233	232	233	231	233	235	235	236	235	231	232
Wind Cave NP	246	248	250	250	247	249	252	250	247	249	248	246
Wolf Island Wilderness	173	175	176	177	176	172	172	170	170	171	173	172
Yellowstone NP	280	282	283	284	284	287	290	291	288	285	280	280
Yolla Bolly-Middle Eel Wilderness	246	251	254	258	259	262	261	260	260	258	251	248
Yosemite NP	243	245	246	252	253	257	259	259	258	256	251	246
Zion NP	247	249	254	257	259	262	262	260	260	258	254	250

3.4. Ozone

3.4.1. Introduction (Revised)

Ozone is an air pollutant that forms on warm, sunny days when precursor emissions—nitrogen oxides (NO_x) and volatile organic compounds (VOCs)—react in the presence of sunlight. Because ozone is a regional pollutant, precursor sources both near and far from FLM areas can contribute to ozone formation.

Ozone is phytotoxic, causing damage to vegetation throughout the world (Ashmore et al. 2004). Some plant species are more sensitive to ozone than are humans (EPA 2007b). Ozone pollution has been shown to reduce plant growth, alter species composition, and predispose trees to insect and disease attack. Ozone also causes direct foliar injury to many plant species. Affected leaves are often marked with discoloration and lesions, and they age more rapidly than normal leaves (EPA 2007b).

FLAG is intended to provide information to assist the FLMs in identifying ozone impacts to vegetation on lands they manage. Therefore, the objectives of this chapter are to document information currently known about vegetation response to ozone exposure, and to describe FLM procedures for responding to new source review (NSR) permit applications. If the FLMs have evidence that ozone is adversely impacting an area they manage, they will recommend that additional emissions of ozone precursors are minimized until those adverse impacts are mitigated.

3.4.2. Ozone Effects on Vegetation (Revised)

Most ozone effects research has focused on agricultural crops. However, research has identified many native plants in natural ecosystems that are sensitive to ozone (EPA 1996e). Some of these ozone-sensitive plant species have been used as "bioindicators" of ozone to document phytotoxicity of ozone in the field due to ambient ozone. A listing of key literature describing known ozone effects on native vegetation is provided in Appendix G.

The definitions for ozone injury and damage used by FLMs are based on the classical definitions (for example, see Guderian 1977). Injury is all physical or biological responses to pollutants, such as change in metabolism, reduced photosynthesis, leaf necrosis, premature leaf drop, and chlorosis. Damage is reduction in the intended use or value of the biological or physical resource; for example, economic production, ecological structure and function, aesthetic value, and biological or genetic diversity that may be altered through the impact of pollutants.

Ozone enters plants through leaf stomata. It oxidizes plant tissue, causing changes in biochemical and physiological processes. These biochemical and physiological changes occur within the leaf long before visible necrotic symptoms appear (Guderian et al. 1985). Plants must expend energy to detoxify ozone and repair injured tissue that could otherwise be used for growth or for maintenance of plant health. The injured plant cells eventually die if detoxification and repair cannot keep up with ozone uptake. The mesophyll cells under the upper epidermis of leaves are the most sensitive to ozone, and those are the first cells to die. The adjacent epidermal cells then die, forming a small black or brown interveinal necrotic lesion that becomes visible on the upper surface of the leaf. These visible lesions most frequently begin to develop on leaves that have just become fully matured, with older leaves on a stem showing increased amounts of injury. These lesions, termed oxidant stipple[7], are quite specific indicators that the plant has been exposed to ozone. Other plant symptoms that can result from exposure to ozone, with or without the presence of oxidant stipple, include chlorosis, premature senescence, and reduced growth. However, these symptoms are non-specific for ozone since other stressors (e.g., disease, insects) can also cause them to occur. Further, these non-specific symptoms are difficult to quantify in natural ecosystems, although limited data are available from exposure response experiments to estimate growth losses from specific ozone exposures. In general, the only indicator that a FLM has to document that ozone has impacted vegetation is visible symptoms of injury such as oxidant stipple.

In addition to affecting individual plants, ozone can also affect entire ecosystems. Research shows that plants growing in areas with high exposure to ambient ozone may undergo natural selection for ozone tolerance (EPA 2007b). The final result could be the elimination of the most ozone-sensitive genotypes from the area. Regardless of the amount of ozone exposure, the magnitude of plant response may vary depending on the geographic area because of changes in meteorological and climatic conditions, and differences in plant conditions in space and time. Factors of most importance that influence plant response to ozone are the species/genotype, soil moisture, and nitrogen availability. Other factors influencing plant response to ozone include nutrient status, atmospheric humidity, temperature, solar radiation, phenological stage of development, carbon dioxide concentrations, day length, regional climatic differences, other pollutant interactions, and population/ecosystem interactions (EPA 2007b).

Changes in growth, ecosystem form or function, or biological or genetic diversity caused by ozone have been difficult to document in natural ecosystems. However, recent research in Great Smoky Mountains National Park showed that in years with high ozone, tree growth was

7. Specific symptoms of ozone injury in some plant species are different. A few species develop white or tan rather than brown or black lesions. This is termed "fleck" or "weather fleck" instead of oxidant stipple. In conifers, ozone causes banding of necrotic and green tissue near the tips of older needles, termed "chlorotic mottle."

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significantly reduced and trees had increased rates of water loss (McLaughlin et al. 2007a). Increased water loss resulted in soil moisture depletion and reduced late-season streamflows (McLaughlin et al. 2007b). The experiment was conducted over a range of forest types and included several different tree species. These findings may have implications for climate change. Climate change is predicted to increase temperatures and drought conditions in some areas. Ozone may exacerbate the effects of drought by increasing water loss from trees.

Given the difficulty in determining ozone-induced physiological or growth changes in natural ecosystems, FLMs will utilize as indicators of ozone effects on vegetation (1) symptoms that are clearly ozone induced such as oxidant stipple, and (2) ozone exposures that have been shown to be phytotoxic.

3.4.3. Established Metrics to Determine Phytotoxic Ozone Concentrations (Revised)

EPA has set primary and secondary ozone standards to protect human health and welfare. On March 12, 2008, EPA revised the primary and secondary ozone standards to 0.075 ppm (8-hour standard). On January 6, 2010, the EPA proposed further strengthening of the primary (human health) ozone standard and establishing a new secondary ozone standard to protect ecosystems and sensitive plants (EPA 2010b). For questions regarding site specific issues the applicant is encouraged to consult with the FLM. More detailed discussions regarding other ozone metrics may be available on the respective agency web sites provided in section 3.4.7.

3.4.4. Identification of Ozone Sensitive AQRVs or Sensitive Receptors (Revised)

FLMs have determined that given the high ecological, aesthetic, and intrinsic value of federal lands, special attention should be given to native species. Ideally, protection efforts would focus on the identification and protection of at risk native species in an area. Unfortunately, AQRV identification is limited by incomplete species inventories and/or lack of exposure/response data for most species of native vegetation. Sensitive species identification will improve as more information becomes available. In the meantime, the Agencies are providing lists of sensitive plant species for each Class I area, i.e., those species that have been observed to exhibit ozone symptoms at ambient ozone exposures. This information is available at the respective agency web sites (see below). However, those ambient levels have not necessarily occurred at the specific Class I area where the plants occur.

Since FLAG 2000, the FLMs have acquired additional information regarding ozone effects to vegetation, including lists of ozone sensitive species. Much of this information is included in the NPS and FWS ARIS data base referenced previously, and will be updated as necessary. The ARIS web site is as follows:

- http://www.nature.nps.gov/air/permits/aris/index.cfm

In addition, the NPS has evaluated the risk to vegetation from ozone exposure at approximately 270 park units. The ozone risk assessment can be found at:

- http://www.nature.nps.gov/air/Permits/ARIS/networks/ozonerisk.cfm

Forest Service pertinent ozone information, including a list of ozone sensitive species, can be found at:

- http://www.fs.fed.us/air

3.4.5. Review Process for Sources that Could Affect Ozone Levels or Vegetation in FLM Areas (Revised)

As mentioned above, NO_x and VOC are ozone precursors. States and the EPA have based ozone control strategies in various parts of the country on the determination of which precursor is most likely to influence the formation of ozone. Information suggests that in areas where ozone formation is driven by VOC emissions, i.e., VOC-limited areas, VOC to NO_x ratios are less than 4:1. In VOC-limited areas, minimizing or reducing VOC emissions is the most effective means of limiting or lowering ozone concentrations. Conversely, in NO_x-limited areas, where VOC to NO_x ratios are greater than 15:1, controlling NO_x emissions is most effective. It is generally thought that most rural areas of the U.S. are NO_x-limited, most or all of the time, with the possible exception of the rural areas of southern California. The FLMs do not have current data to show that all areas are not NO_x limited, nor do they consider VOCs to be unimportant as ozone precursors. However, until there is enough information available for FLAG to determine whether ozone formation in each FLM area is primarily limited by NO_x or VOC emissions, we will assume all FLM areas are NO_x-limited and will focus on control of NO_x emissions. Where FLMs have information indicating a specific area is VOC limited, they will shift the ozone protection strategy to focus on VOC rather than NO_x emissions.

The FLMs recognize that oxidant stipple can occur at hourly ozone concentrations that can be considered natural background levels (Singh et al. 1978). Many of the high hourly background concentrations can be attributed to stratospheric intrusions or stratospheric mixing in the upper troposphere (Singh et al. 1978); but stratospheric intrusions rarely occur in the middle and southern latitudes after May (Singh et al. 1980, Wooldridge et al. 1997), and thus do not coincide with the major portion of the growing season.

However, oxidant stipple has been observed on foliage in the spring when these intrusions can occur. In general, oxidant stipple observed on foliage from June through September cannot be attributed to natural background ozone from stratospheric sources. Low levels of ambient ozone may occasionally occur in the troposphere from non-anthropogenic and non-stratospheric sources.

The occurrence of oxidant stipple necrosis on plant foliage may indicate further ozone induced physiological and growth impacts. Point sources emit precursors that could produce ozone at the FLM area, and increased ozone could induce further injury or damage to vegetation. However, we assume that restriction on increases in ozone precursors will prevent additional ambient ozone and subsequent increases in injury or damage to vegetation in FLM managed areas. It is important that ambient ozone monitoring be conducted by the State or Local air pollution control agency or by the FLM to determine the seasonal ozone exposure.

FLM actions or specific requests on a permit application will be based on the existing air pollution situation at the FLM area(s) that may be affected by the source. Some FLMs may, with appropriate documentation, rely on growth loss rather than foliar necrosis to make an adverse impact finding. Each FLM will determine if actions are warranted to limit emissions that might lead to increased ambient ozone, based on the expected impact of ozone in their particular area.

FLM response will depend on whether or not:

- ozone specific vegetation effects have been documented in the area (as evidenced by foliar injury or damage to vegetation);
- ozone exposure levels occurring in the area are high enough that they could affect vegetation (i.e., ozone exposures are at levels shown to be phytotoxic).

For a project that exceeds the initial annual emissions over distance (Q/D) screening criteria, Figure 6 outlines the general FLM review process for responding to NSR permit applications based on ozone exposure and vegetation effects at the receptor site. As noted in Figure 6, ambient ozone concentrations are considered along with data from exposure response studies (EPA 2007b) to determine whether a source will cause or contribute to phytotoxic ozone levels (i.e., levels toxic to plants) at the affected site. The FLM may ask the applicant to calculate the ozone exposure values if these data are not already available. Ozone damage to vegetation is determined from field observations at the impacted site.

Management decisions regarding acceptance of an existing or future ozone exposure will be area-specific and may differ significantly between agencies, or even regionally within agencies. Each FLM will determine if injury and/or damage are necessary to warrant action, based on the expected impact in the area they manage. The decisions are based on the FLM interpretation of regulations, past experience in the NSR arena, availability of ozone effect exposure/response information for species that occur in the area, and other factors. The FLM may also consider current trends in ozone exposures and meteorological conditions during peak ozone exposures (because dry soil conditions may induce plants to close stomates to limit water loss, thus limiting ozone uptake), as well as expected reductions in ozone precursor emissions. The FLM will negotiate with the NSR permit applicant and the permitting authority regarding possible mitigation strategies (e.g., using more efficient emissions control technologies, obtaining emission offsets, etc.).

3.4.6. Further Guidance to FLMs (Revised)

As mentioned above, limited information about ozone exposure/response relationships in plants and lack of an ozone source/receptor model make it difficult to protect FLM areas from the effects of ozone from new sources. However, there are other area-specific gaps in information that also limit protection efforts. It is important for local land managers to attempt to collect the missing information. This section provides guidance specifically to FLMs on what types of data should be collected and how the data could be collected.

Identifying and Monitoring Ozone-sensitive AQRVs

Although many FLM areas have identified ozone-sensitive plant species in their areas, most areas need more details regarding plant species location and abundance. FLAG recommends FLMs gather this information, where needed, and refine their lists of area-specific ozone-sensitive plants. The FLMs have placed ozone sensitive plant species lists for many of their areas in the NRIS-AIR or Air Resources Information System databases.

FLAG recommends that once local FLMs have developed lists of potentially sensitive AQRVs specific for their site, they conduct surveys to detect the presence of ozone-induced foliar injury on the selected species. The USFS Forest Health Monitoring (FHM) Program and the National Park Service Inventory and Monitoring Program have developed foliar injury survey protocols and QA/QC procedures that can be used to collect this information. Another resource is the foliar injury training module developed by the NPS Air Resources Division and The Pennsylvania State University, available at http://www.nature.nps.gov/air/edu/O3Training/index.cfm. This module helps field staff identify and quantify ozone injury symptoms on plant foliage. Field crews should obtain proper training and field experience in identifying foliar injury symptoms before surveys can be conducted.

Ideally, to verify ozone-induced foliar injury symptoms in the field, exposure/response fumigation studies should be conducted on these species, using concentrations that reflect current ambient exposure. Plants should also be tested at

higher exposures, simulating increased levels of ambient ozone that might occur in the future. Due to the expense of constructing and operating such systems, it would be most appropriate for agencies to join resources and develop regional fumigation facilities. At a minimum, such facilities should be constructed both in the eastern and western U.S., since ambient conditions at an eastern facility might not be appropriate for western species and vice versa.

Ambient Ozone Monitoring

Many FLM areas do not currently have either on-site or nearby ambient ozone monitoring data. FLAG recommends that local FLMs make every effort to collect this information and that they use quality-assured ambient ozone monitoring protocols developed by the EPA and the state air quality agency. Continuous monitoring is desirable to determine the temporal dynamics of ozone exposure for vegetation. Unfortunately, continuous monitoring is expensive and requires electric power that is often not available in or near remote FLM areas. When installing a continuous monitor is not an option, FLAG recommends use of passive monitors. Passive monitors give total exposure loading values (SUM00) for a specified period of time. The data are useful for indicating year-to-year changes in total ozone exposure at an individual site, and for indicating where continuous monitors should be installed. However, FLMs recognize the limitation of passive samplers in relating ozone exposure to plant response.

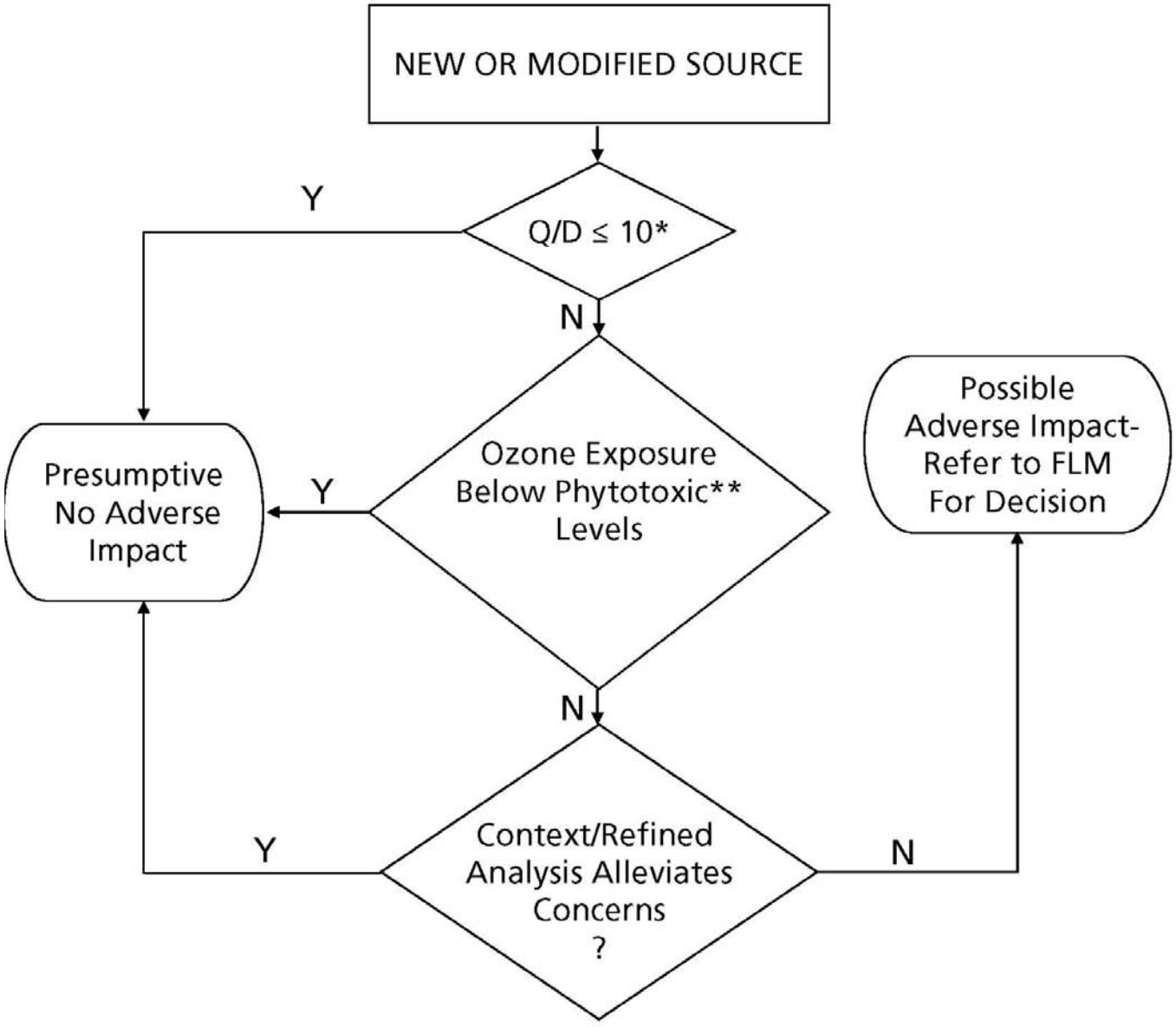

Figure 6. FLM Assessment of Potential Ozone Effects from New Emissions Source (Revised)
*Q/D test only applies to sources located greater that 50 km from a Class I area.
**Note: Ambient ozone concentrations are considered along with data from exposure response studies (EPA 2007b) to determine whether a source will cause or contribute to phytotoxic ozone levels (i.e., levels toxic to plants) at the affected site.

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3.4.7. Ozone Air Pollution Web Sites (Revised)

EPA ozone information:

- http://www.epa.gov/ozone
- http://www.epa.gov/castnet

NPS ozone information:

- http://www.nature.nps.gov/air/permits/aris/index.cfm
- http://www.nature.nps.gov/air/Monitoring/network.cfm
- http://www.nature.nps.gov/air/studies/ecoOzone.cfm

FWS Information:

- http://www.fws.gov/refuges/whm/AirQuality/index.html

U.S. Forest Service information:

- http://www.fs.fed.us/air
- http://www.fs.fed.us/psw/programs/atdep

Ozone effects research, USDA ARS, North Carolina:

- http://www.ars.usda.gov/Main/docs.htm?docid=8453

Ozone exposure metrics for vegetation:

- http://www.asl-associates.com/

3.5. Deposition

3.5.1. Introduction (Revised)

Atmospheric deposition has been studied extensively throughout the world, beginning in the 1800's in England, Sweden, Norway, and Germany. Research has primarily focused on the deposition of acidic pollutants and long-term acidification. Many publications describe current conditions, monitoring and modeling methods, and the results of acidification experiments. In the United States, research on acidification was first begun in 1962 at Hubbard Brook, New Hampshire. Subsequent work in the Adirondack lakes and other areas furthered the understanding of acid deposition effects. It is now recognized that, in addition to causing acidification, deposition of pollutants can affect many ecosystem characteristics, including nutrient cycling and biological diversity.

Although much progress has been made to control sulfur dioxide and nitrogen oxide emissions, deposition of sulfur (S) and nitrogen (N) compounds continues to be a problem in North America and Europe (EPA 2007a). As a result, certain sensitive freshwater lakes and streams continue to lose acid-neutralizing capacity (ANC) and sensitive soils continue to be acidified. Other ecosystems, including forests, grasslands, estuaries, and N-limited lakes exhibit unwanted fertilization and other effects from excess N deposition.

In this section, the Agencies focus on S and N deposition and associated effects to ecosystems, but other potentially damaging pollutants are routinely deposited. For example, mercury emitted from coal-fired powerplants, incinerators, and other sources deposits into ecosystems and accumulates to sometimes toxic levels in fish and wildlife (EPA 1997). EPA sampled fish from over 75,000 lakes nationwide and found that mercury concentrations in large predatory fish exceeded the human health screening value for mercury in nearly half the lakes (EPA 2009b). The Great Waters Program found that, in addition to mercury, airborne toxics including dioxins, furans, polycyclic organic matter, polychlorinated biphenyls (PCBs), and pesticides are deposited widely across the Great Lakes, the Chesapeake Bay, Lake Champlain, and many coastal estuaries, posing ecological and human health risks (EPA 2000a). Even in relatively remote western and Alaska national parks, deposition has increased concentrations of certain toxic compounds in fish and wildlife above health thresholds (Landers et al. 2008).

Federal Land Managers (FLMs) have documented the effects of S and N deposition on many air quality related values (AQRVs). Documented effects include acidification of lakes, streams, and soils; leaching of nutrients from soils; injury to high-elevation spruce forests; changes in terrestrial and aquatic species composition and abundance; changes in nutrient cycling; unnatural fertilization of terrestrial ecosystems; and eutrophication of estuarine and some lake systems. FLMs recognize that other undocumented effects may also be occurring.

The FLAG deposition subgroup was formed to identify common approaches among these agencies for evaluating atmospheric deposition and its effects on AQRVs. In addition, the subgroup was directed to recommend methods for establishing critical deposition loading values ("critical loads") and, where possible, recommend such critical loads for specific areas. These tasks were assigned to Phase I or Phase II, depending on their degree of difficulty.

During the scoping process, the FLAG Deposition Subgroup determined that Phase I tasks would include the summarization of information currently available about deposition and its effects on FLM areas and the development of recommendations on methods to model and evaluate current and future deposition and its effects on AQRVs. In addition, critical load values, where available from previous FLM guidance documents, would be referenced. FLMs agreed that site-specific AQRV and critical load information would be maintained on FLM web sites, rather than included in the Phase I report. In this way, the information can be updated and the most recent versions made quickly available to the public. Some of this information is already available on FLM web sites, and the FLMs are committed to entering remaining available information as soon as possible.

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The subgroup recognizes that the development and refinement of site-specific critical load values for all FLM areas are crucial for AQRV protection. However, because of the complexity of this undertaking, and the lack of information for many areas, it was deferred to future FLAG development.

Future deposition effects work will involve developing methods for establishing critical deposition loading values for FLM areas, and establishing critical loads for areas with adequate information. For areas lacking sufficient information to determine critical loads, strategies will be developed to obtain needed information. Previously established critical loads will be reviewed and refined as necessary. The subgroup will also explore alternative methods for estimating background deposition rates, including extrapolation techniques or modeling that considers the spatial scale of ecosystems and differences in elevation. Methods for addressing problems with dry deposition and cloud and fog deposition measurements will also be considered. In addition, future work may provide research or monitoring recommendations to improve our understanding of deposition and its effects, including effects on cultural resources.

3.5.2. Current Trends in Deposition (Revised)

Title IV of the Clean Air Act was passed by Congress as part of the 1990 Clean Air Act Amendments to reduce emissions of sulfur dioxide and nitrogen oxides from fossil fuel-burning power plants in order to reduce deposition of S and N compounds and protect ecosystems suffering damage from acid deposition. Since the implementation of Title IV, wet sulfate deposition, a major component of acid rain, has significantly decreased. Average annual sulfate deposition in the Northeast in 2000–2002 was 40% lower than it was in 1989–1991, deposition in the mid-Atlantic and Midwest was 35% lower, and deposition in the Southeast was 25% lower (NAPAP 2005).

Wet nitrate deposition, on the other hand, has not decreased regionally from historical levels because of the relatively moderate reduction in nitrogen oxides from power plants and the continuing large contribution (over 50% of total nitrogen oxides emissions) from other sources of nitrogen oxides such as vehicles and nonroad vehicles (NAPAP 2005).

Deposition monitoring data can be used to identify decreases in S and N deposition due to decreases in emissions. The National Atmospheric Deposition Program (NADP) provides one of the best and most comprehensive long-term records of wet deposition chemistry in the U.S. Annual reports on deposition nationwide as well as deposition trend plots for all NADP sites are available at http://nadp.sws.uiuc.edu/. An analysis of long-term trends (1985-2004) in precipitation chemistry from NADP sites across the U.S. found that concentrations of sulfate have decreased in nearly all parts of the country. Nitrate, however, has increased in many areas and ammonium, another component of N deposition, has also increased significantly in many areas, particularly in the West (Lehmann et al. 2005). Publications on trends in deposition are available from NADP at:

- http://nadp.sws.uiuc.edu/lib/

In this chapter, it is assumed that S is deposited into the environment primarily as sulfate ion and N is deposited primarily as inorganic nitrate and ammonium ions. Other ionic forms of S and N occur in the atmosphere, but information on their deposition into ecosystems is limited. For example, organic N in deposition is not routinely measured because of the expense and complexity of the measurements. Organic N includes peroxyacetyl nitrate (PAN) (produced in the atmosphere by nitrogen oxides and hydrocarbon reactions), urea, and amino acids. Both natural and anthropogenic processes contribute to organic N formation, including industry, agriculture, biomass burning, and biological activity. Limited monitoring suggests that organic N deposition varies widely, but on average constitutes about 30 percent of total N (Neff et al. 2002)

3.5.3. Identification and Assessment of AQRVs (Revised)

AQRVs sensitive to pollutant deposition have been identified in various documents published by the USFS, NPS, and FWS, which are listed in the 'General References' of Appendix G of this report. The FLMs have previously used a combination of approaches to identify AQRVs, including national and regional workshops, regional reviews, and site-specific studies. AQRV identification was based on information from peer-reviewed scientific literature and expert judgment. Because information on AQRVs may change as new data become available, the FLMs agree that AQRV information will be made available on FLM web sites to allow for updating and improve accessibility, as discussed in the Introduction to this chapter.

Information on AQRVs for many USFS Class I areas can be found at

- http://www.fs.fed.us/air

The USFS is currently adding to and updating this information.

Information on AQRVs for NPS Class I areas and some FWS Class I areas is available from NPS Air Web at:

- http://www.nature.nps.gov/air

Information on AQRVs for FWS Class I areas is under development at:

- http://www.fws.gov/refuges/whm/AirQuality/index.html

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Table 11. Indicators for monitoring and evaluating effects from deposition of S and N (Revised)

Ecosystem	Indicators for Sulfur Deposition
Freshwater	Chemical change (ANC depression), changes in phytoplankton and benthic community composition, species diversity, biomass
Terrestrial	Leaching of soil cations, soil acidification, mobilization of aluminum ions; Lichen species and vitality
Estuarine	Saltwater not sensitive to S deposition; leaching of nutrients may occur in sandy nearshore soils
Ecosystem	**Indicators for Nitrogen Deposition**
Freshwater	Chemical change (ANC depression), changes in phytoplankton and benthic community composition, species diversity, biomass
Terrestrial	Changes in: litter and soil carbon and N dynamics; biomass; soil N processes; litter decomposition rates; soil microbe functional groups; soil organic matter quality and quantity; soil water chemistry; Lichen species and vitality
Estuarine	Changes in: phytoplankton species composition and biomass; aquatic invertebrates; seagrass health and distribution; nutrient ratios; dissolved oxygen; trophic status

FLMs recommend that permit applicants consult with the appropriate FLM to determine the need for an AQRV analysis and, if applicable, the methods for the analysis.

All FLMs use a similar conceptual approach to identify AQRVs that reflects the FLMs' interest in maintaining the integrity of ecosystem structure and function and protecting the most sensitive ecosystem components. AQRVs can be categorized by the type of ecosystem in which they are found, such as terrestrial, freshwater, and estuarine ecosystems. Each ecosystem and its AQRVs responds somewhat differently to deposition and approaches to evaluating deposition effects must therefore be developed accordingly. In terrestrial ecosystems, detection of changes in production, decomposition, and nutrient cycling processes provide information on deposition stress. In aquatic and estuarine ecosystems, detection of changes in water chemistry and aquatic community composition and structure provide similar information. Table 11 summarizes AQRV indicators that may be used to assess effects in various ecosystems.

Terrestrial, freshwater, and estuarine AQRVs are discussed below. In addition, methods to evaluate S- and N-induced deposition stress are discussed.

Terrestrial Ecosystems

Terrestrial ecosystem AQRVs include flora, fauna, and soils. FLMs have identified, where possible, AQRVs, or characteristics of AQRVs, most likely to be sensitive to S and N deposition ("sensitive receptors"). For example, high-elevation spruce forests may be sensitive receptors. FLMs assess the condition of these sensitive receptors by evaluating some aspect of the receptor (the "sensitive receptor indicator" or "indicator"). For example, an indicator for high-elevation red spruce forests is the occurrence and extent of winter foliar injury. In general, the FLM has focused on deposition effects to vegetation and chemical receptors in terrestrial ecosystems, with little emphasis on fauna. In addition, there is increasing awareness among FLMs that certain soil fauna (e.g., microorganisms and invertebrates) are very sensitive to deposition and can be used as sensitive receptors.

In terrestrial ecosystems, sulfate production is regulated primarily by chemical processes (Johnson et al. 1983) and it is rarely a limiting nutrient. Soil response to acidic deposition can be evaluated by monitoring the leaching of essential soil cations, soil acidification, and mobilization of ionic aluminum. These processes have been studied both in field and laboratory experiments, and are defined in detail in the literature (Mollitor and Raynal 1983; Richter et al. 1983; Johnson et al. 1983; Reuss and Johnson 1986). Effects of S deposition can be detected by monitoring calcium and magnesium ions and S in the litter layer and surface soils; calcium, magnesium, potassium, and sulfate ions in soil solution; cation exchange capacity (CEC); and base saturation.

In general, biological AQRVs do not provide reliable indicators of S deposition in terrestrial ecosystems except under extreme S deposition. Lichens have been used in some areas as biomonitors to demonstrate spatial trends in S deposition, particularly in areas with pronounced S deposition gradients. For example, isotopic analysis of lichens from Mt. Zirkel Wilderness, Colorado, indicated that power plants in the nearby Yampa Valley were the source of elevated S in the lichens (Jackson et al. 1996).

Unlike S, the production and mobility of N in ecosystems is regulated almost entirely by biological processes. N is a limiting nutrient in many terrestrial ecosystems. In these ecosystems, growth of plants is limited by N availability; additional N from atmospheric inputs increases plant growth. Most ecosystems can retain and process significant additions of N, with resulting increases in production and changes in species diversity, biomass, and nutrient cycling. However, these changes are usually considered to be inconsistent with desired ecosystem conditions for natural areas. The ability to retain and process N varies significantly

depending on watershed successional status, site and fire history, soil conditions, vegetation, and other non-human factors. When N inputs exceed an ecosystem's assimilation capacity, N is lost or leached, usually as nitrate, from the soil and can be detected in adjacent streams or lakes. This may occur following a major disturbance such as fire, logging, land use change, grazing, agriculture, or where atmospheric N deposition or experimental inputs exceed what the ecosystem can assimilate (Fenn and Dunn 1989; Fenn 1991, Fenn et al. 1996; Adams et al. 1997).

Studies in northern Europe (Dise and Wright 1995) found that European forests leached detectable levels of nitrate at inputs of about 10-25 kilograms N per hectare per year (kg N $ha^{-}1yr^{-1}$). Tundra and high-elevation alpine sites may leach N at much lower levels of input. Mountain watersheds in the western U.S. show signs of N leakage at wet deposition levels of 3-5 kg N $ha^{-1}yr^{-1}$ (Eilers et al. 1994; Williams et al. 1996; Williams and Tonnessen, in review). However, even high elevation, poorly vegetated ecosystems with limited soil development can process more than 80% of the atmospheric N input before it reaches the aquatic system (Campbell et al. 1995, Kendall et al. 1995). Although nitrogen leaching has often been used as an indicator of excess N deposition, major changes occur in below- and above-ground biomass, species diversity, and nutrient cycling long before N input levels are sufficient to cause nitrate leaching (NAPAP 1993; Tilman et al. 1997; Vitousek et al. 1997). For example, with ambient deposition rates of 7-10 kg N $ha^{-1}yr^{-1}$, a Minnesota Long-Term Ecological Research (LTER) grassland study observed shifts from native, warm-season grasses to low diversity mixtures dominated by cool-season grasses and a greater than 50% decline in species richness (Wedin and Tilman 1996; Tilman et al. 1997). Significant losses in terrestrial diversity may have already occurred over extensive areas of the U.S., particularly in forest understories, shrublands, grasslands, and in soil microbial communities. (Suding et al. 2005; Weiss 2006).

Because significant ecological changes may occur before nitrate loss can be detected, more sensitive indicators than nitrate leaching are needed to evaluate N deposition effects. Such indicators include changes in carbon and N dynamics of litter and soil and biomass (Aber and Driscoll 1997; Magill et al. 1997). With knowledge of inputs and small-scale N fertilization studies, changes in soil organic matter quality and quantity in response to N deposition can be evaluated. Soil microbial communities control the quantity and quality of N available to ecosystems and may be very sensitive indicators of N deposition. Changes in soil microbe functional groups or biomass may provide good estimates of ecosystem critical loads and incremental effects. Soil N mineralization, small root growth, and carbon:nitrogen ratios of soil and microbial biomass are also sensitive to N deposition. Evidence suggests that current deposition rates may alter the production of dissolved organic carbon and organic N compounds in soils, which are important nutrient and energy sources for both terrestrial and aquatic ecosystems (Grandy et al. 2008; Aber et al. 1995; Sinsabaugh et al. 2005). These could also be used as indicators of N deposition effects. However, because there are many other variables that also affect soil processes, it may be very difficult to discern effects on any soil indicators that are solely attributable to N.

Freshwater Ecosystems

AQRVs in freshwater ecosystems include lakes and streams and their associated flora and fauna. Sensitive receptors include water chemistry and clarity, phytoplankton, zooplankton, fish, amphibians, macroinvertebrates, and benthic organisms. Water chemistry indicators that respond to deposition include pH, ANC, conductance, cations and anions, metals, and dissolved oxygen. Physical indicators, such as water clarity, and biological indicators, including species diversity, abundance, condition factor and productivity of fish, amphibians, macroinvertebrates, and plankton can also be used to detect deposition effects in aquatic ecosystems. Much research has been done on the sensitivity of aquatic species to deposition, many of which are discussed in the 1990 National Acid Precipitation Assessment Program (NAPAP) State of Science report (NAPAP 1991a) and the 1998 NAPAP report (NAPAP 1998).

Sulfur is not a limiting nutrient in freshwater ecosystems. However, there are regions of the U.S. where a relatively high percentage of surface water is sensitive to current acidic inputs. These include portions of the Northeast (particularly Maine and the Adirondack and Catskill Mountains), southeastern streams, and some high elevation western lakes, particularly in the Rocky Mountains (NAPAP 2005). There are a number of FLM areas in acid-sensitive regions, including national parks, national forests, and wilderness areas. In these areas, S deposition can cause decreases in ANC and pH. For these sensitive or low-ANC waters, the best approach to quantify S deposition effects is the procedure currently used, monitoring changes in ANC and pH.

Nitrogen deposition, like S deposition, can cause episodic acidification of surface water in certain sensitive high-elevation ecosystems that have low-ANC headwater lakes and streams. Episodic acidification occurs in these areas when deposition is as low as 3-5 kg N $ha^{-1}yr^{-1}$ (Williams et al. 1996).

Estuarine Ecosystems

AQRV sensitive receptors in estuarine ecosystems include plankton, sea grasses, and water chemistry and clarity. Associated coastal forest and dune soils may also be useful as sensitive receptors. Water and soil nutrient concentrations, phytoplankton species composition and abundance, sea

grass health, and dissolved oxygen concentrations can be used to evaluate deposition effects.

In estuaries, S is not a limiting nutrient. In addition, estuarine waters are highly buffered and, therefore, not subject to acidification. However, many coastal forest and dune soils are dominated by sandy soils that are sensitive to leaching of limiting nutrients because of very low cation exchange capacity (Au 1974). Monitoring for change in estuarine areas with high S deposition should therefore focus on soil ion mobility. As soil calcium and magnesium levels are generally adequate because of deposition from marine sources, potassium is likely the only limiting nutrient subject to significant loss by sulfate leaching.

The role of N in estuaries is probably the best-documented example of anthropogenic alteration with a literature record dating back to the 1950s. Production and use of fertilizers, land use changes, and fossil fuel combustion have greatly increased the available N, normally a limiting nutrient, which enters coastal waters (Galloway et al. 2003). This has increased estuarine production and accelerated the process of eutrophication. Eutrophication can result in dramatic algae blooms, anoxia, the production of toxic hydrogen sulfide gas, and species extirpation in estuarine ecosystems. Human induced eutrophication has been documented for many areas along the Atlantic and Gulf coasts, including the Chesapeake Bay, Tampa Bay, Sarasota Bay, Florida Bay, and Long Island Sound.

A number of FLM areas along the Atlantic and Gulf coasts contain significant coastal waters that may be sensitive to eutrophication. Little is known about excess N effects in most of these areas, although eutrophication is well documented in Florida Bay, located in Everglades National Park. Also, recent evidence indicates that coastal waters in Chassahowitzka Wilderness (Florida) experience N-induced algal blooms (Dixon and Estevez in draft). In most coastal waters, 10-45% of the N entering the system is atmospheric, either from direct deposition to surface water or deposition to the watershed. Complete elimination of atmospheric N inputs would not entirely mitigate ecosystem change due to N because of the substantial contributions from agricultural and urban runoff. However, for most estuaries, any reduction in N input would be beneficial in restoring ecosystem structure and function.

The monitoring procedures recommended, and currently used, in estuaries are similar to those used in freshwater, with emphasis on incremental changes in plankton, aquatic plant, benthic, and invertebrate community composition; species diversity, distribution, and biomass; and ecosystem trophic status.

Significance of Long-Term Monitoring to Evaluate Trends and Validate Modeling

Long-term monitoring is critical to evaluate trends in deposition and deposition effects. Monitoring programs should concentrate not only on areas with high past and/or present sulfate, nitrate, or ammonium deposition, but also in areas that are very sensitive to deposition and in areas where deposition is expected to increase. For selected monitoring sites, the FLM should (1) obtain ion deposition data for the site, as from NADP or CASTNet, (2) identify sensitive AQRVs and appropriate variables to monitor, (3) evaluate the present condition of the sensitive AQRVs, (4) determine the degree to which results from one site can be extrapolated to other FLM areas in the region, and lastly (5) implement a long-term monitoring program, using carefully selected variables.

Long-term monitoring data are also needed to support and validate models used to predict deposition and deposition effects, including the effects of increases or decreases of S and N on ecosystems. Long term studies in both aquatic and terrestrial ecosystems such as Hubbard Brook, Lake Tahoe, and the Experimental Lakes Area have provided useful information for modeling (Bormann and Likens 1967; Holm-Hanson et al. 1976; Likens and Bormann 1977, Leonard et al. 1979; Byron and Eloranta 1984; Schindler et al. 1985; Schindler 1987; Schindler et al. 1990; Jassby et al. 1995). NAPAP and the National Science Foundation LTER program have addressed monitoring to meet modeling needs in both terrestrial and aquatic ecosystems.

Data requirements to support models vary, but the quality of input data will determine the quality of a model's predictions. Modeling is further discussed in the 'Other AQRV Identification and Assessment Tools' (see section 3.5.5).

3.5.4. Determining Critical Loads (Revised)

FLAG 2000 introduced the concept of critical loads as it relates to air resource management in Class I areas. Since FLAG 2000 was published, the Agencies have adopted the widely used definition of critical load, "the quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge" (Nilsson and Grennfelt 1988). Critical loads have been widely accepted in Europe and Canada as a basis for negotiating control strategies for transboundary air pollution (Posch et al. 1997).

In Canada, researchers have estimated the critical loads of S in wet deposition necessary to protect moderately sensitive lakes in eastern provinces. That value, equivalent to 6.7 kg $ha^{-1}yr^{-1}$ of S in wet deposition, was used by Canada to argue for the U.S. to implement the Clean Air Act Amendments of 1990, which call for the initial reduction of sulfur dioxide

emissions in the eastern U.S. and later from all electric utilities nationwide. With additional data on lake and stream chemistry available for sensitive systems in Nova Scotia, Ontario, and Quebec, the Canadians are now recommending a more stringent critical load, equivalent to 2.7 kg $ha^{-1}yr^{-1}$ of wet deposition S.

In both European countries and in North America, attention has expanded beyond ecosystem damage caused by S deposition to ecosystem damage caused by N deposition. In some European forests, chronically high N deposition has exceeded the assimilation capacity of local ecosystems, resulting in the release of nitrate into surface waters (Dise and Wright 1995). Watersheds that are leaking nitrate into surface waters during the growing season, are referred to as "N saturated" (Aber et al. 1989). Nitrogen saturation has been linked to forest decline in Europe (Schulze 1989). Based on a set of regional N addition experiments conducted at sites in northern Europe (NITREX), Wright (1995) recommended a N critical load of less than 10 kg $ha^{-1}yr^{-1}$ to protect European forests and fresh waters from N saturation. However, this critical load does not protect ecosystems from the changes caused by N deposition prior to actual N saturation, including shifts in composition and abundance of soil fauna species and alterations in soil chemistry. (Fenn et al. 2003; Driscoll et al. 2003)

In the United States, two states have attempted to set deposition standards or critical loads to protect sensitive ecosystems. In 1982, the State of Minnesota passed the Acid Deposition Control Act to limit wet sulfate deposition to 11 kg $ha^{-1}yr^{-1}$, which is equivalent to 3.7 kg S $ha^{-1}yr^{-1}$. At this sulfate level, precipitation pH was likely to remain above 4.7, which would protect lakes with ANC less than 50 microequivalents per liter (µeq l^{-1}).

In 1989, the California legislature adopted the Atmospheric Acidity Protection Act, which required the Air Resources Board (CARB) to "develop and adopt standards, to the extent supportable by scientific data, at levels which are necessary and appropriate to protect public health and sensitive ecosystems from adverse effects resulting from atmospheric acidity" (CARB 1993). An assessment of existing data identified the high elevation watersheds, surface waters, and mixed conifer forests of the Sierra Nevada and the Los Angeles Basin as sensitive ecosystems. CARB analyses suggested that appropriate standards would include a critical load value for inorganic N to protect forests, and critical loads for both N and S to protect poorly buffered lakes and streams. However, no acidity standards to protect human health or critical loads to protect ecosystems have been set in California to date.

The Clean Air Act Amendments of 1990, Title IV, section 404, called on the Environmental Protection Agency (EPA) to prepare a report on the feasibility and effectiveness of setting deposition standards nationwide to protect sensitive aquatic and terrestrial resources. The completed report includes a number of modeling analyses that project the effect of reductions in both S and N deposition in areas studied during NAPAP. EPA concluded that deposition standards could not be set at this time because of 1) the lack of clearly defined policy regarding appropriate or desired goals for protecting sensitive aquatic or terrestrial resources, and 2) key scientific uncertainties, particularly regarding nitrogen watershed processes. In addition, EPA recognized that a national deposition standard might be inappropriate because of differences among ecosystems. However, in response to public comments on the report, EPA stated that "Given an adequate level of monitoring and assessment data, Class I areas could serve as potential targets for standard setting activities." (EPA 1995)

Since FLAG 2000, other U.S. agencies and organizations have started considering how to work with critical loads. A National Academy of Sciences Report, *Air Quality Management in the United States* (2004), recognized the potential of critical loads for establishing standards to protect ecosystems, prompting the EPA to explore critical loads as an accountability tool to assess ongoing programs. Also, in the 2005 Prevention of Significant Deterioration for Nitrogen Oxides Final Rule, EPA stated it would consider critical loads information from any state as part of their air quality management approach, including whether such an approach satisfies PSD requirements. (EPA 2005.) The U.S. has signed, but not ratified, the European Union's protocol for establishing critical loads, contained in the 1999 *Protocol to Abate Acidification, Eutrophication and Ground-level Ozone (AKA The Gothenburg Protocol)*, available at:

- http://www.unece.org/env/lrtap/multi_h1.htm

In 2006, EPA held the Multiagency Critical Loads Workshop to share information on critical loads and to develop a broad federal strategy for planning, executing, and evaluating critical loads projects, and to consider critical load use in a policy or management framework. As a result of recommendations from the workshop, the Critical Loads Ad-Hoc Committee (CLAD) was formed to foster critical loads science and development. Information on CLAD and the Multiagency Critical Loads Workshop Report are available at:

- http://nadp.sws.uiuc.edu/clad/

In 2008, EPA used critical loads to assess progress under the Acid Rain and related programs. For the analysis, EPA compared critical loads exceedances in Adirondack lakes before and after implementation of acid rain controls (EPA 2009a).

Critical Loads in FLM Areas (Revised)

In the Clean Air Act, as amended in 1977, Congress gave FLMs an "affirmative responsibility" to protect AQRVs in Class I areas from the adverse effects of air pollution.

Congress' intent was, "…In cases of doubt the land manager should err on the side of protecting the air quality-related values for future generations…" (Senate Report No. 95-127, 95th Congress, 1st Session 1977). In an effort to ensure AQRV protection, FLMs have established critical loads for many FLM areas. FLMs agree that a critical load should protect the most sensitive AQRVs within each FLM area and should be based on the best science available. As new scientific information becomes available, critical loads should be reviewed and updated. Critical loads should ensure that no unacceptable change occurs to the resource.

A journal article published in the July 2005 issue of *BioScience*, entitled "Protecting Resources on Federal Lands: Implications of Critical Loads for Atmospheric Deposition of Nitrogen and Sulfur" (Porter, Blett, Potter, Huber 2005) provides an update on the Agencies' perspectives with respect to critical loads. Among other things, the article describes the history of critical loads, the advances in science related to critical loads, and how to apply the concept of critical loads (including some specific case studies). Subsequent articles provide additional information and perspectives on critical loads (Burns et al. 2008; Dennis et al. 2007). These and other articles and reports on critical loads are available from:

- http://www.nature.nps.gov/air/Studies/criticalLoads/index.cfm
- http://www.nrs.fs.fed.us/clean_air_water/clean_water/critical_loads/

FLMs have used a combination of approaches to establish critical loads, including national and regional workshops, regional reviews, and site-specific studies (see Appendix G). In all cases, the FLMs have used peer-reviewed scientific literature and expert judgment to make their decisions. For example, the NPS has compiled regional reviews that have evaluated existing information on air quality, deposition, and effects on AQRVs in national parks. For these reviews, NPS grouped parks by region and ecosystem type, including the Pacific Northwest, the Colorado Plateau, and the Rocky Mountains, and conducted an empirical assessment of the status of aquatic and terrestrial resources. An analysis of deposition effects was done, using current deposition data for S and N and effects information from field observations and research. These reviews provide the basis for critical load development by identifying sensitive resources and impacts to those resources. Park-specific information on sensitive resources, impacts, and critical loads is available at:

- http://www.nature.nps.gov/air/permits/aris/index.cfm

The USFS has conducted a series of national and regional workshops to establish critical loads and concern thresholds. In the late 1980s, the USFS published prototype methods for evaluating the effects of acid deposition on AQRVs (Fox et al. 1989; Fox et al. 1987). Subsequently, the USFS held regional workshops to develop updated and more area-specific screening procedures for new air pollutant emissions sources (Adams et al. 1991; Peterson et al. 1992; Haddow et al. 1998; Peterson et al. 1993; Stanford et al. 1997). These workshops were comprised of national and regional USFS land managers, deposition experts from the academic and air pollution research community, and agency air quality professionals. Dependent on the workshop leadership, each regional workshop followed a slightly different process and a variety of outputs and formats resulted. However, all workshops used a collaborative process to determine S and N deposition rates that would pose a risk to the aquatic and terrestrial ecosystems protected in FLM areas, while addressing the scientific uncertainty inherent in ecosystem response to acidic deposition. Critical load guidelines for many USFS Class I areas are published in the regional workshop reports (see Appendix G) and are available at:

- http://www.fs.fed.us/air

As resources permit, the Agencies will develop methods and a process for establishing critical deposition loading values for all FLM areas and for recommending critical loads for areas where adequate information exists. For areas lacking sufficient information to determine critical loads, the Agencies are developing strategies to obtain needed information.

Current information and links on critical loads work being done by the U.S. Forest Service can be found at the following web site:

- http://www.fs.fed.us/air

The Agencies anticipate using critical loads as they are developed as an assessment tool, and, in concert with the Deposition Analysis Thresholds and Concern Thresholds (see below), a tool for assessing new source impacts. The Agencies also intend to continue to consult with States and the EPA as critical load development work progresses.

3.5.5. Other AQRV Identification and Assessment Tools (Revised)

In addition to AQRV monitoring, there are several tools available to the FLM for identifying AQRVs and assessing the response of sensitive AQRVs to pollutant deposition. These include the Air Resources Information System (ARIS), the Natural Resource Information System – Air Module (NRIS-Air), and deposition models such as the Model of Acidification of Groundwater in Catchments (MAGIC) and MAGIC-With Aggregated Nitrogen Dynamics (MAGIC-WAND).

Air Resources Information System (ARIS)

FLAG 2000 also introduced "Air Synthesis" as an information management and decision-support computer system under development by NPS and FWS. The NPS and FWS have since redesigned and renamed Air Synthesis, now called Air Resources Information System (ARIS). ARIS provides information on air quality related values in NPS and FWS Class I areas, as well as in many NPS Class II areas. Information can be accessed for specific areas or for all units within NPS Inventory & Monitoring (I & M) networks.[8] ARIS identifies specific AQRVs, and provides information on air quality and its effects in parks and wildernesses. ARIS maintains information for all 48 NPS Class I air quality areas and several FWS Class I areas. Information is being developed for the remaining FWS Class I areas, and additional Class II areas. Additional information on ARIS can be found at:

- http://www.nature.nps.gov/air/permits/aris/index.cfm

Information for FWS Class I areas is under development at:

- http://www.fws.gov/refuges/whm/AirQuality/index.html

Natural Resource Information System – Air Module (NRIS-Air)

Publicly available USDA Forest Service Class I and II area information and related resource data can be linked to or found at http://www.fs.fed.us/air. If desired information and data cannot be found, contact any air program manager or specialist at national or regional offices for assistance.

Information from NRIS-Air, including USFS Class I area AQRV information, is available at:

- http://www.fs.fed.us/air

Deposition Effects Models

A number of watershed process models have been developed and tested in an attempt to simulate the effects of S and N on soils, forests, and surface waters. These models are used by FLMs to predict effects from increases in deposition and vary from detailed, compartment models of watersheds to lumped parameter models that do not track different ions through each soil compartment. For a review of models developed under NAPAP see NAPAP 1991.

A commonly applied watershed model is MAGIC. MAGIC was first developed for eastern U.S. watersheds and then extensively tested and validated throughout Europe and North America (Cosby et al. 1985, 1995, 1996). The model was used by NAPAP in its 1990 Integrated Assessment to project surface water chemistry resulting from various deposition scenarios (NAPAP 1991b). In another application in the eastern U.S., MAGIC has been linked with a simple, empirical, dose/response fish model developed at University of Virginia that makes it possible to predict changes in fish productivity based on modeled changes in stream water chemistry.

As a result of NAPAP, there was increased awareness of the potential impacts of inorganic N deposition on watersheds and surface waters. In response, the MAGIC model was updated with a module called With Aggregated Nitrogen Dynamics (WAND). MAGIC-WAND is a process-based model that uses site-specific information on hydrology, soils, and hydrochemistry. The model predicts changes through time in lake or stream chemistry. These time-series of changes in pH and ANC can subsequently be used by FLMs to calculate critical S or N loads for watersheds.

MAGIC-WAND has been extensively tested in the Adirondacks and at watersheds in Maine. For example, the Bear Brook Watershed Manipulation Project uses MAGIC-WAND to predict the effects of experimentally added N and S on a test watershed. MAGIC-WAND has also been applied to watersheds in FLM areas in the Cascades, the Sierra Nevada, the Rocky Mountains, and the Wind River Range in an effort to quantify critical S and N loads to aquatic and terrestrial resources. In the southeastern U.S., MAGIC-WAND is being used under the auspices of the Southern Appalachian Mountains Initiative (SAMI) to predict the effects of future deposition scenarios on FLM areas. Future SAMI modeling efforts will link watershed model results with fish dose/response models. The ultimate goal is to calibrate MAGIC-WAND with landscape level data in order to set regional critical loads.

Other models are also in use. For example, the USFS Rocky Mountain Region recommends using either CALPUFF or AERMOD (or other approved models) to estimate S and N deposition. *The Screening Methodology for Calculating ANC Change to High Elevation Lakes* (USDA Forest Service 2000) summarizes procedures for estimating total deposition of S and N. The document also recommends computations for estimating alkalinity changes in lakes caused by increases in S and N deposition. Another model, the Nutrient Cycling Model (NuCM) has been used in the East to predict the effect of changes in deposition on nutrient concentrations in soils and vegetation.

3.5.6. Recommendations for Evaluating Potential Effects from Proposed Increases in Deposition to an FLM Area (Revised)

FLAG 2000 described a process to help the Agencies and permit applicants assess the total sulfur and/or total nitrogen deposition impacts of proposed new or modified sources.

8. The NPS I & M program consists of over 270 park units organized into 32 networks to conduct long-term natural resource monitoring on park "vital signs," that is, selected physical, chemical, and biological elements and processes of park ecosystems that represent the overall health or condition of the park.

Since that time, the Agencies have refined the concept of using concern thresholds, pollutant exposures, and deposition analysis thresholds in the permit review process. The approaches used by the respective agencies may vary somewhat, but in essence are all similar.

Deposition Analysis Thresholds (DATs)

The NPS and FWS have introduced and developed the concept of Deposition Analysis Thresholds (DATs) to use as screening level values for the additional modeled amount of sulfur and nitrogen deposition within FLM areas from new or modified PSD sources. A DAT is defined as the additional amount of nitrogen or sulfur deposition within an FLM area, below which estimated impacts from a proposed new or modified source are considered negligible. In other words, if the new or modified source has a predicted nitrogen or sulfur deposition impact below the respective DAT, the NPS and FWS will consider that impact to be negligible, and no further analysis would be required for that pollutant. In cases where a source's impact equals or exceeds the DAT, the NPS/FWS will make a project specific assessment of whether the projected increase in deposition would likely result in an "adverse impact" on resources considering existing AQRV conditions, the magnitude of the expected increase, and other factors.

The DATs are based on "naturally occurring deposition" that park and wilderness ecosystems may have experienced prior to anthropogenic influences and are scaled to enable assessment of the impacts of individual sources of air pollution. The DAT established for both nitrogen and sulfur in eastern and western FLM areas and wildernesses is 0.010 and 0.005 kilograms/hectare/year (kg/ha/yr), respectively. More information regarding the sulfur and nitrogen DATs can be found at:

- http://www.nature.nps.gov/air/Pubs/pdf/flag/nsDATGuidance.pdf

While DATs are a tool to assess the impact of a single new source, these levels may not be protective in areas that are already impaired or where there are multiple new sources impacting a single area. The critical load concept, discussed above, may be a more effective tool for assessing cumulative impacts.

Concern Thresholds and Pollutant Exposures

The Forest Service has continued to develop AQRV concern thresholds and pollutant exposure(s) thresholds (for sulfur or nitrogen deposition) that when exceeded may indicate an adverse impact to one or more AQRVs. These thresholds are very similar to the NPS/FWS Deposition Analysis Thresholds (DATs) in that they establish a point below which adverse impacts are not expected. Impacts above the thresholds may or may not cause an adverse impact; depending on current levels of deposition and resource condition. The values for these thresholds vary between FS Class I areas; therefore an applicant will need to check for Class I area-specific thresholds on the following Internet site:

- http://www.fs.fed.us/air/technical/class_1/alpha.php

FLM Response to Potential Deposition Impacts

For a project that exceeds the initial annual emissions over distance (Q/D) screening criteria, the permit applicant should consult with the appropriate regulatory agency and FLM for the affected area(s) to determine if a deposition impact analysis should be done (e.g., expected sulfur and/or nitrogen deposition impacts are above the DAT) or respective concern threshold). For such cases, FLMs request that proponents provide sufficient information for the FLM to evaluate the potential effects of emissions increases on AQRVs. FLMs have provided information to applicants through guidance documents, correspondence, meetings, and phone consultations. This chapter summarizes current information for evaluating new emissions on deposition and sensitive AQRVs and includes recommendations for:

- the types of data, information, and analysis needed before a permit application can be considered complete, including analytical and modeling protocols for a proponent's use in conducting an AQRV impact analysis;
- approaches and sources of appropriate values for estimating wet and dry deposition; and
- permit conditions to mitigate source impacts.

The process begins with the question "Q/D ≤ 10?" as the first level screening criteria (see Figure 7). The next question is whether or not the DAT/concern threshold is exceeded. If not, no adverse impacts are expected. If so, the Agencies will determine if the contextual considerations (see section 4.3) or any refined analyses alleviate any deposition concerns. If not, the Agencies will defer to the FLM to make a case-by-case adverse impact finding. In determining if the proposed action will cause or contribute to an adverse effect to AQRVs, the FLM will consider information on deposition-sensitive AQRVs, deposition loads at which these AQRVs are affected (i.e., critical loads), the current pollutant deposition rates in the area, and the expected impacts from the proposed source. Procedures for estimating the source's impacts are found in 'Estimation of Current and Future Deposition Rates' section of this report. In areas where no information is available, information from a nearby, or ecologically similar area, may be used. An adverse effect may occur if the critical load is exceeded for an area, and the new source impact is above the levels of concern (i.e., DAT/concern threshold). AQRV and critical load information are discussed earlier in this report.

If the available information is insufficient for the FLM to determine if the proposed action will cause or contribute to an adverse effect to AQRVs, the FLM may ask for deposition and deposition effects monitoring and/or

research in the FLM area. If the proposed action will likely cause or contribute to an adverse effect to AQRVs, the FLM may recommend permit conditions that ensure mitigation, including stricter emissions controls and effective emissions offsets. If no mitigation is possible, the FLM may recommend denial of the permit.

Available Deposition Monitoring Data

Atmospheric pollutants are deposited to ecosystems primarily through wet deposition and dry deposition. FLMs participate in national monitoring programs to monitor wet and dry deposition, including the National Atmospheric Deposition Program (NADP) and the Clean Air Status and Trends Network (CASTNet). A 1999 report, "The Role of Monitoring Networks in the Management of the Nation's Air Quality," (CENR, 1999) identified these two networks as being critical for characterizing baseline air quality data in the U.S.

Wet Deposition (Revised)

Wet deposition includes rain, snow, fog, cloud water, and dew. In most FLM areas, rain and snow are the primary contributors to wet deposition. However, in some high elevation areas, fog, cloud water, and dew are significant contributors, as discussed below.

Because rain and snow are the primary constituents of wet deposition at most FLM areas, the FLM generally relies on data from NADP to evaluate wet deposition of pollutants. NADP samplers collect rain and snow and NADP has documented deposition for many years in a nationwide network that currently includes over 220 monitoring

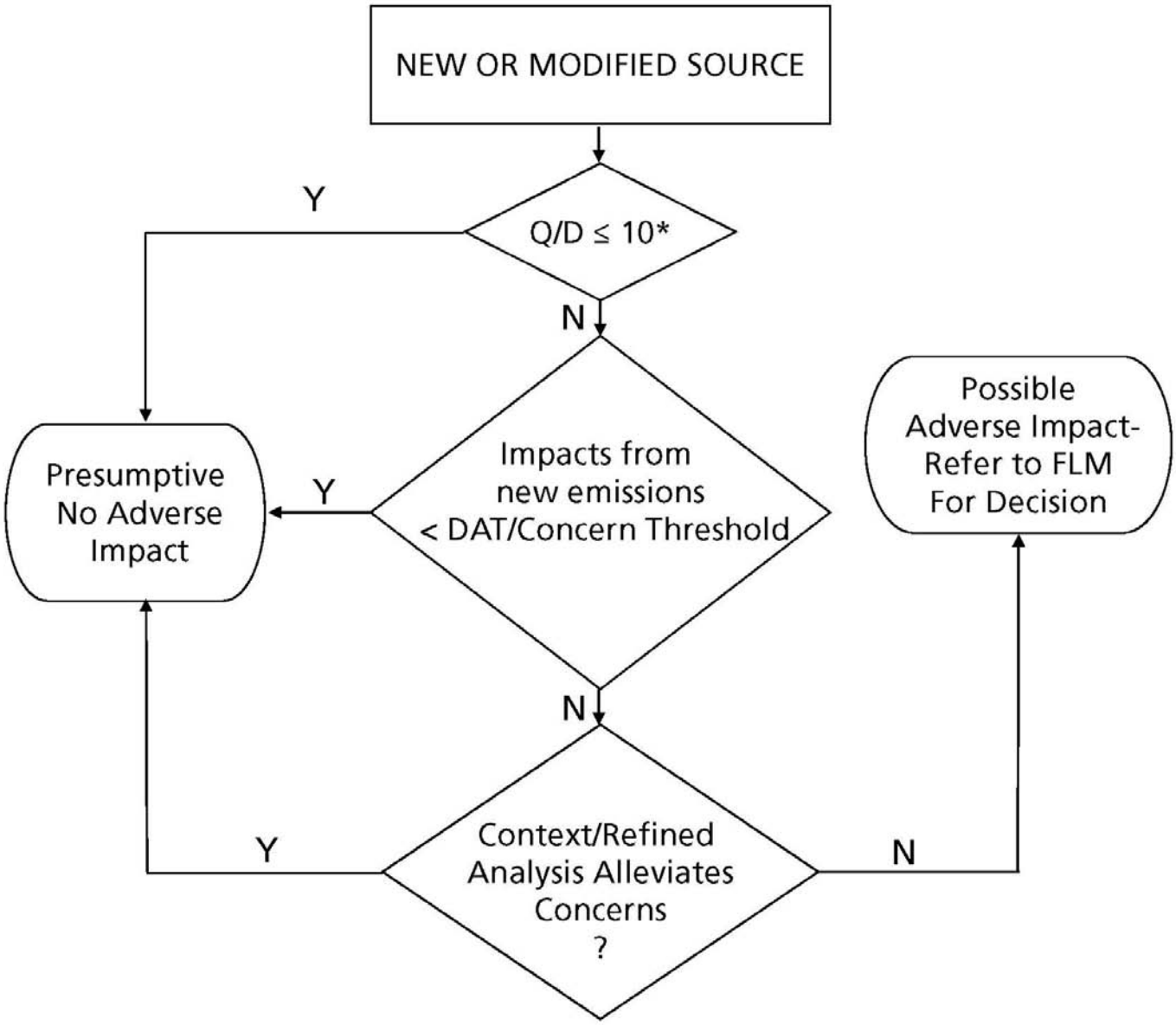

Figure 7. FLM Assessment of Potential Deposition Effects from New Emissions Sources (Revised)
*Q/D test only applies to sources located greater that 50 km from a Class I area.

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sites. The network collects data to evaluate spatial and temporal long-term trends in precipitation chemistry. The precipitation at each site is collected weekly and sent to a central analytical laboratory for analysis of hydrogen (acidity as pH), sulfate, nitrate, ammonium, chloride, and base cations, including calcium, magnesium, potassium, and sodium. Data and isopleth maps of pollutant concentrations and deposition are available on the NADP web site at:

- http://nadp.sws.uiuc.edu/

FLMs agree that it is preferable to obtain NADP data from the web site, rather than summarizing wet deposition data in this report. In this way, current data can be easily accessed by FLMs and the public.

Approximately 50 FLM areas have NADP samplers in or immediately adjacent to them. Because some of these areas are classified as wilderness, FLMs install sampling equipment in adjacent non-wilderness areas in order to preserve the wilderness character of the area. Ambient air in these adjacent areas is considered representative of air in the wilderness area.

A number of FLM areas do not have an NADP sampler in or adjacent to them. Where possible, the FLM has identified an NADP site whose data may be used to characterize deposition at the area. Deposition rates generally increase with elevation and deposition in high-elevation areas may be difficult to characterize with data from a lower-elevation NADP site. FLM consultation may be necessary to estimate deposition in these areas.

Areas that experience significant deposition from fog and cloud water or large amounts of snow may need to use alternate sampling methods and data in addition to NADP protocols and NADP data to characterize them. Wet deposition in these areas may need to be sampled with alternate methods, including cloud water samplers and snowpack sampling or estimated by modeling. At sites where such data or modeled estimates are available, they should be used to calculate total deposition. At mountain sites frequented by clouds and fog, deposition from clouds may equal or exceed that from precipitation. Cloud water is generally more acidic and contains higher concentrations of base cations than rain water; therefore, it can contribute significantly to total loadings of S and N (Hemmerlein and Perkins 1992). Various methods have been developed to measure deposition from cloud water. The Mountain Acid Deposition Program (MADPro) used automated cloud water collectors to sample at three high-elevation eastern sites (Anderson et al. 1999). Forests covered by fog for significant periods of time may be especially susceptible to injury from acid deposition. Acidic cloud water has predisposed red spruce in the high elevations of the northeast U.S. Appalachians to winter injury and cumulative impacts with other biotic and abiotic stresses have caused mortality. The contribution of clouds and fog to deposition at high elevations may overshadow both deposition from precipitation and dry deposition (Hidy 1998). The EPA estimated that as a result of cloud cover, high elevation forests might experience four times the amount of total pollutant deposition as lower elevation forests without cloud cover (NAPAP 1991). High elevation lakes are also impacted by fog and clouds, as well as rain and snow. Measurements in high elevation areas that do not include all contributions to wet deposition will result in under-estimates.

Modeling has been used to estimate total wet deposition in some areas. For example, the Southern Appalachian Man and the Biosphere Cooperative (as part of the Southern Appalachian Assessment) has used NADP data, topographical data, and meteorological data to model wet deposition loading at locations in the southeastern U.S.

Dry Deposition (Revised)

Dry deposition includes gases, aerosols and particles. The primary gases involved with N and S deposition are ammonia (NH_3), nitric oxide (NO), nitrogen dioxide (NO_2), nitric acid (HNO_3), and sulfur dioxide (SO_2), while the primary particles are nitrate (NO_3^-), ammonium (NH_4^+), and sulfate (SO_4^{2-}) ions (Hanson and Lindberg 1991). Ammonia, NO, NO_2 and SO_2 are taken up by plants through stomata, while HNO_3, due to its high deposition velocity, is deposited to plant surfaces in addition to being taken up by stomata. Nitrate, ammonium, and sulfate particles deposit to surfaces (Bytnerowicz and Fenn 1996).

Dry deposition is much more difficult to estimate than wet deposition. The estimation of dry deposition rates requires information on the ambient concentrations of pollutants, meteorological data, and information on land use, vegetation, and surface conditions, all of which are site-specific. Because of this site-specificity, it is difficult to spatially extrapolate dry deposition data as is often done for wet deposition data.

In general, FLMs rely on data from CASTNet for estimates of dry deposition in FLM areas (http://www.epa.gov/castnet). CASTNet was developed by EPA, as a result of the Clean Air Act Amendments of 1990, and currently includes over 70 sites. These include a combination of former National Dry Deposition Network sites, Park Research and Intensive Monitoring of Ecosystems Network sites (PRIMENet), and others. Dry deposition is measured at 26 NPS areas and 2 USFS areas. FLMs agree that it is preferable to obtain CASTNet data from the web site, rather than summarizing dry deposition data in this report. In this way, current data can be easily accessed by FLMs and the public.

Other methods for measuring dry deposition are available. For example, information on vertical changes in concentrations of major gases and particles of interest over plant canopies can be used for calculation of deposition of

these compounds to forests and other ecosystems (Hicks et al. 1987). Models, such as "Big-Leaf" (Baldocchi et al. 1987) allow estimating dry deposition to uniform canopies, such as agricultural crops or lowland forests. However, no models have been developed so far for reliable estimates of deposition of gases and particles to forests and other ecosystems in complex mountain terrain (Bytnerowicz et al. 1997). Therefore, no good large-scale estimates of dry deposition are available for western U.S. forests.

Another approach to evaluating dry deposition is net throughfall technique. By measuring concentrations of ions in throughfall (bulk precipitation) and after subtracting concentrations of the same ions in precipitation in an open area, fluxes of ions such as nitrate, ammonium, and sulfate can be calculated. A branch washing technique is similar to the net throughfall approach and is used when no wet precipitation is present. The pre-washed branches are exposed to ambient air for a certain time period and then carefully rinsed with water (Lindberg and Lovett 1985). Information about amounts of nitrate, ammonium and sulfate rinsed from branches of a known surface area, time of exposure, and leaf area index of a given forest stand allow the calculation of fluxes of the measured ions to trees. Adding stomatal uptake of gases (calculated from information on gas concentration and stomatal conductance), and estimates of deposition to other landscape forms (such as soils and rocks) allow for quite reliable estimates of dry deposition at a forest stand level (Bytnerowicz et al. 2000). Such estimates have been made for the subalpine zone of the eastern Sierra Nevada and mixed conifer forests on the western Sierra Nevada and the San Bernardino Mountains (Bytnerowicz and Fenn 1996; Bytnerowicz et al. 1999). Both the net throughfall and branch washing techniques, although providing relatively accurate estimates of deposition to certain ecosystems, cannot be applied to every type of vegetation. These techniques work well for conifers with relatively thick cuticles. For plants with thinner cuticle, extraction of ions from plant interior or transcuticular uptake of deposited ions may not allow for making good estimates of dry deposition to plant surfaces.

Recent developments, such as passive samplers that allow for relatively inexpensive determinations of nitric oxide, nitrogen dioxide, ammonia, nitric acid and sulfur dioxide concentrations, provide some promising opportunities for large-scale estimates of distribution of these pollutants. This, together with information on landscape-level vegetation coverage, leaf area index, and deposition velocity of the monitored pollutants, will allow calculating deposition of the measured gases to various landscape forms. Although this approach would not include deposition fluxes of particulate pollutants, a large portion of dry N and S deposition (gases) would be covered. Information on fluxes of the N and S particulate component (nitrate, ammonium, and sulfate ion concentrations) can be estimated based on their concentrations from annular denuder/filter pack systems or other comparable techniques and literature values of deposition velocities of these ions.

For many FLM areas, detailed site-specific information and monitoring needed for dry deposition measurements are not available. Therefore, the FLM may choose to recommend a reasonable estimate of dry deposition. NAPAP's 1991 summary report concluded that dry deposition of sulfur is 30-60% of the total (wet plus dry) deposition at regionally representative sites; dry deposition of nitrogen is 30-70% of the total (wet plus dry) deposition at regionally representative sites (NAPAP 1991a). An analysis of one year (1991) of NADP, CASTNet, and IMPROVE (Interagency Monitoring of Protected Visual Environments) data from national parks and wildernesses found that wet deposition dominated total deposition in both the East and the West. Dry deposition of sulfur was 20-50% of the total; dry deposition of nitrogen was 30-60% of the total (Hidy 1998). These estimates, and similar ones, have led to the common assumption that dry deposition is approximately 50% of the total deposition. Therefore, for many FLM areas without on-site or nearby representative dry deposition sampling, the FLM may recommend that dry deposition is equal to wet deposition. The FLM recommends this as a "best available estimate," recognizing that in some areas it may result in under- or over-estimating total deposition. Total deposition, which is the sum of wet plus dry deposition, therefore equals twice the wet deposition.

In summary,

Total Deposition = Wet Deposition + Dry Deposition

Or,

Total Deposition = 2 x Wet Deposition (assuming Dry Deposition = Wet Deposition)

There are numerous monitoring stations in or near FLM areas for estimating wet and dry deposition values. For some areas the FLM assumes that dry deposition equals wet deposition, recognizing that this may result in under- or over-estimates of total deposition. Deposition monitoring data and information on the appropriate dry deposition data to use at sites where data are available are included on the respective Agencies web sites referenced previously.

FLMs will continue to participate in monitoring and research to further our understanding of dry deposition dynamics and improve our measurements of dry deposition.

Other Deposition Measurement Methods

Pollutant deposition, particularly in areas where traditional wet and dry deposition sampling is impractical, can also be estimated by other methods. These methods include bulk samplers that collect both wet and dry deposition and snowpack measurements that estimate the total amount of

pollutants in the snow column at the time of maximum snow accumulation. Special methods have also been developed for collecting fog and cloud water (Anderson et al. 1999).

In addition, methods are being developed to estimate dry deposition rates from pollutant concentrations obtained by IMPROVE fine particle samplers. IMPROVE samplers are located at many FLM areas and expanded coverage is planned for 1999.

Modeling Deposition Rates

Deposition from existing sources can be estimated from deposition monitoring data, but contributions to deposition from the proposed source and other sources permitted but not yet operating should be modeled.

Modeling should be done in accordance with recommendations developed by the Interagency Work Group on Air Quality Modeling (IWAQM) Phase 2:

- http://www.epa.gov/scram001/7thconf/calpuff/phase2.pdf

IWAQM provides the procedures that can be used to estimate S and N deposition from a proposed source and other sources permitted but not yet operating. The FLMs propose that these procedures be used to estimate S and N deposition. For S deposition, the wet and dry fluxes of sulfur dioxide and sulfate are calculated, normalized by the molecular weight of S, and expressed as total S. For N deposition, IWAQM recommends that the wet and dry fluxes of nitric acid (HNO_3) and nitrate (NO_3^-) and the dry flux of nitrogen oxides (NO_x) be calculated, normalized by the molecular weight of N, and expressed as total N. In addition, the FLMs agree that wet and dry fluxes of ammonium sulfate ($(NH_4)_2SO_4$) and ammonium nitrate (NH_4NO_3) should be calculated, normalized by the molecular weight of N, and added to the estimate of total N. Therefore, total N deposition is the sum of N contributed by dry and wet fluxes of HNO_3, NO_3^-, $(NH_4)_2SO_4$, and NH_4NO_3 and the dry flux of NO_x.

The FLMs recognize that the ammonia (NH_3) in these compounds is derived from both man-made and natural sources. Free gaseous NH_3 has a high deposition velocity and tends to deposit quickly. However, if sulfates and nitrates (which are primarily man-made) are present in the atmosphere, free NH_3 quickly reacts to form $(NH_4)_2SO_4$ and NH_4NO_3. These compounds, because of their fine particle size and slower deposition velocity than free gaseous NH_3, can be transported long distances and deposited in a FLM area, adding to the total N deposition loading.

An appropriate estimate of ambient free gaseous NH_3 is needed for the modeling analysis. IWAQM refers to Langford et al. (1992), who suggest that typical (within a factor of 2) background values of NH_3 are: 10 parts per billion (ppb) for grasslands, 0.5 ppb for forest, and 1 ppb for arid lands at 20°C. Langford et al. (1992) provide strong evidence that background levels of NH_3 show strong dependence with ambient temperature (variations of a factor of 3 or 4) and a strong dependence on the soil pH. However, given all the uncertainties in NH_3 data, IWAQM recommends use of the background levels provided above, unless better data are available for the specific modeling domain. IWAQM notes that in areas where there are high ambient levels of sulfate, values such as 10 ppb might overestimate the formation of particulate nitrate from a given source, for these polluted conditions. IWAQM further notes that areas in the vicinity of strong point sources of NH_3, such as feed lots or other agricultural areas, may experience locally high levels of background NH_3.

Questions regarding these recommendations should be resolved through consultation with the appropriate FLM and the appropriate State and/or EPA modeling representative. Applicants should provide a modeling protocol to the appropriate FLM prior to conducting modeling analyses.

Estimation of Current and Future Deposition Rates (Revised)

In order to evaluate a proposed source's contribution to total (wet + dry) deposition in a FLM area, it is necessary to first estimate current pollutant deposition rates. The current rate is a result of deposition from all existing natural and anthropogenic sources. FLMs use two approaches to estimating the current rate of deposition. One approach estimates the current rate by averaging data from an appropriate monitoring site for the pollutant of interest, using all years with complete data records. The second, more conservative, approach assumes that the current rate is equivalent to the highest rate for the pollutant of interest in the data record.

The method for estimating future total deposition rates is:

- From the respective Agency web sites, identify available on-site or representative wet and dry deposition data for the FLM area. Wet deposition data can be obtained through NADP (http://nadp.sws.uiuc.edu/). For NPS sites without an NADP sampler, use estimates of total wet nitrogen and total wet sulfur from the Air Quality Estimates for 1999-2003 at http://www.nature.nps.gov/air/Maps/AirAtlas/index.cfm.

  Dry deposition data can be obtained through CASTNet at (http://www.epa.gov/castnet).

  Verify if dry deposition is assumed to equal wet deposition for the site. For high-elevation sites, consult with the FLM to determine if deposition from cloud water, fog, dew, or snowpack should be considered. For sites without on-site data, consult FLM for further guidance.

- After consulting with the FLM, estimate either:

  - the average annual or seasonal wet and dry deposition rates for the appropriate pollutant using all years with complete data records; or
  - the highest annual or seasonal wet and dry deposition rates for the appropriate pollutant using all years with complete data records.
- Calculate current total deposition (wet + dry = total).
- Estimate, using the appropriate dispersion model as described in the 'Modeling Deposition Rates' section above, the proposed source's contribution to future total deposition on an annual or seasonal basis.
- Estimate, using appropriate dispersion model as described in the 'Modeling Deposition Rates' section above, the contribution of any sources permitted but not yet operating to future total deposition and the affect of any enforceable emission reductions. This estimate may be available from the State permitting authority.
- The current pollutant deposition rate plus the proposed source's contribution to deposition plus the contribution from other sources permitted but not yet operating minus credit for enforceable emission reductions equals the future total deposition rate.

Current + Proposed + Permitted (not yet operating) – credit for enforceable reductions = Future Total Deposition

This future total deposition rate for a given pollutant can then be used to determine the potential for adverse effects to AQRVs. If appropriate, the change in deposition rate can be used to estimate changes in pH or ANC in an ecosystem. If the future total deposition rate is expected to cause an adverse effect to AQRVs and/or exceeds the critical load established for a FLM area, the FLM may recommend mitigation. If no critical load has been established for the FLM area, the FLM will use the best information available in determining whether to recommend mitigation.

3.5.7. Summary (Revised)

- Deposition of S and N has the potential to affect terrestrial, freshwater, and estuarine ecosystems on FLM lands.
- The FLM has identified, where possible, AQRVs sensitive to deposition of S and N on FLM lands and the critical loads associated with those AQRVs.
- A proponent of a source of new emissions with the potential to contribute to S or N deposition in an FLM area should consult with the FLM to determine what analyses are needed to assess AQRV effects. The FLM may request a deposition impact analysis, described in detail in this chapter and summarized below.
  - Estimate the current deposition rate to the FLM area. A list of monitoring sites providing data to characterize deposition in FLM areas is included on the respective Agencies web sites.
  - Estimate the future deposition rate by adding the existing rate, the new emissions' contribution to deposition, the contribution of sources permitted but not yet operating, and then subtracting the credit for enforceable emission reductions. Modeling of new, reduced, and permitted but not yet operating emissions' contribution to deposition should be conducted following current EPA modeling guidance.
  - Compare the future deposition rate with the recommended screening criteria (e.g., critical load, concern threshold, or screening level value) for the affected FLM area. A list of documents summarizing these screening criteria, where available, can be found in Appendix G.

    Information for USFS Class I areas is also available at:

    http://www.fs.fed.us/air

    Information for NPS and FWS Class I areas is available at:

    http://www.nature.nps.gov/air/Permits/ARIS/

    Information for FWS Class I areas is under development at:

    http://www.fws.gov/refuges/whm/AirQuality/index.html

    The appropriate FLM should be contacted for additional information.

3.5.8. Web sites for Deposition and Related Information (Revised)

Clean Air Status and Trends Network (CASTNet) dry deposition data:

- http://www.epa.gov/castnet

National Acid Precipitation Assessment Program 2005 Report:

- http://www.esrl.noaa.gov/csd/AQRS/reports/napapreport05.pdf

National Atmospheric Deposition Program (NADP) wet deposition data:

- http://nadp.sws.uiuc.edu/

National Park Service Airweb:

- http://www.nature.nps.gov/air/

Natural Resources Conservation Service, Snow Water Equivalent Information (SNOTEL):

- http://www.wcc.nrcs.usda.gov/snow

Southern Appalachian Mountain Initiative:

- http://www.tva.gov/sami

USDA Forest Service National Air Resource Management Web Site:

- http://www.fs.fed.us/air/

EPA Office of Air and Radiation:

- http://www.epa.gov/oar

EPA, Deposition to Estuaries:

- http://epa.gov/owow/airdeposition/

EPA, STOrage and RETrieval System for Water and Biological Monitoring Data (STORET):

- http://www.epa.gov/storet

U.S. Fish and Wildlife Service Air Quality Branch:

- http://www.fws.gov/refuges/whm/AirQuality/index.html

U.S. Geological Survey, National Water-Quality Assessment (NAWQA) Program:

- http://water.usgs.gov/nawqa

U.S. Geological Survey, Acid Rain Program:

- http://bqs.usgs.gov/acidrain

U.S. Geological Survey, Water Data Storage and Retrieval System (WATSTORE):

- http://water.usgs.gov/owq/data.html

4. Expansion of Discussion of Process for Adverse Impact Determination (New Chapter)

Based on feedback from permit applicants and State permitting authorities, the Agencies are providing a more detailed description of the adverse impact decision making process once a source analysis has raised concerns during a first-level and any subsequent analyses.

If the first-level analysis yields impacts above the defined threshold(s), the applicant may propose to address preliminary FLM concerns directly through proposed emission reductions for the project, or through implementation of other measures to mitigate emission impacts. Alternatively, the applicant may undertake a more refined analysis to potentially alleviate preliminary concerns. Of course, this refined analysis should occur in a time-frame that enables permitting authorities to adhere to their regulatory guidelines.

Additional emission reductions, mitigation proposals, or more refined analysis are not legal requirements. They are options that can be utilized to help alleviate preliminary FLM concerns about emission impacts on Class I areas. Permit applicants can request that FLMs conduct their evaluation based on information provided in the application.

4.1. Background

The FLAG visibility thresholds have been interpreted by some as a one-dimensional or bright line test that inevitably leads to an adverse impact determination. This, however, is not the intent; these screening-levels were envisioned as a "visibility analysis threshold" similar to the newer deposition analysis thresholds (DATs) discussed above for sulfur and nitrogen deposition.

The Agencies want to emphasize that the FLAG report provides criteria as to when the FLMs will definitively not object to, or declare an adverse impact for, a proposed new source. FLAG assures an applicant that, if they conduct their analyses correctly and demonstrate that change in extinction or deposition falls below the specified thresholds, the FLMs will not raise concerns regarding the project. However, the converse does not necessarily apply — a FLAG threshold exceedance does not mean the FLM will certainly find that a project will adversely affect air quality related values. If a threshold is exceeded, the FLMs will consider the factors discussed below and make a project-specific determination as to whether or not the impacts are adverse.

Seney National Wildlife Refuge, Michigan.
Credit: Atlee Hart

4.2. Regulatory Factors

According to the EPA definition of "adverse impact on visibility," the FLM must determine whether the proposed source's predicted impact "interferes with the management, protection, preservation, or enjoyment of the visitor's visual experience" taking into account the "geographic extent, intensity, duration, frequency and time of visibility impairments, and how these factors correlate with (1) times of visitor use of the Federal Class I area, and (2) the frequency and timing of natural conditions that reduce visibility." (40 C.F.R. §51.301).

Considering the regulatory factors is inherent in the first-level modeling exercise. The model describes the geographic area predicted to be impacted. The visibility extinction values describe the intensity of the impact. Similarly, the model provides some level of assessment regarding duration, frequency, and time of impact. A more refined modeling analysis should further inform consideration of these factors. Regarding how these factors correlate with visitor use, the responsibilities of the Agencies include protecting the resources for all visitors. Visitor data show that nearly all Class I areas have some level of visitation each month. Regarding correlation with the frequency and timing of natural conditions that reduce visibility, the first-level modeling analysis will not provide this information directly, but, by using the percentile approach and monthly relative

humidity values, the Agencies have attempted to provide a reasonable approach to addressing weather impacts.

Similarly, if the sulfur or nitrogen DAT is exceeded, or if high ozone levels are anticipated, the FLMs should determine if those impacts would adversely affect sensitive AQRVs. This adverse impact determination should be made on a project-specific basis and will be largely driven by management objectives for the area.

4.3. Contextual Considerations

The Agencies recognize that the context within which new source permitting occurs is shifting. Many older major stationary sources will be installing pollution controls over the next 10 to 15 years (e.g., in response to the Regional Haze Rule). New motor vehicle emission and fuel standards will reduce tailpipe pollution from mobile sources gradually, but significantly, over a similar time frame. States are developing visibility protection plans that ensure "reasonable progress" toward natural conditions, pursuant to the EPA's Regional Haze Rule. These plans will be reviewed and revised every five to ten years, and thus provide a mechanism for revisiting sources as better technology becomes available or as otherwise needed to maintain progress toward visibility goals. The location and effect of pending pollution control programs on specific Class I areas remains somewhat uncertain; however, the Agencies recognize and appreciate that significant emission reductions are anticipated, especially in the eastern U.S.

As part of the discussions with permitting authorities or permit applicants when screening level thresholds are exceeded, the Agencies will consider contextual information, including, for example:

- Current pollutant concentrations and AQRV impacts in the Class I area
- Air quality trends in the Class I area
- Emission changes that have occurred or would occur (i.e., enforceable) by the time the new source begins operation
- Whether there are approved SIPs that account for new source growth and demonstrate attainment of national ambient air quality standards and "reasonable progress" toward visibility goals
- The expected useful life of the source
- The stringency of the emission limits (e.g., Best Available Control Technology)
- Other considerations such as options put forth by the applicant that would produce ancillary environmental benefits to AQRVs (e.g., reductions in toxic air contaminants, pollution prevention investments)
- Comments received from the public or other agencies during the comment period prior to issuing the permit.

4.4. Preliminary Adverse Impact Concerns

After considering the regulatory factors and contextual considerations listed above, the Agencies, in consultation with the FLM, will evaluate, on a project-specific basis, whether the evidence supports a finding that the new source would possibly cause or contribute to an adverse impact on air quality related values. If so, the Agencies will notify the permit applicant and the permitting agency and provide the permit applicant the opportunity to consider mitigation strategies that will alleviate the potential adverse impact concerns. These strategies may include:

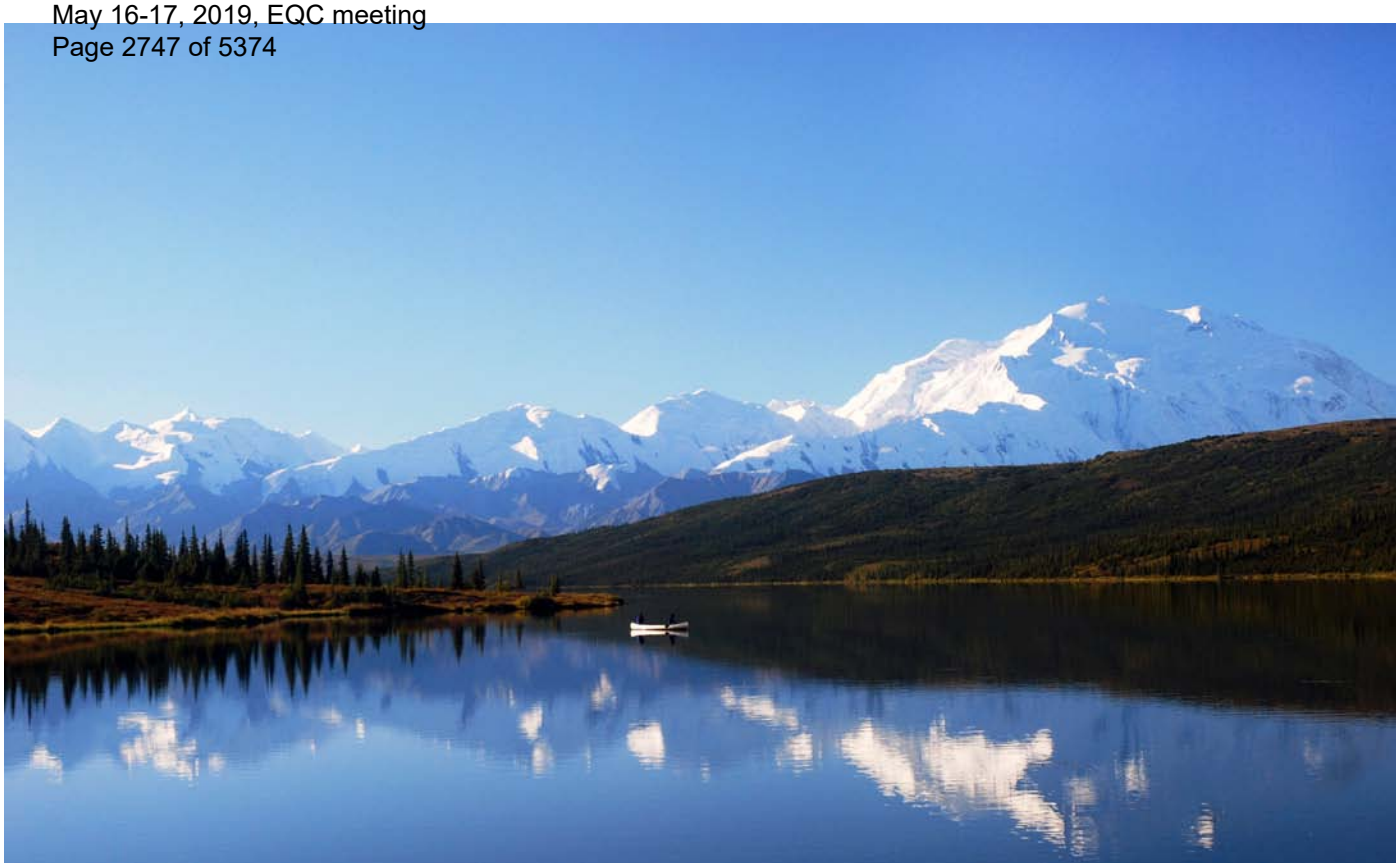
- Obtaining emission offsets for pollutants that cause or contribute to the potential adverse impacts on Class I area resources;
- Reducing emission rates through more stringent pollution control technology or operational or design changes; and
- Monitoring or special studies that increase understanding of how Class I area resources or visitors are affected by air pollution, which may serve as a basis for revisiting permit conditions in future years. (Note: monitoring and study alone does not constitute mitigation.)

Again, proposing any such mitigation strategy is voluntary. Nevertheless, if the FLMs deem a proposed mitigation strategy as adequate to protect AQRVs, and the mitigation strategy is made enforceable via the PSD permit or some other mechanism, the FLM will not make an adverse impact finding with respect to the issues addressed by the mitigation strategy.

4.5. Adverse Impact Determination

If an applicant is unable or unwilling to implement an appropriate mitigation strategy to alleviate potential adverse impact concerns, the FLM will determine whether or not the potential impacts of the project as proposed should be formally deemed adverse to air quality related values in the affected Class I areas. If the FLM concludes that there are potential adverse impacts, he will inform the permitting authority of this decision.

Historically, the FLMs have made adverse impact findings for less that one percent of the permit applications that the Agencies review. In those rare cases, the FLMs will strive to provide the permitting authority with an ample technical and policy/management-related foundation, including a discussion of the analysis results and the regulatory and contextual factors discussed above. The FLMs' ability to provide this foundation will depend on the completeness and adequacy of information provided by the permit applicant. Where information is lacking, or uncertain, the FLMs will err on the side of protecting air quality related values.



Denali National Park and Preserve, Alaska.
Credit: National Park Service/Trey Simmons.

5. Future FLAG Work

5.1. Implementing FLAG Recommendations (Revised)

FLAG participants believe that the recommendations in this revised document should be implemented as soon as possible. Therefore, an attempt has been made to present thorough and clear information on the processes that will be used to protect and improve AQRVs in FLM areas.

Many of the issues and recommendations discussed herein are complex and require specialized knowledge. Consequently, State agencies and others who intend to use this information in NSR/PSD permitting, land planning and use, and other activities, may want or require further guidance and implementation assistance. The Agencies anticipate that much of this guidance and assistance will be provided locally through established formal and informal links between FLMs, States, EPA and others. For example, the Agencies intend to provide further information through their respective web sites, and through participating in related training sessions and/or workshops.

5.2. Phase I Updates (Revised)

This revised *FLAG Phase I Report* is intended to clearly state FLM positions regarding NSR/PSD as it currently exists. As the FLMs learn more about how to better assess the health and status of AQRVs, and as EPA produces new modeling tools, the FLAG report may be revised again. Any such revisions to the report will be announced on the Agencies' web sites.

5.3. Phase II Tasks (Revised)

FLAG Phase I focused on issues that could be resolved relatively quickly, without extensive research or the collection of new data. The FLMs envisioned a Phase II that would address the more complex issues and concerns, including those that may require additional data collection. Unfortunately, lack of available resources has prevented the Agencies from embarking on a formal FLAG Phase II process. Nevertheless, the Agencies continue to gather effects-based information as part of their ongoing resource protection responsibilities. The new information gathered since FLAG 2000 is reflected in this revision. As the Agencies generate additional data or information, they will make that available to interested parties via their respective web sites.

Appendix A: Glossary

The list below contains definitions for some of the terms used in the *FLAG Phase I Report*. These terms are defined in the sense that they relate to the work of the Federal Land Managers (FLMs) in protecting air resources.

For terms whose definition is lengthy or complex, the associated *Code of Federal Regulations* (CFR) section or other reference is cited.

Air Quality Related Value (AQRV). A resource, as identified by the FLM for one or more Federal areas, that may be adversely affected by a change in air quality. The resource may include visibility or a specific scenic, cultural, physical, biological, ecological, or recreational resource identified by the FLM for a particular area.

Adverse Impact on an AQRV. An unacceptable effect, as identified by an FLM, that results from current, or would result from predicted, deterioration of air quality in a Federal Class I or Class II area. A determination of unacceptable effect shall be made on a case-by-case basis for each area taking into account existing air quality conditions. It should be based on a demonstration that the current or predicted deterioration of air quality will cause or contribute to a diminishment of the area's national significance, impairment of the structure and functioning of the area's ecosystem, or impairment of the quality of the visitor experience in the area.

Adverse Impact on Visibility. Visibility impairment which interferes with the management, protection, preservation, or enjoyment of a visitor's visual experience of a Federal Class I or Class II area. This determination must be made on a case-by-case basis taking into account the geographic extent, intensity, duration, frequency and time of visibility impairments, and how these factors correlate with (1) times of visitor use of the Class I area, and (2) the frequency and timing of natural conditions that reduce visibility. This term does not include effects on integral vistas. [40 CFR §51.301(a)]

Absorption. The process by which incident light is removed from the atmosphere and retained by a particle.

Absorption Coefficient. A number that is proportional to the "amount" of light removed from a sight path by absorption per unit distance.

Acidification. The decrease of acid neutralizing capacity in water or base saturation in soil caused by natural or anthropogenic processes.

Aerosol. A mixture of microscopic solid or liquid particles in a gaseous medium. Smoke, haze, and fog are aerosol examples.

Airshed. A geographic area that, because of topography, meteorology, and/or climate, is frequently affected by the same air mass.

AOT40. Sum of all hourly average concentrations after subtracting 40 ppb from each hourly value.

BACT (Best Available Control Technology). The control level (or control measures) required for sources subject to PSD. (See 40 CFR §52.21(b)(12), or 40 CFR §51.166(b)(12)).

Class I Area. As defined in the Clean Air Act, the following areas that were in existence as of August 7, 1977: national parks over 6,000 acres, national wilderness areas and national memorial parks over 5,000 acres, and international parks.

Critical Load. The quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge.

Cumulative. The impact on an AQRV resulting from the total pollutant loading from all sources including the contributing effects of known and reasonably foreseeable new and modified sources of air pollution. A single source may cause individually minor, but cumulatively significant, effects on AQRVs.

Damage. Any reduction in the intended use or value of a biological or physical resource. For example, economic production, ecological structure or function, aesthetic value, or biological or genetic diversity that may be altered by a pollutant.

Deposition Analysis Threshold. A screening threshold developed by NPS and FWS that defines the additional amount of nitrogen or sulfur deposition within an FLM area, below which estimated impacts from a proposed new or modified source are considered negligible.

Emission Offset. A Federally enforceable reduction in emissions from an existing source that mitigates the impacts of a proposed new or modified source on AQRVs, PSD increments, and/or NAAQS. Also, Federally enforceable reductions in actual emissions from existing sources in a nonattainment area such that the total allowable emissions from a new or modified source and existing sources will be sufficiently less than the total emissions from existing sources before the application for a permit to construct so as to represent reasonable further progress towards attainment of the NAAQS. (See 42 U.S.C. § 7503(a)(1)(A))

Extinction. The attenuation of light due to scattering and absorption as it passes through a medium.

Fugitive Emissions. Emissions which do not pass through a stack, chimney, vent, or other functionally equivalent opening.

Federal Land Manager (FLM). The Secretary of the Department with authority over such lands. [40 CFR §51.166(b)(24)] The FLM for the Department of the Interior has been delegated to the Assistant Secretary for Fish and Wildlife and Parks; the FLM for the Department of Agriculture has been delegated to the Forest Service, and has been redelegated to the Regional Forester or individual Forest Supervisor.

Flux. Gaseous uptake into plant tissue.

Green Line. The total pollutant loading (contributions from existing and proposed sources) below which there is a very high degree of certainty that no AQRV will be adversely affected.

Haze. An atmospheric aerosol of sufficient concentration to be visible. The particles are so small that they cannot be seen individually, but are still effective attenuating light and reducing visual range.

Hydrocarbons. Compounds containing only hydrogen and carbon. Examples: methane, benzene, and decane.

Hygroscopic. Readily absorbing moisture, as from the atmosphere.

Injury. Any physical or biological response to pollutants, such as a change in metabolism, reduced photosynthesis, leaf necrosis, premature leaf drop, or chlorosis.

LAER (Lowest Achievable Emissions Rate. The control level required of a source subject to nonattainment review. (See 40 CFR §51.165(a)(1)(xiii))

Limit of Acceptable Change. The amount of change that could occur without significantly altering an AQRV or sensitive receptor.

Micrometer. A unit of length equal to one millionth of a meter; the unit of measure for particle size.

Mie Theory. A complex mathematical model that allows the computation of the amount of energy (light) scattered by spherical particles.

N100. Number of hourly average concentrations ≥100 ppb.

Natural Conditions. Conditions substantially unaltered by humans or human activities. As applied in the context of visibility, natural conditions include naturally occurring phenomena that reduce visibility as measured in terms of light extinction, visual range, contrast, or coloration.

Natural Visibility Conditions. Visibility conditions attributable to Rayleigh scattering and aerosol associated with natural processes.

Nephelometer. An instrument that measures the amount of light scattered.

Nitrates. Those gases and aerosols that have origins in the gas-to-aerosol conversion of nitrogen oxides, e.g., NO_2 ; of primary interest are nitric acid and ammonium nitrate. Ammonium nitrate is very hygroscopic so its contribution to visibility impairment is magnified in the presence of water vapor.

Nitrogen Dioxide (NO_2). A gas consisting of one nitrogen and two oxygen atoms It absorbs blue light and therefore has a reddish-brown color associated with it.

Nonattainment Area. An area designated by the EPA Administrator pursuant to Section 107(d) of the Clean Air Act as having air quality which does not meet one or more National Ambient Air Quality Standard (NAAQS). For a list of nonattainment areas, see 40 CFR Part 81, Subpart C.

Oxidant Stipple. Small brown or black interveinal necrotic lesions on the adaxial surface of leaf tissue that can be attributed to exposure to ozone.

Phytotoxic. Poisonous to plants.

Post-Construction Monitoring. Monitoring required as a permit condition that the permitting authority considers necessary to determine the effect emissions from a stationary source may have, or are having, on the air quality or on the AQRVs of an area. Such monitoring includes both "ambient" monitoring and "AQRV" monitoring and may involve short-term and long-term measurements made at locations representative of the greatest expected impacts.

PSD Increments. The maximum increases in ambient pollution concentrations allowed over baselines concentrations. See 40 CFR §51.166 (c) for increments for specific pollutants.

RACT (Reasonable Available Control Technology). The lowest emissions limit that a particular source can meet by the application of control technology that is reasonably available considering technological and economic feasibility.

Rayleigh Scattering. The scattering of light by particles much smaller than the wavelength of the light, e.g., molecular scattering in the natural atmosphere.

Reconstructed Extinction. Extinction estimate that results from summing up the product of the mass of each measured particle species and the appropriate absorption or extinction coefficient.

Red Line. The total pollutant loading (contributions from existing and proposed sources) at which there is a very high degree of certainty that at least one AQRV will be adversely affected.

Regional Haze Visibility Impairment. Any humanly perceptible change in visibility (light extinction, visual range, contrast, coloration) from that which would have existed under natural conditions, caused predominantly by a combination of many sources from, and occurring over, a wide geographic area.

Re-opener. A permit condition that requires the permitting authority, at a specified time after permit issuance, to review and revise, if necessary, the permit based on new information such as the findings from post-construction monitoring, updated emissions inventories, updated modeling, research, or information on air pollution effects to terrestrial, aquatic, and visibility resources.

Scattering. An interaction of a light with an object (e.g., a fine particle) that causes the light to be redirected in its path.

Scattering Coefficient. Measure of the ability of particles to scatter light; measured in number proportional to the "amount" of light scattered per unit distance.

Screening Level or Screening Level Value (SLV). The concentration or dose of air pollution below which estimated impacts from a proposed new or modified source are considered insignificant. The SLV is dependent on existing air quality and on the condition of the AQRV of concern.

Sensitive Receptor. The AQRV, or part thereof, that is the most responsive to, or the most easily affected by the type of air pollution in question. For example, at Great Smoky Mountains National Park, spruce-fir forest is a sensitive receptor of the AQRV flora.

Sensitive Receptor Indicator. A measurable physical, chemical, biological, or social (e.g., odor) characteristic of a sensitive receptor. For example, for the sensitive receptor, Crater Lake, water clarity is a sensitive receptor indicator.

Stationary Source. A source of pollution that is well defined, such as the smokestack of a coal-fired power plant or smelter.

Sulfates. Those aerosols that have origins in the gas-to-aerosol conversion of sulfur dioxide; of primary interest are sulfuric acid and ammonium sulfate. Sulfuric acid and ammonium sulfate are very hygroscopic so their contribution to visibility impairment is magnified in the presence of water vapor.

Sulfur Dioxide (SO_2). A gas consisting of one sulfur and two oxygen atoms. Of interest because sulfur dioxide converts to an aerosol.

SUM00. The sum of all hourly average concentrations above 0 ppb.

SUM06. The sum of all hourly average concentrations at or above 60 ppb.

Target Load. The acceptable concentration or dose of an air pollutant that provides a reasonable margin of safety below the critical load. The target load should be achievable under existing conditions.

Transmissometer. An instrument that measures the amount of light extinction over a fixed, specified path length.

Visibility Impairment. Any humanly perceptible change in visibility (visual range, contrast, coloration) from that which would have existed under natural conditions. [40 CFR §51.301(x)]

Visual Range. The distance at which a large black object would just disappear from view.

Volatile Organic Compound (VOC). Any compound of carbon, except those excluded by EPA that participates in atmospheric photochemical reactions. (See 40 CFR §51.100(s))

W126. An ozone index that multiplies each specific concentration by a sigmoidal weighted function, then sums all values. $Wi = 1/[1 + Me^{-(A \times Ci)}]$, where M and A are constants 4403 and 126 ppm^{-1}, respectively, w_i is the weighting factor for c_i, and c_i is concentration in ppm.

Appendix B: Legal Framework for Managing Air Quality and Air Quality Effects on Federal Lands

Introduction

The regulation of air pollution sources has clearly been delegated to EPA, and as applicable, the States. However, Federal Land Managers (FLMs) have the responsibility to protect the particular values of the lands over which they have jurisdiction, to the extent they have been delegated the authority, from the adverse impacts of activities inside and outside these areas.

This Appendix sets out the basic legal authorities and responsibilities with which the FLMs comprising FLAG must comply, in addition to those authorities which they can utilize to protect AQRVs on public lands.

For the purposes of this Appendix only, the term "public lands" is defined to include units of the National Park, National Wildlife Refuge, and National Forest Systems.

Agency Organic Acts

Department of the Interior: National Park Service (NPS):

This Organic Act is very specific in that it mandates national park unit managers:

[T]o conserve the scenery and the natural and historic objects and wild life therein and to provide for the enjoyment of the same in such manner and by such means as will leave them unimpaired for the enjoyment of future generations.

16 U.S.C. §1(1997); and

[T]he authorization of activities shall be construed and the protection, management, and administration of these areas shall be conducted in light of the high public value and integrity of the National Park System and shall not be exercised in derogation of the values and purposes for which these various areas have been established, except as may have been or shall be directly and specifically provided for by Congress.

16 U.S.C. § 1a-1 (1997)

Department of the Interior: Fish and Wildlife Service (FWS):

With respect to National Wildlife Refuge System lands (Refuge System lands under the jurisdiction of the United States Fish and Wildlife Service (FWS)), FWS managers are required to manage Refuge System lands so to:

[E]nsure that the biological integrity, diversity, and environmental health of the System are maintained for the benefit of present and future generations of Americans.

16 U.S.C. §668dd(a)(4)(B)(1997)

Department of Agriculture: Forest Service (Forest Service)

National Forest System lands are defined as:

[A]ll National Forests reserved or withdrawn from the public domain of the United States, all national forests acquired through purchase, exchange, donation, or other means, all national grasslands and land utilization projects...and all lands waters, and other interests administered by the Forest Service.

16 U.S.C. §1609(a)(1997)

The Forest Service's Organic Administration Act of 1897 directs the Secretary of Agriculture to:

[M]ake provisions for the protection against destruction by fire and depredations upon the public forests and national forests...

16 U.S.C. Sec. §551(1997)

The National Forest units are managed consistent with Land and Resource Management Plans (LRMPs) under the provisions of the National Forest Management Act (NFMA). 16 §U.S.C. 1604 (1997). Any measures addressing AQRVs on National Forest System lands will be implemented through, and be consistent with, the provisions of an applicable LRMP or its revision (16 U.S.C. §1604(i)).

The Secretary of Agriculture is required by law to prepare a Renewable Resource Assessment by 1979, and every 10 years thereafter. By law this Assessment is required to address:

- A description of Forest Service programs in research, cooperative programs and management of the National Forest System, their relationships, and the relationships of these programs and responsibilities to public and private activities; and
- An analysis of the potential effects of global climate change on the condition of renewable resources on the Forests and rangelands of the United States; and
- An analysis of the rural and urban forestry opportunities to mitigate the buildup of atmospheric carbon dioxide and reduce the risk of global climate change.

16 U.S.C. §1601(a) (1997)

In addition, the Secretary of Agriculture is required to prepare and transmit to the President, a Renewable Resource Program (the Program) every 5 years. This Program must include program recommendations which reflect the fundamental need to protect, and where appropriate,

improve the quality of . . . air resources. 16 U.S.C. §1602(5)(C).

The Forest Service's implementing regulations for NFMA are found at 36 C.F.R. §219 et seq. LRMPs are, in part, specifically based on:

[R]ecognition that the National Forests are ecosystems and their management for goods and services requires an awareness and consideration of the interrelationships among plants, animals, soil, water, air, and other environmental factors within such ecosystems.

36 C.F.R. §219.1(b)(3)

The Wilderness Act. 16 U.S.C. §1131 (1997)

AQRVs in Wilderness areas may receive further protection by the language of the Wilderness Act itself which states:

Wilderness areas... shall be administered for the use of the American people in such a manner as will leave them unimpaired for future use and enjoyment as wilderness .... (16 U.S.C. Sec. §1131).

For Wilderness Areas in the National Forest System, the Act's implementing regulations are found at 36 C.F.R. §293. These Wilderness Areas shall be administered:

...[For] such other purposes for which it may have been established in such a manner as to preserve and protect [their] wilderness character. In carrying out such purposes, National Forest Wilderness resources shall be managed to promote, perpetuate, and, where necessary, restore the wilderness character of the land...

36 C.F.R. §293.2 (1997)

The Clean Air Act, 42 U.S.C. §7401 et seq.

Because of a perceived need for national and regional air quality research to support State programs, Congress passed its first federal air quality initiative in 1955. (Air Pollution Control Act of 1955, Ch. 360, 69 Stat. 322). In response to increasing harm to public health and welfare and to inadequate controls and enforcement, Congress has slowly but steadily expanded and refined the law, now known as the Clean Air Act (CAA), to cover more types of pollutants and emitters; e.g., stationary and mobile sources of pollution. These efforts have culminated in the 1990 Amendments to the CAA, which represent the most comprehensive and detailed set of measures to date to both prevent and curtail air pollution.

The declaration of purpose, as revised in 1990 states in part:

The purposes of this subchapter are: to protect and enhance the quality of the Nation's air resources so as to promote the public health and welfare and the productive capacity of its population.

42 U.S.C. § 7401(b)(1); and

A primary goal of this Act is to encourage or otherwise promote reasonable Federal, State, and local government actions, consistent with the provisions of this Act, for pollution prevention.

42 U.S.C. §7401(c)

The CAA provides an additional legal framework for FLMs to preserve and protect AQRVs from pollution sources emanating both within and outside National Park, Forest, and Refuge boundaries.

National Ambient Air Quality Standards (NAAQS) and State Implementation Plans (SIPs):

The CAA establishes a regulatory program with the goal of achieving and maintaining "national ambient air quality standards" (NAAQS) through state or, if necessary, federal implementation plans (SIPs or FIPs).[1]

The U.S. Environmental Protection Agency (EPA) is charged with promulgating:

- "primary" NAAQS for "criteria" pollutants "to protect the public health," allowing an adequate margin of safety;" and
- "secondary" NAAQS "to protect the public welfare from any known or anticipated adverse effects associated with the presence of such air pollutant in the ambient air."[2]

The above secondary standards may help protect public land AQRVs.[3] To date, EPA has promulgated NAAQS for six criteria pollutants: sulfur dioxide, particulate matter, nitrogen dioxide, carbon monoxide, ozone and lead. In 2006, EPA issued revised, and more stringent NAAQS for "fine particulate matter." In 2008 EPA revised the ozone standard, to address human health and welfare concerns. In 2010, EPA promulgated one-hour standards for nitrogen dioxide and sulfur dioxide. However, EPA openly acknowledged that these revised NAAQS were not fully adequate to protect the above "secondary" values, in particular those sensitive AQRVs on public lands. EPA proposed further revisions to the primary and secondary ozone standards in January 2010 and is currently developing a proposal for secondary NO_x and SO_x standards that are intended to address aquatic acidification due to acid deposition.

Prevention of Significant Deterioration (PSD):

The CAA, as amended in 1977, includes the following major purposes regarding the "prevention of significant deterioration" (PSD) provisions:

[T]o protect public health and welfare from any actual or potential adverse effect . . . from air pollution . . .

notwithstanding attainment and maintenance of all national ambient air quality standards.

42 U.S.C. § 7470(1)

[T]o preserve, protect, and enhance the air quality in national parks, national wilderness areas, national monuments, national seashores, and other areas of special national or regional natural, recreational, scenic, or historic value.

42 U.S.C. §7470(2)

The PSD section provides some protection for park and wilderness AQRVs through establishment of ceilings on additional amounts of air pollution over baseline levels in clean air areas (increments). It requires EPA or the State to provide to the FLM notice of any proposed major emitting facility[4] whose emissions may affect a Class I area (42 U.S.C. §7475(d)(2)(A), and also by charging:

[T]he Federal Land Manager[1] and the Federal official charged with direct responsibility for management of such lands with "an affirmative responsibility to protect the air quality related values (including visibility) of any such lands within a class I area and to consider, in consultation with the Administrator, whether a proposed major emitting facility will have an adverse impact on such values.

42 U.S.C. §7475(d)(2)(B).

Class I areas include national parks larger than 6,000 acres and national wilderness areas and national memorial parks which exceed 5,000 acres, in existence on August 7, 1977. The 1990 Amendments provided that subsequent additions to the boundaries of such areas are also Class I areas. Currently, 48 areas in the National Park system, 21 Refuge System units, and 88 areas under the administration of the Forest Service are designated as Class I.

Under the PSD provisions and implementing regulations (40 C.F.R. §51.166(p)), for Class I areas, once baseline concentrations come under review by submission of a PSD preconstruction permit application for a major new or modified emissions source, only the smallest increment of certain pollutants — sulfur dioxide, nitrogen oxide and particulate matter — may be added to the air by the proposed new source, and other "increment consuming" sources.

Under the PSD provisions a FLM has several tools he/she may use to protect AQRVs.

A state may not issue a PSD permit to allow construction or modification of a major emitting facility when the applicable Federal Land Manager files a notice alleging the facility may cause or contribute to a change in the Class I area's air quality and by identifying the potential adverse impact of such a change, unless:

The facility owner demonstrates that the facility's emissions of particulate matter, sulfur dioxide, and nitrogen oxides will not cause or contribute to concentrations which will exceed the maximum allowable increases for that Class I area.

42 U.S.C. §7475(d)(2)(C)(i)(paraphrased) and 42 U.S.C. §7476.

Even if no increment violation is predicted,

[T]he state may not issue a PSD permit, if the Federal Land Manager demonstrates to the satisfaction of the State that the emissions from such facility will have an adverse impact on the air quality-related values (including visibility) of Class I lands.

42 U.S.C. §7475(d)(2)(C)(ii)(paraphrased)

Neither the CAA nor the implementing regulations specify criteria for the FLM to "satisfy" state permitting agencies. Consequently, some states have taken a liberal view of their discretion to reject an FLM's adverse impact determination. However, EPA's Environmental Appeals Board (the Board) has ruled that state discretion in rejecting a FLM's finding of adverse impacts is not "unfettered" (see the Board's decisions regarding the permit appeals for the Old Dominion Electric Cooperative and Hadson Power projects in Virginia). Nevertheless, the appropriate role of the FLM in the PSD permit process was addressed in EPA's 1996 proposed New Source Review Reform regulations. The final regulations have not yet been promulgated.

Visibility Protection. Subpart II, 42 U.S.C. §7491 et seq. (1997)

The Visibility portion of the CAA:

"... [D]eclares as a national goal the prevention of any future, and the remedying of any existing, impairment of visibility in mandatory class I Federal areas which impairment results from man made air pollution."

42 U.S.C. §7491(a)(1).

To help carry out this goal, the Secretaries of the Interior and Agriculture are charged with identifying Class I areas where visibility is an important value. EPA is charged with reporting to Congress on methods to implement the national goal and with promulgating regulations to ensure reasonable progress toward meeting the goal.

In 1980, EPA issued enforceable regulations for visibility impairment "reasonably attributable" to a specific source or small group of sources. In particular, major stationary sources emitting any pollutant which may "reasonably be anticipated to cause or contribute to any impairment of visibility" is required to install best available retrofit technology (BART). In addition, in April 1999 EPA promulgated final regulations addressing regional haze.

The regional haze rule protects air quality in Class I areas by requiring States to plan to achieve "natural" visibility conditions over a 60-year time frame.

The 1990 Amendments added a new section on visibility, which authorizes EPA in conjunction with NPS and other federal agencies, to conduct visibility research and to evaluate clean air corridors and emissions sources and source regions causing visibility impairment in Class I areas. In this regard, EPA was required to establish the Grand Canyon Visibility Transport Commission (GCVTC) by 1991 and consider the recommendations GCVTC would make (42 U.S.C. §7492(f). NPS, FS, FWS, and BLM played a vital role in the work of the GCVTC and committees in an effort to improve air quality in the Grand Canyon and other parks and wilderness areas in the "Golden Circle" on the Colorado Plateau.

As part of the visibility protection process, states are required to promulgate a plan to prevent any future, and remedy any existing impairment of visibility in Class I areas... 40 C.F.R. §51.300 (1997). EPA has defined "visibility impairment" as:

[A]ny humanly perceptible change in visibility (visual range, contrast, coloration) from that which would have existed under natural conditions.

40 C.F.R. §51.301(x)(1997).7

However, EPA has promulgated its visibility regulations to allow FLMs to use their existing authorities to address "visibility impairment" (rather than "significant impairment") so that "the affected Federal Land Manager may certify to the State, at any time, that there exists impairment of visibility in any mandatory Class I Federal area." 40 C.F.R. §51.302(c).

Nonattainment Areas, 42 U.S.C. §7501 et seq.:

Areas that have failed to meet NAAQS for one or more criteria pollutants are designated as "nonattainment" areas. Under the 1990 Amendments, Congress provides for further classification of nonattainment areas based on severity of the nonattainment and availability and feasibility of appropriate pollution control measures and for a compliance schedule ranging from 1993 in marginal nonattainment areas to 2010 for Los Angeles.

The 1990 Amendments authorize EPA to issue control technique guidance documents (CTGs) covering a variety of topics, such as control of idling vehicles and voluntary removal of pre-1980 model year light duty vehicles (cash for clunker programs). (42 U.S.C. §7408.) EPA is authorized to issue CTGs, in lieu of regulations, to reduce "volatile organic compounds" (VOC) emissions from any consumer or commercial product. (42 U.S.C. §7511b.)

Proposed new or modified major stationary sources within nonattainment areas are required to meet emissions limits based on "lowest achievable emission rate" technology (LAER) and may be constructed only if their emissions are sufficiently offset by reductions in emissions from other sources. The 1990 Amendments also require analysis of alternative sites, sizes, production processes, and control techniques and a finding that the benefits of the source outweigh its environmental and social costs. (42 U.S.C. §7501-15.)

General

CAA Subchapter III 42 U.S.C. §7601 et seq. contains definitions, requirements for reports to Congress, authorizations for appropriations, and procedures for EPA rule making and judicial review. Citizen suits are authorized: 1) against EPA for failure to perform a nondiscretionary duty under the CAA, or 2) against others for alleged violations of an emission limitation, standard, or order. (42 U.S.C.§7601 et seq.)

Acid Deposition

The 1990 Amendments add Title IV, which contains requirements for electric utilities to reduce emissions associated with acid rain. To reduce the adverse effects of acid deposition, Title IV requires a reduction in annual emissions of sulfur dioxide of ten million tons from 1980 emission levels and a reduction of nitrogen oxides emissions of approximately two million tons from 1980 emission levels, in the 48 contiguous states and the District of Columbia. (42 U.S.C. §7651.) The Title creates a system of market-based emission allowances, which can be traded among sources. See (42 U.S.C. §7651a-o.)

Operating Permits

The 1990 Amendments add Subchapter V, 42 U.S.C. §7661 et seq., which establishes a nation-wide permit program for existing stationary sources. Permit requirements will include emission limitations. EPA may veto state permits, which do not comply with provisions of the CAA. (42 U.S.C. §7661a-f.)

Conformity, 42 U.S.C. §7506 (1997)

(Paraphrased) No federal agency may engage in, support in any way,... license or permit, or otherwise approve any activity which does not conform to an approved state (or federal) implementation plan. Conformity shall be an affirmative responsibility of the head of each agency. Conformity means:

- Conforming to the SIP's purpose of eliminating or reducing the number of NAAQS violations;
- That any such activities will not:
  - Cause or contribute to new violations in any area; or

- Increase the frequency or severity of any existing standard violation...

EPA, in its "criteria and procedures" for implementing "conformity" has decided that only those activities that "a federal agency can practicably control, and will maintain control over due to a continuing program responsibility" are subject to same. 40 C.F.R. §93.152.

Although required to comply with the conformity provisions (42 U.S.C. §7618(1997)), the FLM cannot use these provisions to protect AQRVs from adverse impacts from off site sources.

Impact on Federal Land Managers

The CAA reinforces the FLMs' Organic Act and Wilderness Act roles as protectors of AQRVs on public lands.

The CAA also imposes on FLMs an obligation to comply with the Act's many provisions regarding the abatement of air pollution to the same extent as any private person (42 U.S.C. §7418).

Thus, under various authorities, FLMs are responsible for protecting AQRVs within their respective unit boundaries and taking appropriate action to do so, when reviewing emission sources both within units, and in proximity to unit boundaries.

FLMs, under the CAA, have an affirmative responsibility for protecting AQRVs (including visibility) in reviewing proposed PSD permits. However, because of the uncertainty involved in "satisfying" State permitting agencies in the PSD process, and the appropriate delegated role for FLMs in non-PSD situations, the existing framework may provide an inadequate means for FLMs to protect AQRVs from adverse impacts caused by sources outside unit boundaries.

Endnotes

1) Clean Air Act, 42 U.S.C. §7401-7671q (as amended 1990).

2) *Clean Air Deskbook*, The Environmental Law Reporter, Environmental Law Institute, 1992.

3) *Managing National Park System Resources: A Handbook on Legal Duties, Opportunities, and Tools*, Chap. 4 "The Clean Air Act" by Molly Ross at pp. 51-65, The Conservation Foundation, 1990.

4) *Atmospheric Environment* Vol. 27B, No. 1, "The 20-Year History of the Evolution of Air Pollution Control Legislation in the U.S.A." by Richard H. Schulze at pp. 15-25., 1993

5) Wilderness Act of 1964, 16 U.S.C. §1131 et seq, P.L. 577, 78 stat 890 as amended.

6) *The Principal Laws Relating to Forest Service Activities*, USDA - Forest Service ISBN 0-16-041927-1, 1993

7) Organic Administration Act of 1897, 16 U.S.C. §473-475, §477-482, §551.

Appendix C: General Policy for Managing Air Quality Related Values in Class I Areas

Most Federal Land Manager (FLM) enabling legislation and regulations developed to implement Federal Laws do not directly address air quality, or air pollution effects on Parks or Wildernesses. They do, however, provide broad direction on what should be protected in Parks and Wildernesses (the earth and its community of life) and to what degree (preserve natural conditions or conserve resources unimpaired). Accordingly, FLMs have developed the following policies related to air quality and Class I areas:

1. Class I areas are not merely a commodity for human use and consumption. Park and Wilderness ecosystems have intrinsic values other than user/public concerns.
2. A principal objective of FLM management is to offer a natural user experience, rather than strictly an enjoyable one. The amount of enjoyment is purely a personal matter for the individual user to decide.
3. All Class I components are equally important; none is of lesser value than another.
4. A Class I component is important even if users of the area are unaware of its existence.
5. All life forms are equally important. For example, microorganisms are as essential as elk, wild flowers, or grizzly bears.
6. The goal of Class I management is to protect not only resources with immediate aesthetic appeal (i.e., sparkling clean streams) but also unseen ecological processes (such as natural biodiversity and gene pools).
7. The most sensitive Class I components are to be emphasized more than those of "average" or "normal" sensitivity. Sensitivity is generally determined by inertia (resistance to change), elasticity (how far the component can be stretched from its natural condition without being permanently modified), and resiliency (the number of times it can revert to its natural condition after experiencing human-caused change).
8. Each Class I component is important in itself; as well as in terms of how it interacts with other components of the ecosystem. That is, the individual parts of the Class I ecosystem are as significant as the sum of the parts.
9. The physical components of the ecosystem (for instance, lake chemistry) are as essential as its biological constituents (i.e., salamanders). That is, the earth is as essential as the community of life.
10. Class I components are to be protected from "human-caused change" rather than from "damage." Terms such as "damage" and "harm" are prejudicial, whereas "human-caused change" is value-neutral. (For example, deposits of nitrogen in a lake from nitrogen oxide, a common air pollutant, might result in more plant growth and larger fish. This would, however, be an unnatural - and therefore unacceptable - change in the aquatic ecosystem).
11. The goal of Class I management is to protect natural conditions, rather than the conditions when first monitored. That is, if initial monitoring in a Class I area identifies human-caused changes, appropriate actions should be taken to remedy them, in order to move towards a more natural condition.
12. The designation of a Park or Wilderness as Class I or II does not dictate the management goals for it; these are identified in the enabling legislation. The designation only determines which options are available to meet the goals. Class I Parks or Wildernesses, for instance, can be protected through AQRV analysis, whereas the protection of Class II Parks and Wildernesses can be achieved using BACT requirements.
13. The FLMs will do their best to manage and protect resources at every area that they administer.
14. Although monitoring is critical to many air resource management decisions, it must not interfere needlessly with Park or Wilderness. Where possible, the most intrusive monitoring and instrumentation should be conducted adjacent to the Class I area - if such areas adequately represent the area of concern.

Appendix D: Best Available Control Technology (BACT) Analysis

Given the need to minimize emissions and their resulting air quality impacts, the FLMs recommend that the applicant conduct the BACT analysis using EPA's top-down approach. In brief, a top-down process ranks all available control technologies in descending order of control effectiveness. All of the available control systems for the source, including the most stringent, must be considered. The applicant first examines the most effective, or top, alternative. That alternative is established as the BACT unless the applicant demonstrates, and the permitting authority agrees, that technical considerations, or energy, environmental, or economic impacts justify a conclusion that the most stringent technology is not achievable in that case. FLMs utilize EPA's BACT/RACT/LAER Clearinghouse, and other information, for assessing control technologies proposed by permit applicants.

If the most stringent technology is eliminated in this fashion, then the next most stringent alternative is considered, and so on. Permit applicants should refer to chapter B of the EPA Draft New Source Review Workshop Manual for a detailed discussion of the top-down policy (EPA 1990).

The FLM reviews the applicant's BACT analysis to determine if the best available pollution control technology is being proposed, thereby minimizing the proposed emission increases and their corresponding impact on the FLM area in question. The FLM does this by comparing the proposed controls to recent BACT determinations for similar facilities. If the FLM disagrees with the applicant's BACT analysis, technical comments are submitted to the permitting authority that has the ultimate responsibility to make the BACT determination and issue the permit.

The environmental impacts analysis of the BACT review is not to be confused with the air quality-related analysis. The environmental impacts analysis of the BACT review should concentrate on impacts other than ambient air quality impacts of the regulated pollutant in question, such as solid or hazardous waste generation, discharges of polluted water from a control device, or emissions of unregulated pollutants. Thus, the fact that a given control alternative would result in only a slight improvement in ambient concentrations of the pollutant in question when compared with a less stringent control alternative, should not be viewed as a basis for rejecting the more stringent control alternative.

Regarding the economic impact analysis, given the special protection Class I areas are afforded under the Clean Air Act, FLMs believe that the need to minimize potential impacts on a Class I area should be a major consideration in the BACT determination for a project proposed near such an area. Therefore, if a source proposes to locate near a Class I area, additional costs to minimize impacts on sensitive Class I resources may be warranted, even though such costs may be considered economically unjustified under other circumstances.

Appendix E. Maps of Federal Class I Areas

Figure 8. National Park Service Class I Areas
Map produced by the National Park Service Air Resources Division March 2010.

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Figure 9. Fish and Wildlife Service Class I Areas
Map produced by the National Park Service Air Resources Division March 2010.

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Figure 10. Forest Service Class I Wilderness Areas
Map produced by the National Park Service Air Resources Division March 2010.

Item E 002774

Appendix E: FLAG 2000 Participants

The individuals listed in the attached table participated in the development of the *FLAG Phase I Report* (December 2000). The contact information was not updated as part of this FLAG 2010 revision. The abbreviations for the FLAG subgroup or committee on which participants served are shown below.

LC = Leadership Committee

CC = Coordinating Committee

P = Policy Subgroup

V = Visibility Subgroup

O = Ozone Subgroup

D = Deposition Subgroup

T = Terminology (Glossary) Subgroup

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NPS 999/105412, October 2010

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U. S. Forest Service
Air Quality Program
www.fs.fed.us/air

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proposed changes to be made to the existing approved plan, where applicable.

(d) The requirements of paragraphs 2.1(e)–2.1(h) shall not apply to plans submitted for parallel processing.

2.3.2. The exceptions granted in paragraph 2.3.1 shall apply only to EPA's determination of proposed action and all requirements of paragraph 2.1 shall be met prior to publication of EPA's final determination of plan approvability.

3.0. GUIDELINES

The EPA requests that the State adhere to the following voluntary guidelines when making plan submissions.

3.1 All Submissions

(a) The State should identify any copyrighted material in its submission, as EPA does not place such material on the web when creating the E-Docket for loading into the Federal Document Management System (FDMS).

(b) The State is advised not to include any material considered Confidential Business Information (CBI) in their SIP submissions. In rare instances where such information is necessary to justify the control requirements and emissions limitations established in the plan, the State should confer with its Regional Offices prior to submission and must clearly identify such material as CBI in the submission itself. EPA does not place such material in any paper or web-based docket. However, where any such material is considered emissions data within the meaning of Section 114 of the CAA, it cannot be withheld as CBI and must be made publicly available.

3.2 Paper Plan Submissions

(a) The EPA requires that the submission option of submitting one paper plan must be accompanied by an electronic duplicate of the entire paper submission, preferably as a word searchable portable document format (PDF), at the same time the paper copy is submitted. The electronic duplicate should be made available through email, from a File Transfer Protocol (FTP) site, from the State Web site, on a Universal Serial Bus (USB) flash drive, on a compact disk, or using another format agreed upon by the State and Regional Office.

(b) If a state prefers the submission option of submitting three paper copies and has no means of making an electronic copy available to EPA, EPA requests that the state confer with its EPA Regional Office regarding additional guidelines for submitting the plan to EPA.

[55 FR 5830, Feb. 16, 1990, as amended at 56 FR 42219, Aug. 26, 1991; 56 FR 57288, Nov. 8, 1991; 72 FR 38793, July 16, 2007; 80 FR 7340, Feb. 10, 2015]

APPENDIX W TO PART 51—GUIDELINE ON AIR QUALITY MODELS

PREFACE

a. Industry and control agencies have long expressed a need for consistency in the application of air quality models for regulatory purposes. In the 1977 Clean Air Act (CAA), Congress mandated such consistency and encouraged the standardization of model applications. The *Guideline on Air Quality Models* (hereafter, *Guideline*) was first published in April 1978 to satisfy these requirements by specifying models and providing guidance for their use. The *Guideline* provides a common basis for estimating the air quality concentrations of criteria pollutants used in assessing control strategies and developing emissions limits.

b. The continuing development of new air quality models in response to regulatory requirements and the expanded requirements for models to cover even more complex problems have emphasized the need for periodic review and update of guidance on these techniques. Historically, three primary activities have provided direct input to revisions of the *Guideline*. The first is a series of periodic EPA workshops and modeling conferences conducted for the purpose of ensuring consistency and providing clarification in the application of models. The second activity was the solicitation and review of new models from the technical and user community. In the March 27, 1980, FEDERAL REGISTER, a procedure was outlined for the submittal to the EPA of privately developed models. After extensive evaluation and scientific review, these models, as well as those made available by the EPA, have been considered for recognition in the *Guideline*. The third activity is the extensive on-going research efforts by the EPA and others in air quality and meteorological modeling.

c. Based primarily on these three activities, new sections and topics have been included as needed. The EPA does not make changes to the guidance on a predetermined schedule, but rather on an as-needed basis. The EPA believes that revisions of the *Guideline* should be timely and responsive to user needs and should involve public participation to the greatest possible extent. All future changes to the guidance will be proposed and finalized in the FEDERAL REGISTER. Information on the current status of modeling guidance can always be obtained from the EPA's Regional Offices.

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8–1	Point Source Model Emission Inputs for SIP Revisions of Inert Pollutants.
8–2	Point Source Model Emission Inputs for NAAQS Compliance in PSD Demonstrations.

1.0 INTRODUCTION

a. The *Guideline* provides air quality modeling techniques that should be applied to State Implementation Plan (SIP) submittals and revisions, to New Source Review (NSR), including new or modifying sources under Prevention of Significant Deterioration (PSD),[1 2 3] conformity analyses,[4] and other air quality assessments required under EPA regulation. Applicable only to criteria air pollutants, the *Guideline* is intended for use by the EPA Regional Offices in judging the adequacy of modeling analyses performed by the EPA, by state, local, and tribal permitting authorities, and by industry. It is appropriate for use by other federal government agencies and by state, local, and tribal agencies with air quality and land management responsibilities. The *Guideline* serves to identify, for all interested parties, those modeling techniques and databases that the EPA considers acceptable. The *Guideline* is not intended to be a compendium of modeling techniques. Rather, it should serve as a common measure of acceptable technical analysis when supported by sound scientific judgment.

b. Air quality measurements[5] are routinely used to characterize ambient concentrations of criteria pollutants throughout the nation but are rarely sufficient for characterizing the ambient impacts of individual sources or demonstrating adequacy of emissions limits for an existing source due to limitations in spatial and temporal coverage of ambient monitoring networks. The impacts of new sources that do not yet exist, and modifications to existing sources that have yet to be implemented, can only be determined through modeling. Thus, models have become a primary analytical tool in most air quality assessments. Air quality measurements can be used in a complementary manner to air quality models, with due regard for the strengths and weaknesses of both analysis techniques, and are particularly useful in assessing the accuracy of model estimates.

c. It would be advantageous to categorize the various regulatory programs and to apply a designated model to each proposed source needing analysis under a given program. However, the diversity of the nation's topography and climate, and variations in source configurations and operating characteristics dictate against a strict modeling ''cookbook.'' There is no one model capable of properly addressing all conceivable situations even within a broad category such as point sources. Meteorological phenomena associated with threats to air quality standards are rarely amenable to a single mathematical treatment; thus, case-by-case analysis and judgment are frequently required. As modeling efforts become more complex, it is increasingly important that they be directed by highly competent individuals with a broad range of experience and knowledge in air quality meteorology. Further, they should be coordinated closely with specialists in emissions characteristics, air monitoring and data processing. The judgment of experienced meteorologists, atmospheric scientists, and analysts is essential.

d. The model that most accurately estimates concentrations in the area of interest is always sought. However, it is clear from the needs expressed by the EPA Regional Offices, by state, local, and tribal agencies, by many industries and trade associations, and also by the deliberations of Congress, that consistency in the selection and application of models and databases should also be sought, even in case-by-case analyses. Consistency ensures that air quality control agencies and the general public have a common basis for estimating pollutant concentrations, assessing control strategies, and specifying emissions limits. Such consistency is not, however, promoted at the expense of model and database accuracy. The *Guideline* provides a consistent basis for selection of the most accurate models and databases for use in air quality assessments.

e. Recommendations are made in the *Guideline* concerning air quality models and techniques, model evaluation procedures, and model input databases and related requirements. The guidance provided here should be followed in air quality analyses relative to SIPs, NSR, and in supporting analyses required by the EPA and by state, local, and tribal permitting authorities. Specific models are identified for particular applications. The EPA may approve the use of an alternative model or technique that can be demonstrated to be more appropriate than those recommended in the *Guideline*. In all cases, the model or technique applied to a given situation should be the one that provides the most accurate representation of atmospheric transport, dispersion, and chemical transformations in the area of interest. However, to ensure consistency, deviations from the *Guideline* should be carefully documented as part of the public record and fully supported by the appropriate reviewing authority, as discussed later.

f. From time to time, situations arise requiring clarification of the intent of the guidance on a specific topic. Periodic workshops are held with EPA headquarters, EPA Regional Offices, and state, local, and tribal agency modeling representatives to ensure consistency in modeling guidance and to promote the use of more accurate air quality models, techniques, and databases. The workshops serve to provide further explanations of *Guideline* requirements to the EPA Regional Offices and workshop materials are issued with this clarifying information. In addition, findings from ongoing research programs, new model development, or results

from model evaluations and applications are continuously evaluated. Based on this information, changes in the applicable guidance may be indicated and appropriate revisions to the *Guideline* may be considered.

g. All changes to the *Guideline* must follow rulemaking requirements since the *Guideline* is codified in appendix W to 40 Code of Federal Regulations (CFR) part 51. The EPA will promulgate proposed and final rules in the FEDERAL REGISTER to amend this appendix. The EPA utilizes the existing procedures under CAA section 320 that requires the EPA to conduct a Conference on Air Quality Modeling at least every 3 years (CAA 320, 42 U.S.C. 7620). These modeling conferences are intended to develop standardized air quality modeling procedures and form the basis for associated revisions to this *Guideline* in support of the EPA's continuing effort to prescribe with ''reasonable particularity'' air quality models and meteorological and emission databases suitable for modeling National Ambient Air Quality Standards (NAAQS)[6] and PSD increments. Ample opportunity for public comment will be provided for each proposed change and public hearings scheduled.

h. A wide range of topics on modeling and databases are discussed in the *Guideline*. Section 2 gives an overview of models and their suitability for use in regulatory applications. Section 3 provides specific guidance on the determination of preferred air quality models and on the selection of alternative models or techniques. Sections 4 through 6 provide recommendations on modeling techniques for assessing criteria pollutant impacts from single and multiple sources with specific modeling requirements for selected regulatory applications. Section 7 discusses general considerations common to many modeling analyses for stationary and mobile sources. Section 8 makes recommendations for data inputs to models including source, background air quality, and meteorological data. Section 9 summarizes how estimates and measurements of air quality are used in assessing source impact and in evaluating control strategies.

i. Appendix W to 40 CFR part 51 contains an appendix: Appendix A. Thus, when reference is made to ''appendix A'' in this document, it refers to appendix A to appendix W to 40 CFR part 51. Appendix A contains summaries of refined air quality models that are ''preferred'' for particular applications; both EPA models and models developed by others are included.

2.0 OVERVIEW OF MODEL USE

a. Increasing reliance has been placed on concentration estimates from air quality models as the primary basis for regulatory decisions concerning source permits and emission control requirements. In many situations, such as review of a proposed new source, no practical alternative exists. Before attempting to implement the guidance contained in this document, the reader should be aware of certain general information concerning air quality models and their evaluation and use. Such information is provided in this section.

2.1 Suitability of Models

a. The extent to which a specific air quality model is suitable for the assessment of source impacts depends upon several factors. These include: (1) The topographic and meteorological complexities of the area; (2) the detail and accuracy of the input databases, *i.e.*, emissions inventory, meteorological data, and air quality data; (3) the manner in which complexities of atmospheric processes are handled in the model; (4) the technical competence of those undertaking such simulation modeling; and (5) the resources available to apply the model. Any of these factors can have a significant influence on the overall model performance, which must be thoroughly evaluated to determine the suitability of an air quality model to a particular application or range of applications.

b. Air quality models are most accurate and reliable in areas that have gradual transitions of land use and topography. Meteorological conditions in these areas are spatially uniform such that observations are broadly representative and air quality model projections are not further complicated by a heterogeneous environment. Areas subject to major topographic influences experience meteorological complexities that are often difficult to measure and simulate. Models with adequate performance are available for increasingly complex environments. However, they are resource intensive and frequently require site-specific observations and formulations. Such complexities and the related challenges for the air quality simulation should be considered when selecting the most appropriate air quality model for an application.

c. Appropriate model input data should be available before an attempt is made to evaluate or apply an air quality model. Assuming the data are adequate, the greater the detail with which a model considers the spatial and temporal variations in meteorological conditions and permit-enforceable emissions, the greater the ability to evaluate the source impact and to distinguish the effects of various control strategies.

d. There are three types of models that have historically been used in the regulatory demonstrations applicable in the *Guideline*, each having strengths and weaknesses that lend themselves to particular regulatory applications.

i. Gaussian plume models use a ''steady-state'' approximation, which assumes that

over the model time step, the emissions, meteorology and other model inputs, are constant throughout the model domain, resulting in a resolved plume with the emissions distributed throughout the plume according to a Gaussian distribution. This formulation allows Gaussian models to estimate near-field impacts of a limited number of sources at a relatively high resolution, with temporal scales of an hour and spatial scales of meters. However, this formulation allows for only relatively inert pollutants, with very limited considerations of transformation and removal (*e.g.,* deposition), and further limits the domain for which the model may be used. Thus, Gaussian models may not be appropriate if model inputs are changing sharply over the model time step or within the desired model domain, or if more advanced considerations of chemistry are needed.

ii. Lagrangian puff models, on the other hand, are non-steady-state, and assume that model input conditions are changing over the model domain and model time step. Lagrangian models can also be used to determine near- and far-field impacts from a limited number of sources. Traditionally, Lagrangian models have been used for relatively inert pollutants, with slightly more complex considerations of removal than Gaussian models. Some Lagrangian models treat in-plume gas and particulate chemistry. However, these models require time and space varying concentration fields of oxidants and, in the case of fine particulate matter ($PM_{2.5}$), neutralizing agents, such as ammonia. Reliable background fields are critical for applications involving secondary pollutant formation because secondary impacts generally occur when in-plume precursors mix and react with species in the background atmosphere.[7 8] These oxidant and neutralizing agents are not routinely measured, but can be generated with a three-dimensional photochemical grid model.

iii. Photochemical grid models are three-dimensional Eulerian grid-based models that treat chemical and physical processes in each grid cell and use diffusion and transport processes to move chemical species between grid cells.[9] Eulerian models assume that emissions are spread evenly throughout each model grid cell. At coarse grid resolutions, Eulerian models have difficulty with fine scale resolution of individual plumes. However, these types of models can be appropriately applied for assessment of near-field and regional scale reactive pollutant impacts from specific sources[7 10 11 12] or all sources.[13 14 15] Photochemical grid models simulate a more realistic environment for chemical transformation,[7 12] but simulations can be more resource intensive than Lagrangian or Gaussian plume models.

e. Competent and experienced meteorologists, atmospheric scientists, and analysts are an essential prerequisite to the successful application of air quality models. The need for such specialists is critical when sophisticated models are used or the area has complicated meteorological or topographic features. It is important to note that a model applied improperly or with inappropriate data can lead to serious misjudgments regarding the source impact or the effectiveness of a control strategy.

f. The resource demands generated by use of air quality models vary widely depending on the specific application. The resources required may be important factors in the selection and use of a model or technique for a specific analysis. These resources depend on the nature of the model and its complexity, the detail of the databases, the difficulty of the application, the amount and level of expertise required, and the costs of manpower and computational facilities.

2.1.1 Model Accuracy and Uncertainty

a. The formulation and application of air quality models are accompanied by several sources of uncertainty. ''Irreducible'' uncertainty stems from the ''unknown'' conditions, which may not be explicitly accounted for in the model (*e.g.*, the turbulent velocity field). Thus, there are likely to be deviations from the observed concentrations in individual events due to variations in the unknown conditions. ''Reducible'' uncertainties[16] are caused by: (1) Uncertainties in the ''known'' input conditions (*e.g.*, emission characteristics and meteorological data); (2) errors in the measured concentrations; and (3) inadequate model physics and formulation.

b. Evaluations of model accuracy should focus on the reducible uncertainty associated with physics and the formulation of the model. The accuracy of the model is normally determined by an evaluation procedure which involves the comparison of model concentration estimates with measured air quality data.[17] The statement of model accuracy is based on statistical tests or performance measures such as bias, error, correlation, etc.[18 19]

c. Since the 1980's, the EPA has worked with the modeling community to encourage development of standardized model evaluation methods and the development of continually improved methods for the characterization of model performance.[16 18 20 21 22] There is general consensus on what should be considered in the evaluation of air quality models; namely, quality assurance planning, documentation and scrutiny should be consistent with the intended use and should include:

- Scientific peer review;
- Supportive analyses (diagnostic evaluations, code verification, sensitivity analyses);
- Diagnostic and performance evaluations with data obtained in trial locations; and

• Statistical performance evaluations in the circumstances of the intended applications.

Performance evaluations and diagnostic evaluations assess different qualities of how well a model is performing, and both are needed to establish credibility within the client and scientific community.

d. Performance evaluations allow the EPA and model users to determine the relative performance of a model in comparison with alternative modeling systems. Diagnostic evaluations allow determination of a model capability to simulate individual processes that affect the results, and usually employ smaller spatial/temporal scale data sets (*e.g.*, field studies). Diagnostic evaluations enable the EPA and model users to build confidence that model predictions are accurate for the right reasons. However, the objective comparison of modeled concentrations with observed field data provides only a partial means for assessing model performance. Due to the limited supply of evaluation datasets, there are practical limits in assessing model performance. For this reason, the conclusions reached in the science peer reviews and the supportive analyses have particular relevance in deciding whether a model will be useful for its intended purposes.

2.2 Levels of Sophistication of Air Quality Analyses and Models

a. It is desirable to begin an air quality analysis by using simplified and conservative methods followed, as appropriate, by more complex and refined methods. The purpose of this approach is to streamline the process and sufficiently address regulatory requirements by eliminating the need of more detailed modeling when it is not necessary in a specific regulatory application. For example, in the context of a PSD permit application, a simplified and conservative analysis may be sufficient where it shows the proposed construction clearly will not cause or contribute to ambient concentrations in excess of either the NAAQS or the PSD increments.[2 3]

b. There are two general levels of sophistication of air quality models. The first level consists of screening models that provide conservative modeled estimates of the air quality impact of a specific source or source category based on simplified assumptions of the model inputs (*e.g.*, preset, worst-case meteorological conditions). In the case of a PSD assessment, if a screening model indicates that the increase in concentration attributable to the source could cause or contribute to a violation of any NAAQS or PSD increment, then the second level of more sophisticated models should be applied unless appropriate controls or operational restrictions are implemented based on the screening modeling.

c. The second level consists of refined models that provide more detailed treatment of physical and chemical atmospheric processes, require more detailed and precise input data, and provide spatially and temporally resolved concentration estimates. As a result, they provide a more sophisticated and, at least theoretically, a more accurate estimate of source impact and the effectiveness of control strategies.

d. There are situations where a screening model or a refined model is not available such that screening and refined modeling are not viable options to determine source-specific air quality impacts. In such situations, a screening technique or reduced-form model may be viable options for estimating source impacts.

i. Screening techniques are differentiated from a screening model in that screening techniques are approaches that make simplified and conservative assumptions about the physical and chemical atmospheric processes important to determining source impacts, while screening models make assumptions about conservative inputs to a specific model. The complexity of screening techniques ranges from simplified assumptions of chemistry applied to refined or screening model output to sophisticated approximations of the chemistry applied within a refined model.

ii. Reduced-form models are computationally efficient simulation tools for characterizing the pollutant response to specific types of emission reductions for a particular geographic area or background environmental conditions that reflect underlying atmospheric science of a refined model but reduce the computational resources of running a complex, numerical air quality model such as a photochemical grid model.

In such situations, an attempt should be made to acquire or improve the necessary databases and to develop appropriate analytical techniques, but the screening technique or reduced-form model may be sufficient in conducting regulatory modeling applications when applied in consultation with the EPA Regional Office.

e. Consistent with the general principle described in paragraph 2.2(a), the EPA may establish a demonstration tool or method as a sufficient means for a user or applicant to make a demonstration required by regulation, either by itself or as part of a modeling demonstration. To be used for such regulatory purposes, such a tool or method must be reflected in a codified regulation or have a well-documented technical basis and reasoning that is contained or incorporated in the record of the regulatory decision in which it is applied.

2.3 Availability of Models

a. For most of the screening and refined models discussed in the *Guideline*, codes, associated documentation and other useful information are publicly available for download from the EPA's Support Center for Regulatory Atmospheric Modeling (SCRAM) Web site at *https://www.epa.gov/scram*. This is a Web site with which air quality modelers should become familiar and regularly visit for important model updates and additional clarifications and revisions to modeling guidance documents that are applicable to EPA programs and regulations. Codes and documentation may also be available from the National Technical Information Service (NTIS), *http://www.ntis.gov*, and, when available, is referenced with the appropriate NTIS accession number.

3.0 PREFERRED AND ALTERNATIVE AIR QUALITY MODELS

a. This section specifies the approach to be taken in determining preferred models for use in regulatory air quality programs. The status of models developed by the EPA, as well as those submitted to the EPA for review and possible inclusion in this *Guideline*, is discussed in this section. The section also provides the criteria and process for obtaining EPA approval for use of alternative models for individual cases in situations where the preferred models are not applicable or available. Additional sources of relevant modeling information are: the EPA's Model Clearinghouse[23] (section 3.3); EPA modeling conferences; periodic Regional, State, and Local Modelers' Workshops; and the EPA's SCRAM Web site (section 2.3).

b. When approval is required for a specific modeling technique or analytical procedure in this *Guideline*, we refer to the ''*appropriate reviewing authority*.'' Many states and some local agencies administer NSR permitting under programs approved into SIPs. In some EPA regions, federal authority to administer NSR permitting and related activities has been delegated to state or local agencies. In these cases, such agencies ''*stand in the shoes*'' of the respective EPA Region. Therefore, depending on the circumstances, the appropriate reviewing authority may be an EPA Regional Office, a state, local, or tribal agency, or perhaps the Federal Land Manager (FLM). In some cases, the *Guideline* requires review and approval of the use of an alternative model by the EPA Regional Office (sometimes stated as ''*Regional Administrator*''). For all approvals of alternative models or techniques, the EPA Regional Office will coordinate and shall seek concurrence with the EPA's Model Clearinghouse. If there is any question as to the appropriate reviewing authority, you should contact the EPA Regional Office modeling contact (*https://www3.epa.gov/ttn/scram/guidance_cont_regions.htm*), whose jurisdiction generally includes the physical location of the source in question and its expected impacts.

c. In all regulatory analyses, early discussions among the EPA Regional Office staff, state, local, and tribal agency staff, industry representatives, and where appropriate, the FLM, are invaluable and are strongly encouraged. Prior to the actual analyses, agreement on the databases to be used, modeling techniques to be applied, and the overall technical approach helps avoid misunderstandings concerning the final results and may reduce the later need for additional analyses. The preparation of a written modeling protocol that is vetted with the appropriate reviewing authority helps to keep misunderstandings and resource expenditures at a minimum.

d. The identification of preferred models in this *Guideline* should not be construed as a determination that the preferred models identified here are to be permanently used to the exclusion of all others or that they are the only models available for relating emissions to air quality. The model that most accurately estimates concentrations in the area of interest is always sought. However, designation of specific preferred models is needed to promote consistency in model selection and application.

3.1 Preferred Models

3.1.1 Discussion

a. The EPA has developed some models suitable for regulatory application, while other models have been submitted by private developers for possible inclusion in the *Guideline*. Refined models that are preferred and required by the EPA for particular applications have undergone the necessary peer scientific reviews[24][25] and model performance evaluation exercises[26][27] that include statistical measures of model performance in comparison with measured air quality data as described in section 2.1.1.

b. An American Society for Testing and Materials (ASTM) reference[28] provides a general philosophy for developing and implementing advanced statistical evaluations of atmospheric dispersion models, and provides an example statistical technique to illustrate the application of this philosophy. Consistent with this approach, the EPA has determined and applied a specific evaluation protocol that provides a statistical technique for evaluating model performance for predicting peak concentration values, as might be observed at individual monitoring locations.[29]

c. When a single model is found to perform better than others, it is recommended for application as a preferred model and listed in

appendix A. If no one model is found to clearly perform better through the evaluation exercise, then the preferred model listed in appendix A may be selected on the basis of other factors such as past use, public familiarity, resource requirements, and availability. Accordingly, the models listed in appendix A meet these conditions:

i. The model must be written in a common programming language, and the executable(s) must run on a common computer platform.

ii. The model must be documented in a user's guide or model formulation report which identifies the mathematics of the model, data requirements and program operating characteristics at a level of detail comparable to that available for other recommended models in appendix A.

iii. The model must be accompanied by a complete test dataset including input parameters and output results. The test data must be packaged with the model in computer-readable form.

iv. The model must be useful to typical users, *e.g.*, state air agencies, for specific air quality control problems. Such users should be able to operate the computer program(s) from available documentation.

v. The model documentation must include a robust comparison with air quality data (and/or tracer measurements) or with other well-established analytical techniques.

vi. The developer must be willing to make the model and source code available to users at reasonable cost or make them available for public access through the Internet or National Technical Information Service. The model and its code cannot be proprietary.

d. The EPA's process of establishing a preferred model includes a determination of technical merit, in accordance with the above six items, including the practicality of the model for use in ongoing regulatory programs. Each model will also be subjected to a performance evaluation for an appropriate database and to a peer scientific review. Models for wide use (not just an isolated case) that are found to perform better will be proposed for inclusion as preferred models in future *Guideline* revisions.

e. No further evaluation of a preferred model is required for a particular application if the EPA requirements for regulatory use specified for the model in the *Guideline* are followed. Alternative models to those listed in appendix A should generally be compared with measured air quality data when they are used for regulatory applications consistent with recommendations in section 3.2.

3.1.2 Requirements

a. Appendix A identifies refined models that are preferred for use in regulatory applications. If a model is required for a particular application, the user must select a model from appendix A or follow procedures in section 3.2.2 for use of an alternative model or technique. Preferred models may be used without a formal demonstration of applicability as long as they are used as indicated in each model summary in appendix A. Further recommendations for the application of preferred models to specific source applications are found in subsequent sections of the *Guideline*.

b. If changes are made to a preferred model without affecting the modeled concentrations, the preferred status of the model is unchanged. Examples of modifications that do not affect concentrations are those made to enable use of a different computer platform or those that only affect the format or averaging time of the model results. The integration of a graphical user interface (GUI) to facilitate setting up the model inputs and/or analyzing the model results without otherwise altering the preferred model code is another example of a modification that does not affect concentrations. However, when any changes are made, the Regional Administrator must require a test case example to demonstrate that the modeled concentrations are not affected.

c. A preferred model must be operated with the options listed in appendix A for its intended regulatory application. If the regulatory options are not applied, the model is no longer ''preferred.'' Any other modification to a preferred model that would result in a change in the concentration estimates likewise alters its status so that it is no longer a preferred model. Use of the modified model must then be justified as an alternative model on a case-by-case basis to the appropriate reviewing authority and approved by the Regional Administrator.

d. Where the EPA has not identified a preferred model for a particular pollutant or situation, the EPA may establish a multi-tiered approach for making a demonstration required under PSD or another CAA program. The initial tier or tiers may involve use of demonstration tools, screening models, screening techniques, or reduced-form models; while the last tier may involve the use of demonstration tools, refined models or techniques, or alternative models approved under section 3.2.

3.2 Alternative Models

3.2.1 Discussion

a. Selection of the best model or techniques for each individual air quality analysis is always encouraged, but the selection should be done in a consistent manner. A simple listing of models in this *Guideline* cannot alone achieve that consistency nor can it necessarily provide the best model for all possible situations. As discussed in section 3.1.1, the EPA has determined and applied a specific evaluation protocol that provides a statistical technique for evaluating

model performance for predicting peak concentration values, as might be observed at individual monitoring locations.[29] This protocol is available to assist in developing a consistent approach when justifying the use of other-than-preferred models recommended in the *Guideline* (*i.e.*, alternative models). The procedures in this protocol provide a general framework for objective decision-making on the acceptability of an alternative model for a given regulatory application. These objective procedures may be used for conducting both the technical evaluation of the model and the field test or performance evaluation.

b. This subsection discusses the use of alternate models and defines three situations when alternative models may be used. This subsection also provides a procedure for implementing 40 CFR 51.166(l)(2) in PSD permitting. This provision requires written approval of the Administrator for any modification or substitution of an applicable model. An applicable model for purposes of 40 CFR 51.166(l) is a preferred model in appendix A to the *Guideline*. Approval to use an alternative model under section 3.2 of the *Guideline* qualifies as approval for the modification or substitution of a model under 40 CFR 51.166(l)(2). The Regional Administrators have delegated authority to issue such approvals under section 3.2 of the *Guideline*, provided that such approval is issued after consultation with the EPA's Model Clearinghouse and formally documented in a concurrence memorandum from the EPA's Model Clearinghouse which demonstrates that the requirements within section 3.2 for use of an alternative model have been met.

3.2.2 Requirements

a. Determination of acceptability of an alternative model is an EPA Regional Office responsibility in consultation with the EPA's Model Clearinghouse as discussed in paragraphs 3.0(b) and 3.2.1(b). Where the Regional Administrator finds that an alternative model is more appropriate than a preferred model, that model may be used subject to the approval of the EPA Regional Office based on the requirements of this subsection. This finding will normally result from a determination that: (1) A preferred air quality model is not appropriate for the particular application; or (2) a more appropriate model or technique is available and applicable.

b. An alternative model shall be evaluated from both a theoretical and a performance perspective before it is selected for use. There are three separate conditions under which such a model may be approved for use:

1. If a demonstration can be made that the model produces concentration estimates equivalent to the estimates obtained using a preferred model;

2. If a statistical performance evaluation has been conducted using measured air quality data and the results of that evaluation indicate the alternative model performs better for the given application than a comparable model in appendix A; or

3. If there is no preferred model.

Any one of these three separate conditions may justify use of an alternative model. Some known alternative models that are applicable for selected situations are listed on the EPA's SCRAM Web site (section 2.3). However, inclusion there does not confer any unique status relative to other alternative models that are being or will be developed in the future.

c. Equivalency, condition (1) in paragraph (b) of this subsection, is established by demonstrating that the appropriate regulatory metric(s) are within ± 2 percent of the estimates obtained from the preferred model. The option to show equivalency is intended as a simple demonstration of acceptability for an alternative model that is nearly identical (or contains options that can make it identical) to a preferred model that it can be treated for practical purposes as the preferred model. However, notwithstanding this demonstration, models that are not equivalent may be used when one of the two other conditions described in paragraphs (d) and (e) of this subsection are satisfied.

d. For condition (2) in paragraph (b) of this subsection, established statistical performance evaluation procedures and techniques[28 29] for determining the acceptability of a model for an individual case based on superior performance should be followed, as appropriate. Preparation and implementation of an evaluation protocol that is acceptable to both control agencies and regulated industry is an important element in such an evaluation.

e. Finally, for condition (3) in paragraph (b) of this subsection, an alternative model or technique may be approved for use provided that:

i. The model or technique has received a scientific peer review;

ii. The model or technique can be demonstrated to be applicable to the problem on a theoretical basis;

iii. The databases which are necessary to perform the analysis are available and adequate;

iv. Appropriate performance evaluations of the model or technique have shown that the model or technique is not inappropriately biased for regulatory application[a]; and

[a] For PSD and other applications that use the model results in an absolute sense, the model should not be biased toward underestimates. Alternatively, for ozone and $PM_{2.5}$ SIP attainment demonstrations and other applications that use the model results in a

v. A protocol on methods and procedures to be followed has been established.

f. To formally document that the requirements of section 3.2 for use of an alternative model are satisfied for a particular application or range of applications, a memorandum will be prepared by the EPA's Model Clearinghouse through a consultative process with the EPA Regional Office.

3.3 EPA's Model Clearinghouse

a. The Regional Administrator has the authority to select models that are appropriate for use in a given situation. However, there is a need for assistance and guidance in the selection process so that fairness, consistency, and transparency in modeling decisions are fostered among the EPA Regional Offices and the state, local, and tribal agencies. To satisfy that need, the EPA established the Model Clearinghouse[23] to serve a central role of coordination and collaboration between EPA headquarters and the EPA Regional Offices. Additionally, the EPA holds periodic workshops with EPA Headquarters, EPA Regional Offices, and state, local, and tribal agency modeling representatives.

b. The appropriate EPA Regional Office should always be consulted for information and guidance concerning modeling methods and interpretations of modeling guidance, and to ensure that the air quality model user has available the latest most up-to-date policy and procedures. As appropriate, the EPA Regional Office may also request assistance from the EPA's Model Clearinghouse on other applications of models, analytical techniques, or databases or to clarify interpretation of the *Guideline* or related modeling guidance.

c. The EPA Regional Office will coordinate with the EPA's Model Clearinghouse after an initial evaluation and decision has been developed concerning the application of an alternative model. The acceptability and formal approval process for an alternative model is described in section 3.2.

4.0 Models for Carbon Monoxide, Lead, Sulfur Dioxide, Nitrogen Dioxide and Primary Particulate Matter

4.1 Discussion

a. This section identifies modeling approaches generally used in the air quality impact analysis of sources that emit the criteria pollutants carbon monoxide (CO), lead, sulfur dioxide (SO_2), nitrogen dioxide (NO_2), and primary particulates ($PM_{2.5}$ and PM_{10}).

b. The guidance in this section is specific to the application of the Gaussian plume models identified in appendix A. Gaussian plume models assume that emissions and meteorology are in a steady-state, which is typically based on an hourly time step. This approach results in a plume that has an hourly-averaged distribution of emission mass according to a Gaussian curve through the plume. Though Gaussian steady-state models conserve the mass of the primary pollutant throughout the plume, they can still take into account a limited consideration of first-order removal processes (*e.g.*, wet and dry deposition) and limited chemical conversion (*e.g.*, OH oxidation).

c. Due to the steady-state assumption, Gaussian plume models are generally considered applicable to distances less than 50 km, beyond which, modeled predictions of plume impact are likely conservative. The locations of these impacts are expected to be unreliable due to changes in meteorology that are likely to occur during the travel time.

d. The applicability of Gaussian plume models may vary depending on the topography of the modeling domain, *i.e.*, simple or complex. Simple terrain is considered to be an area where terrain features are all lower in elevation than the top of the stack(s) of the source(s) in question. Complex terrain is defined as terrain exceeding the height of the stack(s) being modeled.

e. Gaussian models determine source impacts at discrete locations (receptors) for each meteorological and emission scenario, and generally attempt to estimate concentrations at specific sites that represent an ensemble average of numerous repetitions of the same ''event.'' Uncertainties in model estimates are driven by this formulation, and as noted in section 2.1.1, evaluations of model accuracy should focus on the reducible uncertainty associated with physics and the formulation of the model. The ''irreducible'' uncertainty associated with Gaussian plume models may be responsible for variation in concentrations of as much as ± 50 percent.[30] ''Reducible'' uncertainties[16] can be on a similar scale. For example, Pasquill[31] estimates that, apart from data input errors, maximum ground-level concentrations at a given hour for a point source in flat terrain could be in error by 50 percent due to these uncertainties. Errors of 5 to 10 degrees in the measured wind direction can result in concentration errors of 20 to 70 percent for a particular time and location, depending on stability and station location. Such uncertainties do not indicate that an estimated concentration does not occur, only that the precise time and locations are in doubt. Composite errors in highest estimated concentrations of 10 to 40 percent are found to be typical.[32 33] However, estimates of concentrations paired in time and space with observed concentrations are less certain.

f. Model evaluations and inter-comparisons should take these aspects of uncertainty into

relative sense, the model should not be biased toward overestimates.

account. For a regulatory application of a model, the emphasis of model evaluations is generally placed on the highest modeled impacts. Thus, the Cox-Tikvart model evaluation approach, which compares the highest modeled impacts on several timescales, is recommended for comparisons of models and measurements and model inter-comparisons. The approach includes bootstrap techniques to determine the significance of various modeled predictions and increases the robustness of such comparisons when the number of available measurements are limited.[34] [35] Because of the uncertainty in paired modeled and observed concentrations, any attempts at calibration of models based on these comparisons is of questionable benefit and shall not be done.

4.2 Requirements

a. For NAAQS compliance demonstrations under PSD, use of the screening and preferred models for the pollutants listed in this subsection shall be limited to the near-field at a nominal distance of 50 km or less. Near-field application is consistent with capabilities of Gaussian plume models and, based on the EPA's assessment, is sufficient to address whether a source will cause or contribute to ambient concentrations in excess of a NAAQS. In most cases, maximum source impacts of inert pollutants will occur within the first 10 to 20 km from the source. Therefore, the EPA does not consider a long-range transport assessment beyond 50 km necessary for these pollutants if a near-field NAAQS compliance demonstration is required.[36]

b. For assessment of PSD increments within the near-field distance of 50 km or less, use of the screening and preferred models for the pollutants listed in this subsection shall be limited to the same screening and preferred models approved for NAAQS compliance demonstrations.

c. To determine if a compliance demonstration for NAAQS and/or PSD increments may be necessary beyond 50 km (*i.e.,* long-range transport assessment), the following screening approach shall be used to determine if a significant ambient impact will occur with particular focus on Class I areas and/or the applicable receptors that may be threatened at such distances.

i. Based on application in the near-field of the appropriate screening and/or preferred model, determine the significance of the ambient impacts at or about 50 km from the new or modifying source. If a near-field assessment is not available or this initial analysis indicates there may be significant ambient impacts at that distance, then further assessment is necessary.

ii. For assessment of the significance of ambient impacts for NAAQS and/or PSD increments, there is not a preferred model or screening approach for distances beyond 50 km. Thus, the appropriate reviewing authority (paragraph 3.0(b)) and the EPA Regional Office shall be consulted in determining the appropriate and agreed upon screening technique to conduct the second level assessment. Typically, a Lagrangian model is most appropriate to use for these second level assessments, but applicants shall reach agreement on the specific model and modeling parameters on a case-by-case basis in consultation with the appropriate reviewing authority (paragraph 3.0(b)) and EPA Regional Office. When Lagrangian models are used in this manner, they shall not include plume-depleting processes, such that model estimates are considered conservative, as is generally appropriate for screening assessments.

d. In those situations where a cumulative impact analysis for NAAQS and/or PSD increments analysis beyond 50 km is necessary, the selection and use of an alternative model shall occur in agreement with the appropriate reviewing authority (paragraph 3.0(b)) and approval by the EPA Regional Office based on the requirements of paragraph 3.2.2(e).

4.2.1 Screening Models and Techniques

a. Where a preliminary or conservative estimate is desired, point source screening techniques are an acceptable approach to air quality analyses.

b. As discussed in paragraph 2.2(a), screening models or techniques are designed to provide a conservative estimate of concentrations. The screening models used in most applications are the screening versions of the preferred models for refined applications. The two screening models, AERSCREEN[37] [38] and CTSCREEN, are screening versions of AERMOD (American Meteorological Society (AMS)/EPA Regulatory Model) and CTDMPLUS (Complex Terrain Dispersion Model Plus Algorithms for Unstable Situations), respectively. AERSCREEN is the recommended screening model for most applications in all types of terrain and for applications involving building downwash. For those applications in complex terrain where the application involves a well-defined hill or ridge, CTSCREEN[39] can be used.

c. Although AERSCREEN and CTSCREEN are designed to address a single-source scenario, there are approaches that can be used on a case-by-case basis to address multi-source situations using screening meteorology or other conservative model assumptions. However, the appropriate reviewing authority (paragraph 3.0(b)) shall be consulted, and concurrence obtained, on the protocol for modeling multiple sources with AERSCREEN or CTSCREEN to ensure that the worst case is identified and assessed.

d. As discussed in section 4.2.3.4, there are also screening techniques built into AERMOD that use simplified or limited chemistry assumptions for determining the

partitioning of NO and NO_2 for NO_2 modeling. These screening techniques are part of the EPA's preferred modeling approach for NO_2 and do not need to be approved as an alternative model. However, as with other screening models and techniques, their usage shall occur in agreement with the appropriate reviewing authority (paragraph 3.0(b)).

e. As discussed in section 4.2(c)(ii), there are screening techniques needed for long-range transport assessments that will typically involve the use of a Lagrangian model. Based on the long-standing practice and documented capabilities of these models for long-range transport assessments, the use of a Lagrangian model as a screening technique for this purpose does not need to be approved as an alternative model. However, their usage shall occur in consultation with the appropriate reviewing authority (paragraph 3.0(b)) and EPA Regional Office.

f. All screening models and techniques shall be configured to appropriately address the site and problem at hand. Close attention must be paid to whether the area should be classified urban or rural in accordance with section 7.2.1.1. The climatology of the area must be studied to help define the worst-case meteorological conditions. Agreement shall be reached between the model user and the appropriate reviewing authority (paragraph 3.0(b)) on the choice of the screening model or technique for each analysis, on the input data and model settings, and the appropriate metric for satisfying regulatory requirements.

4.2.1.1 AERSCREEN

a. Released in 2011, AERSCREEN is the EPA's recommended screening model for simple and complex terrain for single sources including point sources, area sources, horizontal stacks, capped stacks, and flares. AERSCREEN runs AERMOD in a screening mode and consists of two main components: 1) the MAKEMET program which generates a site-specific matrix of meteorological conditions for input to the AERMOD model; and 2) the AERSCREEN command-prompt interface.

b. The MAKEMET program generates a matrix of meteorological conditions, in the form of AERMOD-ready surface and profile files, based on user-specified surface characteristics, ambient temperatures, minimum wind speed, and anemometer height. The meteorological matrix is generated based on looping through a range of wind speeds, cloud covers, ambient temperatures, solar elevation angles, and convective velocity scales (w*, for convective conditions only) based on user-specified surface characteristics for surface roughness (Z_o), Bowen ratio (B_o), and albedo (r). For unstable cases, the convective mixing height (Z_{ic}) is calculated based on w*, and the mechanical mixing height (Z_{im}) is calculated for unstable and stable conditions based on the friction velocity, u*.

c. For applications involving simple or complex terrain, AERSCREEN interfaces with AERMAP. AERSCREEN also interfaces with BPIPPRM to provide the necessary building parameters for applications involving building downwash using the Plume Rise Model Enhancements (PRIME) downwash algorithm. AERSCREEN generates inputs to AERMOD via MAKEMET, AERMAP, and BPIPPRM and invokes AERMOD in a screening mode. The screening mode of AERMOD forces the AERMOD model calculations to represent values for the plume centerline, regardless of the source-receptor-wind direction orientation. The maximum concentration output from AERSCREEN represents a worst-case 1-hour concentration. Averaging-time scaling factors of 1.0 for 3-hour, 0.9 for 8-hour, 0.60 for 24-hour, and 0.10 for annual concentration averages are applied internally by AERSCREEN to the highest 1-hour concentration calculated by the model for non-area type sources. For area type source concentrations for averaging times greater than one hour, the concentrations are equal to the 1-hour estimates.[37 40]

4.2.1.2 CTSCREEN

a. CTSCREEN[39 41] can be used to obtain conservative, yet realistic, worst-case estimates for receptors located on terrain above stack height. CTSCREEN accounts for the three-dimensional nature of plume and terrain interaction and requires detailed terrain data representative of the modeling domain. The terrain data must be digitized in the same manner as for CTDMPLUS and a terrain processor is available.[42] CTSCREEN is designed to execute a fixed matrix of meteorological values for wind speed (u), standard deviation of horizontal and vertical wind speeds (σv, σw), vertical potential temperature gradient ($d\theta/dz$), friction velocity (u*), Monin-Obukhov length (L), mixing height (z_i) as a function of terrain height, and wind directions for both neutral/stable conditions and unstable convective conditions. The maximum concentration output from CTSCREEN represents a worst-case 1-hour concentration. Time-scaling factors of 0.7 for 3-hour, 0.15 for 24-hour and 0.03 for annual concentration averages are applied internally by CTSCREEN to the highest 1-hour concentration calculated by the model.

4.2.1.3 Screening in Complex Terrain

a. For applications utilizing AERSCREEN, AERSCREEN automatically generates a polar-grid receptor network with spacing determined by the maximum distance to model. If the application warrants a different receptor network than that generated by AERSCREEN, it may be necessary to run

AERMOD in screening mode with a user-defined network. For CTSCREEN applications or AERMOD in screening mode outside of AERSCREEN, placement of receptors requires very careful attention when modeling in complex terrain. Often the highest concentrations are predicted to occur under very stable conditions, when the plume is near or impinges on the terrain. Under such conditions, the plume may be quite narrow in the vertical, so that even relatively small changes in a receptor's location may substantially affect the predicted concentration. Receptors within about a kilometer of the source may be even more sensitive to location. Thus, a dense array of receptors may be required in some cases.

b. For applications involving AERSCREEN, AERSCREEN interfaces with AERMAP to generate the receptor elevations. For applications involving CTSCREEN, digitized contour data must be preprocessed[42] to provide hill shape parameters in suitable input format. The user then supplies receptor locations either through an interactive program that is part of the model or directly, by using a text editor; using both methods to select receptor locations will generally be necessary to assure that the maximum concentrations are estimated by either model. In cases where a terrain feature may ''appear to the plume'' as smaller, multiple hills, it may be necessary to model the terrain both as a single feature and as multiple hills to determine design concentrations.

c. Other screening techniques may be acceptable for complex terrain cases where established procedures[43] are used. The user is encouraged to confer with the appropriate reviewing authority (paragraph 3.0(b)) if any unforeseen problems are encountered, *e.g.*, applicability, meteorological data, receptor siting, or terrain contour processing issues.

4.2.2 Refined Models

a. A brief description of each preferred model for refined applications is found in appendix A. Also listed in that appendix are availability, the model input requirements, the standard options that shall be selected when running the program, and output options.

4.2.2.1 AERMOD

a. For a wide range of regulatory applications in all types of terrain, and for aerodynamic building downwash, the required model is AERMOD.[44][45] The AERMOD regulatory modeling system consists of the AERMOD dispersion model, the AERMET meteorological processor, and the AERMAP terrain processor. AERMOD is a steady-state Gaussian plume model applicable to directly emitted air pollutants that employs best state-of-practice parameterizations for characterizing the meteorological influences and dispersion. Differentiation of simple versus complex terrain is unnecessary with AERMOD. In complex terrain, AERMOD employs the well-known dividing-streamline concept in a simplified simulation of the effects of plume-terrain interactions.

b. The AERMOD modeling system has been extensively evaluated across a wide range of scenarios based on numerous field studies, including tall stacks in flat and complex terrain settings, sources subject to building downwash influences, and low-level nonbuoyant sources.[27] These evaluations included several long-term field studies associated with operating plants as well as several intensive tracer studies. Based on these evaluations, AERMOD has shown consistently good performance, with ''errors'' in predicted versus observed peak concentrations, based on the Robust Highest Concentration (RHC) metric, consistently within the range of 10 to 40 percent (cited in paragraph 4.1(e)).

c. AERMOD incorporates the PRIME algorithm to account for enhanced plume growth and restricted plume rise for plumes affected by building wake effects.[46] The PRIME algorithm accounts for entrainment of plume mass into the cavity recirculation region, including re-entrainment of plume mass into the wake region beyond the cavity.

d. AERMOD incorporates the Buoyant Line and Point Source (BLP) Dispersion model to account for buoyant plume rise from line sources. The BLP option utilizes the standard meteorological inputs provided by the AERMET meteorological processor.

e. The state-of-the-science for modeling atmospheric deposition is evolving, new modeling techniques are continually being assessed, and their results are being compared with observations. Consequently, while deposition treatment is available in AERMOD, the approach taken for any purpose shall be coordinated with the appropriate reviewing authority (paragraph 3.0(b)).

4.2.2.2 CTDMPLUS

a. If the modeling application involves an elevated point source with a well-defined hill or ridge and a detailed dispersion analysis of the spatial pattern of plume impacts is of interest, CTDMPLUS is available. CTDMPLUS provides greater resolution of concentrations about the contour of the hill feature than does AERMOD through a different plume-terrain interaction algorithm.

4.2.2.3 OCD

a. If the modeling application involves determining the impact of offshore emissions from point, area, or line sources on the air quality of coastal regions, the recommended model is the OCD (Offshore and Coastal Dispersion) Model. OCD is a straight-line Gaussian model that incorporates overwater

plume transport and dispersion as well as changes that occur as the plume crosses the shoreline. OCD is also applicable for situations that involve platform building downwash.

4.2.3 Pollutant Specific Modeling Requirements

4.2.3.1 Models for Carbon Monoxide

a. Models for assessing the impact of CO emissions are needed to meet NSR requirements to address compliance with the CO NAAQS and to determine localized impacts from transportations projects. Examples include evaluating effects of point sources, congested roadway intersections and highways, as well as the cumulative effect of numerous sources of CO in an urban area.

b. The general modeling recommendations and requirements for screening models in section 4.2.1 and refined models in section 4.2.2 shall be applied for CO modeling. Given the relatively low CO background concentrations, screening techniques are likely to be adequate in most cases. In applying these recommendations and requirements, the existing 1992 EPA guidance for screening CO impacts from highways may be consulted.[47]

4.2.3.2 Models for Lead

a. In January 1999 (40 CFR part 58, appendix D), the EPA gave notice that concern about ambient lead impacts was being shifted away from roadways and toward a focus on stationary point sources. Thus, models for assessing the impact of lead emissions are needed to meet NSR requirements to address compliance with the lead NAAQS and for SIP attainment demonstrations. The EPA has also issued guidance on siting ambient monitors in the vicinity of stationary point sources.[48] For lead, the SIP should contain an air quality analysis to determine the maximum rolling 3-month average lead concentration resulting from major lead point sources, such as smelters, gasoline additive plants, etc. The EPA has developed a post-processor to calculate rolling 3-month average concentrations from model output.[49] General guidance for lead SIP development is also available.[50]

b. For major lead point sources, such as smelters, which contribute fugitive emissions and for which deposition is important, professional judgment should be used, and there shall be coordination with the appropriate reviewing authority (paragraph 3.0(b)). For most applications, the general requirements for screening and refined models of section 4.2.1 and 4.2.2 are applicable to lead modeling.

4.2.3.3 Models for Sulfur Dioxide

a. Models for SO_2 are needed to meet NSR requirements to address compliance with the SO_2 NAAQS and PSD increments, for SIP attainment demonstrations,[51] and for characterizing current air quality via modeling.[52] SO_2 is one of a group of highly reactive gases known as ''oxides of sulfur'' with largest emissions sources being fossil fuel combustion at power plants and other industrial facilities.

b. Given the relatively inert nature of SO_2 on the short-term time scales of interest (*i.e.*, 1-hour) and the sources of SO_2 (*i.e.*, stationary point sources), the general modeling requirements for screening models in section 4.2.1 and refined models in section 4.2.2 are applicable for SO_2 modeling applications. For urban areas, AERMOD automatically invokes a half-life of 4 hours[53] to SO_2. Therefore, care must be taken when determining whether a source is urban or rural (*see* section 7.2.1.1 for urban/rural determination methodology).

4.2.3.4 Models for Nitrogen Dioxide

a. Models for assessing the impact of sources on ambient NO_2 concentrations are needed to meet NSR requirements to address compliance with the NO_2 NAAQS and PSD increments. Impact of an individual source on ambient NO_2 depends, in part, on the chemical environment into which the source's plume is to be emitted. This is due to the fact that NO_2 sources co-emit NO along with NO_2 and any emitted NO may react with ambient ozone to convert to additional NO_2 downwind. Thus, comprehensive modeling of NO_2 would need to consider the ratio of emitted NO and NO_2, the ambient levels of ozone and subsequent reactions between ozone and NO, and the photolysis of NO_2 to NO.

b. Due to the complexity of NO_2 modeling, a multi-tiered screening approach is required to obtain hourly and annual average estimates of NO_2.[54] Since these methods are considered screening techniques, their usage shall occur in agreement with the appropriate reviewing authority (paragraph 3.0(b)). Additionally, since screening techniques are conservative by their nature, there are limitations to how these options can be used. Specifically, modeling of negative emissions rates should only be done after consultation with the EPA Regional Office to ensure that decreases in concentrations would not be overestimated. Each tiered approach (*see* Figure 4–1) accounts for increasingly complex considerations of NO_2 chemistry and is described in paragraphs c through e of this subsection. The tiers of NO_2 modeling include:

i. A first-tier (most conservative) ''full'' conversion approach;

ii. A second-tier approach that assumes ambient equilibrium between NO and NO_2; and

iii. A third-tier consisting of several detailed screening techniques that account for

ambient ozone and the relative amount of NO and NO_2 emitted from a source.

c. For Tier 1, use an appropriate refined model (section 4.2.2) to estimate nitrogen oxides (NO_X) concentrations and assume a total conversion of NO to NO_2.

d. For Tier 2, multiply the Tier 1 result(s) by the Ambient Ratio Method 2 (ARM2), which provides estimates of representative equilibrium ratios of NO_2/NO_X value based ambient levels of NO_2 and NO_X derived from national data from the EPA's Air Quality System (AQS).[55] The national default for ARM2 includes a minimum ambient NO_2/NO_X ratio of 0.5 and a maximum ambient ratio of 0.9. The reviewing agency may establish alternative minimum ambient NO_2/NO_X values based on the source's in-stack emissions ratios, with alternative minimum ambient ratios reflecting the source's in-stack NO_2/NO_X ratios. Preferably, alternative minimum ambient NO_2/NO_X ratios should be based on source-specific data which satisfies all quality assurance procedures that ensure data accuracy for both NO_2 and NO_X within the typical range of measured values. However, alternate information may be used to justify a source's anticipated NO_2/NO_X in-stack ratios, such as manufacturer test data, state or local agency guidance, peer-reviewed literature, and/or the EPA's NO_2/NO_X ratio database.

e. For Tier 3, a detailed screening technique shall be applied on a case-by-case basis. Because of the additional input data requirements and complexities associated with the Tier 3 options, their usage shall occur in consultation with the EPA Regional Office in addition to the appropriate reviewing authority. The Ozone Limiting Method (OLM)[56] and the Plume Volume Molar Ratio Method (PVMRM)[57] are two detailed screening techniques that may be used for most sources. These two techniques use an appropriate section 4.2.2 model to estimate NO_X concentrations and then estimate the conversion of primary NO emissions to NO_2 based on the ambient levels of ozone and the plume characteristics. OLM only accounts for NO_2 formation based on the ambient levels of ozone while PVMRM also accommodates distance-dependent conversion ratios based on ambient ozone. Both PVMRM and OLM require that ambient ozone concentrations be provided on an hourly basis and explicit specification of the NO_2/NO_X in-stack ratios. PVMRM works best for relatively isolated and elevated point source modeling while OLM works best for large groups of sources, area sources, and near-surface releases, including roadway sources.

f. Alternative models or techniques may be considered on a case-by-case basis and their usage shall be approved by the EPA Regional Office (section 3.2). Such models or techniques should consider individual quantities of NO and NO_2 emissions, atmospheric transport and dispersion, and atmospheric transformation of NO to NO_2. Dispersion models that account for more explicit photochemistry may also be considered as an alternative model to estimate ambient impacts of NO_X sources.

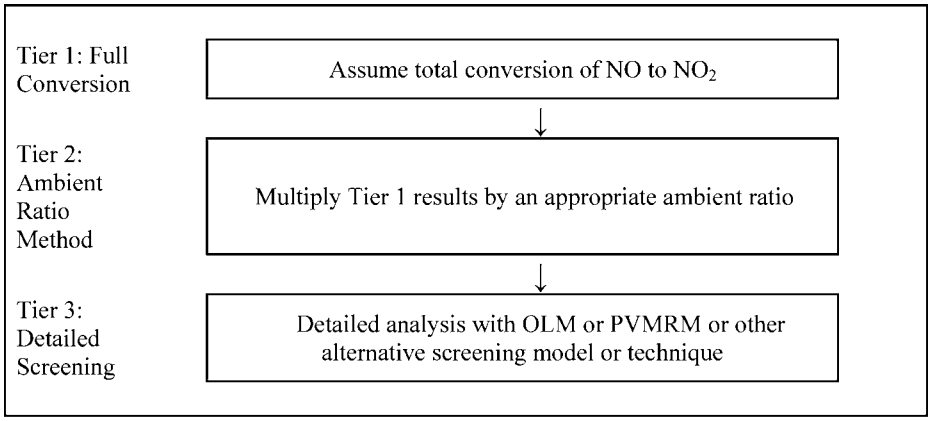

Figure 4-1: Multi-tiered Approach for Estimating NO2 Concentrations

4.2.3.5 Models for $PM_{2.5}$

a. $PM_{2.5}$ is a mixture consisting of several diverse components.[58] Ambient $PM_{2.5}$ generally consists of two components: (1) The primary component, emitted directly from a source; and (2) the secondary component,

formed in the atmosphere from other pollutants emitted from the source. Models for $PM_{2.5}$ are needed to meet NSR requirements to address compliance with the $PM_{2.5}$ NAAQS and PSD increments and for SIP attainment demonstrations.

b. For NSR modeling assessments, the general modeling requirements for screening models in section 4.2.1 and refined models in section 4.2.2 are applicable for the primary component of $PM_{2.5}$, while the methods in section 5.4 are applicable for addressing the secondary component of $PM_{2.5}$. Guidance for PSD assessments is available for determining the best approach to handling sources of primary and secondary $PM_{2.5}$.[59]

c. For SIP attainment demonstrations and regional haze reasonable progress goal analyses, effects of a control strategy on $PM_{2.5}$ are estimated from the sum of the effects on the primary and secondary components composing $PM_{2.5}$. Model users should refer to section 5.4.1 and associated SIP modeling guidance[60] for further details concerning appropriate modeling approaches.

d. The general modeling requirements for the refined models discussed in section 4.2.2 shall be applied for $PM_{2.5}$ hot-spot modeling for mobile sources. Specific guidance is available for analyzing direct $PM_{2.5}$ impacts from highways, terminals, and other transportation projects.[61]

4.2.3.6 Models for PM_{10}

a. Models for PM_{10} are needed to meet NSR requirements to address compliance with the PM_{10} NAAQS and PSD increments and for SIP attainment demonstrations.

b. For most sources, the general modeling requirements for screening models in section 4.2.1 and refined models in section 4.2.2 shall be applied for PM_{10} modeling. In cases where the particle size and its effect on ambient concentrations need to be considered, particle deposition may be used on a case-by-case basis and their usage shall be coordinated with the appropriate reviewing authority. A SIP development guide[62] is also available to assist in PM_{10} analyses and control strategy development.

c. Fugitive dust usually refers to dust put into the atmosphere by the wind blowing over plowed fields, dirt roads, or desert or sandy areas with little or no vegetation. Fugitive emissions include the emissions resulting from the industrial process that are not captured and vented through a stack, but may be released from various locations within the complex. In some unique cases, a model developed specifically for the situation may be needed. Due to the difficult nature of characterizing and modeling fugitive dust and fugitive emissions, the proposed procedure shall be determined in consultation with the appropriate reviewing authority (paragraph 3.0(b)) for each specific situation before the modeling exercise is begun. Re-entrained dust is created by vehicles driving over dirt roads (*e.g.*, haul roads) and dust-covered roads typically found in arid areas. Such sources can be characterized as line, area or volume sources.[61] [63] Emission rates may be based on site-specific data or values from the general literature.

d. Under certain conditions, recommended dispersion models may not be suitable to appropriately address the nature of ambient PM_{10}. In these circumstances, the alternative modeling approach shall be approved by the EPA Regional Office (section 3.2).

e. The general modeling requirements for the refined models discussed in section 4.2.2 shall be applied for PM_{10} hot-spot modeling for mobile sources. Specific guidance is available for analyzing direct PM_{10} impacts from highways, terminals, and other transportation projects.[61]

5.0 Models for Ozone and Secondarily Formed Particulate Matter

5.1 Discussion

a. Air pollutants formed through chemical reactions in the atmosphere are referred to as secondary pollutants. For example, ground-level ozone and a portion of $PM_{2.5}$ are secondary pollutants formed through photochemical reactions. Ozone and secondarily formed particulate matter are closely related to each other in that they share common sources of emissions and are formed in the atmosphere from chemical reactions with similar precursors.

b. Ozone formation is driven by emissions of NO_X and volatile organic compounds (VOCs). Ozone formation is a complicated nonlinear process that requires favorable meteorological conditions in addition to VOC and NO_X emissions. Sometimes complex terrain features also contribute to the build-up of precursors and subsequent ozone formation or destruction.

c. $PM_{2.5}$ can be either primary (*i.e.*, emitted directly from sources) or secondary in nature. The fraction of $PM_{2.5}$ which is primary versus secondary varies by location and season. In the United States, $PM_{2.5}$ is dominated by a variety of chemical species or components of atmospheric particles, such as ammonium sulfate, ammonium nitrate, organic carbon mass, elemental carbon, and other soil compounds and oxidized metals. $PM_{2.5}$ sulfate, nitrate, and ammonium ions are predominantly the result of chemical reactions of the oxidized products of SO_2 and NO_X emissions with direct ammonia emissions.[64]

d. Control measures reducing ozone and $PM_{2.5}$ precursor emissions may not lead to proportional reductions in ozone and $PM_{2.5}$. Modeled strategies designed to reduce ozone or $PM_{2.5}$ levels typically need to consider the chemical coupling between these pollutants. This coupling is important in understanding

processes that control the levels of both pollutants. Thus, when feasible, it is important to use models that take into account the chemical coupling between ozone and $PM_{2.5}$. In addition, using such a multi-pollutant modeling system can reduce the resource burden associated with applying and evaluating separate models for each pollutant and promotes consistency among the strategies themselves.

e. $PM_{2.5}$ is a mixture consisting of several diverse chemical species or components of atmospheric particles. Because chemical and physical properties and origins of each component differ, it may be appropriate to use either a single model capable of addressing several of the important components or to model primary and secondary components using different models. Effects of a control strategy on $PM_{2.5}$ is estimated from the sum of the effects on the specific components comprising $PM_{2.5}$.

5.2 Recommendations

a. Chemical transformations can play an important role in defining the concentrations and properties of certain air pollutants. Models that take into account chemical reactions and physical processes of various pollutants (including precursors) are needed for determining the current state of air quality, as well as predicting and projecting the future evolution of these pollutants. It is important that a modeling system provide a realistic representation of chemical and physical processes leading to secondary pollutant formation and removal from the atmosphere.

b. Chemical transport models treat atmospheric chemical and physical processes such as deposition and motion. There are two types of chemical transport models, Eulerian (grid based) and Lagrangian. These types of models are differentiated from each other by their frame of reference. Eulerian models are based on a fixed frame of reference and Lagrangian models use a frame of reference that moves with parcels of air between the source and receptor point.[9] Photochemical grid models are three-dimensional Eulerian grid-based models that treat chemical and physical processes in each grid cell and use diffusion and transport processes to move chemical species between grid cells.[9] These types of models are appropriate for assessment of near-field and regional scale reactive pollutant impacts from specific sources[7 10 11 12] or all sources.[13 14 15] In some limited cases, the secondary processes can be treated with a box model, ideally in combination with a number of other modeling techniques and/or analyses to treat individual source sectors.

c. Regardless of the modeling system used to estimate secondary impacts of ozone and/or $PM_{2.5}$, model results should be compared to observation data to generate confidence that the modeling system is representative of the local and regional air quality. For ozone related projects, model estimates of ozone should be compared with observations in both time and space. For $PM_{2.5}$, model estimates of speciated $PM_{2.5}$ components (such as sulfate ion, nitrate ion, etc.) should be compared with observations in both time and space.[65]

d. Model performance metrics comparing observations and predictions are often used to summarize model performance. These metrics include mean bias, mean error, fractional bias, fractional error, and correlation coefficient. [65] There are no specific levels of any model performance metric that indicate ''acceptable'' model performance. The EPA's preferred approach for providing context about model performance is to compare model performance metrics with similar contemporary applications. [60 65] Because model application purpose and scope vary, model users should consult with the appropriate reviewing authority (paragraph 3.0(b)) to determine what model performance elements should be emphasized and presented to provide confidence in the regulatory model application.

e. There is no preferred modeling system or technique for estimating ozone or secondary $PM_{2.5}$ for specific source impacts or to assess impacts from multiple sources. For assessing secondary pollutant impacts from single sources, the degree of complexity required to assess potential impacts varies depending on the nature of the source, its emissions, and the background environment. The EPA recommends a two-tiered approach where the first tier consists of using existing technically credible and appropriate relationships between emissions and impacts developed from previous modeling that is deemed sufficient for evaluating a source's impacts. The second tier consists of more sophisticated case-specific modeling analyses. The appropriate tier for a given application should be selected in consultation with the appropriate reviewing authority (paragraph 3.0(b)) and be consistent with EPA guidance.[66]

5.3 Recommended Models and Approaches for Ozone

a. Models that estimate ozone concentrations are needed to guide the choice of strategies for the purposes of a nonattainment area demonstrating future year attainment of the ozone NAAQS. Additionally, models that estimate ozone concentrations are needed to assess impacts from specific sources or source complexes to satisfy requirements for NSR and other regulatory programs. Other purposes for ozone modeling include estimating the impacts of specific events on air

quality, ozone deposition impacts, and planning for areas that may be attaining the ozone NAAQS.

5.3.1 Models for NAAQS Attainment Demonstrations and Multi-Source Air Quality Assessments

a. Simulation of ozone formation and transport is a complex exercise. Control agencies with jurisdiction over areas with ozone problems should use photochemical grid models to evaluate the relationship between precursor species and ozone. Use of photochemical grid models is the recommended means for identifying control strategies needed to address high ozone concentrations in such areas. Judgment on the suitability of a model for a given application should consider factors that include use of the model in an attainment test, development of emissions and meteorological inputs to the model, and choice of episodes to model. Guidance on the use of models and other analyses for demonstrating attainment of the air quality goals for ozone is available. [59] [60] Users should consult with the appropriate reviewing authority (paragraph 3.0(b)) to ensure the most current modeling guidance is applied.

5.3.2 Models for Single-Source Air Quality Assessments

a. Depending on the magnitude of emissions, estimating the impact of an individual source's emissions of NO_X and VOC on ambient ozone is necessary for obtaining a permit. The simulation of ozone formation and transport requires realistic treatment of atmospheric chemistry and deposition. Models (*e.g.*, Lagrangian and photochemical grid models) that integrate chemical and physical processes important in the formation, decay, and transport of ozone and important precursor species should be applied. Photochemical grid models are primarily designed to characterize precursor emissions and impacts from a wide variety of sources over a large geographic area but can also be used to assess the impacts from specific sources. [7] [11] [12]

b. The first tier of assessment for ozone impacts involves those situations where existing technical information is available (*e.g.*, results from existing photochemical grid modeling, published empirical estimates of source specific impacts, or reduced-form models) in combination with other supportive information and analysis for the purposes of estimating secondary impacts from a particular source. The existing technical information should provide a credible and representative estimate of the secondary impacts from the project source. The appropriate reviewing authority (paragraph 3.0(b)) and appropriate EPA guidance [66] should be consulted to determine what types of assessments may be appropriate on a case-by-case basis.

c. The second tier of assessment for ozone impacts involves those situations where existing technical information is not available or a first tier demonstration indicates a more refined assessment is needed. For these situations, chemical transport models should be used to address single-source impacts. Special considerations are needed when using these models to evaluate the ozone impact from an individual source. Guidance on the use of models and other analyses for demonstrating the impacts of single sources for ozone is available. [66] This guidance document provides a more detailed discussion of the appropriate approaches to obtaining estimates of ozone impacts from a single source. Model users should use the latest version of the guidance in consultation with the appropriate reviewing authority (paragraph 3.0(b)) to determine the most suitable refined approach for single-source ozone modeling on a case-by-case basis.

5.4 Recommended Models and Approaches for Secondarily Formed $PM_{2.5}$

a. Models that estimate $PM_{2.5}$ concentrations are needed to guide the choice of strategies for the purposes of a nonattainment area demonstrating future year attainment of the $PM_{2.5}$ NAAQS. Additionally, models that estimate $PM_{2.5}$ concentrations are needed to assess impacts from specific sources or source complexes to satisfy requirements for NSR and other regulatory programs. Other purposes for $PM_{2.5}$ modeling include estimating the impacts of specific events on air quality, visibility, deposition impacts, and planning for areas that may be attaining the $PM_{2.5}$ NAAQS.

5.4.1 Models for NAAQS Attainment Demonstrations and Multi-Source Air Quality Assessments

a. Models for $PM_{2.5}$ are needed to assess the adequacy of a proposed strategy for meeting the annual and 24-hour $PM_{2.5}$ NAAQS. Modeling primary and secondary $PM_{2.5}$ can be a multi-faceted and complex problem, especially for secondary components of $PM_{2.5}$ such as sulfates and nitrates. Control agencies with jurisdiction over areas with secondary $PM_{2.5}$ problems should use models that integrate chemical and physical processes important in the formation, decay, and transport of these species (*e.g.*, photochemical grid models). Suitability of a modeling approach or mix of modeling approaches for a given application requires technical judgment as well as professional experience in choice of models, use of the model(s) in an attainment test, development of emissions and meteorological inputs to the model, and selection of days to model. Guidance on the use of models and other

analyses for demonstrating attainment of the air quality goals for $PM_{2.5}$ is available.[59][60] Users should consult with the appropriate reviewing authority (paragraph 3.0(b)) to ensure the most current modeling guidance is applied.

5.4.2 Models for Single-Source Air Quality Assessments

a. Depending on the magnitude of emissions, estimating the impact of an individual source's emissions on secondary particulate matter concentrations may be necessary for obtaining a permit. Primary $PM_{2.5}$ components shall be simulated using the general modeling requirements in section 4.2.3.5. The simulation of secondary particulate matter formation and transport is a complex exercise requiring realistic treatment of atmospheric chemistry and deposition. Models should be applied that integrate chemical and physical processes important in the formation, decay, and transport of these species (*e.g.*, Lagrangian and photochemical grid models). Photochemical grid models are primarily designed to characterize precursor emissions and impacts from a wide variety of sources over a large geographic area and can also be used to assess the impacts from specific sources.[7][10] For situations where a project source emits both primary $PM_{2.5}$ and $PM_{2.5}$ precursors, the contribution from both should be combined for use in determining the source's ambient impact. Approaches for combining primary and secondary impacts are provided in appropriate guidance for single source permit related demonstrations. [66]

b. The first tier of assessment for secondary $PM_{2.5}$ impacts involves those situations where existing technical information is available (*e.g.*, results from existing photochemical grid modeling, published empirical estimates of source specific impacts, or reduced-form models) in combination with other supportive information and analysis for the purposes of estimating secondary impacts from a particular source. The existing technical information should provide a credible and representative estimate of the secondary impacts from the project source. The appropriate reviewing authority (paragraph 3.0(b)) and appropriate EPA guidance[66] should be consulted to determine what types of assessments may be appropriate on a case-by-case basis.

c. The second tier of assessment for secondary $PM_{2.5}$ impacts involves those situations where existing technical information is not available or a first tier demonstration indicates a more refined assessment is needed. For these situations, chemical transport models should be used for assessments of single-source impacts. Special considerations are needed when using these models to evaluate the secondary particulate matter impact from an individual source. Guidance on the use of models and other analyses for demonstrating the impacts of single sources for secondary $PM_{2.5}$ is available. [66] This guidance document provides a more detailed discussion of the appropriate approaches to obtaining estimates of secondary particulate matter concentrations from a single source. Model users should use the latest version of this guidance in consultation with the appropriate reviewing authority (paragraph 3.0(b)) to determine the most suitable single-source modeling approach for secondary $PM_{2.5}$ on a case-by-case basis.

6.0 Modeling for Air Quality Related Values and Other Governmental Programs

6.1 Discussion

a. Other federal government agencies and state, local, and tribal agencies with air quality and land management responsibilities have also developed specific modeling approaches for their own regulatory or other requirements. Although such regulatory requirements and guidance have come about because of EPA rules or standards, the implementation of such regulations and the use of the modeling techniques is under the jurisdiction of the agency issuing the guidance or directive. This section covers such situations with reference to those guidance documents, when they are available.

b. When using the model recommended or discussed in the *Guideline* in support of programmatic requirements not specifically covered by EPA regulations, the model user should consult the appropriate federal, state, local, or tribal agency to ensure the proper application and use of the models and/or techniques. These agencies have developed specific modeling approaches for their own regulatory or other requirements. Most of the programs have, or will have when fully developed, separate guidance documents that cover the program and a discussion of the tools that are needed. The following paragraphs reference those guidance documents, when they are available.

6.2 Air Quality Related Values

a. The 1990 CAA Amendments give FLMs an ''affirmative responsibility'' to protect the natural and cultural resources of Class I areas from the adverse impacts of air pollution and to provide the appropriate procedures and analysis techniques. The CAA identifies the FLM as the Secretary of the department, or their designee, with authority over these lands. Mandatory Federal Class I areas are defined in the CAA as international parks, national parks over 6,000 acres, and wilderness areas and memorial parks over 5,000 acres, established as of 1977. The FLMs are also concerned with the protection of resources in federally managed

Class II areas because of other statutory mandates to protect these areas. Where state or tribal agencies have successfully petitioned the EPA and lands have been redesignated to Class I status, these agencies may have equivalent responsibilities to that of the FLMs for these non-federal Class I areas as described throughout the remainder of section 6.2.

b. The FLM agency responsibilities include the review of air quality permit applications from proposed new or modified major pollution sources that may affect these Class I areas to determine if emissions from a proposed or modified source will cause or contribute to adverse impacts on air quality related values (AQRVs) of a Class I area and making recommendations to the FLM. AQRVs are resources, identified by the FLM agencies, that have the potential to be affected by air pollution. These resources may include visibility, scenic, cultural, physical, or ecological resources for a particular area. The FLM agencies take into account the particular resources and AQRVs that would be affected; the frequency and magnitude of any potential impacts; and the direct, indirect, and cumulative effects of any potential impacts in making their recommendations.

c. While the AQRV notification and impact analysis requirements are outlined in the PSD regulations at 40 CFR 51.166(p) and 40 CFR 52.21(p), determination of appropriate analytical methods and metrics for AQRV's are determined by the FLM agencies and are published in guidance external to the general recommendations of this paragraph.

d. To develop greater consistency in the application of air quality models to assess potential AQRV impacts in both Class I areas and protected Class II areas, the FLM agencies have developed the Federal Land Managers' Air Quality Related Values Work Group Phase I Report (FLAG).[67] FLAG focuses upon specific technical and policy issues associated with visibility impairment, effects of pollutant deposition on soils and surface waters, and ozone effects on vegetation. Model users should consult the latest version of the FLAG report for current modeling guidance and with affected FLM agency representatives for any application specific guidance which is beyond the scope of the *Guideline*.

6.2.1 Visibility

a. Visibility in important natural areas (*e.g.,* Federal Class I areas) is protected under a number of provisions of the CAA, including sections 169A and 169B (addressing impacts primarily from existing sources) and section 165 (new source review). Visibility impairment is caused by light scattering and light absorption associated with particles and gases in the atmosphere. In most areas of the country, light scattering by $PM_{2.5}$ is the most significant component of visibility impairment. The key components of $PM_{2.5}$ contributing to visibility impairment include sulfates, nitrates, organic carbon, elemental carbon, and crustal material.[67]

b. Visibility regulations (40 CFR 51.300 through 51.309) require state, local, and tribal agencies to mitigate current and prevent future visibility impairment in any of the 156 mandatory Federal Class I areas where visibility is considered an important attribute. In 1999, the EPA issued revisions to the regulations to address visibility impairment in the form of regional haze, which is caused by numerous, diverse sources (*e.g.,* stationary, mobile, and area sources) located across a broad region (40 CFR 51.308 through 51.309). The state of relevant scientific knowledge has expanded significantly since that time. A number of studies and reports[68][69] have concluded that long-range transport (*e.g.,* up to hundreds of kilometers) of fine particulate matter plays a significant role in visibility impairment across the country. Section 169A of the CAA requires states to develop SIPs containing long-term strategies for remedying existing and preventing future visibility impairment in the 156 mandatory Class I Federal areas, where visibility is considered an important attribute. In order to develop long-term strategies to address regional haze, many state, local, and tribal agencies will need to conduct regional-scale modeling of fine particulate concentrations and associated visibility impairment.

c. The FLAG visibility modeling recommendations are divided into two distinct sections to address different requirements for: (1) Near field modeling where plumes or layers are compared against a viewing background, and (2) distant/multi-source modeling for plumes and aggregations of plumes that affect the general appearance of a scene.[67] The recommendations separately address visibility assessments for sources proposing to locate relatively near and at farther distances from these areas.[67]

6.2.1.1 Models for Estimating Near-Field Visibility Impairment

a. To calculate the potential impact of a plume of specified emissions for specific transport and dispersion conditions (''plume blight'') for source-receptor distances less than 50 km, a screening model and guidance are available.[67][70] If a more comprehensive analysis is necessary, a refined model should be selected. The model selection, procedures, and analyses should be determined in consultation with the appropriate reviewing authority (paragraph 3.0(b)) and the affected FLM(s).

6.2.1.2 Models for Estimating Visibility Impairment for Long-Range Transport

a. Chemical transformations can play an important role in defining the concentrations and properties of certain air pollutants. Models that take into account chemical reactions and physical processes of various pollutants (including precursors) are needed for determining the current state of air quality, as well as predicting and projecting the future evolution of these pollutants. It is important that a modeling system provide a realistic representation of chemical and physical processes leading to secondary pollutant formation and removal from the atmosphere.

b. Chemical transport models treat atmospheric chemical and physical processes such as deposition and motion. There are two types of chemical transport models, Eulerian (grid based) and Lagrangian. These types of models are differentiated from each other by their frame of reference. Eulerian models are based on a fixed frame of reference and Lagrangian models use a frame of reference that moves with parcels of air between the source and receptor point.[9] Photochemical grid models are three-dimensional Eulerian grid-based models that treat chemical and physical processes in each grid cell and use diffusion and transport processes to move chemical species between grid cells.[9] These types of models are appropriate for assessment of near-field and regional scale reactive pollutant impacts from specific sources[7 10 11 12] or all sources.[13 14 15]

c. Development of the requisite meteorological and emissions databases necessary for use of photochemical grid models to estimate AQRVs should conform to recommendations in section 8 and those outlined in the EPA's *Modeling Guidance for Demonstrating Attainment of Air Quality Goals for Ozone, $PM_{2.5}$, and Regional Haze*.[60] Demonstration of the adequacy of prognostic meteorological fields can be established through appropriate diagnostic and statistical performance evaluations consistent with recommendations provided in the appropriate guidance.[60] Model users should consult the latest version of this guidance and with the appropriate reviewing authority (paragraph 3.0(b)) for any application-specific guidance that is beyond the scope of this subsection.

6.2.2 Models for Estimating Deposition Impacts

a. For many Class I areas, AQRVs have been identified that are sensitive to atmospheric deposition of air pollutants. Emissions of NO_X, sulfur oxides, NH_3, mercury, and secondary pollutants such as ozone and particulate matter affect components of ecosystems. In sensitive ecosystems, these compounds can acidify soils and surface waters, add nutrients that change biodiversity, and affect the ecosystem services provided by forests and natural areas.[67] To address the relationship between deposition and ecosystem effects, the FLM agencies have developed estimates of critical loads. A critical load is defined as, ''A quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge.'' [71]

b. The FLM deposition modeling recommendations are divided into two distinct sections to address different requirements for: (1) Near field modeling, and (2) distant/multi-source modeling for cumulative effects. The recommendations separately address deposition assessments for sources proposing to locate relatively near and at farther distances from these areas.[67] Where the source and receptors are not in close proximity, chemical transport (*e.g.*, photochemical grid) models generally should be applied for an assessment of deposition impacts due to one or a small group of sources. Over these distances, chemical and physical transformations can change atmospheric residence time due to different propensity for deposition to the surface of different forms of nitrate and sulfate. Users should consult the latest version of the FLAG report[67] and relevant FLM representatives for guidance on the use of models for deposition. Where source and receptors are in close proximity, users should contact the appropriate FLM for application-specific guidance.

6.3 Modeling Guidance for Other Governmental Programs

a. Dispersion and photochemical grid modeling may need to be conducted to ensure that individual and cumulative offshore oil and gas exploration, development, and production plans and activities do not significantly affect the air quality of any state as required under the Outer Continental Shelf Lands Act (OCSLA). Air quality modeling requires various input datasets, including emissions sources, meteorology, and pre-existing pollutant concentrations. For sources under the reviewing authority of the Department of Interior, Bureau of Ocean Energy Management (BOEM), guidance for the development of all necessary Outer Continental Shelf (OCS) air quality modeling inputs and appropriate model selection and application is available from the BOEM's Web site: *https://www.boem.gov/GOMR-Environmental-Compliance*.

b. The Federal Aviation Administration (FAA) is the appropriate reviewing authority for air quality assessments of primary pollutant impacts at airports and air bases. The Aviation Environmental Design Tool (AEDT) is developed and supported by the FAA, and

is appropriate for air quality assessment of primary pollutant impacts at airports or air bases. AEDT has adopted AERMOD for treating dispersion. Application of AEDT is intended for estimating the change in emissions for aircraft operations, point source, and mobile source emissions on airport property and quantify the associated pollutant level- concentrations. AEDT is not intended for PSD, SIP, or other regulatory air quality analyses of point or mobile sources at or peripheral to airport property that are unrelated to airport operations. The latest version of AEDT may be obtained from the FAA at: *https://aedt.faa.gov*.

7.0 General Modeling Considerations

7.1 Discussion

a. This section contains recommendations concerning a number of different issues not explicitly covered in other sections of the *Guideline*. The topics covered here are not specific to any one program or modeling area, but are common to dispersion modeling analyses for criteria pollutants.

7.2 Recommendations

7.2.1 All Sources

7.2.1.1 Dispersion Coefficients

a. For any dispersion modeling exercise, the urban or rural determination of a source is critical in determining the boundary layer characteristics that affect the model's prediction of downwind concentrations. Historically, steady-state Gaussian plume models used in most applications have employed dispersion coefficients based on Pasquill-Gifford[72] in rural areas and McElroy-Pooler[73] in urban areas. These coefficients are still incorporated in the BLP and OCD models. However, the AERMOD model incorporates a more up-to-date characterization of the atmospheric boundary layer using continuous functions of parameterized horizontal and vertical turbulence based on Monin-Obukhov similarity (scaling) relationships.[44] Another key feature of AERMOD's formulation is the option to use directly observed variables of the boundary layer to parameterize dispersion.[44 45]

b. The selection of rural or urban dispersion coefficients in a specific application should follow one of the procedures suggested by Irwin[74] to determine whether the character of an area is primarily urban or rural (of the two methods, the land use procedure is considered more definitive.):

i. Land Use Procedure: (1) Classify the land use within the total area, A_o, circumscribed by a 3 km radius circle about the source using the meteorological land use typing scheme proposed by Auer;[75] (2) if land use types I1, I2, C1, R2, and R3 account for 50 percent or more of A_o, use urban dispersion coefficients; otherwise, use appropriate rural dispersion coefficients.

ii. Population Density Procedure: (1) Compute the average population density, $\bar{p}$ per square kilometer with A_o as defined above; (2) If $\bar{p}$ is greater than 750 people per square kilometer, use urban dispersion coefficients; otherwise use appropriate rural dispersion coefficients.

c. Population density should be used with caution and generally not be applied to highly industrialized areas where the population density may be low and, thus, a rural classification would be indicated. However, the area is likely to be sufficiently built-up so that the urban land use criteria would be satisfied. Therefore, in this case, the classification should be ''urban'' and urban dispersion parameters should be used.

d. For applications of AERMOD in urban areas, under either the Land Use Procedure or the Population Density Procedure, the user needs to estimate the population of the urban area affecting the modeling domain because the urban influence in AERMOD is scaled based on a user-specified population. For non-population oriented urban areas, or areas influenced by both population and industrial activity, the user will need to estimate an equivalent population to adequately account for the combined effects of industrialized areas and populated areas within the modeling domain. Selection of the appropriate population for these applications should be determined in consultation with the appropriate reviewing authority (paragraph 3.0(b)) and the latest version of the AERMOD Implementation Guide.[76]

e. It should be noted that AERMOD allows for modeling rural and urban sources in a single model run. For analyses of whole urban complexes, the entire area should be modeled as an urban region if most of the sources are located in areas classified as urban. For tall stacks located within or adjacent to small or moderate sized urban areas, the stack height or effective plume height may extend above the urban boundary layer and, therefore, may be more appropriately modeled using rural coefficients. Model users should consult with the appropriate reviewing authority (paragraph 3.0(b)) and the latest version of the AERMOD Implementation Guide[76] when evaluating this situation.

f. Buoyancy-induced dispersion (BID), as identified by Pasquill,[77] is included in the preferred models and should be used where buoyant sources (*e.g.,* those involving fuel combustion) are involved.

7.2.1.2 Complex Winds

a. *Inhomogeneous local winds.* In many parts of the United States, the ground is neither

flat nor is the ground cover (or land use) uniform. These geographical variations can generate local winds and circulations, and modify the prevailing ambient winds and circulations. Typically, geographic effects are more apparent when the ambient winds are light or calm, as stronger synoptic or mesoscale winds can modify, or even eliminate the weak geographic circulations.[78] In general, these geographically induced wind circulation effects are named after the source location of the winds, *e.g.*, lake and sea breezes, and mountain and valley winds. In very rugged hilly or mountainous terrain, along coastlines, or near large land use variations, the characteristics of the winds are a balance of various forces, such that the assumptions of steady-state straight-line transport both in time and space are inappropriate. In such cases, a model should be chosen to fully treat the time and space variations of meteorology effects on transport and dispersion. The setup and application of such a model should be determined in consultation with the appropriate reviewing authority (paragraph 3.0(b)) consistent with limitations of paragraph 3.2.2(e). The meteorological input data requirements for developing the time and space varying three-dimensional winds and dispersion meteorology for these situations are discussed in paragraph 8.4.1.2(c). Examples of inhomogeneous winds include, but are not limited to, situations described in the following paragraphs:

i. *Inversion breakup fumigation.* Inversion breakup fumigation occurs when a plume (or multiple plumes) is emitted into a stable layer of air and that layer is subsequently mixed to the ground through convective transfer of heat from the surface or because of advection to less stable surroundings. Fumigation may cause excessively high concentrations, but is usually rather short-lived at a given receptor. There are no recommended refined techniques to model this phenomenon. There are, however, screening procedures[40] that may be used to approximate the concentrations. Considerable care should be exercised in using the results obtained from the screening techniques.

ii. *Shoreline fumigation.* Fumigation can be an important phenomenon on and near the shoreline of bodies of water. This can affect both individual plumes and area-wide emissions. When fumigation conditions are expected to occur from a source or sources with tall stacks located on or just inland of a shoreline, this should be addressed in the air quality modeling analysis. The EPA has evaluated several coastal fumigation models, and the evaluation results of these models are available for their possible application on a case-by-case basis when air quality estimates under shoreline fumigation conditions are needed.[79] Selection of the appropriate model for applications where shoreline fumigation is of concern should be determined in consultation with the appropriate reviewing authority (paragraph 3.0(b)).

iii. *Stagnation.* Stagnation conditions are characterized by calm or very low wind speeds, and variable wind directions. These stagnant meteorological conditions may persist for several hours to several days. During stagnation conditions, the dispersion of air pollutants, especially those from low-level emissions sources, tends to be minimized, potentially leading to relatively high ground-level concentrations. If point sources are of interest, users should note the guidance provided in paragraph (a) of this subsection. Selection of the appropriate model for applications where stagnation is of concern should be determined in consultation with the appropriate reviewing authority (paragraph 3.0(b)).

7.2.1.3 Gravitational Settling and Deposition

a. Gravitational settling and deposition may be directly included in a model if either is a significant factor. When particulate matter sources can be quantified and settling and dry deposition are problems, use professional judgment along with coordination with the appropriate reviewing authority (paragraph 3.0(b)). AERMOD contains algorithms for dry and wet deposition of gases and particles.[80] For other Gaussian plume models, an ''infinite half-life'' may be used for estimates of particle concentrations when only exponential decay terms are used for treating settling and deposition. Lagrangian models have varying degrees of complexity for dealing with settling and deposition and the selection of a parameterization for such should be included in the approval process for selecting a Lagrangian model. Eulerian grid models tend to have explicit parameterizations for gravitational settling and deposition as well as wet deposition parameters already included as part of the chemistry scheme.

7.2.2 Stationary Sources

7.2.2.1 Good Engineering Practice Stack Height

a. The use of stack height credit in excess of Good Engineering Practice (GEP) stack height or credit resulting from any other dispersion technique is prohibited in the development of emissions limits by 40 CFR 51.118 and 40 CFR 51.164. The definition of GEP stack height and dispersion technique are contained in 40 CFR 51.100. Methods and procedures for making the appropriate stack height calculations, determining stack height credits and an example of applying those techniques are found in several references,[81 82 83 84] that provide a great deal of additional information for evaluating and describing building cavity and wake effects.

b. If stacks for new or existing major sources are found to be less than the height defined by the EPA's refined formula for determining GEP height, then air quality impacts associated with cavity or wake effects due to the nearby building structures should be determined. The EPA refined formula height is defined as H + 1.5L.[83] Since the definition of GEP stack height defines excessive concentrations as a maximum ground-level concentration due in whole or in part to downwash of at least 40 percent in excess of the maximum concentration without downwash, the potential air quality impacts associated with cavity and wake effects should also be considered for stacks that equal or exceed the EPA formula height for GEP. The AERSCREEN model can be used to obtain screening estimates of potential downwash influences, based on the PRIME downwash algorithm incorporated in the AERMOD model. If more refined concentration estimates are required, AERMOD should be used (section 4.2.2).

7.2.2.2 Plume Rise

a. The plume rise methods of Briggs[85 86] are incorporated in many of the preferred models and are recommended for use in many modeling applications. In AERMOD,[44 45] for the stable boundary layer, plume rise is estimated using an iterative approach, similar to that in the CTDMPLUS model. In the convective boundary layer, plume rise is superposed on the displacements by random convective velocities.[87] In AERMOD, plume rise is computed using the methods of Briggs, except in cases involving building downwash, in which a numerical solution of the mass, energy, and momentum conservation laws is performed.[88] No explicit provisions in these models are made for multistack plume rise enhancement or the handling of such special plumes as flares.

b. Gradual plume rise is generally recommended where its use is appropriate: (1) In AERMOD; (2) in complex terrain screening procedures to determine close-in impacts; and (3) when calculating the effects of building wakes. The building wake algorithm in AERMOD incorporates and exercises the thermodynamically based gradual plume rise calculations as described in paragraph (a) of this subsection. If the building wake is calculated to affect the plume for any hour, gradual plume rise is also used in downwind dispersion calculations to the distance of final plume rise, after which final plume rise is used. Plumes captured by the near wake are re-emitted to the far wake as a ground-level volume source.

c. Stack tip downwash generally occurs with poorly constructed stacks and when the ratio of the stack exit velocity to wind speed is small. An algorithm developed by Briggs[86] is the recommended technique for this situation and is used in preferred models for point sources.

d. On a case-by-case basis, refinements to the preferred model may be considered for plume rise and downwash effects and shall occur in agreement with the appropriate reviewing authority (paragraph 3.0(b)) and approval by the EPA Regional Office based on the requirements of section 3.2.2.

7.2.3 Mobile Sources

a. Emissions of primary pollutants from mobile sources can be modeled with an appropriate model identified in section 4.2. Screening of mobile sources can be accomplished by using screening meteorology, *e.g.*, worst-case meteorological conditions. Maximum hourly concentrations computed from screening modeling can be converted to longer averaging periods using the scaling ratios specified in the AERSCREEN User's Guide.[37]

b. Mobile sources can be modeled in AERMOD as either line (*i.e.*, elongated area) sources or as a series of volume sources. However, since mobile source modeling usually includes an analysis of very near-source impacts (*e.g.*, hot-spot modeling, which can include receptors within 5–10 meters (m) of the roadway), the results can be highly sensitive to the characterization of the mobile emissions. Important characteristics for both line/area and volume sources include the plume release height, source width, and initial dispersion characteristics, and should also take into account the impact of traffic-induced turbulence that can cause roadway sources to have larger initial dimensions than might normally be used for representing line sources.

c. The EPA's quantitative PM hot-spot guidance[61] and Haul Road Workgroup Final Report[63] provide guidance on the appropriate characterization of mobile sources as a function of the roadway and vehicle characteristics. The EPA's quantitative PM hot-spot guidance includes important considerations and should be consulted when modeling roadway links. Area, line or volume sources may be used for modeling mobile sources. However, experience in the field has shown that area sources may be easier to characterize correctly compared to volume sources. If volume sources are used, it is particularly important to ensure that roadway emissions are appropriately spaced when using volume source so that the emissions field is uniform across the roadway. Additionally, receptor placement is particularly important for volume sources that have ''exclusion zones'' where concentrations are not calculated for receptors located ''within'' the volume sources, *i.e.*, less than 2.15 times the initial lateral dispersion coefficient from the center of the volume.[61] Placing receptors in these ''exclusion zones'' will result in underestimates of roadway impacts.

8.0 MODEL INPUT DATA

a. Databases and related procedures for estimating input parameters are an integral part of the modeling process. The most appropriate input data available should always be selected for use in modeling analyses. Modeled concentrations can vary widely depending on the source data or meteorological data used. This section attempts to minimize the uncertainty associated with database selection and use by identifying requirements for input data used in modeling. More specific data requirements and the format required for the individual models are described in detail in the user's guide and/or associated documentation for each model.

8.1 Modeling Domain

8.1.1 Discussion

a. The modeling domain is the geographic area for which the required air quality analyses for the NAAQS and PSD increments are conducted.

8.1.2 Requirements

a. For a NAAQS or PSD increments assessment, the modeling domain or project's impact area shall include all locations where the emissions of a pollutant from the new or modifying source(s) may cause a significant ambient impact. This impact area is defined as an area with a radius extending from the new or modifying source to: (1) The most distant location where air quality modeling predicts a significant ambient impact will occur, or (2) the nominal 50 km distance considered applicable for Gaussian dispersion models, whichever is less. The required air quality analysis shall be carried out within this geographical area with characterization of source impacts, nearby source impacts, and background concentrations, as recommended later in this section.

b. For SIP attainment demonstrations for ozone and $PM_{2.5}$, or regional haze reasonable progress goal analyses, the modeling domain is determined by the nature of the problem being modeled and the spatial scale of the emissions that impact the nonattainment or Class I area(s). The modeling domain shall be designed so that all major upwind source areas that influence the downwind nonattainment area are included in addition to all monitor locations that are currently or recently violating the NAAQS or close to violating the NAAQS in the nonattainment area. Similarly, all Class I areas to be evaluated in a regional haze modeling application shall be included and sufficiently distant from the edge of the modeling domain. Guidance on the determination of the appropriate modeling domain for photochemical grid models in demonstrating attainment of these air quality goals is available.[60] Users should consult the latest version of this guidance for the most current modeling guidance and the appropriate reviewing authority (paragraph 3.0(b)) for any application specific guidance that is beyond the scope of this section.

8.2 Source Data

8.2.1 Discussion

a. Sources of pollutants can be classified as point, line, area, and volume sources. Point sources are defined in terms of size and may vary between regulatory programs. The line sources most frequently considered are roadways and streets along which there are well-defined movements of motor vehicles. They may also be lines of roof vents or stacks, such as in aluminum refineries. Area and volume sources are often collections of a multitude of minor sources with individually small emissions that are impractical to consider as separate point or line sources. Large area sources are typically treated as a grid network of square areas, with pollutant emissions distributed uniformly within each grid square. Generally, input data requirements for air quality models necessitate the use of metric units. As necessary, any English units common to engineering applications should be appropriately converted to metric.

b. For point sources, there are many source characteristics and operating conditions that may be needed to appropriately model the facility. For example, the plant layout (*e.g.*, location of stacks and buildings), stack parameters (*e.g.*, height and diameter), boiler size and type, potential operating conditions, and pollution control equipment parameters. Such details are required inputs to air quality models and are needed to determine maximum potential impacts.

c. Modeling mobile emissions from streets and highways requires data on the road layout, including the width of each traveled lane, the number of lanes, and the width of the median strip. Additionally, traffic patterns should be taken into account (*e.g.*, daily cycles of rush hour, differences in weekday and weekend traffic volumes, and changes in the distribution of heavy-duty trucks and light-duty passenger vehicles), as these patterns will affect the types and amounts of pollutant emissions allocated to each lane and the height of emissions.

d. Emission factors can be determined through source-specific testing and measurements (*e.g.*, stack test data) from existing sources or provided from a manufacturing association or vendor. Additionally, emissions factors for a variety of source types are compiled in an EPA publication commonly known as AP–42.[89] AP–42 also provides an indication of the quality and amount of data on which many of the factors are based. Other information concerning emissions is

available in EPA publications relating to specific source categories. The appropriate reviewing authority (paragraph 3.0(b)) should be consulted to determine appropriate source definitions and for guidance concerning the determination of emissions from and techniques for modeling the various source types.

8.2.2 Requirements

a. For SIP attainment demonstrations for the purpose of projecting future year NAAQS attainment for ozone, $PM_{2.5}$, and regional haze reasonable progress goal analyses, emissions which reflect actual emissions during the base modeling year time period should be input to models for base year modeling. Emissions projections to future years should account for key variables such as growth due to increased or decreased activity, expected emissions controls due to regulations, settlement agreements or consent decrees, fuel switches, and any other relevant information. Guidance on emissions estimation techniques (including future year projections) for SIP attainment demonstrations is available.[60 90]

b. For the purpose of SIP revisions for stationary point sources, the regulatory modeling of inert pollutants shall use the emissions input data shown in Table 8–1 for short-term and long-term NAAQS. To demonstrate compliance and/or establish the appropriate SIP emissions limits, Table 8–1 generally provides for the use of ''allowable'' emissions in the regulatory dispersion modeling of the stationary point source(s) of interest. In such modeling, these source(s) should be modeled sequentially with these loads for every hour of the year. As part of a cumulative impact analysis, Table 8–1 allows for the model user to account for actual operations in developing the emissions inputs for dispersion modeling of nearby sources, while other sources are best represented by air quality monitoring data. Consultation with the appropriate reviewing authority (paragraph 3.0(b)) is advisable on the establishment of the appropriate emissions inputs for regulatory modeling applications with respect to SIP revisions for stationary point sources.

c. For the purposes of demonstrating NAAQS compliance in a PSD assessment, the regulatory modeling of inert pollutants shall use the emissions input data shown in Table 8–2 for short and long-term NAAQS. The new or modifying stationary point source shall be modeled with ''allowable'' emissions in the regulatory dispersion modeling. As part of a cumulative impact analysis, Table 8–2 allows for the model user to account for actual operations in developing the emissions inputs for dispersion modeling of nearby sources, while other sources are best represented by air quality monitoring data. For purposes of situations involving emissions trading, refer to current EPA policy and guidance to establish input data. Consultation with the appropriate reviewing authority (paragraph 3.0(b)) is advisable on the establishment of the appropriate emissions inputs for regulatory modeling applications with respect to PSD assessments for a proposed new or modifying source.

d. For stationary source applications, changes in operating conditions that affect the physical emission parameters (*e.g.*, release height, initial plume volume, and exit velocity) shall be considered to ensure that maximum potential impacts are appropriately determined in the assessment. For example, the load or operating condition for point sources that causes maximum ground-level concentrations shall be established. As a minimum, the source should be modeled using the design capacity (100 percent load). If a source operates at greater than design capacity for periods that could result in violations of the NAAQS or PSD increments, this load should be modeled. Where the source operates at substantially less than design capacity, and the changes in the stack parameters associated with the operating conditions could lead to higher ground level concentrations, loads such as 50 percent and 75 percent of capacity should also be modeled. Malfunctions which may result in excess emissions are not considered to be a normal operating condition. They generally should not be considered in determining allowable emissions. However, if the excess emissions are the result of poor maintenance, careless operation, or other preventable conditions, it may be necessary to consider them in determining source impact. A range of operating conditions should be considered in screening analyses. The load causing the highest concentration, in addition to the design load, should be included in refined modeling.

e. Emissions from mobile sources also have physical and temporal characteristics that should be appropriately accounted. For example, an appropriate emissions model shall be used to determine emissions profiles. Such emissions should include speciation specific for the vehicle types used on the roadway (*e.g.*, light duty and heavy duty trucks), and subsequent parameterizations of the physical emissions characteristics (*e.g.*, release height) should reflect those emissions sources. For long-term standards, annual average emissions may be appropriate, but for short-term standards, discrete temporal representation of emissions should be used (*e.g.*, variations in weekday and weekend traffic or the diurnal rush-hour profile typical of many cities). Detailed information and data requirements for modeling mobile sources of pollution are provided in the user's manuals for each of the models applicable to mobile sources.[61 63]

Table 8-1. - Point Source Model Emission Inputs for SIP Revisions of Inert Pollutants[1]

Averaging time	Emissions limit (lb/MMBtu)[2]	X	Operating level (MMBtu/hr)[2]	X	Operating factor (*e.g.* , hr/yr, hr/day)
Stationary Point Source(s) Subject to SIP Emissions Limit(s) Evaluation for Compliance with Ambient Standards *(Including Areawide Demonstrations)*					
Annual & quarterly	Maximum allowable emission limit or federally enforceable permit limit.		Actual or design capacity (whichever is greater), or federally enforceable permit condition.		Actual operating factor averaged over the most recent 2 years.[3]
Short term (≤ 24 hours)	Maximum allowable emission limit or federally enforceable permit limit.		Actual or design capacity (whichever is greater), or federally enforceable permit condition.[4]		Continuous operation, i.e., all hours of each time period under consideration (for all hours of the meteorological database).[5]
Nearby Source(s) [6]					
Annual & quarterly	Maximum allowable emission limit or federally enforceable permit limit.[6]		Annual level when actually operating, averaged over the most recent 2 years.[3]		Actual operating factor averaged over the most recent 2 years.[3, 8]
Short term (≤ 24 hours)	Maximum allowable emission limit or federally enforceable permit limit.[6]		Temporally representative level when actually operating, reflective of the most recent 2 years.[3, 7]		Continuous operation, i.e., all hours of each time period under consideration (for all hours of the meteorological database).[5]
Other Source(s) [6, 9]					

The ambient impacts from Non-nearby or Other Sources (*e.g.* , natural sources, minor sources and ,distant major sources, and unidentified sources) can be represented by air quality monitoring data unless adequate data do not exist.

1 . For purposes of emissions trading, NSR, or PSD, other model input criteria may apply. See Section 8.2 for more information regarding attainment demonstrations of primary PM2.5.
2. Terminology applicable to fuel burning sources; analogous terminology (*e.g.* , lb/throughput) may be used for other types of sources.
3. Unless it is determined that this period is not representative.
4. Operating levels such as 50 percent and 75 percent of capacity should also be modeled to determine the load causing the highest concentration.
5. If operation does not occur for all hours of the time period of consideration (*e.g.* , 3 or 24-hours) and the source operation is constrained by a federally enforceable permit condition, an appropriate adjustment to the modeled emission rate may be made (*e.g.* , if operation is only 8 a.m. to 4 p.m. each day, only these hours will be modeled with emissions from the source. Modeled emissions should not be averaged across non-operating time periods.)
6. See Section 8.3.3.
7. Temporally representative operating level could be based on Continuous Emissions Monitoring (CEM) data or other information and should be determined through consultation with the appropriate reviewing authority (Paragraph 3.0(b)).
8. For those permitted sources not in operation or that have not established an appropriate factor, continuous operation (i.e., 8760) should be used.
9. See Section 8.3.2.

Table 8-2. - Point Source Model Emission Inputs for NAAQS Compliance in PSD Demonstrations

Averaging time	Emissions limit (lb/MMBtu)[1]	X	Operating level (MMBtu/hr)[2]	X	Operating factor (*e.g.*, hr/yr, hr/day)
Proposed Major New or Modified Source					
Annual & quarterly	Maximum allowable emission limit or federally enforceable permit limit.		Design capacity or federally enforceable permit condition.		Continuous operation (i.e., 8760 hours).[2]
Short term (≤ 24 hours)	Maximum allowable emission limit or federally enforceable permit limit.		Design capacity or federally enforceable permit condition.[3]		Continuous operation, i.e., all hours of each time period under consideration (for all hours of the meteorological database).[2]
Nearby Source(s) [4,5]					
Annual & quarterly	Maximum allowable emission limit or federally enforceable permit limit.[5]		Annual level when actually operating, averaged over the most recent 2 years.[6]		Actual operating factor averaged over the most recent 2 years.[6,8]
Short term (≤ 24 hours)	Maximum allowable emission limit or federally enforceable permit limit.[5]		Temporally representative level when actually operating, reflective of the most recent 2 years.[6,7]		Continuous operation, i.e., all hours of each time period under consideration (for all hours of the meteorological database).[2]
Other Source(s) [5,9]					

The ambient impacts from Non-nearby or Other Sources (*e.g.*, natural sources, minor sources and ,distant major sources, and unidentified sources) can be represented by air quality monitoring data unless adequate data do not exist.

1. Terminology applicable to fuel burning sources; analogous terminology (*e.g.*, lb/throughput) may be used for other types of sources.
2. If operation does not occur for all hours of the time period of consideration (*e.g.*, 3 or 24-hours) and the source operation is constrained by a federally enforceable permit condition, an appropriate adjustment to the modeled emission rate may be made (*e.g.*, if operation is only 8 a.m. to 4 p.m. each day, only these hours will be modeled with emissions from the source. Modeled emissions should not be averaged across non-operating time periods.
3. Operating levels such as 50 percent and 75 percent of capacity should also be modeled to determine the load causing the highest concentration.
4. Includes existing facility to which modification is proposed if the emissions from the existing facility will not be affected by the modification. Otherwise use the same parameters as for major modification.
5. See Section 8.3.3.
6. Unless it is determined that this period is not representative.
7. Temporally representative operating level could be based on Continuous Emissions Monitoring (CEM) data or other information and should be determined through consultation with the appropriate reviewing authority (Paragraph 3.0(b)).
8. For those permitted sources not in operation or that have not established an appropriate factor, continuous operation (*i.e.*, 8760) should be used.
9. See Section 8.3.2.

8.3 Background Concentrations

8.3.1 Discussion

a. Background concentrations are essential in constructing the design concentration, or total air quality concentration, as part of a cumulative impact analysis for NAAQS and PSD increments (section 9.2.3). Background air quality should not include the ambient impacts of the project source under consideration. Instead, it should include:

i. Nearby sources: These are individual sources located in the vicinity of the source(s) under consideration for emissions limits that are not adequately represented by ambient monitoring data. Typically, sources that cause a significant concentration gradient in the vicinity of the source(s) under consideration for emissions limits are not adequately represented by background ambient monitoring. The ambient contributions from these nearby sources are thereby accounted for by explicitly modeling their emissions (section 8.2).

ii. Other sources: That portion of the background attributable to natural sources, other unidentified sources in the vicinity of the project, and regional transport contributions from more distant sources (domestic and international). The ambient contributions from these sources are typically accounted for through use of ambient monitoring data or, in some cases, regional-scale photochemical grid modeling results.

b. The monitoring network used for developing background concentrations is expected to conform to the same quality assurance and other requirements as those networks established for PSD purposes.[91] Accordingly, the air quality monitoring data should be of sufficient completeness and follow appropriate data validation procedures. These data should be adequately representative of the area to inform calculation of the design concentration for comparison to the applicable NAAQS (section 9.2.2).

c. For photochemical grid modeling conducted in SIP attainment demonstrations for ozone, $PM_{2.5}$ and regional haze, the emissions from nearby and other sources are included as model inputs and fully accounted for in the modeling application and predicted concentrations. The concept of adding individual components to develop a design concentration, therefore, do not apply in these SIP applications. However, such modeling results may then be appropriate for consideration in characterizing background concentrations for other regulatory applications. Also, as noted in section 5, this modeling approach does provide for an appropriate atmospheric environment to assess single-source impacts for ozone and secondary $PM_{2.5}$.

d. For NAAQS assessments and SIP attainment demonstrations for inert pollutants, the development of the appropriate background concentration for a cumulative impact analysis involves proper accounting of each contribution to the design concentration and will depend upon whether the project area's situation consists of either an isolated single source(s) or a multitude of sources. For PSD increment assessments, all impacts after the appropriate baseline dates (*i.e.*, trigger date, major source baseline date, and minor source baseline date) from all increment-consuming and increment-expanding sources should be considered in the design concentration (section 9.2.2).

8.3.2 Recommendations for Isolated Single Sources

a. In areas with an isolated source(s), determining the appropriate background concentration should focus on characterization of contributions from all other sources through adequately representative ambient monitoring data.

b. The EPA recommends use of the most recent quality assured air quality monitoring data collected in the vicinity of the source to determine the background concentration for the averaging times of concern. In most cases, the EPA recommends using data from the monitor closest to and upwind of the project area. If several monitors are available, preference should be given to the monitor with characteristics that are most similar to the project area. If there are no monitors located in the vicinity of the new or modifying source, a ''regional site'' may be used to determine background concentrations. A regional site is one that is located away from the area of interest but is impacted by similar or adequately representative sources.

c. Many of the challenges related to cumulative impact analyses arise in the context of defining the appropriate metric to characterize background concentrations from ambient monitoring data and determining the appropriate method for combining this monitor-based background contribution to the modeled impact of the project and other nearby sources. For many cases, the best starting point would be use of the current design value for the applicable NAAQS as a uniform monitored background contribution across the project area. However, there are cases in which the current design value may not be appropriate. Such cases include but are not limited to:

i. For situations involving a modifying source where the existing facility is determined to impact the ambient monitor, the background concentration at each monitor can be determined by excluding values when the source in question is impacting the monitor. In such cases, monitoring sites inside a 90° sector downwind of the source may be used to determine the area of impact.

ii. There may be other circumstances which would necessitate modifications to the ambient data record. Such cases could include removal of data from specific days or hours when a monitor is being impacted by activities that are not typical or not expected to occur again in the future (*e.g.*, construction, roadway repairs, forest fires, or unusual agricultural activities). There may also be cases where it may be appropriate to scale (multiplying the monitored concentrations with a scaling factor) or adjust (adding or subtracting a constant value the monitored concentrations) data from specific days or hours. Such adjustments would make the monitored background concentrations more temporally and/or spatially representative of the area around the new or modifying source for the purposes of the regulatory assessment.

iii. For short-term standards, the diurnal or seasonal patterns of the air quality monitoring data may differ significantly from the patterns associated with the modeled concentrations. When this occurs, it may be appropriate to pair the air quality monitoring data in a temporal manner that reflects these patterns (*e.g.*, pairing by season and/or hour of day).[92]

iv. For situations where monitored air quality concentrations vary across the modeling domain, it may be appropriate to consider air quality monitoring data from multiple monitors within the project area.

d. Determination of the appropriate background concentrations should be consistent with appropriate EPA modeling guidance[59 60] and justified in the modeling protocol that is vetted with the appropriate reviewing authority (paragraph 3.0(b)).

e. Considering the spatial and temporal variability throughout a typical modeling domain on an hourly basis and the complexities and limitations of hourly observations from the ambient monitoring network, the EPA does not recommend hourly or daily pairing of monitored background and modeled concentrations except in rare cases of

relatively isolated sources where the available monitor can be shown to be representative of the ambient concentration levels in the areas of maximum impact from the proposed new source. The implicit assumption underlying hourly pairing is that the background monitored levels for each hour are spatially uniform and that the monitored values are fully representative of background levels at each receptor for each hour. Such an assumption clearly ignores the many factors that contribute to the temporal and spatial variability of ambient concentrations across a typical modeling domain on an hourly basis. In most cases, the seasonal (or quarterly) pairing of monitored and modeled concentrations should sufficiently address situations to which the impacts from modeled emissions are not temporally correlated with background monitored levels.

f. In those cases where adequately representative monitoring data to characterize background concentrations are not available, it may be appropriate to use results from a regional-scale photochemical grid model, or other representative model application, as background concentrations consistent with the considerations discussed above and in consultation with the appropriate reviewing authority (paragraph 3.0(b)).

8.3.3 Recommendations for Multi-Source Areas

a. In multi-source areas, determining the appropriate background concentration involves: (1) Identification and characterization of contributions from nearby sources through explicit modeling, and (2) characterization of contributions from other sources through adequately representative ambient monitoring data. A key point here is the interconnectedness of each component in that the question of which nearby sources to include in the cumulative modeling is inextricably linked to the question of what the ambient monitoring data represents within the project area.

b. *Nearby sources:* All sources in the vicinity of the source(s) under consideration for emissions limits that are not adequately represented by ambient monitoring data should be explicitly modeled. Since an ambient monitor is limited to characterizing air quality at a fixed location, sources that cause a significant concentration gradient in the vicinity of the source(s) under consideration for emissions limits are not likely to be adequately characterized by the monitored data due to the high degree of variability of the source's impact.

i. The pattern of concentration gradients can vary significantly based on the averaging period being assessed. In general, concentration gradients will be smaller and more spatially uniform for annual averages than for short-term averages, especially for hourly averages. The spatial distribution of annual impacts around a source will often have a single peak downwind of the source based on the prevailing wind direction, except in cases where terrain or other geographic effects are important. By contrast, the spatial distribution of peak short-term impacts will typically show several localized concentration peaks with more significant gradient.

ii. Concentration gradients associated with a particular source will generally be largest between that source's location and the distance to the maximum ground-level concentrations from that source. Beyond the maximum impact distance, concentration gradients will generally be much smaller and more spatially uniform. Thus, the magnitude of a concentration gradient will be greatest in the proximity of the source and will generally not be significant at distances greater than 10 times the height of the stack(s) at that source without consideration of terrain influences.

iii. The number of nearby sources to be explicitly modeled in the air quality analysis is expected to be few except in unusual situations. In most cases, the few nearby sources will be located within the first 10 to 20 km from the source(s) under consideration. Owing to both the uniqueness of each modeling situation and the large number of variables involved in identifying nearby sources, no attempt is made here to comprehensively define a ''significant concentration gradient.'' Rather, identification of nearby sources calls for the exercise of professional judgment by the appropriate reviewing authority (paragraph 3.0(b)). This guidance is not intended to alter the exercise of that judgment or to comprehensively prescribe which sources should be included as nearby sources.

c. For cumulative impact analyses of short-term and annual ambient standards, the nearby sources as well as the project source(s) must be evaluated using an appropriate appendix A model or approved alternative model with the emission input data shown in Table 8–1 or 8–2.

i. When modeling a nearby source that does not have a permit and the emissions limits contained in the SIP for a particular source category is greater than the emissions possible given the source's maximum physical capacity to emit, the ''maximum allowable emissions limit'' for such a nearby source may be calculated as the emissions rate representative of the nearby source's maximum physical capacity to emit, considering its design specifications and allowable fuels and process materials. However, the burden is on the permit applicant to sufficiently document what the maximum physical capacity to emit is for such a nearby source.

ii. It is appropriate to model nearby sources only during those times when they, by their nature, operate at the same time as the primary source(s) or could have impact on the averaging period of concern. Accordingly, it is not necessary to model impacts of a nearby source that does not, by its nature, operate at the same time as the primary source or could have impact on the averaging period of concern, regardless of an identified significant concentration gradient from the nearby source. The burden is on the permit applicant to adequately justify the exclusion of nearby sources to the satisfaction of the appropriate reviewing authority (paragraph 3.0(b)). The following examples illustrate two cases in which a nearby source may be shown not to operate at the same time as the primary source(s) being modeled: (1) Seasonal sources (only used during certain seasons of the year). Such sources would not be modeled as nearby sources during times in which they do not operate; and (2) Emergency backup generators, to the extent that they do not operate simultaneously with the sources that they back up. Such emergency equipment would not be modeled as nearby sources.

d. *Other sources.* That portion of the background attributable to all other sources (*e.g.*, natural sources, minor and distant major sources) should be accounted for through use of ambient monitoring data and determined by the procedures found in section 8.3.2 in keeping with eliminating or reducing the source-oriented impacts from nearby sources to avoid potential double-counting of modeled and monitored contributions.

8.4 Meteorological Input Data

8.4.1 Discussion

a. This subsection covers meteorological input data for use in dispersion modeling for regulatory applications and is separate from recommendations made for photochemical grid modeling. Recommendations for meteorological data for photochemical grid modeling applications are outlined in the latest version of EPA's *Modeling Guidance for Demonstrating Attainment of Air Quality Goals for Ozone*, $PM_{2.5}$, and *Regional Haze*.[60] In cases where Lagrangian models are applied for regulatory purposes, appropriate meteorological inputs should be determined in consultation with the appropriate reviewing authority (paragraph 3.0(b)).

b. The meteorological data used as input to a dispersion model should be selected on the basis of spatial and climatological (temporal) representativeness as well as the ability of the individual parameters selected to characterize the transport and dispersion conditions in the area of concern. The representativeness of the measured data is dependent on numerous factors including, but not limited to: (1) The proximity of the meteorological monitoring site to the area under consideration; (2) the complexity of the terrain; (3) the exposure of the meteorological monitoring site; and (4) the period of time during which data are collected. The spatial representativeness of the data can be adversely affected by large distances between the source and receptors of interest and the complex topographic characteristics of the area. Temporal representativeness is a function of the year-to-year variations in weather conditions. Where appropriate, data representativeness should be viewed in terms of the appropriateness of the data for constructing realistic boundary layer profiles and, where applicable, three-dimensional meteorological fields, as described in paragraphs (c) and (d) of this subsection.

c. The meteorological data should be adequately representative and may be site-specific data, data from a nearby National Weather Service (NWS) or comparable station, or prognostic meteorological data. The implementation of NWS Automated Surface Observing Stations (ASOS) in the early 1990's should not preclude the use of NWS ASOS data if such a station is determined to be representative of the modeled area.[93]

d. Model input data are normally obtained either from the NWS or as part of a site-specific measurement program. State climatology offices, local universities, FAA, military stations, industry, and pollution control agencies may also be sources of such data. In specific cases, prognostic meteorological data may be appropriate for use and obtained from similar sources. Some recommendations and requirements for the use of each type of data are included in this subsection.

8.4.2 Recommendations and Requirements

a. AERMET[94] shall be used to preprocess all meteorological data, be it observed or prognostic, for use with AERMOD in regulatory applications. The AERMINUTE[95] processor, in most cases, should be used to process 1-minute ASOS wind data for input to AERMET when processing NWS ASOS sites in AERMET. When processing prognostic meteorological data for AERMOD, the Mesoscale Model Interface Program (MMIF)[103] should be used to process data for input to AERMET. Other methods of processing prognostic meteorological data for input to AERMET should be approved by the appropriate reviewing authority. Additionally, the following meteorological preprocessors are recommended by the EPA: PCRAMMET,[96] MPRM,[97] and METPRO.[98] PCRAMMET is the recommended meteorological data preprocessor for use in applications of OCD employing hourly NWS data. MPRM is the recommended meteorological data preprocessor for applications of OCD employing site-specific meteorological data.

METPRO is the recommended meteorological data preprocessor for use with CTDMPLUS.[99]

b. Regulatory application of AERMOD necessitates careful consideration of the meteorological data for input to AERMET. Data representativeness, in the case of AERMOD, means utilizing data of an appropriate type for constructing realistic boundary layer profiles. Of particular importance is the requirement that all meteorological data used as input to AERMOD should be adequately representative of the transport and dispersion within the analysis domain. Where surface conditions vary significantly over the analysis domain, the emphasis in assessing representativeness should be given to adequate characterization of transport and dispersion between the source(s) of concern and areas where maximum design concentrations are anticipated to occur. The EPA recommends that the surface characteristics input to AERMET should be representative of the land cover in the vicinity of the meteorological data, *i.e.*, the location of the meteorological tower for measured data or the representative grid cell for prognostic data. Therefore, the model user should apply the latest version AERSURFACE,[100] [101] where applicable, for determining surface characteristics when processing measured meteorological data through AERMET. In areas where it is not possible to use AERSURFACE output, surface characteristics can be determined using techniques that apply the same analysis as AERSURFACE. In the case of prognostic meteorological data, the surface characteristics associated with the prognostic meteorological model output for the representative grid cell should be used.[102] [103] Furthermore, since the spatial scope of each variable could be different, representativeness should be judged for each variable separately. For example, for a variable such as wind direction, the data should ideally be collected near plume height to be adequately representative, especially for sources located in complex terrain. Whereas, for a variable such as temperature, data from a station several kilometers away from the source may be considered to be adequately representative. More information about meteorological data, representativeness, and surface characteristics can be found in the AERMOD Implementation Guide.[76]

c. Regulatory application of CTDMPLUS requires the input of multi-level measurements of wind speed, direction, temperature, and turbulence from an appropriately sited meteorological tower. The measurements should be obtained up to the representative plume height(s) of interest. Plume heights of interest can be determined by use of screening procedures such as CTSCREEN.

d. Regulatory application of OCD requires meteorological data over land and over water. The over land or surface data, processed through PCRAMMET[96] or MPRM,[97] that provides hourly stability class, wind direction and speed, ambient temperature, and mixing height, are required. Data over water requires hourly mixing height, relative humidity, air temperature, and water surface temperature. Missing winds are substituted with the surface winds. Vertical wind direction shear, vertical temperature gradient, and turbulence intensities are optional.

e. The model user should acquire enough meteorological data to ensure that worst-case meteorological conditions are adequately represented in the model results. The use of 5 years of adequately representative NWS or comparable meteorological data, at least 1 year of site-specific, or at least 3 years of prognostic meteorological data, are required. If 1 year or more, up to 5 years, of site-specific data are available, these data are preferred for use in air quality analyses. Depending on completeness of the data record, consecutive years of NWS, site-specific, or prognostic data are preferred. Such data must be subjected to quality assurance procedures as described in section 8.4.4.2.

f. Objective analysis in meteorological modeling is to improve meteorological analyses (the ''*first guess field*'') used as initial conditions for prognostic meteorological models by incorporating information from meteorological observations. Direct and indirect (using remote sensing techniques) observations of temperature, humidity, and wind from surface and radiosonde reports are commonly employed to improve these analysis fields. For long-range transport applications, it is recommended that objective analysis procedures, using direct and indirect meteorological observations, be employed in preparing input fields to produce prognostic meteorological datasets. The length of record of observations should conform to recommendations outlined in paragraph 8.4.2(e) for prognostic meteorological model datasets.

8.4.3 National Weather Service Data

8.4.3.1 Discussion

a. The NWS meteorological data are routinely available and familiar to most model users. Although the NWS does not provide direct measurements of all the needed dispersion model input variables, methods have been developed and successfully used to translate the basic NWS data to the needed model input. Site-specific measurements of model input parameters have been made for many modeling studies, and those methods and techniques are becoming more widely applied, especially in situations such as complex terrain applications, where available NWS data are not adequately representative.

However, there are many modeling applications where NWS data are adequately representative and the applications still rely heavily on the NWS data.

b. Many models use the standard hourly weather observations available from the National Centers for Environmental Information (NCEI).[b] These observations are then preprocessed before they can be used in the models. Prior to the advent of ASOS in the early 1990's, the standard ''hourly'' weather observation was a human-based observation reflecting a single 2-minute average generally taken about 10 minutes before the hour. However, beginning in January 2000 for first-order stations and in March 2005 for all stations, the NCEI has archived the 1-minute ASOS wind data (*i.e.*, the rolling 2-minute average winds) for the NWS ASOS sites. The AERMINUTE processor[95] was developed to reduce the number of calm and missing hours in AERMET processing by substituting standard hourly observations with full hourly average winds calculated from 1-minute ASOS wind data.

8.4.3.2 Recommendations

a. The preferred models listed in appendix A all accept, as input, the NWS meteorological data preprocessed into model compatible form. If NWS data are judged to be adequately representative for a specific modeling application, they may be used. The NCEI makes available surface[104][105] and upper air[106] meteorological data online and in CD–ROM format. Upper air data are also available at the Earth System Research Laboratory Global Systems Divisions Web site (*http://esrl.noaa.gov/gsd*).

b. Although most NWS wind measurements are made at a standard height of 10 m, the actual anemometer height should be used as input to the preferred meteorological processor and model.

c. Standard hourly NWS wind directions are reported to the nearest 10 degrees. Due to the coarse resolution of these data, a specific set of randomly generated numbers has been developed by the EPA and should be used when processing standard hourly NWS data for use in the preferred EPA models to ensure a lack of bias in wind direction assignments within the models.

d. Beginning with year 2000, NCEI began archiving 2-minute winds, reported every minute to the nearest degree for NWS ASOS sites. The AERMINUTE processor was developed to read those winds and calculate hourly average winds for input to AERMET. When such data are available for the NWS ASOS site being processed, the AERMINUTE processor should be used, in most cases, to calculate hourly average wind speed and direction when processing NWS ASOS data for input to AERMOD.[93]

e. Data from universities, FAA, military stations, industry and pollution control agencies may be used if such data are equivalent in accuracy and detail (*e.g.*, siting criteria, frequency of observations, data completeness, etc.) to the NWS data, they are judged to be adequately representative for the particular application, and have undergone quality assurance checks.

f. After valid data retrieval requirements have been met,[107] large number of hours in the record having missing data should be treated according to an established data substitution protocol provided that adequately representative alternative data are available. Data substitution guidance is provided in section 5.3 of reference.[107] If no representative alternative data are available for substitution, the absent data should be coded as missing using missing data codes appropriate to the applicable meteorological pre-processor. Appropriate model options for treating missing data, if available in the model, should be employed.

8.4.4 Site-Specific Data

8.4.4.1 Discussion

a. Spatial or geographical representativeness is best achieved by collection of all of the needed model input data in close proximity to the actual site of the source(s). Site-specific measured data are, therefore, preferred as model input, provided that appropriate instrumentation and quality assurance procedures are followed, and that the data collected are adequately representative (free from inappropriate local or microscale influences) and compatible with the input requirements of the model to be used. It should be noted that, while site-specific measurements are frequently made ''on-property'' (*i.e.*, on the source's premises), acquisition of adequately representative site-specific data does not preclude collection of data from a location off property. Conversely, collection of meteorological data on a source's property does not of itself guarantee adequate representativeness. For help in determining representativeness of site-specific measurements, technical guidance[107] is available. Site-specific data should always be reviewed for representativeness and adequacy by an experienced meteorologist, atmospheric scientist, or other qualified scientist in consultation with the appropriate reviewing authority (paragraph 3.0(b)).

8.4.4.2 Recommendations

a. The EPA guidance[107] provides recommendations on the collection and use of site-specific meteorological data. Recommendations on characteristics, siting, and exposure of meteorological instruments and on data recording, processing, completeness

[b] Formerly the National Climatic Data Center (NCDC).

requirements, reporting, and archiving are also included. This publication should be used as a supplement to other limited guidance on these subjects.[5 91 108 109] Detailed information on quality assurance is also available.[110] As a minimum, site-specific measurements of ambient air temperature, transport wind speed and direction, and the variables necessary to estimate atmospheric dispersion should be available in meteorological datasets to be used in modeling. Care should be taken to ensure that meteorological instruments are located to provide an adequately representative characterization of pollutant transport between sources and receptors of interest. The appropriate reviewing authority (paragraph 3.0(b)) is available to help determine the appropriateness of the measurement locations.

i. *Solar radiation measurements.* Total solar radiation or net radiation should be measured with a reliable pyranometer or net radiometer sited and operated in accordance with established site-specific meteorological guidance.[107 110]

ii. *Temperature measurements.* Temperature measurements should be made at standard shelter height (2m) in accordance with established site-specific meteorological guidance.[107]

iii. *Temperature difference measurements.* Temperature difference (DT) measurements should be obtained using matched thermometers or a reliable thermocouple system to achieve adequate accuracy. Siting, probe placement, and operation of DT systems should be based on guidance found in Chapter 3 of reference 107 and such guidance should be followed when obtaining vertical temperature gradient data. AERMET may employ the Bulk Richardson scheme, which requires measurements of temperature difference, in lieu of cloud cover or insolation data. To ensure correct application and acceptance, AERMOD users should consult with the appropriate reviewing authority (paragraph 3.0(b)) before using the Bulk Richardson scheme for their analysis.

iv. *Wind measurements.* For simulation of plume rise and dispersion of a plume emitted from a stack, characterization of the wind profile up through the layer in which the plume disperses is desirable. This is especially important in complex terrain and/or complex wind situations where wind measurements at heights up to hundreds of meters above stack base may be required in some circumstances. For tall stacks when site-specific data are needed, these winds have been obtained traditionally using meteorological sensors mounted on tall towers. A feasible alternative to tall towers is the use of meteorological remote sensing instruments (*e.g.*, acoustic sounders or radar wind profilers) to provide winds aloft, coupled with 10-meter towers to provide the near-surface winds. Note that when site-specific wind measurements are used, AERMOD, at a minimum, requires wind observations at a height above ground between seven times the local surface roughness height and 100 m. (For additional requirements for AERMOD and CTDMPLUS, *see* appendix A.) Specifications for wind measuring instruments and systems are contained in reference 107.

b. All processed site-specific data should be in the form of hourly averages for input to the dispersion model.

i. *Turbulence data.* There are several dispersion models that are capable of using direct measurements of turbulence (wind fluctuations) in the characterization of the vertical and lateral dispersion (*e.g.*, CTDMPLUS or AERMOD). When turbulence data are used to directly characterize the vertical and lateral dispersion, the averaging time for the turbulence measurements should be 1 hour. For technical guidance on processing of turbulence parameters for use in dispersion modeling, refer to the user's guide to the meteorological processor for each model (*see* section 8.4.2(a)).

ii. *Stability categories.* For dispersion models that employ P–G stability categories for the characterization of the vertical and lateral dispersion, the P–G stability categories, as originally defined, couple near-surface measurements of wind speed with subjectively determined insolation assessments based on hourly cloud cover and ceiling height observations. The wind speed measurements are made at or near 10 m. The insolation rate is typically assessed using observations of cloud cover and ceiling height based on criteria outlined by Turner.[72] It is recommended that the P–G stability category be estimated using the Turner method with site-specific wind speed measured at or near 10 m and representative cloud cover and ceiling height. Implementation of the Turner method, as well as considerations in determining representativeness of cloud cover and ceiling height in cases for which site-specific cloud observations are unavailable, may be found in section 6 of reference 107. In the absence of requisite data to implement the Turner method, the solar radiation/delta-T (SRDT) method or wind fluctuation statistics (*i.e.*, the σ_E and σ_A methods) may be used.

iii. The SRDT method, described in section 6.4.4.2 of reference 107, is modified slightly from that published from earlier work[111] and has been evaluated with three site-specific databases.[112] The two methods of stability classification that use wind fluctuation statistics, the σ_E and σ_A methods, are also described in detail in section 6.4.4 of reference 107 (note applicable tables in section 6). For additional information on the wind fluctuation methods, several references are available.[113 114 115 116]

c. *Missing data substitution.* After valid data retrieval requirements have been met,[107]

hours in the record having missing data should be treated according to an established data substitution protocol provided that adequately representative alternative data are available. Such protocols are usually part of the approved monitoring program plan. Data substitution guidance is provided in section 5.3 of reference 107. If no representative alternative data are available for substitution, the absent data should be coded as missing, using missing data codes appropriate to the applicable meteorological pre-processor. Appropriate model options for treating missing data, if available in the model, should be employed.

8.4.5 Prognostic Meteorological Data

8.4.5.1 Discussion

a. For some modeling applications, there may not be a representative NWS or comparable meteorological station available (*e.g.*, complex terrain), and it may be cost prohibitive or infeasible to collect adequately representative site-specific data. For these cases, it may be appropriate to use prognostic meteorological data, if deemed adequately representative, in a regulatory modeling application. However, if prognostic meteorological data are not representative of transport and dispersion conditions in the area of concern, the collection of site-specific data is necessary.

b. The EPA has developed a processor, the MMIF,[102] to process MM5 (Mesoscale Model 5) or WRF (Weather Research and Forecasting) model data for input to various models including AERMOD. MMIF can process data for input to AERMET or AERMOD for a single grid cell or multiple grid cells. MMIF output has been found to compare favorably against observed data (site-specific or NWS).[117] Specific guidance on processing MMIF for AERMOD can be found in reference 103. When using MMIF to process prognostic data for regulatory applications, the data should be processed to generate AERMET inputs and the data subsequently processed through AERMET for input to AERMOD. If an alternative method of processing data for input to AERMET is used, it must be approved by the appropriate reviewing authority (paragraph 3.0(b)).

8.4.5.2 Recommendations

a. *Prognostic model evaluation*. Appropriate effort by the applicant should be devoted to the process of evaluating the prognostic meteorological data. The modeling data should be compared to NWS observational data or other comparable data in an effort to show that the data are adequately replicating the observed meteorological conditions of the time periods modeled. An operational evaluation of the modeling data for all model years (*i.e.*, statistical, graphical) should be completed.[60] The use of output from prognostic mesoscale meteorological models is contingent upon the concurrence with the appropriate reviewing authority (paragraph 3.0(b)) that the data are of acceptable quality, which can be demonstrated through statistical comparisons with meteorological observations aloft and at the surface at several appropriate locations.[60]

b. *Representativeness*. When processing MMIF data for use with AERMOD, the grid cell used for the dispersion modeling should be adequately spatially representative of the analysis domain. In most cases, this may be the grid cell containing the emission source of interest. Since the dispersion modeling may involve multiple sources and the domain may cover several grid cells, depending on grid resolution of the prognostic model, professional judgment may be needed to select the appropriate grid cell to use. In such cases, the selected grid cells should be adequately representative of the entire domain.

c. *Grid resolution*. The grid resolution of the prognostic meteorological data should be considered and evaluated appropriately, particularly for projects involving complex terrain. The operational evaluation of the modeling data should consider whether a finer grid resolution is needed to ensure that the data are representative. The use of output from prognostic mesoscale meteorological models is contingent upon the concurrence with the appropriate reviewing authority (paragraph 3.0(b)) that the data are of acceptable quality.

8.4.6 Treatment of Near-Calms and Calms

8.4.6.1 Discussion

a. Treatment of calm or light and variable wind poses a special problem in modeling applications since steady-state Gaussian plume models assume that concentration is inversely proportional to wind speed, depending on model formulations. Procedures have been developed to prevent the occurrence of overly conservative concentration estimates during periods of calms. These procedures acknowledge that a steady-state Gaussian plume model does not apply during calm conditions, and that our knowledge of wind patterns and plume behavior during these conditions does not, at present, permit the development of a better technique. Therefore, the procedures disregard hours that are identified as calm. The hour is treated as missing and a convention for handling missing hours is recommended. With the advent of the AERMINUTE processor, when processing NWS ASOS data, the inclusion of hourly averaged winds from AERMINUTE will, in some instances, dramatically reduce the number of calm and missing hours, especially when the ASOS wind are derived from a sonic anemometer. To alleviate concerns

about these issues, especially those introduced with AERMINUTE, the EPA implemented a wind speed threshold in AERMET for use with ASOS derived winds.[93 94] Winds below the threshold will be treated as calms.

b. AERMOD, while fundamentally a steady-state Gaussian plume model, contains algorithms for dealing with low wind speed (near calm) conditions. As a result, AERMOD can produce model estimates for conditions when the wind speed may be less than 1m/s, but still greater than the instrument threshold. Required input to AERMET for site-specific data, the meteorological processor for AERMOD, includes a threshold wind speed and a reference wind speed. The threshold wind speed is the greater of the threshold of the instrument used to collect the wind speed data or wind direction sensor.[107] The reference wind speed is selected by the model as the lowest level of non-missing wind speed and direction data where the speed is greater than the wind speed threshold, and the height of the measurement is between seven times the local surface roughness length and 100 m. If the only valid observation of the reference wind speed between these heights is less than the threshold, the hour is considered calm, and no concentration is calculated. None of the observed wind speeds in a measured wind profile that are less than the threshold speed are used in construction of the modeled wind speed profile in AERMOD.

8.4.6.2 Recommendations

a. Hourly concentrations calculated with steady-state Gaussian plume models using calms should not be considered valid; the wind and concentration estimates for these hours should be disregarded and considered to be missing. Model predicted concentrations for 3-, 8-, and 24-hour averages should be calculated by dividing the sum of the hourly concentrations for the period by the number of valid or non-missing hours. If the total number of valid hours is less than 18 for 24-hour averages, less than 6 for 8-hour averages, or less than 3 for 3-hour averages, the total concentration should be divided by 18 for the 24-hour average, 6 for the 8-hour average, and 3 for the 3-hour average. For annual averages, the sum of all valid hourly concentrations is divided by the number of non-calm hours during the year. AERMOD has been coded to implement these instructions. For hours that are calm or missing, the AERMOD hourly concentrations will be zero. For other models listed in appendix A, a post-processor computer program, CALMPRO[118] has been prepared, is available on the EPA's SCRAM Web site (section 2.3), and should be used.

b. Stagnant conditions that include extended periods of calms often produce high concentrations over wide areas for relatively long averaging periods. The standard steady-state Gaussian plume models are often not applicable to such situations. When stagnation conditions are of concern, other modeling techniques should be considered on a case-by-case basis (*see* also section 7.2.1.2).

c. When used in steady-state Gaussian plume models other than AERMOD, measured site-specific wind speeds of less than 1 m/s but higher than the response threshold of the instrument should be input as 1 m/s; the corresponding wind direction should also be input. Wind observations below the response threshold of the instrument should be set to zero, with the input file in ASCII format. For input to AERMOD, no such adjustment should be made to the site-specific wind data, as AERMOD has algorithms to account for light or variable winds as discussed in section 8.4.6.1(a). For NWS ASOS data, especially data using the 1-minute ASOS winds, a wind speed threshold option is allowed with a recommended speed of 0.5 m/s.[93] When using prognostic data processed by MMIF, a 0.5 m/s threshold is also invoked by MMIF for input to AERMET. Observations with wind speeds less than the threshold are considered calm, and no concentration is calculated. In all cases involving steady-state Gaussian plume models, calm hours should be treated as missing, and concentrations should be calculated as in paragraph (a) of this subsection.

9.0 Regulatory Application of Models

9.1 Discussion

a. Standardized procedures are valuable in the review of air quality modeling and data analyses conducted to support SIP submittals and revisions, NSR, or other EPA requirements to ensure consistency in their regulatory application. This section recommends procedures specific to NSR that facilitate some degree of standardization while at the same time allowing the flexibility needed to assure the technically best analysis for each regulatory application. For SIP attainment demonstrations, refer to the appropriate EPA guidance[51 60] for the recommended procedures.

b. Air quality model estimates, especially with the support of measured air quality data, are the preferred basis for air quality demonstrations. A number of actions have been taken to ensure that the best air quality model is used correctly for each regulatory application and that it is not arbitrarily imposed.

• First, the *Guideline* clearly recommends that the most appropriate model be used in each case. Preferred models are identified, based on a number of factors, for many uses.

• Second, the preferred models have been subjected to a systematic performance evaluation and a scientific peer review. Statistical performance measures, including measures of difference (or residuals) such as bias, variance of difference and gross variability of the difference, and measures of correlation such as time, space, and time and space combined, as described in section 2.1.1, were generally followed.

• Third, more specific information has been provided for considering the incorporation of new models into the *Guideline* (section 3.1), and the *Guideline* contains procedures for justifying the case-by-case use of alternative models and obtaining EPA approval (section 3.2).

c. Air quality modeling is the preferred basis for air quality demonstrations. Nevertheless, there are rare circumstances where the performance of the preferred air quality model may be shown to be less than reasonably acceptable or where no preferred air quality model, screening model or technique, or alternative model are suitable for the situation. In these unique instances, there is the possibility of assuring compliance and establishing emissions limits for an existing source solely on the basis of observed air quality data in lieu of an air quality modeling analysis. Comprehensive air quality monitoring in the vicinity of the existing source with proposed modifications will be necessary in these cases. The same attention should be given to the detailed analyses of the air quality data as would be applied to a model performance evaluation.

d. The current levels and forms of the NAAQS for the six criteria pollutants can be found on the EPA's NAAQS Web site at *https://www.epa.gov/criteria-air-pollutants*. As required by the CAA, the NAAQS are subjected to extensive review every 5 years and the standards, including the level and the form, may be revised as part of that review. The criteria pollutants have either long-term (annual or quarterly) and/or short-term (24-hour or less) forms that are not to be exceeded more than a certain frequency over a period of time (*e.g.*, no exceedance on a rolling 3-month average, no more than once per year, or no more than once per year averaged over 3 years), are averaged over a period of time (*e.g.*, an annual mean or an annual mean averaged over 3 years), or are some percentile that is averaged over a period of time (*e.g.*, annual 99th or 98th percentile averaged over 3 years). The 3-year period for ambient monitoring design values does not dictate the length of the data periods recommended for modeling (*i.e.*, 5 years of NWS meteorological data, at least 1 year of site-specific, or at least 3 years of prognostic meteorological data).

e. This section discusses general recommendations on the regulatory application of models for the purposes of NSR, including PSD permitting, and particularly for estimating design concentration(s), appropriately comparing these estimates to NAAQS and PSD increments, and developing emissions limits. This section also provides the criteria necessary for considering use of an analysis based on measured ambient data in lieu of modeling as the sole basis for demonstrating compliance with NAAQS and PSD increments.

9.2 Recommendations

9.2.1 Modeling Protocol

a. Every effort should be made by the appropriate reviewing authority (paragraph 3.0(b)) to meet with all parties involved in either a SIP submission or revision or a PSD permit application prior to the start of any work on such a project. During this meeting, a protocol should be established between the preparing and reviewing parties to define the procedures to be followed, the data to be collected, the model to be used, and the analysis of the source and concentration data to be performed. An example of the content for such an effort is contained in the Air Quality Analysis Checklist posted on the EPA's SCRAM Web site (section 2.3). This checklist suggests the appropriate level of detail to assess the air quality resulting from the proposed action. Special cases may require additional data collection or analysis and this should be determined and agreed upon at the pre-application meeting. The protocol should be written and agreed upon by the parties concerned, although it is not intended that this protocol be a binding, formal legal document. Changes in such a protocol or deviations from the protocol are often necessary as the data collection and analysis progresses. However, the protocol establishes a common understanding of how the demonstration required to meet regulatory requirements will be made.

9.2.2 Design Concentration and Receptor Sites

a. Under the PSD permitting program, an air quality analysis for criteria pollutants is required to demonstrate that emissions from the construction or operation of a proposed new source or modification will not cause or contribute to a violation of the NAAQS or PSD increments.

i. For a NAAQS assessment, the design concentration is the combination of the appropriate background concentration (section 8.3) with the estimated modeled impact of the proposed source. The NAAQS design concentration is then compared to the applicable NAAQS.

ii. For a PSD increment assessment, the design concentration includes impacts occurring after the appropriate baseline date from all increment-consuming and increment-expanding sources. The PSD increment design

concentration is then compared to the applicable PSD increment.

b. The specific form of the NAAQS for the pollutant(s) of concern will also influence how the background and modeled data should be combined for appropriate comparison with the respective NAAQS in such a modeling demonstration. Given the potential for revision of the form of the NAAQS and the complexities of combining background and modeled data, specific details on this process can be found in the applicable modeling guidance available on the EPA's SCRAM Web site (section 2.3). Modeled concentrations should not be rounded before comparing the resulting design concentration to the NAAQS or PSD increments. Ambient monitoring and dispersion modeling address different issues and needs relative to each aspect of the overall air quality assessment.

c. The PSD increments for criteria pollutants are listed in 40 CFR 52.21(c) and 40 CFR 51.166(c). For short-term increments, these maximum allowable increases in pollutant concentrations may be exceeded once per year at each site, while the annual increment may not be exceeded. The highest, second-highest increase in estimated concentrations for the short-term averages, as determined by a model, must be less than or equal to the permitted increment. The modeled annual averages must not exceed the increment.

d. Receptor sites for refined dispersion modeling should be located within the modeling domain (section 8.1). In designing a receptor network, the emphasis should be placed on receptor density and location, not total number of receptors. Typically, the density of receptor sites should be progressively more resolved near the new or modifying source, areas of interest, and areas with the highest concentrations with sufficient detail to determine where possible violations of a NAAQS or PSD increments are most likely to occur. The placement of receptor sites should be determined on a case-by-case basis, taking into consideration the source characteristics, topography, climatology, and monitor sites. Locations of particular importance include: (1) The area of maximum impact of the point source; (2) the area of maximum impact of nearby sources; and (3) the area where all sources combine to cause maximum impact. Depending on the complexities of the source and the environment to which the source is located, a dense array of receptors may be required in some cases. In order to avoid unreasonably large computer runs due to an excessively large array of receptors, it is often desirable to model the area twice. The first model run would use a moderate number of receptors more resolved near the new or modifying source and over areas of interest. The second model run would modify the receptor network from the first model run with a denser array of receptors in areas showing potential for high concentrations and possible violations, as indicated by the results of the first model run. Accordingly, the EPA neither anticipates nor encourages that numerous iterations of modeling runs be made to continually refine the receptor network.

9.2.3 NAAQS and PSD Increments Compliance Demonstrations for New or Modifying Sources

a. As described in this subsection, the recommended procedure for conducting either a NAAQS or PSD increments assessment under PSD permitting is a multi-stage approach that includes the following two stages:

i. The EPA describes the first stage as a single-source impact analysis, since this stage involves considering only the impact of the new or modifying source. There are two possible levels of detail in conducting a single-source impact analysis with the model user beginning with use of a screening model and proceeding to use of a refined model as necessary.

ii. The EPA describes the second stage as a cumulative impact analysis, since it takes into account all sources affecting the air quality in an area. In addition to the project source impact, this stage includes consideration of background, which includes contributions from nearby sources and other sources (*e.g.*, natural, minor, and distant major sources).

b. Each stage should involve increasing complexity and details, as required, to fully demonstrate that a new or modifying source will not cause or contribute to a violation of any NAAQS or PSD increment. As such, starting with a single-source impact analysis is recommended because, where the analysis at this stage is sufficient to demonstrate that a source will not cause or contribute to any potential violation, this may alleviate the need for a more time-consuming and comprehensive cumulative modeling analysis.

c. The single-source impact analysis, or first stage of an air quality analysis, should begin by determining the potential of a proposed new or modifying source to cause or contribute to a NAAQS or PSD increment violation. In certain circumstances, a screening model or technique may be used instead of the preferred model because it will provide estimated worst-case ambient impacts from the proposed new or modifying source. If these worst case ambient concentration estimates indicate that the source will not cause or contribute to any potential violation of a NAAQS or PSD increment, then the screening analysis should generally be sufficient for the required demonstration under PSD. If the ambient concentration estimates indicate that the source's emissions have the potential to

cause or contribute to a violation, then the use of a refined model to estimate the source's impact should be pursued. The refined modeling analysis should use a model or technique consistent with the *Guideline* (either a preferred model or technique or an alternative model or technique) and follow the requirements and recommendations for model inputs outlined in section 8. If the ambient concentration increase predicted with refined modeling indicates that the source will not cause or contribute to any potential violation of a NAAQS or PSD increment, then the refined analysis should generally be sufficient for the required demonstration under PSD. However, if the ambient concentration estimates from the refined modeling analysis indicate that the source's emissions have the potential to cause or contribute to a violation, then a cumulative impact analysis should be undertaken. The receptors that indicate the location of significant ambient impacts should be used to define the modeling domain for use in the cumulative impact analysis (section 8.2.2).

d. The cumulative impact analysis, or the second stage of an air quality analysis, should be conducted with the same refined model or technique to characterize the project source and then include the appropriate background concentrations (section 8.3). The resulting design concentrations should be used to determine whether the source will cause or contribute to a NAAQS or PSD increment violation. This determination should be based on: (1) The appropriate design concentration for each applicable NAAQS (and averaging period); and (2) whether the source's emissions cause or contribute to a violation at the time and location of any modeled violation (*i.e.*, when and where the predicted design concentration is greater than the NAAQS). For PSD increments, the cumulative impact analysis should also consider the amount of the air quality increment that has already been consumed by other sources, or, conversely, whether increment has expanded relative to the baseline concentration. Therefore, the applicant should model the existing or permitted nearby increment-consuming and increment-expanding sources, rather than using past modeling analyses of those sources as part of background concentration. This would permit the use of newly acquired data or improved modeling techniques if such data and/or techniques have become available since the last source was permitted.

9.2.3.1 Considerations in Developing Emissions Limits

a. Emissions limits and resulting control requirements should be established to provide for compliance with each applicable NAAQS (and averaging period) and PSD increment. It is possible that multiple emissions limits will be required for a source to demonstrate compliance with several criteria pollutants (and averaging periods) and PSD increments. Case-by-case determinations must be made as to the appropriate form of the limits, *i.e.*, whether the emissions limits restrict the emission factor (*e.g.*, limiting lb/MMBTU), the emission rate (*e.g.*, lb/hr), or both. The appropriate reviewing authority (paragraph 3.0(b)) and appropriate EPA guidance should be consulted to determine the appropriate emissions limits on a case-by-case basis.

9.2.4 Use of Measured Data in Lieu of Model Estimates

a. As described throughout the *Guideline*, modeling is the preferred method for demonstrating compliance with the NAAQS and PSD increments and for determining the most appropriate emissions limits for new and existing sources. When a preferred model or adequately justified and approved alternative model is available, model results, including the appropriate background, are sufficient for air quality demonstrations and establishing emissions limits, if necessary. In instances when the modeling technique available is only a screening technique, the addition of air quality monitoring data to the analysis may lend credence to the model results. However, air quality monitoring data alone will normally not be acceptable as the sole basis for demonstrating compliance with the NAAQS and PSD increments or for determining emissions limits.

b. There may be rare circumstances where the performance of the preferred air quality model will be shown to be less than reasonably acceptable when compared with air quality monitoring data measured in the vicinity of an existing source. Additionally, there may not be an applicable preferred air quality model, screening technique, or justifiable alternative model suitable for the situation. In these unique instances, there may be the possibility of establishing emissions limits and demonstrating compliance with the NAAQS and PSD increments solely on the basis of analysis of observed air quality data in lieu of an air quality modeling analysis. However, only in the case of a modification to an existing source should air quality monitoring data alone be a basis for determining adequate emissions limits or for demonstration that the modification will not cause or contribute to a violation of any NAAQS or PSD increment.

c. The following items should be considered prior to the acceptance of an analysis of measured air quality data as the sole basis for an air quality demonstration or determining an emissions limit:

i. Does a monitoring network exist for the pollutants and averaging times of concern in the vicinity of the existing source?

ii. Has the monitoring network been designed to locate points of maximum concentration?

iii. Do the monitoring network and the data reduction and storage procedures meet EPA monitoring and quality assurance requirements?

iv. Do the dataset and the analysis allow impact of the most important individual sources to be identified if more than one source or emission point is involved?

v. Is at least one full year of valid ambient data available?

vi. Can it be demonstrated through the comparison of monitored data with model results that available air quality models and techniques are not applicable?

d. Comprehensive air quality monitoring in the area affected by the existing source with proposed modifications will be necessary in these cases. Additional meteorological monitoring may also be necessary. The appropriate number of air quality and meteorological monitors from a scientific and technical standpoint is a function of the situation being considered. The source configuration, terrain configuration, and meteorological variations all have an impact on number and optimal placement of monitors. Decisions on the monitoring network appropriate for this type of analysis can only be made on a case-by-case basis.

e. Sources should obtain approval from the appropriate reviewing authority (paragraph 3.0(b)) and the EPA Regional Office for the monitoring network prior to the start of monitoring. A monitoring protocol agreed to by all parties involved is necessary to assure that ambient data are collected in a consistent and appropriate manner. The design of the network, the number, type, and location of the monitors, the sampling period, averaging time, as well as the need for meteorological monitoring or the use of mobile sampling or plume tracking techniques, should all be specified in the protocol and agreed upon prior to start-up of the network.

f. Given the uniqueness and complexities of these rare circumstances, the procedures can only be established on a case-by-case basis for analyzing the source's emissions data and the measured air quality monitoring data, and for projecting with a reasoned basis the air quality impact of a proposed modification to an existing source in order to demonstrate that emissions from the construction or operation of the modification will not cause or contribute to a violation of the applicable NAAQS and PSD increment, and to determine adequate emissions limits. The same attention should be given to the detailed analyses of the air quality data as would be applied to a comprehensive model performance evaluation. In some cases, the monitoring data collected for use in the performance evaluation of preferred air quality models, screening technique, or existing alternative models may help inform the development of a suitable new alternative model. Early coordination with the appropriate reviewing authority (paragraph 3.0(b)) and the EPA Regional Office is fundamental with respect to any potential use of measured data in lieu of model estimates.

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Appendix A to Appendix W of Part 51—Summaries of Preferred Air Quality Models

Table of Contents

A.0 Introduction and Availability

A.1 AERMOD (AMS/EPA Regulatory Model)
A.2 CTDMPLUS (Complex Terrain Dispersion Model Plus Algorithms for Unstable Situations)
A.3 OCD (Offshore and Coastal Dispersion Model)

A.0 Introduction and Availability

(1) This appendix summarizes key features of refined air quality models preferred for specific regulatory applications. For each model, information is provided on availability, approximate cost (where applicable), regulatory use, data input, output format and options, simulation of atmospheric physics, and accuracy. These models may be used without a formal demonstration of applicability provided they satisfy the recommendations for regulatory use; not all options in the models are necessarily recommended for regulatory use.

(2) Many of these models have been subjected to a performance evaluation using comparisons with observed air quality data. Where possible, several of the models contained herein have been subjected to evaluation exercises, including: (1) Statistical performance tests recommended by the American Meteorological Society, and (2) peer scientific reviews. The models in this appendix have been selected on the basis of the results of the model evaluations, experience with previous use, familiarity of the model to various air quality programs, and the costs and resource requirements for use.

(3) Codes and documentation for all models listed in this appendix are available from the EPA's Support Center for Regulatory Air Models (SCRAM) Web site at *https://www.epa.gov/scram*. Codes and documentation may also available from the National Technical Information Service (NTIS), *http://www.ntis.gov*, and, when available, are referenced with the appropriate NTIS accession number.

A.1 AERMOD (AMS/EPA Regulatory Model)

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Availability

The model codes and associated documentation are available on EPA's SCRAM Web site (paragraph A.0(3)).

Abstract

AERMOD is a steady-state plume dispersion model for assessment of pollutant concentrations from a variety of sources. AERMOD simulates transport and dispersion from multiple point, area, or volume sources based on an up-to-date characterization of the atmospheric boundary layer. Sources may be located in rural or urban areas, and receptors may be located in simple or complex terrain. AERMOD accounts for building wake effects (*i.e.*, plume downwash) based on the PRIME building downwash algorithms. The model employs hourly sequential preprocessed meteorological data to estimate concentrations for averaging times from 1-hour to 1-year (also multiple years). AERMOD can be used to estimate the concentrations of nonreactive pollutants from highway traffic. AERMOD also handles unique modeling problems associated with aluminum reduction plants, and other industrial sources where plume rise and downwash effects from stationary buoyant line sources are important. AERMOD is designed to operate in concert with two pre-processor codes: AERMET processes meteorological data for input to AERMOD, and AERMAP processes

terrain elevation data and generates receptor and hill height information for input to AERMOD.

a. Regulatory Use

(1) AERMOD is appropriate for the following applications:

- Point, volume, and area sources;
- Buoyant, elevated line sources (*e.g.*, aluminum reduction plants);
- Mobile sources;
- Surface, near-surface, and elevated releases;
- Rural or urban areas;
- Simple and complex terrain;
- Transport distances over which steady-state assumptions are appropriate, up to 50km;
- 1-hour to annual averaging times; and
- Continuous toxic air emissions.

(2) For regulatory applications of AERMOD, the regulatory default option should be set, *i.e.*, the parameter DFAULT should be employed in the MODELOPT record in the COntrol Pathway. The DFAULT option requires the use of meteorological data processed with the regulatory options in AERMET, the use of terrain elevation data processed through the AERMAP terrain processor, stack-tip downwash, sequential date checking, and does not permit the use of the model in the SCREEN mode. In the regulatory default mode, pollutant half-life or decay options are not employed, except in the case of an urban source of sulfur dioxide where a 4-hour half-life is applied. Terrain elevation data from the U.S. Geological Survey (USGS) 7.5-Minute Digital Elevation Model (DEM), or equivalent (approx. 30-meter resolution), (processed through AERMAP) should be used in all applications. Starting in 2011, data from the National Elevation Dataset (NED, *https://nationalmap.gov/elevation.html*) can also be used in AERMOD, which includes a range of resolutions, from 1-m to 2 arc seconds and such high resolution would always be preferred. In some cases, exceptions from the terrain data requirement may be made in consultation with the appropriate reviewing authority (paragraph 3.0(b)).

b. Input Requirements

(1) Source data: Required inputs include source type, location, emission rate, stack height, stack inside diameter, stack gas exit velocity, stack gas exit temperature, area and volume source dimensions, and source base elevation. For point sources subject to the influence of building downwash, direction-specific building dimensions (processed through the BPIPPRM building processor) should be input. Variable emission rates are optional. Buoyant line sources require coordinates of the end points of the line, release height, emission rate, average line source width, average building width, average spacing between buildings, and average line source buoyancy parameter. For mobile sources, traffic volume; emission factor, source height, and mixing zone width are needed to determine appropriate model inputs.

(2) Meteorological data: The AERMET meteorological preprocessor requires input of surface characteristics, including surface roughness (zo), Bowen ratio, and albedo, as well as, hourly observations of wind speed between 7zo and 100 m (reference wind speed measurement from which a vertical profile can be developed), wind direction, cloud cover, and temperature between zo and 100 m (reference temperature measurement from which a vertical profile can be developed). Meteorological data can be in the form of observed data or prognostic modeled data as discussed in paragraph 8.4.1(d). Surface characteristics may be varied by wind sector and by season or month. When using observed meteorological data, a morning sounding (in National Weather Service format) from a representative upper air station is required. Latitude, longitude, and time zone of the surface, site-specific (if applicable) and upper air meteorological stations are required. The wind speed starting threshold is also required in AERMET for applications involving site-specific data. When using prognostic data, modeled profiles of temperature and winds are input to AERMET. These can be hourly or a time that represents a morning sounding. Additionally, measured profiles of wind, temperature, vertical and lateral turbulence may be required in certain applications (*e.g.*, in complex terrain) to adequately represent the meteorology affecting plume transport and dispersion. Optionally, measurements of solar and/or net radiation may be input to AERMET. Two files are produced by the AERMET meteorological preprocessor for input to the AERMOD dispersion model. When using observed data, the surface file contains observed and calculated surface variables, one record per hour. For applications with multi-level site-specific meteorological data, the profile contains the observations made at each level of the meteorological tower (or remote sensor). When using prognostic data, the surface file contains surface variables calculated by the prognostic model and AERMET. The profile file contains the observations made at each level of a meteorological tower (or remote sensor), the one-level observations taken from other representative data (*e.g.*, National Weather Service surface observations), one record per level per hour, or in the case of prognostic data, the prognostic modeled values of temperature and winds at user-specified levels.

(i) Data used as input to AERMET should possess an adequate degree of representativeness to ensure that the wind, temperature and turbulence profiles derived by AERMOD

are both laterally and vertically representative of the source impact area. The adequacy of input data should be judged independently for each variable. The values for surface roughness, Bowen ratio, and albedo should reflect the surface characteristics in the vicinity of the meteorological tower or representative grid cell when using prognostic data, and should be adequately representative of the modeling domain. Finally, the primary atmospheric input variables, including wind speed and direction, ambient temperature, cloud cover, and a morning upper air sounding, should also be adequately representative of the source area when using observed data.

(ii) For applications involving the use of site-specific meteorological data that includes turbulences parameters (*i.e.,* sigma-theta and/or sigma-w), the application of the ADJ_U* option in AERMET would require approval as an alternative model application under section 3.2.

(iii) For recommendations regarding the length of meteorological record needed to perform a regulatory analysis with AERMOD, *see* section 8.4.2.

(3) Receptor data: Receptor coordinates, elevations, height above ground, and hill height scales are produced by the AERMAP terrain preprocessor for input to AERMOD. Discrete receptors and/or multiple receptor grids, Cartesian and/or polar, may be employed in AERMOD. AERMAP requires input of DEM or NED terrain data produced by the USGS, or other equivalent data. AERMAP can be used optionally to estimate source elevations.

c. Output

Printed output options include input information, high concentration summary tables by receptor for user-specified averaging periods, maximum concentration summary tables, and concurrent values summarized by receptor for each day processed. Optional output files can be generated for: A listing of occurrences of exceedances of user-specified threshold value; a listing of concurrent (raw) results at each receptor for each hour modeled, suitable for post-processing; a listing of design values that can be imported into graphics software for plotting contours; a listing of results suitable for NAAQS analyses including NAAQS exceedances and culpability analyses; an unformatted listing of raw results above a threshold value with a special structure for use with the TOXX model component of TOXST; a listing of concentrations by rank (*e.g.,* for use in quantile-quantile plots); and a listing of concentrations, including arc-maximum normalized concentrations, suitable for model evaluation studies.

d. Type of Model

AERMOD is a steady-state plume model, using Gaussian distributions in the vertical and horizontal for stable conditions, and in the horizontal for convective conditions. The vertical concentration distribution for convective conditions results from an assumed bi-Gaussian probability density function of the vertical velocity.

e. Pollutant Types

AERMOD is applicable to primary pollutants and continuous releases of toxic and hazardous waste pollutants. Chemical transformation is treated by simple exponential decay.

f. Source-Receptor Relationships

AERMOD applies user-specified locations for sources and receptors. Actual separation between each source-receptor pair is used. Source and receptor elevations are user input or are determined by AERMAP using USGS DEM or NED terrain data. Receptors may be located at user-specified heights above ground level.

g. Plume Behavior

(1) In the convective boundary layer (CBL), the transport and dispersion of a plume is characterized as the superposition of three modeled plumes: (1) The direct plume (from the stack); (2) the indirect plume; and (3) the penetrated plume, where the indirect plume accounts for the lofting of a buoyant plume near the top of the boundary layer, and the penetrated plume accounts for the portion of a plume that, due to its buoyancy, penetrates above the mixed layer, but can disperse downward and re-enter the mixed layer. In the CBL, plume rise is superposed on the displacements by random convective velocities (Weil *et al.*, 1997).

(2) In the stable boundary layer, plume rise is estimated using an iterative approach to account for height-dependent lapse rates, similar to that in the CTDMPLUS model (*see* A.2 in this appendix).

(3) Stack-tip downwash and buoyancy induced dispersion effects are modeled. Building wake effects are simulated for stacks subject to building downwash using the methods contained in the PRIME downwash algorithms (Schulman, *et al.*, 2000). For plume rise affected by the presence of a building, the PRIME downwash algorithm uses a numerical solution of the mass, energy and momentum conservation laws (Zhang and Ghoniem, 1993). Streamline deflection and the position of the stack relative to the building affect plume trajectory and dispersion. Enhanced dispersion is based on the approach of Weil (1996). Plume mass captured by the cavity is well-mixed within the cavity. The captured plume mass is re-emitted to the far wake as a volume source.

(4) For elevated terrain, AERMOD incorporates the concept of the critical dividing streamline height, in which flow below this height remains horizontal, and flow above this height tends to rise up and over terrain (Snyder *et al.*, 1985). Plume concentration estimates are the weighted sum of these two limiting plume states. However, consistent with the steady-state assumption of uniform horizontal wind direction over the modeling domain, straight-line plume trajectories are assumed, with adjustment in the plume/receptor geometry used to account for the terrain effects.

h. Horizontal Winds

Vertical profiles of wind are calculated for each hour based on measurements and surface-layer similarity (scaling) relationships. At a given height above ground, for a given hour, winds are assumed constant over the modeling domain. The effect of the vertical variation in horizontal wind speed on dispersion is accounted for through simple averaging over the plume depth.

i. Vertical Wind Speed

In convective conditions, the effects of random vertical updraft and downdraft velocities are simulated with a bi-Gaussian probability density function. In both convective and stable conditions, the mean vertical wind speed is assumed equal to zero.

j. Horizontal Dispersion

Gaussian horizontal dispersion coefficients are estimated as continuous functions of the parameterized (or measured) ambient lateral turbulence and also account for buoyancy-induced and building wake-induced turbulence. Vertical profiles of lateral turbulence are developed from measurements and similarity (scaling) relationships. Effective turbulence values are determined from the portion of the vertical profile of lateral turbulence between the plume height and the receptor height. The effective lateral turbulence is then used to estimate horizontal dispersion.

k. Vertical Dispersion

In the stable boundary layer, Gaussian vertical dispersion coefficients are estimated as continuous functions of parameterized vertical turbulence. In the convective boundary layer, vertical dispersion is characterized by a bi-Gaussian probability density function and is also estimated as a continuous function of parameterized vertical turbulence. Vertical turbulence profiles are developed from measurements and similarity (scaling) relationships. These turbulence profiles account for both convective and mechanical turbulence. Effective turbulence values are determined from the portion of the vertical profile of vertical turbulence between the plume height and the receptor height. The effective vertical turbulence is then used to estimate vertical dispersion.

l. Chemical Transformation

Chemical transformations are generally not treated by AERMOD. However, AERMOD does contain an option to treat chemical transformation using simple exponential decay, although this option is typically not used in regulatory applications except for sources of sulfur dioxide in urban areas. Either a decay coefficient or a half-life is input by the user. Note also that the Plume Volume Molar Ratio Method and the Ozone Limiting Method (section 4.2.3.4) for NO_2 analyses are available.

m. Physical Removal

AERMOD can be used to treat dry and wet deposition for both gases and particles.

n. Evaluation Studies

American Petroleum Institute, 1998. Evaluation of State of the Science of Air Quality Dispersion Model, Scientific Evaluation, prepared by Woodward-Clyde Consultants, Lexington, Massachusetts, for American Petroleum Institute, Washington, DC 20005–4070.

Brode, R.W., 2002. Implementation and Evaluation of PRIME in AERMOD. Preprints of the 12th Joint Conference on Applications of Air Pollution Meteorology, May 20–24, 2002; American Meteorological Society, Boston, MA.

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U.S. Environmental Protection Agency, 2003. AERMOD: Latest Features and Evaluation Results. Publication No. EPA–454/R–03–003. Office of Air Quality Planning and Standards, Research Triangle Park, NC.

Heist, D., et al, 2013. Estimating near-road pollutant dispersion: A model inter-comparison. *Transportation Research Part D: Transport and Environment,* 25: pp 93–105.

A.2 CTDMPLUS (Complex Terrain Dispersion Model Plus Algorithms for Unstable Situations)

References

Perry, S.G., D.J. Burns, L.H. Adams, R.J. Paine, M.G. Dennis, M.T. Mills, D.G. Strimaitis, R.J. Yamartino and E.M. Insley, 1989. User's Guide to the Complex Terrain Dispersion Model Plus Algorithms for Unstable Situations

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(CTDMPLUS). Volume 1: Model Descriptions and User Instructions. EPA Publication No. EPA–600/8–89–041. U.S. Environmental Protection Agency, Research Triangle Park, NC. (NTIS No. PB 89–181424).

Perry, S.G., 1992. CTDMPLUS: A Dispersion Model for Sources near Complex Topography. Part I: Technical Formulations. *Journal of Applied Meteorology*, 31(7): 633–645.

Availability

The model codes and associated documentation are available on the EPA's SCRAM Web site (paragraph A.0(3)).

Abstract

CTDMPLUS is a refined point source Gaussian air quality model for use in all stability conditions for complex terrain applications. The model contains, in its entirety, the technology of CTDM for stable and neutral conditions. However, CTDMPLUS can also simulate daytime, unstable conditions, and has a number of additional capabilities for improved user friendliness. Its use of meteorological data and terrain information is different from other EPA models; considerable detail for both types of input data is required and is supplied by preprocessors specifically designed for CTDMPLUS. CTDMPLUS requires the parameterization of individual hill shapes using the terrain preprocessor and the association of each model receptor with a particular hill.

a. Regulatory Use

CTDMPLUS is appropriate for the following applications:

- Elevated point sources;
- Terrain elevations above stack top;
- Rural or urban areas;
- Transport distances less than 50 kilometers; and
- 1-hour to annual averaging times when used with a post-processor program such as CHAVG.

b. Input Requirements

(1) Source data: For each source, user supplies source location, height, stack diameter, stack exit velocity, stack exit temperature, and emission rate; if variable emissions are appropriate, the user supplies hourly values for emission rate, stack exit velocity, and stack exit temperature.

(2) Meteorological data: For applications of CTDMPLUS, multiple level (typically three or more) measurements of wind speed and direction, temperature and turbulence (wind fluctuation statistics) are required to create the basic meteorological data file (''PROFILE''). Such measurements should be obtained up to the representative plume height(s) of interest (*i.e.*, the plume height(s) under those conditions important to the determination of the design concentration). The representative plume height(s) of interest should be determined using an appropriate complex terrain screening procedure (*e.g.*, CTSCREEN) and should be documented in the monitoring/modeling protocol. The necessary meteorological measurements should be obtained from an appropriately sited meteorological tower augmented by SODAR and/or RASS if the representative plume height(s) of interest is above the levels represented by the tower measurements. Meteorological preprocessors then create a SURFACE data file (hourly values of mixed layer heights, surface friction velocity, Monin-Obukhov length and surface roughness length) and a RAWINsonde data file (upper air measurements of pressure, temperature, wind direction, and wind speed).

(3) Receptor data: Receptor names (up to 400) and coordinates, and hill number (each receptor must have a hill number assigned).

(4) Terrain data: User inputs digitized contour information to the terrain preprocessor which creates the TERRAIN data file (for up to 25 hills).

c. Output

(1) When CTDMPLUS is run, it produces a concentration file, in either binary or text format (user's choice), and a list file containing a verification of model inputs, *i.e.*,

- Input meteorological data from ''SURFACE'' and ''PROFILE,''
- Stack data for each source,
- Terrain information,
- Receptor information, and
- Source-receptor location (line printer map).

(2) In addition, if the case-study option is selected, the listing includes:

- Meteorological variables at plume height,
- Geometrical relationships between the source and the hill, and
- Plume characteristics at each receptor, *i.e.*,

—Distance in along-flow and cross flow direction
—Effective plume-receptor height difference
—Effective σy & σz values, both flat terrain and hill induced (the difference shows the effect of the hill)
—Concentration components due to WRAP, LIFT and FLAT.

(3) If the user selects the TOPN option, a summary table of the top four concentrations at each receptor is given. If the ISOR option is selected, a source contribution table for every hour will be printed.

(4) A separate output file of predicted (1-hour only) concentrations (''CONC'') is written if the user chooses this option. Three forms of output are possible:

Item E 002837

(i) A binary file of concentrations, one value for each receptor in the hourly sequence as run;

(ii) A text file of concentrations, one value for each receptor in the hourly sequence as run; or

(iii) A text file as described above, but with a listing of receptor information (names, positions, hill number) at the beginning of the file.

(5) Hourly information provided to these files besides the concentrations themselves includes the year, month, day, and hour information as well as the receptor number with the highest concentration.

d. Type of Model

CTDMPLUS is a refined steady-state, point source plume model for use in all stability conditions for complex terrain applications.

e. Pollutant Types

CTDMPLUS may be used to model non- reactive, primary pollutants.

f. Source-Receptor Relationship

Up to 40 point sources, 400 receptors and 25 hills may be used. Receptors and sources are allowed at any location. Hill slopes are assumed not to exceed 15°, so that the linearized equation of motion for Boussinesq flow are applicable. Receptors upwind of the impingement point, or those associated with any of the hills in the modeling domain, require separate treatment.

g. Plume Behavior

(1) As in CTDM, the basic plume rise algorithms are based on Briggs' (1975) recommendations.

(2) A central feature of CTDMPLUS for neutral/stable conditions is its use of a critical dividing-streamline height (H_c) to separate the flow in the vicinity of a hill into two separate layers. The plume component in the upper layer has sufficient kinetic energy to pass over the top of the hill while streamlines in the lower portion are constrained to flow in a horizontal plane around the hill. Two separate components of CTDMPLUS compute ground-level concentrations resulting from plume material in each of these flows.

(3) The model calculates on an hourly (or appropriate steady averaging period) basis how the plume trajectory (and, in stable/neutral conditions, the shape) is deformed by each hill. Hourly profiles of wind and temperature measurements are used by CTDMPLUS to compute plume rise, plume penetration (a formulation is included to handle penetration into elevated stable layers, based on Briggs (1984)), convective scaling parameters, the value of H_c, and the Froude number above H_c.

h. Horizontal Winds

CTDMPLUS does not simulate calm meteorological conditions. Both scalar and vector wind speed observations can be read by the model. If vector wind speed is unavailable, it is calculated from the scalar wind speed. The assignment of wind speed (either vector or scalar) at plume height is done by either:

- Interpolating between observations above and below the plume height, or
- Extrapolating (within the surface layer) from the nearest measurement height to the plume height.

i. Vertical Wind Speed

Vertical flow is treated for the plume component above the critical dividing streamline height (H_c); *see* ''Plume Behavior.''

j. Horizontal Dispersion

Horizontal dispersion for stable/neutral conditions is related to the turbulence velocity scale for lateral fluctuations, σv, for which a minimum value of 0.2 m/s is used. Convective scaling formulations are used to estimate horizontal dispersion for unstable conditions.

k. Vertical Dispersion

Direct estimates of vertical dispersion for stable/neutral conditions are based on observed vertical turbulence intensity, *e.g.*, σw (standard deviation of the vertical velocity fluctuation). In simulating unstable (convective) conditions, CTDMPLUS relies on a skewed, bi-Gaussian probability density function (pdf) description of the vertical velocities to estimate the vertical distribution of pollutant concentration.

l. Chemical Transformation

Chemical transformation is not treated by CTDMPLUS.

m. Physical Removal

Physical removal is not treated by CTDMPLUS (complete reflection at the ground/hill surface is assumed).

n. Evaluation Studies

Burns, D.J., L.H. Adams and S.G. Perry, 1990. Testing and Evaluation of the CTDMPLUS Dispersion Model: Daytime Convective Conditions. U.S. Environmental Protection Agency, Research Triangle Park, NC.

Paumier, J.O., S.G. Perry and D.J. Burns, 1990. An Analysis of CTDMPLUS Model Predictions with the Lovett Power Plant Data Base. U.S. Environmental Protection Agency, Research Triangle Park, NC.

Paumier, J.O., S.G. Perry and D.J. Burns, 1992. CTDMPLUS: A Dispersion Model for Sources near Complex Topography. Part

II: Performance Characteristics. *Journal of Applied Meteorology*, 31(7): 646–660.

A.3 OCD (Offshore and Coastal Dispersion Model)

Reference

DiCristofaro, D.C. and S.R. Hanna, 1989. OCD: The Offshore and Coastal Dispersion Model, Version 4. Volume I: User's Guide, and Volume II: Appendices. Sigma Research Corporation, Westford, MA. (NTIS Nos. PB 93–144384 and PB 93–144392).

Availability

The model codes and associated documentation are available on EPA's SCRAM Web site (paragraph A.0(3)).

Abstract

(1) OCD is a straight-line Gaussian model developed to determine the impact of offshore emissions from point, area or line sources on the air quality of coastal regions. OCD incorporates overwater plume transport and dispersion as well as changes that occur as the plume crosses the shoreline. Hourly meteorological data are needed from both offshore and onshore locations. These include water surface temperature, overwater air temperature, mixing height, and relative humidity.

(2) Some of the key features include platform building downwash, partial plume penetration into elevated inversions, direct use of turbulence intensities for plume dispersion, interaction with the overland internal boundary layer, and continuous shoreline fumigation.

a. Regulatory Use

OCD has been recommended for use by the Bureau of Ocean Energy Management for emissions located on the Outer Continental Shelf (50 FR 12248; 28 March 1985). OCD is applicable for overwater sources where onshore receptors are below the lowest source height. Where onshore receptors are above the lowest source height, offshore plume transport and dispersion may be modeled on a case-by-case basis in consultation with the appropriate reviewing authority (paragraph 3.0(b)).

b. Input Requirements

(1) Source data: Point, area or line source location, pollutant emission rate, building height, stack height, stack gas temperature, stack inside diameter, stack gas exit velocity, stack angle from vertical, elevation of stack base above water surface and gridded specification of the land/water surfaces. As an option, emission rate, stack gas exit velocity and temperature can be varied hourly.

(2) Meteorological data: PCRAMMET is the recommended meteorological data preprocessor for use in applications of OCD employing hourly NWS data. MPRM is the recommended meteorological data preprocessor for applications of OCD employing site-specific meteorological data.

(i) Over land: Surface weather data including hourly stability class, wind direction, wind speed, ambient temperature, and mixing height are required.

(ii) Over water: Hourly values for mixing height, relative humidity, air temperature, and water surface temperature are required; if wind speed/direction are missing, values over land will be used (if available); vertical wind direction shear, vertical temperature gradient, and turbulence intensities are optional.

(3) Receptor data: Location, height above local ground-level, ground-level elevation above the water surface.

c. Output

(1) All input options, specification of sources, receptors and land/water map including locations of sources and receptors.

(2) Summary tables of five highest concentrations at each receptor for each averaging period, and average concentration for entire run period at each receptor.

(3) Optional case study printout with hourly plume and receptor characteristics. Optional table of annual impact assessment from non-permanent activities.

(4) Concentration output files can be used by ANALYSIS postprocessor to produce the highest concentrations for each receptor, the cumulative frequency distributions for each receptor, the tabulation of all concentrations exceeding a given threshold, and the manipulation of hourly concentration files.

d. Type of Model

OCD is a Gaussian plume model constructed on the framework of the MPTER model.

e. Pollutant Types

OCD may be used to model primary pollutants. Settling and deposition are not treated.

f. Source-Receptor Relationship

(1) Up to 250 point sources, 5 area sources, or 1 line source and 180 receptors may be used.

(2) Receptors and sources are allowed at any location.

(3) The coastal configuration is determined by a grid of up to 3600 rectangles. Each element of the grid is designated as either land or water to identify the coastline.

g. Plume Behavior

(1) The basic plume rise algorithms are based on Briggs' recommendations.

(2) Momentum rise includes consideration of the stack angle from the vertical.

(3) The effect of drilling platforms, ships, or any overwater obstructions near the source are used to decrease plume rise using a revised platform downwash algorithm based on laboratory experiments.

(4) Partial plume penetration of elevated inversions is included using the suggestions of Briggs (1975) and Weil and Brower (1984).

(5) Continuous shoreline fumigation is parameterized using the Turner method where complete vertical mixing through the thermal internal boundary layer (TIBL) occurs as soon as the plume intercepts the TIBL.

h. Horizontal Winds

(1) Constant, uniform wind is assumed for each hour.

(2) Overwater wind speed can be estimated from overland wind speed using relationship of Hsu (1981).

(3) Wind speed profiles are estimated using similarity theory (Businger, 1973). Surface layer fluxes for these formulas are calculated from bulk aerodynamic methods.

i. Vertical Wind Speed

Vertical wind speed is assumed equal to zero.

j. Horizontal Dispersion

(1) Lateral turbulence intensity is recommended as a direct estimate of horizontal dispersion. If lateral turbulence intensity is not available, it is estimated from boundary layer theory. For wind speeds less than 8 m/s, lateral turbulence intensity is assumed inversely proportional to wind speed.

(2) Horizontal dispersion may be enhanced because of obstructions near the source. A virtual source technique is used to simulate the initial plume dilution due to downwash.

(3) Formulas recommended by Pasquill (1976) are used to calculate buoyant plume enhancement and wind direction shear enhancement.

(4) At the water/land interface, the change to overland dispersion rates is modeled using a virtual source. The overland dispersion rates can be calculated from either lateral turbulence intensity or Pasquill-Gifford curves. The change is implemented where the plume intercepts the rising internal boundary layer.

k. Vertical Dispersion

(1) Observed vertical turbulence intensity is not recommended as a direct estimate of vertical dispersion. Turbulence intensity should be estimated from boundary layer theory as default in the model. For very stable conditions, vertical dispersion is also a function of lapse rate.

(2) Vertical dispersion may be enhanced because of obstructions near the source. A virtual source technique is used to simulate the initial plume dilution due to downwash.

(3) Formulas recommended by Pasquill (1976) are used to calculate buoyant plume enhancement.

(4) At the water/land interface, the change to overland dispersion rates is modeled using a virtual source. The overland dispersion rates can be calculated from either vertical turbulence intensity or the Pasquill-Gifford coefficients. The change is implemented where the plume intercepts the rising internal boundary layer.

l. Chemical Transformation

Chemical transformations are treated using exponential decay. Different rates can be specified by month and by day or night.

m. Physical Removal

Physical removal is also treated using exponential decay.

n. Evaluation Studies

DiCristofaro, D.C. and S.R. Hanna, 1989. OCD: The Offshore and Coastal Dispersion Model. Volume I: User's Guide. Sigma Research Corporation, Westford, MA.

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Hanna, S.R. and D.C. DiCristofaro, 1988. Development and Evaluation of the OCD/API Model. Final Report, API Pub. 4461, American Petroleum Institute, Washington, DC.

[82 FR 5203, Jan. 17, 2017]

APPENDIX X TO PART 51—EXAMPLES OF ECONOMIC INCENTIVE PROGRAMS

I. INTRODUCTION AND PURPOSE

This appendix contains examples of EIP's which are covered by the EIP rules. Program descriptions identify key provisions which distinguish the different model program types. The examples provide additional information and guidance on various types of regulatory programs collectively referred to as EIP's. The examples include programs involving stationary, area, and mobile sources. The definition section at 40 CFR 51.491 defines an EIP as a program which may include State established emission fees or a system of marketable permits, or a system of State fees on sale or manufacture of products the

State of Oregon Department of Environmental Quality

OAR 340-225-0070 Federal Land Managers' Air Quality Related Values Work Group Phase I Report - Revised

National Park Service
U.S. Department of the Interior

Natural Resource Program Center

Federal Land Managers' Air Quality Related Values Work Group (FLAG)

Phase I Report—Revised (2010)

Natural Resource Report NPS/NRPC/NRR—2010/232

ON THE COVER

Courthouse Towers, Arches National Park, Utah.
Photo by Debbie Miller.

THIS PAGE:

Jumping Cholla, Superstition Wilderness, Arizona.
Photo by Steve Boutcher

Federal Land Managers' Air Quality Related Values Work Group (FLAG)

Phase I Report—Revised (2010)

Natural Resource Report NPS/NRPC/NRR—2010/232

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October 2010

The National Park Service, Natural Resource Program Center publishes a range of reports that address natural resource topics of interest and applicability to a broad audience in the National Park Service and others in natural resource management, including scientists, conservation and environmental constituencies, and the public.

The Natural Resource Report Series is used to disseminate high-priority, current natural resource management information with managerial application. The series targets a general, diverse audience, and may contain NPS policy considerations or address sensitive issues of management applicability.

All manuscripts in the series receive the appropriate level of peer review to ensure that the information is scientifically credible, technically accurate, appropriately written for the intended audience, and designed and published in a professional manner.

This guidance document was jointly prepared by the National Park Service, U.S. Forest Service, and the U.S. Fish and Wildlife Service, in collaboration with the Environmental Protection Agency. Guidance contained herein has been reviewed by subject matter experts and the general public through formal public review and comment period. This guidance document provides information for Federal Land Managers, permitting authorities, and permit applicants to use when assessing air quality impacts to air quality related values. Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. Government.

This report is available from the Air Resources Division of the NPS (http://www.nature.nps.gov/air) and the Natural Resource Publications Management Web site (http://www.nature.nps.gov/publications/NRPM) on the Internet.

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NPS 999/105412, October 2010

United States Department of the Interior

OFFICE OF THE SECRETARY
Washington, D.C. 20240

OCT - 7 2010

Dear FLAG User:

We are pleased to provide the final revised FLAG report (FLAG 2010). FLAG was formed at the request of permit applicants and State permit review authorities to develop a more consistent and objective approach for the Federal Land Managers (FLMs), *i.e.*, National Park Service, U.S. Fish and Wildlife Service, and U.S. Department of Agriculture Forest Service, to evaluate air pollution effects on their Air Quality Related Values (AQRVs). The FLAG effort focused on how air pollutants – primarily particulate matter, nitrogen dioxide, sulfur dioxide, nitrates, sulfates, ozone – affect the health and status of resources in areas managed by the three agencies. FLAG subgroups concentrated on four key issues: (1) visibility; (2) aquatic and terrestrial effects of wet and dry pollutant deposition; (3) terrestrial effects of ozone; and (4) process and policy issues. In December 2000, the FLMs published a final Phase I report (FLAG 2000). Based on knowledge gained and regulatory developments since FLAG 2000, the FLMs believe certain revisions to FLAG 2000 are now appropriate. The final revised FLAG 2010 report reflects those changes.

The FLAG 2010 report contains a wealth of information and should continue to be a very useful tool; we support its recommendations. The FLAG report is guidance and reflects agency direction, but it is not a rule. Nevertheless, we encourage all FLMs, permitting authorities, permit applicants, and other interested parties to take advantage of the helpful information contained in the FLAG report when assessing air pollution impacts on AQRVs.

We want to thank the many people who contributed to this important and worthwhile project.

Sincerely,

Thomas L. Strickland
Assistant Secretary for Fish and Wildlife and Parks
Department of the Interior

Sincerely,

Harris Sherman, Under Secretary
Natural Resources and the Environment
Department of Agriculture

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Preface to this Edition of the FLAG Phase I Report (New)

Under the Clean Air Act, the Federal Land Manager (FLM) and the Federal official with direct responsibility for management of Federal Class I parks and wilderness areas (i.e., Park Superintendent, Refuge Manager, Forest Supervisor) have an affirmative responsibility to protect the air quality related values (AQRVs) (including visibility) of such lands, and to consider whether a proposed major emitting facility will have an adverse impact on such values. The FLM's decision regarding whether there is an adverse impact is then conveyed to the permitting authority – usually a State agency – for consideration in its determinations regarding the permit. The permitting authority's determinations generally consider a wide range of factors, including the potential impact of the new source or major modification on the AQRVs of Class I areas, if applicable.

Both State permitting agencies and permit applicants requested that the FLMs provide better consistency pertaining to their role in the review of new source permit applications near Federal Class I areas. To address this concern, the FLMs formed the Federal Land Managers' Air Quality Related Values Work Group (FLAG). The official "FLM" is the Secretary of the department with authority over the Federal Class I areas (or the Secretary's designee). For the Department of the Interior, the Secretary has designated the Assistant Secretary for Fish and Wildlife and Parks as the FLM, whereas the Secretary of Agriculture has delegated the FLM responsibilities to the Regional Forester, and in some cases, the Forest Supervisor.

The purpose of FLAG is twofold: (1) to develop a more consistent and objective approach for the FLMs to evaluate air pollution effects on public AQRVs in Class I areas, including a process to identify those resources and any potential adverse impacts, and (2) to provide State permitting authorities and potential permit applicants consistency on how to assess the impacts of new and existing sources on AQRVs in Class I areas, especially in the review of Prevention of Significant Deterioration (PSD) of air quality permit applications. Under the Clean Air Act, the FLM formal "affirmative responsibility" role in the permitting process is limited to the extent a proposed new or modified source may affect AQRVs in a Class I area.[1]

Adult Brown Pelicans on Breton Island National Wildlife Refuge, Louisiana.
Credit: USFWS

FLAG members include representatives from three of the federal land management agencies that administer Federal Class I areas: the U.S. Forest Service (USFS), under the Department of Agriculture, and the National Park Service (NPS) and U.S. Fish and Wildlife Service (FWS) under the Department of the Interior, hereafter referred to as "the Agencies" or the "FLMs." In addition, five Tribal governments each administer their redesignated Class I areas, and the Bureau of Land Management (BLM) jointly administers four mandatory Federal Class I areas with the USFS. BLM is not a member of FLAG. However, because BLM does manage federal PSD Class I lands, as well as large amounts of acres in the vicinity of many FLAG Agencies' Class I areas, they may apply, when appropriate, the assessment methodologies outlined in the FLAG report. Applicants with the potential to adversely impact visibility or other AQRVs at PSD Class I areas administered by the BLM should contact that agency directly to discuss their considerations. The Agencies review permit applications for projects that may impact their areas, and make recommendations to their respective FLM as to whether or not those impacts might be considered adverse. The FLM will then make the final decision regarding the nature of the potential impacts to AQRVs, which is then conveyed to the permitting authority for its consideration.

In December 2000, after undergoing a public review and comment process that included a 90 day public comment period announced in the *Federal Register* and a public meeting, the FLMs published a *FLAG Phase I Report* (FLAG 2000), along with an accompanying "Response to Public Comments" document. The FLAG 2000 report described the work accomplished in Phase I of the FLAG effort. FLAG 2000 provided State permitting authorities and potential permit applicants a consistent methodology for conducting Class I area impact analyses. At that time, the Agencies envisioned a FLAG Phase II to address unresolved issues

1. Nevertheless, the FLMs are also concerned about resources in Class II parks and wilderness areas because they have other mandates to protect those areas as well. The information and procedures outlined in this document are generally applicable to evaluating the effect of new or modified sources on the AQRVs in both Class I and Class II areas, including the evaluation of effects as part of Environmental Assessments and/or Environmental Impact Statements under the National Environmental Policy Act (NEPA). However, FLAG does not preclude more refined or regional analyses being performed under NEPA or other programs.

including those that will require research and the collection of new data. However, resource constraints have prevented the Agencies from embarking on a formal FLAG Phase II process, but the Agencies have made significant progress in obtaining effects-based information as part of their resource-protection responsibilities. This information is included in this revised report.

The Agencies formed three separate subgroups to deal with area specific technical and policy issues associated with visibility impairment, ozone effects on vegetation, and effects of pollutant deposition on soils and surface waters. FLAG 2000 consolidated the results of those three subgroups.

FLAG 2000 included recommendations for completing and evaluating New Source Review (NSR) projects that may affect federally protected areas. It was intended to be a screening tool to help the Agencies and permit applicants determine whether impacts would be negligible. It was not intended to provide a bright-line test that would allow one to determine whether or not a proposed source of air pollution would cause or contribute to an adverse impact on AQRVs. That determination remains a project-specific management decision of the FLM. Among other factors, the FLMs' assessment of whether or not an adverse impact would occur is based on the sensitivity of the AQRVs at the particular federally protected area under consideration, and the magnitude, frequency, duration, timing, and geographic extent of the estimated new source impacts. This report (FLAG 2010) reaffirms these intentions.

FLAG 2000 has been a useful tool to the Agencies, State permitting authorities, and permit applicants. It was intended to be a working document that would be revised as necessary as the Agencies learn more about how to better assess the health and status of AQRVs. Based on knowledge gained and regulatory developments since FLAG 2000, the Agencies believe certain revisions to FLAG 2000 are now appropriate. This revised report (FLAG 2010) reflects those changes. However, it is important to emphasize that in this revision the Agencies have made certain changes to update specific information and data, but retain intact much of the background and general information contained in FLAG 2000 (e.g., Appendices A through H). Therefore, while this version replaces FLAG 2000, FLAG 2010 does not constitute a comprehensive update of all the information and material contained in FLAG 2000. Instead, the Agencies have focused their efforts on those areas of FLAG 2000 that have received the most attention and concern from permit applicants and permitting authorities. In that regard, the Agencies have included substantial changes to the visibility analysis sections, as well as included a more detailed discussion of the factors that the FLMs will use in the decision making process for an adverse impact determination. The Agencies have also taken this opportunity to discuss some key regulatory developments since FLAG 2000, as well as update some information in the FLAG 2000 deposition and ozone sections. To aid the FLAG user wanting to focus on the most recent changes, the Agencies have identified those new and revised sections throughout the FLAG 2010 report.

The most significant changes in this FLAG 2010 revision are summarized as follows:

- Adopts similar criteria derived from EPA's 2005 Best Available Retrofit Technology (BART) guidelines for the Regional Haze Rule to screen out from AQRV review those sources with relatively small amounts of emissions located a large distance from a Class I area (i.e., Q/D ≤ 10, for sources located greater than 50 km away).
- Utilizes the most recent EPA estimates to determine annual average or 20% best natural visibility conditions for Class I areas, using the new EPA-approved visibility algorithm.
- Adopts criteria derived from the 2005 BART guidelines that utilizes monthly average relative humidity adjustment factors to minimize the effects of weather events (i.e., short-term meteorological phenomena) on modeled visibility impacts.
- Adopts criteria derived from the 2005 BART guidelines that sets a 98th percentile value to screen out roughly seven days of haze-type visibility impairment per year.
- Includes deposition analysis thresholds and concern thresholds for nitrogen and sulfur deposition impacts on vegetation, soils, and water.
- Increases transparency and consistency of factors considered for adverse impact determinations.

A comparison of these FLAG 2010 changes to information contained in FLAG 2000 is provided in Table 1:

Other changes of note included in FLAG 2010 are:

- Clarifies the near field visibility analysis techniques for analyzing plumes or layers viewed against a background;
- Expands discussion of "Critical Loads" to reflect some significant developments in this area since FLAG 2000;
- Updates ozone sensitive species lists contained in Appendix 3.A of the FLAG 2000 report, but now includes that information on individual agency web sites rather than in the FLAG 2010 report;
- Replaces Appendix 3.B of FLAG 2000 (W126 and N100 ozone values) with current information on the individual agency web sites;
- Updates the information contained in Table D-2 of FLAG 2000 to reflect current information, but now includes that information on individual agency web sites rather than in the FLAG 2010 report;
- Replaces the dated sulfate, nitrate, and ammonium ion concentration maps (Figures D-2, D-3, and D-4 of FLAG 2000), with a reference to the NADP site for current trends data.

Table 1. FLAG 2000 vs. FLAG 2010 Analyses

	FLAG 2000	FLAG 2010
Annual emissions/Distance (Q/D) screening criteria. (Not applicable for Class I increment analyses).	None	≤10 (sum of certain pollutant emissions (TPY) divided by distance (km) from Class I area; applies to all AQRVs, not just visibility. See section 3.2.
Background Visibility Conditions.	Based on annual average natural, using NAPAP estimates.	Based on annual average natural, or 20% best natural, using EPA data from Regional Haze Rule development. See section 3.3.3.
Relative Humidity Adjustment Factor (f(RH)).	Hour-by-hour (with RH capped at 98%).	Monthly average (with RH capped at 95%). See section 3.3.3.
First Level Screening Model.	CALPUFF or CALPUFF-lite.	CALPUFF only. See section 3.3.3.
Visibility Assessment Criteria.	Maximum modeled value.	98th percentile modeled value at any receptor. See section 3.3.3.
Deposition Analysis Thresholds/ Concern Thresholds	None	Provided for nitrogen and sulfur deposition. See section 3.5.6.
Adverse Impact Determination Criteria.	"Likely to Object" if 10% threshold exceeded; regulatory factors implicitly considered.	Adverse impact determination process more explicit; considers regulatory and other factors. See sections 4.2-4.4

Executive Summary (Revised)

The Federal Land Managers' Air Quality Related Values Work Group (FLAG) formed to develop a more consistent approach for the Federal Land Managers (FLMs) to evaluate air pollution effects on resources. As discussed in the Preface, the *FLAG Phase I Report* (FLAG 2000) is being revised in part at this time. The primary—but not sole—focus of FLAG is the New Source Review (NSR) program, especially in the review of Prevention of Significant Deterioration (PSD) of air quality permit applications. The goals of FLAG have been to provide consistent policies and processes both for identifying air quality related values (AQRVs) and for evaluating the effects of air pollution on AQRVs, primarily in Federal Class I air quality areas, but also in some instances, in other national parks, national forests, national wildlife refuges, wilderness areas, and national monuments. Federal Class I areas are defined in the Clean Air Act as national parks over 6,000 acres and wilderness areas and memorial parks over 5,000 acres, established as of 1977. All other FLM areas are designated Class II. Maps of the Agencies' Federal Class I areas are provided in Appendix E.

FLMs have an "affirmative responsibility" to protect AQRVs. In this respect, the FLM role consists of considering whether emissions from a new or modified source may have an adverse impact on AQRVs and providing comments to permitting authorities (States or EPA). FLMs have no permitting authority under the Clean Air Act, and they have no authority under the Clean Air Act to establish air quality-related rules or standards. It is important to emphasize that the FLAG report only explains factors and information the FLMs expect to use when carrying out their consultative role. It is separate from Federal regulatory programs.

FLAG members include representatives from the three primary agencies that administer the nation's Federal Class I areas: the U.S. Forest Service (USFS), the National Park Service (NPS), and the U.S. Fish and Wildlife Service (FWS). (Subsequently in this report, these three agencies collectively will be referred to as "the Agencies" or the "FLMs." Class I and Class II air quality areas are called "FLM areas" in this report.) Appendix F contains a list of participants that worked on the original FLAG 2000 report.

This report describes the work accomplished in Phase I of the FLAG effort as revised to reflect current developments. That work includes identifying policies and processes common to the FLMs (herein called "commonalities") and developing new policies and processes using readily available information. This report provides State permitting authorities and potential permit applicants a consistent and predictable process for assessing the impacts of new and existing sources on AQRVs, including a process to identify those AQRVs and potential adverse impacts. The report also discusses considerations unrelated to new source review and managing emissions in Federal areas. If and when the Agencies embark on Phase II, FLAG will address unresolved issues including those that will require research and the collection of new data.

Marble Mountain Wilderness, California.
Credit: Steve Boutcher

This revised *FLAG Phase I Report* consolidates the results of the FLAG Visibility, Ozone, and Deposition subgroups. The chapters prepared by these subgroups contain issue-specific technical and policy analyses, recommendations for evaluating AQRVs, and information for completing and evaluating NSR permit applications. This information and the associated recommendations are intended for use by the FLMs, permitting authorities, NSR permit applicants, and other interested parties. The report includes background information on the roles and responsibilities of the FLMs under the NSR program.

This document includes recommendations for completing and evaluating NSR applications that may affect Class I FLM areas. This information can also be used to evaluate impacts on Class II parks and wilderness areas. It does not provide a universal formula that would, in all situations, allow one to determine whether or not a source of air pollution causes or contributes to an adverse impact. That determination remains a project-specific management decision, the responsibility for which remains with the FLM, as delegated by Congress. The FLM's assessment of whether or not an adverse impact would occur is based on the sensitivity of the AQRVs at the particular FLM area under consideration, as well as the consideration of several other factors, including the magnitude, frequency, duration, timing, and geographic extent of the new source's impacts.

To provide information for the FLM's assessment of adverse impacts on AQRVs, the permit applicant should identify the potential impacts of the source on all applicable AQRVs of that area. An FLM may ask that an applicant address any or all of the areas of concern. The primary areas of concern to the FLMs with respect to air pollution emissions are

visibility impairment, ozone effects on vegetation, and effects of pollutant deposition on soils and surface waters.

The *FLAG Phase I Report* also describes the FLAG effort, including the FLAG approach, organization, and plans for future FLAG work. Appendix A of the report contains a glossary of technical terms, abbreviations, and acronyms used in the report along with associated definitions. Appendix G provides a list of all references cited in the FLAG report.

The key recommendations developed by the Visibility, Ozone, and Deposition subgroups are summarized below, and updated in part in this FLAG 2010 revision. However, for all three subject matter areas, FLAG recommends that the permit applicant consult with the appropriate permitting authority and with the FLM for the affected area(s) for confirmation of preferred procedures. This consultation should take place in the early stages of the permit application process.

Recommendations for Evaluating Visibility Impacts (Revised)

FLAG provides recommendations, specific procedures, and interpretation of results for assessing visibility impacts of new or modified sources on Class I area resources.[2]

FLAG addresses assessments for sources proposed for locations near (generally within 50 km) and at large distances (greater than 50 km) from these areas. The key components of the recommendations are highlighted below.

In general, FLAG recommends that an applicant:

- Apply the Q/D test (see "INITIAL SCREENING TEST" below) for proposed sources greater than 50 km from a Class I area to determine whether or not any further visibility analysis is necessary.
- Consult with the appropriate regulatory agency and with the FLM for the affected Class I area(s) or other affected area for confirmation of preferred visibility analysis procedures.
- Obtain FLM recommendation for the specified reference levels (estimate of natural conditions) and, if applicable, FLM recommended plume/observer geometries and model receptor locations.
- Apply the applicable EPA Guideline, steady-state models for regions within the Class I area that are affected by plumes or layers that are viewed against a background (generally within 50 km of the source).
  - Calculate hourly estimates of changes in visibility, as characterized by the change in the color difference index (ΔE) and plume contrast (C), with respect to natural conditions, and compare these estimates with the thresholds given in section 3.3.3.
- For regions of the Class I area where visibility impairment from the source would cause a general alteration of the appearance of the scene (generally 50 km or more away from the source or from the interaction of the emissions from multiple sources), apply a non-steady-state air quality model with chemical transformation capabilities (refer to EPA's *Guideline on Air Quality Models*), which yields ambient concentrations of visibility-impairing pollutants. At each Class I receptor:
  - Calculate the change in extinction due to the source being analyzed, compare these changes with the reference conditions, and then compare these results with the thresholds given in section 3.3.3.
  - Utilize estimates of annual average natural visibility conditions for each Class I area as presented in Table 6, unless otherwise recommended by the FLM or permitting authority. Alternative estimates of visibility conditions are provided in Table 5 for consistency with State agencies that elected to use 20% best visibility for regional haze or BART implementations, or when FLMs recommend using the 20% best visibility as natural background.
- If first-level modeling results are above levels of concern, continue to consult with the Agencies to discuss other considerations (e.g., possible impact mitigation, more refined analyses).

This review process for distant/multi-source applications is portrayed schematically in Figure 1.

Recommendations for Evaluating Ozone Impacts (Revised)

- FLM actions or specific requests on a permit application will be based on the existing air pollution situation at the area they manage. These conditions include (1) whether or not actual ozone damage has occurred in the area, and (2) whether or not ozone exposure levels occurring in the area are high enough to cause damage to vegetation (i.e., phytotoxic O_3 exposures). Figure 2 shows the FLM review process to assess ozone impacts for a project that exceeds the initial annual emissions over distance (Q/D) screening criteria. As noted in Figure 2, ambient ozone concentrations are considered along with data from exposure response studies (EPA 2007a) to determine whether a source will cause or contribute to phytotoxic

2. Nevertheless, the FLMs are also concerned about resources in Class II parks and wilderness areas because they have other mandates to protect those areas as well. The information and procedures outlined in this document are generally applicable to evaluating the effect of new or modified sources on the AQRVs in both Class I and Class II areas, including the evaluation of effects as part of Environmental Assessments and/or Environmental Impact Statements under the National Environmental Policy Act (NEPA). However, FLAG does not preclude more refined or regional analyses being performed under NEPA or other programs.

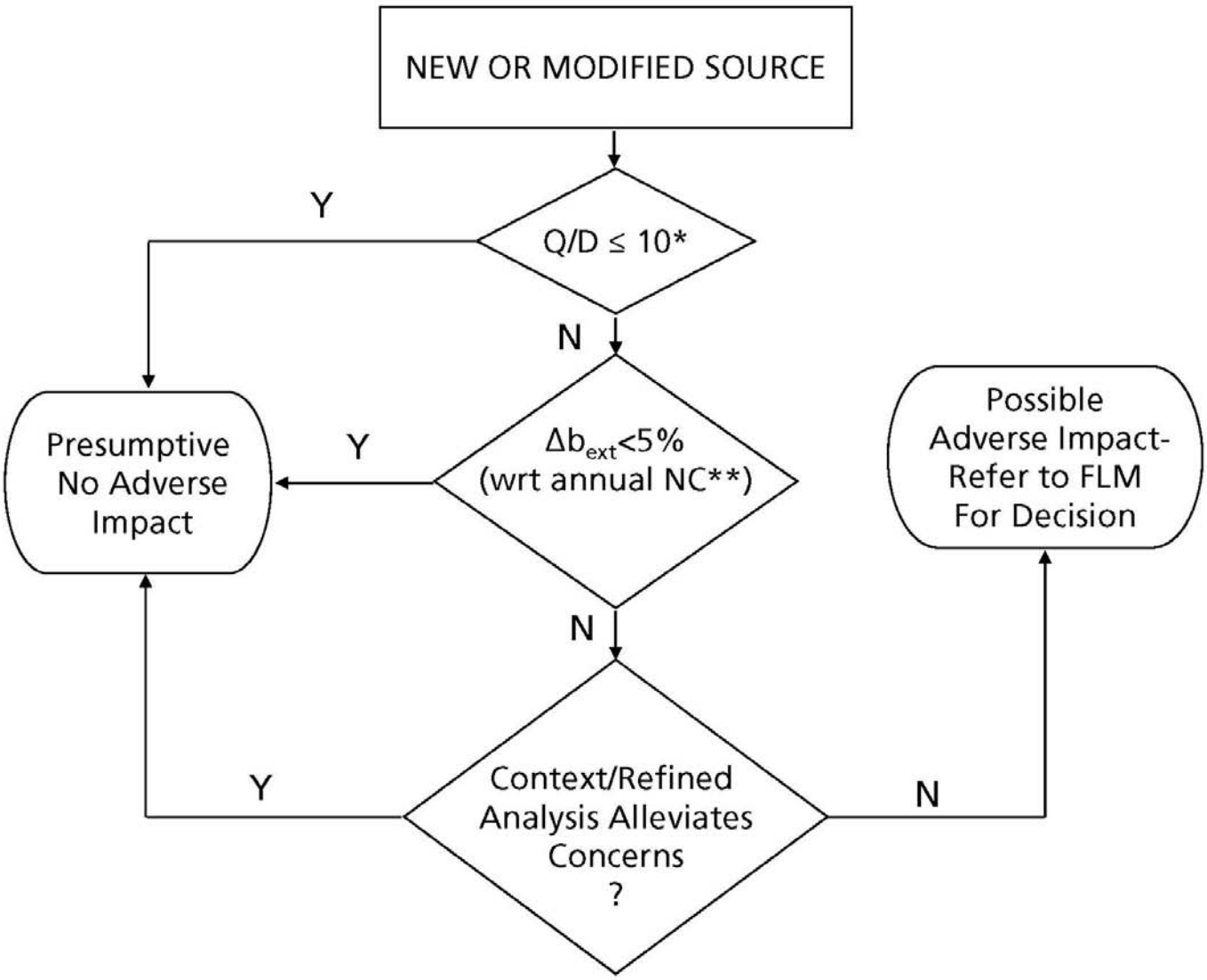

Figure 1. Procedure for Visibility Assessment for Distant/Multi-Source Applications (Revised)
*Q/D test only applies to sources located greater that 50 km from a Class I area.
**Difference Change in the 98th percentile with respect to (wrt) the annual average Natural Condition (NC). Applicant should use the 20th percentile best natural condition background if recommended by the FLM or permitting authority.

ozone levels (i.e., levels toxic to plants) at the affected site. The FLM may ask the applicant to calculate the ozone exposure values if these data are not already available. Ozone damage to vegetation is determined from field observations at the impacted site.

- Oxidant stipple necrosis on plant foliage and ozone-induced senescence infer adverse physiological or ecological effects, and are considered to be damage if they are determined to have a negative impact on aesthetic value.
- Established ozone metrics to describe ozone exposure are referenced.
- NO_x and VOC emissions are of concern because they are precursors of ozone. Current information indicates most FLM areas are NO_x limited. Until we determine the VOC or NO_x status of each area, we will focus on NO_x emission sources.

Recommendations for Evaluating Deposition Impacts (Revised)

For a project that exceeds the initial annual emissions over distance (Q/D) screening criteria, the permit applicant should consult with the appropriate regulatory agency and FLM for the affected area(s) to determine if a deposition impact analysis should be done (i.e., expected sulfur and/

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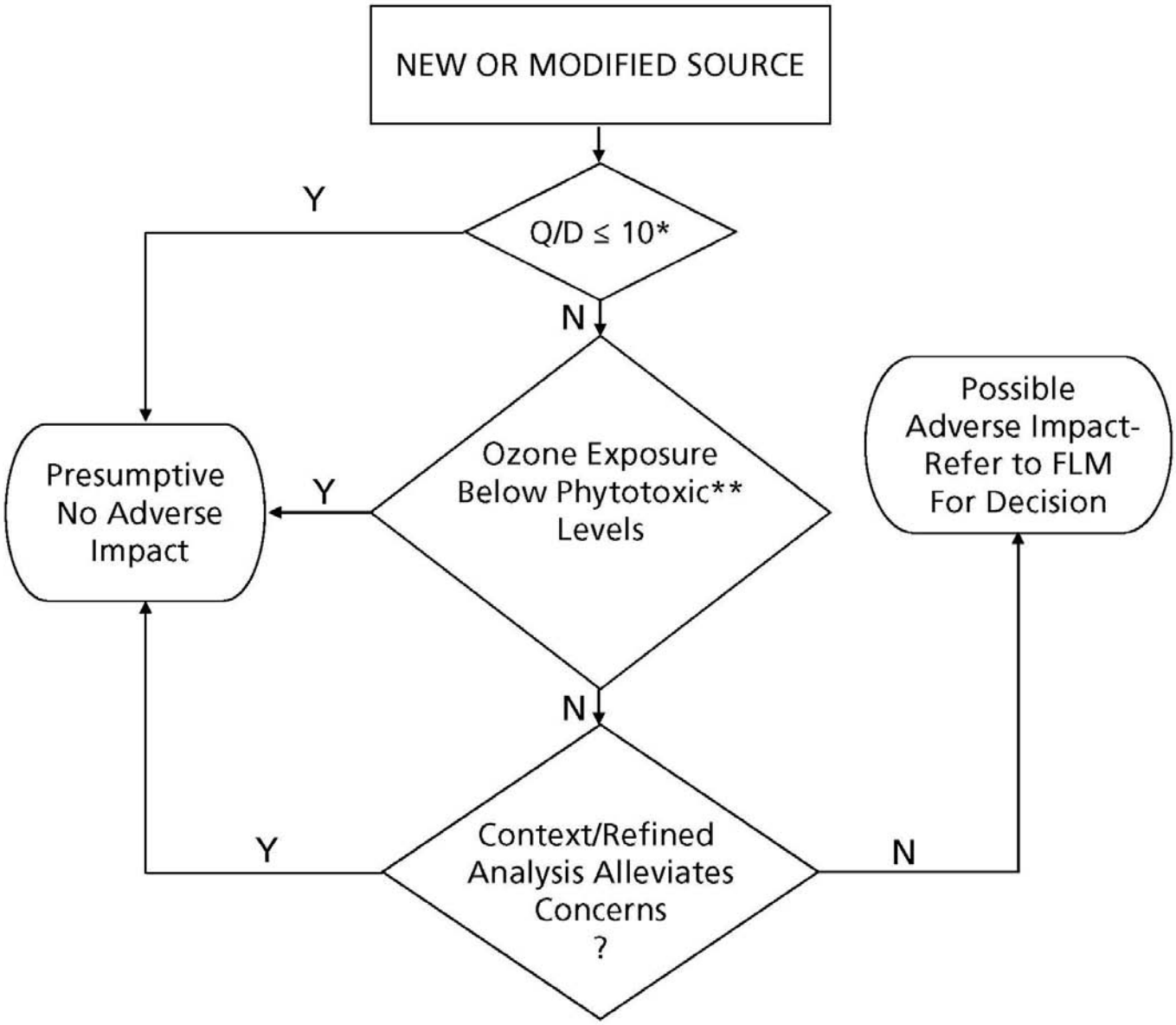

Figure 2. FLM Assessment of Potential Ozone Effects from New Emissions Source (Revised)
*Q/D test only applies to sources located greater that 50 km from a Class I area.
**Note: Ambient ozone concentrations are considered along with data from exposure response studies (EPA 2007b) to determine whether a source will cause or contribute to phytotoxic ozone levels (i.e., levels toxic to plants) at the affected site.

or nitrogen deposition impacts are above the Deposition Analysis Threshold (DAT) or concern threshold (see section 3.5.6). Please note that although mercury and other toxic emissions are of interest to the FLM, the deposition impact analyses discussed here applies only to nitrogen and sulfur emissions. If an analysis is advised, the permit applicant should obtain available information on Class I AQRVs, critical loads, and concern thresholds from the FLM. In addition, the applicant should refer to section 3.5.6 'Recommendations for Evaluating Potential Effects from Proposed Increases in Deposition to an FLM Area' section of the Deposition Chapter. The following steps summarize that process.

- From the respective Agency web sites, identify available on-site or representative wet and dry deposition data for the FLM area.
- Estimate the future deposition rate by adding the existing rate, the new emissions' contribution to deposition, and the contribution of sources permitted but not yet operating, while subtracting emission reductions that will occur before the proposed source begins operation. Modeling of new, reduced, and permitted but not yet operating emissions' contribution to deposition should be conducted following EPA recommendations.
- Compare the future deposition rate with the recommended screening criteria (e.g., critical load,

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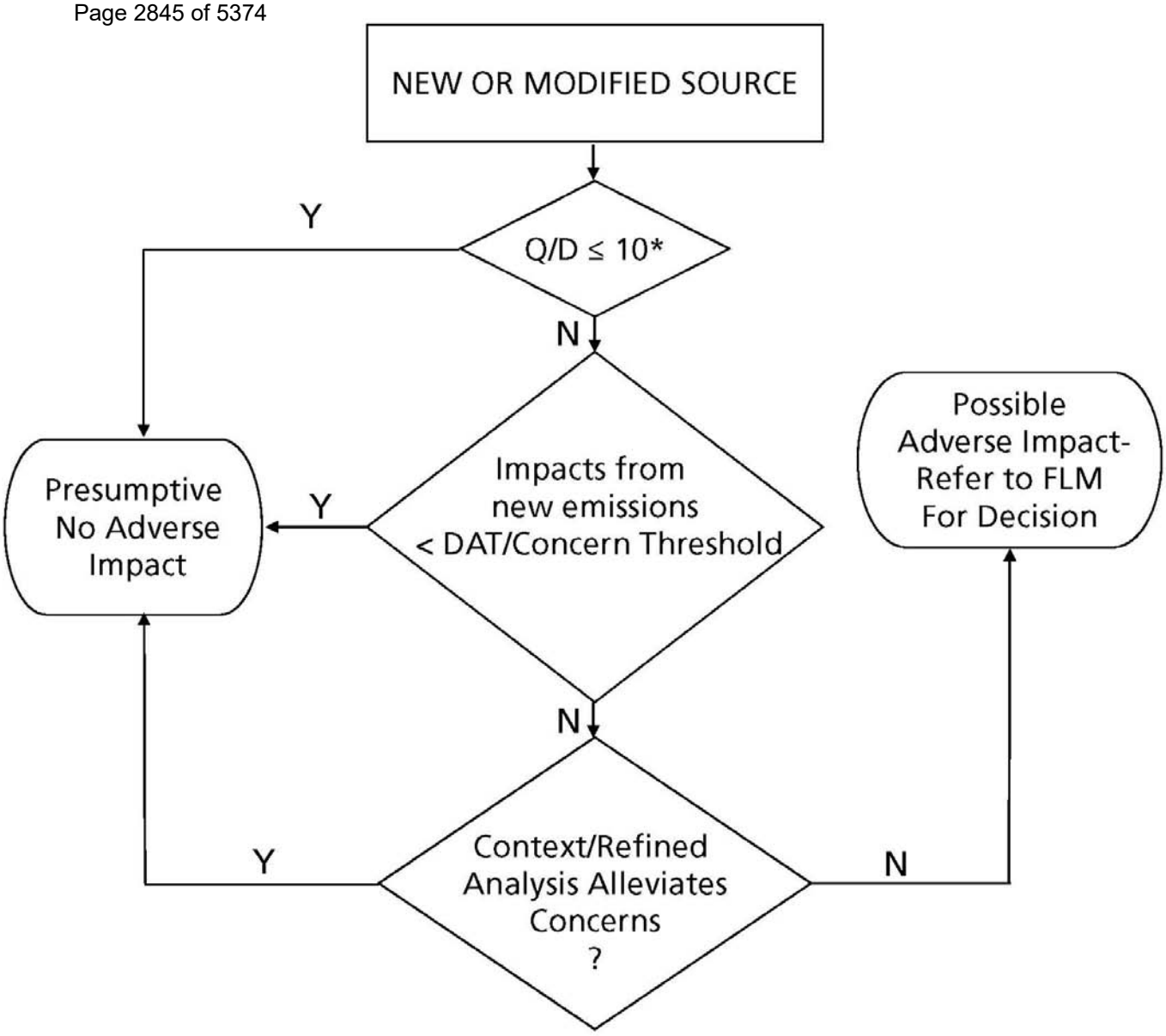

Figure 3. FLM Assessment of Potential Deposition Effects from New Emissions Sources (Revised)
*Q/D test only applies to sources located greater that 50 km from a Class I area.

concern threshold, or screening level value) for the affected FLM area. A list of documents summarizing these screening criteria, where available, can be found in Appendix G.

- Information for USFS Class I areas is also available at: http://www.fs.fed.us/air
- NPS and FWS Class I area information is available at: http://www.nature.nps.gov/air

- Figure 3 shows the FLM review process to assess deposition impacts from new emission sources.

1. Background

1.1. History (Revised)

The Clean Air Act Amendments of 1977 give Federal Land Managers (FLMs) an "affirmative responsibility" to protect the natural and cultural resources of Class I areas from the adverse impacts of air pollution (see Appendix B: 'Legal Framework for Managing Air Quality and Air Quality Effects on Federal Lands'). FLM responsibilities include the review of air quality permit applications from proposed new or modified major pollution sources near these Class I areas. If, in its permit review, an FLM demonstrates that emissions from a proposed source will cause or contribute to adverse impacts on the air quality related values (AQRVs) of a Class I area, the permitting authority, typically the State, can deny the permit.

The FLMs' role in the reviewing of permit applications focuses on impacts to Class I areas.[3] Individually, FLMs have developed different approaches to identifying AQRVs and defining adverse impacts on AQRVs in Class I areas. For example, in 1988, the U.S. Department of Agriculture Forest Service (USFS) conducted a national screening process to identify the AQRVs for each of its Class I areas. Using this national process as a starting point, each USFS Region refined the screening parameters and identified sensitive AQRVs for many Class I areas. However, this resulted in differences in the approaches and levels used by USFS Regions. The U.S. Department of the Interior National Park Service (NPS) and the U.S. Fish and Wildlife Service (FWS) have adopted a case-by-case approach to permit review, considering the most recent information available for each area. NPS and FWS have included lists of sensitive AQRVs for their Class I areas in their Air Resources Information System (ARIS) database.

1.1.1. FLAG Approach (Revised)

Air resource managers from the USFS, NPS, and FWS recognized the need for a more consistent approach among their agencies with respect to their efforts to protect AQRVs. In April 1997, an interagency Work Group was formed whose objective was "to achieve greater consistency in the procedures each agency uses in identifying and evaluating AQRVs." The Work Group named itself the

UL Bend National Wildlife Refuge, Montana.
Credit: Maribeth Oaks/The Wilderness Society

Federal Land Managers' Air Quality Related Values Work Group, or FLAG. Although FLAG membership comprises air resource managers and subject matter experts from the three agencies, representatives from the Bureau of Land Management, the U.S. Environmental Protection Agency (EPA), U.S. Geological Survey, and State air agencies have also participated in FLAG efforts.

FLAG participants have collaborated to:

- define sensitive AQRVs,
- identify the critical loads (or pollutant levels) that would protect an area and identify the criteria that define adverse impacts, and
- standardize the methods and procedures for conducting AQRV analyses.

To accomplish its objective, FLAG started with (and will continue to build on) the procedures, terms, definitions, and screening levels common to the three agencies. Many such "commonalities" were identified early in the FLAG planning sessions (see section 1.4, 'Commonalities Among Federal Land Managers').

FLAG's "Action Plan" stipulates a phased approach. Phase I addressed issues that could be resolved without research or the collection of new data. When the Agencies embark on FLAG Phase II, they will address the more complex and unresolved issues from Phase I that may require additional data collection (see section 5, 'Future FLAG Work').

The FLAG effort focuses on the effects of the air pollutants that could affect the health of resources in Class I areas, primarily pollutants such as ozone, particulate matter, nitrogen dioxide, sulfur dioxide, nitrates, and sulfates. In Phase I, FLAG concentrated on four issues: (1) terrestrial effects of ozone; (2) aquatic and terrestrial effects of wet and dry pollutant deposition; (3) visibility impairment; and (4) process and policy issues. Four subgroups, one for each of

3. Nevertheless, the FLMs are also concerned about resources in Class II parks and wilderness areas because they have other mandates to protect those areas as well. The information and procedures outlined in this document are generally applicable to evaluating the effect of new or modified sources on the AQRVs in both Class I and Class II areas, including the evaluation of effects as part of Environmental Assessments and/or Environmental Impact Statements under the National Environmental Policy Act (NEPA). However, FLAG does not preclude more refined or regional analyses being performed under NEPA or other programs.

these issues, were formed and charged with developing a set of recommendations for consistent policies and processes.

FLAG 2000's findings and technical recommendations underwent scientific peer review, as well as review by agency decision-makers such as Class I area Park Superintendents, Refuge Managers, and Forest Supervisors; Regional Foresters; and the Assistant Secretary for Fish and Wildlife and Parks. (Note: USFS has designated the FLM as the Regional Foresters and, in some cases, Forest Supervisors.) FLAG products have also undergone public review and comment. A "notice of availability" of the draft FLAG 2000 report was published in the *Federal Register*, and the FLMs conducted a public meeting to discuss the draft FLAG report and provided a 90 day public comment period. For the FLAG 2010 revisions, the FLMs announced the availability of the draft report in the *Federal Register* and provided a 60 day public comment period. There was not sufficient public interest to conduct a public meeting to discuss the proposed revisions to the FLAG report.

1.1.2. FLAG Organization

In addition to the four subgroups (policy, deposition, ozone, and visibility), the FLAG organization included Leadership and Coordinating Committees and a Project Manager. The Leadership Committee, which includes the air quality program chiefs from the three FLM agencies, was responsible for providing direction to the Work Group and the resources necessary for FLAG to accomplish its objective. The Coordinating Committee, which also includes representatives from each agency, was responsible for communications within the Work Group, including coordination among the agencies and subgroups. The FLAG Project Manager coordinated FLAG activities, served as a single point-of-contact for the subgroups, and performed other administrative functions.

1.2. Overview of Resource Issues (Revised)

Research conducted on Federal lands by FLMs and others has characterized natural resource effects associated with air pollution, and has helped identify those particular resources that are vulnerable to pollution in different areas. This effort does not address the impacts from air pollution on cultural resources. Documented effects include impairment of visibility, injury and reduced growth of vegetation, and acidification and fertilization of soils and surface waters. Air pollution effects on resources have been identified in a number of FLM areas; a few examples are provided below. It is important to note that similar, or even more serious, air pollution effects may be occurring on all Federal lands, but FLMs have not had the financial resources to perform the inventorying, monitoring, and/or research necessary to document such effects. Furthermore, the sensitivity of resources may vary from area to area because the nature of the resource, as well as geological, meteorological, biological, and other factors, vary from place to place.

1.2.1. Visibility

Visitors to national parks and wildernesses list the ability to view unobscured scenic vistas as a significant part of a satisfying experience. Unfortunately, visibility impairment has been documented in all Class I areas with visibility monitoring. Most visibility impairment is in the form of regional haze. The greatest visibility impairment due to regional haze occurs in the eastern United States and in southern California, while the least impairment occurs in the Colorado Plateau and Nevada Great Basin areas, and in Alaska. Ammonium sulfate contributes at least 50% to visibility impairment at most Class I areas in the eastern United States. The contribution to visibility impairment from ammonium nitrate is highest in central and southern California and in the Midwest. The largest region of high rural organic carbon visibility impairment is in the southeastern United States; impairment in this range is also present in the Sierra Nevada region of California and in the northern Rockies of Montana. The highest contribution to visibility impairment from fine soil is found in the arid Southwest. The highest coarse particle contribution to impairment is also in the arid Southwest and southern California. (DeBell et al. 2006) Visibility impairment on Federal lands can also result from plume intrusion and has been documented in Mount Zirkel Wilderness, Moosehorn National Wildlife Refuge, and Grand Canyon National Park.

1.2.2. Vegetation

While several components of air pollution (e.g., sulfur dioxide, nitrogen dioxide, and peroxyacyl nitrates) can affect vegetation, ozone is generally acknowledged as the air pollutant causing the greatest amount of injury and damage to vegetation. The most common visible effects are stipple (dark colored lesions on leaves resulting from pigmentation of injured cells), fleck (collapse of a few cells in isolated areas of the upper layers of the leaf, resulting in tiny light-colored lesions), mottle (degeneration of the chlorophyll in certain areas of the leaf giving the leaf a blotchy appearance), necrosis (death of tissue), and in extreme cases, mortality. Aside from visible injury, ozone exposure can result in less obvious physiological impairment such as decreased growth or altered carbon allocation.

Ozone fumigation experiments have identified a number of plant species that are sensitive to ozone. For example, fumigations were conducted in Great Smoky Mountains National Park (Tennessee and North Carolina) from 1987 to 1992. On the basis of foliar injury, thirty species were rated as sensitive to ozone levels that occurred in the park. The species with foliar injury included black cherry (*Prunus serotina*) and American sycamore (*Platanus occidentalis*). Additional observations and physiological measurements

indicated elevated ozone concentrations reduced leaf, root, and total dry weights, and increased the severity of leaf stipple and premature leaf abscission in these two species (Neufeld and Renfro 1993a,b). Field observations have documented foliar injury of these species in other eastern United States areas such as Brigantine Wilderness (New Jersey) and Cape Romain Wilderness (South Carolina).

Ponderosa pine (*Pinus ponderosa*) and Jeffrey pine (*Pinus jeffreyi*) are recognized as good candidates for ozone-injury surveys in the western United States, based on their documented sensitivity. For example, these species were examined for ozone injury in national parks and national forests in the California Sierra Nevada from 1991 to 1995. The sites surveyed included Lassen Volcanic, Yosemite, and Sequoia/Kings Canyon National Parks and the Tahoe, Eldorado, Stanislaus, Sierra, and Sequoia National Forests. Foliar injury attributable to ozone was found at all areas, and the extent of injury generally increased in a southward direction along the Sierra Nevada (Miller 1995).

1.2.3. Soils and Surface Waters

Acidity in rain, snow, cloud water, and dry deposition can affect soil fertility and nutrient cycling processes in watersheds and can result in acidification of lakes and streams with low buffering capacity. Deposition of sulfate to sensitive watersheds results in leaching of base cations, soil acidification, and surface-water acidification. In some soils, sulfate adsorption results in "delayed" acidification of surface waters. Deposition of excess nitrogen species (nitrate and ammonium) to both terrestrial and aquatic systems can result in acidifying streams, lakes, and soils. There is also evidence that nitrogen deposition can cause shifts in phytoplankton composition in lakes in which biological activity is limited by nitrogen availability, i.e., increased nitrogen deposition can cause phytoplankton species that use nitrogen more efficiently to eventually dominate the lake.

Water chemistry surveys and on-going monitoring show that many high elevation lakes on Federal lands in the Sierra Nevada, Cascades, and Rocky Mountains are sensitive to acid deposition. In general, these lakes are on bedrock that provides them with very little buffering capacity. Some of these lakes, for example, Loch Vale in Rocky Mountain National Park (Colorado) experience episodic acidification during Spring snow melt (Baron and Campbell 1997).

Through funding provided by the Southern Appalachian Mountains Initiative, Herlihy et al. (1996) compiled information on surface water sensitivity of streams in nine of the eleven Class I areas in the Southern Appalachians. The nine Class I areas were grouped according to geology, physiography, and stream chemistry, then the groupings were ranked in terms of effects. Class I areas in the West Virginia Plateau (Otter Creek and Dolly Sods Wildernesses) had the highest percentage of acidic stream length and lowest pH values. Class I areas in the Northern and Southern Blue Ridge (e.g., Shenandoah National Park in Virginia and Joyce Kilmer/Slickrock Wilderness in North Carolina) had a lower percentage of acidic stream length, however, streams with low buffering capacity were common. The Alabama Plateau Class I area (Sipsey Wilderness) had streams with the highest buffering capacity. (Note that the authors based their report on surveys conducted by others and did not account for potential differences in methods of data collection.)

A number of Federal areas contain estuarine and coastal areas that may experience eutrophication as a result of excess nitrogen deposition resulting from air pollution and other sources of nitrogen. For example, symptoms of eutrophication, including nutrient enrichment and algal blooms, have been observed in Everglades National Park and Chassahowitzka Wilderness (Florida).

1.3. Legal Responsibilities (Revised)

The specific legal responsibilities that Congress has given FLMs to protect natural, cultural, and scenic resources on the public lands from air pollution are identified in Appendix B. Statutes described in Appendix B include agency organic acts, the Wilderness Act, and the Clean Air Act (CAA).

The fundamental Congressional direction for managing public lands arises out of respective organic acts. Each of these laws is essentially a charter from Congress to the Executive Branch providing a purpose for parks, wildernesses, and refuges, respectively, and establishing broad management objectives for these areas. The Wilderness Act sets aside a subset of these public lands where natural processes are allowed to dominate. The agency stewards develop specific management objectives building on the organic acts using public involvement, regulations, best available science, and additional direction provided by Congress.

Among this additional Congressional direction is the Clean Air Act (CAA). It further characterizes some of the public lands as "Class I" areas and bestows on the land managers an affirmative responsibility to protect these areas from air pollution. The CAA directs that the FLMs identify and protect air quality related values, including visibility. This direction is consistent with the underlying charters provided by the organic acts and the Wilderness Act. The similarities of management objectives, and of the policies and procedures necessary for protecting Class I areas, are at the core of the FLAG process. Please note that although all wilderness is not Class I, and the FLMs have not proposed that non-Class I wilderness be classified as Class I, management actions (e.g., limiting human activities) that satisfy wilderness management objectives for Class II areas, are often substantially the same as those used in Class I area management.

In implementing laws, it is essential to understand the intent of Congress. In the case of the CAA, the FLM gleans additional insight from a passage in Senate Report No. 95-127, 95th Congress, 1st Session, 1977 which states:

> The Federal Land Manager holds a powerful tool. He is required to protect Federal lands from deterioration of an established value, even when Class I [increments] are not exceeded. . . . While the general scope of the Federal Government's activities in preventing significant deterioration has been carefully limited, the FLM should assume an aggressive role in protecting the air quality values of land areas under their jurisdiction. In cases of doubt the land manager should err on the side of protecting the air quality-related values for future generations.

Although the FLMs have an "affirmative responsibility" to protect AQRVs, they have no permitting authority under the CAA, and they have no authority under the CAA to establish air quality-related rules or standards. The FLM role within the regulatory context consists of considering whether emissions from a new source, or emission increases from a modified source, may have an adverse impact on AQRVs and providing comments to permitting authorities (States or EPA). It is important to emphasize that the FLAG report only explains factors and information the FLMs expect to use when carrying out their consultative role. It is not a rule or standard.

The FLAG report describes the steps and process that the FLMs intend to go through in order to perform their statutory duties. Consequently, the scope of the FLAG report is to provide a more consistent approach for the three FLM agencies to evaluate air pollution effects on resources, and to provide guidance to permitting authorities and permit applicants regarding necessary AQRV analyses. Although FLAG strives to be consistent with regulatory programs and initiatives such as the Regional Haze Rule and New Source Review Reform, no direct ties exist between FLAG and these regulatory requirements.

1.4. Commonalities Among Federal Land Managers

If a new source is proposed near two or more areas managed by different FLMs, the FLMs generally try to coordinate in their interactions with the permitting authority and with the applicant. For example, two or more FLMs involved in pre-application meetings typically try to minimize the workload for the applicant by reaching agreement on the types of analyses the application should contain. Beyond coordinating during permit review, FLMs currently base requests and decisions on similar principles regarding resource protection and FLM responsibilities. Listed below are the common principles in five areas of air resource management. In addition, Appendix C provides the FLM's 'General Policy for Managing Air Quality Related Values in Class I Areas.'

1.4.1. Identifying AQRVs (Revised)

FLMs agree on the following definition of an AQRV:

> A resource, as identified by the FLM for one or more Federal areas that may be adversely affected by a change in air quality. The resource may include visibility or a specific scenic, cultural, physical, biological, ecological, or recreational resource identified by the FLM for a particular area.

This definition is compatible with the general definition of AQRV that appears in the *Federal Register* (45 FR 43003, June 25, 1980). That definition includes visibility, flora, fauna, odor, water, soils, geologic features, and cultural resources. FLMs have the responsibility to identify specific AQRVs of areas they manage. To this end, FLMs further refine AQRVs beyond the above definition to be more site-specific (i.e., area specific) by using on-site information. To the extent possible, the FLMs have identified specific AQRVs for many Class I areas. Site-specific AQRV lists are available on the respective Agency web sites, or by contacting the Agencies directly. The FLMs also recognize that, ideally, inventories should be developed for all Class I areas. The FLMs may identify additional AQRVs in the future as more is learned through science about the sensitivity of resources to air pollution. A public process involving the regulated community and other interested members of the public is necessary and will be accomplished through participation in the land management planning process or reply to an announcement in the *Federal Register*. Finally, FLMs agree on the need for continued inventory, research, and monitoring to improve their ability to determine which AQRVs are most sensitive to air pollution and the sensitivity of these AQRVs.

1.4.2. Determining the Levels of Pollution that Trigger Concern for the Well-Being of AQRVs (Revised)

FLMs acknowledge the importance of being able to agree among themselves on the levels of pollution that trigger concerns for AQRVs. FLMs recognize the need to assess cumulative impacts and the difficulties associated with this process. Difficulties arise when a large number of minor source impacts eventually lead to an unacceptable cumulative impact or when a new source applies for a PSD permit in an area that has a high background concentration of pollution from existing sources. The agencies will evaluate a proposed new source within the context of the total impacts that are occurring or that potentially could occur from permitted/existing sources on the AQRVs of the area and should consider the effects of both emission increases and decreases.

1.4.3. Visibility

FLMs use EPA-approved models [Appendix W of Part 51 (EPA's *Guideline on Air Quality Models*, revised November 2005), as required under the PSD regulations at 40 CFR 51.166(1) and 52.21(1)] and the recommendations of the Interagency Work Group on Air Quality Modeling (IWAQM) to evaluate visibility impacts. The models use thresholds of visibility degradation measured in light extinction to evaluate source impacts to haze (far-field/multi-source impacts), and EPA established criteria for coherent plume impacts (near-field impacts). Currently all FLMs use Interagency Monitoring of Protected Visual Environments (IMPROVE) monitoring data to determine current conditions for visibility in FLM areas.

1.4.4. Biological and Physical Effects

All FLMs rely on research, monitoring, models, and effects experts to identify and understand physical, biological, and chemical changes resulting from air pollution and relating them to changes in AQRVs. Further, they focus on sensitive AQRVs (defined as either species or processes) to assess this biological/physical/chemical change.

1.4.5. Determining Pollution Levels of Concern (Revised)

FLMs rely on the best scientific information available in the published literature and best available data to make informed decisions regarding levels of pollution likely to cause adverse impacts. FLMs re-evaluate, update, and assess this information as appropriate. They consider specific Agency and Class I area legislative mandates in their decisions and, in cases of doubt, "err on the side of protecting the AQRVs for future generations." (Senate Report No. 95-127, 95th Congress, 1st Session, 1977)

For air quality dispersion modeling analyses, FLMs follow Appendix W of Part 51 (EPA's *Guideline on Air Quality Models*, revised November 2005), as required under the PSD regulations at 40 CFR 51.166(1) and 52.21(1), and the recommendations of the Interagency Work Group on Air Quality Modeling (IWAQM). FLMs recommend protocols for modeling analyses to permit applicants on a case-by-case basis considering types and amount of emissions, location of source, and meteorology. When reviewing modeling and impact analysis results, all FLMs consider frequency, magnitude, duration, location of impacts, and other factors, in determining whether impacts are adverse.

1.4.6. FLM Databases (Revised)

Air Resources Information System (ARIS) (Formerly Air Synthesis) (Revised)

ARIS provides information on air quality related values in NPS and FWS Class I areas, as well as in many NPS Class II areas. ARIS identifies specific AQRVs, and provides information on air quality and its effects in parks and wildernesses.

Natural Resource Information System – Air Module (NRIS-AIR) (Revised)

Publicly available USDA Forest Service Class I and II area information and related resource data can be linked to or found at http://www.fs.fed.us/air. If desired information and data cannot be found, contact any air program manager or specialist at national or regional offices for assistance.

1.5. Regulatory Developments Since FLAG 2000 (New)

Several regulatory developments have occurred since the FLMs published the FLAG report in December 2000. Some of these regulatory developments may have a significant effect on air resource management in mandatory Class I areas, or how these effects are assessed. First, on April 15, 2003, the Environmental Protection Agency (EPA) promulgated revisions to Appendix W of 40 C.F.R. §51 (*Guideline on Air Quality Models*). EPA revised the Guideline to adopt the CALPUFF model as a preferred long-range transport model for inclusion in Appendix A of that document. Prior to that date, FLAG 2000 relied on CALPUFF as the suggested model of choice for long-range transport assessments in accordance with recommendations of the Interagency Work Group on Air Quality Models (IWAQM). EPA's adoption of CALPUFF substantiates the Agencies' model choice. In addition, EPA's action, combined with improved computer technology, has resulted in the availability of more meteorological data. These improvements have enhanced the ability of permitting authorities and applicants to perform the types of modeling analyses suggested in FLAG. However, the FLMs will continue to work with the EPA on recommendations for future long-range transport model development.

On May 12, 2005, the EPA published the Clean Air Interstate Rule (CAIR) to reduce interstate transport of fine particulate matter and ozone. The CAIR applied to 28 eastern states and the District of Columbia, and required those areas to significantly reduce emissions of sulfur dioxide (SO_2) and/or nitrogen oxides (NO_x) from utilities. Although EPA developed the CAIR to address violations of the National Ambient Air Quality Standards (NAAQS) for fine particulates ($PM_{2.5}$) and ozone, the associated SO_2 and NO_x emission reductions would also benefit visibility and other AQRVs at many eastern Class I areas. The Agencies supported the CAIR, however, because it did not apply to western states, the majority of the Class I areas would not have directly benefited from the rule. Please note that at the time of this writing CAIR has been remanded to the EPA for revision to address various court challenges, and EPA has proposed a new transport rule as a replacement (EPA 2010a).

On July 6, 2005, the EPA published a final rule and associated guidelines that detail the Best Available Retrofit Technology (BART) requirements of the Regional Haze Rule. Among other things, the BART guidelines advise States to rely on the CALPUFF model for long-range visibility impairment assessments, provide thresholds for what constitutes causing or contributing to regional haze visibility impairment, and includes screening level values that exempt certain sources from further analysis. As discussed in more detail below, the Agencies believe the assumptions and methodology included in the BART guidelines also have merit with respect to evaluating haze-like visibility impairment for New Source Review under the PSD and other programs. Consequently, the Agencies are paralleling some of those BART guidelines in this FLAG revision.

Please note that FLAG 2000 acknowledges the EPA's July 1999 Regional Haze Rule, and discusses possible changes to FLAG that may be necessary as States implement the Regional Haze Rule. Although the EPA promulgated the Regional Haze Rule before the FLMs published FLAG 2000, there were several improvements and differences in the associated EPA guidance documents (e.g., those related to Natural Conditions and Tracking Progress) that were not finalized until December 2003. Therefore, these documents were not reflected in FLAG 2000, but have been considered in this revision. Currently, State Implementation Plans (SIPs) under the Regional Haze Rule are being developed, and submitted to the EPA for approval. If the new visibility SIPs adequately account for new source growth, the Agencies may need to make further revisions to the FLAG recommendations to reflect progress made through the SIP process that could minimize the focus the FLMs place on individual sources.

EPA has also developed other regulations, standards, and policies that will help reduce air pollution and resulting impacts at FLM areas (e.g., revised ozone, sulfur dioxide, nitrogen dioxide, and particulate matter standards; mobile source controls).

2. Federal Land Managers' Approach to AQRV Protection

FLM responsibilities for resource protection on Federal lands are clear and there should be no misunderstanding regarding the tools the FLM uses to fulfill these responsibilities. Opportunities to influence decisions regarding pollution sources external to the park or wilderness are limited. However, FLMs strive to minimize emissions from internal sources and their effects. Approaches for minimizing air pollution from external and internal sources are discussed in detail below.

2.1. AQRV Protection and Identification (Revised)

Congress assigned the FLMs an affirmative responsibility to protect AQRVs in Federal Class I areas. The FLMs interpret this assignment as a responsibility to:

- Identify AQRVs in each of the Class I areas.
- Establish inventorying and monitoring protocols for AQRVs.
- Prioritize AQRV inventorying and monitoring.
- Specify a process for evaluating air pollution effects on AQRVs, including the use of sensitive indicators.
- Specify adverse effects for each AQRV.

To the extent possible, AQRVs have been identified for each Class I area. As noted above, the FLMs may identify additional AQRVs in the future as more is learned about the sensitivity of resources to air pollution. The FLMs will provide a public process involving the regulated community and other interested members of the public in order to seek public input regarding AQRV-identification issues. This desired public involvement will be accomplished through participation in the land management planning process or reply to an announcement in the *Federal Register*.

While the sensitivity of an AQRV to air pollution may be known, long-term monitoring of the health or status of the AQRV may not have been accomplished. The expense of monitoring all AQRVs simultaneously is prohibitive. Consequently, FLMs seek opportunities through the permitting process and through partnerships to gather more information about condition of AQRVs.

Because AQRVs themselves are often difficult to measure, surrogates are used as indicators, or sensitive indicators, of the health or status of the AQRV. A working process for Class I area management and AQRV protection is outlined ahead in this document.

An adverse impact is determined for each AQRV. An adverse impact from air pollution results in a diminishment of

Sipsey Wilderness, Alabama.
Credit: Steve Boutcher

the Class I area's national significance, that is, the reason the Class I area was created. Adverse impacts can also be an impairment of the structure or functioning of the ecosystem, as well as an impairment of the quality of the visitor experience. The FLMs make an adverse impact determination on a case-by-case basis, based on technical and other information, which is then conveyed to the permitting authority.[4] The permitting authority then considers this, along with other factors, in its determination regarding the permit application.

2.2. New Source Review (Revised)

Section 165 of the CAA spells out the roles and responsibilities for FLMs in New Source Review, including the Prevention of Significant Deterioration (PSD) permitting program. Other laws, such as the respective agency organic acts and the Wilderness Act, provide the fundamental underpinning of land management direction to land managers. The following discussion merges this complex labyrinth of legal responsibilities as it relates to air resource management.

2.2.1. Roles and Responsibilities of FLMs (Revised)

The federal officials directly responsible for the national parks, national wildlife refuges, and national forests (e.g., park superintendents, refuge managers, and forest supervisors, respectively) derive their responsibility from the respective agency organic acts. Furthermore, these officials, and the FLM for the respective agencies, have an affirmative responsibility under Section 165 of the CAA to protect and

4. As discussed elsewhere in this report, if a proposed source's impacts on AQRVs exceed established significance criteria, the FLMs will consider the magnitude, frequency, geographic extent, etc. of the impacts, and other relevant factors, in determining whether or not the impacts are adverse.

enhance the AQRVs of Class I areas from the adverse effects of air pollution. The FLM for the USFS is the Regional Forester or the Forest Supervisor depending on the specific location. The FLM for the NPS and FWS is the Department of the Interior's Assistant Secretary for Fish and Wildlife and Parks.

The FLMs have visibility protection responsibility under 40 CFR §51.307 (New source review), which spells out the requirements for State Implementation Plan (SIP) visibility protection programs, as well as 40 CFR §52.27 (Protection of visibility from sources in attainment areas) and 40 CFR §52.28 (Protection of visibility from sources in non-attainment areas). These three provisions, taken together along with the SIP-approved rules, establish the visibility protection program for new and modified sources throughout the country.

Notification

Section 165 (42 USC 7475) of the CAA requires the EPA, or the State/local permitting authority, to notify the FLM if emissions from a proposed project may impact a Class I area. The permitting authority should forward PSD applications to the FLM for review and analysis as soon as possible after receipt, giving the FLM an opportunity to review the application concurrently with the permitting authority.

Generally, the permitting authority should notify the FLM of all new or modified major facilities proposing to locate within 100 km (62 miles) of a Class I area. In addition, the permitting authority should notify the FLM of "very large sources" with the potential to affect Class I areas proposing to locate at distances greater than 100 km. (Reference March 19, 1979, memorandum from EPA Assistant Administrator for Air, Noise, and Radiation to Regional Administrators, Regions I - X). Given the multitude of possible size/distance combinations, the FLMs can not precisely define in advance what constitutes a "very large source" located more than 100 km away that may impact a particular Class I area. However, as discussed elsewhere in this report, the Agencies have adopted a size (Q)/distance (D) criteria to screen out from AQRV review those sources with relatively small amounts of emissions located a large distance from a Class I area. Consequently, as a minimum, the permitting authority should notify the FLM of all sources that exceed this Q/D criteria. Nevertheless, the FLM and permitting authority should still work together to determine which other PSD applications the FLM is to be made aware of in excess of 100 km. In making this determination, the FLM and permitting authority should consider, on a case-by-case basis, such factors as:

- Current conditions of sensitive AQRVs;
- Magnitude of emissions;
- Distance from the Class I area;
- Potential for source growth in an area/region;
- Existing/prevailing meteorological conditions;
- Cumulative effects of several sources to AQRVs, as well as changes in their emissions.

Additionally, such dialogue facilitates coordination between permitting authorities and the FLMs. The significance of the impact to AQRVs is more important than the distance of the source. Not all PSD permit applications that the FLM is notified of will be analyzed in-depth by the FLM. FLM notification of a PSD permit application for a project located greater than 100 km does not mean that the permit application will be reviewed by the FLM in detail. Notification of PSD permit applications in excess of 100 km by the permitting authority allows the FLM to gauge the level of potential cumulative effects. As indicated above, the FLM decides which PSD permit applications to review on a case-by-case basis depending on the potential impacts to AQRVs.

Pre-Application Meetings

To expedite the PSD permit review process, the FLM encourages pre-application meetings with permitting authorities and permit applicants to discuss air quality concerns for a specific Class I area in question. Given preliminary information, such as the source's location and the types and quantity of projected air emissions, the FLM can discuss specific AQRVs for an area and advise the applicant of the analyses needed to assess potential impacts on these resources.

Completeness Determination

To further minimize delays, the FLMs encourage the permitting authority to use comments provided by the FLM concerning the completeness of the application, and to not deem the application complete until the applicant performs all necessary air quality impact analyses, including all relevant AQRV impact information. The permitting authority should then notify the FLM when they deem the application to be complete.

Visibility Protection Procedures

Additional procedural requirements apply when a proposed source has the potential to impair visibility in a Class I area (40 CFR §52.27(d)(2007); 40 CFR §51.307(a)(2007)). Specifically, the permitting authority must, upon receiving a permit application for a source that may affect visibility in any Class I area, notify the FLM in writing. Such notification shall include a copy of all information relevant to the permit application, including the proposed source's anticipated impacts on visibility in a Class I area. The permitting authority shall notify the FLM within 30 days of receipt and at least 60 days prior to the close of the comment period.

If the FLM notifies the permitting authority that the proposed source may adversely impact visibility in a Class I area, or may adversely impact visibility in a previously identified integral (scenic) vista, then the permitting

authority is to work with the FLM to address their concerns. If the permitting authority agrees with the FLM's finding that visibility in a Class I area may be adversely affected, the permit may not be issued. Even though the permitting authority may agree with the FLM's adverse impact finding regarding integral vistas, the permitting authority may still issue a permit if the emissions from the source are consistent with reasonable progress toward the national goal of preventing or remedying visibility impairment. In making this decision, the permitting authority may take into account the costs of compliance, the time needed for compliance, the energy and non-air quality environmental impacts of compliance, and the useful life of the source.

The FLM will make a preliminary determination regarding possible adverse visibility impacts upon receipt of all relevant information, including the draft permit and any associated staff analysis.

2.2.2. Elements of Permit Review

The FLM review of a PSD application for a proposed project that may impact a Class I area generally consists of three main analyses:

1. Air quality impact analysis to ensure that predicted pollutant levels in Class I areas do not exceed National Ambient Air Quality Standards (NAAQS) and PSD increments, and to provide sufficient information for the FLM to conduct an AQRV impact analysis. Ensuring that permit applicants meet these requirements is the direct responsibility of the permitting authority (see discussion below);
2. AQRV impact analysis to ensure that the Class I area resources (i.e., visibility, flora, fauna, etc.) are not adversely affected by the proposed emissions. The AQRV impact analysis includes interpreting the significance of the results from the applicant's air quality impact analysis and is the responsibility of the FLM (see discussion below); and
3. Best Available Control Technology (BACT) analysis to help ensure that the source installs the best control technology to minimize emission increases from the proposed project (See Appendix D for a summary of this analysis). The final BACT determination is a direct responsibility of the permitting authority.

Air Quality Impact Analysis

The permit applicant must perform an air quality impact analysis for each pollutant subject to PSD review (40 CFR §51.166). This analysis must show the contribution of the proposed emissions to increment consumption and to the existing ambient pollution levels in a Class I park or wilderness area. The applicant must perform a cumulative increment analysis for each pollutant and averaging time for which the proposed source will have a significant impact.

Because proposed sources are not yet operating, the air quality analysis should rely on mathematical dispersion models to estimate the air quality impact of the proposed emissions. The FLMs provide the applicants with guidance on where to place model receptors within the Class I area. The applicant is responsible to provide sufficient information for the FLM to make a decision about the acceptability of potential AQRV impacts as a consequence of the new source.

The applicant must perform the air quality impact analysis using approved models and procedures as specified in Appendix W of Part 51 (EPA's *Guideline on Air Quality Models*, revised November 2005), as required under the PSD regulations at 40 CFR 51.166(1) and 52.21(1). The applicant should explicitly state all assumptions for the analysis, and furnish sufficient information on modeling input so that the FLM can validate and duplicate the model results. FLMs encourage the permit applicant to submit a modeling protocol for review before performing the Class I modeling analyses. This protocol should include the proposed air quality analysis methodology and model input (i.e., emissions, stack data, meteorological data, etc.), and the proposed location of the receptors in the FLM area.

AQRV Impact Analysis

According to the CAA's legislative history and current EPA regulations and guidance, the air quality impact analysis that provides sufficient information to enable the FLM to conduct the AQRV impact analysis is one part of a permit application just as are the BACT analysis and the air quality impact analysis relative to the increments and NAAQS. The applicant bears the entire cost of preparing the permit application including the complete air quality impact analysis.

It is important to highlight the distinction between the air quality impact analyses that the applicant performs and the AQRV impact analyses that FLMs perform. Whereas the permit applicant calculates changes in pollutant concentrations, deposition rates, or visibility extinction, the FLM assesses the extent to which these impacts affect sensitive visual, aquatic, or terrestrial resources. Given the FLM's statutory responsibilities and expertise, the FLM must have responsibility to consider whether the amount of pollution dispersed into the air or deposited on the ground (or in water) would have an adverse impact on any AQRV, and if so, to demonstrate that claim to the permitting authority. In making an adverse impact finding, FLMs consider such factors as magnitude, frequency, duration, location, geographic extent, and timing of impacts, as well as current and projected conditions of AQRVs based on cumulative impacts.

The FLM uses the results from the applicant's air quality impact analysis and other information to conduct the

AQRV impact analysis and make an informed decision about whether or not AQRVs will be adversely affected. If the FLM concludes that AQRVs will be adversely affected, the FLM will so demonstrate to the permitting authority. The following sections of this document give guidance to applicants on how to conduct an air quality impact analysis and how the FLM uses this information to make an AQRV impact decision.

Cumulative Impact Analysis

The FLM will evaluate on a case-by-case basis both the permit applicant's contribution to the AQRV impacts, as well as the cumulative source impacts on AQRVs, taking into account expected emission reductions. A cumulative air quality analysis in which the proposed source and any recently permitted (but not yet operating) sources in the area are modeled is an important part of any AQRV impact analysis. This cumulative modeled impact is then added to measured ambient levels (to the extent that such monitoring data are available) so that the FLM can assess the total effect of the anticipated ambient concentrations on AQRVs. If no representative monitoring data are available, the total pollutant concentrations should be estimated by modeling emissions from all contributing sources in the area.

Information Provided by the FLM to the Applicant

To assist the permit applicant in performing air quality impact analyses, the FLMs will provide all available information about AQRVs for a particular Class I area that may be adversely affected by emissions from the proposed source. FLMs will recommend available methods the applicant should use to analyze the potential effects (i.e., pollutant concentration, deposition rates, and visibility extinction) in the Class I area. In addition to identifying AQRVs, FLMs will, to the extent possible:

- identify inventories, surveys, monitoring data, scientific studies, or other published reports that are the basis for identification of AQRVs;
- identify specific receptors known to be most sensitive to air pollution and the pollutant or pollutants that individually or in combination can cause or contribute to an adverse effect on each receptor;
- identify the critical pollutant concentrations above which adverse effects are known or suspected to occur;
- recommend methods the applicant should use for predicting ambient pollutant concentrations and other related impacts (e.g., deposition, visibility) which may cause or contribute to an adverse effect on each receptor; and
- suggest screening level values or criteria that would be used to assess whether a proposed emissions increase would have a *de minimis* impact on AQRVs.

2.2.3. FLM Permit Review Process

The FLM's current permit review process for any application that may impact a FLM area is described below.

1. **Pre-application.** If possible, participate in any pre-application meeting to learn specifics of the proposed project (size, emissions, location, etc.) and to provide information regarding recommended Class I analyses.
2. **Modeling Protocol.** The FLMs encourage the permit applicant to submit a modeling protocol for review before performing the Class I modeling analyses. This protocol should include the proposed air quality analysis methodology and model input (i.e., emissions, stack data, meteorological data, etc.), and the proposed location of the receptors in the FLM area.
3. **Completeness Determination.** Upon receipt, the FLM will review the application and provide comments to the permitting authority regarding the completeness of the application and the need for additional information regarding the BACT, Air Quality Impacts, and AQRV Impacts analyses. The FLM will coordinate with the permitting authority and the permit applicant to ensure that all the necessary information to enable the FLM to make an impact determination is included.
4. **Public Comment Period.** After review of all relevant information, the FLM will provide pertinent comments to the permitting authority, before or during the official public comment period, and/or at scheduled public hearings.
5. **No Class I Increment Violated and No Adverse Impacts.** If no Class I increment is violated and no adverse impacts to AQRVs are expected, the FLM will inform the permitting authority of this determination and no further FLM action is necessary. The FLM may still provide BACT comments.
6. **No Class I Increment Violated but AQRV Impacts Uncertain.** If no Class I increment is violated but uncertainty exists regarding potential adverse impacts to AQRVs, the FLM may request that the permitting authority include a permit condition that requires the permittee to conduct relevant post-construction AQRV or air quality monitoring. The FLM may also request certain control technologies or methods to reduce impacts.
7. **Class I Increment Violated, but No Adverse AQRV Impacts.** If the Class I increment is violated, but no adverse AQRV impacts are anticipated, the applicant requests the FLM to "certify" no adverse impact under Section 165(d)(2)C)(iii) of the Clean Air Act [42 USC 7475(d)(2)(C)(iii)(1998)]. If the FLM concurs, (s)he makes a preliminary determination that no adverse impacts will occur.

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- The FLM will inform the applicant, the State/local permitting authority, and EPA of the preliminary no adverse impact determination.
- The FLM will notify the public of its preliminary no adverse impact determination either through the permitting authority's notice procedures, or through separate notice in the *Federal Register*. Such notice should include a statement as to the availability of supporting documentation for inspection and copying, and an announcement of at least a 30 day public comment period on issues directly relevant to the determination in question.
- The FLM will review and prepare response to public comments.
- The FLM will make a final determination regarding no adverse impacts, with a clear and concise statement of reasons supporting that determination.
- The FLM will inform the permit applicant, the permitting authority, and EPA of its final determination and if the final determination is "no adverse impact," the FLM shall so "certify" in a letter to the affected parties.
- Simultaneous with above, the FLM will publish a final determination in the 'Notice' section of the *Federal Register*, including a clear and concise statement of reasons supporting that determination, statement as to availability of supporting documentation for inspection and copying, and statement as to immediate effective date (date signed) of final determination.
- The FLM will contact the permitting authority and request a revision to the State Implementation Plan (SIP) to eliminate the Class I increment violations.

8. **Adverse Impact Determination**. Regardless of increment status, the FLM may make a preliminary determination that the proposed project will cause, or contribute to, an adverse impact on AQRVs. Before officially declaring an adverse impact, the FLM will inform the proposed new source and the permitting authority that an adverse impact determination is imminent and suggest that the draft permit be modified. If the draft permit is modified to satisfy the concerns of the FLM, then an adverse determination is avoided.
   - The FLM will inform the applicant, the permitting authority, and EPA of a preliminary adverse impact determination.
   - The FLM will notify the public of the preliminary adverse impact determination either through the permitting authority's notice procedures, or through separate notice in the *Federal Register*. Such notice should include a statement as to the availability of supporting documentation for inspection and copying, and an announcement of at least a 30 day public comment period on issues directly relevant to the determination in question.
   - The FLM will review and prepare response to public comments.
   - The FLM will make a final determination regarding adverse impacts, with a clear and concise statement of reasons supporting that determination.
   - The FLM will inform the permit applicant, the permitting authority, and EPA of its final determination.
   - Simultaneous with above, the FLM will publish a final determination in the 'Notice' section of the *Federal Register*, including a clear and concise statement of reasons supporting that determination, statement as to availability of supporting documentation for inspection and copying, and statement as to immediate effective date (date signed) of final determination.
   - If the FLM makes a final determination that a source will have an adverse impact, the FLM will oppose the permit. However, the permit applicant may propose to mitigate any adverse impacts (via reducing emissions, obtaining emission offsets, etc.). If the applicant adequately mitigates the adverse impacts to the satisfaction of the FLM, the FLM will withdraw his objection to the permit. If the adverse impacts are not adequately mitigated and the permitting authority nevertheless issues the permit, the FLM may appeal the permit.

Note: If the permitting authority's SIP makes execution of the above listed steps impossible (e.g., inadequate time allotments for the FLM's determination or lack of timely FLM notice) the procedures shall be adjusted as appropriate. In addition, the above procedures (6 and 7) could also be modified to accommodate those situations when the FLM chooses to certify that existing impacts are adverse, absent a proposed new source. Such an action would alert potential permit applicants that adverse impacts exist and any new source would need to mitigate its potential impacts. Although each FLM may implement the above procedures somewhat differently, the FLAG goal is to reduce the differences in implementing the above steps.

Furthermore, FLMs intend to coordinate on air permit modeling requirements for new or modified sources that are geographically near more than one FLM area. For example, a proposed source in eastern Tennessee that lies equidistant from NPS-administered Great Smoky Mountains National Park and the FS-administered Joyce Kilmer/ Slickrock Wilderness would receive coordinated guidance on modeling requirements from the FLMs. The FLMs may or may not have common AQRVs and Class I areas, making coordination beneficial. The FLMs may also

coordinate on potential permit conditions and mitigation strategies.

2.2.4. Criteria for Decision Making (Adverse Impact Considerations) (Revised)

As previously mentioned, the legislative history of the CAA provides direction to the FLM on how to comply with the affirmative responsibility to protect AQRVs in Class I areas, and in cases of doubt, the land manager should err on the side of protecting air quality-related values for future generations.

The FLMs define adverse impact on AQRVs as:

> An unacceptable effect, as identified by an FLM that results from current, or would result from predicted, deterioration of air quality in a Federal Class I or Class II area. A determination of unacceptable effect shall be made on a case-by-case basis for each area taking into account existing air quality conditions. It should be based on a demonstration that the current or predicted deterioration of air quality will cause or contribute to a diminishment of the area's national significance, impairment of the structure and functioning of the area's ecosystem, or impairment of the quality of the visitor experience in the area.

Also, the Federal visibility protection regulations (40 CFR §51.300, et seq., §52.27) define adverse impact on visibility as:

> [V]isibility impairment which interferes with the management, protection, preservation or enjoyment of the visitor's visual experience of the Federal class I area. This determination must be made on a case-by-case basis taking into account the geographic extent, intensity, duration, frequency, and time of visibility impairment, and how these factors correlate with: (1) times of visitor use of the Federal class I area, and (2) the frequency and timing of natural conditions that reduce visibility. (Id. §51.301(a))

FLMs typically address adverse impacts on a case-by-case basis in response to PSD permit applications. The factors the FLMs will consider in making an adverse impact determination are discussed in more detail below (see section 4.3). When an adverse impact is predicted, FLMs recommend that permits either be modified to protect AQRVs or be denied. FLMs can also address adverse conditions outside of the PSD process. They do so through a variety of mechanisms: certify visibility impairment; participate in regional assessments; informally collaborate with States and EPA; review lease permits, SIP revisions, National Environmental Policy Act (NEPA) analyses, Park/Refuge/Forest management plans, CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act) reviews, and other documents.

In some States, FLMs use screening procedures or thresholds that indicate when the condition of an AQRV is acceptable or unacceptable. The pollutant concentration or loading rate that will adversely impact an AQRV can vary among Class I areas, and depends on current conditions. After a threshold is reached, an increase in pollutant concentrations is likely to be unacceptable. A concern threshold can be an adverse impact threshold or other quantifiable level in resource condition or pollutant exposure identified by the FLM.

2.2.5. Air Pollution Permit Conditions that Benefit Class I Areas

The FLM does not determine what permit conditions will be required or administer permit conditions; that is the responsibility of the permitting authority. However, the FLMs may request permit conditions or agree to withdraw objections to permit issuance if requested conditions are included. The FLMs view the inclusion of certain PSD permit conditions by the permitting authority as a means to help protect or enhance the condition of AQRVs when:

1. Air pollution source(s) may cause impacts that exceed protection thresholds for AQRVs;
2. Terrestrial resources, aquatic resources, and/or visibility are currently adversely impacted by air pollution and proposed emissions will exacerbate these adverse conditions;
3. FLM policies require improvement or restoration of AQRVs in parks and wildernesses; and
4. There is uncertainty on the extent and magnitude of air pollution effects on AQRVs.

Recommended permit conditions may include requiring emission offsets, AQRV and/or air quality monitoring, inventories, post-construction reassessment, LAER (or other improved control technologies), or other measures to protect, enhance, or restore resources and values of parks and wildernesses. Permit conditions may:

1. Result in net air quality benefits at a protected area or within a region;
2. Contribute to a reduction of air pollution within a region;
3. Promote ecosystem inventories and/or monitoring to evaluate physical and biological resource damage caused by air pollution emissions; and
4. Promote ecosystem restoration or improve the condition of resources that have been damaged by air pollution emissions.

The basis of an air permit condition should be identified in the public notice for the draft permit. To be effective, permit conditions must be federally enforceable and guaranteed. Air permit provisions may be temporary or permanent depending on the nature of the permit requirements.

Procedures to implement an air permit condition must be acceptable to the FLM (e.g., an agreement between parties [memorandum of understanding, interagency agreement] is an option to accomplish inventory, monitoring, or other requirements).

2.2.6. Reducing Pollution in Nonattainment Areas (Nonattainment Permit Process)

The PSD program does not apply with respect to a particular pollutant when the source locates in an area designated non-attainment for that pollutant. Instead, pollution sources are regulated by Non-attainment Area New Source Review (NNSR). NNSR includes air quality planning and regulation of stationary sources. Air quality planning addresses issues such as lowest achievable emission rate (LAER), offsets, reasonably available control technology (RACT), and mobile and stationary source control strategies. New major stationary sources and major modifications of sources in designated non-attainment areas must satisfy NNSR before construction begins. For visibility protection, SIPs must include either EPA-approved provisions to comply with 40 CFR §51.307 for the non-attainment pollutant, otherwise, the federally promulgated visibility provisions at 40 CFR §52.28 would apply to all sources located in non-attainment areas. Therefore, FLMs can provide suggestions to the permitting authority regarding these conditions during the permitting and planning processes.

SIPs provide a mechanism to address AQRV impacts when the source or the Class I area is located in a non-attainment area. FLMs may recommend that States adopt policies, rules, or regulations in their SIPs requiring a demonstration that offsets will result in a net air quality benefit within any Class I area likely to be impacted by emissions from the source to be permitted. FLMs may also request emissions reductions greater than 1:1, perhaps offset rates of 1.5 or 2.0 to 1, or higher, depending on the nature and magnitude of impacts to be offset. Such recommendations can be developed jointly in a meeting with the regulatory authority or in a letter from the FLM.

Mitigation measures recommended by FLMs may include stringent control technologies to minimize the increase in emissions and the impact on AQRVs. Monitoring can determine whether predicted resource conditions are observed. Offsets ensure that net emissions reductions from all sources will occur within a geographic area and their resulting air quality impacts at the Class I area will be mitigated.

2.3. Other Air Quality Review Considerations (Revised)

At all Class I areas where visibility has been monitored, visibility conditions have been found to be impaired by human-caused pollution. The impairment comes primarily from older sources, not new sources. From a regional perspective, new or modified sources (using new/cleaner technologies) contribute far less to impaired AQRV conditions than old sources. EPA has implemented a call for reducing NO_x emissions from older sources in the eastern U.S. to meet existing ozone standards. In addition to complying with national ambient standards, States are now developing plans to implement EPA's Regional Haze Regulations. If these requirements are implemented, then progress toward remedying impaired AQRVs is likely. However, given the sensitivity of some AQRVs to low levels of pollution, programs focused on reaching national goals, such as the NAAQS or visibility, may not fully remedy impacts on AQRVs in all locations. It is for this reason that the FLM does pursue other strategies to protect AQRVs. The following sections discuss FLM issues that go beyond NSR.

2.3.1. Remedying Existing Adverse Impacts

Allowing the existence of adverse impacts would be inconsistent with the mandates of the FLM agencies. Consequently, FLMs may request or participate in regional assessments to protect AQRVs, and remedy any existing adverse impacts on AQRVs, as appropriate. Regional assessments often use a multi-faceted approach to remedy impairment. For example, categories addressed by the Grand Canyon Visibility Transport Commission (GCVTC) include air pollution prevention; clean air corridors; stationary sources; sources in and near Class I areas; mobile sources; road dust; fire; and future regional coordination.

Clean Air Act requirements for remedying existing visibility impairment provide a mechanism for addressing impacts from specific sources or groups of sources [42 USC 7491). Negotiations at the Centralia Power Plant in the state of Washington provide an example of how to build partnerships and work collaboratively to obtain retrofit controls or more stringent control technologies for sources that affect a FLM area. Through a collaborative decision making process, owners of the Centralia plant agreed to reduce sulfur dioxide emissions at the plant by 90%. In another case, the FWS identified plume impacts from a pulp and paper mill located seven miles upwind of the Moosehorn Wilderness Area. Using cameras provided by the IMPROVE monitoring network, plumes from the mill were documented entering the Moosehorn Wilderness Area. In collaboration with the State of Maine, additional controls for nitrogen oxides and updated particulate controls were incorporated into the mill's PSD permit to address the plume impacts.

FLMs may also coordinate with others to ensure that emission reductions in nonattainment areas will improve air quality in FLM areas. Recommendations on urban planning were developed with FLM involvement to address nonattainment areas in California. Data documenting ozone effects on vegetation were provided to the planning authority.

2.3.2. Requesting State Implementation Plan (SIP) Revisions to Address AQRV Adverse Impacts (Revised)

A SIP is the mechanism that states use to develop the pollution control programs that will be used to achieve and maintain the NAAQS, as well as prevent significant deterioration of air quality. It is important for FLMs to be involved in SIP development, as participation provides an opportunity to influence planning of pollution control programs that can benefit air quality in FLM areas. Once a SIP is fully approved by EPA, it is legally enforceable under both State and Federal law. FLMs assist in the development of SIPs by providing analysis and comment to address existing impacts of concern. This approach is particularly useful for addressing impacts on AQRVs other than visibility, since the Clean Air Act does not provide specific requirements for other AQRVs.

SIP revisions could be used to address multiple sources and regional pollution that adversely affect AQRVs in all Class I areas. For example, in South Coast and San Diego, California, SIP revisions included FLM recommendations to reduce the impact of minor sources on AQRVs. South Coast recommendations addressed visibility while the San Diego recommendations addressed all AQRVs. EPA's NO_x SIP Call in the east is another example of obtaining emission reductions through the SIP revision process. The NO_x SIP Call was directed at 20 eastern States and the District of Columbia to address NO_x emissions from existing large sources. Significant reductions in ozone formation and nitrogen deposition have occurred as a result of these efforts.

2.3.3. Periodic Increment Consumption Review (Revised)

EPA has indicated its intention to establish a SIP revision requirement to address existing adverse impacts on AQRVs. The FLMs strongly support EPA exercising its authority in this way. In the interim, however, there are existing SIP revision requirements that are not being fully utilized. EPA's current regulations require States to conduct a periodic review of the adequacy of their PSD plan and program. [40 CFR §51.166(a)(4)] This would include an assessment of increment consumption in Class I and Class II areas. Few States have ever conducted a comprehensive, cumulative increment consumption analysis for one or more Class I areas. In addition, many PSD sources have not exceeded the significant impact levels for increment consumption; thus, few PSD permit applicants have had to perform a cumulative increment consumption analysis for Class I areas. Such a periodic increment consumption review would be beneficial given that the burden of proof for AQRV adverse impact determinations shifts from the FLM to the applicant when the increment has been consumed.

In its 1990 report, *Air Pollution: Protecting Parks and Wilderness From Nearby Pollution Sources,* the U.S. General Accounting Office (GAO) found that only 1 percent of the sources within 100 kilometers of five Class I areas it investigated were required to have permits under the PSD program, with 99 percent of the sources being minor or grandfathered sources. It also found that "non-PSD sources contribute from 53 to 90 percent of five of the six criteria pollutants emitted within a 100-kilometer radius of each of the five Class I areas." As part of its investigation, GAO noted that "a significant portion of total emissions of volatile organic compounds generally comes from small sources...and suggested that as part of the overall control strategy, States may want to consider lowering thresholds for regulating new sources to 25 tons of volatile organic compounds a year." According to the investigation, 55 percent of anthropogenic VOC emissions come from new sources or modifications totaling five tons per year or less. In a review of PSD permit applications near Mesa Verde National Park (a Class I area in Colorado), a cumulative modeling analysis of increment-consuming sources found that approximately 80 percent of the NO_2 Class I increment at the park had been consumed, but much of it by minor sources.

The FLMs have encouraged EPA to provide clearer direction on how often these periodic reviews should occur as the lack of a prescribed time-frame for conducting such analyses has clearly led to noncompliance with this requirement over the past twenty years by States.

2.4. Managing Emissions Generated in and Near FLM Areas (Revised)

Specific strategies need to be developed and implemented for reducing and preventing pollution from the many diverse sources and activities in communities surrounding FLM areas, including "gateway" communities (i.e., those adjacent to FLM areas). Accountability mechanisms are needed to ensure that appropriate actions are taken, reported and incorporated into SIPs, visibility protection plans, and Federal land management plans. Various forums (e.g., the Western Regional Air Partnership, and the Southern Appalachian Mountains Initiative) addressed some of the emissions sources of concern and developed regional strategies. In addition, EPA has formed other "regional planning organizations" for implementing its regional haze rule. FLMs participate in these forums, consistent with Federal law (e.g., Federal Advisory Committee Act), to the

maximum extent possible and coordinate their activities within those forums to ensure that comprehensive strategies are developed and implemented to address all the key emissions sources near FLM areas.

A systematic assessment of emission sources in and near FLM areas would be extremely helpful for formulating strategies aimed at mitigating or eliminating adverse impacts on area resources, and the NPS has performed micro-emission inventories for several of its Class I areas. However, without this assessment for all areas it is not possible to accurately quantify the extent to which these emissions contribute to the overall problem. Nevertheless, FLMs can, and should, take steps to minimize emissions generated on FLM lands even without an accurate inventory of emissions sources.

2.4.1. Prescribed Fire

Prescribed fire is a land management tool used for multiple landscape objectives. Prescribed fire allows the FLM to mimic natural fire return intervals under controlled conditions where smoke management can minimize air quality impacts. The alternative is wildfires, which can be very difficult to control and may cause much more severe air quality impacts. A modeling assessment suggests that using prescribed fire to minimize wildfires can result in a net reduction in fine particle ($PM_{2.5}$) emissions in the long-term. In the Pacific Northwest wildfire emissions were found to be greater than prescribed fire emissions in the same airshed (Ottmar 1996).

Since the early 1900s, wildfire has been aggressively suppressed on most of the nation's public lands to protect public safety, property, and to prevent what was thought to be the destruction of our natural and cultural resources. Fire-exclusion practices have resulted in forests, shrub lands, and grasslands plagued with a variety of problems, including overcrowding, resulting from the encroachment of species normally suppressed by fire; vulnerability of trees to insects and disease; and inadequate reproduction of certain species. In addition, heavy accumulation of fuels (such as dead vegetation on the forest floor) can cause fires to be catastrophic, which threatens firefighter and public safety, impairs forest and ecosystem health, destroys property and natural and cultural resources, and degrades air quality. The intense or extended periods of smoke associated with wildfires can also cause serious health effects and significantly decrease visibility.

FLMs recognize prescribed fire as a valuable tool; they also recognize that emissions from prescribed fire can be a significant source of air pollution. Smoke particles are also in the size range (< 2.5 µm) that they play a significant role in visibility impairment. Particulate matter is the main pollutant of concern from smoke because it can cause serious health problems, especially for people with respiratory illness.

The FLMs are committed to minimizing the impacts from smoke by following sound smoke management practices, and if practical, using non-burning alternatives (i.e., mechanical clearing, chipping, mulching) to achieve land management objectives. Each prescribed burn site will have unique characteristics, but in general, smoke impacts can be minimized by burning during weather conditions that provide optimal humidity levels and dispersion conditions for the type of materials being burned, in addition to limiting the amount of materials and acreage burned at one time.

EPA has worked in partnership with land management agencies in the U.S. Departments of Agriculture, Defense, and the Interior; State Foresters; State air regulators; Tribes; and others to obtain recommendations and develop a national policy that addresses how best to improve the quality of wildland ecosystems (including forests and grasslands) and reduce threats of catastrophic wildfires through the increased use of managed fire, while achieving national clean air goals (EPA 1998b). EPA's interim air quality policy on fire describes criteria for wildland managers (federal, state, tribal, and private), and state and tribal air pollution agencies, to use in planning for and implementing prescribed fires, and recommends a variety of smoke management techniques that land managers can use to help reduce smoke impacts from prescribed fires. The policy is available at EPA's web site: http://www.epa.gov/ttn/faca/fa08.html. In addition, on March 22, 2007, EPA promulgated its Exceptional Events Rule that clarifies how ambient air quality standard exceedances from wildland fire will be treated in determining attainment and nonattainment status. In that rule, EPA committed to revising its 1998 wildland fire policy (72 FR 13560, March 22, 2007).

2.4.2. Strategies to Minimize Emissions from Sources In and Near FLM Areas (Revised)

Aside from prescribed fire, other activities in and near FLM areas that generate air pollution include vehicle emissions, road building, operation of generators, oil and gas development, etc. Developing strategies for addressing natural resource impacts in or near an FLM area should not only take into consideration the type of activities generating the emissions and their amount, but also the existing condition of the resources of that area. More stringent measures should be recommended for sources in and near FLM areas that are already experiencing adverse effects from air pollution.

Examples of potential air pollution prevention practices that FLM agencies may encourage or develop and use are categorized under the following three strategies:

Pollution Prevention Strategies

- Review land management plans for affected FLM areas to assess whether they include strategies to limit and reduce air pollution emissions and incorporate protective measures into planning and decision documents.
- Place priority on pollution prevention.
- Encourage zero and near-zero emitting technologies.
- Promote energy conservation and the use of renewable energy sources.
- Promote use of clean fuels.

Mobile Source Strategies

- Promote the adoption of Low Emission Vehicle standards or the conversion of Federal fleets to alternative fuels.
- Improve control of evaporative emissions.
- Promote more stringent emission standards for the tour bus industry and other high-emitting vehicles used in federal areas (e.g., park shuttle vehicles).
- Considering restricting access of high emitting vehicles to sensitive areas.
- Retire high-emitting vehicles from Federal fleets as quickly as practicable and/or relocate high-emitting vehicles to less sensitive areas until they can be retired.
- Establish emission budgets from the transportation sector for selected FLM areas.
- Develop mass transit systems in some NPS units (e.g., light rail in Grand Canyon NP and a bus system in Zion NP).

Minor Source Strategies (Revised)

- Apply RACT, BACT, LAER, best and reasonably available control measures, etc., to existing federal sources, as appropriate.
- Recommend going beyond conformity requirements to include the protection of AQRVs in FLM areas, and ensure all actions FLMs can practicably control in and near FLM areas will not cause, or contribute to, an adverse impact on any AQRV.

Improved involvement with interested parties in gateway communities will likely be required to ensure growth in these communities occurs in a manner that mitigates the impact on natural resources. These communities may need to enhance their participation in the planning processes of FLMs. Similarly, FLMs should participate in planning activities for public lands located in the FLM area and communities adjacent to FLM areas to ensure air quality concerns are adequately addressed. Mechanisms should be identified and developed for community involvement in developing, implementing, and enforcing emission management strategies for sources near and in FLM areas.

Implementing strategies to achieve emission reductions in and near FLM areas will require efforts in at least three specific areas:

1. FLMs should ensure that sufficient emphasis is placed in agency planning documents requiring the minimization of air pollution emissions from new activities or practices.
2. FLMs should inventory air pollution emissions within FLM areas. After emissions have been quantified, FLMs, States, and adjacent communities will be able to assess the impact of these emissions through the use of appropriate models. Knowledge of Class I area emissions will also improve FLM ability to consult with States during the development and review of their SIPs (especially visibility SIPs). The NPS has developed an emissions inventory tool, the Climate Leadership in Parks (CLIP) Tool, that can be utilized by FLMs to inventory both greenhouse gases and all criteria air pollutants.
3. FLMs should cooperate with States and local communities in assessing the need for, and the development of, appropriate emission reduction strategies in and near FLM areas that address non-PSD sources. For Class I areas, the Regional Planning Organizations have completed analyses of emissions from nearby communities and activities that will serve as the basis for identifying strategies to reduce emissions. Without an acknowledgment from States and local communities that these sources may pose a threat to FLM areas and a systematic assessment of these potential impacts, current efforts to protect FLM area resources may be insufficient.

2.4.3. Conformity Requirements in Nonattainment Areas

Conformity criteria and procedures ensure that actions on lands administered by Federal agencies do not cause a violation of the NAAQS, increase the frequency of any standards violations, or delay attainment of a standard. Conformity to SIPs is only required for activities within nonattainment areas for non-transportation related sources if emissions are above de minimis levels and regionally significant. Any activity that represents 10 percent, or more, of the emission inventory for that pollutant in the non-attainment or maintenance area is regionally significant. Examples of actions that may require a conformity determination include road paving projects, ski area development, or mining. Activities such as prescribed fire, that are included in a conforming land management plan, are exempt from conformity requirements. Please note that conformity determinations must be made in accordance with applicable EPA regulations, are typically done before a project is approved, and are part of the NEPA process.

The FLM should define the process to be used in conformity determinations and perform the conformity analysis before

a project is implemented. A conformity analysis typically includes emission calculations, public participation, mitigation measures/implementation schedules, and reporting methods. The Pacific Southwest Region of the USFS has published a *Conformity Handbook for FLMs* to assist in conformity compliance. In an approved Plan of Operation, FLMs can require monitoring. For example, in the case of Carlota Mine, located on National Forest land in Arizona, the USFS requested additional mitigation measures to protect AQRVs in the Superstition Wilderness.

Transportation projects in FLM areas classified as nonattainment are subject to a more complicated transportation conformity process. Consultation with State and local air quality and transportation agencies will be required to comply with applicable regulations.

3. Subgroup Reports: Technical Analyses and Recommendations

3.1. Subgroup Objectives and Tasks

Subgroups were formed to address the four key issues relevant to AQRV identification and evaluation issues: policy (and procedures), visibility, ozone, and deposition. Each of these subgroups reviewed the commonalities among the FLMs then addressed the tasks assigned to them by FLAG. One of their first tasks was to differentiate between Phase I tasks, those which could be resolved in the short term without significant additional resources, and Phase II issues, those that would require a longer period or greater effort.

Subgroups were asked to reach common ground among the FLMs on the issues. The intent was to develop, to the extent possible, consistent policies, processes, and terminology that could be used when identifying AQRVs and evaluating impacts on AQRVs. This involves recommending consistent approaches for identifying air pollution effects on AQRVs, for determining adverse impacts, and for attributing adverse impacts to specific pollution sources. In addition, the FLMs consider that AQRV protection from visibility, ozone, and deposition impacts are equally important. However, we also recognize that given the current state of the science, attributing adverse impacts to specific sources are easier to document for visibility than for deposition and ozone, and easier for deposition than ozone.

The individual subgroup reports document the common policies, procedures, and definitions identified or developed during Phase I activities. The Visibility, Ozone, and Deposition subgroup reports are included below. The FLAG Policy Subgroup Report was used as the basis for much of the rest of this *FLAG Phase I Report*, including much of section 1 'Background' and section 2 'Federal Land Managers' Approach to AQRV Protection'.

3.2. Initial Screening Criteria (New)

Experience with the FLAG 2000 recommendations in dealing with many new source review applications led the Agencies to believe that an initial screen that would exempt a source from AQRV impact review based on its annual emissions and distance from a Class I area may be appropriate in most situations. As part of its Regional Haze Regulation, the EPA has introduced a screening criteria in its BART guidelines based on a source's annual emission strength and distance from a Class I area. The EPA stated that it would be reasonable to conclude that the following sources would not be considered to cause or contribute to visibility impairment:

Acadia National Park, Maine.
Credit: National Park Service

- those located more than 50 km from any Class I area that emit less than 500 tons per year of NO_x or SO_2 (or combined NO_x and SO_2), and
- those located more than 100 km from any Class I area that emit less than 1,000 tons per year of NO_x or SO_2 (or combined NO_x and SO_2).

In both cases, the annual emissions over distance factor equates to 10.

The Agencies have concluded that a similar approach has merit with respect to new source impacts at Class I areas, for air pollution sources with relatively steady emissions throughout each year. However, the Agencies are modifying the size criteria to also include Particulate Matter less than 10 microns in size (PM_{10}) and sulfuric acid mist (H_2SO_4) emissions because those pollutants also impair visibility and contribute to other resource impacts. In addition, rather than the two-step BART test, the Agencies are using a fixed Q/D factor of 10 as a screening criteria for sources locating/located greater than 50 km from a Class I area. Furthermore, the Agencies are expanding the screening criteria to include all AQRVs, not just visibility. Therefore, the Agencies will consider a source locating greater than 50 km from a Class I area to have negligible impacts with respect to Class I AQRVs if its total SO_2, NO_x, PM_{10}, and H_2SO_4 annual emissions (in tons per year, based on 24-hour maximum allowable emissions), divided by the distance (in km) from the Class I

area (Q/D) is 10 or less. The Agencies would not request any further Class I AQRV impact analyses from such sources.

In cases where a source's operations which generate visibility-affecting emissions are limited to time periods shorter than a year, the short-term potential to impact visibility may not be adequately expressed by the Q/D concept. For example, a source that is operated either seasonally or intermittently, and has zero emissions for substantial portions of a year, would have a total annual emission rate that under-represents its potential emission strength over a shorter time frame, such as a day or week. Because visibility is an air quality related value that is sensitive to immediate and short-term conditions, in order to apply the Q/D≤10 screening tool, these types of sources need to first adjust the tons-per-year emissions to reflect what the emissions would be if the source operated year-round. For instance, if operations are restricted to 3,000 hours per year, then the annual steady-state-equivalent emission rate (Q) is found by multiplying the permitted total tons per year for SO_2, NO_x, PM_{10} , and H_2SO_4 by the ratio of hours: 8,760 hours per year/3,000 hours operation.[5] Then, using this annual equivalent Q in the Q/D test, the Agencies will consider a source locating greater than 50 km and showing that its ratio of annual equivalent Q (tons per year) divided by distance from the Class I area (km) of 10 or less, as having negligible impacts with respect to Class I visibility impacts, and would not request any further Class I visibility impact analyses from such sources.

3.3. Visibility

3.3.1. Introduction (Revised)

This chapter describes methods for analyzing the impacts on visibility from new or modified air pollution sources. This includes sources that fall under the purview of the Prevention of Significant Deterioration (PSD) regulations and sources that are being analyzed for Environmental Assessments and/or Environmental Impact Statements under the National Environmental Policy Act (NEPA). The basis for some of the decisions outlined in this chapter is Section 169A of the Clean Air Act. The opening statement of this section states: "Congress hereby declares as a national goal the prevention of any future, and the remedying of any existing, impairment of visibility in mandatory class I Federal areas which impairment results from man made air pollution." Under the regulations promulgated for visibility protection (40 CFR §51.301 (x)) visibility impairment is defined as "…any humanly perceptible change in visibility (visual range, contrast, coloration) from that which would have existed under natural conditions." The remainder of this chapter describes methods that allow for new source growth to be analyzed against the constraint of preventing visibility impairment as defined in 40 CFR §51.301 (x), that is, new source growth should not allow any humanly perceptible change in visibility as compared against natural conditions.

Visibility Impairment

Before proceeding with the discussion, it is useful to identify the ways that visibility impairment can manifest itself. First, the pollutant loading of a section of the atmosphere can become visible, by the contrast or color difference between a layer or plume and a viewed background, such as a landscape feature or the sky. The second way that visibility is impaired is a general alteration in the appearance of landscape features or the sky, changing the color or the contrast between landscape features or causing features of a view to disappear. The first phenomenon is commonly referred to as plume impairment, whereas the second phenomenon is sometimes referred to as uniform haze impairment. As plumes are transported within a stable atmospheric layer, they may become a layered haze. As plumes and other more diffuse emission sources are transported and become well mixed in the atmosphere, they may develop into a uniform haze.

Visibility Parameters (Revised)

The analysis methods for new source growth, described in this chapter, deal with the visibility effects of discrete plumes and the aggregation of discrete plumes into a uniform haze. The difference in these phenomena, as treated in this chapter, is whether the visibility effect is primarily seen as a section of the atmosphere which exhibits a change in contrast or color as compared with a viewed background, or whether the effect is due to an alteration of the appearance of the background features themselves. For the first situation, the contrast (C) and color difference index (ΔE) of the plume and the viewing background are calculated. For the second situation, the change in atmospheric light extinction (Δb_{ext}), relative to natural conditions, is calculated. The light extinction is inversely proportional to "visual range." An approximation for which situation applies is the distance from the point of emission. (Distance serves as an indicator of where steady state conditions may apply.) The visibility impairment from sources within 50 kilometers of a view is usually calculated using contrast and color difference, whereas visibility impairment from sources greater than 50 kilometers from a view, or the aggregation of a number of plumes, regardless of distance, is usually calculated using the change in light extinction. The distance approximation is useful for distinguishing these two phenomena; the terms "near field" and "distant/multi-source" are sometimes used in the remainder of this document to make this distinction.

5. Or, an intermittent hourly emission limit could be annualized by multiplying by 8,760 hours per year/2,000 lb/ton (= 4.38).

3.3.2. Recommendations for Evaluating Visibility Impacts (Revised)

There are two fundamentally different approaches one could adopt to determine visibility impairment. One is a technically rigorous, complex, and situation-specific method, while the other is a more generalized approach. The more rigorous approach requires determination of particle concentrations and size distributions, calculation of particle growth dynamics, and application of elaborate physics (e.g., Mie Theory) to determine the optical characteristics of the aerosol distribution. Sophisticated radiative transfer models are then applied, using aerosol optical characteristics, lighting and scene characteristics, and spatial distribution of the pollutants to calculate the path and wavelength of image-forming and non-image-forming light that reaches a specific observer from all points in the scene being viewed.

While such a detailed analysis may be useful for assessing specific cases, it is usually impractical for situations in which visibility could be experienced in a nearly infinite variety of circumstances. Practical limitations frequently dictate that it is more reasonable to use a generalized approach to determine the change in extinction by using bulk-averaged aerosol-specific extinction efficiencies rather than trying to reproduce the complex optical phenomena that may occur in the atmosphere.

Consequently, as a first-level analysis, FLAG recommends the generalized approach for determining the effects on visibility from a proposed new source's emissions. The procedure is to estimate the atmospheric concentrations of visibility impairing pollutants, apply representative visibility parameters, calculate the change from specified reference levels, and compare this change with prescribed threshold values. The more detailed analysis described above may be appropriate as a refined analysis in the event the source fails the first-level analysis.

FLAG is using EPA's estimates of natural visibility conditions under its Regional Haze Rule as reference levels for Class I visibility analyses. Comparison with natural conditions will help ensure that those conditions will not be impaired in keeping with Section 169A of the CAA. Because of the different requirements of the two modeling approaches discussed below, natural conditions should be expressed using two different metrics:

- Standard visual range (visual range adjusted to a Rayleigh condition of 10 Mm^{-1}), for near field modeling. Present EPA guideline visibility models traditionally accept visibility conditions expressed in these terms.
- Extinction, for distant/multi-source modeling. Visibility conditions should be expressed in terms of the averaged extinction efficiencies of the individual atmospheric constituents that comprise the total extinction. The relative humidity effects of the hygroscopic particles should be accounted for when the change in extinction is calculated.

Information needed to calculate the above indices for all 156 Class I areas for which visibility is an important attribute is provided in Tables 5 through 10 at the end of this chapter. If estimates are needed for Class II areas, the FLM can provide them.

3.3.3. Air Quality Models and Visibility Assessment Procedures (Revised)

The modeling discussion will be divided into two parts to address the very different requirements for 1) near field modeling where plumes or layers are compared against a viewing background, and 2) distant/multi-source modeling for plumes and aggregations of plumes that affect the general appearance of a scene. Note that both of the above analyses might apply depending on the source's proximity to all portions of the Class I area or multiple Class I areas.

FLAG 2000 provided information in the form of recommendations, specific processes, and interpretations of results for assessing visibility impacts of sources affecting Class I areas (although some of this information is generally applicable to Class II areas, as well). The information separately addressed assessments for sources proposing to locate relatively near (within 50 km) and at farther distances (greater than 50 km) from these areas. It also recommended impairment thresholds and identified the conditions for which cumulative analyses could be warranted. This revision (FLAG 2010) updates the Distant/Multi-source analysis discussed in FLAG 2000, and clarifies the recommendations regarding the near-field (within 50 km)/steady-state analysis.

Near Field Analysis Technique for Analyzing Plumes or Layers Viewed Against a Background (Revised)

The Model (Near Field – Steady State Conditions Applicable) (Revised)

EPA has recommended a methodology to assess impacts due to coherent plumes. A guideline for when these steady state conditions apply is the distance from the source to the view of concern. This technique is usually applied for sources locating within 50 km of a Class I area. Applicants should first model their potential plume impacts using the screening model, VISCREEN (EPA 1992a), or, if the next level of analysis is called for, PLUVUE II (EPA 1992b and 1996a). Both of these models use steady-state, gaussian-based plume dispersion techniques to calculate one-hour concentrations within an elevated plume. These two models calculate the change in the color difference index (ΔE) and contrast between the plume and the viewing background. Values of ΔE and plume contrast are based on the concentrations of fine primary particulates (including sulfates), nitrogen dioxide (NO_2), and the geometry of the observer, target, plume, and the position of the sun. PLUVUE II also allows

consideration of the effects of secondarily formed sulfates. Plume contrast results from an increase or decrease in light transmitted from the viewing background through the plume to the observer. The specifics of the emission scenarios and plume/observer geometries for modeling should be selected in consultation with the appropriate Agency representatives. At the present time there is no recommended procedure for conducting analyses of multiple sources with these modeling tools, so multiple coherent plumes should be treated individually, or combined into a representative single source if appropriate. Alternatively, the techniques outlined in the Distant/Multi-Source section below may be used on a case-by-case basis.

The Recommended Procedures (Near Field – Steady State Conditions) (Revised)

Until better modeling tools are available, FLAG recommends using the present EPA techniques for plume visual impact screening analyses (EPA 1992c). However, unlike those procedures, which suggest the use of current average annual visibility conditions, FLAG recommends that for Class I areas the visual range corresponding to natural conditions be used to generate the hourly estimates of ΔE and plume contrast. FLAG recommends this change in order for the analysis technique to be consistent with the national visibility goal. For plume analyses, FLAG recommends using the monthly average natural visual range conditions provided for each area in Table 10.

If a screening analysis of a new or modified source can demonstrate that its emissions will not cause a plume with any hourly estimates of ΔE greater than or equal to 2.0, or the absolute value of the contrast values ($|C|$) greater than or equal to 0.05, the FLM is likely not to object to the issuance of the PSD permit based on near field visibility impacts and no further near field visibility analyses will be requested. More refined analyses (i.e., PLUVUE II) would be undertaken if the above conditions are not met and would be compared against lower levels of concern. For PLUVUE II analyses, the FLM would likely not object if $\Delta E < 1.0$ and $|C| < 0.02$.

All analysis for Class I visibility impacts should include all visibility impairing emissions. This means that even if a facility is only considered a significant emitter of one pollutant, all pollutants that may contribute to impairment should be modeled together. Furthermore, since visibility is an instantaneous value, short-term (24-hour) maximum allowable emissions should be used.

- Level-1 Near Field Screening. Conducting a complete refined plume blight analysis can become rather complex, so three levels of evaluation are available to an applicant. The first, Level-1 screening, is the simplest and most conservative method. As described in the EPA's Workbook for Estimating Visibility Impairment (EPA-450/4-80-031):

  > Level-1 Screening: Level-1 screening is designed to provide a conservative estimate of plume visual impacts (i.e., impacts that would be larger than those calculated with more realistic input and modeling assumptions). This conservatism is achieved by the use within the screening model VISCREEN of worst-case meteorological conditions: extremely stable (F) atmospheric condition, coupled with a very low wind speed (1 m/s) persisting for 12 hours, with a wind that would transport the plume directly adjacent to the observer (as shown schematically in Figure 7).

  Since little project specific information is used for a Level-1 screening analysis, documentation requirements are minimal. Basic information of emissions, meteorological parameters, and model results should be provided. Applicants are encouraged to supply electronic copies of all files necessary to reproduce the results. If an application shows estimated impact values within the thresholds, it is unlikely that additional evaluation will be necessary.

- Level-2 Near Field Screening. If Level-2 screening is necessary, more project specific information is now incorporated. Actual meteorology from the area and emission characteristics of the facility are used. Again, as described in the EPA's Workbook for Estimating Visibility Impairment:

  > Level-2 Screening: As shown in Figure 1, Level-2 plume visual impact screening is done if the Level-1 results exceed the screening criteria. The objective of Level-2 screening is identical to that of Level-1—the estimation of worst-day plume visual impacts—but in Level-2 screening more realistic (less conservative) input, representative of the given source and the Class I area, is provided. This situation-specific input may include particle size distributions for plume and background that are different from those used in the default Level-1 analysis. Median background visual range based on on-site measurements rather than the map shown in Figure 9 might be used. However, the most important potential difference in input between Level-1 and Level-2 analysis centers on meteorology and plume transport and dispersion patterns. While the Level-1 analysis assumes F stability, a 1 m/s wind speed, and a wind direction that would carry plume material very close to the observer, in the Level-2 analysis, meteorological data and topography representative of the source area and Class I area may suggest that worst-case plume dispersion conditions are different.

  It is important to note that the Agency's guidance contained the recommendation that all applicants compare

estimated modeled impacts from a facility against natural conditions. This is true for all analysis levels. The use of five years of site-representative meteorology and facility-specific emission characteristics is what makes this analysis different.

As a result of the increased project-specific information, documentation also should include summaries and/or tables describing the additional data sets and evaluation steps taken to conduct the analysis.

Once again, meeting screening thresholds means that it is likely that the Agencies' Class I air quality modeling procedures will have been satisfied.

- Level-3 Near Field Refined Analysis. A Level-3 analysis is the final assessment. An applicant can conduct a full refined analysis demonstrating estimates of frequency, magnitude, and spatial extent of a proposed project's visibility impacts. The EPA's Workbook for Estimating Visibility Impairment says:

  > Level-3 Analysis: In Level-3 analysis, the objective is broadened from conservative analysis of worst-case conditions to a realistic analysis of all conditions that would be expected to occur in a typical year in the region that includes both the emission source and the observer. Level-3 analysis is no longer considered screening because it is a comprehensive analysis of the magnitude and frequency of occurrence of plume visual impacts as observed at a sensitive Class I area vista.
  >
  > It is important to determine the frequency of occurrence of visual impact because the adversity or significance of impact is dependent on how frequently an impact of a given magnitude occurs. For example, if a plume is perceptible from a Class I area a third of the time, the impact would be considered much more significant than if it were perceptible only one day per year. The assessment of frequency of occurrence of impact should be an integral part of Level-3 visual impact analysis.

  As mentioned above, the threshold values for this analysis step changed. For this step, EPA's PLUVUE II model is currently recommended. One main difference with PLUVUE II is its inability to evaluate more than one hour of impact per run. Because it is customary to evaluate five years of site-specific meteorology, it can become an extensive process. Applicants may want to develop and utilize tools to group hourly meteorological and post processing scenarios. The analysis identifies specific locations for plume/observer relationships. These observation points should be established within each potentially impacted Class I area. With each observer, potential impacts are calculated for all possible views. As with the meteorology, PLUVUE II is only able to assess one observer location per model run. Specific information on setup methods can be found in EPA's Workbook for Estimating Visibility Impairment and PLUVUE II manual.

  Substantial documentation is needed for this more refined analysis. The discussion should summarize data sources, processing methods, and modeling utilities used, and information regarding all assumptions or consolidation criteria. In short, sufficient information and electronic files should be provided to the Agencies that will allow reviewers to reproduce the results. Due to the complexity of this refined analysis, the Agencies suggest that consultation occur between the applicant and the Agencies before working on the impact analysis begins. Furthermore, selection of model parameters and input data should be documented in a written protocol and agreed upon by the affected Agencies in advance of any modeling being conducted.

If the estimated plume parameters exceed the aforementioned values, the FLM would rely on a case-by-case effects-based test (NPS 1993), taking into account magnitude, frequency, duration, and other factors, to decide whether to make an adverse impact determination.

Distant/Multi-Source Techniques for Analyzing Whether a Plume or an Aggregation of Plumes Alters the General Appearance of a Scene (Revised)

This analysis is generally more complex than the near field, coherent plume modeling analyses and the guidance from EPA is less definitive, though it is evolving. The modeling system should include the capability to assess single and multiple sources in a temporally and spatially varying meteorological domain, accommodate modeling domains measuring hundreds of kilometers, include rough and complex terrain, provide pollutant concentration estimates for averaging times from one-hour to annual, and address inert and secondarily formed pollutants and dry and wet deposition. In the early 1990s the FLMs and the EPA recognized the need for a consistent, technically credible technique to estimate contributions to air quality of multiple new sources locating more than 50 km from Class I areas. Towards that end, on April 15, 2003, the EPA promulgated revisions to Appendix W of 40 C.F.R. §51 (*Guideline on Air Quality Models*). The EPA revised the Guideline to adopt the CALPUFF model as the preferred long-range transport model for inclusion in Appendix A of that document. This technique is usually applied when sources are located more than 50 kilometers from portions of a Class I area, when an aggregation of plumes may impact an area, or when the assumptions inherent in steady state visibility models do not apply.

The first-level analysis procedures discussed in this revision differ from FLAG 2000 in several discrete areas, but

generally remain the same. The primary differences are in the areas of the reference natural conditions that are used in the comparisons for thresholds of concern and using the average monthly relative humidity adjustment factors rather than the hour-by-hour factors identified in FLAG 2000. CALPUFF is still the preferred first-level air quality model for calculating pollutant concentrations, however, using "CALPUFF Lite" with single station meteorology is no longer recommended. We wish to emphasize that the first-level procedures defined herein are to be taken as a whole; any deviations from these procedures or ostensible refinements compromise the integrity of the analysis, and may warrant an hourly analysis for all hours in the analysis. Furthermore, the metric used for the first-level analysis (relative change in light extinction) is not necessarily the appropriate metric for a refined analysis. The procedures and metrics for refined analyses will need to be agreed upon by the affected Agencies.

The initial step in conducting the first-level analysis is to run CALPUFF using a minimum of three years of mesoscale meteorological model output, and preferably five years, consistent with current EPA guidance. Selection of model parameters and input data should be documented in a written protocol and agreed upon by the affected Agencies in advance of any modeling being conducted. Please note emissions input considerations and model receptor grid data are discussed below. The indices for comparison with the Agencies' levels of concern are calculated in CALPOST. The remainder of this discussion is focused on CALPOST.

After CALPUFF is run, CALPOST is used to evaluate whether the proposed source or modification will be below the Agencies' threshold for concern (i.e., 5% change in light extinction). The CALPOST parameter MVISBK is set to eight (8), sub-mode five (M8_MODE = 5), and the background hygroscopic and non-hygroscopic aerosol levels are derived from the annual average natural conditions provided in Table 6. The monthly relative humidity adjustment factors for the Class I area are input to the RHFAC array (Tables 7-9) in CALPOST. The 98th percentile test applies to the number of days that any model receptor in the Class I area exceeds the threshold. The visibility threshold for concern is not exceeded if the 98th percentile change in light extinction is less than 5% for each year modeled, when compared to the annual average natural condition value for that Class I area.

If this analysis indicates that the 98th percentile values for change in light extinction are equal to or greater than 5% for any year, then the Agencies will further scrutinize the applicant's proposal. The Agencies will consider the full range of factors discussed below (in the "Expansion of Discussion of Process for Adverse Impact Determination" chapter) and any refined analyses provided by the applicant before making a recommendation to the FLM regarding potential adverse impacts. As noted above, these refined analyses should account for the relevant physicochemical processes that produce visibility impairing pollutants and accurately treat the relevant radiative transfer properties affecting visibility. This will likely entail using different meteorological and air quality models capable of producing hourly concentrations, or less, and using a three dimensional radiative transfer model (see refined analysis discussion below).

For consistency with implementation of BART or the regional haze rule to specific Class I areas, the FLM or permitting authority may recommend use of the 20% best natural background values provided in Table 5 in lieu of annual averages on a case-by-case basis.

Background Information on Thresholds

In its BART guidelines, EPA indicated that for regional haze, a source whose 98th percentile value of the haze index is greater than 0.5 deciview (dv) (approximately a 5% change in light extinction) is considered to contribute to regional haze visibility impairment. Similarly, a source that exceeds 1.0 dv (approximately a 10% change in light extinction) causes visibility impairment. The 0.5 dv and 1.0 dv thresholds are similar to what the Agencies used in FLAG 2000. Therefore, for consistency between visibility protection programs and to address similar concerns, the Agencies will also use the 98th percentile value as a threshold in the first-level visibility analyses for new source impacts.

In its 2005 BART guidelines, the EPA also concluded that by using the 98th percentile of CALPUFF modeled impacts the sources that contribute 0.5 deciview to regional haze visibility impairment in a Class I area would effectively be captured, while minimizing the likelihood that the highest modeled visibility impacts might be caused by conservative assumptions in the model. Similarly, using the monthly average relative humidity adjustment factors, rather than the hour-by-hour factors, reduces some of the higher (e.g., weather –related) values seen in FLAG 2000.

Using the 98th percentile of modeled visibility values to compare to the 5% change in extinction threshold would exclude roughly seven days per year from consideration for each Class I area. However, consistent with the BART guidelines, the 98th percentile test applies to the number of days that any model receptor in the Class I area exceeds the threshold. Also, this test is limited to haze-like, first-level analyses. Therefore, all applicable sources locating within 50 km of a Class I area would still need to assess coherent plume impacts in accordance with the procedure described above. Furthermore, applicable sources would need to assess sulfur and nitrogen deposition impacts at the Class I area.

Natural Conditions

FLAG 2000 discussed assessing the change in visibility due to a proposed new source relative to annual average natural conditions. Therefore, it is important to define

natural conditions for each Class I area. At the time of FLAG 2000, the Agencies acknowledged that the EPA was working on defining natural conditions in support of their visibility regulations. In the absence of more specific data, the FLMs at that time adopted the appropriate aerosol concentrations developed by the National Acid Precipitation Assessment Program (NAPAP) as estimates of natural conditions for each Class I area. The EPA has since published natural condition estimates for each Class I area. The natural condition values provided in FLAG 2000 and those developed by the EPA are based on similar underlying assumptions; consequently, the estimates are similar. Regardless, the EPA estimates should be used by applicants in future visibility impact assessments. Please note that Tables 5 and 6 contain estimates for the 20% best natural visibility and annual average natural visibility conditions for each Class I area, respectively.

Relative Humidity Adjustment Factor

FLAG 2000 discussed the importance of the relative humidity adjustment factor (f(RH)) when calculating the sulfate and nitrate components of the visibility extinction coefficient. These aerosols are hygroscopic and the addition of water enhances their scattering efficiencies. FLAG 2000 recommended using hour-by-hour f(RH) for the analysis. The EPA, in its 2005 BART guidelines, concluded that by using a monthly average f(RH) the likelihood that the highest modeled visibility impacts were caused by short-term and geographically different meteorological phenomena (e.g., weather events) would be minimized. The Agencies agree with the EPA that using the monthly f(RH) effectively neutralizes short-term weather events and are adopting a similar approach for Class I visibility impact analyses for new sources. Therefore, new sources performing Class I visibility analyses should use monthly average f(RH) values developed by EPA for large hygroscopic particles (Table 7), small hygroscopic particles (Table 8), and sea salt (Table 9), rather than the hourly values discussed in FLAG 2000.

Emissions Input

There are two other aspects of the visibility impact analysis that the Agencies would like to clarify at this time: (1) emissions input, and (2) the model receptor grid. Regarding the emission inputs, because applicants are assessing a 24-hour average regional haze visibility impact, it is important that they model a corresponding maximum allowable 24-hour mass emission rate, as opposed to monthly or annual average emissions. Using a 30 day average emission rate as input to the visibility modeling analyses does not restrict the facility from emitting pollution at a higher rate for shorter time periods (e.g., 24-hour average). A 30 day average emission rate smooths out days with high emissions, and therefore, would underestimate the predicted 24-hour visibility impacts. Because the emission rates and the corresponding averaging times influence the outcome of the analyses, it is critical that appropriate emissions are matched to the averaging time being assessed, and that these emission rates ultimately are included as enforceable permit conditions. This approach is consistent with the *Guideline on Air Quality Models* (Appendix W of 40 C.F.R. §51) and the EPA BART guidelines. Furthermore, if an applicant chooses to conduct any refined analyses, where visibility impairment is assessed at no more than an hourly basis, maximum hourly emissions should be analyzed.

Please note that all visibility impairing pollutants should be modeled from all modified or affected emission unit(s), regardless of which pollutants actually triggered NSR. Particulate Matter (PM) should also be speciated into filterable PM (coarse, fine, elemental carbon) and Condensable PM (organic carbon and sulfates) based on the best available information. Particulate speciation data for several source types can be found on the NPS Air Resources Division's web site at:

- http://www.nature.nps.gov/air/permits/ect/index.cfm

Applicants should calculate the 24-hour average net emission increase for each pollutant from modified facilities as the maximum allowable 24-hour average minus the actual hourly rate averaged over the past two years (annual emissions over past two years/hours of operation over last two years).[6]

Model Receptor Grid

Since FLAG 2000 was published, the NPS Air Resources Division has developed a database of modeling receptors for all of the Class I areas in the contiguous United States. A file conversion program to convert the data from latitude/longitude to other common mapping coordinates (currently Lambert Conformal and Universal Transverse Mercator (UTM)) has also been developed. Alaska and Hawaii are not yet complete, but will be included in the data sets when they are available.

Permit applicants can download the Class I Receptor Data files, as well as the Conversion program, from the link below. For modeling consistency, the Agencies ask that permit applicants use the uniform receptor grids provided. Also available are the Class I boundary shape files that were used to create the receptor data files.

- http://www.nature.nps.gov/air/Maps/Receptors/index.cfm

Receptor grids for FLM Class II areas should be dense enough to determine Class II increment consumption and

6. Note that this is different from the emission change calculation used for short-term increment, which is calculated as the maximum allowable 24-hour average minus the highest occurrence over the past two years.

to perform any required "secondary impacts" (i.e., soils, vegetation and visibility) analyses.

Refined Analysis

It is important to reiterate that the FLAG distant/multi-source visibility analysis is only a first-level screening technique, primarily designed to identify those sources that are unlikely to significantly affect visibility and warrant no further analysis, and those that may adversely impact visibility and warrant further scrutiny. Visibility is experienced instantaneously, not on a 24-hour average basis. The 24-hour average visibility calculation in FLAG is acceptable because of a number of simplifying assumptions in the prescribed technique. Accepting certain EPA BART guideline procedures as an update to the FLAG techniques does not alter the first-level nature of the procedure. Modifying those simplifying assumptions negates the acceptability of using a 24-hour average. Consequently, any applicant whose visibility analysis deviates from the recommended FLAG screening procedures warrants performing an hour-by-hour analysis.

Deviations from the first-level screening procedure should lead to refinements in the modeling and visibility analyses, not arbitrary adjustments to the prescribed first-level technique. This is especially important in dealing with weather-related events. The Agencies believe that by paralleling the BART guideline procedures they have adequately taken into account the effects of meteorological extremes, and model uncertainty. Therefore, given the Agencies' desire to balance the positive and negative biases of the FLAG screening methodology, any modifications to the screening technique invalidate the Level 1 model results. Consequently, the Agencies do not expect permit applicants that exceed the visibility effects thresholds to scrutinize the data and attempt to disregard specific impact days due to weather. Under those circumstances, the permit applicant can accept the modeling results at face value, and then the FLM will decide whether or not those impacts are adverse. Alternatively, the applicant could conduct an hour-by-hour analysis (as opposed to using a 24-hour average) by performing a refined analysis using a more sophisticated approach that requires determining particle concentrations and size distributions, calculation of particle growth dynamics, and application of Mie Theory to determine the optical characteristics of the aerosol distribution. Sophisticated radiative transfer models can then be applied, using aerosol optical characteristics, lighting and scene characteristics, and spatial distribution of the pollutants to calculate the path and wavelength of image-forming and non-image-forming light that reaches a specific observer from all points in the scene being viewed. The concept of this more refined approach is discussed in FLAG 2000, and one possible approach is included in "*Proposed FLAG Level II and III Visibility Assessment*" (Schichtel et al. 2006). However, if this situation arises, permit applicants are encouraged to consult with the Agencies and discuss the specifics of this refined analysis.

3.3.4. Summary (Revised)

FLAG provides recommendations, specific procedures, and interpretation of results for assessing visibility impacts of new or modified sources on Class I area resources. Although FLMs only have a formal role in the permitting process for applications that affect Class I areas, this information can be used for Class II areas as well. FLAG addresses assessments for sources proposed for locations near (generally within 50 km) and at large distances (greater than 50 km) from these areas. The key components of the recommendations are highlighted below.

In general, FLAG recommends that an applicant:

- Apply the Q/D test (see section 3.2, 'Initial Screening Criteria') for proposed sources greater than 50 km from a Class I area to determine whether or not any further visibility analysis is necessary.
- Consult with the appropriate regulatory agency and with the FLM for the affected Class I area(s) or other affected area for confirmation of preferred visibility analysis procedures.
- Obtain FLM recommendation for the specified reference levels (estimate of natural conditions) and, if applicable, FLM recommended plume/observer geometries and model receptor locations.
- Apply the applicable EPA Guideline, steady-state models for regions within the Class I area that are affected by plumes or layers that are viewed against a background (generally within 50 km of the source).
    - Calculate hourly estimates of changes in visibility, as characterized by the change in the color difference index (ΔE) and plume contrast (C), with respect to natural conditions, and compare these estimates with the thresholds given in section 3.3.3.
- For regions of the Class I area where visibility impairment from the source would cause a general alteration of the appearance of the scene (generally 50 km or more away from the source or from the interaction of the emissions from multiple sources), apply a non-steady-state air quality model with chemical transformation capabilities (refer to EPA guidance documents), which yields ambient concentrations of visibility-impairing pollutants. At each Class I receptor:
    - Calculate the change in extinction due to the source being analyzed, compare these changes with the reference conditions, and then compare these results with the thresholds given in section 3.3.3.
    - Utilize estimates of annual average natural visibility conditions for each Class I area as presented in Table 6, unless otherwise recommended by the

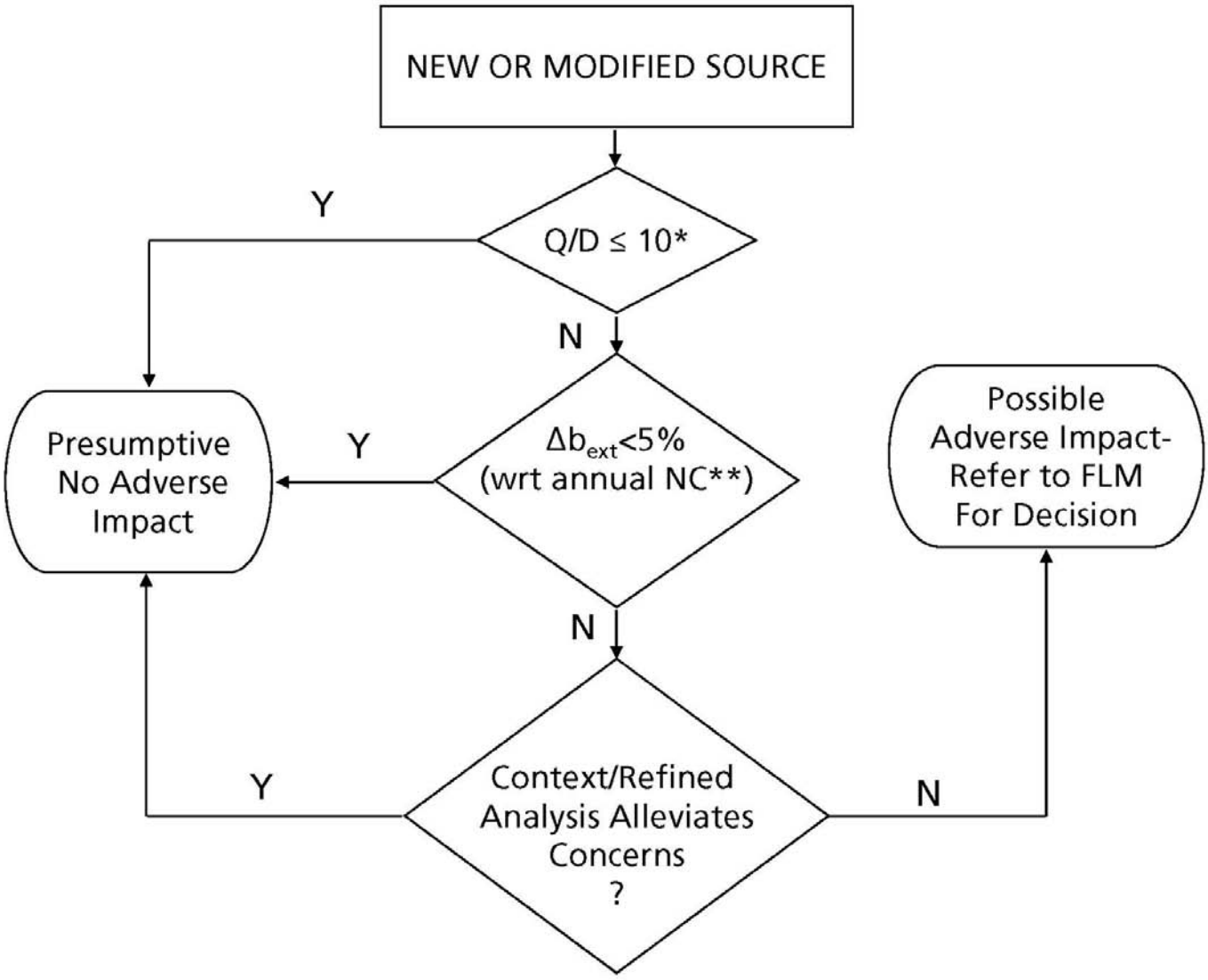

Figure 4. Procedure for Visibility Assessment for Distant/Multi-Source Applications (Revised)
*Q/D test only applies to sources located greater that 50 km from a Class I area.
**Difference Change in the 98th percentile with respect to (wrt) the annual average Natural Condition (NC). Applicant should use the 20th percentile best natural condition background if recommended by the FLM or permitting authority.

FLM or permitting authority. Alternative estimates of visibility conditions are provided in Table 5 for consistency with State agencies that elected to use 20% best visibility for regional haze or BART implementations.

- If first-level modeling results are above levels of concern, continue to consult with the Agencies to discuss other considerations (e.g., possible impact mitigation, more refined analyses).

This review process for distant/multi-source applications is portrayed schematically in Figure 4.

3.3.5. Natural Visibility Conditions and Analysis Methods (New)

Both distant/multi-source applications and near-field analyses require an estimate of natural visibility conditions. The effects of visibility impairing emissions from a source are compared to the natural visibility conditions to determine the potential for unacceptable visibility impacts. The methods and data for calculating natural visibility conditions in FLAG are presented in this section. The calculation of visibility metrics under the distant/multi-source application is also described. For the distant/multi-source application, aerosol species components are provided from the CALPUFF modeling system, which is the suggested model

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for most of these applications. For near-field analyses, visual ranges under natural conditions are provided for input to the VISCREEN and PLUVUE-II models.

Natural visibility conditions

Distant/Multi-source: Natural visibility conditions are affected by the light scattering of air molecules (Rayleigh scattering) and by naturally occurring aerosols. The majority of aerosols, both natural and anthropogenic, that affect light extinction can be categorized as sulfates ($(NH_4)_2SO_4$), nitrates (NH_4NO_3), organic mass (OM), elemental carbon (EC), soil, sea salt, and coarse mass (CM). The light scattering efficiency of aerosols is affected by the size of the aerosol relative to the wavelength of light. Sulfates, nitrates, and sea salt are all hygroscopic, which affects their size and their light scattering efficiency as they acquire or shed water molecules. The relationship between the aerosol components and light extinction is shown through the equations in Figure 5. The hygroscopic effects are accounted for through the relative humidity adjustment factors (f(RH)) terms in the equations in Figure 5. The aerosol concentrations and monthly relative humidity adjustment factors for calculating natural visibility conditions are found in Tables 5 through 10.

Table 2. Section of Table 6 Used for Step 1 Calculations of the Alpine Lakes Wilderness Example

Class I Area	$(NH_4)_2SO_4$ µg/m³	NH_4NO_3 µg/m³	OM µg/m³	EC µg/m³	Soil µg/m³	CM µg/m³	Sea Salt µg/m³	Rayleigh Mm^{-1}
Acadia NP	0.23	0.10	1.67	0.02	0.24	2.14	0.14	12
Agua Tibia Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.14	11
Alpine Lakes Wilderness	0.12	0.10	0.60	0.02	0.23	1.30	0.06	11
…	…	…	…	…	…	…	…	…

The aerosol concentrations for the 20% best natural conditions are found in Table 5 and the annual average natural concentrations are found in Table 6.

Near-field: The near-field visibility analysis is generally performed using either VISCREEN or PLUVUE-II. For calculating the effect of a plume on visibility, a background visibility, expressed as a visual range, must be input to these models. Appropriate average natural conditions, by month and Class I area are listed in Table 10. The values in Table 10 were determined by calculating the month by month light extinction values and calculating the visual range (VR) ($VR=3912/b_{ext}$).

Example Calculation of Natural Conditions and Change in Light Extinction

The annual average concentration and the relative humidity adjustment factors ($f_{\{L,S,SS\}}(RH)$) for the Alpine Lakes Wilderness for January will be used for illustration of the calculations.

1. Look up the Alpine Lakes Wilderness annual average concentration values in Table 6 for sulfate ($(NH_4)_2SO_4$), nitrate (NH_4NO_3), organic mass (OM), Elemental Carbon (EC), soil, coarse mass (CM), sea salt, and Rayleigh scattering.
2. Look up the f(RH) factors for large sulfate/nitrate (table 7), small sulfate/nitrate (table 8), and sea salt (table 9); January in this example.
   a. $f_L(RH) = 3.86$
   b. $f_S(RH) = 5.87$
   c. $f_{SS}(RH) = 5.35$
3. Calculate the large and small sulfate, nitrate, and organic mass, as defined in Figure 5.

Table 3. Step 3 Calculation Results for the Alpine Lakes Wilderness Example

	Total	Large	Small
Sulfate	0.12	0.00072	0.11928
Nitrate	0.10	0.0005	0.0995
Organic Mass	0.60	0.018	0.582

4. Apply to b_{ext} equation in Figure 5:

b_{ext}=

$2.2 \times 5.87 \times 0.11928 + 4.8 \times 3.86 \times 0.00072$	{Sulfate}
$+ 2.4 \times 5.87 \times 0.0995 + 5.1 \times 3.86 \times 0.0005$	{Nitrate}
$+ 2.8 \times 0.582 + 6.1 \times 0.018$	{Organic Mass}
$+ 10 \times 0.02$	{Elemental Carbon}
$+ 1 \times 0.23$	{Soil}
$+ 0.6 \times 1.30$	{Coarse Mass}
$+ 1.7 \times 5.35 \times 0.06\}$	{Sea Salt
$+ 11$	{Rayleigh}
$+ 0.33 \times 0$	{NO_2}

b_{ext} $=17.46\ Mm^{-1}$

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To calculate the change in light extinction from the impacts from an air pollution source, the species concentrations from the source are added to the total species concentrations in steps 3 and 4 above and the new total light extinction is calculated. Therefore, if a source contributed 0.05 µg/m^3 of sulfate ($(NH_4)_2SO_4$) and 0.01 µg/m^3 of nitrate (NH_4NO_3) at a receptor, the total, large and small sulfate and nitrate values would be:

Table 4. Step 4 Calculation Results for the Alpine Lakes Wilderness Example

	Total	Large	Small
Sulfate	0.17 (0.12+0.05)	0.001445	0.168555
Nitrate	0.11 (0.10+0.01)	0.000605	0.109395

The other concentrations and the relative humidity adjustment factors would remain as in step 4 of the natural condition example. After recalculating the light extinction accounting for the effect of the source ($b_{ext(source+nat\ cond)}$), the new light extinction would be 18.25 Mm^{-1}.

The change in light extinction (Δb_{ext}) would simply be:

$$\Delta b_{ext} = (b_{ext(source+nat\ cond)} - b_{ext(nat\ cond)}) / b_{ext(nat\ cond)} \text{ or:}$$

$$\Delta b_{ext} = (18.25 - 17.46) / 17.46$$

$$\Delta b_{ext} = 0.045\ (4.5\%)$$

The example provided here is to illustrate the process. Usually the concentrations and relative humidity adjustment factors would be extracted from the appropriate tables and input to one of the air quality model post processing programs.

$$b_{ext} = 2.2 \times f_S(RH) \times [\text{Small Sulfate}] + 4.8 \times f_L(RH) \times [\text{Large Sulfate}]$$
$$+ 2.4 \times f_S(RH) \times [\text{Small Nitrate}] + 5.1 \times f_L(RH) \times [\text{Large Nitrate}]$$
$$+ 2.8 \times [\text{Small Organic Mass}] + 6.1 \times [\text{Large Organic Mass}]$$
$$+ 10 \times [\text{Elemental Carbon}]$$
$$+ 1 \times [\text{Fine Soil}]$$
$$+ 0.6 \times [\text{Coarse Mass}]$$
$$+ 1.7 \times f_{SS}(RH) \times [\text{Sea Salt}]$$
$$+ \text{Rayleigh Scattering (Site Specific)}$$
$$+ 0.33 \times [NO_2 \text{ (ppb)}] \quad \{\text{or as: } 0.1755 \times [NO_2 \text{ (}\mu g/m^3\text{)}]\}$$

Where:

[ ] indicates concentrations in $\mu g/m^3$

$f_S(RH)$ = Relative humidity adjustment factor for small sulfate and nitrate

$f_L(RH)$ = Relative humidity adjustment factor for large sulfate and nitrate

$f_{SS}(RH)$ = Relative humidity adjustment factor for sea salt

For Total Sulfate $< 20\ \mu g/m^3$:

$$[\text{Large Sulfate}] = ([\text{Total Sulfate}] / 20\ \mu g/m^3) \times [\text{Total Sulfate}]$$

For Total Sulfate $\geq 20\ \mu g/m^3$:

$$[\text{Large Sulfate}] = [\text{Total Sulfate}]$$

And:

$$[\text{Small Sulfate}] = [\text{Total Sulfate}] - [\text{Large Sulfate}]$$

To calculate large and small nitrate and organic mass, substitute ({Large, Small, Total} {Nitrate, Organic Mass}) for Sulfate.

Figure 5. IMPROVE Equation for Calculating Light Extinction
http://vista.cira.colostate.edu/improve/Publications/GrayLit/019_RevisedIMPROVEeq/RevisedIMPROVEAlgorithm3.doc

Table 5. Page Best Natural Conditions – Concentrations and Rayleigh Scattering By Class I Area

Class I Area	$(NH_4)_2SO_4$ µg/m3	NH_4NO_3 µg/m3	OM µg/m³	EC µg/m³	Soil µg/m³	CM µg/m³	Sea Salt µg/m³	Rayleigh Mm^{-1}	Type
Acadia NP	0.09	0.03	0.68	0.01	0.10	0.94	0.03	12	B20%
Agua Tibia Wilderness	0.03	0.04	0.26	0.01	0.26	1.20	0.04	11	B20%
Alpine Lakes Wilderness	0.04	0.03	0.15	0.01	0.05	0.30	0.02	11	B20%
Anaconda Pintler Wilderness	0.04	0.03	0.12	0.01	0.07	0.31	0.00	10	B20%
Ansel Adams Wilderness	0.02	0.01	0.12	0.01	0.07	0.44	0.01	9	B20%
Arches NP	0.07	0.06	0.23	0.01	0.14	0.89	0.01	9	B20%
Badlands NP	0.05	0.05	0.23	0.01	0.22	0.99	0.00	11	B20%
Bandelier NM	0.07	0.06	0.31	0.01	0.16	0.91	0.00	9	B20%
Bering Sea Wilderness									B20%
Big Bend NP	0.05	0.04	0.24	0.01	0.11	0.80	0.00	10	B20%
Black Canyon of the Gunnison NP	0.06	0.04	0.24	0.01	0.13	0.88	0.00	9	B20%
Bob Marshall Wilderness	0.05	0.04	0.19	0.01	0.08	0.37	0.00	10	B20%
Bosque del Apache Wilderness	0.08	0.06	0.30	0.01	0.15	0.97	0.02	10	B20%
Boundary Waters Canoe Area Wilderness	0.11	0.02	0.50	0.01	0.13	0.86	0.01	11	B20%
Breton Wilderness	0.14	0.05	0.73	0.01	0.27	2.26	0.07	11	B20%
Bridger Wilderness	0.05	0.04	0.14	0.01	0.07	0.33	0.00	9	B20%
Brigantine Wilderness	0.12	0.04	0.86	0.01	0.24	1.73	0.04	12	B20%
Bryce Canyon NP	0.04	0.05	0.18	0.01	0.10	0.60	0.00	9	B20%
Cabinet Mountains Wilderness	0.05	0.05	0.13	0.01	0.09	0.42	0.01	10	B20%
Caney Creek Wilderness	0.07	0.06	0.68	0.01	0.14	1.51	0.02	11	B20%
Canyonlands NP	0.07	0.06	0.23	0.01	0.14	0.89	0.01	9	B20%
Cape Romain Wilderness	0.14	0.06	0.88	0.01	0.24	1.99	0.04	12	B20%
Capitol Reef NP	0.06	0.07	0.26	0.01	0.15	0.79	0.01	9	B20%
Caribou Wilderness	0.03	0.02	0.12	0.01	0.08	0.24	0.01	10	B20%
Carlsbad Caverns NP	0.06	0.05	0.26	0.01	0.12	0.82	0.00	9	B20%
Chassahowitzka Wilderness	0.14	0.08	1.02	0.01	0.28	2.46	0.02	11	B20%
Chiricahua NM	0.06	0.05	0.27	0.01	0.13	0.81	0.00	10	B20%
Chiricahua Wilderness	0.06	0.05	0.27	0.01	0.13	0.81	0.00	10	B20%
Cohutta Wilderness	0.09	0.08	0.69	0.01	0.15	1.06	0.01	11	B20%
Crater Lake NP	0.02	0.02	0.08	0.01	0.07	0.23	0.01	9	B20%
Craters of the Moon NM	0.06	0.05	0.19	0.01	0.12	0.69	0.01	10	B20%
Cucamonga Wilderness	0.03	0.03	0.15	0.01	0.14	0.67	0.01	9	B20%
Denali NP & Pres	0.04	0.02	0.08	0.01	0.05	0.31	0.01	11	B20%
Desolation Wilderness	0.04	0.03	0.15	0.01	0.09	0.51	0.01	9	B20%
Diamond Peak Wilderness	0.02	0.02	0.08	0.01	0.07	0.23	0.01	9	B20%
Dolly Sods Wilderness	0.10	0.05	0.80	0.01	0.17	0.96	0.01	10	B20%
Dome Land Wilderness	0.03	0.02	0.18	0.01	0.08	0.43	0.01	10	B20%
Eagle Cap Wilderness	0.05	0.02	0.17	0.01	0.10	0.50	0.01	10	B20%
Eagles Nest Wilderness	0.04	0.03	0.14	0.01	0.08	0.36	0.00	8	B20%
Emigrant Wilderness	0.03	0.02	0.10	0.00	0.08	0.50	0.01	10	B20%
Everglades NP	0.16	0.07	0.77	0.01	0.16	1.86	0.12	11	B20%
Fitzpatrick Wilderness	0.05	0.04	0.14	0.01	0.07	0.33	0.00	9	B20%
Flat Tops Wilderness	0.04	0.03	0.14	0.01	0.08	0.36	0.00	8	B20%
Galiuro Wilderness	0.06	0.05	0.27	0.01	0.13	0.81	0.00	10	B20%

Table 9. 20% Best Natural Conditions – Concentrations and Rayleigh Scattering By Class I Area

Class I Area	$(NH_4)_2SO_4$ µg/m3	NH_4NO_3 µg/m3	OM µg/m³	EC µg/m³	Soil µg/m³	CM µg/m³	Sea Salt µg/m³	Rayleigh Mm^{-1}	Type
Gates of the Mountains Wilderness	0.04	0.04	0.13	0.01	0.07	0.49	0.00	9	B20%
Gearhart Mountain Wilderness	0.02	0.02	0.08	0.01	0.07	0.23	0.01	9	B20%
Gila Wilderness	0.06	0.04	0.22	0.01	0.09	0.45	0.00	9	B20%
Glacier NP	0.05	0.03	0.17	0.01	0.11	0.57	0.00	11	B20%
Glacier Peak Wilderness	0.02	0.03	0.09	0.00	0.04	0.28	0.01	11	B20%
Goat Rocks Wilderness	0.02	0.01	0.06	0.00	0.04	0.21	0.01	10	B20%
Grand Canyon NP	0.04	0.03	0.12	0.01	0.10	0.59	0.00	9	B20%
Grand Teton NP	0.06	0.05	0.17	0.01	0.08	0.33	0.00	9	B20%
Great Gulf Wilderness	0.09	0.04	0.56	0.01	0.10	1.05	0.02	11	B20%
Great Sand Dunes NP & Pres	0.06	0.05	0.29	0.01	0.15	0.90	0.00	9	B20%
Great Smoky Mountains NP	0.09	0.06	0.78	0.01	0.16	1.47	0.01	11	B20%
Guadalupe Mountains NP	0.06	0.05	0.26	0.01	0.12	0.82	0.00	9	B20%
Haleakala NP	0.05	0.04	0.24	0.01	0.11	1.59	0.13	10	B20%
Hawaii Volcanoes NP	0.03	0.04	0.27	0.01	0.06	0.64	0.11	10	B20%
Hells Canyon Wilderness	0.06	0.02	0.19	0.01	0.14	0.81	0.01	11	B20%
Hercules-Glades Wilderness	0.09	0.06	0.78	0.01	0.16	1.86	0.02	11	B20%
Hoover Wilderness	0.03	0.02	0.08	0.01	0.06	0.55	0.00	9	B20%
Isle Royale NP	0.10	0.02	0.34	0.01	0.09	0.79	0.01	12	B20%
James River Face Wilderness	0.11	0.06	0.71	0.01	0.20	1.39	0.01	11	B20%
Jarbidge Wilderness	0.05	0.03	0.14	0.01	0.05	0.33	0.00	10	B20%
John Muir Wilderness	0.02	0.01	0.12	0.01	0.07	0.44	0.01	9	B20%
Joshua Tree NP	0.04	0.02	0.20	0.01	0.17	0.94	0.02	10	B20%
Joyce Kilmer-Slickrock Wilderness	0.09	0.06	0.78	0.01	0.16	1.47	0.01	11	B20%
Kaiser Wilderness	0.02	0.01	0.12	0.01	0.07	0.44	0.01	9	B20%
Kalmiopsis Wilderness	0.03	0.02	0.31	0.01	0.05	0.99	0.04	12	B20%
Kings Canyon	0.03	0.03	0.18	0.01	0.08	0.73	0.02	11	B20%
La Garita Wilderness	0.06	0.04	0.24	0.01	0.13	0.88	0.00	9	B20%
Lassen Volcanic NP	0.03	0.02	0.12	0.01	0.08	0.24	0.01	10	B20%
Lava Beds NM	0.03	0.03	0.14	0.01	0.06	0.46	0.00	10	B20%
Linville Gorge Wilderness	0.08	0.06	0.67	0.01	0.14	1.04	0.01	11	B20%
Lostwood Wilderness	0.06	0.04	0.23	0.01	0.22	1.05	0.01	11	B20%
Lye Brook Wilderness	0.05	0.03	0.36	0.01	0.09	0.63	0.01	11	B20%
Mammoth Cave NP	0.11	0.08	0.86	0.01	0.24	1.54	0.01	11	B20%
Marble Mountain Wilderness	0.03	0.02	0.12	0.01	0.06	0.36	0.01	10	B20%
Maroon Bells-Snowmass Wilderness	0.04	0.03	0.14	0.01	0.08	0.36	0.00	8	B20%
Mazatzal Wilderness	0.06	0.05	0.30	0.01	0.14	0.80	0.00	10	B20%
Medicine Lake Wilderness	0.06	0.05	0.24	0.01	0.20	1.13	0.00	11	B20%
Mesa Verde NP	0.06	0.05	0.24	0.01	0.17	0.67	0.00	9	B20%
Mingo Wilderness	0.12	0.04	0.88	0.01	0.21	1.49	0.01	12	B20%
Mission Mountains Wilderness	0.05	0.04	0.19	0.01	0.08	0.37	0.00	10	B20%
Mokelumne Wilderness	0.04	0.03	0.15	0.01	0.09	0.51	0.01	9	B20%
Moosehorn Wilderness	0.11	0.04	0.76	0.01	0.12	1.25	0.02	12	B20%
Mount Adams Wilderness	0.02	0.01	0.06	0.00	0.04	0.21	0.01	10	B20%
Mount Baldy Wilderness	0.05	0.04	0.19	0.01	0.11	0.53	0.00	9	B20%
Mount Hood Wilderness	0.02	0.02	0.06	0.00	0.05	0.15	0.01	10	B20%

Table 5. 20% Best Natural Conditions – Concentrations and Rayleigh Scattering By Class I Area

Class I Area	$(NH_4)_2SO_4$ µg/m3	NH_4NO_3 µg/m3	OM µg/m³	EC µg/m³	Soil µg/m³	CM µg/m³	Sea Salt µg/m³	Rayleigh Mm^{-1}	Type
Mount Jefferson Wilderness	0.02	0.02	0.08	0.00	0.03	0.31	0.01	11	B20%
Mount Rainier NP	0.03	0.02	0.18	0.01	0.06	0.83	0.02	11	B20%
Mount Washington Wilderness	0.02	0.02	0.08	0.00	0.03	0.31	0.01	11	B20%
Mount Zirkel Wilderness	0.06	0.04	0.16	0.01	0.09	0.60	0.00	8	B20%
Mountain Lakes Wilderness	0.02	0.02	0.08	0.01	0.07	0.23	0.01	9	B20%
North Absaroka Wilderness	0.05	0.04	0.16	0.00	0.11	0.82	0.00	9	B20%
North Cascades NP	0.02	0.03	0.09	0.00	0.04	0.28	0.01	11	B20%
Okefenokee Wilderness	0.13	0.07	0.92	0.01	0.22	1.69	0.03	11	B20%
Olympic NP	0.04	0.03	0.23	0.01	0.03	0.50	0.04	11	B20%
Otter Creek Wilderness	0.10	0.05	0.80	0.01	0.17	0.96	0.01	10	B20%
Pasayten Wilderness	0.04	0.03	0.07	0.00	0.07	0.24	0.01	10	B20%
Pecos Wilderness	0.04	0.03	0.16	0.01	0.08	0.67	0.00	8	B20%
Petrified Forest NP	0.06	0.06	0.28	0.01	0.15	0.75	0.00	9	B20%
Pine Mountain Wilderness	0.06	0.05	0.30	0.01	0.14	0.80	0.00	10	B20%
Pinnacles NM	0.06	0.04	0.31	0.01	0.16	1.50	0.06	11	B20%
Point Reyes NS	0.12	0.04	0.33	0.01	0.13	1.08	0.25	12	B20%
Presidential Range-Dry River Wilderness	0.09	0.04	0.56	0.01	0.10	1.05	0.02	11	B20%
Rawah Wilderness	0.06	0.04	0.16	0.01	0.09	0.60	0.00	8	B20%
Red Rock Lakes Wilderness	0.06	0.05	0.17	0.01	0.08	0.33	0.00	9	B20%
Redwood NP	0.05	0.03	0.28	0.01	0.06	1.02	0.10	11	B20%
Rocky Mountain NP	0.04	0.02	0.15	0.01	0.09	0.68	0.00	9	B20%
Roosevelt Campobello International Park	0.11	0.04	0.76	0.01	0.12	1.25	0.02	12	B20%
Saguaro NP	0.07	0.05	0.32	0.01	0.22	1.15	0.03	10	B20%
Saint Marks Wilderness	0.14	0.06	0.81	0.01	0.24	2.17	0.04	11	B20%
Salt Creek Wilderness	0.05	0.06	0.31	0.01	0.17	1.00	0.02	10	B20%
San Gabriel Wilderness	0.03	0.03	0.15	0.01	0.14	0.67	0.01	9	B20%
San Gorgonio Wilderness	0.03	0.02	0.15	0.01	0.10	0.62	0.02	10	B20%
San Jacinto Wilderness	0.03	0.02	0.15	0.01	0.10	0.62	0.02	10	B20%
San Pedro Parks Wilderness	0.05	0.04	0.14	0.01	0.09	0.34	0.01	8	B20%
San Rafael Wilderness	0.03	0.04	0.22	0.01	0.11	0.79	0.02	10	B20%
Sawtooth Wilderness	0.05	0.04	0.23	0.01	0.10	0.37	0.00	10	B20%
Scapegoat Wilderness	0.05	0.04	0.19	0.01	0.08	0.37	0.00	10	B20%
Selway-Bitterroot Wilderness	0.04	0.03	0.12	0.01	0.07	0.31	0.00	10	B20%
Seney Wilderness	0.08	0.01	0.38	0.01	0.09	0.80	0.01	12	B20%
Sequoia NP	0.03	0.03	0.18	0.01	0.08	0.73	0.02	11	B20%
Shenandoah NP	0.08	0.07	0.56	0.01	0.14	1.20	0.01	10	B20%
Shining Rock Wilderness	0.05	0.05	0.51	0.01	0.13	0.56	0.01	10	B20%
Sierra Ancha Wilderness	0.06	0.05	0.33	0.02	0.14	0.73	0.01	10	B20%
Simeonof Wilderness	0.06	0.05	0.25	0.02	0.04	1.18	0.25	12	B20%
Sipsey Wilderness	0.11	0.10	0.81	0.01	0.25	1.66	0.01	11	B20%
South Warner Wilderness	0.03	0.03	0.14	0.01	0.06	0.46	0.00	10	B20%
Strawberry Mountain Wilderness	0.05	0.02	0.17	0.01	0.10	0.50	0.01	10	B20%
Superstition Wilderness	0.07	0.05	0.31	0.01	0.16	0.84	0.00	10	B20%

Table 9. 20% Best Natural Conditions – Concentrations and Rayleigh Scattering By Class I Area

Class I Area	$(NH_4)_2SO_4$ µg/m3	NH_4NO_3 µg/m3	OM µg/m³	EC µg/m³	Soil µg/m³	CM µg/m³	Sea Salt µg/m³	Rayleigh Mm^{-1}	Type
Swanquarter Wilderness	0.12	0.06	0.65	0.01	0.23	2.38	0.05	12	B20%
Sycamore Canyon Wilderness	0.06	0.05	0.28	0.01	0.12	0.62	0.00	9	B20%
Teton Wilderness	0.06	0.05	0.17	0.01	0.08	0.33	0.00	9	B20%
Theodore Roosevelt NP	0.07	0.04	0.26	0.01	0.21	1.20	0.01	11	B20%
Thousand Lakes Wilderness	0.03	0.02	0.12	0.01	0.08	0.24	0.01	10	B20%
Three Sisters Wilderness	0.02	0.02	0.08	0.00	0.03	0.31	0.01	11	B20%
Tuxedni Wilderness	0.03	0.04	0.09	0.01	0.03	0.52	0.05	12	B20%
UL Bend Wilderness	0.05	0.03	0.18	0.01	0.15	0.93	0.01	11	B20%
Upper Buffalo Wilderness	0.08	0.06	0.68	0.01	0.16	1.33	0.01	11	B20%
Ventana Wilderness	0.06	0.04	0.31	0.01	0.16	1.50	0.06	11	B20%
Virgin Islands NP	0.18	0.07	0.21	0.01	0.12	1.53	0.26	11	B20%
Voyageurs NP	0.12	0.02	0.56	0.01	0.10	0.86	0.01	12	B20%
Washakie Wilderness	0.05	0.04	0.16	0.00	0.11	0.82	0.00	9	B20%
Weminuche Wilderness	0.06	0.04	0.24	0.01	0.13	0.88	0.00	9	B20%
West Elk Wilderness	0.04	0.03	0.14	0.01	0.08	0.36	0.00	8	B20%
Wheeler Peak Wilderness	0.04	0.03	0.16	0.01	0.08	0.67	0.00	8	B20%
White Mountain Wilderness	0.05	0.03	0.24	0.01	0.08	0.67	0.01	9	B20%
Wichita Mountains Wilderness	0.03	0.04	0.28	0.01	0.15	1.52	0.01	11	B20%
Wind Cave NP	0.05	0.04	0.20	0.01	0.19	1.05	0.00	10	B20%
Wolf Island Wilderness	0.13	0.07	0.92	0.01	0.22	1.69	0.03	11	B20%
Yellowstone NP	0.06	0.05	0.17	0.01	0.08	0.33	0.00	9	B20%
Yolla Bolly-Middle Eel Wilderness	0.03	0.02	0.12	0.01	0.06	0.36	0.01	10	B20%
Yosemite NP	0.03	0.02	0.10	0.00	0.08	0.50	0.01	10	B20%
Zion NP	0.05	0.06	0.28	0.01	0.10	0.60	0.01	10	B20%

Table 6. Page 2 Average Natural Conditions - Concentrations and Rayleigh Scattering By Class I Area

Class I Area	$(NH_4)_2SO_4$ µg/m3	NH_4NO_3 µg/m3	OM µg/m³	EC µg/m³	Soil µg/m³	CM µg/m³	Sea Salt µg/m³	Rayleigh Mm^{-1}	Type
Acadia NP	0.23	0.10	1.67	0.02	0.25	2.14	0.14	12	Annual
Agua Tibia Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.14	11	Annual
Alpine Lakes Wilderness	0.12	0.10	0.60	0.02	0.23	1.30	0.06	11	Annual
Anaconda Pintler Wilderness	0.12	0.10	0.60	0.02	0.39	1.79	0.02	10	Annual
Ansel Adams Wilderness	0.12	0.10	0.58	0.02	0.46	2.88	0.03	9	Annual
Arches NP	0.12	0.10	0.60	0.02	0.50	2.92	0.01	9	Annual
Badlands NP	0.12	0.10	0.60	0.02	0.50	3.00	0.01	11	Annual
Bandelier NM	0.12	0.10	0.60	0.02	0.50	2.86	0.02	9	Annual
Bering Sea Wilderness									Annual
Big Bend NP	0.12	0.10	0.60	0.02	0.50	3.00	0.03	10	Annual
Black Canyon of the Gunnison NP	0.12	0.10	0.60	0.02	0.49	2.59	0.01	9	Annual
Bob Marshall Wilderness	0.12	0.10	0.60	0.02	0.44	2.34	0.01	10	Annual
Bosque del Apache Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.04	10	Annual
Boundary Waters Canoe Area Wilderness	0.23	0.10	1.71	0.02	0.31	2.53	0.02	11	Annual
Breton Wilderness	0.23	0.10	1.78	0.02	0.48	3.01	0.19	11	Annual
Bridger Wilderness	0.12	0.10	0.60	0.02	0.44	1.88	0.01	9	Annual
Brigantine Wilderness	0.23	0.10	1.80	0.02	0.47	3.00	0.22	12	Annual
Bryce Canyon NP	0.12	0.10	0.60	0.02	0.50	2.87	0.01	9	Annual
Cabinet Mountains Wilderness	0.12	0.10	0.60	0.02	0.41	2.31	0.02	10	Annual
Caney Creek Wilderness	0.23	0.10	1.80	0.02	0.50	3.00	0.03	11	Annual
Canyonlands NP	0.12	0.10	0.60	0.02	0.50	2.92	0.01	9	Annual
Cape Romain Wilderness	0.23	0.10	1.80	0.02	0.45	3.00	0.20	12	Annual
Capitol Reef NP	0.11	0.10	0.58	0.02	0.50	2.78	0.00	9	Annual
Caribou Wilderness	0.12	0.10	0.60	0.02	0.44	1.82	0.01	10	Annual
Carlsbad Caverns NP	0.12	0.10	0.60	0.02	0.50	3.00	0.02	9	Annual
Chassahowitzka Wilderness	0.23	0.10	1.81	0.02	0.50	3.00	0.08	11	Annual
Chiricahua NM	0.12	0.10	0.60	0.02	0.50	3.00	0.02	10	Annual
Chiricahua Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.02	10	Annual
Cohutta Wilderness	0.23	0.10	1.71	0.02	0.50	2.45	0.02	11	Annual
Crater Lake NP	0.12	0.10	0.60	0.02	0.39	1.67	0.02	9	Annual
Craters of the Moon NM	0.12	0.10	0.60	0.02	0.50	2.92	0.01	10	Annual
Cucamonga Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.04	9	Annual
Denali NP & Pres	0.12	0.05	0.60	0.02	0.14	1.12	0.04	11	Annual
Desolation Wilderness	0.12	0.10	0.60	0.02	0.43	1.92	0.01	9	Annual
Diamond Peak Wilderness	0.12	0.10	0.60	0.02	0.39	1.67	0.02	9	Annual
Dolly Sods Wilderness	0.23	0.10	1.80	0.02	0.43	2.19	0.02	10	Annual
Dome Land Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.03	10	Annual
Eagle Cap Wilderness	0.12	0.10	0.60	0.02	0.50	2.99	0.04	10	Annual
Eagles Nest Wilderness	0.12	0.10	0.60	0.02	0.48	2.12	0.00	8	Annual
Emigrant Wilderness	0.12	0.10	0.60	0.02	0.44	3.00	0.02	10	Annual
Everglades NP	0.23	0.10	1.79	0.02	0.50	3.00	0.31	11	Annual
Fitzpatrick Wilderness	0.12	0.10	0.60	0.02	0.44	1.88	0.01	9	Annual
Flat Tops Wilderness	0.12	0.10	0.60	0.02	0.48	2.12	0.00	8	Annual
Galiuro Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.02	10	Annual

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Table 9. Annual Average Natural Conditions - Concentrations and Rayleigh Scattering By Class I Area

Class I Area	$(NH_4)_2SO_4$ µg/m3	NH_4NO_3 µg/m3	OM µg/m³	EC µg/m³	Soil µg/m³	CM µg/m³	Sea Salt µg/m³	Rayleigh Mm^{-1}	Type
Gates of the Mountains Wilderness	0.12	0.10	0.60	0.02	0.35	1.55	0.01	9	Annual
Gearhart Mountain Wilderness	0.12	0.10	0.60	0.02	0.39	1.67	0.02	9	Annual
Gila Wilderness	0.12	0.10	0.60	0.02	0.50	2.54	0.01	9	Annual
Glacier NP	0.11	0.10	0.59	0.02	0.50	3.00	0.01	11	Annual
Glacier Peak Wilderness	0.11	0.10	0.60	0.02	0.19	1.32	0.02	11	Annual
Goat Rocks Wilderness	0.12	0.10	0.60	0.02	0.23	1.23	0.03	10	Annual
Grand Canyon NP	0.12	0.10	0.60	0.02	0.50	2.88	0.02	9	Annual
Grand Teton NP	0.12	0.10	0.60	0.02	0.41	1.92	0.01	9	Annual
Great Gulf Wilderness	0.23	0.10	1.70	0.02	0.25	2.65	0.03	11	Annual
Great Sand Dunes NP & Pres	0.12	0.10	0.60	0.02	0.50	2.99	0.01	9	Annual
Great Smoky Mountains NP	0.23	0.10	1.80	0.02	0.48	2.92	0.02	11	Annual
Guadalupe Mountains NP	0.12	0.10	0.60	0.02	0.50	3.00	0.02	9	Annual
Haleakala NP	0.12	0.10	0.57	0.02	0.23	2.93	0.25	10	Annual
Hawaii Volcanoes NP	0.12	0.10	0.45	0.02	0.16	1.42	0.29	10	Annual
Hells Canyon Wilderness	0.12	0.10	0.60	0.02	0.48	2.97	0.01	11	Annual
Hercules-Glades Wilderness	0.23	0.10	1.80	0.02	0.50	3.00	0.02	11	Annual
Hoover Wilderness	0.12	0.10	0.60	0.02	0.50	2.97	0.01	9	Annual
Isle Royale NP	0.23	0.10	1.55	0.02	0.24	2.89	0.03	12	Annual
James River Face Wilderness	0.23	0.10	1.80	0.02	0.48	3.00	0.02	11	Annual
Jarbidge Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.02	10	Annual
John Muir Wilderness	0.12	0.10	0.58	0.02	0.46	2.88	0.03	9	Annual
Joshua Tree NP	0.12	0.10	0.60	0.02	0.50	3.00	0.03	10	Annual
Joyce Kilmer-Slickrock Wilderness	0.23	0.10	1.80	0.02	0.48	2.92	0.02	11	Annual
Kaiser Wilderness	0.12	0.10	0.58	0.02	0.46	2.88	0.03	9	Annual
Kalmiopsis Wilderness	0.12	0.10	0.60	0.02	0.20	2.24	0.23	12	Annual
Kings Canyon	0.11	0.10	0.60	0.02	0.50	3.00	0.04	11	Annual
La Garita Wilderness	0.12	0.10	0.60	0.02	0.49	2.59	0.01	9	Annual
Lassen Volcanic NP	0.12	0.10	0.60	0.02	0.44	1.82	0.01	10	Annual
Lava Beds NM	0.12	0.10	0.60	0.02	0.44	2.36	0.01	10	Annual
Linville Gorge Wilderness	0.23	0.10	1.80	0.02	0.45	2.60	0.02	11	Annual
Lostwood Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.03	11	Annual
Lye Brook Wilderness	0.23	0.10	1.59	0.02	0.28	1.79	0.02	11	Annual
Mammoth Cave NP	0.23	0.10	1.80	0.02	0.50	2.73	0.02	11	Annual
Marble Mountain Wilderness	0.12	0.10	0.52	0.02	0.42	2.08	0.04	10	Annual
Maroon Bells-Snowmass Wilderness	0.12	0.10	0.60	0.02	0.48	2.12	0.00	8	Annual
Mazatzal Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.02	10	Annual
Medicine Lake Wilderness	0.12	0.10	0.60	0.02	0.48	3.00	0.01	11	Annual
Mesa Verde NP	0.12	0.10	0.60	0.02	0.50	2.88	0.00	9	Annual
Mingo Wilderness	0.23	0.10	1.83	0.02	0.51	3.05	0.04	12	Annual
Mission Mountains Wilderness	0.12	0.10	0.60	0.02	0.44	2.34	0.01	10	Annual
Mokelumne Wilderness	0.12	0.10	0.60	0.02	0.43	1.92	0.01	9	Annual
Moosehorn Wilderness	0.23	0.10	1.79	0.02	0.23	2.56	0.11	12	Annual
Mount Adams Wilderness	0.12	0.10	0.60	0.02	0.23	1.23	0.03	10	Annual

Table 6. Annual Average Natural Conditions - Concentrations and Rayleigh Scattering By Class I Area

Class I Area	$(NH_4)_2SO_4$ µg/m3	NH_4NO_3 µg/m3	OM µg/m³	EC µg/m³	Soil µg/m³	CM µg/m³	Sea Salt µg/m³	Rayleigh Mm^{-1}	Type
Mount Baldy Wilderness	0.12	0.10	0.57	0.02	0.50	2.82	0.01	9	Annual
Mount Hood Wilderness	0.12	0.10	0.60	0.02	0.29	1.58	0.05	10	Annual
Mount Jefferson Wilderness	0.12	0.10	0.60	0.02	0.26	1.98	0.05	11	Annual
Mount Rainier NP	0.12	0.10	0.60	0.02	0.24	2.27	0.07	11	Annual
Mount Washington Wilderness	0.12	0.10	0.60	0.02	0.26	1.98	0.05	11	Annual
Mount Zirkel Wilderness	0.12	0.10	0.60	0.02	0.45	2.69	0.00	8	Annual
Mountain Lakes Wilderness	0.12	0.10	0.60	0.02	0.39	1.67	0.02	9	Annual
North Absaroka Wilderness	0.12	0.10	0.60	0.02	0.43	2.84	0.01	9	Annual
North Cascades NP	0.11	0.10	0.60	0.02	0.19	1.32	0.02	11	Annual
Okefenokee Wilderness	0.23	0.10	1.80	0.02	0.50	3.00	0.08	11	Annual
Olympic NP	0.12	0.10	0.60	0.02	0.15	1.88	0.14	11	Annual
Otter Creek Wilderness	0.23	0.10	1.80	0.02	0.43	2.19	0.02	10	Annual
Pasayten Wilderness	0.12	0.10	0.60	0.02	0.33	1.50	0.01	10	Annual
Pecos Wilderness	0.12	0.10	0.60	0.02	0.50	2.29	0.03	8	Annual
Petrified Forest NP	0.12	0.10	0.60	0.02	0.50	3.00	0.01	9	Annual
Pine Mountain Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.02	10	Annual
Pinnacles NM	0.12	0.10	0.60	0.02	0.35	3.00	0.19	11	Annual
Point Reyes NS	0.12	0.10	0.60	0.02	0.24	3.00	2.11	12	Annual
Presidential Range-Dry River Wilderness	0.23	0.10	1.70	0.02	0.25	2.65	0.03	11	Annual
Rawah Wilderness	0.12	0.10	0.60	0.02	0.45	2.69	0.00	8	Annual
Red Rock Lakes Wilderness	0.12	0.10	0.60	0.02	0.41	1.92	0.01	9	Annual
Redwood NP	0.12	0.10	0.60	0.02	0.16	3.00	0.96	11	Annual
Rocky Mountain NP	0.12	0.10	0.60	0.02	0.50	2.90	0.00	9	Annual
Roosevelt Campobello International Park	0.23	0.10	1.79	0.02	0.23	2.56	0.11	12	Annual
Saguaro NP	0.12	0.10	0.60	0.02	0.50	3.00	0.06	10	Annual
Saint Marks Wilderness	0.23	0.10	1.80	0.02	0.50	3.00	0.10	11	Annual
Salt Creek Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.04	10	Annual
San Gabriel Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.04	9	Annual
San Gorgonio Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.05	10	Annual
San Jacinto Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.05	10	Annual
San Pedro Parks Wilderness	0.12	0.10	0.60	0.02	0.50	2.19	0.01	8	Annual
San Rafael Wilderness	0.11	0.10	0.60	0.02	0.50	3.00	0.11	10	Annual
Sawtooth Wilderness	0.12	0.08	0.60	0.02	0.41	1.64	0.01	10	Annual
Scapegoat Wilderness	0.12	0.10	0.60	0.02	0.44	2.34	0.01	10	Annual
Selway-Bitterroot Wilderness	0.12	0.10	0.60	0.02	0.39	1.79	0.02	10	Annual
Seney Wilderness	0.23	0.10	1.74	0.02	0.26	1.95	0.02	12	Annual
Sequoia NP	0.11	0.10	0.60	0.02	0.50	3.00	0.04	11	Annual
Shenandoah NP	0.23	0.10	1.80	0.02	0.41	2.88	0.02	10	Annual
Shining Rock Wilderness	0.23	0.10	1.76	0.02	0.50	1.76	0.02	10	Annual
Sierra Ancha Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.02	10	Annual
Simeonof Wilderness	0.12	0.10	0.46	0.02	0.13	3.00	1.26	12	Annual
Sipsey Wilderness	0.23	0.10	1.80	0.02	0.50	3.00	0.04	11	Annual
South Warner Wilderness	0.12	0.10	0.60	0.02	0.44	2.36	0.01	10	Annual

Table 9. Annual Average Natural Conditions - Concentrations and Rayleigh Scattering By Class I Area

Class I Area	$(NH_4)_2SO_4$ µg/m3	NH_4NO_3 µg/m3	OM µg/m³	EC µg/m³	Soil µg/m³	CM µg/m³	Sea Salt µg/m³	Rayleigh Mm^{-1}	Type
Strawberry Mountain Wilderness	0.12	0.10	0.60	0.02	0.50	2.99	0.04	10	Annual
Superstition Wilderness	0.11	0.10	0.59	0.02	0.50	3.00	0.02	10	Annual
Swanquarter Wilderness	0.23	0.10	1.63	0.02	0.41	3.00	0.14	12	Annual
Sycamore Canyon Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.03	9	Annual
Teton Wilderness	0.12	0.10	0.60	0.02	0.41	1.92	0.01	9	Annual
Theodore Roosevelt NP	0.12	0.10	0.60	0.02	0.50	3.00	0.01	11	Annual
Thousand Lakes Wilderness	0.12	0.10	0.60	0.02	0.44	1.82	0.01	10	Annual
Three Sisters Wilderness	0.12	0.10	0.60	0.02	0.26	1.98	0.05	11	Annual
Tuxedni Wilderness	0.12	0.09	0.60	0.02	0.10	2.06	0.38	12	Annual
UL Bend Wilderness	0.12	0.10	0.60	0.02	0.45	3.00	0.00	11	Annual
Upper Buffalo Wilderness	0.23	0.10	1.80	0.02	0.50	3.00	0.03	11	Annual
Ventana Wilderness	0.12	0.10	0.60	0.02	0.35	3.00	0.19	11	Annual
Virgin Islands NP	0.23	0.10	0.35	0.02	0.50	3.00	0.84	11	Annual
Voyageurs NP	0.23	0.10	1.75	0.02	0.26	2.73	0.04	12	Annual
Washakie Wilderness	0.12	0.10	0.60	0.02	0.43	2.84	0.01	9	Annual
Weminuche Wilderness	0.12	0.10	0.60	0.02	0.49	2.59	0.01	9	Annual
West Elk Wilderness	0.12	0.10	0.60	0.02	0.48	2.12	0.00	8	Annual
Wheeler Peak Wilderness	0.12	0.10	0.60	0.02	0.50	2.29	0.03	8	Annual
White Mountain Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.03	9	Annual
Wichita Mountains Wilderness	0.12	0.10	0.60	0.02	0.50	3.00	0.03	11	Annual
Wind Cave NP	0.12	0.10	0.60	0.02	0.49	2.98	0.01	10	Annual
Wolf Island Wilderness	0.23	0.10	1.80	0.02	0.50	3.00	0.08	11	Annual
Yellowstone NP	0.12	0.10	0.60	0.02	0.41	1.92	0.01	9	Annual
Yolla Bolly-Middle Eel Wilderness	0.12	0.10	0.52	0.02	0.42	2.08	0.04	10	Annual
Yosemite NP	0.12	0.10	0.60	0.02	0.44	3.00	0.02	10	Annual
Zion NP	0.12	0.10	0.60	0.02	0.50	3.00	0.01	10	Annual

Table 7. Monthly $f_L(RH)$ - Large $(NH_4)_2SO_4$ and NH_4NO_3 Relative Humidity Adjustment Factor

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Acadia NP	2.74	2.46	2.45	2.66	2.67	2.73	2.99	3.03	3.16	2.91	2.89	2.96
Agua Tibia Wilderness	2.10	2.08	2.11	1.98	1.98	1.93	1.93	2.01	2.02	1.99	1.87	1.95
Alpine Lakes Wilderness	3.86	3.58	3.04	2.92	2.99	2.58	2.62	2.67	2.97	3.60	4.00	3.99
Anaconda Pintler Wilderness	2.75	2.46	2.24	2.08	2.06	2.01	1.76	1.72	1.88	2.22	2.66	2.74
Ansel Adams Wilderness	2.56	2.34	2.20	1.88	1.79	1.59	1.52	1.52	1.59	1.70	2.01	2.34
Arches NP	2.28	2.12	1.73	1.57	1.50	1.28	1.34	1.47	1.51	1.56	1.90	2.13
Badlands NP	2.31	2.31	2.31	2.21	2.34	2.25	2.08	2.05	2.02	2.05	2.38	2.33
Bandelier NM	2.10	1.90	1.72	1.51	1.53	1.38	1.63	1.87	1.80	1.59	1.87	2.04
Bering Sea Wilderness	3.02	3.17	3.20	3.19	3.23	3.34	3.78	4.16	3.64	3.19	3.12	3.13
Big Bend NP	1.72	1.61	1.44	1.38	1.47	1.48	1.58	1.74	1.83	1.63	1.63	1.70
Black Canyon of the Gunnison NP	2.15	2.05	1.83	1.75	1.74	1.51	1.59	1.78	1.80	1.68	1.96	2.06
Bob Marshall Wilderness	2.82	2.54	2.35	2.22	2.21	2.19	1.98	1.92	2.15	2.43	2.78	2.81
Bosque del Apache Wilderness	2.03	1.82	1.55	1.37	1.36	1.27	1.61	1.79	1.73	1.54	1.73	2.00
Boundary Waters Canoe Area Wilderness	2.50	2.25	2.28	2.09	2.20	2.43	2.57	2.71	2.78	2.38	2.64	2.64
Breton Wilderness	2.91	2.76	2.74	2.72	2.83	2.94	3.10	3.07	2.97	2.82	2.83	2.90
Bridger Wilderness	2.22	2.10	2.04	1.95	1.95	1.67	1.46	1.44	1.68	1.83	2.19	2.16
Brigantine Wilderness	2.49	2.32	2.38	2.28	2.50	2.56	2.69	2.81	2.82	2.71	2.45	2.50
Bryce Canyon NP	2.31	2.16	1.82	1.56	1.47	1.26	1.30	1.46	1.46	1.55	1.87	2.15
Cabinet Mountains Wilderness	3.07	2.73	2.45	2.26	2.24	2.21	1.98	1.92	2.19	2.53	3.03	3.11
Caney Creek Wilderness	2.77	2.53	2.37	2.43	2.68	2.71	2.59	2.60	2.71	2.69	2.67	2.79
Canyonlands NP	2.32	2.16	1.78	1.58	1.51	1.28	1.36	1.53	1.55	1.58	1.93	2.17
Cape Romain Wilderness	2.66	2.47	2.42	2.32	2.56	2.80	2.82	3.04	3.03	2.86	2.65	2.70
Capitol Reef NP	2.36	2.22	1.84	1.63	1.54	1.31	1.36	1.52	1.55	1.61	1.95	2.22
Caribou Wilderness	2.96	2.58	2.35	2.10	2.01	1.85	1.79	1.82	1.88	2.03	2.50	2.82
Carlsbad Caverns NP	2.07	1.81	1.50	1.42	1.51	1.48	1.72	1.90	2.03	1.64	1.76	2.00
Chassahowitzka Wilderness	3.03	2.82	2.74	2.65	2.63	3.00	3.02	3.15	3.14	3.03	2.97	3.09
Chiricahua NM	1.87	1.79	1.52	1.24	1.22	1.13	1.64	1.87	1.66	1.45	1.55	1.89
Chiricahua Wilderness	1.84	1.76	1.49	1.22	1.20	1.12	1.64	1.86	1.64	1.43	1.53	1.87
Cohutta Wilderness	2.84	2.61	2.49	2.36	2.72	2.97	3.00	3.07	3.08	2.89	2.72	2.85
Crater Lake NP	3.71	3.25	3.07	2.91	2.70	2.50	2.31	2.33	2.49	2.99	3.67	3.74
Craters of the Moon NM	2.58	2.34	2.03	1.84	1.83	1.65	1.40	1.39	1.52	1.80	2.35	2.54
Cucamonga Wilderness	2.21	2.14	2.13	1.96	1.95	1.90	1.91	1.96	1.98	1.96	1.90	2.02
Denali NP & Pres	2.48	2.44	2.15	1.96	1.98	2.13	2.47	2.90	2.95	2.84	2.69	2.68
Desolation Wilderness	2.73	2.42	2.18	1.84	1.74	1.56	1.47	1.49	1.58	1.73	2.12	2.54
Diamond Peak Wilderness	3.82	3.38	3.18	3.04	2.79	2.60	2.33	2.35	2.58	3.18	3.80	3.86
Dolly Sods Wilderness	2.53	2.39	2.38	2.20	2.63	2.65	2.74	2.90	2.94	2.65	2.45	2.61
Dome Land Wilderness	2.26	2.07	2.00	1.79	1.73	1.63	1.61	1.64	1.68	1.71	1.81	2.01
Eagle Cap Wilderness	3.44	3.02	2.54	2.31	2.28	2.01	1.78	1.75	1.97	2.61	3.34	3.56
Eagles Nest Wilderness	2.02	2.01	1.87	1.87	1.92	1.69	1.68	1.83	1.86	1.73	1.96	1.97
Emigrant Wilderness	2.67	2.42	2.26	1.92	1.81	1.59	1.49	1.50	1.58	1.72	2.08	2.45
Everglades NP	2.43	2.31	2.26	2.16	2.15	2.38	2.32	2.49	2.55	2.42	2.34	2.39
Fitzpatrick Wilderness	2.22	2.10	2.04	1.95	1.94	1.68	1.47	1.44	1.68	1.83	2.18	2.16
Flat Tops Wilderness	2.09	2.04	1.87	1.84	1.86	1.62	1.59	1.70	1.79	1.72	1.97	2.03
Galiuro Wilderness	1.80	1.67	1.47	1.21	1.18	1.10	1.43	1.66	1.53	1.42	1.57	1.87
Gates of the Mountains Wilderness	2.46	2.25	2.15	2.05	2.02	2.00	1.81	1.77	1.91	2.15	2.37	2.41

Table 3. Monthly $f_L(RH)$ – Large $(NH_4)_2SO_4$ and NH_4NO_3 Relative Humidity Adjustment Factor

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Gearhart Mountain Wilderness	3.30	2.89	2.62	2.45	2.29	2.13	1.88	1.90	2.03	2.47	3.09	3.27
Gila Wilderness	1.93	1.78	1.52	1.31	1.28	1.23	1.72	1.76	1.68	1.50	1.67	1.96
Glacier NP	3.21	2.84	2.69	2.55	2.58	2.56	2.24	2.22	2.57	2.81	3.08	3.13
Glacier Peak Wilderness	3.69	3.39	2.97	2.85	2.79	2.54	2.49	2.59	2.91	3.45	3.83	3.84
Goat Rocks Wilderness	3.83	3.44	3.10	2.97	2.82	2.60	2.48	2.55	2.88	3.49	3.91	3.98
Grand Canyon NP	2.13	2.01	1.74	1.46	1.36	1.19	1.29	1.49	1.47	1.50	1.75	1.98
Grand Teton NP	2.27	2.14	2.01	1.91	1.90	1.68	1.48	1.44	1.64	1.84	2.16	2.24
Great Gulf Wilderness	2.51	2.32	2.36	2.41	2.45	2.55	2.72	2.87	2.98	2.80	2.67	2.60
Great Sand Dunes NP & Pres	2.11	2.04	1.85	1.77	1.80	1.62	1.70	1.97	1.92	1.72	2.04	2.09
Great Smoky Mountains NP	2.85	2.57	2.51	2.35	2.72	2.98	2.98	3.08	3.10	2.87	2.71	2.85
Guadalupe Mountains NP	2.14	1.82	1.49	1.38	1.48	1.47	1.78	1.98	2.10	1.60	1.78	2.08
Haleakala NP	2.34	2.27	2.25	2.20	2.13	2.09	2.16	2.14	2.10	2.19	2.33	2.30
Hawaii Volcanoes NP	2.56	2.45	2.47	2.47	2.47	2.45	2.53	2.59	2.55	2.57	2.78	2.55
Hells Canyon Wilderness	3.05	2.65	2.22	1.97	1.91	1.81	1.55	1.52	1.68	2.15	2.90	3.15
Hercules-Glades Wilderness	2.70	2.48	2.30	2.30	2.57	2.59	2.56	2.60	2.69	2.54	2.57	2.72
Hoover Wilderness	2.63	2.38	2.21	1.88	1.77	1.56	1.46	1.47	1.55	1.69	2.05	2.42
Isle Royale NP	2.53	2.21	2.26	2.07	1.99	2.32	2.65	2.69	2.82	2.28	2.76	2.74
James River Face Wilderness	2.44	2.30	2.29	2.12	2.47	2.58	2.65	2.78	2.82	2.57	2.36	2.51
Jarbidge Wilderness	2.51	2.28	1.90	1.92	1.97	1.82	1.51	1.37	1.34	1.56	2.14	2.42
John Muir Wilderness	2.51	2.29	2.20	1.95	1.86	1.65	1.60	1.61	1.69	1.78	2.03	2.28
Joshua Tree NP	2.06	1.99	1.97	1.82	1.81	1.74	1.68	1.82	1.83	1.81	1.75	1.87
Joyce Kilmer-Slickrock Wilderness	2.86	2.58	2.51	2.36	2.71	2.97	2.98	3.06	3.08	2.87	2.72	2.85
Kaiser Wilderness	2.58	2.35	2.22	1.90	1.80	1.62	1.56	1.57	1.64	1.75	2.03	2.36
Kalmiopsis Wilderness	3.57	3.17	3.03	2.88	2.75	2.60	2.52	2.53	2.60	2.92	3.51	3.55
Kings Canyon	2.47	2.26	2.18	1.94	1.85	1.65	1.59	1.60	1.68	1.77	2.01	2.24
La Garita Wilderness	2.14	2.03	1.81	1.70	1.69	1.49	1.63	1.87	1.83	1.67	1.98	2.08
Lassen Volcanic NP	2.99	2.61	2.38	2.13	2.03	1.86	1.81	1.84	1.90	2.06	2.54	2.86
Lava Beds NM	3.31	2.88	2.64	2.44	2.29	2.13	1.98	1.99	2.10	2.43	3.03	3.26
Linville Gorge Wilderness	2.71	2.54	2.48	2.31	2.70	2.96	3.00	3.20	3.19	2.84	2.62	2.74
Lostwood Wilderness	2.51	2.45	2.54	2.06	2.03	2.21	2.23	2.05	2.02	2.13	2.69	2.67
Lye Brook Wilderness	2.46	2.30	2.34	2.31	2.42	2.47	2.60	2.76	2.84	2.70	2.54	2.51
Mammoth Cave NP	2.79	2.57	2.47	2.56	3.29	3.76	3.67	2.92	2.95	2.71	2.61	2.82
Marble Mountain Wilderness	3.48	3.08	2.95	2.78	2.67	2.53	2.50	2.52	2.55	2.78	3.32	3.42
Maroon Bells-Snowmass Wilderness	2.02	1.99	1.84	1.84	1.83	1.59	1.69	1.90	1.89	1.71	1.94	1.96
Mazatzal Wilderness	1.91	1.80	1.59	1.32	1.25	1.13	1.38	1.61	1.51	1.45	1.63	1.89
Medicine Lake Wilderness	2.53	2.46	2.46	2.02	2.00	2.13	2.12	1.95	1.98	2.10	2.63	2.65
Mesa Verde NP	2.45	2.25	1.98	1.57	1.61	1.31	1.62	1.87	1.75	1.66	2.01	2.30
Mingo Wilderness	2.73	2.52	2.34	2.28	2.53	2.60	2.64	2.67	2.71	2.56	2.56	2.73
Mission Mountains Wilderness	2.93	2.62	2.37	2.20	2.21	2.19	1.98	1.92	2.15	2.46	2.91	2.96
Mokelumne Wilderness	2.72	2.42	2.20	1.86	1.75	1.57	1.48	1.50	1.58	1.73	2.11	2.52
Moosehorn Wilderness	2.65	2.39	2.38	2.52	2.49	2.57	2.83	2.95	3.07	2.83	2.77	2.78
Mount Adams Wilderness	3.78	3.40	3.10	2.98	2.78	2.60	2.43	2.52	2.84	3.45	3.87	3.92
Mount Baldy Wilderness	2.00	1.86	1.62	1.34	1.29	1.18	1.50	1.73	1.60	1.51	1.73	2.01
Mount Hood Wilderness	3.71	3.33	3.08	2.96	2.74	2.55	2.34	2.42	2.72	3.35	3.81	3.84
Mount Jefferson Wilderness	3.89	3.48	3.27	3.16	2.89	2.66	2.35	2.35	2.63	3.34	3.82	3.95

Table 7. Hygroscopic Large $(NH_4)_2SO_4$ and NH_4NO_3 Relative Humidity Adjustment Factor

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Mount Rainier NP	3.93	3.54	3.23	3.12	2.96	2.75	2.61	2.69	3.04	3.66	4.04	4.07
Mount Washington Wilderness	4.09	3.63	3.49	3.41	3.06	2.80	2.37	2.34	2.62	3.41	4.07	4.10
Mount Zirkel Wilderness	2.00	1.99	1.89	1.92	1.98	1.72	1.63	1.70	1.81	1.75	1.97	1.95
Mountain Lakes Wilderness	3.51	3.03	2.80	2.62	2.44	2.25	2.08	2.09	2.23	2.65	3.37	3.52
North Absaroka Wilderness	2.16	2.05	2.01	1.95	1.94	1.77	1.58	1.50	1.67	1.87	2.12	2.14
North Cascades NP	3.60	3.32	2.99	2.88	2.74	2.59	2.49	2.63	2.97	3.43	3.77	3.76
Okefenokee Wilderness	2.94	2.73	2.73	2.65	2.74	3.11	3.00	3.17	3.16	3.05	2.96	3.03
Olympic NP	3.80	3.50	3.30	3.21	2.76	2.89	2.61	2.94	3.23	3.73	3.99	3.95
Otter Creek Wilderness	2.55	2.41	2.40	2.23	2.64	2.69	2.80	2.96	3.00	2.69	2.48	2.63
Pasayten Wilderness	3.65	3.34	2.97	2.84	2.72	2.53	2.45	2.56	2.88	3.39	3.78	3.81
Pecos Wilderness	2.09	1.93	1.73	1.57	1.58	1.44	1.65	1.90	1.84	1.63	1.90	2.05
Petrified Forest NP	2.11	1.95	1.64	1.40	1.32	1.18	1.46	1.72	1.58	1.53	1.81	2.09
Pine Mountain Wilderness	1.96	1.86	1.64	1.35	1.28	1.15	1.38	1.62	1.53	1.48	1.66	1.93
Pinnacles NM	2.84	2.86	2.87	2.27	2.15	1.99	1.91	1.97	1.98	2.10	2.16	2.46
Point Reyes NS	2.96	2.73	2.61	2.28	2.20	2.04	2.12	2.16	2.18	2.23	2.47	2.75
Presidential Range-Dry River Wilderness	2.52	2.32	2.37	2.42	2.49	2.61	2.78	2.93	3.03	2.83	2.68	2.59
Rawah Wilderness	1.91	1.96	1.89	1.96	2.04	1.79	1.71	1.78	1.86	1.75	1.94	1.90
Red Rock Lakes Wilderness	2.39	2.20	2.06	1.95	1.92	1.80	1.60	1.54	1.69	1.93	2.30	2.37
Redwood NP	3.31	3.10	3.16	3.04	3.11	3.08	3.26	3.28	3.11	2.99	3.20	3.12
Rocky Mountain NP	1.77	1.85	1.84	1.95	2.04	1.80	1.73	1.77	1.84	1.70	1.84	1.76
Roosevelt Campobello International Park	2.66	2.39	2.38	2.53	2.49	2.57	2.82	2.93	3.05	2.83	2.78	2.79
Saguaro NP	1.69	1.56	1.40	1.13	1.12	1.05	1.37	1.62	1.47	1.38	1.50	1.83
Saint Marks Wilderness	2.98	2.78	2.73	2.69	2.74	3.04	3.17	3.21	3.10	2.96	2.94	3.06
Salt Creek Wilderness	2.01	1.79	1.51	1.45	1.55	1.48	1.64	1.80	1.91	1.64	1.72	1.91
San Gabriel Wilderness	2.25	2.17	2.14	1.96	1.95	1.90	1.91	1.95	1.98	1.97	1.91	2.04
San Gorgonio Wilderness	2.21	2.23	2.13	1.90	1.90	1.69	1.62	1.71	1.72	1.70	1.73	1.92
San Jacinto Wilderness	2.12	2.09	2.06	1.90	1.90	1.81	1.71	1.88	1.89	1.87	1.80	1.92
San Pedro Parks Wilderness	2.14	1.97	1.73	1.55	1.53	1.38	1.59	1.83	1.77	1.61	1.91	2.08
San Rafael Wilderness	2.50	2.37	2.34	2.12	2.10	2.05	2.10	2.15	2.20	2.15	2.07	2.25
Sawtooth Wilderness	2.79	2.44	2.05	1.83	1.80	1.66	1.37	1.35	1.43	1.77	2.47	2.75
Scapegoat Wilderness	2.74	2.47	2.30	2.18	2.16	2.14	1.93	1.87	2.07	2.35	2.70	2.72
Selway-Bitterroot Wilderness	2.90	2.57	2.26	2.05	2.03	1.95	1.67	1.63	1.81	2.19	2.76	2.91
Seney Wilderness	2.75	2.42	2.49	2.35	2.30	2.55	2.75	3.01	3.03	2.78	2.88	2.85
Sequoia NP	2.40	2.22	2.21	2.05	1.95	1.67	1.60	1.59	1.69	1.78	2.04	2.17
Shenandoah NP	2.44	2.28	2.29	2.12	2.45	2.56	2.65	2.79	2.81	2.53	2.34	2.55
Shining Rock Wilderness	2.78	2.56	2.48	2.33	2.72	2.98	3.02	3.17	3.18	2.91	2.68	2.79
Sierra Ancha Wilderness	1.92	1.81	1.59	1.32	1.25	1.13	1.42	1.65	1.54	1.47	1.66	1.93
Simeonof Wilderness	3.39	3.40	3.15	3.26	3.40	3.69	4.00	4.14	3.61	3.09	3.21	3.44
Sipsey Wilderness	2.79	2.58	2.42	2.36	2.64	2.86	2.94	2.92	2.93	2.78	2.64	2.80
South Warner Wilderness	3.06	2.67	2.39	2.16	2.05	1.90	1.68	1.69	1.79	2.11	2.67	2.97
Strawberry Mountain Wilderness	3.55	3.10	2.69	2.47	2.37	2.10	1.82	1.81	2.05	2.73	3.45	3.65
Superstition Wilderness	1.84	1.72	1.53	1.26	1.20	1.11	1.36	1.56	1.46	1.40	1.58	1.85
Swanquarter Wilderness	2.48	2.35	2.31	2.18	2.38	2.55	2.67	2.72	2.64	2.55	2.40	2.49
Sycamore Canyon Wilderness	2.01	1.93	1.70	1.40	1.33	1.17	1.38	1.67	1.58	1.52	1.70	1.97
Teton Wilderness	2.22	2.09	2.01	1.92	1.91	1.72	1.52	1.47	1.65	1.86	2.15	2.19

Table 6. Monthly $f_L(RH)$ – Large $(NH_4)_2SO_4$ and NH_4NO_3 Relative Humidity Adjustment Factor

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Theodore Roosevelt NP	2.47	2.42	2.45	2.12	2.14	2.21	2.14	1.99	1.99	2.10	2.58	2.57
Thousand Lakes Wilderness	3.04	2.63	2.42	2.17	2.06	1.88	1.82	1.85	1.91	2.08	2.61	2.91
Three Sisters Wilderness	4.03	3.59	3.43	3.34	3.02	2.78	2.40	2.38	2.65	3.39	4.02	4.04
Tuxedni Wilderness	2.97	2.83	2.47	2.40	2.38	2.50	2.96	3.19	3.18	2.91	2.91	3.03
UL Bend Wilderness	2.33	2.20	2.19	2.03	1.96	1.95	1.80	1.66	1.76	2.00	2.31	2.32
Upper Buffalo Wilderness	2.71	2.48	2.31	2.33	2.61	2.64	2.57	2.59	2.71	2.58	2.59	2.72
Ventana Wilderness	2.80	2.67	2.63	2.20	2.10	1.96	1.97	2.01	2.05	2.11	2.21	2.51
Virgin Islands NP	2.04	2.00	1.94	2.03	2.06	2.04	2.05	2.14	2.14	2.18	2.20	2.12
Voyageurs NP	2.46	2.22	2.22	2.07	2.09	2.46	2.46	2.59	2.70	2.35	2.58	2.55
Washakie Wilderness	2.16	2.05	2.01	1.94	1.93	1.74	1.54	1.48	1.66	1.86	2.12	2.14
Weminuche Wilderness	2.19	2.05	1.81	1.65	1.64	1.44	1.60	1.85	1.79	1.65	1.97	2.11
West Elk Wilderness	2.11	2.04	1.84	1.77	1.77	1.54	1.63	1.83	1.83	1.69	1.96	2.04
Wheeler Peak Wilderness	2.14	2.00	1.78	1.65	1.67	1.52	1.66	1.94	1.89	1.68	1.98	2.10
White Mountain Wilderness	2.00	1.79	1.51	1.40	1.44	1.37	1.64	1.82	1.85	1.59	1.72	1.95
Wichita Mountains Wilderness	2.39	2.25	2.10	2.11	2.39	2.24	2.02	2.13	2.35	2.22	2.28	2.41
Wind Cave NP	2.23	2.22	2.22	2.18	2.32	2.18	2.00	1.97	1.95	2.00	2.30	2.24
Wolf Island Wilderness	2.86	2.67	2.61	2.54	2.63	2.96	2.94	3.13	3.12	2.99	2.88	2.95
Yellowstone NP	2.24	2.11	2.03	1.95	1.94	1.78	1.59	1.53	1.69	1.91	2.19	2.22
Yolla Bolly-Middle Eel Wilderness	3.12	2.76	2.60	2.37	2.29	2.13	2.14	2.18	2.21	2.33	2.75	2.98
Yosemite NP	2.61	2.45	2.34	1.99	1.88	1.61	1.48	1.46	1.54	1.69	2.06	2.38
Zion NP	2.32	2.18	1.83	1.56	1.45	1.26	1.24	1.38	1.40	1.51	1.84	2.14

Table 8. Hygroscopicity ($f(RH)$) Small $(NH_4)_2SO_4$ and NH_4NO_3 Relative Humidity Adjustment Factor

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Acadia NP	3.80	3.28	3.30	3.71	3.72	3.81	4.28	4.34	4.58	4.10	4.06	4.19
Agua Tibia Wilderness	2.68	2.61	2.63	2.42	2.40	2.33	2.33	2.45	2.49	2.46	2.29	2.42
Alpine Lakes Wilderness	5.87	5.35	4.34	4.13	4.30	3.50	3.61	3.69	4.27	5.43	6.15	6.08
Anaconda Pintler Wilderness	3.72	3.23	2.87	2.62	2.60	2.52	2.14	2.07	2.33	2.87	3.60	3.71
Ansel Adams Wilderness	3.51	3.11	2.87	2.34	2.18	1.86	1.75	1.76	1.88	2.05	2.55	3.12
Arches NP	2.96	2.70	2.09	1.84	1.75	1.40	1.49	1.69	1.76	1.83	2.33	2.69
Badlands NP	2.94	2.96	3.01	2.87	3.10	2.91	2.64	2.59	2.56	2.58	3.11	2.98
Bandelier NM	2.66	2.36	2.10	1.77	1.80	1.55	1.93	2.30	2.21	1.87	2.32	2.60
Bering Sea Wilderness	4.16	4.48	4.52	4.50	4.64	4.86	5.71	6.43	5.40	4.52	4.36	4.37
Big Bend NP	2.11	1.92	1.65	1.56	1.67	1.67	1.83	2.07	2.22	1.92	1.92	2.04
Black Canyon of the Gunnison NP	2.71	2.56	2.23	2.12	2.12	1.75	1.87	2.17	2.21	2.00	2.42	2.57
Bob Marshall Wilderness	3.84	3.35	3.06	2.86	2.86	2.84	2.49	2.39	2.77	3.22	3.81	3.83
Bosque del Apache Wilderness	2.56	2.23	1.83	1.54	1.54	1.39	1.90	2.16	2.09	1.79	2.09	2.53
Boundary Waters Canoe Area Wilderness	3.23	2.81	2.93	2.63	2.89	3.22	3.44	3.71	3.83	3.08	3.49	3.49
Breton Wilderness	4.08	3.82	3.79	3.74	3.94	4.12	4.41	4.37	4.18	3.92	3.93	4.06
Bridger Wilderness	2.78	2.60	2.55	2.43	2.45	1.99	1.65	1.63	2.03	2.25	2.78	2.68
Brigantine Wilderness	3.34	3.07	3.17	2.99	3.37	3.45	3.68	3.90	3.91	3.73	3.27	3.36
Bryce Canyon NP	3.02	2.77	2.23	1.84	1.70	1.38	1.42	1.67	1.67	1.81	2.30	2.75
Cabinet Mountains Wilderness	4.30	3.69	3.23	2.91	2.91	2.87	2.50	2.40	2.84	3.40	4.26	4.37
Caney Creek Wilderness	3.85	3.44	3.14	3.24	3.66	3.71	3.49	3.51	3.73	3.72	3.68	3.88
Canyonlands NP	3.03	2.77	2.17	1.86	1.76	1.40	1.52	1.78	1.81	1.87	2.38	2.77
Cape Romain Wilderness	3.66	3.33	3.24	3.07	3.46	3.88	3.91	4.31	4.30	4.00	3.62	3.73
Capitol Reef NP	3.10	2.86	2.27	1.94	1.81	1.45	1.52	1.77	1.81	1.91	2.43	2.86
Caribou Wilderness	4.17	3.50	3.11	2.68	2.54	2.28	2.21	2.26	2.36	2.60	3.39	3.93
Carlsbad Caverns NP	2.70	2.25	1.75	1.63	1.77	1.70	2.06	2.34	2.59	1.95	2.16	2.57
Chassahowitzka Wilderness	4.31	3.92	3.79	3.62	3.57	4.22	4.26	4.50	4.49	4.29	4.18	4.43
Chiricahua NM	2.29	2.19	1.75	1.34	1.31	1.18	1.94	2.28	1.95	1.64	1.79	2.34
Chiricahua Wilderness	2.25	2.14	1.71	1.30	1.28	1.17	1.95	2.26	1.93	1.61	1.75	2.31
Cohutta Wilderness	3.99	3.59	3.38	3.16	3.76	4.19	4.24	4.37	4.41	4.09	3.77	4.00
Crater Lake NP	5.58	4.73	4.37	4.09	3.70	3.37	3.05	3.08	3.38	4.26	5.52	5.64
Craters of the Moon NM	3.40	3.00	2.52	2.22	2.23	1.94	1.56	1.55	1.76	2.17	3.04	3.32
Cucamonga Wilderness	2.87	2.73	2.68	2.40	2.37	2.29	2.31	2.38	2.43	2.42	2.34	2.54
Denali NP & Pres	3.21	3.19	2.71	2.39	2.46	2.69	3.27	4.05	4.17	3.90	3.59	3.58
Desolation Wilderness	3.77	3.22	2.82	2.26	2.09	1.80	1.67	1.71	1.84	2.08	2.72	3.44
Diamond Peak Wilderness	5.79	4.97	4.61	4.35	3.90	3.55	3.08	3.12	3.55	4.63	5.75	5.88
Dolly Sods Wilderness	3.39	3.16	3.17	2.87	3.63	3.62	3.78	4.06	4.15	3.63	3.27	3.53
Dome Land Wilderness	2.97	2.64	2.51	2.17	2.08	1.91	1.89	1.93	2.01	2.06	2.23	2.56
Eagle Cap Wilderness	5.05	4.28	3.45	3.05	3.02	2.56	2.20	2.15	2.53	3.62	4.89	5.26
Eagles Nest Wilderness	2.48	2.48	2.29	2.32	2.42	2.03	2.02	2.24	2.31	2.09	2.42	2.42
Emigrant Wilderness	3.69	3.25	2.98	2.39	2.21	1.86	1.71	1.73	1.85	2.07	2.68	3.32
Everglades NP	3.14	2.93	2.83	2.67	2.63	3.03	2.91	3.22	3.33	3.12	2.95	3.08
Fitzpatrick Wilderness	2.78	2.60	2.54	2.43	2.44	1.99	1.66	1.63	2.02	2.25	2.77	2.68
Flat Tops Wilderness	2.61	2.53	2.28	2.26	2.31	1.91	1.86	2.04	2.19	2.06	2.42	2.51
Galiuro Wilderness	2.17	1.99	1.68	1.30	1.26	1.14	1.62	1.96	1.75	1.60	1.82	2.31
Gates of the Mountains Wilderness	3.20	2.85	2.71	2.57	2.53	2.50	2.21	2.14	2.37	2.74	3.09	3.12

Table 3. Monthly $f_S(RH)$ – Small $(NH_4)_2SO_4$ and NH_4NO_3 Relative Humidity Adjustment Factor

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Gearhart Mountain Wilderness	4.80	4.05	3.60	3.30	3.04	2.76	2.37	2.39	2.62	3.36	4.45	4.76
Gila Wilderness	2.40	2.16	1.77	1.45	1.41	1.33	2.11	2.12	2.00	1.73	1.99	2.45
Glacier NP	4.53	3.87	3.63	3.39	3.51	3.48	2.91	2.87	3.47	3.86	4.29	4.37
Glacier Peak Wilderness	5.53	4.98	4.21	3.99	3.90	3.43	3.35	3.54	4.14	5.12	5.80	5.80
Goat Rocks Wilderness	5.81	5.08	4.46	4.23	3.97	3.57	3.35	3.48	4.11	5.22	5.98	6.09
Grand Canyon NP	2.73	2.53	2.12	1.69	1.52	1.27	1.42	1.72	1.69	1.74	2.11	2.49
Grand Teton NP	2.88	2.66	2.48	2.35	2.34	2.00	1.68	1.62	1.94	2.25	2.73	2.82
Great Gulf Wilderness	3.34	3.02	3.12	3.23	3.31	3.46	3.76	4.03	4.22	3.90	3.64	3.50
Great Sand Dunes NP & Pres	2.66	2.55	2.27	2.16	2.22	1.92	2.04	2.47	2.41	2.07	2.57	2.63
Great Smoky Mountains NP	4.01	3.52	3.43	3.14	3.76	4.20	4.21	4.39	4.45	4.05	3.76	3.99
Guadalupe Mountains NP	2.85	2.28	1.74	1.57	1.73	1.69	2.16	2.48	2.74	1.90	2.20	2.71
Haleakala NP	2.98	2.85	2.81	2.72	2.60	2.53	2.65	2.63	2.56	2.69	2.95	2.89
Hawaii Volcanoes NP	3.35	3.10	3.14	3.13	3.14	3.11	3.24	3.42	3.34	3.38	3.76	3.34
Hells Canyon Wilderness	4.28	3.56	2.83	2.42	2.34	2.19	1.80	1.75	2.01	2.75	4.03	4.45
Hercules-Glades Wilderness	3.70	3.33	3.01	3.01	3.47	3.48	3.41	3.51	3.67	3.43	3.46	3.73
Hoover Wilderness	3.63	3.18	2.89	2.33	2.16	1.82	1.66	1.68	1.81	2.02	2.62	3.25
Isle Royale NP	3.26	2.74	2.87	2.58	2.46	3.00	3.59	3.68	3.92	2.88	3.72	3.67
James River Face Wilderness	3.25	3.03	3.02	2.72	3.31	3.48	3.59	3.83	3.91	3.48	3.11	3.38
Jarbidge Wilderness	3.29	2.92	2.31	2.34	2.44	2.22	1.73	1.51	1.48	1.80	2.70	3.13
John Muir Wilderness	3.42	3.02	2.86	2.44	2.29	1.94	1.86	1.87	2.01	2.16	2.60	3.03
Joshua Tree NP	2.62	2.49	2.44	2.19	2.16	2.05	1.97	2.18	2.21	2.19	2.11	2.31
Joyce Kilmer-Slickrock Wilderness	4.02	3.54	3.42	3.15	3.74	4.19	4.21	4.35	4.41	4.04	3.77	4.00
Kaiser Wilderness	3.55	3.13	2.89	2.36	2.21	1.90	1.81	1.83	1.95	2.12	2.59	3.16
Kalmiopsis Wilderness	5.32	4.56	4.30	4.02	3.79	3.54	3.43	3.44	3.56	4.12	5.21	5.28
Kings Canyon	3.35	2.97	2.82	2.42	2.28	1.93	1.85	1.87	2.01	2.15	2.56	2.96
La Garita Wilderness	2.71	2.54	2.21	2.04	2.05	1.72	1.93	2.31	2.26	2.00	2.46	2.62
Lassen Volcanic NP	4.24	3.55	3.16	2.73	2.58	2.31	2.24	2.29	2.39	2.64	3.46	4.00
Lava Beds NM	4.84	4.05	3.63	3.28	3.04	2.76	2.53	2.55	2.75	3.29	4.35	4.75
Linville Gorge Wilderness	3.76	3.46	3.37	3.07	3.74	4.18	4.24	4.62	4.61	4.00	3.59	3.80
Lostwood Wilderness	3.21	3.15	3.36	2.60	2.54	2.86	2.89	2.60	2.53	2.72	3.60	3.52
Lye Brook Wilderness	3.25	2.99	3.10	3.06	3.24	3.30	3.52	3.80	3.95	3.71	3.42	3.35
Mammoth Cave NP	3.86	3.47	3.32	3.54	4.90	5.77	5.58	4.09	4.15	3.73	3.54	3.91
Marble Mountain Wilderness	5.15	4.40	4.15	3.84	3.67	3.44	3.41	3.44	3.50	3.89	4.87	5.04
Maroon Bells-Snowmass Wilderness	2.48	2.44	2.23	2.25	2.25	1.87	2.02	2.35	2.35	2.04	2.36	2.38
Mazatzal Wilderness	2.36	2.20	1.88	1.46	1.36	1.18	1.54	1.89	1.74	1.66	1.91	2.33
Medicine Lake Wilderness	3.25	3.15	3.21	2.52	2.49	2.71	2.71	2.42	2.46	2.65	3.48	3.48
Mesa Verde NP	3.32	2.96	2.55	1.88	1.96	1.46	1.94	2.35	2.13	2.04	2.57	3.06
Mingo Wilderness	3.74	3.38	3.07	2.97	3.39	3.52	3.57	3.64	3.72	3.47	3.43	3.74
Mission Mountains Wilderness	4.03	3.51	3.08	2.82	2.84	2.83	2.49	2.40	2.78	3.28	4.04	4.08
Mokelumne Wilderness	3.75	3.23	2.86	2.29	2.12	1.81	1.68	1.72	1.84	2.08	2.71	3.41
Moosehorn Wilderness	3.59	3.14	3.16	3.44	3.38	3.49	3.98	4.18	4.40	3.94	3.82	3.82
Mount Adams Wilderness	5.71	5.00	4.46	4.23	3.89	3.55	3.26	3.41	4.02	5.13	5.89	5.98
Mount Baldy Wilderness	2.51	2.30	1.92	1.51	1.43	1.25	1.73	2.08	1.88	1.76	2.08	2.54
Mount Hood Wilderness	5.56	4.87	4.40	4.19	3.79	3.44	3.07	3.22	3.79	4.93	5.76	5.81
Mount Jefferson Wilderness	5.95	5.16	4.78	4.57	4.09	3.65	3.10	3.11	3.63	4.91	5.88	6.05

Table 8. Hygroscopic (RH) > small $(NH_4)_2SO_4$ and NH_4NO_3 Relative Humidity Adjustment Factor

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Mount Rainier NP	6.01	5.29	4.71	4.51	4.23	3.82	3.59	3.73	4.39	5.55	6.23	6.27
Mount Washington Wilderness	6.35	5.47	5.22	5.07	4.42	3.93	3.16	3.09	3.63	5.07	6.31	6.35
Mount Zirkel Wilderness	2.43	2.44	2.31	2.37	2.51	2.07	1.92	2.02	2.23	2.12	2.41	2.37
Mountain Lakes Wilderness	5.20	4.32	3.90	3.58	3.26	2.96	2.69	2.70	2.94	3.67	4.96	5.24
North Absaroka Wilderness	2.68	2.51	2.50	2.42	2.40	2.13	1.83	1.72	1.98	2.31	2.65	2.65
North Cascades NP	5.37	4.86	4.24	4.04	3.80	3.51	3.34	3.61	4.23	5.08	5.68	5.66
Okefenokee Wilderness	4.16	3.79	3.80	3.65	3.79	4.46	4.24	4.55	4.55	4.35	4.18	4.33
Olympic NP	5.76	5.20	4.81	4.64	3.81	4.04	3.52	4.16	4.70	5.63	6.11	6.02
Otter Creek Wilderness	3.41	3.20	3.20	2.91	3.64	3.70	3.88	4.18	4.26	3.72	3.32	3.56
Pasayten Wilderness	5.46	4.89	4.20	3.96	3.77	3.42	3.28	3.49	4.08	5.00	5.72	5.74
Pecos Wilderness	2.65	2.40	2.10	1.85	1.88	1.65	1.96	2.34	2.27	1.94	2.36	2.60
Petrified Forest NP	2.67	2.43	1.96	1.59	1.46	1.26	1.67	2.06	1.85	1.79	2.20	2.66
Pine Mountain Wilderness	2.44	2.29	1.95	1.51	1.41	1.20	1.54	1.91	1.77	1.70	1.96	2.39
Pinnacles NM	4.02	4.05	4.09	3.01	2.81	2.54	2.40	2.52	2.54	2.74	2.82	3.36
Point Reyes NS	4.16	3.74	3.53	2.96	2.80	2.55	2.69	2.77	2.80	2.90	3.30	3.80
Presidential Range-Dry River Wilderness	3.36	3.02	3.15	3.26	3.37	3.56	3.86	4.14	4.33	3.96	3.68	3.50
Rawah Wilderness	2.31	2.39	2.32	2.44	2.61	2.19	2.05	2.16	2.31	2.12	2.37	2.29
Red Rock Lakes Wilderness	3.09	2.76	2.57	2.41	2.38	2.17	1.86	1.77	2.01	2.39	2.96	3.05
Redwood NP	4.81	4.41	4.51	4.27	4.40	4.37	4.73	4.76	4.46	4.24	4.62	4.45
Rocky Mountain NP	2.09	2.24	2.24	2.45	2.62	2.22	2.09	2.15	2.29	2.04	2.23	2.08
Roosevelt Campobello International Park	3.61	3.14	3.16	3.45	3.37	3.49	3.95	4.15	4.36	3.93	3.84	3.85
Saguaro NP	1.99	1.80	1.56	1.18	1.16	1.07	1.51	1.89	1.66	1.54	1.72	2.25
Saint Marks Wilderness	4.24	3.89	3.79	3.72	3.79	4.32	4.56	4.63	4.43	4.19	4.16	4.39
Salt Creek Wilderness	2.57	2.19	1.75	1.67	1.82	1.69	1.93	2.16	2.37	1.94	2.07	2.38
San Gabriel Wilderness	2.94	2.78	2.72	2.41	2.37	2.29	2.32	2.39	2.44	2.44	2.36	2.58
San Gorgonio Wilderness	2.94	2.94	2.74	2.36	2.34	2.00	1.88	2.02	2.05	2.04	2.10	2.43
San Jacinto Wilderness	2.73	2.65	2.59	2.33	2.30	2.16	2.02	2.26	2.30	2.28	2.19	2.38
San Pedro Parks Wilderness	2.73	2.45	2.10	1.81	1.80	1.55	1.87	2.24	2.16	1.91	2.36	2.65
San Rafael Wilderness	3.38	3.13	3.07	2.68	2.64	2.57	2.66	2.74	2.84	2.77	2.63	2.94
Sawtooth Wilderness	3.78	3.18	2.55	2.20	2.17	1.95	1.51	1.50	1.61	2.11	3.26	3.70
Scapegoat Wilderness	3.70	3.24	2.97	2.79	2.78	2.75	2.41	2.31	2.65	3.09	3.67	3.68
Selway-Bitterroot Wilderness	3.99	3.41	2.90	2.56	2.54	2.43	2.00	1.93	2.21	2.82	3.78	4.01
Seney Wilderness	3.69	3.10	3.30	3.10	3.03	3.45	3.80	4.27	4.31	3.82	3.97	3.87
Sequoia NP	3.25	2.91	2.87	2.59	2.46	1.97	1.85	1.84	2.02	2.18	2.64	2.85
Shenandoah NP	3.26	2.99	3.02	2.72	3.28	3.46	3.59	3.85	3.91	3.41	3.08	3.44
Shining Rock Wilderness	3.89	3.51	3.37	3.11	3.77	4.22	4.29	4.58	4.60	4.12	3.69	3.88
Sierra Ancha Wilderness	2.38	2.21	1.87	1.46	1.36	1.19	1.60	1.95	1.78	1.69	1.96	2.41
Simeonof Wilderness	4.86	4.88	4.44	4.64	4.92	5.46	6.08	6.35	5.30	4.29	4.52	4.98
Sipsey Wilderness	3.89	3.52	3.23	3.13	3.60	3.99	4.13	4.09	4.12	3.87	3.61	3.89
South Warner Wilderness	4.36	3.67	3.20	2.81	2.64	2.39	2.04	2.07	2.24	2.76	3.71	4.20
Strawberry Mountain Wilderness	5.26	4.45	3.71	3.32	3.18	2.70	2.26	2.24	2.66	3.84	5.11	5.44
Superstition Wilderness	2.25	2.06	1.77	1.38	1.29	1.15	1.52	1.81	1.66	1.58	1.83	2.28
Swanquarter Wilderness	3.31	3.09	3.01	2.78	3.09	3.39	3.57	3.68	3.55	3.40	3.14	3.33
Sycamore Canyon Wilderness	2.52	2.41	2.05	1.59	1.47	1.23	1.53	1.98	1.85	1.77	2.03	2.45
Teton Wilderness	2.78	2.59	2.49	2.37	2.36	2.06	1.75	1.67	1.96	2.28	2.70	2.73

Table 8. Monthly $f_{(RH)}$ – Small $(NH_4)_2SO_4$ and NH_4NO_3 Relative Humidity Adjustment Factor

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Theodore Roosevelt NP	3.17	3.11	3.22	2.71	2.74	2.85	2.73	2.49	2.48	2.66	3.42	3.37
Thousand Lakes Wilderness	4.34	3.60	3.22	2.79	2.62	2.34	2.26	2.31	2.41	2.69	3.58	4.11
Three Sisters Wilderness	6.22	5.38	5.09	4.92	4.35	3.89	3.21	3.17	3.68	5.02	6.20	6.24
Tuxedni Wilderness	4.11	3.89	3.26	3.14	3.11	3.31	4.13	4.57	4.57	4.04	4.04	4.23
UL Bend Wilderness	2.94	2.75	2.77	2.55	2.44	2.41	2.19	1.97	2.12	2.50	2.96	2.95
Upper Buffalo Wilderness	3.73	3.33	3.03	3.07	3.54	3.57	3.43	3.50	3.71	3.51	3.52	3.74
Ventana Wilderness	3.92	3.69	3.61	2.86	2.69	2.46	2.46	2.55	2.61	2.72	2.89	3.43
Virgin Islands NP	2.41	2.36	2.27	2.39	2.44	2.40	2.43	2.57	2.58	2.63	2.68	2.54
Voyageurs NP	3.16	2.77	2.82	2.59	2.65	3.28	3.25	3.48	3.66	3.02	3.37	3.32
Washakie Wilderness	2.68	2.52	2.49	2.40	2.40	2.09	1.77	1.68	1.98	2.29	2.66	2.65
Weminuche Wilderness	2.80	2.58	2.22	1.97	1.97	1.64	1.89	2.28	2.20	1.97	2.45	2.69
West Elk Wilderness	2.64	2.53	2.24	2.15	2.16	1.79	1.92	2.24	2.26	2.02	2.41	2.53
Wheeler Peak Wilderness	2.72	2.50	2.17	1.97	2.02	1.76	1.98	2.42	2.36	2.01	2.48	2.66
White Mountain Wilderness	2.54	2.19	1.76	1.58	1.65	1.53	1.94	2.20	2.29	1.87	2.07	2.45
Wichita Mountains Wilderness	3.17	2.94	2.69	2.68	3.15	2.86	2.49	2.70	3.07	2.87	2.97	3.20
Wind Cave NP	2.81	2.81	2.86	2.82	3.06	2.81	2.50	2.46	2.44	2.52	2.97	2.83
Wolf Island Wilderness	4.02	3.68	3.58	3.45	3.59	4.17	4.13	4.47	4.46	4.23	4.05	4.18
Yellowstone NP	2.82	2.61	2.53	2.42	2.41	2.16	1.86	1.76	2.02	2.36	2.78	2.80
Yolla Bolly-Middle Eel Wilderness	4.48	3.82	3.53	3.13	3.00	2.75	2.81	2.87	2.93	3.11	3.84	4.24
Yosemite NP	3.62	3.32	3.13	2.52	2.34	1.89	1.69	1.67	1.78	2.04	2.65	3.22
Zion NP	3.05	2.81	2.26	1.84	1.67	1.37	1.33	1.54	1.58	1.75	2.25	2.72

Table 9. Hygroscopic (f_{ss}(RH)) Sea Salt Relative Humidity Adjustment Factor

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Acadia NP	3.90	3.48	3.40	3.66	3.71	3.81	4.19	4.27	4.44	4.13	4.10	4.19
Agua Tibia Wilderness	2.94	2.95	3.02	2.85	2.88	2.81	2.78	2.90	2.90	2.83	2.56	2.69
Alpine Lakes Wilderness	5.35	4.96	4.27	4.11	4.18	3.64	3.68	3.73	4.12	4.98	5.51	5.53
Anaconda Pintler Wilderness	4.00	3.56	3.18	2.90	2.85	2.75	2.33	2.25	2.52	3.10	3.81	3.97
Ansel Adams Wilderness	3.55	3.25	3.04	2.54	2.38	2.05	1.91	1.91	2.03	2.21	2.72	3.21
Arches NP	3.25	2.99	2.26	1.97	1.86	1.48	1.59	1.82	1.88	1.96	2.60	3.02
Badlands NP	3.37	3.33	3.27	3.05	3.25	3.15	2.89	2.81	2.74	2.82	3.41	3.38
Bandelier NM	2.91	2.59	2.22	1.87	1.90	1.67	2.11	2.54	2.37	2.00	2.49	2.78
Bering Sea Wilderness	4.39	4.57	4.60	4.58	4.57	4.70	5.26	5.73	5.11	4.59	4.52	4.54
Big Bend NP	2.20	2.03	1.75	1.67	1.84	1.87	2.03	2.34	2.47	2.09	2.10	2.22
Black Canyon of the Gunnison NP	3.05	2.89	2.47	2.31	2.28	1.89	2.04	2.36	2.37	2.18	2.71	2.92
Bob Marshall Wilderness	4.08	3.66	3.35	3.11	3.08	3.04	2.68	2.59	2.94	3.42	3.98	4.05
Bosque del Apache Wilderness	2.77	2.43	1.95	1.62	1.62	1.47	2.06	2.40	2.29	1.92	2.27	2.71
Boundary Waters Canoe Area Wilderness	3.73	3.35	3.29	2.91	3.00	3.44	3.68	3.88	3.98	3.45	3.89	3.91
Breton Wilderness	4.10	3.89	3.87	3.85	4.02	4.21	4.44	4.38	4.23	3.99	4.01	4.11
Bridger Wilderness	3.25	3.05	2.90	2.67	2.62	2.17	1.81	1.79	2.17	2.43	3.15	3.17
Brigantine Wilderness	3.53	3.24	3.30	3.15	3.49	3.63	3.84	4.02	4.02	3.82	3.48	3.55
Bryce Canyon NP	3.24	3.00	2.40	1.96	1.80	1.45	1.52	1.80	1.78	1.93	2.52	2.99
Cabinet Mountains Wilderness	4.42	3.93	3.50	3.18	3.13	3.06	2.67	2.59	3.01	3.58	4.33	4.46
Caney Creek Wilderness	3.90	3.52	3.31	3.41	3.83	3.88	3.69	3.68	3.82	3.76	3.77	3.93
Canyonlands NP	3.30	3.04	2.33	1.99	1.87	1.48	1.63	1.90	1.94	2.00	2.64	3.07
Cape Romain Wilderness	3.74	3.44	3.37	3.23	3.62	3.99	4.04	4.32	4.29	4.03	3.74	3.81
Capitol Reef NP	3.35	3.11	2.45	2.08	1.93	1.54	1.62	1.90	1.94	2.05	2.68	3.13
Caribou Wilderness	4.16	3.63	3.28	2.89	2.75	2.47	2.33	2.37	2.49	2.74	3.48	3.97
Carlsbad Caverns NP	2.75	2.36	1.86	1.72	1.89	1.86	2.27	2.59	2.75	2.09	2.29	2.68
Chassahowitzka Wilderness	4.29	3.99	3.89	3.76	3.77	4.29	4.34	4.51	4.49	4.33	4.23	4.38
Chiricahua NM	2.53	2.38	1.91	1.41	1.38	1.21	2.12	2.55	2.18	1.78	1.99	2.56
Chiricahua Wilderness	2.48	2.33	1.86	1.37	1.35	1.20	2.12	2.54	2.16	1.75	1.94	2.52
Cohutta Wilderness	3.97	3.62	3.44	3.26	3.82	4.20	4.24	4.35	4.35	4.05	3.82	4.02
Crater Lake NP	5.15	4.56	4.31	4.12	3.80	3.52	3.20	3.23	3.44	4.17	5.10	5.19
Craters of the Moon NM	3.78	3.41	2.86	2.51	2.48	2.16	1.72	1.69	1.93	2.43	3.38	3.72
Cucamonga Wilderness	3.07	3.01	3.03	2.79	2.80	2.72	2.72	2.80	2.81	2.76	2.58	2.77
Denali NP & Pres	3.68	3.57	3.07	2.74	2.74	3.01	3.53	4.13	4.19	4.09	3.92	3.94
Desolation Wilderness	3.85	3.39	3.02	2.48	2.32	2.01	1.84	1.87	2.02	2.28	2.94	3.58
Diamond Peak Wilderness	5.29	4.72	4.45	4.27	3.92	3.65	3.23	3.26	3.56	4.43	5.26	5.34
Dolly Sods Wilderness	3.60	3.35	3.31	3.03	3.66	3.76	3.91	4.12	4.16	3.72	3.47	3.72
Dome Land Wilderness	3.10	2.86	2.75	2.42	2.33	2.15	2.11	2.16	2.22	2.26	2.40	2.71
Eagle Cap Wilderness	4.84	4.27	3.57	3.22	3.14	2.74	2.33	2.27	2.60	3.61	4.68	4.99
Eagles Nest Wilderness	2.86	2.82	2.54	2.52	2.57	2.20	2.20	2.44	2.46	2.27	2.73	2.79
Emigrant Wilderness	3.70	3.37	3.13	2.60	2.42	2.05	1.88	1.88	2.01	2.24	2.84	3.39
Everglades NP	3.60	3.44	3.37	3.22	3.21	3.58	3.50	3.72	3.78	3.61	3.50	3.55
Fitzpatrick Wilderness	3.25	3.05	2.88	2.66	2.62	2.18	1.82	1.79	2.16	2.43	3.13	3.18
Flat Tops Wilderness	2.99	2.88	2.54	2.47	2.47	2.07	2.03	2.23	2.35	2.25	2.75	2.89
Galiuro Wilderness	2.42	2.19	1.82	1.35	1.31	1.16	1.76	2.18	1.94	1.73	2.00	2.52
Gates of the Mountains Wilderness	3.62	3.27	3.05	2.85	2.80	2.74	2.43	2.35	2.58	2.99	3.41	3.52

Table 9. Monthly $f_{ss}(RH)$ – Sea Salt Relative Humidity Adjustment Factor

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Gearhart Mountain Wilderness	4.63	4.06	3.67	3.40	3.16	2.90	2.49	2.50	2.70	3.39	4.31	4.60
Gila Wilderness	2.63	2.35	1.91	1.52	1.48	1.36	2.22	2.36	2.19	1.87	2.17	2.65
Glacier NP	4.61	4.12	3.87	3.64	3.63	3.59	3.11	3.11	3.63	4.03	4.43	4.51
Glacier Peak Wilderness	5.14	4.73	4.19	4.03	3.93	3.60	3.51	3.63	4.04	4.79	5.31	5.34
Goat Rocks Wilderness	5.30	4.79	4.32	4.15	3.94	3.65	3.46	3.55	3.99	4.83	5.40	5.51
Grand Canyon NP	2.93	2.73	2.26	1.78	1.61	1.32	1.50	1.85	1.79	1.84	2.29	2.70
Grand Teton NP	3.34	3.10	2.82	2.59	2.56	2.21	1.85	1.78	2.12	2.48	3.10	3.29
Great Gulf Wilderness	3.60	3.29	3.29	3.34	3.41	3.58	3.85	4.07	4.20	3.96	3.81	3.73
Great Sand Dunes NP & Pres	2.98	2.84	2.48	2.33	2.36	2.08	2.24	2.66	2.56	2.26	2.82	2.94
Great Smoky Mountains NP	4.01	3.57	3.47	3.22	3.82	4.23	4.24	4.37	4.38	4.03	3.81	4.02
Guadalupe Mountains NP	2.82	2.35	1.84	1.64	1.82	1.83	2.36	2.72	2.85	2.01	2.28	2.76
Haleakala NP	3.52	3.43	3.40	3.35	3.25	3.18	3.29	3.27	3.22	3.33	3.52	3.47
Hawaii Volcanoes NP	3.80	3.68	3.71	3.72	3.72	3.69	3.79	3.83	3.79	3.83	4.08	3.80
Hells Canyon Wilderness	4.39	3.81	3.15	2.75	2.63	2.44	1.97	1.90	2.19	3.00	4.13	4.51
Hercules-Glades Wilderness	3.86	3.51	3.23	3.22	3.66	3.72	3.69	3.73	3.81	3.57	3.65	3.88
Hoover Wilderness	3.66	3.31	3.05	2.53	2.36	2.00	1.82	1.82	1.96	2.18	2.79	3.34
Isle Royale NP	3.78	3.34	3.28	2.93	2.78	3.31	3.83	3.87	4.06	3.40	4.05	4.04
James River Face Wilderness	3.43	3.19	3.16	2.90	3.46	3.69	3.79	3.97	4.00	3.61	3.31	3.56
Jarbidge Wilderness	3.65	3.28	2.62	2.69	2.71	2.44	1.95	1.67	1.60	2.01	3.03	3.51
John Muir Wilderness	3.46	3.18	3.07	2.68	2.51	2.17	2.06	2.08	2.20	2.35	2.75	3.12
Joshua Tree NP	2.83	2.76	2.75	2.52	2.53	2.41	2.28	2.53	2.53	2.48	2.32	2.54
Joyce Kilmer-Slickrock Wilderness	4.01	3.58	3.46	3.24	3.81	4.22	4.23	4.35	4.35	4.03	3.82	4.02
Kaiser Wilderness	3.58	3.27	3.08	2.58	2.42	2.10	1.99	2.00	2.12	2.29	2.75	3.24
Kalmiopsis Wilderness	4.98	4.45	4.28	4.09	3.89	3.66	3.49	3.51	3.60	4.08	4.90	4.96
Kings Canyon	3.40	3.13	3.03	2.66	2.50	2.16	2.05	2.07	2.20	2.33	2.71	3.05
La Garita Wilderness	3.03	2.83	2.41	2.21	2.19	1.86	2.10	2.50	2.42	2.16	2.72	2.93
Lassen Volcanic NP	4.21	3.66	3.33	2.93	2.78	2.50	2.36	2.40	2.51	2.78	3.54	4.02
Lava Beds NM	4.64	4.04	3.68	3.37	3.15	2.89	2.62	2.65	2.82	3.32	4.21	4.56
Linville Gorge Wilderness	3.80	3.52	3.43	3.18	3.80	4.20	4.25	4.51	4.48	3.97	3.67	3.86
Lostwood Wilderness	3.77	3.66	3.67	2.86	2.79	3.07	3.11	2.82	2.80	2.99	3.93	3.95
Lye Brook Wilderness	3.53	3.26	3.27	3.20	3.36	3.48	3.70	3.93	4.04	3.82	3.63	3.61
Mammoth Cave NP	3.99	3.63	3.45	3.50	4.52	5.19	5.08	4.16	4.17	3.81	3.73	4.03
Marble Mountain Wilderness	4.85	4.32	4.16	3.92	3.76	3.53	3.44	3.46	3.51	3.86	4.63	4.78
Maroon Bells-Snowmass Wilderness	2.89	2.82	2.52	2.49	2.45	2.04	2.22	2.57	2.54	2.26	2.71	2.80
Mazatzal Wilderness	2.60	2.40	2.03	1.53	1.42	1.21	1.66	2.06	1.90	1.77	2.10	2.55
Medicine Lake Wilderness	3.79	3.66	3.56	2.80	2.75	2.94	2.93	2.66	2.73	2.95	3.85	3.92
Mesa Verde NP	3.40	3.10	2.61	1.95	2.00	1.53	2.04	2.45	2.28	2.05	2.69	3.15
Mingo Wilderness	3.92	3.58	3.30	3.19	3.58	3.72	3.80	3.82	3.85	3.61	3.66	3.90
Mission Mountains Wilderness	4.24	3.79	3.38	3.10	3.08	3.04	2.68	2.59	2.96	3.48	4.17	4.26
Mokelumne Wilderness	3.81	3.38	3.04	2.51	2.34	2.02	1.86	1.88	2.02	2.27	2.91	3.52
Moosehorn Wilderness	3.80	3.42	3.32	3.50	3.47	3.60	3.98	4.15	4.31	4.02	3.97	3.99
Mount Adams Wilderness	5.24	4.74	4.34	4.18	3.91	3.66	3.41	3.51	3.93	4.78	5.36	5.44
Mount Baldy Wilderness	2.74	2.50	2.05	1.58	1.50	1.29	1.87	2.28	2.06	1.87	2.26	2.74
Mount Hood Wilderness	5.16	4.67	4.33	4.18	3.87	3.61	3.29	3.38	3.78	4.67	5.29	5.33
Mount Jefferson Wilderness	5.38	4.84	4.55	4.42	4.05	3.74	3.27	3.28	3.63	4.64	5.41	5.46
Mount Rainier NP	5.42	4.92	4.50	4.36	4.13	3.86	3.67	3.76	4.20	5.05	5.56	5.62

Table 9. Hygroscopic ($f(RH)$) Sea Salt Relative Humidity Adjustment Factor

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Mount Washington Wilderness	5.61	5.03	4.81	4.71	4.24	3.91	3.31	3.25	3.60	4.73	5.59	5.62
Mount Zirkel Wilderness	2.85	2.83	2.61	2.61	2.67	2.24	2.10	2.23	2.38	2.31	2.75	2.78
Mountain Lakes Wilderness	4.89	4.26	3.93	3.67	3.40	3.11	2.82	2.83	3.04	3.67	4.68	4.91
North Absaroka Wilderness	3.18	2.97	2.83	2.66	2.64	2.35	2.02	1.89	2.16	2.53	3.03	3.13
North Cascades NP	5.03	4.65	4.22	4.08	3.88	3.68	3.53	3.70	4.13	4.78	5.24	5.25
Okefenokee Wilderness	4.13	3.83	3.82	3.69	3.85	4.38	4.28	4.51	4.48	4.31	4.18	4.27
Olympic NP	5.27	4.87	4.61	4.51	3.94	4.12	3.76	4.16	4.51	5.17	5.51	5.46
Otter Creek Wilderness	3.63	3.40	3.34	3.06	3.67	3.82	3.98	4.19	4.23	3.78	3.51	3.76
Pasayten Wilderness	5.09	4.67	4.18	4.00	3.84	3.58	3.45	3.58	3.99	4.71	5.25	5.30
Pecos Wilderness	2.91	2.64	2.25	1.97	2.00	1.78	2.15	2.57	2.44	2.09	2.56	2.83
Petrified Forest NP	2.93	2.66	2.11	1.66	1.53	1.30	1.81	2.26	2.03	1.91	2.40	2.88
Pine Mountain Wilderness	2.69	2.50	2.11	1.60	1.47	1.24	1.67	2.09	1.92	1.82	2.16	2.62
Pinnacles NM	3.94	3.97	3.99	3.12	2.94	2.67	2.54	2.63	2.65	2.80	2.96	3.36
Point Reyes NS	4.20	3.88	3.72	3.25	3.12	2.88	2.96	3.01	3.05	3.12	3.48	3.90
Presidential Range-Dry River Wilderness	3.60	3.28	3.31	3.36	3.45	3.66	3.92	4.14	4.27	3.99	3.83	3.72
Rawah Wilderness	2.70	2.74	2.58	2.65	2.76	2.36	2.23	2.37	2.45	2.31	2.69	2.66
Red Rock Lakes Wilderness	3.51	3.18	2.91	2.67	2.63	2.41	2.06	1.94	2.20	2.63	3.29	3.46
Redwood NP	4.66	4.38	4.48	4.34	4.41	4.35	4.56	4.59	4.34	4.19	4.51	4.44
Rocky Mountain NP	2.44	2.56	2.47	2.64	2.75	2.37	2.26	2.36	2.41	2.20	2.51	2.41
Roosevelt Campobello International Park	3.82	3.43	3.32	3.52	3.47	3.61	3.96	4.13	4.29	4.02	3.99	4.01
Saguaro NP	2.24	2.00	1.69	1.21	1.20	1.08	1.67	2.13	1.86	1.65	1.89	2.44
Saint Marks Wilderness	4.18	3.89	3.82	3.76	3.85	4.30	4.49	4.54	4.39	4.19	4.15	4.30
Salt Creek Wilderness	2.72	2.37	1.88	1.77	1.96	1.87	2.15	2.44	2.59	2.12	2.26	2.56
San Gabriel Wilderness	3.12	3.04	3.04	2.77	2.78	2.69	2.69	2.77	2.79	2.74	2.59	2.79
San Gorgonio Wilderness	2.97	3.06	2.93	2.60	2.63	2.28	2.13	2.30	2.31	2.24	2.25	2.55
San Jacinto Wilderness	2.92	2.91	2.91	2.67	2.69	2.55	2.33	2.64	2.64	2.57	2.40	2.60
San Pedro Parks Wilderness	3.00	2.71	2.25	1.94	1.91	1.66	2.04	2.45	2.33	2.05	2.57	2.88
San Rafael Wilderness	3.49	3.35	3.34	3.00	2.99	2.90	2.97	3.04	3.09	3.00	2.86	3.12
Sawtooth Wilderness	4.05	3.53	2.89	2.53	2.44	2.18	1.66	1.61	1.76	2.38	3.55	4.00
Scapegoat Wilderness	3.97	3.57	3.27	3.04	3.01	2.96	2.60	2.51	2.83	3.30	3.86	3.93
Selway-Bitterroot Wilderness	4.20	3.71	3.21	2.86	2.80	2.66	2.18	2.09	2.39	3.06	3.96	4.20
Seney Wilderness	4.05	3.60	3.60	3.30	3.20	3.58	3.91	4.28	4.30	4.00	4.19	4.16
Sequoia NP	3.27	3.07	3.10	2.84	2.66	2.21	2.06	2.05	2.21	2.35	2.75	2.93
Shenandoah NP	3.44	3.17	3.17	2.90	3.42	3.66	3.78	3.97	3.98	3.56	3.28	3.62
Shining Rock Wilderness	3.90	3.55	3.43	3.21	3.82	4.22	4.28	4.48	4.48	4.06	3.76	3.92
Sierra Ancha Wilderness	2.62	2.42	2.02	1.53	1.42	1.22	1.73	2.14	1.95	1.81	2.15	2.62
Simeonof Wilderness	4.83	4.85	4.54	4.68	4.83	5.20	5.57	5.72	5.11	4.48	4.62	4.89
Sipsey Wilderness	3.94	3.60	3.36	3.28	3.72	4.06	4.18	4.14	4.13	3.91	3.74	3.96
South Warner Wilderness	4.32	3.75	3.31	2.94	2.77	2.51	2.13	2.15	2.31	2.83	3.71	4.19
Strawberry Mountain Wilderness	4.97	4.37	3.77	3.44	3.28	2.88	2.41	2.38	2.73	3.77	4.82	5.10
Superstition Wilderness	2.49	2.27	1.92	1.44	1.34	1.17	1.64	1.98	1.82	1.69	2.01	2.49
Swanquarter Wilderness	3.52	3.30	3.25	3.09	3.42	3.71	3.88	3.96	3.83	3.67	3.43	3.55
Sycamore Canyon Wilderness	2.78	2.62	2.22	1.68	1.55	1.27	1.67	2.17	2.00	1.90	2.25	2.69
Teton Wilderness	3.26	3.04	2.83	2.61	2.59	2.27	1.93	1.83	2.14	2.50	3.07	3.21
Theodore Roosevelt NP	3.67	3.56	3.51	2.93	2.97	3.09	2.96	2.72	2.72	2.93	3.75	3.78

Table 9. Monthly $f_{ss}(RH)$ – Sea Salt Relative Humidity Adjustment Factor

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Thousand Lakes Wilderness	4.27	3.70	3.38	2.99	2.82	2.52	2.37	2.42	2.53	2.82	3.62	4.08
Three Sisters Wilderness	5.53	4.97	4.74	4.63	4.20	3.89	3.35	3.31	3.65	4.70	5.53	5.56
Tuxedni Wilderness	4.28	4.06	3.53	3.46	3.44	3.64	4.26	4.56	4.51	4.17	4.17	4.37
UL Bend Wilderness	3.44	3.22	3.12	2.79	2.70	2.67	2.42	2.18	2.35	2.77	3.34	3.40
Upper Buffalo Wilderness	3.85	3.47	3.23	3.27	3.72	3.78	3.69	3.70	3.84	3.64	3.67	3.86
Ventana Wilderness	3.91	3.76	3.70	3.08	2.93	2.69	2.69	2.75	2.80	2.87	3.06	3.48
Virgin Islands NP	3.17	3.12	3.04	3.15	3.19	3.17	3.18	3.31	3.30	3.36	3.39	3.28
Voyageurs NP	3.69	3.31	3.20	2.90	2.89	3.46	3.55	3.71	3.87	3.42	3.83	3.80
Washakie Wilderness	3.18	2.98	2.83	2.64	2.62	2.31	1.96	1.85	2.15	2.50	3.04	3.14
Weminuche Wilderness	3.08	2.85	2.39	2.11	2.09	1.77	2.05	2.46	2.36	2.12	2.69	2.95
West Elk Wilderness	3.00	2.87	2.49	2.36	2.33	1.94	2.10	2.44	2.43	2.20	2.72	2.89
Wheeler Peak Wilderness	3.00	2.76	2.35	2.11	2.15	1.92	2.17	2.63	2.52	2.18	2.71	2.93
White Mountain Wilderness	2.71	2.37	1.89	1.68	1.76	1.66	2.14	2.46	2.49	2.02	2.25	2.63
Wichita Mountains Wilderness	3.35	3.12	2.91	2.94	3.40	3.21	2.84	3.01	3.32	3.10	3.20	3.40
Wind Cave NP	3.25	3.20	3.13	3.01	3.22	3.06	2.75	2.68	2.63	2.75	3.28	3.24
Wolf Island Wilderness	4.03	3.74	3.66	3.55	3.72	4.20	4.20	4.46	4.42	4.22	4.08	4.15
Yellowstone NP	3.29	3.05	2.87	2.66	2.65	2.39	2.05	1.93	2.21	2.59	3.14	3.25
Yolla Bolly-Middle Eel Wilderness	4.38	3.89	3.66	3.31	3.18	2.92	2.89	2.94	3.00	3.20	3.84	4.19
Yosemite NP	3.58	3.38	3.23	2.71	2.54	2.08	1.84	1.79	1.93	2.18	2.78	3.25
Zion NP	3.26	3.03	2.44	1.96	1.78	1.44	1.41	1.66	1.67	1.88	2.48	2.98

Table 10. Monthly Average Natural Conditions Visual Range In Kilometers

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Acadia NP	173	177	177	174	174	173	170	169	167	171	171	170
Agua Tibia Wilderness	226	227	226	228	228	229	229	228	228	228	230	229
Alpine Lakes Wilderness	224	228	236	238	236	243	242	242	237	227	222	222
Anaconda Pintler Wilderness	256	259	262	267	268	271	273	272	271	269	265	259
Ansel Adams Wilderness	258	263	266	269	269	270	274	275	272	267	259	258
Arches NP	265	268	274	276	277	281	280	278	277	276	271	268
Badlands NP	233	233	233	234	232	233	235	236	236	236	232	233
Bandelier NM	269	272	276	280	281	283	278	274	276	277	274	269
Bering Sea Wilderness												
Big Bend NP	236	234	233	234	233	231	225	220	227	233	235	235
Black Canyon of the Gunnison NP	278	280	282	283	282	282	281	278	276	280	280	278
Bob Marshall Wilderness	257	259	262	263	263	266	265	262	262	264	260	258
Bosque del Apache Wilderness	249	252	256	259	259	260	255	252	253	256	253	249
Boundary Waters Canoe Area Wilderness	184	187	189	190	190	191	193	194	191	188	184	184
Breton Wilderness	173	176	176	179	177	174	172	170	169	174	171	171
Bridger Wilderness	278	280	286	290	292	296	295	292	292	291	285	280
Brigantine Wilderness	159	161	161	161	160	158	156	157	158	160	160	159
Bryce Canyon NP	268	269	270	271	271	275	279	279	275	273	268	268
Cabinet Mountains Wilderness	252	254	253	255	251	251	249	247	247	248	252	251
Caney Creek Wilderness	174	177	180	183	183	183	186	186	183	179	174	173
Canyonlands NP	257	261	264	263	259	259	260	260	258	258	259	257
Cape Romain Wilderness	167	169	174	177	178	181	180	178	177	177	172	169
Capitol Reef NP	269	271	277	280	281	285	284	281	281	280	275	271
Caribou Wilderness	250	256	259	263	264	267	267	267	266	264	257	252
Carlsbad Caverns NP	266	271	276	277	275	276	272	270	267	274	271	267
Chassahowitzka Wilderness	171	173	174	175	175	171	171	169	169	171	171	170
Chiricahua NM	253	254	258	261	262	263	256	253	256	259	257	252
Chiricahua Wilderness	253	254	258	262	262	263	256	253	256	259	258	252
Cohutta Wilderness	181	184	185	187	183	180	180	179	179	181	183	181
Crater Lake NP	255	263	266	269	273	276	280	279	276	267	256	255
Craters of the Moon NM	245	248	252	255	255	257	261	261	259	255	248	246
Cucamonga Wilderness	263	264	264	267	267	268	268	267	267	267	268	266
Denali NP & Pres	257	257	261	263	263	261	257	251	250	252	254	254
Desolation Wilderness	270	275	279	285	287	290	292	292	290	287	280	273
Diamond Peak Wilderness	253	261	264	267	271	275	279	279	275	264	254	253
Dolly Sods Wilderness	197	200	201	203	204	206	206	205	205	204	203	200
Dome Land Wilderness	242	244	244	247	241	241	239	237	236	241	243	241
Eagle Cap Wilderness	229	234	241	245	245	249	252	253	249	240	230	227
Eagles Nest Wilderness	302	302	304	304	303	308	308	305	304	307	303	303
Emigrant Wilderness	242	245	248	253	254	258	259	259	258	256	250	245
Everglades NP	168	170	171	172	172	169	170	167	166	168	169	168
Fitzpatrick Wilderness	280	282	283	284	284	289	292	293	288	286	280	281
Flat Tops Wilderness	301	302	305	305	304	309	310	307	306	307	303	302
Galiuro Wilderness	254	255	258	262	262	263	259	256	258	259	257	252
Gates of the Mountains Wilderness	281	285	287	288	289	289	292	293	291	286	283	282

Table 9a. Monthly Average Natural Conditions Visual Range In Kilometers

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Gearhart Mountain Wilderness	262	269	274	277	280	283	287	287	285	277	266	263
Gila Wilderness	275	278	282	285	285	286	278	278	279	282	279	275
Glacier NP	224	228	230	231	231	231	235	235	231	228	225	225
Glacier Peak Wilderness	233	237	243	245	245	249	250	248	244	236	231	231
Goat Rocks Wilderness	243	249	254	256	259	263	265	263	258	248	241	241
Grand Canyon NP	267	269	273	278	280	282	281	277	278	277	273	269
Grand Teton NP	274	278	277	276	275	273	270	268	266	269	272	273
Great Gulf Wilderness	192	192	195	195	195	197	196	193	193	196	192	192
Great Sand Dunes NP & Pres	255	260	260	263	257	254	253	252	251	255	257	255
Great Smoky Mountains NP	184	185	187	188	188	190	192	193	190	188	185	184
Guadalupe Mountains NP	265	270	276	278	276	276	271	268	266	274	271	266
Haleakala NP	232	234	234	235	237	238	236	236	237	235	232	233
Hawaii Volcanoes NP	243	246	246	246	246	246	244	243	244	243	238	243
Hells Canyon Wilderness	224	229	234	237	238	239	242	243	241	235	226	223
Hercules-Glades Wilderness	178	180	182	182	179	179	180	179	178	180	179	178
Hoover Wilderness	259	263	265	271	273	276	278	277	276	274	268	262
Isle Royale NP	182	185	184	186	187	183	179	179	177	184	179	179
James River Face Wilderness	181	183	187	187	186	188	192	193	193	191	185	182
Jarbidge Wilderness	245	246	246	249	244	243	242	240	239	243	246	243
John Muir Wilderness	256	260	261	264	258	254	254	253	252	255	258	256
Joshua Tree NP	242	246	247	251	252	255	256	256	255	253	249	246
Joyce Kilmer-Slickrock Wilderness	186	187	187	189	189	190	190	189	188	189	189	188
Kaiser Wilderness	260	264	266	272	273	277	278	278	276	274	269	264
Kalmiopsis Wilderness	194	200	202	205	207	209	211	210	209	204	195	195
Kings Canyon	229	232	233	236	237	240	240	240	239	238	235	232
La Garita Wilderness	252	259	263	266	268	271	273	273	271	266	256	253
Lassen Volcanic NP	263	264	267	269	269	272	270	266	267	269	265	263
Lava Beds NM	244	250	253	257	258	261	261	261	260	258	251	246
Linville Gorge Wilderness	180	182	183	185	180	177	177	175	175	178	181	180
Lostwood Wilderness	229	230	228	234	235	232	232	234	235	233	227	227
Lye Brook Wilderness	196	198	197	197	196	195	194	192	191	192	195	195
Mammoth Cave NP	187	188	189	189	189	192	191	188	188	191	188	188
Marble Mountain Wilderness	251	255	256	254	242	235	237	249	248	252	254	250
Maroon Bells-Snowmass Wilderness	274	281	284	287	289	291	292	291	291	286	276	275
Mazatzal Wilderness	252	253	256	260	261	263	259	256	258	258	256	252
Medicine Lake Wilderness	231	232	231	236	237	235	235	237	237	236	230	229
Mesa Verde NP	264	267	271	277	276	281	276	272	275	275	270	266
Mingo Wilderness	166	169	172	174	173	173	176	176	174	171	166	166
Mission Mountains Wilderness	249	252	254	255	251	250	250	249	249	251	251	249
Mokelumne Wilderness	252	259	263	266	269	272	275	273	268	257	251	250
Moosehorn Wilderness	159	163	166	167	170	172	174	173	170	162	158	157
Mount Adams Wilderness	242	248	251	253	258	262	267	267	262	250	241	241
Mount Baldy Wilderness	261	266	269	275	276	280	281	281	279	277	271	264
Mount Hood Wilderness	241	249	253	256	259	262	265	265	262	255	243	241
Mount Jefferson Wilderness	237	240	240	238	239	238	234	232	230	234	235	235

Table 10. Monthly Average Natural Conditions Visual Range In Kilometers

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Mount Rainier NP	215	220	224	226	228	231	233	232	227	218	213	213
Mount Washington Wilderness	216	223	224	225	230	234	240	241	237	225	217	216
Mount Zirkel Wilderness	296	296	297	296	295	300	301	300	298	299	296	296
Mountain Lakes Wilderness	284	285	286	287	287	290	294	295	292	288	284	284
North Absaroka Wilderness	246	251	256	258	260	262	264	261	256	249	244	244
North Cascades NP	243	246	246	247	246	241	243	240	240	242	243	242
Okefenokee Wilderness	162	166	168	169	174	173	176	172	169	163	160	161
Olympic NP	233	235	235	238	231	230	228	226	225	230	234	231
Otter Creek Wilderness	180	183	188	190	191	194	195	193	189	183	178	178
Pasayten Wilderness	269	271	274	277	276	279	276	272	272	276	272	269
Pecos Wilderness	294	297	303	308	310	313	307	302	304	305	300	294
Petrified Forest NP	269	271	274	279	280	282	278	275	276	277	274	270
Pine Mountain Wilderness	238	238	238	247	248	251	252	251	251	249	248	244
Pinnacles NM	211	215	216	222	223	226	225	224	224	223	219	214
Point Reyes NS	128	134	133	132	130	127	122	119	117	121	124	126
Presidential Range-Dry River Wilderness	186	188	189	191	192	192	192	191	190	191	192	190
Rawah Wilderness	297	296	297	296	294	298	300	299	297	299	296	297
Red Rock Lakes Wilderness	261	264	263	266	264	265	261	261	264	266	262	264
Redwood NP	176	182	187	191	192	196	204	206	201	192	180	177
Rocky Mountain NP	261	265	265	262	263	262	258	256	254	258	259	259
Roosevelt Campobello Int Pk	170	173	173	175	172	169	169	166	166	168	171	170
Saguaro NP	252	250	250	248	247	251	252	251	250	252	250	252
Saint Marks Wilderness	182	185	189	190	188	189	187	185	184	187	186	184
Salt Creek Wilderness	245	247	247	250	250	251	251	250	250	250	251	249
San Gabriel Wilderness	262	262	264	268	268	272	273	271	271	271	271	267
San Gorgonio Wilderness	253	255	258	262	262	263	258	254	257	258	256	251
San Jacinto Wilderness	247	247	248	250	250	252	253	251	250	251	252	250
San Pedro Parks Wilderness	280	284	285	286	285	279	277	276	278	281	281	279
San Rafael Wilderness	243	246	250	253	253	256	252	248	249	252	247	244
Sawtooth Wilderness	259	263	269	272	272	274	278	278	277	273	263	259
Scapegoat Wilderness	249	253	255	257	257	257	260	261	258	254	249	249
Selway-Bitterroot Wilderness	251	256	261	264	265	266	270	271	268	262	253	251
Seney Wilderness	179	182	181	182	183	180	178	175	175	178	177	177
Sequoia NP	230	232	232	234	236	239	240	240	239	238	234	233
Shenandoah NP	191	193	193	195	191	190	189	187	186	190	192	190
Shining Rock Wilderness	193	196	197	199	194	191	190	188	188	192	195	193
Sierra Ancha Wilderness	252	253	256	260	261	263	259	256	257	258	256	252
Simeonof Wilderness	138	138	143	141	138	133	128	127	135	144	142	138
Sipsey Wilderness	176	178	180	181	178	175	174	174	174	176	178	176
South Warner Wilderness	243	249	253	256	258	260	263	263	261	257	249	245
Strawberry Mountain Wilderness	227	233	239	242	244	248	252	252	248	238	228	226
Superstition Wilderness	254	256	259	262	263	264	261	258	259	260	258	254
Swanquarter Wilderness	172	174	174	176	174	171	170	169	170	171	173	172
Sycamore Canyon Wilderness	267	268	272	277	278	281	277	273	274	275	272	268
Teton Wilderness	280	282	283	285	285	288	291	292	289	286	281	281

Table 9. Monthly Average Natural Conditions Visual Range In Kilometers

Class I Area	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Theodore Roosevelt NP	223	228	231	234	235	238	238	238	237	235	229	225
Thousand Lakes Wilderness	258	259	258	263	262	261	262	265	265	263	256	257
Three Sisters Wilderness	217	223	225	227	231	234	240	240	236	226	217	217
Tuxedni Wilderness	195	198	205	206	206	204	195	192	192	196	196	194
UL Bend Wilderness	235	236	236	237	238	238	240	242	241	238	234	235
Upper Buffalo Wilderness	177	180	182	182	178	178	179	179	177	179	179	177
Ventana Wilderness	213	215	216	223	225	227	227	227	226	225	223	218
Virgin Islands NP	188	189	190	188	187	188	187	185	185	184	183	185
Voyageurs NP	177	179	179	181	180	176	176	175	174	178	175	176
Washakie Wilderness	270	272	272	273	273	276	279	280	277	274	270	270
Weminuche Wilderness	272	273	276	277	277	281	280	276	276	279	275	273
West Elk Wilderness	298	301	305	308	308	312	309	305	306	308	303	300
Wheeler Peak Wilderness	296	300	306	308	307	309	303	300	299	304	301	297
White Mountain Wilderness	265	267	271	273	272	275	273	268	269	272	267	265
Wichita Mountains Wilderness	232	233	232	233	231	233	235	235	236	235	231	232
Wind Cave NP	246	248	250	250	247	249	252	250	247	249	248	246
Wolf Island Wilderness	173	175	176	177	176	172	172	170	170	171	173	172
Yellowstone NP	280	282	283	284	284	287	290	291	288	285	280	280
Yolla Bolly-Middle Eel Wilderness	246	251	254	258	259	262	261	260	260	258	251	248
Yosemite NP	243	245	246	252	253	257	259	259	258	256	251	246
Zion NP	247	249	254	257	259	262	262	260	260	258	254	250

3.4. Ozone

3.4.1. Introduction (Revised)

Ozone is an air pollutant that forms on warm, sunny days when precursor emissions—nitrogen oxides (NO_x) and volatile organic compounds (VOCs)—react in the presence of sunlight. Because ozone is a regional pollutant, precursor sources both near and far from FLM areas can contribute to ozone formation.

Ozone is phytotoxic, causing damage to vegetation throughout the world (Ashmore et al. 2004). Some plant species are more sensitive to ozone than are humans (EPA 2007b). Ozone pollution has been shown to reduce plant growth, alter species composition, and predispose trees to insect and disease attack. Ozone also causes direct foliar injury to many plant species. Affected leaves are often marked with discoloration and lesions, and they age more rapidly than normal leaves (EPA 2007b).

FLAG is intended to provide information to assist the FLMs in identifying ozone impacts to vegetation on lands they manage. Therefore, the objectives of this chapter are to document information currently known about vegetation response to ozone exposure, and to describe FLM procedures for responding to new source review (NSR) permit applications. If the FLMs have evidence that ozone is adversely impacting an area they manage, they will recommend that additional emissions of ozone precursors are minimized until those adverse impacts are mitigated.

3.4.2. Ozone Effects on Vegetation (Revised)

Most ozone effects research has focused on agricultural crops. However, research has identified many native plants in natural ecosystems that are sensitive to ozone (EPA 1996e). Some of these ozone-sensitive plant species have been used as "bioindicators" of ozone to document phytotoxicity of ozone in the field due to ambient ozone. A listing of key literature describing known ozone effects on native vegetation is provided in Appendix G.

The definitions for ozone injury and damage used by FLMs are based on the classical definitions (for example, see Guderian 1977). Injury is all physical or biological responses to pollutants, such as change in metabolism, reduced photosynthesis, leaf necrosis, premature leaf drop, and chlorosis. Damage is reduction in the intended use or value of the biological or physical resource; for example, economic production, ecological structure and function, aesthetic value, and biological or genetic diversity that may be altered through the impact of pollutants.

Ozone enters plants through leaf stomata. It oxidizes plant tissue, causing changes in biochemical and physiological processes. These biochemical and physiological changes occur within the leaf long before visible necrotic symptoms appear (Guderian et al. 1985). Plants must expend energy to detoxify ozone and repair injured tissue that could otherwise be used for growth or for maintenance of plant health. The injured plant cells eventually die if detoxification and repair cannot keep up with ozone uptake. The mesophyll cells under the upper epidermis of leaves are the most sensitive to ozone, and those are the first cells to die. The adjacent epidermal cells then die, forming a small black or brown interveinal necrotic lesion that becomes visible on the upper surface of the leaf. These visible lesions most frequently begin to develop on leaves that have just become fully matured, with older leaves on a stem showing increased amounts of injury. These lesions, termed oxidant stipple[7], are quite specific indicators that the plant has been exposed to ozone. Other plant symptoms that can result from exposure to ozone, with or without the presence of oxidant stipple, include chlorosis, premature senescence, and reduced growth. However, these symptoms are non-specific for ozone since other stressors (e.g., disease, insects) can also cause them to occur. Further, these non-specific symptoms are difficult to quantify in natural ecosystems, although limited data are available from exposure response experiments to estimate growth losses from specific ozone exposures. In general, the only indicator that a FLM has to document that ozone has impacted vegetation is visible symptoms of injury such as oxidant stipple.

In addition to affecting individual plants, ozone can also affect entire ecosystems. Research shows that plants growing in areas with high exposure to ambient ozone may undergo natural selection for ozone tolerance (EPA 2007b). The final result could be the elimination of the most ozone-sensitive genotypes from the area. Regardless of the amount of ozone exposure, the magnitude of plant response may vary depending on the geographic area because of changes in meteorological and climatic conditions, and differences in plant conditions in space and time. Factors of most importance that influence plant response to ozone are the species/genotype, soil moisture, and nitrogen availability. Other factors influencing plant response to ozone include nutrient status, atmospheric humidity, temperature, solar radiation, phenological stage of development, carbon dioxide concentrations, day length, regional climatic differences, other pollutant interactions, and population/ecosystem interactions (EPA 2007b).

Changes in growth, ecosystem form or function, or biological or genetic diversity caused by ozone have been difficult to document in natural ecosystems. However, recent research in Great Smoky Mountains National Park showed that in years with high ozone, tree growth was

7. Specific symptoms of ozone injury in some plant species are different. A few species develop white or tan rather than brown or black lesions. This is termed "fleck" or "weather fleck" instead of oxidant stipple. In conifers, ozone causes banding of necrotic and green tissue near the tips of older needles, termed "chlorotic mottle."

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significantly reduced and trees had increased rates of water loss (McLaughlin et al. 2007a). Increased water loss resulted in soil moisture depletion and reduced late-season streamflows (McLaughlin et al. 2007b). The experiment was conducted over a range of forest types and included several different tree species. These findings may have implications for climate change. Climate change is predicted to increase temperatures and drought conditions in some areas. Ozone may exacerbate the effects of drought by increasing water loss from trees.

Given the difficulty in determining ozone-induced physiological or growth changes in natural ecosystems, FLMs will utilize as indicators of ozone effects on vegetation (1) symptoms that are clearly ozone induced such as oxidant stipple, and (2) ozone exposures that have been shown to be phytotoxic.

3.4.3. Established Metrics to Determine Phytotoxic Ozone Concentrations (Revised)

EPA has set primary and secondary ozone standards to protect human health and welfare. On March 12, 2008, EPA revised the primary and secondary ozone standards to 0.075 ppm (8-hour standard). On January 6, 2010, the EPA proposed further strengthening of the primary (human health) ozone standard and establishing a new secondary ozone standard to protect ecosystems and sensitive plants (EPA 2010b). For questions regarding site specific issues the applicant is encouraged to consult with the FLM. More detailed discussions regarding other ozone metrics may be available on the respective agency web sites provided in section 3.4.7.

3.4.4. Identification of Ozone Sensitive AQRVs or Sensitive Receptors (Revised)

FLMs have determined that given the high ecological, aesthetic, and intrinsic value of federal lands, special attention should be given to native species. Ideally, protection efforts would focus on the identification and protection of at risk native species in an area. Unfortunately, AQRV identification is limited by incomplete species inventories and/or lack of exposure/response data for most species of native vegetation. Sensitive species identification will improve as more information becomes available. In the meantime, the Agencies are providing lists of sensitive plant species for each Class I area, i.e., those species that have been observed to exhibit ozone symptoms at ambient ozone exposures. This information is available at the respective agency web sites (see below). However, those ambient levels have not necessarily occurred at the specific Class I area where the plants occur.

Since FLAG 2000, the FLMs have acquired additional information regarding ozone effects to vegetation, including lists of ozone sensitive species. Much of this information is included in the NPS and FWS ARIS data base referenced previously, and will be updated as necessary. The ARIS web site is as follows:

- http://www.nature.nps.gov/air/permits/aris/index.cfm

In addition, the NPS has evaluated the risk to vegetation from ozone exposure at approximately 270 park units. The ozone risk assessment can be found at:

- http://www.nature.nps.gov/air/Permits/ARIS/networks/ozonerisk.cfm

Forest Service pertinent ozone information, including a list of ozone sensitive species, can be found at:

- http://www.fs.fed.us/air

3.4.5. Review Process for Sources that Could Affect Ozone Levels or Vegetation in FLM Areas (Revised)

As mentioned above, NO_x and VOC are ozone precursors. States and the EPA have based ozone control strategies in various parts of the country on the determination of which precursor is most likely to influence the formation of ozone. Information suggests that in areas where ozone formation is driven by VOC emissions, i.e., VOC-limited areas, VOC to NO_x ratios are less than 4:1. In VOC-limited areas, minimizing or reducing VOC emissions is the most effective means of limiting or lowering ozone concentrations. Conversely, in NO_x-limited areas, where VOC to NO_x ratios are greater than 15:1, controlling NO_x emissions is most effective. It is generally thought that most rural areas of the U.S. are NO_x-limited, most or all of the time, with the possible exception of the rural areas of southern California. The FLMs do not have current data to show that all areas are not NO_x limited, nor do they consider VOCs to be unimportant as ozone precursors. However, until there is enough information available for FLAG to determine whether ozone formation in each FLM area is primarily limited by NO_x or VOC emissions, we will assume all FLM areas are NO_x-limited and will focus on control of NO_x emissions. Where FLMs have information indicating a specific area is VOC limited, they will shift the ozone protection strategy to focus on VOC rather than NO_x emissions.

The FLMs recognize that oxidant stipple can occur at hourly ozone concentrations that can be considered natural background levels (Singh et al. 1978). Many of the high hourly background concentrations can be attributed to stratospheric intrusions or stratospheric mixing in the upper troposphere (Singh et al. 1978); but stratospheric intrusions rarely occur in the middle and southern latitudes after May (Singh et al. 1980, Wooldridge et al. 1997), and thus do not coincide with the major portion of the growing season.

However, oxidant stipple has been observed on foliage in the spring when these intrusions can occur. In general, oxidant stipple observed on foliage from June through September cannot be attributed to natural background ozone from stratospheric sources. Low levels of ambient ozone may occasionally occur in the troposphere from non-anthropogenic and non-stratospheric sources.

The occurrence of oxidant stipple necrosis on plant foliage may indicate further ozone induced physiological and growth impacts. Point sources emit precursors that could produce ozone at the FLM area, and increased ozone could induce further injury or damage to vegetation. However, we assume that restriction on increases in ozone precursors will prevent additional ambient ozone and subsequent increases in injury or damage to vegetation in FLM managed areas. It is important that ambient ozone monitoring be conducted by the State or Local air pollution control agency or by the FLM to determine the seasonal ozone exposure.

FLM actions or specific requests on a permit application will be based on the existing air pollution situation at the FLM area(s) that may be affected by the source. Some FLMs may, with appropriate documentation, rely on growth loss rather than foliar necrosis to make an adverse impact finding. Each FLM will determine if actions are warranted to limit emissions that might lead to increased ambient ozone, based on the expected impact of ozone in their particular area.

FLM response will depend on whether or not:

- ozone specific vegetation effects have been documented in the area (as evidenced by foliar injury or damage to vegetation);
- ozone exposure levels occurring in the area are high enough that they could affect vegetation (i.e., ozone exposures are at levels shown to be phytotoxic).

For a project that exceeds the initial annual emissions over distance (Q/D) screening criteria, Figure 6 outlines the general FLM review process for responding to NSR permit applications based on ozone exposure and vegetation effects at the receptor site. As noted in Figure 6, ambient ozone concentrations are considered along with data from exposure response studies (EPA 2007b) to determine whether a source will cause or contribute to phytotoxic ozone levels (i.e., levels toxic to plants) at the affected site. The FLM may ask the applicant to calculate the ozone exposure values if these data are not already available. Ozone damage to vegetation is determined from field observations at the impacted site.

Management decisions regarding acceptance of an existing or future ozone exposure will be area-specific and may differ significantly between agencies, or even regionally within agencies. Each FLM will determine if injury and/or damage are necessary to warrant action, based on the expected impact in the area they manage. The decisions are based on the FLM interpretation of regulations, past experience in the NSR arena, availability of ozone effect exposure/response information for species that occur in the area, and other factors. The FLM may also consider current trends in ozone exposures and meteorological conditions during peak ozone exposures (because dry soil conditions may induce plants to close stomates to limit water loss, thus limiting ozone uptake), as well as expected reductions in ozone precursor emissions. The FLM will negotiate with the NSR permit applicant and the permitting authority regarding possible mitigation strategies (e.g., using more efficient emissions control technologies, obtaining emission offsets, etc.).

3.4.6. Further Guidance to FLMs (Revised)

As mentioned above, limited information about ozone exposure/response relationships in plants and lack of an ozone source/receptor model make it difficult to protect FLM areas from the effects of ozone from new sources. However, there are other area-specific gaps in information that also limit protection efforts. It is important for local land managers to attempt to collect the missing information. This section provides guidance specifically to FLMs on what types of data should be collected and how the data could be collected.

Identifying and Monitoring Ozone-sensitive AQRVs

Although many FLM areas have identified ozone-sensitive plant species in their areas, most areas need more details regarding plant species location and abundance. FLAG recommends FLMs gather this information, where needed, and refine their lists of area-specific ozone-sensitive plants. The FLMs have placed ozone sensitive plant species lists for many of their areas in the NRIS-AIR or Air Resources Information System databases.

FLAG recommends that once local FLMs have developed lists of potentially sensitive AQRVs specific for their site, they conduct surveys to detect the presence of ozone-induced foliar injury on the selected species. The USFS Forest Health Monitoring (FHM) Program and the National Park Service Inventory and Monitoring Program have developed foliar injury survey protocols and QA/QC procedures that can be used to collect this information. Another resource is the foliar injury training module developed by the NPS Air Resources Division and The Pennsylvania State University, available at http://www.nature.nps.gov/air/edu/O3Training/index.cfm. This module helps field staff identify and quantify ozone injury symptoms on plant foliage. Field crews should obtain proper training and field experience in identifying foliar injury symptoms before surveys can be conducted.

Ideally, to verify ozone-induced foliar injury symptoms in the field, exposure/response fumigation studies should be conducted on these species, using concentrations that reflect current ambient exposure. Plants should also be tested at

higher exposures, simulating increased levels of ambient ozone that might occur in the future. Due to the expense of constructing and operating such systems, it would be most appropriate for agencies to join resources and develop regional fumigation facilities. At a minimum, such facilities should be constructed both in the eastern and western U.S., since ambient conditions at an eastern facility might not be appropriate for western species and vice versa.

Ambient Ozone Monitoring

Many FLM areas do not currently have either on-site or nearby ambient ozone monitoring data. FLAG recommends that local FLMs make every effort to collect this information and that they use quality-assured ambient ozone monitoring protocols developed by the EPA and the state air quality agency. Continuous monitoring is desirable to determine the temporal dynamics of ozone exposure for vegetation. Unfortunately, continuous monitoring is expensive and requires electric power that is often not available in or near remote FLM areas. When installing a continuous monitor is not an option, FLAG recommends use of passive monitors. Passive monitors give total exposure loading values (SUM00) for a specified period of time. The data are useful for indicating year-to-year changes in total ozone exposure at an individual site, and for indicating where continuous monitors should be installed. However, FLMs recognize the limitation of passive samplers in relating ozone exposure to plant response.

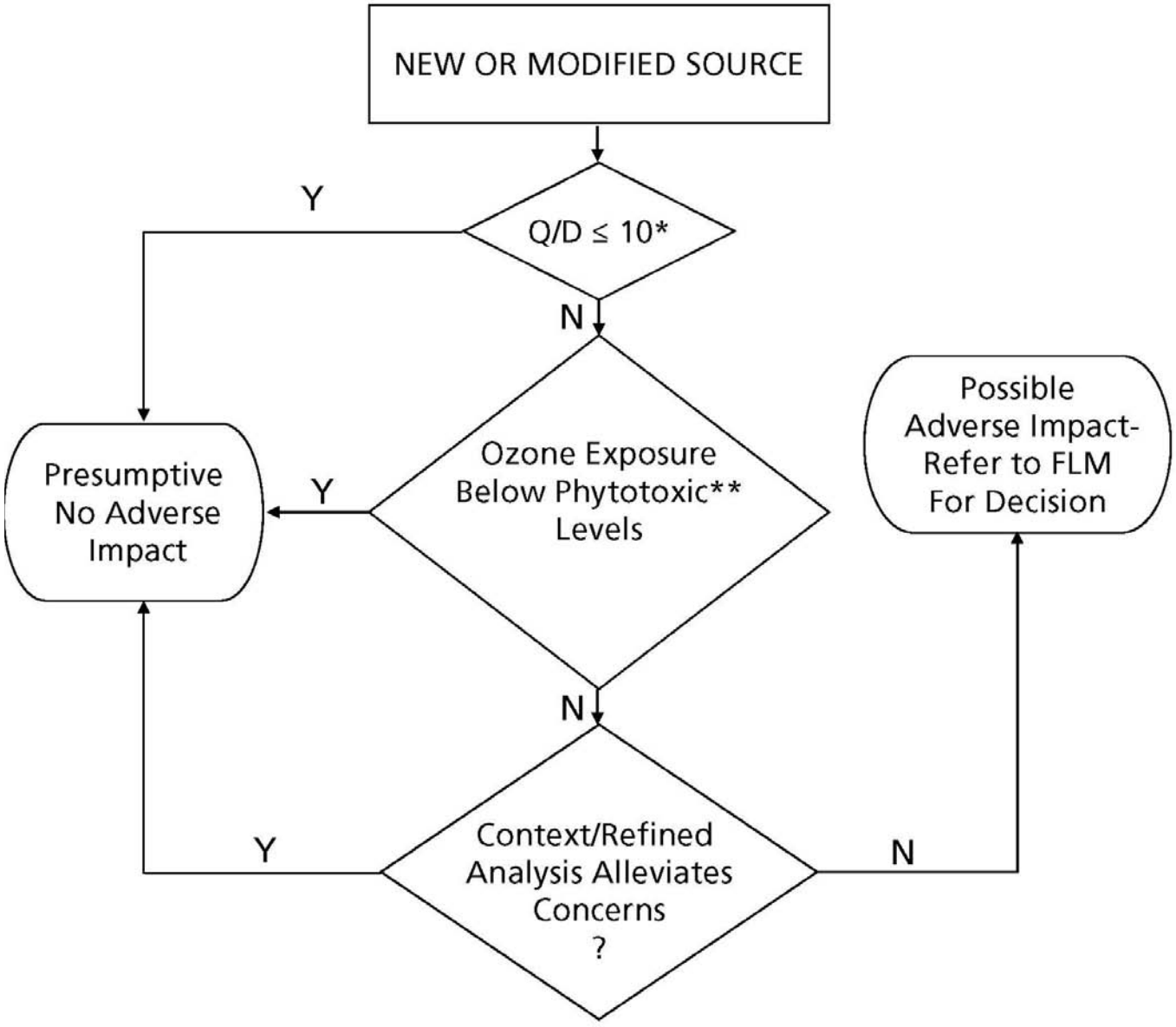

Figure 6. FLM Assessment of Potential Ozone Effects from New Emissions Source (Revised)
*Q/D test only applies to sources located greater that 50 km from a Class I area.
**Note: Ambient ozone concentrations are considered along with data from exposure response studies (EPA 2007b) to determine whether a source will cause or contribute to phytotoxic ozone levels (i.e., levels toxic to plants) at the affected site.

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3.4.7. Ozone Air Pollution Web Sites (Revised)

EPA ozone information:

- http://www.epa.gov/ozone
- http://www.epa.gov/castnet

NPS ozone information:

- http://www.nature.nps.gov/air/permits/aris/index.cfm
- http://www.nature.nps.gov/air/Monitoring/network.cfm
- http://www.nature.nps.gov/air/studies/ecoOzone.cfm

FWS Information:

- http://www.fws.gov/refuges/whm/AirQuality/index.html

U.S. Forest Service information:

- http://www.fs.fed.us/air
- http://www.fs.fed.us/psw/programs/atdep

Ozone effects research, USDA ARS, North Carolina:

- http://www.ars.usda.gov/Main/docs.htm?docid=8453

Ozone exposure metrics for vegetation:

- http://www.asl-associates.com/

3.5. Deposition

3.5.1. Introduction (Revised)

Atmospheric deposition has been studied extensively throughout the world, beginning in the 1800's in England, Sweden, Norway, and Germany. Research has primarily focused on the deposition of acidic pollutants and long-term acidification. Many publications describe current conditions, monitoring and modeling methods, and the results of acidification experiments. In the United States, research on acidification was first begun in 1962 at Hubbard Brook, New Hampshire. Subsequent work in the Adirondack lakes and other areas furthered the understanding of acid deposition effects. It is now recognized that, in addition to causing acidification, deposition of pollutants can affect many ecosystem characteristics, including nutrient cycling and biological diversity.

Although much progress has been made to control sulfur dioxide and nitrogen oxide emissions, deposition of sulfur (S) and nitrogen (N) compounds continues to be a problem in North America and Europe (EPA 2007a). As a result, certain sensitive freshwater lakes and streams continue to lose acid-neutralizing capacity (ANC) and sensitive soils continue to be acidified. Other ecosystems, including forests, grasslands, estuaries, and N-limited lakes exhibit unwanted fertilization and other effects from excess N deposition. In this section, the Agencies focus on S and N deposition and associated effects to ecosystems, but other potentially damaging pollutants are routinely deposited. For example, mercury emitted from coal-fired powerplants, incinerators, and other sources deposits into ecosystems and accumulates to sometimes toxic levels in fish and wildlife (EPA 1997). EPA sampled fish from over 75,000 lakes nationwide and found that mercury concentrations in large predatory fish exceeded the human health screening value for mercury in nearly half the lakes (EPA 2009b). The Great Waters Program found that, in addition to mercury, airborne toxics including dioxins, furans, polycyclic organic matter, polychlorinated biphenyls (PCBs), and pesticides are deposited widely across the Great Lakes, the Chesapeake Bay, Lake Champlain, and many coastal estuaries, posing ecological and human health risks (EPA 2000a). Even in relatively remote western and Alaska national parks, deposition has increased concentrations of certain toxic compounds in fish and wildlife above health thresholds (Landers et al. 2008).

Federal Land Managers (FLMs) have documented the effects of S and N deposition on many air quality related values (AQRVs). Documented effects include acidification of lakes, streams, and soils; leaching of nutrients from soils; injury to high-elevation spruce forests; changes in terrestrial and aquatic species composition and abundance; changes in nutrient cycling; unnatural fertilization of terrestrial ecosystems; and eutrophication of estuarine and some lake systems. FLMs recognize that other undocumented effects may also be occurring.

The FLAG deposition subgroup was formed to identify common approaches among these agencies for evaluating atmospheric deposition and its effects on AQRVs. In addition, the subgroup was directed to recommend methods for establishing critical deposition loading values ("critical loads") and, where possible, recommend such critical loads for specific areas. These tasks were assigned to Phase I or Phase II, depending on their degree of difficulty.

During the scoping process, the FLAG Deposition Subgroup determined that Phase I tasks would include the summarization of information currently available about deposition and its effects on FLM areas and the development of recommendations on methods to model and evaluate current and future deposition and its effects on AQRVs. In addition, critical load values, where available from previous FLM guidance documents, would be referenced. FLMs agreed that site-specific AQRV and critical load information would be maintained on FLM web sites, rather than included in the Phase I report. In this way, the information can be updated and the most recent versions made quickly available to the public. Some of this information is already available on FLM web sites, and the FLMs are committed to entering remaining available information as soon as possible.

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The subgroup recognizes that the development and refinement of site-specific critical load values for all FLM areas are crucial for AQRV protection. However, because of the complexity of this undertaking, and the lack of information for many areas, it was deferred to future FLAG development.

Future deposition effects work will involve developing methods for establishing critical deposition loading values for FLM areas, and establishing critical loads for areas with adequate information. For areas lacking sufficient information to determine critical loads, strategies will be developed to obtain needed information. Previously established critical loads will be reviewed and refined as necessary. The subgroup will also explore alternative methods for estimating background deposition rates, including extrapolation techniques or modeling that considers the spatial scale of ecosystems and differences in elevation. Methods for addressing problems with dry deposition and cloud and fog deposition measurements will also be considered. In addition, future work may provide research or monitoring recommendations to improve our understanding of deposition and its effects, including effects on cultural resources.

3.5.2. Current Trends in Deposition (Revised)

Title IV of the Clean Air Act was passed by Congress as part of the 1990 Clean Air Act Amendments to reduce emissions of sulfur dioxide and nitrogen oxides from fossil fuel-burning power plants in order to reduce deposition of S and N compounds and protect ecosystems suffering damage from acid deposition. Since the implementation of Title IV, wet sulfate deposition, a major component of acid rain, has significantly decreased. Average annual sulfate deposition in the Northeast in 2000–2002 was 40% lower than it was in 1989–1991, deposition in the mid-Atlantic and Midwest was 35% lower, and deposition in the Southeast was 25% lower (NAPAP 2005).

Wet nitrate deposition, on the other hand, has not decreased regionally from historical levels because of the relatively moderate reduction in nitrogen oxides from power plants and the continuing large contribution (over 50% of total nitrogen oxides emissions) from other sources of nitrogen oxides such as vehicles and nonroad vehicles (NAPAP 2005).

Deposition monitoring data can be used to identify decreases in S and N deposition due to decreases in emissions. The National Atmospheric Deposition Program (NADP) provides one of the best and most comprehensive long-term records of wet deposition chemistry in the U.S. Annual reports on deposition nationwide as well as deposition trend plots for all NADP sites are available at http://nadp.sws.uiuc.edu/. An analysis of long-term trends (1985-2004) in precipitation chemistry from NADP sites across the U.S. found that concentrations of sulfate have decreased in nearly all parts of the country. Nitrate, however, has increased in many areas and ammonium, another component of N deposition, has also increased significantly in many areas, particularly in the West (Lehmann et al. 2005). Publications on trends in deposition are available from NADP at:

- http://nadp.sws.uiuc.edu/lib/

In this chapter, it is assumed that S is deposited into the environment primarily as sulfate ion and N is deposited primarily as inorganic nitrate and ammonium ions. Other ionic forms of S and N occur in the atmosphere, but information on their deposition into ecosystems is limited. For example, organic N in deposition is not routinely measured because of the expense and complexity of the measurements. Organic N includes peroxyacetyl nitrate (PAN) (produced in the atmosphere by nitrogen oxides and hydrocarbon reactions), urea, and amino acids. Both natural and anthropogenic processes contribute to organic N formation, including industry, agriculture, biomass burning, and biological activity. Limited monitoring suggests that organic N deposition varies widely, but on average constitutes about 30 percent of total N (Neff et al. 2002)

3.5.3. Identification and Assessment of AQRVs (Revised)

AQRVs sensitive to pollutant deposition have been identified in various documents published by the USFS, NPS, and FWS, which are listed in the 'General References' of Appendix G of this report. The FLMs have previously used a combination of approaches to identify AQRVs, including national and regional workshops, regional reviews, and site-specific studies. AQRV identification was based on information from peer-reviewed scientific literature and expert judgment. Because information on AQRVs may change as new data become available, the FLMs agree that AQRV information will be made available on FLM web sites to allow for updating and improve accessibility, as discussed in the Introduction to this chapter.

Information on AQRVs for many USFS Class I areas can be found at

- http://www.fs.fed.us/air

The USFS is currently adding to and updating this information.

Information on AQRVs for NPS Class I areas and some FWS Class I areas is available from NPS Air Web at:

- http://www.nature.nps.gov/air

Information on AQRVs for FWS Class I areas is under development at:

- http://www.fws.gov/refuges/whm/AirQuality/index.html

Table 11. Indicators for monitoring and evaluating effects from deposition of S and N (Revised)

Ecosystem	Indicators for Sulfur Deposition
Freshwater	Chemical change (ANC depression), changes in phytoplankton and benthic community composition, species diversity, biomass
Terrestrial	Leaching of soil cations, soil acidification, mobilization of aluminum ions; Lichen species and vitality
Estuarine	Saltwater not sensitive to S deposition; leaching of nutrients may occur in sandy nearshore soils
Ecosystem	**Indicators for Nitrogen Deposition**
Freshwater	Chemical change (ANC depression), changes in phytoplankton and benthic community composition, species diversity, biomass
Terrestrial	Changes in: litter and soil carbon and N dynamics; biomass; soil N processes; litter decomposition rates; soil microbe functional groups; soil organic matter quality and quantity; soil water chemistry; Lichen species and vitality
Estuarine	Changes in: phytoplankton species composition and biomass; aquatic invertebrates; seagrass health and distribution; nutrient ratios; dissolved oxygen; trophic status

FLMs recommend that permit applicants consult with the appropriate FLM to determine the need for an AQRV analysis and, if applicable, the methods for the analysis.

All FLMs use a similar conceptual approach to identify AQRVs that reflects the FLMs' interest in maintaining the integrity of ecosystem structure and function and protecting the most sensitive ecosystem components. AQRVs can be categorized by the type of ecosystem in which they are found, such as terrestrial, freshwater, and estuarine ecosystems. Each ecosystem and its AQRVs responds somewhat differently to deposition and approaches to evaluating deposition effects must therefore be developed accordingly. In terrestrial ecosystems, detection of changes in production, decomposition, and nutrient cycling processes provide information on deposition stress. In aquatic and estuarine ecosystems, detection of changes in water chemistry and aquatic community composition and structure provide similar information. Table 11 summarizes AQRV indicators that may be used to assess effects in various ecosystems.

Terrestrial, freshwater, and estuarine AQRVs are discussed below. In addition, methods to evaluate S- and N-induced deposition stress are discussed.

Terrestrial Ecosystems

Terrestrial ecosystem AQRVs include flora, fauna, and soils. FLMs have identified, where possible, AQRVs, or characteristics of AQRVs, most likely to be sensitive to S and N deposition ("sensitive receptors"). For example, high-elevation spruce forests may be sensitive receptors. FLMs assess the condition of these sensitive receptors by evaluating some aspect of the receptor (the "sensitive receptor indicator" or "indicator"). For example, an indicator for high-elevation red spruce forests is the occurrence and extent of winter foliar injury. In general, the FLM has focused on deposition effects to vegetation and chemical receptors in terrestrial ecosystems, with little emphasis on fauna. In addition, there is increasing awareness among FLMs that certain soil fauna (e.g., microorganisms and invertebrates) are very sensitive to deposition and can be used as sensitive receptors.

In terrestrial ecosystems, sulfate production is regulated primarily by chemical processes (Johnson et al. 1983) and it is rarely a limiting nutrient. Soil response to acidic deposition can be evaluated by monitoring the leaching of essential soil cations, soil acidification, and mobilization of ionic aluminum. These processes have been studied both in field and laboratory experiments, and are defined in detail in the literature (Mollitor and Raynal 1983; Richter et al. 1983; Johnson et al. 1983; Reuss and Johnson 1986). Effects of S deposition can be detected by monitoring calcium and magnesium ions and S in the litter layer and surface soils; calcium, magnesium, potassium, and sulfate ions in soil solution; cation exchange capacity (CEC); and base saturation.

In general, biological AQRVs do not provide reliable indicators of S deposition in terrestrial ecosystems except under extreme S deposition. Lichens have been used in some areas as biomonitors to demonstrate spatial trends in S deposition, particularly in areas with pronounced S deposition gradients. For example, isotopic analysis of lichens from Mt. Zirkel Wilderness, Colorado, indicated that power plants in the nearby Yampa Valley were the source of elevated S in the lichens (Jackson et al. 1996).

Unlike S, the production and mobility of N in ecosystems is regulated almost entirely by biological processes. N is a limiting nutrient in many terrestrial ecosystems. In these ecosystems, growth of plants is limited by N availability; additional N from atmospheric inputs increases plant growth. Most ecosystems can retain and process significant additions of N, with resulting increases in production and changes in species diversity, biomass, and nutrient cycling. However, these changes are usually considered to be inconsistent with desired ecosystem conditions for natural areas. The ability to retain and process N varies significantly

depending on watershed successional status, site and fire history, soil conditions, vegetation, and other non-human factors. When N inputs exceed an ecosystem's assimilation capacity, N is lost or leached, usually as nitrate, from the soil and can be detected in adjacent streams or lakes. This may occur following a major disturbance such as fire, logging, land use change, grazing, agriculture, or where atmospheric N deposition or experimental inputs exceed what the ecosystem can assimilate (Fenn and Dunn 1989; Fenn 1991, Fenn et al. 1996; Adams et al. 1997).

Studies in northern Europe (Dise and Wright 1995) found that European forests leached detectable levels of nitrate at inputs of about 10-25 kilograms N per hectare per year (kg N $ha^{-}1yr^{-1}$). Tundra and high-elevation alpine sites may leach N at much lower levels of input. Mountain watersheds in the western U.S. show signs of N leakage at wet deposition levels of 3-5 kg N $ha^{-1}yr^{-1}$ (Eilers et al. 1994; Williams et al. 1996; Williams and Tonnessen, in review). However, even high elevation, poorly vegetated ecosystems with limited soil development can process more than 80% of the atmospheric N input before it reaches the aquatic system (Campbell et al. 1995, Kendall et al. 1995). Although nitrogen leaching has often been used as an indicator of excess N deposition, major changes occur in below- and above-ground biomass, species diversity, and nutrient cycling long before N input levels are sufficient to cause nitrate leaching (NAPAP 1993; Tilman et al. 1997; Vitousek et al. 1997). For example, with ambient deposition rates of 7-10 kg N $ha^{-1}yr^{-1}$, a Minnesota Long-Term Ecological Research (LTER) grassland study observed shifts from native, warm-season grasses to low diversity mixtures dominated by cool-season grasses and a greater than 50% decline in species richness (Wedin and Tilman 1996; Tilman et al. 1997). Significant losses in terrestrial diversity may have already occurred over extensive areas of the U.S., particularly in forest understories, shrublands, grasslands, and in soil microbial communities. (Suding et al. 2005; Weiss 2006).

Because significant ecological changes may occur before nitrate loss can be detected, more sensitive indicators than nitrate leaching are needed to evaluate N deposition effects. Such indicators include changes in carbon and N dynamics of litter and soil and biomass (Aber and Driscoll 1997; Magill et al. 1997). With knowledge of inputs and small-scale N fertilization studies, changes in soil organic matter quality and quantity in response to N deposition can be evaluated. Soil microbial communities control the quantity and quality of N available to ecosystems and may be very sensitive indicators of N deposition. Changes in soil microbe functional groups or biomass may provide good estimates of ecosystem critical loads and incremental effects. Soil N mineralization, small root growth, and carbon:nitrogen ratios of soil and microbial biomass are also sensitive to N deposition. Evidence suggests that current deposition rates may alter the production of dissolved organic carbon and organic N compounds in soils, which are important nutrient and energy sources for both terrestrial and aquatic ecosystems (Grandy et al. 2008; Aber et al. 1995; Sinsabaugh et al. 2005). These could also be used as indicators of N deposition effects. However, because there are many other variables that also affect soil processes, it may be very difficult to discern effects on any soil indicators that are solely attributable to N.

Freshwater Ecosystems

AQRVs in freshwater ecosystems include lakes and streams and their associated flora and fauna. Sensitive receptors include water chemistry and clarity, phytoplankton, zooplankton, fish, amphibians, macroinvertebrates, and benthic organisms. Water chemistry indicators that respond to deposition include pH, ANC, conductance, cations and anions, metals, and dissolved oxygen. Physical indicators, such as water clarity, and biological indicators, including species diversity, abundance, condition factor and productivity of fish, amphibians, macroinvertebrates, and plankton can also be used to detect deposition effects in aquatic ecosystems. Much research has been done on the sensitivity of aquatic species to deposition, many of which are discussed in the 1990 National Acid Precipitation Assessment Program (NAPAP) State of Science report (NAPAP 1991a) and the 1998 NAPAP report (NAPAP 1998).

Sulfur is not a limiting nutrient in freshwater ecosystems. However, there are regions of the U.S. where a relatively high percentage of surface water is sensitive to current acidic inputs. These include portions of the Northeast (particularly Maine and the Adirondack and Catskill Mountains), southeastern streams, and some high elevation western lakes, particularly in the Rocky Mountains (NAPAP 2005). There are a number of FLM areas in acid-sensitive regions, including national parks, national forests, and wilderness areas. In these areas, S deposition can cause decreases in ANC and pH. For these sensitive or low-ANC waters, the best approach to quantify S deposition effects is the procedure currently used, monitoring changes in ANC and pH.

Nitrogen deposition, like S deposition, can cause episodic acidification of surface water in certain sensitive high-elevation ecosystems that have low-ANC headwater lakes and streams. Episodic acidification occurs in these areas when deposition is as low as 3-5 kg N $ha^{-1}yr^{-1}$ (Williams et al. 1996).

Estuarine Ecosystems

AQRV sensitive receptors in estuarine ecosystems include plankton, sea grasses, and water chemistry and clarity. Associated coastal forest and dune soils may also be useful as sensitive receptors. Water and soil nutrient concentrations, phytoplankton species composition and abundance, sea

grass health, and dissolved oxygen concentrations can be used to evaluate deposition effects.

In estuaries, S is not a limiting nutrient. In addition, estuarine waters are highly buffered and, therefore, not subject to acidification. However, many coastal forest and dune soils are dominated by sandy soils that are sensitive to leaching of limiting nutrients because of very low cation exchange capacity (Au 1974). Monitoring for change in estuarine areas with high S deposition should therefore focus on soil ion mobility. As soil calcium and magnesium levels are generally adequate because of deposition from marine sources, potassium is likely the only limiting nutrient subject to significant loss by sulfate leaching.

The role of N in estuaries is probably the best-documented example of anthropogenic alteration with a literature record dating back to the 1950s. Production and use of fertilizers, land use changes, and fossil fuel combustion have greatly increased the available N, normally a limiting nutrient, which enters coastal waters (Galloway et al. 2003). This has increased estuarine production and accelerated the process of eutrophication. Eutrophication can result in dramatic algae blooms, anoxia, the production of toxic hydrogen sulfide gas, and species extirpation in estuarine ecosystems. Human induced eutrophication has been documented for many areas along the Atlantic and Gulf coasts, including the Chesapeake Bay, Tampa Bay, Sarasota Bay, Florida Bay, and Long Island Sound.

A number of FLM areas along the Atlantic and Gulf coasts contain significant coastal waters that may be sensitive to eutrophication. Little is known about excess N effects in most of these areas, although eutrophication is well documented in Florida Bay, located in Everglades National Park. Also, recent evidence indicates that coastal waters in Chassahowitzka Wilderness (Florida) experience N-induced algal blooms (Dixon and Estevez in draft). In most coastal waters, 10-45% of the N entering the system is atmospheric, either from direct deposition to surface water or deposition to the watershed. Complete elimination of atmospheric N inputs would not entirely mitigate ecosystem change due to N because of the substantial contributions from agricultural and urban runoff. However, for most estuaries, any reduction in N input would be beneficial in restoring ecosystem structure and function.

The monitoring procedures recommended, and currently used, in estuaries are similar to those used in freshwater, with emphasis on incremental changes in plankton, aquatic plant, benthic, and invertebrate community composition; species diversity, distribution, and biomass; and ecosystem trophic status.

Significance of Long-Term Monitoring to Evaluate Trends and Validate Modeling

Long-term monitoring is critical to evaluate trends in deposition and deposition effects. Monitoring programs should concentrate not only on areas with high past and/or present sulfate, nitrate, or ammonium deposition, but also in areas that are very sensitive to deposition and in areas where deposition is expected to increase. For selected monitoring sites, the FLM should (1) obtain ion deposition data for the site, as from NADP or CASTNet, (2) identify sensitive AQRVs and appropriate variables to monitor, (3) evaluate the present condition of the sensitive AQRVs, (4) determine the degree to which results from one site can be extrapolated to other FLM areas in the region, and lastly (5) implement a long-term monitoring program, using carefully selected variables.

Long-term monitoring data are also needed to support and validate models used to predict deposition and deposition effects, including the effects of increases or decreases of S and N on ecosystems. Long term studies in both aquatic and terrestrial ecosystems such as Hubbard Brook, Lake Tahoe, and the Experimental Lakes Area have provided useful information for modeling (Bormann and Likens 1967; Holm-Hanson et al. 1976; Likens and Bormann 1977, Leonard et al. 1979; Byron and Eloranta 1984; Schindler et al. 1985; Schindler 1987; Schindler et al. 1990; Jassby et al. 1995). NAPAP and the National Science Foundation LTER program have addressed monitoring to meet modeling needs in both terrestrial and aquatic ecosystems.

Data requirements to support models vary, but the quality of input data will determine the quality of a model's predictions. Modeling is further discussed in the 'Other AQRV Identification and Assessment Tools' (see section 3.5.5).

3.5.4. Determining Critical Loads (Revised)

FLAG 2000 introduced the concept of critical loads as it relates to air resource management in Class I areas. Since FLAG 2000 was published, the Agencies have adopted the widely used definition of critical load, "the quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge" (Nilsson and Grennfelt 1988). Critical loads have been widely accepted in Europe and Canada as a basis for negotiating control strategies for transboundary air pollution (Posch et al. 1997).

In Canada, researchers have estimated the critical loads of S in wet deposition necessary to protect moderately sensitive lakes in eastern provinces. That value, equivalent to 6.7 kg $ha^{-1}yr^{-1}$ of S in wet deposition, was used by Canada to argue for the U.S. to implement the Clean Air Act Amendments of 1990, which call for the initial reduction of sulfur dioxide

emissions in the eastern U.S. and later from all electric utilities nationwide. With additional data on lake and stream chemistry available for sensitive systems in Nova Scotia, Ontario, and Quebec, the Canadians are now recommending a more stringent critical load, equivalent to 2.7 kg $ha^{-1}yr^{-1}$ of wet deposition S.

In both European countries and in North America, attention has expanded beyond ecosystem damage caused by S deposition to ecosystem damage caused by N deposition. In some European forests, chronically high N deposition has exceeded the assimilation capacity of local ecosystems, resulting in the release of nitrate into surface waters (Dise and Wright 1995). Watersheds that are leaking nitrate into surface waters during the growing season, are referred to as "N saturated" (Aber et al. 1989). Nitrogen saturation has been linked to forest decline in Europe (Schulze 1989). Based on a set of regional N addition experiments conducted at sites in northern Europe (NITREX), Wright (1995) recommended a N critical load of less than 10 kg $ha^{-1}yr^{-1}$ to protect European forests and fresh waters from N saturation. However, this critical load does not protect ecosystems from the changes caused by N deposition prior to actual N saturation, including shifts in composition and abundance of soil fauna species and alterations in soil chemistry. (Fenn et al. 2003; Driscoll et al. 2003)

In the United States, two states have attempted to set deposition standards or critical loads to protect sensitive ecosystems. In 1982, the State of Minnesota passed the Acid Deposition Control Act to limit wet sulfate deposition to 11 kg $ha^{-1}yr^{-1}$, which is equivalent to 3.7 kg S $ha^{-1}yr^{-1}$. At this sulfate level, precipitation pH was likely to remain above 4.7, which would protect lakes with ANC less than 50 microequivalents per liter (µeq l^{-1}).

In 1989, the California legislature adopted the Atmospheric Acidity Protection Act, which required the Air Resources Board (CARB) to "develop and adopt standards, to the extent supportable by scientific data, at levels which are necessary and appropriate to protect public health and sensitive ecosystems from adverse effects resulting from atmospheric acidity" (CARB 1993). An assessment of existing data identified the high elevation watersheds, surface waters, and mixed conifer forests of the Sierra Nevada and the Los Angeles Basin as sensitive ecosystems. CARB analyses suggested that appropriate standards would include a critical load value for inorganic N to protect forests, and critical loads for both N and S to protect poorly buffered lakes and streams. However, no acidity standards to protect human health or critical loads to protect ecosystems have been set in California to date.

The Clean Air Act Amendments of 1990, Title IV, section 404, called on the Environmental Protection Agency (EPA) to prepare a report on the feasibility and effectiveness of setting deposition standards nationwide to protect sensitive aquatic and terrestrial resources. The completed report includes a number of modeling analyses that project the effect of reductions in both S and N deposition in areas studied during NAPAP. EPA concluded that deposition standards could not be set at this time because of 1) the lack of clearly defined policy regarding appropriate or desired goals for protecting sensitive aquatic or terrestrial resources, and 2) key scientific uncertainties, particularly regarding nitrogen watershed processes. In addition, EPA recognized that a national deposition standard might be inappropriate because of differences among ecosystems. However, in response to public comments on the report, EPA stated that "Given an adequate level of monitoring and assessment data, Class I areas could serve as potential targets for standard setting activities." (EPA 1995)

Since FLAG 2000, other U.S. agencies and organizations have started considering how to work with critical loads. A National Academy of Sciences Report, *Air Quality Management in the United States* (2004), recognized the potential of critical loads for establishing standards to protect ecosystems, prompting the EPA to explore critical loads as an accountability tool to assess ongoing programs. Also, in the 2005 Prevention of Significant Deterioration for Nitrogen Oxides Final Rule, EPA stated it would consider critical loads information from any state as part of their air quality management approach, including whether such an approach satisfies PSD requirements. (EPA 2005.) The U.S. has signed, but not ratified, the European Union's protocol for establishing critical loads, contained in the 1999 *Protocol to Abate Acidification, Eutrophication and Ground-level Ozone (AKA The Gothenburg Protocol)*, available at:

- http://www.unece.org/env/lrtap/multi_h1.htm

In 2006, EPA held the Multiagency Critical Loads Workshop to share information on critical loads and to develop a broad federal strategy for planning, executing, and evaluating critical loads projects, and to consider critical load use in a policy or management framework. As a result of recommendations from the workshop, the Critical Loads Ad-Hoc Committee (CLAD) was formed to foster critical loads science and development. Information on CLAD and the Multiagency Critical Loads Workshop Report are available at:

- http://nadp.sws.uiuc.edu/clad/

In 2008, EPA used critical loads to assess progress under the Acid Rain and related programs. For the analysis, EPA compared critical loads exceedances in Adirondack lakes before and after implementation of acid rain controls (EPA 2009a).

Critical Loads in FLM Areas (Revised)

In the Clean Air Act, as amended in 1977, Congress gave FLMs an "affirmative responsibility" to protect AQRVs in Class I areas from the adverse effects of air pollution.

Congress' intent was, "…In cases of doubt the land manager should err on the side of protecting the air quality-related values for future generations…" (Senate Report No. 95-127, 95th Congress, 1st Session 1977). In an effort to ensure AQRV protection, FLMs have established critical loads for many FLM areas. FLMs agree that a critical load should protect the most sensitive AQRVs within each FLM area and should be based on the best science available. As new scientific information becomes available, critical loads should be reviewed and updated. Critical loads should ensure that no unacceptable change occurs to the resource.

A journal article published in the July 2005 issue of *BioScience*, entitled "Protecting Resources on Federal Lands: Implications of Critical Loads for Atmospheric Deposition of Nitrogen and Sulfur" (Porter, Blett, Potter, Huber 2005) provides an update on the Agencies' perspectives with respect to critical loads. Among other things, the article describes the history of critical loads, the advances in science related to critical loads, and how to apply the concept of critical loads (including some specific case studies). Subsequent articles provide additional information and perspectives on critical loads (Burns et al. 2008; Dennis et al. 2007). These and other articles and reports on critical loads are available from:

- http://www.nature.nps.gov/air/Studies/criticalLoads/index.cfm
- http://www.nrs.fs.fed.us/clean_air_water/clean_water/critical_loads/

FLMs have used a combination of approaches to establish critical loads, including national and regional workshops, regional reviews, and site-specific studies (see Appendix G). In all cases, the FLMs have used peer-reviewed scientific literature and expert judgment to make their decisions. For example, the NPS has compiled regional reviews that have evaluated existing information on air quality, deposition, and effects on AQRVs in national parks. For these reviews, NPS grouped parks by region and ecosystem type, including the Pacific Northwest, the Colorado Plateau, and the Rocky Mountains, and conducted an empirical assessment of the status of aquatic and terrestrial resources. An analysis of deposition effects was done, using current deposition data for S and N and effects information from field observations and research. These reviews provide the basis for critical load development by identifying sensitive resources and impacts to those resources. Park-specific information on sensitive resources, impacts, and critical loads is available at:

- http://www.nature.nps.gov/air/permits/aris/index.cfm

The USFS has conducted a series of national and regional workshops to establish critical loads and concern thresholds. In the late 1980s, the USFS published prototype methods for evaluating the effects of acid deposition on AQRVs (Fox et al. 1989; Fox et al. 1987). Subsequently, the USFS held regional workshops to develop updated and more area-specific screening procedures for new air pollutant emissions sources (Adams et al. 1991; Peterson et al. 1992; Haddow et al. 1998; Peterson et al. 1993; Stanford et al. 1997). These workshops were comprised of national and regional USFS land managers, deposition experts from the academic and air pollution research community, and agency air quality professionals. Dependent on the workshop leadership, each regional workshop followed a slightly different process and a variety of outputs and formats resulted. However, all workshops used a collaborative process to determine S and N deposition rates that would pose a risk to the aquatic and terrestrial ecosystems protected in FLM areas, while addressing the scientific uncertainty inherent in ecosystem response to acidic deposition. Critical load guidelines for many USFS Class I areas are published in the regional workshop reports (see Appendix G) and are available at:

- http://www.fs.fed.us/air

As resources permit, the Agencies will develop methods and a process for establishing critical deposition loading values for all FLM areas and for recommending critical loads for areas where adequate information exists. For areas lacking sufficient information to determine critical loads, the Agencies are developing strategies to obtain needed information.

Current information and links on critical loads work being done by the U.S. Forest Service can be found at the following web site:

- http://www.fs.fed.us/air

The Agencies anticipate using critical loads as they are developed as an assessment tool, and, in concert with the Deposition Analysis Thresholds and Concern Thresholds (see below), a tool for assessing new source impacts. The Agencies also intend to continue to consult with States and the EPA as critical load development work progresses.

3.5.5. Other AQRV Identification and Assessment Tools (Revised)

In addition to AQRV monitoring, there are several tools available to the FLM for identifying AQRVs and assessing the response of sensitive AQRVs to pollutant deposition. These include the Air Resources Information System (ARIS), the Natural Resource Information System – Air Module (NRIS-Air), and deposition models such as the Model of Acidification of Groundwater in Catchments (MAGIC) and MAGIC-With Aggregated Nitrogen Dynamics (MAGIC-WAND).

Air Resources Information System (ARIS)

FLAG 2000 also introduced "Air Synthesis" as an information management and decision-support computer system under development by NPS and FWS. The NPS and FWS have since redesigned and renamed Air Synthesis, now called Air Resources Information System (ARIS). ARIS provides information on air quality related values in NPS and FWS Class I areas, as well as in many NPS Class II areas. Information can be accessed for specific areas or for all units within NPS Inventory & Monitoring (I & M) networks.[8] ARIS identifies specific AQRVs, and provides information on air quality and its effects in parks and wildernesses. ARIS maintains information for all 48 NPS Class I air quality areas and several FWS Class I areas. Information is being developed for the remaining FWS Class I areas, and additional Class II areas. Additional information on ARIS can be found at:

- http://www.nature.nps.gov/air/permits/aris/index.cfm

Information for FWS Class I areas is under development at:

- http://www.fws.gov/refuges/whm/AirQuality/index.html

Natural Resource Information System – Air Module (NRIS-Air)

Publicly available USDA Forest Service Class I and II area information and related resource data can be linked to or found at http://www.fs.fed.us/air. If desired information and data cannot be found, contact any air program manager or specialist at national or regional offices for assistance.

Information from NRIS-Air, including USFS Class I area AQRV information, is available at:

- http://www.fs.fed.us/air

Deposition Effects Models

A number of watershed process models have been developed and tested in an attempt to simulate the effects of S and N on soils, forests, and surface waters. These models are used by FLMs to predict effects from increases in deposition and vary from detailed, compartment models of watersheds to lumped parameter models that do not track different ions through each soil compartment. For a review of models developed under NAPAP see NAPAP 1991.

A commonly applied watershed model is MAGIC. MAGIC was first developed for eastern U.S. watersheds and then extensively tested and validated throughout Europe and North America (Cosby et al. 1985, 1995, 1996). The model was used by NAPAP in its 1990 Integrated Assessment to project surface water chemistry resulting from various deposition scenarios (NAPAP 1991b). In another application in the eastern U.S., MAGIC has been linked with a simple, empirical, dose/response fish model developed at University of Virginia that makes it possible to predict changes in fish productivity based on modeled changes in stream water chemistry.

As a result of NAPAP, there was increased awareness of the potential impacts of inorganic N deposition on watersheds and surface waters. In response, the MAGIC model was updated with a module called With Aggregated Nitrogen Dynamics (WAND). MAGIC-WAND is a process-based model that uses site-specific information on hydrology, soils, and hydrochemistry. The model predicts changes through time in lake or stream chemistry. These time-series of changes in pH and ANC can subsequently be used by FLMs to calculate critical S or N loads for watersheds.

MAGIC-WAND has been extensively tested in the Adirondacks and at watersheds in Maine. For example, the Bear Brook Watershed Manipulation Project uses MAGIC-WAND to predict the effects of experimentally added N and S on a test watershed. MAGIC-WAND has also been applied to watersheds in FLM areas in the Cascades, the Sierra Nevada, the Rocky Mountains, and the Wind River Range in an effort to quantify critical S and N loads to aquatic and terrestrial resources. In the southeastern U.S., MAGIC-WAND is being used under the auspices of the Southern Appalachian Mountains Initiative (SAMI) to predict the effects of future deposition scenarios on FLM areas. Future SAMI modeling efforts will link watershed model results with fish dose/response models. The ultimate goal is to calibrate MAGIC-WAND with landscape level data in order to set regional critical loads.

Other models are also in use. For example, the USFS Rocky Mountain Region recommends using either CALPUFF or AERMOD (or other approved models) to estimate S and N deposition. *The Screening Methodology for Calculating ANC Change to High Elevation Lakes* (USDA Forest Service 2000) summarizes procedures for estimating total deposition of S and N. The document also recommends computations for estimating alkalinity changes in lakes caused by increases in S and N deposition. Another model, the Nutrient Cycling Model (NuCM) has been used in the East to predict the effect of changes in deposition on nutrient concentrations in soils and vegetation.

3.5.6. Recommendations for Evaluating Potential Effects from Proposed Increases in Deposition to an FLM Area (Revised)

FLAG 2000 described a process to help the Agencies and permit applicants assess the total sulfur and/or total nitrogen deposition impacts of proposed new or modified sources.

8. The NPS I & M program consists of over 270 park units organized into 32 networks to conduct long-term natural resource monitoring on park "vital signs," that is, selected physical, chemical, and biological elements and processes of park ecosystems that represent the overall health or condition of the park.

Since that time, the Agencies have refined the concept of using concern thresholds, pollutant exposures, and deposition analysis thresholds in the permit review process. The approaches used by the respective agencies may vary somewhat, but in essence are all similar.

Deposition Analysis Thresholds (DATs)

The NPS and FWS have introduced and developed the concept of Deposition Analysis Thresholds (DATs) to use as screening level values for the additional modeled amount of sulfur and nitrogen deposition within FLM areas from new or modified PSD sources. A DAT is defined as the additional amount of nitrogen or sulfur deposition within an FLM area, below which estimated impacts from a proposed new or modified source are considered negligible. In other words, if the new or modified source has a predicted nitrogen or sulfur deposition impact below the respective DAT, the NPS and FWS will consider that impact to be negligible, and no further analysis would be required for that pollutant. In cases where a source's impact equals or exceeds the DAT, the NPS/FWS will make a project specific assessment of whether the projected increase in deposition would likely result in an "adverse impact" on resources considering existing AQRV conditions, the magnitude of the expected increase, and other factors.

The DATs are based on "naturally occurring deposition" that park and wilderness ecosystems may have experienced prior to anthropogenic influences and are scaled to enable assessment of the impacts of individual sources of air pollution. The DAT established for both nitrogen and sulfur in eastern and western FLM areas and wildernesses is 0.010 and 0.005 kilograms/hectare/year (kg/ha/yr), respectively. More information regarding the sulfur and nitrogen DATs can be found at:

- http://www.nature.nps.gov/air/Pubs/pdf/flag/nsDATGuidance.pdf

While DATs are a tool to assess the impact of a single new source, these levels may not be protective in areas that are already impaired or where there are multiple new sources impacting a single area. The critical load concept, discussed above, may be a more effective tool for assessing cumulative impacts.

Concern Thresholds and Pollutant Exposures

The Forest Service has continued to develop AQRV concern thresholds and pollutant exposure(s) thresholds (for sulfur or nitrogen deposition) that when exceeded may indicate an adverse impact to one or more AQRVs. These thresholds are very similar to the NPS/FWS Deposition Analysis Thresholds (DATs) in that they establish a point below which adverse impacts are not expected. Impacts above the thresholds may or may not cause an adverse impact; depending on current levels of deposition and resource condition. The values for these thresholds vary between FS Class I areas; therefore an applicant will need to check for Class I area-specific thresholds on the following Internet site:

- http://www.fs.fed.us/air/technical/class_1/alpha.php

FLM Response to Potential Deposition Impacts

For a project that exceeds the initial annual emissions over distance (Q/D) screening criteria, the permit applicant should consult with the appropriate regulatory agency and FLM for the affected area(s) to determine if a deposition impact analysis should be done (e.g., expected sulfur and/or nitrogen deposition impacts are above the DAT) or respective concern threshold). For such cases, FLMs request that proponents provide sufficient information for the FLM to evaluate the potential effects of emissions increases on AQRVs. FLMs have provided information to applicants through guidance documents, correspondence, meetings, and phone consultations. This chapter summarizes current information for evaluating new emissions on deposition and sensitive AQRVs and includes recommendations for:

- the types of data, information, and analysis needed before a permit application can be considered complete, including analytical and modeling protocols for a proponent's use in conducting an AQRV impact analysis;
- approaches and sources of appropriate values for estimating wet and dry deposition; and
- permit conditions to mitigate source impacts.

The process begins with the question "Q/D ≤ 10?" as the first level screening criteria (see Figure 7). The next question is whether or not the DAT/concern threshold is exceeded. If not, no adverse impacts are expected. If so, the Agencies will determine if the contextual considerations (see section 4.3) or any refined analyses alleviate any deposition concerns. If not, the Agencies will defer to the FLM to make a case-by-case adverse impact finding. In determining if the proposed action will cause or contribute to an adverse effect to AQRVs, the FLM will consider information on deposition-sensitive AQRVs, deposition loads at which these AQRVs are affected (i.e., critical loads), the current pollutant deposition rates in the area, and the expected impacts from the proposed source. Procedures for estimating the source's impacts are found in 'Estimation of Current and Future Deposition Rates' section of this report. In areas where no information is available, information from a nearby, or ecologically similar area, may be used. An adverse effect may occur if the critical load is exceeded for an area, and the new source impact is above the levels of concern (i.e., DAT/concern threshold). AQRV and critical load information are discussed earlier in this report.

If the available information is insufficient for the FLM to determine if the proposed action will cause or contribute to an adverse effect to AQRVs, the FLM may ask for deposition and deposition effects monitoring and/or

research in the FLM area. If the proposed action will likely cause or contribute to an adverse effect to AQRVs, the FLM may recommend permit conditions that ensure mitigation, including stricter emissions controls and effective emissions offsets. If no mitigation is possible, the FLM may recommend denial of the permit.

Available Deposition Monitoring Data

Atmospheric pollutants are deposited to ecosystems primarily through wet deposition and dry deposition. FLMs participate in national monitoring programs to monitor wet and dry deposition, including the National Atmospheric Deposition Program (NADP) and the Clean Air Status and Trends Network (CASTNet). A 1999 report, "The Role of Monitoring Networks in the Management of the Nation's Air Quality," (CENR, 1999) identified these two networks as being critical for characterizing baseline air quality data in the U.S.

Wet Deposition (Revised)

Wet deposition includes rain, snow, fog, cloud water, and dew. In most FLM areas, rain and snow are the primary contributors to wet deposition. However, in some high elevation areas, fog, cloud water, and dew are significant contributors, as discussed below.

Because rain and snow are the primary constituents of wet deposition at most FLM areas, the FLM generally relies on data from NADP to evaluate wet deposition of pollutants. NADP samplers collect rain and snow and NADP has documented deposition for many years in a nationwide network that currently includes over 220 monitoring

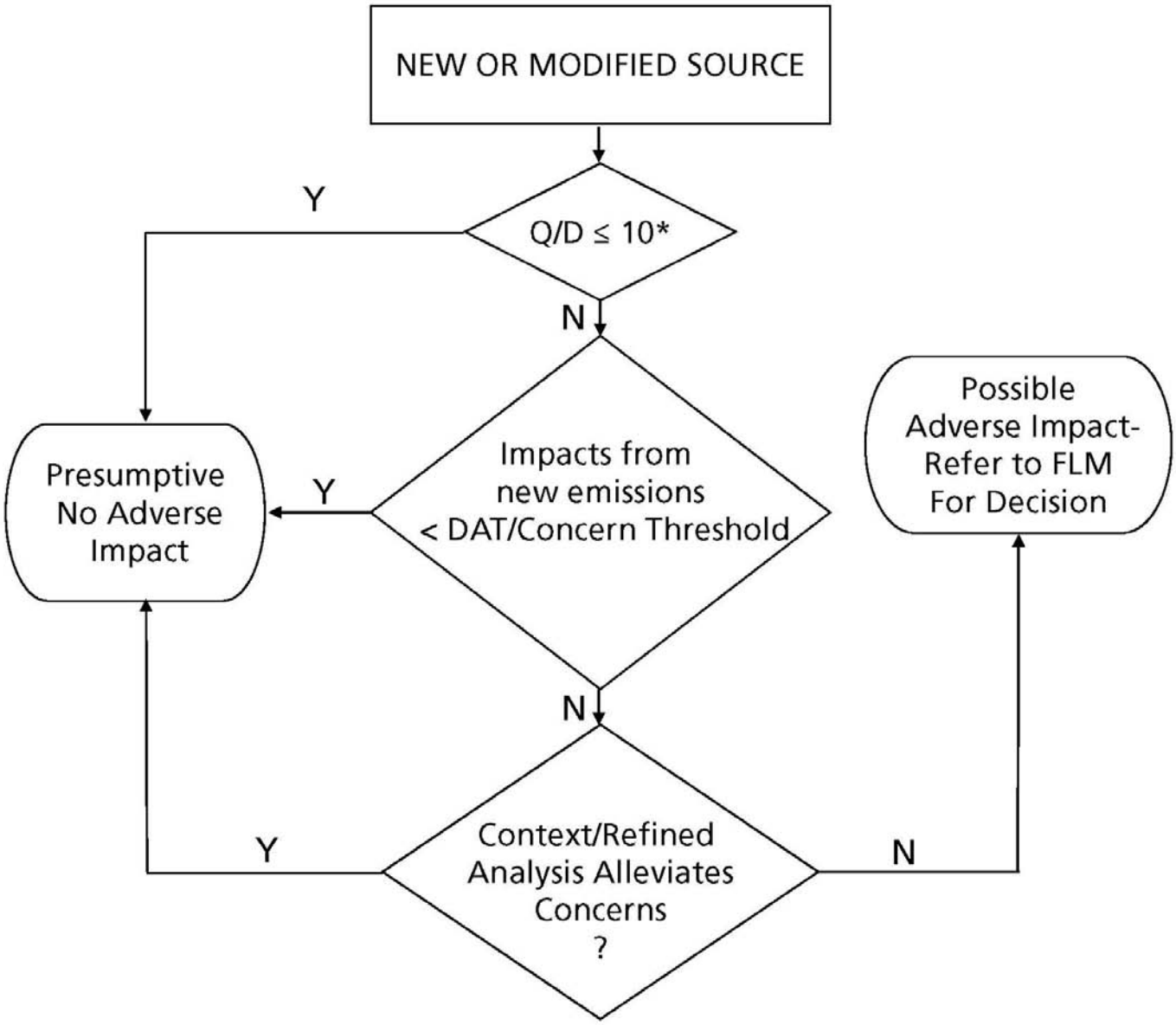

Figure 7. FLM Assessment of Potential Deposition Effects from New Emissions Sources (Revised)
*Q/D test only applies to sources located greater that 50 km from a Class I area.

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sites. The network collects data to evaluate spatial and temporal long-term trends in precipitation chemistry. The precipitation at each site is collected weekly and sent to a central analytical laboratory for analysis of hydrogen (acidity as pH), sulfate, nitrate, ammonium, chloride, and base cations, including calcium, magnesium, potassium, and sodium. Data and isopleth maps of pollutant concentrations and deposition are available on the NADP web site at:

- http://nadp.sws.uiuc.edu/

FLMs agree that it is preferable to obtain NADP data from the web site, rather than summarizing wet deposition data in this report. In this way, current data can be easily accessed by FLMs and the public.

Approximately 50 FLM areas have NADP samplers in or immediately adjacent to them. Because some of these areas are classified as wilderness, FLMs install sampling equipment in adjacent non-wilderness areas in order to preserve the wilderness character of the area. Ambient air in these adjacent areas is considered representative of air in the wilderness area.

A number of FLM areas do not have an NADP sampler in or adjacent to them. Where possible, the FLM has identified an NADP site whose data may be used to characterize deposition at the area. Deposition rates generally increase with elevation and deposition in high-elevation areas may be difficult to characterize with data from a lower-elevation NADP site. FLM consultation may be necessary to estimate deposition in these areas.

Areas that experience significant deposition from fog and cloud water or large amounts of snow may need to use alternate sampling methods and data in addition to NADP protocols and NADP data to characterize them. Wet deposition in these areas may need to be sampled with alternate methods, including cloud water samplers and snowpack sampling or estimated by modeling. At sites where such data or modeled estimates are available, they should be used to calculate total deposition. At mountain sites frequented by clouds and fog, deposition from clouds may equal or exceed that from precipitation. Cloud water is generally more acidic and contains higher concentrations of base cations than rain water; therefore, it can contribute significantly to total loadings of S and N (Hemmerlein and Perkins 1992). Various methods have been developed to measure deposition from cloud water. The Mountain Acid Deposition Program (MADPro) used automated cloud water collectors to sample at three high-elevation eastern sites (Anderson et al. 1999). Forests covered by fog for significant periods of time may be especially susceptible to injury from acid deposition. Acidic cloud water has predisposed red spruce in the high elevations of the northeast U.S. Appalachians to winter injury and cumulative impacts with other biotic and abiotic stresses have caused mortality. The contribution of clouds and fog to deposition at high elevations may overshadow both deposition from precipitation and dry deposition (Hidy 1998). The EPA estimated that as a result of cloud cover, high elevation forests might experience four times the amount of total pollutant deposition as lower elevation forests without cloud cover (NAPAP 1991). High elevation lakes are also impacted by fog and clouds, as well as rain and snow. Measurements in high elevation areas that do not include all contributions to wet deposition will result in under-estimates.

Modeling has been used to estimate total wet deposition in some areas. For example, the Southern Appalachian Man and the Biosphere Cooperative (as part of the Southern Appalachian Assessment) has used NADP data, topographical data, and meteorological data to model wet deposition loading at locations in the southeastern U.S.

Dry Deposition (Revised)

Dry deposition includes gases, aerosols and particles. The primary gases involved with N and S deposition are ammonia (NH_3), nitric oxide (NO), nitrogen dioxide (NO_2), nitric acid (HNO_3), and sulfur dioxide (SO_2), while the primary particles are nitrate (NO_3^-), ammonium (NH_4^+), and sulfate (SO_4^{2-}) ions (Hanson and Lindberg 1991). Ammonia, NO, NO_2 and SO_2 are taken up by plants through stomata, while HNO_3, due to its high deposition velocity, is deposited to plant surfaces in addition to being taken up by stomata. Nitrate, ammonium, and sulfate particles deposit to surfaces (Bytnerowicz and Fenn 1996).

Dry deposition is much more difficult to estimate than wet deposition. The estimation of dry deposition rates requires information on the ambient concentrations of pollutants, meteorological data, and information on land use, vegetation, and surface conditions, all of which are site-specific. Because of this site-specificity, it is difficult to spatially extrapolate dry deposition data as is often done for wet deposition data.

In general, FLMs rely on data from CASTNet for estimates of dry deposition in FLM areas (http://www.epa.gov/castnet). CASTNet was developed by EPA, as a result of the Clean Air Act Amendments of 1990, and currently includes over 70 sites. These include a combination of former National Dry Deposition Network sites, Park Research and Intensive Monitoring of Ecosystems Network sites (PRIMENet), and others. Dry deposition is measured at 26 NPS areas and 2 USFS areas. FLMs agree that it is preferable to obtain CASTNet data from the web site, rather than summarizing dry deposition data in this report. In this way, current data can be easily accessed by FLMs and the public.

Other methods for measuring dry deposition are available. For example, information on vertical changes in concentrations of major gases and particles of interest over plant canopies can be used for calculation of deposition of

these compounds to forests and other ecosystems (Hicks et al. 1987). Models, such as "Big-Leaf" (Baldocchi et al. 1987) allow estimating dry deposition to uniform canopies, such as agricultural crops or lowland forests. However, no models have been developed so far for reliable estimates of deposition of gases and particles to forests and other ecosystems in complex mountain terrain (Bytnerowicz et al. 1997). Therefore, no good large-scale estimates of dry deposition are available for western U.S. forests.

Another approach to evaluating dry deposition is net throughfall technique. By measuring concentrations of ions in throughfall (bulk precipitation) and after subtracting concentrations of the same ions in precipitation in an open area, fluxes of ions such as nitrate, ammonium, and sulfate can be calculated. A branch washing technique is similar to the net throughfall approach and is used when no wet precipitation is present. The pre-washed branches are exposed to ambient air for a certain time period and then carefully rinsed with water (Lindberg and Lovett 1985). Information about amounts of nitrate, ammonium and sulfate rinsed from branches of a known surface area, time of exposure, and leaf area index of a given forest stand allow the calculation of fluxes of the measured ions to trees. Adding stomatal uptake of gases (calculated from information on gas concentration and stomatal conductance), and estimates of deposition to other landscape forms (such as soils and rocks) allow for quite reliable estimates of dry deposition at a forest stand level (Bytnerowicz et al. 2000). Such estimates have been made for the subalpine zone of the eastern Sierra Nevada and mixed conifer forests on the western Sierra Nevada and the San Bernardino Mountains (Bytnerowicz and Fenn 1996; Bytnerowicz et al. 1999). Both the net throughfall and branch washing techniques, although providing relatively accurate estimates of deposition to certain ecosystems, cannot be applied to every type of vegetation. These techniques work well for conifers with relatively thick cuticles. For plants with thinner cuticle, extraction of ions from plant interior or transcuticular uptake of deposited ions may not allow for making good estimates of dry deposition to plant surfaces.

Recent developments, such as passive samplers that allow for relatively inexpensive determinations of nitric oxide, nitrogen dioxide, ammonia, nitric acid and sulfur dioxide concentrations, provide some promising opportunities for large-scale estimates of distribution of these pollutants. This, together with information on landscape-level vegetation coverage, leaf area index, and deposition velocity of the monitored pollutants, will allow calculating deposition of the measured gases to various landscape forms. Although this approach would not include deposition fluxes of particulate pollutants, a large portion of dry N and S deposition (gases) would be covered. Information on fluxes of the N and S particulate component (nitrate, ammonium, and sulfate ion concentrations) can be estimated based on their concentrations from annular denuder/filter pack systems or other comparable techniques and literature values of deposition velocities of these ions.

For many FLM areas, detailed site-specific information and monitoring needed for dry deposition measurements are not available. Therefore, the FLM may choose to recommend a reasonable estimate of dry deposition. NAPAP's 1991 summary report concluded that dry deposition of sulfur is 30-60% of the total (wet plus dry) deposition at regionally representative sites; dry deposition of nitrogen is 30-70% of the total (wet plus dry) deposition at regionally representative sites (NAPAP 1991a). An analysis of one year (1991) of NADP, CASTNet, and IMPROVE (Interagency Monitoring of Protected Visual Environments) data from national parks and wildernesses found that wet deposition dominated total deposition in both the East and the West. Dry deposition of sulfur was 20-50% of the total; dry deposition of nitrogen was 30-60% of the total (Hidy 1998). These estimates, and similar ones, have led to the common assumption that dry deposition is approximately 50% of the total deposition. Therefore, for many FLM areas without on-site or nearby representative dry deposition sampling, the FLM may recommend that dry deposition is equal to wet deposition. The FLM recommends this as a "best available estimate," recognizing that in some areas it may result in under- or over-estimating total deposition. Total deposition, which is the sum of wet plus dry deposition, therefore equals twice the wet deposition.

In summary,

Total Deposition = Wet Deposition + Dry Deposition

Or,

Total Deposition = 2 x Wet Deposition (assuming Dry Deposition = Wet Deposition)

There are numerous monitoring stations in or near FLM areas for estimating wet and dry deposition values. For some areas the FLM assumes that dry deposition equals wet deposition, recognizing that this may result in under- or over-estimates of total deposition. Deposition monitoring data and information on the appropriate dry deposition data to use at sites where data are available are included on the respective Agencies web sites referenced previously.

FLMs will continue to participate in monitoring and research to further our understanding of dry deposition dynamics and improve our measurements of dry deposition.

Other Deposition Measurement Methods

Pollutant deposition, particularly in areas where traditional wet and dry deposition sampling is impractical, can also be estimated by other methods. These methods include bulk samplers that collect both wet and dry deposition and snowpack measurements that estimate the total amount of

pollutants in the snow column at the time of maximum snow accumulation. Special methods have also been developed for collecting fog and cloud water (Anderson et al. 1999).

In addition, methods are being developed to estimate dry deposition rates from pollutant concentrations obtained by IMPROVE fine particle samplers. IMPROVE samplers are located at many FLM areas and expanded coverage is planned for 1999.

Modeling Deposition Rates

Deposition from existing sources can be estimated from deposition monitoring data, but contributions to deposition from the proposed source and other sources permitted but not yet operating should be modeled.

Modeling should be done in accordance with recommendations developed by the Interagency Work Group on Air Quality Modeling (IWAQM) Phase 2:

- http://www.epa.gov/scram001/7thconf/calpuff/phase2.pdf

IWAQM provides the procedures that can be used to estimate S and N deposition from a proposed source and other sources permitted but not yet operating. The FLMs propose that these procedures be used to estimate S and N deposition. For S deposition, the wet and dry fluxes of sulfur dioxide and sulfate are calculated, normalized by the molecular weight of S, and expressed as total S. For N deposition, IWAQM recommends that the wet and dry fluxes of nitric acid (HNO_3) and nitrate (NO_3^-) and the dry flux of nitrogen oxides (NO_x) be calculated, normalized by the molecular weight of N, and expressed as total N. In addition, the FLMs agree that wet and dry fluxes of ammonium sulfate ($(NH_4)_2SO_4$) and ammonium nitrate (NH_4NO_3) should be calculated, normalized by the molecular weight of N, and added to the estimate of total N. Therefore, total N deposition is the sum of N contributed by dry and wet fluxes of HNO_3, NO_3^-, $(NH_4)_2SO_4$, and NH_4NO_3 and the dry flux of NO_x.

The FLMs recognize that the ammonia (NH_3) in these compounds is derived from both man-made and natural sources. Free gaseous NH_3 has a high deposition velocity and tends to deposit quickly. However, if sulfates and nitrates (which are primarily man-made) are present in the atmosphere, free NH_3 quickly reacts to form $(NH_4)_2SO_4$ and NH_4NO_3. These compounds, because of their fine particle size and slower deposition velocity than free gaseous NH_3, can be transported long distances and deposited in a FLM area, adding to the total N deposition loading.

An appropriate estimate of ambient free gaseous NH_3 is needed for the modeling analysis. IWAQM refers to Langford et al. (1992), who suggest that typical (within a factor of 2) background values of NH_3 are: 10 parts per billion (ppb) for grasslands, 0.5 ppb for forest, and 1 ppb for arid lands at 20°C. Langford et al. (1992) provide strong evidence that background levels of NH_3 show strong dependence with ambient temperature (variations of a factor of 3 or 4) and a strong dependence on the soil pH. However, given all the uncertainties in NH_3 data, IWAQM recommends use of the background levels provided above, unless better data are available for the specific modeling domain. IWAQM notes that in areas where there are high ambient levels of sulfate, values such as 10 ppb might overestimate the formation of particulate nitrate from a given source, for these polluted conditions. IWAQM further notes that areas in the vicinity of strong point sources of NH_3, such as feed lots or other agricultural areas, may experience locally high levels of background NH_3.

Questions regarding these recommendations should be resolved through consultation with the appropriate FLM and the appropriate State and/or EPA modeling representative. Applicants should provide a modeling protocol to the appropriate FLM prior to conducting modeling analyses.

Estimation of Current and Future Deposition Rates (Revised)

In order to evaluate a proposed source's contribution to total (wet + dry) deposition in a FLM area, it is necessary to first estimate current pollutant deposition rates. The current rate is a result of deposition from all existing natural and anthropogenic sources. FLMs use two approaches to estimating the current rate of deposition. One approach estimates the current rate by averaging data from an appropriate monitoring site for the pollutant of interest, using all years with complete data records. The second, more conservative, approach assumes that the current rate is equivalent to the highest rate for the pollutant of interest in the data record.

The method for estimating future total deposition rates is:

- From the respective Agency web sites, identify available on-site or representative wet and dry deposition data for the FLM area. Wet deposition data can be obtained through NADP (http://nadp.sws.uiuc.edu/). For NPS sites without an NADP sampler, use estimates of total wet nitrogen and total wet sulfur from the Air Quality Estimates for 1999-2003 at http://www.nature.nps.gov/air/Maps/AirAtlas/index.cfm.

  Dry deposition data can be obtained through CASTNet at (http://www.epa.gov/castnet).

  Verify if dry deposition is assumed to equal wet deposition for the site. For high-elevation sites, consult with the FLM to determine if deposition from cloud water, fog, dew, or snowpack should be considered. For sites without on-site data, consult FLM for further guidance.

- After consulting with the FLM, estimate either:

- the average annual or seasonal wet and dry deposition rates for the appropriate pollutant using all years with complete data records; or
- the highest annual or seasonal wet and dry deposition rates for the appropriate pollutant using all years with complete data records.

- Calculate current total deposition (wet + dry = total).
- Estimate, using the appropriate dispersion model as described in the 'Modeling Deposition Rates' section above, the proposed source's contribution to future total deposition on an annual or seasonal basis.
- Estimate, using appropriate dispersion model as described in the 'Modeling Deposition Rates' section above, the contribution of any sources permitted but not yet operating to future total deposition and the affect of any enforceable emission reductions. This estimate may be available from the State permitting authority.
- The current pollutant deposition rate plus the proposed source's contribution to deposition plus the contribution from other sources permitted but not yet operating minus credit for enforceable emission reductions equals the future total deposition rate.

Current + Proposed + Permitted (not yet operating) – credit for enforceable reductions = Future Total Deposition

This future total deposition rate for a given pollutant can then be used to determine the potential for adverse effects to AQRVs. If appropriate, the change in deposition rate can be used to estimate changes in pH or ANC in an ecosystem. If the future total deposition rate is expected to cause an adverse effect to AQRVs and/or exceeds the critical load established for a FLM area, the FLM may recommend mitigation. If no critical load has been established for the FLM area, the FLM will use the best information available in determining whether to recommend mitigation.

3.5.7. Summary (Revised)

- Deposition of S and N has the potential to affect terrestrial, freshwater, and estuarine ecosystems on FLM lands.
- The FLM has identified, where possible, AQRVs sensitive to deposition of S and N on FLM lands and the critical loads associated with those AQRVs.
- A proponent of a source of new emissions with the potential to contribute to S or N deposition in an FLM area should consult with the FLM to determine what analyses are needed to assess AQRV effects. The FLM may request a deposition impact analysis, described in detail in this chapter and summarized below.
  - Estimate the current deposition rate to the FLM area. A list of monitoring sites providing data to characterize deposition in FLM areas is included on the respective Agencies web sites.
  - Estimate the future deposition rate by adding the existing rate, the new emissions' contribution to deposition, the contribution of sources permitted but not yet operating, and then subtracting the credit for enforceable emission reductions. Modeling of new, reduced, and permitted but not yet operating emissions' contribution to deposition should be conducted following current EPA modeling guidance.
  - Compare the future deposition rate with the recommended screening criteria (e.g., critical load, concern threshold, or screening level value) for the affected FLM area. A list of documents summarizing these screening criteria, where available, can be found in Appendix G.

    Information for USFS Class I areas is also available at:

    http://www.fs.fed.us/air

    Information for NPS and FWS Class I areas is available at:

    http://www.nature.nps.gov/air/Permits/ARIS/

    Information for FWS Class I areas is under development at:

    http://www.fws.gov/refuges/whm/AirQuality/index.html

    The appropriate FLM should be contacted for additional information.

3.5.8. Web sites for Deposition and Related Information (Revised)

Clean Air Status and Trends Network (CASTNet) dry deposition data:

- http://www.epa.gov/castnet

National Acid Precipitation Assessment Program 2005 Report:

- http://www.esrl.noaa.gov/csd/AQRS/reports/napapreport05.pdf

National Atmospheric Deposition Program (NADP) wet deposition data:

- http://nadp.sws.uiuc.edu/

National Park Service Airweb:

- http://www.nature.nps.gov/air/

Natural Resources Conservation Service, Snow Water Equivalent Information (SNOTEL):

- http://www.wcc.nrcs.usda.gov/snow

Southern Appalachian Mountain Initiative:

- http://www.tva.gov/sami

USDA Forest Service National Air Resource Management Web Site:

- http://www.fs.fed.us/air/

EPA Office of Air and Radiation:

- http://www.epa.gov/oar

EPA, Deposition to Estuaries:

- http://epa.gov/owow/airdeposition/

EPA, STOrage and RETrieval System for Water and Biological Monitoring Data (STORET):

- http://www.epa.gov/storet

U.S. Fish and Wildlife Service Air Quality Branch:

- http://www.fws.gov/refuges/whm/AirQuality/index.html

U.S. Geological Survey, National Water-Quality Assessment (NAWQA) Program:

- http://water.usgs.gov/nawqa

U.S. Geological Survey, Acid Rain Program:

- http://bqs.usgs.gov/acidrain

U.S. Geological Survey, Water Data Storage and Retrieval System (WATSTORE):

- http://water.usgs.gov/owq/data.html

4. Expansion of Discussion of Process for Adverse Impact Determination (New Chapter)

Based on feedback from permit applicants and State permitting authorities, the Agencies are providing a more detailed description of the adverse impact decision making process once a source analysis has raised concerns during a first-level and any subsequent analyses.

If the first-level analysis yields impacts above the defined threshold(s), the applicant may propose to address preliminary FLM concerns directly through proposed emission reductions for the project, or through implementation of other measures to mitigate emission impacts. Alternatively, the applicant may undertake a more refined analysis to potentially alleviate preliminary concerns. Of course, this refined analysis should occur in a time-frame that enables permitting authorities to adhere to their regulatory guidelines.

Additional emission reductions, mitigation proposals, or more refined analysis are not legal requirements. They are options that can be utilized to help alleviate preliminary FLM concerns about emission impacts on Class I areas. Permit applicants can request that FLMs conduct their evaluation based on information provided in the application.

4.1. Background

The FLAG visibility thresholds have been interpreted by some as a one-dimensional or bright line test that inevitably leads to an adverse impact determination. This, however, is not the intent; these screening-levels were envisioned as a "visibility analysis threshold" similar to the newer deposition analysis thresholds (DATs) discussed above for sulfur and nitrogen deposition.

The Agencies want to emphasize that the FLAG report provides criteria as to when the FLMs will definitively not object to, or declare an adverse impact for, a proposed new source. FLAG assures an applicant that, if they conduct their analyses correctly and demonstrate that change in extinction or deposition falls below the specified thresholds, the FLMs will not raise concerns regarding the project. However, the converse does not necessarily apply — a FLAG threshold exceedance does not mean the FLM will certainly find that a project will adversely affect air quality related values. If a threshold is exceeded, the FLMs will consider the factors discussed below and make a project-specific determination as to whether or not the impacts are adverse.

Seney National Wildlife Refuge, Michigan.
Credit: Atlee Hart

4.2. Regulatory Factors

According to the EPA definition of "adverse impact on visibility," the FLM must determine whether the proposed source's predicted impact "interferes with the management, protection, preservation, or enjoyment of the visitor's visual experience" taking into account the "geographic extent, intensity, duration, frequency and time of visibility impairments, and how these factors correlate with (1) times of visitor use of the Federal Class I area, and (2) the frequency and timing of natural conditions that reduce visibility." (40 C.F.R. §51.301).

Considering the regulatory factors is inherent in the first-level modeling exercise. The model describes the geographic area predicted to be impacted. The visibility extinction values describe the intensity of the impact. Similarly, the model provides some level of assessment regarding duration, frequency, and time of impact. A more refined modeling analysis should further inform consideration of these factors. Regarding how these factors correlate with visitor use, the responsibilities of the Agencies include protecting the resources for all visitors. Visitor data show that nearly all Class I areas have some level of visitation each month. Regarding correlation with the frequency and timing of natural conditions that reduce visibility, the first-level modeling analysis will not provide this information directly, but, by using the percentile approach and monthly relative

humidity values, the Agencies have attempted to provide a reasonable approach to addressing weather impacts.

Similarly, if the sulfur or nitrogen DAT is exceeded, or if high ozone levels are anticipated, the FLMs should determine if those impacts would adversely affect sensitive AQRVs. This adverse impact determination should be made on a project-specific basis and will be largely driven by management objectives for the area.

4.3. Contextual Considerations

The Agencies recognize that the context within which new source permitting occurs is shifting. Many older major stationary sources will be installing pollution controls over the next 10 to 15 years (e.g., in response to the Regional Haze Rule). New motor vehicle emission and fuel standards will reduce tailpipe pollution from mobile sources gradually, but significantly, over a similar time frame. States are developing visibility protection plans that ensure "reasonable progress" toward natural conditions, pursuant to the EPA's Regional Haze Rule. These plans will be reviewed and revised every five to ten years, and thus provide a mechanism for revisiting sources as better technology becomes available or as otherwise needed to maintain progress toward visibility goals. The location and effect of pending pollution control programs on specific Class I areas remains somewhat uncertain; however, the Agencies recognize and appreciate that significant emission reductions are anticipated, especially in the eastern U.S.

As part of the discussions with permitting authorities or permit applicants when screening level thresholds are exceeded, the Agencies will consider contextual information, including, for example:

- Current pollutant concentrations and AQRV impacts in the Class I area
- Air quality trends in the Class I area
- Emission changes that have occurred or would occur (i.e., enforceable) by the time the new source begins operation
- Whether there are approved SIPs that account for new source growth and demonstrate attainment of national ambient air quality standards and "reasonable progress" toward visibility goals
- The expected useful life of the source
- The stringency of the emission limits (e.g., Best Available Control Technology)
- Other considerations such as options put forth by the applicant that would produce ancillary environmental benefits to AQRVs (e.g., reductions in toxic air contaminants, pollution prevention investments)
- Comments received from the public or other agencies during the comment period prior to issuing the permit.

4.4. Preliminary Adverse Impact Concerns

After considering the regulatory factors and contextual considerations listed above, the Agencies, in consultation with the FLM, will evaluate, on a project-specific basis, whether the evidence supports a finding that the new source would possibly cause or contribute to an adverse impact on air quality related values. If so, the Agencies will notify the permit applicant and the permitting agency and provide the permit applicant the opportunity to consider mitigation strategies that will alleviate the potential adverse impact concerns. These strategies may include:

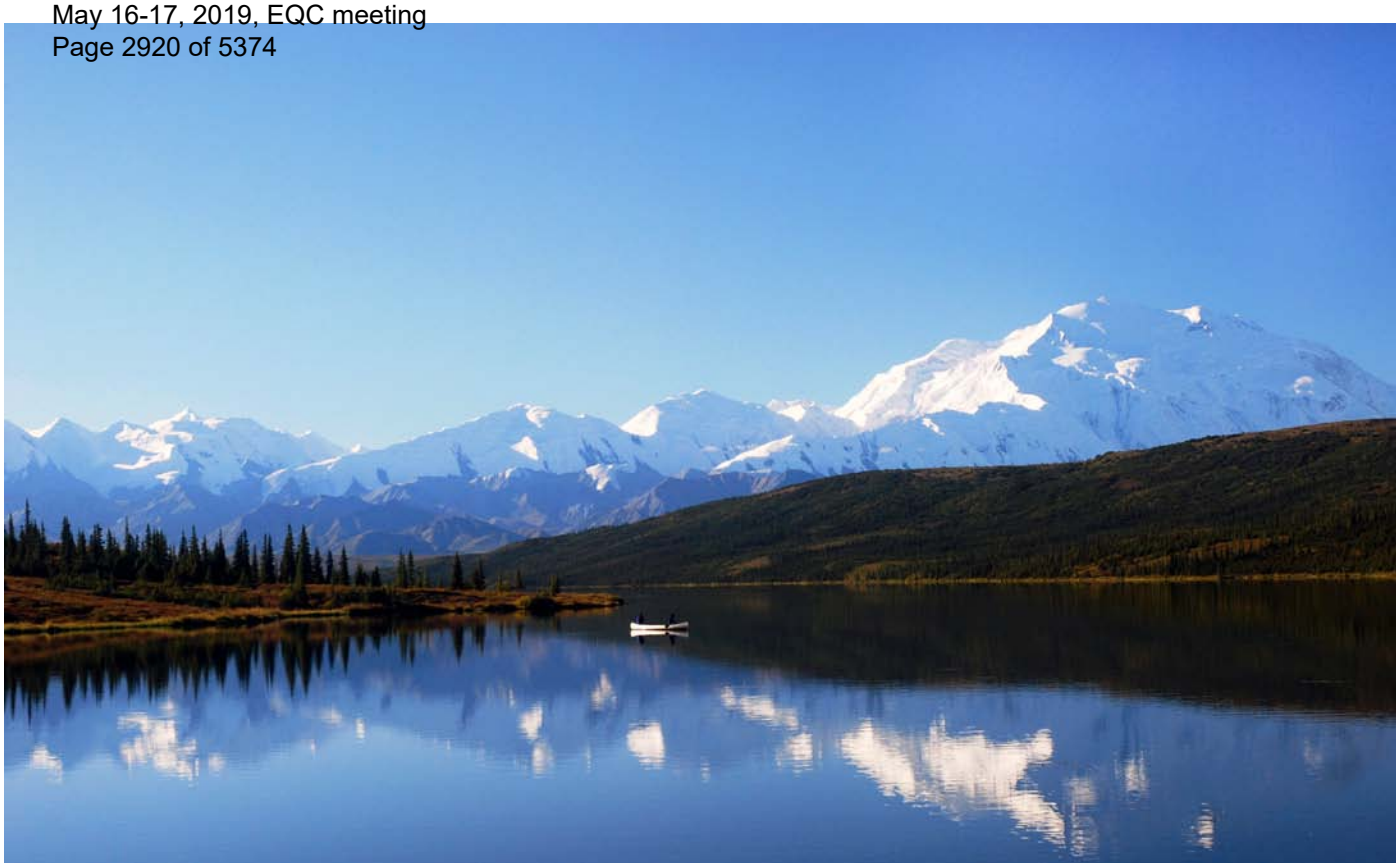
- Obtaining emission offsets for pollutants that cause or contribute to the potential adverse impacts on Class I area resources;
- Reducing emission rates through more stringent pollution control technology or operational or design changes; and
- Monitoring or special studies that increase understanding of how Class I area resources or visitors are affected by air pollution, which may serve as a basis for revisiting permit conditions in future years. (Note: monitoring and study alone does not constitute mitigation.)

Again, proposing any such mitigation strategy is voluntary. Nevertheless, if the FLMs deem a proposed mitigation strategy as adequate to protect AQRVs, and the mitigation strategy is made enforceable via the PSD permit or some other mechanism, the FLM will not make an adverse impact finding with respect to the issues addressed by the mitigation strategy.

4.5. Adverse Impact Determination

If an applicant is unable or unwilling to implement an appropriate mitigation strategy to alleviate potential adverse impact concerns, the FLM will determine whether or not the potential impacts of the project as proposed should be formally deemed adverse to air quality related values in the affected Class I areas. If the FLM concludes that there are potential adverse impacts, he will inform the permitting authority of this decision.

Historically, the FLMs have made adverse impact findings for less that one percent of the permit applications that the Agencies review. In those rare cases, the FLMs will strive to provide the permitting authority with an ample technical and policy/management-related foundation, including a discussion of the analysis results and the regulatory and contextual factors discussed above. The FLMs' ability to provide this foundation will depend on the completeness and adequacy of information provided by the permit applicant. Where information is lacking, or uncertain, the FLMs will err on the side of protecting air quality related values.



Denali National Park and Preserve, Alaska.
Credit: National Park Service/Trey Simmons.

5. Future FLAG Work

5.1. Implementing FLAG Recommendations (Revised)

FLAG participants believe that the recommendations in this revised document should be implemented as soon as possible. Therefore, an attempt has been made to present thorough and clear information on the processes that will be used to protect and improve AQRVs in FLM areas.

Many of the issues and recommendations discussed herein are complex and require specialized knowledge. Consequently, State agencies and others who intend to use this information in NSR/PSD permitting, land planning and use, and other activities, may want or require further guidance and implementation assistance. The Agencies anticipate that much of this guidance and assistance will be provided locally through established formal and informal links between FLMs, States, EPA and others. For example, the Agencies intend to provide further information through their respective web sites, and through participating in related training sessions and/or workshops.

5.2. Phase I Updates (Revised)

This revised *FLAG Phase I Report* is intended to clearly state FLM positions regarding NSR/PSD as it currently exists. As the FLMs learn more about how to better assess the health and status of AQRVs, and as EPA produces new modeling tools, the FLAG report may be revised again. Any such revisions to the report will be announced on the Agencies' web sites.

5.3. Phase II Tasks (Revised)

FLAG Phase I focused on issues that could be resolved relatively quickly, without extensive research or the collection of new data. The FLMs envisioned a Phase II that would address the more complex issues and concerns, including those that may require additional data collection. Unfortunately, lack of available resources has prevented the Agencies from embarking on a formal FLAG Phase II process. Nevertheless, the Agencies continue to gather effects-based information as part of their ongoing resource protection responsibilities. The new information gathered since FLAG 2000 is reflected in this revision. As the Agencies generate additional data or information, they will make that available to interested parties via their respective web sites.

Appendix A: Glossary

The list below contains definitions for some of the terms used in the *FLAG Phase I Report*. These terms are defined in the sense that they relate to the work of the Federal Land Managers (FLMs) in protecting air resources.

For terms whose definition is lengthy or complex, the associated *Code of Federal Regulations* (CFR) section or other reference is cited.

Air Quality Related Value (AQRV). A resource, as identified by the FLM for one or more Federal areas, that may be adversely affected by a change in air quality. The resource may include visibility or a specific scenic, cultural, physical, biological, ecological, or recreational resource identified by the FLM for a particular area.

Adverse Impact on an AQRV. An unacceptable effect, as identified by an FLM, that results from current, or would result from predicted, deterioration of air quality in a Federal Class I or Class II area. A determination of unacceptable effect shall be made on a case-by-case basis for each area taking into account existing air quality conditions. It should be based on a demonstration that the current or predicted deterioration of air quality will cause or contribute to a diminishment of the area's national significance, impairment of the structure and functioning of the area's ecosystem, or impairment of the quality of the visitor experience in the area.

Adverse Impact on Visibility. Visibility impairment which interferes with the management, protection, preservation, or enjoyment of a visitor's visual experience of a Federal Class I or Class II area. This determination must be made on a case-by-case basis taking into account the geographic extent, intensity, duration, frequency and time of visibility impairments, and how these factors correlate with (1) times of visitor use of the Class I area, and (2) the frequency and timing of natural conditions that reduce visibility. This term does not include effects on integral vistas. [40 CFR §51.301(a)]

Absorption. The process by which incident light is removed from the atmosphere and retained by a particle.

Absorption Coefficient. A number that is proportional to the "amount" of light removed from a sight path by absorption per unit distance.

Acidification. The decrease of acid neutralizing capacity in water or base saturation in soil caused by natural or anthropogenic processes.

Aerosol. A mixture of microscopic solid or liquid particles in a gaseous medium. Smoke, haze, and fog are aerosol examples.

Airshed. A geographic area that, because of topography, meteorology, and/or climate, is frequently affected by the same air mass.

AOT40. Sum of all hourly average concentrations after subtracting 40 ppb from each hourly value.

BACT (Best Available Control Technology). The control level (or control measures) required for sources subject to PSD. (See 40 CFR §52.21(b)(12), or 40 CFR §51.166(b)(12)).

Class I Area. As defined in the Clean Air Act, the following areas that were in existence as of August 7, 1977: national parks over 6,000 acres, national wilderness areas and national memorial parks over 5,000 acres, and international parks.

Critical Load. The quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge.

Cumulative. The impact on an AQRV resulting from the total pollutant loading from all sources including the contributing effects of known and reasonably foreseeable new and modified sources of air pollution. A single source may cause individually minor, but cumulatively significant, effects on AQRVs.

Damage. Any reduction in the intended use or value of a biological or physical resource. For example, economic production, ecological structure or function, aesthetic value, or biological or genetic diversity that may be altered by a pollutant.

Deposition Analysis Threshold. A screening threshold developed by NPS and FWS that defines the additional amount of nitrogen or sulfur deposition within an FLM area, below which estimated impacts from a proposed new or modified source are considered negligible.

Emission Offset. A Federally enforceable reduction in emissions from an existing source that mitigates the impacts of a proposed new or modified source on AQRVs, PSD increments, and/or NAAQS. Also, Federally enforceable reductions in actual emissions from existing sources in a nonattainment area such that the total allowable emissions from a new or modified source and existing sources will be sufficiently less than the total emissions from existing sources before the application for a permit to construct so as to represent reasonable further progress towards attainment of the NAAQS. (See 42 U.S.C. § 7503(a)(1)(A))

Extinction. The attenuation of light due to scattering and absorption as it passes through a medium.

Fugitive Emissions. Emissions which do not pass through a stack, chimney, vent, or other functionally equivalent opening.

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Federal Land Manager (FLM). The Secretary of the Department with authority over such lands. [40 CFR §51.166(b)(24)] The FLM for the Department of the Interior has been delegated to the Assistant Secretary for Fish and Wildlife and Parks; the FLM for the Department of Agriculture has been delegated to the Forest Service, and has been redelegated to the Regional Forester or individual Forest Supervisor.

Flux. Gaseous uptake into plant tissue.

Green Line. The total pollutant loading (contributions from existing and proposed sources) below which there is a very high degree of certainty that no AQRV will be adversely affected.

Haze. An atmospheric aerosol of sufficient concentration to be visible. The particles are so small that they cannot be seen individually, but are still effective attenuating light and reducing visual range.

Hydrocarbons. Compounds containing only hydrogen and carbon. Examples: methane, benzene, and decane.

Hygroscopic. Readily absorbing moisture, as from the atmosphere.

Injury. Any physical or biological response to pollutants, such as a change in metabolism, reduced photosynthesis, leaf necrosis, premature leaf drop, or chlorosis.

LAER (Lowest Achievable Emissions Rate. The control level required of a source subject to nonattainment review. (See 40 CFR §51.165(a)(1)(xiii))

Limit of Acceptable Change. The amount of change that could occur without significantly altering an AQRV or sensitive receptor.

Micrometer. A unit of length equal to one millionth of a meter; the unit of measure for particle size.

Mie Theory. A complex mathematical model that allows the computation of the amount of energy (light) scattered by spherical particles.

N100. Number of hourly average concentrations ≥100 ppb.

Natural Conditions. Conditions substantially unaltered by humans or human activities. As applied in the context of visibility, natural conditions include naturally occurring phenomena that reduce visibility as measured in terms of light extinction, visual range, contrast, or coloration.

Natural Visibility Conditions. Visibility conditions attributable to Rayleigh scattering and aerosol associated with natural processes.

Nephelometer. An instrument that measures the amount of light scattered.

Nitrates. Those gases and aerosols that have origins in the gas-to-aerosol conversion of nitrogen oxides, e.g., NO_2 ; of primary interest are nitric acid and ammonium nitrate. Ammonium nitrate is very hygroscopic so its contribution to visibility impairment is magnified in the presence of water vapor.

Nitrogen Dioxide (NO_2). A gas consisting of one nitrogen and two oxygen atoms It absorbs blue light and therefore has a reddish-brown color associated with it.

Nonattainment Area. An area designated by the EPA Administrator pursuant to Section 107(d) of the Clean Air Act as having air quality which does not meet one or more National Ambient Air Quality Standard (NAAQS). For a list of nonattainment areas, see 40 CFR Part 81, Subpart C.

Oxidant Stipple. Small brown or black interveinal necrotic lesions on the adaxial surface of leaf tissue that can be attributed to exposure to ozone.

Phytotoxic. Poisonous to plants.

Post-Construction Monitoring. Monitoring required as a permit condition that the permitting authority considers necessary to determine the effect emissions from a stationary source may have, or are having, on the air quality or on the AQRVs of an area. Such monitoring includes both "ambient" monitoring and "AQRV" monitoring and may involve short-term and long-term measurements made at locations representative of the greatest expected impacts.

PSD Increments. The maximum increases in ambient pollution concentrations allowed over baselines concentrations. See 40 CFR §51.166 (c) for increments for specific pollutants.

RACT (Reasonable Available Control Technology). The lowest emissions limit that a particular source can meet by the application of control technology that is reasonably available considering technological and economic feasibility.

Rayleigh Scattering. The scattering of light by particles much smaller than the wavelength of the light, e.g., molecular scattering in the natural atmosphere.

Reconstructed Extinction. Extinction estimate that results from summing up the product of the mass of each measured particle species and the appropriate absorption or extinction coefficient.

Red Line. The total pollutant loading (contributions from existing and proposed sources) at which there is a very high degree of certainty that at least one AQRV will be adversely affected.

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Regional Haze Visibility Impairment. Any humanly perceptible change in visibility (light extinction, visual range, contrast, coloration) from that which would have existed under natural conditions, caused predominantly by a combination of many sources from, and occurring over, a wide geographic area.

Re-opener. A permit condition that requires the permitting authority, at a specified time after permit issuance, to review and revise, if necessary, the permit based on new information such as the findings from post-construction monitoring, updated emissions inventories, updated modeling, research, or information on air pollution effects to terrestrial, aquatic, and visibility resources.

Scattering. An interaction of a light with an object (e.g., a fine particle) that causes the light to be redirected in its path.

Scattering Coefficient. Measure of the ability of particles to scatter light; measured in number proportional to the "amount" of light scattered per unit distance.

Screening Level or Screening Level Value (SLV). The concentration or dose of air pollution below which estimated impacts from a proposed new or modified source are considered insignificant. The SLV is dependent on existing air quality and on the condition of the AQRV of concern.

Sensitive Receptor. The AQRV, or part thereof, that is the most responsive to, or the most easily affected by the type of air pollution in question. For example, at Great Smoky Mountains National Park, spruce-fir forest is a sensitive receptor of the AQRV flora.

Sensitive Receptor Indicator. A measurable physical, chemical, biological, or social (e.g., odor) characteristic of a sensitive receptor. For example, for the sensitive receptor, Crater Lake, water clarity is a sensitive receptor indicator.

Stationary Source. A source of pollution that is well defined, such as the smokestack of a coal-fired power plant or smelter.

Sulfates. Those aerosols that have origins in the gas-to-aerosol conversion of sulfur dioxide; of primary interest are sulfuric acid and ammonium sulfate. Sulfuric acid and ammonium sulfate are very hygroscopic so their contribution to visibility impairment is magnified in the presence of water vapor.

Sulfur Dioxide (SO_2). A gas consisting of one sulfur and two oxygen atoms. Of interest because sulfur dioxide converts to an aerosol.

SUM00. The sum of all hourly average concentrations above 0 ppb.

SUM06. The sum of all hourly average concentrations at or above 60 ppb.

Target Load. The acceptable concentration or dose of an air pollutant that provides a reasonable margin of safety below the critical load. The target load should be achievable under existing conditions.

Transmissometer. An instrument that measures the amount of light extinction over a fixed, specified path length.

Visibility Impairment. Any humanly perceptible change in visibility (visual range, contrast, coloration) from that which would have existed under natural conditions. [40 CFR §51.301(x)]

Visual Range. The distance at which a large black object would just disappear from view.

Volatile Organic Compound (VOC). Any compound of carbon, except those excluded by EPA that participates in atmospheric photochemical reactions. (See 40 CFR §51.100(s))

W126. An ozone index that multiplies each specific concentration by a sigmoidal weighted function, then sums all values. $Wi = 1/[1 + Me^{-(A \times Ci)}]$, where M and A are constants 4403 and 126 ppm^{-1}, respectively, w_i is the weighting factor for c_i, and c_i is concentration in ppm.

Appendix B: Legal Framework for Managing Air Quality and Air Quality Effects on Federal Lands

Introduction

The regulation of air pollution sources has clearly been delegated to EPA, and as applicable, the States. However, Federal Land Managers (FLMs) have the responsibility to protect the particular values of the lands over which they have jurisdiction, to the extent they have been delegated the authority, from the adverse impacts of activities inside and outside these areas.

This Appendix sets out the basic legal authorities and responsibilities with which the FLMs comprising FLAG must comply, in addition to those authorities which they can utilize to protect AQRVs on public lands.

For the purposes of this Appendix only, the term "public lands" is defined to include units of the National Park, National Wildlife Refuge, and National Forest Systems.

Agency Organic Acts

Department of the Interior: National Park Service (NPS):

This Organic Act is very specific in that it mandates national park unit managers:

[T]o conserve the scenery and the natural and historic objects and wild life therein and to provide for the enjoyment of the same in such manner and by such means as will leave them unimpaired for the enjoyment of future generations.

16 U.S.C. §1(1997); and

[T]he authorization of activities shall be construed and the protection, management, and administration of these areas shall be conducted in light of the high public value and integrity of the National Park System and shall not be exercised in derogation of the values and purposes for which these various areas have been established, except as may have been or shall be directly and specifically provided for by Congress.

16 U.S.C. § 1a-1 (1997)

Department of the Interior: Fish and Wildlife Service (FWS):

With respect to National Wildlife Refuge System lands (Refuge System lands under the jurisdiction of the United States Fish and Wildlife Service (FWS)), FWS managers are required to manage Refuge System lands so to:

[E]nsure that the biological integrity, diversity, and environmental health of the System are maintained for the benefit of present and future generations of Americans.

16 U.S.C. §668dd(a)(4)(B)(1997)

Department of Agriculture: Forest Service (Forest Service)

National Forest System lands are defined as:

[A]ll National Forests reserved or withdrawn from the public domain of the United States, all national forests acquired through purchase, exchange, donation, or other means, all national grasslands and land utilization projects...and all lands waters, and other interests administered by the Forest Service.

16 U.S.C. §1609(a)(1997)

The Forest Service's Organic Administration Act of 1897 directs the Secretary of Agriculture to:

[M]ake provisions for the protection against destruction by fire and depredations upon the public forests and national forests...

16 U.S.C. Sec. §551(1997)

The National Forest units are managed consistent with Land and Resource Management Plans (LRMPs) under the provisions of the National Forest Management Act (NFMA). 16 §U.S.C. 1604 (1997). Any measures addressing AQRVs on National Forest System lands will be implemented through, and be consistent with, the provisions of an applicable LRMP or its revision (16 U.S.C. §1604(i)).

The Secretary of Agriculture is required by law to prepare a Renewable Resource Assessment by 1979, and every 10 years thereafter. By law this Assessment is required to address:

- A description of Forest Service programs in research, cooperative programs and management of the National Forest System, their relationships, and the relationships of these programs and responsibilities to public and private activities; and
- An analysis of the potential effects of global climate change on the condition of renewable resources on the Forests and rangelands of the United States; and
- An analysis of the rural and urban forestry opportunities to mitigate the buildup of atmospheric carbon dioxide and reduce the risk of global climate change.

16 U.S.C. §1601(a) (1997)

In addition, the Secretary of Agriculture is required to prepare and transmit to the President, a Renewable Resource Program (the Program) every 5 years. This Program must include program recommendations which reflect the fundamental need to protect, and where appropriate,

improve the quality of . . . air resources. 16 U.S.C. §1602(5)(C).

The Forest Service's implementing regulations for NFMA are found at 36 C.F.R. §219 et seq. LRMPs are, in part, specifically based on:

[R]ecognition that the National Forests are ecosystems and their management for goods and services requires an awareness and consideration of the interrelationships among plants, animals, soil, water, air, and other environmental factors within such ecosystems.

36 C.F.R. §219.1(b)(3)

The Wilderness Act. 16 U.S.C. §1131 (1997)

AQRVs in Wilderness areas may receive further protection by the language of the Wilderness Act itself which states:

Wilderness areas... shall be administered for the use of the American people in such a manner as will leave them unimpaired for future use and enjoyment as wilderness .... (16 U.S.C. Sec. §1131).

For Wilderness Areas in the National Forest System, the Act's implementing regulations are found at 36 C.F.R. §293. These Wilderness Areas shall be administered:

...[For] such other purposes for which it may have been established in such a manner as to preserve and protect [their] wilderness character. In carrying out such purposes, National Forest Wilderness resources shall be managed to promote, perpetuate, and, where necessary, restore the wilderness character of the land...

36 C.F.R. §293.2 (1997)

The Clean Air Act, 42 U.S.C. §7401 et seq.

Because of a perceived need for national and regional air quality research to support State programs, Congress passed its first federal air quality initiative in 1955. (Air Pollution Control Act of 1955, Ch. 360, 69 Stat. 322). In response to increasing harm to public health and welfare and to inadequate controls and enforcement, Congress has slowly but steadily expanded and refined the law, now known as the Clean Air Act (CAA), to cover more types of pollutants and emitters; e.g., stationary and mobile sources of pollution. These efforts have culminated in the 1990 Amendments to the CAA, which represent the most comprehensive and detailed set of measures to date to both prevent and curtail air pollution.

The declaration of purpose, as revised in 1990 states in part:

The purposes of this subchapter are: to protect and enhance the quality of the Nation's air resources so as to promote the public health and welfare and the productive capacity of its population.

42 U.S.C. § 7401(b)(1); and

A primary goal of this Act is to encourage or otherwise promote reasonable Federal, State, and local government actions, consistent with the provisions of this Act, for pollution prevention.

42 U.S.C. §7401(c)

The CAA provides an additional legal framework for FLMs to preserve and protect AQRVs from pollution sources emanating both within and outside National Park, Forest, and Refuge boundaries.

National Ambient Air Quality Standards (NAAQS) and State Implementation Plans (SIPs):

The CAA establishes a regulatory program with the goal of achieving and maintaining "national ambient air quality standards" (NAAQS) through state or, if necessary, federal implementation plans (SIPs or FIPs).[1]

The U.S. Environmental Protection Agency (EPA) is charged with promulgating:

- "primary" NAAQS for "criteria" pollutants "to protect the public health," allowing an adequate margin of safety;" and
- "secondary" NAAQS "to protect the public welfare from any known or anticipated adverse effects associated with the presence of such air pollutant in the ambient air."[2]

The above secondary standards may help protect public land AQRVs.[3] To date, EPA has promulgated NAAQS for six criteria pollutants: sulfur dioxide, particulate matter, nitrogen dioxide, carbon monoxide, ozone and lead. In 2006, EPA issued revised, and more stringent NAAQS for "fine particulate matter." In 2008 EPA revised the ozone standard, to address human health and welfare concerns. In 2010, EPA promulgated one-hour standards for nitrogen dioxide and sulfur dioxide. However, EPA openly acknowledged that these revised NAAQS were not fully adequate to protect the above "secondary" values, in particular those sensitive AQRVs on public lands. EPA proposed further revisions to the primary and secondary ozone standards in January 2010 and is currently developing a proposal for secondary NO_x and SO_x standards that are intended to address aquatic acidification due to acid deposition.

Prevention of Significant Deterioration (PSD):

The CAA, as amended in 1977, includes the following major purposes regarding the "prevention of significant deterioration" (PSD) provisions:

[T]o protect public health and welfare from any actual or potential adverse effect . . . from air pollution . . .

notwithstanding attainment and maintenance of all national ambient air quality standards.

42 U.S.C. § 7470(1)

[T]o preserve, protect, and enhance the air quality in national parks, national wilderness areas, national monuments, national seashores, and other areas of special national or regional natural, recreational, scenic, or historic value.

42 U.S.C. §7470(2)

The PSD section provides some protection for park and wilderness AQRVs through establishment of ceilings on additional amounts of air pollution over baseline levels in clean air areas (increments). It requires EPA or the State to provide to the FLM notice of any proposed major emitting facility[4] whose emissions may affect a Class I area (42 U.S.C. §7475(d)(2)(A), and also by charging:

[T]he Federal Land Manager[1] and the Federal official charged with direct responsibility for management of such lands with "an affirmative responsibility to protect the air quality related values (including visibility) of any such lands within a class I area and to consider, in consultation with the Administrator, whether a proposed major emitting facility will have an adverse impact on such values.

42 U.S.C. §7475(d)(2)(B).

Class I areas include national parks larger than 6,000 acres and national wilderness areas and national memorial parks which exceed 5,000 acres, in existence on August 7, 1977. The 1990 Amendments provided that subsequent additions to the boundaries of such areas are also Class I areas. Currently, 48 areas in the National Park system, 21 Refuge System units, and 88 areas under the administration of the Forest Service are designated as Class I.

Under the PSD provisions and implementing regulations (40 C.F.R. §51.166(p)), for Class I areas, once baseline concentrations come under review by submission of a PSD preconstruction permit application for a major new or modified emissions source, only the smallest increment of certain pollutants — sulfur dioxide, nitrogen oxide and particulate matter — may be added to the air by the proposed new source, and other "increment consuming" sources.

Under the PSD provisions a FLM has several tools he/she may use to protect AQRVs.

A state may not issue a PSD permit to allow construction or modification of a major emitting facility when the applicable Federal Land Manager files a notice alleging the facility may cause or contribute to a change in the Class I area's air quality and by identifying the potential adverse impact of such a change, unless:

The facility owner demonstrates that the facility's emissions of particulate matter, sulfur dioxide, and nitrogen oxides will not cause or contribute to concentrations which will exceed the maximum allowable increases for that Class I area.

42 U.S.C. §7475(d)(2)(C)(i)(paraphrased) and 42 U.S.C. §7476.

Even if no increment violation is predicted,

[T]he state may not issue a PSD permit, if the Federal Land Manager demonstrates to the satisfaction of the State that the emissions from such facility will have an adverse impact on the air quality-related values (including visibility) of Class I lands.

42 U.S.C. §7475(d)(2)(C)(ii)(paraphrased)

Neither the CAA nor the implementing regulations specify criteria for the FLM to "satisfy" state permitting agencies. Consequently, some states have taken a liberal view of their discretion to reject an FLM's adverse impact determination. However, EPA's Environmental Appeals Board (the Board) has ruled that state discretion in rejecting a FLM's finding of adverse impacts is not "unfettered" (see the Board's decisions regarding the permit appeals for the Old Dominion Electric Cooperative and Hadson Power projects in Virginia). Nevertheless, the appropriate role of the FLM in the PSD permit process was addressed in EPA's 1996 proposed New Source Review Reform regulations. The final regulations have not yet been promulgated.

Visibility Protection. Subpart II, 42 U.S.C. §7491 et seq. (1997)

The Visibility portion of the CAA:

"... [D]eclares as a national goal the prevention of any future, and the remedying of any existing, impairment of visibility in mandatory class I Federal areas which impairment results from man made air pollution."

42 U.S.C. §7491(a)(1).

To help carry out this goal, the Secretaries of the Interior and Agriculture are charged with identifying Class I areas where visibility is an important value. EPA is charged with reporting to Congress on methods to implement the national goal and with promulgating regulations to ensure reasonable progress toward meeting the goal.

In 1980, EPA issued enforceable regulations for visibility impairment "reasonably attributable" to a specific source or small group of sources. In particular, major stationary sources emitting any pollutant which may "reasonably be anticipated to cause or contribute to any impairment of visibility" is required to install best available retrofit technology (BART). In addition, in April 1999 EPA promulgated final regulations addressing regional haze.

The regional haze rule protects air quality in Class I areas by requiring States to plan to achieve "natural" visibility conditions over a 60-year time frame.

The 1990 Amendments added a new section on visibility, which authorizes EPA in conjunction with NPS and other federal agencies, to conduct visibility research and to evaluate clean air corridors and emissions sources and source regions causing visibility impairment in Class I areas. In this regard, EPA was required to establish the Grand Canyon Visibility Transport Commission (GCVTC) by 1991 and consider the recommendations GCVTC would make (42 U.S.C. §7492(f). NPS, FS, FWS, and BLM played a vital role in the work of the GCVTC and committees in an effort to improve air quality in the Grand Canyon and other parks and wilderness areas in the "Golden Circle" on the Colorado Plateau.

As part of the visibility protection process, states are required to promulgate a plan to prevent any future, and remedy any existing impairment of visibility in Class I areas... 40 C.F.R. §51.300 (1997). EPA has defined "visibility impairment" as:

[A]ny humanly perceptible change in visibility (visual range, contrast, coloration) from that which would have existed under natural conditions.

40 C.F.R. §51.301(x)(1997).7

However, EPA has promulgated its visibility regulations to allow FLMs to use their existing authorities to address "visibility impairment" (rather than "significant impairment") so that "the affected Federal Land Manager may certify to the State, at any time, that there exists impairment of visibility in any mandatory Class I Federal area." 40 C.F.R. §51.302(c).

Nonattainment Areas, 42 U.S.C. §7501 et seq.:

Areas that have failed to meet NAAQS for one or more criteria pollutants are designated as "nonattainment" areas. Under the 1990 Amendments, Congress provides for further classification of nonattainment areas based on severity of the nonattainment and availability and feasibility of appropriate pollution control measures and for a compliance schedule ranging from 1993 in marginal nonattainment areas to 2010 for Los Angeles.

The 1990 Amendments authorize EPA to issue control technique guidance documents (CTGs) covering a variety of topics, such as control of idling vehicles and voluntary removal of pre-1980 model year light duty vehicles (cash for clunker programs). (42 U.S.C. §7408.) EPA is authorized to issue CTGs, in lieu of regulations, to reduce "volatile organic compounds" (VOC) emissions from any consumer or commercial product. (42 U.S.C. §7511b.)

Proposed new or modified major stationary sources within nonattainment areas are required to meet emissions limits based on "lowest achievable emission rate" technology (LAER) and may be constructed only if their emissions are sufficiently offset by reductions in emissions from other sources. The 1990 Amendments also require analysis of alternative sites, sizes, production processes, and control techniques and a finding that the benefits of the source outweigh its environmental and social costs. (42 U.S.C. §7501-15.)

General

CAA Subchapter III 42 U.S.C. §7601 et seq. contains definitions, requirements for reports to Congress, authorizations for appropriations, and procedures for EPA rule making and judicial review. Citizen suits are authorized: 1) against EPA for failure to perform a nondiscretionary duty under the CAA, or 2) against others for alleged violations of an emission limitation, standard, or order. (42 U.S.C.§7601 et seq.)

Acid Deposition

The 1990 Amendments add Title IV, which contains requirements for electric utilities to reduce emissions associated with acid rain. To reduce the adverse effects of acid deposition, Title IV requires a reduction in annual emissions of sulfur dioxide of ten million tons from 1980 emission levels and a reduction of nitrogen oxides emissions of approximately two million tons from 1980 emission levels, in the 48 contiguous states and the District of Columbia. (42 U.S.C. §7651.) The Title creates a system of market-based emission allowances, which can be traded among sources. See (42 U.S.C. §7651a-o.)

Operating Permits

The 1990 Amendments add Subchapter V, 42 U.S.C. §7661 et seq., which establishes a nation-wide permit program for existing stationary sources. Permit requirements will include emission limitations. EPA may veto state permits, which do not comply with provisions of the CAA. (42 U.S.C. §7661a-f.)

Conformity, 42 U.S.C. §7506 (1997)

(Paraphrased) No federal agency may engage in, support in any way,... license or permit, or otherwise approve any activity which does not conform to an approved state (or federal) implementation plan. Conformity shall be an affirmative responsibility of the head of each agency. Conformity means:

- Conforming to the SIP's purpose of eliminating or reducing the number of NAAQS violations;
- That any such activities will not:
  - Cause or contribute to new violations in any area; or

- Increase the frequency or severity of any existing standard violation...

EPA, in its "criteria and procedures" for implementing "conformity" has decided that only those activities that "a federal agency can practicably control, and will maintain control over due to a continuing program responsibility" are subject to same. 40 C.F.R. §93.152.

Although required to comply with the conformity provisions (42 U.S.C. §7618(1997)), the FLM cannot use these provisions to protect AQRVs from adverse impacts from off site sources.

Impact on Federal Land Managers

The CAA reinforces the FLMs' Organic Act and Wilderness Act roles as protectors of AQRVs on public lands.

The CAA also imposes on FLMs an obligation to comply with the Act's many provisions regarding the abatement of air pollution to the same extent as any private person (42 U.S.C. §7418).

Thus, under various authorities, FLMs are responsible for protecting AQRVs within their respective unit boundaries and taking appropriate action to do so, when reviewing emission sources both within units, and in proximity to unit boundaries.

FLMs, under the CAA, have an affirmative responsibility for protecting AQRVs (including visibility) in reviewing proposed PSD permits. However, because of the uncertainty involved in "satisfying" State permitting agencies in the PSD process, and the appropriate delegated role for FLMs in non-PSD situations, the existing framework may provide an inadequate means for FLMs to protect AQRVs from adverse impacts caused by sources outside unit boundaries.

Endnotes

1) Clean Air Act, 42 U.S.C. §7401-7671q (as amended 1990).

2) *Clean Air Deskbook*, The Environmental Law Reporter, Environmental Law Institute, 1992.

3) *Managing National Park System Resources: A Handbook on Legal Duties, Opportunities, and Tools*, Chap. 4 "The Clean Air Act" by Molly Ross at pp. 51-65, The Conservation Foundation, 1990.

4) *Atmospheric Environment* Vol. 27B, No. 1, "The 20-Year History of the Evolution of Air Pollution Control Legislation in the U.S.A." by Richard H. Schulze at pp. 15-25., 1993

5) Wilderness Act of 1964, 16 U.S.C. §1131 et seq, P.L. 577, 78 stat 890 as amended.

6) *The Principal Laws Relating to Forest Service Activities*, USDA - Forest Service ISBN 0-16-041927-1, 1993

7) Organic Administration Act of 1897, 16 U.S.C. §473-475, §477-482, §551.

Appendix C: General Policy for Managing Air Quality Related Values in Class I Areas

Most Federal Land Manager (FLM) enabling legislation and regulations developed to implement Federal Laws do not directly address air quality, or air pollution effects on Parks or Wildernesses. They do, however, provide broad direction on what should be protected in Parks and Wildernesses (the earth and its community of life) and to what degree (preserve natural conditions or conserve resources unimpaired). Accordingly, FLMs have developed the following policies related to air quality and Class I areas:

1. Class I areas are not merely a commodity for human use and consumption. Park and Wilderness ecosystems have intrinsic values other than user/public concerns.
2. A principal objective of FLM management is to offer a natural user experience, rather than strictly an enjoyable one. The amount of enjoyment is purely a personal matter for the individual user to decide.
3. All Class I components are equally important; none is of lesser value than another.
4. A Class I component is important even if users of the area are unaware of its existence.
5. All life forms are equally important. For example, microorganisms are as essential as elk, wild flowers, or grizzly bears.
6. The goal of Class I management is to protect not only resources with immediate aesthetic appeal (i.e., sparkling clean streams) but also unseen ecological processes (such as natural biodiversity and gene pools).
7. The most sensitive Class I components are to be emphasized more than those of "average" or "normal" sensitivity. Sensitivity is generally determined by inertia (resistance to change), elasticity (how far the component can be stretched from its natural condition without being permanently modified), and resiliency (the number of times it can revert to its natural condition after experiencing human-caused change).
8. Each Class I component is important in itself; as well as in terms of how it interacts with other components of the ecosystem. That is, the individual parts of the Class I ecosystem are as significant as the sum of the parts.
9. The physical components of the ecosystem (for instance, lake chemistry) are as essential as its biological constituents (i.e., salamanders). That is, the earth is as essential as the community of life.
10. Class I components are to be protected from "human-caused change" rather than from "damage." Terms such as "damage" and "harm" are prejudicial, whereas "human-caused change" is value-neutral. (For example, deposits of nitrogen in a lake from nitrogen oxide, a common air pollutant, might result in more plant growth and larger fish. This would, however, be an unnatural - and therefore unacceptable - change in the aquatic ecosystem).
11. The goal of Class I management is to protect natural conditions, rather than the conditions when first monitored. That is, if initial monitoring in a Class I area identifies human-caused changes, appropriate actions should be taken to remedy them, in order to move towards a more natural condition.
12. The designation of a Park or Wilderness as Class I or II does not dictate the management goals for it; these are identified in the enabling legislation. The designation only determines which options are available to meet the goals. Class I Parks or Wildernesses, for instance, can be protected through AQRV analysis, whereas the protection of Class II Parks and Wildernesses can be achieved using BACT requirements.
13. The FLMs will do their best to manage and protect resources at every area that they administer.
14. Although monitoring is critical to many air resource management decisions, it must not interfere needlessly with Park or Wilderness. Where possible, the most intrusive monitoring and instrumentation should be conducted adjacent to the Class I area - if such areas adequately represent the area of concern.

Appendix D: Best Available Control Technology (BACT) Analysis

Given the need to minimize emissions and their resulting air quality impacts, the FLMs recommend that the applicant conduct the BACT analysis using EPA's top-down approach. In brief, a top-down process ranks all available control technologies in descending order of control effectiveness. All of the available control systems for the source, including the most stringent, must be considered. The applicant first examines the most effective, or top, alternative. That alternative is established as the BACT unless the applicant demonstrates, and the permitting authority agrees, that technical considerations, or energy, environmental, or economic impacts justify a conclusion that the most stringent technology is not achievable in that case. FLMs utilize EPA's BACT/RACT/LAER Clearinghouse, and other information, for assessing control technologies proposed by permit applicants.

If the most stringent technology is eliminated in this fashion, then the next most stringent alternative is considered, and so on. Permit applicants should refer to chapter B of the EPA Draft New Source Review Workshop Manual for a detailed discussion of the top-down policy (EPA 1990).

The FLM reviews the applicant's BACT analysis to determine if the best available pollution control technology is being proposed, thereby minimizing the proposed emission increases and their corresponding impact on the FLM area in question. The FLM does this by comparing the proposed controls to recent BACT determinations for similar facilities. If the FLM disagrees with the applicant's BACT analysis, technical comments are submitted to the permitting authority that has the ultimate responsibility to make the BACT determination and issue the permit.

The environmental impacts analysis of the BACT review is not to be confused with the air quality-related analysis. The environmental impacts analysis of the BACT review should concentrate on impacts other than ambient air quality impacts of the regulated pollutant in question, such as solid or hazardous waste generation, discharges of polluted water from a control device, or emissions of unregulated pollutants. Thus, the fact that a given control alternative would result in only a slight improvement in ambient concentrations of the pollutant in question when compared with a less stringent control alternative, should not be viewed as a basis for rejecting the more stringent control alternative.

Regarding the economic impact analysis, given the special protection Class I areas are afforded under the Clean Air Act, FLMs believe that the need to minimize potential impacts on a Class I area should be a major consideration in the BACT determination for a project proposed near such an area. Therefore, if a source proposes to locate near a Class I area, additional costs to minimize impacts on sensitive Class I resources may be warranted, even though such costs may be considered economically unjustified under other circumstances.

Appendix E. Maps of Federal Class I Areas

Figure 8. National Park Service Class I Areas
Map produced by the National Park Service Air Resources Division March 2010.

Item E 002945

Figure 9. Fish and Wildlife Service Class I Areas
Map produced by the National Park Service Air Resources Division March 2010.

Item E 002946

Figure 10. Forest Service Class I Wilderness Areas
Map produced by the National Park Service Air Resources Division March 2010.

Item E 002947

Appendix E: FLAG 2000 Participants

The individuals listed in the attached table participated in the development of the *FLAG Phase I Report* (December 2000). The contact information was not updated as part of this FLAG 2010 revision. The abbreviations for the FLAG subgroup or committee on which participants served are shown below.

LC = Leadership Committee

CC = Coordinating Committee

P = Policy Subgroup

V = Visibility Subgroup

O = Ozone Subgroup

D = Deposition Subgroup

T = Terminology (Glossary) Subgroup

FLAG 2000 Participants

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Appendix G: Bibliography (Revised)

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NPS 999/105412, October 2010

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OAR 340-226-8010
Particulate Matter Emissions Standards for Process Equipment

Process lbs/hr	Emissions lbs/hr	Process lbs/hr	Emissions lbs/hr	Process lbs/hr	Emissions lbs/hr
50	0.24	2300	4.44	7500	8.39
100	0.46	2400	4.55	8000	8.71
150	0.66	2500	4.64	8500	9.03
200	0.85	2600	4.74	9000	9.36
250	1.03	2700	4.84	9500	9.67
300	1.20	2800	4.92	10000	10.00
350	1.35	2900	5.02	11000	10.63
400	1.50	3000	5.10	12000	11.28
450	1.63	3100	5.18	13000	11.89
500	1.77	3200	5.27	14000	12.50
550	1.89	3300	5.36	15000	13.13
600	2.01	3400	5.44	16000	13.74
650	2.12	3500	5.52	17000	14.36
700	2.24	3600	5.61	18000	14.97
750	2.34	3700	5.69	19000	15.58
800	2.43	3800	5.77	20000	16.19
850	2.53	3900	5.85	30000	22.22
900	2.62	4000	5.93	40000	28.30
950	2.72	4100	6.01	50000	34.30
1000	2.80	4200	6.08	60000	40.00
1100	2.97	4300	6.15	70000	41.30
1200	3.12	4400	6.22	80000	42.50
1300	3.26	4500	6.30	90000	43.60
1400	3.40	4600	6.37	100000	44.60
1500	3.54	4700	6.45	120000	46.30
1600	3.66	4800	6.52	140000	47.80
1700	3.79	4900	6.60	160000	49.00
1800	3.91	5000	6.67	200000	51.20

OAR 340-226-8010
Particulate Matter Emissions Standards for Process Equipment

Process lbs/hr	Emissions lbs/hr	Process lbs/hr	Emissions lbs/hr	Process lbs/hr	Emissions lbs/hr
1900	4.03	5500	7.03	1000000	69.00
2000	4.14	6000	7.37	2000000	77.60
2100	4.24	6500	7.71	6000000	92.70
2200	4.34	7000	8.05		

Interpolation and extrapolation of the data for process unit weight rates in excess of 6,000,000 pounds/hour shall be accomplished by using the equation:

$$E = 55.0P^{0.11} - 40$$

Where: E = rate of process unit emission in pounds/hour, and

P = process weight in tons/hour

State of Oregon Department of Environmental Quality

OAR 340-228-0639 Tables

OAR 340-228-0639 Table 4 Fuel Analysis Requirements	
The owner or operator must:	**Using:**
1. Collect fuel samples	Procedures in OAR 340-228-0639(3) or ASTM D2234-00 or equivalent.
2. Composite fuel samples	Procedures in OAR 340-228-0639(4) or equivalent
3. Prepare composited fuel samples	ASTM D2013-01 or equivalent
4. Determine heat content of the fuel	ASTM D5865-03a or equivalent
5. Determine moisture content of the fuel type	ASTM D3173-02 or ASTM E871 (1998) or equivalent
6. Measure mercury concentration in fuel sample	ASTM D3684-01
7. Convert concentrations into units of pounds of pollutant per MMBtu of heat content	

State of Oregon Department of Environmental Quality

OAR 340-230-0120
Formula for Design and Operation

(6) Combustion efficiency. Except during periods of startup and shutdown, all waste incinerators shall achieve a combustion efficiency of 99.9 percent based on a running eight-hour average, computed as follows:

$CE = (CO_2 / (CO_2 + CO)) X 100$

State of Oregon Department of Environmental Quality

OAR 340-230-0200
EPA Method 9

APPENDIX A–4 TO PART 60—TEST METHODS 6 THROUGH 10B

Method 6—Determination of sulfur dioxide emissions from stationary sources
Method 6A—Determination of sulfur dioxide, moisture, and carbon dioxide emissions from fossil fuel combustion sources
Method 6B—Determination of sulfur dioxide and carbon dioxide daily average emissions from fossil fuel combustion sources
Method 6C—Determination of Sulfur Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure)
Method 7—Determination of nitrogen oxide emissions from stationary sources
Method 7A—Determination of nitrogen oxide emissions from stationary sources—Ion chromatographic method
Method 7B—Determination of nitrogen oxide emissions from stationary sources (Ultraviolet spectrophotometry)
Method 7C—Determination of nitrogen oxide emissions from stationary sources—Alkaline-permanganate/colorimetric method
Method 7D—Determination of nitrogen oxide emissions from stationary sources—Alkaline-permanganate/ion chromatographic method
Method 7E—Determination of Nitrogen Oxides Emissions From Stationary Sources (Instrumental Analyzer Procedure)
Method 8—Determination of sulfuric acid mist and sulfur dioxide emissions from stationary sources
Method 9—Visual determination of the opacity of emissions from stationary sources
Alternate method 1—Determination of the opacity of emissions from stationary sources remotely by lidar
Method 10—Determination of carbon monoxide emissions from stationary sources
Method 10A—Determination of carbon monoxide emissions in certifying continuous emission monitoring systems at petroleum refineries
Method 10B—Determination of carbon monoxide emissions from stationary sources

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that

the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

METHOD 6—DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, and Method 8.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
SO_2	7449–09–5	3.4 mg SO_2/m^3 $(2.12 \times 10)_{-7}$ lb/ft^3

1.2 Applicability. This method applies to the measurement of sulfur dioxide (SO_2) emissions from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the sampling point in the stack. The SO_2 and the sulfur trioxide, including those fractions in any sulfur acid mist, are separated. The SO_2 fraction is measured by the barium-thorin titration method.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Free Ammonia. Free ammonia interferes with this method by reacting with SO_2 to form particulate sulfite and by reacting with the indicator. If free ammonia is present (this can be determined by knowledge of the process and/or noticing white particulate matter in the probe and isopropanol bubbler), alternative methods, subject to the approval of the Administrator are required. One approved alternative is listed in Reference 13 of section 17.0.

4.2 Water-Soluble Cations and Fluorides. The cations and fluorides are removed by a glass wool filter and an isopropanol bubbler; therefore, they do not affect the SO_2 analysis. When samples are collected from a gas stream with high concentrations of metallic fumes (*i.e.*, very fine cation aerosols) a high-efficiency glass fiber filter must be used in place of the glass wool plug (*i.e.*, the one in the probe) to remove the cation interferent.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations before performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs. 30% H_2O_2 is a strong oxidizing agent. Avoid contact with skin, eyes, and combustible material. Wear gloves when handling.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

6.1 Sample Collection. The following items are required for sample collection:

6.1.1 Sampling Train. A schematic of the sampling train is shown in Figure 6–1. The sampling equipment described in Method 8 may be substituted in place of the midget impinger equipment of Method 6. However, the Method 8 train must be modified to include a heated filter between the probe and isopropanol impinger, and the operation of the sampling train and sample analysis must be at the flow rates and solution volumes defined in Method 8. Alternatively, SO_2 may be determined simultaneously with particulate

matter and moisture determinations by either (1) replacing the water in a Method 5 impinger system with a 3 percent H_2O_2 solution, or (2) replacing the Method 5 water impinger system with a Method 8 isopropanol-filter-H_2O_2 system. The analysis for SO_2 must be consistent with the procedure of Method 8. The Method 6 sampling train consists of the following components:

6.1.1.1 Probe. Borosilicate glass or stainless steel (other materials of construction may be used, subject to the approval of the Administrator), approximately 6 mm (0.25 in.) inside diameter, with a heating system to prevent water condensation and a filter (either in-stack or heated out-of-stack) to remove particulate matter, including sulfuric acid mist. A plug of glass wool is a satisfactory filter.

6.1.1.2 Bubbler and Impingers. One midget bubbler with medium-coarse glass frit and borosilicate or quartz glass wool packed in top (see Figure 6–1) to prevent sulfuric acid mist carryover, and three 30-ml midget impingers. The midget bubbler and midget impingers must be connected in series with leak-free glass connectors. Silicone grease may be used, if necessary, to prevent leakage. A midget impinger may be used in place of the midget bubbler.

NOTE: Other collection absorbers and flow rates may be used, subject to the approval of the Administrator, but the collection efficiency must be shown to be at least 99 percent for each test run and must be documented in the report. If the efficiency is found to be acceptable after a series of three tests, further documentation is not required. To conduct the efficiency test, an extra absorber must be added and analyzed separately. This extra absorber must not contain more than 1 percent of the total SO_2.

6.1.1.3 Glass Wool. Borosilicate or quartz.

6.1.1.4 Stopcock Grease. Acetone-insoluble, heat-stable silicone grease may be used, if necessary.

6.1.1.5 Temperature Sensor. Dial thermometer, or equivalent, to measure temperature of gas leaving impinger train to within 1 °C (2 °F).

6.1.1.6 Drying Tube. Tube packed with 6- to 16- mesh indicating-type silica gel, or equivalent, to dry the gas sample and to protect the meter and pump. If silica gel is previously used, dry at 177 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

6.1.1.7 Valve. Needle valve, to regulate sample gas flow rate.

6.1.1.8 Pump. Leak-free diaphragm pump, or equivalent, to pull gas through the train. Install a small surge tank between the pump and rate meter to negate the pulsation effect of the diaphragm pump on the rate meter.

6.1.1.9 Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of the selected flow rate of about 1 liter/min (0.035 cfm).

6.1.1.10 Volume Meter. Dry gas meter (DGM), sufficiently accurate to measure the sample volume to within 2 percent, calibrated at the selected flow rate and conditions actually encountered during sampling, and equipped with a temperature sensor (dial thermometer, or equivalent) capable of measuring temperature accurately to within 3 °C (5.4 °F). A critical orifice may be used in place of the DGM specified in this section provided that it is selected, calibrated, and used as specified in section 16.0.

6.1.2 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). See the note in Method 5, section 6.1.2.

6.1.3 Vacuum Gauge and Rotameter. At least 760-mm Hg (30-in. Hg) gauge and 0- to 40-ml/min rotameter, to be used for leak-check of the sampling train.

6.2 Sample Recovery. The following items are needed for sample recovery:

6.2.1 Wash Bottles. Two polyethylene or glass bottles, 500-ml.

6.2.2 Storage Bottles. Polyethylene bottles, 100-ml, to store impinger samples (one per sample).

6.3 Sample Analysis. The following equipment is needed for sample analysis:

6.3.1 Pipettes. Volumetric type, 5-ml, 20-ml (one needed per sample), and 25-ml sizes.

6.3.2 Volumetric Flasks. 100-ml size (one per sample) and 1000-ml size.

6.3.3 Burettes. 5- and 50-ml sizes.

6.3.4 Erlenmeyer Flasks. 250-ml size (one for each sample, blank, and standard).

6.3.5 Dropping Bottle. 125-ml size, to add indicator.

6.3.6 Graduated Cylinder. 100-ml size.

6.3.7 Spectrophotometer. To measure absorbance at 352 nm.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Water. Deionized distilled to conform to ASTM Specification D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17). The $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.1.2 Isopropanol, 80 Percent by Volume. Mix 80 ml of isopropanol with 20 ml of water.

7.1.2.1 Check each lot of isopropanol for peroxide impurities as follows: Shake 10 ml of isopropanol with 10 ml of freshly prepared 10 percent potassium iodide solution. Prepare a blank by similarly treating 10 ml of water. After 1 minute, read the absorbance at 352 nm on a spectrophotometer using a 1-cm path length. If absorbance exceeds 0.1, reject alcohol for use.

7.1.2.2 Peroxides may be removed from isopropanol by redistilling or by passage through a column of activated alumina; however, reagent grade isopropanol with suitably low peroxide levels may be obtained from commercial sources. Rejection of contaminated lots may, therefore, be a more efficient procedure.

7.1.3 Hydrogen Peroxide (H_2O_2), 3 Percent by Volume. Add 10 ml of 30 percent H_2O_2 to 90 ml of water. Prepare fresh daily.

7.1.4 Potassium Iodide Solution, 10 Percent Weight by Volume (w/v). Dissolve 10.0 g of KI in water, and dilute to 100 ml. Prepare when needed.

7.2 Sample Recovery. The following reagents are required for sample recovery:

7.2.1 Water. Same as in section 7.1.1.

7.2.2 Isopropanol, 80 Percent by Volume. Same as in section 7.1.2.

7.3 Sample Analysis. The following reagents and standards are required for sample analysis:

7.3.1 Water. Same as in section 7.1.1.

7.3.2 Isopropanol, 100 Percent.

7.3.3 Thorin Indicator. 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, disodium salt, or equivalent. Dissolve 0.20 g in 100 ml of water.

7.3.4 Barium Standard Solution, 0.0100 N. Dissolve 1.95 g of barium perchlorate trihydrate [$Ba(ClO_4)_2$ $3H_2O$] in 200 ml water, and dilute to 1 liter with isopropanol. Alternatively, 1.22 g of barium chloride dihydrate [$BaCl_2$ $2H_2O$] may be used instead of the barium perchlorate trihydrate. Standardize as in section 10.5.

7.3.5 Sulfuric Acid Standard, 0.0100 N. Purchase or standardize to ±0.0002 N against 0.0100 N NaOH which has previously been standardized against potassium acid phthalate (primary standard grade).

8.0 Sample Collection, Preservation, Storage and Transport

8.1 Preparation of Sampling Train. Measure 15 ml of 80 percent isopropanol into the midget bubbler and 15 ml of 3 percent H_2O_2 into each of the first two midget impingers. Leave the final midget impinger dry. Assemble the train as shown in Figure 6–1. Adjust the probe heater to a temperature sufficient to prevent water condensation. Place crushed ice and water around the impingers.

8.2 Sampling Train Leak-Check Procedure. A leak-check prior to the sampling run is recommended, but not required. A leak-check after the sampling run is mandatory. The leak-check procedure is as follows:

8.2.1 Temporarily attach a suitable (*e.g.*, 0- to 40- ml/min) rotameter to the outlet of the DGM, and place a vacuum gauge at or near the probe inlet. Plug the probe inlet, pull a vacuum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter. A leakage rate in excess of 2 percent of the average sampling rate is not acceptable.

NOTE: Carefully (*i.e.*, slowly) release the probe inlet plug before turning off the pump.

8.2.2 It is suggested (not mandatory) that the pump be leak-checked separately, either prior to or after the sampling run. To leak-check the pump, proceed as follows: Disconnect the drying tube from the probe-impinger assembly. Place a vacuum gauge at the inlet to either the drying tube or the pump, pull a vacuum of 250 mm Hg (10 in. Hg), plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum should remain stable for at least 30 seconds.

If performed prior to the sampling run, the pump leak-check shall precede the leak-check of the sampling train described immediately above; if performed after the sampling run, the pump leak-check shall follow the sampling train leak-check.

8.2.3 Other leak-check procedures may be used, subject to the approval of the Administrator.

8.3 Sample Collection.

8.3.1 Record the initial DGM reading and barometric pressure. To begin sampling, position the tip of the probe at the sampling point, connect the probe to the bubbler, and start the pump. Adjust the sample flow to a constant rate of approximately 1.0 liter/min as indicated by the rate meter. Maintain this constant rate (±10 percent) during the entire sampling run.

8.3.2 Take readings (DGM volume, temperatures at DGM and at impinger outlet, and rate meter flow rate) at least every 5 minutes. Add more ice during the run to keep the temperature of the gases leaving the last impinger at 20 °C (68 °F) or less.

8.3.3 At the conclusion of each run, turn off the pump, remove the probe from the stack, and record the final readings. Conduct a leak-check as described in section 8.2. (This leak-check is mandatory.) If a leak is detected, void the test run or use procedures acceptable to the Administrator to adjust the sample volume for the leakage.

8.3.4 Drain the ice bath, and purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at the sampling rate. Clean ambient air can be provided by passing air through a charcoal filter or through an extra midget impinger containing 15 ml of 3 percent H_2O_2. Alternatively, ambient air without purification may be used.

8.4 Sample Recovery. Disconnect the impingers after purging. Discard the contents of the midget bubbler. Pour the contents of the midget impingers into a leak-free polyethylene bottle for shipment. Rinse the three midget impingers and the connecting tubes with water, and add the rinse to the same storage container. Mark the fluid level. Seal and identify the sample container.

9.0 Quality Control

Section	Quality control measure	Effect
7.1.2	Isopropanol check	Ensure acceptable level of peroxide impurities in isopropanol.
8.2, 10.1–10.4	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.
10.5	Barium standard solution standardization	Ensure precision of normality determination
11.2.3	Replicate titrations	Ensure precision of titration determinations.

10.0 Calibration and Standardization

10.1 Volume Metering System.

10.1.1 Initial Calibration.

10.1.1.1 Before its initial use in the field, leak-check the metering system (drying tube, needle valve, pump, rate meter, and DGM) as follows: Place a vacuum gauge at the inlet to the drying tube and pull a vacuum of 250 mm Hg (10 in. Hg). Plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum must remain stable for at least 30 seconds. Carefully release the vacuum gauge before releasing the flow meter end.

10.1.1.2 Remove the drying tube, and calibrate the metering system (at the sampling flow rate specified by the method) as follows: Connect an appropriately sized wet-test meter (*e.g.*, 1 liter per revolution) to the inlet of the needle valve. Make three independent calibration runs, using at least five revolutions of the DGM per run. Calculate the calibration factor Y (wet-test meter calibration volume divided by the DGM volume, both volumes adjusted to the same reference temperature and pressure) for each run, and average the results (Y_i). If any Y-value deviates by more than 2 percent from (Y_i), the metering system is unacceptable for use. If the metering system is acceptable, use (Y_i) as the calibration factor for subsequent test runs.

10.1.2 Post-Test Calibration Check. After each field test series, conduct a calibration check using the procedures outlined in section 10.1.1.2, except that three or more revolutions of the DGM may be used, and only two independent runs need be made. If the average of the two post-test calibration factors does not deviate by more than 5 percent from Y_i, then Y_i is accepted as the DGM calibration factor (Y), which is used in Equation 6–1 to calculate collected sample volume (see section 12.2). If the deviation is more than 5 percent, recalibrate the metering system as in section 10.1.1, and determine a post-test calibration factor (Y_f). Compare Y_i and Y_f; the smaller of the two factors is accepted as the DGM calibration factor. If recalibration indicates that the metering system is unacceptable for use, either void the test run or use methods, subject to the approval of the Administrator, to determine an acceptable value for the collected sample volume.

10.1.3 DGM as a Calibration Standard. A DGM may be used as a calibration standard for volume measurements in place of the wet-test meter specified in section 10.1.1.2, provided that it is calibrated initially and recalibrated periodically according to the same procedures outlined in Method 5, section 10.3 with the following exceptions: (a) the DGM is calibrated against a wet-test meter having a capacity of 1 liter/rev (0.035 ft^3/rev) or 3 liters/rev (0.1 ft^3/rev) and having the capability of measuring volume to within 1 percent; (b) the DGM is calibrated at 1 liter/min (0.035 cfm); and (c) the meter box of the Method 6 sampling train is calibrated at the same flow rate.

10.2 Temperature Sensors. Calibrate against mercury-in-glass thermometers. An alternative mercury-free thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

10.3 Rate Meter. The rate meter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instructions.

10.4 Barometer. Calibrate against a mercury barometer or NIST-traceable barometer prior to the field test.

10.5 Barium Standard Solution. Standardize the barium perchlorate or chloride solution against 25 ml of standard sulfuric acid to which 100 ml of 100 percent isopropanol has been added. Run duplicate analyses. Calculate the normality using the average of duplicate analyses where the titrations agree within 1 percent or 0.2 ml, whichever is larger.

11.0 Analytical Procedure

11.1 Sample Loss Check. Note level of liquid in container and confirm whether any sample was lost during shipment; note this

finding on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Analysis.

11.2.1 Transfer the contents of the storage container to a 100-ml volumetric flask, dilute to exactly 100 ml with water, and mix the diluted sample.

11.2.2 Pipette a 20-ml aliquot of the diluted sample into a 250-ml Erlenmeyer flask and add 80 ml of 100 percent isopropanol plus two to four drops of thorin indicator. While stirring the solution, titrate to a pink endpoint using 0.0100 N barium standard solution.

11.2.3 Repeat the procedures in section 11.2.2, and average the titration volumes. Run a blank with each series of samples. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is larger.

NOTE: Protect the 0.0100 N barium standard solution from evaporation at all times.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 NOMENCLATURE

C_{SO2} = Concentration of SO_2, dry basis, corrected to standard conditions, mg/dscm (lb/dscf).

N = Normality of barium standard titrant, meq/ml.

P_{bar} = Barometric pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

T_m = Average DGM absolute temperature, °K (°R).

T_{std} = Standard absolute temperature, 293 °K (528 °R).

V_a = Volume of sample aliquot titrated, ml.

V_m = Dry gas volume as measured by the DGM, dcm (dcf).

$V_{m(std)}$ = Dry gas volume measured by the DGM, corrected to standard conditions, dscm (dscf).

V_{soln} = Total volume of solution in which the SO_2 sample is contained, 100 ml.

V_t = Volume of barium standard titrant used for the sample (average of replicate titration), ml.

V_{tb} = Volume of barium standard titrant used for the blank, ml.

Y = DGM calibration factor.

12.2 Dry Sample Gas Volume, Corrected to Standard Conditions.

$$V_{m(std)} = \frac{\left(V_m Y T_{std} P_{bar}\right)}{\left(T_m P_{std}\right)} = \frac{K_1 Y V_m P_{bar}}{T_m} \quad \text{Eq. 6-1}$$

Where:

K_1 = 0.3855 °K/mm Hg for metric units,

K_1 = 17.65 °R/in. Hg for English units.

12.3 SO_2 Concentration.

$$C_{so_2} = \frac{K_2 N \left(V_t - V_{tb}\right)\left(V_{soln}/V_a\right)}{V_{m(std)}} \quad \text{Eq. 6-2}$$

Where:

K_2 = 32.03 mg SO_2/meq for metric units,

$K_2 = 7.061 \times 10^{-5}$ lb SO_2/meq for English units.

13.0 Method Performance

13.1 Range. The minimum detectable limit of the method has been determined to be 3.4 mg SO_2/m^3 (2.12×10^{-7} lb/ft³). Although no upper limit has been established, tests have shown that concentrations as high as 80,000 mg/m³ (0.005 lb/ft³) of SO_2 can be collected efficiently at a rate of 1.0 liter/min (0.035 cfm) for 20 minutes in two midget impingers, each containing 15 ml of 3 percent H_2O_2. Based on theoretical calculations, the upper concentration limit in a 20 liter (0.7 ft³) sample is about 93,300 mg/m³ (0.00583 lb/ft³).

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Nomenclature. Same as section 12.1, with the following additions:

B_{wa} = Water vapor in ambient air, proportion by volume.

M_a = Molecular weight of the ambient air saturated at impinger temperature, g/g-mole (lb/lb-mole).

M_s = Molecular weight of the sample gas saturated at impinger temperature, g/g-mole (lb/lb-mole).

P_c = Inlet vacuum reading obtained during the calibration run, mm Hg (in. Hg).

P_{sr} = Inlet vacuum reading obtained during the sampling run, mm Hg (in. Hg).

$\bar{Q}_{std}$ = Volumetric flow rate through critical orifice, scm/min (scf/min).
Q_{std} = Average flow rate of pre-test and post-test calibration runs, scm/min (scf/min).
T_{amb} = Ambient absolute temperature of air, °K (°R).
V_{sb} = Volume of gas as measured by the soap bubble meter, m^3 (ft^3).
$V_{sb(std)}$ = Volume of gas as measured by the soap bubble meter, corrected to standard conditions, scm (scf).
θ = Soap bubble travel time, min.
θ_s = Time, min.

16.2 Critical Orifices for Volume and Rate Measurements. A critical orifice may be used in place of the DGM specified in section 6.1.1.10, provided that it is selected, calibrated, and used as follows:

16.2.1 Preparation of Sampling Train. Assemble the sampling train as shown in Figure 6–2. The rate meter and surge tank are optional but are recommended in order to detect changes in the flow rate.

NOTE: The critical orifices can be adapted to a Method 6 type sampling train as follows: Insert sleeve type, serum bottle stoppers into two reducing unions. Insert the needle into the stoppers as shown in Figure 6–3.

16.2.2 Selection of Critical Orifices.

16.2.2.1 The procedure that follows describes the use of hypodermic needles and stainless steel needle tubings, which have been found suitable for use as critical orifices. Other materials and critical orifice designs may be used provided the orifices act as true critical orifices, (*i.e.*, a critical vacuum can be obtained) as described in this section. Select a critical orifice that is sized to operate at the desired flow rate. The needle sizes and tubing lengths shown in Table 6–1 give the following approximate flow rates.

16.2.2.2 Determine the suitability and the appropriate operating vacuum of the critical orifice as follows: If applicable, temporarily attach a rate meter and surge tank to the outlet of the sampling train, if said equipment is not present (see section 16.2.1). Turn on the pump and adjust the valve to give an outlet vacuum reading corresponding to about half of the atmospheric pressure. Observe the rate meter reading. Slowly increase the vacuum until a stable reading is obtained on the rate meter. Record the critical vacuum, which is the outlet vacuum when the rate meter first reaches a stable value. Orifices that do not reach a critical value must not be used.

16.2.3 Field Procedures.

16.2.3.1 Leak-Check Procedure. A leak-check before the sampling run is recommended, but not required. The leak-check procedure is as follows: Temporarily attach a suitable (*e.g.*, 0–40 ml/min) rotameter and surge tank, or a soap bubble meter and surge tank to the outlet of the pump. Plug the probe inlet, pull an outlet vacuum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter or bubble meter. A leakage rate in excess of 2 percent of the average sampling rate ($\bar{Q}_{std}$) is not acceptable. Carefully release the probe inlet plug before turning off the pump.

16.2.3.2 Moisture Determination. At the sampling location, prior to testing, determine the percent moisture of the ambient air using the wet and dry bulb temperatures or, if appropriate, a relative humidity meter.

16.2.3.3 Critical Orifice Calibration. At the sampling location, prior to testing, calibrate the entire sampling train (*i.e.*, determine the flow rate of the sampling train when operated at critical conditions). Attach a 500-ml soap bubble meter to the inlet of the probe, and operate the sampling train at an outlet vacuum of 25 to 50 mm Hg (1 to 2 in. Hg) above the critical vacuum. Record the information listed in Figure 6–4. Calculate the standard volume of air measured by the soap bubble meter and the volumetric flow rate using the equations below:

$$V_{sb(std)} = V_{sb}\left(T_{std}/T_{amb}\right)\left(P_{bar}/P_{std}\right) \qquad \text{Eq. 6-4}$$

$$Q_{std} = \frac{V_{sb(std)}}{\theta} \qquad \text{Eq. 6-5}$$

16.2.3.4 Sampling.

16.2.3.4.1 Operate the sampling train for sample collection at the same vacuum used during the calibration run. Start the watch and pump simultaneously. Take readings (temperature, rate meter, inlet vacuum, and outlet vacuum) at least every 5 minutes. At the end of the sampling run, stop the watch and pump simultaneously.

16.2.3.4.2 Conduct a post-test calibration run using the calibration procedure outlined in section 16.2.3.3. If the Q_{std} obtained before and after the test differ by more than 5 percent, void the test run; if not, calculate the volume of the gas measured with the critical orifice using Equation 6–6 as follows:

$$V_{m(std)} = \frac{\overline{Q}_{std}\ \theta_s\ (1-B_{wa})(P_{bar}+P_{sr})}{(P_{bar}+P_c)} \quad \text{Eq. 6-6}$$

16.2.3.4.3 If the percent difference between the molecular weight of the ambient air at saturated conditions and the sample gas is more that ±3 percent, then the molecular weight of the gas sample must be considered in the calculations using the following equation:

$$_{(std)} = \frac{\overline{Q}_{std}\ \theta_s\ (1-B_{wa})(P_{bar}+P_{sr})(M_a/M_s)^1}{(P_{bar}+P_c)} \quad \text{Eq. 6-7}$$

NOTE: A post-test leak-check is not necessary because the post-test calibration run results will indicate whether there is any leakage.

16.2.3.4.4 Drain the ice bath, and purge the sampling train using the procedure described in section 8.3.4.

16.3 Elimination of Ammonia Interference. The following alternative procedures must be used in addition to those specified in the method when sampling at sources having ammonia emissions.

16.3.1 Sampling. The probe shall be maintained at 275 °C (527 °F) and equipped with a high-efficiency in-stack filter (glass fiber) to remove particulate matter. The filter material shall be unreactive to SO_2. Whatman 934AH (formerly Reeve Angel 934AH) filters treated as described in Reference 10 in section 17.0 of Method 5 is an example of a filter that has been shown to work. Where alkaline particulate matter and condensed moisture are present in the gas stream, the filter shall be heated above the moisture dew point but below 225 °C (437 °F).

16.3.2 Sample Recovery. Recover the sample according to section 8.4 except for discarding the contents of the midget bubbler. Add the bubbler contents, including the rinsings of the bubbler with water, to a separate polyethylene bottle from the rest of the sample. Under normal testing conditions where sulfur trioxide will not be present significantly, the tester may opt to delete the midget bubbler from the sampling train. If an approximation of the sulfur trioxide concentration is desired, transfer the contents of the midget bubbler to a separate polyethylene bottle.

16.3.3 Sample Analysis. Follow the procedures in sections 11.1 and 11.2, except add 0.5 ml of 0.1 N HCl to the Erlenmeyer flask and mix before adding the indicator. The following analysis procedure may be used for an approximation of the sulfur trioxide concentration. The accuracy of the calculated concentration will depend upon the ammonia to SO_2 ratio and the level of oxygen present in the gas stream. A fraction of the SO_2 will be counted as sulfur trioxide as the ammonia to SO_2 ratio and the sample oxygen content increases. Generally, when this ratio is 1 or less and the oxygen content is in the range of 5 percent, less than 10 percent of the SO_2 will be counted as sulfur trioxide. Analyze the peroxide and isopropanol sample portions separately. Analyze the peroxide portion as described above. Sulfur trioxide is determined by difference using sequential titration of the isopropanol portion of the sample. Transfer the contents of the isopropanol storage container to a 100-ml volumetric flask, and dilute to exactly 100 ml with water. Pipette a 20-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 0.5 ml of 0.1 N HCl, 80 ml of 100 percent isopropanol, and two to four drops of thorin indicator. Titrate to a pink endpoint using 0.0100 N barium perchlorate. Repeat and average the titration volumes that agree within 1 percent or 0.2 ml, whichever is larger. Use this volume in Equation 6–2 to determine the sulfur trioxide concentration. From the flask containing the remainder of the isopropanol sample, determine the fraction of SO_2 collected in the bubbler by pipetting 20-ml aliquots into 250-ml Erlenmeyer flasks. Add 5 ml of 3 percent H_2O_2, 100 ml of 100 percent isopropanol, and two to four drips of thorin indicator, and titrate as before. From this titration volume, subtract the titrant volume determined for sulfur trioxide, and add the titrant volume determined for the peroxide portion. This final volume constitutes V_t, the volume of barium perchlorate used for the SO_2 sample.

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18.0 Tables, Diagrams, Flowcharts and Validation Data

TABLE 6–1—APPROXIMATE FLOW RATES FOR VARIOUS NEEDLE SIZES

Needle size (gauge)	Needle length (cm)	Flow rate (ml/min)
21	7.6	1,100
22	2.9	1,000
22	3.8	900
23	3.8	500
23	5.1	450
24	3.2	400

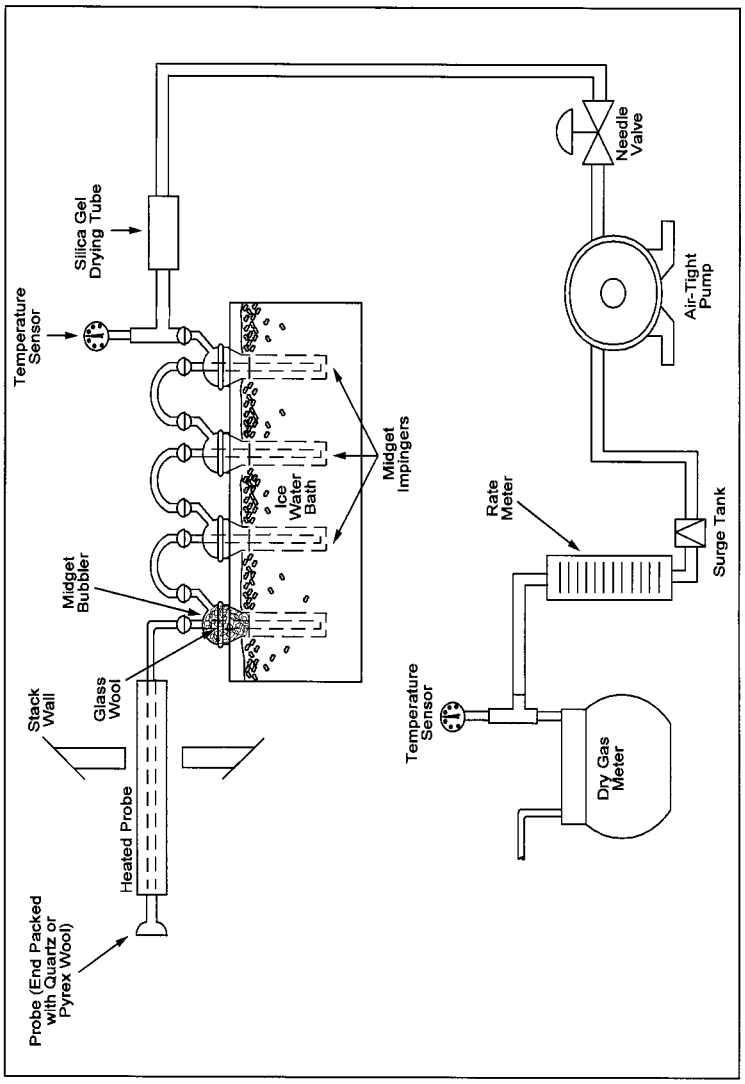

Figure 6-1. Sulfur Dioxide Sampling Train.

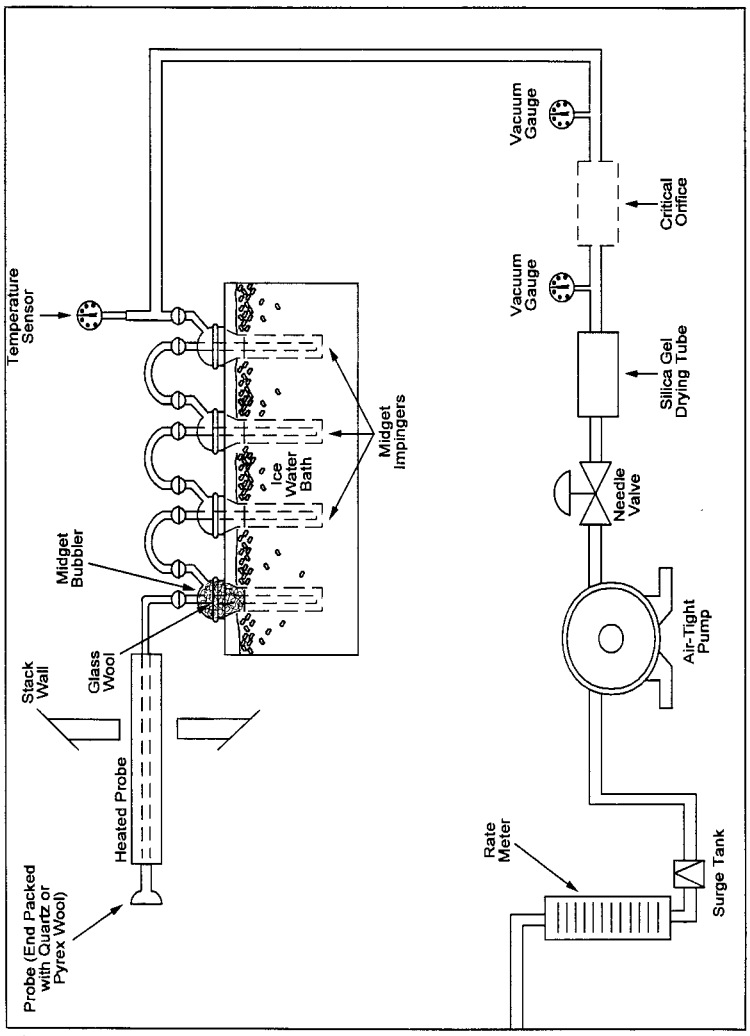

Figure 6-2. Sulfur Dioxide Sampling Train Using a Critical Orifice.

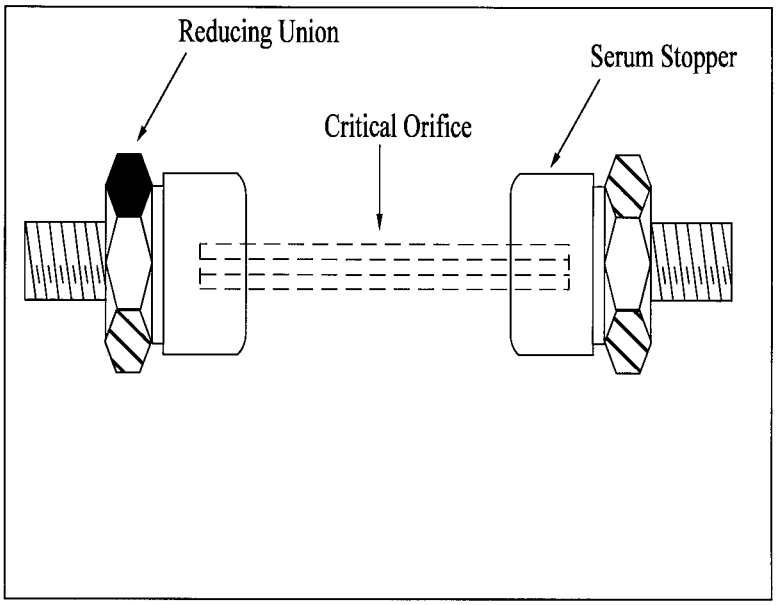

Figure 6-3. Critical Orifice Adaptation for the Method 6 Sampling Train.

Date _____ Train ID _____

Critical orifice size _____ Critical vacuum _____

		Pretest	Post-test
Soap bubble meter volume, V_{sb}	cc		
	m^3 (ft^3)		
Time, θ	sec		
	min		
Barometric pressure, P_{bar}	mm Hg (in. Hg)		
Ambient temperature, t_{amb}	°C (°F)		
Inlet vacuum, P_c	mm Hg (in. Hg)		
Outlet vacuum	mm Hg (in. Hg)		
$V_{sb(std)}$	m^3 (ft^3)		
Flow rate, Q_{std}	$\frac{m^3}{min}\left(\frac{ft^3}{min}\right)$		

Figure 6-4. Critical Orifice Calibration Data Sheet.

METHOD 6A—DETERMINATION OF SULFUR DIOXIDE, MOISTURE, AND CARBON DIOXIDE FROM FOSSIL FUEL COMBUSTION SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, Method 6, and Method 19.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
SO_2	7449–09–05	3.4 mg SO_2/m^3 (2.12×10^{-7} lb/ft^3)
CO_2	124–38–9	N/A
H_2O	7732–18–5	N/A

1.2 Applicability. This method is applicable for the determination of sulfur dioxide (SO_2) emissions from fossil fuel combustion sources in terms of concentration (mg/dscm or lb/dscf) and in terms of emission rate (ng/J or lb/10^6 Btu) and for the determination of carbon dioxide (CO_2) concentration (percent). Moisture content (percent), if desired, may also be determined by this method.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from a sampling point in the stack. The SO_2 and the sulfur trioxide, including those fractions in any sulfur acid mist, are separated. The SO_2 fraction is measured by the barium-thorin titration method. Moisture and CO_2 fractions are collected in the same sampling train, and are determined gravimetrically.

3.0 Definitions [Reserved]

4.0 Interferences

Same as Method 6, section 4.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. Same as Method 6, section 5.2.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 6, section 6.1, with the exception of the following:

6.1.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 6A–1.

6.1.1.1 Impingers and Bubblers. Two 30 = ml midget impingers with a 1 = mm restricted tip and two 30 = ml midget bubblers with unrestricted tips. Other types of impingers and bubblers (*e.g.*, Mae West for SO_2 collection and rigid cylinders containing Drierite for moisture absorbers), may be used with proper attention to reagent volumes and levels, subject to the approval of the Administrator.

6.1.1.2 CO_2 Absorber. A sealable rigid cylinder or bottle with an inside diameter between 30 and 90 mm , a length between 125 and 250 mm, and appropriate connections at both ends. The filter may be a separate heated unit or may be within the heated portion of the probe. If the filter is within the sampling probe, the filter should not be within 15 cm of the probe inlet or any unheated section of the probe, such as the connection to the first bubbler. The probe and filter should be heated to at least 20 °C (68 °F) above the source temperature, but not greater than 120 °C (248 °F). The filter temperature (*i.e.*, the sample gas temperature) should be monitored to assure the desired temperature is maintained. A heated Teflon connector may be used to connect the filter holder or probe to the first impinger.

NOTE: For applications downstream of wet scrubbers, a heated out-of-stack filter (either borosilicate glass wool or glass fiber mat) is necessary.

6.2 Sample Recovery. Same as Method 6, section 6.2.

6.3 Sample Analysis. Same as Method 6, section 6.3, with the addition of a balance to measure within 0.05 g.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

7.1 Sample Collection. Same as Method 6, section 7.1, with the addition of the following:

7.1.1 Drierite. Anhydrous calcium sulfate ($CaSO_4$) desiccant, 8 mesh, indicating type is recommended.

NOTE: Do not use silica gel or similar desiccant in this application.

7.1.2 CO_2 Absorbing Material. Ascarite II. Sodium hydroxide-coated silica, 8- to 20-mesh.

7.2 Sample Recovery and Analysis. Same as Method 6, sections 7.2 and 7.3, respectively.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Preparation of Sampling Train.

8.1.1 Measure 15 ml of 80 percent isopropanol into the first midget bubbler and 15 ml of 3 percent hydrogen peroxide into each of the two midget impingers (the second

and third vessels in the train) as described in Method 6, section 8.1. Insert the glass wool into the top of the isopropanol bubbler as shown in Figure 6A–1. Place about 25 g of Drierite into the second midget bubbler (the fourth vessel in the train). Clean the outside of the bubblers and impingers and allow the vessels to reach room temperature. Weigh the four vessels simultaneously to the nearest 0.1 g, and record this initial weight (m_{wi}).

8.1.2 With one end of the CO_2 absorber sealed, place glass wool into the cylinder to a depth of about 1 cm (0.5 in.). Place about 150 g of CO_2 absorbing material in the cylinder on top of the glass wool, and fill the remaining space in the cylinder with glass wool. Assemble the cylinder as shown in figure 6A–2. With the cylinder in a horizontal position, rotate it around the horizontal axis. The CO_2 absorbing material should remain in position during the rotation, and no open spaces or channels should be formed. If necessary, pack more glass wool into the cylinder to make the CO_2 absorbing material stable. Clean the outside of the cylinder of loose dirt and moisture and allow the cylinder to reach room temperature. Weigh the cylinder to the nearest 0.1 g, and record this initial weight (m_{ai}).

8.1.3 Assemble the train as shown in figure 6A–1. Adjust the probe heater to a temperature sufficient to prevent condensation (see note in section 6.1). Place crushed ice and water around the impingers and bubblers. Mount the CO_2 absorber outside the water bath in a vertical flow position with the sample gas inlet at the bottom. Flexible tubing (*e.g.*, Tygon) may be used to connect the last SO_2 absorbing impinger to the moisture absorber and to connect the moisture absorber to the CO_2 absorber. A second, smaller CO_2 absorber containing Ascarite II may be added in-line downstream of the primary CO_2 absorber as a breakthrough indicator. Ascarite II turns white when CO_2 is absorbed.

8.2 Sampling Train Leak-Check Procedure and Sample Collection. Same as Method 6, sections 8.2 and 8.3, respectively.

8.3 Sample Recovery.

8.3.1 Moisture Measurement. Disconnect the isopropanol bubbler, the SO_2 impingers, and the moisture absorber from the sample train. Allow about 10 minutes for them to reach room temperature, clean the outside of loose dirt and moisture, and weigh them simultaneously in the same manner as in section 8.1. Record this final weight (m_{wf}).

8.3.2 Peroxide Solution. Discard the contents of the isopropanol bubbler and pour the contents of the midget impingers into a leak-free polyethylene bottle for shipping. Rinse the two midget impingers and connecting tubes with water, and add the washing to the same storage container.

8.3.3 CO_2 Absorber. Allow the CO_2 absorber to warm to room temperature (about 10 minutes), clean the outside of loose dirt and moisture, and weigh to the nearest 0.1 g in the same manner as in section 8.1. Record this final weight (m_{af}). Discard used Ascarite II material.

9.0 Quality Control

Same as Method 6, section 9.0.

10.0 Calibration and Standardization

Same as Method 6, section 10.0.

11.0 Analytical Procedure

11.1 Sample Analysis. The sample analysis procedure for SO_2 is the same as that specified in Method 6, section 11.0.

12.0 Data Analysis and Calculations

Same as Method 6, section 12.0, with the addition of the following:

12.1 Nomenclature.

C_w = Concentration of moisture, percent.
C_{CO2} = Concentration of CO_2, dry basis, percent.
E_{SO2} = Emission rate of SO_2, ng/J (lb/10^6 Btu).
F_C = Carbon F-factor from Method 19 for the fuel burned, dscm/J (dscf/10^6 Btu).
m_{wi} = Initial weight of impingers, bubblers, and moisture absorber, g.
m_{wf} = Final weight of impingers, bubblers, and moisture absorber, g.
m_{ai} = Initial weight of CO_2 absorber, g.
m_{af} = Final weight of CO_2 absorber, g.
m_{SO2} = Mass of SO_2 collected, mg.
$V_{CO2(std)}$ = Equivalent volume of CO_2 collected at standard conditions, dscm (dscf).
$V_{w(std)}$ = Equivalent volume of moisture collected at standard conditions, scm (scf).

12.2 CO_2 Volume Collected, Corrected to Standard Conditions.

$$V_{CO_2(std)} = K_3 \left(m_{af} - m_{ai}\right) \qquad \text{Eq. 6A-1}$$

Where:

K_3 = Equivalent volume of gaseous CO_2 at standard conditions, 5.467×10^{-4} dscm/g (1.930×10^{-2} dscf/g).

12.3 Moisture Volume Collected, Corrected to Standard Conditions.

$$V_{w(std)} = K_4 \left(m_{wf} - m_{wi}\right) \qquad \text{Eq. 6A-2}$$

Where:

K_4 = Equivalent volume of water vapor at standard conditions, 1.336×10^{-3} scm/g (4.717×10^{-2} scf/g).

12.4 SO_2 Concentration.

$$C_{so_2} = \frac{K_2 N (V_t - V_{tb})(V_{so\,ln}/V_a)}{V_{m(std)} + V_{co_2(std)}} \qquad \text{Eq. 6A-3}$$

Where:

K_2 = 32.03 mg SO_2/meq. SO_2 (7.061×10^{-5} lb SO_2/meq. SO_2)

12.5 CO_2 Concentration.

$$C_{co_2} = \frac{V_{co_2(std)}}{V_{m(std)} + V_{co_2(std)}} \qquad \text{Eq. 6A-4}$$

12.6 Moisture Concentration.

$$C_w = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)} + V_{co_2(std)}} \qquad \text{Eq. 6A-5}$$

13.0 Method Performance

13.1 Range and Precision. The minimum detectable limit and the upper limit for the measurement of SO_2 are the same as for Method 6. For a 20-liter sample, this method has a precision of ±0.5 percent CO_2 for concentrations between 2.5 and 25 percent CO_2 and ±1.0 percent moisture for moisture concentrations greater than 5 percent.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Methods

If the only emission measurement desired is in terms of emission rate of SO_2 (ng/J or lb/10^6 Btu), an abbreviated procedure may be used. The differences between the above procedure and the abbreviated procedure are described below.

16.1 Sampling Train. The sampling train is the same as that shown in Figure 6A–1 and as described in section 6.1, except that the dry gas meter is not needed.

16.2 Preparation of the Sampling Train. Follow the same procedure as in section 8.1, except do not weigh the isopropanol bubbler, the SO_2 absorbing impingers, or the moisture absorber.

16.3 Sampling Train Leak-Check Procedure and Sample Collection. Leak-check and operate the sampling train as described in section 8.2, except that dry gas meter readings, barometric pressure, and dry gas meter temperatures need not be recorded during sampling.

16.4 Sample Recovery. Follow the procedure in section 8.3, except do not weigh the isopropanol bubbler, the SO_2 absorbing impingers, or the moisture absorber.

16.5 Sample Analysis. Analysis of the peroxide solution is the same as that described in section 11.1.

16.6 Calculations.

16.6.1 SO_2 Collected.

$$m_{SO_2} = K_2 N (V_t - V_{tb})(V_{soln}/V_a) \qquad \text{Eq. 6A-6}$$

Where:

K_2 = 32.03 mg SO_2/meq. SO_2
$K_2 = 7.061 \times 10^{-5}$ lb SO_2/meq. SO_2

16.6.2 Sulfur Dioxide Emission Rate.

$$E_{SO_2} = K_5 F_c m_{so_2} / (m_{af} - m_{ai}) \qquad \text{Eq. 6A-7}$$

Where:

$K_5 = 1.829 \times 10^9$ mg/dscm
$K_2 = 0.1142$ lb/dscf

17.0 References

Same as Method 6, section 17.0, References 1 through 8, with the addition of the following:

1. Stanley, Jon and P.R. Westlin. An Alternate Method for Stack Gas Moisture Determination. Source Evaluation Society Newsletter. *3*(4). November 1978.

2. Whittle, Richard N. and P.R. Westlin. Air Pollution Test Report: Development and Evaluation of an Intermittent Integrated SO_2/CO_2 Emission Sampling Procedure. Environmental Protection Agency, Emission Standard and Engineering Division, Emission Measurement Branch. Research Triangle Park, NC. December 1979. 14 pp.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

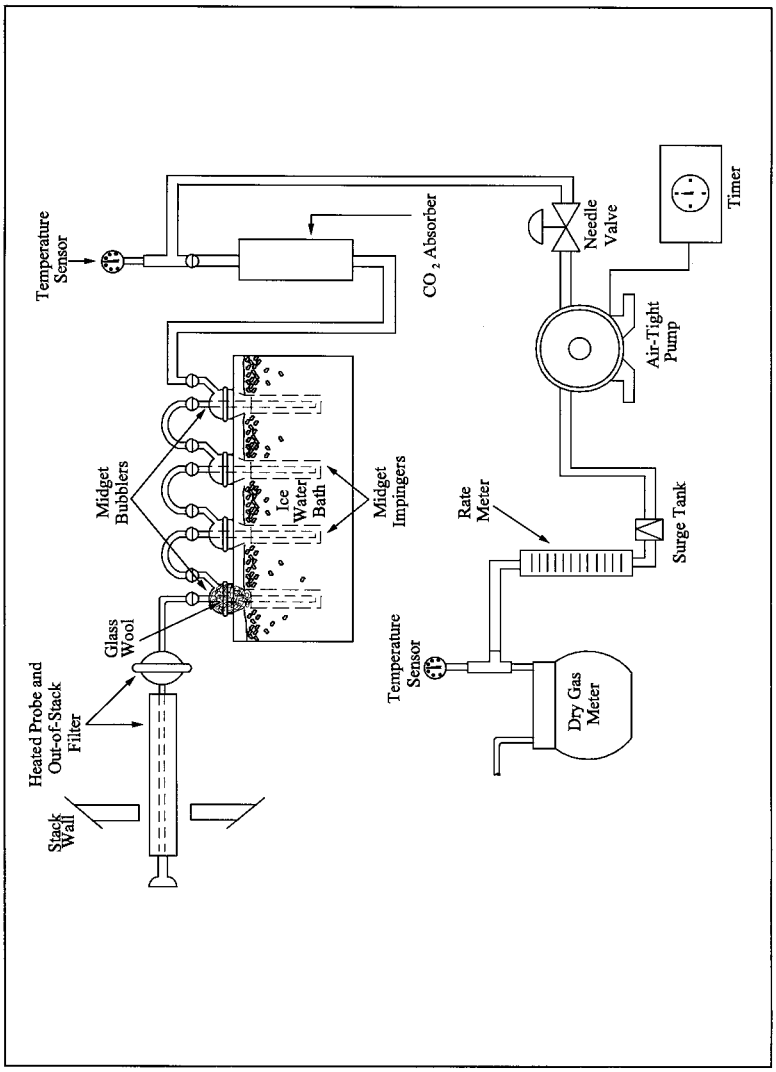

Figure 6A-1. Sampling train.

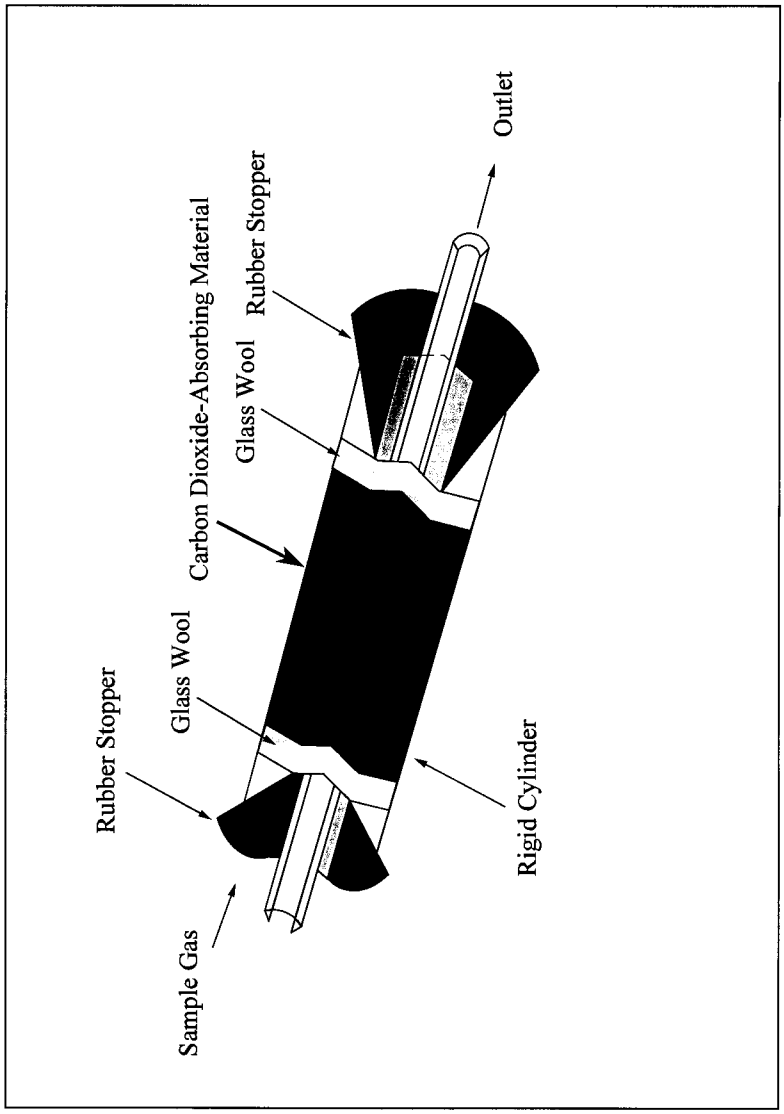

Figure 6A-2. CO_2 Absorber

METHOD 6B—DETERMINATION OF SULFUR DIOXIDE AND CARBON DIOXIDE DAILY AVERAGE EMISSIONS FROM FOSSIL FUEL COMBUSTION SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, Method 6, and Method 6A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Sulfur dioxide (SO_2)	7449–09–05	3.4 mg SO_2/m^3 (2.12×10^{-7} lb/ft^3)
Carbon dioxide (CO_2)	124–38–9	N/A

1.2 Applicability. This method is applicable for the determination of SO_2 emissions from combustion sources in terms of concentration (ng/dscm or lb/dscf) and emission rate (ng/J or lb/10^6 Btu), and for the determination of CO_2 concentration (percent) on a daily (24 hours) basis.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the sampling point in the stack intermittently over a 24-hour or other specified time period. The SO_2 fraction is measured by the barium-thorin titration method. Moisture and CO_2 fractions are collected in the same sampling train, and are determined gravimetrically.

3.0 Definitions [Reserved]

4.0 Interferences

Same as Method 6, section 4.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. Same as Method 6, section 5.2.

6.0 Equipment and Supplies

Same as Method 6A, section 6.0, with the following exceptions and additions:

6.1 The isopropanol bubbler is not used. An empty bubbler for the collection of liquid droplets, that does not allow direct contact between the collected liquid and the gas sample, may be included in the sampling train.

6.2 For intermittent operation, include an industrial timer-switch designed to operate in the ''on'' position at least 2 minutes continuously and ''off'' the remaining period over a repeating cycle. The cycle of operation is designated in the applicable regulation. At a minimum, the sampling operation should include at least 12, equal, evenly-spaced periods per 24 hours.

6.3 Stainless steel sampling probes, type 316, are not recommended for use with Method 6B because of potential sample contamination due to corrosion. Glass probes or other types of stainless steel, *e.g.*, Hasteloy or Carpenter 20, are recommended for long-term use.

NOTE: For applications downstream of wet scrubbers, a heated out-of-stack filter (either borosilicate glass wool or glass fiber mat) is necessary. Probe and filter heating systems capable of maintaining a sample gas temperature of between 20 and 120 °C (68 and 248 °F) at the filter are also required in these cases. The electric supply for these heating systems should be continuous and separate from the timed operation of the sample pump.

7.0 Reagents and Standards

Same as Method 6A, section 7.0, with the following exceptions:

7.1 Isopropanol is not used for sampling.

7.2 The hydrogen peroxide absorbing solution shall be diluted to no less than 6 percent by volume, instead of 3 percent as specified in Methods 6 and 6A.

7.3 If the Method 6B sampling train is to be operated in a low sample flow condition (less than 100 ml/min or 0.21 ft^3/hr), molecular sieve material may be substituted for Ascarite II as the CO_2 absorbing material. The recommended molecular sieve material is Union Carbide 1/16 inch pellets, 5 A°, or equivalent. Molecular sieve material need not be discarded following the sampling run, provided that it is regenerated as per the manufacturer's instruction. Use of molecular sieve material at flow rates higher than 100 ml/min (0.21 ft^3/hr) may cause erroneous CO_2 results.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Preparation of Sampling Train. Same as Method 6A, section 8.1, with the addition of the following:

8.1.1 The sampling train is assembled as shown in Figure 6A–1 of Method 6A, except that the isopropanol bubbler is not included.

8.1.2 Adjust the timer-switch to operate in the ''on'' position from 2 to 4 minutes on a 2-hour repeating cycle or other cycle specified in the applicable regulation. Other timer sequences may be used with the restriction that the total sample volume collected is between 25 and 60 liters (0.9 and 2.1 ft^3) for the amounts of sampling reagents prescribed in this method.

8.1.3 Add cold water to the tank until the impingers and bubblers are covered at least two-thirds of their length. The impingers and bubbler tank must be covered and protected from intense heat and direct sunlight. If freezing conditions exist, the impinger solution and the water bath must be protected.

NOTE: Sampling may be conducted continuously if a low flow-rate sample pump [20

to 40 ml/min (0.04 to 0.08 ft^3/hr) for the reagent volumes described in this method] is used. If sampling is continuous, the timer-switch is not necessary. In addition, if the sample pump is designed for constant rate sampling, the rate meter may be deleted. The total gas volume collected should be between 25 and 60 liters (0.9 and 2.1 ft^3) for the amounts of sampling reagents prescribed in this method.

8.2 Sampling Train Leak-Check Procedure. Same as Method 6, section 8.2.

8.3 Sample Collection.

8.3.1 The probe and filter (either in-stack, out-of-stack, or both) must be heated to a temperature sufficient to prevent water condensation.

8.3.2 Record the initial dry gas meter reading. To begin sampling, position the tip of the probe at the sampling point, connect the probe to the first impinger (or filter), and start the timer and the sample pump. Adjust the sample flow to a constant rate of approximately 1.0 liter/min (0.035 cfm) as indicated by the rotameter. Observe the operation of the timer, and determine that it is operating as intended (*i.e.*, the timer is in the ''on'' position for the desired period, and the cycle repeats as required).

8.3.3 One time between 9 a.m. and 11 a.m. during the 24-hour sampling period, record the dry gas meter temperature (T_m) and the barometric pressure ($P_{(bar)}$).

8.3.4 At the conclusion of the run, turn off the timer and the sample pump, remove the probe from the stack, and record the final gas meter volume reading. Conduct a leak-check as described in section 8.2. If a leak is found, void the test run or use procedures acceptable to the Administrator to adjust the sample volume for leakage. Repeat the steps in sections 8.3.1 to 8.3.4 for successive runs.

8.4 Sample Recovery. The procedures for sample recovery (moisture measurement, peroxide solution, and CO_2 absorber) are the same as those in Method 6A, section 8.3.

9.0 Quality Control

Same as Method 6, section 9.0., with the exception of the isopropanol-check.

10.0 Calibration and Standardization

Same as Method 6, section 10.0, with the addition of the following:

10.1 Periodic Calibration Check. After 30 days of operation of the test train, conduct a calibration check according to the same procedures as the post-test calibration check (Method 6, section 10.1.2). If the deviation between initial and periodic calibration factors exceeds 5 percent, use the smaller of the two factors in calculations for the preceding 30 days of data, but use the most recent calibration factor for succeeding test runs.

11.0 Analytical Procedures

11.1 Sample Loss Check and Analysis. Same as Method 6, sections 11.1 and 11.2, respectively.

12.0 Data Analysis and Calculations

Same as Method 6A, section 12.0, except that P_{bar} and T_m correspond to the values recorded in section 8.3.3 of this method. The values are as follows:

P_{bar} = Initial barometric pressure for the test period, mm Hg.

T_m = Absolute meter temperature for the test period, °K.

13.0 Method Performance

13.1 Range.

13.1.1 Sulfur Dioxide. Same as Method 6.

13.1.2 Carbon Dioxide. Not determined.

13.2 Repeatability and Reproducibility. EPA-sponsored collaborative studies were undertaken to determine the magnitude of repeatability and reproducibility achievable by qualified testers following the procedures in this method. The results of the studies evolve from 145 field tests including comparisons with Methods 3 and 6. For measurements of emission rates from wet, flue gas desulfurization units in (ng/J), the repeatability (intra-laboratory precision) is 8.0 percent and the reproducibility (inter-laboratory precision) is 11.1 percent.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Methods

Same as Method 6A, section 16.0, except that the timer is needed and is operated as outlined in this method.

17.0 References

Same as Method 6A, section 17.0, with the addition of the following:

1. Butler, Frank E., et. al. The Collaborative Test of Method 6B: Twenty-Four-Hour Analysis of SO_2 and CO_2. JAPCA. Vol. 33, No. 10. October 1983.

18.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 6C—DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES (INSTRUMENTAL ANALYZER PROCEDURE)

1.0 Scope and Application

What is Method 6C?

Method 6C is a procedure for measuring sulfur dioxide (SO_2) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that

you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis.

This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 4—Determination of Moisture Content in Stack Gases.

(c) Method 6—Determination of Sulfur Dioxide Emissions from Stationary Sources.

(d) Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure).

1.1 Analytes. What does this method determine? This method measures the concentration of sulfur dioxide.

Analyte	CAS No.	Sensitivity
SO_2	7446–09–5	Typically <2% of Calibration Span.

1.2 Applicability. When is this method required? The use of Method 6C may be required by specific New Source Performance Standards, Clean Air Marketing rules, State Implementation Plans, and permits where SO_2 concentrations in stationary source emissions must be measured, either to determine compliance with an applicable emission standard or to conduct performance testing of a continuous emission monitoring system (CEMS). Other regulations may also require the use of Method 6C.

1.3 Data Quality Objectives. How good must my collected data be? Refer to section 1.3 of Method 7E.

2.0 Summary of Method

In this method, you continuously sample the effluent gas and convey the sample to an analyzer that measures the concentration of SO_2. You must meet the performance requirements of this method to validate your data.

3.0 Definitions

Refer to section 3.0 of Method 7E for the applicable definitions.

4.0 Interferences

Refer to Section 4.0 of Method 7E.

5.0 Safety

Refer to section 5.0 of Method 7E.

6.0 Equipment and Supplies

Figure 7E–1 of Method 7E is a schematic diagram of an acceptable measurement system.

6.1 What do I need for the measurement system? The essential components of the measurement system are the same as those in sections 6.1 and 6.2 of Method 7E, except that the SO_2 analyzer described in section 6.2 of this method must be used instead of the analyzer described in section 6.2 of Method 7E. You must follow the noted specifications in section 6.1 of Method 7E.

6.2 What analyzer must I use? You may use an instrument that uses an ultraviolet, nondispersive infrared, fluorescence, or other detection principle to continuously measure SO_2 in the gas stream and meets the performance specifications in section 13.0. The low-range and dual-range analyzer provisions in sections 6.2.8.1 and 6.2.8.2 of Method 7E apply.

7.0 Reagents and Standards

7.1 Calibration Gas. What calibration gases do I need? Refer to section 7.1 of Method 7E for the calibration gas requirements. Example calibration gas mixtures are listed below.

(a) SO_2 in nitrogen (N_2).

(b) SO_2 in air.

(c) SO_2 and CO_2 in N_2.

(d) SO_2 andO_2 in N_2.

(e) $SO_2/CO_2/O_2$ gas mixture in N_2.

(f) CO_2/NO_X gas mixture in N_2.

(g) $CO_2/SO_2/NO_X$ gas mixture in N_2.

7.2 Interference Check. What additional reagents do I need for the interference check? The test gases for the interference check are listed in Table 7E–3 of Method 7E. For the alternative interference check, you must use the reagents described in section 7.0 of Method 6.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling Site and Sampling Points. You must follow the procedures of section 8.1 of Method 7E.

8.2 Initial Measurement System Performance Tests. You must follow the procedures in section 8.2 of Method 7E. If a dilution-type measurement system is used, the special considerations in section 8.3 of Method 7E also apply.

8.3 Interference Check. You must follow the procedures of section 8.2.7 of Method 7E

to conduct an interference check, substituting SO_2 for NO_X as the method pollutant. For dilution-type measurement systems, you must use the alternative interference check procedure in section 16 and a co-located, unmodified Method 6 sampling train.

8.4 Sample Collection. You must follow the procedures of section 8.4 of Method 7E.

8.5 Post-Run System Bias Check and Drift Assessment. You must follow the procedures of section 8.5 of Method 7E.

9.0 Quality Control

Follow quality control procedures in section 9.0 of Method 7E.

10.0 Calibration and Standardization

Follow the procedures for calibration and standardization in section 10.0 of Method 7E.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the applicable procedures for calculations and data analysis in section 12.0 of Method 7E as applicable, substituting SO_2 for NO_X as appropriate.

13.0 Method Performance

13.1 The specifications for the applicable performance checks are the same as in section 13.0 of Method 7E.

13.2 Alternative Interference Check. The results are acceptable if the difference between the Method 6C result and the modified Method 6 result is less than 7.0 percent of the Method 6 result for each of the three test runs. For the purposes of comparison, the Method 6 and 6C results must be expressed in the same units of measure.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Alternative Interference Check. You may perform an alternative interference check consisting of at least three comparison runs between Method 6C and Method 6. This check validates the Method 6C results at each particular source category (type of facility) where the check is performed. When testing under conditions of low concentrations (<15 ppm), this alternative interference check is not allowed.

NOTE: The procedure described below applies to non-dilution sampling systems only. If this alternative interference check is used for a dilution sampling system, use a standard Method 6 sampling train and extract the sample directly from the exhaust stream at points collocated with the Method 6C sample probe.

a. Build the modified Method 6 sampling train (flow control valve, two midget impingers containing 3 percent hydrogen peroxide, and dry gas meter) shown in Figure 6C–1. Connect the sampling train to the sample bypass discharge vent. Record the dry gas meter reading before you begin sampling. Simultaneously collect modified Method 6 and Method 6C samples. Open the flow control valve in the modified Method 6 train as you begin to sample with Method 6C. Adjust the Method 6 sampling rate to 1 liter per minute (.10 percent). The sampling time per run must be the same as for Method 6 plus twice the average measurement system response time. If your modified Method 6 train does not include a pump, you risk biasing the results high if you over-pressurize the midget impingers and cause a leak. You can reduce this risk by cautiously increasing the flow rate as sampling begins.

b. After completing a run, record the final dry gas meter reading, meter temperature, and barometric pressure. Recover and analyze the contents of the midget impingers using the procedures in Method 6. Determine the average gas concentration reported by Method 6C for the run.

17.0 References

1. ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards'' September 1997 as amended, EPA–600/R–97/121

18.0 Tables, Diagrams, Flowcharts, and Validation Data

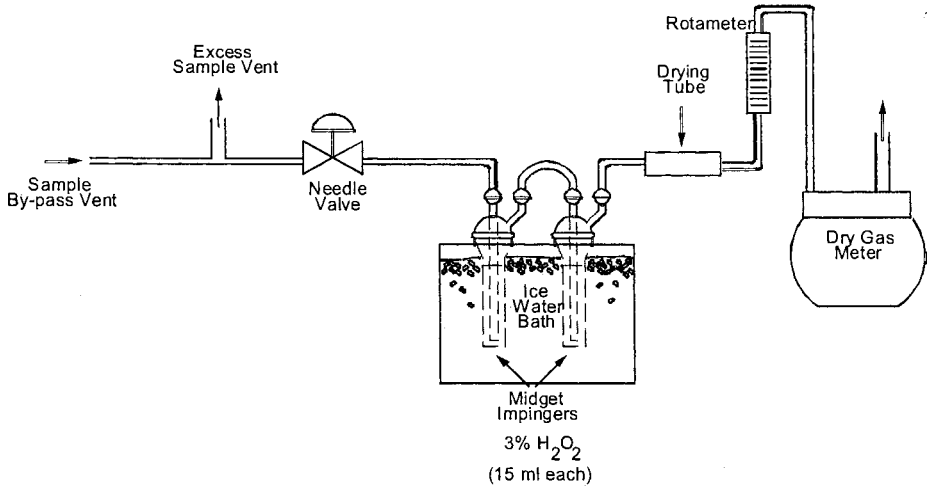

Figure 6C-1. Modified Method 6
Alternative Interference Check Sampling Train

METHOD 7—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1 and Method 5.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–0	2–400 mg/dscm

1.2 Applicability. This method is applicable for the measurement of nitrogen oxides (NO_X) emitted from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sample methods.

2.0 Summary of Method

A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution, and the nitrogen oxides, except nitrous oxide, are measured colorimetrically using the phenoldisulfonic acid (PDS) procedure.

3.0 Definitions [Reserved]

4.0 Interferences

Biased results have been observed when sampling under conditions of high sulfur dioxide concentrations. At or above 2100 ppm SO_2, use five times the H_2O_2 concentration of the Method 7 absorbing solution. Laboratory tests have shown that high concentrations of SO_2 (about 2100 ppm) cause low results in Method 7 and 7A. Increasing the H_2O_2 concentration to five times the original concentration eliminates this bias. However, when no SO_2 is present, increasing the concentration by five times results in a low bias.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs.

5.2.2 Phenoldisulfonic Acid. Irritating to eyes and skin.

5.2.3 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.4 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

5.2.5 Phenol. Poisonous and caustic. Do not handle with bare hands as it is absorbed through the skin.

6.0 Equipment and Supplies

6.1 Sample Collection. A schematic of the sampling train used in performing this method is shown in Figure 7–1. Other grab sampling systems or equipment, capable of measuring sample volume to within 2.0 percent and collecting a sufficient sample volume to allow analytical reproducibility to within 5 percent, will be considered acceptable alternatives, subject to the approval of the Administrator. The following items are required for sample collection:

6.1.1 Probe. Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or heated out-of-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Stainless steel or Teflon tubing may also be used for the probe. Heating is not necessary if the probe remains dry during the purging period.

6.1.2 Collection Flask. Two-liter borosilicate, round bottom flask, with short neck and 24/40 standard taper opening, protected against implosion or breakage.

6.1.3 Flask Valve. T-bore stopcock connected to a 24/40 standard taper joint.

6.1.4 Temperature Gauge. Dial-type thermometer, or other temperature gauge, capable of measuring 1 °C (2 °F) intervals from −5 to 50 °C (23 to 122 °F).

6.1.5 Vacuum Line. Tubing capable of withstanding a vacuum of 75 mm (3 in.) Hg absolute pressure, with ''T'' connection and T-bore stopcock.

6.1.6 Vacuum Gauge. U-tube manometer, 1 meter (39 in.), with 1 mm (0.04 in.) divisions, or other gauge capable of measuring pressure to within 2.5 mm (0.10 in.) Hg.

6.1.7 Pump. Capable of evacuating the collection flask to a pressure equal to or less than 75 mm (3 in.) Hg absolute.

6.1.8 Squeeze Bulb. One-way.

6.1.9 Volumetric Pipette. 25-ml.

6.1.10 Stopcock and Ground Joint Grease. A high-vacuum, high-temperature chlorofluorocarbon grease is required. Halocarbon 25–5S has been found to be effective.

6.1.11 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg. See note in Method 5, section 6.1.2.

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Graduated Cylinder. 50-ml with 1 ml divisions.

6.2.2 Storage Containers. Leak-free polyethylene bottles.

6.2.3 Wash Bottle. Polyethylene or glass.

6.2.4 Glass Stirring Rod.

6.2.5 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

6.3 Analysis. The following items are required for analysis:

6.3.1 Volumetric Pipettes. Two 1-ml, two 2-ml, one 3-ml, one 4-ml, two 10-ml, and one 25-ml for each sample and standard.

6.3.2 Porcelain Evaporating Dishes. 175- to 250-ml capacity with lip for pouring, one for each sample and each standard. The Coors No. 45006 (shallowform, 195-ml) has been found to be satisfactory. Alternatively, polymethyl pentene beakers (Nalge No. 1203, 150-ml), or glass beakers (150-ml) may be used. When glass beakers are used, etching of the beakers may cause solid matter to be present in the analytical step; the solids should be removed by filtration.

6.3.3 Steam Bath. Low-temperature ovens or thermostatically controlled hot plates kept below 70 °C (160 °F) are acceptable alternatives.

6.3.4 Dropping Pipette or Dropper. Three required.

6.3.5 Polyethylene Policeman. One for each sample and each standard.

6.3.6 Graduated Cylinder. 100-ml with 1-ml divisions.

6.3.7 Volumetric Flasks. 50-ml (one for each sample and each standard), 100-ml (one for each sample and each standard, and one for the working standard KNO_3 solution), and 1000-ml (one).

6.3.8 Spectrophotometer. To measure at 410 nm.

6.3.9 Graduated Pipette. 10-ml with 0.1-ml divisions.

6.3.10 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

6.3.11 Analytical Balance. To measure to within 0.1 mg.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. The following reagents are required for sampling:

7.1.1 Water. Deionized distilled to conform to ASTM D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17). The $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.1.2 Absorbing Solution. Cautiously add 2.8 ml concentrated H_2SO_4 to a 1-liter flask partially filled with water. Mix well, and add 6 ml of 3 percent hydrogen peroxide, freshly prepared from 30 percent hydrogen peroxide solution. Dilute to 1 liter of water and mix well. The absorbing solution should be used within 1 week of its preparation. Do not expose to extreme heat or direct sunlight.

7.2 Sample Recovery. The following reagents are required for sample recovery:

7.2.1 Water. Same as in 7.1.1.

7.2.2 Sodium Hydroxide, 1 N. Dissolve 40 g NaOH in water, and dilute to 1 liter.

7.3 Analysis. The following reagents and standards are required for analysis:

7.3.1 Water. Same as in 7.1.1.

7.3.2 Fuming Sulfuric Acid. 15 to 18 percent by weight free sulfur trioxide. HANDLE WITH CAUTION.

7.3.3 Phenol. White solid.

7.3.4 Sulfuric Acid. Concentrated, 95 percent minimum assay.

7.3.5 Potassium Nitrate (KNO_3). Dried at 105 to 110 °C (221 to 230 °F) for a minimum of 2 hours just prior to preparation of standard solution.

7.3.6 Standard KNO_3 Solution. Dissolve exactly 2.198 g of dried KNO_3 in water, and dilute to 1 liter with water in a 1000-ml volumetric flask.

7.3.7 Working Standard KNO_3 Solution. Dilute 10 ml of the standard solution to 100 ml with water. One ml of the working standard solution is equivalent to 100 μg nitrogen dioxide (NO_2).

7.3.8 Phenoldisulfonic Acid Solution. Dissolve 25 g of pure white phenol solid in 150 ml concentrated sulfuric acid on a steam bath. Cool, add 75 ml fuming sulfuric acid (15 to 18 percent by weight free sulfur trioxide—HANDLE WITH CAUTION), and heat at 100 °C (212 °F) for 2 hours. Store in a dark, stoppered bottle.

7.3.9 Concentrated Ammonium Hydroxide.

8.0 Sample Collection, Preservation, Storage and Transport

8.1 Sample Collection.

8.1.1 Flask Volume. The volume of the collection flask and flask valve combination must be known prior to sampling. Assemble the flask and flask valve, and fill with water to the stopcock. Measure the volume of water to ±10 ml. Record this volume on the flask.

8.1.2 Pipette 25 ml of absorbing solution into a sample flask, retaining a sufficient quantity for use in preparing the calibration standards. Insert the flask valve stopper into the flask with the valve in the ''purge'' position. Assemble the sampling train as shown in Figure 7–1, and place the probe at the sampling point. Make sure that all fittings are tight and leak-free, and that all ground glass joints have been greased properly with a high-vacuum, high temperature chlorofluorocarbon-based stopcock grease. Turn the flask valve and the pump valve to their ''evacuate'' positions. Evacuate the flask to 75 mm (3 in.) Hg absolute pressure, or less. Evacuation to a pressure approaching the vapor pressure of water at the existing temperature is desirable. Turn the pump valve to its ''vent'' position, and turn off the pump. Check for leakage by observing the manometer for any pressure fluctuation. (Any variation greater than 10 mm (0.4 in.) Hg over a period of 1 minute is not acceptable, and the flask is not to be used until the leakage problem is corrected. Pressure in the flask is not to exceed 75 mm (3 in.) Hg absolute at the time sampling is commenced.) Record the volume of the flask and valve (V_f), the flask temperature (T_i), and the barometric pressure. Turn the flask valve counterclockwise to its ''purge'' position, and do the same with the pump valve. Purge the probe and the vacuum tube using the squeeze bulb. If condensation occurs in the probe and the flask valve area, heat the probe, and purge until the condensation disappears. Next, turn the pump valve to its ''vent'' position. Turn the flask valve clockwise to its ''evacuate'' position, and record the difference in the mercury levels in the manometer. The absolute internal pressure in the flask (P_i) is equal to the barometric pressure less the manometer reading. Immediately turn the flask valve to the ''sample'' position, and permit the gas to enter the flask until pressures in the flask and sample line (*i.e.*, duct, stack) are equal. This will usually require about 15 seconds; a longer period indicates a plug in the probe, which must be

corrected before sampling is continued. After collecting the sample, turn the flask valve to its ''purge'' position, and disconnect the flask from the sampling train.

8.1.3 Shake the flask for at least 5 minutes.

8.1.4 If the gas being sampled contains insufficient oxygen for the conversion of NO to NO_2 (*e.g.,* an applicable subpart of the standards may require taking a sample of a calibration gas mixture of NO in N_2), then introduce oxygen into the flask to permit this conversion. Oxygen may be introduced into the flask by one of three methods: (1) Before evacuating the sampling flask, flush with pure cylinder oxygen, then evacuate flask to 75 mm (3 in.) Hg absolute pressure or less; or (2) inject oxygen into the flask after sampling; or (3) terminate sampling with a minimum of 50 mm (2 in.) Hg vacuum remaining in the flask, record this final pressure, and then vent the flask to the atmosphere until the flask pressure is almost equal to atmospheric pressure.

8.2 Sample Recovery. Let the flask sit for a minimum of 16 hours, and then shake the contents for 2 minutes.

8.2.1 Connect the flask to a mercury filled U-tube manometer. Open the valve from the flask to the manometer, and record the flask temperature (T_f), the barometric pressure, and the difference between the mercury levels in the manometer. The absolute internal pressure in the flask (P_f) is the barometric pressure less the manometer reading. Transfer the contents of the flask to a leak-free polyethylene bottle. Rinse the flask twice with 5 ml portions of water, and add the rinse water to the bottle. Adjust the pH to between 9 and 12 by adding 1 N NaOH, dropwise (about 25 to 35 drops). Check the pH by dipping a stirring rod into the solution and then touching the rod to the pH test paper. Remove as little material as possible during this step. Mark the height of the liquid level so that the container can be checked for leakage after transport. Label the container to identify clearly its contents. Seal the container for shipping.

9.0 Quality Control

Section	Quality control measure	Effect
10.1	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.

10.0 Calibration and Standardization

10.1 Spectrophotometer.

10.1.1 Optimum Wavelength Determination.

10.1.1.1 Calibrate the wavelength scale of the spectrophotometer every 6 months. The calibration may be accomplished by using an energy source with an intense line emission such as a mercury lamp, or by using a series of glass filters spanning the measuring range of the spectrophotometer. Calibration materials are available commercially and from the National Institute of Standards and Technology. Specific details on the use of such materials should be supplied by the vendor; general information about calibration techniques can be obtained from general reference books on analytical chemistry. The wavelength scale of the spectrophotometer must read correctly within 5 nm at all calibration points; otherwise, repair and recalibrate the spectrophotometer. Once the wavelength scale of the spectrophotometer is in proper calibration, use 410 nm as the optimum wavelength for the measurement of the absorbance of the standards and samples.

10.1.1.2 Alternatively, a scanning procedure may be employed to determine the proper measuring wavelength. If the instrument is a double-beam spectrophotometer, scan the spectrum between 400 and 415 nm using a 200 μg NO_2 standard solution in the sample cell and a blank solution in the reference cell. If a peak does not occur, the spectrophotometer is probably malfunctioning and should be repaired. When a peak is obtained within the 400 to 415 nm range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of absorbance of both the standards and the samples. For a single-beam spectrophotometer, follow the scanning procedure described above, except scan separately the blank and standard solutions. The optimum wavelength shall be the wavelength at which the maximum difference in absorbance between the standard and the blank occurs.

10.1.2 Determination of Spectrophotometer Calibration Factor K_c. Add 0 ml, 2.0 ml, 4.0 ml, 6.0 ml, and 8.0 ml of the KNO_3 working standard solution (1 ml = 100 μg NO_2) to a series of five 50-ml volumetric flasks. To each flask, add 25 ml of absorbing solution and 10 ml water. Add 1 N NaOH to each flask until the pH is between 9 and 12 (about 25 to 35 drops). Dilute to the mark with water. Mix thoroughly, and pipette a 25-ml aliquot of each solution into a separate porcelain evaporating dish. Beginning with the evaporation step, follow the analysis procedure of section 11.2 until the solution has been transferred to the 100-ml volumetric flask and diluted to the mark. Measure the absorbance of each solution at the optimum wavelength as determined in section 10.2.1. This calibration procedure must be repeated on each day that samples are analyzed. Calculate the spectrophotometer calibration factor as shown in section 12.2.

10.1.3 Spectrophotometer Calibration Quality Control. Multiply the absorbance value obtained for each standard by the K_c factor (reciprocal of the least squares slope) to determine the distance each calibration point lies from the theoretical calibration line. The difference between the calculated concentration values and the actual concentrations (*i.e.*, 100, 200, 300, and 400 µg NO_2) should be less than 7 percent for all standards.

10.2 Barometer. Calibrate against a mercury barometer or NIST-traceable barometer prior to the field test.

10.3 Temperature Gauge. Calibrate dial thermometers against mercury-in-glass thermometers. An alternative mercury-free thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

10.4 Vacuum Gauge. Calibrate mechanical gauges, if used, against a mercury manometer such as that specified in section 6.1.6.

10.5 Analytical Balance. Calibrate against standard weights.

11.0 Analytical Procedures

11.1 Sample Loss Check. Note the level of the liquid in the container, and confirm whether any sample was lost during shipment. Note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Preparation. Immediately prior to analysis, transfer the contents of the shipping container to a 50 ml volumetric flask, and rinse the container twice with 5 ml portions of water. Add the rinse water to the flask, and dilute to mark with water; mix thoroughly. Pipette a 25-ml aliquot into the porcelain evaporating dish. Return any unused portion of the sample to the polyethylene storage bottle. Evaporate the 25-ml aliquot to dryness on a steam bath, and allow to cool. Add 2 ml phenoldisulfonic acid solution to the dried residue, and triturate thoroughly with a polyethylene policeman. Make sure the solution contacts all the residue. Add 1 ml water and 4 drops of concentrated sulfuric acid. Heat the solution on a steam bath for 3 minutes with occasional stirring. Allow the solution to cool, add 20 ml water, mix well by stirring, and add concentrated ammonium hydroxide, dropwise, with constant stirring, until the pH is 10 (as determined by pH paper). If the sample contains solids, these must be removed by filtration (centrifugation is an acceptable alternative, subject to the approval of the Administrator) as follows: Filter through Whatman No. 41 filter paper into a 100-ml volumetric flask. Rinse the evaporating dish with three 5-ml portions of water. Filter these three rinses. Wash the filter with at least three 15-ml portions of water. Add the filter washings to the contents of the volumetric flask, and dilute to the mark with water. If solids are absent, the solution can be transferred directly to the 100-ml volumetric flask and diluted to the mark with water.

11.3 Sample Analysis. Mix the contents of the flask thoroughly, and measure the absorbance at the optimum wavelength used for the standards (Section 10.2.1), using the blank solution as a zero reference. Dilute the sample and the blank with equal volumes of water if the absorbance exceeds A_4, the absorbance of the 400-µg NO_2 standard (see section 10.2.2).

12.0 Data Analysis and Calculations

Carry out the calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculations.

12.1 12.1 Nomenclature

A = Absorbance of sample.
A_1 = Absorbance of the 100-µg NO_2 standard.
A_2 = Absorbance of the 200-µg NO_2 standard.
A_3 = Absorbance of the 300-µg NO_2 standard.
A_4 = Absorbance of the 400-µg NO_2 standard.
C = Concentration of NO_X as NO_2, dry basis, corrected to standard conditions, mg/dsm^3 (lb/dscf).
F = Dilution factor (*i.e.*, 25/5, 25/10, *etc.*, required only if sample dilution was needed to reduce the absorbance into the range of the calibration).
K_c = Spectrophotometer calibration factor.
M = Mass of NO_X as NO_2 in gas sample, µg.
P_f = Final absolute pressure of flask, mm Hg (in. Hg).
P_i = Initial absolute pressure of flask, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
T_f = Final absolute temperature of flask, °K (°R).
T_i = Initial absolute temperature of flask, °K (°R).
T_{std} = Standard absolute temperature, 293 °K (528°R).
V_{sc} = Sample volume at standard conditions (dry basis), ml.
V_f = Volume of flask and valve, ml.
V_a = Volume of absorbing solution, 25 ml.

12.2 Spectrophotometer Calibration Factor.

$$K_c = 100\frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^{\,2} + A_2^{\,2} + A_3^{\,2} + A_4^{\,2}} \qquad \text{Eq. 7-1}$$

12.3 Sample Volume, Dry Basis, Corrected to Standard Conditions.

$$V_{sc} = \left(V_f - V_a\right)\frac{T_{std}}{P_{std}}\left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right] \qquad \text{Eq. 7-2}$$

$$= K_1\left(V_f - 25\right)\left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right]$$

Where:

K_1 = 0.3858 °K/mm Hg for metric units,
K_1 = 17.65 °R/in. Hg for English units.

12.4 Total µg NO_2 per sample.

$$m = 2K_c AF \qquad \text{Eq. 7-3}$$

Where:

2 = 50/25, the aliquot factor.

NOTE: If other than a 25-ml aliquot is used for analysis, the factor 2 must be replaced by a corresponding factor.

12.5 Sample Concentration, Dry Basis, Corrected to Standard Conditions.

$$C = K_2\left(m/V_{sc}\right) \qquad \text{Eq. 7-4}$$

Where:

K2 = 10^3 (mg/m^3)/(µg/ml) for metric units,
K_2 = 6.242 × 10^{-5} (lb/scf)/(µg/ml) for English units.

13.0 Method Performance

13.1 Range. The analytical range of the method has been determined to be 2 to 400 milligrams NO_X (as NO_2) per dry standard cubic meter, without having to dilute the sample.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Standard Methods of Chemical Analysis. 6th ed. New York, D. Van Nostrand Co., Inc. 1962. Vol. 1, pp. 329–330.

2. Standard Method of Test for Oxides of Nitrogen in Gaseous Combustion Products (Phenoldisulfonic Acid Procedure). In: 1968 Book of ASTM Standards, Part 26. Philadelphia, PA. 1968. ASTM Designation D 1608–60, pp. 725–729.

3. Jacob, M.B. The Chemical Analysis of Air Pollutants. New York. Interscience Publishers, Inc. 1960. Vol. 10, pp. 351–356.

4. Beatty, R.L., L.B. Berger, and H.H. Schrenk. Determination of Oxides of Nitrogen by the Phenoldisulfonic Acid Method. Bureau of Mines, U.S. Dept. of Interior. R.I. 3687. February 1943.

5. Hamil, H.F. and D.E. Camann. Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Fossil Fuel-Fired Steam Generators). Southwest Research Institute Report for Environmental Protection Agency. Research Triangle Park, NC. October 5, 1973.

6. Hamil, H.F. and R.E. Thomas. Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Nitric Acid Plants). Southwest Research Institute Report for Environmental Protection Agency. Research Triangle Park, NC. May 8, 1974.

7. Stack Sampling Safety Manual (Draft). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC. September 1978.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

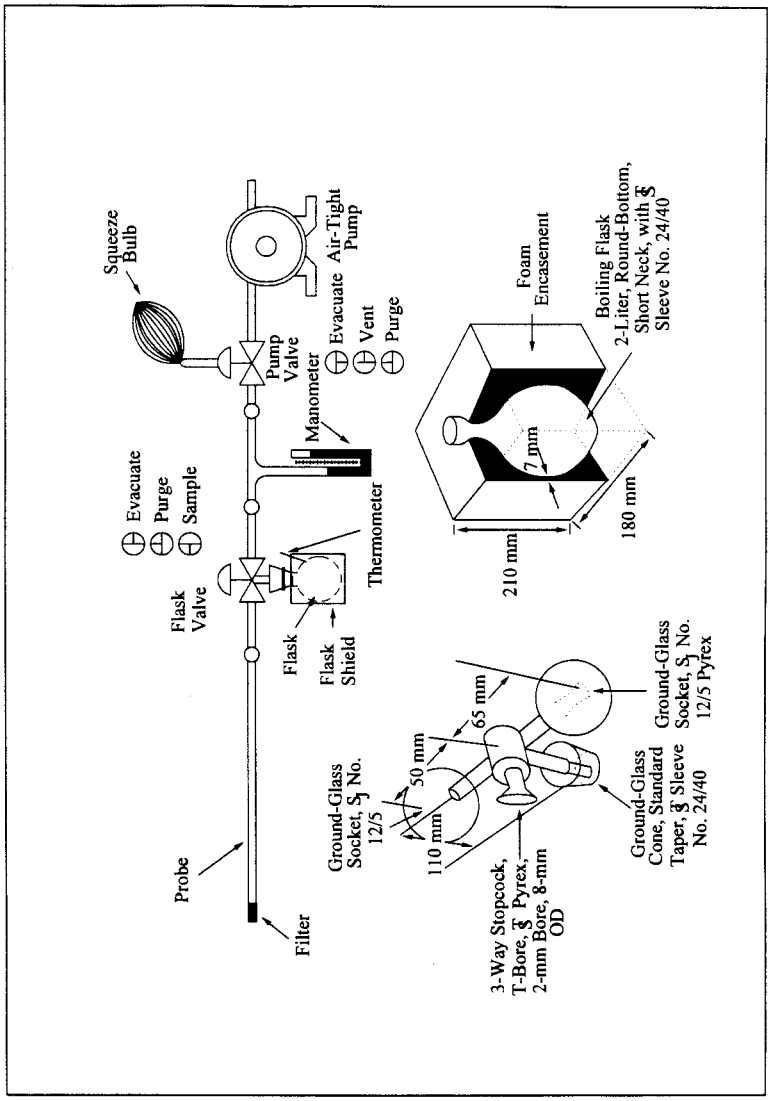

Figure 7-1. Sampling Train, Flask Valve, and Flask.

METHOD 7A—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ION CHROMATOGRAPHIC METHOD)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 3, Method 5, and Method 7.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–0	65–655 ppmv

1.2 Applicability. This method is applicable for the determination of NO_X emissions from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution. The nitrogen oxides, excluding nitrous oxide (N_2O), are oxidized to nitrate and measured by ion chromatography.

3.0 Definitions [Reserved]

4.0 Interferences

Biased results have been observed when sampling under conditions of high sulfur dioxide concentrations. At or above 2100 ppm SO_2, use five times the H_2O_2 concentration of the Method 7 absorbing solution. Laboratory tests have shown that high concentrations of SO_2 (about 2100 ppm) cause low results in Method 7 and 7A. Increasing the H_2O_2 concentration to five times the original concentration eliminates this bias. However, when no SO_2 is present, increasing the concentration by five times results in a low bias.

5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs.

5.2.2 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m^3 will cause lung damage in uninitiated. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as in Method 7, section 6.1.

6.2 Sample Recovery. Same as in Method 7, section 6.2, except the stirring rod and pH paper are not needed.

6.3 Analysis. For the analysis, the following equipment and supplies are required. Alternative instrumentation and procedures will be allowed provided the calibration precision requirement in section 10.1.2 can be met.

6.3.1 Volumetric Pipets. Class A;1-, 2-, 4-, 5-ml (two for the set of standards and one per sample), 6-, 10-, and graduated 5-ml sizes.

6.3.2 Volumetric Flasks. 50-ml (two per sample and one per standard), 200-ml, and 1-liter sizes.

6.3.3 Analytical Balance. To measure to within 0.1 mg.

6.3.4 Ion Chromatograph. The ion chromatograph should have at least the following components:

6.3.4.1 Columns. An anion separation or other column capable of resolving the nitrate ion from sulfate and other species present and a standard anion suppressor column (optional). Suppressor columns are produced as proprietary items; however, one can be produced in the laboratory using the resin available from BioRad Company, 32nd and Griffin Streets, Richmond, California. Peak resolution can be optimized by varying the eluent strength or column flow rate, or by experimenting with alternative columns that may offer more efficient separation. When using guard columns with the stronger reagent to protect the separation column, the analyst should allow rest periods between injection intervals to purge possible sulfate buildup in the guard column.

6.3.4.2 Pump. Capable of maintaining a steady flow as required by the system.

6.3.4.3 Flow Gauges. Capable of measuring the specified system flow rate.

6.3.4.4 Conductivity Detector.

6.3.4.5 Recorder. Compatible with the output voltage range of the detector.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 7, section 7.1.

7.2 Sample Recovery. Same as Method 7, section 7.1.1.

7.3 Analysis. The following reagents and standards are required for analysis:

7.3.1 Water. Same as Method 7, section 7.1.1.

7.3.2 Stock Standard Solution, 1 mg NO_2/ml. Dry an adequate amount of sodium nitrate ($NaNO_3$) at 105 to 110 °C (221 to 230 °F) for a minimum of 2 hours just before preparing the standard solution. Then dissolve exactly 1.847 g of dried $NaNO_3$ in water, and dilute to 1 liter in a volumetric flask. Mix well. This solution is stable for 1 month and should not be used beyond this time.

7.3.3 Working Standard Solution, 25 μg/ml. Dilute 5 ml of the standard solution to 200 ml with water in a volumetric flask, and mix well.

7.3.4 Eluent Solution. Weigh 1.018 g of sodium carbonate (Na_2CO_3) and 1.008 g of sodium bicarbonate ($NaHCO_3$), and dissolve in 4 liters of water. This solution is 0.0024 M Na_2CO_3/0.003 M $NaHCO_3$. Other eluents appropriate to the column type and capable of resolving nitrate ion from sulfate and other species present may be used.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling. Same as in Method 7, section 8.1.

8.2 Sample Recovery. Same as in Method 7, section 8.2, except delete the steps on adjusting and checking the pH of the sample. Do not store the samples more than 4 days between collection and analysis.

9.0 Quality Control

Section	Quality control measure	Effect
10.1	Ion chromatographn calibration	Ensure linearity of ion chromatograph response to standards.

10.0 Calibration and Standardizations

10.1 Ion Chromatograph.

10.1.1 Determination of Ion Chromatograph Calibration Factor S. Prepare a series of five standards by adding 1.0, 2.0, 4.0, 6.0, and 10.0 ml of working standard solution (25 μg/ml) to a series of five 50-ml volumetric flasks. (The standard masses will equal 25, 50, 100, 150, and 250 μg.) Dilute each flask to the mark with water, and mix well. Analyze with the samples as described in section 11.2, and subtract the blank from each value. Prepare or calculate a linear regression plot of the standard masses in μg (x-axis) versus their peak height responses in millimeters (y-axis). (Take peak height measurements with symmetrical peaks; in all other cases, calculate peak areas.) From this curve, or equation, determine the slope, and calculate its reciprocal to denote as the calibration factor, S.

10.1.2 Ion Chromatograph Calibration Quality Control. If any point on the calibration curve deviates from the line by more than 7 percent of the concentration at that point, remake and reanalyze that standard. This deviation can be determined by multiplying S times the peak height response for each standard. The resultant concentrations must not differ by more than 7 percent from each known standard mass (*i.e.*, 25, 50, 100, 150, and 250 μg).

10.2 Conductivity Detector. Calibrate according to manufacturer's specifications prior to initial use.

10.3 Barometer. Calibrate against a mercury barometer.

10.4 Temperature Gauge. Calibrate dial thermometers against mercury-in-glass thermometers. An alternative mercury-free thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

10.5 Vacuum Gauge. Calibrate mechanical gauges, if used, against a mercury manometer such as that specified in section 6.1.6 of Method 7.

10.6 Analytical Balance. Calibrate against standard weights.

11.0 Analytical Procedures

11.1 Sample Preparation.

11.1.1 Note on the analytical data sheet, the level of the liquid in the container, and whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Immediately before analysis, transfer the contents of the shipping container to a 50-ml volumetric flask, and rinse the container twice with 5 ml portions of water. Add the rinse water to the flask, and dilute to the mark with water. Mix thoroughly.

11.1.2 Pipet a 5-ml aliquot of the sample into a 50-ml volumetric flask, and dilute to the mark with water. Mix thoroughly. For each set of determinations, prepare a reagent

blank by diluting 5 ml of absorbing solution to 50 ml with water. (Alternatively, eluent solution may be used instead of water in all sample, standard, and blank dilutions.)

11.2 Analysis.

11.2.1 Prepare a standard calibration curve according to section 10.1.1. Analyze the set of standards followed by the set of samples using the same injection volume for both standards and samples. Repeat this analysis sequence followed by a final analysis of the standard set. Average the results. The two sample values must agree within 5 percent of their mean for the analysis to be valid. Perform this duplicate analysis sequence on the same day. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

11.2.2 Document each sample chromatogram by listing the following analytical parameters: injection point, injection volume, nitrate and sulfate retention times, flow rate, detector sensitivity setting, and recorder chart speed.

12.0 Data Analysis and Calculations

Carry out the calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculations.

12.1 Sample Volume. Calculate the sample volume Vsc (in ml), on a dry basis, corrected to standard conditions, using Equation 7–2 of Method 7.

12.2 Sample Concentration of NO_X as NO_2.

12.2.1 Calculate the sample concentration C (in mg/dscm) as follows:

$$C = (H)(S)(F)\left(10^4\right)/V_{sc} \qquad \text{Eq. 7A-1}$$

Where:

H = Sample peak height, mm.

S = Calibration factor, µg/mm.

F = Dilution factor (required only if sample dilution was needed to reduce the concentration into the range of calibration), dimensionless.

10^4 = 1:10 dilution times conversion factor of: $(mg/10^3\ \mu g)(10^6\ ml/m^3)$.

12.2.2 If desired, the concentration of NO_2 may be calculated as ppm NO_2 at standard conditions as follows:

$$\text{ppm } NO_2 = 0.5228C \qquad \text{Eq. 7A-2}$$

Where:

0.5228 = ml/mg NO_2.

13.0 Method Performance

13.1 Range. The analytical range of the method is from 125 to 1250 mg NO_X/m^3 as NO_2 (65 to 655 ppmv), and higher concentrations may be analyzed by diluting the sample. The lower detection limit is approximately 19 mg/m^3 (10 ppmv), but may vary among instruments.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Mulik, J.D., and E. Sawicki. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor, Ann Arbor Science Publishers, Inc. Vol. 2, 1979.

2. Sawicki, E., J.D. Mulik, and E. Wittgenstein. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor, Ann Arbor Science Publishers, Inc. Vol. 1. 1978.

3. Siemer, D.D. Separation of Chloride and Bromide from Complex Matrices Prior to Ion Chromatographic Determination. Anal. Chem. *52*(12):1874–1877. October 1980.

4. Small, H., T.S. Stevens, and W.C. Bauman. Novel Ion Exchange Chromatographic Method Using Conductimetric Determination. Anal. Chem. *47*(11):1801. 1975.

5. Yu, K.K., and P.R. Westlin. Evaluation of Reference Method 7 Flask Reaction Time. Source Evaluation Society Newsletter. *4*(4). November 1979. 10 pp.

6. Stack Sampling Safety Manual (Draft). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standard, Research Triangle Park, NC. September 1978.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 7B—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ULTRAVIOLET SPECTROPHOTOMETRIC METHOD)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 5, and Method 7.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		

Analyte	CAS No.	Sensitivity
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–0	30–786 ppmv

1.2 Applicability. This method is applicable for the determination of NO_X emissions from nitric acid plants.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution; the NO_X, excluding nitrous oxide (N_2O), are measured by ultraviolet spectrophotometry.

3.0 Definition [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m^3 will cause lung damage in uninitiated. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 7, section 6.1.

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Wash Bottle. Polyethylene or glass.

6.2.2 Volumetric Flasks. 100-ml (one for each sample).

6.3 Analysis. The following items are required for analysis:

6.3.1 Volumetric Pipettes. 5-, 10-, 15-, and 20-ml to make standards and sample dilutions.

6.3.2 Volumetric Flasks. 1000- and 100-ml for preparing standards and dilution of samples.

6.3.3 Spectrophotometer. To measure ultraviolet absorbance at 210 nm.

6.3.4 Analytical Balance. To measure to within 0.1 mg.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents are to conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 7, section 7.1. It is important that the amount of hydrogen peroxide in the absorbing solution not be increased. Higher concentrations of peroxide may interfere with sample analysis.

7.2 Sample Recovery. Same as Method 7, section 7.2.

7.3 Analysis. Same as Method 7, sections 7.3.1, 7.3.3, and 7.3.4, with the addition of the following:

7.3.1 Working Standard KNO_3 Solution. Dilute 10 ml of the standard solution to 1000 ml with water. One milliliter of the working standard is equivalent to 10 μg NO_2.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sample Collection. Same as Method 7, section 8.1.

8.2 Sample Recovery.

8.2.1 Let the flask sit for a minimum of 16 hours, and then shake the contents for 2 minutes.

8.2.2 Connect the flask to a mercury filled U-tube manometer. Open the valve from the flask to the manometer, and record the flask temperature (T_f), the barometric pressure, and the difference between the mercury levels in the manometer. The absolute internal pressure in the flask (P_f) is the barometric pressure less the manometer reading.

8.2.3 Transfer the contents of the flask to a leak-free wash bottle. Rinse the flask three times with 10-ml portions of water, and add

to the bottle. Mark the height of the liquid level so that the container can be checked for leakage after transport. Label the container to identify clearly its contents. Seal the container for shipping.

9.0 Quality Control

Section	Quality control measure	Effect
10.1	Spectrophotometer calibration	Ensures linearity of spectrophotometer response to standards.

10.0 Calibration and Standardizations

Same as Method 7, sections 10.2 through 10.5, with the addition of the following:

10.1 Determination of Spectrophotometer Standard Curve. Add 0 ml, 5 ml, 10 ml, 15 ml, and 20 ml of the KNO_3 working standard solution (1 ml = 10 µg NO_2) to a series of five 100-ml volumetric flasks. To each flask, add 5 ml of absorbing solution. Dilute to the mark with water. The resulting solutions contain 0.0, 50, 100, 150, and 200 µg NO_2, respectively. Measure the absorbance by ultraviolet spectrophotometry at 210 nm, using the blank as a zero reference. Prepare a standard curve plotting absorbance vs. µg NO_2.

NOTE: If other than a 20-ml aliquot of sample is used for analysis, then the amount of absorbing solution in the blank and standards must be adjusted such that the same amount of absorbing solution is in the blank and standards as is in the aliquot of sample used.

10.1.1 Calculate the spectrophotometer calibration factor as follows:

$$K_c = \frac{\sum_{i=1}^{n} M_i A_i}{\sum_{i=1}^{n} A_i^2} \qquad \text{Eq. 7B-1}$$

Where:

Mi = Mass of NO_2 in standard i, µg.
Ai = Absorbance of NO_2 standard i.
n = Total number of calibration standards.

10.1.2 For the set of calibration standards specified here, Equation 7B–1 simplifies to the following:

$$K_c = 50\frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2} \qquad \text{Eq. 7B-2}$$

10.2 Spectrophotometer Calibration Quality Control. Multiply the absorbance value obtained for each standard by the K_c factor (reciprocal of the least squares slope) to determine the distance each calibration point lies from the theoretical calibration line. The difference between the calculated concentration values and the actual concentrations (*i.e.*, 50, 100, 150, and 200 µg NO_2) should be less than 7 percent for all standards.

11.0 Analytical Procedures

11.1 Sample Loss Check. Note the level of the liquid in the container, and confirm whether any sample was lost during shipment. Note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Preparation. Immediately prior to analysis, transfer the contents of the shipping container to a 100-ml volumetric flask, and rinse the container twice with 5-ml portions of water. Add the rinse water to the flask, and dilute to mark with water.

11.3 Sample Analysis. Mix the contents of the flask thoroughly and pipette a 20 ml-aliquot of sample into a 100-ml volumetric flask. Dilute to the mark with water. Using the blank as zero reference, read the absorbance of the sample at 210 nm.

11.4 Audit Sample Analysis. Same as Method 7, section 11.4, except that a set of audit samples must be analyzed with each set of compliance samples or once per analysis day, or once per week when averaging continuous samples.

12.0 Data Analysis and Calculations

Same as Method 7, section 12.0, except replace section 12.3 with the following:

12.1 Total µg NO_2 Per Sample.

$$m = 5\,K_c\,A\,F \qquad \text{Eq. 7B-3}$$

Where:

5 = 100/20, the aliquot factor.

NOTE: If other than a 20-ml aliquot is used for analysis, the factor 5 must be replaced by a corresponding factor.

13.0 Method Performance

13.1 Range. The analytical range of the method as outlined has been determined to be 57 to 1500 milligrams NO_X (as NO_2) per dry standard cubic meter, or 30 to 786 parts per million by volume (ppmv) NO_X.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. National Institute for Occupational Safety and Health. Recommendations for Occupational Exposure to Nitric Acid. In: Occupational Safety and Health Reporter. Washington, D.C. Bureau of National Affairs, Inc. 1976. p. 149.

2. Rennie, P.J., A.M. Sumner, and F.B. Basketter. Determination of Nitrate in Raw, Potable, and Waste Waters by Ultraviolet Spectrophotometry. Analyst. *104*:837. September 1979.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 7C—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ALKALINE PERMANGANATE/COLORIMETRIC METHOD)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 3, Method 6 and Method 7.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS no.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–07	ppmv

1.2 Applicability. This method applies to the measurement of NO_X emissions from fossil-fuel fired steam generators, electric utility plants, nitric acid plants, or other sources as specified in the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

An integrated gas sample is extracted from the stack and passed through impingers containing an alkaline potassium permanganate solution; NO_X (NO + NO_2) emissions are oxidized to NO_2 and NO_3. Then NO_3^- is reduced to NO_2^- with cadmium, and the NO_2^- is analyzed colorimetrically.

3.0 Definitions [Reserved]

4.0 Interferences

Possible interferents are sulfur dioxides (SO_2) and ammonia (NH_3).

4.1 High concentrations of SO_2 could interfere because SO_2 consumes MnO_4 (as does NO_X) and, therefore, could reduce the NO_X collection efficiency. However, when sampling emissions from a coal-fired electric utility plant burning 2.1 percent sulfur coal with no control of SO_2 emissions, collection efficiency was not reduced. In fact, calculations show that sampling 3000 ppm SO_2 will reduce the MnO_4 concentration by only 5 percent if all the SO_2 is consumed in the first impinger.

4.2 Ammonia (NH_3) is slowly oxidized to NO_3^- by the absorbing solution. At 100 ppm NH_3 in the gas stream, an interference of 6 ppm NO_X (11 mg NO_2/m^3) was observed when the sample was analyzed 10 days after collection. Therefore, the method may not be applicable to plants using NH_3 injection to control NO_X emissions unless means are taken to correct the results. An equation has been developed to allow quantification of the interference and is discussed in Reference 5 of section 16.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrochloric Acid (HCl). Highly toxic and corrosive. Causes severe damage to skin. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to vapor concentrations of 0.13 to 0.2 percent can be lethal in minutes. Will react with metals, producing hydrogen.

5.2.2 Oxalic Acid $(COOH)_2$. Poisonous. Irritating to eyes, skin, nose, and throat.

5.2.3 Sodium Hydroxide (NaOH). Causes severe damage to eye tissues and to skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with small amounts of water.

5.2.4 Potassium Permanganate ($KMnO_4$). Caustic, strong oxidizer. Avoid bodily contact with.

6.0 Equipment and Supplies

6.1 Sample Collection and Sample Recovery. A schematic of the Method 7C sampling train is shown in Figure 7C–1, and component parts are discussed below. Alternative apparatus and procedures are allowed provided acceptable accuracy and precision can be demonstrated to the satisfaction of the Administrator.

6.1.1 Probe. Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or heated out-of-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Stainless steel or Teflon tubing may also be used for the probe.

6.1.2 Impingers. Three restricted-orifice glass impingers, having the specifications given in Figure 7C–2, are required for each sampling train. The impingers must be connected in series with leak-free glass connectors. Stopcock grease may be used, if necessary, to prevent leakage. (The impingers can be fabricated by a glass blower if not available commercially.)

6.1.3 Glass Wool, Stopcock Grease, Drying Tube, Valve, Pump, Barometer, and Vacuum Gauge and Rotameter. Same as in Method 6, sections 6.1.1.3, 6.1.1.4, 6.1.1.6, 6.1.1.7, 6.1.1.8, 6.1.2, and 6.1.3, respectively.

6.1.4 Rate Meter. Rotameter, or equivalent, accurate to within 2 percent at the selected flow rate of between 400 and 500 ml/min (0.014 to 0.018 cfm). For rotameters, a range of 0 to 1 liter/min (0 to 0.035 cfm) is recommended.

6.1.5 Volume Meter. Dry gas meter (DGM) capable of measuring the sample volume under the sampling conditions of 400 to 500 ml/min (0.014 to 0.018 cfm) for 60 minutes within an accuracy of 2 percent.

6.1.6 Filter. To remove NO_X from ambient air, prepared by adding 20 g of 5-angstrom molecular sieve to a cylindrical tube (*e.g.*, a polyethylene drying tube).

6.1.7 Polyethylene Bottles. 1-liter, for sample recovery.

6.1.8 Funnel and Stirring Rods. For sample recovery.

6.2 Sample Preparation and Analysis.

6.2.1 Hot Plate. Stirring type with 50- by 10-mm Teflon-coated stirring bars.

6.2.2 Beakers. 400-, 600-, and 1000-ml capacities.

6.2.3 Filtering Flask. 500-ml capacity with side arm.

6.2.4 Buchner Funnel. 75-mm ID, with spout equipped with a 13-mm ID by 90-mm long piece of Teflon tubing to minimize possibility of aspirating sample solution during filtration.

6.2.5 Filter Paper. Whatman GF/C, 7.0-cm diameter.

6.2.6 Stirring Rods.

6.2.7 Volumetric Flasks. 100-, 200- or 250-, 500-, and 1000-ml capacity.

6.2.8 Watch Glasses. To cover 600- and 1000-ml beakers.

6.2.9 Graduated Cylinders. 50- and 250-ml capacities.

6.2.10 Pipettes. Class A.

6.2.11 pH Meter. To measure pH from 0.5 to 12.0.

6.2.12 Burette. 50-ml with a micrometer type stopcock. (The stopcock is Catalog No. 8225–t–05, Ace Glass, Inc., Post Office Box 996, Louisville, Kentucky 50201.) Place a glass wool plug in bottom of burette. Cut off burette at a height of 43 cm (17 in.) from the top of plug, and have a blower attach a glass funnel to top of burette such that the diameter of the burette remains essentially unchanged. Other means of attaching the funnel are acceptable.

6.2.13 Glass Funnel. 75-mm ID at the top.

6.2.14 Spectrophotometer. Capable of measuring absorbance at 540 nm; 1-cm cells are adequate.

6.2.15 Metal Thermometers. Bimetallic thermometers, range 0 to 150 °C (32 to 300 °F).

6.2.16 Culture Tubes. 20-by 150-mm, Kimax No. 45048.

6.2.17 Parafilm ''M.'' Obtained from American Can Company, Greenwich, Connecticut 06830.

6.2.18 CO_2 Measurement Equipment. Same as in Method 3, section 6.0.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection.

7.1.1 Water. Deionized distilled to conform to ASTM Specification D 1193–77 or 91 Type 3 (incorporated by reference—see § 60.17).

7.1.2 Potassium Permanganate, 4.0 Percent (w/w), Sodium Hydroxide, 2.0 Percent (w/w) solution ($KMnO_4$/NaOH solution). Dissolve 40.0 g of $KMnO_4$ and 20.0 g of NaOH in 940 ml of water.

7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in section 7.1.1.

7.2.2 Oxalic Acid Solution. Dissolve 48 g of oxalic acid [$(COOH)_2 \cdot 2H_2O$] in water, and dilute to 500 ml. Do not heat the solution.

7.2.3 Sodium Hydroxide, 0.5 N. Dissolve 20 g of NaOH in water, and dilute to 1 liter.

7.2.4 Sodium Hydroxide, 10 N. Dissolve 40 g of NaOH in water, and dilute to 100 ml.

7.2.5 Ethylenediamine Tetraacetic Acid (EDTA) Solution, 6.5 percent (w/v). Dissolve 6.5 g of EDTA (disodium salt) in water, and dilute to 100 ml. Dissolution is best accomplished by using a magnetic stirrer.

7.2.6 Column Rinse Solution. Add 20 ml of 6.5 percent EDTA solution to 960 ml of water, and adjust the pH to between 11.7 and 12.0 with 0.5 N NaOH.

7.2.7 Hydrochloric Acid (HCl), 2 N. Add 86 ml of concentrated HCl to a 500 ml-volumetric flask containing water, dilute to volume, and mix well. Store in a glass-stoppered bottle.

7.2.8 Sulfanilamide Solution. Add 20 g of sulfanilamide (melting point 165 to 167 °C (329 to 333 °F)) to 700 ml of water. Add, with mixing, 50 ml concentrated phosphoric acid (85 percent), and dilute to 1000 ml. This solution is stable for at least 1 month, if refrigerated.

7.2.9 N-(1-Naphthyl)-Ethylenediamine Dihydrochloride (NEDA) Solution. Dissolve 0.5 g of NEDA in 500 ml of water. An aqueous solution should have one absorption peak at 320 nm over the range of 260 to 400 nm. NEDA that shows more than one absorption peak over this range is impure and should not be used. This solution is stable for at least 1 month if protected from light and refrigerated.

7.2.10 Cadmium. Obtained from Matheson Coleman and Bell, 2909 Highland Avenue, Norwood, Ohio 45212, as EM Laboratories Catalog No. 2001. Prepare by rinsing in 2 N HCl for 5 minutes until the color is silver-grey. Then rinse the cadmium with water until the rinsings are neutral when tested with pH paper. CAUTION: H_2 is liberated during preparation. Prepare in an exhaust hood away from any flame or combustion source.

7.2.11 Sodium Sulfite ($NaNO_2$) Standard Solution, Nominal Concentration, 1000 μg NO_2^-/ml. Desiccate NaNO2 overnight. Accurately weigh 1.4 to 1.6 g of $NaNO_2$ (assay of 97 percent $NaNO_2$ or greater), dissolve in water, and dilute to 1 liter. Calculate the exact NO_2^- concentration using Equation 7C–1 in section 12.2. This solution is stable for at least 6 months under laboratory conditions.

7.2.12 Potassium Nitrate (KNO_3) Standard Solution. Dry KNO_3 at 110 °C (230 °F) for 2 hours, and cool in a desiccator. Accurately weigh 9 to 10 g of KNO_3 to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact NO_3^- concentration using Equation 7C–2 in section 12.3. This solution is stable for 2 months without preservative under laboratory conditions.

7.2.13 Spiking Solution. Pipette 7 ml of the KNO_3 standard into a 100-ml volumetric flask, and dilute to volume.

7.2.14 Blank Solution. Dissolve 2.4 g of $KMnO_4$ and 1.2 g of NaOH in 96 ml of water. Alternatively, dilute 60 ml of $KMnO_4$/NaOH solution to 100 ml.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Preparation of Sampling Train. Add 200 ml of $KMnO_4$/NaOH solution (Section 7.1.2) to each of three impingers, and assemble the train as shown in Figure 7C–1. Adjust the probe heater to a temperature sufficient to prevent water condensation.

8.2 Leak-Checks. Same as in Method 6, section 8.2.

8.3 Sample Collection.

8.3.1 Record the initial DGM reading and barometric pressure. Determine the sampling point or points according to the appropriate regulations (*e.g.*, §60.46(b)(5) of 40 CFR Part 60). Position the tip of the probe at the sampling point, connect the probe to the first impinger, and start the pump. Adjust the sample flow to a value between 400 and 500 ml/min (0.014 and 0.018 cfm). CAUTION: DO NOT EXCEED THESE FLOW RATES. Once adjusted, maintain a constant flow rate during the entire sampling run. Sample for 60 minutes. For relative accuracy (RA) testing of continuous emission monitors, the minimum sampling time is 1 hour, sampling 20 minutes at each traverse point.

NOTE: When the SO_2 concentration is greater than 1200 ppm, the sampling time may have to be reduced to 30 minutes to eliminate plugging of the impinger orifice with MnO_2. For RA tests with SO_2 greater than 1200 ppm, sample for 30 minutes (10 minutes at each point).

8.3.2 Record the DGM temperature, and check the flow rate at least every 5 minutes. At the conclusion of each run, turn off the pump, remove the probe from the stack, and record the final readings. Divide the sample volume by the sampling time to determine the average flow rate. Conduct the mandatory post-test leak-check. If a leak is found, void the test run, or use procedures acceptable to the Administrator to adjust the sample volume for the leakage.

8.4 CO_2 Measurement. During sampling, measure the CO_2 content of the stack gas near the sampling point using Method 3. The single-point grab sampling procedure is adequate, provided the measurements are made at least three times (near the start, midway, and before the end of a run), and the average CO_2 concentration is computed. The Orsat or Fyrite analyzer may be used for this analysis.

8.5 Sample Recovery. Disconnect the impingers. Pour the contents of the impingers into a 1-liter polyethylene bottle

using a funnel and a stirring rod (or other means) to prevent spillage. Complete the quantitative transfer by rinsing the impingers and connecting tubes with water until the rinsings are clear to light pink, and add the rinsings to the bottle. Mix the sample, and mark the solution level. Seal and identify the sample container.

9.0 Quality Control

Section	Quality control measure	Effect
8.2, 10.1–10.3	Sampling equipment leak-check and calibration.	Ensure accurate measurement of sample volume.
10.4	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards
11.3	Spiked sample analysis.	Ensure reduction efficiency of column.

10.0 Calibration and Standardizations

10.1 Volume Metering System. Same as Method 6, section 10.1. For detailed instructions on carrying out these calibrations, it is suggested that section 3.5.2 of Reference 4 of section 16.0 be consulted.

10.2 Temperature Sensors and Barometer. Same as in Method 6, sections 10.2 and 10.4, respectively.

10.3 Check of Rate Meter Calibration Accuracy (Optional). Disconnect the probe from the first impinger, and connect the filter. Start the pump, and adjust the rate meter to read between 400 and 500 ml/min (0.014 and 0.018 cfm). After the flow rate has stabilized, start measuring the volume sampled, as recorded by the dry gas meter and the sampling time. Collect enough volume to measure accurately the flow rate. Then calculate the flow rate. This average flow rate must be less than 500 ml/min (0.018 cfm) for the sample to be valid; therefore, it is recommended that the flow rate be checked as above prior to each test.

10.4 Spectrophotometer.

10.4.1 Dilute 5.0 ml of the $NaNO_2$ standard solution to 200 ml with water. This solution nominally contains 25 μg NO_2^-/ml. Use this solution to prepare calibration standards to cover the range of 0.25 to 3.00 μg NO_2^-/ml. Prepare a minimum of three standards each for the linear and slightly nonlinear (described below) range of the curve. Use pipettes for all additions.

10.4.2 Measure the absorbance of the standards and a water blank as instructed in section 11.5. Plot the net absorbance vs. μg NO_2^-/ml. Draw a smooth curve through the points. The curve should be linear up to an absorbance of approximately 1.2 with a slope of approximately 0.53 absorbance units/μg NO_2^-/ml. The curve should pass through the origin. The curve is slightly nonlinear from an absorbance of 1.2 to 1.6.

11.0 Analytical Procedures

11.1 Sample Stability. Collected samples are stable for at least four weeks; thus, analysis must occur within 4 weeks of collection.

11.2 Sample Preparation.

11.2.1 Prepare a cadmium reduction column as follows: Fill the burette with water. Add freshly prepared cadmium slowly, with tapping, until no further settling occurs. The height of the cadmium column should be 39 cm (15 in). When not in use, store the column under rinse solution.

NOTE: The column should not contain any bands of cadmium fines. This may occur if regenerated cadmium is used and will greatly reduce the column lifetime.

11.2.2 Note the level of liquid in the sample container, and determine whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume lost can be determined from the difference between initial and final solution levels, and this value can then be used to correct the analytical result. Quantitatively transfer the contents to a 1-liter volumetric flask, and dilute to volume.

11.2.3 Take a 100-ml aliquot of the sample and blank (unexposed $KMnO_4$/NaOH) solutions, and transfer to 400-ml beakers containing magnetic stirring bars. Using a pH meter, add concentrated H_2SO_4 with stirring until a pH of 0.7 is obtained. Allow the solutions to stand for 15 minutes. Cover the beakers with watch glasses, and bring the temperature of the solutions to 50 °C (122 °F). Keep the temperature below 60 °C (140 °F). Dissolve 4.8 g of oxalic acid in a minimum volume of water, approximately 50 ml, at room temperature. Do not heat the solution. Add this solution slowly, in increments, until the $KMnO_4$ solution becomes colorless. If the color is not completely removed, prepare some more of the above oxalic acid solution, and add until a colorless solution is obtained. Add an excess of oxalic acid by dissolving 1.6 g of oxalic acid in 50 ml of water, and add 6 ml of this solution to the colorless solution. If suspended matter is present, add concentrated H_2SO_4 until a clear solution is obtained.

11.2.4 Allow the samples to cool to near room temperature, being sure that the samples are still clear. Adjust the pH to between 11.7 and 12.0 with 10 N NaOH. Quantitatively transfer the mixture to a Buchner funnel containing GF/C filter paper, and filter the

precipitate. Filter the mixture into a 500-ml filtering flask. Wash the solid material four times with water. When filtration is complete, wash the Teflon tubing, quantitatively transfer the filtrate to a 500-ml volumetric flask, and dilute to volume. The samples are now ready for cadmium reduction. Pipette a 50-ml aliquot of the sample into a 150-ml beaker, and add a magnetic stirring bar. Pipette in 1.0 ml of 6.5 percent EDTA solution, and mix.

11.3 Determine the correct stopcock setting to establish a flow rate of 7 to 9 ml/min of column rinse solution through the cadmium reduction column. Use a 50-ml graduated cylinder to collect and measure the solution volume. After the last of the rinse solution has passed from the funnel into the burette, but before air entrapment can occur, start adding the sample, and collect it in a 250-ml graduated cylinder. Complete the quantitative transfer of the sample to the column as the sample passes through the column. After the last of the sample has passed from the funnel into the burette, start adding 60 ml of column rinse solution, and collect the rinse solution until the solution just disappears from the funnel. Quantitatively transfer the sample to a 200-ml volumetric flask (a 250-ml flask may be required), and dilute to volume. The samples are now ready for NO_2-analysis.

NOTE: Two spiked samples should be run with every group of samples passed through the column. To do this, prepare two additional 50-ml aliquots of the sample suspected to have the highest NO_2-concentration, and add 1 ml of the spiking solution to these aliquots. If the spike recovery or column efficiency (see section 12.2) is below 95 percent, prepare a new column, and repeat the cadmium reduction.

11.5 Sample Analysis. Pipette 10 ml of sample into a culture tube. Pipette in 10 ml of sulfanilamide solution and 1.4 ml of NEDA solution. Cover the culture tube with parafilm, and mix the solution. Prepare a blank in the same manner using the sample from treatment of the unexposed $KMnO_4$/NaOH solution. Also, prepare a calibration standard to check the slope of the calibration curve. After a 10-minute color development interval, measure the absorbance at 540 nm against water. Read μg NO_2^-/ml from the calibration curve. If the absorbance is greater than that of the highest calibration standard, use less than 10 ml of sample, and repeat the analysis. Determine the NO_2^-concentration using the calibration curve obtained in section 10.4.

NOTE: Some test tubes give a high blank NO_2^- value but culture tubes do not.

11.6 Audit Sample Analysis. Same as in Method 7, section 11.4.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature.

B = Analysis of blank, μg NO_2^-/ml.
C = Concentration of NO_X as NO_2, dry basis, mg/dsm³.
E = Column efficiency, dimensionless
$K_2 = 10^{-3}$ mg/μg.
m = Mass of NO_X, as NO_2, in sample, μg.
P_{bar} = Barometric pressure, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
s = Concentration of spiking solution, μg NO_3/ml.
S = Analysis of sample, μg NO_2^-/ml.
T_m = Average dry gas meter absolute temperature, °K.
T_{std} = Standard absolute temperature, 293 °K (528 °R).
$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).
V_m = Dry gas volume as measured by the dry gas meter, scm (scf).
x = Analysis of spiked sample, μg NO_2^-/ml.
X = Correction factor for CO_2 collection = $100/(100 - \%CO_2(V/V))$.
y = Analysis of unspiked sample, μg NO_2^-/ml.
Y = Dry gas meter calibration factor.
1.0 ppm NO = 1.247 mg NO/m³ at STP.
1.0 ppm NO_2 = 1.912 mg NO_2/m³ at STP.
1 ft³ = 2.832×10^{-2} m³.

12.2 NO_2 Concentration. Calculate the NO_2 concentration of the solution (see section 7.2.11) using the following equation:

$$\frac{\mu g\ NO_2^-}{ml} = g\ NaNO_2 \times \frac{purity,\ \%}{100} \times 10^3 \times \frac{46.01}{69.01} \qquad \text{Eq. 7C-1}$$

12.3 NO_3 Concentration. Calculate the NO_3 concentration of the KNO_3 solution (see section 7.2.12) using the following equation:

$$\frac{\mu g\ NO_3^-}{ml} = g\ KNO_3 \times \left(10^3\right) \times \frac{62.01}{101.10} \qquad \text{Eq. 7C-2}$$

12.4 Sample Volume, Dry Basis, Corrected to Standard Conditions.

$$V_{m(std)} = V_m\ X\ Y \frac{T_{std}}{T_m} \frac{P_{bar}}{P_{std}} \qquad \text{Eq. 7C-3}$$

$$= K_1\ X\ Y\ V_m \frac{P_{bar}}{T_m}$$

Where:

K_1 = 0.3855 °K/mm Hg for metric units.
K_1 = 17.65 °R/in. Hg for English units.

12.5 Efficiency of Cadmium Reduction Column. Calculate this value as follows:

$$E = \frac{200\ (x-y)}{1.0\ s\ \frac{46.01}{62.01}} = \frac{269.6\ (x-y)}{s} \qquad \text{Eq. 7C-4}$$

Where:

200 = Final volume of sample and blank after passing through the column, ml.
1.0 = Volume of spiking solution added, ml.
46.01=μg NO_2^-/μmole.
62.01=μg NO_3^-/μmole.

12.6 Total μg NO_2.

$$m = 200\left(\frac{500}{50}\right)\left(\frac{1000}{100}\right)\left(\frac{(S-B)}{E}\right) = \frac{(2\times10^4)(S-B)}{E} \qquad \text{Eq. 7C-5}$$

Where:

500 = Total volume of prepared sample, ml.
50 = Aliquot of prepared sample processed through cadmium column, ml.
100 = Aliquot of $KMnO_4$/NaOH solution, ml.
1000 = Total volume of $KMnO_4$/NaOH solution, ml.

12.7 Sample Concentration.

$$C = K_2 \frac{m}{V_{m(std)}} \qquad \text{Eq. 7C-6}$$

13.0 Method Performance

13.1 Precision. The intra-laboratory relative standard deviation for a single measurement is 2.8 and 2.9 percent at 201 and 268 ppm NO_X, respectively.

13.2 Bias. The method does not exhibit any bias relative to Method 7.

13.3 Range. The lower detectable limit is 13 mg NO_X/m^3, as NO_2 (7 ppm NO_X) when sampling at 500 ml/min for 1 hour. No upper limit has been established; however, when using the recommended sampling conditions, the method has been found to collect NO_X emissions quantitatively up to 1782 mg NO_X/m^3, as NO_2 (932 ppm NO_X).

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Margeson, J.H., W.J. Mitchell, J.C. Suggs, and M.R. Midgett. Integrated Sampling and Analysis Methods for Determining NO_X Emissions at Electric Utility Plants. U.S. Environmental Protection Agency, Research Triangle Park, NC. Journal of the Air Pollution Control Association. *32*:1210–1215. 1982.

2. Memorandum and attachment from J.H. Margeson, Source Branch, Quality Assurance Division, Environmental Monitoring Systems Laboratory, to The Record, EPA. March 30, 1983. NH_3 Interference in Methods 7C and 7D.

3. Margeson, J.H., J.C. Suggs, and M.R. Midgett. Reduction of Nitrate to Nitrite with Cadmium. Anal. Chem. *52*:1955–57. 1980.

4. Quality Assurance Handbook for Air Pollution Measurement Systems. Volume III—Stationary Source Specific Methods. U.S.

Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA–600/4–77–027b. August 1977.

5. Margeson, J.H., *et al.* An Integrated Method for Determining NO_X Emissions at Nitric Acid Plants. Analytical Chemistry. *47* (11):1801. 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

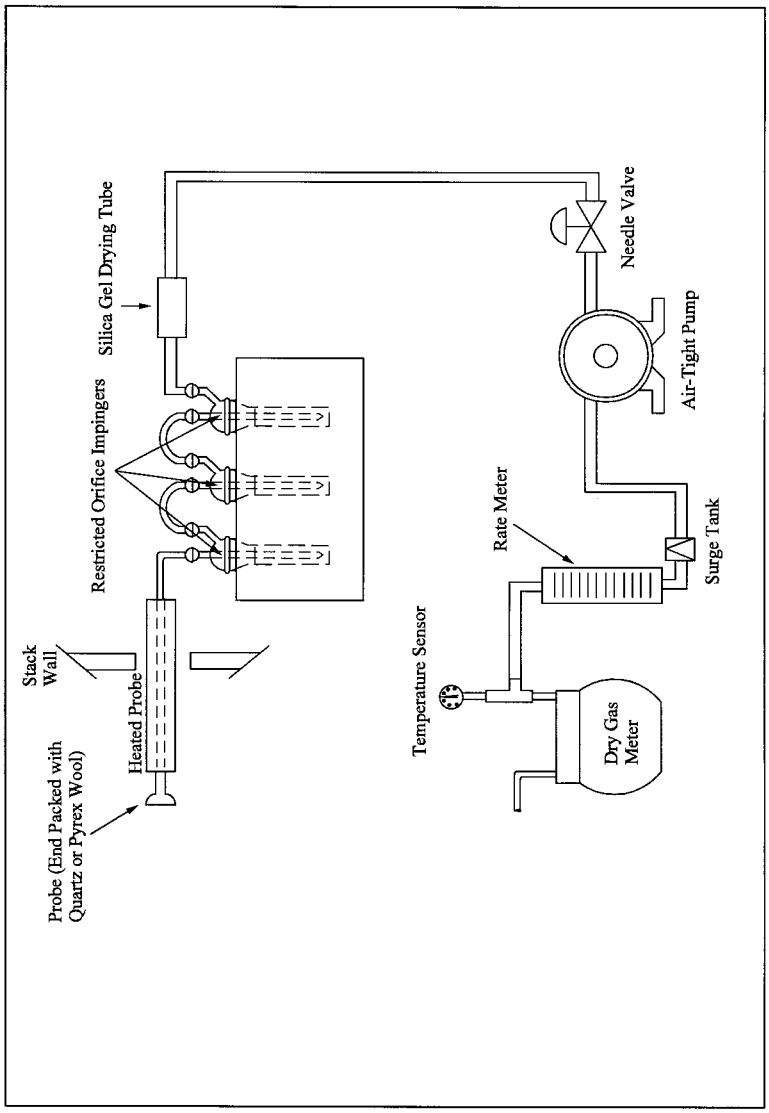

Figure 7C-1. NO_x Sampling Train.

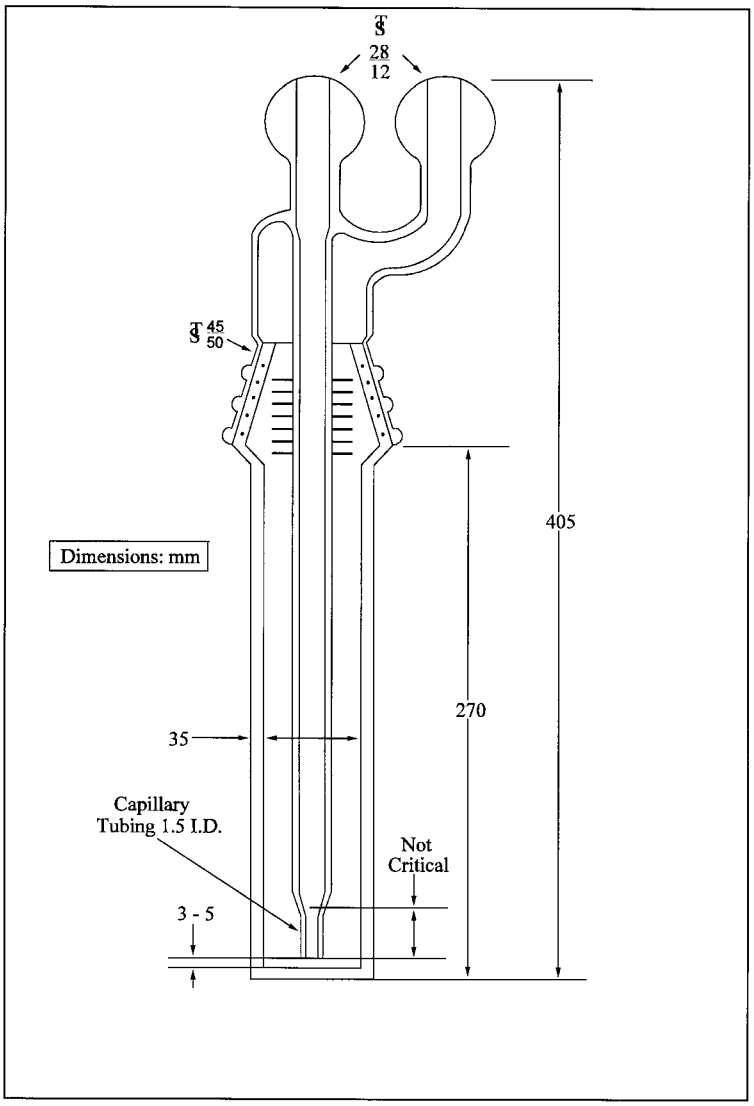

Figure 7C-2. Restricted-Orifice Impinger.

METHOD 7D—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ALKALINE-PERMANGANATE/ION CHROMATOGRAPHIC METHOD)

NOTE: This method is not inclusive with respect to specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 3, Method 6, Method 7, and Method 7C.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–0	7 ppmv

1.2 Applicability. This method applies to the measurement of NO_X emissions from fossil-fuel fired steam generators, electric utility plants, nitric acid plants, or other sources as specified in the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

An integrated gas sample is extracted from the stack and passed through impingers containing an alkaline-potassium permanganate solution; NO_X ($NO + NO_2$) emissions are oxidized to NO_3^-. Then NO_3^- is analyzed by ion chromatography.

3.0 Definitions [Reserved]

4.0 Interferences

Same as in Method 7C, section 4.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs. 30% H_2O_2 is a strong oxidizing agent; avoid contact with skin, eyes, and combustible material. Wear gloves when handling.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eye tissues and to skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Potassium Permanganate ($KMnO_4$). Caustic, strong oxidizer. Avoid bodily contact with.

6.0 Equipment and Supplies

6.1 Sample Collection and Sample Recovery. Same as Method 7C, section 6.1. A schematic of the sampling train used in performing this method is shown in Figure 7C–1 of Method 7C.

6.2 Sample Preparation and Analysis.

6.2.1 Magnetic Stirrer. With 25- by 10-mm Teflon-coated stirring bars.

6.2.2 Filtering Flask. 500-ml capacity with sidearm.

6.2.3 Buchner Funnel. 75-mm ID, with spout equipped with a 13-mm ID by 90-mm long piece of Teflon tubing to minimize possibility of aspirating sample solution during filtration.

6.2.4 Filter Paper. Whatman GF/C, 7.0-cm diameter.

6.2.5 Stirring Rods.

6.2.6 Volumetric Flask. 250-ml.

6.2.7 Pipettes. Class A.

6.2.8 Erlenmeyer Flasks. 250-ml.

6.2.9 Ion Chromatograph. Equipped with an anion separator column to separate NO_3^-, H_3^+ suppressor, and necessary auxiliary equipment. Nonsuppressed and other forms of ion chromatography may also be used provided that adequate resolution of NO_3^- is obtained. The system must also be able to resolve and detect NO_2^-.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection.

7.1.1 Water. Deionized distilled to conform to ASTM specification D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17).

7.1.2 Potassium Permanganate, 4.0 Percent (w/w), Sodium Hydroxide, 2.0 Percent (w/w). Dissolve 40.0 g of $KMnO_4$ and 20.0 g of NaOH in 940 ml of water.

7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in section 7.1.1.

7.2.2 Hydrogen Peroxide (H_2O_2), 5 Percent. Dilute 30 percent H_2O_2 1:5 (v/v) with water.

7.2.3 Blank Solution. Dissolve 2.4 g of $KMnO_4$ and 1.2 g of NaOH in 96 ml of water. Alternatively, dilute 60 ml of $KMnO_4$/NaOH solution to 100 ml.

7.2.4 KNO_3 Standard Solution. Dry KNO_3 at 110 °C for 2 hours, and cool in a desiccator. Accurately weigh 9 to 10 g of KNO_3 to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact NO_3^- concentration using Equation 7D–1 in section 12.2. This

solution is stable for 2 months without preservative under laboratory conditions.

7.2.5 Eluent, 0.003 M $NaHCO_3$/0.0024 M Na_2CO_3. Dissolve 1.008 g $NaHCO_3$ and 1.018 g Na_2CO_3 in water, and dilute to 4 liters. Other eluents capable of resolving nitrate ion from sulfate and other species present may be used.

8.0 Sample Collection, Preservation, Transport, and Storage.

8.1 Sampling. Same as in Method 7C, section 8.1.

8.2 Sample Recovery. Same as in Method 7C, section 8.2.

8.3 Sample Preparation for Analysis.

NOTE: Samples must be analyzed within 28 days of collection.

8.3.1 Note the level of liquid in the sample container, and determine whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume lost can be determined from the difference between initial and final solution levels, and this value can then be used to correct the analytical result. Quantitatively transfer the contents to a 1-liter volumetric flask, and dilute to volume.

8.3.2 Sample preparation can be started 36 hours after collection. This time is necessary to ensure that all NO_2^- is converted to NO_3^- in the collection solution. Take a 50-ml aliquot of the sample and blank, and transfer to 250-ml Erlenmeyer flasks. Add a magnetic stirring bar. Adjust the stirring rate to as fast a rate as possible without loss of solution. Add 5 percent H_2O_2 in increments of approximately 5 ml using a 5-ml pipette. When the $KMnO_4$ color appears to have been removed, allow the precipitate to settle, and examine the supernatant liquid. If the liquid is clear, the H_2O_2 addition is complete. If the $KMnO_4$ color persists, add more H_2O_2, with stirring, until the supernatant liquid is clear.

NOTE: The faster the stirring rate, the less volume of H_2O_2 that will be required to remove the $KMnO_4$.) Quantitatively transfer the mixture to a Buchner funnel containing GF/C filter paper, and filter the precipitate. The spout of the Buchner funnel should be equipped with a 13-mm ID by 90-mm long piece of Teflon tubing. This modification minimizes the possibility of aspirating sample solution during filtration. Filter the mixture into a 500-ml filtering flask. Wash the solid material four times with water. When filtration is complete, wash the Teflon tubing, quantitatively transfer the filtrate to a 250-ml volumetric flask, and dilute to volume. The sample and blank are now ready for NO_3^- analysis.

9.0 Quality Control

Section	Quality control measure	Effect
8.2, 10.1–10.3	Sampling equipment leak-check and calibration.	Ensure accurate measurement of sample volume.
10.4	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.
11.3	Spiked sample analysis	Ensure reduction efficiency of column.

10.0 Calibration and Standardizations

10.1 Dry Gas Meter (DGM) System.

10.1.1 Initial Calibration. Same as in Method 6, section 10.1.1. For detailed instructions on carrying out this calibration, it is suggested that section 3.5.2 of Citation 4 in section 16.0 of Method 7C be consulted.

10.1.2 Post-Test Calibration Check. Same as in Method 6, section 10.1.2.

10.2 Thermometers for DGM and Barometer. Same as in Method 6, sections 10.2 and 10.4, respectively.

10.3 Ion Chromatograph.

10.3.1 Dilute a given volume (1.0 ml or greater) of the KNO_3 standard solution to a convenient volume with water, and use this solution to prepare calibration standards. Prepare at least four standards to cover the range of the samples being analyzed. Use pipettes for all additions. Run standards as instructed in section 11.2. Determine peak height or area, and plot the individual values versus concentration in µg NO_3^-/ml.

10.3.2 Do not force the curve through zero. Draw a smooth curve through the points. The curve should be linear. With the linear curve, use linear regression to determine the calibration equation.

11.0 Analytical Procedures

11.1 The following chromatographic conditions are recommended: 0.003 M $NaHCO_3$/0.0024 Na_2CO_3 eluent solution (Section 7.2.5), full scale range, 3 µMHO; sample loop, 0.5 ml; flow rate, 2.5 ml/min. These conditions should give a NO_3^- retention time of approximately 15 minutes (Figure 7D–1).

11.2 Establish a stable baseline. Inject a sample of water, and determine whether any NO_3^- appears in the chromatogram. If NO_3^- is present, repeat the water load/injection procedure approximately five times; then reinject a water sample and observe the chromatogram. When no NO_3^- is present, the instrument is ready for use. Inject calibration standards. Then inject samples and a blank. Repeat the injection of the calibration

standards (to compensate for any drift in response of the instrument). Measure the NO_3^- peak height or peak area, and determine the sample concentration from the calibration curve.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature. Same as in Method 7C, section 12.1.

12.2 NO_3^- concentration. Calculate the NO_3^- concentration in the KNO_3 standard solution (see section 7.2.4) using the following equation:

$$\frac{\mu g\ NO_3^-}{ml} = g\ of\ KNO_3 \times 10^3 \times \frac{62.01}{101.10} \qquad \text{Eq. 7D-1}$$

12.3 Sample Volume, Dry Basis, Corrected to Standard Conditions. Same as in Method 7C, section 12.4.

12.4 Total μg NO_2 Per Sample.

$$m = 250\left(\frac{1000}{50}\right)\left(\frac{46.01}{62.01}\right)(S-B) \qquad \text{Eq. 7D-2}$$
$$= 3710\ (S-B)$$

Where:

250 = Volume of prepared sample, ml.

1000 = Total volume of $KMnO_4$ solution, ml.

50 = Aliquot of $KMnO_4$/NaOH solution, ml.

46.01 = Molecular weight of NO_3^-.

62.01 = Molecular weight of NO_3^-.

12.5 Sample Concentration. Same as in Method 7C, section 12.7.

13.0 Method Performance

13.1 Precision. The intra-laboratory relative standard deviation for a single measurement is approximately 6 percent at 200 to 270 ppm NO_X.

13.2 Bias. The method does not exhibit any bias relative to Method 7.

13.3 Range. The lower detectable limit is similar to that of Method 7C. No upper limit has been established; however, when using the recommended sampling conditions, the method has been found to collect NO_X emissions quantitatively up to 1782 mg NO_X/m^3, as NO_2 (932 ppm NO_X).

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 7C, section 16.0, References 1, 2, 4, and 5.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

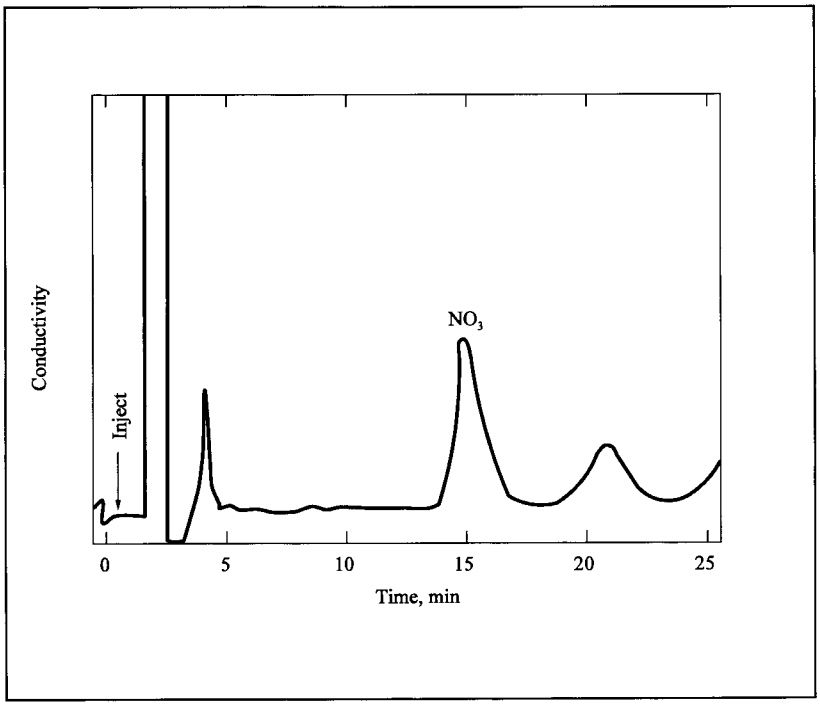

Figure 7D-1. Ion Chromatograph of a Prepared Sample.

METHOD 7E—DETERMINATION OF NITROGEN OXIDES EMISSIONS FROM STATIONARY SOURCES (INSTRUMENTAL ANALYZER PROCEDURE)

1.0 Scope and Application

What is Method 7E?

Method 7E is a procedure for measuring nitrogen oxides (NO_X) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis. This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 4—Determination of Moisture Content in Stack Gases.

1.1 Analytes. What does this method determine? This method measures the concentration of nitrogen oxides as NO_2.

Analyte	CAS No.	Sensitivity
Nitric oxide (NO)	10102–43–9	Typically <2% of
Nitrogen dioxide (NO_2)	10102–44–0	Calibration Span.

1.2 Applicability. When is this method required? The use of Method 7E may be required by specific New Source Performance Standards, Clean Air Marketing rules, State Implementation Plans, and permits where measurement of NO_X concentrations in stationary source emissions is required, either to determine compliance with an applicable

emissions standard or to conduct performance testing of a continuous monitoring system (CEMS). Other regulations may also require the use of Method 7E.

1.3 Data Quality Objectives (DQO). How good must my collected data be? Method 7E is designed to provide high-quality data for determining compliance with Federal and State emission standards and for relative accuracy testing of CEMS. In these and other applications, the principal objective is to ensure the accuracy of the data at the actual emission levels encountered. To meet this objective, the use of EPA traceability protocol calibration gases and measurement system performance tests are required.

1.4 Data Quality Assessment for Low Emitters. Is performance relief granted when testing low-emission units? Yes. For low-emitting sources, there are alternative performance specifications for analyzer calibration error, system bias, drift, and response time. Also, the alternative dynamic spiking procedure in section 16 may provide performance relief for certain low-emitting units.

2.0 Summary of Method

In this method, a sample of the effluent gas is continuously sampled and conveyed to the analyzer for measuring the concentration of NO_X. You may measure NO and NO_2 separately or simultaneously together but, for the purposes of this method, NO_X is the sum of NO and NO_2. You must meet the performance requirements of this method to validate your data.

3.0 Definitions

3.1 Analyzer Calibration Error, for non-dilution systems, means the difference between the manufacturer certified concentration of a calibration gas and the measured concentration of the same gas when it is introduced into the analyzer in direct calibration mode.

3.2 Calibration Curve means the relationship between an analyzer's response to the injection of a series of calibration gases and the actual concentrations of those gases.

3.3 Calibration Gas means the gas mixture containing NO_X at a known concentration and produced and certified in accordance with ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards,'' September 1997, as amended August 25, 1999, EPA–600/R–97/121 or more recent updates. The tests for analyzer calibration error, drift, and system bias require the use of calibration gas prepared according to this protocol. If a zero gas is used for the low-level gas, it must meet the requirements under the definition for ''zero air material'' in 40 CFR 72.2 in place of being prepared by the traceability protocol.

3.3.1 Low-Level Gas means a calibration gas with a concentration that is less than 20 percent of the calibration span and may be a zero gas.

3.3.2 Mid-Level Gas means a calibration gas with a concentration that is 40 to 60 percent of the calibration span.

3.3.3 High-Level Gas means a calibration gas with a concentration that is equal to the calibration span.

3.4 Calibration Span means the upper limit of the analyzer's calibration that is set by the choice of high-level calibration gas. No valid run average concentration may exceed the calibration span. To the extent practicable, the measured emissions should be between 20 to 100 percent of the selected calibration span. This may not be practicable in some cases of low-concentration measurements or testing for compliance with an emission limit when emissions are substantially less than the limit. In such cases, calibration spans that are practicable to achieving the data quality objectives without being excessively high should be chosen.

3.5 Centroidal Area means the central area of the stack or duct that is no greater than 1 percent of the stack or duct cross section. This area has the same geometric shape as the stack or duct.

3.6 Converter Efficiency Gas means a calibration gas with a known NO or NO_2 concentration and of Traceability Protocol quality.

3.7 Data Recorder means the equipment that permanently records the concentrations reported by the analyzer.

3.8 Direct Calibration Mode means introducing the calibration gases directly into the analyzer (or into the assembled measurement system at a point downstream of all sample conditioning equipment) according to manufacturer's recommended calibration procedure. This mode of calibration applies to non-dilution-type measurement systems.

3.9 Drift means the difference between the pre- and post-run system bias (or system calibration error) checks at a specific calibration gas concentration level (*i.e.* low-, mid- or high-).

3.10 Gas Analyzer means the equipment that senses the gas being measured and generates an output proportional to its concentration.

3.11 Interference Check means the test to detect analyzer responses to compounds other than the compound of interest, usually a gas present in the measured gas stream, that is not adequately accounted for in the calibration procedure and may cause measurement bias.

3.12 Low-Concentration Analyzer means any analyzer that operates with a calibration span of 20 ppm NO_X or lower. Each analyzer model used routinely to measure low NO_X concentrations must pass a manufacturer's stability test (MST). An MST subjects the analyzer to a range of line voltages and temperatures that reflect potential field conditions to demonstrate its stability following

procedures similar to those provided in 40 CFR 53.23. Ambient-level analyzers are exempt from the MST requirements of section 16.3. A copy of this information must be included in each test report. Table 7E–5 lists the criteria to be met.

3.13 Measurement System means all of the equipment used to determine the NO_x concentration. The measurement system comprises six major subsystems: Sample acquisition, sample transport, sample conditioning, calibration gas manifold, gas analyzer, and data recorder.

3.14 Response Time means the time it takes the measurement system to respond to a change in gas concentration occurring at the sampling point when the system is operating normally at its target sample flow rate or dilution ratio.

3.15 Run means a series of gas samples taken successively from the stack or duct. A test normally consists of a specific number of runs.

3.16 System Bias means the difference between a calibration gas measured in direct calibration mode and in system calibration mode. System bias is determined before and after each run at the low- and mid- or high-concentration levels. For dilution-type systems, pre- and post-run system calibration error is measured rather than system bias.

3.17 System Calibration Error applies to dilution-type systems and means the difference between the measured concentration of low-, mid-, or high-level calibration gas and the certified concentration for each gas when introduced in system calibration mode. For dilution-type systems, a 3-point system calibration error test is conducted in lieu of the analyzer calibration error test, and 2-point system calibration error tests are conducted in lieu of system bias tests.

3.18 System Calibration Mode means introducing the calibration gases into the measurement system at the probe, upstream of the filter and all sample conditioning components.

3.19 Test refers to the series of runs required by the applicable regulation.

4.0 Interferences

Note that interferences may vary among instruments and that instrument-specific interferences must be evaluated through the interference test.

5.0 Safety

What safety measures should I consider when using this method? This method may require you to work with hazardous materials and in hazardous conditions. We encourage you to establish safety procedures before using the method. Among other precautions, you should become familiar with the safety recommendations in the gas analyzer user's manual. Occupational Safety and Health Administration (OSHA) regulations concerning cylinder and noxious gases may apply. Nitric oxide and NO_2 are toxic and dangerous gases. Nitric oxide is immediately converted to NO_2 upon reaction with air. Nitrogen dioxide is a highly poisonous and insidious gas. Inflammation of the lungs from exposure may cause only slight pain or pass unnoticed, but the resulting edema several days later may cause death. A concentration of 100 ppm is dangerous for even a short exposure, and 200 ppm may be fatal. Calibration gases must be handled with utmost care and with adequate ventilation. Emission-level exposure to these gases should be avoided.

6.0 Equipment and Supplies

The performance criteria in this method will be met or exceeded if you are properly using equipment designed for this application.

6.1 What do I need for the measurement system? You may use any equipment and supplies meeting the following specifications:

(1) Sampling system components that are not evaluated in the system bias or system calibration error test must be glass, Teflon, or stainless steel. Other materials are potentially acceptable, subject to approval by the Administrator.

(2) The interference, calibration error, and system bias criteria must be met.

(3) Sample flow rate must be maintained within 10 percent of the flow rate at which the system response time was measured.

(4) All system components (excluding sample conditioning components, if used) must maintain the sample temperature above the moisture dew point. Ensure minimal contact between any condensate and the sample gas. Section 6.2 provides example equipment specifications for a NO_x measurement system. Figure 7E–1 is a diagram of an example dry-basis measurement system that is likely to meet the method requirements and is provided as guidance. For wet-basis systems, you may use alternative equipment and supplies as needed (some of which are described in Section 6.2), provided that the measurement system meets the applicable performance specifications of this method.

6.2 Measurement System Components

6.2.1 Sample Probe. Glass, stainless steel, or other approved material, of sufficient length to traverse the sample points.

6.2.2 Particulate Filter. An in-stack or out-of-stack filter. The filter must be made of material that is non-reactive to the gas being sampled. The filter media for out-of-stack filters must be included in the system bias test. The particulate filter requirement may be waived in applications where no significant particulate matter is expected (*e.g.*, for emission testing of a combustion turbine firing natural gas).

6.2.3 Sample Line. The sample line from the probe to the conditioning system/sample pump should be made of Teflon or other material that does not absorb or otherwise alter the sample gas. For a dry-basis measurement system (as shown in Figure 7E–1), the temperature of the sample line must be maintained at a sufficiently high level to prevent condensation before the sample conditioning components. For wet-basis measurement systems, the temperature of the sample line must be maintained at a sufficiently high level to prevent condensation before the analyzer.

6.2.4 Conditioning Equipment. For dry basis measurements, a condenser, dryer or other suitable device is required to remove moisture continuously from the sample gas. Any equipment needed to heat the probe or sample line to avoid condensation prior to the sample conditioning component is also required.

For wet basis systems, you must keep the sample above its dew point either by: (1) Heating the sample line and all sample transport components up to the inlet of the analyzer (and, for hot-wet extractive systems, also heating the analyzer) or (2) by diluting the sample prior to analysis using a dilution probe system. The components required to do either of the above are considered to be conditioning equipment.

6.2.5 Sampling Pump. For systems similar to the one shown in Figure 7E–1, a leak-free pump is needed to pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system. The pump may be constructed of any material that is non-reactive to the gas being sampled. For dilution-type measurement systems, an ejector pump (eductor) is used to create a vacuum that draws the sample through a critical orifice at a constant rate.

6.2.6 Calibration Gas Manifold. Prepare a system to allow the introduction of calibration gases either directly to the gas analyzer in direct calibration mode or into the measurement system, at the probe, in system calibration mode, or both, depending upon the type of system used. In system calibration mode, the system should be able to flood the sampling probe and vent excess gas. Alternatively, calibration gases may be introduced at the calibration valve following the probe. Maintain a constant pressure in the gas manifold. For in-stack dilution-type systems, a gas dilution subsystem is required to transport large volumes of purified air to the sample probe and a probe controller is needed to maintain the proper dilution ratio.

6.2.7 Sample Gas Manifold. For the type of system shown in Figure 7E–1, the sample gas manifold diverts a portion of the sample to the analyzer, delivering the remainder to the by-pass discharge vent. The manifold should also be able to introduce calibration gases directly to the analyzer (except for dilution-type systems). The manifold must be made of material that is non-reactive to the gas sampled or the calibration gas and be configured to safely discharge the bypass gas.

6.2.8 NO_X Analyzer. An instrument that continuously measures NO_X in the gas stream and meets the applicable specifications in section 13.0. An analyzer that operates on the principle of chemiluminescence with an NO_2 to NO converter is one example of an analyzer that has been used successfully in the past. Analyzers operating on other principles may also be used provided the performance criteria in section 13.0 are met.

6.2.8.1 Dual Range Analyzers. For certain applications, a wide range of gas concentrations may be encountered, necessitating the use of two measurement ranges. Dual-range analyzers are readily available for these applications. These analyzers are often equipped with automated range-switching capability, so that when readings exceed the full-scale of the low measurement range, they are recorded on the high range. As an alternative to using a dual-range analyzer, you may use two segments of a single, large measurement scale to serve as the low and high ranges. In all cases, when two ranges are used, you must quality-assure both ranges using the proper sets of calibration gases. You must also meet the interference, calibration error, system bias, and drift checks. However, we caution that when you use two segments of a large measurement scale for dual range purposes, it may be difficult to meet the performance specifications on the low range due to signal-to-noise ratio considerations.

6.2.8.2 Low Concentration Analyzer. When an analyzer is routinely calibrated with a calibration span of 20 ppmv or less, the manufacturer's stability test (MST) is required. See Table 7E–5 for test parameters.

6.2.9 Data Recording. A strip chart recorder, computerized data acquisition system, digital recorder, or data logger for recording measurement data may be used.

7.0 Reagents and Standards

7.1 Calibration Gas. What calibration gases do I need? Your calibration gas must be NO in N_2 and certified (or recertified) within an uncertainty of 2.0 percent in accordance with ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards'' September 1997, as amended August 25, 1999, EPA–600/R–97/121. Blended gases meeting the Traceability Protocol are allowed if the additional gas components are shown not to interfere with the analysis. If a zero gas is used for the low-level gas, it must meet the requirements under the definition for ''zero air material'' in 40 CFR 72.2. The calibration gas must not be used after its expiration date. Except for applications under part 75 of

this chapter, it is acceptable to prepare calibration gas mixtures from EPA Traceability Protocol gases in accordance with Method 205 in appendix M to part 51 of this chapter. For part 75 applications, the use of Method 205 is subject to the approval of the Administrator. The goal and recommendation for selecting calibration gases is to bracket the sample concentrations. The following calibration gas concentrations are required:

7.1.1 *High-Level Gas.* This concentration is chosen to set the calibration span as defined in Section 3.4.

7.1.2 Mid-Level Gas. 40 to 60 percent of the calibration span.

7.1.3 Low-Level Gas. Less than 20 percent of the calibration span.

7.1.4 Converter Efficiency Gas. What reagents do I need for the converter efficiency test? The converter efficiency gas is a manufacturer-certified gas with a concentration sufficient to show NO_2 conversion at the concentrations encountered in the source. A test gas concentration in the 40 to 60 ppm range is suggested, but other concentrations may be more appropriate to specific sources. For the test described in section 8.2.4.1, NO_2 is required. For the alternative converter efficiency tests in section 16.2, NO is required.

7.2 Interference Check. What reagents do I need for the interference check? Use the appropriate test gases listed in Table 7E–3 or others not listed that can potentially interfere (as indicated by the test facility type, instrument manufacturer, etc.) to conduct the interference check. These gases should be manufacturer certified but do not have to be prepared by the EPA traceability protocol.

8.0 Sample Collection, Preservation, Storage, and Transport

Emission Test Procedure

Since you are allowed to choose different options to comply with some of the performance criteria, it is your responsibility to identify the specific options you have chosen, to document that the performance criteria for that option have been met, and to identify any deviations from the method.

8.1 What sampling site and sampling points do I select?

8.1.1 Unless otherwise specified in an applicable regulation or by the Administrator, when this method is used to determine compliance with an emission standard, conduct a stratification test as described in section 8.1.2 to determine the sampling traverse points to be used. For performance testing of continuous emission monitoring systems, follow the sampling site selection and traverse point layout procedures described in the appropriate performance specification or applicable regulation (e.g., Performance Specification 2 in appendix B to this part).

8.1.2 Determination of Stratification. Perform a stratification test at each test site to determine the appropriate number of sample traverse points. If testing for multiple pollutants or diluents at the same site, a stratification test using only one pollutant or diluent satisfies this requirement. A stratification test is not required for small stacks that are less than 4 inches in diameter. To test for stratification, use a probe of appropriate length to measure the NO_X (or pollutant of interest) concentration at 12 traverse points located according to Table 1–1 or Table 1–2 of Method 1. Alternatively, you may measure at three points on a line passing through the centroidal area. Space the three points at 16.7, 50.0, and 83.3 percent of the measurement line. Sample for a minimum of twice the system response time (see section 8.2.6) at each traverse point. Calculate the individual point and mean NO_X concentrations. If the concentration at each traverse point differs from the mean concentration for all traverse points by no more than: ±5.0 percent of the mean concentration; or ±0.5 ppm (whichever is less restrictive), the gas stream is considered unstratified, and you may collect samples from a single point that most closely matches the mean. If the 5.0 percent or 0.5 ppm criterion is not met, but the concentration at each traverse point differs from the mean concentration for all traverse points by not more than: ±10.0 percent of the mean concentration; or ±1.0 ppm (whichever is less restrictive), the gas stream is considered to be minimally stratified and you may take samples from three points. Space the three points at 16.7, 50.0, and 83.3 percent of the measurement line. Alternatively, if a 12-point stratification test was performed and the emissions were shown to be minimally stratified (all points within ± 10.0 percent of their mean or within ±1.0 ppm), and if the stack diameter (or equivalent diameter, for a rectangular stack or duct) is greater than 2.4 meters (7.8 ft), then you may use 3-point sampling and locate the three points along the measurement line exhibiting the highest average concentration during the stratification test at 0.4, 1.2 and 2.0 meters from the stack or duct wall. If the gas stream is found to be stratified because the 10.0 percent or 1.0 ppm criterion for a 3-point test is not met, locate 12 traverse points for the test in accordance with Table 1–1 or Table 1–2 of Method 1.

8.2 Initial Measurement System Performance Tests. What initial performance criteria must my system meet before I begin collecting samples? Before measuring emissions, perform the following procedures:

(a) Calibration gas verification,

(b) Measurement system preparation,

(c) Calibration error test,

(d) NO_2 to NO conversion efficiency test, if applicable,

(e) System bias check,

(f) System response time test, and

(g) Interference check

8.2.1 Calibration Gas Verification. How must I verify the concentrations of my calibration gases? Obtain a certificate from the gas manufacturer documenting the quality of the gas. Confirm that the manufacturer certification is complete and current. Ensure that your calibration gas certifications have not expired. This documentation should be available on-site for inspection. To the extent practicable, select a high-level gas concentration that will result in the measured emissions being between 20 and 100 percent of the calibration span.

8.2.2 Measurement System Preparation. How do I prepare my measurement system? Assemble, prepare, and precondition the measurement system according to your standard operating procedure. Adjust the system to achieve the correct sampling rate or dilution ratio (as applicable).

8.2.3 Calibration Error Test. How do I confirm my analyzer calibration is correct? After you have assembled, prepared and calibrated your sampling system and analyzer, you must conduct a 3-point analyzer calibration error test (or a 3-point system calibration error test for dilution systems) before the first run and again after any failed system bias test (or 2-point system calibration error test for dilution systems) or failed drift test. Introduce the low-, mid-, and high-level calibration gases sequentially. For non-dilution-type measurement systems, introduce the gases in direct calibration mode. For dilution-type measurement systems, introduce the gases in system calibration mode.

(1) For non-dilution systems, you may adjust the system to maintain the correct flow rate at the analyzer during the test, but you may not make adjustments for any other purpose. For dilution systems, you must operate the measurement system at the appropriate dilution ratio during all system calibration error checks, and may make only the adjustments necessary to maintain the proper ratio.

(2) Record the analyzer's response to each calibration gas on a form similar to Table 7E–1. For each calibration gas, calculate the analyzer calibration error using Equation 7E–1 in section 12.2 or the system calibration error using Equation 7E–3 in section 12.4 (as applicable). The calibration error specification in section 13.1 must be met for the low-, mid-, and high-level gases. If the calibration error specification is not met, take corrective action and repeat the test until an acceptable 3-point calibration is achieved.

8.2.4 NO_2 to NO Conversion Efficiency Test. Before or after each field test, you must conduct an NO_2 to NO conversion efficiency test if your system converts NO_2 to NO before analyzing for NO_X. You may risk testing multiple facilities before performing this test provided you pass this test at the conclusion of the final facility test. A failed final conversion efficiency test in this case will invalidate all tests performed subsequent to the test in which the converter efficiency test was passed. Follow the procedures in section 8.2.4.1, or 8.2.4.2. If desired, the converter efficiency factor derived from this test may be used to correct the test results for converter efficiency if the NO_2 fraction in the measured test gas is known. Use Equation 7E–8 in section 12.8 for this correction.

8.2.4.1 Introduce NO_2 converter efficiency gas to the analyzer in direct calibration mode and record the NO_X concentration displayed by the analyzer. Calculate the converter efficiency using Equation 7E–7 in section 12.7. The specification for converter efficiency in section 13.5 must be met. The user is cautioned that state-of-the-art NO_2 calibration gases may have limited shelf lives, and this could affect the ability to pass the 90-percent conversion efficiency requirement.

8.2.4.2 Alternatively, either of the procedures for determining conversion efficiency using NO in section 16.2 may be used.

8.2.5 Initial System Bias and System Calibration Error Checks. Before sampling begins, determine whether the high-level or mid-level calibration gas best approximates the emissions and use it as the upscale gas. Introduce the upscale gas at the probe upstream of all sample conditioning components in system calibration mode. Record the time it takes for the measured concentration to increase to a value that is at least 95 percent or within 0.5 ppm (whichever is less restrictive) of a stable response for both the low-level and upscale gases. Continue to observe the gas concentration reading until it has reached a final, stable value. Record this value on a form similar to Table 7E–2.

(1) Next, introduce the low-level gas in system calibration mode and record the time required for the concentration response to decrease to a value that is within 5.0 percent or 0.5 ppm (whichever is less restrictive) of the certified low-range gas concentration. If the low-level gas is a zero gas, use the procedures described above and observe the change in concentration until the response is 0.5 ppm or 5.0 percent of the upscale gas concentration (whichever is less restrictive).

(2) Continue to observe the low-level gas reading until it has reached a final, stable value and record the result on a form similar to Table 7E–2. Operate the measurement system at the normal sampling rate during all system bias checks. Make only the adjustments necessary to achieve proper calibration gas flow rates at the analyzer.

(3) From these data, calculate the measurement system response time (see section 8.2.6) and then calculate the initial system bias using Equation 7E–2 in section 12.3. For dilution systems, calculate the system calibration error in lieu of system bias using

equation 7E–3 in section 12.4. See section 13.2 for acceptable performance criteria for system bias and system calibration error. If the initial system bias (or system calibration error) specification is not met, take corrective action. Then, you must repeat the applicable calibration error test from section 8.2.3 and the initial system bias (or 2-point system calibration error) check until acceptable results are achieved, after which you may begin sampling.

(NOTE: For dilution-type systems, data from the 3-point system calibration error test described in section 8.2.3 may be used to meet the initial 2-point system calibration error test requirement of this section, if the calibration gases were injected as described in this section, and if response time data were recorded).

8.2.6 Measurement System Response Time. As described in section 8.2.5, you must determine the measurement system response time during the initial system bias (or 2-point system calibration error) check. Observe the times required to achieve 95 percent of a stable response for both the low-level and upscale gases. The longer interval is the response time.

8.2.7 Interference Check. Conduct an interference response test of the gas analyzer prior to its initial use in the field. If you have multiple analyzers of the same make and model, you need only perform this alternative interference check on one analyzer. You may also meet the interference check requirement if the instrument manufacturer performs this or a similar check on an analyzer of the same make and model of the analyzer that you use and provides you with documented results.

(1) You may introduce the appropriate interference test gases (that are potentially encountered during a test; see examples in Table 7E–3) into the analyzer separately or as mixtures. Test the analyzer with the interference gas alone at the highest concentration expected at a test source and again with the interference gas and NO_X at a representative NO_X test concentration. For analyzers measuring NO_X greater than 20 ppm, use a calibration gas with a NO_X concentration of 80 to 100 ppm and set this concentration equal to the calibration span. For analyzers measuring less than 20 ppm NO_X, select an NO concentration for the calibration span that reflects the emission levels at the sources to be tested, and perform the interference check at that level. Measure the total interference response of the analyzer to these gases in ppmv. Record the responses and determine the interference using Table 7E–4. The specification in section 13.4 must be met.

(2) A copy of this data, including the date completed and signed certification, must be available for inspection at the test site and included with each test report. This interference test is valid for the life of the instrument unless major analytical components (*e.g.,* the detector) are replaced with different model parts. If major components are replaced with different model parts, the interference gas check must be repeated before returning the analyzer to service. If major components are replaced, the interference gas check must be repeated before returning the analyzer to service. The tester must ensure that any specific technology, equipment, or procedures that are intended to remove interference effects are operating properly during testing.

8.3 Dilution-Type Systems—Special Considerations. When a dilution-type measurement system is used, there are three important considerations that must be taken into account to ensure the quality of the emissions data. First, the critical orifice size and dilution ratio must be selected properly so that the sample dew point will be below the sample line and analyzer temperatures. Second, a high-quality, accurate probe controller must be used to maintain the dilution ratio during the test. The probe controller should be capable of monitoring the dilution air pressure, eductor vacuum, and sample flow rates. Third, differences between the molecular weight of calibration gas mixtures and the stack gas molecular weight must be addressed because these can affect the dilution ratio and introduce measurement bias.

8.4 Sample Collection.

(1) Position the probe at the first sampling point. Purge the system for at least two times the response time before recording any data. Then, traverse all required sampling points, sampling at each point for an equal length of time and maintaining the appropriate sample flow rate or dilution ratio (as applicable). You must record at least one valid data point per minute during the test run.

(2) Each time the probe is removed from the stack and replaced, you must recondition the sampling system for at least two times the system response time prior to your next recording. If the average of any run exceeds the calibration span value, that run is invalid.

(3) You may satisfy the multipoint traverse requirement by sampling sequentially using a single-hole probe or a multi-hole probe designed to sample at the prescribed points with a flow within 10 percent of mean flow rate. Notwithstanding, for applications under part 75 of this chapter, the use of multi-hole probes is subject to the approval of the Administrator.

8.5 Post-Run System Bias Check and Drift Assessment.

How do I confirm that each sample I collect is valid? After each run, repeat the system bias check or 2-point system calibration error check (for dilution systems) to validate

the run. Do not make adjustments to the measurement system (other than to maintain the target sampling rate or dilution ratio) between the end of the run and the completion of the post-run system bias or system calibration error check. Note that for all post-run system bias or 2-point system calibration error checks, you may inject the low-level gas first and the upscale gas last, or vice-versa. You may risk sampling for multiple runs before performing the post-run bias or system calibration error check provided you pass this test at the conclusion of the group of runs. A failed final test in this case will invalidate all runs subsequent to the last passed test.

(1) If you do not pass the post-run system bias (or system calibration error) check, then the run is invalid. You must diagnose and fix the problem and pass another calibration error test (Section 8.2.3) and system bias (or 2-point system calibration error) check (Section 8.2.5) before repeating the run. Record the system bias (or system calibration error) results on a form similar to Table 7E–2.

(2) After each run, calculate the low-level and upscale drift, using Equation 7E–4 in section 12.5. If the post-run low- and upscale bias (or 2-point system calibration error) checks are passed, but the low-or upscale drift exceeds the specification in section 13.3, the run data are valid, but a 3-point calibration error test and a system bias (or 2-point system calibration error) check must be performed and passed before any more test runs are done.

(3) For dilution systems, data from a 3-point system calibration error test may be used to met the pre-run 2-point system calibration error requirement for the first run in a test sequence. Also, the post-run bias (or 2-point calibration error) check data may be used as the pre-run data for the next run in the test sequence at the discretion of the tester.

8.6 Alternative Interference and System Bias Checks (Dynamic Spike Procedure). If I want to use the dynamic spike procedure to validate my data, what procedure should I follow? Except for applications under part 75 of this chapter, you may use the dynamic spiking procedure and requirements provided in section 16.1 during each test as an alternative to the interference check and the pre- and post-run system bias checks. The calibration error test is still required under this option. Use of the dynamic spiking procedure for Part 75 applications is subject to the approval of the Administrator.

8.7 Moisture correction. You must determine the moisture content of the flue gas and correct the measured gas concentrations to a dry basis using Method 4 or other appropriate methods, subject to the approval of the Administrator, when the moisture basis (wet or dry) of the measurements made with this method is different from the moisture basis of either: (1) The applicable emissions limit; or (2) the CEMS being evaluated for relative accuracy. Moisture correction is also required if the applicable limit is in lb/mmBtu and the moisture basis of the Method 7E NO_X analyzer is different from the moisture basis of the Method 3A diluent gas (CO_2 or O_2) analyzer.

9.0 Quality Control

What quality control measures must I take?

The following table is a summary of the mandatory, suggested, and alternative quality assurance and quality control measures and the associated frequency and acceptance criteria. All of the QC data, along with the sample run data, must be documented and included in the test report.

SUMMARY TABLE OF AQ/QC

Status	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
S	Identify Data User		Regulatory Agency or other primary end user of data.	Before designing test.
S	Analyzer Design	Analyzer resolution or sensitivity.	<2.0% of full-scale range	Manufacturer design.
M		Interference gas check.	Sum of responses ≤2.5% of calibration span Alternatively, sum of responses: ≤0.5 ppmv for calibration spans of 5 to 10 ppmv. ≤0.2 ppmv for calibration spans <5 ppmv. See Table 7E-3.	
M	Calibration Gases	Traceability protocol (G1, G2).	Valid certificate required Uncertainty ≤2.0% of tag value.	
M		High-level gas	Equal to the calibration span	Each test.
M		Mid-level gas	40 to 60% of calibration span	Each test.
M		Low-level gas	<20% of calibration span	Each test.
S	Data Recorder Design.	Data resolution	≤0.5% of full-scale range	Manufacturer design.
S	Sample Extraction	Probe material	SS or quartz if stack >500 °F	East test.
M	Sample Extraction	Probe, filter and sample line temperature.	For dry-basis analyzers, keep sample above the dew point by heating, prior to sample conditioning.	Each run.

SUMMARY TABLE OF AQ/QC—Continued

Status	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
			For wet-basis analyzers, keep sample above dew point at all times, by heating or dilution.	
S	Sample Extraction	Calibration valve material.	SS	Each test.
S	Sample Extraction	Sample pump material.	Inert to sample constituents	Each test.
S	Sample Extraction	Manifolding material	Inert to sample constituents	Each test.
S	Moisture Removal	Equipment efficiency	<5% target compound removal	Verified through system bias check.
S	Particulate Removal	Filter inertness	Pass system bias check	Each bias check.
M	Analyzer & Calibration Gas Performance.	Analyzer calibration error (of 3-point system calibration error for dilution systems).	Within ±2.0 percent of the calibration span of the analyzer for the low-, mid-, and high-level calibration gases. Alternative specification: ≤0.5 ppmv absolute difference.	Before initial run and after a failed system bias test or drift test.
M	System Performance	System bias (or pre- and post-run 2-point system calibration error for dilution (Systems).	Within ±5.0% of the analyzer calibration span for low-sacle and upscale calibration gases. Alternative specification: ≤0.5 ppmv absolute difference.	Before and after each run.
M	System Performance	System response time.	Determines minimum sampling time per point.	During initial sampling system bias test.
M	System Performance	Drift	≤3.0% of calibration span for low-level and mid- or high-level gases. Alternative specification: ≤0.5 ppmv absolute difference.	After each test run.
M	System Performance	NO_2-NO conversion efficiency.	≥90% of certified test gas concentration	Before or after each test.
M	System Performance	Purge time	≥2 times system response time	Before starting the first run and when probe is removed from and re-inserted into the stack.
M	System Performance	Minimum sample time at each point.	Two times the system response time	Each sample point.
M	System Performance	Stable sample flow rate (surrogate for maintaining system response time).	Within 10% of flow rate established during system response time check.	Each run.
M	Sample Point Selection.	Stratification test	All points within: ±5% of mean for 1-point sampling. ±10% of mean for 3-point. Alternatively, all points within: ±0.5 ppm of mean for 1-point sampling. ±1.0 ppm of mean for 3-point sampling.	Prior to first run.
A	Multiple sample points simultaneously.	No. of openings in probe.	Multi-hole probe with verifiable constant flow through all holes within 10% of mean flow rate (requires Administrative approval for Part 75).	Each run.
M	Data Recording	Frequency	≤1 minute average	During run.
S	Data Parameters	Sample concentration range.	All 1-minute averages within calibration span.	Each run.
M	Date Parameters	Average concentration for the run.	Run average ≤calibration span	Each run.

S = Suggest.
M = Mandatory.
A = Alternative.
Agency.

10.0 Calibration and Standardization

What measurement system calibrations are required?

(1) The initial 3-point calibration error test as described in section 8.2.3 and the system bias (or system calibration error) checks described in section 8.2.5 are required and must meet the specifications in section 13 before you start the test. Make all necessary adjustments to calibrate the gas analyzer and data recorder. Then, after the test commences, the system bias or system calibration error checks described in section 8.5 are required before and after each run. Your analyzer must be calibrated for all species of NO_X that it detects. Analyzers that measure NO and NO_2 separately without using a converter must be calibrated with both NO and NO_2.

(2) You must include a copy of the manufacturer's certification of the calibration gases used in the testing as part of the test report. This certification must include the 13 documentation requirements in the EPA Traceability Protocol For Assay and Certification of Gaseous Calibration Standards, September 1997, as amended August 25, 1999. When Method 205 is used to produce diluted calibration gases, you must document that the specifications for the gas dilution system are met for the test. You must also include the date of the most recent dilution system calibration against flow standards and the name of the person or manufacturer who carried out the calibration in the test report.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the procedures for calculations and data analysis listed in this section.

12.1 *Nomenclature.* The terms used in the equations are defined as follows:

ACE = Analyzer calibration error, percent of calibration span.

B_{WS} = Moisture content of sample gas as measured by Method 4 or other approved method, percent/100.

C_{Avg} = Average unadjusted gas concentration indicated by data recorder for the test run, ppmv.

C_D = Pollutant concentration adjusted to dry conditions, ppmv.

C_{Dir} = Measured concentration of a calibration gas (low, mid, or high) when introduced in direct calibration mode, ppmv.

C_{Gas} = Average effluent gas concentration adjusted for bias, ppmv.

C_M = Average of initial and final system calibration bias (or 2-point system calibration error) check responses for the upscale calibration gas, ppmv.

C_{MA} = Actual concentration of the upscale calibration gas, ppmv.

C_{Native} = NO_X concentration in the stack gas as calculated in section 12.6, ppmv.

C_O = Average of the initial and final system calibration bias (or 2-point system calibration error) check responses from the low-level (or zero) calibration gas, ppmv.

C_{OA} = Actual concentration of the low-level calibration gas, ppmv.

C_S = Measured concentration of a calibration gas (low, mid, or high) when introduced in system calibration mode, ppmv.

C_{SS} = Concentration of NO_X measured in the spiked sample, ppmv.

C_{Spike} = Concentration of NO_X in the undiluted spike gas, ppmv.

C_{Calc} = Calculated concentration of NO_X in the spike gas diluted in the sample, ppmv.

C_V = Manufacturer certified concentration of a calibration gas (low, mid, or high), ppmv.

C_W = Pollutant concentration measured under moist sample conditions, wet basis, ppmv.

CS = Calibration span, ppmv.

D = Drift assessment, percent of calibration span.

DF = Dilution system dilution factor or spike gas dilution factor, dimensionless.

Eff_{NO2} = NO_2 to NO converter efficiency, percent.

NO_{XCorr} = The NO_X concentration corrected for the converter efficiency, ppmv.

NOX_{Final} = The final NO_X concentration observed during the converter efficiency test in section 16.2.2, ppmv.

NO_{XPeak} = The highest NO_X concentration observed during the converter efficiency test in section 16.2.2, ppmv.

Q_{Spike} = Flow rate of spike gas introduced in system calibration mode, L/min.

Q_{Total} = Total sample flow rate during the spike test, L/min.

R = Spike recovery, percent.

SB = System bias, percent of calibration span.

SB_i = Pre-run system bias, percent of calibration span.

SB_{final} = Post-run system bias, percent of calibration span.

SCE = System calibration error, percent of calibration span.

SCE_i = Pre-run system calibration error, percent of calibration span.

SCE_{Final} = Post-run system calibration error, percent of calibration span.

12.2 Analyzer Calibration Error. For non-dilution systems, use Equation 7E–1 to calculate the analyzer calibration error for the low-, mid-, and high-level calibration gases.

$$ACE = \frac{C_{Dir} - C_v}{CS} \times 100 \qquad \text{Eq. 7E-1}$$

12.3 System Bias. For non-dilution systems, use Equation 7E–2 to calculate the system bias separately for the low-level and upscale calibration gases.

$$SB = \frac{C_S - C_{Dir}}{CS} \times 100 \qquad \text{Eq. 7E-2}$$

12.4 System Calibration Error. Use Equation 7E–3 to calculate the system calibration error for dilution systems. Equation 7E–3 applies to both the initial 3-point system calibration error test and the subsequent 2-point calibration error checks between test runs. In this equation, the term ''C_s'' refers to the diluted calibration gas concentration measured by the analyzer.

$$SCE = \frac{(C_S \quad DF) - C_V}{CS} \times 100 \qquad \text{Eq. 7E-3}$$

12.5 Drift Assessment. Use Equation 7E–4 to separately calculate the low-level and upscale drift over each test run. For dilution systems, replace ''SB_{final}'' and ''SB_i'' with ''SCE_{final}'' and ''SCE_i'', respectively, to calculate and evaluate drift.

$$D = \left|SB_{final} - SB_i\right| \qquad \text{Eq. 7E-4}$$

12.6 Effluent Gas Concentration. For each test run, calculate C_{avg}, the arithmetic average of all valid NO_X concentration values (*e.g.*, 1-minute averages). Then adjust the value of C_{avg} for bias using Equation 7E–5a if you use a non-zero gas as your low-level calibration gas, or Equation 7E–5b if you use a zero gas as your low-level calibration gas.

$$C_{Gas} = \left(C_{Avg} - C_M\right)\frac{C_{MA} - C_{OA}}{C_M - C_O} + C_{MA} \qquad \text{Eq. 7E-5a}$$

$$C_{Gas} = \left(C_{Avg} - C_O\right)\frac{C_{MA}}{C_M - C_O} \qquad \text{Eq. 7E-5b}$$

12.7 NO_2—NO Conversion Efficiency. If the NO_X converter efficiency test described in section 8.2.4.1 is performed, calculate the efficiency using Equation 7E–7.

$$Eff_{NO2} = \frac{C_{Dir}}{C_V} \times 100 \qquad \text{Eq. 7E-7}$$

12.8 NO_2—NO Conversion Efficiency Correction. If desired, calculate the total NO_X concentration with a correction for converter efficiency using Equation 7E–8.

$$NO_{x\,Corr} = NO + \left(\frac{(NO_X - NO)}{Eff_{NO_2}} x\ 100\right) \qquad \text{Eq. 7E-8}$$

12.9 Alternative NO_2 Converter Efficiency. If the alternative procedure of section 16.2.2 is used, determine the NO_X concentration decrease from NO_{XPeak} after the minimum 30-minute test interval using Equation 7E–9.

This decrease from NO_{XPeak} must meet the requirement in section 13.5 for the converter to be acceptable.

$$\%\,Decrease = \frac{NO_{XPeak} - NO_{XFinal}}{NO_{XPeak}} \times 100 \qquad \text{Eq. 7E-9}$$

12.10 Moisture Correction. Use Equation 7E–10 if your measurements need to be corrected to a dry basis.

$$C_D = \frac{C_W}{1 - B_{WS}} \qquad \text{Eq. 7E-10}$$

12.11 Calculated Spike Gas Concentration and Spike Recovery for the Example Alternative Dynamic Spiking Procedure in section 16.1.3. Use Equation 7E–11 to determine the calculated spike gas concentration. Use Equation 7E–12 to calculate the spike recovery.

$$C_{Calc} = \frac{\left(C_{Spike}\right)\left(Q_{Spike}\right)}{Q_{Total}} \qquad \text{Eq. 7E-11}$$

$$R = \frac{DF\left(C_{ss} - C_{native}\right) + C_{native}}{C_{Spike}} \times 100 \qquad \text{Eq. 7E-12}$$

13.0 Method Performance

13.1 Calibration Error. This specification is applicable to both the analyzer calibration error and the 3-point system calibration error tests described in section 8.2.3. At each calibration gas level (low, mid, and high) the calibration error must either be within ±2.0 percent of the calibration span. Alternatively, the results are acceptable if $|C_{dir} - C_v|$ or $|C_s - C_v|$ (as applicable) is ≤0.5 ppmv.

13.2 System Bias. This specification is applicable to both the system bias and 2-point system calibration error tests described in section 8.2.5 and 8.5. The pre- and post-run system bias (or system calibration error) must be within ±5.0 percent of the calibration span for the low-level and upscale calibration gases. Alternatively, the results are acceptable if $|C_s - C_{dir}|$ is ≤0.5 ppmv or if $|C_s - C_v|$ is ≤0.5 ppmv (as applicable).

13.3 Drift. For each run, the low-level and upscale drift must be less than or equal to 3.0 percent of the calibration span. The drift is also acceptable if the pre- and post-run bias (or the pre- and post-run system calibration error) responses do not differ by more than 0.5 ppmv at each gas concentration (i.e. $|C_{s\ post\text{-}run} - C_{s\ pre\text{-}run}| \leq 0.5$ ppmv).

13.4 Interference Check. The total interference response (i.e., the sum of the interference responses of all tested gaseous components) must not be greater than 2.50 percent of the calibration span for the analyzer tested. In summing the interferences, use the larger of the absolute values obtained for the interferent tested with and without the pollutant present. The results are also acceptable if the sum of the responses does not exceed 0.5 ppmv for a calibration span of 5 to 10 ppmv, or 0.2 ppmv for a calibration span <5 ppmv.

13.5 NO_2 to NO Conversion Efficiency Test (as applicable). The NO_2 to NO conversion efficiency, calculated according to Equation 7E–7, must be greater than or equal to 90 percent. The alternative conversion efficiency check, described in section 16.2.2 and calculated according to Equation 7E–9, must not result in a decrease from NO_{XPeak} by more than 2.0 percent.

13.6 Alternative Dynamic Spike Procedure. Recoveries of both pre-test spikes and post-test spikes must be within 100 ±10 percent. If the absolute difference between the calculated spike value and measured spike value is equal to or less than 0.20 ppmv, then the requirements of the ADSC are met.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Dynamic Spike Procedure. Except for applications under part 75 of this chapter, you may use a dynamic spiking procedure to validate your test data for a specific test matrix in place of the interference check and pre- and post-run system bias checks. For part 75 applications, use of this procedure is subject to the approval of the Administrator.

Best results are obtained for this procedure when source emissions are steady and not varying. Fluctuating emissions may render this alternative procedure difficult to pass. To use this alternative, you must meet the following requirements.

16.1.1 Procedure Documentation. You must detail the procedure you followed in the test report, including how the spike was measured, added, verified during the run, and calculated after the test.

16.1.2 Spiking Procedure Requirements. The spikes must be prepared from EPA Traceability Protocol gases. Your procedure must be designed to spike field samples at two target levels both before and after the test. Your target spike levels should bracket the average sample NO_X concentrations. The higher target concentration must be less than the calibration span. You must collect at least 5 data points for each target concentration. The spiking procedure must be performed before the first run and repeated after the last run of the test program.

16.1.3 Example Spiking Procedure. Determine the NO concentration needed to generate concentrations that are 50 and 150 percent of the anticipated NO_X concentration in the stack at the total sampling flow rate while keeping the spike flow rate at or below 10 percent of this total. Use a mass flow meter (accurate within 2.0 percent) to generate these NO spike gas concentrations at a constant flow rate. Use Equation 7E–11 in section 12.11 to determine the calculated spike concentration in the collected sample.

(1) Prepare the measurement system and conduct the analyzer calibration error test as described in sections 8.2.2 and 8.2.3. Following the sampling procedures in section 8.1, determine the stack NO_X concentration and use this concentration as the average stack concentration (C_{avg}) for the first spike level, or if desired, for both pre-test spike levels. Introduce the first level spike gas into the system in system calibration mode and begin sample collection. Wait for at least two times the system response time before measuring the spiked sample concentration. Then record at least five successive 1-minute averages of the spiked sample gas. Monitor the spike gas flow rate and maintain at the determined addition rate. Average the five 1-minute averages and determine the spike recovery using Equation 7E–12. Repeat this procedure for the other pre-test spike level. The recovery at each level must be within the limits in section 13.6 before proceeding with the test.

(2) Conduct the number of runs required for the test. Then repeat the above procedure for the post-test spike evaluation. The last run of the test may serve as the average stack concentration for the post-test spike test calculations. The results of the post-test spikes must meet the limits in section 13.6.

16.2 Alternative NO_2 to NO Conversion Efficiency Procedures. You may use either of the following procedures to determine converter efficiency in place of the procedure in section 8.2.4.1.

16.2.1 The procedure for determining conversion efficiency using NO in 40 CFR 86.123–78.

16.2.2 Bag Procedure. Perform the analyzer calibration error test to document the calibration (both NO and NO_X modes, as applicable). Fill a Tedlar or equivalent bag approximately half full with either ambient air, pure oxygen, or an oxygen standard gas with at least 19.5 percent by volume oxygen content. Fill the remainder of the bag with mid- to high-level NO in N_2 (or other appropriate concentration) calibration gas. (Note that the concentration of the NO standard should be sufficiently high enough for the diluted concentration to be easily and accurately measured on the scale used. The size of the bag should be large enough to accommodate the procedure and time required. Verify through the manufacturer that the Tedlar alternative is suitable for NO and make this verifed information available for inspection.)

(1) Immediately attach the bag to the inlet of the NO_X analyzer (or external converter if used). In the case of a dilution-system, introduce the gas at a point upstream of the dilution assembly. Measure the NO_X concentration for a period of 30 minutes. If the NO_X concentration drops more than 2 percent absolute from the peak value observed, then the NO_2 converter has failed to meet the criteria of this test. Take corrective action. The highest NO_X value observed is considered to be NO_{XPeak}. The final NO_X value observed is considered to be NO_{Xfinal}.

(2) [Reserved]

16.3 Manufacturer's Stability Test. A manufacturer's stability test is required for all analyzers that routinely measure emissions below 20 ppmv and is optional but recommended for other analyzers. This test evaluates each analyzer model by subjecting it to the tests listed in Table 7E–5 following procedures similar to those in 40 CFR 53.23 for thermal stability and insensitivity to supply voltage variations. If the analyzer will be used under temperature conditions that are outside the test conditions in Table B–4 of Part 53.23, alternative test temperatures that better reflect the analyzer field environment should be used. Alternative procedures or documentation that establish the analyzer's stability over the appropriate line voltages and temperatures are acceptable.

17.0 References

1. ''ERA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards'' September 1997 as amended, ERA–600/R–97/121.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

Figure 7E-1. Measurement System

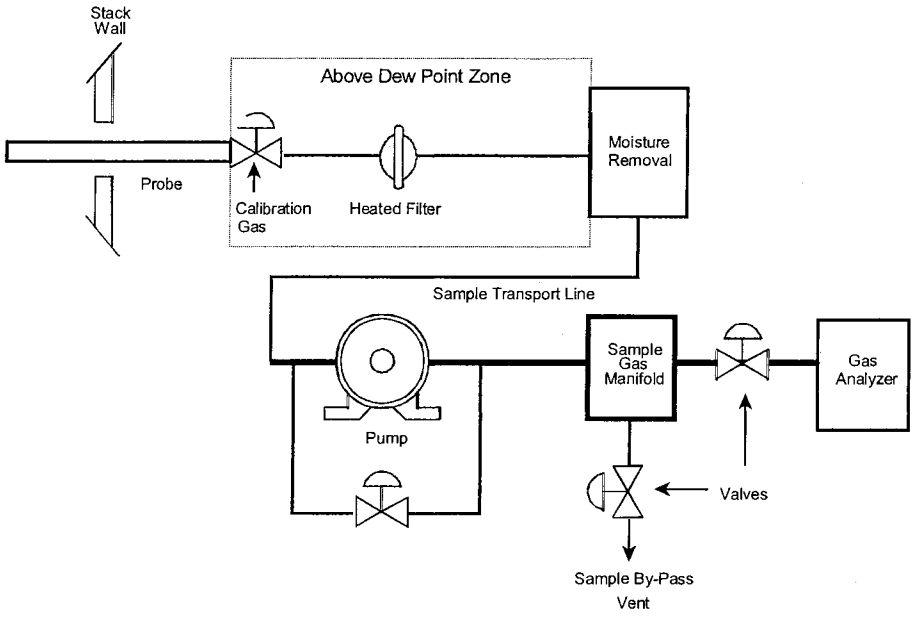

Figure 7E-2. Testing Flow Chart

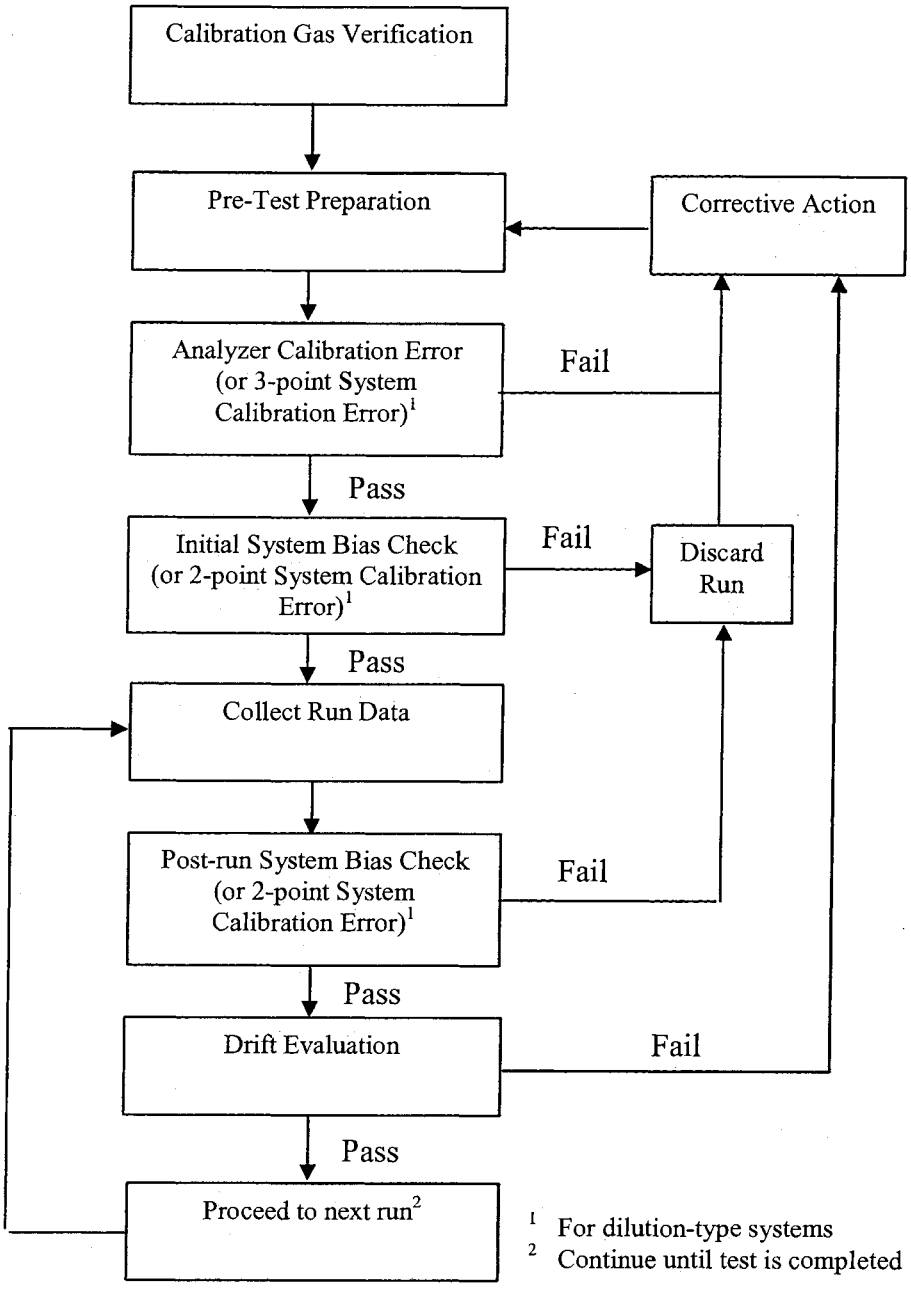

Table 7E-1 - Analyzer (or System) Calibration Error Data

Source Identification: _____ Test personnel: _____ Date: _____ Time: _____		Analyzer[1] or System[2] calibration error data for sampling runs: _____ Analyzer Model No. _____ Serial No. _____ Calibration Span (CS):		
	Manufacturer Certified Cylinder Value (indicate units) A	Analyzer calibration response (indicate units) B	Absolute difference (indicate units) A-B	Calibration Error (percent of calibration span) $\frac{A-B}{CS} \times 100$
Low-level (or zero) calibration gas	.....	.....	.....	.....
Mid-level calibration gas	.....	.....	.....	.....
High-level calibration gas	.....	.....	.....	.....

[1] Refers to data from the analyzer calibration error test of a non-dilution system.
[2] Refers to data from a 3-point system calibration error test of a dilution system.

Table 7E-2 - System Bias (or System Calibration Error) and Drift Data

Source Identification: _____ Run Number: _____
Test personnel: _____ Calibration Span: _____
Date: _____ Response Time: _____
Analyzer Model No. _____ Serial No. _____

	Initial values			Final values		
Calibration Gas Level	Certified Calibration gas value (indicate units)	System Response (indicate units)	System Bias[1] or Calibration Error[2] (% of calibration span)	System response (indicate units)	System Bias[1] or Calibration Error[2] (% of calibration span)	Drift (% of calibration span)
Low-level gas.....	.....	.....	.....	.....	.....	
Upscale (high- or mid-) level gas.....	.....	.....	.....	.....	.....	

[1] Refers to the pre- and post-run system bias checks of a non-dilution system.
[2] Refers to the pre- and post-run system calibration error checks of a dilution system.

TABLE 7E–3—EXAMPLE INTERFERENCE CHECK GAS CONCENTRATIONS

Potential interferent gas [1]	Concentrations [2] sample conditioning type	
	Hot wet	Dried
CO_2	5 and 15%	5 and 15%
H_2O	25%	1%
NO	15 ppmv	15 ppmv
NO_2	15 ppmv	15 ppmv
N_2O	10 ppmv	10 ppmv
CO	50 ppmv	50 ppmv
NH_3	10 ppmv	10 ppmv
CH_4	50 ppmv	50 ppmv
SO_2	20 ppmv	20 ppmv
H_2	50 ppmv	50 ppmv
HCl	10 ppmv	10 ppmv

[1] Any applicable gas may be eliminated or tested at a reduced level if the manufacturer has provided reliable means for limiting or scrubbing that gas to a specified level.
[2] As practicable, gas concentrations should be the highest expected at test sites.

TABLE 7E–4—INTERFERENCE RESPONSE

Date of Test: _____

Analyzer Type: _____
Model No.: _____
Serial No: _____
Calibration Span: _____

Test gas type	Concentration (ppm)	Analyzer response
	Sum of Responses	
	% of Calibration Span	

TABLE 7E–5—MANUFACTURER STABILITY TEST

Test description	Acceptance criteria (note 1)
Thermal Stability	Temperature range when drift does not exceed 3.0% of analyzer range over a 12-hour run when measured with NO_X present @ 80% of calibration span.
Fault Conditions	Identify conditions which, when they occur, result in performance which is not in compliance with the Manufacturer's Stability Test criteria. These are to be indicated visually or electrically to alert the operator of the problem.
Insensitivity to Supply Voltage Variations.	±10.0% (or manufacturers alternative) variation from nominal voltage must produce a drift of ≤2.0% of calibration span for either zero or concentration ≥80% NO_X present.
Analyzer Calibration Error.	For a low-, medium-, and high-calibration gas, the difference between the manufacturer certified value and the analyzer response in direct calibration mode, no more than 2.0% of calibration span.

Note 1: If the instrument is to be used as a Low Range analyzer, all tests must be performed at a calibration span of 20 ppm or less.

METHOD 8—DETERMINATION OF SULFURIC ACID AND SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, and Method 6.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Sulfuric acid, including: Sulfuric acid (H_2SO_4) mist, Sulfur trioxide (SO_3).	7664–93–9, 7449–11–9	0.05 mg/m³ (0.03×10^{-7} lb/ft³).
Sulfur dioxide (SO_2)	7449–09–5	1.2 mg/m³ (3×10^{-9} lb/ft³).

1.2 Applicability. This method is applicable for the determination of H_2SO_4 (including H_2SO_4 mist and SO_3) and gaseous SO_2 emissions from stationary sources.

NOTE: Filterable particulate matter may be determined along with H_2SO_4 and SO_2 (subject to the approval of the Administrator) by inserting a heated glass fiber filter between the probe and isopropanol impinger (see section 6.1.1 of Method 6). If this option is chosen, particulate analysis is gravimetric only; sulfuric acid is not determined separately.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

A gas sample is extracted isokinetically from the stack. The H_2SO_4 and the SO_2 are separated, and both fractions are measured separately by the barium-thorin titration method.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Possible interfering agents of this method are fluorides, free ammonia, and dimethyl aniline. If any of these interfering agents is present (this can be determined by knowledge of the process), alternative methods, subject to the approval of the Administrator, are required.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. Same as Method 6, section 5.2.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 5, section 6.1, with the following additions and exceptions:

6.1.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 8–1; it is similar to the Method 5 sampling train, except that the filter position is different, and the filter holder does not have to be heated. See Method 5, section 6.1.1, for details and guidelines on operation and maintenance.

6.1.1.1 Probe Liner. Borosilicate or quartz glass, with a heating system to prevent visible condensation during sampling. Do not use metal probe liners.

6.1.1.2 Filter Holder. Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other gasket materials (*e.g.*, Teflon or Viton) may be used, subject to the approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The filter holder shall be placed between the first and second impingers. Do not heat the filter holder.

6.1.1.3 Impingers. Four, of the Greenburg-Smith design, as shown in Figure 8–1. The first and third impingers must have standard tips. The second and fourth impingers must be modified by replacing the insert with an approximately 13-mm (½-in.) ID glass tube, having an unconstricted tip located 13 mm (½ in.) from the bottom of the impinger. Similar collection systems, subject to the approval of the Administrator, may be used.

6.1.1.4 Temperature Sensor. Thermometer, or equivalent, to measure the temperature of the gas leaving the impinger train to within 1 °C (2 °F).

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Wash Bottles. Two polyethylene or glass bottles, 500-ml.

6.2.2 Graduated Cylinders. Two graduated cylinders (volumetric flasks may be used), 250-ml, 1-liter.

6.2.3 Storage Bottles. Leak-free polyethylene bottles, 1-liter size (two for each sampling run).

6.2.4 Trip Balance. 500-g capacity, to measure to ±0.5 g (necessary only if a moisture content analysis is to be done).

6.3 Analysis. The following items are required for sample analysis:

6.3.1 Pipettes. Volumetric 10-ml, 100-ml.

6.3.2 Burette. 50-ml.

6.3.3 Erlenmeyer Flask. 250-ml (one for each sample, blank, and standard).

6.3.4 Graduated Cylinder. 100-ml.

6.3.5 Dropping Bottle. To add indicator solution, 125-ml size.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents are to conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Filters and Silica Gel. Same as in Method 5, sections 7.1.1 and 7.1.2, respectively.

7.1.2 Water. Same as in Method 6, section 7.1.1.

7.1.3 Isopropanol, 80 Percent by Volume. Mix 800 ml of isopropanol with 200 ml of water.

NOTE: Check for peroxide impurities using the procedure outlined in Method 6, section 7.1.2.1.

7.1.4 Hydrogen Peroxide (H^2O^2), 3 Percent by Volume. Dilute 100 ml of 30 percent H_2O_2) to 1 liter with water. Prepare fresh daily.

7.1.5 Crushed Ice.

7.2 Sample Recovery. The reagents and standards required for sample recovery are:

7.2.1 Water. Same as in section 7.1.2.

7.2.2 Isopropanol, 80 Percent. Same as in section 7.1.3.

7.3 Sample Analysis. Same as Method 6, section 7.3.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation. Same as Method 5, section 8.1, except that filters should be inspected but need not be desiccated, weighed, or identified. If the effluent gas can be considered dry (i.e., moisture-free), the silica gel need not be weighed.

8.2 Preliminary Determinations. Same as Method 5, section 8.2.

8.3 Preparation of Sampling Train. Same as Method 5, section 8.3, with the following exceptions:

8.3.1 Use Figure 8–1 instead of Figure 5–1.

8.3.2 Replace the second sentence of Method 5, section 8.3.1 with: Place 100 ml of 80 percent isopropanol in the first impinger, 100 ml of 3 percent H_2O_2 in both the second and third impingers; retain a portion of each reagent for use as a blank solution. Place about 200 g of silica gel in the fourth impinger.

8.3.3 Ignore any other statements in section 8.3 of Method 5 that are obviously not applicable to the performance of Method 8.

NOTE: If moisture content is to be determined by impinger analysis, weigh each of the first three impingers (plus absorbing solution) to the nearest 0.5 g, and record these weights. Weigh also the silica gel (or silica gel plus container) to the nearest 0.5 g, and record.)

8.4 Metering System Leak-Check Procedure. Same as Method 5, section 8.4.1.

8.5 Pretest Leak-Check Procedure. Follow the basic procedure in Method 5, section 8.4.2, noting that the probe heater shall be adjusted to the minimum temperature required to prevent condensation, and also that verbage such as ''* * * plugging the inlet to the filter holder * * * '' found in section 8.4.2.2 of Method 5 shall be replaced by '' * * * plugging the inlet to the first impinger * * * ''. The pretest leak-check is recommended, but is not required.

8.6 Sampling Train Operation. Follow the basic procedures in Method 5, section 8.5, in conjunction with the following special instructions:

8.6.1 Record the data on a sheet similar to that shown in Figure 8–2 (alternatively, Figure 5–2 in Method 5 may be used). The sampling rate shall not exceed 0.030 m^3/min (1.0 cfm) during the run. Periodically during the test, observe the connecting line between the probe and first impinger for signs of condensation. If condensation does occur, adjust the probe heater setting upward to the minimum temperature required to prevent condensation. If component changes become necessary during a run, a leak-check shall be performed immediately before each change, according to the procedure outlined in section 8.4.3 of Method 5 (with appropriate modifications, as mentioned in section 8.5 of this method); record all leak rates. If the leakage rate(s) exceeds the specified rate, the tester shall either void the run or plan to correct the sample volume as outlined in section 12.3 of Method 5. Leak-checks immediately after component changes are recommended, but not required. If these leak-checks are performed, the procedure in section 8.4.2 of Method 5 (with appropriate modifications) shall be used.

8.6.2 After turning off the pump and recording the final readings at the conclusion of each run, remove the probe from the stack. Conduct a post-test (mandatory) leak-check as outlined in section 8.4.4 of Method 5 (with appropriate modifications), and record the leak rate. If the post-test leakage rate exceeds the specified acceptable rate, either correct the sample volume, as outlined in section 12.3 of Method 5, or void the run.

8.6.3 Drain the ice bath and, with the probe disconnected, purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at the average flow rate used for sampling.

NOTE: Clean ambient air can be provided by passing air through a charcoal filter. Alternatively, ambient air (without cleaning) may be used.

8.7 Calculation of Percent Isokinetic. Same as Method 5, section 8.6.

8.8 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. Treat the samples as follows:

8.8.1 Container No. 1.

8.8.1.1 If a moisture content analysis is to be performed, clean and weigh the first impinger (plus contents) to the nearest 0.5 g, and record this weight.

8.8.1.2 Transfer the contents of the first impinger to a 250-ml graduated cylinder. Rinse the probe, first impinger, all connecting glassware before the filter, and the front half of the filter holder with 80 percent isopropanol. Add the isopropanol rinse solution to the cylinder. Dilute the contents of the cylinder to 225 ml with 80 percent isopropanol, and transfer the cylinder contents to the storage container. Rinse the cylinder with 25 ml of 80 percent isopropanol, and transfer the rinse to the storage container. Add the filter to the solution in the storage container and mix. Seal the container to protect the solution against evaporation. Mark the level of liquid on the container, and identify the sample container.

8.8.2 Container No. 2.

8.8.2.1 If a moisture content analysis is to be performed, clean and weigh the second and third impingers (plus contents) to the nearest 0.5 g, and record the weights. Also, weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g, and record the weight.

8.8.2.2 Transfer the solutions from the second and third impingers to a 1-liter graduated cylinder. Rinse all connecting glassware (including back half of filter holder) between the filter and silica gel impinger with water, and add this rinse water to the cylinder. Dilute the contents of the cylinder to 950 ml with water. Transfer the solution to a storage container. Rinse the cylinder with 50 ml of water, and transfer the rinse to the storage container. Mark the level of liquid on the container. Seal and identify the sample container.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
7.1.3	Isopropanol check	Ensure acceptable level of peroxide impurities in isopropanol.
8.4, 8.5, 10.1	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.
10.2	Barium standard solution standardization	Ensure normality determination.
11.2	Replicate titrations	Ensure precision of titration determinations.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

10.1 Sampling Equipment. Same as Method 5, section 10.0.

10.2 Barium Standard Solution. Same as Method 6, section 10.5.

11.0 Analytical Procedure

11.1. Sample Loss. Same as Method 6, section 11.1.

11.2. Sample Analysis.

11.2.1 Container No. 1. Shake the container holding the isopropanol solution and the filter. If the filter breaks up, allow the fragments to settle for a few minutes before removing a sample aliquot. Pipette a 100-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 2 to 4 drops of thorin indicator, and titrate to a pink endpoint using 0.0100 N barium standard solution. Repeat the titration with a second aliquot of sample, and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater.

11.2.2 Container No. 2. Thoroughly mix the solution in the container holding the contents of the second and third impingers. Pipette a 10-ml aliquot of sample into a 250-ml Erlenmeyer flask. Add 40 ml of isopropanol, 2 to 4 drops of thorin indicator, and titrate to a pink endpoint using 0.0100 N barium standard solution. Repeat the titration with a second aliquot of sample, and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater.

11.2.3 Blanks. Prepare blanks by adding 2 to 4 drops of thorin indicator to 100 ml of 80 percent isopropanol. Titrate the blanks in the same manner as the samples.

12.0 Data Analysis and Calculations

Carry out calculations retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature. Same as Method 5, section 12.1, with the following additions and exceptions:

$C_{H_2SO_4}$ = Sulfuric acid (including SO_3) concentration, g/dscm (lb/dscf).

C_{SO_2} = Sulfur dioxide concentration, g/dscm (lb/dscf).

N = Normality of barium perchlorate titrant, meq/ml.

V_a = Volume of sample aliquot titrated, 100 ml for H_2SO_4 and 10 ml for SO_2.

V_{soln} = Total volume of solution in which the sample is contained, 1000 ml for the SO_2 sample and 250 ml for the H_2SO_4 sample.

V_t = Volume of barium standard solution titrant used for the sample, ml.

V_{tb} = Volume of barium standard solution titrant used for the blank, ml.

12.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 8–2).

12.3 Dry Gas Volume. Same as Method 5, section 12.3.

12.4 Volume of Water Vapor Condensed and Moisture Content. Calculate the volume of water vapor using Equation 5–2 of Method 5; the weight of water collected in the impingers and silica gel can be converted directly to milliliters (the specific gravity of water is 1 g/ml). Calculate the moisture content of the stack gas (B_{ws}) using Equation 5–3 of Method 5. The note in section 12.5 of Method 5 also applies to this method. Note that if the effluent gas stream can be considered dry, the volume of water vapor and moisture content need not be calculated.

12.5 Sulfuric Acid Mist (Including SO_3) Concentration.

$$C_{H_2SO_4} = K_3\left[N\left(V_t - V_{tb}\right)\left(V_{soln}/V_a\right)\right]/V_{m(std)} \qquad \text{Eq. 8-1}$$

Where:

K_3 = 0.04904 g/meq for metric units,

$K_3 = 1.081 \times 10^{-4}$ lb/meq for English units.

12.6 Sulfur Dioxide Concentration.

$$C_{SO_2} = K_4\left[N\left(V_t - V_{tb}\right)\left(V_{soln}/V_a\right)\right]/V_{m(std)} \qquad \text{Eq. 8-2}$$

Where:

K_4 = 0.03203 g/meq for metric units,

$K_4 = 7.061 \times 10^{-5}$ lb/meq for English units.

12.7 Isokinetic Variation. Same as Method 5, section 12.11.

12.8 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate, if needed, using data obtained in this method and the equations in sections 12.6 and 12.7 of Method 2.

13.0 Method Performance

13.1 Analytical Range. Collaborative tests have shown that the minimum detectable limits of the method are 0.06 mg/m^3 (4×10^{-9} lb/ft^3) for H_2SO_4 and 1.2 mg/m^3 (74×10^{-9} lb/ft^3) for SO_2. No upper limits have been established. Based on theoretical calculations for 200 ml of 3 percent H_2O_2 solution, the upper concentration limit for SO_2 in a 1.0 m^3 (35.3 ft^3) gas sample is about 12,000 mg/m^3 (7.7×10^{-4} lb/ft^3). The upper limit can be extended by increasing the quantity of peroxide solution in the impingers.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as section 17.0 of Methods 5 and 6.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

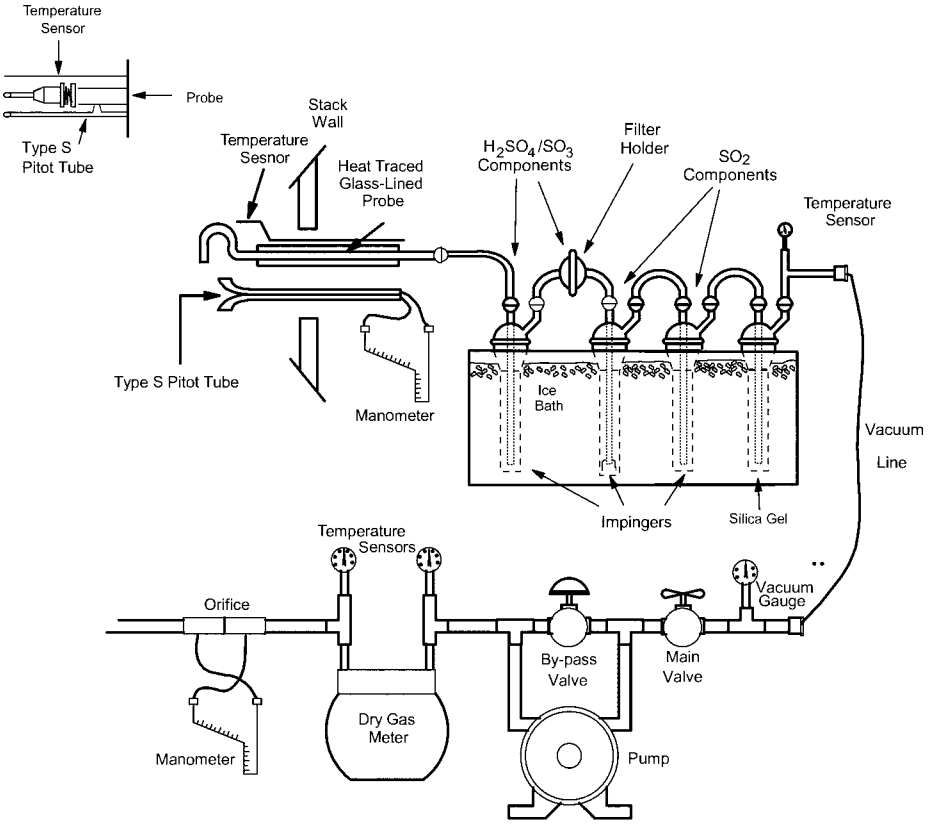

Figure 8-1. Sulfuric Acid Sampling Train

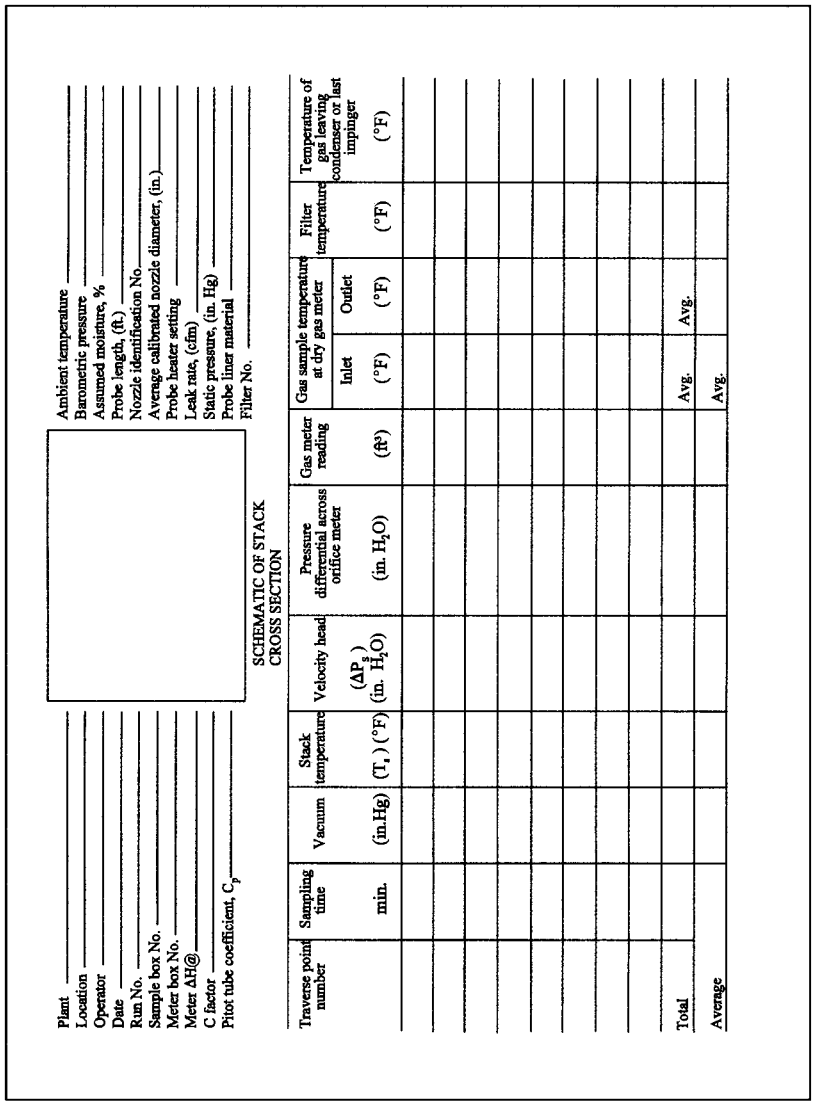

Figure 8-2. Field Data Sheet.

METHOD 9—VISUAL DETERMINATION OF THE OPACITY OF EMISSIONS FROM STATIONARY SOURCES

Many stationary sources discharge visible emissions into the atmosphere; these emissions are usually in the shape of a plume. This method involves the determination of plume opacity by qualified observers. The method includes procedures for the training and certification of observers, and procedures to be used in the field for determination of plume opacity. The appearance of a plume as viewed by an observer depends upon a number of variables, some of which may be controllable and some of which may not be controllable in the field. Variables which can be controlled to an extent to which they no longer exert a significant influence upon

plume appearance include: Angle of the observer with respect to the plume; angle of the observer with respect to the sun; point of observation of attached and detached steam plume; and angle of the observer with respect to a plume emitted from a rectangular stack with a large length to width ratio. The method includes specific criteria applicable to these variables.

Other variables which may not be controllable in the field are luminescence and color contrast between the plume and the background against which the plume is viewed. These variables exert an influence upon the appearance of a plume as viewed by an observer, and can affect the ability of the observer to accurately assign opacity values to the observed plume. Studies of the theory of plume opacity and field studies have demonstrated that a plume is most visible and presents the greatest apparent opacity when viewed against a contrasting background. It follows from this, and is confirmed by field trials, that the opacity of a plume, viewed under conditions where a contrasting background is present can be assigned with the greatest degree of accuracy. However, the potential for a positive error is also the greatest when a plume is viewed under such contrasting conditions. Under conditions presenting a less contrasting background, the apparent opacity of a plume is less and approaches zero as the color and luminescence contrast decrease toward zero. As a result, significant negative bias and negative errors can be made when a plume is viewed under less contrasting conditions. A negative bias decreases rather than increases the possibility that a plant operator will be cited for a violation of opacity standards due to observer error.

Studies have been undertaken to determine the magnitude of positive errors which can be made by qualified observers while reading plumes under contrasting conditions and using the procedures set forth in this method. The results of these studies (field trials) which involve a total of 769 sets of 25 readings each are as follows:

(1) For black plumes (133 sets at a smoke generator), 100 percent of the sets were read with a positive error[1] of less than 7.5 percent opacity; 99 percent were read with a positive error of less than 5 percent opacity.

(2) For white plumes (170 sets at a smoke generator, 168 sets at a coal-fired power plant, 298 sets at a sulfuric acid plant), 99 percent of the sets were read with a positive error of less than 7.5 percent opacity; 95 percent were read with a positive error of less than 5 percent opacity.

[1] For a set, positive error = average opacity determined by observers' 25 observations—average opacity determined from transmissometer's 25 recordings.

The positive observational error associated with an average of twenty-five readings is therefore established. The accuracy of the method must be taken into account when determining possible violations of applicable opacity standards.

1. Principle and Applicability

1.1 Principle. The opacity of emissions from stationary sources is determined visually by a qualified observer.

1.2 Applicability. This method is applicable for the determination of the opacity of emissions from stationary sources pursuant to §60.11(b) and for qualifying observers for visually determining opacity of emissions.

2. Procedures

The observer qualified in accordance with section 3 of this method shall use the following procedures for visually determining the opacity of emissions:

2.1 Position. The qualified observer shall stand at a distance sufficient to provide a clear view of the emissions with the sun oriented in the 140° sector to his back. Consistent with maintaining the above requirement, the observer shall, as much as possible, make his observations from a position such that his line of vision is approximately perpendicular to the plume direction, and when observing opacity of emissions from rectangular outlets (e.g., roof monitors, open baghouses, noncircular stacks), approximately perpendicular to the longer axis of the outlet. The observer's line of sight should not include more than one plume at a time when multiple stacks are involved, and in any case the observer should make his observations with his line of sight perpendicular to the longer axis of such a set of multiple stacks (e.g., stub stacks on baghouses).

2.2 Field Records. The observer shall record the name of the plant, emission location, type facility, observer's name and affiliation, a sketch of the observer's position relative to the source, and the date on a field data sheet (Figure 9–1). The time, estimated distance to the emission location, approximate wind direction, estimated wind speed, description of the sky condition (presence and color of clouds), and plume background are recorded on a field data sheet at the time opacity readings are initiated and completed.

2.3 Observations. Opacity observations shall be made at the point of greatest opacity in that portion of the plume where condensed water vapor is not present. The observer shall not look continuously at the plume, but instead shall observe the plume momentarily at 15-second intervals.

2.3.1 Attached Steam Plumes. When condensed water vapor is present within the

plume as it emerges from the emission outlet, opacity observations shall be made beyond the point in the plume at which condensed water vapor is no longer visible. The observer shall record the approximate distance from the emission outlet to the point in the plume at which the observations are made.

2.3.2 Detached Steam Plume. When water vapor in the plume condenses and becomes visible at a distinct distance from the emission outlet, the opacity of emissions should be evaluated at the emission outlet prior to the condensation of water vapor and the formation of the steam plume.

2.4 Recording Observations. Opacity observations shall be recorded to the nearest 5 percent at 15-second intervals on an observational record sheet. (See Figure 9–2 for an example.) A minimum of 24 observations shall be recorded. Each momentary observation recorded shall be deemed to represent the average opacity of emissions for a 15-second period.

2.5 Data Reduction. Opacity shall be determined as an average of 24 consecutive observations recorded at 15-second intervals. Divide the observations recorded on the record sheet into sets of 24 consecutive observations. A set is composed of any 24 consecutive observations. Sets need not be consecutive in time and in no case shall two sets overlap. For each set of 24 observations, calculate the average by summing the opacity of the 24 observations and dividing this sum by 24. If an applicable standard specifies an averaging time requiring more than 24 observations, calculate the average for all observations made during the specified time period. Record the average opacity on a record sheet. (See Figure 9–1 for an example.)

3. Qualifications and Testing

3.1 Certification Requirements. To receive certification as a qualified observer, a candidate must be tested and demonstrate the ability to assign opacity readings in 5 percent increments to 25 different black plumes and 25 different white plumes, with an error not to exceed 15 percent opacity on any one reading and an average error not to exceed 7.5 percent opacity in each category. Candidates shall be tested according to the procedures described in section 3.2. Smoke generators used pursuant to section 3.2 shall be equipped with a smoke meter which meets the requirements of section 3.3.

The certification shall be valid for a period of 6 months, at which time the qualification procedure must be repeated by any observer in order to retain certification.

3.2 Certification Procedure. The certification test consists of showing the candidate a complete run of 50 plumes—25 black plumes and 25 white plumes—generated by a smoke generator. Plumes within each set of 25 black and 25 white runs shall be presented in random order. The candidate assigns an opacity value to each plume and records his observation on a suitable form. At the completion of each run of 50 readings, the score of the candidate is determined. If a candidate fails to qualify, the complete run of 50 readings must be repeated in any retest. The smoke test may be administered as part of a smoke school or training program, and may be preceded by training or familiarization runs of the smoke generator during which candidates are shown black and white plumes of known opacity.

3.3 Smoke Generator Specifications. Any smoke generator used for the purposes of section 3.2 shall be equipped with a smoke meter installed to measure opacity across the diameter of the smoke generator stack. The smoke meter output shall display instack opacity based upon a pathlength equal to the stack exit diameter, on a full 0 to 100 percent chart recorder scale. The smoke meter optical design and performance shall meet the specifications shown in Table 9–1. The smoke meter shall be calibrated as prescribed in section 3.3.1 prior to the conduct of each smoke reading test. At the completion of each test, the zero and span drift shall be checked and if the drift exceeds ±1 percent opacity, the condition shall be corrected prior to conducting any subsequent test runs. The smoke meter shall be demonstrated, at the time of installation, to meet the specifications listed in Table 9–1. This demonstration shall be repeated following any subsequent repair or replacement of the photocell or associated electronic circuitry including the chart recorder or output meter, or every 6 months, whichever occurs first.

TABLE 9–1—SMOKE METER DESIGN AND PERFORMANCE SPECIFICATIONS

Parameter	Specification
a. Light source	Incandescent lamp operated at nominal rated voltage.
b. Spectral response of photocell.	Photopic (daylight spectral response of the human eye—Citation 3).
c. Angle of view	15° maximum total angle.
d. Angle of projection	15° maximum total angle.
e. Calibration error	±3% opacity, maximum.
f. Zero and span drift	±1% opacity, 30 minutes.
g. Response time	5 seconds.

3.3.1 Calibration. The smoke meter is calibrated after allowing a minimum of 30 minutes warmup by alternately producing simulated opacity of 0 percent and 100 percent. When stable response at 0 percent or 100 percent is noted, the smoke meter is adjusted to produce an output of 0 percent or 100 percent, as appropriate. This calibration shall be repeated until stable 0 percent and 100

percent readings are produced without adjustment. Simulated 0 percent and 100 percent opacity values may be produced by alternately switching the power to the light source on and off while the smoke generator is not producing smoke.

3.3.2 Smoke Meter Evaluation. The smoke meter design and performance are to be evaluated as follows:

3.3.2.1 Light Source. Verify from manufacturer's data and from voltage measurements made at the lamp, as installed, that the lamp is operated within ±5 percent of the nominal rated voltage.

3.3.2.2 Spectral Response of Photocell. Verify from manufacturer's data that the photocell has a photopic response; i.e., the spectral sensitivity of the cell shall closely approximate the standard spectral-luminosity curve for photopic vision which is referenced in (b) of Table 9–1.

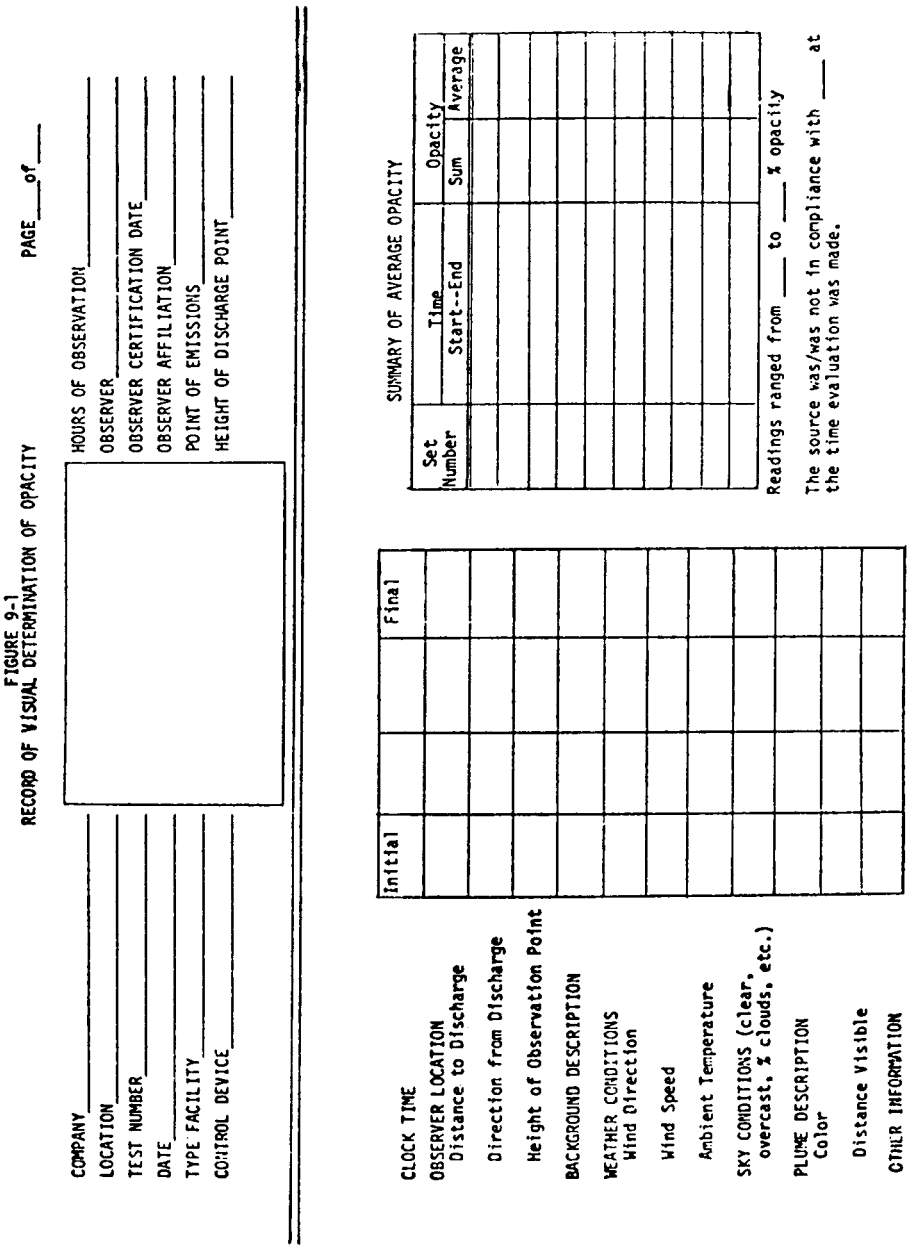

FIGURE 9–2—OBSERVATION RECORD

Page ___ of ___

Company .....
Location .....
Test Number .....
Date.

Observer .....
Type facility .....
Point of emissions .....

Hr.	Min.	Seconds				Steam plume (check if applicable)		Comments
		0	15	30	45	Attached	Detached	
	0							
	1							
	2							
	3							
	4							
	5							
	6							
	7							
	8							
	9							
	10							
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	25							
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	27							
	28							
	29							

FIGURE 9–2—OBSERVATION RECORD (CONTINUED)

Page ____ of ____

Company ..... Observer .....
Location ..... Type facility .....
Test Number ..... Point of emissions .....
Date.

Hr.	Min.	Seconds				Steam plume (check if applicable)		Comments
		0	15	30	45	Attached	Detached	
	30							

Hr.	Min.	Seconds				Steam plume (check if applicable)		Comments
		0	15	30	45	Attached	Detached	
	31							
	32							
	33							
	34							
	35							
	36							
	37							
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3.3.2.3 Angle of View. Check construction geometry to ensure that the total angle of view of the smoke plume, as seen by the photocell, does not exceed 15°. The total angle of view may be calculated from: $\theta = 2 \tan^{-1} d/2L$, where θ = total angle of view; d = the sum of the photocell diameter + the diameter of the limiting aperture; and L = the distance from the photocell to the limiting aperture. The limiting aperture is the point in the path between the photocell and the smoke plume where the angle of view is most restricted. In smoke generator smoke meters this is normally an orifice plate.

3.3.2.4 Angle of Projection. Check construction geometry to ensure that the total angle of projection of the lamp on the smoke plume does not exceed 15°. The total angle of projection may be calculated from: $\theta = 2 \tan^{-1} d/2L$, where θ = total angle of projection; d = the sum of the length of the lamp

filament + the diameter of the limiting aperture; and L = the distance from the lamp to the limiting aperture.

3.3.2.5 Calibration Error. Using neutral-density filters of known opacity, check the error between the actual response and the theoretical linear response of the smoke meter. This check is accomplished by first calibrating the smoke meter according to 3.3.1 and then inserting a series of three neutral-density filters of nominal opacity of 20, 50, and 75 percent in the smoke meter pathlength. Filters calibrated within ±2 percent shall be used. Care should be taken when inserting the filters to prevent stray light from affecting the meter. Make a total of five nonconsecutive readings for each filter. The maximum error on any one reading shall be 3 percent opacity.

3.3.2.6 Zero and Span Drift. Determine the zero and span drift by calibrating and operating the smoke generator in a normal manner over a 1-hour period. The drift is measured by checking the zero and span at the end of this period.

3.3.2.7 Response Time. Determine the response time by producing the series of five simulated 0 percent and 100 percent opacity values and observing the time required to reach stable response. Opacity values of 0 percent and 100 percent may be simulated by alternately switching the power to the light source off and on while the smoke generator is not operating.

4. Bibliography

1. Air Pollution Control District Rules and Regulations, Los Angeles County Air Pollution Control District, Regulation IV, Prohibitions, Rule 50.

2. Weisburd, Melvin I., Field Operations and Enforcement Manual for Air, U.S. Environmental Protection Agency, Research Triangle Park, NC. APTD–1100, August 1972, pp. 4.1–4.36.

3. Condon, E.U., and Odishaw, H., Handbook of Physics, McGraw-Hill Co., New York, NY, 1958, Table 3.1, p. 6–52.

Alternate Method 1—Determination of the Opacity of Emissions From Stationary Sources Remotely by Lidar

This alternate method provides the quantitative determination of the opacity of an emissions plume remotely by a mobile lidar system (laser radar; Light Detection and Ranging). The method includes procedures for the calibration of the lidar and procedures to be used in the field for the lidar determination of plume opacity. The lidar is used to measure plume opacity during either day or nighttime hours because it contains its own pulsed light source or transmitter. The operation of the lidar is not dependent upon ambient lighting conditions (light, dark, sunny or cloudy).

The lidar mechanism or technique is applicable to measuring plume opacity at numerous wavelengths of laser radiation. However, the performance evaluation and calibration test results given in support of this method apply only to a lidar that employs a ruby (red light) laser [Reference 5.1].

1. Principle and Applicability

1.1 Principle. The opacity of visible emissions from stationary sources (stacks, roof vents, etc.) is measured remotely by a mobile lidar (laser radar).

1.2 Applicability. This method is applicable for the remote measurement of the opacity of visible emissions from stationary sources during both nighttime and daylight conditions, pursuant to 40 CFR §60.11(b). It is also applicable for the calibration and performance verification of the mobile lidar for the measurement of the opacity of emissions. A performance/design specification for a basic lidar system is also incorporated into this method.

1.3 Definitions.

Azimuth angle: The angle in the horizontal plane that designates where the laser beam is pointed. It is measured from an arbitrary fixed reference line in that plane.

Backscatter: The scattering of laser light in a direction opposite to that of the incident laser beam due to reflection from particulates along the beam's atmospheric path which may include a smoke plume.

Backscatter signal: The general term for the lidar return signal which results from laser light being backscattered by atmospheric and smoke plume particulates.

Convergence distance: The distance from the lidar to the point of overlap of the lidar receiver's field-of-view and the laser beam.

Elevation angle: The angle of inclination of the laser beam referenced to the horizontal plane.

Far region: The region of the atmosphere's path along the lidar line-of-sight beyond or behind the plume being measured.

Lidar: Acronym for Light Detection and Ranging.

Lidar range: The range or distance from the lidar to a point of interest along the lidar line-of-sight.

Near region: The region of the atmospheric path along the lidar line-of-sight between the lidar's convergence distance and the plume being measured.

Opacity: One minus the optical transmittance of a smoke plume, screen target, etc.

Pick interval: The time or range intervals in the lidar backscatter signal whose minimum average amplitude is used to calculate opacity. Two pick intervals are required, one in the near region and one in the far region.

Plume: The plume being measured by lidar.

Plume signal: The backscatter signal resulting from the laser light pulse passing through a plume.

$1/R^2$Correction: The correction made for the systematic decrease in lidar backscatter signal amplitude with range.

Reference signal: The backscatter signal resulting from the laser light pulse passing through ambient air.

Sample interval: The time period between successive samples for a digital signal or between successive measurements for an analog signal.

Signal spike: An abrupt, momentary increase and decrease in signal amplitude.

Source: The source being tested by lidar.

Time reference: The time (t_o) when the laser pulse emerges from the laser, used as the reference in all lidar time or range measurements.

2. Procedures

The mobile lidar calibrated in accordance with Paragraph 3 of this method shall use the following procedures for remotely measuring the opacity of stationary source emissions:

2.1 Lidar Position. The lidar shall be positioned at a distance from the plume sufficient to provide an unobstructed view of the source emissions. The plume must be at a range of at least 50 meters or three consecutive pick intervals (whichever is greater) from the lidar's transmitter/receiver convergence distance along the line-of-sight. The maximum effective opacity measurement distance of the lidar is a function of local atmospheric conditions, laser beam diameter, and plume diameter. The test position of the lidar shall be selected so that the diameter of the laser beam at the measurement point within the plume shall be no larger than three-fourths the plume diameter. The beam diameter is calculated by Equation (AM1–1):

$$D(\text{lidar}) = A + R\varphi \leq 0.75\ D(\text{Plume}) \quad \text{(AM1–1)}$$

Where:

D(Plume) = diameter of the plume (cm),
φ = laser beam divergence measured in radians
R = range from the lidar to the source (cm)
D(Lidar) = diameter of the laser beam at range R (cm),
A = diameter of the laser beam or pulse where it leaves the laser.

The lidar range, R, is obtained by aiming and firing the laser at the emissions source structure immediately below the outlet. The range value is then determined from the backscatter signal which consists of a signal spike (return from source structure) and the atmospheric backscatter signal [Reference 5.1]. This backscatter signal should be recorded.

When there is more than one source of emissions in the immediate vicinity of the plume, the lidar shall be positioned so that the laser beam passes through only a single plume, free from any interference of the other plumes for a minimum of 50 meters or three consecutive pick intervals (whichever is greater) in each region before and beyond the plume along the line-of-sight (determined from the backscatter signals). The lidar shall initially be positioned so that its line-of-sight is approximately perpendicular to the plume.

When measuring the opacity of emissions from rectangular outlets (e.g., roof monitors, open baghouses, noncircular stacks, etc.), the lidar shall be placed in a position so that its line-of-sight is approximately perpendicular to the longer (major) axis of the outlet.

2.2 Lidar Operational Restrictions. The lidar receiver shall not be aimed within an angle of ±15° (cone angle) of the sun.

This method shall not be used to make opacity measurements if thunderstorms, snowstorms, hail storms, high wind, high-ambient dust levels, fog or other atmospheric conditions cause the reference signals to consistently exceed the limits specified in section 2.3.

2.3 Reference Signal Requirements. Once placed in its proper position for opacity measurement, the laser is aimed and fired with the line-of-sight near the outlet height and rotated horizontally to a position clear of the source structure and the associated plume. The backscatter signal obtained from this position is called the ambient-air or reference signal. The lidar operator shall inspect this signal [Section V of Reference 5.1] to: (1) determine if the lidar line-of-sight is free from interference from other plumes and from physical obstructions such as cables, power lines, etc., for a minimum of 50 meters or three consecutive pick intervals (whichever is greater) in each region before and beyond the plume, and (2) obtain a qualitative measure of the homogeneity of the ambient air by noting any signal spikes.

Should there be any signal spikes on the reference signal within a minimum of 50 meters or three consecutive pick intervals (whichever is greater) in each region before and beyond the plume, the laser shall be fired three more times and the operator shall inspect the reference signals on the display. If the spike(s) remains, the azimuth angle shall be changed and the above procedures conducted again. If the spike(s) disappears in all three reference signals, the lidar line-of-sight is acceptable if there is shot-to-shot consistency and there is no interference from other plumes.

Shot-to-shot consistency of a series of reference signals over a period of twenty seconds is verified in either of two ways. (1) The lidar operator shall observe the reference signal amplitudes. For shot-to-shot consistency the ratio of R_f to R_n [amplitudes of the near and far region pick intervals (Section 2.6.1)] shall vary by not more than ±6% between shots; or (2) the lidar operator shall accept any one of the reference signals and

treat the other two as plume signals; then the opacity for each of the subsequent reference signals is calculated (Equation AM1–2). For shot-to-shot consistency, the opacity values shall be within ±3% of 0% opacity and the associated S_o values less than or equal to 8% (full scale) [Section 2.6].

If a set of reference signals fails to meet the requirements of this section, then all plume signals [Section 2.4] from the last set of acceptable reference signals to the failed set shall be discarded.

2.3.1 Initial and Final Reference Signals. Three reference signals shall be obtained within a 90-second time period prior to any data run. A final set of three reference signals shall be obtained within three (3) minutes after the completion of the same data run.

2.3.2 Temporal Criterion for Additional Reference Signals. An additional set of reference signals shall be obtained during a data run if there is a change in wind direction or plume drift of 30° or more from the direction that was prevalent when the last set of reference signals was obtained. An additional set of reference signals shall also be obtained if there is an increase in value of S_{In} (near region standard deviation, Equation AM1–5) or S_{If} (far region standard deviation, Equation AM1–6) that is greater than 6% (full scale) over the respective values calculated from the immediately previous plume signal, and this increase in value remains for 30 seconds or longer. An additional set of reference signals shall also be obtained if there is a change in amplitude in either the near or the far region of the plume signal, that is greater than 6% of the near signal amplitude and this change in amplitude remains for 30 seconds or more.

2.4 Plume Signal Requirements. Once properly aimed, the lidar is placed in operation with the nominal pulse or firing rate of six pulses/minute (1 pulse/10 seconds). The lidar operator shall observe the plume backscatter signals to determine the need for additional reference signals as required by section 2.3.2. The plume signals are recorded from lidar start to stop and are called a data run. The length of a data run is determined by operator discretion. Short-term stops of the lidar to record additional reference signals do not constitute the end of a data run if plume signals are resumed within 90 seconds after the reference signals have been recorded, and the total stop or interrupt time does not exceed 3 minutes.

2.4.1 Non-hydrated Plumes. The laser shall be aimed at the region of the plume which displays the greatest opacity. The lidar operator must visually verify that the laser is aimed clearly above the source exit structure.

2.4.2 Hydrated Plumes. The lidar will be used to measure the opacity of hydrated or so-called steam plumes. As listed in the reference method, there are two types, i.e., attached and detached steam plumes.

2.4.2.1 Attached Steam Plumes. When condensed water vapor is present within a plume, lidar opacity measurements shall be made at a point within the residual plume where the condensed water vapor is no longer visible. The laser shall be aimed into the most dense region (region of highest opacity) of the residual plume.

During daylight hours the lidar operator locates the most dense portion of the residual plume visually. During nighttime hours a high-intensity spotlight, night vision scope, or low light level TV, etc., can be used as an aid to locate the residual plume. If visual determination is ineffective, the lidar may be used to locate the most dense region of the residual plume by repeatedly measuring opacity, along the longitudinal axis or center of the plume from the emissions outlet to a point just beyond the steam plume. The lidar operator should also observe color differences and plume reflectivity to ensure that the lidar is aimed completely within the residual plume. If the operator does not obtain a clear indication of the location of the residual plume, this method shall not be used.

Once the region of highest opacity of the residual plume has been located, aiming adjustments shall be made to the laser line-of-sight to correct for the following: movement to the region of highest opacity out of the lidar line-of-sight (away from the laser beam) for more than 15 seconds, expansion of the steam plume (air temperature lowers and/or relative humidity increases) so that it just begins to encroach on the field-of-view of the lidar's optical telescope receiver, or a decrease in the size of the steam plume (air temperature higher and/or relative humidity decreases) so that regions within the residual plume whose opacity is higher than the one being monitored, are present.

2.4.2.2 Detached Steam Plumes. When the water vapor in a hydrated plume condenses and becomes visible at a finite distance from the stack or source emissions outlet, the opacity of the emissions shall be measured in the region of the plume clearly above the emissions outlet and below condensation of the water vapor.

During daylight hours the lidar operators can visually determine if the steam plume is detached from the stack outlet. During nighttime hours a high-intensity spotlight, night vision scope, low light level TV, etc., can be used as an aid in determining if the steam plume is detached. If visual determination is ineffective, the lidar may be used to determine if the steam plume is detached by repeatedly measuring plume opacity from the outlet to the steam plume along the plume's longitudinal axis or center line. The lidar operator should also observe color differences and plume reflectivity to detect a

detached plume. If the operator does not obtain a clear indication of the location of the detached plume, this method shall not be used to make opacity measurements between the outlet and the detached plume.

Once the determination of a detached steam plume has been confirmed, the laser shall be aimed into the region of highest opacity in the plume between the outlet and the formation of the steam plume. Aiming adjustments shall be made to the lidar's line-of-sight within the plume to correct for changes in the location of the most dense region of the plume due to changes in wind direction and speed or if the detached steam plume moves closer to the source outlet encroaching on the most dense region of the plume. If the detached steam plume should move too close to the source outlet for the lidar to make interference-free opacity measurements, this method shall not be used.

2.5 Field Records. In addition to the recording recommendations listed in other sections of this method the following records should be maintained. Each plume measured should be uniquely identified. The name of the facility, type of facility, emission source type, geographic location of the lidar with respect to the plume, and plume characteristics should be recorded. The date of the test, the time period that a source was monitored, the time (to the nearest second) of each opacity measurement, and the sample interval should also be recorded. The wind speed, wind direction, air temperature, relative humidity, visibility (measured at the lidar's position), and cloud cover should be recorded at the beginning and end of each time period for a given source. A small sketch depicting the location of the laser beam within the plume should be recorded.

If a detached or attached steam plume is present at the emissions source, this fact should be recorded. Figures AM1–I and AM1–II are examples of logbook forms that may be used to record this type of data. Magnetic tape or paper tape may also be used to record data.

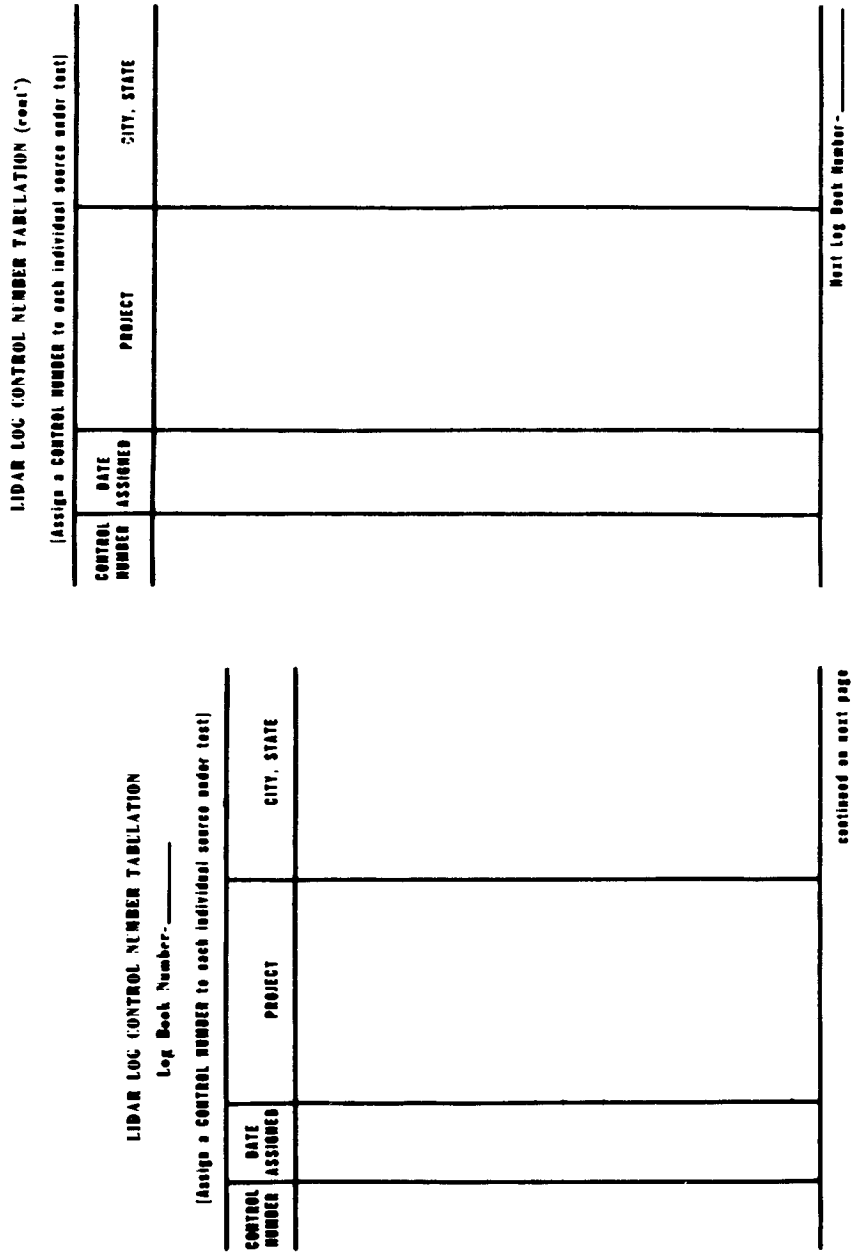


Figure AM1-1 Lidar Log Control Number Tabulation

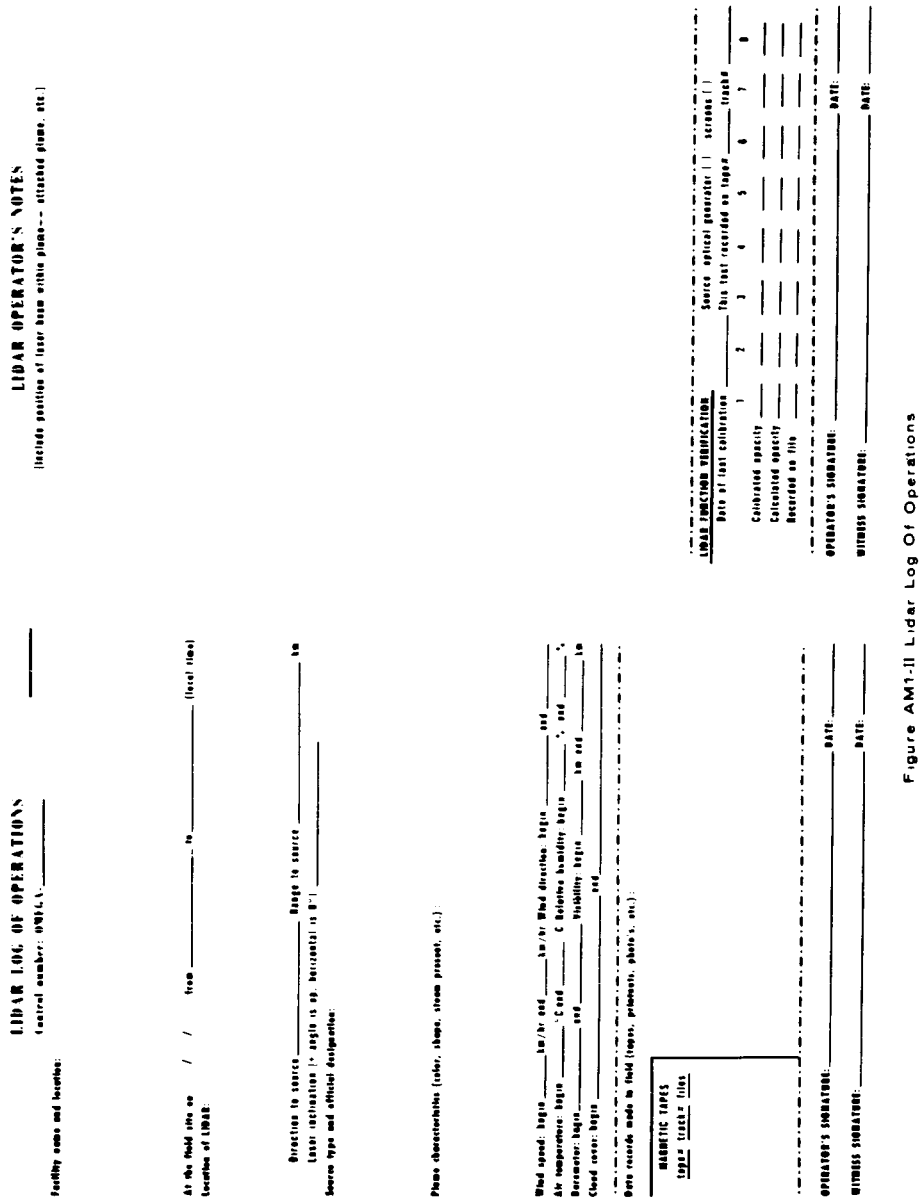
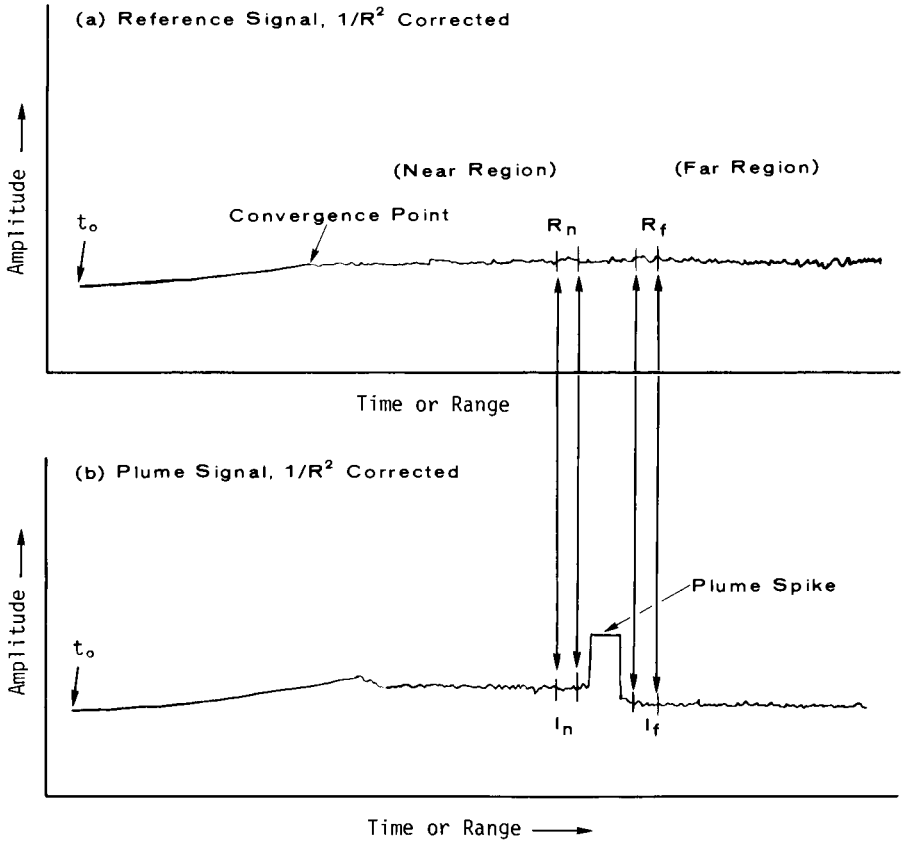


Figure AM1-11 Lidar Log Of Operations



(a) Reference signal, $1/R^2$-corrected. This reference signal is for plume signal (b). R_n, R_f are chosen to coincide with I_n, I_f.

(b) Plume signal, $1/R^2$-corrected. The plume spike and the decrease in the backscatter signal amplitude in the far region are due to the opacity of the plume. I_n, I_f are chosen as indicated in Section 2.6.

Figure AM1-III. Plots of Lidar Backscatter Signals

2.6 Opacity Calculation and Data Analysis. Referring to the reference signal and plume signal in Figure AM1–III, the measured opacity (O_p) in percent for each lidar measurement is calculated using Equation AM1–2. ($O_p = 1 - T_p$; T_p is the plume transmittance.)

$$O_p = (100\%)\left[1 - \left(\frac{I_f}{R_f}\frac{R_n}{I_n}\right)^{\frac{1}{2}}\right], \qquad \text{(AM1-2)}$$

Where:

I_n = near-region pick interval signal amplitude, plume signal, $1/R^2$ corrected,

I_f = far-region pick interval signal amplitude, plume signal, $1/R^2$ corrected,

R_n = near-region pick interval signal amplitude, reference signal, $1/R^2$ corrected, and

R_f = far-region pick interval signal amplitude, reference signal, $1/R^2$ corrected.

The $1/R^2$ correction to the plume and reference signal amplitudes is made by multiplying the amplitude for each successive sample interval from the time reference, by the square of the lidar time (or range) associated with that sample interval [Reference 5.1].

The first step in selecting the pick intervals for Equation AM1–2 is to divide the plume signal amplitude by the reference signal amplitude at the same respective ranges to obtain a ''normalized'' signal. The pick intervals selected using this normalized signal, are a minimum of 15 m (100 nanoseconds) in length and consist of at least 5 contiguous sample intervals. In addition, the following criteria, listed in order of importance, govern pick interval selection. (1) The intervals shall be in a region of the normalized signal where the reference signal meets the requirements of section 2.3 and is everywhere greater than zero. (2) The intervals (near and far) with the minimum average amplitude are chosen. (3) If more than one interval with the same minimum average amplitude is found, the interval closest to the plume is chosen. (4) The standard deviation, S_o, for the calculated opacity shall be 8% or less. (S_o is calculated by Equation AM1–7).

If S_o is greater than 8%, then the far pick interval shall be changed to the next interval of minimal average amplitude. If S_o is still greater than 8%, then this procedure is repeated for the far pick interval. This procedure may be repeated once again for the near pick interval, but if S_o remains greater than 8%, the plume signal shall be discarded.

The reference signal pick intervals, R_n and R_f, must be chosen over the same time interval as the plume signal pick intervals, I_n and I_f, respectively [Figure AM1–III]. Other methods of selecting pick intervals may be used if they give equivalent results. Field-oriented examples of pick interval selection are available in Reference 5.1.

The average amplitudes for each of the pick intervals, I_n, I_f, R_n, R_f, shall be calculated by averaging the respective individual amplitudes of the sample intervals from the plume signal and the associated reference signal each corrected for $1/R^2$. The amplitude of I_n shall be calculated according to Equation (AM–3).

$$I_n = \frac{1}{m}\sum_{i=1}^{m} I_{ni}, \qquad \text{(AM1-3)}$$

Where:

I_{ni} = the amplitude of the ith sample interval (near-region),

Σ = sum of the individual amplitudes for the sample intervals,

m = number of sample intervals in the pick interval, and

I_n = average amplitude of the near-region pick interval.

Similarly, the amplitudes for I_f, R_n, and R_f are calculated with the three expressions in Equation (AM1–4).

$$I_f = \frac{1}{m}\sum_{i=1}^{m} I_{fi}, \quad R_n = \frac{1}{m}\sum_{i=1}^{m} R_{ni}, \quad R_f = \frac{1}{m}\sum_{i=1}^{m} R_{fi}. \qquad \text{(AM1-4)}$$

The standard deviation, S_{In}, of the set of amplitudes for the near-region pick interval, I_n, shall be calculated using Equation (AM1–5).

Similarly, the standard deviations S_{If}, S_{Rn}, and S_{Rf} are calculated with the three expressions in Equation (AM1–6).

$$S_{In} = \left[\sum_{i=1}^{m} \frac{(I_{ni} - I_n)^2}{(m-1)} \right]^{1/2} \qquad S_{If} = \left[\sum_{i=1}^{m} \frac{(I_{fi} - I_f)^2}{(m-1)} \right]^{1/2} \qquad \text{(AM1-5)}$$

$$S_{Rn} = \left[\sum_{i=1}^{m} \frac{(R_{ni} - R_n)^2}{(m-1)} \right]^{1/2},$$

$$S_{Rf} = \left[\sum_{i=1}^{m} \frac{(R_{fi} - R_f)^2}{(m-1)} \right]^{1/2}. \qquad \text{(AM1-6)}$$

The standard deviation, S_o, for each associated opacity value, O_p, shall be calculated using Equation (AM1–7).

$$S_o = \frac{(100\%)}{2} \left(\frac{I_f}{R_f} \frac{R_n}{I_n} \right)^{1/2} \left[\frac{S_{In}^2}{I_n^2} + \frac{S_{If}^2}{I_f^2} + \frac{S_{Rn}^2}{R_n^2} + \frac{S_{Rf}^2}{R_f^2} \right]^{1/2} \qquad \text{(AM1-7)}$$

The calculated values of I_n, I_f, R_n, R_f, S_{In}, S_{If}, S_{Rn}, S_{Rf}, O_p, and S_o should be recorded. Any plume signal with an S_o greater than 8% shall be discarded.

2.6.1 Azimuth Angle Correction. If the azimuth angle correction to opacity specified in this section is performed, then the elevation angle correction specified in section 2.6.2 shall not be performed. When opacity is measured in the residual region of an attached steam plume, and the lidar line-of-sight is not perpendicular to the plume, it may be necessary to correct the opacity measured by the lidar to obtain the opacity that would be measured on a path perpendicular to the plume. The following method, or any other method which produces equivalent results, shall be used to determine the need for a correction, to calculate the correction, and to document the point within the plume at which the opacity was measured.

Figure AM1–IV(b) shows the geometry of the opacity correction. L′ is the path through the plume along which the opacity measurement is made. P′ is the path perpendicular to the plume at the same point. The angle ε is the angle between L′ and the plume center line. The angle (π/2-ε), is the angle between the L′ and P′. The measured opacity, O_p, measured along the path L′ shall be corrected to obtain the corrected opacity, O_{pc}, for the path P′, using Equation (AM1–8).

$$O_{pc} = (100\%)\left[1 - (1 - 0.01\, O_p)^{\mathrm{Cos}\,(\pi/2-\varepsilon)} \right]$$

$$= (100\%)\left[1 - (1 - 0.01\, O_p)^{\mathrm{Sin}\,\varepsilon} \right] \qquad \text{(AM1-8)}$$

The correction in Equation (AM1–8) shall be performed if the inequality in Equation (AM1–9) is true.

$$\varepsilon \geq \mathrm{Sin}^{-1}\left[\frac{\ln(101 - O_p)}{\ln(100 - O_p)}\right] \qquad \text{(AM1-9)}$$

Figure AM1–IV(a) shows the geometry used to calculate ε and the position in the plume at which the lidar measurement is made. This analysis assumes that for a given lidar measurement, the range from the lidar to the plume, the elevation angle of the lidar from the horizontal plane, and the azimuth angle of the lidar from an arbitrary fixed reference in the horizontal plane can all be obtained directly.

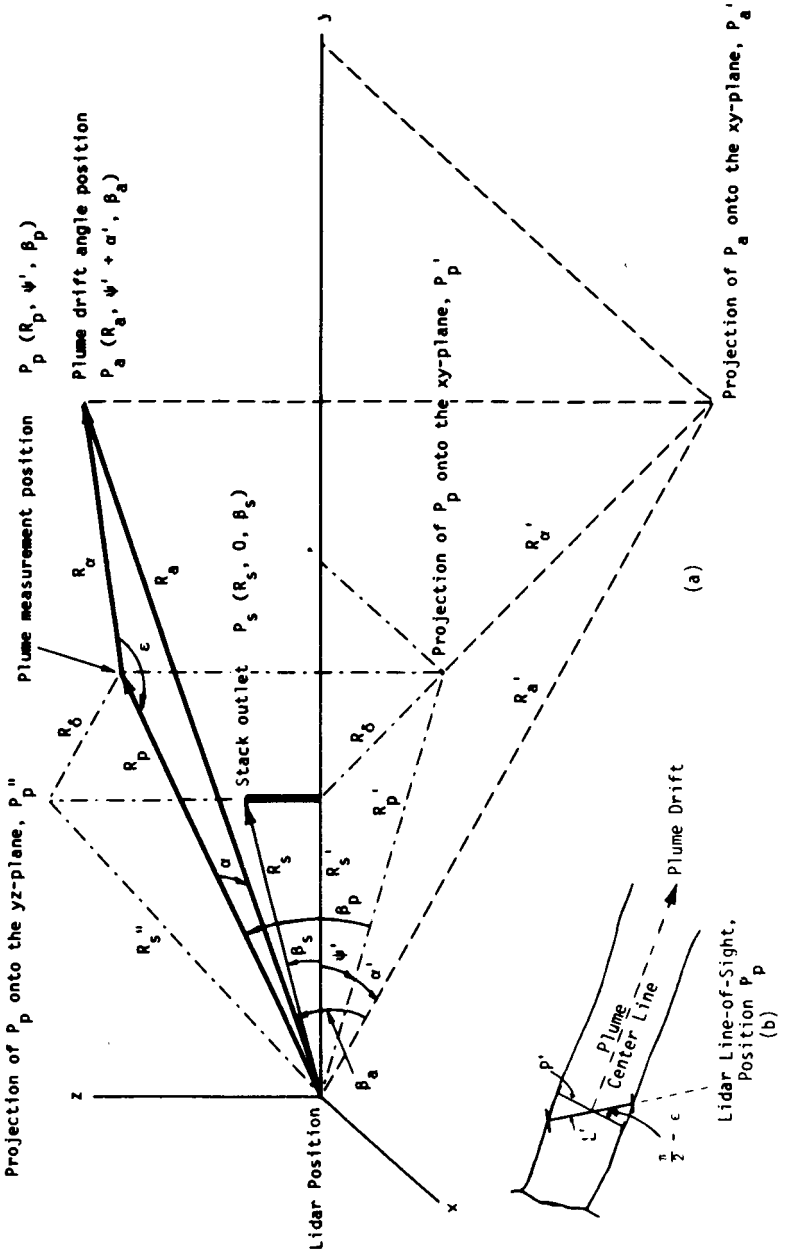


Figure AMI - IV. Correction in Opacity for Drift of the Residual Region of an Attached Steam Plume.

R_s = range from lidar to source*
β_s = elevation angle of R_s*
R_p = range from lidar to plume at the opacity measurement point*
β_p = elevation angle of R_p*
R_a = range from lidar to plume at some arbitrary point, P_a, so the drift angle of the plume can be determined*

β_a = elevation angle of R_a*
α = angle between R_p and R_a
R'_s = projection of R_s in the horizontal plane
R'_p = projection of R_p in the horizontal plane
R'_a = projection of R_a in the horizontal plane
ψ' = angle between R'_s and R'_p*
α' = angle between R'_p and R'_a*
R≤ = distance from the source to the opacity measurement point projected in the horizontal plane
Rθ = distance from opacity measurement point P_p to the point in the plume P_a.

$$O_{pc} = 1 - (1 - O_p)^{\mathrm{Cos}\,(\pi/2-\varepsilon)} = 1 - (1 - O_p)^{\mathrm{Sin}\,\varepsilon} \qquad \text{(AMI-8)}$$

The correction angle ε shall be determined using Equation AM1–10.

Where:

$\alpha = \mathrm{Cos}^{-1}\,(\mathrm{Cos}\beta_p\,\mathrm{Cos}\beta_a\,\mathrm{Cos}\alpha' + \mathrm{Sin}\beta_p\,\mathrm{Sin}\beta_a)$, and

$R\theta = (R_p 2 + R_a 2 - 2\,R_p\,R_a\,\mathrm{Cos}\alpha)^{1/2}$

R≤, the distance from the source to the opacity measurement point projected in the horizontal plane, shall be determined using Equation AM1–11.

$$R_\delta = (R'^2_s + R'^2_p - 2R'_sR'_p\mathrm{Cos}\psi')^{\frac{1}{2}}, \qquad \text{(AM1-11)}$$

Where:

$R'_s = R_s\,\mathrm{Cos}\,\beta_s$, and
$R'_p = R_p\,\mathrm{Cos}\,\beta_p$.

In the special case where the plume centerline at the opacity measurement point is horizontal, parallel to the ground, Equation AM1–12 may be used to determine ε instead of Equation AM1–10.

$$\varepsilon = \mathrm{Cos}^{-1}\left[\frac{R_p^2 + R_\delta^2 - R''^2_s}{2\,R_p\,R_\delta}\right] \qquad \text{(AM1-12)}$$

Where:

$R''_s = (R'^2_s + R_p^2\mathrm{Sin}^2\beta_p)^{1/2}$.

If the angle ε is such that ε≤30° or ε ≥150°, the azimuth angle correction shall not be performed and the associated opacity value shall be discarded.

2.6.2 Elevation Angle Correction. An individual lidar-measured opacity, O_p, shall be corrected for elevation angle if the laser elevation or inclination angle, β_p [Figure AM1–V], is greater than or equal to the value calculated in Equation AM1–13.

$$\beta_p \geq \mathrm{Cos}^{-1}\left[\frac{\ln\,(101 - O_p)}{\ln\,(100 - O_p)}\right] \qquad \text{(AM1-13)}$$

The measured opacity, O_p, along the lidar path L, is adjusted to obtain the corrected opacity, O_{pc}, for the actual plume (horizontal) path, P, by using Equation (AM1–14).

*Obtained directly from lidar. These values should be recorded.

$$O_{pc} = (100\%)\left[1-\left(1-0.01\,O_p\right)^{Cos\beta}p\right], \qquad (AM1\text{-}14)$$

Where:

β_p = lidar elevation or inclination angle,
O_p = measured opacity along path L, and
O_{pc} = corrected opacity for the actual plume thickness P.

The values for β_p, O_p and O_{pc} should be recorded.

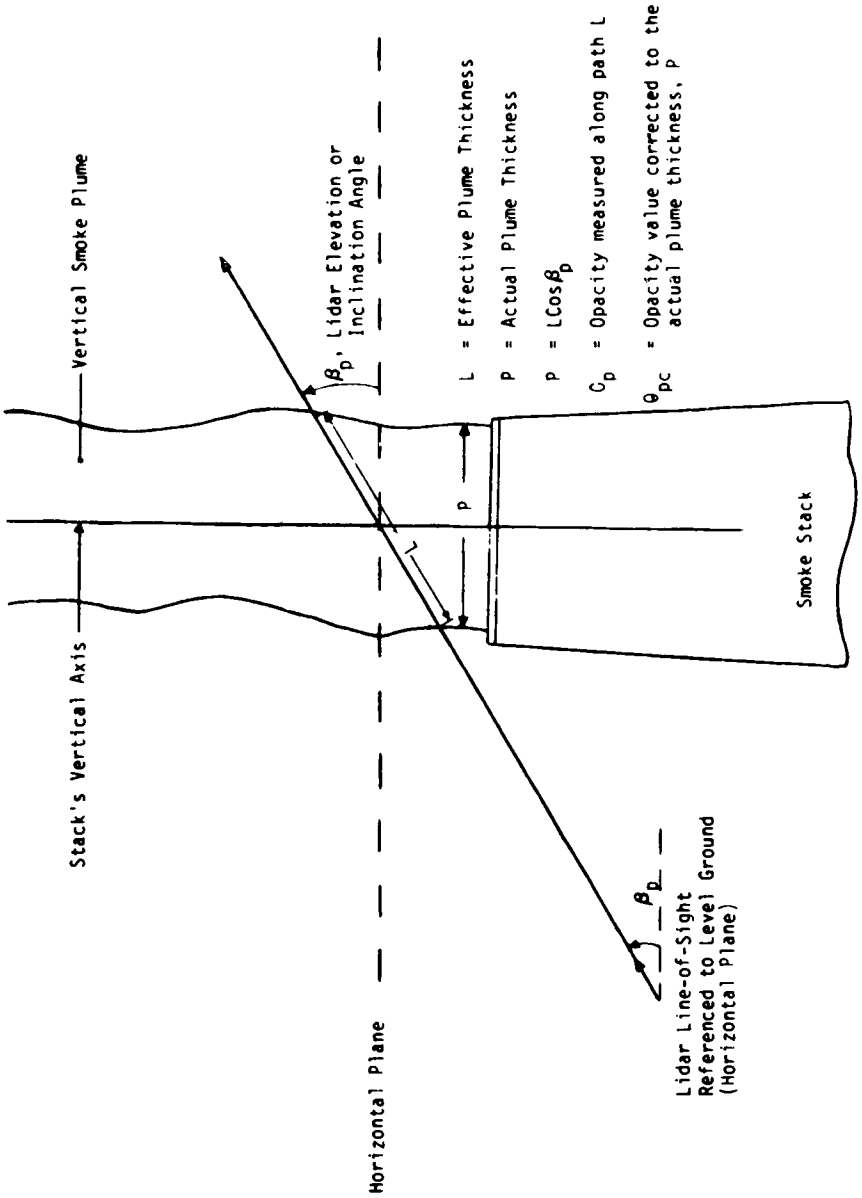


Figure AM1-V. Elevation Angle Correction for Vertical Plumes.

2.6.3 Determination of Actual Plume Opacity. Actual opacity of the plume shall be determined by Equation AM1–15.

$$O_{pa} = O_{pc} - [2\ S_o + 5\%]. \quad \text{(AM1-15)}$$

2.6.4 Calculation of Average Actual Plume Opacity. The average of the actual plume opacity, O_{pa}, shall be calculated as the average of the consecutive individual actual opacity values, O_{pa}, by Equation AM1–16.

$$\bar{O}_{pa} = \frac{1}{n}\sum_{k=1}^{n}(O_{pa})_k \quad , \qquad \text{(AM1-16)}$$

Where:

$(O_{pa})_k$ = the kth actual opacity value in an averaging interval containing n opacity values; k is a summing index.

Σ = the sum of the individual actual opacity values.

n = the number of individual actual opacity values contained in the averaging interval.

O_{pa} = average actual opacity calculated over the averaging interval.

3. Lidar Performance Verification

The lidar shall be subjected to two types of performance verifications that shall be performed in the field. The annual calibration, conducted at least once a year, shall be used to directly verify operation and performance of the entire lidar system. The routine verification, conducted for each emission source measured, shall be used to insure proper performance of the optical receiver and associated electronics.

3.1 Annual Calibration Procedures. Either a plume from a smoke generator or screen targets shall be used to conduct this calibration.

If the screen target method is selected, five screens shall be fabricated by placing an opaque mesh material over a narrow frame (wood, metal extrusion, etc.). The screen shall have a surface area of at least one square meter. The screen material should be chosen for precise optical opacities of about 10, 20, 40, 60, and 80%. Opacity of each target shall be optically determined and should be recorded. If a smoke generator plume is selected, it shall meet the requirements of section 3.3 of Reference Method 9. This calibration shall be performed in the field during calm (as practical) atmospheric conditions. The lidar shall be positioned in accordance with section 2.1.

The screen targets must be placed perpendicular to and coincident with the lidar line-of-sight at sufficient height above the ground (suggest about 30 ft) to avoid ground-level dust contamination. Reference signals shall be obtained just prior to conducting the calibration test.

The lidar shall be aimed through the center of the plume within 1 stack diameter of the exit, or through the geometric center of the screen target selected. The lidar shall be set in operation for a 6-minute data run at a nominal pulse rate of 1 pulse every 10 seconds. Each backscatter return signal and each respective opacity value obtained from the smoke generator transmissometer, shall be obtained in temporal coincidence. The data shall be analyzed and reduced in accordance with section 2.6 of this method. This calibration shall be performed for 0% (clean air), and at least five other opacities (nominally 10, 20, 40, 60, and 80%).

The average of the lidar opacity values obtained during a 6-minute calibration run shall be calculated and should be recorded. Also the average of the opacity values obtained from the smoke generator transmissometer for the same 6-minute run shall be calculated and should be recorded.

Alternate calibration procedures that do not meet the above requirements but produce equivalent results may be used.

3.2 Routine Verification Procedures. Either one of two techniques shall be used to conduct this verification. It shall be performed at least once every 4 hours for each emission source measured. The following parameters shall be directly verified.

1) The opacity value of 0% plus a minimum of 5 (nominally 10, 20, 40, 60, and 80%) opacity values shall be verified through the PMT detector and data processing electronics.

2) The zero-signal level (receiver signal with no optical signal from the source present) shall be inspected to insure that no spurious noise is present in the signal. With the entire lidar receiver and analog/digital electronics turned on and adjusted for normal operating performance, the following procedures shall be used for Techniques 1 and 2, respectively.

3.2.1 Procedure for Technique 1. This test shall be performed with no ambient or stray light reaching the PMT detector. The narrow band filter (694.3 nanometers peak) shall be removed from its position in front of the PMT detector. Neutral density filters of nominal opacities of 10, 20, 40, 60, and 80% shall be used. The recommended test configuration is depicted in Figure AM1–VI.

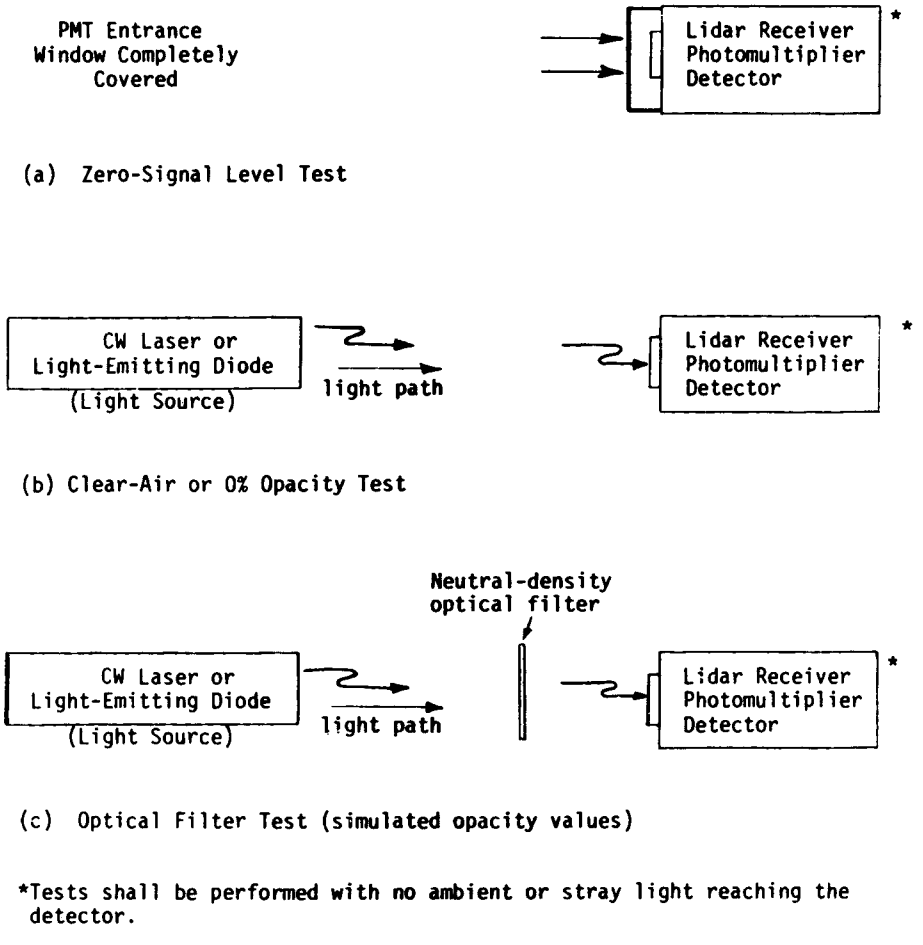


Figure AM1–VI. Test Configuration for Technique 1.

The zero-signal level shall be measured and should be recorded, as indicated in Figure AM1–VI(a). This simulated clear-air or 0% opacity value shall be tested in using the selected light source depicted in Figure AM1–VI(b).

The light source either shall be a continuous wave (CW) laser with the beam mechanically chopped or a light emitting diode controlled with a pulse generator (rectangular pulse). (A laser beam may have to be attenuated so as not to saturate the PMT detector). This signal level shall be measured

and should be recorded. The opacity value is calculated by taking two pick intervals [Section 2.6] about 1 microsecond apart in time and using Equation (AM1–2) setting the ratio $R_n/R_f = 1$. This calculated value should be recorded.

The simulated clear-air signal level is also employed in the optical test using the neutral density filters. Using the test configuration in Figure AM1–VI(c), each neutral density filter shall be separately placed into the light path from the light source to the PMT detector. The signal level shall be measured and should be recorded. The opacity value for each filter is calculated by taking the signal level for that respective filter (I_f), dividing it by the 0% opacity signal level (I_n) and performing the remainder of the calculation by Equation (AM1–2) with $R_n/R_f = 1$. The calculated opacity value for each filter should be recorded.

The neutral density filters used for Technique 1 shall be calibrated for actual opacity with accuracy of ±2% or better. This calibration shall be done monthly while the filters are in use and the calibrated values should be recorded.

3.2.2 Procedure for Technique 2. An optical generator (built-in calibration mechanism) that contains a light-emitting diode (red light for a lidar containing a ruby laser) is used. By injecting an optical signal into the lidar receiver immediately ahead of the PMT detector, a backscatter signal is simulated. With the entire lidar receiver electronics turned on and adjusted for normal operating performance, the optical generator is turned on and the simulation signal (corrected for $1/R^2$) is selected with no plume spike signal and with the opacity value equal to 0%. This simulated clear-air atmospheric return signal is displayed on the system's video display. The lidar operator then makes any fine adjustments that may be necessary to maintain the system's normal operating range.

The opacity values of 0% and the other five values are selected one at a time in any order. The simulated return signal data should be recorded. The opacity value shall be calculated. This measurement/calculation shall be performed at least three times for each selected opacity value. While the order is not important, each of the opacity values from the optical generator shall be verified. The calibrated optical generator opacity value for each selection should be recorded.

The optical generator used for Technique 2 shall be calibrated for actual opacity with an accuracy of ±1% or better. This calibration shall be done monthly while the generator is in use and calibrated value should be recorded.

Alternate verification procedures that do not meet the above requirements but produce equivalent results may be used.

3.3 Deviation. The permissible error for the annual calibration and routine verification are:

3.3.1 Annual Calibration Deviation.

3.3.1.1 Smoke Generator. If the lidar-measured average opacity for each data run is not within ±5% (full scale) of the respective smoke generator's average opacity over the range of 0% through 80%, then the lidar shall be considered out of calibration.

3.3.1.2 Screens. If the lidar-measured average opacity for each data run is not within ±3% (full scale) of the laboratory-determined opacity for each respective simulation screen target over the range of 0% through 80%, then the lidar shall be considered out of calibration.

3.3.2 Routine Verification Error. If the lidar-measured average opacity for each neutral density filter (Technique 1) or optical generator selection (Technique 2) is not within ±3% (full scale) of the respective laboratory calibration value then the lidar shall be considered non-operational.

4. Performance/Design Specification for Basic Lidar System

4.1 Lidar Design Specification. The essential components of the basic lidar system are a pulsed laser (transmitter), optical receiver, detector, signal processor, recorder, and an aiming device that is used in aiming the lidar transmitter and receiver. Figure AM1–VII shows a functional block diagram of a basic lidar system.

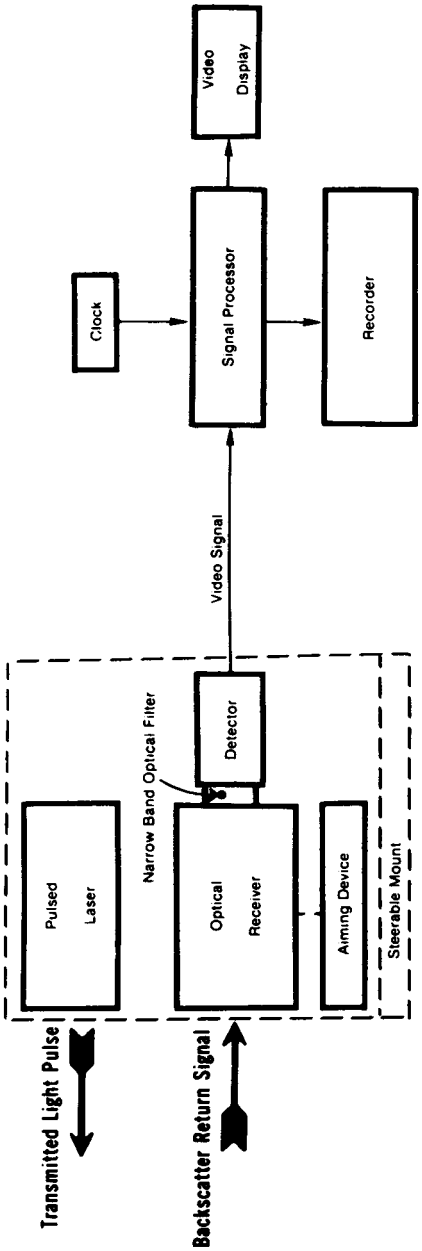


Figure AM1-VII. Functional Block Diagram of a Basic Lidar System

4.2 Performance Evaluation Tests. The owner of a lidar system shall subject such a lidar system to the performance verification tests described in section 3, prior to first use of this method. The annual calibration shall be performed for three separate, complete

runs and the results of each should be recorded. The requirements of section 3.3.1 must be fulfilled for each of the three runs.

Once the conditions of the annual calibration are fulfilled the lidar shall be subjected to the routine verification for three separate complete runs. The requirements of section 3.3.2 must be fulfilled for each of the three runs and the results should be recorded. The Administrator may request that the results of the performance evaluation be submitted for review.

5. References

5.1 The Use of Lidar for Emissions Source Opacity Determination, U.S. Environmental Protection Agency, National Enforcement Investigations Center, Denver, CO. EPA–330/1–79–003–R, Arthur W. Dybdahl, current edition [NTIS No. PB81–246662].

5.2 Field Evaluation of Mobile Lidar for the Measurement of Smoke Plume Opacity, U.S. Environmental Protection Agency, National Enforcement Investigations Center, Denver, CO. EPA/NEIC-TS-128, February 1976.

5.3 Remote Measurement of Smoke Plume Transmittance Using Lidar, C. S. Cook, G. W. Bethke, W. D. Conner (EPA/RTP). Applied Optics 11, pg 1742. August 1972.

5.4 Lidar Studies of Stack Plumes in Rural and Urban Environments, EPA–650/4–73–002, October 1973.

5.5 American National Standard for the Safe Use of Lasers ANSI Z 136.1–176, March 8, 1976.

5.6 U.S. Army Technical Manual TB MED 279, Control of Hazards to Health from Laser Radiation, February 1969.

5.7 Laser Institute of America Laser Safety Manual, 4th Edition.

5.8 U.S. Department of Health, Education and Welfare, Regulations for the Administration and Enforcement of the Radiation Control for Health and Safety Act of 1968, January 1976.

5.9 Laser Safety Handbook, Alex Mallow, Leon Chabot, Van Nostrand Reinhold Co., 1978.

Method 10—Determination of Carbon Monoxide Emissions From Stationary Sources (Instrumental Analyzer Procedure)

1.0 Scope and Application

What is Method 10?

Method 10 is a procedure for measuring carbon monoxide (CO) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis. This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 4—Determination of Moisture Content in Stack Gases.

(c) Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure).

1.1 Analytes. What does this method determine? This method measures the concentration of carbon monoxide.

Analyte	CAS No.	Sensitivity
CO	630–08–0	Typically <2% of Calibration Span.

1.2 Applicability. When is this method required? The use of Method 10 may be required by specific New Source Performance Standards, State Implementation Plans, and permits where CO concentrations in stationary source emissions must be measured, either to determine compliance with an applicable emission standard or to conduct performance testing of a continuous emission monitoring system (CEMS). Other regulations may also require the use of Method 10.

1.3 Data Quality Objectives. Refer to section 1.3 of Method 7E.

2.0 Summary of Method

In this method, you continuously or intermittently sample the effluent gas and convey the sample to an analyzer that measures the concentration of CO. You must meet the performance requirements of this method to validate your data.

3.0 Definitions

Refer to section 3.0 of Method 7E for the applicable definitions.

4.0 Interferences

Substances having a strong absorption of infrared energy may interfere to some extent in some analyzers. Instrumental correction may be used to compensate for the interference. You may also use silica gel and ascarite traps to eliminate the interferences. If this option is used, correct the measured

gas volume for the carbon dioxide (CO_2) removed in the trap.

5.0 Safety

Refer to section 5.0 of Method 7E.

6.0 Equipment and Supplies

What do I need for the measurement system?

6.1 Continuous Sampling. Figure 7E–1 of Method 7E is a schematic diagram of an acceptable measurement system. The components are the same as those in sections 6.1 and 6.2 of Method 7E, except that the CO analyzer described in section 6.2 of this method must be used instead of the analyzer described in section 6.2 of Method 7E. You must follow the noted specifications in section 6.1 of Method 7E except that the requirements to use stainless steel, Teflon, or non-reactive glass filters do not apply. Also, a heated sample line is not required to transport dry gases or for systems that measure the CO concentration on a dry basis.

6.2 Integrated Sampling.

6.2.1 Air-Cooled Condenser or Equivalent. To remove any excess moisture.

6.2.2 Valve. Needle valve, or equivalent, to adjust flow rate.

6.2.3 Pump. Leak-free diaphragm type, or equivalent, to transport gas.

6.2.4 Rate Meter. Rotameter, or equivalent, to measure a flow range from 0 to 1.0 liter per minute (0.035 cfm).

6.2.5 Flexible Bag. Tedlar, or equivalent, with a capacity of 60 to 90 liters (2 to 3 ft^3). (Verify through the manufacturer that the Tedlar alternative is suitable for CO and make this verified information available for inspection.) Leak-test the bag in the laboratory before using by evacuating with a pump followed by a dry gas meter. When the evacuation is complete, there should be no flow through the meter.

6.2.6 Sample Tank. Stainless steel or aluminum tank equipped with a pressure indicator with a minimum volume of 4 liters.

6.3 What analyzer must I use? You must use an instrument that continuously measures CO in the gas stream and meets the specifications in section 13.0. The dual-range analyzer provisions in section 6.2.8.1 of Method 7E apply.

7.0 Reagents and Standards

7.1 Calibration Gas. What calibration gases do I need? Refer to section 7.1 of Method 7E for the calibration gas requirements.

7.2 Interference Check. What additional reagents do I need for the interference check? Use the appropriate test gases listed in Table 7E–3 of Method 7E (i.e., potential interferents, as identified by the instrument manufacturer) to conduct the interference check.

8.0 Sample Collection, Preservation, Storage, and Transport

Emission Test Procedure

8.1 Sampling Site and Sampling Points. You must follow section 8.1 of Method 7E.

8.2 Initial Measurement System Performance Tests. You must follow the procedures in section 8.2 of Method 7E. If a dilution-type measurement system is used, the special considerations in section 8.3 of Method 7E also apply.

8.3 Interference Check. You must follow the procedures of section 8.2.7 of Method 7E.

8.4 Sample Collection.

8.4.1 Continuous Sampling. You must follow the procedures of section 8.4 of Method 7E.

8.4.2 Integrated Sampling. Evacuate the flexible bag or sample tank. Set up the equipment as shown in Figure 10–1 with the bag disconnected. Place the probe in the stack and purge the sampling line. Connect the bag, making sure that all connections are leak-free. Sample at a rate proportional to the stack velocity. If needed, the CO_2 content of the gas may be determined by using the Method 3 integrated sample procedures, or by weighing an ascarite CO_2 removal tube used and computing CO_2 concentration from the gas volume sampled and the weight gain of the tube. Data may be recorded on a form similar to Table 10–1. If a sample tank is used for sample collection, follow procedures similar to those in sections 8.1.2, 8.2.3, 8.3, and 12.4 of Method 25 as appropriate to prepare the tank, conduct the sampling, and correct the measured sample concentration.

8.5 Post-Run System Bias Check, Drift Assessment, and Alternative Dynamic Spike Procedure. You must follow the procedures in sections 8.5 and 8.6 of Method 7E.

9.0 Quality Control

Follow the quality control procedures in section 9.0 of Method 7E.

10.0 Calibration and Standardization

Follow the procedures for calibration and standardization in section 10.0 of Method 7E.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the procedures for calculations and data analysis in section 12.0 of Method 7E, as applicable, substituting CO for NO_X as applicable.

12.1 Concentration Correction for CO_2 Removal. Correct the CO concentration for CO_2 removal (if applicable) using Eq. 10–1.

$$C_{Avg} = C_{CO\ stack}\left(1 - F_{CO2}\right)$$

Where:

C_{Avg} = Average gas concentration for the test run, ppm.

$C_{CO\ stack}$ = Average unadjusted stack gas CO concentration indicated by the data recorder for the test run, ppmv.

F_{CO2} = Volume fraction of CO_2 in the sample, i.e., percent CO_2 from Orsat analysis divided by 100.

13.0 Method Performance

The specifications for analyzer calibration error, system bias, drift, interference check, and alternative dynamic spike procedure are the same as in section 13.0 of Method 7E.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

The dynamic spike procedure and the manufacturer stability test are the same as in sections 16.1 and 16.3 of Method 7E

17.0 References

1. ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards— September 1997 as amended, EPA–600/R–97/121

18.0 Tables, Diagrams, Flowcharts, and Validation Data

Figure 10-1. Integrated Gas Sampling Train.

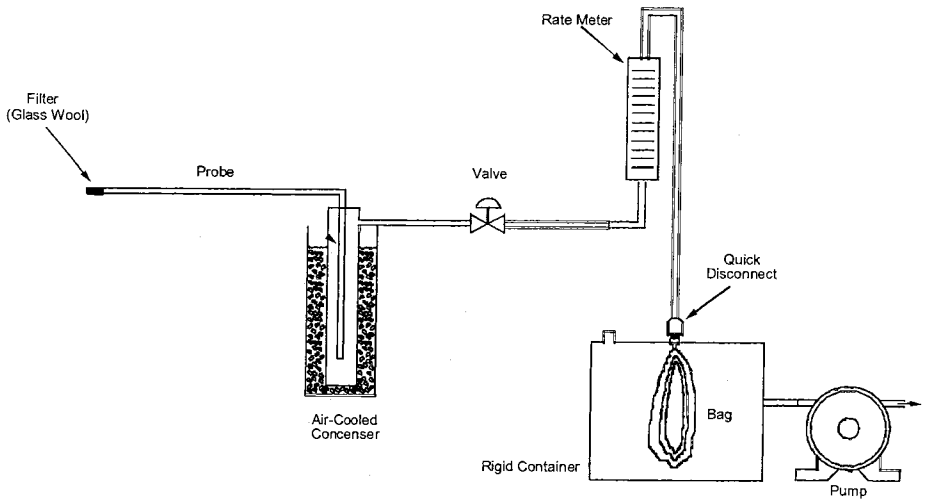


TABLE 10–1—FIELD DATA

[Integrated sampling]

Location:	Date:	
Test:	Operator:	
Clock Time	Rotameter Reading liters/min (cfm)	Comments

TABLE 10–1—FIELD DATA—Continued

[Integrated sampling]

METHOD 10A—DETERMINATION OF CARBON MONOXIDE EMISSIONS IN CERTIFYING CONTINUOUS EMISSION MONITORING SYSTEMS AT PETROLEUM REFINERIES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 4, and Method 5.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Carbon monoxide (CO)	630–08–0	3 ppmv

1.2 Applicability. This method is applicable for the determination of CO emissions at petroleum refineries. This method serves as the reference method in the relative accuracy test for nondispersive infrared (NDIR) CO continuous emission monitoring systems (CEMS) that are required to be installed in petroleum refineries on fluid catalytic cracking unit catalyst regenerators (§60.105(a)(2) of this part).

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

An integrated gas sample is extracted from the stack, passed through an alkaline permanganate solution to remove sulfur oxides and nitrogen oxides, and collected in a Tedlar or equivalent bag. (Verify through the manufacturer that the Tedlar alternative is suitable for NO and make this verified information available for inspection.) The CO concentration in the sample is measured spectrophotometrically using the reaction of CO with *p*-sulfaminobenzoic acid.

3.0 Definitions [Reserved]

4.0 Interferences

Sulfur oxides, nitric oxide, and other acid gases interfere with the colorimetric reaction. They are removed by passing the sampled gas through an alkaline potassium permanganate scrubbing solution. Carbon dioxide (CO_2) does not interfere, but, because it is removed by the scrubbing solution, its concentration must be measured independently and an appropriate volume correction made to the sampled gas.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs.

Reacts exothermically with limited amounts of water.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling train shown in Figure 10A–1 is required for sample collection. Component parts are described below:

6.1.1 Probe. Stainless steel, sheathed Pyrex glass, or equivalent, equipped with a glass wool plug to remove particulate matter.

6.1.2 Sample Conditioning System. Three Greenburg-Smith impingers connected in series with leak-free connections.

6.1.3 Pump. Leak-free pump with stainless steel and Teflon parts to transport sample at a flow rate of 300 ml/min (0.01 ft^3/min) to the flexible bag.

6.1.4 Surge Tank. Installed between the pump and the rate meter to eliminate the pulsation effect of the pump on the rate meter.

6.1.5 Rate Meter. Rotameter, or equivalent, to measure flow rate at 300 ml/min (0.01 ft^3/min). Calibrate according to section 10.2.

6.1.6 Flexible Bag. Tedlar, or equivalent, with a capacity of 10 liters (0.35 ft^3) and equipped with a sealing quick-connect plug. The bag must be leak-free according to section 8.1. For protection, it is recommended that the bag be enclosed within a rigid container.

6.1.7 Sample Tank. Stainless steel or aluminum tank equipped with a pressure indicator with a minimum volume of 10 liters.

6.1.8 Valves. Stainless-steel needle valve to adjust flow rate, and stainless-steel 3-way valve, or equivalent.

6.1.9 CO_2 Analyzer. Fyrite, or equivalent, to measure CO_2 concentration to within 0.5 percent.

6.1.10 Volume Meter. Dry gas meter, capable of measuring the sample volume under calibration conditions of 300 ml/min (0.01 ft^3/min) for 10 minutes.

6.1.11 Pressure Gauge. A water filled U-tube manometer, or equivalent, of about 30 cm (12 in.) to leak-check the flexible bag.

6.2 Sample Analysis.

6.2.1 Spectrophotometer. Single- or double-beam to measure absorbance at 425 and 600 nm. Slit width should not exceed 20 nm.

6.2.2 Spectrophotometer Cells. 1-cm pathlength.

6.2.3 Vacuum Gauge. U-tube mercury manometer, 1 meter (39 in.), with 1-mm divisions, or other gauge capable of measuring pressure to within 1 mm Hg.

6.2.4 Pump. Capable of evacuating the gas reaction bulb to a pressure equal to or less than 40 mm Hg absolute, equipped with coarse and fine flow control valves.

6.2.5 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm Hg.

6.2.6 Reaction Bulbs. Pyrex glass, 100-ml with Teflon stopcock (Figure 10A–2), leak-free at 40 mm Hg, designed so that 10 ml of the colorimetric reagent can be added and removed easily and accurately. Commercially available gas sample bulbs such as Supelco Catalog No. 2–2161 may also be used.

6.2.7 Manifold. Stainless steel, with connections for three reaction bulbs and the appropriate connections for the manometer and sampling bag as shown in Figure 10A–3.

6.2.8 Pipets. Class A, 10–ml size.

6.2.9 Shaker Table. Reciprocating-stroke type such as Eberbach Corporation, Model 6015. A rocking arm or rotary-motion type shaker may also be used. The shaker must be large enough to accommodate at least six gas sample bulbs simultaneously. It may be necessary to construct a table top extension for most commercial shakers to provide sufficient space for the needed bulbs (Figure 10A–4).

6.2.10 Valve. Stainless steel shut-off valve.

6.2.11 Analytical Balance. Capable of weighing to 0.1 mg.

7.0 Reagents and Standards

Unless otherwise indicated, all reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, the best available grade shall be used.

7.1 Sample Collection.

7.1.1 Water. Deionized distilled, to conform to ASTM D 1193–77 or 91, Type 3 (incorporated by reference—see §60.17). If high concentrations of organic matter are not expected to be present, the potassium permanganate test for oxidizable organic matter may be omitted.

7.1.2 Alkaline Permanganate Solution, 0.25 M $KMnO_4$/1.5 M Sodium Hydroxide (NaOH). Dissolve 40 g $KMnO_4$ and 60 g NaOH in approximately 900 ml water, cool, and dilute to 1 liter.

7.2 Sample Analysis.

7.2.1 Water. Same as in section 7.1.1.

7.2.2 1 M Sodium Hydroxide Solution. Dissolve 40 g NaOH in approximately 900 ml of water, cool, and dilute to 1 liter.

7.2.3 0.1 M NaOH Solution. Dilute 50 ml of the 1 M NaOH solution prepared in section 7.2.2 to 500 ml.

7.2.4 0.1 M Silver Nitrate ($AgNO_3$) Solution. Dissolve 8.5 g $AgNO_3$ in water, and dilute to 500 ml.

7.2.5 0.1 M Para-Sulfaminobenzoic Acid (p-SABA) Solution. Dissolve 10.0 g p-SABA in 0.1 M NaOH, and dilute to 500 ml with 0.1 M NaOH.

7.2.6 Colorimetric Solution. To a flask, add 100 ml of 0.1 M p-SABA solution and 100 ml of 0.1 M $AgNO_3$ solution. Mix, and add 50 ml of 1 M NaOH with shaking. The resultant solution should be clear and colorless. This solution is acceptable for use for a period of 2 days.

7.2.7 Standard Gas Mixtures. Traceable to National Institute of Standards and Technology (NIST) standards and containing between 50 and 1000 ppm CO in nitrogen. At least two concentrations are needed to span each calibration range used (Section 10.3). The calibration gases must be certified by the manufacturer to be within 2 percent of the specified concentrations.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sample Bag or Tank Leak-Checks. While a leak-check is required after bag or sample tank use, it should also be done before the bag or sample tank is used for sample collection. The tank should be leak-checked according to the procedure specified in section 8.1.2 of Method 25. The bag should be leak-checked in the inflated and deflated condition according to the following procedure:

8.1.1 Connect the bag to a water manometer, and pressurize the bag to 5 to 10 cm H_2O (2 to 4 in H_2O). Allow the bag to stand for 60 minutes. Any displacement in the water manometer indicates a leak.

8.1.2 Evacuate the bag with a leakless pump that is connected to the downstream side of a flow indicating device such as a 0- to 100-ml/min rotameter or an impinger containing water. When the bag is completely evacuated, no flow should be evident if the bag is leak-free.

8.2 Sample Collection.

8.2.1 Evacuate and leak check the sample bag or tank as specified in section 8.1. Assemble the apparatus as shown in Figure 10A–1. Loosely pack glass wool in the tip of the probe. Place 400 ml of alkaline permanganate solution in the first two impingers and 250 ml in the third. Connect the pump to the third impinger, and follow this with the surge tank, rate meter, and 3-way valve. Do not connect the bag or sample tank to the system at this time.

8.2.2 Leak-check the sampling system by plugging the probe inlet, opening the 3-way valve, and pulling a vacuum of approximately 250 mm Hg on the system while observing the rate meter for flow. If flow is indicated on the rate meter, do not proceed further until the leak is found and corrected.

8.2.3 Purge the system with sample gas by inserting the probe into the stack and drawing the sample gas through the system at 300 ml/min ±10 percent for 5 minutes. Connect the evacuated bag or sample tank to the system, record the starting time, and sample at a rate of 300 ml/min for 30 minutes, or until the bag is nearly full, or the sample tank reaches ambient pressure. Record the sampling time, the barometric pressure, and the ambient temperature. Purge the system as described above immediately before each sample.

8.2.4 The scrubbing solution is adequate for removing sulfur oxides and nitrogen oxides from 50 liters (1.8 ft^3) of stack gas when the concentration of each is less than 1,000 ppm and the CO_2 concentration is less than 15 percent. Replace the scrubber solution after every fifth sample.

8.3 Carbon Dioxide Measurement. Measure the CO_2 content in the stack to the nearest 0.5 percent each time a CO sample is collected. A simultaneous grab sample analyzed by the Fyrite analyzer is acceptable.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.1	Sampling equipment leak-checks and calibration.	Ensure accuracy and precision of sampling measurements.
10.3	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Gas Bulb Calibration. Weigh the empty bulb to the nearest 0.1 g. Fill the bulb to the stopcock with water, and again weigh to the nearest 0.1 g. Subtract the tare weight, and calculate the volume in liters to three significant figures using the density of water at the measurement temperature. Record the volume on the bulb. Alternatively, mark an identification number on the bulb, and record the volume in a notebook.

10.2 Rate Meter Calibration. Assemble the system as shown in Figure 10A–1 (the impingers may be removed), and attach a volume meter to the probe inlet. Set the rotameter at 300 ml/min, record the volume meter reading, start the pump, and pull ambient air through the system for 10 minutes. Record the final volume meter reading. Repeat the procedure and average the results to determine the volume of gas that passed through the system.

10.3 Spectrophotometer Calibration Curve.

10.3.1 Collect the standards as described in section 8.2. Prepare at least two sets of three bulbs as standards to span the 0 to 400 or 400 to 1000 ppm range. If any samples span both

concentration ranges, prepare a calibration curve for each range using separate reagent blanks. Prepare a set of three bulbs containing colorimetric reagent but no CO to serve as a reagent blank. Analyze each standard and blank according to the sample analysis procedure of section 11.0 Reject the standard set where any of the individual bulb absorbances differs from the set mean by more than 10 percent.

10.3.2 Calculate the average absorbance for each set (3 bulbs) of standards using Equation 10A–1 and Table 10A–1. Construct a graph of average absorbance for each standard against its corresponding concentration. Draw a smooth curve through the points. The curve should be linear over the two concentration ranges discussed in section 13.3.

11.0 Analytical Procedure

11.1 Assemble the system shown in Figure 10A–3, and record the information required in Table 10A–1 as it is obtained. Pipet 10.0 ml of the colorimetric reagent into each gas reaction bulb, and attach the bulbs to the system. Open the stopcocks to the reaction bulbs, but leave the valve to the bag closed. Turn on the pump, fully open the coarse-adjust flow valve, and slowly open the fine-adjust valve until the pressure is reduced to at least 40 mm Hg. Now close the coarse adjust valve, and observe the manometer to be certain that the system is leak-free. Wait a minimum of 2 minutes. If the pressure has increased less than 1 mm Hg, proceed as described below. If a leak is present, find and correct it before proceeding further.

11.2 Record the vacuum pressure (P_v) to the nearest 1 mm Hg, and close the reaction bulb stopcocks. Open the bag valve, and allow the system to come to atmospheric pressure. Close the bag valve, open the pump coarse adjust valve, and evacuate the system again. Repeat this fill/evacuation procedure at least twice to flush the manifold completely. Close the pump coarse adjust valve, open the bag valve, and let the system fill to atmospheric pressure. Open the stopcocks to the reaction bulbs, and let the entire system come to atmospheric pressure. Close the bulb stopcocks, remove the bulbs, record the room temperature and barometric pressure (P_{bar}, to nearest mm Hg), and place the bulbs on the shaker table with their main axis either parallel to or perpendicular to the plane of the table top. Purge the bulb-filling system with ambient air for several minutes between samples. Shake the samples for exactly 2 hours.

11.3 Immediately after shaking, measure the absorbance (A) of each bulb sample at 425 nm if the concentration is less than or equal to 400 ppm CO or at 600 nm if the concentration is above 400 ppm.

NOTE: This may be accomplished with multiple bulb sets by sequentially collecting sets and adding to the shaker at staggered intervals, followed by sequentially removing sets from the shaker for absorbance measurement after the two-hour designated intervals have elapsed.

11.4 Use a small portion of the sample to rinse a spectrophotometer cell several times before taking an aliquot for analysis. If one cell is used to analyze multiple samples, rinse the cell with deionized distilled water several times between samples. Prepare and analyze standards and a reagent blank as described in section 10.3. Use water as the reference. Reject the analysis if the blank absorbance is greater than 0.1. All conditions should be the same for analysis of samples and standards. Measure the absorbances as soon as possible after shaking is completed.

11.5 Determine the CO concentration of each bag sample using the calibration curve for the appropriate concentration range as discussed in section 10.3.

12.0 Calculations and Data Analysis

Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature.

A = Sample absorbance, uncorrected for the reagent blank.
A_r = Absorbance of the reagent blank.
A_s = Average sample absorbance per liter, units/liter.
B_w = Moisture content in the bag sample.
C = CO concentration in the stack gas, dry basis, ppm.
C_b = CO concentration of the bag sample, dry basis, ppm.
C_g = CO concentration from the calibration curve, ppm.
F = Volume fraction of CO_2 in the stack.
n = Number of reaction bulbs used per bag sample.
P_b = Barometric pressure, mm Hg.
P_v = Residual pressure in the sample bulb after evacuation, mm Hg.
P_w = Vapor pressure of H_2O in the bag (from Table 10A–2), mm Hg.
V_b = Volume of the sample bulb, liters.
V_r = Volume of reagent added to the sample bulb, 0.0100 liter.

12.2 Average Sample Absorbance per Liter. Calculate A_s for each gas bulb using Equation 10A–1, and record the value in Table 10A–1. Calculate the average A_s for each bag sample, and compare the three values to the average. If any single value differs by more than 10 percent from the average, reject this value, and calculate a new average using the two remaining values.

$$A_s = \frac{(A - A_r)(P_b)}{(V_b - V_r)(P_b - P_v)} \qquad \text{Eq. 10A-1}$$

NOTE: A and A_r must be at the same wavelength.

12.3 CO Concentration in the Bag. Calculate C_b using Equations 10A–2 and 10A–3. If condensate is visible in the bag, calculate B_w using Table 10A–2 and the temperature and barometric pressure in the analysis room. If condensate is not visible, calculate B_w using the temperature and barometric pressure at the sampling site.

$$B_w = \frac{P_w}{P_b} \qquad \text{Eq. 10A-2}$$

$$C_b = \frac{C_g}{(1 - B_w)} \qquad \text{Eq. 10A-3}$$

12.4 CO Concentration in the Stack.

$$C = C_b\,(1 - F) \qquad \text{Eq. 10A-4}$$

13.0 Method Performance

13.1 Precision. The estimated intralaboratory standard deviation of the method is 3 percent of the mean for gas samples analyzed in duplicate in the concentration range of 39 to 412 ppm. The interlaboratory precision has not been established.

13.2 Accuracy. The method contains no significant biases when compared to an NDIR analyzer calibrated with NIST standards.

13.3 Range. Approximately 3 to 1800 ppm CO. Samples having concentrations below 400 ppm are analyzed at 425 nm, and samples having concentrations above 400 ppm are analyzed at 600 nm.

13.4 Sensitivity. The detection limit is 3 ppmv based on a change in concentration equal to three times the standard deviation of the reagent blank solution.

13.5 Stability. The individual components of the colorimetric reagent are stable for at least one month. The colorimetric reagent must be used within two days after preparation to avoid excessive blank correction. The samples in the bag should be stable for at least one week if the bags are leak-free.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Butler, F.E., J.E. Knoll, and M.R. Midgett. Development and Evaluation of Methods for Determining Carbon Monoxide Emissions. U.S. Environmental Protection Agency, Research Triangle Park, N.C. June 1985. 33 pp.

2. Ferguson, B.B., R.E. Lester, and W.J. Mitchell. Field Evaluation of Carbon Monoxide and Hydrogen Sulfide Continuous Emission Monitors at an Oil Refinery. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA–600/4–82–054. August 1982. 100 pp.

3. Lambert, J.L., and R.E. Weins. Induced Colorimetric Method for Carbon Monoxide. Analytical Chemistry. *46*(7):929–930. June 1974.

4. Levaggi, D.A., and M. Feldstein. The Colorimetric Determination of Low Concentrations of Carbon Monoxide. Industrial Hygiene Journal. *25*:64–66. January-February 1964.

5. Repp, M. Evaluation of Continuous Monitors For Carbon Monoxide in Stationary Sources. U.S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA–600/2–77–063. March 1977. 155 pp.

6. Smith, F., D.E. Wagoner, and R.P. Donovan. Guidelines for Development of a Quality Assurance Program: Volume VIII—Determination of CO Emissions from Stationary Sources by NDIR Spectrometry. U.S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA–650/4–74–005–h. February 1975. 96 pp.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 10A–1—DATA RECORDING SHEET FOR SAMPLES ANALYZED IN TRIPLICATE

Sample No./type	Room temp °C	Stack %CO_2	Bulb No.	Bulb vol. liters	Reagent vol. in bulb, liter	Partial pressure of gas in bulb, mm Hg	$P_{b,r}$, mm Hg	Shaking time, min	Abs versus water	A-A_r	A_s	Avg A_s
blank												
Std. 1												
Std. 2												
Sample 1												
Sample 2												
Sample 3												

TABLE 10A–2—MOISTURE CORRECTION

Temperature °C	Vapor pressure of H_2O, mm Hg	Temperature °C	Vapor pressure of H_2, mm Hg
4	6.1	18	15.5
6	7.0	20	17.5
8	8.0	22	19.8
10	9.2	24	22.4
12	10.5	26	25.2
14	12.0	28	28.3
16	13.6	30	31.8

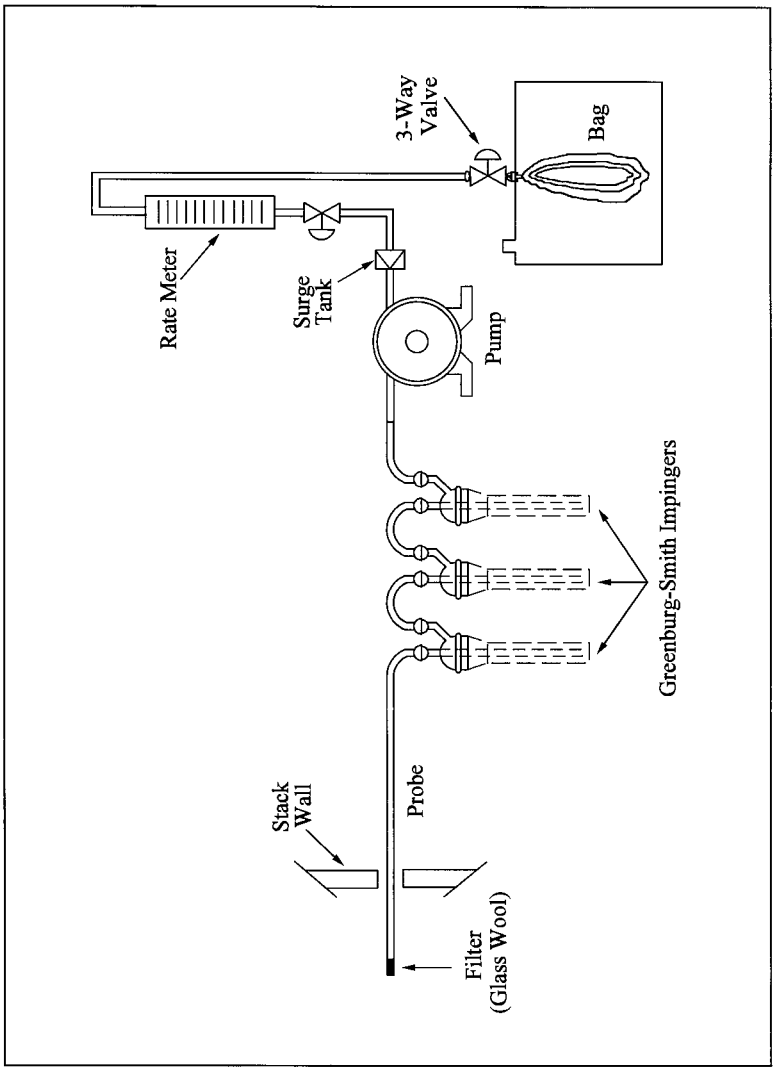


Figure 10A-1. Sampling Train.

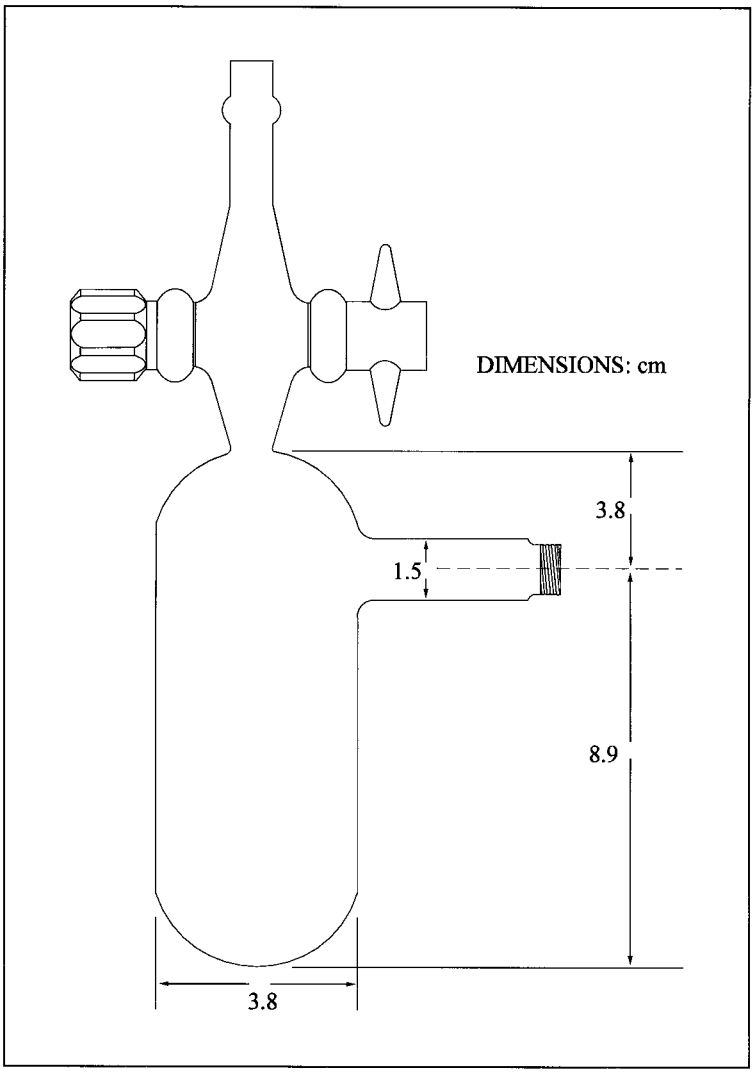


Figure 10A-2. Sample Reaction Bulbs.

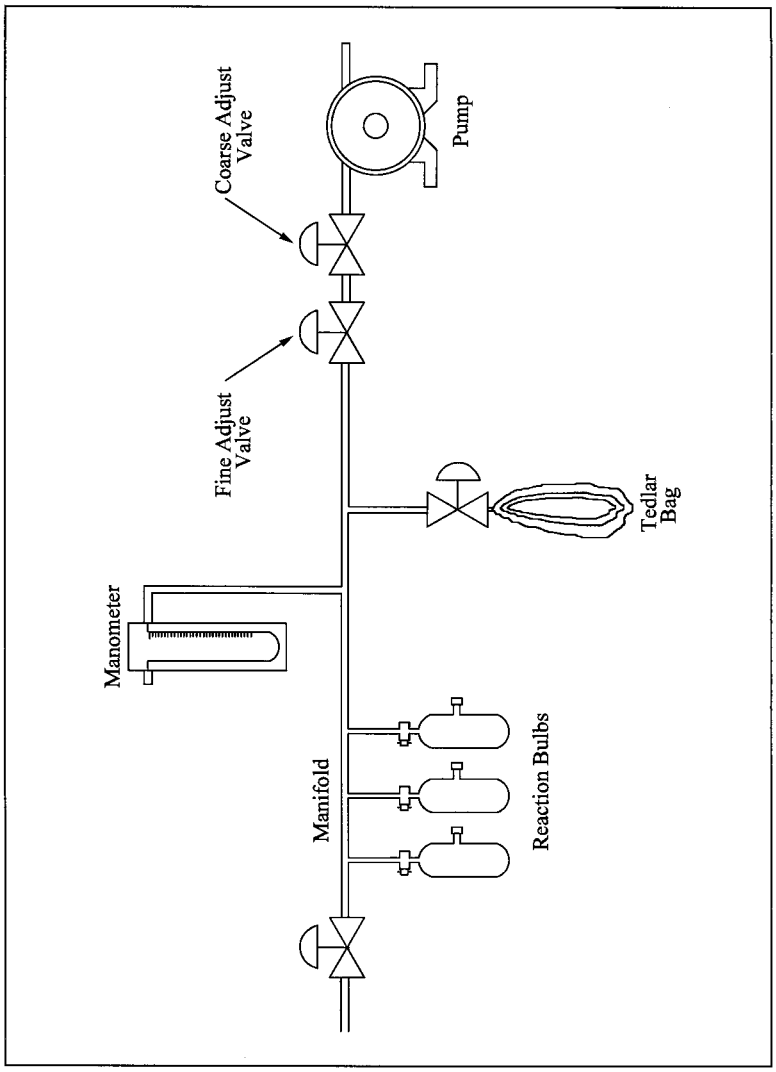


Figure 10A-3. Sample Bulb Filling System.

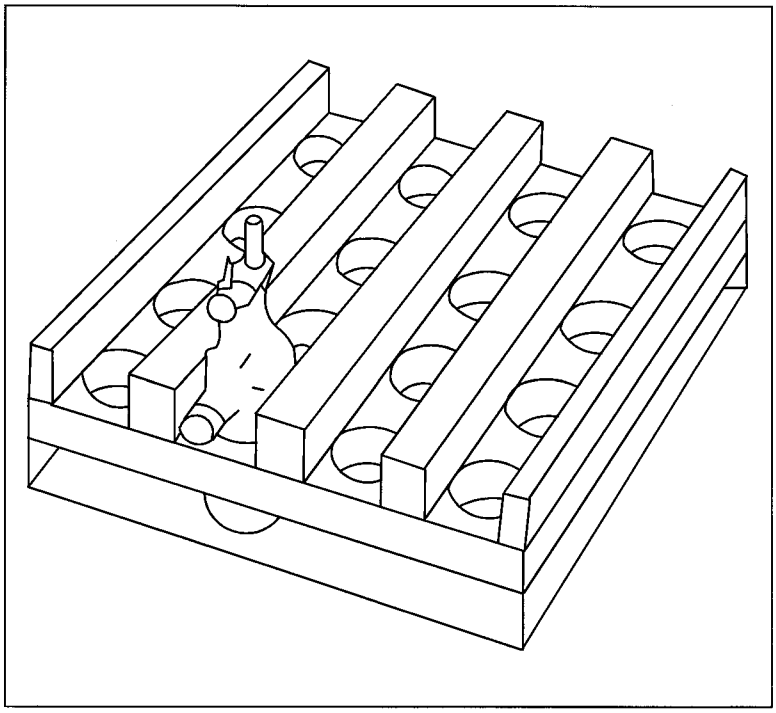


Figure 10A-4. Shaker Table Adapter.

METHOD 10B—DETERMINATION OF CARBON MONOXIDE EMISSIONS FROM STATIONARY SOURCES

NOTE: This method is not inclusive with respect to specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 4, Method 10A, and Method 25.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Carbon monoxide (CO)	630–08–0	Not determined.

1.2 Applicability. This method applies to the measurement of CO emissions at petroleum refineries and from other sources when specified in an applicable subpart of the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 An integrated gas sample is extracted from the sampling point, passed through a conditioning system to remove interferences, and collected in a Tedlar or equivalent bag. (Verify through the manufacturer that the Tedlar alternative is suitable for NO and make this verifying information available for inspection.) The CO is separated from the sample by gas chromatography (GC) and catalytically reduced to methane (CH_4) which is determined by flame ionization detection (FID). The analytical portion of this method is identical to applicable sections in Method 25 detailing CO measurement.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Carbon dioxide (CO_2) and organics potentially can interfere with the analysis. Most of the CO_2 is removed from the sample by the alkaline permanganate conditioning system; any residual CO_2 and organics are separated from the CO by GC.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions concerning the analytical procedure.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as in Method 10A, section 6.1 (paragraphs 6.1.1 through 6.1.11).

6.2 Sample Analysis. A GC/FID analyzer, capable of quantifying CO in the sample and consisting of at least the following major components, is required for sample analysis. [Alternatively, complete Method 25 analytical systems (Method 25, section 6.3) are acceptable alternatives when calibrated for CO and operated in accordance with the Method 25 analytical procedures (Method 25, section 11.0).]

6.2.1 Separation Column. A column capable of separating CO from CO_2 and organic compounds that may be present. A 3.2-mm (⅛-in.) OD stainless steel column packed with 1.7 m (5.5 ft.) of 60/80 mesh Carbosieve S-II (available from Supelco) has been used successfully for this purpose.

6.2.2 Reduction Catalyst. Same as in Method 25, section 6.3.1.2.

6.2.3 Sample Injection System. Same as in Method 25, Section 6.3.1.4, equipped to accept a sample line from the bag.

6.2.4 Flame Ionization Detector. Meeting the linearity specifications of section 10.3 and having a minimal instrument range of 10 to 1,000 ppm CO.

6.2.5 Data Recording System. Analog strip chart recorder or digital integration system, compatible with the FID, for permanently recording the analytical results.

7.0 Reagents and Standards

7.1 Sample Collection. Same as in Method 10A, section 7.1.

7.2 Sample Analysis.

7.2.1 Carrier, Fuel, and Combustion Gases. Same as in Method 25, sections 7.2.1, 7.2.2, and 7.2.3, respectively.

7.2.2 Calibration Gases. Three standard gases with nominal CO concentrations of 20, 200, and 1,000 ppm CO in nitrogen. The calibration gases shall be certified by the manufacturer to be ±2 percent of the specified concentrations.

7.2.3 Reduction Catalyst Efficiency Check Calibration Gas. Standard CH_4 gas with a nominal concentration of 1,000 ppm in air.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as in Method 10A, section 8.0.

9.0 Quality Control

Section	Quality control measure	Effect
8.0	Sample bag/sampling system leak-checks	Ensures that negative bias introduced through leakage is minimized.
10.1	Carrier gas blank check	Ensures that positive bias introduced by contamination of carrier gas is less than 5 ppmv.
10.2	Reduction catalyst efficiency check	Ensures that negative bias introduced by inefficient reduction catalyst is less than 5 percent.
10.3	Analyzer calibration	Ensures linearity of analyzer response to standards.
11.2	Triplicate sample analyses	Ensures precision of analytical results.

10.0 Calibration and Standardization

10.1 Carrier Gas Blank Check. Analyze each new tank of carrier gas with the GC analyzer according to section 11.2 to check for contamination. The corresponding concentration must be less than 5 ppm for the tank to be acceptable for use.

10.2 Reduction Catalyst Efficiency Check. Prior to initial use, the reduction catalyst shall be tested for reduction efficiency. With the heated reduction catalyst bypassed, make triplicate injections of the 1,000 ppm CH_4 gas (Section 7.2.3) to calibrate the analyzer. Repeat the procedure using 1,000 ppm CO gas (Section 7.2.2) with the catalyst in operation. The reduction catalyst operation is acceptable if the CO response is within 5 percent of the certified gas value.

10.3 Analyzer Calibration. Perform this test before the system is first placed into operation. With the reduction catalyst in operation, conduct a linearity check of the analyzer using the standards specified in section 7.2.2. Make triplicate injections of each calibration gas, and then calculate the average

response factor (area/ppm) for each gas, as well as the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within 2.5 percent of the overall mean value and if the relative standard deviation (calculated in section 12.8 of Method 25) for each set of triplicate injections is less than 2 percent. Record the overall mean of the response factor values as the calibration response factor (R).

11.0 Analytical Procedure

11.1 Preparation for Analysis. Before putting the GC analyzer into routine operation, conduct the calibration procedures listed in section 10.0. Establish an appropriate carrier flow rate and detector temperature for the specific instrument used.

11.2 Sample Analysis. Purge the sample loop with sample, and then inject the sample. Analyze each sample in triplicate, and calculate the average sample area (A). Determine the bag CO concentration according to section 12.2.

12.0 Calculations and Data Analysis

Carry out calculations retaining at least one extra significant figure beyond that of the acquired data. Round off results only after the final calculation.

12.1 Nomenclature.

A = Average sample area.
B_w = Moisture content in the bag sample, fraction.
C = CO concentration in the stack gas, dry basis, ppm.
C_b = CO concentration in the bag sample, dry basis, ppm.
F = Volume fraction of CO_2 in the stack, fraction.
P_{bar} = Barometric pressure, mm Hg.
P_w = Vapor pressure of the H_2O in the bag (from Table 10A–2, Method 10A), mm Hg.
R = Mean calibration response factor, area/ppm.

12.2 CO Concentration in the Bag. Calculate C_b using Equations 10B–1 and 10B–2. If condensate is visible in the bag, calculate B_w using Table 10A–2 of Method 10A and the temperature and barometric pressure in the analysis room. If condensate is not visible, calculate B_w using the temperature and barometric pressure at the sampling site.

$$B_w = \frac{P_w}{P_{bar}} \qquad \text{Eq. 10B-1}$$

$$C_b = \frac{A}{R\left(1 - B_w\right)} \qquad \text{Eq. 10B-2}$$

12.3 CO Concentration in the Stack

$$C = C_b\left(1 - F\right) \qquad \text{Eq. 10B-3}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as in Method 25, section 16.0, with the addition of the following:

1. Butler, F.E, J.E. Knoll, and M.R. Midgett. Development and Evaluation of Methods for Determining Carbon Monoxide Emissions. Quality Assurance Division, Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC. June 1985. 33 pp.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–4 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

APPENDIX A–5 TO PART 60—TEST METHODS 11 THROUGH 15A

Method 11—Determination of hydrogen sulfide content of fuel gas streams in petroleum refineries
Method 12—Determination of inorganic lead emissions from stationary sources
Method 13A—Determination of total fluoride emissions from stationary sources—SPADNS zirconium lake method
Method 13B—Determination of total fluoride emissions from stationary sources—Specific ion electrode method
Method 14—Determination of fluoride emissions from potroom roof monitors for primary aluminum plants
Method 14A—Determination of Total Fluoride Emissions from Selected Sources at Primary Aluminum Production Facilities
Method 15—Determination of hydrogen sulfide, carbonyl sulfide, and carbon disulfide emissions from stationary sources
Method 15A—Determination of total reduced sulfur emissions from sulfur recovery plants in petroleum refineries

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods

State of Oregon Department of Environmental Quality

OAR 340-230-0310
EPA Reference Method 22

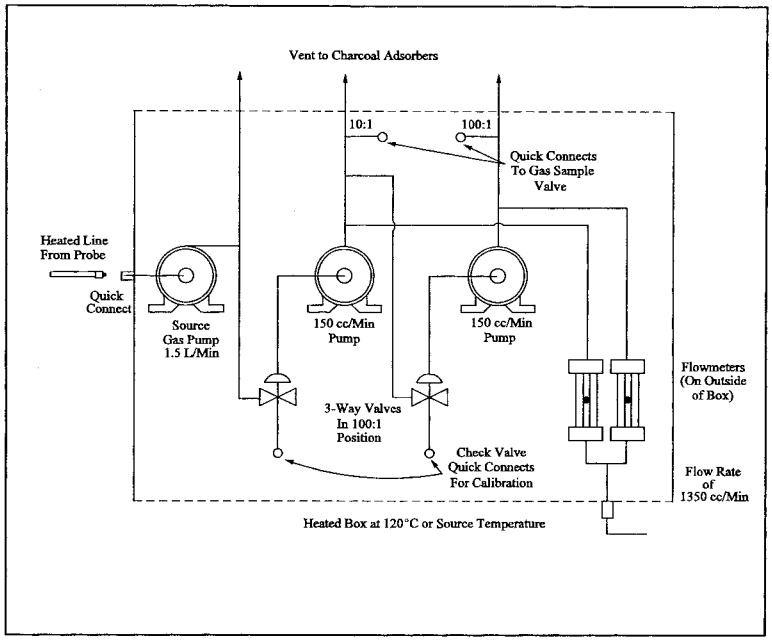


Figure 18-13. Schematic Diagram of the Heated Box Required for Dilution of Sample Gas.

GASEOUS ORGANIC SAMPLING AND ANALYSIS CHECK LIST

[Respond with initials or number as appropriate]

1. Presurvey data:		
A. Grab sample collected	☐	_____
B. Grab sample analyzed for composition	☐	_____
Method GC	☐	_____
GC/MS	☐	_____
Other	☐	_____
C. GC-FID analysis performed	☐	_____
2. Laboratory calibration data:		
A. Calibration curves prepared	☐	_____
Number of components	☐	_____
Number of concentrations/component (3 required).	☐	_____
B. Audit samples (optional):		
Analysis completed	☐	_____
Verified for concentration	☐	_____
OK obtained for field work	☐	_____
3. Sampling procedures:		
A. Method:		
Bag sample	☐	_____
Direct interface	☐	_____
Dilution interface	☐	_____
B. Number of samples collected	☐	_____
4. Field Analysis:		
A. Total hydrocarbon analysis performed	☐	_____
B. Calibration curve prepared	☐	_____
Number of components	☐	_____
Number of concentrations per component (3 required).	☐	_____

Gaseous Organic Sampling and Analysis Data

Date _____
Location _____

Plant _____

GASEOUS ORGANIC SAMPLING AND ANALYSIS CHECK LIST (RESPOND WITH INITIALS OR NUMBER AS APPROPRIATE)

	Date
1. Pre-survey data	
A. Grab sample collected	_____
B. Grab sample analyzed for composition	_____
Method GC	_____
GC/MS	_____
Other_____	_____
C. GC–FID analysis performed	_____
2. Laboratory calibration curves prepared	_____
A. Number of components	_____
B. Number of concentrations per component (3 required)	_____
C. OK obtained for field work	_____
3. Sampling procedures.	
A. Method.	
Bag sample	_____
Direct interface	_____
Dilution interface	_____
B. Number of samples collected	_____
4. Field Analysis.	
A. Total hydrocarbon analysis performed	_____
B. Calibration curve prepared	_____
Number of components	_____
Number of concentrations per component (3 required)	_____

Figure 18–14. Sampling and Analysis Sheet

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–6 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

APPENDIX A–7 TO PART 60—TEST METHODS 19 THROUGH 25E

Method 19—Determination of sulfur dioxide removal efficiency and particulate, sulfur dioxide and nitrogen oxides emission rates
Method 20—Determination of nitrogen oxides, sulfur dioxide, and diluent emissions from stationary gas turbines
Method 21—Determination of volatile organic compound leaks
Method 22—Visual determination of fugitive emissions from material sources and smoke emissions from flares
Method 23—Determination of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans From Stationary Sources
Method 24—Determination of volatile matter content, water content, density, volume solids, and weight solids of surface coatings
Method 24A—Determination of volatile matter content and density of printing inks and related coatings
Method 25—Determination of total gaseous nonmethane organic emissions as carbon
Method 25A—Determination of total gaseous organic concentration using a flame ionization analyzer
Method 25B—Determination of total gaseous organic concentration using a nondispersive infrared analyzer
Method 25C—Determination of nonmethane organic compounds (NMOC) in MSW landfill gases
Method 25D—Determination of the Volatile Organic Concentration of Waste Samples
Method 25E—Determination of Vapor Phase Organic Concentration in Waste Samples

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

Method 19—Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates

1.0 Scope and Application

1.1 Analytes. This method provides data reduction procedures relating to the following pollutants, but does not include any sample collection or analysis procedures.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), including:		
Nitric oxide (NO)	10102–43–9	N/A
Nitrogen dioxide (NO_2)	10102–44–0.	
Particulate matter (PM)	None assigned	N/A
Sulfur dioxide (SO_2)	7499–09–05	N/A

1.2 Applicability. Where specified by an applicable subpart of the regulations, this method is applicable for the determination of (a) PM, SO_2, and NO_X emission rates; (b) sulfur removal efficiencies of fuel pretreatment and SO_2 control devices; and (c) overall reduction of potential SO_2 emissions.

2.0 Summary of Method

2.1 Emission Rates. Oxygen (O_2) or carbon dioxide (CO_2) concentrations and appropriate F factors (ratios of combustion gas volumes to heat inputs) are used to calculate pollutant emission rates from pollutant concentrations.

2.2 Sulfur Reduction Efficiency and SO_2 Removal Efficiency. An overall SO_2 emission reduction efficiency is computed from the efficiency of fuel pretreatment systems, where applicable, and the efficiency of SO_2 control devices.

2.2.1 The sulfur removal efficiency of a fuel pretreatment system is determined by fuel sampling and analysis of the sulfur and heat contents of the fuel before and after the pretreatment system.

2.2.2 The SO_2 removal efficiency of a control device is determined by measuring the SO_2 rates before and after the control device.

2.2.2.1 The inlet rates to SO_2 control systems (or, when SO_2 control systems are not used, SO_2 emission rates to the atmosphere) are determined by fuel sampling and analysis.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety [Reserved]

6.0 Equipment and Supplies [Reserved]

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transport [Reserved]

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedures [Reserved]

12.0 Data Analysis and Calculations

12.1 Nomenclature

B_{wa} = Moisture fraction of ambient air, percent.

B_{ws} = Moisture fraction of effluent gas, percent.

%C = Concentration of carbon from an ultimate analysis of fuel, weight percent.

C_d = Pollutant concentration, dry basis, ng/scm (lb/scf)

$\%CO_{2d}$,$\%CO_{2w}$ = Concentration of carbon dioxide on a dry and wet basis, respectively, percent.

C_w = Pollutant concentration, wet basis, ng/scm (lb/scf).

D = Number of sampling periods during the performance test period.

E = Pollutant emission rate, ng/J (lb/million Btu).

E_a = Average pollutant rate for the specified performance test period, ng/J (lb/million Btu).

E_{ao}, E_{ai} = Average pollutant rate of the control device, outlet and inlet, respectively, for the performance test period, ng/J (lb/million Btu).

E_{bi} = Pollutant rate from the steam generating unit, ng/J (lb/million Btu)

E_{bo} = Pollutant emission rate from the steam generating unit, ng/J (lb/million Btu).

E_{ci} = Pollutant rate in combined effluent, ng/J (lb/million Btu).

E_{co} = Pollutant emission rate in combined effluent, ng/J (lb/million Btu).

E_d = Average pollutant rate for each sampling period (*e.g.*, 24-hr Method 6B sample or 24-hr fuel sample) or for each fuel lot (*e.g.*, amount of fuel bunkered), ng/J (lb/million Btu).

E_{di} = Average inlet SO_2 rate for each sampling period d, ng/J (lb/million Btu)

E_g = Pollutant rate from gas turbine, ng/J (lb/million Btu).

E_{ga} = Daily geometric average pollutant rate, ng/J (lbs/million Btu) or ppm corrected to 7 percent O_2.

E_{jo},E_{ji} = Matched pair hourly arithmetic average pollutant rate, outlet and inlet, respectively, ng/J (lb/million Btu) or ppm corrected to 7 percent O_2.

E_h = Hourly average pollutant, ng/J (lb/million Btu).

E_{hj} = Hourly arithmetic average pollutant rate for hour ''j,'' ng/J (lb/million Btu) or ppm corrected to 7 percent O_2.

EXP = Natural logarithmic base (2.718) raised to the value enclosed by brackets.

F_d, F_w, F_c = Volumes of combustion components per unit of heat content, scm/J (scf/million Btu).

GCV = Gross calorific value of the fuel consistent with the ultimate analysis, kJ/kg (Btu/lb).

GCV_p, GCV_r = Gross calorific value for the product and raw fuel lots, respectively, dry basis, kJ/kg (Btu/lb).

%H = Concentration of hydrogen from an ultimate analysis of fuel, weight percent.

H = Total number of operating hours for which pollutant rates are determined in the performance test period.

H_b = Heat input rate to the steam generating unit from fuels fired in the steam generating unit, J/hr (million Btu/hr).

H_g = Heat input rate to gas turbine from all fuels fired in the gas turbine, J/hr (million Btu/hr).

$\%H_2O$ = Concentration of water from an ultimate analysis of fuel, weight percent.
H_r = Total numbers of hours in the performance test period (*e.g.*, 720 hours for 30-day performance test period).
K = Conversion factor, 10^{-5} (kJ/J)/(%) [10^6 Btu/million Btu].
K_c = (9.57 scm/kg)/% [(1.53 scf/lb)/%].
K_{cc} = (2.0 scm/kg)/% [(0.321 scf/lb)/%].
K_{hd} = (22.7 scm/kg)/% [(3.64 scf/lb)/%].
K_{hw} = (34.74 scm/kg)/% [(5.57 scf/lb)/%].
K_n = (0.86 scm/kg)/% [(0.14 scf/lb)/%].
K_o = (2.85 scm/kg)/% [(0.46 scf/lb)/%].
K_s = (3.54 scm/kg)/% [(0.57 scf/lb)/%].
K_w = (1.30 scm/kg)/% [(0.21 scf/lb)/%].
ln = Natural log of indicated value.
L_p,L_r = Weight of the product and raw fuel lots, respectively, metric ton (ton).
%N = Concentration of nitrogen from an ultimate analysis of fuel, weight percent.
N = Number of fuel lots during the averaging period.
n = Number of fuels being burned in combination.
n_d = Number of operating hours of the affected facility within the performance test period for each E_d determined.
n_t = Total number of hourly averages for which paired inlet and outlet pollutant rates are available within the 24-hr midnight to midnight daily period.
%O = Concentration of oxygen from an ultimate analysis of fuel, weight percent.
$\%O_{2d}$, $\%O_{2w}$ = Concentration of oxygen on a dry and wet basis, respectively, percent.
P_s = Potential SO_2 emissions, percent.
$\%R_f$ = SO_2 removal efficiency from fuel pretreatment, percent.
$\%R_g$ = SO_2 removal efficiency of the control device, percent.
$\%R_{ga}$ = Daily geometric average percent reduction.
$\%R_o$ = Overall SO_2 reduction, percent.
%S = Sulfur content of as-fired fuel lot, dry basis, weight percent.
S_e = Standard deviation of the hourly average pollutant rates for each performance test period, ng/J (lb/million Btu).
$\%S_f$ = Concentration of sulfur from an ultimate analysis of fuel, weight percent.
S_i = Standard deviation of the hourly average inlet pollutant rates for each performance test period, ng/J (lb/million Btu).
S_o = Standard deviation of the hourly average emission rates for each performance test period, ng/J (lb/million Btu).
$\%S_p$, $\%S_r$ = Sulfur content of the product and raw fuel lots respectively, dry basis, weight percent.
$t_{0.95}$ = Values shown in Table 19–3 for the indicated number of data points n.
X_k = Fraction of total heat input from each type of fuel k.

12.2 Emission Rates of PM, SO_2, and NO_X. Select from the following sections the applicable procedure to compute the PM, S_{O2}, or NO_X emission rate (E) in ng/J (lb/million Btu). The pollutant concentration must be in ng/scm (lb/scf) and the F factor must be in scm/J (scf/million Btu). If the pollutant concentration (C) is not in the appropriate units, use Table 19–1 in section 17.0 to make the proper conversion. An F factor is the ratio of the gas volume of the products of combustion to the heat content of the fuel. The dry F factor (F_d) includes all components of combustion less water, the wet F factor (F_w) includes all components of combustion, and the carbon F factor (F_c) includes only carbon dioxide.

NOTE: Since F_w factors include water resulting only from the combustion of hydrogen in the fuel, the procedures using F_w factors are not applicable for computing E from steam generating units with wet scrubbers or with other processes that add water (*e.g.*, steam injection).

12.2.1 Oxygen-Based F Factor, Dry Basis. When measurements are on a dry basis for both O ($\%O_{2d}$) and pollutant (C_d) concentrations, use the following equation:

$$E = C_d F_d \frac{20.9}{(20.9 - \%O_{2d})} \qquad \text{Eq. 19-1}$$

12.2.2 Oxygen-Based F Factor, Wet Basis. When measurements are on a wet basis for both O_2 ($\%O_{2w}$) and pollutant (C_w) concentrations, use either of the following:

12.2.2.1 If the moisture fraction of ambient air (B_{wa}) is measured:

$$E = C_w F_w \frac{20.9}{\left[20.9(1 - B_{wa}) - \%O_{2w}\right]} \qquad \text{Eq. 19-2}$$

Instead of actual measurement, B_{wa} may be estimated according to the procedure below.

NOTE: The estimates are selected to ensure that negative errors will not be larger than −1.5 percent. However, positive errors, or over-estimation of emissions by as much as 5 percent may be introduced depending upon the geographic location of the facility and the associated range of ambient moisture.

12.2.2.1.1 B_{wa} = 0.027. This value may be used at any location at all times.

12.2.2.1.2 B_{wa} = Highest monthly average of B_{wa} that occurred within the previous calendar year at the nearest Weather Service Station. This value shall be determined annually and may be used as an estimate for the entire current calendar year.

12.2.2.1.3 B_{wa} = Highest daily average of Bwa that occurred within a calendar month at the nearest Weather Service Station, calculated from the data from the past 3 years. This value shall be computed for each month and may be used as an estimate for the current respective calendar month.

12.2.2.2 If the moisture fraction (B_{ws}) of the effluent gas is measured:

$$E = C_w F_d \frac{20.9}{\left[20.9\left(1-B_{ws}\right)-\%O_{2w}\right]} \qquad \text{Eq. 19-3}$$

12.2.3 Oxygen-Based F Factor, Dry/Wet Basis.

12.2.3.1 When the pollutant concentration is measured on a wet basis (C_w) and O_2 concentration is measured on a dry basis ($\%O_{2d}$), use the following equation:

$$E = \frac{\left(C_w F_d\right)(20.9)}{\left(1-B_{ws}\right)\left(20.9-\%O_{2d}\right)} \qquad \text{Eq. 19-4}$$

12.2.3.2 When the pollutant concentration is measured on a dry basis (C_d) and the O_2 concentration is measured on a wet basis ($\%O_{2w}$), use the following equation:

$$E = \frac{C_d F_d 20.9}{\frac{\left(20.9-\%O_{2w}\right)}{\left(1-B_{ws}\right)}} \qquad \text{Eq. 19-5}$$

12.2.4 Carbon Dioxide-Based F Factor, Dry Basis. When measurements are on a dry basis for both CO_2 ($\%CO_{2d}$) and pollutant (C_d) concentrations, use the following equation:

$$E = C_d F_c \frac{100}{\%CO_{2d}} \qquad \text{Eq. 19-6}$$

12.2.5 Carbon Dioxide-Based F Factor, Wet Basis. When measurements are on a wet basis for both CO_2 ($\%CO_{2w}$) and pollutant (C_w) concentrations, use the following equation:

$$E = C_w F_c \frac{100}{\%CO_{2w}} \qquad \text{Eq. 19-7}$$

12.2.6 Carbon Dioxide-Based F Factor, Dry/Wet Basis.

12.2.6.1 When the pollutant concentration is measured on a wet basis (C_w) and CO_2 concentration is measured on a dry basis ($\%CO_{2d}$), use the following equation:

$$E = \frac{C_w F_c}{\left(1-B_{ws}\right)} \frac{100}{\%CO_{2d}} \qquad \text{Eq. 19-8}$$

12.2.6.2 When the pollutant concentration is measured on a dry basis (C_d) and CO_2 concentration is measured on a wet basis ($\%CO_{2w}$), use the following equation:

$$E = C_d F_c \left(1-B_{ws}\right) \frac{100}{\%CO_{2w}} \qquad \text{Eq. 19-9}$$

12.2.7 Direct-Fired Reheat Fuel Burning. The effect of direct-fired reheat fuel burning (for the purpose of raising the temperature of the exhaust effluent from wet scrubbers to above the moisture dew-point) on emission rates will be less than 1.0 percent and, therefore, may be ignored.

12.2.8 Combined Cycle-Gas Turbine Systems. For gas turbine-steam generator combined cycle systems, determine the emissions from the steam generating unit or the percent reduction in potential SO_2 emissions as follows:

12.2.8.1 Compute the emission rate from the steam generating unit using the following equation:

$$E_{bo} = E_{co} + \frac{H_g}{H_b}\left(E_{co} - E_g\right) \qquad \text{Eq. 19-10}$$

12.2.8.1.1 Use the test methods and procedures section of 40 CFR Part 60, Subpart GG to obtain E_{co} and E_g. Do not use F_w factors for determining E_g or E_{co}. If an SO_2 control device is used, measure E_{co} after the control device.

12.2.8.1.2 Suitable methods shall be used to determine the heat input rates to the steam generating units (H_b) and the gas turbine (H_g).

12.2.8.2 If a control device is used, compute the percent of potential SO_2 emissions (P_s) using the following equations:

$$E_{bi} = E_{ci} - \frac{H_g}{H_b}\left(E_{ci} - E_g\right) \qquad \text{Eq. 19-11}$$

$$P_s = 100\left(1 - \frac{E_{bo}}{E_{bi}}\right) \qquad \text{Eq. 19-12}$$

NOTE: Use the test methods and procedures section of Subpart GG to obtain E_{ci} and E_g. Do not use F_w factors for determining E_g or E_{ci}.

12.3 F Factors. Use an average F factor according to section 12.3.1 or determine an applicable F factor according to section 12.3.2. If combined fuels are fired, prorate the applicable F factors using the procedure in section 12.3.3.

12.3.1 Average F Factors. Average F factors (F_d, F_w, or F_c) from Table 19–2 in section 17.0 may be used.

12.3.2 Determined F Factors. If the fuel burned is not listed in Table 19–2 or if the owner or operator chooses to determine an F factor rather than use the values in Table 19–2, use the procedure below:

12.3.2.1 Equations. Use the equations below, as appropriate, to compute the F factors:

$$F_d = \frac{K\left(K_{hd}\%H + K_c\%C + K_s\%S + K_n\%N - K_o\%O\right)}{GCV} \qquad \text{Eq. 19-13}$$

$$F_w = \frac{K\left[K_{hw}\%H + K_c\%C + K_s\%S + K_n\%N - K_o\%O + K_w\%H_2O\right]}{GCV_w} \qquad \text{Eq. 19-14}$$

$$F_c = \frac{K\left(K_{cc}\%C\right)}{GCV} \qquad \text{Eq. 19-15}$$

NOTE: Omit the $\%H_2O$ term in the equations for F_w if %H and %O include the unavailable hydrogen and oxygen in the form of H_2O.)

12.3.2.2 Use applicable sampling procedures in section 12.5.2.1 or 12.5.2.2 to obtain samples for analyses.

12.3.2.3 Use ASTM D 3176–74 or 89 (all cited ASTM standards are incorporated by reference—see §60.17) for ultimate analysis of the fuel.

12.3.2.4 Use applicable methods in section 12.5.2.1 or 12.5.2.2 to determine the heat content of solid or liquid fuels. For gaseous fuels, use ASTM D 1826–77 or 94 (incorporated by reference—see §60.17) to determine the heat content.

12.3.3 F Factors for Combination of Fuels. If combinations of fuels are burned, use the following equations, as applicable unless otherwise specified in an applicable subpart:

$$F_d = \sum_{k=1}^{n}\left(X_k F_{dk}\right) \qquad \text{Eq. 19-16}$$

$$F_w = \sum_{k=1}^{n}\left(X_k F_{wk}\right) \qquad \text{Eq. 19-17}$$

$$F_c = \sum_{k=1}^{n}\left(X_k F_{ck}\right) \qquad \text{Eq. 19-18}$$

12.4 Determination of Average Pollutant Rates.

12.4.1 Average Pollutant Rates from Hourly Values. When hourly average pollutant rates (E_h), inlet or outlet, are obtained (*e.g.*, CEMS values), compute the average pollutant rate (E_a) for the performance test period (*e.g.*, 30 days) specified in the applicable regulation using the following equation:

$$E_a = \frac{1}{H}\sum_{j=1}^{n} E_{hj} \qquad \text{Eq. 19-19}$$

12.4.2 Average Pollutant Rates from Other than Hourly Averages. When pollutant rates are determined from measured values representing longer than 1-hour periods (*e.g.*, daily fuel sampling and analyses or Method 6B values), or when pollutant rates are determined from combinations of 1-hour and longer than 1-hour periods (*e.g.*, CEMS and Method 6B values), compute the average pollutant rate (E_a) for the performance test period (*e.g.*, 30 days) specified in the applicable regulation using the following equation:

$$E_a = \frac{\sum_{j=1}^{D}\left(n_d E_d\right)_j}{\sum_{j=1}^{D} n_{dj}} \qquad \text{Eq. 19-20}$$

12.4.3 Daily Geometric Average Pollutant Rates from Hourly Values. The geometric average pollutant rate (E_{ga}) is computed using the following equation:

$$E_{ga} = \exp\left[\frac{1}{n_t}\sum_{j=1}^{n_t}\left[\ln\left(E_{hj}\right)\right]\right] \quad \text{Eq. 19-21}$$

12.5 Determination of Overall Reduction in Potential Sulfur Dioxide Emission.

12.5.1 Overall Percent Reduction. Compute the overall percent SO_2 reduction ($\%R_o$) using the following equation:

$$\%R_o = 100\left[1.0 - \left(1.0 - \frac{\%R_f}{100}\right)\left(1.0 - \frac{\%R_g}{100}\right)\right] \quad \text{Eq. 19-22}$$

12.5.2 Pretreatment Removal Efficiency (Optional). Compute the SO_2 removal efficiency from fuel pretreatment ($\%R_f$) for the averaging period (*e.g.*, 90 days) as specified in the applicable regulation using the following equation:

$$\%R_f = 100\left[1.0 - \frac{\sum_{j=1}^{N}\left(\frac{\%S_{pj}}{GCV_{pj}}\right)L_{pj}}{\sum_{j=1}^{N}\left(\frac{\%S_{rj}}{GCV_{rj}}\right)L_{rj}}\right] \quad \text{Eq. 19-23}$$

NOTE: In calculating $\%R_f$, include %S and GCV values for all fuel lots that are not pretreated and are used during the averaging period.

12.5.2.1 Solid Fossil (Including Waste) Fuel/Sampling and Analysis.

NOTE: For the purposes of this method, raw fuel (coal or oil) is the fuel delivered to the desulfurization (pretreatment) facility. For oil, the input oil to the oil desulfurization process (*e.g.*, hydrotreatment) is considered to be the raw fuel.

12.5.2.1.1 Sample Increment Collection. Use ASTM D 2234–76, 96, 97a, or 98 (incorporated by reference—see §60.17), Type I, Conditions A, B, or C, and systematic spacing. As used in this method, systematic spacing is intended to include evenly spaced increments in time or increments based on equal weights of coal passing the collection area. As a minimum, determine the number and weight of increments required per gross sample representing each coal lot according to Table 2 or Paragraph 7.1.5.2 of ASTM D 2234. Collect one gross sample for each lot of raw coal and one gross sample for each lot of product coal.

12.5.2.1.2 ASTM Lot Size. For the purpose of section 12.5.2 (fuel pretreatment), the lot size of product coal is the weight of product coal from one type of raw coal. The lot size of raw coal is the weight of raw coal used to produce one lot of product coal. Typically, the lot size is the weight of coal processed in a 1-day (24-hour) period. If more than one type of coal is treated and produced in 1 day, then gross samples must be collected and analyzed for each type of coal. A coal lot size equaling the 90-day quarterly fuel quantity for a steam generating unit may be used if representative sampling can be conducted for each raw coal and product coal.

NOTE: Alternative definitions of lot sizes may be used, subject to prior approval of the Administrator.

12.5.2.1.3 Gross Sample Analysis. Use ASTM D 2013–72 or 86 to prepare the sample, ASTM D 3177–75 or 89 or ASTM D 4239–85, 94, or 97 to determine sulfur content (%S), ASTM D 3173–73 or 87 to determine moisture content, and ASTM D 2015–77 (Reapproved 1978) or 96, D 3286–85 or 96, or D 5865–98 or 10 to determine gross calorific value (GCV) (all standards cited are incorporated by reference—see §60.17 for acceptable versions of the standards) on a dry basis for each gross sample.

12.5.2.2 Liquid Fossil Fuel-Sampling and Analysis. See Note under section 12.5.2.1.

12.5.2.2.1 Sample Collection. Follow the procedures for continuous sampling in ASTM D 270 or D 4177–95 (incorporated by reference—see §60.17) for each gross sample from each fuel lot.

12.5.2.2.2 Lot Size. For the purpose of section 12.5.2 (fuel pretreatment), the lot size of a product oil is the weight of product oil from one pretreatment facility and intended as one shipment (ship load, barge load, etc.). The lot size of raw oil is the weight of each crude liquid fuel type used to produce a lot of product oil.

NOTE: Alternative definitions of lot sizes may be used, subject to prior approval of the Administrator.

12.5.2.2.3 Sample Analysis. Use ASTM D 129–64, 78, or 95, ASTM D 1552–83 or 95, or ASTM D 4057–81 or 95 to determine the sulfur content (%S) and ASTM D 240–76 or 92 (all standards cited are incorporated by reference—see §60.17) to determine the GCV of each gross sample. These values may be assumed to be on a dry basis. The owner or operator of an affected facility may elect to determine the GCV by sampling the oil combusted on the first steam generating unit operating day of each calendar month and then using the lowest GCV value of the three GCV values per quarter for the GCV of all oil combusted in that calendar quarter.

12.5.2.3 Use appropriate procedures, subject to the approval of the Administrator, to determine the fraction of total mass input derived from each type of fuel.

12.5.3 Control Device Removal Efficiency. Compute the percent removal efficiency ($\%R_g$) of the control device using the following equation:

$$\%R_g = 100\left(1.0 - \frac{E_{ao}}{E_{ai}}\right) \qquad \text{Eq. 19-24}$$

12.5.3.1 Use continuous emission monitoring systems or test methods, as appropriate, to determine the outlet SO_2 rates and, if appropriate, the inlet SO_2 rates. The rates may be determined as hourly (E_h) or other sampling period averages (E_d). Then, compute the average pollutant rates for the performance test period (E_{ao} and E_{ai}) using the procedures in section 12.4.

12.5.3.2 As an alternative, as-fired fuel sampling and analysis may be used to determine inlet SO_2 rates as follows:

12.5.3.2.1 Compute the average inlet SO_2 rate (E_{di}) for each sampling period using the following equation:

$$E_{di} = K\frac{\%S}{GCV} \qquad \text{Eq. 19-25}$$

Where:

$$K = 2\times10^7\left(\frac{\text{ng SO}_2}{\%S}\right)\left(\frac{(\text{kJ})}{\text{J}}\right)\left(\frac{1}{\text{kg coal}}\right)\left[2\times10^4\left(\frac{\text{lb SO}_2}{\%S}\right)\left(\frac{\text{Btu}}{\text{million Btu}}\right)\left(\frac{1}{\text{lb coal}}\right)\right]$$

After calculating E_{di}, use the procedures in section 12.4 to determine the average inlet SO_2 rate for the performance test period (E_{ai}).

12.5.3.2.2 Collect the fuel samples from a location in the fuel handling system that provides a sample representative of the fuel bunkered or consumed during a steam generating unit operating day. For the purpose of as-fired fuel sampling under section 12.5.3.2 or section 12.6, the lot size for coal is the weight of coal bunkered or consumed during each steam generating unit operating day. The lot size for oil is the weight of oil supplied to the ''day'' tank or consumed during each steam generating unit operating day. For reporting and calculation purposes, the gross sample shall be identified with the calendar day on which sampling began. For steam generating unit operating days when a coal-fired steam generating unit is operated without coal being added to the bunkers, the coal analysis from the previous ''as bunkered'' coal sample shall be used until coal is bunkered again. For steam generating unit operating days when an oil-fired steam generating unit is operated without oil being added to the oil ''day'' tank, the oil analysis from the previous day shall be used until the ''day'' tank is filled again. Alternative definitions of fuel lot size may be used, subject to prior approval of the Administrator.

12.5.3.2.3 Use ASTM procedures specified in section 12.5.2.1 or 12.5.2.2 to determine %S and GCV.

12.5.4 Daily Geometric Average Percent Reduction from Hourly Values. The geometric average percent reduction ($\%R_{ga}$) is computed using the following equation:

$$\%R_{ga} = 100\left[1 - \text{EXP}\left(\frac{1}{n_t}\sum_{j=1}^{n_t} 1n\frac{E_{jo}}{E_{ji}}\right)\right] \qquad \text{Eq. 19-26}$$

NOTE: The calculation includes only paired data sets (hourly average) for the inlet and outlet pollutant measurements.

12.6 Sulfur Retention Credit for Compliance Fuel. If fuel sampling and analysis procedures in section 12.5.2.1 are being used to determine average SO_2 emission rates (E_{as}) to the atmosphere from a coal-fired steam generating unit when there is no SO_2 control device, the following equation may be used to adjust the emission rate for sulfur retention credits (no credits are allowed for oil-fired systems) (E_{di}) for each sampling period using the following equation:

$$E_{di} = 0.97K\ \frac{\%S}{GDV} \qquad \text{Eq. 19-27}$$

Where:

$$K = 2\times10^{7}\left(\frac{\text{ng } SO_2}{\%S}\right)\left(\frac{kJ}{J}\right)\left(\frac{1}{\text{kg coal}}\right)\left[2\times10^{4}\left(\frac{\text{lb } SO_2}{\%S}\right)\left(\frac{\text{Btu}}{\text{million Btu}}\right)\left(\frac{1}{\text{lb coal}}\right)\right]$$

After calculating E_{di}, use the procedures in section 12.4.2 to determine the average SO_2 emission rate to the atmosphere for the performance test period (E_{ao}).

12.7 Determination of Compliance When Minimum Data Requirement Is Not Met.

12.7.1 Adjusted Emission Rates and Control Device Removal Efficiency. When the minimum data requirement is not met, the Administrator may use the following adjusted emission rates or control device removal efficiencies to determine compliance with the applicable standards.

12.7.1.1 Emission Rate. Compliance with the emission rate standard may be determined by using the lower confidence limit of the emission rate (E_{ao}*) as follows:

$$E^{*}_{ao} = E_{ao} - t_{0.95}S_o \qquad \text{Eq. 19-28}$$

12.7.1.2 Control Device Removal Efficiency. Compliance with the overall emission reduction ($\%R_o$) may be determined by using the lower confidence limit of the emission rate (E_{ao}*) and the upper confidence limit of the inlet pollutant rate (E_{ai}*) in calculating the control device removal efficiency ($\%R_g$) as follows:

$$\%R_g = 100\left(1.0 - \frac{E^{*}_{ao}}{E^{*}_{ai}}\right) \qquad \text{Eq. 19-29}$$

$$E^{*}_{ai} = E_{ai} + t_{0.95}S_i \qquad \text{Eq. 19-30}$$

12.7.2 Standard Deviation of Hourly Average Pollutant Rates. Compute the standard deviation (S_e) of the hourly average pollutant rates using the following equation:

$$S_e = \sqrt{\frac{1}{H} - \frac{1}{H_r}}\ \sqrt{\frac{\sum_{j=1}^{H}\left(E_{hj} - E_a\right)^2}{H-1}} \qquad \text{Eq. 19-31}$$

Equation 19–19 through 19–31 may be used to compute the standard deviation for both the outlet (S_o) and, if applicable, inlet (S_i) pollutant rates.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References [Reserved]

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 19–1—CONVERSION FACTORS FOR CONCENTRATION

From	To	Multiply by
g/scm	ng/scm	10^9
mg/scm	ng/scm	10^6
lb/scf	ng/scm	1.602×10^{13}

TABLE 19–1—CONVERSION FACTORS FOR CONCENTRATION—Continued

From	To	Multiply by
ppm SO_2	ng/scm	2.66×10^6
ppm NO_X	ng/scm	1.912×10^6
ppm SO_2	lb/scf	1.660×10^{-7}
ppm NO_X	lb/scf	1.194×10^{-7}

TABLE 19–2—F FACTORS FOR VARIOUS FUELS[1]

Fuel Type	F_d		F_w		F_c	
	dscm/J	dscf/10^6 Btu	wscm/J	wscf/10^6 Btu	scm/J	scf/10^6 Btu
Coal:						
Anthracite[2]	2.71×10^{-7}	10,100	2.83×10^{-7}	10,540	0.530×10^{-7}	1,970
Bituminus[2]	2.63×10^{-7}	9,780	2.86×10^{-7}	10,640	0.484×10^{-7}	1,800
Lignite	2.65×10^{-7}	9,860	3.21×10^{-7}	11,950	0.513×10^{-7}	1,910
Oil[3]	2.47×10^{-7}	9,190	2.77×10^{-7}	10,320	0.383×10^{-7}	1,420
Gas:.						
Natural	2.34×10^{-7}	8,710	2.85×10^{-7}	10,610	0.287×10^{-7}	1,040
Propane	2.34×10^{-7}	8,710	2.74×10^{-7}	10,200	0.321×10^{-7}	1,190
Butane	2.34×10^{-7}	8,710	2.79×10^{-7}	10,390	0.337×10^{-7}	1,250
Wood	2.48×10^{-7}	9,240			0.492×10^{-7}	1,830
Wood Bark	2.58×10^{-7}	9,600			0.516×10^{-7}	1,920
Municipal	2.57×10^{-7}	9,570			0.488×10^{-7}	1,820
Solid Waste						

[1] Determined at standard conditions: 20 °C (68 °F) and 760 mm Hg (29.92 in Hg)
[2] As classified according to ASTM D 388.
[3] Crude, residual, or distillate.

TABLE 19–3—VALUES FOR $T_{0.95*}$

n[1]	$t_{0.95}$	n[1]	$t_{0.95}$	n[1]	$t_{0.95}$
2	6.31	8	1.89	22–26	1.71
3	2.42	9	1.86	27–31	1.70
4	2.35	10	1.83	32–51	1.68
5	2.13	11	1.81	52–91	1.67
6	2.02	12–16	1.77	92–151	1.66
7	1.94	17–21	1.73	152 or more	1.65

[1] The values of this table are corrected for n-1 degrees of freedom. Use n equal to the number (H) of hourly average data points.

METHOD 20—DETERMINATION OF NITROGEN OXIDES, SULFUR DIOXIDE, AND DILUENT EMISSIONS FROM STATIONARY GAS TURBINES

1.0 Scope and Application

What is Method 20?

Method 20 contains the details you must follow when using an instrumental analyzer to determine concentrations of nitrogen oxides, oxygen, carbon dioxide, and sulfur dioxide in the emissions from stationary gas turbines. This method follows the specific instructions for equipment and performance requirements, supplies, sample collection and analysis, calculations, and data analysis in the methods listed in section 2.0.

1.1 Analytes. What does this method determine?

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X) as nitrogen dioxide:	10102–43–9	Typically <2% of Calibration Span.
Nitric oxide (NO)	10102–44–0	
Nitrogen dioxide NO_2.		
Diluent oxygen (O_2) or carbon dioxide (CO_2)		Typically <2% of Calibration Span.
Sulfur dioxide (SO_X)	7446–09–5	Typically <2% of Calibration Span.

1.2 Applicability. When is this method required? The use of Method 20 may be required by specific New Source Performance Standards, Clean Air Marketing rules, and State Implementation Plans and permits where

measuring SO_2, NO_X, CO_2, and/or O_2 concentrations in stationary gas turbines emissions are required. Other regulations may also require its use.

1.3 Data Quality Objectives. How good must my collected data be? Refer to section 1.3 of Method 7E.

2.0 Summary of Method

In this method, NO_X, O_2 (or CO_2), and SO_X are measured using the following methods found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 3A—Determination of Oxygen and Carbon Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(c) Method 6C—Determination of Sulfur Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(d) Method 7E—Determination of Nitrogen Oxides Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(e) Method 19—Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates.

3.0 Definitions

Refer to section 3.0 of Method 7E for the applicable definitions.

4.0 Interferences

Refer to section 4.0 of Methods 3A, 6C, and 7E as applicable.

5.0 Safety

Refer to section 5.0 of Method 7E.

6.0 Equipment and Supplies

The measurement system design is shown in Figure 7E–1 of Method 7E. Refer to the appropriate methods listed in section 2.0 for equipment and supplies.

7.0 Reagents and Standards

Refer to the appropriate methods listed in section 2.0 for reagents and standards.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling Site and Sampling Points. Follow the procedures of section 8.1 of Method 7E. For the stratification test in section 8.1.2, determine the diluent-corrected pollutant concentration at each traverse point.

8.2 Initial Measurement System Performance Tests. You must refer to the appropriate methods listed in section 2.0 for the measurement system performance tests as applicable.

8.3 Interference Check. You must follow the procedures in section 8.3 of Method 3A or 6C, or section 8.2.7 of Method 7E (as appropriate).

8.4 Sample Collection. You must follow the procedures of section 8.4 of the appropriate methods listed in section 2.0. A test run must have a duration of at least 21 minutes.

8.5 Post-Run System Bias Check, Drift Assessment, and Alternative Dynamic Spike Procedure. You must follow the procedures of sections 8.5 and 8.6 of the appropriate methods listed in section 2.0. A test run must have a duration of at least 21 minutes.

9.0 Quality Control

Follow quality control procedures in section 9.0 of Method 7E.

10.0 Calibration and Standardization

Follow the procedures for calibration and standardization in section 10.0 of Method 7E.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the procedures for calculations and data analysis in section 12.0 of the appropriate method listed in section 2.0. Follow the procedures in section 12.0 of Method 19 for calculating fuel-specific F factors, diluent-corrected pollutant concentrations, and emission rates.

13.0 Method Performance

The specifications for the applicable performance checks are the same as in section 13.0 of Method 7E.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

Refer to section 16.0 of the appropriate method listed in section 2.0 for alternative procedures.

17.0 References

Refer to section 17.0 of the appropriate method listed in section 2.0 for references.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

Refer to section 18.0 of the appropriate method listed in section 2.0 for tables, diagrams, flowcharts, and validation data.

METHOD 21—DETERMINATION OF VOLATILE ORGANIC COMPOUND LEAKS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile Organic Compounds (VOC).	No CAS number assigned.

1.2 Scope. This method is applicable for the determination of VOC leaks from process equipment. These sources include, but are not limited to, valves, flanges and other connections, pumps and compressors, pressure relief devices, process drains, open-ended valves, pump and compressor seal system degassing vents, accumulator vessel vents, agitator seals, and access door seals.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A portable instrument is used to detect VOC leaks from individual sources. The instrument detector type is not specified, but it must meet the specifications and performance criteria contained in section 6.0. A leak definition concentration based on a reference compound is specified in each applicable regulation. This method is intended to locate and classify leaks only, and is not to be used as a direct measure of mass emission rate from individual sources.

3.0 Definitions

3.1 *Calibration gas* means the VOC compound used to adjust the instrument meter reading to a known value. The calibration gas is usually the reference compound at a known concentration approximately equal to the leak definition concentration.

3.2 *Calibration precision* means the degree of agreement between measurements of the same known value, expressed as the relative percentage of the average difference between the meter readings and the known concentration to the known concentration.

3.3 *Leak definition concentration* means the local VOC concentration at the surface of a leak source that indicates that a VOC emission (leak) is present. The leak definition is an instrument meter reading based on a reference compound.

3.4 *No detectable emission* means a local VOC concentration at the surface of a leak source, adjusted for local VOC ambient concentration, that is less than 2.5 percent of the specified leak definition concentration. that indicates that a VOC emission (leak) is not present.

3.5 *Reference compound* means the VOC species selected as the instrument calibration basis for specification of the leak definition concentration. (For example, if a leak definition concentration is 10,000 ppm as methane, then any source emission that results in a local concentration that yields a meter reading of 10,000 on an instrument meter calibrated with methane would be classified as a leak. In this example, the leak definition concentration is 10,000 ppm and the reference compound is methane.)

3.6 *Response factor* means the ratio of the known concentration of a VOC compound to the observed meter reading when measured using an instrument calibrated with the reference compound specified in the applicable regulation.

3.7 *Response time* means the time interval from a step change in VOC concentration at the input of the sampling system to the time at which 90 percent of the corresponding final value is reached as displayed on the instrument readout meter.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Pollutants. Several of the compounds, leaks of which may be determined by this method, may be irritating or corrosive to tissues (*e.g.*, heptane) or may be toxic (*e.g.*, benzene, methyl alcohol). Nearly all are fire hazards. Compounds in emissions should be determined through familiarity with the source. Appropriate precautions can be found in reference documents, such as reference No. 4 in section 16.0.

6.0 Equipment and Supplies

A VOC monitoring instrument meeting the following specifications is required:

6.1 The VOC instrument detector shall respond to the compounds being processed. Detector types that may meet this requirement include, but are not limited to, catalytic oxidation, flame ionization, infrared absorption, and photoionization.

6.2 The instrument shall be capable of measuring the leak definition concentration specified in the regulation.

6.3 The scale of the instrument meter shall be readable to ±2.5 percent of the specified leak definition concentration.

6.4 The instrument shall be equipped with an electrically driven pump to ensure that a sample is provided to the detector at a constant flow rate. The nominal sample flow rate, as measured at the sample probe tip, shall be 0.10 to 3.0 l/min (0.004 to 0.1 ft^3/min) when the probe is fitted with a glass wool plug or filter that may be used to prevent plugging of the instrument.

6.5 The instrument shall be equipped with a probe or probe extension or sampling not to exceed 6.4 mm (¼ in) in outside diameter,

with a single end opening for admission of sample.

6.6 The instrument shall be intrinsically safe for operation in explosive atmospheres as defined by the National Electrical Code by the National Fire Prevention Association or other applicable regulatory code for operation in any explosive atmospheres that may be encountered in its use. The instrument shall, at a minimum, be intrinsically safe for Class 1, Division 1 conditions, and/or Class 2, Division 1 conditions, as appropriate, as defined by the example code. The instrument shall not be operated with any safety device, such as an exhaust flame arrestor, removed.

7.0 Reagents and Standards

7.1 Two gas mixtures are required for instrument calibration and performance evaluation:

7.1.1 Zero Gas. Air, less than 10 parts per million by volume (ppmv) VOC.

7.1.2 Calibration Gas. For each organic species that is to be measured during individual source surveys, obtain or prepare a known standard in air at a concentration approximately equal to the applicable leak definition specified in the regulation.

7.2 Cylinder Gases. If cylinder calibration gas mixtures are used, they must be analyzed and certified by the manufacturer to be within 2 percent accuracy, and a shelf life must be specified. Cylinder standards must be either reanalyzed or replaced at the end of the specified shelf life.

7.3 Prepared Gases. Calibration gases may be prepared by the user according to any accepted gaseous preparation procedure that will yield a mixture accurate to within 2 percent. Prepared standards must be replaced each day of use unless it is demonstrated that degradation does not occur during storage.

7.4 Mixtures with non-Reference Compound Gases. Calibrations may be performed using a compound other than the reference compound. In this case, a conversion factor must be determined for the alternative compound such that the resulting meter readings during source surveys can be converted to reference compound results.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Instrument Performance Evaluation. Assemble and start up the instrument according to the manufacturer's instructions for recommended warmup period and preliminary adjustments.

8.1.1 Response Factor. A response factor must be determined for each compound that is to be measured, either by testing or from reference sources. The response factor tests are required before placing the analyzer into service, but do not have to be repeated at subsequent intervals.

8.1.1.1 Calibrate the instrument with the reference compound as specified in the applicable regulation. Introduce the calibration gas mixture to the analyzer and record the observed meter reading. Introduce zero gas until a stable reading is obtained. Make a total of three measurements by alternating between the calibration gas and zero gas. Calculate the response factor for each repetition and the average response factor.

8.1.1.2 The instrument response factors for each of the individual VOC to be measured shall be less than 10 unless otherwise specified in the applicable regulation. When no instrument is available that meets this specification when calibrated with the reference VOC specified in the applicable regulation, the available instrument may be calibrated with one of the VOC to be measured, or any other VOC, so long as the instrument then has a response factor of less than 10 for each of the individual VOC to be measured.

8.1.1.3 Alternatively, if response factors have been published for the compounds of interest for the instrument or detector type, the response factor determination is not required, and existing results may be referenced. Examples of published response factors for flame ionization and catalytic oxidation detectors are included in References 1–3 of section 17.0.

8.1.2 Calibration Precision. The calibration precision test must be completed prior to placing the analyzer into service and at subsequent 3-month intervals or at the next use, whichever is later.

8.1.2.1 Make a total of three measurements by alternately using zero gas and the specified calibration gas. Record the meter readings. Calculate the average algebraic difference between the meter readings and the known value. Divide this average difference by the known calibration value and multiply by 100 to express the resulting calibration precision as a percentage.

8.1.2.2 The calibration precision shall be equal to or less than 10 percent of the calibration gas value.

8.1.3 Response Time. The response time test is required before placing the instrument into service. If a modification to the sample pumping system or flow configuration is made that would change the response time, a new test is required before further use.

8.1.3.1 Introduce zero gas into the instrument sample probe. When the meter reading has stabilized, switch quickly to the specified calibration gas. After switching, measure the time required to attain 90 percent of the final stable reading. Perform this test sequence three times and record the results. Calculate the average response time.

8.1.3.2 The instrument response time shall be equal to or less than 30 seconds. The instrument pump, dilution probe (if any), sample probe, and probe filter that will be used

during testing shall all be in place during the response time determination.

8.2 Instrument Calibration. Calibrate the VOC monitoring instrument according to section 10.0.

8.3 Individual Source Surveys.

8.3.1 Type I—Leak Definition Based on Concentration. Place the probe inlet at the surface of the component interface where leakage could occur. Move the probe along the interface periphery while observing the instrument readout. If an increased meter reading is observed, slowly sample the interface where leakage is indicated until the maximum meter reading is obtained. Leave the probe inlet at this maximum reading location for approximately two times the instrument response time. If the maximum observed meter reading is greater than the leak definition in the applicable regulation, record and report the results as specified in the regulation reporting requirements. Examples of the application of this general technique to specific equipment types are:

8.3.1.1 Valves. The most common source of leaks from valves is the seal between the stem and housing. Place the probe at the interface where the stem exits the packing gland and sample the stem circumference. Also, place the probe at the interface of the packing gland take-up flange seat and sample the periphery. In addition, survey valve housings of multipart assembly at the surface of all interfaces where a leak could occur.

8.3.1.2 Flanges and Other Connections. For welded flanges, place the probe at the outer edge of the flange-gasket interface and sample the circumference of the flange. Sample other types of nonpermanent joints (such as threaded connections) with a similar traverse.

8.3.1.3 Pumps and Compressors. Conduct a circumferential traverse at the outer surface of the pump or compressor shaft and seal interface. If the source is a rotating shaft, position the probe inlet within 1 cm of the shaft-seal interface for the survey. If the housing configuration prevents a complete traverse of the shaft periphery, sample all accessible portions. Sample all other joints on the pump or compressor housing where leakage could occur.

8.3.1.4 Pressure Relief Devices. The configuration of most pressure relief devices prevents sampling at the sealing seat interface. For those devices equipped with an enclosed extension, or horn, place the probe inlet at approximately the center of the exhaust area to the atmosphere.

8.3.1.5 Process Drains. For open drains, place the probe inlet at approximately the center of the area open to the atmosphere. For covered drains, place the probe at the surface of the cover interface and conduct a peripheral traverse.

8.3.1.6 Open-ended Lines or Valves. Place the probe inlet at approximately the center of the opening to the atmosphere.

8.3.1.7 Seal System Degassing Vents and Accumulator Vents. Place the probe inlet at approximately the center of the opening to the atmosphere.

8.3.1.8 Access door seals. Place the probe inlet at the surface of the door seal interface and conduct a peripheral traverse.

8.3.2 Type II—''No Detectable Emission''. Determine the local ambient VOC concentration around the source by moving the probe randomly upwind and downwind at a distance of one to two meters from the source. If an interference exists with this determination due to a nearby emission or leak, the local ambient concentration may be determined at distances closer to the source, but in no case shall the distance be less than 25 centimeters. Then move the probe inlet to the surface of the source and determine the concentration as outlined in section 8.3.1. The difference between these concentrations determines whether there are no detectable emissions. Record and report the results as specified by the regulation. For those cases where the regulation requires a specific device installation, or that specified vents be ducted or piped to a control device, the existence of these conditions shall be visually confirmed. When the regulation also requires that no detectable emissions exist, visual observations and sampling surveys are required. Examples of this technique are:

8.3.2.1 Pump or Compressor Seals. If applicable, determine the type of shaft seal. Perform a survey of the local area ambient VOC concentration and determine if detectable emissions exist as described in section 8.3.2.

8.3.2.2 Seal System Degassing Vents, Accumulator Vessel Vents, Pressure Relief Devices. If applicable, observe whether or not the applicable ducting or piping exists. Also, determine if any sources exist in the ducting or piping where emissions could occur upstream of the control device. If the required ducting or piping exists and there are no sources where the emissions could be vented to the atmosphere upstream of the control device, then it is presumed that no detectable emissions are present. If there are sources in the ducting or piping where emissions could be vented or sources where leaks could occur, the sampling surveys described in section 8.3.2 shall be used to determine if detectable emissions exist.

8.3.3 Alternative Screening Procedure.

8.3.3.1 A screening procedure based on the formation of bubbles in a soap solution that is sprayed on a potential leak source may be used for those sources that do not have continuously moving parts, that do not have surface temperatures greater than the boiling point or less than the freezing point of the soap solution, that do not have open

areas to the atmosphere that the soap solution cannot bridge, or that do not exhibit evidence of liquid leakage. Sources that have these conditions present must be surveyed using the instrument technique of section 8.3.1 or 8.3.2.

8.3.3.2 Spray a soap solution over all potential leak sources. The soap solution may be a commercially available leak detection solution or may be prepared using concentrated detergent and water. A pressure sprayer or squeeze bottle may be used to dispense the solution. Observe the potential leak sites to determine if any bubbles are formed. If no bubbles are observed, the source is presumed to have no detectable emissions or leaks as applicable. If any bubbles are observed, the instrument techniques of section 8.3.1 or 8.3.2 shall be used to determine if a leak exists, or if the source has detectable emissions, as applicable.

9.0 Quality Control

Section	Quality control measure	Effect
8.1.2	Instrument calibration precision check	Ensure precision and accuracy, respectively, of instrument response to standard.
10.0	Instrument calibration.	

10.0 Calibration and Standardization

10.1 Calibrate the VOC monitoring instrument as follows. After the appropriate warmup period and zero internal calibration procedure, introduce the calibration gas into the instrument sample probe. Adjust the instrument meter readout to correspond to the calibration gas value.

NOTE: If the meter readout cannot be adjusted to the proper value, a malfunction of the analyzer is indicated and corrective actions are necessary before use.

11.0 Analytical Procedures [Reserved]

12.0 Data Analyses and Calculations [Reserved]

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Dubose, D.A., and G.E. Harris. Response Factors of VOC Analyzers at a Meter Reading of 10,000 ppmv for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81051. September 1981.

2. Brown, G.E., *et al.* Response Factors of VOC Analyzers Calibrated with Methane for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81–022. May 1981.

3. DuBose, D.A. *et al.* Response of Portable VOC Analyzers to Chemical Mixtures. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81–110. September 1981.

4. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 22—VISUAL DETERMINATION OF FUGITIVE EMISSIONS FROM MATERIAL SOURCES AND SMOKE EMISSIONS FROM FLARES

NOTE: This method is not inclusive with respect to observer certification. Some material is incorporated by reference from Method 9.

1.0 Scope and Application

This method is applicable for the determination of the frequency of fugitive emissions from stationary sources, only as specified in an applicable subpart of the regulations. This method also is applicable for the determination of the frequency of visible smoke emissions from flares.

2.0 Summary of Method

2.1 Fugitive emissions produced during material processing, handling, and transfer operations or smoke emissions from flares are visually determined by an observer without the aid of instruments.

2.2 This method is used also to determine visible smoke emissions from flares used for combustion of waste process materials.

2.3 This method determines the amount of time that visible emissions occur during the observation period (*i.e.*, the accumulated emission time). This method does not require that the opacity of emissions be determined. Since this procedure requires only the determination of whether visible emissions occur and does not require the determination of opacity levels, observer certification according to the procedures of Method 9 is not required. However, it is necessary that the observer is knowledgeable with respect to the general procedures for determining the presence of visible emissions. At a minimum, the observer must be trained and knowledgeable regarding the effects of background contrast, ambient lighting, observer position relative

to lighting, wind, and the presence of uncombined water (condensing water vapor) on the visibility of emissions. This training is to be obtained from written materials found in References 1 and 2 or from the lecture portion of the Method 9 certification course.

3.0 Definitions

3.1 *Emission frequency* means the percentage of time that emissions are visible during the observation period.

3.2 *Emission time* means the accumulated amount of time that emissions are visible during the observation period.

3.3 *Fugitive emissions* means emissions generated by an affected facility which is not collected by a capture system and is released to the atmosphere. This includes emissions that (1) escape capture by process equipment exhaust hoods; (2) are emitted during material transfer; (3) are emitted from buildings housing material processing or handling equipment; or (4) are emitted directly from process equipment.

3.4 *Observation period* means the accumulated time period during which observations are conducted, not to be less than the period specified in the applicable regulation.

3.5 *Smoke emissions* means a pollutant generated by combustion in a flare and occurring immediately downstream of the flame. Smoke occurring within the flame, but not downstream of the flame, is not considered a smoke emission.

4.0 Interferences

4.1 Occasionally, fugitive emissions from sources other than the affected facility (*e.g.*, road dust) may prevent a clear view of the affected facility. This may particularly be a problem during periods of high wind. If the view of the potential emission points is obscured to such a degree that the observer questions the validity of continuing observations, then the observations shall be terminated, and the observer shall clearly note this fact on the data form.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment

6.1 Stopwatches (two). Accumulative type with unit divisions of at least 0.5 seconds.

6.2 Light Meter. Light meter capable of measuring illuminance in the 50 to 200 lux range, required for indoor observations only.

7.0 Reagents and Supplies [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transfer [Reserved]

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

11.1 Selection of Observation Location. Survey the affected facility, or the building or structure housing the process to be observed, and determine the locations of potential emissions. If the affected facility is located inside a building, determine an observation location that is consistent with the requirements of the applicable regulation (*i.e.*, outside observation of emissions escaping the building/structure or inside observation of emissions directly emitted from the affected facility process unit). Then select a position that enables a clear view of the potential emission point(s) of the affected facility or of the building or structure housing the affected facility, as appropriate for the applicable subpart. A position at least 4.6 m (15 feet), but not more than 400 m (0.25 miles), from the emission source is recommended. For outdoor locations, select a position where the sunlight is not shining directly in the observer's eyes.

11.2 Field Records.

11.2.1 Outdoor Location. Record the following information on the field data sheet (Figure 22–1): Company name, industry, process unit, observer's name, observer's affiliation, and date. Record also the estimated wind speed, wind direction, and sky condition. Sketch the process unit being observed, and note the observer location relative to the source and the sun. Indicate the potential and actual emission points on the sketch.

11.2.2 Indoor Location. Record the following information on the field data sheet (Figure 22–2): Company name, industry, process unit, observer's name, observer's affiliation, and date. Record as appropriate the type, location, and intensity of lighting on the data sheet. Sketch the process unit being observed, and note the observer location relative to the source. Indicate the potential and actual fugitive emission points on the sketch.

11.3 Indoor Lighting Requirements. For indoor locations, use a light meter to measure the level of illumination at a location as close to the emission source(s) as is feasible. An illumination of greater than 100 lux (10 foot candles) is considered necessary for proper application of this method.

11.4 Observations.

11.4.1 Procedure. Record the clock time when observations begin. Use one stopwatch to monitor the duration of the observation

period. Start this stopwatch when the observation period begins. If the observation period is divided into two or more segments by process shutdowns or observer rest breaks (see section 11.4.3), stop the stopwatch when a break begins and restart the stopwatch without resetting it when the break ends. Stop the stopwatch at the end of the observation period. The accumulated time indicated by this stopwatch is the duration of observation period. When the observation period is completed, record the clock time. During the observation period, continuously watch the emission source. Upon observing an emission (condensed water vapor is not considered an emission), start the second accumulative stopwatch; stop the watch when the emission stops. Continue this procedure for the entire observation period. The accumulated elapsed time on this stopwatch is the total time emissions were visible during the observation period (*i.e.*, the emission time.)

11.4.2 Observation Period. Choose an observation period of sufficient length to meet the requirements for determining compliance with the emission standard in the applicable subpart of the regulations. When the length of the observation period is specifically stated in the applicable subpart, it may not be necessary to observe the source for this entire period if the emission time required to indicate noncompliance (based on the specified observation period) is observed in a shorter time period. In other words, if the regulation prohibits emissions for more than 6 minutes in any hour, then observations may (optional) be stopped after an emission time of 6 minutes is exceeded. Similarly, when the regulation is expressed as an emission frequency and the regulation prohibits emissions for greater than 10 percent of the time in any hour, then observations may (optional) be terminated after 6 minutes of emission are observed since 6 minutes is 10 percent of an hour. In any case, the observation period shall not be less than 6 minutes in duration. In some cases, the process operation may be intermittent or cyclic. In such cases, it may be convenient for the observation period to coincide with the length of the process cycle.

11.4.3 Observer Rest Breaks. Do not observe emissions continuously for a period of more than 15 to 20 minutes without taking a rest break. For sources requiring observation periods of greater than 20 minutes, the observer shall take a break of not less than 5 minutes and not more than 10 minutes after every 15 to 20 minutes of observation. If continuous observations are desired for extended time periods, two observers can alternate between making observations and taking breaks.

11.5 Recording Observations. Record the accumulated time of the observation period on the data sheet as the observation period duration. Record the accumulated time emissions were observed on the data sheet as the emission time. Record the clock time the observation period began and ended, as well as the clock time any observer breaks began and ended.

12.0 Data Analysis and Calculations

If the applicable subpart requires that the emission rate be expressed as an emission frequency (in percent), determine this value as follows: Divide the accumulated emission time (in seconds) by the duration of the observation period (in seconds) or by any minimum observation period required in the applicable subpart, if the actual observation period is less than the required period, and multiply this quotient by 100.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Missan, R., and A. Stein. Guidelines for Evaluation of Visible Emissions Certification, Field Procedures, Legal Aspects, and Background Material. EPA Publication No. EPA–340/1–75–007. April 1975.

2. Wohlschlegel, P., and D.E. Wagoner. Guideline for Development of a Quality Assurance Program: Volume IX—Visual Determination of Opacity Emissions from Stationary Sources. EPA Publication No. EPA–650/4–74–005i. November 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

FUGITIVE OR SMOKE EMISSION INSPECTION
OUTDOOR LOCATION

Company Location Company Rep.	Observer Affiliation Date
Sky Conditions Precipitation	Wind Direction Wind Speed
Industry	Process Unit

Sketch process unit: indicate observer position relative to source; indicate potential emission points and/or actual emission points.

OBSERVATIONS	Clock Time	Observation period duration, min:sec	Accumulated emission time, min:sec
Begin Observation			
End Observation			

Figure 22-1

FUGITIVE OR SMOKE EMISSION INSPECTION
INDOOR LOCATION

Company Location Company Rep.	Observer Affiliation Date
Industry	Process Unit

Light type (fluorescent, incandescent, natural)
Light location (overhead, behind observer, etc.)
Illuminance (lux or footcandles)
Sketch process unit: indicate observer position relative to source; indicate potential emission points and/or actual emission points.

OBSERVATIONS	Clock Time	Observation period duration, min:sec	Accumulated emission time, min:sec
Begin			
End Observation			

Figure 22-2

METHOD 23—DETERMINATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS FROM STATIONARY SOURCES

1. Applicability and Principle

1.1 Applicability. This method is applicable to the determination of polychlorinated dibenzo-p-dioxins (PCDD's) and polychlorinated dibenzofurans (PCDF's) from stationary sources.

1.2 Principle. A sample is withdrawn from the gas stream isokinetically and collected in the sample probe, on a glass fiber filter, and on a packed column of adsorbent material. The sample cannot be separated into a particle vapor fraction. The PCDD's and

PCDF's are extracted from the sample, separated by high resolution gas chromatography, and measured by high resolution mass spectrometry.

2. Apparatus

2.1 Sampling. A schematic of the sampling train used in this method is shown in Figure 23–1. Sealing greases may not be used in assembling the train. The train is identical to that described in section 2.1 of Method 5 of this appendix with the following additions:

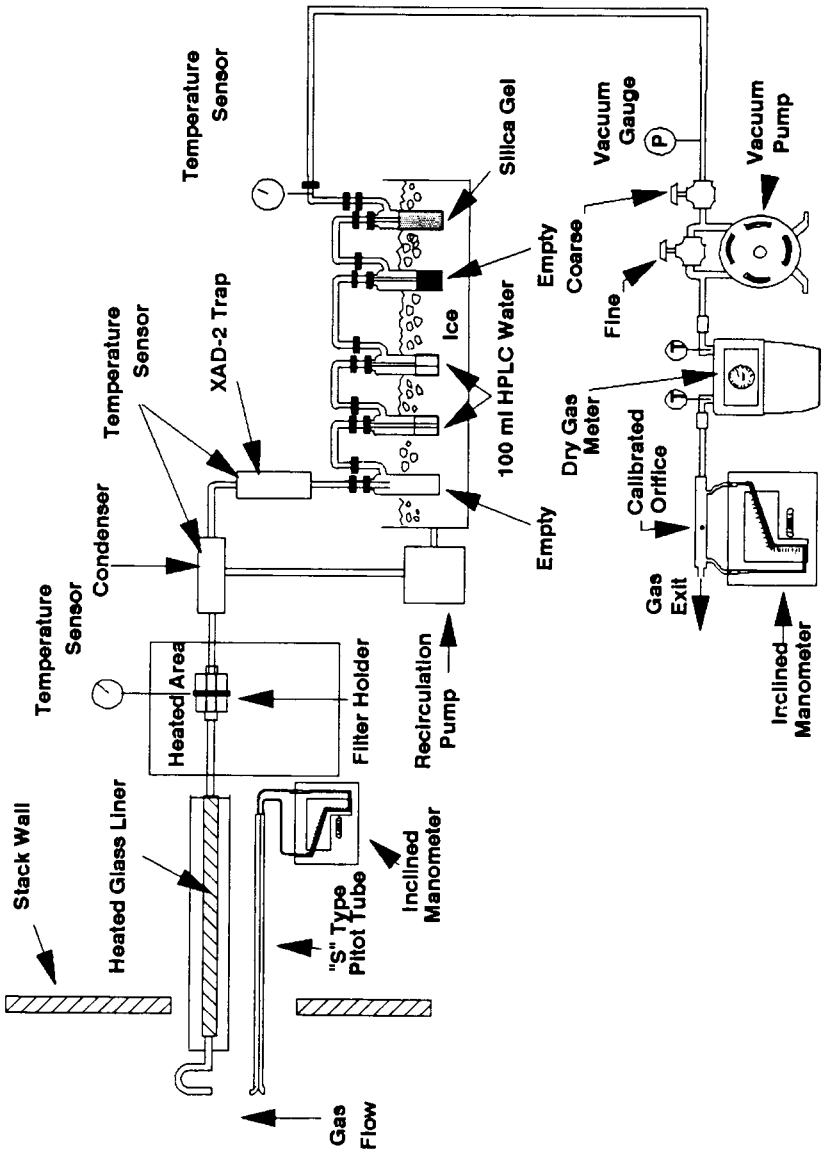


Figure 23.1 Sampling train

2.1.1 Nozzle. The nozzle shall be made of nickel, nickel-plated stainless steel, quartz, or borosilicate glass.

2.1.2 Sample Transfer Lines. The sample transfer lines, if needed, shall be heat traced, heavy walled TFE (½ in. OD with ⅛ in. wall) with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases. The line shall be as short as possible and must be maintained at 120 °C.

2.1.1 Filter Support. Teflon or Teflon-coated wire.

2.1.2 Condenser. Glass, coil type with compatible fittings. A schematic diagram is shown in Figure 23–2.

2.1.3 Water Bath. Thermostatically controlled to maintain the gas temperature exiting the condenser at <20 °C (68 °F).

2.1.4 Adsorbent Module. Glass container to hold the solid adsorbent. A shematic diagram is shown in Figure 23–2. Other physical configurations of the resin trap/condenser assembly are acceptable. The connecting fittings shall form leak-free, vacuum tight seals. No sealant greases shall be used in the sampling train. A coarse glass frit is included to retain the adsorbent.

2.2 Sample Recovery.

2.2.1 Fitting Caps. Ground glass, Teflon tape, or aluminum foil (Section 2.2.6) to cap off the sample exposed sections of the train.

2.2.2 Wash Bottles. Teflon, 500-ml.

2.2.3 Probe-Liner Probe-Nozzle, and Filter-Holder Brushes. Inert bristle brushes with precleaned stainless steel or Teflon handles. The probe brush shall have extensions of stainless steel or Teflon, at least as long as the probe. The brushes shall be properly sized and shaped to brush out the nozzle, probe liner, and transfer line, if used.

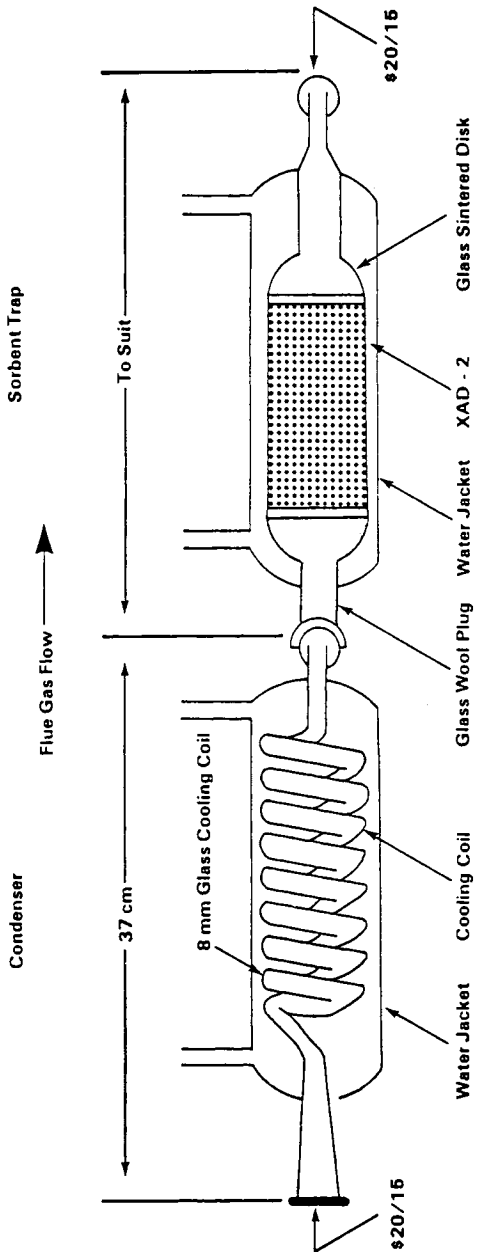


Figure 23.2. Condenser and adsorbent trap

2.2.4 Filter Storage Container. Sealed filter holder, wide-mouth amber glass jar with Teflon-lined cap, or glass petri dish.

2.2.5 Balance. Triple beam.

2.2.6 Aluminum Foil. Heavy duty, hexane-rinsed.

2.2.7 Storage Container. Air-tight container to store silica gel.

2.2.8 Graduated Cylinder. Glass, 250-ml with 2-ml graduation.

2.2.9 Glass Sample Storage Container. Amber glass bottle for sample glassware washes, 500- or 1000-ml, with leak free Teflon-lined caps.

2.3 Analysis.

2.3.1 Sample Container. 125- and 250-ml flint glass bottles with Teflon-lined caps.

2.3.2 Test Tube. Glass.

2.3.3 Soxhlet Extraction Apparatus. Capable of holding 43 × 123 mm extraction thimbles.

2.3.4 Extraction Thimble. Glass, precleaned cellulosic, or glass fiber.

2.3.5 Pasteur Pipettes. For preparing liquid chromatographic columns.

2.3.6 Reacti-vials. Amber glass, 2-ml, silanized prior to use.

2.3.7 Rotary Evaporator. Buchi/Brinkman RF–121 or equivalent.

2.3.8 Nitrogen Evaporative Concentrator. N-Evap Analytical Evaporator Model III or equivalent.

2.3.9 Separatory Funnels. Glass, 2-liter.

2.3.10 Gas Chromatograph. Consisting of the following components:

2.3.10.1 Oven. Capable of maintaining the separation column at the proper operating temperature ±°C and performing programmed increases in temperature at rates of at least 40 °C/min.

2.3.10.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperatures ±1 °C.

2.3.10.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

2.3.10.4 Capillary Columns. A fused silica column, 60 × 0.25 mm inside diameter (ID), coated with DB–5 and a fused silica column, 30 m × 0.25 mm ID coated with DB–225. Other column systems may be used provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of section 6.1.2.2.

2.3.11 Mass Spectrometer. Capable of routine operation at a resolution of 1:10000 with a stability of ±5 ppm.

2.3.12 Data System. Compatible with the mass spectrometer and capable of monitoring at least five groups of 25 ions.

2.3.13 Analytical Balance. To measure within 0.1 mg.

3. Reagents

3.1 Sampling.

3.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D 2986–71 (Reapproved 1978) (incorporated by reference—see §60.17).

3.1.1.1 Precleaning. All filters shall be cleaned before their initial use. Place a glass extraction thimble and 1 g of silica gel and a plug of glass wool into a Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Place no more than 50 filters in the thimble onto the silica gel bed and top with the cleaned glass wool. Charge the Soxhlet with toluene and reflux for 16 hours. After extraction, allow the Soxhlet to cool, remove the filters, and dry them under a clean N_2 stream. Store the filters in a glass petri dish sealed with Teflon tape.

3.1.2 Adsorbent Resin. Amberlite XAD–2 resin. Thoroughly cleaned before initial use.

3.1.2.1 Cleaning Procedure. This procedure may be carried out in a giant Soxhlet extractor. An all-glass filter thimble containing an extra-course frit is used for extraction of XAD–2. The frit is recessed 10–15 mm above a crenelated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass wool plug and a stainless steel ring because it floats on methylene chloride. This process involves sequential extraction in the following order.

Solvent	Procedure
Water	Initial rinse: Place resin in a beaker, rinse once with water, and discard. Fill with water a second time, let stand overnight, and discard.
Water	Extract with water for 8 hours.
Methanol	Extract for 22 hours.
Methylene Chloride	Extract for 22 hours.
Toluene	Extract for 22 hours.

3.1.2.2 Drying.

3.1.2.2.1 Drying Column. Pyrex pipe, 10.2 cm ID by 0.6 m long, with suitable retainers.

3.1.2.2.2 Procedure. The adsorbent must be dried with clean inert gas. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has proven to be a reliable source of large volumes of gas free from organic contaminants. Connect the liquid nitrogen cylinder to the column by a length of cleaned copper tubing, 0.95 cm ID, coiled to pass through a heat source. A convenient heat source is a water-bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40 °C. Continue flowing nitrogen through the adsorbent until all the residual solvent is removed. The flow rate should be sufficient to gently agitate the particles but not so excessive as the cause the particles to fracture.

3.1.2.3 Quality Control Check. The adsorbent must be checked for residual toluene.

3.1.2.3.1 Extraction. Weigh 1.0 g sample of dried resin into a small vial, add 3 ml of toluene, cap the vial, and shake it well.

3.1.2.3.2 Analysis. Inject a 2 µl sample of the extract into a gas chromatograph operated under the following conditions:

Column: 6 ft × ⅛ in stainless steel containing 10 percent OV–101 on 100/120 Supelcoport.
Carrier Gas: Helium at a rate of 30 ml/min.
Detector: Flame ionization detector operated at a sensitivity of 4×10^{-11} A/mV.
Injection Port Temperature: 250 °C.
Detector Temperature: 305 °C.
Oven Temperature: 30 °C for 4 min; programmed to rise at 40 °C/min until it reaches 250 °C; return to 30 °C after 17 minutes.

Compare the results of the analysis to the results from the reference solution. Prepare the reference solution by injection 2.5 µl of methylene chloride into 100 ml of toluene. This corresponds to 100 µg of methylene chloride per g of adsorbent. The maximum acceptable concentration is 1000 µg/g of adsorbent. If the adsorbent exceeds this level, drying must be continued until the excess methylene chloride is removed.

3.1.2.4 Storage. The adsorbent must be used within 4 weeks of cleaning. After cleaning, it may be stored in a wide mouth amber glass container with a Teflon-lined cap or placed in one of the glass adsorbent modules tightly sealed with glass stoppers. If precleaned adsorbent is purchased in sealed containers, it must be used within 4 weeks after the seal is broken.

3.1.3 Glass Wool. Cleaned by sequential immersion in three aliquots of methylene chloride, dried in a 110 °C oven, and stored in a methylene chloride-washed glass jar with a Teflon-lined screw cap.

3.1.4 Water. Deionized distilled and stored in a methylene chloride-rinsed glass container with a Teflon-lined screw cap.

3.1.5 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175 °C (350 °F) for two hours. New silica gel may be used as received. Alternately other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

3.1.6 Chromic Acid Cleaning Solution. Dissolve 20 g of sodium dichromate in 15 ml of water, and then carefully add 400 ml of concentrated sulfuric acid.

3.2 Sample Recovery.

3.2.2 Acetone. Pesticide quality.

3.2.2 Methylene Chloride. Pesticide qualtity.

3.2.3 Toluene. Pesticide quality.

3.3 Analysis.

3.3.1 Potassium Hydroxide. ACS grade, 2-percent (weight/volume) in water.

3.3.2 Sodium Sulfate. Granulated, reagent grade. Purify prior to use by rinsing with methylene chloride and oven drying. Store the cleaned material in a glass container with a Teflon-lined screw cap.

3.3.3 Sulfuric Acid. Reagent grade.

3.3.4 Sodium Hydroxide. 1.0 N. Weigh 40 g of sodium hydroxide into a 1-liter volumetric flask. Dilute to 1 liter with water.

3.3.5 Hexane. Pesticide grade.

3.3.6 Methylene Chloride. Pesticide grade.

3.3.7 Benzene. Pesticide Grade.

3.3.8 Ethyl Acetate.

3.3.9 Methanol. Pesticide Grade.

3.3.10 Toluene. Pesticide Grade.

3.3.11 Nonane. Pesticide Grade.

3.3.12 Cyclohexane. Pesticide Grade.

3.3.13 Basic Alumina. Activity grade 1, 100–200 mesh. Prior to use, activate the alumina by heating for 16 hours at 130 °C before use. Store in a desiccator. Pre-activated alumina may be purchased from a supplier and may be used as received.

3.3.14 Silica Gel. Bio-Sil A, 100–200 mesh. Prior to use, activate the silica gel by heating for at least 30 minutes at 180 °C. After cooling, rinse the silica gel sequentially with methanol and methylene chloride. Heat the rinsed silica gel at 50 °C for 10 minutes, then increase the temperature gradually to 180 °C over 25 minutes and maintain it at this temperature for 90 minutes. Cool at room temperature and store in a glass container with a Teflon-lined screw cap.

3.3.15 Silica Gel Impregnated with Sulfuric Acid. Combine 100 g of silica gel with 44 g of concentrated sulfuric acid in a screw capped glass bottle and agitate thoroughly. Disperse the solids with a stirring rod until a uniform mixture is obtained. Store the mixture in a glass container with a Teflon-lined screw cap.

3.3.16 Silica Gel Impregnated with Sodium Hydroxide. Combine 39 g of 1 N sodium hydroxide with 100 g of silica gel in a screw capped glass bottle and agitate thoroughly. Disperse solids with a stirring rod until a uniform mixture is obtained. Store the mixture in glass container with a Teflon-lined screw cap.

3.3.17 Carbon/Celite. Combine 10.7 g of AX–21 carbon with 124 g of Celite 545 in a 250-ml glass bottle with a Teflon-lined screw cap. Agitate the mixture thoroughly until a uniform mixture is obtained. Store in the glass container.

3.3.18 Nitrogen. Ultra high purity.

3.3.19 Hydrogen. Ultra high purity.

3.3.20 Internal Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Internal Standards'' in 10 ml of nonane.

3.3.21 Surrogate Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Surrogate Standards'' in 10 ml of nonane.

3.3.22 Recovery Standard Solution. Prepare a stock standard solution containing the

isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Recovery Standards'' in 10 ml of nonane.

4. Procedure

4.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, testers should be trained and experienced with the test procedures.

4.1.1 Pretest Preparation.

4.1.1.1 Cleaning Glassware. All glass components of the train upstream of and including the adsorbent module, shall be cleaned as described in section 3A of the ''Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples.'' Special care shall be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. Any residue shall be removed by soaking the glassware for several hours in a chromic acid cleaning solution prior to cleaning as described above.

4.1.1.2 Adsorbent Trap. The traps must be loaded in a clean area to avoid contamination. They may not be loaded in the field. Fill a trap with 20 to 40 g of XAD–2. Follow the XAD–2 with glass wool and tightly cap both ends of the trap. Add 100 μl of the surrogate standard solution (section 3.3.21) to each trap.

4.1.1.3 Sample Train. It is suggested that all components be maintained according to the procedure described in APTD–0576. Alternative mercury-free thermometers may be used if the thermometers are, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

4.1.1.4 Silica Gel. Weigh several 200 to 300 g portions of silica gel in an air tight container to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel may be weighed directly in its impinger or sampling holder just prior to sampling.

4.1.1.5 Filter. Check each filter against light for irregularities and flaws or pinhole leaks. Pack the filters flat in a clean glass container.

4.1.2 Preliminary Determinations. Same as section 4.1.2 of Method 5.

4.1.3 Preparation of Collection Train.

4.1.3.1 During preparation and assembly of the sampling train, keep all train openings where contamination can enter, sealed until just prior to assembly or until sampling is about to begin.

NOTE: Do not use sealant grease in assembling the train.

4.1.3.2 Place approximately 100 ml of water in the second and third impingers, leave the first and fourth impingers empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fifth impinger.

4.1.3.3 Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

4.1.3.4 Assemble the train as shown in Figure 23–1.

4.1.3.5 Turn on the adsorbent module and condenser coil recirculating pump and begin monitoring the adsorbent module gas entry temperature. Ensure proper sorbent temperature gas entry temperature before proceeding and before sampling is initiated. It is extremely important that the XAD–2 adsorbent resin temperature never exceed 50 °C because thermal decomposition will occur. During testing, the XAD–2 temperature must not exceed 20 °C for efficient capture of the PCDD's and PCDF's.

4.1.4 Leak-Check Procedure. Same as Method 5, section 4.1.4.

4.1.5 Sample Train Operation. Same as Method 5, section 4.1.5.

4.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Seal the nozzle end of the sampling probe with Teflon tape or aluminum foil.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe. Remove the probe from the train and close off both ends with aluminum foil. Seal off the inlet to the train with Teflon tape, a ground glass cap, or aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area shall be clean and enclosed so that the chances of losing or contaminating the sample are minimized. Smoking, which could contaminate the sample, shall not be allowed in the cleanup area.

Inspect the train prior to and during disassembly and note any abnormal conditions, e.g., broken filters, colored impinger liquid, etc. Treat the samples as follows:

4.2.1 Container No. 1. Either seal the filter holder or carefully remove the filter from the filter holder and place it in its identified container. Use a pair of cleaned tweezers to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and filter fibers which adhere to the filter holder gasket, by using a dry inert bristle brush and a sharp-edged blade. Seal the container.

4.2.2 Adsorbent Module. Remove the module from the train, tightly cap both ends, label it, cover with aluminum foil, and store it on ice for transport to the laboratory.

4.2.3 Container No. 2. Quantitatively recover material deposited in the nozzle, probe transfer lines, the front half of the filter holder, and the cyclone, if used, first, by

brushing while rinsing three times each with acetone and then, by rinsing the probe three times with methylene chloride. Collect all the rinses in Container No. 2.

Rinse the back half of the filter holder three times with acetone. Rinse the connecting line between the filter and the condenser three times with acetone. Soak the connecting line with three separate portions of methylene chloride for 5 minutes each. If using a separate condenser and adsorbent trap, rinse the condenser in the same manner as the connecting line. Collect all the rinses in Container No. 2 and mark the level of the liquid on the container.

4.2.4 Container No. 3. Repeat the methylene chloride-rinsing described in section 4.2.3 using toluene as the rinse solvent. Collect the rinses in Container No. 3 and mark the level of the liquid on the container.

4.2.5 Impinger Water. Measure the liquid in the first three impingers to within ±1 ml by using a graduated cylinder or by weighing it to within ±0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

Discard the liquid after measuring and recording the volume or weight.

4.2.7 Silica Gel. Note the color of the indicating silica gel to determine if it has been completely spent and make a mention of its condition. Transfer the silica gel from the fifth impinger to its original container and seal. If a moisture determination is made, follow the applicable procedures in sections 8.7.6.3 and 11.2.3 of Method 5 to handle and weigh the silica gel. If moisture is not measured, the silica gel may be disposed.

5. Analysis

All glassware shall be cleaned as described in section 3A of the ''Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples.'' All samples must be extracted within 30 days of collection and analyzed within 45 days of extraction.

5.1 Sample Extraction.

5.1.1 Extraction System. Place an extraction thimble (section 2.3.4), 1 g of silica gel, and a plug of glass wool into the Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Remove the extraction thimble from the extraction system and place it in a glass beaker to catch the solvent rinses.

5.1.2 Container No. 1 (Filter). Transfer the contents directly to the glass thimble of the extraction system and extract them simultaneously with the XAD–2 resin.

5.1.3 Adsorbent Cartridge. Suspend the adsorbent module directly over the extraction thimble in the beaker (See section 5.1.1). The glass frit of the module should be in the up position. Using a Teflon squeeze bottle containing toluene, flush the XAD–2 into the thimble onto the bed of cleaned silica gel. Thoroughly rinse the glass module catching the rinsings in the beaker containing the thimble. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. Add the XAD–2 glass wool plug into the thimble.

5.1.4 Container No. 2 (Acetone and Methylene Chloride). Concentrate the sample to a volume of about 1–5 ml using the rotary evaporator apparatus, at a temperature of less than 37 °C. Rinse the sample container three times with small portions of methylene chloride and add these to the concentrated solution and concentrate further to near dryness. This residue contains particulate matter removed in the rinse of the train probe and nozzle. Add the concentrate to the filter and the XAD–2 resin in the Soxhlet apparatus described in section 5.1.1.

5.1.5 Extraction. Add 100 µl of the internal standard solution (Section 3.3.20) to the extraction thimble containing the contents of the adsorbent cartridge, the contents of Container No. 1, and the concentrate from section 5.1.4. Cover the contents of the extraction thimble with the cleaned glass wool plug to prevent the XAD–2 resin from floating into the solvent reservoir of the extractor. Place the thimble in the extractor, and add the toluene contained in the beaker to the solvent reservoir. Pour additional toluene to fill the reservoir approximately ⅔ full. Add Teflon boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle three times per hour. Extract the sample for 16 hours. After extraction, allow the Soxhlet to cool. Transfer the toluene extract and three 10-ml rinses to the rotary evaporator. Concentrate the extract to approximately 10 ml. At this point the analyst may choose to split the sample in half. If so, split the sample, store one half for future use, and analyze the other according to the procedures in sections 5.2 and 5.3. In either case, use a nitrogen evaporative concentrator to reduce the volume of the sample being analyzed to near dryness. Dissolve the residue in 5 ml of hexane.

5.1.6 Container No. 3 (Toluene Rinse). Add 100 µl of the Internal Standard solution (section 3.3.2) to the contents of the container. Concentrate the sample to a volume of about 1–5 ml using the rotary evaporator apparatus at a temperature of less than 37 °C. Rinse the sample container apparatus at a temperature of less than 37 °C. Rinse the sample container three times with small portions of toluene and add these to the concentrated solution and concentrate further to near dryness. Analyze the extract separately according to the procedures in sections 5.2 and 5.3, but concentrate the solution in a rotary evaporator apparatus rather than a nitrogen evaporative concentrator.

5.2 Sample Cleanup and Fractionation.

5.2.1 Silica Gel Column. Pack one end of a glass column, 20 mm × 230 mm, with glass wool. Add in sequence, 1 g silica gel, 2 g of sodium hydroxide impregnated silica gel, 1 g silica gel, 4 g of acid-modified silica gel, and 1 g of silica gel. Wash the column with 30 ml of hexane and discard it. Add the sample extract, dissolved in 5 ml of hexane to the column with two additional 5-ml rinses. Elute the column with an additional 90 ml of hexane and retain the entire eluate. Concentrate this solution to a volume of about 1 ml using the nitrogen evaporative concentrator (section 2.3.7).

5.2.2 Basic Alumina Column. Shorten a 25-ml disposable Pasteur pipette to about 16 ml. Pack the lower section with glass wool and 12 g of basic alumina. Transfer the concentrated extract from the silica gel column to the top of the basic alumina column and elute the column sequentially with 120 ml of 0.5 percent methylene chloride in hexane followed by 120 ml of 35 percent methylene chloride in hexane. Discard the first 120 ml of eluate. Collect the second 120 ml of eluate and concentrate it to about 0.5 ml using the nitrogen evaporative concentrator.

5.2.3 AX–21 Carbon/Celite 545 Column. Remove the botton 0.5 in. from the tip of a 9-ml disposable Pasteur pipette. Insert a glass fiber filter disk in the top of the pipette 2.5 cm from the constriction. Add sufficient carbon/celite mixture to form a 2 cm column. Top with a glass wool plug. In some cases AX–21 carbon fines may wash through the glass wool plug and enter the sample. This may be prevented by adding a celite plug to the exit end of the column. Rinse the column in sequence with 2 ml of 50 percent benzene in ethyl acetate, 1 ml of 50 percent methylene chloride in cyclohexane, and 2 ml of hexane. Discard these rinses. Transfer the concentrate in 1 ml of hexane from the basic alumina column to the carbon/celite column along with 1 ml of hexane rinse. Elute the column sequentially with 2 ml of 50 percent methylene chloride in hexane and 2 ml of 50 percent benzene in ethyl acetate and discard these eluates. Invert the column and elute in the reverse direction with 13 ml of toluene. Collect this eluate. Concentrate the eluate in a rotary evaporator at 50 °C to about 1 ml. Transfer the concentrate to a Reacti-vial using a toluene rinse and concentrate to a volume of 200 µl using a stream of N_2. Store extracts at room temperature, shielded from light, until the analysis is performed.

5.3 Analysis. Analyze the sample with a gas chromatograph coupled to a mass spectrometer (GC/MS) using the instrumental parameters in sections 5.3.1 and 5.3.2. Immediately prior to analysis, add a 20 µl aliquot of the Recovery Standard solution from Table 1 to each sample. A 2 µl aliquot of the extract is injected into the GC. Sample extracts are first analyzed using the DB–5 capillary column to determine the concentration of each isomer of PCDD's and PCDF's (tetra-through octa-). If tetra-chlorinated dibenzofurans are detected in this analysis, then analyze another aliquot of the sample in a separate run, using the DB–225 column to measure the 2,3,7,8 tetra-chloro dibenzofuran isomer. Other column systems may be used, provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of section 6.1.2.2.

5.3.1 Gas Chromatograph Operating Conditions.

5.3.1.1 Injector. Configured for capillary column, splitless, 250 °C.

5.3.1.2 Carrier Gas. Helium, 1–2 ml/min.

5.3.1.3 Oven. Initially at 150 °C. Raise by at least 40 °C/min to 190 °C and then at 3 °C/min up to 300 °C.

5.3.2 High Resolution Mass Spectrometer.

5.3.2.1 Resolution. 10000 m/e.

5.3.2.2 Ionization Mode. Electron impact.

5.3.2.3 Source Temperature 250 °C.

5.3.2.4 Monitoring Mode. Selected ion monitoring. A list of the various ions to be monitored is summarized in Table 3.

5.3.2.5 Identification Criteria. The following identification criteria shall be used for the characterization of polychlorinated dibenzodioxins and dibenzofurans.

1. The integrated ion-abundance ratio (M/M + 2 or M + 2/M + 4) shall be within 15 percent of the theoretical value. The acceptable ion-abundance ratio ranges for the identification of chlorine-containing compounds are given in Table 4.

2. The retention time for the analytes must be within 3 seconds of the corresponding ^{13}C-labeled internal standard, surrogate or alternate standard.

3. The monitored ions, shown in Table 3 for a given analyte, shall reach their maximum within 2 seconds of each other.

4. The identification of specific isomers that do not have corresponding ^{13}C-labeled standards is done by comparison of the relative retention time (RRT) of the analyte to the nearest internal standard retention time with reference (i.e., within 0.005 RRT units) to the comparable RRT's found in the continuing calibration.

5. The signal to noise ratio for all monitored ions must be greater than 2.5.

6. The confirmation of 2, 3, 7, 8–TCDD and 2, 3, 7, 8–TCDF shall satisfy all of the above identification criteria.

7. For the identification of PCDF's, no signal may be found in the corresponding PCDPE channels.

5.3.2.6 Quantification. The peak areas for the two ions monitored for each analyte are summed to yield the total response for each analyte. Each internal standard is used to quantify the indigenous PCDD's or PCDF's in its homologous series. For example, the $^{13}C_{12}$–2,3,7,8-tetra chlorinated dibenzodioxin is used to calculate the concentrations of all

other tetra chlorinated isomers. Recoveries of the tetra- and penta- internal standards are calculated using the $^{13}C_{12}$–1,2,3,4–TCDD. Recoveries of the hexa- through octa- internal standards are calculated using $^{13}C_{12}$–1,2,3,7,8,9–HxCDD. Recoveries of the surrogate standards are calculated using the corresponding homolog from the internal standard.

6. Calibration

Same as Method 5 with the following additions.

6.1 GC/MS System.

6.1.1 Initial Calibration. Calibrate the GC/MS system using the set of five standards shown in Table 2. The relative standard deviation for the mean response factor from each of the unlabeled analytes (Table 2) and of the internal, surrogate, and alternate standards shall be less than or equal to the values in Table 5. The signal to noise ratio for the GC signal present in every selected ion current profile shall be greater than or equal to 2.5. The ion abundance ratios shall be within the control limits in Table 4.

6.1.2 Daily Performance Check.

6.1.2.1 Calibration Check. Inject on µl of solution Number 3 from Table 2. Calculate the relative response factor (RRF) for each compound and compare each RRF to the corresponding mean RRF obtained during the initial calibration. The analyzer performance is acceptable if the measured RRF's for the labeled and unlabeled compounds for the daily run are within the limits of the mean values shown in Table 5. In addition, the ion-abundance ratios shall be within the allowable control limits shown in Table 4.

6.1.2.2 Column Separation Check. Inject a solution of a mixture of PCDD's and PCDF's that documents resolution between 2,3,7,8–TCDD and other TCDD isomers. Resolution is defined as a valley between peaks that is less than 25 percent of the lower of the two peaks. Identify and record the retention time windows for each homologous series.

Perform a similar resolution check on the confirmation column to document the resolution between 2,3,7,8 TCDF and other TCDF isomers.

6.2 Lock Channels. Set mass spectrometer lock channels as specified in Table 3. Monitor the quality control check channels specified in Table 3 to verify instrument stability during the analysis.

7. Quality Control

7.1 Sampling Train Collection Efficiency Check. Add 100 µl of the surrogate standards in Table 1 to the absorbent cartridge of each train before collecting the field samples.

7.2 Internal Standard Percent Recoveries. A group of nine carbon labeled PCDD's and PCDF's representing, the tetra-through octachlorinated homologues, is added to every sample prior to extraction. The role of the internal standards is to quantify the native PCDD's and PCDF's present in the sample as well as to determine the overall method efficiency. Recoveries of the internal standards must be between 40 to 130 percent for the tetra-through hexachlorinated compounds while the range is 25 to 130 percent for the higher hepta- and octachlorinated homologues.

7.3 Surrogate Recoveries. The five surrogate compounds in Table 2 are added to the resin in the adsorbent sampling cartridge before the sample is collected. The surrogate recoveries are measured relative to the internal standards and are a measure of collection efficiency. They are not used to measure native PCDD's and PCDF's. All recoveries shall be between 70 and 130 percent. Poor recoveries for all the surrogates may be an indication of breakthrough in the sampling train. If the recovery of all standards is below 70 percent, the sampling runs must be repeated. As an alternative, the sampling runs do not have to be repeated if the final results are divided by the fraction of surrogate recovery. Poor recoveries of isolated surrogate compounds should not be grounds for rejecting an entire set of the samples.

7.4 Toluene QA Rinse. Report the results of the toluene QA rinse separately from the total sample catch. Do not add it to the total sample.

8.0 [Reserved]

9. Calculations

Same as Method 5, section 6 with the following additions.

9.1 Nomenclature.

A_{ai} = Integrated ion current of the noise at the retention time of the analyte.

A^*_{ci} = Integrated ion current of the two ions characteristic of the internal standard i in the calibration standard.

A_{cij} = Integrated ion current of the two ions characteristic of compound i in the jth calibration standard.

A^*_{cij} = Integrated ion current of the two ions characteristic of the internal standard i in the jth calibration standard.

A_{csi} = Integrated ion current of the two ions characteristic of surrogate compound i in the calibration standard.

A_i = Integrated ion current of the two ions characteristic of compound i in the sample.

A^*_i = Integrated ion current of the two ions characteristic of internal standard i in the sample.

A_{rs} = Integrated ion current of the two ions characteristic of the recovery standard.

A_{si} = Integrated ion current of the two ions characteristic of surrogate compound i in the sample.

C_i = Concentration of PCDD or PCDF i in the sample, pg/M^3.

C_T = Total concentration of PCDD's or PCDF's in the sample, pg/M^3.
m_{ci} = Mass of compound i in the calibration standard injected into the analyzer, pg.
m_{rs} = Mass of recovery standard in the calibration standard injected into the analyzer, pg.
m_{si} = Mass of surrogate compound in the calibration standard, pg.
RRF_i = Relative response factor.
RRF_{rs} = Recovery standard response factor.
RRF_s = Surrogate compound response factor.

9.2 Average Relative Response Factor.

$$RRF_i = \frac{1}{n}\sum_{j=1}^{n}\frac{A_{cij}\, m^*_{ci}}{A^*_{cij}\, m_{ci}} \qquad \text{Eq. 23-1}$$

9.3 Concentration of the PCDD's and PCDF's.

$$C_i = \frac{m_i^* A_i}{A_i^* RRF_i V_{mstd}} \qquad \text{Eq. 23-2}$$

9.4 Recovery Standard Response Factor.

$$RRF_{rs} = \frac{A_{ci}^* m_{rs}}{A_{rs} m_{ci}^*} \qquad \text{Eq. 23-3}$$

9.5 Recovery of Internal Standards (R*).

$$R^* = \frac{A_i^* m_{rs}}{A_{rs} RF_{rs} m_i^*} \times 100\% \qquad \text{Eq. 23-4}$$

9.6 Surrogate Compound Response Factor.

$$RRF_s = \frac{A_{ci}^* m_s}{A_{cis} m_{ci}^*} \qquad \text{Eq. 23-5}$$

9.7 Recovery of Surrogate Compounds (R_s).

$$R_s = \frac{A_s m_i^*}{A_i^* RRF_s m_s} \times 100\% \qquad \text{Eq. 23-6}$$

9.8 Minimum Detectable Limit (MDL).

$$MDL = \frac{2.5\, A_{ai} m_i^*}{A_{ci}^* RRF_i} \qquad \text{Eq. 23-7}$$

9.9 Total Concentration of PCDD's and PCDF's in the Sample.

$$C_{Tr} = \sum_{i=1}^{n} C_i \qquad \text{Eq. 23-8}$$

Any PCDD's or PCDF's that are reported as nondetected (below the MDL) shall be counted as zero for the purpose of calculating the total concentration of PCDD's and PCDF's in the sample.

10. Bibliography

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TABLE 1—COMPOSITION OF THE SAMPLE FORTIFICATION AND RECOVERY STANDARDS SOLUTIONS

Analyte	Concentration (pg/µl)
Internal Standards:	
$^{13}C_{12}$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100
$^{13}C_{12}$-OCDD	100
$^{13}C_{12}$-2,3,7,8-TCDF	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100
Surrogate Standards:	
$^{37}Cl_4$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100
Recovery Standards:	
$^{13}C_{12}$-1,2,3,4-TCDD	500
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	500

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS

Compound	Concentrations (pg/µL)				
	Solution No.				
	1	2	3	4	5
Alternate Standard:					
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	2.5	5	25	250	500

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS—Continued

Compound	Concentrations (pg/μL)				
	Solution No.				
	1	2	3	4	5
Recovery Standards:					
$^{13}C_{12}$-1,2,3,4-TCDD ..	100	100	100	100	100

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS—Continued

Compound	Concentrations (pg/μL)				
	Solution No.				
	1	2	3	4	5
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

TABLE 3—ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HIGH RESOLUTION MASS SPECTROMETRY FOR PCDD'S AND PCDF'S

Descriptor No.	Accurate mass	Ion type	Elemental composition	Analyte
2	292.9825	LOCK	C_7F_{11}	PFK
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M + 2	$C_{12}H_4{}^{35}Cl^{37}O$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M + 2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}ClO_2$	TCDD
	321.8936	M + 2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD (S)
	330.9792	QC	C_7F_{13}	PFK
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9339	M + 2	$^{13}C_{12}H_4{}^{35}Cl^{37}ClO_2$	TCDD (S)
	339.8597	M + 2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PECDF
	341.8567	M + 4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M + 2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M + 4	$^{13}C_{12}H_3{}^{35}Cl^{3537}Cl_2O$	PeCDF (S)
	355.8546	M + 2	$C_{12}H_3{}^{35}Cl_3{}37ClO_2$	PeCDD
	357.8516	M + 4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M + 2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M + 4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}\ Cl_2O_2$	PeCDD (S)
	375.8364	M + 2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
	409.7974	M + 2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCPDE
3	373.8208	M + 2	$C_{12}H_2{}35Cl_5{}^{37}ClO$	HxCDF
	375.8178	M + 4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M + 2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8157	M + 2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M + 4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	392.9760	LOCK	C_9F_{15}	PFK
	401.8559	M + 2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M + 4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDD (S)
	445.7555	M + 4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	430.9729	QC	C_9F_{17}	PFK
4	407.7818	M + 2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M + 4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8253	M	$^{13}C_{12}H^{35}Cl_7O$	HpCDF (S)
	419.8220	M + 2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF (S)
	423.7766	M + 2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M + 4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M + 2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M + 4	$^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S)
	479.7165	M + 4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCPDE
	430.9729	LOCK	C_9F_{17}	PFK
	441.7428	M + 2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M + 4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M + 2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M + 4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M + 2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M + 4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S)
	513.6775	M + 4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O_2$	DCDPE
	442.9728	QC	$C_{10}F_{17}$	PFK

(a) The following nuclidic masses were used:
H = 1.007825
C = 12.000000
^{13}C = 13.003355
F = 18.9984
O = 15.994915
^{35}Cl = 34.968853
^{37}Cl = 36.965903

S = Labeled Standard
QC = Ion selected for monitoring instrument stability during the GC/MS analysis.

TABLE 4—ACCEPTABLE RANGES FOR ION-ABUNDANCE RATIOS OF PCDD'S AND PCDF'S

No. of chlorine atoms	Ion type	Theoretical ratio	Control limits	
			Lower	Upper
4	M/M + 2	0.77	0.65	0.89
5	M + 2/M + 4	1.55	1.32	1.78
6	M + 2/M + 4	1.24	1.05	1.43
6[a]	M/M + 2	0.51	0.43	0.59
7[b]	M/M + 2	0.44	0.37	0.51
7	M + 2/M + 4	1.04	0.88	1.20
8	M + 2/M + 4	0.89	0.76	1.02

[a] Used only for ^{13}C-HxCDF.
[b] Used only for ^{13}C-HpCDF.

TABLE 5—MINIMUM REQUIREMENTS FOR INITIAL AND DAILY CALIBRATION RESPONSE FACTORS

Compound	Relative response factors	
	Initial calibration RSD	Daily calibration % difference
Unlabeled Analytes:		
2,3,7,8-TCDD	25	25
2,3,7,8-TCDF	25	25
1,2,3,7,8-PeCDD	25	25
1,2,3,7,8-PeCDF	25	25
2,3,4,7,8-PeCDF	25	25
1,2,4,5,7,8-HxCDD	25	25
1,2,3,6,7,8-HxCDD	25	25
1,2,3,7,8,9-HxCDD	25	25
1,2,3,4,7,8-HxCDF	25	25
1,2,3,6,7,8-HxCDF	25	25
1,2,3,7,8,9-HxCDF	25	25
2,3,4,6,7,8-HxCDF	25	25
1,2,3,4,6,7,8-HpCDD	25	25
1,2,3,4,6,7,8-HpCDF	25	25
OCDD	25	25
OCDF	30	30
Internal Standards:		
$^{13}C_{12}$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-1,2,3,7,8-PeCDD	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	30	30
$^{13}C_{12}$-OCDD	30	30
$^{13}C_{12}$-2,3,7,8-TCDF	30	30
$^{13}C_{12}$-1,2,3,7,8-PeCDF	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	30	30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	30	30
Surrogate Standards:		
$^{37}Cl_4$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-2,3,4,7,8-PeCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	25	25
Alternate Standard:		
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	25	25

METHOD 24—DETERMINATION OF VOLATILE MATTER CONTENT, WATER CONTENT, DENSITY, VOLUME SOLIDS, AND WEIGHT SOLIDS OF SURFACE COATINGS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile organic compounds	No CAS Number assigned
Water.	7732–18–5

1.2 Applicability. This method is applicable for the determination of volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or other related surface coatings.

1.3 Precision and Bias. Intra-and inter-laboratory analytical precision statements are presented in section 13.1. No bias has been identified.

2.0 Summary of Method

2.1 Standard methods are used to determine the volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or other related surface coatings.

3.0 Definitions

3.1 *Waterborne coating* means any coating which contains more than 5 percent water by weight in its volatile fraction.

3.2 *Multicomponent coatings* are coatings that are packaged in two or more parts, which are combined before application. Upon combination a coreactant from one part of the coating chemically reacts, at ambient conditions, with a coreactant from another part of the coating.

3.3 *Ultraviolet (UV) radiation-cured coatings* are coatings which contain unreacted monomers that are polymerized by exposure to ultraviolet light.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Components. Several of the compounds that may be contained in the coatings analyzed by this method may be irritating or corrosive to tissues (e.g., heptane) or may be toxic (e.g., benzene, methyl alcohol). Nearly all are fire hazards.

Appropriate precautions can be found in reference documents, such as Reference 3 of section 16.0.

6.0 Equipment and Supplies

The equipment and supplies specified in the ASTM methods listed in sections 6.1 through 6.6 (incorporated by reference—see §60.17 for acceptable versions of the methods) are required:

6.1 ASTM D 1475–60, 80, or 90, Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products.

6.2 ASTM D 2369–81, 87, 90, 92, 93, or 95, Standard Test Method for Volatile Content of Coatings.

6.3 ASTM D 3792–79 or 91, Standard Test Method for Water Content of Water Reducible Paints by Direct Injection into a Gas Chromatograph.

6.4 ASTM D 4017–81, 90, or 96a, Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Titration Method.

6.5 ASTM 4457–85 91, Standard Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph.

6.6 ASTM D 5403–93, Standard Test Methods for Volatile Content of Radiation Curable Materials.

6.7 ASTM D 6419–00, Test Method for Volatile Content of Sheet-Fed and Coldset Web Offset Printing Inks.

7.0 Reagents and Standards

7.1 The reagents and standards specified in the ASTM methods listed in sections 6.1 through 6.6 are required.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Follow the sample collection, preservation, storage, and transport procedures described in Reference 1 of section 16.0.

9.0 Quality Control

9.1 Reproducibility

NOTE: Not applicable to UV radiation-cured coatings). The variety of coatings that may be subject to analysis makes it necessary to verify the ability of the analyst and the analytical procedures to obtain reproducible results for the coatings tested. Verification is accomplished by running duplicate analyses on each sample tested (Sections 11.2 through 11.4) and comparing the results with the intra-laboratory precision statements (Section 13.1) for each parameter.

9.2 Confidence Limits for Waterborne Coatings. Because of the inherent increased imprecision in the determination of the VOC content of waterborne coatings as the weight percent of water increases, measured parameters for waterborne coatings are replaced with appropriate confidence limits (Section 12.6). These confidence limits are based on measured parameters and inter-laboratory precision statements.

10.0 Calibration and Standardization

10.1 Perform the calibration and standardization procedures specified in the ASTM methods listed in sections 6.1 through 6.6.

11.0 Analytical Procedure

Additional guidance can be found in Reference 2 of section 16.0.

11.1 Non Thin-film Ultraviolet Radiation-cured (UV radiation-cured) Coatings.

11.1.1 Volatile Content. Use the procedure in ASTM D 5403 to determine the volatile matter content of the coating except the curing test described in NOTE 2 of ASTM D 5403 is required.

11.1.2 Water Content. To determine water content, follow section 11.3.2.

11.1.3 Coating Density. To determine coating density, follow section 11.3.3.

11.1.4 Solids Content. To determine solids content, follow section 11.3.4.

11.1.5 To determine if a coating or ink can be classified as a thin-film UV cured coating or ink, use the equation in section 12.2. If C is less than 0.2 g and A is greater than or equal to 225 cm^2 (35 in^2) then the coating or ink is considered a thin-film UV radiation-cured coating and ASTM D 5403 is not applicable.

NOTE: As noted in section 1.4 of ASTM D 5403, this method may not be applicable to radiation curable materials wherein the volatile material is water.

11.2 Multi-component Coatings.

11.2.1 Sample Preparation.

11.2.1.1 Prepare about 100 ml of sample by mixing the components in a storage container, such as a glass jar with a screw top or a metal can with a cap. The storage container should be just large enough to hold the mixture. Combine the components (by weight or volume) in the ratio recommended by the manufacturer. Tightly close the container between additions and during mixing to prevent loss of volatile materials. However, most manufacturers mixing instructions are by volume. Because of possible error caused by expansion of the liquid when measuring the volume, it is recommended that the components be combined by weight. When weight is used to combine the components and the manufacturer's recommended ratio is by volume, the density must be determined by section 11.3.3.

11.2.1.2 Immediately after mixing, take aliquots from this 100 ml sample for determination of the total volatile content, water content, and density.

11.2.2 Volatile Content. To determine total volatile content, use the apparatus and

reagents described in ASTM D2369 (incorporated by reference; see §60.17 for the approved versions of the standard), respectively, and use the following procedures:

11.2.2.1 Weigh and record the weight of an aluminum foil weighing dish. Add 3 ±1 ml of suitable solvent as specified in ASTM D2369 to the weighing dish. Using a syringe as specified in ASTM D2369, weigh to 1 mg, by difference, a sample of coating into the weighing dish. For coatings believed to have a volatile content less than 40 weight percent, a suitable size is 0.3 + 0.10 g, but for coatings believed to have a volatile content greater than 40 weight percent, a suitable size is 0.5 ±0.1 g.

NOTE: If the volatile content determined pursuant to section 12.4 is not in the range corresponding to the sample size chosen repeat the test with the appropriate sample size. Add the specimen dropwise, shaking (swirling) the dish to disperse the specimen completely in the solvent. If the material forms a lump that cannot be dispersed, discard the specimen and prepare a new one. Similarly, prepare a duplicate. The sample shall stand for a minimum of 1 hour, but no more than 24 hours prior to being oven cured at 110 ±5 °C (230 ±9 °F) for 1 hour.

11.2.2.2 Heat the aluminum foil dishes containing the dispersed specimens in the forced draft oven for 60 min at 110 ±5 °C (230 ±9 °F). Caution—provide adequate ventilation, consistent with accepted laboratory practice, to prevent solvent vapors from accumulating to a dangerous level.

11.2.2.3 Remove the dishes from the oven, place immediately in a desiccator, cool to ambient temperature, and weigh to within 1 mg.

11.2.2.4 Run analyses in pairs (duplicate sets) for each coating mixture until the criterion in section 11.4 is met. Calculate W_v following Equation 24–2 and record the arithmetic average.

11.2.3 Water Content. To determine water content, follow section 11.3.2.

11.2.4 Coating Density. To determine coating density, follow section 11.3.3.

11.2.5 Solids Content. To determine solids content, follow section 11.3.4.

11.2.6 Exempt Solvent Content. To determine the exempt solvent content, follow section 11.3.5.

NOTE: For all other coatings (*i.e.*, water-or solvent-borne coatings) not covered by multicomponent or UV radiation-cured coatings, analyze as shown below:

11.3 Water-or Solvent-borne coatings.

11.3.1 Volatile Content. Use the procedure in ASTM D 2369 to determine the volatile matter content (may include water) of the coating.

11.3.1.1 Record the following information:

W_1 = weight of dish and sample before heating, g

W_2 = weight of dish and sample after heating, g

W_3 = sample weight, g.

11.3.1.2 Calculate the weight fraction of the volatile matter (W_v) for each analysis as shown in section 12.3.

11.3.1.3 Run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement in section 13.1.

11.3.1.4 Record the arithmetic average (W_v).

11.3.2 Water Content. For waterborne coatings only, determine the weight fraction of water (W_w) using either ASTM D 3792 or ASTM D 4017.

11.3.2.1 Run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement in section 13.1.

11.3.2.2 Record the arithmetic average (w_w).

11.3.3 Coating Density. Determine the density (Dc, kg/l) of the surface coating using the procedure in ASTM D 1475.

11.3.3.1 Run duplicate analyses until each value in a set deviates from the mean of the set by no more than the intra-laboratory precision statement in section 13.1.

11.3.3.2 Record the arithmetic average (D_c).

11.3.4 Solids Content. Determine the volume fraction (V_s) solids of the coating by calculation using the manufacturer's formulation.

11.3.5 Exempt Solvent Content. Determine the weight fraction of exempt solvents (W_E) by using ASTM Method D4457. Run a duplicate set of determinations and record the arithmetic average (W_E).

11.4 Sample Analysis Criteria. For W_v and W_w, run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement for that parameter. For D_c, run duplicate analyses until each value in a set deviates from the mean of the set by no more than the intra-laboratory precision statement. If, after several attempts, it is concluded that the ASTM procedures cannot be used for the specific coating with the established intra-laboratory precision (excluding UV radiation-cured coatings), the U.S. Environmental Protection Agency (EPA) will assume responsibility for providing the necessary procedures for revising the method or precision statements upon written request to: Director, Emissions, Monitoring, and Analysis Division, MD–14, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

12.0 Calculations and Data Analysis

12.1 Nomenclature.

A = Area of substrate, cm^2, (in^2).

C = Amount of coating or ink added to the substrate, g.

D_c = Density of coating or ink, g/cm^3 (g/in^3).

F = Manufacturer's recommended film thickness, cm (in).
W_o = Weight fraction of nonaqueous volatile matter, g/g.
W_s = Weight fraction of solids, g/g.
W_v = Weight fraction of the volatile matter, g/g.
W_w = Weight fraction of the water, g/g.

12.2 To determine if a coating or ink can be classified as a thin-film UV cured coating or ink, use the following equation:

$$C = F A D_c \qquad \text{Eq. 24-1}$$

12.3 Calculate W_v for each analysis as shown below:

$$W_v = \frac{W_1 - W_2}{W_3} \qquad \text{Eq. 24-2}$$

12.4 Nonaqueous Volatile Matter.
12.4.1 Solvent-borne Coatings.

$$W_o = W_v \qquad \text{Eq. 24-3}$$

12.4.2 Waterborne Coatings.

$$W_o = W_v - W_w \qquad \text{Eq. 24-4}$$

12.4.3 Coatings Containing Exempt Solvents.

$$W_o = W_v - W_E - W_w \qquad \text{Eq. 24-5}$$

12.5 Weight Fraction Solids.

$$W_s = 1 - W_v \qquad \text{Eq. 24-6}$$

12.6 Confidence Limit Calculations for Waterborne Coatings. To calculate the lower confidence limit, subtract the appropriate inter-laboratory precision value from the measured mean value for that parameter. To calculate the upper confidence limit, add the appropriate inter-laboratory precision value to the measured mean value for that parameter. For W_v and D_c, use the lower confidence limits; for W_w, use the upper confidence limit. Because W_s is calculated, there is no adjustment for this parameter.

13.0 Method Performance

13.1 Analytical Precision Statements. The intra-and inter-laboratory precision statements are given in Table 24–1 in section 17.0.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as specified in section 6.0, with the addition of the following:

1. Standard Procedure for Collection of Coating and Ink Samples for Analysis by Reference Methods 24 and 24A. EPA–340/1–91–010. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

2. Standard Operating Procedure for Analysis of Coating and Ink Samples by Reference Methods 24 and 24A.

EPA–340/1–91–011. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

3. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 24–1—ANALYTICAL PRECISION STATEMENTS

	Intra-laboratory	Inter-laboratory
Volatile matter content, W_v	±0.015 $\overline{W}_v$	±0.047 $\overline{W}_v$
Water content, W_w	±0.029 $\overline{W}_w$	±0.075 $\overline{W}_w$
Density, D_c	±0.001 kg/l	±0.002 kg/l

METHOD 24A—DETERMINATION OF VOLATILE MATTER CONTENT AND DENSITY OF PUBLICATION ROTOGRAVURE INKS AND RELATED PUBLICATION ROTOGRAVURE COATINGS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile organic compounds (VOC).	No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of the VOC content and density of solvent-borne (solvent-reducible) publication rotogravure inks and related publication rotogravure coatings.

2.0 Summary of Method

2.1 Separate procedures are used to determine the VOC weight fraction and density of the ink or related coating and the density of the solvent in the ink or related coating. The VOC weight fraction is determined by measuring the weight loss of a known sample quantity which has been heated for a specified length of time at a specified temperature. The density of both the ink or related coating and solvent are measured by a standard procedure. From this information, the VOC volume fraction is calculated.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Components. Some of the compounds that may be contained in the inks or related coatings analyzed by this method may be irritating or corrosive to tissues or may be toxic. Nearly all are fire hazards. Appropriate precautions can be found in reference documents, such as Reference 6 of section 16.0.

6.0 Equipment and Supplies

The following equipment and supplies are required for sample analysis:

6.1 Weighing Dishes. Aluminum foil, 58 mm (2.3 in.) in diameter by 18 mm (0.7 in.) high, with a flat bottom. There must be at least three weighing dishes per sample.

6.2 Disposable Syringe. 5 ml.

6.3 Analytical Balance. To measure to within 0.1 mg.

6.4 Oven. Vacuum oven capable of maintaining a temperature of 120 ±2 °C (248 ±4 °F) and an absolute pressure of 510 ±51 mm Hg (20 ±2 in. Hg) for 4 hours. Alternatively, a forced draft oven capable of maintaining a temperature of 120 ±2 °C (248 ±4 °F) for 24 hours.

6.5 The equipment and supplies specified in ASTM D 1475–60, 80, or 90 (incorporated by reference—see §60.17).

7.0 Reagents and Standards

7.1 The reagents and standards specified in ASTM D 1475–60, 80, or 90 are required.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Follow the sample collection, preservation, storage, and transport procedures described in Reference 4 of section 16.0.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

Additional guidance can be found in Reference 5 of section 16.0.

11.1 VOC Weight Fraction. Shake or mix the ink or related coating sample thoroughly to assure that all the solids are completely suspended. Label and weigh to the nearest 0.1 mg a weighing dish and record this weight (M_{x1}). Using a 5 ml syringe, without a needle, extract an aliquot from the ink or related coating sample. Weigh the syringe and aliquot to the nearest 0.1 mg and record this weight (M_{cy1}). Transfer 1 to 3 g of the aliquot to the tared weighing dish. Reweigh the syringe and remaining aliquot to the nearest 0.1 mg and record this weight (M_{cy2}). Heat the weighing dish with the transferred aliquot in a vacuum oven at an absolute pressure of 510 ±51 mm Hg (20 ±2 in. Hg) and a temperature of 120 ±2 °C (248 ±4 °F) for 4 hours. Alternatively, heat the weighing dish with the transferred aliquot in a forced draft oven at a temperature of 120 ±2 °C for 24 hours. After the weighing dish has cooled, reweigh it to the nearest 0.1 mg and record the weight (M_{x2}). Repeat this procedure two times for each ink or related coating sample, for a total of three samples.

11.2 Ink or Related Coating Density. Determine the density of the ink or related coating (D_c) according to the procedure outlined in ASTM D 1475. Make a total of three determinations for each ink or related coating sample. Report the ink or related coating density as the arithmetic average (D_c) of the three determinations.

11.3 Solvent Density. Determine the density of the solvent (D_o) according to the procedure outlined in ASTM D 1475. Make a total of three determinations for each ink or related coating sample. Report the solvent density as the arithmetic average (D_o) of the three determinations.

12.0 Calculations and Data Analysis

12.1 VOC Weight Fraction. For each determination, calculate the volatile organic content weight fraction (W_o) using the following equation:

$$W_o = \frac{M_{x1} + M_{cy1} - M_{cy2} - M_{x2}}{M_{cy1} - M_{cy2}} \qquad \text{Eq. 24A-1}$$

Make a total of three determinations. Report the VOC weight fraction as the arithmetic average ($\bar{W}_o$) of the three determinations.

12.2 VOC Volume Fraction. Calculate the volume fraction volatile organic content (V_o) using the following equation:

$$V_o = \frac{\overline{W}_o \overline{D}_c}{\overline{D}_o} \qquad \text{Eq. 24A-2}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products. ASTM Designation D 1475.

2. Teleconversation. Wright, Chuck, Inmont Corporation with Reich, R., A., Radian Corporation. September 25, 1979, Gravure Ink Analysis.

3. Teleconversation. Oppenheimer, Robert, Gravure Research Institute with Burt, Rick, Radian Corporation, November 5, 1979, Gravure Ink Analysis.

4. Standard Procedure for Collection of Coating and Ink Samples for Analysis by Reference Methods 24 and 24A. EPA–340/1–91–010. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

5. Standard Operating Procedure for Analysis of Coating and Ink Samples by Reference Methods 24 and 24A. EPA–340/1–91–011. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

6. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

Method 25—Determination of Total Gaseous Nonmethane Organic Emissions as Carbon

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total gaseous nonmethane organic compounds (TGNMO)	N/A	Dependent upon analytical equipment.

1.2 Applicability.

1.2.1 This method is applicable for the determination of volatile organic compounds (VOC) (measured as total gaseous nonmethane organics (TGNMO) and reported as carbon) in stationary source emissions. This method is not applicable for the determination of organic particulate matter.

1.2.2 This method is not the only method that applies to the measurement of VOC. Costs, logistics, and other practicalities of source testing may make other test methods more desirable for measuring VOC contents of certain effluent streams. Proper judgment is required in determining the most applicable VOC test method. For example, depending upon the molecular composition of the organics in the effluent stream, a totally automated semicontinuous nonmethane organics (NMO) analyzer interfaced directly to the source may yield accurate results. This approach has the advantage of providing emission data semicontinuously over an extended time period.

1.2.3 Direct measurement of an effluent with a flame ionization detector (FID) analyzer may be appropriate with prior characterization of the gas stream and knowledge that the detector responds predictably to the organic compounds in the stream. If present, methane (CH_4) will, of course, also be measured. The FID can be used under any of the following limited conditions: (1) Where only one compound is known to exist; (2) when the organic compounds consist of only hydrogen and carbon; (3) where the relative percentages of the compounds are known or can be determined, and the FID responses to the compounds are known; (4) where a consistent mixture of the compounds exists before and after emission control and only the relative concentrations are to be assessed; or (5) where the FID can be calibrated against mass standards of the compounds emitted (solvent emissions, for example).

1.2.4 Another example of the use of a direct FID is as a screening method. If there is enough information available to provide a rough estimate of the analyzer accuracy, the FID analyzer can be used to determine the VOC content of an uncharacterized gas stream. With a sufficient buffer to account for possible inaccuracies, the direct FID can be a useful tool to obtain the desired results without costly exact determination.

1.2.5 In situations where a qualitative/quantitative analysis of an effluent stream is desired or required, a gas chromatographic FID system may apply. However, for sources emitting numerous organics, the time and expense of this approach will be formidable.

2.0 Summary of Method

2.1 An emission sample is withdrawn from the stack at a constant rate through a heated filter and a chilled condensate trap by means of an evacuated sample tank. After sampling is completed, the TGNMO are determined by independently analyzing the condensate trap and sample tank fractions and combining the analytical results. The organic content of the condensate trap fraction is determined by oxidizing the NMO to carbon dioxide (CO_2) and quantitatively collecting in the effluent in an evacuated vessel; then a portion of the CO_2 is reduced to CH_4 and measured by an FID. The organic content of the sample tank fraction is measured by injecting a portion of the sample into a gas chromatographic column to separate the NMO from carbon monoxide (CO), CO_2, and CH_4; the NMO are oxidized to CO_2, reduced to CH_4, and measured by an FID. In this manner, the variable response of the FID associated with different types of organics is eliminated.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Carbon Dioxide and Water Vapor. When carbon dioxide (CO_2) and water vapor are present together in the stack, they can produce a positive bias in the sample. The magnitude of the bias depends on the concentrations of CO_2 and water vapor. As a guideline, multiply the CO_2 concentration, expressed as volume percent, times the water vapor concentration. If this product does not exceed 100, the bias can be considered insignificant. For example, the bias is not significant for a source having 10 percent CO_2 and 10 percent water vapor, but it might be significant for a source having 10 percent CO_2 and 20 percent water vapor.

4.2. Particulate Matter. Collection of organic particulate matter in the condensate trap would produce a positive bias. A filter is included in the sampling equipment to minimize this bias.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling system consists of a heated probe, heated filter, condensate trap, flow control system, and sample tank (see Figure 25–1). The TGNMO sampling equipment can be constructed from commercially available components and components fabricated in a machine shop. The following equipment is required:

6.1.1 Heated Probe. 6.4-mm (¼-in.) OD stainless steel tubing with a heating system capable of maintaining a gas temperature at the exit end of at least 129 °C (265 °F). The probe shall be equipped with a temperature sensor at the exit end to monitor the gas temperature. A suitable probe is shown in Figure 25–1. The nozzle is an elbow fitting attached to the front end of the probe while the temperature sensor is inserted in the side arm of a tee fitting attached to the rear of the probe. The probe is wrapped with a suitable length of high temperature heating tape, and then covered with two layers of glass cloth insulation and one layer of aluminum foil or an equivalent wrapping.

NOTE: If it is not possible to use a heating system for safety reasons, an unheated system with an in-stack filter is a suitable alternative.

6.1.2 Filter Holder. 25-mm (15/16-in.) ID Gelman filter holder with 303 stainless steel body and 316 stainless steel support screen with the Viton O-ring replaced by a Teflon O-ring.

6.1.3 Filter Heating System.

6.1.3.1 A metal box consisting of an inner and an outer shell separated by insulating material with a heating element in the inner shell capable of maintaining a gas temperature at the filter of 121 ±3 °C (250 ±5 °F). The heating box shall include temperature sensors to monitor the gas temperature immediately upstream and immediately downstream of the filter.

6.1.3.2 A suitable heating box is shown in Figure 25–2. The outer shell is a metal box that measures 102 mm × 280 mm × 292 mm (4 in. × 11 in. × 11½ in.), while the inner shell is a metal box measuring 76 mm × 229 mm × 241 mm (3 in. × 9 in. × 9½ in.). The inner box is supported by 13-mm (½-in.) phenolic rods. The void space between the boxes is filled with ceramic fiber insulation which is sealed in place by means of a silicon rubber bead around the upper sides of the box. A removable lid made in a similar manner, with a 25-mm (1-in.) gap between the parts is used to cover the heating chamber. The inner box is heated with a 250-watt cartridge heater, shielded by a stainless steel shroud. The heater is regulated by a thermostatic temperature controller which is set to maintain a gas temperature of 121 °C (250 °F) as measured by the temperature sensor upstream of the filter.

NOTE: If it is not possible to use a heating system for safety reasons, an unheated system with an in-stack filter is a suitable alternative.

6.1.4 Condensate Trap. 9.5-mm (⅜-in.) OD 316 stainless steel tubing bent into a U-shape. Exact dimensions are shown in Figure

25–3. The tubing shall be packed with coarse quartz wool, to a density of approximately 0.11 g/cm^3 before bending. While the condensate trap is packed with dry ice in the Dewar, an ice bridge may form between the arms of the condensate trap making it difficult to remove the condensate trap. This problem can be prevented by attaching a steel plate between the arms of the condensate trap in the same plane as the arms to completely fill the intervening space.

6.1.5 Valve. Stainless steel control valve for starting and stopping sample flow.

6.1.6 Metering Valve. Stainless steel valve for regulating the sample flow rate through the sample train.

6.1.7 Rate Meter. Rotameter, or equivalent, capable of measuring sample flow in the range of 60 to 100 cm^3/min (0.13 to 0.21 ft^3/hr).

6.1.8 Sample Tank. Stainless steel or aluminum tank with a minimum volume of 4 liters (0.14 ft^3).

NOTE: Sample volumes greater than 4 liters may be required for sources with low organic concentrations.

6.1.9 Mercury Manometer. U-tube manometer or absolute pressure gauge capable of measuring pressure to within 1 mm Hg in the range of 0 to 900 mm.

6.1.10 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

6.2 Condensate Recovery. The system for the recovery of the organics captured in the condensate trap consists of a heat source, an oxidation catalyst, a nondispersive infrared (NDIR) analyzer, and an intermediate collection vessel (ICV). Figure 25–4 is a schematic of a typical system. The system shall be capable of proper oxidation and recovery, as specified in section 10.1.1. The following major components are required:

6.2.1 Heat Source. Sufficient to heat the condensate trap (including probe) to a temperature of 200 °C (390 °F). A system using both a heat gun and an electric tube furnace is recommended.

6.2.2 Heat Tape. Sufficient to heat the connecting tubing between the water trap and the oxidation catalyst to 100 °C (212 °F).

6.2.3 Oxidation Catalyst. A suitable length of 9.5 mm (3/8-in.) OD Inconel 600 tubing packed with 15 cm (6 in.) of 3.2 mm (3/8-in.) diameter 19 percent chromia on alumina pellets. The catalyst material is packed in the center of the catalyst tube with quartz wool packed on either end to hold it in place.

6.2.4 Water Trap. Leak-proof, capable of removing moisture from the gas stream.

6.2.5 Syringe Port. A 6.4-mm (1/4-in.) OD stainless steel tee fitting with a rubber septum placed in the side arm.

6.2.6 NDIR Detector. Capable of indicating CO_2 concentration in the range of zero to 5 percent, to monitor the progress of combustion of the organic compounds from the condensate trap.

6.2.7 Flow-Control Valve. Stainless steel, to maintain the trap conditioning system near atmospheric pressure.

6.2.8 Intermediate Collection Vessel. Stainless steel or aluminum, equipped with a female quick connect. Tanks with nominal volumes of at least 6 liters (0.2 ft^3) are recommended.

6.2.9 Mercury Manometer. Same as described in section 6.1.9.

6.2.10 Syringe. 10-ml gas-tight glass syringe equipped with an appropriate needle.

6.2.11 Syringes. 10-µl and 50-µl liquid injection syringes.

6.2.12 Liquid Sample Injection Unit. 316 Stainless steel U-tube fitted with an injection septum (see Figure 25–7).

6.3 Analysis.

6.3.1 NMO Analyzer. The NMO analyzer is a gas chromatograph (GC) with backflush capability for NMO analysis and is equipped with an oxidation catalyst, reduction catalyst, and FID. Figures 25–5 and 25–6 are schematics of a typical NMO analyzer. This semicontinuous GC/FID analyzer shall be capable of: (1) Separating CO, CO_2, and CH_4 from NMO, (2) reducing the CO_2 to CH_4 and quantifying as CH_4, and (3) oxidizing the NMO to CO_2, reducing the CO_2 to CH_4 and quantifying as CH_4, according to section 10.1.2. The analyzer consists of the following major components:

6.3.1.1 Oxidation Catalyst. A suitable length of 9.5-mm (3/8-in.) OD Inconel 600 tubing packed with 5.1 cm (2 in.) of 19 percent chromia on 3.2-mm (1/8-in.) alumina pellets. The catalyst material is packed in the center of the tube supported on either side by quartz wool. The catalyst tube must be mounted vertically in a 650 °C (1200 °F) furnace. Longer catalysts mounted horizontally may be used, provided they can meet the specifications of section 10.1.2.1.

6.3.1.2 Reduction Catalyst. A 7.6-cm (3-in.) length of 6.4-mm (1/4-in.) OD Inconel tubing fully packed with 100-mesh pure nickel powder. The catalyst tube must be mounted vertically in a 400 °C (750 °F) furnace.

6.3.1.3 Separation Column(s). A 30-cm (1-ft) length of 3.2-mm (1/8-in.) OD stainless steel tubing packed with 60/80 mesh Unibeads 1S followed by a 61-cm (2-ft) length of 3.2-mm (1/8-in.) OD stainless steel tubing packed with 60/80 mesh Carbosieve G. The Carbosieve and Unibeads columns must be baked separately at 200 °C (390 °F) with carrier gas flowing through them for 24 hours before initial use.

6.3.1.4 Sample Injection System. A single 10-port GC sample injection valve or a group of valves with sufficient ports fitted with a sample loop properly sized to interface with the NMO analyzer (1-cc loop recommended).

6.3.1.5 FID. An FID meeting the following specifications is required:

6.3.1.5.1 Linearity. A linear response (±5 percent) over the operating range as demonstrated by the procedures established in section 10.1.2.3.

6.3.1.5.2 Range. A full scale range of 10 to 50,000 ppm CH_4. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.3.1.6 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the analytical results.

6.3.2 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm Hg.

6.3.3 Temperature Sensor. Capable of measuring the laboratory temperature within 1 °C (2 °F).

6.3.4 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

7.0 Reagents and Standards

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Dry Ice. Solid CO2, crushed.

7.1.2 Coarse Quartz Wool. 8 to 15 um.

7.1.3 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Method D2986–71, 78, or 95a (incorporated by reference—see §60.17). Test data from the supplier's quality control program are sufficient for this purpose.

7.2 NMO Analysis. The following gases are required for NMO analysis:

7.2.1 Carrier Gases. Helium (He) and oxygen (O_2) containing less than 1 ppm CO_2 and less than 0.1 ppm hydrocarbon.

7.2.2 Fuel Gas. Hydrogen (H_2), at least 99.999 percent pure.

7.2.3 Combustion Gas. Either air (less than 0.1 ppm total hydrocarbon content) or O_2 (purity 99.99 percent or greater), as required by the detector.

7.3 Condensate Analysis. The following are required for condensate analysis:

7.3.1 Gases. Containing less than 1 ppm carbon.

7.3.1.1 Air.

7.3.1.2 Oxygen.

7.3.2 Liquids. To conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society.

7.3.2.1 Hexane.

7.3.2.2 Decane.

7.4 Calibration. For all calibration gases, the manufacturer must recommend a maximum shelf life for each cylinder (i.e., the length of time the gas concentration is not expected to change more than ±5 percent from its certified value). The date of gas cylinder preparation, certified organic concentration, and recommended maximum shelf life must be affixed to each cylinder before shipment from the gas manufacturer to the buyer. The following calibration gases are required:

7.4.1 Oxidation Catalyst Efficiency Check Calibration Gas. Gas mixture standard with nominal concentration of 1 percent methane in air.

7.4.2 FID Linearity and NMO Calibration Gases. Three gas mixture standards with nominal propane concentrations of 20 ppm, 200 ppm, and 3000 ppm, in air.

7.4.3 CO_2 Calibration Gases. Three gas mixture standards with nominal CO_2 concentrations of 50 ppm, 500 ppm, and 1 percent, in air.

NOTE: Total NMO less than 1 ppm required for 1 percent mixture.

7.4.4 NMO Analyzer System Check Calibration Gases. Four calibration gases are needed as follows:

7.4.4.1 Propane Mixture. Gas mixture standard containing (nominal) 50 ppm CO, 50 ppm CH_4, 1 percent CO_2, and 20 ppm C_3H_8, prepared in air.

7.4.4.2 Hexane. Gas mixture standard containing (nominal) 50 ppm hexane in air.

7.4.4.3 Toluene. Gas mixture standard containing (nominal) 20 ppm toluene in air.

7.4.4.4 Methanol. Gas mixture standard containing (nominal) 100 ppm methanol in air.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Sampling Equipment Preparation.

8.1.1 Condensate Trap Cleaning. Before its initial use and after each use, a condensate trap should be thoroughly cleaned and checked to ensure that it is not contaminated. Both cleaning and checking can be accomplished by installing the trap in the condensate recovery system and treating it as if it were a sample. The trap should be heated as described in section 11.1.3. A trap may be considered clean when the CO_2 concentration in its effluent gas drops below 10 ppm. This check is optional for traps that most recently have been used to collect samples which were then recovered according to the procedure in section 11.1.3.

8.1.2 Sample Tank Evacuation and Leak-Check. Evacuate the sample tank to 10 mm Hg absolute pressure or less. Then close the sample tank valve, and allow the tank to sit for 60 minutes. The tank is acceptable if a change in tank vacuum of less than 1 mm Hg is noted. The evacuation and leak-check may be conducted either in the laboratory or the field.

8.1.3 Sampling Train Assembly. Just before assembly, measure the tank vacuum using a mercury manometer. Record this vacuum, the ambient temperature, and the barometric pressure at this time. Close the sample tank valve and assemble the sampling

system as shown in Figure 25–1. Immerse the condensate trap body in dry ice at least 30 minutes before commencing sampling to improve collection efficiency. The point where the inlet tube joins the trap body should be 2.5 to 5 cm (1 to 2 in.) above the top of the dry ice.

8.1.4 Pretest Leak-Check. A pretest leak-check is required. Calculate or measure the approximate volume of the sampling train from the probe tip to the sample tank valve. After assembling the sampling train, plug the probe tip, and make certain that the sample tank valve is closed. Turn on the vacuum pump, and evacuate the sampling system from the probe tip to the sample tank valve to an absolute pressure of 10 mm Hg or less. Close the purge valve, turn off the pump, wait a minimum period of 10 minutes, and recheck the indicated vacuum. Calculate the maximum allowable pressure change based on a leak rate of 1 percent of the sampling rate using Equation 25–1, section 12.2. If the measured pressure change exceeds the allowable, correct the problem and repeat the leak-check before beginning sampling.

8.2 Sample Collection.

8.2.1 Unplug the probe tip, and place the probe into the stack such that the probe is perpendicular to the duct or stack axis; locate the probe tip at a single preselected point of average velocity facing away from the direction of gas flow. For stacks having a negative static pressure, seal the sample port sufficiently to prevent air in-leakage around the probe. Set the probe temperature controller to 129 °C (265 °F) and the filter temperature controller to 121 °C (250 °F). Allow the probe and filter to heat for about 30 minutes before purging the sample train.

8.2.2 Close the sample valve, open the purge valve, and start the vacuum pump. Set the flow rate between 60 and 100 cm^3/min (0.13 and 0.21 ft^3/hr), and purge the train with stack gas for at least 10 minutes.

8.2.3 When the temperatures at the exit ends of the probe and filter are within the corresponding specified ranges, check the dry ice level around the condensate trap, and add dry ice if necessary. Record the clock time. To begin sampling, close the purge valve and stop the pump. Open the sample valve and the sample tank valve. Using the flow control valve, set the flow through the sample train to the proper rate. Adjust the flow rate as necessary to maintain a constant rate (±10 percent) throughout the duration of the sampling period. Record the sample tank vacuum and flowmeter setting at 5-minute intervals. (See Figure 25–8.) Select a total sample time greater than or equal to the minimum sampling time specified in the applicable subpart of the regulations; end the sampling when this time period is reached or when a constant flow rate can no longer be maintained because of reduced sample tank vacuum.

NOTE: If sampling had to be stopped before obtaining the minimum sampling time (specified in the applicable subpart) because a constant flow rate could not be maintained, proceed as follows: After closing the sample tank valve, remove the used sample tank from the sampling train (without disconnecting other portions of the sampling train). Take another evacuated and leak-checked sample tank, measure and record the tank vacuum, and attach the new tank to the sampling train. After the new tank is attached to the sample train, proceed with the sampling until the required minimum sampling time has been exceeded.

8.3 Sample Recovery. After sampling is completed, close the flow control valve, and record the final tank vacuum; then record the tank temperature and barometric pressure. Close the sample tank valve, and disconnect the sample tank from the sample system. Disconnect the condensate trap at the inlet to the rate meter, and tightly seal both ends of the condensate trap. Do not include the probe from the stack to the filter as part of the condensate sample.

8.4 Sample Storage and Transport. Keep the trap packed in dry ice until the samples are returned to the laboratory for analysis. Ensure that run numbers are identified on the condensate trap and the sample tank(s).

9.0 Quality Control

Section	Quality control measure	Effect
10.1.1	Initial performance check of condensate recovery apparatus.	Ensure acceptable condensate recovery efficiency.
10.1.2, 10.2	NMO analyzer initial and daily performance checks.	Ensure precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Initial Performance Checks.

10.1.1 Condensate Recovery Apparatus. Perform these tests before the system is first placed in operation, after any shutdown of 6 months or more, and after any major modification of the system, or at the frequency recommended by the manufacturer.

10.1.1.1 Carrier Gas and Auxiliary O_2 Blank Check. Analyze each new tank of carrier gas or auxiliary O_2 with the NMO analyzer to

check for contamination. Treat the gas cylinders as noncondensible gas samples, and analyze according to the procedure in section 11.2.3. Add together any measured CH_4, CO, CO_2, or NMO. The total concentration must be less than 5 ppm.

10.1.1.2 Oxidation Catalyst Efficiency Check.

10.1.1.2.1 With a clean condensate trap installed in the recovery system or a ⅛″ stainless steel connector tube, replace the carrier gas cylinder with the high level methane standard gas cylinder (Section 7.4.1). Set the four-port valve to the recovery position, and attach an ICV to the recovery system. With the sample recovery valve in vent position and the flow-control and ICV valves fully open, evacuate the manometer or gauge, the connecting tubing, and the ICV to 10 mm Hg absolute pressure. Close the flow-control and vacuum pump valves.

10.1.1.2.2 After the NDIR response has stabilized, switch the sample recovery valve from vent to collect. When the manometer or pressure gauge begins to register a slight positive pressure, open the flow-control valve. Keep the flow adjusted such that the pressure in the system is maintained within 10 percent of atmospheric pressure. Continue collecting the sample in a normal manner until the ICV is filled to a nominal gauge pressure of 300 mm Hg. Close the ICV valve, and remove the ICV from the system. Place the sample recovery valve in the vent position, and return the recovery system to its normal carrier gas and normal operating conditions. Analyze the ICV for CO_2 using the NMO analyzer; the catalyst efficiency is acceptable if the CO_2 concentration is within 2 percent of the methane standard concentration.

10.1.1.3 System Performance Check. Construct a liquid sample injection unit similar in design to the unit shown in Figure 25–7. Insert this unit into the condensate recovery and conditioning system in place of a condensate trap, and set the carrier gas and auxiliary O_2 flow rates to normal operating levels. Attach an evacuated ICV to the system, and switch from system vent to collect. With the carrier gas routed through the injection unit and the oxidation catalyst, inject a liquid sample (see sections 10.1.1.3.1 to 10.1.1.3.4) into the injection port. Operate the trap recovery system as described in section 11.1.3. Measure the final ICV pressure, and then analyze the vessel to determine the CO_2 concentration. For each injection, calculate the percent recovery according to section 12.7. Calculate the relative standard deviation for each set of triplicate injections according to section 12.8. The performance test is acceptable if the average percent recovery is 100 ±5 percent and the relative standard deviation is less than 2 percent for each set of triplicate injections.

10.1.1.3.1 50 µl hexane.

10.1.1.3.2 10 µl hexane.

10.1.1.3.3 50 µl decane.

10.1.1.3.4 10 µl decane.

10.1.2 NMO Analyzer. Perform these tests before the system is first placed in operation, after any shutdown longer than 6 months, and after any major modification of the system.

10.1.2.1 Oxidation Catalyst Efficiency Check. Turn off or bypass the NMO analyzer reduction catalyst. Make triplicate injections of the high level methane standard (Section 7.4.1). The oxidation catalyst operation is acceptable if the FID response is less than 1 percent of the injected methane concentration.

10.1.2.2 Reduction Catalyst Efficiency Check. With the oxidation catalyst unheated or bypassed and the heated reduction catalyst bypassed, make triplicate injections of the high level methane standard (Section 7.4.1). Repeat this procedure with both catalysts operative. The reduction catalyst operation is acceptable if the responses under both conditions agree within 5 percent of their average.

10.1.2.3 NMO Analyzer Linearity Check Calibration. While operating both the oxidation and reduction catalysts, conduct a linearity check of the analyzer using the propane standards specified in section 7.4.2. Make triplicate injections of each calibration gas. For each gas (*i.e.*, each set of triplicate injections), calculate the average response factor (area/ppm C) for each gas, as well as and the relative standard deviation (according to section 12.8). Then calculate the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within 2.5 percent of the overall mean value and if the relative standard deviation gas is less than 2 percent of the overall mean value. Record the overall mean of the propane response factor values as the NMO calibration response factor (RF_{NMO}). Repeat the linearity check using the CO_2 standards specified in section 7.4.3. Make triplicate injections of each gas, and then calculate the average response factor (area/ppm C) for each gas, as well as the overall mean of the response factor values. Record the overall mean of the response factor values as the CO_2 calibration response factor (RF_{CO2}). The RF_{CO2} must be within 10 percent of the RF_{NMO}.

10.1.2.4 System Performance Check. Check the column separation and overall performance of the analyzer by making triplicate injections of the calibration gases listed in section 7.4.4. The analyzer performance is acceptable if the measured NMO value for each gas (average of triplicate injections) is within 5 percent of the expected value.

10.2 NMO Analyzer Daily Calibration. The following calibration procedures shall be performed before and immediately after the

analysis of each set of samples, or on a daily basis, whichever is more stringent:

10.2.1 CO_2 Response Factor. Inject triplicate samples of the high level CO_2 calibration gas (Section 7.4.3), and calculate the average response factor. The system operation is adequate if the calculated response factor is within 5 percent of the RF_{CO2} calculated during the initial performance test (Section 10.1.2.3). Use the daily response factor (DRF_{CO2}) for analyzer calibration and the calculation of measured CO_2 concentrations in the ICV samples.

10.2.2 NMO Response Factors. Inject triplicate samples of the mixed propane calibration cylinder gas (Section 7.4.4.1), and calculate the average NMO response factor. The system operation is adequate if the calculated response factor is within 10 percent of the RF_{NMO} calculated during the initial performance test (Section 10.1.2.4). Use the daily response factor (DRF_{NMO}) for analyzer calibration and calculation of NMO concentrations in the sample tanks.

10.3 Sample Tank and ICV Volume. The volume of the gas sampling tanks used must be determined. Determine the tank and ICV volumes by weighing them empty and then filled with deionized distilled water; weigh to the nearest 5 g, and record the results. Alternatively, measure the volume of water used to fill them to the nearest 5 ml.

11.0 Analytical Procedure

11.1 Condensate Recovery. See Figure 25–9. Set the carrier gas flow rate, and heat the catalyst to its operating temperature to condition the apparatus.

11.1.1 Daily Performance Checks. Each day before analyzing any samples, perform the following tests:

11.1.1.1 Leak-Check. With the carrier gas inlets and the sample recovery valve closed, install a clean condensate trap in the system, and evacuate the system to 10 mm Hg absolute pressure or less. Monitor the system pressure for 10 minutes. The system is acceptable if the pressure change is less than 2 mm Hg.

11.1.1.2 System Background Test. Adjust the carrier gas and auxiliary oxygen flow rate to their normal values of 100 cc/min and 150 cc/min, respectively, with the sample recovery valve in vent position. Using a 10-ml syringe, withdraw a sample from the system effluent through the syringe port. Inject this sample into the NMO analyzer, and measure the CO_2 content. The system background is acceptable if the CO_2 concentration is less than 10 ppm.

11.1.1.3 Oxidation Catalyst Efficiency Check. Conduct a catalyst efficiency test as specified in section 10.1.1.2. If the criterion of this test cannot be met, make the necessary repairs to the system before proceeding.

11.1.2 Condensate Trap CO_2 Purge and Sample Tank Pressurization.

11.1.2.1 After sampling is completed, the condensate trap will contain condensed water and organics and a small volume of sampled gas. This gas from the stack may contain a significant amount of CO_2 which must be removed from the condensate trap before the sample is recovered. This is accomplished by purging the condensate trap with zero air and collecting the purged gas in the original sample tank.

11.1.2.2 Begin with the sample tank and condensate trap from the test run to be analyzed. Set the four-port valve of the condensate recovery system in the CO_2 purge position as shown in Figure 25–9. With the sample tank valve closed, attach the sample tank to the sample recovery system. With the sample recovery valve in the vent position and the flow control valve fully open, evacuate the manometer or pressure gauge to the vacuum of the sample tank. Next, close the vacuum pump valve, open the sample tank valve, and record the tank pressure.

11.1.2.3 Attach the dry ice-cooled condensate trap to the recovery system, and initiate the purge by switching the sample recovery valve from vent to collect position. Adjust the flow control valve to maintain atmospheric pressure in the recovery system. Continue the purge until the CO_2 concentration of the trap effluent is less than 5 ppm. CO_2 concentration in the trap effluent should be measured by extracting syringe samples from the recovery system and analyzing the samples with the NMO analyzer. This procedure should be used only after the NDIR response has reached a minimum level. Using a 10-ml syringe, extract a sample from the syringe port prior to the NDIR, and inject this sample into the NMO analyzer.

11.1.2.4 After the completion of the CO_2 purge, use the carrier gas bypass valve to pressurize the sample tank to approximately 1,060 mm Hg absolute pressure with zero air.

11.1.3 Recovery of the Condensate Trap Sample (See Figure 25–10).

11.1.3.1 Attach the ICV to the sample recovery system. With the sample recovery valve in a closed position, between vent and collect, and the flow control and ICV valves fully open, evacuate the manometer or gauge, the connecting tubing, and the ICV to 10 mm Hg absolute pressure. Close the flow-control and vacuum pump valves.

11.1.3.2 Begin auxiliary oxygen flow to the oxidation catalyst at a rate of 150 cc/min, then switch the four-way valve to the trap recovery position and the sample recovery valve to collect position. The system should now be set up to operate as indicated in Figure 25–10. After the manometer or pressure gauge begins to register a slight positive pressure, open the flow control valve. Adjust the flow-control valve to maintain atmospheric pressure in the system within 10 percent.

11.1.3.3 Remove the condensate trap from the dry ice, and allow it to warm to ambient temperature while monitoring the NDIR response. If, after 5 minutes, the CO_2 concentration of the catalyst effluent is below 10,000 ppm, discontinue the auxiliary oxygen flow to the oxidation catalyst. Begin heating the trap by placing it in a furnace preheated to 200 °C (390 °F). Once heating has begun, carefully monitor the NDIR response to ensure that the catalyst effluent concentration does not exceed 50,000 ppm. Whenever the CO_2 concentration exceeds 50,000 ppm, supply auxiliary oxygen to the catalyst at the rate of 150 cc/min. Begin heating the tubing that connected the heated sample box to the condensate trap only after the CO_2 concentration falls below 10,000 ppm. This tubing may be heated in the same oven as the condensate trap or with an auxiliary heat source such as a heat gun. Heating temperature must not exceed 200 °C (390 °F). If a heat gun is used, heat the tubing slowly along its entire length from the upstream end to the downstream end, and repeat the pattern for a total of three times. Continue the recovery until the CO_2 concentration drops to less than 10 ppm as determined by syringe injection as described under the condensate trap CO_2 purge procedure (Section 11.1.2).

11.1.3.4 After the sample recovery is completed, use the carrier gas bypass valve to pressurize the ICV to approximately 1060 mm Hg absolute pressure with zero air.

11.2 Analysis. Once the initial performance test of the NMO analyzer has been successfully completed (see section 10.1.2) and the daily CO_2 and NMO response factors have been determined (see section 10.2), proceed with sample analysis as follows:

11.2.1 Operating Conditions. The carrier gas flow rate is 29.5 cc/min He and 2.2 cc/min O_2. The column oven is heated to 85 °C (185 °F). The order of elution for the sample from the column is CO, CH_4, CO_2, and NMO.

11.2.2 Analysis of Recovered Condensate Sample. Purge the sample loop with sample, and then inject the sample. Under the specified operating conditions, the CO_2 in the sample will elute in approximately 100 seconds. As soon as the detector response returns to baseline following the CO_2 peak, switch the carrier gas flow to backflush, and raise the column oven temperature to 195 °C (380 °F) as rapidly as possible. A rate of 30 °C/min (90 °F) has been shown to be adequate. Record the value obtained for the condensible organic material (C_{cm}) measured as CO_2 and any measured NMO. Return the column oven temperature to 85 °C (185 °F) in preparation for the next analysis. Analyze each sample in triplicate, and report the average C_{cm}.

11.2.3 Analysis of Sample Tank. Perform the analysis as described in section 11.2.2, but record only the value measured for NMO (C_{tm}).

12.0 Data Analysis and Calculations

Carry out the calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculations. All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge or manometer pressure.

12.1 Nomenclature.

C = TGNMO concentration of the effluent, ppm C equivalent.
C_c = Calculated condensible organic (condensate trap) concentration of the effluent, ppm C equivalent.
C_{cm} = Measured concentration (NMO analyzer) for the condensate trap ICV, ppm CO_2.
C_t = Calculated noncondensible organic concentration (sample tank) of the effluent, ppm C equivalent.
C_{tm} = Measured concentration (NMO analyzer) for the sample tank, ppm NMO.
F = Sampling flow rate, cc/min.
L = Volume of liquid injected, µl.
M = Molecular weight of the liquid injected, g/g-mole.
M_c = TGNMO mass concentration of the effluent, mg C/dsm³.
N = Carbon number of the liquid compound injected (N = 12 for decane, N = 6 for hexane).
n = Number of data points.
P_f = Final pressure of the intermediate collection vessel, mm Hg absolute.
P_b = Barometric pressure, cm Hg.
P_{ti} = Gas sample tank pressure before sampling, mm Hg absolute.
P_t = Gas sample tank pressure after sampling, but before pressurizing, mm Hg absolute.
P_{tf} = Final gas sample tank pressure after pressurizing, mm Hg absolute.
q = Total number of analyzer injections of intermediate collection vessel during analysis (where k = injection number, 1 * * * q).
r = Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 * * * r).
r = Density of liquid injected, g/cc.
T_f = Final temperature of intermediate collection vessel, °K.
T_{ti} = Sample tank temperature before sampling, °K.
T_t = Sample tank temperature at completion of sampling, °K.
T_{tf} = Sample tank temperature after pressurizing, °K.
V = Sample tank volume, m³.
V_t = Sample train volume, cc.
V_v = Intermediate collection vessel volume, m³.
V_s = Gas volume sampled, dsm³.
x_i = Individual measurements.
$\bar{x}$ = Mean value.

ΔP = Allowable pressure change, cm Hg.
Θ = Leak-check period, min.

12.2 Allowable Pressure Change. For the pretest leak-check, calculate the allowable pressure change using Equation 25–1:

$$\Delta P = 0.01 \frac{F P_b \Theta}{V_t} \qquad \text{Eq. 25-1}$$

12.3 Sample Volume. For each test run, calculate the gas volume sampled using Equation 25–2:

$$V_s = 0.3857\, V \left(\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}} \right) \qquad \text{Eq. 25-2}$$

12.4 Noncondensible Organics. For each sample tank, determine the concentration of nonmethane organics (ppm C) using Equation 25–3:

$$C_t = \left(\frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}} \right) \left(\frac{1}{r} \sum_{j=1}^{r} C_{tm_j} \right) \qquad \text{Eq. 25-3}$$

12.5 Condensible Organics. For each condensate trap determine the concentration of organics (ppm C) using Equation 25–4:

$$C_c = 0.3857 \frac{V_v P_f}{V_s T_f} \left(\frac{1}{q} \sum_{k=1}^{q} C_{cm_k} \right) \qquad \text{Eq. 25-4}$$

12.6 TGNMO Mass Concentration. Determine the TGNMO mass concentration as carbon for each test run, using Equation 25–5:

$$M_c = 0.4993 \left(C_t + C_c \right) \qquad \text{Eq. 25-5}$$

12.7 Percent Recovery. Calculate the percent recovery for the liquid injections to the condensate recovery and conditioning system using Equation 25–6:

$$\text{Percent Recovery} = K \frac{M V_v P_t C_{cm}}{L P T_f N} \qquad \text{Eq. 25-6}$$

where K = 1.604 (°K)(g-mole)(%)/(mm Hg)(ml)(m^3)(ppm).

12.8 Relative Standard Deviation. Use Equation 25–7 to calculate the relative standard deviation (RSD) of percent recovery and analyzer linearity.

$$RSD = \frac{100}{\bar{x}} \left[\frac{\sum_{i=1}^{n} \left(x_i - \bar{x} \right)^2}{n-1} \right]^{\frac{1}{2}} \qquad \text{Eq. 25-7}$$

13.0 Method Performance

13.1 Range. The minimum detectable limit of the method has been determined to be 50 parts per million by volume (ppm). No upper limit has been established.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, A.E., S. Witz, and R.D. MacPhee. Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, MA. June 15–20, 1975.) 14 p.

2. Salo, A.E., W.L. Oaks, and R.D. MacPhee. Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, CO. June 9–13, 1974.) 25 p.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

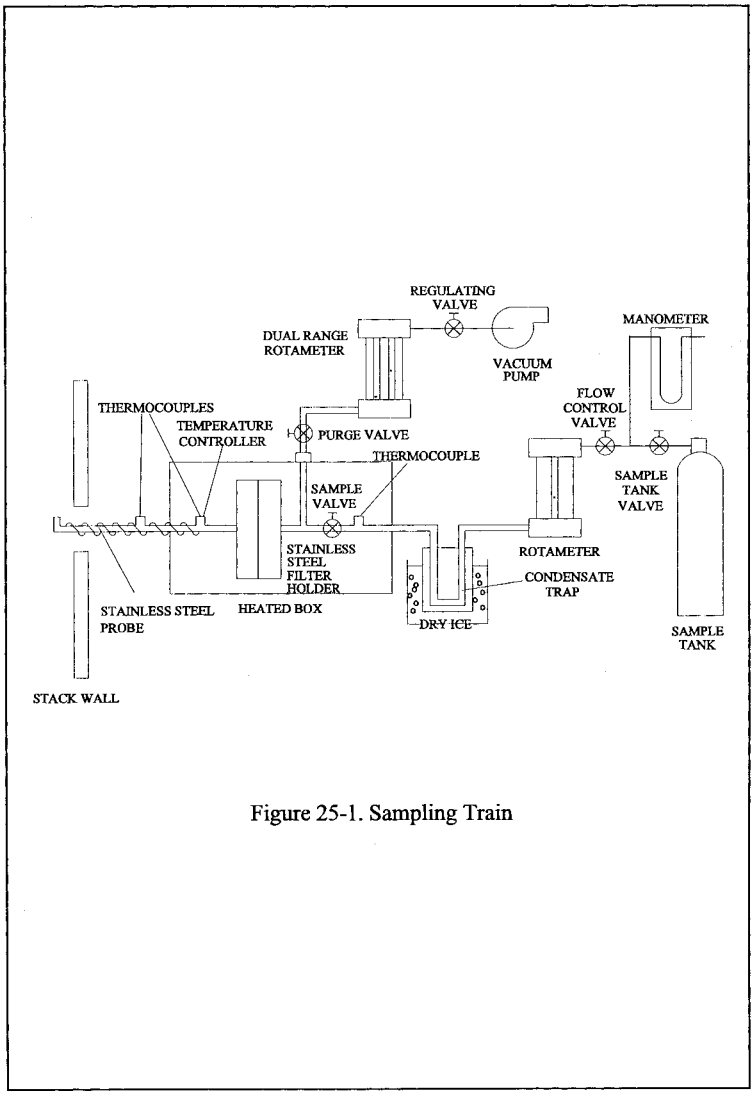


Figure 25-1. Sampling Train

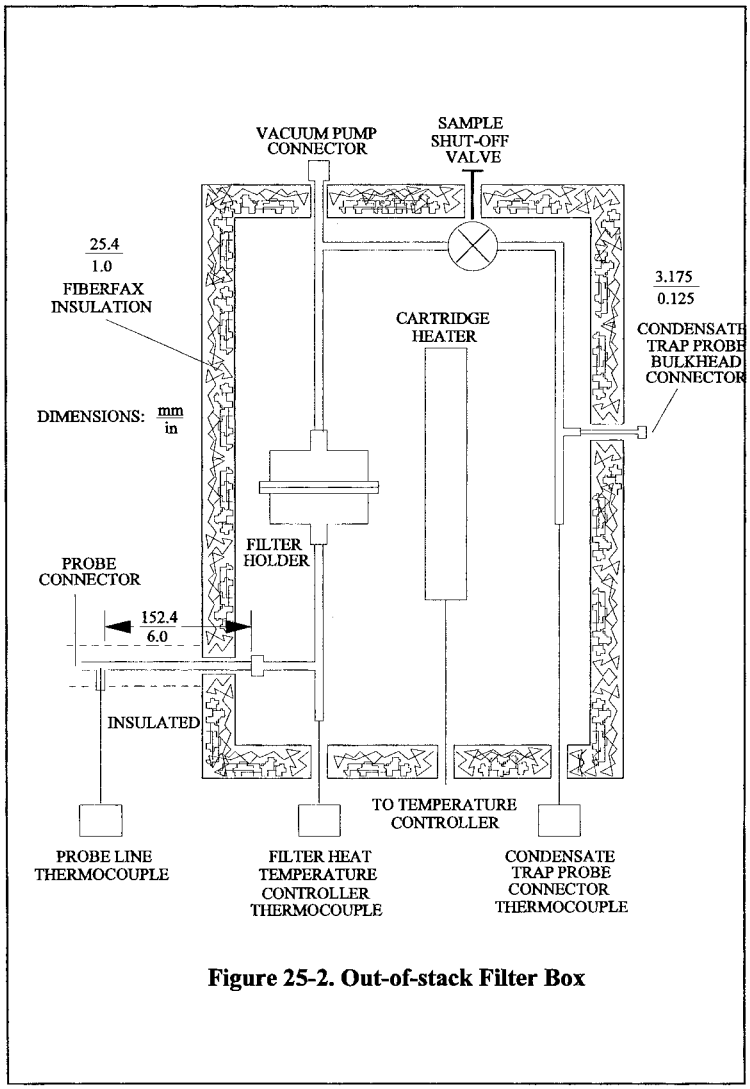


Figure 25-2. Out-of-stack Filter Box

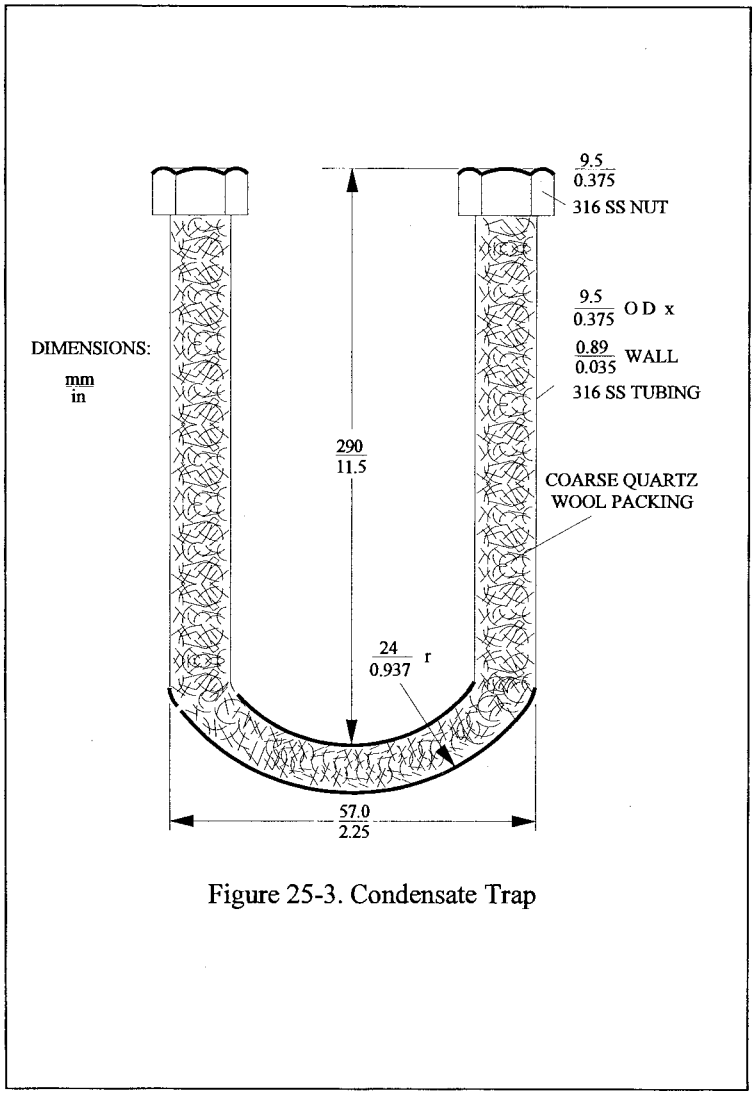


Figure 25-3. Condensate Trap

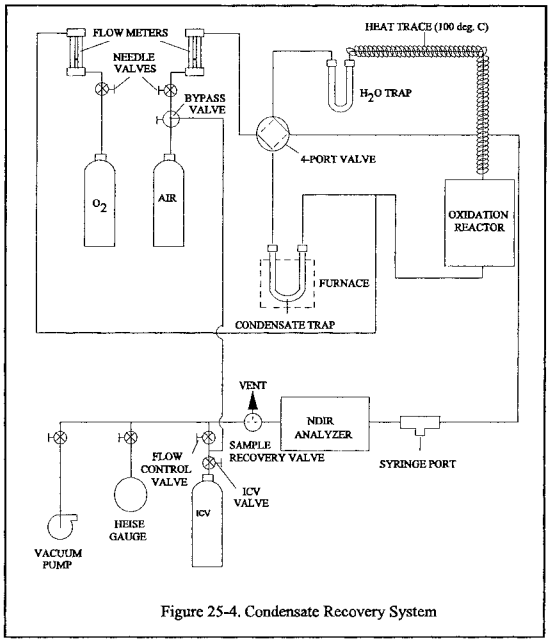


Figure 25-4. Condensate Recovery System

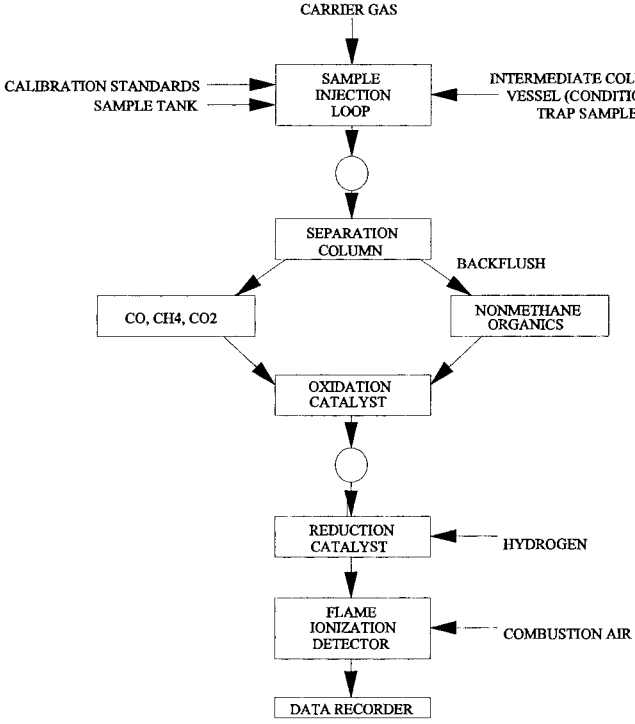


Figure 25-5. Simplified Schematic of Nonmethane Organic (NMO) Analyzer

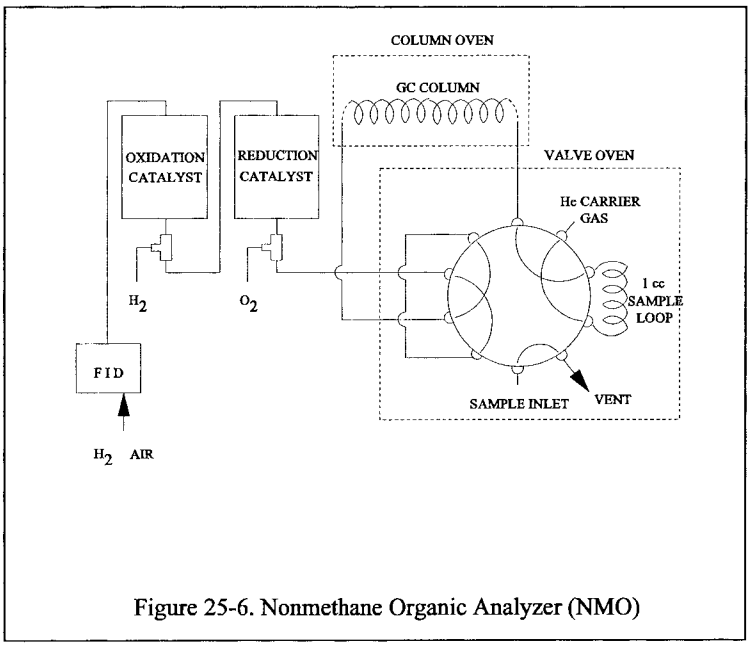


Figure 25-6. Nonmethane Organic Analyzer (NMO)

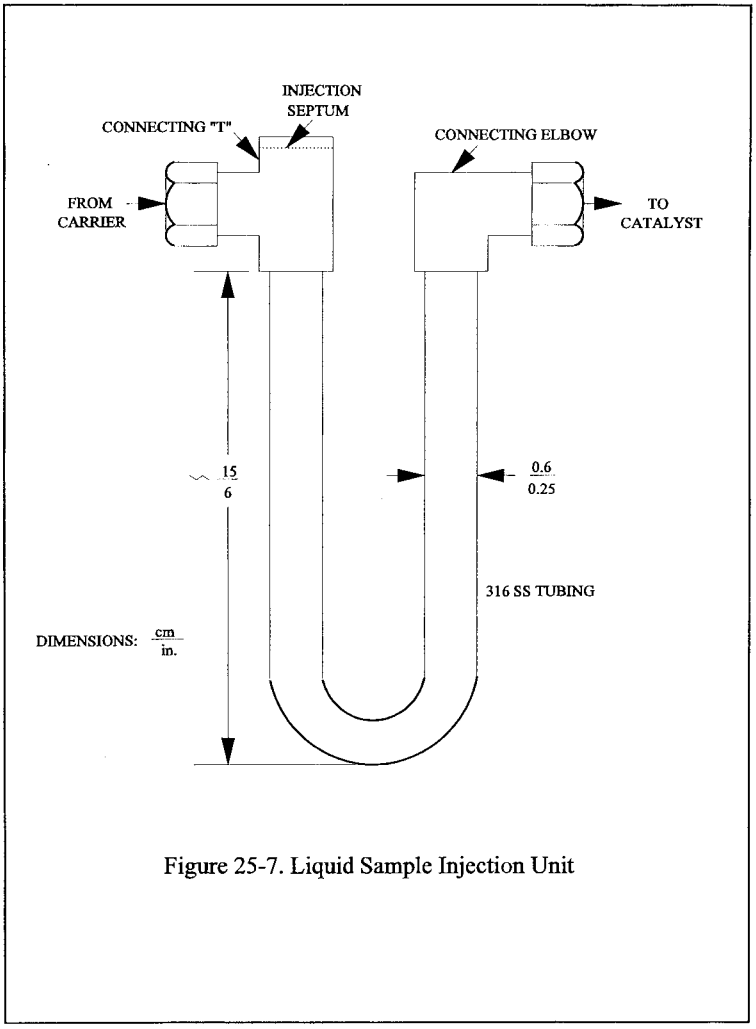


Figure 25-7. Liquid Sample Injection Unit

VOLATILE ORGANIC CARBON

FACILITY _____ SAMPLE LOCATION _____

LOCATION _____ OPERATOR _____

DATE _____ RUN NUMBER _____

TANK NUMBER _____ TRAP NUMBER _____ SAMPLE ID NUMBER _____

TANK VACUUM mm HG	TANK VACUUM cm Hg	BAROMETRIC PRESSURE mm Hg	AMBIENT TEMPERATURE °C
PRETEST (MANOMETER)	(GAUGE)		
POST-TEST (MANOMETER)	(GAUGE)		

LEAK RATE _____ cm Hg / l fl min _____

PRETEST _____

TIME CLOCK/SAMPLE	VACUUM cm Hg	FLOWMETER SETTINGS	COMMENTS

Figure 25-8. Example Field Data Form

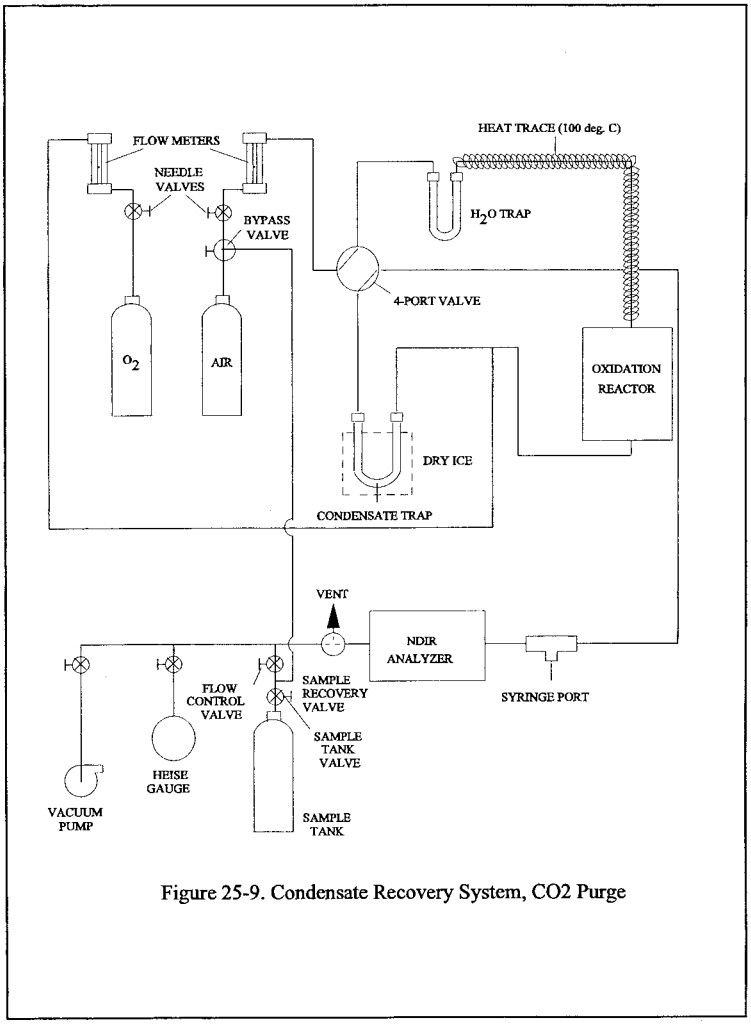


Figure 25-9. Condensate Recovery System, CO2 Purge

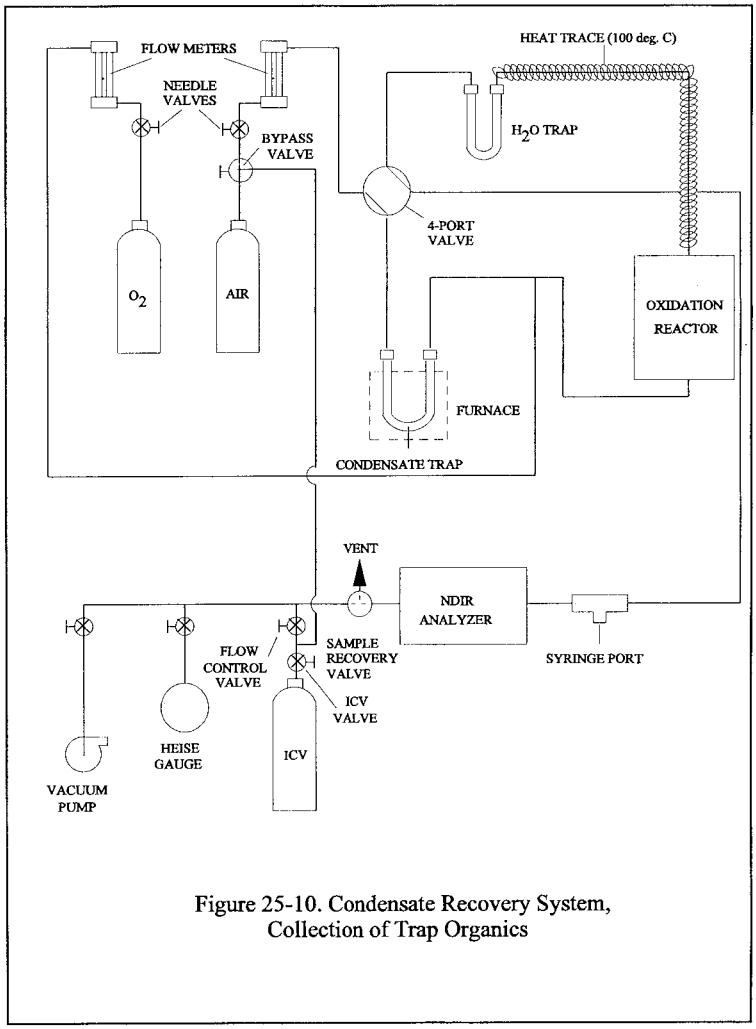


Figure 25-10. Condensate Recovery System, Collection of Trap Organics

METHOD 25A—DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A FLAME IONIZATION ANALYZER

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total Organic Compounds	N/A	<2% of span.

1.2 Applicability. This method is applicable for the determination of total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the source through a heated sample line and glass fiber filter to a flame ionization analyzer (FIA). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

3.0 Definitions

3.1 *Calibration drift* means the difference in the measurement system response to a mid-level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

3.2 *Calibration error* means the difference between the gas concentration indicated by the measurement system and the know concentration of the calibration gas.

3.3 *Calibration gas* means a known concentration of a gas in an appropriate diluent gas.

3.4 *Measurement system* means the total equipment required for the determination of the gas concentration. The system consists of the following major subsystems:

3.4.1 *Sample interface* means that portion of a system used for one or more of the following: sample acquisition, sample transportation, sample conditioning, or protection of the analyzer(s) from the effects of the stack effluent.

3.4.2 *Organic analyzer* means that portion of the measurement system that senses the gas to be measured and generates an output proportional to its concentration.

3.5 *Response time* means the time interval from a step change in pollutant concentration at the inlet to the emission measurement system to the time at which 95 percent of the corresponding final value is reached as displayed on the recorder.

3.6 *Span Value* means the upper limit of a gas concentration measurement range that is specified for affected source categories in the applicable part of the regulations. The span value is established in the applicable regulation and is usually 1.5 to 2.5 times the applicable emission limit. If no span value is provided, use a span value equivalent to 1.5 to 2.5 times the expected concentration. For convenience, the span value should correspond to 100 percent of the recorder scale.

3.7 *Zero drift* means the difference in the measurement system response to a zero level calibration gas before or after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

5.2 Explosive Atmosphere. This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

6.0 Equipment and Supplies

6.1 Measurement System. Any measurement system for total organic concentration that meets the specifications of this method. A schematic of an acceptable measurement system is shown in Figure 25A–1. All sampling components leading to the analyzer shall be heated ≥110 °C (220 °F) throughout the sampling period, unless safety reasons are cited (Section 5.2) The essential components of the measurement system are described below:

6.1.1 Organic Concentration Analyzer. A flame ionization analyzer (FIA) capable of meeting or exceeding the specifications of this method. The flame ionization detector block shall be heated >120 °C (250 °F).

6.1.2 Sample Probe. Stainless steel, or equivalent, three-hole rake type. Sample holes shall be 4 mm (0.16-in.) in diameter or smaller and located at 16.7, 50, and 83.3 percent of the equivalent stack diameter. Alternatively, a single opening probe may be used so that a gas sample is collected from the centrally located 10 percent area of the stack cross-section.

6.1.3 Heated Sample Line. Stainless steel or Teflon'' tubing to transport the sample gas

to the analyzer. The sample line should be heated (≥110 °C) to prevent any condensation.

6.1.4 Calibration Valve Assembly. A three-way valve assembly to direct the zero and calibration gases to the analyzers is recommended. Other methods, such as quick-connect lines, to route calibration gas to the analyzers are applicable.

6.1.5 Particulate Filter. An in-stack or an out-of-stack glass fiber filter is recommended if exhaust gas particulate loading is significant. An out-of-stack filter should be heated to prevent any condensation.

6.1.6 Recorder. A strip-chart recorder, analog computer, or digital recorder for recording measurement data. The minimum data recording requirement is one measurement value per minute.

7.0 Reagents and Standards

7.1 Calibration Gases. The calibration gases for the gas analyzer shall be propane in air or propane in nitrogen. Alternatively, organic compounds other than propane can be used; the appropriate corrections for response factor must be made. Calibration gases shall be prepared in accordance with the procedure listed in Citation 2 of section 16. Additionally, the manufacturer of the cylinder should provide a recommended shelf life for each calibration gas cylinder over which the concentration does not change more than ±2 percent from the certified value. For calibration gas values not generally available (*i.e.*, organics between 1 and 10 percent by volume), alternative methods for preparing calibration gas mixtures, such as dilution systems (Test Method 205, 40 CFR Part 51, Appendix M), may be used with prior approval of the Administrator.

7.1.1 Fuel. A 40 percent H_2/60 percent N_2 gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value.

7.1.2 Zero Gas. High purity air with less than 0.1 part per million by volume (ppmv) of organic material (propane or carbon equivalent) or less than 0.1 percent of the span value, whichever is greater.

7.1.3 Low-level Calibration Gas. An organic calibration gas with a concentration equivalent to 25 to 35 percent of the applicable span value.

7.1.4 Mid-level Calibration Gas. An organic calibration gas with a concentration equivalent to 45 to 55 percent of the applicable span value.

7.1.5 High-level Calibration Gas. An organic calibration gas with a concentration equivalent to 80 to 90 percent of the applicable span value.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Selection of Sampling Site. The location of the sampling site is generally specified by the applicable regulation or purpose of the test (*i.e.*, exhaust stack, inlet line, etc.). The sample port shall be located to meet the testing requirements of Method 1.

8.2 Location of Sample Probe. Install the sample probe so that the probe is centrally located in the stack, pipe, or duct and is sealed tightly at the stack port connection.

8.3 Measurement System Preparation. Prior to the emission test, assemble the measurement system by following the manufacturer's written instructions for preparing sample interface and the organic analyzer. Make the system operable (Section 10.1).

8.4 Calibration Error Test. Immediately prior to the test series (within 2 hours of the start of the test), introduce zero gas and high-level calibration gas at the calibration valve assembly. Adjust the analyzer output to the appropriate levels, if necessary. Calculate the predicted response for the low-level and mid-level gases based on a linear response line between the zero and high-level response. Then introduce low-level and mid-level calibration gases successively to the measurement system. Record the analyzer responses for low-level and mid-level calibration gases and determine the differences between the measurement system responses and the predicted responses. These differences must be less than 5 percent of the respective calibration gas value. If not, the measurement system is not acceptable and must be replaced or repaired prior to testing. No adjustments to the measurement system shall be conducted after the calibration and before the drift check (Section 8.6.2). If adjustments are necessary before the completion of the test series, perform the drift checks prior to the required adjustments and repeat the calibration following the adjustments. If multiple electronic ranges are to be used, each additional range must be checked with a mid-level calibration gas to verify the multiplication factor.

8.5 Response Time Test. Introduce zero gas into the measurement system at the calibration valve assembly. When the system output has stabilized, switch quickly to the high-level calibration gas. Record the time from the concentration change to the measurement system response equivalent to 95 percent of the step change. Repeat the test three times and average the results.

8.6 Emission Measurement Test Procedure.

8.6.1 Organic Measurement. Begin sampling at the start of the test period, recording time and any required process information as appropriate. In particulate, note on the recording chart, periods of process interruption or cyclic operation.

8.6.2 Drift Determination. Immediately following the completion of the test period and hourly during the test period, reintroduce the zero and mid-level calibration gases, one at a time, to the measurement system at the calibration valve assembly. (Make no adjustments to the measurement system until both the zero and calibration drift checks are made.) Record the analyzer response. If the drift values exceed the specified limits, invalidate the test results preceding the check and repeat the test following corrections to the measurement system. Alternatively, recalibrate the test measurement system as in section 8.4 and report the results using both sets of calibration data (i.e., data determined prior to the test period and data determined following the test period).

NOTE: Note on the recording chart periods of process interruption or cyclic operation.

9.0 Quality Control

Method section	Quality control measure	Effect
8.4	Zero and calibration drift tests	Ensures that bias introduced by drift in the measurement system output during the run is no greater than 3 percent of span.

10.0 Calibration and Standardization

10.1 FIA equipment can be calibrated for almost any range of total organic concentrations. For high concentrations of organics (>1.0 percent by volume as propane), modifications to most commonly available analyzers are necessary. One accepted method of equipment modification is to decrease the size of the sample to the analyzer through the use of a smaller diameter sample capillary. Direct and continuous measurement of organic concentration is a necessary consideration when determining any modification design.

11.0 Analytical Procedure

The sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Calculations and Data Analysis

12.1 Determine the average organic concentration in terms of ppmv as propane or other calibration gas. The average shall be determined by integration of the output recording over the period specified in the applicable regulation. If results are required in terms of ppmv as carbon, adjust measured concentrations using Equation 25A–1.

$$C_c = K C_{meas} \qquad \text{Eq. 25A-1}$$

Where:

C_c = Organic concentration as carbon, ppmv.
C_{meas} = Organic concentration as measured, ppmv.
K = Carbon equivalent correction factor.
= 2 for ethane.
= 3 for propane.
= 4 for butane.
= Appropriate response factor for other organic calibration gases.

13.0 Method Performance

13.1 Measurement System Performance Specifications.

13.1.1 Zero Drift. Less than ±3 percent of the span value.

13.1.2 Calibration Drift. Less than ±3 percent of span value.

13.1.3 Calibration Error. Less than ±5 percent of the calibration gas value.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Measurement of Volatile Organic Compounds—Guideline Series. U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA–450/2–78–041. June 1978. p. 46–54.

2. EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards. U.S. Environmental Protection Agency, Quality Assurance and Technical Support Division. Research Triangle Park, N.C. September 1993.

3. Gasoline Vapor Emission Laboratory Evaluation—Part 2. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, NC. EMB Report No. 75–GAS–6. August 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

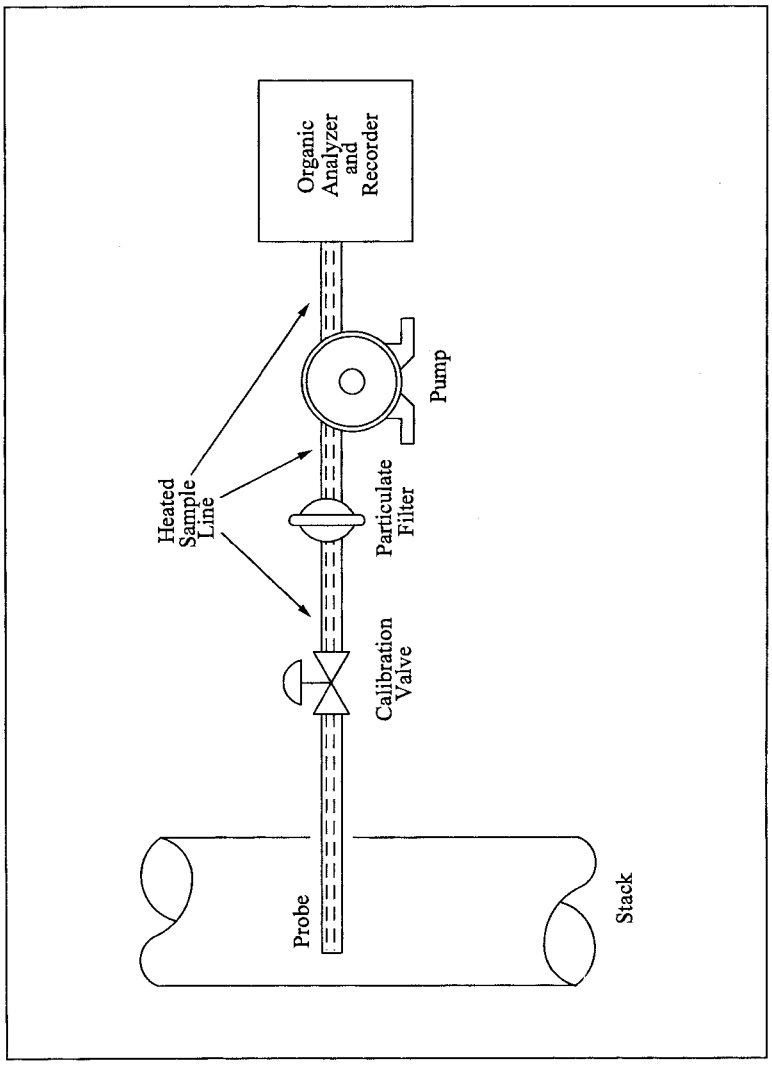


Figure 25A-1. Organic Concentration Measurement System.

METHOD 25B—DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A NONDISPERSIVE INFRARED ANALYZER

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 6C, and Method 25A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total Organic Compounds	N/A	<2% of span.

1.2 Applicability. This method is applicable for the determination of total gaseous organic concentration of vapors consisting primarily of alkanes. Other organic materials may be measured using the general procedure in this method, the appropriate calibration gas, and an analyzer set to the appropriate absorption band.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

A gas sample is extracted from the source through a heated sample line, if necessary, and glass fiber filter to a nondispersive infrared analyzer (NDIR). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

3.0 Definitions

Same as Method 25A, section 3.0.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

5.2 Explosive Atmosphere. This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

6.0 Equipment and Supplies

Same as Method 25A, section 6.0, with the exception of the following:

6.1 Organic Concentration Analyzer. A nondispersive infrared analyzer designed to measure alkane organics and capable of meeting or exceeding the specifications in this method.

7.0 Reagents and Standards

Same as Method 25A, section 7.1. No fuel gas is required for an NDIR.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as Method 25A, section 8.0.

9.0 Quality Control

Same as Method 25A, section 9.0.

10.0 Calibration and Standardization

Same as Method 25A, section 10.0.

11.0 Analytical Procedure

The sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Calculations and Data Analysis

Same as Method 25A, section 12.0.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 25A, section 16.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 25C—DETERMINATION OF NONMETHANE ORGANIC COMPOUNDS (NMOC) IN LANDFILL GASES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should also have a thorough knowledge of EPA Method 25.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Nonmethane organic compounds (NMOC).	No CAS number assigned.

1.2 Applicability. This method is applicable to the sampling and measurement of NMOC as carbon in landfill gases (LFG).

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A sample probe that has been perforated at one end is driven or augured to a depth of 0.9 m (3 ft) below the bottom of the landfill cover. A sample of the landfill gas is extracted with an evacuated cylinder. The NMOC content of the gas is determined by

injecting a portion of the gas into a gas chromatographic column to separate the NMOC from carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4); the NMOC are oxidized to CO_2, reduced to CH_4, and measured by a flame ionization detector (FID). In this manner, the variable response of the FID associated with different types of organics is eliminated.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Since this method is complex, only experienced personnel should perform this test. LFG contains methane, therefore explosive mixtures may exist on or near the landfill. It is advisable to take appropriate safety precautions when testing landfills, such as refraining from smoking and installing explosion-proof equipment.

6.0 Equipment and Supplies

6.1 Sample Probe. Stainless steel, with the bottom third perforated. Teflon probe liners and sampling lines are also allowed. Non-perforated probes are allowed as long as they are withdrawn to create a gap equivalent to having the bottom third perforated. The sample probe must be capped at the bottom and must have a threaded cap with a sampling attachment at the top. The sample probe must be long enough to go through and extend no less than 0.9 m (3 ft) below the landfill cover. If the sample probe is to be driven into the landfill, the bottom cap should be designed to facilitate driving the probe into the landfill.

6.2 Sampling Train.

6.2.1 Rotameter with Flow Control Valve. Capable of measuring a sample flow rate of 100 ±10 ml/min. The control valve must be made of stainless steel.

6.2.2 Sampling Valve. Stainless steel.

6.2.3 Pressure Gauge. U-tube mercury manometer, or equivalent, capable of measuring pressure to within 1 mm Hg (0.5 in H_2O) in the range of 0 to 1,100 mm Hg (0 to 590 in H_2O).

6.2.4 Sample Tank. Stainless steel or aluminum cylinder, equipped with a stainless steel sample tank valve.

6.3 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg (5.4 in H_2O).

6.4 Purging Pump. Portable, explosion proof, and suitable for sampling NMOC.

6.5 Pilot Probe Procedure. The following are needed only if the tester chooses to use the procedure described in section 8.2.1.

6.5.1 Pilot Probe. Tubing of sufficient strength to withstand being driven into the landfill by a post driver and an outside diameter of at least 6 mm (0.25 in.) smaller than the sample probe. The pilot probe shall be capped on both ends and long enough to go through the landfill cover and extend no less than 0.9 m (3 ft) into the landfill.

6.5.2 Post Driver and Compressor. Capable of driving the pilot probe and the sampling probe into the landfill. The Kitty Hawk portable post driver has been found to be acceptable.

6.6 Auger Procedure. The following are needed only if the tester chooses to use the procedure described in section 8.2.2.

6.6.1 Auger. Capable of drilling through the landfill cover and to a depth of no less than 0.9 m (3 ft) into the landfill.

6.6.2 Pea Gravel.

6.6.3 Bentonite.

6.7 NMOC Analyzer, Barometer, Thermometer, and Syringes. Same as in sections 6.3.1, 6.3.2, 6.33, and 6.2.10, respectively, of Method 25.

7.0 Reagents and Standards

7.1 NMOC Analysis. Same as in Method 25, section 7.2.

7.2 Calibration. Same as in Method 25, section 7.4, except omit section 7.4.3.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sample Tank Evacuation and Leak-Check. Conduct the sample tank evacuation and leak-check either in the laboratory or the field. Connect the pressure gauge and sampling valve to the sample tank. Evacuate the sample tank to 10 mm Hg (5.4 in H_2O) absolute pressure or less. Close the sampling valve, and allow the tank to sit for 30 minutes. The tank is acceptable if no change more than ±2 mm is noted. Include the results of the leak-check in the test report.

8.2 Sample Probe Installation. The tester may use the procedure in section 8.2.1 or 8.2.2.

8.2.1 Pilot Probe Procedure. Use the post driver to drive the pilot probe at least 0.9 m (3 ft) below the landfill cover. Alternative procedures to drive the probe into the landfill may be used subject to the approval of the Administrator's designated representative.

8.2.1.1 Remove the pilot probe and drive the sample probe into the hole left by the pilot probe. The sample probe shall extend at least 0.9 m (3 ft) below the landfill cover and shall protrude about 0.3 m (1 ft) above the landfill cover. Seal around the sampling probe with bentonite and cap the sampling probe with the sampling probe cap.

8.2.2 Auger Procedure. Use an auger to drill a hole to at least 0.9 m (3 ft) below the landfill cover. Place the sample probe in the hole and backfill with pea gravel to a level 0.6 m (2 ft) from the surface. The sample probe shall protrude at least 0.3 m (1 ft) above the landfill cover. Seal the remaining area around the probe with bentonite. Allow 24

hours for the landfill gases to equilibrate inside the augured probe before sampling.

8.2.3 Driven Probes. Closed-point probes may be driven directly into the landfill in a single step. This method may not require backfilling if the probe is adequately sealed by its insertion. Unperforated probes that are inserted in this manner and withdrawn at a distance from a detachable tip to create an open space are also acceptable.

8.3 Sample Train Assembly. Just before assembling the sample train, measure the sample tank vacuum using the pressure gauge. Record the vacuum, the ambient temperature, and the barometric pressure at this time. Assemble the sampling probe purging system as shown in Figure 25C–1.

8.4 Sampling Procedure. Open the sampling valve and use the purge pump and the flow control valve to evacuate at least two sample probe volumes from the system at a flow rate of 500 ml/min or less. Close the sampling valve and replace the purge pump with the sample tank apparatus as shown in Figure 25C–2. Open the sampling valve and the sample tank valve and, using the flow control valve, sample at a flow rate of 500 ml/min or less until either a constant flow rate can no longer be maintained because of reduced sample tank vacuum or the appropriate composite volume is attained. Disconnect the sampling tank apparatus and pressurize the sample cylinder to approximately 1,060 mm Hg (567 in. H_2O) absolute pressure with helium, and record the final pressure. Alternatively, the sample tank may be pressurized in the lab.

8.4.1 The following restrictions apply to compositing samples from different probe sites into a single cylinder: (1) Individual composite samples per cylinder must be of equal volume; this must be verified by recording the flow rate, sampling time, vacuum readings, or other appropriate volume measuring data, (2) individual composite samples must have a minimum volume of 1 liter unless data is provided showing smaller volumes can be accurately measured, and (3) composite samples must not be collected using the final cylinder vacuum as it diminishes to ambient pressure.

8.4.2 Use Method 3C to determine the percent N_2 in each cylinder. The presence of N_2 indicates either infiltration of ambient air into the landfill gas sample or an inappropriate testing site has been chosen where anaerobic decomposition has not begun. The landfill gas sample is acceptable if the concentration of N_2 is less than 20 percent. Alternatively, Method 3C may be used to determine the oxygen content of each cylinder as an air infiltration test. With this option, the oxygen content of each cylinder must be less than 5 percent.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4.2	Verify that landfill gas sample contains less than 20 percent N_2 or 5 percent O_2.	Ensures that ambient air was not drawn into the landfill gas sample and gas was sampled from an appropriate location.
10.1, 10.2	NMOC analyzer initial and daily performance checks.	Ensures precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Initial NMOC Analyzer Performance Test. Same as in Method 25, section 10.1, except omit the linearity checks for CO_2 standards.

10.2 NMOC Analyzer Daily Calibration.

10.2.1 NMOC Response Factors. Same as in Method 25, section 10.2.2.

10.3 Sample Tank Volume. The volume of the gas sampling tanks must be determined. Determine the tank volumes by weighing them empty and then filled with deionized water; weigh to the nearest 5 g, and record the results. Alternatively, measure the volume of water used to fill them to the nearest 5 ml.

11.0 Analytical Procedures

11.1 The oxidation, reduction, and measurement of NMOC's is similar to Method 25. Before putting the NMOC analyzer into routine operation, conduct an initial performance test. Start the analyzer, and perform all the necessary functions in order to put the analyzer into proper working order. Conduct the performance test according to the procedures established in section 10.1. Once the performance test has been successfully completed and the NMOC calibration response factor has been determined, proceed with sample analysis as follows:

11.1.1 Daily Operations and Calibration Checks. Before and immediately after the analysis of each set of samples or on a daily basis (whichever occurs first), conduct a calibration test according to the procedures established in section 10.2. If the criteria of the daily calibration test cannot be met, repeat

the NMOC analyzer performance test (Section 10.1) before proceeding.

11.1.2 Operating Conditions. Same as in Method 25, section 11.2.1.

11.1.3 Analysis of Sample Tank. Purge the sample loop with sample, and then inject the sample. Under the specified operating conditions, the CO_2 in the sample will elute in approximately 100 seconds. As soon as the detector response returns to baseline following the CO_2 peak, switch the carrier gas flow to backflush, and raise the column oven temperature to 195 °C (383 °F) as rapidly as possible. A rate of 30 °C/min (54 °F/min) has been shown to be adequate. Record the value obtained for any measured NMOC. Return the column oven temperature to 85 °C (185 °F) in preparation for the next analysis. Analyze each sample in triplicate, and report the average as C_{tm}.

12.0 Data Analysis and Calculations

NOTE: All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge or manometer pressure.

12.1 Nomenclature

B_w = Moisture content in the sample, fraction.
C_{N2} = N_2 concentration in the diluted sample gas.
C_{mN2} = Measured N_2 concentration, fraction in landfill gas.
C_{mOx} = Measured Oxygen concentration, fraction in landfill gas.
C_{Ox} = Oxygen concentration in the diluted sample gas.
C_t = Calculated NMOC concentration, ppmv C equivalent.
C_{tm} = Measured NMOC concentration, ppmv C equivalent.
P_b = Barometric pressure, mm Hg.
P_t = Gas sample tank pressure after sampling, but before pressurizing, mm Hg absolute.
P_{tf} = Final gas sample tank pressure after pressurizing, mm Hg absolute.
P_{ti} = Gas sample tank pressure after evacuation, mm Hg absolute.
P_w = Vapor pressure of H_2O (from Table 25C–1), mm Hg.
r = Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 . . . r).
T_t = Sample tank temperature at completion of sampling, °K.
T_{ti} = Sample tank temperature before sampling, °K.
T_{tf} = Sample tank temperature after pressuring, °K.

12.2 Water Correction. Use Table 25C–1 (Section 17.0), the LFG temperature, and barometric pressure at the sampling site to calculate B_w.

$$B_w = \frac{P_w}{P_b} \qquad \text{Eq. 25C-1}$$

12.3 Nitrogen Concentration in the landfill gas. Use equation 25C–2 to calculate the measured concentration of nitrogen in the original landfill gas.

$$C_{N2} = \left[\frac{\left(\frac{P_{tf}}{T_{tf}}\right)}{\left(\left(\frac{P_t}{T_t}\right)-\left(\frac{P_{ti}}{T_{ti}}\right)\right)}\right] C_{mN2} \qquad \text{Eq.25C-2}$$

12.4 Oxygen Concentration in the landfill gas. Use equation 25C–3 to calculate the measured concentration of oxygen in the original landfill gas.

$$C_{Ox} = \left[\frac{\left(\frac{P_{tf}}{T_{tf}}\right)}{\left(\left(\frac{P_t}{T_t}\right)-\left(\frac{P_{ti}}{T_{ti}}\right)\right)}\right] C_{mOx} \qquad \text{Eq.25C-3}$$

12.5 You must correct the NMOC Concentration for the concentration of nitrogen or oxygen based on which gas or gases passes the requirements in section 9.1.

12.5.1 NMOC Concentration with nitrogen correction. Use Equation 25C–4 to calculate the concentration of NMOC for each sample tank when the nitrogen concentration is less than 20 percent.

$$C_t = \frac{\frac{P_{tf}}{T_{tf}}}{\left(\frac{P_t}{T_t}-\frac{P_{ti}}{T_{ti}}\right)\left(1-\frac{99}{78}C_{N2}\right)-B_w}\frac{1}{r}\sum_{j=1}^{r} C_{tm(j)} \qquad \text{Eq. 25C-4}$$

12.5.2 NMOC Concentration with oxygen correction. Use Equation 25C–5 to calculate the concentration of NMOC for each sample tank if the landfill gas oxygen is less than 5 percent and the landfill gas nitrogen concentration is greater than 20 percent.

$$C_t = \frac{\frac{P_{tf}}{T_{tf}}}{\left(\frac{P_t}{T_t}-\frac{P_{ti}}{T_{ti}}\right)\left(1-\frac{99}{21}C_{Ox}\right)-B_w}\frac{1}{r}\sum_{j=1}^{r} C_{tm(j)} \qquad \text{Eq. 25C-5}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, Albert E., Samuel Witz, and Robert D. MacPhee. Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, Massachusetts. June 15–20, 1975.) 14 p.

2. Salo, Albert E., William L. Oaks, and Robert D. MacPhee. Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, Colorado. June 9–13, 1974.) 25 p.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

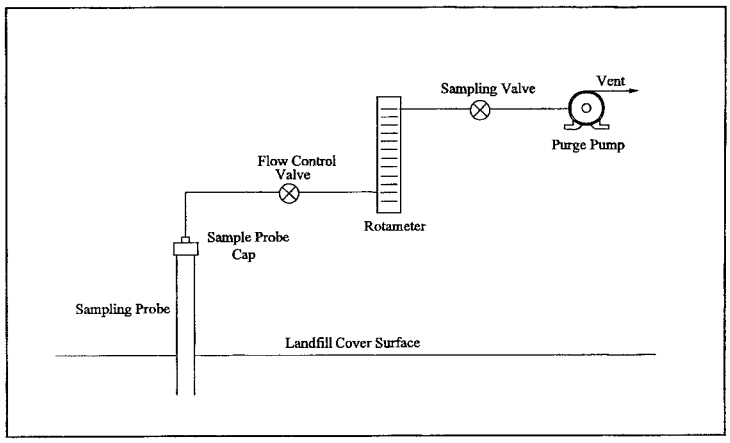


Figure 25C-1. Schematic of Sampling Probe Purging System

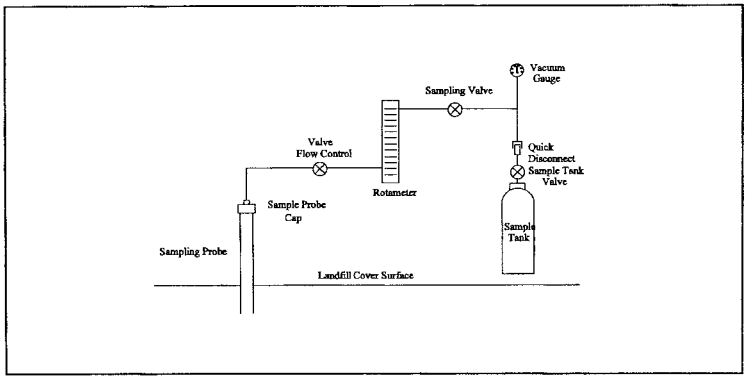


Figure 25C-2. Schematic of Sampling Train.

TABLE 25C–1—MOISTURE CORRECTION

Temperature, °C	Vapor Pressure of H_2O, mm Hg	Temperature, °C	Vapor Pressure of H_2O, mm Hg
4	6.1	18	15.5
6	7.0	20	17.5
8	8.0	22	19.8
10	9.2	24	22.4
12	10.5	26	25.2
14	12.0	28	28.3

TABLE 25C–1—MOISTURE CORRECTION—Continued

Temperature, °C	Vapor Pressure of H_2O, mm Hg	Temperature, °C	Vapor Pressure of H_2O, mm Hg
16	13.6	30	31.8

METHOD 25D—DETERMINATION OF THE VOLATILE ORGANIC CONCENTRATION OF WASTE SAMPLES

NOTE: Performance of this method should not be attempted by persons unfamiliar with the operation of a flame ionization detector (FID) or an electrolytic conductivity detector (ELCD) because knowledge beyond the scope of this presentation is required.

1.0 Scope and Application

1.1 Analyte. Volatile Organic Compounds. No CAS No. assigned.

1.2 Applicability. This method is applicable for determining the volatile organic (VO) concentration of a waste sample.

2.0 Summary of Method

2.1 Principle. A sample of waste is obtained at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to the atmosphere). The sample is suspended in an organic/aqueous matrix, then heated and purged with nitrogen for 30 min. in order to separate certain organic compounds. Part of the sample is analyzed for carbon concentration, as methane, with an FID, and part of the sample is analyzed for chlorine concentration, as chloride, with an ELCD. The VO concentration is the sum of the carbon and chlorine content of the sample.

3.0 Definitions

3.1 *Well-mixed* in the context of this method refers to turbulent flow which results in multiple-phase waste in effect behaving as single-phase waste due to good mixing.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1 Sampling. The following equipment is required:

6.1.1 Sampling Tube. Flexible Teflon, 0.25 in. ID (6.35 mm).

6.1.2 Sample Container. Borosilicate glass, 40-mL, and a Teflon-lined screw cap capable of forming an air tight seal.

6.1.3 Cooling Coil. Fabricated from 0.25 in (6.35 mm). ID 304 stainless steel tubing with a thermocouple at the coil outlet.

6.2 Analysis. The following equipment is required.

6.2.1 Purging Apparatus. For separating the VO from the waste sample. A schematic of the system is shown in Figure 25D–1. The purging apparatus consists of the following major components.

6.2.1.1 Purging Flask. A glass container to hold the sample while it is heated and purged with dry nitrogen. The cap of the purging flask is equipped with three fittings: one for a purging lance (fitting with the #7 Ace-thread), one for the Teflon exit tubing (side fitting, also a #7 Ace-thread), and a third (a 50-mm Ace-thread) to attach the base of the purging flask as shown in Figure 25D–2. The base of the purging flask is a 50-mm ID (2 in) cylindrical glass tube. One end of the tube is open while the other end is sealed. Exact dimensions are shown in Figure 25D–2.

6.2.1.2 Purging Lance. Glass tube, 6-mm OD (0.2 in) by 30 cm (12 in) long. The purging end of the tube is fitted with a four-arm bubbler with each tip drawn to an opening 1 mm (0.04 in) in diameter. Details and exact dimensions are shown in Figure 25D–2.

6.2.1.3 Coalescing Filter. Porous fritted disc incorporated into a container with the same dimensions as the purging flask. The details of the design are shown in Figure 25D–3.

6.2.1.4 Constant Temperature Chamber. A forced draft oven capable of maintaining a uniform temperature around the purging flask and coalescing filter of 75 ±2 °C (167 ±3.6 °F).

6.2.1.5 Three-way Valve. Manually operated, stainless steel. To introduce calibration gas into system.

6.2.1.6 Flow Controllers. Two, adjustable. One capable of maintaining a purge gas flow rate of 6 ±0.06 L/min (0.2 ±0.002 ft^3/min) The other capable of maintaining a calibration gas flow rate of 1–100 mL/min (0.00004–0.004 ft^3/min).

6.2.1.7 Rotameter. For monitoring the air flow through the purging system (0–10 L/min)(0–0.4 ft^3/min).

6.2.1.8 Sample Splitters. Two heated flow restrictors (placed inside oven or heated to 120 ±10 °C (248 ±18 °F)). At a purge rate of 6 L/min (0.2 ft^3/min), one will supply a constant flow to the first detector (the rest of the flow will be directed to the second sample splitter). The second splitter will split the analytical flow between the second detector and the flow restrictor. The approximate flow to the FID will be 40 mL/min (0.0014 ft^3/min) and to the ELCD will be 15 mL/min (0.0005 ft^3/min), but the exact flow must be adjusted to be compatible with the individual detector and to meet its linearity requirement. The two sample splitters will be connected to each other by 1/8″ OD (3.175 mm) stainless steel tubing.

6.2.1.9 Flow Restrictor. Stainless steel tubing, 1/8″ OD (3.175 mm), connecting the second sample splitter to the ice bath. Length is determined by the resulting pressure in the purging flask (as measured by the pressure gauge). The resulting pressure from the use of the flow restrictor shall be 6–7 psig.

6.2.1.10 Filter Flask. With one-hole stopper. Used to hold ice bath. Excess purge gas is vented through the flask to prevent condensation in the flowmeter and to trap volatile organic compounds.

6.2.1.11 Four-way Valve. Manually operated, stainless steel. Placed inside oven, used to bypass purging flask.

6.2.1.12 On/Off Valves. Two, stainless steel. One heat resistant up to 130 °C (266 °F) and placed between oven and ELCD. The other a toggle valve used to control purge gas flow.

6.2.1.13 Pressure Gauge. Range 0–40 psi. To monitor pressure in purging flask and coalescing filter.

6.2.1.14 Sample Lines. Teflon, 1/4″ OD (6.35 mm), used inside the oven to carry purge gas to and from purging chamber and to and from coalescing filter to four-way valve. Also used to carry sample from four-way valve to first sample splitter.

6.2.1.15 Detector Tubing. Stainless steel, 1/8″ OD (3.175 mm), heated to 120 ±10 °C (248 ±18 °F) . Used to carry sample gas from each sample splitter to a detector. Each piece of tubing must be wrapped with heat tape and insulating tape in order to insure that no cold spots exist. The tubing leading to the ELCD will also contain a heat-resistant on-off valve (Section 6.2.1.12) which shall also be wrapped with heat-tape and insulation.

6.2.2 Volatile Organic Measurement System. Consisting of an FID to measure the carbon concentration of the sample and an ELCD to measure the chlorine concentration.

6.2.2.1 FID. A heated FID meeting the following specifications is required.

6.2.2.1.1 Linearity. A linear response (±5 percent) over the operating range as demonstrated by the procedures established in section 10.1.1.

6.2.2.1.2 Range. A full scale range of 50 pg carbon/sec to 50 µg carbon/sec. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.2.2.1.3 Data Recording System. A digital integration system compatible with the FID for permanently recording the output of the detector. The recorder shall have the capability to start and stop integration at points selected by the operator or it shall be capable of the ''integration by slices'' technique (this technique involves breaking down the chromatogram into smaller increments, integrating the area under the curve for each portion, subtracting the background for each portion, and then adding all of the areas together for the final area count).

6.2.2.2 ELCD. An ELCD meeting the following specifications is required. 1-propanol must be used as the electrolyte. The electrolyte flow through the conductivity cell shall be 1 to 2 mL/min (0.00004 to 0.00007 ft^3/min).

NOTE: A ¼-in. ID (6.35 mm) quartz reactor tube is strongly recommended to reduce carbon buildup and the resulting detector maintenance.

6.2.2.2.1 Linearity. A linear response (±10 percent) over the response range as demonstrated by the procedures in section 10.1.2.

6.2.2.2.2 Range. A full scale range of 5.0 pg/sec to 500 ng/sec chloride. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.2.2.2.3 Data Recording System. A digital integration system compatible with the output voltage range of the ELCD. The recorder must have the capability to start and stop integration at points selected by the operator or it shall be capable of performing the ''integration by slices'' technique.

7.0 Reagents and Standards

7.1 Sampling.

7.1.1 Polyethylene Glycol (PEG). Ninety-eight percent pure with an average molecular weight of 400. Before using the PEG, remove any organic compounds that might be detected as volatile organics by heating it to 120 °C (248 °F) and purging it with nitrogen at a flow rate of 1 to 2 L/min (0.04 to 0.07 ft^3/min) for 2 hours. The cleaned PEG must be stored under a 1 to 2 L/min (0.04 to 0.07 ft^3/min) nitrogen purge until use. The purge apparatus is shown in Figure 25D–4.

7.2 Analysis.

7.2.1 Sample Separation. The following are required for the sample purging step.

7.2.1.1 PEG. Same as section 7.1.1.

7.2.1.2 Purge Gas. Zero grade nitrogen (N_2), containing less than 1 ppm carbon.

7.2.2 Volatile Organics Measurement. The following are required for measuring the VO concentration.

7.2.2.1 Hydrogen (H_2). Zero grade H_2, 99.999 percent pure.

7.2.2.2 Combustion Gas. Zero grade air or oxygen as required by the FID.

7.2.2.3 Calibration Gas. Pressurized gas cylinder containing 10 percent propane and 1 percent 1,1-dichloroethylene by volume in nitrogen.

7.2.2.4 Water. Deionized distilled water that conforms to American Society for Testing and Materials Specification D 1193–74, Type 3, is required for analysis. At the option of the analyst, the $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations are not expected to be present.

7.2.2.5 1-Propanol. ACS grade or better. Electrolyte Solution. For use in the ELCD.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling.

8.1.1 Sampling Plan Design and Development. Use the procedures in chapter nine of Reference 1 in section 16 as guidance in developing a sampling plan.

8.1.2 Single Phase or Well-mixed Waste.

8.1.2.1 Install a sampling tap to obtain the sample at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to the atmosphere). Assemble the sampling apparatus as shown in Figure 25D–5.

8.1.2.2 Prepare the sampling containers as follows: Pour 30 mL of clean PEG into the container. PEG will reduce but not eliminate the loss of organics during sample collection. Weigh the sample container with the screw cap, the PEG, and any labels to the nearest 0.01 g and record the weight (m_{st}). Store the containers in an ice bath until 1 hour before sampling (PEG will solidify at ice bath temperatures; allow the containers to reach room temperature before sampling).

8.1.2.3 Begin sampling by purging the sample lines and cooling coil with at least four volumes of waste. Collect the purged material in a separate container and dispose of it properly.

8.1.2.4 After purging, stop the sample flow and direct the sampling tube to a preweighed sample container, prepared as described in section 8.1.2.2. Keep the tip of the tube below the surface of the PEG during sampling to minimize contact with the atmosphere. Sample at a flow rate such that the temperature of the waste is less than 10 °C (50 °F). Fill the sample container and immediately cap it (within 5 seconds) so that a minimum headspace exists in the container. Store immediately in a cooler and cover with ice.

8.1.3 Multiple-phase Waste. Collect a 10 g sample of each phase of waste generated using the procedures described in section 8.1.2 or 8.1.5. Each phase of the waste shall be analyzed as a separate sample. Calculate the weighted average VO concentration of the waste using Equation 25D–13 (Section 12.14).

8.1.4 Solid waste. Add approximately 10 g of the solid waste to a container prepared in the manner described in section 8.1.2.2, minimizing headspace. Cap and chill immediately.

8.1.5 Alternative to Tap Installation. If tap installation is impractical or impossible, fill a large, clean, empty container by submerging the container into the waste below the surface of the waste. Immediately fill a container prepared in the manner described in section 8.1.2.2 with approximately 10 g of the waste collected in the large container. Minimize headspace, cap and chill immediately.

8.1.6 Alternative sampling techniques may be used upon the approval of the Administrator.

8.2 Sample Recovery.

8.2.1 Assemble the purging apparatus as shown in Figures 25D–1 and 25D–2. The oven shall be heated to 75 ±2 °C (167 ±3.6 °F). The sampling lines leading from the oven to the detectors shall be heated to 120 ±10 °C (248 ±18 °F) with no cold spots. The flame ionization detector shall be operated with a heated block. Adjust the purging lance so that it reaches the bottom of the chamber.

8.2.2 Remove the sample container from the cooler, and wipe the exterior of the container to remove any extraneous ice, water, or other debris. Reweigh the sample container to the nearest 0.01 g, and record the weight (m_{sf}). Pour the contents of the sample container into the purging flask, rinse the sample container three times with a total of 20 mL of PEG (since the sample container originally held 30 mL of PEG, the total volume of PEG added to the purging flask will be 50 mL), transferring the rinsings to the purging flask after each rinse. Cap purging flask between rinses. The total volume of PEG in the purging flask shall be 50 mL. Add 50 mL of water to the purging flask.

9.0 Quality Control

9.1 Quality Control Samples. If audit samples are not available, prepare and analyze the two types of quality control samples (QCS) listed in Sections 9.1.1 and 9.1.2. Before placing the system in operation, after a shutdown of greater than six months, and after any major modifications, analyze each QCS in triplicate. For each detector, calculate the percent recovery by dividing measured concentration by theoretical concentration and multiplying by 100. Determine the mean percent recovery for each detector for each QCS triplicate analysis. The RSD for any triplicate analysis shall be ≤10 percent. For QCS 1 (methylene chloride), the percent recovery shall be ≥90 percent for carbon as methane, and ≥55 percent for chlorine as chloride. For QCS 2 (1,3-dichloro-2-propanol), the percent recovery shall be ≤15 percent for carbon as methane, and ≤6 percent for chlorine as chloride. If the analytical system does not meet the above-mentioned criteria for both detectors, check the system parameters (temperature, system pressure, purge rate, etc.), correct the problem, and repeat the triplicate analysis of each QCS.

9.1.1 QCS 1, Methylene Chloride. Prepare a stock solution by weighing, to the nearest 0.1 mg, 55 µL of HPLC grade methylene chloride in a tared 5 mL volumetric flask. Record the weight in milligrams, dilute to 5 mL with cleaned PEG, and inject 100 µL of the stock solution into a sample prepared as a water blank (50 mL of cleaned PEG and 60 mL of water in the purging flask). Analyze

the QCS according to the procedures described in sections 10.2 and 10.3, excluding section 10.2.2. To calculate the theoretical carbon concentration (in mg) in QCS 1, multiply mg of methylene chloride in the stock solution by 3.777×10^{-3}. To calculate the theoretical chlorine concentration (in mg) in QCS 1, multiply mg of methylene chloride in the stock solution by 1.670×10^{-2}.

9.1.2 QCS 2, 1,3-dichloro-2-propanol. Prepare a stock solution by weighing, to the nearest 0.1 mg, 60 μL of high purity grade 1,3-dichloro-2-propanol in a tared 5 mL volumetric flask. Record the weight in milligrams, dilute to 5 mL with cleaned PEG, and inject 100 μL of the stock solution into a sample prepared as a water blank (50 mL of cleaned PEG and 60 mL of water in the purging flask). Analyze the QCS according to the procedures described in sections 10.2 and 10.3, excluding section 10.2.2. To calculate the theoretical carbon concentration (in mg) in QCS 2, multiply mg of 1,3-dichloro-2-propanol in the stock solution by 7.461×10^{-3}. To calculate the theoretical chlorine concentration (in mg) in QCS 2, multiply mg of 1,3-dichloro-2-propanol in the stock solution by 1.099×10^{-2}.

9.1.3 Routine QCS Analysis. For each set of compliance samples (in this context, set is per facility, per compliance test), analyze one QCS 1 and one QCS 2 sample. The percent recovery for each sample for each detector shall be ±13 percent of the mean recovery established for the most recent set of QCS triplicate analysis (Section 9.4). If the sample does not meet this criteria, check the system components and analyze another QCS 1 and 2 until a single set of QCS meet the ±13 percent criteria.

10.0 Calibration and Standardization

10.1 Initial Performance Check of Purging System. Before placing the system in operation, after a shutdown of greater than six months, after any major modifications, and at least once per month during continuous operation, conduct the linearity checks described in sections 10.1.1 and 10.1.2. Install calibration gas at the three-way calibration gas valve. See Figure 25D–1.

10.1.1 Linearity Check Procedure. Using the calibration standard described in section 7.2.2.3 and by varying the injection time, it is possible to calibrate at multiple concentration levels. Use Equation 25D–3 to calculate three sets of calibration gas flow rates and run times needed to introduce a total mass of carbon, as methane, (m_c) of 1, 5, and 10 mg into the system (low, medium and high FID calibration, respectively). Use Equation 25D–4 to calculate three sets of calibration gas flow rates and run times needed to introduce a total chloride mass (m_{ch}) of 1, 5, and 10 mg into the system (low, medium and high ELCD calibration, respectively). With the system operating in standby mode, allow the FID and the ELCD to establish a stable baseline. Set the secondary pressure regulator of the calibration gas cylinder to the same pressure as the purge gas cylinder and set the proper flow rate with the calibration flow controller (see Figure 25D–1). The calibration gas flow rate can be measured with a flowmeter attached to the vent position of the calibration gas valve. Set the four-way bypass valve to standby position so that the calibration gas flows through the coalescing filter only. Inject the calibration gas by turning the calibration gas valve from vent position to inject position. Continue the calibration gas flow for the appropriate period of time before switching the calibration valve to vent position. Continue recording the response of the FID and the ELCD for 5 min after switching off calibration gas flow. Make triplicate injections of all six levels of calibration.

10.1.2 Linearity Criteria. Calculate the average response factor (Equations 25D–5 and 25D–6) and the relative standard deviation (RSD) (Equation 25D–10) at each level of the calibration curve for both detectors. Calculate the overall mean of the three response factor averages for each detector. The FID linearity is acceptable if each response factor is within 5 percent of the overall mean and if the RSD for each set of triplicate injections is less than 5 percent. The ELCD linearity is acceptable if each response factor is within 10 percent of the overall mean and if the RSD for each set of triplicate injections is less than 10 percent. Record the overall mean value of the response factors for the FID and the ELCD. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat sections 10.1.1 and 10.1.2.

10.2 Daily Calibrations.

10.2.1 Daily Linearity Check. Follow the procedures outlined in section 10.1.1 to analyze the medium level calibration for both the FID and the ELCD in duplicate at the start of the day. Calculate the response factors and the RSDs for each detector. For the FID, the calibration is acceptable if the average response factor is within 5 percent of the overall mean response factor (Section 10.1.2) and if the RSD for the duplicate injection is less than 5 percent. For the ELCD, the calibration is acceptable if the average response factor is within 10 percent of the overall mean response factor (Section 10.1.2) and if the RSD for the duplicate injection is less than 10 percent. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat sections 10.1.1 and 10.1.2.

10.2.2 Calibration Range Check.

10.2.2.1 If the waste concentration for either detector falls below the range of calibration for that detector, use the procedure outlined in section 10.1.1 to choose two calibration points that bracket the new target

concentration. Analyze each of these points in triplicate (as outlined in section 10.1.1) and use the criteria in section 10.1.2 to determine the linearity of the detector in this ''mini-calibration'' range.

10.2.2.2 After the initial linearity check of the mini-calibration curve, it is only necessary to test one of the points in duplicate for the daily calibration check (in addition to the points specified in section 10.2.1). The average daily mini-calibration point should fit the linearity criteria specified in section 10.2.1. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat the calibration procedure mentioned in the first paragraph of section 10.2.2. A mini-calibration curve for waste concentrations above the calibration curve for either detector is optional.

10.3 Analytical Balance. Calibrate against standard weights.

11.0 Analysis

11.1 Sample Analysis.

11.1.1 Turn on the constant temperature chamber and allow the temperature to equilibrate at 75 ±2 °C (167 ±3.6 °F). Turn the four-way valve so that the purge gas bypasses the purging flask, the purge gas flowing through the coalescing filter and to the detectors (standby mode). Turn on the purge gas. Allow both the FID and the ELCD to warm up until a stable baseline is achieved on each detector. Pack the filter flask with ice. Replace ice after each run and dispose of the waste water properly. When the temperature of the oven reaches 75 ±2 °C (167 ±3.6 °F), start both integrators and record baseline. After 1 min, turn the four-way valve so that the purge gas flows through the purging flask, to the coalescing filter and to the sample splitters (purge mode). Continue recording the response of the FID and the ELCD. Monitor the readings of the pressure gauge and the rotameter. If the readings fall below established setpoints, stop the purging, determine the source of the leak, and resolve the problem before resuming. Leaks detected during a sampling period invalidate that sample.

11.1.2 As the purging continues, monitor the output of the detectors to make certain that the analysis is proceeding correctly and that the results are being properly recorded. Every 10 minutes read and record the purge flow rate, the pressure and the chamber temperature. Continue the purging for 30 minutes.

11.1.3 For each detector output, integrate over the entire area of the peak starting at 1 minute and continuing until the end of the run. Subtract the established baseline area from the peak area. Record the corrected area of the peak. See Figure 25D–6 for an example integration.

11.2 Water Blank. A water blank shall be analyzed for each batch of cleaned PEG prepared. Transfer about 60 mL of water into the purging flask. Add 50 mL of the cleaned PEG to the purging flask. Treat the blank as described in sections 8.2 and 8.3, excluding section 8.2.2. Calculate the concentration of carbon and chlorine in the blank sample (assume 10 g of waste as the mass). A VO concentration equivalent to ≤10 percent of the applicable standard may be subtracted from the measured VO concentration of the waste samples. Include all blank results and documentation in the test report.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

A_b = Area under the water blank response curve, counts.
A_c = Area under the calibration response curve, counts.
A_s = Area under the sample response curve, counts.
C = Concentration of volatile organics in the sample, ppmw.
C_c = Concentration of carbon, as methane, in the calibration gas, mg/L.
C_{ch} = Concentration of chloride in the calibration gas, mg/L.
C_j = VO concentration of phase j, ppmw.
DR_t = Average daily response factor of the FID, mg CH_4/counts.
Dr_{th} = Average daily response factor of the ELCD, mg Cl^-/counts.
F_j = Weight fraction of phase j present in the waste.
m_c = Mass of carbon, as methane, in a calibration run, mg.
m_{ch} = Mass of chloride in a calibration run, mg.
m_s = Mass of the waste sample, g.
m_{sc} = Mass of carbon, as methane, in the sample, mg.
m_{sf} = Mass of sample container and waste sample, g.
m_{sh} = Mass of chloride in the sample, mg.
m_{st} = Mass of sample container prior to sampling, g.
m_{VO} = Mass of volatile organics in the sample, mg.
n = Total number of phases present in the waste.
P_p = Percent propane in calibration gas (L/L).
P_{vc} = Percent 1,1-dichloroethylene in calibration gas (L/L).
Q_c = Flow rate of calibration gas, L/min.
t_c = Length of time standard gas is delivered to the analyzer, min.
W = Weighted average VO concentration, ppmw.

12.2 Concentration of Carbon, as Methane, in the Calibration Gas.

$$C_c = (19.681 \times P_p) + (13.121 \times P_{vc}) \qquad \text{Eq. 25D-1}$$

12.3 Concentration of Chloride in the Calibration Gas.

$$C_{ch} = 28.998 \times P_{vc} \qquad \text{Eq. 25D-2}$$

12.4 Mass of Carbon, as Methane, in a Calibration Run.

$$M_c = C_c \times Q_c \times t_c \qquad \text{Eq. 25D-3}$$

12.5 Mass of Chloride in a Calibration Run.

$$m_{ch} = C_{ch} \times Q_c \times t_c \qquad \text{Eq. 25D-4}$$

12.6 FID Response Factor, mg/counts.

$$DR_t = \frac{m_c}{A_c} \qquad \text{Eq. 25D-5}$$

12.7 ELCD Response Factor, mg/counts.

$$DR_{th} = \frac{m_{ch}}{A_c} \qquad \text{Eq. 25D-6}$$

12.8 Mass of Carbon in the Sample.

$$m_{sc} = DR_t(A_s - A_b) \qquad \text{Eq. 25D-7}$$

12.9 Mass of Chloride in the Sample.

$$m_{sh} = DR_{th}(A_s - A_b) \qquad \text{Eq. 25D-8}$$

12.10 Mass of Volatile Organics in the Sample.

$$m_{vo} = m_{sc} + m_{sh} \qquad \text{Eq. 25D-9}$$

12.11 Relative Standard Deviation.

$$RSD = \frac{100}{\bar{x}} \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}} \qquad \text{Eq. 25D-10}$$

12.12 Mass of Sample.

$$m_s = m_{sf} - m_{st} \qquad \text{Eq. 25D-11}$$

12.13 Concentration of Volatile Organics in Waste.

$$C = \frac{(m_{vo} \times 1000)}{m_s} \qquad \text{Eq. 25D-12}$$

12.14 Weighted Average VO Concentration of Multi-phase Waste.

$$W = \sum_{j=1}^{n} F_j x \overline{C}_j \qquad \text{Eq. 25D-13}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. ''Test Methods for Evaluating Solid Waste, Physical/Chemistry Methods'', U.S. Environmental Protection Agency. Publication SW–846, 3rd Edition, November 1986 as amended by Update I, November 1990.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

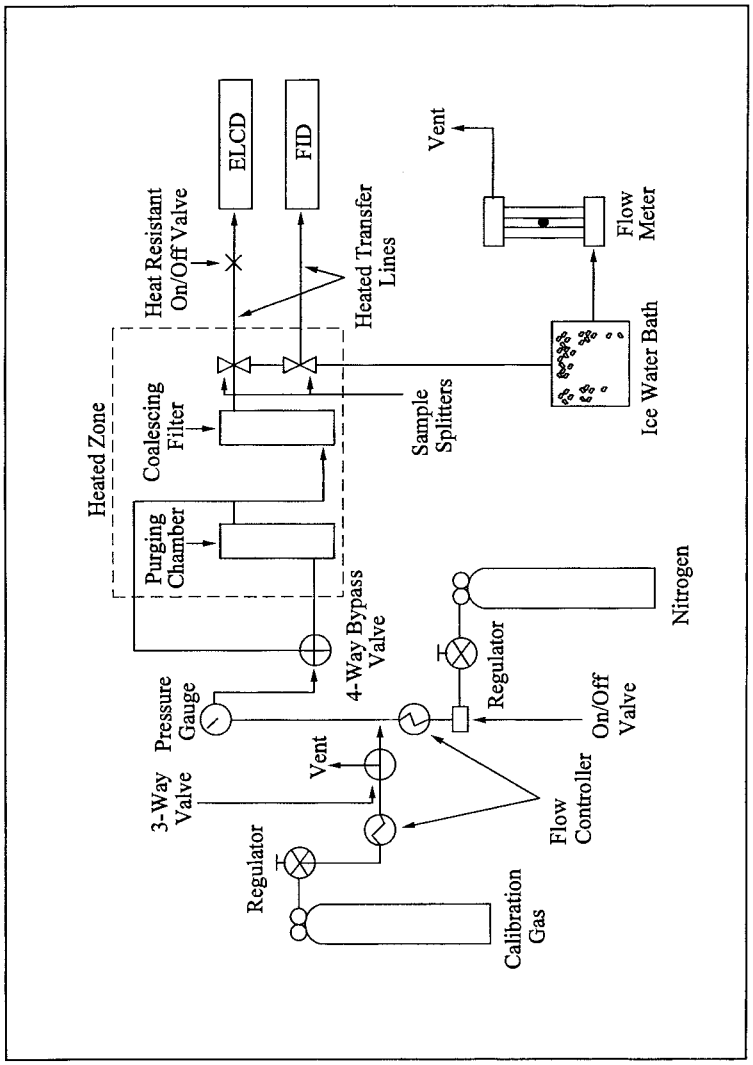


Figure 25D-1. Schematic of Purging Apparatus.

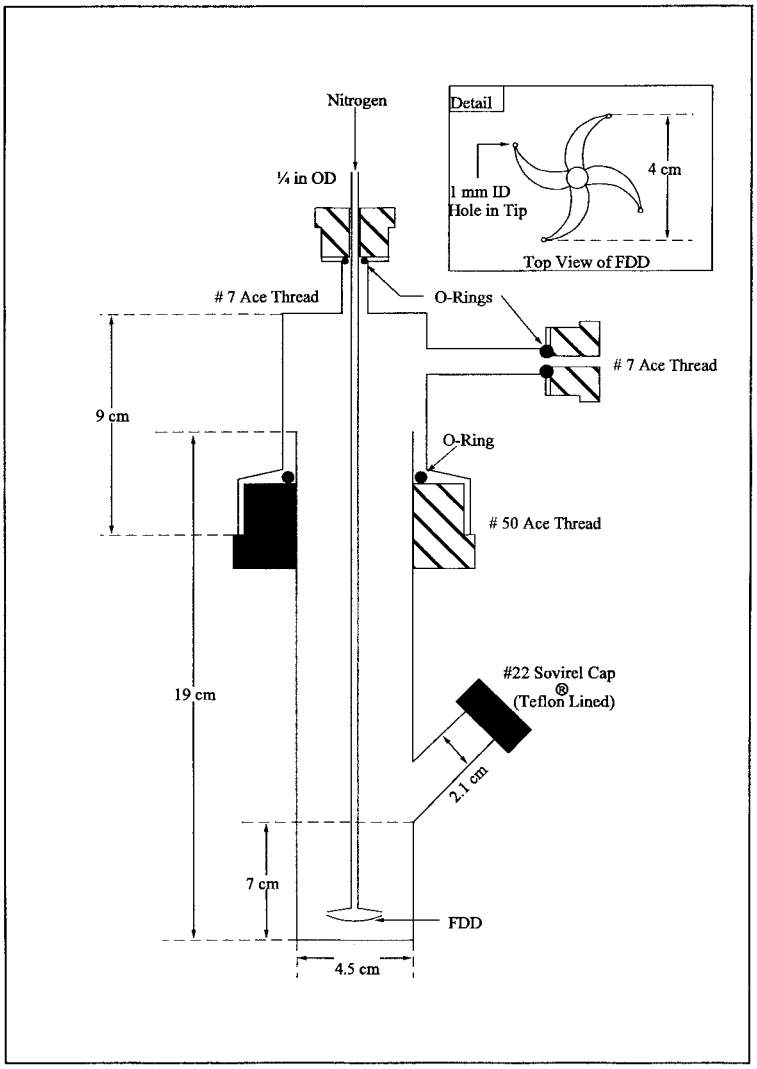
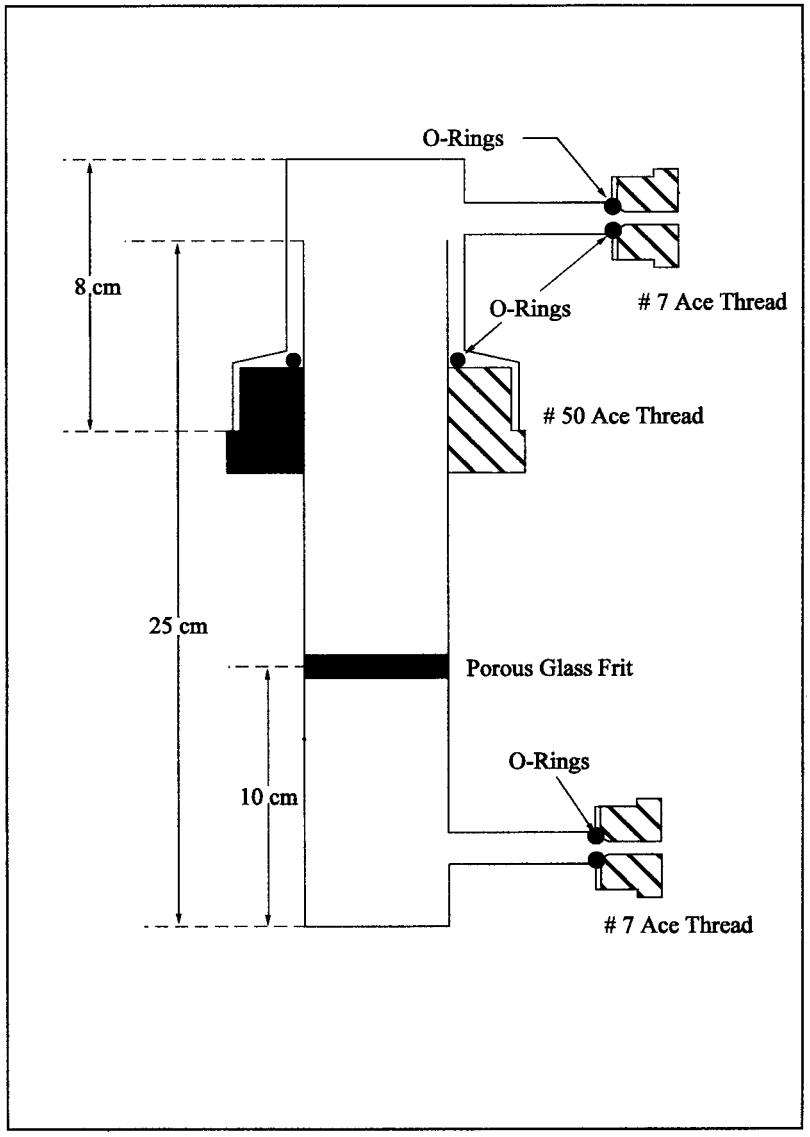


Figure 25D-2. Purging Lance.


O-Rings
8 cm
O-Rings
7 Ace Thread
50 Ace Thread
25 cm
Porous Glass Frit
O-Rings
10 cm
7 Ace Thread

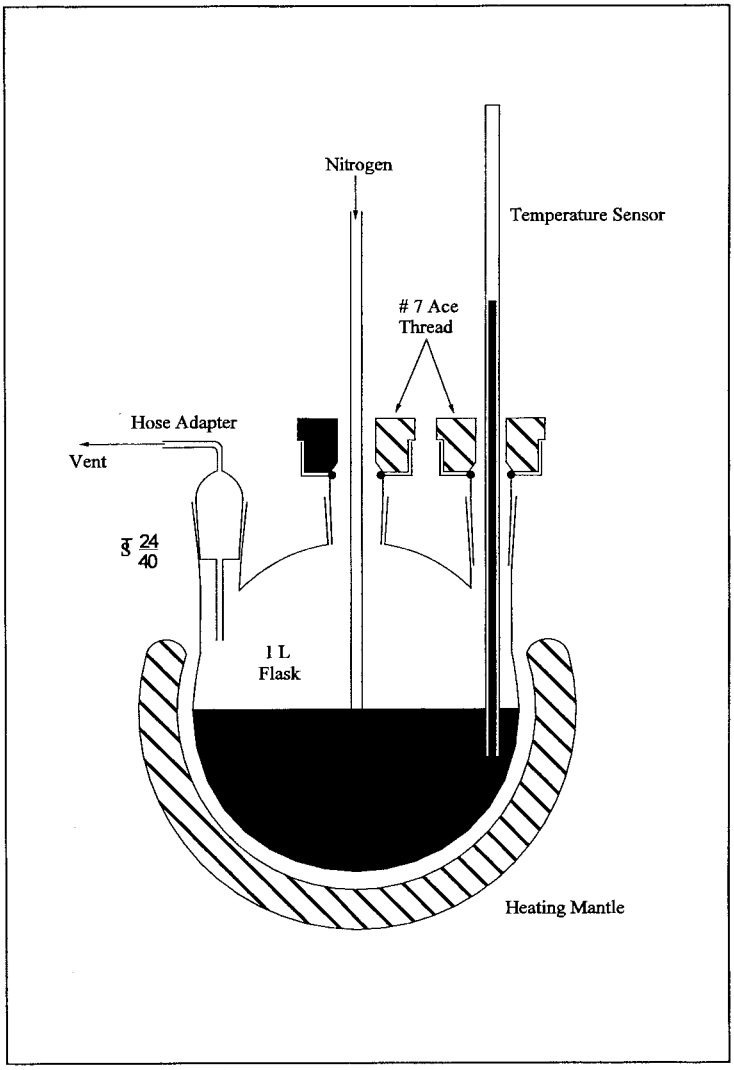


Figure 25D-4. Schematic of PEG Cleaning System.

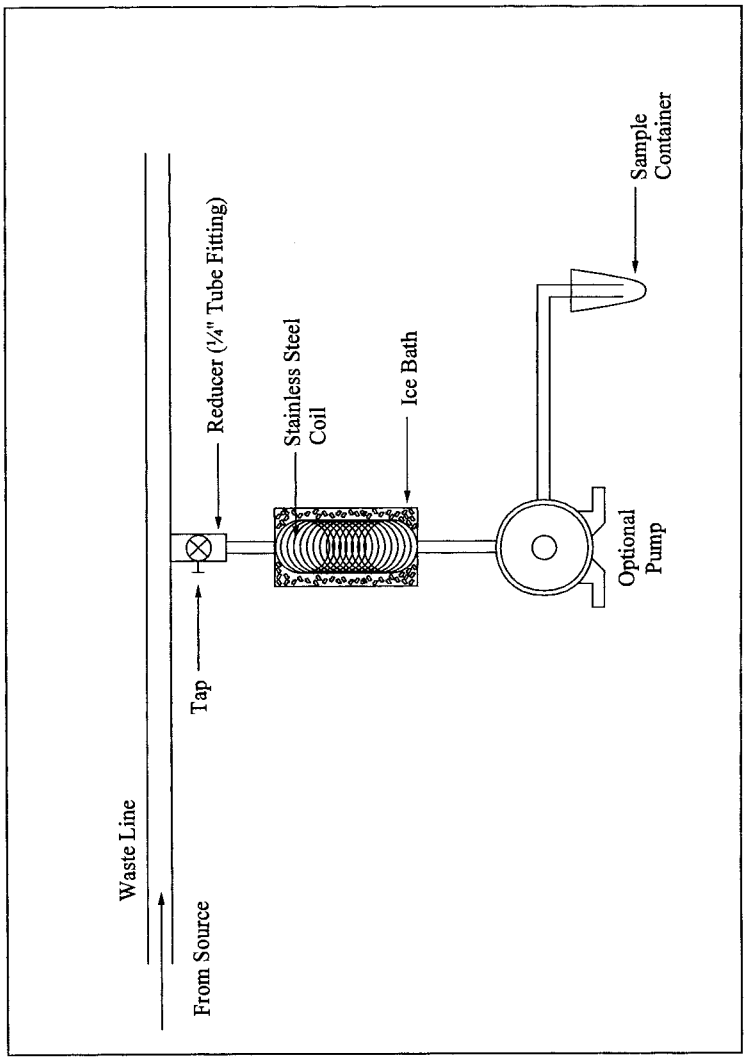


Figure 25D-5. Schematic of Sampling Apparatus.

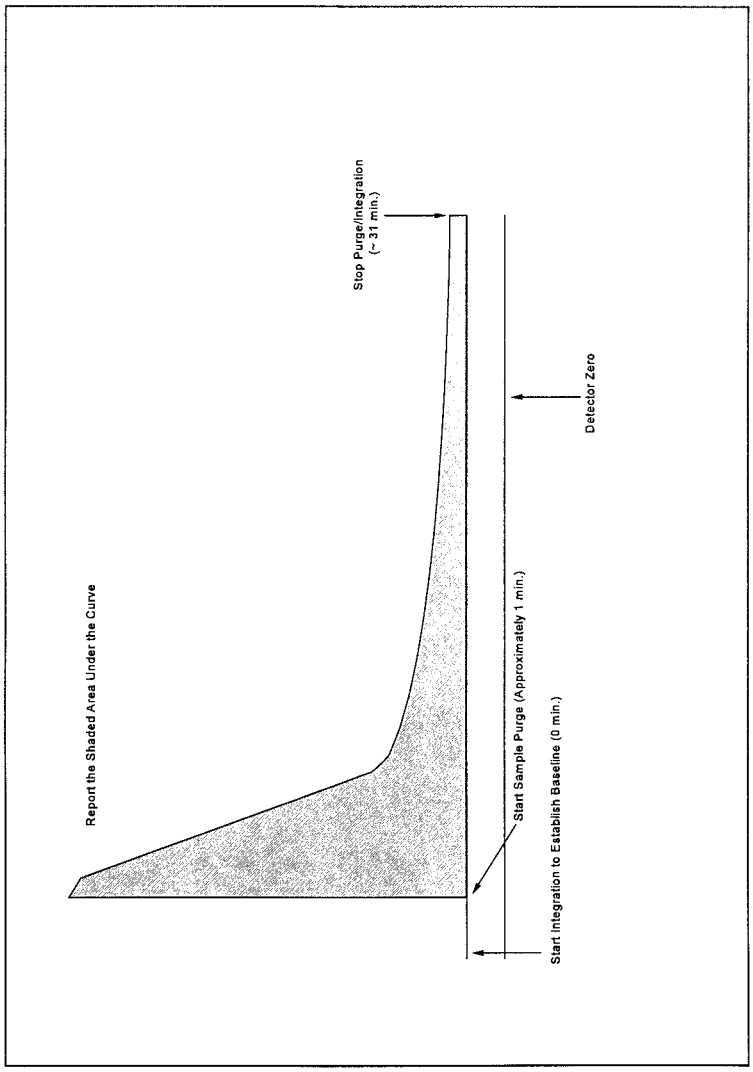


Figure 25D-6. Example Integration of Either Detector.

METHOD 25E—DETERMINATION OF VAPOR PHASE ORGANIC CONCENTRATION IN WASTE SAMPLES

NOTE: Performance of this method should not be attempted by persons unfamiliar with the operation of a flame ionization detector (FID) nor by those who are unfamiliar with source sampling because knowledge beyond the scope of this presentation is required. This method is not inclusive with respect to specifications (*e.g.*, reagents and standards) and calibration procedures. Some material is incorporated by reference from other methods. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 106, part 61, Appendix B, and Method 18, part 60, Appendix A.

1.0 Scope and Application

1.1 Applicability. This method is applicable for determining the vapor pressure of waste cited by an applicable regulation.

1.2 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 The headspace vapor of the sample is analyzed for carbon content by a headspace analyzer, which uses an FID.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 The analyst shall select the operating parameters best suited to the requirements for a particular analysis. The analyst shall produce confirming data through an adequate supplemental analytical technique and have the data available for review by the Administrator.

5.0 Safety [Reserved]

6.0 Equipment and Supplies

6.1 Sampling. The following equipment is required:

6.1.1 Sample Containers. Vials, glass, with butyl rubber septa, Perkin-Elmer Corporation Numbers 0105–0129 (glass vials), B001–0728 (gray butyl rubber septum, plug style), 0105–0131 (butyl rubber septa), or equivalent. The seal must be made from butyl rubber. Silicone rubber seals are not acceptable.

6.1.2 Vial Sealer. Perkin-Elmer Number 105–0106, or equivalent.

6.1.3 Gas-Tight Syringe. Perkin-Elmer Number 00230117, or equivalent.

6.1.4 The following equipment is required for sampling.

6.1.4.1 Tap.

6.1.4.2 Tubing. Teflon, 0.25-in. ID.

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1.4.3 Cooling Coil. Stainless steel (304), 0.25 in.-ID, equipped with a thermocouple at the coil outlet.

6.2 Analysis. The following equipment is required.

6.2.1 Balanced Pressure Headspace Sampler. Perkin-Elmer HS–6, HS–100, or equivalent, equipped with a glass bead column instead of a chromatographic column.

6.2.2 FID. An FID meeting the following specifications is required.

6.2.2.1 Linearity. A linear response (±5 percent) over the operating range as demonstrated by the procedures established in section 10.2.

6.2.2.2 Range. A full scale range of 1 to 10,000 parts per million (ppm) propane (C_3H_8). Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.2.3 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the output of the detector.

6.2.4 Temperature Sensor. Capable of reading temperatures in the range of 30 to 60 °C (86 to 140 °F) with an accuracy of ±0.1 °C (±0.2 °F).

7.0 Reagents and Standards

7.1 Analysis. The following items are required for analysis.

7.1.1 Hydrogen (H_2). Zero grade hydrogen, as required by the FID.

7.1.2 Carrier Gas. Zero grade nitrogen, containing less than 1 ppm carbon (C) and less than 1 ppm carbon dioxide.

7.1.3 Combustion Gas. Zero grade air or oxygen as required by the FID.

7.2 Calibration and Linearity Check.

7.2.1 Stock Cylinder Gas Standard. 100 percent propane. The manufacturer shall: (a) Certify the gas composition to be accurate to ±3 percent or better (see section 7.2.1.1); (b) recommend a maximum shelf life over which the gas concentration does not change by greater than ±5 percent from the certified value; and (c) affix the date of gas cylinder preparation, certified propane concentration, and recommended maximum shelf life to the cylinder before shipment to the buyer.

7.2.1.1 Cylinder Standards Certification. The manufacturer shall certify the concentration of the calibration gas in the cylinder by (a) directly analyzing the cylinder and (b) calibrating his analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use, as a minimum, a three-point calibration curve.

7.2.1.2 Verification of Manufacturer's Calibration Standards. Before using, the manufacturer shall verify each calibration standard by (a) comparing it to gas mixtures prepared in accordance with the procedure described in section 7.1 of Method 106 of Part 61, Appendix B, or by (b) calibrating it against Standard Reference Materials (SRM's) prepared by the National Bureau of Standards, if such SRM's are available. The agreement between the initially determined concentration value and the verification concentration value must be within ±5 percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

8.0 Sampling Collection, Preservation, Storage, and Transport

8.1 Install a sampling tap to obtain a sample at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to

the atmosphere). Assemble the sampling apparatus as shown in Figure 25E–1.

8.2 Begin sampling by purging the sample lines and cooling coil with at least four volumes of waste. Collect the purged material in a separate container and dispose of it properly.

8.3 After purging, stop the sample flow and transfer the Teflon sampling tube to a sample container. Sample at a flow rate such that the temperature of the waste is <10 °C (<50 °F). Fill the sample container halfway (±5 percent) and cap it within 5 seconds. Store immediately in a cooler and cover with ice.

8.4 Alternative sampling techniques may be used upon the approval of the Administrator.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
10.2, 10.3	FID calibration and response check	Ensure precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Use the procedures in sections 10.2 to calibrate the headspace analyzer and FID and check for linearity before the system is first placed in operation, after any shutdown longer than 6 months, and after any modification of the system.

10.2 Calibration and Linearity. Use the procedures in section 10 of Method 18 of Part 60, Appendix A, to prepare the standards and calibrate the flowmeters, using propane as the standard gas. Fill the calibration standard vials halfway (±5 percent) with deionized water. Purge and fill the airspace with calibration standard. Prepare a minimum of three concentrations of calibration standards in triplicate at concentrations that will bracket the applicable cutoff. For a cutoff of 5.2 kPa (0.75 psi), prepare nominal concentrations of 30,000, 50,000, and 70,000 ppm as propane. For a cutoff of 27.6 kPa (4.0 psi), prepare nominal concentrations of 200,000, 300,000, and 400,000 ppm as propane.

10.2.1 Use the procedures in section 11.3 to measure the FID response of each standard. Use a linear regression analysis to calculate the values for the slope (k) and the y-intercept (b). Use the procedures in sections 12.3 and 12.2 to test the calibration and the linearity.

10.3 Daily FID Calibration Check. Check the calibration at the beginning and at the end of the daily runs by using the following procedures. Prepare 2 calibration standards at the nominal cutoff concentration using the procedures in section 10.2. Place one at the beginning and one at the end of the daily run. Measure the FID response of the daily calibration standard and use the values for k and b from the most recent calibration to calculate the concentration of the daily standard. Use an equation similar to 25E–2 to calculate the percent difference between the daily standard and C_s. If the difference is within 5 percent, then the previous values for k and b can be used. Otherwise, use the procedures in section 10.2 to recalibrate the FID.

11.0 Analytical Procedures

11.1 Allow one hour for the headspace vials to equilibrate at the temperature specified in the regulation. Allow the FID to warm up until a stable baseline is achieved on the detector.

11.2 Check the calibration of the FID daily using the procedures in section 10.3.

11.3 Follow the manufacturer's recommended procedures for the normal operation of the headspace sampler and FID.

11.4 Use the procedures in sections 12.4 and 12.5 to calculate the vapor phase organic vapor pressure in the samples.

11.5 Monitor the output of the detector to make certain that the results are being properly recorded.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

A = Measurement of the area under the response curve, counts.
b = y-intercept of the linear regression line.
C_a = Measured vapor phase organic concentration of sample, ppm as propane.
C_{ma} = Average measured vapor phase organic concentration of standard, ppm as propane.
C_m = Measured vapor phase organic concentration of standard, ppm as propane.
C_s = Calculated standard concentration, ppm as propane.
k = Slope of the linear regression line.
P_{bar} = Atmospheric pressure at analysis conditions, mm Hg (in. Hg).
P* = Organic vapor pressure in the sample, kPa (psi).
PD = Percent difference between the average measured vapor phase organic concentration (C_m) and the calculated standard concentration (C_s).
RSD = Relative standard deviation.
$\beta = 1.333 \times 10^{-7}$ kPa/[(mm Hg)(ppm)], $(4.91 \times 10^{-7}$ psi/[(in. Hg)(ppm)])

12.2 Linearity. Use the following equation to calculate the measured standard concentration for each standard vial.

$$C_m = kA + b \qquad \text{Eq. 25E-1}$$

12.2.1 Calculate the average measured standard concentration (C_{ma}) for each set of triplicate standards and use the following equation to calculate PD between C_{ma} and C_s. The instrument linearity is acceptable if the PD is within five for each standard.

$$PD = \frac{C_s - C_{ma}}{C_s} \times 100 \qquad \text{Eq. 25E-2}$$

12.3. Relative Standard Deviation (RSD). Use the following equation to calculate the RSD for each triplicate set of standards.

$$RSD = \frac{100}{C_{ma}} \sqrt{\frac{\sum (C_m - C_{ma})^2}{2}} \qquad \text{Eq. 25E-3}$$

The calibration is acceptable if the RSD is within five for each standard concentration.

12.4 Concentration of organics in the headspace. Use the following equation to calculate the concentration of vapor phase organics in each sample.

$$C_a = kA + b \qquad \text{Eq. 25E-4}$$

12.5 Vapor Pressure of Organics in the Headspace Sample. Use the following equation to calculate the vapor pressure of organics in the sample.

$$P^* = \beta P_{bar} C_a \qquad \text{Eq. 25E-5}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, Albert E., Samuel Witz, and Robert D. MacPhee. ''Determination of Solvent Vapor Concentrations by Total Combustion Analysis: a Comparison of Infared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, Massachusetts.

2. Salo, Albert E., William L. Oaks, and Robert D. MacPhee. ''Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, Colorado. June 9–13, 1974.) p. 25.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

State of Oregon Department of Environmental Quality

OAR 340-230-0335
EPA Method 22

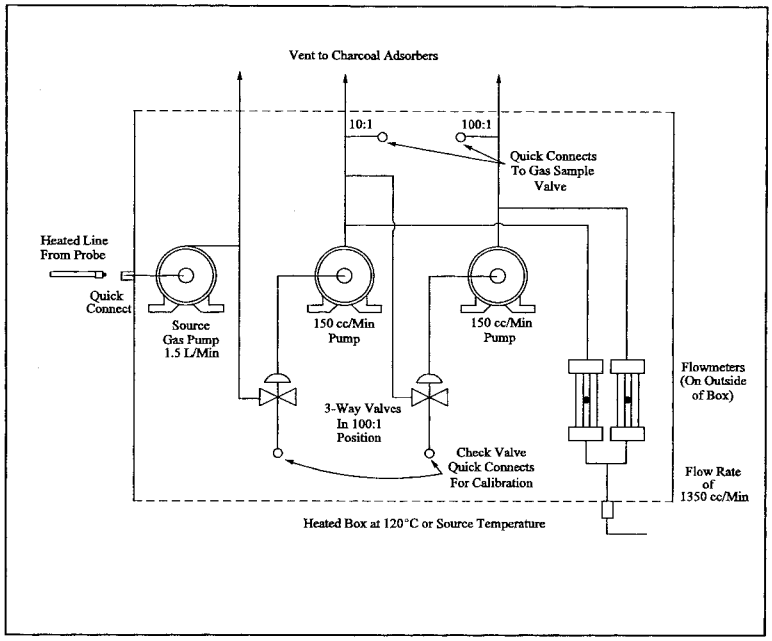


Figure 18-13. Schematic Diagram of the Heated Box Required for Dilution of Sample Gas.

GASEOUS ORGANIC SAMPLING AND ANALYSIS CHECK LIST

[Respond with initials or number as appropriate]

1. Presurvey data:		
A. Grab sample collected	☐	_____
B. Grab sample analyzed for composition	☐	_____
Method GC	☐	_____
GC/MS	☐	_____
Other	☐	_____
C. GC-FID analysis performed	☐	_____
2. Laboratory calibration data:		
A. Calibration curves prepared	☐	_____
Number of components	☐	_____
Number of concentrations/component (3 required).	☐	_____
B. Audit samples (optional):		
Analysis completed	☐	_____
Verified for concentration	☐	_____
OK obtained for field work	☐	_____
3. Sampling procedures:		
A. Method:		
Bag sample	☐	_____
Direct interface	☐	_____
Dilution interface	☐	_____
B. Number of samples collected	☐	_____
4. Field Analysis:		
A. Total hydrocarbon analysis performed	☐	_____
B. Calibration curve prepared	☐	_____
Number of components	☐	_____
Number of concentrations per component (3 required).	☐	_____

Gaseous Organic Sampling and Analysis Data

Date _____
Location _____

Plant _____

GASEOUS ORGANIC SAMPLING AND ANALYSIS CHECK LIST (RESPOND WITH INITIALS OR NUMBER AS APPROPRIATE)

	Date
1. Pre-survey data	
A. Grab sample collected	_____
B. Grab sample analyzed for composition	_____
Method GC	_____
GC/MS	_____
Other_____	_____
C. GC–FID analysis performed	_____
2. Laboratory calibration curves prepared	_____
A. Number of components	_____
B. Number of concentrations per component (3 required)	_____
C. OK obtained for field work	_____
3. Sampling procedures.	
A. Method.	
Bag sample	_____
Direct interface	_____
Dilution interface	_____
B. Number of samples collected	_____
4. Field Analysis.	
A. Total hydrocarbon analysis performed	_____
B. Calibration curve prepared	_____
Number of components	_____
Number of concentrations per component (3 required)	_____

Figure 18–14. Sampling and Analysis Sheet

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–6 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

APPENDIX A–7 TO PART 60—TEST METHODS 19 THROUGH 25E

Method 19—Determination of sulfur dioxide removal efficiency and particulate, sulfur dioxide and nitrogen oxides emission rates
Method 20—Determination of nitrogen oxides, sulfur dioxide, and diluent emissions from stationary gas turbines
Method 21—Determination of volatile organic compound leaks
Method 22—Visual determination of fugitive emissions from material sources and smoke emissions from flares
Method 23—Determination of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans From Stationary Sources
Method 24—Determination of volatile matter content, water content, density, volume solids, and weight solids of surface coatings
Method 24A—Determination of volatile matter content and density of printing inks and related coatings
Method 25—Determination of total gaseous nonmethane organic emissions as carbon
Method 25A—Determination of total gaseous organic concentration using a flame ionization analyzer
Method 25B—Determination of total gaseous organic concentration using a nondispersive infrared analyzer
Method 25C—Determination of nonmethane organic compounds (NMOC) in MSW landfill gases
Method 25D—Determination of the Volatile Organic Concentration of Waste Samples
Method 25E—Determination of Vapor Phase Organic Concentration in Waste Samples

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

Method 19—Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates

1.0 Scope and Application

1.1 Analytes. This method provides data reduction procedures relating to the following pollutants, but does not include any sample collection or analysis procedures.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), including:		
Nitric oxide (NO)	10102–43–9	N/A
Nitrogen dioxide (NO_2)	10102–44–0.	
Particulate matter (PM)	None assigned	N/A
Sulfur dioxide (SO_2)	7499–09–05	N/A

1.2 Applicability. Where specified by an applicable subpart of the regulations, this method is applicable for the determination of (a) PM, SO_2, and NO_X emission rates; (b) sulfur removal efficiencies of fuel pretreatment and SO_2 control devices; and (c) overall reduction of potential SO_2 emissions.

2.0 Summary of Method

2.1 Emission Rates. Oxygen (O_2) or carbon dioxide (CO_2) concentrations and appropriate F factors (ratios of combustion gas volumes to heat inputs) are used to calculate pollutant emission rates from pollutant concentrations.

2.2 Sulfur Reduction Efficiency and SO_2 Removal Efficiency. An overall SO_2 emission reduction efficiency is computed from the efficiency of fuel pretreatment systems, where applicable, and the efficiency of SO_2 control devices.

2.2.1 The sulfur removal efficiency of a fuel pretreatment system is determined by fuel sampling and analysis of the sulfur and heat contents of the fuel before and after the pretreatment system.

2.2.2 The SO_2 removal efficiency of a control device is determined by measuring the SO_2 rates before and after the control device.

2.2.2.1 The inlet rates to SO_2 control systems (or, when SO_2 control systems are not used, SO_2 emission rates to the atmosphere) are determined by fuel sampling and analysis.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety [Reserved]

6.0 Equipment and Supplies [Reserved]

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transport [Reserved]

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedures [Reserved]

12.0 Data Analysis and Calculations

12.1 Nomenclature

B_{wa} = Moisture fraction of ambient air, percent.

B_{ws} = Moisture fraction of effluent gas, percent.

%C = Concentration of carbon from an ultimate analysis of fuel, weight percent.

C_d = Pollutant concentration, dry basis, ng/scm (lb/scf)

$\%CO_{2d}$,$\%CO_{2w}$ = Concentration of carbon dioxide on a dry and wet basis, respectively, percent.

C_w = Pollutant concentration, wet basis, ng/scm (lb/scf).

D = Number of sampling periods during the performance test period.

E = Pollutant emission rate, ng/J (lb/million Btu).

E_a = Average pollutant rate for the specified performance test period, ng/J (lb/million Btu).

E_{ao}, E_{ai} = Average pollutant rate of the control device, outlet and inlet, respectively, for the performance test period, ng/J (lb/million Btu).

E_{bi} = Pollutant rate from the steam generating unit, ng/J (lb/million Btu)

E_{bo} = Pollutant emission rate from the steam generating unit, ng/J (lb/million Btu).

E_{ci} = Pollutant rate in combined effluent, ng/J (lb/million Btu).

E_{co} = Pollutant emission rate in combined effluent, ng/J (lb/million Btu).

E_d = Average pollutant rate for each sampling period (*e.g.*, 24-hr Method 6B sample or 24-hr fuel sample) or for each fuel lot (*e.g.*, amount of fuel bunkered), ng/J (lb/million Btu).

E_{di} = Average inlet SO_2 rate for each sampling period d, ng/J (lb/million Btu)

E_g = Pollutant rate from gas turbine, ng/J (lb/million Btu).

E_{ga} = Daily geometric average pollutant rate, ng/J (lbs/million Btu) or ppm corrected to 7 percent O_2.

E_{jo},E_{ji} = Matched pair hourly arithmetic average pollutant rate, outlet and inlet, respectively, ng/J (lb/million Btu) or ppm corrected to 7 percent O_2.

E_h = Hourly average pollutant, ng/J (lb/million Btu).

E_{hj} = Hourly arithmetic average pollutant rate for hour ''j,'' ng/J (lb/million Btu) or ppm corrected to 7 percent O_2.

EXP = Natural logarithmic base (2.718) raised to the value enclosed by brackets.

F_d, F_w, F_c = Volumes of combustion components per unit of heat content, scm/J (scf/million Btu).

GCV = Gross calorific value of the fuel consistent with the ultimate analysis, kJ/kg (Btu/lb).

GCV_p, GCV_r = Gross calorific value for the product and raw fuel lots, respectively, dry basis, kJ/kg (Btu/lb).

%H = Concentration of hydrogen from an ultimate analysis of fuel, weight percent.

H = Total number of operating hours for which pollutant rates are determined in the performance test period.

H_b = Heat input rate to the steam generating unit from fuels fired in the steam generating unit, J/hr (million Btu/hr).

H_g = Heat input rate to gas turbine from all fuels fired in the gas turbine, J/hr (million Btu/hr).

$\%H_2O$ = Concentration of water from an ultimate analysis of fuel, weight percent.
H_r = Total numbers of hours in the performance test period (*e.g.*, 720 hours for 30-day performance test period).
K = Conversion factor, 10^{-5} (kJ/J)/(%) [10^6 Btu/million Btu].
K_c = (9.57 scm/kg)/% [(1.53 scf/lb)/%].
K_{cc} = (2.0 scm/kg)/% [(0.321 scf/lb)/%].
K_{hd} = (22.7 scm/kg)/% [(3.64 scf/lb)/%].
K_{hw} = (34.74 scm/kg)/% [(5.57 scf/lb)/%].
K_n = (0.86 scm/kg)/% [(0.14 scf/lb)/%].
K_o = (2.85 scm/kg)/% [(0.46 scf/lb)/%].
K_s = (3.54 scm/kg)/% [(0.57 scf/lb)/%].
K_w = (1.30 scm/kg)/% [(0.21 scf/lb)/%].
ln = Natural log of indicated value.
L_p,L_r = Weight of the product and raw fuel lots, respectively, metric ton (ton).
%N = Concentration of nitrogen from an ultimate analysis of fuel, weight percent.
N = Number of fuel lots during the averaging period.
n = Number of fuels being burned in combination.
n_d = Number of operating hours of the affected facility within the performance test period for each E_d determined.
n_t = Total number of hourly averages for which paired inlet and outlet pollutant rates are available within the 24-hr midnight to midnight daily period.
%O = Concentration of oxygen from an ultimate analysis of fuel, weight percent.
$\%O_{2d}$, $\%O_{2w}$ = Concentration of oxygen on a dry and wet basis, respectively, percent.
P_s = Potential SO_2 emissions, percent.
$\%R_f$ = SO_2 removal efficiency from fuel pretreatment, percent.
$\%R_g$ = SO_2 removal efficiency of the control device, percent.
$\%R_{ga}$ = Daily geometric average percent reduction.
$\%R_o$ = Overall SO_2 reduction, percent.
%S = Sulfur content of as-fired fuel lot, dry basis, weight percent.
S_e = Standard deviation of the hourly average pollutant rates for each performance test period, ng/J (lb/million Btu).
$\%S_f$ = Concentration of sulfur from an ultimate analysis of fuel, weight percent.
S_i = Standard deviation of the hourly average inlet pollutant rates for each performance test period, ng/J (lb/million Btu).
S_o = Standard deviation of the hourly average emission rates for each performance test period, ng/J (lb/million Btu).
$\%S_p$, $\%S_r$ = Sulfur content of the product and raw fuel lots respectively, dry basis, weight percent.
$t_{0.95}$ = Values shown in Table 19–3 for the indicated number of data points n.
X_k = Fraction of total heat input from each type of fuel k.

12.2 Emission Rates of PM, SO_2, and NO_X. Select from the following sections the applicable procedure to compute the PM, S_{O2}, or NO_X emission rate (E) in ng/J (lb/million Btu). The pollutant concentration must be in ng/scm (lb/scf) and the F factor must be in scm/J (scf/million Btu). If the pollutant concentration (C) is not in the appropriate units, use Table 19–1 in section 17.0 to make the proper conversion. An F factor is the ratio of the gas volume of the products of combustion to the heat content of the fuel. The dry F factor (F_d) includes all components of combustion less water, the wet F factor (F_w) includes all components of combustion, and the carbon F factor (F_c) includes only carbon dioxide.

NOTE: Since F_w factors include water resulting only from the combustion of hydrogen in the fuel, the procedures using F_w factors are not applicable for computing E from steam generating units with wet scrubbers or with other processes that add water (*e.g.*, steam injection).

12.2.1 Oxygen-Based F Factor, Dry Basis. When measurements are on a dry basis for both O ($\%O_{2d}$) and pollutant (C_d) concentrations, use the following equation:

$$E = C_d F_d \frac{20.9}{(20.9 - \%O_{2d})} \qquad \text{Eq. 19-1}$$

12.2.2 Oxygen-Based F Factor, Wet Basis. When measurements are on a wet basis for both O_2 ($\%O_{2w}$) and pollutant (C_w) concentrations, use either of the following:

12.2.2.1 If the moisture fraction of ambient air (B_{wa}) is measured:

$$E = C_w F_w \frac{20.9}{\left[20.9(1 - B_{wa}) - \%O_{2w}\right]} \qquad \text{Eq. 19-2}$$

Instead of actual measurement, B_{wa} may be estimated according to the procedure below.

NOTE: The estimates are selected to ensure that negative errors will not be larger than −1.5 percent. However, positive errors, or over-estimation of emissions by as much as 5 percent may be introduced depending upon the geographic location of the facility and the associated range of ambient moisture.

12.2.2.1.1 B_{wa} = 0.027. This value may be used at any location at all times.

12.2.2.1.2 B_{wa} = Highest monthly average of B_{wa} that occurred within the previous calendar year at the nearest Weather Service Station. This value shall be determined annually and may be used as an estimate for the entire current calendar year.

12.2.2.1.3 B_{wa} = Highest daily average of Bwa that occurred within a calendar month at the nearest Weather Service Station, calculated from the data from the past 3 years. This value shall be computed for each month and may be used as an estimate for the current respective calendar month.

12.2.2.2 If the moisture fraction (B_{ws}) of the effluent gas is measured:

$$E = C_w F_d \frac{20.9}{\left[20.9\left(1-B_{ws}\right)-\%O_{2w}\right]} \qquad \text{Eq. 19-3}$$

12.2.3 Oxygen-Based F Factor, Dry/Wet Basis.

12.2.3.1 When the pollutant concentration is measured on a wet basis (C_w) and O_2 concentration is measured on a dry basis ($\%O_{2d}$), use the following equation:

$$E = \frac{\left(C_w F_d\right)(20.9)}{\left(1-B_{ws}\right)\left(20.9-\%O_{2d}\right)} \qquad \text{Eq. 19-4}$$

12.2.3.2 When the pollutant concentration is measured on a dry basis (C_d) and the O_2 concentration is measured on a wet basis ($\%O_{2w}$), use the following equation:

$$E = \frac{C_d F_d 20.9}{\frac{\left(20.9-\%O_{2w}\right)}{\left(1-B_{ws}\right)}} \qquad \text{Eq. 19-5}$$

12.2.4 Carbon Dioxide-Based F Factor, Dry Basis. When measurements are on a dry basis for both CO_2 ($\%CO_{2d}$) and pollutant (C_d) concentrations, use the following equation:

$$E = C_d F_c \frac{100}{\%CO_{2d}} \qquad \text{Eq. 19-6}$$

12.2.5 Carbon Dioxide-Based F Factor, Wet Basis. When measurements are on a wet basis for both CO_2 ($\%CO_{2w}$) and pollutant (C_w) concentrations, use the following equation:

$$E = C_w F_c \frac{100}{\%CO_{2w}} \qquad \text{Eq. 19-7}$$

12.2.6 Carbon Dioxide-Based F Factor, Dry/Wet Basis.

12.2.6.1 When the pollutant concentration is measured on a wet basis (C_w) and CO_2 concentration is measured on a dry basis ($\%CO_{2d}$), use the following equation:

$$E = \frac{C_w F_c}{\left(1-B_{ws}\right)} \frac{100}{\%CO_{2d}} \qquad \text{Eq. 19-8}$$

12.2.6.2 When the pollutant concentration is measured on a dry basis (C_d) and CO_2 concentration is measured on a wet basis ($\%CO_{2w}$), use the following equation:

$$E = C_d F_c \left(1-B_{ws}\right) \frac{100}{\%CO_{2w}} \qquad \text{Eq. 19-9}$$

12.2.7 Direct-Fired Reheat Fuel Burning. The effect of direct-fired reheat fuel burning (for the purpose of raising the temperature of the exhaust effluent from wet scrubbers to above the moisture dew-point) on emission rates will be less than 1.0 percent and, therefore, may be ignored.

12.2.8 Combined Cycle-Gas Turbine Systems. For gas turbine-steam generator combined cycle systems, determine the emissions from the steam generating unit or the percent reduction in potential SO_2 emissions as follows:

12.2.8.1 Compute the emission rate from the steam generating unit using the following equation:

$$E_{bo} = E_{co} + \frac{H_g}{H_b}\left(E_{co} - E_g\right) \qquad \text{Eq. 19-10}$$

12.2.8.1.1 Use the test methods and procedures section of 40 CFR Part 60, Subpart GG to obtain E_{co} and E_g. Do not use F_w factors for determining E_g or E_{co}. If an SO_2 control device is used, measure E_{co} after the control device.

12.2.8.1.2 Suitable methods shall be used to determine the heat input rates to the steam generating units (H_b) and the gas turbine (H_g).

12.2.8.2 If a control device is used, compute the percent of potential SO_2 emissions (P_s) using the following equations:

$$E_{bi} = E_{ci} - \frac{H_g}{H_b}\left(E_{ci} - E_g\right) \qquad \text{Eq. 19-11}$$

$$P_s = 100\left(1 - \frac{E_{bo}}{E_{bi}}\right) \qquad \text{Eq. 19-12}$$

NOTE: Use the test methods and procedures section of Subpart GG to obtain E_{ci} and E_g. Do not use F_w factors for determining E_g or E_{ci}.

12.3 F Factors. Use an average F factor according to section 12.3.1 or determine an applicable F factor according to section 12.3.2. If combined fuels are fired, prorate the applicable F factors using the procedure in section 12.3.3.

12.3.1 Average F Factors. Average F factors (F_d, F_w, or F_c) from Table 19–2 in section 17.0 may be used.

12.3.2 Determined F Factors. If the fuel burned is not listed in Table 19–2 or if the owner or operator chooses to determine an F factor rather than use the values in Table 19–2, use the procedure below:

12.3.2.1 Equations. Use the equations below, as appropriate, to compute the F factors:

$$F_d = \frac{K\left(K_{hd}\%H + K_c\%C + K_s\%S + K_n\%N - K_o\%O\right)}{GCV} \qquad \text{Eq. 19-13}$$

$$F_w = \frac{K\left[K_{hw}\%H + K_c\%C + K_s\%S + K_n\%N - K_o\%O + K_w\%H_2O\right]}{GCV_w} \qquad \text{Eq. 19-14}$$

$$F_c = \frac{K\left(K_{cc}\%C\right)}{GCV} \qquad \text{Eq. 19-15}$$

NOTE: Omit the $\%H_2O$ term in the equations for F_w if %H and %O include the unavailable hydrogen and oxygen in the form of H_2O.)

12.3.2.2 Use applicable sampling procedures in section 12.5.2.1 or 12.5.2.2 to obtain samples for analyses.

12.3.2.3 Use ASTM D 3176–74 or 89 (all cited ASTM standards are incorporated by reference—see §60.17) for ultimate analysis of the fuel.

12.3.2.4 Use applicable methods in section 12.5.2.1 or 12.5.2.2 to determine the heat content of solid or liquid fuels. For gaseous fuels, use ASTM D 1826–77 or 94 (incorporated by reference—see §60.17) to determine the heat content.

12.3.3 F Factors for Combination of Fuels. If combinations of fuels are burned, use the following equations, as applicable unless otherwise specified in an applicable subpart:

$$F_d = \sum_{k=1}^{n}\left(X_k F_{dk}\right) \qquad \text{Eq. 19-16}$$

$$F_w = \sum_{k=1}^{n}\left(X_k F_{wk}\right) \qquad \text{Eq. 19-17}$$

$$F_c = \sum_{k=1}^{n}\left(X_k F_{ck}\right) \qquad \text{Eq. 19-18}$$

12.4 Determination of Average Pollutant Rates.

12.4.1 Average Pollutant Rates from Hourly Values. When hourly average pollutant rates (E_h), inlet or outlet, are obtained (*e.g.*, CEMS values), compute the average pollutant rate (E_a) for the performance test period (*e.g.*, 30 days) specified in the applicable regulation using the following equation:

$$E_a = \frac{1}{H}\sum_{j=1}^{n} E_{hj} \qquad \text{Eq. 19-19}$$

12.4.2 Average Pollutant Rates from Other than Hourly Averages. When pollutant rates are determined from measured values representing longer than 1-hour periods (*e.g.*, daily fuel sampling and analyses or Method 6B values), or when pollutant rates are determined from combinations of 1-hour and longer than 1-hour periods (*e.g.*, CEMS and Method 6B values), compute the average pollutant rate (E_a) for the performance test period (*e.g.*, 30 days) specified in the applicable regulation using the following equation:

$$E_a = \frac{\sum_{j=1}^{D}\left(n_d E_d\right)_j}{\sum_{j=1}^{D} n_{dj}} \qquad \text{Eq. 19-20}$$

12.4.3 Daily Geometric Average Pollutant Rates from Hourly Values. The geometric average pollutant rate (E_{ga}) is computed using the following equation:

$$E_{ga} = \exp\left[\frac{1}{n_t}\sum_{j=1}^{n_t}\left[\ln\left(E_{hj}\right)\right]\right] \quad \text{Eq. 19-21}$$

12.5 Determination of Overall Reduction in Potential Sulfur Dioxide Emission.

12.5.1 Overall Percent Reduction. Compute the overall percent SO_2 reduction ($\%R_o$) using the following equation:

$$\%R_o = 100\left[1.0 - \left(1.0 - \frac{\%R_f}{100}\right)\left(1.0 - \frac{\%R_g}{100}\right)\right] \quad \text{Eq. 19-22}$$

12.5.2 Pretreatment Removal Efficiency (Optional). Compute the SO_2 removal efficiency from fuel pretreatment ($\%R_f$) for the averaging period (*e.g.*, 90 days) as specified in the applicable regulation using the following equation:

$$\%R_f = 100\left[1.0 - \frac{\sum_{j=1}^{N}\left(\frac{\%S_{pj}}{GCV_{pj}}\right)L_{pj}}{\sum_{j=1}^{N}\left(\frac{\%S_{rj}}{GCV_{rj}}\right)L_{rj}}\right] \quad \text{Eq. 19-23}$$

NOTE: In calculating $\%R_f$, include %S and GCV values for all fuel lots that are not pretreated and are used during the averaging period.

12.5.2.1 Solid Fossil (Including Waste) Fuel/Sampling and Analysis.

NOTE: For the purposes of this method, raw fuel (coal or oil) is the fuel delivered to the desulfurization (pretreatment) facility. For oil, the input oil to the oil desulfurization process (*e.g.*, hydrotreatment) is considered to be the raw fuel.

12.5.2.1.1 Sample Increment Collection. Use ASTM D 2234–76, 96, 97a, or 98 (incorporated by reference—see §60.17), Type I, Conditions A, B, or C, and systematic spacing. As used in this method, systematic spacing is intended to include evenly spaced increments in time or increments based on equal weights of coal passing the collection area. As a minimum, determine the number and weight of increments required per gross sample representing each coal lot according to Table 2 or Paragraph 7.1.5.2 of ASTM D 2234. Collect one gross sample for each lot of raw coal and one gross sample for each lot of product coal.

12.5.2.1.2 ASTM Lot Size. For the purpose of section 12.5.2 (fuel pretreatment), the lot size of product coal is the weight of product coal from one type of raw coal. The lot size of raw coal is the weight of raw coal used to produce one lot of product coal. Typically, the lot size is the weight of coal processed in a 1-day (24-hour) period. If more than one type of coal is treated and produced in 1 day, then gross samples must be collected and analyzed for each type of coal. A coal lot size equaling the 90-day quarterly fuel quantity for a steam generating unit may be used if representative sampling can be conducted for each raw coal and product coal.

NOTE: Alternative definitions of lot sizes may be used, subject to prior approval of the Administrator.

12.5.2.1.3 Gross Sample Analysis. Use ASTM D 2013–72 or 86 to prepare the sample, ASTM D 3177–75 or 89 or ASTM D 4239–85, 94, or 97 to determine sulfur content (%S), ASTM D 3173–73 or 87 to determine moisture content, and ASTM D 2015–77 (Reapproved 1978) or 96, D 3286–85 or 96, or D 5865–98 or 10 to determine gross calorific value (GCV) (all standards cited are incorporated by reference—see §60.17 for acceptable versions of the standards) on a dry basis for each gross sample.

12.5.2.2 Liquid Fossil Fuel-Sampling and Analysis. See Note under section 12.5.2.1.

12.5.2.2.1 Sample Collection. Follow the procedures for continuous sampling in ASTM D 270 or D 4177–95 (incorporated by reference—see §60.17) for each gross sample from each fuel lot.

12.5.2.2.2 Lot Size. For the purpose of section 12.5.2 (fuel pretreatment), the lot size of a product oil is the weight of product oil from one pretreatment facility and intended as one shipment (ship load, barge load, etc.). The lot size of raw oil is the weight of each crude liquid fuel type used to produce a lot of product oil.

NOTE: Alternative definitions of lot sizes may be used, subject to prior approval of the Administrator.

12.5.2.2.3 Sample Analysis. Use ASTM D 129–64, 78, or 95, ASTM D 1552–83 or 95, or ASTM D 4057–81 or 95 to determine the sulfur content (%S) and ASTM D 240–76 or 92 (all standards cited are incorporated by reference—see §60.17) to determine the GCV of each gross sample. These values may be assumed to be on a dry basis. The owner or operator of an affected facility may elect to determine the GCV by sampling the oil combusted on the first steam generating unit operating day of each calendar month and then using the lowest GCV value of the three GCV values per quarter for the GCV of all oil combusted in that calendar quarter.

12.5.2.3 Use appropriate procedures, subject to the approval of the Administrator, to determine the fraction of total mass input derived from each type of fuel.

12.5.3 Control Device Removal Efficiency. Compute the percent removal efficiency ($\%R_g$) of the control device using the following equation:

$$\%R_g = 100\left(1.0 - \frac{E_{ao}}{E_{ai}}\right) \qquad \text{Eq. 19-24}$$

12.5.3.1 Use continuous emission monitoring systems or test methods, as appropriate, to determine the outlet SO_2 rates and, if appropriate, the inlet SO_2 rates. The rates may be determined as hourly (E_h) or other sampling period averages (E_d). Then, compute the average pollutant rates for the performance test period (E_{ao} and E_{ai}) using the procedures in section 12.4.

12.5.3.2 As an alternative, as-fired fuel sampling and analysis may be used to determine inlet SO_2 rates as follows:

12.5.3.2.1 Compute the average inlet SO_2 rate (E_{di}) for each sampling period using the following equation:

$$E_{di} = K\frac{\%S}{GCV} \qquad \text{Eq. 19-25}$$

Where:

$$K = 2\times10^7\left(\frac{\text{ng SO}_2}{\%S}\right)\left(\frac{(\text{kJ})}{\text{J}}\right)\left(\frac{1}{\text{kg coal}}\right)\left[2\times10^4\left(\frac{\text{lb SO}_2}{\%S}\right)\left(\frac{\text{Btu}}{\text{million Btu}}\right)\left(\frac{1}{\text{lb coal}}\right)\right]$$

After calculating E_{di}, use the procedures in section 12.4 to determine the average inlet SO_2 rate for the performance test period (E_{ai}).

12.5.3.2.2 Collect the fuel samples from a location in the fuel handling system that provides a sample representative of the fuel bunkered or consumed during a steam generating unit operating day. For the purpose of as-fired fuel sampling under section 12.5.3.2 or section 12.6, the lot size for coal is the weight of coal bunkered or consumed during each steam generating unit operating day. The lot size for oil is the weight of oil supplied to the ''day'' tank or consumed during each steam generating unit operating day. For reporting and calculation purposes, the gross sample shall be identified with the calendar day on which sampling began. For steam generating unit operating days when a coal-fired steam generating unit is operated without coal being added to the bunkers, the coal analysis from the previous ''as bunkered'' coal sample shall be used until coal is bunkered again. For steam generating unit operating days when an oil-fired steam generating unit is operated without oil being added to the oil ''day'' tank, the oil analysis from the previous day shall be used until the ''day'' tank is filled again. Alternative definitions of fuel lot size may be used, subject to prior approval of the Administrator.

12.5.3.2.3 Use ASTM procedures specified in section 12.5.2.1 or 12.5.2.2 to determine %S and GCV.

12.5.4 Daily Geometric Average Percent Reduction from Hourly Values. The geometric average percent reduction ($\%R_{ga}$) is computed using the following equation:

$$\%R_{ga} = 100\left[1 - \text{EXP}\left(\frac{1}{n_t}\sum_{j=1}^{n_t}\ln\frac{E_{jo}}{E_{ji}}\right)\right] \qquad \text{Eq. 19-26}$$

NOTE: The calculation includes only paired data sets (hourly average) for the inlet and outlet pollutant measurements.

12.6 Sulfur Retention Credit for Compliance Fuel. If fuel sampling and analysis procedures in section 12.5.2.1 are being used to determine average SO_2 emission rates (E_{as}) to the atmosphere from a coal-fired steam generating unit when there is no SO_2 control device, the following equation may be used to adjust the emission rate for sulfur retention credits (no credits are allowed for oil-fired systems) (E_{di}) for each sampling period using the following equation:

$$E_{di} = 0.97K\ \frac{\%S}{GDV} \qquad \text{Eq. 19-27}$$

Where:

$$K = 2\times10^{7}\left(\frac{\text{ng } SO_2}{\%S}\right)\left(\frac{kJ}{J}\right)\left(\frac{1}{\text{kg coal}}\right)\left[2\times10^{4}\left(\frac{\text{lb } SO_2}{\%S}\right)\left(\frac{Btu}{\text{million Btu}}\right)\left(\frac{1}{\text{lb coal}}\right)\right]$$

After calculating E_{di}, use the procedures in section 12.4.2 to determine the average SO_2 emission rate to the atmosphere for the performance test period (E_{ao}).

12.7 Determination of Compliance When Minimum Data Requirement Is Not Met.

12.7.1 Adjusted Emission Rates and Control Device Removal Efficiency. When the minimum data requirement is not met, the Administrator may use the following adjusted emission rates or control device removal efficiencies to determine compliance with the applicable standards.

12.7.1.1 Emission Rate. Compliance with the emission rate standard may be determined by using the lower confidence limit of the emission rate (E_{ao}*) as follows:

$$E^{*}_{ao} = E_{ao} - t_{0.95}S_o \qquad \text{Eq. 19-28}$$

12.7.1.2 Control Device Removal Efficiency. Compliance with the overall emission reduction ($\%R_o$) may be determined by using the lower confidence limit of the emission rate (E_{ao}*) and the upper confidence limit of the inlet pollutant rate (E_{ai}*) in calculating the control device removal efficiency ($\%R_g$) as follows:

$$\%R_g = 100\left(1.0 - \frac{E^{*}_{ao}}{E^{*}_{ai}}\right) \qquad \text{Eq. 19-29}$$

$$E^{*}_{ai} = E_{ai} + t_{0.95}S_i \qquad \text{Eq. 19-30}$$

12.7.2 Standard Deviation of Hourly Average Pollutant Rates. Compute the standard deviation (S_e) of the hourly average pollutant rates using the following equation:

$$S_e = \sqrt{\frac{1}{H} - \frac{1}{H_r}}\ \sqrt{\frac{\sum_{j=1}^{H}\left(E_{hj} - E_a\right)^2}{H-1}} \qquad \text{Eq. 19-31}$$

Equation 19–19 through 19–31 may be used to compute the standard deviation for both the outlet (S_o) and, if applicable, inlet (S_i) pollutant rates.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References [Reserved]

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 19–1—CONVERSION FACTORS FOR CONCENTRATION

From	To	Multiply by
g/scm	ng/scm	10^9
mg/scm	ng/scm	10^6
lb/scf	ng/scm	1.602×10^{13}

TABLE 19–1—CONVERSION FACTORS FOR CONCENTRATION—Continued

From	To	Multiply by
ppm SO_2	ng/scm	2.66×10^6
ppm NO_X	ng/scm	1.912×10^6
ppm SO_2	lb/scf	1.660×10^{-7}
ppm NO_X	lb/scf	1.194×10^{-7}

TABLE 19–2—F FACTORS FOR VARIOUS FUELS[1]

Fuel Type	F_d		F_w		F_c	
	dscm/J	dscf/10^6 Btu	wscm/J	wscf/10^6 Btu	scm/J	scf/10^6 Btu
Coal:						
Anthracite[2]	2.71×10^{-7}	10,100	2.83×10^{-7}	10,540	0.530×10^{-7}	1,970
Bituminus[2]	2.63×10^{-7}	9,780	2.86×10^{-7}	10,640	0.484×10^{-7}	1,800
Lignite	2.65×10^{-7}	9,860	3.21×10^{-7}	11,950	0.513×10^{-7}	1,910
Oil[3]	2.47×10^{-7}	9,190	2.77×10^{-7}	10,320	0.383×10^{-7}	1,420
Gas:.						
Natural	2.34×10^{-7}	8,710	2.85×10^{-7}	10,610	0.287×10^{-7}	1,040
Propane	2.34×10^{-7}	8,710	2.74×10^{-7}	10,200	0.321×10^{-7}	1,190
Butane	2.34×10^{-7}	8,710	2.79×10^{-7}	10,390	0.337×10^{-7}	1,250
Wood	2.48×10^{-7}	9,240			0.492×10^{-7}	1,830
Wood Bark	2.58×10^{-7}	9,600			0.516×10^{-7}	1,920
Municipal	2.57×10^{-7}	9,570			0.488×10^{-7}	1,820
Solid Waste						

[1] Determined at standard conditions: 20 °C (68 °F) and 760 mm Hg (29.92 in Hg)
[2] As classified according to ASTM D 388.
[3] Crude, residual, or distillate.

TABLE 19–3—VALUES FOR $T_{0.95*}$

n[1]	$t_{0.95}$	n[1]	$t_{0.95}$	n[1]	$t_{0.95}$
2	6.31	8	1.89	22–26	1.71
3	2.42	9	1.86	27–31	1.70
4	2.35	10	1.83	32–51	1.68
5	2.13	11	1.81	52–91	1.67
6	2.02	12–16	1.77	92–151	1.66
7	1.94	17–21	1.73	152 or more	1.65

[1] The values of this table are corrected for n-1 degrees of freedom. Use n equal to the number (H) of hourly average data points.

METHOD 20—DETERMINATION OF NITROGEN OXIDES, SULFUR DIOXIDE, AND DILUENT EMISSIONS FROM STATIONARY GAS TURBINES

1.0 Scope and Application

What is Method 20?

Method 20 contains the details you must follow when using an instrumental analyzer to determine concentrations of nitrogen oxides, oxygen, carbon dioxide, and sulfur dioxide in the emissions from stationary gas turbines. This method follows the specific instructions for equipment and performance requirements, supplies, sample collection and analysis, calculations, and data analysis in the methods listed in section 2.0.

1.1 Analytes. What does this method determine?

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X) as nitrogen dioxide:	10102–43–9	Typically <2% of Calibration Span.
Nitric oxide (NO)	10102–44–0	
Nitrogen dioxide NO_2.		
Diluent oxygen (O_2) or carbon dioxide (CO_2)		Typically <2% of Calibration Span.
Sulfur dioxide (SO_X)	7446–09–5	Typically <2% of Calibration Span.

1.2 Applicability. When is this method required? The use of Method 20 may be required by specific New Source Performance Standards, Clean Air Marketing rules, and State Implementation Plans and permits where

measuring SO_2, NO_X, CO_2, and/or O_2 concentrations in stationary gas turbines emissions are required. Other regulations may also require its use.

1.3 Data Quality Objectives. How good must my collected data be? Refer to section 1.3 of Method 7E.

2.0 Summary of Method

In this method, NO_X, O_2 (or CO_2), and SO_X are measured using the following methods found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 3A—Determination of Oxygen and Carbon Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(c) Method 6C—Determination of Sulfur Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(d) Method 7E—Determination of Nitrogen Oxides Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(e) Method 19—Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates.

3.0 Definitions

Refer to section 3.0 of Method 7E for the applicable definitions.

4.0 Interferences

Refer to section 4.0 of Methods 3A, 6C, and 7E as applicable.

5.0 Safety

Refer to section 5.0 of Method 7E.

6.0 Equipment and Supplies

The measurement system design is shown in Figure 7E–1 of Method 7E. Refer to the appropriate methods listed in section 2.0 for equipment and supplies.

7.0 Reagents and Standards

Refer to the appropriate methods listed in section 2.0 for reagents and standards.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling Site and Sampling Points. Follow the procedures of section 8.1 of Method 7E. For the stratification test in section 8.1.2, determine the diluent-corrected pollutant concentration at each traverse point.

8.2 Initial Measurement System Performance Tests. You must refer to the appropriate methods listed in section 2.0 for the measurement system performance tests as applicable.

8.3 Interference Check. You must follow the procedures in section 8.3 of Method 3A or 6C, or section 8.2.7 of Method 7E (as appropriate).

8.4 Sample Collection. You must follow the procedures of section 8.4 of the appropriate methods listed in section 2.0. A test run must have a duration of at least 21 minutes.

8.5 Post-Run System Bias Check, Drift Assessment, and Alternative Dynamic Spike Procedure. You must follow the procedures of sections 8.5 and 8.6 of the appropriate methods listed in section 2.0. A test run must have a duration of at least 21 minutes.

9.0 Quality Control

Follow quality control procedures in section 9.0 of Method 7E.

10.0 Calibration and Standardization

Follow the procedures for calibration and standardization in section 10.0 of Method 7E.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the procedures for calculations and data analysis in section 12.0 of the appropriate method listed in section 2.0. Follow the procedures in section 12.0 of Method 19 for calculating fuel-specific F factors, diluent-corrected pollutant concentrations, and emission rates.

13.0 Method Performance

The specifications for the applicable performance checks are the same as in section 13.0 of Method 7E.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

Refer to section 16.0 of the appropriate method listed in section 2.0 for alternative procedures.

17.0 References

Refer to section 17.0 of the appropriate method listed in section 2.0 for references.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

Refer to section 18.0 of the appropriate method listed in section 2.0 for tables, diagrams, flowcharts, and validation data.

METHOD 21—DETERMINATION OF VOLATILE ORGANIC COMPOUND LEAKS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile Organic Compounds (VOC).	No CAS number assigned.

1.2 Scope. This method is applicable for the determination of VOC leaks from process equipment. These sources include, but are not limited to, valves, flanges and other connections, pumps and compressors, pressure relief devices, process drains, open-ended valves, pump and compressor seal system degassing vents, accumulator vessel vents, agitator seals, and access door seals.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A portable instrument is used to detect VOC leaks from individual sources. The instrument detector type is not specified, but it must meet the specifications and performance criteria contained in section 6.0. A leak definition concentration based on a reference compound is specified in each applicable regulation. This method is intended to locate and classify leaks only, and is not to be used as a direct measure of mass emission rate from individual sources.

3.0 Definitions

3.1 *Calibration gas* means the VOC compound used to adjust the instrument meter reading to a known value. The calibration gas is usually the reference compound at a known concentration approximately equal to the leak definition concentration.

3.2 *Calibration precision* means the degree of agreement between measurements of the same known value, expressed as the relative percentage of the average difference between the meter readings and the known concentration to the known concentration.

3.3 *Leak definition concentration* means the local VOC concentration at the surface of a leak source that indicates that a VOC emission (leak) is present. The leak definition is an instrument meter reading based on a reference compound.

3.4 *No detectable emission* means a local VOC concentration at the surface of a leak source, adjusted for local VOC ambient concentration, that is less than 2.5 percent of the specified leak definition concentration. that indicates that a VOC emission (leak) is not present.

3.5 *Reference compound* means the VOC species selected as the instrument calibration basis for specification of the leak definition concentration. (For example, if a leak definition concentration is 10,000 ppm as methane, then any source emission that results in a local concentration that yields a meter reading of 10,000 on an instrument meter calibrated with methane would be classified as a leak. In this example, the leak definition concentration is 10,000 ppm and the reference compound is methane.)

3.6 *Response factor* means the ratio of the known concentration of a VOC compound to the observed meter reading when measured using an instrument calibrated with the reference compound specified in the applicable regulation.

3.7 *Response time* means the time interval from a step change in VOC concentration at the input of the sampling system to the time at which 90 percent of the corresponding final value is reached as displayed on the instrument readout meter.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Pollutants. Several of the compounds, leaks of which may be determined by this method, may be irritating or corrosive to tissues (*e.g.*, heptane) or may be toxic (*e.g.*, benzene, methyl alcohol). Nearly all are fire hazards. Compounds in emissions should be determined through familiarity with the source. Appropriate precautions can be found in reference documents, such as reference No. 4 in section 16.0.

6.0 Equipment and Supplies

A VOC monitoring instrument meeting the following specifications is required:

6.1 The VOC instrument detector shall respond to the compounds being processed. Detector types that may meet this requirement include, but are not limited to, catalytic oxidation, flame ionization, infrared absorption, and photoionization.

6.2 The instrument shall be capable of measuring the leak definition concentration specified in the regulation.

6.3 The scale of the instrument meter shall be readable to ±2.5 percent of the specified leak definition concentration.

6.4 The instrument shall be equipped with an electrically driven pump to ensure that a sample is provided to the detector at a constant flow rate. The nominal sample flow rate, as measured at the sample probe tip, shall be 0.10 to 3.0 l/min (0.004 to 0.1 ft^3/min) when the probe is fitted with a glass wool plug or filter that may be used to prevent plugging of the instrument.

6.5 The instrument shall be equipped with a probe or probe extension or sampling not to exceed 6.4 mm (¼ in) in outside diameter,

with a single end opening for admission of sample.

6.6 The instrument shall be intrinsically safe for operation in explosive atmospheres as defined by the National Electrical Code by the National Fire Prevention Association or other applicable regulatory code for operation in any explosive atmospheres that may be encountered in its use. The instrument shall, at a minimum, be intrinsically safe for Class 1, Division 1 conditions, and/or Class 2, Division 1 conditions, as appropriate, as defined by the example code. The instrument shall not be operated with any safety device, such as an exhaust flame arrestor, removed.

7.0 Reagents and Standards

7.1 Two gas mixtures are required for instrument calibration and performance evaluation:

7.1.1 Zero Gas. Air, less than 10 parts per million by volume (ppmv) VOC.

7.1.2 Calibration Gas. For each organic species that is to be measured during individual source surveys, obtain or prepare a known standard in air at a concentration approximately equal to the applicable leak definition specified in the regulation.

7.2 Cylinder Gases. If cylinder calibration gas mixtures are used, they must be analyzed and certified by the manufacturer to be within 2 percent accuracy, and a shelf life must be specified. Cylinder standards must be either reanalyzed or replaced at the end of the specified shelf life.

7.3 Prepared Gases. Calibration gases may be prepared by the user according to any accepted gaseous preparation procedure that will yield a mixture accurate to within 2 percent. Prepared standards must be replaced each day of use unless it is demonstrated that degradation does not occur during storage.

7.4 Mixtures with non-Reference Compound Gases. Calibrations may be performed using a compound other than the reference compound. In this case, a conversion factor must be determined for the alternative compound such that the resulting meter readings during source surveys can be converted to reference compound results.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Instrument Performance Evaluation. Assemble and start up the instrument according to the manufacturer's instructions for recommended warmup period and preliminary adjustments.

8.1.1 Response Factor. A response factor must be determined for each compound that is to be measured, either by testing or from reference sources. The response factor tests are required before placing the analyzer into service, but do not have to be repeated at subsequent intervals.

8.1.1.1 Calibrate the instrument with the reference compound as specified in the applicable regulation. Introduce the calibration gas mixture to the analyzer and record the observed meter reading. Introduce zero gas until a stable reading is obtained. Make a total of three measurements by alternating between the calibration gas and zero gas. Calculate the response factor for each repetition and the average response factor.

8.1.1.2 The instrument response factors for each of the individual VOC to be measured shall be less than 10 unless otherwise specified in the applicable regulation. When no instrument is available that meets this specification when calibrated with the reference VOC specified in the applicable regulation, the available instrument may be calibrated with one of the VOC to be measured, or any other VOC, so long as the instrument then has a response factor of less than 10 for each of the individual VOC to be measured.

8.1.1.3 Alternatively, if response factors have been published for the compounds of interest for the instrument or detector type, the response factor determination is not required, and existing results may be referenced. Examples of published response factors for flame ionization and catalytic oxidation detectors are included in References 1–3 of section 17.0.

8.1.2 Calibration Precision. The calibration precision test must be completed prior to placing the analyzer into service and at subsequent 3-month intervals or at the next use, whichever is later.

8.1.2.1 Make a total of three measurements by alternately using zero gas and the specified calibration gas. Record the meter readings. Calculate the average algebraic difference between the meter readings and the known value. Divide this average difference by the known calibration value and multiply by 100 to express the resulting calibration precision as a percentage.

8.1.2.2 The calibration precision shall be equal to or less than 10 percent of the calibration gas value.

8.1.3 Response Time. The response time test is required before placing the instrument into service. If a modification to the sample pumping system or flow configuration is made that would change the response time, a new test is required before further use.

8.1.3.1 Introduce zero gas into the instrument sample probe. When the meter reading has stabilized, switch quickly to the specified calibration gas. After switching, measure the time required to attain 90 percent of the final stable reading. Perform this test sequence three times and record the results. Calculate the average response time.

8.1.3.2 The instrument response time shall be equal to or less than 30 seconds. The instrument pump, dilution probe (if any), sample probe, and probe filter that will be used

during testing shall all be in place during the response time determination.

8.2 Instrument Calibration. Calibrate the VOC monitoring instrument according to section 10.0.

8.3 Individual Source Surveys.

8.3.1 Type I—Leak Definition Based on Concentration. Place the probe inlet at the surface of the component interface where leakage could occur. Move the probe along the interface periphery while observing the instrument readout. If an increased meter reading is observed, slowly sample the interface where leakage is indicated until the maximum meter reading is obtained. Leave the probe inlet at this maximum reading location for approximately two times the instrument response time. If the maximum observed meter reading is greater than the leak definition in the applicable regulation, record and report the results as specified in the regulation reporting requirements. Examples of the application of this general technique to specific equipment types are:

8.3.1.1 Valves. The most common source of leaks from valves is the seal between the stem and housing. Place the probe at the interface where the stem exits the packing gland and sample the stem circumference. Also, place the probe at the interface of the packing gland take-up flange seat and sample the periphery. In addition, survey valve housings of multipart assembly at the surface of all interfaces where a leak could occur.

8.3.1.2 Flanges and Other Connections. For welded flanges, place the probe at the outer edge of the flange-gasket interface and sample the circumference of the flange. Sample other types of nonpermanent joints (such as threaded connections) with a similar traverse.

8.3.1.3 Pumps and Compressors. Conduct a circumferential traverse at the outer surface of the pump or compressor shaft and seal interface. If the source is a rotating shaft, position the probe inlet within 1 cm of the shaft-seal interface for the survey. If the housing configuration prevents a complete traverse of the shaft periphery, sample all accessible portions. Sample all other joints on the pump or compressor housing where leakage could occur.

8.3.1.4 Pressure Relief Devices. The configuration of most pressure relief devices prevents sampling at the sealing seat interface. For those devices equipped with an enclosed extension, or horn, place the probe inlet at approximately the center of the exhaust area to the atmosphere.

8.3.1.5 Process Drains. For open drains, place the probe inlet at approximately the center of the area open to the atmosphere. For covered drains, place the probe at the surface of the cover interface and conduct a peripheral traverse.

8.3.1.6 Open-ended Lines or Valves. Place the probe inlet at approximately the center of the opening to the atmosphere.

8.3.1.7 Seal System Degassing Vents and Accumulator Vents. Place the probe inlet at approximately the center of the opening to the atmosphere.

8.3.1.8 Access door seals. Place the probe inlet at the surface of the door seal interface and conduct a peripheral traverse.

8.3.2 Type II—''No Detectable Emission''. Determine the local ambient VOC concentration around the source by moving the probe randomly upwind and downwind at a distance of one to two meters from the source. If an interference exists with this determination due to a nearby emission or leak, the local ambient concentration may be determined at distances closer to the source, but in no case shall the distance be less than 25 centimeters. Then move the probe inlet to the surface of the source and determine the concentration as outlined in section 8.3.1. The difference between these concentrations determines whether there are no detectable emissions. Record and report the results as specified by the regulation. For those cases where the regulation requires a specific device installation, or that specified vents be ducted or piped to a control device, the existence of these conditions shall be visually confirmed. When the regulation also requires that no detectable emissions exist, visual observations and sampling surveys are required. Examples of this technique are:

8.3.2.1 Pump or Compressor Seals. If applicable, determine the type of shaft seal. Perform a survey of the local area ambient VOC concentration and determine if detectable emissions exist as described in section 8.3.2.

8.3.2.2 Seal System Degassing Vents, Accumulator Vessel Vents, Pressure Relief Devices. If applicable, observe whether or not the applicable ducting or piping exists. Also, determine if any sources exist in the ducting or piping where emissions could occur upstream of the control device. If the required ducting or piping exists and there are no sources where the emissions could be vented to the atmosphere upstream of the control device, then it is presumed that no detectable emissions are present. If there are sources in the ducting or piping where emissions could be vented or sources where leaks could occur, the sampling surveys described in section 8.3.2 shall be used to determine if detectable emissions exist.

8.3.3 Alternative Screening Procedure.

8.3.3.1 A screening procedure based on the formation of bubbles in a soap solution that is sprayed on a potential leak source may be used for those sources that do not have continuously moving parts, that do not have surface temperatures greater than the boiling point or less than the freezing point of the soap solution, that do not have open

areas to the atmosphere that the soap solution cannot bridge, or that do not exhibit evidence of liquid leakage. Sources that have these conditions present must be surveyed using the instrument technique of section 8.3.1 or 8.3.2.

8.3.3.2 Spray a soap solution over all potential leak sources. The soap solution may be a commercially available leak detection solution or may be prepared using concentrated detergent and water. A pressure sprayer or squeeze bottle may be used to dispense the solution. Observe the potential leak sites to determine if any bubbles are formed. If no bubbles are observed, the source is presumed to have no detectable emissions or leaks as applicable. If any bubbles are observed, the instrument techniques of section 8.3.1 or 8.3.2 shall be used to determine if a leak exists, or if the source has detectable emissions, as applicable.

9.0 Quality Control

Section	Quality control measure	Effect
8.1.2	Instrument calibration precision check	Ensure precision and accuracy, respectively, of instrument response to standard.
10.0	Instrument calibration.	

10.0 Calibration and Standardization

10.1 Calibrate the VOC monitoring instrument as follows. After the appropriate warmup period and zero internal calibration procedure, introduce the calibration gas into the instrument sample probe. Adjust the instrument meter readout to correspond to the calibration gas value.

NOTE: If the meter readout cannot be adjusted to the proper value, a malfunction of the analyzer is indicated and corrective actions are necessary before use.

11.0 Analytical Procedures [Reserved]

12.0 Data Analyses and Calculations [Reserved]

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Dubose, D.A., and G.E. Harris. Response Factors of VOC Analyzers at a Meter Reading of 10,000 ppmv for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81051. September 1981.

2. Brown, G.E., *et al.* Response Factors of VOC Analyzers Calibrated with Methane for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81–022. May 1981.

3. DuBose, D.A. *et al.* Response of Portable VOC Analyzers to Chemical Mixtures. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81–110. September 1981.

4. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 22—VISUAL DETERMINATION OF FUGITIVE EMISSIONS FROM MATERIAL SOURCES AND SMOKE EMISSIONS FROM FLARES

NOTE: This method is not inclusive with respect to observer certification. Some material is incorporated by reference from Method 9.

1.0 Scope and Application

This method is applicable for the determination of the frequency of fugitive emissions from stationary sources, only as specified in an applicable subpart of the regulations. This method also is applicable for the determination of the frequency of visible smoke emissions from flares.

2.0 Summary of Method

2.1 Fugitive emissions produced during material processing, handling, and transfer operations or smoke emissions from flares are visually determined by an observer without the aid of instruments.

2.2 This method is used also to determine visible smoke emissions from flares used for combustion of waste process materials.

2.3 This method determines the amount of time that visible emissions occur during the observation period (*i.e.*, the accumulated emission time). This method does not require that the opacity of emissions be determined. Since this procedure requires only the determination of whether visible emissions occur and does not require the determination of opacity levels, observer certification according to the procedures of Method 9 is not required. However, it is necessary that the observer is knowledgeable with respect to the general procedures for determining the presence of visible emissions. At a minimum, the observer must be trained and knowledgeable regarding the effects of background contrast, ambient lighting, observer position relative

to lighting, wind, and the presence of uncombined water (condensing water vapor) on the visibility of emissions. This training is to be obtained from written materials found in References 1 and 2 or from the lecture portion of the Method 9 certification course.

3.0 Definitions

3.1 *Emission frequency* means the percentage of time that emissions are visible during the observation period.

3.2 *Emission time* means the accumulated amount of time that emissions are visible during the observation period.

3.3 *Fugitive emissions* means emissions generated by an affected facility which is not collected by a capture system and is released to the atmosphere. This includes emissions that (1) escape capture by process equipment exhaust hoods; (2) are emitted during material transfer; (3) are emitted from buildings housing material processing or handling equipment; or (4) are emitted directly from process equipment.

3.4 *Observation period* means the accumulated time period during which observations are conducted, not to be less than the period specified in the applicable regulation.

3.5 *Smoke emissions* means a pollutant generated by combustion in a flare and occurring immediately downstream of the flame. Smoke occurring within the flame, but not downstream of the flame, is not considered a smoke emission.

4.0 Interferences

4.1 Occasionally, fugitive emissions from sources other than the affected facility (*e.g.*, road dust) may prevent a clear view of the affected facility. This may particularly be a problem during periods of high wind. If the view of the potential emission points is obscured to such a degree that the observer questions the validity of continuing observations, then the observations shall be terminated, and the observer shall clearly note this fact on the data form.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment

6.1 Stopwatches (two). Accumulative type with unit divisions of at least 0.5 seconds.

6.2 Light Meter. Light meter capable of measuring illuminance in the 50 to 200 lux range, required for indoor observations only.

7.0 Reagents and Supplies [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transfer [Reserved]

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

11.1 Selection of Observation Location. Survey the affected facility, or the building or structure housing the process to be observed, and determine the locations of potential emissions. If the affected facility is located inside a building, determine an observation location that is consistent with the requirements of the applicable regulation (*i.e.*, outside observation of emissions escaping the building/structure or inside observation of emissions directly emitted from the affected facility process unit). Then select a position that enables a clear view of the potential emission point(s) of the affected facility or of the building or structure housing the affected facility, as appropriate for the applicable subpart. A position at least 4.6 m (15 feet), but not more than 400 m (0.25 miles), from the emission source is recommended. For outdoor locations, select a position where the sunlight is not shining directly in the observer's eyes.

11.2 Field Records.

11.2.1 Outdoor Location. Record the following information on the field data sheet (Figure 22–1): Company name, industry, process unit, observer's name, observer's affiliation, and date. Record also the estimated wind speed, wind direction, and sky condition. Sketch the process unit being observed, and note the observer location relative to the source and the sun. Indicate the potential and actual emission points on the sketch.

11.2.2 Indoor Location. Record the following information on the field data sheet (Figure 22–2): Company name, industry, process unit, observer's name, observer's affiliation, and date. Record as appropriate the type, location, and intensity of lighting on the data sheet. Sketch the process unit being observed, and note the observer location relative to the source. Indicate the potential and actual fugitive emission points on the sketch.

11.3 Indoor Lighting Requirements. For indoor locations, use a light meter to measure the level of illumination at a location as close to the emission source(s) as is feasible. An illumination of greater than 100 lux (10 foot candles) is considered necessary for proper application of this method.

11.4 Observations.

11.4.1 Procedure. Record the clock time when observations begin. Use one stopwatch to monitor the duration of the observation

period. Start this stopwatch when the observation period begins. If the observation period is divided into two or more segments by process shutdowns or observer rest breaks (see section 11.4.3), stop the stopwatch when a break begins and restart the stopwatch without resetting it when the break ends. Stop the stopwatch at the end of the observation period. The accumulated time indicated by this stopwatch is the duration of observation period. When the observation period is completed, record the clock time. During the observation period, continuously watch the emission source. Upon observing an emission (condensed water vapor is not considered an emission), start the second accumulative stopwatch; stop the watch when the emission stops. Continue this procedure for the entire observation period. The accumulated elapsed time on this stopwatch is the total time emissions were visible during the observation period (*i.e.*, the emission time.)

11.4.2 Observation Period. Choose an observation period of sufficient length to meet the requirements for determining compliance with the emission standard in the applicable subpart of the regulations. When the length of the observation period is specifically stated in the applicable subpart, it may not be necessary to observe the source for this entire period if the emission time required to indicate noncompliance (based on the specified observation period) is observed in a shorter time period. In other words, if the regulation prohibits emissions for more than 6 minutes in any hour, then observations may (optional) be stopped after an emission time of 6 minutes is exceeded. Similarly, when the regulation is expressed as an emission frequency and the regulation prohibits emissions for greater than 10 percent of the time in any hour, then observations may (optional) be terminated after 6 minutes of emission are observed since 6 minutes is 10 percent of an hour. In any case, the observation period shall not be less than 6 minutes in duration. In some cases, the process operation may be intermittent or cyclic. In such cases, it may be convenient for the observation period to coincide with the length of the process cycle.

11.4.3 Observer Rest Breaks. Do not observe emissions continuously for a period of more than 15 to 20 minutes without taking a rest break. For sources requiring observation periods of greater than 20 minutes, the observer shall take a break of not less than 5 minutes and not more than 10 minutes after every 15 to 20 minutes of observation. If continuous observations are desired for extended time periods, two observers can alternate between making observations and taking breaks.

11.5 Recording Observations. Record the accumulated time of the observation period on the data sheet as the observation period duration. Record the accumulated time emissions were observed on the data sheet as the emission time. Record the clock time the observation period began and ended, as well as the clock time any observer breaks began and ended.

12.0 Data Analysis and Calculations

If the applicable subpart requires that the emission rate be expressed as an emission frequency (in percent), determine this value as follows: Divide the accumulated emission time (in seconds) by the duration of the observation period (in seconds) or by any minimum observation period required in the applicable subpart, if the actual observation period is less than the required period, and multiply this quotient by 100.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Missan, R., and A. Stein. Guidelines for Evaluation of Visible Emissions Certification, Field Procedures, Legal Aspects, and Background Material. EPA Publication No. EPA–340/1–75–007. April 1975.

2. Wohlschlegel, P., and D.E. Wagoner. Guideline for Development of a Quality Assurance Program: Volume IX—Visual Determination of Opacity Emissions from Stationary Sources. EPA Publication No. EPA–650/4–74–005i. November 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

FUGITIVE OR SMOKE EMISSION INSPECTION
OUTDOOR LOCATION

Company Location Company Rep.	Observer Affiliation Date
Sky Conditions Precipitation	Wind Direction Wind Speed
Industry	Process Unit

Sketch process unit: indicate observer position relative to source; indicate potential emission points and/or actual emission points.

OBSERVATIONS	Clock Time	Observation period duration, min:sec	Accumulated emission time, min:sec
Begin Observation			
End Observation			

Figure 22-1

FUGITIVE OR SMOKE EMISSION INSPECTION
INDOOR LOCATION

Company Location Company Rep.	Observer Affiliation Date
Industry	Process Unit

Light type (fluorescent, incandescent, natural)
Light location (overhead, behind observer, etc.)
Illuminance (lux or footcandles)
Sketch process unit: indicate observer position relative to source; indicate potential emission points and/or actual emission points.

OBSERVATIONS	Clock Time	Observation period duration, min:sec	Accumulated emission time, min:sec
Begin			
End Observation			

Figure 22-2

METHOD 23—DETERMINATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS FROM STATIONARY SOURCES

1. Applicability and Principle

1.1 Applicability. This method is applicable to the determination of polychlorinated dibenzo-p-dioxins (PCDD's) and polychlorinated dibenzofurans (PCDF's) from stationary sources.

1.2 Principle. A sample is withdrawn from the gas stream isokinetically and collected in the sample probe, on a glass fiber filter, and on a packed column of adsorbent material. The sample cannot be separated into a particle vapor fraction. The PCDD's and

PCDF's are extracted from the sample, separated by high resolution gas chromatography, and measured by high resolution mass spectrometry.

2. Apparatus

2.1 Sampling. A schematic of the sampling train used in this method is shown in Figure 23–1. Sealing greases may not be used in assembling the train. The train is identical to that described in section 2.1 of Method 5 of this appendix with the following additions:

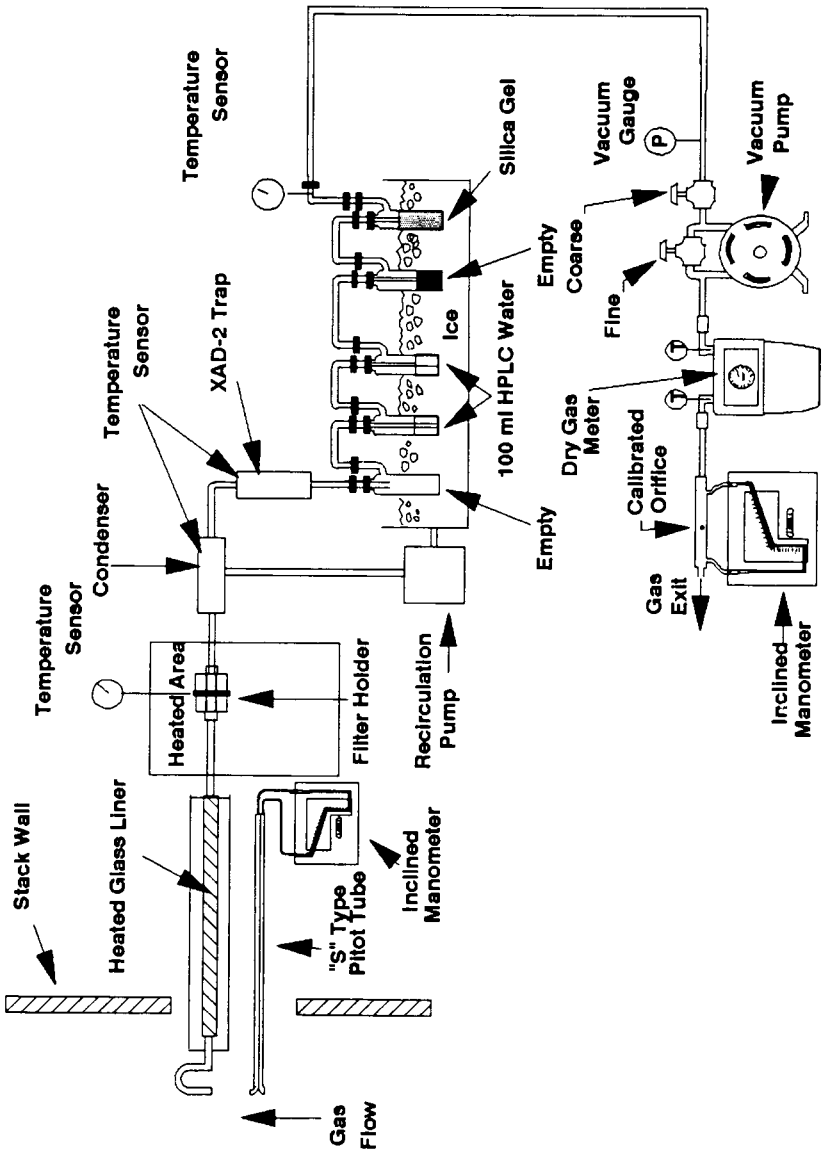


Figure 23.1 Sampling train

2.1.1 Nozzle. The nozzle shall be made of nickel, nickel-plated stainless steel, quartz, or borosilicate glass.

2.1.2 Sample Transfer Lines. The sample transfer lines, if needed, shall be heat traced, heavy walled TFE (½ in. OD with ⅛ in. wall) with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases. The line shall be as short as possible and must be maintained at 120 °C.

2.1.1 Filter Support. Teflon or Teflon-coated wire.

2.1.2 Condenser. Glass, coil type with compatible fittings. A schematic diagram is shown in Figure 23–2.

2.1.3 Water Bath. Thermostatically controlled to maintain the gas temperature exiting the condenser at <20 °C (68 °F).

2.1.4 Adsorbent Module. Glass container to hold the solid adsorbent. A shematic diagram is shown in Figure 23–2. Other physical configurations of the resin trap/condenser assembly are acceptable. The connecting fittings shall form leak-free, vacuum tight seals. No sealant greases shall be used in the sampling train. A coarse glass frit is included to retain the adsorbent.

2.2 Sample Recovery.

2.2.1 Fitting Caps. Ground glass, Teflon tape, or aluminum foil (Section 2.2.6) to cap off the sample exposed sections of the train.

2.2.2 Wash Bottles. Teflon, 500-ml.

2.2.3 Probe-Liner Probe-Nozzle, and Filter-Holder Brushes. Inert bristle brushes with precleaned stainless steel or Teflon handles. The probe brush shall have extensions of stainless steel or Teflon, at least as long as the probe. The brushes shall be properly sized and shaped to brush out the nozzle, probe liner, and transfer line, if used.

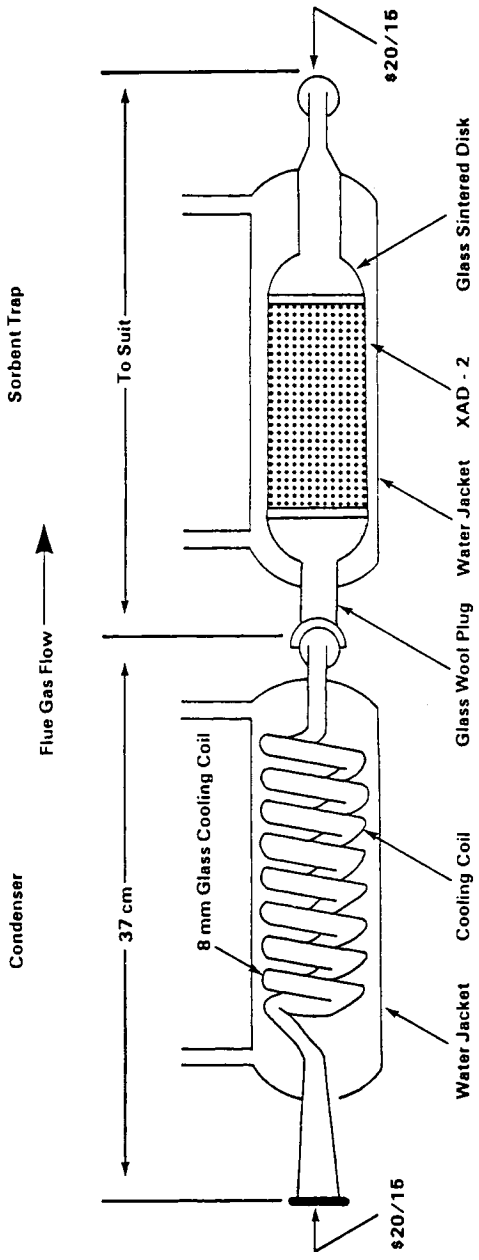


Figure 23.2. Condenser and adsorbent trap

2.2.4 Filter Storage Container. Sealed filter holder, wide-mouth amber glass jar with Teflon-lined cap, or glass petri dish.

2.2.5 Balance. Triple beam.

2.2.6 Aluminum Foil. Heavy duty, hexane-rinsed.

2.2.7 Storage Container. Air-tight container to store silica gel.

2.2.8 Graduated Cylinder. Glass, 250-ml with 2-ml graduation.

2.2.9 Glass Sample Storage Container. Amber glass bottle for sample glassware washes, 500- or 1000-ml, with leak free Teflon-lined caps.

2.3 Analysis.

2.3.1 Sample Container. 125- and 250-ml flint glass bottles with Teflon-lined caps.

2.3.2 Test Tube. Glass.

2.3.3 Soxhlet Extraction Apparatus. Capable of holding 43 × 123 mm extraction thimbles.

2.3.4 Extraction Thimble. Glass, precleaned cellulosic, or glass fiber.

2.3.5 Pasteur Pipettes. For preparing liquid chromatographic columns.

2.3.6 Reacti-vials. Amber glass, 2-ml, silanized prior to use.

2.3.7 Rotary Evaporator. Buchi/Brinkman RF–121 or equivalent.

2.3.8 Nitrogen Evaporative Concentrator. N-Evap Analytical Evaporator Model III or equivalent.

2.3.9 Separatory Funnels. Glass, 2-liter.

2.3.10 Gas Chromatograph. Consisting of the following components:

2.3.10.1 Oven. Capable of maintaining the separation column at the proper operating temperature ±°C and performing programmed increases in temperature at rates of at least 40 °C/min.

2.3.10.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperatures ±1 °C.

2.3.10.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

2.3.10.4 Capillary Columns. A fused silica column, 60 × 0.25 mm inside diameter (ID), coated with DB–5 and a fused silica column, 30 m × 0.25 mm ID coated with DB–225. Other column systems may be used provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of section 6.1.2.2.

2.3.11 Mass Spectrometer. Capable of routine operation at a resolution of 1:10000 with a stability of ±5 ppm.

2.3.12 Data System. Compatible with the mass spectrometer and capable of monitoring at least five groups of 25 ions.

2.3.13 Analytical Balance. To measure within 0.1 mg.

3. Reagents

3.1 Sampling.

3.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D 2986–71 (Reapproved 1978) (incorporated by reference—see §60.17).

3.1.1.1 Precleaning. All filters shall be cleaned before their initial use. Place a glass extraction thimble and 1 g of silica gel and a plug of glass wool into a Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Place no more than 50 filters in the thimble onto the silica gel bed and top with the cleaned glass wool. Charge the Soxhlet with toluene and reflux for 16 hours. After extraction, allow the Soxhlet to cool, remove the filters, and dry them under a clean N_2 stream. Store the filters in a glass petri dish sealed with Teflon tape.

3.1.2 Adsorbent Resin. Amberlite XAD–2 resin. Thoroughly cleaned before initial use.

3.1.2.1 Cleaning Procedure. This procedure may be carried out in a giant Soxhlet extractor. An all-glass filter thimble containing an extra-course frit is used for extraction of XAD–2. The frit is recessed 10–15 mm above a crenelated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass wool plug and a stainless steel ring because it floats on methylene chloride. This process involves sequential extraction in the following order.

Solvent	Procedure
Water	Initial rinse: Place resin in a beaker, rinse once with water, and discard. Fill with water a second time, let stand overnight, and discard.
Water	Extract with water for 8 hours.
Methanol	Extract for 22 hours.
Methylene Chloride	Extract for 22 hours.
Toluene	Extract for 22 hours.

3.1.2.2 Drying.

3.1.2.2.1 Drying Column. Pyrex pipe, 10.2 cm ID by 0.6 m long, with suitable retainers.

3.1.2.2.2 Procedure. The adsorbent must be dried with clean inert gas. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has proven to be a reliable source of large volumes of gas free from organic contaminants. Connect the liquid nitrogen cylinder to the column by a length of cleaned copper tubing, 0.95 cm ID, coiled to pass through a heat source. A convenient heat source is a water-bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40 °C. Continue flowing nitrogen through the adsorbent until all the residual solvent is removed. The flow rate should be sufficient to gently agitate the particles but not so excessive as the cause the particles to fracture.

3.1.2.3 Quality Control Check. The adsorbent must be checked for residual toluene.

3.1.2.3.1 Extraction. Weigh 1.0 g sample of dried resin into a small vial, add 3 ml of toluene, cap the vial, and shake it well.

3.1.2.3.2 Analysis. Inject a 2 µl sample of the extract into a gas chromatograph operated under the following conditions:

Column: 6 ft × ⅛ in stainless steel containing 10 percent OV–101 on 100/120 Supelcoport.
Carrier Gas: Helium at a rate of 30 ml/min.
Detector: Flame ionization detector operated at a sensitivity of 4×10^{-11} A/mV.
Injection Port Temperature: 250 °C.
Detector Temperature: 305 °C.
Oven Temperature: 30 °C for 4 min; programmed to rise at 40 °C/min until it reaches 250 °C; return to 30 °C after 17 minutes.

Compare the results of the analysis to the results from the reference solution. Prepare the reference solution by injection 2.5 µl of methylene chloride into 100 ml of toluene. This corresponds to 100 µg of methylene chloride per g of adsorbent. The maximum acceptable concentration is 1000 µg/g of adsorbent. If the adsorbent exceeds this level, drying must be continued until the excess methylene chloride is removed.

3.1.2.4 Storage. The adsorbent must be used within 4 weeks of cleaning. After cleaning, it may be stored in a wide mouth amber glass container with a Teflon-lined cap or placed in one of the glass adsorbent modules tightly sealed with glass stoppers. If precleaned adsorbent is purchased in sealed containers, it must be used within 4 weeks after the seal is broken.

3.1.3 Glass Wool. Cleaned by sequential immersion in three aliquots of methylene chloride, dried in a 110 °C oven, and stored in a methylene chloride-washed glass jar with a Teflon-lined screw cap.

3.1.4 Water. Deionized distilled and stored in a methylene chloride-rinsed glass container with a Teflon-lined screw cap.

3.1.5 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175 °C (350 °F) for two hours. New silica gel may be used as received. Alternately other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

3.1.6 Chromic Acid Cleaning Solution. Dissolve 20 g of sodium dichromate in 15 ml of water, and then carefully add 400 ml of concentrated sulfuric acid.

3.2 Sample Recovery.

3.2.2 Acetone. Pesticide quality.

3.2.2 Methylene Chloride. Pesticide qualtity.

3.2.3 Toluene. Pesticide quality.

3.3 Analysis.

3.3.1 Potassium Hydroxide. ACS grade, 2-percent (weight/volume) in water.

3.3.2 Sodium Sulfate. Granulated, reagent grade. Purify prior to use by rinsing with methylene chloride and oven drying. Store the cleaned material in a glass container with a Teflon-lined screw cap.

3.3.3 Sulfuric Acid. Reagent grade.

3.3.4 Sodium Hydroxide. 1.0 N. Weigh 40 g of sodium hydroxide into a 1-liter volumetric flask. Dilute to 1 liter with water.

3.3.5 Hexane. Pesticide grade.

3.3.6 Methylene Chloride. Pesticide grade.

3.3.7 Benzene. Pesticide Grade.

3.3.8 Ethyl Acetate.

3.3.9 Methanol. Pesticide Grade.

3.3.10 Toluene. Pesticide Grade.

3.3.11 Nonane. Pesticide Grade.

3.3.12 Cyclohexane. Pesticide Grade.

3.3.13 Basic Alumina. Activity grade 1, 100–200 mesh. Prior to use, activate the alumina by heating for 16 hours at 130 °C before use. Store in a desiccator. Pre-activated alumina may be purchased from a supplier and may be used as received.

3.3.14 Silica Gel. Bio-Sil A, 100–200 mesh. Prior to use, activate the silica gel by heating for at least 30 minutes at 180 °C. After cooling, rinse the silica gel sequentially with methanol and methylene chloride. Heat the rinsed silica gel at 50 °C for 10 minutes, then increase the temperature gradually to 180 °C over 25 minutes and maintain it at this temperature for 90 minutes. Cool at room temperature and store in a glass container with a Teflon-lined screw cap.

3.3.15 Silica Gel Impregnated with Sulfuric Acid. Combine 100 g of silica gel with 44 g of concentrated sulfuric acid in a screw capped glass bottle and agitate thoroughly. Disperse the solids with a stirring rod until a uniform mixture is obtained. Store the mixture in a glass container with a Teflon-lined screw cap.

3.3.16 Silica Gel Impregnated with Sodium Hydroxide. Combine 39 g of 1 N sodium hydroxide with 100 g of silica gel in a screw capped glass bottle and agitate thoroughly. Disperse solids with a stirring rod until a uniform mixture is obtained. Store the mixture in glass container with a Teflon-lined screw cap.

3.3.17 Carbon/Celite. Combine 10.7 g of AX–21 carbon with 124 g of Celite 545 in a 250-ml glass bottle with a Teflon-lined screw cap. Agitate the mixture thoroughly until a uniform mixture is obtained. Store in the glass container.

3.3.18 Nitrogen. Ultra high purity.

3.3.19 Hydrogen. Ultra high purity.

3.3.20 Internal Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Internal Standards'' in 10 ml of nonane.

3.3.21 Surrogate Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Surrogate Standards'' in 10 ml of nonane.

3.3.22 Recovery Standard Solution. Prepare a stock standard solution containing the

isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Recovery Standards'' in 10 ml of nonane.

4. Procedure

4.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, testers should be trained and experienced with the test procedures.

4.1.1 Pretest Preparation.

4.1.1.1 Cleaning Glassware. All glass components of the train upstream of and including the adsorbent module, shall be cleaned as described in section 3A of the ''Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples.'' Special care shall be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. Any residue shall be removed by soaking the glassware for several hours in a chromic acid cleaning solution prior to cleaning as described above.

4.1.1.2 Adsorbent Trap. The traps must be loaded in a clean area to avoid contamination. They may not be loaded in the field. Fill a trap with 20 to 40 g of XAD–2. Follow the XAD–2 with glass wool and tightly cap both ends of the trap. Add 100 μl of the surrogate standard solution (section 3.3.21) to each trap.

4.1.1.3 Sample Train. It is suggested that all components be maintained according to the procedure described in APTD–0576. Alternative mercury-free thermometers may be used if the thermometers are, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

4.1.1.4 Silica Gel. Weigh several 200 to 300 g portions of silica gel in an air tight container to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel may be weighed directly in its impinger or sampling holder just prior to sampling.

4.1.1.5 Filter. Check each filter against light for irregularities and flaws or pinhole leaks. Pack the filters flat in a clean glass container.

4.1.2 Preliminary Determinations. Same as section 4.1.2 of Method 5.

4.1.3 Preparation of Collection Train.

4.1.3.1 During preparation and assembly of the sampling train, keep all train openings where contamination can enter, sealed until just prior to assembly or until sampling is about to begin.

NOTE: Do not use sealant grease in assembling the train.

4.1.3.2 Place approximately 100 ml of water in the second and third impingers, leave the first and fourth impingers empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fifth impinger.

4.1.3.3 Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

4.1.3.4 Assemble the train as shown in Figure 23–1.

4.1.3.5 Turn on the adsorbent module and condenser coil recirculating pump and begin monitoring the adsorbent module gas entry temperature. Ensure proper sorbent temperature gas entry temperature before proceeding and before sampling is initiated. It is extremely important that the XAD–2 adsorbent resin temperature never exceed 50 °C because thermal decomposition will occur. During testing, the XAD–2 temperature must not exceed 20 °C for efficient capture of the PCDD's and PCDF's.

4.1.4 Leak-Check Procedure. Same as Method 5, section 4.1.4.

4.1.5 Sample Train Operation. Same as Method 5, section 4.1.5.

4.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Seal the nozzle end of the sampling probe with Teflon tape or aluminum foil.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe. Remove the probe from the train and close off both ends with aluminum foil. Seal off the inlet to the train with Teflon tape, a ground glass cap, or aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area shall be clean and enclosed so that the chances of losing or contaminating the sample are minimized. Smoking, which could contaminate the sample, shall not be allowed in the cleanup area.

Inspect the train prior to and during disassembly and note any abnormal conditions, e.g., broken filters, colored impinger liquid, etc. Treat the samples as follows:

4.2.1 Container No. 1. Either seal the filter holder or carefully remove the filter from the filter holder and place it in its identified container. Use a pair of cleaned tweezers to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and filter fibers which adhere to the filter holder gasket, by using a dry inert bristle brush and a sharp-edged blade. Seal the container.

4.2.2 Adsorbent Module. Remove the module from the train, tightly cap both ends, label it, cover with aluminum foil, and store it on ice for transport to the laboratory.

4.2.3 Container No. 2. Quantitatively recover material deposited in the nozzle, probe transfer lines, the front half of the filter holder, and the cyclone, if used, first, by

brushing while rinsing three times each with acetone and then, by rinsing the probe three times with methylene chloride. Collect all the rinses in Container No. 2.

Rinse the back half of the filter holder three times with acetone. Rinse the connecting line between the filter and the condenser three times with acetone. Soak the connecting line with three separate portions of methylene chloride for 5 minutes each. If using a separate condenser and adsorbent trap, rinse the condenser in the same manner as the connecting line. Collect all the rinses in Container No. 2 and mark the level of the liquid on the container.

4.2.4 Container No. 3. Repeat the methylene chloride-rinsing described in section 4.2.3 using toluene as the rinse solvent. Collect the rinses in Container No. 3 and mark the level of the liquid on the container.

4.2.5 Impinger Water. Measure the liquid in the first three impingers to within ±1 ml by using a graduated cylinder or by weighing it to within ±0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

Discard the liquid after measuring and recording the volume or weight.

4.2.7 Silica Gel. Note the color of the indicating silica gel to determine if it has been completely spent and make a mention of its condition. Transfer the silica gel from the fifth impinger to its original container and seal. If a moisture determination is made, follow the applicable procedures in sections 8.7.6.3 and 11.2.3 of Method 5 to handle and weigh the silica gel. If moisture is not measured, the silica gel may be disposed.

5. Analysis

All glassware shall be cleaned as described in section 3A of the ''Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples.'' All samples must be extracted within 30 days of collection and analyzed within 45 days of extraction.

5.1 Sample Extraction.

5.1.1 Extraction System. Place an extraction thimble (section 2.3.4), 1 g of silica gel, and a plug of glass wool into the Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Remove the extraction thimble from the extraction system and place it in a glass beaker to catch the solvent rinses.

5.1.2 Container No. 1 (Filter). Transfer the contents directly to the glass thimble of the extraction system and extract them simultaneously with the XAD–2 resin.

5.1.3 Adsorbent Cartridge. Suspend the adsorbent module directly over the extraction thimble in the beaker (See section 5.1.1). The glass frit of the module should be in the up position. Using a Teflon squeeze bottle containing toluene, flush the XAD–2 into the thimble onto the bed of cleaned silica gel. Thoroughly rinse the glass module catching the rinsings in the beaker containing the thimble. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. Add the XAD–2 glass wool plug into the thimble.

5.1.4 Container No. 2 (Acetone and Methylene Chloride). Concentrate the sample to a volume of about 1–5 ml using the rotary evaporator apparatus, at a temperature of less than 37 °C. Rinse the sample container three times with small portions of methylene chloride and add these to the concentrated solution and concentrate further to near dryness. This residue contains particulate matter removed in the rinse of the train probe and nozzle. Add the concentrate to the filter and the XAD–2 resin in the Soxhlet apparatus described in section 5.1.1.

5.1.5 Extraction. Add 100 µl of the internal standard solution (Section 3.3.20) to the extraction thimble containing the contents of the adsorbent cartridge, the contents of Container No. 1, and the concentrate from section 5.1.4. Cover the contents of the extraction thimble with the cleaned glass wool plug to prevent the XAD–2 resin from floating into the solvent reservoir of the extractor. Place the thimble in the extractor, and add the toluene contained in the beaker to the solvent reservoir. Pour additional toluene to fill the reservoir approximately ⅔ full. Add Teflon boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle three times per hour. Extract the sample for 16 hours. After extraction, allow the Soxhlet to cool. Transfer the toluene extract and three 10-ml rinses to the rotary evaporator. Concentrate the extract to approximately 10 ml. At this point the analyst may choose to split the sample in half. If so, split the sample, store one half for future use, and analyze the other according to the procedures in sections 5.2 and 5.3. In either case, use a nitrogen evaporative concentrator to reduce the volume of the sample being analyzed to near dryness. Dissolve the residue in 5 ml of hexane.

5.1.6 Container No. 3 (Toluene Rinse). Add 100 µl of the Internal Standard solution (section 3.3.2) to the contents of the container. Concentrate the sample to a volume of about 1–5 ml using the rotary evaporator apparatus at a temperature of less than 37 °C. Rinse the sample container apparatus at a temperature of less than 37 °C. Rinse the sample container three times with small portions of toluene and add these to the concentrated solution and concentrate further to near dryness. Analyze the extract separately according to the procedures in sections 5.2 and 5.3, but concentrate the solution in a rotary evaporator apparatus rather than a nitrogen evaporative concentrator.

5.2 Sample Cleanup and Fractionation.

5.2.1 Silica Gel Column. Pack one end of a glass column, 20 mm × 230 mm, with glass wool. Add in sequence, 1 g silica gel, 2 g of sodium hydroxide impregnated silica gel, 1 g silica gel, 4 g of acid-modified silica gel, and 1 g of silica gel. Wash the column with 30 ml of hexane and discard it. Add the sample extract, dissolved in 5 ml of hexane to the column with two additional 5-ml rinses. Elute the column with an additional 90 ml of hexane and retain the entire eluate. Concentrate this solution to a volume of about 1 ml using the nitrogen evaporative concentrator (section 2.3.7).

5.2.2 Basic Alumina Column. Shorten a 25-ml disposable Pasteur pipette to about 16 ml. Pack the lower section with glass wool and 12 g of basic alumina. Transfer the concentrated extract from the silica gel column to the top of the basic alumina column and elute the column sequentially with 120 ml of 0.5 percent methylene chloride in hexane followed by 120 ml of 35 percent methylene chloride in hexane. Discard the first 120 ml of eluate. Collect the second 120 ml of eluate and concentrate it to about 0.5 ml using the nitrogen evaporative concentrator.

5.2.3 AX–21 Carbon/Celite 545 Column. Remove the botton 0.5 in. from the tip of a 9-ml disposable Pasteur pipette. Insert a glass fiber filter disk in the top of the pipette 2.5 cm from the constriction. Add sufficient carbon/celite mixture to form a 2 cm column. Top with a glass wool plug. In some cases AX–21 carbon fines may wash through the glass wool plug and enter the sample. This may be prevented by adding a celite plug to the exit end of the column. Rinse the column in sequence with 2 ml of 50 percent benzene in ethyl acetate, 1 ml of 50 percent methylene chloride in cyclohexane, and 2 ml of hexane. Discard these rinses. Transfer the concentrate in 1 ml of hexane from the basic alumina column to the carbon/celite column along with 1 ml of hexane rinse. Elute the column sequentially with 2 ml of 50 percent methylene chloride in hexane and 2 ml of 50 percent benzene in ethyl acetate and discard these eluates. Invert the column and elute in the reverse direction with 13 ml of toluene. Collect this eluate. Concentrate the eluate in a rotary evaporator at 50 °C to about 1 ml. Transfer the concentrate to a Reacti-vial using a toluene rinse and concentrate to a volume of 200 µl using a stream of N_2. Store extracts at room temperature, shielded from light, until the analysis is performed.

5.3 Analysis. Analyze the sample with a gas chromatograph coupled to a mass spectrometer (GC/MS) using the instrumental parameters in sections 5.3.1 and 5.3.2. Immediately prior to analysis, add a 20 µl aliquot of the Recovery Standard solution from Table 1 to each sample. A 2 µl aliquot of the extract is injected into the GC. Sample extracts are first analyzed using the DB–5 capillary column to determine the concentration of each isomer of PCDD's and PCDF's (tetra-through octa-). If tetra-chlorinated dibenzofurans are detected in this analysis, then analyze another aliquot of the sample in a separate run, using the DB–225 column to measure the 2,3,7,8 tetra-chloro dibenzofuran isomer. Other column systems may be used, provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of section 6.1.2.2.

5.3.1 Gas Chromatograph Operating Conditions.

5.3.1.1 Injector. Configured for capillary column, splitless, 250 °C.

5.3.1.2 Carrier Gas. Helium, 1–2 ml/min.

5.3.1.3 Oven. Initially at 150 °C. Raise by at least 40 °C/min to 190 °C and then at 3 °C/min up to 300 °C.

5.3.2 High Resolution Mass Spectrometer.

5.3.2.1 Resolution. 10000 m/e.

5.3.2.2 Ionization Mode. Electron impact.

5.3.2.3 Source Temperature 250 °C.

5.3.2.4 Monitoring Mode. Selected ion monitoring. A list of the various ions to be monitored is summarized in Table 3.

5.3.2.5 Identification Criteria. The following identification criteria shall be used for the characterization of polychlorinated dibenzodioxins and dibenzofurans.

1. The integrated ion-abundance ratio (M/M + 2 or M + 2/M + 4) shall be within 15 percent of the theoretical value. The acceptable ion-abundance ratio ranges for the identification of chlorine-containing compounds are given in Table 4.

2. The retention time for the analytes must be within 3 seconds of the corresponding ^{13}C-labeled internal standard, surrogate or alternate standard.

3. The monitored ions, shown in Table 3 for a given analyte, shall reach their maximum within 2 seconds of each other.

4. The identification of specific isomers that do not have corresponding ^{13}C-labeled standards is done by comparison of the relative retention time (RRT) of the analyte to the nearest internal standard retention time with reference (i.e., within 0.005 RRT units) to the comparable RRT's found in the continuing calibration.

5. The signal to noise ratio for all monitored ions must be greater than 2.5.

6. The confirmation of 2, 3, 7, 8–TCDD and 2, 3, 7, 8–TCDF shall satisfy all of the above identification criteria.

7. For the identification of PCDF's, no signal may be found in the corresponding PCDPE channels.

5.3.2.6 Quantification. The peak areas for the two ions monitored for each analyte are summed to yield the total response for each analyte. Each internal standard is used to quantify the indigenous PCDD's or PCDF's in its homologous series. For example, the $^{13}C_{12}$–2,3,7,8-tetra chlorinated dibenzodioxin is used to calculate the concentrations of all

other tetra chlorinated isomers. Recoveries of the tetra- and penta- internal standards are calculated using the $^{13}C_{12}$–1,2,3,4–TCDD. Recoveries of the hexa- through octa- internal standards are calculated using $^{13}C_{12}$–1,2,3,7,8,9–HxCDD. Recoveries of the surrogate standards are calculated using the corresponding homolog from the internal standard.

6. Calibration

Same as Method 5 with the following additions.

6.1 GC/MS System.

6.1.1 Initial Calibration. Calibrate the GC/MS system using the set of five standards shown in Table 2. The relative standard deviation for the mean response factor from each of the unlabeled analytes (Table 2) and of the internal, surrogate, and alternate standards shall be less than or equal to the values in Table 5. The signal to noise ratio for the GC signal present in every selected ion current profile shall be greater than or equal to 2.5. The ion abundance ratios shall be within the control limits in Table 4.

6.1.2 Daily Performance Check.

6.1.2.1 Calibration Check. Inject on µl of solution Number 3 from Table 2. Calculate the relative response factor (RRF) for each compound and compare each RRF to the corresponding mean RRF obtained during the initial calibration. The analyzer performance is acceptable if the measured RRF's for the labeled and unlabeled compounds for the daily run are within the limits of the mean values shown in Table 5. In addition, the ion-abundance ratios shall be within the allowable control limits shown in Table 4.

6.1.2.2 Column Separation Check. Inject a solution of a mixture of PCDD's and PCDF's that documents resolution between 2,3,7,8–TCDD and other TCDD isomers. Resolution is defined as a valley between peaks that is less than 25 percent of the lower of the two peaks. Identify and record the retention time windows for each homologous series.

Perform a similar resolution check on the confirmation column to document the resolution between 2,3,7,8 TCDF and other TCDF isomers.

6.2 Lock Channels. Set mass spectrometer lock channels as specified in Table 3. Monitor the quality control check channels specified in Table 3 to verify instrument stability during the analysis.

7. Quality Control

7.1 Sampling Train Collection Efficiency Check. Add 100 µl of the surrogate standards in Table 1 to the absorbent cartridge of each train before collecting the field samples.

7.2 Internal Standard Percent Recoveries. A group of nine carbon labeled PCDD's and PCDF's representing, the tetra-through octachlorinated homologues, is added to every sample prior to extraction. The role of the internal standards is to quantify the native PCDD's and PCDF's present in the sample as well as to determine the overall method efficiency. Recoveries of the internal standards must be between 40 to 130 percent for the tetra-through hexachlorinated compounds while the range is 25 to 130 percent for the higher hepta- and octachlorinated homologues.

7.3 Surrogate Recoveries. The five surrogate compounds in Table 2 are added to the resin in the adsorbent sampling cartridge before the sample is collected. The surrogate recoveries are measured relative to the internal standards and are a measure of collection efficiency. They are not used to measure native PCDD's and PCDF's. All recoveries shall be between 70 and 130 percent. Poor recoveries for all the surrogates may be an indication of breakthrough in the sampling train. If the recovery of all standards is below 70 percent, the sampling runs must be repeated. As an alternative, the sampling runs do not have to be repeated if the final results are divided by the fraction of surrogate recovery. Poor recoveries of isolated surrogate compounds should not be grounds for rejecting an entire set of the samples.

7.4 Toluene QA Rinse. Report the results of the toluene QA rinse separately from the total sample catch. Do not add it to the total sample.

8.0 [Reserved]

9. Calculations

Same as Method 5, section 6 with the following additions.

9.1 Nomenclature.

A_{ai} = Integrated ion current of the noise at the retention time of the analyte.

A^*_{ci} = Integrated ion current of the two ions characteristic of the internal standard i in the calibration standard.

A_{cij} = Integrated ion current of the two ions characteristic of compound i in the jth calibration standard.

A^*_{cij} = Integrated ion current of the two ions characteristic of the internal standard i in the jth calibration standard.

A_{csi} = Integrated ion current of the two ions characteristic of surrogate compound i in the calibration standard.

A_i = Integrated ion current of the two ions characteristic of compound i in the sample.

A^*_i = Integrated ion current of the two ions characteristic of internal standard i in the sample.

A_{rs} = Integrated ion current of the two ions characteristic of the recovery standard.

A_{si} = Integrated ion current of the two ions characteristic of surrogate compound i in the sample.

C_i = Concentration of PCDD or PCDF i in the sample, pg/M^3.

C_T = Total concentration of PCDD's or PCDF's in the sample, pg/M^3.
m_{ci} = Mass of compound i in the calibration standard injected into the analyzer, pg.
m_{rs} = Mass of recovery standard in the calibration standard injected into the analyzer, pg.
m_{si} = Mass of surrogate compound in the calibration standard, pg.
RRF_i = Relative response factor.
RRF_{rs} = Recovery standard response factor.
RRF_s = Surrogate compound response factor.

9.2 Average Relative Response Factor.

$$RRF_i = \frac{1}{n}\sum_{j=1}^{n}\frac{A_{cij}\, m^*_{ci}}{A^*_{cij}\, m_{ci}} \qquad \text{Eq. 23-1}$$

9.3 Concentration of the PCDD's and PCDF's.

$$C_i = \frac{m_i^* A_i}{A_i^* RRF_i V_{mstd}} \qquad \text{Eq. 23-2}$$

9.4 Recovery Standard Response Factor.

$$RRF_{rs} = \frac{A_{ci}^* m_{rs}}{A_{rs} m_{ci}^*} \qquad \text{Eq. 23-3}$$

9.5 Recovery of Internal Standards (R*).

$$R^* = \frac{A_i^* m_{rs}}{A_{rs} RF_{rs} m_i^*} \times 100\% \qquad \text{Eq. 23-4}$$

9.6 Surrogate Compound Response Factor.

$$RRF_s = \frac{A_{ci}^* m_s}{A_{cis} m_{ci}^*} \qquad \text{Eq. 23-5}$$

9.7 Recovery of Surrogate Compounds (R_s).

$$R_s = \frac{A_s m_i^*}{A_i^* RRF_s m_s} \times 100\% \qquad \text{Eq. 23-6}$$

9.8 Minimum Detectable Limit (MDL).

$$MDL = \frac{2.5\, A_{ai} m_i^*}{A_{ci}^* RRF_i} \qquad \text{Eq. 23-7}$$

9.9 Total Concentration of PCDD's and PCDF's in the Sample.

$$C_{Tr} = \sum_{i=1}^{n} C_i \qquad \text{Eq. 23-8}$$

Any PCDD's or PCDF's that are reported as nondetected (below the MDL) shall be counted as zero for the purpose of calculating the total concentration of PCDD's and PCDF's in the sample.

10. Bibliography

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TABLE 1—COMPOSITION OF THE SAMPLE FORTIFICATION AND RECOVERY STANDARDS SOLUTIONS

Analyte	Concentration (pg/µl)
Internal Standards:	
$^{13}C_{12}$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100
$^{13}C_{12}$-OCDD	100
$^{13}C_{12}$-2,3,7,8-TCDF	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100
Surrogate Standards:	
$^{37}Cl_4$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100
Recovery Standards:	
$^{13}C_{12}$-1,2,3,4-TCDD	500
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	500

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS

Compound	Concentrations (pg/µL)				
	Solution No.				
	1	2	3	4	5
Alternate Standard:					
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	2.5	5	25	250	500

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS—Continued

Compound	Concentrations (pg/μL)				
	Solution No.				
	1	2	3	4	5
Recovery Standards:					
$^{13}C_{12}$-1,2,3,4-TCDD ..	100	100	100	100	100

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS—Continued

Compound	Concentrations (pg/μL)				
	Solution No.				
	1	2	3	4	5
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

TABLE 3—ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HIGH RESOLUTION MASS SPECTROMETRY FOR PCDD'S AND PCDF'S

Descriptor No.	Accurate mass	Ion type	Elemental composition	Analyte
2	292.9825	LOCK	C_7F_{11}	PFK
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M + 2	$C_{12}H_4{}^{35}Cl^{37}O$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M + 2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}ClO_2$	TCDD
	321.8936	M + 2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD (S)
	330.9792	QC	C_7F_{13}	PFK
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9339	M + 2	$^{13}C_{12}H_4{}^{35}Cl^{37}ClO_2$	TCDD (S)
	339.8597	M + 2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PECDF
	341.8567	M + 4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M + 2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M + 4	$^{13}C_{12}H_3{}^{35}Cl^{3537}Cl_2O$	PeCDF (S)
	355.8546	M + 2	$C_{12}H_3{}^{35}Cl_3{}37ClO_2$	PeCDD
	357.8516	M + 4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M + 2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M + 4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}\ Cl_2O_2$	PeCDD (S)
	375.8364	M + 2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
	409.7974	M + 2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCPDE
3	373.8208	M + 2	$C_{12}H_2{}35Cl_5{}^{37}ClO$	HxCDF
	375.8178	M + 4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M + 2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8157	M + 2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M + 4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	392.9760	LOCK	C_9F_{15}	PFK
	401.8559	M + 2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M + 4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDD (S)
	445.7555	M + 4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	430.9729	QC	C_9F_{17}	PFK
4	407.7818	M + 2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M + 4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8253	M	$^{13}C_{12}H^{35}Cl_7O$	HpCDF (S)
	419.8220	M + 2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF (S)
	423.7766	M + 2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M + 4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M + 2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M + 4	$^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S)
	479.7165	M + 4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCPDE
	430.9729	LOCK	C_9F_{17}	PFK
	441.7428	M + 2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M + 4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M + 2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M + 4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M + 2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M + 4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S)
	513.6775	M + 4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O_2$	DCDPE
	442.9728	QC	$C_{10}F_{17}$	PFK

(a) The following nuclidic masses were used:
H = 1.007825
C = 12.000000
^{13}C = 13.003355
F = 18.9984
O = 15.994915
^{35}Cl = 34.968853
^{37}Cl = 36.965903

S = Labeled Standard
QC = Ion selected for monitoring instrument stability during the GC/MS analysis.

TABLE 4—ACCEPTABLE RANGES FOR ION-ABUNDANCE RATIOS OF PCDD'S AND PCDF'S

No. of chlorine atoms	Ion type	Theoretical ratio	Control limits	
			Lower	Upper
4	M/M + 2	0.77	0.65	0.89
5	M + 2/M + 4	1.55	1.32	1.78
6	M + 2/M + 4	1.24	1.05	1.43
6[a]	M/M + 2	0.51	0.43	0.59
7[b]	M/M + 2	0.44	0.37	0.51
7	M + 2/M + 4	1.04	0.88	1.20
8	M + 2/M + 4	0.89	0.76	1.02

[a] Used only for ^{13}C-HxCDF.
[b] Used only for ^{13}C-HpCDF.

TABLE 5—MINIMUM REQUIREMENTS FOR INITIAL AND DAILY CALIBRATION RESPONSE FACTORS

Compound	Relative response factors	
	Initial calibration RSD	Daily calibration % difference
Unlabeled Analytes:		
2,3,7,8-TCDD	25	25
2,3,7,8-TCDF	25	25
1,2,3,7,8-PeCDD	25	25
1,2,3,7,8-PeCDF	25	25
2,3,4,7,8-PeCDF	25	25
1,2,4,5,7,8-HxCDD	25	25
1,2,3,6,7,8-HxCDD	25	25
1,2,3,7,8,9-HxCDD	25	25
1,2,3,4,7,8-HxCDF	25	25
1,2,3,6,7,8-HxCDF	25	25
1,2,3,7,8,9-HxCDF	25	25
2,3,4,6,7,8-HxCDF	25	25
1,2,3,4,6,7,8-HpCDD	25	25
1,2,3,4,6,7,8-HpCDF	25	25
OCDD	25	25
OCDF	30	30
Internal Standards:		
$^{13}C_{12}$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-1,2,3,7,8-PeCDD	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	30	30
$^{13}C_{12}$-OCDD	30	30
$^{13}C_{12}$-2,3,7,8-TCDF	30	30
$^{13}C_{12}$-1,2,3,7,8-PeCDF	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	30	30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	30	30
Surrogate Standards:		
$^{37}Cl_4$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-2,3,4,7,8-PeCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	25	25
Alternate Standard:		
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	25	25

METHOD 24—DETERMINATION OF VOLATILE MATTER CONTENT, WATER CONTENT, DENSITY, VOLUME SOLIDS, AND WEIGHT SOLIDS OF SURFACE COATINGS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile organic compounds	No CAS Number assigned
Water.	7732–18–5

1.2 Applicability. This method is applicable for the determination of volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or other related surface coatings.

1.3 Precision and Bias. Intra-and inter-laboratory analytical precision statements are presented in section 13.1. No bias has been identified.

2.0 Summary of Method

2.1 Standard methods are used to determine the volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or other related surface coatings.

3.0 Definitions

3.1 *Waterborne coating* means any coating which contains more than 5 percent water by weight in its volatile fraction.

3.2 *Multicomponent coatings* are coatings that are packaged in two or more parts, which are combined before application. Upon combination a coreactant from one part of the coating chemically reacts, at ambient conditions, with a coreactant from another part of the coating.

3.3 *Ultraviolet (UV) radiation-cured coatings* are coatings which contain unreacted monomers that are polymerized by exposure to ultraviolet light.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Components. Several of the compounds that may be contained in the coatings analyzed by this method may be irritating or corrosive to tissues (e.g., heptane) or may be toxic (e.g., benzene, methyl alcohol). Nearly all are fire hazards.

Appropriate precautions can be found in reference documents, such as Reference 3 of section 16.0.

6.0 Equipment and Supplies

The equipment and supplies specified in the ASTM methods listed in sections 6.1 through 6.6 (incorporated by reference—see §60.17 for acceptable versions of the methods) are required:

6.1 ASTM D 1475–60, 80, or 90, Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products.

6.2 ASTM D 2369–81, 87, 90, 92, 93, or 95, Standard Test Method for Volatile Content of Coatings.

6.3 ASTM D 3792–79 or 91, Standard Test Method for Water Content of Water Reducible Paints by Direct Injection into a Gas Chromatograph.

6.4 ASTM D 4017–81, 90, or 96a, Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Titration Method.

6.5 ASTM 4457–85 91, Standard Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph.

6.6 ASTM D 5403–93, Standard Test Methods for Volatile Content of Radiation Curable Materials.

6.7 ASTM D 6419–00, Test Method for Volatile Content of Sheet-Fed and Coldset Web Offset Printing Inks.

7.0 Reagents and Standards

7.1 The reagents and standards specified in the ASTM methods listed in sections 6.1 through 6.6 are required.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Follow the sample collection, preservation, storage, and transport procedures described in Reference 1 of section 16.0.

9.0 Quality Control

9.1 Reproducibility

NOTE: Not applicable to UV radiation-cured coatings). The variety of coatings that may be subject to analysis makes it necessary to verify the ability of the analyst and the analytical procedures to obtain reproducible results for the coatings tested. Verification is accomplished by running duplicate analyses on each sample tested (Sections 11.2 through 11.4) and comparing the results with the intra-laboratory precision statements (Section 13.1) for each parameter.

9.2 Confidence Limits for Waterborne Coatings. Because of the inherent increased imprecision in the determination of the VOC content of waterborne coatings as the weight percent of water increases, measured parameters for waterborne coatings are replaced with appropriate confidence limits (Section 12.6). These confidence limits are based on measured parameters and inter-laboratory precision statements.

10.0 Calibration and Standardization

10.1 Perform the calibration and standardization procedures specified in the ASTM methods listed in sections 6.1 through 6.6.

11.0 Analytical Procedure

Additional guidance can be found in Reference 2 of section 16.0.

11.1 Non Thin-film Ultraviolet Radiation-cured (UV radiation-cured) Coatings.

11.1.1 Volatile Content. Use the procedure in ASTM D 5403 to determine the volatile matter content of the coating except the curing test described in NOTE 2 of ASTM D 5403 is required.

11.1.2 Water Content. To determine water content, follow section 11.3.2.

11.1.3 Coating Density. To determine coating density, follow section 11.3.3.

11.1.4 Solids Content. To determine solids content, follow section 11.3.4.

11.1.5 To determine if a coating or ink can be classified as a thin-film UV cured coating or ink, use the equation in section 12.2. If C is less than 0.2 g and A is greater than or equal to 225 cm^2 (35 in^2) then the coating or ink is considered a thin-film UV radiation-cured coating and ASTM D 5403 is not applicable.

NOTE: As noted in section 1.4 of ASTM D 5403, this method may not be applicable to radiation curable materials wherein the volatile material is water.

11.2 Multi-component Coatings.

11.2.1 Sample Preparation.

11.2.1.1 Prepare about 100 ml of sample by mixing the components in a storage container, such as a glass jar with a screw top or a metal can with a cap. The storage container should be just large enough to hold the mixture. Combine the components (by weight or volume) in the ratio recommended by the manufacturer. Tightly close the container between additions and during mixing to prevent loss of volatile materials. However, most manufacturers mixing instructions are by volume. Because of possible error caused by expansion of the liquid when measuring the volume, it is recommended that the components be combined by weight. When weight is used to combine the components and the manufacturer's recommended ratio is by volume, the density must be determined by section 11.3.3.

11.2.1.2 Immediately after mixing, take aliquots from this 100 ml sample for determination of the total volatile content, water content, and density.

11.2.2 Volatile Content. To determine total volatile content, use the apparatus and

reagents described in ASTM D2369 (incorporated by reference; see §60.17 for the approved versions of the standard), respectively, and use the following procedures:

11.2.2.1 Weigh and record the weight of an aluminum foil weighing dish. Add 3 ±1 ml of suitable solvent as specified in ASTM D2369 to the weighing dish. Using a syringe as specified in ASTM D2369, weigh to 1 mg, by difference, a sample of coating into the weighing dish. For coatings believed to have a volatile content less than 40 weight percent, a suitable size is 0.3 + 0.10 g, but for coatings believed to have a volatile content greater than 40 weight percent, a suitable size is 0.5 ±0.1 g.

NOTE: If the volatile content determined pursuant to section 12.4 is not in the range corresponding to the sample size chosen repeat the test with the appropriate sample size. Add the specimen dropwise, shaking (swirling) the dish to disperse the specimen completely in the solvent. If the material forms a lump that cannot be dispersed, discard the specimen and prepare a new one. Similarly, prepare a duplicate. The sample shall stand for a minimum of 1 hour, but no more than 24 hours prior to being oven cured at 110 ±5 °C (230 ±9 °F) for 1 hour.

11.2.2.2 Heat the aluminum foil dishes containing the dispersed specimens in the forced draft oven for 60 min at 110 ±5 °C (230 ±9 °F). Caution—provide adequate ventilation, consistent with accepted laboratory practice, to prevent solvent vapors from accumulating to a dangerous level.

11.2.2.3 Remove the dishes from the oven, place immediately in a desiccator, cool to ambient temperature, and weigh to within 1 mg.

11.2.2.4 Run analyses in pairs (duplicate sets) for each coating mixture until the criterion in section 11.4 is met. Calculate W_V following Equation 24–2 and record the arithmetic average.

11.2.3 Water Content. To determine water content, follow section 11.3.2.

11.2.4 Coating Density. To determine coating density, follow section 11.3.3.

11.2.5 Solids Content. To determine solids content, follow section 11.3.4.

11.2.6 Exempt Solvent Content. To determine the exempt solvent content, follow section 11.3.5.

NOTE: For all other coatings (*i.e.*, water-or solvent-borne coatings) not covered by multicomponent or UV radiation-cured coatings, analyze as shown below:

11.3 Water-or Solvent-borne coatings.

11.3.1 Volatile Content. Use the procedure in ASTM D 2369 to determine the volatile matter content (may include water) of the coating.

11.3.1.1 Record the following information:

W_1 = weight of dish and sample before heating, g

W_2 = weight of dish and sample after heating, g

W_3 = sample weight, g.

11.3.1.2 Calculate the weight fraction of the volatile matter (W_v) for each analysis as shown in section 12.3.

11.3.1.3 Run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement in section 13.1.

11.3.1.4 Record the arithmetic average (W_v).

11.3.2 Water Content. For waterborne coatings only, determine the weight fraction of water (W_w) using either ASTM D 3792 or ASTM D 4017.

11.3.2.1 Run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement in section 13.1.

11.3.2.2 Record the arithmetic average (w_w).

11.3.3 Coating Density. Determine the density (Dc, kg/l) of the surface coating using the procedure in ASTM D 1475.

11.3.3.1 Run duplicate analyses until each value in a set deviates from the mean of the set by no more than the intra-laboratory precision statement in section 13.1.

11.3.3.2 Record the arithmetic average (D_c).

11.3.4 Solids Content. Determine the volume fraction (V_s) solids of the coating by calculation using the manufacturer's formulation.

11.3.5 Exempt Solvent Content. Determine the weight fraction of exempt solvents (W_E) by using ASTM Method D4457. Run a duplicate set of determinations and record the arithmetic average (W_E).

11.4 Sample Analysis Criteria. For W_v and W_w, run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement for that parameter. For D_c, run duplicate analyses until each value in a set deviates from the mean of the set by no more than the intra-laboratory precision statement. If, after several attempts, it is concluded that the ASTM procedures cannot be used for the specific coating with the established intra-laboratory precision (excluding UV radiation-cured coatings), the U.S. Environmental Protection Agency (EPA) will assume responsibility for providing the necessary procedures for revising the method or precision statements upon written request to: Director, Emissions, Monitoring, and Analysis Division, MD–14, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

12.0 Calculations and Data Analysis

12.1 Nomenclature.

A = Area of substrate, cm^2, (in^2).

C = Amount of coating or ink added to the substrate, g.

D_c = Density of coating or ink, g/cm^3 (g/in^3).

F = Manufacturer's recommended film thickness, cm (in).
W_o = Weight fraction of nonaqueous volatile matter, g/g.
W_s = Weight fraction of solids, g/g.
W_v = Weight fraction of the volatile matter, g/g.
W_w = Weight fraction of the water, g/g.

12.2 To determine if a coating or ink can be classified as a thin-film UV cured coating or ink, use the following equation:

$$C = F A D_c \qquad \text{Eq. 24-1}$$

12.3 Calculate W_v for each analysis as shown below:

$$W_v = \frac{W_1 - W_2}{W_3} \qquad \text{Eq. 24-2}$$

12.4 Nonaqueous Volatile Matter.
12.4.1 Solvent-borne Coatings.

$$W_o = W_v \qquad \text{Eq. 24-3}$$

12.4.2 Waterborne Coatings.

$$W_o = W_v - W_w \qquad \text{Eq. 24-4}$$

12.4.3 Coatings Containing Exempt Solvents.

$$W_o = W_v - W_E - W_w \qquad \text{Eq. 24-5}$$

12.5 Weight Fraction Solids.

$$W_s = 1 - W_v \qquad \text{Eq. 24-6}$$

12.6 Confidence Limit Calculations for Waterborne Coatings. To calculate the lower confidence limit, subtract the appropriate inter-laboratory precision value from the measured mean value for that parameter. To calculate the upper confidence limit, add the appropriate inter-laboratory precision value to the measured mean value for that parameter. For W_v and D_c, use the lower confidence limits; for W_w, use the upper confidence limit. Because W_s is calculated, there is no adjustment for this parameter.

13.0 Method Performance

13.1 Analytical Precision Statements. The intra-and inter-laboratory precision statements are given in Table 24–1 in section 17.0.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as specified in section 6.0, with the addition of the following:

1. Standard Procedure for Collection of Coating and Ink Samples for Analysis by Reference Methods 24 and 24A. EPA–340/1–91–010. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.
2. Standard Operating Procedure for Analysis of Coating and Ink Samples by Reference Methods 24 and 24A.
EPA–340/1–91–011. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.
3. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 24–1—ANALYTICAL PRECISION STATEMENTS

	Intra-laboratory	Inter-laboratory
Volatile matter content, W_v	±0.015 $\overline{W}_v$	±0.047 $\overline{W}_v$
Water content, W_w	±0.029 $\overline{W}_w$	±0.075 $\overline{W}_w$
Density, D_c	±0.001 kg/l	±0.002 kg/l

METHOD 24A—DETERMINATION OF VOLATILE MATTER CONTENT AND DENSITY OF PUBLICATION ROTOGRAVURE INKS AND RELATED PUBLICATION ROTOGRAVURE COATINGS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile organic compounds (VOC).	No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of the VOC content and density of solvent-borne (solvent-reducible) publication rotogravure inks and related publication rotogravure coatings.

2.0 Summary of Method

2.1 Separate procedures are used to determine the VOC weight fraction and density of the ink or related coating and the density of the solvent in the ink or related coating. The VOC weight fraction is determined by measuring the weight loss of a known sample quantity which has been heated for a specified length of time at a specified temperature. The density of both the ink or related coating and solvent are measured by a standard procedure. From this information, the VOC volume fraction is calculated.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Components. Some of the compounds that may be contained in the inks or related coatings analyzed by this method may be irritating or corrosive to tissues or may be toxic. Nearly all are fire hazards. Appropriate precautions can be found in reference documents, such as Reference 6 of section 16.0.

6.0 Equipment and Supplies

The following equipment and supplies are required for sample analysis:

6.1 Weighing Dishes. Aluminum foil, 58 mm (2.3 in.) in diameter by 18 mm (0.7 in.) high, with a flat bottom. There must be at least three weighing dishes per sample.

6.2 Disposable Syringe. 5 ml.

6.3 Analytical Balance. To measure to within 0.1 mg.

6.4 Oven. Vacuum oven capable of maintaining a temperature of 120 ±2 °C (248 ±4 °F) and an absolute pressure of 510 ±51 mm Hg (20 ±2 in. Hg) for 4 hours. Alternatively, a forced draft oven capable of maintaining a temperature of 120 ±2 °C (248 ±4 °F) for 24 hours.

6.5 The equipment and supplies specified in ASTM D 1475–60, 80, or 90 (incorporated by reference—see §60.17).

7.0 Reagents and Standards

7.1 The reagents and standards specified in ASTM D 1475–60, 80, or 90 are required.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Follow the sample collection, preservation, storage, and transport procedures described in Reference 4 of section 16.0.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

Additional guidance can be found in Reference 5 of section 16.0.

11.1 VOC Weight Fraction. Shake or mix the ink or related coating sample thoroughly to assure that all the solids are completely suspended. Label and weigh to the nearest 0.1 mg a weighing dish and record this weight (M_{x1}). Using a 5 ml syringe, without a needle, extract an aliquot from the ink or related coating sample. Weigh the syringe and aliquot to the nearest 0.1 mg and record this weight (M_{cy1}). Transfer 1 to 3 g of the aliquot to the tared weighing dish. Reweigh the syringe and remaining aliquot to the nearest 0.1 mg and record this weight (M_{cy2}). Heat the weighing dish with the transferred aliquot in a vacuum oven at an absolute pressure of 510 ±51 mm Hg (20 ±2 in. Hg) and a temperature of 120 ±2 °C (248 ±4 °F) for 4 hours. Alternatively, heat the weighing dish with the transferred aliquot in a forced draft oven at a temperature of 120 ±2 °C for 24 hours. After the weighing dish has cooled, reweigh it to the nearest 0.1 mg and record the weight (M_{x2}). Repeat this procedure two times for each ink or related coating sample, for a total of three samples.

11.2 Ink or Related Coating Density. Determine the density of the ink or related coating (D_c) according to the procedure outlined in ASTM D 1475. Make a total of three determinations for each ink or related coating sample. Report the ink or related coating density as the arithmetic average (D_c) of the three determinations.

11.3 Solvent Density. Determine the density of the solvent (D_o) according to the procedure outlined in ASTM D 1475. Make a total of three determinations for each ink or related coating sample. Report the solvent density as the arithmetic average (D_o) of the three determinations.

12.0 Calculations and Data Analysis

12.1 VOC Weight Fraction. For each determination, calculate the volatile organic content weight fraction (W_o) using the following equation:

$$W_o = \frac{M_{x1} + M_{cy1} - M_{cy2} - M_{x2}}{M_{cy1} - M_{cy2}} \qquad \text{Eq. 24A-1}$$

Make a total of three determinations. Report the VOC weight fraction as the arithmetic average ($\bar{W}_o$) of the three determinations.

12.2 VOC Volume Fraction. Calculate the volume fraction volatile organic content (V_o) using the following equation:

$$V_o = \frac{\overline{W}_o \overline{D}_c}{\overline{D}_o} \qquad \text{Eq. 24A-2}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products. ASTM Designation D 1475.

2. Teleconversation. Wright, Chuck, Inmont Corporation with Reich, R., A., Radian Corporation. September 25, 1979, Gravure Ink Analysis.

3. Teleconversation. Oppenheimer, Robert, Gravure Research Institute with Burt, Rick, Radian Corporation, November 5, 1979, Gravure Ink Analysis.

4. Standard Procedure for Collection of Coating and Ink Samples for Analysis by Reference Methods 24 and 24A. EPA–340/1–91–010. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

5. Standard Operating Procedure for Analysis of Coating and Ink Samples by Reference Methods 24 and 24A. EPA–340/1–91–011. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

6. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

Method 25—Determination of Total Gaseous Nonmethane Organic Emissions as Carbon

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total gaseous nonmethane organic compounds (TGNMO)	N/A	Dependent upon analytical equipment.

1.2 Applicability.

1.2.1 This method is applicable for the determination of volatile organic compounds (VOC) (measured as total gaseous nonmethane organics (TGNMO) and reported as carbon) in stationary source emissions. This method is not applicable for the determination of organic particulate matter.

1.2.2 This method is not the only method that applies to the measurement of VOC. Costs, logistics, and other practicalities of source testing may make other test methods more desirable for measuring VOC contents of certain effluent streams. Proper judgment is required in determining the most applicable VOC test method. For example, depending upon the molecular composition of the organics in the effluent stream, a totally automated semicontinuous nonmethane organics (NMO) analyzer interfaced directly to the source may yield accurate results. This approach has the advantage of providing emission data semicontinuously over an extended time period.

1.2.3 Direct measurement of an effluent with a flame ionization detector (FID) analyzer may be appropriate with prior characterization of the gas stream and knowledge that the detector responds predictably to the organic compounds in the stream. If present, methane (CH_4) will, of course, also be measured. The FID can be used under any of the following limited conditions: (1) Where only one compound is known to exist; (2) when the organic compounds consist of only hydrogen and carbon; (3) where the relative percentages of the compounds are known or can be determined, and the FID responses to the compounds are known; (4) where a consistent mixture of the compounds exists before and after emission control and only the relative concentrations are to be assessed; or (5) where the FID can be calibrated against mass standards of the compounds emitted (solvent emissions, for example).

1.2.4 Another example of the use of a direct FID is as a screening method. If there is enough information available to provide a rough estimate of the analyzer accuracy, the FID analyzer can be used to determine the VOC content of an uncharacterized gas stream. With a sufficient buffer to account for possible inaccuracies, the direct FID can be a useful tool to obtain the desired results without costly exact determination.

1.2.5 In situations where a qualitative/quantitative analysis of an effluent stream is desired or required, a gas chromatographic FID system may apply. However, for sources emitting numerous organics, the time and expense of this approach will be formidable.

2.0 Summary of Method

2.1 An emission sample is withdrawn from the stack at a constant rate through a heated filter and a chilled condensate trap by means of an evacuated sample tank. After sampling is completed, the TGNMO are determined by independently analyzing the condensate trap and sample tank fractions and combining the analytical results. The organic content of the condensate trap fraction is determined by oxidizing the NMO to carbon dioxide (CO_2) and quantitatively collecting in the effluent in an evacuated vessel; then a portion of the CO_2 is reduced to CH_4 and measured by an FID. The organic content of the sample tank fraction is measured by injecting a portion of the sample into a gas chromatographic column to separate the NMO from carbon monoxide (CO), CO_2, and CH_4; the NMO are oxidized to CO_2, reduced to CH_4, and measured by an FID. In this manner, the variable response of the FID associated with different types of organics is eliminated.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Carbon Dioxide and Water Vapor. When carbon dioxide (CO_2) and water vapor are present together in the stack, they can produce a positive bias in the sample. The magnitude of the bias depends on the concentrations of CO_2 and water vapor. As a guideline, multiply the CO_2 concentration, expressed as volume percent, times the water vapor concentration. If this product does not exceed 100, the bias can be considered insignificant. For example, the bias is not significant for a source having 10 percent CO_2 and 10 percent water vapor, but it might be significant for a source having 10 percent CO_2 and 20 percent water vapor.

4.2. Particulate Matter. Collection of organic particulate matter in the condensate trap would produce a positive bias. A filter is included in the sampling equipment to minimize this bias.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling system consists of a heated probe, heated filter, condensate trap, flow control system, and sample tank (see Figure 25–1). The TGNMO sampling equipment can be constructed from commercially available components and components fabricated in a machine shop. The following equipment is required:

6.1.1 Heated Probe. 6.4-mm (¼-in.) OD stainless steel tubing with a heating system capable of maintaining a gas temperature at the exit end of at least 129 °C (265 °F). The probe shall be equipped with a temperature sensor at the exit end to monitor the gas temperature. A suitable probe is shown in Figure 25–1. The nozzle is an elbow fitting attached to the front end of the probe while the temperature sensor is inserted in the side arm of a tee fitting attached to the rear of the probe. The probe is wrapped with a suitable length of high temperature heating tape, and then covered with two layers of glass cloth insulation and one layer of aluminum foil or an equivalent wrapping.

NOTE: If it is not possible to use a heating system for safety reasons, an unheated system with an in-stack filter is a suitable alternative.

6.1.2 Filter Holder. 25-mm (15/16-in.) ID Gelman filter holder with 303 stainless steel body and 316 stainless steel support screen with the Viton O-ring replaced by a Teflon O-ring.

6.1.3 Filter Heating System.

6.1.3.1 A metal box consisting of an inner and an outer shell separated by insulating material with a heating element in the inner shell capable of maintaining a gas temperature at the filter of 121 ±3 °C (250 ±5 °F). The heating box shall include temperature sensors to monitor the gas temperature immediately upstream and immediately downstream of the filter.

6.1.3.2 A suitable heating box is shown in Figure 25–2. The outer shell is a metal box that measures 102 mm × 280 mm × 292 mm (4 in. × 11 in. × 11½ in.), while the inner shell is a metal box measuring 76 mm × 229 mm × 241 mm (3 in. × 9 in. × 9½ in.). The inner box is supported by 13-mm (½-in.) phenolic rods. The void space between the boxes is filled with ceramic fiber insulation which is sealed in place by means of a silicon rubber bead around the upper sides of the box. A removable lid made in a similar manner, with a 25-mm (1-in.) gap between the parts is used to cover the heating chamber. The inner box is heated with a 250-watt cartridge heater, shielded by a stainless steel shroud. The heater is regulated by a thermostatic temperature controller which is set to maintain a gas temperature of 121 °C (250 °F) as measured by the temperature sensor upstream of the filter.

NOTE: If it is not possible to use a heating system for safety reasons, an unheated system with an in-stack filter is a suitable alternative.

6.1.4 Condensate Trap. 9.5-mm (⅜-in.) OD 316 stainless steel tubing bent into a U-shape. Exact dimensions are shown in Figure

25–3. The tubing shall be packed with coarse quartz wool, to a density of approximately 0.11 g/cm^3 before bending. While the condensate trap is packed with dry ice in the Dewar, an ice bridge may form between the arms of the condensate trap making it difficult to remove the condensate trap. This problem can be prevented by attaching a steel plate between the arms of the condensate trap in the same plane as the arms to completely fill the intervening space.

6.1.5 Valve. Stainless steel control valve for starting and stopping sample flow.

6.1.6 Metering Valve. Stainless steel valve for regulating the sample flow rate through the sample train.

6.1.7 Rate Meter. Rotameter, or equivalent, capable of measuring sample flow in the range of 60 to 100 cm^3/min (0.13 to 0.21 ft^3/hr).

6.1.8 Sample Tank. Stainless steel or aluminum tank with a minimum volume of 4 liters (0.14 ft^3).

NOTE: Sample volumes greater than 4 liters may be required for sources with low organic concentrations.

6.1.9 Mercury Manometer. U-tube manometer or absolute pressure gauge capable of measuring pressure to within 1 mm Hg in the range of 0 to 900 mm.

6.1.10 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

6.2 Condensate Recovery. The system for the recovery of the organics captured in the condensate trap consists of a heat source, an oxidation catalyst, a nondispersive infrared (NDIR) analyzer, and an intermediate collection vessel (ICV). Figure 25–4 is a schematic of a typical system. The system shall be capable of proper oxidation and recovery, as specified in section 10.1.1. The following major components are required:

6.2.1 Heat Source. Sufficient to heat the condensate trap (including probe) to a temperature of 200 °C (390 °F). A system using both a heat gun and an electric tube furnace is recommended.

6.2.2 Heat Tape. Sufficient to heat the connecting tubing between the water trap and the oxidation catalyst to 100 °C (212 °F).

6.2.3 Oxidation Catalyst. A suitable length of 9.5 mm (3/8-in.) OD Inconel 600 tubing packed with 15 cm (6 in.) of 3.2 mm (3/8-in.) diameter 19 percent chromia on alumina pellets. The catalyst material is packed in the center of the catalyst tube with quartz wool packed on either end to hold it in place.

6.2.4 Water Trap. Leak-proof, capable of removing moisture from the gas stream.

6.2.5 Syringe Port. A 6.4-mm (1/4-in.) OD stainless steel tee fitting with a rubber septum placed in the side arm.

6.2.6 NDIR Detector. Capable of indicating CO_2 concentration in the range of zero to 5 percent, to monitor the progress of combustion of the organic compounds from the condensate trap.

6.2.7 Flow-Control Valve. Stainless steel, to maintain the trap conditioning system near atmospheric pressure.

6.2.8 Intermediate Collection Vessel. Stainless steel or aluminum, equipped with a female quick connect. Tanks with nominal volumes of at least 6 liters (0.2 ft^3) are recommended.

6.2.9 Mercury Manometer. Same as described in section 6.1.9.

6.2.10 Syringe. 10-ml gas-tight glass syringe equipped with an appropriate needle.

6.2.11 Syringes. 10-µl and 50-µl liquid injection syringes.

6.2.12 Liquid Sample Injection Unit. 316 Stainless steel U-tube fitted with an injection septum (see Figure 25–7).

6.3 Analysis.

6.3.1 NMO Analyzer. The NMO analyzer is a gas chromatograph (GC) with backflush capability for NMO analysis and is equipped with an oxidation catalyst, reduction catalyst, and FID. Figures 25–5 and 25–6 are schematics of a typical NMO analyzer. This semicontinuous GC/FID analyzer shall be capable of: (1) Separating CO, CO_2, and CH_4 from NMO, (2) reducing the CO_2 to CH_4 and quantifying as CH_4, and (3) oxidizing the NMO to CO_2, reducing the CO_2 to CH_4 and quantifying as CH_4, according to section 10.1.2. The analyzer consists of the following major components:

6.3.1.1 Oxidation Catalyst. A suitable length of 9.5-mm (3/8-in.) OD Inconel 600 tubing packed with 5.1 cm (2 in.) of 19 percent chromia on 3.2-mm (1/8-in.) alumina pellets. The catalyst material is packed in the center of the tube supported on either side by quartz wool. The catalyst tube must be mounted vertically in a 650 °C (1200 °F) furnace. Longer catalysts mounted horizontally may be used, provided they can meet the specifications of section 10.1.2.1.

6.3.1.2 Reduction Catalyst. A 7.6-cm (3-in.) length of 6.4-mm (1/4-in.) OD Inconel tubing fully packed with 100-mesh pure nickel powder. The catalyst tube must be mounted vertically in a 400 °C (750 °F) furnace.

6.3.1.3 Separation Column(s). A 30-cm (1-ft) length of 3.2-mm (1/8-in.) OD stainless steel tubing packed with 60/80 mesh Unibeads 1S followed by a 61-cm (2-ft) length of 3.2-mm (1/8-in.) OD stainless steel tubing packed with 60/80 mesh Carbosieve G. The Carbosieve and Unibeads columns must be baked separately at 200 °C (390 °F) with carrier gas flowing through them for 24 hours before initial use.

6.3.1.4 Sample Injection System. A single 10-port GC sample injection valve or a group of valves with sufficient ports fitted with a sample loop properly sized to interface with the NMO analyzer (1-cc loop recommended).

6.3.1.5 FID. An FID meeting the following specifications is required:

6.3.1.5.1 Linearity. A linear response (±5 percent) over the operating range as demonstrated by the procedures established in section 10.1.2.3.

6.3.1.5.2 Range. A full scale range of 10 to 50,000 ppm CH_4. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.3.1.6 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the analytical results.

6.3.2 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm Hg.

6.3.3 Temperature Sensor. Capable of measuring the laboratory temperature within 1 °C (2 °F).

6.3.4 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

7.0 Reagents and Standards

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Dry Ice. Solid CO2, crushed.

7.1.2 Coarse Quartz Wool. 8 to 15 um.

7.1.3 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Method D2986–71, 78, or 95a (incorporated by reference—see §60.17). Test data from the supplier's quality control program are sufficient for this purpose.

7.2 NMO Analysis. The following gases are required for NMO analysis:

7.2.1 Carrier Gases. Helium (He) and oxygen (O_2) containing less than 1 ppm CO_2 and less than 0.1 ppm hydrocarbon.

7.2.2 Fuel Gas. Hydrogen (H_2), at least 99.999 percent pure.

7.2.3 Combustion Gas. Either air (less than 0.1 ppm total hydrocarbon content) or O_2 (purity 99.99 percent or greater), as required by the detector.

7.3 Condensate Analysis. The following are required for condensate analysis:

7.3.1 Gases. Containing less than 1 ppm carbon.

7.3.1.1 Air.

7.3.1.2 Oxygen.

7.3.2 Liquids. To conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society.

7.3.2.1 Hexane.

7.3.2.2 Decane.

7.4 Calibration. For all calibration gases, the manufacturer must recommend a maximum shelf life for each cylinder (i.e., the length of time the gas concentration is not expected to change more than ±5 percent from its certified value). The date of gas cylinder preparation, certified organic concentration, and recommended maximum shelf life must be affixed to each cylinder before shipment from the gas manufacturer to the buyer. The following calibration gases are required:

7.4.1 Oxidation Catalyst Efficiency Check Calibration Gas. Gas mixture standard with nominal concentration of 1 percent methane in air.

7.4.2 FID Linearity and NMO Calibration Gases. Three gas mixture standards with nominal propane concentrations of 20 ppm, 200 ppm, and 3000 ppm, in air.

7.4.3 CO_2 Calibration Gases. Three gas mixture standards with nominal CO_2 concentrations of 50 ppm, 500 ppm, and 1 percent, in air.

NOTE: Total NMO less than 1 ppm required for 1 percent mixture.

7.4.4 NMO Analyzer System Check Calibration Gases. Four calibration gases are needed as follows:

7.4.4.1 Propane Mixture. Gas mixture standard containing (nominal) 50 ppm CO, 50 ppm CH_4, 1 percent CO_2, and 20 ppm C_3H_8, prepared in air.

7.4.4.2 Hexane. Gas mixture standard containing (nominal) 50 ppm hexane in air.

7.4.4.3 Toluene. Gas mixture standard containing (nominal) 20 ppm toluene in air.

7.4.4.4 Methanol. Gas mixture standard containing (nominal) 100 ppm methanol in air.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Sampling Equipment Preparation.

8.1.1 Condensate Trap Cleaning. Before its initial use and after each use, a condensate trap should be thoroughly cleaned and checked to ensure that it is not contaminated. Both cleaning and checking can be accomplished by installing the trap in the condensate recovery system and treating it as if it were a sample. The trap should be heated as described in section 11.1.3. A trap may be considered clean when the CO_2 concentration in its effluent gas drops below 10 ppm. This check is optional for traps that most recently have been used to collect samples which were then recovered according to the procedure in section 11.1.3.

8.1.2 Sample Tank Evacuation and Leak-Check. Evacuate the sample tank to 10 mm Hg absolute pressure or less. Then close the sample tank valve, and allow the tank to sit for 60 minutes. The tank is acceptable if a change in tank vacuum of less than 1 mm Hg is noted. The evacuation and leak-check may be conducted either in the laboratory or the field.

8.1.3 Sampling Train Assembly. Just before assembly, measure the tank vacuum using a mercury manometer. Record this vacuum, the ambient temperature, and the barometric pressure at this time. Close the sample tank valve and assemble the sampling

system as shown in Figure 25–1. Immerse the condensate trap body in dry ice at least 30 minutes before commencing sampling to improve collection efficiency. The point where the inlet tube joins the trap body should be 2.5 to 5 cm (1 to 2 in.) above the top of the dry ice.

8.1.4 Pretest Leak-Check. A pretest leak-check is required. Calculate or measure the approximate volume of the sampling train from the probe tip to the sample tank valve. After assembling the sampling train, plug the probe tip, and make certain that the sample tank valve is closed. Turn on the vacuum pump, and evacuate the sampling system from the probe tip to the sample tank valve to an absolute pressure of 10 mm Hg or less. Close the purge valve, turn off the pump, wait a minimum period of 10 minutes, and recheck the indicated vacuum. Calculate the maximum allowable pressure change based on a leak rate of 1 percent of the sampling rate using Equation 25–1, section 12.2. If the measured pressure change exceeds the allowable, correct the problem and repeat the leak-check before beginning sampling.

8.2 Sample Collection.

8.2.1 Unplug the probe tip, and place the probe into the stack such that the probe is perpendicular to the duct or stack axis; locate the probe tip at a single preselected point of average velocity facing away from the direction of gas flow. For stacks having a negative static pressure, seal the sample port sufficiently to prevent air in-leakage around the probe. Set the probe temperature controller to 129 °C (265 °F) and the filter temperature controller to 121 °C (250 °F). Allow the probe and filter to heat for about 30 minutes before purging the sample train.

8.2.2 Close the sample valve, open the purge valve, and start the vacuum pump. Set the flow rate between 60 and 100 cm^3/min (0.13 and 0.21 ft^3/hr), and purge the train with stack gas for at least 10 minutes.

8.2.3 When the temperatures at the exit ends of the probe and filter are within the corresponding specified ranges, check the dry ice level around the condensate trap, and add dry ice if necessary. Record the clock time. To begin sampling, close the purge valve and stop the pump. Open the sample valve and the sample tank valve. Using the flow control valve, set the flow through the sample train to the proper rate. Adjust the flow rate as necessary to maintain a constant rate (±10 percent) throughout the duration of the sampling period. Record the sample tank vacuum and flowmeter setting at 5-minute intervals. (See Figure 25–8.) Select a total sample time greater than or equal to the minimum sampling time specified in the applicable subpart of the regulations; end the sampling when this time period is reached or when a constant flow rate can no longer be maintained because of reduced sample tank vacuum.

NOTE: If sampling had to be stopped before obtaining the minimum sampling time (specified in the applicable subpart) because a constant flow rate could not be maintained, proceed as follows: After closing the sample tank valve, remove the used sample tank from the sampling train (without disconnecting other portions of the sampling train). Take another evacuated and leak-checked sample tank, measure and record the tank vacuum, and attach the new tank to the sampling train. After the new tank is attached to the sample train, proceed with the sampling until the required minimum sampling time has been exceeded.

8.3 Sample Recovery. After sampling is completed, close the flow control valve, and record the final tank vacuum; then record the tank temperature and barometric pressure. Close the sample tank valve, and disconnect the sample tank from the sample system. Disconnect the condensate trap at the inlet to the rate meter, and tightly seal both ends of the condensate trap. Do not include the probe from the stack to the filter as part of the condensate sample.

8.4 Sample Storage and Transport. Keep the trap packed in dry ice until the samples are returned to the laboratory for analysis. Ensure that run numbers are identified on the condensate trap and the sample tank(s).

9.0 Quality Control

Section	Quality control measure	Effect
10.1.1	Initial performance check of condensate recovery apparatus.	Ensure acceptable condensate recovery efficiency.
10.1.2, 10.2	NMO analyzer initial and daily performance checks.	Ensure precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Initial Performance Checks.

10.1.1 Condensate Recovery Apparatus. Perform these tests before the system is first placed in operation, after any shutdown of 6 months or more, and after any major modification of the system, or at the frequency recommended by the manufacturer.

10.1.1.1 Carrier Gas and Auxiliary O_2 Blank Check. Analyze each new tank of carrier gas or auxiliary O_2 with the NMO analyzer to

check for contamination. Treat the gas cylinders as noncondensible gas samples, and analyze according to the procedure in section 11.2.3. Add together any measured CH_4, CO, CO_2, or NMO. The total concentration must be less than 5 ppm.

10.1.1.2 Oxidation Catalyst Efficiency Check.

10.1.1.2.1 With a clean condensate trap installed in the recovery system or a ⅛″ stainless steel connector tube, replace the carrier gas cylinder with the high level methane standard gas cylinder (Section 7.4.1). Set the four-port valve to the recovery position, and attach an ICV to the recovery system. With the sample recovery valve in vent position and the flow-control and ICV valves fully open, evacuate the manometer or gauge, the connecting tubing, and the ICV to 10 mm Hg absolute pressure. Close the flow-control and vacuum pump valves.

10.1.1.2.2 After the NDIR response has stabilized, switch the sample recovery valve from vent to collect. When the manometer or pressure gauge begins to register a slight positive pressure, open the flow-control valve. Keep the flow adjusted such that the pressure in the system is maintained within 10 percent of atmospheric pressure. Continue collecting the sample in a normal manner until the ICV is filled to a nominal gauge pressure of 300 mm Hg. Close the ICV valve, and remove the ICV from the system. Place the sample recovery valve in the vent position, and return the recovery system to its normal carrier gas and normal operating conditions. Analyze the ICV for CO_2 using the NMO analyzer; the catalyst efficiency is acceptable if the CO_2 concentration is within 2 percent of the methane standard concentration.

10.1.1.3 System Performance Check. Construct a liquid sample injection unit similar in design to the unit shown in Figure 25–7. Insert this unit into the condensate recovery and conditioning system in place of a condensate trap, and set the carrier gas and auxiliary O_2 flow rates to normal operating levels. Attach an evacuated ICV to the system, and switch from system vent to collect. With the carrier gas routed through the injection unit and the oxidation catalyst, inject a liquid sample (see sections 10.1.1.3.1 to 10.1.1.3.4) into the injection port. Operate the trap recovery system as described in section 11.1.3. Measure the final ICV pressure, and then analyze the vessel to determine the CO_2 concentration. For each injection, calculate the percent recovery according to section 12.7. Calculate the relative standard deviation for each set of triplicate injections according to section 12.8. The performance test is acceptable if the average percent recovery is 100 ±5 percent and the relative standard deviation is less than 2 percent for each set of triplicate injections.

10.1.1.3.1 50 µl hexane.

10.1.1.3.2 10 µl hexane.

10.1.1.3.3 50 µl decane.

10.1.1.3.4 10 µl decane.

10.1.2 NMO Analyzer. Perform these tests before the system is first placed in operation, after any shutdown longer than 6 months, and after any major modification of the system.

10.1.2.1 Oxidation Catalyst Efficiency Check. Turn off or bypass the NMO analyzer reduction catalyst. Make triplicate injections of the high level methane standard (Section 7.4.1). The oxidation catalyst operation is acceptable if the FID response is less than 1 percent of the injected methane concentration.

10.1.2.2 Reduction Catalyst Efficiency Check. With the oxidation catalyst unheated or bypassed and the heated reduction catalyst bypassed, make triplicate injections of the high level methane standard (Section 7.4.1). Repeat this procedure with both catalysts operative. The reduction catalyst operation is acceptable if the responses under both conditions agree within 5 percent of their average.

10.1.2.3 NMO Analyzer Linearity Check Calibration. While operating both the oxidation and reduction catalysts, conduct a linearity check of the analyzer using the propane standards specified in section 7.4.2. Make triplicate injections of each calibration gas. For each gas (*i.e.*, each set of triplicate injections), calculate the average response factor (area/ppm C) for each gas, as well as and the relative standard deviation (according to section 12.8). Then calculate the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within 2.5 percent of the overall mean value and if the relative standard deviation gas is less than 2 percent of the overall mean value. Record the overall mean of the propane response factor values as the NMO calibration response factor (RF_{NMO}). Repeat the linearity check using the CO_2 standards specified in section 7.4.3. Make triplicate injections of each gas, and then calculate the average response factor (area/ppm C) for each gas, as well as the overall mean of the response factor values. Record the overall mean of the response factor values as the CO_2 calibration response factor (RF_{CO2}). The RF_{CO2} must be within 10 percent of the RF_{NMO}.

10.1.2.4 System Performance Check. Check the column separation and overall performance of the analyzer by making triplicate injections of the calibration gases listed in section 7.4.4. The analyzer performance is acceptable if the measured NMO value for each gas (average of triplicate injections) is within 5 percent of the expected value.

10.2 NMO Analyzer Daily Calibration. The following calibration procedures shall be performed before and immediately after the

analysis of each set of samples, or on a daily basis, whichever is more stringent:

10.2.1 CO_2 Response Factor. Inject triplicate samples of the high level CO_2 calibration gas (Section 7.4.3), and calculate the average response factor. The system operation is adequate if the calculated response factor is within 5 percent of the RF_{CO2} calculated during the initial performance test (Section 10.1.2.3). Use the daily response factor (DRF_{CO2}) for analyzer calibration and the calculation of measured CO_2 concentrations in the ICV samples.

10.2.2 NMO Response Factors. Inject triplicate samples of the mixed propane calibration cylinder gas (Section 7.4.4.1), and calculate the average NMO response factor. The system operation is adequate if the calculated response factor is within 10 percent of the RF_{NMO} calculated during the initial performance test (Section 10.1.2.4). Use the daily response factor (DRF_{NMO}) for analyzer calibration and calculation of NMO concentrations in the sample tanks.

10.3 Sample Tank and ICV Volume. The volume of the gas sampling tanks used must be determined. Determine the tank and ICV volumes by weighing them empty and then filled with deionized distilled water; weigh to the nearest 5 g, and record the results. Alternatively, measure the volume of water used to fill them to the nearest 5 ml.

11.0 Analytical Procedure

11.1 Condensate Recovery. See Figure 25–9. Set the carrier gas flow rate, and heat the catalyst to its operating temperature to condition the apparatus.

11.1.1 Daily Performance Checks. Each day before analyzing any samples, perform the following tests:

11.1.1.1 Leak-Check. With the carrier gas inlets and the sample recovery valve closed, install a clean condensate trap in the system, and evacuate the system to 10 mm Hg absolute pressure or less. Monitor the system pressure for 10 minutes. The system is acceptable if the pressure change is less than 2 mm Hg.

11.1.1.2 System Background Test. Adjust the carrier gas and auxiliary oxygen flow rate to their normal values of 100 cc/min and 150 cc/min, respectively, with the sample recovery valve in vent position. Using a 10-ml syringe, withdraw a sample from the system effluent through the syringe port. Inject this sample into the NMO analyzer, and measure the CO_2 content. The system background is acceptable if the CO_2 concentration is less than 10 ppm.

11.1.1.3 Oxidation Catalyst Efficiency Check. Conduct a catalyst efficiency test as specified in section 10.1.1.2. If the criterion of this test cannot be met, make the necessary repairs to the system before proceeding.

11.1.2 Condensate Trap CO_2 Purge and Sample Tank Pressurization.

11.1.2.1 After sampling is completed, the condensate trap will contain condensed water and organics and a small volume of sampled gas. This gas from the stack may contain a significant amount of CO_2 which must be removed from the condensate trap before the sample is recovered. This is accomplished by purging the condensate trap with zero air and collecting the purged gas in the original sample tank.

11.1.2.2 Begin with the sample tank and condensate trap from the test run to be analyzed. Set the four-port valve of the condensate recovery system in the CO_2 purge position as shown in Figure 25–9. With the sample tank valve closed, attach the sample tank to the sample recovery system. With the sample recovery valve in the vent position and the flow control valve fully open, evacuate the manometer or pressure gauge to the vacuum of the sample tank. Next, close the vacuum pump valve, open the sample tank valve, and record the tank pressure.

11.1.2.3 Attach the dry ice-cooled condensate trap to the recovery system, and initiate the purge by switching the sample recovery valve from vent to collect position. Adjust the flow control valve to maintain atmospheric pressure in the recovery system. Continue the purge until the CO_2 concentration of the trap effluent is less than 5 ppm. CO_2 concentration in the trap effluent should be measured by extracting syringe samples from the recovery system and analyzing the samples with the NMO analyzer. This procedure should be used only after the NDIR response has reached a minimum level. Using a 10-ml syringe, extract a sample from the syringe port prior to the NDIR, and inject this sample into the NMO analyzer.

11.1.2.4 After the completion of the CO_2 purge, use the carrier gas bypass valve to pressurize the sample tank to approximately 1,060 mm Hg absolute pressure with zero air.

11.1.3 Recovery of the Condensate Trap Sample (See Figure 25–10).

11.1.3.1 Attach the ICV to the sample recovery system. With the sample recovery valve in a closed position, between vent and collect, and the flow control and ICV valves fully open, evacuate the manometer or gauge, the connecting tubing, and the ICV to 10 mm Hg absolute pressure. Close the flow-control and vacuum pump valves.

11.1.3.2 Begin auxiliary oxygen flow to the oxidation catalyst at a rate of 150 cc/min, then switch the four-way valve to the trap recovery position and the sample recovery valve to collect position. The system should now be set up to operate as indicated in Figure 25–10. After the manometer or pressure gauge begins to register a slight positive pressure, open the flow control valve. Adjust the flow-control valve to maintain atmospheric pressure in the system within 10 percent.

11.1.3.3 Remove the condensate trap from the dry ice, and allow it to warm to ambient temperature while monitoring the NDIR response. If, after 5 minutes, the CO_2 concentration of the catalyst effluent is below 10,000 ppm, discontinue the auxiliary oxygen flow to the oxidation catalyst. Begin heating the trap by placing it in a furnace preheated to 200 °C (390 °F). Once heating has begun, carefully monitor the NDIR response to ensure that the catalyst effluent concentration does not exceed 50,000 ppm. Whenever the CO_2 concentration exceeds 50,000 ppm, supply auxiliary oxygen to the catalyst at the rate of 150 cc/min. Begin heating the tubing that connected the heated sample box to the condensate trap only after the CO_2 concentration falls below 10,000 ppm. This tubing may be heated in the same oven as the condensate trap or with an auxiliary heat source such as a heat gun. Heating temperature must not exceed 200 °C (390 °F). If a heat gun is used, heat the tubing slowly along its entire length from the upstream end to the downstream end, and repeat the pattern for a total of three times. Continue the recovery until the CO_2 concentration drops to less than 10 ppm as determined by syringe injection as described under the condensate trap CO_2 purge procedure (Section 11.1.2).

11.1.3.4 After the sample recovery is completed, use the carrier gas bypass valve to pressurize the ICV to approximately 1060 mm Hg absolute pressure with zero air.

11.2 Analysis. Once the initial performance test of the NMO analyzer has been successfully completed (see section 10.1.2) and the daily CO_2 and NMO response factors have been determined (see section 10.2), proceed with sample analysis as follows:

11.2.1 Operating Conditions. The carrier gas flow rate is 29.5 cc/min He and 2.2 cc/min O_2. The column oven is heated to 85 °C (185 °F). The order of elution for the sample from the column is CO, CH_4, CO_2, and NMO.

11.2.2 Analysis of Recovered Condensate Sample. Purge the sample loop with sample, and then inject the sample. Under the specified operating conditions, the CO_2 in the sample will elute in approximately 100 seconds. As soon as the detector response returns to baseline following the CO_2 peak, switch the carrier gas flow to backflush, and raise the column oven temperature to 195 °C (380 °F) as rapidly as possible. A rate of 30 °C/min (90 °F) has been shown to be adequate. Record the value obtained for the condensible organic material (C_{cm}) measured as CO_2 and any measured NMO. Return the column oven temperature to 85 °C (185 °F) in preparation for the next analysis. Analyze each sample in triplicate, and report the average C_{cm}.

11.2.3 Analysis of Sample Tank. Perform the analysis as described in section 11.2.2, but record only the value measured for NMO (C_{tm}).

12.0 Data Analysis and Calculations

Carry out the calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculations. All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge or manometer pressure.

12.1 Nomenclature.

C = TGNMO concentration of the effluent, ppm C equivalent.
C_c = Calculated condensible organic (condensate trap) concentration of the effluent, ppm C equivalent.
C_{cm} = Measured concentration (NMO analyzer) for the condensate trap ICV, ppm CO_2.
C_t = Calculated noncondensible organic concentration (sample tank) of the effluent, ppm C equivalent.
C_{tm} = Measured concentration (NMO analyzer) for the sample tank, ppm NMO.
F = Sampling flow rate, cc/min.
L = Volume of liquid injected, µl.
M = Molecular weight of the liquid injected, g/g-mole.
M_c = TGNMO mass concentration of the effluent, mg C/dsm³.
N = Carbon number of the liquid compound injected (N = 12 for decane, N = 6 for hexane).
n = Number of data points.
P_f = Final pressure of the intermediate collection vessel, mm Hg absolute.
P_b = Barometric pressure, cm Hg.
P_{ti} = Gas sample tank pressure before sampling, mm Hg absolute.
P_t = Gas sample tank pressure after sampling, but before pressurizing, mm Hg absolute.
P_{tf} = Final gas sample tank pressure after pressurizing, mm Hg absolute.
q = Total number of analyzer injections of intermediate collection vessel during analysis (where k = injection number, 1 * * * q).
r = Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 * * * r).
r = Density of liquid injected, g/cc.
T_f = Final temperature of intermediate collection vessel, °K.
T_{ti} = Sample tank temperature before sampling, °K.
T_t = Sample tank temperature at completion of sampling, °K.
T_{tf} = Sample tank temperature after pressurizing, °K.
V = Sample tank volume, m³.
V_t = Sample train volume, cc.
V_v = Intermediate collection vessel volume, m³.
V_s = Gas volume sampled, dsm³.
x_i = Individual measurements.
$\bar{x}$ = Mean value.

ΔP = Allowable pressure change, cm Hg.
Θ = Leak-check period, min.

12.2 Allowable Pressure Change. For the pretest leak-check, calculate the allowable pressure change using Equation 25–1:

$$\Delta P = 0.01 \frac{F P_b \Theta}{V_t} \qquad \text{Eq. 25-1}$$

12.3 Sample Volume. For each test run, calculate the gas volume sampled using Equation 25–2:

$$V_s = 0.3857\, V \left(\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}} \right) \qquad \text{Eq. 25-2}$$

12.4 Noncondensible Organics. For each sample tank, determine the concentration of nonmethane organics (ppm C) using Equation 25–3:

$$C_t = \left(\frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}} \right) \left(\frac{1}{r} \sum_{j=1}^{r} C_{tm_j} \right) \qquad \text{Eq. 25-3}$$

12.5 Condensible Organics. For each condensate trap determine the concentration of organics (ppm C) using Equation 25–4:

$$C_c = 0.3857 \frac{V_v P_f}{V_s T_f} \left(\frac{1}{q} \sum_{k=1}^{q} C_{cm_k} \right) \qquad \text{Eq. 25-4}$$

12.6 TGNMO Mass Concentration. Determine the TGNMO mass concentration as carbon for each test run, using Equation 25–5:

$$M_c = 0.4993 \left(C_t + C_c \right) \qquad \text{Eq. 25-5}$$

12.7 Percent Recovery. Calculate the percent recovery for the liquid injections to the condensate recovery and conditioning system using Equation 25–6:

$$\text{Percent Recovery} = K \frac{M V_v P_t C_{cm}}{L P T_f N} \qquad \text{Eq. 25-6}$$

where K = 1.604 (°K)(g-mole)(%)/(mm Hg)(ml)(m^3)(ppm).

12.8 Relative Standard Deviation. Use Equation 25–7 to calculate the relative standard deviation (RSD) of percent recovery and analyzer linearity.

$$RSD = \frac{100}{\bar{x}} \left[\frac{\sum_{i=1}^{n} \left(x_i - \bar{x} \right)^2}{n - 1} \right]^{\frac{1}{2}} \qquad \text{Eq. 25-7}$$

13.0 Method Performance

13.1 Range. The minimum detectable limit of the method has been determined to be 50 parts per million by volume (ppm). No upper limit has been established.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, A.E., S. Witz, and R.D. MacPhee. Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, MA. June 15–20, 1975.) 14 p.

2. Salo, A.E., W.L. Oaks, and R.D. MacPhee. Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, CO. June 9–13, 1974.) 25 p.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

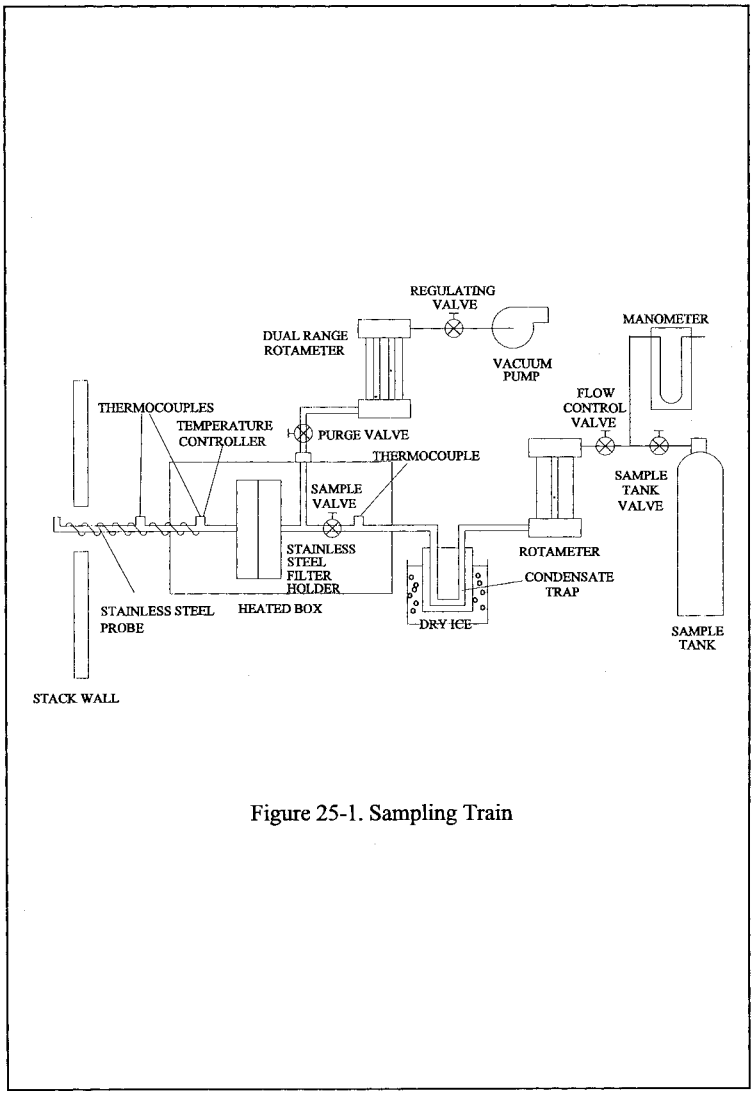


Figure 25-1. Sampling Train

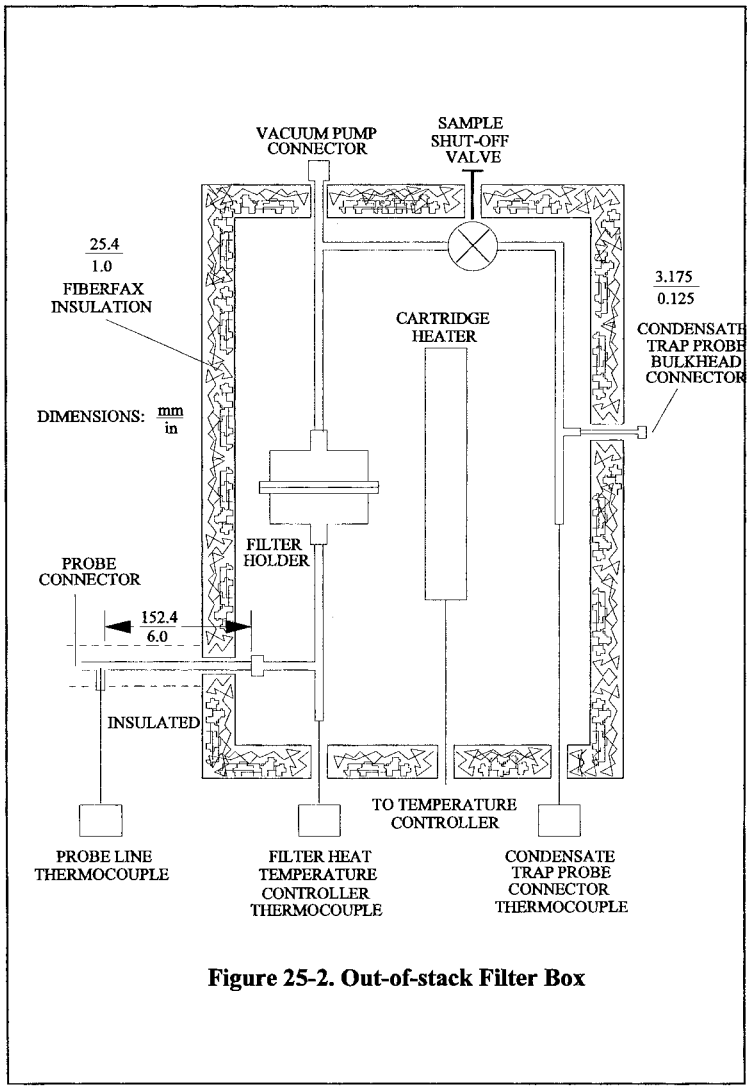


Figure 25-2. Out-of-stack Filter Box

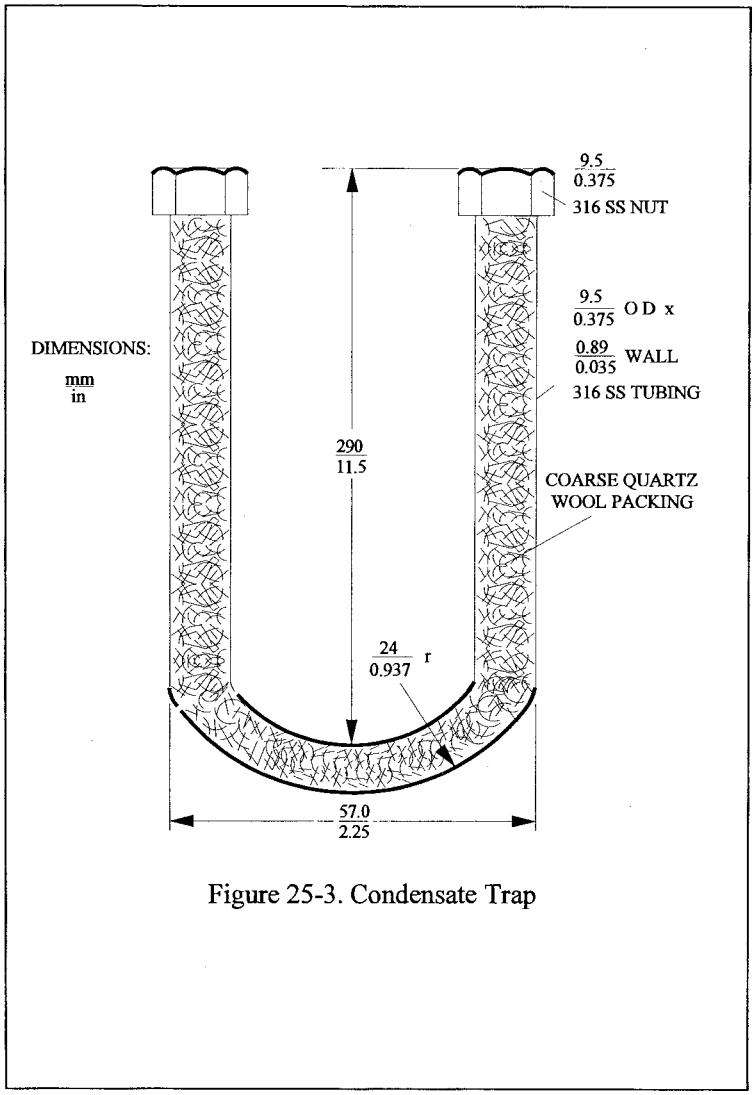


Figure 25-3. Condensate Trap

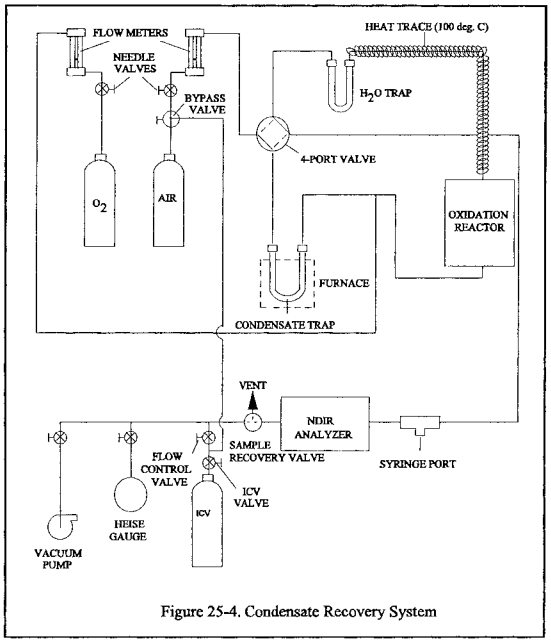


Figure 25-4. Condensate Recovery System

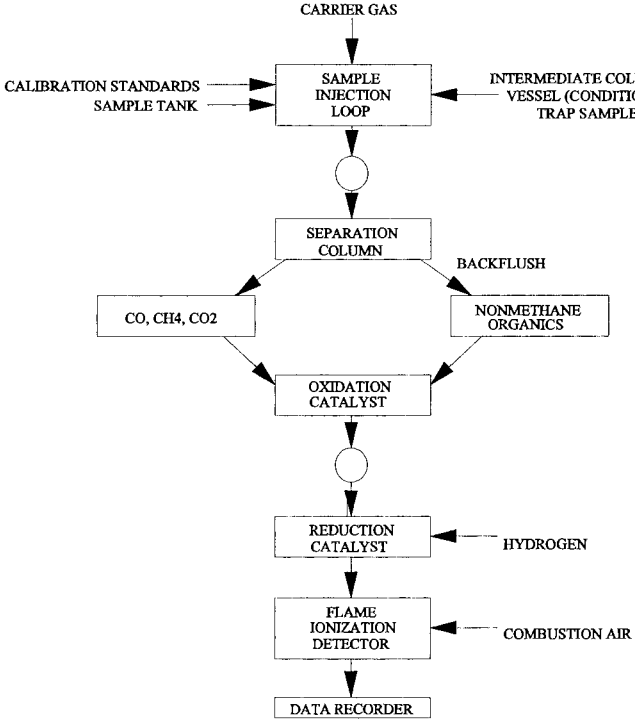


Figure 25-5. Simplified Schematic of Nonmethane Organic (NMO) Analyzer

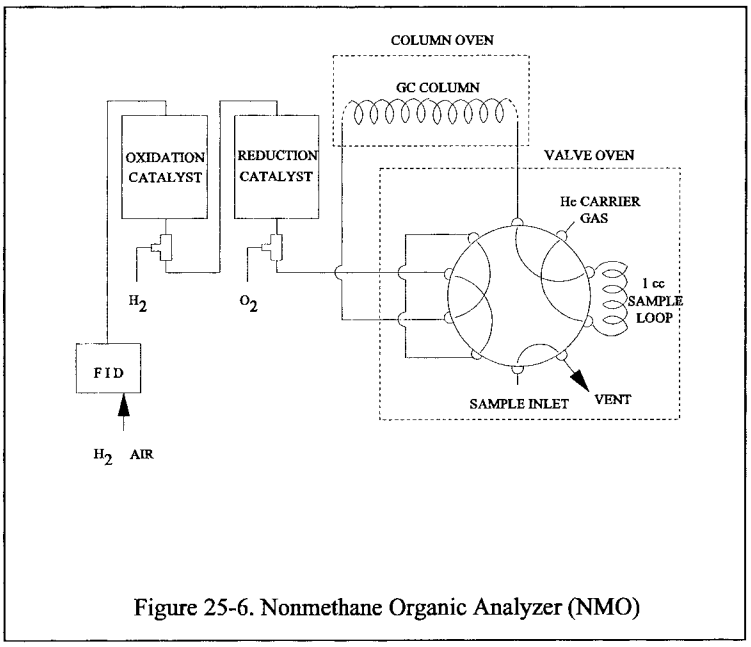


Figure 25-6. Nonmethane Organic Analyzer (NMO)

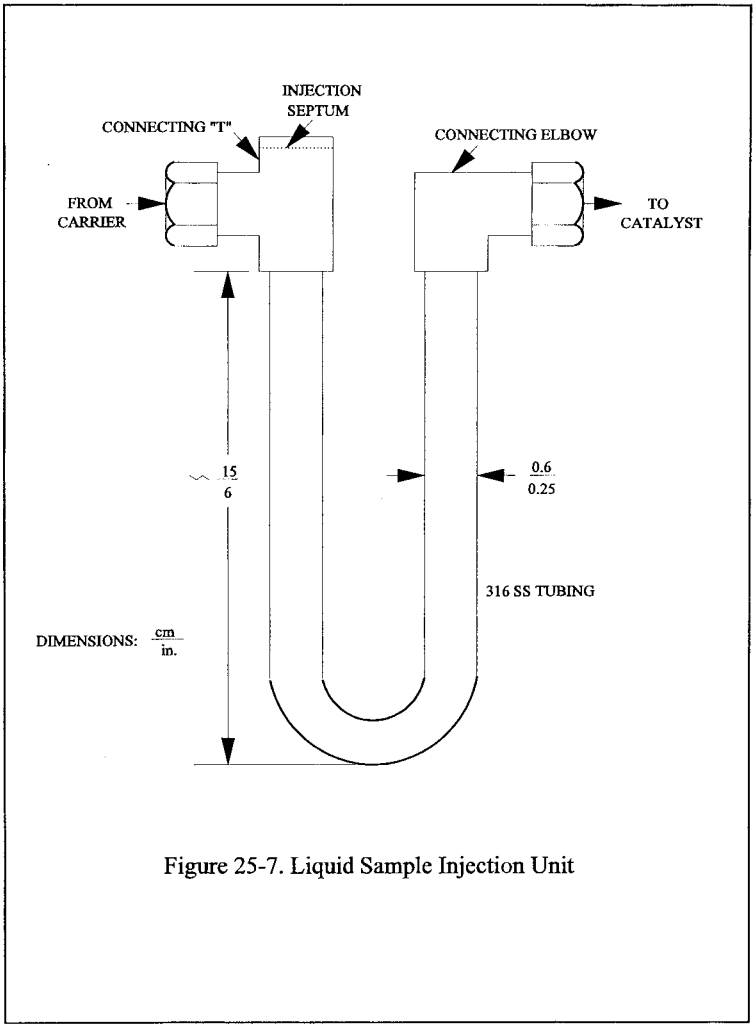


Figure 25-7. Liquid Sample Injection Unit

VOLATILE ORGANIC CARBON

FACILITY _____ SAMPLE LOCATION _____

LOCATION _____ OPERATOR _____

DATE _____ RUN NUMBER _____

TANK NUMBER _____ TRAP NUMBER _____ SAMPLE ID NUMBER _____

TANK VACUUM mm HG	TANK VACUUM cm Hg	BAROMETRIC PRESSURE mm Hg	AMBIENT TEMPERATURE °C
PRETEST (MANOMETER)	(GAUGE)		
POST-TEST (MANOMETER)	(GAUGE)		

LEAK RATE _____ cm Hg / l.0 min _____

PRETEST _____

TIME CLOCK/SAMPLE	VACUUM cm Hg	FLOWMETER SETTINGS	COMMENTS

Figure 25-8. Example Field Data Form

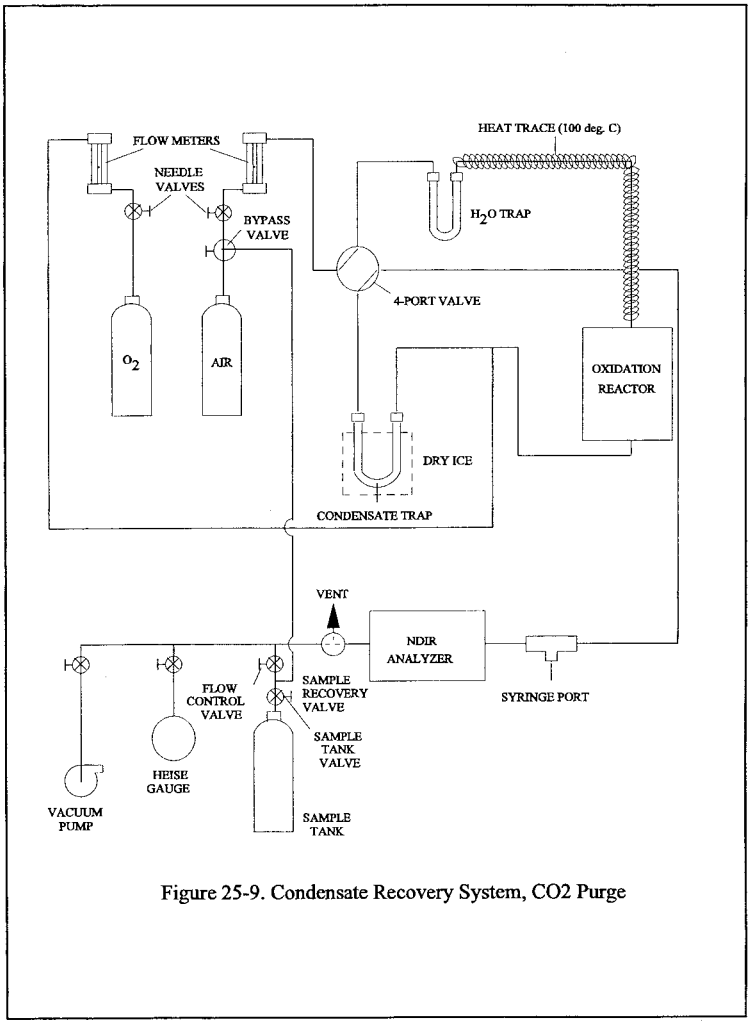


Figure 25-9. Condensate Recovery System, CO2 Purge

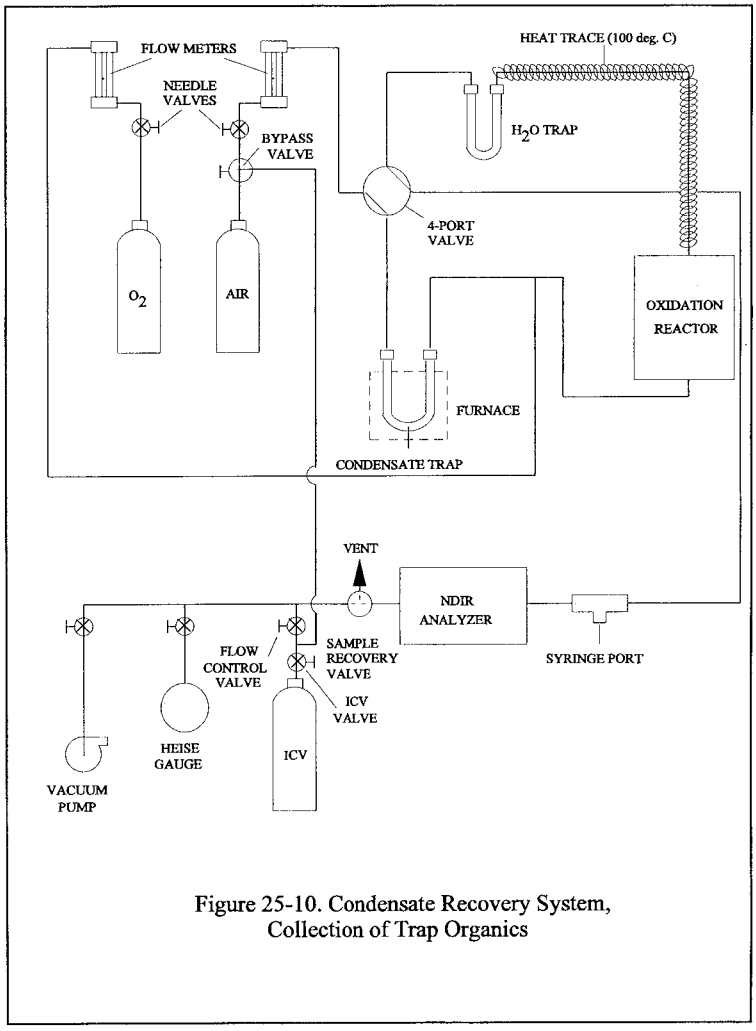


Figure 25-10. Condensate Recovery System, Collection of Trap Organics

METHOD 25A—DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A FLAME IONIZATION ANALYZER

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total Organic Compounds	N/A	<2% of span.

1.2 Applicability. This method is applicable for the determination of total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the source through a heated sample line and glass fiber filter to a flame ionization analyzer (FIA). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

3.0 Definitions

3.1 *Calibration drift* means the difference in the measurement system response to a mid-level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

3.2 *Calibration error* means the difference between the gas concentration indicated by the measurement system and the know concentration of the calibration gas.

3.3 *Calibration gas* means a known concentration of a gas in an appropriate diluent gas.

3.4 *Measurement system* means the total equipment required for the determination of the gas concentration. The system consists of the following major subsystems:

3.4.1 *Sample interface* means that portion of a system used for one or more of the following: sample acquisition, sample transportation, sample conditioning, or protection of the analyzer(s) from the effects of the stack effluent.

3.4.2 *Organic analyzer* means that portion of the measurement system that senses the gas to be measured and generates an output proportional to its concentration.

3.5 *Response time* means the time interval from a step change in pollutant concentration at the inlet to the emission measurement system to the time at which 95 percent of the corresponding final value is reached as displayed on the recorder.

3.6 *Span Value* means the upper limit of a gas concentration measurement range that is specified for affected source categories in the applicable part of the regulations. The span value is established in the applicable regulation and is usually 1.5 to 2.5 times the applicable emission limit. If no span value is provided, use a span value equivalent to 1.5 to 2.5 times the expected concentration. For convenience, the span value should correspond to 100 percent of the recorder scale.

3.7 *Zero drift* means the difference in the measurement system response to a zero level calibration gas before or after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

5.2 Explosive Atmosphere. This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

6.0 Equipment and Supplies

6.1 Measurement System. Any measurement system for total organic concentration that meets the specifications of this method. A schematic of an acceptable measurement system is shown in Figure 25A–1. All sampling components leading to the analyzer shall be heated ≥110 °C (220 °F) throughout the sampling period, unless safety reasons are cited (Section 5.2) The essential components of the measurement system are described below:

6.1.1 Organic Concentration Analyzer. A flame ionization analyzer (FIA) capable of meeting or exceeding the specifications of this method. The flame ionization detector block shall be heated >120 °C (250 °F).

6.1.2 Sample Probe. Stainless steel, or equivalent, three-hole rake type. Sample holes shall be 4 mm (0.16-in.) in diameter or smaller and located at 16.7, 50, and 83.3 percent of the equivalent stack diameter. Alternatively, a single opening probe may be used so that a gas sample is collected from the centrally located 10 percent area of the stack cross-section.

6.1.3 Heated Sample Line. Stainless steel or Teflon'' tubing to transport the sample gas

to the analyzer. The sample line should be heated (≥110 °C) to prevent any condensation.

6.1.4 Calibration Valve Assembly. A three-way valve assembly to direct the zero and calibration gases to the analyzers is recommended. Other methods, such as quick-connect lines, to route calibration gas to the analyzers are applicable.

6.1.5 Particulate Filter. An in-stack or an out-of-stack glass fiber filter is recommended if exhaust gas particulate loading is significant. An out-of-stack filter should be heated to prevent any condensation.

6.1.6 Recorder. A strip-chart recorder, analog computer, or digital recorder for recording measurement data. The minimum data recording requirement is one measurement value per minute.

7.0 Reagents and Standards

7.1 Calibration Gases. The calibration gases for the gas analyzer shall be propane in air or propane in nitrogen. Alternatively, organic compounds other than propane can be used; the appropriate corrections for response factor must be made. Calibration gases shall be prepared in accordance with the procedure listed in Citation 2 of section 16. Additionally, the manufacturer of the cylinder should provide a recommended shelf life for each calibration gas cylinder over which the concentration does not change more than ±2 percent from the certified value. For calibration gas values not generally available (*i.e.*, organics between 1 and 10 percent by volume), alternative methods for preparing calibration gas mixtures, such as dilution systems (Test Method 205, 40 CFR Part 51, Appendix M), may be used with prior approval of the Administrator.

7.1.1 Fuel. A 40 percent H_2/60 percent N_2 gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value.

7.1.2 Zero Gas. High purity air with less than 0.1 part per million by volume (ppmv) of organic material (propane or carbon equivalent) or less than 0.1 percent of the span value, whichever is greater.

7.1.3 Low-level Calibration Gas. An organic calibration gas with a concentration equivalent to 25 to 35 percent of the applicable span value.

7.1.4 Mid-level Calibration Gas. An organic calibration gas with a concentration equivalent to 45 to 55 percent of the applicable span value.

7.1.5 High-level Calibration Gas. An organic calibration gas with a concentration equivalent to 80 to 90 percent of the applicable span value.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Selection of Sampling Site. The location of the sampling site is generally specified by the applicable regulation or purpose of the test (*i.e.*, exhaust stack, inlet line, etc.). The sample port shall be located to meet the testing requirements of Method 1.

8.2 Location of Sample Probe. Install the sample probe so that the probe is centrally located in the stack, pipe, or duct and is sealed tightly at the stack port connection.

8.3 Measurement System Preparation. Prior to the emission test, assemble the measurement system by following the manufacturer's written instructions for preparing sample interface and the organic analyzer. Make the system operable (Section 10.1).

8.4 Calibration Error Test. Immediately prior to the test series (within 2 hours of the start of the test), introduce zero gas and high-level calibration gas at the calibration valve assembly. Adjust the analyzer output to the appropriate levels, if necessary. Calculate the predicted response for the low-level and mid-level gases based on a linear response line between the zero and high-level response. Then introduce low-level and mid-level calibration gases successively to the measurement system. Record the analyzer responses for low-level and mid-level calibration gases and determine the differences between the measurement system responses and the predicted responses. These differences must be less than 5 percent of the respective calibration gas value. If not, the measurement system is not acceptable and must be replaced or repaired prior to testing. No adjustments to the measurement system shall be conducted after the calibration and before the drift check (Section 8.6.2). If adjustments are necessary before the completion of the test series, perform the drift checks prior to the required adjustments and repeat the calibration following the adjustments. If multiple electronic ranges are to be used, each additional range must be checked with a mid-level calibration gas to verify the multiplication factor.

8.5 Response Time Test. Introduce zero gas into the measurement system at the calibration valve assembly. When the system output has stabilized, switch quickly to the high-level calibration gas. Record the time from the concentration change to the measurement system response equivalent to 95 percent of the step change. Repeat the test three times and average the results.

8.6 Emission Measurement Test Procedure.

8.6.1 Organic Measurement. Begin sampling at the start of the test period, recording time and any required process information as appropriate. In particulate, note on the recording chart, periods of process interruption or cyclic operation.

8.6.2 Drift Determination. Immediately following the completion of the test period and hourly during the test period, reintroduce the zero and mid-level calibration gases, one at a time, to the measurement system at the calibration valve assembly. (Make no adjustments to the measurement system until both the zero and calibration drift checks are made.) Record the analyzer response. If the drift values exceed the specified limits, invalidate the test results preceding the check and repeat the test following corrections to the measurement system. Alternatively, recalibrate the test measurement system as in section 8.4 and report the results using both sets of calibration data (i.e., data determined prior to the test period and data determined following the test period).

NOTE: Note on the recording chart periods of process interruption or cyclic operation.

9.0 Quality Control

Method section	Quality control measure	Effect
8.4	Zero and calibration drift tests	Ensures that bias introduced by drift in the measurement system output during the run is no greater than 3 percent of span.

10.0 Calibration and Standardization

10.1 FIA equipment can be calibrated for almost any range of total organic concentrations. For high concentrations of organics (>1.0 percent by volume as propane), modifications to most commonly available analyzers are necessary. One accepted method of equipment modification is to decrease the size of the sample to the analyzer through the use of a smaller diameter sample capillary. Direct and continuous measurement of organic concentration is a necessary consideration when determining any modification design.

11.0 Analytical Procedure

The sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Calculations and Data Analysis

12.1 Determine the average organic concentration in terms of ppmv as propane or other calibration gas. The average shall be determined by integration of the output recording over the period specified in the applicable regulation. If results are required in terms of ppmv as carbon, adjust measured concentrations using Equation 25A–1.

$$C_c = K C_{meas} \qquad \text{Eq. 25A-1}$$

Where:

C_c = Organic concentration as carbon, ppmv.
C_{meas} = Organic concentration as measured, ppmv.
K = Carbon equivalent correction factor.
= 2 for ethane.
= 3 for propane.
= 4 for butane.
= Appropriate response factor for other organic calibration gases.

13.0 Method Performance

13.1 Measurement System Performance Specifications.

13.1.1 Zero Drift. Less than ±3 percent of the span value.

13.1.2 Calibration Drift. Less than ±3 percent of span value.

13.1.3 Calibration Error. Less than ±5 percent of the calibration gas value.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Measurement of Volatile Organic Compounds—Guideline Series. U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA–450/2–78–041. June 1978. p. 46–54.

2. EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards. U.S. Environmental Protection Agency, Quality Assurance and Technical Support Division. Research Triangle Park, N.C. September 1993.

3. Gasoline Vapor Emission Laboratory Evaluation—Part 2. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, NC. EMB Report No. 75–GAS–6. August 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

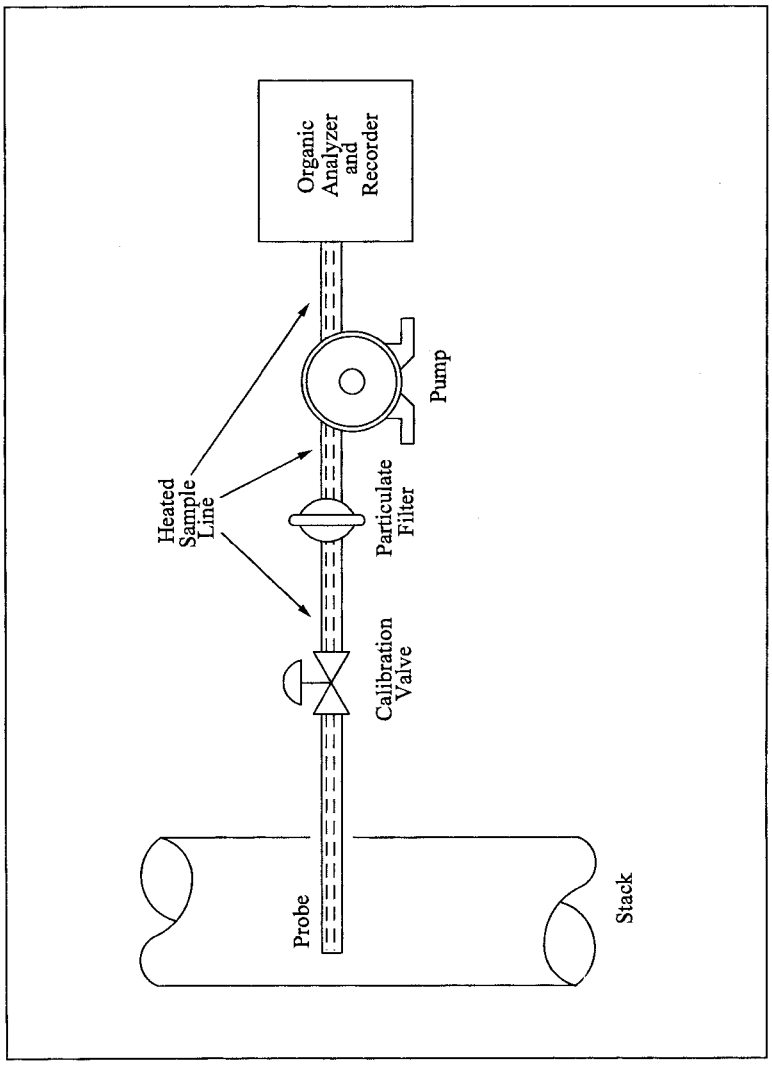


Figure 25A-1. Organic Concentration Measurement System.

METHOD 25B—DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A NONDISPERSIVE INFRARED ANALYZER

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 6C, and Method 25A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total Organic Compounds	N/A	<2% of span.

1.2 Applicability. This method is applicable for the determination of total gaseous organic concentration of vapors consisting primarily of alkanes. Other organic materials may be measured using the general procedure in this method, the appropriate calibration gas, and an analyzer set to the appropriate absorption band.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

A gas sample is extracted from the source through a heated sample line, if necessary, and glass fiber filter to a nondispersive infrared analyzer (NDIR). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

3.0 Definitions

Same as Method 25A, section 3.0.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

5.2 Explosive Atmosphere. This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

6.0 Equipment and Supplies

Same as Method 25A, section 6.0, with the exception of the following:

6.1 Organic Concentration Analyzer. A nondispersive infrared analyzer designed to measure alkane organics and capable of meeting or exceeding the specifications in this method.

7.0 Reagents and Standards

Same as Method 25A, section 7.1. No fuel gas is required for an NDIR.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as Method 25A, section 8.0.

9.0 Quality Control

Same as Method 25A, section 9.0.

10.0 Calibration and Standardization

Same as Method 25A, section 10.0.

11.0 Analytical Procedure

The sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Calculations and Data Analysis

Same as Method 25A, section 12.0.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 25A, section 16.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 25C—DETERMINATION OF NONMETHANE ORGANIC COMPOUNDS (NMOC) IN LANDFILL GASES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should also have a thorough knowledge of EPA Method 25.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Nonmethane organic compounds (NMOC).	No CAS number assigned.

1.2 Applicability. This method is applicable to the sampling and measurement of NMOC as carbon in landfill gases (LFG).

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A sample probe that has been perforated at one end is driven or augured to a depth of 0.9 m (3 ft) below the bottom of the landfill cover. A sample of the landfill gas is extracted with an evacuated cylinder. The NMOC content of the gas is determined by

injecting a portion of the gas into a gas chromatographic column to separate the NMOC from carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4); the NMOC are oxidized to CO_2, reduced to CH_4, and measured by a flame ionization detector (FID). In this manner, the variable response of the FID associated with different types of organics is eliminated.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Since this method is complex, only experienced personnel should perform this test. LFG contains methane, therefore explosive mixtures may exist on or near the landfill. It is advisable to take appropriate safety precautions when testing landfills, such as refraining from smoking and installing explosion-proof equipment.

6.0 Equipment and Supplies

6.1 Sample Probe. Stainless steel, with the bottom third perforated. Teflon probe liners and sampling lines are also allowed. Non-perforated probes are allowed as long as they are withdrawn to create a gap equivalent to having the bottom third perforated. The sample probe must be capped at the bottom and must have a threaded cap with a sampling attachment at the top. The sample probe must be long enough to go through and extend no less than 0.9 m (3 ft) below the landfill cover. If the sample probe is to be driven into the landfill, the bottom cap should be designed to facilitate driving the probe into the landfill.

6.2 Sampling Train.

6.2.1 Rotameter with Flow Control Valve. Capable of measuring a sample flow rate of 100 ±10 ml/min. The control valve must be made of stainless steel.

6.2.2 Sampling Valve. Stainless steel.

6.2.3 Pressure Gauge. U-tube mercury manometer, or equivalent, capable of measuring pressure to within 1 mm Hg (0.5 in H_2O) in the range of 0 to 1,100 mm Hg (0 to 590 in H_2O).

6.2.4 Sample Tank. Stainless steel or aluminum cylinder, equipped with a stainless steel sample tank valve.

6.3 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg (5.4 in H_2O).

6.4 Purging Pump. Portable, explosion proof, and suitable for sampling NMOC.

6.5 Pilot Probe Procedure. The following are needed only if the tester chooses to use the procedure described in section 8.2.1.

6.5.1 Pilot Probe. Tubing of sufficient strength to withstand being driven into the landfill by a post driver and an outside diameter of at least 6 mm (0.25 in.) smaller than the sample probe. The pilot probe shall be capped on both ends and long enough to go through the landfill cover and extend no less than 0.9 m (3 ft) into the landfill.

6.5.2 Post Driver and Compressor. Capable of driving the pilot probe and the sampling probe into the landfill. The Kitty Hawk portable post driver has been found to be acceptable.

6.6 Auger Procedure. The following are needed only if the tester chooses to use the procedure described in section 8.2.2.

6.6.1 Auger. Capable of drilling through the landfill cover and to a depth of no less than 0.9 m (3 ft) into the landfill.

6.6.2 Pea Gravel.

6.6.3 Bentonite.

6.7 NMOC Analyzer, Barometer, Thermometer, and Syringes. Same as in sections 6.3.1, 6.3.2, 6.33, and 6.2.10, respectively, of Method 25.

7.0 Reagents and Standards

7.1 NMOC Analysis. Same as in Method 25, section 7.2.

7.2 Calibration. Same as in Method 25, section 7.4, except omit section 7.4.3.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sample Tank Evacuation and Leak-Check. Conduct the sample tank evacuation and leak-check either in the laboratory or the field. Connect the pressure gauge and sampling valve to the sample tank. Evacuate the sample tank to 10 mm Hg (5.4 in H_2O) absolute pressure or less. Close the sampling valve, and allow the tank to sit for 30 minutes. The tank is acceptable if no change more than ±2 mm is noted. Include the results of the leak-check in the test report.

8.2 Sample Probe Installation. The tester may use the procedure in section 8.2.1 or 8.2.2.

8.2.1 Pilot Probe Procedure. Use the post driver to drive the pilot probe at least 0.9 m (3 ft) below the landfill cover. Alternative procedures to drive the probe into the landfill may be used subject to the approval of the Administrator's designated representative.

8.2.1.1 Remove the pilot probe and drive the sample probe into the hole left by the pilot probe. The sample probe shall extend at least 0.9 m (3 ft) below the landfill cover and shall protrude about 0.3 m (1 ft) above the landfill cover. Seal around the sampling probe with bentonite and cap the sampling probe with the sampling probe cap.

8.2.2 Auger Procedure. Use an auger to drill a hole to at least 0.9 m (3 ft) below the landfill cover. Place the sample probe in the hole and backfill with pea gravel to a level 0.6 m (2 ft) from the surface. The sample probe shall protrude at least 0.3 m (1 ft) above the landfill cover. Seal the remaining area around the probe with bentonite. Allow 24

hours for the landfill gases to equilibrate inside the augured probe before sampling.

8.2.3 Driven Probes. Closed-point probes may be driven directly into the landfill in a single step. This method may not require backfilling if the probe is adequately sealed by its insertion. Unperforated probes that are inserted in this manner and withdrawn at a distance from a detachable tip to create an open space are also acceptable.

8.3 Sample Train Assembly. Just before assembling the sample train, measure the sample tank vacuum using the pressure gauge. Record the vacuum, the ambient temperature, and the barometric pressure at this time. Assemble the sampling probe purging system as shown in Figure 25C–1.

8.4 Sampling Procedure. Open the sampling valve and use the purge pump and the flow control valve to evacuate at least two sample probe volumes from the system at a flow rate of 500 ml/min or less. Close the sampling valve and replace the purge pump with the sample tank apparatus as shown in Figure 25C–2. Open the sampling valve and the sample tank valve and, using the flow control valve, sample at a flow rate of 500 ml/min or less until either a constant flow rate can no longer be maintained because of reduced sample tank vacuum or the appropriate composite volume is attained. Disconnect the sampling tank apparatus and pressurize the sample cylinder to approximately 1,060 mm Hg (567 in. H_2O) absolute pressure with helium, and record the final pressure. Alternatively, the sample tank may be pressurized in the lab.

8.4.1 The following restrictions apply to compositing samples from different probe sites into a single cylinder: (1) Individual composite samples per cylinder must be of equal volume; this must be verified by recording the flow rate, sampling time, vacuum readings, or other appropriate volume measuring data, (2) individual composite samples must have a minimum volume of 1 liter unless data is provided showing smaller volumes can be accurately measured, and (3) composite samples must not be collected using the final cylinder vacuum as it diminishes to ambient pressure.

8.4.2 Use Method 3C to determine the percent N_2 in each cylinder. The presence of N_2 indicates either infiltration of ambient air into the landfill gas sample or an inappropriate testing site has been chosen where anaerobic decomposition has not begun. The landfill gas sample is acceptable if the concentration of N_2 is less than 20 percent. Alternatively, Method 3C may be used to determine the oxygen content of each cylinder as an air infiltration test. With this option, the oxygen content of each cylinder must be less than 5 percent.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4.2	Verify that landfill gas sample contains less than 20 percent N_2 or 5 percent O_2.	Ensures that ambient air was not drawn into the landfill gas sample and gas was sampled from an appropriate location.
10.1, 10.2	NMOC analyzer initial and daily performance checks.	Ensures precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Initial NMOC Analyzer Performance Test. Same as in Method 25, section 10.1, except omit the linearity checks for CO_2 standards.

10.2 NMOC Analyzer Daily Calibration.

10.2.1 NMOC Response Factors. Same as in Method 25, section 10.2.2.

10.3 Sample Tank Volume. The volume of the gas sampling tanks must be determined. Determine the tank volumes by weighing them empty and then filled with deionized water; weigh to the nearest 5 g, and record the results. Alternatively, measure the volume of water used to fill them to the nearest 5 ml.

11.0 Analytical Procedures

11.1 The oxidation, reduction, and measurement of NMOC's is similar to Method 25. Before putting the NMOC analyzer into routine operation, conduct an initial performance test. Start the analyzer, and perform all the necessary functions in order to put the analyzer into proper working order. Conduct the performance test according to the procedures established in section 10.1. Once the performance test has been successfully completed and the NMOC calibration response factor has been determined, proceed with sample analysis as follows:

11.1.1 Daily Operations and Calibration Checks. Before and immediately after the analysis of each set of samples or on a daily basis (whichever occurs first), conduct a calibration test according to the procedures established in section 10.2. If the criteria of the daily calibration test cannot be met, repeat

the NMOC analyzer performance test (Section 10.1) before proceeding.

11.1.2 Operating Conditions. Same as in Method 25, section 11.2.1.

11.1.3 Analysis of Sample Tank. Purge the sample loop with sample, and then inject the sample. Under the specified operating conditions, the CO_2 in the sample will elute in approximately 100 seconds. As soon as the detector response returns to baseline following the CO_2 peak, switch the carrier gas flow to backflush, and raise the column oven temperature to 195 °C (383 °F) as rapidly as possible. A rate of 30 °C/min (54 °F/min) has been shown to be adequate. Record the value obtained for any measured NMOC. Return the column oven temperature to 85 °C (185 °F) in preparation for the next analysis. Analyze each sample in triplicate, and report the average as C_{tm}.

12.0 Data Analysis and Calculations

NOTE: All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge or manometer pressure.

12.1 Nomenclature

B_w = Moisture content in the sample, fraction.
C_{N2} = N_2 concentration in the diluted sample gas.
C_{mN2} = Measured N_2 concentration, fraction in landfill gas.
C_{mOx} = Measured Oxygen concentration, fraction in landfill gas.
C_{Ox} = Oxygen concentration in the diluted sample gas.
C_t = Calculated NMOC concentration, ppmv C equivalent.
C_{tm} = Measured NMOC concentration, ppmv C equivalent.
P_b = Barometric pressure, mm Hg.
P_t = Gas sample tank pressure after sampling, but before pressurizing, mm Hg absolute.
P_{tf} = Final gas sample tank pressure after pressurizing, mm Hg absolute.
P_{ti} = Gas sample tank pressure after evacuation, mm Hg absolute.
P_w = Vapor pressure of H_2O (from Table 25C–1), mm Hg.
r = Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 . . . r).
T_t = Sample tank temperature at completion of sampling, °K.
T_{ti} = Sample tank temperature before sampling, °K.
T_{tf} = Sample tank temperature after pressuring, °K.

12.2 Water Correction. Use Table 25C–1 (Section 17.0), the LFG temperature, and barometric pressure at the sampling site to calculate B_w.

$$B_w = \frac{P_w}{P_b} \qquad \text{Eq. 25C-1}$$

12.3 Nitrogen Concentration in the landfill gas. Use equation 25C–2 to calculate the measured concentration of nitrogen in the original landfill gas.

$$C_{N2} = \left[\frac{\left(\frac{P_{tf}}{T_{tf}}\right)}{\left(\left(\frac{P_t}{T_t}\right)-\left(\frac{P_{ti}}{T_{ti}}\right)\right)}\right] C_{mN2} \qquad \text{Eq.25C-2}$$

12.4 Oxygen Concentration in the landfill gas. Use equation 25C–3 to calculate the measured concentration of oxygen in the original landfill gas.

$$C_{Ox} = \left[\frac{\left(\frac{P_{tf}}{T_{tf}}\right)}{\left(\left(\frac{P_t}{T_t}\right)-\left(\frac{P_{ti}}{T_{ti}}\right)\right)}\right] C_{mOx} \qquad \text{Eq.25C-3}$$

12.5 You must correct the NMOC Concentration for the concentration of nitrogen or oxygen based on which gas or gases passes the requirements in section 9.1.

12.5.1 NMOC Concentration with nitrogen correction. Use Equation 25C–4 to calculate the concentration of NMOC for each sample tank when the nitrogen concentration is less than 20 percent.

$$C_t = \frac{\frac{P_{tf}}{T_{tf}}}{\left(\frac{P_t}{T_t}-\frac{P_{ti}}{T_{ti}}\right)\left(1-\frac{99}{78}C_{N2}\right)-B_w}\frac{1}{r}\sum_{j=1}^{r} C_{tm(j)} \qquad \text{Eq. 25C-4}$$

12.5.2 NMOC Concentration with oxygen correction. Use Equation 25C–5 to calculate the concentration of NMOC for each sample tank if the landfill gas oxygen is less than 5 percent and the landfill gas nitrogen concentration is greater than 20 percent.

$$C_t = \frac{\frac{P_{tf}}{T_{tf}}}{\left(\frac{P_t}{T_t}-\frac{P_{ti}}{T_{ti}}\right)\left(1-\frac{99}{21}C_{Ox}\right)-B_w}\frac{1}{r}\sum_{j=1}^{r} C_{tm(j)} \qquad \text{Eq. 25C-5}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, Albert E., Samuel Witz, and Robert D. MacPhee. Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, Massachusetts. June 15–20, 1975.) 14 p.

2. Salo, Albert E., William L. Oaks, and Robert D. MacPhee. Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, Colorado. June 9–13, 1974.) 25 p.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

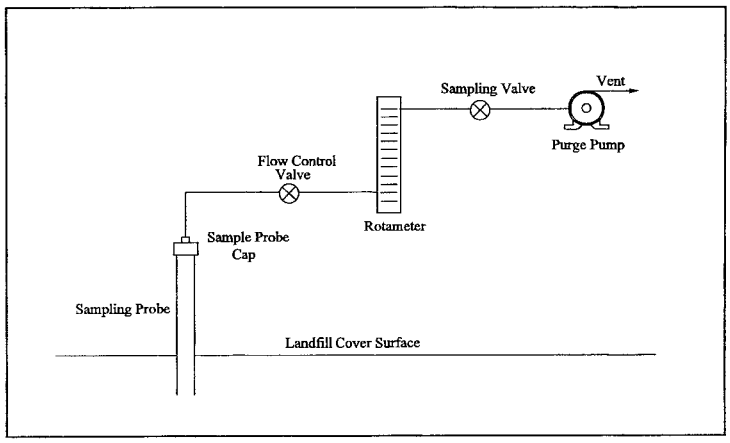


Figure 25C-1. Schematic of Sampling Probe Purging System

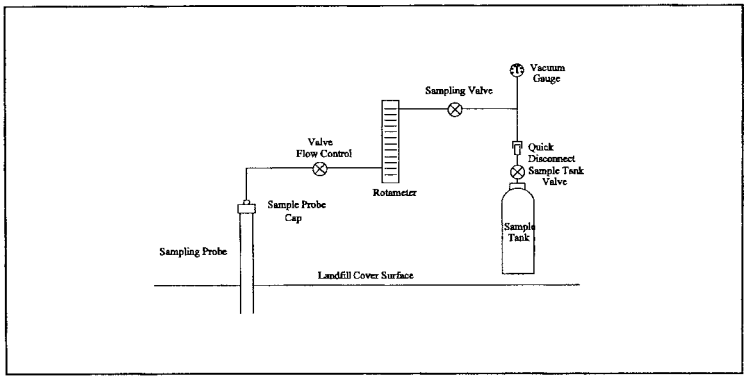


Figure 25C-2. Schematic of Sampling Train.

TABLE 25C–1—MOISTURE CORRECTION

Temperature, °C	Vapor Pressure of H_2O, mm Hg	Temperature, °C	Vapor Pressure of H_2O, mm Hg
4	6.1	18	15.5
6	7.0	20	17.5
8	8.0	22	19.8
10	9.2	24	22.4
12	10.5	26	25.2
14	12.0	28	28.3

TABLE 25C–1—MOISTURE CORRECTION—Continued

Temperature, °C	Vapor Pressure of H_2O, mm Hg	Temperature, °C	Vapor Pressure of H_2O, mm Hg
16	13.6	30	31.8

METHOD 25D—DETERMINATION OF THE VOLATILE ORGANIC CONCENTRATION OF WASTE SAMPLES

NOTE: Performance of this method should not be attempted by persons unfamiliar with the operation of a flame ionization detector (FID) or an electrolytic conductivity detector (ELCD) because knowledge beyond the scope of this presentation is required.

1.0 Scope and Application

1.1 Analyte. Volatile Organic Compounds. No CAS No. assigned.

1.2 Applicability. This method is applicable for determining the volatile organic (VO) concentration of a waste sample.

2.0 Summary of Method

2.1 Principle. A sample of waste is obtained at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to the atmosphere). The sample is suspended in an organic/aqueous matrix, then heated and purged with nitrogen for 30 min. in order to separate certain organic compounds. Part of the sample is analyzed for carbon concentration, as methane, with an FID, and part of the sample is analyzed for chlorine concentration, as chloride, with an ELCD. The VO concentration is the sum of the carbon and chlorine content of the sample.

3.0 Definitions

3.1 *Well-mixed* in the context of this method refers to turbulent flow which results in multiple-phase waste in effect behaving as single-phase waste due to good mixing.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1 Sampling. The following equipment is required:

6.1.1 Sampling Tube. Flexible Teflon, 0.25 in. ID (6.35 mm).

6.1.2 Sample Container. Borosilicate glass, 40-mL, and a Teflon-lined screw cap capable of forming an air tight seal.

6.1.3 Cooling Coil. Fabricated from 0.25 in (6.35 mm). ID 304 stainless steel tubing with a thermocouple at the coil outlet.

6.2 Analysis. The following equipment is required.

6.2.1 Purging Apparatus. For separating the VO from the waste sample. A schematic of the system is shown in Figure 25D–1. The purging apparatus consists of the following major components.

6.2.1.1 Purging Flask. A glass container to hold the sample while it is heated and purged with dry nitrogen. The cap of the purging flask is equipped with three fittings: one for a purging lance (fitting with the #7 Ace-thread), one for the Teflon exit tubing (side fitting, also a #7 Ace-thread), and a third (a 50-mm Ace-thread) to attach the base of the purging flask as shown in Figure 25D–2. The base of the purging flask is a 50-mm ID (2 in) cylindrical glass tube. One end of the tube is open while the other end is sealed. Exact dimensions are shown in Figure 25D–2.

6.2.1.2 Purging Lance. Glass tube, 6-mm OD (0.2 in) by 30 cm (12 in) long. The purging end of the tube is fitted with a four-arm bubbler with each tip drawn to an opening 1 mm (0.04 in) in diameter. Details and exact dimensions are shown in Figure 25D–2.

6.2.1.3 Coalescing Filter. Porous fritted disc incorporated into a container with the same dimensions as the purging flask. The details of the design are shown in Figure 25D–3.

6.2.1.4 Constant Temperature Chamber. A forced draft oven capable of maintaining a uniform temperature around the purging flask and coalescing filter of 75 ±2 °C (167 ±3.6 °F).

6.2.1.5 Three-way Valve. Manually operated, stainless steel. To introduce calibration gas into system.

6.2.1.6 Flow Controllers. Two, adjustable. One capable of maintaining a purge gas flow rate of 6 ±0.06 L/min (0.2 ±0.002 ft^3/min) The other capable of maintaining a calibration gas flow rate of 1–100 mL/min (0.00004–0.004 ft^3/min).

6.2.1.7 Rotameter. For monitoring the air flow through the purging system (0–10 L/min)(0–0.4 ft^3/min).

6.2.1.8 Sample Splitters. Two heated flow restrictors (placed inside oven or heated to 120 ±10 °C (248 ±18 °F)). At a purge rate of 6 L/min (0.2 ft^3/min), one will supply a constant flow to the first detector (the rest of the flow will be directed to the second sample splitter). The second splitter will split the analytical flow between the second detector and the flow restrictor. The approximate flow to the FID will be 40 mL/min (0.0014 ft^3/min) and to the ELCD will be 15 mL/min (0.0005 ft^3/min), but the exact flow must be adjusted to be compatible with the individual detector and to meet its linearity requirement. The two sample splitters will be connected to each other by 1/8″ OD (3.175 mm) stainless steel tubing.

6.2.1.9 Flow Restrictor. Stainless steel tubing, 1/8″ OD (3.175 mm), connecting the second sample splitter to the ice bath. Length is determined by the resulting pressure in the purging flask (as measured by the pressure gauge). The resulting pressure from the use of the flow restrictor shall be 6–7 psig.

6.2.1.10 Filter Flask. With one-hole stopper. Used to hold ice bath. Excess purge gas is vented through the flask to prevent condensation in the flowmeter and to trap volatile organic compounds.

6.2.1.11 Four-way Valve. Manually operated, stainless steel. Placed inside oven, used to bypass purging flask.

6.2.1.12 On/Off Valves. Two, stainless steel. One heat resistant up to 130 °C (266 °F) and placed between oven and ELCD. The other a toggle valve used to control purge gas flow.

6.2.1.13 Pressure Gauge. Range 0–40 psi. To monitor pressure in purging flask and coalescing filter.

6.2.1.14 Sample Lines. Teflon, 1/4″ OD (6.35 mm), used inside the oven to carry purge gas to and from purging chamber and to and from coalescing filter to four-way valve. Also used to carry sample from four-way valve to first sample splitter.

6.2.1.15 Detector Tubing. Stainless steel, 1/8″ OD (3.175 mm), heated to 120 ±10 °C (248 ±18 °F) . Used to carry sample gas from each sample splitter to a detector. Each piece of tubing must be wrapped with heat tape and insulating tape in order to insure that no cold spots exist. The tubing leading to the ELCD will also contain a heat-resistant on-off valve (Section 6.2.1.12) which shall also be wrapped with heat-tape and insulation.

6.2.2 Volatile Organic Measurement System. Consisting of an FID to measure the carbon concentration of the sample and an ELCD to measure the chlorine concentration.

6.2.2.1 FID. A heated FID meeting the following specifications is required.

6.2.2.1.1 Linearity. A linear response (±5 percent) over the operating range as demonstrated by the procedures established in section 10.1.1.

6.2.2.1.2 Range. A full scale range of 50 pg carbon/sec to 50 µg carbon/sec. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.2.2.1.3 Data Recording System. A digital integration system compatible with the FID for permanently recording the output of the detector. The recorder shall have the capability to start and stop integration at points selected by the operator or it shall be capable of the ''integration by slices'' technique (this technique involves breaking down the chromatogram into smaller increments, integrating the area under the curve for each portion, subtracting the background for each portion, and then adding all of the areas together for the final area count).

6.2.2.2 ELCD. An ELCD meeting the following specifications is required. 1-propanol must be used as the electrolyte. The electrolyte flow through the conductivity cell shall be 1 to 2 mL/min (0.00004 to 0.00007 ft^3/min).

NOTE: A ¼-in. ID (6.35 mm) quartz reactor tube is strongly recommended to reduce carbon buildup and the resulting detector maintenance.

6.2.2.2.1 Linearity. A linear response (±10 percent) over the response range as demonstrated by the procedures in section 10.1.2.

6.2.2.2.2 Range. A full scale range of 5.0 pg/sec to 500 ng/sec chloride. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.2.2.2.3 Data Recording System. A digital integration system compatible with the output voltage range of the ELCD. The recorder must have the capability to start and stop integration at points selected by the operator or it shall be capable of performing the ''integration by slices'' technique.

7.0 Reagents and Standards

7.1 Sampling.

7.1.1 Polyethylene Glycol (PEG). Ninety-eight percent pure with an average molecular weight of 400. Before using the PEG, remove any organic compounds that might be detected as volatile organics by heating it to 120 °C (248 °F) and purging it with nitrogen at a flow rate of 1 to 2 L/min (0.04 to 0.07 ft^3/min) for 2 hours. The cleaned PEG must be stored under a 1 to 2 L/min (0.04 to 0.07 ft^3/min) nitrogen purge until use. The purge apparatus is shown in Figure 25D–4.

7.2 Analysis.

7.2.1 Sample Separation. The following are required for the sample purging step.

7.2.1.1 PEG. Same as section 7.1.1.

7.2.1.2 Purge Gas. Zero grade nitrogen (N_2), containing less than 1 ppm carbon.

7.2.2 Volatile Organics Measurement. The following are required for measuring the VO concentration.

7.2.2.1 Hydrogen (H_2). Zero grade H_2, 99.999 percent pure.

7.2.2.2 Combustion Gas. Zero grade air or oxygen as required by the FID.

7.2.2.3 Calibration Gas. Pressurized gas cylinder containing 10 percent propane and 1 percent 1,1-dichloroethylene by volume in nitrogen.

7.2.2.4 Water. Deionized distilled water that conforms to American Society for Testing and Materials Specification D 1193–74, Type 3, is required for analysis. At the option of the analyst, the $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations are not expected to be present.

7.2.2.5 1-Propanol. ACS grade or better. Electrolyte Solution. For use in the ELCD.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling.

8.1.1 Sampling Plan Design and Development. Use the procedures in chapter nine of Reference 1 in section 16 as guidance in developing a sampling plan.

8.1.2 Single Phase or Well-mixed Waste.

8.1.2.1 Install a sampling tap to obtain the sample at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to the atmosphere). Assemble the sampling apparatus as shown in Figure 25D–5.

8.1.2.2 Prepare the sampling containers as follows: Pour 30 mL of clean PEG into the container. PEG will reduce but not eliminate the loss of organics during sample collection. Weigh the sample container with the screw cap, the PEG, and any labels to the nearest 0.01 g and record the weight (m_{st}). Store the containers in an ice bath until 1 hour before sampling (PEG will solidify at ice bath temperatures; allow the containers to reach room temperature before sampling).

8.1.2.3 Begin sampling by purging the sample lines and cooling coil with at least four volumes of waste. Collect the purged material in a separate container and dispose of it properly.

8.1.2.4 After purging, stop the sample flow and direct the sampling tube to a preweighed sample container, prepared as described in section 8.1.2.2. Keep the tip of the tube below the surface of the PEG during sampling to minimize contact with the atmosphere. Sample at a flow rate such that the temperature of the waste is less than 10 °C (50 °F). Fill the sample container and immediately cap it (within 5 seconds) so that a minimum headspace exists in the container. Store immediately in a cooler and cover with ice.

8.1.3 Multiple-phase Waste. Collect a 10 g sample of each phase of waste generated using the procedures described in section 8.1.2 or 8.1.5. Each phase of the waste shall be analyzed as a separate sample. Calculate the weighted average VO concentration of the waste using Equation 25D–13 (Section 12.14).

8.1.4 Solid waste. Add approximately 10 g of the solid waste to a container prepared in the manner described in section 8.1.2.2, minimizing headspace. Cap and chill immediately.

8.1.5 Alternative to Tap Installation. If tap installation is impractical or impossible, fill a large, clean, empty container by submerging the container into the waste below the surface of the waste. Immediately fill a container prepared in the manner described in section 8.1.2.2 with approximately 10 g of the waste collected in the large container. Minimize headspace, cap and chill immediately.

8.1.6 Alternative sampling techniques may be used upon the approval of the Administrator.

8.2 Sample Recovery.

8.2.1 Assemble the purging apparatus as shown in Figures 25D–1 and 25D–2. The oven shall be heated to 75 ±2 °C (167 ±3.6 °F). The sampling lines leading from the oven to the detectors shall be heated to 120 ±10 °C (248 ±18 °F) with no cold spots. The flame ionization detector shall be operated with a heated block. Adjust the purging lance so that it reaches the bottom of the chamber.

8.2.2 Remove the sample container from the cooler, and wipe the exterior of the container to remove any extraneous ice, water, or other debris. Reweigh the sample container to the nearest 0.01 g, and record the weight (m_{sf}). Pour the contents of the sample container into the purging flask, rinse the sample container three times with a total of 20 mL of PEG (since the sample container originally held 30 mL of PEG, the total volume of PEG added to the purging flask will be 50 mL), transferring the rinsings to the purging flask after each rinse. Cap purging flask between rinses. The total volume of PEG in the purging flask shall be 50 mL. Add 50 mL of water to the purging flask.

9.0 Quality Control

9.1 Quality Control Samples. If audit samples are not available, prepare and analyze the two types of quality control samples (QCS) listed in Sections 9.1.1 and 9.1.2. Before placing the system in operation, after a shutdown of greater than six months, and after any major modifications, analyze each QCS in triplicate. For each detector, calculate the percent recovery by dividing measured concentration by theoretical concentration and multiplying by 100. Determine the mean percent recovery for each detector for each QCS triplicate analysis. The RSD for any triplicate analysis shall be ≤10 percent. For QCS 1 (methylene chloride), the percent recovery shall be ≥90 percent for carbon as methane, and ≥55 percent for chlorine as chloride. For QCS 2 (1,3-dichloro-2-propanol), the percent recovery shall be ≤15 percent for carbon as methane, and ≤6 percent for chlorine as chloride. If the analytical system does not meet the above-mentioned criteria for both detectors, check the system parameters (temperature, system pressure, purge rate, etc.), correct the problem, and repeat the triplicate analysis of each QCS.

9.1.1 QCS 1, Methylene Chloride. Prepare a stock solution by weighing, to the nearest 0.1 mg, 55 µL of HPLC grade methylene chloride in a tared 5 mL volumetric flask. Record the weight in milligrams, dilute to 5 mL with cleaned PEG, and inject 100 µL of the stock solution into a sample prepared as a water blank (50 mL of cleaned PEG and 60 mL of water in the purging flask). Analyze

the QCS according to the procedures described in sections 10.2 and 10.3, excluding section 10.2.2. To calculate the theoretical carbon concentration (in mg) in QCS 1, multiply mg of methylene chloride in the stock solution by 3.777×10^{-3}. To calculate the theoretical chlorine concentration (in mg) in QCS 1, multiply mg of methylene chloride in the stock solution by 1.670×10^{-2}.

9.1.2 QCS 2, 1,3-dichloro-2-propanol. Prepare a stock solution by weighing, to the nearest 0.1 mg, 60 μL of high purity grade 1,3-dichloro-2-propanol in a tared 5 mL volumetric flask. Record the weight in milligrams, dilute to 5 mL with cleaned PEG, and inject 100 μL of the stock solution into a sample prepared as a water blank (50 mL of cleaned PEG and 60 mL of water in the purging flask). Analyze the QCS according to the procedures described in sections 10.2 and 10.3, excluding section 10.2.2. To calculate the theoretical carbon concentration (in mg) in QCS 2, multiply mg of 1,3-dichloro-2-propanol in the stock solution by 7.461×10^{-3}. To calculate the theoretical chlorine concentration (in mg) in QCS 2, multiply mg of 1,3-dichloro-2-propanol in the stock solution by 1.099×10^{-2}.

9.1.3 Routine QCS Analysis. For each set of compliance samples (in this context, set is per facility, per compliance test), analyze one QCS 1 and one QCS 2 sample. The percent recovery for each sample for each detector shall be ±13 percent of the mean recovery established for the most recent set of QCS triplicate analysis (Section 9.4). If the sample does not meet this criteria, check the system components and analyze another QCS 1 and 2 until a single set of QCS meet the ±13 percent criteria.

10.0 Calibration and Standardization

10.1 Initial Performance Check of Purging System. Before placing the system in operation, after a shutdown of greater than six months, after any major modifications, and at least once per month during continuous operation, conduct the linearity checks described in sections 10.1.1 and 10.1.2. Install calibration gas at the three-way calibration gas valve. See Figure 25D–1.

10.1.1 Linearity Check Procedure. Using the calibration standard described in section 7.2.2.3 and by varying the injection time, it is possible to calibrate at multiple concentration levels. Use Equation 25D–3 to calculate three sets of calibration gas flow rates and run times needed to introduce a total mass of carbon, as methane, (m_c) of 1, 5, and 10 mg into the system (low, medium and high FID calibration, respectively). Use Equation 25D–4 to calculate three sets of calibration gas flow rates and run times needed to introduce a total chloride mass (m_{ch}) of 1, 5, and 10 mg into the system (low, medium and high ELCD calibration, respectively). With the system operating in standby mode, allow the FID and the ELCD to establish a stable baseline. Set the secondary pressure regulator of the calibration gas cylinder to the same pressure as the purge gas cylinder and set the proper flow rate with the calibration flow controller (see Figure 25D–1). The calibration gas flow rate can be measured with a flowmeter attached to the vent position of the calibration gas valve. Set the four-way bypass valve to standby position so that the calibration gas flows through the coalescing filter only. Inject the calibration gas by turning the calibration gas valve from vent position to inject position. Continue the calibration gas flow for the appropriate period of time before switching the calibration valve to vent position. Continue recording the response of the FID and the ELCD for 5 min after switching off calibration gas flow. Make triplicate injections of all six levels of calibration.

10.1.2 Linearity Criteria. Calculate the average response factor (Equations 25D–5 and 25D–6) and the relative standard deviation (RSD) (Equation 25D–10) at each level of the calibration curve for both detectors. Calculate the overall mean of the three response factor averages for each detector. The FID linearity is acceptable if each response factor is within 5 percent of the overall mean and if the RSD for each set of triplicate injections is less than 5 percent. The ELCD linearity is acceptable if each response factor is within 10 percent of the overall mean and if the RSD for each set of triplicate injections is less than 10 percent. Record the overall mean value of the response factors for the FID and the ELCD. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat sections 10.1.1 and 10.1.2.

10.2 Daily Calibrations.

10.2.1 Daily Linearity Check. Follow the procedures outlined in section 10.1.1 to analyze the medium level calibration for both the FID and the ELCD in duplicate at the start of the day. Calculate the response factors and the RSDs for each detector. For the FID, the calibration is acceptable if the average response factor is within 5 percent of the overall mean response factor (Section 10.1.2) and if the RSD for the duplicate injection is less than 5 percent. For the ELCD, the calibration is acceptable if the average response factor is within 10 percent of the overall mean response factor (Section 10.1.2) and if the RSD for the duplicate injection is less than 10 percent. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat sections 10.1.1 and 10.1.2.

10.2.2 Calibration Range Check.

10.2.2.1 If the waste concentration for either detector falls below the range of calibration for that detector, use the procedure outlined in section 10.1.1 to choose two calibration points that bracket the new target

concentration. Analyze each of these points in triplicate (as outlined in section 10.1.1) and use the criteria in section 10.1.2 to determine the linearity of the detector in this ''mini-calibration'' range.

10.2.2.2 After the initial linearity check of the mini-calibration curve, it is only necessary to test one of the points in duplicate for the daily calibration check (in addition to the points specified in section 10.2.1). The average daily mini-calibration point should fit the linearity criteria specified in section 10.2.1. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat the calibration procedure mentioned in the first paragraph of section 10.2.2. A mini-calibration curve for waste concentrations above the calibration curve for either detector is optional.

10.3 Analytical Balance. Calibrate against standard weights.

11.0 Analysis

11.1 Sample Analysis.

11.1.1 Turn on the constant temperature chamber and allow the temperature to equilibrate at 75 ±2 °C (167 ±3.6 °F). Turn the four-way valve so that the purge gas bypasses the purging flask, the purge gas flowing through the coalescing filter and to the detectors (standby mode). Turn on the purge gas. Allow both the FID and the ELCD to warm up until a stable baseline is achieved on each detector. Pack the filter flask with ice. Replace ice after each run and dispose of the waste water properly. When the temperature of the oven reaches 75 ±2 °C (167 ±3.6 °F), start both integrators and record baseline. After 1 min, turn the four-way valve so that the purge gas flows through the purging flask, to the coalescing filter and to the sample splitters (purge mode). Continue recording the response of the FID and the ELCD. Monitor the readings of the pressure gauge and the rotameter. If the readings fall below established setpoints, stop the purging, determine the source of the leak, and resolve the problem before resuming. Leaks detected during a sampling period invalidate that sample.

11.1.2 As the purging continues, monitor the output of the detectors to make certain that the analysis is proceeding correctly and that the results are being properly recorded. Every 10 minutes read and record the purge flow rate, the pressure and the chamber temperature. Continue the purging for 30 minutes.

11.1.3 For each detector output, integrate over the entire area of the peak starting at 1 minute and continuing until the end of the run. Subtract the established baseline area from the peak area. Record the corrected area of the peak. See Figure 25D–6 for an example integration.

11.2 Water Blank. A water blank shall be analyzed for each batch of cleaned PEG prepared. Transfer about 60 mL of water into the purging flask. Add 50 mL of the cleaned PEG to the purging flask. Treat the blank as described in sections 8.2 and 8.3, excluding section 8.2.2. Calculate the concentration of carbon and chlorine in the blank sample (assume 10 g of waste as the mass). A VO concentration equivalent to ≤10 percent of the applicable standard may be subtracted from the measured VO concentration of the waste samples. Include all blank results and documentation in the test report.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

A_b = Area under the water blank response curve, counts.
A_c = Area under the calibration response curve, counts.
A_s = Area under the sample response curve, counts.
C = Concentration of volatile organics in the sample, ppmw.
C_c = Concentration of carbon, as methane, in the calibration gas, mg/L.
C_{ch} = Concentration of chloride in the calibration gas, mg/L.
C_j = VO concentration of phase j, ppmw.
DR_t = Average daily response factor of the FID, mg CH_4/counts.
Dr_{th} = Average daily response factor of the ELCD, mg Cl^-/counts.
F_j = Weight fraction of phase j present in the waste.
m_c = Mass of carbon, as methane, in a calibration run, mg.
m_{ch} = Mass of chloride in a calibration run, mg.
m_s = Mass of the waste sample, g.
m_{sc} = Mass of carbon, as methane, in the sample, mg.
m_{sf} = Mass of sample container and waste sample, g.
m_{sh} = Mass of chloride in the sample, mg.
m_{st} = Mass of sample container prior to sampling, g.
m_{VO} = Mass of volatile organics in the sample, mg.
n = Total number of phases present in the waste.
P_p = Percent propane in calibration gas (L/L).
P_{vc} = Percent 1,1-dichloroethylene in calibration gas (L/L).
Q_c = Flow rate of calibration gas, L/min.
t_c = Length of time standard gas is delivered to the analyzer, min.
W = Weighted average VO concentration, ppmw.

12.2 Concentration of Carbon, as Methane, in the Calibration Gas.

$$C_c = \left(19.681 \times P_p\right) + \left(13.121 \times P_{vc}\right) \qquad \text{Eq. 25D-1}$$

12.3 Concentration of Chloride in the Calibration Gas.

$$C_{ch} = 28.998 \times P_{vc} \qquad \text{Eq. 25D-2}$$

12.4 Mass of Carbon, as Methane, in a Calibration Run.

$$M_c = C_c \times Q_c \times t_c \qquad \text{Eq. 25D-3}$$

12.5 Mass of Chloride in a Calibration Run.

$$m_{ch} = C_{ch} \times Q_c \times t_c \qquad \text{Eq. 25D-4}$$

12.6 FID Response Factor, mg/counts.

$$DR_t = \frac{m_c}{A_c} \qquad \text{Eq. 25D-5}$$

12.7 ELCD Response Factor, mg/counts.

$$DR_{th} = \frac{m_{ch}}{A_c} \qquad \text{Eq. 25D-6}$$

12.8 Mass of Carbon in the Sample.

$$m_{sc} = DR_t\left(A_s - A_b\right) \qquad \text{Eq. 25D-7}$$

12.9 Mass of Chloride in the Sample.

$$m_{sh} = DR_{th}\left(A_s - A_b\right) \qquad \text{Eq. 25D-8}$$

12.10 Mass of Volatile Organics in the Sample.

$$m_{vo} = m_{sc} + m_{sh} \qquad \text{Eq. 25D-9}$$

12.11 Relative Standard Deviation.

$$RSD = \frac{100}{\bar{x}} \sqrt{\frac{\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2}{n-1}} \qquad \text{Eq. 25D-10}$$

12.12 Mass of Sample.

$$m_s = m_{sf} - m_{st} \qquad \text{Eq. 25D-11}$$

12.13 Concentration of Volatile Organics in Waste.

$$C = \frac{\left(m_{vo} \times 1000\right)}{m_s} \qquad \text{Eq. 25D-12}$$

12.14 Weighted Average VO Concentration of Multi-phase Waste.

$$W = \sum_{j=1}^{n} F_j x \overline{C}_j \qquad \text{Eq. 25D-13}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. ''Test Methods for Evaluating Solid Waste, Physical/Chemistry Methods'', U.S. Environmental Protection Agency. Publication SW–846, 3rd Edition, November 1986 as amended by Update I, November 1990.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

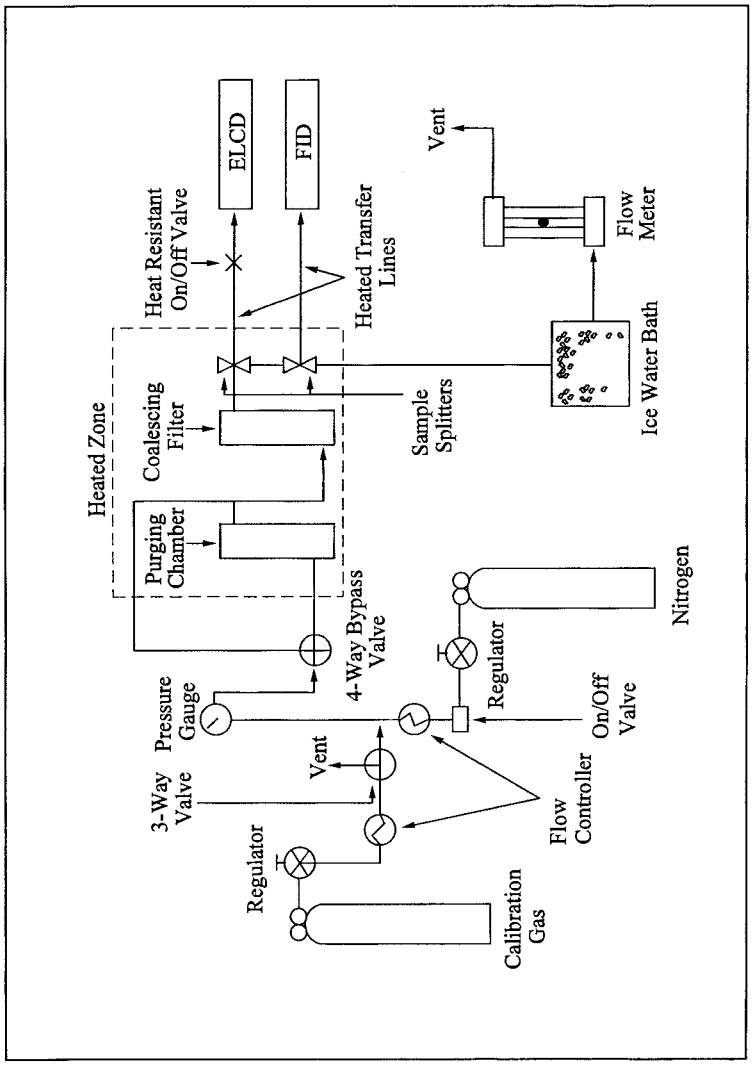


Figure 25D-1. Schematic of Purging Apparatus.

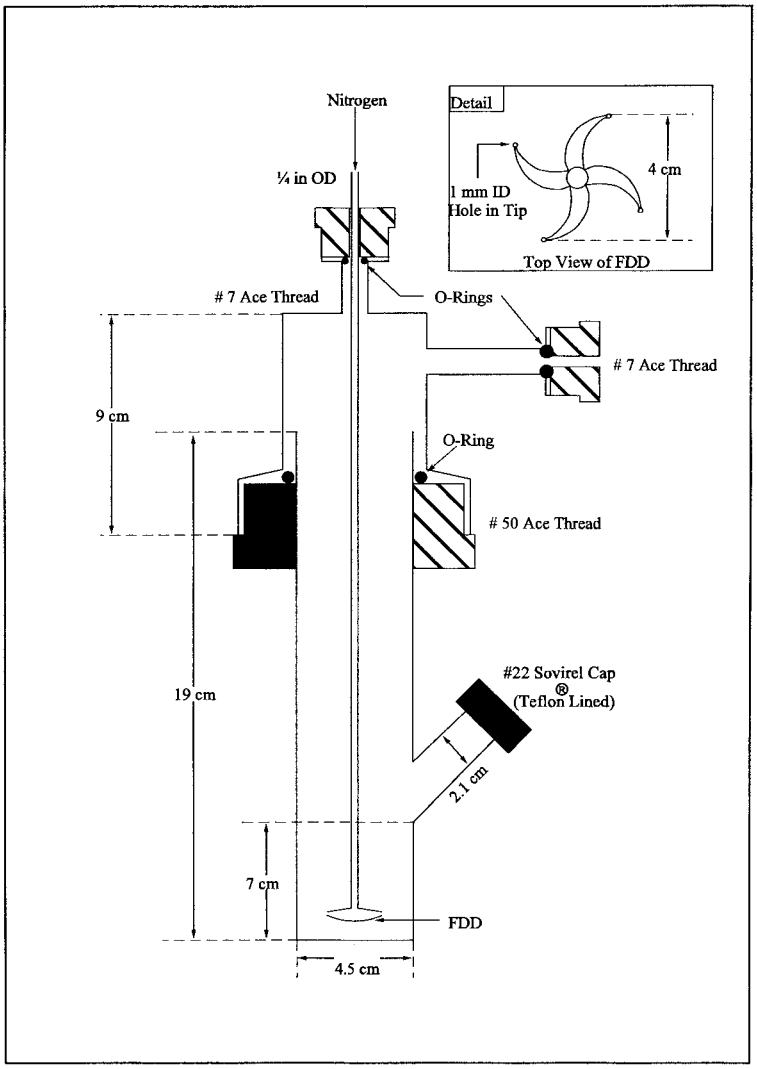
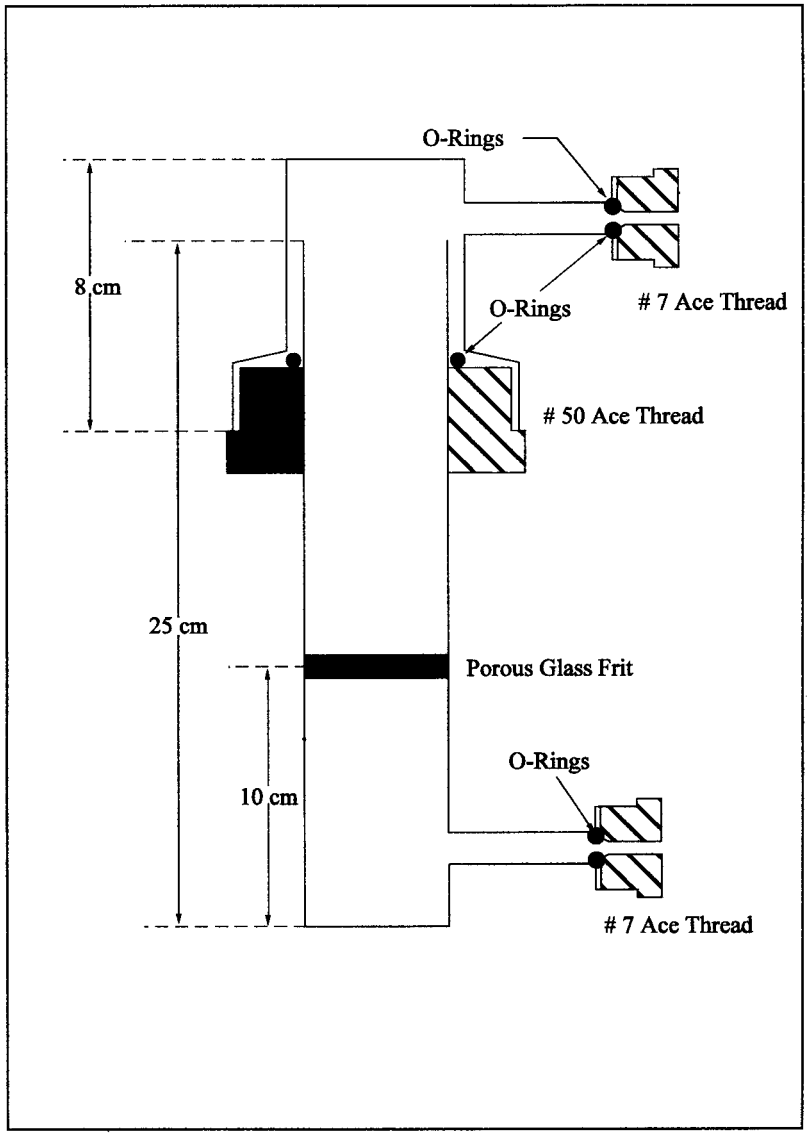


Figure 25D-2. Purging Lance.


O-Rings
8 cm
O-Rings
7 Ace Thread
50 Ace Thread
25 cm
Porous Glass Frit
O-Rings
10 cm
7 Ace Thread

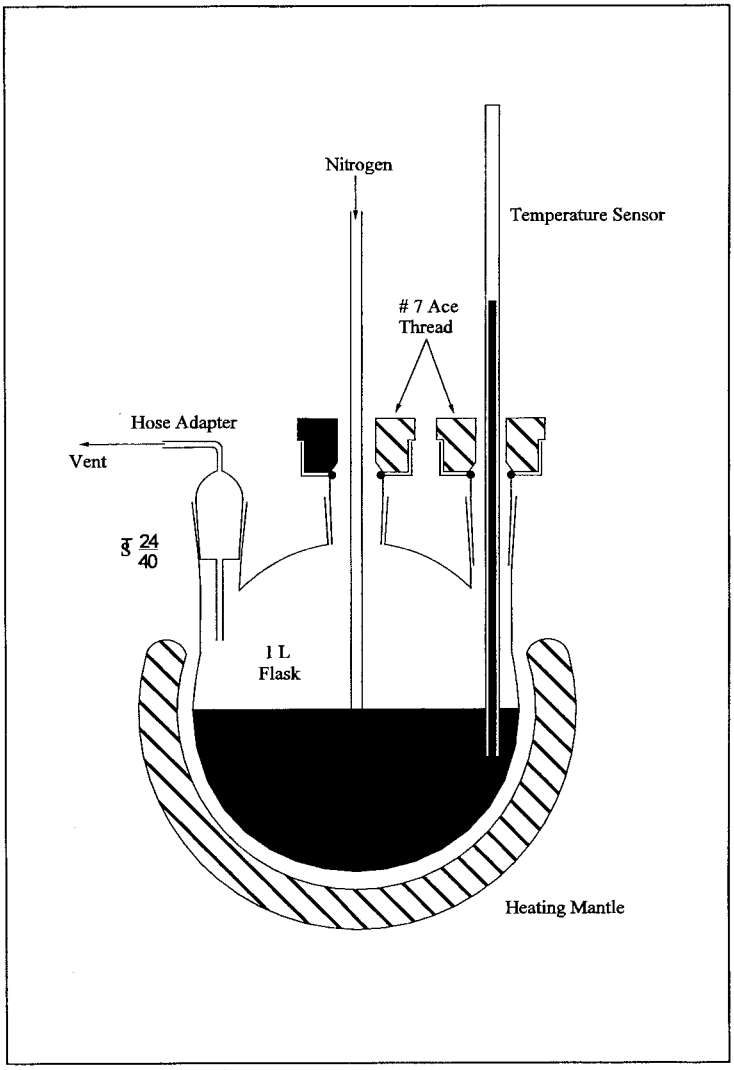


Figure 25D-4. Schematic of PEG Cleaning System.

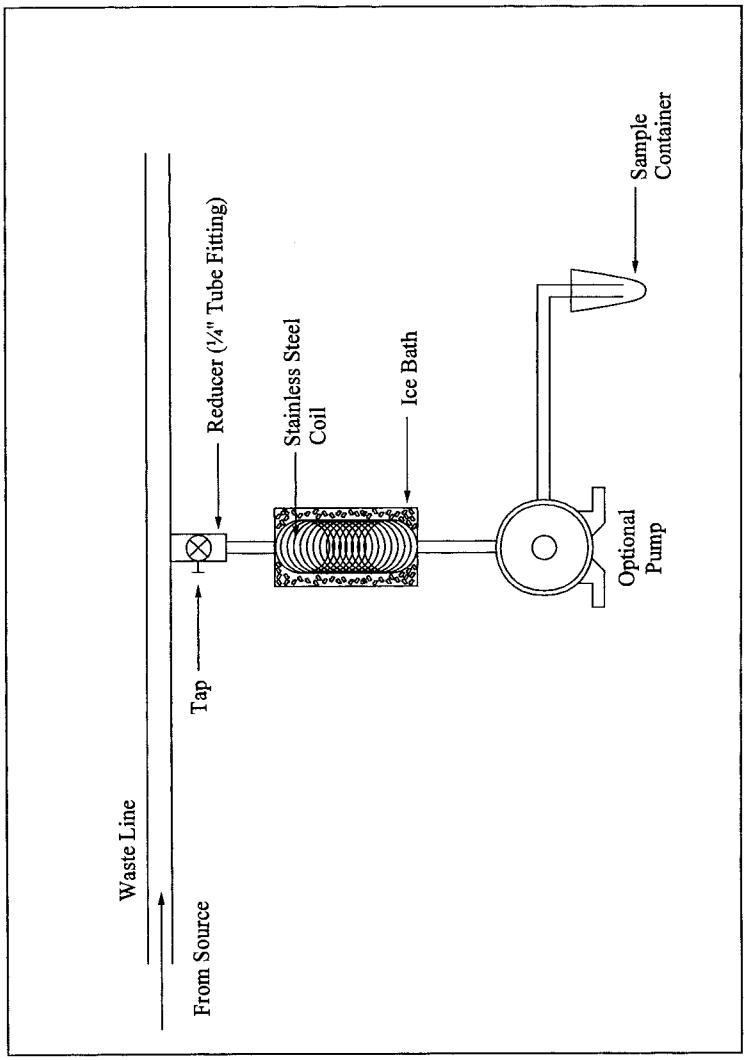


Figure 25D-5. Schematic of Sampling Apparatus.

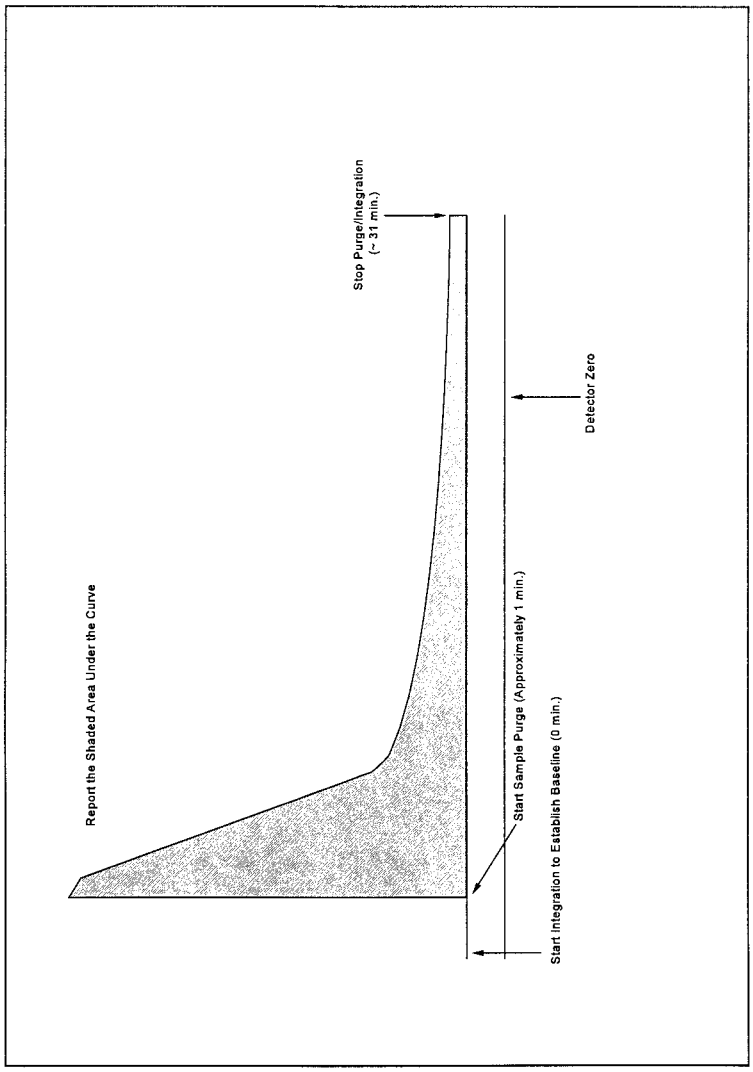


Figure 25D-6. Example Integration of Either Detector.

METHOD 25E—DETERMINATION OF VAPOR PHASE ORGANIC CONCENTRATION IN WASTE SAMPLES

NOTE: Performance of this method should not be attempted by persons unfamiliar with the operation of a flame ionization detector (FID) nor by those who are unfamiliar with source sampling because knowledge beyond the scope of this presentation is required. This method is not inclusive with respect to specifications (*e.g.*, reagents and standards) and calibration procedures. Some material is incorporated by reference from other methods. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 106, part 61, Appendix B, and Method 18, part 60, Appendix A.

1.0 Scope and Application

1.1 Applicability. This method is applicable for determining the vapor pressure of waste cited by an applicable regulation.

1.2 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 The headspace vapor of the sample is analyzed for carbon content by a headspace analyzer, which uses an FID.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 The analyst shall select the operating parameters best suited to the requirements for a particular analysis. The analyst shall produce confirming data through an adequate supplemental analytical technique and have the data available for review by the Administrator.

5.0 Safety [Reserved]

6.0 Equipment and Supplies

6.1 Sampling. The following equipment is required:

6.1.1 Sample Containers. Vials, glass, with butyl rubber septa, Perkin-Elmer Corporation Numbers 0105–0129 (glass vials), B001–0728 (gray butyl rubber septum, plug style), 0105–0131 (butyl rubber septa), or equivalent. The seal must be made from butyl rubber. Silicone rubber seals are not acceptable.

6.1.2 Vial Sealer. Perkin-Elmer Number 105–0106, or equivalent.

6.1.3 Gas-Tight Syringe. Perkin-Elmer Number 00230117, or equivalent.

6.1.4 The following equipment is required for sampling.

6.1.4.1 Tap.

6.1.4.2 Tubing. Teflon, 0.25-in. ID.

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1.4.3 Cooling Coil. Stainless steel (304), 0.25 in.-ID, equipped with a thermocouple at the coil outlet.

6.2 Analysis. The following equipment is required.

6.2.1 Balanced Pressure Headspace Sampler. Perkin-Elmer HS–6, HS–100, or equivalent, equipped with a glass bead column instead of a chromatographic column.

6.2.2 FID. An FID meeting the following specifications is required.

6.2.2.1 Linearity. A linear response (±5 percent) over the operating range as demonstrated by the procedures established in section 10.2.

6.2.2.2 Range. A full scale range of 1 to 10,000 parts per million (ppm) propane (C_3H_8). Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.2.3 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the output of the detector.

6.2.4 Temperature Sensor. Capable of reading temperatures in the range of 30 to 60 °C (86 to 140 °F) with an accuracy of ±0.1 °C (±0.2 °F).

7.0 Reagents and Standards

7.1 Analysis. The following items are required for analysis.

7.1.1 Hydrogen (H_2). Zero grade hydrogen, as required by the FID.

7.1.2 Carrier Gas. Zero grade nitrogen, containing less than 1 ppm carbon (C) and less than 1 ppm carbon dioxide.

7.1.3 Combustion Gas. Zero grade air or oxygen as required by the FID.

7.2 Calibration and Linearity Check.

7.2.1 Stock Cylinder Gas Standard. 100 percent propane. The manufacturer shall: (a) Certify the gas composition to be accurate to ±3 percent or better (see section 7.2.1.1); (b) recommend a maximum shelf life over which the gas concentration does not change by greater than ±5 percent from the certified value; and (c) affix the date of gas cylinder preparation, certified propane concentration, and recommended maximum shelf life to the cylinder before shipment to the buyer.

7.2.1.1 Cylinder Standards Certification. The manufacturer shall certify the concentration of the calibration gas in the cylinder by (a) directly analyzing the cylinder and (b) calibrating his analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use, as a minimum, a three-point calibration curve.

7.2.1.2 Verification of Manufacturer's Calibration Standards. Before using, the manufacturer shall verify each calibration standard by (a) comparing it to gas mixtures prepared in accordance with the procedure described in section 7.1 of Method 106 of Part 61, Appendix B, or by (b) calibrating it against Standard Reference Materials (SRM's) prepared by the National Bureau of Standards, if such SRM's are available. The agreement between the initially determined concentration value and the verification concentration value must be within ±5 percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

8.0 Sampling Collection, Preservation, Storage, and Transport

8.1 Install a sampling tap to obtain a sample at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to

the atmosphere). Assemble the sampling apparatus as shown in Figure 25E–1.

8.2 Begin sampling by purging the sample lines and cooling coil with at least four volumes of waste. Collect the purged material in a separate container and dispose of it properly.

8.3 After purging, stop the sample flow and transfer the Teflon sampling tube to a sample container. Sample at a flow rate such that the temperature of the waste is <10 °C (<50 °F). Fill the sample container halfway (±5 percent) and cap it within 5 seconds. Store immediately in a cooler and cover with ice.

8.4 Alternative sampling techniques may be used upon the approval of the Administrator.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
10.2, 10.3	FID calibration and response check	Ensure precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Use the procedures in sections 10.2 to calibrate the headspace analyzer and FID and check for linearity before the system is first placed in operation, after any shutdown longer than 6 months, and after any modification of the system.

10.2 Calibration and Linearity. Use the procedures in section 10 of Method 18 of Part 60, Appendix A, to prepare the standards and calibrate the flowmeters, using propane as the standard gas. Fill the calibration standard vials halfway (±5 percent) with deionized water. Purge and fill the airspace with calibration standard. Prepare a minimum of three concentrations of calibration standards in triplicate at concentrations that will bracket the applicable cutoff. For a cutoff of 5.2 kPa (0.75 psi), prepare nominal concentrations of 30,000, 50,000, and 70,000 ppm as propane. For a cutoff of 27.6 kPa (4.0 psi), prepare nominal concentrations of 200,000, 300,000, and 400,000 ppm as propane.

10.2.1 Use the procedures in section 11.3 to measure the FID response of each standard. Use a linear regression analysis to calculate the values for the slope (k) and the y-intercept (b). Use the procedures in sections 12.3 and 12.2 to test the calibration and the linearity.

10.3 Daily FID Calibration Check. Check the calibration at the beginning and at the end of the daily runs by using the following procedures. Prepare 2 calibration standards at the nominal cutoff concentration using the procedures in section 10.2. Place one at the beginning and one at the end of the daily run. Measure the FID response of the daily calibration standard and use the values for k and b from the most recent calibration to calculate the concentration of the daily standard. Use an equation similar to 25E–2 to calculate the percent difference between the daily standard and C_s. If the difference is within 5 percent, then the previous values for k and b can be used. Otherwise, use the procedures in section 10.2 to recalibrate the FID.

11.0 Analytical Procedures

11.1 Allow one hour for the headspace vials to equilibrate at the temperature specified in the regulation. Allow the FID to warm up until a stable baseline is achieved on the detector.

11.2 Check the calibration of the FID daily using the procedures in section 10.3.

11.3 Follow the manufacturer's recommended procedures for the normal operation of the headspace sampler and FID.

11.4 Use the procedures in sections 12.4 and 12.5 to calculate the vapor phase organic vapor pressure in the samples.

11.5 Monitor the output of the detector to make certain that the results are being properly recorded.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

A = Measurement of the area under the response curve, counts.
b = y-intercept of the linear regression line.
C_a = Measured vapor phase organic concentration of sample, ppm as propane.
C_{ma} = Average measured vapor phase organic concentration of standard, ppm as propane.
C_m = Measured vapor phase organic concentration of standard, ppm as propane.
C_s = Calculated standard concentration, ppm as propane.
k = Slope of the linear regression line.
P_{bar} = Atmospheric pressure at analysis conditions, mm Hg (in. Hg).
P* = Organic vapor pressure in the sample, kPa (psi).
PD = Percent difference between the average measured vapor phase organic concentration (C_m) and the calculated standard concentration (C_s).
RSD = Relative standard deviation.
$\beta = 1.333 \times 10^{-7}$ kPa/[(mm Hg)(ppm)], $(4.91 \times 10^{-7}$ psi/[(in. Hg)(ppm)])

12.2 Linearity. Use the following equation to calculate the measured standard concentration for each standard vial.

$$C_m = kA + b \qquad \text{Eq. 25E-1}$$

12.2.1 Calculate the average measured standard concentration (C_{ma}) for each set of triplicate standards and use the following equation to calculate PD between C_{ma} and C_s. The instrument linearity is acceptable if the PD is within five for each standard.

$$PD = \frac{C_s - C_{ma}}{C_s} \times 100 \qquad \text{Eq. 25E-2}$$

12.3. Relative Standard Deviation (RSD). Use the following equation to calculate the RSD for each triplicate set of standards.

$$RSD = \frac{100}{C_{ma}} \sqrt{\frac{\sum (C_m - C_{ma})^2}{2}} \qquad \text{Eq. 25E-3}$$

The calibration is acceptable if the RSD is within five for each standard concentration.

12.4 Concentration of organics in the headspace. Use the following equation to calculate the concentration of vapor phase organics in each sample.

$$C_a = kA + b \qquad \text{Eq. 25E-4}$$

12.5 Vapor Pressure of Organics in the Headspace Sample. Use the following equation to calculate the vapor pressure of organics in the sample.

$$P^* = \beta P_{bar} C_a \qquad \text{Eq. 25E-5}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, Albert E., Samuel Witz, and Robert D. MacPhee. ''Determination of Solvent Vapor Concentrations by Total Combustion Analysis: a Comparison of Infared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, Massachusetts.

2. Salo, Albert E., William L. Oaks, and Robert D. MacPhee. ''Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, Colorado. June 9–13, 1974.) p. 25.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

State of Oregon Department of Environmental Quality

OAR 340-230-0340 Attachments

State of Oregon Department of Environmental Quality

OAR 340-230-0340
Monitoring and Testing

Equation 1:

(4)(b)(E) The percent reduction in the potential mercury emissions (%P_{Hg}) is computed using equation 1:

$(\%P_{Hg}) = (E_i - E_o \div E_i) \times 100$

$\%P_{Hg}$ = percent reduction of the potential mercury emissions achieved.

E_i = potential mercury emission concentration measured at the control device inlet, corrected to 7 percent oxygen (dry basis).

E_o = controlled mercury emission concentration measured at the mercury control device outlet, corrected to 7 percent oxygen (dry basis).

Equation 2:

(6)(c) The percent reduction in potential hydrogen chloride emissions (% P_{HCl}) is computed using equation 2:

$(\%P_{HCl}) = (E_i - E_o \div E_i) \times 100$

$\%P_{HCl}$ = percent reduction of the potential hydrogen chloride emissions achieved.

E_i = potential hydrogen chloride emission concentration measured at the control device inlet, corrected to 7 percent oxygen (dry basis).

E_o = controlled hydrogen chloride emission concentration measured at the control device outlet, corrected to 7 percent oxygen (dry basis).

APPENDIX D TO PART 60—REQUIRED EMISSION INVENTORY INFORMATION

(a) Completed NEDS point source form(s) for the entire plant containing the designated facility, including information on the applicable criteria pollutants. If data concerning the plant are already in NEDS, only that information must be submitted which is necessary to update the existing NEDS record for that plant. Plant and point identification codes for NEDS records shall correspond to those previously assigned in NEDS; for plants not in NEDS, these codes shall be obtained from the appropriate Regional Office.

(b) Accompanying the basic NEDS information shall be the following information on each designated facility:

(1) The state and county identification codes, as well as the complete plant and point identification codes of the designated facility in NEDS. (The codes are needed to match these data with the NEDS data.)

(2) A description of the designated facility including, where appropriate:

(i) Process name.

(ii) Description and quantity of each product (maximum per hour and average per year).

(iii) Description and quantity of raw materials handled for each product (maximum per hour and average per year).

(iv) Types of fuels burned, quantities and characteristics (maximum and average quantities per hour, average per year).

(v) Description and quantity of solid wastes generated (per year) and method of disposal.

(3) A description of the air pollution control equipment in use or proposed to control the designated pollutant, including:

(i) Verbal description of equipment.

(ii) Optimum control efficiency, in percent. This shall be a combined efficiency when more than one device operates in series. The method of control efficiency determination shall be indicated (e.g., design efficiency, measured efficiency, estimated efficiency).

(iii) Annual average control efficiency, in percent, taking into account control equipment down time. This shall be a combined efficiency when more than one device operates in series.

(4) An estimate of the designated pollutant emissions from the designated facility (maximum per hour and average per year). The method of emission determination shall also be specified (e.g., stack test, material balance, emission factor).

[40 FR 53349, Nov. 17, 1975]

APPENDIX E TO PART 60 [RESERVED]

APPENDIX F TO PART 60—QUALITY ASSURANCE PROCEDURES

PROCEDURE 1. QUALITY ASSURANCE REQUIREMENTS FOR GAS CONTINUOUS EMISSION MONITORING SYSTEMS USED FOR COMPLIANCE DETERMINATION

1. Applicability and Principle

1.1 Applicability. Procedure 1 is used to evaluate the effectiveness of quality control (QC) and quality assurance (QA) procedures and the quality of data produced by any continuous emission monitoring system (CEMS) that is used for determining compliance with the emission standards on a continuous basis as specified in the applicable regulation. The CEMS may include pollutant (e.g., $S0_2$ and $N0_x$) and diluent (e.g., 0_2 or $C0_2$) monitors.

This procedure specifies the minimum QA requirements necessary for the control and assessment of the quality of CEMS data submitted to the Environmental Protection Agency (EPA). Source owners and operators responsible for one or more CEMS's used for compliance monitoring must meet these minimum requirements and are encouraged to develop and implement a more extensive QA program or to continue such programs where they already exist.

Data collected as a result of QA and QC measures required in this procedure are to be submitted to the Agency. These data are to be used by both the Agency and the CEMS operator in assessing the effectiveness of the CEMS QC and QA procedures in the maintenance of acceptable CEMS operation and valid emission data.

Appendix F, Procedure 1 is applicable December 4, 1987. The first CEMS accuracy assessment shall be a relative accuracy test audit (RATA) (see section 5) and shall be completed by March 4, 1988 or the date of the initial performance test required by the applicable regulation, whichever is later.

1.2 Principle. The QA procedures consist of two distinct and equally important functions. One function is the assessment of the quality of the CEMS data by estimating accuracy. The other function is the control and improvement of the quality of the CEMS data by implementing QC policies and corrective actions. These two functions form a control loop: When the assessment function indicates that the data quality is inadequate, the control effort must be increased until the data quality is acceptable. In order to provide uniformity in the assessment and reporting of data quality, this procedure explicitly specifies the assessment methods for response drift and accuracy. The methods are based on procedures included in the applicable performance specifications (PS's) in appendix B of 40 CFR part 60. Procedure 1 also requires the analysis of the EPA audit

samples concurrent with certain reference method (RM) analyses as specified in the applicable RM's.

Because the control and corrective action function encompasses a variety of policies, specifications, standards, and corrective measures, this procedure treats QC requirements in general terms to allow each source owner or operator to develop a QC system that is most effective and efficient for the circumstances.

2. Definitions

2.1 Continuous Emission Monitoring System. The total equipment required for the determination of a gas concentration or emission rate.

2.2 Diluent Gas. A major gaseous constituent in a gaseous pollutant mixture. For combustion sources, CO_2 and O_2 are the major gaseous constituents of interest.

2.3 Span Value. The upper limit of a gas concentration measurement range that is specified for affected source categories in the applicable subpart of the regulation.

2.4 Zero, Low-Level, and High-Level Values. The CEMS response values related to the source specific span value. Determination of zero, low-level, and high-level values is defined in the appropriate PS in appendix B of this part.

2.5 Calibration Drift (CD). The difference in the CEMS output reading from a reference value after a period of operation during which no unscheduled maintenance, repair or adjustment took place. The reference value may be supplied by a cylinder gas, gas cell, or optical filter and need not be certified.

2.6 Relative Accuracy (RA). The absolute mean difference between the gas concentration or emission rate determined by the CEMS and the value determined by the RM's plus the 2.5 percent error confidence coefficient of a series of tests divided by the mean of the RM tests or the applicable emission limit.

3. QC Requirements

Each source owner or operator must develop and implement a QC program. As a minimum, each QC program must include written procedures which should describe in detail, complete, step-by-step procedures and operations for each of the following activities:

1. Calibration of CEMS.
2. CD determination and adjustment of CEMS.
3. Preventive maintenance of CEMS (including spare parts inventory).
4. Data recording, calculations, and reporting.
5. Accuracy audit procedures including sampling and analysis methods.
6. Program of corrective action for malfunctioning CEMS.

As described in Section 5.2, whenever excessive inaccuracies occur for two consecutive quarters, the source owner or operator must revise the current written procedures or modify or replace the CEMS to correct the deficiency causing the excessive inaccuracies.

These written procedures must be kept on record and available for inspection by the enforcement agency.

4. CD Assessment

4.1 CD Requirement. As described in 40 CFR 60.13(d), source owners and operators of CEMS must check, record, and quantify the CD at two concentration values at least once daily (approximately 24 hours) in accordance with the method prescribed by the manufacturer. The CEMS calibration must, as minimum, be adjusted whenever the daily zero (or low-level) CD or the daily high-level CD exceeds two times the limits of the applicable PS's in appendix B of this regulation.

4.2 Recording Requirement for Automatic CD Adjusting Monitors. Monitors that automatically adjust the data to the corrected calibration values (e.g., microprocessor control) must be programmed to record the unadjusted concentration measured in the CD prior to resetting the calibration, if performed, or record the amount of adjustment.

4.3 Criteria for Excessive CD. If either the zero (or low-level) or high-level CD result exceeds twice the applicable drift specification in appendix B for five, consecutive, daily periods, the CEMS is out-of-control. If either the zero (or low-level) or high-level CD result exceeds four times the applicable drift specification in appendix B during any CD check, the CEMS is out-of-control. If the CEMS is out-of-control, take necessary corrective action. Following corrective action, repeat the CD checks.

4.3.1 Out-Of-Control Period Definition. The beginning of the out-of-control period is the time corresponding to the completion of the fifth, consecutive, daily CD check with a CD in excess of two times the allowable limit, or the time corresponding to the completion of the daily CD check preceding the daily CD check that results in a CD in excess of four times the allowable limit. The end of the out-of-control period is the time corresponding to the completion of the CD check following corrective action that results in the CD's at both the zero (or low-level) and high-level measurement points being within the corresponding allowable CD limit (i.e., either two times or four times the allowable limit in appendix B).

4.3.2 CEMS Data Status During Out-of-Control Period. During the period the CEMS is out-of-control, the CEMS data may not be used in calculating emission compliance nor be counted towards meeting minimum data availability as required and described in the applicable subpart [e.g., §60.47a(f)].

4.4 Data Recording and Reporting. As required in §60.7(d) of this regulation (40 CFR part 60), all measurements from the CEMS must be retained on file by the source owner for at least 2 years. However, emission data obtained on each successive day while the CEMS is out-of-control may not be included as part of the minimum daily data requirement of the applicable subpart [e.g., §60.47a(f)] nor be used in the calculation of reported emissions for that period.

5. Data Accuracy Assessment

5.1 Auditing Requirements. Each CEMS must be audited at least once each calendar quarter. Successive quarterly audits shall occur no closer than 2 months. The audits shall be conducted as follows:

5.1.1 Relative Accuracy Test Audit (RATA). The RATA must be conducted at least once every four calendar quarters, except as otherwise noted in section 5.1.4 of this appendix. Conduct the RATA as described for the RA test procedure in the applicable PS in appendix B (e.g., PS 2 for SO_2 and NO_X). In addition, analyze the appropriate performance audit samples received from EPA as described in the applicable sampling methods (e.g., Methods 6 and 7).

5.1.2 Cylinder Gas Audit (CGA). If applicable, a CGA may be conducted in three of four calendar quarters, but in no more than three quarters in succession.

To conduct a CGA: (1) Challenge the CEMS (both pollutant and diluent portions of the CEMS, if applicable) with an audit gas of known concentration at two points within the following ranges:

Audit point	Audit range		
	Pollutant monitors	Diluent monitors for—	
		CO_2	O_2
1	20 to 30% of span value.	5 to 8% by volume.	4 to 6% by volume.
2	50 to 60% of span value.	10 to 14% by volume.	8 to 12% by volume.

Challenge the CEMS three times at each audit point, and use the average of the three responses in determining accuracy.

Use of separate audit gas cylinder for audit points 1 and 2. Do not dilute gas from audit cylinder when challenging the CEMS.

The monitor should be challenged at each audit point for a sufficient period of time to assure adsorption-desorption of the CEMS sample transport surfaces has stabilized.

(2) Operate each monitor in its normal sampling mode, i.e., pass the audit gas through all filters, scrubbers, conditioners, and other monitor components used during normal sampling, and as much of the sampling probe as is practical. At a minimum, the audit gas should be introduced at the connection between the probe and the sample line.

(3) Use Certified Reference Materials (CRM's) (See Citation 1) audit gases that have been certified by comparison to National Institute of Standards and Technology (NIST) or EPA Traceability Protocol Materials (ETPM's) following the most recent edition of EPA's Traceability Protocol No. 1 (See Citation 2). Procedures for preparation of CRM's are described in Citation 1. Procedures for preparation of ETPM's are described in Citation 2. As an alternative to CRM's or ETPM gases, Method 205 (See Citation 3) may be used. The difference between the actual concentration of the audit gas and the concentration indicated by the monitor is used to assess the accuracy of the CEMS.

5.1.3 Relative Accuracy Audit (RAA). The RAA may be conducted three of four calendar quarters, but in no more than three quarters in succession. To conduct a RAA, follow the procedure described in the applicable PS in appendix B for the relative accuracy test, except that only three sets of measurement data are required. Analyses of EPA performance audit samples are also required.

The relative difference between the mean of the RM values and the mean of the CEMS responses will be used to assess the accuracy of the CEMS.

5.1.4 Other Alternative Audits. Other alternative audit procedures may be used as approved by the Administrator for three of four calendar quarters. One RATA is required at least every four calendar quarters, except in the case where the affected facility is off-line (does not operate) in the fourth calendar quarter since the quarter of the previous RATA. In that case, the RATA shall be performed in the quarter in which the unit recommences operation. Also, cylinder gas audits are not be required for calendar quarters in which the affected facility does not operate.

5.2 Excessive Audit Inaccuracy. If the RA, using the RATA, CGA, or RAA exceeds the criteria in section 5.2.3, the CEMS is out-of-control. If the CEMS is out-of-control, take necessary corrective action to eliminate the problem. Following corrective action, the source owner or operator must audit the CEMS with a RATA, CGA, or RAA to determine if the CEMS is operating within the specifications. A RATA must always be used following an out-of-control period resulting from a RATA. The audit following corrective action does not require analysis of EPA performance audit samples. If audit results show the CEMS to be out-of-control, the CEMS operator shall report both the audit showing the CEMS to be out-of-control and the results of the audit following corrective action showing the CEMS to be operating within specifications.

5.2.1 Out-Of-Control Period Definition. The beginning of the out-of-control period is the time corresponding to the completion of the sampling for the RATA, RAA, or CGA. The end of the out-of-control period is the time corresponding to the completion of the sampling of the subsequent successful audit.

5.2.2 CEMS Data Status During Out-Of-Control Period. During the period the monitor is out-of-control, the CEMS data may not be used in calculating emission compliance nor be counted towards meeting minimum data availabilty as required and described in the applicable subpart [e.g., §60.47a(f)].

5.2.3 Criteria for Excessive Audit Inaccuracy. Unless specified otherwise in the applicable subpart, the criteria for excessive inaccuracy are:

(1) For the RATA, the allowable RA in the applicable PS in appendix B.

(2) For the CGA, ±15 percent of the average audit value or ±5 ppm, whichever is greater.

(3) For the RAA, ±15 percent of the three run average or ±7.5 percent of the applicable standard, whichever is greater.

5.3 Criteria for Acceptable QC Procedure. Repeated excessive inaccuracies (i.e., out-of-control conditions resulting from the quarterly audits) indicates the QC procedures are inadequate or that the CEMS is incapable of providing quality data. Therefore, whenever excessive inaccuracies occur for two consective quarters, the source owner or operator must revise the QC procedures (see Section 3) or modify or replace the CEMS.

6. Calculations for CEMS Data Accuracy

6.1 RATA RA Calculation. Follow the equations described in Section 8 of appendix B, PS 2 to calculate the RA for the RATA. The RATA must be calculated in units of the applicable emission standard (e.g., ng/J).

6.2 RAA Accuracy Calculation. Use Equation 1–1 to calculate the accuracy for the RAA. The RAA must be calculated in units of the applicable emission standard (e.g., ng/J).

6.3 CGA Accuracy Calculation. Use Equation 1–1 to calculate the accuracy for the CGA, which is calculated in units of the appropriate concentration (e.g., ppm SO_2 or percent O_2). Each component of the CEMS must meet the acceptable accuracy requirement.

$$A = \frac{C_m - C_a}{C_a} \times 100 \qquad \text{Eq. 1-1}$$

where:

A=Accuracy of the CEMS, percent.

C_m=Average CEMS response during audit in units of applicable standard or appropriate concentration.

C_a=Average audit value (CGA certified value or three-run average for RAA) in units of applicable standard or appropriate concentration.

6.4 Example Accuracy Calculations. Example calculations for the RATA, RAA, and CGA are available in Citation 3.

7. Reporting Requirements

At the reporting interval specified in the applicable regulation, report for each CEMS the accuracy results from Section 6 and the CD assessment results from Section 4. Report the drift and accuracy information as a Data Assessment Report (DAR), and include one copy of this DAR for each quarterly audit with the report of emissions required under the applicable subparts of this part.

As a minimum, the DAR must contain the following information:

1. Source owner or operator name and address.

2. Identification and location of monitors in the CEMS.

3. Manufacturer and model number of each monitor in the CEMS.

4. Assessment of CEMS data accuracy and date of assessment as determined by a RATA, RAA, or CGA described in Section 5 including the RA for the RATA, the A for the RAA or CGA, the RM results, the cylinder gases certified values, the CEMS responses, and the calculations results as defined in Section 6. If the accuracy audit results show the CEMS to be out-of-control, the CEMS operator shall report both the audit results showing the CEMS to be out-of-control and the results of the audit following corrective action showing the CEMS to be operating within specifications.

5. Results from EPA performance audit samples described in Section 5 and the applicable RM's.

6. Summary of all corrective actions taken when CEMS was determined out-of-control, as described in Sections 4 and 5.

An example of a DAR format is shown in Figure 1.

8. Bibliography

1. ''A Procedure for Establishing Traceability of Gas Mixtures to Certain National Bureau of Standards Standard Reference Materials.'' Joint publication by NBS and EPA–600/7–81–010, Revised 1989. Available from the U.S. Environmental Protection Agency. Quality Assurance Division (MD–77). Research Triangle Park, NC 27711.

2. ''EPA Traceability Protocol For Assay And Certification Of Gaseous Calibration Standards.'' EPA–600/R–97/121, September 1997. Available from EPA's Emission Measurement Center at *http://www.epa.gov/ttn/emc*.

3. Method 205, ''Verification of Gas Dilution Systems for Field Instrument Calibrations,'' 40 CFR 51, appendix M.

FIGURE 1—EXAMPLE FORMAT FOR DATA ASSESSMENT REPORT

Period ending date _____
Year _____
Company name _____
Plant name _____
Source unit no. _____
CEMS manufacturer _____
Model no. _____
CEMS serial no. _____
CEMS type (e.g., in situ) _____
CEMS sampling location (e.g., control device outlet) _____
CEMS span values as per the applicable regulation: _____ (e.g., SO_2 _____ ppm, NO_x _____ ppm). _____

I. Accuracy assessment results (Complete A, B, or C below for each CEMS or for each pollutant and diluent analyzer, as applicable.) If the quarterly audit results show the CEMS to be out-of-control, report the results of both the quarterly audit and the audit following corrective action showing the CEMS to be operating properly.

A. Relative accuracy test audit (RATA) for _____ (e.g., SO_2 in ng/J).

1. Date of audit _____.
2. Reference methods (RM's) used _____ (e.g., Methods 3 and 6).
3. Average RM value _____ (e.g., ng/J, mg/dsm^3, or percent volume).
4. Average CEMS value _____.
5. Absolute value of mean difference [d] _____.
6. Confidence coefficient [CC] _____.
7. Percent relative accuracy (RA) _____ percent.
8. EPA performance audit results:
a. Audit lot number (1) _____ (2) _____
b. Audit sample number (1) _____ (2) _____
c. Results (mg/dsm^3) (1) _____ (2) _____
d. Actual value (mg/dsm^3)* (1) _____ (2) _____
e. Relative error* (1) _____ (2) _____

B. Cylinder gas audit (CGA) for _____ (e.g., SO_2 in ppm).

	Audit point 1	Audit point 2	
1. Date of audit.			
2. Cylinder ID number.			
3. Date of certification.			
4. Type of certification	.....	.....	(e.g., EPA Protocol 1 or CRM).
5. Certified audit value	.....	.....	(e.g., ppm).
6. CEMS response value	.....	.....	(e.g., ppm).
7. Accuracy	.....	.....	percent.

C. Relative accuracy audit (RAA) for _____ (e.g., SO_2 in ng/J).

1. Date of audit _____.
2. Reference methods (RM's) used _____ (e.g., Methods 3 and 6).
3. Average RM value _____ (e.g., ng/J).
4. Average CEMS value _____.
5. Accuracy _____ percent.
6. EPA performance audit results:
a. Audit lot number (1) _____ (2) _____
b. Audit sample number (1) _____ (2) _____
c. Results (mg/dsm^3) (1) _____ (2) _____
d. Actual value (mg/dsm^3) *(1) _____ (2) _____
e. Relative error* (1) _____ (2) _____

D. Corrective action for excessive inaccuracy.

1. Out-of-control periods.
a. Date(s) _____.
b. Number of days _____.
2. Corrective action taken _____
3. Results of audit following corrective action. (Use format of A, B, or C above, as applicable.)

II. Calibration drift assessment.

A. Out-of-control periods.
1. Date(s) _____.
2. Number of days _____.

B. Corrective action taken _____

PROCEDURE 2—QUALITY ASSURANCE REQUIREMENTS FOR PARTICULATE MATTER CONTINUOUS EMISSION MONITORING SYSTEMS AT STATIONARY SOURCES

1.0 What Are the Purpose and Applicability of Procedure 2?

The purpose of Procedure 2 is to establish the minimum requirements for evaluating the effectiveness of quality control (QC) and quality assurance (QA) procedures and the quality of data produced by your particulate matter (PM) continuous emission monitoring system (CEMS). Procedure 2 applies to PM CEMS used for continuously determining compliance with emission standards or operating permit limits as specified in an applicable regulation or permit. Other QC procedures may apply to diluent (*e.g.*, O_2) monitors and other auxiliary monitoring equipment included with your CEMS to facilitate PM measurement or determination of PM concentration in units specified in an applicable regulation.

1.1 What measurement parameter does Procedure 2 address? Procedure 2 covers the instrumental measurement of PM as defined by your source's applicable reference method (no Chemical Abstract Service number assigned).

1.2 For what types of devices must I comply with Procedure 2? You must comply with Procedure 2 for the total equipment that:

(1) We require you to install and operate on a continuous basis under the applicable regulation, and

*To be completed by the Agency.

(2) You use to monitor the PM mass concentration associated with the operation of a process or emission control device.

1.3 What are the data quality objectives (DQOs) of Procedure 2? The overall DQO of Procedure 2 is the generation of valid, representative data that can be transferred into useful information for determining PM CEMS concentrations averaged over a prescribed interval. Procedure 2 is also closely associated with Performance Specification 11 (PS–11).

(1) Procedure 2 specifies the minimum requirements for controlling and assessing the quality of PM CEMS data submitted to us or the delegated permitting authority.

(2) You must meet these minimum requirements if you are responsible for one or more PM CEMS used for compliance monitoring. We encourage you to develop and implement a more extensive QA program or to continue such programs where they already exist.

1.4 What is the intent of the QA/QC procedures specified in Procedure 2? Procedure 2 is intended to establish the minimum QA/QC requirements for PM CEMS and is presented in general terms to allow you to develop a program that is most effective for your circumstances. You may adopt QA/QC procedures that go beyond these minimum requirements to ensure compliance with applicable regulations.

1.5 When must I comply with Procedure 2? You must comply with the basic requirements of Procedure 2 immediately following successful completion of the initial correlation test of PS–11.

2.0 What Are the Basic Requirements of Procedure 2?

Procedure 2 requires you to perform periodic evaluations of PM CEMS performance and to develop and implement QA/QC programs to ensure that PM CEMS data quality is maintained.

2.1 What are the basic functions of Procedure 2?

(1) Assessment of the quality of your PM CEMS data by estimating measurement accuracy;

(2) Control and improvement of the quality of your PM CEMS data by implementing QC requirements and corrective actions until the data quality is acceptable; and

(3) Specification of requirements for daily instrument zero and upscale drift checks and daily sample volume checks, as well as routine response correlation audits, absolute correlation audits, sample volume audits, and relative response audits.

3.0 What Special Definitions Apply to Procedure 2?

The definitions in Procedure 2 include those provided in PS–11 of Appendix B, with the following additions:

3.1 ''Absolute Correlation Audit (ACA)'' means an evaluation of your PM CEMS response to a series of reference standards covering the full measurement range of the instrument (*e.g.*, 4 mA to 20 mA).

3.2 ''Correlation Range'' means the range of PM CEMS responses used in the complete set of correlation test data.

3.3 ''PM CEMS Correlation'' means the site-specific relationship (*i.e.*, a regression equation) between the output from your PM CEMS (*e.g.*, mA) and the particulate concentration, as determined by the reference method. The PM CEMS correlation is expressed in the same units as the PM concentration measured by your PM CEMS (*e.g.*, mg/acm). You must derive this relation from PM CEMS response data and manual reference method data that were gathered simultaneously. These data must be representative of the full range of source and control device operating conditions that you expect to occur. You must develop the correlation by performing the steps presented in sections 12.2 and 12.3 of PS–11.

3.4 ''Reference Method Sampling Location'' means the location in your source's exhaust duct from which you collect manual reference method data for developing your PM CEMS correlation and for performing relative response audits (RRAs) and response correlation audits (RCAs).

3.5 ''Response Correlation Audit (RCA)'' means the series of tests specified in section 10.3(8) of this procedure that you conduct to ensure the continued validity of your PM CEMS correlation.

3.6 ''Relative Response Audit (RRA)'' means the brief series of tests specified in section 10.3(6) of this procedure that you conduct between consecutive RCAs to ensure the continued validity of your PM CEMS correlation.

3.7 ''Sample Volume Audit (SVA)'' means an evaluation of your PM CEMS measurement of sample volume if your PM CEMS determines PM concentration based on a measure of PM mass in an extracted sample volume and an independent determination of sample volume.

4.0 Interferences [Reserved]

5.0 What Do I Need To Know To Ensure the Safety of Persons Using Procedure 2?

People using Procedure 2 may be exposed to hazardous materials, operations, and equipment. Procedure 2 does not purport to address all of the safety issues associated with its use. It is your responsibility to establish appropriate safety and health practices and determine the applicable regulatory limitations before performing this procedure. You must consult your CEMS user's manual for specific precautions to be taken with regard to your PM CEMS procedures.

6.0 What Equipment and Supplies Do I Need? [Reserved]

7.0 What Reagents and Standards Do I Need?

You will need reference standards or procedures to perform the zero drift check, the upscale drift check, and the sample volume check.

7.1 What is the reference standard value for the zero drift check? You must use a zero check value that is no greater than 20 percent of the PM CEMS's response range. You must obtain documentation on the zero check value from your PM CEMS manufacturer.

7.2 What is the reference standard value for the upscale drift check? You must use an upscale check value that produces a response between 50 and 100 percent of the PM CEMS's response range. For a PM CEMS that produces output over a range of 4 mA to 20 mA, the upscale check value must produce a response in the range of 12 mA to 20 mA. You must obtain documentation on the upscale check value from your PM CEMS manufacturer.

7.3 What is the reference standard value for the sample volume check? You must use a reference standard value or procedure that produces a sample volume value equivalent to the normal sampling rate. You must obtain documentation on the sample volume value from your PM CEMS manufacturer.

8.0 What Sample Collection, Preservation, Storage, and Transport Are Relevant to This Procedure? [Reserved]

9.0 What Quality Control Measures Are Required by This Procedure for My PM CEMS?

You must develop and implement a QC program for your PM CEMS. Your QC program must, at a minimum, include written procedures that describe, in detail, complete step-by-step procedures and operations for the activities in paragraphs (1) through (8) of this section.

(1) Procedures for performing drift checks, including both zero drift and upscale drift and the sample volume check (see sections 10.2(1), (2), and (5)).

(2) Methods for adjustment of PM CEMS based on the results of drift checks, sample volume checks (if applicable), and the periodic audits specified in this procedure.

(3) Preventative maintenance of PM CEMS (including spare parts inventory and sampling probe integrity).

(4) Data recording, calculations, and reporting.

(5) RCA and RRA procedures, including sampling and analysis methods, sampling strategy, and structuring test conditions over the prescribed range of PM concentrations.

(6) Procedures for performing ACAs and SVAs and methods for adjusting your PM CEMS response based on ACA and SVA results.

(7) Program of corrective action for malfunctioning PM CEMS, including flagged data periods.

(8) For extractive PM CEMS, procedures for checking extractive system ducts for material accumulation.

9.1 What QA/QC documentation must I have? You are required to keep the written QA/QC procedures on record and available for inspection by us, the State, and/or local enforcement agency for the life of your CEMS or until you are no longer subject to the requirements of this procedure.

9.2 How do I know if I have acceptable QC procedures for my PM CEMS? Your QC procedures are inadequate or your PM CEMS is incapable of providing quality data if you fail two consecutive QC audits (*i.e.*, out-of-control conditions resulting from the annual audits, quarterly audits, or daily checks). Therefore, if you fail the same two consecutive audits, you must revise your QC procedures or modify or replace your PM CEMS to correct the deficiencies causing the excessive inaccuracies (see section 10.4 for limits for excessive audit inaccuracy).

10.0 What Calibration/Correlation and Standardization Procedures Must I Perform for My PM CEMS?

You must generate a site-specific correlation for each of your PM CEMS installation(s) relating response from your PM CEMS to results from simultaneous PM reference method testing. The PS–11 defines procedures for developing the correlation and defines a series of statistical parameters for assessing acceptability of the correlation. However, a critical component of your PM CEMS correlation process is ensuring the accuracy and precision of reference method data. The activities listed in sections 10.1 through 10.10 assure the quality of the correlation.

10.1 When should I use paired trains for reference method testing? Although not required, we recommend that you should use paired-train reference method testing to generate data used to develop your PM CEMS correlation and for RCA testing. Guidance on the use of paired sampling trains can be found in the PM CEMS Knowledge Document (see section 16.5 of PS–11).

10.2 What routine system checks must I perform on my PM CEMS? You must perform routine checks to ensure proper operation of system electronics and optics, light and radiation sources and detectors, and electric or electro-mechanical systems. Necessary components of the routine system checks will depend on design details of your PM CEMS. As a minimum, you must verify the system operating parameters listed in paragraphs (1) through (5) of this section on a daily basis. Some PM CEMS may perform one or more of

these functions automatically or as an integral portion of unit operations; for other PM CEMS, you must initiate or perform one or more of these functions manually.

(1) You must check the zero drift to ensure stability of your PM CEMS response to the zero check value. You must determine system output on the most sensitive measurement range when the PM CEMS is challenged with a zero reference standard or procedure. You must, at a minimum, adjust your PM CEMS whenever the daily zero drift exceeds 4 percent.

(2) You must check the upscale drift to ensure stability of your PM CEMS response to the upscale check value. You must determine system output when the PM CEMS is challenged with a reference standard or procedure corresponding to the upscale check value. You must, at a minimum, adjust your PM CEMS whenever the daily upscale drift check exceeds 4 percent.

(3) For light-scattering and extinction-type PM CEMS, you must check the system optics to ensure that system response has not been altered by the condition of optical components, such as fogging of lens and performance of light monitoring devices.

(4) You must record data from your automatic drift-adjusting PM CEMS before any adjustment is made. If your PM CEMS automatically adjusts its response to the corrected calibration values (*e.g.*, microprocessor control), you must program your PM CEMS to record the unadjusted concentration measured in the drift check before resetting the calibration. Alternately, you may program your PM CEMS to record the amount of adjustment.

(5) For extractive PM CEMS that measure the sample volume and use the measured sample volume as part of calculating the output value, you must check the sample volume on a daily basis to verify the accuracy of the sample volume measuring equipment. This sample volume check must be done at the normal sampling rate of your PM CEMS. You must adjust your PM CEMS sample volume measurement whenever the daily sample volume check error exceeds 10 percent.

10.3 What are the auditing requirements for my PM CEMS? You must subject your PM CEMS to an ACA and an SVA, as applicable, at least once each calender quarter. Successive quarterly audits must occur no closer than 2 months apart. You must conduct an RCA and an RRA at the frequencies specified in the applicable regulation or facility operating permit. An RRA or RCA conducted during any calendar quarter can take the place of the ACA required for that calendar quarter. An RCA conducted during the period in which an RRA is required can take the place of the RRA for that period.

(1) When must I perform an ACA? You must perform an ACA each quarter unless you conduct an RRA or RCA during that same quarter.

(2) How do I perform an ACA? You perform an ACA according to the procedure specified in paragraphs (2)(i) through (v) of this section.

(i) You must challenge your PM CEMS with an audit standard or an equivalent audit reference to reproduce the PM CEMS's measurement at three points within the following ranges:

Audit point	Audit range
1	0 to 20 percent of measurement range
2	40 to 60 percent of measurement range
3	70 to 100 percent of measurement range

(ii) You must then challenge your PM CEMS three times at each audit point and use the average of the three responses in determining accuracy at each audit point. Use a separate audit standard for audit points 1, 2, and 3. Challenge the PM CEMS at each audit point for a sufficient period of time to ensure that your PM CEMS response has stabilized.

(iii) Operate your PM CEMS in the mode, manner, and range specified by the manufacturer.

(iv) Store, maintain, and use audit standards as recommended by the manufacturer.

(v) Use the difference between the actual known value of the audit standard and the response of your PM CEMS to assess the accuracy of your PM CEMS.

(3) When must I perform an SVA? You must perform an audit of the measured sample volume (*e.g.*, the sampling flow rate for a known time) once per quarter for applicable PM CEMS with an extractive sampling system. Also, you must perform and pass an SVA prior to initiation of any of the reference method data collection runs for an RCA or RRA.

(4) How do I perform an SVA? You perform an SVA according to the procedure specified in paragraphs (4)(i) through (iii) of this section.

(i) You perform an SVA by independently measuring the volume of sample gas extracted from the stack or duct over each batch cycle or time period with a calibrated device. You may make this measurement either at the inlet or outlet of your PM CEMS, so long as it measures the sample gas volume without including any dilution or recycle air. Compare the measured volume with the volume reported by your PM CEMS for the same cycle or time period to calculate sample volume accuracy.

(ii) You must make measurements during three sampling cycles for batch extractive monitors (*e.g.*, Beta-gauge) or during three periods of at least 20 minutes for continuous extractive PM CEMS.

(iii) You may need to condense, collect, and measure moisture from the sample gas prior to the calibrated measurement device (*e.g.*, dry gas meter) and correct the results for moisture content. In any case, the volumes measured by the calibrated device and your PM CEMS must be on a consistent temperature, pressure, and moisture basis.

(5) How often must I perform an RRA? You must perform an RRA at the frequency specified in the applicable regulation or facility operating permit. You may conduct an RCA instead of an RRA during the period when the RRA is required.

(6) How do I perform an RRA? You must perform the RRA according to the procedure specified in paragraphs (6)(i) and (ii) of this section.

(i) You perform an RRA by collecting three simultaneous reference method PM concentration measurements and PM CEMS measurements at the as-found source operating conditions and PM concentration.

(ii) We recommend that you use paired trains for reference method sampling. Guidance on the use of paired sampling trains can be found in the PM CEMS Knowledge Document (see section 16.5 of PS–11).

(7) How often must I perform an RCA? You must perform an RCA at the frequency specified in the applicable regulation or facility operating permit.

(8) How do I perform an RCA? You must perform the RCA according to the procedures for the PM CEMS correlation test described in PS–11, section 8.6, except that the minimum number of runs required is 12 in the RCA instead of 15 as specified in PS–11.

(9) What other alternative audits can I use? You can use other alternative audit procedures as approved by us, the State, or local agency for the quarters when you would conduct ACAs.

10.4 What are my limits for excessive audit inaccuracy? Unless specified otherwise in the applicable subpart, the criteria for excessive audit inaccuracy are listed in paragraphs (1) through (6) of this section.

(1) What are the criteria for excessive zero or upscale drift? Your PM CEMS is out of control if the zero drift check or upscale drift check either exceeds 4 percent for five consecutive daily periods or exceeds 8 percent for any one day.

(2) What are the criteria for excessive sample volume measurement error? Your PM CEMS is out of control if sample volume check error exceeds 10 percent for five consecutive daily periods or exceeds 20 percent for any one day.

(3) What are the criteria for excessive ACA error? Your PM CEMS is out of control if the results of any ACA exceed ± 10 percent of the average audit value, as calculated using Equation 2–1a, or 7.5 percent of the applicable standard, as calculated using Equation 2–1b, whichever is greater.

(4) What is the criterion for excessive SVA error? Your PM CEMS is out of control if results exceed ±5 percent of the average sample volume audit value.

(5) What are the criteria for passing an RCA? To pass an RCA, you must meet the criteria specified in paragraphs (5)(i) through (iii) of this section. If your PM CEMS fails to meet these RCA criteria, it is out of control.

(i) For all 12 data points, the PM CEMS response value can be no greater than the greatest PM CEMS response value used to develop your correlation curve.

(ii) For 9 of the 12 data points, the PM CEMS response value must lie within the PM CEMS output range used to develop your correlation curve.

(iii) At least 75 percent of a minimum number of 12 sets of PM CEMS and reference method measurements must fall within a specified area on a graph of the correlation regression line. The specified area on the graph of the correlation regression line is defined by two lines parallel to the correlation regression line, offset at a distance of ±25 percent of the numerical emission limit value from the correlation regression line.

(6) What are the criteria to pass an RRA? To pass an RRA, you must meet the criteria specified in paragraphs (6)(i) and (ii) of this section. If your PM CEMS fails to meet these RRA criteria, it is out of control.

(i) For all three data points, the PM CEMS response value can be no greater than the greatest PM CEMS response value used to develop your correlation curve.

(ii) For two of the three data points, the PM CEMS response value must lie within the PM CEMS output range used to develop your correlation curve.

(iii) At least two of the three sets of PM CEMS and reference method measurements must fall within the same specified area on a graph of the correlation regression line as required for the RCA and described in paragraph (5)(iii) of this section.

10.5 What do I do if my PM CEMS is out of control? If your PM CEMS is out of control, you must take the actions listed in paragraphs (1) and (2) of this section.

(1) You must take necessary corrective action to eliminate the problem and perform tests, as appropriate, to ensure that the corrective action was successful.

(i) Following corrective action, you must repeat the previously failed audit to confirm that your PM CEMS is operating within the specifications.

(ii) If your PM CEMS failed an RRA, you must take corrective action until your PM CEMS passes the RRA criteria. If the RRA criteria cannot be achieved, you must perform an RCA.

(iii) If your PM CEMS failed an RCA, you must follow procedures specified in section 10.6 of this procedure.

(2) You must report both the audit showing your PM CEMS to be out of control and the results of the audit following corrective action showing your PM CEMS to be operating within specifications.

10.6 What do I do if my PM CEMS fails an RCA? After an RCA failure, you must take all applicable actions listed in paragraphs (1) through (3) of this section.

(1) Combine RCA data with data from the active PM CEMS correlation and perform the mathematical evaluations defined in PS–11 for development of a PM CEMS correlation, including examination of alternate correlation models (*i.e.,* linear, polynomial, logarithmic, exponential, and power). If the expanded data base and revised correlation meet PS–11 statistical criteria, use the revised correlation.

(2) If the criteria specified in paragraph (1) of this section are not achieved, you must develop a new PM CEMS correlation based on revised data. The revised data set must consist of the test results from only the RCA. The new data must meet all requirements of PS–11 to develop a revised PM CEMS correlation, except that the minimum number of sets of PM CEMS and reference method measurements is 12 instead of the minimum of 15 sets required by PS–11. Your PM CEMS is considered to be back in controlled status when the revised correlation meets all of the performance criteria specified in section 13.2 of PS–11.

(3) If the actions in paragraphs (1) and (2) of this section do not result in an acceptable correlation, you must evaluate the cause(s) and comply with the actions listed in paragraphs (3)(i) through (iv) of this section within 90 days after the completion of the failed RCA.

(i) Completely inspect your PM CEMS for mechanical or operational problems. If you find a mechanical or operational problem, repair your PM CEMS and repeat the RCA.

(ii) You may need to relocate your PM CEMS to a more appropriate measurement location. If you relocate your PM CEMS, you must perform a new correlation test according to the procedures specified in PS–11.

(iii) The characteristics of the PM or gas in your source's flue gas stream may have changed such that your PM CEMS measurement technology is no longer appropriate. If this is the case, you must install a PM CEMS with measurement technology that is appropriate for your source's flue gas characteristics. You must perform a new correlation test according to the procedures specified in PS–11.

(iv) If the corrective actions in paragraphs (3)(i) through (iii) of this section were not successful, you must petition us, the State, or local agency for approval of alternative criteria or an alternative for continuous PM monitoring.

10.7 When does the out-of-control period begin and end? The out-of-control period begins immediately after the last test run or check of an unsuccessful RCA, RRA, ACA, SVA, drift check, or sample volume check. The out-of-control period ends immediately after the last test run or check of the subsequent successful audit or drift check.

10.8 Can I use the data recorded by my PM CEMS during out-of-control periods? During any period when your PM CEMS is out of control, you may not use your PM CEMS data to calculate emission compliance or to meet minimum data availability requirements described in the applicable regulation.

10.9 What are the QA/QC reporting requirements for my PM CEMS? You must report the accuracy results for your PM CEMS, specified in section 10.4 of this procedure, at the interval specified in the applicable regulation. Report the drift and accuracy information as a Data Assessment Report (DAR), and include one copy of this DAR for each quarterly audit with the report of emissions required under the applicable regulation. An example DAR is provided in Procedure 1, Appendix F of this part.

10.10 What minimum information must I include in my DAR? As a minimum, you must include the information listed in paragraphs (1) through (5) of this section in the DAR:

(1) Your name and address.

(2) Identification and location of monitors in your CEMS.

(3) Manufacturer and model number of each monitor in your CEMS.

(4) Assessment of PM CEMS data accuracy/acceptability, and date of assessment, as determined by an RCA, RRA, ACA, or SVA described in section 10, including the acceptability determination for the RCA or RRA, the accuracy for the ACA or SVA, the reference method results, the audit standards, your PM CEMS responses, and the calculation results as defined in section 12. If the accuracy audit results show your PM CEMS to be out of control, you must report both the audit results showing your PM CEMS to be out of control and the results of the audit following corrective action showing your PM CEMS to be operating within specifications.

(5) Summary of all corrective actions you took when you determined your PM CEMS to be out of control, as described in section 10.5, or after failing on RCA, as described in section 10.6.

10.7 Where and how long must I retain the QA data that this procedure requires me to record for my PM CEMS? You must keep the records required by this procedure for your PM CEMS onsite and available for inspection by us, the State, and/or local enforcement agency for a period of 5 years.

11.0 What Analytical Procedures Apply to This Procedure?

Sample collection and analysis are concurrent for this procedure. You must refer to the appropriate reference method for the specific analytical procedures.

12.0 What Calculations and Data Analysis Must I Perform for my PM CEMS?

(1) How do I determine RCA and RRA acceptability? You must plot each of your PM CEMS and reference method data sets from an RCA or RRA on a graph based on your PM CEMS correlation line to determine if the criteria in paragraphs 10.4(5) or (6), respectively, are met.

(2) How do I calculate ACA accuracy? You must use either Equation 2–1a or 2–1b to calculate ACA accuracy for each of the three audit points. However, when calculating ACA accuracy for the first audit point (0 to 20 percent of measurement range), you must use Equation 2–1b to calculate ACA accuracy if the reference standard value (R_v) equals zero.

$$\text{ACA Accuracy} = \frac{|R_{CEM} - R_V|}{R_V} \times 100\% \qquad \text{Eq. 2-1a}$$

Where:

ACA Accuracy = The ACA accuracy at each audit point, in percent,

R_{CEM} = Your PM CEMS response to the reference standard, and

R_V = The reference standard value.

$$\text{ACA Accuracy} = \frac{|C_{CEM} - C_{RV}|}{C_S} \times 100\% \qquad \text{Eq. 2-1b}$$

Where:

ACA Accuracy = The ACA accuracy at each audit point, in percent,

C_{CEM} = The PM concentration that corresponds to your PM CEMS response to the reference standard, as calculated using the correlation equation for your PM CEMS,

C_{RV} = The PM concentration that corresponds to the reference standard value in units consistent with C_{CEM}, and

C_s = The PM concentration that corresponds to the applicable emission limit in units consistent with C_{CEM}.

(3) How do I calculate daily upscale and zero drift? You must calculate the upscale drift using to Equation 2–2 and the zero drift according to Equation 2–3:

$$UD = \frac{|R_{CEM} - R_U|}{R_U} \times 100 \qquad \text{(Eq. 2-2)}$$

Where:

UD = The upscale drift of your PM CEMS, in percent,

R_{CEM} = Your PM CEMS response to the upscale check value, and

R_U = The upscale check value.

$$ZD = \frac{|R_{CEM} - R_L|}{R_U} \times 100 \qquad \text{(Eq. 2-3)}$$

Where:

ZD = The zero (low-level) drift of your PM CEMS, in percent,

R_{CEM} = Your PM CEMS response of the zero check value,

R_L = The zero check value, and

R_U = The upscale check value.

(4) How do I calculate SVA accuracy? You must use Equation 2–4 to calculate the accuracy, in percent, for each of the three SVA tests or the daily sample volume check:

$$\text{Accuracy} = \frac{(V_R - V_M)}{FS} \times 100 \qquad \text{(Eq. 2-4)}$$

Where:

V_M = Sample gas volume determined/reported by your PM CEMS (*e.g.*, dscm),

V_R = Sample gas volume measured by the independent calibrated reference device (*e.g.*, dscm) for the SVA or the reference value for the daily sample volume check, and

FS = Full-scale value.

NOTE: Before calculating SVA accuracy, you must correct the sample gas volumes

measured by your PM CEMS and the independent calibrated reference device to the same basis of temperature, pressure, and moisture content. You must document all data and calculations.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Which References are Relevant to This Method? [Reserved]

17.0 What Tables, Diagrams, Flowcharts, and Validation Data Are Relevant to This Method? [Reserved]

[52 FR 21008, June 4, 1987; 52 FR 27612, July 22, 1987, as amended at 56 FR 5527, Feb. 11, 1991; 69 FR 1816, Jan. 12, 2004; 72 FR 32768, June 13, 2007; 74 FR 12590, Mar. 25, 2009]

APPENDIX G TO PART 60—PROVISIONS FOR AN ALTERNATIVE METHOD OF DEMONSTRATING COMPLIANCE WITH 40 CFR 60.43 FOR THE NEWTON POWER STATION OF CENTRAL ILLINOIS PUBLIC SERVICE COMPANY

1. *Designation of Affected Facilities*

1.1 The affected facilities to which this alternative compliance method applies are the Unit 1 and 2 coal-fired steam generating units located at the Central Illinois Public Service Company's (CIPS) Newton Power Station in Jasper County, Illinois. Each of these units is subject to the Standards of Performance for Fossil-Fuel-Fired Steam Generators for Which Construction Commenced After August 17, 1971 (subpart D).

2. *Definitions*

2.1 All definitions in subparts D and Da of part 60 apply to this provision except that:

24-hour period means the period of time between 12:00 midnight and the following midnight.

Boiler operating day means a 24-hour period during which any fossil is combusted in either the Unit 1 or Unit 2 steam generating unit and during which the provisions of §60.43(e) are applicable.

CEMs means continuous emission monitoring system.

Coal bunker means a single or group of coal trailers, hoppers, silos or other containers that:

(1) are physically attached to the affected facility; and

(2) provide coal to the coal pulverizers.

DAFGDS means the dual alkali flue gas desulfurization system for the Newton Unit 1 steam generating unit.

3. *Compliance Provisions*

3.1 If the owner or operator of the affected facility elects to comply with the 470 ng/J (1.1 lbs/MMBTU) of combined heat input emission limit under §60.43(e), he shall notify the Regional Administrator, of the United States Environmental Protection Agency (USEPA), Region 5 and the Director, of the Illinois Environmental Protection Agency (IEPA) at least 30 days in advance of the date such election is to take effect, stating the date such operation is to commence. When the owner or operator elects to comply with this limit after one or more periods of reverting to the 520 ng/J heat input (1.2 lbs/MMBTU) limit of §60.43(a)(2), as provided under 3.4, he shall notify the Regional Administrator of the USEPA, Region 5 and the Director of the (IEPA) in writing at least ten (10) days in advance of the date such election is to take effect.

3.2 Compliance with the sulfur dioxide emission limit under §60.43(e) is determined on a continuous basis by performance testing using CEMs. Within 60 days after the initial operation of Units 1 and 2 subject to the combined emission limit in §60.43(e), the owner or operator shall conduct an initial performance test, as required by §60.8, to determine compliance with the combined emission limit. This initial performance test is to be scheduled so that the thirtieth boiler operating day of the 30 successive boiler operating days is completed within 60 days after initial operation subject to the 470 ng/J (1.1 lbs/MMBTU) combined emission limit. Following the initial performance test, a separate performance test is completed at the end of each boiler operating day Unit 1 and Unit 2 are subject to §60.43(e), and a new 30 day average emission rate calculated.

3.2.1 Following the initial performance test, a new 30 day average emission rate is calculated for each boiler operating day the affected facility is subject to §60.43(e). If the owner or operator of the affected facility elects to comply with §60.43(e) after one or more periods of reverting to the 520 ng/J heat input (1.2 lbs/MMBTU) limit under §60.43(a)(2), as provided under 3.4, the 30 day average emission rate under §60.43(e) is calculated using emissions data of the current boiler operating day and data for the previous 29 boiler operating days when the affected facility was subject to §60.43(e). Periods of operation of the affected facility under §60.43(a)(2) are not considered boiler operating days. Emissions data collected during operation under §60.43(a)(2) are not considered relative to 4.6 and emissions data are not included in calculations of emission under §60.43(e).

3.2.2 When the affected facility is operated under the provisions of §60.43(e), the Unit 1 DAFGDS bypass damper must be fully closed. The DAFGDS bypass may be opened only during periods of DAFGDS startup, shutdown, malfunction or testing as described under Sections 3.5.1, 3.5.2, 3.5.3, 3.5.4, and 4.8.2.

While we have taken steps to ensure the accuracy of this Internet version of the document, it is not the official version. The most recent edits to this method were published here: https://www.gpo.gov/fdsys/pkg/FR-2016-08-30/pdf/2016-19642.pdf. To see a complete version including any recent edits, visit: https://www.ecfr.gov/cgi-bin/ECFR?page=browse and search under Title 40, Protection of Environment.

PERFORMANCE SPECIFICATION 1—SPECIFICATIONS AND TEST PROCEDURES FOR CONTINUOUS OPACITY MONITORING SYSTEMS IN STATIONARY SOURCES

1.0 What Is the Purpose and Applicability of Performance Specification 1?

Performance Specification 1 (PS-1) provides (1) requirements for the design, performance, and installation of a continuous opacity monitoring system (COMS) and (2) data computation procedures for evaluating the acceptability of a COMS. It specifies activities for two groups (1) the owner or operator and (2) the opacity monitor manufacturer.

1.1 Measurement Parameter. PS-1 covers the instrumental measurement of opacity caused by attenuation of projected light due to absorption and scatter of the light by particulate matter in the effluent gas stream.

1.2 What COMS must comply with PS-1? If you are an owner or operator of a facility with a COMS as a result of this Part, then PS-1 applies to your COMS if one of the following is true:

(1) Your facility has a new COMS installed after February 6, 2001; or

(2) Your COMS is replaced, relocated, or substantially refurbished (in the opinion of the regulatory authority) after February 6, 2001; or

(3) Your COMS was installed before February 6, 2001 and is specifically required by regulatory action other than the promulgation of PS-1 to be recertified.

If you are an opacity monitor manufacturer, then paragraph 8.2 applies to you.

1.3 Does PS-1 apply to a facility with an applicable opacity limit less than 10 percent? If you are an owner or operator of a facility with a COMS as a result of this Part and the applicable opacity limit is less than 10 percent, then PS-1 applies to your COMS as described in section 1.2; taking into account (through statistical procedures or otherwise) the uncertainties associated with opacity measurements, and following the conditions for attenuators selection for low opacity applications as outlined in section 8.1(3)(ii). At your option, you, the source owner or operator, may select to establish a reduced full scale range of no less than 50 percent opacity instead of the 80 percent as prescribed in section 3.5, if the applicable opacity limit for your facility is less than 10 percent. The EPA recognizes that reducing the range of the analyzer to 50 percent does not necessarily result in any measurable improvement in measurement accuracy at opacity levels less than 10 percent; however, it may allow improved chart recorder interpretation.

1.4 What data uncertainty issues apply to COMS data? The measurement uncertainties associated with COMS data result from several design and performance factors including

limitations on the availability of calibration attenuators for opacities less than about 6 percent (3 percent for single-pass instruments), calibration error tolerances, zero and upscale drift tolerances, and allowance for dust compensation that are significant relative to low opacity levels. The full scale requirements of this PS may also contribute to measurement uncertainty for opacity measurements where the applicable limits are below 10 percent opacity.

2.0 What Are the Basic Requirements of PS-1?

PS-1 requires (1) opacity monitor manufacturers comply with a comprehensive series of design and performance specifications and test procedures to certify opacity monitoring equipment before shipment to the end user, (2) the owner or operator to follow installation guidelines, and (3) the owner or operator to conduct a set of field performance tests that confirm the acceptability of the COMS after it is installed.

2.1 ASTM D 6216-98 is the reference for design specifications, manufacturer's performance specifications, and test procedures. The opacity monitor manufacturer must periodically select and test an opacity monitor, that is representative of a group of monitors produced during a specified period or lot, for conformance with the design specifications in ASTM D 6216-98. The opacity monitor manufacturer must test each opacity monitor for conformance with the manufacturer's performance specifications in ASTM D 6216-98.

2.2 section 8.1(2) provides guidance for locating an opacity monitor in vertical and horizontal ducts. You are encouraged to seek approval for the opacity monitor location from the appropriate regulatory authority prior to installation.

2.3 After the COMS is installed and calibrated, the owner or operator must test the COMS for conformance with the field performance specifications in PS-1.

3.0 What Special Definitions Apply to PS-1?

3.1 All definitions and discussions from section 3 of ASTM D 6216-98 are applicable to PS-1.

3.2 *Centroid Area.* A concentric area that is geometrically similar to the stack or duct cross-section and is no greater than 1 percent of the stack or duct cross-sectional area.

3.3 *Data Recorder.* That portion of the installed COMS that provides a permanent record of the opacity monitor output in terms of opacity. The data recorder may include automatic data reduction capabilities.

3.4 *External Audit Device.* The inherent design, equipment, or accommodation of the opacity monitor allowing the independent assessment of the COMS's calibration and operation.

3.5 *Full Scale.* The maximum data display output of the COMS. For purposes of recordkeeping and reporting, full scale will be greater than 80 percent opacity.

3.6 *Operational Test Period.* A period of time (168 hours) during which the COMS is expected to operate within the established performance specifications without any unscheduled maintenance, repair, or adjustment.

3.7 *Primary Attenuators.* Those devices (glass or grid filter that reduce the transmission of light) calibrated according to procedures in section 7.1.

3.8 *Secondary Attenuators.* Those devices (glass or grid filter that reduce the transmission of light) calibrated against primary attenuators according to procedures in section 7.2.

3.9 *System Response Time.* The amount of time the COMS takes to display 95 percent of a step change in opacity on the COMS data recorder.

4.0 Interferences. Water Droplets

5.0 What Do I Need To Know To Ensure the Safety of Persons Using PS-1?

The procedures required under PS-1 may involve hazardous materials, operations, and equipment. PS-1 does not purport to address all of the safety problems associated with these procedures. Before performing these procedures, you must establish appropriate safety and health practices, and you must determine the applicable regulatory limitations. You should consult the COMS user's manual for specific precautions to take.

6.0 What Equipment and Supplies Do I Need?

6.1 *Continuous Opacity Monitoring System.* You, as owner or operator, are responsible for purchasing an opacity monitor that meets the specifications of ASTM D 6216-98, including a suitable data recorder or automated data acquisition handling system. Example data recorders include an analog strip chart recorder or more appropriately an electronic data acquisition and reporting system with an input signal range compatible with the analyzer output.

6.2 *Calibration Attenuators.* You, as owner or operator, are responsible for purchasing a minimum of three calibration attenuators that meet the requirements of PS-1. Calibration attenuators are optical filters with neutral spectral characteristics. Calibration attenuators must meet the requirements in section 7 and must be of sufficient size to attenuate the entire light beam received by the detector of the COMS. For transmissometers operating over a narrow bandwidth (*e.g.,* laser), a calibration attenuator's value is determined for the actual operating wavelengths of the transmissometer. Some filters may not be uniform across the face. If errors result in the daily calibration drift or calibration error test, you may want to examine the across-face uniformity of the filter.

6.3 *Calibration Spectrophotometer.* Whoever calibrates the attenuators must have a spectrophotometer that meets the following minimum design specifications:

Parameter	Specification
Wavelength range	300-800 nm.
Detector angle of view	<10°.
Accuracy	<0.5% transmittance, NIST traceable calibration.

7.0 What Reagents and Standards Do I Need?

You will need to use attenuators (*i.e.,* neutral density filters) to check the daily calibration drift and calibration error of a COMS. Attenuators are designated as either primary or secondary based on how they are calibrated.

7.1 Attenuators are designated primary in one of two ways:

(1) They are calibrated by NIST; or

(2) They are calibrated on a 6-month frequency through the assignment of a luminous transmittance value in the following manner:

(i) Use a spectrophotometer meeting the specifications of section 6.3 to calibrate the required filters. Verify the spectrophotometer calibration through use of a NIST 930D Standard Reference Material (SRM). A SRM 930D consists of three neutral density glass filters and a blank, each mounted in a cuvette. The wavelengths and temperature to be used in the calibration are listed on the NIST certificate that accompanies the reported values. Determine and record a transmittance of the SRM values at the NIST wavelengths (three filters at five wavelengths each for a total of 15 determinations). Calculate a percent difference between the NIST certified values and the spectrophotometer response. At least 12 of the 15 differences (in percent) must be within ±0.5 percent of the NIST SRM values. No difference can be greater than ±1.0 percent. Recalibrate the SRM or service the spectrophotometer if the calibration results fail the criteria.

(ii) Scan the filter to be tested and the NIST blank from wavelength 380 to 780 nm, and record the spectrophotometer percent transmittance responses at 10 nm intervals. Test in this sequence: blank filter, tested filter, tested filter rotated 90 degrees in the plane of the filter, blank filter. Calculate the average transmittance at each 10 nm interval. If any pair of the tested filter transmittance values (for the same filter and wavelength) differ by more than ±0.25 percent, rescan the tested filter. If the filter fails to achieve this tolerance, do not use the filter in the calibration tests of the COMS.

(iii) Correct the tested filter transmittance values by dividing the average tested filter transmittance by the average blank filter transmittance at each 10 nm interval.

(iv) Calculate the weighted (to the response of the human eye), tested filter transmittance by multiplying the transmittance value by the corresponding response factor shown in table 1-1, to obtain the Source C Human Eye Response.

(v) Recalibrate the primary attenuators semi-annually if they are used for the required calibration error test. Recalibrate the primary attenuators annually if they are used only for calibration of secondary attenuators.

7.2 Attenuators are designated secondary if the filter calibration is done using a laboratory-based transmissometer. Conduct the secondary attenuator calibration using a laboratory-based transmissometer calibrated as follows:

(i) Use at least three primary filters of nominal luminous transmittance 50, 70 and 90 percent, calibrated as specified in section 7.1(2)(i), to calibrate the laboratory-based transmissometer. Determine and record the slope of the calibration line using linear regression through zero opacity. The slope of the calibration line must be between 0.99 and 1.01, and the laboratory-based transmissometer reading for each primary filter must not deviate by more than ±2 percent from the linear regression line. If the calibration of the laboratory-based transmissometer yields a slope or individual readings outside the specified ranges, secondary filter calibrations cannot be performed. Determine the source of the variations (either transmissometer performance or changes in the primary filters) and repeat the transmissometer calibration before proceeding with the attenuator calibration.

(ii) Immediately following the laboratory-based transmissometer calibration, insert the secondary attenuators and determine and record the percent effective opacity value per secondary attenuator from the calibration curve (linear regression line).

(iii) Recalibrate the secondary attenuators semi-annually if they are used for the required calibration error test.

8.0 What Performance Procedures Are Required To Comply With PS-1?

Procedures to verify the performance of the COMS are divided into those completed by the owner or operator and those completed by the opacity monitor manufacturer.

8.1 What procedures must I follow as the Owner or Operator?

(1) You must purchase an opacity monitor that complies with ASTM D 6216-98 and obtain a certificate of conformance from the opacity monitor manufacturer.

(2) You must install the opacity monitor at a location where the opacity measurements are representative of the total emissions from the affected facility. You must meet this requirement by choosing a measurement location and a light beam path as follows:

(i) Measurement Location. Select a measurement location that is (1) at least 4 duct diameters downstream from all particulate control equipment or flow disturbance, (2) at least 2 duct diameters upstream of a flow disturbance, (3) where condensed water vapor is not present, and (4) accessible in order to permit maintenance.

Alternatively, you may select a measurement location specified in paragraph 8.1(2)(ii) or 8.1(2)(iii).

(ii) Light Beam Path. Select a light beam path that passes through the centroidal area of the stack or duct. Also, you must follow these additional requirements or modifications for these measurement locations:

If your measurement location is in a:	**And is:**	**Then use a light beam path that is:**
1. Straight vertical section of stack or duct	Less than 4 equivalent diameters downstream from a bend	In the plane defined by the upstream bend (see figure 1-1).
2. Straight vertical section of stack or duct	Less than 4 equivalent diameters upstream from a bend	In the plane defined by the downstream bend (see figure 1-2).
3. Straight vertical section of stack or duct	Less than 4 equivalent diameters downstream and is also less than 1 diameter upstream from a bend	In the plane defined by the upstream bend (see figure 1-3).
4. Horizontal section of stack or duct	At least 4 equivalent diameters downstream from a vertical bend	In the horizontal plane that is between 1/3 and 1/2 the distance up the vertical axis from the bottom of the duct (see figure 1-4).
5. Horizontal section of duct	Less than 4 equivalent diameters downstream from a vertical bend	In the horizontal plane that is between 1/2 and 2/3 the distance up the vertical axis from the bottom of the duct for upward flow in the vertical section, and is between 1/3 and 1/2 the distance up the vertical axis from the bottom of the duct for downward flow (figure 1-5).

(iii) Alternative Locations and Light Beam Paths. You may select locations and light beam paths, other than those cited above, if you demonstrate, to the satisfaction of the Administrator or delegated agent, that the average opacity measured at the alternative location or path is equivalent to the opacity as measured at a location meeting the criteria of sections 8.1(2)(i) and 8.1(2)(ii). The opacity at the alternative location is considered equivalent if (1) the average opacity value measured at the alternative location is within ±10 percent of the average opacity value measured at the location meeting the installation criteria, and (2) the difference between any two average opacity values is less than 2 percent opacity (absolute). You use the following procedure to conduct this demonstration: simultaneously measure the opacities at the two locations or paths for a minimum period of time (*e.g.,* 180-minutes) covering the range of normal operating conditions and compare the results. The opacities of the two locations or paths may be measured at different times, but must represent the same process operating conditions. You may

use alternative procedures for determining acceptable locations if those procedures are approved by the Administrator.

(3) Field Audit Performance Tests. After you install the COMS, you must perform the following procedures and tests on the COMS.

(i) Optical Alignment Assessment. Verify and record that all alignment indicator devices show proper alignment. A clear indication of alignment is one that is objectively apparent relative to reference marks or conditions.

(ii) Calibration Error Check. Conduct a three-point calibration error test using three calibration attenuators that produce outlet pathlength corrected, single-pass opacity values shown in ASTM D 6216-98, section 7.5. If your applicable limit is less than 10 percent opacity, use attenuators as described in ASTM D 6216-98, section 7.5 for applicable standards of 10 to 19 percent opacity. Confirm the external audit device produces the proper zero value on the COMS data recorder. Separately, insert each calibration attenuators (low, mid, and high-level) into the external audit device. While inserting each attenuator, (1) ensure that the entire light beam passes through the attenuator, (2) minimize interference from reflected light, and (3) leave the attenuator in place for at least two times the shortest recording interval on the COMS data recorder. Make a total of five nonconsecutive readings for each attenuator. At the end of the test, correlate each attenuator insertion to the corresponding value from the data recorder. Subtract the single-pass calibration attenuator values corrected to the stack exit conditions from the COMS responses. Calculate the arithmetic mean difference, standard deviation, and confidence coefficient of the five measurements value using equations 1-3, 1-4, and 1-5. Calculate the calibration error as the sum of the absolute value of the mean difference and the 95 percent confidence coefficient for each of the three test attenuators using equation 1-6. Report the calibration error test results for each of the three attenuators.

(iii) System Response Time Check. Using a high-level calibration attenuator, alternately insert the filter five times and remove it from the external audit device. For each filter insertion and removal, measure the amount of time required for the COMS to display 95 percent of the step change in opacity on the COMS data recorder. For the upscale response time, measure the time from insertion to display of 95 percent of the final, steady upscale reading. For the downscale response time, measure the time from removal to display 5 percent of the initial upscale reading. Calculate the mean of the five upscale response time measurements and the mean of the five downscale response time measurements. Report both the upscale and downscale response times.

(iv) Averaging Period Calculation and Recording Check. After the calibration error check, conduct a check of the averaging period calculation (e.g., 6-minute integrated average). Consecutively insert each of the calibration error check attenuators (low, mid, and high-level) into the external audit device for a period of two times the averaging period plus 1 minute (e.g., 13 minutes for a 6-minute averaging period). Compare the path length corrected opacity value of each attenuator to the valid average value calculated by the COMS data recording device for that attenuator.

(4) Operational Test Period. Before conducting the operational testing, you must have successfully completed the field audit tests described in sections 8.1(3)(i) through 8.1(3)(iv). Then, you operate the COMS for an initial 168-hour test period while the source is operating under normal operating conditions. If normal operations contain routine source shutdowns, include the source's down periods in the 168-hour operational test period. However, you must ensure that the following minimum source operating time is included in the operational test period: (1) For a batch operation, the operational test period must include at least one full cycle of batch operation during the 168-hour period unless the batch operation is longer than 168 hours or (2) for continuous operating processes, the unit must be operating for at least 50 percent of the 168-hour period. Except during times of instrument zero and upscale calibration drift checks, you must analyze the effluent gas for opacity and produce a permanent record of the COMS output. During this period, you may not perform unscheduled maintenance, repair, or adjustment to the COMS. Automatic zero and calibration adjustments (*i.e.,* intrinsic adjustments), made by the COMS without operator intervention or initiation, are allowable at any time. At the end of the operational test period, verify and record that the COMS optical alignment is still correct. If the test period is interrupted because of COMS failure, record the time when the failure occurred. After the failure is corrected, you restart the 168-hour period and tests from the beginning (0-hour). During the operational test period, perform the following test procedures:

(i) Zero Calibration Drift Test. At the outset of the 168-hour operational test period and at each 24-hour interval, the automatic calibration check system must initiate the simulated zero device to allow the zero drift to be determined. Record the COMS response to the simulated zero device. After each 24-hour period, subtract the COMS zero reading from the nominal value of the simulated zero device to calculate the 24-hour zero drift (ZD). At the end of the 168-hour period, calculate the arithmetic mean, standard deviation, and confidence coefficient of the 24-hour ZDs using equations 1-3, 1-4, and 1-5. Calculate the sum of the absolute value of the mean and the absolute value of the confidence coefficient using equation 1-6, and report this value as the 24-hour ZD error.

(ii) Upscale Calibration Drift Test. At each 24-hour interval after the simulated zero device value has been checked, check and record the COMS response to the upscale calibration device. After each 24-hour period, subtract the COMS upscale reading from the nominal value of the upscale calibration device to calculate the 24-hour calibration drift (CD). At the end of the 168-hour period, calculate the arithmetic mean, standard deviation, and confidence coefficient of the 24-hour CD using equations 1-3, 1-4, and 1-5. Calculate the sum of the absolute value of the mean and the absolute value of the confidence coefficient using equation 1-6, and report this value as the 24-hour CD error.

(5) Retesting. If the COMS fails to meet the specifications for the tests conducted under the operational test period, make the necessary corrections and restart the operational test period. Depending on the opinion of the enforcing agency, you may have to repeat some or all of the field audit tests.

8.2 What are the responsibilities of the Opacity Monitor Manufacturer?

You, the manufacturer, must carry out the following activities:

(1) Conduct the verification procedures for design specifications in section 6 of ASTM D 6216-98.

(2) Conduct the verification procedures for performance specifications in section 7 of ASTM D 6216-98.

(3) Provide to the owner or operator, a report of the opacity monitor's conformance to the design and performance specifications required in sections 6 and 7 of ASTM D 6216-98 in accordance with the reporting requirements of section 9 in ASTM D 6216-98.

9.0 What quality control measures are required by PS-1?

Opacity monitor manufacturers must initiate a quality program following the requirements of ASTM D 6216-98, section 8. The quality program must include (1) a quality system and (2) a corrective action program.

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure [Reserved]

12.0 What Calculations Are Needed for PS-1?

12.1 Desired Attenuator Values. Calculate the desired attenuator value corrected to the emission outlet path length as follows:

$$OP_2 = 1 - (1 - OP_1)^{\frac{L_2}{L_1}} \qquad Eq.\ 1\text{-}1$$

Where:

OP_1 = Nominal opacity value of required low-, mid-, or high-range calibration attenuators.

OP_2 = Desired attenuator opacity value from ASTM D 6216-98, section 7.5 at the opacity limit required by the applicable subpart.

L_1 = Monitoring pathlength.

L_2 = Emission outlet pathlength.

12.2 Luminous Transmittance Value of a Filter. Calculate the luminous transmittance of a filter as follows:

$$LT = \frac{\sum_{i=300_{nm}}^{i=800_{nm}} T_i}{100,000} \qquad Eq.\ 1\text{-}2$$

Where:

LT = Luminous transmittance

T_i = Weighted tested filter transmittance.

12.3 Arithmetic Mean. Calculate the arithmetic mean of a data set as follows:

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i \qquad Eq.\ 1\text{-}3$$

Where:

$\bar{x}$ = Arithmetic mean

n=Number of data points

$\sum_{i=1}^{n} x_i$ = Algebraic sum of the individual measurements,

x_i.

12.4 Standard Deviation. Calculate the standard deviation as follows:

$$S_d = \sqrt{\frac{\sum_{i=1}^{n} x_i^2 - \frac{\left(\sum_{i=1}^{n} x_i\right)^2}{n}}{n-1}} \qquad \text{Eq. 1-4}$$

Where:

S_d = Standard deviation of a data set.

12.5 Confidence Coefficient. Calculate the 2.5 percent error confidence coefficient (one-tailed) as follows:

$$CC = \frac{t_{0.975} S_d}{\sqrt{n}} \qquad \text{Eq. 1-5}$$

Where:

CC = Confidence coefficient

$t_{0.975}$ = t − value (see table 1-2).

12.6 Calibration Error. Calculate the error (calibration error, zero drift error, and calibration drift error) as follows:

$$Er = |\bar{x}| + |CC| \qquad \text{Eq. 1-6}$$

Where:

Er = Error.

12.7 Conversion of Opacity Values for Monitor Pathlength to Emission Outlet Pathlength. When the monitor pathlength is different from the emission outlet pathlength, use either of the following equations to convert from one basis to the other (this conversion may be automatically calculated by the monitoring system):

$$\log\ (1-Op_2) = \frac{L_2}{L_1} \log\ (1-Op_1) \qquad Eq.\ 1\text{-}7$$

$$OD_2 = \frac{L_2}{L_1} \times OD_1 \qquad Eq.\ 1\text{-}8$$

Where:

Op_1 = Opacity of the effluent based upon L_1.

Op_2 = Opacity of the effluent based upon L_2.

L_1 = Monitor pathlength.

L_2 = Emission outlet pathlength.

OD_1 = Optical density of the effluent based upon L_1.

OD_2 = Optical density of the effluent based upon L_2.

12.8 Mean Response Wavelength. Calculate the mean of the effective spectral response curve from the individual responses at the specified wavelength values as follows:

$$L = \frac{\sum_{i=1}^{n} L_i g_i}{\sum_{i=1}^{n} g_i} \qquad Eq.\ 1\text{-}9$$

Where:

L = mean of the effective spectral response curve

L_i = The specified wavelength at which the response g_i is calculated at 20 nm intervals.

g_i = The individual response value at L_i.

13.0 What Specifications Does a COMS Have To Meet for Certification?

A COMS must meet the following design, manufacturer's performance, and field audit performance specifications:

13.1 Design Specifications. The opacity monitoring equipment must comply with the design specifications of ASTM D 6216-98.

13.2 Manufacturer's Performance Specifications. The opacity monitor must comply with the manufacturer's performance specifications of ASTM D 6216-98.

13.3 Field Audit Performance Specifications. The installed COMS must comply with the following performance specifications:

(1) Optical Alignment. Objectively indicate proper alignment relative to reference marks (*e.g.,* bull's-eye) or conditions.

(2) Calibration Error. The calibration error must be ≤3 percent opacity for each of the three calibration attenuators.

(3) System Response Time. The COMS upscale and downscale response times must be ≤10 seconds as measured at the COMS data recorder.

(4) Averaging Period Calculation and Recording. The COMS data recorder must average and record each calibration attenuator value to within ±2 percent opacity of the certified value of the attenuator.

(5) Operational Test Period. The COMS must be able to measure and record opacity and to perform daily calibration drift assessments for 168 hours without unscheduled maintenance, repair, or adjustment.

(6) Zero and Upscale Calibration Drift Error. The COMS zero and upscale calibration drift error must not exceed 2 percent opacity over a 24 hour period.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Which references are relevant to this method?

1. Experimental Statistics. Department of Commerce. National Bureau of Standards Handbook 91. Paragraph 3-3.1.4. 1963. 3-31 p.

2. Performance Specifications for Stationary Source Monitoring Systems for Gases and Visible Emissions, EPA-650/2-74-013, January 1974, U. S. Environmental Protection Agency, Research Triangle Park, NC.

3. Koontz, E.C., Walton, J. Quality Assurance Programs for Visible Emission Evaluations. Tennessee Division of Air Pollution Control. Nashville, TN. 78th Meeting of the Air Pollution Control Association. Detroit, MI. June 16-21, 1985.

4. Evaluation of Opacity CEMS Reliability and Quality Assurance Procedures. Volume 1. U. S. Environmental Protection Agency. Research Triangle Park, NC. EPA-340/1-86-009a.

5. Nimeroff, I. "Colorimetry Precision Measurement and Calibration." NBS Special Publication 300. Volume 9. June 1972.

6. Technical Assistance Document: Performance Audit Procedures for Opacity Monitors. U. S. Environmental Protection Agency. Research Triangle Park, NC. EPA-600/8-87-025. April 1987.

7. Technical Assistance Document: Performance Audit Procedures for Opacity Monitors. U. S. Environmental Protection Agency. Research Triangle Park, NC. EPA-450/4-92-010. April 1992.

8. ASTM D 6216-98: Standard Practice for Opacity Monitor Manufacturers to Certify Conformance with Design and Performance Specifications. American Society for Testing and Materials (ASTM). April 1998.

17.0 What tables and diagrams are relevant to this method?

17.1 Reference Tables.

TABLE 1-1—SOURCE C, HUMAN EYE RESPONSE FACTOR

Wavelength nanometers	Weighting factor[a]	Wavelength nanometers	Weighting factor[a]
380	0	590	6627
390	0	600	5316
400	2	610	4176
410	9	620	3153
420	37	630	2190
430	122	640	1443
440	262	650	886
450	443	660	504
460	694	670	259

470	1058	680	134
480	1618	690	62
490	2358	700	29
500	3401	720	14
510	4833	720	6
520	6462	730	3
530	7934	740	2
540	9194	750	1
550	9832	760	1
560	9841	770	0
570	9147	780	0
580	7992		

[1]Total of weighting factors = 100,000.

TABLE 1-2[T] VALUES

n[a]	**t0.975**	**n[a]**	**t0.975**	**n[a]**	**t0.975**
2	12.706	7	2.447	12	2.201
3	4.303	8	2.365	13	2.179
4	3.182	9	2.306	14	2.160
5	2.776	10	2.262	15	2.145
6	2.571	11	2.228	16	2.131

[a]The values in this table are already corrected for n-1 degrees of freedom. Use n equal to the number of individual values.

17.2 Diagrams.

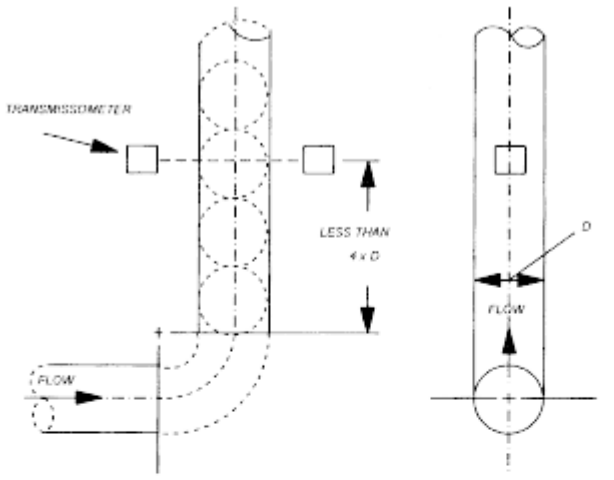


Figure 1-1. Transmissometer location downstream of a bend in a vertical stack.

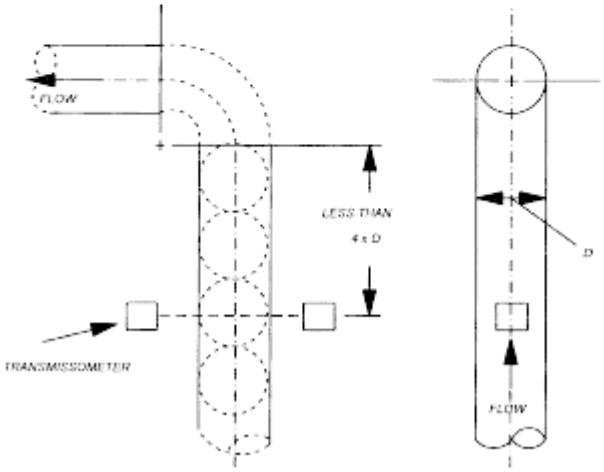


Figure 1-2. Transmissometer location upstream of a bend in a vertical stack.

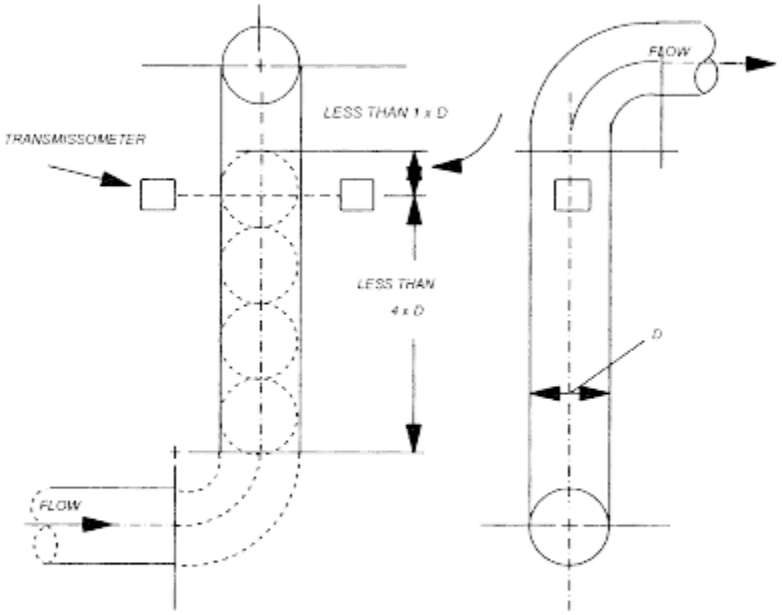


Figure 1-3. Transmissometer location between bends in a vertical stack.

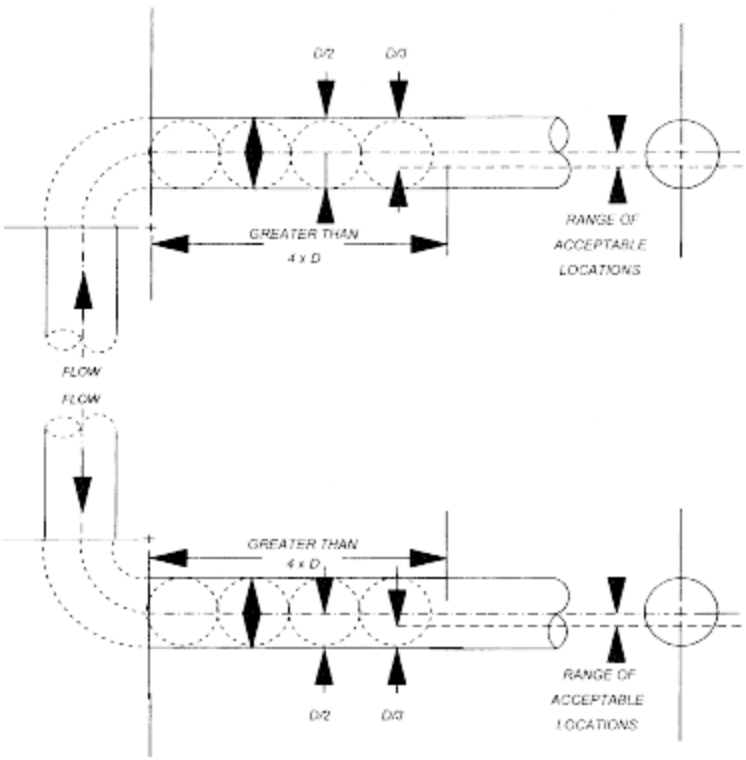


Figure 1-4. Transmissometer location greater than four diameters downstream of a vertical bend in a horizontal stack or duct.

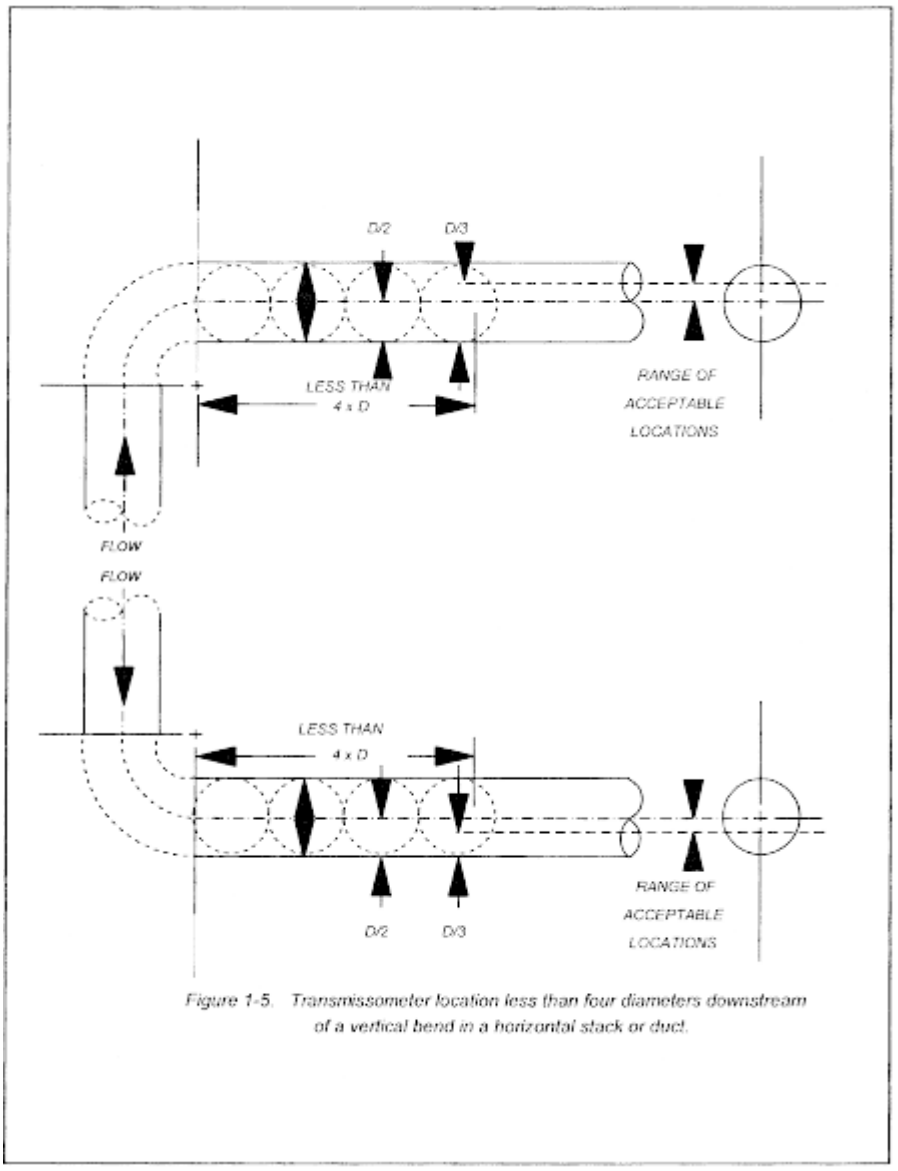


Figure 1-5. Transmissometer location less than four diameters downstream of a vertical bend in a horizontal stack or duct.

While we have taken steps to ensure the accuracy of this Internet version of the document, it is not the official version. The most recent edits to this method were published here: https://www.gpo.gov/fdsys/pkg/FR-2016-08-30/pdf/2016-19642.pdf. To see a complete version including any recent edits, visit: https://www.ecfr.gov/cgi-bin/ECFR?page=browse and search under Title 40, Protection of Environment.

PERFORMANCE SPECIFICATION 2—SPECIFICATIONS AND TEST PROCEDURES FOR SO_2 AND NO_X CONTINUOUS EMISSION MONITORING SYSTEMS IN STATIONARY SOURCES

1.0 Scope and Application

1.1 Analytes

Analyte	**CAS Nos.**
Sulfur Dioxide (SO_2)	7449-09-5
Nitrogen Oxides (NO_X)	10102-44-0 (NO_2), 10024-97-2 (NO)

1.2 Applicability.

1.2.1 This specification is for evaluating the acceptability of SO_2 and NO_X continuous emission monitoring systems (CEMS) at the time of installation or soon after and whenever specified in the regulations. The CEMS may include, for certain stationary sources, a diluent (O_2 or CO_2) monitor.

1.2.2 This specification is not designed to evaluate the installed CEMS performance over an extended period of time nor does it identify specific calibration techniques and other auxiliary procedures to assess the CEMS performance. The source owner or operator is responsible to calibrate, maintain, and operate the CEMS properly. The Administrator may require, under section 114 of the Act, the operator to conduct CEMS performance evaluations at other times besides the initial test to evaluate the CEMS performance. See 40 CFR Part 60, §60.13(c).

2.0 Summary of Performance Specification

Procedures for measuring CEMS relative accuracy and calibration drift are outlined. CEMS installation and measurement location specifications, equipment specifications, performance specifications, and data reduction procedures are included. Conformance of the CEMS with the Performance Specification is determined.

3.0 Definitions

3.1 *Calibration Drift (CD)* means the difference in the CEMS output readings from the established reference value after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

3.2 *Centroidal Area* means a concentric area that is geometrically similar to the stack or duct cross section and is no greater than l percent of the stack or duct cross-sectional area.

3.3 *Continuous Emission Monitoring System* means the total equipment required for the determination of a gas concentration or emission rate. The sample interface, pollutant analyzer, diluent analyzer, and data recorder are the major subsystems of the CEMS.

3.4 *Data Recorder* means that portion of the CEMS that provides a permanent record of the analyzer output. The data recorder may include automatic data reduction capabilities.

3.5 *Diluent Analyzer* means that portion of the CEMS that senses the diluent gas (*i.e.,* CO_2 or O_2) and generates an output proportional to the gas concentration.

3.6 *Path CEMS* means a CEMS that measures the gas concentration along a path greater than 10 percent of the equivalent diameter of the stack or duct cross section.

3.7 *Point CEMS* means a CEMS that measures the gas concentration either at a single point or along a path equal to or less than 10 percent of the equivalent diameter of the stack or duct cross section.

3.8 *Pollutant Analyzer* means that portion of the CEMS that senses the pollutant gas and generates an output proportional to the gas concentration.

3.9 *Relative Accuracy (RA)* means the absolute mean difference between the gas concentration or emission rate determined by the CEMS and the value determined by the reference method (RM), plus the 2.5 percent error confidence coefficient of a series of tests, divided by the mean of the RM tests or the applicable emission limit.

3.10 *Sample Interface* means that portion of the CEMS used for one or more of the following: sample acquisition, sample delivery, sample conditioning, or protection of the monitor from the effects of the stack effluent.

3.11 *Span Value* means the calibration portion of the measurement range as specified in the applicable regulation or other requirement. If the span is not specified in the applicable regulation or other requirement, then it must be a value approximately equivalent to two times the emission standard. For spans less than 500 ppm, the span value may either be rounded upward to the next highest multiple of 10 ppm, or to the next highest multiple of 100 ppm such that the equivalent emission concentration is not less than 30 percent of the selected span value.

4.0 Interferences [Reserved]

5.0 Safety

The procedures required under this performance specification may involve hazardous materials, operations, and equipment. This performance specification may not address all of the safety problems associated with these procedures. It is the responsibility of the user to establish

appropriate safety and health practices and determine the applicable regulatory limitations prior to performing these procedures. The CEMS user's manual and materials recommended by the reference method should be consulted for specific precautions to be taken.

6.0 Equipment and Supplies

6.1 CEMS Equipment Specifications.

6.1.1 Data Recorder. The portion of the CEMS that provides a record of analyzer output. The data recorder may record other pertinent data such as effluent flow rates, various instrument temperatures or abnormal CEMS operation. The data recorder output range must include the full range of expected concentration values in the gas stream to be sampled including zero and span values.

6.1.2 The CEMS design should also allow the determination of calibration drift at the zero and span values. If this is not possible or practical, the design must allow these determinations to be conducted at a low-level value (zero to 20 percent of the span value) and at a value between 50 and 100 percent of the span value. In special cases, the Administrator may approve a single-point calibration drift determination.

6.2 Other equipment and supplies, as needed by the applicable reference method(s) (see section 8.4.2 of this Performance Specification), may be required.

7.0 Reagents and Standards

7.1 Reference Gases, Gas Cells, or Optical Filters. As specified by the CEMS manufacturer for calibration of the CEMS (these need not be certified).

7.2 Reagents and Standards. May be required as needed by the applicable reference method(s) (see section 8.4.2 of this Performance Specification).

8.0 Performance Specification Test Procedure

8.1 Installation and Measurement Location Specifications.

8.1.1 CEMS Installation. Install the CEMS at an accessible location where the pollutant concentration or emission rate measurements are directly representative or can be corrected so as to be representative of the total emissions from the affected facility or at the measurement location cross section. Then select representative measurement points or paths for monitoring in locations that the CEMS will pass the RA test (see section 8.4). If the cause of failure to meet the RA test is determined to be the measurement location and a satisfactory correction technique cannot be established, the Administrator may require the CEMS to be relocated. Suggested measurement locations and points or paths that are most likely to provide data that will meet the RA requirements are listed below.

8.1.2 CEMS Measurement Location. It is suggested that the measurement location be (1) at least two equivalent diameters downstream from the nearest control device, the point of pollutant

generation, or other point at which a change in the pollutant concentration or emission rate may occur and (2) at least a half equivalent diameter upstream from the effluent exhaust or control device.

8.1.2.1 Point CEMS. It is suggested that the measurement point be (1) no less than 1.0 meter (3.3 ft) from the stack or duct wall or (2) within or centrally located over the centroidal area of the stack or duct cross section.

8.1.2.2 Path CEMS. It is suggested that the effective measurement path (1) be totally within the inner area bounded by a line 1.0 meter (3.3 ft) from the stack or duct wall, or (2) have at least 70 percent of the path within the inner 50 percent of the stack or duct cross-sectional area, or (3) be centrally located over any part of the centroidal area.

8.1.3 Reference Method Measurement Location and Traverse Points.

8.1.3.1 Select, as appropriate, an accessible RM measurement point at least two equivalent diameters downstream from the nearest control device, the point of pollutant generation, or other point at which a change in the pollutant concentration or emission rate may occur, and at least a half equivalent diameter upstream from the effluent exhaust or control device. When pollutant concentration changes are due solely to diluent leakage (*e.g.,* air heater leakages) and pollutants and diluents are simultaneously measured at the same location, a half diameter may be used in lieu of two equivalent diameters. The CEMS and RM locations need not be the same.

8.1.3.2 Select traverse points that assure acquisition of representative samples over the stack or duct cross section. The minimum requirements are as follows: Establish a “measurement line” that passes through the centroidal area and in the direction of any expected stratification. If this line interferes with the CEMS measurements, displace the line up to 30 cm (12 in.) (or 5 percent of the equivalent diameter of the cross section, whichever is less) from the centroidal area. Locate three traverse points at 16.7, 50.0, and 83.3 percent of the measurement line. If the measurement line is longer than 2.4 meters (7.8 ft) and pollutant stratification is not expected, the three traverse points may be located on the line at 0.4, 1.2, and 2.0 meters from the stack or duct wall. This option must not be used after wet scrubbers or at points where two streams with different pollutant concentrations are combined. If stratification is suspected, the following procedure is suggested. For rectangular ducts, locate at least nine sample points in the cross section such that sample points are the centroids of similarly-shaped, equal area divisions of the cross section. Measure the pollutant concentration, and, if applicable, the diluent concentration at each point using appropriate reference methods or other appropriate instrument methods that give responses relative to pollutant concentrations. Then calculate the mean value for all sample points. For circular ducts, conduct a 12-point traverse (*i.e.,* six points on each of the two perpendicular diameters) locating the sample points as described in 40 CFR 60, Appendix A, Method 1. Perform the measurements and calculations as described above. Determine if the mean pollutant concentration is more than 10% different from any single point. If so, the cross section is considered to be stratified, and the tester may not use the alternative traverse point locations (...0.4, 1.2, and 2.0 meters from the stack or duct wall.) but must use the three traverse points at 16.7, 50.0, and 83.3 percent of the entire measurement line. Other traverse points may be selected, provided that they can be shown to the satisfaction of the Administrator to provide a

representative sample over the stack or duct cross section. Conduct all necessary RM tests within 3 cm (1.2 in.) of the traverse points, but no closer than 3 cm (1.2 in.) to the stack or duct wall.

8.2 Pretest Preparation. Install the CEMS, prepare the RM test site according to the specifications in section 8.1, and prepare the CEMS for operation according to the manufacturer's written instructions.

8.3 Calibration Drift Test Procedure.

8.3.1 *CD Test Period.* While the affected facility is operating, determine the magnitude of the CD once each day (at 24-hour intervals) for 7 consecutive calendar days according to the procedure given in sections 8.3.2 through 8.3.4. Alternatively, the CD test may be conducted over 7 consecutive unit operating days.

8.3.2 The purpose of the CD measurement is to verify the ability of the CEMS to conform to the established CEMS calibration used for determining the emission concentration or emission rate. Therefore, if periodic automatic or manual adjustments are made to the CEMS zero and calibration settings, conduct the CD test immediately before these adjustments, or conduct it in such a way that the CD can be determined.

8.3.3 Conduct the CD test at the two points specified in section 6.1.2. Introduce to the CEMS the reference gases, gas cells, or optical filters (these need not be certified). Record the CEMS response and subtract this value from the reference value (see example data sheet in Figure 2-1).

8.4 Relative Accuracy Test Procedure.

8.4.1 RA Test Period. Conduct the RA test according to the procedure given in sections 8.4.2 through 8.4.6 while the affected facility is operating at more than 50 percent of normal load, or as specified in an applicable subpart. The RA test may be conducted during the CD test period.

8.4.2 Reference Methods. Unless otherwise specified in an applicable subpart of the regulations, Methods 3B, 4, 6, and 7, or their approved alternatives, are the reference methods for diluent (O_2 and CO_2), moisture, SO_2, and NO_X, respectively.

8.4.3 Sampling Strategy for RM Tests. Conduct the RM tests in such a way that they will yield results representative of the emissions from the source and can be correlated to the CEMS data. It is preferable to conduct the diluent (if applicable), moisture (if needed), and pollutant measurements simultaneously. However, diluent and moisture measurements that are taken within an hour of the pollutant measurements may be used to calculate dry pollutant concentration and emission rates. In order to correlate the CEMS and RM data properly, note the beginning and end of each RM test period of each run (including the exact time of day) on the CEMS chart recordings or other permanent record of output. Use the following strategies for the RM tests:

8.4.3.1 For integrated samples (*e.g.,* Methods 6 and Method 4), make a sample traverse of at least 21 minutes, sampling for an equal time at each traverse point (see section 8.1.3.2 for discussion of traverse points.

8.4.3.2 For grab samples (*e.g.,* Method 7), take one sample at each traverse point, scheduling the grab samples so that they are taken simultaneously (within a 3-minute period) or at an equal interval of time apart over the span of time the CEM pollutant is measured. A test run for grab samples must be made up of at least three separate measurements.

NOTE: At times, CEMS RA tests are conducted during new source performance standards performance tests. In these cases, RM results obtained during CEMS RA tests may be used to determine compliance as long as the source and test conditions are consistent with the applicable regulations.

8.4.4 Number of RM Tests. Conduct a minimum of nine sets of all necessary RM test runs.

NOTE: More than nine sets of RM tests may be performed. If this option is chosen, a maximum of three sets of the test results may be rejected so long as the total number of test results used to determine the RA is greater than or equal to nine. However, all data must be reported, including the rejected data.

8.4.5 Correlation of RM and CEMS Data. Correlate the CEMS and the RM test data as to the time and duration by first determining from the CEMS final output (the one used for reporting) the integrated average pollutant concentration or emission rate for each pollutant RM test period. Consider system response time, if important, and confirm that the pair of results are on a consistent moisture, temperature, and diluent concentration basis. Then, compare each integrated CEMS value against the corresponding average RM value. Use the following guidelines to make these comparisons.

8.4.5.1 If the RM has an integrated sampling technique, make a direct comparison of the RM results and CEMS integrated average value.

8.4.5.2 If the RM has a grab sampling technique, first average the results from all grab samples taken during the test run, and then compare this average value against the integrated value obtained from the CEMS chart recording or output during the run. If the pollutant concentration is varying with time over the run, the arithmetic average of the CEMS value recorded at the time of each grab sample may be used.

8.4.6 Calculate the mean difference between the RM and CEMS values in the units of the emission standard, the standard deviation, the confidence coefficient, and the relative accuracy according to the procedures in section 12.0.

8.5 Reporting. At a minimum (check with the appropriate regional office, State, or Local agency for additional requirements, if any), summarize in tabular form the results of the CD tests and the RA tests or alternative RA procedure, as appropriate. Include all data sheets, calculations, charts (records of CEMS responses), cylinder gas concentration certifications, and calibration cell

response certifications (if applicable) necessary to confirm that the performance of the CEMS met the performance specifications.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

Sample collection and analysis are concurrent for this Performance Specification (see section 8.0). Refer to the RM for specific analytical procedures.

12.0 Calculations and Data Analysis

Summarize the results on a data sheet similar to that shown in Figure 2-2 (in section 18.0).

12.1 All data from the RM and CEMS must be on a consistent dry basis and, as applicable, on a consistent diluent basis and in the units of the emission standard. Correct the RM and CEMS data for moisture and diluent as follows:

12.1.1 Moisture Correction (as applicable). Correct each wet RM run for moisture with the corresponding Method 4 data; correct each wet CEMS run using the corresponding CEMS moisture monitor date using Equation 2-1.

$$\text{Concentration}_{(\text{dry})} = \frac{Concentration_{wet}}{(1 - B_{ws})} \qquad \text{Eq. 2-1}$$

12.1.2 Correction to Units of Standard (as applicable). Correct each dry RM run to the units of the emission standard with the corresponding Method 3B data; correct each dry CEMS run using the corresponding CEMS diluent monitor data as follows:

12.1.2.1 Correct to Diluent Basis. The following is an example of concentration (ppm) correction to 7% oxygen.

$$\text{ppm}_{(\text{corr})} = \text{ppm}_{(\text{uncorr})}\left[\frac{20.9 - 7.0}{20.9 - \%O_{2(dry)}}\right] \qquad \text{Eq. 2-2}$$

The following is an example of mass/gross calorific value (lbs/million Btu) correction.
lbs/MMBtu = $\text{Conc}_{(\text{dry})}$ (F-factor) (20.9/20.9-%0_2)

12.2 Arithmetic Mean. Calculate the arithmetic mean of the difference, d, of a data set as follows:

$$\bar{d} = \frac{1}{n}\sum_{i=1}^{n} d_i \qquad \text{Eq. 2-3}$$

Where:

n = Number of data points.

$\sum_{i=1}^{n} d_i$ = Algebraic summation of the individual differences d_i.

12.3 Standard Deviation. Calculate the standard deviation, S_d, as follows:

$$S_d = \left[\frac{\sum_{i=1}^{n} d_i^2 - \frac{\left[\sum_{i=1}^{n} d_i\right]^2}{n}}{n-1} \right]^{\frac{1}{2}} \qquad Eq.\ 2\text{-}4$$

12.4 Confidence Coefficient. Calculate the 2.5 percent error confidence coefficient (one-tailed), CC, as follows:

$$CC = t_{0.975} \frac{S_d}{\sqrt{n}} \qquad Eq.\ 2\text{-}5$$

Where:

$t_{0.975}$ = t-value (see Table 2-1).

12.5 Relative Accuracy. Calculate the RA of a set of data as follows:

$$RA = \frac{\left[\left|\bar{d}\right| + \left|CC\right|\right]}{\overline{RM}} \times 100 \qquad Eq.\ 2\text{-}6$$

Where:

$|\bar{d}|$ = Absolute value of the mean differences (from Equation 2-3).

|CC| = Absolute value of the confidence coefficient (from Equation 2-3).

RM = Average RM value. In cases where the average emissions for the test are less than 50 percent of the applicable standard, substitute the emission standard value in the denominator of Eq. 2-6 in place of RM. In all other cases, use RM.

13.0 Method Performance

13.1 Calibration Drift Performance Specification. The CEMS calibration must not drift or deviate from the reference value of the gas cylinder, gas cell, or optical filter by more than 2.5 percent of the span value. If the CEMS includes pollutant and diluent monitors, the CD must be determined separately for each in terms of concentrations (See Performance Specification 3 for the diluent specifications), and none of the CDs may exceed the specification.

13.2 Relative Accuracy Performance Specification. The RA of the CEMS must be no greater than 20 percent when $R\bar{M}$ is used in the denominator of Eq. 2-6 (average emissions during test are greater than 50 percent of the emission standard) or 10 percent when the applicable emission standard is used in the denominator of Eq. 2-6 (average emissions during test are less than 50 percent of the emission standard). For SO_2 emission standards of 130 to and including 86 ng/J (0.30 and 0.20 lb/million Btu), inclusive, use 15 percent of the applicable standard; below 86 ng/J (0.20 lb/million Btu), use 20 percent of the emission standard.

13.3 For instruments that use common components to measure more than one effluent gas constituent, all channels must simultaneously pass the RA requirement, unless it can be demonstrated that any adjustments made to one channel did not affect the others.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

Paragraphs 60.13(j)(1) and (2) of 40 CFR part 60 contain criteria for which the reference method procedure for determining relative accuracy (see section 8.4 of this Performance Specification) may be waived and the following procedure substituted.

16.1 Conduct a complete CEMS status check following the manufacturer's written instructions. The check should include operation of the light source, signal receiver, timing mechanism functions, data acquisition and data reduction functions, data recorders, mechanically operated functions (mirror movements, zero pipe operation, calibration gas valve operations, etc.), sample filters, sample line heaters, moisture traps, and other related functions of the CEMS, as applicable. All parts of the CEMS shall be functioning properly before proceeding to the alternative RA procedure.

16.2 Alternative RA Procedure.

16.2.1 Challenge each monitor (both pollutant and diluent, if applicable) with cylinder gases of known concentrations or calibration cells that produce known responses at two measurement points within the ranges shown in Table 2-2 (Section 18).

16.2.2 Use a separate cylinder gas (for point CEMS only) or calibration cell (for path CEMS or where compressed gas cylinders can not be used) for measurement points 1 and 2. Challenge the

CEMS and record the responses three times at each measurement point. The Administrator may allow dilution of cylinder gas using the performance criteria in Test Method 205, 40 CFR Part 51, Appendix M. Use the average of the three responses in determining relative accuracy.

16.2.3 Operate each monitor in its normal sampling mode as nearly as possible. When using cylinder gases, pass the cylinder gas through all filters, scrubbers, conditioners, and other monitor components used during normal sampling and as much of the sampling probe as practical. When using calibration cells, the CEMS components used in the normal sampling mode should not be by-passed during the RA determination. These include light sources, lenses, detectors, and reference cells. The CEMS should be challenged at each measurement point for a sufficient period of time to assure adsorption-desorption reactions on the CEMS surfaces have stabilized.

16.2.4 Use cylinder gases that have been certified by comparison to National Institute of Standards and Technology (NIST) gaseous standard reference material (SRM) or NIST/EPA approved gas manufacturer's certified reference material (CRM) (See Reference 2 in section 17.0) following EPA Traceability Protocol Number 1 (See Reference 3 in section 17.0). As an alternative to Protocol Number 1 gases, CRM's may be used directly as alternative RA cylinder gases. A list of gas manufacturers that have prepared approved CRM's is available from EPA at the address shown in Reference 2. Procedures for preparation of CRM's are described in Reference 2.

16.2.5 Use calibration cells certified by the manufacturer to produce a known response in the CEMS. The cell certification procedure shall include determination of CEMS response produced by the calibration cell in direct comparison with measurement of gases of known concentration. This can be accomplished using SRM or CRM gases in a laboratory source simulator or through extended tests using reference methods at the CEMS location in the exhaust stack. These procedures are discussed in Reference 4 in section 17.0. The calibration cell certification procedure is subject to approval of the Administrator.
16.3 The differences between the known concentrations of the cylinder gases and the concentrations indicated by the CEMS are used to assess the accuracy of the CEMS. The calculations and limits of acceptable relative accuracy are as follows:

16.3.1 For pollutant CEMS:

$$RA = \left| \left(\frac{\bar{d}}{AC} \right) 100 \right| \leq 15 \text{ percent} \qquad \text{Eq. 2-7}$$

Where:

$\bar{d}$ = Average difference between responses and the concentration/responses (see section 16.2.2).

AC = The known concentration/response of the cylinder gas or calibration cell.

16.3.2 For diluent CEMS:

RA=$\bar{d}$; ≤0.7 percent O_2 or CO_2, as applicable.

Note: Waiver of the relative accuracy test in favor of the alternative RA procedure does not preclude the requirements to complete the CD tests nor any other requirements specified in an applicable subpart for reporting CEMS data and performing CEMS drift checks or audits.

17.0 References

1. Department of Commerce. Experimental Statistics. Handbook 91. Washington, D.C. p. 3-31, paragraphs 3-3.1.4.

2. "A Procedure for Establishing Traceability of Gas Mixtures to Certain National Bureau of Standards Standard Reference Materials." Joint publication by NBS and EPA. EPA 600/7-81-010. Available from U.S. Environmental Protection Agency, Quality Assurance Division (MD-77), Research Triangle Park, North Carolina 27711.

3. "Traceability Protocol for Establishing True Concentrations of Gases Used for Calibration and Audits of Continuous Source Emission Monitors. (Protocol Number 1)." June 1978. Protocol Number 1 is included in the Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Stationary Source Specific Methods. EPA-600/4-77-027b. August 1977.

4. "Gaseous Continuous Emission Monitoring Systems—Performance Specification Guidelines for SO_2, NO_X, CO_2, O_2, and TRS." EPA-450/3-82-026. Available from the U.S. EPA, Emission Measurement Center, Emission Monitoring and Data Analysis Division (MD-19), Research Triangle Park, North Carolina 27711.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

Table 2-1—t-Values

n^a	$t_{0.975}$	n^a	$t_{0.975}$	n^a	$t_{0.975}$
2	12.706	7	2.447	12	2.201
3	4.303	8	2.365	13	2.179
4	3.182	9	2.306	14	2.160
5	2.776	10	2.262	15	2.145
6	2.571	11	2.228	16	2.131

[A] The values in this table are already corrected for n-1 degrees of freedom. Use n equal to the number of individual values.

Table 2–2 Measurement Range

Measurement point	Pollutant monitor	Diluent monitor for	
		CO_2	O_2
1	20–30% of span value	5–8% by volume	4–6% by volume.
2	50–60% of span value	10–14% by volume	8–12% by volume.

Figure 2-1. Calibration Drift Determination

	Day	Date and time	Calibration value (C)	Monitor value (M)	Difference (C-M)	Percent of span value (C-M)/span value × 100
Low-level						
High-level						

FIGURE 2-2. RELATIVE ACCURACY DETERMINATION.

Run No.	Date and time	SO_2			NO_X[b]			CO_2 or O_2[a]		SO_2[a]			NO_X[a]		
		RM	CEMS	Diff	RM	CEMS	Diff	RM	CEMS	RM	CEMS	Diff	RM	CEMS	Diff
		ppm[c]			ppm[c]			%[c]	%[c]	mass/GCV			mass/GCV		
1															
2															
3															
4															
5															
6															
7															
8															
9															
10															
11															
12															
Average															
Confidence Interval															
Accuracy															

[a] For steam generators.

[b] Average of three samples.

[c] Make sure that RM and CEMS data are on a consistent basis, either wet or dry.

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PERFORMANCE SPECIFICATION 3—SPECIFICATIONS AND TEST PROCEDURES FOR O_2 AND CO_2 CONTINUOUS EMISSION MONITORING SYSTEMS IN STATIONARY SOURCES

1.0 Scope and Application

1.1 Analytes.

Analytes	**CAS No.**
Carbon Dioxide (CO_2)	124-38-9
Oxygen (O_2)	7782-44-7

1.2 Applicability.

1.2.1 This specification is for evaluating acceptability of O_2 and CO_2 continuous emission monitoring systems (CEMS) at the time of installation or soon after and whenever specified in an applicable subpart of the regulations. This specification applies to O_2 or CO_2 monitors that are not included under Performance Specification 2 (PS 2).

1.2.2 This specification is not designed to evaluate the installed CEMS performance over an extended period of time, nor does it identify specific calibration techniques and other auxiliary procedures to assess the CEMS performance. The source owner or operator, is responsible to calibrate, maintain, and operate the CEMS properly. The Administrator may require, under section 114 of the Act, the operator to conduct CEMS performance evaluations at other times besides the initial test to evaluate the CEMS performance. See 40 CFR part 60, section 60.13(c).

1.2.3 The definitions, installation and measurement location specifications, calculations and data analysis, and references are the same as in PS 2, sections 3, 8.1, 12, and 17, respectively, and also apply to O_2 and CO_2 CEMS under this specification. The performance and equipment specifications and the relative accuracy (RA) test procedures for O_2 and CO_2 CEMS do not differ from those for SO_2 and NO_X CEMS (see PS 2), except as noted below.

2.0 Summary of Performance Specification

The RA and calibration drift (CD) tests are conducted to determine conformance of the CEMS to the specification.

3.0 Definitions

Same as in section 3.0 of PS 2.

4.0 Interferences [Reserved]

5.0 Safety

This performance specification may involve hazardous materials, operations, and equipment. This performance specification may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicable regulatory limitations prior to performing this performance specification. The CEMS users manual should be consulted for specific precautions to be taken with regard to the analytical procedures.

6.0 Equipment and Supplies

Same as section 6.0 of PS2.

7.0 Reagents and Standards

Same as section 7.0 of PS2.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Relative Accuracy Test Procedure. Sampling Strategy for reference method (RM) Tests, Correlation of RM and CEMS Data, and Number of RM Tests. Same as PS 2, sections 8.4.3, 8.4.5, and 8.4.4, respectively.

8.2 Reference Method. Unless otherwise specified in an applicable subpart of the regulations, Method 3B or other approved alternative is the RM for O_2 or CO_2.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

Sample collection and analyses are concurrent for this performance specification (see section 8). Refer to the RM for specific analytical procedures.

12.0 Calculations and Data Analysis

Summarize the results on a data sheet similar to that shown in Figure 2.2 of PS2. Calculate the arithmetic difference between the RM and the CEMS output for each run. The average difference of the nine (or more) data sets constitute the RA.

13.0 Method Performance

13.1 Calibration Drift Performance Specification. The CEMS calibration must not drift by more than 0.5 percent O_2 or CO_2 from the reference value of the gas, gas cell, or optical filter.

13.2 CEMS Relative Accuracy Performance Specification. The RA of the CEMS must be no greater than 20.0 percent of the mean value of the reference method (RM) data when calculated using equation 3-1. The results are also acceptable if the result of Equation 3-2 is less than or equal to 1.0 percent O_2 (or CO_2).

$$RA = \frac{\left[\left|\bar{d}\right| + \left|CC\right|\right]}{\overline{RM}} \times 100 \qquad \text{Eq. 3-1}$$

Where:

$\left|\bar{d}\right|$ = Absolute value of the mean of the differences (from Equation 2-3 of Performance Specification 2).

|CC| = Absolute value of the confidence coefficient (from Equation 2-5 of Performance Specification 2).

$\overline{RM}$ = Average Reference Method Value

$$RA = \left|\overline{RM} - \overline{CEMS}\right| \qquad Eq. 3-2$$

$\overline{RM}$ = Average Reference Method Value

$\overline{CEMS}$ = Average CEMS Value

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as in section 17.0 of PS 2.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

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PERFORMANCE SPECIFICATION 4A—SPECIFICATIONS AND TEST PROCEDURES FOR CARBON MONOXIDE CONTINUOUS EMISSION MONITORING SYSTEMS IN STATIONARY SOURCES

1.0 Scope and Application

1.1 Analytes.

Analyte	**CAS No.**
Carbon Monoxide (CO)	630-80-0

1.2 Applicability.

1.2.1 This specification is for evaluating the acceptability of carbon monoxide (CO) continuous emission monitoring systems (CEMS) at the time of installation or soon after and whenever specified in an applicable subpart of the regulations. This specification was developed primarily for CEMS that comply with low emission standards (less than 200 ppmv).

1.2.2 This specification is not designed to evaluate the installed CEMS performance over an extended period of time nor does it identify specific calibration techniques and other auxiliary procedures to assess CEMS performance. The source owner or operator is responsible to calibrate, maintain, and operate the CEMS. The Administrator may require, under section 114 of the Act, the source owner or operator to conduct CEMS performance evaluations at other times besides the initial test to evaluate CEMS performance. See 40 CFR Part 60, section 60.13(c).

1.2.3 The definitions, performance specification, test procedures, calculations and data analysis procedures for determining calibration drifts (CD) and relative accuracy (RA), of Performance Specification 2 (PS 2), sections 3, 8.0, and 12, respectively, apply to this specification.

2.0 Summary of Performance Specification

The CD and RA tests are conducted to determine conformance of the CEMS to the specification.

3.0 Definitions

Same as in section 3.0 of PS 2.

4.0 Interferences [Reserved]

5.0 Safety

This performance specification may involve hazardous materials, operations, and equipment. This performance specification may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicable regulatory limitations prior to performing this performance specification. The CEMS users manual should be consulted for specific precautions to be taken with regard to the analytical procedures.

6.0 Equipment and Supplies

Same as section 6.0 of PS 2 with the following additions.

6.1 Data Recorder Scale.

6.1.1 This specification is the same as section 6.1 of PS 2. The CEMS shall be capable of measuring emission levels under normal conditions and under periods of short-duration peaks of high concentrations. This dual-range capability may be met using two separate analyzers (one for each range) or by using dual-range units which have the capability of measuring both levels with a single unit. In the latter case, when the reading goes above the full-scale measurement value of the lower range, the higher-range operation shall be started automatically. The CEMS recorder range must include zero and a high-level value. Under applications of consistent low emissions, a single-range analyzer is allowed provided normal and spike emissions can be quantified. In this case, set an appropriate high-level value to include all emissions.

6.1.2 For the low-range scale of dual-range units, the high-level value shall be between 1.5 times the pollutant concentration corresponding to the emission standard level and the span value. For the high-range scale, the high-level value shall be set at 2000 ppm, as a minimum, and the range shall include the level of the span value. There shall be no concentration gap between the low- and high-range scales.

7.0 Reagents and Standards

Same as section 7.0 of PS 2.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Relative Accuracy Test Procedure. Sampling Strategy for reference method (RM) Tests, Number of RM Tests, and Correlation of RM and CEMS Data are the same as PS 2, sections 8.4.3, 8.4.4, and 8.4.5, respectively.

8.2 Reference Methods. Unless otherwise specified in an applicable subpart of the regulation, Methods 10, 10A, 10B, or other approved alternative is the RM for this PS. When evaluating nondispersive infrared CEMS using Method 10 as the RM, the alternative interference trap specified in section 16.0 of Method 10 shall be used.

8.3 Response Time Test Procedure. The response time test applies to all types of CEMS, but will generally have significance only for extractive systems. The entire system is checked with this

procedure including applicable sample extraction and transport, sample conditioning, gas analyses, and data recording.

8.3.1 Introduce zero gas into the system. When the system output has stabilized (no change greater than 1 percent of full scale for 30 sec), introduce an upscale calibration gas and wait for a stable value. Record the time (upscale response time) required to reach 95 percent of the final stable value. Next, reintroduce the zero gas and wait for a stable reading before recording the response time (downscale response time). Repeat the entire procedure until you have three sets of data to determine the mean upscale and downscale response times. The slower or longer of the two means is the system response time.

8.4 Interference Check. The CEMS must be shown to be free from the effects of any interferences.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

Sample collection and analysis are concurrent for this performance specification (see section 8.0). Refer to the RM for specific analytical procedures.

12.0 Calculations and Data Analysis. Same as section 12.0 of PS 2

13.0 Method Performance

13.1 Calibration Drift. The CEMS calibration must not drift or deviate from the reference value of the calibration gas, gas cell, or optical filter by more than 5 percent of the established span value for 6 out of 7 test days.

13.2 Relative Accuracy. The RA of the CEMS must be no greater than 10 percent when the average RM value is used to calculate RA, 5 percent when the applicable emission standard is used to calculate RA, or within 5 ppmv when the RA is calculated as the absolute average difference between the RM and CEMS plus the 2.5 percent confidence coefficient.

13.3 Response Time. The CEMS response time shall not exceed 240 seconds to achieve 95 percent of the final stable value.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Under conditions where the average CO emissions are less than 10 percent of the standard and this is verified by Method 10, a cylinder gas audit may be performed in place of the RA test to determine compliance with these limits. In this case, the cylinder gas shall contain CO in 12 percent carbon dioxide as an interference check. If this option is exercised, Method 10 must be used to verify that emission levels are less than 10 percent of the standard.

17.0 References

Same as section 17 of PS 4.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

Same as section 18.0 of PS 2.

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PERFORMANCE SPECIFICATION 11—SPECIFICATIONS AND TEST PROCEDURES FOR PARTICULATE MATTER CONTINUOUS EMISSION MONITORING SYSTEMS AT STATIONARY SOURCES

1.0 What Are the Purpose and Applicability of Performance Specification 11?

The purpose of Performance Specification 11 (PS-11) is to establish the initial installation and performance procedures that are required for evaluating the acceptability of a particulate matter (PM) continuous emission monitoring system (CEMS); it is not to evaluate the ongoing performance of your PM CEMS over an extended period of time, nor to identify specific calibration techniques and auxiliary procedures to assess CEMS performance. You will find procedures for evaluating the ongoing performance of a PM CEMS in Procedure 2 of Appendix F—Quality Assurance Requirements for Particulate Matter Continuous Emission Monitoring Systems Used at Stationary Sources.

1.1 Under what conditions does PS-11 apply to my PM CEMS? The PS-11 applies to your PM CEMS if you are required by any provision of Title 40 of the Code of Federal Regulations (CFR) to install and operate PM CEMS.

1.2 When must I comply with PS-11? You must comply with PS-11 when directed by the applicable rule that requires you to install and operate a PM CEMS.

1.3 What other monitoring must I perform? To report your PM emissions in units of the emission standard, you may need to monitor additional parameters to correct the PM concentration reported by your PM CEMS. Your CEMS may include the components listed in paragraphs (1) through (3) of this section:

(1) A diluent monitor (*i.e.,* O_2, CO_2, or other CEMS specified in the applicable regulation), which must meet its own performance specifications (also found in this appendix),

(2) Auxiliary monitoring equipment to allow measurement, determination, or input of the flue gas temperature, pressure, moisture content, and/or dry volume of stack effluent sampled, and

(3) An automatic sampling system. The performance of your PM CEMS and the establishment of its correlation to manual reference method measurements must be determined in units of mass concentration as measured by your PM CEMS (*e.g.,* milligrams per actual cubic meter (mg/acm) or milligrams per dry standard cubic meter (mg/dscm)).

2.0 What Are the Basic Requirements of PS-11?

The PS-11 requires you to perform initial installation and calibration procedures that confirm the acceptability of your CEMS when it is installed and placed into operation. You must develop a site-specific correlation of your PM CEMS response against manual gravimetric reference method measurements (including those made using EPA Methods 5, 5I, or 17).

2.1 What types of PM CEMS technologies are covered? Several different types of PM CEMS technologies (*e.g.,* light scattering, Beta attenuation, etc.) can be designed with in-situ or extractive sample gas handling systems. Each PM CEMS technology and sample gas handling technology has certain site-specific advantages. You should select and install a PM CEMS that is appropriate for the flue gas conditions at your source.

2.2 How is PS-11 different from other performance specifications? The PS-11 is based on a technique of correlating PM CEMS responses relative to emission concentrations determined by the reference method. This technique is called "the correlation." This differs from CEMS used to measure gaseous pollutants that have available calibration gases of known concentration. Because the type and characteristics of PM vary from source to source, a single PM correlation, applicable to all sources, is not possible.

2.3 How are the correlation data handled? You must carefully review your manual reference method data and your PM CEMS responses to include only valid, high-quality data. For the correlation, you must convert the manual reference method data to measurement conditions (*e.g.,* wet or dry basis) that are consistent with your PM CEMS. Then, you must correlate the manual method and PM CEMS data in terms of the output as received from the monitor (*e.g.,* milliamps). At the appropriate PM CEMS response specified in section 13.2 of this performance specification, you must calculate the confidence interval half range and tolerance interval half range as a percentage of the applicable PM concentration emission limit and compare the confidence interval and tolerance interval percentages with the performance criteria. Also, you must calculate the correlation coefficient and compare the correlation coefficient with the applicable performance criterion specified in section 13.2 of this performance specification.

Situations may arise where you will need two or more correlations. If you need multiple correlations, you must collect sufficient data for each correlation, and each correlation must satisfy the performance criteria specified in section 13.2 of this performance specification.

2.4 How do I design my PM CEMS correlation program? When planning your PM CEMS correlation effort, you must address each of the items in paragraphs (1) through (7) of this section to enhance the probability of success. You will find each of these elements further described in this performance specification or in the applicable reference method procedure.

(1) What type of PM CEMS should I select? You should select a PM CEMS that is appropriate for your source with technical consideration for potential factors such as interferences, site-specific configurations, installation location, flue gas conditions, PM concentration range, and other PM characteristics. You can find guidance on which technology is best suited for specific situations in our report "Current Knowledge of Particulate Matter (PM) Continuous Emission Monitoring" (PM CEMS Knowledge Document, see section 16.5).

(2) Where should I install my PM CEMS? Your PM CEMS must be installed in a location that is most representative of PM emissions, as determined by the reference method, such that the correlation between PM CEMS response and emissions determined by the reference method will meet these performance specifications. Care must be taken in selecting a location and measurement point to minimize problems due to flow disturbances, cyclonic flow, and varying PM stratification.

(3) How should I record my CEMS data? You need to ensure that your PM CEMS and data logger are set up to collect and record all normal emission levels and excursions. You must ensure that your data logger and PM CEMS have been properly programmed to accept and transfer status signals of valid monitor operation (*e.g.,* flags for internal calibration, suspect data, or maintenance periods).

(4) What CEMS data should I review? You must review drift data daily to document proper operation. You must also ensure that any audit material is appropriate for the typical operating range of your PM CEMS.

(5) How long should I operate my PM CEMS before conducting the initial correlation test? You should allow sufficient time for your PM CEMS to operate for you to become familiar with your PM CEMS.

(i) You should observe PM CEMS response over time during normal and varying process conditions. This will ensure that your PM CEMS has been properly set up to operate at a range that is compatible with the concentrations and characteristics of PM emissions for your source. You should use this information to establish the range of operating conditions necessary to determine the correlations of PM CEMS data to manual reference method measurements over a wide operating range.

(ii) You must determine the types of process changes that will influence, on a definable and repeatable basis, flue gas PM concentrations and the resulting PM CEMS responses. You may find this period useful to make adjustments to your planned approach for operating your PM CEMS at your source. For instance, you may change the measurement range or batch sampling period to something other than those you initially planned to use.

(6) How do I conduct the initial correlation test? When conducting the initial correlation test of your PM CEMS response to PM emissions determined by the reference method, you must pay close attention to accuracy and details. Your PM CEMS must be operating properly. You must perform the manual reference method testing accurately, with attention to eliminating site-specific systemic errors. You must coordinate the timing of the manual reference method testing with the sampling cycle of your PM CEMS. You must complete a minimum of 15 manual reference method tests. You must perform the manual reference method testing over the full range of PM CEMS responses that correspond to normal operating conditions for your source and control device and will result in the widest range of emission concentrations.

(7) How should I perform the manual reference method testing? You must perform the manual reference method testing in accordance with specific rule requirements, coordinated closely with

PM CEMS and process operations. It is highly recommended that you use paired trains for the manual reference method testing. You must perform the manual reference method testing over a suitable PM concentration range that corresponds to the full range of normal process and control device operating conditions. Because the manual reference method testing for this correlation test is not for compliance reporting purposes, you may conduct the reference method test runs for less than the typical minimum test run duration of 1 hour.

(8) What do I do with the manual reference method data and PM CEMS data? You must complete each of the activities in paragraphs (8)(i) through (v) of this section.

(i) Screen the manual reference method data for validity (*e.g.,* isokinetics, leak checks), quality assurance, and quality control (*e.g.,* outlier identification).

(ii) Screen your PM CEMS data for validity (*e.g.,* daily drift check requirements) and quality assurance (*e.g.,* flagged data).

(iii) Convert the manual reference method test data into measurement units (*e.g.,* mg/acm) consistent with the measurement conditions of your PM CEMS.

(iv) Calculate the correlation equation(s) as specified in section 12.3.

(v) Calculate the correlation coefficient, confidence interval half range, and tolerance interval half range for the complete set of PM CEMS and reference method correlation data for comparison with the correlation performance criteria specified in section 13.2.

2.5 What other procedures must I perform? Before conducting the initial correlation test, you must successfully complete a 7-day drift test (See section 8.5).

3.0 What Special Definitions Apply to PS-11?

3.1 “Appropriate Measurement Range of your PM CEMS” means a measurement range that is capable of recording readings over the complete range of your source's PM emission concentrations during routine operations. The appropriate range is determined during the pretest preparations as specified in section 8.4.

3.2 “Appropriate Data Range for PM CEMS Correlation” means the data range that reflects the full range of your source's PM emission concentrations recorded by your PM CEMS during the correlation test planning period or other normal operations as defined in the applicable regulations.

3.3 “Batch Sampling” means that gas is sampled on an intermittent basis and concentrated on a collection medium before intermittent analysis and follow-up reporting. Beta gauge PM CEMS are an example of batch sampling devices.

3.4 “Confidence Interval Half Range (CI)” is a statistical term and means one-half of the width of the 95 percent confidence interval around the predicted mean PM concentration (y value)

calculated at the PM CEMS response value (x value) where the confidence interval is narrowest. Procedures for calculating CI are specified in section 12.3. The CI as a percent of the emission limit value (CI%) is calculated at the appropriate PM CEMS response value and must satisfy the criteria specified in section 13.2 (2).

3.5 "Continuous Emission Monitoring System (CEMS)" means all of the equipment required for determination of PM mass concentration in units of the emission standard. The sample interface, pollutant monitor, diluent monitor, other auxiliary data monitor(s), and data recorder are the major subsystems of your CEMS.

3.6 "Correlation" means the primary mathematical relationship for correlating the output from your PM CEMS to a PM concentration, as determined by the PM reference method. The correlation is expressed in the measurement units that are consistent with the measurement conditions (*e.g.,* mg/dscm, mg/acm) of your PM CEMS.

3.7 "Correlation Coefficient (r)" means a quantitative measure of the association between your PM CEMS outputs and the reference method measurements. Equations for calculating the r value are provided in section 12.3(1)(iv) for linear correlations and in section 12.3(2)(iv) for polynomial correlations.

3.8 "Cycle Time" means the time required to complete one sampling, measurement, and reporting cycle. For a batch sampling PM CEMS, the cycle time would start when sample gas is first extracted from the stack/duct and end when the measurement of that batch sample is complete and a new result for that batch sample is produced on the data recorder.

3.9 "Data Recorder" means the portion of your CEMS that provides a permanent record of the monitor output in terms of response and status (flags). The data recorder may also provide automatic data reduction and CEMS control capabilities (see section 6.6).

3.10 "Diluent Monitor and Other Auxiliary Data Monitor(s) (if applicable)" means the portion of your CEMS that provides the diluent gas concentration (such as O_2 or CO_2, as specified by the applicable regulations), temperature, pressure, and/or moisture content, and generates an output proportional to the diluent gas concentration or gas property.

3.11 "Drift Check" means a check of the difference between your PM CEMS output readings and the established reference value of a reference standard or procedure after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place. The procedures used to determine drift are specific to the operating principles of your specific PM CEMS. A drift check includes both a zero drift check and an upscale drift check.

3.12 "Exponential Correlation" means an exponential equation used to define the relationship between your PM CEMS output and the reference method PM concentration, as indicated by Equation 11-37.

3.13 “Flagged Data” means data marked by your CEMS indicating that the response value(s) from one or more CEMS subsystems is suspect or invalid or that your PM CEMS is not in source-measurement operating mode.

3.14 “Linear Correlation” means a first-order mathematical relationship between your PM CEMS output and the reference method PM concentration that is linear in form, as indicated by Equation 11-3.

3.15 “Logarithmic Correlation” means a first-order mathematical relationship between the natural logarithm of your PM CEMS output and the reference method PM concentration that is linear in form, as indicated by Equation 11-34.

3.16 “Low-Emitting Source” means a source that operated at no more than 50 percent of the emission limit during the most recent performance test, and, based on the PM CEMS correlation, the daily average emissions for the source, measured in the units of the applicable emission limit, have not exceeded 50 percent of the emission limit for any day since the most recent performance test.

3.17 “Paired Trains” means two reference method trains that are used to conduct simultaneous measurements of PM concentrations. Guidance on the use of paired sampling trains can be found in the PM CEMS Knowledge Document (see section 16.5).

3.18 “Polynomial Correlation” means a second-order equation used to define the relationship between your PM CEMS output and reference method PM concentration, as indicated by Equation 11-16.

3.19 “Power Correlation” means an equation used to define a power function relationship between your PM CEMS output and the reference method concentration, as indicated by Equation 11-42.

3.20 “Reference Method” means the method defined in the applicable regulations, but commonly refers to those methods collectively known as EPA Methods 5, 5I, and 17 (for particulate matter), found in Appendix A of 40 CFR 60. Only the front half and dry filter catch portions of the reference method can be correlated to your PM CEMS output.

3.21 “Reference Standard” means a reference material or procedure that produces a known and unchanging response when presented to the pollutant monitor portion of your CEMS. You must use these standards to evaluate the overall operation of your PM CEMS, but not to develop a PM CEMS correlation.

3.22 “Response Time” means the time interval between the start of a step change in the system input and the time when the pollutant monitor output reaches 95 percent of the final value (see sections 6.5 and 13.3 for procedures and acceptance criteria).

3.23 “Sample Interface” means the portion of your CEMS used for one or more of the following: sample acquisition, sample delivery, sample conditioning, or protection of the monitor from the effects of the stack effluent.

3.24 “Sample Volume Check” means a check of the difference between your PM CEMS sample volume reading and the sample volume reference value.

3.25 “Tolerance Interval half range (TI)” means one-half of the width of the tolerance interval with upper and lower limits, within which a specified percentage of the future data population is contained with a given level of confidence, as defined by the respective tolerance interval half range equations in section 12.3(1)(iii) for linear correlations and in section 12.3(2)(iii) for polynomial correlations. The TI as a percent of the emission limit value (TI%) is calculated at the appropriate PM CEMS response value specified in section 13.2(3).

3.26 “Upscale Check Value” means the expected response to a reference standard or procedure used to check the upscale response of your PM CEMS.

3.27 “Upscale Drift (UD) Check” means a check of the difference between your PM CEMS output reading and the upscale check value.

3.28 “Zero Check Value” means the expected response to a reference standard or procedure used to check the response of your PM CEMS to particulate-free or low-particulate concentration conditions.

3.29 “Zero Drift (ZD) Check” means a check of the difference between your PM CEMS output reading and the zero check value.

3.30 “Zero Point Correlation Value” means a value added to PM CEMS correlation data to represent low or near zero PM concentration data (see section 8.6 for rationale and procedures).

4.0 Are There Any Potential Interferences for My PM CEMS?

Yes, condensible water droplets or condensible acid gas aerosols (*i.e.,* those with condensation temperatures above those specified by the reference method) at the measurement location can be interferences for your PM CEMS if the necessary precautions are not met.

4.1 Where are interferences likely to occur? Interferences may develop if your CEMS is installed downstream of a wet air pollution control system or any other conditions that produce flue gases, which, at your PM CEMS measurement point, normally or occasionally contain entrained water droplets or condensible salts before release to the atmosphere.

4.2 How do I deal with interferences? We recommend that you use a PM CEMS that extracts and heats representative samples of the flue gas for measurement to simulate results produced by the reference method for conditions such as those described in section 4.1. Independent of your PM CEMS measurement technology and extractive technique, you should have a configuration simulating the reference method to ensure that:

(1) No formation of new PM or deposition of PM occurs in sample delivery from the stack or duct; and

(2) No condensate accumulates in the sample flow measurement apparatus.

4.3 What PM CEMS measurement technologies should I use? You should use a PM CEMS measurement technology that is free of interferences from any condensible constituent in the flue gas.

5.0 What Do I Need To Know To Ensure the Safety of Persons Using PS-11?

People using the procedures required under PS-11 may be exposed to hazardous materials, operations, site conditions, and equipment. This performance specification does not purport to address all of the safety issues associated with its use. It is your responsibility to establish appropriate safety and health practices and determine the applicable regulatory limitations before performing these procedures. You must consult your CEMS user's manual and other reference materials recommended by the reference method for specific precautions to be taken.

6.0 What Equipment and Supplies Do I Need?

Different types of PM CEMS use different operating principles. You should select an appropriate PM CEMS based on your site-specific configurations, flue gas conditions, and PM characteristics.

(1) Your PM CEMS must sample the stack effluent continuously or, for batch sampling PM CEMS, intermittently.

(2) You must ensure that the averaging time, the number of measurements in an average, the minimum data availability, and the averaging procedure for your CEMS conform with those specified in the applicable emission regulation.

(3) Your PM CEMS must include, as a minimum, the equipment described in sections 6.1 through 6.7.

6.1 What equipment is needed for my PM CEMS's sample interface? Your PM CEMS's sample interface must be capable of delivering a representative sample of the flue gas to your PM CEMS. This subsystem may be required to heat the sample gas to avoid PM deposition or moisture condensation, provide dilution air, perform other gas conditioning to prepare the sample for analysis, or measure the sample volume or flow rate.

(1) If your PM CEMS is installed downstream of a wet air pollution control system such that the flue gases normally or occasionally contain entrained water droplets, we recommend that you select a sampling system that includes equipment to extract and heat a representative sample of the flue gas for measurement so that the pollutant monitor portion of your CEMS measures only dry PM. Heating should be sufficient to raise the temperature of the extracted flue gas above the water condensation temperature and should be maintained at all times and at all points in the

sample line from where the flue gas is extracted, including the pollutant monitor and any sample flow measurement devices.

(2) You must consider the measured conditions of the sample gas stream to ensure that manual reference method test data are converted to units of PM concentration that are appropriate for the correlation calculations. Additionally, you must identify what, if any, additional auxiliary data from other monitoring and handling systems are necessary to convert your PM CEMS response into the units of the PM standard.

(3) If your PM CEMS is an extractive type and your source's flue gas volumetric flow rate varies by more than 10 percent from nominal, your PM CEMS should maintain an isokinetic sampling rate (within 10 percent of true isokinetic). If your extractive-type PM CEMS does not maintain an isokinetic sampling rate, you must use actual site-specific data or data from a similar installation to prove to us, the State, and/or local enforcement agency that isokinetic sampling is not necessary.

6.2 What type of equipment is needed for my PM CEMS? Your PM CEMS must be capable of providing an electronic output that can be correlated to the PM concentration.

(1) Your PM CEMS must be able to perform zero and upscale drift checks. You may perform these checks manually, but performing these checks automatically is preferred.

(2) We recommend that you select a PM CEMS that is capable of performing automatic diagnostic checks and sending instrument status signals (flags) to the data recorder.

(3) If your PM CEMS is an extractive type that measures the sample volume and uses the measured sample volume as part of calculating the output value, your PM CEMS must be able to perform a check of the sample volume to verify the accuracy of the sample volume measuring equipment. The sample volume check must be conducted daily and at the normal sampling rate of your PM CEMS.

6.3 What is the appropriate measurement range for my PM CEMS? Initially, your PM CEMS must be set up to measure over the expected range of your source's PM emission concentrations during routine operations. You may change the measurement range to a more appropriate range prior to correlation testing.

6.4 What if my PM CEMS does automatic range switching? Your PM CEMS may be equipped to perform automatic range switching so that it is operating in a range most sensitive to the detected concentrations. If your PM CEMS does automatic range switching, you must configure the data recorder to handle the recording of data values in multiple ranges during range-switching intervals.

6.5 What averaging time and sample intervals should be used? Your CEMS must sample the stack effluent such that the averaging time, the number of measurements in an average, the minimum sampling time, and the averaging procedure for reporting and determining compliance conform with those specified in the applicable regulation. Your PM CEMS must be designed to

meet the specified response time and cycle time established in this performance specification (see section 13.3).

6.6 What type of equipment is needed for my data recorder? Your CEMS data recorder must be able to accept and record electronic signals from all the monitors associated with your PM CEMS.

(1) Your data recorder must record the signals from your PM CEMS that can be correlated to PM mass concentrations. If your PM CEMS uses multiple ranges, your data recorder must identify what range the measurement was made in and provide range-adjusted results.

(2) Your data recorder must accept and record monitor status signals (flagged data).

(3) Your data recorder must accept signals from auxiliary data monitors, as appropriate.

6.7 What other equipment and supplies might I need? You may need other supporting equipment as defined by the applicable reference method(s) (see section 7) or as specified by your CEMS manufacturer.

7.0 What Reagents and Standards Do I Need?

You will need reference standards or procedures to perform the zero drift check, the upscale drift check, and the sample volume check.

7.1 What is the reference standard value for the zero drift check? You must use a zero check value that is no greater than 20 percent of the PM CEMS's response range. You must obtain documentation on the zero check value from your PM CEMS manufacturer.

7.2 What is the reference standard value for the upscale drift check? You must use an upscale check value that produces a response between 50 and 100 percent of the PM CEMS's response range. For a PM CEMS that produces output over a range of 4 mA to 20 mA, the upscale check value must produce a response in the range of 12 mA to 20 mA. You must obtain documentation on the upscale check value from your PM CEMS manufacturer.

7.3 What is the reference standard value for the sample volume check? You must use a reference standard value or procedure that produces a sample volume value equivalent to the normal sampling rate. You must obtain documentation on the sample volume value from your PM CEMS manufacturer.

8.0 What Performance Specification Test Procedure Do I Follow?

You must complete each of the activities in sections 8.1 through 8.8 for your performance specification test.

8.1 How should I select and set up my equipment? You should select a PM CEMS that is appropriate for your source, giving consideration to potential factors such as flue gas conditions,

interferences, site-specific configuration, installation location, PM concentration range, and other PM characteristics. Your PM CEMS must meet the equipment specifications in sections 6.1 and 6.2.

(1) You should select a PM CEMS that is appropriate for the flue gas conditions at your source. If your source's flue gas contains entrained water droplets, we recommend that your PM CEMS include a sample delivery and conditioning system that is capable of extracting and heating a representative sample.

(i) Your PM CEMS must maintain the sample at a temperature sufficient to prevent moisture condensation in the sample line before analysis of PM.

(ii) If condensible PM is an issue, we recommend that you operate your PM CEMS to maintain the sample gas temperature at the same temperature as the reference method filter.

(iii) Your PM CEMS must avoid condensation in the sample flow rate measurement lines.

(2) Some PM CEMS do not have a wide measurement range capability. Therefore, you must select a PM CEMS that is capable of measuring the full range of PM concentrations expected from your source from normal levels through the emission limit concentration.

(3) Some PM CEMS are sensitive to particle size changes, water droplets in the gas stream, particle charge, stack gas velocity changes, or other factors. Therefore, you should select a PM CEMS appropriate for the emission characteristics of your source.

(4) We recommend that you consult your PM CEMS vendor to obtain basic recommendations on the instrument capabilities and setup configuration. You are ultimately responsible for setup and operation of your PM CEMS.

8.2 Where do I install my PM CEMS? You must install your PM CEMS at an accessible location downstream of all pollution control equipment. You must perform your PM CEMS concentration measurements from a location considered representative or be able to provide data that can be corrected to be representative of the total PM emissions as determined by the manual reference method.

(1) You must select a measurement location that minimizes problems due to flow disturbances, cyclonic flow, and varying PM stratification (refer to Method 1 for guidance).

(2) If you plan to achieve higher emissions for correlation test purposes by adjusting the performance of the air pollution control device (per section 8.6(4)(i)), you must locate your PM CEMS and reference method sampling points well downstream of the control device (*e.g.,* downstream of the induced draft fan), in order to minimize PM stratification that may be created in these cases.

8.3 How do I select the reference method measurement location and traverse points? You must follow EPA Method 1 for identifying manual reference method traverse points. Ideally, you

should perform your manual reference method measurements at locations that satisfy the measurement site selection criteria specified in EPA Method 1 of at least eight duct diameters downstream and at least two duct diameters upstream of any flow disturbance. Where necessary, you may conduct testing at a location that is two diameters downstream and 0.5 diameters upstream of flow disturbances. If your location does not meet the minimum downstream and upstream requirements, you must obtain approval from us to test at your location.

8.4 What are my pretest preparation steps? You must install your CEMS and prepare the reference method test site according to the specifications in sections 8.2 and 8.3.

(1) After completing the initial field installation, we recommend that you operate your PM CEMS according to the manufacturer's instructions to familiarize yourself with its operation before you begin correlation testing.

(i) During this initial period of operation, we recommend that you conduct daily checks (zero and upscale drift and sample volume, as appropriate), and, when any check exceeds the daily specification (see section 13.1), make adjustments and perform any necessary maintenance to ensure reliable operation.

(2) When you are confident that your PM CEMS is operating properly, we recommend that you operate your CEMS over a correlation test planning period of sufficient duration to identify the full range of operating conditions and PM emissions to be used in your PM CEMS correlation test.

(i) During the correlation test planning period, you should operate the process and air pollution control equipment over the normal range of operating conditions, except when you attempt to produce higher emissions.

(ii) Your data recorder should record PM CEMS response during the full range of routine process operating conditions.

(iii) You should try to establish the relationships between operating conditions and PM CEMS response, especially those conditions that produce the highest PM CEMS response over 15-minute averaging periods, and the lowest PM CEMS response as well. The objective is to be able to reproduce the conditions for purposes of the actual correlation testing discussed in section 8.6.

(3) You must set the response range of your PM CEMS such that the instrument measures the full range of responses that correspond to the range of source operating conditions that you will implement during correlation testing.

(4) We recommend that you perform preliminary reference method testing after the correlation test planning period. During this preliminary testing, you should measure the PM emission concentration corresponding to the highest PM CEMS response observed during the full range of normal operation, when perturbing the control equipment, or as the result of PM spiking.

(5) Before performing correlation testing, you must perform a 7-day zero and upscale drift test (see section 8.5).

(6) You must not change the response range of the monitor once the response range has been set and the drift test successfully completed.

8.5 How do I perform the 7-day drift test? You must check the zero (or low-level value between 0 and 20 percent of the response range of the instrument) and upscale (between 50 and 100 percent of the instrument's response range) drift. You must perform this check at least once daily over 7 consecutive days. Your PM CEMS must quantify and record the zero and upscale measurements and the time of the measurements. If you make automatic or manual adjustments to your PM CEMS zero and upscale settings, you must conduct the drift test immediately before these adjustments, or conduct it in such a way that you can determine the amount of drift. You will find the calculation procedures for drift in section 12.1 and the acceptance criteria for allowable drift in section 13.1.

(1) What is the purpose of 7-day drift tests? The purpose of the 7-day drift test is to demonstrate that your system is capable of operating in a stable manner and maintaining its calibration for at least a 7-day period.

(2) How do I conduct the 7-day drift test? To conduct the 7-day drift test, you must determine the magnitude of the drift once each day, at 24-hour intervals, for 7 consecutive days while your source is operating normally.

(i) You must conduct the 7-day drift test at the two points specified in section 8.5. You may perform the 7-day drift tests automatically or manually by introducing to your PM CEMS suitable reference standards (these need not be certified) or by using other appropriate procedures.

(ii) You must record your PM CEMS zero and upscale response and evaluate them against the zero check value and upscale check value.

(3) When must I conduct the 7-day drift test? You must complete a valid 7-day drift test before attempting the correlation test.

8.6 How do I conduct my PM CEMS correlation test? You must conduct the correlation test according to the procedure given in paragraphs (1) through (5) of this section. If you need multiple correlations, you must conduct testing and collect at least 15 sets of reference method and PM CEMS data for calculating each separate correlation.

(1) You must use the reference method for PM (usually EPA Methods 5, 5I, or 17) that is prescribed by the applicable regulations. You may need to perform other reference methods or performance specifications (*e.g.,* Method 3 for oxygen, Method 4 for moisture, etc.) depending on the units in which your PM CEMS reports PM concentration.

(i) We recommend that you use paired reference method trains when collecting manual PM data to identify and screen the reference method data for imprecision and bias. Procedures for checking reference method data for bias and precision can be found in the PM CEMS Knowledge Document (see section 16.5).

(ii) You may use test runs that are shorter than 60 minutes in duration (*e.g.,* 20 or 30 minutes). You may perform your PM CEMS correlation tests during new source performance standards performance tests or other compliance tests subject to the Clean Air Act or other statutes, such as the Resource Conservation and Recovery Act. In these cases, your reference method results obtained during the PM CEMS correlation test may be used to determine compliance so long as your source and the test conditions and procedures (*e.g.,* reference method sample run durations) are consistent with the applicable regulations and the reference method.

(iii) You must convert the reference method results to units consistent with the conditions of your PM CEMS measurements. For example, if your PM CEMS measures and reports PM emissions in the units of mass per actual volume of stack gas, you must convert your reference method results to those units (*e.g.,* mg/acm). If your PM CEMS extracts and heats the sample gas to eliminate water droplets, then measures and reports PM emissions under those actual conditions, you must convert your reference method results to those same conditions (*e.g.,* mg/acm at 160 °C).

(2) During each test run, you must coordinate process operations, reference method sampling, and PM CEMS operations. For example, you must ensure that the process is operating at the targeted conditions, both reference method trains are sampling simultaneously (if paired sampling trains are being used), and your PM CEMS and data logger are operating properly.

(i) You must coordinate the start and stop times of each run between the reference method sampling and PM CEMS operation. For a batch sampling PM CEMS, you must start the reference method at the same time as your PM CEMS sampling.

(ii) You must note the times for port changes (and other periods when the reference method sampling may be suspended) on the data sheets so that you can adjust your PM CEMS data accordingly, if necessary.

(iii) You must properly align the time periods for your PM CEMS and your reference method measurements to account for your PM CEMS response time.

(3) You must conduct a minimum of 15 valid runs each consisting of simultaneous PM CEMS and reference method measurement sets.

(i) You may conduct more than 15 sets of CEMS and reference method measurements. If you choose this option, you may reject certain test results so long as the total number of valid test results you use to determine the correlation is greater than or equal to 15.

(ii) You must report all data, including the rejected data.

(iii) You may reject the results of up to five test runs without explanation.

(iv) If you reject the results of more than five test runs, the basis for rejecting the results of the additional test runs must be explicitly stated in the reference method, this performance specification, Procedure 2 of appendix F, or your quality assurance plan.

(4) Simultaneous PM CEMS and reference method measurements must be performed in a manner to ensure that the range of data that will be used to establish the correlation for your PM CEMS is maximized. You must first attempt to maximize your correlation range by following the procedures described in paragraphs (4)(i) through (iv) of this section. If you cannot obtain the three levels as described in paragraphs (i) through (iv), then you must use the procedure described in section 8.6(5).

(i) You must attempt to obtain the three different levels of PM mass concentration by varying process operating conditions, varying PM control device conditions, or by means of PM spiking.

(ii) The three PM concentration levels you use in the correlation tests must be distributed over the complete operating range experienced by your source.

(iii) At least 20 percent of the minimum 15 measured data points you use should be contained in each of the following levels:

• Level 1: From no PM (zero concentration) emissions to 50 percent of the maximum PM concentration;

• Level 2: 25 to 75 percent of the maximum PM concentration; and

• Level 3: 50 to 100 percent of the maximum PM concentration.

(iv) Although the above levels overlap, you may only apply individual run data to one level.

(5) If you cannot obtain three distinct levels of PM concentration as described, you must perform correlation testing over the maximum range of PM concentrations that is practical for your PM CEMS. To ensure that the range of data used to establish the correlation for your PM CEMS is maximized, you must follow one or more of the steps in paragraphs (5)(i) through (iv) of this section.

(i) Zero point data for *in-situ* instruments should be obtained, to the extent possible, by removing the instrument from the stack and monitoring ambient air on a test bench.

(ii) Zero point data for extractive instruments should be obtained by removing the extractive probe from the stack and drawing in clean ambient air.

(iii) Zero point data also can be obtained by performing manual reference method measurements when the flue gas is free of PM emissions or contains very low PM concentrations (*e.g.,* when

your process is not operating, but the fans are operating or your source is combusting only natural gas).

(iv) If none of the steps in paragraphs (5)(i) through (iii) of this section are possible, you must estimate the monitor response when no PM is in the flue gas (*e.g.,* 4 mA = 0 mg/acm).

8.7 What do I do with the initial correlation test data for my PM CEMS? You must calculate and report the results of the correlation testing, including the correlation coefficient, confidence interval, and tolerance interval for the PM CEMS response and reference method correlation data that are use to establish the correlation, as specified in section 12. You must include all data sheets, calculations, charts (records of PM CEMS responses), process data records including PM control equipment operating parameters, and reference media certifications necessary to confirm that your PM CEMS met the requirements of this performance specification. In addition, you must:

(1) Determine the integrated (arithmetic average) PM CEMS output over each reference method test period;

(2) Adjust your PM CEMS outputs and reference method test data to the same clock time (considering response time of your PM CEMS);

(3) Confirm that the reference method results are consistent with your PM CEMS response in terms of, where applicable, moisture, temperature, pressure, and diluent concentrations; and

(4) Determine whether any of the reference method test results do not meet the test method criteria.

8.8 What is the limitation on the range of my PM CEMS correlation? Although the data you collect during the correlation testing should be representative of the full range of normal operating conditions at your source, you must conduct additional correlation testing if either of the conditions specified in paragraphs (1) and (2) of this section occurs.

(1) If your source is a low-emitting source, as defined in section 3.16 of this specification, you must conduct additional correlation testing if either of the events specified in paragraphs (1)(i) or (ii) of this section occurs while your source is operating under normal conditions.

(i) Your source generates 24 consecutive hourly average PM CEMS responses that are greater than 125 percent of the highest PM CEMS response (*e.g.,* mA reading) used for the correlation curve or are greater than the PM CEMS response that corresponds to 50 percent of the emission limit, whichever is greater, or

(ii) The cumulative hourly average PM CEMS responses generated by your source are greater than 125 percent of the highest PM CEMS response used for the correlation curve or are greater than the PM CEMS response that corresponds to 50 percent of the emission limit, whichever is greater, for more than 5 percent of your PM CEMS operating hours for the previous 30-day period.

(2) If your source is not a low-emitting source, as defined in section 3.16 of this specification, you must conduct additional correlation testing if either of the events specified in paragraph (i) or (ii) of this section occurs while your source is operating under normal conditions.

(i) Your source generates 24 consecutive hourly average PM CEMS responses that are greater than 125 percent of the highest PM CEMS response (*e.g.,* mA reading) used for the correlation curve, or

(ii) The cumulative hourly average PM CEMS responses generated by your source are greater than 125 percent of the highest PM CEMS response used for the correlation curve for more than 5 percent of your PM CEMS operating hours for the previous 30-day period.

(3) If additional correlation testing is required, you must conduct at least three additional test runs under the conditions that caused the higher PM CEMS response.

(i) You must complete the additional testing and use the resulting new data along with the previous data to calculate a revised correlation equation within 60 days after the occurrence of the event that requires additional testing, as specified in paragraphs 8.8(1) and (2).

(4) If your source generates consecutive PM CEMS hourly responses that are greater than 125 percent of the highest PM CEMS response used to develop the correlation curve for 24 hours or for a cumulative period that amounts to more than 5 percent of the PM CEMS operating hours for the previous 30-day period, you must report the reason for the higher PM CEMS responses.

9.0 What Quality Control Measures Are Required?

Quality control measures for PM CEMS are specified in 40 CFR 60, Appendix F, Procedure 2.

10.0 What Calibration and Standardization Procedures Must I Perform? [Reserved]

11.0 What Analytical Procedures Apply to This Procedure?

Specific analytical procedures are outlined in the applicable reference method(s).

12.0 What Calculations and Data Analyses Are Needed?

You must determine the primary relationship for correlating the output from your PM CEMS to a PM concentration, typically in units of mg/acm or mg/dscm of flue gas, using the calculations and data analysis process in sections 12.2 and 12.3. You develop the correlation by performing an appropriate regression analysis between your PM CEMS response and your reference method data.

12.1 How do I calculate upscale drift and zero drift? You must determine the difference in your PM CEMS output readings from the established reference values (zero and upscale check values) after a stated period of operation during which you performed no unscheduled maintenance, repair or adjustment.

(1) Calculate the upscale drift (UD) using Equation 11-1:

$$UD = \frac{|R_{CEM} - R_U|}{R_r} \times 100 \qquad \text{Eq. 11-1}$$

Where:

UD = The upscale (high-level) drift of your PM CEMS in percent,

R_{CEM} = The measured PM CEMS response to the upscale reference standard,

R_U = The pre-established numerical value of the upscale reference standard, and

R_r = The response range of the analyzer.

(2) Calculate the zero drift (ZD) using Equation 11-2:

$$ZD = \frac{|R_{CEM} - R_L|}{R_r} \times 100 \qquad \text{Eq. 11-2}$$

Where:

ZD = The zero (low-level) drift of your PM CEMS in percent,

R_{CEM} = The measured PM CEMS response to the zero reference standard,

R_L = The pre-established numerical value of the zero reference standard, and

R_r = The response range of the analyzer.

(3) Summarize the results on a data sheet similar to that shown in Table 2 (see section 17).

12.2 How do I perform the regression analysis? You must couple each reference method PM concentration measurement, y, in the appropriate units, with an average PM CEMS response, x, over corresponding time periods. You must complete your PM CEMS correlation calculations using data deemed acceptable by quality control procedures identified in 40 CFR 60, Appendix F, Procedure 2.

(1) You must evaluate all flagged or suspect data produced during measurement periods and determine whether they should be excluded from your PM CEMS's average.
(2) You must assure that the reference method and PM CEMS results are on a consistent moisture, temperature, and diluent basis. You must convert the reference method PM concentration measurements (dry standard conditions) to the units of your PM CEMS measurement conditions. The conditions of your PM CEMS measurement are monitor-specific. You must obtain from your PM CEMS vendor or instrument manufacturer the conditions and units of measurement for your PM CEMS.

(i) If your sample gas contains entrained water droplets and your PM CEMS is an extractive system that measures at actual conditions (*i.e.,* wet basis), you must use the measured moisture content determined from the impinger analysis when converting your reference method PM data to PM CEMS conditions; do not use the moisture content calculated from a psychrometric chart based on saturated conditions.

12.3 How do I determine my PM CEMS correlation? To predict PM concentrations from PM CEMS responses, you must use the calculation method of least squares presented in paragraphs (1) through (5) of this section. When performing the calculations, each reference method PM concentration measurement must be treated as a discrete data point; if using paired sampling trains, do not average reference method data pairs for any test run.

This performance specification describes procedures for evaluating five types of correlation models: linear, polynomial, logarithmic, exponential, and power. Procedures for selecting the most appropriate correlation model are presented in section 12.4 of this specification.

(1) How do I evaluate a linear correlation for my correlation test data? To evaluate a linear correlation, follow the procedures described in paragraphs (1)(i) through (iv) of this section.

(i) Calculate the linear correlation equation, which gives the predicted PM concentration () as a function of the PM CEMS response (x), as indicated by Equation 11-3:

$$\hat{y}=b_0+b_1x \qquad \text{(Eq. 11-3)}$$

Where:

$\hat{y}$ = the predicted PM concentration,

b_0 = the intercept for the correlation curve, as calculated using Equation 11-4,

b_1 = the slope of the correlation curve, as calculated using Equation 11-6, and

x = the PM CEMS response value.

Calculate the y intercept (b_0) of the correlation curve using Equation 11-4:

$$b_0=\bar{y}-b_1\cdot\bar{x} \qquad \text{(Eq. 11-4)}$$

Where:

$\bar{x}$ = the mean value of the PM CEMS response data, as calculated using Equation 11-5, and

$\bar{y}$ = the mean value of the PM concentration data, as calculated using Equation 11-5:

$$\bar{x}=\frac{1}{n}\sum_{i=1}^{n}x_i,\ \bar{y}=\frac{1}{n}\sum_{i=1}^{n}y_i \qquad \text{(Eq. 11-5)}$$

Where:

x_i = the PM CEMS response value for run i,

y_i = the PM concentration value for run i, and

n = the number of data points.

Calculate the slope (b_1) of the correlation curve using Equation 11-6:

$$b_1 = \frac{S_{xy}}{S_{xx}} \qquad \text{(Eq. 11-6)}$$

Where:

S_{xx}, S_{xy} = as calculated using Equation 11-7:

$$S_{xx} = \sum_{i=1}^{n}(x_i - \bar{x})^2, \; S_{xy} = \sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y}) \qquad \text{(Eq. 11-7)}$$

(ii) Calculate the half range of the 95 percent confidence interval (CI) for the predicted PM concentration () at the mean value of x, using Equation 11-8:

$$Cl = t_{df,1-a/2} S_L \sqrt{\frac{1}{n}} \qquad \text{(Eq. 11-8)}$$

Where:

CI = the half range of the 95 percent confidence interval for the predicted PM concentration at the mean x value,

$t_{df,1-a/2}$ = the value for the t statistic provided in Table 1 for df = (n - 2), and

S_L = the scatter or deviation of values about the correlation curve, which is determined using Equation 11-9:

$$S_L = \sqrt{\frac{1}{n-2}\sum_{i=1}^{n}(\hat{y}_i - y_i)^2} \qquad \text{(Eq. 11-9)}$$

Calculate the confidence interval half range for the predicted PM concentration () at the mean x value as a percentage of the emission limit (CI%) using Equation 11-10:

$$CI\% = \frac{CI}{EL} \cdot 100\% \qquad \text{(Eq. 11-10)}$$

Where:

CI = the half range of the 95 percent confidence interval for the predicted PM concentration at the mean x value, and

EL = PM emission limit, as described in section 13.2.

(iii) Calculate the half range of the tolerance interval (TI) for the predicted PM concentration () at the mean x value using Equation 11-11:

$$TI = k_T \cdot S_L \qquad \text{(Eq. 11-11)}$$

Where:

TI = the half range of the tolerance interval for the predicted PM concentration () at the mean x value,

k_T = as calculated using Equation 11-12, and

S_L = as calculated using Equation 11-9:

$$k_T = u_{n'} \cdot v_{df} \qquad \text{(Eq. 11-12)}$$

Where:

n′ = the number of test runs (n),

$u_{n'}$ = the tolerance factor for 75 percent coverage at 95 percent confidence provided in Table 1 for df = (n−2), and

v_{df} = the value from Table 1 for df = (n−2).

Calculate the half range of the tolerance interval for the predicted PM concentration () at the mean x value as a percentage of the emission limit (TI%) using Equation 11-13:

$$TI\% = \frac{TI}{EL} \cdot 100\% \qquad \text{(Eq. 11-13)}$$

Where:

TI = the half range of the tolerance interval for the predicted PM concentration () at the mean x value, and

EL = PM emission limit, as described in section 13.2.

(iv) Calculate the linear correlation coefficient (r) using Equation 11-14:

$$r = \sqrt{1 - \frac{S_L^2}{S_y^2}} \qquad \text{(Eq. 11-14)}$$

Where:

S_L = as calculated using Equation 11-9, and

S_y = as calculated using Equation 11-15:

$$S_y = \sqrt{\frac{\sum_{i=1}^{n}(y_i - \bar{y})^2}{n-1}} \qquad (Eq.\ 11\text{-}15)$$

(2) How do I evaluate a polynomial correlation for my correlation test data? To evaluate a polynomial correlation, follow the procedures described in paragraphs (2)(i) through (iv) of this section.

(i) Calculate the polynomial correlation equation, which is indicated by Equation 11-16, using Equations 11-17 through 11-22:

$$\hat{y} = b_0 + b_1 x + b_2 x^2 \qquad \text{(Eq. 11-16)}$$

Where:

= the PM CEMS concentration predicted by the polynomial correlation equation, and

b_0, b_1, b_2 = the coefficients determined from the solution to the matrix equation Ab=B

Where:

$$A = \begin{bmatrix} n & S_1 & S_2 \\ S_1 & S_2 & S_3 \\ S_2 & S_3 & S_4 \end{bmatrix}, \qquad b = \begin{bmatrix} b_0 \\ b_1 \\ b_2 \end{bmatrix}, \qquad B = \begin{bmatrix} S_5 \\ S_6 \\ S_7 \end{bmatrix}.$$

$$S_1 = \sum_{i=1}^{n}(x_i), S_2 = \sum_{i=1}^{n}(x_i^2), S_3 = \sum_{i=1}^{n}(x_i^3), S_4 = \sum_{i=1}^{n}(x_i^4) \qquad (Eq.\ 11\text{-}17)$$

$$S_5 = \sum_{i=1}^{n}(y_i), S_6 = \sum_{i=1}^{n}(x_i y_i), S_7 = \sum_{i=1}^{n}(x_i^2 y_i). \qquad (Eq.\ 11\text{-}18)$$

Where:

X_i = the PM CEMS response for run i,

Y_i = the reference method PM concentration for run i, and

n = the number of test runs.

Calculate the polynomial correlation curve coefficients (b_0, b_1, and b_2) using Equations 11-19 through 11-21, respectively:

$$b_0 = \frac{\left(S_5 \cdot S_2 \cdot S_4 + S_1 \cdot S_3 \cdot S_7 + S_2 \cdot S_6 \cdot S_3 - S_7 \cdot S_2 \cdot S_2 - S_3 \cdot S_3 \cdot S_5 - S_4 \cdot S_6 \cdot S_1\right)}{\det A} \quad \text{(Eq. 11-19)}$$

$$b_1 = \frac{\left(n \cdot S_6 \cdot S_4 + S_5 \cdot S_3 \cdot S_2 + S_2 \cdot S_1 \cdot S_7 - S_2 \cdot S_6 \cdot S_2 - S_7 \cdot S_3 \cdot n - S_4 \cdot S_1 \cdot S_5\right)}{\det A} \quad \text{(Eq. 11-20)}$$

$$b_2 = \frac{\left(n \cdot S_2 \cdot S_7 + S_1 \cdot S_6 \cdot S_2 + S_5 \cdot S_1 \cdot S_3 - S_2 \cdot S_2 \cdot S_5 - S_3 \cdot S_6 \cdot n - S_7 \cdot S_1 \cdot S_1\right)}{\det A} \quad \text{(Eq. 11-21)}$$

Where:

$$\det A = n \cdot S_2 \cdot S_4 - S_2 \cdot S_2 \cdot S_2 + S_1 \cdot S_3 \cdot S_2 - S_3 \cdot S_3 \cdot n + S_2 \cdot S_1 \cdot S_3 - S_4 \cdot S_1 \cdot S_1 \quad \text{(Eq. 11-22)}$$

(ii) Calculate the 95 percent confidence interval half range (CI) by first calculating the C coefficients (C_o to C_5) using Equations 11-23 and 11-24:

$$C_0 = \frac{\left(S_2 \cdot S_4 - S_3^2\right)}{D}, \quad C_1 = \frac{\left(S_3 \cdot S_2 - S_1 \cdot S_4\right)}{D}, \quad C_2 = \frac{\left(S_1 \cdot S_3 - S_2^2\right)}{D},$$

$$C_3 = \frac{\left(nS_4 - S_2^2\right)}{D}, \quad C_4 = \frac{\left(S_1 \cdot S_2 - nS_3\right)}{D}, \quad C_5 = \frac{\left(nS_2 - S_1^2\right)}{D} \quad \text{(Eq. 11-23)}$$

Where:

$$D = n\left(S_2 \cdot S_4 - S_3^2\right) + S_1\left(S_3 \cdot S_2 - S_1 \cdot S_4\right) + S_2\left(S_1 \cdot S_3 - S_2^2\right) \quad \text{(Eq. 11-24)}$$

Calculate Δ using Equation 11-25 for each x value:

$$\Delta = C_0 + 2C_1 x + \left(2C_2 + C_3\right)x^2 + 2C_4 x^3 + C_5 x^4 \quad \text{(Eq. 11-25)}$$

Determine the x value that corresponds to the minimum value of Δ (Δ_{min}). Determine the scatter or deviation of values about the polynomial correlation curve (S_P) using Equation 11-26:

$$S_r = \sqrt{\frac{1}{n-3}\sum_{i=1}^{n}\left(\hat{y}_i - y_i\right)^2} \quad \text{(Eq. 11-26)}$$

Calculate the half range of the 95 percent confidence interval (CI) for the predicted PM concentration () at the x value that corresponds to Δ_{min} using Equation 11-27:

$$CI = t_{df} \cdot S_p \sqrt{\Delta_{min}} \quad \text{(Eq. 11-27)}$$

Where:

df = (n-3), and

tdf = as listed in Table 1 (see section 17).

Calculate the half range of the 95 percent confidence interval for the predicted PM concentration at the x value that corresponds to Δ_{min} as a percentage of the emission limit (CI%) using Equation 11-28:

$$CI\% = \frac{CI}{EL} \cdot 100\% \qquad \text{(Eq. 11-28)}$$

Where:

CI = the half range of the 95 percent confidence interval for the predicted PM concentration at the x value that corresponds to Δ_{min}, and

EL = PM emission limit, as described in section 13.2.

(iii) Calculate the tolerance interval half range (TI) for the predicted PM concentration at the x value that corresponds to Δ_{min}, as indicated in Equation 11-29 for the polynomial correlation, using Equations 11-30 and 11-31:

$$TI = k_T \cdot S_p \qquad \text{(Eq. 11-29)}$$

Where:

$$k_T = u_{n'} \cdot v_{df} \qquad \text{(Eq. 11-30)}$$

$$n' = \frac{1}{\Delta} \qquad \text{(Eq. 11-31)}$$

$u_{n'}$ = the value indicated in Table 1 for df = (n′-3), and

v_{df} = the value indicated in Table 1 for df = (n′—3).

Calculate the tolerance interval half range for the predicted PM concentration at the x value that corresponds to Δ_{min} as a percentage of the emission limit (TI%) using Equation 11-32:

$$TI\% = \frac{TI}{EL} \cdot 100 \qquad \text{(Eq. 11-32)}$$

Where:

TI = the tolerance interval half range for the predicted PM concentration at the x value that corresponds to Δ_{min}, and

EL = PM emission limit, as described in section 13.2.

(iv) Calculate the polynomial correlation coefficient (r) using Equation 11-33:

$$r = \sqrt{1 - \frac{s_p^2}{s_y^2}} \qquad \text{(Eq. 11-33)}$$

Where:

S_P = as calculated using Equation 11-26, and

S_y = as calculated using Equation 11-15.

(3) How do I evaluate a logarithmic correlation for my correlation test data? To evaluate a logarithmic correlation, which has the form indicated by Equation 11-34, follow the procedures described in paragraphs (3)(i) through (iii) of this section.

$$\hat{y}=b_0+b_1 Ln(x) \qquad \text{(Eq. 11-34)}$$

(i) Perform a logarithmic transformation of each PM CEMS response value (x values) using Equation 11-35:

$$x_i'=Ln(x_i) \qquad \text{(Eq. 11-35)}$$

Where:

x_i' = is the transformed value of x_i, and

$Ln(x_i)$ = the natural logarithm of the PM CEMS response for run i.

(ii) Using the values for x_i' in place of the values for x_i, perform the same procedures used to develop the linear correlation equation described in paragraph (1)(i) of this section. The resulting equation has the form indicated by Equation 11-36:

$$\hat{y}=b_0+b_1 x' \qquad \text{(Eq. 11-36)}$$

Where:

x' = the natural logarithm of the PM CEMS response, and the variables , b_0, and b_1 are as defined in paragraph (1)(i) of this section.

(iii) Using the values for x_i' in place of the values for x_i, calculate the confidence interval half range at the mean x' value as a percentage of the emission limit (CI%), the tolerance interval half range at the mean x' value as a percentage of the emission limit (TI%), and the correlation coefficient (*r*) using the procedures described in paragraphs (1)(ii) through (iv) of this section.

(4) How do I evaluate an exponential correlation for my correlation test data? To evaluate an exponential correlation, which has the form indicated by Equation 11-37, follow the procedures described in paragraphs (4)(i) through (v) of this section:

$$\hat{y} = b_1 e^{b_0 x} \qquad \text{(Eq. 11-37)}$$

(i) Perform a logarithmic transformation of each PM concentration measurement (y values) using Equation 11-38:

$$y_i' = \mathrm{Ln}(y_i) \quad \text{(Eq. 11-38)}$$

Where:

y'_i = is the transformed value of y_i, and

$\mathrm{Ln}(y_i)$ = the natural logarithm of the PM concentration measurement for run i.

(ii) Using the values for y'_i in place of the values for y_i, perform the same procedures used to develop the linear correlation equation described in paragraph (1)(i) of this section. The resulting equation will have the form indicated by Equation 11-39.

$$\widehat{y'} = b_0 + b_1 x \quad \text{(Eq. 11-39)}$$

Where:

′ = the predicted log PM concentration value,

b'_0 = the natural logarithm of b_0, and the variables b_0, b_1, and x are as defined in paragraph (1)(i) of this section.

(iii) Using the values for y''_i in place of the values for y_i, calculate the half range of the 95 percent confidence interval (CI′), as described in paragraph (1)(ii) of this section for CI. Note that CI′ is on the log scale. Next, calculate the upper and lower 95 percent confidence limits for the mean value $\underline{y}'$ using Equations 11-40 and 11-41:

$$LCL' = \underline{y}' - CI' \quad \text{(Eq. 11-40)}$$

$$UCL' = \underline{y}' + CI' \quad \text{(Eq. 11-41)}$$

Where:

LCL′ = the lower 95 percent confidence limit for the mean value $\underline{y}'$,

UCL′ = the upper 95 percent confidence limit for the mean value $\underline{y}'$,

$\underline{y}'$ = the mean value of the log-transformed PM concentrations, and

CI′ = the half range of the 95 percent confidence interval for the predicted PM concentration (′), as calculated in Equation 11-8.

Calculate the half range of the 95 percent confidence interval (CI) on the original PM concentration scale using Equation 11-42:

$$CI = \frac{e^{UCL'} - e^{LCL'}}{2} \quad \text{(Eq. 11-42)}$$

Where:

CI = the half range of the 95 percent confidence interval on the original PM concentration scale, and UCL′ and LCL′ are as defined previously.

Calculate the half range of the 95 percent confidence interval for the predicted PM concentration corresponding to the mean value of x as a percentage of the emission limit (CI%) using Equation 11-10.

(iv) Using the values for y'_i in place of the values for y_i, calculate the half range tolerance interval (TI′), as described in paragraph (1)(iii) of this section for TI. Note that TI′ is on the log scale. Next, calculate the half range tolerance limits for the mean value $\underline{y}'$ using Equations 11-43 and 11-44:

$$LTL' = \underline{y}' - TI' \quad \text{(Eq. 11-43)}$$

$$UTL' = \underline{y}' + TI' \quad \text{(Eq. 11-44)}$$

Where:

LTL′ = the lower 95 percent tolerance limit for the mean value $\underline{y}'$,

UTL′ = the upper 95 percent tolerance limit for the mean value $\underline{y}'$,

$\underline{y}'$, = the mean value of the log-transformed PM concentrations, and

TI′ = the half range of the 95 percent tolerance interval for the predicted PM concentration (′), as calculated in Equation 11-11.

Calculate the half range tolerance interval (TI) on the original PM concentration scale using Equation 11-45:

$$TI = \frac{e^{UTL'} - e^{LTL'}}{2} \quad \text{(Eq. 11-45)}$$

TI = the half range of the 95 percent tolerance interval on the original PM scale, and UTL′ and LTL′ are as defined previously.

Calculate the tolerance interval half range for the predicted PM concentration corresponding to the mean value of x as a percentage of the emission limit (TI%) using Equation 11-13.

(v) Using the values for y''_i in place of the values for y_i, calculate the correlation coefficient (r) using the procedure described in paragraph (1)(iv) of this section.

(5) How do I evaluate a power correlation for my correlation test data? To evaluate a power correlation, which has the form indicated by Equation 11-46, follow the procedures described in paragraphs (5)(i) through (v) of this section.

$$\hat{y} = b_0 x^{b_1} \qquad \text{(Eq. 11-46)}$$

(i) Perform logarithmic transformations of each PM CEMS response (x values) and each PM concentration measurement (y values) using Equations 11-35 and 11-38, respectively.

(ii) Using the values for x''_i in place of the values for x_i, and the values for y''_i in place of the values for y_i, perform the same procedures used to develop the linear correlation equation described in paragraph (1)(i) of this section. The resulting equation will have the form indicated by Equation 11-47:

$$\hat{Y}' = b'_0 + b_1 x' \qquad \text{(Eq. 11-47)}$$

Where:

′ = the predicted log PM concentration value, and

x′ = the natural logarithm of the PM CEMS response values,

b′$_0$ = the natural logarithm of b_0, and the variables b_0, b_1, and x are as defined in paragraph (1)(i) of this section.

(iii) Using the same procedure described for exponential models in paragraph (4)(iii) of this section, calculate the half range of the 95 percent confidence interval for the predicted PM concentration corresponding to the mean value of x′ as a percentage of the emission limit.

(iv) Using the same procedure described for exponential models in paragraph (4)(iv) of this section, calculate the tolerance interval half range for the predicted PM concentration corresponding to the mean value of x′ as a percentage of the emission limit.

(v) Using the values for y'_i in place of the values for y_i, calculate the correlation coefficient (r) using the procedure described in paragraph (1)(iv) of this section.

Note: PS-11 does not address the application of correlation equations to calculate PM emission concentrations using PM CEMS response data during normal operations of a PM CEMS. However, we will provide guidance on the use of specific correlation models (i.e., logarithmic, exponential, and power models) to calculate PM concentrations in an operating PM CEMS in situations when the PM CEMS response values are equal to or less than zero, and the correlation model is undefined.

12.4 Which correlation model should I use? Follow the procedures described in paragraphs (1) through (4) of this section to determine which correlation model you should use.

(1) For each correlation model that you develop using the procedures described in section 12.3 of this specification, compare the confidence interval half range percentage, tolerance interval half range percentage, and correlation coefficient to the performance criteria specified in section 13.2 of this specification. You can use the linear, logarithmic, exponential, or power correlation model if the model satisfies all of the performance criteria specified in section 13.2 of this specification. However, to use the polynomial model you first must check that the polynomial correlation curve satisfies the criteria for minimum and maximum values specified in paragraph (3) of this section.

(2) If you develop more than one correlation curve that satisfy the performance criteria specified in section 13.2 of this specification, you should use the correlation curve with the greatest correlation coefficient. If the polynomial model has the greatest correlation coefficient, you first must check that the polynomial correlation curve satisfies the criteria for minimum and maximum values specified in paragraph (3) of this section.

(3) You can use the polynomial model that you develop using the procedures described in section 12.3(2) if the model satisfies the performance criteria specified in section 13.2 of this specification, and the minimum or maximum value of the polynomial correlation curve does not occur within the expanded data range. The minimum or maximum value of the polynomial correlation curve is the point where the slope of the curve equals zero. To determine if the minimum or maximum value occurs within the expanded data range, follow the procedure described in paragraphs (3)(i) through (iv) of this section.

(i) Determine if your polynomial correlation curve has a minimum or maximum point by comparing the polynomial coefficient b_2 to zero. If b_2 is less than zero, the curve has a maximum value. If b_2 is greater than zero, the curve has a minimum value. (Note: If b_2 equals zero, the correlation curve is linear.)

(ii) Calculate the minimum value using Equation 11-48.

$$\text{min or max} = -\frac{b_1}{2b_2} \qquad \text{(Eq. 11-48)}$$

(iii) If your polynomial correlation curve has a minimum point, you must compare the minimum value to the minimum PM CEMS response used to develop the correlation curve. If the correlation curve minimum value is less than or equal to the minimum PM CEMS response value, you can use the polynomial correlation curve, provided the correlation curve also satisfies all of the performance criteria specified in section 13.2 of this specification. If the correlation curve minimum value is greater than the minimum PM CEMS response value, you cannot use the polynomial correlation curve to predict PM concentrations.

(iv) If your polynomial correlation curve has a maximum, the maximum value must be greater than the allowable extrapolation limit. If your source is not a low-emitting source, as defined in section 3.16 of this specification, the allowable extrapolation limit is 125 percent of the highest PM CEMS response used to develop the correlation curve. If your source is a low-emitting source, the allowable extrapolation limit is 125 percent of the highest PM CEMS response used

to develop the correlation curve or the PM CEMS response that corresponds to 50 percent of the emission limit, whichever is greater. If the polynomial correlation curve maximum value is greater than the extrapolation limit, and the correlation curve satisfies all of the performance criteria specified in section 13.2 of this specification, you can use the polynomial correlation curve to predict PM concentrations. If the correlation curve maximum value is less than the extrapolation limit, you cannot use the polynomial correlation curve to predict PM concentrations.

(4) You may petition the Administrator for alternative solutions or sampling recommendations if the correlation models described in section 12.3 of this specification do not satisfy the performance criteria specified in section 13.2 of this specification.

13.0 What Are the Performance Criteria for My PM CEMS?

You must evaluate your PM CEMS based on the 7-day drift check, the accuracy of the correlation, and the sampling periods and cycle/response time.

13.1 What is the 7-day drift check performance specification? Your daily PM CEMS internal drift checks must demonstrate that the average daily drift of your PM CEMS does not deviate from the value of the reference light, optical filter, Beta attenuation signal, or other technology-suitable reference standard by more than 2 percent of the response range. If your CEMS includes diluent and/or auxiliary monitors (for temperature, pressure, and/or moisture) that are employed as a necessary part of this performance specification, you must determine the calibration drift separately for each ancillary monitor in terms of its respective output (see the appropriate performance specification for the diluent CEMS specification). None of the calibration drifts may exceed their individual specification.

13.2 What performance criteria must my PM CEMS correlation satisfy? Your PM CEMS correlation must meet each of the minimum specifications in paragraphs (1), (2), and (3) of this section. Before confidence and tolerance interval half range percentage calculations are made, you must convert the emission limit to the appropriate units of your PM CEMS measurement conditions using the average of emissions gas property values (*e.g.,* diluent concentration, temperature, pressure, and moisture) measured during the correlation test.

(1) The correlation coefficient must satisfy the criterion specified in paragraph (1)(i) or (ii), whichever applies.

(i) If your source is not a low-emitting source, as defined in section 3.16 of this specification, the correlation coefficient (r) must be greater than or equal to 0.85.

(ii) If your source is a low-emitting source, as defined in section 3.16 of this specification, the correlation coefficient (r) must be greater than or equal to 0.75.

(2) The confidence interval half range must satisfy the applicable criterion specified in paragraph (2)(i), (ii), or (iii) of this section, based on the type of correlation model.

(i) For linear or logarithmic correlations, the 95 percent confidence interval half range at the mean PM CEMS response value from the correlation test must be within 10 percent of the PM emission limit value specified in the applicable regulation. Therefore, the CI% calculated using Equation 11-10 must be less than or equal to 10 percent.

(ii) For polynomial correlations, the 95 percent confidence interval half range at the PM CEMS response value from the correlation test that corresponds to the minimum value for Δ must be within 10 percent of the PM emission limit value specified in the applicable regulation. Therefore, the CI% calculated using Equation 11-28 must be less than or equal to 10 percent.

(iii) For exponential or power correlations, the 95 percent confidence interval half range at the mean of the logarithm of the PM CEMS response values from the correlation test must be within 10 percent of the PM emission limit value specified in the applicable regulation. Therefore, the CI% calculated using Equation 11-10 must be less than or equal to 10 percent.

(3) The tolerance interval half range must satisfy the applicable criterion specified in paragraph (3)(i), (ii), or (iii) of this section, based on the type of correlation model.

(i) For linear or logarithmic correlations, the half range tolerance interval with 95 percent confidence and 75 percent coverage at the mean PM CEMS response value from the correlation test must be within 25 percent of the PM emission limit value specified in the applicable regulation. Therefore, the TI% calculated using Equation 11-13 must be less than or equal to 25 percent.

(ii) For polynomial correlations, the half range tolerance interval with 95 percent confidence and 75 percent coverage at the PM CEMS response value from the correlation test that corresponds to the minimum value for Δ must be within 25 percent of the PM emission limit value specified in the applicable regulation. Therefore, the TI% calculated using Equation 11-32 must be less than or equal to 25 percent.

(iii) For exponential or power correlations, the half range tolerance interval with 95 percent confidence and 75 percent coverage at the mean of the logarithm of the PM CEMS response values from the correlation test must be within 25 percent of the PM emission limit value specified in the applicable regulation. Therefore, the TI% calculated using Equation 11-13 must be less than or equal to 25 percent.

13.3 What are the sampling periods and cycle/response time? You must document and maintain the response time and any changes in the response time following installation.

(1) If you have a batch sampling PM CEMS, you must evaluate the limits presented in paragraphs (1)(i) and (ii) of this section.

(i) The response time of your PM CEMS, which is equivalent to the cycle time, must be no longer than 15 minutes. In addition, the delay between the end of the sampling time and reporting of the sample analysis must be no greater than 3 minutes. You must document any changes in the response time following installation.

(ii) The sampling time of your PM CEMS must be no less than 30 percent of the cycle time. If you have a batch sampling PM CEMS, sampling must be continuous except during pauses when the collected pollutant on the capture media is being analyzed and the next capture medium starts collecting a new sample.

13.4 What PM compliance monitoring must I do? You must report your CEMS measurements in the units of the standard expressed in the regulations (*e.g.,* mg/dscm @ 7 percent oxygen, pounds per million Btu (lb/mmBtu), etc.). You may need to install auxiliary data monitoring equipment to convert the units reported by your PM CEMS into units of the PM emission standard.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Which References Are Relevant to This Performance Specification?

16.1 Technical Guidance Document: Compliance Assurance Monitoring. U.S. Environmental Protection Agency Office of Air Quality Planning and Standards Emission Measurement Center. August 1998.

16.2 40 CFR 60, Appendix B, "Performance Specification 2—Specifications and Test Procedures for SO_2, and NO_X, Continuous Emission Monitoring Systems in Stationary Sources."

16.3 40 CFR 60, Appendix B, "Performance Specification 1—Specification and Test Procedures for Opacity Continuous Emission Monitoring Systems in Stationary Sources."

16.4 40 CFR 60, Appendix A, "Method 1—Sample and Velocity Traverses for Stationary Sources."

16.5 "Current Knowledge of Particulate Matter (PM) Continuous Emission Monitoring." EPA-454/R-00-039. U.S. Environmental Protection Agency, Research Triangle Park, NC. September 2000.

16.6 40 CFR 266, Appendix IX, section 2, "Performance Specifications for Continuous Emission Monitoring Systems."

16.7 ISO 10155, "Stationary Source Emissions—Automated Monitoring of Mass Concentrations of Particles: Performance Characteristics, Test Procedures, and Specifications." American National Standards Institute, New York City. 1995.

16.8 Snedecor, George W. and Cochran, William G. (1989), Statistical Methods, Eighth Edition, Iowa State University Press.

16.9 Wallis, W. A. (1951) "Tolerance Intervals for Linear Regression," in Second Berkeley Symposium on Mathematical Statistics and Probability, ed. J. Neyman, Berkeley: University of California Press, pp. 43-51.

17.0 What Reference Tables and Validation Data Are Relevant to PS-11?

Use the information in Table 1 for determining the confidence and tolerance interval half ranges. Use Table 2 to record your 7-day drift test data.

TABLE 1—FACTORS FOR CALCULATION OF CONFIDENCE AND TOLERANCE INTERVAL HALF RANGES

		Tolerance interval with 75% coverage and 95% confidence level		
df	**Student's t, t_{df}**	**v_{df} (95%)**	**$u_{n'}$ (75%)**	**k_T**
3	3.182	2.920	1.266	3.697
4	2.776	2.372	1.247	2.958
5	2.571	2.089	1.233	2.576
6	2.447	1.915	1.223	2.342
7	2.365	1.797	1.214	2.183
8	2.306	1.711	1.208	2.067
9	2.262	1.645	1.203	1.979
10	2.228	1.593	1.198	1.909
11	2.201	1.551	1.195	1.853
12	2.179	1.515	1.192	1.806
13	2.160	1.485	1.189	1.766
14	2.145	1.460	1.186	1.732
15	2.131	1.437	1.184	1.702
16	2.120	1.418	1.182	1.676
17	2.110	1.400	1.181	1.653
18	2.101	1.384	1.179	1.633
19	2.093	1.370	1.178	1.614
20	2.086	1.358	1.177	1.597
21	2.080	1.346	1.175	1.582
22	2.074	1.335	1.174	1.568
23	2.069	1.326	1.173	1.555
24	2.064	1.316	1.172	1.544
25	2.060	1.308	1.172	1.533

26	2.056	1.300	1.171	1.522
27	2.052	1.293	1.170	1.513
28	2.048	1.286	1.170	1.504
29	2.045	1.280	1.169	1.496
30	2.042	1.274	1.168	1.488
31	2.040	1.268	1.168	1.481
32	2.037	1.263	1.167	1.474
33	2.035	1.258	1.167	1.467
34	2.032	1.253	1.166	1.461
35	2.030	1.248	1.166	1.455
36	2.028	1.244	1.165	1.450
37	2.026	1.240	1.165	1.444
38	2.024	1.236	1.165	1.439
39	2.023	1.232	1.164	1.435
40	2.021	1.228	1.164	1.430
41	2.020	1.225	1.164	1.425
42	2.018	1.222	1.163	1.421
43	2.017	1.218	1.163	1.417
44	2.015	1.215	1.163	1.413
45	2.014	1.212	1.163	1.410
46	2.013	1.210	1.162	1.406
47	2.012	1.207	1.162	1.403
48	2.011	1.204	1.162	1.399
49	2.010	1.202	1.162	1.396
50	2.009	1.199	1.161	1.393
51	2.008	1.197	1.161	1.390
52	2.007	1.195	1.161	1.387
53	2.006	1.192	1.161	1.384
54	2.005	1.190	1.161	1.381
55	2.004	1.188	1.160	1.379

56	2.003	1.186	1.160	1.376
57	2.002	1.184	1.160	1.374
58	2.002	1.182	1.160	1.371
59	2.001	1.180	1.160	1.369
60	2.000	1.179	1.160	1.367

References 16.8 (t values) and 16.9 (v_{df} and $u_{n'}$ values).

TABLE 2—7-DAY DRIFT TEST DATA

Zero drift day #	Date and time	Zero check value (R_L)	PM CEMS response (R_{CEMS})	Difference ($R_{CEMS} - R_L$)	Zero drift $((R_{CEMS} - R_L) / R_U) \times 100$
1					
2					
3					
4					
5					
6					
7					
Upscale drift day #	**Date and time**	**Upscale check value (R_U)**	**PM CEMS response (R_{CEMS})**	**Difference ($R_{CEMS} - R_U$)**	**Upscale drift $((R_{CEMS} - R_U)/R_U) \times 100\%$**
1					
2					
3					
4					
5					
6					
7					

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PERFORMANCE SPECIFICATION 12A—SPECIFICATIONS AND TEST PROCEDURES FOR TOTAL VAPOR PHASE MERCURY CONTINUOUS EMISSION MONITORING SYSTEMS IN STATIONARY SOURCES

1.0 Scope and Application

1.1 Analyte. The analyte measured by these procedures and specifications is total vapor phase mercury (Hg) in the flue gas, which represents the sum of elemental Hg (Hg°, CAS Number 7439-97-6) and oxidized forms of gaseous Hg (Hg^{+2}), in concentration units of micrograms per cubic meter ($\mu g/m^3$).

1.2 Applicability.

1.2.1 This specification is for evaluating the acceptability of total vapor phase Hg continuous emission monitoring systems (CEMS) installed at stationary sources at the time of or soon after installation and whenever specified in the regulations. The Hg CEMS must be capable of measuring the total concentration in $\mu g/m^3$ of vapor phase Hg, regardless of speciation, and recording that concentration at standard conditions on a wet or dry basis. These specifications do not address measurement of particle bound Hg.

1.2.2 This specification is not designed to evaluate an installed CEMS's performance over an extended period of time nor does it identify specific calibration techniques and auxiliary procedures to assess the CEMS's performance. The source owner or operator, however, is responsible to calibrate, maintain, and operate the CEMS properly. The Administrator may require, under section 114 of the Clean Air Act, the operator to conduct CEMS performance evaluations at other times besides the initial performance evaluation test. *See* §§60.13(c) and 63.8(e)(1).

1.2.3 Mercury monitoring approaches not entirely suited to these specifications may be approvable under the alternative monitoring or alternative test method provisions of §60.13(i) and §63.8(f) or §60.8(b)(3) and §63.7(f), respectively.

2.0 Summary of Performance Specification

Procedures for determining CEMS relative accuracy, linearity, and calibration drift are outlined. CEMS installation and measurement location specifications, data reduction procedures, and performance criteria are included.

3.0 Definitions

3.1 *Continuous Emission Monitoring System (CEMS)* means the total equipment required to measure a pollutant concentration. The system generally consists of the following three major subsystems:

3.2 *Sample Interface* means that portion of the CEMS used for one or more of the following: sample acquisition, sample transport, sample conditioning, and protection of the monitor from the effects of the stack effluent.

3.3 *Hg Analyzer* means that portion of the Hg CEMS that measures the total vapor phase Hg mass concentration and generates a proportional output.

3.4 *Data Recorder* means that portion of the CEMS that provides a permanent electronic record of the analyzer output. The data recorder may provide automatic data reduction and CEMS control capabilities.

3.5 *Span Value* means the measurement range as specified in the applicable regulation or other requirement. If the span is not specified in the applicable regulation or other requirement, then it must be a value approximately equivalent to two times the emission standard. Unless otherwise specified, the span value may be rounded up to the nearest multiple of 10.

3.6 *Measurement Error Test* means a test procedure in which the accuracy of the concentrations measured by a CEMS at three or more points over its measurement range is evaluated using reference gases. For Hg CEMS, elemental and oxidized Hg (Hg^0 and mercuric chloride, $HgCl_2$) gas standards of known concentration are used for this procedure.

3.7 *Measurement Error (ME)* means the absolute value of the difference between the concentration indicated by the CEMS and the known concentration of a reference gas, expressed as a percentage of the span value, when the entire CEMS, including the sampling interface, is challenged.

3.8 *Calibration Drift (CD)* means the absolute value of the difference between the CEMS output response and either an upscale Hg reference gas or a zero-level Hg reference gas, expressed as a percentage of the span value, when the entire CEMS, including the sampling interface, is challenged after a stated period of operation during which no unscheduled maintenance or repair took place.

3.9 *Relative Accuracy Test Procedure* means a test procedure consisting of at least nine test runs, in which the accuracy of the concentrations measured by a CEMS is evaluated by comparison against concurrent measurements made with a reference method (RM). Relative accuracy tests repeated on a regular, on-going basis are referred to as relative accuracy test audits or RATAs.

3.10 *Relative Accuracy (RA)* means the absolute mean difference between the pollutant concentrations determined by the CEMS and the values determined by the RM plus the 2.5 percent error confidence coefficient of a series of tests divided by the mean of the RM tests. Alternatively, for sources with an average RM concentration less than 5.0 micrograms per

standard cubic meter (µg/scm), the RA may be expressed as the absolute value of the difference between the mean CEMS and RM values.

4.0 Interferences [Reserved]

5.0 Safety

The procedures required under this performance specification may involve hazardous materials, operations, and equipment. This performance specification may not address all of the safety problems associated with these procedures. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicable regulatory limitations prior to performing these procedures. The CEMS user's manual and materials recommended by the RM should be consulted for specific precautions to be taken.

6.0 Equipment and Supplies

6.1 CEMS Equipment Specifications.

6.1.1 Data Recorder Scale. The Hg CEMS data recorder output range must include the full range of expected Hg concentration values in the gas stream to be sampled including zero and the span value.

6.1.2 The Hg CEMS design should also provide for the determination of CD and ME at a zero value (zero to 20 percent of the span value) and at upscale values (between 50 and 100 percent of the span value). The Hg CEMS must be constructed to permit the introduction of known concentrations of Hg and $HgCl_2$ separately into the sampling system of the CEMS immediately preceding the sample extraction filtration system such that the entire CEMS can be challenged.

6.2 Reference Gas Delivery System. The reference gas delivery system must be designed so that the flowrate exceeds the sampling system flow requirements of the CEMS and that the gas is delivered to the CEMS at atmospheric pressure.

6.3 Other equipment and supplies, as needed by the reference method used for the Relative Accuracy Test Procedure.*See* section 8.6.2.

7.0 Reagents and Standards

7.1 Reference Gases. Reference gas standards are required for both elemental and oxidized Hg (Hg and mercuric chloride, $HgCl_2$). The use of National Institute of Standards and Technology (NIST)-traceable standards and reagents is required. The following gas concentrations are required.

7.1.1 Zero-level. 0 to 20 percent of the span value.

7.1.2 Mid-level. 50 to 60 percent of the span value.

7.1.3 High-level. 80 to 100 percent of the span value.

7.2 Reference gas standards may also be required for the reference methods. *See* section 8.6.2.

8.0 Performance Specification Test Procedure

8.1 Installation and Measurement Location Specifications.

8.1.1 CEMS Installation. Install the CEMS at an accessible location downstream of all pollution control equipment. Place the probe outlet or other sampling interface at a point or location in the stack (or vent) representative of the stack gas concentration of Hg. Since the Hg CEMS sample system normally extracts gas from a single point in the stack, a location that has been shown to be free of stratification for Hg or, alternatively, SO_2 is recommended. If the cause of failure to meet the RA test requirement is determined to be the measurement location and a satisfactory correction technique cannot be established, the Administrator may require the CEMS to be relocated. Measurement locations and points or paths that are most likely to provide data that will meet the RA requirements are described in sections 8.1.2 and 8.1.3 below.

8.1.2 Measurement Location. The measurement location should be (1) at least two equivalent diameters downstream of the nearest control device, point of pollutant generation or other point at which a change of pollutant concentration may occur, and (2) at least half an equivalent diameter upstream from the effluent exhaust. The equivalent duct diameter is calculated according to Method 1 in appendix A-1 to this part.

8.1.3 Hg CEMS Sample Extraction Point. Use a sample extraction point either (1) no less than 1.0 meter from the stack or duct wall, or (2) within the centroidal velocity traverse area of the stack or duct cross section. This does not apply to cross-stack, in-situ measurement systems.

8.2 Measurement Error (ME) Test Procedure. Sequentially inject each of at least three elemental Hg reference gases (zero, mid-level, and high level, as defined in section 7.1), three times each for a total of nine injections. Inject the gases in such a manner that the entire CEMS is challenged. Do not inject the same gas concentration twice in succession. At each reference gas concentration, determine the average of the three CEMS responses and subtract the average response from the reference gas value. Calculate the measurement error (ME) using Equation 12-1 by expressing the absolute value of the difference between the average CEMS response (A) and the reference gas value (R) as a percentage of the span (*see*example data sheet in Figure 12A-1). For each elemental Hg reference gas, the absolute value of the difference between the CEMS response and the reference value must not exceed 5 percent of the span value. If this specification is not met, identify and correct the problem before proceeding. Repeat the measurement error test procedure using oxidized Hg reference gases. For each oxidized Hg reference gas, the absolute value of the difference between the CEMS response and the reference value shall not exceed 10 percent of the span value. If this specification is not met, identify and correct the problem before proceeding.

$$ME = \frac{|R - A|}{Span} x100 \qquad \text{(Equation 12A-1)}$$

8.3 Seven-Day Calibration Drift (CD) Test Procedure.

8.3.1 CD Test Period. While the affected facility is operating normally, or as specified in an applicable regulation, determine the magnitude of the CD once each day (at 24-hour intervals, to the extent practicable) for 7 consecutive unit operating days according to the procedures in sections 8.3.2 and 8.3.3. The 7 consecutive unit operating days need not be 7 consecutive calendar days. Use either Hg° or $HgCl_2$ standards for this test.

8.3.2 The purpose of the CD measurement is to verify the ability of the CEMS to conform to the established CEMS response used for determining emission concentrations or emission rates. Therefore, if periodic automatic or manual adjustments are made to the CEMS zero and upscale response settings, conduct the CD test immediately before these adjustments, or conduct it in such a way that the CD can be determined.

8.3.3 Conduct the CD test using the zero gas specified and either the mid-level or high-level gas as specified in section 7.1. Sequentially introduce the reference gases to the CEMS at the sampling system of the CEMS immediately preceding the sample extraction filtration system. Record the CEMS response (A) for each reference gas and, using Equation 12A-2, subtract the corresponding reference value (R) from the CEMS value, and express the absolute value of the difference as a percentage of the span value (*see also* example data sheet in Figure 12A-2). For each reference gas, the absolute value of the difference between the CEMS response and the reference value must not exceed 5 percent of the span value. If these specifications are not met, identify and correct the problem before proceeding.

$$CD = \frac{|R - A|}{Span} x100 \qquad \text{(Equation 12A-2)}$$

8.4 Relative Accuracy (RA) Test Procedure.

8.4.1 RA Test Period. Conduct the RA test according to the procedure given in sections 8.4.2 through 8.4.6 while the affected facility is operating normally, or as specified in an applicable subpart. The RA test may be conducted during the CD test period.

8.4.2 Reference Methods (RM). Unless otherwise specified in an applicable subpart of the regulations, use Method 29, Method 30A, or Method 30B in appendix A-8 to this part or American Society of Testing and Materials (ASTM) Method D6784-02 (incorporated by reference, *see* §60.17) as the RM for Hg concentration. For Method 29 and ASTM Method D6784-02 only, the filterable portion of the sample need not be included when making comparisons to the CEMS results. When Method 29, Method 30B, or ASTM D6784-02 is used, conduct the RM test runs with paired or duplicate sampling systems and use the average of the vapor phase Hg concentrations measured by the two trains. When Method 30A is used, paired sampling systems are not required. If the RM and CEMS measure on a different moisture basis, data derived with Method 4 in appendix A-3 to this part must also be obtained during the RA test.

8.4.3 Sampling Strategy for RM Tests. Conduct the RM tests in such a way that they will yield results representative of the emissions from the source and can be compared to the CEMS data. The RM and CEMS locations need not be immediately adjacent. Locate the RM measurement

points in accordance with section 8.1.3 of Performance Specification 2 (PS 2) in this appendix. It is preferable to conduct moisture measurements (if needed) and Hg measurements simultaneously, although moisture measurements that are taken within an hour of the Hg measurements may be used to adjust the Hg concentrations to a consistent moisture basis. In order to correlate the CEMS and RM data properly, note the beginning and end of each RM test period for each paired RM run (including the exact time of day) on the CEMS chart recordings or other permanent record of output.

8.4.4 Number and Length of RM Test Runs. Conduct a minimum of nine RM test runs. When Method 29, Method 30B, or ASTM D6784-02 is used, only test runs for which the paired RM trains meet the relative deviation criteria (RD) of this PS must be used in the RA calculations. In addition, for Method 29 and ASTM D6784-02, use a minimum sample time of 2 hours and for Methods 30A and 30B use a minimum sample time of 30 minutes.

NOTE: More than nine sets of RM test runs may be performed. If this option is chosen, RM test run results may be excluded so long as the total number of RM test run results used to determine the CEMS RA is greater than or equal to nine. However, all data must be reported including the excluded test run data.

8.4.5 Correlation of RM and CEMS Data. Correlate the CEMS and the RM test data as to the time and duration by first determining from the CEMS final output (the one used for reporting) the integrated average pollutant concentration for each RM test period. Consider system response time, if important, and confirm that the results are on a consistent moisture basis with the RM test. Then, compare each integrated CEMS value against the corresponding RM value. When Method 29, Method 30B, or ASTM D6784-02 is used, compare each CEMS value against the corresponding average of the paired RM values.

8.4.6 Paired RM Outliers.

8.4.6.1 When Method 29, Method 30B, or ASTM D6784-02 is used, outliers are identified through the determination of relative deviation (RD) of the paired RM tests. Data that do not meet the RD criteria must be flagged as a data quality problem and may not be used in the calculation of RA. The primary reason for performing paired RM sampling is to ensure the quality of the RM data. The percent RD of paired data is the parameter used to quantify data quality. Determine RD for paired data points as follows:

$$RD = \frac{|C_a - C_b|}{C_a + C_b} x\,100 \quad \text{(Equation 12A-3)}$$

Where:

C_a and C_b are the Hg concentration values determined from the paired samples.

8.4.6.2 The minimum performance criteria for RM Hg data is that RD for any data pair must be ≤10 percent as long as the mean Hg concentration is greater than 1.0 μg/m^3. If the mean Hg concentration is less than or equal to 1.0 μg/m^3, the RD must be ≤20 percent or ≤0.2

$\mu g/m^3$ absolute difference. Pairs of RM data exceeding these RD criteria should be eliminated from the data set used to develop a Hg CEMS correlation or to assess CEMS RA.

8.4.7 Calculate the mean difference between the RM and CEMS values in the units of micrograms per cubic meter ($\mu g/m^3$), the standard deviation, the confidence coefficient, and the RA according to the procedures in section 12.0.

8.5 Reporting. At a minimum (check with the appropriate EPA Regional Office, State or local Agency for additional requirements, if any), summarize in tabular form the results of the CD tests, the linearity tests, and the RA test or alternative RA procedure, as appropriate. Include all data sheets, calculations, charts (records of CEMS responses), reference gas concentration certifications, and any other information necessary to confirm that the CEMS meets the performance criteria.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

For Method 30A, sample collection and analysis are concurrent. For the other RM, post-run sample analyses are performed. Refer to the RM employed for specific analytical procedures.

12.0 Calculations and Data Analysis

Calculate and summarize the RA test results on a data sheet similar to Figure 12A-3.

12.1 Consistent Basis. All data from the RM and CEMS must be compared in units of micrograms per standard cubic meter (µg/scm), on a consistent and identified moisture basis. The values must be standardized to 20 °C, 760 mm Hg.

12.1.1 Moisture Correction (as applicable). If the RM and CEMS measure Hg on a different moisture basis, they will need to be corrected to a consistent basis. Use Equation 12A-4a to correct data from a wet basis to a dry basis.

$$Concentration_{(dry)} = \frac{Concentration_{(wet)}}{(1 - B_{ws})} \qquad \text{(Equation 12A-4a)}$$

Use Equation 12A-4b to correct data from a dry basis to a wet basis.

$Concentration_{(wet)} = Concentration_{(dry)} \times (1-B_{ws})$ (Equation 12A-4b)

Where:

B_{ws} is the moisture content of the flue gas from Method 4, expressed as a decimal fraction (e.g., for 8.0 percent H_2O, B_{ws}= 0.08).

12.2 Arithmetic Mean. Calculate $\bar{d}$, the arithmetic mean of the differences (d_i) of a data set as follows:

$$\bar{d} = \frac{1}{n}\sum_{i=1}^{n} d_i \qquad \text{(Equation 12A-5)}$$

Where:

n = Number of data points.

12.3 Standard Deviation. Calculate the standard deviation, S_d, as follows:

$$S_d = \left[\frac{\sum_{i=1}^{n} d_i^2 - \frac{\left[\sum_{i=1}^{n} d_i\right]^2}{n}}{n-1}\right]^{\frac{1}{2}} \qquad \text{(Equation 12A-6)}$$

Where:

$\sum_{i=1}^{n} d_i$ = Algebraic sum of the individual differences d_i.

12.3 Confidence Coefficient (CC). Calculate the 2.5 percent error confidence coefficient (one-tailed), CC, as follows:

$$CC = t_{0.975}\frac{S_d}{\sqrt{n}} \qquad \text{(Equation 12A-7)}$$

12.4 Relative Accuracy. Calculate the RA of a set of data as follows:

$$RA = \frac{\left|\left|\bar{d}\right| + |CC|\right|}{\overline{RM}} x\ 100 \qquad \text{(Equation 12A-8)}$$

Where:

$|\bar{d}|$ = Absolute value of the mean of the differences (from Equation 12A-5)

$|CC|$ = Absolute value of the confidence coefficient (from Equation 12A-7)

RM = Average reference method value

13.0 Method Performance

13.1 Measurement Error (ME). For Hg^0, the ME must not exceed 5 percent of the span value at the zero-, mid-, and high-level reference gas concentrations. For $HgCl_2$, the ME must not exceed 10 percent of the span value at the zero-, mid-, and high-level reference gas concentrations.

13.2 Calibration Drift (CD). The CD must not exceed 5 percent of the span value on any of the 7 days of the CD test.

13.3 Relative Accuracy (RA). The RA of the CEMS must be no greater than 20 percent of the mean value of the RM test data in terms of units of µg/scm. Alternatively, if the mean RM is less than 5.0 µg/scm, the results are acceptable if the absolute value of the difference between the mean RM and CEMS values does not exceed 1.0 µg/scm.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures [Reserved]

17.0 Bibliography

17.1 40 CFR part 60, appendix B, "Performance Specification 2—Specifications and Test Procedures for SO_2 and NO_XContinuous Emission Monitoring Systems in Stationary Sources."

17.2 40 CFR part 60, appendix A, "Method 29—Determination of Metals Emissions from Stationary Sources."

17.3 40 CFR part 60, appendix A, "Method 30A—Determination of Total Vapor Phase Mercury Emissions From Stationary Sources (Instrumental Analyzer Procedure).

17.4 40 CFR part 60, appendix A, "Method 30B—Determination of Total Vapor Phase Mercury Emissions From Coal-Fired Combustion Sources Using Carbon Sorbent Traps."

17.5 ASTM Method D6784-02, "Standard Test Method for Elemental, Oxidized, Particle-Bound and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method)."

18.0 Tables and Figures

TABLE 12A-1—T-VALUES

n^a	$t_{0.975}$	n^a	$t_{0.975}$	n^a	$t_{0.975}$
2	12.706	7	2.447	12	2.201
3	4.303	8	2.365	13	2.179
4	3.182	9	2.306	14	2.160
5	2.776	10	2.262	15	2.145
6	2.571	11	2.228	16	2.131

[a]The values in this table are already corrected for n-1 degrees of freedom. Use n equal to the number of individual values.

FIGURE 12A-1—ME DETERMINATION

	Date	Time	Reference gas value (µg/m³)	CEMS measured value (µg/m³)	Absolute difference (µg/m³)	ME (% of span value)
Zero level						
	Average					
Mid level						
	Average					
High level						
	Average					

FIGURE 12A-2—7-DAY CALIBRATION DRIFT DETERMINATION

	Date	Time	Reference gas value (µg/m^3)	CEMS measured value (µg/m^3)	Absolute difference (µg/m^3)	CD (% of span value)
Zero level						
Upscale (Mid or High)						

FIGURE 12A-3—RELATIVE ACCURACY TEST DATA

Run No.	Date	Begin time	End time	RM value (µg/m^3)	CEMS value (µg/m^3)	Difference (µg/m^3)	Run used? (Yes/No)	RD[1]
1								
2								
3								
4								
5								
6								
7								
8								
9								
10								
11								
12								
Average Values								
Arithmetic Mean Difference:								
Standard Deviation:								
Confidence Coefficient:								
T-Value:								
% Relative Accuracy:								
$\lvert (RM)_{avg} - (CEMS)_{avg} \rvert$:								

[1]Calculate the RD only if paired samples are taken using RM 30B, RM 29, or ASTM 6784-08. Express RD as a percentage or, for very low RM concentrations (≤1.0 µg/m^3), as the absolute difference between C_a and C_b.

APPENDIX D TO PART 60—REQUIRED EMISSION INVENTORY INFORMATION

(a) Completed NEDS point source form(s) for the entire plant containing the designated facility, including information on the applicable criteria pollutants. If data concerning the plant are already in NEDS, only that information must be submitted which is necessary to update the existing NEDS record for that plant. Plant and point identification codes for NEDS records shall correspond to those previously assigned in NEDS; for plants not in NEDS, these codes shall be obtained from the appropriate Regional Office.

(b) Accompanying the basic NEDS information shall be the following information on each designated facility:

(1) The state and county identification codes, as well as the complete plant and point identification codes of the designated facility in NEDS. (The codes are needed to match these data with the NEDS data.)

(2) A description of the designated facility including, where appropriate:

(i) Process name.

(ii) Description and quantity of each product (maximum per hour and average per year).

(iii) Description and quantity of raw materials handled for each product (maximum per hour and average per year).

(iv) Types of fuels burned, quantities and characteristics (maximum and average quantities per hour, average per year).

(v) Description and quantity of solid wastes generated (per year) and method of disposal.

(3) A description of the air pollution control equipment in use or proposed to control the designated pollutant, including:

(i) Verbal description of equipment.

(ii) Optimum control efficiency, in percent. This shall be a combined efficiency when more than one device operates in series. The method of control efficiency determination shall be indicated (e.g., design efficiency, measured efficiency, estimated efficiency).

(iii) Annual average control efficiency, in percent, taking into account control equipment down time. This shall be a combined efficiency when more than one device operates in series.

(4) An estimate of the designated pollutant emissions from the designated facility (maximum per hour and average per year). The method of emission determination shall also be specified (e.g., stack test, material balance, emission factor).

[40 FR 53349, Nov. 17, 1975]

APPENDIX E TO PART 60 [RESERVED]

APPENDIX F TO PART 60—QUALITY ASSURANCE PROCEDURES

PROCEDURE 1. QUALITY ASSURANCE REQUIREMENTS FOR GAS CONTINUOUS EMISSION MONITORING SYSTEMS USED FOR COMPLIANCE DETERMINATION

1. Applicability and Principle

1.1 Applicability. Procedure 1 is used to evaluate the effectiveness of quality control (QC) and quality assurance (QA) procedures and the quality of data produced by any continuous emission monitoring system (CEMS) that is used for determining compliance with the emission standards on a continuous basis as specified in the applicable regulation. The CEMS may include pollutant (e.g., $S0_2$ and $N0_x$) and diluent (e.g., 0_2 or $C0_2$) monitors.

This procedure specifies the minimum QA requirements necessary for the control and assessment of the quality of CEMS data submitted to the Environmental Protection Agency (EPA). Source owners and operators responsible for one or more CEMS's used for compliance monitoring must meet these minimum requirements and are encouraged to develop and implement a more extensive QA program or to continue such programs where they already exist.

Data collected as a result of QA and QC measures required in this procedure are to be submitted to the Agency. These data are to be used by both the Agency and the CEMS operator in assessing the effectiveness of the CEMS QC and QA procedures in the maintenance of acceptable CEMS operation and valid emission data.

Appendix F, Procedure 1 is applicable December 4, 1987. The first CEMS accuracy assessment shall be a relative accuracy test audit (RATA) (see section 5) and shall be completed by March 4, 1988 or the date of the initial performance test required by the applicable regulation, whichever is later.

1.2 Principle. The QA procedures consist of two distinct and equally important functions. One function is the assessment of the quality of the CEMS data by estimating accuracy. The other function is the control and improvement of the quality of the CEMS data by implementing QC policies and corrective actions. These two functions form a control loop: When the assessment function indicates that the data quality is inadequate, the control effort must be increased until the data quality is acceptable. In order to provide uniformity in the assessment and reporting of data quality, this procedure explicitly specifies the assessment methods for response drift and accuracy. The methods are based on procedures included in the applicable performance specifications (PS's) in appendix B of 40 CFR part 60. Procedure 1 also requires the analysis of the EPA audit

samples concurrent with certain reference method (RM) analyses as specified in the applicable RM's.

Because the control and corrective action function encompasses a variety of policies, specifications, standards, and corrective measures, this procedure treats QC requirements in general terms to allow each source owner or operator to develop a QC system that is most effective and efficient for the circumstances.

2. Definitions

2.1 Continuous Emission Monitoring System. The total equipment required for the determination of a gas concentration or emission rate.

2.2 Diluent Gas. A major gaseous constituent in a gaseous pollutant mixture. For combustion sources, CO_2 and O_2 are the major gaseous constituents of interest.

2.3 Span Value. The upper limit of a gas concentration measurement range that is specified for affected source categories in the applicable subpart of the regulation.

2.4 Zero, Low-Level, and High-Level Values. The CEMS response values related to the source specific span value. Determination of zero, low-level, and high-level values is defined in the appropriate PS in appendix B of this part.

2.5 Calibration Drift (CD). The difference in the CEMS output reading from a reference value after a period of operation during which no unscheduled maintenance, repair or adjustment took place. The reference value may be supplied by a cylinder gas, gas cell, or optical filter and need not be certified.

2.6 Relative Accuracy (RA). The absolute mean difference between the gas concentration or emission rate determined by the CEMS and the value determined by the RM's plus the 2.5 percent error confidence coefficient of a series of tests divided by the mean of the RM tests or the applicable emission limit.

3. QC Requirements

Each source owner or operator must develop and implement a QC program. As a minimum, each QC program must include written procedures which should describe in detail, complete, step-by-step procedures and operations for each of the following activities:

1. Calibration of CEMS.
2. CD determination and adjustment of CEMS.
3. Preventive maintenance of CEMS (including spare parts inventory).
4. Data recording, calculations, and reporting.
5. Accuracy audit procedures including sampling and analysis methods.
6. Program of corrective action for malfunctioning CEMS.

As described in Section 5.2, whenever excessive inaccuracies occur for two consecutive quarters, the source owner or operator must revise the current written procedures or modify or replace the CEMS to correct the deficiency causing the excessive inaccuracies.

These written procedures must be kept on record and available for inspection by the enforcement agency.

4. CD Assessment

4.1 CD Requirement. As described in 40 CFR 60.13(d), source owners and operators of CEMS must check, record, and quantify the CD at two concentration values at least once daily (approximately 24 hours) in accordance with the method prescribed by the manufacturer. The CEMS calibration must, as minimum, be adjusted whenever the daily zero (or low-level) CD or the daily high-level CD exceeds two times the limits of the applicable PS's in appendix B of this regulation.

4.2 Recording Requirement for Automatic CD Adjusting Monitors. Monitors that automatically adjust the data to the corrected calibration values (e.g., microprocessor control) must be programmed to record the unadjusted concentration measured in the CD prior to resetting the calibration, if performed, or record the amount of adjustment.

4.3 Criteria for Excessive CD. If either the zero (or low-level) or high-level CD result exceeds twice the applicable drift specification in appendix B for five, consecutive, daily periods, the CEMS is out-of-control. If either the zero (or low-level) or high-level CD result exceeds four times the applicable drift specification in appendix B during any CD check, the CEMS is out-of-control. If the CEMS is out-of-control, take necessary corrective action. Following corrective action, repeat the CD checks.

4.3.1 Out-Of-Control Period Definition. The beginning of the out-of-control period is the time corresponding to the completion of the fifth, consecutive, daily CD check with a CD in excess of two times the allowable limit, or the time corresponding to the completion of the daily CD check preceding the daily CD check that results in a CD in excess of four times the allowable limit. The end of the out-of-control period is the time corresponding to the completion of the CD check following corrective action that results in the CD's at both the zero (or low-level) and high-level measurement points being within the corresponding allowable CD limit (i.e., either two times or four times the allowable limit in appendix B).

4.3.2 CEMS Data Status During Out-of-Control Period. During the period the CEMS is out-of-control, the CEMS data may not be used in calculating emission compliance nor be counted towards meeting minimum data availability as required and described in the applicable subpart [e.g., §60.47a(f)].

4.4 Data Recording and Reporting. As required in §60.7(d) of this regulation (40 CFR part 60), all measurements from the CEMS must be retained on file by the source owner for at least 2 years. However, emission data obtained on each successive day while the CEMS is out-of-control may not be included as part of the minimum daily data requirement of the applicable subpart [e.g., §60.47a(f)] nor be used in the calculation of reported emissions for that period.

5. Data Accuracy Assessment

5.1 Auditing Requirements. Each CEMS must be audited at least once each calendar quarter. Successive quarterly audits shall occur no closer than 2 months. The audits shall be conducted as follows:

5.1.1 Relative Accuracy Test Audit (RATA). The RATA must be conducted at least once every four calendar quarters, except as otherwise noted in section 5.1.4 of this appendix. Conduct the RATA as described for the RA test procedure in the applicable PS in appendix B (e.g., PS 2 for SO_2 and NO_X). In addition, analyze the appropriate performance audit samples received from EPA as described in the applicable sampling methods (e.g., Methods 6 and 7).

5.1.2 Cylinder Gas Audit (CGA). If applicable, a CGA may be conducted in three of four calendar quarters, but in no more than three quarters in succession.

To conduct a CGA: (1) Challenge the CEMS (both pollutant and diluent portions of the CEMS, if applicable) with an audit gas of known concentration at two points within the following ranges:

Audit point	Audit range		
	Pollutant monitors	Diluent monitors for—	
		CO_2	O_2
1	20 to 30% of span value.	5 to 8% by volume.	4 to 6% by volume.
2	50 to 60% of span value.	10 to 14% by volume.	8 to 12% by volume.

Challenge the CEMS three times at each audit point, and use the average of the three responses in determining accuracy.

Use of separate audit gas cylinder for audit points 1 and 2. Do not dilute gas from audit cylinder when challenging the CEMS.

The monitor should be challenged at each audit point for a sufficient period of time to assure adsorption-desorption of the CEMS sample transport surfaces has stabilized.

(2) Operate each monitor in its normal sampling mode, i.e., pass the audit gas through all filters, scrubbers, conditioners, and other monitor components used during normal sampling, and as much of the sampling probe as is practical. At a minimum, the audit gas should be introduced at the connection between the probe and the sample line.

(3) Use Certified Reference Materials (CRM's) (See Citation 1) audit gases that have been certified by comparison to National Institute of Standards and Technology (NIST) or EPA Traceability Protocol Materials (ETPM's) following the most recent edition of EPA's Traceability Protocol No. 1 (See Citation 2). Procedures for preparation of CRM's are described in Citation 1. Procedures for preparation of ETPM's are described in Citation 2. As an alternative to CRM's or ETPM gases, Method 205 (See Citation 3) may be used. The difference between the actual concentration of the audit gas and the concentration indicated by the monitor is used to assess the accuracy of the CEMS.

5.1.3 Relative Accuracy Audit (RAA). The RAA may be conducted three of four calendar quarters, but in no more than three quarters in succession. To conduct a RAA, follow the procedure described in the applicable PS in appendix B for the relative accuracy test, except that only three sets of measurement data are required. Analyses of EPA performance audit samples are also required.

The relative difference between the mean of the RM values and the mean of the CEMS responses will be used to assess the accuracy of the CEMS.

5.1.4 Other Alternative Audits. Other alternative audit procedures may be used as approved by the Administrator for three of four calendar quarters. One RATA is required at least every four calendar quarters, except in the case where the affected facility is off-line (does not operate) in the fourth calendar quarter since the quarter of the previous RATA. In that case, the RATA shall be performed in the quarter in which the unit recommences operation. Also, cylinder gas audits are not be required for calendar quarters in which the affected facility does not operate.

5.2 Excessive Audit Inaccuracy. If the RA, using the RATA, CGA, or RAA exceeds the criteria in section 5.2.3, the CEMS is out-of-control. If the CEMS is out-of-control, take necessary corrective action to eliminate the problem. Following corrective action, the source owner or operator must audit the CEMS with a RATA, CGA, or RAA to determine if the CEMS is operating within the specifications. A RATA must always be used following an out-of-control period resulting from a RATA. The audit following corrective action does not require analysis of EPA performance audit samples. If audit results show the CEMS to be out-of-control, the CEMS operator shall report both the audit showing the CEMS to be out-of-control and the results of the audit following corrective action showing the CEMS to be operating within specifications.

5.2.1 Out-Of-Control Period Definition. The beginning of the out-of-control period is the time corresponding to the completion of the sampling for the RATA, RAA, or CGA. The end of the out-of-control period is the time corresponding to the completion of the sampling of the subsequent successful audit.

5.2.2 CEMS Data Status During Out-Of-Control Period. During the period the monitor is out-of-control, the CEMS data may not be used in calculating emission compliance nor be counted towards meeting minimum data availabilty as required and described in the applicable subpart [e.g., §60.47a(f)].

5.2.3 Criteria for Excessive Audit Inaccuracy. Unless specified otherwise in the applicable subpart, the criteria for excessive inaccuracy are:

(1) For the RATA, the allowable RA in the applicable PS in appendix B.

(2) For the CGA, ±15 percent of the average audit value or ±5 ppm, whichever is greater.

(3) For the RAA, ±15 percent of the three run average or ±7.5 percent of the applicable standard, whichever is greater.

5.3 Criteria for Acceptable QC Procedure. Repeated excessive inaccuracies (i.e., out-of-control conditions resulting from the quarterly audits) indicates the QC procedures are inadequate or that the CEMS is incapable of providing quality data. Therefore, whenever excessive inaccuracies occur for two consective quarters, the source owner or operator must revise the QC procedures (see Section 3) or modify or replace the CEMS.

6. Calculations for CEMS Data Accuracy

6.1 RATA RA Calculation. Follow the equations described in Section 8 of appendix B, PS 2 to calculate the RA for the RATA. The RATA must be calculated in units of the applicable emission standard (e.g., ng/J).

6.2 RAA Accuracy Calculation. Use Equation 1–1 to calculate the accuracy for the RAA. The RAA must be calculated in units of the applicable emission standard (e.g., ng/J).

6.3 CGA Accuracy Calculation. Use Equation 1–1 to calculate the accuracy for the CGA, which is calculated in units of the appropriate concentration (e.g., ppm SO_2 or percent O_2). Each component of the CEMS must meet the acceptable accuracy requirement.

$$A = \frac{C_m - C_a}{C_a} \times 100 \qquad \text{Eq. 1-1}$$

where:

A=Accuracy of the CEMS, percent.

C_m=Average CEMS response during audit in units of applicable standard or appropriate concentration.

C_a=Average audit value (CGA certified value or three-run average for RAA) in units of applicable standard or appropriate concentration.

6.4 Example Accuracy Calculations. Example calculations for the RATA, RAA, and CGA are available in Citation 3.

7. Reporting Requirements

At the reporting interval specified in the applicable regulation, report for each CEMS the accuracy results from Section 6 and the CD assessment results from Section 4. Report the drift and accuracy information as a Data Assessment Report (DAR), and include one copy of this DAR for each quarterly audit with the report of emissions required under the applicable subparts of this part.

As a minimum, the DAR must contain the following information:

1. Source owner or operator name and address.

2. Identification and location of monitors in the CEMS.

3. Manufacturer and model number of each monitor in the CEMS.

4. Assessment of CEMS data accuracy and date of assessment as determined by a RATA, RAA, or CGA described in Section 5 including the RA for the RATA, the A for the RAA or CGA, the RM results, the cylinder gases certified values, the CEMS responses, and the calculations results as defined in Section 6. If the accuracy audit results show the CEMS to be out-of-control, the CEMS operator shall report both the audit results showing the CEMS to be out-of-control and the results of the audit following corrective action showing the CEMS to be operating within specifications.

5. Results from EPA performance audit samples described in Section 5 and the applicable RM's.

6. Summary of all corrective actions taken when CEMS was determined out-of-control, as described in Sections 4 and 5.

An example of a DAR format is shown in Figure 1.

8. Bibliography

1. ''A Procedure for Establishing Traceability of Gas Mixtures to Certain National Bureau of Standards Standard Reference Materials.'' Joint publication by NBS and EPA–600/7–81–010, Revised 1989. Available from the U.S. Environmental Protection Agency. Quality Assurance Division (MD–77). Research Triangle Park, NC 27711.

2. ''EPA Traceability Protocol For Assay And Certification Of Gaseous Calibration Standards.'' EPA–600/R–97/121, September 1997. Available from EPA's Emission Measurement Center at *http://www.epa.gov/ttn/emc*.

3. Method 205, ''Verification of Gas Dilution Systems for Field Instrument Calibrations,'' 40 CFR 51, appendix M.

FIGURE 1—EXAMPLE FORMAT FOR DATA ASSESSMENT REPORT

Period ending date _____
Year _____
Company name _____
Plant name _____
Source unit no. _____
CEMS manufacturer _____
Model no. _____
CEMS serial no. _____
CEMS type (e.g., in situ) _____
CEMS sampling location (e.g., control device outlet) _____
CEMS span values as per the applicable regulation: _____ (e.g., SO_2 _____ ppm, NO_x _____ ppm). _____

I. Accuracy assessment results (Complete A, B, or C below for each CEMS or for each pollutant and diluent analyzer, as applicable.) If the quarterly audit results show the CEMS to be out-of-control, report the results of both the quarterly audit and the audit following corrective action showing the CEMS to be operating properly.

A. Relative accuracy test audit (RATA) for _____ (e.g., SO_2 in ng/J).

1. Date of audit _____.
2. Reference methods (RM's) used _____ (e.g., Methods 3 and 6).
3. Average RM value _____ (e.g., ng/J, mg/dsm^3, or percent volume).
4. Average CEMS value _____.
5. Absolute value of mean difference [d] _____.
6. Confidence coefficient [CC] _____.
7. Percent relative accuracy (RA) _____ percent.
8. EPA performance audit results:
a. Audit lot number (1) _____ (2) _____
b. Audit sample number (1) _____ (2) _____
c. Results (mg/dsm^3) (1) _____ (2) _____
d. Actual value (mg/dsm^3)* (1) _____ (2) _____
e. Relative error* (1) _____ (2) _____

B. Cylinder gas audit (CGA) for _____ (e.g., SO_2 in ppm).

	Audit point 1	Audit point 2	
1. Date of audit.			
2. Cylinder ID number.			
3. Date of certification.			
4. Type of certification	.....	.....	(e.g., EPA Protocol 1 or CRM).
5. Certified audit value	.....	.....	(e.g., ppm).
6. CEMS response value	.....	.....	(e.g., ppm).
7. Accuracy	.....	.....	percent.

C. Relative accuracy audit (RAA) for _____ (e.g., SO_2 in ng/J).

1. Date of audit _____.
2. Reference methods (RM's) used _____ (e.g., Methods 3 and 6).
3. Average RM value _____ (e.g., ng/J).
4. Average CEMS value _____.
5. Accuracy _____ percent.
6. EPA performance audit results:
a. Audit lot number (1) _____ (2) _____
b. Audit sample number (1) _____ (2) _____
c. Results (mg/dsm^3) (1) _____ (2) _____
d. Actual value (mg/dsm^3) *(1) _____ (2)
e. Relative error* (1) _____ (2) _____

D. Corrective action for excessive inaccuracy.

1. Out-of-control periods.
a. Date(s) _____.
b. Number of days _____.
2. Corrective action taken _____
3. Results of audit following corrective action. (Use format of A, B, or C above, as applicable.)

II. Calibration drift assessment.

A. Out-of-control periods.
1. Date(s) _____.
2. Number of days _____.

B. Corrective action taken _____

PROCEDURE 2—QUALITY ASSURANCE REQUIREMENTS FOR PARTICULATE MATTER CONTINUOUS EMISSION MONITORING SYSTEMS AT STATIONARY SOURCES

1.0 What Are the Purpose and Applicability of Procedure 2?

The purpose of Procedure 2 is to establish the minimum requirements for evaluating the effectiveness of quality control (QC) and quality assurance (QA) procedures and the quality of data produced by your particulate matter (PM) continuous emission monitoring system (CEMS). Procedure 2 applies to PM CEMS used for continuously determining compliance with emission standards or operating permit limits as specified in an applicable regulation or permit. Other QC procedures may apply to diluent (*e.g.*, O_2) monitors and other auxiliary monitoring equipment included with your CEMS to facilitate PM measurement or determination of PM concentration in units specified in an applicable regulation.

1.1 What measurement parameter does Procedure 2 address? Procedure 2 covers the instrumental measurement of PM as defined by your source's applicable reference method (no Chemical Abstract Service number assigned).

1.2 For what types of devices must I comply with Procedure 2? You must comply with Procedure 2 for the total equipment that:

(1) We require you to install and operate on a continuous basis under the applicable regulation, and

*To be completed by the Agency.

(2) You use to monitor the PM mass concentration associated with the operation of a process or emission control device.

1.3 What are the data quality objectives (DQOs) of Procedure 2? The overall DQO of Procedure 2 is the generation of valid, representative data that can be transferred into useful information for determining PM CEMS concentrations averaged over a prescribed interval. Procedure 2 is also closely associated with Performance Specification 11 (PS–11).

(1) Procedure 2 specifies the minimum requirements for controlling and assessing the quality of PM CEMS data submitted to us or the delegated permitting authority.

(2) You must meet these minimum requirements if you are responsible for one or more PM CEMS used for compliance monitoring. We encourage you to develop and implement a more extensive QA program or to continue such programs where they already exist.

1.4 What is the intent of the QA/QC procedures specified in Procedure 2? Procedure 2 is intended to establish the minimum QA/QC requirements for PM CEMS and is presented in general terms to allow you to develop a program that is most effective for your circumstances. You may adopt QA/QC procedures that go beyond these minimum requirements to ensure compliance with applicable regulations.

1.5 When must I comply with Procedure 2? You must comply with the basic requirements of Procedure 2 immediately following successful completion of the initial correlation test of PS–11.

2.0 What Are the Basic Requirements of Procedure 2?

Procedure 2 requires you to perform periodic evaluations of PM CEMS performance and to develop and implement QA/QC programs to ensure that PM CEMS data quality is maintained.

2.1 What are the basic functions of Procedure 2?

(1) Assessment of the quality of your PM CEMS data by estimating measurement accuracy;

(2) Control and improvement of the quality of your PM CEMS data by implementing QC requirements and corrective actions until the data quality is acceptable; and

(3) Specification of requirements for daily instrument zero and upscale drift checks and daily sample volume checks, as well as routine response correlation audits, absolute correlation audits, sample volume audits, and relative response audits.

3.0 What Special Definitions Apply to Procedure 2?

The definitions in Procedure 2 include those provided in PS–11 of Appendix B, with the following additions:

3.1 ''Absolute Correlation Audit (ACA)'' means an evaluation of your PM CEMS response to a series of reference standards covering the full measurement range of the instrument (*e.g.*, 4 mA to 20 mA).

3.2 ''Correlation Range'' means the range of PM CEMS responses used in the complete set of correlation test data.

3.3 ''PM CEMS Correlation'' means the site-specific relationship (*i.e.*, a regression equation) between the output from your PM CEMS (*e.g.*, mA) and the particulate concentration, as determined by the reference method. The PM CEMS correlation is expressed in the same units as the PM concentration measured by your PM CEMS (*e.g.*, mg/acm). You must derive this relation from PM CEMS response data and manual reference method data that were gathered simultaneously. These data must be representative of the full range of source and control device operating conditions that you expect to occur. You must develop the correlation by performing the steps presented in sections 12.2 and 12.3 of PS–11.

3.4 ''Reference Method Sampling Location'' means the location in your source's exhaust duct from which you collect manual reference method data for developing your PM CEMS correlation and for performing relative response audits (RRAs) and response correlation audits (RCAs).

3.5 ''Response Correlation Audit (RCA)'' means the series of tests specified in section 10.3(8) of this procedure that you conduct to ensure the continued validity of your PM CEMS correlation.

3.6 ''Relative Response Audit (RRA)'' means the brief series of tests specified in section 10.3(6) of this procedure that you conduct between consecutive RCAs to ensure the continued validity of your PM CEMS correlation.

3.7 ''Sample Volume Audit (SVA)'' means an evaluation of your PM CEMS measurement of sample volume if your PM CEMS determines PM concentration based on a measure of PM mass in an extracted sample volume and an independent determination of sample volume.

4.0 Interferences [Reserved]

5.0 What Do I Need To Know To Ensure the Safety of Persons Using Procedure 2?

People using Procedure 2 may be exposed to hazardous materials, operations, and equipment. Procedure 2 does not purport to address all of the safety issues associated with its use. It is your responsibility to establish appropriate safety and health practices and determine the applicable regulatory limitations before performing this procedure. You must consult your CEMS user's manual for specific precautions to be taken with regard to your PM CEMS procedures.

6.0 What Equipment and Supplies Do I Need? [Reserved]

7.0 What Reagents and Standards Do I Need?

You will need reference standards or procedures to perform the zero drift check, the upscale drift check, and the sample volume check.

7.1 What is the reference standard value for the zero drift check? You must use a zero check value that is no greater than 20 percent of the PM CEMS's response range. You must obtain documentation on the zero check value from your PM CEMS manufacturer.

7.2 What is the reference standard value for the upscale drift check? You must use an upscale check value that produces a response between 50 and 100 percent of the PM CEMS's response range. For a PM CEMS that produces output over a range of 4 mA to 20 mA, the upscale check value must produce a response in the range of 12 mA to 20 mA. You must obtain documentation on the upscale check value from your PM CEMS manufacturer.

7.3 What is the reference standard value for the sample volume check? You must use a reference standard value or procedure that produces a sample volume value equivalent to the normal sampling rate. You must obtain documentation on the sample volume value from your PM CEMS manufacturer.

8.0 What Sample Collection, Preservation, Storage, and Transport Are Relevant to This Procedure? [Reserved]

9.0 What Quality Control Measures Are Required by This Procedure for My PM CEMS?

You must develop and implement a QC program for your PM CEMS. Your QC program must, at a minimum, include written procedures that describe, in detail, complete step-by-step procedures and operations for the activities in paragraphs (1) through (8) of this section.

(1) Procedures for performing drift checks, including both zero drift and upscale drift and the sample volume check (see sections 10.2(1), (2), and (5)).

(2) Methods for adjustment of PM CEMS based on the results of drift checks, sample volume checks (if applicable), and the periodic audits specified in this procedure.

(3) Preventative maintenance of PM CEMS (including spare parts inventory and sampling probe integrity).

(4) Data recording, calculations, and reporting.

(5) RCA and RRA procedures, including sampling and analysis methods, sampling strategy, and structuring test conditions over the prescribed range of PM concentrations.

(6) Procedures for performing ACAs and SVAs and methods for adjusting your PM CEMS response based on ACA and SVA results.

(7) Program of corrective action for malfunctioning PM CEMS, including flagged data periods.

(8) For extractive PM CEMS, procedures for checking extractive system ducts for material accumulation.

9.1 What QA/QC documentation must I have? You are required to keep the written QA/QC procedures on record and available for inspection by us, the State, and/or local enforcement agency for the life of your CEMS or until you are no longer subject to the requirements of this procedure.

9.2 How do I know if I have acceptable QC procedures for my PM CEMS? Your QC procedures are inadequate or your PM CEMS is incapable of providing quality data if you fail two consecutive QC audits (*i.e.*, out-of-control conditions resulting from the annual audits, quarterly audits, or daily checks). Therefore, if you fail the same two consecutive audits, you must revise your QC procedures or modify or replace your PM CEMS to correct the deficiencies causing the excessive inaccuracies (see section 10.4 for limits for excessive audit inaccuracy).

10.0 What Calibration/Correlation and Standardization Procedures Must I Perform for My PM CEMS?

You must generate a site-specific correlation for each of your PM CEMS installation(s) relating response from your PM CEMS to results from simultaneous PM reference method testing. The PS–11 defines procedures for developing the correlation and defines a series of statistical parameters for assessing acceptability of the correlation. However, a critical component of your PM CEMS correlation process is ensuring the accuracy and precision of reference method data. The activities listed in sections 10.1 through 10.10 assure the quality of the correlation.

10.1 When should I use paired trains for reference method testing? Although not required, we recommend that you should use paired-train reference method testing to generate data used to develop your PM CEMS correlation and for RCA testing. Guidance on the use of paired sampling trains can be found in the PM CEMS Knowledge Document (see section 16.5 of PS–11).

10.2 What routine system checks must I perform on my PM CEMS? You must perform routine checks to ensure proper operation of system electronics and optics, light and radiation sources and detectors, and electric or electro-mechanical systems. Necessary components of the routine system checks will depend on design details of your PM CEMS. As a minimum, you must verify the system operating parameters listed in paragraphs (1) through (5) of this section on a daily basis. Some PM CEMS may perform one or more of

these functions automatically or as an integral portion of unit operations; for other PM CEMS, you must initiate or perform one or more of these functions manually.

(1) You must check the zero drift to ensure stability of your PM CEMS response to the zero check value. You must determine system output on the most sensitive measurement range when the PM CEMS is challenged with a zero reference standard or procedure. You must, at a minimum, adjust your PM CEMS whenever the daily zero drift exceeds 4 percent.

(2) You must check the upscale drift to ensure stability of your PM CEMS response to the upscale check value. You must determine system output when the PM CEMS is challenged with a reference standard or procedure corresponding to the upscale check value. You must, at a minimum, adjust your PM CEMS whenever the daily upscale drift check exceeds 4 percent.

(3) For light-scattering and extinction-type PM CEMS, you must check the system optics to ensure that system response has not been altered by the condition of optical components, such as fogging of lens and performance of light monitoring devices.

(4) You must record data from your automatic drift-adjusting PM CEMS before any adjustment is made. If your PM CEMS automatically adjusts its response to the corrected calibration values (*e.g.*, microprocessor control), you must program your PM CEMS to record the unadjusted concentration measured in the drift check before resetting the calibration. Alternately, you may program your PM CEMS to record the amount of adjustment.

(5) For extractive PM CEMS that measure the sample volume and use the measured sample volume as part of calculating the output value, you must check the sample volume on a daily basis to verify the accuracy of the sample volume measuring equipment. This sample volume check must be done at the normal sampling rate of your PM CEMS. You must adjust your PM CEMS sample volume measurement whenever the daily sample volume check error exceeds 10 percent.

10.3 What are the auditing requirements for my PM CEMS? You must subject your PM CEMS to an ACA and an SVA, as applicable, at least once each calender quarter. Successive quarterly audits must occur no closer than 2 months apart. You must conduct an RCA and an RRA at the frequencies specified in the applicable regulation or facility operating permit. An RRA or RCA conducted during any calendar quarter can take the place of the ACA required for that calendar quarter. An RCA conducted during the period in which an RRA is required can take the place of the RRA for that period.

(1) When must I perform an ACA? You must perform an ACA each quarter unless you conduct an RRA or RCA during that same quarter.

(2) How do I perform an ACA? You perform an ACA according to the procedure specified in paragraphs (2)(i) through (v) of this section.

(i) You must challenge your PM CEMS with an audit standard or an equivalent audit reference to reproduce the PM CEMS's measurement at three points within the following ranges:

Audit point	Audit range
1	0 to 20 percent of measurement range
2	40 to 60 percent of measurement range
3	70 to 100 percent of measurement range

(ii) You must then challenge your PM CEMS three times at each audit point and use the average of the three responses in determining accuracy at each audit point. Use a separate audit standard for audit points 1, 2, and 3. Challenge the PM CEMS at each audit point for a sufficient period of time to ensure that your PM CEMS response has stabilized.

(iii) Operate your PM CEMS in the mode, manner, and range specified by the manufacturer.

(iv) Store, maintain, and use audit standards as recommended by the manufacturer.

(v) Use the difference between the actual known value of the audit standard and the response of your PM CEMS to assess the accuracy of your PM CEMS.

(3) When must I perform an SVA? You must perform an audit of the measured sample volume (*e.g.*, the sampling flow rate for a known time) once per quarter for applicable PM CEMS with an extractive sampling system. Also, you must perform and pass an SVA prior to initiation of any of the reference method data collection runs for an RCA or RRA.

(4) How do I perform an SVA? You perform an SVA according to the procedure specified in paragraphs (4)(i) through (iii) of this section.

(i) You perform an SVA by independently measuring the volume of sample gas extracted from the stack or duct over each batch cycle or time period with a calibrated device. You may make this measurement either at the inlet or outlet of your PM CEMS, so long as it measures the sample gas volume without including any dilution or recycle air. Compare the measured volume with the volume reported by your PM CEMS for the same cycle or time period to calculate sample volume accuracy.

(ii) You must make measurements during three sampling cycles for batch extractive monitors (*e.g.*, Beta-gauge) or during three periods of at least 20 minutes for continuous extractive PM CEMS.

(iii) You may need to condense, collect, and measure moisture from the sample gas prior to the calibrated measurement device (*e.g.*, dry gas meter) and correct the results for moisture content. In any case, the volumes measured by the calibrated device and your PM CEMS must be on a consistent temperature, pressure, and moisture basis.

(5) How often must I perform an RRA? You must perform an RRA at the frequency specified in the applicable regulation or facility operating permit. You may conduct an RCA instead of an RRA during the period when the RRA is required.

(6) How do I perform an RRA? You must perform the RRA according to the procedure specified in paragraphs (6)(i) and (ii) of this section.

(i) You perform an RRA by collecting three simultaneous reference method PM concentration measurements and PM CEMS measurements at the as-found source operating conditions and PM concentration.

(ii) We recommend that you use paired trains for reference method sampling. Guidance on the use of paired sampling trains can be found in the PM CEMS Knowledge Document (see section 16.5 of PS–11).

(7) How often must I perform an RCA? You must perform an RCA at the frequency specified in the applicable regulation or facility operating permit.

(8) How do I perform an RCA? You must perform the RCA according to the procedures for the PM CEMS correlation test described in PS–11, section 8.6, except that the minimum number of runs required is 12 in the RCA instead of 15 as specified in PS–11.

(9) What other alternative audits can I use? You can use other alternative audit procedures as approved by us, the State, or local agency for the quarters when you would conduct ACAs.

10.4 What are my limits for excessive audit inaccuracy? Unless specified otherwise in the applicable subpart, the criteria for excessive audit inaccuracy are listed in paragraphs (1) through (6) of this section.

(1) What are the criteria for excessive zero or upscale drift? Your PM CEMS is out of control if the zero drift check or upscale drift check either exceeds 4 percent for five consecutive daily periods or exceeds 8 percent for any one day.

(2) What are the criteria for excessive sample volume measurement error? Your PM CEMS is out of control if sample volume check error exceeds 10 percent for five consecutive daily periods or exceeds 20 percent for any one day.

(3) What are the criteria for excessive ACA error? Your PM CEMS is out of control if the results of any ACA exceed ± 10 percent of the average audit value, as calculated using Equation 2–1a, or 7.5 percent of the applicable standard, as calculated using Equation 2–1b, whichever is greater.

(4) What is the criterion for excessive SVA error? Your PM CEMS is out of control if results exceed ±5 percent of the average sample volume audit value.

(5) What are the criteria for passing an RCA? To pass an RCA, you must meet the criteria specified in paragraphs (5)(i) through (iii) of this section. If your PM CEMS fails to meet these RCA criteria, it is out of control.

(i) For all 12 data points, the PM CEMS response value can be no greater than the greatest PM CEMS response value used to develop your correlation curve.

(ii) For 9 of the 12 data points, the PM CEMS response value must lie within the PM CEMS output range used to develop your correlation curve.

(iii) At least 75 percent of a minimum number of 12 sets of PM CEMS and reference method measurements must fall within a specified area on a graph of the correlation regression line. The specified area on the graph of the correlation regression line is defined by two lines parallel to the correlation regression line, offset at a distance of ±25 percent of the numerical emission limit value from the correlation regression line.

(6) What are the criteria to pass an RRA? To pass an RRA, you must meet the criteria specified in paragraphs (6)(i) and (ii) of this section. If your PM CEMS fails to meet these RRA criteria, it is out of control.

(i) For all three data points, the PM CEMS response value can be no greater than the greatest PM CEMS response value used to develop your correlation curve.

(ii) For two of the three data points, the PM CEMS response value must lie within the PM CEMS output range used to develop your correlation curve.

(iii) At least two of the three sets of PM CEMS and reference method measurements must fall within the same specified area on a graph of the correlation regression line as required for the RCA and described in paragraph (5)(iii) of this section.

10.5 What do I do if my PM CEMS is out of control? If your PM CEMS is out of control, you must take the actions listed in paragraphs (1) and (2) of this section.

(1) You must take necessary corrective action to eliminate the problem and perform tests, as appropriate, to ensure that the corrective action was successful.

(i) Following corrective action, you must repeat the previously failed audit to confirm that your PM CEMS is operating within the specifications.

(ii) If your PM CEMS failed an RRA, you must take corrective action until your PM CEMS passes the RRA criteria. If the RRA criteria cannot be achieved, you must perform an RCA.

(iii) If your PM CEMS failed an RCA, you must follow procedures specified in section 10.6 of this procedure.

(2) You must report both the audit showing your PM CEMS to be out of control and the results of the audit following corrective action showing your PM CEMS to be operating within specifications.

10.6 What do I do if my PM CEMS fails an RCA? After an RCA failure, you must take all applicable actions listed in paragraphs (1) through (3) of this section.

(1) Combine RCA data with data from the active PM CEMS correlation and perform the mathematical evaluations defined in PS–11 for development of a PM CEMS correlation, including examination of alternate correlation models (*i.e.,* linear, polynomial, logarithmic, exponential, and power). If the expanded data base and revised correlation meet PS–11 statistical criteria, use the revised correlation.

(2) If the criteria specified in paragraph (1) of this section are not achieved, you must develop a new PM CEMS correlation based on revised data. The revised data set must consist of the test results from only the RCA. The new data must meet all requirements of PS–11 to develop a revised PM CEMS correlation, except that the minimum number of sets of PM CEMS and reference method measurements is 12 instead of the minimum of 15 sets required by PS–11. Your PM CEMS is considered to be back in controlled status when the revised correlation meets all of the performance criteria specified in section 13.2 of PS–11.

(3) If the actions in paragraphs (1) and (2) of this section do not result in an acceptable correlation, you must evaluate the cause(s) and comply with the actions listed in paragraphs (3)(i) through (iv) of this section within 90 days after the completion of the failed RCA.

(i) Completely inspect your PM CEMS for mechanical or operational problems. If you find a mechanical or operational problem, repair your PM CEMS and repeat the RCA.

(ii) You may need to relocate your PM CEMS to a more appropriate measurement location. If you relocate your PM CEMS, you must perform a new correlation test according to the procedures specified in PS–11.

(iii) The characteristics of the PM or gas in your source's flue gas stream may have changed such that your PM CEMS measurement technology is no longer appropriate. If this is the case, you must install a PM CEMS with measurement technology that is appropriate for your source's flue gas characteristics. You must perform a new correlation test according to the procedures specified in PS–11.

(iv) If the corrective actions in paragraphs (3)(i) through (iii) of this section were not successful, you must petition us, the State, or local agency for approval of alternative criteria or an alternative for continuous PM monitoring.

10.7 When does the out-of-control period begin and end? The out-of-control period begins immediately after the last test run or check of an unsuccessful RCA, RRA, ACA, SVA, drift check, or sample volume check. The out-of-control period ends immediately after the last test run or check of the subsequent successful audit or drift check.

10.8 Can I use the data recorded by my PM CEMS during out-of-control periods? During any period when your PM CEMS is out of control, you may not use your PM CEMS data to calculate emission compliance or to meet minimum data availability requirements described in the applicable regulation.

10.9 What are the QA/QC reporting requirements for my PM CEMS? You must report the accuracy results for your PM CEMS, specified in section 10.4 of this procedure, at the interval specified in the applicable regulation. Report the drift and accuracy information as a Data Assessment Report (DAR), and include one copy of this DAR for each quarterly audit with the report of emissions required under the applicable regulation. An example DAR is provided in Procedure 1, Appendix F of this part.

10.10 What minimum information must I include in my DAR? As a minimum, you must include the information listed in paragraphs (1) through (5) of this section in the DAR:

(1) Your name and address.

(2) Identification and location of monitors in your CEMS.

(3) Manufacturer and model number of each monitor in your CEMS.

(4) Assessment of PM CEMS data accuracy/acceptability, and date of assessment, as determined by an RCA, RRA, ACA, or SVA described in section 10, including the acceptability determination for the RCA or RRA, the accuracy for the ACA or SVA, the reference method results, the audit standards, your PM CEMS responses, and the calculation results as defined in section 12. If the accuracy audit results show your PM CEMS to be out of control, you must report both the audit results showing your PM CEMS to be out of control and the results of the audit following corrective action showing your PM CEMS to be operating within specifications.

(5) Summary of all corrective actions you took when you determined your PM CEMS to be out of control, as described in section 10.5, or after failing on RCA, as described in section 10.6.

10.7 Where and how long must I retain the QA data that this procedure requires me to record for my PM CEMS? You must keep the records required by this procedure for your PM CEMS onsite and available for inspection by us, the State, and/or local enforcement agency for a period of 5 years.

11.0 What Analytical Procedures Apply to This Procedure?

Sample collection and analysis are concurrent for this procedure. You must refer to the appropriate reference method for the specific analytical procedures.

12.0 What Calculations and Data Analysis Must I Perform for my PM CEMS?

(1) How do I determine RCA and RRA acceptability? You must plot each of your PM CEMS and reference method data sets from an RCA or RRA on a graph based on your PM CEMS correlation line to determine if the criteria in paragraphs 10.4(5) or (6), respectively, are met.

(2) How do I calculate ACA accuracy? You must use either Equation 2–1a or 2–1b to calculate ACA accuracy for each of the three audit points. However, when calculating ACA accuracy for the first audit point (0 to 20 percent of measurement range), you must use Equation 2–1b to calculate ACA accuracy if the reference standard value (R_v) equals zero.

$$\text{ACA Accuracy} = \frac{|R_{CEM} - R_V|}{R_V} \times 100\% \qquad \text{Eq. 2-1a}$$

Where:

ACA Accuracy = The ACA accuracy at each audit point, in percent,

R_{CEM} = Your PM CEMS response to the reference standard, and

R_V = The reference standard value.

$$\text{ACA Accuracy} = \frac{|C_{CEM} - C_{RV}|}{C_S} \times 100\% \qquad \text{Eq. 2-1b}$$

Where:

ACA Accuracy = The ACA accuracy at each audit point, in percent,

C_{CEM} = The PM concentration that corresponds to your PM CEMS response to the reference standard, as calculated using the correlation equation for your PM CEMS,

C_{RV} = The PM concentration that corresponds to the reference standard value in units consistent with C_{CEM}, and

C_s = The PM concentration that corresponds to the applicable emission limit in units consistent with C_{CEM}.

(3) How do I calculate daily upscale and zero drift? You must calculate the upscale drift using to Equation 2–2 and the zero drift according to Equation 2–3:

$$UD = \frac{|R_{CEM} - R_U|}{R_U} \times 100 \qquad \text{(Eq. 2-2)}$$

Where:

UD = The upscale drift of your PM CEMS, in percent,

R_{CEM} = Your PM CEMS response to the upscale check value, and

R_U = The upscale check value.

$$ZD = \frac{|R_{CEM} - R_L|}{R_U} \times 100 \qquad \text{(Eq. 2-3)}$$

Where:

ZD = The zero (low-level) drift of your PM CEMS, in percent,

R_{CEM} = Your PM CEMS response of the zero check value,

R_L = The zero check value, and

R_U = The upscale check value.

(4) How do I calculate SVA accuracy? You must use Equation 2–4 to calculate the accuracy, in percent, for each of the three SVA tests or the daily sample volume check:

$$\text{Accuracy} = \frac{(V_R - V_M)}{FS} \times 100 \qquad \text{(Eq. 2-4)}$$

Where:

V_M = Sample gas volume determined/reported by your PM CEMS (*e.g.*, dscm),

V_R = Sample gas volume measured by the independent calibrated reference device (*e.g.*, dscm) for the SVA or the reference value for the daily sample volume check, and

FS = Full-scale value.

NOTE: Before calculating SVA accuracy, you must correct the sample gas volumes

measured by your PM CEMS and the independent calibrated reference device to the same basis of temperature, pressure, and moisture content. You must document all data and calculations.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Which References are Relevant to This Method? [Reserved]

17.0 What Tables, Diagrams, Flowcharts, and Validation Data Are Relevant to This Method? [Reserved]

[52 FR 21008, June 4, 1987; 52 FR 27612, July 22, 1987, as amended at 56 FR 5527, Feb. 11, 1991; 69 FR 1816, Jan. 12, 2004; 72 FR 32768, June 13, 2007; 74 FR 12590, Mar. 25, 2009]

APPENDIX G TO PART 60—PROVISIONS FOR AN ALTERNATIVE METHOD OF DEMONSTRATING COMPLIANCE WITH 40 CFR 60.43 FOR THE NEWTON POWER STATION OF CENTRAL ILLINOIS PUBLIC SERVICE COMPANY

1. *Designation of Affected Facilities*

1.1 The affected facilities to which this alternative compliance method applies are the Unit 1 and 2 coal-fired steam generating units located at the Central Illinois Public Service Company's (CIPS) Newton Power Station in Jasper County, Illinois. Each of these units is subject to the Standards of Performance for Fossil-Fuel-Fired Steam Generators for Which Construction Commenced After August 17, 1971 (subpart D).

2. *Definitions*

2.1 All definitions in subparts D and Da of part 60 apply to this provision except that:

24-hour period means the period of time between 12:00 midnight and the following midnight.

Boiler operating day means a 24-hour period during which any fossil is combusted in either the Unit 1 or Unit 2 steam generating unit and during which the provisions of §60.43(e) are applicable.

CEMs means continuous emission monitoring system.

Coal bunker means a single or group of coal trailers, hoppers, silos or other containers that:

(1) are physically attached to the affected facility; and

(2) provide coal to the coal pulverizers.

DAFGDS means the dual alkali flue gas desulfurization system for the Newton Unit 1 steam generating unit.

3. *Compliance Provisions*

3.1 If the owner or operator of the affected facility elects to comply with the 470 ng/J (1.1 lbs/MMBTU) of combined heat input emission limit under §60.43(e), he shall notify the Regional Administrator, of the United States Environmental Protection Agency (USEPA), Region 5 and the Director, of the Illinois Environmental Protection Agency (IEPA) at least 30 days in advance of the date such election is to take effect, stating the date such operation is to commence. When the owner or operator elects to comply with this limit after one or more periods of reverting to the 520 ng/J heat input (1.2 lbs/MMBTU) limit of §60.43(a)(2), as provided under 3.4, he shall notify the Regional Administrator of the USEPA, Region 5 and the Director of the (IEPA) in writing at least ten (10) days in advance of the date such election is to take effect.

3.2 Compliance with the sulfur dioxide emission limit under §60.43(e) is determined on a continuous basis by performance testing using CEMs. Within 60 days after the initial operation of Units 1 and 2 subject to the combined emission limit in §60.43(e), the owner or operator shall conduct an initial performance test, as required by §60.8, to determine compliance with the combined emission limit. This initial performance test is to be scheduled so that the thirtieth boiler operating day of the 30 successive boiler operating days is completed within 60 days after initial operation subject to the 470 ng/J (1.1 lbs/MMBTU) combined emission limit. Following the initial performance test, a separate performance test is completed at the end of each boiler operating day Unit 1 and Unit 2 are subject to §60.43(e), and a new 30 day average emission rate calculated.

3.2.1 Following the initial performance test, a new 30 day average emission rate is calculated for each boiler operating day the affected facility is subject to §60.43(e). If the owner or operator of the affected facility elects to comply with §60.43(e) after one or more periods of reverting to the 520 ng/J heat input (1.2 lbs/MMBTU) limit under §60.43(a)(2), as provided under 3.4, the 30 day average emission rate under §60.43(e) is calculated using emissions data of the current boiler operating day and data for the previous 29 boiler operating days when the affected facility was subject to §60.43(e). Periods of operation of the affected facility under §60.43(a)(2) are not considered boiler operating days. Emissions data collected during operation under §60.43(a)(2) are not considered relative to 4.6 and emissions data are not included in calculations of emission under §60.43(e).

3.2.2 When the affected facility is operated under the provisions of §60.43(e), the Unit 1 DAFGDS bypass damper must be fully closed. The DAFGDS bypass may be opened only during periods of DAFGDS startup, shutdown, malfunction or testing as described under Sections 3.5.1, 3.5.2, 3.5.3, 3.5.4, and 4.8.2.

State of Oregon Department of Environmental Quality

OAR 340-230-0350 Attachments

APPENDIX D TO PART 60—REQUIRED EMISSION INVENTORY INFORMATION

(a) Completed NEDS point source form(s) for the entire plant containing the designated facility, including information on the applicable criteria pollutants. If data concerning the plant are already in NEDS, only that information must be submitted which is necessary to update the existing NEDS record for that plant. Plant and point identification codes for NEDS records shall correspond to those previously assigned in NEDS; for plants not in NEDS, these codes shall be obtained from the appropriate Regional Office.

(b) Accompanying the basic NEDS information shall be the following information on each designated facility:

(1) The state and county identification codes, as well as the complete plant and point identification codes of the designated facility in NEDS. (The codes are needed to match these data with the NEDS data.)

(2) A description of the designated facility including, where appropriate:

(i) Process name.

(ii) Description and quantity of each product (maximum per hour and average per year).

(iii) Description and quantity of raw materials handled for each product (maximum per hour and average per year).

(iv) Types of fuels burned, quantities and characteristics (maximum and average quantities per hour, average per year).

(v) Description and quantity of solid wastes generated (per year) and method of disposal.

(3) A description of the air pollution control equipment in use or proposed to control the designated pollutant, including:

(i) Verbal description of equipment.

(ii) Optimum control efficiency, in percent. This shall be a combined efficiency when more than one device operates in series. The method of control efficiency determination shall be indicated (e.g., design efficiency, measured efficiency, estimated efficiency).

(iii) Annual average control efficiency, in percent, taking into account control equipment down time. This shall be a combined efficiency when more than one device operates in series.

(4) An estimate of the designated pollutant emissions from the designated facility (maximum per hour and average per year). The method of emission determination shall also be specified (e.g., stack test, material balance, emission factor).

[40 FR 53349, Nov. 17, 1975]

APPENDIX E TO PART 60 [RESERVED]

APPENDIX F TO PART 60—QUALITY ASSURANCE PROCEDURES

PROCEDURE 1. QUALITY ASSURANCE REQUIREMENTS FOR GAS CONTINUOUS EMISSION MONITORING SYSTEMS USED FOR COMPLIANCE DETERMINATION

1. Applicability and Principle

1.1 Applicability. Procedure 1 is used to evaluate the effectiveness of quality control (QC) and quality assurance (QA) procedures and the quality of data produced by any continuous emission monitoring system (CEMS) that is used for determining compliance with the emission standards on a continuous basis as specified in the applicable regulation. The CEMS may include pollutant (e.g., $S0_2$ and $N0_x$) and diluent (e.g., 0_2 or $C0_2$) monitors.

This procedure specifies the minimum QA requirements necessary for the control and assessment of the quality of CEMS data submitted to the Environmental Protection Agency (EPA). Source owners and operators responsible for one or more CEMS's used for compliance monitoring must meet these minimum requirements and are encouraged to develop and implement a more extensive QA program or to continue such programs where they already exist.

Data collected as a result of QA and QC measures required in this procedure are to be submitted to the Agency. These data are to be used by both the Agency and the CEMS operator in assessing the effectiveness of the CEMS QC and QA procedures in the maintenance of acceptable CEMS operation and valid emission data.

Appendix F, Procedure 1 is applicable December 4, 1987. The first CEMS accuracy assessment shall be a relative accuracy test audit (RATA) (see section 5) and shall be completed by March 4, 1988 or the date of the initial performance test required by the applicable regulation, whichever is later.

1.2 Principle. The QA procedures consist of two distinct and equally important functions. One function is the assessment of the quality of the CEMS data by estimating accuracy. The other function is the control and improvement of the quality of the CEMS data by implementing QC policies and corrective actions. These two functions form a control loop: When the assessment function indicates that the data quality is inadequate, the control effort must be increased until the data quality is acceptable. In order to provide uniformity in the assessment and reporting of data quality, this procedure explicitly specifies the assessment methods for response drift and accuracy. The methods are based on procedures included in the applicable performance specifications (PS's) in appendix B of 40 CFR part 60. Procedure 1 also requires the analysis of the EPA audit

samples concurrent with certain reference method (RM) analyses as specified in the applicable RM's.

Because the control and corrective action function encompasses a variety of policies, specifications, standards, and corrective measures, this procedure treats QC requirements in general terms to allow each source owner or operator to develop a QC system that is most effective and efficient for the circumstances.

2. Definitions

2.1 Continuous Emission Monitoring System. The total equipment required for the determination of a gas concentration or emission rate.

2.2 Diluent Gas. A major gaseous constituent in a gaseous pollutant mixture. For combustion sources, CO_2 and O_2 are the major gaseous constituents of interest.

2.3 Span Value. The upper limit of a gas concentration measurement range that is specified for affected source categories in the applicable subpart of the regulation.

2.4 Zero, Low-Level, and High-Level Values. The CEMS response values related to the source specific span value. Determination of zero, low-level, and high-level values is defined in the appropriate PS in appendix B of this part.

2.5 Calibration Drift (CD). The difference in the CEMS output reading from a reference value after a period of operation during which no unscheduled maintenance, repair or adjustment took place. The reference value may be supplied by a cylinder gas, gas cell, or optical filter and need not be certified.

2.6 Relative Accuracy (RA). The absolute mean difference between the gas concentration or emission rate determined by the CEMS and the value determined by the RM's plus the 2.5 percent error confidence coefficient of a series of tests divided by the mean of the RM tests or the applicable emission limit.

3. QC Requirements

Each source owner or operator must develop and implement a QC program. As a minimum, each QC program must include written procedures which should describe in detail, complete, step-by-step procedures and operations for each of the following activities:

1. Calibration of CEMS.
2. CD determination and adjustment of CEMS.
3. Preventive maintenance of CEMS (including spare parts inventory).
4. Data recording, calculations, and reporting.
5. Accuracy audit procedures including sampling and analysis methods.
6. Program of corrective action for malfunctioning CEMS.

As described in Section 5.2, whenever excessive inaccuracies occur for two consecutive quarters, the source owner or operator must revise the current written procedures or modify or replace the CEMS to correct the deficiency causing the excessive inaccuracies.

These written procedures must be kept on record and available for inspection by the enforcement agency.

4. CD Assessment

4.1 CD Requirement. As described in 40 CFR 60.13(d), source owners and operators of CEMS must check, record, and quantify the CD at two concentration values at least once daily (approximately 24 hours) in accordance with the method prescribed by the manufacturer. The CEMS calibration must, as minimum, be adjusted whenever the daily zero (or low-level) CD or the daily high-level CD exceeds two times the limits of the applicable PS's in appendix B of this regulation.

4.2 Recording Requirement for Automatic CD Adjusting Monitors. Monitors that automatically adjust the data to the corrected calibration values (e.g., microprocessor control) must be programmed to record the unadjusted concentration measured in the CD prior to resetting the calibration, if performed, or record the amount of adjustment.

4.3 Criteria for Excessive CD. If either the zero (or low-level) or high-level CD result exceeds twice the applicable drift specification in appendix B for five, consecutive, daily periods, the CEMS is out-of-control. If either the zero (or low-level) or high-level CD result exceeds four times the applicable drift specification in appendix B during any CD check, the CEMS is out-of-control. If the CEMS is out-of-control, take necessary corrective action. Following corrective action, repeat the CD checks.

4.3.1 Out-Of-Control Period Definition. The beginning of the out-of-control period is the time corresponding to the completion of the fifth, consecutive, daily CD check with a CD in excess of two times the allowable limit, or the time corresponding to the completion of the daily CD check preceding the daily CD check that results in a CD in excess of four times the allowable limit. The end of the out-of-control period is the time corresponding to the completion of the CD check following corrective action that results in the CD's at both the zero (or low-level) and high-level measurement points being within the corresponding allowable CD limit (i.e., either two times or four times the allowable limit in appendix B).

4.3.2 CEMS Data Status During Out-of-Control Period. During the period the CEMS is out-of-control, the CEMS data may not be used in calculating emission compliance nor be counted towards meeting minimum data availability as required and described in the applicable subpart [e.g., §60.47a(f)].

4.4 Data Recording and Reporting. As required in §60.7(d) of this regulation (40 CFR part 60), all measurements from the CEMS must be retained on file by the source owner for at least 2 years. However, emission data obtained on each successive day while the CEMS is out-of-control may not be included as part of the minimum daily data requirement of the applicable subpart [e.g., §60.47a(f)] nor be used in the calculation of reported emissions for that period.

5. Data Accuracy Assessment

5.1 Auditing Requirements. Each CEMS must be audited at least once each calendar quarter. Successive quarterly audits shall occur no closer than 2 months. The audits shall be conducted as follows:

5.1.1 Relative Accuracy Test Audit (RATA). The RATA must be conducted at least once every four calendar quarters, except as otherwise noted in section 5.1.4 of this appendix. Conduct the RATA as described for the RA test procedure in the applicable PS in appendix B (e.g., PS 2 for SO_2 and NO_X). In addition, analyze the appropriate performance audit samples received from EPA as described in the applicable sampling methods (e.g., Methods 6 and 7).

5.1.2 Cylinder Gas Audit (CGA). If applicable, a CGA may be conducted in three of four calendar quarters, but in no more than three quarters in succession.

To conduct a CGA: (1) Challenge the CEMS (both pollutant and diluent portions of the CEMS, if applicable) with an audit gas of known concentration at two points within the following ranges:

Audit point	Audit range		
	Pollutant monitors	Diluent monitors for—	
		CO_2	O_2
1	20 to 30% of span value.	5 to 8% by volume.	4 to 6% by volume.
2	50 to 60% of span value.	10 to 14% by volume.	8 to 12% by volume.

Challenge the CEMS three times at each audit point, and use the average of the three responses in determining accuracy.

Use of separate audit gas cylinder for audit points 1 and 2. Do not dilute gas from audit cylinder when challenging the CEMS.

The monitor should be challenged at each audit point for a sufficient period of time to assure adsorption-desorption of the CEMS sample transport surfaces has stabilized.

(2) Operate each monitor in its normal sampling mode, i.e., pass the audit gas through all filters, scrubbers, conditioners, and other monitor components used during normal sampling, and as much of the sampling probe as is practical. At a minimum, the audit gas should be introduced at the connection between the probe and the sample line.

(3) Use Certified Reference Materials (CRM's) (See Citation 1) audit gases that have been certified by comparison to National Institute of Standards and Technology (NIST) or EPA Traceability Protocol Materials (ETPM's) following the most recent edition of EPA's Traceability Protocol No. 1 (See Citation 2). Procedures for preparation of CRM's are described in Citation 1. Procedures for preparation of ETPM's are described in Citation 2. As an alternative to CRM's or ETPM gases, Method 205 (See Citation 3) may be used. The difference between the actual concentration of the audit gas and the concentration indicated by the monitor is used to assess the accuracy of the CEMS.

5.1.3 Relative Accuracy Audit (RAA). The RAA may be conducted three of four calendar quarters, but in no more than three quarters in succession. To conduct a RAA, follow the procedure described in the applicable PS in appendix B for the relative accuracy test, except that only three sets of measurement data are required. Analyses of EPA performance audit samples are also required.

The relative difference between the mean of the RM values and the mean of the CEMS responses will be used to assess the accuracy of the CEMS.

5.1.4 Other Alternative Audits. Other alternative audit procedures may be used as approved by the Administrator for three of four calendar quarters. One RATA is required at least every four calendar quarters, except in the case where the affected facility is off-line (does not operate) in the fourth calendar quarter since the quarter of the previous RATA. In that case, the RATA shall be performed in the quarter in which the unit recommences operation. Also, cylinder gas audits are not be required for calendar quarters in which the affected facility does not operate.

5.2 Excessive Audit Inaccuracy. If the RA, using the RATA, CGA, or RAA exceeds the criteria in section 5.2.3, the CEMS is out-of-control. If the CEMS is out-of-control, take necessary corrective action to eliminate the problem. Following corrective action, the source owner or operator must audit the CEMS with a RATA, CGA, or RAA to determine if the CEMS is operating within the specifications. A RATA must always be used following an out-of-control period resulting from a RATA. The audit following corrective action does not require analysis of EPA performance audit samples. If audit results show the CEMS to be out-of-control, the CEMS operator shall report both the audit showing the CEMS to be out-of-control and the results of the audit following corrective action showing the CEMS to be operating within specifications.

5.2.1 Out-Of-Control Period Definition. The beginning of the out-of-control period is the time corresponding to the completion of the sampling for the RATA, RAA, or CGA. The end of the out-of-control period is the time corresponding to the completion of the sampling of the subsequent successful audit.

5.2.2 CEMS Data Status During Out-Of-Control Period. During the period the monitor is out-of-control, the CEMS data may not be used in calculating emission compliance nor be counted towards meeting minimum data availabilty as required and described in the applicable subpart [e.g., §60.47a(f)].

5.2.3 Criteria for Excessive Audit Inaccuracy. Unless specified otherwise in the applicable subpart, the criteria for excessive inaccuracy are:

(1) For the RATA, the allowable RA in the applicable PS in appendix B.

(2) For the CGA, ±15 percent of the average audit value or ±5 ppm, whichever is greater.

(3) For the RAA, ±15 percent of the three run average or ±7.5 percent of the applicable standard, whichever is greater.

5.3 Criteria for Acceptable QC Procedure. Repeated excessive inaccuracies (i.e., out-of-control conditions resulting from the quarterly audits) indicates the QC procedures are inadequate or that the CEMS is incapable of providing quality data. Therefore, whenever excessive inaccuracies occur for two consective quarters, the source owner or operator must revise the QC procedures (see Section 3) or modify or replace the CEMS.

6. Calculations for CEMS Data Accuracy

6.1 RATA RA Calculation. Follow the equations described in Section 8 of appendix B, PS 2 to calculate the RA for the RATA. The RATA must be calculated in units of the applicable emission standard (e.g., ng/J).

6.2 RAA Accuracy Calculation. Use Equation 1–1 to calculate the accuracy for the RAA. The RAA must be calculated in units of the applicable emission standard (e.g., ng/J).

6.3 CGA Accuracy Calculation. Use Equation 1–1 to calculate the accuracy for the CGA, which is calculated in units of the appropriate concentration (e.g., ppm SO_2 or percent O_2). Each component of the CEMS must meet the acceptable accuracy requirement.

$$A = \frac{C_m - C_a}{C_a} \times 100 \qquad \text{Eq. 1-1}$$

where:

A=Accuracy of the CEMS, percent.

C_m=Average CEMS response during audit in units of applicable standard or appropriate concentration.

C_a=Average audit value (CGA certified value or three-run average for RAA) in units of applicable standard or appropriate concentration.

6.4 Example Accuracy Calculations. Example calculations for the RATA, RAA, and CGA are available in Citation 3.

7. Reporting Requirements

At the reporting interval specified in the applicable regulation, report for each CEMS the accuracy results from Section 6 and the CD assessment results from Section 4. Report the drift and accuracy information as a Data Assessment Report (DAR), and include one copy of this DAR for each quarterly audit with the report of emissions required under the applicable subparts of this part.

As a minimum, the DAR must contain the following information:

1. Source owner or operator name and address.

2. Identification and location of monitors in the CEMS.

3. Manufacturer and model number of each monitor in the CEMS.

4. Assessment of CEMS data accuracy and date of assessment as determined by a RATA, RAA, or CGA described in Section 5 including the RA for the RATA, the A for the RAA or CGA, the RM results, the cylinder gases certified values, the CEMS responses, and the calculations results as defined in Section 6. If the accuracy audit results show the CEMS to be out-of-control, the CEMS operator shall report both the audit results showing the CEMS to be out-of-control and the results of the audit following corrective action showing the CEMS to be operating within specifications.

5. Results from EPA performance audit samples described in Section 5 and the applicable RM's.

6. Summary of all corrective actions taken when CEMS was determined out-of-control, as described in Sections 4 and 5.

An example of a DAR format is shown in Figure 1.

8. Bibliography

1. ''A Procedure for Establishing Traceability of Gas Mixtures to Certain National Bureau of Standards Standard Reference Materials.'' Joint publication by NBS and EPA–600/7–81–010, Revised 1989. Available from the U.S. Environmental Protection Agency. Quality Assurance Division (MD–77). Research Triangle Park, NC 27711.

2. ''EPA Traceability Protocol For Assay And Certification Of Gaseous Calibration Standards.'' EPA–600/R–97/121, September 1997. Available from EPA's Emission Measurement Center at *http://www.epa.gov/ttn/emc*.

3. Method 205, ''Verification of Gas Dilution Systems for Field Instrument Calibrations,'' 40 CFR 51, appendix M.

FIGURE 1—EXAMPLE FORMAT FOR DATA ASSESSMENT REPORT

Period ending date _____
Year _____
Company name _____
Plant name _____
Source unit no. _____
CEMS manufacturer _____
Model no. _____
CEMS serial no. _____
CEMS type (e.g., in situ) _____
CEMS sampling location (e.g., control device outlet) _____
CEMS span values as per the applicable regulation: _____ (e.g., SO_2 _____ ppm, NO_x _____ ppm). _____

I. Accuracy assessment results (Complete A, B, or C below for each CEMS or for each pollutant and diluent analyzer, as applicable.) If the quarterly audit results show the CEMS to be out-of-control, report the results of both the quarterly audit and the audit following corrective action showing the CEMS to be operating properly.

A. Relative accuracy test audit (RATA) for _____ (e.g., SO_2 in ng/J).

1. Date of audit _____.
2. Reference methods (RM's) used _____ (e.g., Methods 3 and 6).
3. Average RM value _____ (e.g., ng/J, mg/dsm^3, or percent volume).
4. Average CEMS value _____.
5. Absolute value of mean difference [d] _____.
6. Confidence coefficient [CC] _____.
7. Percent relative accuracy (RA) _____ percent.
8. EPA performance audit results:
a. Audit lot number (1) _____ (2) _____
b. Audit sample number (1) _____ (2) _____
c. Results (mg/dsm^3) (1) _____ (2) _____
d. Actual value (mg/dsm^3)* (1) _____ (2) _____
e. Relative error* (1) _____ (2) _____

B. Cylinder gas audit (CGA) for _____ (e.g., SO_2 in ppm).

	Audit point 1	Audit point 2	
1. Date of audit.			
2. Cylinder ID number.			
3. Date of certification.			
4. Type of certification	.....	.....	(e.g., EPA Protocol 1 or CRM).
5. Certified audit value	.....	.....	(e.g., ppm).
6. CEMS response value	.....	.....	(e.g., ppm).
7. Accuracy	.....	.....	percent.

C. Relative accuracy audit (RAA) for _____ (e.g., SO_2 in ng/J).

1. Date of audit _____.
2. Reference methods (RM's) used _____ (e.g., Methods 3 and 6).
3. Average RM value _____ (e.g., ng/J).
4. Average CEMS value _____.
5. Accuracy _____ percent.
6. EPA performance audit results:
a. Audit lot number (1) _____ (2) _____
b. Audit sample number (1) _____ (2) _____
c. Results (mg/dsm^3) (1) _____ (2) _____
d. Actual value (mg/dsm^3) *(1) _____ (2)
e. Relative error* (1) _____ (2) _____

D. Corrective action for excessive inaccuracy.

1. Out-of-control periods.
a. Date(s) _____.
b. Number of days _____.
2. Corrective action taken _____
3. Results of audit following corrective action. (Use format of A, B, or C above, as applicable.)

II. Calibration drift assessment.

A. Out-of-control periods.
1. Date(s) _____.
2. Number of days _____.

B. Corrective action taken _____

PROCEDURE 2—QUALITY ASSURANCE REQUIREMENTS FOR PARTICULATE MATTER CONTINUOUS EMISSION MONITORING SYSTEMS AT STATIONARY SOURCES

1.0 What Are the Purpose and Applicability of Procedure 2?

The purpose of Procedure 2 is to establish the minimum requirements for evaluating the effectiveness of quality control (QC) and quality assurance (QA) procedures and the quality of data produced by your particulate matter (PM) continuous emission monitoring system (CEMS). Procedure 2 applies to PM CEMS used for continuously determining compliance with emission standards or operating permit limits as specified in an applicable regulation or permit. Other QC procedures may apply to diluent (*e.g.*, O_2) monitors and other auxiliary monitoring equipment included with your CEMS to facilitate PM measurement or determination of PM concentration in units specified in an applicable regulation.

1.1 What measurement parameter does Procedure 2 address? Procedure 2 covers the instrumental measurement of PM as defined by your source's applicable reference method (no Chemical Abstract Service number assigned).

1.2 For what types of devices must I comply with Procedure 2? You must comply with Procedure 2 for the total equipment that:

(1) We require you to install and operate on a continuous basis under the applicable regulation, and

*To be completed by the Agency.

(2) You use to monitor the PM mass concentration associated with the operation of a process or emission control device.

1.3 What are the data quality objectives (DQOs) of Procedure 2? The overall DQO of Procedure 2 is the generation of valid, representative data that can be transferred into useful information for determining PM CEMS concentrations averaged over a prescribed interval. Procedure 2 is also closely associated with Performance Specification 11 (PS–11).

(1) Procedure 2 specifies the minimum requirements for controlling and assessing the quality of PM CEMS data submitted to us or the delegated permitting authority.

(2) You must meet these minimum requirements if you are responsible for one or more PM CEMS used for compliance monitoring. We encourage you to develop and implement a more extensive QA program or to continue such programs where they already exist.

1.4 What is the intent of the QA/QC procedures specified in Procedure 2? Procedure 2 is intended to establish the minimum QA/QC requirements for PM CEMS and is presented in general terms to allow you to develop a program that is most effective for your circumstances. You may adopt QA/QC procedures that go beyond these minimum requirements to ensure compliance with applicable regulations.

1.5 When must I comply with Procedure 2? You must comply with the basic requirements of Procedure 2 immediately following successful completion of the initial correlation test of PS–11.

2.0 What Are the Basic Requirements of Procedure 2?

Procedure 2 requires you to perform periodic evaluations of PM CEMS performance and to develop and implement QA/QC programs to ensure that PM CEMS data quality is maintained.

2.1 What are the basic functions of Procedure 2?

(1) Assessment of the quality of your PM CEMS data by estimating measurement accuracy;

(2) Control and improvement of the quality of your PM CEMS data by implementing QC requirements and corrective actions until the data quality is acceptable; and

(3) Specification of requirements for daily instrument zero and upscale drift checks and daily sample volume checks, as well as routine response correlation audits, absolute correlation audits, sample volume audits, and relative response audits.

3.0 What Special Definitions Apply to Procedure 2?

The definitions in Procedure 2 include those provided in PS–11 of Appendix B, with the following additions:

3.1 ''Absolute Correlation Audit (ACA)'' means an evaluation of your PM CEMS response to a series of reference standards covering the full measurement range of the instrument (*e.g.*, 4 mA to 20 mA).

3.2 ''Correlation Range'' means the range of PM CEMS responses used in the complete set of correlation test data.

3.3 ''PM CEMS Correlation'' means the site-specific relationship (*i.e.*, a regression equation) between the output from your PM CEMS (*e.g.*, mA) and the particulate concentration, as determined by the reference method. The PM CEMS correlation is expressed in the same units as the PM concentration measured by your PM CEMS (*e.g.*, mg/acm). You must derive this relation from PM CEMS response data and manual reference method data that were gathered simultaneously. These data must be representative of the full range of source and control device operating conditions that you expect to occur. You must develop the correlation by performing the steps presented in sections 12.2 and 12.3 of PS–11.

3.4 ''Reference Method Sampling Location'' means the location in your source's exhaust duct from which you collect manual reference method data for developing your PM CEMS correlation and for performing relative response audits (RRAs) and response correlation audits (RCAs).

3.5 ''Response Correlation Audit (RCA)'' means the series of tests specified in section 10.3(8) of this procedure that you conduct to ensure the continued validity of your PM CEMS correlation.

3.6 ''Relative Response Audit (RRA)'' means the brief series of tests specified in section 10.3(6) of this procedure that you conduct between consecutive RCAs to ensure the continued validity of your PM CEMS correlation.

3.7 ''Sample Volume Audit (SVA)'' means an evaluation of your PM CEMS measurement of sample volume if your PM CEMS determines PM concentration based on a measure of PM mass in an extracted sample volume and an independent determination of sample volume.

4.0 Interferences [Reserved]

5.0 What Do I Need To Know To Ensure the Safety of Persons Using Procedure 2?

People using Procedure 2 may be exposed to hazardous materials, operations, and equipment. Procedure 2 does not purport to address all of the safety issues associated with its use. It is your responsibility to establish appropriate safety and health practices and determine the applicable regulatory limitations before performing this procedure. You must consult your CEMS user's manual for specific precautions to be taken with regard to your PM CEMS procedures.

6.0 What Equipment and Supplies Do I Need? [Reserved]

7.0 What Reagents and Standards Do I Need?

You will need reference standards or procedures to perform the zero drift check, the upscale drift check, and the sample volume check.

7.1 What is the reference standard value for the zero drift check? You must use a zero check value that is no greater than 20 percent of the PM CEMS's response range. You must obtain documentation on the zero check value from your PM CEMS manufacturer.

7.2 What is the reference standard value for the upscale drift check? You must use an upscale check value that produces a response between 50 and 100 percent of the PM CEMS's response range. For a PM CEMS that produces output over a range of 4 mA to 20 mA, the upscale check value must produce a response in the range of 12 mA to 20 mA. You must obtain documentation on the upscale check value from your PM CEMS manufacturer.

7.3 What is the reference standard value for the sample volume check? You must use a reference standard value or procedure that produces a sample volume value equivalent to the normal sampling rate. You must obtain documentation on the sample volume value from your PM CEMS manufacturer.

8.0 What Sample Collection, Preservation, Storage, and Transport Are Relevant to This Procedure? [Reserved]

9.0 What Quality Control Measures Are Required by This Procedure for My PM CEMS?

You must develop and implement a QC program for your PM CEMS. Your QC program must, at a minimum, include written procedures that describe, in detail, complete step-by-step procedures and operations for the activities in paragraphs (1) through (8) of this section.

(1) Procedures for performing drift checks, including both zero drift and upscale drift and the sample volume check (see sections 10.2(1), (2), and (5)).

(2) Methods for adjustment of PM CEMS based on the results of drift checks, sample volume checks (if applicable), and the periodic audits specified in this procedure.

(3) Preventative maintenance of PM CEMS (including spare parts inventory and sampling probe integrity).

(4) Data recording, calculations, and reporting.

(5) RCA and RRA procedures, including sampling and analysis methods, sampling strategy, and structuring test conditions over the prescribed range of PM concentrations.

(6) Procedures for performing ACAs and SVAs and methods for adjusting your PM CEMS response based on ACA and SVA results.

(7) Program of corrective action for malfunctioning PM CEMS, including flagged data periods.

(8) For extractive PM CEMS, procedures for checking extractive system ducts for material accumulation.

9.1 What QA/QC documentation must I have? You are required to keep the written QA/QC procedures on record and available for inspection by us, the State, and/or local enforcement agency for the life of your CEMS or until you are no longer subject to the requirements of this procedure.

9.2 How do I know if I have acceptable QC procedures for my PM CEMS? Your QC procedures are inadequate or your PM CEMS is incapable of providing quality data if you fail two consecutive QC audits (*i.e.*, out-of-control conditions resulting from the annual audits, quarterly audits, or daily checks). Therefore, if you fail the same two consecutive audits, you must revise your QC procedures or modify or replace your PM CEMS to correct the deficiencies causing the excessive inaccuracies (see section 10.4 for limits for excessive audit inaccuracy).

10.0 What Calibration/Correlation and Standardization Procedures Must I Perform for My PM CEMS?

You must generate a site-specific correlation for each of your PM CEMS installation(s) relating response from your PM CEMS to results from simultaneous PM reference method testing. The PS–11 defines procedures for developing the correlation and defines a series of statistical parameters for assessing acceptability of the correlation. However, a critical component of your PM CEMS correlation process is ensuring the accuracy and precision of reference method data. The activities listed in sections 10.1 through 10.10 assure the quality of the correlation.

10.1 When should I use paired trains for reference method testing? Although not required, we recommend that you should use paired-train reference method testing to generate data used to develop your PM CEMS correlation and for RCA testing. Guidance on the use of paired sampling trains can be found in the PM CEMS Knowledge Document (see section 16.5 of PS–11).

10.2 What routine system checks must I perform on my PM CEMS? You must perform routine checks to ensure proper operation of system electronics and optics, light and radiation sources and detectors, and electric or electro-mechanical systems. Necessary components of the routine system checks will depend on design details of your PM CEMS. As a minimum, you must verify the system operating parameters listed in paragraphs (1) through (5) of this section on a daily basis. Some PM CEMS may perform one or more of

these functions automatically or as an integral portion of unit operations; for other PM CEMS, you must initiate or perform one or more of these functions manually.

(1) You must check the zero drift to ensure stability of your PM CEMS response to the zero check value. You must determine system output on the most sensitive measurement range when the PM CEMS is challenged with a zero reference standard or procedure. You must, at a minimum, adjust your PM CEMS whenever the daily zero drift exceeds 4 percent.

(2) You must check the upscale drift to ensure stability of your PM CEMS response to the upscale check value. You must determine system output when the PM CEMS is challenged with a reference standard or procedure corresponding to the upscale check value. You must, at a minimum, adjust your PM CEMS whenever the daily upscale drift check exceeds 4 percent.

(3) For light-scattering and extinction-type PM CEMS, you must check the system optics to ensure that system response has not been altered by the condition of optical components, such as fogging of lens and performance of light monitoring devices.

(4) You must record data from your automatic drift-adjusting PM CEMS before any adjustment is made. If your PM CEMS automatically adjusts its response to the corrected calibration values (*e.g.*, microprocessor control), you must program your PM CEMS to record the unadjusted concentration measured in the drift check before resetting the calibration. Alternately, you may program your PM CEMS to record the amount of adjustment.

(5) For extractive PM CEMS that measure the sample volume and use the measured sample volume as part of calculating the output value, you must check the sample volume on a daily basis to verify the accuracy of the sample volume measuring equipment. This sample volume check must be done at the normal sampling rate of your PM CEMS. You must adjust your PM CEMS sample volume measurement whenever the daily sample volume check error exceeds 10 percent.

10.3 What are the auditing requirements for my PM CEMS? You must subject your PM CEMS to an ACA and an SVA, as applicable, at least once each calender quarter. Successive quarterly audits must occur no closer than 2 months apart. You must conduct an RCA and an RRA at the frequencies specified in the applicable regulation or facility operating permit. An RRA or RCA conducted during any calendar quarter can take the place of the ACA required for that calendar quarter. An RCA conducted during the period in which an RRA is required can take the place of the RRA for that period.

(1) When must I perform an ACA? You must perform an ACA each quarter unless you conduct an RRA or RCA during that same quarter.

(2) How do I perform an ACA? You perform an ACA according to the procedure specified in paragraphs (2)(i) through (v) of this section.

(i) You must challenge your PM CEMS with an audit standard or an equivalent audit reference to reproduce the PM CEMS's measurement at three points within the following ranges:

Audit point	Audit range
1	0 to 20 percent of measurement range
2	40 to 60 percent of measurement range
3	70 to 100 percent of measurement range

(ii) You must then challenge your PM CEMS three times at each audit point and use the average of the three responses in determining accuracy at each audit point. Use a separate audit standard for audit points 1, 2, and 3. Challenge the PM CEMS at each audit point for a sufficient period of time to ensure that your PM CEMS response has stabilized.

(iii) Operate your PM CEMS in the mode, manner, and range specified by the manufacturer.

(iv) Store, maintain, and use audit standards as recommended by the manufacturer.

(v) Use the difference between the actual known value of the audit standard and the response of your PM CEMS to assess the accuracy of your PM CEMS.

(3) When must I perform an SVA? You must perform an audit of the measured sample volume (*e.g.*, the sampling flow rate for a known time) once per quarter for applicable PM CEMS with an extractive sampling system. Also, you must perform and pass an SVA prior to initiation of any of the reference method data collection runs for an RCA or RRA.

(4) How do I perform an SVA? You perform an SVA according to the procedure specified in paragraphs (4)(i) through (iii) of this section.

(i) You perform an SVA by independently measuring the volume of sample gas extracted from the stack or duct over each batch cycle or time period with a calibrated device. You may make this measurement either at the inlet or outlet of your PM CEMS, so long as it measures the sample gas volume without including any dilution or recycle air. Compare the measured volume with the volume reported by your PM CEMS for the same cycle or time period to calculate sample volume accuracy.

(ii) You must make measurements during three sampling cycles for batch extractive monitors (*e.g.*, Beta-gauge) or during three periods of at least 20 minutes for continuous extractive PM CEMS.

(iii) You may need to condense, collect, and measure moisture from the sample gas prior to the calibrated measurement device (*e.g.*, dry gas meter) and correct the results for moisture content. In any case, the volumes measured by the calibrated device and your PM CEMS must be on a consistent temperature, pressure, and moisture basis.

(5) How often must I perform an RRA? You must perform an RRA at the frequency specified in the applicable regulation or facility operating permit. You may conduct an RCA instead of an RRA during the period when the RRA is required.

(6) How do I perform an RRA? You must perform the RRA according to the procedure specified in paragraphs (6)(i) and (ii) of this section.

(i) You perform an RRA by collecting three simultaneous reference method PM concentration measurements and PM CEMS measurements at the as-found source operating conditions and PM concentration.

(ii) We recommend that you use paired trains for reference method sampling. Guidance on the use of paired sampling trains can be found in the PM CEMS Knowledge Document (see section 16.5 of PS–11).

(7) How often must I perform an RCA? You must perform an RCA at the frequency specified in the applicable regulation or facility operating permit.

(8) How do I perform an RCA? You must perform the RCA according to the procedures for the PM CEMS correlation test described in PS–11, section 8.6, except that the minimum number of runs required is 12 in the RCA instead of 15 as specified in PS–11.

(9) What other alternative audits can I use? You can use other alternative audit procedures as approved by us, the State, or local agency for the quarters when you would conduct ACAs.

10.4 What are my limits for excessive audit inaccuracy? Unless specified otherwise in the applicable subpart, the criteria for excessive audit inaccuracy are listed in paragraphs (1) through (6) of this section.

(1) What are the criteria for excessive zero or upscale drift? Your PM CEMS is out of control if the zero drift check or upscale drift check either exceeds 4 percent for five consecutive daily periods or exceeds 8 percent for any one day.

(2) What are the criteria for excessive sample volume measurement error? Your PM CEMS is out of control if sample volume check error exceeds 10 percent for five consecutive daily periods or exceeds 20 percent for any one day.

(3) What are the criteria for excessive ACA error? Your PM CEMS is out of control if the results of any ACA exceed ± 10 percent of the average audit value, as calculated using Equation 2–1a, or 7.5 percent of the applicable standard, as calculated using Equation 2–1b, whichever is greater.

(4) What is the criterion for excessive SVA error? Your PM CEMS is out of control if results exceed ±5 percent of the average sample volume audit value.

(5) What are the criteria for passing an RCA? To pass an RCA, you must meet the criteria specified in paragraphs (5)(i) through (iii) of this section. If your PM CEMS fails to meet these RCA criteria, it is out of control.

(i) For all 12 data points, the PM CEMS response value can be no greater than the greatest PM CEMS response value used to develop your correlation curve.

(ii) For 9 of the 12 data points, the PM CEMS response value must lie within the PM CEMS output range used to develop your correlation curve.

(iii) At least 75 percent of a minimum number of 12 sets of PM CEMS and reference method measurements must fall within a specified area on a graph of the correlation regression line. The specified area on the graph of the correlation regression line is defined by two lines parallel to the correlation regression line, offset at a distance of ±25 percent of the numerical emission limit value from the correlation regression line.

(6) What are the criteria to pass an RRA? To pass an RRA, you must meet the criteria specified in paragraphs (6)(i) and (ii) of this section. If your PM CEMS fails to meet these RRA criteria, it is out of control.

(i) For all three data points, the PM CEMS response value can be no greater than the greatest PM CEMS response value used to develop your correlation curve.

(ii) For two of the three data points, the PM CEMS response value must lie within the PM CEMS output range used to develop your correlation curve.

(iii) At least two of the three sets of PM CEMS and reference method measurements must fall within the same specified area on a graph of the correlation regression line as required for the RCA and described in paragraph (5)(iii) of this section.

10.5 What do I do if my PM CEMS is out of control? If your PM CEMS is out of control, you must take the actions listed in paragraphs (1) and (2) of this section.

(1) You must take necessary corrective action to eliminate the problem and perform tests, as appropriate, to ensure that the corrective action was successful.

(i) Following corrective action, you must repeat the previously failed audit to confirm that your PM CEMS is operating within the specifications.

(ii) If your PM CEMS failed an RRA, you must take corrective action until your PM CEMS passes the RRA criteria. If the RRA criteria cannot be achieved, you must perform an RCA.

(iii) If your PM CEMS failed an RCA, you must follow procedures specified in section 10.6 of this procedure.

(2) You must report both the audit showing your PM CEMS to be out of control and the results of the audit following corrective action showing your PM CEMS to be operating within specifications.

10.6 What do I do if my PM CEMS fails an RCA? After an RCA failure, you must take all applicable actions listed in paragraphs (1) through (3) of this section.

(1) Combine RCA data with data from the active PM CEMS correlation and perform the mathematical evaluations defined in PS–11 for development of a PM CEMS correlation, including examination of alternate correlation models (*i.e.,* linear, polynomial, logarithmic, exponential, and power). If the expanded data base and revised correlation meet PS–11 statistical criteria, use the revised correlation.

(2) If the criteria specified in paragraph (1) of this section are not achieved, you must develop a new PM CEMS correlation based on revised data. The revised data set must consist of the test results from only the RCA. The new data must meet all requirements of PS–11 to develop a revised PM CEMS correlation, except that the minimum number of sets of PM CEMS and reference method measurements is 12 instead of the minimum of 15 sets required by PS–11. Your PM CEMS is considered to be back in controlled status when the revised correlation meets all of the performance criteria specified in section 13.2 of PS–11.

(3) If the actions in paragraphs (1) and (2) of this section do not result in an acceptable correlation, you must evaluate the cause(s) and comply with the actions listed in paragraphs (3)(i) through (iv) of this section within 90 days after the completion of the failed RCA.

(i) Completely inspect your PM CEMS for mechanical or operational problems. If you find a mechanical or operational problem, repair your PM CEMS and repeat the RCA.

(ii) You may need to relocate your PM CEMS to a more appropriate measurement location. If you relocate your PM CEMS, you must perform a new correlation test according to the procedures specified in PS–11.

(iii) The characteristics of the PM or gas in your source's flue gas stream may have changed such that your PM CEMS measurement technology is no longer appropriate. If this is the case, you must install a PM CEMS with measurement technology that is appropriate for your source's flue gas characteristics. You must perform a new correlation test according to the procedures specified in PS–11.

(iv) If the corrective actions in paragraphs (3)(i) through (iii) of this section were not successful, you must petition us, the State, or local agency for approval of alternative criteria or an alternative for continuous PM monitoring.

10.7 When does the out-of-control period begin and end? The out-of-control period begins immediately after the last test run or check of an unsuccessful RCA, RRA, ACA, SVA, drift check, or sample volume check. The out-of-control period ends immediately after the last test run or check of the subsequent successful audit or drift check.

10.8 Can I use the data recorded by my PM CEMS during out-of-control periods? During any period when your PM CEMS is out of control, you may not use your PM CEMS data to calculate emission compliance or to meet minimum data availability requirements described in the applicable regulation.

10.9 What are the QA/QC reporting requirements for my PM CEMS? You must report the accuracy results for your PM CEMS, specified in section 10.4 of this procedure, at the interval specified in the applicable regulation. Report the drift and accuracy information as a Data Assessment Report (DAR), and include one copy of this DAR for each quarterly audit with the report of emissions required under the applicable regulation. An example DAR is provided in Procedure 1, Appendix F of this part.

10.10 What minimum information must I include in my DAR? As a minimum, you must include the information listed in paragraphs (1) through (5) of this section in the DAR:

(1) Your name and address.

(2) Identification and location of monitors in your CEMS.

(3) Manufacturer and model number of each monitor in your CEMS.

(4) Assessment of PM CEMS data accuracy/acceptability, and date of assessment, as determined by an RCA, RRA, ACA, or SVA described in section 10, including the acceptability determination for the RCA or RRA, the accuracy for the ACA or SVA, the reference method results, the audit standards, your PM CEMS responses, and the calculation results as defined in section 12. If the accuracy audit results show your PM CEMS to be out of control, you must report both the audit results showing your PM CEMS to be out of control and the results of the audit following corrective action showing your PM CEMS to be operating within specifications.

(5) Summary of all corrective actions you took when you determined your PM CEMS to be out of control, as described in section 10.5, or after failing on RCA, as described in section 10.6.

10.7 Where and how long must I retain the QA data that this procedure requires me to record for my PM CEMS? You must keep the records required by this procedure for your PM CEMS onsite and available for inspection by us, the State, and/or local enforcement agency for a period of 5 years.

11.0 What Analytical Procedures Apply to This Procedure?

Sample collection and analysis are concurrent for this procedure. You must refer to the appropriate reference method for the specific analytical procedures.

12.0 What Calculations and Data Analysis Must I Perform for my PM CEMS?

(1) How do I determine RCA and RRA acceptability? You must plot each of your PM CEMS and reference method data sets from an RCA or RRA on a graph based on your PM CEMS correlation line to determine if the criteria in paragraphs 10.4(5) or (6), respectively, are met.

(2) How do I calculate ACA accuracy? You must use either Equation 2–1a or 2–1b to calculate ACA accuracy for each of the three audit points. However, when calculating ACA accuracy for the first audit point (0 to 20 percent of measurement range), you must use Equation 2–1b to calculate ACA accuracy if the reference standard value (R_v) equals zero.

$$\text{ACA Accuracy} = \frac{|R_{CEM} - R_V|}{R_V} \times 100\% \qquad \text{Eq. 2-1a}$$

Where:

ACA Accuracy = The ACA accuracy at each audit point, in percent,

R_{CEM} = Your PM CEMS response to the reference standard, and

R_V = The reference standard value.

$$\text{ACA Accuracy} = \frac{|C_{CEM} - C_{RV}|}{C_S} \times 100\% \qquad \text{Eq. 2-1b}$$

Where:

ACA Accuracy = The ACA accuracy at each audit point, in percent,

C_{CEM} = The PM concentration that corresponds to your PM CEMS response to the reference standard, as calculated using the correlation equation for your PM CEMS,

C_{RV} = The PM concentration that corresponds to the reference standard value in units consistent with C_{CEM}, and

C_s = The PM concentration that corresponds to the applicable emission limit in units consistent with C_{CEM}.

(3) How do I calculate daily upscale and zero drift? You must calculate the upscale drift using to Equation 2–2 and the zero drift according to Equation 2–3:

$$UD = \frac{|R_{CEM} - R_U|}{R_U} \times 100 \qquad \text{(Eq. 2-2)}$$

Where:

UD = The upscale drift of your PM CEMS, in percent,

R_{CEM} = Your PM CEMS response to the upscale check value, and

R_U = The upscale check value.

$$ZD = \frac{|R_{CEM} - R_L|}{R_U} \times 100 \qquad \text{(Eq. 2-3)}$$

Where:

ZD = The zero (low-level) drift of your PM CEMS, in percent,

R_{CEM} = Your PM CEMS response of the zero check value,

R_L = The zero check value, and

R_U = The upscale check value.

(4) How do I calculate SVA accuracy? You must use Equation 2–4 to calculate the accuracy, in percent, for each of the three SVA tests or the daily sample volume check:

$$\text{Accuracy} = \frac{(V_R - V_M)}{FS} \times 100 \qquad \text{(Eq. 2-4)}$$

Where:

V_M = Sample gas volume determined/reported by your PM CEMS (*e.g.*, dscm),

V_R = Sample gas volume measured by the independent calibrated reference device (*e.g.*, dscm) for the SVA or the reference value for the daily sample volume check, and

FS = Full-scale value.

NOTE: Before calculating SVA accuracy, you must correct the sample gas volumes

measured by your PM CEMS and the independent calibrated reference device to the same basis of temperature, pressure, and moisture content. You must document all data and calculations.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Which References are Relevant to This Method? [Reserved]

17.0 What Tables, Diagrams, Flowcharts, and Validation Data Are Relevant to This Method? [Reserved]

[52 FR 21008, June 4, 1987; 52 FR 27612, July 22, 1987, as amended at 56 FR 5527, Feb. 11, 1991; 69 FR 1816, Jan. 12, 2004; 72 FR 32768, June 13, 2007; 74 FR 12590, Mar. 25, 2009]

APPENDIX G TO PART 60—PROVISIONS FOR AN ALTERNATIVE METHOD OF DEMONSTRATING COMPLIANCE WITH 40 CFR 60.43 FOR THE NEWTON POWER STATION OF CENTRAL ILLINOIS PUBLIC SERVICE COMPANY

1. *Designation of Affected Facilities*

1.1 The affected facilities to which this alternative compliance method applies are the Unit 1 and 2 coal-fired steam generating units located at the Central Illinois Public Service Company's (CIPS) Newton Power Station in Jasper County, Illinois. Each of these units is subject to the Standards of Performance for Fossil-Fuel-Fired Steam Generators for Which Construction Commenced After August 17, 1971 (subpart D).

2. *Definitions*

2.1 All definitions in subparts D and Da of part 60 apply to this provision except that:

24-hour period means the period of time between 12:00 midnight and the following midnight.

Boiler operating day means a 24-hour period during which any fossil is combusted in either the Unit 1 or Unit 2 steam generating unit and during which the provisions of §60.43(e) are applicable.

CEMs means continuous emission monitoring system.

Coal bunker means a single or group of coal trailers, hoppers, silos or other containers that:

(1) are physically attached to the affected facility; and

(2) provide coal to the coal pulverizers.

DAFGDS means the dual alkali flue gas desulfurization system for the Newton Unit 1 steam generating unit.

3. *Compliance Provisions*

3.1 If the owner or operator of the affected facility elects to comply with the 470 ng/J (1.1 lbs/MMBTU) of combined heat input emission limit under §60.43(e), he shall notify the Regional Administrator, of the United States Environmental Protection Agency (USEPA), Region 5 and the Director, of the Illinois Environmental Protection Agency (IEPA) at least 30 days in advance of the date such election is to take effect, stating the date such operation is to commence. When the owner or operator elects to comply with this limit after one or more periods of reverting to the 520 ng/J heat input (1.2 lbs/MMBTU) limit of §60.43(a)(2), as provided under 3.4, he shall notify the Regional Administrator of the USEPA, Region 5 and the Director of the (IEPA) in writing at least ten (10) days in advance of the date such election is to take effect.

3.2 Compliance with the sulfur dioxide emission limit under §60.43(e) is determined on a continuous basis by performance testing using CEMs. Within 60 days after the initial operation of Units 1 and 2 subject to the combined emission limit in §60.43(e), the owner or operator shall conduct an initial performance test, as required by §60.8, to determine compliance with the combined emission limit. This initial performance test is to be scheduled so that the thirtieth boiler operating day of the 30 successive boiler operating days is completed within 60 days after initial operation subject to the 470 ng/J (1.1 lbs/MMBTU) combined emission limit. Following the initial performance test, a separate performance test is completed at the end of each boiler operating day Unit 1 and Unit 2 are subject to §60.43(e), and a new 30 day average emission rate calculated.

3.2.1 Following the initial performance test, a new 30 day average emission rate is calculated for each boiler operating day the affected facility is subject to §60.43(e). If the owner or operator of the affected facility elects to comply with §60.43(e) after one or more periods of reverting to the 520 ng/J heat input (1.2 lbs/MMBTU) limit under §60.43(a)(2), as provided under 3.4, the 30 day average emission rate under §60.43(e) is calculated using emissions data of the current boiler operating day and data for the previous 29 boiler operating days when the affected facility was subject to §60.43(e). Periods of operation of the affected facility under §60.43(a)(2) are not considered boiler operating days. Emissions data collected during operation under §60.43(a)(2) are not considered relative to 4.6 and emissions data are not included in calculations of emission under §60.43(e).

3.2.2 When the affected facility is operated under the provisions of §60.43(e), the Unit 1 DAFGDS bypass damper must be fully closed. The DAFGDS bypass may be opened only during periods of DAFGDS startup, shutdown, malfunction or testing as described under Sections 3.5.1, 3.5.2, 3.5.3, 3.5.4, and 4.8.2.

State of Oregon Department of Environmental Quality

OAR 340-230-0390 Attachments

APPENDIX D TO PART 60—REQUIRED EMISSION INVENTORY INFORMATION

(a) Completed NEDS point source form(s) for the entire plant containing the designated facility, including information on the applicable criteria pollutants. If data concerning the plant are already in NEDS, only that information must be submitted which is necessary to update the existing NEDS record for that plant. Plant and point identification codes for NEDS records shall correspond to those previously assigned in NEDS; for plants not in NEDS, these codes shall be obtained from the appropriate Regional Office.

(b) Accompanying the basic NEDS information shall be the following information on each designated facility:

(1) The state and county identification codes, as well as the complete plant and point identification codes of the designated facility in NEDS. (The codes are needed to match these data with the NEDS data.)

(2) A description of the designated facility including, where appropriate:

(i) Process name.

(ii) Description and quantity of each product (maximum per hour and average per year).

(iii) Description and quantity of raw materials handled for each product (maximum per hour and average per year).

(iv) Types of fuels burned, quantities and characteristics (maximum and average quantities per hour, average per year).

(v) Description and quantity of solid wastes generated (per year) and method of disposal.

(3) A description of the air pollution control equipment in use or proposed to control the designated pollutant, including:

(i) Verbal description of equipment.

(ii) Optimum control efficiency, in percent. This shall be a combined efficiency when more than one device operates in series. The method of control efficiency determination shall be indicated (e.g., design efficiency, measured efficiency, estimated efficiency).

(iii) Annual average control efficiency, in percent, taking into account control equipment down time. This shall be a combined efficiency when more than one device operates in series.

(4) An estimate of the designated pollutant emissions from the designated facility (maximum per hour and average per year). The method of emission determination shall also be specified (e.g., stack test, material balance, emission factor).

[40 FR 53349, Nov. 17, 1975]

APPENDIX E TO PART 60 [RESERVED]

APPENDIX F TO PART 60—QUALITY ASSURANCE PROCEDURES

PROCEDURE 1. QUALITY ASSURANCE REQUIREMENTS FOR GAS CONTINUOUS EMISSION MONITORING SYSTEMS USED FOR COMPLIANCE DETERMINATION

1. Applicability and Principle

1.1 Applicability. Procedure 1 is used to evaluate the effectiveness of quality control (QC) and quality assurance (QA) procedures and the quality of data produced by any continuous emission monitoring system (CEMS) that is used for determining compliance with the emission standards on a continuous basis as specified in the applicable regulation. The CEMS may include pollutant (e.g., $S0_2$ and $N0_x$) and diluent (e.g., 0_2 or $C0_2$) monitors.

This procedure specifies the minimum QA requirements necessary for the control and assessment of the quality of CEMS data submitted to the Environmental Protection Agency (EPA). Source owners and operators responsible for one or more CEMS's used for compliance monitoring must meet these minimum requirements and are encouraged to develop and implement a more extensive QA program or to continue such programs where they already exist.

Data collected as a result of QA and QC measures required in this procedure are to be submitted to the Agency. These data are to be used by both the Agency and the CEMS operator in assessing the effectiveness of the CEMS QC and QA procedures in the maintenance of acceptable CEMS operation and valid emission data.

Appendix F, Procedure 1 is applicable December 4, 1987. The first CEMS accuracy assessment shall be a relative accuracy test audit (RATA) (see section 5) and shall be completed by March 4, 1988 or the date of the initial performance test required by the applicable regulation, whichever is later.

1.2 Principle. The QA procedures consist of two distinct and equally important functions. One function is the assessment of the quality of the CEMS data by estimating accuracy. The other function is the control and improvement of the quality of the CEMS data by implementing QC policies and corrective actions. These two functions form a control loop: When the assessment function indicates that the data quality is inadequate, the control effort must be increased until the data quality is acceptable. In order to provide uniformity in the assessment and reporting of data quality, this procedure explicitly specifies the assessment methods for response drift and accuracy. The methods are based on procedures included in the applicable performance specifications (PS's) in appendix B of 40 CFR part 60. Procedure 1 also requires the analysis of the EPA audit

samples concurrent with certain reference method (RM) analyses as specified in the applicable RM's.

Because the control and corrective action function encompasses a variety of policies, specifications, standards, and corrective measures, this procedure treats QC requirements in general terms to allow each source owner or operator to develop a QC system that is most effective and efficient for the circumstances.

2. Definitions

2.1 Continuous Emission Monitoring System. The total equipment required for the determination of a gas concentration or emission rate.

2.2 Diluent Gas. A major gaseous constituent in a gaseous pollutant mixture. For combustion sources, CO_2 and O_2 are the major gaseous constituents of interest.

2.3 Span Value. The upper limit of a gas concentration measurement range that is specified for affected source categories in the applicable subpart of the regulation.

2.4 Zero, Low-Level, and High-Level Values. The CEMS response values related to the source specific span value. Determination of zero, low-level, and high-level values is defined in the appropriate PS in appendix B of this part.

2.5 Calibration Drift (CD). The difference in the CEMS output reading from a reference value after a period of operation during which no unscheduled maintenance, repair or adjustment took place. The reference value may be supplied by a cylinder gas, gas cell, or optical filter and need not be certified.

2.6 Relative Accuracy (RA). The absolute mean difference between the gas concentration or emission rate determined by the CEMS and the value determined by the RM's plus the 2.5 percent error confidence coefficient of a series of tests divided by the mean of the RM tests or the applicable emission limit.

3. QC Requirements

Each source owner or operator must develop and implement a QC program. As a minimum, each QC program must include written procedures which should describe in detail, complete, step-by-step procedures and operations for each of the following activities:

1. Calibration of CEMS.
2. CD determination and adjustment of CEMS.
3. Preventive maintenance of CEMS (including spare parts inventory).
4. Data recording, calculations, and reporting.
5. Accuracy audit procedures including sampling and analysis methods.
6. Program of corrective action for malfunctioning CEMS.

As described in Section 5.2, whenever excessive inaccuracies occur for two consecutive quarters, the source owner or operator must revise the current written procedures or modify or replace the CEMS to correct the deficiency causing the excessive inaccuracies.

These written procedures must be kept on record and available for inspection by the enforcement agency.

4. CD Assessment

4.1 CD Requirement. As described in 40 CFR 60.13(d), source owners and operators of CEMS must check, record, and quantify the CD at two concentration values at least once daily (approximately 24 hours) in accordance with the method prescribed by the manufacturer. The CEMS calibration must, as minimum, be adjusted whenever the daily zero (or low-level) CD or the daily high-level CD exceeds two times the limits of the applicable PS's in appendix B of this regulation.

4.2 Recording Requirement for Automatic CD Adjusting Monitors. Monitors that automatically adjust the data to the corrected calibration values (e.g., microprocessor control) must be programmed to record the unadjusted concentration measured in the CD prior to resetting the calibration, if performed, or record the amount of adjustment.

4.3 Criteria for Excessive CD. If either the zero (or low-level) or high-level CD result exceeds twice the applicable drift specification in appendix B for five, consecutive, daily periods, the CEMS is out-of-control. If either the zero (or low-level) or high-level CD result exceeds four times the applicable drift specification in appendix B during any CD check, the CEMS is out-of-control. If the CEMS is out-of-control, take necessary corrective action. Following corrective action, repeat the CD checks.

4.3.1 Out-Of-Control Period Definition. The beginning of the out-of-control period is the time corresponding to the completion of the fifth, consecutive, daily CD check with a CD in excess of two times the allowable limit, or the time corresponding to the completion of the daily CD check preceding the daily CD check that results in a CD in excess of four times the allowable limit. The end of the out-of-control period is the time corresponding to the completion of the CD check following corrective action that results in the CD's at both the zero (or low-level) and high-level measurement points being within the corresponding allowable CD limit (i.e., either two times or four times the allowable limit in appendix B).

4.3.2 CEMS Data Status During Out-of-Control Period. During the period the CEMS is out-of-control, the CEMS data may not be used in calculating emission compliance nor be counted towards meeting minimum data availability as required and described in the applicable subpart [e.g., §60.47a(f)].

4.4 Data Recording and Reporting. As required in §60.7(d) of this regulation (40 CFR part 60), all measurements from the CEMS must be retained on file by the source owner for at least 2 years. However, emission data obtained on each successive day while the CEMS is out-of-control may not be included as part of the minimum daily data requirement of the applicable subpart [e.g., §60.47a(f)] nor be used in the calculation of reported emissions for that period.

5. Data Accuracy Assessment

5.1 Auditing Requirements. Each CEMS must be audited at least once each calendar quarter. Successive quarterly audits shall occur no closer than 2 months. The audits shall be conducted as follows:

5.1.1 Relative Accuracy Test Audit (RATA). The RATA must be conducted at least once every four calendar quarters, except as otherwise noted in section 5.1.4 of this appendix. Conduct the RATA as described for the RA test procedure in the applicable PS in appendix B (e.g., PS 2 for SO_2 and NO_X). In addition, analyze the appropriate performance audit samples received from EPA as described in the applicable sampling methods (e.g., Methods 6 and 7).

5.1.2 Cylinder Gas Audit (CGA). If applicable, a CGA may be conducted in three of four calendar quarters, but in no more than three quarters in succession.

To conduct a CGA: (1) Challenge the CEMS (both pollutant and diluent portions of the CEMS, if applicable) with an audit gas of known concentration at two points within the following ranges:

Audit point	Audit range		
	Pollutant monitors	Diluent monitors for—	
		CO_2	O_2
1	20 to 30% of span value.	5 to 8% by volume.	4 to 6% by volume.
2	50 to 60% of span value.	10 to 14% by volume.	8 to 12% by volume.

Challenge the CEMS three times at each audit point, and use the average of the three responses in determining accuracy.

Use of separate audit gas cylinder for audit points 1 and 2. Do not dilute gas from audit cylinder when challenging the CEMS.

The monitor should be challenged at each audit point for a sufficient period of time to assure adsorption-desorption of the CEMS sample transport surfaces has stabilized.

(2) Operate each monitor in its normal sampling mode, i.e., pass the audit gas through all filters, scrubbers, conditioners, and other monitor components used during normal sampling, and as much of the sampling probe as is practical. At a minimum, the audit gas should be introduced at the connection between the probe and the sample line.

(3) Use Certified Reference Materials (CRM's) (See Citation 1) audit gases that have been certified by comparison to National Institute of Standards and Technology (NIST) or EPA Traceability Protocol Materials (ETPM's) following the most recent edition of EPA's Traceability Protocol No. 1 (See Citation 2). Procedures for preparation of CRM's are described in Citation 1. Procedures for preparation of ETPM's are described in Citation 2. As an alternative to CRM's or ETPM gases, Method 205 (See Citation 3) may be used. The difference between the actual concentration of the audit gas and the concentration indicated by the monitor is used to assess the accuracy of the CEMS.

5.1.3 Relative Accuracy Audit (RAA). The RAA may be conducted three of four calendar quarters, but in no more than three quarters in succession. To conduct a RAA, follow the procedure described in the applicable PS in appendix B for the relative accuracy test, except that only three sets of measurement data are required. Analyses of EPA performance audit samples are also required.

The relative difference between the mean of the RM values and the mean of the CEMS responses will be used to assess the accuracy of the CEMS.

5.1.4 Other Alternative Audits. Other alternative audit procedures may be used as approved by the Administrator for three of four calendar quarters. One RATA is required at least every four calendar quarters, except in the case where the affected facility is off-line (does not operate) in the fourth calendar quarter since the quarter of the previous RATA. In that case, the RATA shall be performed in the quarter in which the unit recommences operation. Also, cylinder gas audits are not be required for calendar quarters in which the affected facility does not operate.

5.2 Excessive Audit Inaccuracy. If the RA, using the RATA, CGA, or RAA exceeds the criteria in section 5.2.3, the CEMS is out-of-control. If the CEMS is out-of-control, take necessary corrective action to eliminate the problem. Following corrective action, the source owner or operator must audit the CEMS with a RATA, CGA, or RAA to determine if the CEMS is operating within the specifications. A RATA must always be used following an out-of-control period resulting from a RATA. The audit following corrective action does not require analysis of EPA performance audit samples. If audit results show the CEMS to be out-of-control, the CEMS operator shall report both the audit showing the CEMS to be out-of-control and the results of the audit following corrective action showing the CEMS to be operating within specifications.

5.2.1 Out-Of-Control Period Definition. The beginning of the out-of-control period is the time corresponding to the completion of the sampling for the RATA, RAA, or CGA. The end of the out-of-control period is the time corresponding to the completion of the sampling of the subsequent successful audit.

5.2.2 CEMS Data Status During Out-Of-Control Period. During the period the monitor is out-of-control, the CEMS data may not be used in calculating emission compliance nor be counted towards meeting minimum data availabilty as required and described in the applicable subpart [e.g., §60.47a(f)].

5.2.3 Criteria for Excessive Audit Inaccuracy. Unless specified otherwise in the applicable subpart, the criteria for excessive inaccuracy are:

(1) For the RATA, the allowable RA in the applicable PS in appendix B.

(2) For the CGA, ±15 percent of the average audit value or ±5 ppm, whichever is greater.

(3) For the RAA, ±15 percent of the three run average or ±7.5 percent of the applicable standard, whichever is greater.

5.3 Criteria for Acceptable QC Procedure. Repeated excessive inaccuracies (i.e., out-of-control conditions resulting from the quarterly audits) indicates the QC procedures are inadequate or that the CEMS is incapable of providing quality data. Therefore, whenever excessive inaccuracies occur for two consective quarters, the source owner or operator must revise the QC procedures (see Section 3) or modify or replace the CEMS.

6. Calculations for CEMS Data Accuracy

6.1 RATA RA Calculation. Follow the equations described in Section 8 of appendix B, PS 2 to calculate the RA for the RATA. The RATA must be calculated in units of the applicable emission standard (e.g., ng/J).

6.2 RAA Accuracy Calculation. Use Equation 1–1 to calculate the accuracy for the RAA. The RAA must be calculated in units of the applicable emission standard (e.g., ng/J).

6.3 CGA Accuracy Calculation. Use Equation 1–1 to calculate the accuracy for the CGA, which is calculated in units of the appropriate concentration (e.g., ppm SO_2 or percent O_2). Each component of the CEMS must meet the acceptable accuracy requirement.

$$A = \frac{C_m - C_a}{C_a} \times 100 \qquad \text{Eq. 1-1}$$

where:

A=Accuracy of the CEMS, percent.

C_m=Average CEMS response during audit in units of applicable standard or appropriate concentration.

C_a=Average audit value (CGA certified value or three-run average for RAA) in units of applicable standard or appropriate concentration.

6.4 Example Accuracy Calculations. Example calculations for the RATA, RAA, and CGA are available in Citation 3.

7. Reporting Requirements

At the reporting interval specified in the applicable regulation, report for each CEMS the accuracy results from Section 6 and the CD assessment results from Section 4. Report the drift and accuracy information as a Data Assessment Report (DAR), and include one copy of this DAR for each quarterly audit with the report of emissions required under the applicable subparts of this part.

As a minimum, the DAR must contain the following information:

1. Source owner or operator name and address.

2. Identification and location of monitors in the CEMS.

3. Manufacturer and model number of each monitor in the CEMS.

4. Assessment of CEMS data accuracy and date of assessment as determined by a RATA, RAA, or CGA described in Section 5 including the RA for the RATA, the A for the RAA or CGA, the RM results, the cylinder gases certified values, the CEMS responses, and the calculations results as defined in Section 6. If the accuracy audit results show the CEMS to be out-of-control, the CEMS operator shall report both the audit results showing the CEMS to be out-of-control and the results of the audit following corrective action showing the CEMS to be operating within specifications.

5. Results from EPA performance audit samples described in Section 5 and the applicable RM's.

6. Summary of all corrective actions taken when CEMS was determined out-of-control, as described in Sections 4 and 5.

An example of a DAR format is shown in Figure 1.

8. Bibliography

1. ''A Procedure for Establishing Traceability of Gas Mixtures to Certain National Bureau of Standards Standard Reference Materials.'' Joint publication by NBS and EPA–600/7–81–010, Revised 1989. Available from the U.S. Environmental Protection Agency. Quality Assurance Division (MD–77). Research Triangle Park, NC 27711.

2. ''EPA Traceability Protocol For Assay And Certification Of Gaseous Calibration Standards.'' EPA–600/R–97/121, September 1997. Available from EPA's Emission Measurement Center at *http://www.epa.gov/ttn/emc*.

3. Method 205, ''Verification of Gas Dilution Systems for Field Instrument Calibrations,'' 40 CFR 51, appendix M.

FIGURE 1—EXAMPLE FORMAT FOR DATA ASSESSMENT REPORT

Period ending date _____
Year _____
Company name _____
Plant name _____
Source unit no. _____
CEMS manufacturer _____
Model no. _____
CEMS serial no. _____
CEMS type (e.g., in situ) _____
CEMS sampling location (e.g., control device outlet) _____
CEMS span values as per the applicable regulation: _____ (e.g., SO_2 _____ ppm, NO_x _____ ppm). _____

I. Accuracy assessment results (Complete A, B, or C below for each CEMS or for each pollutant and diluent analyzer, as applicable.) If the quarterly audit results show the CEMS to be out-of-control, report the results of both the quarterly audit and the audit following corrective action showing the CEMS to be operating properly.

A. Relative accuracy test audit (RATA) for _____ (e.g., SO_2 in ng/J).

1. Date of audit _____.
2. Reference methods (RM's) used _____ (e.g., Methods 3 and 6).
3. Average RM value _____ (e.g., ng/J, mg/dsm^3, or percent volume).
4. Average CEMS value _____.
5. Absolute value of mean difference [d] _____.
6. Confidence coefficient [CC] _____.
7. Percent relative accuracy (RA) _____ percent.
8. EPA performance audit results:
a. Audit lot number (1) _____ (2) _____
b. Audit sample number (1) _____ (2) _____
c. Results (mg/dsm^3) (1) _____ (2) _____
d. Actual value (mg/dsm^3)* (1) _____ (2) _____
e. Relative error* (1) _____ (2) _____

B. Cylinder gas audit (CGA) for _____ (e.g., SO_2 in ppm).

	Audit point 1	Audit point 2	
1. Date of audit.			
2. Cylinder ID number.			
3. Date of certification.			
4. Type of certification	.....	.....	(e.g., EPA Protocol 1 or CRM).
5. Certified audit value	.....	.....	(e.g., ppm).
6. CEMS response value	.....	.....	(e.g., ppm).
7. Accuracy	.....	.....	percent.

C. Relative accuracy audit (RAA) for _____ (e.g., SO_2 in ng/J).

1. Date of audit _____.
2. Reference methods (RM's) used _____ (e.g., Methods 3 and 6).
3. Average RM value _____ (e.g., ng/J).
4. Average CEMS value _____.
5. Accuracy _____ percent.
6. EPA performance audit results:
a. Audit lot number (1) _____ (2) _____
b. Audit sample number (1) _____ (2) _____
c. Results (mg/dsm^3) (1) _____ (2) _____
d. Actual value (mg/dsm^3) *(1) _____ (2) _____
e. Relative error* (1) _____ (2) _____

D. Corrective action for excessive inaccuracy.

1. Out-of-control periods.
a. Date(s) _____.
b. Number of days _____.
2. Corrective action taken _____
3. Results of audit following corrective action. (Use format of A, B, or C above, as applicable.)

II. Calibration drift assessment.

A. Out-of-control periods.
1. Date(s) _____.
2. Number of days _____.

B. Corrective action taken _____

PROCEDURE 2—QUALITY ASSURANCE REQUIREMENTS FOR PARTICULATE MATTER CONTINUOUS EMISSION MONITORING SYSTEMS AT STATIONARY SOURCES

1.0 What Are the Purpose and Applicability of Procedure 2?

The purpose of Procedure 2 is to establish the minimum requirements for evaluating the effectiveness of quality control (QC) and quality assurance (QA) procedures and the quality of data produced by your particulate matter (PM) continuous emission monitoring system (CEMS). Procedure 2 applies to PM CEMS used for continuously determining compliance with emission standards or operating permit limits as specified in an applicable regulation or permit. Other QC procedures may apply to diluent (*e.g.*, O_2) monitors and other auxiliary monitoring equipment included with your CEMS to facilitate PM measurement or determination of PM concentration in units specified in an applicable regulation.

1.1 What measurement parameter does Procedure 2 address? Procedure 2 covers the instrumental measurement of PM as defined by your source's applicable reference method (no Chemical Abstract Service number assigned).

1.2 For what types of devices must I comply with Procedure 2? You must comply with Procedure 2 for the total equipment that:

(1) We require you to install and operate on a continuous basis under the applicable regulation, and

*To be completed by the Agency.

(2) You use to monitor the PM mass concentration associated with the operation of a process or emission control device.

1.3 What are the data quality objectives (DQOs) of Procedure 2? The overall DQO of Procedure 2 is the generation of valid, representative data that can be transferred into useful information for determining PM CEMS concentrations averaged over a prescribed interval. Procedure 2 is also closely associated with Performance Specification 11 (PS–11).

(1) Procedure 2 specifies the minimum requirements for controlling and assessing the quality of PM CEMS data submitted to us or the delegated permitting authority.

(2) You must meet these minimum requirements if you are responsible for one or more PM CEMS used for compliance monitoring. We encourage you to develop and implement a more extensive QA program or to continue such programs where they already exist.

1.4 What is the intent of the QA/QC procedures specified in Procedure 2? Procedure 2 is intended to establish the minimum QA/QC requirements for PM CEMS and is presented in general terms to allow you to develop a program that is most effective for your circumstances. You may adopt QA/QC procedures that go beyond these minimum requirements to ensure compliance with applicable regulations.

1.5 When must I comply with Procedure 2? You must comply with the basic requirements of Procedure 2 immediately following successful completion of the initial correlation test of PS–11.

2.0 What Are the Basic Requirements of Procedure 2?

Procedure 2 requires you to perform periodic evaluations of PM CEMS performance and to develop and implement QA/QC programs to ensure that PM CEMS data quality is maintained.

2.1 What are the basic functions of Procedure 2?

(1) Assessment of the quality of your PM CEMS data by estimating measurement accuracy;

(2) Control and improvement of the quality of your PM CEMS data by implementing QC requirements and corrective actions until the data quality is acceptable; and

(3) Specification of requirements for daily instrument zero and upscale drift checks and daily sample volume checks, as well as routine response correlation audits, absolute correlation audits, sample volume audits, and relative response audits.

3.0 What Special Definitions Apply to Procedure 2?

The definitions in Procedure 2 include those provided in PS–11 of Appendix B, with the following additions:

3.1 ''Absolute Correlation Audit (ACA)'' means an evaluation of your PM CEMS response to a series of reference standards covering the full measurement range of the instrument (*e.g.*, 4 mA to 20 mA).

3.2 ''Correlation Range'' means the range of PM CEMS responses used in the complete set of correlation test data.

3.3 ''PM CEMS Correlation'' means the site-specific relationship (*i.e.*, a regression equation) between the output from your PM CEMS (*e.g.*, mA) and the particulate concentration, as determined by the reference method. The PM CEMS correlation is expressed in the same units as the PM concentration measured by your PM CEMS (*e.g.*, mg/acm). You must derive this relation from PM CEMS response data and manual reference method data that were gathered simultaneously. These data must be representative of the full range of source and control device operating conditions that you expect to occur. You must develop the correlation by performing the steps presented in sections 12.2 and 12.3 of PS–11.

3.4 ''Reference Method Sampling Location'' means the location in your source's exhaust duct from which you collect manual reference method data for developing your PM CEMS correlation and for performing relative response audits (RRAs) and response correlation audits (RCAs).

3.5 ''Response Correlation Audit (RCA)'' means the series of tests specified in section 10.3(8) of this procedure that you conduct to ensure the continued validity of your PM CEMS correlation.

3.6 ''Relative Response Audit (RRA)'' means the brief series of tests specified in section 10.3(6) of this procedure that you conduct between consecutive RCAs to ensure the continued validity of your PM CEMS correlation.

3.7 ''Sample Volume Audit (SVA)'' means an evaluation of your PM CEMS measurement of sample volume if your PM CEMS determines PM concentration based on a measure of PM mass in an extracted sample volume and an independent determination of sample volume.

4.0 Interferences [Reserved]

5.0 What Do I Need To Know To Ensure the Safety of Persons Using Procedure 2?

People using Procedure 2 may be exposed to hazardous materials, operations, and equipment. Procedure 2 does not purport to address all of the safety issues associated with its use. It is your responsibility to establish appropriate safety and health practices and determine the applicable regulatory limitations before performing this procedure. You must consult your CEMS user's manual for specific precautions to be taken with regard to your PM CEMS procedures.

6.0 What Equipment and Supplies Do I Need? [Reserved]

7.0 What Reagents and Standards Do I Need?

You will need reference standards or procedures to perform the zero drift check, the upscale drift check, and the sample volume check.

7.1 What is the reference standard value for the zero drift check? You must use a zero check value that is no greater than 20 percent of the PM CEMS's response range. You must obtain documentation on the zero check value from your PM CEMS manufacturer.

7.2 What is the reference standard value for the upscale drift check? You must use an upscale check value that produces a response between 50 and 100 percent of the PM CEMS's response range. For a PM CEMS that produces output over a range of 4 mA to 20 mA, the upscale check value must produce a response in the range of 12 mA to 20 mA. You must obtain documentation on the upscale check value from your PM CEMS manufacturer.

7.3 What is the reference standard value for the sample volume check? You must use a reference standard value or procedure that produces a sample volume value equivalent to the normal sampling rate. You must obtain documentation on the sample volume value from your PM CEMS manufacturer.

8.0 What Sample Collection, Preservation, Storage, and Transport Are Relevant to This Procedure? [Reserved]

9.0 What Quality Control Measures Are Required by This Procedure for My PM CEMS?

You must develop and implement a QC program for your PM CEMS. Your QC program must, at a minimum, include written procedures that describe, in detail, complete step-by-step procedures and operations for the activities in paragraphs (1) through (8) of this section.

(1) Procedures for performing drift checks, including both zero drift and upscale drift and the sample volume check (see sections 10.2(1), (2), and (5)).

(2) Methods for adjustment of PM CEMS based on the results of drift checks, sample volume checks (if applicable), and the periodic audits specified in this procedure.

(3) Preventative maintenance of PM CEMS (including spare parts inventory and sampling probe integrity).

(4) Data recording, calculations, and reporting.

(5) RCA and RRA procedures, including sampling and analysis methods, sampling strategy, and structuring test conditions over the prescribed range of PM concentrations.

(6) Procedures for performing ACAs and SVAs and methods for adjusting your PM CEMS response based on ACA and SVA results.

(7) Program of corrective action for malfunctioning PM CEMS, including flagged data periods.

(8) For extractive PM CEMS, procedures for checking extractive system ducts for material accumulation.

9.1 What QA/QC documentation must I have? You are required to keep the written QA/QC procedures on record and available for inspection by us, the State, and/or local enforcement agency for the life of your CEMS or until you are no longer subject to the requirements of this procedure.

9.2 How do I know if I have acceptable QC procedures for my PM CEMS? Your QC procedures are inadequate or your PM CEMS is incapable of providing quality data if you fail two consecutive QC audits (*i.e.*, out-of-control conditions resulting from the annual audits, quarterly audits, or daily checks). Therefore, if you fail the same two consecutive audits, you must revise your QC procedures or modify or replace your PM CEMS to correct the deficiencies causing the excessive inaccuracies (see section 10.4 for limits for excessive audit inaccuracy).

10.0 What Calibration/Correlation and Standardization Procedures Must I Perform for My PM CEMS?

You must generate a site-specific correlation for each of your PM CEMS installation(s) relating response from your PM CEMS to results from simultaneous PM reference method testing. The PS–11 defines procedures for developing the correlation and defines a series of statistical parameters for assessing acceptability of the correlation. However, a critical component of your PM CEMS correlation process is ensuring the accuracy and precision of reference method data. The activities listed in sections 10.1 through 10.10 assure the quality of the correlation.

10.1 When should I use paired trains for reference method testing? Although not required, we recommend that you should use paired-train reference method testing to generate data used to develop your PM CEMS correlation and for RCA testing. Guidance on the use of paired sampling trains can be found in the PM CEMS Knowledge Document (see section 16.5 of PS–11).

10.2 What routine system checks must I perform on my PM CEMS? You must perform routine checks to ensure proper operation of system electronics and optics, light and radiation sources and detectors, and electric or electro-mechanical systems. Necessary components of the routine system checks will depend on design details of your PM CEMS. As a minimum, you must verify the system operating parameters listed in paragraphs (1) through (5) of this section on a daily basis. Some PM CEMS may perform one or more of

these functions automatically or as an integral portion of unit operations; for other PM CEMS, you must initiate or perform one or more of these functions manually.

(1) You must check the zero drift to ensure stability of your PM CEMS response to the zero check value. You must determine system output on the most sensitive measurement range when the PM CEMS is challenged with a zero reference standard or procedure. You must, at a minimum, adjust your PM CEMS whenever the daily zero drift exceeds 4 percent.

(2) You must check the upscale drift to ensure stability of your PM CEMS response to the upscale check value. You must determine system output when the PM CEMS is challenged with a reference standard or procedure corresponding to the upscale check value. You must, at a minimum, adjust your PM CEMS whenever the daily upscale drift check exceeds 4 percent.

(3) For light-scattering and extinction-type PM CEMS, you must check the system optics to ensure that system response has not been altered by the condition of optical components, such as fogging of lens and performance of light monitoring devices.

(4) You must record data from your automatic drift-adjusting PM CEMS before any adjustment is made. If your PM CEMS automatically adjusts its response to the corrected calibration values (*e.g.*, microprocessor control), you must program your PM CEMS to record the unadjusted concentration measured in the drift check before resetting the calibration. Alternately, you may program your PM CEMS to record the amount of adjustment.

(5) For extractive PM CEMS that measure the sample volume and use the measured sample volume as part of calculating the output value, you must check the sample volume on a daily basis to verify the accuracy of the sample volume measuring equipment. This sample volume check must be done at the normal sampling rate of your PM CEMS. You must adjust your PM CEMS sample volume measurement whenever the daily sample volume check error exceeds 10 percent.

10.3 What are the auditing requirements for my PM CEMS? You must subject your PM CEMS to an ACA and an SVA, as applicable, at least once each calender quarter. Successive quarterly audits must occur no closer than 2 months apart. You must conduct an RCA and an RRA at the frequencies specified in the applicable regulation or facility operating permit. An RRA or RCA conducted during any calendar quarter can take the place of the ACA required for that calendar quarter. An RCA conducted during the period in which an RRA is required can take the place of the RRA for that period.

(1) When must I perform an ACA? You must perform an ACA each quarter unless you conduct an RRA or RCA during that same quarter.

(2) How do I perform an ACA? You perform an ACA according to the procedure specified in paragraphs (2)(i) through (v) of this section.

(i) You must challenge your PM CEMS with an audit standard or an equivalent audit reference to reproduce the PM CEMS's measurement at three points within the following ranges:

Audit point	Audit range
1	0 to 20 percent of measurement range
2	40 to 60 percent of measurement range
3	70 to 100 percent of measurement range

(ii) You must then challenge your PM CEMS three times at each audit point and use the average of the three responses in determining accuracy at each audit point. Use a separate audit standard for audit points 1, 2, and 3. Challenge the PM CEMS at each audit point for a sufficient period of time to ensure that your PM CEMS response has stabilized.

(iii) Operate your PM CEMS in the mode, manner, and range specified by the manufacturer.

(iv) Store, maintain, and use audit standards as recommended by the manufacturer.

(v) Use the difference between the actual known value of the audit standard and the response of your PM CEMS to assess the accuracy of your PM CEMS.

(3) When must I perform an SVA? You must perform an audit of the measured sample volume (*e.g.*, the sampling flow rate for a known time) once per quarter for applicable PM CEMS with an extractive sampling system. Also, you must perform and pass an SVA prior to initiation of any of the reference method data collection runs for an RCA or RRA.

(4) How do I perform an SVA? You perform an SVA according to the procedure specified in paragraphs (4)(i) through (iii) of this section.

(i) You perform an SVA by independently measuring the volume of sample gas extracted from the stack or duct over each batch cycle or time period with a calibrated device. You may make this measurement either at the inlet or outlet of your PM CEMS, so long as it measures the sample gas volume without including any dilution or recycle air. Compare the measured volume with the volume reported by your PM CEMS for the same cycle or time period to calculate sample volume accuracy.

(ii) You must make measurements during three sampling cycles for batch extractive monitors (*e.g.*, Beta-gauge) or during three periods of at least 20 minutes for continuous extractive PM CEMS.

(iii) You may need to condense, collect, and measure moisture from the sample gas prior to the calibrated measurement device (*e.g.*, dry gas meter) and correct the results for moisture content. In any case, the volumes measured by the calibrated device and your PM CEMS must be on a consistent temperature, pressure, and moisture basis.

(5) How often must I perform an RRA? You must perform an RRA at the frequency specified in the applicable regulation or facility operating permit. You may conduct an RCA instead of an RRA during the period when the RRA is required.

(6) How do I perform an RRA? You must perform the RRA according to the procedure specified in paragraphs (6)(i) and (ii) of this section.

(i) You perform an RRA by collecting three simultaneous reference method PM concentration measurements and PM CEMS measurements at the as-found source operating conditions and PM concentration.

(ii) We recommend that you use paired trains for reference method sampling. Guidance on the use of paired sampling trains can be found in the PM CEMS Knowledge Document (see section 16.5 of PS–11).

(7) How often must I perform an RCA? You must perform an RCA at the frequency specified in the applicable regulation or facility operating permit.

(8) How do I perform an RCA? You must perform the RCA according to the procedures for the PM CEMS correlation test described in PS–11, section 8.6, except that the minimum number of runs required is 12 in the RCA instead of 15 as specified in PS–11.

(9) What other alternative audits can I use? You can use other alternative audit procedures as approved by us, the State, or local agency for the quarters when you would conduct ACAs.

10.4 What are my limits for excessive audit inaccuracy? Unless specified otherwise in the applicable subpart, the criteria for excessive audit inaccuracy are listed in paragraphs (1) through (6) of this section.

(1) What are the criteria for excessive zero or upscale drift? Your PM CEMS is out of control if the zero drift check or upscale drift check either exceeds 4 percent for five consecutive daily periods or exceeds 8 percent for any one day.

(2) What are the criteria for excessive sample volume measurement error? Your PM CEMS is out of control if sample volume check error exceeds 10 percent for five consecutive daily periods or exceeds 20 percent for any one day.

(3) What are the criteria for excessive ACA error? Your PM CEMS is out of control if the results of any ACA exceed ± 10 percent of the average audit value, as calculated using Equation 2–1a, or 7.5 percent of the applicable standard, as calculated using Equation 2–1b, whichever is greater.

(4) What is the criterion for excessive SVA error? Your PM CEMS is out of control if results exceed ±5 percent of the average sample volume audit value.

(5) What are the criteria for passing an RCA? To pass an RCA, you must meet the criteria specified in paragraphs (5)(i) through (iii) of this section. If your PM CEMS fails to meet these RCA criteria, it is out of control.

(i) For all 12 data points, the PM CEMS response value can be no greater than the greatest PM CEMS response value used to develop your correlation curve.

(ii) For 9 of the 12 data points, the PM CEMS response value must lie within the PM CEMS output range used to develop your correlation curve.

(iii) At least 75 percent of a minimum number of 12 sets of PM CEMS and reference method measurements must fall within a specified area on a graph of the correlation regression line. The specified area on the graph of the correlation regression line is defined by two lines parallel to the correlation regression line, offset at a distance of ±25 percent of the numerical emission limit value from the correlation regression line.

(6) What are the criteria to pass an RRA? To pass an RRA, you must meet the criteria specified in paragraphs (6)(i) and (ii) of this section. If your PM CEMS fails to meet these RRA criteria, it is out of control.

(i) For all three data points, the PM CEMS response value can be no greater than the greatest PM CEMS response value used to develop your correlation curve.

(ii) For two of the three data points, the PM CEMS response value must lie within the PM CEMS output range used to develop your correlation curve.

(iii) At least two of the three sets of PM CEMS and reference method measurements must fall within the same specified area on a graph of the correlation regression line as required for the RCA and described in paragraph (5)(iii) of this section.

10.5 What do I do if my PM CEMS is out of control? If your PM CEMS is out of control, you must take the actions listed in paragraphs (1) and (2) of this section.

(1) You must take necessary corrective action to eliminate the problem and perform tests, as appropriate, to ensure that the corrective action was successful.

(i) Following corrective action, you must repeat the previously failed audit to confirm that your PM CEMS is operating within the specifications.

(ii) If your PM CEMS failed an RRA, you must take corrective action until your PM CEMS passes the RRA criteria. If the RRA criteria cannot be achieved, you must perform an RCA.

(iii) If your PM CEMS failed an RCA, you must follow procedures specified in section 10.6 of this procedure.

(2) You must report both the audit showing your PM CEMS to be out of control and the results of the audit following corrective action showing your PM CEMS to be operating within specifications.

10.6 What do I do if my PM CEMS fails an RCA? After an RCA failure, you must take all applicable actions listed in paragraphs (1) through (3) of this section.

(1) Combine RCA data with data from the active PM CEMS correlation and perform the mathematical evaluations defined in PS–11 for development of a PM CEMS correlation, including examination of alternate correlation models (*i.e.,* linear, polynomial, logarithmic, exponential, and power). If the expanded data base and revised correlation meet PS–11 statistical criteria, use the revised correlation.

(2) If the criteria specified in paragraph (1) of this section are not achieved, you must develop a new PM CEMS correlation based on revised data. The revised data set must consist of the test results from only the RCA. The new data must meet all requirements of PS–11 to develop a revised PM CEMS correlation, except that the minimum number of sets of PM CEMS and reference method measurements is 12 instead of the minimum of 15 sets required by PS–11. Your PM CEMS is considered to be back in controlled status when the revised correlation meets all of the performance criteria specified in section 13.2 of PS–11.

(3) If the actions in paragraphs (1) and (2) of this section do not result in an acceptable correlation, you must evaluate the cause(s) and comply with the actions listed in paragraphs (3)(i) through (iv) of this section within 90 days after the completion of the failed RCA.

(i) Completely inspect your PM CEMS for mechanical or operational problems. If you find a mechanical or operational problem, repair your PM CEMS and repeat the RCA.

(ii) You may need to relocate your PM CEMS to a more appropriate measurement location. If you relocate your PM CEMS, you must perform a new correlation test according to the procedures specified in PS–11.

(iii) The characteristics of the PM or gas in your source's flue gas stream may have changed such that your PM CEMS measurement technology is no longer appropriate. If this is the case, you must install a PM CEMS with measurement technology that is appropriate for your source's flue gas characteristics. You must perform a new correlation test according to the procedures specified in PS–11.

(iv) If the corrective actions in paragraphs (3)(i) through (iii) of this section were not successful, you must petition us, the State, or local agency for approval of alternative criteria or an alternative for continuous PM monitoring.

10.7 When does the out-of-control period begin and end? The out-of-control period begins immediately after the last test run or check of an unsuccessful RCA, RRA, ACA, SVA, drift check, or sample volume check. The out-of-control period ends immediately after the last test run or check of the subsequent successful audit or drift check.

10.8 Can I use the data recorded by my PM CEMS during out-of-control periods? During any period when your PM CEMS is out of control, you may not use your PM CEMS data to calculate emission compliance or to meet minimum data availability requirements described in the applicable regulation.

10.9 What are the QA/QC reporting requirements for my PM CEMS? You must report the accuracy results for your PM CEMS, specified in section 10.4 of this procedure, at the interval specified in the applicable regulation. Report the drift and accuracy information as a Data Assessment Report (DAR), and include one copy of this DAR for each quarterly audit with the report of emissions required under the applicable regulation. An example DAR is provided in Procedure 1, Appendix F of this part.

10.10 What minimum information must I include in my DAR? As a minimum, you must include the information listed in paragraphs (1) through (5) of this section in the DAR:

(1) Your name and address.

(2) Identification and location of monitors in your CEMS.

(3) Manufacturer and model number of each monitor in your CEMS.

(4) Assessment of PM CEMS data accuracy/acceptability, and date of assessment, as determined by an RCA, RRA, ACA, or SVA described in section 10, including the acceptability determination for the RCA or RRA, the accuracy for the ACA or SVA, the reference method results, the audit standards, your PM CEMS responses, and the calculation results as defined in section 12. If the accuracy audit results show your PM CEMS to be out of control, you must report both the audit results showing your PM CEMS to be out of control and the results of the audit following corrective action showing your PM CEMS to be operating within specifications.

(5) Summary of all corrective actions you took when you determined your PM CEMS to be out of control, as described in section 10.5, or after failing on RCA, as described in section 10.6.

10.7 Where and how long must I retain the QA data that this procedure requires me to record for my PM CEMS? You must keep the records required by this procedure for your PM CEMS onsite and available for inspection by us, the State, and/or local enforcement agency for a period of 5 years.

11.0 What Analytical Procedures Apply to This Procedure?

Sample collection and analysis are concurrent for this procedure. You must refer to the appropriate reference method for the specific analytical procedures.

12.0 What Calculations and Data Analysis Must I Perform for my PM CEMS?

(1) How do I determine RCA and RRA acceptability? You must plot each of your PM CEMS and reference method data sets from an RCA or RRA on a graph based on your PM CEMS correlation line to determine if the criteria in paragraphs 10.4(5) or (6), respectively, are met.

(2) How do I calculate ACA accuracy? You must use either Equation 2–1a or 2–1b to calculate ACA accuracy for each of the three audit points. However, when calculating ACA accuracy for the first audit point (0 to 20 percent of measurement range), you must use Equation 2–1b to calculate ACA accuracy if the reference standard value (R_v) equals zero.

$$\text{ACA Accuracy} = \frac{|R_{CEM} - R_V|}{R_V} \times 100\% \qquad \text{Eq. 2-1a}$$

Where:

ACA Accuracy = The ACA accuracy at each audit point, in percent,

R_{CEM} = Your PM CEMS response to the reference standard, and

R_V = The reference standard value.

$$\text{ACA Accuracy} = \frac{|C_{CEM} - C_{RV}|}{C_S} \times 100\% \qquad \text{Eq. 2-1b}$$

Where:

ACA Accuracy = The ACA accuracy at each audit point, in percent,

C_{CEM} = The PM concentration that corresponds to your PM CEMS response to the reference standard, as calculated using the correlation equation for your PM CEMS,

C_{RV} = The PM concentration that corresponds to the reference standard value in units consistent with C_{CEM}, and

C_s = The PM concentration that corresponds to the applicable emission limit in units consistent with C_{CEM}.

(3) How do I calculate daily upscale and zero drift? You must calculate the upscale drift using to Equation 2–2 and the zero drift according to Equation 2–3:

$$UD = \frac{|R_{CEM} - R_U|}{R_U} \times 100 \qquad \text{(Eq. 2-2)}$$

Where:

UD = The upscale drift of your PM CEMS, in percent,

R_{CEM} = Your PM CEMS response to the upscale check value, and

R_U = The upscale check value.

$$ZD = \frac{|R_{CEM} - R_L|}{R_U} \times 100 \qquad \text{(Eq. 2-3)}$$

Where:

ZD = The zero (low-level) drift of your PM CEMS, in percent,

R_{CEM} = Your PM CEMS response of the zero check value,

R_L = The zero check value, and

R_U = The upscale check value.

(4) How do I calculate SVA accuracy? You must use Equation 2–4 to calculate the accuracy, in percent, for each of the three SVA tests or the daily sample volume check:

$$\text{Accuracy} = \frac{(V_R - V_M)}{FS} \times 100 \qquad \text{(Eq. 2-4)}$$

Where:

V_M = Sample gas volume determined/reported by your PM CEMS (*e.g.*, dscm),

V_R = Sample gas volume measured by the independent calibrated reference device (*e.g.*, dscm) for the SVA or the reference value for the daily sample volume check, and

FS = Full-scale value.

NOTE: Before calculating SVA accuracy, you must correct the sample gas volumes

measured by your PM CEMS and the independent calibrated reference device to the same basis of temperature, pressure, and moisture content. You must document all data and calculations.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Which References are Relevant to This Method? [Reserved]

17.0 What Tables, Diagrams, Flowcharts, and Validation Data Are Relevant to This Method? [Reserved]

[52 FR 21008, June 4, 1987; 52 FR 27612, July 22, 1987, as amended at 56 FR 5527, Feb. 11, 1991; 69 FR 1816, Jan. 12, 2004; 72 FR 32768, June 13, 2007; 74 FR 12590, Mar. 25, 2009]

APPENDIX G TO PART 60—PROVISIONS FOR AN ALTERNATIVE METHOD OF DEMONSTRATING COMPLIANCE WITH 40 CFR 60.43 FOR THE NEWTON POWER STATION OF CENTRAL ILLINOIS PUBLIC SERVICE COMPANY

1. *Designation of Affected Facilities*

1.1 The affected facilities to which this alternative compliance method applies are the Unit 1 and 2 coal-fired steam generating units located at the Central Illinois Public Service Company's (CIPS) Newton Power Station in Jasper County, Illinois. Each of these units is subject to the Standards of Performance for Fossil-Fuel-Fired Steam Generators for Which Construction Commenced After August 17, 1971 (subpart D).

2. *Definitions*

2.1 All definitions in subparts D and Da of part 60 apply to this provision except that:

24-hour period means the period of time between 12:00 midnight and the following midnight.

Boiler operating day means a 24-hour period during which any fossil is combusted in either the Unit 1 or Unit 2 steam generating unit and during which the provisions of §60.43(e) are applicable.

CEMs means continuous emission monitoring system.

Coal bunker means a single or group of coal trailers, hoppers, silos or other containers that:

(1) are physically attached to the affected facility; and

(2) provide coal to the coal pulverizers.

DAFGDS means the dual alkali flue gas desulfurization system for the Newton Unit 1 steam generating unit.

3. *Compliance Provisions*

3.1 If the owner or operator of the affected facility elects to comply with the 470 ng/J (1.1 lbs/MMBTU) of combined heat input emission limit under §60.43(e), he shall notify the Regional Administrator, of the United States Environmental Protection Agency (USEPA), Region 5 and the Director, of the Illinois Environmental Protection Agency (IEPA) at least 30 days in advance of the date such election is to take effect, stating the date such operation is to commence. When the owner or operator elects to comply with this limit after one or more periods of reverting to the 520 ng/J heat input (1.2 lbs/MMBTU) limit of §60.43(a)(2), as provided under 3.4, he shall notify the Regional Administrator of the USEPA, Region 5 and the Director of the (IEPA) in writing at least ten (10) days in advance of the date such election is to take effect.

3.2 Compliance with the sulfur dioxide emission limit under §60.43(e) is determined on a continuous basis by performance testing using CEMs. Within 60 days after the initial operation of Units 1 and 2 subject to the combined emission limit in §60.43(e), the owner or operator shall conduct an initial performance test, as required by §60.8, to determine compliance with the combined emission limit. This initial performance test is to be scheduled so that the thirtieth boiler operating day of the 30 successive boiler operating days is completed within 60 days after initial operation subject to the 470 ng/J (1.1 lbs/MMBTU) combined emission limit. Following the initial performance test, a separate performance test is completed at the end of each boiler operating day Unit 1 and Unit 2 are subject to §60.43(e), and a new 30 day average emission rate calculated.

3.2.1 Following the initial performance test, a new 30 day average emission rate is calculated for each boiler operating day the affected facility is subject to §60.43(e). If the owner or operator of the affected facility elects to comply with §60.43(e) after one or more periods of reverting to the 520 ng/J heat input (1.2 lbs/MMBTU) limit under §60.43(a)(2), as provided under 3.4, the 30 day average emission rate under §60.43(e) is calculated using emissions data of the current boiler operating day and data for the previous 29 boiler operating days when the affected facility was subject to §60.43(e). Periods of operation of the affected facility under §60.43(a)(2) are not considered boiler operating days. Emissions data collected during operation under §60.43(a)(2) are not considered relative to 4.6 and emissions data are not included in calculations of emission under §60.43(e).

3.2.2 When the affected facility is operated under the provisions of §60.43(e), the Unit 1 DAFGDS bypass damper must be fully closed. The DAFGDS bypass may be opened only during periods of DAFGDS startup, shutdown, malfunction or testing as described under Sections 3.5.1, 3.5.2, 3.5.3, 3.5.4, and 4.8.2.

State of Oregon Department of Environmental Quality

OAR 340-230-8010 Attachments

SUBCHAPTER C—AIR PROGRAMS (CONTINUED)

PART 60—STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES (CONTINUED)

App.

APPENDIX A–1 TO PART 60—TEST METHODS 1 THROUGH 2F
APPENDIX A–2 TO PART 60—TEST METHODS 2G THROUGH 3C
APPENDIX A–3 TO PART 60—TEST METHODS 4 THROUGH 5I
APPENDIX A–4 TO PART 60—TEST METHODS 6 THROUGH 10B
APPENDIX A–5 TO PART 60—TEST METHODS 11 THROUGH 15A
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APPENDIX B TO PART 60—PERFORMANCE SPECIFICATIONS
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APPENDIX E TO PART 60 [RESERVED]
APPENDIX F TO PART 60—QUALITY ASSURANCE PROCEDURES
APPENDIX G TO PART 60—PROVISIONS FOR AN ALTERNATIVE METHOD OF DEMONSTRATING COMPLIANCE WITH 40 CFR 60.43 FOR THE NEWTON POWER STATION OF CENTRAL ILLINOIS PUBLIC SERVICE COMPANY
APPENDIX H TO PART 60 [RESERVED]
APPENDIX I TO PART 60—OWNER'S MANUALS AND TEMPORARY LABELS FOR WOOD HEATERS SUBJECT TO SUBPARTS AAA AND QQQQ OF PART 60

AUTHORITY: 42 U.S.C. 7401–7601.

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APPENDIX A–1 TO PART 60—TEST METHODS 1 THROUGH 2F

Method 1—Sample and velocity traverses for stationary sources
Method 1A—Sample and velocity traverses for stationary sources with small stacks or ducts
Method 2—Determination of stack gas velocity and volumetric flow rate (Type S pitot tube)
Method 2A—Direct measurement of gas volume through pipes and small ducts
Method 2B—Determination of exhaust gas volume flow rate from gasoline vapor incinerators
Method 2C—Determination of gas velocity and volumetric flow rate in small stacks or ducts (standard pitot tube)
Method 2D—Measurement of gas volume flow rates in small pipes and ducts
Method 2E—Determination of landfill gas production flow rate
Method 2F—Determination of Stack Gas Velocity and Volumetric Flow Rate With Three-Dimensional Probes

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to

specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

METHOD 1—SAMPLE AND VELOCITY TRAVERSES FOR STATIONARY SOURCES

NOTE: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test method: Method 2.

1.0 Scope and Application

1.1 Measured Parameters. The purpose of the method is to provide guidance for the selection of sampling ports and traverse points at which sampling for air pollutants will be performed pursuant to regulations set forth in this part. Two procedures are presented: a simplified procedure, and an alternative procedure (see section 11.5). The magnitude of cyclonic flow of effluent gas in a stack or duct is the only parameter quantitatively measured in the simplified procedure.

1.2 Applicability. This method is applicable to gas streams flowing in ducts, stacks, and flues. This method cannot be used when: (1) the flow is cyclonic or swirling; or (2) a stack is smaller than 0.30 meter (12 in.) in diameter, or 0.071 m^2 (113 $in.^2$) in cross-sectional area. The simplified procedure cannot be used when the measurement site is less than two stack or duct diameters downstream or less than a half diameter upstream from a flow disturbance.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

NOTE: The requirements of this method must be considered before construction of a new facility from which emissions are to be measured; failure to do so may require subsequent alterations to the stack or deviation from the standard procedure. Cases involving variants are subject to approval by the Administrator.

2.0 Summary of Method

2.1 This method is designed to aid in the representative measurement of pollutant emissions and/or total volumetric flow rate from a stationary source. A measurement site where the effluent stream is flowing in a known direction is selected, and the cross-section of the stack is divided into a number of equal areas. Traverse points are then located within each of these equal areas.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies.

6.1 Apparatus. The apparatus described below is required only when utilizing the alternative site selection procedure described in section 11.5 of this method.

6.1.1 Directional Probe. Any directional probe, such as United Sensor Type DA Three-Dimensional Directional Probe, capable of measuring both the pitch and yaw angles of gas flows is acceptable. Before using the probe, assign an identification number to the

directional probe, and permanently mark or engrave the number on the body of the probe. The pressure holes of directional probes are susceptible to plugging when used in particulate-laden gas streams. Therefore, a procedure for cleaning the pressure holes by ''back-purging'' with pressurized air is required.

6.1.2 Differential Pressure Gauges. Inclined manometers, U-tube manometers, or other differential pressure gauges (*e.g.*, magnehelic gauges) that meet the specifications described in Method 2, section 6.2.

NOTE: If the differential pressure gauge produces both negative and positive readings, then both negative and positive pressure readings shall be calibrated at a minimum of three points as specified in Method 2, section 6.2.

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transport [Reserved]

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Procedure

11.1 Selection of Measurement Site.

11.1.1 Sampling and/or velocity measurements are performed at a site located at least eight stack or duct diameters downstream and two diameters upstream from any flow disturbance such as a bend, expansion, or contraction in the stack, or from a visible flame. If necessary, an alternative location may be selected, at a position at least two stack or duct diameters downstream and a half diameter upstream from any flow disturbance.

11.1.2 An alternative procedure is available for determining the acceptability of a measurement location not meeting the criteria above. This procedure described in section 11.5 allows for the determination of gas flow angles at the sampling points and comparison of the measured results with acceptability criteria.

11.2 Determining the Number of Traverse Points.

11.2.1 Particulate Traverses.

11.2.1.1 When the eight- and two-diameter criterion can be met, the minimum number of traverse points shall be: (1) twelve, for circular or rectangular stacks with diameters (or equivalent diameters) greater than 0.61 meter (24 in.); (2) eight, for circular stacks with diameters between 0.30 and 0.61 meter (12 and 24 in.); and (3) nine, for rectangular stacks with equivalent diameters between 0.30 and 0.61 meter (12 and 24 in.).

11.2.1.2 When the eight- and two-diameter criterion cannot be met, the minimum number of traverse points is determined from Figure 1–1. Before referring to the figure, however, determine the distances from the measurement site to the nearest upstream and downstream disturbances, and divide each distance by the stack diameter or equivalent diameter, to determine the distance in terms of the number of duct diameters. Then, determine from Figure 1–1 the minimum number of traverse points that corresponds:

(1) To the number of duct diameters upstream; and

(2) To the number of diameters downstream. Select the higher of the two minimum numbers of traverse points, or a greater value, so that for circular stacks, the number is a multiple of 4, and for rectangular stacks, the number is one of those shown in Table 1–1.

11.2.2 Velocity (Non-Particulate) Traverses. When velocity or volumetric flow rate is to be determined (but not particulate matter), the same procedure as that used for particulate traverses (Section 11.2.1) is followed, except that Figure 1–2 may be used instead of Figure 1–1.

11.3 Cross-Sectional Layout and Location of Traverse Points.

11.3.1 Circular Stacks.

11.3.1.1 Locate the traverse points on two perpendicular diameters according to Table 1–2 and the example shown in Figure 1–3. Any equation (see examples in References 2 and 3 in section 16.0) that gives the same values as those in Table 1–2 may be used in lieu of Table 1–2.

11.3.1.2 For particulate traverses, one of the diameters must coincide with the plane containing the greatest expected concentration variation (*e.g.*, after bends); one diameter shall be congruent to the direction of the bend. This requirement becomes less critical as the distance from the disturbance increases; therefore, other diameter locations may be used, subject to the approval of the Administrator.

11.3.1.3 In addition, for elliptical stacks having unequal perpendicular diameters, separate traverse points shall be calculated and located along each diameter. To determine the cross-sectional area of the elliptical stack, use the following equation:

$$\text{Square Area} = D_1 \times D_2 \times 0.7854$$

Where: D_1 = Stack diameter 1

D_2 = Stack diameter 2

11.3.1.4 In addition, for stacks having diameters greater than 0.61 m (24 in.), no traverse points shall be within 2.5 centimeters (1.00 in.) of the stack walls; and for stack diameters equal to or less than 0.61 m (24 in.), no traverse points shall be located within 1.3 cm (0.50 in.) of the stack walls. To meet these criteria, observe the procedures given below.

11.3.2 Stacks With Diameters Greater Than 0.61 m (24 in.).

11.3.2.1 When any of the traverse points as located in section 11.3.1 fall within 2.5 cm (1.0 in.) of the stack walls, relocate them away from the stack walls to: (1) a distance of 2.5 cm (1.0 in.); or (2) a distance equal to the nozzle inside diameter, whichever is larger. These relocated traverse points (on each end of a diameter) shall be the ''adjusted'' traverse points.

11.3.2.2 Whenever two successive traverse points are combined to form a single adjusted traverse point, treat the adjusted point as two separate traverse points, both in the sampling and/or velocity measurement procedure, and in recording of the data.

11.3.3 Stacks With Diameters Equal To or Less Than 0.61 m (24 in.). Follow the procedure in section 11.3.1.1, noting only that any ''adjusted'' points should be relocated away from the stack walls to: (1) a distance of 1.3 cm (0.50 in.); or (2) a distance equal to the nozzle inside diameter, whichever is larger.

11.3.4 Rectangular Stacks.

11.3.4.1 Determine the number of traverse points as explained in sections 11.1 and 11.2 of this method. From Table 1–1, determine the grid configuration. Divide the stack cross-section into as many equal rectangular elemental areas as traverse points, and then locate a traverse point at the centroid of each equal area according to the example in Figure 1–4.

11.3.4.2 To use more than the minimum number of traverse points, expand the ''minimum number of traverse points'' matrix (see Table 1–1) by adding the extra traverse points along one or the other or both legs of the matrix; the final matrix need not be balanced. For example, if a 4×3 ''minimum number of points'' matrix were expanded to 36 points, the final matrix could be 9×4 or 12×3, and would not necessarily have to be 6×6. After constructing the final matrix, divide the stack cross-section into as many equal rectangular, elemental areas as traverse points, and locate a traverse point at the centroid of each equal area.

11.3.4.3 The situation of traverse points being too close to the stack walls is not expected to arise with rectangular stacks. If this problem should ever arise, the Administrator must be contacted for resolution of the matter.

11.4 Verification of Absence of Cyclonic Flow.

11.4.1 In most stationary sources, the direction of stack gas flow is essentially parallel to the stack walls. However, cyclonic flow may exist (1) after such devices as cyclones and inertial demisters following venturi scrubbers, or (2) in stacks having tangential inlets or other duct configurations which tend to induce swirling; in these instances, the presence or absence of cyclonic flow at the sampling location must be determined. The following techniques are acceptable for this determination.

11.4.2 Level and zero the manometer. Connect a Type S pitot tube to the manometer and leak-check system. Position the Type S pitot tube at each traverse point, in succession, so that the planes of the face openings of the pitot tube are perpendicular to the stack cross-sectional plane; when the Type S pitot tube is in this position, it is at ''0° reference.'' Note the differential pressure (Δp) reading at each traverse point. If a null (zero) pitot reading is obtained at 0° reference at a given traverse point, an acceptable flow condition exists at that point. If the pitot reading is not zero at 0° reference, rotate the pitot tube (up to ±90° yaw angle), until a null reading is obtained. Carefully determine and record the value of the rotation angle (α) to the nearest degree. After the null technique has been applied at each traverse point, calculate the average of the absolute values of α; assign α values of 0° to those points for which no rotation was required, and include these in the overall average. If the average value of α is greater than 20°, the overall flow condition in the stack is unacceptable, and alternative methodology, subject to the approval of the Administrator, must be used to perform accurate sample and velocity traverses.

11.5 The alternative site selection procedure may be used to determine the rotation angles in lieu of the procedure outlined in section 11.4.

11.5.1 Alternative Measurement Site Selection Procedure. This alternative applies to sources where measurement locations are less than 2 equivalent or duct diameters downstream or less than one-half duct diameter upstream from a flow disturbance. The alternative should be limited to ducts larger than 24 in. in diameter where blockage and wall effects are minimal. A directional flow-sensing probe is used to measure pitch and yaw angles of the gas flow at 40 or more traverse points; the resultant angle is calculated and compared with acceptable criteria for mean and standard deviation.

NOTE: Both the pitch and yaw angles are measured from a line passing through the traverse point and parallel to the stack axis. The pitch angle is the angle of the gas flow component in the plane that INCLUDES the traverse line and is parallel to the stack axis. The yaw angle is the angle of the gas flow component in the plane PERPENDICULAR to the traverse line at the traverse point and is measured from the line passing through the traverse point and parallel to the stack axis.

11.5.2 Traverse Points. Use a minimum of 40 traverse points for circular ducts and 42 points for rectangular ducts for the gas flow angle determinations. Follow the procedure outlined in section 11.3 and Table 1–1 or 1–2 for the location and layout of the traverse

points. If the measurement location is determined to be acceptable according to the criteria in this alternative procedure, use the same traverse point number and locations for sampling and velocity measurements.

11.5.3 Measurement Procedure.

11.5.3.1 Prepare the directional probe and differential pressure gauges as recommended by the manufacturer. Capillary tubing or surge tanks may be used to dampen pressure fluctuations. It is recommended, but not required, that a pretest leak check be conducted. To perform a leak check, pressurize or use suction on the impact opening until a reading of at least 7.6 cm (3 in.) H_2O registers on the differential pressure gauge, then plug the impact opening. The pressure of a leak-free system will remain stable for at least 15 seconds.

11.5.3.2 Level and zero the manometers. Since the manometer level and zero may drift because of vibrations and temperature changes, periodically check the level and zero during the traverse.

11.5.3.3 Position the probe at the appropriate locations in the gas stream, and rotate until zero deflection is indicated for the yaw angle pressure gauge. Determine and record the yaw angle. Record the pressure gauge readings for the pitch angle, and determine the pitch angle from the calibration curve. Repeat this procedure for each traverse point. Complete a ''back-purge'' of the pressure lines and the impact openings prior to measurements of each traverse point.

11.5.3.4 A post-test check as described in section 11.5.3.1 is required. If the criteria for a leak-free system are not met, repair the equipment, and repeat the flow angle measurements.

11.5.4 Calibration. Use a flow system as described in sections 10.1.2.1 and 10.1.2.2 of Method 2. In addition, the flow system shall have the capacity to generate two test-section velocities: one between 365 and 730 m/min (1,200 and 2,400 ft/min) and one between 730 and 1,100 m/min (2,400 and 3,600 ft/min).

11.5.4.1 Cut two entry ports in the test section. The axes through the entry ports shall be perpendicular to each other and intersect in the centroid of the test section. The ports should be elongated slots parallel to the axis of the test section and of sufficient length to allow measurement of pitch angles while maintaining the pitot head position at the test-section centroid. To facilitate alignment of the directional probe during calibration, the test section should be constructed of plexiglass or some other transparent material. All calibration measurements should be made at the same point in the test section, preferably at the centroid of the test section.

11.5.4.2 To ensure that the gas flow is parallel to the central axis of the test section, follow the procedure outlined in section 11.4 for cyclonic flow determination to measure the gas flow angles at the centroid of the test section from two test ports located 90° apart. The gas flow angle measured in each port must be ±2° of 0°. Straightening vanes should be installed, if necessary, to meet this criterion.

11.5.4.3 Pitch Angle Calibration. Perform a calibration traverse according to the manufacturer's recommended protocol in 5° increments for angles from −60° to + 60° at one velocity in each of the two ranges specified above. Average the pressure ratio values obtained for each angle in the two flow ranges, and plot a calibration curve with the average values of the pressure ratio (or other suitable measurement factor as recommended by the manufacturer) versus the pitch angle. Draw a smooth line through the data points. Plot also the data values for each traverse point. Determine the differences between the measured data values and the angle from the calibration curve at the same pressure ratio. The difference at each comparison must be within 2° for angles between 0° and 40° and within 3° for angles between 40° and 60°.

11.5.4.4 Yaw Angle Calibration. Mark the three-dimensional probe to allow the determination of the yaw position of the probe. This is usually a line extending the length of the probe and aligned with the impact opening. To determine the accuracy of measurements of the yaw angle, only the zero or null position need be calibrated as follows: Place the directional probe in the test section, and rotate the probe until the zero position is found. With a protractor or other angle measuring device, measure the angle indicated by the yaw angle indicator on the three-dimensional probe. This should be within 2° of 0°. Repeat this measurement for any other points along the length of the pitot where yaw angle measurements could be read in order to account for variations in the pitot markings used to indicate pitot head positions.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

L = length.
n = total number of traverse points.
P_i = pitch angle at traverse point i, degree.
R_{avg} = average resultant angle, degree.
R_i = resultant angle at traverse point i, degree.
S_d = standard deviation, degree.
W = width.
Y_i = yaw angle at traverse point i, degree.

12.2 For a rectangular cross section, an equivalent diameter (D_e) shall be calculated using the following equation, to determine the upstream and downstream distances:

$$D_e = \frac{2(L)(W)}{L + W} \qquad \text{Eq. 1-1}$$

12.3 If use of the alternative site selection procedure (Section 11.5 of this method) is required, perform the following calculations using the equations below: the resultant angle at each traverse point, the average resultant angle, and the standard deviation. Complete the calculations retaining at least one extra significant figure beyond that of the acquired data. Round the values after the final calculations.

12.3.1 Calculate the resultant angle at each traverse point:

$$R_i = \text{arc cosine}\left[(\text{cosine } Y_i)(\text{cosine } P_i)\right] \qquad \text{Eq. 1-2}$$

12.3.2 Calculate the average resultant for the measurements:

$$R_{avg} = \sum R_i/n \qquad \text{Eq. 1-3}$$

12.3.3 Calculate the standard deviations:

$$S_d = \sqrt{\frac{\sum_{i=1}^{n}\left(R_i - R_{avg}\right)^2}{(n-1)}} \qquad \text{Eq. 1-4}$$

12.3.4 Acceptability Criteria. The measurement location is acceptable if $R_{avg} \leq 20°$ and $S_d \leq 10°$.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

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17.0 Tables, Diagrams, Flowcharts, and Validation Data

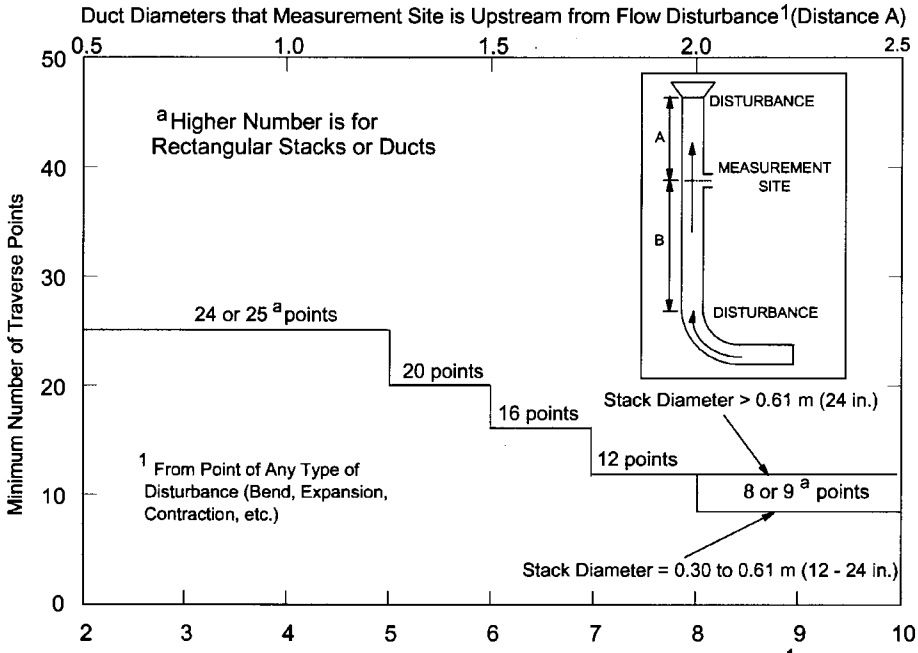

Figure 1-1. Minimum number of traverse points for particulate traverses

TABLE 1–1 CROSS-SECTION LAYOUT FOR RECTANGULAR STACKS

Number of tranverse points layout	Matrix
9	3 × 3
12	4 × 3
16	4 × 4
20	5 × 4
25	5 × 5

TABLE 1–1 CROSS-SECTION LAYOUT FOR RECTANGULAR STACKS—Continued

Number of tranverse points layout	Matrix
30	6 × 5
36	6 × 6
42	7 × 6
49	7 × 7

TABLE 1–2—LOCATION OF TRAVERSE POINTS IN CIRCULAR STACKS

[Percent of stack diameter from inside wall to tranverse point]

Traverse point number on a diameter	Number of traverse points on a diameter											
	2	4	6	8	10	12	14	16	18	20	22	24
1	14.6	6.7	4.4	3.2	2.6	2.1	1.8	1.6	1.4	1.3	1.1	1.1
2	85.4	25.0	14.6	10.5	8.2	6.7	5.7	4.9	4.4	3.9	3.5	3.2
3		75.0	29.6	19.4	14.6	11.8	9.9	8.5	7.5	6.7	6.0	5.5
4		93.3	70.4	32.3	22.6	17.7	14.6	12.5	10.9	9.7	8.7	7.9
5			85.4	67.7	34.2	25.0	20.1	16.9	14.6	12.9	11.6	10.5
6			95.6	80.6	65.8	35.6	26.9	22.0	18.8	16.5	14.6	13.2
7				89.5	77.4	64.4	36.6	28.3	23.6	20.4	18.0	16.1
8				96.8	85.4	75.0	63.4	37.5	29.6	25.0	21.8	19.4
9					91.8	82.3	73.1	62.5	38.2	30.6	26.2	23.0
10					97.4	88.2	79.9	71.7	61.8	38.8	31.5	27.2
11						93.3	85.4	78.0	70.4	61.2	39.3	32.3
12						97.9	90.1	83.1	76.4	69.4	60.7	39.8
13							94.3	87.5	81.2	75.0	68.5	60.2
14							98.2	91.5	85.4	79.6	73.8	67.7
15								95.1	89.1	83.5	78.2	72.8
16								98.4	92.5	87.1	82.0	77.0
17									95.6	90.3	85.4	80.6

TABLE 1–2—LOCATION OF TRAVERSE POINTS IN CIRCULAR STACKS—Continued

[Percent of stack diameter from inside wall to tranverse point]

Traverse point number on a diameter	Number of traverse points on a diameter											
	2	4	6	8	10	12	14	16	18	20	22	24
18									98.6	93.3	88.4	83.9
19										96.1	91.3	86.8
20										98.7	94.0	89.5
21											96.5	92.1
22											98.9	94.5
23												96.8
24												99.9

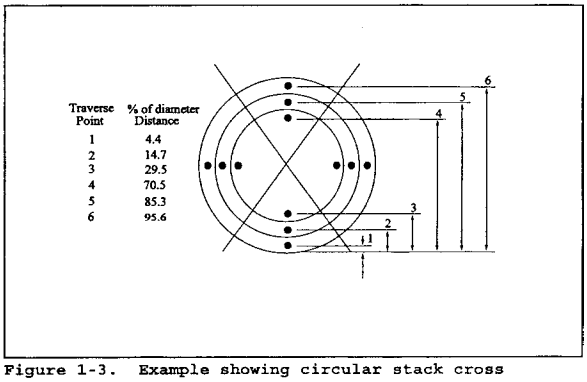

Figure 1-3. Example showing circular stack cross section divided into 12 equal areas, with location of traverse points.

METHOD 1A—SAMPLE AND VELOCITY TRAVERSES FOR STATIONARY SOURCES WITH SMALL STACKS OR DUCTS

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test method: Method 1.

1.0 Scope and Application

1.1 Measured Parameters. The purpose of the method is to provide guidance for the selection of sampling ports and traverse points at which sampling for air pollutants will be performed pursuant to regulations set forth in this part.

1.2 Applicability. The applicability and principle of this method are identical to Method 1, except its applicability is limited to stacks or ducts. This method is applicable to flowing gas streams in ducts, stacks, and flues of less than about 0.30 meter (12 in.) in diameter, or 0.071 m^2 (113 $in.^2$) in cross-sectional area, but equal to or greater than about 0.10 meter (4 in.) in diameter, or 0.0081 m^2 (12.57 $in.^2$) in cross-sectional area. This method cannot be used when the flow is cyclonic or swirling.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 The method is designed to aid in the representative measurement of pollutant emissions and/or total volumetric flow rate from a stationary source. A measurement site or a pair of measurement sites where the effluent stream is flowing in a known direction is (are) selected. The cross-section of the stack is divided into a number of equal areas. Traverse points are then located within each of these equal areas.

2.2 In these small diameter stacks or ducts, the conventional Method 5 stack assembly (consisting of a Type S pitot tube attached to a sampling probe, equipped with a nozzle and thermocouple) blocks a significant portion of the cross-section of the duct and causes inaccurate measurements. Therefore, for particulate matter (PM) sampling in small stacks or ducts, the gas velocity is measured using a standard pitot tube downstream of the actual emission sampling site.

The straight run of duct between the PM sampling and velocity measurement sites allows the flow profile, temporarily disturbed by the presence of the sampling probe, to redevelop and stabilize.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies [Reserved]

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transport [Reserved]

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Procedure

11.1 Selection of Measurement Site.

11.1.1 Particulate Measurements—Steady or Unsteady Flow. Select a particulate measurement site located preferably at least eight equivalent stack or duct diameters downstream and 10 equivalent diameters upstream from any flow disturbances such as bends, expansions, or contractions in the stack, or from a visible flame. Next, locate the velocity measurement site eight equivalent diameters downstream of the particulate measurement site (see Figure 1A–1). If such locations are not available, select an alternative particulate measurement location at least two equivalent stack or duct diameters downstream and two and one-half diameters upstream from any flow disturbance. Then, locate the velocity measurement site two equivalent diameters downstream from the particulate measurement site. (See section 12.2 of Method 1 for calculating equivalent diameters for a rectangular cross-section.)

11.1.2 PM Sampling (Steady Flow) or Velocity (Steady or Unsteady Flow) Measurements. For PM sampling when the volumetric flow rate in a duct is constant with respect to time, section 11.1.1 of Method 1 may be followed, with the PM sampling and velocity measurement performed at one location. To demonstrate that the flow rate is constant (within 10 percent) when PM measurements are made, perform complete velocity traverses before and after the PM sampling run, and calculate the deviation of the flow rate derived after the PM sampling run from the one derived before the PM sampling run. The PM sampling run is acceptable if the deviation does not exceed 10 percent.

11.2 Determining the Number of Traverse Points.

11.2.1 Particulate Measurements (Steady or Unsteady Flow). Use Figure 1–1 of Method 1 to determine the number of traverse points to use at both the velocity measurement and PM sampling locations. Before referring to the figure, however, determine the distances between both the velocity measurement and PM sampling sites to the nearest upstream and downstream disturbances. Then divide each distance by the stack diameter or equivalent diameter to express the distances in terms of the number of duct diameters. Then, determine the number of traverse points from Figure 1–1 of Method 1 corresponding to each of these four distances. Choose the highest of the four numbers of traverse points (or a greater number) so that, for circular ducts the number is a multiple of four; and for rectangular ducts, the number is one of those shown in Table 1–1 of Method 1. When the optimum duct diameter location criteria can be satisfied, the minimum number of traverse points required is eight for circular ducts and nine for rectangular ducts.

11.2.2 PM Sampling (Steady Flow) or only Velocity (Non-Particulate) Measurements. Use Figure 1–2 of Method 1 to determine number of traverse points, following the same procedure used for PM sampling as described in section 11.2.1 of Method 1. When the optimum duct diameter location criteria can be satisfied, the minimum number of traverse points required is eight for circular ducts and nine for rectangular ducts.

11.3 Cross-sectional Layout, Location of Traverse Points, and Verification of the Absence of Cyclonic Flow. Same as Method 1, sections 11.3 and 11.4, respectively.

12.0 Data Analysis and Calculations [Reserved]

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 1, section 16.0, References 1 through 6, with the addition of the following:

1. Vollaro, Robert F. Recommended Procedure for Sample Traverses in Ducts Smaller Than 12 Inches in Diameter. U.S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, North Carolina. January 1977.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

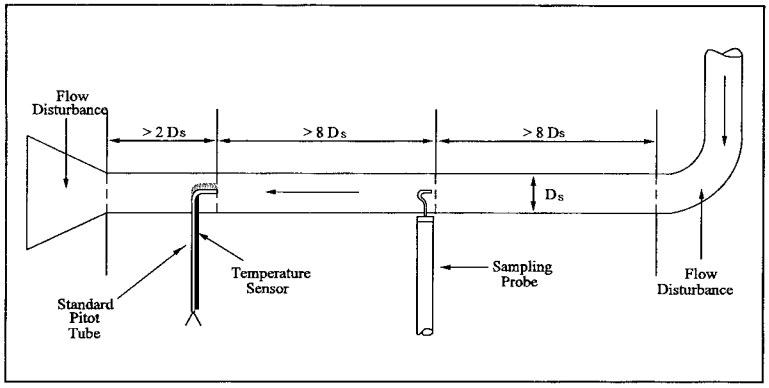

Figure 1A-1. Recommended sampling arrangement for small ducts

METHOD 2—DETERMINATION OF STACK GAS VELOCITY AND VOLUMETRIC FLOW RATE (TYPE S PITOT TUBE)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test method: Method 1.

1.0 Scope and Application.

1.1 This method is applicable for the determination of the average velocity and the volumetric flow rate of a gas stream.

1.2 This method is not applicable at measurement sites that fail to meet the criteria of Method 1, section 11.1. Also, the method cannot be used for direct measurement in cyclonic or swirling gas streams; section 11.4 of Method 1 shows how to determine cyclonic or swirling flow conditions. When unacceptable conditions exist, alternative procedures, subject to the approval of the Administrator, must be employed to produce accurate flow rate determinations. Examples of such alternative procedures are: (1) to install straightening vanes; (2) to calculate the total volumetric flow rate stoichiometrically, or (3) to move to another measurement site at which the flow is acceptable.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method.

2.1 The average gas velocity in a stack is determined from the gas density and from measurement of the average velocity head with a Type S (Stausscheibe or reverse type) pitot tube.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

Specifications for the apparatus are given below. Any other apparatus that has been demonstrated (subject to approval of the Administrator) to be capable of meeting the specifications will be considered acceptable.

6.1 Type S Pitot Tube.

6.1.1 Pitot tube made of metal tubing (*e.g.*, stainless steel) as shown in Figure 2–1. It is recommended that the external tubing diameter (dimension D_t, Figure 2–2b) be between 0.48 and 0.95 cm (3⁄16 and 3⁄8 inch). There shall be an equal distance from the base of each leg of the pitot tube to its face-opening plane (dimensions P_A and P_B, Figure 2–2b); it is recommended that this distance be between 1.05 and 1.50 times the external tubing diameter. The face openings of the pitot tube shall, preferably, be aligned as shown in Figure 2–2; however, slight misalignments of the openings are permissible (see Figure 2–3).

6.1.2 The Type S pitot tube shall have a known coefficient, determined as outlined in section 10.0. An identification number shall be assigned to the pitot tube; this number shall be permanently marked or engraved on

the body of the tube. A standard pitot tube may be used instead of a Type S, provided that it meets the specifications of sections 6.7 and 10.2. Note, however, that the static and impact pressure holes of standard pitot tubes are susceptible to plugging in particulate-laden gas streams. Therefore, whenever a standard pitot tube is used to perform a traverse, adequate proof must be furnished that the openings of the pitot tube have not plugged up during the traverse period. This can be accomplished by comparing the velocity head (Δp) measurement recorded at a selected traverse point (readable Δp value) with a second Δp measurement recorded after ''back purging'' with pressurized air to clean the impact and static holes of the standard pitot tube. If the before and after Δp measurements are within 5 percent, then the traverse data are acceptable. Otherwise, the data should be rejected and the traverse measurements redone. Note that the selected traverse point should be one that demonstrates a readable Δp value. If ''back purging'' at regular intervals is part of a routine procedure, then comparative Δp measurements shall be conducted as above for the last two traverse points that exhibit suitable Δp measurements.

6.2 Differential Pressure Gauge. An inclined manometer or equivalent device. Most sampling trains are equipped with a 10 in. (water column) inclined-vertical manometer, having 0.01 in. H_20 divisions on the 0 to 1 in. inclined scale, and 0.1 in. H_20 divisions on the 1 to 10 in. vertical scale. This type of manometer (or other gauge of equivalent sensitivity) is satisfactory for the measurement of Δp values as low as 1.27 mm (0.05 in.) H_20. However, a differential pressure gauge of greater sensitivity shall be used (subject to the approval of the Administrator), if any of the following is found to be true: (1) the arithmetic average of all Δp readings at the traverse points in the stack is less than 1.27 mm (0.05 in.) H_20; (2) for traverses of 12 or more points, more than 10 percent of the individual Δp readings are below 1.27 mm (0.05 in.) H_20; or (3) for traverses of fewer than 12 points, more than one Δp reading is below 1.27 mm (0.05 in.) H_20. Reference 18 (see section 17.0) describes commercially available instrumentation for the measurement of low-range gas velocities.

6.2.1 As an alternative to criteria (1) through (3) above, Equation 2–1 (Section 12.2) may be used to determine the necessity of using a more sensitive differential pressure gauge. If T is greater than 1.05, the velocity head data are unacceptable and a more sensitive differential pressure gauge must be used.

NOTE: If differential pressure gauges other than inclined manometers are used (*e.g.*, magnehelic gauges), their calibration must be checked after each test series. To check the calibration of a differential pressure gauge, compare Δp readings of the gauge with those of a gauge-oil manometer at a minimum of three points, approximately representing the range of Δp values in the stack. If, at each point, the values of Δp as read by the differential pressure gauge and gauge-oil manometer agree to within 5 percent, the differential pressure gauge shall be considered to be in proper calibration. Otherwise, the test series shall either be voided, or procedures to adjust the measured Δp values and final results shall be used, subject to the approval of the Administrator.

6.3 Temperature Sensor. A thermocouple, liquid-filled bulb thermometer, bimetallic thermometer, mercury-in-glass thermometer, or other gauge capable of measuring temperatures to within 1.5 percent of the minimum absolute stack temperature. The temperature sensor shall be attached to the pitot tube such that the sensor tip does not touch any metal; the gauge shall be in an interference-free arrangement with respect to the pitot tube face openings (see Figure 2–1 and Figure 2–4). Alternative positions may be used if the pitot tube-temperature gauge system is calibrated according to the procedure of section 10.0. Provided that a difference of not more than 1 percent in the average velocity measurement is introduced, the temperature gauge need not be attached to the pitot tube. This alternative is subject to the approval of the Administrator.

6.4 Pressure Probe and Gauge. A piezometer tube and mercury- or water-filled U-tube manometer capable of measuring stack pressure to within 2.5 mm (0.1 in.) Hg. The static tap of a standard type pitot tube or one leg of a Type S pitot tube with the face opening planes positioned parallel to the gas flow may also be used as the pressure probe.

6.5 Barometer. A mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.54 mm (0.1 in.) Hg.

NOTE: The barometric pressure reading may be obtained from a nearby National Weather Service station. In this case, the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be made at a rate of minus 2.5 mm (0.1 in.) Hg per 30 m (100 ft) elevation increase or plus 2.5 mm (0.1 in.) Hg per 30 m (100 ft.) for elevation decrease.

6.6 Gas Density Determination Equipment. Method 3 equipment, if needed (see section 8.6), to determine the stack gas dry molecular weight, and Method 4 (reference method) or Method 5 equipment for moisture content determination. Other methods may be used subject to approval of the Administrator.

6.7 Calibration Pitot Tube. Calibration of the Type S pitot tube requires a standard pitot tube for a reference. When calibration of the Type S pitot tube is necessary (see Section 10.1), a standard pitot tube shall be used for a reference. The standard pitot tube shall, preferably, have a known coefficient, obtained directly from the National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899, (301) 975–2002; or by calibration against another standard pitot tube with a NIST-traceable coefficient. Alternatively, a standard pitot tube designed according to the criteria given in sections 6.7.1 through 6.7.5 below and illustrated in Figure 2–5 (see also References 7, 8, and 17 in section 17.0) may be used. Pitot tubes designed according to these specifications will have baseline coefficients of 0.99 ±0.01.

6.7.1 Standard Pitot Design.

6.7.1.1 Hemispherical (shown in Figure 2–5), ellipsoidal, or conical tip.

6.7.1.2 A minimum of six diameters straight run (based upon D, the external diameter of the tube) between the tip and the static pressure holes.

6.7.1.3 A minimum of eight diameters straight run between the static pressure holes and the centerline of the external tube, following the 90° bend.

6.7.1.4 Static pressure holes of equal size (approximately 0.1 D), equally spaced in a piezometer ring configuration.

6.7.1.5 90° bend, with curved or mitered junction.

6.8 Differential Pressure Gauge for Type S Pitot Tube Calibration. An inclined manometer or equivalent. If the single-velocity calibration technique is employed (see section 10.1.2.3), the calibration differential pressure gauge shall be readable to the nearest 0.127 mm (0.005 in.) H_20. For multivelocity calibrations, the gauge shall be readable to the nearest 0.127 mm (0.005 in.) H_20 for Δp values between 1.27 and 25.4 mm (0.05 and 1.00 in.) H_20, and to the nearest 1.27 mm (0.05 in.) H_20 for Δp values above 25.4 mm (1.00 in.) H_20. A special, more sensitive gauge will be required to read Δp values below 1.27 mm (0.05 in.) H_20 (see Reference 18 in section 16.0).

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection and Analysis

8.1 Set up the apparatus as shown in Figure 2–1. Capillary tubing or surge tanks installed between the manometer and pitot tube may be used to dampen ΔP fluctuations. It is recommended, but not required, that a pretest leak-check be conducted as follows: (1) blow through the pitot impact opening until at least 7.6 cm (3.0 in.) H_2O velocity head registers on the manometer; then, close off the impact opening. The pressure shall remain stable (±2.5 mm H_2O, ±0.10 in. H_2O) for at least 15 seconds; (2) do the same for the static pressure side, except using suction to obtain the minimum of 7.6 cm (3.0 in.) H_2O. Other leak-check procedures, subject to the approval of the Administrator, may be used.

8.2 Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse (at least once per hour). Record all necessary data on a form similar to that shown in Figure 2–6.

8.3 Measure the velocity head and temperature at the traverse points specified by Method 1. Ensure that the proper differential pressure gauge is being used for the range of Δp values encountered (see section 6.2). If it is necessary to change to a more sensitive gauge, do so, and remeasure the Δp and temperature readings at each traverse point. Conduct a post-test leak-check (mandatory), as described in section 8.1 above, to validate the traverse run.

8.4 Measure the static pressure in the stack. One reading is usually adequate.

8.5 Determine the atmospheric pressure.

8.6 Determine the stack gas dry molecular weight. For combustion processes or processes that emit essentially CO_2, O_2, CO, and N_2, use Method 3. For processes emitting essentially air, an analysis need not be conducted; use a dry molecular weight of 29.0. For other processes, other methods, subject to the approval of the Administrator, must be used.

8.7 Obtain the moisture content from Method 4 (reference method, or equivalent) or from Method 5.

8.8 Determine the cross-sectional area of the stack or duct at the sampling location. Whenever possible, physically measure the stack dimensions rather than using blueprints. Do not assume that stack diameters are equal. Measure each diameter distance to verify its dimensions.

9.0 Quality Control

Section	Quality control measure	Effect
10.1–10.4	Sampling equipment calibration	Ensure accurate measurement of stack gas flow rate, sample volume.

10.0 Calibration and Standardization

10.1 Type S Pitot Tube. Before its initial use, carefully examine the Type S pitot tube top, side, and end views to verify that the face openings of the tube are aligned within the specifications illustrated in Figures 2–2

and 2–3. The pitot tube shall not be used if it fails to meet these alignment specifications. After verifying the face opening alignment, measure and record the following dimensions of the pitot tube: (a) the external tubing diameter (dimension D_t, Figure 2–2b); and (b) the base-to-opening plane distances (dimensions P_A and P_B, Figure 2–2b). If D_t is between 0.48 and 0.95 cm 3⁄16 and 3⁄8 in.), and if P_A and P_B are equal and between 1.05 and 1.50 D_t, there are two possible options: (1) the pitot tube may be calibrated according to the procedure outlined in sections 10.1.2 through 10.1.5, or (2) a baseline (isolated tube) coefficient value of 0.84 may be assigned to the pitot tube. Note, however, that if the pitot tube is part of an assembly, calibration may still be required, despite knowledge of the baseline coefficient value (see section 10.1.1). If D_t, P_A, and P_B are outside the specified limits, the pitot tube must be calibrated as outlined in sections 10.1.2 through 10.1.5.

10.1.1 Type S Pitot Tube Assemblies. During sample and velocity traverses, the isolated Type S pitot tube is not always used; in many instances, the pitot tube is used in combination with other source-sampling components (e.g., thermocouple, sampling probe, nozzle) as part of an ''assembly.'' The presence of other sampling components can sometimes affect the baseline value of the Type S pitot tube coefficient (Reference 9 in section 17.0); therefore, an assigned (or otherwise known) baseline coefficient value may or may not be valid for a given assembly. The baseline and assembly coefficient values will be identical only when the relative placement of the components in the assembly is such that aerodynamic interference effects are eliminated. Figures 2–4, 2–7, and 2–8 illustrate interference-free component arrangements for Type S pitot tubes having external tubing diameters between 0.48 and 0.95 cm (3⁄16 and 3⁄8 in.). Type S pitot tube assemblies that fail to meet any or all of the specifications of Figures 2–4, 2–7, and 2-8 shall be calibrated according to the procedure outlined in sections 10.1.2 through 10.1.5, and prior to calibration, the values of the intercomponent spacings (pitot-nozzle, pitot-thermocouple, pitot-probe sheath) shall be measured and recorded.

NOTE: Do not use a Type S pitot tube assembly that is constructed such that the impact pressure opening plane of the pitot tube is below the entry plane of the nozzle (see Figure 2–7B).

10.1.2 Calibration Setup. If the Type S pitot tube is to be calibrated, one leg of the tube shall be permanently marked A, and the other, B. Calibration shall be performed in a flow system having the following essential design features:

10.1.2.1 The flowing gas stream must be confined to a duct of definite cross-sectional area, either circular or rectangular. For circular cross sections, the minimum duct diameter shall be 30.48 cm (12 in.); for rectangular cross sections, the width (shorter side) shall be at least 25.4 cm (10 in.).

10.1.2.2 The cross-sectional area of the calibration duct must be constant over a distance of 10 or more duct diameters. For a rectangular cross section, use an equivalent diameter, calculated according to Equation 2–2 (see section 12.3), to determine the number of duct diameters. To ensure the presence of stable, fully developed flow patterns at the calibration site, or ''test section,'' the site must be located at least eight diameters downstream and two diameters upstream from the nearest disturbances.

NOTE: The eight- and two-diameter criteria are not absolute; other test section locations may be used (subject to approval of the Administrator), provided that the flow at the test site has been demonstrated to be or found stable and parallel to the duct axis.

10.1.2.3 The flow system shall have the capacity to generate a test-section velocity around 910 m/min (3,000 ft/min). This velocity must be constant with time to guarantee constant and steady flow during the entire period of calibration. A centrifugal fan is recommended for this purpose, as no flow rate adjustment for back pressure of the fan is allowed during the calibration process. Note that Type S pitot tube coefficients obtained by single-velocity calibration at 910 m/min (3,000 ft/min) will generally be valid to ±3 percent for the measurement of velocities above 300 m/min (1,000 ft/min) and to ±6 percent for the measurement of velocities between 180 and 300 m/min (600 and 1,000 ft/min). If a more precise correlation between the pitot tube coefficient (Cp) and velocity is desired, the flow system should have the capacity to generate at least four distinct, time-invariant test-section velocities covering the velocity range from 180 to 1,500 m/min (600 to 5,000 ft/min), and calibration data shall be taken at regular velocity intervals over this range (see References 9 and 14 in section 17.0 for details).

10.1.2.4 Two entry ports, one for each of the standard and Type S pitot tubes, shall be cut in the test section. The standard pitot entry port shall be located slightly downstream of the Type S port, so that the standard and Type S impact openings will lie in the same cross-sectional plane during calibration. To facilitate alignment of the pitot tubes during calibration, it is advisable that the test section be constructed of Plexiglas™ or some other transparent material.

10.1.3 Calibration Procedure. Note that this procedure is a general one and must not be used without first referring to the special considerations presented in section 10.1.5. Note also that this procedure applies only to

single-velocity calibration. To obtain calibration data for the A and B sides of the Type S pitot tube, proceed as follows:

10.1.3.1 Make sure that the manometer is properly filled and that the oil is free from contamination and is of the proper density. Inspect and leak-check all pitot lines; repair or replace if necessary.

10.1.3.2 Level and zero the manometer. Switch on the fan, and allow the flow to stabilize. Seal the Type S pitot tube entry port.

10.1.3.3 Ensure that the manometer is level and zeroed. Position the standard pitot tube at the calibration point (determined as outlined in section 10.1.5.1), and align the tube so that its tip is pointed directly into the flow. Particular care should be taken in aligning the tube to avoid yaw and pitch angles. Make sure that the entry port surrounding the tube is properly sealed.

10.1.3.4 Read Δp_{std}, and record its value in a data table similar to the one shown in Figure 2–9. Remove the standard pitot tube from the duct, and disconnect it from the manometer. Seal the standard entry port. Make no adjustment to the fan speed or other wind tunnel volumetric flow control device between this reading and the corresponding Type S pitot reading.

10.1.3.5 Connect the Type S pitot tube to the manometer and leak-check. Open the Type S tube entry port. Check the manometer level and zero. Insert and align the Type S pitot tube so that its A side impact opening is at the same point as was the standard pitot tube and is pointed directly into the flow. Make sure that the entry port surrounding the tube is properly sealed.

10.1.3.6 Read Δp_s, and enter its value in the data table. Remove the Type S pitot tube from the duct, and disconnect it from the manometer.

10.1.3.7 Repeat Steps 10.1.3.3 through 10.1.3.6 until three pairs of Δp readings have been obtained for the A side of the Type S pitot tube, with all the paired observations conducted at a constant fan speed (no changes to fan velocity between observed readings).

10.1.3.8 Repeat Steps 10.1.3.3 through 10.1.3.7 for the B side of the Type S pitot tube.

10.1.3.9 Perform calculations as described in section 12.4. Use the Type S pitot tube only if the values of σ_A and σ_B are less than or equal to 0.01 and if the absolute value of the difference between $\bar{C}_{p(A)}$ and $\bar{C}_{p(B)}$ is 0.01 or less.

10.1.4 Special Considerations.

10.1.4.1 Selection of Calibration Point.

10.1.4.1.1 When an isolated Type S pitot tube is calibrated, select a calibration point at or near the center of the duct, and follow the procedures outlined in section 10.1.3. The Type S pitot coefficients measured or calculated, (*i.e.*, $\bar{C}_{p(A)}$ and $\bar{C}_{p(B)}$) will be valid, so long as either: (1) the isolated pitot tube is used; or (2) the pitot tube is used with other components (nozzle, thermocouple, sample probe) in an arrangement that is free from aerodynamic interference effects (see Figures 2–4, 2–7, and 2–8).

10.1.4.1.2 For Type S pitot tube-thermocouple combinations (without probe assembly), select a calibration point at or near the center of the duct, and follow the procedures outlined in section 10.1.3. The coefficients so obtained will be valid so long as the pitot tube-thermocouple combination is used by itself or with other components in an interference-free arrangement (Figures 2–4, 2–7, and 2–8).

10.1.4.1.3 For Type S pitot tube combinations with complete probe assemblies, the calibration point should be located at or near the center of the duct; however, insertion of a probe sheath into a small duct may cause significant cross-sectional area interference and blockage and yield incorrect coefficient values (Reference 9 in section 17.0). Therefore, to minimize the blockage effect, the calibration point may be a few inches off-center if necessary, but no closer to the outer wall of the wind tunnel than 4 inches. The maximum allowable blockage, as determined by a projected-area model of the probe sheath, is 2 percent or less of the duct cross-sectional area (Figure 2–10a). If the pitot and/or probe assembly blocks more than 2 percent of the cross-sectional area at an insertion point only 4 inches inside the wind tunnel, the diameter of the wind tunnel must be increased.

10.1.4.2 For those probe assemblies in which pitot tube-nozzle interference is a factor (i.e., those in which the pitot-nozzle separation distance fails to meet the specifications illustrated in Figure 2–7A), the value of $C_{p(s)}$ depends upon the amount of free space between the tube and nozzle and, therefore, is a function of nozzle size. In these instances, separate calibrations shall be performed with each of the commonly used nozzle sizes in place. Note that the single-velocity calibration technique is acceptable for this purpose, even though the larger nozzle sizes (>0.635 cm or ¼ in.) are not ordinarily used for isokinetic sampling at velocities around 910 m/min (3,000 ft/min), which is the calibration velocity. Note also that it is not necessary to draw an isokinetic sample during calibration (see Reference 19 in section 17.0).

10.1.4.3 For a probe assembly constructed such that its pitot tube is always used in the same orientation, only one side of the pitot tube needs to be calibrated (the side which will face the flow). The pitot tube must still meet the alignment specifications of Figure 2–2 or 2–3, however, and must have an average deviation (σ) value of 0.01 or less (see section 12.4.4).

10.1.5 Field Use and Recalibration.

10.1.5.1 Field Use.

10.1.5.1.1 When a Type S pitot tube (isolated or in an assembly) is used in the field, the appropriate coefficient value (whether

assigned or obtained by calibration) shall be used to perform velocity calculations. For calibrated Type S pitot tubes, the A side coefficient shall be used when the A side of the tube faces the flow, and the B side coefficient shall be used when the B side faces the flow. Alternatively, the arithmetic average of the A and B side coefficient values may be used, irrespective of which side faces the flow.

10.1.5.1.2 When a probe assembly is used to sample a small duct, 30.5 to 91.4 cm (12 to 36 in.) in diameter, the probe sheath sometimes blocks a significant part of the duct cross-section, causing a reduction in the effective value of $C_{p(s)}$. Consult Reference 9 (see section 17.0) for details. Conventional pitot-sampling probe assemblies are not recommended for use in ducts having inside diameters smaller than 30.5 cm (12 in.) (see Reference 16 in section 17.0).

10.1.5.2 Recalibration.

10.1.5.2.1 Isolated Pitot Tubes. After each field use, the pitot tube shall be carefully re-examined in top, side, and end views. If the pitot face openings are still aligned within the specifications illustrated in Figure 2–2 and Figure 2–3, it can be assumed that the baseline coefficient of the pitot tube has not changed. If, however, the tube has been damaged to the extent that it no longer meets the specifications of Figure 2–2 and Figure 2–3, the damage shall either be repaired to restore proper alignment of the face openings, or the tube shall be discarded.

10.1.5.2.2 Pitot Tube Assemblies. After each field use, check the face opening alignment of the pitot tube, as in section 10.1.5.2.1. Also, remeasure the intercomponent spacings of the assembly. If the intercomponent spacings have not changed and the face opening alignment is acceptable, it can be assumed that the coefficient of the assembly has not changed. If the face opening alignment is no longer within the specifications of Figure 2–2 and Figure 2–3, either repair the damage or replace the pitot tube (calibrating the new assembly, if necessary). If the intercomponent spacings have changed, restore the original spacings, or recalibrate the assembly.

10.2 Standard Pitot Tube (if applicable). If a standard pitot tube is used for the velocity traverse, the tube shall be constructed according to the criteria of section 6.7 and shall be assigned a baseline coefficient value of 0.99. If the standard pitot tube is used as part of an assembly, the tube shall be in an interference-free arrangement (subject to the approval of the Administrator).

10.3 Temperature Sensors.

10.3.1 After each field use, calibrate dial thermometers, liquid-filled bulb thermometers, thermocouple-potentiometer systems, and other sensors at a temperature within 10 percent of the average absolute stack temperature. For temperatures up to 405 °C (761 °F), use an ASTM mercury-in-glass reference thermometer, or equivalent, as a reference. Alternatively, either a reference thermocouple and potentiometer (calibrated against NIST standards) or thermometric fixed points (*e.g.*, ice bath and boiling water, corrected for barometric pressure) may be used. For temperatures above 405 °C (761 °F), use a reference thermocouple-potentiometer system calibrated against NIST standards or an alternative reference, subject to the approval of the Administrator.

10.3.2 The temperature data recorded in the field shall be considered valid. If, during calibration, the absolute temperature measured with the sensor being calibrated and the reference sensor agree within 1.5 percent, the temperature data taken in the field shall be considered valid. Otherwise, the pollutant emission test shall either be considered invalid or adjustments (if appropriate) of the test results shall be made, subject to the approval of the Administrator.

10.4 Barometer. Calibrate the barometer used against a mercury barometer or NIST-traceable barometer prior to each field test.

11.0 Analytical Procedure

Sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature.

A = Cross-sectional area of stack, m^2 (ft^2).

B_{ws} = Water vapor in the gas stream (from Method 4 (reference method) or Method 5), proportion by volume.

C_p = Pitot tube coefficient, dimensionless.

$C_{p(s)}$ = Type S pitot tube coefficient, dimensionless.

$C_{p(std)}$ = Standard pitot tube coefficient; use 0.99 if the coefficient is unknown and the tube is designed according to the criteria of sections 6.7.1 to 6.7.5 of this method.

D_e = Equivalent diameter.

K = 0.127 mm H_2O (metric units). 0.005 in. H_2O (English units).

K_p = Velocity equation constant.

L = Length.

M_d = Molecular weight of stack gas, dry basis (see section 8.6), g/g-mole (lb/lb-mole).

M_s = Molecular weight of stack gas, wet basis, g/g-mole (lb/lb-mole).

n = Total number of traverse points.

P_{bar} = Barometric pressure at measurement site, mm Hg (in. Hg).

P_g = Stack static pressure, mm Hg (in. Hg).

P_s = Absolute stack pressure ($P_{bar} + P_g$), mm Hg (in. Hg),

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

Q_{sd} = Dry volumetric stack gas flow rate corrected to standard conditions, dscm/hr (dscf/hr).
T = Sensitivity factor for differential pressure gauges.
$T_{s(abavg)}$ = Average absolute stack temperature, °K (°R).
= 273 + T_s for metric units,
= 460 + T_s for English units.
T_s = Stack temperature, °C (°F).
= 273 + T_s for metric units,
= 460 + T_s for English units.
T_{std} = Standard absolute temperature, 293 °K (528 °R).
V_s = Average stack gas velocity, m/sec (ft/sec).
W = Width.
Δp = Velocity head of stack gas, mm H_2O (in. H_{20}).
Δp_i = Individual velocity head reading at traverse point ''i'', mm (in.) H_2O.
Δp_{std} = Velocity head measured by the standard pitot tube, cm (in.) H_2O.
Δp_s = Velocity head measured by the Type S pitot tube, cm (in.) H_2O.
3600 = Conversion Factor, sec/hr.
18.0 = Molecular weight of water, g/g-mole (lb/lb-mole).

12.2 Calculate T as follows:

$$T = \frac{\sum_{i=1}^{n} \sqrt{\Delta p_i + K}}{\sum_{i=1}^{n} \sqrt{\Delta p_i}} \qquad \text{Eq. 2-1}$$

12.3 Calculate D_e as follows:

$$D_e = \frac{2LW}{L+W} \qquad \text{Eq. 2-2}$$

12.4 Calibration of Type S Pitot Tube.

12.4.1 For each of the six pairs of Δp readings (i.e., three from side A and three from side B) obtained in section 10.1.3, calculate the value of the Type S pitot tube coefficient according to Equation 2–3:

$$C_{p(s)} = C_{p(std)} \sqrt{\frac{\Delta p_{std}}{\Delta p}} \qquad \text{Eq. 2-3}$$

12.4.2 Calculate $\bar{C}_{p(A)}$, the mean A-side coefficient, and $\bar{C}_{p(B)}$, the mean B-side coefficient. Calculate the difference between these two average values.

12.4.3 Calculate the deviation of each of the three A-side values of $C_{p(s)}$ from $\bar{C}_{p(A)}$, and the deviation of each of the three B-side values of $C_{p(s)}$ from $\bar{C}_{p(B)}$, using Equation 2–4:

$$\text{Deviation} = C_{p(s)} - \overline{C}_{p(A \text{ or } B)} \qquad \text{Eq. 2-4}$$

12.4.4 Calculate σ the average deviation from the mean, for both the A and B sides of the pitot tube. Use Equation 2–5:

$$\sigma_{A \text{ or } B} = \frac{\sum_{i=1}^{3} \left| C_{p(s)} - \overline{C}_{p(A \text{ or } B)} \right|}{3} \qquad \text{Eq. 2-5}$$

12.5 Molecular Weight of Stack Gas.

$$M_s = M_d\left(1 - B_{ws}\right) + 18.0\ B_{ws} \qquad \text{Eq. 2-6}$$

12.6 Average Stack Gas Velocity.

$$V_s = K_p\, C_p \left[\frac{\sum_{i=1}^{n}\sqrt{\Delta p_i}}{n}\right]\sqrt{\frac{T_{s(abavg)}}{P_s\ M_s}} \qquad \text{Eq. 2-7}$$

Where:

$$K_p = 34.97\,\frac{m}{\sec}\left[\frac{(g/g-mole)(mm\ Hg)}{(^oK)(mm\ H_2O)}\right]^{1/2} \qquad Metric$$

$$= 85.49\,\frac{ft}{\sec}\left[\frac{(lb/lb-mole)(in.\ Hg)}{(^oR)(in.\ H_2O)}\right]^{1/2} \qquad English$$

12.7 Average Stack Gas Dry Volumetric Flow Rate.

$$Q = 3600(1 - B_{ws})v_s A\left[\frac{T_{std}P_s}{T_{s(abavg)}P_{std}}\right] \qquad Eq.2-8$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

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11. Vollaro, R.F. The Effects of Impact Opening Misalignment on the Value of the Type S Pitot Tube Coefficient. U.S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, NC. October 1976.

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of Determining Type S Pitot Tube Coefficients. U.S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, NC. August 1975.

14. Vollaro, R.F. The Use of Type S Pitot Tubes for the Measurement of Low Velocities. U.S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, NC. November 1976.

15. Smith, Marvin L. Velocity Calibration of EPA Type Source Sampling Probe. United Technologies Corporation, Pratt and Whitney Aircraft Division, East Hartford, CT. 1975.

16. Vollaro, R.F. Recommended Procedure for Sample Traverses in Ducts Smaller than 12 Inches in Diameter. U.S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, NC. November 1976.

17. Ower, E. and R.C. Pankhurst. The Measurement of Air Flow, 4th Ed. London, Pergamon Press. 1966.

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19. Gnyp, A.W., et al. An Experimental Investigation of the Effect of Pitot Tube-Sampling Probe Configurations on the Magnitude of the S Type Pitot Tube Coefficient for Commercially Available Source Sampling Probes. Prepared by the University of Windsor for the Ministry of the Environment, Toronto, Canada. February 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

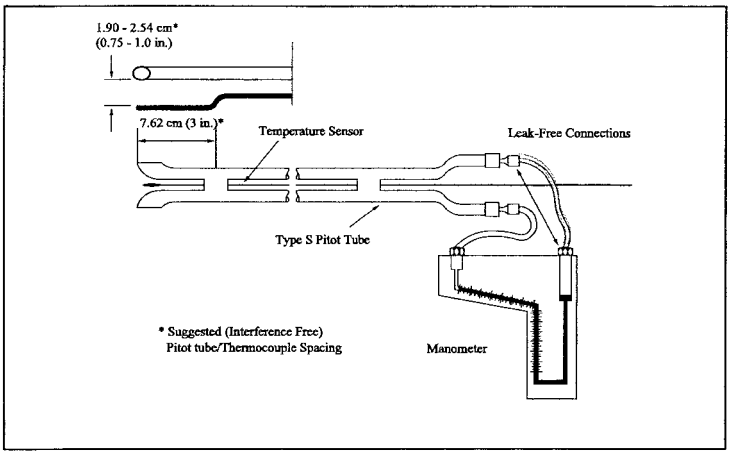

Figure 2-1. Type S Pitot Tube Manometer Assembly.

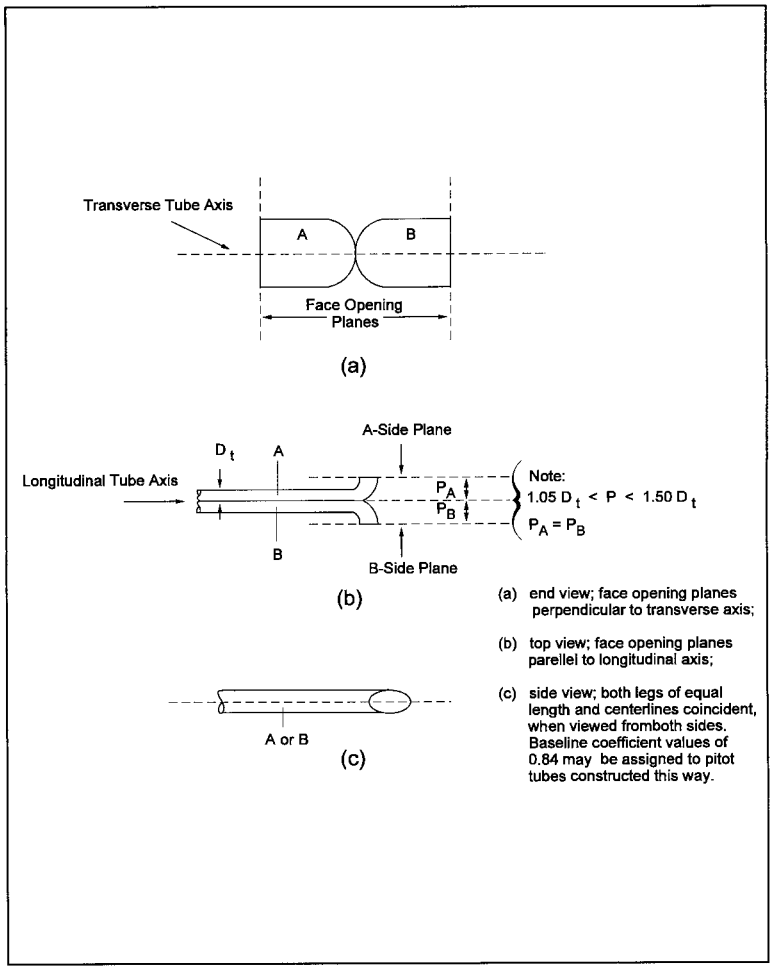

Figure 2-2. Properly Constructed Type S Pitot Tube.

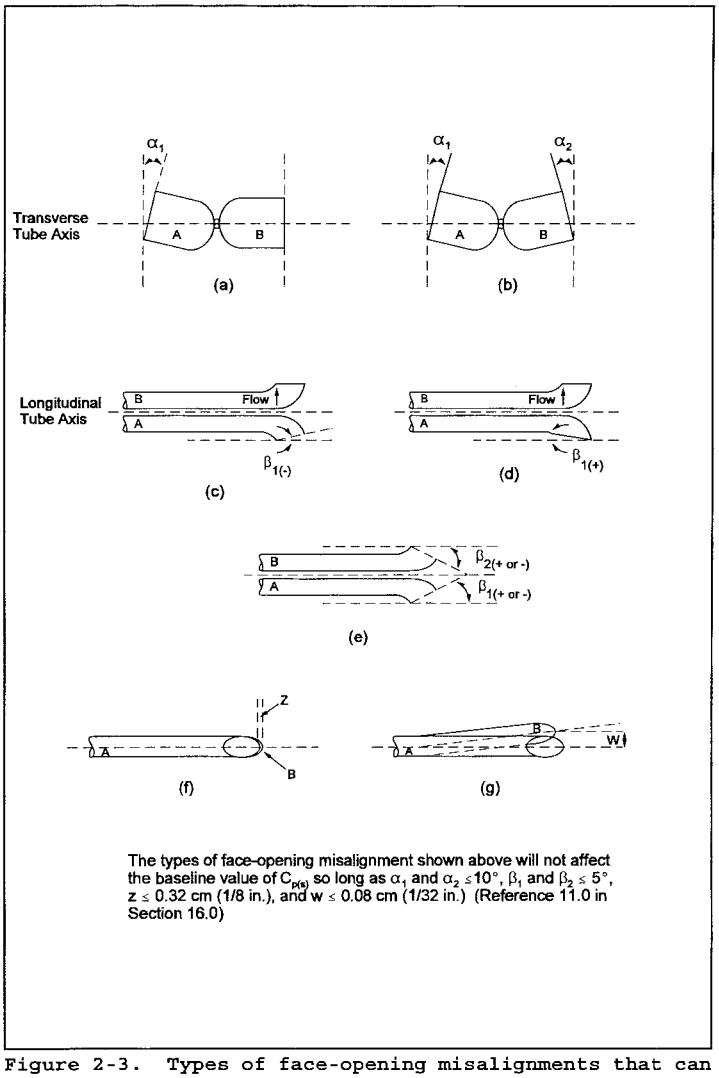

Figure 2-3. Types of face-opening misalignments that can result from field use or improper construction of type S pitot tubes.

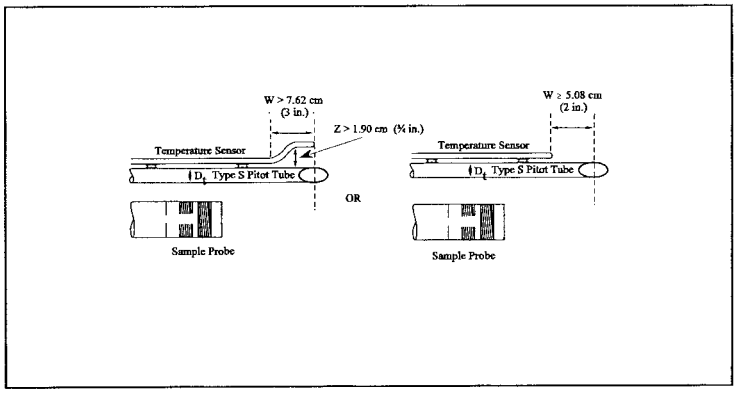

Figure 2-4. Proper temperature sensor placement to prevent interference; D_t between 0.48 and 0.95 cm (3/16 and 3/8 in).

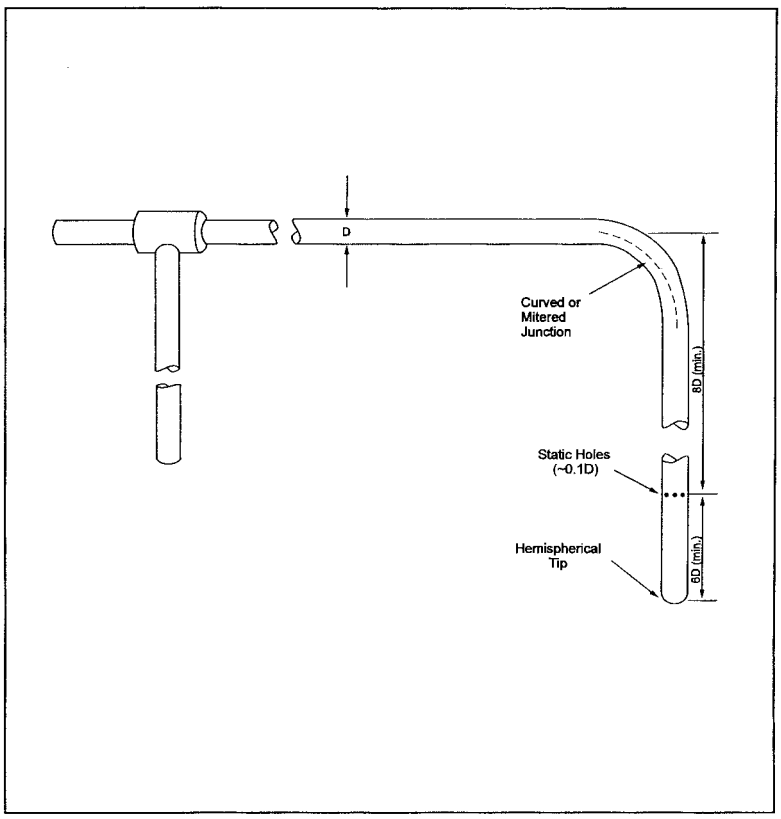

Figure 2-5. Standard pitot tube design specifications.

PLANT _____ DATE _____

RUN NO. _____ OPERATORS _____
STACK DIA. OR DIMENSIONS, m (in.) _____ PITOT TUBE I.D. NO. _____
BAROMETRIC PRESS., mm Hg (in. Hg) _____ AVG. COEFFICIENT, Cp = _____
CROSS SECTIONAL AREA, m^2 (ft^2) _____ LAST DATE CALIBRATED _____

SCHEMATIC OF STACK CROSS SECTION

Traverse Pt. No.	Vel. Hd., Δp mm (in.) H_2O	Stack temperature		P_g mm Hg (in. Hg)	$(\Delta p)^{1/2}$
		T_s, °C (°F)	T_s, °K (°R)		
	Average(1)				

Figure 2–6. Velocity Traverse Data

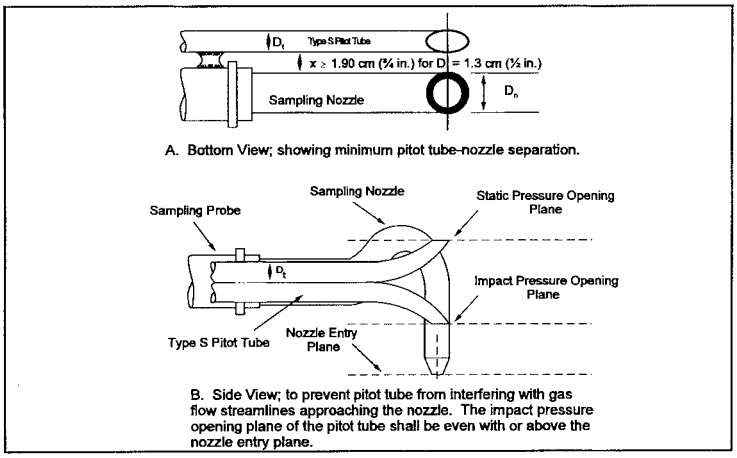

Figure 2-7. Proper pitot tube-sampling nozzle configuration.

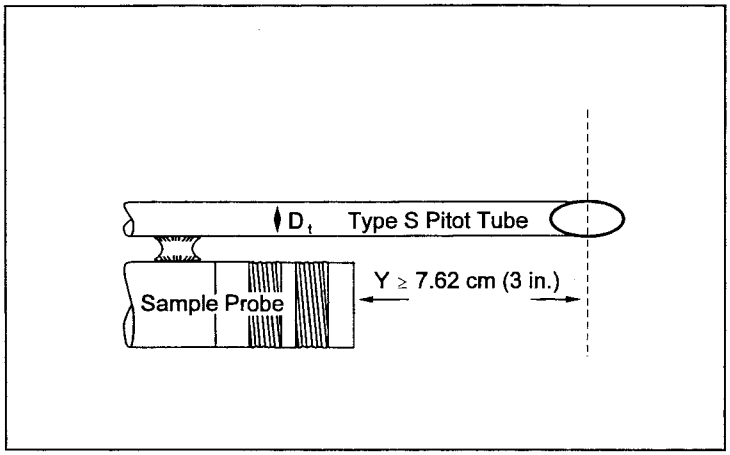

Figure 2-8. Minimum pitot-sample probe separation needed to prevent interference; D_t between 0.48 and 0.95 cm (3/16 and 3/8 in).

PITOT TUBE IDENTIFICATION NUMBER: CALIBRATED BY: _____
DATE: _____

"A" SIDE CALIBRATION

Run No.	ΔP_{std} cm H_2O (in H_2O)	$\Delta P_{(s)}$ cm H_2O (in H_2O)	$C_{p(s)}$	Deviation $C_{p(s)}$—C_p(A)
1				
2				
3				

"A" SIDE CALIBRATION—Continued

Run No.	ΔP_{std} cm H_2O (in H_2O)	$\Delta P_{(s)}$ cm H_2O (in H_2O)	$C_{p(s)}$	Deviation $C_{p(s)}$—C_p(A)
		$C_{p,\ avg}$ (SIDE A)		

"B" SIDE CALIBRATION

Run No.	ΔP_{std} cm H_2O (in H_2O)	$\Delta P_{(s)}$ cm H_2O (in H_2O)	$C_{p(s)}$	Deviation $C_{p(s)}$—C_p(B)
1				
2				
3				
		$C_{p,\ avg}$ (SIDE B)		

$$\sigma_{A\ or\ B} = \frac{\sum_{i=1}^{3}\left|C_{p(s)} - \overline{C}_{p\ (A\ or\ B)}\right|}{3} \qquad \text{Eq. 2-5}$$

[Cp, avg (side A)—Cp, avg (side B)]*
*Must be less than or equal to 0.01

Figure 2–9. Pitot Tube Calibration Data

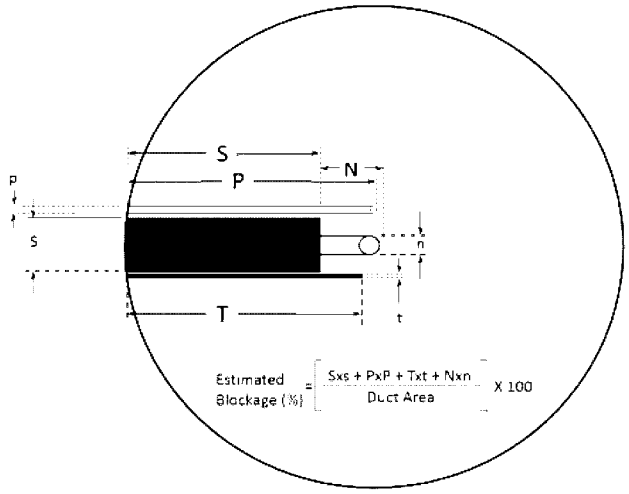

Figure 2-10. Projected-area model for a typical pitot tube assembly.

METHOD 2A—DIRECT MEASUREMENT OF GAS VOLUME THROUGH PIPES AND SMALL DUCTS

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have

a thorough knowledge of at least the following additional test methods: Method 1, Method 2.

1.0 Scope and Application

1.1 This method is applicable for the determination of gas flow rates in pipes and small ducts, either in-line or at exhaust positions, within the temperature range of 0 to 50 °C (32 to 122 °F).

1.2 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas volume meter is used to measure gas volume directly. Temperature and pressure measurements are made to allow correction of the volume to standard conditions.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

Specifications for the apparatus are given below. Any other apparatus that has been demonstrated (subject to approval of the Administrator) to be capable of meeting the specifications will be considered acceptable.

6.1 Gas Volume Meter. A positive displacement meter, turbine meter, or other direct measuring device capable of measuring volume to within 2 percent. The meter shall be equipped with a temperature sensor (accurate to within ±2 percent of the minimum absolute temperature) and a pressure gauge (accurate to within ±2.5 mm Hg). The manufacturer's recommended capacity of the meter shall be sufficient for the expected maximum and minimum flow rates for the sampling conditions. Temperature, pressure, corrosive characteristics, and pipe size are factors necessary to consider in selecting a suitable gas meter.

6.2 Barometer. A mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within ±2.5 mm Hg.

NOTE: In many cases, the barometric reading may be obtained from a nearby National Weather Service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm (0.1 in.) Hg per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

6.3 Stopwatch. Capable of measurement to within 1 second.

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection and Analysis

8.1 Installation. As there are numerous types of pipes and small ducts that may be subject to volume measurement, it would be difficult to describe all possible installation schemes. In general, flange fittings should be used for all connections wherever possible. Gaskets or other seal materials should be used to assure leak-tight connections. The volume meter should be located so as to avoid severe vibrations and other factors that may affect the meter calibration.

8.2 Leak Test.

8.2.1 A volume meter installed at a location under positive pressure may be leak-checked at the meter connections by using a liquid leak detector solution containing a surfactant. Apply a small amount of the solution to the connections. If a leak exists, bubbles will form, and the leak must be corrected.

8.2.2 A volume meter installed at a location under negative pressure is very difficult to test for leaks without blocking flow at the inlet of the line and watching for meter movement. If this procedure is not possible, visually check all connections to assure leak-tight seals.

8.3 Volume Measurement.

8.3.1 For sources with continuous, steady emission flow rates, record the initial meter volume reading, meter temperature(s), meter pressure, and start the stopwatch. Throughout the test period, record the meter temperatures and pressures so that average values can be determined. At the end of the test, stop the timer, and record the elapsed time, the final volume reading, meter temperature, and pressure. Record the barometric pressure at the beginning and end of the test run. Record the data on a table similar to that shown in Figure 2A–1.

8.3.2 For sources with noncontinuous, nonsteady emission flow rates, use the procedure in section 8.3.1 with the addition of the following: Record all the meter parameters and the start and stop times corresponding to each process cyclical or noncontinuous event.

9.0 Quality Control

Section	Quality control measure	Effect
10.1–10.4	Sampling equipment calibration	Ensure accurate measurement of stack gas flow rate, sample volume.

10.0 Calibration and Standardization

10.1 Volume Meter.

10.1.1 The volume meter is calibrated against a standard reference meter prior to its initial use in the field. The reference meter is a spirometer or liquid displacement meter with a capacity consistent with that of the test meter.

10.1.2 Alternatively, a calibrated, standard pitot may be used as the reference meter in conjunction with a wind tunnel assembly. Attach the test meter to the wind tunnel so that the total flow passes through the test meter. For each calibration run, conduct a 4-point traverse along one stack diameter at a position at least eight diameters of straight tunnel downstream and two diameters upstream of any bend, inlet, or air mover. Determine the traverse point locations as specified in Method 1. Calculate the reference volume using the velocity values following the procedure in Method 2, the wind tunnel cross-sectional area, and the run time.

10.1.3 Set up the test meter in a configuration similar to that used in the field installation (*i.e.*, in relation to the flow moving device). Connect the temperature sensor and pressure gauge as they are to be used in the field. Connect the reference meter at the inlet of the flow line, if appropriate for the meter, and begin gas flow through the system to condition the meters. During this conditioning operation, check the system for leaks.

10.1.4 The calibration shall be performed during at least three different flow rates. The calibration flow rates shall be about 0.3, 0.6, and 0.9 times the rated maximum flow rate of the test meter.

10.1.5 For each calibration run, the data to be collected include: reference meter initial and final volume readings, the test meter initial and final volume reading, meter average temperature and pressure, barometric pressure, and run time. Repeat the runs at each flow rate at least three times.

10.1.6 Calculate the test meter calibration coefficient as indicated in section 12.2.

10.1.7 Compare the three Y_m values at each of the flow rates tested and determine the maximum and minimum values. The difference between the maximum and minimum values at each flow rate should be no greater than 0.030. Extra runs may be required to complete this requirement. If this specification cannot be met in six successive runs, the test meter is not suitable for use. In addition, the meter coefficients should be between 0.95 and 1.05. If these specifications are met at all the flow rates, average all the Y_m values from runs meeting the specifications to obtain an average meter calibration coefficient, Y_m.

10.1.8 The procedure above shall be performed at least once for each volume meter. Thereafter, an abbreviated calibration check shall be completed following each field test. The calibration of the volume meter shall be checked with the meter pressure set at the average value encountered during the field test. Three calibration checks (runs) shall be performed using this average flow rate value. Calculate the average value of the calibration factor. If the calibration has changed by more than 5 percent, recalibrate the meter over the full range of flow as described above.

NOTE: If the volume meter calibration coefficient values obtained before and after a test series differ by more than 5 percent, the test series shall either be voided, or calculations for the test series shall be performed using whichever meter coefficient value (*i.e.*, before or after) gives the greater value of pollutant emission rate.

10.2 Temperature Sensor. After each test series, check the temperature sensor at ambient temperature. Use an American Society for Testing and Materials (ASTM) mercury-in-glass reference thermometer, or equivalent, as a reference. If the sensor being checked agrees within 2 percent (absolute temperature) of the reference, the temperature data collected in the field shall be considered valid. Otherwise, the test data shall be considered invalid or adjustments of the results shall be made, subject to the approval of the Administrator.

10.3 Barometer. Calibrate the barometer used against a mercury barometer or NIST-traceable barometer prior to the field test.

11.0 Analytical Procedure

Sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature.

f = Final reading.
i = Initial reading.
P_{bar} = Barometric pressure, mm Hg.
P_g = Average static pressure in volume meter, mm Hg.
Q_s = Gas flow rate, m^3/min, standard conditions.

s = Standard conditions, 20 °C and 760 mm Hg.
T_r = Reference meter average temperature, °K (°R).
T_m = Test meter average temperature, °K (°R).
V_r = Reference meter volume reading, m^3.
V_m = Test meter volume reading, m^3.
Y_m = Test meter calibration coefficient, dimensionless.
θ = Elapsed test period time, min.

12.2 Test Meter Calibration Coefficient.

$$Y_m = \frac{\left(V_{rf} - V_{ri}\right) P_b \, T_{m(abs)}}{\left(V_{mf} - V_{mi}\right)\left(P_b + P_g\right) T_{r(abs)}} \qquad \text{Eq. 2A-1}$$

12.3 Volume.

$$Y_{m_s} = Y_m \left[\frac{\left(P_{bar} + P_g\right)\left(V_{m_f} - V_{m_i}\right)(293\,°K)}{\left(T_m\right)(760\ mmHg)} \right] \qquad \text{Eq. 2-2}$$

12.4 Gas Flow Rate.

$$Q_s = \frac{V_{m_s}}{\theta} \qquad \text{Eq. 2A-3}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Rom, Jerome J. Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. APTD–0576. March 1972.

2. Wortman, Martin, R. Vollaro, and P.R. Westlin. Dry Gas Volume Meter Calibrations. Source Evaluation Society Newsletter. Vol. 2, No. 2. May 1977.

3. Westlin, P.R., and R.T. Shigehara. Procedure for Calibrating and Using Dry Gas Volume Meters as Calibration Standards. Source Evaluation Society Newsletter. Vol. 3, No. 1. February 1978.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

Method 2B—Determination of Exhaust Gas Volume Flow Rate From Gasoline Vapor Incinerators

Note: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should also have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 2A, Method 10, Method 25A, Method 25B.

1.0 Scope and Application

1.1 This method is applicable for the determination of exhaust volume flow rate from incinerators that process gasoline vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). It is assumed that the amount of auxiliary fuel is negligible.

1.2 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Organic carbon concentration and volume flow rate are measured at the incinerator inlet using either Method 25A or Method 25B and Method 2A, respectively. Organic carbon, carbon dioxide (CO_2), and carbon monoxide (CO) concentrations are measured at the outlet using either Method 25A or Method 25B and Method 10, respectively. The ratio of total carbon at the incinerator inlet and outlet is multiplied by the inlet volume to determine the exhaust volume flow rate.

3.0 Definitions

Same as section 3.0 of Method 10 and Method 25A.

4.0 Interferences

Same as section 4.0 of Method 10.

5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

Same as section 6.0 of Method 2A, Method 10, and Method 25A and/or Method 25B as applicable, with the addition of the following:

6.1 This analyzer must meet the specifications set forth in section 6.1.2 of Method 10, except that the span shall be 15 percent CO_2 by volume.

7.0 Reagents and Standards

Same as section 7.0 of Method 10 and Method 25A, with the following addition and exceptions:

7.1 Carbon Dioxide Analyzer Calibration. CO_2 gases meeting the specifications set forth in section 7 of Method 6C are required.

7.2 Hydrocarbon Analyzer Calibration. Methane shall not be used as a calibration gas when performing this method.

7.3 Fuel Gas. If Method 25B is used to measure the organic carbon concentrations at both the inlet and exhaust, no fuel gas is required.

8.0 Sample Collection and Analysis

8.1 Pre-test Procedures. Perform all pretest procedures (*e.g.*, system performance checks, leak checks) necessary to determine gas volume flow rate and organic carbon concentration in the vapor line to the incinerator inlet and to determine organic carbon, carbon monoxide, and carbon dioxide concentrations at the incinerator exhaust, as outlined in Method 2A, Method 10, and Method 25A and/or Method 25B as applicable.

8.2 Sampling. At the beginning of the test period, record the initial parameters for the inlet volume meter according to the procedures in Method 2A and mark all of the recorder strip charts to indicate the start of the test. Conduct sampling and analysis as outlined in Method 2A, Method 10, and Method 25A and/or Method 25B as applicable. Continue recording inlet organic and exhaust CO_2, CO, and organic concentrations throughout the test. During periods of process interruption and halting of gas flow, stop the timer and mark the recorder strip charts so that data from this interruption are not included in the calculations. At the end of the test period, record the final parameters for the inlet volume meter and mark the end on all of the recorder strip charts.

8.3 Post-test Procedures. Perform all post-test procedures (*e.g.*, drift tests, leak checks), as outlined in Method 2A, Method 10, and Method 25A and/or Method 25B as applicable.

9.0 Quality Control

Same as section 9.0 of Method 2A, Method 10, and Method 25A.

10.0 Calibration and Standardization

Same as section 10.0 of Method 2A, Method 10, and Method 25A.

NOTE: If a manifold system is used for the exhaust analyzers, all the analyzers and sample pumps must be operating when the analyzer calibrations are performed.

10.1 If an analyzer output does not meet the specifications of the method, invalidate the test data for the period. Alternatively, calculate the exhaust volume results using initial calibration data and using final calibration data and report both resulting volumes. Then, for emissions calculations, use the volume measurement resulting in the greatest emission rate or concentration.

11.0 Analytical Procedure

Sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Data Analysis and Calculations

Carry out the calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation.

12.1 Nomenclature.

CO_e = Mean carbon monoxide concentration in system exhaust, ppm.
$(CO_2)_a$ = Ambient carbon dioxide concentration, ppm (if not measured during the test period, may be assumed to equal 380 ppm).
$(CO_2)_e$ = Mean carbon dioxide concentration in system exhaust, ppm.
HC_e = Mean organic concentration in system exhaust as defined by the calibration gas, ppm.
Hc_i = Mean organic concentration in system inlet as defined by the calibration gas, ppm.
K_e = Hydrocarbon calibration gas factor for the exhaust hydrocarbon analyzer, unitless [equal to the number of carbon atoms per molecule of the gas used to calibrate the analyzer (2 for ethane, 3 for propane, etc.)].
K_i = Hydrocarbon calibration gas factor for the inlet hydrocarbon analyzer, unitless.
V_{es} = Exhaust gas volume, m^3.
V_{is} = Inlet gas volume, m^3.
Q_{es} = Exhaust gas volume flow rate, m^3/min.
Q_{is} = Inlet gas volume flow rate, m^3/min.
θ = Sample run time, min.
S = Standard conditions: 20 °C, 760 mm Hg.

12.2 Concentrations. Determine mean concentrations of inlet organics, outlet CO_2,

outlet CO, and outlet organics according to the procedures in the respective methods and the analyzers' calibration curves, and for the time intervals specified in the applicable regulations.

12.3 Exhaust Gas Volume. Calculate the exhaust gas volume as follows:

$$V_{es} = V_{is}\frac{K_i(HC_i)}{K_e(HC_e)+\left[(CO_2)_e-(CO_2)_a\right]+CO_e} \qquad \text{Eq. 2B-1}$$

12.4 Exhaust Gas Volume Flow Rate. Calculate the exhaust gas volume flow rate as follows:

$$Q_{es} = \frac{V_{es}}{\Theta} \qquad \text{Eq. 2B-2}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as section 16.0 of Method 2A, Method 10, and Method 25A.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

Method 2C—Determination of Gas Velocity and Volumetric Flow Rate in Small Stacks or Ducts (Standard Pitot Tube)

NOTE: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should also have a thorough knowledge of at least the following additional test methods: Method 1, Method 2.

1.0 Scope and Application

1.1 This method is applicable for the determination of average velocity and volumetric flow rate of gas streams in small stacks or ducts. Limits on the applicability of this method are identical to those set forth in Method 2, section 1.0, except that this method is limited to stationary source stacks or ducts less than about 0.30 meter (12 in.) in diameter, or 0.071 m^2 (113 $in.^2$) in cross-sectional area, but equal to or greater than about 0.10 meter (4 in.) in diameter, or 0.0081 m^2 (12.57 $in.^2$) in cross-sectional area.

1.2 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 The average gas velocity in a stack or duct is determined from the gas density and from measurement of velocity heads with a standard pitot tube.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

Same as Method 2, section 6.0, with the exception of the following:

6.1 Standard Pitot Tube (instead of Type S). A standard pitot tube which meets the specifications of section 6.7 of Method 2. Use a coefficient of 0.99 unless it is calibrated against another standard pitot tube with a NIST-traceable coefficient (see section 10.2 of Method 2).

6.2 Alternative Pitot Tube. A modified hemispherical-nosed pitot tube (see Figure 2C–1), which features a shortened stem and enlarged impact and static pressure holes. Use a coefficient of 0.99 unless it is calibrated as mentioned in section 6.1 above. This pitot tube is useful in particulate liquid droplet-laden gas streams when a ''back purge'' is ineffective.

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection and Analysis

8.1 Follow the general procedures in section 8.0 of Method 2, except conduct the measurements at the traverse points specified in Method 1A. The static and impact pressure holes of standard pitot tubes are susceptible to plugging in particulate-laden gas streams. Therefore, adequate proof that the openings of the pitot tube have not plugged during the traverse period must be

furnished; this can be done by taking the velocity head (Δp) heading at the final traverse point, cleaning out the impact and static holes of the standard pitot tube by ''back-purging'' with pressurized air, and then taking another Δp reading. If the Δp readings made before and after the air purge are the same (within ±5 percent) the traverse is acceptable. Otherwise, reject the run. Note that if the Δp at the final traverse point is unsuitably low, another point may be selected. If ''back purging'' at regular intervals is part of the procedure, then take comparative Δp readings, as above, for the last two back purges at which suitably high Δp readings are observed.

9.0 Quality Control

Section	Quality control measure	Effect
10.0	Sampling equipment calibration	Ensure accurate measurement of stack gas velocity head.

10.0 Calibration and Standardization

Same as Method 2, sections 10.2 through 10.4.

11.0 Analytical Procedure

Sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Calculations and Data Analysis

Same as Method 2, section 12.0.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 2, section 16.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

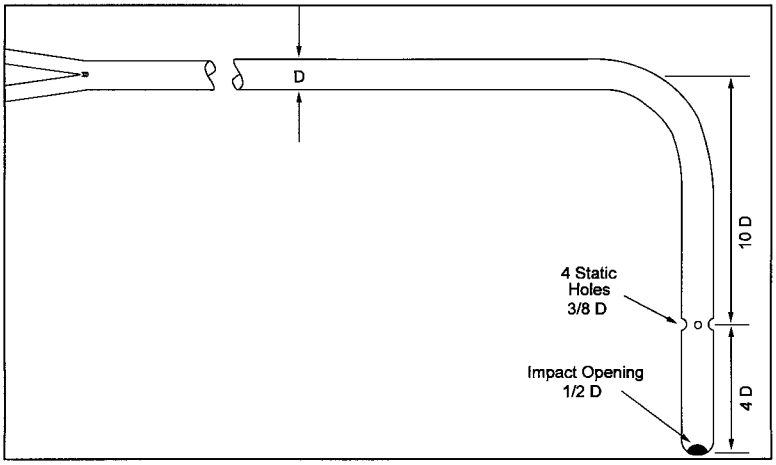

Figure 2C-1. Modified Hemispherical-Nosed Pitot Tube.

METHOD 2D—MEASUREMENT OF GAS VOLUME FLOW RATES IN SMALL PIPES AND DUCTS

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (e.g., sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should also have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, and Method 2A.

1.0 Scope and Application

1.1 This method is applicable for the determination of the volumetric flow rates of gas streams in small pipes and ducts. It can be applied to intermittent or variable gas flows only with particular caution.

1.2 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 All the gas flow in the pipe or duct is directed through a rotameter, orifice plate or similar device to measure flow rate or pressure drop. The device has been previously calibrated in a manner that insures its proper calibration for the gas being measured. Absolute temperature and pressure measurements are made to allow correction of volumetric flow rates to standard conditions.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

Specifications for the apparatus are given below. Any other apparatus that has been demonstrated (subject to approval of the Administrator) to be capable of meeting the specifications will be considered acceptable.

6.1 Gas Metering Rate or Flow Element Device. A rotameter, orifice plate, or other volume rate or pressure drop measuring device capable of measuring the stack flow rate to within ±5 percent. The metering device shall be equipped with a temperature gauge accurate to within ±2 percent of the minimum absolute stack temperature and a pressure gauge (accurate to within ±5 mm Hg). The capacity of the metering device shall be sufficient for the expected maximum and minimum flow rates at the stack gas conditions. The magnitude and variability of stack gas flow rate, molecular weight, temperature, pressure, dewpoint, and corrosive characteristics, and pipe or duct size are factors to consider in choosing a suitable metering device.

6.2 Barometer. Same as Method 2, section 6.5.

6.3 Stopwatch. Capable of measurement to within 1 second.

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection and Analysis

8.1 Installation and Leak Check. Same as Method 2A, sections 8.1 and 8.2, respectively.

8.2 Volume Rate Measurement.

8.2.1 Continuous, Steady Flow. At least once an hour, record the metering device flow rate or pressure drop reading, and the metering device temperature and pressure. Make a minimum of 12 equally spaced readings of each parameter during the test period. Record the barometric pressure at the beginning and end of the test period. Record the data on a table similar to that shown in Figure 2D–1.

8.2.2 Noncontinuous and Nonsteady Flow. Use volume rate devices with particular caution. Calibration will be affected by variation in stack gas temperature, pressure and molecular weight. Use the procedure in section 8.2.1 with the addition of the following: Record all the metering device parameters on a time interval frequency sufficient to adequately profile each process cyclical or noncontinuous event. A multichannel continuous recorder may be used.

9.0 Quality Control

Section	Quality control measure	Effect
10.0	Sampling equipment calibration	Ensure accurate measurement of stack gas flow rate or sample volume.

10.0 Calibration and Standardization

Same as Method 2A, section 10.0, with the following exception:

10.1 Gas Metering Device. Same as Method 2A, section 10.1, except calibrate the metering device with the principle stack gas to be measured (examples: air, nitrogen) against a standard reference meter. A calibrated dry gas meter is an acceptable reference meter. Ideally, calibrate the metering device in the field with the actual gas to be metered. For metering devices that have a volume rate readout, calculate the test metering device calibration coefficient, Y_m, for each run shown in Equation 2D–2 section 12.3.

10.2 For metering devices that do not have a volume rate readout, refer to the manufacturer's instructions to calculate the V_{m2} corresponding to each V_r.

10.3 Temperature Gauge. Use the procedure and specifications in Method 2A, section 10.2. Perform the calibration at a temperature that approximates field test conditions.

10.4 Barometer. Calibrate the barometer used against a mercury barometer or NIST-traceable barometer prior to the field test.

11.0 Analytical Procedure.

Sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Data Analysis and Calculations

12.1 Nomenclature.

P_{bar} = Barometric pressure, mm Hg (in. Hg).
P_m = Test meter average static pressure, mm Hg (in. Hg).
Q_r = Reference meter volume flow rate reading, m^3/min (ft^3/min).
Q_m = Test meter volume flow rate reading, m^3/min (ft^3/min).
T_r = Absolute reference meter average temperature, °K (°R).
T_m = Absolute test meter average temperature, °K (°R).
K_1 = 0.3855 °K/mm Hg for metric units, = 17.65 °R/in. Hg for English units.

12.2 Gas Flow Rate.

$$Q_s = K_1 Y_m Q_m \frac{(P_{bar} + P_m)}{T_m} \qquad \text{Eq. 2D-1}$$

12.3 Test Meter Device Calibration Coefficient. Calculation for testing metering device calibration coefficient, Y_m.

$$Y_m = \frac{Q_r T_r P_{bar}}{Q_m T_m (P_{bar} + P_m)} \qquad \text{Eq. 2D-2}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Spink, L.K. Principles and Practice of Flowmeter Engineering. The Foxboro Company. Foxboro, MA. 1967.

2. Benedict, R.P. Fundamentals of Temperature, Pressure, and Flow Measurements. John Wiley & Sons, Inc. New York, NY. 1969.

3. Orifice Metering of Natural Gas. American Gas Association. Arlington, VA. Report No. 3. March 1978. 88 pp.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

Plant _____
Date _____
Run No. _____
Sample location _____
Barometric pressure (mm Hg):
Start _____
Finish _____
Operators _____
Metering device No. _____
Calibration coefficient _____
Calibration gas _____
Date to recalibrate _____

Time	Flow rate reading	Static Pressure [mm Hg (in. Hg)]	Temperature	
			°C (°F)	°K (°R)
Average				

Figure 2D–1. Volume Flow Rate Measurement Data

METHOD 2E—DETERMINATION OF LANDFILL GAS PRODUCTION FLOW RATE

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this

method should also have a thorough knowledge of at least the following additional test methods: Methods 2 and 3C.

1.0 Scope and Application

1.1 Applicability. This method applies to the measurement of landfill gas (LFG) production flow rate from municipal solid waste landfills and is used to calculate the flow rate of nonmethane organic compounds (NMOC) from landfills.

1.2 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Extraction wells are installed either in a cluster of three or at five dispersed locations in the landfill. A blower is used to extract LFG from the landfill. LFG composition, landfill pressures, and orifice pressure differentials from the wells are measured and the landfill gas production flow rate is calculated.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Since this method is complex, only experienced personnel should perform the test. Landfill gas contains methane, therefore explosive mixtures may exist at or near the landfill. It is advisable to take appropriate safety precautions when testing landfills, such as refraining from smoking and installing explosion-proof equipment.

6.0 Equipment and Supplies

6.1 Well Drilling Rig. Capable of boring a 0.61 m (24 in.) diameter hole into the landfill to a minimum of 75 percent of the landfill depth. The depth of the well shall not extend to the bottom of the landfill or the liquid level.

6.2 Gravel. No fines. Gravel diameter should be appreciably larger than perforations stated in sections 6.10 and 8.2.

6.3 Bentonite.

6.4 Backfill Material. Clay, soil, and sandy loam have been found to be acceptable.

6.5 Extraction Well Pipe. Minimum diameter of 3 in., constructed of polyvinyl chloride (PVC), high density polyethylene (HDPE), fiberglass, stainless steel, or other suitable nonporous material capable of transporting landfill gas.

6.6 Above Ground Well Assembly. Valve capable of adjusting gas flow, such as a gate, ball, or butterfly valve; sampling ports at the well head and outlet; and a flow measuring device, such as an in-line orifice meter or pitot tube. A schematic of the above-ground well head assembly is shown in Figure 2E–1.

6.7 Cap. Constructed of PVC or HDPE.

6.8 Header Piping. Constructed of PVC or HDPE.

6.9 Auger. Capable of boring a 0.15-to 0.23-m (6-to 9-in.) diameter hole to a depth equal to the top of the perforated section of the extraction well, for pressure probe installation.

6.10 Pressure Probe. Constructed of PVC or stainless steel (316), 0.025-m (1-in.). Schedule 40 pipe. Perforate the bottom two-thirds. A minimum requirement for perforations is slots or holes with an open area equivalent to four 0.006-m (¼-in.) diameter holes spaced 90° apart every 0.15 m (6 in.).

6.11 Blower and Flare Assembly. Explosion-proof blower, capable of extracting LFG at a flow rate of 8.5 m^3/min (300 ft^3/min), a water knockout, and flare or incinerator.

6.12 Standard Pitot Tube and Differential Pressure Gauge for Flow Rate Calibration with Standard Pitot. Same as Method 2, sections 6.7 and 6.8.

6.13 Orifice Meter. Orifice plate, pressure tabs, and pressure measuring device to measure the LFG flow rate.

6.14 Barometer. Same as Method 4, section 6.1.5.

6.15 Differential Pressure Gauge. Water-filled U-tube manometer or equivalent, capable of measuring within 0.02 mm Hg (0.01 in. H_2O), for measuring the pressure of the pressure probes.

7.0 Reagents and Standards. Not Applicable

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Placement of Extraction Wells. The landfill owner or operator may install a single cluster of three extraction wells in a test area or space five equal-volume wells over the landfill. The cluster wells are recommended but may be used only if the composition, age of the refuse, and the landfill depth of the test area can be determined.

8.1.1 Cluster Wells. Consult landfill site records for the age of the refuse, depth, and composition of various sections of the landfill. Select an area near the perimeter of the landfill with a depth equal to or greater than the average depth of the landfill and with the average age of the refuse between 2 and 10 years old. Avoid areas known to contain nondecomposable materials, such as concrete and asbestos. Locate the cluster wells as shown in Figure 2E–2.

8.1.1.1 The age of the refuse in a test area will not be uniform, so calculate a weighted average age of the refuse as shown in section 12.2.

8.1.2 Equal Volume Wells. Divide the sections of the landfill that are at least 2 years old into five areas representing equal volumes. Locate an extraction well near the center of each area.

8.2 Installation of Extraction Wells. Use a well drilling rig to dig a 0.6 m (24 in.) diameter hole in the landfill to a minimum of 75 percent of the landfill depth, not to extend to the bottom of the landfill or the liquid level. Perforate the bottom two thirds of the extraction well pipe. A minimum requirement for perforations is holes or slots with an open area equivalent to 0.01-m (0.5-in.) diameter holes spaced 90° apart every 0.1 to 0.2 m (4 to 8 in.). Place the extraction well in the center of the hole and backfill with gravel to a level 0.30 m (1 ft) above the perforated section. Add a layer of backfill material 1.2 m (4 ft) thick. Add a layer of bentonite 0.9 m (3 ft) thick, and backfill the remainder of the hole with cover material or material equal in permeability to the existing cover material. The specifications for extraction well installation are shown in Figure 2E–3.

8.3 Pressure Probes. Shallow pressure probes are used in the check for infiltration of air into the landfill, and deep pressure probes are use to determine the radius of influence. Locate pressure probes along three radial arms approximately 120° apart at distances of 3, 15, 30, and 45 m (10, 50, 100, and 150 ft) from the extraction well. The tester has the option of locating additional pressure probes at distances every 15 m (50 feet) beyond 45 m (150 ft). Example placements of probes are shown in Figure 2E–4. The 15-, 30-, and 45-m, (50-, 100-, and 150-ft) probes from each well, and any additional probes located along the three radial arms (deep probes), shall extend to a depth equal to the top of the perforated section of the extraction wells. All other probes (shallow probes) shall extend to a depth equal to half the depth of the deep probes.

8.3.1 Use an auger to dig a hole, 0.15- to 0.23-m (6-to 9-in.) in diameter, for each pressure probe. Perforate the bottom two thirds of the pressure probe. A minimum requirement for perforations is holes or slots with an open area equivalent to four 0.006-m (0.25-in.) diameter holes spaced 90° apart every 0.15 m (6 in.). Place the pressure probe in the center of the hole and backfill with gravel to a level 0.30 m (1 ft) above the perforated section. Add a layer of backfill material at least 1.2 m (4 ft) thick. Add a layer of bentonite at least 0.3 m (1 ft) thick, and backfill the remainder of the hole with cover material or material equal in permeability to the existing cover material. The specifications for pressure probe installation are shown in Figure 2E–5.

8.4 LFG Flow Rate Measurement. Place the flow measurement device, such as an orifice meter, as shown in Figure 2E–1. Attach the wells to the blower and flare assembly. The individual wells may be ducted to a common header so that a single blower, flare assembly, and flow meter may be used. Use the procedures in section 10.1 to calibrate the flow meter.

8.5 Leak-Check. A leak-check of the above ground system is required for accurate flow rate measurements and for safety. Sample LFG at the well head sample port and at the outlet sample port. Use Method 3C to determine nitrogen (N_2) concentrations. Determine the difference between the well head and outlet N_2 concentrations using the formula in section 12.3. The system passes the leak-check if the difference is less than 10,000 ppmv.

8.6 Static Testing. Close the control valves on the well heads during static testing. Measure the gauge pressure (P_g) at each deep pressure probe and the barometric pressure (P_{bar}) every 8 hours (hr) for 3 days. Convert the gauge pressure of each deep pressure probe to absolute pressure using the equation in section 12.4. Record as P_i (initial absolute pressure).

8.6.1 For each probe, average all of the 8-hr deep pressure probe readings (P_i) and record as P_{ia} (average absolute pressure). P_{ia} is used in section 8.7.5 to determine the maximum radius of influence.

8.6.2 Measure the static flow rate of each well once during static testing.

8.7 Short-Term Testing. The purpose of short-term testing is to determine the maximum vacuum that can be applied to the wells without infiltration of ambient air into the landfill. The short-term testing is performed on one well at a time. Burn all LFG with a flare or incinerator.

8.7.1 Use the blower to extract LFG from a single well at a rate at least twice the static flow rate of the respective well measured in section 8.6.2. If using a single blower and flare assembly and a common header system, close the control valve on the wells not being measured. Allow 24 hr for the system to stabilize at this flow rate.

8.7.2 Test for infiltration of air into the landfill by measuring the gauge pressures of the shallow pressure probes and using Method 3C to determine the LFG N_2 concentration. If the LFG N_2 concentration is less than 5 percent and all of the shallow probes have a positive gauge pressure, increase the blower vacuum by 3.7 mm Hg (2 in. H_2O), wait 24 hr, and repeat the tests for infiltration. Continue the above steps of increasing blower vacuum by 3.7 mm Hg (2 in. H_2O), waiting 24 hr, and testing for infiltration until the concentration of N_2 exceeds 5 percent or any of the shallow probes have a negative gauge pressure. When this occurs,reduce the blower vacuum to the maximum setting at which the N_2 concentration was less than 5 percent and the gauge pressures of the shallow probes are positive.

8.7.3 At this blower vacuum, measure atmospheric pressure (P_{bar}) every 8 hr for 24 hr, and record the LFG flow rate (Q_s) and the probe gauge pressures (P_f) for all of the probes. Convert the gauge pressures of the

deep probes to absolute pressures for each 8-hr reading at Q_s as shown in section 12.4.

8.7.4 For each probe, average the 8-hr deep pressure probe absolute pressure readings and record as P_{fa} (the final average absolute pressure).

8.7.5 For each probe, compare the initial average pressure (P_{ia}) from section 8.6.1 to the final average pressure (P_{fa}). Determine the furthermost point from the well head along each radial arm where $P_{fa} \leq P_{ia}$. This distance is the maximum radius of influence (R_m), which is the distance from the well affected by the vacuum. Average these values to determine the average maximum radius of influence (R_{ma}).

8.7.6 Calculate the depth (D_{st}) affected by the extraction well during the short term test as shown in section 12.6. If the computed value of D_{st} exceeds the depth of the landfill, set D_{st} equal to the landfill depth.

8.7.7 Calculate the void volume (V) for the extraction well as shown in section 12.7.

8.7.8 Repeat the procedures in section 8.7 for each well.

8.8 Calculate the total void volume of the test wells (V_v) by summing the void volumes (V) of each well.

8.9 Long-Term Testing. The purpose of long-term testing is to extract two void volumes of LFG from the extraction wells. Use the blower to extract LFG from the wells. If a single Blower and flare assembly and common header system are used, open all control valves and set the blower vacuum equal to the highest stabilized blower vacuum demonstrated by any individual well in section 8.7. Every 8 hr, sample the LFG from the well head sample port, measure the gauge pressures of the shallow pressure probes, the blower vacuum, the LFG flow rate, and use the criteria for infiltration in section 8.7.2 and Method 3C to test for infiltration. If infiltration is detected, do not reduce the blower vacuum, instead reduce the LFG flow rate from the well by adjusting the control valve on the well head. Adjust each affected well individually. Continue until the equivalent of two total void volumes (V_v) have been extracted, or until $V_t = 2V_v$.

8.9.1 Calculate V_t, the total volume of LFG extracted from the wells, as shown in section 12.8.

8.9.2 Record the final stabilized flow rate as Q_f and the gauge pressure for each deep probe. If, during the long term testing, the flow rate does not stabilize, calculate Q_f by averaging the last 10 recorded flow rates.

8.9.3 For each deep probe, convert each gauge pressure to absolute pressure as in section 12.4. Average these values and record as P_{sa}. For each probe, compare P_{ia} to P_{sa}. Determine the furthermost point from the well head along each radial arm where $P_{sa} \leq P_{ia}$. This distance is the stabilized radius of influence. Average these values to determine the average stabilized radius of influence (R_{sa}).

8.10 Determine the NMOC mass emission rate using the procedures in section 12.9 through 12.15.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
10.1	LFG flow rate meter calibration	Ensures accurate measurement of LFG flow rate and sample volume

10.0 Calibration and Standardization

10.1 LFG Flow Rate Meter (Orifice) Calibration Procedure. Locate a standard pitot tube in line with an orifice meter. Use the procedures in section 8, 12.5, 12.6, and 12.7 of Method 2 to determine the average dry gas volumetric flow rate for at least five flow rates that bracket the expected LFG flow rates, except in section 8.1, use a standard pitot tube rather than a Type S pitot tube. Method 3C may be used to determine the dry molecular weight. It may be necessary to calibrate more than one orifice meter in order to bracket the LFG flow rates. Construct a calibration curve by plotting the pressure drops across the orifice meter for each flow rate versus the average dry gas volumetric flow rate in m^3/min of the gas.

11.0 Procedures [Reserved]

12.0 Data Analysis and Calculations

12.1 Nomenclature.

A = Age of landfill, yr.
A_{avg} = Average age of the refuse tested, yr.
A_i = Age of refuse in the ith fraction, yr.
A_r = Acceptance rate, Mg/yr.
C_{NMOC} = NMOC concentration, ppmv as hexane ($C_{NMOC} = C_t/6$).
C_o = Concentration of N_2 at the outlet, ppmv.
C_t = NMOC concentration, ppmv (carbon equivalent) from Method 25C.
C_w = Concentration of N_2 at the wellhead, ppmv.
D = Depth affected by the test wells, m.
D_{st} = Depth affected by the test wells in the short-term test, m.
e = Base number for natural logarithms (2.718).
f = Fraction of decomposable refuse in the landfill.

f_i = Fraction of the refuse in the ith section.
k = Landfill gas generation constant, yr^{-1}.
L_o = Methane generation potential, m^3/Mg.
L_o' = Revised methane generation potential to account for the amount of nondecomposable material in the landfill, m^3/Mg.
M_i = Mass of refuse in the ith section, Mg.
M_r = Mass of decomposable refuse affected by the test well, Mg.
P_{bar} = Atmospheric pressure, mm Hg.
P_f = Final absolute pressure of the deep pressure probes during short-term testing, mm Hg.
P_{fa} = Average final absolute pressure of the deep pressure probes during short-term testing, mm Hg.
P_{gf} = final gauge pressure of the deep pressure probes, mm Hg.
P_{gi} = Initial gauge pressure of the deep pressure probes, mm Hg.
P_i = Initial absolute pressure of the deep pressure probes during static testing, mm Hg.
P_{ia} = Average initial absolute pressure of the deep pressure probes during static testing, mm Hg.
P_s = Final absolute pressure of the deep pressure probes during long-term testing, mm Hg.
P_{sa} = Average final absolute pressure of the deep pressure probes during long-term testing, mm Hg.
Q_f = Final stabilized flow rate, m^3/min.
Q_i = LFG flow rate measured at orifice meter during the ith interval, m^3/min.
Q_s = Maximum LFG flow rate at each well determined by short-term test, m^3/min.
Q_t = NMOC mass emission rate, m^3/min.
R_m = Maximum radius of influence, m.
R_{ma} = Average maximum radius of influence, m.
R_s = Stabilized radius of influence for an individual well, m.
R_{sa} = Average stabilized radius of influence, m.
t_i = Age of section i, yr.
t_t = Total time of long-term testing, yr.
t_{vi} = Time of the ith interval (usually 8), hr.
V = Void volume of test well, m^3.
V_r = Volume of refuse affected by the test well, m^3.
V_t = Total volume of refuse affected by the long-term testing, m^3.
V_v = Total void volume affected by test wells, m^3.
WD = Well depth, m.
ρ = Refuse density, Mg/m^3 (Assume 0.64 Mg/m^3 if data are unavailable).

12.2 Use the following equation to calculate a weighted average age of landfill refuse.

$$A_{avg} = \sum_{i=1}^{n} f_i A_i \qquad \text{Eq. 2E-1}$$

12.3 Use the following equation to determine the difference in N_2 concentrations (ppmv) at the well head and outlet location.

$$\text{Difference} = C_o - C_w \qquad \text{Eq. 2E-2}$$

12.4 Use the following equation to convert the gauge pressure (P_g) of each initial deep pressure probe to absolute pressure (P_i).

$$P_i = P_{bar} + P_{gi} \qquad \text{Eq. 2E-3}$$

12.5 Use the following equation to convert the gauge pressures of the deep probes to absolute pressures for each 8-hr reading at Q_s.

$$P_f = P_{bar} + P_{gf} \qquad \text{Eq. 2E-4}$$

12.6 Use the following equation to calculate the depth (D_{st}) affected by the extraction well during the short-term test.

$$D_{st} = WD + R_{ma} \qquad \text{Eq. 2E-5}$$

12.7 Use the following equation to calculate the void volume for the extraction well (V).

$$V = 0.40\ \Pi\ R_{ma}{}^2\ D_{st} \qquad \text{Eq. 2E-6}$$

12.8 Use the following equation to calculate V_t, the total volume of LFG extracted from the wells.

$$V_t = \sum_{i=1}^{n} 60\ Q_i t_{vi} \qquad \text{Eq. 2E-7}$$

12.9 Use the following equation to calculate the depth affected by the test well. If using cluster wells, use the average depth of the wells for WD. If the value of D is greater than the depth of the landfill, set D equal to the landfill depth.

$$D = WD + R_{sa} \qquad \text{Eq. 2E-8}$$

12.10 Use the following equation to calculate the volume of refuse affected by the test well.

$$V_r = R_{sa}{}^2\ \Pi D \qquad \text{Eq. 2E-9}$$

12.11 Use the following equation to calculate the mass affected by the test well.

$$M_r = V_r \rho \qquad \text{Eq. 2E-10}$$

12.12 Modify L_o to account for the nondecomposable refuse in the landfill.

$$L_o' = f\ L_o \qquad \text{Eq. 2E-11}$$

12.13 In the following equation, solve for k (landfill gas generation constant) by iteration. A suggested procedure is to select a value for k, calculate the left side of the equation, and if not equal to zero, select another value for k. Continue this process until the left hand side of the equation equals zero, ±0.001.

$$k_e^{-k} A_{avg} - \frac{Q_f}{2\,L_o' M_r} = 0 \qquad \text{Eq. 2E-12}$$

12.14 Use the following equation to determine landfill NMOC mass emission rate if the yearly acceptance rate of refuse has been consistent (10 percent) over the life of the landfill.

$$Q_t = 2\,L_o' A_r \left(1 - e^{-kA}\right) C_{NMOC} \left(3.595 \times 10^{-9}\right) \qquad \text{Eq. 2E-13}$$

12.15 Use the following equation to determine landfill NMOC mass emission rate if the acceptance rate has not been consistent over the life of the landfill.

$$Q_t = 2\,k\,L_o' C_{NMOC} \left(3.595 \times 10^{-9}\right) \sum_{i=1}^{n} M_i e^{-kt_i} \qquad \text{Eq. 2E-14}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Same as Method 2, Appendix A, 40 CFR Part 60.

2. Emcon Associates, Methane Generation and Recovery from Landfills. Ann Arbor Science, 1982.

3. The Johns Hopkins University, Brown Station Road Landfill Gas Resource Assessment, Volume 1: Field Testing and Gas Recovery Projections. Laurel, Maryland: October 1982.

4. Mandeville and Associates, Procedure Manual for Landfill Gases Emission Testing.

5. Letter and attachments from Briggum, S., Waste Management of North America, to Thorneloe, S., EPA. Response to July 28, 1988 request for additional information. August 18, 1988.

6. Letter and attachments from Briggum, S., Waste Management of North America, to Wyatt, S., EPA. Response to December 7, 1988 request for additional information. January 16, 1989.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

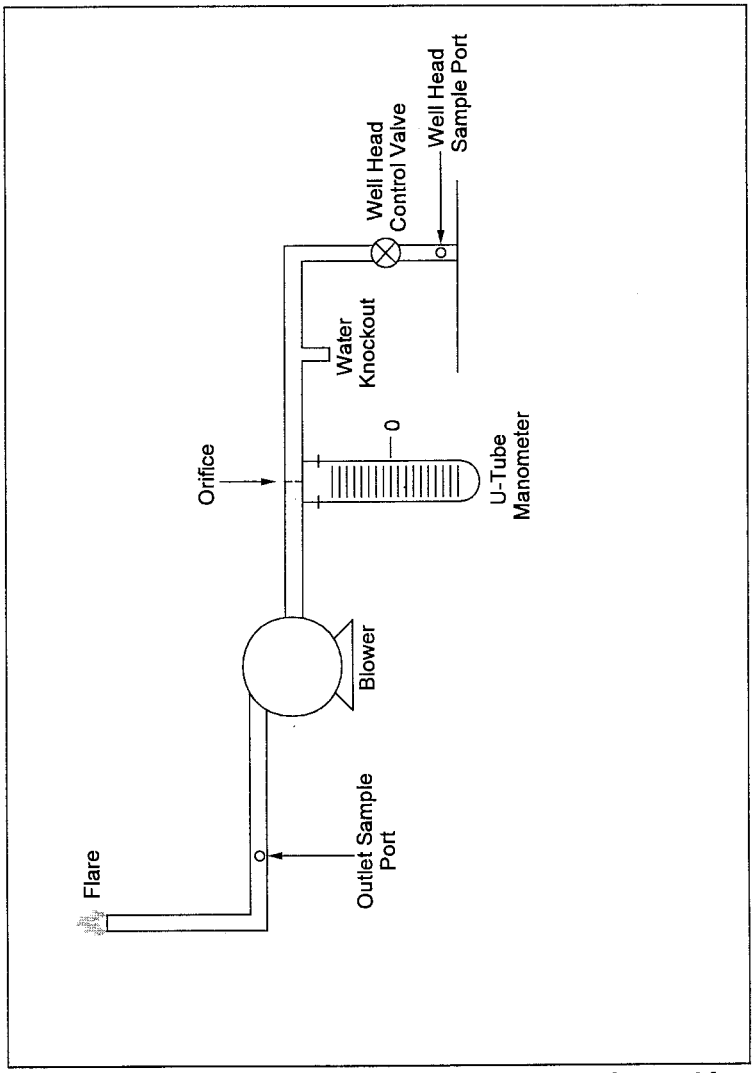

Figure 2E-1. Schematic of Aboveground Well Head Assembly.

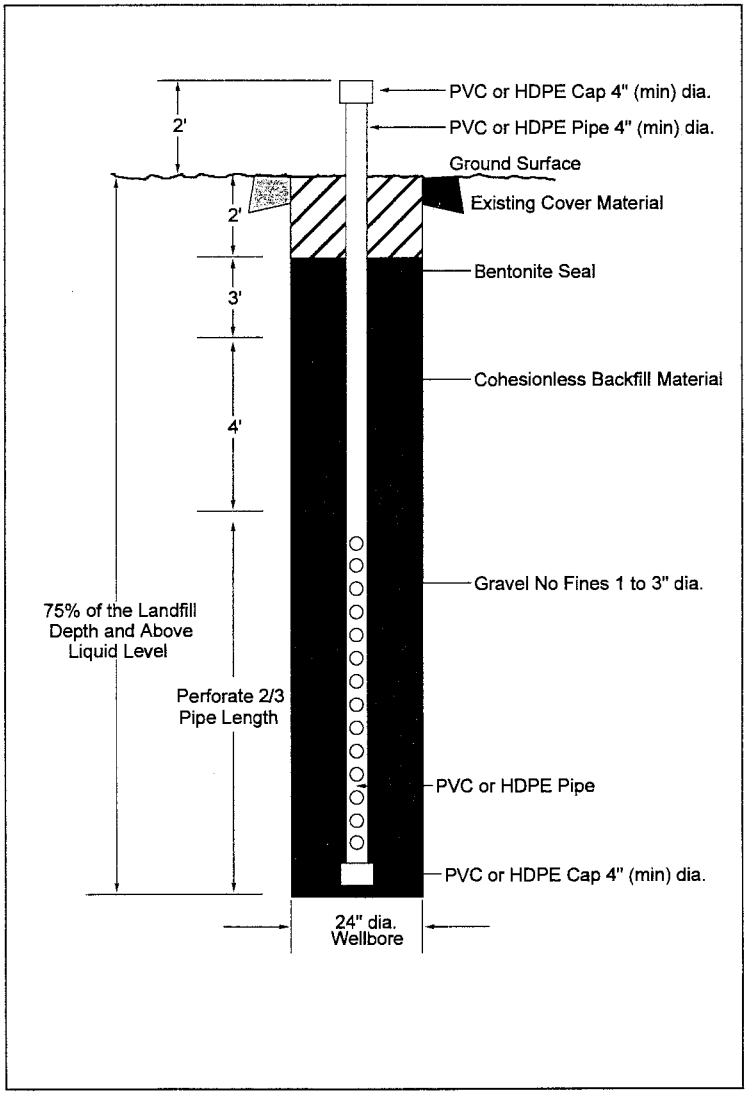

Figure 2E-3. Gas Extraction Well.

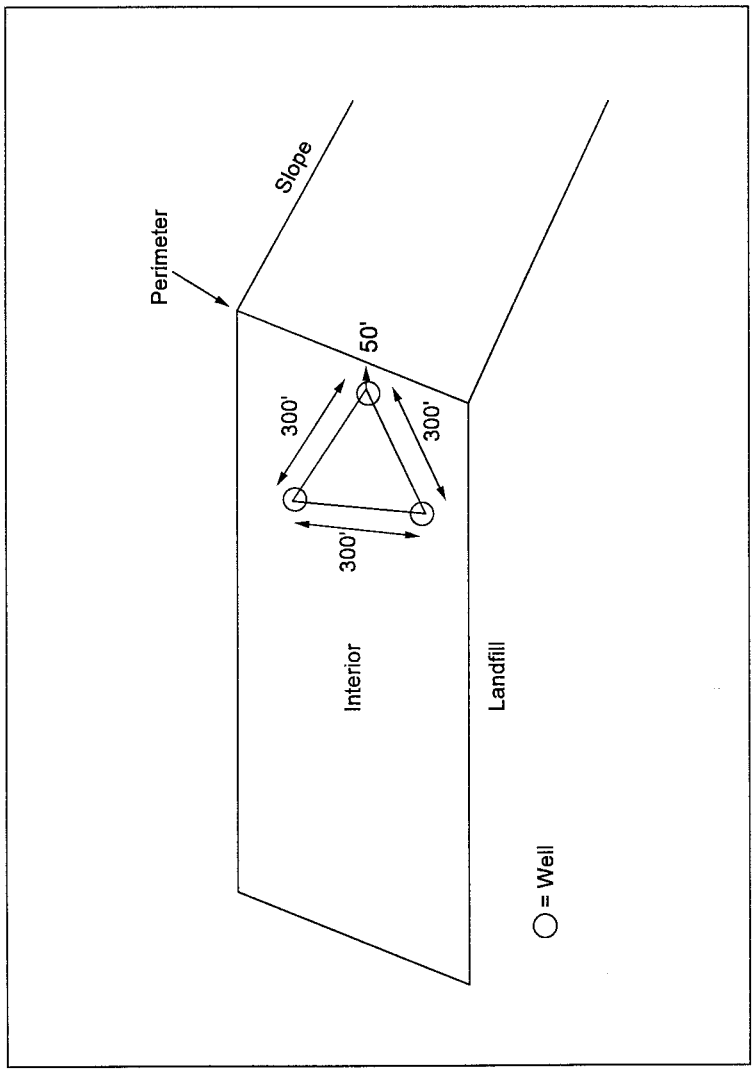

Figure 2E-2. Cluster Well Placement.

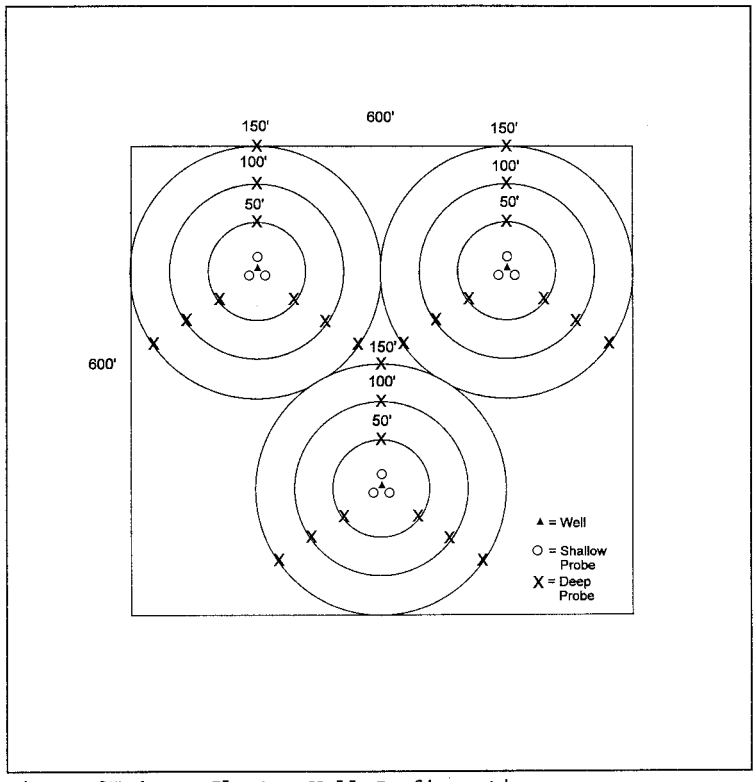

Figure 2E-4. Cluster Well Configuration.

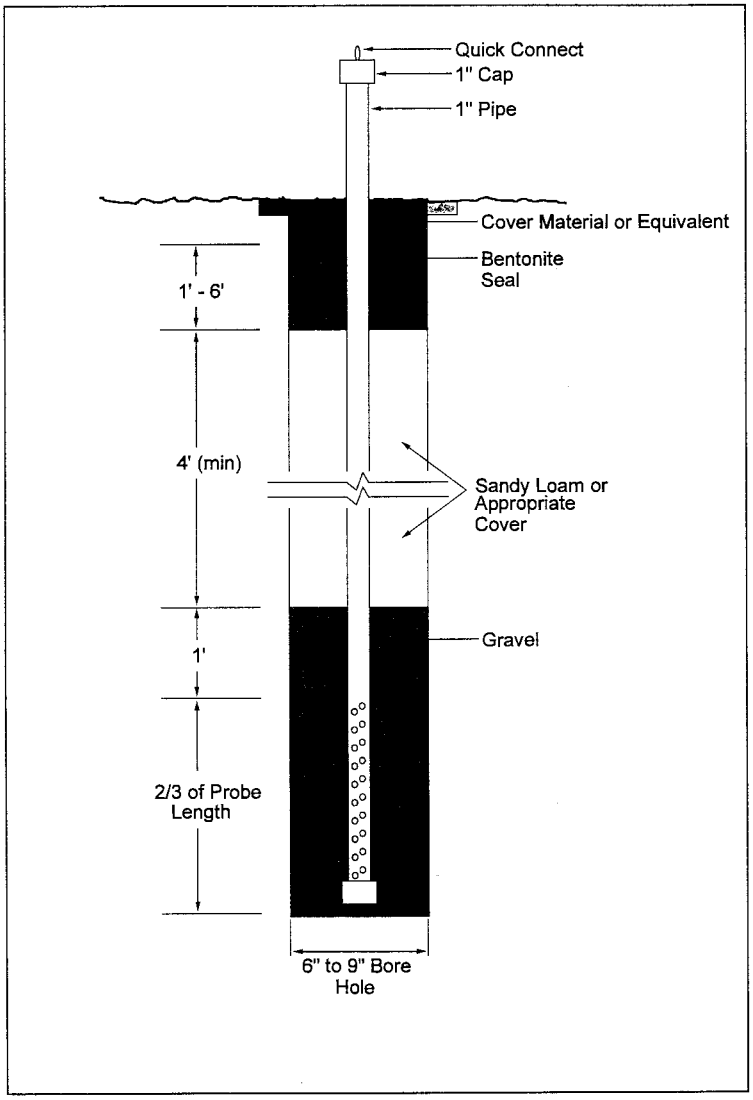

Figure 2E-5. Pressure Probe.

METHOD 2F—DETERMINATION OF STACK GAS VELOCITY AND VOLUMETRIC FLOW RATE WITH THREE-DIMENSIONAL PROBES

NOTE: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling) essential to its performance. Some material has been incorporated from other methods in this part. Therefore, to obtain reliable results, those using this method should have a thorough knowledge of at least the following additional test methods: Methods 1, 2, 3 or 3A, and 4.

1.0 Scope and Application

1.1 This method is applicable for the determination of yaw angle, pitch angle, axial velocity and the volumetric flow rate of a gas

stream in a stack or duct using a three-dimensional (3–D) probe. This method may be used only when the average stack or duct gas velocity is greater than or equal to 20 ft/sec. When the above condition cannot be met, alternative procedures, approved by the Administrator, U.S. Environmental Protection Agency, shall be used to make accurate flow rate determinations.

2.0 Summary of Method

2.1 A 3–D probe is used to determine the velocity pressure and the yaw and pitch angles of the flow velocity vector in a stack or duct. The method determines the yaw angle directly by rotating the probe to null the pressure across a pair of symmetrically placed ports on the probe head. The pitch angle is calculated using probe-specific calibration curves. From these values and a determination of the stack gas density, the average axial velocity of the stack gas is calculated. The average gas volumetric flow rate in the stack or duct is then determined from the average axial velocity.

3.0 Definitions

3.1. *Angle-measuring Device Rotational Offset* (R_{ADO}). The rotational position of an angle-measuring device relative to the reference scribe line, as determined during the pre-test rotational position check described in section 8.3.

3.2 *Axial Velocity*. The velocity vector parallel to the axis of the stack or duct that accounts for the yaw and pitch angle components of gas flow. The term ''axial'' is used herein to indicate that the velocity and volumetric flow rate results account for the measured yaw and pitch components of flow at each measurement point.

3.3 *Calibration Pitot Tube*. The standard (Prandtl type) pitot tube used as a reference when calibrating a 3–D probe under this method.

3.4 *Field Test*. A set of measurements conducted at a specific unit or exhaust stack/duct to satisfy the applicable regulation (e.g., a three-run boiler performance test, a single-or multiple-load nine-run relative accuracy test).

3.5 *Full Scale of Pressure-measuring Device*. Full scale refers to the upper limit of the measurement range displayed by the device. For bi-directional pressure gauges, full scale includes the entire pressure range from the lowest negative value to the highest positive value on the pressure scale.

3.6 *Main probe*. Refers to the probe head and that section of probe sheath directly attached to the probe head. The main probe sheath is distinguished from probe extensions, which are sections of sheath added onto the main probe to extend its reach.

3.7 *''May,'' ''Must,'' ''Shall,'' ''Should,''* and the imperative form of verbs.

3.7.1 *''May''* is used to indicate that a provision of this method is optional.

3.7.2 *''Must,'' ''Shall,''* and the imperative form of verbs (such as ''record'' or ''enter'') are used to indicate that a provision of this method is mandatory.

3.7.3 *''Should''* is used to indicate that a provision of this method is not mandatory, but is highly recommended as good practice.

3.8 *Method 1*. Refers to 40 CFR part 60, appendix A, ''Method 1—Sample and velocity traverses for stationary sources.''

3.9 *Method 2*. Refers to 40 CFR part 60, appendix A, ''Method 2—Determination of stack gas velocity and volumetric flow rate (Type S pitot tube).''

3.10 *Method 2G*. Refers to 40 CFR part 60, appendix A, ''Method 2G—Determination of stack gas velocity and volumetric flow rate with two-dimensional probes.''

3.11 *Nominal Velocity*. Refers to a wind tunnel velocity setting that approximates the actual wind tunnel velocity to within ±1.5 m/sec (±5 ft/sec).

3.12 *Pitch Angle*. The angle between the axis of the stack or duct and the pitch component of flow, i.e., the component of the total velocity vector in a plane defined by the traverse line and the axis of the stack or duct. (Figure 2F–1 illustrates the ''pitch plane.'') From the standpoint of a tester facing a test port in a vertical stack, the pitch component of flow is the vector of flow moving from the center of the stack toward or away from that test port. The pitch angle is the angle described by this pitch component of flow and the vertical axis of the stack.

3.13 *Readability*. For the purposes of this method, readability for an analog measurement device is one half of the smallest scale division. For a digital measurement device, it is the number of decimals displayed by the device.

3.14 *Reference Scribe Line*. A line permanently inscribed on the main probe sheath (in accordance with section 6.1.6.1) to serve as a reference mark for determining yaw angles.

3.15 *Reference Scribe Line Rotational Offset* (R_{SLO}). The rotational position of a probe's reference scribe line relative to the probe's yaw-null position, as determined during the yaw angle calibration described in section 10.5.

3.16 *Response Time*. The time required for the measurement system to fully respond to a change from zero differential pressure and ambient temperature to the stable stack or duct pressure and temperature readings at a traverse point.

3.17 *Tested Probe*. A 3–D probe that is being calibrated.

3.18 *Three-dimensional (3–D) Probe*. A directional probe used to determine the velocity pressure and yaw and pitch angles in a flowing gas stream.

3.19 *Traverse Line*. A diameter or axis extending across a stack or duct on which measurements of differential pressure and flow angles are made.

3.20 *Wind Tunnel Calibration Location*. A point, line, area, or volume within the wind tunnel test section at, along, or within which probes are calibrated. At a particular wind tunnel velocity setting, the average velocity pressures at specified points at, along, or within the calibration location shall vary by no more than 2 percent or 0.3 mm H_2O (0.01 in. H_2O), whichever is less restrictive, from the average velocity pressure at the calibration pitot tube location. Air flow at this location shall be axial, i.e., yaw and pitch angles within ±3°. Compliance with these flow criteria shall be demonstrated by performing the procedures prescribed in sections 10.1.1 and 10.1.2. For circular tunnels, no part of the calibration location may be closer to the tunnel wall than 10.2 cm (4 in.) or 25 percent of the tunnel diameter, whichever is farther from the wall. For elliptical or rectangular tunnels, no part of the calibration location may be closer to the tunnel wall than 10.2 cm (4 in.) or 25 percent of the applicable cross-sectional axis, whichever is farther from the wall.

3.21 *Wind Tunnel with Documented Axial Flow*. A wind tunnel facility documented as meeting the provisions of sections 10.1.1 (velocity pressure cross-check) and 10.1.2 (axial flow verification) using the procedures described in these sections or alternative procedures determined to be technically equivalent.

3.22 *Yaw Angle*. The angle between the axis of the stack or duct and the yaw component of flow, i.e., the component of the total velocity vector in a plane perpendicular to the traverse line at a particular traverse point. (Figure 2F–1 illustrates the ''yaw plane.'') From the standpoint of a tester facing a test port in a vertical stack, the yaw component of flow is the vector of flow moving to the left or right from the center of the stack as viewed by the tester. (This is sometimes referred to as ''vortex flow,'' i.e., flow around the centerline of a stack or duct.) The yaw angle is the angle described by this yaw component of flow and the vertical axis of the stack. The algebraic sign convention is illustrated in Figure 2F–2.

3.23 *Yaw Nulling*. A procedure in which a probe is rotated about its axis in a stack or duct until a zero differential pressure reading (''yaw null'') is obtained. When a 3–D probe is yaw-nulled, its impact pressure port (P_1) faces directly into the direction of flow in the stack or duct and the differential pressure between pressure ports P_2 and P_3 is zero.

4.0 Interferences [Reserved]

5.0 Safety

5.1 This test method may involve hazardous operations and the use of hazardous materials or equipment. This method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user to establish and implement appropriate safety and health practices and to determine the applicability of regulatory limitations before using this test method.

6.0 Equipment and Supplies

6.1 *Three-dimensional Probes*. The 3–D probes as specified in subsections 6.1.1 through 6.1.3 below qualify for use based on comprehensive wind tunnel and field studies involving both inter-and intra-probe comparisons by multiple test teams. Other types of probes shall not be used unless approved by the Administrator. Each 3–D probe shall have a unique identification number or code permanently marked on the main probe sheath. The minimum recommended diameter of the sensing head of any probe used under this method is 2.5 cm (1 in.). Each probe shall be calibrated prior to use according to the procedures in section 10. Manufacturer-supplied calibration data shall be used as example information only, except when the manufacturer calibrates the 3–D probe as specified in section 10 and provides complete documentation.

6.1.1 *Five-hole prism-shaped probe*. This type of probe consists of five pressure taps in the flat facets of a prism-shaped sensing head. The pressure taps are numbered 1 through 5, with the pressures measured at each hole referred to as P_1, P_2, P_3, P_4, and P_5, respectively. Figure 2F–3 is an illustration of the placement of pressure taps on a commonly available five-hole prism-shaped probe, the 2.5-cm (1-in.) DAT probe. (Note: Mention of trade names or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.) The numbering arrangement for the prism-shaped sensing head presented in Figure 2F–3 shall be followed for correct operation of the probe. A brief description of the probe measurements involved is as follows: the differential pressure P_2–P_3 is used to yaw null the probe and determine the yaw angle; the differential pressure P_4–P_5 is a function of pitch angle; and the differential pressure P_1–P_2 is a function of total velocity.

6.1.2 *Five-hole spherical probe*. This type of probe consists of five pressure taps in a spherical sensing head. As with the prism-shaped probe, the pressure taps are numbered 1 through 5, with the pressures measured at each hole referred to as P_1, P_2, P_3, P_4, and P_5, respectively. However, the P_4 and P_5 pressure taps are in the reverse location

from their respective positions on the prism-shaped probe head. The differential pressure P_2–P_3 is used to yaw null the probe and determine the yaw angle; the differential pressure P_4–P_5 is a function of pitch angle; and the differential pressure P_1–P_2 is a function of total velocity. A diagram of a typical spherical probe sensing head is presented in Figure 2F–4. Typical probe dimensions are indicated in the illustration.

6.1.3 *A manual 3–D probe* refers to a five-hole prism-shaped or spherical probe that is positioned at individual traverse points and yaw nulled manually by an operator. An automated 3–D probe refers to a system that uses a computer-controlled motorized mechanism to position the five-hole prism-shaped or spherical head at individual traverse points and perform yaw angle determinations.

6.1.4 *Other three-dimensional probes.* [Reserved]

6.1.5 *Probe sheath.* The probe shaft shall include an outer sheath to: (1) provide a surface for inscribing a permanent reference scribe line, (2) accommodate attachment of an angle-measuring device to the probe shaft, and (3) facilitate precise rotational movement of the probe for determining yaw angles. The sheath shall be rigidly attached to the probe assembly and shall enclose all pressure lines from the probe head to the farthest position away from the probe head where an angle-measuring device may be attached during use in the field. The sheath of the fully assembled probe shall be sufficiently rigid and straight at all rotational positions such that, when one end of the probe shaft is held in a horizontal position, the fully extended probe meets the horizontal straightness specifications indicated in section 8.2 below.

6.1.6 *Scribe lines.*

6.1.6.1 *Reference scribe line.* A permanent line, no greater than 1.6 mm (1/16 in.) in width, shall be inscribed on each manual probe that will be used to determine yaw angles of flow. This line shall be placed on the main probe sheath in accordance with the procedures described in section 10.4 and is used as a reference position for installation of the yaw angle-measuring device on the probe. At the discretion of the tester, the scribe line may be a single line segment placed at a particular position on the probe sheath (e.g., near the probe head), multiple line segments placed at various locations along the length of the probe sheath (e.g., at every position where a yaw angle-measuring device may be mounted), or a single continuous line extending along the full length of the probe sheath.

6.1.6.2 *Scribe line on probe extensions.* A permanent line may also be inscribed on any probe extension that will be attached to the main probe in performing field testing. This allows a yaw angle-measuring device mounted on the extension to be readily aligned with the reference scribe line on the main probe sheath.

6.1.6.3 *Alignment specifications.* This specification shall be met separately, using the procedures in section 10.4.1, on the main probe and on each probe extension. The rotational position of the scribe line or scribe line segments on the main probe or any probe extension must not vary by more than 2°. That is, the difference between the minimum and maximum of all of the rotational angles that are measured along the full length of the main probe or the probe extension must not exceed 2°.

6.1.7 Probe and system characteristics to ensure horizontal stability.

6.1.7.1 For manual probes, it is recommended that the effective length of the probe (coupled with a probe extension, if necessary) be at least 0.9 m (3 ft.) longer than the farthest traverse point mark on the probe shaft away from the probe head. The operator should maintain the probe's horizontal stability when it is fully inserted into the stack or duct. If a shorter probe is used, the probe should be inserted through a bushing sleeve, similar to the one shown in Figure 2F–5, that is installed on the test port; such a bushing shall fit snugly around the probe and be secured to the stack or duct entry port in such a manner as to maintain the probe's horizontal stability when fully inserted into the stack or duct.

6.1.7.2 An automated system that includes an external probe casing with a transport system shall have a mechanism for maintaining horizontal stability comparable to that obtained by manual probes following the provisions of this method. The automated probe assembly shall also be constructed to maintain the alignment and position of the pressure ports during sampling at each traverse point. The design of the probe casing and transport system shall allow the probe to be removed from the stack or duct and checked through direct physical measurement for angular position and insertion depth.

6.1.8 The tubing that is used to connect the probe and the pressure-measuring device should have an inside diameter of at least 3.2 mm (1/8 in.), to reduce the time required for pressure equilibration, and should be as short as practicable.

6.2 Yaw Angle-measuring Device. One of the following devices shall be used for measurement of the yaw angle of flow.

6.2.1 Digital inclinometer. This refers to a digital device capable of measuring and displaying the rotational position of the probe to within ±1°. The device shall be able to be locked into position on the probe sheath or probe extension, so that it indicates the probe's rotational position throughout the test. A rotational position collar block that can be attached to the probe sheath (similar

to the collar shown in Figure 2F–6) may be required to lock the digital inclinometer into position on the probe sheath.

6.2.2 Protractor wheel and pointer assembly. This apparatus, similar to that shown in Figure 2F–7, consists of the following components.

6.2.2.1 A protractor wheel that can be attached to a port opening and set in a fixed rotational position to indicate the yaw angle position of the probe's scribe line relative to the longitudinal axis of the stack or duct. The protractor wheel must have a measurement ring on its face that is no less than 17.8 cm (7 in.) in diameter, shall be able to be rotated to any angle and then locked into position on the stack or duct port, and shall indicate angles to a resolution of 1°.

6.2.2.2 A pointer assembly that includes an indicator needle mounted on a collar that can slide over the probe sheath and be locked into a fixed rotational position on the probe sheath. The pointer needle shall be of sufficient length, rigidity, and sharpness to allow the tester to determine the probe's angular position to within 1° from the markings on the protractor wheel. Corresponding to the position of the pointer, the collar must have a scribe line to be used in aligning the pointer with the scribe line on the probe sheath.

6.2.3 Other yaw angle-measuring devices. Other angle-measuring devices with a manufacturer's specified precision of 1° or better may be used, if approved by the Administrator.

6.3 Probe Supports and Stabilization Devices. When probes are used for determining flow angles, the probe head should be kept in a stable horizontal position. For probes longer than 3.0 m (10 ft.), the section of the probe that extends outside the test port shall be secured. Three alternative devices are suggested for maintaining the horizontal position and stability of the probe shaft during flow angle determinations and velocity pressure measurements: (1) Monorails installed above each port, (2) probe stands on which the probe shaft may be rested, or (3) bushing sleeves of sufficient length secured to the test ports to maintain probes in a horizontal position. Comparable provisions shall be made to ensure that automated systems maintain the horizontal position of the probe in the stack or duct. The physical characteristics of each test platform may dictate the most suitable type of stabilization device. Thus, the choice of a specific stabilization device is left to the judgment of the testers.

6.4 Differential Pressure Gauges. The pressure (ΔP) measuring devices used during wind tunnel calibrations and field testing shall be either electronic manometers (e.g., pressure transducers), fluid manometers, or mechanical pressure gauges (e.g., MagnehelicΔ gauges). Use of electronic manometers is recommended. Under low velocity conditions, use of electronic manometers may be necessary to obtain acceptable measurements.

6.4.1 Differential pressure-measuring device. This refers to a device capable of measuring pressure differentials and having a readability of ±1 percent of full scale. The device shall be capable of accurately measuring the maximum expected pressure differential. Such devices are used to determine the following pressure measurements: velocity pressure, static pressure, yaw-null pressure, and pitch-angle pressure. For an inclined-vertical manometer, the readability specification of ±1 percent shall be met separately using the respective full-scale upper limits of the inclined and vertical portions of the scales. To the extent practicable, the device shall be selected such that most of the pressure readings are between 10 and 90 percent of the device's full-scale measurement range (as defined in section 3.5). Typical velocity pressure (P_1–P_2) ranges for both the prism-shaped probe and the spherical probe are 0 to 1.3 cm H_2O (0 to 0.5 in. H_2O), 0 to 5.1 cm H_2O (0 to 2 in. H_2O), and 0 to 12.7 cm H_2O (0 to 5 in. H_2O). The pitch angle (P_4–P_5) pressure range is typically −6.4 to + 6.4 mm H_2O (−0.25 to + 0.25 in. H_2O) or −12.7 to + 12.7 mm H_2O (−0.5 to + 0.5 in. H_2O) for the prism-shaped probe, and −12.7 to + 12.7 mm H_2O (−0.5 to + 0.5 in. H_2O) or −5.1 to + 5.1 cm H_2O (−2 to + 2 in. H_2O) for the spherical probe. The pressure range for the yaw null (P_2–P_3) readings is typically −12.7 to + 12.7 mm H_2O (−0.5 to + 0.5 in. H_2O) for both probe types. In addition, pressure-measuring devices should be selected such that the zero does not drift by more than 5 percent of the average expected pressure readings to be encountered during the field test. This is particularly important under low pressure conditions.

6.4.2 Gauge used for yaw nulling. The differential pressure-measuring device chosen for yaw nulling the probe during the wind tunnel calibrations and field testing shall be bi-directional, i.e., capable of reading both positive and negative differential pressures. If a mechanical, bi-directional pressure gauge is chosen, it shall have a full-scale range no greater than 2.6 cm H_2O (1 in. H_2O) [i.e., −1.3 to + 1.3 cm H_2O (−0.5 in. to + 0.5 in.)].

6.4.3 Devices for calibrating differential pressure-measuring devices. A precision manometer (e.g., a U-tube, inclined, or inclined-vertical manometer, or micromanometer) or NIST (National Institute of Standards and Technology) traceable pressure source shall be used for calibrating differential pressure-measuring devices. The device shall be maintained under laboratory conditions or in a similar protected environment (e.g., a climate-controlled trailer). It shall not be used in field tests. The precision manometer shall have a scale gradation of 0.3 mm H_2O (0.01 in. H_2O), or less, in the range of 0 to 5.1 cm H_2O

(0 to 2 in. H_2O) and 2.5 mm H_2O (0.1 in. H_2O), or less, in the range of 5.1 to 25.4 cm H_2O (2 to 10 in. H_2O). The manometer shall have manufacturer's documentation that it meets an accuracy specification of at least 0.5 percent of full scale. The NIST-traceable pressure source shall be recertified annually.

6.4.4 Devices used for post-test calibration check. A precision manometer meeting the specifications in section 6.4.3, a pressure-measuring device or pressure source with a documented calibration traceable to NIST, or an equivalent device approved by the Administrator shall be used for the post-test calibration check. The pressure-measuring device shall have a readability equivalent to or greater than the tested device. The pressure source shall be capable of generating pressures between 50 and 90 percent of the range of the tested device and known to within ±1 percent of the full scale of the tested device. The pressure source shall be recertified annually.

6.5 Data Display and Capture Devices. Electronic manometers (if used) shall be coupled with a data display device (such as a digital panel meter, personal computer display, or strip chart) that allows the tester to observe and validate the pressure measurements taken during testing. They shall also be connected to a data recorder (such as a data logger or a personal computer with data capture software) that has the ability to compute and retain the appropriate average value at each traverse point, identified by collection time and traverse point.

6.6 Temperature Gauges. For field tests, a thermocouple or resistance temperature detector (RTD) capable of measuring temperature to within ±3 °C (±5 °F) of the stack or duct temperature shall be used. The thermocouple shall be attached to the probe such that the sensor tip does not touch any metal and is located on the opposite side of the probe head from the pressure ports so as not to interfere with the gas flow around the probe head. The position of the thermocouple relative to the pressure port face openings shall be in the same configuration as used for the probe calibrations in the wind tunnel. Temperature gauges used for wind tunnel calibrations shall be capable of measuring temperature to within ±0.6 °C (±1 °F) of the temperature of the flowing gas stream in the wind tunnel.

6.7 Stack or Duct Static Pressure Measurement. The pressure-measuring device used with the probe shall be as specified in section 6.4 of this method. The static tap of a standard (Prandtl type) pitot tube or one leg of a Type S pitot tube with the face opening planes positioned parallel to the gas flow may be used for this measurement. Also acceptable is the pressure differential reading of $P_1–P_{bar}$ from a five-hole prism-shaped probe (e.g., Type DA or DAT probe) with the P_1 pressure port face opening positioned parallel to the gas flow in the same manner as the Type S probe. However, the spherical probe, as specified in section 6.1.2, is unable to provide this measurement and shall not be used to take static pressure measurements. Static pressure measurement is further described in section 8.11.

6.8 Barometer. Same as Method 2, section 2.5.

6.9 Gas Density Determination Equipment. Method 3 or 3A shall be used to determine the dry molecular weight of the stack gas. Method 4 shall be used for moisture content determination and computation of stack gas wet molecular weight. Other methods may be used, if approved by the Administrator.

6.10 Calibration Pitot Tube. Same as Method 2, section 2.7.

6.11 Wind Tunnel for Probe Calibration. Wind tunnels used to calibrate velocity probes must meet the following design specifications.

6.11.1 Test section cross-sectional area. The flowing gas stream shall be confined within a circular, rectangular, or elliptical duct. The cross-sectional area of the tunnel must be large enough to ensure fully developed flow in the presence of both the calibration pitot tube and the tested probe. The calibration site, or ''test section,'' of the wind tunnel shall have a minimum diameter of 30.5 cm (12 in.) for circular or elliptical duct cross-sections or a minimum width of 30.5 cm (12 in.) on the shorter side for rectangular cross-sections. Wind tunnels shall meet the probe blockage provisions of this section and the qualification requirements prescribed in section 10.1. The projected area of the portion of the probe head, shaft, and attached devices inside the wind tunnel during calibration shall represent no more than 4 percent of the cross-sectional area of the tunnel. The projected area shall include the combined area of the calibration pitot tube and the tested probe if both probes are placed simultaneously in the same cross-sectional plane in the wind tunnel, or the larger projected area of the two probes if they are placed alternately in the wind tunnel.

6.11.2 Velocity range and stability. The wind tunnel should be capable of maintaining velocities between 6.1 m/sec and 30.5 m/sec (20 ft/sec and 100 ft/sec). The wind tunnel shall produce fully developed flow patterns that are stable and parallel to the axis of the duct in the test section.

6.11.3 Flow profile at the calibration location. The wind tunnel shall provide axial flow within the test section calibration location (as defined in section 3.20). Yaw and pitch angles in the calibration location shall be within ±3° of 0°. The procedure for determining that this requirement has been met is described in section 10.1.2.

6.11.4 Entry ports in the wind tunnel test section.

6.11.4.1 Port for tested probe. A port shall be constructed for the tested probe. The port should have an elongated slot parallel to the axis of the duct at the test section. The elongated slot should be of sufficient length to allow attaining all the pitch angles at which the probe will be calibrated for use in the field. To facilitate alignment of the probe during calibration, the test section should include a window constructed of a transparent material to allow the tested probe to be viewed. This port shall be located to allow the head of the tested probe to be positioned within the calibration location (as defined in section 3.20) at all pitch angle settings.

6.11.4.2 Port for verification of axial flow. Depending on the equipment selected to conduct the axial flow verification prescribed in section 10.1.2, a second port, located 90° from the entry port for the tested probe, may be needed to allow verification that the gas flow is parallel to the central axis of the test section. This port should be located and constructed so as to allow one of the probes described in section 10.1.2.2 to access the same test point(s) that are accessible from the port described in section 6.11.4.1.

6.11.4.3 Port for calibration pitot tube. The calibration pitot tube shall be used in the port for the tested probe or a separate entry port. In either case, all measurements with the calibration pitot tube shall be made at the same point within the wind tunnel over the course of a probe calibration. The measurement point for the calibration pitot tube shall meet the same specifications for distance from the wall and for axial flow as described in section 3.20 for the wind tunnel calibration location.

6.11.5 Pitch angle protractor plate. A protractor plate shall be attached directly under the port used with the tested probe and set in a fixed position to indicate the pitch angle position of the probe relative to the longitudinal axis of the wind tunnel duct (similar to Figure 2F–8). The protractor plate shall indicate angles in 5° increments with a minimum resolution of ±2°. The tested probe shall be able to be locked into position at the desired pitch angle delineated on the protractor. The probe head position shall be maintained within the calibration location (as defined in section 3.20) in the test section of the wind tunnel during all tests across the range of pitch angles.

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection and Analysis

8.1 Equipment Inspection and Set-Up

8.1.1 All probes, differential pressure-measuring devices, yaw angle-measuring devices, thermocouples, and barometers shall have a current, valid calibration before being used in a field test. (See sections 10.3.3, 10.3.4, and 10.5 through10.10 for the applicable calibration requirements.)

8.1.2 Before each field use of a 3-D probe, perform a visual inspection to verify the physical condition of the probe head according to the procedures in section 10.2. Record the inspection results on a form similar to Table 2F–1. If there is visible damage to the 3-D probe, the probe shall not be used until it is recalibrated.

8.1.3 After verifying that the physical condition of the probe head is acceptable, set up the apparatus using lengths of flexible tubing that are as short as practicable. Surge tanks installed between the probe and pressure-measuring device may be used to dampen pressure fluctuations provided that an adequate measurement response time (see section 8.8) is maintained.

8.2 Horizontal Straightness Check. A horizontal straightness check shall be performed before the start of each field test, except as otherwise specified in this section. Secure the fully assembled probe (including the probe head and all probe shaft extensions) in a horizontal position using a stationary support at a point along the probe shaft approximating the location of the stack or duct entry port when the probe is sampling at the farthest traverse point from the stack or duct wall. The probe shall be rotated to detect bends. Use an angle-measuring device or trigonometry to determine the bend or sag between the probe head and the secured end. (See Figure 2F–9.) Probes that are bent or sag by more than 5° shall not be used. Although this check does not apply when the probe is used for a vertical traverse, care should be taken to avoid the use of bent probes when conducting vertical traverses. If the probe is constructed of a rigid steel material and consists of a main probe without probe extensions, this check need only be performed before the initial field use of the probe, when the probe is recalibrated, when a change is made to the design or material of the probe assembly, and when the probe becomes bent. With such probes, a visual inspection shall be made of the fully assembled probe before each field test to determine if a bend is visible. The probe shall be rotated to detect bends. The inspection results shall be documented in the field test report. If a bend in the probe is visible, the horizontal straightness check shall be performed before the probe is used.

8.3 Rotational Position Check. Before each field test, and each time an extension is added to the probe during a field test, a rotational position check shall be performed on all manually operated probes (except as noted in section 8.3.5, below) to ensure that, throughout testing, the angle-measuring device is either: aligned to within ±1° of the rotational position of the reference scribe line; or is affixed to the probe such that the rotational offset of the device from the reference scribe line is known to within ±1°. This check shall consist of direct measurements of the

rotational positions of the reference scribe line and angle-measuring device sufficient to verify that these specifications are met. Annex A in section 18 of this method gives recommended procedures for performing the rotational position check, and Table 2F–2 gives an example data form. Procedures other than those recommended in Annex A in section 18 may be used, provided they demonstrate whether the alignment specification is met and are explained in detail in the field test report.

8.3.1 Angle-measuring device rotational offset. The tester shall maintain a record of the angle-measuring device rotational offset, R_{ADO}, as defined in section 3.1. Note that R_{ADO} is assigned a value of 0° when the angle-measuring device is aligned to within ±1° of the rotational position of the reference scribe line. The R_{ADO} shall be used to determine the yaw angle of flow in accordance with section 8.9.4.

8.3.2 Sign of angle-measuring device rotational offset. The sign of R_{ADO} is positive when the angle-measuring device (as viewed from the ''tail'' end of the probe) is positioned in a clockwise direction from the reference scribe line and negative when the device is positioned in a counterclockwise direction from the reference scribe line.

8.3.3 Angle-measuring devices that can be independently adjusted (e.g., by means of a set screw), after being locked into position on the probe sheath, may be used. However, the R_{ADO} must also take into account this adjustment.

8.3.4 Post-test check. If probe extensions remain attached to the main probe throughout the field test, the rotational position check shall be repeated, at a minimum, at the completion of the field test to ensure that the angle-measuring device has remained within ±2° of its rotational position established prior to testing. At the discretion of the tester, additional checks may be conducted after completion of testing at any sample port or after any test run. If the ±2° specification is not met, all measurements made since the last successful rotational position check must be repeated. section 18.1.1.3 of Annex A provides an example procedure for performing the post-test check.

8.3.5 Exceptions.

8.3.5.1 A rotational position check need not be performed if, for measurements taken at all velocity traverse points, the yaw angle-measuring device is mounted and aligned directly on the reference scribe line specified in sections 6.1.6.1 and 6.1.6.3 and no independent adjustments, as described in section 8.3.3, are made to the device's rotational position.

8.3.5.2 If extensions are detached and re-attached to the probe during a field test, a rotational position check need only be performed the first time an extension is added to the probe, rather than each time the extension is re-attached, if the probe extension is designed to be locked into a mechanically fixed rotational position (e.g., through use of interlocking grooves) that can re-establish the initial rotational position to within ±1°.

8.4 Leak Checks. A pre-test leak check shall be conducted before each field test. A post-test check shall be performed at the end of the field test, but additional leak checks may be conducted after any test run or group of test runs. The post-test check may also serve as the pre-test check for the next group of test runs. If any leak check is failed, all runs since the last passed leak check are invalid. While performing the leak check procedures, also check each pressure device's responsiveness to the changes in pressure.

8.4.1 To perform the leak check, pressurize the probe's P_1 pressure port until at least 7.6 cm H_2O (3 in. H_2O) pressure, or a pressure corresponding to approximately 75 percent of the pressure-measuring device's measurement scale, whichever is less, registers on the device; then, close off the pressure port. The pressure shall remain stable [±2.5 mm H_2O (±0.10 in. H_2O)] for at least 15 seconds. Check the P_2, P_3, P_4, and P_5 pressure ports in the same fashion. Other leak-check procedures may be used, if approved by the Administrator.

8.5 Zeroing the Differential Pressure-measuring Device. Zero each differential pressure-measuring device, including the device used for yaw nulling, before each field test. At a minimum, check the zero after each field test. A zero check may also be performed after any test run or group of test runs. For fluid manometers and mechanical pressure gauges (e.g., Magnehelic∆ gauges), the zero reading shall not deviate from zero by more than ±0.8 mm H_2O (±0.03 in. H_2O) or one minor scale division, whichever is greater, between checks. For electronic manometers, the zero reading shall not deviate from zero between checks by more than: ±0.3 mm H_2O (±0.01 in. H_2O), for full scales less than or equal to 5.1 cm H_2O (2.0 in. H_2O); or ±0.8 mm H_2O (±0.03 in. H_2O), for full scales greater than 5.1 cm H_2O (2.0 in. H_2O). (Note: If negative zero drift is not directly readable, estimate the reading based on the position of the gauge oil in the manometer or of the needle on the pressure gauge.) In addition, for all pressure-measuring devices except those used exclusively for yaw nulling, the zero reading shall not deviate from zero by more than 5 percent of the average measured differential pressure at any distinct process condition or load level. If any zero check is failed at a specific process condition or load level, all runs conducted at that process condition or load level since the last passed zero check are invalid.

8.6 Traverse Point Verification. The number and location of the traverse points shall be selected based on Method 1 guidelines.

The stack or duct diameter and port nipple lengths, including any extension of the port nipples into stack or duct, shall be verified the first time the test is performed; retain and use this information for subsequent field tests, updating it as required. Physically measure the stack or duct dimensions or use a calibrated laser device; do not use engineering drawings of the stack or duct. The probe length necessary to reach each traverse point shall be recorded to within ±6.4 mm (±1/4 in.) and, for manual probes, marked on the probe sheath. In determining these lengths, the tester shall take into account both the distance that the port flange projects outside of the stack and the depth that any port nipple extends into the gas stream. The resulting point positions shall reflect the true distances from the inside wall of the stack or duct, so that when the tester aligns any of the markings with the outside face of the stack port, the probe's impact port shall be located at the appropriate distance from the inside wall for the respective Method 1 traverse point. Before beginning testing at a particular location, an out-of-stack or duct verification shall be performed on each probe that will be used to ensure that these position markings are correct. The distances measured during the verification must agree with the previously calculated distances to within ±1/4 in. For manual probes, the traverse point positions shall be verified by measuring the distance of each mark from the probe's P_1 pressure port. A comparable out-of-stack test shall be performed on automated probe systems. The probe shall be extended to each of the prescribed traverse point positions. Then, the accuracy of the positioning for each traverse point shall be verified by measuring the distance between the port flange and the probe's P_1 pressure port.

8.7 Probe Installation. Insert the probe into the test port. A solid material shall be used to seal the port.

8.8 System Response Time. Determine the response time of the probe measurement system. Insert and position the ''cold'' probe (at ambient temperature and pressure) at any Method 1 traverse point. Read and record the probe's P_1–P_2 differential pressure, temperature, and elapsed time at 15-second intervals until stable readings for both pressure and temperature are achieved. The response time is the longer of these two elapsed times. Record the response time.

8.9 Sampling.

8.9.1 Yaw angle measurement protocol. With manual probes, yaw angle measurements may be obtained in two alternative ways during the field test, either by using a yaw angle-measuring device (e.g., digital inclinometer) affixed to the probe, or using a protractor wheel and pointer assembly. For horizontal traversing, either approach may be used. For vertical traversing, i.e., when measuring from on top or into the bottom of a horizontal duct, only the protractor wheel and pointer assembly may be used. With automated probes, curve-fitting protocols may be used to obtain yaw-angle measurements.

8.9.1.1 If a yaw angle-measuring device affixed to the probe is to be used, lock the device on the probe sheath, aligning it either on the reference scribe line or in the rotational offset position established under section 8.3.1.

8.9.1.2 If a protractor wheel and pointer assembly is to be used, follow the procedures in Annex B of this method.

8.9.1.3 Other yaw angle-determination procedures. If approved by the Administrator, other procedures for determining yaw angle may be used, provided that they are verified in a wind tunnel to be able to perform the yaw angle calibration procedure as described in section 10.5.

8.9.2 Sampling strategy. At each traverse point, first yaw-null the probe, as described in section 8.9.3, below. Then, with the probe oriented into the direction of flow, measure and record the yaw angle, the differential pressures and the temperature at the traverse point, after stable readings are achieved, in accordance with sections 8.9.4 and 8.9.5. At the start of testing in each port (i.e., after a probe has been inserted into the flue gas stream), allow at least the response time to elapse before beginning to take measurements at the first traverse point accessed from that port. Provided that the probe is not removed from the flue gas stream, measurements may be taken at subsequent traverse points accessed from the same test port without waiting again for the response time to elapse.

8.9.3 Yaw-nulling procedure. In preparation for yaw angle determination, the probe must first be yaw nulled. After positioning the probe at the appropriate traverse point, perform the following procedures.

8.9.3.1 Rotate the probe until a null differential pressure reading (the difference in pressures across the P_2 and P_3 pressure ports is zero, i.e., $P_2 = P_3$) is indicated by the yaw angle pressure gauge. Read and record the angle displayed by the angle-measuring device.

8.9.3.2 Sign of the measured angle. The angle displayed on the angle-measuring device is considered positive when the probe's impact pressure port (as viewed from the ''tail'' end of the probe) is oriented in a clockwise rotational position relative to the stack or duct axis and is considered negative when the probe's impact pressure port is oriented in a counterclockwise rotational position (see Figure 2F–10).

8.9.4 Yaw angle determination. After performing the yaw-nulling procedure in section

8.9.3, determine the yaw angle of flow according to one of the following procedures. Special care must be observed to take into account the signs of the recorded angle and all offsets.

8.9.4.1 Direct-reading. If all rotational offsets are zero or if the angle-measuring device rotational offset (R_{ADO}) determined in section 8.3 exactly compensates for the scribe line rotational offset (R_{SLO}) determined in section 10.5, then the magnitude of the yaw angle is equal to the displayed angle-measuring device reading from section 8.9.3.1. The algebraic sign of the yaw angle is determined in accordance with section 8.9.3.2.

NOTE: Under certain circumstances (e.g., testing of horizontal ducts), a 90° adjustment to the angle-measuring device readings may be necessary to obtain the correct yaw angles.

8.9.4.2 Compensation for rotational offsets during data reduction. When the angle-measuring device rotational offset does not compensate for reference scribe line rotational offset, the following procedure shall be used to determine the yaw angle:

(a) Enter the reading indicated by the angle-measuring device from section 8.9.3.1.

(b) Associate the proper algebraic sign from section 8.9.3.2 with the reading in step (a).

(c) Subtract the reference scribe line rotational offset, R_{SLO}, from the reading in step (b).

(d) Subtract the angle-measuring device rotational offset, R_{ADO}, if any, from the result obtained in step (c).

(e) The final result obtained in step (d) is the yaw angle of flow.

NOTE: It may be necessary to first apply a 90° adjustment to the reading in step (a), in order to obtain the correct yaw angle.

8.9.4.3 Record the yaw angle measurements on a form similar to Table 2F–3.

8.9.5 Velocity determination. Maintain the probe rotational position established during the yaw angle determination. Then, begin recording the pressure-measuring device readings for the impact pressure (P_1–P_2) and pitch angle pressure (P_4–P_5). These pressure measurements shall be taken over a sampling period of sufficiently long duration to ensure representative readings at each traverse point. If the pressure measurements are determined from visual readings of the pressure device or display, allow sufficient time to observe the pulsation in the readings to obtain a sight-weighted average, which is then recorded manually. If an automated data acquisition system (e.g., data logger, computer-based data recorder, strip chart recorder) is used to record the pressure measurements, obtain an integrated average of all pressure readings at the traverse point. Stack or duct gas temperature measurements shall be recorded, at a minimum, once at each traverse point. Record all necessary data as shown in the example field data form (Table 2F–3).

8.9.6 Alignment check. For manually operated probes, after the required yaw angle and differential pressure and temperature measurements have been made at each traverse point, verify (e.g., by visual inspection) that the yaw angle-measuring device has remained in proper alignment with the reference scribe line or with the rotational offset position established in section 8.3. If, for a particular traverse point, the angle-measuring device is found to be in proper alignment, proceed to the next traverse point; otherwise, re-align the device and repeat the angle and differential pressure measurements at the traverse point. In the course of a traverse, if a mark used to properly align the angle-measuring device (e.g., as described in section 18.1.1.1) cannot be located, re-establish the alignment mark before proceeding with the traverse.

8.10 Probe Plugging. Periodically check for plugging of the pressure ports by observing the responses on pressure differential readouts. Plugging causes erratic results or sluggish responses. Rotate the probe to determine whether the readouts respond in the expected direction. If plugging is detected, correct the problem and repeat the affected measurements.

8.11 Static Pressure. Measure the static pressure in the stack or duct using the equipment described in section 6.7.

8.11.1 If a Type DA or DAT probe is used for this measurement, position the probe at or between any traverse point(s) and rotate the probe until a null differential pressure reading is obtained at P_2–P_3. Rotate the probe 90°. Disconnect the P_2 pressure side of the probe and read the pressure P_1-P_{bar} and record as the static pressure. (NOTE: The spherical probe, specified in section 6.1.2, is unable to provide this measurement and shall not be used to take static pressure measurements.)

8.11.2 If a Type S probe is used for this measurement, position the probe at or between any traverse point(s) and rotate the probe until a null differential pressure reading is obtained. Disconnect the tubing from one of the pressure ports; read and record the ΔP. For pressure devices with one-directional scales, if a deflection in the positive direction is noted with the negative side disconnected, then the static pressure is positive. Likewise, if a deflection in the positive direction is noted with the positive side disconnected, then the static pressure is negative.

8.12 Atmospheric Pressure. Determine the atmospheric pressure at the sampling elevation during each test run following the procedure described in section 2.5 of Method 2.

8.13 Molecular Weight. Determine the stack gas dry molecular weight. For combustion processes or processes that emit essentially CO_2, O_2, CO, and N_2, use Method 3 or 3A. For processes emitting essentially air, an analysis need not be conducted; use a dry molecular weight of 29.0. Other methods may be used, if approved by the Administrator.

8.14 Moisture. Determine the moisture content of the stack gas using Method 4 or equivalent.

8.15 Data Recording and Calculations. Record all required data on a form similar to Table 2F–3.

8.15.1 Selection of appropriate calibration curves. Choose the appropriate pair of F_1 and F_2 versus pitch angle calibration curves, created as described in section 10.6.

8.15.2 Pitch angle derivation. Use the appropriate calculation procedures in section 12.2 to find the pitch angle ratios that are applicable at each traverse point. Then, find the pitch angles corresponding to these pitch angle ratios on the ''F_1 versus pitch angle'' curve for the probe.

8.15.3 Velocity calibration coefficient derivation. Use the pitch angle obtained following the procedures described in section 8.15.2 to find the corresponding velocity calibration coefficients from the ''F_2 versus pitch angle'' calibration curve for the probe.

8.15.4 Calculations. Calculate the axial velocity at each traverse point using the equations presented in section 12.2 to account for the yaw and pitch angles of flow. Calculate the test run average stack gas velocity by finding the arithmetic average of the point velocity results in accordance with sections 12.3 and 12.4, and calculate the stack gas volumetric flow rate in accordance with section 12.5 or 12.6, as applicable.

9.0 Quality Control

9.1 Quality Control Activities. In conjunction with the yaw angle determination and the pressure and temperature measurements specified in section 8.9, the following quality control checks should be performed.

9.1.1 Range of the differential pressure gauge. In accordance with the specifications in section 6.4, ensure that the proper differential pressure gauge is being used for the range of ΔP values encountered. If it is necessary to change to a more sensitive gauge, replace the gauge with a gauge calibrated according to section 10.3.3, perform the leak check described in section 8.4 and the zero check described in section 8.5, and repeat the differential pressure and temperature readings at each traverse point.

9.1.2 Horizontal stability check. For horizontal traverses of a stack or duct, visually check that the probe shaft is maintained in a horizontal position prior to taking a pressure reading. Periodically, during a test run, the probe's horizontal stability should be verified by placing a carpenter's level, a digital inclinometer, or other angle-measuring device on the portion of the probe sheath that extends outside of the test port. A comparable check should be performed by automated systems.

10.0 Calibration

10.1 Wind Tunnel Qualification Checks. To qualify for use in calibrating probes, a wind tunnel shall have the design features specified in section 6.11 and satisfy the following qualification criteria. The velocity pressure cross-check in section 10.1.1 and axial flow verification in section 10.1.2 shall be performed before the initial use of the wind tunnel and repeated immediately after any alteration occurs in the wind tunnel's configuration, fans, interior surfaces, straightening vanes, controls, or other properties that could reasonably be expected to alter the flow pattern or velocity stability in the tunnel. The owner or operator of a wind tunnel used to calibrate probes according to this method shall maintain records documenting that the wind tunnel meets the requirements of sections 10.1.1 and 10.1.2 and shall provide these records to the Administrator upon request.

10.1.1 Velocity pressure cross-check. To verify that the wind tunnel produces the same velocity at the tested probe head as at the calibration pitot tube impact port, perform the following cross-check. Take three differential pressure measurements at the fixed calibration pitot tube location, using the calibration pitot tube specified in section 6.10, and take three measurements with the calibration pitot tube at the wind tunnel calibration location, as defined in section 3.20. Alternate the measurements between the two positions. Perform this procedure at the lowest and highest velocity settings at which the probes will be calibrated. Record the values on a form similar to Table 2F–4. At each velocity setting, the average velocity pressure obtained at the wind tunnel calibration location shall be within ±2 percent or 2.5 mm H_2O (0.01 in. H_2O), whichever is less restrictive, of the average velocity pressure obtained at the fixed calibration pitot tube location. This comparative check shall be performed at 2.5-cm (1-in.), or smaller, intervals across the full length, width, and depth (if applicable) of the wind tunnel calibration location. If the criteria are not met at every tested point, the wind tunnel calibration location must be redefined, so that acceptable results are obtained at every point. Include the results of the velocity pressure cross-check in the calibration data section of the field test report. (See section 16.1.4.)

10.1.2 Axial flow verification. The following procedures shall be performed to demonstrate that there is fully developed axial flow within the calibration location and at

the calibration pitot tube location. Two testing options are available to conduct this check.

10.1.2.1 Using a calibrated 3–D probe. A 3–D probe that has been previously calibrated in a wind tunnel with documented axial flow (as defined in section 3.21) may be used to conduct this check. Insert the calibrated 3–D probe into the wind tunnel test section using the tested probe port. Following the procedures in sections 8.9 and 12.2 of this method, determine the yaw and pitch angles at all the point(s) in the test section where the velocity pressure cross-check, as specified in section 10.1.1, is performed. This includes all the points in the calibration location and the point where the calibration pitot tube will be located. Determine the yaw and pitch angles at each point. Repeat these measurements at the highest and lowest velocities at which the probes will be calibrated. Record the values on a form similar to Table 2F–5. Each measured yaw and pitch angle shall be within ±3° of 0°. Exceeding the limits indicates unacceptable flow in the test section. Until the problem is corrected and acceptable flow is verified by repetition of this procedure, the wind tunnel shall not be used for calibration of probes. Include the results of the axial flow verification in the calibration data section of the field test report. (See section 16.1.4.)

10.1.2.2 Using alternative probes. Axial flow verification may be performed using an uncalibrated prism-shaped 3–D probe (e.g., DA or DAT probe) or an uncalibrated wedge probe. (Figure 2F–11 illustrates a typical wedge probe.) This approach requires use of two ports: the tested probe port and a second port located 90° from the tested probe port. Each port shall provide access to all the points within the wind tunnel test section where the velocity pressure cross-check, as specified in section 10.1.1, is conducted. The probe setup shall include establishing a reference yaw-null position on the probe sheath to serve as the location for installing the angle-measuring device. Physical design features of the DA, DAT, and wedge probes are relied on to determine the reference position. For the DA or DAT probe, this reference position can be determined by setting a digital inclinometer on the flat facet where the P_1 pressure port is located and then identifying the rotational position on the probe sheath where a second angle-measuring device would give the same angle reading. The reference position on a wedge probe shaft can be determined either geometrically or by placing a digital inclinometer on each side of the wedge and rotating the probe until equivalent readings are obtained. With the latter approach, the reference position is the rotational position on the probe sheath where an angle-measuring device would give a reading of 0°. After installing the angle-measuring device in the reference yaw-null position on the probe sheath, determine the yaw angle from the tested port. Repeat this measurement using the 90° offset port, which provides the pitch angle of flow. Determine the yaw and pitch angles at all the point(s) in the test section where the velocity pressure cross-check, as specified in section 10.1.1, is performed. This includes all the points in the wind tunnel calibration location and the point where the calibration pitot tube will be located. Perform this check at the highest and lowest velocities at which the probes will be calibrated. Record the values on a form similar to Table 2F–5. Each measured yaw and pitch angle shall be within ±3° of 0°. Exceeding the limits indicates unacceptable flow in the test section. Until the problem is corrected and acceptable flow is verified by repetition of this procedure, the wind tunnel shall not be used for calibration of probes. Include the results in the probe calibration report.

10.1.3 Wind tunnel audits.

10.1.3.1 Procedure. Upon the request of the Administrator, the owner or operator of a wind tunnel shall calibrate a 3–D audit probe in accordance with the procedures described in sections 10.3 through 10.6. The calibration shall be performed at two velocities and over a pitch angle range that encompasses the velocities and pitch angles typically used for this method at the facility. The resulting calibration data and curves shall be submitted to the Agency in an audit test report. These results shall be compared by the Agency to reference calibrations of the audit probe at the same velocity and pitch angle settings obtained at two different wind tunnels.

10.1.3.2 Acceptance criteria. The audited tunnel's calibration is acceptable if all of the following conditions are satisfied at each velocity and pitch setting for the reference calibration obtained from at least one of the wind tunnels. For pitch angle settings between −15° and + 15°, no velocity calibration coefficient (i.e., F_2) may differ from the corresponding reference value by more than 3 percent. For pitch angle settings outside of this range (i.e., less than −15° and greater than + 15°), no velocity calibration coefficient may differ by more than 5 percent from the corresponding reference value. If the acceptance criteria are not met, the audited wind tunnel shall not be used to calibrate probes for use under this method until the problems are resolved and acceptable results are obtained upon completion of a subsequent audit.

10.2 Probe Inspection. Before each calibration of a 3–D probe, carefully examine the physical condition of the probe head. Particular attention shall be paid to the edges of the pressure ports and the surfaces surrounding these ports. Any dents, scratches, or asymmetries on the edges of the pressure ports and any scratches or indentations on

the surfaces surrounding the pressure ports shall be noted because of the potential effect on the probe's pressure readings. If the probe has been previously calibrated, compare the current condition of the probe's pressure ports and surfaces to the results of the inspection performed during the probe's most recent wind tunnel calibration. Record the results of this inspection on a form and in diagrams similar to Table 2F–1. The information in Table 2F–1 will be used as the basis for comparison during the probe head inspections performed before each subsequent field use.

10.3 Pre-Calibration Procedures. Prior to calibration, a scribe line shall have been placed on the probe in accordance with section 10.4. The yaw angle and velocity calibration procedures shall not begin until the pretest requirements in sections 10.3.1 through 10.3.4 have been met.

10.3.1 Perform the horizontal straightness check described in section 8.2 on the probe assembly that will be calibrated in the wind tunnel.

10.3.2 Perform a leak check in accordance with section 8.4.

10.3.3 Except as noted in section 10.3.3.3, calibrate all differential pressure-measuring devices to be used in the probe calibrations, using the following procedures. At a minimum, calibrate these devices on each day that probe calibrations are performed.

10.3.3.1 Procedure. Before each wind tunnel use, all differential pressure-measuring devices shall be calibrated against the reference device specified in section 6.4.3 using a common pressure source. Perform the calibration at three reference pressures representing 30, 60, and 90 percent of the full-scale range of the pressure-measuring device being calibrated. For an inclined-vertical manometer, perform separate calibrations on the inclined and vertical portions of the measurement scale, considering each portion of the scale to be a separate full-scale range. [For example, for a manometer with a 0- to 2.5-cm H_2O (0- to 1-in. H_2O) inclined scale and a 2.5- to 12.7-cm H_2O (1- to 5-in. H_2O) vertical scale, calibrate the inclined portion at 7.6, 15.2, and 22.9 mm H_2O (0.3, 0.6, and 0.9 in. H_2O), and calibrate the vertical portion at 3.8, 7.6, and 11.4 cm H_2O (1.5, 3.0, and 4.5 in. H_2O).] Alternatively, for the vertical portion of the scale, use three evenly spaced reference pressures, one of which is equal to or higher than the highest differential pressure expected in field applications.

10.3.3.2 Acceptance criteria. At each pressure setting, the two pressure readings made using the reference device and the pressure-measuring device being calibrated shall agree to within ±2 percent of full scale of the device being calibrated or 0.5 mm H_2O (0.02 in. H_2O), whichever is less restrictive. For an inclined-vertical manometer, these requirements shall be met separately using the respective full-scale upper limits of the inclined and vertical portions of the scale. Differential pressure-measuring devices not meeting the #2 percent of full scale or 0.5 mm H_2O (0.02 in. H_2O) calibration requirement shall not be used.

10.3.3.3 Exceptions. Any precision manometer that meets the specifications for a reference device in section 6.4.3 and that is not used for field testing does not require calibration, but must be leveled and zeroed before each wind tunnel use. Any pressure device used exclusively for yaw nulling does not require calibration, but shall be checked for responsiveness to rotation of the probe prior to each wind tunnel use.

10.3.4 Calibrate digital inclinometers on each day of wind tunnel or field testing (prior to beginning testing) using the following procedures. Calibrate the inclinometer according to the manufacturer's calibration procedures. In addition, use a triangular block (illustrated in Figure 2F–12) with a known angle, θ independently determined using a protractor or equivalent device, between two adjacent sides to verify the inclinometer readings.

NOTE: If other angle-measuring devices meeting the provisions of section 6.2.3 are used in place of a digital inclinometer, comparable calibration procedures shall be performed on such devices.)

Secure the triangular block in a fixed position. Place the inclinometer on one side of the block (side A) to measure the angle of inclination (R_1). Repeat this measurement on the adjacent side of the block (side B) using the inclinometer to obtain a second angle reading (R_2). The difference of the sum of the two readings from 180° (i.e., $180° - R_1 - R_2$) shall be within ±2° of the known angle, Θ

10.4 Placement of Reference Scribe Line. Prior to the first calibration of a probe, a line shall be permanently inscribed on the main probe sheath to serve as a reference mark for determining yaw angles. Annex C in section 18 of this method gives a guideline for placement of the reference scribe line.

10.4.1 This reference scribe line shall meet the specifications in sections 6.1.6.1 and 6.1.6.3 of this method. To verify that the alignment specification in section 6.1.6.3 is met, secure the probe in a horizontal position and measure the rotational angle of each scribe line and scribe line segment using an angle-measuring device that meets the specifications in section 6.2.1 or 6.2.3. For any scribe line that is longer than 30.5 cm (12 in.), check the line's rotational position at 30.5-cm (12-in.) intervals. For each line segment that is 30.5 cm (12 in.) or less in length, check the rotational position at the two endpoints of the segment. To meet the alignment specification in section 6.1.6.3, the minimum and maximum of all of the rotational angles that are measured along the full

length of the main probe must not differ by more than 2°.

NOTE: A short reference scribe line segment [e.g., 15.2 cm (6 in.) or less in length] meeting the alignment specifications in section 6.1.6.3 is fully acceptable under this method. See section 18.1.1.1 of Annex A for an example of a probe marking procedure, suitable for use with a short reference scribe line.

10.4.2 The scribe line should be placed on the probe first and then its offset from the yaw-null position established (as specified in section 10.5). The rotational position of the reference scribe line relative to the yaw-null position of the probe, as determined by the yaw angle calibration procedure in section 10.5, is defined as the reference scribe line rotational offset, R_{SLO}. The reference scribe line rotational offset shall be recorded and retained as part of the probe's calibration record.

10.4.3 Scribe line for automated probes. A scribe line may not be necessary for an automated probe system if a reference rotational position of the probe is built into the probe system design. For such systems, a ''flat'' (or comparable, clearly identifiable physical characteristic) should be provided on the probe casing or flange plate to ensure that the reference position of the probe assembly remains in a vertical or horizontal position. The rotational offset of the flat (or comparable, clearly identifiable physical characteristic) needed to orient the reference position of the probe assembly shall be recorded and maintained as part of the automated probe system's specifications.

10.5 Yaw Angle Calibration Procedure. For each probe used to measure yaw angles with this method, a calibration procedure shall be performed in a wind tunnel meeting the specifications in section 10.1 to determine the rotational position of the reference scribe line relative to the probe's yaw-null position. This procedure shall be performed on the main probe with all devices that will be attached to the main probe in the field [such as thermocouples or resistance temperature detectors (RTDs)] that may affect the flow around the probe head. Probe shaft extensions that do not affect flow around the probe head need not be attached during calibration. At a minimum, this procedure shall include the following steps.

10.5.1 Align and lock the angle-measuring device on the reference scribe line. If a marking procedure (such as that described in section 18.1.1.1) is used, align the angle-measuring device on a mark within ±1° of the rotational position of the reference scribe line. Lock the angle-measuring device onto the probe sheath at this position.

10.5.2 Zero the pressure-measuring device used for yaw nulling.

10.5.3 Insert the probe assembly into the wind tunnel through the entry port, positioning the probe's impact port at the calibration location. Check the responsiveness of the pressure-measurement device to probe rotation, taking corrective action if the response is unacceptable.

10.5.4 Ensure that the probe is in a horizontal position, using a carpenter's level.

10.5.5 Rotate the probe either clockwise or counterclockwise until a yaw null ($P_2 = P_3$) is obtained.

10.5.6 Use the reading displayed by the angle-measuring device at the yaw-null position to determine the magnitude of the reference scribe line rotational offset, R_{SLO}, as defined in section 3.15. Annex D in section 18 of this method provides a recommended procedure for determining the magnitude of R_{SLO} with a digital inclinometer and a second procedure for determining the magnitude of R_{SLO} with a protractor wheel and pointer device. Table 2F–6 presents an example data form and Table 2F–7 is a look-up table with the recommended procedure. Procedures other than those recommended in Annex D in section 18 may be used, if they can determine R_{SLO} to within ±1° and are explained in detail in the field test report. The algebraic sign of R_{SLO} will either be positive, if the rotational position of the reference scribe line (as viewed from the ''tail'' end of the probe) is clockwise, or negative, if counterclockwise with respect to the probe's yaw-null position. (This is illustrated in Figure 2F–13.)

10.5.7 The steps in sections 10.5.3 through 10.5.6 shall be performed twice at each of the velocities at which the probe will be calibrated (in accordance with section 10.6). Record the values of R_{SLO}.

10.5.8 The average of all of the R_{SLO} values shall be documented as the reference scribe line rotational offset for the probe.

10.5.9 Use of reference scribe line offset. The reference scribe line rotational offset shall be used to determine the yaw angle of flow in accordance with section 8.9.4.

10.6 Pitch Angle and Velocity Pressure Calibrations. Use the procedures in sections 10.6.1 through 10.6.16 to generate an appropriate set (or sets) of pitch angle and velocity pressure calibration curves for each probe. The calibration procedure shall be performed on the main probe and all devices that will be attached to the main probe in the field (e.g., thermocouple or RTDs) that may affect the flow around the probe head. Probe shaft extensions that do not affect flow around the probe head need not be attached during calibration. (Note: If a sampling nozzle is part of the assembly, a wind tunnel demonstration shall be performed that shows the probe's ability to measure velocity and yaw null is not impaired when the nozzle is drawing a sample.) The calibration

procedure involves generating two calibration curves, F_1 versus pitch angle and F_2 versus pitch angle. To generate these two curves, F_1 and F_2 shall be derived using Equations 2F–1 and 2F–2, below. Table 2F–8 provides an example wind tunnel calibration data sheet, used to log the measurements needed to derive these two calibration curves.

10.6.1 Calibration velocities. The tester may calibrate the probe at two nominal wind tunnel velocity settings of 18.3 m/sec and 27.4 m/sec (60 ft/sec and 90 ft/sec) and average the results of these calibrations, as described in section 10.6.16.1, in order to generate a set of calibration curves. If this option is selected, this single set of calibration curves may be used for all field applications over the entire velocity range allowed by the method. Alternatively, the tester may customize the probe calibration for a particular field test application (or for a series of applications), based on the expected average velocity(ies) at the test site(s). If this option is selected, generate each set of calibration curves by calibrating the probe at two nominal wind tunnel velocity settings, at least one of which is greater than or equal to the expected average velocity(ies) for the field application(s), and average the results as described in section 10.6.16.1. Whichever calibration option is selected, the probe calibration coefficients (F_2 values) obtained at the two nominal calibration velocities shall, for the same pitch angle setting, meet the conditions specified in section 10.6.16.

10.6.2 Pitch angle calibration curve (F_1 versus pitch angle). The pitch angle calibration involves generating a calibration curve of calculated F_1 values versus tested pitch angles, where F_1 is the ratio of the pitch pressure to the velocity pressure, i.e.,

$$F_1 = \frac{(P_4 - P_5)}{(P_1 - P_2)} \qquad \text{Eq. 2F-1}$$

See Figure 2F–14 for an example F_1 versus pitch angle calibration curve.

10.6.3 Velocity calibration curve (F_2 versus pitch angle). The velocity calibration involves generating a calibration curve of the 3–D probe's F_2 coefficient against the tested pitch angles, where

$$F_2 = C_p \sqrt{\frac{\Delta P_{std}}{(P_1 - P_2)}} \qquad \text{Eq. 2F-2}$$

and

C_p = calibration pitot tube coefficient, and

ΔP_{std} = velocity pressure from the calibration pitot tube.

See Figure 2F–15 for an example F_2 versus pitch angle calibration curve.

10.6.4 Connect the tested probe and calibration pitot probe to their respective pressure-measuring devices. Zero the pressure-measuring devices. Inspect and leak-check all pitot lines; repair or replace, if necessary. Turn on the fan, and allow the wind tunnel air flow to stabilize at the first of the two selected nominal velocity settings.

10.6.5 Position the calibration pitot tube at its measurement location (determined as outlined in section 6.11.4.3), and align the tube so that its tip is pointed directly into the flow. Ensure that the entry port surrounding the tube is properly sealed. The calibration pitot tube may either remain in the wind tunnel throughout the calibration, or be removed from the wind tunnel while measurements are taken with the probe being calibrated.

10.6.6 Set up the pitch protractor plate on the tested probe's entry port to establish the pitch angle positions of the probe to within ±2°.

10.6.7 Check the zero setting of each pressure-measuring device.

10.6.8 Insert the tested probe into the wind tunnel and align it so that its P_1 pressure port is pointed directly into the flow and is positioned within the calibration location (as defined in section 3.20). Secure the probe at the 0° pitch angle position. Ensure that the entry port surrounding the probe is properly sealed.

10.6.9 Read the differential pressure from the calibration pitot tube (ΔP_{std}), and record its value. Read the barometric pressure to within ±2.5 mm Hg (±0.1 in. Hg) and the temperature in the wind tunnel to within 0.6 °C (1 °F). Record these values on a data form similar to Table 2F–8.

10.6.10 After the tested probe's differential pressure gauges have had sufficient time to stabilize, yaw null the probe, then obtain differential pressure readings for (P_1–P_2) and (P_4–P_5). Record the yaw angle and differential pressure readings. After taking these readings, ensure that the tested probe has remained at the yaw-null position.

10.6.11 Either take paired differential pressure measurements with both the calibration pitot tube and tested probe (according to sections 10.6.9 and 10.6.10) or take readings only with the tested probe (according to section 10.6.10) in 5° increments over the pitch-angle range for which the probe is to be calibrated. The calibration pitch-angle range shall be symmetric around 0° and shall exceed the largest pitch angle expected in the field by 5°. At a minimum, probes shall be calibrated over the range of −15° to + 15°. If paired calibration pitot tube and tested probe measurements are not taken at each pitch angle setting, the differential pressure from the calibration pitot tube shall be read, at a minimum, before taking the tested probe's differential pressure reading at the first pitch angle setting and after taking the tested probe's differential pressure readings at the last pitch angle setting in each replicate.

10.6.12 Perform a second replicate of the procedures in sections 10.6.5 through 10.6.11 at the same nominal velocity setting.

10.6.13 For each replicate, calculate the F_1 and F_2 values at each pitch angle. At each pitch angle, calculate the percent difference between the two F_2 values using Equation 2F–3.

$$\%\text{Diff} = \frac{F_2^{max} - F_2^{min}}{F_2^{min}} \times 100\% \quad \text{Eq. 2F-3}$$

If the percent difference is less than or equal to 2 percent, calculate an average F_1 value and an average F_2 value at that pitch angle. If the percent difference is greater than 2 percent and less than or equal to 5 percent, perform a third repetition at that angle and calculate an average F_1 value and an average F_2 value using all three repetitions. If the percent difference is greater than 5 percent, perform four additional repetitions at that angle and calculate an average F_1 value and an average F_2 value using all six repetitions. When additional repetitions are required at any pitch angle, move the probe by at least 5° and then return to the specified pitch angle before taking the next measurement. Record the average values on a form similar to Table 2F–9.

10.6.14 Repeat the calibration procedures in sections 10.6.5 through 10.6.13 at the second selected nominal wind tunnel velocity setting.

10.6.15 Velocity drift check. The following check shall be performed, except when paired calibration pitot tube and tested probe pressure measurements are taken at each pitch angle setting. At each velocity setting, calculate the percent difference between consecutive differential pressure measurements made with the calibration pitot tube. If a measurement differs from the previous measurement by more than 2 percent or 0.25 mm H_2O (0.01 in. H_2O), whichever is less restrictive, the calibration data collected between these calibration pitot tube measurements may not be used, and the measurements shall be repeated.

10.6.16 Compare the averaged F_2 coefficients obtained from the calibrations at the two selected nominal velocities, as follows. At each pitch angle setting, use Equation 2F–3 to calculate the difference between the corresponding average F_2 values at the two calibration velocities. At each pitch angle in the −15° to + 15° range, the percent difference between the average F_2 values shall not exceed 3.0 percent. For pitch angles outside this range (i.e., less than −15°0 and greater than + 15°), the percent difference shall not exceed 5.0 percent.

10.6.16.1 If the applicable specification in section 10.6.16 is met at each pitch angle setting, average the results obtained at the two nominal calibration velocities to produce a calibration record of F_1 and F_2 at each pitch angle tested. Record these values on a form similar to Table 2F–9. From these values, generate one calibration curve representing F_1 versus pitch angle and a second curve representing F_2 versus pitch angle. Computer spreadsheet programs may be used to graph the calibration data and to develop polynomial equations that can be used to calculate pitch angles and axial velocities.

10.6.16.2 If the applicable specification in section 10.6.16 is exceeded at any pitch angle setting, the probe shall not be used unless: (1) the calibration is repeated at that pitch angle and acceptable results are obtained or (2) values of F_1 and F_2 are obtained at two nominal velocities for which the specifications in section 10.6.16 are met across the entire pitch angle range.

10.7 Recalibration. Recalibrate the probe using the procedures in section 10 either within 12 months of its first field use after its most recent calibration or after 10 field tests (as defined in section 3.4), whichever occurs later. In addition, whenever there is visible damage to the 3-D head, the probe shall be recalibrated before it is used again.

10.8 Calibration of pressure-measuring devices used in field tests. Before its initial use in a field test, calibrate each pressure-measuring device (except those used exclusively for yaw nulling) using the three-point calibration procedure described in section 10.3.3. The device shall be recalibrated according to the procedure in section 10.3.3 no later than 90 days after its first field use following its most recent calibration. At the discretion of the tester, more frequent calibrations (e.g., after a field test) may be performed. No adjustments, other than adjustments to the zero setting, shall be made to the device between calibrations.

10.8.1 Post-test calibration check. A single-point calibration check shall be performed on each pressure-measuring device after completion of each field test. At the discretion of the tester, more frequent single-point calibration checks (e.g., after one or more field test runs) may be performed. It is recommended that the post-test check be performed before leaving the field test site. The check shall be performed at a pressure between 50 and 90 percent of full scale by taking a common pressure reading with the tested device and a reference pressure-measuring device (as described in section 6.4.4) or by challenging the tested device with a reference pressure source (as described in section 6.4.4) or by performing an equivalent check using a reference device approved by the Administrator.

10.8.2 Acceptance criterion. At the selected pressure setting, the pressure readings made using the reference device and the tested device shall agree to within 3 percent of full scale of the tested device or 0.8 mm H_2O (0.03 in. H_2O), whichever is less restrictive. If this

specification is met, the test data collected during the field test are valid. If the specification is not met, all test data collected since the last successful calibration or calibration check are invalid and shall be repeated using a pressure-measuring device with a current, valid calibration. Any device that fails the calibration check shall not be used in a field test until a successful recalibration is performed according to the procedures in section 10.3.3.

10.9 Temperature Gauges. Same as Method 2, section 4.3. The alternative thermocouple calibration procedures outlined in Emission Measurement Center (EMC) Approved Alternative Method (ALT–011) ''Alternative Method 2 Thermocouple Calibration Procedure'' may be performed. Temperature gauges shall be calibrated no more than 30 days prior to the start of a field test or series of field tests and recalibrated no more than 30 days after completion of a field test or series of field tests.

10.10 Barometer. Same as Method 2, section 4.4. The barometer shall be calibrated no more than 30 days prior to the start of a field test or series of field tests.

11.0 Analytical Procedure

Sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Data Analysis and Calculations

These calculations use the measured yaw angle, derived pitch angle, and the differential pressure and temperature measurements at individual traverse points to derive the axial flue gas velocity ($v_{a(i)}$) at each of those points. The axial velocity values at all traverse points that comprise a full stack or duct traverse are then averaged to obtain the average axial flue gas velocity ($v_{a\ (avg)}$). Round off figures only in the final calculation of reported values.

12.1 Nomenclature

A = Cross-sectional area of stack or duct, m^2 (ft^2).

B_{ws} = Water vapor in the gas stream (from Method 4 or alternative), proportion by volume.

K_p Conversion factor (a constant),

$$34.97\frac{m}{sec}\left[\frac{(g/g\text{-}mole)(mm\ Hg)}{(^\circ K)(mm\ H_2O)}\right]^{1/2}$$

for the metric system, and

$$85.49\frac{ft}{sec}\left[\frac{(lb/lb\text{-}mole)(in.\ Hg)}{(^\circ R)(in.\ H_2O)}\right]^{1/2}$$

for the English system.

M_d = Molecular weight of stack or duct gas, dry basis (see section 8.13), g/g-mole (lb/lb-mole).

M_s = Molecular weight of stack or duct gas, wet basis, g/g-mole (lb/lb-mole).

$$M_s = M_d(1-B_{ws}) + 18.0B_{ws} \qquad \text{Eq. 2F-4}$$

P_{bar} = Barometric pressure at measurement site, mm Hg (in. Hg).

P_g = Stack or duct static pressure, mm H_2O (in. H_2O).

P_s = Absolute stack or duct pressure, mm Hg (in. Hg),

$$P_s = P_{bar} + \frac{P_g}{13.6} \qquad \text{Eq. 2F-5}$$

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

13.6 = Conversion from mm H_2O (in. H_2O) to mm Hg (in. Hg).

Q_{sd} = Average dry-basis volumetric stack or duct gas flow rate corrected to standard conditions, dscm/hr (dscf/hr).

Q_{sw} = Average wet-basis volumetric stack or duct gas flow rate corrected to standard conditions, wscm/hr (wscf/hr).

$T_{s(avg)}$ = Average absolute stack or duct gas temperature across all traverse points.

$t_{s(i)}$ = Stack or duct gas temperature, C (F), at traverse point i.

$T_{s(i)}$ = Absolute stack or duct gas temperature, K (R), at traverse point i,

$$T_{s(i)} = 273 + t_{s(i)} \qquad \text{Eq. 2F-6}$$

for the metric system, and

$$T_{s(i)} = 460 + t_{s(i)} \qquad \text{Eq. 2F-7}$$

for the English system.

T_{std} = Standard absolute temperature, 293 °K (528 °R).

$F_{1(i)}$ = Pitch angle ratio, applicable at traverse point i, dimensionless.

$F_{2(i)}$ = 3-D probe velocity calibration coefficient, applicable at traverse point i, dimensionless.

$(P_4\text{-}P_5)_i$ = Pitch differential pressure of stack or duct gas flow, mm H_2O (in. H_2O), at traverse point i.

$(P_1\text{-}P_2)_i$ = Velocity head (differential pressure) of stack or duct gas flow, mm H_2O (in. H_2O), at traverse point i.

$v_{a(i)}$ = Reported stack or duct gas axial velocity, m/sec (ft/sec), at traverse point i.

$v_{a(avg)}$ = Average stack or duct gas axial velocity, m/sec (ft/sec), across all traverse points.

3,600 = Conversion factor, sec/hr.

18.0 = Molecular weight of water, g/g-mole (lb/lb-mole).

$\theta_{y(i)}$ = Yaw angle, degrees, at traverse point i.

$\theta_{p(i)}$ = Pitch angle, degrees, at traverse point i.

n = Number of traverse points.

12.2 Traverse Point Velocity Calculations. Perform the following calculations from the measurements obtained at each traverse point.

12.2.1 Selection of calibration curves. Select calibration curves as described in section 10.6.1.

12.2.2 Traverse point pitch angle ratio. Use Equation 2F–1, as described in section 10.6.2, to calculate the pitch angle ratio, $F_{1(i)}$, at each traverse point.

12.2.3 Pitch angle. Use the pitch angle ratio, $F_{1(i)}$, to derive the pitch angle, $\theta_{p(i)}$, at traverse point i from the F_1 versus pitch angle calibration curve generated under section 10.6.16.1.

12.2.4 Velocity calibration coefficient. Use the pitch angle, $\theta_{p(i)}$, to obtain the probe velocity calibration coefficient, $F_{2(i)}$, at traverse point i from the ''velocity pressure calibration curve,'' i.e., the F_2 versus pitch angle calibration curve generated under section 10.6.16.1.

12.2.5 Axial velocity. Use the following equation to calculate the axial velocity, $v_{a(i)}$, from the differential pressure $(P_1\text{-}P_2)_i$ and yaw angle, $\theta_{y(i)}$, measured at traverse point i and the previously calculated values for the velocity calibration coefficient, $F_{2(i)}$, absolute stack or duct standard temperature, $T_{s(i)}$, absolute stack or duct pressure, P_s, molecular weight, M_s, and pitch angle, ''$\theta_{p(i)}$.

$$v_{a(i)} = K_p F_{2(i)} \sqrt{\frac{(P_1 - P_2)_i T_{s(i)}}{P_s M_s}} \left(\cos\theta_{y(i)}\right)\left(\cos\theta_{p(i)}\right) \qquad \text{Eq. 2F-8}$$

12.2.6 Handling multiple measurements at a traverse point. For pressure or temperature devices that take multiple measurements at a traverse point, the multiple measurements (or where applicable, their square roots) may first be averaged and the resulting average values used in the equations above. Alternatively, the individual measurements may be used in the equations above and the resulting multiple calculated values may then be averaged to obtain a single traverse point value. With either approach, all of the individual measurements recorded at a traverse point must be used in calculating the applicable traverse point value.

12.3 Average Axial Velocity in Stack or Duct. Use the reported traverse point axial velocity in the following equation.

$$v_{a(avg)} = \frac{\sum_{i=1}^{n} v_{a(i)}}{n} \qquad \text{Eq. 2F-9}$$

12.4 Acceptability of Results. The test results are acceptable and the calculated value of $v_{a(avg)}$ may be reported as the average axial velocity for the test run if the conditions in either section 12.4.1 or 12.4.2 are met.

12.4.1 The calibration curves were generated at nominal velocities of 18.3 m/sec and 27.4 m/sec (60 ft/sec and 90 ft/sec).

12.4.2 The calibration curves were generated at nominal velocities other than 18.3 m/sec and 27.4 m/sec (60 ft/sec and 90 ft/sec), and the value of $v_{a(avg)}$ obtained using Equation 2F–9 is less than or equal to at least one of the nominal velocities used to derive the F_1 and F_2 calibration curves.

12.4.3 If the conditions in neither section 12.4.1 nor section 12.4.2 are met, the test results obtained in Equation 2F–9 are not acceptable, and the steps in sections 12.2 and 12.3 must be repeated using a set of F_1 and F_2 calibration curves that satisfies the conditions specified in section 12.4.1 or 12.4.2.

12.5 Average Gas Wet Volumetric Flow Rate in Stack or Duct. Use the following equation to compute the average volumetric flow rate on a wet basis.

$$Q_{sw} = 3{,}600\left(v_{a(avg)}\right)(A)\left(\frac{T_{std}}{T_{s(avg)}}\right)\left(\frac{P_s}{P_{std}}\right) \qquad \text{Eq. 2F-10}$$

12.6 Average Gas Dry Volumetric Flow Rate in Stack or Duct. Use the following equation to compute the average volumetric flow rate on a dry basis.

$$Q_{sd} = 3{,}600(1 - B_{ws})(v_{a(avg)})(A)\left(\frac{T_{std}}{T_{s(avg)}}\right)\left(\frac{P_s}{P_{std}}\right) \qquad \text{Eq. 2F-11}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Reporting

16.1 Field Test Reports. Field test reports shall be submitted to the Agency according to applicable regulatory requirements. Field test reports should, at a minimum, include the following elements.

16.1.1 Description of the source. This should include the name and location of the test site, descriptions of the process tested, a description of the combustion source, an accurate diagram of stack or duct cross-sectional area at the test site showing the dimensions of the stack or duct, the location of the test ports, and traverse point locations and identification numbers or codes. It should also include a description and diagram of the stack or duct layout, showing the distance of the test location from the nearest upstream and downstream disturbances and all structural elements (including breachings, baffles, fans, straighteners, etc.) affecting the flow pattern. If the source and test location descriptions have been previously submitted to the Agency in a document (e.g., a monitoring plan or test plan), referencing the document in lieu of including this information in the field test report is acceptable.

16.1.2 Field test procedures. These should include a description of test equipment and test procedures. Testing conventions, such as traverse point numbering and measurement sequence (e.g., sampling from center to wall, or wall to center), should be clearly stated. Test port identification and directional reference for each test port should be included on the appropriate field test data sheets.

16.1.3 Field test data.

16.1.3.1 Summary of results. This summary should include the dates and times of testing and the average axial gas velocity and the average flue gas volumetric flow results for each run and tested condition.

16.1.3.2 Test data. The following values for each traverse point should be recorded and reported:

(a) P_1-P_2 and P_4-P_5 differential pressures

(b) Stack or duct gas temperature at traverse point i ($t_{s(i)}$)

(c) Absolute stack or duct gas temperature at traverse point i ($T_{s(i)}$)

(d) Yaw angle at each traverse point i ($\theta_{y(i)}$)

(e) Pitch angle at each traverse point i ($\theta_{p(i)}$)

(f) Stack or duct gas axial velocity at traverse point i ($v_{a(i)}$)

16.1.3.3 The following values should be reported once per run:

(a) Water vapor in the gas stream (from Method 4 or alternative), proportion by volume (B_{ws}), measured at the frequency specified in the applicable regulation

(b) Molecular weight of stack or duct gas, dry basis (M_d)

(c) Molecular weight of stack or duct gas, wet basis (M_s)

(d) Stack or duct static pressure (P_g)

(e) Absolute stack or duct pressure (P_s)

(f) Carbon dioxide concentration in the flue gas, dry basis (%$_d$ CO_2)

(g) Oxygen concentration in the flue gas, dry basis (%$_d$ O_2)

(h) Average axial stack or duct gas velocity ($v_{a(avg)}$) across all traverse points

(i) Gas volumetric flow rate corrected to standard conditions, dry or wet basis as required by the applicable regulation (Q_{sd} or Q_{sw})

16.1.3.4 The following should be reported once per complete set of test runs:

(a) Cross-sectional area of stack or duct at the test location (A)

(b) Measurement system response time (sec)

(c) Barometric pressure at measurement site (P_{bar})

16.1.4 Calibration data. The field test report should include calibration data for all probes and test equipment used in the field test. At a minimum, the probe calibration data reported to the Agency should include the following:

(a) Date of calibration

(b) Probe type

(c) Probe identification number(s) or code(s)

(d) Probe inspection sheets

(e) Pressure measurements and intermediate calculations of F_1 and F_2 at each pitch angle used to obtain calibration curves in accordance with section 10.6 of this method

(f) Calibration curves (in graphic or equation format) obtained in accordance with sections 10.6.11 of this method

(g) Description and diagram of wind tunnel used for the calibration, including dimensions of cross-sectional area and position and size of the test section

(h) Documentation of wind tunnel qualification tests performed in accordance with section 10.1 of this method

16.1.5 Quality Assurance. Specific quality assurance and quality control procedures used during the test should be described.

17.0 Bibliography

(1) 40 CFR Part 60, Appendix A, Method 1—Sample and velocity traverses for stationary sources.

(2) 40 CFR Part 60, Appendix A, Method 2H—Determination of stack gas velocity taking into account velocity decay near the stack wall.

(3) 40 CFR Part 60, Appendix A, Method 2—Determination of stack gas velocity and volumetric flow rate (Type S pitot tube).

(4) 40 CFR Part 60, Appendix A, Method 3—Gas analysis for carbon dioxide, oxygen, excess air, and dry molecular weight.

(5) 40 CFR Part 60, Appendix A, Method 3A—Determination of oxygen and carbon dioxide concentrations in emissions from stationary sources (instrumental analyzer procedure).

(6) 40 CFR Part 60, Appendix A, Method 4—Determination of moisture content in stack gases.

(7) Emission Measurement Center (EMC) Approved Alternative Method (ALT–011) ''Alternative Method 2 Thermocouple Calibration Procedure.''

(8) Electric Power Research Institute, Interim Report EPRI TR–106698, ''Flue Gas Flow Rate Measurement Errors,'' June 1996.

(9) Electric Power Research Institute, Final Report EPRI TR–108110, ''Evaluation of Heat Rate Discrepancy from Continuous Emission Monitoring Systems,'' August 1997.

(10) Fossil Energy Research Corporation, Final Report, ''Velocity Probe Tests in Non-axial Flow Fields,'' November 1998, Prepared for the U.S. Environmental Protection Agency.

(11) Fossil Energy Research Corporation, ''Additional Swirl Tunnel Tests: E-DAT and T-DAT Probes,'' February 24, 1999, Technical Memorandum Prepared for U.S. Environmental Protection Agency, P.O. No. 7W–1193–NALX.

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(15) National Institute of Standards and Technology, 1998, ''Report of Special Test of Air Speed Instrumentation, Five Autoprobes,'' Prepared for the U.S. Environmental Protection Agency under IAG #DW13938432–01–0.

(16) National Institute of Standards and Technology, 1998, ''Report of Special Test of Air Speed Instrumentation, Eight Spherical Probes,'' Prepared for the U.S. Environmental Protection Agency under IAG #DW13938432–01–0.

(17) National Institute of Standards and Technology, 1998, ''Report of Special Test of Air Speed Instrumentation, Four DAT Probes,'' Prepared for the U.S. Environmental Protection Agency under IAG #DW13938432–01–0.

(18) Norfleet, S.K., ''An Evaluation of Wall Effects on Stack Flow Velocities and Related Overestimation Bias in EPA's Stack Flow Reference Methods,'' EPRI CEMS User's Group Meeting, New Orleans, Louisiana, May 13–15, 1998.

(19) Page, J.J., E.A. Potts, and R.T. Shigehara, ''3–D Pitot Tube Calibration Study,'' EPA Contract No. 68–D1–0009, Work Assignment No. I–121, March 11, 1993.

(20) Shigehara, R.T., W.F. Todd, and W.S. Smith, ''Significance of Errors in Stack Sampling Measurements,'' Presented at the Annual Meeting of the Air Pollution Control Association, St. Louis, Missouri, June 14–19, 1970.

(21) The Cadmus Group, Inc., May 1999, ''EPA Flow Reference Method Testing and Analysis: Findings Report,'' EPA/430–R–99–009.

(22) The Cadmus Group, Inc., 1998, ''EPA Flow Reference Method Testing and Analysis: Data Report, Texas Utilities, DeCordova Steam Electric Station, Volume I: Test Description and Appendix A (Data Distribution Package),'' EPA/430–R–98–015a.

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18.0 Annexes

Annex A, C, and D describe recommended procedures for meeting certain provisions in sections 8.3, 10.4, and 10.5 of this method. Annex B describes procedures to be followed

when using the protractor wheel and pointer assembly to measure yaw angles, as provided under section 8.9.1.

18.1 Annex A—Rotational Position Check. The following are recommended procedures that may be used to satisfy the rotational position check requirements of section 8.3 of this method and to determine the angle-measuring device rotational offset R_{ADO}.

18.1.1 Rotational position check with probe outside stack. Where physical constraints at the sampling location allow full assembly of the probe outside the stack and insertion into the test port, the following procedures should be performed before the start of testing. Two angle-measuring devices that meet the specifications in section 6.2.1 or 6.2.3 are required for the rotational position check. An angle measuring device whose position can be independently adjusted (e.g., by means of a set screw) after being locked into position on the probe sheath shall not be used for this check unless the independent adjustment is set so that the device performs exactly like a device without the capability for independent adjustment. That is, when aligned on the probe such a device must give the same reading as a device that does not have the capability of being independently adjusted. With the fully assembled probe (including probe shaft extensions, if any) secured in a horizontal position, affix one yaw angle-measuring device to the probe sheath and lock it into position on the reference scribe line specified in section 6.1.6.1. Position the second angle-measuring device using the procedure in section 18.1.1.1 or 18.1.1.2.

18.1.1.1 Marking procedure. The procedures in this section should be performed at each location on the fully assembled probe where the yaw angle-measuring device will be mounted during the velocity traverse. Place the second yaw angle-measuring device on the main probe sheath (or extension) at the position where a yaw angle will be measured during the velocity traverse. Adjust the position of the second angle-measuring device until it indicates the same angle (±1°) as the reference device, and affix the second device to the probe sheath (or extension). Record the angles indicated by the two angle-measuring devices on a form similar to Table 2F–2. In this position, the second angle-measuring device is considered to be properly positioned for yaw angle measurement. Make a mark, no wider than 1.6 mm (1/16 in.), on the probe sheath (or extension), such that the yaw angle-measuring device can be re-affixed at this same properly aligned position during the velocity traverse.

18.1.1.2 Procedure for probe extensions with scribe lines. If, during a velocity traverse the angle-measuring device will be affixed to a probe extension having a scribe line as specified in section 6.1.6.2, the following procedure may be used to align the extension's scribe line with the reference scribe line instead of marking the extension as described in section 18.1.1.1. Attach the probe extension to the main probe. Align and lock the second angle-measuring device on the probe extension's scribe line. Then, rotate the extension until both measuring devices indicate the same angle (±1°). Lock the extension at this rotational position. Record the angles indicated by the two angle-measuring devices on a form similar to Table 2F–2. An angle-measuring device may be aligned at any position on this scribe line during the velocity traverse, if the scribe line meets the alignment specification in section 6.1.6.3.

18.1.1.3 Post-test rotational position check. If the fully assembled probe includes one or more extensions, the following check should be performed immediately after the completion of a velocity traverse. At the discretion of the tester, additional checks may be conducted after completion of testing at any sample port. Without altering the alignment of any of the components of the probe assembly used in the velocity traverse, secure the fully assembled probe in a horizontal position. Affix an angle-measuring device at the reference scribe line specified in section 6.1.6.1. Use the other angle-measuring device to check the angle at each location where the device was checked prior to testing. Record the readings from the two angle-measuring devices.

18.1.2 Rotational position check with probe in stack. This section applies only to probes that, due to physical constraints, cannot be inserted into the test port as fully assembled with all necessary extensions needed to reach the inner-most traverse point(s).

18.1.2.1 Perform the out-of-stack procedure in section 18.1.1 on the main probe and any attached extensions that will be initially inserted into the test port.

18.1.2.2 Use the following procedures to perform additional rotational position check(s) with the probe in the stack, each time a probe extension is added. Two angle-measuring devices are required. The first of these is the device that was used to measure yaw angles at the preceding traverse point, left in its properly aligned measurement position. The second angle-measuring device is positioned on the added probe extension. Use the applicable procedures in section 18.1.1.1 or 18.1.1.2 to align, adjust, lock, and mark (if necessary) the position of the second angle-measuring device to within ±1° of the first device. Record the readings of the two devices on a form similar to Table 2F–2.

18.1.2.3 The procedure in section 18.1.2.2 should be performed at the first port where measurements are taken. The procedure should be repeated each time a probe extension is re-attached at a subsequent port, unless the probe extensions are designed to be locked into a mechanically fixed rotational position (e.g., through use of interlocking

grooves), which can be reproduced from port to port as specified in section 8.3.5.2.

18.2 Annex B—Angle Measurement Protocol for Protractor Wheel and Pointer Device. The following procedure shall be used when a protractor wheel and pointer assembly, such as the one described in section 6.2.2 and illustrated in Figure 2F–7 is used to measure the yaw angle of flow. With each move to a new traverse point, unlock, realign, and re-lock the probe, angle-pointer collar, and protractor wheel to each other. At each such move, particular attention is required to ensure that the scribe line on the angle pointer collar is either aligned with the reference scribe line on the main probe sheath or is at the rotational offset position established under section 8.3.1. The procedure consists of the following steps:

18.2.1 Affix a protractor wheel to the entry port for the test probe in the stack or duct.

18.2.2 Orient the protractor wheel so that the 0° mark corresponds to the longitudinal axis of the stack or duct. For stacks, vertical ducts, or ports on the side of horizontal ducts, use a digital inclinometer meeting the specifications in section 6.2.1 to locate the 0° orientation. For ports on the top or bottom of horizontal ducts, identify the longitudinal axis at each test port and permanently mark the duct to indicate the 0° orientation. Once the protractor wheel is properly aligned, lock it into position on the test port.

18.2.3 Move the pointer assembly along the probe sheath to the position needed to take measurements at the first traverse point. Align the scribe line on the pointer collar with the reference scribe line or at the rotational offset position established under section 8.3.1. Maintaining this rotational alignment, lock the pointer device onto the probe sheath. Insert the probe into the entry port to the depth needed to take measurements at the first traverse point.

18.2.4 Perform the yaw angle determination as specified in sections 8.9.3 and 8.9.4 and record the angle as shown by the pointer on the protractor wheel. Then, take velocity pressure and temperature measurements in accordance with the procedure in section 8.9.5. Perform the alignment check described in section 8.9.6.

18.2.5 After taking velocity pressure measurements at that traverse point, unlock the probe from the collar and slide the probe through the collar to the depth needed to reach the next traverse point.

18.2.6 Align the scribe line on the pointer collar with the reference scribe line on the main probe or at the rotational offset position established under section 8.3.1. Lock the collar onto the probe.

18.2.7 Repeat the steps in sections 18.2.4 through 18.2.6 at the remaining traverse points accessed from the current stack or duct entry port.

18.2.8 After completing the measurement at the last traverse point accessed from a port, verify that the orientation of the protractor wheel on the test port has not changed over the course of the traverse at that port. For stacks, vertical ducts, or ports on the side of horizontal ducts, use a digital inclinometer meeting the specifications in section 6.2.1 to check the rotational position of the 0° mark on the protractor wheel. For ports on the top or bottom of horizontal ducts, observe the alignment of the angle wheel 0° mark relative to the permanent 0° mark on the duct at that test port. If these observed comparisons exceed ±2° of 0°, all angle and pressure measurements taken at that port since the protractor wheel was last locked into position on the port shall be repeated.

18.2.9 Move to the next stack or duct entry port and repeat the steps in sections 18.2.1 through 18.2.8.

18.3 Annex C—Guideline for Reference Scribe Line Placement. Use of the following guideline is recommended to satisfy the requirements of section 10.4 of this method. The rotational position of the reference scribe line should be either 90° or 180° from the probe's impact pressure port.

18.4 Annex D—Determination of Reference Scribe Line Rotational Offset. The following procedures are recommended for determining the magnitude and sign of a probe's reference scribe line rotational offset, R_{SLO}. Separate procedures are provided for two types of angle-measuring devices: digital inclinometers and protractor wheel and pointer assemblies.

18.4.1 Perform the following procedures on the main probe with all devices that will be attached to the main probe in the field [such as thermocouples or resistance temperature detectors (RTDs)] that may affect the flow around the probe head. Probe shaft extensions that do not affect flow around the probe head need not be attached during calibration.

18.4.2 The procedures below assume that the wind tunnel duct used for probe calibration is horizontal and that the flow in the calibration wind tunnel is axial as determined by the axial flow verification check described in section 10.1.2. Angle-measuring devices are assumed to display angles in alternating 0° to 90° and 90° to 0° intervals. If angle-measuring devices with other readout conventions are used or if other calibration wind tunnel duct configurations are used, make the appropriate calculational corrections.

18.4.2.1 Position the angle-measuring device in accordance with one of the following procedures.

18.4.2.1.1 If using a digital inclinometer, affix the calibrated digital inclinometer to the probe. If the digital inclinometer can be independently adjusted after being locked

into position on the probe sheath (e.g., by means of a set screw), the independent adjustment must be set so that the device performs exactly like a device without the capability for independent adjustment. That is, when aligned on the probe the device must give the same readings as a device that does not have the capability of being independently adjusted. Either align it directly on the reference scribe line or on a mark aligned with the scribe line determined according to the procedures in section 18.1.1.1. Maintaining this rotational alignment, lock the digital inclinometer onto the probe sheath.

18.4.2.1.2 If using a protractor wheel and pointer device, orient the protractor wheel on the test port so that the 0° mark is aligned with the longitudinal axis of the wind tunnel duct. Maintaining this alignment, lock the wheel into place on the wind tunnel test port. Align the scribe line on the pointer collar with the reference scribe line or with a mark aligned with the reference scribe line, as determined under section 18.1.1.1. Maintaining this rotational alignment, lock the pointer device onto the probe sheath.

18.4.2.2 Zero the pressure-measuring device used for yaw nulling.

18.4.2.3 Insert the probe assembly into the wind tunnel through the entry port, positioning the probe's impact port at the calibration location. Check the responsiveness of the pressure-measuring device to probe rotation, taking corrective action if the response is unacceptable.

18.4.2.4 Ensure that the probe is in a horizontal position using a carpenter's level.

18.4.2.5 Rotate the probe either clockwise or counterclockwise until a yaw null ($P_2 = P_3$) is obtained.

18.4.2.6 Read and record the value of θ_{null}, the angle indicated by the angle-measuring device at the yaw-null position. Record the angle reading on a form similar to Table 2F–6. Do not associate an algebraic sign with this reading.

18.4.2.7 Determine the magnitude and algebraic sign of the reference scribe line rotational offset, R_{SLO}. The magnitude of R_{SLO} will be equal to either θ_{null} or $(90° - \theta_{null})$, depending on the angle-measuring device used. (See Table 2F–7 for a summary.) The algebraic sign of R_{SLO} will either be positive, if the rotational position of the reference scribe line is clockwise, or negative, if counterclockwise with respect to the probe's yaw-null position. Figure 2F–13 illustrates how the magnitude and sign of R_{SLO} are determined.

18.4.2.8 Perform the steps in sections 18.4.2.3 through 18.4.2.7 twice at each of the two calibration velocities selected for the probe under section 10.6. Record the values of R_{SLO} in a form similar to Table 2F–6.

18.4.2.9 The average of all R_{SLO} values is the reference scribe line rotational offset for the probe.

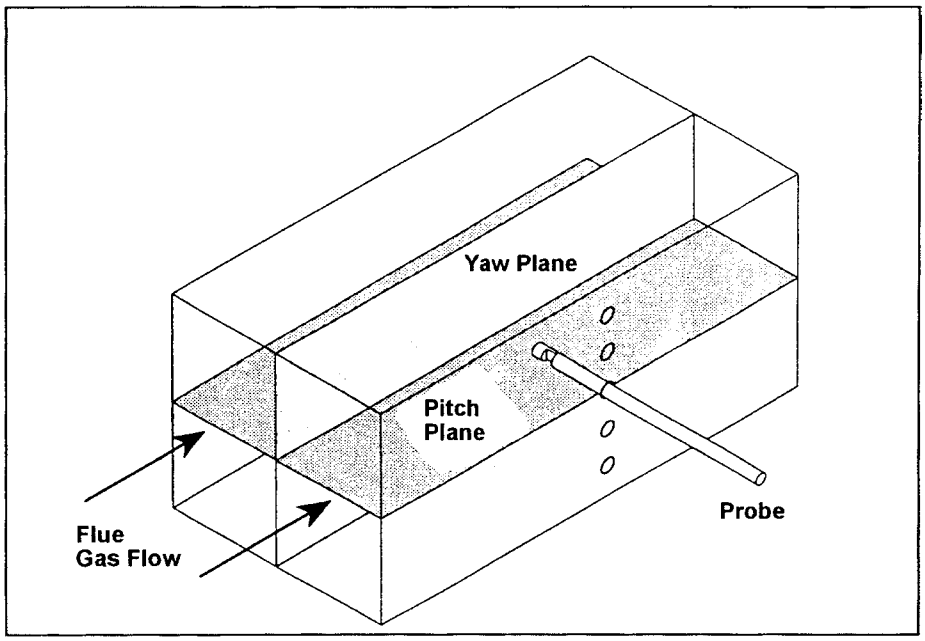


Figure 2F-1. Illustration of yaw and pitch planes in stack or duct.

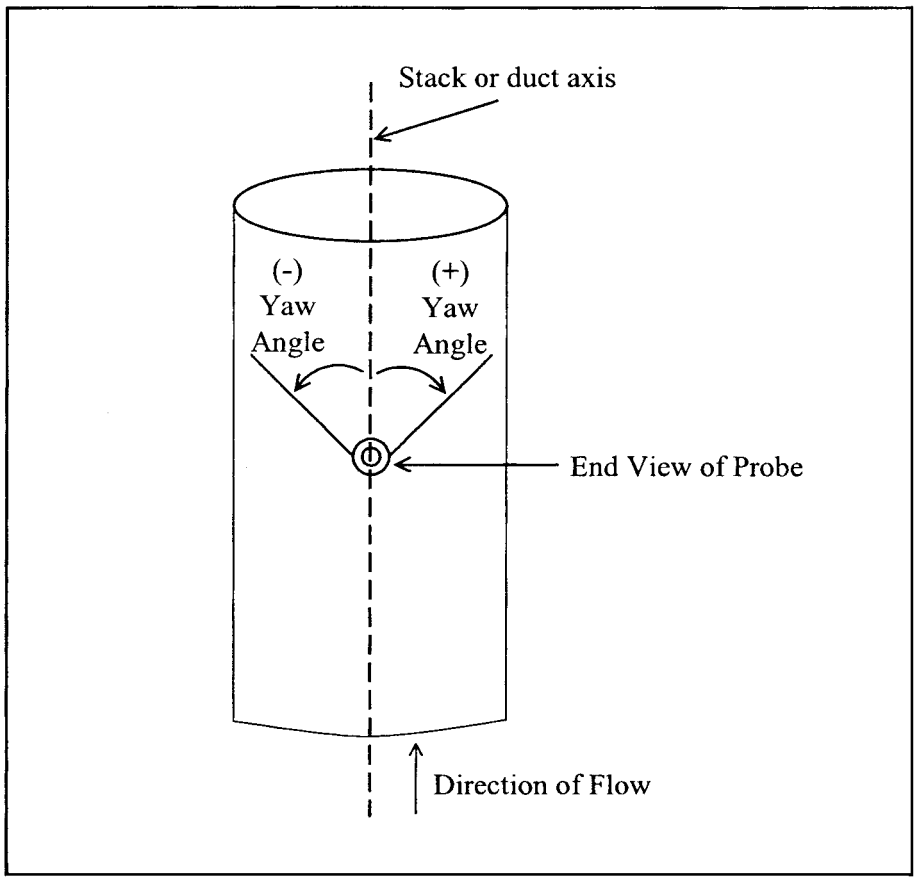


Figure 2F-2. Illustration of probe rotation representing positive and negative yaw angles.

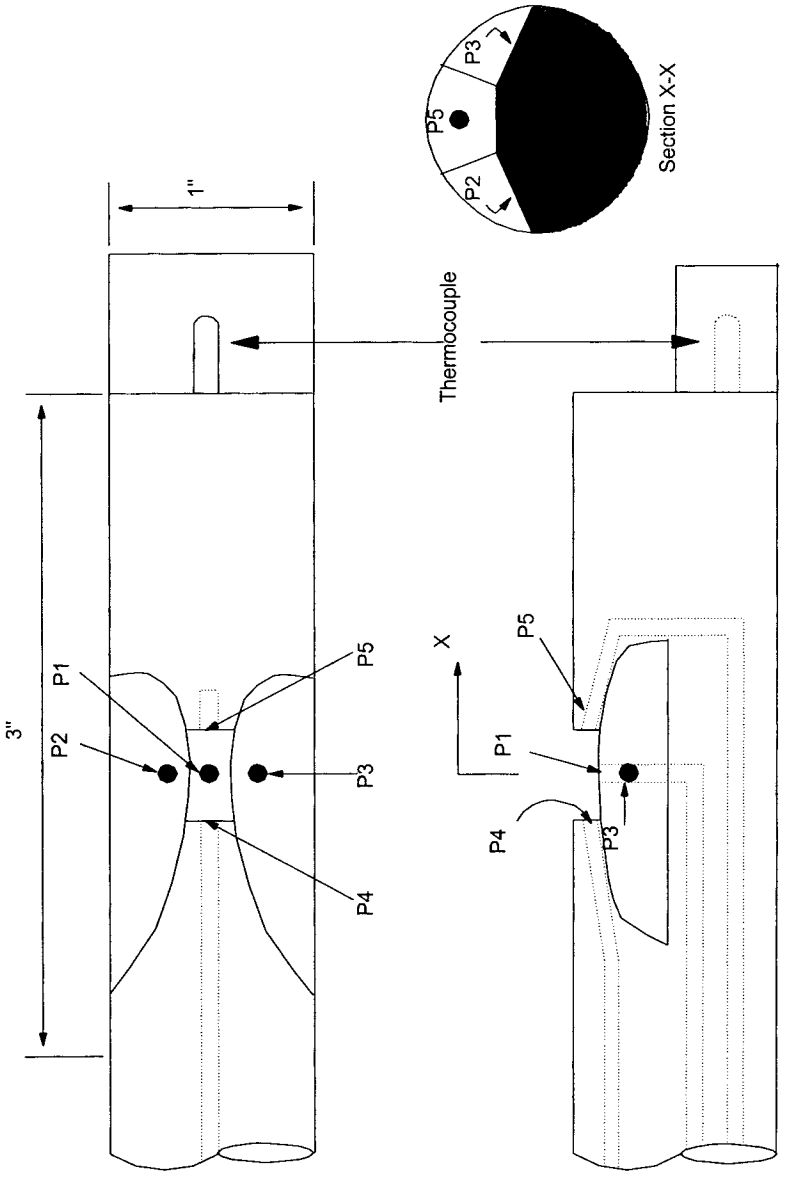


Figure 2F-3. Illustration of a five-hole prism-shaped (DAT) probe.

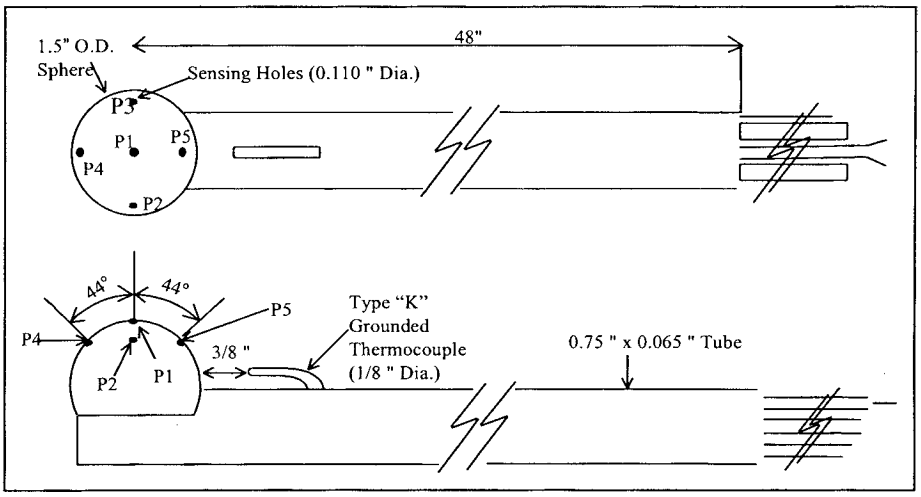


Figure 2F-4. Illustration of front and side view of spherical probe.

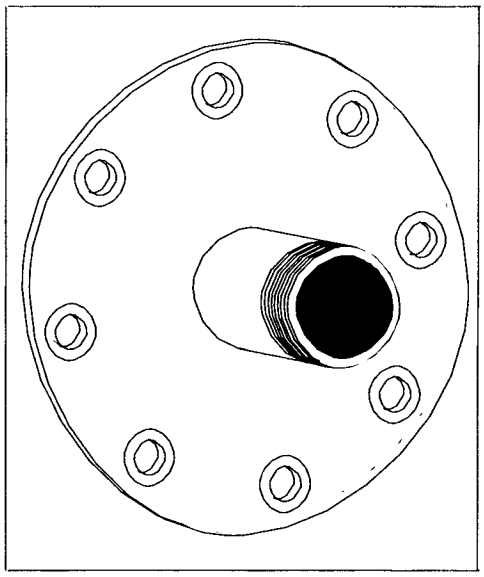


Figure 2F-5. Example bushing sleeve.

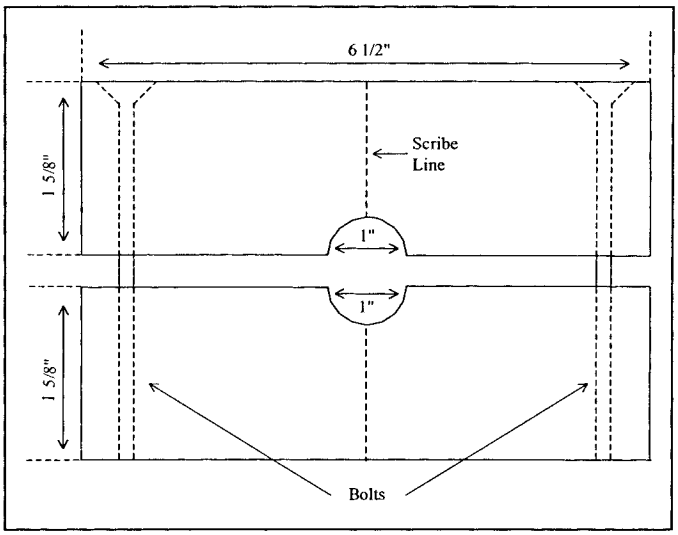


Figure 2F-6. Rotational position collar block.

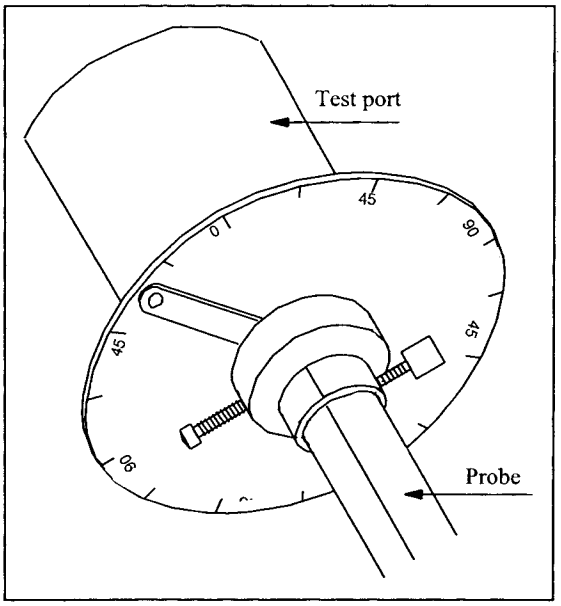


Figure 2F-7. Yaw angle protractor wheel and pointer.

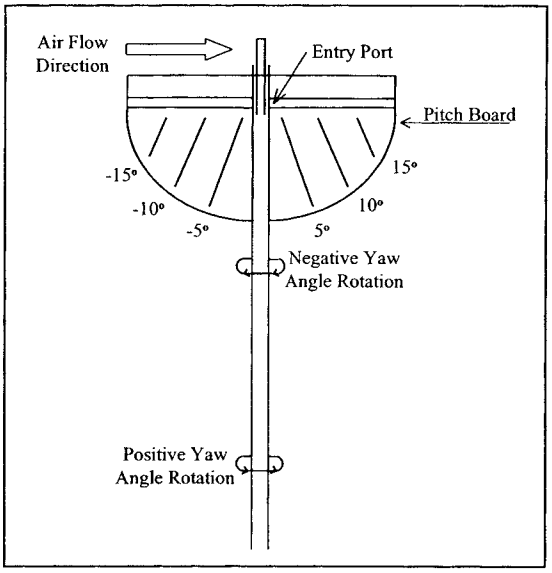


Figure 2F-8. Pitch angle protractor plate.

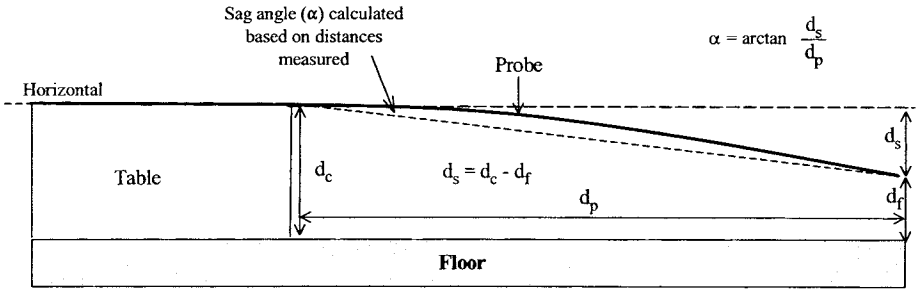


Figure 2F-9. Elements in horizontal straightness test using trigonometry.

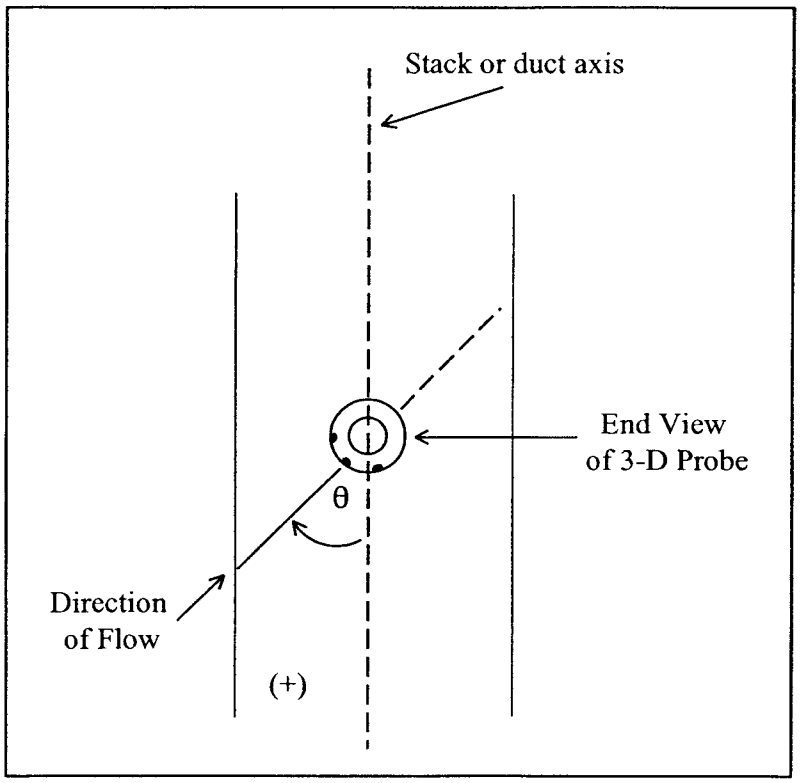


Figure 2F-10. Sign convention for the measured angle (θ) when the probe impact port is pointed directly into the flow. The angle θ is positive when the probe's impact pressure port is oriented in a clockwise rotational position relative to the stack or duct axis, as shown above and negative for a counterclockwise orientation.

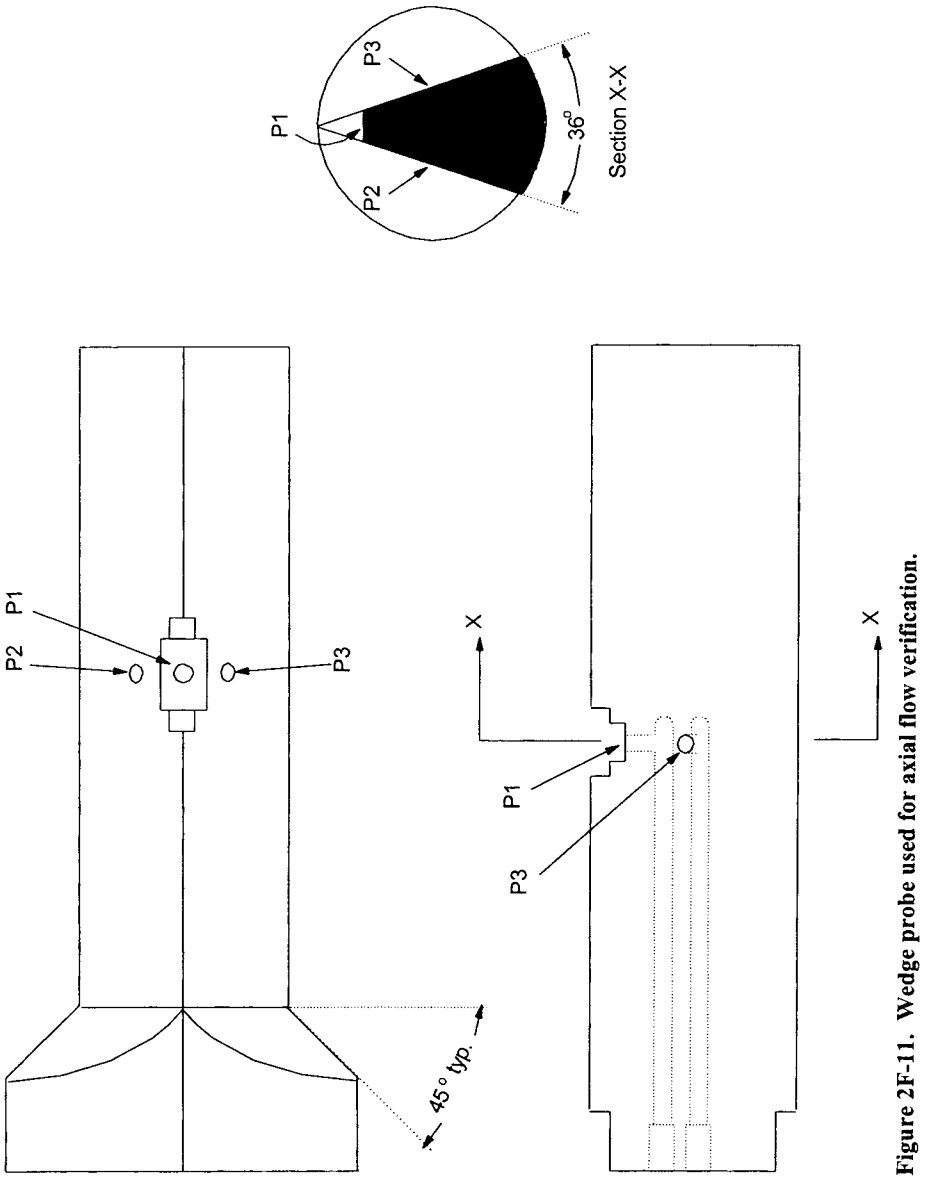


Figure 2F-11. Wedge probe used for axial flow verification.

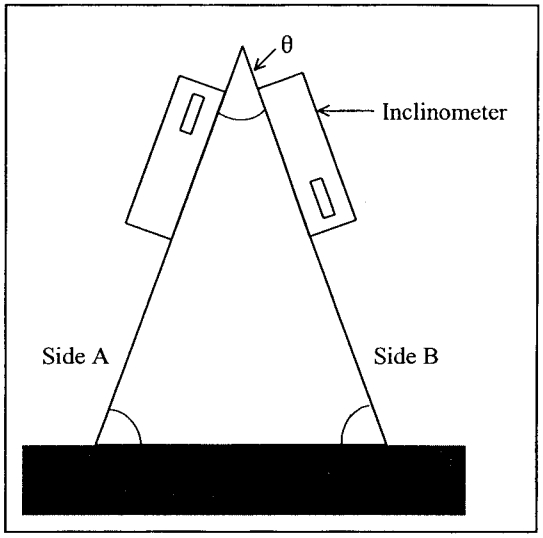


Figure 2F-12. Triangular block used for digital inclinometer calibration.

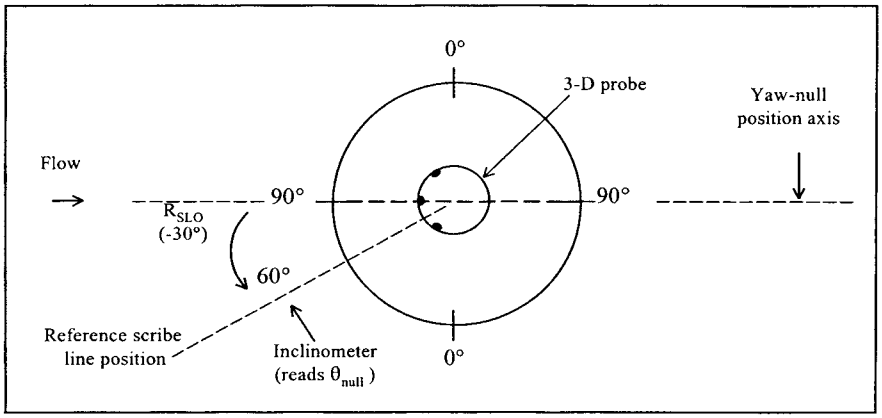


Figure 2F-13. Determination of reference scribe line rotational offset (R_{SLO}) in a horizontal wind tunnel with axial flow for a 3-D probe. The probe impact pressure port is aligned with the yaw-null position and is pointed into the flow. The inclinometer reads θ_{null}. The magnitude of $R_{SLO}=90°-\theta_{null}$ and the sign is a negative (counterclockwise from yaw-null position axis).

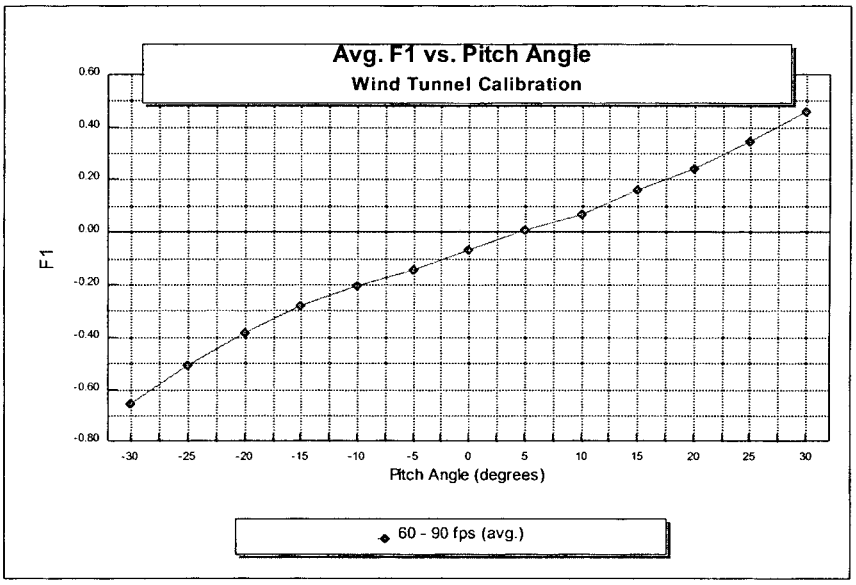


Figure 2F-14. Example F_1 calibration curve for the DAT probe.

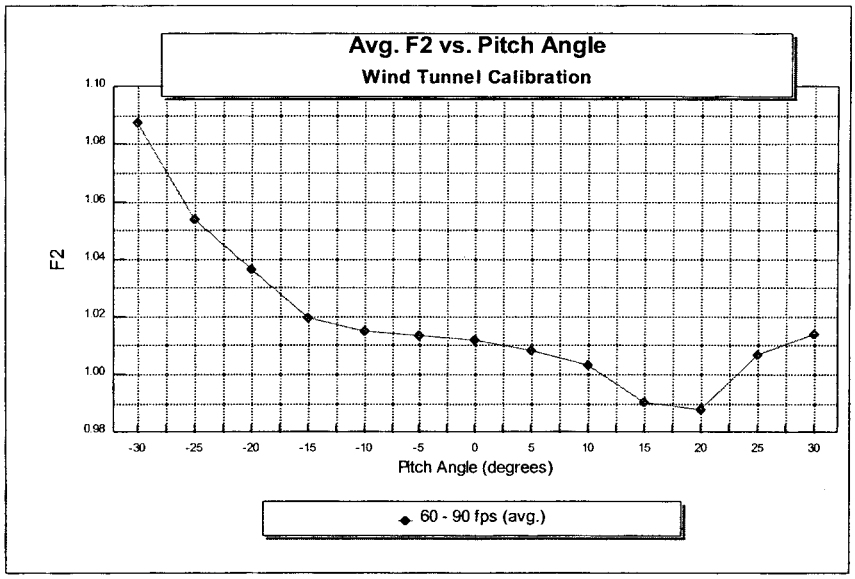


Figure 2F-15. Example F_2 calibration curve for the DAT probe.

Table 2F-1. 3-D Probe Inspection Sheet

Probe Type and ID # _____ **Date of most recent calibration**: _____
Fill in the tables below. For any item assigned a value of "1", show its location in the accompanying probe diagrams.

Inspection of Probe Ports

Port ID	Current Inspection (1=present, 0=absent)			Compared to Previous Calibration (1=changed, 0=unchanged)			Brief Description of Any Item with a Value of "1" in Preceding Columns
	Dents	Scratches	Asymmetries	Dents	Scratches	Asymmetries	
P1							
P2							
P3							
P4							
P5							

Inspection of Probe Surfaces

Surface ID	Current Inspection (1=present, 0=absent)		Compared to Previous Calibration (1=changed, 0=unchanged)		Brief Description of Any Item with a Value of "1" in Preceding Columns
	Scratches	Indentations	Scratches	Indentations	
S1					
S2					
S3					
S4					
S5					

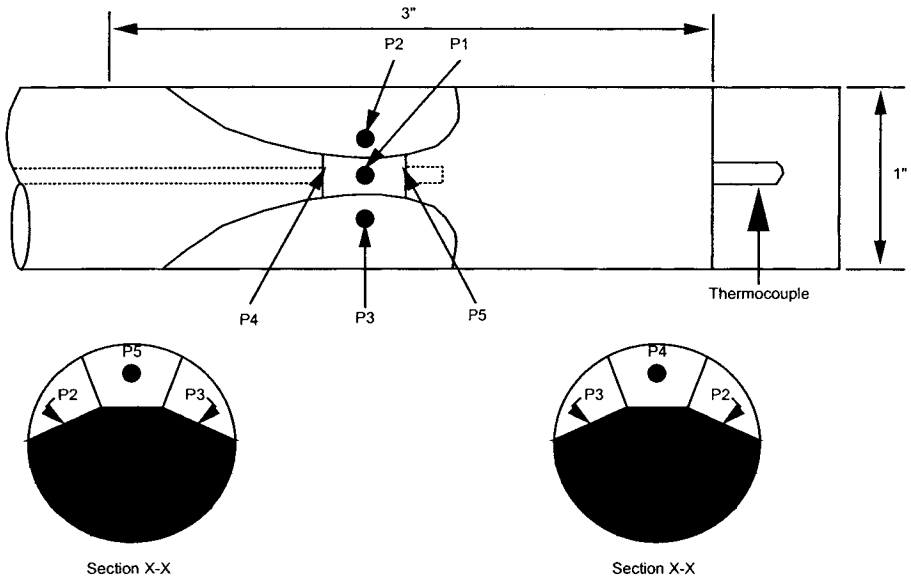
Surface IDs S1 through S5 refer to the surfaces adjacent to pressure ports with the corresponding numbers, e.g., S3 refers to the surface adjacent to pressure port P3.

QA/QC Check
Completeness ___ Legibility ___ Accuracy ___ Specifications ___ Reasonableness ___

Certification
I certify that the Probe ID _____ meets or exceeds all specifications, criteria, and/or applicable design features required under Method 2F.

Certified by: _____ Date: _____

Table 2F-1. 3-D Probe Inspection Sheet (continued)



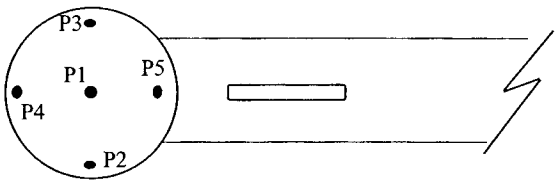


Table 2F-2. Rotational Position Check

Source: _____ Date: _____

Test Location: _____ Tester(s): _____

Probe Type: _____ Affiliation: _____

Probe ID: _____ Fully-Assembled Probe Length (in.): _____

Position	Angle Comparisons		
Distance of 2nd measurement device from probe head impact port in mm (in.)	1st Device Angle measured by device aligned on the reference scribe line, including algebraic sign (degrees)	2nd Device Angle measured by device mounted at each position to be used during testing, including algebraic sign (degrees)	R_{ADO} Difference between readings by 1st and 2nd angle-measuring devices (degrees)[a]
(Col. A)	(Col. B)	(Col. C)	(Col. C - Col. B)

[a] The algebraic sign must be consistent with section 8.3.2.

Specifications: For the pre-test rotational position check, the value of R_{ADO} at each location along the probe shaft must be determined to within ±1°. In the post-test check, R_{ADO} at each location must remain within ±2° of the value obtained in the pre-test check.

Table 2F-3. Example EPA Method 2F Field Data Form

Source: _____ Date: _____

Source Location: _____ Test Personnel: _____

Measurement Location: _____ Probe Type / ID: _____

Run ID:	
Start Time:	
End Time:	
Pressure Gauge ID:	
Pressure Gauge Readability:	in. H_2O
Temperature Gauge ID:	
Measurement Response Time:	sec.
R_{SLO}	
R_{ADO}	

Stack Diameter:		
Stack Area:		
Barometric Pressure (P_{bar}):		in. Hg
Static Pressure (P_g):		in. H_2O

	Pre-Test	Post-Test
Probe Head Condition: Damage Noted?		
Leak Check Performed?		

Clock Time	Traverse Point	Yaw Angle, including algebraic sign (degrees)	Velocity Differential Pressure (P_1-P_2)	Pitch Differential Pressure (P_4-P_5)	Stack or Duct Gas Temperature (°F)

Table 2F-4. Wind Tunnel Velocity Pressure Cross-Check

Wind Tunnel Facility: _____
Date: _____
Wind Tunnel Temperature: _____
Barometric Pressure: _____
Test Point Locations: _____
Lowest Test Velocity in m/sec (ft/sec): _____
Highest Test Velocity in m/sec (ft/sec): _____

Port		Rep.	Velocity Pressure (ΔP_{std})	
			@ Lowest Test Velocity	@ Highest Test Velocity
Calibration Pitot Tube Location		1		
		2		
		3		
		Average		
Calibration Location Test Points *	1	1		
		2		
		3		
		Average		
		% Difference **		
	2	1		
		2		
		3		
		Average		
		% Difference **		
		1		
		2		
		3		
		Average		
		% Difference **		

* Measurements must be taken at all points in the calibration location as specified in section 10.1.1

** Percent Difference = $\frac{(Calibration\ Location\ Test\ Point\ Avg - Cal.\ Pitot\ Tube\ Location\ Avg)}{Cal.\ Pitot\ Tube\ Location\ Avg} \times 100\%$

Specification: At each velocity setting, the average velocity pressure obtained at the calibration location shall be within ±2 percent or 0.01 in. H_2O, whichever is less restrictive, of the average velocity pressure obtained at the fixed calibration pitot tube location.

Table 2F-5. Wind Tunnel Axial Flow Verification

Wind Tunnel Facility: _____
Date: _____
Wind Tunnel Temperature: _____
Barometric Pressure: _____
Probe Type/I.D. Used To Conduct Check: _____
Test Point Locations: _____
Lowest Test Velocity in m/sec (ft/sec): _____
Highest Test Velocity in m/sec (ft/sec): _____

Port		@ Lowest Test Velocity		@ Highest Test Velocity	
		Yaw Angle * (degrees)	Pitch Angle * (degrees)	Yaw Angle * (degrees)	Pitch Angle * (degrees)
Calibration Location Test Points **	1				
	2				
	3				
	..				
Calibration Pitot Tube Location					

* When following the procedures in section 10.1.2.1, both the yaw and pitch angles are obtained from the same port. When following the procedures in section 10.1.2.2, the yaw angle is obtained using the port for the tested probe, and the pitch angle is obtained using the port for verification of axial flow.

** Yaw and pitch angle measurements must be taken at all points that define the calibration location (as per the requirements in section 10.1.1)

Specification: At each velocity setting, each measured yaw and pitch angle shall be within ±3° of 0° in accordance with the requirements in section 10.1.2.

Table 2F-6. Yaw Angle Calibration

Probe Type:_____ Tester(s):_____

Probe ID:_____ Affiliation:_____

Test Location:_____ Date:_____

	Repetition 1		Repetition 2	
Nominal Velocity Setting in m/sec (ft/sec)	θ_{null} (degrees)	R_{SLO} (degrees)*	θ_{null} (degrees)	R_{SLO} (degrees)*

Average of all recorded R_{SLO} values: _____

* Include magnitude and algebraic sign in accordance with section 10.5.7.

Table 2F-7. Determining the Magnitude of Reference Scribe Line Offset

Probe/Angle-Measuring Device	Magnitude of R_{SLO}
3-D probe with inclinometer	$90° - \theta_{null}$
3-D probe with protractor wheel and pointer	θ_{null}

Table 2F-8. Wind Tunnel Calibration of Three-Dimensional Probe

Wind Tunnel Facility: _____
Wind Tunnel Location: _____
Probe Type: _____
Probe ID: _____
Probe Calibration Date: _____
Test Location: _____
Calibration Pitot Tube Coeff. (C_p):_____
Ambient Temperature (° F): _____
Barometric Pressure (P_{bar}): _____

Velocity Setting (ft/sec)	Pitch Angle	Calibration Pitot Tube		Tested Probe			Calc. F_1	Calc. F_2
		ΔP_{std} (in. H_2O)*	Temp. (°F)	P_1-P_2 (in. H_2O)	P_4-P_5 (in. H_2O)	Yaw Angle (degrees)		
	-30°							
	-25°							
	-20°							
	-15°							
	-10°							
	-5°							
	0°							
	5°							
	10°							
	15°							
	20°							
	25°							
	30°							

* Calibration pitot tube measurements must, at a minimum, be taken before the tested probe reading at the first pitch angle setting, and after the tested probe reading at the last pitch angle setting in each replicate. See section 10.6.11.

Table 2F-9. Calibration Log for Three-Dimensional Probe

Probe ID: _____

Probe Type: _____

Probe Calibration Date:_____

Test Location: _____

Nominal Velocity: _____

Pitch Angle	Average of All Repetitions		Number of Repetitions
	F_1	F_2	
-35°			
-30°			
-25°			
-20°			
-15°			
-10°			
-5°			
0°			
5°			
10°			
15°			
20°			
25°			
30°			
35°			

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–1 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

EDITORIAL NOTE: At 79 FR 11257, Feb. 27, 2014, Figure 1-2 was added to part 60, appendix A-1, method 1, section 17. However, this amendment could not be performed because Figure 1-2 already existed.

APPENDIX A–2 TO PART 60—TEST METHODS 2G THROUGH 3C

Method 2G—Determination of Stack Gas Velocity and Volumetric Flow Rate With Two-Dimensional Probes
Method 2H—Determination of Stack Gas Velocity Taking Into Account Velocity Decay Near the Stack Wall
Method 3—Gas analysis for the determination of dry molecular weight
Method 3A—Determination of Oxygen and Carbon Dioxide Concentrations in Emissions From Stationary Sources (Instrumental Analyzer Procedure)
Method 3B—Gas analysis for the determination of emission rate correction factor or excess air
Method 3C—Determination of carbon dioxide, methane, nitrogen, and oxygen from stationary sources

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

EDITORIAL NOTE: At 79 FR 11257, Feb. 27, 2014, Figure 1-2 was added to part 60, appendix A-1, method 1, section 17. However, this amendment could not be performed because Figure 1-2 already existed.

APPENDIX A–2 TO PART 60—TEST METHODS 2G THROUGH 3C

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Method 3A—Determination of Oxygen and Carbon Dioxide Concentrations in Emissions From Stationary Sources (Instrumental Analyzer Procedure)
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The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

METHOD 2G—DETERMINATION OF STACK GAS VELOCITY AND VOLUMETRIC FLOW RATE WITH TWO-DIMENSIONAL PROBES

NOTE: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling) essential to its performance. Some material has been incorporated from other methods in this part. Therefore, to obtain reliable results, those using this method should have a thorough knowledge of at least the following additional test methods: Methods 1, 2, 3 or 3A, and 4.

1.0 Scope and Application

1.1 This method is applicable for the determination of yaw angle, near-axial velocity, and the volumetric flow rate of a gas stream in a stack or duct using a two-dimensional (2–D) probe.

2.0 Summary of Method

2.1 A 2–D probe is used to measure the velocity pressure and the yaw angle of the flow velocity vector in a stack or duct. Alternatively, these measurements may be made by operating one of the three-dimensional (3–D) probes described in Method 2F, in yaw determination mode only. From these measurements and a determination of the stack gas density, the average near-axial velocity of the stack gas is calculated. The near-axial velocity accounts for the yaw, but not the pitch, component of flow. The average gas volumetric flow rate in the stack or duct is then determined from the average near-axial velocity.

3.0 Definitions

3.1. *Angle-measuring Device Rotational Offset (R_{ADO}).* The rotational position of an angle-measuring device relative to the reference scribe line, as determined during the pre-test rotational position check described in section 8.3.

3.2 *Calibration Pitot Tube.* The standard (Prandtl type) pitot tube used as a reference when calibrating a probe under this method.

3.3 *Field Test.* A set of measurements conducted at a specific unit or exhaust stack/duct to satisfy the applicable regulation (e.g., a three-run boiler performance test, a single-or multiple-load nine-run relative accuracy test).

3.4 *Full Scale of Pressure-measuring Device.* Full scale refers to the upper limit of the measurement range displayed by the device. For bi-directional pressure gauges, full scale includes the entire pressure range from the lowest negative value to the highest positive value on the pressure scale.

3.5 *Main probe.* Refers to the probe head and that section of probe sheath directly attached to the probe head. The main probe sheath is distinguished from probe extensions, which are sections of sheath added onto the main probe to extend its reach.

3.6 *''May,'' ''Must,'' ''Shall,'' ''Should,''* and the imperative form of verbs.

3.6.1 *''May''* is used to indicate that a provision of this method is optional.

3.6.2 *''Must,'' ''Shall,''* and the imperative form of verbs (such as ''record'' or ''enter'') are used to indicate that a provision of this method is mandatory.

3.6.3 *''Should''* is used to indicate that a provision of this method is not mandatory, but is highly recommended as good practice.

3.7 *Method 1.* Refers to 40 CFR part 60, appendix A, ''Method 1—Sample and velocity traverses for stationary sources.''

3.8 *Method 2.* Refers to 40 CFR part 60, appendix A, ''Method 2—Determination of stack gas velocity and volumetric flow rate (Type S pitot tube).''

3.9 *Method 2F.* Refers to 40 CFR part 60, appendix A, ''Method 2F—Determination of stack gas velocity and volumetric flow rate with three-dimensional probes.''

3.10 *Near-axial Velocity.* The velocity vector parallel to the axis of the stack or duct that accounts for the yaw angle component of gas flow. The term ''near-axial'' is used herein to indicate that the velocity and volumetric flow rate results account for the measured yaw angle component of flow at each measurement point.

3.11 *Nominal Velocity.* Refers to a wind tunnel velocity setting that approximates the actual wind tunnel velocity to within ±1.5 m/sec (±5 ft/sec).

3.12 *Pitch Angle.* The angle between the axis of the stack or duct and the pitch component of flow, i.e., the component of the total velocity vector in a plane defined by the traverse line and the axis of the stack or duct. (Figure 2G–1 illustrates the ''pitch plane.'') From the standpoint of a tester facing a test port in a vertical stack, the pitch component of flow is the vector of flow moving from the center of the stack toward or away from that test port. The pitch angle is the angle described by this pitch component of flow and the vertical axis of the stack.

3.13 *Readability.* For the purposes of this method, readability for an analog measurement device is one half of the smallest scale division. For a digital measurement device, it is the number of decimals displayed by the device.

3.14 *Reference Scribe Line.* A line permanently inscribed on the main probe sheath (in accordance with section 6.1.5.1) to serve as a reference mark for determining yaw angles.

3.15 *Reference Scribe Line Rotational Offset (R_{SLO}).* The rotational position of a probe's reference scribe line relative to the probe's yaw-null position, as determined during the yaw angle calibration described in section 10.5.

3.16 *Response Time*. The time required for the measurement system to fully respond to a change from zero differential pressure and ambient temperature to the stable stack or duct pressure and temperature readings at a traverse point.

3.17 *Tested Probe*. A probe that is being calibrated.

3.18 *Three-dimensional (3–D) Probe*. A directional probe used to determine the velocity pressure and the yaw and pitch angles in a flowing gas stream.

3.19 *Two-dimensional (2–D) Probe*. A directional probe used to measure velocity pressure and yaw angle in a flowing gas stream.

3.20 *Traverse Line*. A diameter or axis extending across a stack or duct on which measurements of velocity pressure and flow angles are made.

3.21 *Wind Tunnel Calibration Location*. A point, line, area, or volume within the wind tunnel test section at, along, or within which probes are calibrated. At a particular wind tunnel velocity setting, the average velocity pressures at specified points at, along, or within the calibration location shall vary by no more than 2 percent or 0.3 mm H_20 (0.01 in. H_2O), whichever is less restrictive, from the average velocity pressure at the calibration pitot tube location. Air flow at this location shall be axial, i.e., yaw and pitch angles within ±3° of 0°. Compliance with these flow criteria shall be demonstrated by performing the procedures prescribed in sections 10.1.1 and 10.1.2. For circular tunnels, no part of the calibration location may be closer to the tunnel wall than 10.2 cm (4 in.) or 25 percent of the tunnel diameter, whichever is farther from the wall. For elliptical or rectangular tunnels, no part of the calibration location may be closer to the tunnel wall than 10.2 cm (4 in.) or 25 percent of the applicable cross-sectional axis, whichever is farther from the wall.

3.22 *Wind Tunnel with Documented Axial Flow*. A wind tunnel facility documented as meeting the provisions of sections 10.1.1 (velocity pressure cross-check) and 10.1.2 (axial flow verification) using the procedures described in these sections or alternative procedures determined to be technically equivalent.

3.23 *Yaw Angle*. The angle between the axis of the stack or duct and the yaw component of flow, i.e., the component of the total velocity vector in a plane perpendicular to the traverse line at a particular traverse point. (Figure 2G–1 illustrates the ''yaw plane.'') From the standpoint of a tester facing a test port in a vertical stack, the yaw component of flow is the vector of flow moving to the left or right from the center of the stack as viewed by the tester. (This is sometimes referred to as ''vortex flow,'' i.e., flow around the centerline of a stack or duct.) The yaw angle is the angle described by this yaw component of flow and the vertical axis of the stack. The algebraic sign convention is illustrated in Figure 2G–2.

3.24 *Yaw Nulling*. A procedure in which a Type-S pitot tube or a 3–D probe is rotated about its axis in a stack or duct until a zero differential pressure reading (''yaw null'') is obtained. When a Type S probe is yaw-nulled, the rotational position of its impact port is 90° from the direction of flow in the stack or duct and the ΔP reading is zero. When a 3–D probe is yaw-nulled, its impact pressure port (P_1) faces directly into the direction of flow in the stack or duct and the differential pressure between pressure ports P_2 and P_3 is zero.

4.0 Interferences [Reserved]

5.0 Safety

5.1 This test method may involve hazardous operations and the use of hazardous materials or equipment. This method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user to establish and implement appropriate safety and health practices and to determine the applicability of regulatory limitations before using this test method.

6.0 Equipment and Supplies

6.1 Two-dimensional Probes. Probes that provide both the velocity pressure and the yaw angle of the flow vector in a stack or duct, as listed in sections 6.1.1 and 6.1.2, qualify for use based on comprehensive wind tunnel and field studies involving both inter-and intra-probe comparisons by multiple test teams. Each 2–D probe shall have a unique identification number or code permanently marked on the main probe sheath. Each probe shall be calibrated prior to use according to the procedures in section 10. Manufacturer-supplied calibration data shall be used as example information only, except when the manufacturer calibrates the probe as specified in section 10 and provides complete documentation.

6.1.1 Type S (Stausscheibe or reverse type) pitot tube. This is the same as specified in Method 2, section 2.1, except for the following additional specifications that enable the pitot tube to accurately determine the yaw component of flow. For the purposes of this method, the external diameter of the tubing used to construct the Type S pitot tube (dimension D_t in Figure 2–2 of Method 2) shall be no less than 9.5 mm (3/8 in.). The pitot tube shall also meet the following alignment specifications. The angles α_1, α_2, β_1, and β_2, as shown in Method 2, Figure 2–3, shall not exceed ±2°. The dimensions w and z, shown in Method 2, Figure 2–3 shall not exceed 0.5 mm (0.02 in.).

6.1.1.1 Manual Type S probe. This refers to a Type S probe that is positioned at individual traverse points and yaw nulled manually by an operator.

6.1.1.2 Automated Type S probe. This refers to a system that uses a computer-controlled motorized mechanism to position the Type S pitot head at individual traverse points and perform yaw angle determinations.

6.1.2 Three-dimensional probes used in 2–D mode. A 3–D probe, as specified in sections 6.1.1 through 6.1.3 of Method 2F, may, for the purposes of this method, be used in a two-dimensional mode (i.e., measuring yaw angle, but not pitch angle). When the 3–D probe is used as a 2–D probe, only the velocity pressure and yaw-null pressure are obtained using the pressure taps referred to as P_1, P_2, and P_3. The differential pressure P_1–P_2 is a function of total velocity and corresponds to the ΔP obtained using the Type S probe. The differential pressure P_2–P_3 is used to yaw null the probe and determine the yaw angle. The differential pressure P_4–P_5, which is a function of pitch angle, is not measured when the 3–D probe is used in 2–D mode.

6.1.3 Other probes. [Reserved]

6.1.4 Probe sheath. The probe shaft shall include an outer sheath to: (1) provide a surface for inscribing a permanent reference scribe line, (2) accommodate attachment of an angle-measuring device to the probe shaft, and (3) facilitate precise rotational movement of the probe for determining yaw angles. The sheath shall be rigidly attached to the probe assembly and shall enclose all pressure lines from the probe head to the farthest position away from the probe head where an angle-measuring device may be attached during use in the field. The sheath of the fully assembled probe shall be sufficiently rigid and straight at all rotational positions such that, when one end of the probe shaft is held in a horizontal position, the fully extended probe meets the horizontal straightness specifications indicated in section 8.2 below.

6.1.5 Scribe lines.

6.1.5.1 Reference scribe line. A permanent line, no greater than 1.6 mm (1/16 in.) in width, shall be inscribed on each manual probe that will be used to determine yaw angles of flow. This line shall be placed on the main probe sheath in accordance with the procedures described in section 10.4 and is used as a reference position for installation of the yaw angle-measuring device on the probe. At the discretion of the tester, the scribe line may be a single line segment placed at a particular position on the probe sheath (e.g., near the probe head), multiple line segments placed at various locations along the length of the probe sheath (e.g., at every position where a yaw angle-measuring device may be mounted), or a single continuous line extending along the full length of the probe sheath.

6.1.5.2 Scribe line on probe extensions. A permanent line may also be inscribed on any probe extension that will be attached to the main probe in performing field testing. This allows a yaw angle-measuring device mounted on the extension to be readily aligned with the reference scribe line on the main probe sheath.

6.1.5.3 Alignment specifications. This specification shall be met separately, using the procedures in section 10.4.1, on the main probe and on each probe extension. The rotational position of the scribe line or scribe line segments on the main probe or any probe extension must not vary by more than 2°. That is, the difference between the minimum and maximum of all of the rotational angles that are measured along the full length of the main probe or the probe extension must not exceed 2°.

6.1.6 Probe and system characteristics to ensure horizontal stability.

6.1.6.1 For manual probes, it is recommended that the effective length of the probe (coupled with a probe extension, if necessary) be at least 0.9 m (3 ft.) longer than the farthest traverse point mark on the probe shaft away from the probe head. The operator should maintain the probe's horizontal stability when it is fully inserted into the stack or duct. If a shorter probe is used, the probe should be inserted through a bushing sleeve, similar to the one shown in Figure 2G–3, that is installed on the test port; such a bushing shall fit snugly around the probe and be secured to the stack or duct entry port in such a manner as to maintain the probe's horizontal stability when fully inserted into the stack or duct.

6.1.6.2 An automated system that includes an external probe casing with a transport system shall have a mechanism for maintaining horizontal stability comparable to that obtained by manual probes following the provisions of this method. The automated probe assembly shall also be constructed to maintain the alignment and position of the pressure ports during sampling at each traverse point. The design of the probe casing and transport system shall allow the probe to be removed from the stack or duct and checked through direct physical measurement for angular position and insertion depth.

6.1.7 The tubing that is used to connect the probe and the pressure-measuring device should have an inside diameter of at least 3.2 mm (⅛ in.), to reduce the time required for pressure equilibration, and should be as short as practicable.

6.1.8 If a detachable probe head without a sheath [e.g., a pitot tube, typically 15.2 to 30.5 cm (6 to 12 in.) in length] is coupled with a probe sheath and calibrated in a wind tunnel in accordance with the yaw angle calibration procedure in section 10.5, the probe head shall remain attached to the probe

sheath during field testing in the same configuration and orientation as calibrated. Once the detachable probe head is uncoupled or re-oriented, the yaw angle calibration of the probe is no longer valid and must be repeated before using the probe in subsequent field tests.

6.2 Yaw Angle-measuring Device. One of the following devices shall be used for measurement of the yaw angle of flow.

6.2.1 Digital inclinometer. This refers to a digital device capable of measuring and displaying the rotational position of the probe to within ±1°. The device shall be able to be locked into position on the probe sheath or probe extension, so that it indicates the probe's rotational position throughout the test. A rotational position collar block that can be attached to the probe sheath (similar to the collar shown in Figure 2G–4) may be required to lock the digital inclinometer into position on the probe sheath.

6.2.2 Protractor wheel and pointer assembly. This apparatus, similar to that shown in Figure 2G–5, consists of the following components.

6.2.2.1 A protractor wheel that can be attached to a port opening and set in a fixed rotational position to indicate the yaw angle position of the probe's scribe line relative to the longitudinal axis of the stack or duct. The protractor wheel must have a measurement ring on its face that is no less than 17.8 cm (7 in.) in diameter, shall be able to be rotated to any angle and then locked into position on the stack or duct test port, and shall indicate angles to a resolution of 1°.

6.2.2.2 A pointer assembly that includes an indicator needle mounted on a collar that can slide over the probe sheath and be locked into a fixed rotational position on the probe sheath. The pointer needle shall be of sufficient length, rigidity, and sharpness to allow the tester to determine the probe's angular position to within 1° from the markings on the protractor wheel. Corresponding to the position of the pointer, the collar must have a scribe line to be used in aligning the pointer with the scribe line on the probe sheath.

6.2.3 Other yaw angle-measuring devices. Other angle-measuring devices with a manufacturer's specified precision of 1° or better may be used, if approved by the Administrator.

6.3 Probe Supports and Stabilization Devices. When probes are used for determining flow angles, the probe head should be kept in a stable horizontal position. For probes longer than 3.0 m (10 ft.), the section of the probe that extends outside the test port shall be secured. Three alternative devices are suggested for maintaining the horizontal position and stability of the probe shaft during flow angle determinations and velocity pressure measurements: (1) monorails installed above each port, (2) probe stands on which the probe shaft may be rested, or (3) bushing sleeves of sufficient length secured to the test ports to maintain probes in a horizontal position. Comparable provisions shall be made to ensure that automated systems maintain the horizontal position of the probe in the stack or duct. The physical characteristics of each test platform may dictate the most suitable type of stabilization device. Thus, the choice of a specific stabilization device is left to the judgement of the testers.

6.4 Differential Pressure Gauges. The velocity pressure (ΔP) measuring devices used during wind tunnel calibrations and field testing shall be either electronic manometers (e.g., pressure transducers), fluid manometers, or mechanical pressure gauges (e.g., MagnehelicΔ gauges). Use of electronic manometers is recommended. Under low velocity conditions, use of electronic manometers may be necessary to obtain acceptable measurements.

6.4.1 Differential pressure-measuring device. This refers to a device capable of measuring pressure differentials and having a readability of ±1 percent of full scale. The device shall be capable of accurately measuring the maximum expected pressure differential. Such devices are used to determine the following pressure measurements: velocity pressure, static pressure, and yaw-null pressure. For an inclined-vertical manometer, the readability specification of ±1 percent shall be met separately using the respective full-scale upper limits of the inclined anvertical portions of the scales. To the extent practicable, the device shall be selected such that most of the pressure readings are between 10 and 90 percent of the device's full-scale measurement range (as defined in section 3.4). In addition, pressure-measuring devices should be selected such that the zero does not drift by more than 5 percent of the average expected pressure readings to be encountered during the field test. This is particularly important under low pressure conditions.

6.4.2 Gauge used for yaw nulling. The differential pressure-measuring device chosen for yaw nulling the probe during the wind tunnel calibrations and field testing shall be bi-directional, i.e., capable of reading both positive and negative differential pressures. If a mechanical, bi-directional pressure gauge is chosen, it shall have a full-scale range no greater than 2.6 cm (i.e., −1.3 to + 1.3 cm) [1 in. H_2O (i.e., −0.5 in. to + 0.5 in.)].

6.4.3 Devices for calibrating differential pressure-measuring devices. A precision manometer (e.g., a U-tube, inclined, or inclined-vertical manometer, or micromanometer) or NIST (National Institute of Standards and Technology) traceable pressure source shall be used for calibrating differential pressure-measuring devices. The device shall be maintained under laboratory conditions or in a similar protected environment (e.g., a climate-controlled trailer). It shall not be used

in field tests. The precision manometer shall have a scale gradation of 0.3 mm H_2O (0.01 in. H_2O), or less, in the range of 0 to 5.1 cm H_2O (0 to 2 in. H_2O) and 2.5 mm H_2O (0.1 in. H_2O), or less, in the range of 5.1 to 25.4 cm H_2O (2 to 10 in. H_2O). The manometer shall have manufacturer's documentation that it meets an accuracy specification of at least 0.5 percent of full scale. The NIST-traceable pressure source shall be recertified annually.

6.4.4 Devices used for post-test calibration check. A precision manometer meeting the specifications in section 6.4.3, a pressure-measuring device or pressure source with a documented calibration traceable to NIST, or an equivalent device approved by the Administrator shall be used for the post-test calibration check. The pressure-measuring device shall have a readability equivalent to or greater than the tested device. The pressure source shall be capable of generating pressures between 50 and 90 percent of the range of the tested device and known to within ±1 percent of the full scale of the tested device. The pressure source shall be recertified annually.

6.5 Data Display and Capture Devices. Electronic manometers (if used) shall be coupled with a data display device (such as a digital panel meter, personal computer display, or strip chart) that allows the tester to observe and validate the pressure measurements taken during testing. They shall also be connected to a data recorder (such as a data logger or a personal computer with data capture software) that has the ability to compute and retain the appropriate average value at each traverse point, identified by collection time and traverse point.

6.6 Temperature Gauges. For field tests, a thermocouple or resistance temperature detector (RTD) capable of measuring temperature to within ±3 °C (±5 °F) of the stack or duct temperature shall be used. The thermocouple shall be attached to the probe such that the sensor tip does not touch any metal. The position of the thermocouple relative to the pressure port face openings shall be in the same configuration as used for the probe calibrations in the wind tunnel. Temperature gauges used for wind tunnel calibrations shall be capable of measuring temperature to within ±0.6 °C (±1 °F) of the temperature of the flowing gas stream in the wind tunnel.

6.7 Stack or Duct Static Pressure Measurement. The pressure-measuring device used with the probe shall be as specified in section 6.4 of this method. The static tap of a standard (Prandtl type) pitot tube or one leg of a Type S pitot tube with the face opening planes positioned parallel to the gas flow may be used for this measurement. Also acceptable is the pressure differential reading of P_1-P_{bar} from a five-hole prism-shaped 3–D probe, as specified in section 6.1.1 of Method 2F (such as the Type DA or DAT probe), with the P_1 pressure port face opening positioned parallel to the gas flow in the same manner as the Type S probe. However, the 3–D spherical probe, as specified in section 6.1.2 of Method 2F, is unable to provide this measurement and shall not be used to take static pressure measurements. Static pressure measurement is further described in section 8.11.

6.8 Barometer. Same as Method 2, section 2.5.

6.9 Gas Density Determination Equipment. Method 3 or 3A shall be used to determine the dry molecular weight of the stack or duct gas. Method 4 shall be used for moisture content determination and computation of stack or duct gas wet molecular weight. Other methods may be used, if approved by the Administrator.

6.10 Calibration Pitot Tube. Same as Method 2, section 2.7.

6.11 Wind Tunnel for Probe Calibration. Wind tunnels used to calibrate velocity probes must meet the following design specifications.

6.11.1 Test section cross-sectional area. The flowing gas stream shall be confined within a circular, rectangular, or elliptical duct. The cross-sectional area of the tunnel must be large enough to ensure fully developed flow in the presence of both the calibration pitot tube and the tested probe. The calibration site, or ''test section,'' of the wind tunnel shall have a minimum diameter of 30.5 cm (12 in.) for circular or elliptical duct cross-sections or a minimum width of 30.5 cm (12 in.) on the shorter side for rectangular cross-sections. Wind tunnels shall meet the probe blockage provisions of this section and the qualification requirements prescribed in section 10.1. The projected area of the portion of the probe head, shaft, and attached devices inside the wind tunnel during calibration shall represent no more than 2 percent of the cross-sectional area of the tunnel. If the pitot and/or probe assembly blocks more than 2 percent of the cross-sectional area at an insertion point only 4 inches inside the wind tunnel, the diameter of the wind tunnel must be increased.

6.11.2 Velocity range and stability. The wind tunnel should be capable of achieving and maintaining a constant and steady velocity between 6.1 m/sec and 30.5 m/sec (20 ft/sec and 100 ft/sec) for the entire calibration period for each selected calibration velocity. The wind tunnel shall produce fully developed flow patterns that are stable and parallel to the axis of the duct in the test section.

6.11.3 Flow profile at the calibration location. The wind tunnel shall provide axial flow within the test section calibration location (as defined in section 3.21). Yaw and pitch angles in the calibration location shall be within ±3° of 0°. The procedure for determining that this requirement has been met is described in section 10.1.2.

6.11.4 Entry ports in the wind tunnel test section.

6.11.4.1 Port for tested probe. A port shall be constructed for the tested probe. This port shall be located to allow the head of the tested probe to be positioned within the wind tunnel calibration location (as defined in section 3.21). The tested probe shall be able to be locked into the 0° pitch angle position. To facilitate alignment of the probe during calibration, the test section should include a window constructed of a transparent material to allow the tested probe to be viewed.

6.11.4.2 Port for verification of axial flow. Depending on the equipment selected to conduct the axial flow verification prescribed in section 10.1.2, a second port, located 90° from the entry port for the tested probe, may be needed to allow verification that the gas flow is parallel to the central axis of the test section. This port should be located and constructed so as to allow one of the probes described in section 10.1.2.2 to access the same test point(s) that are accessible from the port described in section 6.11.4.1.

6.11.4.3 Port for calibration pitot tube. The calibration pitot tube shall be used in the port for the tested probe or in a separate entry port. In either case, all measurements with the calibration pitot tube shall be made at the same point within the wind tunnel over the course of a probe calibration. The measurement point for the calibration pitot tube shall meet the same specifications for distance from the wall and for axial flow as described in section 3.21 for the wind tunnel calibration location.

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection and Analysis

8.1 Equipment Inspection and Set Up

8.1.1 All 2–D and 3–D probes, differential pressure-measuring devices, yaw angle-measuring devices, thermocouples, and barometers shall have a current, valid calibration before being used in a field test. (See sections 10.3.3, 10.3.4, and 10.5 through 10.10 for the applicable calibration requirements.)

8.1.2 Before each field use of a Type S probe, perform a visual inspection to verify the physical condition of the pitot tube. Record the results of the inspection. If the face openings are noticeably misaligned or there is visible damage to the face openings, the probe shall not be used until repaired, the dimensional specifications verified (according to the procedures in section 10.2.1), and the probe recalibrated.

8.1.3 Before each field use of a 3–D probe, perform a visual inspection to verify the physical condition of the probe head according to the procedures in section 10.2 of Method 2F. Record the inspection results on a form similar to Table 2F–1 presented in Method 2F. If there is visible damage to the 3–D probe, the probe shall not be used until it is recalibrated.

8.1.4 After verifying that the physical condition of the probe head is acceptable, set up the apparatus using lengths of flexible tubing that are as short as practicable. Surge tanks installed between the probe and pressure-measuring device may be used to dampen pressure fluctuations provided that an adequate measurement system response time (see section 8.8) is maintained.

8.2 Horizontal Straightness Check. A horizontal straightness check shall be performed before the start of each field test, except as otherwise specified in this section. Secure the fully assembled probe (including the probe head and all probe shaft extensions) in a horizontal position using a stationary support at a point along the probe shaft approximating the location of the stack or duct entry port when the probe is sampling at the farthest traverse point from the stack or duct wall. The probe shall be rotated to detect bends. Use an angle-measuring device or trigonometry to determine the bend or sag between the probe head and the secured end. (See Figure 2G–6.) Probes that are bent or sag by more than 5° shall not be used. Although this check does not apply when the probe is used for a vertical traverse, care should be taken to avoid the use of bent probes when conducting vertical traverses. If the probe is constructed of a rigid steel material and consists of a main probe without probe extensions, this check need only be performed before the initial field use of the probe, when the probe is recalibrated, when a change is made to the design or material of the probe assembly, and when the probe becomes bent. With such probes, a visual inspection shall be made of the fully assembled probe before each field test to determine if a bend is visible. The probe shall be rotated to detect bends. The inspection results shall be documented in the field test report. If a bend in the probe is visible, the horizontal straightness check shall be performed before the probe is used.

8.3 Rotational Position Check. Before each field test, and each time an extension is added to the probe during a field test, a rotational position check shall be performed on all manually operated probes (except as noted in section 8.3.5 below) to ensure that, throughout testing, the angle-measuring device is either: aligned to within ±1° of the rotational position of the reference scribe line; or is affixed to the probe such that the rotational offset of the device from the reference scribe line is known to within ±1°. This check shall consist of direct measurements of the rotational positions of the reference scribe line and angle-measuring device sufficient to verify that these specifications are met. Annex A in section 18 of this method gives recommended procedures for performing the rotational position check, and Table 2G–2

gives an example data form. Procedures other than those recommended in Annex A in section 18 may be used, provided they demonstrate whether the alignment specification is met and are explained in detail in the field test report.

8.3.1 Angle-measuring device rotational offset. The tester shall maintain a record of the angle-measuring device rotational offset, R_{ADO}, as defined in section 3.1. Note that R_{ADO} is assigned a value of 0° when the angle-measuring device is aligned to within ±1° of the rotational position of the reference scribe line. The R_{ADO} shall be used to determine the yaw angle of flow in accordance with section 8.9.4.

8.3.2 Sign of angle-measuring device rotational offset. The sign of R_{ADO} is positive when the angle-measuring device (as viewed from the ''tail'' end of the probe) is positioned in a clockwise direction from the reference scribe line and negative when the device is positioned in a counterclockwise direction from the reference scribe line.

8.3.3 Angle-measuring devices that can be independently adjusted (e.g., by means of a set screw), after being locked into position on the probe sheath, may be used. However, the R_{ADO} must also take into account this adjustment.

8.3.4 Post-test check. If probe extensions remain attached to the main probe throughout the field test, the rotational position check shall be repeated, at a minimum, at the completion of the field test to ensure that the angle-measuring device has remained within ±2° of its rotational position established prior to testing. At the discretion of the tester, additional checks may be conducted after completion of testing at any sample port or after any test run. If the ±2° specification is not met, all measurements made since the last successful rotational position check must be repeated. section 18.1.1.3 of Annex A provides an example procedure for performing the post-test check.

8.3.5 Exceptions.

8.3.5.1 A rotational position check need not be performed if, for measurements taken at all velocity traverse points, the yaw angle-measuring device is mounted and aligned directly on the reference scribe line specified in sections 6.1.5.1 and 6.1.5.3 and no independent adjustments, as described in section 8.3.3, are made to device's rotational position.

8.3.5.2 If extensions are detached and re-attached to the probe during a field test, a rotational position check need only be performed the first time an extension is added to the probe, rather than each time the extension is re-attached, if the probe extension is designed to be locked into a mechanically fixed rotational position (e.g., through the use of interlocking grooves), that can re-establish the initial rotational position to within ±1°.

8.4 Leak Checks. A pre-test leak check shall be conducted before each field test. A post-test check shall be performed at the end of the field test, but additional leak checks may be conducted after any test run or group of test runs. The post-test check may also serve as the pre-test check for the next group of test runs. If any leak check is failed, all runs since the last passed leak check are invalid. While performing the leak check procedures, also check each pressure device's responsiveness to changes in pressure.

8.4.1 To perform the leak check on a Type S pitot tube, pressurize the pitot impact opening until at least 7.6 cm H_2O (3 in. H_2O) velocity pressure, or a pressure corresponding to approximately 75 percent of the pressure device's measurement scale, whichever is less, registers on the pressure device; then, close off the impact opening. The pressure shall remain stable (±2.5 mm H_2O, ±0.10 in. H_2O) for at least 15 seconds. Repeat this procedure for the static pressure side, except use suction to obtain the required pressure. Other leak-check procedures may be used, if approved by the Administrator.

8.4.2 To perform the leak check on a 3–D probe, pressurize the probe's impact (P_1) opening until at least 7.6 cm H_2O (3 in. H_2O) velocity pressure, or a pressure corresponding to approximately 75 percent of the pressure device's measurement scale, whichever is less, registers on the pressure device; then, close off the impact opening. The pressure shall remain stable (±2.5 mm H_2O, ±0.10 in. H_2O) for at least 15 seconds. Check the P_2 and P_3 pressure ports in the same fashion. Other leak-check procedures may be used, if approved by the Administrator.

8.5 Zeroing the Differential Pressure-measuring Device. Zero each differential pressure-measuring device, including the device used for yaw nulling, before each field test. At a minimum, check the zero after each field test. A zero check may also be performed after any test run or group of test runs. For fluid manometers and mechanical pressure gauges (e.g., Magnehelic∆ gauges), the zero reading shall not deviate from zero by more than ±0.8 mm H_2O (±0.03 in. H_2O) or one minor scale division, whichever is greater, between checks. For electronic manometers, the zero reading shall not deviate from zero between checks by more than: ±0.3 mm H_2O (±0.01 in. H_2O), for full scales less than or equal to 5.1 cm H_2O (2.0 in. H_2O); or ±0.8 mm H_2O (±0.03 in. H_2O), for full scales greater than 5.1 cm H_2O (2.0 in. H_2O). (NOTE: If negative zero drift is not directly readable, estimate the reading based on the position of the gauge oil in the manometer or of the needle on the pressure gauge.) In addition, for all pressure-measuring devices except those used exclusively for yaw nulling, the zero

reading shall not deviate from zero by more than 5 percent of the average measured differential pressure at any distinct process condition or load level. If any zero check is failed at a specific process condition or load level, all runs conducted at that process condition or load level since the last passed zero check are invalid.

8.6 Traverse Point Verification. The number and location of the traverse points shall be selected based on Method 1 guidelines. The stack or duct diameter and port nipple lengths, including any extension of the port nipples into the stack or duct, shall be verified the first time the test is performed; retain and use this information for subsequent field tests, updating it as required. Physically measure the stack or duct dimensions or use a calibrated laser device; do not use engineering drawings of the stack or duct. The probe length necessary to reach each traverse point shall be recorded to within ±6.4 mm (±¼ in.) and, for manual probes, marked on the probe sheath. In determining these lengths, the tester shall take into account both the distance that the port flange projects outside of the stack and the depth that any port nipple extends into the gas stream. The resulting point positions shall reflect the true distances from the inside wall of the stack or duct, so that when the tester aligns any of the markings with the outside face of the stack port, the probe's impact port shall be located at the appropriate distance from the inside wall for the respective Method 1 traverse point. Before beginning testing at a particular location, an out-of-stack or duct verification shall be performed on each probe that will be used to ensure that these position markings are correct. The distances measured during the verification must agree with the previously calculated distances to within ±¼ in. For manual probes, the traverse point positions shall be verified by measuring the distance of each mark from the probe's impact pressure port (the P_1 port for a 3-D probe). A comparable out-of-stack test shall be performed on automated probe systems. The probe shall be extended to each of the prescribed traverse point positions. Then, the accuracy of the positioning for each traverse point shall be verified by measuring the distance between the port flange and the probe's impact pressure port.

8.7 Probe Installation. Insert the probe into the test port. A solid material shall be used to seal the port.

8.8 System Response Time. Determine the response time of the probe measurement system. Insert and position the ''cold'' probe (at ambient temperature and pressure) at any Method 1 traverse point. Read and record the probe differential pressure, temperature, and elapsed time at 15-second intervals until stable readings for both pressure and temperature are achieved. The response time is the longer of these two elapsed times. Record the response time.

8.9 Sampling.

8.9.1 Yaw angle measurement protocol. With manual probes, yaw angle measurements may be obtained in two alternative ways during the field test, either by using a yaw angle-measuring device (e.g., digital inclinometer) affixed to the probe, or using a protractor wheel and pointer assembly. For horizontal traversing, either approach may be used. For vertical traversing, i.e., when measuring from on top or into the bottom of a horizontal duct, only the protractor wheel and pointer assembly may be used. With automated probes, curve-fitting protocols may be used to obtain yaw-angle measurements.

8.9.1.1 If a yaw angle-measuring device affixed to the probe is to be used, lock the device on the probe sheath, aligning it either on the reference scribe line or in the rotational offset position established under section 8.3.1.

8.9.1.2 If a protractor wheel and pointer assembly is to be used, follow the procedures in Annex B of this method.

8.9.1.3 Curve-fitting procedures. Curve-fitting routines sweep through a range of yaw angles to create curves correlating pressure to yaw position. To find the zero yaw position and the yaw angle of flow, the curve found in the stack is computationally compared to a similar curve that was previously generated under controlled conditions in a wind tunnel. A probe system that uses a curve-fitting routine for determining the yaw-null position of the probe head may be used, provided that it is verified in a wind tunnel to be able to determine the yaw angle of flow to within ±1°.

8.9.1.4 Other yaw angle determination procedures. If approved by the Administrator, other procedures for determining yaw angle may be used, provided that they are verified in a wind tunnel to be able to perform the yaw angle calibration procedure as described in section 10.5.

8.9.2 Sampling strategy. At each traverse point, first yaw-null the probe, as described in section 8.9.3, below. Then, with the probe oriented into the direction of flow, measure and record the yaw angle, the differential pressure and the temperature at the traverse point, after stable readings are achieved, in accordance with sections 8.9.4 and 8.9.5. At the start of testing in each port (i.e., after a probe has been inserted into the flue gas stream), allow at least the response time to elapse before beginning to take measurements at the first traverse point accessed from that port. Provided that the probe is not removed from the flue gas stream, measurements may be taken at subsequent traverse points accessed from the same test port without waiting again for the response time to elapse.

8.9.3 Yaw-nulling procedure. In preparation for yaw angle determination, the probe must first be yaw nulled. After positioning the probe at the appropriate traverse point, perform the following procedures.

8.9.3.1 For Type S probes, rotate the probe until a null differential pressure reading is obtained. The direction of the probe rotation shall be such that the thermocouple is located downstream of the probe pressure ports at the yaw-null position. Rotate the probe 90° back from the yaw-null position to orient the impact pressure port into the direction of flow. Read and record the angle displayed by the angle-measuring device.

8.9.3.2 For 3-D probes, rotate the probe until a null differential pressure reading (the difference in pressures across the P_2 and P_3 pressure ports is zero, i.e., $P_2 = P_3$) is indicated by the yaw angle pressure gauge. Read and record the angle displayed by the angle-measuring device.

8.9.3.3 Sign of the measured angle. The angle displayed on the angle-measuring device is considered positive when the probe's impact pressure port (as viewed from the ''tail'' end of the probe) is oriented in a clockwise rotational position relative to the stack or duct axis and is considered negative when the probe's impact pressure port is oriented in a counterclockwise rotational position (see Figure 2G–7).

8.9.4 Yaw angle determination. After performing the applicable yaw-nulling procedure in section 8.9.3, determine the yaw angle of flow according to one of the following procedures. Special care must be observed to take into account the signs of the recorded angle reading and all offsets.

8.9.4.1 Direct-reading. If all rotational offsets are zero or if the angle-measuring device rotational offset (R_{ADO}) determined in section 8.3 exactly compensates for the scribe line rotational offset (R_{SLO}) determined in section 10.5, then the magnitude of the yaw angle is equal to the displayed angle-measuring device reading from section 8.9.3.1 or 8.9.3.2. The algebraic sign of the yaw angle is determined in accordance with section 8.9.3.3. [NOTE: Under certain circumstances (e.g., testing of horizontal ducts) a 90° adjustment to the angle-measuring device readings may be necessary to obtain the correct yaw angles.]

8.9.4.2 Compensation for rotational offsets during data reduction. When the angle-measuring device rotational offset does not compensate for reference scribe line rotational offset, the following procedure shall be used to determine the yaw angle:

(a) Enter the reading indicated by the angle-measuring device from section 8.9.3.1 or 8.9.3.2.

(b) Associate the proper algebraic sign from section 8.9.3.3 with the reading in step (a).

(c) Subtract the reference scribe line rotational offset, R_{SLO}, from the reading in step (b).

(d) Subtract the angle-measuring device rotational offset, R_{ADO}, if any, from the result obtained in step (c).

(e) The final result obtained in step (d) is the yaw angle of flow.

[NOTE: It may be necessary to first apply a 90° adjustment to the reading in step (a), in order to obtain the correct yaw angle.]

8.9.4.3 Record the yaw angle measurements on a form similar to Table 2G–3.

8.9.5 Impact velocity determination. Maintain the probe rotational position established during the yaw angle determination. Then, begin recording the pressure-measuring device readings. These pressure measurements shall be taken over a sampling period of sufficiently long duration to ensure representative readings at each traverse point. If the pressure measurements are determined from visual readings of the pressure device or display, allow sufficient time to observe the pulsation in the readings to obtain a sight-weighted average, which is then recorded manually. If an automated data acquisition system (e.g., data logger, computer-based data recorder, strip chart recorder) is used to record the pressure measurements, obtain an integrated average of all pressure readings at the traverse point. Stack or duct gas temperature measurements shall be recorded, at a minimum, once at each traverse point. Record all necessary data as shown in the example field data form (Table 2G–3).

8.9.6 Alignment check. For manually operated probes, after the required yaw angle and differential pressure and temperature measurements have been made at each traverse point, verify (e.g., by visual inspection) that the yaw angle-measuring device has remained in proper alignment with the reference scribe line or with the rotational offset position established in section 8.3. If, for a particular traverse point, the angle-measuring device is found to be in proper alignment, proceed to the next traverse point; otherwise, re-align the device and repeat the angle and differential pressure measurements at the traverse point. In the course of a traverse, if a mark used to properly align the angle-measuring device (e.g., as described in section 18.1.1.1) cannot be located, re-establish the alignment mark before proceeding with the traverse.

8.10 Probe Plugging. Periodically check for plugging of the pressure ports by observing the responses on the pressure differential readouts. Plugging causes erratic results or sluggish responses. Rotate the probe to determine whether the readouts respond in the expected direction. If plugging is detected, correct the problem and repeat the affected measurements.

8.11 Static Pressure. Measure the static pressure in the stack or duct using the equipment described in section 6.7.

8.11.1 If a Type S probe is used for this measurement, position the probe at or between any traverse point(s) and rotate the probe until a null differential pressure reading is obtained. Disconnect the tubing from one of the pressure ports; read and record the ΔP. For pressure devices with one-directional scales, if a deflection in the positive direction is noted with the negative side disconnected, then the static pressure is positive. Likewise, if a deflection in the positive direction is noted with the positive side disconnected, then the static pressure is negative.

8.11.2 If a 3–D probe is used for this measurement, position the probe at or between any traverse point(s) and rotate the probe until a null differential pressure reading is obtained at P_2–P_3. Rotate the probe 90°. Disconnect the P_2 pressure side of the probe and read the pressure P_1–P_{bar} and record as the static pressure. (NOTE: The spherical probe, specified in section 6.1.2 of Method 2F, is unable to provide this measurement and shall not be used to take static pressure measurements.)

8.12 Atmospheric Pressure. Determine the atmospheric pressure at the sampling elevation during each test run following the procedure described in section 2.5 of Method 2.

8.13 Molecular Weight. Determine the stack or duct gas dry molecular weight. For combustion processes or processes that emit essentially CO_2, O_2, CO, and N_2, use Method 3 or 3A. For processes emitting essentially air, an analysis need not be conducted; use a dry molecular weight of 29.0. Other methods may be used, if approved by the Administrator.

8.14 Moisture. Determine the moisture content of the stack gas using Method 4 or equivalent.

8.15 Data Recording and Calculations. Record all required data on a form similar to Table 2G–3.

8.15.1 2–D probe calibration coefficient. When a Type S pitot tube is used in the field, the appropriate calibration coefficient as determined in section 10.6 shall be used to perform velocity calculations. For calibrated Type S pitot tubes, the A-side coefficient shall be used when the A-side of the tube faces the flow, and the B-side coefficient shall be used when the B-side faces the flow.

8.15.2 3–D calibration coefficient. When a 3–D probe is used to collect data with this method, follow the provisions for the calibration of 3–D probes in section 10.6 of Method 2F to obtain the appropriate velocity calibration coefficient (F_2 as derived using Equation 2F–2 in Method 2F) corresponding to a pitch angle position of 0°.

8.15.3 Calculations. Calculate the yaw-adjusted velocity at each traverse point using the equations presented in section 12.2. Calculate the test run average stack gas velocity by finding the arithmetic average of the point velocity results in accordance with sections 12.3 and 12.4, and calculate the stack gas volumetric flow rate in accordance with section 12.5 or 12.6, as applicable.

9.0 Quality Control

9.1 Quality Control Activities. In conjunction with the yaw angle determination and the pressure and temperature measurements specified in section 8.9, the following quality control checks should be performed.

9.1.1 Range of the differential pressure gauge. In accordance with the specifications in section 6.4, ensure that the proper differential pressure gauge is being used for the range of ΔP values encountered. If it is necessary to change to a more sensitive gauge, replace the gauge with a gauge calibrated according to section 10.3.3, perform the leak check described in section 8.4 and the zero check described in section 8.5, and repeat the differential pressure and temperature readings at each traverse point.

9.1.2 Horizontal stability check. For horizontal traverses of a stack or duct, visually check that the probe shaft is maintained in a horizontal position prior to taking a pressure reading. Periodically, during a test run, the probe's horizontal stability should be verified by placing a carpenter's level, a digital inclinometer, or other angle-measuring device on the portion of the probe sheath that extends outside of the test port. A comparable check should be performed by automated systems.

10.0 Calibration

10.1 Wind Tunnel Qualification Checks. To qualify for use in calibrating probes, a wind tunnel shall have the design features specified in section 6.11 and satisfy the following qualification criteria. The velocity pressure cross-check in section 10.1.1 and axial flow verification in section 10.1.2 shall be performed before the initial use of the wind tunnel and repeated immediately after any alteration occurs in the wind tunnel's configuration, fans, interior surfaces, straightening vanes, controls, or other properties that could reasonably be expected to alter the flow pattern or velocity stability in the tunnel. The owner or operator of a wind tunnel used to calibrate probes according to this method shall maintain records documenting that the wind tunnel meets the requirements of sections 10.1.1 and 10.1.2 and shall provide these records to the Administrator upon request.

10.1.1 Velocity pressure cross-check. To verify that the wind tunnel produces the same velocity at the tested probe head as at the calibration pitot tube impact port, perform the following cross-check. Take three

differential pressure measurements at the fixed calibration pitot tube location, using the calibration pitot tube specified in section 6.10, and take three measurements with the calibration pitot tube at the wind tunnel calibration location, as defined in section 3.21. Alternate the measurements between the two positions. Perform this procedure at the lowest and highest velocity settings at which the probes will be calibrated. Record the values on a form similar to Table 2G–4. At each velocity setting, the average velocity pressure obtained at the wind tunnel calibration location shall be within ±2 percent or 2.5 mm H_2O (0.01 in. H_2O), whichever is less restrictive, of the average velocity pressure obtained at the fixed calibration pitot tube location. This comparative check shall be performed at 2.5-cm (1-in.), or smaller, intervals across the full length, width, and depth (if applicable) of the wind tunnel calibration location. If the criteria are not met at every tested point, the wind tunnel calibration location must be redefined, so that acceptable results are obtained at every point. Include the results of the velocity pressure cross-check in the calibration data section of the field test report. (See section 16.1.4.)

10.1.2 Axial flow verification. The following procedures shall be performed to demonstrate that there is fully developed axial flow within the wind tunnel calibration location and at the calibration pitot tube location. Two options are available to conduct this check.

10.1.2.1 Using a calibrated 3–D probe. A probe that has been previously calibrated in a wind tunnel with documented axial flow (as defined in section 3.22) may be used to conduct this check. Insert the calibrated 3–D probe into the wind tunnel test section using the tested probe port. Following the procedures in sections 8.9 and 12.2 of Method 2F, determine the yaw and pitch angles at all the point(s) in the test section where the velocity pressure cross-check, as specified in section 10.1.1, is performed. This includes all the points in the calibration location and the point where the calibration pitot tube will be located. Determine the yaw and pitch angles at each point. Repeat these measurements at the highest and lowest velocities at which the probes will be calibrated. Record the values on a form similar to Table 2G–5. Each measured yaw and pitch angle shall be within ±3° of 0°. Exceeding the limits indicates unacceptable flow in the test section. Until the problem is corrected and acceptable flow is verified by repetition of this procedure, the wind tunnel shall not be used for calibration of probes. Include the results of the axial flow verification in the calibration data section of the field test report. (See section 16.1.4.)

10.1.2.2 Using alternative probes. Axial flow verification may be performed using an uncalibrated prism-shaped 3–D probe (e.g., DA or DAT probe) or an uncalibrated wedge probe. (Figure 2G–8 illustrates a typical wedge probe.) This approach requires use of two ports: the tested probe port and a second port located 90° from the tested probe port. Each port shall provide access to all the points within the wind tunnel test section where the velocity pressure cross-check, as specified in section 10.1.1, is conducted. The probe setup shall include establishing a reference yaw-null position on the probe sheath to serve as the location for installing the angle-measuring device. Physical design features of the DA, DAT, and wedge probes are relied on to determine the reference position. For the DA or DAT probe, this reference position can be determined by setting a digital inclinometer on the flat facet where the P_1 pressure port is located and then identifying the rotational position on the probe sheath where a second angle-measuring device would give the same angle reading. The reference position on a wedge probe shaft can be determined either geometrically or by placing a digital inclinometer on each side of the wedge and rotating the probe until equivalent readings are obtained. With the latter approach, the reference position is the rotational position on the probe sheath where an angle-measuring device would give a reading of 0°. After installation of the angle-measuring device in the reference yaw-null position on the probe sheath, determine the yaw angle from the tested port. Repeat this measurement using the 90° offset port, which provides the pitch angle of flow. Determine the yaw and pitch angles at all the point(s) in the test section where the velocity pressure cross-check, as specified in section 10.1.1, is performed. This includes all the points in the wind tunnel calibration location and the point where the calibration pitot tube will be located. Perform this check at the highest and lowest velocities at which the probes will be calibrated. Record the values on a form similar to Table 2G–5. Each measured yaw and pitch angle shall be within ±3° of 0°. Exceeding the limits indicates unacceptable flow in the test section. Until the problem is corrected and acceptable flow is verified by repetition of this procedure, the wind tunnel shall not be used for calibration of probes. Include the results in the probe calibration report.

10.1.3 Wind tunnel audits.

10.1.3.1 Procedure. Upon the request of the Administrator, the owner or operator of a wind tunnel shall calibrate a 2-D audit probe in accordance with the procedures described in sections 10.3 through 10.6. The calibration shall be performed at two velocities that encompass the velocities typically used for this method at the facility. The resulting calibration data shall be submitted to the Agency in an audit test report. These results shall be

compared by the Agency to reference calibrations of the audit probe at the same velocity settings obtained at two different wind tunnels.

10.1.3.2 Acceptance criterion. The audited tunnel's calibration coefficient is acceptable if it is within ±3 percent of the reference calibrations obtained at each velocity setting by one (or both) of the wind tunnels. If the acceptance criterion is not met at each calibration velocity setting, the audited wind tunnel shall not be used to calibrate probes for use under this method until the problems are resolved and acceptable results are obtained upon completion of a subsequent audit.

10.2 Probe Inspection.

10.2.1 Type S probe. Before each calibration of a Type S probe, verify that one leg of the tube is permanently marked A, and the other, B. Carefully examine the pitot tube from the top, side, and ends. Measure the angles (α_1, α_2, β_1, and β_2) and the dimensions (w and z) illustrated in Figures 2–2 and 2–3 in Method 2. Also measure the dimension A, as shown in the diagram in Table 2G–1, and the external tubing diameter (dimension D_t, Figure 2–2b in Method 2). For the purposes of this method, D_t shall be no less than 9.5 mm (3/8 in.). The base-to-opening plane distances P_A and P_B in Figure 2–3 of Method 2 shall be equal, and the dimension A in Table 2G–1 should be between $2.10D_t$ and $3.00D_t$. Record the inspection findings and probe measurements on a form similar to Table CD2–1 of the ''Quality Assurance Handbook for Air Pollution Measurement Systems: Volume III, Stationary Source-Specific Methods'' (EPA/600/R–94/038c, September 1994). For reference, this form is reproduced herein as Table 2G–1. The pitot tube shall not be used under this method if it fails to meet the specifications in this section and the alignment specifications in section 6.1.1. All Type S probes used to collect data with this method shall be calibrated according to the procedures outlined in sections 10.3 through 10.6 below. During calibration, each Type S pitot tube shall be configured in the same manner as used, or planned to be used, during the field test, including all components in the probe assembly (e.g., thermocouple, probe sheath, sampling nozzle). Probe shaft extensions that do not affect flow around the probe head need not be attached during calibration.

10.2.2 3-D probe. If a 3-D probe is used to collect data with this method, perform the pre-calibration inspection according to procedures in Method 2F, section 10.2.

10.3 Pre-Calibration Procedures. Prior to calibration, a scribe line shall have been placed on the probe in accordance with section 10.4. The yaw angle and velocity calibration procedures shall not begin until the pretest requirements in sections 10.3.1 through 10.3.4 have been met.

10.3.1 Perform the horizontal straightness check described in section 8.2 on the probe assembly that will be calibrated in the wind tunnel.

10.3.2 Perform a leak check in accordance with section 8.4.

10.3.3 Except as noted in section 10.3.3.3, calibrate all differential pressure-measuring devices to be used in the probe calibrations, using the following procedures. At a minimum, calibrate these devices on each day that probe calibrations are performed.

10.3.3.1 Procedure. Before each wind tunnel use, all differential pressure-measuring devices shall be calibrated against the reference device specified in section 6.4.3 using a common pressure source. Perform the calibration at three reference pressures representing 30, 60, and 90 percent of the full-scale range of the pressure-measuring device being calibrated. For an inclined-vertical manometer, perform separate calibrations on the inclined and vertical portions of the measurement scale, considering each portion of the scale to be a separate full-scale range. [For example, for a manometer with a 0-to 2.5-cm H_2O (0-to 1-in. H_2O) inclined scale and a 2.5-to 12.7-cm H_2O (1-to 5-in. H_2O) vertical scale, calibrate the inclined portion at 7.6, 15.2, and 22.9 mm H_2O (0.3, 0.6, and 0.9 in. H_2O), and calibrate the vertical portion at 3.8, 7.6, and 11.4 cm H_2O (1.5, 3.0, and 4.5 in. H_2O).] Alternatively, for the vertical portion of the scale, use three evenly spaced reference pressures, one of which is equal to or higher than the highest differential pressure expected in field applications.

10.3.3.2 Acceptance criteria. At each pressure setting, the two pressure readings made using the reference device and the pressure-measuring device being calibrated shall agree to within ±2 percent of full scale of the device being calibrated or 0.5 mm H_2O (0.02 in. H_2O), whichever is less restrictive. For an inclined-vertical manometer, these requirements shall be met separately using the respective full-scale upper limits of the inclined and vertical portions of the scale. Differential pressure-measuring devices not meeting the ±2 percent of full scale or 0.5 mm H_2O (0.02 in. H_2O) calibration requirement shall not be used.

10.3.3.3 Exceptions. Any precision manometer that meets the specifications for a reference device in section 6.4.3 and that is not used for field testing does not require calibration, but must be leveled and zeroed before each wind tunnel use. Any pressure device used exclusively for yaw nulling does not require calibration, but shall be checked for responsiveness to rotation of the probe prior to each wind tunnel use.

10.3.4 Calibrate digital inclinometers on each day of wind tunnel or field testing

(prior to beginning testing) using the following procedures. Calibrate the inclinometer according to the manufacturer's calibration procedures. In addition, use a triangular block (illustrated in Figure 2G–9) with a known angle θ, independently determined using a protractor or equivalent device, between two adjacent sides to verify the inclinometer readings. (NOTE: If other angle-measuring devices meeting the provisions of section 6.2.3 are used in place of a digital inclinometer, comparable calibration procedures shall be performed on such devices.) Secure the triangular block in a fixed position. Place the inclinometer on one side of the block (side A) to measure the angle of inclination (R_1). Repeat this measurement on the adjacent side of the block (side B) using the inclinometer to obtain a second angle reading (R_2). The difference of the sum of the two readings from 180° (i.e., 180°-R_1-R_2) shall be within ±2° of the known angle, θ.

10.4 Placement of Reference Scribe Line. Prior to the first calibration of a probe, a line shall be permanently inscribed on the main probe sheath to serve as a reference mark for determining yaw angles. Annex C in section 18 of this method gives a guideline for placement of the reference scribe line.

10.4.1 This reference scribe line shall meet the specifications in sections 6.1.5.1 and 6.1.5.3 of this method. To verify that the alignment specification in section 6.1.5.3 is met, secure the probe in a horizontal position and measure the rotational angle of each scribe line and scribe line segment using an angle-measuring device that meets the specifications in section 6.2.1 or 6.2.3. For any scribe line that is longer than 30.5 cm (12 in.), check the line's rotational position at 30.5-cm (12-in.) intervals. For each line segment that is 12 in. or less in length, check the rotational position at the two endpoints of the segment. To meet the alignment specification in section 6.1.5.3, the minimum and maximum of all of the rotational angles that are measured along the full length of main probe must not differ by more than 2°. (NOTE: A short reference scribe line segment [e.g., 15.2 cm (6 in.) or less in length] meeting the alignment specifications in section 6.1.5.3 is fully acceptable under this method. See section 18.1.1.1 of Annex A for an example of a probe marking procedure, suitable for use with a short reference scribe line.)

10.4.2 The scribe line should be placed on the probe first and then its offset from the yaw-null position established (as specified in section 10.5). The rotational position of the reference scribe line relative to the yaw-null position of the probe, as determined by the yaw angle calibration procedure in section 10.5, is the reference scribe line rotational offset, R_{SLO}. The reference scribe line rotational offset shall be recorded and retained as part of the probe's calibration record.

10.4.3 Scribe line for automated probes. A scribe line may not be necessary for an automated probe system if a reference rotational position of the probe is built into the probe system design. For such systems, a ''flat'' (or comparable, clearly identifiable physical characteristic) should be provided on the probe casing or flange plate to ensure that the reference position of the probe assembly remains in a vertical or horizontal position. The rotational offset of the flat (or comparable, clearly identifiable physical characteristic) needed to orient the reference position of the probe assembly shall be recorded and maintained as part of the automated probe system's specifications.

10.5 Yaw Angle Calibration Procedure. For each probe used to measure yaw angles with this method, a calibration procedure shall be performed in a wind tunnel meeting the specifications in section 10.1 to determine the rotational position of the reference scribe line relative to the probe's yaw-null position. This procedure shall be performed on the main probe with all devices that will be attached to the main probe in the field [such as thermocouples, resistance temperature detectors (RTDs), or sampling nozzles] that may affect the flow around the probe head. Probe shaft extensions that do not affect flow around the probe head need not be attached during calibration. At a minimum, this procedure shall include the following steps.

10.5.1 Align and lock the angle-measuring device on the reference scribe line. If a marking procedure (such as described in section 18.1.1.1) is used, align the angle-measuring device on a mark within ±1° of the rotational position of the reference scribe line. Lock the angle-measuring device onto the probe sheath at this position.

10.5.2 Zero the pressure-measuring device used for yaw nulling.

10.5.3 Insert the probe assembly into the wind tunnel through the entry port, positioning the probe's impact port at the calibration location. Check the responsiveness of the pressure-measurement device to probe rotation, taking corrective action if the response is unacceptable.

10.5.4 Ensure that the probe is in a horizontal position, using a carpenter's level.

10.5.5 Rotate the probe either clockwise or counterclockwise until a yaw null [zero ΔP for a Type S probe or zero (P_2-P_3) for a 3–D probe] is obtained. If using a Type S probe with an attached thermocouple, the direction of the probe rotation shall be such that the thermocouple is located downstream of the probe pressure ports at the yaw-null position.

10.5.6 Use the reading displayed by the angle-measuring device at the yaw-null position to determine the magnitude of the reference scribe line rotational offset, R_{SLO}, as defined in section 3.15. Annex D in section 18

of this method gives a recommended procedure for determining the magnitude of R_{SLO} with a digital inclinometer and a second procedure for determining the magnitude of R_{SLO} with a protractor wheel and pointer device. Table 2G–6 gives an example data form and Table 2G–7 is a look-up table with the recommended procedure. Procedures other than those recommended in Annex D in section 18 may be used, if they can determine R_{SLO} to within 1° and are explained in detail in the field test report. The algebraic sign of R_{SLO} will either be positive if the rotational position of the reference scribe line (as viewed from the ''tail'' end of the probe) is clockwise, or negative, if counterclockwise with respect to the probe's yaw-null position. (This is illustrated in Figure 2G–10.)

10.5.7 The steps in sections 10.5.3 through 10.5.6 shall be performed twice at each of the velocities at which the probe will be calibrated (in accordance with section 10.6). Record the values of R_{SLO}.

10.5.8 The average of all of the R_{SLO} values shall be documented as the reference scribe line rotational offset for the probe.

10.5.9 Use of reference scribe line offset. The reference scribe line rotational offset shall be used to determine the yaw angle of flow in accordance with section 8.9.4.

10.6 Velocity Calibration Procedure. When a 3–D probe is used under this method, follow the provisions for the calibration of 3–D probes in section 10.6 of Method 2F to obtain the necessary velocity calibration coefficients (F_2 as derived using Equation 2F–2 in Method 2F) corresponding to a pitch angle position of 0°. The following procedure applies to Type S probes. This procedure shall be performed on the main probe and all devices that will be attached to the main probe in the field (e.g., thermocouples, RTDs, sampling nozzles) that may affect the flow around the probe head. Probe shaft extensions that do not affect flow around the probe head need not be attached during calibration. (Note: If a sampling nozzle is part of the assembly, two additional requirements must be satisfied before proceeding. The distance between the nozzle and the pitot tube shall meet the minimum spacing requirement prescribed in Method 2, and a wind tunnel demonstration shall be performed that shows the probe's ability to yaw null is not impaired when the nozzle is drawing sample.) To obtain velocity calibration coefficient(s) for the tested probe, proceed as follows.

10.6.1 Calibration velocities. The tester may calibrate the probe at two nominal wind tunnel velocity settings of 18.3 m/sec and 27.4 m/sec (60 ft/sec and 90 ft/sec) and average the results of these calibrations, as described in sections 10.6.12 through 10.6.14, in order to generate the calibration coefficient, C_p. If this option is selected, this calibration coefficient may be used for all field applications where the velocities are 9.1 m/sec (30 ft/sec) or greater. Alternatively, the tester may customize the probe calibration for a particular field test application (or for a series of applications), based on the expected average velocity(ies) at the test site(s). If this option is selected, generate the calibration coefficients by calibrating the probe at two nominal wind tunnel velocity settings, one of which is less than or equal to and the other greater than or equal to the expected average velocity(ies) for the field application(s), and average the results as described in sections 10.6.12 through 10.6.14. Whichever calibration option is selected, the probe calibration coefficient(s) obtained at the two nominal calibration velocities shall meet the conditions specified in sections 10.6.12 through 10.6.14.

10.6.2 Connect the tested probe and calibration pitot tube to their respective pressure-measuring devices. Zero the pressure-measuring devices. Inspect and leak-check all pitot lines; repair or replace them, if necessary. Turn on the fan, and allow the wind tunnel air flow to stabilize at the first of the selected nominal velocity settings.

10.6.3 Position the calibration pitot tube at its measurement location (determined as outlined in section 6.11.4.3), and align the tube so that its tip is pointed directly into the flow. Ensure that the entry port surrounding the tube is properly sealed. The calibration pitot tube may either remain in the wind tunnel throughout the calibration, or be removed from the wind tunnel while measurements are taken with the probe being calibrated.

10.6.4 Check the zero setting of each pressure-measuring device.

10.6.5 Insert the tested probe into the wind tunnel and align it so that the designated pressure port (e.g., either the A-side or B-side of a Type S probe) is pointed directly into the flow and is positioned within the wind tunnel calibration location (as defined in section 3.21). Secure the probe at the 0° pitch angle position. Ensure that the entry port surrounding the probe is properly sealed.

10.6.6 Read the differential pressure from the calibration pitot tube (ΔP_{std}), and record its value. Read the barometric pressure to within ±2.5 mm Hg (±0.1 in. Hg) and the temperature in the wind tunnel to within 0.6 °C (1 °F). Record these values on a data form similar to Table 2G–8. Record the rotational speed of the fan or indicator of wind tunnel velocity control (damper setting, variac rheostat, etc.) and make no adjustment to fan speed or wind tunnel velocity control between this observation and the Type S probe reading.

10.6.7 After the tested probe's differential pressure gauges have had sufficient time to stabilize, yaw null the probe (and then rotate it back 90° for Type S probes), then obtain the differential pressure reading (ΔP). Record

the yaw angle and differential pressure readings.

10.6.8 Take paired differential pressure measurements with the calibration pitot tube and tested probe (according to sections 10.6.6 and 10.6.7). The paired measurements in each replicate can be made either simultaneously (*i.e.*, with both probes in the wind tunnel) or by alternating the measurements of the two probes (*i.e.*, with only one probe at a time in the wind tunnel). Adjustments made to the fan speed or other changes to the system designed to change the air flow velocity of the wind tunnel between observation of the calibration pitot tube (ΔP_{std}) and the Type S pitot tube invalidates the reading and the observation must be repeated.

10.6.9 Repeat the steps in sections 10.6.6 through 10.6.8 at the same nominal velocity setting until three pairs of ΔP readings have been obtained from the calibration pitot tube and the tested probe.

10.6.10 Repeat the steps in sections 10.6.6 through 10.6.9 above for the A-side and B-side of the Type S pitot tube. For a probe assembly constructed such that its pitot tube is always used in the same orientation, only one side of the pitot tube need be calibrated (the side that will face the flow). However, the pitot tube must still meet the alignment and dimension specifications in section 6.1.1 and must have an average deviation (σ) value of 0.01 or less as provided in section 10.6.12.4.

10.6.11 Repeat the calibration procedures in sections 10.6.6 through 10.6.10 at the second selected nominal wind tunnel velocity setting.

10.6.12 Perform the following calculations separately on the A-side and B-side values.

10.6.12.1 Calculate a C_p value for each of the three replicates performed at the lower velocity setting where the calibrations were performed using Equation 2–2 in section 4.1.4 of Method 2.

10.6.12.2 Calculate the arithmetic average, $C_{p(avg\text{-}low)}$, of the three C_p values.

10.6.12.3 Calculate the deviation of each of the three individual values of C_p from the A-side average $C_{p(avg\text{-}low)}$ value using Equation 2–3 in Method 2.

10.6.12.4 Calculate the average deviation (σ) of the three individual C_p values from $C_{p(avg\text{-}low)}$ using Equation 2–4 in Method 2. Use the Type S pitot tube only if the values of σ (side A) and σ (side B) are less than or equal to 0.01. If both A-side and B-side calibration coefficients are calculated, the absolute value of the difference between $C_{p(avg\text{-}low)}$ (side A) and $C_{p(avg\text{-}low)}$ (side B) must not exceed 0.01.

10.6.13 Repeat the calculations in section 10.6.12 using the data obtained at the higher velocity setting to derive the arithmetic C_p values at the higher velocity setting, $C_{p(avg\text{-}high)}$, and to determine whether the conditions in 10.6.12.4 are met by both the A-side and B-side calibrations at this velocity setting.

10.6.14 Use equation 2G–1 to calculate the percent difference of the averaged C_p values at the two calibration velocities.

$$\%\text{Difference} = \frac{C_{p(avg\text{-}low)} - C_{p(avg\text{-}high)}}{C_{p(avg\text{-}low)}} \times 100\% \quad \text{Eq. 2G-1}$$

The percent difference between the averaged C_p values shall not exceed ±3 percent. If the specification is met, average the A-side values of $C_{p(avg\text{-}low)}$ and $C_{p(avg\text{-}high)}$ to produce a single A-side calibration coefficient, C_p. Repeat for the B-side values if calibrations were performed on that side of the pitot. If the specification is not met, make necessary adjustments in the selected velocity settings and repeat the calibration procedure until acceptable results are obtained.

10.6.15 If the two nominal velocities used in the calibration were 18.3 and 27.4 m/sec (60 and 90 ft/sec), the average C_p from section 10.6.14 is applicable to all velocities 9.1 m/sec (30 ft/sec) or greater. If two other nominal velocities were used in the calibration, the resulting average C_p value shall be applicable only in situations where the velocity calculated using the calibration coefficient is neither less than the lower nominal velocity nor greater than the higher nominal velocity.

10.7 Recalibration. Recalibrate the probe using the procedures in section 10 either within 12 months of its first field use after its most recent calibration or after 10 field tests (as defined in section 3.3), whichever occurs later. In addition, whenever there is visible damage to the probe head, the probe shall be recalibrated before it is used again.

10.8 Calibration of pressure-measuring devices used in the field. Before its initial use in a field test, calibrate each pressure-measuring device (except those used exclusively for yaw nulling) using the three-point calibration procedure described in section 10.3.3. The device shall be recalibrated according to the procedure in section 10.3.3 no later than 90 days after its first field use following its most recent calibration. At the discretion of the tester, more frequent calibrations (e.g.,

after a field test) may be performed. No adjustments, other than adjustments to the zero setting, shall be made to the device between calibrations.

10.8.1 Post-test calibration check. A single-point calibration check shall be performed on each pressure-measuring device after completion of each field test. At the discretion of the tester, more frequent single-point calibration checks (e.g., after one or more field test runs) may be performed. It is recommended that the post-test check be performed before leaving the field test site. The check shall be performed at a pressure between 50 and 90 percent of full scale by taking a common pressure reading with the tested probe and a reference pressure-measuring device (as described in section 6.4.4) or by challenging the tested device with a reference pressure source (as described in section 6.4.4) or by performing an equivalent check using a reference device approved by the Administrator.

10.8.2 Acceptance criterion. At the selected pressure setting, the pressure readings made using the reference device and the tested device shall agree to within ±3 percent of full scale of the tested device or 0.8 mm H_2O (0.03 in. H_2O), whichever is less restrictive. If this specification is met, the test data collected during the field test are valid. If the specification is not met, all test data collected since the last successful calibration or calibration check are invalid and shall be repeated using a pressure-measuring device with a current, valid calibration. Any device that fails the calibration check shall not be used in a field test until a successful recalibration is performed according to the procedures in section 10.3.3.

10.9 Temperature Gauges. Same as Method 2, section 4.3. The alternative thermocouple calibration procedures outlined in Emission Measurement Center (EMC) Approved Alternative Method (ALT–011) ''Alternative Method 2 Thermocouple Calibration Procedure'' may be performed. Temperature gauges shall be calibrated no more than 30 days prior to the start of a field test or series of field tests and recalibrated no more than 30 days after completion of a field test or series of field tests.

10.10 Barometer. Same as Method 2, section 4.4. The barometer shall be calibrated no more than 30 days prior to the start of a field test or series of field tests.

11.0 Analytical Procedure

Sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Data Analysis and Calculations

These calculations use the measured yaw angle and the differential pressure and temperature measurements at individual traverse points to derive the near-axial flue gas velocity ($v_{a(i)}$) at each of those points. The near-axial velocity values at all traverse points that comprise a full stack or duct traverse are then averaged to obtain the average near-axial stack or duct gas velocity ($v_{a(avg)}$).

12.1 Nomenclature

A = Cross-sectional area of stack or duct at the test port location, m^2 (ft^2).

B_{ws} = Water vapor in the gas stream (from Method 4 or alternative), proportion by volume.

C_p = Pitot tube calibration coefficient, dimensionless.

$F_{2(i)}$ = 3-D probe velocity coefficient at 0 pitch, applicable at traverse point i.

K_p = Pitot tube constant,

$$34.97\frac{m}{sec}\left[\frac{(g/g\text{-}mole)(mm\ Hg)}{(^\circ K)(mm\ H_2O)}\right]^{1/2}$$

for the metric system, and

$$85.49\frac{ft}{sec}\left[\frac{(lb/lb\text{-}mole)(in.\ Hg)}{(^\circ R)(in.\ H_2O)}\right]^{1/2}$$

for the English system.

M_d = Molecular weight of stack or duct gas, dry basis (see section 8.13), g/g-mole (lb/lb-mole).

M_s = Molecular weight of stack or duct gas, wet basis, g/g-mole (lb/lb-mole).

$$M_s = M_d(1-B_{ws}) + 18.0B_{ws} \quad \text{Eq. 2G-2}$$

P_{bar} = Barometric pressure at velocity measurement site, mm Hg (in. Hg).

P_g = Stack or duct static pressure, mm H_2O (in. H_2O).

P_s = Absolute stack or duct pressure, mm Hg (in. Hg),

$$P_s = P_{bar} + \frac{P_g}{13.6} \quad \text{Eq. 2G-3}$$

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

13.6 = Conversion from mm H_2O (in. H_2O) to mm Hg (in. Hg).

Q_{sd} = Average dry-basis volumetric stack or duct gas flow rate corrected to standard conditions, dscm/hr (dscf/hr).

Q_{sw} = Average wet-basis volumetric stack or duct gas flow rate corrected to standard conditions, wscm/hr (wscf/hr).

$t_{s(i)}$ = Stack or duct temperature, °C (°F), at traverse point i.

$T_{s(i)}$ = Absolute stack or duct temperature, °K (°R), at traverse point i.

$$T_{s(i)} = 273 + t_{s(i)} \quad \text{Eq. 2G-4}$$

for the metric system, and

$$T_{s(i)} = 460 + t_{s(i)} \qquad \text{Eq. 2G-5}$$

for the English system.

$T_{s(avg)}$ = Average absolute stack or duct gas temperature across all traverse points.

T_{std} = Standard absolute temperature, 293 °K (528 °R).

$v_{a(i)}$ = Measured stack or duct gas impact velocity, m/sec (ft/sec), at traverse point i.

$v_{a(avg)}$ = Average near-axial stack or duct gas velocity, m/sec (ft/sec) across all traverse points.

ΔP_i = Velocity head (differential pressure) of stack or duct gas, mm H_2O (in. H_2O), applicable at traverse point i.

$(P_1\text{-}P_2)$ = Velocity head (differential pressure) of stack or duct gas measured by a 3-D probe, mm H_2O (in. H_2O), applicable at traverse point i.

3,600 = Conversion factor, sec/hr.

18.0 = Molecular weight of water, g/g-mole (lb/lb-mole).

$\theta_{y(i)}$ = Yaw angle of the flow velocity vector, at traverse point i.

n = Number of traverse points.

12.2 Traverse Point Velocity Calculations. Perform the following calculations from the measurements obtained at each traverse point.

12.2.1 Selection of calibration coefficient. Select the calibration coefficient as described in section 10.6.1.

12.2.2 Near-axial traverse point velocity. When using a Type S probe, use the following equation to calculate the traverse point near-axial velocity ($v_{a(i)}$) from the differential pressure (ΔP_i), yaw angle ($\theta_{y(i)}$), absolute stack or duct standard temperature ($T_{s(i)}$) measured at traverse point i, the absolute stack or duct pressure (P_s), and molecular weight (M_s).

$$v_{a(i)} = K_p C_p \sqrt{\frac{(\Delta P)_i T_{s(i)}}{P_s M_s}} \left(\cos\theta_{y(i)}\right) \qquad \text{Eq. 2G-6}$$

Use the following equation when using a 3–D probe.

$$v_{a(i)} = K_p F_2 \sqrt{\frac{(P_1 - P_2)_i T_{s(i)}}{P_s M_s}} \left(\cos\theta_{y(i)}\right) \qquad \text{Eq. 2G-7}$$

12.2.3 Handling multiple measurements at a traverse point. For pressure or temperature devices that take multiple measurements at a traverse point, the multiple measurements (or where applicable, their square roots) may first be averaged and the resulting average values used in the equations above. Alternatively, the individual measurements may be used in the equations above and the resulting calculated values may then be averaged to obtain a single traverse point value. With either approach, all of the individual measurements recorded at a traverse point must be used in calculating the applicable traverse point value.

12.3 Average Near-Axial Velocity in Stack or Duct. Use the reported traverse point near-axial velocity in the following equation.

$$v_{a(avg)} = \frac{\sum_{i=1}^{n} v_{a(i)}}{n} \qquad \text{Eq. 2G-8}$$

12.4 Acceptability of Results. The acceptability provisions in section 12.4 of Method 2F apply to 3-D probes used under Method 2G. The following provisions apply to Type S probes. For Type S probes, the test results are acceptable and the calculated value of $v_{a(avg)}$ may be reported as the average near-axial velocity for the test run if the conditions in either section 12.4.1 or 12.4.2 are met.

12.4.1 The average calibration coefficient C_p used in Equation 2G–6 was generated at nominal velocities of 18.3 and 27.4 m/sec (60 and 90 ft/sec) and the value of $v_{a(avg)}$ calculated using Equation 2G–8 is greater than or equal to 9.1 m/sec (30 ft/sec).

12.4.2 The average calibration coefficient C_p used in Equation 2G–6 was generated at nominal velocities other than 18.3 or 27.4 m/

sec (60 or 90 ft/sec) and the value of $v_{a(avg)}$ calculated using Equation 2G–8 is greater than or equal to the lower nominal velocity and less than or equal to the higher nominal velocity used to derive the average C_p.

12.4.3 If the conditions in neither section 12.4.1 nor section 12.4.2 are met, the test results obtained from Equation 2G–8 are not acceptable, and the steps in sections 12.2 and 12.3 must be repeated using an average calibration coefficient C_p that satisfies the conditions in section 12.4.1 or 12.4.2.

12.5 Average Gas Volumetric Flow Rate in Stack or Duct (Wet Basis). Use the following equation to compute the average volumetric flow rate on a wet basis.

$$Q_{sw} = 3{,}600\left(v_{a(avg)}\right)(A)\left(\frac{T_{std}}{T_{s(avg)}}\right)\left(\frac{P_s}{P_{std}}\right) \qquad \text{Eq. 2G-9}$$

12.6 Average Gas Volumetric Flow Rate in Stack or Duct (Dry Basis). Use the following equation to compute the average volumetric flow rate on a dry basis.

$$Q_{sd} = 3{,}600\left(1 - B_{ws}\right)\left(v_{a(avg)}\right)(A)\left(\frac{T_{std}}{T_{s(avg)}}\right)\left(\frac{P_s}{P_{std}}\right) \qquad \text{Eq. 2G-10}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Reporting.

16.1 Field Test Reports. Field test reports shall be submitted to the Agency according to applicable regulatory requirements. Field test reports should, at a minimum, include the following elements.

16.1.1 Description of the source. This should include the name and location of the test site, descriptions of the process tested, a description of the combustion source, an accurate diagram of stack or duct cross-sectional area at the test site showing the dimensions of the stack or duct, the location of the test ports, and traverse point locations and identification numbers or codes. It should also include a description and diagram of the stack or duct layout, showing the distance of the test location from the nearest upstream and downstream disturbances and all structural elements (including breachings, baffles, fans, straighteners, etc.) affecting the flow pattern. If the source and test location descriptions have been previously submitted to the Agency in a document (e.g., a monitoring plan or test plan), referencing the document in lieu of including this information in the field test report is acceptable.

16.1.2 Field test procedures. These should include a description of test equipment and test procedures. Testing conventions, such as traverse point numbering and measurement sequence (e.g., sampling from center to wall, or wall to center), should be clearly stated. Test port identification and directional reference for each test port should be included on the appropriate field test data sheets.

16.1.3 Field test data.

16.1.3.1 Summary of results. This summary should include the dates and times of testing, and the average near-axial gas velocity and the average flue gas volumetric flow results for each run and tested condition.

16.1.3.2 Test data. The following values for each traverse point should be recorded and reported:

(a) Differential pressure at traverse point i (ΔP_i)

(b) Stack or duct temperature at traverse point i ($t_{s(i)}$)

(c) Absolute stack or duct temperature at traverse point i ($T_{s(i)}$)

(d) Yaw angle at traverse point i ($\theta_{y(i)}$)

(e) Stack gas near-axial velocity at traverse point i ($v_{a(i)}$)

16.1.3.3 The following values should be reported once per run:

(a) Water vapor in the gas stream (from Method 4 or alternative), proportion by volume (B_{ws}), measured at the frequency specified in the applicable regulation

(b) Molecular weight of stack or duct gas, dry basis (M_d)

(c) Molecular weight of stack or duct gas, wet basis (M_s)

(d) Stack or duct static pressure (P_g)

(e) Absolute stack or duct pressure (P_s)

(f) Carbon dioxide concentration in the flue gas, dry basis ($\%_d$ CO_2)

(g) Oxygen concentration in the flue gas, dry basis (%$_d$ O_2)

(h) Average near-axial stack or duct gas velocity ($v_{a(avg)}$) across all traverse points

(i) Gas volumetric flow rate corrected to standard conditions, dry or wet basis as required by the applicable regulation (Q_{sd} or Q_{sw})

16.1.3.4 The following should be reported once per complete set of test runs:

(a) Cross-sectional area of stack or duct at the test location (A)

(b) Pitot tube calibration coefficient (C_p)

(c) Measurement system response time (sec)

(d) Barometric pressure at measurement site (P_{bar})

16.1.4 Calibration data. The field test report should include calibration data for all probes and test equipment used in the field test. At a minimum, the probe calibration data reported to the Agency should include the following:

(a) Date of calibration

(b) Probe type

(c) Probe identification number(s) or code(s)

(d) Probe inspection sheets

(e) Pressure measurements and calculations used to obtain calibration coefficients in accordance with section 10.6 of this method

(f) Description and diagram of wind tunnel used for the calibration, including dimensions of cross-sectional area and position and size of the test section

(g) Documentation of wind tunnel qualification tests performed in accordance with section 10.1 of this method

16.1.5 Quality assurance. Specific quality assurance and quality control procedures used during the test should be described.

17.0 Bibliography.

(1) 40 CFR Part 60, Appendix A, Method 1—Sample and velocity traverses for stationary sources.

(2) 40 CFR Part 60, Appendix A, Method 2—Determination of stack gas velocity and volumetric flow rate (Type S pitot tube) .

(3) 40 CFR Part 60, Appendix A, Method 2F—Determination of stack gas velocity and volumetric flow rate with three-dimensional probes.

(4) 40 CFR Part 60, Appendix A, Method 2H—Determination of stack gas velocity taking into account velocity decay near the stack wall.

(5) 40 CFR Part 60, Appendix A, Method 3—Gas analysis for carbon dioxide, oxygen, excess air, and dry molecular weight.

(6) 40 CFR Part 60, Appendix A, Method 3A—Determination of oxygen and carbon dioxide concentrations in emissions from stationary sources (instrumental analyzer procedure).

(7) 40 CFR Part 60, Appendix A, Method 4—Determination of moisture content in stack gases.

(8) Emission Measurement Center (EMC) Approved Alternative Method (ALT–011) ''Alternative Method 2 Thermocouple Calibration Procedure.''

(9) Electric Power Research Institute, Interim Report EPRI TR–106698, ''Flue Gas Flow Rate Measurement Errors,'' June 1996.

(10) Electric Power Research Institute, Final Report EPRI TR–108110, ''Evaluation of Heat Rate Discrepancy from Continuous Emission Monitoring Systems,'' August 1997.

(11) Fossil Energy Research Corporation, Final Report, ''Velocity Probe Tests in Non-axial Flow Fields,'' November 1998, Prepared for the U.S. Environmental Protection Agency.

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(17) National Institute of Standards and Technology, 1998, ''Report of Special Test of Air Speed Instrumentation, Eight Spherical Probes,'' Prepared for the U.S. Environmental Protection Agency under IAG #DW13938432–01–0.

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Flow Reference Methods,'' EPRI CEMS User's Group Meeting, New Orleans, Louisiana, May 13–15, 1998.

(20) Page, J.J., E.A. Potts, and R.T. Shigehara, ''3–D Pitot Tube Calibration Study,'' EPA Contract No. 68D10009, Work Assignment No. I–121, March 11, 1993.

(21) Shigehara, R.T., W.F. Todd, and W.S. Smith, ''Significance of Errors in Stack Sampling Measurements,'' Presented at the Annual Meeting of the Air Pollution Control Association, St. Louis, Missouri, June 1419, 1970.

(22) The Cadmus Group, Inc., May 1999, ''EPA Flow Reference Method Testing and Analysis: Findings Report,'' EPA/430–R–99–009.

(23) The Cadmus Group, Inc., 1998, ''EPA Flow Reference Method Testing and Analysis: Data Report, Texas Utilities, DeCordova Steam Electric Station, Volume I: Test Description and Appendix A (Data Distribution Package),'' EPA/430–R–98–015a.

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18.0 Annexes

Annex A, C, and D describe recommended procedures for meeting certain provisions in sections 8.3, 10.4, and 10.5 of this method. Annex B describes procedures to be followed when using the protractor wheel and pointer assembly to measure yaw angles, as provided under section 8.9.1.

18.1 Annex A—Rotational Position Check. The following are recommended procedures that may be used to satisfy the rotational position check requirements of section 8.3 of this method and to determine the angle-measuring device rotational offset (R_{ADO}).

18.1.1 Rotational position check with probe outside stack. Where physical constraints at the sampling location allow full assembly of the probe outside the stack and insertion into the test port, the following procedures should be performed before the start of testing. Two angle-measuring devices that meet the specifications in section 6.2.1 or 6.2.3 are required for the rotational position check. An angle measuring device whose position can be independently adjusted (e.g., by means of a set screw) after being locked into position on the probe sheath shall not be used for this check unless the independent adjustment is set so that the device performs exactly like a device without the capability for independent adjustment. That is, when aligned on the probe such a device must give the same reading as a device that does not have the capability of being independently adjusted. With the fully assembled probe (including probe shaft extensions, if any) secured in a horizontal position, affix one yaw angle-measuring device to the probe sheath and lock it into position on the reference scribe line specified in section 6.1.5.1. Position the second angle-measuring device using the procedure in section 18.1.1.1 or 18.1.1.2.

18.1.1.1 Marking procedure. The procedures in this section should be performed at each location on the fully assembled probe where the yaw angle-measuring device will be mounted during the velocity traverse. Place the second yaw angle-measuring device on the main probe sheath (or extension) at the position where a yaw angle will be measured during the velocity traverse. Adjust the position of the second angle-measuring device until it indicates the same angle (±1°) as the reference device, and affix the second device to the probe sheath (or extension). Record the angles indicated by the two angle-measuring devices on a form similar to table 2G–2. In this position, the second angle-measuring device is considered to be properly positioned for yaw angle measurement. Make a mark, no wider than 1.6 mm (1/16 in.), on the probe sheath (or extension), such that the yaw angle-measuring device can be re-affixed at this same properly aligned position during the velocity traverse.

18.1.1.2 Procedure for probe extensions with scribe lines. If, during a velocity traverse the angle-measuring device will be affixed to a probe extension having a scribe line as specified in section 6.1.5.2, the following procedure may be used to align the extension's scribe line with the reference scribe line instead of marking the extension as described in section 18.1.1.1. Attach the probe extension to the main probe. Align and lock the second angle-measuring device on the probe extension's scribe line. Then, rotate the extension until both measuring devices indicate the same angle (±1°). Lock the extension at this rotational position. Record the angles indicated by the two angle-measuring devices on a form similar to table 2G–2. An angle-measuring device may be aligned at any position on this scribe line during the velocity traverse, if the scribe line meets the alignment specification in section 6.1.5.3.

18.1.1.3 Post-test rotational position check. If the fully assembled probe includes one or more extensions, the following check should be performed immediately after the completion of a velocity traverse. At the discretion

of the tester, additional checks may be conducted after completion of testing at any sample port. Without altering the alignment of any of the components of the probe assembly used in the velocity traverse, secure the fully assembled probe in a horizontal position. Affix an angle-measuring device at the reference scribe line specified in section 6.1.5.1. Use the other angle-measuring device to check the angle at each location where the device was checked prior to testing. Record the readings from the two angle-measuring devices.

18.1.2 Rotational position check with probe in stack. This section applies only to probes that, due to physical constraints, cannot be inserted into the test port as fully assembled with all necessary extensions needed to reach the inner-most traverse point(s).

18.1.2.1 Perform the out-of-stack procedure in section 18.1.1 on the main probe and any attached extensions that will be initially inserted into the test port.

18.1.2.2 Use the following procedures to perform additional rotational position check(s) with the probe in the stack, each time a probe extension is added. Two angle-measuring devices are required. The first of these is the device that was used to measure yaw angles at the preceding traverse point, left in its properly aligned measurement position. The second angle-measuring device is positioned on the added probe extension. Use the applicable procedures in section 18.1.1.1 or 18.1.1.2 to align, adjust, lock, and mark (if necessary) the position of the second angle-measuring device to within ±1° of the first device. Record the readings of the two devices on a form similar to Table 2G–2.

18.1.2.3 The procedure in section 18.1.2.2 should be performed at the first port where measurements are taken. The procedure should be repeated each time a probe extension is re-attached at a subsequent port, unless the probe extensions are designed to be locked into a mechanically fixed rotational position (e.g., through use of interlocking grooves), which can be reproduced from port to port as specified in section 8.3.5.2.

18.2 Annex B—Angle Measurement Protocol for Protractor Wheel and Pointer Device. The following procedure shall be used when a protractor wheel and pointer assembly, such as the one described in section 6.2.2 and illustrated in Figure 2G–5 is used to measure the yaw angle of flow. With each move to a new traverse point, unlock, re-align, and re-lock the probe, angle-pointer collar, and protractor wheel to each other. At each such move, particular attention is required to ensure that the scribe line on the angle pointer collar is either aligned with the reference scribe line on the main probe sheath or is at the rotational offset position established under section 8.3.1. The procedure consists of the following steps:

18.2.1 Affix a protractor wheel to the entry port for the test probe in the stack or duct.

18.2.2 Orient the protractor wheel so that the 0° mark corresponds to the longitudinal axis of the stack or duct. For stacks, vertical ducts, or ports on the side of horizontal ducts, use a digital inclinometer meeting the specifications in section 6.2.1 to locate the 0° orientation. For ports on the top or bottom of horizontal ducts, identify the longitudinal axis at each test port and permanently mark the duct to indicate the 0° orientation. Once the protractor wheel is properly aligned, lock it into position on the test port.

18.2.3 Move the pointer assembly along the probe sheath to the position needed to take measurements at the first traverse point. Align the scribe line on the pointer collar with the reference scribe line or at the rotational offset position established under section 8.3.1. Maintaining this rotational alignment, lock the pointer device onto the probe sheath. Insert the probe into the entry port to the depth needed to take measurements at the first traverse point.

18.2.4 Perform the yaw angle determination as specified in sections 8.9.3 and 8.9.4 and record the angle as shown by the pointer on the protractor wheel. Then, take velocity pressure and temperature measurements in accordance with the procedure in section 8.9.5. Perform the alignment check described in section 8.9.6.

18.2.5 After taking velocity pressure measurements at that traverse point, unlock the probe from the collar and slide the probe through the collar to the depth needed to reach the next traverse point.

18.2.6 Align the scribe line on the pointer collar with the reference scribe line on the main probe or at the rotational offset position established under section 8.3.1. Lock the collar onto the probe.

18.2.7 Repeat the steps in sections 18.2.4 through 18.2.6 at the remaining traverse points accessed from the current stack or duct entry port.

18.2.8 After completing the measurement at the last traverse point accessed from a port, verify that the orientation of the protractor wheel on the test port has not changed over the course of the traverse at that port. For stacks, vertical ducts, or ports on the side of horizontal ducts, use a digital inclinometer meeting the specifications in section 6.2.1 to check the rotational position of the 0° mark on the protractor wheel. For ports on the top or bottom of horizontal ducts, observe the alignment of the angle wheel 0° mark relative to the permanent 0° mark on the duct at that test port. If these observed comparisons exceed ±2° of 0°, all angle and pressure measurements taken at that port since the protractor wheel was last locked into position on the port shall be repeated.

18.2.9 Move to the next stack or duct entry port and repeat the steps in sections 18.2.1 through 18.2.8.

18.3 Annex C—Guideline for Reference Scribe Line Placement. Use of the following guideline is recommended to satisfy the requirements of section 10.4 of this method. The rotational position of the reference scribe line should be either 90° or 180° from the probe's impact pressure port. For Type-S probes, place separate scribe lines, on opposite sides of the probe sheath, if both the A and B sides of the pitot tube are to be used for yaw angle measurements.

18.4 Annex D—Determination of Reference Scribe Line Rotational Offset. The following procedures are recommended for determining the magnitude and sign of a probe's reference scribe line rotational offset, R_{SLO}. Separate procedures are provided for two types of angle-measuring devices: digital inclinometers and protractor wheel and pointer assemblies.

18.4.1 Perform the following procedures on the main probe with all devices that will be attached to the main probe in the field [such as thermocouples, resistance temperature detectors (RTDs), or sampling nozzles] that may affect the flow around the probe head. Probe shaft extensions that do not affect flow around the probe head need not be attached during calibration.

18.4.2 The procedures below assume that the wind tunnel duct used for probe calibration is horizontal and that the flow in the calibration wind tunnel is axial as determined by the axial flow verification check described in section 10.1.2. Angle-measuring devices are assumed to display angles in alternating 0° to 90° and 90° to 0° intervals. If angle-measuring devices with other readout conventions are used or if other calibration wind tunnel duct configurations are used, make the appropriate calculational corrections. For Type-S probes, calibrate the A-side and B-sides separately, using the appropriate scribe line (see section 18.3, above), if both the A and B sides of the pitot tube are to be used for yaw angle determinations.

18.4.2.1 Position the angle-measuring device in accordance with one of the following procedures.

18.4.2.1.1 If using a digital inclinometer, affix the calibrated digital inclinometer to the probe. If the digital inclinometer can be independently adjusted after being locked into position on the probe sheath (e.g., by means of a set screw), the independent adjustment must be set so that the device performs exactly like a device without the capability for independent adjustment. That is, when aligned on the probe the device must give the same readings as a device that does not have the capability of being independently adjusted. Either align it directly on the reference scribe line or on a mark aligned with the scribe line determined according to the procedures in section 18.1.1.1. Maintaining this rotational alignment, lock the digital inclinometer onto the probe sheath.

18.4.2.1.2 If using a protractor wheel and pointer device, orient the protractor wheel on the test port so that the 0° mark is aligned with the longitudinal axis of the wind tunnel duct. Maintaining this alignment, lock the wheel into place on the wind tunnel test port. Align the scribe line on the pointer collar with the reference scribe line or with a mark aligned with the reference scribe line, as determined under section 18.1.1.1. Maintaining this rotational alignment, lock the pointer device onto the probe sheath.

18.4.2.2 Zero the pressure-measuring device used for yaw nulling.

18.4.2.3 Insert the probe assembly into the wind tunnel through the entry port, positioning the probe's impact port at the calibration location. Check the responsiveness of the pressure-measuring device to probe rotation, taking corrective action if the response is unacceptable.

18.4.2.4 Ensure that the probe is in a horizontal position using a carpenter's level.

18.4.2.5 Rotate the probe either clockwise or counterclockwise until a yaw null [zero ΔP for a Type S probe or zero (P_2–P_3) for a 3–D probe] is obtained. If using a Type S probe with an attached thermocouple, the direction of the probe rotation shall be such that the thermocouple is located downstream of the probe pressure ports at the yaw-null position.

18.4.2.6 Read and record the value of θ_{null}, the angle indicated by the angle-measuring device at the yaw-null position. Record the angle reading on a form similar to Table 2G–6. Do not associate an algebraic sign with this reading.

18.4.2.7 Determine the magnitude and algebraic sign of the reference scribe line rotational offset, R_{SLO}. The magnitude of R_{SLO} will be equal to either θ_{null} or $(90° - \theta_{null})$, depending on the type of probe being calibrated and the type of angle-measuring device used. (See Table 2G–7 for a summary.) The algebraic sign of R_{SLO} will either be positive if the rotational position of the reference scribe line is clockwise or negative if counterclockwise with respect to the probe's yaw-null position. Figure 2G–10 illustrates how the magnitude and sign of R_{SLO} are determined.

18.4.2.8 Perform the steps in sections 18.3.2.3 through 18.3.2.7 twice at each of the two calibration velocities selected for the probe under section 10.6. Record the values of R_{SLO} in a form similar to Table 2G–6.

18.4.2.9 The average of all R_{SLO} values is the reference scribe line rotational offset for the probe.

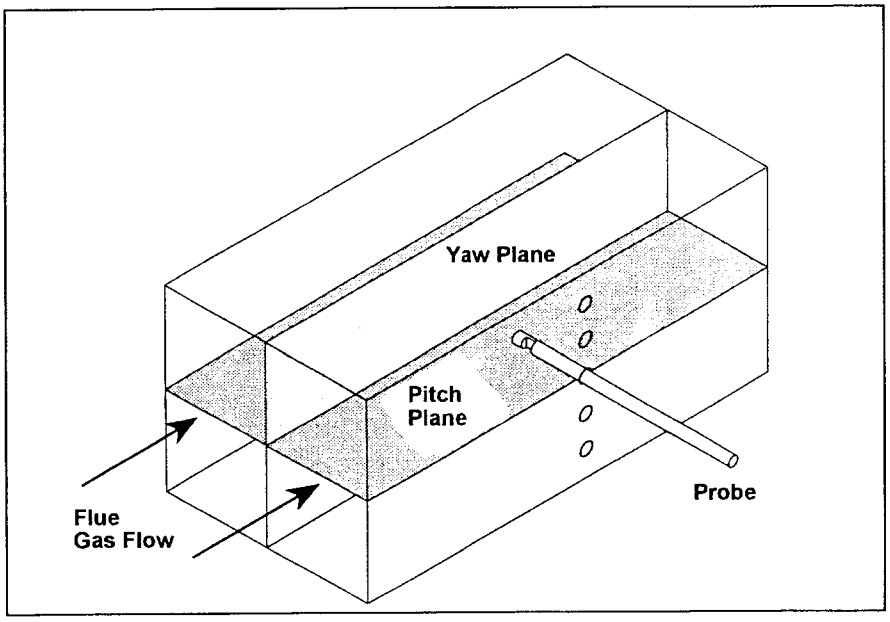


Figure 2G-1. Illustration of yaw and pitch planes in stack or duct.

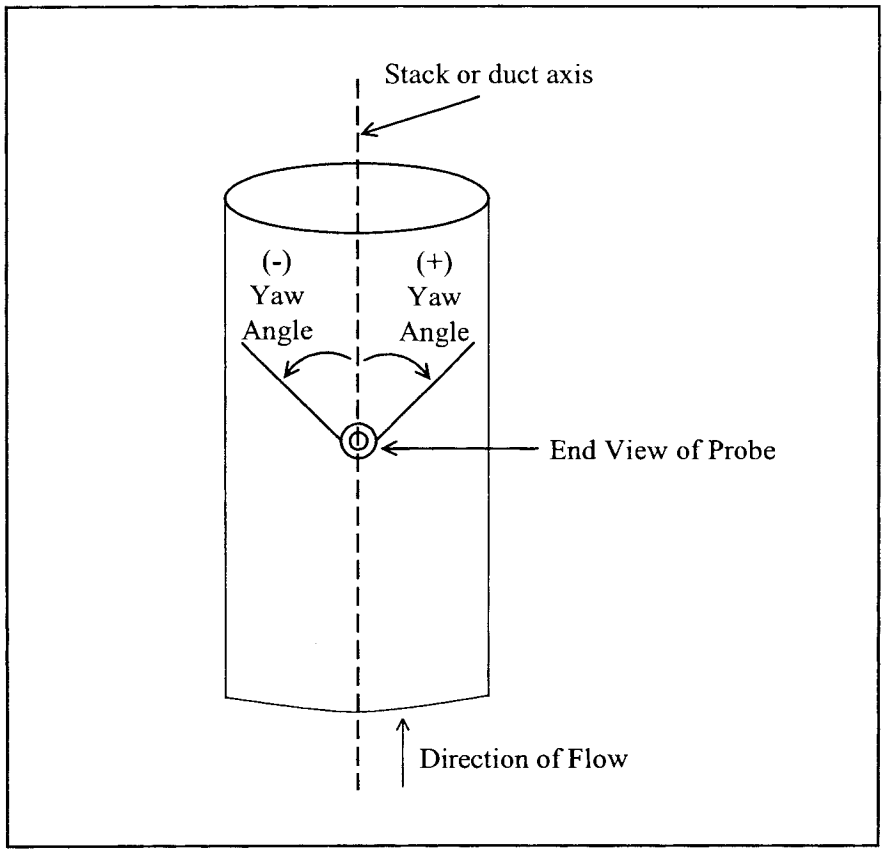


Figure 2G-2. Illustration of probe rotation representing positive and negative yaw angles.

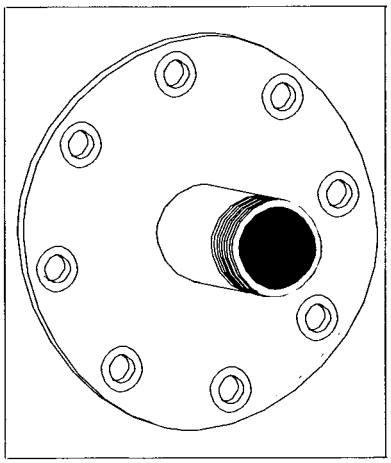


Figure 2G-3. Example bushing sleeve.

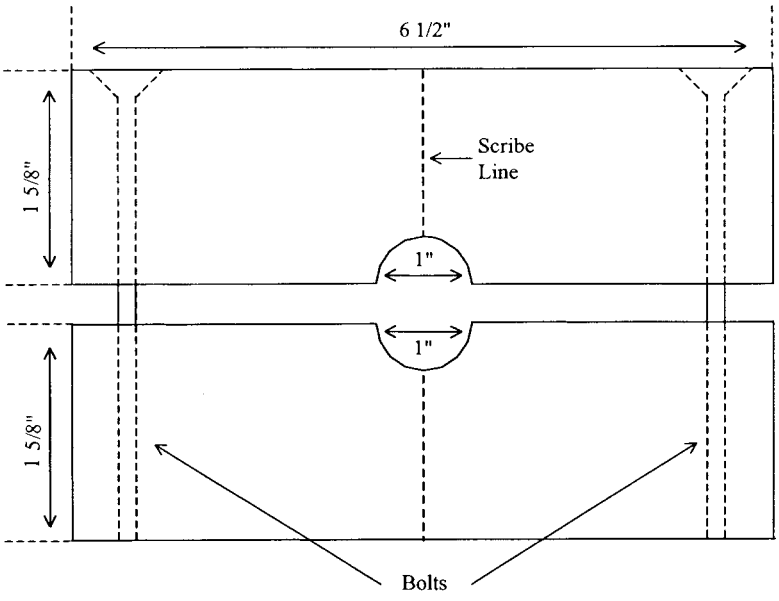


Figure 2G-4. Rotational position collar block.

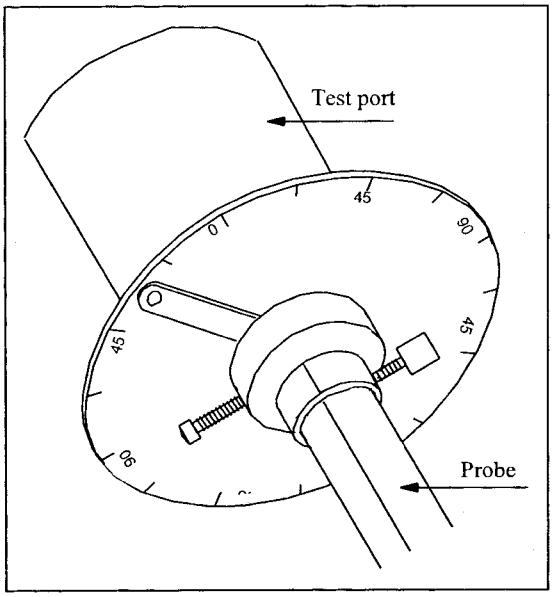


Figure 2G-5. Yaw angle protractor wheel and pointer.

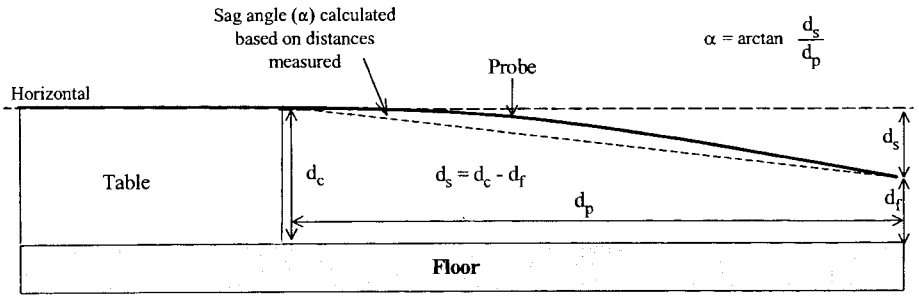


Figure 2G-6. Elements in horizontal straightness test based on trigonometry.

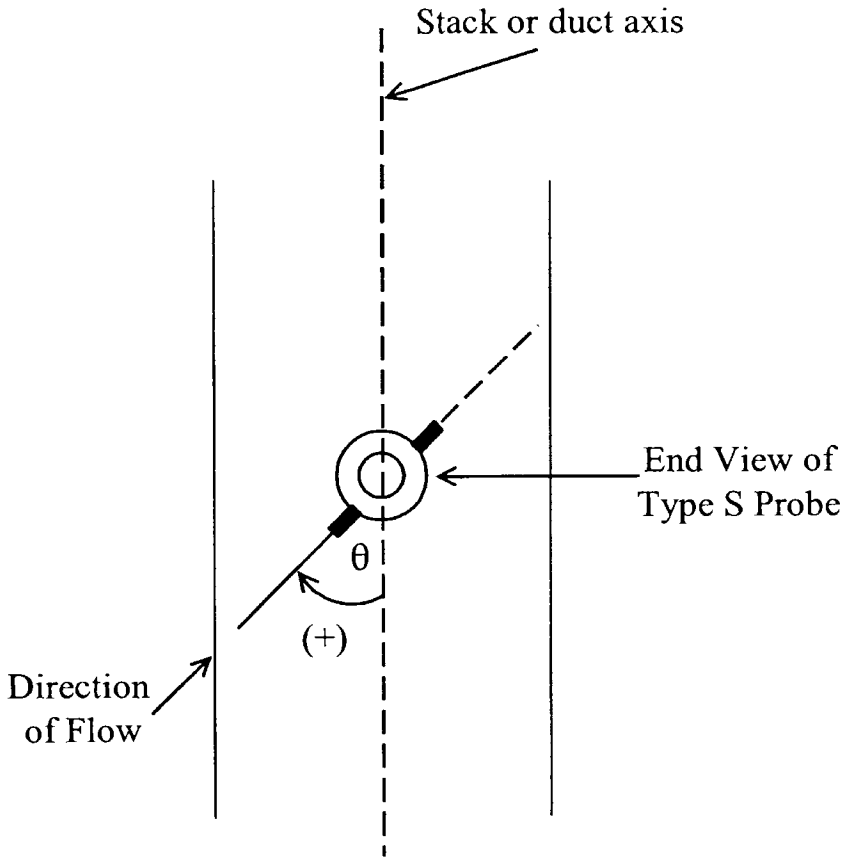


Figure 2G-7. Sign convention for the measured angle (θ) when the probe impact port is pointed directly into the flow. The angle θ is positive when the probe's impact pressure port is oriented in a clockwise rotational position relative to the stack or duct axis, as shown above, and negative for a counter-clockwise orientation.

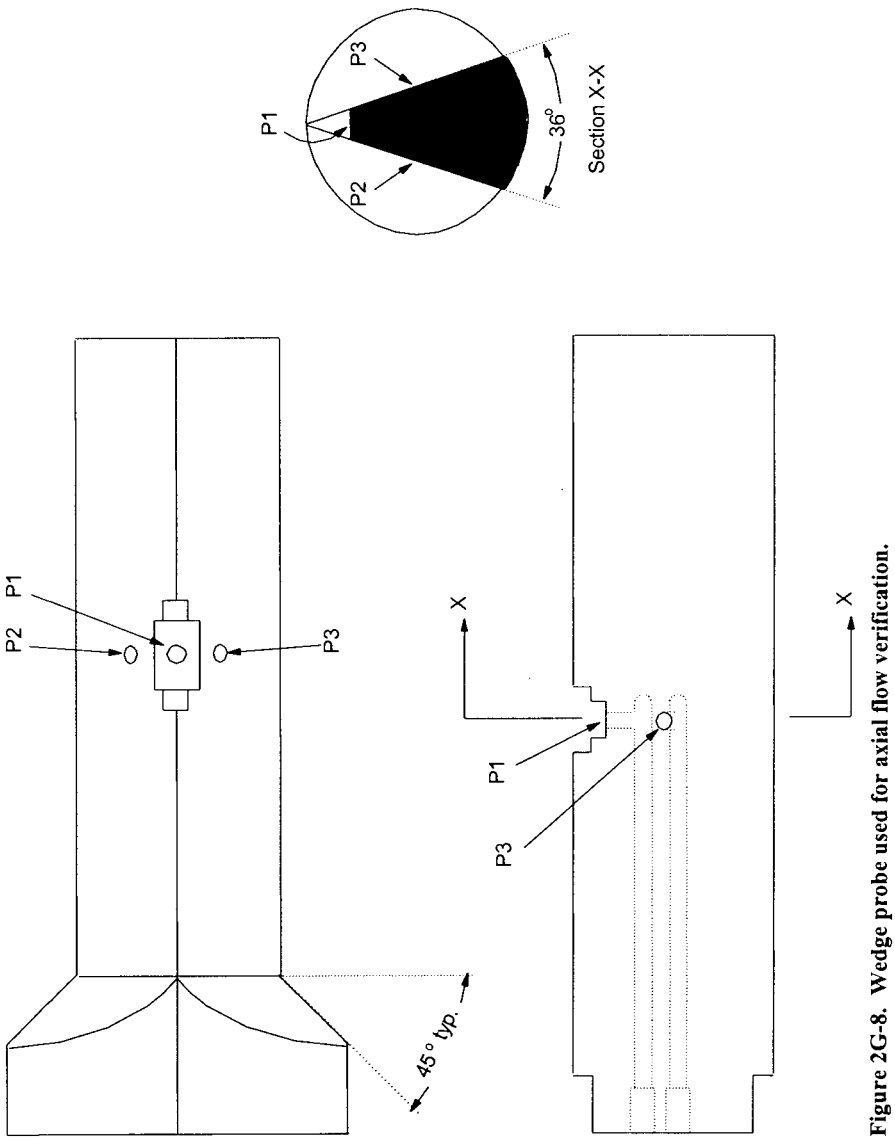


Figure 2G-8. Wedge probe used for axial flow verification.

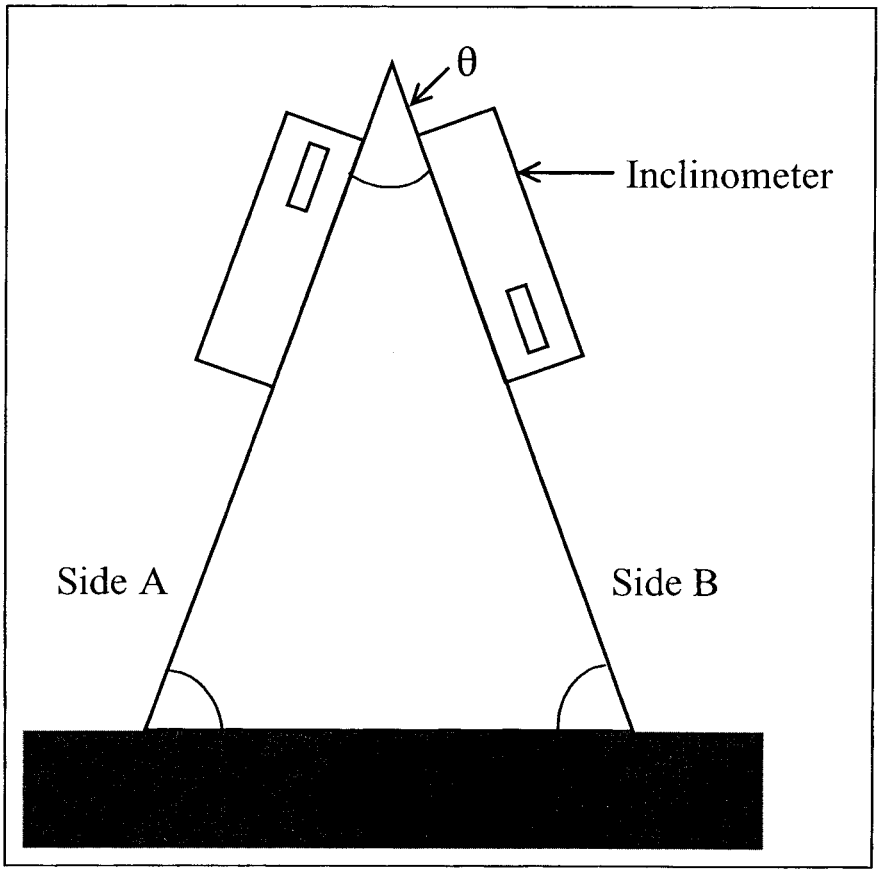


Figure 2G-9. Triangular block used for digital inclinometer calibration.

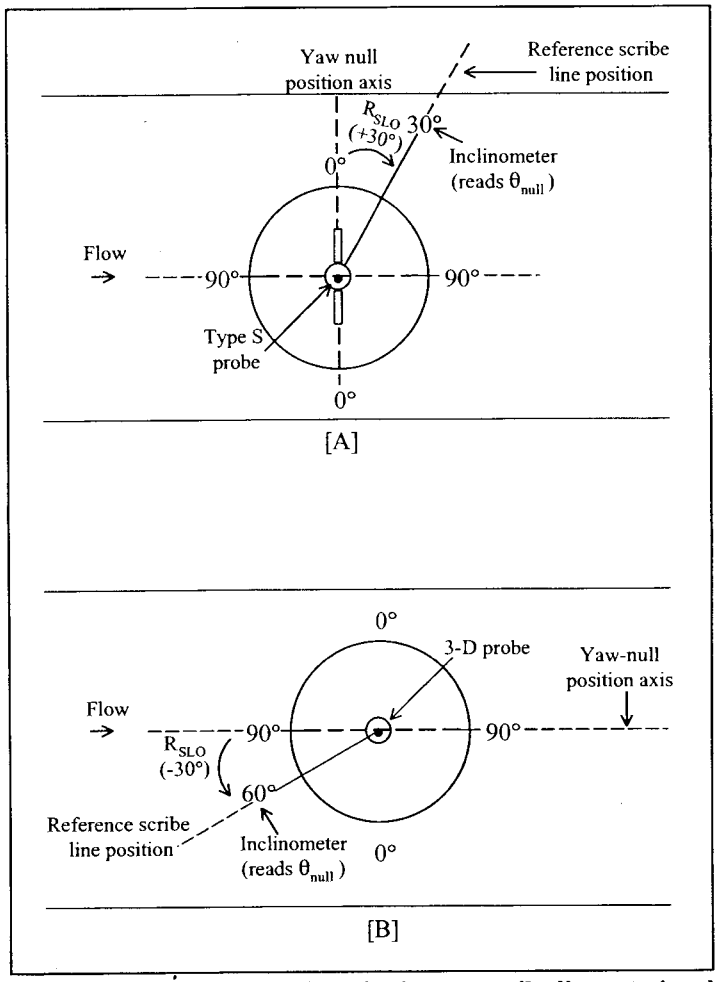
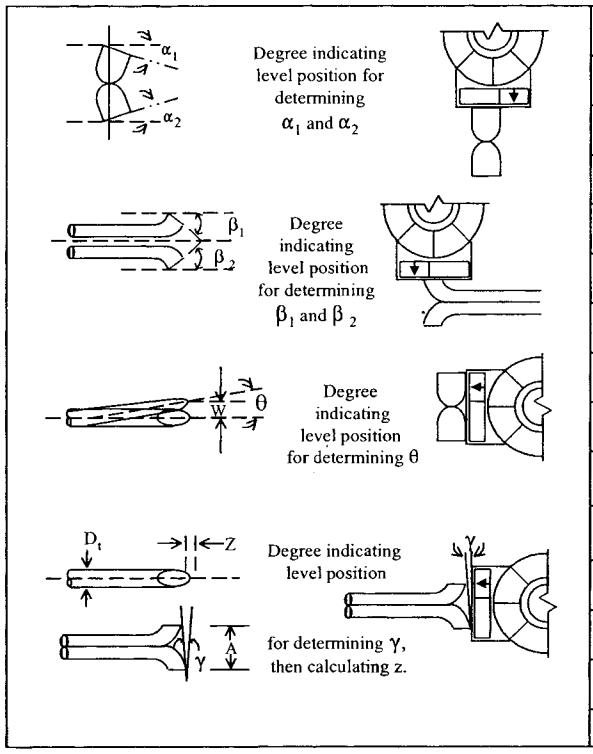


Figure 2G-10. Determination of reference scribe line rotational offset (R_{SLO}) in a horizontal wind tunnel with axial flow for: [A], a Type S probe, and [B], a 3-D probe. In [A] and [B], the probe impact pressure port is aligned with the yaw-null position axis and the inclinometer reads θ_{null}. In [A], the magnitude of R_{SLO} = θ_{null} and the sign is positive (clockwise from yaw-null position axis). In [B], the magnitude of $R_{SLO} = 90° - \theta_{null}$ and the sign is negative (counterclockwise from yaw-null position axis).

Table 2G-1. Type S Probe Inspection Sheet

Note: Method 2 provides the criteria for an acceptably constructed Type S pitot tube. However, the procedure for making the necessary measurements is not specified. One approach is given below.

1. Use a vise with parallel and perpendicular faces. Use an angle-measuring device (analog or digital) for this check.
2. Place the pitot tube in the vise, and level the pitot tube horizontally using the angle-measuring device.
3. Place the angle-measuring device as shown below.
4. Measure distance A, which is P_A plus P_B. Method 2 specifies that $P_A = P_B$, but provides no tolerance for this measurement. Because this measurement is very difficult, it is suggested that $P_A = P_B = A/2$.
5. Measure the external tube diameter (D_t) with a micrometer, machinist's rule, or internal caliper.
6. Record all data as shown on the form below.
7. Calculate dimensions w and z as shown below.



Level and perpendicular?	
Obstruction?	
Damaged?	
α_1 ($-2° \le \alpha_1 \le +2°$)	
α_2 ($-2° \le \alpha_2 \le +2°$)	
β_1 ($-2° \le \beta_1 \le +2°$)	
β_2 ($-2° \le \beta_2 \le +2°$)	
γ	
θ	
$z = A (\tan\gamma)$ [≤ 0.5 mm (0.02 in.)]	
$w = A (\tan\theta)$ [≤ 0.5 mm (0.02 in.)]	
D_t [≥ 9.5 mm (3/8 in.)]	
A	
$A/2D_t$ ($1.05 \le P_A/D_t \le 1.5$) *	
* Recommended dimensions	

QA/QC Check

Completeness_____ Legibility_____ Accuracy_____

Specifications_____ Reasonableness_____

Certification

I certify that the Type S probe ID _____ meets or exceeds all specifications, criteria, and applicable design features.

Certified by:_____ Date:_____

Table 2G-2. Rotational Position Check

Source:_____ Date:_____

Test Location:_____ Tester(s):_____

Probe Type:_____ Affiliation:_____

Probe ID:_____ Fully-Assembled Probe Length in mm (in.):_____

Position	Angle Comparisons		
Distance of 2nd measurement device from probe head impact port in mm (in.)	1st Device Angle measured by device aligned on the reference scribe line, including algebraic sign (degrees)	2nd Device Angle measured by device mounted at each position to be used during testing, including algebraic sign (degrees)	R_{ADO} Difference between readings by 1st and 2nd angle-measuring devices (degrees)[a]
(Col. A)	(Col. B)	(Col. C)	(Col. C - Col. B)

[a] The algebraic sign must be consistent with section 8.3.2.

Specifications: For the pre-test rotational position check, the value of R_{ADO} at each location along the probe shaft must be determined to within ±1°. In the post-test check, R_{ADO} at each location must remain within ±2° of the value obtained in the pre-test check.

Table 2G-3. Example EPA Method 2G Field Data Form

Source: _____ Date: _____

Source Location: _____ Test Personnel: _____

Measurement Location: _____ Probe Type: _____

Run ID:		Stack Diameter:		
Start Time:		Stack Area:		
End Time:		Barometric Pressure (P_{bar}):		in. Hg
Pitot Tube ID:		Static Pressure (P_g):		in. H_2O
Pitot Tube Coefficient (C_p):		R_{SLO}		
Pressure Gauge ID:		R_{ADO}		
Pressure Gauge Readability:	in. H_2O		Pre-test	Post-test
Temperature Gauge ID:		Pitot Tube Condition: Damage Noted?		
Measurement System Response Time	sec.	Leak Check Performed?		

Clock Time	Traverse Point	Yaw Angle, including algebraic sign (degrees)	Differential Pressure (Δ P)	Stack or Duct Gas Temperature (° F)

Table 2G-4. Wind Tunnel Velocity Pressure Cross-Check

Wind Tunnel Facility: _____
Date: _____
Wind Tunnel Temperature: _____
Barometric Pressure: _____
Test Point Locations: _____
Lowest Test Velocity in m/sec (ft/sec): _____
Highest Test Velocity in m/sec (ft/sec): _____

Port		Rep.	Velocity Pressure (ΔP_{std})	
			@ Lowest Test Velocity	@ Highest Test Velocity
Calibration Pitot Tube Location		1		
		2		
		3		
		Average		
Calibration Location Test Points *	1	1		
		2		
		3		
		Average		
		% Difference **		
	2	1		
		2		
		3		
		Average		
		% Difference **		
	..	1		
		2		
		3		
		Average		
		% Difference **		

* Measurements must be taken at all points in the calibration location as specified in section 10.1.1

** Percent Difference = $\frac{(Calibration\ Location\ Test\ Point\ Avg - Cal.\ Pitot\ Tube\ Location\ Avg)}{Cal.\ Pitot\ Tube\ Location\ Avg} \times 100\%$

Specification: At each velocity setting, the average velocity pressure obtained at the calibration location shall be within ±2 percent or 0.01 in. H_2O, whichever is less restrictive, of the average velocity pressure obtained at the fixed calibration pitot tube location.

Table 2G-5. Wind Tunnel Axial Flow Verification

Wind Tunnel Facility: _____
Date: _____
Wind Tunnel Temperature: _____
Barometric Pressure: _____
Probe Type/I.D. Used To Conduct Check: _____
Test Point Locations: _____
Lowest Test Velocity in m/sec (ft/sec): _____
Highest Test Velocity in m/sec (ft/sec): _____

Port		@ Lowest Test Velocity		@ Highest Test Velocity	
		Yaw Angle * (degrees)	Pitch Angle * (degrees)	Yaw Angle * (degrees)	Pitch Angle * (degrees)
Calibration Location Test Points **	1				
	2				
	3				
	..				
Calibration Pitot Tube Location					

* When following the procedures in section 10.1.2.1, both the yaw and pitch angles are obtained from the same port. When following the procedures in section 10.1.2.2, the yaw angle is obtained using the port for the tested probe, and the pitch angle is obtained using the port for verification of axial flow.

** Yaw and pitch angle measurements must be taken at all points that define the calibration location (as per the requirements in section 10.1.1)

Specification: At each velocity setting, each measured yaw and pitch angle shall be within ±3° of 0° in accordance with the requirements in section 10.1.2.

Table 2G-6. Yaw Angle Calibration

Probe Type: _____ **Tester(s):** _____

Probe ID: _____ **Affiliation:** _____

Test Location: _____ **Date:** _____

	Repetition 1		Repetition 2	
Nominal Velocity Setting in m/sec (ft/sec)	**θ_{null} (degrees)**	**R_{SLO} (degrees)***	**θ_{null} (degrees)**	**R_{SLO} (degrees)***

Average of all recorded R_{SLO} values: _____

* Include magnitude and algebraic sign in accordance with section 10.5.6.

Table 2G-7. Determining the Magnitude of Reference Scribe Line Offset

Probe/Angle-Measuring Device	Magnitude of R_{SLO}
Type S probe with inclinometer	θ_{null}
Type S probe with protractor wheel and pointer	$90° - \theta_{null}$
3-D probe with inclinometer	$90° - \theta_{null}$
3-D probe with protractor wheel and pointer	θ_{null}

Table 2G-8. Probe Calibration for Method 2G

Wind Tunnel Facility: _____
Wind Tunnel Location: _____
Probe Type: _____
Probe ID: _____
Probe Calibration Date: _____
Test Point Location: _____
Ambient Temperature (°F): _____
Barometric Pressure (P_{bar}): _____

Repetition	Low Velocity Setting (ft/sec)	Calibration Pitot		Tested Probe		Calculated C_p or F_2
		ΔP_{std} (in. H_2O)	Temp. (°F)	ΔP or P_1-P_2 (in. H_2O)	Yaw Angle (°)	
1						
2						
3						
					Average ($C_{p(avg\text{-}low)}$) =	

Repetition	High Velocity Setting (ft/sec)	Calibration Pitot		Tested Probe		Calculated C_p or F_2
		ΔP_{std} (in. H_2O)	Temp. (°F)	ΔP or P_1-P_2 (in. H_2O)	Yaw Angle (°)	
1						
2						
3						
					Average ($C_{p(avg\text{-}high)}$) =	

$$\% \text{ Difference} = \frac{C_{p(avg\text{-}low)} - C_{p(avg\text{-}high)}}{C_{p(avg\text{-}low)}} \times 100\% = _____\%$$

Note: (1) The percent difference between the low and high velocity setting C_p values shall be within ±3 percent.
(2) If calibrating a 3-D probe for this method, the pitch angle setting must be 0°.

METHOD 2H—DETERMINATION OF STACK GAS VELOCITY TAKING INTO ACCOUNT VELOCITY DECAY NEAR THE STACK WALL

1.0 Scope and Application

1.1 This method is applicable in conjunction with Methods 2, 2F, and 2G (40 CFR Part 60, Appendix A) to account for velocity decay near the wall in circular stacks and ducts.

1.2 This method is not applicable for testing stacks and ducts less than 3.3 ft (1.0 m) in diameter.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A wall effects adjustment factor is determined. It is used to adjust the average stack gas velocity obtained under Method 2, 2F, or 2G of this appendix to take into account velocity decay near the stack or duct wall.

2.2 The method contains two possible procedures: a calculational approach which derives an adjustment factor from velocity measurements and a default procedure which assigns a generic adjustment factor based on the construction of the stack or duct.

2.2.1 The calculational procedure derives a wall effects adjustment factor from velocity measurements taken using Method 2, 2F, or 2G at 16 (or more) traverse points specified under Method 1 of this appendix and a total of eight (or more) wall effects traverse points specified under this method. The calculational procedure based on velocity measurements is not applicable for horizontal circular ducts where build-up of particulate matter or other material in the bottom of the duct is present.

2.2.2 A default wall effects adjustment factor of 0.9900 for brick and mortar stacks and 0.9950 for all other types of stacks and ducts may be used without taking wall effects measurements in a stack or duct.

2.3 When the calculational procedure is conducted as part of a relative accuracy test audit (RATA) or other multiple-run test procedure, the wall effects adjustment factor derived from a single traverse (i.e., single RATA run) may be applied to all runs of the same RATA without repeating the wall effects measurements. Alternatively, wall effects adjustment factors may be derived for several traverses and an average wall effects adjustment factor applied to all runs of the same RATA.

3.0 Definitions.

3.1 *Complete wall effects traverse* means a traverse in which measurements are taken at d_{rem} (see section 3.3) and at 1-in. intervals in each of the four Method 1 equal-area sectors closest to the wall, beginning not farther than 4 in. (10.2 cm) from the wall and extending either (1) across the entire width of the Method 1 equal-area sector or (2) for stacks or ducts where this width exceeds 12 in. (30.5 cm) (i.e., stacks or ducts greater than or equal to 15.6 ft [4.8 m] in diameter), to a distance of not less than 12 in. (30.5 cm) from the wall. Note: Because this method specifies that measurements must be taken at whole number multiples of 1 in. from a stack or duct wall, for clarity numerical quantities in this method are expressed in English units followed by metric units in parentheses. To enhance readability, hyphenated terms such as ''1-in. intervals'' or ''1-in. incremented,'' are expressed in English units only.

3.2 d_{last} Depending on context, d_{last} means either (1) the distance from the wall of the last 1-in. incremented wall effects traverse point or (2) the traverse point located at that distance (see Figure 2H–2).

3.3 d_{rem} Depending on context, d_{rem} means either (1) the distance from the wall of the centroid of the area between d_{last} and the interior edge of the Method 1 equal-area sector closest to the wall or (2) the traverse point located at that distance (see Figure 2H–2).

3.4 ''*May,*'' ''*Must,*'' ''*Shall,*'' ''*Should,*'' and the imperative form of verbs.

3.4.1 ''*May*'' is used to indicate that a provision of this method is optional.

3.4.2 ''*Must,*'' ''*Shall,*'' and the imperative form of verbs (such as ''record'' or ''enter'') are used to indicate that a provision of this method is mandatory.

3.4.3 ''*Should*'' is used to indicate that a provision of this method is not mandatory but is highly recommended as good practice.

3.5 *Method 1* refers to 40 CFR part 60, appendix A, ''Method 1—Sample and velocity traverses for stationary sources.''

3.6 *Method 1 exterior equal-area sector and Method 1 equal-area sector closest to the wall* mean any one of the four equal-area sectors that are closest to the wall for a circular stack or duct laid out in accordance with section 2.3.1 of Method 1 (see Figure 2H–1).

3.7 *Method 1 interior equal-area sector* means any of the equal-area sectors other than the Method 1 exterior equal-area sectors (as defined in section 3.6) for a circular stack or duct laid out in accordance with section 2.3.1 of Method 1 (see Figure 2H–1).

3.8 *Method 1 traverse point and Method 1 equal-area traverse point* mean a traverse point located at the centroid of an equal-area sector of a circular stack laid out in accordance with section 2.3.1 of Method 1.

3.9 *Method 2* refers to 40 CFR part 60, appendix A, ''Method 2—Determination of stack gas velocity and volumetric flow rate (Type S pitot tube).''

3.10 *Method 2F* refers to 40 CFR part 60, appendix A, ''Method 2F—Determination of stack gas velocity and volumetric flow rate with three-dimensional probes.''

3.11 *Method 2G* refers to 40 CFR part 60, appendix A, ''Method 2G—Determination of stack gas velocity and volumetric flow rate with two-dimensional probes.''

3.12 *1-in. incremented wall effects traverse point* means any of the wall effects traverse points that are located at 1-in. intervals, i.e., traverse points d_1 through d_{last} (see Figure 2H–2).

3.13 *Partial wall effects traverse* means a traverse in which measurements are taken at fewer than the number of traverse points required for a ''complete wall effects traverse'' (as defined in section 3.1), but are taken at a minimum of two traverse points in each Method 1 equal-area sector closest to the wall, as specified in section 8.2.2.

3.14 *Relative accuracy test audit (RATA)* is a field test procedure performed in a stack or duct in which a series of concurrent measurements of the same stack gas stream is taken by a reference method and an installed monitoring system. A RATA usually consists of series of 9 to 12 sets of such concurrent measurements, each of which is referred to as a RATA run. In a volumetric flow RATA, each reference method run consists of a complete traverse of the stack or duct.

3.15 *Wall effects-unadjusted average velocity* means the average stack gas velocity, not accounting for velocity decay near the wall, as determined in accordance with Method 2, 2F, or 2G for a Method 1 traverse consisting of 16 or more points.

3.16 *Wall effects-adjusted average velocity* means the average stack gas velocity, taking into account velocity decay near the wall, as calculated from measurements at 16 or more Method 1 traverse points and at the additional wall effects traverse points specified in this method.

3.17 *Wall effects traverse point* means a traverse point located in accordance with sections 8.2.2 or 8.2.3 of this method.

4.0 Interferences [Reserved]

5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This method does not purport to address all of the health and safety considerations associated with its use. It is the responsibility of the user of this method to establish appropriate health and safety practices and to determine the applicability of occupational health and safety regulatory requirements prior to performing this method.

6.0 Equipment and Supplies

6.1 The provisions pertaining to equipment and supplies in the method that is used to take the traverse point measurements (i.e., Method 2, 2F, or 2G) are applicable under this method.

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection and Analysis

8.1 Default Wall Effects Adjustment Factors. A default wall effects adjustment factor of 0.9900 for brick and mortar stacks and 0.9950 for all other types of stacks and ducts may be used without conducting the following procedures.

8.2 Traverse Point Locations. Determine the location of the Method 1 traverse points in accordance with section 8.2.1 and the location of the traverse points for either a partial wall effects traverse in accordance with section 8.2.2 or a complete wall effects traverse in accordance with section 8.2.3.

8.2.1 Method 1 equal-area traverse point locations. Determine the location of the Method 1 equal-area traverse points for a traverse consisting of 16 or more points using Table 1–2 (Location of Traverse Points in Circular Stacks) of Method 1.

8.2.2 Partial wall effects traverse. For a partial wall effects traverse, measurements must be taken at a minimum of the following two wall effects traverse point locations in all four Method 1 equal-area sectors closest to the wall: (1) 1 in. (2.5 cm) from the wall (except as provided in section 8.2.2.1) and (2) d_{rem}, as determined using Equation 2H–1 or 2H–2 (see section 8.2.2.2).

8.2.2.1 If the probe cannot be positioned at 1 in. (2.5 cm) from the wall (e.g., because of insufficient room to withdraw the probe shaft) or if velocity pressure cannot be detected at 1 in. (2.5 cm) from the wall (for any reason other than build-up of particulate matter in the bottom of a duct), take measurements at the 1-in. incremented wall effects traverse point closest to the wall where the probe can be positioned and velocity pressure can be detected.

8.2.2.2 Calculate the distance of d_{rem} from the wall to within ±¼ in. (6.4 mm) using Equation 2H–1 or Equation 2H–2 (for a 16-point traverse).

$$d_{last} \leq d_b \qquad \text{Eq. 2H-3}$$

Where:

r = the stack or duct radius determined from direct measurement of the stack or duct diameter in accordance with section 8.6 of Method 2F or Method 2G, in. (cm);

p = the number of Method 1 equal-area traverse points on a diameter, $p \geq 8$ (e.g., for a 16-point traverse, $p = 8$); d_{last} and d_{rem} are defined in sections 3.2 and 3.3 respectively, in. (cm).

For a 16-point Method 1 traverse, Equation 2H–1 becomes:

$$d_{rem} = r - \sqrt{\frac{7}{8}r^2 - rd_{last} + \frac{1}{2}d_{last}^2} \qquad \text{Eq. 2H-2}$$

8.2.2.3 Measurements may be taken at any number of additional wall effects traverse points, with the following provisions.

(a) d_{last} must not be closer to the center of the stack or duct than the distance of the interior edge (boundary), d_b, of the Method 1 equal-area sector closest to the wall (see Figure 2H–2 or 2H–3). That is,

Where:

$$d_b = r\left(1 - \sqrt{1 - \frac{2}{p}}\right) \qquad \text{Eq. 2H-4}$$

Table 2H–1 shows d_b as a function of the stack or duct radius, r, for traverses ranging from 16 to 48 points (i.e., for values of p ranging from 8 to 24).

(b) Each point must be located at a distance that is a whole number (e.g., 1, 2, 3) multiple of 1 in. (2.5 cm).

(c) Points do not have to be located at consecutive 1-in. intervals. That is, one or more 1-in. incremented points may be skipped. For example, it would be acceptable for points to be located at 1 in. (2.5 cm), 3 in. (7.6 cm), 5 in. (12.7 cm), d_{last}, and d_{rem}; or at 1 in. (2.5 cm), 2 in. (5.1 cm), 4 in. (10.2 cm), 7 in. (17.8 cm), d_{last}, and d_{rem}. Follow the instructions in section 8.7.1.2 of this method for recording results for wall effects traverse points that are skipped. It should be noted that the full extent of velocity decay may not be accounted for if measurements are not taken at all 1-in. incremented points close to the wall.

8.2.3 Complete wall effects traverse. For a complete wall effects traverse, measurements must be taken at the following points in all four Method 1 equal-area sectors closest to the wall.

(a) The 1-in. incremented wall effects traverse point closest to the wall where the probe can be positioned and velocity can be detected, but no farther than 4 in. (10.2 cm) from the wall.

(b) Every subsequent 1-in. incremented wall effects traverse point out to the interior edge of the Method 1 equal-area sector or to 12 in. (30.5 cm) from the wall, whichever comes first. Note: In stacks or ducts with diameters greater than 15.6 ft (4.8 m) the interior edge of the Method 1 equal-area sector is farther from the wall than 12 in. (30.5 cm).

(c) d_{rem}, as determined using Equation 2H–1 or 2H–2 (as applicable). Note: For a complete traverse of a stack or duct with a diameter less than 16.5 ft (5.0 m), the distance between d_{rem} and d_{last} is less than or equal to ½ in. (12.7 mm). As discussed in section 8.2.4.2, when the distance between d_{rem} and d_{last} is less than or equal to ½ in. (12.7 mm), the velocity measured at d_{last} may be used for d_{rem}. Thus, it is not necessary to calculate the distance of d_{rem} or to take measurements at d_{rem} when conducting a complete traverse of a stack or duct with a diameter less than 16.5 ft (5.0 m).

8.2.4 Special considerations. The following special considerations apply when the distance between traverse points is less than or equal to ½ in. (12.7 mm).

8.2.4.1 A wall effects traverse point and the Method 1 traverse point. If the distance between a wall effects traverse point and the Method 1 traverse point is less than or equal to ½ in. (12.7 mm), taking measurements at both points is allowed but not required or recommended; if measurements are taken at only one point, take the measurements at the point that is farther from the wall and use the velocity obtained at that point as the value for both points (see sections 8.2.3 and 9.2 for related requirements).

8.2.4.2 d_{rem} and d_{last}. If the distance between d_{rem} and d_{last} is less than or equal to ½ in. (12.7 mm), taking measurements at d_{rem} is allowed but not required or recommended; if measurements are not taken at d_{rem}, the measured velocity value at d_{last} must be used as the value for both d_{last} and d_{rem}.

8.3 Traverse Point Sampling Order and Probe Selection. Determine the sampling order of the Method 1 and wall effects traverse points and select the appropriate probe for the measurements, taking into account the following considerations.

8.3.1 Traverse points on any radius may be sampled in either direction (i.e., from the wall toward the center of the stack or duct, or vice versa).

8.3.2 To reduce the likelihood of velocity variations during the time of the traverse and the attendant potential impact on the wall effects-adjusted and unadjusted average velocities, the following provisions of this method shall be met.

8.3.2.1 Each complete set of Method 1 and wall effects traverse points accessed from the same port shall be sampled without interruption. Unless traverses are performed simultaneously in all ports using separate probes at each port, this provision disallows first sampling all Method 1 points at all ports and then sampling all the wall effects points.

8.3.2.2 The entire integrated Method 1 and wall effects traverse across all test ports shall be as short as practicable, consistent with the measurement system response time

(see section 8.4.1.1) and sampling (see section 8.4.1.2) provisions of this method.

8.3.3 It is recommended but not required that in each Method 1 equal-area sector closest to the wall, the Method 1 equal-area traverse point should be sampled in sequence between the adjacent wall effects traverse points. For example, for the traverse point configuration shown in Figure 2H–2, it is recommended that the Method 1 equal-area traverse point be sampled between d_{last} and d_{rem}. In this example, if the traverse is conducted from the wall toward the center of the stack or duct, it is recommended that measurements be taken at points in the following order: d_1, d_2, d_{last}, the Method 1 traverse point, d_{rem}, and then at the traverse points in the three Method 1 interior equal-area sectors.

8.3.4 The same type of probe must be used to take measurements at all Method 1 and wall effects traverse points. However, different copies of the same type of probe may be used at different ports (e.g., Type S probe 1 at port A, Type S probe 2 at port B) or at different traverse points accessed from a particular port (e.g., Type S probe 1 for Method 1 interior traverse points accessed from port A, Type S probe 2 for wall effects traverse points and the Method 1 exterior traverse point accessed from port A). The identification number of the probe used to obtain measurements at each traverse point must be recorded.

8.4 Measurements at Method 1 and Wall Effects Traverse Points. Conduct measurements at Method 1 and wall effects traverse points in accordance with Method 2, 2F, or 2G and in accordance with the provisions of the following subsections (some of which are included in Methods 2F and 2G but not in Method 2), which are particularly important for wall effects testing.

8.4.1 Probe residence time at wall effects traverse points. Due to the steep temperature and pressure gradients that can occur close to the wall, it is very important for the probe residence time (i.e., the total time spent at a traverse point) to be long enough to ensure collection of representative temperature and pressure measurements. The provisions of Methods 2F and 2G in the following subsections shall be observed.

8.4.1.1 System response time. Determine the response time of each probe measurement system by inserting and positioning the ''cold'' probe (at ambient temperature and pressure) at any Method 1 traverse point. Read and record the probe differential pressure, temperature, and elapsed time at 15-second intervals until stable readings for both pressure and temperature are achieved. The response time is the longer of these two elapsed times. Record the response time.

8.4.1.2 Sampling. At the start of testing in each port (i.e., after a probe has been inserted into the stack gas stream), allow at least the response time to elapse before beginning to take measurements at the first traverse point accessed from that port. Provided that the probe is not removed from the stack gas stream, measurements may be taken at subsequent traverse points accessed from the same test port without waiting again for the response time to elapse.

8.4.2 Temperature measurement for wall effects traverse points. Either (1) take temperature measurements at each wall effects traverse point in accordance with the applicable provisions of Method 2, 2F, or 2G; or (2) use the temperature measurement at the Method 1 traverse point closest to the wall as the temperature measurement for all the wall effects traverse points in the corresponding equal-area sector.

8.4.3 Non-detectable velocity pressure at wall effects traverse points. If the probe cannot be positioned at a wall effects traverse point or if no velocity pressure can be detected at a wall effects point, measurements shall be taken at the first subsequent wall effects traverse point farther from the wall where velocity can be detected. Follow the instructions in section 8.7.1.2 of this method for recording results for wall effects traverse points where velocity pressure cannot be detected. It should be noted that the full extent of velocity decay may not be accounted for if measurements are not taken at the 1-in. incremented wall effects traverse points closest to the wall.

8.5 Data Recording. For each wall effects and Method 1 traverse point where measurements are taken, record all pressure, temperature, and attendant measurements prescribed in section 3 of Method 2 or section 8.0 of Method 2F or 2G, as applicable.

8.6 Point Velocity Calculation. For each wall effects and Method 1 traverse point, calculate the point velocity value (v_i) in accordance with sections 12.1 and 12.2 of Method 2F for tests using Method 2F and in accordance with sections 12.1 and 12.2 of Method 2G for tests using Method 2 and Method 2G. (Note that the term (v_i) in this method corresponds to the term ($v_{a(i)}$) in Methods 2F and 2G.) When the equations in the indicated sections of Method 2G are used in deriving point velocity values for Method 2 tests, set the value of the yaw angles appearing in the equations to 0°.

8.7 Tabulating Calculated Point Velocity Values for Wall Effects Traverse Points. Enter the following values in a hardcopy or electronic form similar to Form 2H–1 (for 16-point Method 1 traverses) or Form 2H–2 (for Method 1 traverses consisting of more than 16 points). A separate form must be completed for each of the four Method 1 equal-area sectors that are closest to the wall.

(a) Port ID (e.g., A, B, C, or D)

(b) Probe type

(c) Probe ID

(d) Stack or duct diameter in ft (m) (determined in accordance with section 8.6 of Method 2F or Method 2G)

(e) Stack or duct radius in in. (cm)

(f) Distance from the wall of wall effects traverse points at 1-in. intervals, in ascending order starting with 1 in. (2.5 cm) (column A of Form 2H–1 or 2H–2)

(g) Point velocity values (v_d) for 1-in. incremented traverse points (see section 8.7.1), including d_{last} (see section 8.7.2)

(h) Point velocity value (v_{drem}) at d_{rem} (see section 8.7.3).

8.7.1 Point velocity values at wall effects traverse points other than d_{last}. For every 1-in. incremented wall effects traverse point other than d_{last}, enter in column B of Form 2H–1 or 2H–2 either the velocity measured at the point (see section 8.7.1.1) or the velocity measured at the first subsequent traverse point farther from the wall (see section 8.7.1.2). A velocity value must be entered in column B of Form 2H–1 or 2H–2 for every 1-in. incremented traverse point from d_1 (representing the wall effects traverse point 1 in. [2.5 cm] from the wall) to d_{last}.

8.7.1.1 For wall effects traverse points where the probe can be positioned and velocity pressure can be detected, enter the value obtained in accordance with section 8.6.

8.7.1.2 For wall effects traverse points that were skipped [see section 8.2.2.3(c)] and for points where the probe cannot be positioned or where no velocity pressure can be detected, enter the value obtained at the first subsequent traverse point farther from the wall where velocity pressure was detected and measured and follow the entered value with a ''flag,'' such as the notation ''NM,'' to indicate that ''no measurements'' were actually taken at this point.

8.7.2 Point velocity value at d_{last}. For d_{last}, enter in column B of Form 2H–1 or 2H–2 the measured value obtained in accordance with section 8.6.

8.7.3 Point velocity value (v_{drem}) at d_{rem}. Enter the point velocity value obtained at d_{rem} in column G of row 4a in Form 2H–1 or 2H–2. If the distance between d_{rem} and d_{last} is less than or equal to ½ in. (12.7 mm), the measured velocity value at d_{last} may be used as the value at d_{rem} (see section 8.2.4.2).

9.0 Quality Control.

9.1 Particulate Matter Build-up in Horizontal Ducts. Wall effects testing of horizontal circular ducts should be conducted only if build-up of particulate matter or other material in the bottom of the duct is not present.

9.2 Verifying Traverse Point Distances. In taking measurements at wall effects traverse points, it is very important for the probe impact pressure port to be positioned as close as practicable to the traverse point locations in the gas stream. For this reason, before beginning wall effects testing, it is important to calculate and record the traverse point positions that will be marked on each probe for each port, taking into account the distance that each port nipple (or probe mounting flange for automated probes) extends out of the stack and any extension of the port nipple (or mounting flange) into the gas stream. To ensure that traverse point positions are properly identified, the following procedures should be performed on each probe used.

9.2.1 Manual probes. Mark the probe insertion distance of the wall effects and Method 1 traverse points on the probe sheath so that when a mark is aligned with the outside face of the stack port, the probe impact port is located at the calculated distance of the traverse point from the stack inside wall. The use of different colored marks is recommended for designating the wall effects and Method 1 traverse points. Before the first use of each probe, check to ensure that the distance of each mark from the center of the probe impact pressure port agrees with the previously calculated traverse point positions to within ±¼ in. (6.4 mm).

9.2.2 Automated probe systems. For automated probe systems that mechanically position the probe head at prescribed traverse point positions, activate the system with the probe assemblies removed from the test ports and sequentially extend the probes to the programmed location of each wall effects traverse point and the Method 1 traverse points. Measure the distance between the center of the probe impact pressure port and the inside of the probe assembly mounting flange for each traverse point. The measured distances must agree with the previously calculated traverse point positions to within ±¼ in. (6.4 mm).

9.3 Probe Installation. Properly sealing the port area is particularly important in taking measurements at wall effects traverse points. For testing involving manual probes, the area between the probe sheath and the port should be sealed with a tightly fitting flexible seal made of an appropriate material such as heavy cloth so that leakage is minimized. For automated probe systems, the probe assembly mounting flange area should be checked to verify that there is no leakage.

9.4 Velocity Stability. This method should be performed only when the average gas velocity in the stack or duct is relatively constant over the duration of the test. If the average gas velocity changes significantly during the course of a wall effects test, the test results should be discarded.

10.0 Calibration

10.1 The calibration coefficient(s) or curves obtained under Method 2, 2F, or 2G and used to perform the Method 1 traverse are applicable under this method.

11.0 Analytical Procedure

11.1 Sample collection and analysis are concurrent for this method (see section 8).

12.0 Data Analysis and Calculations

12.1 The following calculations shall be performed to obtain a wall effects adjustment factor (*WAF*) from (1) the wall effects-unadjusted average velocity (*T4avg*), (2) the replacement velocity ($\hat{v}e_j$) for each of the four Method 1 sectors closest to the wall, and (3) the average stack gas velocity that accounts for velocity decay near the wall ($\hat{v}_{avg}$).

12.2 Nomenclature. The following terms are listed in the order in which they appear in Equations 2H–5 through 2H–21.

v_{avg} = the average stack gas velocity, unadjusted for wall effects, actual ft/sec (m/sec);

vi_i = stack gas point velocity value at Method 1 interior equal-area sectors, actual ft/sec (m/sec);

ve_j = stack gas point velocity value, unadjusted for wall effects, at Method 1 exterior equal-area sectors, actual ft/sec (m/sec);

i = index of Method 1 interior equal-area traverse points;

j = index of Method 1 exterior equal-area traverse points;

n = total number of traverse points in the Method 1 traverse;

$vdec_d$ = the wall effects decay velocity for a sub-sector located between the traverse points at distances $d-1$ (in metric units, $d-2.5$) and d from the wall, actual ft/sec (m/sec);

v_d = the measured stack gas velocity at distance d from the wall, actual ft/sec (m/sec); Note: $v_0 = 0$;

d = the distance of a 1-in. incremented wall effects traverse point from the wall, for traverse points d_1 through d_{last}, in. (cm);

A_d = the cross-sectional area of a sub-sector located between the traverse points at distances $d-1$ (in metric units, $d-2.5$) and d from the wall, in.^{2} (cm^2) (e.g., sub-sector A_2 shown in Figures 2H–3 and 2H–4);

r = the stack or duct radius, in. (cm);

Q_d = the stack gas volumetric flow rate for a sub-sector located between the traverse points at distances $d-1$ (in metric units, $d-2.5$) and d from the wall, actual ft-in.^{2}/sec (m-cm^2/sec);

$Q_{d_1 \rightarrow d_{last}}$ = the total stack gas volumetric flow rate for all sub-sectors located between the wall and d_{last}, actual ft-in.^{2}/sec (m-cm^2/sec);

d_{last} = the distance from the wall of the last 1-in. incremented wall effects traverse point, in. (cm);

A_{drem} = the cross-sectional area of the sub-sector located between d_{last} and the interior edge of the Method 1 equal-area sector closest to the wall, in.^{2} (cm^2) (see Figure 2H–4);

p = the number of Method 1 traverse points per diameter, $p \geq 8$ (e.g., for a 16-point traverse, $p = 8$);

d_{rem} = the distance from the wall of the centroid of the area between d_{last} and the interior edge of the Method 1 equal-area sector closest to the wall, in. (cm);

Q_{drem} = the total stack gas volumetric flow rate for the sub-sector located between d_{last} and the interior edge of the Method 1 equal-area sector closest to the wall, actual ft-in.^{2}/sec (m-cm^2/sec);

v_{drem} = the measured stack gas velocity at distance d_{rem} from the wall, actual ft/sec (m/sec);

Q_T = the total stack gas volumetric flow rate for the Method 1 equal-area sector closest to the wall, actual ft-in.^{2}/sec (m-cm^2/sec);

$\hat{v}e_j$ = the replacement stack gas velocity for the Method 1 equal-area sector closest to the wall, i.e., the stack gas point velocity value, adjusted for wall effects, for the jth Method 1 equal-area sector closest to the wall, actual ft/sec (m/sec);

$\hat{v}_{avg}$ = the average stack gas velocity that accounts for velocity decay near the wall, actual ft/sec (m/sec);

WAF = the wall effects adjustment factor derived from v_{avg} and $\hat{v}_{avg}$ for a single traverse, dimensionless;

$\hat{v}_{final}$ = the final wall effects-adjusted average stack gas velocity that replaces the unadjusted average stack gas velocity obtained using Method 2, 2F, or 2G for a field test consisting of a single traverse, actual ft/sec (m/sec);

$\bar{W}\bar{A}\bar{F}$ = the wall effects adjustment factor that is applied to the average velocity, unadjusted for wall effects, in order to obtain the final wall effects-adjusted stack gas velocity, $\hat{v}_{final}$ or, $\hat{v}_{final(k)}$, dimensionless;

$\hat{v}_{final(k)}$ = the final wall effects-adjusted average stack gas velocity that replaces the unadjusted average stack gas velocity obtained using Method 2, 2F, or 2G on run k of a RATA or other multiple-run field test procedure, actual ft/sec (m/sec);

$v_{avg(k)}$ = the average stack gas velocity, obtained on run k of a RATA or other multiple-run procedure, unadjusted for velocity decay near the wall, actual ft/sec (m/sec);

k=index of runs in a RATA or other multiple-run procedure.

12.3 Calculate the average stack gas velocity that does not account for velocity decay near the wall (v_{avg}) using Equation 2H–5.

$$v_{avg} = \frac{\left(\sum_{i=1}^{n-4} vi_i + \sum_{j=1}^{4} ve_j\right)}{n} \qquad \text{Eq. 2H-5}$$

(Note that v_{avg} in Equation 2H–5 is the same as $v_{(a)avg}$ in Equations 2F–9 and 2G–8 in Methods 2F and 2G, respectively.)

For a 16-point traverse, Equation 2H–5 may be written as follows:

$$v_{avg} = \frac{\left(\sum_{i=1}^{12} vi_i + \sum_{j=1}^{4} ve_j\right)}{16} \qquad \text{Eq. 2H-6}$$

12.4 Calculate the replacement velocity, $\hat{v}e_j$, for each of the four Method 1 equal-area sectors closest to the wall using the procedures described in sections 12.4.1 through 12.4.8. Forms 2H–1 and 2H–2 provide sample tables that may be used in either hardcopy or spreadsheet format to perform the calculations described in sections 12.4.1 through 12.4.8. Forms 2H–3 and 2H–4 provide examples of Form 2H–1 filled in for partial and complete wall effects traverses.

12.4.1 Calculate the average velocity (designated the ''decay velocity,'' $vdec_d$) for each sub-sector located between the wall and d_{last} (see Figure 2H–3) using Equation 2H–7.

$$vdec_d = \frac{v_{d-1} + v_d}{2} \qquad \text{Eq. 2H-7}$$

For each line in column A of Form 2H–1 or 2H–2 that contains a value of d, enter the corresponding calculated value of $vdec_d$ in column C.

12.4.2 Calculate the cross-sectional area between the wall and the first 1-in. incremented wall effects traverse point and between successive 1-in. incremented wall effects traverse points, from the wall to d_{last} (see Figure 2H–3), using Equation 2H–8.

$$A_d = \frac{1}{4}\pi(r-d+1)^2 - \frac{1}{4}\pi(r-d)^2 \qquad \text{Eq. 2H-8}$$

For each line in column A of Form 2H–1 or 2H–2 that contains a value of d, enter the value of the expression $\frac{1}{4}\pi(r-d+1)^2$ in column D, the value of the expression $\frac{1}{4}\pi(r-d)^2$ in column E, and the value of A_d in column F. Note that Equation 2H–8 is designed for use only with English units (in.). If metric units (cm) are used, the first term, $\frac{1}{4}\pi(r-d+1)^2$, must be changed to $\frac{1}{4}\pi(r-d+2.5)^2$. This change must also be made in column D of Form 2H–1 or 2H–2.

12.4.3 Calculate the volumetric flow through each cross-sectional area derived in section 12.4.2 by multiplying the values of $vdec_d$, derived according to section 12.4.1, by the cross-sectional areas derived in section 12.4.2 using Equation 2H–9.

$$Q_d = vdec_d \times A_d \qquad \text{Eq. 2H-9}$$

For each line in column A of Form 2H–1 or 2H–2 that contains a value of d, enter the corresponding calculated value of Q_d in column G.

12.4.4 Calculate the total volumetric flow through all sub-sectors located between the wall and d_{last}, using Equation 2H–10.

$$Q_{d_1 \rightarrow d_{last}} = \sum_{d=1}^{d_{last}} Q_d \qquad \text{Eq. 2H-10}$$

Enter the calculated value of $Q_{d_1 \rightarrow_c d_{last}}$ in line 3 of column G of Form 2H–1 or 2H–2.

12.4.5 Calculate the cross-sectional area of the sub-sector located between d_{last} and the interior edge of the Method 1 equal-area sector (e.g., sub-sector A_{drem} shown in Figures 2H–3 and 2H–4) using Equation 2H–11.

$$A_{drem} = \frac{1}{4}\pi(r-d_{last})^2 - \frac{p-2}{4p}\pi(r)^2 \qquad \text{Eq. 2H-11}$$

For a 16-point traverse (eight points per diameter), Equation 2H–11 may be written as follows:

$$A_{drem} = \frac{1}{4}\pi\left(r - d_{last}\right)^2 - \frac{3}{16}\pi(r)^2 \qquad \text{Eq. 2H-12}$$

Enter the calculated value of A_{drem} in line 4b of column G of Form 2H–1 or 2H–2.

12.4.6 Calculate the volumetric flow for the sub-sector located between d_{last} and the interior edge of the Method 1 equal-area sector, using Equation 2H–13.

$$Q_{drem} = v_{drem} \times A_{drem} \qquad \text{Eq. 2H-13}$$

In Equation 2H–13, v_{drem} is either (1) the measured velocity value at d_{rem} or (2) the measured velocity at d_{last}, if the distance between d_{rem} and d_{last} is less than or equal to ½ in. (12.7 mm) and no velocity measurement is taken at d_{rem} (see section 8.2.4.2). Enter the calculated value of Q_{drem} in line 4c of column G of Form 2H–1 or 2H–2.

12.4.7 Calculate the total volumetric flow for the Method 1 equal-area sector closest to the wall, using Equation 2H–14.

$$Q_T = Q_{d_1 \rightarrow d_{last}} + Q_{drem} \qquad \text{Eq. 2H-14}$$

Enter the calculated value of Q_T in line 5a of column G of Form 2H–1 or 2H–2.

12.4.8 Calculate the wall effects-adjusted replacement velocity value for the Method 1 equal-area sector closest to the wall, using Equation 2H–15.

$$\hat{v}e_j = \frac{Q_T}{\frac{1}{2p}\pi(r)^2} \qquad \text{Eq. 2H-15}$$

For a 16-point traverse (eight points per diameter), Equation 2H–15 may be written as follows:

$$\hat{v}e_j = \frac{Q_T}{\frac{1}{16}\pi(r)^2} \qquad \text{Eq. 2H-16}$$

Enter the calculated value of $\hat{v}e_j$ in line 5B of column G of Form 2H–1 or 2H–2.

12.5 Calculate the wall effects-adjusted average velocity, $\hat{v}_{avg}$, by replacing the four values of ve_j shown in Equation 2H–5 with the four wall effects-adjusted replacement velocity values,$\hat{v}e_j$, calculated according to section 12.4.8, using Equation 2H–17.

$$\hat{v}_{avg} = \frac{\left(\sum_{i=1}^{n-4} vi_i + \sum_{j=1}^{4} \hat{v}e_j\right)}{n} \qquad \text{Eq. 2H-17}$$

For a 16-point traverse, Equation 2H–17 may be written as follows:

$$\hat{v}_{avg} = \frac{\left(\sum_{i=1}^{12} vi_i + \sum_{j=1}^{4} \hat{v}e_j\right)}{16} \qquad \text{Eq. 2H-18}$$

12.6 Calculate the wall effects adjustment factor, WAF, using Equation 2H–19.

$$WAF = \frac{\hat{v}_{avg}}{v_{avg}} \qquad \text{Eq. 2H-19}$$

12.6.1 Partial wall effects traverse. If a partial wall effects traverse (see section 8.2.2) is conducted, the value obtained from Equation 2H–19 is acceptable and may be reported as the wall effects adjustment factor provided that the value is greater than or equal to 0.9800. If the value is less than 0.9800, it shall not be used and a wall effects adjustment factor of 0.9800 may be used instead.

12.6.2 Complete wall effects traverse. If a complete wall effects traverse (see section 8.2.3) is conducted, the value obtained from Equation 2H–19 is acceptable and may be reported as the wall effects adjustment factor provided that the value is greater than or equal to 0.9700. If the value is less than 0.9700, it shall not be used and a wall effects adjustment factor of 0.9700 may be used instead. If the wall effects adjustment factor for a particular stack or duct is less than 0.9700, the tester may (1) repeat the wall effects test, taking measurements at more Method 1 traverse points and (2) recalculate the wall effects adjustment factor from these measurements, in an attempt to obtain a wall effects adjustment factor that meets the 0.9700 specification and completely characterizes the wall effects.

12.7 Applying a Wall Effects Adjustment Factor. A default wall effects adjustment factor, as specified in section 8.1, or a calculated wall effects adjustment factor meeting the requirements of section 12.6.1 or 12.6.2

may be used to adjust the average stack gas velocity obtained using Methods 2, 2F, or 2G to take into account velocity decay near the wall of circular stacks or ducts. Default wall effects adjustment factors specified in section 8.1 and calculated wall effects adjustment factors that meet the requirements of section 12.6.1 and 12.6.2 are summarized in Table 2H–2.

12.7.1 Single-run tests. Calculate the final wall effects-adjusted average stack gas velocity for field tests consisting of a single traverse using Equation 2H–20.

$$\hat{v}_{final} = \overline{WAF} \times v_{avg} \qquad \text{Eq. 2H-20}$$

The wall effects adjustment factor, WAF, shown in Equation 2H–20, may be (1) a default wall effects adjustment factor, as specified in section 8.1, or (2) a calculated adjustment factor that meets the specifications in sections 12.6.1 or 12.6.2. If a calculated adjustment factor is used in Equation 2H–20, the factor must have been obtained during the same traverse in which v_{avg} was obtained.

12.7.2 RATA or other multiple run test procedure. Calculate the final wall effects-adjusted average stack gas velocity for any run k of a RATA or other multiple-run procedure using Equation 2H–21.

$$\hat{v}_{final(k)} = \overline{WAF} \times v_{avg(k)} \qquad \text{Eq. 2H-21}$$

The wall effects adjustment factor, $\bar{W}\bar{A}\bar{F}$, shown in Equation 2H–21 may be (1) a default wall effects adjustment factor, as specified in section 8.1; (2) a calculated adjustment factor (meeting the specifications in sections 12.6.1 or 12.6.2) obtained from any single run of the RATA that includes run k; or (3) the arithmetic average of more than one WAF (each meeting the specifications in sections 12.6.1 or 12.6.2) obtained through wall effects testing conducted during several runs of the RATA that includes run k. If wall effects adjustment factors (meeting the specifications in sections 12.6.1 or 12.6.2) are determined for more than one RATA run, the arithmetic average of all of the resulting calculated wall effects adjustment factors must be used as the value of $\bar{W}\bar{A}\bar{F}$ and applied to all runs of that RATA. If a calculated, not a default, wall effects adjustment factor is used in Equation 2H–21, the average velocity unadjusted for wall effects, $v_{avg(k)}$ must be obtained from runs in which the number of Method 1 traverse points sampled does not exceed the number of Method 1 traverse points in the runs used to derive the wall effects adjustment factor, $\bar{W}\bar{A}\bar{F}$, shown in Equation 2H–21.

12.8 Calculating Volumetric Flow Using Final Wall Effects-Adjusted Average Velocity Value. To obtain a stack gas flow rate that accounts for velocity decay near the wall of circular stacks or ducts, replace v_s in Equation 2–10 in Method 2, or $v_{a(avg)}$ in Equations 2F–10 and 2F–11 in Method 2F, or $v_{a(avg)}$ in Equations 2G–9 and 2G–10 in Method 2G with one of the following.

12.8.1 For single-run test procedures, use the final wall effects-adjusted average stack gas velocity, $\hat{v}_{final}$, calculated according to Equation 2H–20.

12.8.2 For RATA and other multiple run test procedures, use the final wall effects-adjusted average stack gas velocity, $\hat{v}_{final(k)}$, calculated according to Equation 2H–21.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Reporting

16.1 Field Test Reports. Field test reports shall be submitted to the Agency according to the applicable regulatory requirements. When Method 2H is performed in conjunction with Method 2, 2F, or 2G to derive a wall effects adjustment factor, a single consolidated Method 2H/2F (or 2H/2G) field test report should be prepared. At a minimum, the consolidated field test report should contain (1) all of the general information, and data for Method 1 points, specified in section 16.0 of Method 2F (when Method 2H is used in conjunction with Method 2F) or section 16.0 of Method 2G (when Method 2H is used in conjunction with Method 2 or 2G) and (2) the additional general information, and data for Method 1 points and wall effects points, specified in this section (some of which are included in section 16.0 of Methods 2F and 2G and are repeated in this section to ensure complete reporting for wall effects testing).

16.1.1 Description of the source and site. The field test report should include the descriptive information specified in section 16.1.1 of Method 2F (when using Method 2F) or 2G (when using either Method 2 or 2G). It should also include a description of the stack or duct's construction material along with the diagram showing the dimensions of the stack or duct at the test port elevation prescribed in Methods 2F and 2G. The diagram should indicate the location of all wall effects traverse points where measurements were taken as well as the Method 1 traverse points. The diagram should provide a unique identification number for each wall effects and Method 1 traverse point, its distance from the wall, and its location relative to the probe entry ports.

16.1.2 Field test forms. The field test report should include a copy of Form 2H–1, 2H–2, or an equivalent for each Method 1 exterior equal-area sector.

16.1.3 Field test data. The field test report should include the following data for the Method 1 and wall effects traverse.

16.1.3.1 Data for each traverse point. The field test report should include the values

specified in section 16.1.3.2 of Method 2F (when using Method 2F) or 2G (when using either Method 2 or 2G) for each Method 1 and wall effects traverse point. The provisions of section 8.4.2 of Method 2H apply to the temperature measurements reported for wall effects traverse points. For each wall effects and Method 1 traverse point, the following values should also be included in the field test report.

(a) Traverse point identification number for each Method 1 and wall effects traverse point.

(b) Probe type.

(c) Probe identification number.

(d) Probe velocity calibration coefficient (i.e., C_p when Method 2 or 2G is used; F_2 when Method 2F is used).

For each Method 1 traverse point in an exterior equal-area sector, the following additional value should be included.

(e) Calculated replacement velocity, $\hat{v}e_j$, accounting for wall effects.

16.1.3.2 Data for each run. The values specified in section 16.1.3.3 of Method 2F (when using Method 2F) or 2G (when using either Method 2 or 2G) should be included in the field test report once for each run. The provisions of section 12.8 of Method 2H apply for calculating the reported gas volumetric flow rate. In addition, the following Method 2H run values should also be included in the field test report.

(a) Average velocity for run, accounting for wall effects, $\hat{v}_{avg}$.

(b) Wall effects adjustment factor derived from a test run, WAF.

16.1.3.3 Data for a complete set of runs. The values specified in section 16.1.3.4 of Method 2F (when using Method 2F) or 2G (when using either Method 2 or 2G) should be included in the field test report once for each complete set of runs. In addition, the field test report should include the wall effects adjustment factor, $\bar{W}\bar{A}\bar{F}$, that is applied in accordance with section 12.7.1 or 12.7.2 to obtain the final wall effects-adjusted average stack gas velocity $\hat{v}_{final}$ or $\hat{v}_{final(k)}$.

16.1.4 Quality assurance and control. Quality assurance and control procedures, specifically tailored to wall effects testing, should be described.

16.2 Reporting a Default Wall Effects Adjustment Factor. When a default wall effects adjustment factor is used in accordance with section 8.1 of this method, its value and a description of the stack or duct's construction material should be reported in lieu of submitting a test report.

17.0 References.

(1) 40 CFR Part 60, Appendix A, Method 1—Sample and velocity traverses for stationary sources.

(2) 40 CFR Part 60, Appendix A, Method 2—Determination of stack gas velocity and volumetric flow rate (Type S pitot tube).

(3) 40 CFR Part 60, Appendix A, Method 2F—Determination of stack gas velocity and volumetric flow rate with three-dimensional probes.

(4) 40 CFR Part 60, Appendix A, Method 2G—Determination of stack gas velocity and volumetric flow rate with two-dimensional probes.

(5) 40 CFR Part 60, Appendix A, Method 3—Gas analysis for carbon dioxide, oxygen, excess air, and dry molecular weight.

(6) 40 CFR Part 60, Appendix A, Method 3A—Determination of oxygen and carbon dioxide concentrations in emissions from stationary sources (instrumental analyzer procedure).

(7) 40 CFR Part 60, Appendix A, Method 4—Determination of moisture content in stack gases.

(8) Emission Measurement Center (EMC) Approved Alternative Method (ALT–011) ''Alternative Method 2 Thermocouple Calibration Procedure.''

(9) The Cadmus Group, Inc., 1998, ''EPA Flow Reference Method Testing and Analysis: Data Report, Texas Utilities, DeCordova Steam Electric Station, Volume I: Test Description and Appendix A (Data Distribution Package),'' EPA/430–R–98–015a.

(10) The Cadmus Group, Inc., 1998, ''EPA Flow Reference Method Testing and Analysis: Data Report, Texas Utilities, Lake Hubbard Steam Electric Station, Volume I: Test Description and Appendix A (Data Distribution Package),'' EPA/430–R–98–017a.

(11) The Cadmus Group, Inc., 1998, ''EPA Flow Reference Method Testing and Analysis: Data Report, Pennsylvania Electric Co., G.P.U. Genco Homer City Station: Unit 1, Volume I: Test Description and Appendix A (Data Distribution Package),'' EPA/430–R–98–018a.

(12) The Cadmus Group, Inc., May 1999, ''EPA Flow Reference Method Testing and Analysis: Findings Report,'' EPA/430–R–99–009.

(13) The Cadmus Group, Inc., 1997, ''EPA Flow Reference Method Testing and Analysis: Wind Tunnel Experimental Results,'' EPA/430–R–97–013.

(14) National Institute of Standards and Technology, 1998, ''Report of Special Test of Air Speed Instrumentation, Four Prandtl Probes, Four S-Type Probes, Four French Probes, Four Modified Kiel Probes,'' Prepared for the U.S. Environmental Protection Agency under IAG No. DW13938432–01–0.

(15) National Institute of Standards and Technology, 1998, ''Report of Special Test of Air Speed Instrumentation, Five Autoprobes,'' Prepared for the U.S. Environmental Protection Agency under IAG No. DW13938432–01–0.

(16) National Institute of Standards and Technology, 1998, ''Report of Special Test of Air Speed Instrumentation, Eight Spherical Probes,'' Prepared for the U.S. Environmental Protection Agency under IAG No. DW13938432–01–0.

(17) National Institute of Standards and Technology, 1998, ''Report of Special Test of Air Speed Instrumentation, Four DAT Probes,'' Prepared for the U.S. Environmental Protection Agency under IAG No. DW13938432–01–0.

(18) Massachusetts Institute of Technology (MIT), 1998, ''Calibration of Eight Wind Speed Probes Over a Reynolds Number Range of 46,000 to 725,000 per Foot, Text and Summary Plots,'' Plus Appendices, WBWT-TR–1317, Prepared for The Cadmus Group, Inc., under EPA Contract 68–W6–0050, Work Assignment 0007AA–3.

(19) Fossil Energy Research Corporation, Final Report, ''Velocity Probe Tests in Non-axial Flow Fields,'' November 1998, Prepared for the U.S. Environmental Protection Agency.

(20) Fossil Energy Research Corporation, ''Additional Swirl Tunnel Tests: E-DAT and T-DAT Probes,'' February 24, 1999, Technical Memorandum Prepared for U.S. Environmental Protection Agency, P.O. No. 7W–1193–NALX.

Table 2H-1. Distance from the Wall for the Interior Boundary, d_b, of a Method 1 Exterior Equal-Area Sector as a Function of the Stack or Duct Radius, r, and Number of Method 1 Traverse Points

Number of Method 1 Traverse Points	d_b
16	0.134 × r
20	0.106 × r
24	0.087 × r
28	0.074 × r
32	0.065 × r
36	0.057 × r
40	0.051 × r
44	0.047 × r
48	0.043 × r

Table 2H-2 Default and Minimum Acceptable Calculated Wall Effects Adjustment Factors

		Brick and Mortar Stacks	All Other Stacks and Ducts
Default WAF		0.9900	0.9950
Minimum Acceptable WAF	Partial Traverse	0.9800	
	Complete Traverse	0.9700	

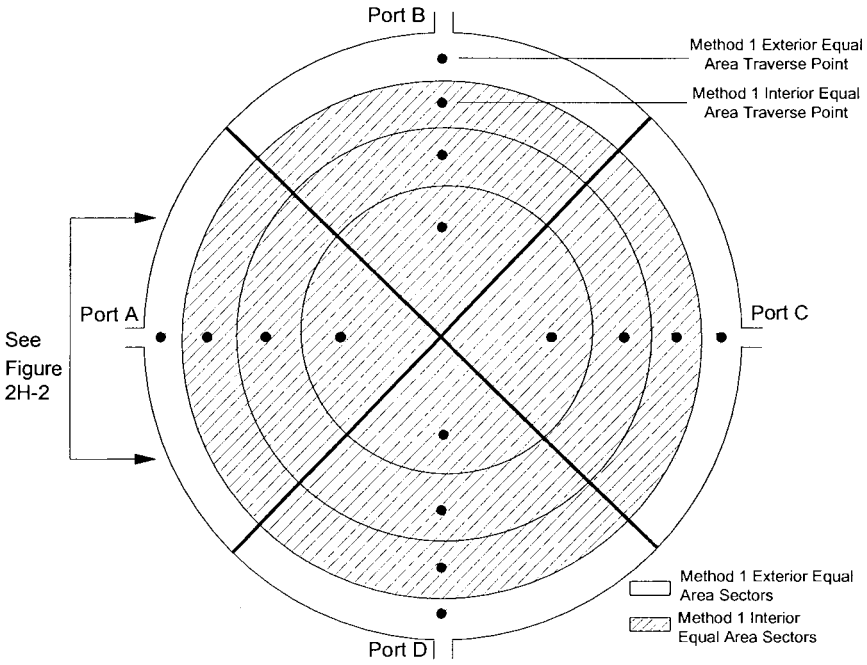


Figure 2H-1. Method 1 exterior and interior equal-area sectors with traverse points indicated.

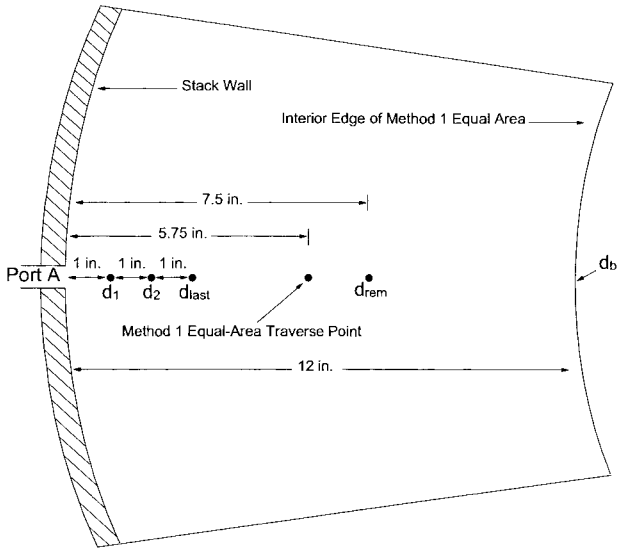


Figure 2H-2. Figure showing part of a Method 1 equal-area sector closest to the stack wall with three illustrative wall effects points at 1 in. intervals, the Method 1 equal-area traverse point, and d_{rem} for a 15 ft diameter stack.[1]

[1] Metric equivalents of English units used in Figure 2H-2 are as follows: 1 in. = 2.5 cm; 5.75 in. = 14.6 cm; 7.5 in. = 19.0 cm; 12 in. = 30.5 cm; and 15 ft = 4.6 m.

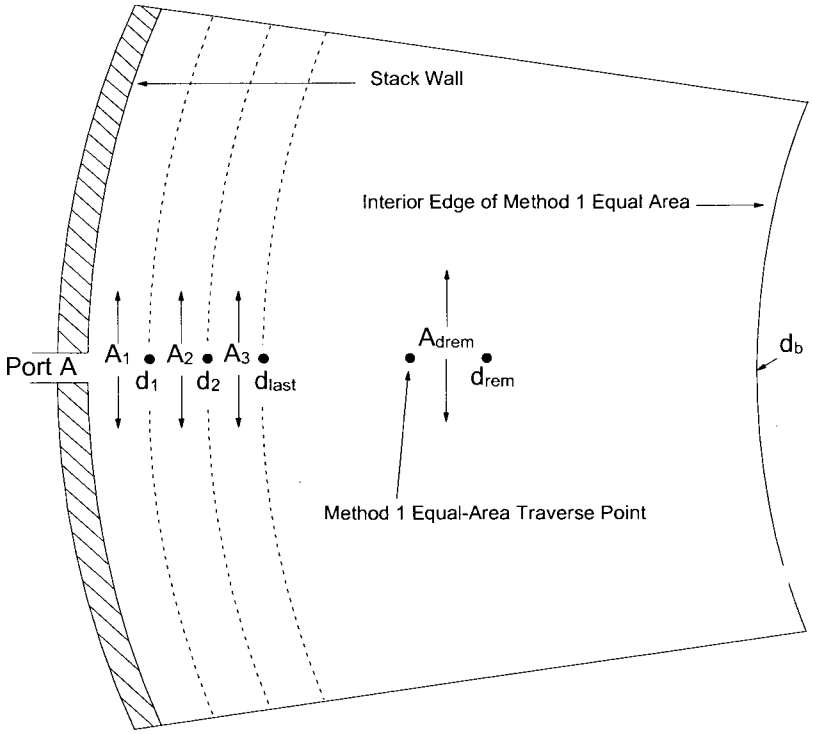


Figure 2H-3. Figure showing part of a Method 1 equal-area sector closest to the stack wall with three illustrative sub-sectors between the stack wall and d_{last} and the sub-sector represented by d_{rem}. A_1 is the area between the stack wall and d_1, A_2 is the area between d_1 and d_2, A_3 is the area between d_2 and d_{last}, and A_{drem} is the area between d_{last} and the interior edge of the Method 1 equal-area sector.

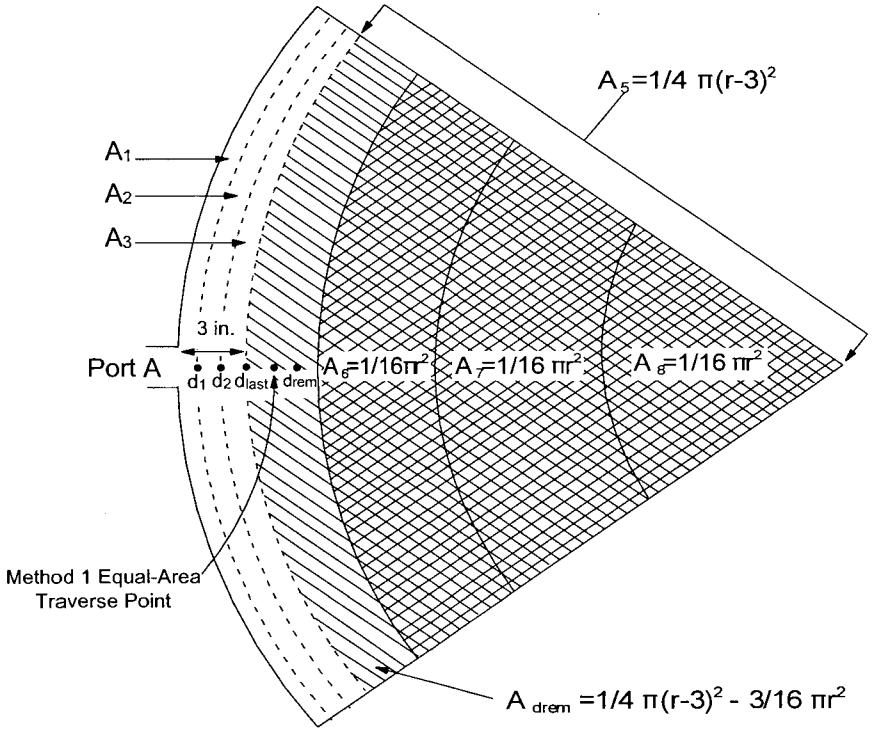


Figure 2H-4. Figure illustrating the calculations in Equation 2H-12 used to calculate the cross sectional area of the sub-sector between d_{last} and the interior edge of the Method 1 sector closest to the stack wall (A_{drem}) for a 16-point Method 1 traverse. The Method 1 equal-area traverse point and four wall effects traverse points (d_1, d_2, d_{last}, and d_{rem}) within the Method 1 sector closest to the stack wall are also shown.[1]

[1] All dimensions are given in in. Metric equivalents (in cm) are as follows: 3 in. = 7.6 cm; A_5 = 1/4 π(r−7.6)²; and A_{drem} = 1/4 π(r−7.6)² − 3/16 πr².

Form 2H-1. Calculation of Wall Effects Replacement Velocity Values (16-Point Method 1 Traverse)

1st Probe Type/ID/Pts. Sampled: _____ Tester(s): _____

2nd Probe Type/ID/Pts. Sampled: _____ Affiliation: _____

Entry Port ID (e.g., A, B, C, or D): _____

1. Diameter of the stack or duct (ft)		Radius, r, of the stack or duct (in.) (= diameter × 6)	

2. Location (column A), measured and decay velocities (columns B and C), and volumetric flow (column G) associated with each successive wall effects traverse point.

(A)	(B)	(C)	(D)	(E)	(F)	(G)
Distance (d) from Wall	Measured Velocity (v_d) at Distance d	Decay Velocity ($vdec_d$)	Intermediate Calculations		Area of Sub-sector (A_d)	Volumetric Flow in Sub-sector (Q_d)
		$\frac{v_{d-1}+v_d}{2}$ Note: $v_0 = 0$	$\frac{1}{4}\pi[r-d+1]^2$	$\frac{1}{4}\pi[r-d]^2$	(Col. D - Col. E)	(Col. C × Col. F)
(*in.*)	(*ft/sec*)	(*ft/sec*)	(*in.*^{2})	(*in.*^{2})	(*in.*^{2})	(*ft-in.*^{2}/*sec*)
$d = 1$						
$d = 2$						
. . .						
d_{last}						

Note: $d_{last} \leq 0.1340\ r$, where r is the radius of the stack or duct. See section 8.2.2.3 of the method.

3. Total volumetric flow for all sub-sectors located between stack wall and d_{last} (total Col. G).	
4. Volumetric flow for remainder of the Method 1 equal-area sector.	
a. Velocity measurement at distance d_{rem} from stack wall (v_{drem}). (If d_{rem}- d_{last} <½ in., then no measurement at d_{rem} is necessary. Enter the velocity at d_{last} on this line.)	
b. Total area in remainder of Method 1 equal-area segment (A_{drem}). Subtract $\frac{3}{16}\pi(r)^2$ from last entry in item 2, column E, and enter the result on this line.	
c. Multiply values on lines 4a and 4b. (Q_{drem})	
5. Wall effects-adjusted velocity in the Method 1 equal-area sector.	
a. Add the values on lines 3 and 4c. (Q_T)	
b. Divide line 5a by $\frac{1}{16}\pi(r)^2$. The resulting value is one of four "replacement" point velocity values adjusted for wall effects, $\hat{v}e_j$, as derived in Equation 2H-16.	
6. Substitute the value shown in 5b for the unadjusted velocity value in the Method 1 sector. (See Eq. 2H-18.)	

Notes: 1. Column B: If no measurement is taken at distance d, enter the velocity value obtained at the first subsequent traverse point where a measurement was taken, followed by the letters "NM". See section 8.7.1.2.

2. For clarity, only English units are shown in this form. Following are metric equivalents of the English units used in the form. In row 2, column A: 1 in. = 2.5 cm; 2 in. = 5.1 cm. In row 2, column D: If metric units (cm) are used, the term $\frac{1}{4}\pi(r-d+1)^2$ must be changed to $\frac{1}{4}\pi(r-d+2.5)^2$. In row 4a: ½ in. = 12.7 mm. Throughout the form, the metric equivalents of *in.*, *in.*^{2}, *ft*, *ft/sec*, and *ft-in*^{2}*/sec* are *cm*, *cm*^{2}, *m*, *m/sec*, and *m-cm*^{2}*/sec*, respectively.

Form 2H-2. Calculation of Wall Effects Replacement Velocity Values (Any Method 1 Traverse ≥16 Points)

1st Probe Type/ID/Pts. Sampled: _____ Tester(s): _____

2nd Probe Type/ID/Pts. Sampled: _____ Affiliation: _____

Entry Port ID (e.g., A, B, C, or D): _____

1. Diameter of the stack or duct (ft)		Radius, r, of the stack or duct (in.) (= diameter × 6)	

2. Location (Column A), measured and decay velocities (Columns B and C), and volumetric flow (Column G) associated with each successive wall effects traverse point.

(A)	(B)	(C)	(D)	(E)	(F)	(G)
Distance (d) from Wall	Measured Velocity (v_d) at Distance d	Decay Velocity ($vdec_d$)	Intermediate Calculations		Area of Sub-sector (A_d)	Volumetric Flow in Sub-sector (Q_d)
		$\frac{v_{d-1}+v_d}{2}$ Note: $v_0 = 0$	$\frac{2}{p}\pi[r-d+1]^2$	$\frac{2}{p}\pi[r-d]^2$	(Col. D - Col. E)	(Col. C × Col. F)
(*in.*)	(*ft/sec*)	(*ft/sec*)	(*in.*^{2})	(*in.*^{2})	(*in.*^{2})	(*ft-in.*^{2}/*sec*)
$d = 1$						
$d = 2$						
. . .						
d_{last}						

Note: $d_{last} \le d_b$, as defined in section 8.2.2.3 of the method.

3. Total volumetric flow for all sub-sectors located between stack wall and d_{last} (total Col. G).	
4. Volumetric flow for remainder of the Method 1 equal-area sector.	
a. Velocity measurement at distance d_{rem} from stack wall (v_{drem}). (If d_{rem}- d_{last} <½ in., then no measurement at d_{rem} is necessary. Enter the velocity at d_{last} on this line.)	
b. Total area in remainder of Method 1 equal-area segment (A_{drem}). Subtract $\left\{\frac{p-2}{4p}\right\}\pi(r)^2$ from last entry in item 2, column E, and enter the result on this line.	
c. Multiply values on lines 4a and 4b. (Q_{drem})	
5. Wall effects-adjusted velocity in the Method 1 near-wall equal-area segment.	
a. Add the values on lines 3 and 4. (Q_T)	
b. Divide line 5a by $\left\{\frac{1}{2p}\right\}\pi(r)^2$. The resulting value is one of four "replacement" point velocity values adjusted for wall effects, $\hat{v}e_j$, as derived in Equation 2H-15.	
6. Substitute the value shown in 5b for the unadjusted velocity value in the Method 1 sector. (See Eq. 2H-17.)	

Notes: 1. Column B: If no measurement is taken at distance d, enter the velocity value obtained at the first subsequent traverse point where a measurement was taken, followed by the letters "NM". See section 8.7.1.2.

2. For clarity, only English units are shown in this form. Following are metric equivalents of the English units used in the form. In row 2, column A: 1 in. = 2.5 cm; 2 in. = 5.1 cm. In row 2, column D: If metric units (cm) are used, the term $¼\,\pi(r-d+1)^2$ must be changed to $¼\,\pi(r-d+2.5)^2$. In row 4a: ½ in. = 12.7 mm. Throughout the form, the metric equivalents of *in.*, *in.*^{2}, *ft*, *ft/sec*, and *ft-in*^{2}*/sec* are *cm*, *cm*^{2}, *m*, *m/sec*, and *m-cm*^{2}*/sec*, respectively.

Form 2H-3. Calculation of Replacement Velocity Values for a Method 1 Equal-Area Sector Closest to the Stack Wall for a 16-Point Method 1 Traverse, Using a Partial Wall Effects Traverse

1st Probe Type/ID/Pts. Sampled: *Type S Straight-up/S-13/All* Tester(s): *Test Team III*

2nd Probe Type/ID/Pts. Sampled: _____ Affiliation: *Contractor III*

Entry Port ID (e.g., A, B, C, or D): *A*

1. Diameter of the stack or duct (ft)	*24*	Radius, r, of the stack or duct (in.) (= diameter × 6)	*144*

2. Location (column A), measured and decay velocities (columns B and C), and volumetric flow (column G) associated with each successive wall effects traverse point.

(A) Distance (d) from Wall	(B) Measured Velocity (v_d) at Distance d	(C) Decay Velocity ($vdec_d$)	(D) Intermediate Calculations	(E) Intermediate Calculations	(F) Area of Sub-sector (A_d)	(G) Volumetric Flow in Sub-sector (Q_d)
		$\frac{v_{d-1}+v_d}{2}$ Note: $v_0 = 0$	$\frac{1}{4}\pi[r-d+1]^2$	$\frac{1}{4}\pi[r-d]^2$	(Col. D - Col. E)	(Col. C × Col. F)
(in.)	(ft/sec)	(ft/sec)	(in.^{2})	(in.^{2})	(in.^{2})	(ft-in.^{2}/sec)
d = 1	51.71 NM	25.85	16,286.00	16,060.59	225.41	5,827.47
d = 2	51.71 NM	51.71	16,060.59	15,836.76	223.84	11,573.72
d_{last} = 3	51.71	51.71	15,836.76	15,614.49	222.27	11,492.51

3. Total volumetric flow for all sub-sectors located between stack wall and d_{last} (total Col. G).	*28,893.70*
4. Volumetric flow for remainder of the Method 1 equal-area sector.	
a. Velocity measurement at distance d_{rem} from stack wall (v_{drem}). (If d_{rem} - d_{last} <½ in., then no measurement at d_{rem} is necessary. Enter the velocity at d_{last} on this line.)	*77.01*
b. Total area in remainder of Method 1 equal-area segment (A_{drem}). Subtract $\frac{3}{16}\pi(r)^2$ from last entry in item 2, column E, and enter the result on this line.	*3,399.99*
c. Multiply values on lines 4a and 4b. (Q_{drem})	*261,832.90*
5. Wall effects-adjusted velocity in the Method 1 equal-area sector.	
a. Add the values on lines 3 and 4c. (Q_T)	*290,726.61*
b. Divide line 5a by $\frac{1}{16}\pi(r)^2$. The resulting value is one of four "replacement" point velocity values adjusted for wall effects, $\hat{v}e_i$, as derived in Equation 2H-16.	*71.41*
6. Substitute the value shown in 5b for the unadjusted velocity value in the Method 1 sector. (See Eq. 2H-18.)	

Form 2H-4 Calculation of Replacement Velocity Values for a Method 1 Equal-Area Sector Closest to the Stack Wall for a 16-Point Method 1 Traverse, Using a Complete Traverse

1st Probe Type/ID/Pts. Sampled: *Type S Straight-up/S-13/All* Tester(s): *Test Team III*

2nd Probe Type/ID/Pts. Sampled: _____ Affiliation: *Contractor III*

Entry Port ID (e.g., A, B, C, or D): *A*

1. Diameter of the stack or duct (ft)	*24*	Radius, r, of the stack or duct (in.) (= diameter × 6)	*144*

2. Location (column A), measured and decay velocities (columns B and C), and volumetric flow (column G) associated with each successive wall effects traverse point.

(A)	(B)	(C)	(D)	(E)	(F)	(G)
Distance (d) from Wall	Measured Velocity (v_d) at Distance d	Decay Velocity ($vdec_d$)	Intermediate Calculations		Area of Sub-sector (A_d)	Volumetric Flow in Sub-sector (Q_s)
		$\frac{v_{d-1}+v_d}{2}$ Note: $v_0 = 0$	$\frac{1}{4}\pi[r-d+1]^2$	$\frac{1}{4}\pi[r-d]^2$	(Col. D - Col. E)	(Col. C × Col. F)
(in.)	(ft/sec)	(ft/sec)	(in.^{2})	(in.^{2})	(in.^{2})	(ft-in.^{2}/sec)
$d = 1$	51.71 NM	25.85	16,286.00	16,060.59	225.41	5,827.47
$d = 2$	51.71 NM	51.71	16,060.59	15,836.76	223.84	11,573.72
$d = 3$	51.71	51.71	15,836.76	15,614.49	222.27	11,492.51
$d = 4$	62.26	56.98	15,614.49	15,393.79	220.70	12,576.24
$d = 5$	67.16	64.71	15,393.79	15,174.67	219.13	14,179.40
$d = 6$	69.44	68.30	15,174.67	14,957.11	217.56	14,858.32
$d = 7$	72.63	71.03	14,957.11	14,741.13	215.98	15,341.75
$d = 8$	71.37	72.00	14,741.13	14,526.71	214.41	15,437.01
$d = 9$	74.37	72.87	14,526.71	14,313.87	212.84	15,510.03
$d = 10$	75.80	75.08	14,313.87	14,102.60	211.27	15,863.30
$d = 11$	77.15	76.47	14,102.60	13,892.90	209.70	16,035.93
$d_{last} = 12$	78.58	77.86	13,892.90	13,684.77	208.13	16,205.92

3. Total volumetric flow for all sub-sectors located between stack wall and d_{last} (total Col. G).	*164,901.59*
4. Volumetric flow for remainder of the Method 1 equal-area sector.	
a. Velocity measurement at distance d_{rem} from stack wall (v_{drem}). (If $d_{rem} - d_{last} < ½$ in., then no measurement at d_{rem} is necessary. Enter the velocity at d_{last} on this line.)	*78.51*
b. Total area in remainder of Method 1 equal-area segment (A_{drem}). Subtract $\frac{3}{16}\pi(r)^2$ from last entry in item 2, column E, and enter the result on this line.	*1,470.26*
c. Multiply values on lines 4a and 4b. (Q_{drem})	*115,430.44*
5. Wall effects-adjusted velocity in the Method 1 equal-area sector.	
a. Add the values on lines 3 and 4c. (Q_T)	*280,332.03*
b. Divide line 5a by $\frac{1}{16}\pi(r)^2$. The resulting value is one of four "replacement" point velocity values adjusted for wall effects, $\hat{v}e_L$, as derived in Equation 2H-16.	*68.85*
6. Substitute the value shown in 5b for the unadjusted velocity value in the Method 1 sector. (See Eq. 2H-18.)	

METHOD 3—GAS ANALYSIS FOR THE DETERMINATION OF DRY MOLECULAR WEIGHT

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should also have a thorough knowledge of Method 1.

1.0 Scope and Application

1.1 Analytes.

Analytes	CAS No.	Sensitivity
Oxygen (O_2)	7782–44–7	2,000 ppmv.
Nitrogen (N_2)	7727–37–9	N/A.
Carbon dioxide (CO_2)	124–38–9	2,000 ppmv.
Carbon monoxide (CO)	630–08–0	N/A.

1.2 Applicability. This method is applicable for the determination of CO_2 and O_2 concentrations and dry molecular weight of a sample from an effluent gas stream of a fossil-fuel combustion process or other process.

1.3 Other methods, as well as modifications to the procedure described herein, are also applicable for all of the above determinations. Examples of specific methods and modifications include: (1) A multi-point grab sampling method using an Orsat analyzer to analyze the individual grab sample obtained at each point; (2) a method for measuring either CO_2 or O_2 and using stoichiometric calculations to determine dry molecular weight; and (3) assigning a value of 30.0 for dry molecular weight, in lieu of actual measurements, for processes burning natural gas, coal, or oil. These methods and modifications may be used, but are subject to the approval of the Administrator. The method may also be applicable to other processes where it has been determined that compounds other than CO_2, O_2, carbon monoxide (CO), and nitrogen (N_2) are not present in concentrations sufficient to affect the results.

1.4 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from a stack by one of the following methods: (1) single-point, grab sampling; (2) single-point, integrated sampling; or (3) multi-point, integrated sampling. The gas sample is analyzed for percent CO_2 and percent O_2. For dry molecular weight determination, either an Orsat or a Fyrite analyzer may be used for the analysis.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Several compounds can interfere, to varying degrees, with the results of Orsat or Fyrite analyses. Compounds that interfere with CO_2 concentration measurement include acid gases (*e.g.*, sulfur dioxide, hydrogen chloride); compounds that interfere with O_2 concentration measurement include unsaturated hydrocarbons (*e.g.*, acetone, acetylene), nitrous oxide, and ammonia. Ammonia reacts chemically with the O_2 absorbing solution, and when present in the effluent gas stream must be removed before analysis.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents.

5.2.1 A typical Orsat analyzer requires four reagents: a gas-confining solution, CO_2 absorbent, O_2 absorbent, and CO absorbent. These reagents may contain potassium hydroxide, sodium hydroxide, cuprous chloride, cuprous sulfate, alkaline pyrogallic acid, and/or chromous chloride. Follow manufacturer's operating instructions and observe all warning labels for reagent use.

5.2.2 A typical Fyrite analyzer contains zinc chloride, hydrochloric acid, and either potassium hydroxide or chromous chloride. Follow manufacturer's operating instructions and observe all warning labels for reagent use.

6.0 Equipment and Supplies

NOTE: As an alternative to the sampling apparatus and systems described herein, other sampling systems (*e.g.*, liquid displacement) may be used, provided such systems are capable of obtaining a representative sample and maintaining a constant sampling rate, and are, otherwise, capable of yielding acceptable results. Use of such systems is subject to the approval of the Administrator.

6.1 Grab Sampling (See Figure 3–1).

6.1.1 Probe. Stainless steel or borosilicate glass tubing equipped with an in-stack or out-of-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Any other materials, resistant to temperature at sampling conditions and inert to all components of the gas stream, may be used for the probe. Examples of such materials may include aluminum, copper, quartz glass, and Teflon.

6.1.2 Pump. A one-way squeeze bulb, or equivalent, to transport the gas sample to the analyzer.

6.2 Integrated Sampling (Figure 3–2).

6.2.1 Probe. Same as in section 6.1.1.

6.2.2 Condenser. An air-cooled or water-cooled condenser, or other condenser no greater than 250 ml that will not remove O_2, CO_2, CO, and N_2, to remove excess moisture which would interfere with the operation of the pump and flowmeter.

6.2.3 Valve. A needle valve, to adjust sample gas flow rate.

6.2.4 Pump. A leak-free, diaphragm-type pump, or equivalent, to transport sample gas to the flexible bag. Install a small surge tank between the pump and rate meter to eliminate the pulsation effect of the diaphragm pump on the rate meter.

6.2.5 Rate Meter. A rotameter, or equivalent, capable of measuring flow rate to ±2 percent of the selected flow rate. A flow rate range of 500 to 1000 ml/min is suggested.

6.2.6 Flexible Bag. Any leak-free plastic (*e.g.*, Tedlar, Mylar, Teflon) or plastic-coated aluminum (*e.g.*, aluminized Mylar) bag, or equivalent, having a capacity consistent with the selected flow rate and duration of the test run. A capacity in the range of 55 to 90 liters (1.9 to 3.2 ft^3) is suggested. To leak-check the bag, connect it to a water manometer, and pressurize the bag to 5 to 10 cm H_2O (2 to 4 in. H_2O). Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak. An alternative leak-check method is to pressurize the bag to 5 to 10 cm (2 to 4 in.) H_2O and allow to stand overnight. A deflated bag indicates a leak.

6.2.7 Pressure Gauge. A water-filled U-tube manometer, or equivalent, of about 30 cm (12 in.), for the flexible bag leak-check.

6.2.8 Vacuum Gauge. A mercury manometer, or equivalent, of at least 760 mm (30 in.) Hg, for the sampling train leak-check.

6.3 Analysis. An Orsat or Fyrite type combustion gas analyzer.

7.0 Reagents and Standards

7.1 Reagents. As specified by the Orsat or Fyrite-type combustion analyzer manufacturer.

7.2 Standards. Two standard gas mixtures, traceable to National Institute of Standards and Technology (NIST) standards, to be used in auditing the accuracy of the analyzer and the analyzer operator technique:

7.2.1. Gas cylinder containing 2 to 4 percent O_2 and 14 to 18 percent CO_2.

7.2.2. Gas cylinder containing 2 to 4 percent CO_2 and about 15 percent O_2.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Single Point, Grab Sampling Procedure.

8.1.1 The sampling point in the duct shall either be at the centroid of the cross section or at a point no closer to the walls than 1.0 m (3.3 ft), unless otherwise specified by the Administrator.

8.1.2 Set up the equipment as shown in Figure 3–1, making sure all connections ahead of the analyzer are tight. If an Orsat analyzer is used, it is recommended that the analyzer be leak-checked by following the procedure in section 11.5; however, the leak-check is optional.

8.1.3 Place the probe in the stack, with the tip of the probe positioned at the sampling point. Purge the sampling line long enough to allow at least five exchanges. Draw a sample into the analyzer, and immediately analyze it for percent CO_2 and percent O_2 according to section 11.2.

8.2 Single-Point, Integrated Sampling Procedure.

8.2.1 The sampling point in the duct shall be located as specified in section 8.1.1.

8.2.2 Leak-check (optional) the flexible bag as in section 6.2.6. Set up the equipment as shown in Figure 3–2. Just before sampling, leak-check (optional) the train by placing a vacuum gauge at the condenser inlet, pulling a vacuum of at least 250 mm Hg (10 in. Hg), plugging the outlet at the quick disconnect, and then turning off the pump. The vacuum should remain stable for at least 0.5 minute. Evacuate the flexible bag. Connect the probe, and place it in the stack, with the tip of the probe positioned at the sampling point. Purge the sampling line. Next, connect the bag, and make sure that all connections are tight.

8.2.3 Sample Collection. Sample at a constant rate (±10 percent). The sampling run should be simultaneous with, and for the same total length of time as, the pollutant emission rate determination. Collection of at least 28 liters (1.0 ft^3) of sample gas is recommended; however, smaller volumes may be collected, if desired.

8.2.4 Obtain one integrated flue gas sample during each pollutant emission rate determination. Within 8 hours after the sample is taken, analyze it for percent CO_2 and percent O_2 using either an Orsat analyzer or a Fyrite type combustion gas analyzer according to section 11.3.

NOTE: When using an Orsat analyzer, periodic Fyrite readings may be taken to verify/confirm the results obtained from the Orsat.

8.3 Multi-Point, Integrated Sampling Procedure.

8.3.1 Unless otherwise specified in an applicable regulation, or by the Administrator, a minimum of eight traverse points shall be used for circular stacks having diameters less than 0.61 m (24 in.), a minimum of nine shall be used for rectangular stacks having equivalent diameters less than 0.61 m (24 in.), and a minimum of 12 traverse points shall be used for all other cases. The traverse points shall be located according to Method 1.

8.3.2 Follow the procedures outlined in sections 8.2.2 through 8.2.4, except for the following: Traverse all sampling points, and sample at each point for an equal length of

time. Record sampling data as shown in Figure 3–3.

9.0 Quality Control

Section	Quality control measure	Effect
8.2	Use of Fyrite to confirm Orsat results	Ensures the accurate measurement of CO_2 and O_2.
10.1	Periodic audit of analyzer and operator technique.	Ensures that the analyzer is operating properly and that the operator performs the sampling procedure correctly and accurately.
11.3	Replicable analyses of integrated samples.	Minimizes experimental error.

10.0 Calibration and Standardization

10.1 Analyzer. The analyzer and analyzer operator's technique should be audited periodically as follows: take a sample from a manifold containing a known mixture of CO_2 and O_2, and analyze according to the procedure in section 11.3. Repeat this procedure until the measured concentration of three consecutive samples agrees with the stated value ±0.5 percent. If necessary, take corrective action, as specified in the analyzer users manual.

10.2 Rotameter. The rotameter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instruction.

11.0 Analytical Procedure

11.1 Maintenance. The Orsat or Fyrite-type analyzer should be maintained and operated according to the manufacturers specifications.

11.2 Grab Sample Analysis. Use either an Orsat analyzer or a Fyrite-type combustion gas analyzer to measure O_2 and CO_2 concentration for dry molecular weight determination, using procedures as specified in the analyzer user's manual. If an Orsat analyzer is used, it is recommended that the Orsat leak-check, described in section 11.5, be performed before this determination; however, the check is optional. Calculate the dry molecular weight as indicated in section 12.0. Repeat the sampling, analysis, and calculation procedures until the dry molecular weights of any three grab samples differ from their mean by no more than 0.3 g/g-mole (0.3 lb/lb-mole). Average these three molecular weights, and report the results to the nearest 0.1 g/g-mole (0.1 lb/lb-mole).

11.3 Integrated Sample Analysis. Use either an Orsat analyzer or a Fyrite-type combustion gas analyzer to measure O_2 and CO_2 concentration for dry molecular weight determination, using procedures as specified in the analyzer user's manual. If an Orsat analyzer is used, it is recommended that the Orsat leak-check, described in section 11.5, be performed before this determination; however, the check is optional. Calculate the dry molecular weight as indicated in section 12.0. Repeat the analysis and calculation procedures until the individual dry molecular weights for any three analyses differ from their mean by no more than 0.3 g/g-mole (0.3 lb/lb-mole). Average these three molecular weights, and report the results to the nearest 0.1 g/g-mole (0.1 lb/lb-mole).

11.4 Standardization. A periodic check of the reagents and of operator technique should be conducted at least once every three series of test runs as outlined in section 10.1.

11.5 Leak-Check Procedure for Orsat Analyzer. Moving an Orsat analyzer frequently causes it to leak. Therefore, an Orsat analyzer should be thoroughly leak-checked on site before the flue gas sample is introduced into it. The procedure for leak-checking an Orsat analyzer is as follows:

11.5.1 Bring the liquid level in each pipette up to the reference mark on the capillary tubing, and then close the pipette stopcock.

11.5.2 Raise the leveling bulb sufficiently to bring the confining liquid meniscus onto the graduated portion of the burette, and then close the manifold stopcock.

11.5.3 Record the meniscus position.

11.5.4 Observe the meniscus in the burette and the liquid level in the pipette for movement over the next 4 minutes.

11.5.5 For the Orsat analyzer to pass the leak-check, two conditions must be met:

11.5.5.1 The liquid level in each pipette must not fall below the bottom of the capillary tubing during this 4-minute interval.

11.5.5.2 The meniscus in the burette must not change by more than 0.2 ml during this 4-minute interval.

11.5.6 If the analyzer fails the leak-check procedure, check all rubber connections and stopcocks to determine whether they might be the cause of the leak. Disassemble, clean, and regrease any leaking stopcocks. Replace leaking rubber connections. After the analyzer is reassembled, repeat the leak-check procedure.

12.0 Calculations and Data Analysis

12.1 Nomenclature.

M_d = Dry molecular weight, g/g-mole (lb/lb-mole).
$\%CO_2$ = Percent CO_2 by volume, dry basis.
$\%O_2$ = Percent O_2 by volume, dry basis.
%CO = Percent CO by volume, dry basis.
$\%N_2$ = Percent N_2 by volume, dry basis.

0.280 = Molecular weight of N_2 or CO, divided by 100.
0.320 = Molecular weight of O_2 divided by 100.
0.440 = Molecular weight of CO_2 divided by 100.

12.2 Nitrogen, Carbon Monoxide Concentration. Determine the percentage of the gas that is N_2 and CO by subtracting the sum of the percent CO_2 and percent O_2 from 100 percent.

12.3 Dry Molecular Weight. Use Equation 3–1 to calculate the dry molecular weight of the stack gas.

$$M_d = 0.440(\%CO_2) + 0.320(\%O_2) + 0.280(\%N_2 + \%CO) \qquad \text{Eq. 3-1}$$

NOTE: The above Equation 3–1 does not consider the effect on calculated dry molecular weight of argon in the effluent gas. The concentration of argon, with a molecular weight of 39.9, in ambient air is about 0.9 percent. A negative error of approximately 0.4 percent is introduced. The tester may choose to include argon in the analysis using procedures subject to approval of the Administrator.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Altshuller, A.P. Storage of Gases and Vapors in Plastic Bags. International Journal of Air and Water Pollution. *6*:75–81. 1963.

2. Conner, William D. and J.S. Nader. Air Sampling with Plastic Bags. Journal of the American Industrial Hygiene Association. *25*:291–297. 1964.

3. Burrell Manual for Gas Analysts, Seventh edition. Burrell Corporation, 2223 Fifth Avenue, Pittsburgh, PA. 15219. 1951.

4. Mitchell, W.J. and M.R. Midgett. Field Reliability of the Orsat Analyzer. Journal of Air Pollution Control Association. *26*:491–495. May 1976.

5. Shigehara, R.T., R.M. Neulicht, and W.S. Smith. Validating Orsat Analysis Data from Fossil Fuel-Fired Units. Stack Sampling News. *4*(2):21–26. August 1976.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

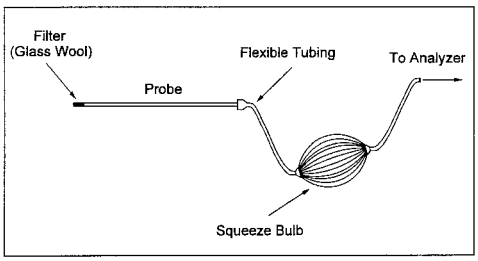


Figure 3-1. Grab-Sampling Train.

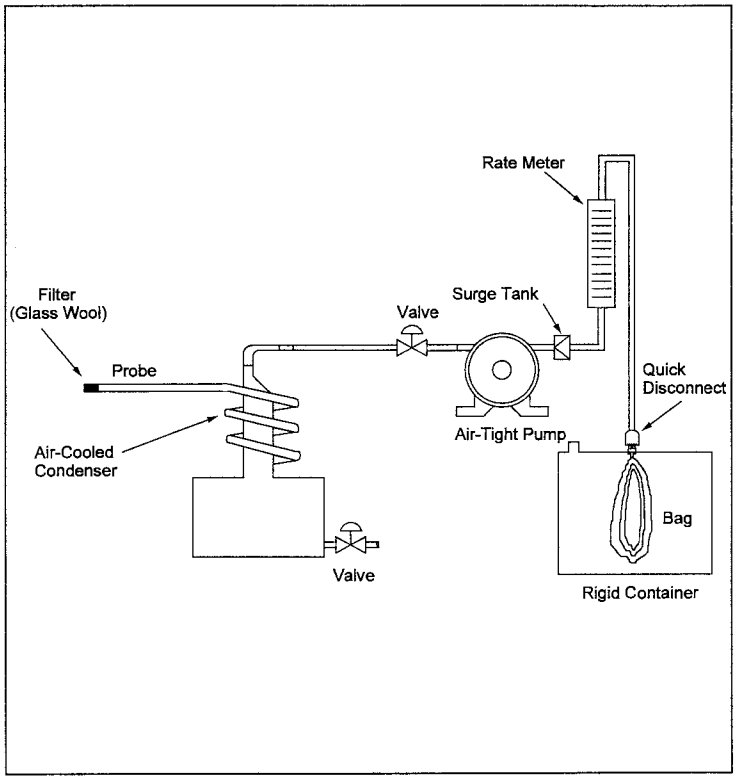


Figure 3-2. Integrated Gas-Sampling Train.

Time	Traverse point	Q (liter/min)	% Deviation [a]
Average			

[a] % Dev.=$[(Q - Q_{avg})/Q_{avg}] \times 100$ (Must be ≤±10%)

Figure 3–3. Sampling Rate Data

METHOD 3A—DETERMINATION OF OXYGEN AND CARBON DIOXIDE CONCENTRATIONS IN EMISSIONS FROM STATIONARY SOURCES (INSTRUMENTAL ANALYZER PROCEDURE)

1.0 Scope and Application

What is Method 3A?

Method 3A is a procedure for measuring oxygen (O_2) and carbon dioxide (CO_2) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis.

This method does not completely describe all equipment, supplies, and sampling and

analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 3—Gas Analysis for the Determination of Molecular Weight.

(c) Method 4—Determination of Moisture Content in Stack Gases.

(d) Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure).

1.1 *Analytes. What does this method determine?* This method measures the concentration of oxygen and carbon dioxide.

Analyte	CAS No.	Sensitivity
Oxygen (O_2)	7782–44–7	Typically <2% of Calibration Span.
Carbon dioxide (CO_2)	124–38–9	Typically <2% of Calibration Span.

1.2 *Applicability. When is this method required?* The use of Method 3A may be required by specific New Source Performance Standards, Clean Air Marketing rules, State Implementation Plans and permits, where measurements of O_2 and CO_2 concentrations in stationary source emissions must be made, either to determine compliance with an applicable emission standard or to conduct performance testing of a continuous emission monitoring system (CEMS). Other regulations may also require the use of Method 3A.

1.3 *Data Quality Objectives. How good must my collected data be?* Refer to section 1.3 of Method 7E.

2.0 Summary of Method

In this method, you continuously or intermittently sample the effluent gas and convey the sample to an analyzer that measures the concentration of O_2 or CO_2. You must meet the performance requirements of this method to validate your data.

3.0 Definitions

Refer to section 3.0 of Method 7E for the applicable definitions.

4.0 Interferences [Reserved]

5.0 Safety

Refer to section 5.0 of Method 7E.

6.0 Equipment and Supplies

Figure 7E–1 in Method 7E is a schematic diagram of an acceptable measurement system.

6.1 What do I need for the measurement system? The components of the measurement system are described (as applicable) in sections 6.1 and 6.2 of Method 7E, except that the analyzer described in section 6.2 of this method must be used instead of the analyzer described in Method 7E. You must follow the noted specifications in section 6.1 of Method 7E except that the requirements to use stainless steel, Teflon, or non-reactive glass filters do not apply. Also, a heated sample line is not required to transport dry gases or for systems that measure the O_2 or CO_2 concentration on a dry basis, provided that the system is not also being used to concurrently measure SO_2 and/or NO_X.

6.2 What analyzer must I use? You must use an analyzer that continuously measures O_2 or CO_2 in the gas stream and meets the specifications in section 13.0.

7.0 Reagents and Standards

7.1 *Calibration Gas.* What calibration gases do I need? Refer to Section 7.1 of Method 7E for the calibration gas requirements. Example calibration gas mixtures are listed below. Pre-cleaned or scrubbed air may be used for the O_2 high-calibration gas provided it does not contain other gases that interfere with the O_2 measurement.

(a) CO_2 in Nitrogen (N_2).

(b) CO_2/SO_2 gas mixture in N_2.

(c) O_2/SO_2 gas mixture in N_2.

(d) $O_2/CO_2/SO_2$ gas mixture in N_2.

(e) CO_2/NO_X gas mixture in N_2.

(f) $CO_2/SO_2/NO_X$ gas mixture in N_2.

The tests for analyzer calibration error and system bias require high-, mid-, and low-level gases.

7.2 Interference Check. What reagents do I need for the interference check? Potential interferences may vary among available analyzers. Table 7E–3 of Method 7E lists a number of gases that should be considered in conducting the interference test.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling Site and Sampling Points. You must follow the procedures of section 8.1 of Method 7E to determine the appropriate sampling points, unless you are using Method 3A only to determine the stack gas molecular weight and for no other purpose. In that case, you may use single-point integrated sampling as described in section 8.2.1 of Method 3. If the stratification test provisions in section 8.1.2 of Method 7E are used to reduce the number of required sampling points, the alternative acceptance criterion for 3-

point sampling will be ±0.5 percent CO_2 or O_2, and the alternative acceptance criterion for single-point sampling will be ±0.3 percent CO_2 or O_2. In that case, you may use single-point integrated sampling as described in section 8.2.1 of Method 3.

8.2 Initial Measurement System Performance Tests. You must follow the procedures in section 8.2 of Method 7E. If a dilution-type measurement system is used, the special considerations in section 8.3 of Method 7E apply.

8.3 Interference Check. The O_2 or CO_2 analyzer must be documented to show that interference effects to not exceed 2.5 percent of the calibration span. The interference test in section 8.2.7 of Method 7E is a procedure that may be used to show this. The effects of all potential interferences at the concentrations encountered during testing must be addressed and documented. This testing and documentation may be done by the instrument manufacturer.

8.4 Sample Collection. You must follow the procedures in section 8.4 of Method 7E.

8.5 Post-Run System Bias Check and Drift Assessment. You must follow the procedures in section 8.5 of Method 7E.

9.0 Quality Control

Follow quality control procedures in section 9.0 of Method 7E.

10.0 Calibration and Standardization

Follow the procedures for calibration and standardization in section 10.0 of Method 7E.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the applicable procedures for calculations and data analysis in section 12.0 of Method 7E, substituting percent O_2 and percent CO_2 for ppmv of NO_X as appropriate.

13.0 Method Performance

The specifications for the applicable performance checks are the same as in section 13.0 of Method 7E except for the alternative specifications for system bias, drift, and calibration error. In these alternative specifications, replace the term ''0.5 ppmv'' with the term ''0.5 percent O_2'' or ''0.5 percent CO_2'' (as applicable).

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures [Reserved]

17.0 References

1. ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards'' September 1997 as amended, EPA–600/R–97/121.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

Refer to section 18.0 of Method 7E.

Method 3B—Gas Analysis for the Determination of Emission Rate Correction Factor or Excess Air

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1 and 3.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Oxygen (O_2)	7782–44–7	2,000 ppmv.
Carbon Dioxide (CO_2)	124–38–9	2,000 ppmv.
Carbon Monoxide (CO)	630–08–0	N/A.

1.2 Applicability. This method is applicable for the determination of O_2, CO_2, and CO concentrations in the effluent from fossil-fuel combustion processes for use in excess air or emission rate correction factor calculations. Where compounds other than CO_2, O_2, CO, and nitrogen (N_2) are present in concentrations sufficient to affect the results, the calculation procedures presented in this method must be modified, subject to the approval of the Administrator.

1.3 Other methods, as well as modifications to the procedure described herein, are also applicable for all of the above determinations. Examples of specific methods and modifications include: (1) A multi-point sampling method using an Orsat analyzer to analyze individual grab samples obtained at each point, and (2) a method using CO_2 or O_2 and stoichiometric calculations to determine excess air. These methods and modifications may be used, but are subject to the approval of the Administrator.

1.4 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from a stack by one of the following methods: (1) Single-point, grab sampling; (2) single-point, integrated sampling; or (3) multi-point, integrated sampling. The gas sample is analyzed for percent CO_2, percent O_2, and, if necessary, percent CO using an Orsat combustion gas analyzer.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Several compounds can interfere, to varying degrees, with the results of Orsat analyses. Compounds that interfere with CO2 concentration measurement include acid gases (*e.g.*, sulfur dioxide, hydrogen chloride); compounds that interfere with O_2 concentration measurement include unsaturated hydrocarbons (*e.g.*, acetone, acetylene), nitrous oxide, and ammonia. Ammonia reacts chemically with the O_2 absorbing solution, and when present in the effluent gas stream must be removed before analysis.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. A typical Orsat analyzer requires four reagents: a gas-confining solution, CO_2 absorbent, O_2 absorbent, and CO absorbent. These reagents may contain potassium hydroxide, sodium hydroxide, cuprous chloride, cuprous sulfate, alkaline pyrogallic acid, and/or chromous chloride. Follow manufacturer's operating instructions and observe all warning labels for reagent use.

6.0 Equipment and Supplies

NOTE: As an alternative to the sampling apparatus and systems described herein, other sampling systems (*e.g.*, liquid displacement) may be used, provided such systems are capable of obtaining a representative sample and maintaining a constant sampling rate, and are, otherwise, capable of yielding acceptable results. Use of such systems is subject to the approval of the Administrator.

6.1 Grab Sampling and Integrated Sampling. Same as in sections 6.1 and 6.2, respectively for Method 3.

6.2 Analysis. An Orsat analyzer only. For low CO_2 (less than 4.0 percent) or high O_2 (greater than 15.0 percent) concentrations, the measuring burette of the Orsat must have at least 0.1 percent subdivisions. For Orsat maintenance and operation procedures, follow the instructions recommended by the manufacturer, unless otherwise specified herein.

7.0 Reagents and Standards

7.1 Reagents. Same as in Method 3, section 7.1.

7.2 Standards. Same as in Method 3, section 7.2.

8.0 Sample Collection, Preservation, Storage, and Transport

NOTE: Each of the three procedures below shall be used only when specified in an applicable subpart of the standards. The use of these procedures for other purposes must have specific prior approval of the Administrator. A Fyrite-type combustion gas analyzer is not acceptable for excess air or emission rate correction factor determinations, unless approved by the Administrator. If both percent CO_2 and percent O_2 are measured, the analytical results of any of the three procedures given below may also be used for calculating the dry molecular weight (see Method 3).

8.1 Single-Point, Grab Sampling and Analytical Procedure.

8.1.1 The sampling point in the duct shall either be at the centroid of the cross section or at a point no closer to the walls than 1.0 m (3.3 ft), unless otherwise specified by the Administrator.

8.1.2 Set up the equipment as shown in Figure 3–1 of Method 3, making sure all connections ahead of the analyzer are tight. Leak-check the Orsat analyzer according to the procedure described in section 11.5 of Method 3. This leak-check is mandatory.

8.1.3 Place the probe in the stack, with the tip of the probe positioned at the sampling point; purge the sampling line long enough to allow at least five exchanges. Draw a sample into the analyzer. For emission rate correction factor determinations, immediately analyze the sample for percent CO_2 or percent O_2, as outlined in section 11.2. For excess air determination, immediately analyze the sample for percent CO_2, O_2, and CO, as outlined in section 11.2, and calculate excess air as outlined in section 12.2.

8.1.4 After the analysis is completed, leak-check (mandatory) the Orsat analyzer once again, as described in section 11.5 of Method 3. For the results of the analysis to be valid, the Orsat analyzer must pass this leak-test before and after the analysis.

8.2 Single-Point, Integrated Sampling and Analytical Procedure.

8.2.1 The sampling point in the duct shall be located as specified in section 8.1.1.

8.2.2 Leak-check (mandatory) the flexible bag as in section 6.2.6 of Method 3. Set up the equipment as shown in Figure 3–2 of Method 3. Just before sampling, leak-check (mandatory) the train by placing a vacuum gauge at the condenser inlet, pulling a vacuum of at least 250 mm Hg (10 in. Hg), plugging the outlet at the quick disconnect, and then turning off the pump. The vacuum should remain stable for at least 0.5 minute. Evacuate the flexible bag. Connect the probe, and place it in the stack, with the tip of the probe positioned at the sampling point; purge the sampling line. Next, connect the bag, and make sure that all connections are tight.

8.2.3 Sample at a constant rate, or as specified by the Administrator. The sampling run must be simultaneous with, and for the same total length of time as, the pollutant emission rate determination. Collect at least 28 liters (1.0 ft^3) of sample gas. Smaller volumes may be collected, subject to approval of the Administrator.

8.2.4 Obtain one integrated flue gas sample during each pollutant emission rate determination. For emission rate correction factor determination, analyze the sample within 4 hours after it is taken for percent CO_2 or percent O_2 (as outlined in section 11.2).

8.3 Multi-Point, Integrated Sampling and Analytical Procedure.

8.3.1 Unless otherwise specified in an applicable regulation, or by the Administrator, a minimum of eight traverse points shall be used for circular stacks having diameters less than 0.61 m (24 in.), a minimum of nine shall be used for rectangular stacks having equivalent diameters less than 0.61 m (24 in.), and a minimum of 12 traverse points shall be used for all other cases. The traverse points shall be located according to Method 1.

8.3.2 Follow the procedures outlined in sections 8.2.2 through 8.2.4, except for the following: Traverse all sampling points, and sample at each point for an equal length of time. Record sampling data as shown in Figure 3–3 of Method 3.

9.0 Quality Control

9.1 Data Validation Using Fuel Factor. Although in most instances, only CO_2 or O_2 measurement is required, it is recommended that both CO_2 and O_2 be measured to provide a check on the quality of the data. The data validation procedure of section 12.3 is suggested.

NOTE: Since this method for validating the CO_2 and O_2 analyses is based on combustion of organic and fossil fuels and dilution of the gas stream with air, this method does not apply to sources that (1) remove CO_2 or O_2 through processes other than combustion, (2) add O_2 (*e.g.*, oxygen enrichment) and N_2 in proportions different from that of air, (3) add CO_2 (*e.g.*, cement or lime kilns), or (4) have no fuel factor, F_O, values obtainable (*e.g.*, extremely variable waste mixtures). This method validates the measured proportions of CO_2 and O_2 for fuel type, but the method does not detect sample dilution resulting from leaks during or after sample collection. The method is applicable for samples collected downstream of most lime or limestone flue-gas desulfurization units as the CO_2 added or removed from the gas stream is not significant in relation to the total CO_2 concentration. The CO_2 concentrations from other types of scrubbers using only water or basic slurry can be significantly affected and would render the fuel factor check minimally useful.

10.0 Calibration and Standardization

10.1 Analyzer. The analyzer and analyzer operator technique should be audited periodically as follows: take a sample from a manifold containing a known mixture of CO_2 and O_2, and analyze according to the procedure in section 11.3. Repeat this procedure until the measured concentration of three consecutive samples agrees with the stated value ±0.5 percent. If necessary, take corrective action, as specified in the analyzer users manual.

10.2 Rotameter. The rotameter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instruction.

11.0 Analytical Procedure

11.1 Maintenance. The Orsat analyzer should be maintained according to the manufacturers specifications.

11.2 Grab Sample Analysis. To ensure complete absorption of the CO_2, O_2, or if applicable, CO, make repeated passes through each absorbing solution until two consecutive readings are the same. Several passes (three or four) should be made between readings. (If constant readings cannot be obtained after three consecutive readings, replace the absorbing solution.) Although in most cases, only CO_2 or O_2 concentration is required, it is recommended that both CO_2 and O_2 be measured, and that the procedure in section 12.3 be used to validate the analytical data.

NOTE: Since this single-point, grab sampling and analytical procedure is normally conducted in conjunction with a single-point, grab sampling and analytical procedure for a pollutant, only one analysis is ordinarily conducted. Therefore, great care must be taken to obtain a valid sample and analysis.

11.3 Integrated Sample Analysis. The Orsat analyzer must be leak-checked (see section 11.5 of Method 3) before the analysis. If excess air is desired, proceed as follows: (1) within 4 hours after the sample is taken, analyze it (as in sections 11.3.1 through

11.3.3) for percent CO_2, O_2, and CO; (2) determine the percentage of the gas that is N_2 by subtracting the sum of the percent CO_2, percent O_2, and percent CO from 100 percent; and (3) calculate percent excess air, as outlined in section 12.2.

11.3.1 To ensure complete absorption of the CO_2, O_2, or if applicable, CO, follow the procedure described in section 11.2.

NOTE: Although in most instances only CO_2 or O_2 is required, it is recommended that both CO_2 and O_2 be measured, and that the procedures in section 12.3 be used to validate the analytical data.

11.3.2 Repeat the analysis until the following criteria are met:

11.3.2.1 For percent CO_2, repeat the analytical procedure until the results of any three analyses differ by no more than (a) 0.3 percent by volume when CO_2 is greater than 4.0 percent or (b) 0.2 percent by volume when CO_2 is less than or equal to 4.0 percent. Average three acceptable values of percent CO_2, and report the results to the nearest 0.2 percent.

11.3.2.2 For percent O_2, repeat the analytical procedure until the results of any three analyses differ by no more than (a) 0.3 percent by volume when O_2 is less than 15.0 percent or (b) 0.2 percent by volume when O_2 is greater than or equal to 15.0 percent. Average the three acceptable values of percent O_2, and report the results to the nearest 0.1 percent.

11.3.2.3 For percent CO, repeat the analytical procedure until the results of any three analyses differ by no more than 0.3 percent. Average the three acceptable values of percent CO, and report the results to the nearest 0.1 percent.

11.3.3 After the analysis is completed, leak-check (mandatory) the Orsat analyzer once again, as described in section 11.5 of Method 3. For the results of the analysis to be valid, the Orsat analyzer must pass this leak-test before and after the analysis.

11.4 Standardization. A periodic check of the reagents and of operator technique should be conducted at least once every three series of test runs as indicated in section 10.1.

12.0 Calculations and Data Analysis

12.1 Nomenclature. Same as section 12.1 of Method 3 with the addition of the following:
%EA = Percent excess air.
0.264 = Ratio of O_2 to N_2 in air, v/v.

12.2 Percent Excess Air. Determine the percentage of the gas that is N_2 by subtracting the sum of the percent CO_2, percent CO, and percent O_2 from 100 percent. Calculate the percent excess air (if applicable) by substituting the appropriate values of percent O_2, CO, and N_2 into Equation 3B–1.

$$\%EA = \frac{\%O_2 - 0.5\ \%CO}{0.264\ \%N_2 - (\%O_2 - 0.5\ \%CO)} \times 100 \qquad \text{Eq. 3B-1}$$

NOTE: The equation above assumes that ambient air is used as the source of O_2 and that the fuel does not contain appreciable amounts of N_2 (as do coke oven or blast furnace gases). For those cases when appreciable amounts of N_2 are present (coal, oil, and natural gas do not contain appreciable amounts of N_2) or when oxygen enrichment is used, alternative methods, subject to approval of the Administrator, are required.

12.3 Data Validation When Both CO_2 and O_2 Are Measured.

12.3.1 Fuel Factor, F_o. Calculate the fuel factor (if applicable) using Equation 3B–2:

$$F_o = \frac{20.9 - \%O_2}{\%CO_2} \qquad \text{Eq. 3B-2}$$

Where:

$\%O_2$ = Percent O_2 by volume, dry basis.
$\%CO_2$ = Percent CO_2 by volume, dry basis.
20.9 = Percent O_2 by volume in ambient air.

If CO is present in quantities measurable by this method, adjust the O_2 and CO_2 values using Equations 3B–3 and 3B–4 before performing the calculation for F_o:

$$\%CO_2(\text{adj}) = \%CO_2 + \%CO \qquad \text{Eq. 3B-3}$$

$$\%O_2(\text{adj}) = \%O_2 - 0.5\ \%CO \qquad \text{Eq. 3B-4}$$

Where:
%CO = Percent CO by volume, dry basis.

12.3.2 Compare the calculated F_o factor with the expected F_o values. Table 3B–1 in section 17.0 may be used in establishing acceptable ranges for the expected F_o if the fuel being burned is known. When fuels are burned in combinations, calculate the combined fuel F_d and F_c factors (as defined in Method 19, section 12.2) according to the procedure in Method 19, sections 12.2 and 12.3. Then calculate the F_o factor according to Equation 3B–5.

$$F_o = \frac{0.209\ F_d}{F_c} \qquad \text{Eq. 3B-5}$$

12.3.3 Calculated F_o values, beyond the acceptable ranges shown in this table, should be investigated before accepting the test results. For example, the strength of the solutions in the gas analyzer and the analyzing technique should be checked by sampling and analyzing a known concentration, such as air; the fuel factor should be reviewed and verified. An acceptability range of ±12 percent is appropriate for the F_o factor of mixed fuels with variable fuel ratios. The level of the emission rate relative to the compliance level should be considered in determining if a retest is appropriate; i.e., if the measured emissions are much lower or much greater than the compliance limit, repetition of the test would not significantly change the compliance status of the source and would be unnecessarily time consuming and costly.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 3, section 16.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 3B–1—F_o FACTORS FOR SELECTED FUELS

Fuel type	F_o range
Coal:	
Anthracite and lignite	1.016–1.130
Bituminous	1.083–1.230
Oil:	
Distillate	1.260–1.413
Residual	1.210–1.370
Gas:	
Natural	1.600–1.836
Propane	1.434–1.586
Butane	1.405–1.553
Wood	1.000–1.120
Wood bark	1.003–1.130

METHOD 3C—DETERMINATION OF CARBON DIOXIDE, METHANE, NITROGEN, AND OXYGEN FROM STATIONARY SOURCES

1. Applicability and Principle

1.1 Applicability. This method applies to the analysis of carbon dioxide (CO_2), methane (CH_4), nitrogen (N_2), and oxygen (O_2) in samples from municipal solid waste landfills and other sources when specified in an applicable subpart.

1.2 Principle. A portion of the sample is injected into a gas chromatograph (GC) and the CO_2, CH_4, N_2, and O_2 concentrations are determined by using a thermal conductivity detector (TCD) and integrator.

2. Range and Sensitivity

2.1 Range. The range of this method depends upon the concentration of samples. The analytical range of TCD's is generally between approximately 10 ppmv and the upper percent range.

2.2 Sensitivity. The sensitivity limit for a compound is defined as the minimum detectable concentration of that compound, or the concentration that produces a signal-to-noise ratio of three to one. For CO_2, CH_4, N_2, and O_2, the sensitivity limit is in the low ppmv range.

3. Interferences

Since the TCD exhibits universal response and detects all gas components except the carrier, interferences may occur. Choosing the appropriate GC or shifting the retention times by changing the column flow rate may help to eliminate resolution interferences.

To assure consistent detector response, helium is used to prepare calibration gases. Frequent exposure to samples or carrier gas containing oxygen may gradually destroy filaments.

4. Apparatus

4.1 Gas Chromatograph. GC having at least the following components:

4.1.1 Separation Column. Appropriate column(s) to resolve CO_2, CH_4, N_2, O_2, and other gas components that may be present in the sample.

4.1.2 Sample Loop. Teflon or stainless steel tubing of the appropriate diameter.

NOTE: Mention of trade names or specific products does not constitute endorsement or recommendation by the U. S. Environmental Protection Agency.

4.1.3 Conditioning System. To maintain the column and sample loop at constant temperature.

4.1.4 Thermal Conductivity Detector.

4.2 Recorder. Recorder with linear strip chart. Electronic integrator (optional) is recommended.

4.3 Teflon Tubing. Diameter and length determined by connection requirements of cylinder regulators and the GC.

4.4 Regulators. To control gas cylinder pressures and flow rates.

4.5 Adsorption Tubes. Applicable traps to remove any O_2 from the carrier gas.

5. Reagents

5.1 Calibration and Linearity Gases. Standard cylinder gas mixtures for each compound of interest with at least three concentration levels spanning the range of suspected sample concentrations. The calibration gases shall be prepared in helium.

5.2 Carrier Gas. Helium, high-purity.

6. Analysis

6.1 Sample Collection. Use the sample collection procedures described in Methods 3 or 25C to collect a sample of landfill gas (LFG).

6.2 Preparation of GC. Before putting the GC analyzer into routine operation, optimize the operational conditions according to the manufacturer's specifications to provide good resolution and minimum analysis time. Establish the appropriate carrier gas flow and set the detector sample and reference cell flow rates at exactly the same levels. Adjust the column and detector temperatures to the recommended levels. Allow sufficient time for temperature stabilization. This may typically require 1 hour for each change in temperature.

6.3 Analyzer Linearity Check and Calibration. Perform this test before sample analysis.

6.3.1 Using the gas mixtures in section 5.1, verify the detector linearity over the range of suspected sample concentrations with at least three concentrations per compound of interest. This initial check may also serve as the initial instrument calibration.

6.3.2 You may extend the use of the analyzer calibration by performing a single-point calibration verification. Calibration verifications shall be performed by triplicate injections of a single-point standard gas. The concentration of the single-point calibration must either be at the midpoint of the calibration curve or at approximately the source emission concentration measured during operation of the analyzer.

6.3.3 Triplicate injections must agree within 5 percent of their mean, and the average calibration verification point must agree within 10 percent of the initial calibration response factor. If these calibration verification criteria are not met, the initial calibration described in section 6.3.1, using at least three concentrations, must be repeated before analysis of samples can continue.

6.3.4 For each instrument calibration, record the carrier and detector flow rates, detector filament and block temperatures, attenuation factor, injection time, chart speed, sample loop volume, and component concentrations.

6.3.5 Plot a linear regression of the standard concentrations versus area values to obtain the response factor of each compound. Alternatively, response factors of uncorrected component concentrations (wet basis) may be generated using instrumental integration.

NOTE: Peak height may be used instead of peak area throughout this method.

6.4 Sample Analysis. Purge the sample loop with sample, and allow to come to atmospheric pressure before each injection. Analyze each sample in duplicate, and calculate the average sample area (A). The results are acceptable when the peak areas for two consecutive injections agree within 5 percent of their average. If they do not agree, run additional samples until consistent area data are obtained. Determine the tank sample concentrations according to section 7.2.

7. Calculations

Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off results only after the final calculation.

7.1 Nomenclature.

B_w = Moisture content in the sample, fraction.

C_{N2} = Measured N_2 concentration (by Method 3C), fraction.

C_{N2Corr} = Measured N_2 concentration corrected only for dilution, fraction.

C_t = Calculated NMOC concentration, ppmv C equivalent.

C_{tm} = Measured NMOC concentration, ppmv C equivalent.

P_b = Barometric pressure, mm Hg.

P_t = Gas sample tank pressure after sampling, but before pressurizing, mm Hg absolute.

P_{tf} = Final gas sample tank pressure after pressurizing, mm Hg absolute.

P_{ti} = Gas sample tank pressure after evacuation, mm Hg absolute.

P_w = Vapor pressure of H_2O (from Table 25C–1), mm Hg.

r = Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 . . . r).

R = Mean calibration response factor for specific sample component, area/ppm.

T_t = Sample tank temperature at completion of sampling, °K.

T_{ti} = Sample tank temperature before sampling, °K.

T_{tf} = Sample tank temperature after pressurizing, °K.

7.2 Concentration of Sample Components. Calculate C for each compound using Equations 3C–1 and 3C–2. Use the temperature and barometric pressure at the sampling site to calculate Bw. If the sample was diluted with helium using the procedures in Method 25C, use Equation 3C–3 to calculate the concentration.

$$B_w = \frac{P_w}{P_{bar}} \qquad 3C\text{-}1$$

$$C = \frac{A}{R(1-B_w)} \qquad 3C\text{-}2$$

$$C = \frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}} \quad \frac{A}{R(1-B_w)} \qquad 3C\text{-}3$$

7.3 Measured N_2 Concentration Correction. Calculate the reported N_2 correction for Method 25–C using Eq. 3C–4. If oxygen is determined in place of N_2, substitute the oxygen concentration for the nitrogen concentration in the equation.

$$C_{N_2 Corr} = \frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}}(C_{N_2}) \quad Eq.\ 3C-4$$

8. Bibliography

1. McNair, H.M., and E.J. Bonnelli. Basic Gas Chromatography. Consolidated Printers, Berkeley, CA. 1969.

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–2 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

APPENDIX A–3 TO PART 60—TEST METHODS 4 THROUGH 5I

Method 4—Determination of moisture content in stack gases
Method 5—Determination of particulate matter emissions from stationary sources
Method 5A—Determination of particulate matter emissions from the asphalt processing and asphalt roofing industry
Method 5B—Determination of nonsulfuric acid particulate matter emissions from stationary sources
Method 5C [Reserved]
Method 5D—Determination of particulate matter emissions from positive pressure fabric filters
Method 5E—Determination of particulate matter emissions from the wool fiberglass insulation manufacturing industry
Method 5F—Determination of nonsulfate particulate matter emissions from stationary sources
Method 5G—Determination of particulate matter emissions from wood heaters (dilution tunnel sampling location)
Method 5H—Determination of particulate emissions from wood heaters from a stack location
Method 5I—Determination of Low Level Particulate Matter Emissions From Stationary Sources

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference

$$B_w = \frac{P_w}{P_{bar}} \qquad 3C\text{-}1$$

$$C = \frac{A}{R(1-B_w)} \qquad 3C\text{-}2$$

$$C = \frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}} \quad \frac{A}{R(1-B_w)} \qquad 3C\text{-}3$$

7.3 Measured N_2 Concentration Correction. Calculate the reported N_2 correction for Method 25–C using Eq. 3C–4. If oxygen is determined in place of N_2, substitute the oxygen concentration for the nitrogen concentration in the equation.

$$C_{N_2 Corr} = \frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}}(C_{N_2}) \quad Eq.\ 3C-4$$

8. Bibliography

1. McNair, H.M., and E.J. Bonnelli. Basic Gas Chromatography. Consolidated Printers, Berkeley, CA. 1969.

[36 FR 24877, Dec. 23, 1971]

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APPENDIX A–3 TO PART 60—TEST METHODS 4 THROUGH 5I

Method 4—Determination of moisture content in stack gases
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Method 5B—Determination of nonsulfuric acid particulate matter emissions from stationary sources
Method 5C [Reserved]
Method 5D—Determination of particulate matter emissions from positive pressure fabric filters
Method 5E—Determination of particulate matter emissions from the wool fiberglass insulation manufacturing industry
Method 5F—Determination of nonsulfate particulate matter emissions from stationary sources
Method 5G—Determination of particulate matter emissions from wood heaters (dilution tunnel sampling location)
Method 5H—Determination of particulate emissions from wood heaters from a stack location
Method 5I—Determination of Low Level Particulate Matter Emissions From Stationary Sources

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference

method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

METHOD 4—DETERMINATION OF MOISTURE CONTENT IN STACK GASES

NOTE: This method does not include all the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 5, and Method 6.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Water vapor (H_2O) ...	7732–18–5	N/A

1.2 Applicability. This method is applicable for the determination of the moisture content of stack gas.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted at a constant rate from the source; moisture is removed from the sample stream and determined either volumetrically or gravimetrically.

2.2 The method contains two possible procedures: a reference method and an approximation method.

2.2.1 The reference method is used for accurate determinations of moisture content (such as are needed to calculate emission data). The approximation method, provides estimates of percent moisture to aid in setting isokinetic sampling rates prior to a pollutant emission measurement run. The approximation method described herein is only a suggested approach; alternative means for approximating the moisture content (*e.g.*, drying tubes, wet bulb-dry bulb techniques, condensation techniques, stoichiometric calculations, previous experience, etc.) are also acceptable.

2.2.2 The reference method is often conducted simultaneously with a pollutant emission measurement run. When it is, calculation of percent isokinetic, pollutant emission rate, etc., for the run shall be based upon the results of the reference method or its equivalent. These calculations shall not

be based upon the results of the approximation method, unless the approximation method is shown, to the satisfaction of the Administrator, to be capable of yielding results within one percent H_2O of the reference method.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 The moisture content of saturated gas streams or streams that contain water droplets, as measured by the reference method, may be positively biased. Therefore, when these conditions exist or are suspected, a second determination of the moisture content shall be made simultaneously with the reference method, as follows: Assume that the gas stream is saturated. Attach a temperature sensor [capable of measuring to ±1 °C (2 °F)] to the reference method probe. Measure the stack gas temperature at each traverse point (see section 8.1.1.1) during the reference method traverse, and calculate the average stack gas temperature. Next, determine the moisture percentage, either by: (1) Using a psychrometric chart and making appropriate corrections if the stack pressure is different from that of the chart, or (2) using saturation vapor pressure tables. In cases where the psychrometric chart or the saturation vapor pressure tables are not applicable (based on evaluation of the process), alternative methods, subject to the approval of the Administrator, shall be used.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Reference Method. A schematic of the sampling train used in this reference method is shown in Figure 4–1.

6.1.1 Probe. Stainless steel or glass tubing, sufficiently heated to prevent water condensation, and equipped with a filter, either in-stack (*e.g.*, a plug of glass wool inserted into the end of the probe) or heated out-of-stack (*e.g.*, as described in Method 5), to remove particulate matter. When stack conditions permit, other metals or plastic tubing may be used for the probe, subject to the approval of the Administrator.

6.1.2 Condenser. Same as Method 5, section 6.1.1.8.

6.1.3 Cooling System. An ice bath container, crushed ice, and water (or equivalent), to aid in condensing moisture.

6.1.4 Metering System. Same as in Method 5, section 6.1.1.9, except do not use sampling systems designed for flow rates higher than 0.0283 m^3/min (1.0 cfm). Other metering systems, capable of maintaining a constant sampling rate to within 10 percent and determining sample gas volume to within 2 percent, may be used, subject to the approval of the Administrator.

6.1.5 Barometer and Graduated Cylinder and/or Balance. Same as Method 5, sections 6.1.2 and 6.2.5, respectively.

6.2. Approximation Method. A schematic of the sampling train used in this approximation method is shown in Figure 4–2.

6.2.1 Probe. Same as section 6.1.1.

6.2.2 Condenser. Two midget impingers, each with 30-ml capacity, or equivalent.

6.2.3 Cooling System. Ice bath container, crushed ice, and water, to aid in condensing moisture in impingers.

6.2.4 Drying Tube. Tube packed with new or regenerated 6- to 16-mesh indicating-type silica gel (or equivalent desiccant), to dry the sample gas and to protect the meter and pump.

6.2.5 Valve. Needle valve, to regulate the sample gas flow rate.

6.2.6 Pump. Leak-free, diaphragm type, or equivalent, to pull the gas sample through the train.

6.2.7 Volume Meter. Dry gas meter, sufficiently accurate to measure the sample volume to within 2 percent, and calibrated over the range of flow rates and conditions actually encountered during sampling.

6.2.8 Rate Meter. Rotameter, or equivalent, to measure the flow range from 0 to 3 liters/min (0 to 0.11 cfm).

6.2.9 Graduated Cylinder. 25-ml.

6.2.10 Barometer. Same as Method 5, section 6.1.2.

6.2.11 Vacuum Gauge. At least 760-mm (30-in.) Hg gauge, to be used for the sampling leak check.

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Reference Method. The following procedure is intended for a condenser system (such as the impinger system described in section 6.1.1.8 of Method 5) incorporating volumetric analysis to measure the condensed moisture, and silica gel and gravimetric analysis to measure the moisture leaving the condenser.

8.1.1 Preliminary Determinations.

8.1.1.1 Unless otherwise specified by the Administrator, a minimum of eight traverse points shall be used for circular stacks having diameters less than 0.61 m (24 in.), a minimum of nine points shall be used for rectangular stacks having equivalent diameters less than 0.61 m (24 in.), and a minimum of twelve traverse points shall be used in all

other cases. The traverse points shall be located according to Method 1. The use of fewer points is subject to the approval of the Administrator. Select a suitable probe and probe length such that all traverse points can be sampled. Consider sampling from opposite sides of the stack (four total sampling ports) for large stacks, to permit use of shorter probe lengths. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

8.1.1.2 Select a total sampling time such that a minimum total gas volume of 0.60 scm (21 scf) will be collected, at a rate no greater than 0.021 m^3/min (0.75 cfm). When both moisture content and pollutant emission rate are to be determined, the moisture determination shall be simultaneous with, and for the same total length of time as, the pollutant emission rate run, unless otherwise specified in an applicable subpart of the standards.

8.1.2 Preparation of Sampling Train.

8.1.2.1 Place known volumes of water in the first two impingers; alternatively, transfer water into the first two impingers and record the weight of each impinger (plus water) to the nearest 0.5 g. Weigh and record the weight of the silica gel to the nearest 0.5 g, and transfer the silica gel to the fourth impinger; alternatively, the silica gel may first be transferred to the impinger, and the weight of the silica gel plus impinger recorded.

8.1.2.2 Set up the sampling train as shown in Figure 4–1. Turn on the probe heater and (if applicable) the filter heating system to temperatures of approximately 120 °C (248 °F), to prevent water condensation ahead of the condenser. Allow time for the temperatures to stabilize. Place crushed ice and water in the ice bath container.

8.1.3 Leak Check Procedures. It is recommended, but not required, that the volume metering system and sampling train be leak-checked as follows:

8.1.3.1 Metering System. Same as Method 5, section 8.4.1.

8.1.3.2 Sampling Train. Disconnect the probe from the first impinger or (if applicable) from the filter holder. Plug the inlet to the first impinger (or filter holder), and pull a 380 mm (15 in.) Hg vacuum. A lower vacuum may be used, provided that it is not exceeded during the test. A leakage rate in excess of 4 percent of the average sampling rate or 0.00057 m^3/min (0.020 cfm), whichever is less, is unacceptable. Following the leak check, reconnect the probe to the sampling train.

8.1.4 Sampling Train Operation. During the sampling run, maintain a sampling rate within 10 percent of constant rate, or as specified by the Administrator. For each run, record the data required on a data sheet similar to that shown in Figure 4–3. Be sure to record the dry gas meter reading at the beginning and end of each sampling time increment and whenever sampling is halted. Take other appropriate readings at each sample point at least once during each time increment.

NOTE: When Method 4 is used concurrently with an isokinetic method (*e.g.*, Method 5) the sampling rate should be maintained at isokinetic conditions rather than 10 percent of constant rate.

8.1.4.1 To begin sampling, position the probe tip at the first traverse point. Immediately start the pump, and adjust the flow to the desired rate. Traverse the cross section, sampling at each traverse point for an equal length of time. Add more ice and, if necessary, salt to maintain a temperature of less than 20 °C (68 °F) at the silica gel outlet.

8.1.4.2 After collecting the sample, disconnect the probe from the first impinger (or from the filter holder), and conduct a leak check (mandatory) of the sampling train as described in section 8.1.3.2. Record the leak rate. If the leakage rate exceeds the allowable rate, either reject the test results or correct the sample volume as in section 12.3 of Method 5.

8.2 Approximation Method.

NOTE: The approximation method described below is presented only as a suggested method (see section 2.0).

8.2.1 Place exactly 5 ml water in each impinger. Leak check the sampling train as follows: Temporarily insert a vacuum gauge at or near the probe inlet. Then, plug the probe inlet and pull a vacuum of at least 250 mm (10 in.) Hg. Note the time rate of change of the dry gas meter dial; alternatively, a rotameter (0 to 40 ml/min) may be temporarily attached to the dry gas meter outlet to determine the leakage rate. A leak rate not in excess of 2 percent of the average sampling rate is acceptable.

NOTE: Release the probe inlet plug slowly before turning off the pump.

8.2.2 Connect the probe, insert it into the stack, and sample at a constant rate of 2 liters/min (0.071 cfm). Continue sampling until the dry gas meter registers about 30 liters (1.1 ft^3) or until visible liquid droplets are carried over from the first impinger to the second. Record temperature, pressure, and dry gas meter readings as indicated by Figure 4–4.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
Section 8.1.1.4	Leak rate of the sampling system cannot exceed four percent of the average sampling rate or 0.00057 m^3/min (0.020 cfm).	Ensures the accuracy of the volume of gas sampled. (Reference Method).
Section 8.2.1	Leak rate of the sampling system cannot exceed two percent of the average sampling rate.	Ensures the accuracy of the volume of gas sampled. (Approximation Method).

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Reference Method. Calibrate the metering system, temperature sensors, and barometer according to Method 5, sections 10.3, 10.5, and 10.6, respectively.

10.2 Approximation Method. Calibrate the metering system and the barometer according to Method 6, section 10.1 and Method 5, section 10.6, respectively.

10.3 Field Balance Calibration Check. Check the calibration of the balance used to weigh impingers with a weight that is at least 500g or within 50g of a loaded impinger. The weight must be ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference-see 40 CFR 60.17) Class 6 (or better). Daily, before use, the field balance must measure the weight within ± 0.5g of the certified mass. If the daily balance calibration check fails, perform corrective measures and repeat the check before using balance.

11.0 Analytical Procedure

11.1 Reference Method. Measure the volume of the moisture condensed in each of the impingers to the nearest ml. Alternatively, if the impingers were weighed prior to sampling, weigh the impingers after sampling and record the difference in weight to the nearest 0.5 g. Determine the increase in weight of the silica gel (or silica gel plus impinger) to the nearest 0.5 g. Record this information (see example data sheet, Figure 4–5), and calculate the moisture content, as described in section 12.0.

11.2 Approximation Method. Combine the contents of the two impingers, and measure the volume to the nearest 0.5 ml.

12.0 Data Analysis and Calculations

Carry out the following calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Reference Method.

12.1.1 Nomenclature.

B_{ws} = Proportion of water vapor, by volume, in the gas stream.

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P_m = Absolute pressure (for this method, same as barometric pressure) at the dry gas meter, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 (mm Hg)(m^3)/(g-mole)(°K) for metric units and 21.85 (in. Hg)(ft^3)/(lb-mole)(°R) for English units.

T_m = Absolute temperature at meter, °K (°R).

T_{std} = Standard absolute temperature, 293 °K (528 °R).

V_f = Final volume of condenser water, ml.

V_i = Initial volume, if any, of condenser water, ml.

V_m = Dry gas volume measured by dry gas meter, dcm (dcf).

$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

$V_{wc(std)}$ = Volume of water vapor condensed, corrected to standard conditions, scm (scf).

$V_{wsg(std)}$ = Volume of water vapor collected in silica gel, corrected to standard conditions, scm (scf).

W_f = Final weight of silica gel or silica gel plus impinger, g.

W_i = Initial weight of silica gel or silica gel plus impinger, g.

Y = Dry gas meter calibration factor.

ΔV_m = Incremental dry gas volume measured by dry gas meter at each traverse point, dcm (dcf).

ρ_w = Density of water, 0.9982 g/ml (0.002201 lb/ml).

12.1.2 Volume of Water Vapor Condensed.

$$V_{wc(std)} = \frac{(V_f - V_i)\,\rho_w R\,T_{std}}{P_{std} M_W} = K_1 (V_f - V_i) \qquad \text{Eq. 4-1}$$

Where:

K_1 = 0.001333 m^3/ml for metric units,
= 0.04706 ft^3/ml for English units.

12.1.3 Volume of Water Collected in Silica Gel.

$$V_{wsg(std)} = \frac{(W_f - W_i)\,R\,T_{std}}{P_{std} M_W K_2} = K_3 (W_f - W_i) \qquad \text{Eq. 4-2}$$

Where:

K_2 = 1.0 g/g for metric units,
= 453.6 g/lb for English units.
K_3 = 0.001335 m^3/g for metric units,
= 0.04715 ft^3/g for English units.

12.1.4 Sample Gas Volume.

$$V_{m(std)} = \frac{V_m\ Y\ P_m T_{std}}{P_{std} T_m} = K_4 Y \frac{V_m P_m}{T_m} \qquad \text{Eq. 4-3}$$

Where:

K_4 = 0.3855 °K/mm Hg for metric units,
= 17.64 °R/in. Hg for English units.

NOTE: If the post-test leak rate (Section 8.1.4.2) exceeds the allowable rate, correct the value of Vm in Equation 4–3, as described in section 12.3 of Method 5.

12.1.5 Moisture Content.

$$B_{ws} = \frac{V_{wc(std)} + V_{wsg(std)}}{V_{wc(std)} + V_{wsg(std)} + V_{m(std)}} \qquad \text{Eq. 4-4}$$

12.1.6 Verification of Constant Sampling Rate. For each time increment, determine the ΔV_m. Calculate the average. If the value for any time increment differs from the average by more than 10 percent, reject the results, and repeat the run.

12.1.7 In saturated or moisture droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one using a value based upon the saturated conditions (see section 4.1), and another based upon the results of the impinger analysis. The lower of these two values of B_{ws} shall be considered correct.

12.2 Approximation Method. The approximation method presented is designed to estimate the moisture in the stack gas; therefore, other data, which are only necessary for accurate moisture determinations, are not collected. The following equations adequately estimate the moisture content for the purpose of determining isokinetic sampling rate settings.

12.2.1 Nomenclature.

B_{wm} = Approximate proportion by volume of water vapor in the gas stream leaving the second impinger, 0.025.
B_{ws} = Water vapor in the gas stream, proportion by volume.
M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
P_m = Absolute pressure (for this method, same as barometric pressure) at the dry gas meter, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
R = Ideal gas constant, 0.06236 [(mm Hg)(m^3)]/[(g-mole)(K)] for metric units and 21.85 [(in. Hg)(ft^3)]/[(lb-mole)(°R)] for English units.
T_m = Absolute temperature at meter, °K (°R).
T_{std} = Standard absolute temperature, 293 °K (528 °R).
V_f = Final volume of impinger contents, ml.
V_i = Initial volume of impinger contents, ml.
V_m = Dry gas volume measured by dry gas meter, dcm (dcf).
$V_{m(std)}$ = Dry gas volume measured by dry gas meter, corrected to standard conditions, dscm (dscf).
$V_{wc(std)}$ = Volume of water vapor condensed, corrected to standard conditions, scm (scf).
Y = Dry gas meter calibration factor.
ρ_w = Density of water, 0.09982 g/ml (0.002201 lb/ml).

12.2.2 Volume of Water Vapor Collected.

$$V_{wc(std)} = \frac{(V_f - V_i)\,\rho_w R\, T_{std}}{P_{std} M_W} = K_5 (V_f - V_i) \qquad \text{Eq. 4-5}$$

Where:

K_5 = 0.001333 m^3/ml for metric units,
= 0.04706 ft^3/ml for English units.

12.2.3 Sample Gas Volume.

$$V_{m(std)} = \frac{V_m\ Y\ P_m T_{std}}{P_{std} T_m} = K_6 Y \frac{V_m P_m}{T_m} \qquad \text{Eq. 4-6}$$

Where:

K_6 = 0.3855 °K/mm Hg for metric units,
= 17.64 °R/in. Hg for English units.

12.2.4 Approximate Moisture Content.

$$B_{ws} = \frac{V_{wc(std)}}{V_{wc(std)} + V_{m(std)}} + B_{wm} = \frac{V_{wc(std)}}{V_{wc(std)} + V_{m(std)}} + (0.025) \qquad \text{Eq. 4-7}$$

12.2.5 Using F-factors to determine approximate moisture for estimating moisture content where no wet scrubber is being used, for the purpose of determining isokinetic sampling rate settings with no fuel sample, is acceptable using the average F_c or F_d factor from Method 19 (see Method 19, section 12.3.1). If this option is selected, calculate the approximate moisture as follows:

$B_{ws} = B_H + B_A + B_F$

Where:

B_A = Mole Fraction of moisture in the ambient air.

$$B_A = \frac{\%RH}{100 * P_{Bar}} * 10^{\left[6.6912 - \left(\frac{3144}{T+390.86}\right)\right]}$$

B_F = Mole fraction of moisture from free water in the fuel.

$$B_F = \left[\frac{0.0036W^2 + 0.075W}{100}\right]\left[\frac{20.9 - O_2}{20.9}\right]$$

B_H = Mole fraction of moisture from the hydrogen in the fuel.

$$B_H = \left[1 - \frac{F_d}{F_w}\right]\frac{(20.9 - O_2)}{20.9}$$

B_{ws} = Mole fraction of moisture in the stack gas.
F_d = Volume of dry combustion components per unit of heat content at 0 percent oxygen, dscf/10^6.
Btu (scm/J). See Table 19–2 in Method 19.
F_w = Volume of wet combustion components per unit of heat content at 0 percent oxygen, wet.
scf/10^6 Btu (scm/J). See Table 19–2 in Method 19.
%RH = Percent relative humidity (calibrated hygrometer acceptable), percent.
P_{Bar} = Barometric pressure, in. Hg.
T = Ambient temperature, °F.
W = Percent free water by weight, percent.
O_2 = Percent oxygen in stack gas, dry basis, percent.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 The procedure described in Method 5 for determining moisture content is an acceptable alternative to Method 4.

16.2 The procedures in Method 6A for determining moisture is an acceptable alternative to Method 4.

16.3 Method 320 is an acceptable alternative to Method 4 for determining moisture.

16.4 Using F-factors to determine moisture is an acceptable alternative to Method 4 for a combustion stack not using a scrubber, and where a fuel sample is taken during the test run and analyzed for development of an F_d factor (see Method 19, section 12.3.2), and where stack O_2 content is measured by Method 3A or 3B during each test run. If this option is selected, calculate the moisture content as follows:

$B_{ws} = B_H + B_A + B_F$

Where:

B_A = Mole fraction of moisture in the ambient air.

$$B_A = \frac{\%RH}{100\ P_{Bar}}\left[10^{\left[6.6912-\left(\frac{3144}{T+390.86}\right)\right]}\right]$$

NOTE: Values of B_A should be between 0.00 and 0.06 with common values being about 0.015.

B_F = Mole fraction of moisture from free water in the fuel.

$$B_F = \left[\frac{0.0036\ W^2 + 0.075\ W}{100}\right]\left[\frac{20.9 - O_2}{20.9}\right]$$

NOTE: Free water in fuel is minimal for distillate oil and gases, such as propane and natural gas, so this step may be omitted for those fuels.

B_H = Mole fraction of moisture from the hydrogen in the fuel.

$$B_H = \left(1 - \frac{F_d}{F_w}\right)\frac{(20.9 - O_2)}{20.9}$$

B_{ws} = Mole fraction of moisture in the stack gas.

F_d = Volume of dry combustion components per unit of heat content at 0 percent oxygen, dscf/10^6 Btu (scm/J). Develop a test specific F_d value using an integrated fuel sample from each test run and Equation 19–13 in section 12.3.2 of Method 19.

F_w = Volume of wet combustion components per unit of heat content at 0 percent oxygen, wet scf/10^6 Btu (scm/J). Develop a test specific F_w value using an integrated fuel sample from each test run and Equation 19–14 in section 12.3.2 of Method 19.

%RH = Percent relative humidity (calibrated hygrometer acceptable), percent.

P_{Bar} = Barometric pressure, in. Hg.

T = Ambient temperature, °F.

W = Percent free water by weight, percent.

O_2 = Percent oxygen in stack gas, dry basis, percent.

17.0 References

1. Air Pollution Engineering Manual (Second Edition). Danielson, J.A. (ed.). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, NC. Publication No. AP–40. 1973.

2. Devorkin, Howard, et al. Air Pollution Source Testing Manual. Air Pollution Control District, Los Angeles, CA. November 1963.

3. Methods for Determination of Velocity, Volume, Dust and Mist Content of Gases. Western Precipitation Division of Joy Manufacturing Co. Los Angeles, CA. Bulletin WP–50. 1968.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

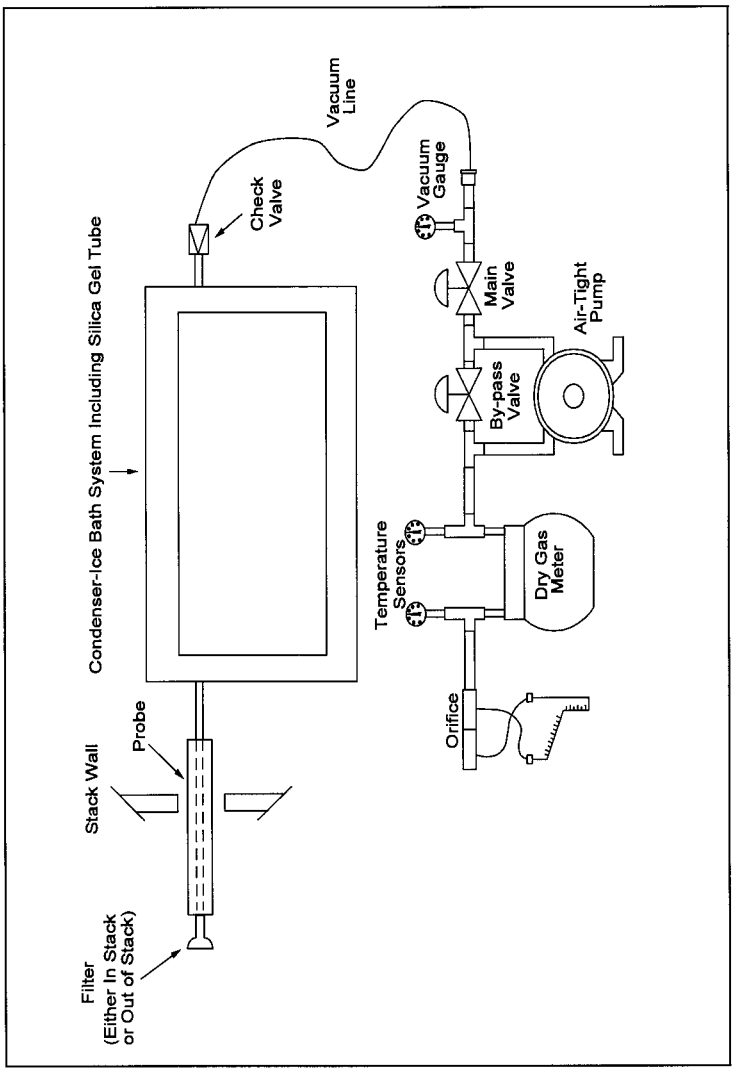

Figure 4-1. Moisture Sampling Train-Reference Method

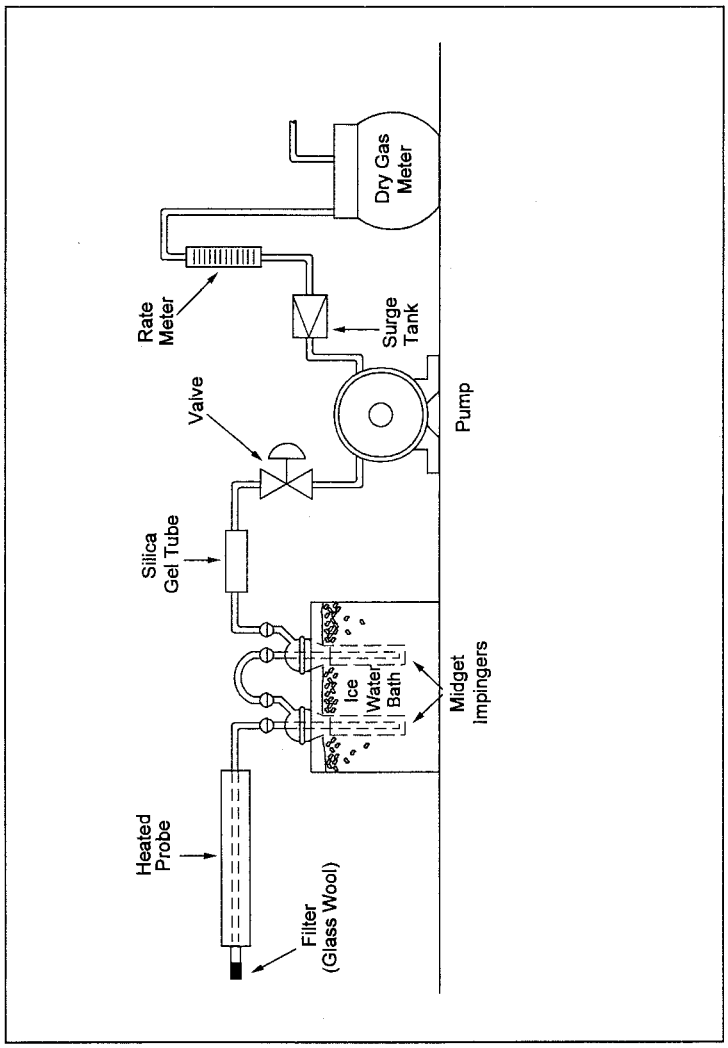

Figure 4-2. Moisture Sampling Train - Approximation Method.

Plant		Run No.	
Location		Ambient temperature	
Operator		Barometric pressure	
Date		Probe Length	

Traverse Pt. No.	Sampling time (Δ), min	Stack temperature °C (°F)	Pressure differential across orifice meter ΔH mm (in.) H_2O	Meter reading gas sample volume m^3 (ft^3)	ΔV_m m^3 (ft^3)	Gas sample temperature at dry gas meter		Temperature of gas leaving condenser or last impinger °C (°F)
						Inlet Tm_{in} °C (°F)	Outlet Tm_{out} °C (°F)	
Average								

Location _____ Barometric pressure _____
Test _____ Comments: _____
Date _____
Operator _____

Figure 4–3. Moisture Determination—Reference Method

Clock time	Gas Volume through meter, (V_m), m^3 (ft^3)	Rate meter setting m^3/min (ft^3/min)	Meter temperature °C (°F)

Figure 4–4. Example Moisture Determination Field Data Sheet—Approximation Method

	Impinger volume, ml	Silica gel weight, g
Final Initial Difference		

Figure 4–5. Analytical Data—Reference Method

METHOD 5—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of PM emissions from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature of 120 ±14 °C (248 ±25 °F) or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. The PM mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after the removal of uncombined water.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. The following items are required for sample collection:

6.1.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 5–1 in section 18.0. Complete construction details are given in APTD–0581 (Reference 2 in section 17.0); commercial models of this train are also available. For

changes from APTD–0581 and for allowable modifications of the train shown in Figure 5–1, see the following subsections.

NOTE: The operating and maintenance procedures for the sampling train are described in APTD–0576 (Reference 3 in section 17.0). Since correct usage is important in obtaining valid results, all users should read APTD–0576 and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein.

6.1.1.1 Probe Nozzle. Stainless steel (316) or glass with a sharp, tapered leading edge. The angle of taper shall be ≤30°, and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. If made of stainless steel, the nozzle shall be constructed from seamless tubing. Other materials of construction may be used, subject to the approval of the Administrator. A range of nozzle sizes suitable for isokinetic sampling should be available. Typical nozzle sizes range from 0.32 to 1.27 cm (⅛ to ½ in) inside diameter (ID) in increments of 0.16 cm (1⁄16 in). Larger nozzles sizes are also available if higher volume sampling trains are used. Each nozzle shall be calibrated, according to the procedures outlined in section 10.1.

6.1.1.2 Probe Liner. Borosilicate or quartz glass tubing with a heating system capable of maintaining a probe gas temperature during sampling of 120 ±14 °C (248 ±25 °F), or such other temperature as specified by an applicable subpart of the standards or as approved by the Administrator for a particular application. Since the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to APTD–0581 and utilizing the calibration curves of APTD–0576 (or calibrated according to the procedure outlined in APTD–0576) will be considered acceptable. Either borosilicate or quartz glass probe liners may be used for stack temperatures up to about 480 °C (900 °F); quartz glass liners shall be used for temperatures between 480 and 900 °C (900 and 1,650 °F). Both types of liners may be used at higher temperatures than specified for short periods of time, subject to the approval of the Administrator. The softening temperature for borosilicate glass is 820 °C (1500 °F), and for quartz glass it is 1500 °C (2700 °F). Whenever practical, every effort should be made to use borosilicate or quartz glass probe liners. Alternatively, metal liners (e.g., 316 stainless steel, Incoloy 825 or other corrosion resistant metals) made of seamless tubing may be used, subject to the approval of the Administrator.

6.1.1.3 Pitot Tube. Type S, as described in section 6.1 of Method 2, or other device approved by the Administrator. The pitot tube shall be attached to the probe (as shown in Figure 5–1) to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see Method 2, Figure 2–7) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in section 10.0 of Method 2.

6.1.1.4 Differential Pressure Gauge. Inclined manometer or equivalent device (two), as described in section 6.2 of Method 2. One manometer shall be used for velocity head (Δp) readings, and the other, for orifice differential pressure readings.

6.1.1.5 Filter Holder. Borosilicate glass, with a glass or Teflon frit filter support and a silicone rubber gasket. Other materials of construction (e.g., stainless steel or Viton) may be used, subject to the approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe (or cyclone, if used).

6.1.1.6 Filter Heating System. Any heating system capable of monitoring and maintaining temperature around the filter shall be used to ensure the sample gas temperature exiting the filter of 120 ±14 °C (248 ±25 °F) during sampling or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. The monitoring and regulation of the temperature around the filter may be done with the filter temperature sensor or another temperature sensor.

6.1.1.7 Filter Temperature Sensor. A temperature sensor capable of measuring temperature to within ±3 °C (5.4 °F) shall be installed so that the sensing tip of the temperature sensor is in direct contact with the sample gas exiting the filter. The sensing tip of the sensor may be encased in glass, Teflon, or metal and must protrude at least ½ in. into the sample gas exiting the filter. The filter temperature sensor must be monitored and recorded during sampling to ensure a sample gas temperature exiting the filter of 120 ±14 °C (248 ±25 °F), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application.

6.1.1.8 Condenser. The following system shall be used to determine the stack gas moisture content: Four impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with a 1.3 cm (½ in.) ID glass tube extending to about 1.3 cm (½ in.) from the bottom of the flask. The second impinger shall be of the Greenburg-Smith design with the standard

tip. Modifications (e.g., using flexible connections between the impingers, using materials other than glass, or using flexible vacuum lines to connect the filter holder to the condenser) may be used, subject to the approval of the Administrator. The first and second impingers shall contain known quantities of water (Section 8.3.1), the third shall be empty, and the fourth shall contain a known weight of silica gel, or equivalent desiccant. A temperature sensor, capable of measuring temperature to within 1 °C (2 °F) shall be placed at the outlet of the fourth impinger for monitoring purposes. Alternatively, any system that cools the sample gas stream and allows measurement of the water condensed and moisture leaving the condenser, each to within 1 ml or 1 g may be used, subject to the approval of the Administrator. An acceptable technique involves the measurement of condensed water either gravimetrically or volumetrically and the determination of the moisture leaving the condenser by: (1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's law of partial pressures; or (2) passing the sample gas stream through a tared silica gel (or equivalent desiccant) trap with exit gases kept below 20 °C (68 °F) and determining the weight gain. If means other than silica gel are used to determine the amount of moisture leaving the condenser, it is recommended that silica gel (or equivalent) still be used between the condenser system and pump to prevent moisture condensation in the pump and metering devices and to avoid the need to make corrections for moisture in the metered volume.

NOTE: If a determination of the PM collected in the impingers is desired in addition to moisture content, the impinger system described above shall be used, without modification. Individual States or control agencies requiring this information shall be contacted as to the sample recovery and analysis of the impinger contents.

6.1.1.9 Metering System. Vacuum gauge, leak-free pump, calibrated temperature sensors, dry gas meter (DGM) capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 5–1. Other metering systems capable of maintaining sampling rates within 10 percent of isokinetic and of determining sample volumes to within 2 percent may be used, subject to the approval of the Administrator. When the metering system is used in conjunction with a pitot tube, the system shall allow periodic checks of isokinetic rates.

6.1.1.10 Sampling trains utilizing metering systems designed for higher flow rates than that described in APTD–0581 or APTD–0576 may be used provided that the specifications of this method are met.

6.1.2 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in.).

NOTE: The barometric pressure reading may be obtained from a nearby National Weather Service station. In this case, the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be made at a rate of minus 2.5 mm Hg (0.1 in.) per 30 m (100 ft) elevation increase or plus 2.5 mm Hg (0.1 in) per 30 m (100 ft) elevation decrease.

6.1.3 Gas Density Determination Equipment. Temperature sensor and pressure gauge, as described in sections 6.3 and 6.4 of Method 2, and gas analyzer, if necessary, as described in Method 3. The temperature sensor shall, preferably, be permanently attached to the pitot tube or sampling probe in a fixed configuration, such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see Method 2, Figure 2–4). As a second alternative, if a difference of not more than 1 percent in the average velocity measurement is to be introduced, the temperature sensor need not be attached to the probe or pitot tube. (This alternative is subject to the approval of the Administrator.)

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Probe-Liner and Probe-Nozzle Brushes. Nylon bristle brushes with stainless steel wire handles. The probe brush shall have extensions (at least as long as the probe) constructed of stainless steel, Nylon, Teflon, or similarly inert material. The brushes shall be properly sized and shaped to brush out the probe liner and nozzle.

6.2.2 Wash Bottles. Two Glass wash bottles are recommended. Alternatively, polyethylene wash bottles may be used. It is recommended that acetone not be stored in polyethylene bottles for longer than a month.

6.2.3 Glass Sample Storage Containers. Chemically resistant, borosilicate glass bottles, for acetone washes, 500 ml or 1000 ml. Screw cap liners shall either be rubber-backed Teflon or shall be constructed so as to be leak-free and resistant to chemical attack by acetone. (Narrow mouth glass bottles have been found to be less prone to leakage.) Alternatively, polyethylene bottles may be used.

6.2.4 Petri Dishes. For filter samples; glass or polyethylene, unless otherwise specified by the Administrator.

6.2.5 Graduated Cylinder and/or Balance. To measure condensed water to within 1 ml or 0.5 g. Graduated cylinders shall have subdivisions no greater than 2 ml.

6.2.6 Plastic Storage Containers. Air-tight containers to store silica gel.

6.2.7 Funnel and Rubber Policeman. To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

6.2.8 Funnel. Glass or polyethylene, to aid in sample recovery.

6.3 Sample Analysis. The following equipment is required for sample analysis:

6.3.1 Glass Weighing Dishes.

6.3.2 Desiccator.

6.3.3 Analytical Balance. To measure to within 0.1 mg.

6.3.4 Balance. To measure to within 0.5 g.

6.3.5 Beakers. 250 ml.

6.3.6 Hygrometer. To measure the relative humidity of the laboratory environment.

6.3.7 Temperature Sensor. To measure the temperature of the laboratory environment.

7.0 Reagents and Standards

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Method D 2986–71, 78, or 95a (incorporated by reference—see §60.17). Test data from the supplier's quality control program are sufficient for this purpose. In sources containing SO_2 or SO_3, the filter material must be of a type that is unreactive to SO_2 or SO_3. Reference 10 in section 17.0 may be used to select the appropriate filter.

7.1.2 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

7.1.3 Water. When analysis of the material caught in the impingers is required, deionized distilled water [to conform to ASTM D1193–77 or 91 Type 3 (incorporated by reference—see §60.17)] with at least <0.001 percent residue shall be used or as specified in the applicable method requiring analysis of the water. Run reagent blanks prior to field use to eliminate a high blank on test samples.

7.1.4 Crushed Ice.

7.2 Sample Recovery. Acetone, reagent grade, ≤0.001 percent residue, in glass bottles, is required. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers; thus, acetone blanks shall be run prior to field use and only acetone with low blank values (≤0.001 percent) shall be used. In no case shall a blank value of greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight.

7.3 Sample Analysis. The following reagents are required for sample analysis:

7.3.1 Acetone. Same as in section 7.2.

7.3.2 Desiccant. Anhydrous calcium sulfate, indicating type. Alternatively, other types of desiccants may be used, subject to the approval of the Administrator.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation. It is suggested that sampling equipment be maintained according to the procedures described in APTD–0576. Alternative mercury-free thermometers may be used if the thermometers are at a minimum equivalent in terms of performance or suitably effective for the specific temperature measurement application.

8.1.1 Place 200 to 300 g of silica gel in each of several air-tight containers. Weigh each container, including silica gel, to the nearest 0.5 g, and record this weight. As an alternative, the silica gel need not be preweighed, but may be weighed directly in its impinger or sampling holder just prior to train assembly.

8.1.2 Check filters visually against light for irregularities, flaws, or pinhole leaks. Label filters of the proper diameter on the back side near the edge using numbering machine ink. As an alternative, label the shipping containers (glass or polyethylene petri dishes), and keep each filter in its identified container at all times except during sampling.

8.1.3 Desiccate the filters at 20 ±5.6 °C (68 ±10 °F) and ambient pressure for at least 24 hours. Weigh each filter (or filter and shipping container) at intervals of at least 6 hours to a constant weight (*i.e.*, ≤0.5 mg change from previous weighing). Record results to the nearest 0.1 mg. During each weighing, the period for which the filter is exposed to the laboratory atmosphere shall be less than 2 minutes. Alternatively (unless otherwise specified by the Administrator), the filters may be oven dried at 105 °C (220 °F) for 2 to 3 hours, desiccated for 2 hours, and weighed. Procedures other than those described, which account for relative humidity effects, may be used, subject to the approval of the Administrator.

8.2 Preliminary Determinations.

8.2.1 Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and the range of velocity heads using Method 2; it is recommended that a leak check of the pitot lines (see Method 2, section 8.1) be performed. Determine the moisture content using Approximation Method 4 or its alternatives for the purpose

of making isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in Method 2, section 8.6; if integrated Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the particulate sample run.

8.2.2 Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see section 8.3 of Method 2).

8.2.3 Select a suitable probe liner and probe length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the required probe length.

8.2.4 Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that (1) the sampling time per point is not less than 2 minutes (or some greater time interval as specified by the Administrator), and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume. The latter is based on an approximate average sampling rate.

8.2.5 The sampling time at each point shall be the same. It is recommended that the number of minutes sampled at each point be an integer or an integer plus one-half minute, in order to avoid timekeeping errors.

8.2.6 In some circumstances (*e.g.*, batch cycles) it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the Administrator's approval must first be obtained.

8.3 Preparation of Sampling Train.

8.3.1 During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin. Place 100 ml of water in each of the first two impingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

8.3.2 Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly is completed.

8.3.3 When glass probe liners are used, install the selected nozzle using a Viton A O-ring when stack temperatures are less than 260 °C (500 °F) or a heat-resistant string gasket when temperatures are higher. See APTD–0576 for details. Other connecting systems using either 316 stainless steel or Teflon ferrules may be used. When metal liners are used, install the nozzle as discussed above or by a leak-free direct mechanical connection. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

8.3.4 Set up the train as shown in Figure 5–1 ensuring that the connections are leaktight. Subject to the approval of the Administrator, a glass cyclone may be used between the probe and filter holder when the total particulate catch is expected to exceed 100 mg or when water droplets are present in the stack gas.

8.3.5 Place crushed ice around the impingers.

8.4 Leak-Check Procedures.

8.4.1 Leak Check of Metering System Shown in Figure 5–1. That portion of the sampling train from the pump to the orifice meter should be leak-checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The following procedure is suggested (see Figure 5–2): Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 to 18 cm (5 to 7 in.) water column by blowing into the rubber tubing. Pinch off the tubing, and observe the manometer for one minute. A loss of pressure on the manometer indicates a leak in the meter box; leaks, if present, must be corrected.

8.4.2 Pretest Leak Check. A pretest leak check of the sampling train is recommended, but not required. If the pretest leak check is conducted, the following procedure should be used.

8.4.2.1 After the sampling train has been assembled, turn on and set the filter and probe heating systems to the desired operating temperatures. Allow time for the temperatures to stabilize. If a Viton A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 380 mm (15 in.) Hg vacuum.

NOTE: A lower vacuum may be used, provided that it is not exceeded during the test.

8.4.2.2 If a heat-resistant string is used, do not connect the probe to the train during the leak check. Instead, leak-check the train by first plugging the inlet to the filter holder (cyclone, if applicable) and pulling a 380 mm (15 in.) Hg vacuum (see note in section 8.4.2.1). Then connect the probe to the train, and leak-check at approximately 25 mm (1 in.) Hg vacuum; alternatively, the probe may be leak-checked with the rest of the sampling train, in one step, at 380 mm (15 in.) Hg vacuum. Leakage rates in excess of 4 percent of the average sampling rate or 0.00057 m^3/min (0.020 cfm), whichever is less, are unacceptable.

8.4.2.3 The following leak-check instructions for the sampling train described in APTD–0576 and APTD–0581 may be helpful. Start the pump with the bypass valve fully open and the coarse adjust valve completely closed. Partially open the coarse adjust valve, and slowly close the bypass valve until the desired vacuum is reached. Do not reverse the direction of the bypass valve, as this will cause water to back up into the filter holder. If the desired vacuum is exceeded, either leak-check at this higher vacuum, or end the leak check and start over.

8.4.2.4 When the leak check is completed, first slowly remove the plug from the inlet to the probe, filter holder, or cyclone (if applicable), and immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the filter holder and the silica gel from being entrained backward into the third impinger.

8.4.3 Leak Checks During Sample Run. If, during the sampling run, a component (*e.g.*, filter assembly or impinger) change becomes necessary, a leak check shall be conducted immediately before the change is made. The leak check shall be done according to the procedure outlined in section 8.4.2 above, except that it shall be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.020 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered; if, however, a higher leakage rate is obtained, either record the leakage rate and plan to correct the sample volume as shown in section 12.3 of this method, or void the sample run.

NOTE: Immediately after component changes, leak checks are optional. If such leak checks are done, the procedure outlined in section 8.4.2 above should be used.

8.4.4 Post-Test Leak Check. A leak check of the sampling train is mandatory at the conclusion of each sampling run. The leak check shall be performed in accordance with the procedures outlined in section 8.4.2, except that it shall be conducted at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m^3 min (0.020 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, either record the leakage rate and correct the sample volume as shown in section 12.3 of this method, or void the sampling run.

8.5 Sampling Train Operation. During the sampling run, maintain an isokinetic sampling rate (within 10 percent of true isokinetic unless otherwise specified by the Administrator) and a sample gas temperature through the filter of 120 ±14 °C (248 ±25 °F) or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator.

8.5.1 For each run, record the data required on a data sheet such as the one shown in Figure 5–3. Be sure to record the initial DGM reading. Record the DGM readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak check, and when sampling is halted. Take other readings indicated by Figure 5–3 at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

8.5.2 Clean the portholes prior to the test run to minimize the chance of collecting deposited material. To begin sampling, verify that the filter and probe heating systems are up to temperature, remove the nozzle cap, verify that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump, and adjust the flow to isokinetic conditions. Nomographs are available which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pitot tube coefficient (C_p) is 0.85 ±0.02, and the stack gas equivalent density [dry molecular weight (M_d)] is equal to 29 ±4. APTD–0576 details the procedure for using the nomographs. If C_p and M_d are outside the above stated ranges, do not use the nomographs unless appropriate steps (see Reference 7 in section 17.0) are taken to compensate for the deviations.

8.5.3 When the stack is under significant negative pressure (*i.e.*, height of impinger stem), take care to close the coarse adjust valve before inserting the probe into the stack to prevent water from backing into the

filter holder. If necessary, the pump may be turned on with the coarse adjust valve closed.

8.5.4 When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

8.5.5 Traverse the stack cross-section, as required by Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the portholes; this minimizes the chance of extracting deposited material.

8.5.6 During the test run, make periodic adjustments to keep the temperature around the filter holder at the proper level to maintain the sample gas temperature exiting the filter; add more ice and, if necessary, salt to maintain a temperature of less than 20 °C (68 °F) at the condenser/silica gel outlet. Also, periodically check the level and zero of the manometer.

8.5.7 If the pressure drop across the filter becomes too high, making isokinetic sampling difficult to maintain, the filter may be replaced in the midst of the sample run. It is recommended that another complete filter assembly be used rather than attempting to change the filter itself. Before a new filter assembly is installed, conduct a leak check (see section 8.4.3). The total PM weight shall include the summation of the filter assembly catches.

8.5.8 A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator.

NOTE: When two or more trains are used, separate analyses of the front-half and (if applicable) impinger catches from each train shall be performed, unless identical nozzle sizes were used on all trains, in which case, the front-half catches from the individual trains may be combined (as may the impinger catches) and one analysis of front-half catch and one analysis of impinger catch may be performed. Consult with the Administrator for details concerning the calculation of results when two or more trains are used.

8.5.9 At the end of the sample run, close the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final DGM meter reading, and conduct a post-test leak check, as outlined in section 8.4.4. Also, leak-check the pitot lines as described in Method 2, section 8.1. The lines must pass this leak check, in order to validate the velocity head data.

8.6 Calculation of Percent Isokinetic. Calculate percent isokinetic (see Calculations, section 12.11) to determine whether the run was valid or another test run should be made. If there was difficulty in maintaining isokinetic rates because of source conditions, consult with the Administrator for possible variance on the isokinetic rates.

8.7 Sample Recovery.

8.7.1 Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

8.7.2 When the probe can be safely handled, wipe off all external PM near the tip of the probe nozzle, and place a cap over it to prevent losing or gaining PM. Do not cap off the probe tip tightly while the sampling train is cooling down. This would create a vacuum in the filter holder, thereby drawing water from the impingers into the filter holder.

8.7.3 Before moving the sample train to the cleanup site, remove the probe from the sample train and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Cap the filter inlet where the probe was fastened. Remove the umbilical cord from the last impinger, and cap the impinger. If a flexible line is used between the first impinger or condenser and the filter holder, disconnect the line at the filter holder, and let any condensed water or liquid drain into the impingers or condenser. Cap off the filter holder outlet and impinger inlet. Either ground-glass stoppers, plastic caps, or serum caps may be used to close these openings.

8.7.4 Transfer the probe and filter-impinger assembly to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

8.7.5 Save a portion of the acetone used for cleanup as a blank. From each storage container of acetone used for cleanup, save 200 ml and place in a glass sample container labeled ''acetone blank.'' To minimize any particulate contamination, rinse the wash bottle prior to filling from the tested container.

8.7.6 Inspect the train prior to and during disassembly, and note any abnormal conditions. Treat the samples as follows:

8.7.6.1 Container No. 1. Carefully remove the filter from the filter holder, and place it in its identified petri dish container. Use a pair of tweezers and/or clean disposable surgical gloves to handle the filter. If it is necessary to fold the filter, do so such that the PM cake is inside the fold. Using a dry Nylon bristle brush and/or a sharp-edged blade, carefully transfer to the petri dish any PM and/or filter fibers that adhere to the filter holder gasket. Seal the container.

8.7.6.2 Container No. 2. Taking care to see that dust on the outside of the probe or other

exterior surfaces does not get into the sample, quantitatively recover PM or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with acetone and placing the wash in a glass container. Deionized distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator. In these cases, save a water blank, and follow the Administrator's directions on analysis. Perform the acetone rinse as follows:

8.7.6.2.1 Carefully remove the probe nozzle. Clean the inside surface by rinsing with acetone from a wash bottle and brushing with a Nylon bristle brush. Brush until the acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

8.7.6.2.2 Brush and rinse the inside parts of the fitting with acetone in a similar way until no visible particles remain.

8.7.6.2.3 Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Let the acetone drain from the lower end into the sample container. A funnel (glass or polyethylene) may be used to aid in transferring liquid washes to the container. Follow the acetone rinse with a probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action through the probe; hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter that is brushed from the probe. Run the brush through the probe three times or more until no visible PM is carried out with the acetone or until none remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times since metal probes have small crevices in which particulate matter can be entrapped. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe.

8.7.6.2.4 It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

8.7.6.2.5 Clean the inside of the front half of the filter holder by rubbing the surfaces with a Nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone, also (if applicable). After all acetone washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to allow determination of whether leakage occurred during transport. Label the container to clearly identify its contents.

8.7.6.3 Container No. 3. Note the color of the indicating silica gel to determine whether it has been completely spent, and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container, and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, follow the procedure for Container No. 3 in section 11.2.3.

8.7.6.4 Impinger Water. Treat the impingers as follows: Make a notation of any color or film in the liquid catch. Measure the liquid that is in the first three impingers to within 1 ml by using a graduated cylinder or by weighing it to within 0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas. Discard the liquid after measuring and recording the volume or weight, unless analysis of the impinger catch is required (see NOTE, section 6.1.1.8). If a different type of condenser is used, measure the amount of moisture condensed either volumetrically or gravimetrically.

8.8 Sample Transport. Whenever possible, containers should be shipped in such a way that they remain upright at all times.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4, 10.1–10.6	Sampling equipment leak check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.

9.2 Volume Metering System Checks. The following procedures are suggested to check the volume metering system calibration values at the field test site prior to sample collection. These procedures are optional.

9.2.1 Meter Orifice Check. Using the calibration data obtained during the calibration procedure described in section 10.3, determine the ΔH@ for the metering system orifice. The ΔH@ is the orifice pressure differential in units of in. H_2O that correlates to 0.75 cfm of air at 528 °R and 29.92 in. Hg. The ΔH@ is calculated as follows:

$$\Delta H@ = 0.0319\ \Delta H \frac{T_M \theta^2}{P_{bar} Y^2 V_m^2}$$

Where:

ΔH = Average pressure differential across the orifice meter, in. H_2O.
T_m = Absolute average DGM temperature, °R.
P_{bar} = Barometric pressure, in. Hg.
θ = Total sampling time, min.
Y = DGM calibration factor, dimensionless.
V_m = Volume of gas sample as measured by DGM, dcf.
0.0319 = (0.0567 in. Hg/°R) (0.75 cfm)^2

9.2.1.1 Before beginning the field test (a set of three runs usually constitutes a field test), operate the metering system (*i.e.*, pump, volume meter, and orifice) at the ΔH@ pressure differential for 10 minutes. Record the volume collected, the DGM temperature, and the barometric pressure. Calculate a DGM calibration check value, Y_c, as follows:

$$Y_c = \frac{10}{V_m}\left[\frac{0.0319\ T_m}{P_{bar}}\right]^{\frac{1}{2}}$$

where:

Y_c = DGM calibration check value, dimensionless.
10 = Run time, min.

9.2.1.2 Compare the Y_c value with the dry gas meter calibration factor Y to determine that: $0.97Y < Y_c < 1.03Y$. If the Y_c value is not within this range, the volume metering system should be investigated before beginning the test.

9.2.2 Calibrated Critical Orifice. A critical orifice, calibrated against a wet test meter or spirometer and designed to be inserted at the inlet of the sampling meter box, may be used as a check by following the procedure of section 16.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Probe Nozzle. Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the ID of the nozzle to the nearest 0.025 mm (0.001 in.). Make three separate measurements using different diameters each time, and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

10.2 Pitot Tube Assembly. The Type S pitot tube assembly shall be calibrated according to the procedure outlined in section 10.1 of Method 2.

10.3 Metering System.

10.3.1 Calibration Prior to Use. Before its initial use in the field, the metering system shall be calibrated as follows: Connect the metering system inlet to the outlet of a wet test meter that is accurate to within 1 percent. Refer to Figure 5–4. The wet test meter should have a capacity of 30 liters/rev (1 ft^3/rev). A spirometer of 400 liters (14 ft^3) or more capacity, or equivalent, may be used for this calibration, although a wet test meter is usually more practical. The wet test meter should be periodically calibrated with a spirometer or a liquid displacement meter to ensure the accuracy of the wet test meter. Spirometers or wet test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained. Run the metering system pump for about 15 minutes with the orifice manometer indicating a median reading as expected in field use to allow the pump to warm up and to permit the interior surface of the wet test meter to be thoroughly wetted. Then, at each of a minimum of three orifice manometer settings, pass an exact quantity of gas through the wet test meter and note the gas volume indicated by the DGM. Also note the barometric pressure and the temperatures of the wet test meter, the inlet of the DGM, and the outlet of the DGM. Select the highest and lowest orifice settings to bracket the expected field operating range of the orifice. Use a minimum volume of 0.14 m^3 (5 ft^3) at all orifice settings. Record all the data on a form similar to Figure 5–5 and calculate Y, the DGM calibration factor, and ΔH , the orifice calibration factor, at each orifice setting as shown on Figure 5–5. Allowable tolerances for individual Y and ΔH values are given in Figure 5–5. Use the average of the Y values in the calculations in section 12.0.

10.3.1.1 Before calibrating the metering system, it is suggested that a leak check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. For these cases the following leak-check procedure is suggested: make a 10-minute calibration run at 0.00057 m^3/min (0.020 cfm). At the end of the run, take the difference of the measured wet test meter and DGM volumes. Divide the difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 m^3/min (0.020 cfm).

10.3.2 Calibration After Use. After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single, intermediate

orifice setting (based on the previous field test), with the vacuum set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet test meter and the inlet of the metering system. Calculate the average value of the DGM calibration factor. If the value has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as detailed in section 10.3.1.

NOTE: Alternative procedures (*e.g.*, rechecking the orifice meter coefficient) may be used, subject to the approval of the Administrator.

10.3.3 Acceptable Variation in Calibration Check. If the DGM coefficient values obtained before and after a test series differ by more than 5 percent, the test series shall either be voided, or calculations for the test series shall be performed using whichever meter coefficient value (*i.e.*, before or after) gives the lower value of total sample volume.

10.4 Probe Heater Calibration. Use a heat source to generate air heated to selected temperatures that approximate those expected to occur in the sources to be sampled. Pass this air through the probe at a typical sample flow rate while measuring the probe inlet and outlet temperatures at various probe heater settings. For each air temperature generated, construct a graph of probe heating system setting versus probe outlet temperature. The procedure outlined in APTD–0576 can also be used. Probes constructed according to APTD–0581 need not be calibrated if the calibration curves in APTD–0576 are used. Also, probes with outlet temperature monitoring capabilities do not require calibration.

NOTE: The probe heating system shall be calibrated before its initial use in the field.

10.5 Temperature Sensors. Use the procedure in Section 10.3 of Method 2 to calibrate in-stack temperature sensors. Dial thermometers, such as are used for the DGM and condenser outlet, shall be calibrated against mercury-in-glass thermometers. An alternative mercury-free NIST-traceable thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application. As an alternative, the following single-point calibration procedure may be used. After each test run series, check the accuracy (and, hence, the calibration) of each thermocouple system at ambient temperature, or any other temperature, within the range specified by the manufacturer, using a reference thermometer (either ASTM reference thermometer or a thermometer that has been calibrated against an ASTM reference thermometer). The temperatures of the thermocouple and reference thermometers shall agree to within ±2 °F.

10.6 Barometer. Calibrate against a mercury barometer or NIST-traceable barometer prior to the field test. Alternatively, barometric pressure may be obtained from a weather report that has been adjusted for the test point (on the stack) elevation.

10.7 Field Balance Calibration Check. Check the calibration of the balance used to weigh impingers with a weight that is at least 500g or within 50g of a loaded impinger. The weight must be ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 6 (or better). Daily before use, the field balance must measure the weight within ±0.5g of the certified mass. If the daily balance calibration check fails, perform corrective measures and repeat the check before using balance.

10.8 Analytical Balance Calibration. Perform a multipoint calibration (at least five points spanning the operational range) of the analytical balance before the first use, and semiannually thereafter. The calibration of the analytical balance must be conducted using ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 2 (or better) tolerance weights. Audit the balance each day it is used for gravimetric measurements by weighing at least one ASTM E617–13 Class 2 tolerance (or better) calibration weight that corresponds to 50 to 150 percent of the weight of one filter or between 1g and 5g. If the scale cannot reproduce the value of the calibration weight to within 0.5 mg of the certified mass, perform corrective measures, and conduct the multipoint calibration before use.

11.0 Analytical Procedure

11.1 Record the data required on a sheet such as the one shown in Figure 5–6.

11.2 Handle each sample container as follows:

11.2.1 Container No. 1. Leave the contents in the shipping container or transfer the filter and any loose PM from the sample container to a tared glass weighing dish. Desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh to a constant weight, and report the results to the nearest 0.1 mg. For the purposes of this section, the term ''constant weight'' means a difference of no more than 0.5 mg or 1 percent of total weight less tare weight, whichever is greater, between two consecutive weighings, with no less than 6 hours of desiccation time between weighings. Alternatively, the sample may be oven dried at 104 °C (220 °F) for 2 to 3 hours, cooled in the desiccator, and weighed to a constant weight, unless otherwise specified by the Administrator. The sample may be oven dried at 104 °C (220 °F) for 2 to 3 hours. Once the

sample has cooled, weigh the sample, and use this weight as a final weight.

11.2.2 Container No. 2. Note the level of liquid in the container, and confirm on the analysis sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to ±1 ml or gravimetrically to ±0.5 g. Transfer the contents to a tared 250 ml beaker, and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours, and weigh to a constant weight. Report the results to the nearest 0.1 mg.

11.2.3 Container No. 3. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. This step may be conducted in the field.

11.2.4 Acetone Blank Container. Measure the acetone in this container either volumetrically or gravimetrically. Transfer the acetone to a tared 250 ml beaker, and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours, and weigh to a constant weight. Report the results to the nearest 0.1 mg.

NOTE: The contents of Container No. 2 as well as the acetone blank container may be evaporated at temperatures higher than ambient. If evaporation is done at an elevated temperature, the temperature must be below the boiling point of the solvent; also, to prevent ''bumping,'' the evaporation process must be closely supervised, and the contents of the beaker must be swirled occasionally to maintain an even temperature. Use extreme care, as acetone is highly flammable and has a low flash point.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used, provided that they give equivalent results.

12.1 Nomenclature.

A_n = Cross-sectional area of nozzle, m^2 (ft^2).
B_{ws} = Water vapor in the gas stream, proportion by volume.
C_a = Acetone blank residue concentration, mg/mg.
c_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (gr/dscf).
I = Percent of isokinetic sampling.
L_1 = Individual leakage rate observed during the leak-check conducted prior to the first component change, m^3/min (ft^3/min)
L_a = Maximum acceptable leakage rate for either a pretest leak-check or for a leak-check following a component change; equal to 0.00057 m^3/min (0.020 cfm) or 4 percent of the average sampling rate, whichever is less.
L_i = Individual leakage rate observed during the leak-check conducted prior to the ''i^{th}'' component change (i = 1, 2, 3 . . . n), m^3/min (cfm).
L_p = Leakage rate observed during the post-test leak-check, m^3/min (cfm).
m_a = Mass of residue of acetone after evaporation, mg.
m_n = Total amount of particulate matter collected, mg.
M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).
P_s = Absolute stack gas pressure, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
R = Ideal gas constant, 0.06236 ((mm Hg)(m^3))/((K)(g-mole)) {21.85 ((in. Hg) (ft^3))/((°R)(lb-mole))}.
T_m = Absolute average DGM temperature (see Figure 5–3), K (°R).
T_s = Absolute average stack gas temperature (see Figure 5–3), K (°R).
T_{std} = Standard absolute temperature, 293 K (528 °R).
V_a = Volume of acetone blank, ml.
V_{aw} = Volume of acetone used in wash, ml.
V_{1c} = Total volume of liquid collected in impingers and silica gel (see Figure 5–6), ml.
V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).
$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).
$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).
V_s = Stack gas velocity, calculated by Method 2, Equation 2–7, using data obtained from Method 5, m/sec (ft/sec).
W_a = Weight of residue in acetone wash, mg.
Y = Dry gas meter calibration factor.
ΔH = Average pressure differential across the orifice meter (see Figure 5–4), mm H_2O (in. H_2O).
ρ_a = Density of acetone, mg/ml (see label on bottle).
ρ_w = Density of water, 0.9982 g/ml. (0.002201 lb/ml).
θ = Total sampling time, min.
θ_1 = Sampling time interval, from the beginning of a run until the first component change, min.
θ_i = Sampling time interval, between two successive component changes, beginning with the interval between the first and second changes, min.
θ_p = Sampling time interval, from the final (n^{th}) component change until the end of the sampling run, min.
13.6 = Specific gravity of mercury.
60 = Sec/min.

100 = Conversion to percent.

12.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 5–3).

12.3 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (20 °C, 760 mm Hg or 68 °F, 29.92 in. Hg) by using Equation 5–1.

$$V_{m(std)} = V_m Y \frac{T_{std}\left(P_{bar} + \frac{\Delta H}{13.6}\right)}{T_m P_{std}} \qquad \text{Eq. 5-1}$$

$$= K_1 V_m Y \frac{P_{bar} + \left(\frac{\Delta H}{13.6}\right)}{T_m}$$

Where:

K_1 = 0.3858 °K/mm Hg for metric units, = 17.64 °R/in. Hg for English units.

NOTE: Equation 5–1 can be used as written unless the leakage rate observed during any of the mandatory leak checks (*i.e.*, the post-test leak check or leak checks conducted prior to component changes) exceeds L_a. If L_p or L_i exceeds L_a, Equation 5–1 must be modified as follows:

(a) Case I. No component changes made during sampling run. In this case, replace V_m in Equation 5–1 with the expression:

$$\left(V_m - \left(L_p - L_a\right)\theta\right)$$

(b) Case II. One or more component changes made during the sampling run. In this case, replace V_m in Equation 5–1 by the expression:

$$\left[V_m - \left(L_1 - L_a\right)\theta_1 - \sum_{i=2}^{n}\left(L_1 - L_a\right)\theta_i - \left(L_p - L_a\right)\theta_p\right]$$

and substitute only for those leakage rates (L_i or L_p) which exceed L_a.

12.4 Volume of Water Vapor Condensed.

$$V_{w(std)} = V_{1c}\frac{\rho_w R T_{std}}{M_w P_{std}} \qquad \text{Eq. 5-2}$$

$$= K_2 V_{1c}$$

Where:

K_2 = 0.001333 m^3/ml for metric units, = 0.04706 ft^3/ml for English units.

12.5 Moisture Content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad \text{Eq. 5-3}$$

NOTE: In saturated or water droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation 5–3), and a second from the assumption of saturated conditions. The lower of the two values of B_{ws} shall be considered correct. The procedure for determining the moisture content based upon the assumption of saturated conditions is given in section 4.0 of Method 4. For the purposes of this method, the average stack gas temperature from Figure 5–3 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is ±1 °C (2 °F).

12.6 Acetone Blank Concentration.

$$C_a = \frac{m_a}{V_a \rho_a} \qquad \text{Eq. 5-4}$$

12.7 Acetone Wash Blank.

$$W_a = C_a V_{aw} \rho_a \qquad \text{Eq. 5-5}$$

12.8 Total Particulate Weight. Determine the total particulate matter catch from the sum of the weights obtained from Containers 1 and 2 less the acetone blank (see Figure 5–6).

NOTE: In no case shall a blank value of greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight. Refer to section 8.5.8 to assist in calculation of results involving two or more filter assemblies or two or more sampling trains.

12.9 Particulate Concentration.

$$C_s = \frac{K_3 m_n}{V_{m(std)}} \qquad \text{Eq. 5-6}$$

Where:

K_3 = 0.001 g/mg for metric units.
= 0.0154 gr/mg for English units.

12.10 Conversion Factors:

From	To	Multiply by
ft^3	m^3	0.02832
gr	mg	64.80004
gr/ft^3	mg/m^3	2288.4
mg	g	0.001
gr	lb	1.429×10^{-4}

12.11 Isokinetic Variation.

12.11.1 Calculation from Raw Data.

$$I = \frac{100\,T_s\left[K_4 V_{1c} + \frac{(V_m Y)}{T_m}\left(P_{bar} + \frac{\Delta H}{13.6}\right)\right]}{60\,\theta\,v_s\,P_s\,A_n} \qquad \text{Eq. 5-7}$$

Where:

K_4 = 0.003454 ((mm Hg)(m^3))/((ml)(°K)) for metric units,
= 0.002669 ((in. Hg)(ft^3))/((ml)(°R)) for English units.

12.11.2 Calculation from Intermediate Values.

$$I = \frac{T_s V_{m(std)} P_{std} 100}{T_{std} v_s \theta A_n P_s 60\left(1 - B_{ws}\right)} \qquad \text{Eq. 5-8}$$

$$= K_5 \frac{T_s V_{m(std)}}{P_s v_s A_n \theta\left(1 - B_{ws}\right)}$$

Where:

K_5 = 4.320 for metric units,
= 0.09450 for English units.

12.11.3 Acceptable Results. If 90 percent ≤I ≤110 percent, the results are acceptable. If the PM results are low in comparison to the standard, and ''I'' is over 110 percent or less than 90 percent, the Administrator may opt to accept the results. Reference 4 in section 17.0 may be used to make acceptability judgments. If ''I'' is judged to be unacceptable, reject the results, and repeat the sampling run.

12.12 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate, if needed, using data obtained in this method and the equations in sections 12.3 and 12.4 of Method 2.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Dry Gas Meter as a Calibration Standard. A DGM may be used as a calibration standard for volume measurements in place of the wet test meter specified in section 10.3, provided that it is calibrated initially and recalibrated periodically as follows:

16.1.1 Standard Dry Gas Meter Calibration.

16.1.1.1. The DGM to be calibrated and used as a secondary reference meter should be of high quality and have an appropriately sized capacity (*e.g.*, 3 liters/rev (0.1 ft^3/rev)). A spirometer (400 liters (14 ft^3) or more capacity), or equivalent, may be used for this calibration, although a wet test meter is usually more practical. The wet test meter should have a capacity of 30 liters/rev (1 ft^3/rev) and capable of measuring volume to within 1.0 percent. Wet test meters should be checked against a spirometer or a liquid displacement meter to ensure the accuracy of the wet test meter. Spirometers or wet test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained.

16.1.1.2 Set up the components as shown in Figure 5–7. A spirometer, or equivalent, may be used in place of the wet test meter in the system. Run the pump for at least 5 minutes at a flow rate of about 10 liters/min (0.35 cfm) to condition the interior surface of the wet test meter. The pressure drop indicated by the manometer at the inlet side of the DGM should be minimized (no greater than 100 mm

H_2O (4 in. H_2O) at a flow rate of 30 liters/min (1 cfm)). This can be accomplished by using large diameter tubing connections and straight pipe fittings.

16.1.1.3 Collect the data as shown in the example data sheet (see Figure 5–8). Make triplicate runs at each of the flow rates and at no less than five different flow rates. The range of flow rates should be between 10 and 34 liters/min (0.35 and 1.2 cfm) or over the expected operating range.

16.1.1.4 Calculate flow rate, Q, for each run using the wet test meter volume, V_w, and the run time, θ. Calculate the DGM coefficient, Y_{ds}, for each run. These calculations are as follows:

$$Q = K_1 \frac{P_{bar} V_w}{(T_w + T_{std})\theta} \qquad \text{Eq. 5-9}$$

$$Y_{ds} = \frac{V_w (T_{ds} + T_{std}) P_{bar}}{V_{ds} (T_w + T_{std}) \left(P_{bar} + \frac{\Delta p}{13.6} \right)} \qquad \text{Eq. 5-10}$$

Where:

K_1 = 0.3858 °C/mm Hg for metric units = 17.64 °F/in. Hg for English units.
V_W = Wet test meter volume, liter (ft^3).
V_{ds} = Dry gas meter volume, liter (ft^3).
T_{ds} = Average dry gas meter temperature, °C (°F).
T_{adj} = 273 °C for metric units = 460 °F for English units.
T_W = Average wet test meter temperature, °C (°F)
P_{bar} = Barometric pressure, mm Hg (in. Hg).
Δp = Dry gas meter inlet differential pressure, mm H_2O (in. H_2O).
θ = Run time, min.

16.1.1.5 Compare the three Y_{ds} values at each of the flow rates and determine the maximum and minimum values. The difference between the maximum and minimum values at each flow rate should be no greater than 0.030. Extra sets of triplicate runs may be made in order to complete this requirement. In addition, the meter coefficients should be between 0.95 and 1.05. If these specifications cannot be met in three sets of successive triplicate runs, the meter is not suitable as a calibration standard and should not be used as such. If these specifications are met, average the three Y_{ds} values at each flow rate resulting in no less than five average meter coefficients, Y_{ds}.

16.1.1.6 Prepare a curve of meter coefficient, Y_{ds}, versus flow rate, Q, for the DGM. This curve shall be used as a reference when the meter is used to calibrate other DGMs and to determine whether recalibration is required.

16.1.2 Standard Dry Gas Meter Recalibration.

16.1.2.1 Recalibrate the standard DGM against a wet test meter or spirometer annually or after every 200 hours of operation, whichever comes first. This requirement is valid provided the standard DGM is kept in a laboratory and, if transported, cared for as any other laboratory instrument. Abuse to the standard meter may cause a change in the calibration and will require more frequent recalibrations.

16.1.2.2 As an alternative to full recalibration, a two-point calibration check may be made. Follow the same procedure and equipment arrangement as for a full recalibration, but run the meter at only two flow rates [suggested rates are 14 and 30 liters/min (0.5 and 1.0 cfm)]. Calculate the meter coefficients for these two points, and compare the values with the meter calibration curve. If the two coefficients are within 1.5 percent of the calibration curve values at the same flow rates, the meter need not be recalibrated until the next date for a recalibration check.

16.2 Critical Orifices As Calibration Standards. Critical orifices may be used as calibration standards in place of the wet test meter specified in section 16.1, provided that they are selected, calibrated, and used as follows:

16.2.1 Selection of Critical Orifices.

16.2.1.1 The procedure that follows describes the use of hypodermic needles or stainless steel needle tubings which have been found suitable for use as critical orifices. Other materials and critical orifice designs may be used provided the orifices act as true critical orifices (*i.e.,* a critical vacuum can be obtained, as described in section 16.2.2.2.3). Select five critical orifices that are appropriately sized to cover the range of flow rates between 10 and 34 liters/min (0.35 and 1.2 cfm) or the expected operating range. Two of the critical orifices should bracket the expected operating range. A minimum of three critical orifices will be needed to calibrate a Method 5 DGM; the other two critical

orifices can serve as spares and provide better selection for bracketing the range of operating flow rates. The needle sizes and tubing lengths shown in Table 5–1 in section 18.0 give the approximate flow rates.

16.2.1.2 These needles can be adapted to a Method 5 type sampling train as follows: Insert a serum bottle stopper, 13 by 20 mm sleeve type, into a ½-inch Swagelok (or equivalent) quick connect. Insert the needle into the stopper as shown in Figure 5–9.

16.2.2 Critical Orifice Calibration. The procedure described in this section uses the Method 5 meter box configuration with a DGM as described in section 6.1.1.9 to calibrate the critical orifices. Other schemes may be used, subject to the approval of the Administrator.

16.2.2.1 Calibration of Meter Box. The critical orifices must be calibrated in the same configuration as they will be used (*i.e.*, there should be no connections to the inlet of the orifice).

16.2.2.1.1 Before calibrating the meter box, leak check the system as follows: Fully open the coarse adjust valve, and completely close the by-pass valve. Plug the inlet. Then turn on the pump, and determine whether there is any leakage. The leakage rate shall be zero (*i.e.*, no detectable movement of the DGM dial shall be seen for 1 minute).

16.2.2.1.2 Check also for leakages in that portion of the sampling train between the pump and the orifice meter. See section 8.4.1 for the procedure; make any corrections, if necessary. If leakage is detected, check for cracked gaskets, loose fittings, worn O-rings, etc., and make the necessary repairs.

16.2.2.1.3 After determining that the meter box is leakless, calibrate the meter box according to the procedure given in section 10.3. Make sure that the wet test meter meets the requirements stated in section 16.1.1.1. Check the water level in the wet test meter. Record the DGM calibration factor, Y.

16.2.2.2 Calibration of Critical Orifices. Set up the apparatus as shown in Figure 5–10.

16.2.2.2.1 Allow a warm-up time of 15 minutes. This step is important to equilibrate the temperature conditions through the DGM.

16.2.2.2.2 Leak check the system as in section 16.2.2.1.1. The leakage rate shall be zero.

16.2.2.2.3 Before calibrating the critical orifice, determine its suitability and the appropriate operating vacuum as follows: Turn on the pump, fully open the coarse adjust valve, and adjust the by-pass valve to give a vacuum reading corresponding to about half of atmospheric pressure. Observe the meter box orifice manometer reading, ΔH. Slowly increase the vacuum reading until a stable reading is obtained on the meter box orifice manometer. Record the critical vacuum for each orifice. Orifices that do not reach a critical value shall not be used.

16.2.2.2.4 Obtain the barometric pressure using a barometer as described in section 6.1.2. Record the barometric pressure, P_{bar}, in mm Hg (in. Hg).

16.2.2.2.5 Conduct duplicate runs at a vacuum of 25 to 50 mm Hg (1 to 2 in. Hg) above the critical vacuum. The runs shall be at least 5 minutes each. The DGM volume readings shall be in increments of complete revolutions of the DGM. As a guideline, the times should not differ by more than 3.0 seconds (this includes allowance for changes in the DGM temperatures) to achieve ±0.5 percent in K′ (see Eq. 5–11). Record the information listed in Figure 5–11.

16.2.2.2.6 Calculate K′ using Equation 5–11.

$$K' = \frac{K_1 V_m Y \left(P_{bar} + \frac{\Delta H}{13.6} \right) T_{amb}^{1/2}}{P_{bar} T_m \theta} \qquad \text{Eq. 5-11}$$

Where:

K′ = Critical orifice coefficient,
$[m^3)(°K)^{1/2}]/$
$[(mm\ Hg)(min)]\ \{[(ft^3)(°R)^{1/2})]\ [(in.\ Hg)(min)]$.
T_{amb} = Absolute ambient temperature, °K (°R).

Calculate the arithmetic mean of the K′ values. The individual K' values should not differ by more than ±0.5 percent from the mean value.

16.2.3 Using the Critical Orifices as Calibration Standards.

16.2.3.1 Record the barometric pressure.

16.2.3.2 Calibrate the metering system according to the procedure outlined in section 16.2.2. Record the information listed in Figure 5–12.

16.2.3.3 Calculate the standard volumes of air passed through the DGM and the critical orifices, and calculate the DGM calibration factor, Y, using the equations below:

$$V_{m(std)} = \frac{K_1 V_m \left[P_{bar} + \left(\frac{\Delta H}{13.6} \right) \right]}{T_m} \qquad \text{Eq. 5-12}$$

$$V_{cr(std)} = K' \frac{P_{bar}\theta}{\sqrt{T_{amb}}} \qquad \text{Eq. 5-13}$$

$$Y = \frac{V_{cr\ (std)}}{V_{m(std)}} \qquad \text{Eq. 5-14}$$

Where:

$V_{cr(std)}$ = Volume of gas sample passed through the critical orifice, corrected to standard conditions, dscm (dscf).

K_1 = 0.3858 K/mm Hg for metric units
= 17.64 °R/in. Hg for English units.

16.2.3.4 Average the DGM calibration values for each of the flow rates. The calibration factor, Y, at each of the flow rates should not differ by more than ±2 percent from the average.

16.2.3.5 To determine the need for recalibrating the critical orifices, compare the DGM Y factors obtained from two adjacent orifices each time a DGM is calibrated; for example, when checking orifice 13/2.5, use orifices 12/10.2 and 13/5.1. If any critical orifice yields a DGM Y factor differing by more than 2 percent from the others, recalibrate the critical orifice according to section 16.2.2.

16.3 Alternative Post-Test Metering System Calibration. The following procedure may be used as an alternative to the post-test calibration described in Section 10.3.2. This alternative procedure does not detect leakages between the inlet of the metering system and the dry gas meter. Therefore, two steps must be included to make it an equivalent alternative:

(1) The metering system must pass the post-test leak-check from either the inlet of the sampling train or the inlet of the metering system. Therefore, if the train fails the former leak-check, another leak-check from the inlet of the metering system must be conducted;

(2) The metering system must pass the leak-check of that portion of the train from the pump to the orifice meter as described in Section 8.4.1.

16.3.1 After each test run, do the following:

16.3.1.1 Ensure that the metering system has passed the post-test leak-check. If not, conduct a leak-check of the metering system from its inlet.

16.3.1.2 Conduct the leak-check of that portion of the train from the pump to the orifice meter as described in Section 10.3.1.1.

16.3.1.3 Calculate Y_{qa} for each test run using the following equation:

$$Y_{qa} = \frac{\theta}{V_m} \sqrt{\frac{0.0319 T_m}{\Delta H@ \left(P_{bar} + \frac{\Delta H_{avg}}{13.6} \right)} \left(\frac{29}{M_d} \right)} \left(\sqrt{\Delta H} \right)_{avg} \qquad \text{Eq. 5-15}$$

Where:

Y_{qa} = Dry gas meter calibration check value, dimensionless.

0.0319 = (29.92/528) (0.75)^2 (in. Hg/°R) cfm^2.

$\Delta H@$ = Orifice meter calibration coefficient, in. H_2O.

M_d = Dry molecular weight of stack gas, lb/lb-mole.

29 = Dry molecular weight of air, lb/lb-mole.

16.3.2 After each test run series, do the following:

16.3.2.1 Average the three or more Y_{qa}'s obtained from the test run series and compare this average Y_{qa} with the dry gas meter calibration factor Y. The average Y_{qa} must be within 5 percent of Y.

16.3.2.2 If the average Y_{qa} does not meet the 5 percent criterion, recalibrate the meter

over the full range of orifice settings as detailed in Section 10.3.1. Then follow the procedure in Section 10.3.3.

17.0 References.

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13. Shigehara, Roger T., P.G. Royals, and E.W. Steward. ''Alternative Method 5 Post-Test Calibration.'' Entropy Incorporated, Research Triangle Park, NC 27709.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 5–1 FLOR RATES FOR VARIOUS NEEDLE SIZES AND TUBE LENGTHS

Gauge/cm	Flow rate liters/min.	Gauge/cm	Flow rate liters/min.
12/7.6	32.56	14/2.5	19.54
12/10.2	30.02	14/5.1	17.27
13/2.5	25.77	14/7.6	16.14
13/5.1	23.50	15/3.2	14.16
13/7.6	22.37	15/7.6	11.61
13/10.2	20.67	15/10.2	10.48

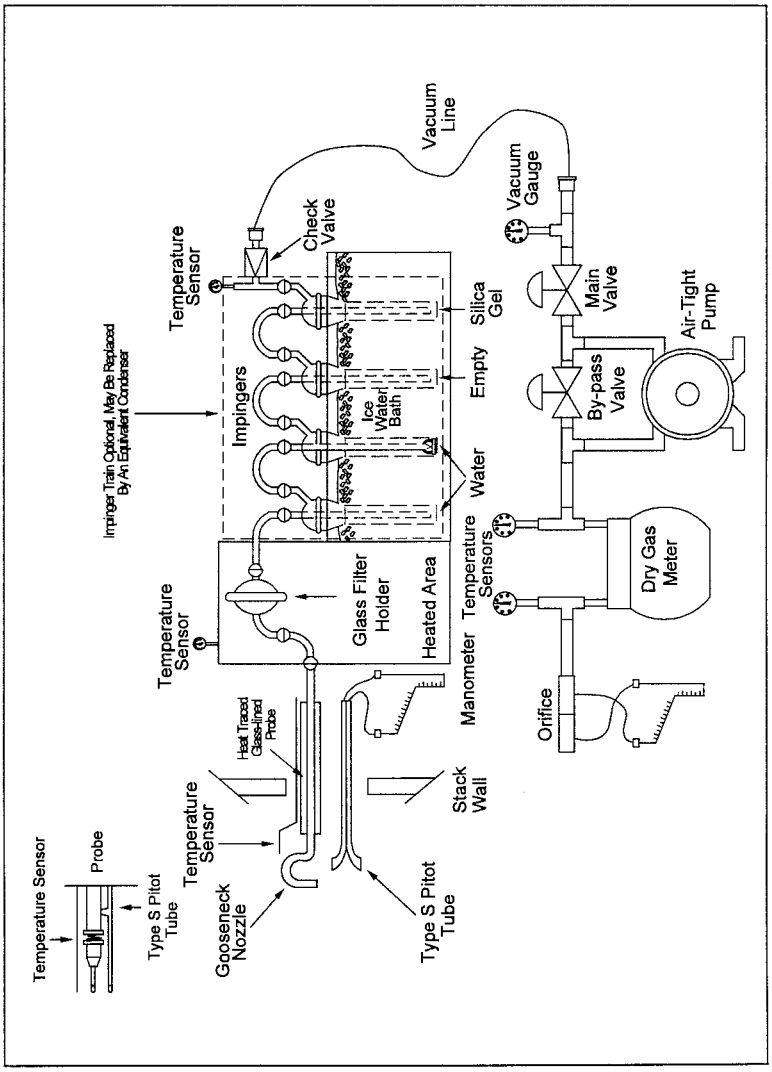


Figure 5-1. Particulate Sampling Train.

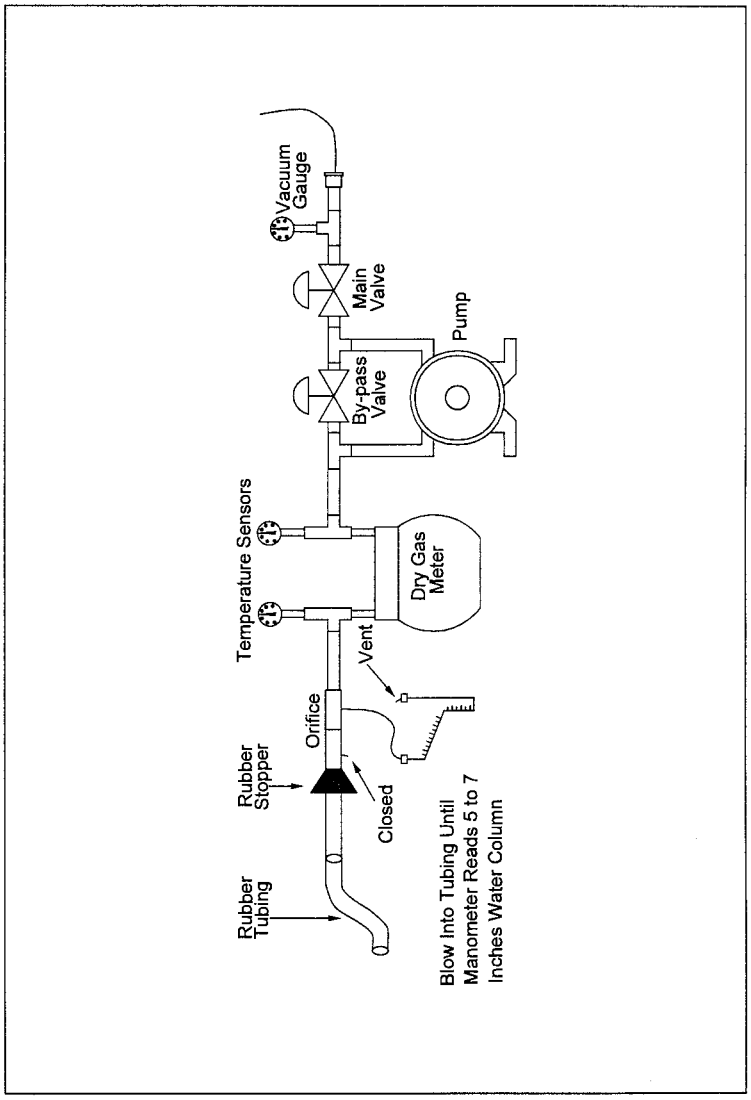


Figure 5-2. Leak Check of Meter Box.

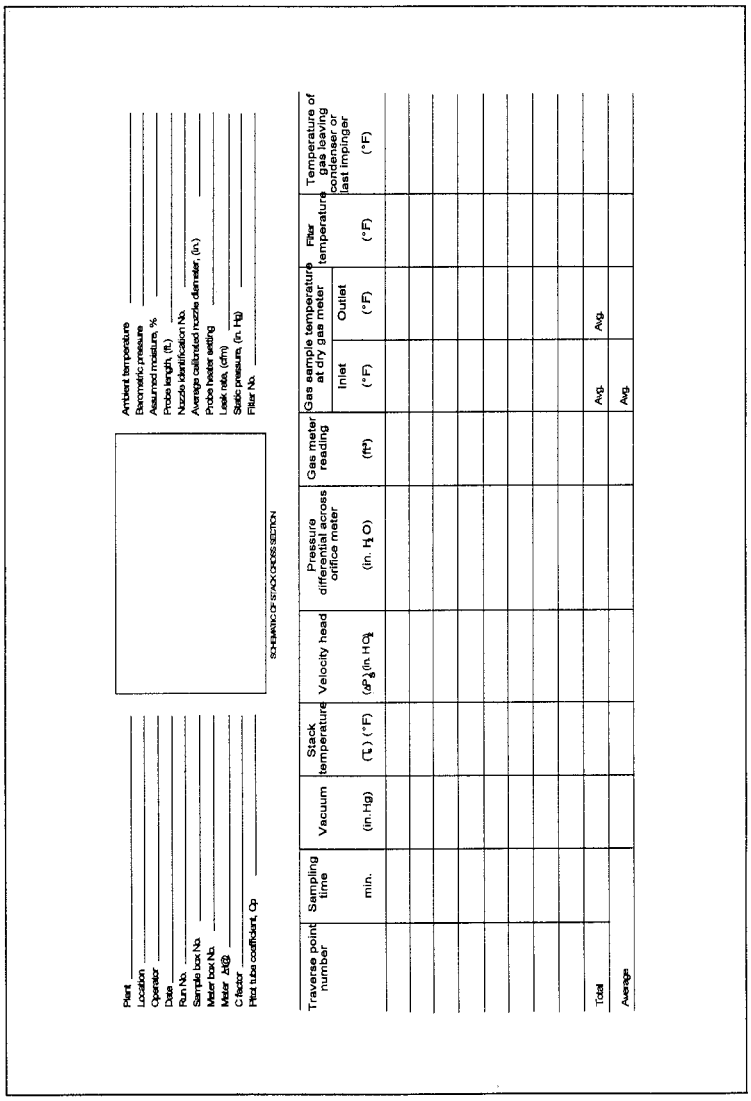


Figure 5-3. Particulate Field Data.

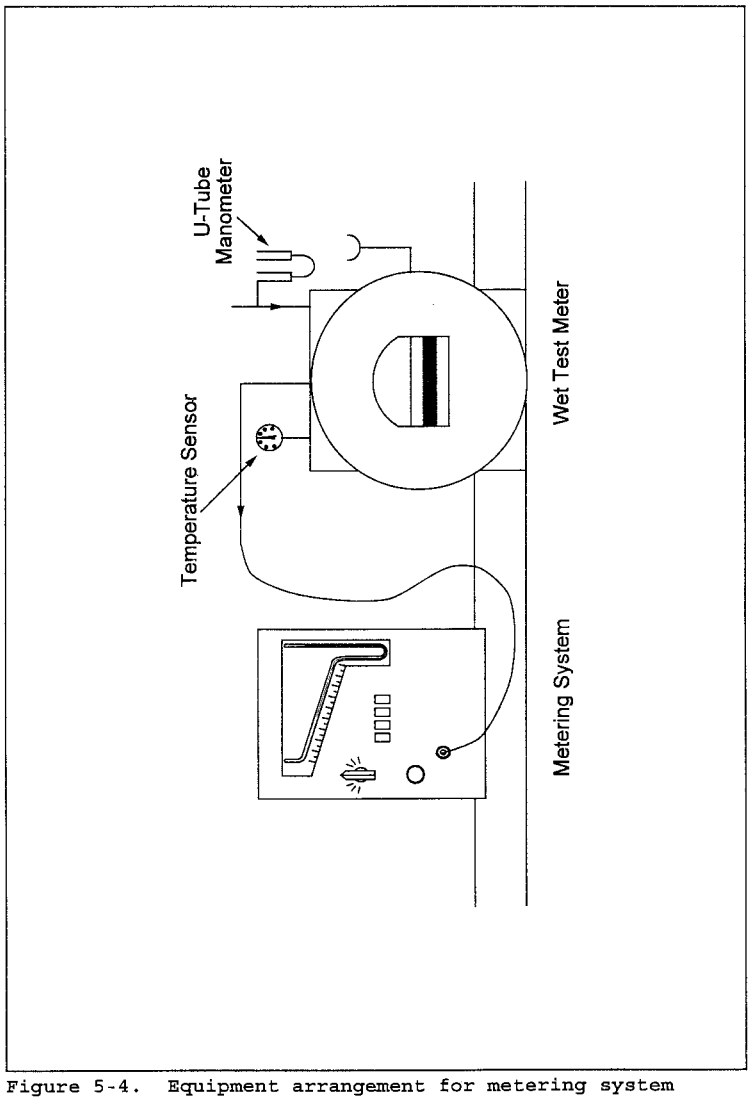


Figure 5-4. Equipment arrangement for metering system calibration.

Date: _____ Metering System Identification: _____
Barometric pressure, P_b = _____ in. Hg

Orifice manometer setting ΔH in. H_2O	Spirometer (wet meter) gas volume, V_w, ft^3	Dry gas meter volume, V_m, ft^3	Temperatures: Spirometer (wet meter) T_w °F	Temperatures: Dry Gas Meter Inlet T_i °F	Temperatures: Dry Gas Meter Outlet T_o °F	Temperatures: Dry Gas Meter Average T_m °F	Time θ min
Average							

Calculations

ΔH in H_2O	Y	ΔH@

Y = Ratio of reading of wet test meter to dry test meter; tolerance for individual values ± 0.02 from average.
$\Delta H_@$ = Orifice pressure differential that equates to 0.75 cfm of air @ 68°F and 29.92 inches of mercury, in. H_2O; tolerance for individual values ± 0.20 from average.

Figure 5-5. Example Data Sheet for Calibration of Metering System (English Units).

Plant _____
Date _____
Run No. _____
Filter No. _____
Amount liquid lost during transport _____

Acetone blank volume, m1 _____
Acetone blank concentration, mg/mg (Equation 5–4) _____
Acetone wash blank, mg (Equation 5–5) ____

Container number	Weight of particulate collected, mg		
	Final weight	Tare weight	Weight gain
1.			
2.			
Total: Less acetone blank. Weight of particulate matter.			

	Volume of liquid water collected	
	Impinger volume, ml	Silica gel weight, g
Final Initial Liquid collected Total volume collected	.....	g* ml

*Convert weight of water to volume by dividing total weight increase by density of water (1 g/ml).

Figure 5–6. Analytical Data Sheet

$$\frac{\text{Increase, g}}{(1\text{g/ml})} = \text{Volume water, ml}$$

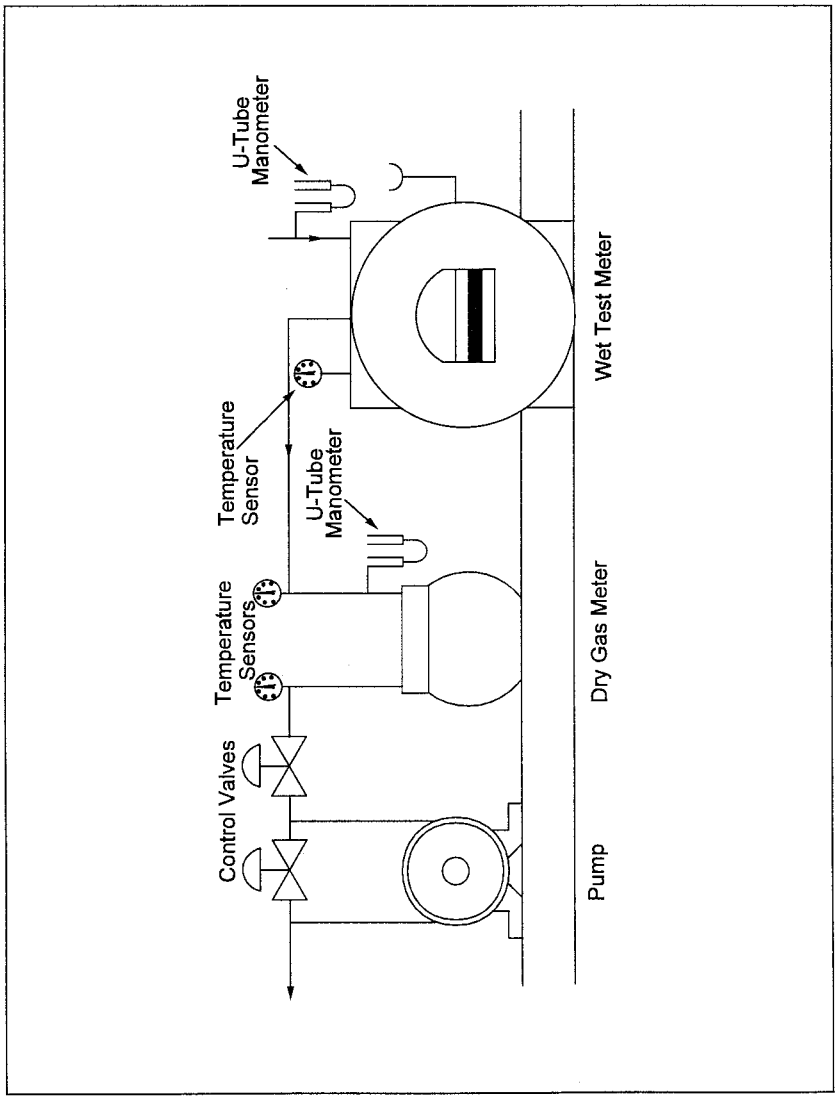


Figure 5-7. Equipment Arrangement for Dry Gas Meter Calibration.

Date: _____

Dry Gas Meter Identification: _____

Barometric Pressure (P): _____ in. Hg

Approximate Flow Rate (Q) cfm	Spirometer (Wet Meter) Gas Volume (V_s) ft³	Dry Gas Meter Volume (V_{dg}) ft³	Temperatures: Spirometer (Wet Meter) (t_g) °F	Temperatures: Dry Gas Meter Inlet (t_i) °F	Temperatures: Dry Gas Meter Outlet (t_o) °F	Temperatures: Dry Gas Meter Average (t_d) °F	Dry Gas Meter Pressure (Δp) in. H_2O	Time (θ) ft³	Flow Rate (Q) cfm	Meter Coefficient (Y_{ds})	Average Meter Coefficient ($\overline{Y}_{ds}$)
0.40											
0.60											
0.80											
1.00											
1.20											

$$Q = K_1 \frac{P_{bar} V_w}{(T_w + T_{std}) \theta}$$

$$Y_{ds} = \frac{V_w (T_{ds} + T_{std}) P_{bar}}{V_{ds} (T_w + T_{std}) (P_{bar} + \Delta P/13.6)}$$

Figure 5-8. Example Data Sheet for Calibration of a Standard Dry Gas Meter for Method 5 Sampling Equipment (English units).

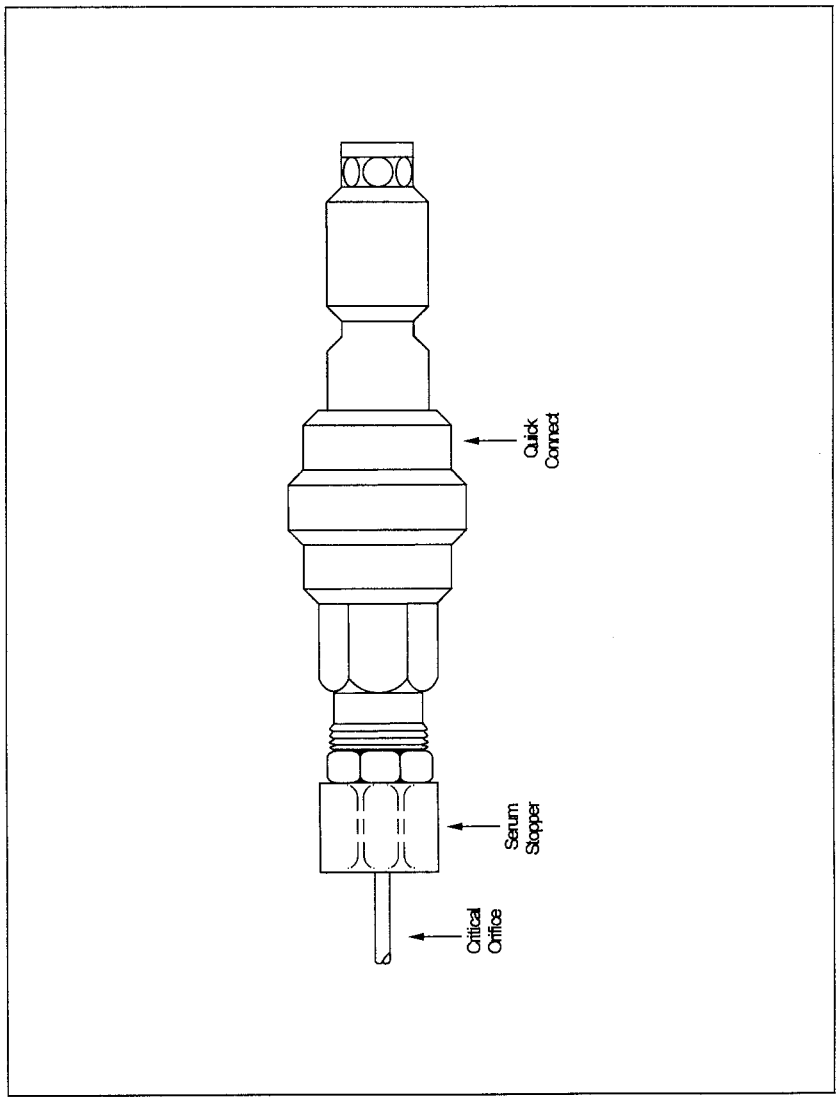


Figure 5-9. Critical Orifice Adaptation to Method 5 Metering System.

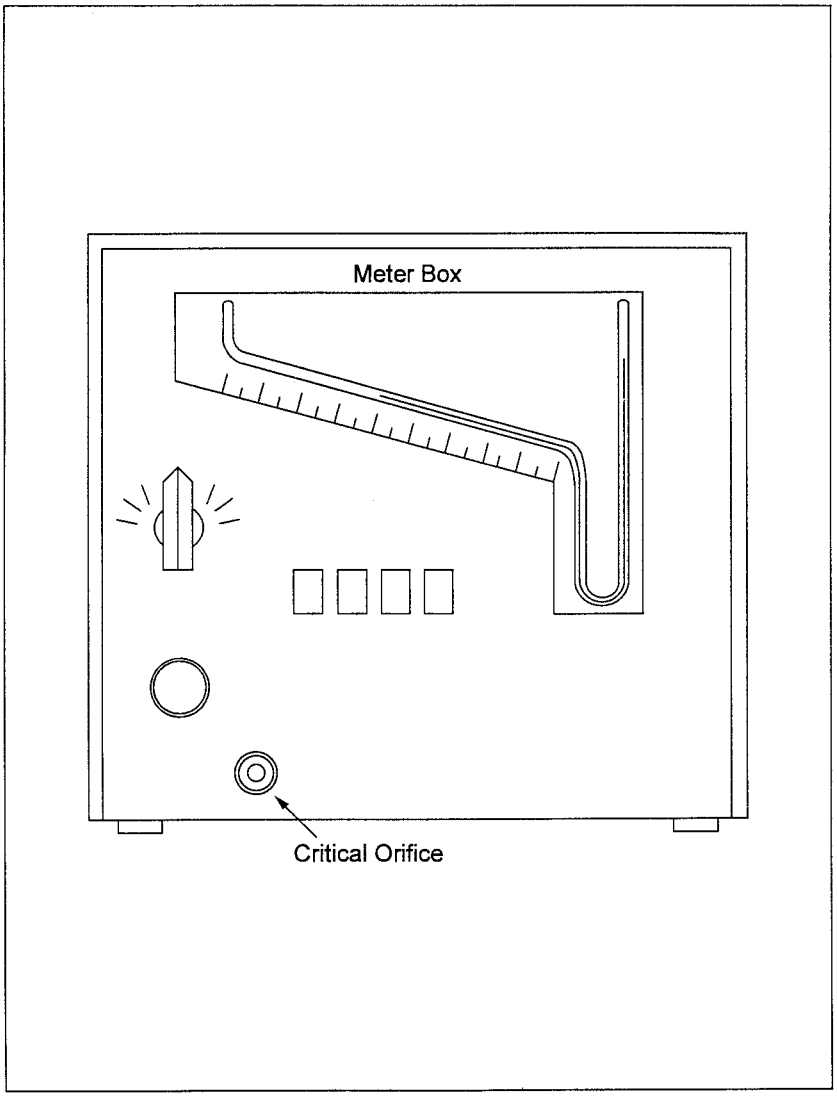


Figure 5-10. Apparatus Setup.

Date _____ DGM cal. factor _____
Train ID _____ Critical orifice ID _____

Dry gas meter		Run No.	
		1	2
Final reading	m^3 (ft^3)		
Initial reading	m^3 (ft^3)		
Difference, V_m	m^3 (ft^3)		
Inlet/Outlet			

Dry gas meter		Run No.	
		1	2
Temperatures:	°C (°F)	/	/
Initial	°C (°F)	/	/
Final	min/sec	/	/
Av. Temeperature, t_m	min		
Time, θ			
Orifice man. rdg., ΔH	mm (in.) H_2		
Bar. pressure, P^{bar}	mm (in.) Hg		
Ambient temperature, t_{amb}	mm (in.) Hg		
Pump vacuum			
K′ factor			
Average			

Figure 5–11. Data sheet of determining K′ factor.

Train ID _____
Critical orifice ID _____
Critical orifice K' factor _____

Date _____

Dry gas meter		Run No.	
		1	2
Final reading	m^3 (ft^3)		
Initial reading	m^3 (ft^3)		
Difference, V_m	m^3 (ft^3)		
Inlet/outlet temperatures	°C (°F)	/	/
Initial	°C (°F)	/	/
Final	°C (°F)		
Avg. Temperature, t_m	min/sec	/	/
Time, θ	min		
Orifice man. rdg., ΔH	min		
Bar. pressure, P_{bar}	mm (in.) H_2O		
Ambient temperature, t_{amb}	mm (in.) Hg		
Pump vacuum	°C (°F)		
$V_{m(std)}$	mm (in.) Hg		
$V_{cr(std)}$	m^3 (ft^3)		
DGM cal. factor, Y	m^3 (ft^3)		

Figure 5–12. Data Sheet for Determining DGM Y Factor

METHOD 5A—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM THE ASPHALT PROCESSING AND ASPHALT ROOFING INDUSTRY

NOTE: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5.

1.0 Scope and Applications

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of PM emissions from asphalt roofing industry process saturators, blowing stills, and other sources as specified in the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature of 42 ±10 °C (108 ±18 °F). The PM mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after the removal of uncombined water.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the

applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 5, section 6.1, with the following exceptions and additions:

6.1.1 Probe Liner. Same as Method 5, section 6.1.1.2, with the note that at high stack gas temperatures greater than 250 °C (480 °F), water-cooled probes may be required to control the probe exit temperature to 42 ±10 °C (108 ±18 °F).

6.1.2 Precollector Cyclone. Borosilicate glass following the construction details shown in Air Pollution Technical Document (APTD)–0581, ''Construction Details of Isokinetic Source-Sampling Equipment'' (Reference 2 in Method 5, section 17.0).

NOTE: The cyclone shall be used when the stack gas moisture is greater than 10 percent, and shall not be used otherwise.

6.1.3 Filter Heating System. Any heating (or cooling) system capable of maintaining a sample gas temperature at the exit end of the filter holder during sampling at 42 ±10 °C (108 ±18 °F).

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Probe-Liner and Probe-Nozzle Brushes, Graduated Cylinder and/or Balance, Plastic Storage Containers, and Funnel and Rubber Policeman. Same as in Method 5, sections 6.2.1, 6.2.5, 6.2.6, and 6.2.7, respectively.

6.2.2 Wash Bottles. Glass.

6.2.3 Sample Storage Containers. Chemically resistant 500-ml or 1,000-ml borosilicate glass bottles, with rubber-backed Teflon screw cap liners or caps that are constructed so as to be leak-free, and resistant to chemical attack by 1,1,1-trichloroethane (TCE). (Narrow-mouth glass bottles have been found to be less prone to leakage.)

6.2.4 Petri Dishes. Glass, unless otherwise specified by the Administrator.

6.2.5 Funnel. Glass.

6.3 Sample Analysis. Same as Method 5, section 6.3, with the following additions:

6.3.1 Beakers. Glass, 250-ml and 500-ml.

6.3.2 Separatory Funnel. 100-ml or greater.

7.0. Reagents and Standards

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Filters, Silica Gel, Water, and Crushed Ice. Same as in Method 5, sections 7.1.1, 7.1.2, 7.1.3, and 7.1.4, respectively.

7.1.2 Stopcock Grease. TCE-insoluble, heat-stable grease (if needed). This is not necessary if screw-on connectors with Teflon sleeves, or similar, are used.

7.2 Sample Recovery. Reagent grade TCE, ≤0.001 percent residue and stored in glass bottles. Run TCE blanks before field use, and use only TCE with low blank values (≤0.001 percent). In no case shall a blank value of greater than 0.001 percent of the weight of TCE used be subtracted from the sample weight.

7.3 Analysis. Two reagents are required for the analysis:

7.3.1 TCE. Same as in section 7.2.

7.3.2 Desiccant. Same as in Method 5, section 7.3.2.

8.0. Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation. Unless otherwise specified, maintain and calibrate all components according to the procedure described in APTD–0576, ''Maintenance, Calibration, and Operation of Isokinetic Source-Sampling Equipment'' (Reference 3 in Method 5, Section 17.0). Alternative mercury-free thermometers may be used if the thermometers are, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

8.1.1 Prepare probe liners and sampling nozzles as needed for use. Thoroughly clean each component with soap and water followed by a minimum of three TCE rinses. Use the probe and nozzle brushes during at least one of the TCE rinses (refer to section 8.7 for rinsing techniques). Cap or seal the open ends of the probe liners and nozzles to prevent contamination during shipping.

8.1.2 Prepare silica gel portions and glass filters as specified in Method 5, section 8.1.

8.2 Preliminary Determinations. Select the sampling site, probe nozzle, and probe length as specified in Method 5, section 8.2. Select a total sampling time greater than or equal to the minimum total sampling time specified in the ''Test Methods and Procedures'' section of the applicable subpart of the regulations. Follow the guidelines outlined in Method 5, section 8.2 for sampling time per point and total sample volume collected.

8.3 Preparation of Sampling Train. Prepare the sampling train as specified in Method 5, section 8.3, with the addition of the precollector cyclone, if used, between the probe and filter holder. The temperature of the precollector cyclone, if used, should be maintained in the same range as that of the filter, *i.e.*, 42 ±10 °C (108 ±18 °F). Use no stopcock grease on ground glass joints unless grease is insoluble in TCE.

8.4 Leak-Check Procedures. Same as Method 5, section 8.4.

8.5 Sampling Train Operation. Operate the sampling train as described in Method 5, section 8.5, except maintain the temperature of the gas exiting the filter holder at 42 ±10 °C (108 ±18 °F).

8.6 Calculation of Percent Isokinetic. Same as Method 5, section 8.6.

8.7 Sample Recovery. Same as Method 5, section 8.7.1 through 8.7.6.1, with the addition of the following:

8.7.1 Container No. 2 (Probe to Filter Holder).

8.7.1.1 Taking care to see that material on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover PM or any condensate from the probe nozzle, probe fitting, probe liner, precollector cyclone and collector flask (if used), and front half of the filter holder by washing these components with TCE and placing the wash in a glass container. Carefully measure the total amount of TCE used in the rinses. Perform the TCE rinses as described in Method 5, section 8.7.6.2, using TCE instead of acetone.

8.7.1.2 Brush and rinse the inside of the cyclone, cyclone collection flask, and the front half of the filter holder. Brush and rinse each surface three times or more, if necessary, to remove visible PM.

8.7.2 Container No. 3 (Silica Gel). Same as in Method 5, section 8.7.6.3.

8.7.3 Impinger Water. Same as Method 5, section 8.7.6.4.

8.8 Blank. Save a portion of the TCE used for cleanup as a blank. Take 200 ml of this TCE directly from the wash bottle being used, and place it in a glass sample container labeled ''TCE Blank.''

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4, 10.0	Sampling equipment leak check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.

9.2 A quality control (QC) check of the volume metering system at the field site is suggested before collecting the sample. Use the procedure outlined in Method 5, section 9.2.

10.0 Calibration and Standardization

Same as Method 5, section 10.0.

11.0 Analytical Procedures

11.1 Analysis. Record the data required on a sheet such as the one shown in Figure 5A–1. Handle each sample container as follows:

11.1.1 Container No. 1 (Filter). Transfer the filter from the sample container to a tared glass weighing dish, and desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Rinse Container No. 1 with a measured amount of TCE, and analyze this rinse with the contents of Container No. 2. Weigh the filter to a constant weight. For the purpose of this analysis, the term ''constant weight'' means a difference of no more than 10 percent of the net filter weight or 2 mg (whichever is greater) between two consecutive weighings made 24 hours apart. Report the ''final weight'' to the nearest 0.1 mg as the average of these two values.

11.1.2 Container No. 2 (Probe to Filter Holder).

11.1.2.1 Before adding the rinse from Container No. 1 to Container No. 2, note the level of liquid in Container No. 2, and confirm on the analysis sheet whether leakage occurred during transport. If noticeable leakage occurred, either void the sample or take steps, subject to the approval of the Administrator, to correct the final results.

11.1.2.2 Add the rinse from Container No. 1 to Container No. 2 and measure the liquid in this container either volumetrically to ±1 ml or gravimetrically to ±0.5 g. Check to see whether there is any appreciable quantity of condensed water present in the TCE rinse (look for a boundary layer or phase separation). If the volume of condensed water appears larger than 5 ml, separate the oil-TCE fraction from the water fraction using a separatory funnel. Measure the volume of the water phase to the nearest ml; adjust the stack gas moisture content, if necessary (see sections 12.3 and 12.4). Next, extract the water phase with several 25-ml portions of TCE until, by visual observation, the TCE does not remove any additional organic material. Transfer the remaining water fraction to a tared beaker and evaporate to dryness at 93 °C (200 °F), desiccate for 24 hours, and weigh to the nearest 0.1 mg.

11.1.2.3 Treat the total TCE fraction (including TCE from the filter container rinse and water phase extractions) as follows: Transfer the TCE and oil to a tared beaker, and evaporate at ambient temperature and pressure. The evaporation of TCE from the solution may take several days. Do not desiccate the sample until the solution reaches an apparent constant volume or until the odor of TCE is not detected. When it appears that the TCE has evaporated, desiccate the sample, and weigh it at 24-hour intervals to obtain a ''constant weight'' (as defined for Container No. 1 above). The ''total weight'' for Container No. 2 is the sum of the evaporated PM weight of the TCE-oil and water phase fractions. Report the results to the nearest 0.1 mg.

11.1.3 Container No. 3 (Silica Gel). This step may be conducted in the field. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance.

11.1.4 ''TCE Blank'' Container. Measure TCE in this container either volumetrically or gravimetrically. Transfer the TCE to a tared 250-ml beaker, and evaporate to dryness at ambient temperature and pressure.

Desiccate for 24 hours, and weigh to a constant weight. Report the results to the nearest 0.1 mg.

NOTE: In order to facilitate the evaporation of TCE liquid samples, these samples may be dried in a controlled temperature oven at temperatures up to 38 °C (100 °F) until the liquid is evaporated.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

12.1 Nomenclature. Same as Method 5, section 12.1, with the following additions:

C_t = TCE blank residue concentration, mg/g.
m_t = Mass of residue of TCE blank after evaporation, mg.
V_{pc} = Volume of water collected in precollector, ml.
V_t = Volume of TCE blank, ml.
V_{tw} = Volume of TCE used in wash, ml.
W_t = Weight of residue in TCE wash, mg.
ρ_t = Density of TCE (see label on bottle), g/ml.

12.2 Dry Gas Meter Temperature, Orifice Pressure Drop, and Dry Gas Volume. Same as Method 5, sections 12.2 and 12.3, except use data obtained in performing this test.

12.3 Volume of Water Vapor.

$$V_{w(std)} = K_2\left(V_{1c} + V_{pc}\right) \qquad \text{Eq. 5A-1}$$

Where:

K_2 = 0.001333 m^3/ml for metric units.
= 0.04706 ft^3/ml for English units.

12.4 Moisture Content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad \text{Eq. 5A-2}$$

NOTE: In saturated or water droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger and precollector analysis (Equations 5A–1 and 5A–2) and a second from the assumption of saturated conditions. The lower of the two values of moisture content shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in section 4.0 of Method 4. For the purpose of this method, the average stack gas temperature from Figure 5–3 of Method 5 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is within 1 °C (2 °F).

12.5 TCE Blank Concentration.

$$C_t = \frac{m_t}{V_t \rho_t} \qquad \text{Eq. 5A-3}$$

NOTE: In no case shall a blank value of greater than 0.001 percent of the weight of TCE used be subtracted from the sample weight.

12.6 TCE Wash Blank.

$$W_t = C_t V_{tw} \rho_t \qquad \text{Eq. 5A-4}$$

12.7 Total PM Weight. Determine the total PM catch from the sum of the weights obtained from Containers 1 and 2, less the TCE blank.

12.8 PM Concentration.

$$c_s = K_3 \frac{m_n}{V_{m(std)}} \qquad \text{Eq. 5A-5}$$

Where:

K_3 = 0.001 g/mg for metric units
= 0.0154 gr/mg for English units

12.9 Isokinetic Variation. Same as in Method 5, section 12.11.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 5, section 17.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

Plant _____
Date _____
Run No. _____
Filter No. _____
Amount liquid lost during transport _____
Acetone blank volume, ml _____
Acetone blank concentration, mg/mg (Equation 5–4) _____
Acetone wash blank, mg (Equation 5–5) _____

Container number	Weight of particulate collected, mg		
	Final weight	Tare weight	Weight gain
1.			
2.			
Total: Less acetone blank.			

Container number	Weight of particulate collected, mg		
	Final weight	Tare weight	Weight gain
Weight of particulate matter.			

	Volume of liquid water collected	
	Impinger volume, ml	Silica gel weight, g
Final		
Initial		
Liquid collected		
Total volume collected		g* ml

*Convert weight of water to volume by dividing total weight increase by density of water (1 g/ml).

$$\frac{\text{Increase, g}}{(1\text{g/ml})} = \text{Volume water, ml}$$

METHOD 5B—DETERMINATION OF NONSULFURIC ACID PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5.

1.0 Scope and Application

1.1 Analyte. Nonsulfuric acid particulate matter. No CAS number assigned.

1.2 Applicability. This method is determining applicable for the determination of nonsulfuric acid particulate matter from stationary sources, only where specified by an applicable subpart of the regulations or where approved by the Administrator for a particular application.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature of 160 ±14 °C (320 ±25 °F). The collected sample is then heated in an oven at 160 °C (320 °F) for 6 hours to volatilize any condensed sulfuric acid that may have been collected, and the nonsulfuric acid particulate mass is determined gravimetrically.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

Same as Method 5, section 6.0, with the following addition and exceptions:

6.1 Sample Collection. The probe liner heating system and filter heating system must be capable of maintaining a sample gas temperature of 160 ±14 °C (320 ±25 °F).

6.2 Sample Preparation. An oven is required for drying the sample.

7.0 Reagents and Standards

Same as Method 5, section 7.0.

8.0 Sample Collection, Preservation, Storage, and Transport.

Same as Method 5, with the exception of the following:

8.1 Initial Filter Tare. Oven dry the filter at 160 ±5 °C (320 ±10 °F) for 2 to 3 hours, cool in a desiccator for 2 hours, and weigh. Desiccate to constant weight to obtain the initial tare weight. Use the applicable specifications and techniques of section 8.1.3 of Method 5 for this determination.

8.2 Probe and Filter Temperatures. Maintain the probe outlet and filter temperatures at 160 ±14 °C (320 ±25 °F).

9.0 Quality Control

Same as Method 5, section 9.0.

10.0 Calibration and Standardization

Same as Method 5, section 10.0.

11.0 Analytical Procedure

Same as Method 5, section 11.0, except replace section

11.2.2 With the following:

11.1 Container No. 2. Note the level of liquid in the container, and confirm on the analysis sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to ±1 ml or gravimetrically to ±0.5 g. Transfer the contents to a tared 250 ml beaker, and evaporate to dryness at ambient temperature and pressure. Then oven dry the probe and filter samples at a temperature of 160 ±5 °C (320 ±10 °F) for 6 hours. Cool in a desiccator for 2 hours, and weigh to constant weight. Report the results to the nearest 0.1 mg.

12.0 Data Analysis and Calculations

Same as in Method 5, section 12.0.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 5, section 17.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 5C [RESERVED]

METHOD 5D—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM POSITIVE PRESSURE FABRIC FILTERS

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, Method 17.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability.

1.2.1 This method is applicable for the determination of PM emissions from positive pressure fabric filters. Emissions are determined in terms of concentration (mg/m^3 or gr/ft^3) and emission rate (kg/hr or lb/hr).

1.2.2 The General Provisions of 40 CFR part 60, §60.8(e), require that the owner or operator of an affected facility shall provide performance testing facilities. Such performance testing facilities include sampling ports, safe sampling platforms, safe access to sampling sites, and utilities for testing. It is intended that affected facilities also provide sampling locations that meet the specification for adequate stack length and minimal flow disturbances as described in Method 1. Provisions for testing are often overlooked factors in designing fabric filters or are extremely costly. The purpose of this procedure is to identify appropriate alternative locations and procedures for sampling the emissions from positive pressure fabric filters. The requirements that the affected facility owner or operator provide adequate access to performance testing facilities remain in effect.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature at or above the exhaust gas temperature up to a nominal 120 °C (248 ±25 °F). The particulate mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after the removal of uncombined water.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

Same as section 6.0 of either Method 5 or Method 17.

7.0 Reagents and Standards

Same as section 7.0 of either Method 5 or Method 17.

8.0 Sample Collection, Preservation, Storage, and Transport

Same section 8.0 of either Method 5 or Method 17, except replace section 8.2.1 of Method 5 with the following:

8.1 Determination of Measurement Site. The configuration of positive pressure fabric filter structures frequently are not amenable

to emission testing according to the requirements of Method 1. Following are several alternatives for determining measurement sites for positive pressure fabric filters.

8.1.1 Stacks Meeting Method 1 Criteria. Use a measurement site as specified in Method 1, section 11.1.

8.1.2 Short Stacks Not Meeting Method 1 Criteria. Use stack extensions and the procedures in Method 1. Alternatively, use flow straightening vanes of the ''egg-crate'' type (see Figure 5D–1). Locate the measurement site downstream of the straightening vanes at a distance equal to or greater than two times the average equivalent diameter of the vane openings and at least one-half of the overall stack diameter upstream of the stack outlet.

8.1.3 Roof Monitor or Monovent. (See Figure 5D–2). For a positive pressure fabric filter equipped with a peaked roof monitor, ridge vent, or other type of monovent, use a measurement site at the base of the monovent. Examples of such locations are shown in Figure 5D–2. The measurement site must be upstream of any exhaust point (*e.g.*, louvered vent).

8.1.4 Compartment Housing. Sample immediately downstream of the filter bags directly above the tops of the bags as shown in the examples in Figure 5D–2. Depending on the housing design, use sampling ports in the housing walls or locate the sampling equipment within the compartment housing.

8.2 Determination of Number and Location of Traverse Points. Locate the traverse points according to Method 1, section 11.3. Because a performance test consists of at least three test runs and because of the varied configurations of positive pressure fabric filters, there are several schemes by which the number of traverse points can be determined and the three test runs can be conducted.

8.2.1 Single Stacks Meeting Method 1 Criteria. Select the number of traverse points according to Method 1. Sample all traverse points for each test run.

8.2.2 Other Single Measurement Sites. For a roof monitor or monovent, single compartment housing, or other stack not meeting Method 1 criteria, use at least 24 traverse points. For example, for a rectangular measurement site, such as a monovent, use a balanced 5×5 traverse point matrix. Sample all traverse points for each test run.

8.2.3 Multiple Measurement Sites. Sampling from two or more stacks or measurement sites may be combined for a test run, provided the following guidelines are met:

8.2.3.1 All measurement sites up to 12 must be sampled. For more than 12 measurement sites, conduct sampling on at least 12 sites or 50 percent of the sites, whichever is greater. The measurement sites sampled should be evenly, or nearly evenly, distributed among the available sites; if not, all sites are to be sampled.

8.2.3.2 The same number of measurement sites must be sampled for each test run.

8.2.3.3 The minimum number of traverse points per test run is 24. An exception to the 24-point minimum would be a test combining the sampling from two stacks meeting Method 1 criteria for acceptable stack length, and Method 1 specifies fewer than 12 points per site.

8.2.3.4 As long as the 24 traverse points per test run criterion is met, the number of traverse points per measurement site may be reduced to eight.

8.2.3.5 Alternatively, conduct a test run for each measurement site individually using the criteria in section 8.2.1 or 8.2.2 to determine the number of traverse points. Each test run shall count toward the total of three required for a performance test. If more than three measurement sites are sampled, the number of traverse points per measurement site may be reduced to eight as long as at least 72 traverse points are sampled for all the tests.

8.2.3.6 The following examples demonstrate the procedures for sampling multiple measurement sites.

8.2.3.6.1 Example 1: A source with nine circular measurement sites of equal areas may be tested as follows: For each test run, traverse three measurement sites using four points per diameter (eight points per measurement site). In this manner, test run number 1 will include sampling from sites 1,2, and 3; run 2 will include samples from sites 4, 5, and 6; and run 3 will include sites 7, 8, and 9. Each test area may consist of a separate test of each measurement site using eight points. Use the results from all nine tests in determining the emission average.

8.2.3.6.2 Example 2: A source with 30 rectangular measurement sites of equal areas may be tested as follows: For each of the three test runs, traverse five measurement sites using a 3×3 matrix of traverse points for each site. In order to distribute the sampling evenly over all the available measurement sites while sampling only 50 percent of the sites, number the sites consecutively from 1 to 30 and sample all the even numbered (or odd numbered) sites. Alternatively, conduct a separate test of each of 15 measurement sites using section 8.2.1 or 8.2.2 to determine the number and location of traverse points, as appropriate.

8.2.3.6.3 Example 3: A source with two measurement sites of equal areas may be tested as follows: For each test of three test runs, traverse both measurement sites, using section 8.2.3 in determining the number of traverse points. Alternatively, conduct two full emission test runs for each measurement site using the criteria in section 8.2.1 or 8.2.2 to determine the number of traverse points.

8.2.3.7 Other test schemes, such as random determination of traverse points for a large number of measurement sites, may be used with prior approval from the Administrator.

8.3 Velocity Determination.

8.3.1 The velocities of exhaust gases from positive pressure baghouses are often too low to measure accurately with the type S pitot tube specified in Method 2 (*i.e.*, velocity head <1.3 mm H_2O (0.05 in. H_2O)). For these conditions, measure the gas flow rate at the fabric filter inlet following the procedures outlined in Method 2. Calculate the average gas velocity at the measurement site as shown in section 12.2 and use this average velocity in determining and maintaining isokinetic sampling rates.

8.3.2 Velocity determinations to determine and maintain isokinetic rates at measurement sites with gas velocities within the range measurable with the type S pitot tube (*i.e.*, velocity head greater than 1.3 mm H_2O (0.05 in. H_2O)) shall be conducted according to the procedures outlined in Method 2.

8.4 Sampling. Follow the procedures specified in sections 8.1 through 8.6 of Method 5 or sections 8.1 through 8.25 in Method 17 with the exceptions as noted above.

8.5 Sample Recovery. Follow the procedures specified in section 8.7 of Method 5 or section 8.2 of Method 17.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.0, 10.0	Sampling equipment leak check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

Same as section 10.0 of either Method 5 or Method 17.

11.0 Analytical Procedure

Same as section 11.0 of either Method 5 or Method 17.

12.0 Data Analysis and Calculations

Same as section 12.0 of either Method 5 or Method 17 with the following exceptions:

12.1 Nomenclature.

A_o = Measurement site(s) total cross-sectional area, m^2 (ft^2).

$\bar{C}$ or C_{avg} = Average concentration of PM for all n runs, mg/scm (gr/scf).

Q_i = Inlet gas volume flow rate, m^3/sec (ft^3/sec).

m_i = Mass collected for run i of n, mg (gr).

T_o = Average temperature of gas at measurement site, °K (°R).

T_i = Average temperature of gas at inlet, °K (°R).

Vol_i = Sample volume collected for run i of n, scm (scf).

$\bar{v}$ = Average gas velocity at the measurement site(s), m/s (ft/s)

Q_o = Total baghouse exhaust volumetric flow rate, m^3/sec (ft^3/sec).

Q_d = Dilution air flow rate, m^3/sec (ft^3/sec).

Tamb = Ambient Temperature, (°K).

12.2 Average Gas Velocity. When following section 8.3.1, calculate the average gas velocity at the measurement site as follows:

$$\bar{v} = \frac{Q_o}{A_o} \qquad \text{Eq. 5D-1}$$

12.3 Volumetric Flow Rate. Total volumetric flow rate may be determined as follows:

$$Q_o = Q_i + Q_d \qquad \text{Eq. 5D-2}$$

12.4 Dilution Air Flow Rate.

$$Q_d = \frac{Q_i\left(T_i - T_o\right)}{T_o - T_{amb}} \qquad \text{Eq. 5D-3}$$

12.5 Average PM Concentration. For multiple measurement sites, calculate the average PM concentration as follows:

$$C_{avg} \text{ or } \bar{C} = \frac{\sum_{i=1}^{n} m_i}{\sum_{i=1}^{n} Vol_i} \qquad \text{Eq. 5D-4}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 5, section 17.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

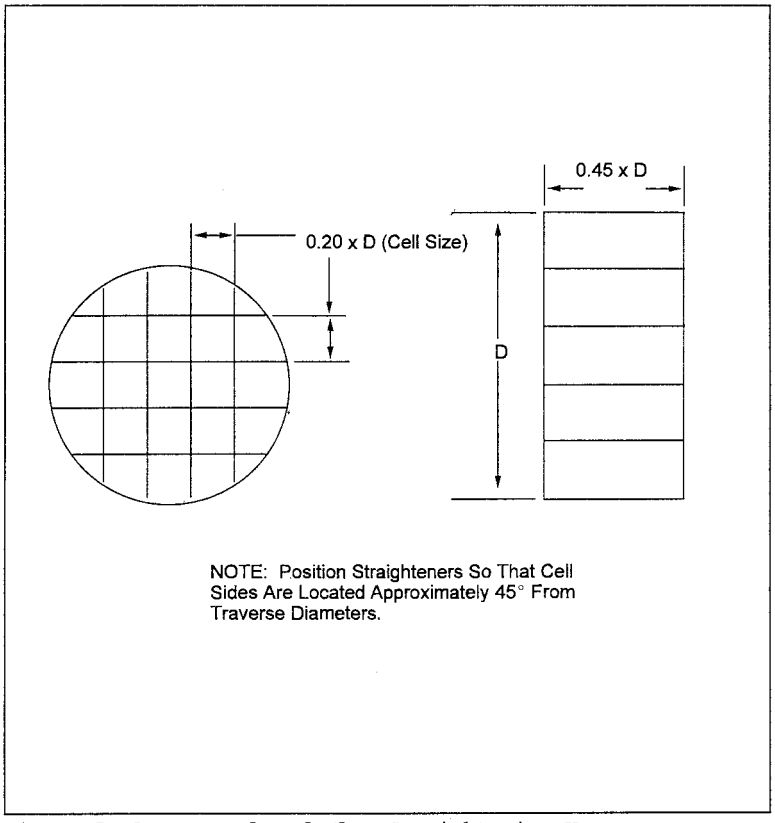


Figure 5D-1. Example of Flow Straightening Vanes.

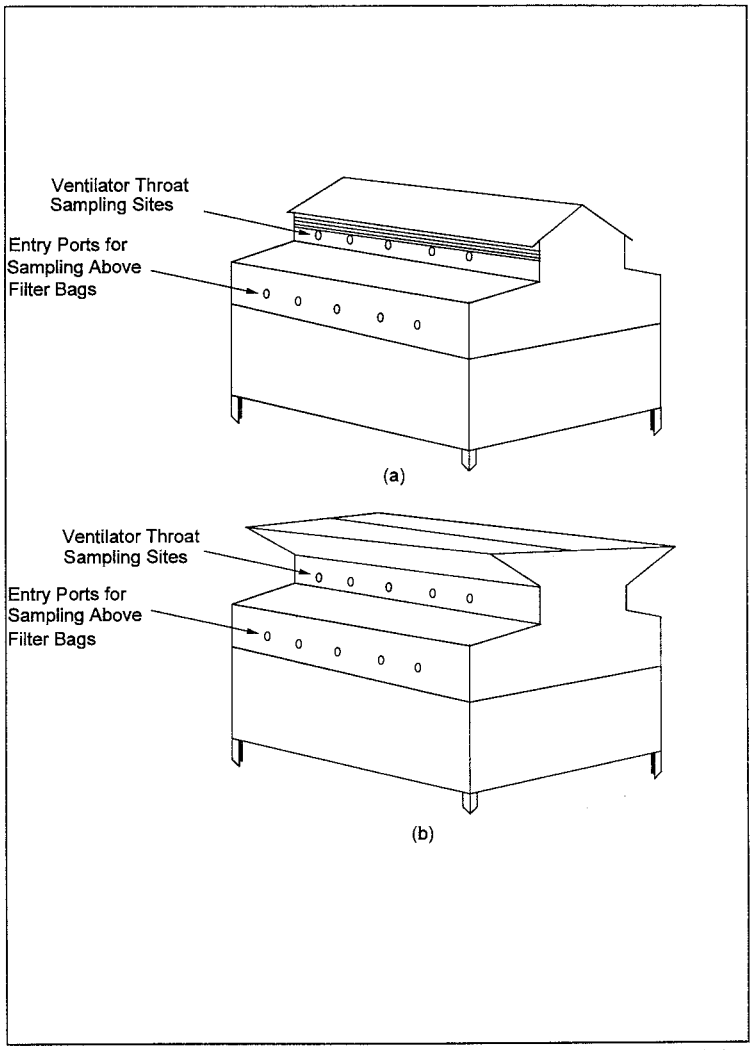


Figure 5D-2. Acceptable Sampling Site Locations for: (a) Peaked Roof; and (b) Ridge Vent Type Fabric Filters

METHOD 5E—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM THE WOOL FIBERGLASS INSULATION MANUFACTURING INDUSTRY

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5.

1.0 Scope and Applications

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of PM emissions from wool fiberglass insulation manufacturing sources.

2.0 Summary of Method

Particulate matter is withdrawn isokinetically from the source and is collected either on a glass fiber filter maintained at a temperature in the range of 120 ±14 °C (248 ±25 °F) and in impingers in solutions of 0.1 N sodium hydroxide (NaOH). The filtered particulate mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after the removal of uncombined water. The condensed PM collected in the impinger solutions is determined as total organic carbon (TOC) using a nondispersive infrared type of analyzer. The sum of the filtered PM mass and the condensed PM is reported as the total PM mass.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Hydrochloric Acid (HCl). Highly toxic. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent in air can be lethal in minutes. Will react with metals, producing hydrogen.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eye tissues and to skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 5, section 6.1, with the exception of the following:

6.1.1 Probe Liner. Same as described in section 6.1.1.2 of Method 5 except use only borosilicate or quartz glass liners.

6.1.2 Filter Holder. Same as described in section 6.1.1.5 of Method 5 with the addition of a leak-tight connection in the rear half of the filter holder designed for insertion of a temperature sensor used for measuring the sample gas exit temperature.

6.2 Sample Recovery. Same as Method 5, section 6.2, except three wash bottles are needed instead of two and only glass storage bottles and funnels may be used.

6.3 Sample Analysis. Same as Method 5, section 6.3, with the additional equipment for TOC analysis as described below:

6.3.1 Sample Blender or Homogenizer. Waring type or ultrasonic.

6.3.2 Magnetic Stirrer.

6.3.3 Hypodermic Syringe. 0- to 100-µl capacity.

6.3.4 Total Organic Carbon Analyzer. Rosemount Model 2100A analyzer or equivalent and a recorder.

6.3.5 Beaker. 30-ml.

6.3.6 Water Bath. Temperature controlled.

6.3.7 Volumetric Flasks. 1000-ml and 500-ml.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 5, section 7.1, with the addition of 0.1 N NaOH (Dissolve 4 g of NaOH in water and dilute to 1 liter).

7.2 Sample Recovery. Same as Method 5, section 7.2, with the addition of the following:

7.2.1 Water. Deionized distilled to conform to ASTM Specification D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17). The potassium permanganate ($KMnO_4$) test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.2.2 Sodium Hydroxide. Same as described in section 7.1.

7.3 Sample Analysis. Same as Method 5, section 7.3, with the addition of the following:

7.3.1 Carbon Dioxide-Free Water. Distilled or deionized water that has been freshly boiled for 15 minutes and cooled to room temperature while preventing exposure to ambient air by using a cover vented with an Ascarite tube.

7.3.2 Hydrochloric Acid. HCl, concentrated, with a dropper.

7.3.3 Organic Carbon Stock Solution. Dissolve 2.1254 g of dried potassium biphthalate ($HOOCC_6H_4COOK$) in CO_2-free water, and dilute to 1 liter in a volumetric flask. This solution contains 1000 mg/L organic carbon.

7.3.4 Inorganic Carbon Stock Solution. Dissolve 4.404 g anhydrous sodium carbonate

(Na_2CO_3.) in about 500 ml of CO_2-free water in a 1-liter volumetric flask. Add 3.497 g anhydrous sodium bicarbonate ($NaHCO_3$) to the flask, and dilute to 1 liter with CO_2 -free water. This solution contains 1000 mg/L inorganic carbon.

7.3.5 Oxygen Gas. CO_2 -free.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation and Preliminary Determinations. Same as Method 5, sections 8.1 and 8.2, respectively.

8.2 Preparation of Sampling Train. Same as Method 5, section 8.3, except that 0.1 N NaOH is used in place of water in the impingers. The volumes of the solutions are the same as in Method 5.

8.3 Leak-Check Procedures, Sampling Train Operation, Calculation of Percent Isokinetic. Same as Method 5, sections 8.4 through 8.6, respectively.

8.4 Sample Recovery. Same as Method 5, sections 8.7.1 through 8.7.4, with the addition of the following:

8.4.1 Save portions of the water, acetone, and 0.1 N NaOH used for cleanup as blanks. Take 200 ml of each liquid directly from the wash bottles being used, and place in glass sample containers labeled ''water blank,'' ''acetone blank,'' and ''NaOH blank,'' respectively.

8.4.2 Inspect the train prior to and during disassembly, and note any abnormal conditions. Treat the samples as follows:

8.4.2.1 Container No. 1. Same as Method 5, section 8.7.6.1.

8.4.2.2 Container No. 2. Use water to rinse the sample nozzle, probe, and front half of the filter holder three times in the manner described in section 8.7.6.2 of Method 5 except that no brushing is done. Put all the water wash in one container, seal, and label.

8.4.2.3 Container No. 3. Rinse and brush the sample nozzle, probe, and front half of the filter holder with acetone as described for Container No. 2 in section 8.7.6.2 of Method 5.

8.4.2.4 Container No. 4. Place the contents of the silica gel impinger in its original container as described for Container No. 3 in section 8.7.6.3 of Method 5.

8.4.2.5 Container No. 5. Measure the liquid in the first three impingers and record the volume or weight as described for the Impinger Water in section 8.7.6.4 of Method 5. Do not discard this liquid, but place it in a sample container using a glass funnel to aid in the transfer from the impingers or graduated cylinder (if used) to the sample container. Rinse each impinger thoroughly with 0.1 N NaOH three times, as well as the graduated cylinder (if used) and the funnel, and put these rinsings in the same sample container. Seal the container and label to clearly identify its contents.

8.5 Sample Transport. Whenever possible, containers should be shipped in such a way that they remain upright at all times.

9.0 Quality Control.

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.3, 10.0	Sampling equipment leak-check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.
10.1.2, 11.2.5.3	Repetitive analyses	Ensures precise measurement of total carbon and inorganic carbon concentration of samples, blank, and standards.
10.1.4	TOC analyzer calibration	Ensures linearity of analyzer response to standards.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

Same as Method 5, section 10.0, with the addition of the following procedures for calibrating the total organic carbon analyzer:

10.1 Preparation of Organic Carbon Standard Curve.

10.1.1 Add 10 ml, 20 ml, 30 ml, 40 ml, and 50 ml of the organic carbon stock solution to a series of five 1000-ml volumetric flasks. Add 30 ml, 40 ml, and 50 ml of the same solution to a series of three 500-ml volumetric flasks. Dilute the contents of each flask to the mark using CO_2-free water. These flasks contain 10, 20, 30, 40, 50, 60, 80, and 100 mg/L organic carbon, respectively.

10.1.2 Use a hypodermic syringe to withdraw a 20- to 50-µl aliquot from the 10 mg/L standard solution and inject it into the total carbon port of the analyzer. Measure the peak height. Repeat the injections until three consecutive peaks are obtained within 10 percent of their arithmetic mean. Repeat this procedure for the remaining organic carbon standard solutions.

10.1.3 Calculate the corrected peak height for each standard by deducting the blank correction (see section 11.2.5.3) as follows:

$$\text{Corrected Peak Height} = A - B \qquad \text{Eq. 5E-1}$$

Where:

A = Peak height of standard or sample, mm or other appropriate unit.

B = Peak height of blank, mm or other appropriate unit.

10.1.4 Prepare a linear regression plot of the arithmetic mean of the three consecutive peak heights obtained for each standard solution against the concentration of that solution. Calculate the calibration factor as the inverse of the slope of this curve. If the product of the arithmetic mean peak height for any standard solution and the calibration factor differs from the actual concentration by more than 5 percent, remake and reanalyze that standard.

10.2 Preparation of Inorganic Carbon Standard Curve. Repeat the procedures outlined in sections 10.1.1 through 10.1.4, substituting the inorganic carbon stock solution for the organic carbon stock solution, and the inorganic carbon port of the analyzer for the total carbon port.

11.0 Analytical Procedure

11.1 Record the data required on a sheet such as the one shown in Figure 5–6 of Method 5.

11.2 Handle each sample container as follows:

11.2.1 Container No. 1. Same as Method 5, section 11.2.1, except that the filters must be dried at 20 ±6 °C (68 ±10 °F) and ambient pressure.

11.2.2 Containers No. 2 and No. 3. Same as Method 5, section 11.2.2, except that evaporation of the samples must be at 20 ±6 °C (68 ±10 °F) and ambient pressure.

11.2.3 Container No. 4. Same as Method 5, section 11.2.3.

11.2.4 ''Water Blank'' and ''Acetone Blank'' Containers. Determine the water and acetone blank values following the procedures for the ''Acetone Blank'' container in section 11.2.4 of Method 5. Evaporate the samples at ambient temperature (20 ±6 °C (68 ±10 °F)) and pressure.

11.2.5 Container No. 5. For the determination of total organic carbon, perform two analyses on successive identical samples, *i.e.*, total carbon and inorganic carbon. The desired quantity is the difference between the two values obtained. Both analyses are based on conversion of sample carbon into carbon dioxide for measurement by a nondispersive infrared analyzer. Results of analyses register as peaks on a strip chart recorder.

11.2.5.1 The principal differences between the operating parameters for the two channels involve the combustion tube packing material and temperature. In the total carbon channel, a high temperature (950 °C (1740 °F)) furnace heats a Hastelloy combustion tube packed with cobalt oxide-impregnated asbestos fiber. The oxygen in the carrier gas, the elevated temperature, and the catalytic effect of the packing result in oxidation of both organic and inorganic carbonaceous material to CO_2, and steam. In the inorganic carbon channel, a low temperature (150 °C (300 °F)) furnace heats a glass tube containing quartz chips wetted with 85 percent phosphoric acid. The acid liberates CO_2 and steam from inorganic carbonates. The operating temperature is below that required to oxidize organic matter. Follow the manufacturer's instructions for assembly, testing, calibration, and operation of the analyzer.

11.2.5.2 As samples collected in 0.1 N NaOH often contain a high measure of inorganic carbon that inhibits repeatable determinations of TOC, sample pretreatment is necessary. Measure and record the liquid volume of each sample (or impinger contents). If the sample contains solids or immiscible liquid matter, homogenize the sample with a blender or ultrasonics until satisfactory repeatability is obtained. Transfer a representative portion of 10 to 15 ml to a 30-ml beaker, and acidify with about 2 drops of concentrated HCl to a pH of 2 or less. Warm the acidified sample at 50 °C (120 °F) in a water bath for 15 minutes.

11.2.5.3 While stirring the sample with a magnetic stirrer, use a hypodermic syringe to withdraw a 20-to 50-µl aliquot from the beaker. Analyze the sample for total carbon and calculate its corrected mean peak height according to the procedures outlined in sections 10.1.2 and 10.1.3. Similarly analyze an aliquot of the sample for inorganic carbon. Repeat the analyses for all the samples and for the 0.1 N NaOH blank.

11.2.5.4 Ascertain the total carbon and inorganic carbon concentrations (C_{TC} and C_{IC}, respectively) of each sample and blank by comparing the corrected mean peak heights for each sample and blank to the appropriate standard curve.

NOTE: If samples must be diluted for analysis, apply an appropriate dilution factor.

12.0 Data Analysis and Calculations

Same as Method 5, section 12.0, with the addition of the following:

12.1 Nomenclature.

C_c = Concentration of condensed particulate matter in stack gas, gas dry basis, corrected to standard conditions, g/dscm (gr/dscf).

C_{IC} = Concentration of condensed TOC in the liquid sample, from section 11.2.5, mg/L.

C_t = Total particulate concentration, dry basis, corrected to standard conditions, g/dscm (gr/dscf).
C_{TC} = Concentration of condensed TOC in the liquid sample, from section 11.2.5, mg/L.
C_{TOC} = Concentration of condensed TOC in the liquid sample, mg/L.
m_{TOC} = Mass of condensed TOC collected in the impingers, mg.
$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, from section 12.3 of Method 5, dscm (dscf).
V_s = Total volume of liquid sample, ml.

12.2 Concentration of Condensed TOC in Liquid Sample.

$$C_{TOC} = C_{TC} - C_{IC} \qquad \text{Eq. 5E-2}$$

12.3 Mass of Condensed TOC Collected.

$$m_{TOC} = 0.001\, C_{TOC} V_s \qquad \text{Eq. 5E-3}$$

Where:

0.001 = Liters per milliliter.

12.4 Concentration of Condensed Particulate Material.

$$C_c = K_4 m_{TOC} / V_{m(std)} \qquad \text{Eq. 5E-4}$$

Where:

K_4 = 0.001 g/mg for metric units.
= 0.0154 gr/mg for English units.

12.5 Total Particulate Concentration.

$$C_t = C_s + C_c \qquad \text{Eq. 5E-4}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Total Organic Carbon Analyzer. Tekmar-Dohrmann analyzers using the single injection technique may be used as an alternative to Rosemount Model 2100A analyzers.

17.0 References.

Same as section 17.0 of Method 5, with the addition of the following:

1. American Public Health Association, American Water Works Association, Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater. Fifteenth Edition. Washington, D.C. 1980.

18.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

Method 5F—Determination of Nonsulfate Particulate Matter Emissions From Stationary Sources

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5.

1.0 Scope and Applications

1.1 Analyte. Nonsulfate particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of nonsulfate PM emissions from stationary sources. Use of this method must be specified by an applicable subpart of the standards, or approved by the Administrator for a particular application.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

Particulate matter is withdrawn isokinetically from the source and collected on a filter maintained at a temperature in the range 160 ±14 °C (320 ±25 °F). The collected sample is extracted with water. A portion of the extract is analyzed for sulfate content by ion chromatography. The remainder is neutralized with ammonium hydroxide (NH_4OH), dried, and weighed. The weight of sulfate in the sample is calculated as ammonium sulfate ($(NH_4)_2SO_4$), and is subtracted from the total particulate weight; the result is reported as nonsulfate particulate matter.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection and Recovery. Same as Method 5, sections 6.1 and 6.2, respectively.

6.2 Sample Analysis. Same as Method 5, section 6.3, with the addition of the following:

6.2.1 Erlenmeyer Flasks. 125-ml, with ground glass joints.

6.2.2 Air Condenser. With ground glass joint compatible with the Erlenmeyer flasks.

6.2.3 Beakers. 600-ml.

6.2.4 Volumetric Flasks. 1-liter, 500-ml (one for each sample), 200-ml, and 50-ml (one for each sample and standard).

6.2.5 Pipet. 5-ml (one for each sample and standard).

6.2.6 Ion Chromatograph. The ion chromatograph should have at least the following components.

6.2.6.1 Columns. An anion separation column or other column capable of resolving the sulfate ion from other species present and a standard anion suppressor column. Suppressor columns are produced as proprietary items; however, one can be produced in the laboratory using the resin available from BioRad Company, 32nd and Griffin Streets, Richmond, California. Other systems which do not use suppressor columns may also be used.

6.2.6.2 Pump. Capable of maintaining a steady flow as required by the system.

6.2.6.3 Flow Gauges. Capable of measuring the specified system flow rate.

6.2.6.4 Conductivity Detector.

6.2.6.5 Recorder. Compatible with the output voltage range of the detector.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 5, section 7.1.

7.2 Sample Recovery. Same as Method 5, section 7.2, with the addition of the following:

7.2.1 Water. Deionized distilled, to conform to ASTM D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17). The potassium permanganate ($KMnO_4$) test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.3 Analysis. Same as Method 5, section 7.3, with the addition of the following:

7.3.1 Water. Same as in section 7.2.1.

7.3.2 Stock Standard Solution, 1 mg $(NH_4)_2SO_4$/ml. Dry an adequate amount of primary standard grade ammonium sulfate ($(NH_4)_2SO_4$) at 105 to 110 °C (220 to 230 °F) for a minimum of 2 hours before preparing the standard solution. Then dissolve exactly 1.000 g of dried $(NH_4)_2SO_4$ in water in a 1-liter volumetric flask, and dilute to 1 liter. Mix well.

7.3.3 Working Standard Solution, 25 µg $(NH_4)_2SO_4$/ml. Pipet 5 ml of the stock standard solution into a 200-ml volumetric flask. Dilute to 200 ml with water.

7.3.4 Eluent Solution. Weigh 1.018 g of sodium carbonate (Na_2CO_3) and 1.008 g of sodium bicarbonate ($NaHCO_3$), and dissolve in 4 liters of water. This solution is 0.0024 M Na_2CO_3/0.003 M $NaHCO_3$. Other eluents appropriate to the column type and capable of resolving sulfate ion from other species present may be used.

7.3.5 Ammonium Hydroxide. Concentrated, 14.8 M.

7.3.6 Phenolphthalein Indicator. 3,3-Bis(4-hydroxyphenyl)-1-(3H)-isobenzo-furanone. Dissolve 0.05 g in 50 ml of ethanol and 50 ml of water.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as Method 5, section 8.0, with the exception of the following:

8.1 Sampling Train Operation. Same as Method 5, section 8.5, except that the probe outlet and filter temperatures shall be maintained at 160 ±14 °C (320 ±25 °F).

8.2 Sample Recovery. Same as Method 5, section 8.7, except that the recovery solvent shall be water instead of acetone, and a clean filter from the same lot as those used during testing shall be saved for analysis as a blank.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures

Section	Quality control measure	Effect
8.3, 10.0	Sampling equipment leak check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.
10.1.2, 11.2.5.3	Repetitive analyses	Ensures precise measurement of total carbon and inorganic carbon concentration of samples, blank, and standards.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

Same as Method 5, section 10.0, with the addition of the following:

10.1 Determination of Ion Chromatograph Calibration Factor S. Prepare a series of five standards by adding 1.0, 2.0, 4.0, 6.0, and 10.0 ml of working standard solution (25 µg/ml) to a series of five 50-ml volumetric flasks. (The standard masses will equal 25, 50, 100, 150, and 250 µg.) Dilute each flask to the mark with water, and mix well. Analyze each standard according to the chromatograph manufacturer's instructions. Take peak height measurements with symmetrical peaks; in all other cases, calculate peak areas. Prepare or calculate a linear regression plot of the standard masses in µg (x-axis) versus their responses (y-axis). From this line, or equation, determine the slope and calculate its reciprocal which is the calibration factor, S. If any point deviates from the line by more than 7 percent of the concentration at that point, remake and reanalyze that standard. This deviation can be determined by multiplying S times the response for each standard. The resultant concentrations must not differ by more than 7 percent from each known standard mass (*i.e.*, 25, 50, 100, 150, and 250 µg).

10.2 Conductivity Detector. Calibrate according to manufacturer's specifications prior to initial use.

11.0 Analytical Procedure

11.1 Sample Extraction.

11.1.1 Note on the analytical data sheet, the level of the liquid in the container, and whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.1.2 Cut the filter into small pieces, and place it in a 125-ml Erlenmeyer flask with a ground glass joint equipped with an air condenser. Rinse the shipping container with water, and pour the rinse into the flask. Add additional water to the flask until it contains about 75 ml, and place the flask on a hot plate. Gently reflux the contents for 6 to 8 hours. Cool the solution, and transfer it to a 500-ml volumetric flask. Rinse the Erlenmeyer flask with water, and transfer the rinsings to the volumetric flask including the pieces of filter.

11.1.3 Transfer the probe rinse to the same 500-ml volumetric flask with the filter sample. Rinse the sample bottle with water, and add the rinsings to the volumetric flask. Dilute the contents of the flask to the mark with water.

11.1.4 Allow the contents of the flask to settle until all solid material is at the bottom of the flask. If necessary, remove and centrifuge a portion of the sample.

11.1.5 Repeat the procedures outlined in sections 11.1.1 through 11.1.4 for each sample and for the filter blank.

11.2 Sulfate (SO_4) Analysis.

11.2.1 Prepare a standard calibration curve according to the procedures outlined in section 10.1.

11.2.2 Pipet 5 ml of the sample into a 50-ml volumetric flask, and dilute to 50 ml with water. (Alternatively, eluent solution may be used instead of water in all sample, standard, and blank dilutions.) Analyze the set of standards followed by the set of samples, including the filter blank, using the same injection volume used for the standards.

11.2.3 Repeat the analyses of the standards and the samples, with the standard set being done last. The two peak height or peak area responses for each sample must agree within 5 percent of their arithmetic mean for the analysis to be valid. Perform this analysis sequence on the same day. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

11.2.4 Document each sample chromatogram by listing the following analytical parameters: injection point, injection volume, sulfate retention time, flow rate, detector sensitivity setting, and recorder chart speed.

11.3 Sample Residue.

11.3.1 Transfer the remaining contents of the volumetric flask to a tared 600-ml beaker or similar container. Rinse the volumetric flask with water, and add the rinsings to the tared beaker. Make certain that all particulate matter is transferred to the beaker. Evaporate the water in an oven at 105 °C (220 °F) until only about 100 ml of water remains. Remove the beakers from the oven, and allow them to cool.

11.3.2 After the beakers have cooled, add five drops of phenolphthalein indicator, and then add concentrated ammonium hydroxide until the solution turns pink. Return the samples to the oven at 105 °C (220 °F), and evaporate the samples to dryness. Cool the samples in a desiccator, and weigh the samples to constant weight.

12.0 Data Analysis and Calculations

Same as Method 5, section 12.0, with the addition of the following:

12.1 Nomenclature.

C_W = Water blank residue concentration, mg/ml.

F = Dilution factor (required only if sample dilution was needed to reduce the concentration into the range of calibration).

H_S = Arithmetic mean response of duplicate sample analyses, mm for height or mm2 for area.

H_b = Arithmetic mean response of duplicate filter blank analyses, mm for height or mm2 for area.
m_b = Mass of beaker used to dry sample, mg.
m_f = Mass of sample filter, mg.
m_n = Mass of nonsulfate particulate matter in the sample as collected, mg.
m_s = Mass of ammonium sulfate in the sample as collected, mg.
m_t = Mass of beaker, filter, and dried sample, mg.
m_w = Mass of residue after evaporation of water blank, mg.
S = Calibration factor, µg/mm.
V_b = Volume of water blank, ml.
V_S = Volume of sample collected, 500 ml.

12.2 Water Blank Concentration.

$$C_w = \frac{m_w}{V_b} \qquad \text{Eq. 5F-1}$$

12.3 Mass of Ammonium Sulfate.

$$m_s = \frac{(99)\, S\, (H_s - H_b)}{(1000)} F \qquad \text{Eq. 5F-2}$$

Where:
100 = Aliquot factor, 495 ml/5 ml
1000 = Constant, µg/mg

12.4 Mass of Nonsulfate Particulate Matter.

$$m_n = m_t - m_b - m_s - m_f - V_s C_w \qquad \text{Eq. 5F-3}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 The following procedure may be used as an alternative to the procedure in section 11.0

16.1.1 Apparatus. Same as for Method 6, sections 6.3.3 to 6.3.6 with the following additions.

16.1.1.1 Beakers. 250-ml, one for each sample, and 600-ml.

16.1.1.2 Oven. Capable of maintaining temperatures of 75 ±5 °C (167 ±9 °F) and 105 ±5 °C (221 ±9 °F).

16.1.1.3 Buchner Funnel.

16.1.1.4 Glass Columns. 25-mm × 305-mm (1-in. × 12-in.) with Teflon stopcock.

16.1.1.5 Volumetric Flasks. 50-ml and 500-ml, one set for each sample, and 100-ml, 200-ml, and 1000-ml.

16.1.1.6 Pipettes. Two 20-ml and one 200-ml, one set for each sample, and 5-ml.

16.1.1.7 Filter Flasks. 500-ml.

16.1.1.8 Polyethylene Bottle. 500-ml, one for each sample.

16.1.2 Reagents. Same as Method 6, sections 7.3.2 to 7.3.5 with the following additions:

16.1.2.1 Water, Ammonium Hydroxide, and Phenolphthalein. Same as sections 7.2.1, 7.3.5, and 7.3.6 of this method, respectively.

16.1.2.2 Filter. Glass fiber to fit Buchner funnel.

16.1.2.3 Hydrochloric Acid (HCl), 1 m. Add 8.3 ml of concentrated HCl (12 M) to 50 ml of water in a 100-ml volumetric flask. Dilute to 100 ml with water.

16.1.2.4 Glass Wool.

16.1.2.5 Ion Exchange Resin. Strong cation exchange resin, hydrogen form, analytical grade.

16.1.2.6 pH Paper. Range of 1 to 7.

16.1.3 Analysis.

16.1.3.1 Ion Exchange Column Preparation. Slurry the resin with 1 M HCl in a 250-ml beaker, and allow to stand overnight. Place 2.5 cm (1 in.) of glass wool in the bottom of the glass column. Rinse the slurried resin twice with water. Resuspend the resin in water, and pour sufficient resin into the column to make a bed 5.1 cm (2 in.) deep. Do not allow air bubbles to become entrapped in the resin or glass wool to avoid channeling, which may produce erratic results. If necessary, stir the resin with a glass rod to remove air bubbles, after the column has been prepared, never let the liquid level fall below the top of the upper glass wool plug. Place a 2.5-cm (1-in.) plug of glass wool on top of the resin. Rinse the column with water until the eluate gives a pH of 5 or greater as measured with pH paper.

16.1.3.2 Sample Extraction. Followup the procedure given in section 11.1.3 except do not dilute the sample to 500 ml.

16.1.3.3 Sample Residue.

16.1.3.3.1 Place at least one clean glass filter for each sample in a Buchner funnel, and rinse the filters with water. Remove the filters from the funnel, and dry them in an oven at 105 ±5 °C (221 ±9 °F); then cool in a desiccator. Weigh each filter to constant weight according to the procedure in Method 5, section 11.0. Record the weight of each filter to the nearest 0.1 mg.

16.1.3.3.2 Assemble the vacuum filter apparatus, and place one of the clean, tared glass fiber filters in the Buchner funnel. Decant the liquid portion of the extracted sample (Section 16.1.3.2) through the tared glass fiber filter into a clean, dry, 500-ml filter flask. Rinse all the particulate matter remaining in the volumetric flask onto the glass fiber filter with water. Rinse the particulate matter with additional water.

Transfer the filtrate to a 500-ml volumetric flask, and dilute to 500 ml with water. Dry the filter overnight at 105 ±5 °C (221 ±9 °F), cool in a desiccator, and weigh to the nearest 0.1 mg.

16.1.3.3.3 Dry a 250-ml beaker at 75 ±5 °C (167 ±9 °F), and cool in a desiccator; then weigh to constant weight to the nearest 0.1 mg. Pipette 200 ml of the filtrate that was saved into a tared 250-ml beaker; add five drops of phenolphthalein indicator and sufficient concentrated ammonium hydroxide to turn the solution pink. Carefully evaporate the contents of the beaker to dryness at 75 ±5 °C (167 ±9 °F). Check for dryness every 30 minutes. Do not continue to bake the sample once it has dried. Cool the sample in a desiccator, and weigh to constant weight to the nearest 0.1 mg.

16.1.3.4 Sulfate Analysis. Adjust the flow rate through the ion exchange column to 3 ml/min. Pipette a 20-ml aliquot of the filtrate onto the top of the ion exchange column, and collect the eluate in a 50-ml volumetric flask. Rinse the column with two 15-ml portions of water. Stop collection of the eluate when the volume in the flask reaches 50-ml. Pipette a 20-ml aliquot of the eluate into a 250-ml Erlenmeyer flask, add 80 ml of 100 percent isopropanol and two to four drops of thorin indicator, and titrate to a pink end point using 0.0100 N barium perchlorate. Repeat and average the titration volumes. Run a blank with each series of samples. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is larger. Perform the ion exchange and titration procedures on duplicate portions of the filtrate. Results should agree within 5 percent. Regenerate or replace the ion exchange resin after 20 sample aliquots have been analyzed or if the end point of the titration becomes unclear.

NOTE: Protect the 0.0100 N barium perchlorate solution from evaporation at all times.

16.1.3.5 Blank Determination. Begin with a sample of water of the same volume as the samples being processed and carry it through the analysis steps described in sections 16.1.3.3 and 16.1.3.4. A blank value larger than 5 mg should not be subtracted from the final particulate matter mass. Causes for large blank values should be investigated and any problems resolved before proceeding with further analyses.

16.1.4 Calibration. Calibrate the barium perchlorate solutions as in Method 6, section 10.5.

16.1.5 Calculations.

16.1.5.1 Nomenclature. Same as section 12.1 with the following additions:

m_a = Mass of clean analytical filter, mg.
m_d = Mass of dissolved particulate matter, mg.
m_e = Mass of beaker and dissolved particulate matter after evaporation of filtrate, mg.
m_p = Mass of insoluble particulate matter, mg.
m_r = Mass of analytical filter, sample filter, and insoluble particulate matter, mg.
m_{bk} = Mass of nonsulfate particulate matter in blank sample, mg.
m_n = Mass of nonsulfate particulate matter, mg.
m_s = Mass of Ammonium sulfate, mg.
N = Normality of $Ba(ClO_4)$ titrant, meq/ml.
V_a = Volume of aliquot taken for titration, 20 ml.
V_c = Volume of titrant used for titration blank, ml.
V_d = Volume of filtrate evaporated, 200 ml.
V_e = Volume of eluate collected, 50 ml.
V_f = Volume of extracted sample, 500 ml.
V_i = Volume of filtrate added to ion exchange column, 20 ml.
V_t = Volume of $Ba(C10_4)_2$ titrant, ml.
W = Equivalent weight of ammonium sulfate, 66.07 mg/meq.

16.1.5.2 Mass of Insoluble Particulate Matter.

$$m_p = m_r - m_a - m_f \qquad \text{Eq. 5F-4}$$

16.1.5.3 Mass of Dissolved Particulate Matter.

$$m_d = \left(m_e - \left(V_f / V_d\right) m_b\right) \qquad \text{Eq. 5F-5}$$

16.1.5.4 Mass of Ammonium Sulfate.

$$m_s = \frac{\left(V_t - V_c\right) N\, W\, V_e V_f}{V_a V_i} \qquad \text{Eq. 5F-6}$$

16.1.5.5 Mass of Nonsulfate Particulate Matter.

$$m_n = m_p + m_d - m_s - m_{bk} \qquad \text{Eq. 5F-7}$$

17.0 References

Same as Method 5, section 17.0, with the addition of the following:

1. Mulik, J.D. and E. Sawicki. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor, Ann Arbor Science Publishers, Inc. Vol. 2, 1979.

2. Sawicki, E., J.D. Mulik, and E. Wittgenstein. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor, Ann Arbor Science Publishers, Inc. Vol. 1. 1978.

3. Siemer, D.D. Separation of Chloride and Bromide from Complex Matrices Prior to Ion Chromatographic Determination. Analytical Chemistry 52(12): 1874–1877. October 1980.

4. Small, H., T.S. Stevens, and W.C. Bauman. Novel Ion Exchange Chromatographic Method Using

Conductimetric Determination. Analytical Chemistry. *47*(11):1801. 1975.

18.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 5G—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM WOOD HEATERS (DILUTION TUNNEL SAMPLING LOCATION)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 4, Method 5, Method 5H, and Method 28.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of PM emissions from wood heaters.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 The exhaust from a wood heater is collected with a total collection hood, and is combined with ambient dilution air. Particulate matter is withdrawn proportionally from a single point in a sampling tunnel, and is collected on two glass fiber filters in series. The filters are maintained at a temperature of no greater than 32 °C (90 °F). The particulate mass is determined gravimetrically after the removal of uncombined water.

2.2 There are three sampling train approaches described in this method: (1) One dual-filter dry sampling train operated at about 0.015 m^3/min (0.5 cfm), (2) One dual-filter plus impingers sampling train operated at about 0.015 m^3/min (0.5 cfm), and (3) two dual-filter dry sampling trains operated simultaneously at any flow rate. Options (2) and (3) are referenced in section 16.0 of this method. The dual-filter dry sampling train equipment and operation, option (1), are described in detail in this method.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. The following items are required for sample collection:

6.1.1 Sampling Train. The sampling train configuration is shown in Figure 5G–1 and consists of the following components:

6.1.1.1 Probe. Stainless steel (*e.g.*, 316 or grade more corrosion resistant) or glass about 9.5 mm (3⁄8 in.) I.D., 0.6 m (24 in.) in length. If made of stainless steel, the probe shall be constructed from seamless tubing.

6.1.1.2 Pitot Tube. Type S, as described in section 6.1 of Method 2. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Method 2, section 10. Alternatively, a standard pitot may be used as described in Method 2, section 6.1.2.

6.1.1.3 Differential Pressure Gauge. Inclined manometer or equivalent device, as described in Method 2, section 6.2. One manometer shall be used for velocity head (Δp) readings and another (optional) for orifice differential pressure readings (ΔH).

6.1.1.4 Filter Holders. Two each made of borosilicate glass, stainless steel, or Teflon, with a glass frit or stainless steel filter support and a silicone rubber, Teflon, or Viton gasket. The holder design shall provide a positive seal against leakage from the outside or around the filters. The filter holders shall be placed in series with the backup filter holder located 25 to 100 mm (1 to 4 in.) downstream from the primary filter holder. The filter holder shall be capable of holding a filter with a 100 mm (4 in.) diameter, except as noted in section 16.

6.1.1.5 Filter Temperature Monitoring System. A temperature sensor capable of measuring temperature to within ±3 °C (±5 °F). The sensor shall be installed at the exit side of the front filter holder so that the sensing tip of the temperature sensor is in direct contact with the sample gas or in a thermowell as shown in Figure 5G–1. The temperature sensor shall comply with the calibration specifications in Method 2, section 10.3. Alternatively, the sensing tip of the temperature sensor may be installed at the inlet side of the front filter holder.

6.1.1.6 Dryer. Any system capable of removing water from the sample gas to less than 1.5 percent moisture (volume percent) prior to the metering system. The system shall include a temperature sensor for demonstrating that sample gas temperature exiting the dryer is less than 20 °C (68 °F).

6.1.1.7 Metering System. Same as Method 5, section 6.1.1.9.

6.1.2 Barometer. Same as Method 5, section 6.1.2.

6.1.3 Dilution Tunnel Gas Temperature Measurement. A temperature sensor capable

of measuring temperature to within ±3 °C (±5 °F).

6.1.4 Dilution Tunnel. The dilution tunnel apparatus is shown in Figure 5G–2 and consists of the following components:

6.1.4.1 Hood. Constructed of steel with a minimum diameter of 0.3 m (1 ft) on the large end and a standard 0.15 to 0.3 m (0.5 to 1 ft) coupling capable of connecting to standard 0.15 to 0.3 m (0.5 to 1 ft) stove pipe on the small end.

6.1.4.2 90° Elbows. Steel 90° elbows, 0.15 to 0.3 m (0.5 to 1 ft) in diameter for connecting mixing duct, straight duct and optional damper assembly. There shall be at least two 90° elbows upstream of the sampling section (see Figure 5G–2).

6.1.4.3 Straight Duct. Steel, 0.15 to 0.3 m (0.5 to 1 ft) in diameter to provide the ducting for the dilution apparatus upstream of the sampling section. Steel duct, 0.15 m (0.5 ft) in diameter shall be used for the sampling section. In the sampling section, at least 1.2 m (4 ft) downstream of the elbow, shall be two holes (velocity traverse ports) at 90° to each other of sufficient size to allow entry of the pitot for traverse measurements. At least 1.2 m (4 ft) downstream of the velocity traverse ports, shall be one hole (sampling port) of sufficient size to allow entry of the sampling probe. Ducts of larger diameter may be used for the sampling section, provided the specifications for minimum gas velocity and the dilution rate range shown in section 8 are maintained. The length of duct from the hood inlet to the sampling ports shall not exceed 9.1 m (30 ft).

6.1.4.4 Mixing Baffles. Steel semicircles (two) attached at 90° to the duct axis on opposite sides of the duct midway between the two elbows upstream of sampling section. The space between the baffles shall be about 0.3 m (1 ft).

6.1.4.5 Blower. Squirrel cage or other fan capable of extracting gas from the dilution tunnel of sufficient flow to maintain the velocity and dilution rate specifications in section 8 and exhausting the gas to the atmosphere.

6.2 Sample Recovery. The following items are required for sample recovery: probe brushes, wash bottles, sample storage containers, petri dishes, and funnel. Same as Method 5, sections 6.2.1 through 6.2.4, and 6.2.8, respectively.

6.3 Sample Analysis. The following items are required for sample analysis: glass weighing dishes, desiccator, analytical balance, beakers (250-ml or smaller), hygrometer, and temperature sensor. Same as Method 5, sections 6.3.1 through 6.3.3 and 6.3.5 through 6.3.7, respectively.

7.0 Reagents and Standards

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Filters. Glass fiber filters with a minimum diameter of 100 mm (4 in.), without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. Gelman A/E 61631 has been found acceptable for this purpose.

7.1.2 Stopcock Grease. Same as Method 5, section 7.1.5. 7.2 Sample Recovery. Acetone-reagent grade, same as Method 5, section 7.2.

7.3 Sample Analysis. Two reagents are required for the sample analysis:

7.3.1 Acetone. Same as in section 7.2.

7.3.2 Desiccant. Anhydrous calcium sulfate, calcium chloride, or silica gel, indicating type.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Dilution Tunnel Assembly and Cleaning. A schematic of a dilution tunnel is shown in Figure 5G–2. The dilution tunnel dimensions and other features are described in section 6.1.4. Assemble the dilution tunnel, sealing joints and seams to prevent air leakage. Clean the dilution tunnel with an appropriately sized wire chimney brush before each certification test.

8.2 Draft Determination. Prepare the wood heater as in Method 28, section 6.2.1. Locate the dilution tunnel hood centrally over the wood heater stack exhaust. Operate the dilution tunnel blower at the flow rate to be used during the test run. Measure the draft imposed on the wood heater by the dilution tunnel (*i.e.*, the difference in draft measured with and without the dilution tunnel operating) as described in Method 28, section 6.2.3. Adjust the distance between the top of the wood heater stack exhaust and the dilution tunnel hood so that the dilution tunnel induced draft is less than 1.25 Pa (0.005 in. H_2O). Have no fire in the wood heater, close the wood heater doors, and open fully the air supply controls during this check and adjustment.

8.3 Pretest Ignition. Same as Method 28, section 8.7.

8.4 Smoke Capture. During the pretest ignition period, operate the dilution tunnel and visually monitor the wood heater stack exhaust. Operate the wood heater with the doors closed and determine that 100 percent of the exhaust gas is collected by the dilution tunnel hood. If less than 100 percent of the wood heater exhaust gas is collected, adjust the distance between the wood heater stack and the dilution tunnel hood until no visible exhaust gas is escaping. Stop the pretest ignition period, and repeat the draft determination procedure described in section 8.2.

8.5 Velocity Measurements. During the pretest ignition period, conduct a velocity traverse to identify the point of average velocity. This single point shall be used for measuring velocity during the test run.

8.5.1 Velocity Traverse. Measure the diameter of the duct at the velocity traverse port location through both ports. Calculate the duct area using the average of the two diameters. A pretest leak-check of pitot lines as in Method 2, section 8.1, is recommended. Place the calibrated pitot tube at the centroid of the stack in either of the velocity traverse ports. Adjust the damper or similar device on the blower inlet until the velocity indicated by the pitot is approximately 220 m/min (720 ft/min). Continue to read the Δp and temperature until the velocity has remained constant (less than 5 percent change) for 1 minute. Once a constant velocity is obtained at the centroid of the duct, perform a velocity traverse as outlined in Method 2, section 8.3 using four points per traverse as outlined in Method 1. Measure the Δp and tunnel temperature at each traverse point and record the readings. Calculate the total gas flow rate using calculations contained in Method 2, section 12. Verify that the flow rate is 4 ±0.40 dscm/min (140 ±14 dscf/min); if not, readjust the damper, and repeat the velocity traverse. The moisture may be assumed to be 4 percent (100 percent relative humidity at 85 °F). Direct moisture measurements (*e.g.*, according to Method 4) are also permissible.

NOTE: If burn rates exceed 3 kg/hr (6.6 lb/hr), dilution tunnel duct flow rates greater than 4 dscm/min (140 dscfm) and sampling section duct diameters larger than 150 mm (6 in.) are allowed. If larger ducts or flow rates are used, the sampling section velocity shall be at least 220 m/min (720 fpm). In order to ensure measurable particulate mass catch, it is recommended that the ratio of the average mass flow rate in the dilution tunnel to the average fuel burn rate be less than 150:1 if larger duct sizes or flow rates are used.

8.5.2 Testing Velocity Measurements. After obtaining velocity traverse results that meet the flow rate requirements, choose a point of average velocity and place the pitot and temperature sensor at that location in the duct. Alternatively, locate the pitot and the temperature sensor at the duct centroid and calculate a velocity correction factor for the centroidal position. Mount the pitot to ensure no movement during the test run and seal the port holes to prevent any air leakage. Align the pitot opening to be parallel with the duct axis at the measurement point. Check that this condition is maintained during the test run (about 30-minute intervals). Monitor the temperature and velocity during the pretest ignition period to ensure that the proper flow rate is maintained. Make adjustments to the dilution tunnel flow rate as necessary.

8.6 Pretest Preparation. Same as Method 5, section 8.1.

8.7 Preparation of Sampling Train. During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin.

Using a tweezer or clean disposable surgical gloves, place one labeled (identified) and weighed filter in each of the filter holders. Be sure that each filter is properly centered and that the gasket is properly placed so as to prevent the sample gas stream from circumventing the filter. Check each filter for tears after assembly is completed.

Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct. Set up the train as shown in Figure 5G–1.

8.8 Leak-Check Procedures.

8.8.1 Leak-Check of Metering System Shown in Figure 5G–1. That portion of the sampling train from the pump to the orifice meter shall be leak-checked prior to initial use and after each certification or audit test. Leakage after the pump will result in less volume being recorded than is actually sampled. Use the procedure described in Method 5, section 8.4.1. Similar leak-checks shall be conducted for other types of metering systems (*i.e.*, without orifice meters).

8.8.2 Pretest Leak-Check. A pretest leak-check of the sampling train is recommended, but not required. If the pretest leak check is conducted, the procedures outlined in Method 5, section 8.4.2 should be used. A vacuum of 130 mm Hg (5 in. Hg) may be used instead of 380 mm Hg (15 in. Hg).

8.8.3 Post-Test Leak-Check. A leak-check of the sampling train is mandatory at the conclusion of each test run. The leak-check shall be performed in accordance with the procedures outlined in Method 5, section 8.4.2. A vacuum of 130 mm Hg (5 in. Hg) or the highest vacuum measured during the test run, whichever is greater, may be used instead of 380 mm Hg (15 in. Hg).

8.9 Preliminary Determinations. Determine the pressure, temperature and the average velocity of the tunnel gases as in section 8.5. Moisture content of diluted tunnel gases is assumed to be 4 percent for making flow rate calculations; the moisture content may be measured directly as in Method 4.

8.10 Sampling Train Operation. Position the probe inlet at the stack centroid, and block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream. Be careful not to bump the probe into the stack wall when removing or inserting the probe through the porthole; this minimizes the chance of extracting deposited material.

8.10.1 Begin sampling at the start of the test run as defined in Method 28, section 8.8.1. During the test run, maintain a sample flow rate proportional to the dilution tunnel flow rate (within 10 percent of the initial proportionality ratio) and a filter holder temperature of no greater than 32 °C (90 °F).

The initial sample flow rate shall be approximately 0.015 m^3/min (0.5 cfm).

8.10.2 For each test run, record the data required on a data sheet such as the one shown in Figure 5G–3. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment and when sampling is halted. Take other readings as indicated on Figure 5G–3 at least once each 10 minutes during the test run. Since the manometer level and zero may drift because of vibrations and temperature changes, make periodic checks during the test run.

8.10.3 For the purposes of proportional sampling rate determinations, data from calibrated flow rate devices, such as glass rotameters, may be used in lieu of incremental dry gas meter readings. Proportional rate calculation procedures must be revised, but acceptability limits remain the same.

8.10.4 During the test run, make periodic adjustments to keep the temperature between (or upstream of) the filters at the proper level. Do not change sampling trains during the test run.

8.10.5 At the end of the test run (see Method 28, section 6.4.6), turn off the coarse adjust valve, remove the probe from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak-check, as outlined in section 8.8.2. Also, leak-check the pitot lines as described in Method 2, section 8.1; the lines must pass this leak-check in order to validate the velocity head data.

8.11 Calculation of Proportional Sampling Rate. Calculate percent proportionality (see section 12.7) to determine whether the run was valid or another test run should be made.

8.12 Sample Recovery. Same as Method 5, section 8.7, with the exception of the following:

8.12.1 An acetone blank volume of about 50-ml or more may be used.

8.12.2 Treat the samples as follows:

8.12.2.1 Container Nos. 1 and 1A. Treat the two filters according to the procedures outlined in Method 5, section 8.7.6.1. The filters may be stored either in a single container or in separate containers. Use the sum of the filter tare weights to determine the sample mass collected.

8.12.2.3 Container No. 2.

8.12.2.3.1 Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe and filter holders by washing and brushing these components with acetone and placing the wash in a labeled glass container. At least three cycles of brushing and rinsing are required.

8.12.2.3.2 Between sampling runs, keep brushes clean and protected from contamination.

8.12.2.3.3 After all acetone washings and particulate matter have been collected in the sample containers, tighten the lids on the sample containers so that the acetone will not leak out when transferred to the laboratory weighing area. Mark the height of the fluid levels to determine whether leakage occurs during transport. Label the containers clearly to identify contents.

8.13 Sample Transport. Whenever possible, containers should be shipped in such a way that they remain upright at all times.

NOTE: Requirements for capping and transport of sample containers are not applicable if sample recovery and analysis occur in the same room.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.8, 10.1–10.4	Sampling equipment leak check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.
10.5	Analytical balance calibration	Ensure accurate and precise measurement of collected particulate.
16.2.5	Simultaneous, dual-train sample collection.	Ensure precision of measured particulate concentration.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory record of all calibrations.

10.1 Pitot Tube. The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Method 2, section 10.1, prior to the first certification test and checked semiannually, thereafter. A standard pitot need not be calibrated but shall be inspected and cleaned, if necessary, prior to each certification test.

10.2 Volume Metering System.

10.2.1 Initial and Periodic Calibration. Before its initial use and at least semiannually thereafter, calibrate the volume metering system as described in Method 5, section 10.3.1, except that the wet test meter with a capacity of 3.0 liters/rev (0.1 ft^3/rev) may be used. Other liquid displacement systems accurate to within ±1 percent, may be used as calibration standards.

NOTE: Procedures and equipment specified in Method 5, section 16.0, for alternative calibration standards, including calibrated dry gas meters and critical orifices, are allowed for calibrating the dry gas meter in the sampling train. A dry gas meter used as a calibration standard shall be recalibrated at least once annually.

10.2.2 Calibration After Use. After each certification or audit test (four or more test runs conducted on a wood heater at the four burn rates specified in Method 28), check calibration of the metering system by performing three calibration runs at a single, intermediate flow rate as described in Method 5, section 10.3.2.

NOTE: Procedures and equipment specified in Method 5, section 16.0, for alternative calibration standards are allowed for the post-test dry gas meter calibration check.

10.2.3 Acceptable Variation in Calibration. If the dry gas meter coefficient values obtained before and after a certification test differ by more than 5 percent, the certification test shall either be voided and repeated, or calculations for the certification test shall be performed using whichever meter coefficient value (*i.e.*, before or after) gives the lower value of total sample volume.

10.3 Temperature Sensors. Use the procedure in Method 2, section 10.3, to calibrate temperature sensors before the first certification or audit test and at least semiannually, thereafter.

10.4 Barometer. Calibrate against a mercury barometer before the first certification test and at least semiannually, thereafter. If a mercury barometer is used, no calibration is necessary. Follow the manufacturer's instructions for operation.

10.5 Analytical Balance. Perform a multipoint calibration (at least five points spanning the operational range) of the analytical balance before the first certification test and semiannually, thereafter. Before each certification test, audit the balance by weighing at least one calibration weight (class F) that corresponds to 50 to 150 percent of the weight of one filter. If the scale cannot reproduce the value of the calibration weight to within 0.1 mg, conduct the multipoint calibration before use.

11.0 Analytical Procedure

11.1 Record the data required on a sheet such as the one shown in Figure 5G–4. Use the same analytical balance for determining tare weights and final sample weights.

11.2 Handle each sample container as follows:

11.2.1 Container Nos. 1 and 1A. Treat the two filters according to the procedures outlined in Method 5, section 11.2.1.

11.2.2 Container No. 2. Same as Method 5, section 11.2.2, except that the beaker may be smaller than 250 ml.

11.2.3 Acetone Blank Container. Same as Method 5, section 11.2.4, except that the beaker may be smaller than 250 ml.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

12.1 Nomenclature.

B_{ws} = Water vapor in the gas stream, proportion by volume (assumed to be 0.04).
c_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (gr/dscf).
E = Particulate emission rate, g/hr (lb/hr).
E_{adj} = Adjusted particulate emission rate, g/hr (lb/hr).
L_a = Maximum acceptable leakage rate for either a pretest or post-test leak-check, equal to 0.00057 m^3/min (0.020 cfm) or 4 percent of the average sampling rate, whichever is less.
L_p = Leakage rate observed during the post-test leak-check, m^3/min (cfm).
m_a = Mass of residue of acetone blank after evaporation, mg.
m_{aw} = Mass of residue from acetone wash after evaporation, mg.
m_n = Total amount of particulate matter collected, mg.
M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).
PR = Percent of proportional sampling rate.
P_s = Absolute gas pressure in dilution tunnel, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
Q_{sd} = Average gas flow rate in dilution tunnel, calculated as in Method 2, Equation 2–8, dscm/hr (dscf/hr).
T_m = Absolute average dry gas meter temperature (see Figure 5G–3), °K (°R).
T_{mi} = Absolute average dry gas meter temperature during each 10-minute interval, i, of the test run, °K (°R).
T_s = Absolute average gas temperature in the dilution tunnel (see Figure 5G–3), °K (°R).
T_{si} = Absolute average gas temperature in the dilution tunnel during each 10 minute interval, i, of the test run, °K (°R).
T_{std} = Standard absolute temperature, 293 °K (528 °R).
V_a = Volume of acetone blank, ml.
V_{aw} = Volume of acetone used in wash, ml.
V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).

V_{mi} = Volume of gas sample as measured by dry gas meter during each 10-minute interval, i, of the test run, dcm.
$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).
V_s = Average gas velocity in the dilution tunnel, calculated by Method 2, Equation 2–7, m/sec (ft/sec). The dilution tunnel dry gas molecular weight may be assumed to be 29 g/g mole (lb/lb mole).
V_{si} = Average gas velocity in dilution tunnel during each 10-minute interval, i, of the test run, calculated by Method 2, Equation 2–7, m/sec (ft/sec).
Y = Dry gas meter calibration factor.
ΔH = Average pressure differential across the orifice meter, if used (see Figure 5G–2), mm H^2O (in. H^2O).
U = Total sampling time, min.
10 = 10 minutes, length of first sampling period.
13.6 = Specific gravity of mercury.
100 = Conversion to percent.

12.2 Dry Gas Volume. Same as Method 5, section 12.2, except that component changes are not allowable.

12.3 Solvent Wash Blank.

$$m_{aw} = \frac{m_a V_{aw}}{V_a} \qquad \text{Eq. 5G-1}$$

12.4 Total Particulate Weight. Determine the total particulate catch, mn, from the sum of the weights obtained from Container Nos. 1, 1A, and 2, less the acetone blank (see Figure 5G–4).

12.5 Particulate Concentration.

$$c_s = K_2 \frac{m_n}{V_{m(std)}} \qquad \text{Eq. 5G-2}$$

Where:
K_2 = 0.001 g/mg for metric units.
= 0.0154 gr/mg for English units.

12.6 Particulate Emission Rate.

$$E = C_s Q_{sd} \qquad \text{Eq. 5G-3}$$

NOTE: Particulate emission rate results produced using the sampling train described in section 6 and shown in Figure 5G–1 shall be adjusted for reporting purposes by the following method adjustment factor:

$$E_{adj} = K_3 E^{0.83} \qquad \text{Eq. 5G-4}$$

Where:
K_3 = constant, 1.82 for metric units.
= constant, 0.643 for English units.

12.7 Proportional Rate Variation. Calculate PR for each 10-minute interval, i, of the test run.

$$PR = \left(\frac{\theta \left(V_{mi} V_s T_m T_{si} \right)}{10 \left(V_m V_{si} T_s T_{mi} \right)} \right) \times 100 \qquad \text{Eq. 5G-5}$$

Alternate calculation procedures for proportional rate variation may be used if other sample flow rate data (e.g., orifice flow meters or rotameters) are monitored to maintain proportional sampling rates. The proportional rate variations shall be calculated for each 10-minute interval by comparing the stack to nozzle velocity ratio for each 10-minute interval to the average stack to nozzle velocity ratio for the test run. Proportional rate variation may be calculated for intervals shorter than 10 minutes with appropriate revisions to Equation 5G–5. If no more than 10 percent of the PR values for all the intervals exceed 90 percent ≤PR ≤110 percent, and if no PR value for any interval exceeds 80 percent ≤PR ≤120 percent, the results are acceptable. If the PR values for the test run are judged to be unacceptable, report the test run emission results, but do not include the results in calculating the weighted average emission rate, and repeat the test run.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Method 5H Sampling Train. The sampling train and sample collection, recovery, and analysis procedures described in Method 5H, sections 6.1.1, 7.1, 7.2, 8.1, 8.10, 8.11, and 11.0, respectively, may be used in lieu of similar sections in Method 5G. Operation of the Method 5H sampling train in the dilution tunnel is as described in section 8.10 of this method. Filter temperatures and condenser conditions are as described in Method 5H. No adjustment to the measured particulate matter emission rate (Equation 5G–4, section 12.6) is to be applied to the particulate emission rate measured by this alternative method.

16.2 Dual Sampling Trains. Two sampling trains may be operated simultaneously at sample flow rates other than that specified

in section 8.10, provided that the following specifications are met.

16.2.1 Sampling Train. The sampling train configuration shall be the same as specified in section 6.1.1, except the probe, filter, and filter holder need not be the same sizes as specified in the applicable sections. Filter holders of plastic materials such as Nalgene or polycarbonate materials may be used (the Gelman 1119 filter holder has been found suitable for this purpose). With such materials, it is recommended that solvents not be used in sample recovery. The filter face velocity shall not exceed 150 mm/sec (30 ft/min) during the test run. The dry gas meter shall be calibrated for the same flow rate range as encountered during the test runs. Two separate, complete sampling trains are required for each test run.

16.2.2 Probe Location. Locate the two probes in the dilution tunnel at the same level (see section 6.1.4.3). Two sample ports are necessary. Locate the probe inlets within the 50 mm (2 in.) diameter centroidal area of the dilution tunnel no closer than 25 mm (1 in.) apart.

16.2.3 Sampling Train Operation. Operate the sampling trains as specified in section 8.10, maintaining proportional sampling rates and starting and stopping the two sampling trains simultaneously. The pitot values as described in section 8.5.2 shall be used to adjust sampling rates in both sampling trains.

16.2.4 Recovery and Analysis of Sample. Recover and analyze the samples from the two sampling trains separately, as specified in sections 8.12 and 11.0, respectively.

16.2.4.1 For this alternative procedure, the probe and filter holder assembly may be weighed without sample recovery (use no solvents) described above in order to determine the sample weight gains. For this approach, weigh the clean, dry probe and filter holder assembly upstream of the front filter (without filters) to the nearest 0.1 mg to establish the tare weights. The filter holder section between the front and second filter need not be weighed. At the end of the test run, carefully clean the outside of the probe, cap the ends, and identify the sample (label). Remove the filters from the filter holder assemblies as described for container Nos. 1 and 1A in section 8.12.2.1. Reassemble the filter holder assembly, cap the ends, identify the sample (label), and transfer all the samples to the laboratory weighing area for final weighing. Requirements for capping and transport of sample containers are not applicable if sample recovery and analysis occur in the same room.

16.2.4.2 For this alternative procedure, filters may be weighed directly without a petri dish. If the probe and filter holder assembly are to be weighed to determine the sample weight, rinse the probe with acetone to remove moisture before desiccating prior to the test run. Following the test run, transport the probe and filter holder to the desiccator, and uncap the openings of the probe and the filter holder assembly. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

16.2.5 Calculations. Calculate an emission rate (Section 12.6) for the sample from each sampling train separately and determine the average emission rate for the two values. The two emission rates shall not differ by more than 7.5 percent from the average emission rate, or 7.5 percent of the weighted average emission rate limit in the applicable subpart of the regulations, whichever is greater. If this specification is not met, the results are unacceptable. Report the results, but do not include the results in calculating the weighted average emission rate. Repeat the test run until acceptable results are achieved, report the average emission rate for the acceptable test run, and use the average in calculating the weighted average emission rate.

17.0 References

Same as Method 5, section 17.0, References 1 through 11, with the addition of the following:

1. Oregon Department of Environmental Quality. Standard Method for Measuring the Emissions and Efficiencies of Woodstoves. June 8, 1984. Pursuant to Oregon Administrative Rules Chapter 340, Division 21.

2. American Society for Testing and Materials. Proposed Test Methods for Heating Performance and Emissions of Residential Wood-fired Closed Combustion-Chamber Heating Appliances. E–6 Proposal P 180. August 1986.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

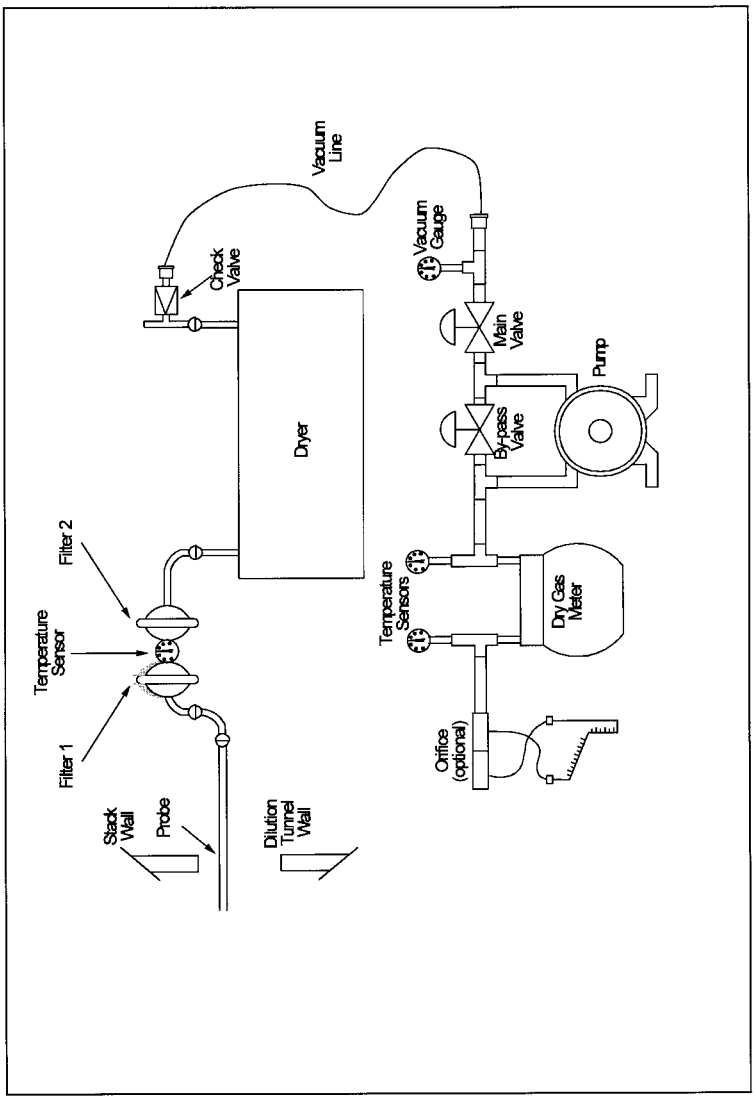


Figure 5G-1. Method 5G Sampling Train.

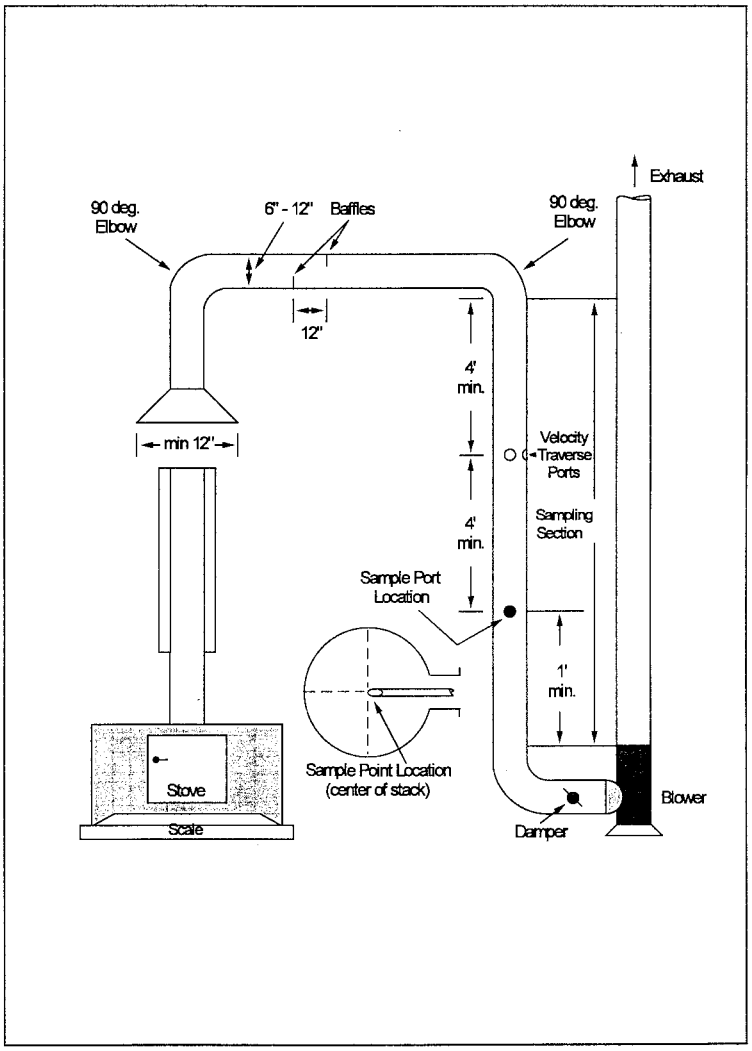


Figure 5G-2. Suggested Construction Details of the Dilution Tunnel.

Stove _____ Pitot tube coefficient, C_p _____
Test Method _____ Room temperature, °C (°F) _____
Operator _____ Barometric pressure mb (in. Hg) _____
Date _____ Measured or assumed moisture, % _____
Run No. _____ Final leak rate, m^3/min, (cfm) _____
Start Time _____ Probe liner material _____
Stop Time _____ Draft or static pressure, mm H_2O (in. H_2O) _____
Sample Box No. _____ Filter No. _____
Meter Box No. _____
Meter ΔH @ (optional) _____

Clock time	Test run time (e) min.	Vacuum mm Hg (in. Hg)	Tunnel temp (T_s) °C (°F)	Velocity head (ΔP_s) mm (in. H_2O)	Sample flow rate indicator (orifice meter optional) mm H_2O (in. H_2O)	Gas meter volume m^3 (ft^3)	Gas sample temp at dry gas meter Inlet °C (°F)	Gas sample temp at dry gas meter Outlet °C (°F)	Filter holder temp °C (°F)	Temperature of gas leaving dryer or last impinger °C (°F)
Total							Avg.	Avg.		
Average							Avg.			

Figure 5G-3. Sampling Data Sheet.

Stove _____
Date _____
Run No. _____
Filter Nos. _____
Liquid lost during transport, ml _____
Acetone blank volume, ml _____
Acetone wash volume, ml _____
Acetone blank concentration, mg/mg _____
Acetone wash blank, mg _____

Container number	Weight of particulate collected, mg	
	Final weight	Tare weight
1		
2		
3		
Total		
Less acetone blank		
Weight of particulate matter		

Stack Moisture Measurement Data
(Optional)

	Volume of liquid water collected	
	Implinger volume, ml	Silica gel weight, g
Final		
Initial		
Liquid collected		
Total volume collected		g[1] or ml

[1]Convert weight of water to volume by dividing total weight increase by density of water (1 g/ml).

$$\frac{\text{Increase, g}}{\text{(1 g/ml)}} = \text{Volume water, ml}$$

Figure 5G-4. Analysis Data Sheet.

METHOD 5H—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM WOOD HEATERS FROM A STACK LOCATION

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 2, Method 3, Method 5, Method 5G, Method 6, Method 6C, Method 16A, and Method 28.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of PM and condensible emissions from wood heaters.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Particulate matter is withdrawn proportionally from the wood heater exhaust and is collected on two glass fiber filters separated by impingers immersed in an ice water bath. The first filter is maintained at a temperature of no greater than 120 °C (248 °F). The second filter and the impinger system are cooled such that the temperature of the gas exiting the second filter is no greater than 20 °C (68 °F). The particulate mass collected in the probe, on the filters, and in the impingers is determined gravimetrically after the removal of uncombined water.

3.0 Definitions

Same as in Method 6C, section 3.0.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. The following items are required for sample collection:

6.1.1 Sampling Train. The sampling train configuration is shown in Figure 5H–1. Same as Method 5, section 6.1.1, with the exception of the following:

6.1.1.1 Probe Nozzle. The nozzle is optional; a straight sampling probe without a nozzle is an acceptable alternative.

6.1.1.2 Probe Liner. Same as Method 5, section 6.1.1.2, except that the maximum length of the sample probe shall be 0.6 m (2 ft) and probe heating is optional.

6.1.1.3 Filter Holders. Two each of borosilicate glass, with a glass frit or stainless steel filter support and a silicone rubber, Teflon, or Viton gasket. The holder design shall provide a positive seal against leakage from the outside or around the filter. The front filter holder shall be attached immediately at the outlet of the probe and prior to the first impinger. The second filter holder shall be attached on the outlet of the third impinger and prior to the inlet of the fourth (silica gel) impinger.

6.1.2 Barometer. Same as Method 5, section 6.2.

6.1.3 Stack Gas Flow Rate Measurement System. A schematic of an example test system is shown in Figure 5H–2. The flow rate measurement system consists of the following components:

6.1.3.1 Sample Probe. A glass or stainless steel sampling probe.

6.1.3.2 Gas Conditioning System. A high density filter to remove particulate matter and a condenser capable of lowering the dew point of the gas to less than 5 °C (40 °F). Desiccant, such as Drierite, may be used to dry the sample gas. Do not use silica gel.

6.1.3.3 Pump. An inert (*e.g.*, Teflon or stainless steel heads) sampling pump capable of delivering more than the total amount of sample required in the manufacturer's instructions for the individual instruments. A means of controlling the analyzer flow rate and a device for determining proper sample flow rate (*e.g.*, precision rotameter, pressure gauge downstream of all flow controls) shall be provided at the analyzer. The requirements for measuring and controlling the analyzer flow rate are not applicable if data are presented that demonstrate that the analyzer is insensitive to flow variations over the range encountered during the test.

6.1.3.4 Carbon Monoxide (CO) Analyzer. Any analyzer capable of providing a measure of CO in the range of 0 to 10 percent by volume at least once every 10 minutes.

6.1.3.5 Carbon Dioxide (CO_2) Analyzer. Any analyzer capable of providing a measure of CO_2 in the range of 0 to 25 percent by volume at least once every 10 minutes.

NOTE: Analyzers with ranges less than those specified above may be used provided actual concentrations do not exceed the range of the analyzer.

6.1.3.6 Manifold. A sampling tube capable of delivering the sample gas to two analyzers and handling an excess of the total amount used by the analyzers. The excess gas is exhausted through a separate port.

6.1.3.7 Recorders (optional). To provide a permanent record of the analyzer outputs.

6.1.4 Proportional Gas Flow Rate System. To monitor stack flow rate changes and provide a measurement that can be used to adjust and maintain particulate sampling flow rates proportional to the stack gas flow rate. A schematic of the proportional flow rate system is shown in Figure 5H–2 and consists of the following components:

6.1.4.1 Tracer Gas Injection System. To inject a known concentration of sulfur dioxide (SO_2) into the flue. The tracer gas injection system consists of a cylinder of SO_2, a gas cylinder regulator, a stainless steel needle valve or flow controller, a nonreactive (stainless steel and glass) rotameter, and an injection loop to disperse the SO_2 evenly in the flue.

6.1.4.2 Sample Probe. A glass or stainless steel sampling probe.

6.1.4.3 Gas Conditioning System. A combustor as described in Method 16A, sections 6.1.5 and 6.1.6, followed by a high density filter to remove particulate matter, and a condenser capable of lowering the dew point of the gas to less than 5 °C (40 °F). Desiccant, such as Drierite, may be used to dry the sample gas. Do not use silica gel.

6.1.4.4 Pump. Same as described in section 6.1.3.3.

6.1.4.5 SO_2 Analyzer. Any analyzer capable of providing a measure of the SO_2 concentration in the range of 0 to 1,000 ppm by volume (or other range necessary to measure the SO_2 concentration) at least once every 10 minutes.

6.1.4.6 Recorder (optional). To provide a permanent record of the analyzer outputs.

NOTE: Other tracer gas systems, including helium gas systems, are acceptable for determination of instantaneous proportional sampling rates.

6.2 Sample Recovery. Same as Method 5, section 6.2.

6.3 Sample Analysis. Same as Method 5, section 6.3, with the addition of the following:

6.3.1 Separatory Funnel. Glass or Teflon, 500-ml or greater.

7.0 Reagents and Standards

7.1 Sample Collection. Same as Method 5, section 7.1, including deionized distilled water.

7.2 Sample Recovery. Same as Method 5, section 7.2.

7.3 Sample Analysis. The following reagents and standards are required for sample analysis:

7.3.1 Acetone. Same as Method 5 section 7.2.

7.3.2 Dichloromethane (Methylene Chloride). Reagent grade, <0.001 percent residue in glass bottles.

7.3.3 Desiccant. Anhydrous calcium sulfate, calcium chloride, or silica gel, indicating type.

7.3.4 Cylinder Gases. For the purposes of this procedure, span value is defined as the upper limit of the range specified for each analyzer as described in section 6.1.3.4 or 6.1.3.5. If an analyzer with a range different from that specified in this method is used, the span value shall be equal to the upper limit of the range for the analyzer used (see note in section 6.1.3.5).

7.3.4.1 Calibration Gases. The calibration gases for the CO_2, CO, and SO_2 analyzers shall be CO_2 in nitrogen (N_2), CO in N_2, and SO_2 in N_2, respectively. CO_2 and CO calibration gases may be combined in a single cylinder. Use three calibration gases as specified in Method 6C, sections 7.2.1 through 7.2.3.

7.3.4.2 SO_2 Injection Gas. A known concentration of SO_2 in N_2. The concentration must be at least 2 percent SO_2 with a maximum of 100 percent SO_2.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Pretest Preparation. Same as Method 5, section 8.1.

8.2 Calibration Gas and SO_2 Injection Gas Concentration Verification, Sampling System Bias Check, Response Time Test, and Zero and Calibration Drift Tests. Same as Method 6C, sections 8.2.1, 8.2.3, 8.2.4, and 8.5, respectively, except that for verification of CO and CO_2 gas concentrations, substitute Method 3 for Method 6.

8.3 Preliminary Determinations.

8.3.1 Sampling Location. The sampling location for the particulate sampling probe shall be 2.45 ±0.15 m (8 ±0.5 ft) above the platform upon which the wood heater is placed (*i.e.*, the top of the scale).

8.3.2 Sampling Probe and Nozzle. Select a nozzle, if used, sized for the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain proportional sampling rates. During the run, do not change the nozzle size. Select a suitable probe liner and probe length to effect minimum blockage.

8.4 Preparation of Particulate Sampling Train. Same as Method 5, section 8.3, with the exception of the following:

8.4.1 The train should be assembled as shown in Figure 5H–1.

8.4.2 A glass cyclone may not be used between the probe and filter holder.

8.5 Leak-Check Procedures.

8.5.1 Leak-Check of Metering System Shown in Figure 5H–1. That portion of the sampling train from the pump to the orifice meter shall be leak-checked after each certification or audit test. Use the procedure described in Method 5, section 8.4.1.

8.5.2 Pretest Leak-Check. A pretest leak-check of the sampling train is recommended, but not required. If the pretest leak-check is conducted, the procedures outlined in Method 5, section 8.5.2 should be used. A vacuum of 130 mm Hg (5 in. Hg) may be used instead of 380 mm Hg (15 in. Hg).

8.5.2 Leak-Checks During Sample Run. If, during the sampling run, a component (*e.g.*, filter assembly or impinger) change becomes necessary, conduct a leak-check as described in Method 5, section 8.4.3.

8.5.3 Post-Test Leak-Check. A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be performed in accordance with the procedures outlined in Method 5, section 8.4.4, except that a vacuum of 130 mm Hg (5 in. Hg) or the greatest vacuum measured during the test run, whichever is greater, may be used instead of 380 mm Hg (15 in. Hg).

8.6 Tracer Gas Procedure. A schematic of the tracer gas injection and sampling systems is shown in Figure 5H–2.

8.6.1 SO_2 Injection Probe. Install the SO_2 injection probe and dispersion loop in the stack at a location 2.9 ±0.15 m (9.5 ±0.5 ft) above the sampling platform.

8.6.2 SO_2 Sampling Probe. Install the SO_2 sampling probe at the centroid of the stack at a location 4.1 ±0.15 m (13.5 ±0.5 ft) above the sampling platform.

8.7 Flow Rate Measurement System. A schematic of the flow rate measurement system is shown in Figure 5H–2. Locate the flow rate measurement sampling probe at the centroid of the stack at a location 2.3 ±0.3 m (7.5 ±1 ft) above the sampling platform.

8.8 Tracer Gas Procedure. Within 1 minute after closing the wood heater door at the start of the test run (as defined in Method 28, section 8.8.1), meter a known concentration of SO_2 tracer gas at a constant flow rate into the wood heater stack. Monitor the SO_2 concentration in the stack, and record the SO_2 concentrations at 10-minute intervals or more often. Adjust the particulate sampling flow rate proportionally to the SO_2 concentration changes using Equation 5H–6 (*e.g.*, the SO_2 concentration at the first 10-minute reading is measured to be 100 ppm; the next 10 minute SO_2 concentration is measured to be 75 ppm: the particulate sample flow rate is adjusted from the initial 0.15 cfm to 0.20 cfm). A check for proportional rate variation shall be made at the completion of the test run using Equation 5H–10.

8.9 Volumetric Flow Rate Procedure. Apply stoichiometric relationships to the wood combustion process in determining the exhaust gas flow rate as follows:

8.9.1 Test Fuel Charge Weight. Record the test fuel charge weight (wet) as specified in Method 28, section 8.8.2. The wood is assumed to have the following weight percent composition: 51 percent carbon, 7.3 percent hydrogen, 41 percent oxygen. Record the wood moisture for each fuel charge as described in Method 28, section 8.6.5. The ash is assumed to have negligible effect on associated C, H, and O concentrations after the test burn.

8.9.2 Measured Values. Record the CO and CO_2 concentrations in the stack on a dry basis every 10 minutes during the test run or more often. Average these values for the test run. Use as a mole fraction (*e.g.*, 10 percent CO_2 is recorded as 0.10) in the calculations to express total flow (see Equation 5H–6).

8.10 Sampling Train Operation.

8.10.1 For each run, record the data required on a data sheet such as the one shown in Figure 5H–3. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak-check, and when sampling is halted. Take other readings as indicated on Figure 5H–3 at least once each 10 minutes during the test run.

8.10.2 Remove the nozzle cap, verify that the filter and probe heating systems are up to temperature, and that the probe is properly positioned. Position the nozzle, if used, facing into gas stream, or the probe tip in the 50 mm (2 in.) centroidal area of the stack.

8.10.3 Be careful not to bump the probe tip into the stack wall when removing or inserting the probe through the porthole; this minimizes the chance of extracting deposited material.

8.10.4 When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

8.10.5 Begin sampling at the start of the test run as defined in Method 28, section 8.8.1, start the sample pump, and adjust the sample flow rate to between 0.003 and 0.014 m^3/min (0.1 and 0.5 cfm). Adjust the sample flow rate proportionally to the stack gas flow during the test run according to the procedures outlined in section 8. Maintain a proportional sampling rate (within 10 percent of the desired value) and a filter holder temperature no greater than 120 °C (248 °F).

8.10.6 During the test run, make periodic adjustments to keep the temperature around the filter holder at the proper level. Add more ice to the impinger box and, if necessary, salt to maintain a temperature of less than 20 °C (68 °F) at the condenser/silica gel outlet.

8.10.7 If the pressure drop across the filter becomes too high, making proportional sampling difficult to maintain, either filter may be replaced during a sample run. It is recommended that another complete filter assembly be used rather than attempting to change the filter itself. Before a new filter assembly is installed, conduct a leak-check (see section 8.5.2). The total particulate weight shall include the summation of all filter assembly catches. The total time for changing sample train components shall not exceed 10 minutes. No more than one component change is allowed for any test run.

8.10.8 At the end of the test run, turn off the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak-check, as outlined in section 8.5.3.

8.11 Sample Recovery. Same as Method 5, section 8.7, with the exception of the following:

8.11.1 Blanks. The volume of the acetone blank may be about 50-ml, rather than 200-ml; a 200-ml water blank shall also be saved for analysis.

8.11.2 Samples.

8.11.2.1 Container Nos. 1 and 1A. Treat the two filters according to the procedures outlined in Method 5, section 8.7.6.1. The filters

may be stored either in a single container or in separate containers.

8.11.2.2 Container No. 2. Same as Method 5, section 8.7.6.2, except that the container should not be sealed until the impinger rinse solution is added (see section 8.10.2.4).

8.11.2.3 Container No. 3. Treat the impingers as follows: Measure the liquid which is in the first three impingers to within 1-ml by using a graduated cylinder or by weighing it to within 0.5 g by using a balance (if one is available). Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas. Transfer the water from the first, second, and third impingers to a glass container. Tighten the lid on the sample container so that water will not leak out.

8.11.2.4 Rinse impingers and graduated cylinder, if used, with acetone three times or more. Avoid direct contact between the acetone and any stopcock grease or collection of any stopcock grease in the rinse solutions. Add these rinse solutions to sample Container No. 2.

8.11.2.5 Container No. 4. Same as Method 5, section 8.7.6.3

8.12 Sample Transport. Whenever possible, containers should be transferred in such a way that they remain upright at all times.

NOTE: Requirements for capping and transport of sample containers are not applicable if sample recovery and analysis occur in the same room.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.2	Sampling system bias check	Ensures that bias introduced by measurement system, minus analyzer, is no greater than 3 percent of span.
8.2	Analyzer zero and calibration drift tests	Ensures that bias introduced by drift in the measurement system output during the run is no greater than 3 percent of span.
8.5, 10.1, 12.13	Sampling equipment leak-check and calibration; proportional sampling rate verification.	Ensures accurate measurement of stack gas flow rate, sample volume.
10.1	Analytical balance calibration	Ensure accurate and precise measurement of collected particulate.
10.3	Analyzer calibration error check	Ensures that bias introduced by analyzer calibration error is no greater than 2 percent of span.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory record of all calibrations.

10.1 Volume Metering System, Temperature Sensors, Barometer, and Analytical Balance. Same as Method 5G, sections 10.2 through 10.5, respectively.

10.2 SO_2 Injection Rotameter. Calibrate the SO_2 injection rotameter system with a soap film flowmeter or similar direct volume measuring device with an accuracy of 2 percent. Operate the rotameter at a single reading for at least three calibration runs for 10 minutes each. When three consecutive calibration flow rates agree within 5 percent, average the three flow rates, mark the rotameter at the calibrated setting, and use the calibration flow rate as the SO_2 injection flow rate during the test run. Repeat the rotameter calibration before the first certification test and semiannually thereafter.

10.3. Gas Analyzers. Same as Method 6C, section 10.0.

10.4 Field Balance Calibration Check. Check the calibration of the balance used to weigh impingers with a weight that is at least 500g or within 50g of a loaded impinger. The weight must be ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 6 (or better). Daily before use, the field balance must measure the weight within ± 0.5g of the certified mass. If the daily balance calibration check fails, perform corrective measures and repeat the check before using balance.

10.5 Analytical Balance Calibration. Perform a multipoint calibration (at least five points spanning the operational range) of the analytical balance before the first use, and semiannually thereafter. The calibration of the analytical balance must be conducted using ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 2 (or better) tolerance weights. Audit the balance each day it is used for gravimetric measurements by weighing at least one ASTM E617–13 Class 2 tolerance (or better) calibration weight that corresponds to 50 to 150 percent of the weight of one filter or between 1g and 5g. If the scale cannot reproduce the value of the calibration weight to within 0.5 mg of the certified mass, perform corrective measures, and conduct the multipoint calibration before use.

11.0 Analytical Procedure

11.1 Record the data required on a sheet such as the one shown in Figure 5H–4.

11.2 Handle each sample container as follows:

11.2.1 Container Nos. 1 and 1A. Treat the two filters according to the procedures outlined in Method 5, section 11.2.1.

11.2.2 Container No. 2. Same as Method 5, section 11.2.2, except that the beaker may be smaller than 250-ml.

11.2.3 Container No. 3. Note the level of liquid in the container and confirm on the analysis sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Determination of sample leakage is not applicable if sample recovery and analysis occur in the same room. Measure the liquid in this container either volumetrically to within 1-ml or gravimetrically to within 0.5 g. Transfer the contents to a 500-ml or larger separatory funnel. Rinse the container with water, and add to the separatory funnel. Add 25-ml of dichloromethane to the separatory funnel, stopper and vigorously shake 1 minute, let separate and transfer the dichloromethane (lower layer) into a tared beaker or evaporating dish. Repeat twice more. It is necessary to rinse Container No. 3 with dichloromethane. This rinse is added to the impinger extract container. Transfer the remaining water from the separatory funnel to a tared beaker or evaporating dish and evaporate to dryness at 104 °C (220 °F). Desiccate and weigh to a constant weight. Evaporate the combined impinger water extracts at ambient temperature and pressure. Desiccate and weigh to a constant weight. Report both results to the nearest 0.1 mg.

11.2.4 Container No. 4. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance.

11.2.5 Acetone Blank Container. Same as Method 5, section 11.2.4, except that the beaker may be smaller than 250 ml.

11.2.6 Dichloromethane Blank Container. Treat the same as the acetone blank.

11.2.7 Water Blank Container. Transfer the water to a tared 250 ml beaker and evaporate to dryness at 104 °C (220 °F). Desiccate and weigh to a constant weight.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

12.1 Nomenclature.

A = Sample flow rate adjustment factor.
BR = Dry wood burn rate, kg/hr (lb/hr), from Method 28, Section 8.3.
B_{ws} = Water vapor in the gas stream, proportion by volume.
C_i = Tracer gas concentration at inlet, ppmv.
C_o = Tracer gas concentration at outlet, ppmv.
C_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (g/dscf).
E = Particulate emission rate, g/hr (lb/hr).
ΔH = Average pressure differential across the orifice meter (see Figure 5H–1), mm H_2O (in. H_2O).
L_a = Maximum acceptable leakage rate for either a post-test leak-check or for a leak-check following a component change; equal to 0.00057 cmm (0.020 cfm) or 4 percent of the average sampling rate, whichever is less.
L_1 = Individual leakage rate observed during the leak-check conducted before a component change, cmm (cfm).
L_p = Leakage rate observed during the post-test leak-check, cmm (cfm).
m_n = Total amount of particulate matter collected, mg.
M_a = Mass of residue of solvent after evaporation, mg.
N_C = Grams of carbon/gram of dry fuel (lb/lb), equal to 0.0425.
N_T = Total dry moles of exhaust gas/kg of dry wood burned, g-moles/kg (lb-moles/lb).
PR = Percent of proportional sampling rate.
P_{bar} = Barometric pressure at the sampling site, mm Hg (in.Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in.Hg).
Q_i = Gas volumetric flow rate at inlet, cfm (l/min).
Q_o = Gas volumetric flow rate at outlet, cfm (l/min).

12.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 5H–3).

12.3 Dry Gas Volume. Same as Method 5, section 12.3.

12.4 Volume of Water Vapor.

$$V_{w(std)} = K_2 V_{1c} \qquad \text{Eq. 5H-1}$$

Where:

K_2 = 0.001333 m^3/ml for metric units.
K_2 = 0.04707 ft^3/ml for English units.

12.5 Moisture Content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad \text{Eq. 5H-2}$$

12.6 Solvent Wash Blank.

$$W_a = \frac{M_a V_{aw}}{V_a} \qquad \text{Eq. 5H-3}$$

12.7 Total Particulate Weight. Determine the total particulate catch from the sum of the weights obtained from containers 1, 2, 3,

and 4 less the appropriate solvent blanks (see Figure 5H–4).

NOTE: Refer to Method 5, section 8.5 to assist in calculation of results involving two filter assemblies.

12.8 Particulate Concentration.

$$C_s = \frac{0.001g}{mg} \frac{m_n}{V_{m(std)}} \qquad \text{Eq. 5H-4}$$

12.9 Sample Flow Rate Adjustment.

$$a = \frac{S_1}{S_i} \qquad \text{Eq. 5H-5}$$

12.10 Carbon Balance for Total Moles of Exhaust Gas (dry)/kg of Wood Burned in the Exhaust Gas.

$$N_T = \frac{K_3 N_C}{Y_{CO_2} + Y_{CO} + Y_{HC}} \qquad \text{Eq. 5H-6}$$

Where:

K_3 = 1000 g/kg for metric units.
K_3 = 1.0 lb/lb for English units.

NOTE: The NO_X/SO_X portion of the gas is assumed to be negligible.

12.11 Total Stack Gas Flow Rate.

$$Q_{sd} = K_4 \, N_T \, BR \qquad \text{Eq. 5H-7}$$

Where:

K_4 = 0.02406 dscm/g-mole for metric units.
K_4 = 384.8 dscf/lb-mole for English units.

12.12 Particulate Emission Rate.

$$E = C_s \, Q_{sd} \qquad \text{Eq. 5H-8}$$

12.13 Proportional Rate Variation. Calculate PR for each 10-minute interval, i, of the test run.

$$PR = \frac{\theta \, S_i V_{mi(std)}}{10 \sum_{i=1}^{N} \left[S_i V_{mi(std)} \right]} \times 100 \qquad \text{Eq. 5H-9}$$

12.14 Acceptable Results. If no more than 15 percent of the PR values for all the intervals fall outside the range 90 percent ≤PR ≤110 percent, and if no PR value for any interval falls outside the range 75 ≤PR ≤125 percent, the results are acceptable. If the PR values for the test runs are judged to be unacceptable, report the test run emission results, but do not include the test run results in calculating the weighted average emission rate, and repeat the test.

12.15 Alternative Tracer Gas Flow Rate Determination.

$$Q_o = \frac{Q_i \times C_i}{C_o} \qquad Eq. 5H - 10$$

NOTE: This gives Q for a single instance only. Repeated multiple determinations are needed to track temporal variations. Very small variations in Q_i, C_i, or C_o may give very large variations in Q_o.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Alternative Stack Gas Volumetric Flow Rate Determination (Tracer Gas).

16.1.1 Apparatus.

16.1.1.1 Tracer Gas Injector System. This is to inject a known concentration of tracer gas into the stack. This system consists of a cylinder of tracer gas, a gas cylinder regulator, a stainless steel needle valve or a flow controller, a nonreactive (stainless steel or glass) rotameter, and an injection loop to disperse the tracer gas evenly in the stack.

16.1.1.2 Tracer Gas Probe. A glass or stainless steel sampling probe.

16.1.1.3 Gas Conditioning System. A gas conditioning system is suitable for delivering a cleaned sample to the analyzer consisting of a filter to remove particulate and a condenser capable of lowering the dew point of the sample gas to less than 5 °C (40 °F). A desiccant such as anhydrous calcium sulfate may be used to dry the sample gas. Desiccants which react or absorb tracer gas or stack gas may not be used, e.g. silica gel absorbs CO_2.

16.1.1.4 Pump. An inert (*i.e.*, stainless steel or Teflon head) pump to deliver more than the total sample required by the manufacturer's specifications for the analyzer used to measure the downstream tracer gas concentration.

16.1.1.5 Gas Analyzer. A gas analyzer is any analyzer capable of measuring the tracer gas concentration in the range necessary at least every 10 minutes. A means of controlling the analyzer flow rate and a device for determining proper sample flow rate shall be provided unless data is provided to show that the analyzer is insensitive to flow variations over the range encountered during the test.

The gas analyzer needs to meet or exceed the following performance specifications:

Linearity	±1 percent of full scale.
Calibration Error	≤2 percent of span.
Response Time	≤10 seconds.
Zero Drift (24 hour)	≤2 percent of full scale.
Span Drift (24 hour)	≤2 percent of full scale.
Resolution	≤0.5 percent of span.

16.1.1.6 Recorder (optional). To provide a permanent record of the analyzer output.

16.1.2 Reagents.

16.1.2.1 Tracer Gas. The tracer gas is sulfur hexafluoride in an appropriate concentration for accurate analyzer measurement or pure sulfur dioxide. The gas used must be nonreactive with the stack effluent and give minimal (<3 percent) interference to measurement by the gas analyzer.

16.1.3 Procedure. Select upstream and downstream locations in the stack or duct for introducing the tracer gas and delivering the sampled gas to the analyzer. The inlet location should be 8 or more duct diameters beyond any upstream flow disturbance. The outlet should be 8 or more undisturbed duct diameters from the inlet and 2 or more duct diameters from the duct exit. After installing the apparatus, meter a known concentration of the tracer gas into the stack at the inlet location. Use the gas sample probe and analyzer to show that no stratification of the tracer gas is found in the stack at the measurement locations. Monitor the tracer gas concentration from the outlet location and record the concentration at 10-minute intervals or more often at the option of the tester. A minimum of three measured intervals is recommended to determine the stack gas volumetric flow rate. Other statistical procedures may be applied for complete flow characterization and additional QA/QC.

17.0 References

Same as Method 5G, section 17.0.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

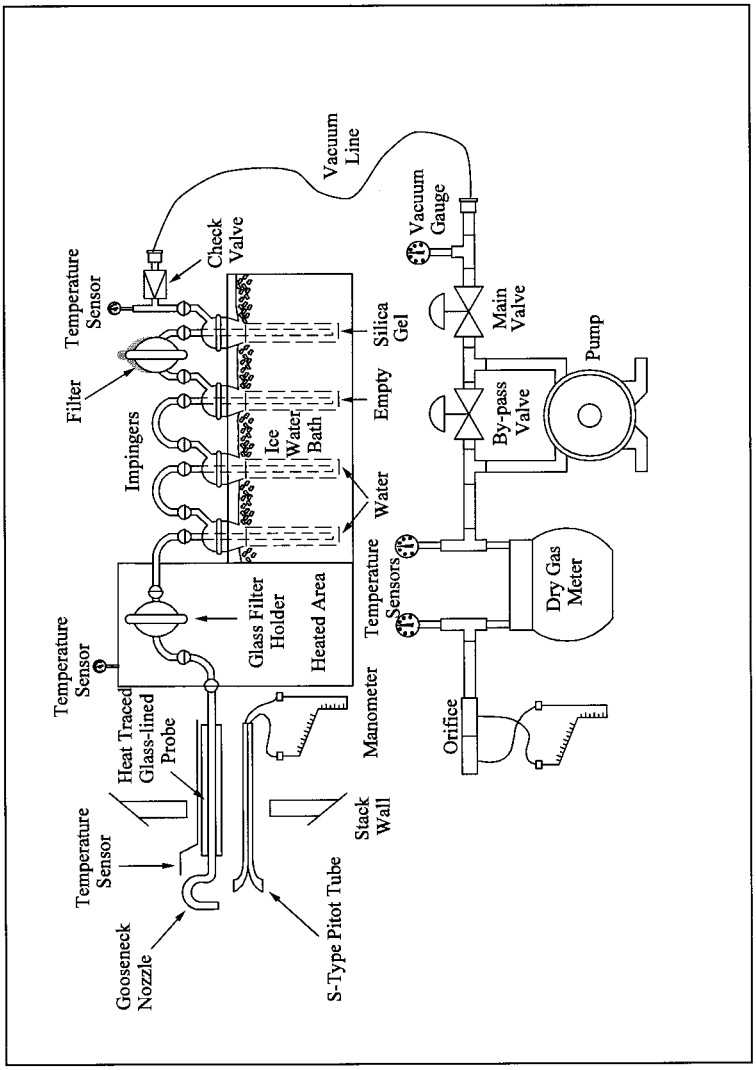


Figure 5H-1. Sampling Train.

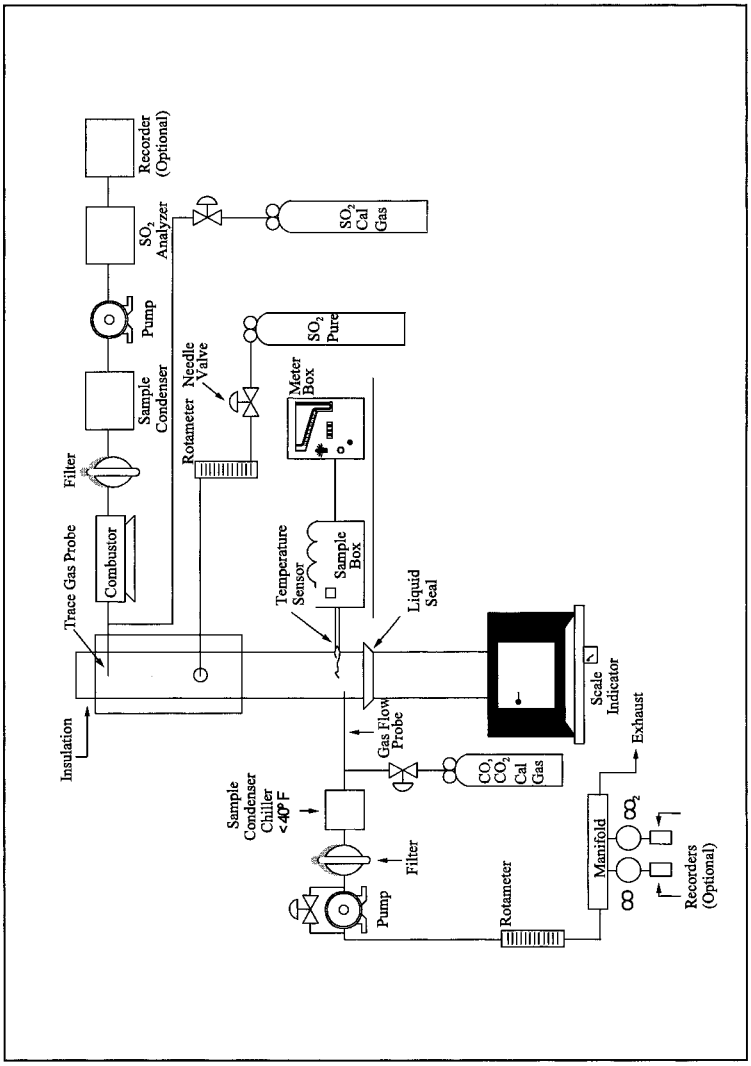
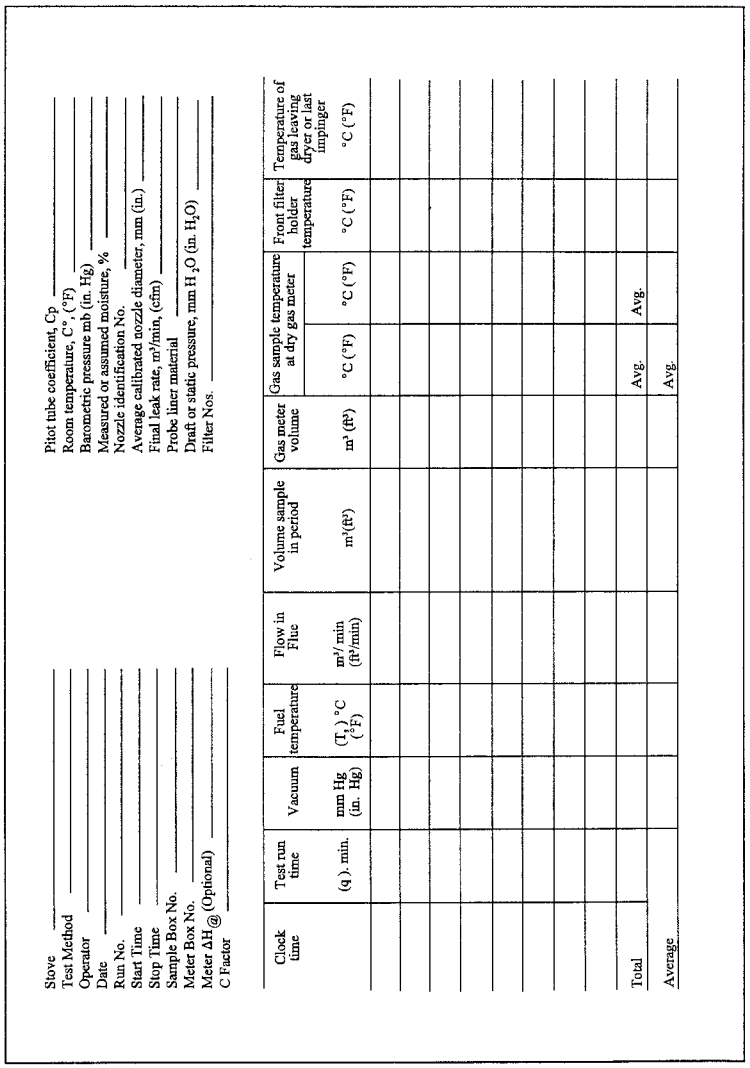


Figure 5H-2. Test System Schematic.



Stove _____
Test Method _____
Operator _____
Date _____
Run No. _____
Start Time _____
Stop Time _____
Sample Box No. _____
Meter Box No. _____
Meter ΔH@ (Optional) _____
C Factor _____

Pitot tube coefficient, Cp _____
Room temperature, C°, (°F) _____
Barometric pressure mb (in. Hg) _____
Measured or assumed moisture, % _____
Nozzle identification No. _____
Average calibrated nozzle diameter, mm (in.) _____
Final leak rate, m³/min, (cfm) _____
Probe liner material _____
Draft or static pressure, mm H_2O (in. H_2O) _____
Filter Nos. _____

Clock time	Test run time (q), min.	Vacuum mm Hg (in. Hg)	Fuel temperature (T_s) °C (°F)	Flow in Flue m³/ min (ft³/min)	Volume sample in period m³(ft³)	Gas meter volume m³ (ft³)	Gas sample temperature at dry gas meter °C (°F)	Gas sample temperature at dry gas meter °C (°F)	Front filter holder temperature °C (°F)	Temperature of gas leaving dryer or last impinger °C (°F)
Total							Avg.	Avg.		
Average							Avg.			

Figure 5H-3. Sampling Data Sheet.

Stove _____
Date _____
Run No. _____
Filter Nos. _____
Amount liquid lost during transport, ml _____
Acetone blank volume, ml _____
Acetone wash volume, ml _____
Acetone blank concentration, mg/ml _____
Acetone wash blank, mg _____

Dichloromethane blank volume, ml _____
Dichloromethane wash volume, ml _____
Dichloromethane blank concentration, mg/ml _____
Dichloromethane wash blank, mg _____
Water blank volume, ml _____
Waster wash volume, ml _____
Water blank concentration, mg/ml _____
Water wash blank, mg _____

Container number	Weight of particulate collected, mg		
	Final weight	Tare weight	Weight gain
1 _____			
2 _____			
3 _____			
4 _____			
5 _____			
Total			
Less acetone blank			
Less dichloromethane blank			
Less water blank			
Weight of particulate matter			

	Volume of liquid water collected	
	Impinger volume, ml	Silica gel weight, g
Final _____		
Initial _____		
Liquid collected _____		
Total volume collected _____		g or ml

* Convert weight of water to volume by dividing total weight increase by density of water (1 g/ml).

$$\frac{\text{Increase, g}}{\text{(1 g/ml)}} = \text{Volume water, ml}$$

Figure 5H-4. Analysis data sheet.

Figure 5H-4. Analysis Data Sheet.

METHOD 5I—DETERMINATION OF LOW LEVEL PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Certain information is contained in other EPA procedures found in this part. Therefore, to obtain reliable results, persons using this method should have experience with and a thorough knowledge of the following Methods: Methods 1, 2, 3, 4 and 5.

1. Scope and Application.

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of low level particulate matter (PM) emissions from stationary sources. The method is most effective for total PM catches of 50 mg or less. This method was initially developed for performing correlation of manual PM measurements to PM continuous emission monitoring systems (CEMS), however it is also useful for other low particulate concentration applications.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods. Method 5I requires the use of paired trains. Acceptance criteria for the identification of data quality outliers from the paired trains are provided in section 12.2 of this Method.

2. Summary of Method.

2.1. Description. The system setup and operation is essentially identical to Method 5. Particulate is withdrawn isokinetically from the source and collected on a 47 mm glass fiber filter maintained at a temperature of 120 ±14 °C (248 ±25 °F). The PM mass is determined by gravimetric analysis after the removal of uncombined water. Specific measures in this procedure designed to improve system performance at low particulate levels include:

1. Improved sample handling procedures
2 Light weight sample filter assembly
3. Use of low residue grade acetone

Accuracy is improved through the minimization of systemic errors associated with sample handling and weighing procedures. High purity reagents, all glass, grease free, sample train components, and light weight filter assemblies and beakers, each contribute to the overall objective of improved precision and accuracy at low particulate concentrations.

2.2 Paired Trains. This method must be performed using a paired train configuration. These trains may be operated as co-located trains (to trains operating collecting from one port) or as simultaneous trains (separate trains operating from different ports at the same time). Procedures for calculating precision of the paired trains are provided in section 12.

2.3 Detection Limit. a. Typical detection limit for manual particulate testing is 0.5 mg. This mass is also cited as the accepted weight variability limit in determination of ''constant weight'' as cited in section 8.1.2 of this Method. EPA has performed studies to provide guidance on minimum PM catch. The minimum detection limit (MDL) is the minimum concentration or amount of an analyte that can be determined with a specified degree of confidence to be different from zero. We have defined the minimum or target catch as a concentration or amount sufficiently larger than the MDL to ensure that the results are reliable and repeatable. The particulate matter catch is the product of the average particulate matter concentration on a mass per volume basis and the volume of gas collected by the sample train. The tester can generally control the volume of gas collected by increasing the sampling time or to a lesser extent by increasing the rate at which sample is collected. If the tester has a reasonable estimate of the PM concentration from the source, the tester can ensure that the target catch is collected by sampling the appropriate gas volume.

b. However, if the source has a very low particulate matter concentration in the stack, the volume of gas sampled may need to be very large which leads to unacceptably long sampling times. When determining compliance with an emission limit, EPA guidance has been that the tester does not always have to collect the target catch. Instead, we have suggested that the tester sample enough stack gas, that if the source were exactly at the level of the emission standard, the sample catch would equal the target catch. Thus, if at the end of the test the catch were smaller than the target, we could still conclude that the source is in compliance though we might not know the exact emission level. This volume of gas becomes a target volume that can be translated into a target sampling time by assuming an average sampling rate. Because the MDL forms the basis for our guidance on target sampling times, EPA has conducted a systematic laboratory study to define what is the MDL for Method 5 and determined the Method to have a calculated practical quantitation limit (PQL) of 3 mg of PM and an MDL of 1 mg.

c. Based on these results, the EPA has concluded that for PM testing, the target catch must be no less than 3 mg. Those sample catches between 1 mg and 3 mg are between the detection limit and the limit of quantitation. If a tester uses the target catch to estimate a target sampling time that results in sample catches that are less than 3 mg, you should not automatically reject the results. If the tester calculated the target sampling time as described above by assuming that the source was at the level of the emission limit, the results would still be valid for determining that the source was in compliance. For purposes other than determining compliance, results should be divided into two categories—those that fall between 3 mg and 1 mg and those that are below 1 mg. A sample catch between 1 and 3 mg may be used for such purposes as calculating emission rates with the understanding that the resulting emission rates can have a high degree of uncertainty. Results of less than 1 mg should not be used for calculating emission rates or pollutant concentrations.

d. When collecting small catches such as 3 mg, bias becomes an important issue. Source testers must use extreme caution to reach the PQL of 3 mg by assuring that sampling

probes are very clean (perhaps confirmed by low blank weights) before use in the field. They should also use low tare weight sample containers, and establish a well-controlled balance room to weigh the samples.

3. Definitions.

3.1 *Light Weight Filter Housing.* A smaller housing that allows the entire filtering system to be weighed before and after sample collection. (See. 6.1.3)

3.2 *Paired Train.* Sample systems trains may be operated as co-located trains (two sample probes attached to each other in the same port) or as simultaneous trains (two separate trains operating from different ports at the same time).

4. Interferences.

a. There are numerous potential interferents that may be encountered during performance of Method 5I sampling and analyses. This Method should be considered more sensitive to the normal interferents typically encountered during particulate testing because of the low level concentrations of the flue gas stream being sampled.

b. Care must be taken to minimize field contamination, especially to the filter housing since the entire unit is weighed (not just the filter media). Care must also be taken to ensure that no sample is lost during the sampling process (such as during port changes, removal of the filter assemblies from the probes, etc.).

c. Balance room conditions are a source of concern for analysis of the low level samples. Relative humidity, ambient temperatures variations, air draft, vibrations and even barometric pressure can affect consistent reproducible measurements of the sample media. Ideally, the same analyst who performs the tare weights should perform the final weights to minimize the effects of procedural differences specific to the analysts.

d. Attention must also be provided to weighing artifacts caused by electrostatic charges which may have to be discharged or neutralized prior to sample analysis. Static charge can affect consistent and reliable gravimetric readings in low humidity environments. Method 5I recommends a relative humidity of less than 50 percent in the weighing room environment used for sample analyses. However, lower humidity may be encountered or required to address sample precision problems. Low humidity conditions can increase the effects of static charge.

e. Other interferences associated with typical Method 5 testing (sulfates, acid gases, etc.) are also applicable to Method 5I.

5. Safety.

Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety concerns associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability and observe all regulatory limitations before using this method.

6. Equipment and Supplies.

6.1 Sample Collection Equipment and Supplies. The sample train is nearly identical in configuration to the train depicted in Figure 5–1 of Method 5. The primary difference in the sample trains is the lightweight Method 5I filter assembly that attaches directly to the exit to the probe. Other exceptions and additions specific to Method 5I include:

6.1.1 Probe Nozzle. Same as Method 5, with the exception that it must be constructed of borosilicate or quartz glass tubing.

6.1.2 Probe Liner. Same as Method 5, with the exception that it must be constructed of borosilicate or quartz glass tubing.

6.1.3 Filter Holder. The filter holder is constructed of borosilicate or quartz glass front cover designed to hold a 47-mm glass fiber filter, with a wafer thin stainless steel (SS) filter support, a silicone rubber or Viton O-ring, and Teflon tape seal. This holder design will provide a positive seal against leakage from the outside or around the filter. The filter holder assembly fits into a SS filter holder and attaches directly to the outlet of the probe. The tare weight of the filter, borosilicate or quartz glass holder, SS filter support, O-ring and Teflon tape seal generally will not exceed approximately 35 grams. The filter holder is designed to use a 47-mm glass fiber filter meeting the quality criteria in of Method 5. These units are commercially available from several source testing equipment vendors. Once the filter holder has been assembled, desiccated and tared, protect it from external sources of contamination by covering the front socket with a ground glass plug. Secure the plug with an impinger clamp or other item that will ensure a leak-free fitting.

6.2 Sample Recovery Equipment and Supplies. Same as Method 5, with the following exceptions:

6.2.1 Probe-Liner and Probe-Nozzle Brushes. Teflon or nylon bristle brushes with stainless steel wire handles, should be used to clean the probe. The probe brush must have extensions (at least as long as the probe) of Teflon, nylon or similarly inert material. The brushes must be properly sized and shaped for brushing out the probe liner and nozzle.

6.2.2 Wash Bottles. Two Teflon wash bottles are recommended however, polyethylene wash bottles may be used at the option of the tester. Acetone should not be stored in polyethylene bottles for longer than one month.

6.2.3 Filter Assembly Transport. A system should be employed to minimize contamination of the filter assemblies during transport to and from the field test location. A carrying case or packet with clean compartments of sufficient size to accommodate each filter assembly can be used. This system should have an air tight seal to further minimize contamination during transport to and from the field.

6.3 Analysis Equipment and Supplies. Same as Method 5, with the following exception:

6.3.1 Lightweight Beaker Liner. Teflon or other lightweight beaker liners are used for the analysis of the probe and nozzle rinses. These light weight liners are used in place of the borosilicate glass beakers typically used for the Method 5 weighings in order to improve sample analytical precision.

6.3.2 Anti-static Treatment. Commercially available gaseous anti-static rinses are recommended for low humidity situations that contribute to static charge problems.

7. Reagents and Standards.

7.1 Sampling Reagents. The reagents used in sampling are the same as Method 5 with the following exceptions:

7.1.1 Filters. The quality specifications for the filters are identical to those cited for Method 5. The only difference is the filter diameter of 47 millimeters.

7.1.2 Stopcock Grease. Stopcock grease cannot be used with this sampling train. We recommend that the sampling train be assembled with glass joints containing O-ring seals or screw-on connectors, or similar.

7.1.3 Acetone. Low residue type acetone, ≤0.001 percent residue, purchased in glass bottles is used for the recovery of particulate matter from the probe and nozzle. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers; thus, acetone blanks must be run prior to field use and only acetone with low blank values (≤0.001 percent residue, as specified by the manufacturer) must be used. Acetone blank correction is not allowed for this method; therefore, it is critical that high purity reagents be purchased and verified prior to use.

7.1.4 Gloves. Disposable, powder-free, latex surgical gloves, or their equivalent are used at all times when handling the filter housings or performing sample recovery.

7.2 Standards. There are no applicable standards commercially available for Method 5I analyses.

8. Sample Collection, Preservation, Storage, and Transport.

8.1 Pretest Preparation. Same as Method 5 with several exceptions specific to filter assembly and weighing.

8.1.1 Filter Assembly. Uniquely identify each filter support before loading filters into the holder assembly. This can be done with an engraving tool or a permanent marker. Use powder free latex surgical gloves whenever handling the filter holder assemblies. Place the O-ring on the back of the filter housing in the O-ring groove. Place a 47 mm glass fiber filter on the O-ring with the face down. Place a stainless steel filter holder against the back of the filter. Carefully wrap 5 mm (¼ inch) wide Teflon'' tape one timearound the outside of the filter holder overlapping the stainless steel filter support by approximately 2.5 mm (⅛ inch). Gently brush the Teflon tape down on the back of the stainless steel filter support. Store the filter assemblies in their transport case until time for weighing or field use.

8.1.2 Filter Weighing Procedures. a. Desiccate the entire filter holder assemblies at 20 ±5.6 °C (68 ±10 °F) and ambient pressure for at least 24 hours. Weigh at intervals of at least 6 hours to a constant weight, *i.e.,* 0.5 mg change from previous weighing. Record the results to the nearest 0.1 mg. During each weighing, the filter holder assemblies must not be exposed to the laboratory atmosphere for a period greater than 2 minutes and a relative humidity above 50 percent. Lower relative humidity may be required in order to improve analytical precision. However, low humidity conditions increase static charge to the sample media.

b. Alternatively (unless otherwise specified by the Administrator), the filters holder assemblies may be oven dried at 105 °C (220 °F) for a minimum of 2 hours, desiccated for 2 hours, and weighed. The procedure used for the tare weigh must also be used for the final weight determination.

c. Experience has shown that weighing uncertainties are not only related to the balance performance but to the entire weighing procedure. Therefore, before performing any measurement, establish and follow standard operating procedures, taking into account the sampling equipment and filters to be used.

8.2 Preliminary Determinations. Select the sampling site, traverse points, probe nozzle, and probe length as specified in Method 5.

8.3 Preparation of Sampling Train. Same as Method 5, section 8.3, with the following exception: During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until justbefore assembly or until sampling is about to begin. Using gloves, place a labeled (identified) and weighed filter holder assembly into the stainless steel holder. Then place this whole unit in the Method 5 hot box, and attach it to the probe. Do not use stopcock grease.

8.4 Leak-Check Procedures. Same as Method 5.

8.5 Sampling Train Operation.

8.5.1. Operation. Operate the sampling train in a manner consistent with those described in Methods 1, 2, 4 and 5 in terms of the number of sample points and minimum time per point. The sample rate and total gas volume should be adjusted based on estimated grain loading of the source being characterized. The total sampling time must be a function of the estimated mass of particulate to be collected for the run. Targeted mass to be collected in a typical Method 5I sample train should be on the order of 10 to 20 mg. Method 5I is most appropriate for total collected masses of less than 50 milligrams, however, there is not an exact particulate loading cutoff, and it is likely that some runs may exceed 50 mg. Exceeding 50 mg (or less than 10 mg) for the sample mass does not necessarily justify invalidating a sample run if all other Method criteria are met.

8.5.2 Paired Train. This Method requires PM samples be collected with paired trains.

8.5.2.1 It is important that the systems be operated truly simultaneously. This implies that both sample systems start and stop at the same times. This also means that if one sample system is stopped during the run, the other sample systems must also be stopped until the cause has been corrected.

8.5.2.2 Care should be taken to maintain the filter box temperature of the paired trains as close as possible to the Method required temperature of 120 ±14 °C (248 ±25 °F). If separate ovens are being used for simultaneously operated trains, it is recommended that the oven temperature of each train be maintained within ±14 °C (±25 °F) of each other.

8.5.2.3 The nozzles for paired trains need not be identically sized.

8.5.2.4 Co-located sample nozzles must be within the same plane perpendicular to the gas flow. Co-located nozzles and pitot assemblies should be within a 6.0 cm × 6.0 cm square (as cited for a quadruple train in Reference Method 301).

8.5.3 Duplicate gas samples for molecular weight determination need not be collected.

8.6 Sample Recovery. Same as Method 5 with several exceptions specific to the filter housing.

8.6.1 Before moving the sampling train to the cleanup site, remove the probe from the train and seal the nozzle inlet and outlet of the probe. Be careful not to lose any condensate that might be present. Cap the filter inlet using a standard ground glass plug and secure the cap with an impinger clamp. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger condenser and the filter holder, disconnect the line at the filter holder and let any condensed water or liquid drain into the impingers or condenser.

8.6.2 Transfer the probe and filter-impinger assembly to the cleanup area. This area must be clean and protected from the wind so that the possibility of losing any of the sample will be minimized.

8.6.3 Inspect the train prior to and during disassembly and note any abnormal conditions such as particulate color, filter loading, impinger liquid color, etc.

8.6.4 Container No. 1, Filter Assembly. Carefully remove the cooled filter holder assembly from the Method 5 hot box and place it in the transport case. Use a pair of clean gloves to handle the filter holder assembly.

8.6.5 Container No. 2, Probe Nozzle and Probe Liner Rinse. Rinse the probe and nozzle components with acetone. Be certain that the probe and nozzle brushes have been thoroughly rinsed prior to use as they can be a source of contamination.

8.6.6 All Other Train Components. (Impingers) Same as Method 5.

8.7 Sample Storage and Transport. Whenever possible, containers should be shipped in such a way that they remain upright at all times. All appropriate dangerous goods shipping requirements must be observed since acetone is a flammable liquid.

9. Quality Control.

9.1 Miscellaneous Field Quality Control Measures.

9.1.1 A quality control (QC) check of the volume metering system at the field site is suggested before collecting the sample using the procedures in Method 5, section 4.4.1.

9.1.2 All other quality control checks outlined in Methods 1, 2, 4 and 5 also apply to Method 5I. This includes procedures such as leak-checks, equipment calibration checks, and independent checks of field data sheets for reasonableness and completeness.

9.2 Quality Control Samples.

9.2.1 Required QC Sample. A laboratory reagent blank must be collected and analyzed for each lot of acetone used for a field program to confirm that it is of suitable purity. The particulate samples cannot be blank corrected.

9.2.2 Recommended QC Samples. These samples may be collected and archived for future analyses.

9.2.2.1 A field reagent blank is a recommended QC sample collected from a portion of the acetone used for cleanup of the probe and nozzle. Take 100 ml of this acetone directly from the wash bottle being used and place it in a glass sample container labeled ''field acetone reagent blank.'' At least one field reagent blank is recommended for every five runs completed. The field reagent blank samples demonstrate the purity of the acetone was maintained throughout the program.

9.2.2.2 A field bias blank train is a recommended QC sample. This sample is collected by recovering a probe and filter assembly that has been assembled, taken to the sample location, leak checked, heated, allowed to sit at the sample location for a similar duration of time as a regular sample run, leak-checked again, and then recovered in the same manner as a regular sample. Field bias blanks are not a Method requirement, however, they are recommended and are very useful for identifying sources of contamination in emission testing samples. Field bias blank train results greater than 5 times the method detection limit may be considered problematic.

10. Calibration and Standardization Same as Method 5, section 5.

10.1 Field Balance Calibration Check. Check the calibration of the balance used to weigh impingers with a weight that is at least 500g or within 50g of a loaded impinger. The weight must be ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 6 (or better). Daily, before use, the field balance must measure the weight within ±0.5g of the certified mass. If the daily balance calibration check fails, perform corrective measures and repeat the check before using balance.

10.2 Analytical Balance Calibration. Perform a multipoint calibration (at least five points spanning the operational range) of the analytical balance before the first use, and semiannually thereafter. The calibration of the analytical balance must be conducted using ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 2 (or better) tolerance weights. Audit the balance each day it is used for gravimetric measurements by weighing at least one ASTM E617–13 Class 2 tolerance (or better) calibration weight that corresponds to 50 to 150 percent of the weight of one filter or between 1g and 5g. If the scale cannot reproduce the value of the calibration weight to within 0.5 mg of the certified mass, perform corrective measures and conduct the multipoint calibration before use.

11. Analytical Procedures.

11.1 Analysis. Same as Method 5, sections 11.1–11.2.4, with the following exceptions:

11.1.1 Container No. 1. Same as Method 5, section 11.2.1, with the following exception: Use disposable gloves to remove each of the filter holder assemblies from the desiccator, transport container, or sample oven (after appropriate cooling).

11.1.2 Container No. 2. Same as Method 5, section 11.2.2, with the following exception: It is recommended that the contents of Container No. 2 be transferred to a 250 ml beaker with a Teflon liner or similar container that has a minimal tare weight before bringing to dryness.

12. Data Analysis and Calculations.

12.1 Particulate Emissions. The analytical results cannot be blank corrected for residual acetone found in any of the blanks. All other sample calculations are identical to Method 5.

12.2 Paired Trains Outliers. a. Outliers are identified through the determination of precision and any systemic bias of the paired trains. Data that do not meet this criteria should be flagged as a data quality problem. The primary reason for performing dual train sampling is to generate information to quantify the precision of the Reference Method data. The relative standard deviation (RSD) of paired data is the parameter used to quantify data precision. RSD for two simultaneously gathered data points is determined according to:

$$RSD = 100\% * \left|\left(C_a - C_b\right)\right| / \left(C_a + C_b\right)$$

where, Ca and Cb are concentration values determined from trains A and B respectively. For RSD calculation, the concentration units are unimportant so long as they are consistent.

b. A minimum precision criteria for Reference Method PM data is that RSD for any data pair must be less than 10% as long as the mean PM concentration is greater than 10 mg/dscm. If the mean PM concentration is less than 10 mg/dscm higher RSD values are acceptable. At mean PM concentration of 1 mg/dscm acceptable RSD for paired trains is 25%. Between 1 and 10 mg/dscm acceptable RSD criteria should be linearly scaled from 25% to 10%. Pairs of manual method data exceeding these RSD criteria should be eliminated from the data set used to develop a PM CEMS correlation or to assess RCA. If the mean PM concentration is less than 1 mg/dscm, RSD does not apply and the mean result is acceptable.

13. Method Performance [Reserved]

14. Pollution Prevention [Reserved]

15. Waste Management [Reserved]

16. Alternative Procedures. Same as Method 5.

17. Bibliography. Same as Method 5.

18. Tables, Diagrams, Flowcharts and Validation Data. Figure 5I–1 is a schematic of the sample train.

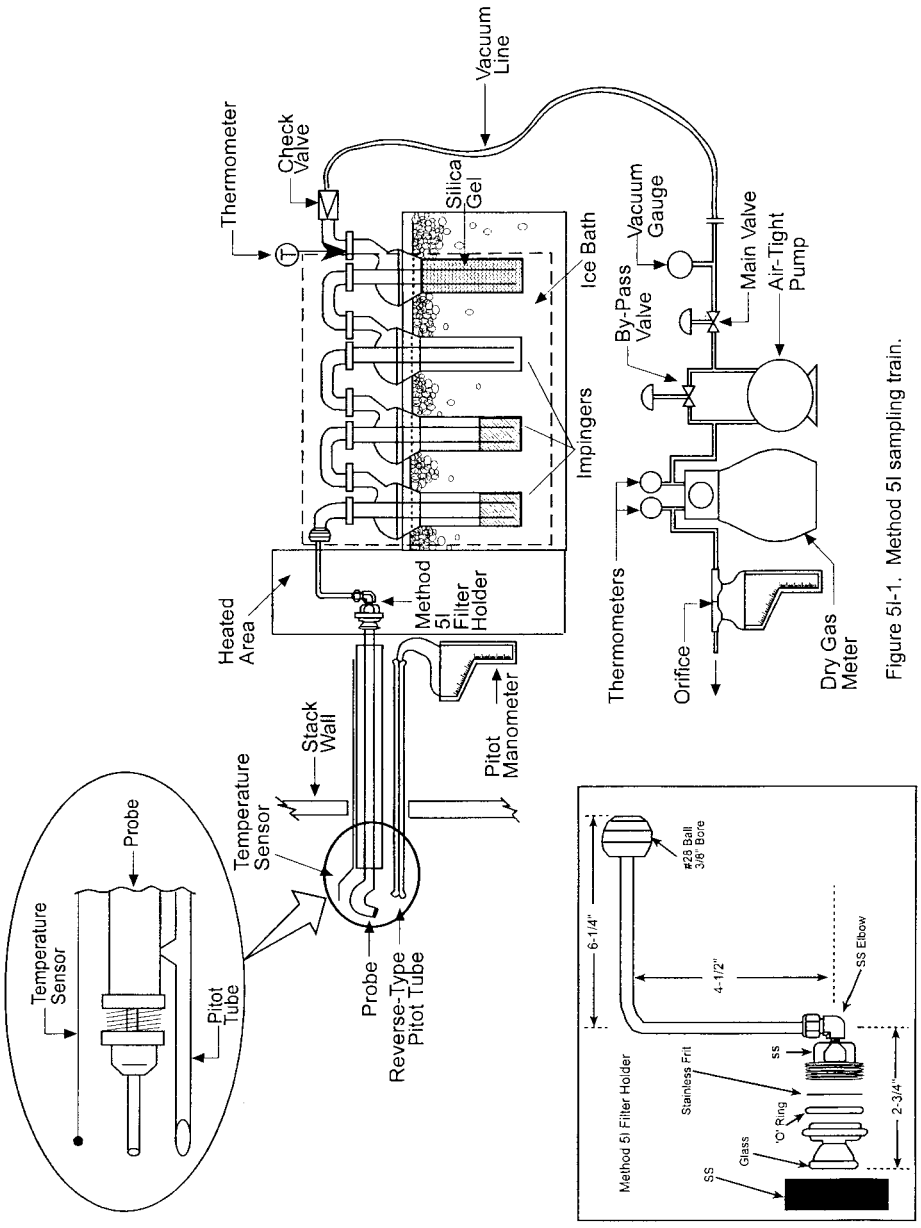


Figure 5I-1. Method 5I sampling train.

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–3 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

APPENDIX A–4 TO PART 60—TEST METHODS 6 THROUGH 10B

Method 6—Determination of sulfur dioxide emissions from stationary sources
Method 6A—Determination of sulfur dioxide, moisture, and carbon dioxide emissions from fossil fuel combustion sources
Method 6B—Determination of sulfur dioxide and carbon dioxide daily average emissions from fossil fuel combustion sources
Method 6C—Determination of Sulfur Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure)
Method 7—Determination of nitrogen oxide emissions from stationary sources
Method 7A—Determination of nitrogen oxide emissions from stationary sources—Ion chromatographic method
Method 7B—Determination of nitrogen oxide emissions from stationary sources (Ultraviolet spectrophotometry)
Method 7C—Determination of nitrogen oxide emissions from stationary sources—Alkaline-permanganate/colorimetric method
Method 7D—Determination of nitrogen oxide emissions from stationary sources—Alkaline-permanganate/ion chromatographic method
Method 7E—Determination of Nitrogen Oxides Emissions From Stationary Sources (Instrumental Analyzer Procedure)
Method 8—Determination of sulfuric acid mist and sulfur dioxide emissions from stationary sources
Method 9—Visual determination of the opacity of emissions from stationary sources
Alternate method 1—Determination of the opacity of emissions from stationary sources remotely by lidar
Method 10—Determination of carbon monoxide emissions from stationary sources
Method 10A—Determination of carbon monoxide emissions in certifying continuous emission monitoring systems at petroleum refineries
Method 10B—Determination of carbon monoxide emissions from stationary sources

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that

the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

METHOD 6—DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, and Method 8.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
SO_2	7449–09–5	3.4 mg SO_2/m^3 $(2.12 \times 10)_{-7}$ lb/ft^3

1.2 Applicability. This method applies to the measurement of sulfur dioxide (SO_2) emissions from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the sampling point in the stack. The SO_2 and the sulfur trioxide, including those fractions in any sulfur acid mist, are separated. The SO_2 fraction is measured by the barium-thorin titration method.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Free Ammonia. Free ammonia interferes with this method by reacting with SO_2 to form particulate sulfite and by reacting with the indicator. If free ammonia is present (this can be determined by knowledge of the process and/or noticing white particulate matter in the probe and isopropanol bubbler), alternative methods, subject to the approval of the Administrator are required. One approved alternative is listed in Reference 13 of section 17.0.

4.2 Water-Soluble Cations and Fluorides. The cations and fluorides are removed by a glass wool filter and an isopropanol bubbler; therefore, they do not affect the SO_2 analysis. When samples are collected from a gas stream with high concentrations of metallic fumes (*i.e.*, very fine cation aerosols) a high-efficiency glass fiber filter must be used in place of the glass wool plug (*i.e.*, the one in the probe) to remove the cation interferent.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations before performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs. 30% H_2O_2 is a strong oxidizing agent. Avoid contact with skin, eyes, and combustible material. Wear gloves when handling.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

6.1 Sample Collection. The following items are required for sample collection:

6.1.1 Sampling Train. A schematic of the sampling train is shown in Figure 6–1. The sampling equipment described in Method 8 may be substituted in place of the midget impinger equipment of Method 6. However, the Method 8 train must be modified to include a heated filter between the probe and isopropanol impinger, and the operation of the sampling train and sample analysis must be at the flow rates and solution volumes defined in Method 8. Alternatively, SO_2 may be determined simultaneously with particulate

matter and moisture determinations by either (1) replacing the water in a Method 5 impinger system with a 3 percent H_2O_2 solution, or (2) replacing the Method 5 water impinger system with a Method 8 isopropanol-filter-H_2O_2 system. The analysis for SO_2 must be consistent with the procedure of Method 8. The Method 6 sampling train consists of the following components:

6.1.1.1 Probe. Borosilicate glass or stainless steel (other materials of construction may be used, subject to the approval of the Administrator), approximately 6 mm (0.25 in.) inside diameter, with a heating system to prevent water condensation and a filter (either in-stack or heated out-of-stack) to remove particulate matter, including sulfuric acid mist. A plug of glass wool is a satisfactory filter.

6.1.1.2 Bubbler and Impingers. One midget bubbler with medium-coarse glass frit and borosilicate or quartz glass wool packed in top (see Figure 6–1) to prevent sulfuric acid mist carryover, and three 30-ml midget impingers. The midget bubbler and midget impingers must be connected in series with leak-free glass connectors. Silicone grease may be used, if necessary, to prevent leakage. A midget impinger may be used in place of the midget bubbler.

NOTE: Other collection absorbers and flow rates may be used, subject to the approval of the Administrator, but the collection efficiency must be shown to be at least 99 percent for each test run and must be documented in the report. If the efficiency is found to be acceptable after a series of three tests, further documentation is not required. To conduct the efficiency test, an extra absorber must be added and analyzed separately. This extra absorber must not contain more than 1 percent of the total SO_2.

6.1.1.3 Glass Wool. Borosilicate or quartz.

6.1.1.4 Stopcock Grease. Acetone-insoluble, heat-stable silicone grease may be used, if necessary.

6.1.1.5 Temperature Sensor. Dial thermometer, or equivalent, to measure temperature of gas leaving impinger train to within 1 °C (2 °F).

6.1.1.6 Drying Tube. Tube packed with 6- to 16- mesh indicating-type silica gel, or equivalent, to dry the gas sample and to protect the meter and pump. If silica gel is previously used, dry at 177 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

6.1.1.7 Valve. Needle valve, to regulate sample gas flow rate.

6.1.1.8 Pump. Leak-free diaphragm pump, or equivalent, to pull gas through the train. Install a small surge tank between the pump and rate meter to negate the pulsation effect of the diaphragm pump on the rate meter.

6.1.1.9 Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of the selected flow rate of about 1 liter/min (0.035 cfm).

6.1.1.10 Volume Meter. Dry gas meter (DGM), sufficiently accurate to measure the sample volume to within 2 percent, calibrated at the selected flow rate and conditions actually encountered during sampling, and equipped with a temperature sensor (dial thermometer, or equivalent) capable of measuring temperature accurately to within 3 °C (5.4 °F). A critical orifice may be used in place of the DGM specified in this section provided that it is selected, calibrated, and used as specified in section 16.0.

6.1.2 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). See the note in Method 5, section 6.1.2.

6.1.3 Vacuum Gauge and Rotameter. At least 760-mm Hg (30-in. Hg) gauge and 0- to 40-ml/min rotameter, to be used for leak-check of the sampling train.

6.2 Sample Recovery. The following items are needed for sample recovery:

6.2.1 Wash Bottles. Two polyethylene or glass bottles, 500-ml.

6.2.2 Storage Bottles. Polyethylene bottles, 100-ml, to store impinger samples (one per sample).

6.3 Sample Analysis. The following equipment is needed for sample analysis:

6.3.1 Pipettes. Volumetric type, 5-ml, 20-ml (one needed per sample), and 25-ml sizes.

6.3.2 Volumetric Flasks. 100-ml size (one per sample) and 1000-ml size.

6.3.3 Burettes. 5- and 50-ml sizes.

6.3.4 Erlenmeyer Flasks. 250-ml size (one for each sample, blank, and standard).

6.3.5 Dropping Bottle. 125-ml size, to add indicator.

6.3.6 Graduated Cylinder. 100-ml size.

6.3.7 Spectrophotometer. To measure absorbance at 352 nm.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Water. Deionized distilled to conform to ASTM Specification D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17). The $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.1.2 Isopropanol, 80 Percent by Volume. Mix 80 ml of isopropanol with 20 ml of water.

7.1.2.1 Check each lot of isopropanol for peroxide impurities as follows: Shake 10 ml of isopropanol with 10 ml of freshly prepared 10 percent potassium iodide solution. Prepare a blank by similarly treating 10 ml of water. After 1 minute, read the absorbance at 352 nm on a spectrophotometer using a 1-cm path length. If absorbance exceeds 0.1, reject alcohol for use.

7.1.2.2 Peroxides may be removed from isopropanol by redistilling or by passage through a column of activated alumina; however, reagent grade isopropanol with suitably low peroxide levels may be obtained from commercial sources. Rejection of contaminated lots may, therefore, be a more efficient procedure.

7.1.3 Hydrogen Peroxide (H_2O_2), 3 Percent by Volume. Add 10 ml of 30 percent H_2O_2 to 90 ml of water. Prepare fresh daily.

7.1.4 Potassium Iodide Solution, 10 Percent Weight by Volume (w/v). Dissolve 10.0 g of KI in water, and dilute to 100 ml. Prepare when needed.

7.2 Sample Recovery. The following reagents are required for sample recovery:

7.2.1 Water. Same as in section 7.1.1.

7.2.2 Isopropanol, 80 Percent by Volume. Same as in section 7.1.2.

7.3 Sample Analysis. The following reagents and standards are required for sample analysis:

7.3.1 Water. Same as in section 7.1.1.

7.3.2 Isopropanol, 100 Percent.

7.3.3 Thorin Indicator. 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, disodium salt, or equivalent. Dissolve 0.20 g in 100 ml of water.

7.3.4 Barium Standard Solution, 0.0100 N. Dissolve 1.95 g of barium perchlorate trihydrate [$Ba(ClO_4)_2$ $3H_2O$] in 200 ml water, and dilute to 1 liter with isopropanol. Alternatively, 1.22 g of barium chloride dihydrate [$BaCl_2$ $2H_2O$] may be used instead of the barium perchlorate trihydrate. Standardize as in section 10.5.

7.3.5 Sulfuric Acid Standard, 0.0100 N. Purchase or standardize to ±0.0002 N against 0.0100 N NaOH which has previously been standardized against potassium acid phthalate (primary standard grade).

8.0 Sample Collection, Preservation, Storage and Transport

8.1 Preparation of Sampling Train. Measure 15 ml of 80 percent isopropanol into the midget bubbler and 15 ml of 3 percent H_2O_2 into each of the first two midget impingers. Leave the final midget impinger dry. Assemble the train as shown in Figure 6–1. Adjust the probe heater to a temperature sufficient to prevent water condensation. Place crushed ice and water around the impingers.

8.2 Sampling Train Leak-Check Procedure. A leak-check prior to the sampling run is recommended, but not required. A leak-check after the sampling run is mandatory. The leak-check procedure is as follows:

8.2.1 Temporarily attach a suitable (*e.g.*, 0- to 40- ml/min) rotameter to the outlet of the DGM, and place a vacuum gauge at or near the probe inlet. Plug the probe inlet, pull a vacuum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter. A leakage rate in excess of 2 percent of the average sampling rate is not acceptable.

NOTE: Carefully (*i.e.*, slowly) release the probe inlet plug before turning off the pump.

8.2.2 It is suggested (not mandatory) that the pump be leak-checked separately, either prior to or after the sampling run. To leak-check the pump, proceed as follows: Disconnect the drying tube from the probe-impinger assembly. Place a vacuum gauge at the inlet to either the drying tube or the pump, pull a vacuum of 250 mm Hg (10 in. Hg), plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum should remain stable for at least 30 seconds.

If performed prior to the sampling run, the pump leak-check shall precede the leak-check of the sampling train described immediately above; if performed after the sampling run, the pump leak-check shall follow the sampling train leak-check.

8.2.3 Other leak-check procedures may be used, subject to the approval of the Administrator.

8.3 Sample Collection.

8.3.1 Record the initial DGM reading and barometric pressure. To begin sampling, position the tip of the probe at the sampling point, connect the probe to the bubbler, and start the pump. Adjust the sample flow to a constant rate of approximately 1.0 liter/min as indicated by the rate meter. Maintain this constant rate (±10 percent) during the entire sampling run.

8.3.2 Take readings (DGM volume, temperatures at DGM and at impinger outlet, and rate meter flow rate) at least every 5 minutes. Add more ice during the run to keep the temperature of the gases leaving the last impinger at 20 °C (68 °F) or less.

8.3.3 At the conclusion of each run, turn off the pump, remove the probe from the stack, and record the final readings. Conduct a leak-check as described in section 8.2. (This leak-check is mandatory.) If a leak is detected, void the test run or use procedures acceptable to the Administrator to adjust the sample volume for the leakage.

8.3.4 Drain the ice bath, and purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at the sampling rate. Clean ambient air can be provided by passing air through a charcoal filter or through an extra midget impinger containing 15 ml of 3 percent H_2O_2. Alternatively, ambient air without purification may be used.

8.4 Sample Recovery. Disconnect the impingers after purging. Discard the contents of the midget bubbler. Pour the contents of the midget impingers into a leak-free polyethylene bottle for shipment. Rinse the three midget impingers and the connecting tubes with water, and add the rinse to the same storage container. Mark the fluid level. Seal and identify the sample container.

9.0 Quality Control

Section	Quality control measure	Effect
7.1.2	Isopropanol check	Ensure acceptable level of peroxide impurities in isopropanol.
8.2, 10.1–10.4	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.
10.5	Barium standard solution standardization	Ensure precision of normality determination
11.2.3	Replicate titrations	Ensure precision of titration determinations.

10.0 Calibration and Standardization

10.1 Volume Metering System.

10.1.1 Initial Calibration.

10.1.1.1 Before its initial use in the field, leak-check the metering system (drying tube, needle valve, pump, rate meter, and DGM) as follows: Place a vacuum gauge at the inlet to the drying tube and pull a vacuum of 250 mm Hg (10 in. Hg). Plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum must remain stable for at least 30 seconds. Carefully release the vacuum gauge before releasing the flow meter end.

10.1.1.2 Remove the drying tube, and calibrate the metering system (at the sampling flow rate specified by the method) as follows: Connect an appropriately sized wet-test meter (*e.g.*, 1 liter per revolution) to the inlet of the needle valve. Make three independent calibration runs, using at least five revolutions of the DGM per run. Calculate the calibration factor Y (wet-test meter calibration volume divided by the DGM volume, both volumes adjusted to the same reference temperature and pressure) for each run, and average the results (Y_i). If any Y-value deviates by more than 2 percent from (Y_i), the metering system is unacceptable for use. If the metering system is acceptable, use (Y_i) as the calibration factor for subsequent test runs.

10.1.2 Post-Test Calibration Check. After each field test series, conduct a calibration check using the procedures outlined in section 10.1.1.2, except that three or more revolutions of the DGM may be used, and only two independent runs need be made. If the average of the two post-test calibration factors does not deviate by more than 5 percent from Y_i, then Y_i is accepted as the DGM calibration factor (Y), which is used in Equation 6–1 to calculate collected sample volume (see section 12.2). If the deviation is more than 5 percent, recalibrate the metering system as in section 10.1.1, and determine a post-test calibration factor (Y_f). Compare Y_i and Y_f; the smaller of the two factors is accepted as the DGM calibration factor. If recalibration indicates that the metering system is unacceptable for use, either void the test run or use methods, subject to the approval of the Administrator, to determine an acceptable value for the collected sample volume.

10.1.3 DGM as a Calibration Standard. A DGM may be used as a calibration standard for volume measurements in place of the wet-test meter specified in section 10.1.1.2, provided that it is calibrated initially and recalibrated periodically according to the same procedures outlined in Method 5, section 10.3 with the following exceptions: (a) the DGM is calibrated against a wet-test meter having a capacity of 1 liter/rev (0.035 ft^3/rev) or 3 liters/rev (0.1 ft^3/rev) and having the capability of measuring volume to within 1 percent; (b) the DGM is calibrated at 1 liter/min (0.035 cfm); and (c) the meter box of the Method 6 sampling train is calibrated at the same flow rate.

10.2 Temperature Sensors. Calibrate against mercury-in-glass thermometers. An alternative mercury-free thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

10.3 Rate Meter. The rate meter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instructions.

10.4 Barometer. Calibrate against a mercury barometer or NIST-traceable barometer prior to the field test.

10.5 Barium Standard Solution. Standardize the barium perchlorate or chloride solution against 25 ml of standard sulfuric acid to which 100 ml of 100 percent isopropanol has been added. Run duplicate analyses. Calculate the normality using the average of duplicate analyses where the titrations agree within 1 percent or 0.2 ml, whichever is larger.

11.0 Analytical Procedure

11.1 Sample Loss Check. Note level of liquid in container and confirm whether any sample was lost during shipment; note this

finding on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Analysis.

11.2.1 Transfer the contents of the storage container to a 100-ml volumetric flask, dilute to exactly 100 ml with water, and mix the diluted sample.

11.2.2 Pipette a 20-ml aliquot of the diluted sample into a 250-ml Erlenmeyer flask and add 80 ml of 100 percent isopropanol plus two to four drops of thorin indicator. While stirring the solution, titrate to a pink endpoint using 0.0100 N barium standard solution.

11.2.3 Repeat the procedures in section 11.2.2, and average the titration volumes. Run a blank with each series of samples. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is larger.

NOTE: Protect the 0.0100 N barium standard solution from evaporation at all times.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 NOMENCLATURE

C_{SO2} = Concentration of SO_2, dry basis, corrected to standard conditions, mg/dscm (lb/dscf).

N = Normality of barium standard titrant, meq/ml.

P_{bar} = Barometric pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

T_m = Average DGM absolute temperature, °K (°R).

T_{std} = Standard absolute temperature, 293 °K (528 °R).

V_a = Volume of sample aliquot titrated, ml.

V_m = Dry gas volume as measured by the DGM, dcm (dcf).

$V_{m(std)}$ = Dry gas volume measured by the DGM, corrected to standard conditions, dscm (dscf).

V_{soln} = Total volume of solution in which the SO_2 sample is contained, 100 ml.

V_t = Volume of barium standard titrant used for the sample (average of replicate titration), ml.

V_{tb} = Volume of barium standard titrant used for the blank, ml.

Y = DGM calibration factor.

12.2 Dry Sample Gas Volume, Corrected to Standard Conditions.

$$V_{m(std)} = \frac{\left(V_m Y T_{std} P_{bar}\right)}{\left(T_m P_{std}\right)} = \frac{K_1 Y V_m P_{bar}}{T_m} \quad \text{Eq. 6-1}$$

Where:

K_1 = 0.3855 °K/mm Hg for metric units,

K_1 = 17.65 °R/in. Hg for English units.

12.3 SO_2 Concentration.

$$C_{so_2} = \frac{K_2 N \left(V_t - V_{tb}\right)\left(V_{soln}/V_a\right)}{V_{m(std)}} \quad \text{Eq. 6-2}$$

Where:

K_2 = 32.03 mg SO_2/meq for metric units,

$K_2 = 7.061 \times 10^{-5}$ lb SO_2/meq for English units.

13.0 Method Performance

13.1 Range. The minimum detectable limit of the method has been determined to be 3.4 mg SO_2/m^3 (2.12×10^{-7} lb/ft³). Although no upper limit has been established, tests have shown that concentrations as high as 80,000 mg/m³ (0.005 lb/ft³) of SO_2 can be collected efficiently at a rate of 1.0 liter/min (0.035 cfm) for 20 minutes in two midget impingers, each containing 15 ml of 3 percent H_2O_2. Based on theoretical calculations, the upper concentration limit in a 20 liter (0.7 ft³) sample is about 93,300 mg/m³ (0.00583 lb/ft³).

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Nomenclature. Same as section 12.1, with the following additions:

B_{wa} = Water vapor in ambient air, proportion by volume.

M_a = Molecular weight of the ambient air saturated at impinger temperature, g/g-mole (lb/lb-mole).

M_s = Molecular weight of the sample gas saturated at impinger temperature, g/g-mole (lb/lb-mole).

P_c = Inlet vacuum reading obtained during the calibration run, mm Hg (in. Hg).

P_{sr} = Inlet vacuum reading obtained during the sampling run, mm Hg (in. Hg).

$\bar{Q}_{std}$ = Volumetric flow rate through critical orifice, scm/min (scf/min).
Q_{std} = Average flow rate of pre-test and post-test calibration runs, scm/min (scf/min).
T_{amb} = Ambient absolute temperature of air, °K (°R).
V_{sb} = Volume of gas as measured by the soap bubble meter, m^3 (ft^3).
$V_{sb(std)}$ = Volume of gas as measured by the soap bubble meter, corrected to standard conditions, scm (scf).
θ = Soap bubble travel time, min.
θ_s = Time, min.

16.2 Critical Orifices for Volume and Rate Measurements. A critical orifice may be used in place of the DGM specified in section 6.1.1.10, provided that it is selected, calibrated, and used as follows:

16.2.1 Preparation of Sampling Train. Assemble the sampling train as shown in Figure 6–2. The rate meter and surge tank are optional but are recommended in order to detect changes in the flow rate.

NOTE: The critical orifices can be adapted to a Method 6 type sampling train as follows: Insert sleeve type, serum bottle stoppers into two reducing unions. Insert the needle into the stoppers as shown in Figure 6–3.

16.2.2 Selection of Critical Orifices.

16.2.2.1 The procedure that follows describes the use of hypodermic needles and stainless steel needle tubings, which have been found suitable for use as critical orifices. Other materials and critical orifice designs may be used provided the orifices act as true critical orifices, (*i.e.*, a critical vacuum can be obtained) as described in this section. Select a critical orifice that is sized to operate at the desired flow rate. The needle sizes and tubing lengths shown in Table 6–1 give the following approximate flow rates.

16.2.2.2 Determine the suitability and the appropriate operating vacuum of the critical orifice as follows: If applicable, temporarily attach a rate meter and surge tank to the outlet of the sampling train, if said equipment is not present (see section 16.2.1). Turn on the pump and adjust the valve to give an outlet vacuum reading corresponding to about half of the atmospheric pressure. Observe the rate meter reading. Slowly increase the vacuum until a stable reading is obtained on the rate meter. Record the critical vacuum, which is the outlet vacuum when the rate meter first reaches a stable value. Orifices that do not reach a critical value must not be used.

16.2.3 Field Procedures.

16.2.3.1 Leak-Check Procedure. A leak-check before the sampling run is recommended, but not required. The leak-check procedure is as follows: Temporarily attach a suitable (*e.g.*, 0–40 ml/min) rotameter and surge tank, or a soap bubble meter and surge tank to the outlet of the pump. Plug the probe inlet, pull an outlet vacuum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter or bubble meter. A leakage rate in excess of 2 percent of the average sampling rate ($\bar{Q}_{std}$) is not acceptable. Carefully release the probe inlet plug before turning off the pump.

16.2.3.2 Moisture Determination. At the sampling location, prior to testing, determine the percent moisture of the ambient air using the wet and dry bulb temperatures or, if appropriate, a relative humidity meter.

16.2.3.3 Critical Orifice Calibration. At the sampling location, prior to testing, calibrate the entire sampling train (*i.e.*, determine the flow rate of the sampling train when operated at critical conditions). Attach a 500-ml soap bubble meter to the inlet of the probe, and operate the sampling train at an outlet vacuum of 25 to 50 mm Hg (1 to 2 in. Hg) above the critical vacuum. Record the information listed in Figure 6–4. Calculate the standard volume of air measured by the soap bubble meter and the volumetric flow rate using the equations below:

$$V_{sb(std)} = V_{sb}\left(T_{std}/T_{amb}\right)\left(P_{bar}/P_{std}\right) \qquad \text{Eq. 6-4}$$

$$Q_{std} = \frac{V_{sb(std)}}{\theta} \qquad \text{Eq. 6-5}$$

16.2.3.4 Sampling.

16.2.3.4.1 Operate the sampling train for sample collection at the same vacuum used during the calibration run. Start the watch and pump simultaneously. Take readings (temperature, rate meter, inlet vacuum, and outlet vacuum) at least every 5 minutes. At the end of the sampling run, stop the watch and pump simultaneously.

16.2.3.4.2 Conduct a post-test calibration run using the calibration procedure outlined in section 16.2.3.3. If the Q_{std} obtained before and after the test differ by more than 5 percent, void the test run; if not, calculate the volume of the gas measured with the critical orifice using Equation 6–6 as follows:

$$V_{m(std)} = \frac{\overline{Q}_{std}\ \theta_s\ (1-B_{wa})(P_{bar}+P_{sr})}{(P_{bar}+P_c)} \quad \text{Eq. 6-6}$$

16.2.3.4.3 If the percent difference between the molecular weight of the ambient air at saturated conditions and the sample gas is more that ±3 percent, then the molecular weight of the gas sample must be considered in the calculations using the following equation:

$$_{(std)} = \frac{\overline{Q}_{std}\ \theta_s\ (1-B_{wa})(P_{bar}+P_{sr})(M_a/M_s)^1}{(P_{bar}+P_c)} \quad \text{Eq. 6-7}$$

NOTE: A post-test leak-check is not necessary because the post-test calibration run results will indicate whether there is any leakage.

16.2.3.4.4 Drain the ice bath, and purge the sampling train using the procedure described in section 8.3.4.

16.3 Elimination of Ammonia Interference. The following alternative procedures must be used in addition to those specified in the method when sampling at sources having ammonia emissions.

16.3.1 Sampling. The probe shall be maintained at 275 °C (527 °F) and equipped with a high-efficiency in-stack filter (glass fiber) to remove particulate matter. The filter material shall be unreactive to SO_2. Whatman 934AH (formerly Reeve Angel 934AH) filters treated as described in Reference 10 in section 17.0 of Method 5 is an example of a filter that has been shown to work. Where alkaline particulate matter and condensed moisture are present in the gas stream, the filter shall be heated above the moisture dew point but below 225 °C (437 °F).

16.3.2 Sample Recovery. Recover the sample according to section 8.4 except for discarding the contents of the midget bubbler. Add the bubbler contents, including the rinsings of the bubbler with water, to a separate polyethylene bottle from the rest of the sample. Under normal testing conditions where sulfur trioxide will not be present significantly, the tester may opt to delete the midget bubbler from the sampling train. If an approximation of the sulfur trioxide concentration is desired, transfer the contents of the midget bubbler to a separate polyethylene bottle.

16.3.3 Sample Analysis. Follow the procedures in sections 11.1 and 11.2, except add 0.5 ml of 0.1 N HCl to the Erlenmeyer flask and mix before adding the indicator. The following analysis procedure may be used for an approximation of the sulfur trioxide concentration. The accuracy of the calculated concentration will depend upon the ammonia to SO_2 ratio and the level of oxygen present in the gas stream. A fraction of the SO_2 will be counted as sulfur trioxide as the ammonia to SO_2 ratio and the sample oxygen content increases. Generally, when this ratio is 1 or less and the oxygen content is in the range of 5 percent, less than 10 percent of the SO_2 will be counted as sulfur trioxide. Analyze the peroxide and isopropanol sample portions separately. Analyze the peroxide portion as described above. Sulfur trioxide is determined by difference using sequential titration of the isopropanol portion of the sample. Transfer the contents of the isopropanol storage container to a 100-ml volumetric flask, and dilute to exactly 100 ml with water. Pipette a 20-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 0.5 ml of 0.1 N HCl, 80 ml of 100 percent isopropanol, and two to four drops of thorin indicator. Titrate to a pink endpoint using 0.0100 N barium perchlorate. Repeat and average the titration volumes that agree within 1 percent or 0.2 ml, whichever is larger. Use this volume in Equation 6–2 to determine the sulfur trioxide concentration. From the flask containing the remainder of the isopropanol sample, determine the fraction of SO_2 collected in the bubbler by pipetting 20-ml aliquots into 250-ml Erlenmeyer flasks. Add 5 ml of 3 percent H_2O_2, 100 ml of 100 percent isopropanol, and two to four drips of thorin indicator, and titrate as before. From this titration volume, subtract the titrant volume determined for sulfur trioxide, and add the titrant volume determined for the peroxide portion. This final volume constitutes V_t, the volume of barium perchlorate used for the SO_2 sample.

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18.0 Tables, Diagrams, Flowcharts and Validation Data

TABLE 6–1—APPROXIMATE FLOW RATES FOR VARIOUS NEEDLE SIZES

Needle size (gauge)	Needle length (cm)	Flow rate (ml/min)
21	7.6	1,100
22	2.9	1,000
22	3.8	900
23	3.8	500
23	5.1	450
24	3.2	400

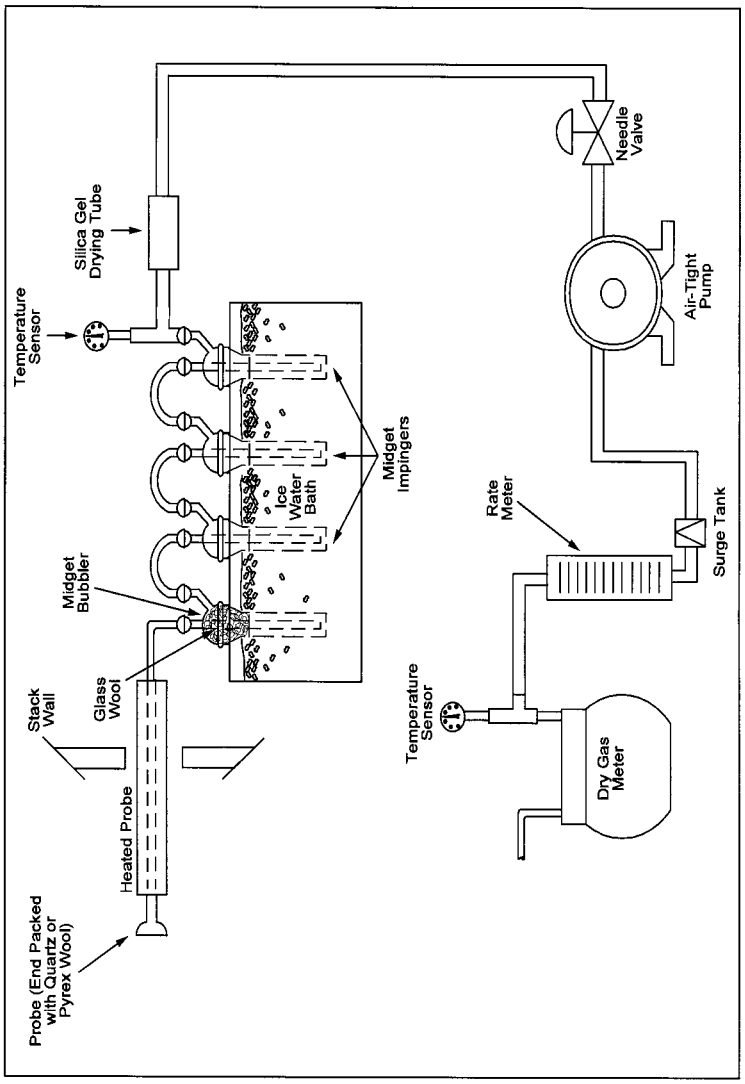

Figure 6-1. Sulfur Dioxide Sampling Train.

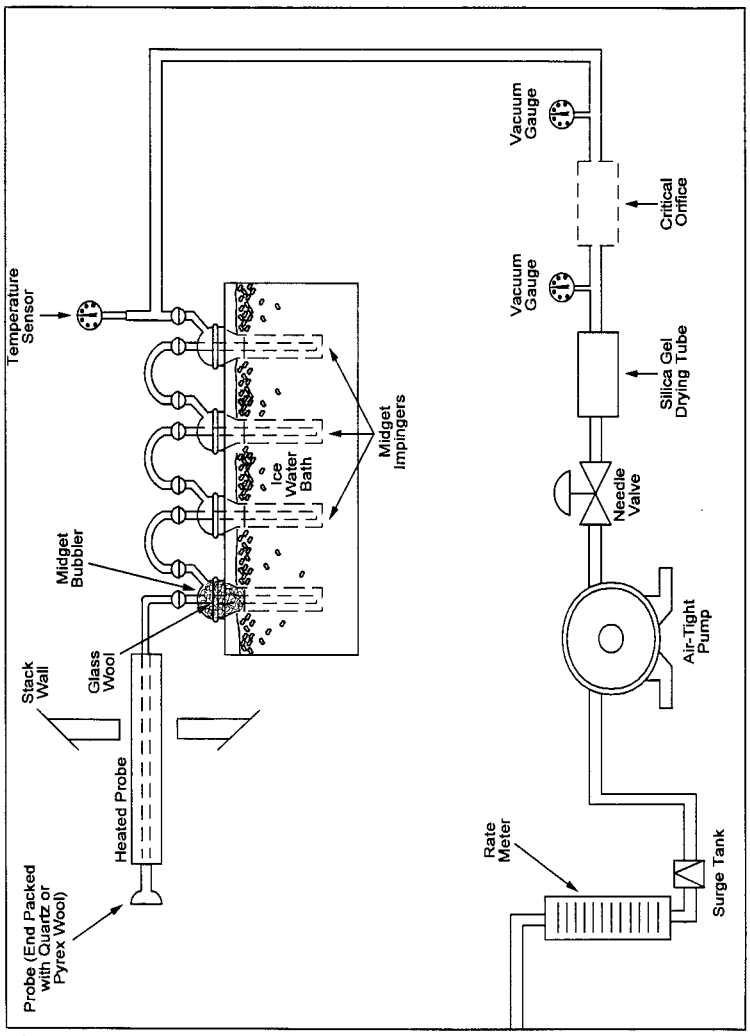

Figure 6-2. Sulfur Dioxide Sampling Train Using a Critical Orifice.

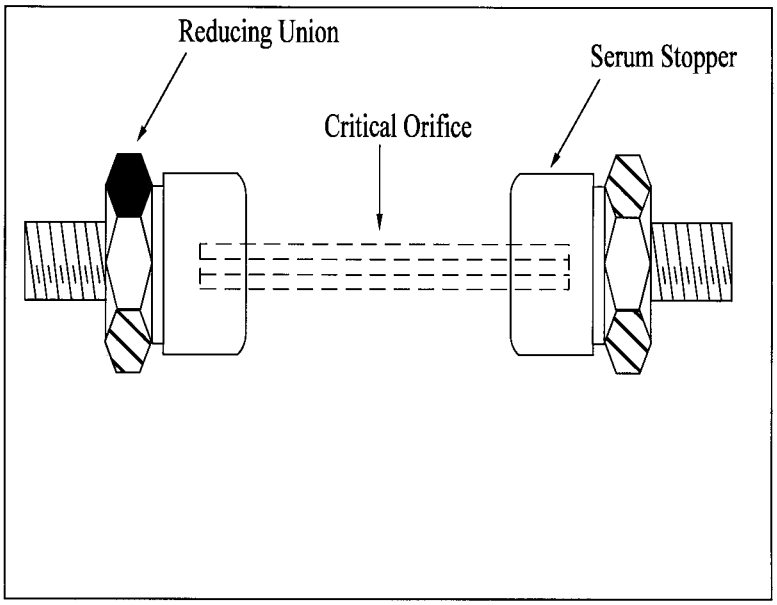

Figure 6-3. Critical Orifice Adaptation for the Method 6 Sampling Train.

Date _____ Train ID _____

Critical orifice size _____ Critical vacuum _____

		Pretest	Post-test
Soap bubble meter volume, V_{sb}	cc		
	m^3 (ft^3)		
Time, θ	sec		
	min		
Barometric pressure, P_{bar}	mm Hg (in. Hg)		
Ambient temperature, t_{amb}	°C (°F)		
Inlet vacuum, P_c	mm Hg (in. Hg)		
Outlet vacuum	mm Hg (in. Hg)		
$V_{sb(std)}$	m^3 (ft^3)		
Flow rate, Q_{std}	$\frac{m^3}{min}\left(\frac{ft^3}{min}\right)$		

Figure 6-4. Critical Orifice Calibration Data Sheet.

METHOD 6A—DETERMINATION OF SULFUR DIOXIDE, MOISTURE, AND CARBON DIOXIDE FROM FOSSIL FUEL COMBUSTION SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, Method 6, and Method 19.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
SO_2	7449–09–05	3.4 mg SO_2/m^3 (2.12×10^{-7} lb/ft^3)
CO_2	124–38–9	N/A
H_2O	7732–18–5	N/A

1.2 Applicability. This method is applicable for the determination of sulfur dioxide (SO_2) emissions from fossil fuel combustion sources in terms of concentration (mg/dscm or lb/dscf) and in terms of emission rate (ng/J or lb/10^6 Btu) and for the determination of carbon dioxide (CO_2) concentration (percent). Moisture content (percent), if desired, may also be determined by this method.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from a sampling point in the stack. The SO_2 and the sulfur trioxide, including those fractions in any sulfur acid mist, are separated. The SO_2 fraction is measured by the barium-thorin titration method. Moisture and CO_2 fractions are collected in the same sampling train, and are determined gravimetrically.

3.0 Definitions [Reserved]

4.0 Interferences

Same as Method 6, section 4.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. Same as Method 6, section 5.2.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 6, section 6.1, with the exception of the following:

6.1.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 6A–1.

6.1.1.1 Impingers and Bubblers. Two 30 = ml midget impingers with a 1 = mm restricted tip and two 30 = ml midget bubblers with unrestricted tips. Other types of impingers and bubblers (*e.g.,* Mae West for SO_2 collection and rigid cylinders containing Drierite for moisture absorbers), may be used with proper attention to reagent volumes and levels, subject to the approval of the Administrator.

6.1.1.2 CO_2 Absorber. A sealable rigid cylinder or bottle with an inside diameter between 30 and 90 mm , a length between 125 and 250 mm, and appropriate connections at both ends. The filter may be a separate heated unit or may be within the heated portion of the probe. If the filter is within the sampling probe, the filter should not be within 15 cm of the probe inlet or any unheated section of the probe, such as the connection to the first bubbler. The probe and filter should be heated to at least 20 °C (68 °F) above the source temperature, but not greater than 120 °C (248 °F). The filter temperature (*i.e.,* the sample gas temperature) should be monitored to assure the desired temperature is maintained. A heated Teflon connector may be used to connect the filter holder or probe to the first impinger.

NOTE: For applications downstream of wet scrubbers, a heated out-of-stack filter (either borosilicate glass wool or glass fiber mat) is necessary.

6.2 Sample Recovery. Same as Method 6, section 6.2.

6.3 Sample Analysis. Same as Method 6, section 6.3, with the addition of a balance to measure within 0.05 g.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

7.1 Sample Collection. Same as Method 6, section 7.1, with the addition of the following:

7.1.1 Drierite. Anhydrous calcium sulfate ($CaSO_4$) desiccant, 8 mesh, indicating type is recommended.

NOTE: Do not use silica gel or similar desiccant in this application.

7.1.2 CO_2 Absorbing Material. Ascarite II. Sodium hydroxide-coated silica, 8- to 20-mesh.

7.2 Sample Recovery and Analysis. Same as Method 6, sections 7.2 and 7.3, respectively.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Preparation of Sampling Train.

8.1.1 Measure 15 ml of 80 percent isopropanol into the first midget bubbler and 15 ml of 3 percent hydrogen peroxide into each of the two midget impingers (the second

and third vessels in the train) as described in Method 6, section 8.1. Insert the glass wool into the top of the isopropanol bubbler as shown in Figure 6A–1. Place about 25 g of Drierite into the second midget bubbler (the fourth vessel in the train). Clean the outside of the bubblers and impingers and allow the vessels to reach room temperature. Weigh the four vessels simultaneously to the nearest 0.1 g, and record this initial weight (m_{wi}).

8.1.2 With one end of the CO_2 absorber sealed, place glass wool into the cylinder to a depth of about 1 cm (0.5 in.). Place about 150 g of CO_2 absorbing material in the cylinder on top of the glass wool, and fill the remaining space in the cylinder with glass wool. Assemble the cylinder as shown in figure 6A–2. With the cylinder in a horizontal position, rotate it around the horizontal axis. The CO_2 absorbing material should remain in position during the rotation, and no open spaces or channels should be formed. If necessary, pack more glass wool into the cylinder to make the CO_2 absorbing material stable. Clean the outside of the cylinder of loose dirt and moisture and allow the cylinder to reach room temperature. Weigh the cylinder to the nearest 0.1 g, and record this initial weight (m_{ai}).

8.1.3 Assemble the train as shown in figure 6A–1. Adjust the probe heater to a temperature sufficient to prevent condensation (see note in section 6.1). Place crushed ice and water around the impingers and bubblers. Mount the CO_2 absorber outside the water bath in a vertical flow position with the sample gas inlet at the bottom. Flexible tubing (*e.g.*, Tygon) may be used to connect the last SO_2 absorbing impinger to the moisture absorber and to connect the moisture absorber to the CO_2 absorber. A second, smaller CO_2 absorber containing Ascarite II may be added in-line downstream of the primary CO_2 absorber as a breakthrough indicator. Ascarite II turns white when CO_2 is absorbed.

8.2 Sampling Train Leak-Check Procedure and Sample Collection. Same as Method 6, sections 8.2 and 8.3, respectively.

8.3 Sample Recovery.

8.3.1 Moisture Measurement. Disconnect the isopropanol bubbler, the SO_2 impingers, and the moisture absorber from the sample train. Allow about 10 minutes for them to reach room temperature, clean the outside of loose dirt and moisture, and weigh them simultaneously in the same manner as in section 8.1. Record this final weight (m_{wf}).

8.3.2 Peroxide Solution. Discard the contents of the isopropanol bubbler and pour the contents of the midget impingers into a leak-free polyethylene bottle for shipping. Rinse the two midget impingers and connecting tubes with water, and add the washing to the same storage container.

8.3.3 CO_2 Absorber. Allow the CO_2 absorber to warm to room temperature (about 10 minutes), clean the outside of loose dirt and moisture, and weigh to the nearest 0.1 g in the same manner as in section 8.1. Record this final weight (m_{af}). Discard used Ascarite II material.

9.0 Quality Control

Same as Method 6, section 9.0.

10.0 Calibration and Standardization

Same as Method 6, section 10.0.

11.0 Analytical Procedure

11.1 Sample Analysis. The sample analysis procedure for SO_2 is the same as that specified in Method 6, section 11.0.

12.0 Data Analysis and Calculations

Same as Method 6, section 12.0, with the addition of the following:

12.1 Nomenclature.

C_w = Concentration of moisture, percent.
C_{CO2} = Concentration of CO_2, dry basis, percent.
E_{SO2} = Emission rate of SO_2, ng/J (lb/10^6 Btu).
F_C = Carbon F-factor from Method 19 for the fuel burned, dscm/J (dscf/10^6 Btu).
m_{wi} = Initial weight of impingers, bubblers, and moisture absorber, g.
m_{wf} = Final weight of impingers, bubblers, and moisture absorber, g.
m_{ai} = Initial weight of CO_2 absorber, g.
m_{af} = Final weight of CO_2 absorber, g.
m_{SO2} = Mass of SO_2 collected, mg.
$V_{CO2(std)}$ = Equivalent volume of CO_2 collected at standard conditions, dscm (dscf).
$V_{w(std)}$ = Equivalent volume of moisture collected at standard conditions, scm (scf).

12.2 CO_2 Volume Collected, Corrected to Standard Conditions.

$$V_{CO_2(std)} = K_3 \left(m_{af} - m_{ai}\right) \qquad \text{Eq. 6A-1}$$

Where:

K_3 = Equivalent volume of gaseous CO_2 at standard conditions, 5.467×10^{-4} dscm/g (1.930×10^{-2} dscf/g).

12.3 Moisture Volume Collected, Corrected to Standard Conditions.

$$V_{w(std)} = K_4 \left(m_{wf} - m_{wi}\right) \qquad \text{Eq. 6A-2}$$

Where:

K_4 = Equivalent volume of water vapor at standard conditions, 1.336×10^{-3} scm/g (4.717×10^{-2} scf/g).

12.4 SO_2 Concentration.

$$C_{so_2} = \frac{K_2 N (V_t - V_{tb})(V_{so\,ln}/V_a)}{V_{m(std)} + V_{co_2(std)}} \qquad \text{Eq. 6A-3}$$

Where:

K_2 = 32.03 mg SO_2/meq. SO_2 (7.061×10^{-5} lb SO_2/meq. SO_2)

12.5 CO_2 Concentration.

$$C_{co_2} = \frac{V_{co_2(std)}}{V_{m(std)} + V_{co_2(std)}} \qquad \text{Eq. 6A-4}$$

12.6 Moisture Concentration.

$$C_w = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)} + V_{co_2(std)}} \qquad \text{Eq. 6A-5}$$

13.0 Method Performance

13.1 Range and Precision. The minimum detectable limit and the upper limit for the measurement of SO_2 are the same as for Method 6. For a 20-liter sample, this method has a precision of ±0.5 percent CO_2 for concentrations between 2.5 and 25 percent CO_2 and ±1.0 percent moisture for moisture concentrations greater than 5 percent.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Methods

If the only emission measurement desired is in terms of emission rate of SO_2 (ng/J or lb/10^6 Btu), an abbreviated procedure may be used. The differences between the above procedure and the abbreviated procedure are described below.

16.1 Sampling Train. The sampling train is the same as that shown in Figure 6A–1 and as described in section 6.1, except that the dry gas meter is not needed.

16.2 Preparation of the Sampling Train. Follow the same procedure as in section 8.1, except do not weigh the isopropanol bubbler, the SO_2 absorbing impingers, or the moisture absorber.

16.3 Sampling Train Leak-Check Procedure and Sample Collection. Leak-check and operate the sampling train as described in section 8.2, except that dry gas meter readings, barometric pressure, and dry gas meter temperatures need not be recorded during sampling.

16.4 Sample Recovery. Follow the procedure in section 8.3, except do not weigh the isopropanol bubbler, the SO_2 absorbing impingers, or the moisture absorber.

16.5 Sample Analysis. Analysis of the peroxide solution is the same as that described in section 11.1.

16.6 Calculations.

16.6.1 SO_2 Collected.

$$m_{SO_2} = K_2 N (V_t - V_{tb})(V_{soln}/V_a) \qquad \text{Eq. 6A-6}$$

Where:

K_2 = 32.03 mg SO_2/meq. SO_2
$K_2 = 7.061 \times 10^{-5}$ lb SO_2/meq. SO_2

16.6.2 Sulfur Dioxide Emission Rate.

$$E_{SO_2} = K_5 F_c m_{so_2} / (m_{af} - m_{ai}) \qquad \text{Eq. 6A-7}$$

Where:

$K_5 = 1.829 \times 10^9$ mg/dscm
$K_2 = 0.1142$ lb/dscf

17.0 References

Same as Method 6, section 17.0, References 1 through 8, with the addition of the following:

1. Stanley, Jon and P.R. Westlin. An Alternate Method for Stack Gas Moisture Determination. Source Evaluation Society Newsletter. *3*(4). November 1978.

2. Whittle, Richard N. and P.R. Westlin. Air Pollution Test Report: Development and Evaluation of an Intermittent Integrated SO_2/CO_2 Emission Sampling Procedure. Environmental Protection Agency, Emission Standard and Engineering Division, Emission Measurement Branch. Research Triangle Park, NC. December 1979. 14 pp.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

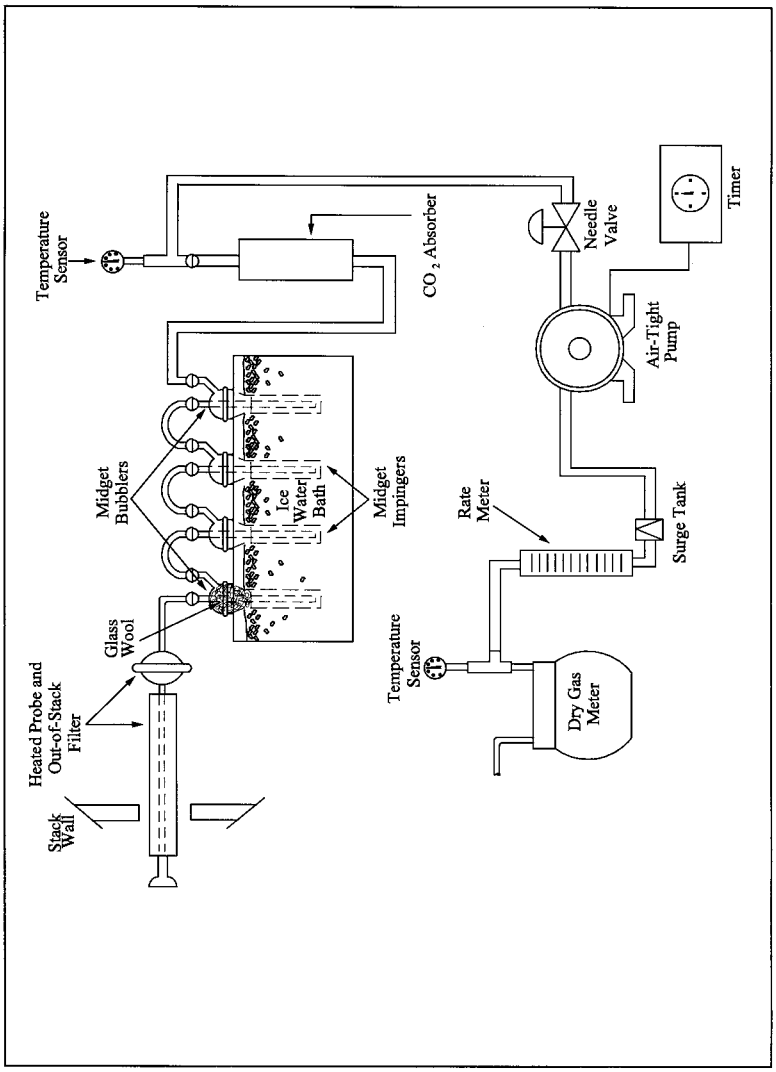

Figure 6A-1. Sampling train.

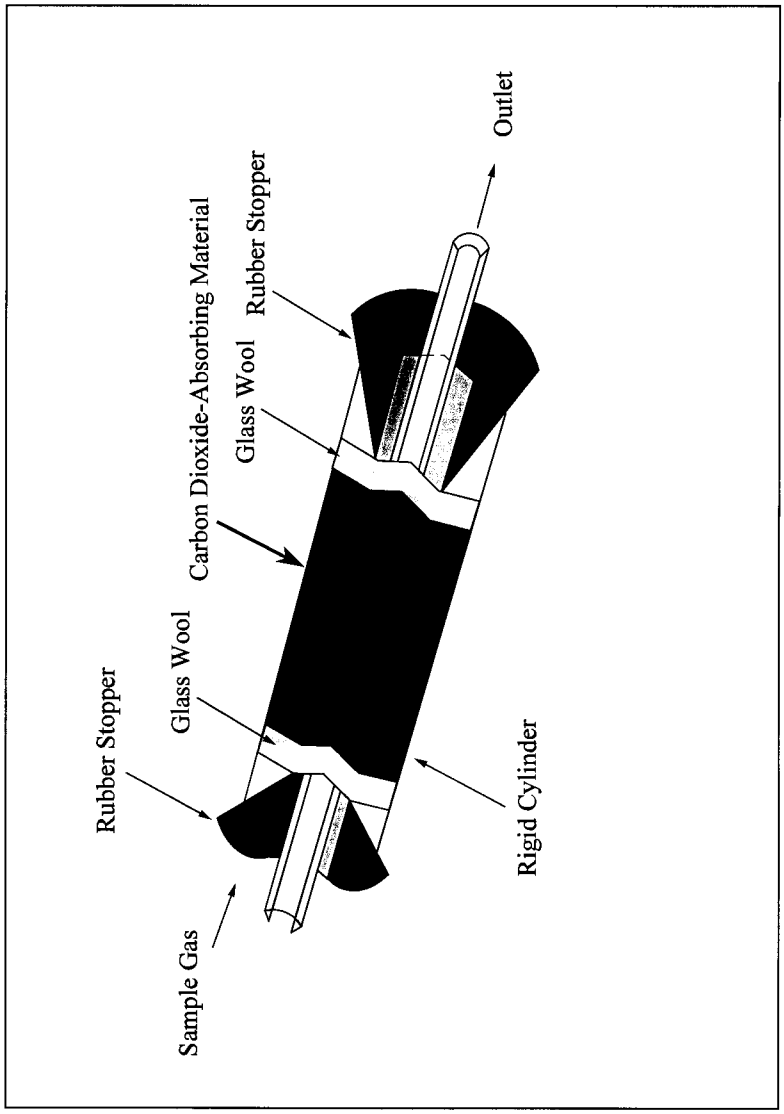

Figure 6A-2. CO_2 Absorber

METHOD 6B—DETERMINATION OF SULFUR DIOXIDE AND CARBON DIOXIDE DAILY AVERAGE EMISSIONS FROM FOSSIL FUEL COMBUSTION SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, Method 6, and Method 6A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Sulfur dioxide (SO_2)	7449–09–05	3.4 mg SO_2/m^3 (2.12×10^{-7} lb/ft^3)
Carbon dioxide (CO_2)	124–38–9	N/A

1.2 Applicability. This method is applicable for the determination of SO_2 emissions from combustion sources in terms of concentration (ng/dscm or lb/dscf) and emission rate (ng/J or lb/10^6 Btu), and for the determination of CO_2 concentration (percent) on a daily (24 hours) basis.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the sampling point in the stack intermittently over a 24-hour or other specified time period. The SO_2 fraction is measured by the barium-thorin titration method. Moisture and CO_2 fractions are collected in the same sampling train, and are determined gravimetrically.

3.0 Definitions [Reserved]

4.0 Interferences

Same as Method 6, section 4.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. Same as Method 6, section 5.2.

6.0 Equipment and Supplies

Same as Method 6A, section 6.0, with the following exceptions and additions:

6.1 The isopropanol bubbler is not used. An empty bubbler for the collection of liquid droplets, that does not allow direct contact between the collected liquid and the gas sample, may be included in the sampling train.

6.2 For intermittent operation, include an industrial timer-switch designed to operate in the ''on'' position at least 2 minutes continuously and ''off'' the remaining period over a repeating cycle. The cycle of operation is designated in the applicable regulation. At a minimum, the sampling operation should include at least 12, equal, evenly-spaced periods per 24 hours.

6.3 Stainless steel sampling probes, type 316, are not recommended for use with Method 6B because of potential sample contamination due to corrosion. Glass probes or other types of stainless steel, *e.g.*, Hasteloy or Carpenter 20, are recommended for long-term use.

NOTE: For applications downstream of wet scrubbers, a heated out-of-stack filter (either borosilicate glass wool or glass fiber mat) is necessary. Probe and filter heating systems capable of maintaining a sample gas temperature of between 20 and 120 °C (68 and 248 °F) at the filter are also required in these cases. The electric supply for these heating systems should be continuous and separate from the timed operation of the sample pump.

7.0 Reagents and Standards

Same as Method 6A, section 7.0, with the following exceptions:

7.1 Isopropanol is not used for sampling.

7.2 The hydrogen peroxide absorbing solution shall be diluted to no less than 6 percent by volume, instead of 3 percent as specified in Methods 6 and 6A.

7.3 If the Method 6B sampling train is to be operated in a low sample flow condition (less than 100 ml/min or 0.21 ft^3/hr), molecular sieve material may be substituted for Ascarite II as the CO_2 absorbing material. The recommended molecular sieve material is Union Carbide 1/16 inch pellets, 5 A°, or equivalent. Molecular sieve material need not be discarded following the sampling run, provided that it is regenerated as per the manufacturer's instruction. Use of molecular sieve material at flow rates higher than 100 ml/min (0.21 ft^3/hr) may cause erroneous CO_2 results.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Preparation of Sampling Train. Same as Method 6A, section 8.1, with the addition of the following:

8.1.1 The sampling train is assembled as shown in Figure 6A–1 of Method 6A, except that the isopropanol bubbler is not included.

8.1.2 Adjust the timer-switch to operate in the ''on'' position from 2 to 4 minutes on a 2-hour repeating cycle or other cycle specified in the applicable regulation. Other timer sequences may be used with the restriction that the total sample volume collected is between 25 and 60 liters (0.9 and 2.1 ft^3) for the amounts of sampling reagents prescribed in this method.

8.1.3 Add cold water to the tank until the impingers and bubblers are covered at least two-thirds of their length. The impingers and bubbler tank must be covered and protected from intense heat and direct sunlight. If freezing conditions exist, the impinger solution and the water bath must be protected.

NOTE: Sampling may be conducted continuously if a low flow-rate sample pump [20

to 40 ml/min (0.04 to 0.08 ft^3/hr) for the reagent volumes described in this method] is used. If sampling is continuous, the timer-switch is not necessary. In addition, if the sample pump is designed for constant rate sampling, the rate meter may be deleted. The total gas volume collected should be between 25 and 60 liters (0.9 and 2.1 ft^3) for the amounts of sampling reagents prescribed in this method.

8.2 Sampling Train Leak-Check Procedure. Same as Method 6, section 8.2.

8.3 Sample Collection.

8.3.1 The probe and filter (either in-stack, out-of-stack, or both) must be heated to a temperature sufficient to prevent water condensation.

8.3.2 Record the initial dry gas meter reading. To begin sampling, position the tip of the probe at the sampling point, connect the probe to the first impinger (or filter), and start the timer and the sample pump. Adjust the sample flow to a constant rate of approximately 1.0 liter/min (0.035 cfm) as indicated by the rotameter. Observe the operation of the timer, and determine that it is operating as intended (*i.e.*, the timer is in the ''on'' position for the desired period, and the cycle repeats as required).

8.3.3 One time between 9 a.m. and 11 a.m. during the 24-hour sampling period, record the dry gas meter temperature (T_m) and the barometric pressure ($P_{(bar)}$).

8.3.4 At the conclusion of the run, turn off the timer and the sample pump, remove the probe from the stack, and record the final gas meter volume reading. Conduct a leak-check as described in section 8.2. If a leak is found, void the test run or use procedures acceptable to the Administrator to adjust the sample volume for leakage. Repeat the steps in sections 8.3.1 to 8.3.4 for successive runs.

8.4 Sample Recovery. The procedures for sample recovery (moisture measurement, peroxide solution, and CO_2 absorber) are the same as those in Method 6A, section 8.3.

9.0 Quality Control

Same as Method 6, section 9.0., with the exception of the isopropanol-check.

10.0 Calibration and Standardization

Same as Method 6, section 10.0, with the addition of the following:

10.1 Periodic Calibration Check. After 30 days of operation of the test train, conduct a calibration check according to the same procedures as the post-test calibration check (Method 6, section 10.1.2). If the deviation between initial and periodic calibration factors exceeds 5 percent, use the smaller of the two factors in calculations for the preceding 30 days of data, but use the most recent calibration factor for succeeding test runs.

11.0 Analytical Procedures

11.1 Sample Loss Check and Analysis. Same as Method 6, sections 11.1 and 11.2, respectively.

12.0 Data Analysis and Calculations

Same as Method 6A, section 12.0, except that P_{bar} and T_m correspond to the values recorded in section 8.3.3 of this method. The values are as follows:

P_{bar} = Initial barometric pressure for the test period, mm Hg.

T_m = Absolute meter temperature for the test period, °K.

13.0 Method Performance

13.1 Range.

13.1.1 Sulfur Dioxide. Same as Method 6.

13.1.2 Carbon Dioxide. Not determined.

13.2 Repeatability and Reproducibility. EPA-sponsored collaborative studies were undertaken to determine the magnitude of repeatability and reproducibility achievable by qualified testers following the procedures in this method. The results of the studies evolve from 145 field tests including comparisons with Methods 3 and 6. For measurements of emission rates from wet, flue gas desulfurization units in (ng/J), the repeatability (intra-laboratory precision) is 8.0 percent and the reproducibility (inter-laboratory precision) is 11.1 percent.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Methods

Same as Method 6A, section 16.0, except that the timer is needed and is operated as outlined in this method.

17.0 References

Same as Method 6A, section 17.0, with the addition of the following:

1. Butler, Frank E., et. al. The Collaborative Test of Method 6B: Twenty-Four-Hour Analysis of SO_2 and CO_2. JAPCA. Vol. 33, No. 10. October 1983.

18.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 6C—DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES (INSTRUMENTAL ANALYZER PROCEDURE)

1.0 Scope and Application

What is Method 6C?

Method 6C is a procedure for measuring sulfur dioxide (SO_2) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that

you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis.

This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 4—Determination of Moisture Content in Stack Gases.

(c) Method 6—Determination of Sulfur Dioxide Emissions from Stationary Sources.

(d) Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure).

1.1 Analytes. What does this method determine? This method measures the concentration of sulfur dioxide.

Analyte	CAS No.	Sensitivity
SO_2	7446–09–5	Typically <2% of Calibration Span.

1.2 Applicability. When is this method required? The use of Method 6C may be required by specific New Source Performance Standards, Clean Air Marketing rules, State Implementation Plans, and permits where SO_2 concentrations in stationary source emissions must be measured, either to determine compliance with an applicable emission standard or to conduct performance testing of a continuous emission monitoring system (CEMS). Other regulations may also require the use of Method 6C.

1.3 Data Quality Objectives. How good must my collected data be? Refer to section 1.3 of Method 7E.

2.0 Summary of Method

In this method, you continuously sample the effluent gas and convey the sample to an analyzer that measures the concentration of SO_2. You must meet the performance requirements of this method to validate your data.

3.0 Definitions

Refer to section 3.0 of Method 7E for the applicable definitions.

4.0 Interferences

Refer to Section 4.0 of Method 7E.

5.0 Safety

Refer to section 5.0 of Method 7E.

6.0 Equipment and Supplies

Figure 7E–1 of Method 7E is a schematic diagram of an acceptable measurement system.

6.1 What do I need for the measurement system? The essential components of the measurement system are the same as those in sections 6.1 and 6.2 of Method 7E, except that the SO_2 analyzer described in section 6.2 of this method must be used instead of the analyzer described in section 6.2 of Method 7E. You must follow the noted specifications in section 6.1 of Method 7E.

6.2 What analyzer must I use? You may use an instrument that uses an ultraviolet, nondispersive infrared, fluorescence, or other detection principle to continuously measure SO_2 in the gas stream and meets the performance specifications in section 13.0. The low-range and dual-range analyzer provisions in sections 6.2.8.1 and 6.2.8.2 of Method 7E apply.

7.0 Reagents and Standards

7.1 Calibration Gas. What calibration gases do I need? Refer to section 7.1 of Method 7E for the calibration gas requirements. Example calibration gas mixtures are listed below.

(a) SO_2 in nitrogen (N_2).

(b) SO_2 in air.

(c) SO_2 and CO_2 in N_2.

(d) SO_2 andO_2 in N_2.

(e) $SO_2/CO_2/O_2$ gas mixture in N_2.

(f) CO_2/NO_X gas mixture in N_2.

(g) $CO_2/SO_2/NO_X$ gas mixture in N_2.

7.2 Interference Check. What additional reagents do I need for the interference check? The test gases for the interference check are listed in Table 7E–3 of Method 7E. For the alternative interference check, you must use the reagents described in section 7.0 of Method 6.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling Site and Sampling Points. You must follow the procedures of section 8.1 of Method 7E.

8.2 Initial Measurement System Performance Tests. You must follow the procedures in section 8.2 of Method 7E. If a dilution-type measurement system is used, the special considerations in section 8.3 of Method 7E also apply.

8.3 Interference Check. You must follow the procedures of section 8.2.7 of Method 7E

to conduct an interference check, substituting SO_2 for NO_X as the method pollutant. For dilution-type measurement systems, you must use the alternative interference check procedure in section 16 and a co-located, unmodified Method 6 sampling train.

8.4 Sample Collection. You must follow the procedures of section 8.4 of Method 7E.

8.5 Post-Run System Bias Check and Drift Assessment. You must follow the procedures of section 8.5 of Method 7E.

9.0 Quality Control

Follow quality control procedures in section 9.0 of Method 7E.

10.0 Calibration and Standardization

Follow the procedures for calibration and standardization in section 10.0 of Method 7E.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the applicable procedures for calculations and data analysis in section 12.0 of Method 7E as applicable, substituting SO_2 for NO_X as appropriate.

13.0 Method Performance

13.1 The specifications for the applicable performance checks are the same as in section 13.0 of Method 7E.

13.2 Alternative Interference Check. The results are acceptable if the difference between the Method 6C result and the modified Method 6 result is less than 7.0 percent of the Method 6 result for each of the three test runs. For the purposes of comparison, the Method 6 and 6C results must be expressed in the same units of measure.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Alternative Interference Check. You may perform an alternative interference check consisting of at least three comparison runs between Method 6C and Method 6. This check validates the Method 6C results at each particular source category (type of facility) where the check is performed. When testing under conditions of low concentrations (<15 ppm), this alternative interference check is not allowed.

NOTE: The procedure described below applies to non-dilution sampling systems only. If this alternative interference check is used for a dilution sampling system, use a standard Method 6 sampling train and extract the sample directly from the exhaust stream at points collocated with the Method 6C sample probe.

a. Build the modified Method 6 sampling train (flow control valve, two midget impingers containing 3 percent hydrogen peroxide, and dry gas meter) shown in Figure 6C–1. Connect the sampling train to the sample bypass discharge vent. Record the dry gas meter reading before you begin sampling. Simultaneously collect modified Method 6 and Method 6C samples. Open the flow control valve in the modified Method 6 train as you begin to sample with Method 6C. Adjust the Method 6 sampling rate to 1 liter per minute (.10 percent). The sampling time per run must be the same as for Method 6 plus twice the average measurement system response time. If your modified Method 6 train does not include a pump, you risk biasing the results high if you over-pressurize the midget impingers and cause a leak. You can reduce this risk by cautiously increasing the flow rate as sampling begins.

b. After completing a run, record the final dry gas meter reading, meter temperature, and barometric pressure. Recover and analyze the contents of the midget impingers using the procedures in Method 6. Determine the average gas concentration reported by Method 6C for the run.

17.0 References

1. ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards'' September 1997 as amended, EPA–600/R–97/121

18.0 Tables, Diagrams, Flowcharts, and Validation Data

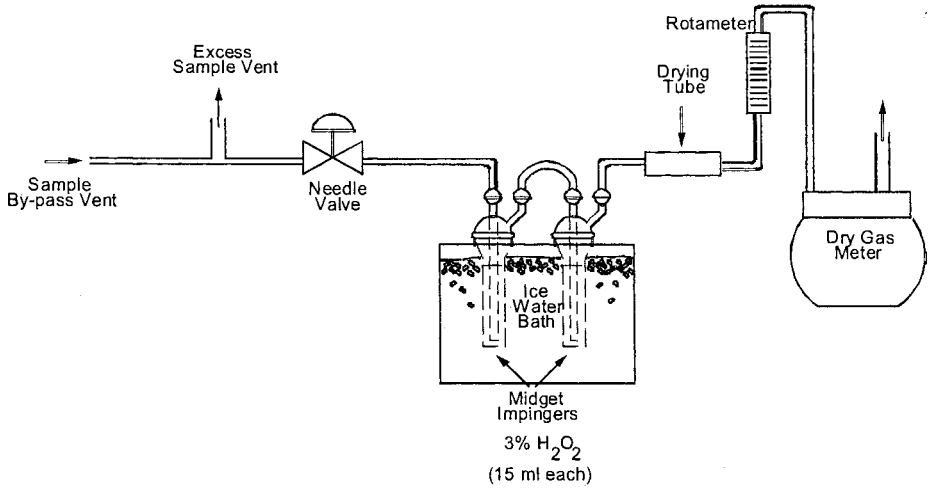

Figure 6C-1. Modified Method 6
Alternative Interference Check Sampling Train

METHOD 7—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1 and Method 5.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–0	2–400 mg/dscm

1.2 Applicability. This method is applicable for the measurement of nitrogen oxides (NO_X) emitted from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sample methods.

2.0 Summary of Method

A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution, and the nitrogen oxides, except nitrous oxide, are measured colorimetrically using the phenoldisulfonic acid (PDS) procedure.

3.0 Definitions [Reserved]

4.0 Interferences

Biased results have been observed when sampling under conditions of high sulfur dioxide concentrations. At or above 2100 ppm SO_2, use five times the H_2O_2 concentration of the Method 7 absorbing solution. Laboratory tests have shown that high concentrations of SO_2 (about 2100 ppm) cause low results in Method 7 and 7A. Increasing the H_2O_2 concentration to five times the original concentration eliminates this bias. However, when no SO_2 is present, increasing the concentration by five times results in a low bias.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs.

5.2.2 Phenoldisulfonic Acid. Irritating to eyes and skin.

5.2.3 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.4 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

5.2.5 Phenol. Poisonous and caustic. Do not handle with bare hands as it is absorbed through the skin.

6.0 Equipment and Supplies

6.1 Sample Collection. A schematic of the sampling train used in performing this method is shown in Figure 7–1. Other grab sampling systems or equipment, capable of measuring sample volume to within 2.0 percent and collecting a sufficient sample volume to allow analytical reproducibility to within 5 percent, will be considered acceptable alternatives, subject to the approval of the Administrator. The following items are required for sample collection:

6.1.1 Probe. Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or heated out-of-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Stainless steel or Teflon tubing may also be used for the probe. Heating is not necessary if the probe remains dry during the purging period.

6.1.2 Collection Flask. Two-liter borosilicate, round bottom flask, with short neck and 24/40 standard taper opening, protected against implosion or breakage.

6.1.3 Flask Valve. T-bore stopcock connected to a 24/40 standard taper joint.

6.1.4 Temperature Gauge. Dial-type thermometer, or other temperature gauge, capable of measuring 1 °C (2 °F) intervals from −5 to 50 °C (23 to 122 °F).

6.1.5 Vacuum Line. Tubing capable of withstanding a vacuum of 75 mm (3 in.) Hg absolute pressure, with ''T'' connection and T-bore stopcock.

6.1.6 Vacuum Gauge. U-tube manometer, 1 meter (39 in.), with 1 mm (0.04 in.) divisions, or other gauge capable of measuring pressure to within 2.5 mm (0.10 in.) Hg.

6.1.7 Pump. Capable of evacuating the collection flask to a pressure equal to or less than 75 mm (3 in.) Hg absolute.

6.1.8 Squeeze Bulb. One-way.

6.1.9 Volumetric Pipette. 25-ml.

6.1.10 Stopcock and Ground Joint Grease. A high-vacuum, high-temperature chlorofluorocarbon grease is required. Halocarbon 25–5S has been found to be effective.

6.1.11 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg. See note in Method 5, section 6.1.2.

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Graduated Cylinder. 50-ml with 1 ml divisions.

6.2.2 Storage Containers. Leak-free polyethylene bottles.

6.2.3 Wash Bottle. Polyethylene or glass.

6.2.4 Glass Stirring Rod.

6.2.5 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

6.3 Analysis. The following items are required for analysis:

6.3.1 Volumetric Pipettes. Two 1-ml, two 2-ml, one 3-ml, one 4-ml, two 10-ml, and one 25-ml for each sample and standard.

6.3.2 Porcelain Evaporating Dishes. 175- to 250-ml capacity with lip for pouring, one for each sample and each standard. The Coors No. 45006 (shallowform, 195-ml) has been found to be satisfactory. Alternatively, polymethyl pentene beakers (Nalge No. 1203, 150-ml), or glass beakers (150-ml) may be used. When glass beakers are used, etching of the beakers may cause solid matter to be present in the analytical step; the solids should be removed by filtration.

6.3.3 Steam Bath. Low-temperature ovens or thermostatically controlled hot plates kept below 70 °C (160 °F) are acceptable alternatives.

6.3.4 Dropping Pipette or Dropper. Three required.

6.3.5 Polyethylene Policeman. One for each sample and each standard.

6.3.6 Graduated Cylinder. 100-ml with 1-ml divisions.

6.3.7 Volumetric Flasks. 50-ml (one for each sample and each standard), 100-ml (one for each sample and each standard, and one for the working standard KNO_3 solution), and 1000-ml (one).

6.3.8 Spectrophotometer. To measure at 410 nm.

6.3.9 Graduated Pipette. 10-ml with 0.1-ml divisions.

6.3.10 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

6.3.11 Analytical Balance. To measure to within 0.1 mg.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. The following reagents are required for sampling:

7.1.1 Water. Deionized distilled to conform to ASTM D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17). The $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.1.2 Absorbing Solution. Cautiously add 2.8 ml concentrated H_2SO_4 to a 1-liter flask partially filled with water. Mix well, and add 6 ml of 3 percent hydrogen peroxide, freshly prepared from 30 percent hydrogen peroxide solution. Dilute to 1 liter of water and mix well. The absorbing solution should be used within 1 week of its preparation. Do not expose to extreme heat or direct sunlight.

7.2 Sample Recovery. The following reagents are required for sample recovery:

7.2.1 Water. Same as in 7.1.1.

7.2.2 Sodium Hydroxide, 1 N. Dissolve 40 g NaOH in water, and dilute to 1 liter.

7.3 Analysis. The following reagents and standards are required for analysis:

7.3.1 Water. Same as in 7.1.1.

7.3.2 Fuming Sulfuric Acid. 15 to 18 percent by weight free sulfur trioxide. HANDLE WITH CAUTION.

7.3.3 Phenol. White solid.

7.3.4 Sulfuric Acid. Concentrated, 95 percent minimum assay.

7.3.5 Potassium Nitrate (KNO_3). Dried at 105 to 110 °C (221 to 230 °F) for a minimum of 2 hours just prior to preparation of standard solution.

7.3.6 Standard KNO_3 Solution. Dissolve exactly 2.198 g of dried KNO_3 in water, and dilute to 1 liter with water in a 1000-ml volumetric flask.

7.3.7 Working Standard KNO_3 Solution. Dilute 10 ml of the standard solution to 100 ml with water. One ml of the working standard solution is equivalent to 100 μg nitrogen dioxide (NO_2).

7.3.8 Phenoldisulfonic Acid Solution. Dissolve 25 g of pure white phenol solid in 150 ml concentrated sulfuric acid on a steam bath. Cool, add 75 ml fuming sulfuric acid (15 to 18 percent by weight free sulfur trioxide—HANDLE WITH CAUTION), and heat at 100 °C (212 °F) for 2 hours. Store in a dark, stoppered bottle.

7.3.9 Concentrated Ammonium Hydroxide.

8.0 Sample Collection, Preservation, Storage and Transport

8.1 Sample Collection.

8.1.1 Flask Volume. The volume of the collection flask and flask valve combination must be known prior to sampling. Assemble the flask and flask valve, and fill with water to the stopcock. Measure the volume of water to ±10 ml. Record this volume on the flask.

8.1.2 Pipette 25 ml of absorbing solution into a sample flask, retaining a sufficient quantity for use in preparing the calibration standards. Insert the flask valve stopper into the flask with the valve in the ''purge'' position. Assemble the sampling train as shown in Figure 7–1, and place the probe at the sampling point. Make sure that all fittings are tight and leak-free, and that all ground glass joints have been greased properly with a high-vacuum, high temperature chlorofluorocarbon-based stopcock grease. Turn the flask valve and the pump valve to their ''evacuate'' positions. Evacuate the flask to 75 mm (3 in.) Hg absolute pressure, or less. Evacuation to a pressure approaching the vapor pressure of water at the existing temperature is desirable. Turn the pump valve to its ''vent'' position, and turn off the pump. Check for leakage by observing the manometer for any pressure fluctuation. (Any variation greater than 10 mm (0.4 in.) Hg over a period of 1 minute is not acceptable, and the flask is not to be used until the leakage problem is corrected. Pressure in the flask is not to exceed 75 mm (3 in.) Hg absolute at the time sampling is commenced.) Record the volume of the flask and valve (V_f), the flask temperature (T_i), and the barometric pressure. Turn the flask valve counterclockwise to its ''purge'' position, and do the same with the pump valve. Purge the probe and the vacuum tube using the squeeze bulb. If condensation occurs in the probe and the flask valve area, heat the probe, and purge until the condensation disappears. Next, turn the pump valve to its ''vent'' position. Turn the flask valve clockwise to its ''evacuate'' position, and record the difference in the mercury levels in the manometer. The absolute internal pressure in the flask (P_i) is equal to the barometric pressure less the manometer reading. Immediately turn the flask valve to the ''sample'' position, and permit the gas to enter the flask until pressures in the flask and sample line (*i.e.*, duct, stack) are equal. This will usually require about 15 seconds; a longer period indicates a plug in the probe, which must be

corrected before sampling is continued. After collecting the sample, turn the flask valve to its ''purge'' position, and disconnect the flask from the sampling train.

8.1.3 Shake the flask for at least 5 minutes.

8.1.4 If the gas being sampled contains insufficient oxygen for the conversion of NO to NO_2 (*e.g.,* an applicable subpart of the standards may require taking a sample of a calibration gas mixture of NO in N_2), then introduce oxygen into the flask to permit this conversion. Oxygen may be introduced into the flask by one of three methods: (1) Before evacuating the sampling flask, flush with pure cylinder oxygen, then evacuate flask to 75 mm (3 in.) Hg absolute pressure or less; or (2) inject oxygen into the flask after sampling; or (3) terminate sampling with a minimum of 50 mm (2 in.) Hg vacuum remaining in the flask, record this final pressure, and then vent the flask to the atmosphere until the flask pressure is almost equal to atmospheric pressure.

8.2 Sample Recovery. Let the flask sit for a minimum of 16 hours, and then shake the contents for 2 minutes.

8.2.1 Connect the flask to a mercury filled U-tube manometer. Open the valve from the flask to the manometer, and record the flask temperature (T_f), the barometric pressure, and the difference between the mercury levels in the manometer. The absolute internal pressure in the flask (P_f) is the barometric pressure less the manometer reading. Transfer the contents of the flask to a leak-free polyethylene bottle. Rinse the flask twice with 5 ml portions of water, and add the rinse water to the bottle. Adjust the pH to between 9 and 12 by adding 1 N NaOH, dropwise (about 25 to 35 drops). Check the pH by dipping a stirring rod into the solution and then touching the rod to the pH test paper. Remove as little material as possible during this step. Mark the height of the liquid level so that the container can be checked for leakage after transport. Label the container to identify clearly its contents. Seal the container for shipping.

9.0 Quality Control

Section	Quality control measure	Effect
10.1	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.

10.0 Calibration and Standardization

10.1 Spectrophotometer.

10.1.1 Optimum Wavelength Determination.

10.1.1.1 Calibrate the wavelength scale of the spectrophotometer every 6 months. The calibration may be accomplished by using an energy source with an intense line emission such as a mercury lamp, or by using a series of glass filters spanning the measuring range of the spectrophotometer. Calibration materials are available commercially and from the National Institute of Standards and Technology. Specific details on the use of such materials should be supplied by the vendor; general information about calibration techniques can be obtained from general reference books on analytical chemistry. The wavelength scale of the spectrophotometer must read correctly within 5 nm at all calibration points; otherwise, repair and recalibrate the spectrophotometer. Once the wavelength scale of the spectrophotometer is in proper calibration, use 410 nm as the optimum wavelength for the measurement of the absorbance of the standards and samples.

10.1.1.2 Alternatively, a scanning procedure may be employed to determine the proper measuring wavelength. If the instrument is a double-beam spectrophotometer, scan the spectrum between 400 and 415 nm using a 200 μg NO_2 standard solution in the sample cell and a blank solution in the reference cell. If a peak does not occur, the spectrophotometer is probably malfunctioning and should be repaired. When a peak is obtained within the 400 to 415 nm range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of absorbance of both the standards and the samples. For a single-beam spectrophotometer, follow the scanning procedure described above, except scan separately the blank and standard solutions. The optimum wavelength shall be the wavelength at which the maximum difference in absorbance between the standard and the blank occurs.

10.1.2 Determination of Spectrophotometer Calibration Factor K_c. Add 0 ml, 2.0 ml, 4.0 ml, 6.0 ml, and 8.0 ml of the KNO_3 working standard solution (1 ml = 100 μg NO_2) to a series of five 50-ml volumetric flasks. To each flask, add 25 ml of absorbing solution and 10 ml water. Add 1 N NaOH to each flask until the pH is between 9 and 12 (about 25 to 35 drops). Dilute to the mark with water. Mix thoroughly, and pipette a 25-ml aliquot of each solution into a separate porcelain evaporating dish. Beginning with the evaporation step, follow the analysis procedure of section 11.2 until the solution has been transferred to the 100-ml volumetric flask and diluted to the mark. Measure the absorbance of each solution at the optimum wavelength as determined in section 10.2.1. This calibration procedure must be repeated on each day that samples are analyzed. Calculate the spectrophotometer calibration factor as shown in section 12.2.

10.1.3 Spectrophotometer Calibration Quality Control. Multiply the absorbance value obtained for each standard by the K_c factor (reciprocal of the least squares slope) to determine the distance each calibration point lies from the theoretical calibration line. The difference between the calculated concentration values and the actual concentrations (*i.e.*, 100, 200, 300, and 400 µg NO_2) should be less than 7 percent for all standards.

10.2 Barometer. Calibrate against a mercury barometer or NIST-traceable barometer prior to the field test.

10.3 Temperature Gauge. Calibrate dial thermometers against mercury-in-glass thermometers. An alternative mercury-free thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

10.4 Vacuum Gauge. Calibrate mechanical gauges, if used, against a mercury manometer such as that specified in section 6.1.6.

10.5 Analytical Balance. Calibrate against standard weights.

11.0 Analytical Procedures

11.1 Sample Loss Check. Note the level of the liquid in the container, and confirm whether any sample was lost during shipment. Note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Preparation. Immediately prior to analysis, transfer the contents of the shipping container to a 50 ml volumetric flask, and rinse the container twice with 5 ml portions of water. Add the rinse water to the flask, and dilute to mark with water; mix thoroughly. Pipette a 25-ml aliquot into the porcelain evaporating dish. Return any unused portion of the sample to the polyethylene storage bottle. Evaporate the 25-ml aliquot to dryness on a steam bath, and allow to cool. Add 2 ml phenoldisulfonic acid solution to the dried residue, and triturate thoroughly with a polyethylene policeman. Make sure the solution contacts all the residue. Add 1 ml water and 4 drops of concentrated sulfuric acid. Heat the solution on a steam bath for 3 minutes with occasional stirring. Allow the solution to cool, add 20 ml water, mix well by stirring, and add concentrated ammonium hydroxide, dropwise, with constant stirring, until the pH is 10 (as determined by pH paper). If the sample contains solids, these must be removed by filtration (centrifugation is an acceptable alternative, subject to the approval of the Administrator) as follows: Filter through Whatman No. 41 filter paper into a 100-ml volumetric flask. Rinse the evaporating dish with three 5-ml portions of water. Filter these three rinses. Wash the filter with at least three 15-ml portions of water. Add the filter washings to the contents of the volumetric flask, and dilute to the mark with water. If solids are absent, the solution can be transferred directly to the 100-ml volumetric flask and diluted to the mark with water.

11.3 Sample Analysis. Mix the contents of the flask thoroughly, and measure the absorbance at the optimum wavelength used for the standards (Section 10.2.1), using the blank solution as a zero reference. Dilute the sample and the blank with equal volumes of water if the absorbance exceeds A_4, the absorbance of the 400-µg NO_2 standard (see section 10.2.2).

12.0 Data Analysis and Calculations

Carry out the calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculations.

12.1 12.1 Nomenclature

A = Absorbance of sample.
A_1 = Absorbance of the 100-µg NO_2 standard.
A_2 = Absorbance of the 200-µg NO_2 standard.
A_3 = Absorbance of the 300-µg NO_2 standard.
A_4 = Absorbance of the 400-µg NO_2 standard.
C = Concentration of NO_X as NO_2, dry basis, corrected to standard conditions, mg/dsm^3 (lb/dscf).
F = Dilution factor (*i.e.*, 25/5, 25/10, *etc.*, required only if sample dilution was needed to reduce the absorbance into the range of the calibration).
K_c = Spectrophotometer calibration factor.
M = Mass of NO_X as NO_2 in gas sample, µg.
P_f = Final absolute pressure of flask, mm Hg (in. Hg).
P_i = Initial absolute pressure of flask, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
T_f = Final absolute temperature of flask, °K (°R).
T_i = Initial absolute temperature of flask, °K (°R).
T_{std} = Standard absolute temperature, 293 °K (528°R).
V_{sc} = Sample volume at standard conditions (dry basis), ml.
V_f = Volume of flask and valve, ml.
V_a = Volume of absorbing solution, 25 ml.

12.2 Spectrophotometer Calibration Factor.

$$K_c = 100\frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^{\,2} + A_2^{\,2} + A_3^{\,2} + A_4^{\,2}} \qquad \text{Eq. 7-1}$$

12.3 Sample Volume, Dry Basis, Corrected to Standard Conditions.

$$V_{sc} = \left(V_f - V_a\right)\frac{T_{std}}{P_{std}}\left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right] \qquad \text{Eq. 7-2}$$

$$= K_1\left(V_f - 25\right)\left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right]$$

Where:

K_1 = 0.3858 °K/mm Hg for metric units,
K_1 = 17.65 °R/in. Hg for English units.

12.4 Total µg NO_2 per sample.

$$m = 2K_c AF \qquad \text{Eq. 7-3}$$

Where:

2 = 50/25, the aliquot factor.

NOTE: If other than a 25-ml aliquot is used for analysis, the factor 2 must be replaced by a corresponding factor.

12.5 Sample Concentration, Dry Basis, Corrected to Standard Conditions.

$$C = K_2\left(m/V_{sc}\right) \qquad \text{Eq. 7-4}$$

Where:

K2 = 10^3 (mg/m^3)/(µg/ml) for metric units,
K_2 = 6.242 × 10^{-5} (lb/scf)/(µg/ml) for English units.

13.0 Method Performance

13.1 Range. The analytical range of the method has been determined to be 2 to 400 milligrams NO_X (as NO_2) per dry standard cubic meter, without having to dilute the sample.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Standard Methods of Chemical Analysis. 6th ed. New York, D. Van Nostrand Co., Inc. 1962. Vol. 1, pp. 329–330.

2. Standard Method of Test for Oxides of Nitrogen in Gaseous Combustion Products (Phenoldisulfonic Acid Procedure). In: 1968 Book of ASTM Standards, Part 26. Philadelphia, PA. 1968. ASTM Designation D 1608–60, pp. 725–729.

3. Jacob, M.B. The Chemical Analysis of Air Pollutants. New York. Interscience Publishers, Inc. 1960. Vol. 10, pp. 351–356.

4. Beatty, R.L., L.B. Berger, and H.H. Schrenk. Determination of Oxides of Nitrogen by the Phenoldisulfonic Acid Method. Bureau of Mines, U.S. Dept. of Interior. R.I. 3687. February 1943.

5. Hamil, H.F. and D.E. Camann. Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Fossil Fuel-Fired Steam Generators). Southwest Research Institute Report for Environmental Protection Agency. Research Triangle Park, NC. October 5, 1973.

6. Hamil, H.F. and R.E. Thomas. Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Nitric Acid Plants). Southwest Research Institute Report for Environmental Protection Agency. Research Triangle Park, NC. May 8, 1974.

7. Stack Sampling Safety Manual (Draft). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC. September 1978.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

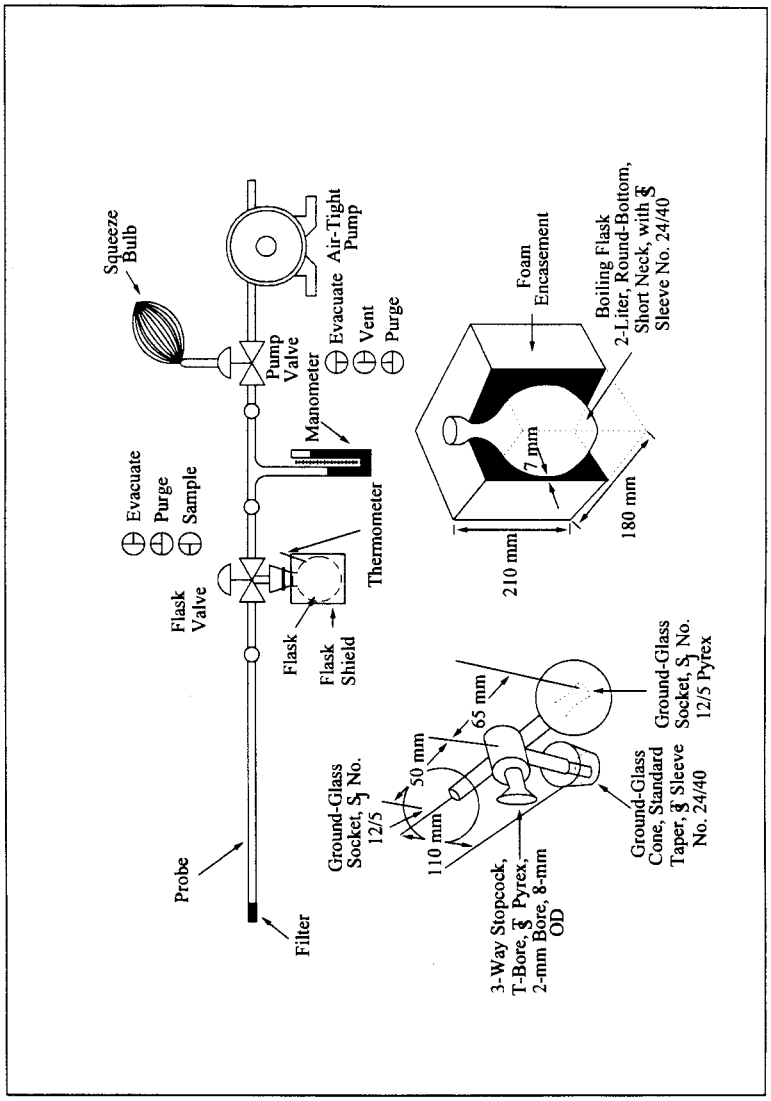

Figure 7-1. Sampling Train, Flask Valve, and Flask.

METHOD 7A—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ION CHROMATOGRAPHIC METHOD)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 3, Method 5, and Method 7.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–0	65–655 ppmv

1.2 Applicability. This method is applicable for the determination of NO_X emissions from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution. The nitrogen oxides, excluding nitrous oxide (N_2O), are oxidized to nitrate and measured by ion chromatography.

3.0 Definitions [Reserved]

4.0 Interferences

Biased results have been observed when sampling under conditions of high sulfur dioxide concentrations. At or above 2100 ppm SO_2, use five times the H_2O_2 concentration of the Method 7 absorbing solution. Laboratory tests have shown that high concentrations of SO_2 (about 2100 ppm) cause low results in Method 7 and 7A. Increasing the H_2O_2 concentration to five times the original concentration eliminates this bias. However, when no SO_2 is present, increasing the concentration by five times results in a low bias.

5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs.

5.2.2 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m^3 will cause lung damage in uninitiated. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as in Method 7, section 6.1.

6.2 Sample Recovery. Same as in Method 7, section 6.2, except the stirring rod and pH paper are not needed.

6.3 Analysis. For the analysis, the following equipment and supplies are required. Alternative instrumentation and procedures will be allowed provided the calibration precision requirement in section 10.1.2 can be met.

6.3.1 Volumetric Pipets. Class A;1-, 2-, 4-, 5-ml (two for the set of standards and one per sample), 6-, 10-, and graduated 5-ml sizes.

6.3.2 Volumetric Flasks. 50-ml (two per sample and one per standard), 200-ml, and 1-liter sizes.

6.3.3 Analytical Balance. To measure to within 0.1 mg.

6.3.4 Ion Chromatograph. The ion chromatograph should have at least the following components:

6.3.4.1 Columns. An anion separation or other column capable of resolving the nitrate ion from sulfate and other species present and a standard anion suppressor column (optional). Suppressor columns are produced as proprietary items; however, one can be produced in the laboratory using the resin available from BioRad Company, 32nd and Griffin Streets, Richmond, California. Peak resolution can be optimized by varying the eluent strength or column flow rate, or by experimenting with alternative columns that may offer more efficient separation. When using guard columns with the stronger reagent to protect the separation column, the analyst should allow rest periods between injection intervals to purge possible sulfate buildup in the guard column.

6.3.4.2 Pump. Capable of maintaining a steady flow as required by the system.

6.3.4.3 Flow Gauges. Capable of measuring the specified system flow rate.

6.3.4.4 Conductivity Detector.

6.3.4.5 Recorder. Compatible with the output voltage range of the detector.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 7, section 7.1.

7.2 Sample Recovery. Same as Method 7, section 7.1.1.

7.3 Analysis. The following reagents and standards are required for analysis:

7.3.1 Water. Same as Method 7, section 7.1.1.

7.3.2 Stock Standard Solution, 1 mg NO_2/ml. Dry an adequate amount of sodium nitrate ($NaNO_3$) at 105 to 110 °C (221 to 230 °F) for a minimum of 2 hours just before preparing the standard solution. Then dissolve exactly 1.847 g of dried $NaNO_3$ in water, and dilute to 1 liter in a volumetric flask. Mix well. This solution is stable for 1 month and should not be used beyond this time.

7.3.3 Working Standard Solution, 25 μg/ml. Dilute 5 ml of the standard solution to 200 ml with water in a volumetric flask, and mix well.

7.3.4 Eluent Solution. Weigh 1.018 g of sodium carbonate (Na_2CO_3) and 1.008 g of sodium bicarbonate ($NaHCO_3$), and dissolve in 4 liters of water. This solution is 0.0024 M Na_2CO_3/0.003 M $NaHCO_3$. Other eluents appropriate to the column type and capable of resolving nitrate ion from sulfate and other species present may be used.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling. Same as in Method 7, section 8.1.

8.2 Sample Recovery. Same as in Method 7, section 8.2, except delete the steps on adjusting and checking the pH of the sample. Do not store the samples more than 4 days between collection and analysis.

9.0 Quality Control

Section	Quality control measure	Effect
10.1	Ion chromatographn calibration	Ensure linearity of ion chromatograph response to standards.

10.0 Calibration and Standardizations

10.1 Ion Chromatograph.

10.1.1 Determination of Ion Chromatograph Calibration Factor S. Prepare a series of five standards by adding 1.0, 2.0, 4.0, 6.0, and 10.0 ml of working standard solution (25 μg/ml) to a series of five 50-ml volumetric flasks. (The standard masses will equal 25, 50, 100, 150, and 250 μg.) Dilute each flask to the mark with water, and mix well. Analyze with the samples as described in section 11.2, and subtract the blank from each value. Prepare or calculate a linear regression plot of the standard masses in μg (x-axis) versus their peak height responses in millimeters (y-axis). (Take peak height measurements with symmetrical peaks; in all other cases, calculate peak areas.) From this curve, or equation, determine the slope, and calculate its reciprocal to denote as the calibration factor, S.

10.1.2 Ion Chromatograph Calibration Quality Control. If any point on the calibration curve deviates from the line by more than 7 percent of the concentration at that point, remake and reanalyze that standard. This deviation can be determined by multiplying S times the peak height response for each standard. The resultant concentrations must not differ by more than 7 percent from each known standard mass (*i.e.*, 25, 50, 100, 150, and 250 μg).

10.2 Conductivity Detector. Calibrate according to manufacturer's specifications prior to initial use.

10.3 Barometer. Calibrate against a mercury barometer.

10.4 Temperature Gauge. Calibrate dial thermometers against mercury-in-glass thermometers. An alternative mercury-free thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

10.5 Vacuum Gauge. Calibrate mechanical gauges, if used, against a mercury manometer such as that specified in section 6.1.6 of Method 7.

10.6 Analytical Balance. Calibrate against standard weights.

11.0 Analytical Procedures

11.1 Sample Preparation.

11.1.1 Note on the analytical data sheet, the level of the liquid in the container, and whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Immediately before analysis, transfer the contents of the shipping container to a 50-ml volumetric flask, and rinse the container twice with 5 ml portions of water. Add the rinse water to the flask, and dilute to the mark with water. Mix thoroughly.

11.1.2 Pipet a 5-ml aliquot of the sample into a 50-ml volumetric flask, and dilute to the mark with water. Mix thoroughly. For each set of determinations, prepare a reagent

blank by diluting 5 ml of absorbing solution to 50 ml with water. (Alternatively, eluent solution may be used instead of water in all sample, standard, and blank dilutions.)

11.2 Analysis.

11.2.1 Prepare a standard calibration curve according to section 10.1.1. Analyze the set of standards followed by the set of samples using the same injection volume for both standards and samples. Repeat this analysis sequence followed by a final analysis of the standard set. Average the results. The two sample values must agree within 5 percent of their mean for the analysis to be valid. Perform this duplicate analysis sequence on the same day. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

11.2.2 Document each sample chromatogram by listing the following analytical parameters: injection point, injection volume, nitrate and sulfate retention times, flow rate, detector sensitivity setting, and recorder chart speed.

12.0 Data Analysis and Calculations

Carry out the calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculations.

12.1 Sample Volume. Calculate the sample volume Vsc (in ml), on a dry basis, corrected to standard conditions, using Equation 7–2 of Method 7.

12.2 Sample Concentration of NO_X as NO_2.

12.2.1 Calculate the sample concentration C (in mg/dscm) as follows:

$$C = (H)(S)(F)\left(10^4\right)/V_{sc} \qquad \text{Eq. 7A-1}$$

Where:

H = Sample peak height, mm.

S = Calibration factor, μg/mm.

F = Dilution factor (required only if sample dilution was needed to reduce the concentration into the range of calibration), dimensionless.

10^4 = 1:10 dilution times conversion factor of: $(mg/10^3\ \mu g)(10^6\ ml/m^3)$.

12.2.2 If desired, the concentration of NO_2 may be calculated as ppm NO_2 at standard conditions as follows:

$$\text{ppm } NO_2 = 0.5228C \qquad \text{Eq. 7A-2}$$

Where:

0.5228 = ml/mg NO_2.

13.0 Method Performance

13.1 Range. The analytical range of the method is from 125 to 1250 mg NO_X/m^3 as NO_2 (65 to 655 ppmv), and higher concentrations may be analyzed by diluting the sample. The lower detection limit is approximately 19 mg/m^3 (10 ppmv), but may vary among instruments.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Mulik, J.D., and E. Sawicki. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor, Ann Arbor Science Publishers, Inc. Vol. 2, 1979.

2. Sawicki, E., J.D. Mulik, and E. Wittgenstein. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor, Ann Arbor Science Publishers, Inc. Vol. 1. 1978.

3. Siemer, D.D. Separation of Chloride and Bromide from Complex Matrices Prior to Ion Chromatographic Determination. Anal. Chem. *52*(12):1874–1877. October 1980.

4. Small, H., T.S. Stevens, and W.C. Bauman. Novel Ion Exchange Chromatographic Method Using Conductimetric Determination. Anal. Chem. *47*(11):1801. 1975.

5. Yu, K.K., and P.R. Westlin. Evaluation of Reference Method 7 Flask Reaction Time. Source Evaluation Society Newsletter. *4*(4). November 1979. 10 pp.

6. Stack Sampling Safety Manual (Draft). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standard, Research Triangle Park, NC. September 1978.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 7B—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ULTRAVIOLET SPECTROPHOTOMETRIC METHOD)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 5, and Method 7.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		

Analyte	CAS No.	Sensitivity
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–0	30–786 ppmv

1.2 Applicability. This method is applicable for the determination of NO_X emissions from nitric acid plants.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution; the NO_X, excluding nitrous oxide (N_2O), are measured by ultraviolet spectrophotometry.

3.0 Definition [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m^3 will cause lung damage in uninitiated. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 7, section 6.1.

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Wash Bottle. Polyethylene or glass.

6.2.2 Volumetric Flasks. 100-ml (one for each sample).

6.3 Analysis. The following items are required for analysis:

6.3.1 Volumetric Pipettes. 5-, 10-, 15-, and 20-ml to make standards and sample dilutions.

6.3.2 Volumetric Flasks. 1000- and 100-ml for preparing standards and dilution of samples.

6.3.3 Spectrophotometer. To measure ultraviolet absorbance at 210 nm.

6.3.4 Analytical Balance. To measure to within 0.1 mg.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents are to conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 7, section 7.1. It is important that the amount of hydrogen peroxide in the absorbing solution not be increased. Higher concentrations of peroxide may interfere with sample analysis.

7.2 Sample Recovery. Same as Method 7, section 7.2.

7.3 Analysis. Same as Method 7, sections 7.3.1, 7.3.3, and 7.3.4, with the addition of the following:

7.3.1 Working Standard KNO_3 Solution. Dilute 10 ml of the standard solution to 1000 ml with water. One milliliter of the working standard is equivalent to 10 μg NO_2.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sample Collection. Same as Method 7, section 8.1.

8.2 Sample Recovery.

8.2.1 Let the flask sit for a minimum of 16 hours, and then shake the contents for 2 minutes.

8.2.2 Connect the flask to a mercury filled U-tube manometer. Open the valve from the flask to the manometer, and record the flask temperature (T_f), the barometric pressure, and the difference between the mercury levels in the manometer. The absolute internal pressure in the flask (P_f) is the barometric pressure less the manometer reading.

8.2.3 Transfer the contents of the flask to a leak-free wash bottle. Rinse the flask three times with 10-ml portions of water, and add

to the bottle. Mark the height of the liquid level so that the container can be checked for leakage after transport. Label the container to identify clearly its contents. Seal the container for shipping.

9.0 Quality Control

Section	Quality control measure	Effect
10.1	Spectrophotometer calibration	Ensures linearity of spectrophotometer response to standards.

10.0 Calibration and Standardizations

Same as Method 7, sections 10.2 through 10.5, with the addition of the following:

10.1 Determination of Spectrophotometer Standard Curve. Add 0 ml, 5 ml, 10 ml, 15 ml, and 20 ml of the KNO_3 working standard solution (1 ml = 10 µg NO_2) to a series of five 100-ml volumetric flasks. To each flask, add 5 ml of absorbing solution. Dilute to the mark with water. The resulting solutions contain 0.0, 50, 100, 150, and 200 µg NO_2, respectively. Measure the absorbance by ultraviolet spectrophotometry at 210 nm, using the blank as a zero reference. Prepare a standard curve plotting absorbance vs. µg NO_2.

NOTE: If other than a 20-ml aliquot of sample is used for analysis, then the amount of absorbing solution in the blank and standards must be adjusted such that the same amount of absorbing solution is in the blank and standards as is in the aliquot of sample used.

10.1.1 Calculate the spectrophotometer calibration factor as follows:

$$K_c = \frac{\sum_{i=1}^{n} M_i A_i}{\sum_{i=1}^{n} A_i^2} \qquad \text{Eq. 7B-1}$$

Where:

Mi = Mass of NO_2 in standard i, µg.
Ai = Absorbance of NO_2 standard i.
n = Total number of calibration standards.

10.1.2 For the set of calibration standards specified here, Equation 7B–1 simplifies to the following:

$$K_c = 50\frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2} \qquad \text{Eq. 7B-2}$$

10.2 Spectrophotometer Calibration Quality Control. Multiply the absorbance value obtained for each standard by the K_c factor (reciprocal of the least squares slope) to determine the distance each calibration point lies from the theoretical calibration line. The difference between the calculated concentration values and the actual concentrations (*i.e.*, 50, 100, 150, and 200 µg NO_2) should be less than 7 percent for all standards.

11.0 Analytical Procedures

11.1 Sample Loss Check. Note the level of the liquid in the container, and confirm whether any sample was lost during shipment. Note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Preparation. Immediately prior to analysis, transfer the contents of the shipping container to a 100-ml volumetric flask, and rinse the container twice with 5-ml portions of water. Add the rinse water to the flask, and dilute to mark with water.

11.3 Sample Analysis. Mix the contents of the flask thoroughly and pipette a 20 ml-aliquot of sample into a 100-ml volumetric flask. Dilute to the mark with water. Using the blank as zero reference, read the absorbance of the sample at 210 nm.

11.4 Audit Sample Analysis. Same as Method 7, section 11.4, except that a set of audit samples must be analyzed with each set of compliance samples or once per analysis day, or once per week when averaging continuous samples.

12.0 Data Analysis and Calculations

Same as Method 7, section 12.0, except replace section 12.3 with the following:

12.1 Total µg NO_2 Per Sample.

$$m = 5\,K_c\,A\,F \qquad \text{Eq. 7B-3}$$

Where:

5 = 100/20, the aliquot factor.

NOTE: If other than a 20-ml aliquot is used for analysis, the factor 5 must be replaced by a corresponding factor.

13.0 Method Performance

13.1 Range. The analytical range of the method as outlined has been determined to be 57 to 1500 milligrams NO_X (as NO_2) per dry standard cubic meter, or 30 to 786 parts per million by volume (ppmv) NO_X.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. National Institute for Occupational Safety and Health. Recommendations for Occupational Exposure to Nitric Acid. In: Occupational Safety and Health Reporter. Washington, D.C. Bureau of National Affairs, Inc. 1976. p. 149.

2. Rennie, P.J., A.M. Sumner, and F.B. Basketter. Determination of Nitrate in Raw, Potable, and Waste Waters by Ultraviolet Spectrophotometry. Analyst. *104*:837. September 1979.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 7C—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ALKALINE PERMANGANATE/COLORIMETRIC METHOD)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 3, Method 6 and Method 7.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS no.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–07	ppmv

1.2 Applicability. This method applies to the measurement of NO_X emissions from fossil-fuel fired steam generators, electric utility plants, nitric acid plants, or other sources as specified in the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

An integrated gas sample is extracted from the stack and passed through impingers containing an alkaline potassium permanganate solution; NO_X (NO + NO_2) emissions are oxidized to NO_2 and NO_3. Then NO_3^- is reduced to NO_2^- with cadmium, and the NO_2^- is analyzed colorimetrically.

3.0 Definitions [Reserved]

4.0 Interferences

Possible interferents are sulfur dioxides (SO_2) and ammonia (NH_3).

4.1 High concentrations of SO_2 could interfere because SO_2 consumes MnO_4 (as does NO_X) and, therefore, could reduce the NO_X collection efficiency. However, when sampling emissions from a coal-fired electric utility plant burning 2.1 percent sulfur coal with no control of SO_2 emissions, collection efficiency was not reduced. In fact, calculations show that sampling 3000 ppm SO_2 will reduce the MnO_4 concentration by only 5 percent if all the SO_2 is consumed in the first impinger.

4.2 Ammonia (NH_3) is slowly oxidized to NO_3^- by the absorbing solution. At 100 ppm NH_3 in the gas stream, an interference of 6 ppm NO_X (11 mg NO_2/m^3) was observed when the sample was analyzed 10 days after collection. Therefore, the method may not be applicable to plants using NH_3 injection to control NO_X emissions unless means are taken to correct the results. An equation has been developed to allow quantification of the interference and is discussed in Reference 5 of section 16.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrochloric Acid (HCl). Highly toxic and corrosive. Causes severe damage to skin. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to vapor concentrations of 0.13 to 0.2 percent can be lethal in minutes. Will react with metals, producing hydrogen.

5.2.2 Oxalic Acid $(COOH)_2$. Poisonous. Irritating to eyes, skin, nose, and throat.

5.2.3 Sodium Hydroxide (NaOH). Causes severe damage to eye tissues and to skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with small amounts of water.

5.2.4 Potassium Permanganate ($KMnO_4$). Caustic, strong oxidizer. Avoid bodily contact with.

6.0 Equipment and Supplies

6.1 Sample Collection and Sample Recovery. A schematic of the Method 7C sampling train is shown in Figure 7C–1, and component parts are discussed below. Alternative apparatus and procedures are allowed provided acceptable accuracy and precision can be demonstrated to the satisfaction of the Administrator.

6.1.1 Probe. Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or heated out-of-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Stainless steel or Teflon tubing may also be used for the probe.

6.1.2 Impingers. Three restricted-orifice glass impingers, having the specifications given in Figure 7C–2, are required for each sampling train. The impingers must be connected in series with leak-free glass connectors. Stopcock grease may be used, if necessary, to prevent leakage. (The impingers can be fabricated by a glass blower if not available commercially.)

6.1.3 Glass Wool, Stopcock Grease, Drying Tube, Valve, Pump, Barometer, and Vacuum Gauge and Rotameter. Same as in Method 6, sections 6.1.1.3, 6.1.1.4, 6.1.1.6, 6.1.1.7, 6.1.1.8, 6.1.2, and 6.1.3, respectively.

6.1.4 Rate Meter. Rotameter, or equivalent, accurate to within 2 percent at the selected flow rate of between 400 and 500 ml/min (0.014 to 0.018 cfm). For rotameters, a range of 0 to 1 liter/min (0 to 0.035 cfm) is recommended.

6.1.5 Volume Meter. Dry gas meter (DGM) capable of measuring the sample volume under the sampling conditions of 400 to 500 ml/min (0.014 to 0.018 cfm) for 60 minutes within an accuracy of 2 percent.

6.1.6 Filter. To remove NO_X from ambient air, prepared by adding 20 g of 5-angstrom molecular sieve to a cylindrical tube (*e.g.*, a polyethylene drying tube).

6.1.7 Polyethylene Bottles. 1-liter, for sample recovery.

6.1.8 Funnel and Stirring Rods. For sample recovery.

6.2 Sample Preparation and Analysis.

6.2.1 Hot Plate. Stirring type with 50- by 10-mm Teflon-coated stirring bars.

6.2.2 Beakers. 400-, 600-, and 1000-ml capacities.

6.2.3 Filtering Flask. 500-ml capacity with side arm.

6.2.4 Buchner Funnel. 75-mm ID, with spout equipped with a 13-mm ID by 90-mm long piece of Teflon tubing to minimize possibility of aspirating sample solution during filtration.

6.2.5 Filter Paper. Whatman GF/C, 7.0-cm diameter.

6.2.6 Stirring Rods.

6.2.7 Volumetric Flasks. 100-, 200- or 250-, 500-, and 1000-ml capacity.

6.2.8 Watch Glasses. To cover 600- and 1000-ml beakers.

6.2.9 Graduated Cylinders. 50- and 250-ml capacities.

6.2.10 Pipettes. Class A.

6.2.11 pH Meter. To measure pH from 0.5 to 12.0.

6.2.12 Burette. 50-ml with a micrometer type stopcock. (The stopcock is Catalog No. 8225–t–05, Ace Glass, Inc., Post Office Box 996, Louisville, Kentucky 50201.) Place a glass wool plug in bottom of burette. Cut off burette at a height of 43 cm (17 in.) from the top of plug, and have a blower attach a glass funnel to top of burette such that the diameter of the burette remains essentially unchanged. Other means of attaching the funnel are acceptable.

6.2.13 Glass Funnel. 75-mm ID at the top.

6.2.14 Spectrophotometer. Capable of measuring absorbance at 540 nm; 1-cm cells are adequate.

6.2.15 Metal Thermometers. Bimetallic thermometers, range 0 to 150 °C (32 to 300 °F).

6.2.16 Culture Tubes. 20-by 150-mm, Kimax No. 45048.

6.2.17 Parafilm ''M.'' Obtained from American Can Company, Greenwich, Connecticut 06830.

6.2.18 CO_2 Measurement Equipment. Same as in Method 3, section 6.0.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection.

7.1.1 Water. Deionized distilled to conform to ASTM Specification D 1193–77 or 91 Type 3 (incorporated by reference—see § 60.17).

7.1.2 Potassium Permanganate, 4.0 Percent (w/w), Sodium Hydroxide, 2.0 Percent (w/w) solution ($KMnO_4$/NaOH solution). Dissolve 40.0 g of $KMnO_4$ and 20.0 g of NaOH in 940 ml of water.

7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in section 7.1.1.

7.2.2 Oxalic Acid Solution. Dissolve 48 g of oxalic acid [$(COOH)_2 \cdot 2H_2O$] in water, and dilute to 500 ml. Do not heat the solution.

7.2.3 Sodium Hydroxide, 0.5 N. Dissolve 20 g of NaOH in water, and dilute to 1 liter.

7.2.4 Sodium Hydroxide, 10 N. Dissolve 40 g of NaOH in water, and dilute to 100 ml.

7.2.5 Ethylenediamine Tetraacetic Acid (EDTA) Solution, 6.5 percent (w/v). Dissolve 6.5 g of EDTA (disodium salt) in water, and dilute to 100 ml. Dissolution is best accomplished by using a magnetic stirrer.

7.2.6 Column Rinse Solution. Add 20 ml of 6.5 percent EDTA solution to 960 ml of water, and adjust the pH to between 11.7 and 12.0 with 0.5 N NaOH.

7.2.7 Hydrochloric Acid (HCl), 2 N. Add 86 ml of concentrated HCl to a 500 ml-volumetric flask containing water, dilute to volume, and mix well. Store in a glass-stoppered bottle.

7.2.8 Sulfanilamide Solution. Add 20 g of sulfanilamide (melting point 165 to 167 °C (329 to 333 °F)) to 700 ml of water. Add, with mixing, 50 ml concentrated phosphoric acid (85 percent), and dilute to 1000 ml. This solution is stable for at least 1 month, if refrigerated.

7.2.9 N-(1-Naphthyl)-Ethylenediamine Dihydrochloride (NEDA) Solution. Dissolve 0.5 g of NEDA in 500 ml of water. An aqueous solution should have one absorption peak at 320 nm over the range of 260 to 400 nm. NEDA that shows more than one absorption peak over this range is impure and should not be used. This solution is stable for at least 1 month if protected from light and refrigerated.

7.2.10 Cadmium. Obtained from Matheson Coleman and Bell, 2909 Highland Avenue, Norwood, Ohio 45212, as EM Laboratories Catalog No. 2001. Prepare by rinsing in 2 N HCl for 5 minutes until the color is silver-grey. Then rinse the cadmium with water until the rinsings are neutral when tested with pH paper. CAUTION: H_2 is liberated during preparation. Prepare in an exhaust hood away from any flame or combustion source.

7.2.11 Sodium Sulfite ($NaNO_2$) Standard Solution, Nominal Concentration, 1000 μg NO_2^-/ml. Desiccate NaNO2 overnight. Accurately weigh 1.4 to 1.6 g of $NaNO_2$ (assay of 97 percent $NaNO_2$ or greater), dissolve in water, and dilute to 1 liter. Calculate the exact NO_2^- concentration using Equation 7C–1 in section 12.2. This solution is stable for at least 6 months under laboratory conditions.

7.2.12 Potassium Nitrate (KNO_3) Standard Solution. Dry KNO_3 at 110 °C (230 °F) for 2 hours, and cool in a desiccator. Accurately weigh 9 to 10 g of KNO_3 to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact NO_3^- concentration using Equation 7C–2 in section 12.3. This solution is stable for 2 months without preservative under laboratory conditions.

7.2.13 Spiking Solution. Pipette 7 ml of the KNO_3 standard into a 100-ml volumetric flask, and dilute to volume.

7.2.14 Blank Solution. Dissolve 2.4 g of $KMnO_4$ and 1.2 g of NaOH in 96 ml of water. Alternatively, dilute 60 ml of $KMnO_4$/NaOH solution to 100 ml.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Preparation of Sampling Train. Add 200 ml of $KMnO_4$/NaOH solution (Section 7.1.2) to each of three impingers, and assemble the train as shown in Figure 7C–1. Adjust the probe heater to a temperature sufficient to prevent water condensation.

8.2 Leak-Checks. Same as in Method 6, section 8.2.

8.3 Sample Collection.

8.3.1 Record the initial DGM reading and barometric pressure. Determine the sampling point or points according to the appropriate regulations (*e.g.*, §60.46(b)(5) of 40 CFR Part 60). Position the tip of the probe at the sampling point, connect the probe to the first impinger, and start the pump. Adjust the sample flow to a value between 400 and 500 ml/min (0.014 and 0.018 cfm). CAUTION: DO NOT EXCEED THESE FLOW RATES. Once adjusted, maintain a constant flow rate during the entire sampling run. Sample for 60 minutes. For relative accuracy (RA) testing of continuous emission monitors, the minimum sampling time is 1 hour, sampling 20 minutes at each traverse point.

NOTE: When the SO_2 concentration is greater than 1200 ppm, the sampling time may have to be reduced to 30 minutes to eliminate plugging of the impinger orifice with MnO_2. For RA tests with SO_2 greater than 1200 ppm, sample for 30 minutes (10 minutes at each point).

8.3.2 Record the DGM temperature, and check the flow rate at least every 5 minutes. At the conclusion of each run, turn off the pump, remove the probe from the stack, and record the final readings. Divide the sample volume by the sampling time to determine the average flow rate. Conduct the mandatory post-test leak-check. If a leak is found, void the test run, or use procedures acceptable to the Administrator to adjust the sample volume for the leakage.

8.4 CO_2 Measurement. During sampling, measure the CO_2 content of the stack gas near the sampling point using Method 3. The single-point grab sampling procedure is adequate, provided the measurements are made at least three times (near the start, midway, and before the end of a run), and the average CO_2 concentration is computed. The Orsat or Fyrite analyzer may be used for this analysis.

8.5 Sample Recovery. Disconnect the impingers. Pour the contents of the impingers into a 1-liter polyethylene bottle

using a funnel and a stirring rod (or other means) to prevent spillage. Complete the quantitative transfer by rinsing the impingers and connecting tubes with water until the rinsings are clear to light pink, and add the rinsings to the bottle. Mix the sample, and mark the solution level. Seal and identify the sample container.

9.0 Quality Control

Section	Quality control measure	Effect
8.2, 10.1–10.3	Sampling equipment leak-check and calibration.	Ensure accurate measurement of sample volume.
10.4	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards
11.3	Spiked sample analysis.	Ensure reduction efficiency of column.

10.0 Calibration and Standardizations

10.1 Volume Metering System. Same as Method 6, section 10.1. For detailed instructions on carrying out these calibrations, it is suggested that section 3.5.2 of Reference 4 of section 16.0 be consulted.

10.2 Temperature Sensors and Barometer. Same as in Method 6, sections 10.2 and 10.4, respectively.

10.3 Check of Rate Meter Calibration Accuracy (Optional). Disconnect the probe from the first impinger, and connect the filter. Start the pump, and adjust the rate meter to read between 400 and 500 ml/min (0.014 and 0.018 cfm). After the flow rate has stabilized, start measuring the volume sampled, as recorded by the dry gas meter and the sampling time. Collect enough volume to measure accurately the flow rate. Then calculate the flow rate. This average flow rate must be less than 500 ml/min (0.018 cfm) for the sample to be valid; therefore, it is recommended that the flow rate be checked as above prior to each test.

10.4 Spectrophotometer.

10.4.1 Dilute 5.0 ml of the $NaNO_2$ standard solution to 200 ml with water. This solution nominally contains 25 μg NO_2^-/ml. Use this solution to prepare calibration standards to cover the range of 0.25 to 3.00 μg NO_2^-/ml. Prepare a minimum of three standards each for the linear and slightly nonlinear (described below) range of the curve. Use pipettes for all additions.

10.4.2 Measure the absorbance of the standards and a water blank as instructed in section 11.5. Plot the net absorbance vs. μg NO_2^-/ml. Draw a smooth curve through the points. The curve should be linear up to an absorbance of approximately 1.2 with a slope of approximately 0.53 absorbance units/μg NO_2^-/ml. The curve should pass through the origin. The curve is slightly nonlinear from an absorbance of 1.2 to 1.6.

11.0 Analytical Procedures

11.1 Sample Stability. Collected samples are stable for at least four weeks; thus, analysis must occur within 4 weeks of collection.

11.2 Sample Preparation.

11.2.1 Prepare a cadmium reduction column as follows: Fill the burette with water. Add freshly prepared cadmium slowly, with tapping, until no further settling occurs. The height of the cadmium column should be 39 cm (15 in). When not in use, store the column under rinse solution.

NOTE: The column should not contain any bands of cadmium fines. This may occur if regenerated cadmium is used and will greatly reduce the column lifetime.

11.2.2 Note the level of liquid in the sample container, and determine whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume lost can be determined from the difference between initial and final solution levels, and this value can then be used to correct the analytical result. Quantitatively transfer the contents to a 1-liter volumetric flask, and dilute to volume.

11.2.3 Take a 100-ml aliquot of the sample and blank (unexposed $KMnO_4$/NaOH) solutions, and transfer to 400-ml beakers containing magnetic stirring bars. Using a pH meter, add concentrated H_2SO_4 with stirring until a pH of 0.7 is obtained. Allow the solutions to stand for 15 minutes. Cover the beakers with watch glasses, and bring the temperature of the solutions to 50 °C (122 °F). Keep the temperature below 60 °C (140 °F). Dissolve 4.8 g of oxalic acid in a minimum volume of water, approximately 50 ml, at room temperature. Do not heat the solution. Add this solution slowly, in increments, until the $KMnO_4$ solution becomes colorless. If the color is not completely removed, prepare some more of the above oxalic acid solution, and add until a colorless solution is obtained. Add an excess of oxalic acid by dissolving 1.6 g of oxalic acid in 50 ml of water, and add 6 ml of this solution to the colorless solution. If suspended matter is present, add concentrated H_2SO_4 until a clear solution is obtained.

11.2.4 Allow the samples to cool to near room temperature, being sure that the samples are still clear. Adjust the pH to between 11.7 and 12.0 with 10 N NaOH. Quantitatively transfer the mixture to a Buchner funnel containing GF/C filter paper, and filter the

precipitate. Filter the mixture into a 500-ml filtering flask. Wash the solid material four times with water. When filtration is complete, wash the Teflon tubing, quantitatively transfer the filtrate to a 500-ml volumetric flask, and dilute to volume. The samples are now ready for cadmium reduction. Pipette a 50-ml aliquot of the sample into a 150-ml beaker, and add a magnetic stirring bar. Pipette in 1.0 ml of 6.5 percent EDTA solution, and mix.

11.3 Determine the correct stopcock setting to establish a flow rate of 7 to 9 ml/min of column rinse solution through the cadmium reduction column. Use a 50-ml graduated cylinder to collect and measure the solution volume. After the last of the rinse solution has passed from the funnel into the burette, but before air entrapment can occur, start adding the sample, and collect it in a 250-ml graduated cylinder. Complete the quantitative transfer of the sample to the column as the sample passes through the column. After the last of the sample has passed from the funnel into the burette, start adding 60 ml of column rinse solution, and collect the rinse solution until the solution just disappears from the funnel. Quantitatively transfer the sample to a 200-ml volumetric flask (a 250-ml flask may be required), and dilute to volume. The samples are now ready for NO_2-analysis.

NOTE: Two spiked samples should be run with every group of samples passed through the column. To do this, prepare two additional 50-ml aliquots of the sample suspected to have the highest NO_2-concentration, and add 1 ml of the spiking solution to these aliquots. If the spike recovery or column efficiency (see section 12.2) is below 95 percent, prepare a new column, and repeat the cadmium reduction.

11.5 Sample Analysis. Pipette 10 ml of sample into a culture tube. Pipette in 10 ml of sulfanilamide solution and 1.4 ml of NEDA solution. Cover the culture tube with parafilm, and mix the solution. Prepare a blank in the same manner using the sample from treatment of the unexposed $KMnO_4$/NaOH solution. Also, prepare a calibration standard to check the slope of the calibration curve. After a 10-minute color development interval, measure the absorbance at 540 nm against water. Read μg NO_2^-/ml from the calibration curve. If the absorbance is greater than that of the highest calibration standard, use less than 10 ml of sample, and repeat the analysis. Determine the NO_2^-concentration using the calibration curve obtained in section 10.4.

NOTE: Some test tubes give a high blank NO_2^- value but culture tubes do not.

11.6 Audit Sample Analysis. Same as in Method 7, section 11.4.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature.

B = Analysis of blank, μg NO_2^-/ml.
C = Concentration of NO_X as NO_2, dry basis, mg/dsm³.
E = Column efficiency, dimensionless
$K_2 = 10^{-3}$ mg/μg.
m = Mass of NO_X, as NO_2, in sample, μg.
P_{bar} = Barometric pressure, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
s = Concentration of spiking solution, μg NO_3/ml.
S = Analysis of sample, μg NO_2^-/ml.
T_m = Average dry gas meter absolute temperature, °K.
T_{std} = Standard absolute temperature, 293 °K (528 °R).
$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).
V_m = Dry gas volume as measured by the dry gas meter, scm (scf).
x = Analysis of spiked sample, μg NO_2^-/ml.
X = Correction factor for CO_2 collection = $100/(100 - \%CO_2(V/V))$.
y = Analysis of unspiked sample, μg NO_2^-/ml.
Y = Dry gas meter calibration factor.
1.0 ppm NO = 1.247 mg NO/m³ at STP.
1.0 ppm NO_2 = 1.912 mg NO_2/m³ at STP.
1 ft³ = 2.832×10^{-2} m³.

12.2 NO_2 Concentration. Calculate the NO_2 concentration of the solution (see section 7.2.11) using the following equation:

$$\frac{\mu g\ NO_2^-}{ml} = g\ NaNO_2 \times \frac{purity,\ \%}{100} \times 10^3 \times \frac{46.01}{69.01} \qquad \text{Eq. 7C-1}$$

12.3 NO_3 Concentration. Calculate the NO_3 concentration of the KNO_3 solution (see section 7.2.12) using the following equation:

$$\frac{\mu g\ NO_3^-}{ml} = g\ KNO_3 \times \left(10^3\right) \times \frac{62.01}{101.10} \qquad \text{Eq. 7C-2}$$

12.4 Sample Volume, Dry Basis, Corrected to Standard Conditions.

$$V_{m(std)} = V_m\ X\ Y \frac{T_{std}}{T_m} \frac{P_{bar}}{P_{std}} \qquad \text{Eq. 7C-3}$$

$$= K_1\ X\ Y\ V_m \frac{P_{bar}}{T_m}$$

Where:

K_1 = 0.3855 °K/mm Hg for metric units.
K_1 = 17.65 °R/in. Hg for English units.

12.5 Efficiency of Cadmium Reduction Column. Calculate this value as follows:

$$E = \frac{200\ (x-y)}{1.0\ s\ \frac{46.01}{62.01}} = \frac{269.6\ (x-y)}{s} \qquad \text{Eq. 7C-4}$$

Where:

200 = Final volume of sample and blank after passing through the column, ml.
1.0 = Volume of spiking solution added, ml.
46.01=μg NO_2^-/μmole.
62.01=μg NO_3^-/μmole.

12.6 Total μg NO_2.

$$m = 200\left(\frac{500}{50}\right)\left(\frac{1000}{100}\right)\left(\frac{(S-B)}{E}\right) = \frac{(2\times10^4)(S-B)}{E} \qquad \text{Eq. 7C-5}$$

Where:

500 = Total volume of prepared sample, ml.
50 = Aliquot of prepared sample processed through cadmium column, ml.
100 = Aliquot of $KMnO_4$/NaOH solution, ml.
1000 = Total volume of $KMnO_4$/NaOH solution, ml.

12.7 Sample Concentration.

$$C = K_2 \frac{m}{V_{m(std)}} \qquad \text{Eq. 7C-6}$$

13.0 Method Performance

13.1 Precision. The intra-laboratory relative standard deviation for a single measurement is 2.8 and 2.9 percent at 201 and 268 ppm NO_X, respectively.

13.2 Bias. The method does not exhibit any bias relative to Method 7.

13.3 Range. The lower detectable limit is 13 mg NO_X/m^3, as NO_2 (7 ppm NO_X) when sampling at 500 ml/min for 1 hour. No upper limit has been established; however, when using the recommended sampling conditions, the method has been found to collect NO_X emissions quantitatively up to 1782 mg NO_X/m^3, as NO_2 (932 ppm NO_X).

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Margeson, J.H., W.J. Mitchell, J.C. Suggs, and M.R. Midgett. Integrated Sampling and Analysis Methods for Determining NO_X Emissions at Electric Utility Plants. U.S. Environmental Protection Agency, Research Triangle Park, NC. Journal of the Air Pollution Control Association. *32*:1210–1215. 1982.

2. Memorandum and attachment from J.H. Margeson, Source Branch, Quality Assurance Division, Environmental Monitoring Systems Laboratory, to The Record, EPA. March 30, 1983. NH_3 Interference in Methods 7C and 7D.

3. Margeson, J.H., J.C. Suggs, and M.R. Midgett. Reduction of Nitrate to Nitrite with Cadmium. Anal. Chem. *52*:1955–57. 1980.

4. Quality Assurance Handbook for Air Pollution Measurement Systems. Volume III—Stationary Source Specific Methods. U.S.

Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA–600/4–77–027b. August 1977.

5. Margeson, J.H., *et al.* An Integrated Method for Determining NO_X Emissions at Nitric Acid Plants. Analytical Chemistry. *47* (11):1801. 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

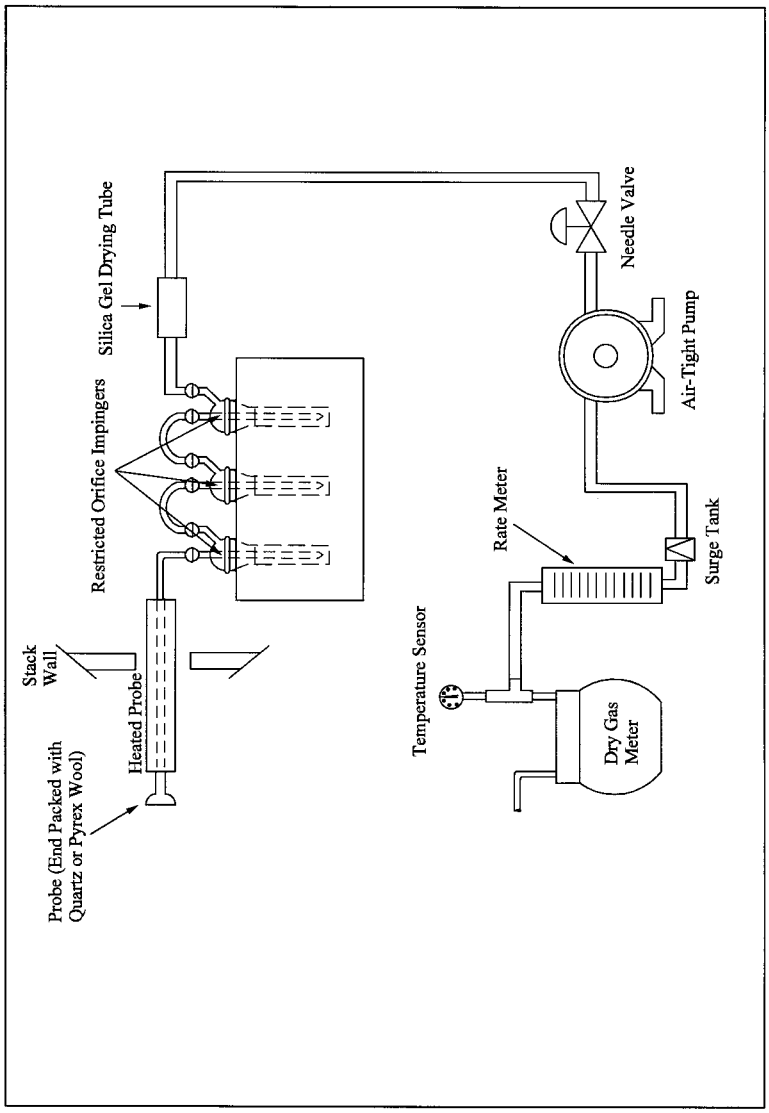

Figure 7C-1. NO_x Sampling Train.

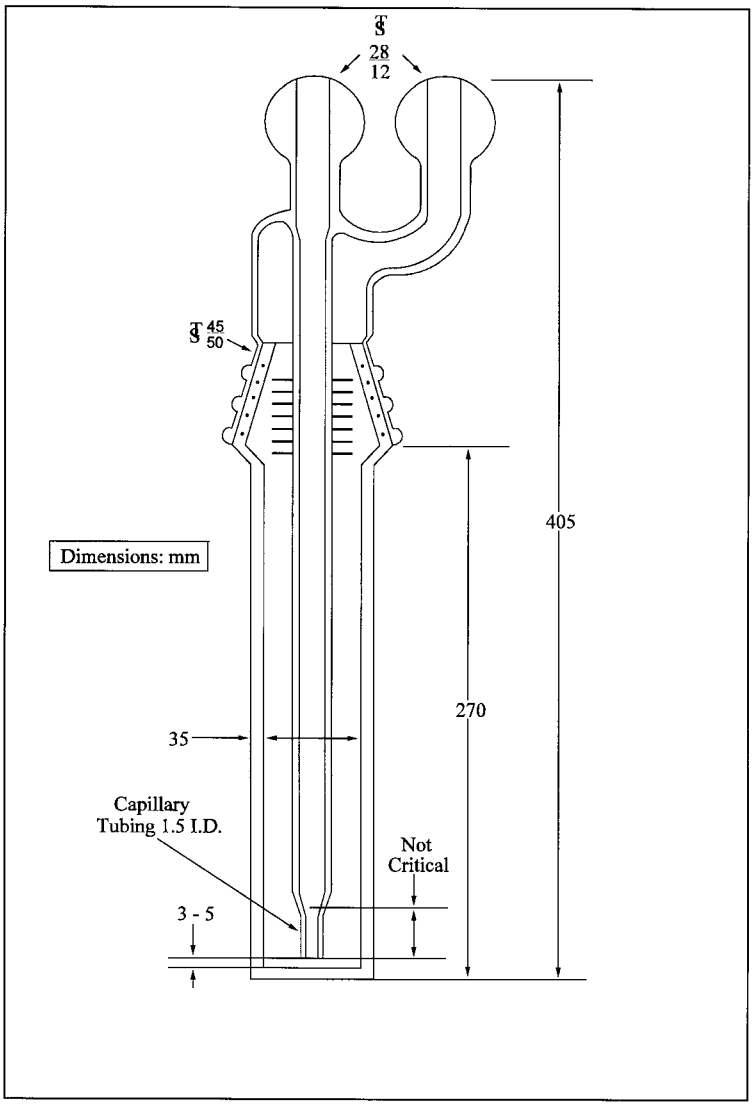

Figure 7C-2. Restricted-Orifice Impinger.

METHOD 7D—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ALKALINE-PERMANGANATE/ION CHROMATOGRAPHIC METHOD)

NOTE: This method is not inclusive with respect to specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 3, Method 6, Method 7, and Method 7C.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–0	7 ppmv

1.2 Applicability. This method applies to the measurement of NO_X emissions from fossil-fuel fired steam generators, electric utility plants, nitric acid plants, or other sources as specified in the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

An integrated gas sample is extracted from the stack and passed through impingers containing an alkaline-potassium permanganate solution; NO_X ($NO + NO_2$) emissions are oxidized to NO_3^-. Then NO_3^- is analyzed by ion chromatography.

3.0 Definitions [Reserved]

4.0 Interferences

Same as in Method 7C, section 4.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs. 30% H_2O_2 is a strong oxidizing agent; avoid contact with skin, eyes, and combustible material. Wear gloves when handling.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eye tissues and to skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Potassium Permanganate ($KMnO_4$). Caustic, strong oxidizer. Avoid bodily contact with.

6.0 Equipment and Supplies

6.1 Sample Collection and Sample Recovery. Same as Method 7C, section 6.1. A schematic of the sampling train used in performing this method is shown in Figure 7C–1 of Method 7C.

6.2 Sample Preparation and Analysis.

6.2.1 Magnetic Stirrer. With 25- by 10-mm Teflon-coated stirring bars.

6.2.2 Filtering Flask. 500-ml capacity with sidearm.

6.2.3 Buchner Funnel. 75-mm ID, with spout equipped with a 13-mm ID by 90-mm long piece of Teflon tubing to minimize possibility of aspirating sample solution during filtration.

6.2.4 Filter Paper. Whatman GF/C, 7.0-cm diameter.

6.2.5 Stirring Rods.

6.2.6 Volumetric Flask. 250-ml.

6.2.7 Pipettes. Class A.

6.2.8 Erlenmeyer Flasks. 250-ml.

6.2.9 Ion Chromatograph. Equipped with an anion separator column to separate NO_3^-, H_3^+ suppressor, and necessary auxiliary equipment. Nonsuppressed and other forms of ion chromatography may also be used provided that adequate resolution of NO_3^- is obtained. The system must also be able to resolve and detect NO_2^-.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection.

7.1.1 Water. Deionized distilled to conform to ASTM specification D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17).

7.1.2 Potassium Permanganate, 4.0 Percent (w/w), Sodium Hydroxide, 2.0 Percent (w/w). Dissolve 40.0 g of $KMnO_4$ and 20.0 g of NaOH in 940 ml of water.

7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in section 7.1.1.

7.2.2 Hydrogen Peroxide (H_2O_2), 5 Percent. Dilute 30 percent H_2O_2 1:5 (v/v) with water.

7.2.3 Blank Solution. Dissolve 2.4 g of $KMnO_4$ and 1.2 g of NaOH in 96 ml of water. Alternatively, dilute 60 ml of $KMnO_4$/NaOH solution to 100 ml.

7.2.4 KNO_3 Standard Solution. Dry KNO_3 at 110 °C for 2 hours, and cool in a desiccator. Accurately weigh 9 to 10 g of KNO_3 to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact NO_3^- concentration using Equation 7D–1 in section 12.2. This

solution is stable for 2 months without preservative under laboratory conditions.

7.2.5 Eluent, 0.003 M $NaHCO_3$/0.0024 M Na_2CO_3. Dissolve 1.008 g $NaHCO_3$ and 1.018 g Na_2CO_3 in water, and dilute to 4 liters. Other eluents capable of resolving nitrate ion from sulfate and other species present may be used.

8.0 Sample Collection, Preservation, Transport, and Storage.

8.1 Sampling. Same as in Method 7C, section 8.1.

8.2 Sample Recovery. Same as in Method 7C, section 8.2.

8.3 Sample Preparation for Analysis.

NOTE: Samples must be analyzed within 28 days of collection.

8.3.1 Note the level of liquid in the sample container, and determine whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume lost can be determined from the difference between initial and final solution levels, and this value can then be used to correct the analytical result. Quantitatively transfer the contents to a 1-liter volumetric flask, and dilute to volume.

8.3.2 Sample preparation can be started 36 hours after collection. This time is necessary to ensure that all NO_2^- is converted to NO_3^- in the collection solution. Take a 50-ml aliquot of the sample and blank, and transfer to 250-ml Erlenmeyer flasks. Add a magnetic stirring bar. Adjust the stirring rate to as fast a rate as possible without loss of solution. Add 5 percent H_2O_2 in increments of approximately 5 ml using a 5-ml pipette. When the $KMnO_4$ color appears to have been removed, allow the precipitate to settle, and examine the supernatant liquid. If the liquid is clear, the H_2O_2 addition is complete. If the $KMnO_4$ color persists, add more H_2O_2, with stirring, until the supernatant liquid is clear.

NOTE: The faster the stirring rate, the less volume of H_2O_2 that will be required to remove the $KMnO_4$.) Quantitatively transfer the mixture to a Buchner funnel containing GF/C filter paper, and filter the precipitate. The spout of the Buchner funnel should be equipped with a 13-mm ID by 90-mm long piece of Teflon tubing. This modification minimizes the possibility of aspirating sample solution during filtration. Filter the mixture into a 500-ml filtering flask. Wash the solid material four times with water. When filtration is complete, wash the Teflon tubing, quantitatively transfer the filtrate to a 250-ml volumetric flask, and dilute to volume. The sample and blank are now ready for NO_3^- analysis.

9.0 Quality Control

Section	Quality control measure	Effect
8.2, 10.1–10.3	Sampling equipment leak-check and calibration.	Ensure accurate measurement of sample volume.
10.4	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.
11.3	Spiked sample analysis	Ensure reduction efficiency of column.

10.0 Calibration and Standardizations

10.1 Dry Gas Meter (DGM) System.

10.1.1 Initial Calibration. Same as in Method 6, section 10.1.1. For detailed instructions on carrying out this calibration, it is suggested that section 3.5.2 of Citation 4 in section 16.0 of Method 7C be consulted.

10.1.2 Post-Test Calibration Check. Same as in Method 6, section 10.1.2.

10.2 Thermometers for DGM and Barometer. Same as in Method 6, sections 10.2 and 10.4, respectively.

10.3 Ion Chromatograph.

10.3.1 Dilute a given volume (1.0 ml or greater) of the KNO_3 standard solution to a convenient volume with water, and use this solution to prepare calibration standards. Prepare at least four standards to cover the range of the samples being analyzed. Use pipettes for all additions. Run standards as instructed in section 11.2. Determine peak height or area, and plot the individual values versus concentration in µg NO_3^-/ml.

10.3.2 Do not force the curve through zero. Draw a smooth curve through the points. The curve should be linear. With the linear curve, use linear regression to determine the calibration equation.

11.0 Analytical Procedures

11.1 The following chromatographic conditions are recommended: 0.003 M $NaHCO_3$/0.0024 Na_2CO_3 eluent solution (Section 7.2.5), full scale range, 3 µMHO; sample loop, 0.5 ml; flow rate, 2.5 ml/min. These conditions should give a NO_3^- retention time of approximately 15 minutes (Figure 7D–1).

11.2 Establish a stable baseline. Inject a sample of water, and determine whether any NO_3^- appears in the chromatogram. If NO_3^- is present, repeat the water load/injection procedure approximately five times; then reinject a water sample and observe the chromatogram. When no NO_3^- is present, the instrument is ready for use. Inject calibration standards. Then inject samples and a blank. Repeat the injection of the calibration

standards (to compensate for any drift in response of the instrument). Measure the NO_3^- peak height or peak area, and determine the sample concentration from the calibration curve.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature. Same as in Method 7C, section 12.1.

12.2 NO_3^- concentration. Calculate the NO_3^- concentration in the KNO_3 standard solution (see section 7.2.4) using the following equation:

$$\frac{\mu g\ NO_3^-}{ml} = g\ of\ KNO_3 \times 10^3 \times \frac{62.01}{101.10} \qquad \text{Eq. 7D-1}$$

12.3 Sample Volume, Dry Basis, Corrected to Standard Conditions. Same as in Method 7C, section 12.4.

12.4 Total μg NO_2 Per Sample.

$$m = 250\left(\frac{1000}{50}\right)\left(\frac{46.01}{62.01}\right)(S-B) \qquad \text{Eq. 7D-2}$$
$$= 3710\ (S-B)$$

Where:

250 = Volume of prepared sample, ml.

1000 = Total volume of $KMnO_4$ solution, ml.

50 = Aliquot of $KMnO_4$/NaOH solution, ml.

46.01 = Molecular weight of NO_3^-.

62.01 = Molecular weight of NO_3^-.

12.5 Sample Concentration. Same as in Method 7C, section 12.7.

13.0 Method Performance

13.1 Precision. The intra-laboratory relative standard deviation for a single measurement is approximately 6 percent at 200 to 270 ppm NO_X.

13.2 Bias. The method does not exhibit any bias relative to Method 7.

13.3 Range. The lower detectable limit is similar to that of Method 7C. No upper limit has been established; however, when using the recommended sampling conditions, the method has been found to collect NO_X emissions quantitatively up to 1782 mg NO_X/m^3, as NO_2 (932 ppm NO_X).

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 7C, section 16.0, References 1, 2, 4, and 5.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

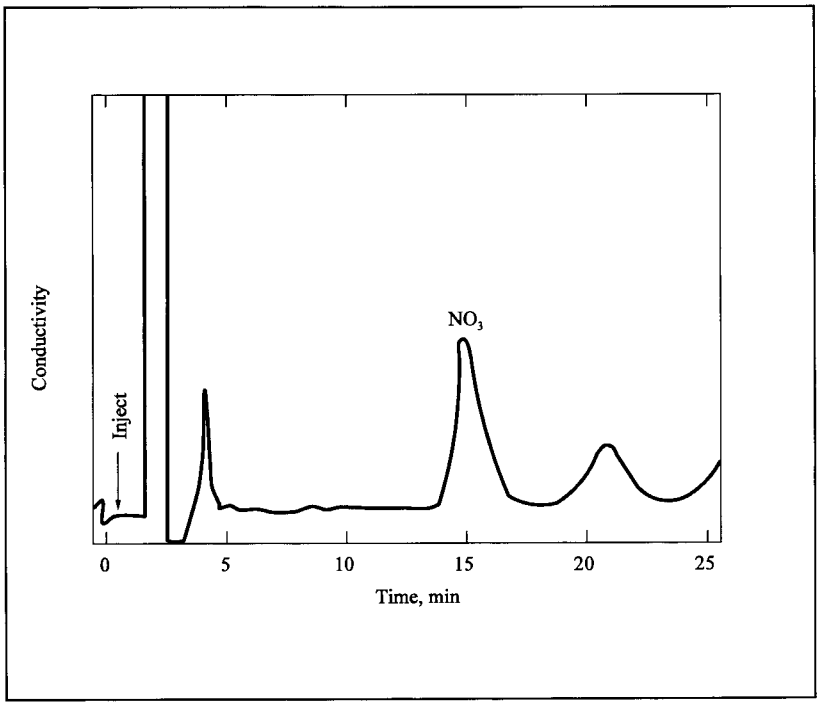

Figure 7D-1. Ion Chromatograph of a Prepared Sample.

METHOD 7E—DETERMINATION OF NITROGEN OXIDES EMISSIONS FROM STATIONARY SOURCES (INSTRUMENTAL ANALYZER PROCEDURE)

1.0 Scope and Application

What is Method 7E?

Method 7E is a procedure for measuring nitrogen oxides (NO_X) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis. This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 4—Determination of Moisture Content in Stack Gases.

1.1 Analytes. What does this method determine? This method measures the concentration of nitrogen oxides as NO_2.

Analyte	CAS No.	Sensitivity
Nitric oxide (NO)	10102–43–9	Typically <2% of
Nitrogen dioxide (NO_2)	10102–44–0	Calibration Span.

1.2 Applicability. When is this method required? The use of Method 7E may be required by specific New Source Performance Standards, Clean Air Marketing rules, State Implementation Plans, and permits where measurement of NO_X concentrations in stationary source emissions is required, either to determine compliance with an applicable

emissions standard or to conduct performance testing of a continuous monitoring system (CEMS). Other regulations may also require the use of Method 7E.

1.3 Data Quality Objectives (DQO). How good must my collected data be? Method 7E is designed to provide high-quality data for determining compliance with Federal and State emission standards and for relative accuracy testing of CEMS. In these and other applications, the principal objective is to ensure the accuracy of the data at the actual emission levels encountered. To meet this objective, the use of EPA traceability protocol calibration gases and measurement system performance tests are required.

1.4 Data Quality Assessment for Low Emitters. Is performance relief granted when testing low-emission units? Yes. For low-emitting sources, there are alternative performance specifications for analyzer calibration error, system bias, drift, and response time. Also, the alternative dynamic spiking procedure in section 16 may provide performance relief for certain low-emitting units.

2.0 Summary of Method

In this method, a sample of the effluent gas is continuously sampled and conveyed to the analyzer for measuring the concentration of NO_X. You may measure NO and NO_2 separately or simultaneously together but, for the purposes of this method, NO_X is the sum of NO and NO_2. You must meet the performance requirements of this method to validate your data.

3.0 Definitions

3.1 Analyzer Calibration Error, for non-dilution systems, means the difference between the manufacturer certified concentration of a calibration gas and the measured concentration of the same gas when it is introduced into the analyzer in direct calibration mode.

3.2 Calibration Curve means the relationship between an analyzer's response to the injection of a series of calibration gases and the actual concentrations of those gases.

3.3 Calibration Gas means the gas mixture containing NO_X at a known concentration and produced and certified in accordance with ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards,'' September 1997, as amended August 25, 1999, EPA–600/R–97/121 or more recent updates. The tests for analyzer calibration error, drift, and system bias require the use of calibration gas prepared according to this protocol. If a zero gas is used for the low-level gas, it must meet the requirements under the definition for ''zero air material'' in 40 CFR 72.2 in place of being prepared by the traceability protocol.

3.3.1 Low-Level Gas means a calibration gas with a concentration that is less than 20 percent of the calibration span and may be a zero gas.

3.3.2 Mid-Level Gas means a calibration gas with a concentration that is 40 to 60 percent of the calibration span.

3.3.3 High-Level Gas means a calibration gas with a concentration that is equal to the calibration span.

3.4 Calibration Span means the upper limit of the analyzer's calibration that is set by the choice of high-level calibration gas. No valid run average concentration may exceed the calibration span. To the extent practicable, the measured emissions should be between 20 to 100 percent of the selected calibration span. This may not be practicable in some cases of low-concentration measurements or testing for compliance with an emission limit when emissions are substantially less than the limit. In such cases, calibration spans that are practicable to achieving the data quality objectives without being excessively high should be chosen.

3.5 Centroidal Area means the central area of the stack or duct that is no greater than 1 percent of the stack or duct cross section. This area has the same geometric shape as the stack or duct.

3.6 Converter Efficiency Gas means a calibration gas with a known NO or NO_2 concentration and of Traceability Protocol quality.

3.7 Data Recorder means the equipment that permanently records the concentrations reported by the analyzer.

3.8 Direct Calibration Mode means introducing the calibration gases directly into the analyzer (or into the assembled measurement system at a point downstream of all sample conditioning equipment) according to manufacturer's recommended calibration procedure. This mode of calibration applies to non-dilution-type measurement systems.

3.9 Drift means the difference between the pre- and post-run system bias (or system calibration error) checks at a specific calibration gas concentration level (*i.e.* low-, mid- or high-).

3.10 Gas Analyzer means the equipment that senses the gas being measured and generates an output proportional to its concentration.

3.11 Interference Check means the test to detect analyzer responses to compounds other than the compound of interest, usually a gas present in the measured gas stream, that is not adequately accounted for in the calibration procedure and may cause measurement bias.

3.12 Low-Concentration Analyzer means any analyzer that operates with a calibration span of 20 ppm NO_X or lower. Each analyzer model used routinely to measure low NO_X concentrations must pass a manufacturer's stability test (MST). An MST subjects the analyzer to a range of line voltages and temperatures that reflect potential field conditions to demonstrate its stability following

procedures similar to those provided in 40 CFR 53.23. Ambient-level analyzers are exempt from the MST requirements of section 16.3. A copy of this information must be included in each test report. Table 7E–5 lists the criteria to be met.

3.13 Measurement System means all of the equipment used to determine the NO_x concentration. The measurement system comprises six major subsystems: Sample acquisition, sample transport, sample conditioning, calibration gas manifold, gas analyzer, and data recorder.

3.14 Response Time means the time it takes the measurement system to respond to a change in gas concentration occurring at the sampling point when the system is operating normally at its target sample flow rate or dilution ratio.

3.15 Run means a series of gas samples taken successively from the stack or duct. A test normally consists of a specific number of runs.

3.16 System Bias means the difference between a calibration gas measured in direct calibration mode and in system calibration mode. System bias is determined before and after each run at the low- and mid- or high-concentration levels. For dilution-type systems, pre- and post-run system calibration error is measured rather than system bias.

3.17 System Calibration Error applies to dilution-type systems and means the difference between the measured concentration of low-, mid-, or high-level calibration gas and the certified concentration for each gas when introduced in system calibration mode. For dilution-type systems, a 3-point system calibration error test is conducted in lieu of the analyzer calibration error test, and 2-point system calibration error tests are conducted in lieu of system bias tests.

3.18 System Calibration Mode means introducing the calibration gases into the measurement system at the probe, upstream of the filter and all sample conditioning components.

3.19 Test refers to the series of runs required by the applicable regulation.

4.0 Interferences

Note that interferences may vary among instruments and that instrument-specific interferences must be evaluated through the interference test.

5.0 Safety

What safety measures should I consider when using this method? This method may require you to work with hazardous materials and in hazardous conditions. We encourage you to establish safety procedures before using the method. Among other precautions, you should become familiar with the safety recommendations in the gas analyzer user's manual. Occupational Safety and Health Administration (OSHA) regulations concerning cylinder and noxious gases may apply. Nitric oxide and NO_2 are toxic and dangerous gases. Nitric oxide is immediately converted to NO_2 upon reaction with air. Nitrogen dioxide is a highly poisonous and insidious gas. Inflammation of the lungs from exposure may cause only slight pain or pass unnoticed, but the resulting edema several days later may cause death. A concentration of 100 ppm is dangerous for even a short exposure, and 200 ppm may be fatal. Calibration gases must be handled with utmost care and with adequate ventilation. Emission-level exposure to these gases should be avoided.

6.0 Equipment and Supplies

The performance criteria in this method will be met or exceeded if you are properly using equipment designed for this application.

6.1 What do I need for the measurement system? You may use any equipment and supplies meeting the following specifications:

(1) Sampling system components that are not evaluated in the system bias or system calibration error test must be glass, Teflon, or stainless steel. Other materials are potentially acceptable, subject to approval by the Administrator.

(2) The interference, calibration error, and system bias criteria must be met.

(3) Sample flow rate must be maintained within 10 percent of the flow rate at which the system response time was measured.

(4) All system components (excluding sample conditioning components, if used) must maintain the sample temperature above the moisture dew point. Ensure minimal contact between any condensate and the sample gas. Section 6.2 provides example equipment specifications for a NO_x measurement system. Figure 7E–1 is a diagram of an example dry-basis measurement system that is likely to meet the method requirements and is provided as guidance. For wet-basis systems, you may use alternative equipment and supplies as needed (some of which are described in Section 6.2), provided that the measurement system meets the applicable performance specifications of this method.

6.2 Measurement System Components

6.2.1 Sample Probe. Glass, stainless steel, or other approved material, of sufficient length to traverse the sample points.

6.2.2 Particulate Filter. An in-stack or out-of-stack filter. The filter must be made of material that is non-reactive to the gas being sampled. The filter media for out-of-stack filters must be included in the system bias test. The particulate filter requirement may be waived in applications where no significant particulate matter is expected (*e.g.*, for emission testing of a combustion turbine firing natural gas).

6.2.3 Sample Line. The sample line from the probe to the conditioning system/sample pump should be made of Teflon or other material that does not absorb or otherwise alter the sample gas. For a dry-basis measurement system (as shown in Figure 7E–1), the temperature of the sample line must be maintained at a sufficiently high level to prevent condensation before the sample conditioning components. For wet-basis measurement systems, the temperature of the sample line must be maintained at a sufficiently high level to prevent condensation before the analyzer.

6.2.4 Conditioning Equipment. For dry basis measurements, a condenser, dryer or other suitable device is required to remove moisture continuously from the sample gas. Any equipment needed to heat the probe or sample line to avoid condensation prior to the sample conditioning component is also required.

For wet basis systems, you must keep the sample above its dew point either by: (1) Heating the sample line and all sample transport components up to the inlet of the analyzer (and, for hot-wet extractive systems, also heating the analyzer) or (2) by diluting the sample prior to analysis using a dilution probe system. The components required to do either of the above are considered to be conditioning equipment.

6.2.5 Sampling Pump. For systems similar to the one shown in Figure 7E–1, a leak-free pump is needed to pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system. The pump may be constructed of any material that is non-reactive to the gas being sampled. For dilution-type measurement systems, an ejector pump (eductor) is used to create a vacuum that draws the sample through a critical orifice at a constant rate.

6.2.6 Calibration Gas Manifold. Prepare a system to allow the introduction of calibration gases either directly to the gas analyzer in direct calibration mode or into the measurement system, at the probe, in system calibration mode, or both, depending upon the type of system used. In system calibration mode, the system should be able to flood the sampling probe and vent excess gas. Alternatively, calibration gases may be introduced at the calibration valve following the probe. Maintain a constant pressure in the gas manifold. For in-stack dilution-type systems, a gas dilution subsystem is required to transport large volumes of purified air to the sample probe and a probe controller is needed to maintain the proper dilution ratio.

6.2.7 Sample Gas Manifold. For the type of system shown in Figure 7E–1, the sample gas manifold diverts a portion of the sample to the analyzer, delivering the remainder to the by-pass discharge vent. The manifold should also be able to introduce calibration gases directly to the analyzer (except for dilution-type systems). The manifold must be made of material that is non-reactive to the gas sampled or the calibration gas and be configured to safely discharge the bypass gas.

6.2.8 NO_X Analyzer. An instrument that continuously measures NO_X in the gas stream and meets the applicable specifications in section 13.0. An analyzer that operates on the principle of chemiluminescence with an NO_2 to NO converter is one example of an analyzer that has been used successfully in the past. Analyzers operating on other principles may also be used provided the performance criteria in section 13.0 are met.

6.2.8.1 Dual Range Analyzers. For certain applications, a wide range of gas concentrations may be encountered, necessitating the use of two measurement ranges. Dual-range analyzers are readily available for these applications. These analyzers are often equipped with automated range-switching capability, so that when readings exceed the full-scale of the low measurement range, they are recorded on the high range. As an alternative to using a dual-range analyzer, you may use two segments of a single, large measurement scale to serve as the low and high ranges. In all cases, when two ranges are used, you must quality-assure both ranges using the proper sets of calibration gases. You must also meet the interference, calibration error, system bias, and drift checks. However, we caution that when you use two segments of a large measurement scale for dual range purposes, it may be difficult to meet the performance specifications on the low range due to signal-to-noise ratio considerations.

6.2.8.2 Low Concentration Analyzer. When an analyzer is routinely calibrated with a calibration span of 20 ppmv or less, the manufacturer's stability test (MST) is required. See Table 7E–5 for test parameters.

6.2.9 Data Recording. A strip chart recorder, computerized data acquisition system, digital recorder, or data logger for recording measurement data may be used.

7.0 Reagents and Standards

7.1 Calibration Gas. What calibration gases do I need? Your calibration gas must be NO in N_2 and certified (or recertified) within an uncertainty of 2.0 percent in accordance with ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards'' September 1997, as amended August 25, 1999, EPA–600/R–97/121. Blended gases meeting the Traceability Protocol are allowed if the additional gas components are shown not to interfere with the analysis. If a zero gas is used for the low-level gas, it must meet the requirements under the definition for ''zero air material'' in 40 CFR 72.2. The calibration gas must not be used after its expiration date. Except for applications under part 75 of

this chapter, it is acceptable to prepare calibration gas mixtures from EPA Traceability Protocol gases in accordance with Method 205 in appendix M to part 51 of this chapter. For part 75 applications, the use of Method 205 is subject to the approval of the Administrator. The goal and recommendation for selecting calibration gases is to bracket the sample concentrations. The following calibration gas concentrations are required:

7.1.1 *High-Level Gas.* This concentration is chosen to set the calibration span as defined in Section 3.4.

7.1.2 Mid-Level Gas. 40 to 60 percent of the calibration span.

7.1.3 Low-Level Gas. Less than 20 percent of the calibration span.

7.1.4 Converter Efficiency Gas. What reagents do I need for the converter efficiency test? The converter efficiency gas is a manufacturer-certified gas with a concentration sufficient to show NO_2 conversion at the concentrations encountered in the source. A test gas concentration in the 40 to 60 ppm range is suggested, but other concentrations may be more appropriate to specific sources. For the test described in section 8.2.4.1, NO_2 is required. For the alternative converter efficiency tests in section 16.2, NO is required.

7.2 Interference Check. What reagents do I need for the interference check? Use the appropriate test gases listed in Table 7E–3 or others not listed that can potentially interfere (as indicated by the test facility type, instrument manufacturer, etc.) to conduct the interference check. These gases should be manufacturer certified but do not have to be prepared by the EPA traceability protocol.

8.0 Sample Collection, Preservation, Storage, and Transport

Emission Test Procedure

Since you are allowed to choose different options to comply with some of the performance criteria, it is your responsibility to identify the specific options you have chosen, to document that the performance criteria for that option have been met, and to identify any deviations from the method.

8.1 What sampling site and sampling points do I select?

8.1.1 Unless otherwise specified in an applicable regulation or by the Administrator, when this method is used to determine compliance with an emission standard, conduct a stratification test as described in section 8.1.2 to determine the sampling traverse points to be used. For performance testing of continuous emission monitoring systems, follow the sampling site selection and traverse point layout procedures described in the appropriate performance specification or applicable regulation (e.g., Performance Specification 2 in appendix B to this part).

8.1.2 Determination of Stratification. Perform a stratification test at each test site to determine the appropriate number of sample traverse points. If testing for multiple pollutants or diluents at the same site, a stratification test using only one pollutant or diluent satisfies this requirement. A stratification test is not required for small stacks that are less than 4 inches in diameter. To test for stratification, use a probe of appropriate length to measure the NO_X (or pollutant of interest) concentration at 12 traverse points located according to Table 1–1 or Table 1–2 of Method 1. Alternatively, you may measure at three points on a line passing through the centroidal area. Space the three points at 16.7, 50.0, and 83.3 percent of the measurement line. Sample for a minimum of twice the system response time (see section 8.2.6) at each traverse point. Calculate the individual point and mean NO_X concentrations. If the concentration at each traverse point differs from the mean concentration for all traverse points by no more than: ±5.0 percent of the mean concentration; or ±0.5 ppm (whichever is less restrictive), the gas stream is considered unstratified, and you may collect samples from a single point that most closely matches the mean. If the 5.0 percent or 0.5 ppm criterion is not met, but the concentration at each traverse point differs from the mean concentration for all traverse points by not more than: ±10.0 percent of the mean concentration; or ±1.0 ppm (whichever is less restrictive), the gas stream is considered to be minimally stratified and you may take samples from three points. Space the three points at 16.7, 50.0, and 83.3 percent of the measurement line. Alternatively, if a 12-point stratification test was performed and the emissions were shown to be minimally stratified (all points within ± 10.0 percent of their mean or within ±1.0 ppm), and if the stack diameter (or equivalent diameter, for a rectangular stack or duct) is greater than 2.4 meters (7.8 ft), then you may use 3-point sampling and locate the three points along the measurement line exhibiting the highest average concentration during the stratification test at 0.4, 1.2 and 2.0 meters from the stack or duct wall. If the gas stream is found to be stratified because the 10.0 percent or 1.0 ppm criterion for a 3-point test is not met, locate 12 traverse points for the test in accordance with Table 1–1 or Table 1–2 of Method 1.

8.2 Initial Measurement System Performance Tests. What initial performance criteria must my system meet before I begin collecting samples? Before measuring emissions, perform the following procedures:

(a) Calibration gas verification,

(b) Measurement system preparation,

(c) Calibration error test,

(d) NO_2 to NO conversion efficiency test, if applicable,

(e) System bias check,

(f) System response time test, and

(g) Interference check

8.2.1 Calibration Gas Verification. How must I verify the concentrations of my calibration gases? Obtain a certificate from the gas manufacturer documenting the quality of the gas. Confirm that the manufacturer certification is complete and current. Ensure that your calibration gas certifications have not expired. This documentation should be available on-site for inspection. To the extent practicable, select a high-level gas concentration that will result in the measured emissions being between 20 and 100 percent of the calibration span.

8.2.2 Measurement System Preparation. How do I prepare my measurement system? Assemble, prepare, and precondition the measurement system according to your standard operating procedure. Adjust the system to achieve the correct sampling rate or dilution ratio (as applicable).

8.2.3 Calibration Error Test. How do I confirm my analyzer calibration is correct? After you have assembled, prepared and calibrated your sampling system and analyzer, you must conduct a 3-point analyzer calibration error test (or a 3-point system calibration error test for dilution systems) before the first run and again after any failed system bias test (or 2-point system calibration error test for dilution systems) or failed drift test. Introduce the low-, mid-, and high-level calibration gases sequentially. For non-dilution-type measurement systems, introduce the gases in direct calibration mode. For dilution-type measurement systems, introduce the gases in system calibration mode.

(1) For non-dilution systems, you may adjust the system to maintain the correct flow rate at the analyzer during the test, but you may not make adjustments for any other purpose. For dilution systems, you must operate the measurement system at the appropriate dilution ratio during all system calibration error checks, and may make only the adjustments necessary to maintain the proper ratio.

(2) Record the analyzer's response to each calibration gas on a form similar to Table 7E–1. For each calibration gas, calculate the analyzer calibration error using Equation 7E–1 in section 12.2 or the system calibration error using Equation 7E–3 in section 12.4 (as applicable). The calibration error specification in section 13.1 must be met for the low-, mid-, and high-level gases. If the calibration error specification is not met, take corrective action and repeat the test until an acceptable 3-point calibration is achieved.

8.2.4 NO_2 to NO Conversion Efficiency Test. Before or after each field test, you must conduct an NO_2 to NO conversion efficiency test if your system converts NO_2 to NO before analyzing for NO_X. You may risk testing multiple facilities before performing this test provided you pass this test at the conclusion of the final facility test. A failed final conversion efficiency test in this case will invalidate all tests performed subsequent to the test in which the converter efficiency test was passed. Follow the procedures in section 8.2.4.1, or 8.2.4.2. If desired, the converter efficiency factor derived from this test may be used to correct the test results for converter efficiency if the NO_2 fraction in the measured test gas is known. Use Equation 7E–8 in section 12.8 for this correction.

8.2.4.1 Introduce NO_2 converter efficiency gas to the analyzer in direct calibration mode and record the NO_X concentration displayed by the analyzer. Calculate the converter efficiency using Equation 7E–7 in section 12.7. The specification for converter efficiency in section 13.5 must be met. The user is cautioned that state-of-the-art NO_2 calibration gases may have limited shelf lives, and this could affect the ability to pass the 90-percent conversion efficiency requirement.

8.2.4.2 Alternatively, either of the procedures for determining conversion efficiency using NO in section 16.2 may be used.

8.2.5 Initial System Bias and System Calibration Error Checks. Before sampling begins, determine whether the high-level or mid-level calibration gas best approximates the emissions and use it as the upscale gas. Introduce the upscale gas at the probe upstream of all sample conditioning components in system calibration mode. Record the time it takes for the measured concentration to increase to a value that is at least 95 percent or within 0.5 ppm (whichever is less restrictive) of a stable response for both the low-level and upscale gases. Continue to observe the gas concentration reading until it has reached a final, stable value. Record this value on a form similar to Table 7E–2.

(1) Next, introduce the low-level gas in system calibration mode and record the time required for the concentration response to decrease to a value that is within 5.0 percent or 0.5 ppm (whichever is less restrictive) of the certified low-range gas concentration. If the low-level gas is a zero gas, use the procedures described above and observe the change in concentration until the response is 0.5 ppm or 5.0 percent of the upscale gas concentration (whichever is less restrictive).

(2) Continue to observe the low-level gas reading until it has reached a final, stable value and record the result on a form similar to Table 7E–2. Operate the measurement system at the normal sampling rate during all system bias checks. Make only the adjustments necessary to achieve proper calibration gas flow rates at the analyzer.

(3) From these data, calculate the measurement system response time (see section 8.2.6) and then calculate the initial system bias using Equation 7E–2 in section 12.3. For dilution systems, calculate the system calibration error in lieu of system bias using

equation 7E–3 in section 12.4. See section 13.2 for acceptable performance criteria for system bias and system calibration error. If the initial system bias (or system calibration error) specification is not met, take corrective action. Then, you must repeat the applicable calibration error test from section 8.2.3 and the initial system bias (or 2-point system calibration error) check until acceptable results are achieved, after which you may begin sampling.

(NOTE: For dilution-type systems, data from the 3-point system calibration error test described in section 8.2.3 may be used to meet the initial 2-point system calibration error test requirement of this section, if the calibration gases were injected as described in this section, and if response time data were recorded).

8.2.6 Measurement System Response Time. As described in section 8.2.5, you must determine the measurement system response time during the initial system bias (or 2-point system calibration error) check. Observe the times required to achieve 95 percent of a stable response for both the low-level and upscale gases. The longer interval is the response time.

8.2.7 Interference Check. Conduct an interference response test of the gas analyzer prior to its initial use in the field. If you have multiple analyzers of the same make and model, you need only perform this alternative interference check on one analyzer. You may also meet the interference check requirement if the instrument manufacturer performs this or a similar check on an analyzer of the same make and model of the analyzer that you use and provides you with documented results.

(1) You may introduce the appropriate interference test gases (that are potentially encountered during a test; see examples in Table 7E–3) into the analyzer separately or as mixtures. Test the analyzer with the interference gas alone at the highest concentration expected at a test source and again with the interference gas and NO_X at a representative NO_X test concentration. For analyzers measuring NO_X greater than 20 ppm, use a calibration gas with a NO_X concentration of 80 to 100 ppm and set this concentration equal to the calibration span. For analyzers measuring less than 20 ppm NO_X, select an NO concentration for the calibration span that reflects the emission levels at the sources to be tested, and perform the interference check at that level. Measure the total interference response of the analyzer to these gases in ppmv. Record the responses and determine the interference using Table 7E–4. The specification in section 13.4 must be met.

(2) A copy of this data, including the date completed and signed certification, must be available for inspection at the test site and included with each test report. This interference test is valid for the life of the instrument unless major analytical components (*e.g.,* the detector) are replaced with different model parts. If major components are replaced with different model parts, the interference gas check must be repeated before returning the analyzer to service. If major components are replaced, the interference gas check must be repeated before returning the analyzer to service. The tester must ensure that any specific technology, equipment, or procedures that are intended to remove interference effects are operating properly during testing.

8.3 Dilution-Type Systems—Special Considerations. When a dilution-type measurement system is used, there are three important considerations that must be taken into account to ensure the quality of the emissions data. First, the critical orifice size and dilution ratio must be selected properly so that the sample dew point will be below the sample line and analyzer temperatures. Second, a high-quality, accurate probe controller must be used to maintain the dilution ratio during the test. The probe controller should be capable of monitoring the dilution air pressure, eductor vacuum, and sample flow rates. Third, differences between the molecular weight of calibration gas mixtures and the stack gas molecular weight must be addressed because these can affect the dilution ratio and introduce measurement bias.

8.4 Sample Collection.

(1) Position the probe at the first sampling point. Purge the system for at least two times the response time before recording any data. Then, traverse all required sampling points, sampling at each point for an equal length of time and maintaining the appropriate sample flow rate or dilution ratio (as applicable). You must record at least one valid data point per minute during the test run.

(2) Each time the probe is removed from the stack and replaced, you must recondition the sampling system for at least two times the system response time prior to your next recording. If the average of any run exceeds the calibration span value, that run is invalid.

(3) You may satisfy the multipoint traverse requirement by sampling sequentially using a single-hole probe or a multi-hole probe designed to sample at the prescribed points with a flow within 10 percent of mean flow rate. Notwithstanding, for applications under part 75 of this chapter, the use of multi-hole probes is subject to the approval of the Administrator.

8.5 Post-Run System Bias Check and Drift Assessment.

How do I confirm that each sample I collect is valid? After each run, repeat the system bias check or 2-point system calibration error check (for dilution systems) to validate

the run. Do not make adjustments to the measurement system (other than to maintain the target sampling rate or dilution ratio) between the end of the run and the completion of the post-run system bias or system calibration error check. Note that for all post-run system bias or 2-point system calibration error checks, you may inject the low-level gas first and the upscale gas last, or vice-versa. You may risk sampling for multiple runs before performing the post-run bias or system calibration error check provided you pass this test at the conclusion of the group of runs. A failed final test in this case will invalidate all runs subsequent to the last passed test.

(1) If you do not pass the post-run system bias (or system calibration error) check, then the run is invalid. You must diagnose and fix the problem and pass another calibration error test (Section 8.2.3) and system bias (or 2-point system calibration error) check (Section 8.2.5) before repeating the run. Record the system bias (or system calibration error) results on a form similar to Table 7E–2.

(2) After each run, calculate the low-level and upscale drift, using Equation 7E–4 in section 12.5. If the post-run low- and upscale bias (or 2-point system calibration error) checks are passed, but the low-or upscale drift exceeds the specification in section 13.3, the run data are valid, but a 3-point calibration error test and a system bias (or 2-point system calibration error) check must be performed and passed before any more test runs are done.

(3) For dilution systems, data from a 3-point system calibration error test may be used to met the pre-run 2-point system calibration error requirement for the first run in a test sequence. Also, the post-run bias (or 2-point calibration error) check data may be used as the pre-run data for the next run in the test sequence at the discretion of the tester.

8.6 Alternative Interference and System Bias Checks (Dynamic Spike Procedure). If I want to use the dynamic spike procedure to validate my data, what procedure should I follow? Except for applications under part 75 of this chapter, you may use the dynamic spiking procedure and requirements provided in section 16.1 during each test as an alternative to the interference check and the pre- and post-run system bias checks. The calibration error test is still required under this option. Use of the dynamic spiking procedure for Part 75 applications is subject to the approval of the Administrator.

8.7 Moisture correction. You must determine the moisture content of the flue gas and correct the measured gas concentrations to a dry basis using Method 4 or other appropriate methods, subject to the approval of the Administrator, when the moisture basis (wet or dry) of the measurements made with this method is different from the moisture basis of either: (1) The applicable emissions limit; or (2) the CEMS being evaluated for relative accuracy. Moisture correction is also required if the applicable limit is in lb/mmBtu and the moisture basis of the Method 7E NO_X analyzer is different from the moisture basis of the Method 3A diluent gas (CO_2 or O_2) analyzer.

9.0 Quality Control

What quality control measures must I take?

The following table is a summary of the mandatory, suggested, and alternative quality assurance and quality control measures and the associated frequency and acceptance criteria. All of the QC data, along with the sample run data, must be documented and included in the test report.

SUMMARY TABLE OF AQ/QC

Status	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
S	Identify Data User		Regulatory Agency or other primary end user of data.	Before designing test.
S	Analyzer Design	Analyzer resolution or sensitivity.	<2.0% of full-scale range	Manufacturer design.
M		Interference gas check.	Sum of responses ≤2.5% of calibration span Alternatively, sum of responses: ≤0.5 ppmv for calibration spans of 5 to 10 ppmv. ≤0.2 ppmv for calibration spans <5 ppmv. See Table 7E-3.	
M	Calibration Gases	Traceability protocol (G1, G2).	Valid certificate required Uncertainty ≤2.0% of tag value.	
M		High-level gas	Equal to the calibration span	Each test.
M		Mid-level gas	40 to 60% of calibration span	Each test.
M		Low-level gas	<20% of calibration span	Each test.
S	Data Recorder Design.	Data resolution	≤0.5% of full-scale range	Manufacturer design.
S	Sample Extraction	Probe material	SS or quartz if stack >500 °F	East test.
M	Sample Extraction	Probe, filter and sample line temperature.	For dry-basis analyzers, keep sample above the dew point by heating, prior to sample conditioning.	Each run.

SUMMARY TABLE OF AQ/QC—Continued

Status	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
			For wet-basis analyzers, keep sample above dew point at all times, by heating or dilution.	
S	Sample Extraction	Calibration valve material.	SS	Each test.
S	Sample Extraction	Sample pump material.	Inert to sample constituents	Each test.
S	Sample Extraction	Manifolding material	Inert to sample constituents	Each test.
S	Moisture Removal	Equipment efficiency	<5% target compound removal	Verified through system bias check.
S	Particulate Removal	Filter inertness	Pass system bias check	Each bias check.
M	Analyzer & Calibration Gas Performance.	Analyzer calibration error (of 3-point system calibration error for dilution systems).	Within ±2.0 percent of the calibration span of the analyzer for the low-, mid-, and high-level calibration gases. Alternative specification: ≤0.5 ppmv absolute difference.	Before initial run and after a failed system bias test or drift test.
M	System Performance	System bias (or pre- and post-run 2-point system calibration error for dilution (Systems).	Within ±5.0% of the analyzer calibration span for low-sacle and upscale calibration gases. Alternative specification: ≤0.5 ppmv absolute difference.	Before and after each run.
M	System Performance	System response time.	Determines minimum sampling time per point.	During initial sampling system bias test.
M	System Performance	Drift	≤3.0% of calibration span for low-level and mid- or high-level gases. Alternative specification: ≤0.5 ppmv absolute difference.	After each test run.
M	System Performance	NO_2-NO conversion efficiency.	≥90% of certified test gas concentration	Before or after each test.
M	System Performance	Purge time	≥2 times system response time	Before starting the first run and when probe is removed from and re-inserted into the stack.
M	System Performance	Minimum sample time at each point.	Two times the system response time	Each sample point.
M	System Performance	Stable sample flow rate (surrogate for maintaining system response time).	Within 10% of flow rate established during system response time check.	Each run.
M	Sample Point Selection.	Stratification test	All points within: ±5% of mean for 1-point sampling. ±10% of mean for 3-point. Alternatively, all points within: ±0.5 ppm of mean for 1-point sampling. ±1.0 ppm of mean for 3-point sampling.	Prior to first run.
A	Multiple sample points simultaneously.	No. of openings in probe.	Multi-hole probe with verifiable constant flow through all holes within 10% of mean flow rate (requires Administrative approval for Part 75).	Each run.
M	Data Recording	Frequency	≤1 minute average	During run.
S	Data Parameters	Sample concentration range.	All 1-minute averages within calibration span.	Each run.
M	Date Parameters	Average concentration for the run.	Run average ≤calibration span	Each run.

S = Suggest.
M = Mandatory.
A = Alternative.
Agency.

10.0 Calibration and Standardization

What measurement system calibrations are required?

(1) The initial 3-point calibration error test as described in section 8.2.3 and the system bias (or system calibration error) checks described in section 8.2.5 are required and must meet the specifications in section 13 before you start the test. Make all necessary adjustments to calibrate the gas analyzer and data recorder. Then, after the test commences, the system bias or system calibration error checks described in section 8.5 are required before and after each run. Your analyzer must be calibrated for all species of NO_X that it detects. Analyzers that measure NO and NO_2 separately without using a converter must be calibrated with both NO and NO_2.

(2) You must include a copy of the manufacturer's certification of the calibration gases used in the testing as part of the test report. This certification must include the 13 documentation requirements in the EPA Traceability Protocol For Assay and Certification of Gaseous Calibration Standards, September 1997, as amended August 25, 1999. When Method 205 is used to produce diluted calibration gases, you must document that the specifications for the gas dilution system are met for the test. You must also include the date of the most recent dilution system calibration against flow standards and the name of the person or manufacturer who carried out the calibration in the test report.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the procedures for calculations and data analysis listed in this section.

12.1 *Nomenclature.* The terms used in the equations are defined as follows:

ACE = Analyzer calibration error, percent of calibration span.

B_{WS} = Moisture content of sample gas as measured by Method 4 or other approved method, percent/100.

C_{Avg} = Average unadjusted gas concentration indicated by data recorder for the test run, ppmv.

C_D = Pollutant concentration adjusted to dry conditions, ppmv.

C_{Dir} = Measured concentration of a calibration gas (low, mid, or high) when introduced in direct calibration mode, ppmv.

C_{Gas} = Average effluent gas concentration adjusted for bias, ppmv.

C_M = Average of initial and final system calibration bias (or 2-point system calibration error) check responses for the upscale calibration gas, ppmv.

C_{MA} = Actual concentration of the upscale calibration gas, ppmv.

C_{Native} = NO_X concentration in the stack gas as calculated in section 12.6, ppmv.

C_O = Average of the initial and final system calibration bias (or 2-point system calibration error) check responses from the low-level (or zero) calibration gas, ppmv.

C_{OA} = Actual concentration of the low-level calibration gas, ppmv.

C_S = Measured concentration of a calibration gas (low, mid, or high) when introduced in system calibration mode, ppmv.

C_{SS} = Concentration of NO_X measured in the spiked sample, ppmv.

C_{Spike} = Concentration of NO_X in the undiluted spike gas, ppmv.

C_{Calc} = Calculated concentration of NO_X in the spike gas diluted in the sample, ppmv.

C_V = Manufacturer certified concentration of a calibration gas (low, mid, or high), ppmv.

C_W = Pollutant concentration measured under moist sample conditions, wet basis, ppmv.

CS = Calibration span, ppmv.

D = Drift assessment, percent of calibration span.

DF = Dilution system dilution factor or spike gas dilution factor, dimensionless.

Eff_{NO2} = NO_2 to NO converter efficiency, percent.

NO_{XCorr} = The NO_X concentration corrected for the converter efficiency, ppmv.

NOX_{Final} = The final NO_X concentration observed during the converter efficiency test in section 16.2.2, ppmv.

NO_{XPeak} = The highest NO_X concentration observed during the converter efficiency test in section 16.2.2, ppmv.

Q_{Spike} = Flow rate of spike gas introduced in system calibration mode, L/min.

Q_{Total} = Total sample flow rate during the spike test, L/min.

R = Spike recovery, percent.

SB = System bias, percent of calibration span.

SB_i = Pre-run system bias, percent of calibration span.

SB_{final} = Post-run system bias, percent of calibration span.

SCE = System calibration error, percent of calibration span.

SCE_i = Pre-run system calibration error, percent of calibration span.

SCE_{Final} = Post-run system calibration error, percent of calibration span.

12.2 Analyzer Calibration Error. For non-dilution systems, use Equation 7E–1 to calculate the analyzer calibration error for the low-, mid-, and high-level calibration gases.

$$ACE = \frac{C_{Dir} - C_v}{CS} \times 100 \qquad \text{Eq. 7E-1}$$

12.3 System Bias. For non-dilution systems, use Equation 7E–2 to calculate the system bias separately for the low-level and upscale calibration gases.

$$SB = \frac{C_S - C_{Dir}}{CS} \times 100 \qquad \text{Eq. 7E-2}$$

12.4 System Calibration Error. Use Equation 7E–3 to calculate the system calibration error for dilution systems. Equation 7E–3 applies to both the initial 3-point system calibration error test and the subsequent 2-point calibration error checks between test runs. In this equation, the term ''C_s'' refers to the diluted calibration gas concentration measured by the analyzer.

$$SCE = \frac{(C_S \quad DF) - C_V}{CS} \times 100 \qquad \text{Eq. 7E-3}$$

12.5 Drift Assessment. Use Equation 7E–4 to separately calculate the low-level and upscale drift over each test run. For dilution systems, replace ''SB_{final}'' and ''SB_i'' with ''SCE_{final}'' and ''SCE_i'', respectively, to calculate and evaluate drift.

$$D = \left|SB_{final} - SB_i\right| \qquad \text{Eq. 7E-4}$$

12.6 Effluent Gas Concentration. For each test run, calculate C_{avg}, the arithmetic average of all valid NO_X concentration values (*e.g.*, 1-minute averages). Then adjust the value of C_{avg} for bias using Equation 7E–5a if you use a non-zero gas as your low-level calibration gas, or Equation 7E–5b if you use a zero gas as your low-level calibration gas.

$$C_{Gas} = \left(C_{Avg} - C_M\right)\frac{C_{MA} - C_{OA}}{C_M - C_O} + C_{MA} \qquad \text{Eq. 7E-5a}$$

$$C_{Gas} = \left(C_{Avg} - C_O\right)\frac{C_{MA}}{C_M - C_O} \qquad \text{Eq. 7E-5b}$$

12.7 NO_2—NO Conversion Efficiency. If the NO_X converter efficiency test described in section 8.2.4.1 is performed, calculate the efficiency using Equation 7E–7.

$$Eff_{NO2} = \frac{C_{Dir}}{C_V} \times 100 \qquad \text{Eq. 7E-7}$$

12.8 NO_2—NO Conversion Efficiency Correction. If desired, calculate the total NO_X concentration with a correction for converter efficiency using Equation 7E–8.

$$NO_{x\,Corr} = NO + \left(\frac{(NO_X - NO)}{Eff_{NO_2}} x\ 100\right) \qquad \text{Eq. 7E-8}$$

12.9 Alternative NO_2 Converter Efficiency. If the alternative procedure of section 16.2.2 is used, determine the NO_X concentration decrease from NO_{XPeak} after the minimum 30-minute test interval using Equation 7E–9.

This decrease from NO_{XPeak} must meet the requirement in section 13.5 for the converter to be acceptable.

$$\%\,Decrease = \frac{NO_{XPeak} - NO_{XFinal}}{NO_{XPeak}} \times 100 \qquad \text{Eq. 7E-9}$$

12.10 Moisture Correction. Use Equation 7E–10 if your measurements need to be corrected to a dry basis.

$$C_D = \frac{C_W}{1 - B_{WS}} \qquad \text{Eq. 7E-10}$$

12.11 Calculated Spike Gas Concentration and Spike Recovery for the Example Alternative Dynamic Spiking Procedure in section 16.1.3. Use Equation 7E–11 to determine the calculated spike gas concentration. Use Equation 7E–12 to calculate the spike recovery.

$$C_{Calc} = \frac{\left(C_{Spike}\right)\left(Q_{Spike}\right)}{Q_{Total}} \qquad \text{Eq. 7E-11}$$

$$R = \frac{DF\left(C_{ss} - C_{native}\right) + C_{native}}{C_{Spike}} \times 100 \qquad \text{Eq. 7E-12}$$

13.0 Method Performance

13.1 Calibration Error. This specification is applicable to both the analyzer calibration error and the 3-point system calibration error tests described in section 8.2.3. At each calibration gas level (low, mid, and high) the calibration error must either be within ±2.0 percent of the calibration span. Alternatively, the results are acceptable if $|C_{dir} - C_v|$ or $|C_s - C_v|$ (as applicable) is ≤0.5 ppmv.

13.2 System Bias. This specification is applicable to both the system bias and 2-point system calibration error tests described in section 8.2.5 and 8.5. The pre- and post-run system bias (or system calibration error) must be within ±5.0 percent of the calibration span for the low-level and upscale calibration gases. Alternatively, the results are acceptable if $|C_s - C_{dir}|$ is ≤0.5 ppmv or if $|C_s - C_v|$ is ≤0.5 ppmv (as applicable).

13.3 Drift. For each run, the low-level and upscale drift must be less than or equal to 3.0 percent of the calibration span. The drift is also acceptable if the pre- and post-run bias (or the pre- and post-run system calibration error) responses do not differ by more than 0.5 ppmv at each gas concentration (i.e. $|C_{s\ post\text{-}run} - C_{s\ pre\text{-}run}| \leq 0.5$ ppmv).

13.4 Interference Check. The total interference response (i.e., the sum of the interference responses of all tested gaseous components) must not be greater than 2.50 percent of the calibration span for the analyzer tested. In summing the interferences, use the larger of the absolute values obtained for the interferent tested with and without the pollutant present. The results are also acceptable if the sum of the responses does not exceed 0.5 ppmv for a calibration span of 5 to 10 ppmv, or 0.2 ppmv for a calibration span <5 ppmv.

13.5 NO_2 to NO Conversion Efficiency Test (as applicable). The NO_2 to NO conversion efficiency, calculated according to Equation 7E–7, must be greater than or equal to 90 percent. The alternative conversion efficiency check, described in section 16.2.2 and calculated according to Equation 7E–9, must not result in a decrease from NO_{XPeak} by more than 2.0 percent.

13.6 Alternative Dynamic Spike Procedure. Recoveries of both pre-test spikes and post-test spikes must be within 100 ±10 percent. If the absolute difference between the calculated spike value and measured spike value is equal to or less than 0.20 ppmv, then the requirements of the ADSC are met.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Dynamic Spike Procedure. Except for applications under part 75 of this chapter, you may use a dynamic spiking procedure to validate your test data for a specific test matrix in place of the interference check and pre- and post-run system bias checks. For part 75 applications, use of this procedure is subject to the approval of the Administrator.

Best results are obtained for this procedure when source emissions are steady and not varying. Fluctuating emissions may render this alternative procedure difficult to pass. To use this alternative, you must meet the following requirements.

16.1.1 Procedure Documentation. You must detail the procedure you followed in the test report, including how the spike was measured, added, verified during the run, and calculated after the test.

16.1.2 Spiking Procedure Requirements. The spikes must be prepared from EPA Traceability Protocol gases. Your procedure must be designed to spike field samples at two target levels both before and after the test. Your target spike levels should bracket the average sample NO_X concentrations. The higher target concentration must be less than the calibration span. You must collect at least 5 data points for each target concentration. The spiking procedure must be performed before the first run and repeated after the last run of the test program.

16.1.3 Example Spiking Procedure. Determine the NO concentration needed to generate concentrations that are 50 and 150 percent of the anticipated NO_X concentration in the stack at the total sampling flow rate while keeping the spike flow rate at or below 10 percent of this total. Use a mass flow meter (accurate within 2.0 percent) to generate these NO spike gas concentrations at a constant flow rate. Use Equation 7E–11 in section 12.11 to determine the calculated spike concentration in the collected sample.

(1) Prepare the measurement system and conduct the analyzer calibration error test as described in sections 8.2.2 and 8.2.3. Following the sampling procedures in section 8.1, determine the stack NO_X concentration and use this concentration as the average stack concentration (C_{avg}) for the first spike level, or if desired, for both pre-test spike levels. Introduce the first level spike gas into the system in system calibration mode and begin sample collection. Wait for at least two times the system response time before measuring the spiked sample concentration. Then record at least five successive 1-minute averages of the spiked sample gas. Monitor the spike gas flow rate and maintain at the determined addition rate. Average the five 1-minute averages and determine the spike recovery using Equation 7E–12. Repeat this procedure for the other pre-test spike level. The recovery at each level must be within the limits in section 13.6 before proceeding with the test.

(2) Conduct the number of runs required for the test. Then repeat the above procedure for the post-test spike evaluation. The last run of the test may serve as the average stack concentration for the post-test spike test calculations. The results of the post-test spikes must meet the limits in section 13.6.

16.2 Alternative NO_2 to NO Conversion Efficiency Procedures. You may use either of the following procedures to determine converter efficiency in place of the procedure in section 8.2.4.1.

16.2.1 The procedure for determining conversion efficiency using NO in 40 CFR 86.123–78.

16.2.2 Bag Procedure. Perform the analyzer calibration error test to document the calibration (both NO and NO_X modes, as applicable). Fill a Tedlar or equivalent bag approximately half full with either ambient air, pure oxygen, or an oxygen standard gas with at least 19.5 percent by volume oxygen content. Fill the remainder of the bag with mid- to high-level NO in N_2 (or other appropriate concentration) calibration gas. (Note that the concentration of the NO standard should be sufficiently high enough for the diluted concentration to be easily and accurately measured on the scale used. The size of the bag should be large enough to accommodate the procedure and time required. Verify through the manufacturer that the Tedlar alternative is suitable for NO and make this verifed information available for inspection.)

(1) Immediately attach the bag to the inlet of the NO_X analyzer (or external converter if used). In the case of a dilution-system, introduce the gas at a point upstream of the dilution assembly. Measure the NO_X concentration for a period of 30 minutes. If the NO_X concentration drops more than 2 percent absolute from the peak value observed, then the NO_2 converter has failed to meet the criteria of this test. Take corrective action. The highest NO_X value observed is considered to be NO_{XPeak}. The final NO_X value observed is considered to be NO_{Xfinal}.

(2) [Reserved]

16.3 Manufacturer's Stability Test. A manufacturer's stability test is required for all analyzers that routinely measure emissions below 20 ppmv and is optional but recommended for other analyzers. This test evaluates each analyzer model by subjecting it to the tests listed in Table 7E–5 following procedures similar to those in 40 CFR 53.23 for thermal stability and insensitivity to supply voltage variations. If the analyzer will be used under temperature conditions that are outside the test conditions in Table B–4 of Part 53.23, alternative test temperatures that better reflect the analyzer field environment should be used. Alternative procedures or documentation that establish the analyzer's stability over the appropriate line voltages and temperatures are acceptable.

17.0 References

1. ''ERA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards'' September 1997 as amended, ERA–600/R–97/121.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

Figure 7E-1. Measurement System

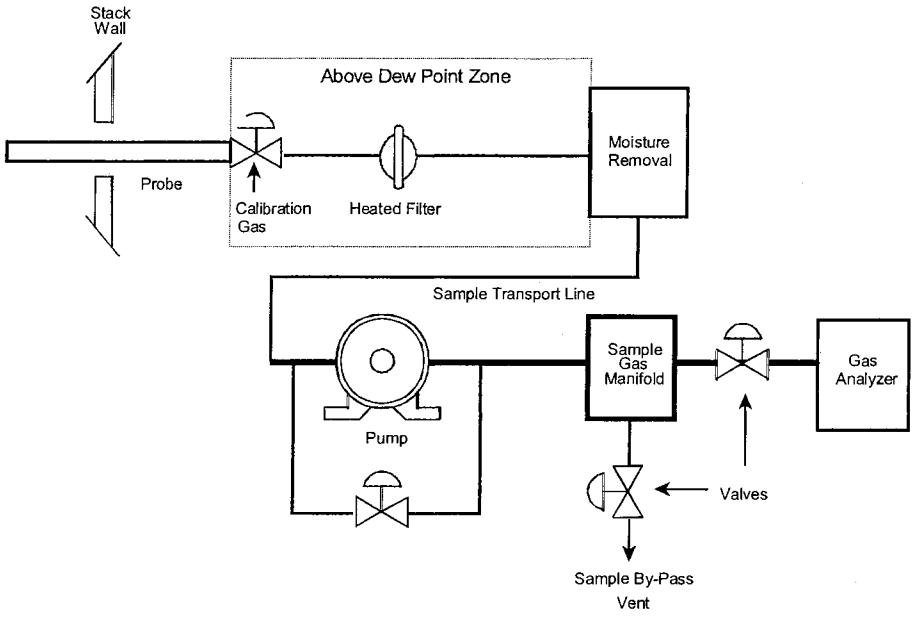

Figure 7E-2. Testing Flow Chart

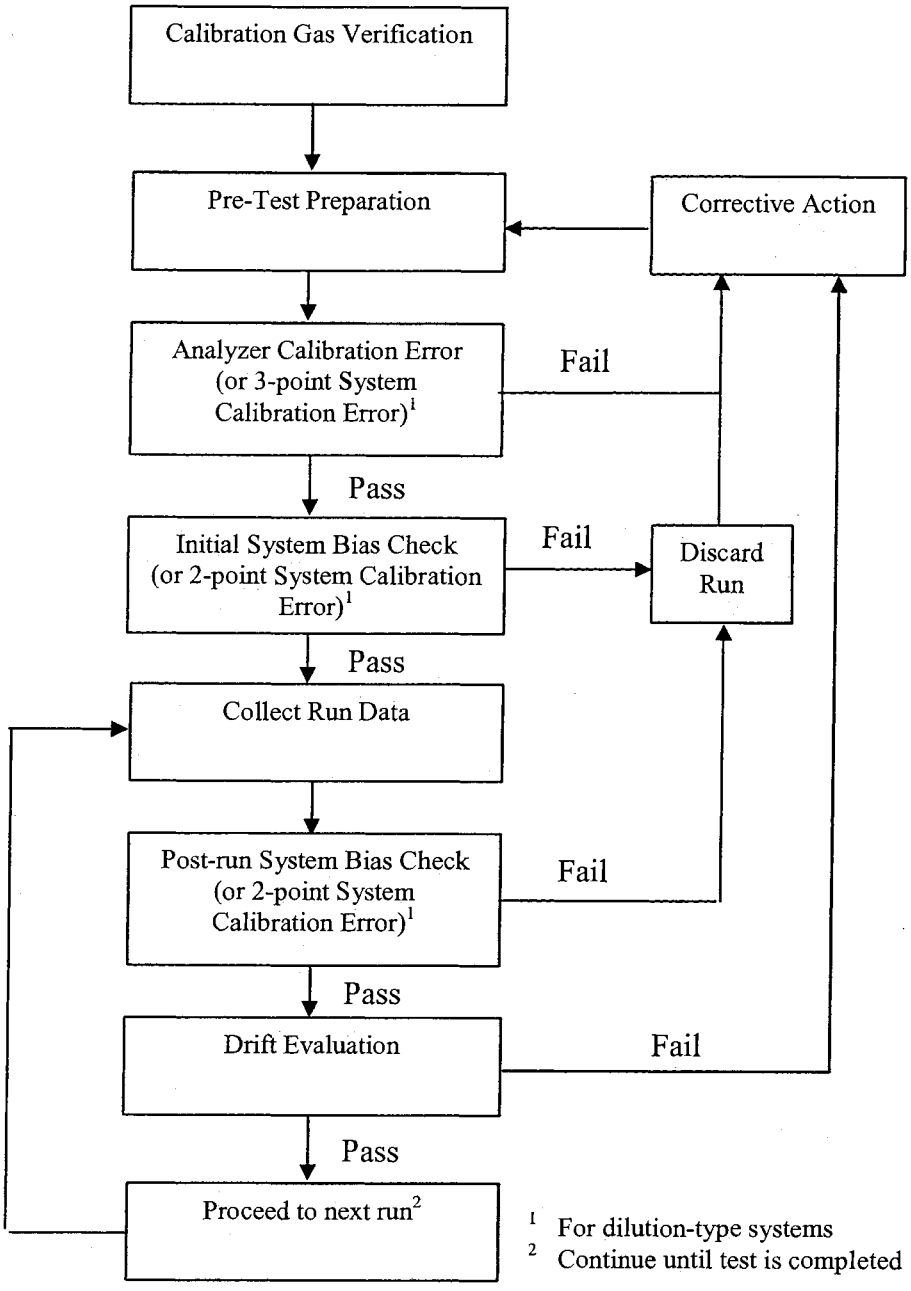

Table 7E-1 - Analyzer (or System) Calibration Error Data

Source Identification: _____ Test personnel: _____ Date: _____ Time: _____		Analyzer[1] or System[2] calibration error data for sampling runs: _____ Analyzer Model No. _____ Serial No. _____ Calibration Span (CS):		
	Manufacturer Certified Cylinder Value (indicate units) A	Analyzer calibration response (indicate units) B	Absolute difference (indicate units) A-B	Calibration Error (percent of calibration span) $\frac{A-B}{CS} \times 100$
Low-level (or zero) calibration gas	.....	.....	.....	.....
Mid-level calibration gas	.....	.....	.....	.....
High-level calibration gas	.....	.....	.....	.....

[1] Refers to data from the analyzer calibration error test of a non-dilution system.
[2] Refers to data from a 3-point system calibration error test of a dilution system.

Table 7E-2 - System Bias (or System Calibration Error) and Drift Data

Source Identification: _____ Run Number: _____
Test personnel: _____ Calibration Span: _____
Date: _____ Response Time: _____
Analyzer Model No. _____ Serial No. _____

	Initial values			Final values		
Calibration Gas Level	Certified Calibration gas value (indicate units)	System Response (indicate units)	System Bias[1] or Calibration Error[2] (% of calibration span)	System response (indicate units)	System Bias[1] or Calibration Error[2] (% of calibration span)	Drift (% of calibration span)
Low-level gas.....	.....	.....	.....	.....	.....	
Upscale (high- or mid-) level gas.....	.....	.....	.....	.....	.....	

[1] Refers to the pre- and post-run system bias checks of a non-dilution system.
[2] Refers to the pre- and post-run system calibration error checks of a dilution system.

TABLE 7E–3—EXAMPLE INTERFERENCE CHECK GAS CONCENTRATIONS

Potential interferent gas[1]	Concentrations[2] sample conditioning type	
	Hot wet	Dried
CO_2	5 and 15%	5 and 15%
H_2O	25%	1%
NO	15 ppmv	15 ppmv
NO_2	15 ppmv	15 ppmv
N_2O	10 ppmv	10 ppmv
CO	50 ppmv	50 ppmv
NH_3	10 ppmv	10 ppmv
CH_4	50 ppmv	50 ppmv
SO_2	20 ppmv	20 ppmv
H_2	50 ppmv	50 ppmv
HCl	10 ppmv	10 ppmv

[1] Any applicable gas may be eliminated or tested at a reduced level if the manufacturer has provided reliable means for limiting or scrubbing that gas to a specified level.
[2] As practicable, gas concentrations should be the highest expected at test sites.

TABLE 7E–4—INTERFERENCE RESPONSE

Date of Test: _____

Analyzer Type: _____
Model No.: _____
Serial No: _____
Calibration Span: _____

Test gas type	Concentration (ppm)	Analyzer response
	Sum of Responses	
	% of Calibration Span	

TABLE 7E–5—MANUFACTURER STABILITY TEST

Test description	Acceptance criteria (note 1)
Thermal Stability	Temperature range when drift does not exceed 3.0% of analyzer range over a 12-hour run when measured with NO_X present @ 80% of calibration span.
Fault Conditions	Identify conditions which, when they occur, result in performance which is not in compliance with the Manufacturer's Stability Test criteria. These are to be indicated visually or electrically to alert the operator of the problem.
Insensitivity to Supply Voltage Variations.	±10.0% (or manufacturers alternative) variation from nominal voltage must produce a drift of ≤2.0% of calibration span for either zero or concentration ≥80% NO_X present.
Analyzer Calibration Error.	For a low-, medium-, and high-calibration gas, the difference between the manufacturer certified value and the analyzer response in direct calibration mode, no more than 2.0% of calibration span.

Note 1: If the instrument is to be used as a Low Range analyzer, all tests must be performed at a calibration span of 20 ppm or less.

METHOD 8—DETERMINATION OF SULFURIC ACID AND SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, and Method 6.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Sulfuric acid, including: Sulfuric acid (H_2SO_4) mist, Sulfur trioxide (SO_3).	7664–93–9, 7449–11–9	0.05 mg/m³ (0.03×10^{-7} lb/ft³).
Sulfur dioxide (SO_2)	7449–09–5	1.2 mg/m³ (3×10^{-9} lb/ft³).

1.2 Applicability. This method is applicable for the determination of H_2SO_4 (including H_2SO_4 mist and SO_3) and gaseous SO_2 emissions from stationary sources.

NOTE: Filterable particulate matter may be determined along with H_2SO_4 and SO_2 (subject to the approval of the Administrator) by inserting a heated glass fiber filter between the probe and isopropanol impinger (see section 6.1.1 of Method 6). If this option is chosen, particulate analysis is gravimetric only; sulfuric acid is not determined separately.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

A gas sample is extracted isokinetically from the stack. The H_2SO_4 and the SO_2 are separated, and both fractions are measured separately by the barium-thorin titration method.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Possible interfering agents of this method are fluorides, free ammonia, and dimethyl aniline. If any of these interfering agents is present (this can be determined by knowledge of the process), alternative methods, subject to the approval of the Administrator, are required.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. Same as Method 6, section 5.2.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 5, section 6.1, with the following additions and exceptions:

6.1.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 8–1; it is similar to the Method 5 sampling train, except that the filter position is different, and the filter holder does not have to be heated. See Method 5, section 6.1.1, for details and guidelines on operation and maintenance.

6.1.1.1 Probe Liner. Borosilicate or quartz glass, with a heating system to prevent visible condensation during sampling. Do not use metal probe liners.

6.1.1.2 Filter Holder. Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other gasket materials (*e.g.*, Teflon or Viton) may be used, subject to the approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The filter holder shall be placed between the first and second impingers. Do not heat the filter holder.

6.1.1.3 Impingers. Four, of the Greenburg-Smith design, as shown in Figure 8–1. The first and third impingers must have standard tips. The second and fourth impingers must be modified by replacing the insert with an approximately 13-mm (½-in.) ID glass tube, having an unconstricted tip located 13 mm (½ in.) from the bottom of the impinger. Similar collection systems, subject to the approval of the Administrator, may be used.

6.1.1.4 Temperature Sensor. Thermometer, or equivalent, to measure the temperature of the gas leaving the impinger train to within 1 °C (2 °F).

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Wash Bottles. Two polyethylene or glass bottles, 500-ml.

6.2.2 Graduated Cylinders. Two graduated cylinders (volumetric flasks may be used), 250-ml, 1-liter.

6.2.3 Storage Bottles. Leak-free polyethylene bottles, 1-liter size (two for each sampling run).

6.2.4 Trip Balance. 500-g capacity, to measure to ±0.5 g (necessary only if a moisture content analysis is to be done).

6.3 Analysis. The following items are required for sample analysis:

6.3.1 Pipettes. Volumetric 10-ml, 100-ml.

6.3.2 Burette. 50-ml.

6.3.3 Erlenmeyer Flask. 250-ml (one for each sample, blank, and standard).

6.3.4 Graduated Cylinder. 100-ml.

6.3.5 Dropping Bottle. To add indicator solution, 125-ml size.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents are to conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Filters and Silica Gel. Same as in Method 5, sections 7.1.1 and 7.1.2, respectively.

7.1.2 Water. Same as in Method 6, section 7.1.1.

7.1.3 Isopropanol, 80 Percent by Volume. Mix 800 ml of isopropanol with 200 ml of water.

NOTE: Check for peroxide impurities using the procedure outlined in Method 6, section 7.1.2.1.

7.1.4 Hydrogen Peroxide (H^2O^2), 3 Percent by Volume. Dilute 100 ml of 30 percent H_2O_2) to 1 liter with water. Prepare fresh daily.

7.1.5 Crushed Ice.

7.2 Sample Recovery. The reagents and standards required for sample recovery are:

7.2.1 Water. Same as in section 7.1.2.

7.2.2 Isopropanol, 80 Percent. Same as in section 7.1.3.

7.3 Sample Analysis. Same as Method 6, section 7.3.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation. Same as Method 5, section 8.1, except that filters should be inspected but need not be desiccated, weighed, or identified. If the effluent gas can be considered dry (i.e., moisture-free), the silica gel need not be weighed.

8.2 Preliminary Determinations. Same as Method 5, section 8.2.

8.3 Preparation of Sampling Train. Same as Method 5, section 8.3, with the following exceptions:

8.3.1 Use Figure 8–1 instead of Figure 5–1.

8.3.2 Replace the second sentence of Method 5, section 8.3.1 with: Place 100 ml of 80 percent isopropanol in the first impinger, 100 ml of 3 percent H_2O_2 in both the second and third impingers; retain a portion of each reagent for use as a blank solution. Place about 200 g of silica gel in the fourth impinger.

8.3.3 Ignore any other statements in section 8.3 of Method 5 that are obviously not applicable to the performance of Method 8.

NOTE: If moisture content is to be determined by impinger analysis, weigh each of the first three impingers (plus absorbing solution) to the nearest 0.5 g, and record these weights. Weigh also the silica gel (or silica gel plus container) to the nearest 0.5 g, and record.)

8.4 Metering System Leak-Check Procedure. Same as Method 5, section 8.4.1.

8.5 Pretest Leak-Check Procedure. Follow the basic procedure in Method 5, section 8.4.2, noting that the probe heater shall be adjusted to the minimum temperature required to prevent condensation, and also that verbage such as ''* * * plugging the inlet to the filter holder * * * '' found in section 8.4.2.2 of Method 5 shall be replaced by '' * * * plugging the inlet to the first impinger * * * ''. The pretest leak-check is recommended, but is not required.

8.6 Sampling Train Operation. Follow the basic procedures in Method 5, section 8.5, in conjunction with the following special instructions:

8.6.1 Record the data on a sheet similar to that shown in Figure 8–2 (alternatively, Figure 5–2 in Method 5 may be used). The sampling rate shall not exceed 0.030 m^3/min (1.0 cfm) during the run. Periodically during the test, observe the connecting line between the probe and first impinger for signs of condensation. If condensation does occur, adjust the probe heater setting upward to the minimum temperature required to prevent condensation. If component changes become necessary during a run, a leak-check shall be performed immediately before each change, according to the procedure outlined in section 8.4.3 of Method 5 (with appropriate modifications, as mentioned in section 8.5 of this method); record all leak rates. If the leakage rate(s) exceeds the specified rate, the tester shall either void the run or plan to correct the sample volume as outlined in section 12.3 of Method 5. Leak-checks immediately after component changes are recommended, but not required. If these leak-checks are performed, the procedure in section 8.4.2 of Method 5 (with appropriate modifications) shall be used.

8.6.2 After turning off the pump and recording the final readings at the conclusion of each run, remove the probe from the stack. Conduct a post-test (mandatory) leak-check as outlined in section 8.4.4 of Method 5 (with appropriate modifications), and record the leak rate. If the post-test leakage rate exceeds the specified acceptable rate, either correct the sample volume, as outlined in section 12.3 of Method 5, or void the run.

8.6.3 Drain the ice bath and, with the probe disconnected, purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at the average flow rate used for sampling.

NOTE: Clean ambient air can be provided by passing air through a charcoal filter. Alternatively, ambient air (without cleaning) may be used.

8.7 Calculation of Percent Isokinetic. Same as Method 5, section 8.6.

8.8 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. Treat the samples as follows:

8.8.1 Container No. 1.

8.8.1.1 If a moisture content analysis is to be performed, clean and weigh the first impinger (plus contents) to the nearest 0.5 g, and record this weight.

8.8.1.2 Transfer the contents of the first impinger to a 250-ml graduated cylinder. Rinse the probe, first impinger, all connecting glassware before the filter, and the front half of the filter holder with 80 percent isopropanol. Add the isopropanol rinse solution to the cylinder. Dilute the contents of the cylinder to 225 ml with 80 percent isopropanol, and transfer the cylinder contents to the storage container. Rinse the cylinder with 25 ml of 80 percent isopropanol, and transfer the rinse to the storage container. Add the filter to the solution in the storage container and mix. Seal the container to protect the solution against evaporation. Mark the level of liquid on the container, and identify the sample container.

8.8.2 Container No. 2.

8.8.2.1 If a moisture content analysis is to be performed, clean and weigh the second and third impingers (plus contents) to the nearest 0.5 g, and record the weights. Also, weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g, and record the weight.

8.8.2.2 Transfer the solutions from the second and third impingers to a 1-liter graduated cylinder. Rinse all connecting glassware (including back half of filter holder) between the filter and silica gel impinger with water, and add this rinse water to the cylinder. Dilute the contents of the cylinder to 950 ml with water. Transfer the solution to a storage container. Rinse the cylinder with 50 ml of water, and transfer the rinse to the storage container. Mark the level of liquid on the container. Seal and identify the sample container.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
7.1.3	Isopropanol check	Ensure acceptable level of peroxide impurities in isopropanol.
8.4, 8.5, 10.1	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.
10.2	Barium standard solution standardization	Ensure normality determination.
11.2	Replicate titrations	Ensure precision of titration determinations.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

10.1 Sampling Equipment. Same as Method 5, section 10.0.

10.2 Barium Standard Solution. Same as Method 6, section 10.5.

11.0 Analytical Procedure

11.1. Sample Loss. Same as Method 6, section 11.1.

11.2. Sample Analysis.

11.2.1 Container No. 1. Shake the container holding the isopropanol solution and the filter. If the filter breaks up, allow the fragments to settle for a few minutes before removing a sample aliquot. Pipette a 100-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 2 to 4 drops of thorin indicator, and titrate to a pink endpoint using 0.0100 N barium standard solution. Repeat the titration with a second aliquot of sample, and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater.

11.2.2 Container No. 2. Thoroughly mix the solution in the container holding the contents of the second and third impingers. Pipette a 10-ml aliquot of sample into a 250-ml Erlenmeyer flask. Add 40 ml of isopropanol, 2 to 4 drops of thorin indicator, and titrate to a pink endpoint using 0.0100 N barium standard solution. Repeat the titration with a second aliquot of sample, and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater.

11.2.3 Blanks. Prepare blanks by adding 2 to 4 drops of thorin indicator to 100 ml of 80 percent isopropanol. Titrate the blanks in the same manner as the samples.

12.0 Data Analysis and Calculations

Carry out calculations retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature. Same as Method 5, section 12.1, with the following additions and exceptions:

$C_{H_2SO_4}$ = Sulfuric acid (including SO_3) concentration, g/dscm (lb/dscf).

C_{SO_2} = Sulfur dioxide concentration, g/dscm (lb/dscf).

N = Normality of barium perchlorate titrant, meq/ml.

V_a = Volume of sample aliquot titrated, 100 ml for H_2SO_4 and 10 ml for SO_2.

V_{soln} = Total volume of solution in which the sample is contained, 1000 ml for the SO_2 sample and 250 ml for the H_2SO_4 sample.

V_t = Volume of barium standard solution titrant used for the sample, ml.

V_{tb} = Volume of barium standard solution titrant used for the blank, ml.

12.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 8–2).

12.3 Dry Gas Volume. Same as Method 5, section 12.3.

12.4 Volume of Water Vapor Condensed and Moisture Content. Calculate the volume of water vapor using Equation 5–2 of Method 5; the weight of water collected in the impingers and silica gel can be converted directly to milliliters (the specific gravity of water is 1 g/ml). Calculate the moisture content of the stack gas (B_{ws}) using Equation 5–3 of Method 5. The note in section 12.5 of Method 5 also applies to this method. Note that if the effluent gas stream can be considered dry, the volume of water vapor and moisture content need not be calculated.

12.5 Sulfuric Acid Mist (Including SO_3) Concentration.

$$C_{H_2SO_4} = K_3\left[N\left(V_t - V_{tb}\right)\left(V_{soln}/V_a\right)\right]/V_{m(std)} \qquad \text{Eq. 8-1}$$

Where:

K_3 = 0.04904 g/meq for metric units,

$K_3 = 1.081 \times 10^{-4}$ lb/meq for English units.

12.6 Sulfur Dioxide Concentration.

$$C_{SO_2} = K_4\left[N\left(V_t - V_{tb}\right)\left(V_{soln}/V_a\right)\right]/V_{m(std)} \qquad \text{Eq. 8-2}$$

Where:

K_4 = 0.03203 g/meq for metric units,

$K_4 = 7.061 \times 10^{-5}$ lb/meq for English units.

12.7 Isokinetic Variation. Same as Method 5, section 12.11.

12.8 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate, if needed, using data obtained in this method and the equations in sections 12.6 and 12.7 of Method 2.

13.0 Method Performance

13.1 Analytical Range. Collaborative tests have shown that the minimum detectable limits of the method are 0.06 mg/m^3 (4×10^{-9} lb/ft^3) for H_2SO_4 and 1.2 mg/m^3 (74×10^{-9} lb/ft^3) for SO_2. No upper limits have been established. Based on theoretical calculations for 200 ml of 3 percent H_2O_2 solution, the upper concentration limit for SO_2 in a 1.0 m^3 (35.3 ft^3) gas sample is about 12,000 mg/m^3 (7.7×10^{-4} lb/ft^3). The upper limit can be extended by increasing the quantity of peroxide solution in the impingers.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as section 17.0 of Methods 5 and 6.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

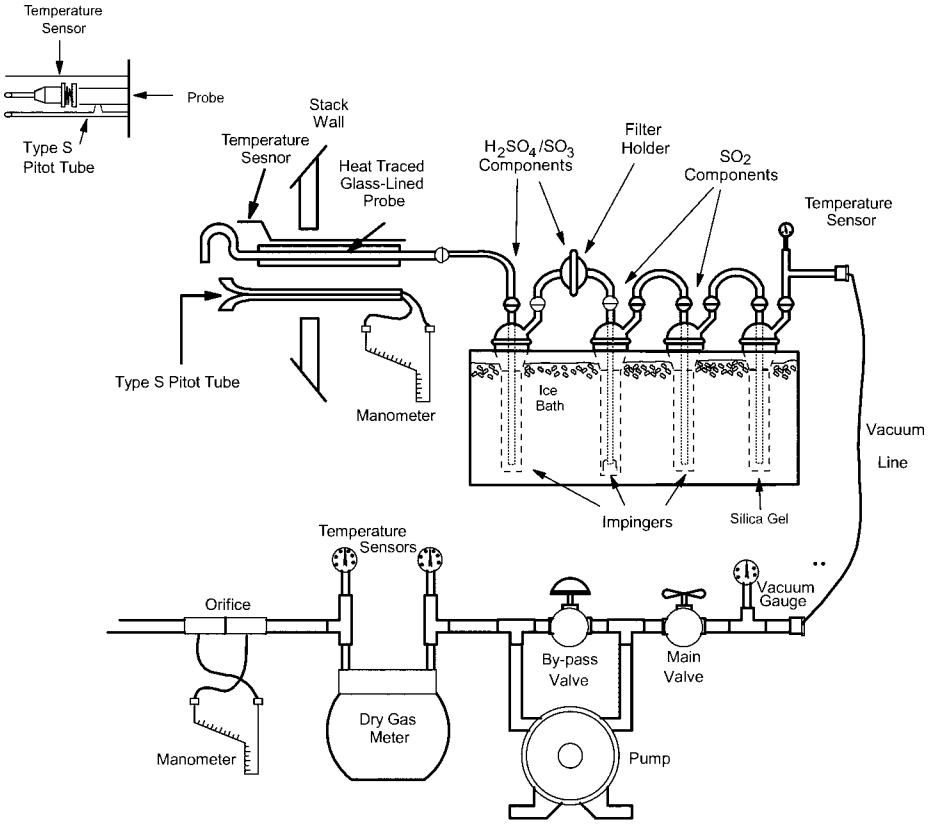

Figure 8-1. Sulfuric Acid Sampling Train

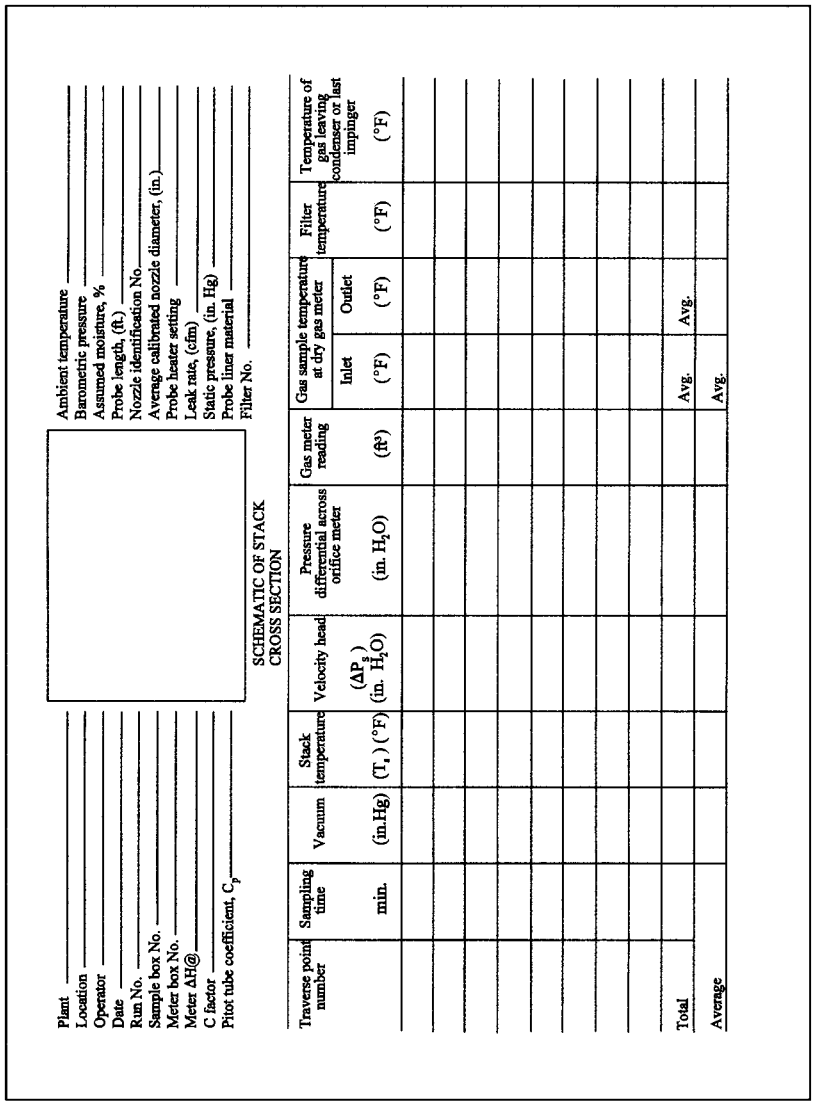

Figure 8-2. Field Data Sheet.

METHOD 9—VISUAL DETERMINATION OF THE OPACITY OF EMISSIONS FROM STATIONARY SOURCES

Many stationary sources discharge visible emissions into the atmosphere; these emissions are usually in the shape of a plume. This method involves the determination of plume opacity by qualified observers. The method includes procedures for the training and certification of observers, and procedures to be used in the field for determination of plume opacity. The appearance of a plume as viewed by an observer depends upon a number of variables, some of which may be controllable and some of which may not be controllable in the field. Variables which can be controlled to an extent to which they no longer exert a significant influence upon

plume appearance include: Angle of the observer with respect to the plume; angle of the observer with respect to the sun; point of observation of attached and detached steam plume; and angle of the observer with respect to a plume emitted from a rectangular stack with a large length to width ratio. The method includes specific criteria applicable to these variables.

Other variables which may not be controllable in the field are luminescence and color contrast between the plume and the background against which the plume is viewed. These variables exert an influence upon the appearance of a plume as viewed by an observer, and can affect the ability of the observer to accurately assign opacity values to the observed plume. Studies of the theory of plume opacity and field studies have demonstrated that a plume is most visible and presents the greatest apparent opacity when viewed against a contrasting background. It follows from this, and is confirmed by field trials, that the opacity of a plume, viewed under conditions where a contrasting background is present can be assigned with the greatest degree of accuracy. However, the potential for a positive error is also the greatest when a plume is viewed under such contrasting conditions. Under conditions presenting a less contrasting background, the apparent opacity of a plume is less and approaches zero as the color and luminescence contrast decrease toward zero. As a result, significant negative bias and negative errors can be made when a plume is viewed under less contrasting conditions. A negative bias decreases rather than increases the possibility that a plant operator will be cited for a violation of opacity standards due to observer error.

Studies have been undertaken to determine the magnitude of positive errors which can be made by qualified observers while reading plumes under contrasting conditions and using the procedures set forth in this method. The results of these studies (field trials) which involve a total of 769 sets of 25 readings each are as follows:

(1) For black plumes (133 sets at a smoke generator), 100 percent of the sets were read with a positive error[1] of less than 7.5 percent opacity; 99 percent were read with a positive error of less than 5 percent opacity.

(2) For white plumes (170 sets at a smoke generator, 168 sets at a coal-fired power plant, 298 sets at a sulfuric acid plant), 99 percent of the sets were read with a positive error of less than 7.5 percent opacity; 95 percent were read with a positive error of less than 5 percent opacity.

[1] For a set, positive error = average opacity determined by observers' 25 observations—average opacity determined from transmissometer's 25 recordings.

The positive observational error associated with an average of twenty-five readings is therefore established. The accuracy of the method must be taken into account when determining possible violations of applicable opacity standards.

1. Principle and Applicability

1.1 Principle. The opacity of emissions from stationary sources is determined visually by a qualified observer.

1.2 Applicability. This method is applicable for the determination of the opacity of emissions from stationary sources pursuant to §60.11(b) and for qualifying observers for visually determining opacity of emissions.

2. Procedures

The observer qualified in accordance with section 3 of this method shall use the following procedures for visually determining the opacity of emissions:

2.1 Position. The qualified observer shall stand at a distance sufficient to provide a clear view of the emissions with the sun oriented in the 140° sector to his back. Consistent with maintaining the above requirement, the observer shall, as much as possible, make his observations from a position such that his line of vision is approximately perpendicular to the plume direction, and when observing opacity of emissions from rectangular outlets (e.g., roof monitors, open baghouses, noncircular stacks), approximately perpendicular to the longer axis of the outlet. The observer's line of sight should not include more than one plume at a time when multiple stacks are involved, and in any case the observer should make his observations with his line of sight perpendicular to the longer axis of such a set of multiple stacks (e.g., stub stacks on baghouses).

2.2 Field Records. The observer shall record the name of the plant, emission location, type facility, observer's name and affiliation, a sketch of the observer's position relative to the source, and the date on a field data sheet (Figure 9–1). The time, estimated distance to the emission location, approximate wind direction, estimated wind speed, description of the sky condition (presence and color of clouds), and plume background are recorded on a field data sheet at the time opacity readings are initiated and completed.

2.3 Observations. Opacity observations shall be made at the point of greatest opacity in that portion of the plume where condensed water vapor is not present. The observer shall not look continuously at the plume, but instead shall observe the plume momentarily at 15-second intervals.

2.3.1 Attached Steam Plumes. When condensed water vapor is present within the

plume as it emerges from the emission outlet, opacity observations shall be made beyond the point in the plume at which condensed water vapor is no longer visible. The observer shall record the approximate distance from the emission outlet to the point in the plume at which the observations are made.

2.3.2 Detached Steam Plume. When water vapor in the plume condenses and becomes visible at a distinct distance from the emission outlet, the opacity of emissions should be evaluated at the emission outlet prior to the condensation of water vapor and the formation of the steam plume.

2.4 Recording Observations. Opacity observations shall be recorded to the nearest 5 percent at 15-second intervals on an observational record sheet. (See Figure 9–2 for an example.) A minimum of 24 observations shall be recorded. Each momentary observation recorded shall be deemed to represent the average opacity of emissions for a 15-second period.

2.5 Data Reduction. Opacity shall be determined as an average of 24 consecutive observations recorded at 15-second intervals. Divide the observations recorded on the record sheet into sets of 24 consecutive observations. A set is composed of any 24 consecutive observations. Sets need not be consecutive in time and in no case shall two sets overlap. For each set of 24 observations, calculate the average by summing the opacity of the 24 observations and dividing this sum by 24. If an applicable standard specifies an averaging time requiring more than 24 observations, calculate the average for all observations made during the specified time period. Record the average opacity on a record sheet. (See Figure 9–1 for an example.)

3. Qualifications and Testing

3.1 Certification Requirements. To receive certification as a qualified observer, a candidate must be tested and demonstrate the ability to assign opacity readings in 5 percent increments to 25 different black plumes and 25 different white plumes, with an error not to exceed 15 percent opacity on any one reading and an average error not to exceed 7.5 percent opacity in each category. Candidates shall be tested according to the procedures described in section 3.2. Smoke generators used pursuant to section 3.2 shall be equipped with a smoke meter which meets the requirements of section 3.3.

The certification shall be valid for a period of 6 months, at which time the qualification procedure must be repeated by any observer in order to retain certification.

3.2 Certification Procedure. The certification test consists of showing the candidate a complete run of 50 plumes—25 black plumes and 25 white plumes—generated by a smoke generator. Plumes within each set of 25 black and 25 white runs shall be presented in random order. The candidate assigns an opacity value to each plume and records his observation on a suitable form. At the completion of each run of 50 readings, the score of the candidate is determined. If a candidate fails to qualify, the complete run of 50 readings must be repeated in any retest. The smoke test may be administered as part of a smoke school or training program, and may be preceded by training or familiarization runs of the smoke generator during which candidates are shown black and white plumes of known opacity.

3.3 Smoke Generator Specifications. Any smoke generator used for the purposes of section 3.2 shall be equipped with a smoke meter installed to measure opacity across the diameter of the smoke generator stack. The smoke meter output shall display instack opacity based upon a pathlength equal to the stack exit diameter, on a full 0 to 100 percent chart recorder scale. The smoke meter optical design and performance shall meet the specifications shown in Table 9–1. The smoke meter shall be calibrated as prescribed in section 3.3.1 prior to the conduct of each smoke reading test. At the completion of each test, the zero and span drift shall be checked and if the drift exceeds ±1 percent opacity, the condition shall be corrected prior to conducting any subsequent test runs. The smoke meter shall be demonstrated, at the time of installation, to meet the specifications listed in Table 9–1. This demonstration shall be repeated following any subsequent repair or replacement of the photocell or associated electronic circuitry including the chart recorder or output meter, or every 6 months, whichever occurs first.

TABLE 9–1—SMOKE METER DESIGN AND PERFORMANCE SPECIFICATIONS

Parameter	Specification
a. Light source	Incandescent lamp operated at nominal rated voltage.
b. Spectral response of photocell.	Photopic (daylight spectral response of the human eye—Citation 3).
c. Angle of view	15° maximum total angle.
d. Angle of projection	15° maximum total angle.
e. Calibration error	±3% opacity, maximum.
f. Zero and span drift	±1% opacity, 30 minutes.
g. Response time	5 seconds.

3.3.1 Calibration. The smoke meter is calibrated after allowing a minimum of 30 minutes warmup by alternately producing simulated opacity of 0 percent and 100 percent. When stable response at 0 percent or 100 percent is noted, the smoke meter is adjusted to produce an output of 0 percent or 100 percent, as appropriate. This calibration shall be repeated until stable 0 percent and 100

percent readings are produced without adjustment. Simulated 0 percent and 100 percent opacity values may be produced by alternately switching the power to the light source on and off while the smoke generator is not producing smoke.

3.3.2 Smoke Meter Evaluation. The smoke meter design and performance are to be evaluated as follows:

3.3.2.1 Light Source. Verify from manufacturer's data and from voltage measurements made at the lamp, as installed, that the lamp is operated within ±5 percent of the nominal rated voltage.

3.3.2.2 Spectral Response of Photocell. Verify from manufacturer's data that the photocell has a photopic response; i.e., the spectral sensitivity of the cell shall closely approximate the standard spectral-luminosity curve for photopic vision which is referenced in (b) of Table 9–1.

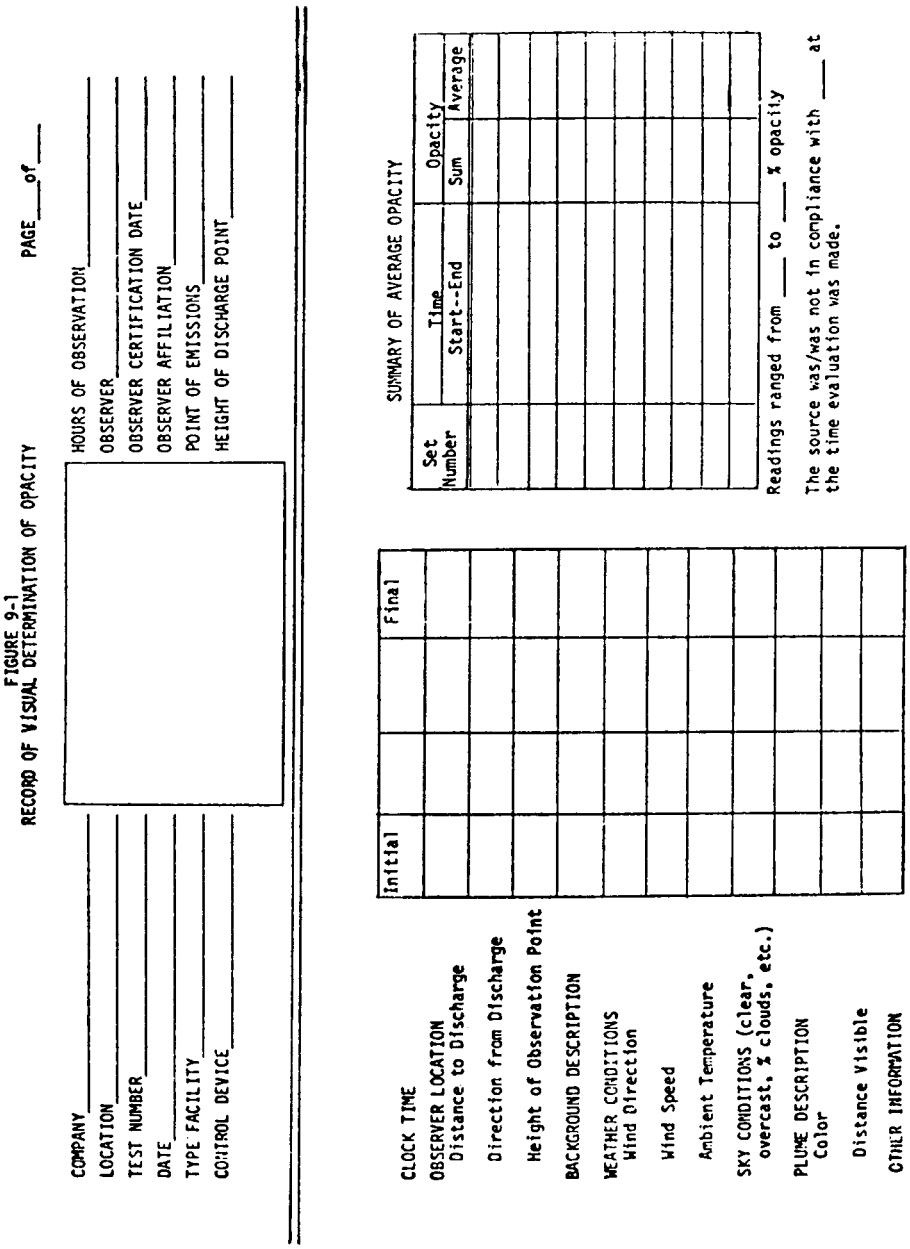

FIGURE 9–2—OBSERVATION RECORD

Page ___ of ___

Company .....
Location .....
Test Number .....
Date.

Observer .....
Type facility .....
Point of emissions .....

Hr.	Min.	Seconds				Steam plume (check if applicable)		Comments
		0	15	30	45	Attached	Detached	
	0							
	1							
	2							
	3							
	4							
	5							
	6							
	7							
	8							
	9							
	10							
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	22							
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	26							
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	29							

FIGURE 9–2—OBSERVATION RECORD (CONTINUED)

Page ____ of ____

Company .....
Location .....
Test Number .....
Date.

Observer .....
Type facility .....
Point of emissions .....

Hr.	Min.	Seconds				Steam plume (check if applicable)		Comments
		0	15	30	45	Attached	Detached	
	30							

Hr.	Min.	Seconds				Steam plume (check if applicable)		Comments
		0	15	30	45	Attached	Detached	
	31							
	32							
	33							
	34							
	35							
	36							
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3.3.2.3 Angle of View. Check construction geometry to ensure that the total angle of view of the smoke plume, as seen by the photocell, does not exceed 15°. The total angle of view may be calculated from: $\theta = 2 \tan^{-1} d/2L$, where θ = total angle of view; d = the sum of the photocell diameter + the diameter of the limiting aperture; and L = the distance from the photocell to the limiting aperture. The limiting aperture is the point in the path between the photocell and the smoke plume where the angle of view is most restricted. In smoke generator smoke meters this is normally an orifice plate.

3.3.2.4 Angle of Projection. Check construction geometry to ensure that the total angle of projection of the lamp on the smoke plume does not exceed 15°. The total angle of projection may be calculated from: $\theta = 2 \tan^{-1} d/2L$, where θ = total angle of projection; d = the sum of the length of the lamp

filament + the diameter of the limiting aperture; and L = the distance from the lamp to the limiting aperture.

3.3.2.5 Calibration Error. Using neutral-density filters of known opacity, check the error between the actual response and the theoretical linear response of the smoke meter. This check is accomplished by first calibrating the smoke meter according to 3.3.1 and then inserting a series of three neutral-density filters of nominal opacity of 20, 50, and 75 percent in the smoke meter pathlength. Filters calibrated within ±2 percent shall be used. Care should be taken when inserting the filters to prevent stray light from affecting the meter. Make a total of five nonconsecutive readings for each filter. The maximum error on any one reading shall be 3 percent opacity.

3.3.2.6 Zero and Span Drift. Determine the zero and span drift by calibrating and operating the smoke generator in a normal manner over a 1-hour period. The drift is measured by checking the zero and span at the end of this period.

3.3.2.7 Response Time. Determine the response time by producing the series of five simulated 0 percent and 100 percent opacity values and observing the time required to reach stable response. Opacity values of 0 percent and 100 percent may be simulated by alternately switching the power to the light source off and on while the smoke generator is not operating.

4. Bibliography

1. Air Pollution Control District Rules and Regulations, Los Angeles County Air Pollution Control District, Regulation IV, Prohibitions, Rule 50.

2. Weisburd, Melvin I., Field Operations and Enforcement Manual for Air, U.S. Environmental Protection Agency, Research Triangle Park, NC. APTD–1100, August 1972, pp. 4.1–4.36.

3. Condon, E.U., and Odishaw, H., Handbook of Physics, McGraw-Hill Co., New York, NY, 1958, Table 3.1, p. 6–52.

Alternate Method 1—Determination of the Opacity of Emissions From Stationary Sources Remotely by Lidar

This alternate method provides the quantitative determination of the opacity of an emissions plume remotely by a mobile lidar system (laser radar; Light Detection and Ranging). The method includes procedures for the calibration of the lidar and procedures to be used in the field for the lidar determination of plume opacity. The lidar is used to measure plume opacity during either day or nighttime hours because it contains its own pulsed light source or transmitter. The operation of the lidar is not dependent upon ambient lighting conditions (light, dark, sunny or cloudy).

The lidar mechanism or technique is applicable to measuring plume opacity at numerous wavelengths of laser radiation. However, the performance evaluation and calibration test results given in support of this method apply only to a lidar that employs a ruby (red light) laser [Reference 5.1].

1. Principle and Applicability

1.1 Principle. The opacity of visible emissions from stationary sources (stacks, roof vents, etc.) is measured remotely by a mobile lidar (laser radar).

1.2 Applicability. This method is applicable for the remote measurement of the opacity of visible emissions from stationary sources during both nighttime and daylight conditions, pursuant to 40 CFR §60.11(b). It is also applicable for the calibration and performance verification of the mobile lidar for the measurement of the opacity of emissions. A performance/design specification for a basic lidar system is also incorporated into this method.

1.3 Definitions.

Azimuth angle: The angle in the horizontal plane that designates where the laser beam is pointed. It is measured from an arbitrary fixed reference line in that plane.

Backscatter: The scattering of laser light in a direction opposite to that of the incident laser beam due to reflection from particulates along the beam's atmospheric path which may include a smoke plume.

Backscatter signal: The general term for the lidar return signal which results from laser light being backscattered by atmospheric and smoke plume particulates.

Convergence distance: The distance from the lidar to the point of overlap of the lidar receiver's field-of-view and the laser beam.

Elevation angle: The angle of inclination of the laser beam referenced to the horizontal plane.

Far region: The region of the atmosphere's path along the lidar line-of-sight beyond or behind the plume being measured.

Lidar: Acronym for Light Detection and Ranging.

Lidar range: The range or distance from the lidar to a point of interest along the lidar line-of-sight.

Near region: The region of the atmospheric path along the lidar line-of-sight between the lidar's convergence distance and the plume being measured.

Opacity: One minus the optical transmittance of a smoke plume, screen target, etc.

Pick interval: The time or range intervals in the lidar backscatter signal whose minimum average amplitude is used to calculate opacity. Two pick intervals are required, one in the near region and one in the far region.

Plume: The plume being measured by lidar.

Plume signal: The backscatter signal resulting from the laser light pulse passing through a plume.

$1/R^2$Correction: The correction made for the systematic decrease in lidar backscatter signal amplitude with range.

Reference signal: The backscatter signal resulting from the laser light pulse passing through ambient air.

Sample interval: The time period between successive samples for a digital signal or between successive measurements for an analog signal.

Signal spike: An abrupt, momentary increase and decrease in signal amplitude.

Source: The source being tested by lidar.

Time reference: The time (t_o) when the laser pulse emerges from the laser, used as the reference in all lidar time or range measurements.

2. Procedures

The mobile lidar calibrated in accordance with Paragraph 3 of this method shall use the following procedures for remotely measuring the opacity of stationary source emissions:

2.1 Lidar Position. The lidar shall be positioned at a distance from the plume sufficient to provide an unobstructed view of the source emissions. The plume must be at a range of at least 50 meters or three consecutive pick intervals (whichever is greater) from the lidar's transmitter/receiver convergence distance along the line-of-sight. The maximum effective opacity measurement distance of the lidar is a function of local atmospheric conditions, laser beam diameter, and plume diameter. The test position of the lidar shall be selected so that the diameter of the laser beam at the measurement point within the plume shall be no larger than three-fourths the plume diameter. The beam diameter is calculated by Equation (AM1–1):

$$D(\text{lidar}) = A + R\varphi \leq 0.75\ D(\text{Plume}) \quad \text{(AM1–1)}$$

Where:

D(Plume) = diameter of the plume (cm),
φ = laser beam divergence measured in radians
R = range from the lidar to the source (cm)
D(Lidar) = diameter of the laser beam at range R (cm),
A = diameter of the laser beam or pulse where it leaves the laser.

The lidar range, R, is obtained by aiming and firing the laser at the emissions source structure immediately below the outlet. The range value is then determined from the backscatter signal which consists of a signal spike (return from source structure) and the atmospheric backscatter signal [Reference 5.1]. This backscatter signal should be recorded.

When there is more than one source of emissions in the immediate vicinity of the plume, the lidar shall be positioned so that the laser beam passes through only a single plume, free from any interference of the other plumes for a minimum of 50 meters or three consecutive pick intervals (whichever is greater) in each region before and beyond the plume along the line-of-sight (determined from the backscatter signals). The lidar shall initially be positioned so that its line-of-sight is approximately perpendicular to the plume.

When measuring the opacity of emissions from rectangular outlets (e.g., roof monitors, open baghouses, noncircular stacks, etc.), the lidar shall be placed in a position so that its line-of-sight is approximately perpendicular to the longer (major) axis of the outlet.

2.2 Lidar Operational Restrictions. The lidar receiver shall not be aimed within an angle of ±15° (cone angle) of the sun.

This method shall not be used to make opacity measurements if thunderstorms, snowstorms, hail storms, high wind, high-ambient dust levels, fog or other atmospheric conditions cause the reference signals to consistently exceed the limits specified in section 2.3.

2.3 Reference Signal Requirements. Once placed in its proper position for opacity measurement, the laser is aimed and fired with the line-of-sight near the outlet height and rotated horizontally to a position clear of the source structure and the associated plume. The backscatter signal obtained from this position is called the ambient-air or reference signal. The lidar operator shall inspect this signal [Section V of Reference 5.1] to: (1) determine if the lidar line-of-sight is free from interference from other plumes and from physical obstructions such as cables, power lines, etc., for a minimum of 50 meters or three consecutive pick intervals (whichever is greater) in each region before and beyond the plume, and (2) obtain a qualitative measure of the homogeneity of the ambient air by noting any signal spikes.

Should there be any signal spikes on the reference signal within a minimum of 50 meters or three consecutive pick intervals (whichever is greater) in each region before and beyond the plume, the laser shall be fired three more times and the operator shall inspect the reference signals on the display. If the spike(s) remains, the azimuth angle shall be changed and the above procedures conducted again. If the spike(s) disappears in all three reference signals, the lidar line-of-sight is acceptable if there is shot-to-shot consistency and there is no interference from other plumes.

Shot-to-shot consistency of a series of reference signals over a period of twenty seconds is verified in either of two ways. (1) The lidar operator shall observe the reference signal amplitudes. For shot-to-shot consistency the ratio of R_f to R_n [amplitudes of the near and far region pick intervals (Section 2.6.1)] shall vary by not more than ±6% between shots; or (2) the lidar operator shall accept any one of the reference signals and

treat the other two as plume signals; then the opacity for each of the subsequent reference signals is calculated (Equation AM1–2). For shot-to-shot consistency, the opacity values shall be within ±3% of 0% opacity and the associated S_o values less than or equal to 8% (full scale) [Section 2.6].

If a set of reference signals fails to meet the requirements of this section, then all plume signals [Section 2.4] from the last set of acceptable reference signals to the failed set shall be discarded.

2.3.1 Initial and Final Reference Signals. Three reference signals shall be obtained within a 90-second time period prior to any data run. A final set of three reference signals shall be obtained within three (3) minutes after the completion of the same data run.

2.3.2 Temporal Criterion for Additional Reference Signals. An additional set of reference signals shall be obtained during a data run if there is a change in wind direction or plume drift of 30° or more from the direction that was prevalent when the last set of reference signals was obtained. An additional set of reference signals shall also be obtained if there is an increase in value of S_{In} (near region standard deviation, Equation AM1–5) or S_{If} (far region standard deviation, Equation AM1–6) that is greater than 6% (full scale) over the respective values calculated from the immediately previous plume signal, and this increase in value remains for 30 seconds or longer. An additional set of reference signals shall also be obtained if there is a change in amplitude in either the near or the far region of the plume signal, that is greater than 6% of the near signal amplitude and this change in amplitude remains for 30 seconds or more.

2.4 Plume Signal Requirements. Once properly aimed, the lidar is placed in operation with the nominal pulse or firing rate of six pulses/minute (1 pulse/10 seconds). The lidar operator shall observe the plume backscatter signals to determine the need for additional reference signals as required by section 2.3.2. The plume signals are recorded from lidar start to stop and are called a data run. The length of a data run is determined by operator discretion. Short-term stops of the lidar to record additional reference signals do not constitute the end of a data run if plume signals are resumed within 90 seconds after the reference signals have been recorded, and the total stop or interrupt time does not exceed 3 minutes.

2.4.1 Non-hydrated Plumes. The laser shall be aimed at the region of the plume which displays the greatest opacity. The lidar operator must visually verify that the laser is aimed clearly above the source exit structure.

2.4.2 Hydrated Plumes. The lidar will be used to measure the opacity of hydrated or so-called steam plumes. As listed in the reference method, there are two types, i.e., attached and detached steam plumes.

2.4.2.1 Attached Steam Plumes. When condensed water vapor is present within a plume, lidar opacity measurements shall be made at a point within the residual plume where the condensed water vapor is no longer visible. The laser shall be aimed into the most dense region (region of highest opacity) of the residual plume.

During daylight hours the lidar operator locates the most dense portion of the residual plume visually. During nighttime hours a high-intensity spotlight, night vision scope, or low light level TV, etc., can be used as an aid to locate the residual plume. If visual determination is ineffective, the lidar may be used to locate the most dense region of the residual plume by repeatedly measuring opacity, along the longitudinal axis or center of the plume from the emissions outlet to a point just beyond the steam plume. The lidar operator should also observe color differences and plume reflectivity to ensure that the lidar is aimed completely within the residual plume. If the operator does not obtain a clear indication of the location of the residual plume, this method shall not be used.

Once the region of highest opacity of the residual plume has been located, aiming adjustments shall be made to the laser line-of-sight to correct for the following: movement to the region of highest opacity out of the lidar line-of-sight (away from the laser beam) for more than 15 seconds, expansion of the steam plume (air temperature lowers and/or relative humidity increases) so that it just begins to encroach on the field-of-view of the lidar's optical telescope receiver, or a decrease in the size of the steam plume (air temperature higher and/or relative humidity decreases) so that regions within the residual plume whose opacity is higher than the one being monitored, are present.

2.4.2.2 Detached Steam Plumes. When the water vapor in a hydrated plume condenses and becomes visible at a finite distance from the stack or source emissions outlet, the opacity of the emissions shall be measured in the region of the plume clearly above the emissions outlet and below condensation of the water vapor.

During daylight hours the lidar operators can visually determine if the steam plume is detached from the stack outlet. During nighttime hours a high-intensity spotlight, night vision scope, low light level TV, etc., can be used as an aid in determining if the steam plume is detached. If visual determination is ineffective, the lidar may be used to determine if the steam plume is detached by repeatedly measuring plume opacity from the outlet to the steam plume along the plume's longitudinal axis or center line. The lidar operator should also observe color differences and plume reflectivity to detect a

detached plume. If the operator does not obtain a clear indication of the location of the detached plume, this method shall not be used to make opacity measurements between the outlet and the detached plume.

Once the determination of a detached steam plume has been confirmed, the laser shall be aimed into the region of highest opacity in the plume between the outlet and the formation of the steam plume. Aiming adjustments shall be made to the lidar's line-of-sight within the plume to correct for changes in the location of the most dense region of the plume due to changes in wind direction and speed or if the detached steam plume moves closer to the source outlet encroaching on the most dense region of the plume. If the detached steam plume should move too close to the source outlet for the lidar to make interference-free opacity measurements, this method shall not be used.

2.5 Field Records. In addition to the recording recommendations listed in other sections of this method the following records should be maintained. Each plume measured should be uniquely identified. The name of the facility, type of facility, emission source type, geographic location of the lidar with respect to the plume, and plume characteristics should be recorded. The date of the test, the time period that a source was monitored, the time (to the nearest second) of each opacity measurement, and the sample interval should also be recorded. The wind speed, wind direction, air temperature, relative humidity, visibility (measured at the lidar's position), and cloud cover should be recorded at the beginning and end of each time period for a given source. A small sketch depicting the location of the laser beam within the plume should be recorded.

If a detached or attached steam plume is present at the emissions source, this fact should be recorded. Figures AM1–I and AM1–II are examples of logbook forms that may be used to record this type of data. Magnetic tape or paper tape may also be used to record data.

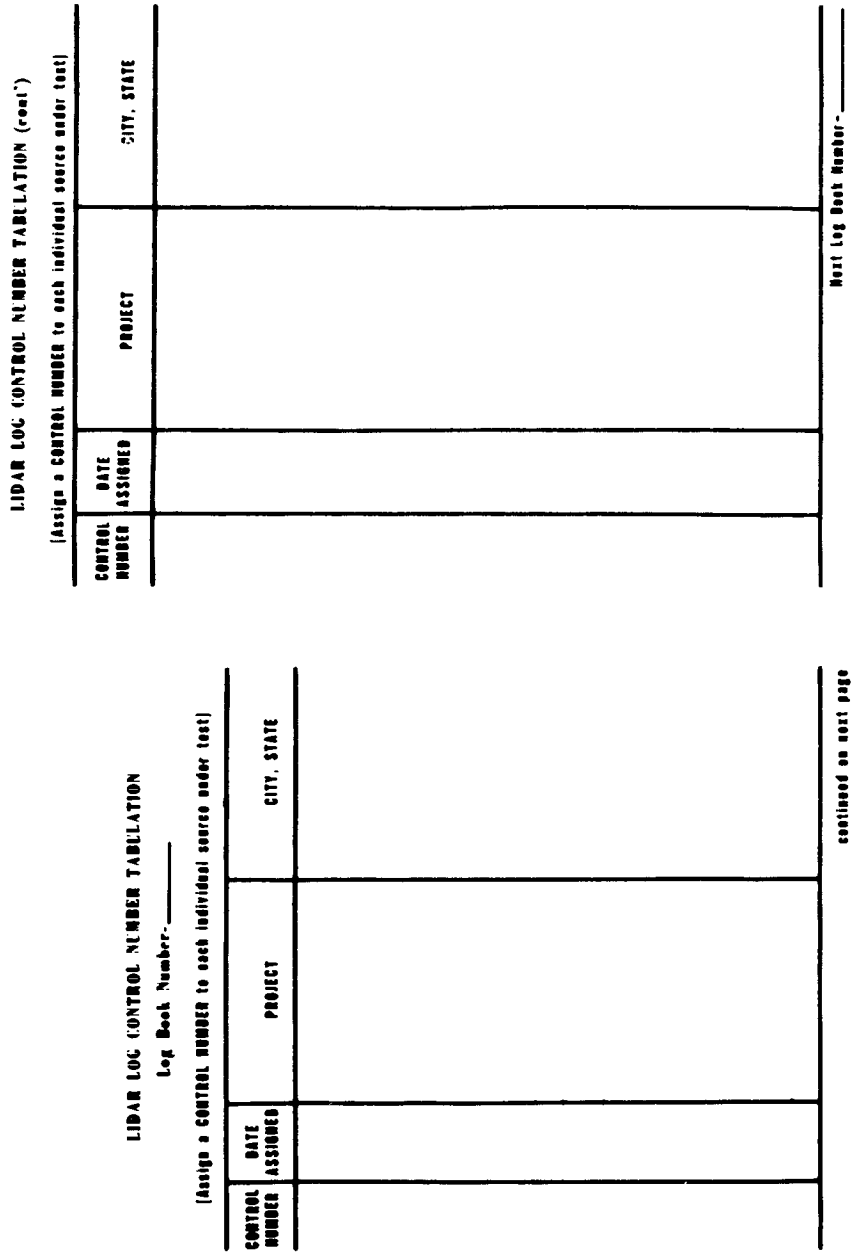


Figure AM1-1 Lidar Log Control Number Tabulation

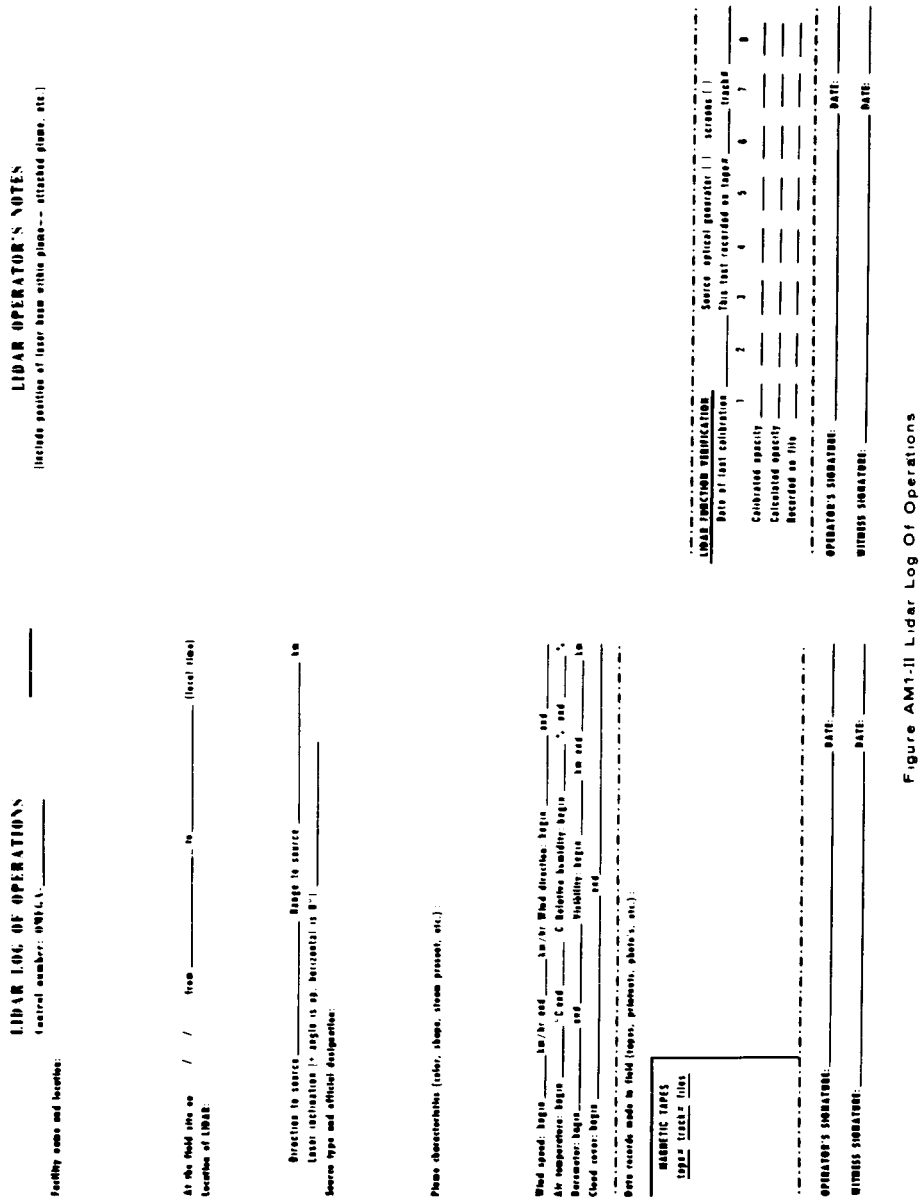
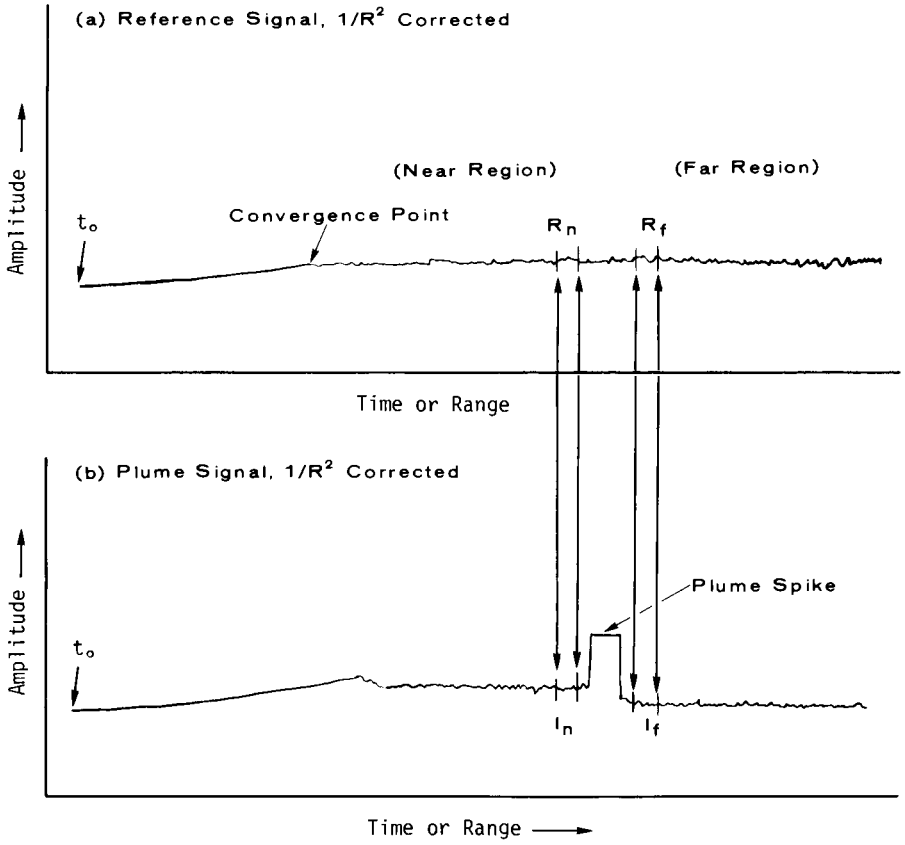


Figure AM1-11 Lidar Log Of Operations



(a) Reference signal, $1/R^2$-corrected. This reference signal is for plume signal (b). R_n, R_f are chosen to coincide with I_n, I_f.

(b) Plume signal, $1/R^2$-corrected. The plume spike and the decrease in the backscatter signal amplitude in the far region are due to the opacity of the plume. I_n, I_f are chosen as indicated in Section 2.6.

Figure AM1-III. Plots of Lidar Backscatter Signals

2.6 Opacity Calculation and Data Analysis. Referring to the reference signal and plume signal in Figure AM1–III, the measured opacity (O_p) in percent for each lidar measurement is calculated using Equation AM1–2. ($O_p = 1 - T_p$; T_p is the plume transmittance.)

$$O_p = (100\%)\left[1 - \left(\frac{I_f}{R_f}\frac{R_n}{I_n}\right)^{\frac{1}{2}}\right], \qquad \text{(AM1-2)}$$

Where:

I_n = near-region pick interval signal amplitude, plume signal, $1/R^2$ corrected,

I_f = far-region pick interval signal amplitude, plume signal, $1/R^2$ corrected,

R_n = near-region pick interval signal amplitude, reference signal, $1/R^2$ corrected, and

R_f = far-region pick interval signal amplitude, reference signal, $1/R^2$ corrected.

The $1/R^2$ correction to the plume and reference signal amplitudes is made by multiplying the amplitude for each successive sample interval from the time reference, by the square of the lidar time (or range) associated with that sample interval [Reference 5.1].

The first step in selecting the pick intervals for Equation AM1–2 is to divide the plume signal amplitude by the reference signal amplitude at the same respective ranges to obtain a ''normalized'' signal. The pick intervals selected using this normalized signal, are a minimum of 15 m (100 nanoseconds) in length and consist of at least 5 contiguous sample intervals. In addition, the following criteria, listed in order of importance, govern pick interval selection. (1) The intervals shall be in a region of the normalized signal where the reference signal meets the requirements of section 2.3 and is everywhere greater than zero. (2) The intervals (near and far) with the minimum average amplitude are chosen. (3) If more than one interval with the same minimum average amplitude is found, the interval closest to the plume is chosen. (4) The standard deviation, S_o, for the calculated opacity shall be 8% or less. (S_o is calculated by Equation AM1–7).

If S_o is greater than 8%, then the far pick interval shall be changed to the next interval of minimal average amplitude. If S_o is still greater than 8%, then this procedure is repeated for the far pick interval. This procedure may be repeated once again for the near pick interval, but if S_o remains greater than 8%, the plume signal shall be discarded.

The reference signal pick intervals, R_n and R_f, must be chosen over the same time interval as the plume signal pick intervals, I_n and I_f, respectively [Figure AM1–III]. Other methods of selecting pick intervals may be used if they give equivalent results. Field-oriented examples of pick interval selection are available in Reference 5.1.

The average amplitudes for each of the pick intervals, I_n, I_f, R_n, R_f, shall be calculated by averaging the respective individual amplitudes of the sample intervals from the plume signal and the associated reference signal each corrected for $1/R^2$. The amplitude of I_n shall be calculated according to Equation (AM–3).

$$I_n = \frac{1}{m}\sum_{i=1}^{m} I_{ni}, \qquad \text{(AM1-3)}$$

Where:

I_{ni} = the amplitude of the ith sample interval (near-region),

Σ = sum of the individual amplitudes for the sample intervals,

m = number of sample intervals in the pick interval, and

I_n = average amplitude of the near-region pick interval.

Similarly, the amplitudes for I_f, R_n, and R_f are calculated with the three expressions in Equation (AM1–4).

$$I_f = \frac{1}{m}\sum_{i=1}^{m} I_{fi}, \quad R_n = \frac{1}{m}\sum_{i=1}^{m} R_{ni}, \quad R_f = \frac{1}{m}\sum_{i=1}^{m} R_{fi}. \qquad \text{(AM1-4)}$$

The standard deviation, S_{In}, of the set of amplitudes for the near-region pick interval, I_n, shall be calculated using Equation (AM1–5).

Similarly, the standard deviations S_{If}, S_{Rn}, and S_{Rf} are calculated with the three expressions in Equation (AM1–6).

$$S_{In} = \left[\sum_{i=1}^{m} \frac{(I_{ni} - I_n)^2}{(m-1)} \right]^{1/2} \qquad S_{If} = \left[\sum_{i=1}^{m} \frac{(I_{fi} - I_f)^2}{(m-1)} \right]^{1/2} \qquad \text{(AM1-5)}$$

$$S_{Rn} = \left[\sum_{i=1}^{m} \frac{(R_{ni} - R_n)^2}{(m-1)} \right]^{1/2},$$

$$S_{Rf} = \left[\sum_{i=1}^{m} \frac{(R_{fi} - R_f)^2}{(m-1)} \right]^{1/2}. \qquad \text{(AM1-6)}$$

The standard deviation, S_o, for each associated opacity value, O_p, shall be calculated using Equation (AM1–7).

$$S_o = \frac{(100\%)}{2} \left(\frac{I_f}{R_f} \frac{R_n}{I_n} \right)^{1/2} \left[\frac{S_{In}^2}{I_n^2} + \frac{S_{If}^2}{I_f^2} + \frac{S_{Rn}^2}{R_n^2} + \frac{S_{Rf}^2}{R_f^2} \right]^{1/2} \qquad \text{(AM1-7)}$$

The calculated values of I_n, I_f, R_n, R_f, S_{In}, S_{If}, S_{Rn}, S_{Rf}, O_p, and S_o should be recorded. Any plume signal with an S_o greater than 8% shall be discarded.

2.6.1 Azimuth Angle Correction. If the azimuth angle correction to opacity specified in this section is performed, then the elevation angle correction specified in section 2.6.2 shall not be performed. When opacity is measured in the residual region of an attached steam plume, and the lidar line-of-sight is not perpendicular to the plume, it may be necessary to correct the opacity measured by the lidar to obtain the opacity that would be measured on a path perpendicular to the plume. The following method, or any other method which produces equivalent results, shall be used to determine the need for a correction, to calculate the correction, and to document the point within the plume at which the opacity was measured.

Figure AM1–IV(b) shows the geometry of the opacity correction. L′ is the path through the plume along which the opacity measurement is made. P′ is the path perpendicular to the plume at the same point. The angle ε is the angle between L′ and the plume center line. The angle (π/2-ε), is the angle between the L′ and P′. The measured opacity, O_p, measured along the path L′ shall be corrected to obtain the corrected opacity, O_{pc}, for the path P′, using Equation (AM1–8).

$$O_{pc} = (100\%)\left[1 - (1 - 0.01\, O_p)^{\mathrm{Cos}\,(\pi/2-\varepsilon)} \right]$$

$$= (100\%)\left[1 - (1 - 0.01\, O_p)^{\mathrm{Sin}\,\varepsilon} \right] \qquad \text{(AM1-8)}$$

The correction in Equation (AM1–8) shall be performed if the inequality in Equation (AM1–9) is true.

$$\varepsilon \geq \mathrm{Sin}^{-1}\left[\frac{\ln(101 - O_p)}{\ln(100 - O_p)}\right] \qquad \text{(AM1-9)}$$

Figure AM1–IV(a) shows the geometry used to calculate ε and the position in the plume at which the lidar measurement is made. This analysis assumes that for a given lidar measurement, the range from the lidar to the plume, the elevation angle of the lidar from the horizontal plane, and the azimuth angle of the lidar from an arbitrary fixed reference in the horizontal plane can all be obtained directly.

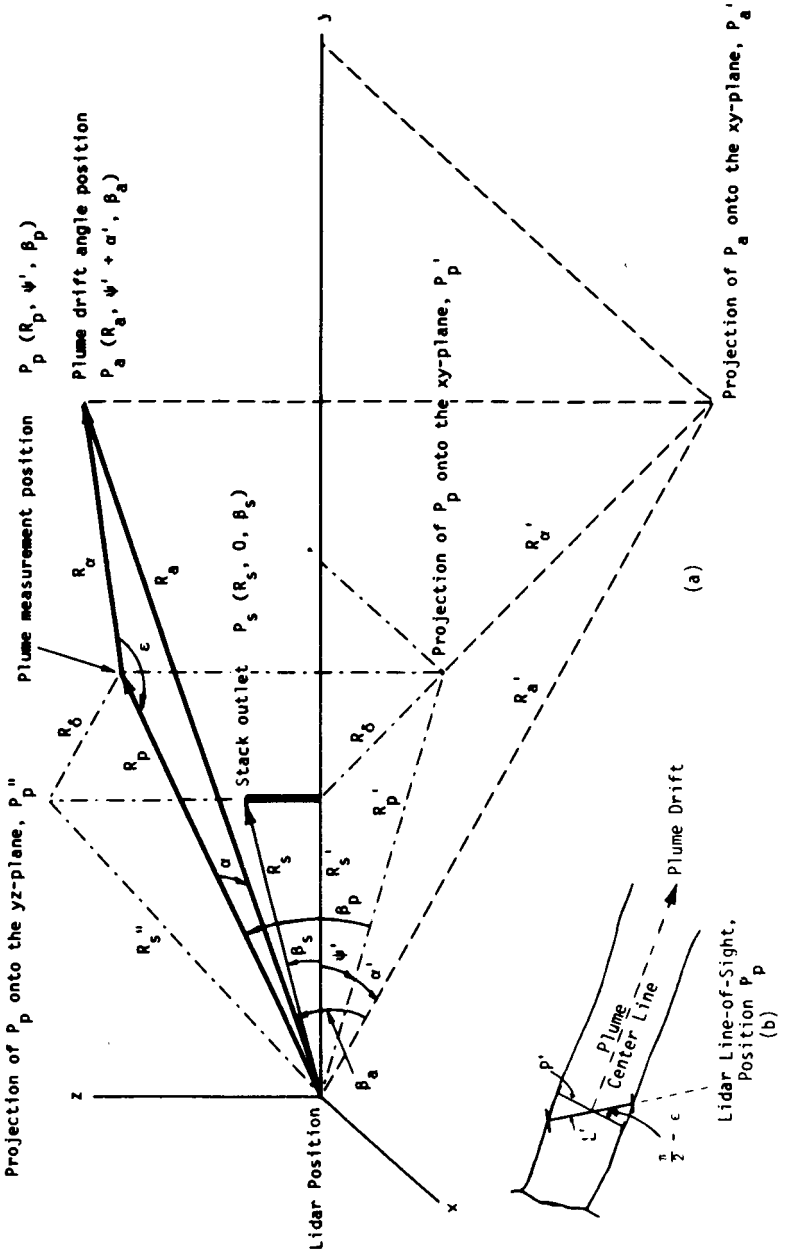


Figure AMI - IV. Correction in Opacity for Drift of the Residual Region of an Attached Steam Plume.

R_s = range from lidar to source*
β_s = elevation angle of R_s*
R_p = range from lidar to plume at the opacity measurement point*
β_p = elevation angle of R_p*
R_a = range from lidar to plume at some arbitrary point, P_a, so the drift angle of the plume can be determined*

β_a = elevation angle of R_a*
α = angle between R_p and R_a
R'_s = projection of R_s in the horizontal plane
R'_p = projection of R_p in the horizontal plane
R'_a = projection of R_a in the horizontal plane
ψ' = angle between R'_s and R'_p*
α' = angle between R'_p and R'_a*
R≤ = distance from the source to the opacity measurement point projected in the horizontal plane
Rθ = distance from opacity measurement point P_p to the point in the plume P_a.

$$O_{pc} = 1 - (1 - O_p)^{\mathrm{Cos}\,(\pi/2-\varepsilon)} = 1 - (1 - O_p)^{\mathrm{Sin}\,\varepsilon} \qquad \text{(AMI-8)}$$

The correction angle ε shall be determined using Equation AM1–10.

Where:

$\alpha = \mathrm{Cos}^{-1}\,(\mathrm{Cos}\beta_p\,\mathrm{Cos}\beta_a\,\mathrm{Cos}\alpha' + \mathrm{Sin}\beta_p\,\mathrm{Sin}\beta_a)$, and

$R\theta = (R_p 2 + R_a 2 - 2\,R_p\,R_a\,\mathrm{Cos}\alpha)^{1/2}$

R≤, the distance from the source to the opacity measurement point projected in the horizontal plane, shall be determined using Equation AM1–11.

$$R_\delta = (R'^2_s + R'^2_p - 2R'_sR'_p\mathrm{Cos}\psi')^{\frac{1}{2}}, \qquad \text{(AM1-11)}$$

Where:

$R'_s = R_s\,\mathrm{Cos}\,\beta_s$, and
$R'_p = R_p\,\mathrm{Cos}\,\beta_p$.

In the special case where the plume centerline at the opacity measurement point is horizontal, parallel to the ground, Equation AM1–12 may be used to determine ε instead of Equation AM1–10.

$$\varepsilon = \mathrm{Cos}^{-1}\left[\frac{R_p^2 + R_\delta^2 - R''^2_s}{2\,R_p\,R_\delta}\right] \qquad \text{(AM1-12)}$$

Where:

$R''_s = (R'^2_s + R_p^2\mathrm{Sin}^2\beta_p)^{1/2}$.

If the angle ε is such that ε≤30° or ε ≥150°, the azimuth angle correction shall not be performed and the associated opacity value shall be discarded.

2.6.2 Elevation Angle Correction. An individual lidar-measured opacity, O_p, shall be corrected for elevation angle if the laser elevation or inclination angle, β_p [Figure AM1–V], is greater than or equal to the value calculated in Equation AM1–13.

$$\beta_p \geq \mathrm{Cos}^{-1}\left[\frac{\ln\,(101 - O_p)}{\ln\,(100 - O_p)}\right] \qquad \text{(AM1-13)}$$

The measured opacity, O_p, along the lidar path L, is adjusted to obtain the corrected opacity, O_{pc}, for the actual plume (horizontal) path, P, by using Equation (AM1–14).

*Obtained directly from lidar. These values should be recorded.

$$O_{pc} = (100\%)\left[1-\left(1-0.01\,O_p\right)^{Cos\beta}p\right], \qquad (AM1\text{-}14)$$

Where:

β_p = lidar elevation or inclination angle,
O_p = measured opacity along path L, and
O_{pc} = corrected opacity for the actual plume thickness P.

The values for β_p, O_p and O_{pc} should be recorded.

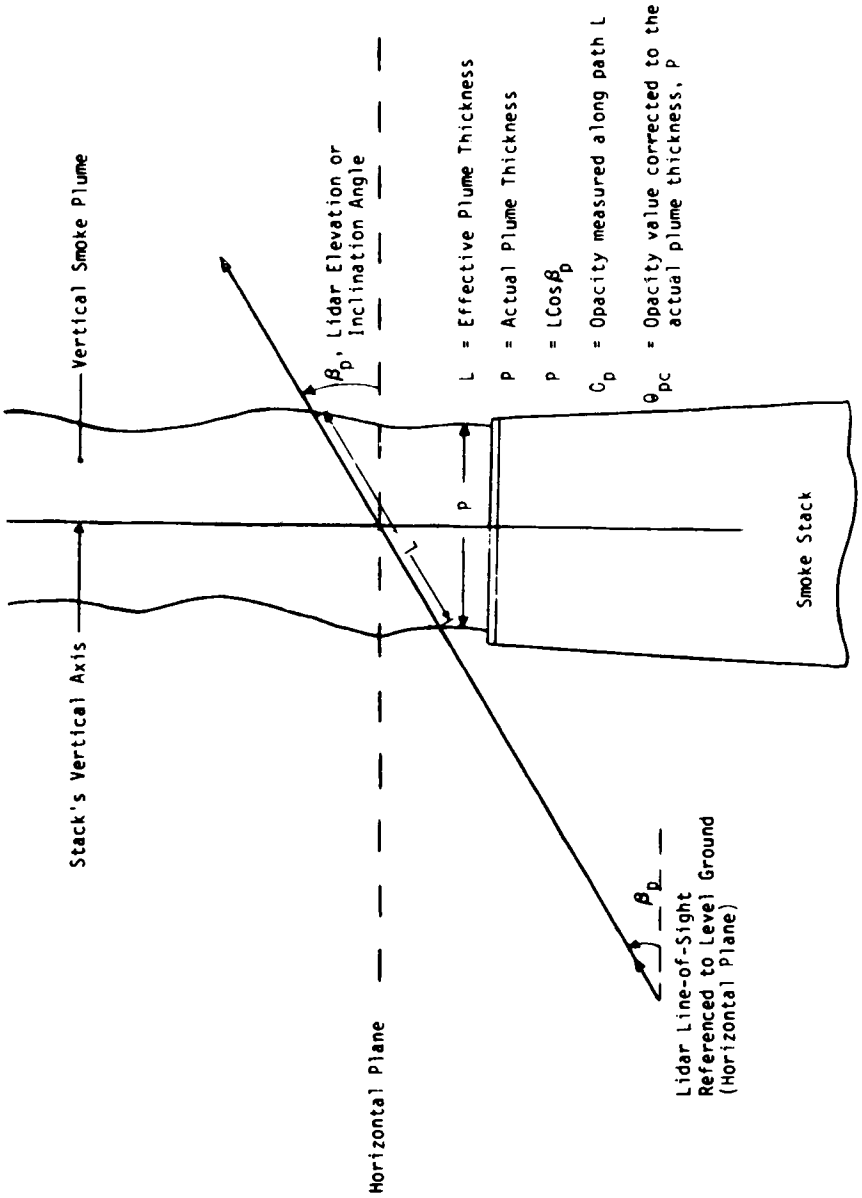


Figure AM1-V. Elevation Angle Correction for Vertical Plumes.

2.6.3 Determination of Actual Plume Opacity. Actual opacity of the plume shall be determined by Equation AM1–15.

$$O_{pa} = O_{pc} - [2\ S_o + 5\%]. \quad \text{(AM1-15)}$$

2.6.4 Calculation of Average Actual Plume Opacity. The average of the actual plume opacity, O_{pa}, shall be calculated as the average of the consecutive individual actual opacity values, O_{pa}, by Equation AM1–16.

$$\bar{O}_{pa} = \frac{1}{n}\sum_{k=1}^{n}(O_{pa})_k \quad , \qquad \text{(AM1-16)}$$

Where:

$(O_{pa})_k$ = the kth actual opacity value in an averaging interval containing n opacity values; k is a summing index.

Σ = the sum of the individual actual opacity values.

n = the number of individual actual opacity values contained in the averaging interval.

O_{pa} = average actual opacity calculated over the averaging interval.

3. Lidar Performance Verification

The lidar shall be subjected to two types of performance verifications that shall be performed in the field. The annual calibration, conducted at least once a year, shall be used to directly verify operation and performance of the entire lidar system. The routine verification, conducted for each emission source measured, shall be used to insure proper performance of the optical receiver and associated electronics.

3.1 Annual Calibration Procedures. Either a plume from a smoke generator or screen targets shall be used to conduct this calibration.

If the screen target method is selected, five screens shall be fabricated by placing an opaque mesh material over a narrow frame (wood, metal extrusion, etc.). The screen shall have a surface area of at least one square meter. The screen material should be chosen for precise optical opacities of about 10, 20, 40, 60, and 80%. Opacity of each target shall be optically determined and should be recorded. If a smoke generator plume is selected, it shall meet the requirements of section 3.3 of Reference Method 9. This calibration shall be performed in the field during calm (as practical) atmospheric conditions. The lidar shall be positioned in accordance with section 2.1.

The screen targets must be placed perpendicular to and coincident with the lidar line-of-sight at sufficient height above the ground (suggest about 30 ft) to avoid ground-level dust contamination. Reference signals shall be obtained just prior to conducting the calibration test.

The lidar shall be aimed through the center of the plume within 1 stack diameter of the exit, or through the geometric center of the screen target selected. The lidar shall be set in operation for a 6-minute data run at a nominal pulse rate of 1 pulse every 10 seconds. Each backscatter return signal and each respective opacity value obtained from the smoke generator transmissometer, shall be obtained in temporal coincidence. The data shall be analyzed and reduced in accordance with section 2.6 of this method. This calibration shall be performed for 0% (clean air), and at least five other opacities (nominally 10, 20, 40, 60, and 80%).

The average of the lidar opacity values obtained during a 6-minute calibration run shall be calculated and should be recorded. Also the average of the opacity values obtained from the smoke generator transmissometer for the same 6-minute run shall be calculated and should be recorded.

Alternate calibration procedures that do not meet the above requirements but produce equivalent results may be used.

3.2 Routine Verification Procedures. Either one of two techniques shall be used to conduct this verification. It shall be performed at least once every 4 hours for each emission source measured. The following parameters shall be directly verified.

1) The opacity value of 0% plus a minimum of 5 (nominally 10, 20, 40, 60, and 80%) opacity values shall be verified through the PMT detector and data processing electronics.

2) The zero-signal level (receiver signal with no optical signal from the source present) shall be inspected to insure that no spurious noise is present in the signal. With the entire lidar receiver and analog/digital electronics turned on and adjusted for normal operating performance, the following procedures shall be used for Techniques 1 and 2, respectively.

3.2.1 Procedure for Technique 1. This test shall be performed with no ambient or stray light reaching the PMT detector. The narrow band filter (694.3 nanometers peak) shall be removed from its position in front of the PMT detector. Neutral density filters of nominal opacities of 10, 20, 40, 60, and 80% shall be used. The recommended test configuration is depicted in Figure AM1–VI.

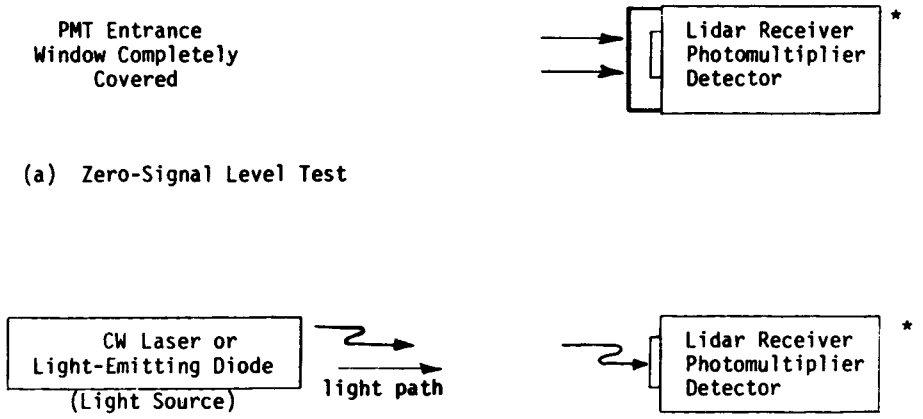


Figure AM1–VI. Test Configuration for Technique 1.

The zero-signal level shall be measured and should be recorded, as indicated in Figure AM1–VI(a). This simulated clear-air or 0% opacity value shall be tested in using the selected light source depicted in Figure AM1–VI(b).

The light source either shall be a continuous wave (CW) laser with the beam mechanically chopped or a light emitting diode controlled with a pulse generator (rectangular pulse). (A laser beam may have to be attenuated so as not to saturate the PMT detector). This signal level shall be measured

and should be recorded. The opacity value is calculated by taking two pick intervals [Section 2.6] about 1 microsecond apart in time and using Equation (AM1–2) setting the ratio $R_n/R_f = 1$. This calculated value should be recorded.

The simulated clear-air signal level is also employed in the optical test using the neutral density filters. Using the test configuration in Figure AM1–VI(c), each neutral density filter shall be separately placed into the light path from the light source to the PMT detector. The signal level shall be measured and should be recorded. The opacity value for each filter is calculated by taking the signal level for that respective filter (I_f), dividing it by the 0% opacity signal level (I_n) and performing the remainder of the calculation by Equation (AM1–2) with $R_n/R_f = 1$. The calculated opacity value for each filter should be recorded.

The neutral density filters used for Technique 1 shall be calibrated for actual opacity with accuracy of ±2% or better. This calibration shall be done monthly while the filters are in use and the calibrated values should be recorded.

3.2.2 Procedure for Technique 2. An optical generator (built-in calibration mechanism) that contains a light-emitting diode (red light for a lidar containing a ruby laser) is used. By injecting an optical signal into the lidar receiver immediately ahead of the PMT detector, a backscatter signal is simulated. With the entire lidar receiver electronics turned on and adjusted for normal operating performance, the optical generator is turned on and the simulation signal (corrected for $1/R^2$) is selected with no plume spike signal and with the opacity value equal to 0%. This simulated clear-air atmospheric return signal is displayed on the system's video display. The lidar operator then makes any fine adjustments that may be necessary to maintain the system's normal operating range.

The opacity values of 0% and the other five values are selected one at a time in any order. The simulated return signal data should be recorded. The opacity value shall be calculated. This measurement/calculation shall be performed at least three times for each selected opacity value. While the order is not important, each of the opacity values from the optical generator shall be verified. The calibrated optical generator opacity value for each selection should be recorded.

The optical generator used for Technique 2 shall be calibrated for actual opacity with an accuracy of ±1% or better. This calibration shall be done monthly while the generator is in use and calibrated value should be recorded.

Alternate verification procedures that do not meet the above requirements but produce equivalent results may be used.

3.3 Deviation. The permissible error for the annual calibration and routine verification are:

3.3.1 Annual Calibration Deviation.

3.3.1.1 Smoke Generator. If the lidar-measured average opacity for each data run is not within ±5% (full scale) of the respective smoke generator's average opacity over the range of 0% through 80%, then the lidar shall be considered out of calibration.

3.3.1.2 Screens. If the lidar-measured average opacity for each data run is not within ±3% (full scale) of the laboratory-determined opacity for each respective simulation screen target over the range of 0% through 80%, then the lidar shall be considered out of calibration.

3.3.2 Routine Verification Error. If the lidar-measured average opacity for each neutral density filter (Technique 1) or optical generator selection (Technique 2) is not within ±3% (full scale) of the respective laboratory calibration value then the lidar shall be considered non-operational.

4. Performance/Design Specification for Basic Lidar System

4.1 Lidar Design Specification. The essential components of the basic lidar system are a pulsed laser (transmitter), optical receiver, detector, signal processor, recorder, and an aiming device that is used in aiming the lidar transmitter and receiver. Figure AM1–VII shows a functional block diagram of a basic lidar system.

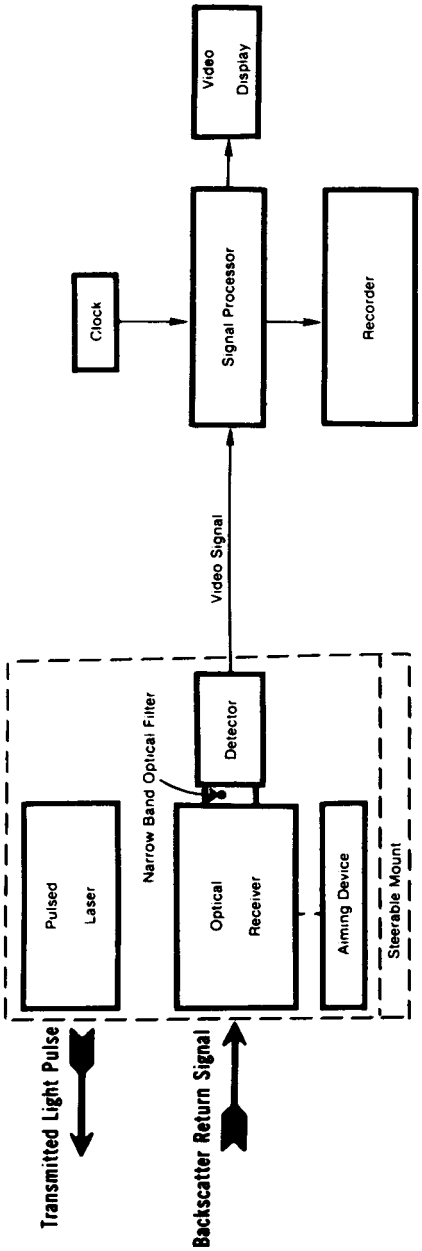


Figure AM1-VII. Functional Block Diagram of a Basic Lidar System

4.2 Performance Evaluation Tests. The owner of a lidar system shall subject such a lidar system to the performance verification tests described in section 3, prior to first use of this method. The annual calibration shall be performed for three separate, complete

runs and the results of each should be recorded. The requirements of section 3.3.1 must be fulfilled for each of the three runs.

Once the conditions of the annual calibration are fulfilled the lidar shall be subjected to the routine verification for three separate complete runs. The requirements of section 3.3.2 must be fulfilled for each of the three runs and the results should be recorded. The Administrator may request that the results of the performance evaluation be submitted for review.

5. References

5.1 The Use of Lidar for Emissions Source Opacity Determination, U.S. Environmental Protection Agency, National Enforcement Investigations Center, Denver, CO. EPA–330/1–79–003–R, Arthur W. Dybdahl, current edition [NTIS No. PB81–246662].

5.2 Field Evaluation of Mobile Lidar for the Measurement of Smoke Plume Opacity, U.S. Environmental Protection Agency, National Enforcement Investigations Center, Denver, CO. EPA/NEIC-TS-128, February 1976.

5.3 Remote Measurement of Smoke Plume Transmittance Using Lidar, C. S. Cook, G. W. Bethke, W. D. Conner (EPA/RTP). Applied Optics 11, pg 1742. August 1972.

5.4 Lidar Studies of Stack Plumes in Rural and Urban Environments, EPA–650/4–73–002, October 1973.

5.5 American National Standard for the Safe Use of Lasers ANSI Z 136.1–176, March 8, 1976.

5.6 U.S. Army Technical Manual TB MED 279, Control of Hazards to Health from Laser Radiation, February 1969.

5.7 Laser Institute of America Laser Safety Manual, 4th Edition.

5.8 U.S. Department of Health, Education and Welfare, Regulations for the Administration and Enforcement of the Radiation Control for Health and Safety Act of 1968, January 1976.

5.9 Laser Safety Handbook, Alex Mallow, Leon Chabot, Van Nostrand Reinhold Co., 1978.

Method 10—Determination of Carbon Monoxide Emissions From Stationary Sources (Instrumental Analyzer Procedure)

1.0 Scope and Application

What is Method 10?

Method 10 is a procedure for measuring carbon monoxide (CO) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis. This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 4—Determination of Moisture Content in Stack Gases.

(c) Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure).

1.1 Analytes. What does this method determine? This method measures the concentration of carbon monoxide.

Analyte	CAS No.	Sensitivity
CO	630–08–0	Typically <2% of Calibration Span.

1.2 Applicability. When is this method required? The use of Method 10 may be required by specific New Source Performance Standards, State Implementation Plans, and permits where CO concentrations in stationary source emissions must be measured, either to determine compliance with an applicable emission standard or to conduct performance testing of a continuous emission monitoring system (CEMS). Other regulations may also require the use of Method 10.

1.3 Data Quality Objectives. Refer to section 1.3 of Method 7E.

2.0 Summary of Method

In this method, you continuously or intermittently sample the effluent gas and convey the sample to an analyzer that measures the concentration of CO. You must meet the performance requirements of this method to validate your data.

3.0 Definitions

Refer to section 3.0 of Method 7E for the applicable definitions.

4.0 Interferences

Substances having a strong absorption of infrared energy may interfere to some extent in some analyzers. Instrumental correction may be used to compensate for the interference. You may also use silica gel and ascarite traps to eliminate the interferences. If this option is used, correct the measured

gas volume for the carbon dioxide (CO_2) removed in the trap.

5.0 Safety

Refer to section 5.0 of Method 7E.

6.0 Equipment and Supplies

What do I need for the measurement system?

6.1 Continuous Sampling. Figure 7E–1 of Method 7E is a schematic diagram of an acceptable measurement system. The components are the same as those in sections 6.1 and 6.2 of Method 7E, except that the CO analyzer described in section 6.2 of this method must be used instead of the analyzer described in section 6.2 of Method 7E. You must follow the noted specifications in section 6.1 of Method 7E except that the requirements to use stainless steel, Teflon, or non-reactive glass filters do not apply. Also, a heated sample line is not required to transport dry gases or for systems that measure the CO concentration on a dry basis.

6.2 Integrated Sampling.

6.2.1 Air-Cooled Condenser or Equivalent. To remove any excess moisture.

6.2.2 Valve. Needle valve, or equivalent, to adjust flow rate.

6.2.3 Pump. Leak-free diaphragm type, or equivalent, to transport gas.

6.2.4 Rate Meter. Rotameter, or equivalent, to measure a flow range from 0 to 1.0 liter per minute (0.035 cfm).

6.2.5 Flexible Bag. Tedlar, or equivalent, with a capacity of 60 to 90 liters (2 to 3 ft^3). (Verify through the manufacturer that the Tedlar alternative is suitable for CO and make this verified information available for inspection.) Leak-test the bag in the laboratory before using by evacuating with a pump followed by a dry gas meter. When the evacuation is complete, there should be no flow through the meter.

6.2.6 Sample Tank. Stainless steel or aluminum tank equipped with a pressure indicator with a minimum volume of 4 liters.

6.3 What analyzer must I use? You must use an instrument that continuously measures CO in the gas stream and meets the specifications in section 13.0. The dual-range analyzer provisions in section 6.2.8.1 of Method 7E apply.

7.0 Reagents and Standards

7.1 Calibration Gas. What calibration gases do I need? Refer to section 7.1 of Method 7E for the calibration gas requirements.

7.2 Interference Check. What additional reagents do I need for the interference check? Use the appropriate test gases listed in Table 7E–3 of Method 7E (i.e., potential interferents, as identified by the instrument manufacturer) to conduct the interference check.

8.0 Sample Collection, Preservation, Storage, and Transport

Emission Test Procedure

8.1 Sampling Site and Sampling Points. You must follow section 8.1 of Method 7E.

8.2 Initial Measurement System Performance Tests. You must follow the procedures in section 8.2 of Method 7E. If a dilution-type measurement system is used, the special considerations in section 8.3 of Method 7E also apply.

8.3 Interference Check. You must follow the procedures of section 8.2.7 of Method 7E.

8.4 Sample Collection.

8.4.1 Continuous Sampling. You must follow the procedures of section 8.4 of Method 7E.

8.4.2 Integrated Sampling. Evacuate the flexible bag or sample tank. Set up the equipment as shown in Figure 10–1 with the bag disconnected. Place the probe in the stack and purge the sampling line. Connect the bag, making sure that all connections are leak-free. Sample at a rate proportional to the stack velocity. If needed, the CO_2 content of the gas may be determined by using the Method 3 integrated sample procedures, or by weighing an ascarite CO_2 removal tube used and computing CO_2 concentration from the gas volume sampled and the weight gain of the tube. Data may be recorded on a form similar to Table 10–1. If a sample tank is used for sample collection, follow procedures similar to those in sections 8.1.2, 8.2.3, 8.3, and 12.4 of Method 25 as appropriate to prepare the tank, conduct the sampling, and correct the measured sample concentration.

8.5 Post-Run System Bias Check, Drift Assessment, and Alternative Dynamic Spike Procedure. You must follow the procedures in sections 8.5 and 8.6 of Method 7E.

9.0 Quality Control

Follow the quality control procedures in section 9.0 of Method 7E.

10.0 Calibration and Standardization

Follow the procedures for calibration and standardization in section 10.0 of Method 7E.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the procedures for calculations and data analysis in section 12.0 of Method 7E, as applicable, substituting CO for NO_X as applicable.

12.1 Concentration Correction for CO_2 Removal. Correct the CO concentration for CO_2 removal (if applicable) using Eq. 10–1.

$$C_{Avg} = C_{CO\ stack}\left(1 - F_{CO2}\right)$$

Where:

C_{Avg} = Average gas concentration for the test run, ppm.

$C_{CO\ stack}$ = Average unadjusted stack gas CO concentration indicated by the data recorder for the test run, ppmv.

F_{CO2} = Volume fraction of CO_2 in the sample, i.e., percent CO_2 from Orsat analysis divided by 100.

13.0 Method Performance

The specifications for analyzer calibration error, system bias, drift, interference check, and alternative dynamic spike procedure are the same as in section 13.0 of Method 7E.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

The dynamic spike procedure and the manufacturer stability test are the same as in sections 16.1 and 16.3 of Method 7E

17.0 References

1. ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards— September 1997 as amended, EPA–600/R–97/121

18.0 Tables, Diagrams, Flowcharts, and Validation Data

Figure 10-1. Integrated Gas Sampling Train.

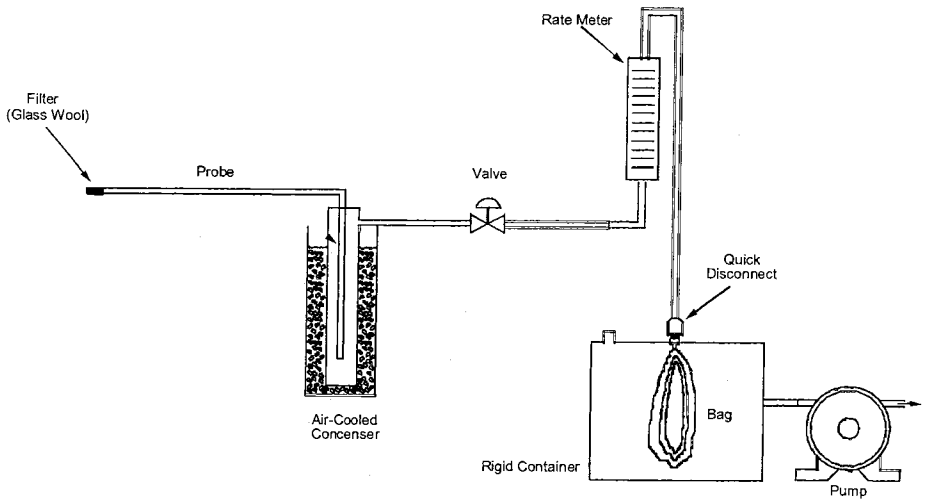


TABLE 10–1—FIELD DATA

[Integrated sampling]

Location:	Date:	
Test:	Operator:	
Clock Time	Rotameter Reading liters/min (cfm)	Comments

TABLE 10–1—FIELD DATA—Continued

[Integrated sampling]

METHOD 10A—DETERMINATION OF CARBON MONOXIDE EMISSIONS IN CERTIFYING CONTINUOUS EMISSION MONITORING SYSTEMS AT PETROLEUM REFINERIES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 4, and Method 5.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Carbon monoxide (CO)	630–08–0	3 ppmv

1.2 Applicability. This method is applicable for the determination of CO emissions at petroleum refineries. This method serves as the reference method in the relative accuracy test for nondispersive infrared (NDIR) CO continuous emission monitoring systems (CEMS) that are required to be installed in petroleum refineries on fluid catalytic cracking unit catalyst regenerators (§60.105(a)(2) of this part).

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

An integrated gas sample is extracted from the stack, passed through an alkaline permanganate solution to remove sulfur oxides and nitrogen oxides, and collected in a Tedlar or equivalent bag. (Verify through the manufacturer that the Tedlar alternative is suitable for NO and make this verified information available for inspection.) The CO concentration in the sample is measured spectrophotometrically using the reaction of CO with *p*-sulfaminobenzoic acid.

3.0 Definitions [Reserved]

4.0 Interferences

Sulfur oxides, nitric oxide, and other acid gases interfere with the colorimetric reaction. They are removed by passing the sampled gas through an alkaline potassium permanganate scrubbing solution. Carbon dioxide (CO_2) does not interfere, but, because it is removed by the scrubbing solution, its concentration must be measured independently and an appropriate volume correction made to the sampled gas.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs.

Reacts exothermically with limited amounts of water.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling train shown in Figure 10A–1 is required for sample collection. Component parts are described below:

6.1.1 Probe. Stainless steel, sheathed Pyrex glass, or equivalent, equipped with a glass wool plug to remove particulate matter.

6.1.2 Sample Conditioning System. Three Greenburg-Smith impingers connected in series with leak-free connections.

6.1.3 Pump. Leak-free pump with stainless steel and Teflon parts to transport sample at a flow rate of 300 ml/min (0.01 ft^3/min) to the flexible bag.

6.1.4 Surge Tank. Installed between the pump and the rate meter to eliminate the pulsation effect of the pump on the rate meter.

6.1.5 Rate Meter. Rotameter, or equivalent, to measure flow rate at 300 ml/min (0.01 ft^3/min). Calibrate according to section 10.2.

6.1.6 Flexible Bag. Tedlar, or equivalent, with a capacity of 10 liters (0.35 ft^3) and equipped with a sealing quick-connect plug. The bag must be leak-free according to section 8.1. For protection, it is recommended that the bag be enclosed within a rigid container.

6.1.7 Sample Tank. Stainless steel or aluminum tank equipped with a pressure indicator with a minimum volume of 10 liters.

6.1.8 Valves. Stainless-steel needle valve to adjust flow rate, and stainless-steel 3-way valve, or equivalent.

6.1.9 CO_2 Analyzer. Fyrite, or equivalent, to measure CO_2 concentration to within 0.5 percent.

6.1.10 Volume Meter. Dry gas meter, capable of measuring the sample volume under calibration conditions of 300 ml/min (0.01 ft^3/min) for 10 minutes.

6.1.11 Pressure Gauge. A water filled U-tube manometer, or equivalent, of about 30 cm (12 in.) to leak-check the flexible bag.

6.2 Sample Analysis.

6.2.1 Spectrophotometer. Single- or double-beam to measure absorbance at 425 and 600 nm. Slit width should not exceed 20 nm.

6.2.2 Spectrophotometer Cells. 1-cm pathlength.

6.2.3 Vacuum Gauge. U-tube mercury manometer, 1 meter (39 in.), with 1-mm divisions, or other gauge capable of measuring pressure to within 1 mm Hg.

6.2.4 Pump. Capable of evacuating the gas reaction bulb to a pressure equal to or less than 40 mm Hg absolute, equipped with coarse and fine flow control valves.

6.2.5 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm Hg.

6.2.6 Reaction Bulbs. Pyrex glass, 100-ml with Teflon stopcock (Figure 10A–2), leak-free at 40 mm Hg, designed so that 10 ml of the colorimetric reagent can be added and removed easily and accurately. Commercially available gas sample bulbs such as Supelco Catalog No. 2–2161 may also be used.

6.2.7 Manifold. Stainless steel, with connections for three reaction bulbs and the appropriate connections for the manometer and sampling bag as shown in Figure 10A–3.

6.2.8 Pipets. Class A, 10–ml size.

6.2.9 Shaker Table. Reciprocating-stroke type such as Eberbach Corporation, Model 6015. A rocking arm or rotary-motion type shaker may also be used. The shaker must be large enough to accommodate at least six gas sample bulbs simultaneously. It may be necessary to construct a table top extension for most commercial shakers to provide sufficient space for the needed bulbs (Figure 10A–4).

6.2.10 Valve. Stainless steel shut-off valve.

6.2.11 Analytical Balance. Capable of weighing to 0.1 mg.

7.0 Reagents and Standards

Unless otherwise indicated, all reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, the best available grade shall be used.

7.1 Sample Collection.

7.1.1 Water. Deionized distilled, to conform to ASTM D 1193–77 or 91, Type 3 (incorporated by reference—see §60.17). If high concentrations of organic matter are not expected to be present, the potassium permanganate test for oxidizable organic matter may be omitted.

7.1.2 Alkaline Permanganate Solution, 0.25 M $KMnO_4$/1.5 M Sodium Hydroxide (NaOH). Dissolve 40 g $KMnO_4$ and 60 g NaOH in approximately 900 ml water, cool, and dilute to 1 liter.

7.2 Sample Analysis.

7.2.1 Water. Same as in section 7.1.1.

7.2.2 1 M Sodium Hydroxide Solution. Dissolve 40 g NaOH in approximately 900 ml of water, cool, and dilute to 1 liter.

7.2.3 0.1 M NaOH Solution. Dilute 50 ml of the 1 M NaOH solution prepared in section 7.2.2 to 500 ml.

7.2.4 0.1 M Silver Nitrate ($AgNO_3$) Solution. Dissolve 8.5 g $AgNO_3$ in water, and dilute to 500 ml.

7.2.5 0.1 M Para-Sulfaminobenzoic Acid (p-SABA) Solution. Dissolve 10.0 g p-SABA in 0.1 M NaOH, and dilute to 500 ml with 0.1 M NaOH.

7.2.6 Colorimetric Solution. To a flask, add 100 ml of 0.1 M p-SABA solution and 100 ml of 0.1 M $AgNO_3$ solution. Mix, and add 50 ml of 1 M NaOH with shaking. The resultant solution should be clear and colorless. This solution is acceptable for use for a period of 2 days.

7.2.7 Standard Gas Mixtures. Traceable to National Institute of Standards and Technology (NIST) standards and containing between 50 and 1000 ppm CO in nitrogen. At least two concentrations are needed to span each calibration range used (Section 10.3). The calibration gases must be certified by the manufacturer to be within 2 percent of the specified concentrations.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sample Bag or Tank Leak-Checks. While a leak-check is required after bag or sample tank use, it should also be done before the bag or sample tank is used for sample collection. The tank should be leak-checked according to the procedure specified in section 8.1.2 of Method 25. The bag should be leak-checked in the inflated and deflated condition according to the following procedure:

8.1.1 Connect the bag to a water manometer, and pressurize the bag to 5 to 10 cm H_2O (2 to 4 in H_2O). Allow the bag to stand for 60 minutes. Any displacement in the water manometer indicates a leak.

8.1.2 Evacuate the bag with a leakless pump that is connected to the downstream side of a flow indicating device such as a 0- to 100-ml/min rotameter or an impinger containing water. When the bag is completely evacuated, no flow should be evident if the bag is leak-free.

8.2 Sample Collection.

8.2.1 Evacuate and leak check the sample bag or tank as specified in section 8.1. Assemble the apparatus as shown in Figure 10A–1. Loosely pack glass wool in the tip of the probe. Place 400 ml of alkaline permanganate solution in the first two impingers and 250 ml in the third. Connect the pump to the third impinger, and follow this with the surge tank, rate meter, and 3-way valve. Do not connect the bag or sample tank to the system at this time.

8.2.2 Leak-check the sampling system by plugging the probe inlet, opening the 3-way valve, and pulling a vacuum of approximately 250 mm Hg on the system while observing the rate meter for flow. If flow is indicated on the rate meter, do not proceed further until the leak is found and corrected.

8.2.3 Purge the system with sample gas by inserting the probe into the stack and drawing the sample gas through the system at 300 ml/min ±10 percent for 5 minutes. Connect the evacuated bag or sample tank to the system, record the starting time, and sample at a rate of 300 ml/min for 30 minutes, or until the bag is nearly full, or the sample tank reaches ambient pressure. Record the sampling time, the barometric pressure, and the ambient temperature. Purge the system as described above immediately before each sample.

8.2.4 The scrubbing solution is adequate for removing sulfur oxides and nitrogen oxides from 50 liters (1.8 ft^3) of stack gas when the concentration of each is less than 1,000 ppm and the CO_2 concentration is less than 15 percent. Replace the scrubber solution after every fifth sample.

8.3 Carbon Dioxide Measurement. Measure the CO_2 content in the stack to the nearest 0.5 percent each time a CO sample is collected. A simultaneous grab sample analyzed by the Fyrite analyzer is acceptable.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.1	Sampling equipment leak-checks and calibration.	Ensure accuracy and precision of sampling measurements.
10.3	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Gas Bulb Calibration. Weigh the empty bulb to the nearest 0.1 g. Fill the bulb to the stopcock with water, and again weigh to the nearest 0.1 g. Subtract the tare weight, and calculate the volume in liters to three significant figures using the density of water at the measurement temperature. Record the volume on the bulb. Alternatively, mark an identification number on the bulb, and record the volume in a notebook.

10.2 Rate Meter Calibration. Assemble the system as shown in Figure 10A–1 (the impingers may be removed), and attach a volume meter to the probe inlet. Set the rotameter at 300 ml/min, record the volume meter reading, start the pump, and pull ambient air through the system for 10 minutes. Record the final volume meter reading. Repeat the procedure and average the results to determine the volume of gas that passed through the system.

10.3 Spectrophotometer Calibration Curve.

10.3.1 Collect the standards as described in section 8.2. Prepare at least two sets of three bulbs as standards to span the 0 to 400 or 400 to 1000 ppm range. If any samples span both

concentration ranges, prepare a calibration curve for each range using separate reagent blanks. Prepare a set of three bulbs containing colorimetric reagent but no CO to serve as a reagent blank. Analyze each standard and blank according to the sample analysis procedure of section 11.0 Reject the standard set where any of the individual bulb absorbances differs from the set mean by more than 10 percent.

10.3.2 Calculate the average absorbance for each set (3 bulbs) of standards using Equation 10A–1 and Table 10A–1. Construct a graph of average absorbance for each standard against its corresponding concentration. Draw a smooth curve through the points. The curve should be linear over the two concentration ranges discussed in section 13.3.

11.0 Analytical Procedure

11.1 Assemble the system shown in Figure 10A–3, and record the information required in Table 10A–1 as it is obtained. Pipet 10.0 ml of the colorimetric reagent into each gas reaction bulb, and attach the bulbs to the system. Open the stopcocks to the reaction bulbs, but leave the valve to the bag closed. Turn on the pump, fully open the coarse-adjust flow valve, and slowly open the fine-adjust valve until the pressure is reduced to at least 40 mm Hg. Now close the coarse adjust valve, and observe the manometer to be certain that the system is leak-free. Wait a minimum of 2 minutes. If the pressure has increased less than 1 mm Hg, proceed as described below. If a leak is present, find and correct it before proceeding further.

11.2 Record the vacuum pressure (P_v) to the nearest 1 mm Hg, and close the reaction bulb stopcocks. Open the bag valve, and allow the system to come to atmospheric pressure. Close the bag valve, open the pump coarse adjust valve, and evacuate the system again. Repeat this fill/evacuation procedure at least twice to flush the manifold completely. Close the pump coarse adjust valve, open the bag valve, and let the system fill to atmospheric pressure. Open the stopcocks to the reaction bulbs, and let the entire system come to atmospheric pressure. Close the bulb stopcocks, remove the bulbs, record the room temperature and barometric pressure (P_{bar}, to nearest mm Hg), and place the bulbs on the shaker table with their main axis either parallel to or perpendicular to the plane of the table top. Purge the bulb-filling system with ambient air for several minutes between samples. Shake the samples for exactly 2 hours.

11.3 Immediately after shaking, measure the absorbance (A) of each bulb sample at 425 nm if the concentration is less than or equal to 400 ppm CO or at 600 nm if the concentration is above 400 ppm.

NOTE: This may be accomplished with multiple bulb sets by sequentially collecting sets and adding to the shaker at staggered intervals, followed by sequentially removing sets from the shaker for absorbance measurement after the two-hour designated intervals have elapsed.

11.4 Use a small portion of the sample to rinse a spectrophotometer cell several times before taking an aliquot for analysis. If one cell is used to analyze multiple samples, rinse the cell with deionized distilled water several times between samples. Prepare and analyze standards and a reagent blank as described in section 10.3. Use water as the reference. Reject the analysis if the blank absorbance is greater than 0.1. All conditions should be the same for analysis of samples and standards. Measure the absorbances as soon as possible after shaking is completed.

11.5 Determine the CO concentration of each bag sample using the calibration curve for the appropriate concentration range as discussed in section 10.3.

12.0 Calculations and Data Analysis

Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature.

A = Sample absorbance, uncorrected for the reagent blank.
A_r = Absorbance of the reagent blank.
A_s = Average sample absorbance per liter, units/liter.
B_w = Moisture content in the bag sample.
C = CO concentration in the stack gas, dry basis, ppm.
C_b = CO concentration of the bag sample, dry basis, ppm.
C_g = CO concentration from the calibration curve, ppm.
F = Volume fraction of CO_2 in the stack.
n = Number of reaction bulbs used per bag sample.
P_b = Barometric pressure, mm Hg.
P_v = Residual pressure in the sample bulb after evacuation, mm Hg.
P_w = Vapor pressure of H_2O in the bag (from Table 10A–2), mm Hg.
V_b = Volume of the sample bulb, liters.
V_r = Volume of reagent added to the sample bulb, 0.0100 liter.

12.2 Average Sample Absorbance per Liter. Calculate A_s for each gas bulb using Equation 10A–1, and record the value in Table 10A–1. Calculate the average A_s for each bag sample, and compare the three values to the average. If any single value differs by more than 10 percent from the average, reject this value, and calculate a new average using the two remaining values.

$$A_s = \frac{(A - A_r)(P_b)}{(V_b - V_r)(P_b - P_v)} \qquad \text{Eq. 10A-1}$$

NOTE: A and A_r must be at the same wavelength.

12.3 CO Concentration in the Bag. Calculate C_b using Equations 10A–2 and 10A–3. If condensate is visible in the bag, calculate B_w using Table 10A–2 and the temperature and barometric pressure in the analysis room. If condensate is not visible, calculate B_w using the temperature and barometric pressure at the sampling site.

$$B_w = \frac{P_w}{P_b} \qquad \text{Eq. 10A-2}$$

$$C_b = \frac{C_g}{(1 - B_w)} \qquad \text{Eq. 10A-3}$$

12.4 CO Concentration in the Stack.

$$C = C_b\,(1 - F) \qquad \text{Eq. 10A-4}$$

13.0 Method Performance

13.1 Precision. The estimated intralaboratory standard deviation of the method is 3 percent of the mean for gas samples analyzed in duplicate in the concentration range of 39 to 412 ppm. The interlaboratory precision has not been established.

13.2 Accuracy. The method contains no significant biases when compared to an NDIR analyzer calibrated with NIST standards.

13.3 Range. Approximately 3 to 1800 ppm CO. Samples having concentrations below 400 ppm are analyzed at 425 nm, and samples having concentrations above 400 ppm are analyzed at 600 nm.

13.4 Sensitivity. The detection limit is 3 ppmv based on a change in concentration equal to three times the standard deviation of the reagent blank solution.

13.5 Stability. The individual components of the colorimetric reagent are stable for at least one month. The colorimetric reagent must be used within two days after preparation to avoid excessive blank correction. The samples in the bag should be stable for at least one week if the bags are leak-free.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Butler, F.E., J.E. Knoll, and M.R. Midgett. Development and Evaluation of Methods for Determining Carbon Monoxide Emissions. U.S. Environmental Protection Agency, Research Triangle Park, N.C. June 1985. 33 pp.

2. Ferguson, B.B., R.E. Lester, and W.J. Mitchell. Field Evaluation of Carbon Monoxide and Hydrogen Sulfide Continuous Emission Monitors at an Oil Refinery. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA–600/4–82–054. August 1982. 100 pp.

3. Lambert, J.L., and R.E. Weins. Induced Colorimetric Method for Carbon Monoxide. Analytical Chemistry. *46*(7):929–930. June 1974.

4. Levaggi, D.A., and M. Feldstein. The Colorimetric Determination of Low Concentrations of Carbon Monoxide. Industrial Hygiene Journal. *25*:64–66. January-February 1964.

5. Repp, M. Evaluation of Continuous Monitors For Carbon Monoxide in Stationary Sources. U.S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA–600/2–77–063. March 1977. 155 pp.

6. Smith, F., D.E. Wagoner, and R.P. Donovan. Guidelines for Development of a Quality Assurance Program: Volume VIII—Determination of CO Emissions from Stationary Sources by NDIR Spectrometry. U.S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA–650/4–74–005–h. February 1975. 96 pp.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 10A–1—DATA RECORDING SHEET FOR SAMPLES ANALYZED IN TRIPLICATE

Sample No./type	Room temp °C	Stack %CO_2	Bulb No.	Bulb vol. liters	Reagent vol. in bulb, liter	Partial pressure of gas in bulb, mm Hg	$P_{b,r}$, mm Hg	Shaking time, min	Abs versus water	A-A_r	A_s	Avg A_s
blank												
Std. 1												
Std. 2												
Sample 1												
Sample 2												
Sample 3												

TABLE 10A–2—MOISTURE CORRECTION

Temperature °C	Vapor pressure of H_2O, mm Hg	Temperature °C	Vapor pressure of H_2, mm Hg
4	6.1	18	15.5
6	7.0	20	17.5
8	8.0	22	19.8
10	9.2	24	22.4
12	10.5	26	25.2
14	12.0	28	28.3
16	13.6	30	31.8

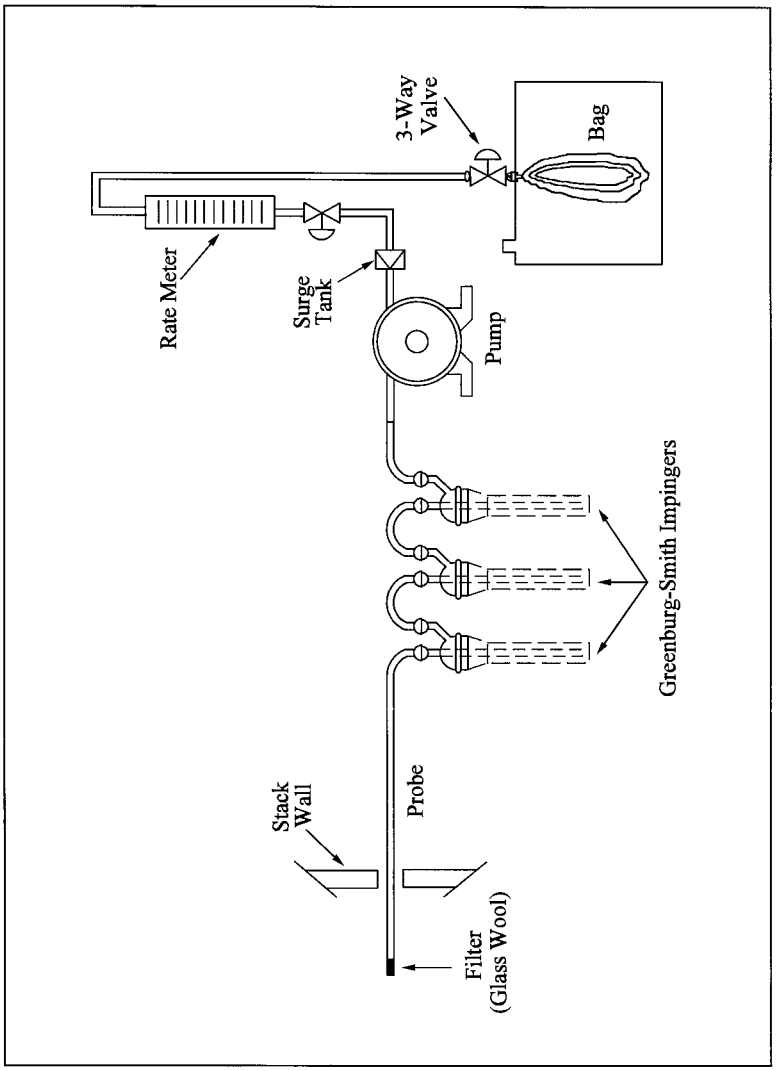


Figure 10A-1. Sampling Train.

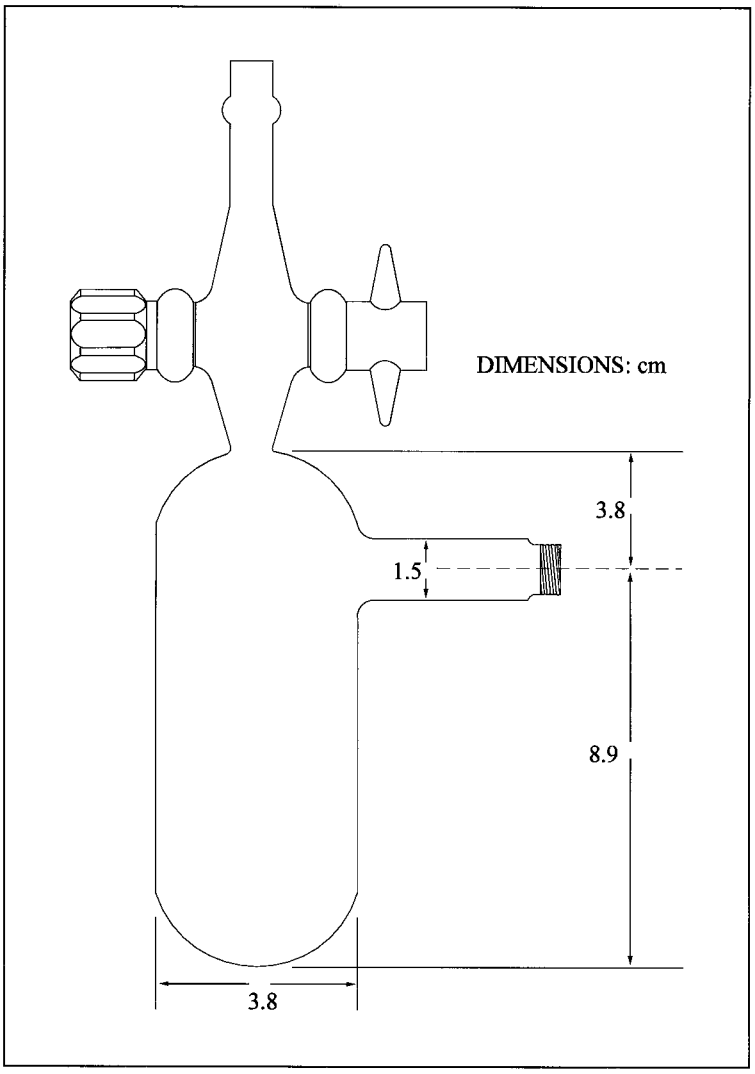


Figure 10A-2. Sample Reaction Bulbs.

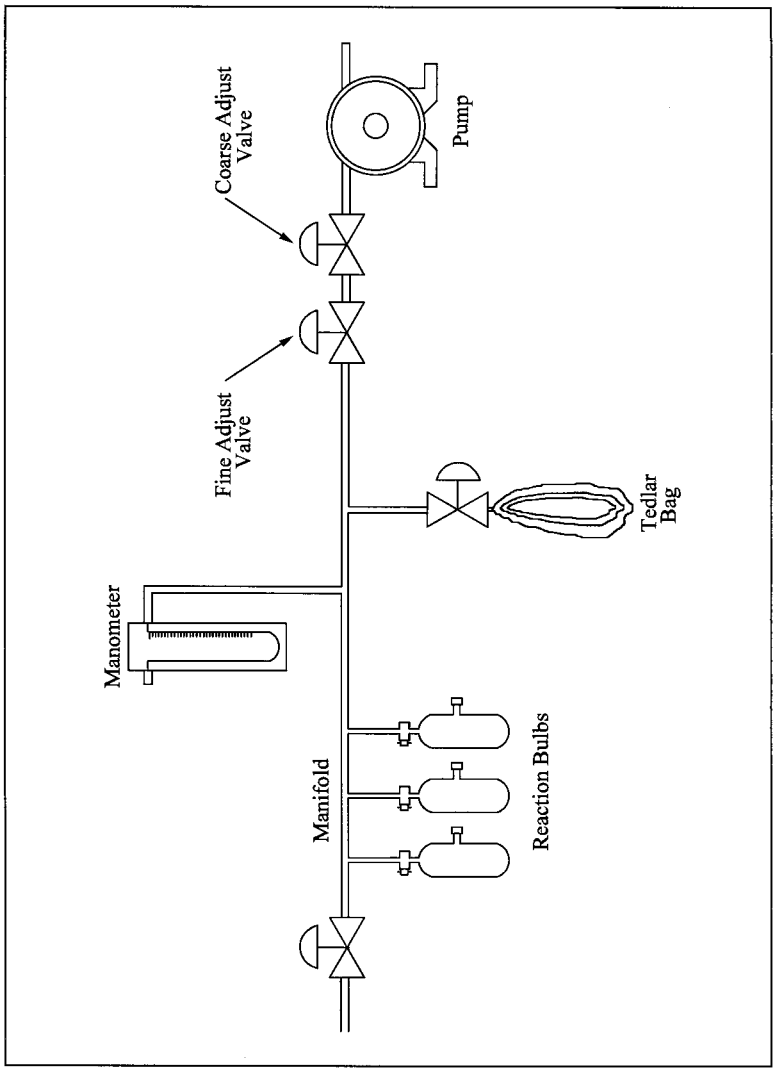


Figure 10A-3. Sample Bulb Filling System.

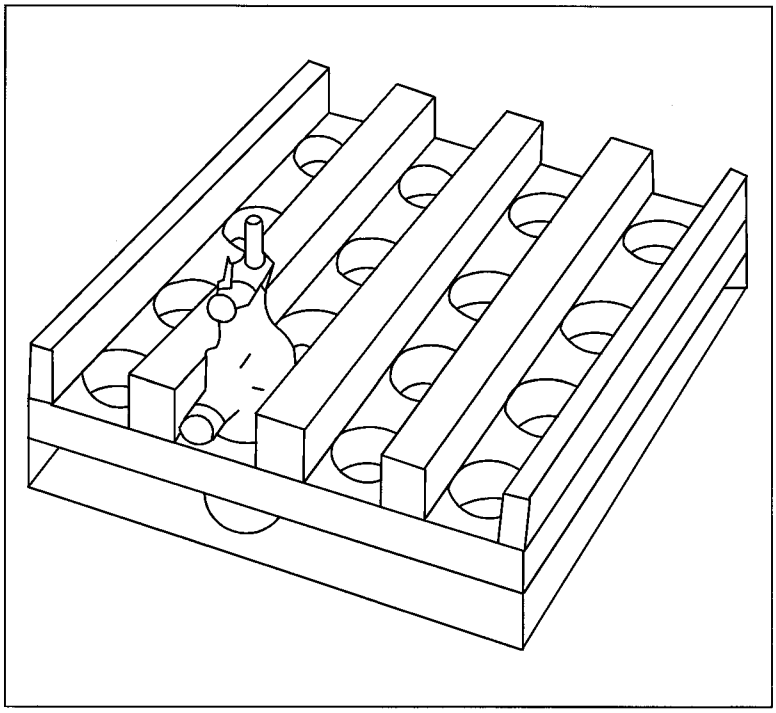


Figure 10A-4. Shaker Table Adapter.

METHOD 10B—DETERMINATION OF CARBON MONOXIDE EMISSIONS FROM STATIONARY SOURCES

NOTE: This method is not inclusive with respect to specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 4, Method 10A, and Method 25.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Carbon monoxide (CO)	630–08–0	Not determined.

1.2 Applicability. This method applies to the measurement of CO emissions at petroleum refineries and from other sources when specified in an applicable subpart of the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 An integrated gas sample is extracted from the sampling point, passed through a conditioning system to remove interferences, and collected in a Tedlar or equivalent bag. (Verify through the manufacturer that the Tedlar alternative is suitable for NO and make this verifying information available for inspection.) The CO is separated from the sample by gas chromatography (GC) and catalytically reduced to methane (CH_4) which is determined by flame ionization detection (FID). The analytical portion of this method is identical to applicable sections in Method 25 detailing CO measurement.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Carbon dioxide (CO_2) and organics potentially can interfere with the analysis. Most of the CO_2 is removed from the sample by the alkaline permanganate conditioning system; any residual CO_2 and organics are separated from the CO by GC.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions concerning the analytical procedure.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as in Method 10A, section 6.1 (paragraphs 6.1.1 through 6.1.11).

6.2 Sample Analysis. A GC/FID analyzer, capable of quantifying CO in the sample and consisting of at least the following major components, is required for sample analysis. [Alternatively, complete Method 25 analytical systems (Method 25, section 6.3) are acceptable alternatives when calibrated for CO and operated in accordance with the Method 25 analytical procedures (Method 25, section 11.0).]

6.2.1 Separation Column. A column capable of separating CO from CO_2 and organic compounds that may be present. A 3.2-mm (⅛-in.) OD stainless steel column packed with 1.7 m (5.5 ft.) of 60/80 mesh Carbosieve S-II (available from Supelco) has been used successfully for this purpose.

6.2.2 Reduction Catalyst. Same as in Method 25, section 6.3.1.2.

6.2.3 Sample Injection System. Same as in Method 25, Section 6.3.1.4, equipped to accept a sample line from the bag.

6.2.4 Flame Ionization Detector. Meeting the linearity specifications of section 10.3 and having a minimal instrument range of 10 to 1,000 ppm CO.

6.2.5 Data Recording System. Analog strip chart recorder or digital integration system, compatible with the FID, for permanently recording the analytical results.

7.0 Reagents and Standards

7.1 Sample Collection. Same as in Method 10A, section 7.1.

7.2 Sample Analysis.

7.2.1 Carrier, Fuel, and Combustion Gases. Same as in Method 25, sections 7.2.1, 7.2.2, and 7.2.3, respectively.

7.2.2 Calibration Gases. Three standard gases with nominal CO concentrations of 20, 200, and 1,000 ppm CO in nitrogen. The calibration gases shall be certified by the manufacturer to be ±2 percent of the specified concentrations.

7.2.3 Reduction Catalyst Efficiency Check Calibration Gas. Standard CH_4 gas with a nominal concentration of 1,000 ppm in air.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as in Method 10A, section 8.0.

9.0 Quality Control

Section	Quality control measure	Effect
8.0	Sample bag/sampling system leak-checks	Ensures that negative bias introduced through leakage is minimized.
10.1	Carrier gas blank check	Ensures that positive bias introduced by contamination of carrier gas is less than 5 ppmv.
10.2	Reduction catalyst efficiency check	Ensures that negative bias introduced by inefficient reduction catalyst is less than 5 percent.
10.3	Analyzer calibration	Ensures linearity of analyzer response to standards.
11.2	Triplicate sample analyses	Ensures precision of analytical results.

10.0 Calibration and Standardization

10.1 Carrier Gas Blank Check. Analyze each new tank of carrier gas with the GC analyzer according to section 11.2 to check for contamination. The corresponding concentration must be less than 5 ppm for the tank to be acceptable for use.

10.2 Reduction Catalyst Efficiency Check. Prior to initial use, the reduction catalyst shall be tested for reduction efficiency. With the heated reduction catalyst bypassed, make triplicate injections of the 1,000 ppm CH_4 gas (Section 7.2.3) to calibrate the analyzer. Repeat the procedure using 1,000 ppm CO gas (Section 7.2.2) with the catalyst in operation. The reduction catalyst operation is acceptable if the CO response is within 5 percent of the certified gas value.

10.3 Analyzer Calibration. Perform this test before the system is first placed into operation. With the reduction catalyst in operation, conduct a linearity check of the analyzer using the standards specified in section 7.2.2. Make triplicate injections of each calibration gas, and then calculate the average

response factor (area/ppm) for each gas, as well as the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within 2.5 percent of the overall mean value and if the relative standard deviation (calculated in section 12.8 of Method 25) for each set of triplicate injections is less than 2 percent. Record the overall mean of the response factor values as the calibration response factor (R).

11.0 Analytical Procedure

11.1 Preparation for Analysis. Before putting the GC analyzer into routine operation, conduct the calibration procedures listed in section 10.0. Establish an appropriate carrier flow rate and detector temperature for the specific instrument used.

11.2 Sample Analysis. Purge the sample loop with sample, and then inject the sample. Analyze each sample in triplicate, and calculate the average sample area (A). Determine the bag CO concentration according to section 12.2.

12.0 Calculations and Data Analysis

Carry out calculations retaining at least one extra significant figure beyond that of the acquired data. Round off results only after the final calculation.

12.1 Nomenclature.

A = Average sample area.
B_w = Moisture content in the bag sample, fraction.
C = CO concentration in the stack gas, dry basis, ppm.
C_b = CO concentration in the bag sample, dry basis, ppm.
F = Volume fraction of CO_2 in the stack, fraction.
P_{bar} = Barometric pressure, mm Hg.
P_w = Vapor pressure of the H_2O in the bag (from Table 10A–2, Method 10A), mm Hg.
R = Mean calibration response factor, area/ppm.

12.2 CO Concentration in the Bag. Calculate C_b using Equations 10B–1 and 10B–2. If condensate is visible in the bag, calculate B_w using Table 10A–2 of Method 10A and the temperature and barometric pressure in the analysis room. If condensate is not visible, calculate B_w using the temperature and barometric pressure at the sampling site.

$$B_w = \frac{P_w}{P_{bar}} \qquad \text{Eq. 10B-1}$$

$$C_b = \frac{A}{R\left(1 - B_w\right)} \qquad \text{Eq. 10B-2}$$

12.3 CO Concentration in the Stack

$$C = C_b\left(1 - F\right) \qquad \text{Eq. 10B-3}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as in Method 25, section 16.0, with the addition of the following:

1. Butler, F.E, J.E. Knoll, and M.R. Midgett. Development and Evaluation of Methods for Determining Carbon Monoxide Emissions. Quality Assurance Division, Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC. June 1985. 33 pp.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–4 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

APPENDIX A–5 TO PART 60—TEST METHODS 11 THROUGH 15A

Method 11—Determination of hydrogen sulfide content of fuel gas streams in petroleum refineries
Method 12—Determination of inorganic lead emissions from stationary sources
Method 13A—Determination of total fluoride emissions from stationary sources—SPADNS zirconium lake method
Method 13B—Determination of total fluoride emissions from stationary sources—Specific ion electrode method
Method 14—Determination of fluoride emissions from potroom roof monitors for primary aluminum plants
Method 14A—Determination of Total Fluoride Emissions from Selected Sources at Primary Aluminum Production Facilities
Method 15—Determination of hydrogen sulfide, carbonyl sulfide, and carbon disulfide emissions from stationary sources
Method 15A—Determination of total reduced sulfur emissions from sulfur recovery plants in petroleum refineries

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods

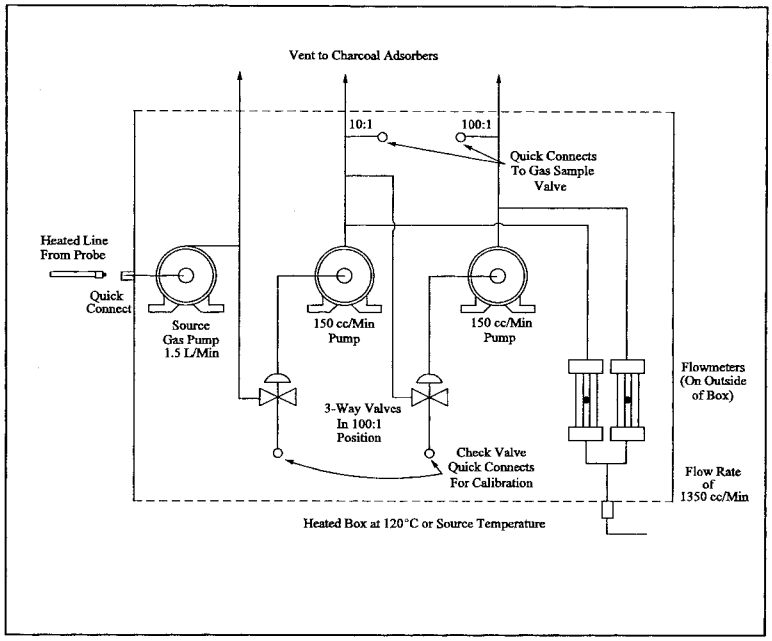


Figure 18-13. Schematic Diagram of the Heated Box Required for Dilution of Sample Gas.

GASEOUS ORGANIC SAMPLING AND ANALYSIS CHECK LIST

[Respond with initials or number as appropriate]

1. Presurvey data:		
A. Grab sample collected	☐	_____
B. Grab sample analyzed for composition	☐	_____
Method GC	☐	_____
GC/MS	☐	_____
Other	☐	_____
C. GC-FID analysis performed	☐	_____
2. Laboratory calibration data:		
A. Calibration curves prepared	☐	_____
Number of components	☐	_____
Number of concentrations/component (3 required).	☐	_____
B. Audit samples (optional):		
Analysis completed	☐	_____
Verified for concentration	☐	_____
OK obtained for field work	☐	_____
3. Sampling procedures:		
A. Method:		
Bag sample	☐	_____
Direct interface	☐	_____
Dilution interface	☐	_____
B. Number of samples collected	☐	_____
4. Field Analysis:		
A. Total hydrocarbon analysis performed	☐	_____
B. Calibration curve prepared	☐	_____
Number of components	☐	_____
Number of concentrations per component (3 required).	☐	_____

Gaseous Organic Sampling and Analysis Data

Date _____
Location _____

Plant _____

GASEOUS ORGANIC SAMPLING AND ANALYSIS CHECK LIST (RESPOND WITH INITIALS OR NUMBER AS APPROPRIATE)

	Date
1. Pre-survey data	
A. Grab sample collected	_____
B. Grab sample analyzed for composition	_____
Method GC	_____
GC/MS	_____
Other_____	_____
C. GC–FID analysis performed	_____
2. Laboratory calibration curves prepared	_____
A. Number of components	_____
B. Number of concentrations per component (3 required)	_____
C. OK obtained for field work	_____
3. Sampling procedures.	
A. Method.	
Bag sample	_____
Direct interface	_____
Dilution interface	_____
B. Number of samples collected	_____
4. Field Analysis.	
A. Total hydrocarbon analysis performed	_____
B. Calibration curve prepared	_____
Number of components	_____
Number of concentrations per component (3 required)	_____

Figure 18–14. Sampling and Analysis Sheet

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–6 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

APPENDIX A–7 TO PART 60—TEST METHODS 19 THROUGH 25E

Method 19—Determination of sulfur dioxide removal efficiency and particulate, sulfur dioxide and nitrogen oxides emission rates
Method 20—Determination of nitrogen oxides, sulfur dioxide, and diluent emissions from stationary gas turbines
Method 21—Determination of volatile organic compound leaks
Method 22—Visual determination of fugitive emissions from material sources and smoke emissions from flares
Method 23—Determination of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans From Stationary Sources
Method 24—Determination of volatile matter content, water content, density, volume solids, and weight solids of surface coatings
Method 24A—Determination of volatile matter content and density of printing inks and related coatings
Method 25—Determination of total gaseous nonmethane organic emissions as carbon
Method 25A—Determination of total gaseous organic concentration using a flame ionization analyzer
Method 25B—Determination of total gaseous organic concentration using a nondispersive infrared analyzer
Method 25C—Determination of nonmethane organic compounds (NMOC) in MSW landfill gases
Method 25D—Determination of the Volatile Organic Concentration of Waste Samples
Method 25E—Determination of Vapor Phase Organic Concentration in Waste Samples

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

Method 19—Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates

1.0 Scope and Application

1.1 Analytes. This method provides data reduction procedures relating to the following pollutants, but does not include any sample collection or analysis procedures.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), including:		
Nitric oxide (NO)	10102–43–9	N/A
Nitrogen dioxide (NO_2)	10102–44–0.	
Particulate matter (PM)	None assigned	N/A
Sulfur dioxide (SO_2)	7499–09–05	N/A

1.2 Applicability. Where specified by an applicable subpart of the regulations, this method is applicable for the determination of (a) PM, SO_2, and NO_X emission rates; (b) sulfur removal efficiencies of fuel pretreatment and SO_2 control devices; and (c) overall reduction of potential SO_2 emissions.

2.0 Summary of Method

2.1 Emission Rates. Oxygen (O_2) or carbon dioxide (CO_2) concentrations and appropriate F factors (ratios of combustion gas volumes to heat inputs) are used to calculate pollutant emission rates from pollutant concentrations.

2.2 Sulfur Reduction Efficiency and SO_2 Removal Efficiency. An overall SO_2 emission reduction efficiency is computed from the efficiency of fuel pretreatment systems, where applicable, and the efficiency of SO_2 control devices.

2.2.1 The sulfur removal efficiency of a fuel pretreatment system is determined by fuel sampling and analysis of the sulfur and heat contents of the fuel before and after the pretreatment system.

2.2.2 The SO_2 removal efficiency of a control device is determined by measuring the SO_2 rates before and after the control device.

2.2.2.1 The inlet rates to SO_2 control systems (or, when SO_2 control systems are not used, SO_2 emission rates to the atmosphere) are determined by fuel sampling and analysis.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety [Reserved]

6.0 Equipment and Supplies [Reserved]

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transport [Reserved]

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedures [Reserved]

12.0 Data Analysis and Calculations

12.1 Nomenclature

B_{wa} = Moisture fraction of ambient air, percent.

B_{ws} = Moisture fraction of effluent gas, percent.

%C = Concentration of carbon from an ultimate analysis of fuel, weight percent.

C_d = Pollutant concentration, dry basis, ng/scm (lb/scf)

$\%CO_{2d}$,$\%CO_{2w}$ = Concentration of carbon dioxide on a dry and wet basis, respectively, percent.

C_w = Pollutant concentration, wet basis, ng/scm (lb/scf).

D = Number of sampling periods during the performance test period.

E = Pollutant emission rate, ng/J (lb/million Btu).

E_a = Average pollutant rate for the specified performance test period, ng/J (lb/million Btu).

E_{ao}, E_{ai} = Average pollutant rate of the control device, outlet and inlet, respectively, for the performance test period, ng/J (lb/million Btu).

E_{bi} = Pollutant rate from the steam generating unit, ng/J (lb/million Btu)

E_{bo} = Pollutant emission rate from the steam generating unit, ng/J (lb/million Btu).

E_{ci} = Pollutant rate in combined effluent, ng/J (lb/million Btu).

E_{co} = Pollutant emission rate in combined effluent, ng/J (lb/million Btu).

E_d = Average pollutant rate for each sampling period (*e.g.*, 24-hr Method 6B sample or 24-hr fuel sample) or for each fuel lot (*e.g.*, amount of fuel bunkered), ng/J (lb/million Btu).

E_{di} = Average inlet SO_2 rate for each sampling period d, ng/J (lb/million Btu)

E_g = Pollutant rate from gas turbine, ng/J (lb/million Btu).

E_{ga} = Daily geometric average pollutant rate, ng/J (lbs/million Btu) or ppm corrected to 7 percent O_2.

E_{jo},E_{ji} = Matched pair hourly arithmetic average pollutant rate, outlet and inlet, respectively, ng/J (lb/million Btu) or ppm corrected to 7 percent O_2.

E_h = Hourly average pollutant, ng/J (lb/million Btu).

E_{hj} = Hourly arithmetic average pollutant rate for hour ''j,'' ng/J (lb/million Btu) or ppm corrected to 7 percent O_2.

EXP = Natural logarithmic base (2.718) raised to the value enclosed by brackets.

F_d, F_w, F_c = Volumes of combustion components per unit of heat content, scm/J (scf/million Btu).

GCV = Gross calorific value of the fuel consistent with the ultimate analysis, kJ/kg (Btu/lb).

GCV_p, GCV_r = Gross calorific value for the product and raw fuel lots, respectively, dry basis, kJ/kg (Btu/lb).

%H = Concentration of hydrogen from an ultimate analysis of fuel, weight percent.

H = Total number of operating hours for which pollutant rates are determined in the performance test period.

H_b = Heat input rate to the steam generating unit from fuels fired in the steam generating unit, J/hr (million Btu/hr).

H_g = Heat input rate to gas turbine from all fuels fired in the gas turbine, J/hr (million Btu/hr).

$\%H_2O$ = Concentration of water from an ultimate analysis of fuel, weight percent.
H_r = Total numbers of hours in the performance test period (*e.g.*, 720 hours for 30-day performance test period).
K = Conversion factor, 10^{-5} (kJ/J)/(%) [10^6 Btu/million Btu].
K_c = (9.57 scm/kg)/% [(1.53 scf/lb)/%].
K_{cc} = (2.0 scm/kg)/% [(0.321 scf/lb)/%].
K_{hd} = (22.7 scm/kg)/% [(3.64 scf/lb)/%].
K_{hw} = (34.74 scm/kg)/% [(5.57 scf/lb)/%].
K_n = (0.86 scm/kg)/% [(0.14 scf/lb)/%].
K_o = (2.85 scm/kg)/% [(0.46 scf/lb)/%].
K_s = (3.54 scm/kg)/% [(0.57 scf/lb)/%].
K_w = (1.30 scm/kg)/% [(0.21 scf/lb)/%].
ln = Natural log of indicated value.
L_p,L_r = Weight of the product and raw fuel lots, respectively, metric ton (ton).
%N = Concentration of nitrogen from an ultimate analysis of fuel, weight percent.
N = Number of fuel lots during the averaging period.
n = Number of fuels being burned in combination.
n_d = Number of operating hours of the affected facility within the performance test period for each E_d determined.
n_t = Total number of hourly averages for which paired inlet and outlet pollutant rates are available within the 24-hr midnight to midnight daily period.
%O = Concentration of oxygen from an ultimate analysis of fuel, weight percent.
$\%O_{2d}$, $\%O_{2w}$ = Concentration of oxygen on a dry and wet basis, respectively, percent.
P_s = Potential SO_2 emissions, percent.
$\%R_f$ = SO_2 removal efficiency from fuel pretreatment, percent.
$\%R_g$ = SO_2 removal efficiency of the control device, percent.
$\%R_{ga}$ = Daily geometric average percent reduction.
$\%R_o$ = Overall SO_2 reduction, percent.
%S = Sulfur content of as-fired fuel lot, dry basis, weight percent.
S_e = Standard deviation of the hourly average pollutant rates for each performance test period, ng/J (lb/million Btu).
$\%S_f$ = Concentration of sulfur from an ultimate analysis of fuel, weight percent.
S_i = Standard deviation of the hourly average inlet pollutant rates for each performance test period, ng/J (lb/million Btu).
S_o = Standard deviation of the hourly average emission rates for each performance test period, ng/J (lb/million Btu).
$\%S_p$, $\%S_r$ = Sulfur content of the product and raw fuel lots respectively, dry basis, weight percent.
$t_{0.95}$ = Values shown in Table 19–3 for the indicated number of data points n.
X_k = Fraction of total heat input from each type of fuel k.

12.2 Emission Rates of PM, SO_2, and NO_X. Select from the following sections the applicable procedure to compute the PM, S_{O2}, or NO_X emission rate (E) in ng/J (lb/million Btu). The pollutant concentration must be in ng/scm (lb/scf) and the F factor must be in scm/J (scf/million Btu). If the pollutant concentration (C) is not in the appropriate units, use Table 19–1 in section 17.0 to make the proper conversion. An F factor is the ratio of the gas volume of the products of combustion to the heat content of the fuel. The dry F factor (F_d) includes all components of combustion less water, the wet F factor (F_w) includes all components of combustion, and the carbon F factor (F_c) includes only carbon dioxide.

NOTE: Since F_w factors include water resulting only from the combustion of hydrogen in the fuel, the procedures using F_w factors are not applicable for computing E from steam generating units with wet scrubbers or with other processes that add water (*e.g.*, steam injection).

12.2.1 Oxygen-Based F Factor, Dry Basis. When measurements are on a dry basis for both O ($\%O_{2d}$) and pollutant (C_d) concentrations, use the following equation:

$$E = C_d F_d \frac{20.9}{(20.9 - \%O_{2d})} \qquad \text{Eq. 19-1}$$

12.2.2 Oxygen-Based F Factor, Wet Basis. When measurements are on a wet basis for both O_2 ($\%O_{2w}$) and pollutant (C_w) concentrations, use either of the following:

12.2.2.1 If the moisture fraction of ambient air (B_{wa}) is measured:

$$E = C_w F_w \frac{20.9}{\left[20.9(1 - B_{wa}) - \%O_{2w}\right]} \qquad \text{Eq. 19-2}$$

Instead of actual measurement, B_{wa} may be estimated according to the procedure below.

NOTE: The estimates are selected to ensure that negative errors will not be larger than −1.5 percent. However, positive errors, or over-estimation of emissions by as much as 5 percent may be introduced depending upon the geographic location of the facility and the associated range of ambient moisture.

12.2.2.1.1 B_{wa} = 0.027. This value may be used at any location at all times.

12.2.2.1.2 B_{wa} = Highest monthly average of B_{wa} that occurred within the previous calendar year at the nearest Weather Service Station. This value shall be determined annually and may be used as an estimate for the entire current calendar year.

12.2.2.1.3 B_{wa} = Highest daily average of Bwa that occurred within a calendar month at the nearest Weather Service Station, calculated from the data from the past 3 years. This value shall be computed for each month and may be used as an estimate for the current respective calendar month.

12.2.2.2 If the moisture fraction (B_{ws}) of the effluent gas is measured:

$$E = C_w F_d \frac{20.9}{\left[20.9\left(1-B_{ws}\right)-\%O_{2w}\right]} \qquad \text{Eq. 19-3}$$

12.2.3 Oxygen-Based F Factor, Dry/Wet Basis.

12.2.3.1 When the pollutant concentration is measured on a wet basis (C_w) and O_2 concentration is measured on a dry basis ($\%O_{2d}$), use the following equation:

$$E = \frac{\left(C_w F_d\right)(20.9)}{\left(1-B_{ws}\right)\left(20.9-\%O_{2d}\right)} \qquad \text{Eq. 19-4}$$

12.2.3.2 When the pollutant concentration is measured on a dry basis (C_d) and the O_2 concentration is measured on a wet basis ($\%O_{2w}$), use the following equation:

$$E = \frac{C_d F_d 20.9}{\frac{\left(20.9-\%O_{2w}\right)}{\left(1-B_{ws}\right)}} \qquad \text{Eq. 19-5}$$

12.2.4 Carbon Dioxide-Based F Factor, Dry Basis. When measurements are on a dry basis for both CO_2 ($\%CO_{2d}$) and pollutant (C_d) concentrations, use the following equation:

$$E = C_d F_c \frac{100}{\%CO_{2d}} \qquad \text{Eq. 19-6}$$

12.2.5 Carbon Dioxide-Based F Factor, Wet Basis. When measurements are on a wet basis for both CO_2 ($\%CO_{2w}$) and pollutant (C_w) concentrations, use the following equation:

$$E = C_w F_c \frac{100}{\%CO_{2w}} \qquad \text{Eq. 19-7}$$

12.2.6 Carbon Dioxide-Based F Factor, Dry/Wet Basis.

12.2.6.1 When the pollutant concentration is measured on a wet basis (C_w) and CO_2 concentration is measured on a dry basis ($\%CO_{2d}$), use the following equation:

$$E = \frac{C_w F_c}{\left(1-B_{ws}\right)} \frac{100}{\%CO_{2d}} \qquad \text{Eq. 19-8}$$

12.2.6.2 When the pollutant concentration is measured on a dry basis (C_d) and CO_2 concentration is measured on a wet basis ($\%CO_{2w}$), use the following equation:

$$E = C_d F_c \left(1-B_{ws}\right) \frac{100}{\%CO_{2w}} \qquad \text{Eq. 19-9}$$

12.2.7 Direct-Fired Reheat Fuel Burning. The effect of direct-fired reheat fuel burning (for the purpose of raising the temperature of the exhaust effluent from wet scrubbers to above the moisture dew-point) on emission rates will be less than 1.0 percent and, therefore, may be ignored.

12.2.8 Combined Cycle-Gas Turbine Systems. For gas turbine-steam generator combined cycle systems, determine the emissions from the steam generating unit or the percent reduction in potential SO_2 emissions as follows:

12.2.8.1 Compute the emission rate from the steam generating unit using the following equation:

$$E_{bo} = E_{co} + \frac{H_g}{H_b}\left(E_{co} - E_g\right) \qquad \text{Eq. 19-10}$$

12.2.8.1.1 Use the test methods and procedures section of 40 CFR Part 60, Subpart GG to obtain E_{co} and E_g. Do not use F_w factors for determining E_g or E_{co}. If an SO_2 control device is used, measure E_{co} after the control device.

12.2.8.1.2 Suitable methods shall be used to determine the heat input rates to the steam generating units (H_b) and the gas turbine (H_g).

12.2.8.2 If a control device is used, compute the percent of potential SO_2 emissions (P_s) using the following equations:

$$E_{bi} = E_{ci} - \frac{H_g}{H_b}\left(E_{ci} - E_g\right) \qquad \text{Eq. 19-11}$$

$$P_s = 100\left(1 - \frac{E_{bo}}{E_{bi}}\right) \qquad \text{Eq. 19-12}$$

NOTE: Use the test methods and procedures section of Subpart GG to obtain E_{ci} and E_g. Do not use F_w factors for determining E_g or E_{ci}.

12.3 F Factors. Use an average F factor according to section 12.3.1 or determine an applicable F factor according to section 12.3.2. If combined fuels are fired, prorate the applicable F factors using the procedure in section 12.3.3.

12.3.1 Average F Factors. Average F factors (F_d, F_w, or F_c) from Table 19–2 in section 17.0 may be used.

12.3.2 Determined F Factors. If the fuel burned is not listed in Table 19–2 or if the owner or operator chooses to determine an F factor rather than use the values in Table 19–2, use the procedure below:

12.3.2.1 Equations. Use the equations below, as appropriate, to compute the F factors:

$$F_d = \frac{K\left(K_{hd}\%H + K_c\%C + K_s\%S + K_n\%N - K_o\%O\right)}{GCV} \qquad \text{Eq. 19-13}$$

$$F_w = \frac{K\left[K_{hw}\%H + K_c\%C + K_s\%S + K_n\%N - K_o\%O + K_w\%H_2O\right]}{GCV_w} \qquad \text{Eq. 19-14}$$

$$F_c = \frac{K\left(K_{cc}\%C\right)}{GCV} \qquad \text{Eq. 19-15}$$

NOTE: Omit the $\%H_2O$ term in the equations for F_w if %H and %O include the unavailable hydrogen and oxygen in the form of H_2O.)

12.3.2.2 Use applicable sampling procedures in section 12.5.2.1 or 12.5.2.2 to obtain samples for analyses.

12.3.2.3 Use ASTM D 3176–74 or 89 (all cited ASTM standards are incorporated by reference—see §60.17) for ultimate analysis of the fuel.

12.3.2.4 Use applicable methods in section 12.5.2.1 or 12.5.2.2 to determine the heat content of solid or liquid fuels. For gaseous fuels, use ASTM D 1826–77 or 94 (incorporated by reference—see §60.17) to determine the heat content.

12.3.3 F Factors for Combination of Fuels. If combinations of fuels are burned, use the following equations, as applicable unless otherwise specified in an applicable subpart:

$$F_d = \sum_{k=1}^{n}\left(X_k F_{dk}\right) \qquad \text{Eq. 19-16}$$

$$F_w = \sum_{k=1}^{n}\left(X_k F_{wk}\right) \qquad \text{Eq. 19-17}$$

$$F_c = \sum_{k=1}^{n}\left(X_k F_{ck}\right) \qquad \text{Eq. 19-18}$$

12.4 Determination of Average Pollutant Rates.

12.4.1 Average Pollutant Rates from Hourly Values. When hourly average pollutant rates (E_h), inlet or outlet, are obtained (*e.g.*, CEMS values), compute the average pollutant rate (E_a) for the performance test period (*e.g.*, 30 days) specified in the applicable regulation using the following equation:

$$E_a = \frac{1}{H}\sum_{j=1}^{n} E_{hj} \qquad \text{Eq. 19-19}$$

12.4.2 Average Pollutant Rates from Other than Hourly Averages. When pollutant rates are determined from measured values representing longer than 1-hour periods (*e.g.*, daily fuel sampling and analyses or Method 6B values), or when pollutant rates are determined from combinations of 1-hour and longer than 1-hour periods (*e.g.*, CEMS and Method 6B values), compute the average pollutant rate (E_a) for the performance test period (*e.g.*, 30 days) specified in the applicable regulation using the following equation:

$$E_a = \frac{\sum_{j=1}^{D}\left(n_d E_d\right)_j}{\sum_{j=1}^{D} n_{dj}} \qquad \text{Eq. 19-20}$$

12.4.3 Daily Geometric Average Pollutant Rates from Hourly Values. The geometric average pollutant rate (E_{ga}) is computed using the following equation:

$$E_{ga} = \exp\left[\frac{1}{n_t}\sum_{j=1}^{n_t}\left[\ln\left(E_{hj}\right)\right]\right] \quad \text{Eq. 19-21}$$

12.5 Determination of Overall Reduction in Potential Sulfur Dioxide Emission.

12.5.1 Overall Percent Reduction. Compute the overall percent SO_2 reduction ($\%R_o$) using the following equation:

$$\%R_o = 100\left[1.0 - \left(1.0 - \frac{\%R_f}{100}\right)\left(1.0 - \frac{\%R_g}{100}\right)\right] \quad \text{Eq. 19-22}$$

12.5.2 Pretreatment Removal Efficiency (Optional). Compute the SO_2 removal efficiency from fuel pretreatment ($\%R_f$) for the averaging period (*e.g.*, 90 days) as specified in the applicable regulation using the following equation:

$$\%R_f = 100\left[1.0 - \frac{\sum_{j=1}^{N}\left(\frac{\%S_{pj}}{GCV_{pj}}\right)L_{pj}}{\sum_{j=1}^{N}\left(\frac{\%S_{rj}}{GCV_{rj}}\right)L_{rj}}\right] \quad \text{Eq. 19-23}$$

NOTE: In calculating $\%R_f$, include %S and GCV values for all fuel lots that are not pretreated and are used during the averaging period.

12.5.2.1 Solid Fossil (Including Waste) Fuel/Sampling and Analysis.

NOTE: For the purposes of this method, raw fuel (coal or oil) is the fuel delivered to the desulfurization (pretreatment) facility. For oil, the input oil to the oil desulfurization process (*e.g.*, hydrotreatment) is considered to be the raw fuel.

12.5.2.1.1 Sample Increment Collection. Use ASTM D 2234–76, 96, 97a, or 98 (incorporated by reference—see §60.17), Type I, Conditions A, B, or C, and systematic spacing. As used in this method, systematic spacing is intended to include evenly spaced increments in time or increments based on equal weights of coal passing the collection area. As a minimum, determine the number and weight of increments required per gross sample representing each coal lot according to Table 2 or Paragraph 7.1.5.2 of ASTM D 2234. Collect one gross sample for each lot of raw coal and one gross sample for each lot of product coal.

12.5.2.1.2 ASTM Lot Size. For the purpose of section 12.5.2 (fuel pretreatment), the lot size of product coal is the weight of product coal from one type of raw coal. The lot size of raw coal is the weight of raw coal used to produce one lot of product coal. Typically, the lot size is the weight of coal processed in a 1-day (24-hour) period. If more than one type of coal is treated and produced in 1 day, then gross samples must be collected and analyzed for each type of coal. A coal lot size equaling the 90-day quarterly fuel quantity for a steam generating unit may be used if representative sampling can be conducted for each raw coal and product coal.

NOTE: Alternative definitions of lot sizes may be used, subject to prior approval of the Administrator.

12.5.2.1.3 Gross Sample Analysis. Use ASTM D 2013–72 or 86 to prepare the sample, ASTM D 3177–75 or 89 or ASTM D 4239–85, 94, or 97 to determine sulfur content (%S), ASTM D 3173–73 or 87 to determine moisture content, and ASTM D 2015–77 (Reapproved 1978) or 96, D 3286–85 or 96, or D 5865–98 or 10 to determine gross calorific value (GCV) (all standards cited are incorporated by reference—see §60.17 for acceptable versions of the standards) on a dry basis for each gross sample.

12.5.2.2 Liquid Fossil Fuel-Sampling and Analysis. See Note under section 12.5.2.1.

12.5.2.2.1 Sample Collection. Follow the procedures for continuous sampling in ASTM D 270 or D 4177–95 (incorporated by reference—see §60.17) for each gross sample from each fuel lot.

12.5.2.2.2 Lot Size. For the purpose of section 12.5.2 (fuel pretreatment), the lot size of a product oil is the weight of product oil from one pretreatment facility and intended as one shipment (ship load, barge load, etc.). The lot size of raw oil is the weight of each crude liquid fuel type used to produce a lot of product oil.

NOTE: Alternative definitions of lot sizes may be used, subject to prior approval of the Administrator.

12.5.2.2.3 Sample Analysis. Use ASTM D 129–64, 78, or 95, ASTM D 1552–83 or 95, or ASTM D 4057–81 or 95 to determine the sulfur content (%S) and ASTM D 240–76 or 92 (all standards cited are incorporated by reference—see §60.17) to determine the GCV of each gross sample. These values may be assumed to be on a dry basis. The owner or operator of an affected facility may elect to determine the GCV by sampling the oil combusted on the first steam generating unit operating day of each calendar month and then using the lowest GCV value of the three GCV values per quarter for the GCV of all oil combusted in that calendar quarter.

12.5.2.3 Use appropriate procedures, subject to the approval of the Administrator, to determine the fraction of total mass input derived from each type of fuel.

12.5.3 Control Device Removal Efficiency. Compute the percent removal efficiency ($\%R_g$) of the control device using the following equation:

$$\%R_g = 100\left(1.0 - \frac{E_{ao}}{E_{ai}}\right) \qquad \text{Eq. 19-24}$$

12.5.3.1 Use continuous emission monitoring systems or test methods, as appropriate, to determine the outlet SO_2 rates and, if appropriate, the inlet SO_2 rates. The rates may be determined as hourly (E_h) or other sampling period averages (E_d). Then, compute the average pollutant rates for the performance test period (E_{ao} and E_{ai}) using the procedures in section 12.4.

12.5.3.2 As an alternative, as-fired fuel sampling and analysis may be used to determine inlet SO_2 rates as follows:

12.5.3.2.1 Compute the average inlet SO_2 rate (E_{di}) for each sampling period using the following equation:

$$E_{di} = K\frac{\%S}{GCV} \qquad \text{Eq. 19-25}$$

Where:

$$K = 2\times10^{7}\left(\frac{\text{ng SO}_2}{\%S}\right)\left(\frac{(\text{kJ})}{\text{J}}\right)\left(\frac{1}{\text{kg coal}}\right)\left[2\times10^{4}\left(\frac{\text{lb SO}_2}{\%S}\right)\left(\frac{\text{Btu}}{\text{million Btu}}\right)\left(\frac{1}{\text{lb coal}}\right)\right]$$

After calculating E_{di}, use the procedures in section 12.4 to determine the average inlet SO_2 rate for the performance test period (E_{ai}).

12.5.3.2.2 Collect the fuel samples from a location in the fuel handling system that provides a sample representative of the fuel bunkered or consumed during a steam generating unit operating day. For the purpose of as-fired fuel sampling under section 12.5.3.2 or section 12.6, the lot size for coal is the weight of coal bunkered or consumed during each steam generating unit operating day. The lot size for oil is the weight of oil supplied to the ''day'' tank or consumed during each steam generating unit operating day. For reporting and calculation purposes, the gross sample shall be identified with the calendar day on which sampling began. For steam generating unit operating days when a coal-fired steam generating unit is operated without coal being added to the bunkers, the coal analysis from the previous ''as bunkered'' coal sample shall be used until coal is bunkered again. For steam generating unit operating days when an oil-fired steam generating unit is operated without oil being added to the oil ''day'' tank, the oil analysis from the previous day shall be used until the ''day'' tank is filled again. Alternative definitions of fuel lot size may be used, subject to prior approval of the Administrator.

12.5.3.2.3 Use ASTM procedures specified in section 12.5.2.1 or 12.5.2.2 to determine %S and GCV.

12.5.4 Daily Geometric Average Percent Reduction from Hourly Values. The geometric average percent reduction ($\%R_{ga}$) is computed using the following equation:

$$\%R_{ga} = 100\left[1 - \text{EXP}\left(\frac{1}{n_t}\sum_{j=1}^{n_t} 1n\frac{E_{jo}}{E_{ji}}\right)\right] \qquad \text{Eq. 19-26}$$

NOTE: The calculation includes only paired data sets (hourly average) for the inlet and outlet pollutant measurements.

12.6 Sulfur Retention Credit for Compliance Fuel. If fuel sampling and analysis procedures in section 12.5.2.1 are being used to determine average SO_2 emission rates (E_{as}) to the atmosphere from a coal-fired steam generating unit when there is no SO_2 control device, the following equation may be used to adjust the emission rate for sulfur retention credits (no credits are allowed for oil-fired systems) (E_{di}) for each sampling period using the following equation:

$$E_{di} = 0.97K\ \frac{\%S}{GDV} \qquad \text{Eq. 19-27}$$

Where:

$$K = 2\times10^{7}\left(\frac{\text{ng } SO_2}{\%S}\right)\left(\frac{kJ}{J}\right)\left(\frac{1}{\text{kg coal}}\right)\left[2\times10^{4}\left(\frac{\text{lb } SO_2}{\%S}\right)\left(\frac{\text{Btu}}{\text{million Btu}}\right)\left(\frac{1}{\text{lb coal}}\right)\right]$$

After calculating E_{di}, use the procedures in section 12.4.2 to determine the average SO_2 emission rate to the atmosphere for the performance test period (E_{ao}).

12.7 Determination of Compliance When Minimum Data Requirement Is Not Met.

12.7.1 Adjusted Emission Rates and Control Device Removal Efficiency. When the minimum data requirement is not met, the Administrator may use the following adjusted emission rates or control device removal efficiencies to determine compliance with the applicable standards.

12.7.1.1 Emission Rate. Compliance with the emission rate standard may be determined by using the lower confidence limit of the emission rate (E_{ao}*) as follows:

$$E^{*}_{ao} = E_{ao} - t_{0.95}S_o \qquad \text{Eq. 19-28}$$

12.7.1.2 Control Device Removal Efficiency. Compliance with the overall emission reduction ($\%R_o$) may be determined by using the lower confidence limit of the emission rate (E_{ao}*) and the upper confidence limit of the inlet pollutant rate (E_{ai}*) in calculating the control device removal efficiency ($\%R_g$) as follows:

$$\%R_g = 100\left(1.0 - \frac{E^{*}_{ao}}{E^{*}_{ai}}\right) \qquad \text{Eq. 19-29}$$

$$E^{*}_{ai} = E_{ai} + t_{0.95}S_i \qquad \text{Eq. 19-30}$$

12.7.2 Standard Deviation of Hourly Average Pollutant Rates. Compute the standard deviation (S_e) of the hourly average pollutant rates using the following equation:

$$S_e = \sqrt{\frac{1}{H} - \frac{1}{H_r}}\ \sqrt{\frac{\sum_{j=1}^{H}\left(E_{hj} - E_a\right)^2}{H-1}} \qquad \text{Eq. 19-31}$$

Equation 19–19 through 19–31 may be used to compute the standard deviation for both the outlet (S_o) and, if applicable, inlet (S_i) pollutant rates.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References [Reserved]

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 19–1—CONVERSION FACTORS FOR CONCENTRATION

From	To	Multiply by
g/scm	ng/scm	10^9
mg/scm	ng/scm	10^6
lb/scf	ng/scm	1.602×10^{13}

TABLE 19–1—CONVERSION FACTORS FOR CONCENTRATION—Continued

From	To	Multiply by
ppm SO_2	ng/scm	2.66×10^6
ppm NO_X	ng/scm	1.912×10^6
ppm SO_2	lb/scf	1.660×10^{-7}
ppm NO_X	lb/scf	1.194×10^{-7}

TABLE 19–2—F FACTORS FOR VARIOUS FUELS[1]

Fuel Type	F_d		F_w		F_c	
	dscm/J	dscf/10^6 Btu	wscm/J	wscf/10^6 Btu	scm/J	scf/10^6 Btu
Coal:						
Anthracite[2]	2.71×10^{-7}	10,100	2.83×10^{-7}	10,540	0.530×10^{-7}	1,970
Bituminus[2]	2.63×10^{-7}	9,780	2.86×10^{-7}	10,640	0.484×10^{-7}	1,800
Lignite	2.65×10^{-7}	9,860	3.21×10^{-7}	11,950	0.513×10^{-7}	1,910
Oil[3]	2.47×10^{-7}	9,190	2.77×10^{-7}	10,320	0.383×10^{-7}	1,420
Gas:.						
Natural	2.34×10^{-7}	8,710	2.85×10^{-7}	10,610	0.287×10^{-7}	1,040
Propane	2.34×10^{-7}	8,710	2.74×10^{-7}	10,200	0.321×10^{-7}	1,190
Butane	2.34×10^{-7}	8,710	2.79×10^{-7}	10,390	0.337×10^{-7}	1,250
Wood	2.48×10^{-7}	9,240			0.492×10^{-7}	1,830
Wood Bark	2.58×10^{-7}	9,600			0.516×10^{-7}	1,920
Municipal	2.57×10^{-7}	9,570			0.488×10^{-7}	1,820
Solid Waste						

[1] Determined at standard conditions: 20 °C (68 °F) and 760 mm Hg (29.92 in Hg)
[2] As classified according to ASTM D 388.
[3] Crude, residual, or distillate.

TABLE 19–3—VALUES FOR $T_{0.95*}$

n[1]	$t_{0.95}$	n[1]	$t_{0.95}$	n[1]	$t_{0.95}$
2	6.31	8	1.89	22–26	1.71
3	2.42	9	1.86	27–31	1.70
4	2.35	10	1.83	32–51	1.68
5	2.13	11	1.81	52–91	1.67
6	2.02	12–16	1.77	92–151	1.66
7	1.94	17–21	1.73	152 or more	1.65

[1] The values of this table are corrected for n-1 degrees of freedom. Use n equal to the number (H) of hourly average data points.

METHOD 20—DETERMINATION OF NITROGEN OXIDES, SULFUR DIOXIDE, AND DILUENT EMISSIONS FROM STATIONARY GAS TURBINES

1.0 Scope and Application

What is Method 20?

Method 20 contains the details you must follow when using an instrumental analyzer to determine concentrations of nitrogen oxides, oxygen, carbon dioxide, and sulfur dioxide in the emissions from stationary gas turbines. This method follows the specific instructions for equipment and performance requirements, supplies, sample collection and analysis, calculations, and data analysis in the methods listed in section 2.0.

1.1 Analytes. What does this method determine?

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X) as nitrogen dioxide:	10102–43–9	Typically <2% of Calibration Span.
Nitric oxide (NO)	10102–44–0	
Nitrogen dioxide NO_2.		
Diluent oxygen (O_2) or carbon dioxide (CO_2)		Typically <2% of Calibration Span.
Sulfur dioxide (SO_X)	7446–09–5	Typically <2% of Calibration Span.

1.2 Applicability. When is this method required? The use of Method 20 may be required by specific New Source Performance Standards, Clean Air Marketing rules, and State Implementation Plans and permits where

measuring SO_2, NO_X, CO_2, and/or O_2 concentrations in stationary gas turbines emissions are required. Other regulations may also require its use.

1.3 Data Quality Objectives. How good must my collected data be? Refer to section 1.3 of Method 7E.

2.0 Summary of Method

In this method, NO_X, O_2 (or CO_2), and SO_X are measured using the following methods found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 3A—Determination of Oxygen and Carbon Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(c) Method 6C—Determination of Sulfur Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(d) Method 7E—Determination of Nitrogen Oxides Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(e) Method 19—Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates.

3.0 Definitions

Refer to section 3.0 of Method 7E for the applicable definitions.

4.0 Interferences

Refer to section 4.0 of Methods 3A, 6C, and 7E as applicable.

5.0 Safety

Refer to section 5.0 of Method 7E.

6.0 Equipment and Supplies

The measurement system design is shown in Figure 7E–1 of Method 7E. Refer to the appropriate methods listed in section 2.0 for equipment and supplies.

7.0 Reagents and Standards

Refer to the appropriate methods listed in section 2.0 for reagents and standards.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling Site and Sampling Points. Follow the procedures of section 8.1 of Method 7E. For the stratification test in section 8.1.2, determine the diluent-corrected pollutant concentration at each traverse point.

8.2 Initial Measurement System Performance Tests. You must refer to the appropriate methods listed in section 2.0 for the measurement system performance tests as applicable.

8.3 Interference Check. You must follow the procedures in section 8.3 of Method 3A or 6C, or section 8.2.7 of Method 7E (as appropriate).

8.4 Sample Collection. You must follow the procedures of section 8.4 of the appropriate methods listed in section 2.0. A test run must have a duration of at least 21 minutes.

8.5 Post-Run System Bias Check, Drift Assessment, and Alternative Dynamic Spike Procedure. You must follow the procedures of sections 8.5 and 8.6 of the appropriate methods listed in section 2.0. A test run must have a duration of at least 21 minutes.

9.0 Quality Control

Follow quality control procedures in section 9.0 of Method 7E.

10.0 Calibration and Standardization

Follow the procedures for calibration and standardization in section 10.0 of Method 7E.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the procedures for calculations and data analysis in section 12.0 of the appropriate method listed in section 2.0. Follow the procedures in section 12.0 of Method 19 for calculating fuel-specific F factors, diluent-corrected pollutant concentrations, and emission rates.

13.0 Method Performance

The specifications for the applicable performance checks are the same as in section 13.0 of Method 7E.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

Refer to section 16.0 of the appropriate method listed in section 2.0 for alternative procedures.

17.0 References

Refer to section 17.0 of the appropriate method listed in section 2.0 for references.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

Refer to section 18.0 of the appropriate method listed in section 2.0 for tables, diagrams, flowcharts, and validation data.

METHOD 21—DETERMINATION OF VOLATILE ORGANIC COMPOUND LEAKS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile Organic Compounds (VOC).	No CAS number assigned.

1.2 Scope. This method is applicable for the determination of VOC leaks from process equipment. These sources include, but are not limited to, valves, flanges and other connections, pumps and compressors, pressure relief devices, process drains, open-ended valves, pump and compressor seal system degassing vents, accumulator vessel vents, agitator seals, and access door seals.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A portable instrument is used to detect VOC leaks from individual sources. The instrument detector type is not specified, but it must meet the specifications and performance criteria contained in section 6.0. A leak definition concentration based on a reference compound is specified in each applicable regulation. This method is intended to locate and classify leaks only, and is not to be used as a direct measure of mass emission rate from individual sources.

3.0 Definitions

3.1 *Calibration gas* means the VOC compound used to adjust the instrument meter reading to a known value. The calibration gas is usually the reference compound at a known concentration approximately equal to the leak definition concentration.

3.2 *Calibration precision* means the degree of agreement between measurements of the same known value, expressed as the relative percentage of the average difference between the meter readings and the known concentration to the known concentration.

3.3 *Leak definition concentration* means the local VOC concentration at the surface of a leak source that indicates that a VOC emission (leak) is present. The leak definition is an instrument meter reading based on a reference compound.

3.4 *No detectable emission* means a local VOC concentration at the surface of a leak source, adjusted for local VOC ambient concentration, that is less than 2.5 percent of the specified leak definition concentration. that indicates that a VOC emission (leak) is not present.

3.5 *Reference compound* means the VOC species selected as the instrument calibration basis for specification of the leak definition concentration. (For example, if a leak definition concentration is 10,000 ppm as methane, then any source emission that results in a local concentration that yields a meter reading of 10,000 on an instrument meter calibrated with methane would be classified as a leak. In this example, the leak definition concentration is 10,000 ppm and the reference compound is methane.)

3.6 *Response factor* means the ratio of the known concentration of a VOC compound to the observed meter reading when measured using an instrument calibrated with the reference compound specified in the applicable regulation.

3.7 *Response time* means the time interval from a step change in VOC concentration at the input of the sampling system to the time at which 90 percent of the corresponding final value is reached as displayed on the instrument readout meter.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Pollutants. Several of the compounds, leaks of which may be determined by this method, may be irritating or corrosive to tissues (*e.g.*, heptane) or may be toxic (*e.g.*, benzene, methyl alcohol). Nearly all are fire hazards. Compounds in emissions should be determined through familiarity with the source. Appropriate precautions can be found in reference documents, such as reference No. 4 in section 16.0.

6.0 Equipment and Supplies

A VOC monitoring instrument meeting the following specifications is required:

6.1 The VOC instrument detector shall respond to the compounds being processed. Detector types that may meet this requirement include, but are not limited to, catalytic oxidation, flame ionization, infrared absorption, and photoionization.

6.2 The instrument shall be capable of measuring the leak definition concentration specified in the regulation.

6.3 The scale of the instrument meter shall be readable to ±2.5 percent of the specified leak definition concentration.

6.4 The instrument shall be equipped with an electrically driven pump to ensure that a sample is provided to the detector at a constant flow rate. The nominal sample flow rate, as measured at the sample probe tip, shall be 0.10 to 3.0 l/min (0.004 to 0.1 ft^3/min) when the probe is fitted with a glass wool plug or filter that may be used to prevent plugging of the instrument.

6.5 The instrument shall be equipped with a probe or probe extension or sampling not to exceed 6.4 mm (¼ in) in outside diameter,

with a single end opening for admission of sample.

6.6 The instrument shall be intrinsically safe for operation in explosive atmospheres as defined by the National Electrical Code by the National Fire Prevention Association or other applicable regulatory code for operation in any explosive atmospheres that may be encountered in its use. The instrument shall, at a minimum, be intrinsically safe for Class 1, Division 1 conditions, and/or Class 2, Division 1 conditions, as appropriate, as defined by the example code. The instrument shall not be operated with any safety device, such as an exhaust flame arrestor, removed.

7.0 Reagents and Standards

7.1 Two gas mixtures are required for instrument calibration and performance evaluation:

7.1.1 Zero Gas. Air, less than 10 parts per million by volume (ppmv) VOC.

7.1.2 Calibration Gas. For each organic species that is to be measured during individual source surveys, obtain or prepare a known standard in air at a concentration approximately equal to the applicable leak definition specified in the regulation.

7.2 Cylinder Gases. If cylinder calibration gas mixtures are used, they must be analyzed and certified by the manufacturer to be within 2 percent accuracy, and a shelf life must be specified. Cylinder standards must be either reanalyzed or replaced at the end of the specified shelf life.

7.3 Prepared Gases. Calibration gases may be prepared by the user according to any accepted gaseous preparation procedure that will yield a mixture accurate to within 2 percent. Prepared standards must be replaced each day of use unless it is demonstrated that degradation does not occur during storage.

7.4 Mixtures with non-Reference Compound Gases. Calibrations may be performed using a compound other than the reference compound. In this case, a conversion factor must be determined for the alternative compound such that the resulting meter readings during source surveys can be converted to reference compound results.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Instrument Performance Evaluation. Assemble and start up the instrument according to the manufacturer's instructions for recommended warmup period and preliminary adjustments.

8.1.1 Response Factor. A response factor must be determined for each compound that is to be measured, either by testing or from reference sources. The response factor tests are required before placing the analyzer into service, but do not have to be repeated at subsequent intervals.

8.1.1.1 Calibrate the instrument with the reference compound as specified in the applicable regulation. Introduce the calibration gas mixture to the analyzer and record the observed meter reading. Introduce zero gas until a stable reading is obtained. Make a total of three measurements by alternating between the calibration gas and zero gas. Calculate the response factor for each repetition and the average response factor.

8.1.1.2 The instrument response factors for each of the individual VOC to be measured shall be less than 10 unless otherwise specified in the applicable regulation. When no instrument is available that meets this specification when calibrated with the reference VOC specified in the applicable regulation, the available instrument may be calibrated with one of the VOC to be measured, or any other VOC, so long as the instrument then has a response factor of less than 10 for each of the individual VOC to be measured.

8.1.1.3 Alternatively, if response factors have been published for the compounds of interest for the instrument or detector type, the response factor determination is not required, and existing results may be referenced. Examples of published response factors for flame ionization and catalytic oxidation detectors are included in References 1–3 of section 17.0.

8.1.2 Calibration Precision. The calibration precision test must be completed prior to placing the analyzer into service and at subsequent 3-month intervals or at the next use, whichever is later.

8.1.2.1 Make a total of three measurements by alternately using zero gas and the specified calibration gas. Record the meter readings. Calculate the average algebraic difference between the meter readings and the known value. Divide this average difference by the known calibration value and multiply by 100 to express the resulting calibration precision as a percentage.

8.1.2.2 The calibration precision shall be equal to or less than 10 percent of the calibration gas value.

8.1.3 Response Time. The response time test is required before placing the instrument into service. If a modification to the sample pumping system or flow configuration is made that would change the response time, a new test is required before further use.

8.1.3.1 Introduce zero gas into the instrument sample probe. When the meter reading has stabilized, switch quickly to the specified calibration gas. After switching, measure the time required to attain 90 percent of the final stable reading. Perform this test sequence three times and record the results. Calculate the average response time.

8.1.3.2 The instrument response time shall be equal to or less than 30 seconds. The instrument pump, dilution probe (if any), sample probe, and probe filter that will be used

during testing shall all be in place during the response time determination.

8.2 Instrument Calibration. Calibrate the VOC monitoring instrument according to section 10.0.

8.3 Individual Source Surveys.

8.3.1 Type I—Leak Definition Based on Concentration. Place the probe inlet at the surface of the component interface where leakage could occur. Move the probe along the interface periphery while observing the instrument readout. If an increased meter reading is observed, slowly sample the interface where leakage is indicated until the maximum meter reading is obtained. Leave the probe inlet at this maximum reading location for approximately two times the instrument response time. If the maximum observed meter reading is greater than the leak definition in the applicable regulation, record and report the results as specified in the regulation reporting requirements. Examples of the application of this general technique to specific equipment types are:

8.3.1.1 Valves. The most common source of leaks from valves is the seal between the stem and housing. Place the probe at the interface where the stem exits the packing gland and sample the stem circumference. Also, place the probe at the interface of the packing gland take-up flange seat and sample the periphery. In addition, survey valve housings of multipart assembly at the surface of all interfaces where a leak could occur.

8.3.1.2 Flanges and Other Connections. For welded flanges, place the probe at the outer edge of the flange-gasket interface and sample the circumference of the flange. Sample other types of nonpermanent joints (such as threaded connections) with a similar traverse.

8.3.1.3 Pumps and Compressors. Conduct a circumferential traverse at the outer surface of the pump or compressor shaft and seal interface. If the source is a rotating shaft, position the probe inlet within 1 cm of the shaft-seal interface for the survey. If the housing configuration prevents a complete traverse of the shaft periphery, sample all accessible portions. Sample all other joints on the pump or compressor housing where leakage could occur.

8.3.1.4 Pressure Relief Devices. The configuration of most pressure relief devices prevents sampling at the sealing seat interface. For those devices equipped with an enclosed extension, or horn, place the probe inlet at approximately the center of the exhaust area to the atmosphere.

8.3.1.5 Process Drains. For open drains, place the probe inlet at approximately the center of the area open to the atmosphere. For covered drains, place the probe at the surface of the cover interface and conduct a peripheral traverse.

8.3.1.6 Open-ended Lines or Valves. Place the probe inlet at approximately the center of the opening to the atmosphere.

8.3.1.7 Seal System Degassing Vents and Accumulator Vents. Place the probe inlet at approximately the center of the opening to the atmosphere.

8.3.1.8 Access door seals. Place the probe inlet at the surface of the door seal interface and conduct a peripheral traverse.

8.3.2 Type II—''No Detectable Emission''. Determine the local ambient VOC concentration around the source by moving the probe randomly upwind and downwind at a distance of one to two meters from the source. If an interference exists with this determination due to a nearby emission or leak, the local ambient concentration may be determined at distances closer to the source, but in no case shall the distance be less than 25 centimeters. Then move the probe inlet to the surface of the source and determine the concentration as outlined in section 8.3.1. The difference between these concentrations determines whether there are no detectable emissions. Record and report the results as specified by the regulation. For those cases where the regulation requires a specific device installation, or that specified vents be ducted or piped to a control device, the existence of these conditions shall be visually confirmed. When the regulation also requires that no detectable emissions exist, visual observations and sampling surveys are required. Examples of this technique are:

8.3.2.1 Pump or Compressor Seals. If applicable, determine the type of shaft seal. Perform a survey of the local area ambient VOC concentration and determine if detectable emissions exist as described in section 8.3.2.

8.3.2.2 Seal System Degassing Vents, Accumulator Vessel Vents, Pressure Relief Devices. If applicable, observe whether or not the applicable ducting or piping exists. Also, determine if any sources exist in the ducting or piping where emissions could occur upstream of the control device. If the required ducting or piping exists and there are no sources where the emissions could be vented to the atmosphere upstream of the control device, then it is presumed that no detectable emissions are present. If there are sources in the ducting or piping where emissions could be vented or sources where leaks could occur, the sampling surveys described in section 8.3.2 shall be used to determine if detectable emissions exist.

8.3.3 Alternative Screening Procedure.

8.3.3.1 A screening procedure based on the formation of bubbles in a soap solution that is sprayed on a potential leak source may be used for those sources that do not have continuously moving parts, that do not have surface temperatures greater than the boiling point or less than the freezing point of the soap solution, that do not have open

areas to the atmosphere that the soap solution cannot bridge, or that do not exhibit evidence of liquid leakage. Sources that have these conditions present must be surveyed using the instrument technique of section 8.3.1 or 8.3.2.

8.3.3.2 Spray a soap solution over all potential leak sources. The soap solution may be a commercially available leak detection solution or may be prepared using concentrated detergent and water. A pressure sprayer or squeeze bottle may be used to dispense the solution. Observe the potential leak sites to determine if any bubbles are formed. If no bubbles are observed, the source is presumed to have no detectable emissions or leaks as applicable. If any bubbles are observed, the instrument techniques of section 8.3.1 or 8.3.2 shall be used to determine if a leak exists, or if the source has detectable emissions, as applicable.

9.0 Quality Control

Section	Quality control measure	Effect
8.1.2	Instrument calibration precision check	Ensure precision and accuracy, respectively, of instrument response to standard.
10.0	Instrument calibration.	

10.0 Calibration and Standardization

10.1 Calibrate the VOC monitoring instrument as follows. After the appropriate warmup period and zero internal calibration procedure, introduce the calibration gas into the instrument sample probe. Adjust the instrument meter readout to correspond to the calibration gas value.

NOTE: If the meter readout cannot be adjusted to the proper value, a malfunction of the analyzer is indicated and corrective actions are necessary before use.

11.0 Analytical Procedures [Reserved]

12.0 Data Analyses and Calculations [Reserved]

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Dubose, D.A., and G.E. Harris. Response Factors of VOC Analyzers at a Meter Reading of 10,000 ppmv for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81051. September 1981.

2. Brown, G.E., *et al.* Response Factors of VOC Analyzers Calibrated with Methane for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81–022. May 1981.

3. DuBose, D.A. *et al.* Response of Portable VOC Analyzers to Chemical Mixtures. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81–110. September 1981.

4. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 22—VISUAL DETERMINATION OF FUGITIVE EMISSIONS FROM MATERIAL SOURCES AND SMOKE EMISSIONS FROM FLARES

NOTE: This method is not inclusive with respect to observer certification. Some material is incorporated by reference from Method 9.

1.0 Scope and Application

This method is applicable for the determination of the frequency of fugitive emissions from stationary sources, only as specified in an applicable subpart of the regulations. This method also is applicable for the determination of the frequency of visible smoke emissions from flares.

2.0 Summary of Method

2.1 Fugitive emissions produced during material processing, handling, and transfer operations or smoke emissions from flares are visually determined by an observer without the aid of instruments.

2.2 This method is used also to determine visible smoke emissions from flares used for combustion of waste process materials.

2.3 This method determines the amount of time that visible emissions occur during the observation period (*i.e.*, the accumulated emission time). This method does not require that the opacity of emissions be determined. Since this procedure requires only the determination of whether visible emissions occur and does not require the determination of opacity levels, observer certification according to the procedures of Method 9 is not required. However, it is necessary that the observer is knowledgeable with respect to the general procedures for determining the presence of visible emissions. At a minimum, the observer must be trained and knowledgeable regarding the effects of background contrast, ambient lighting, observer position relative

to lighting, wind, and the presence of uncombined water (condensing water vapor) on the visibility of emissions. This training is to be obtained from written materials found in References 1 and 2 or from the lecture portion of the Method 9 certification course.

3.0 Definitions

3.1 *Emission frequency* means the percentage of time that emissions are visible during the observation period.

3.2 *Emission time* means the accumulated amount of time that emissions are visible during the observation period.

3.3 *Fugitive emissions* means emissions generated by an affected facility which is not collected by a capture system and is released to the atmosphere. This includes emissions that (1) escape capture by process equipment exhaust hoods; (2) are emitted during material transfer; (3) are emitted from buildings housing material processing or handling equipment; or (4) are emitted directly from process equipment.

3.4 *Observation period* means the accumulated time period during which observations are conducted, not to be less than the period specified in the applicable regulation.

3.5 *Smoke emissions* means a pollutant generated by combustion in a flare and occurring immediately downstream of the flame. Smoke occurring within the flame, but not downstream of the flame, is not considered a smoke emission.

4.0 Interferences

4.1 Occasionally, fugitive emissions from sources other than the affected facility (*e.g.*, road dust) may prevent a clear view of the affected facility. This may particularly be a problem during periods of high wind. If the view of the potential emission points is obscured to such a degree that the observer questions the validity of continuing observations, then the observations shall be terminated, and the observer shall clearly note this fact on the data form.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment

6.1 Stopwatches (two). Accumulative type with unit divisions of at least 0.5 seconds.

6.2 Light Meter. Light meter capable of measuring illuminance in the 50 to 200 lux range, required for indoor observations only.

7.0 Reagents and Supplies [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transfer [Reserved]

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

11.1 Selection of Observation Location. Survey the affected facility, or the building or structure housing the process to be observed, and determine the locations of potential emissions. If the affected facility is located inside a building, determine an observation location that is consistent with the requirements of the applicable regulation (*i.e.*, outside observation of emissions escaping the building/structure or inside observation of emissions directly emitted from the affected facility process unit). Then select a position that enables a clear view of the potential emission point(s) of the affected facility or of the building or structure housing the affected facility, as appropriate for the applicable subpart. A position at least 4.6 m (15 feet), but not more than 400 m (0.25 miles), from the emission source is recommended. For outdoor locations, select a position where the sunlight is not shining directly in the observer's eyes.

11.2 Field Records.

11.2.1 Outdoor Location. Record the following information on the field data sheet (Figure 22–1): Company name, industry, process unit, observer's name, observer's affiliation, and date. Record also the estimated wind speed, wind direction, and sky condition. Sketch the process unit being observed, and note the observer location relative to the source and the sun. Indicate the potential and actual emission points on the sketch.

11.2.2 Indoor Location. Record the following information on the field data sheet (Figure 22–2): Company name, industry, process unit, observer's name, observer's affiliation, and date. Record as appropriate the type, location, and intensity of lighting on the data sheet. Sketch the process unit being observed, and note the observer location relative to the source. Indicate the potential and actual fugitive emission points on the sketch.

11.3 Indoor Lighting Requirements. For indoor locations, use a light meter to measure the level of illumination at a location as close to the emission source(s) as is feasible. An illumination of greater than 100 lux (10 foot candles) is considered necessary for proper application of this method.

11.4 Observations.

11.4.1 Procedure. Record the clock time when observations begin. Use one stopwatch to monitor the duration of the observation

period. Start this stopwatch when the observation period begins. If the observation period is divided into two or more segments by process shutdowns or observer rest breaks (see section 11.4.3), stop the stopwatch when a break begins and restart the stopwatch without resetting it when the break ends. Stop the stopwatch at the end of the observation period. The accumulated time indicated by this stopwatch is the duration of observation period. When the observation period is completed, record the clock time. During the observation period, continuously watch the emission source. Upon observing an emission (condensed water vapor is not considered an emission), start the second accumulative stopwatch; stop the watch when the emission stops. Continue this procedure for the entire observation period. The accumulated elapsed time on this stopwatch is the total time emissions were visible during the observation period (*i.e.*, the emission time.)

11.4.2 Observation Period. Choose an observation period of sufficient length to meet the requirements for determining compliance with the emission standard in the applicable subpart of the regulations. When the length of the observation period is specifically stated in the applicable subpart, it may not be necessary to observe the source for this entire period if the emission time required to indicate noncompliance (based on the specified observation period) is observed in a shorter time period. In other words, if the regulation prohibits emissions for more than 6 minutes in any hour, then observations may (optional) be stopped after an emission time of 6 minutes is exceeded. Similarly, when the regulation is expressed as an emission frequency and the regulation prohibits emissions for greater than 10 percent of the time in any hour, then observations may (optional) be terminated after 6 minutes of emission are observed since 6 minutes is 10 percent of an hour. In any case, the observation period shall not be less than 6 minutes in duration. In some cases, the process operation may be intermittent or cyclic. In such cases, it may be convenient for the observation period to coincide with the length of the process cycle.

11.4.3 Observer Rest Breaks. Do not observe emissions continuously for a period of more than 15 to 20 minutes without taking a rest break. For sources requiring observation periods of greater than 20 minutes, the observer shall take a break of not less than 5 minutes and not more than 10 minutes after every 15 to 20 minutes of observation. If continuous observations are desired for extended time periods, two observers can alternate between making observations and taking breaks.

11.5 Recording Observations. Record the accumulated time of the observation period on the data sheet as the observation period duration. Record the accumulated time emissions were observed on the data sheet as the emission time. Record the clock time the observation period began and ended, as well as the clock time any observer breaks began and ended.

12.0 Data Analysis and Calculations

If the applicable subpart requires that the emission rate be expressed as an emission frequency (in percent), determine this value as follows: Divide the accumulated emission time (in seconds) by the duration of the observation period (in seconds) or by any minimum observation period required in the applicable subpart, if the actual observation period is less than the required period, and multiply this quotient by 100.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Missan, R., and A. Stein. Guidelines for Evaluation of Visible Emissions Certification, Field Procedures, Legal Aspects, and Background Material. EPA Publication No. EPA–340/1–75–007. April 1975.

2. Wohlschlegel, P., and D.E. Wagoner. Guideline for Development of a Quality Assurance Program: Volume IX—Visual Determination of Opacity Emissions from Stationary Sources. EPA Publication No. EPA–650/4–74–005i. November 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

FUGITIVE OR SMOKE EMISSION INSPECTION
OUTDOOR LOCATION

Company Location Company Rep.	Observer Affiliation Date
Sky Conditions Precipitation	Wind Direction Wind Speed
Industry	Process Unit

Sketch process unit: indicate observer position relative to source; indicate potential emission points and/or actual emission points.

OBSERVATIONS	Clock Time	Observation period duration, min:sec	Accumulated emission time, min:sec
Begin Observation			
End Observation			

Figure 22-1

FUGITIVE OR SMOKE EMISSION INSPECTION
INDOOR LOCATION

Company Location Company Rep.	Observer Affiliation Date
Industry	Process Unit

Light type (fluorescent, incandescent, natural)
Light location (overhead, behind observer, etc.)
Illuminance (lux or footcandles)
Sketch process unit: indicate observer position relative to source; indicate potential emission points and/or actual emission points.

OBSERVATIONS	Clock Time	Observation period duration, min:sec	Accumulated emission time, min:sec
Begin			
End Observation			

Figure 22-2

METHOD 23—DETERMINATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS FROM STATIONARY SOURCES

1. Applicability and Principle

1.1 Applicability. This method is applicable to the determination of polychlorinated dibenzo-p-dioxins (PCDD's) and polychlorinated dibenzofurans (PCDF's) from stationary sources.

1.2 Principle. A sample is withdrawn from the gas stream isokinetically and collected in the sample probe, on a glass fiber filter, and on a packed column of adsorbent material. The sample cannot be separated into a particle vapor fraction. The PCDD's and

PCDF's are extracted from the sample, separated by high resolution gas chromatography, and measured by high resolution mass spectrometry.

2. Apparatus

2.1 Sampling. A schematic of the sampling train used in this method is shown in Figure 23–1. Sealing greases may not be used in assembling the train. The train is identical to that described in section 2.1 of Method 5 of this appendix with the following additions:

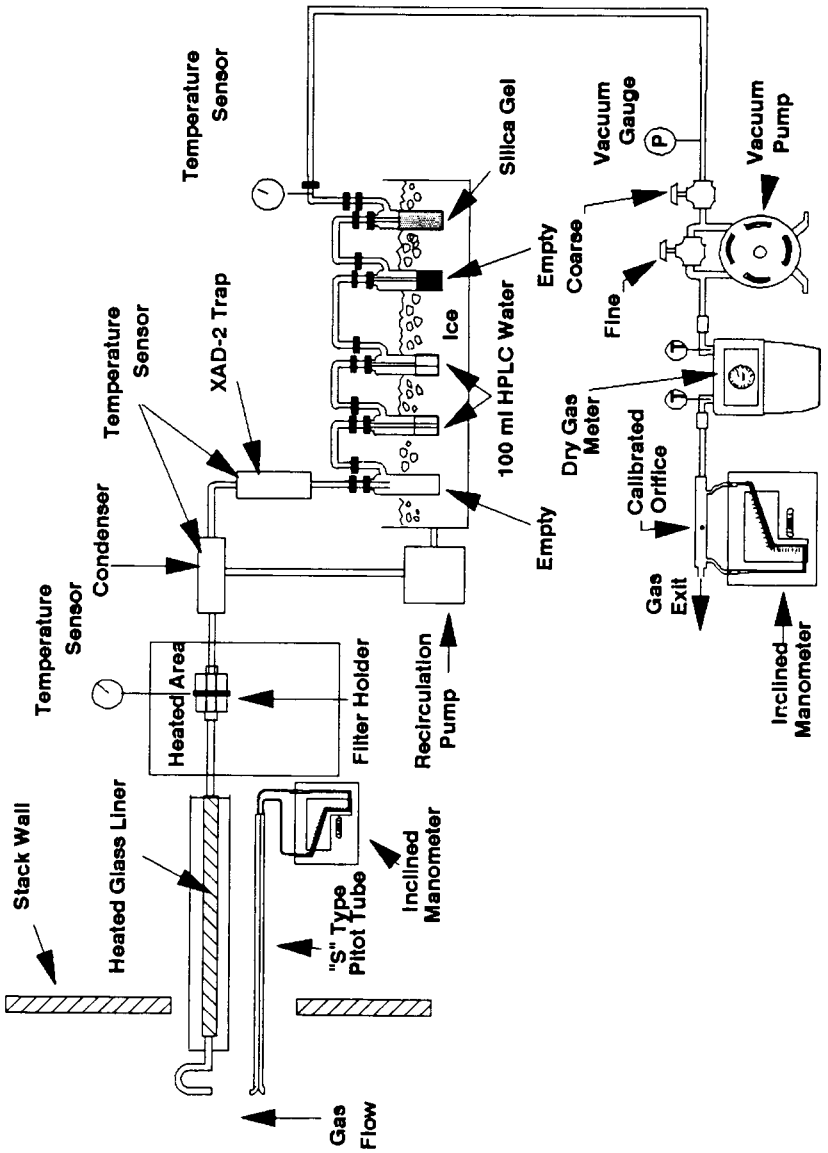


Figure 23.1 Sampling train

2.1.1 Nozzle. The nozzle shall be made of nickel, nickel-plated stainless steel, quartz, or borosilicate glass.

2.1.2 Sample Transfer Lines. The sample transfer lines, if needed, shall be heat traced, heavy walled TFE (½ in. OD with ⅛ in. wall) with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases. The line shall be as short as possible and must be maintained at 120 °C.

2.1.1 Filter Support. Teflon or Teflon-coated wire.

2.1.2 Condenser. Glass, coil type with compatible fittings. A schematic diagram is shown in Figure 23–2.

2.1.3 Water Bath. Thermostatically controlled to maintain the gas temperature exiting the condenser at <20 °C (68 °F).

2.1.4 Adsorbent Module. Glass container to hold the solid adsorbent. A shematic diagram is shown in Figure 23–2. Other physical configurations of the resin trap/condenser assembly are acceptable. The connecting fittings shall form leak-free, vacuum tight seals. No sealant greases shall be used in the sampling train. A coarse glass frit is included to retain the adsorbent.

2.2 Sample Recovery.

2.2.1 Fitting Caps. Ground glass, Teflon tape, or aluminum foil (Section 2.2.6) to cap off the sample exposed sections of the train.

2.2.2 Wash Bottles. Teflon, 500-ml.

2.2.3 Probe-Liner Probe-Nozzle, and Filter-Holder Brushes. Inert bristle brushes with precleaned stainless steel or Teflon handles. The probe brush shall have extensions of stainless steel or Teflon, at least as long as the probe. The brushes shall be properly sized and shaped to brush out the nozzle, probe liner, and transfer line, if used.

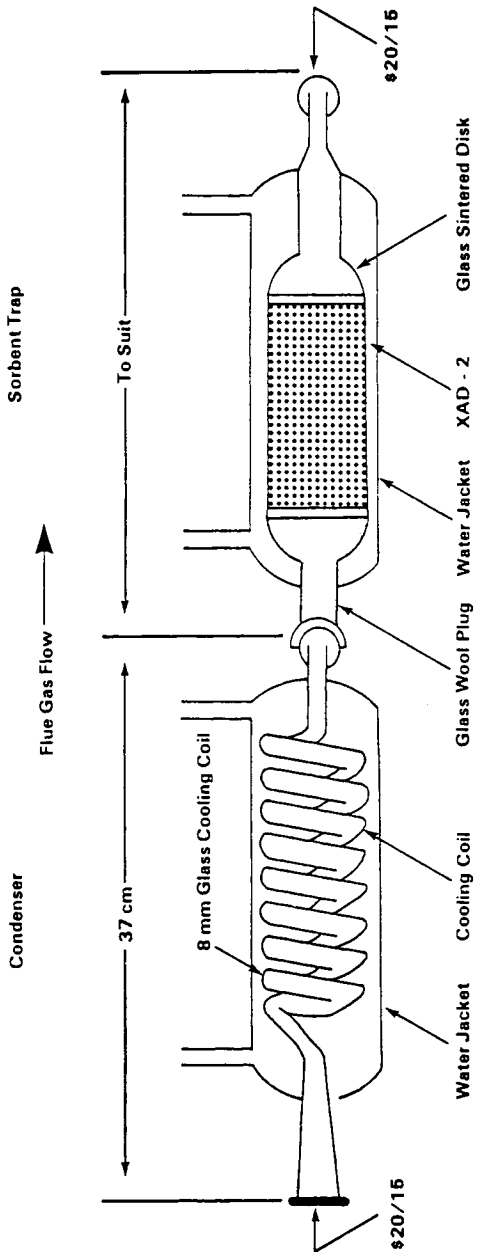


Figure 23.2. Condenser and adsorbent trap

2.2.4 Filter Storage Container. Sealed filter holder, wide-mouth amber glass jar with Teflon-lined cap, or glass petri dish.

2.2.5 Balance. Triple beam.

2.2.6 Aluminum Foil. Heavy duty, hexane-rinsed.

2.2.7 Storage Container. Air-tight container to store silica gel.

2.2.8 Graduated Cylinder. Glass, 250-ml with 2-ml graduation.

2.2.9 Glass Sample Storage Container. Amber glass bottle for sample glassware washes, 500- or 1000-ml, with leak free Teflon-lined caps.

2.3 Analysis.

2.3.1 Sample Container. 125- and 250-ml flint glass bottles with Teflon-lined caps.

2.3.2 Test Tube. Glass.

2.3.3 Soxhlet Extraction Apparatus. Capable of holding 43 × 123 mm extraction thimbles.

2.3.4 Extraction Thimble. Glass, precleaned cellulosic, or glass fiber.

2.3.5 Pasteur Pipettes. For preparing liquid chromatographic columns.

2.3.6 Reacti-vials. Amber glass, 2-ml, silanized prior to use.

2.3.7 Rotary Evaporator. Buchi/Brinkman RF–121 or equivalent.

2.3.8 Nitrogen Evaporative Concentrator. N-Evap Analytical Evaporator Model III or equivalent.

2.3.9 Separatory Funnels. Glass, 2-liter.

2.3.10 Gas Chromatograph. Consisting of the following components:

2.3.10.1 Oven. Capable of maintaining the separation column at the proper operating temperature ±°C and performing programmed increases in temperature at rates of at least 40 °C/min.

2.3.10.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperatures ±1 °C.

2.3.10.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

2.3.10.4 Capillary Columns. A fused silica column, 60 × 0.25 mm inside diameter (ID), coated with DB–5 and a fused silica column, 30 m × 0.25 mm ID coated with DB–225. Other column systems may be used provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of section 6.1.2.2.

2.3.11 Mass Spectrometer. Capable of routine operation at a resolution of 1:10000 with a stability of ±5 ppm.

2.3.12 Data System. Compatible with the mass spectrometer and capable of monitoring at least five groups of 25 ions.

2.3.13 Analytical Balance. To measure within 0.1 mg.

3. Reagents

3.1 Sampling.

3.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D 2986–71 (Reapproved 1978) (incorporated by reference—see §60.17).

3.1.1.1 Precleaning. All filters shall be cleaned before their initial use. Place a glass extraction thimble and 1 g of silica gel and a plug of glass wool into a Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Place no more than 50 filters in the thimble onto the silica gel bed and top with the cleaned glass wool. Charge the Soxhlet with toluene and reflux for 16 hours. After extraction, allow the Soxhlet to cool, remove the filters, and dry them under a clean N_2 stream. Store the filters in a glass petri dish sealed with Teflon tape.

3.1.2 Adsorbent Resin. Amberlite XAD–2 resin. Thoroughly cleaned before initial use.

3.1.2.1 Cleaning Procedure. This procedure may be carried out in a giant Soxhlet extractor. An all-glass filter thimble containing an extra-course frit is used for extraction of XAD–2. The frit is recessed 10–15 mm above a crenelated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass wool plug and a stainless steel ring because it floats on methylene chloride. This process involves sequential extraction in the following order.

Solvent	Procedure
Water	Initial rinse: Place resin in a beaker, rinse once with water, and discard. Fill with water a second time, let stand overnight, and discard.
Water	Extract with water for 8 hours.
Methanol	Extract for 22 hours.
Methylene Chloride	Extract for 22 hours.
Toluene	Extract for 22 hours.

3.1.2.2 Drying.

3.1.2.2.1 Drying Column. Pyrex pipe, 10.2 cm ID by 0.6 m long, with suitable retainers.

3.1.2.2.2 Procedure. The adsorbent must be dried with clean inert gas. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has proven to be a reliable source of large volumes of gas free from organic contaminants. Connect the liquid nitrogen cylinder to the column by a length of cleaned copper tubing, 0.95 cm ID, coiled to pass through a heat source. A convenient heat source is a water-bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40 °C. Continue flowing nitrogen through the adsorbent until all the residual solvent is removed. The flow rate should be sufficient to gently agitate the particles but not so excessive as the cause the particles to fracture.

3.1.2.3 Quality Control Check. The adsorbent must be checked for residual toluene.

3.1.2.3.1 Extraction. Weigh 1.0 g sample of dried resin into a small vial, add 3 ml of toluene, cap the vial, and shake it well.

3.1.2.3.2 Analysis. Inject a 2 µl sample of the extract into a gas chromatograph operated under the following conditions:

Column: 6 ft × ⅛ in stainless steel containing 10 percent OV–101 on 100/120 Supelcoport.
Carrier Gas: Helium at a rate of 30 ml/min.
Detector: Flame ionization detector operated at a sensitivity of 4×10^{-11} A/mV.
Injection Port Temperature: 250 °C.
Detector Temperature: 305 °C.
Oven Temperature: 30 °C for 4 min; programmed to rise at 40 °C/min until it reaches 250 °C; return to 30 °C after 17 minutes.

Compare the results of the analysis to the results from the reference solution. Prepare the reference solution by injection 2.5 µl of methylene chloride into 100 ml of toluene. This corresponds to 100 µg of methylene chloride per g of adsorbent. The maximum acceptable concentration is 1000 µg/g of adsorbent. If the adsorbent exceeds this level, drying must be continued until the excess methylene chloride is removed.

3.1.2.4 Storage. The adsorbent must be used within 4 weeks of cleaning. After cleaning, it may be stored in a wide mouth amber glass container with a Teflon-lined cap or placed in one of the glass adsorbent modules tightly sealed with glass stoppers. If precleaned adsorbent is purchased in sealed containers, it must be used within 4 weeks after the seal is broken.

3.1.3 Glass Wool. Cleaned by sequential immersion in three aliquots of methylene chloride, dried in a 110 °C oven, and stored in a methylene chloride-washed glass jar with a Teflon-lined screw cap.

3.1.4 Water. Deionized distilled and stored in a methylene chloride-rinsed glass container with a Teflon-lined screw cap.

3.1.5 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175 °C (350 °F) for two hours. New silica gel may be used as received. Alternately other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

3.1.6 Chromic Acid Cleaning Solution. Dissolve 20 g of sodium dichromate in 15 ml of water, and then carefully add 400 ml of concentrated sulfuric acid.

3.2 Sample Recovery.

3.2.2 Acetone. Pesticide quality.

3.2.2 Methylene Chloride. Pesticide qualtity.

3.2.3 Toluene. Pesticide quality.

3.3 Analysis.

3.3.1 Potassium Hydroxide. ACS grade, 2-percent (weight/volume) in water.

3.3.2 Sodium Sulfate. Granulated, reagent grade. Purify prior to use by rinsing with methylene chloride and oven drying. Store the cleaned material in a glass container with a Teflon-lined screw cap.

3.3.3 Sulfuric Acid. Reagent grade.

3.3.4 Sodium Hydroxide. 1.0 N. Weigh 40 g of sodium hydroxide into a 1-liter volumetric flask. Dilute to 1 liter with water.

3.3.5 Hexane. Pesticide grade.

3.3.6 Methylene Chloride. Pesticide grade.

3.3.7 Benzene. Pesticide Grade.

3.3.8 Ethyl Acetate.

3.3.9 Methanol. Pesticide Grade.

3.3.10 Toluene. Pesticide Grade.

3.3.11 Nonane. Pesticide Grade.

3.3.12 Cyclohexane. Pesticide Grade.

3.3.13 Basic Alumina. Activity grade 1, 100–200 mesh. Prior to use, activate the alumina by heating for 16 hours at 130 °C before use. Store in a desiccator. Pre-activated alumina may be purchased from a supplier and may be used as received.

3.3.14 Silica Gel. Bio-Sil A, 100–200 mesh. Prior to use, activate the silica gel by heating for at least 30 minutes at 180 °C. After cooling, rinse the silica gel sequentially with methanol and methylene chloride. Heat the rinsed silica gel at 50 °C for 10 minutes, then increase the temperature gradually to 180 °C over 25 minutes and maintain it at this temperature for 90 minutes. Cool at room temperature and store in a glass container with a Teflon-lined screw cap.

3.3.15 Silica Gel Impregnated with Sulfuric Acid. Combine 100 g of silica gel with 44 g of concentrated sulfuric acid in a screw capped glass bottle and agitate thoroughly. Disperse the solids with a stirring rod until a uniform mixture is obtained. Store the mixture in a glass container with a Teflon-lined screw cap.

3.3.16 Silica Gel Impregnated with Sodium Hydroxide. Combine 39 g of 1 N sodium hydroxide with 100 g of silica gel in a screw capped glass bottle and agitate thoroughly. Disperse solids with a stirring rod until a uniform mixture is obtained. Store the mixture in glass container with a Teflon-lined screw cap.

3.3.17 Carbon/Celite. Combine 10.7 g of AX–21 carbon with 124 g of Celite 545 in a 250-ml glass bottle with a Teflon-lined screw cap. Agitate the mixture thoroughly until a uniform mixture is obtained. Store in the glass container.

3.3.18 Nitrogen. Ultra high purity.

3.3.19 Hydrogen. Ultra high purity.

3.3.20 Internal Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Internal Standards'' in 10 ml of nonane.

3.3.21 Surrogate Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Surrogate Standards'' in 10 ml of nonane.

3.3.22 Recovery Standard Solution. Prepare a stock standard solution containing the

isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Recovery Standards'' in 10 ml of nonane.

4. Procedure

4.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, testers should be trained and experienced with the test procedures.

4.1.1 Pretest Preparation.

4.1.1.1 Cleaning Glassware. All glass components of the train upstream of and including the adsorbent module, shall be cleaned as described in section 3A of the ''Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples.'' Special care shall be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. Any residue shall be removed by soaking the glassware for several hours in a chromic acid cleaning solution prior to cleaning as described above.

4.1.1.2 Adsorbent Trap. The traps must be loaded in a clean area to avoid contamination. They may not be loaded in the field. Fill a trap with 20 to 40 g of XAD–2. Follow the XAD–2 with glass wool and tightly cap both ends of the trap. Add 100 μl of the surrogate standard solution (section 3.3.21) to each trap.

4.1.1.3 Sample Train. It is suggested that all components be maintained according to the procedure described in APTD–0576. Alternative mercury-free thermometers may be used if the thermometers are, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

4.1.1.4 Silica Gel. Weigh several 200 to 300 g portions of silica gel in an air tight container to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel may be weighed directly in its impinger or sampling holder just prior to sampling.

4.1.1.5 Filter. Check each filter against light for irregularities and flaws or pinhole leaks. Pack the filters flat in a clean glass container.

4.1.2 Preliminary Determinations. Same as section 4.1.2 of Method 5.

4.1.3 Preparation of Collection Train.

4.1.3.1 During preparation and assembly of the sampling train, keep all train openings where contamination can enter, sealed until just prior to assembly or until sampling is about to begin.

NOTE: Do not use sealant grease in assembling the train.

4.1.3.2 Place approximately 100 ml of water in the second and third impingers, leave the first and fourth impingers empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fifth impinger.

4.1.3.3 Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

4.1.3.4 Assemble the train as shown in Figure 23–1.

4.1.3.5 Turn on the adsorbent module and condenser coil recirculating pump and begin monitoring the adsorbent module gas entry temperature. Ensure proper sorbent temperature gas entry temperature before proceeding and before sampling is initiated. It is extremely important that the XAD–2 adsorbent resin temperature never exceed 50 °C because thermal decomposition will occur. During testing, the XAD–2 temperature must not exceed 20 °C for efficient capture of the PCDD's and PCDF's.

4.1.4 Leak-Check Procedure. Same as Method 5, section 4.1.4.

4.1.5 Sample Train Operation. Same as Method 5, section 4.1.5.

4.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Seal the nozzle end of the sampling probe with Teflon tape or aluminum foil.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe. Remove the probe from the train and close off both ends with aluminum foil. Seal off the inlet to the train with Teflon tape, a ground glass cap, or aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area shall be clean and enclosed so that the chances of losing or contaminating the sample are minimized. Smoking, which could contaminate the sample, shall not be allowed in the cleanup area.

Inspect the train prior to and during disassembly and note any abnormal conditions, e.g., broken filters, colored impinger liquid, etc. Treat the samples as follows:

4.2.1 Container No. 1. Either seal the filter holder or carefully remove the filter from the filter holder and place it in its identified container. Use a pair of cleaned tweezers to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and filter fibers which adhere to the filter holder gasket, by using a dry inert bristle brush and a sharp-edged blade. Seal the container.

4.2.2 Adsorbent Module. Remove the module from the train, tightly cap both ends, label it, cover with aluminum foil, and store it on ice for transport to the laboratory.

4.2.3 Container No. 2. Quantitatively recover material deposited in the nozzle, probe transfer lines, the front half of the filter holder, and the cyclone, if used, first, by

brushing while rinsing three times each with acetone and then, by rinsing the probe three times with methylene chloride. Collect all the rinses in Container No. 2.

Rinse the back half of the filter holder three times with acetone. Rinse the connecting line between the filter and the condenser three times with acetone. Soak the connecting line with three separate portions of methylene chloride for 5 minutes each. If using a separate condenser and adsorbent trap, rinse the condenser in the same manner as the connecting line. Collect all the rinses in Container No. 2 and mark the level of the liquid on the container.

4.2.4 Container No. 3. Repeat the methylene chloride-rinsing described in section 4.2.3 using toluene as the rinse solvent. Collect the rinses in Container No. 3 and mark the level of the liquid on the container.

4.2.5 Impinger Water. Measure the liquid in the first three impingers to within ±1 ml by using a graduated cylinder or by weighing it to within ±0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

Discard the liquid after measuring and recording the volume or weight.

4.2.7 Silica Gel. Note the color of the indicating silica gel to determine if it has been completely spent and make a mention of its condition. Transfer the silica gel from the fifth impinger to its original container and seal. If a moisture determination is made, follow the applicable procedures in sections 8.7.6.3 and 11.2.3 of Method 5 to handle and weigh the silica gel. If moisture is not measured, the silica gel may be disposed.

5. Analysis

All glassware shall be cleaned as described in section 3A of the ''Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples.'' All samples must be extracted within 30 days of collection and analyzed within 45 days of extraction.

5.1 Sample Extraction.

5.1.1 Extraction System. Place an extraction thimble (section 2.3.4), 1 g of silica gel, and a plug of glass wool into the Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Remove the extraction thimble from the extraction system and place it in a glass beaker to catch the solvent rinses.

5.1.2 Container No. 1 (Filter). Transfer the contents directly to the glass thimble of the extraction system and extract them simultaneously with the XAD–2 resin.

5.1.3 Adsorbent Cartridge. Suspend the adsorbent module directly over the extraction thimble in the beaker (See section 5.1.1). The glass frit of the module should be in the up position. Using a Teflon squeeze bottle containing toluene, flush the XAD–2 into the thimble onto the bed of cleaned silica gel. Thoroughly rinse the glass module catching the rinsings in the beaker containing the thimble. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. Add the XAD–2 glass wool plug into the thimble.

5.1.4 Container No. 2 (Acetone and Methylene Chloride). Concentrate the sample to a volume of about 1–5 ml using the rotary evaporator apparatus, at a temperature of less than 37 °C. Rinse the sample container three times with small portions of methylene chloride and add these to the concentrated solution and concentrate further to near dryness. This residue contains particulate matter removed in the rinse of the train probe and nozzle. Add the concentrate to the filter and the XAD–2 resin in the Soxhlet apparatus described in section 5.1.1.

5.1.5 Extraction. Add 100 µl of the internal standard solution (Section 3.3.20) to the extraction thimble containing the contents of the adsorbent cartridge, the contents of Container No. 1, and the concentrate from section 5.1.4. Cover the contents of the extraction thimble with the cleaned glass wool plug to prevent the XAD–2 resin from floating into the solvent reservoir of the extractor. Place the thimble in the extractor, and add the toluene contained in the beaker to the solvent reservoir. Pour additional toluene to fill the reservoir approximately ⅔ full. Add Teflon boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle three times per hour. Extract the sample for 16 hours. After extraction, allow the Soxhlet to cool. Transfer the toluene extract and three 10-ml rinses to the rotary evaporator. Concentrate the extract to approximately 10 ml. At this point the analyst may choose to split the sample in half. If so, split the sample, store one half for future use, and analyze the other according to the procedures in sections 5.2 and 5.3. In either case, use a nitrogen evaporative concentrator to reduce the volume of the sample being analyzed to near dryness. Dissolve the residue in 5 ml of hexane.

5.1.6 Container No. 3 (Toluene Rinse). Add 100 µl of the Internal Standard solution (section 3.3.2) to the contents of the container. Concentrate the sample to a volume of about 1–5 ml using the rotary evaporator apparatus at a temperature of less than 37 °C. Rinse the sample container apparatus at a temperature of less than 37 °C. Rinse the sample container three times with small portions of toluene and add these to the concentrated solution and concentrate further to near dryness. Analyze the extract separately according to the procedures in sections 5.2 and 5.3, but concentrate the solution in a rotary evaporator apparatus rather than a nitrogen evaporative concentrator.

5.2 Sample Cleanup and Fractionation.

5.2.1 Silica Gel Column. Pack one end of a glass column, 20 mm × 230 mm, with glass wool. Add in sequence, 1 g silica gel, 2 g of sodium hydroxide impregnated silica gel, 1 g silica gel, 4 g of acid-modified silica gel, and 1 g of silica gel. Wash the column with 30 ml of hexane and discard it. Add the sample extract, dissolved in 5 ml of hexane to the column with two additional 5-ml rinses. Elute the column with an additional 90 ml of hexane and retain the entire eluate. Concentrate this solution to a volume of about 1 ml using the nitrogen evaporative concentrator (section 2.3.7).

5.2.2 Basic Alumina Column. Shorten a 25-ml disposable Pasteur pipette to about 16 ml. Pack the lower section with glass wool and 12 g of basic alumina. Transfer the concentrated extract from the silica gel column to the top of the basic alumina column and elute the column sequentially with 120 ml of 0.5 percent methylene chloride in hexane followed by 120 ml of 35 percent methylene chloride in hexane. Discard the first 120 ml of eluate. Collect the second 120 ml of eluate and concentrate it to about 0.5 ml using the nitrogen evaporative concentrator.

5.2.3 AX–21 Carbon/Celite 545 Column. Remove the botton 0.5 in. from the tip of a 9-ml disposable Pasteur pipette. Insert a glass fiber filter disk in the top of the pipette 2.5 cm from the constriction. Add sufficient carbon/celite mixture to form a 2 cm column. Top with a glass wool plug. In some cases AX–21 carbon fines may wash through the glass wool plug and enter the sample. This may be prevented by adding a celite plug to the exit end of the column. Rinse the column in sequence with 2 ml of 50 percent benzene in ethyl acetate, 1 ml of 50 percent methylene chloride in cyclohexane, and 2 ml of hexane. Discard these rinses. Transfer the concentrate in 1 ml of hexane from the basic alumina column to the carbon/celite column along with 1 ml of hexane rinse. Elute the column sequentially with 2 ml of 50 percent methylene chloride in hexane and 2 ml of 50 percent benzene in ethyl acetate and discard these eluates. Invert the column and elute in the reverse direction with 13 ml of toluene. Collect this eluate. Concentrate the eluate in a rotary evaporator at 50 °C to about 1 ml. Transfer the concentrate to a Reacti-vial using a toluene rinse and concentrate to a volume of 200 µl using a stream of N_2. Store extracts at room temperature, shielded from light, until the analysis is performed.

5.3 Analysis. Analyze the sample with a gas chromatograph coupled to a mass spectrometer (GC/MS) using the instrumental parameters in sections 5.3.1 and 5.3.2. Immediately prior to analysis, add a 20 µl aliquot of the Recovery Standard solution from Table 1 to each sample. A 2 µl aliquot of the extract is injected into the GC. Sample extracts are first analyzed using the DB–5 capillary column to determine the concentration of each isomer of PCDD's and PCDF's (tetra-through octa-). If tetra-chlorinated dibenzofurans are detected in this analysis, then analyze another aliquot of the sample in a separate run, using the DB–225 column to measure the 2,3,7,8 tetra-chloro dibenzofuran isomer. Other column systems may be used, provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of section 6.1.2.2.

5.3.1 Gas Chromatograph Operating Conditions.

5.3.1.1 Injector. Configured for capillary column, splitless, 250 °C.

5.3.1.2 Carrier Gas. Helium, 1–2 ml/min.

5.3.1.3 Oven. Initially at 150 °C. Raise by at least 40 °C/min to 190 °C and then at 3 °C/min up to 300 °C.

5.3.2 High Resolution Mass Spectrometer.

5.3.2.1 Resolution. 10000 m/e.

5.3.2.2 Ionization Mode. Electron impact.

5.3.2.3 Source Temperature 250 °C.

5.3.2.4 Monitoring Mode. Selected ion monitoring. A list of the various ions to be monitored is summarized in Table 3.

5.3.2.5 Identification Criteria. The following identification criteria shall be used for the characterization of polychlorinated dibenzodioxins and dibenzofurans.

1. The integrated ion-abundance ratio (M/M + 2 or M + 2/M + 4) shall be within 15 percent of the theoretical value. The acceptable ion-abundance ratio ranges for the identification of chlorine-containing compounds are given in Table 4.

2. The retention time for the analytes must be within 3 seconds of the corresponding ^{13}C-labeled internal standard, surrogate or alternate standard.

3. The monitored ions, shown in Table 3 for a given analyte, shall reach their maximum within 2 seconds of each other.

4. The identification of specific isomers that do not have corresponding ^{13}C-labeled standards is done by comparison of the relative retention time (RRT) of the analyte to the nearest internal standard retention time with reference (i.e., within 0.005 RRT units) to the comparable RRT's found in the continuing calibration.

5. The signal to noise ratio for all monitored ions must be greater than 2.5.

6. The confirmation of 2, 3, 7, 8–TCDD and 2, 3, 7, 8–TCDF shall satisfy all of the above identification criteria.

7. For the identification of PCDF's, no signal may be found in the corresponding PCDPE channels.

5.3.2.6 Quantification. The peak areas for the two ions monitored for each analyte are summed to yield the total response for each analyte. Each internal standard is used to quantify the indigenous PCDD's or PCDF's in its homologous series. For example, the $^{13}C_{12}$–2,3,7,8-tetra chlorinated dibenzodioxin is used to calculate the concentrations of all

other tetra chlorinated isomers. Recoveries of the tetra- and penta- internal standards are calculated using the $^{13}C_{12}$–1,2,3,4–TCDD. Recoveries of the hexa- through octa- internal standards are calculated using $^{13}C_{12}$–1,2,3,7,8,9–HxCDD. Recoveries of the surrogate standards are calculated using the corresponding homolog from the internal standard.

6. Calibration

Same as Method 5 with the following additions.

6.1 GC/MS System.

6.1.1 Initial Calibration. Calibrate the GC/MS system using the set of five standards shown in Table 2. The relative standard deviation for the mean response factor from each of the unlabeled analytes (Table 2) and of the internal, surrogate, and alternate standards shall be less than or equal to the values in Table 5. The signal to noise ratio for the GC signal present in every selected ion current profile shall be greater than or equal to 2.5. The ion abundance ratios shall be within the control limits in Table 4.

6.1.2 Daily Performance Check.

6.1.2.1 Calibration Check. Inject on µl of solution Number 3 from Table 2. Calculate the relative response factor (RRF) for each compound and compare each RRF to the corresponding mean RRF obtained during the initial calibration. The analyzer performance is acceptable if the measured RRF's for the labeled and unlabeled compounds for the daily run are within the limits of the mean values shown in Table 5. In addition, the ion-abundance ratios shall be within the allowable control limits shown in Table 4.

6.1.2.2 Column Separation Check. Inject a solution of a mixture of PCDD's and PCDF's that documents resolution between 2,3,7,8–TCDD and other TCDD isomers. Resolution is defined as a valley between peaks that is less than 25 percent of the lower of the two peaks. Identify and record the retention time windows for each homologous series.

Perform a similar resolution check on the confirmation column to document the resolution between 2,3,7,8 TCDF and other TCDF isomers.

6.2 Lock Channels. Set mass spectrometer lock channels as specified in Table 3. Monitor the quality control check channels specified in Table 3 to verify instrument stability during the analysis.

7. Quality Control

7.1 Sampling Train Collection Efficiency Check. Add 100 µl of the surrogate standards in Table 1 to the absorbent cartridge of each train before collecting the field samples.

7.2 Internal Standard Percent Recoveries. A group of nine carbon labeled PCDD's and PCDF's representing, the tetra-through octachlorinated homologues, is added to every sample prior to extraction. The role of the internal standards is to quantify the native PCDD's and PCDF's present in the sample as well as to determine the overall method efficiency. Recoveries of the internal standards must be between 40 to 130 percent for the tetra-through hexachlorinated compounds while the range is 25 to 130 percent for the higher hepta- and octachlorinated homologues.

7.3 Surrogate Recoveries. The five surrogate compounds in Table 2 are added to the resin in the adsorbent sampling cartridge before the sample is collected. The surrogate recoveries are measured relative to the internal standards and are a measure of collection efficiency. They are not used to measure native PCDD's and PCDF's. All recoveries shall be between 70 and 130 percent. Poor recoveries for all the surrogates may be an indication of breakthrough in the sampling train. If the recovery of all standards is below 70 percent, the sampling runs must be repeated. As an alternative, the sampling runs do not have to be repeated if the final results are divided by the fraction of surrogate recovery. Poor recoveries of isolated surrogate compounds should not be grounds for rejecting an entire set of the samples.

7.4 Toluene QA Rinse. Report the results of the toluene QA rinse separately from the total sample catch. Do not add it to the total sample.

8.0 [Reserved]

9. Calculations

Same as Method 5, section 6 with the following additions.

9.1 Nomenclature.

A_{ai} = Integrated ion current of the noise at the retention time of the analyte.

A^*_{ci} = Integrated ion current of the two ions characteristic of the internal standard i in the calibration standard.

A_{cij} = Integrated ion current of the two ions characteristic of compound i in the jth calibration standard.

A^*_{cij} = Integrated ion current of the two ions characteristic of the internal standard i in the jth calibration standard.

A_{csi} = Integrated ion current of the two ions characteristic of surrogate compound i in the calibration standard.

A_i = Integrated ion current of the two ions characteristic of compound i in the sample.

A^*_i = Integrated ion current of the two ions characteristic of internal standard i in the sample.

A_{rs} = Integrated ion current of the two ions characteristic of the recovery standard.

A_{si} = Integrated ion current of the two ions characteristic of surrogate compound i in the sample.

C_i = Concentration of PCDD or PCDF i in the sample, pg/M^3.

C_T = Total concentration of PCDD's or PCDF's in the sample, pg/M^3.
m_{ci} = Mass of compound i in the calibration standard injected into the analyzer, pg.
m_{rs} = Mass of recovery standard in the calibration standard injected into the analyzer, pg.
m_{si} = Mass of surrogate compound in the calibration standard, pg.
RRF_i = Relative response factor.
RRF_{rs} = Recovery standard response factor.
RRF_s = Surrogate compound response factor.

9.2 Average Relative Response Factor.

$$RRF_i = \frac{1}{n}\sum_{j=1}^{n}\frac{A_{cij}\, m^*_{ci}}{A^*_{cij}\, m_{ci}} \qquad \text{Eq. 23-1}$$

9.3 Concentration of the PCDD's and PCDF's.

$$C_i = \frac{m_i^* A_i}{A_i^* RRF_i V_{mstd}} \qquad \text{Eq. 23-2}$$

9.4 Recovery Standard Response Factor.

$$RRF_{rs} = \frac{A_{ci}^* m_{rs}}{A_{rs} m_{ci}^*} \qquad \text{Eq. 23-3}$$

9.5 Recovery of Internal Standards (R*).

$$R^* = \frac{A_i^* m_{rs}}{A_{rs} RF_{rs} m_i^*} \times 100\% \qquad \text{Eq. 23-4}$$

9.6 Surrogate Compound Response Factor.

$$RRF_s = \frac{A_{ci}^* m_s}{A_{cis} m_{ci}^*} \qquad \text{Eq. 23-5}$$

9.7 Recovery of Surrogate Compounds (R_s).

$$R_s = \frac{A_s m_i^*}{A_i^* RRF_s m_s} \times 100\% \qquad \text{Eq. 23-6}$$

9.8 Minimum Detectable Limit (MDL).

$$MDL = \frac{2.5\, A_{ai} m_i^*}{A_{ci}^* RRF_i} \qquad \text{Eq. 23-7}$$

9.9 Total Concentration of PCDD's and PCDF's in the Sample.

$$C_{Tr} = \sum_{i=1}^{n} C_i \qquad \text{Eq. 23-8}$$

Any PCDD's or PCDF's that are reported as nondetected (below the MDL) shall be counted as zero for the purpose of calculating the total concentration of PCDD's and PCDF's in the sample.

10. Bibliography

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2. American Society of Mechanical Engineers. Analytical Procedures to Assay Stack Effluent Samples and Residual Combustion Products for Polychlorinated Dibenzo-p-Dioxins (PCDD) and Polychlorinated Dibenzofurans (PCDF). Prepared for the U.S. Department of Energy and U.S. Environmental Protection Agency. Washington, DC. December 1984. 23 p.

3. Thompson, J. R. (ed.). Analysis of Pesticide Residues in Human and Environmental Samples. U.S. Environmental Protection Agency. Research Triangle Park, NC. 1974.

4. Triangle Laboratories. Case Study: Analysis of Samples for the Presence of Tetra Through Octachloro-p-Dibenzodioxins and Dibenzofurans. Research Triangle Park, NC. 1988. 26 p.

5. U.S. Environmental Protection Agency. Method 8290—The Analysis of Polychlorinated Dibenzo-p-dioxin and Polychlorinated Dibenzofurans by High-Resolution Gas Chromotography/High-Resolution Mass Spectrometry. In: Test Methods for Evaluating Solid Waste. Washington, DC. SW–846.

TABLE 1—COMPOSITION OF THE SAMPLE FORTIFICATION AND RECOVERY STANDARDS SOLUTIONS

Analyte	Concentration (pg/µl)
Internal Standards:	
$^{13}C_{12}$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100
$^{13}C_{12}$-OCDD	100
$^{13}C_{12}$-2,3,7,8-TCDF	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100
Surrogate Standards:	
$^{37}Cl_4$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100
Recovery Standards:	
$^{13}C_{12}$-1,2,3,4-TCDD	500
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	500

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS

Compound	Concentrations (pg/µL)				
	Solution No.				
	1	2	3	4	5
Alternate Standard:					
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	2.5	5	25	250	500

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS—Continued

Compound	Concentrations (pg/μL)				
	Solution No.				
	1	2	3	4	5
Recovery Standards:					
$^{13}C_{12}$-1,2,3,4-TCDD ..	100	100	100	100	100

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS—Continued

Compound	Concentrations (pg/μL)				
	Solution No.				
	1	2	3	4	5
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

TABLE 3—ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HIGH RESOLUTION MASS SPECTROMETRY FOR PCDD'S AND PCDF'S

Descriptor No.	Accurate mass	Ion type	Elemental composition	Analyte
2	292.9825	LOCK	C_7F_{11}	PFK
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M + 2	$C_{12}H_4{}^{35}Cl^{37}O$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M + 2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}ClO_2$	TCDD
	321.8936	M + 2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD (S)
	330.9792	QC	C_7F_{13}	PFK
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9339	M + 2	$^{13}C_{12}H_4{}^{35}Cl^{37}ClO_2$	TCDD (S)
	339.8597	M + 2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PECDF
	341.8567	M + 4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M + 2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M + 4	$^{13}C_{12}H_3{}^{35}Cl^{3537}Cl_2O$	PeCDF (S)
	355.8546	M + 2	$C_{12}H_3{}^{35}Cl_3 37ClO_2$	PeCDD
	357.8516	M + 4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M + 2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M + 4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}\ Cl_2O_2$	PeCDD (S)
	375.8364	M + 2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
	409.7974	M + 2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCPDE
3	373.8208	M + 2	$C_{12}H_2 35Cl_5{}^{37}ClO$	HxCDF
	375.8178	M + 4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M + 2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8157	M + 2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M + 4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	392.9760	LOCK	C_9F_{15}	PFK
	401.8559	M + 2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M + 4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDD (S)
	445.7555	M + 4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	430.9729	QC	C_9F_{17}	PFK
4	407.7818	M + 2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M + 4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8253	M	$^{13}C_{12}H^{35}Cl_7O$	HpCDF (S)
	419.8220	M + 2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF (S)
	423.7766	M + 2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M + 4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M + 2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M + 4	$^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S)
	479.7165	M + 4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCPDE
	430.9729	LOCK	C_9F_{17}	PFK
	441.7428	M + 2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M + 4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M + 2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M + 4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M + 2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M + 4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S)
	513.6775	M + 4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O_2$	DCDPE
	442.9728	QC	$C_{10}F_{17}$	PFK

(a) The following nuclidic masses were used:
H = 1.007825
C = 12.000000
^{13}C = 13.003355
F = 18.9984
O = 15.994915
^{35}Cl = 34.968853
^{37}Cl = 36.965903

S = Labeled Standard
QC = Ion selected for monitoring instrument stability during the GC/MS analysis.

TABLE 4—ACCEPTABLE RANGES FOR ION-ABUNDANCE RATIOS OF PCDD'S AND PCDF'S

No. of chlorine atoms	Ion type	Theoretical ratio	Control limits	
			Lower	Upper
4	M/M + 2	0.77	0.65	0.89
5	M + 2/M + 4	1.55	1.32	1.78
6	M + 2/M + 4	1.24	1.05	1.43
6[a]	M/M + 2	0.51	0.43	0.59
7[b]	M/M + 2	0.44	0.37	0.51
7	M + 2/M + 4	1.04	0.88	1.20
8	M + 2/M + 4	0.89	0.76	1.02

[a] Used only for ^{13}C-HxCDF.
[b] Used only for ^{13}C-HpCDF.

TABLE 5—MINIMUM REQUIREMENTS FOR INITIAL AND DAILY CALIBRATION RESPONSE FACTORS

Compound	Relative response factors	
	Initial calibration RSD	Daily calibration % difference
Unlabeled Analytes:		
2,3,7,8-TCDD	25	25
2,3,7,8-TCDF	25	25
1,2,3,7,8-PeCDD	25	25
1,2,3,7,8-PeCDF	25	25
2,3,4,7,8-PeCDF	25	25
1,2,4,5,7,8-HxCDD	25	25
1,2,3,6,7,8-HxCDD	25	25
1,2,3,7,8,9-HxCDD	25	25
1,2,3,4,7,8-HxCDF	25	25
1,2,3,6,7,8-HxCDF	25	25
1,2,3,7,8,9-HxCDF	25	25
2,3,4,6,7,8-HxCDF	25	25
1,2,3,4,6,7,8-HpCDD	25	25
1,2,3,4,6,7,8-HpCDF	25	25
OCDD	25	25
OCDF	30	30
Internal Standards:		
$^{13}C_{12}$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-1,2,3,7,8-PeCDD	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	30	30
$^{13}C_{12}$-OCDD	30	30
$^{13}C_{12}$-2,3,7,8-TCDF	30	30
$^{13}C_{12}$-1,2,3,7,8-PeCDF	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	30	30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	30	30
Surrogate Standards:		
$^{37}Cl_4$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-2,3,4,7,8-PeCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	25	25
Alternate Standard:		
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	25	25

METHOD 24—DETERMINATION OF VOLATILE MATTER CONTENT, WATER CONTENT, DENSITY, VOLUME SOLIDS, AND WEIGHT SOLIDS OF SURFACE COATINGS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile organic compounds	No CAS Number assigned
Water.	7732–18–5

1.2 Applicability. This method is applicable for the determination of volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or other related surface coatings.

1.3 Precision and Bias. Intra-and inter-laboratory analytical precision statements are presented in section 13.1. No bias has been identified.

2.0 Summary of Method

2.1 Standard methods are used to determine the volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or other related surface coatings.

3.0 Definitions

3.1 *Waterborne coating* means any coating which contains more than 5 percent water by weight in its volatile fraction.

3.2 *Multicomponent coatings* are coatings that are packaged in two or more parts, which are combined before application. Upon combination a coreactant from one part of the coating chemically reacts, at ambient conditions, with a coreactant from another part of the coating.

3.3 *Ultraviolet (UV) radiation-cured coatings* are coatings which contain unreacted monomers that are polymerized by exposure to ultraviolet light.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Components. Several of the compounds that may be contained in the coatings analyzed by this method may be irritating or corrosive to tissues (e.g., heptane) or may be toxic (e.g., benzene, methyl alcohol). Nearly all are fire hazards.

Appropriate precautions can be found in reference documents, such as Reference 3 of section 16.0.

6.0 Equipment and Supplies

The equipment and supplies specified in the ASTM methods listed in sections 6.1 through 6.6 (incorporated by reference—see §60.17 for acceptable versions of the methods) are required:

6.1 ASTM D 1475–60, 80, or 90, Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products.

6.2 ASTM D 2369–81, 87, 90, 92, 93, or 95, Standard Test Method for Volatile Content of Coatings.

6.3 ASTM D 3792–79 or 91, Standard Test Method for Water Content of Water Reducible Paints by Direct Injection into a Gas Chromatograph.

6.4 ASTM D 4017–81, 90, or 96a, Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Titration Method.

6.5 ASTM 4457–85 91, Standard Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph.

6.6 ASTM D 5403–93, Standard Test Methods for Volatile Content of Radiation Curable Materials.

6.7 ASTM D 6419–00, Test Method for Volatile Content of Sheet-Fed and Coldset Web Offset Printing Inks.

7.0 Reagents and Standards

7.1 The reagents and standards specified in the ASTM methods listed in sections 6.1 through 6.6 are required.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Follow the sample collection, preservation, storage, and transport procedures described in Reference 1 of section 16.0.

9.0 Quality Control

9.1 Reproducibility

NOTE: Not applicable to UV radiation-cured coatings). The variety of coatings that may be subject to analysis makes it necessary to verify the ability of the analyst and the analytical procedures to obtain reproducible results for the coatings tested. Verification is accomplished by running duplicate analyses on each sample tested (Sections 11.2 through 11.4) and comparing the results with the intra-laboratory precision statements (Section 13.1) for each parameter.

9.2 Confidence Limits for Waterborne Coatings. Because of the inherent increased imprecision in the determination of the VOC content of waterborne coatings as the weight percent of water increases, measured parameters for waterborne coatings are replaced with appropriate confidence limits (Section 12.6). These confidence limits are based on measured parameters and inter-laboratory precision statements.

10.0 Calibration and Standardization

10.1 Perform the calibration and standardization procedures specified in the ASTM methods listed in sections 6.1 through 6.6.

11.0 Analytical Procedure

Additional guidance can be found in Reference 2 of section 16.0.

11.1 Non Thin-film Ultraviolet Radiation-cured (UV radiation-cured) Coatings.

11.1.1 Volatile Content. Use the procedure in ASTM D 5403 to determine the volatile matter content of the coating except the curing test described in NOTE 2 of ASTM D 5403 is required.

11.1.2 Water Content. To determine water content, follow section 11.3.2.

11.1.3 Coating Density. To determine coating density, follow section 11.3.3.

11.1.4 Solids Content. To determine solids content, follow section 11.3.4.

11.1.5 To determine if a coating or ink can be classified as a thin-film UV cured coating or ink, use the equation in section 12.2. If C is less than 0.2 g and A is greater than or equal to 225 cm^2 (35 in^2) then the coating or ink is considered a thin-film UV radiation-cured coating and ASTM D 5403 is not applicable.

NOTE: As noted in section 1.4 of ASTM D 5403, this method may not be applicable to radiation curable materials wherein the volatile material is water.

11.2 Multi-component Coatings.

11.2.1 Sample Preparation.

11.2.1.1 Prepare about 100 ml of sample by mixing the components in a storage container, such as a glass jar with a screw top or a metal can with a cap. The storage container should be just large enough to hold the mixture. Combine the components (by weight or volume) in the ratio recommended by the manufacturer. Tightly close the container between additions and during mixing to prevent loss of volatile materials. However, most manufacturers mixing instructions are by volume. Because of possible error caused by expansion of the liquid when measuring the volume, it is recommended that the components be combined by weight. When weight is used to combine the components and the manufacturer's recommended ratio is by volume, the density must be determined by section 11.3.3.

11.2.1.2 Immediately after mixing, take aliquots from this 100 ml sample for determination of the total volatile content, water content, and density.

11.2.2 Volatile Content. To determine total volatile content, use the apparatus and

reagents described in ASTM D2369 (incorporated by reference; see §60.17 for the approved versions of the standard), respectively, and use the following procedures:

11.2.2.1 Weigh and record the weight of an aluminum foil weighing dish. Add 3 ±1 ml of suitable solvent as specified in ASTM D2369 to the weighing dish. Using a syringe as specified in ASTM D2369, weigh to 1 mg, by difference, a sample of coating into the weighing dish. For coatings believed to have a volatile content less than 40 weight percent, a suitable size is 0.3 + 0.10 g, but for coatings believed to have a volatile content greater than 40 weight percent, a suitable size is 0.5 ±0.1 g.

NOTE: If the volatile content determined pursuant to section 12.4 is not in the range corresponding to the sample size chosen repeat the test with the appropriate sample size. Add the specimen dropwise, shaking (swirling) the dish to disperse the specimen completely in the solvent. If the material forms a lump that cannot be dispersed, discard the specimen and prepare a new one. Similarly, prepare a duplicate. The sample shall stand for a minimum of 1 hour, but no more than 24 hours prior to being oven cured at 110 ±5 °C (230 ±9 °F) for 1 hour.

11.2.2.2 Heat the aluminum foil dishes containing the dispersed specimens in the forced draft oven for 60 min at 110 ±5 °C (230 ±9 °F). Caution—provide adequate ventilation, consistent with accepted laboratory practice, to prevent solvent vapors from accumulating to a dangerous level.

11.2.2.3 Remove the dishes from the oven, place immediately in a desiccator, cool to ambient temperature, and weigh to within 1 mg.

11.2.2.4 Run analyses in pairs (duplicate sets) for each coating mixture until the criterion in section 11.4 is met. Calculate W_V following Equation 24–2 and record the arithmetic average.

11.2.3 Water Content. To determine water content, follow section 11.3.2.

11.2.4 Coating Density. To determine coating density, follow section 11.3.3.

11.2.5 Solids Content. To determine solids content, follow section 11.3.4.

11.2.6 Exempt Solvent Content. To determine the exempt solvent content, follow section 11.3.5.

NOTE: For all other coatings (*i.e.*, water-or solvent-borne coatings) not covered by multicomponent or UV radiation-cured coatings, analyze as shown below:

11.3 Water-or Solvent-borne coatings.

11.3.1 Volatile Content. Use the procedure in ASTM D 2369 to determine the volatile matter content (may include water) of the coating.

11.3.1.1 Record the following information:

W_1 = weight of dish and sample before heating, g

W_2 = weight of dish and sample after heating, g

W_3 = sample weight, g.

11.3.1.2 Calculate the weight fraction of the volatile matter (W_v) for each analysis as shown in section 12.3.

11.3.1.3 Run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement in section 13.1.

11.3.1.4 Record the arithmetic average (W_v).

11.3.2 Water Content. For waterborne coatings only, determine the weight fraction of water (W_w) using either ASTM D 3792 or ASTM D 4017.

11.3.2.1 Run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement in section 13.1.

11.3.2.2 Record the arithmetic average (w_w).

11.3.3 Coating Density. Determine the density (Dc, kg/l) of the surface coating using the procedure in ASTM D 1475.

11.3.3.1 Run duplicate analyses until each value in a set deviates from the mean of the set by no more than the intra-laboratory precision statement in section 13.1.

11.3.3.2 Record the arithmetic average (D_c).

11.3.4 Solids Content. Determine the volume fraction (V_s) solids of the coating by calculation using the manufacturer's formulation.

11.3.5 Exempt Solvent Content. Determine the weight fraction of exempt solvents (W_E) by using ASTM Method D4457. Run a duplicate set of determinations and record the arithmetic average (W_E).

11.4 Sample Analysis Criteria. For W_v and W_w, run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement for that parameter. For D_c, run duplicate analyses until each value in a set deviates from the mean of the set by no more than the intra-laboratory precision statement. If, after several attempts, it is concluded that the ASTM procedures cannot be used for the specific coating with the established intra-laboratory precision (excluding UV radiation-cured coatings), the U.S. Environmental Protection Agency (EPA) will assume responsibility for providing the necessary procedures for revising the method or precision statements upon written request to: Director, Emissions, Monitoring, and Analysis Division, MD–14, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

12.0 Calculations and Data Analysis

12.1 Nomenclature.

A = Area of substrate, cm^2, (in^2).

C = Amount of coating or ink added to the substrate, g.

D_c = Density of coating or ink, g/cm^3 (g/in^3).

F = Manufacturer's recommended film thickness, cm (in).
W_o = Weight fraction of nonaqueous volatile matter, g/g.
W_s = Weight fraction of solids, g/g.
W_v = Weight fraction of the volatile matter, g/g.
W_w = Weight fraction of the water, g/g.

12.2 To determine if a coating or ink can be classified as a thin-film UV cured coating or ink, use the following equation:

$$C = F A D_c \qquad \text{Eq. 24-1}$$

12.3 Calculate W_v for each analysis as shown below:

$$W_v = \frac{W_1 - W_2}{W_3} \qquad \text{Eq. 24-2}$$

12.4 Nonaqueous Volatile Matter.
12.4.1 Solvent-borne Coatings.

$$W_o = W_v \qquad \text{Eq. 24-3}$$

12.4.2 Waterborne Coatings.

$$W_o = W_v - W_w \qquad \text{Eq. 24-4}$$

12.4.3 Coatings Containing Exempt Solvents.

$$W_o = W_v - W_E - W_w \qquad \text{Eq. 24-5}$$

12.5 Weight Fraction Solids.

$$W_s = 1 - W_v \qquad \text{Eq. 24-6}$$

12.6 Confidence Limit Calculations for Waterborne Coatings. To calculate the lower confidence limit, subtract the appropriate inter-laboratory precision value from the measured mean value for that parameter. To calculate the upper confidence limit, add the appropriate inter-laboratory precision value to the measured mean value for that parameter. For W_v and D_c, use the lower confidence limits; for W_w, use the upper confidence limit. Because W_s is calculated, there is no adjustment for this parameter.

13.0 Method Performance

13.1 Analytical Precision Statements. The intra-and inter-laboratory precision statements are given in Table 24–1 in section 17.0.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as specified in section 6.0, with the addition of the following:

1. Standard Procedure for Collection of Coating and Ink Samples for Analysis by Reference Methods 24 and 24A. EPA–340/1–91–010. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

2. Standard Operating Procedure for Analysis of Coating and Ink Samples by Reference Methods 24 and 24A.

EPA–340/1–91–011. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

3. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 24–1—ANALYTICAL PRECISION STATEMENTS

	Intra-laboratory	Inter-laboratory
Volatile matter content, W_v	±0.015 $\overline{W}_v$	±0.047 $\overline{W}_v$
Water content, W_w	±0.029 $\overline{W}_w$	±0.075 $\overline{W}_w$
Density, D_c	±0.001 kg/l	±0.002 kg/l

METHOD 24A—DETERMINATION OF VOLATILE MATTER CONTENT AND DENSITY OF PUBLICATION ROTOGRAVURE INKS AND RELATED PUBLICATION ROTOGRAVURE COATINGS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile organic compounds (VOC).	No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of the VOC content and density of solvent-borne (solvent-reducible) publication rotogravure inks and related publication rotogravure coatings.

2.0 Summary of Method

2.1 Separate procedures are used to determine the VOC weight fraction and density of the ink or related coating and the density of the solvent in the ink or related coating. The VOC weight fraction is determined by measuring the weight loss of a known sample quantity which has been heated for a specified length of time at a specified temperature. The density of both the ink or related coating and solvent are measured by a standard procedure. From this information, the VOC volume fraction is calculated.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Components. Some of the compounds that may be contained in the inks or related coatings analyzed by this method may be irritating or corrosive to tissues or may be toxic. Nearly all are fire hazards. Appropriate precautions can be found in reference documents, such as Reference 6 of section 16.0.

6.0 Equipment and Supplies

The following equipment and supplies are required for sample analysis:

6.1 Weighing Dishes. Aluminum foil, 58 mm (2.3 in.) in diameter by 18 mm (0.7 in.) high, with a flat bottom. There must be at least three weighing dishes per sample.

6.2 Disposable Syringe. 5 ml.

6.3 Analytical Balance. To measure to within 0.1 mg.

6.4 Oven. Vacuum oven capable of maintaining a temperature of 120 ±2 °C (248 ±4 °F) and an absolute pressure of 510 ±51 mm Hg (20 ±2 in. Hg) for 4 hours. Alternatively, a forced draft oven capable of maintaining a temperature of 120 ±2 °C (248 ±4 °F) for 24 hours.

6.5 The equipment and supplies specified in ASTM D 1475–60, 80, or 90 (incorporated by reference—see §60.17).

7.0 Reagents and Standards

7.1 The reagents and standards specified in ASTM D 1475–60, 80, or 90 are required.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Follow the sample collection, preservation, storage, and transport procedures described in Reference 4 of section 16.0.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

Additional guidance can be found in Reference 5 of section 16.0.

11.1 VOC Weight Fraction. Shake or mix the ink or related coating sample thoroughly to assure that all the solids are completely suspended. Label and weigh to the nearest 0.1 mg a weighing dish and record this weight (M_{x1}). Using a 5 ml syringe, without a needle, extract an aliquot from the ink or related coating sample. Weigh the syringe and aliquot to the nearest 0.1 mg and record this weight (M_{cy1}). Transfer 1 to 3 g of the aliquot to the tared weighing dish. Reweigh the syringe and remaining aliquot to the nearest 0.1 mg and record this weight (M_{cy2}). Heat the weighing dish with the transferred aliquot in a vacuum oven at an absolute pressure of 510 ±51 mm Hg (20 ±2 in. Hg) and a temperature of 120 ±2 °C (248 ±4 °F) for 4 hours. Alternatively, heat the weighing dish with the transferred aliquot in a forced draft oven at a temperature of 120 ±2 °C for 24 hours. After the weighing dish has cooled, reweigh it to the nearest 0.1 mg and record the weight (M_{x2}). Repeat this procedure two times for each ink or related coating sample, for a total of three samples.

11.2 Ink or Related Coating Density. Determine the density of the ink or related coating (D_c) according to the procedure outlined in ASTM D 1475. Make a total of three determinations for each ink or related coating sample. Report the ink or related coating density as the arithmetic average (D_c) of the three determinations.

11.3 Solvent Density. Determine the density of the solvent (D_o) according to the procedure outlined in ASTM D 1475. Make a total of three determinations for each ink or related coating sample. Report the solvent density as the arithmetic average (D_o) of the three determinations.

12.0 Calculations and Data Analysis

12.1 VOC Weight Fraction. For each determination, calculate the volatile organic content weight fraction (W_o) using the following equation:

$$W_o = \frac{M_{x1} + M_{cy1} - M_{cy2} - M_{x2}}{M_{cy1} - M_{cy2}} \qquad \text{Eq. 24A-1}$$

Make a total of three determinations. Report the VOC weight fraction as the arithmetic average ($\bar{W}_o$) of the three determinations.

12.2 VOC Volume Fraction. Calculate the volume fraction volatile organic content (V_o) using the following equation:

$$V_o = \frac{\overline{W}_o \overline{D}_c}{\overline{D}_o} \qquad \text{Eq. 24A-2}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products. ASTM Designation D 1475.

2. Teleconversation. Wright, Chuck, Inmont Corporation with Reich, R., A., Radian Corporation. September 25, 1979, Gravure Ink Analysis.

3. Teleconversation. Oppenheimer, Robert, Gravure Research Institute with Burt, Rick, Radian Corporation, November 5, 1979, Gravure Ink Analysis.

4. Standard Procedure for Collection of Coating and Ink Samples for Analysis by Reference Methods 24 and 24A. EPA–340/1–91–010. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

5. Standard Operating Procedure for Analysis of Coating and Ink Samples by Reference Methods 24 and 24A. EPA–340/1–91–011. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

6. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

Method 25—Determination of Total Gaseous Nonmethane Organic Emissions as Carbon

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total gaseous nonmethane organic compounds (TGNMO)	N/A	Dependent upon analytical equipment.

1.2 Applicability.

1.2.1 This method is applicable for the determination of volatile organic compounds (VOC) (measured as total gaseous nonmethane organics (TGNMO) and reported as carbon) in stationary source emissions. This method is not applicable for the determination of organic particulate matter.

1.2.2 This method is not the only method that applies to the measurement of VOC. Costs, logistics, and other practicalities of source testing may make other test methods more desirable for measuring VOC contents of certain effluent streams. Proper judgment is required in determining the most applicable VOC test method. For example, depending upon the molecular composition of the organics in the effluent stream, a totally automated semicontinuous nonmethane organics (NMO) analyzer interfaced directly to the source may yield accurate results. This approach has the advantage of providing emission data semicontinuously over an extended time period.

1.2.3 Direct measurement of an effluent with a flame ionization detector (FID) analyzer may be appropriate with prior characterization of the gas stream and knowledge that the detector responds predictably to the organic compounds in the stream. If present, methane (CH_4) will, of course, also be measured. The FID can be used under any of the following limited conditions: (1) Where only one compound is known to exist; (2) when the organic compounds consist of only hydrogen and carbon; (3) where the relative percentages of the compounds are known or can be determined, and the FID responses to the compounds are known; (4) where a consistent mixture of the compounds exists before and after emission control and only the relative concentrations are to be assessed; or (5) where the FID can be calibrated against mass standards of the compounds emitted (solvent emissions, for example).

1.2.4 Another example of the use of a direct FID is as a screening method. If there is enough information available to provide a rough estimate of the analyzer accuracy, the FID analyzer can be used to determine the VOC content of an uncharacterized gas stream. With a sufficient buffer to account for possible inaccuracies, the direct FID can be a useful tool to obtain the desired results without costly exact determination.

1.2.5 In situations where a qualitative/quantitative analysis of an effluent stream is desired or required, a gas chromatographic FID system may apply. However, for sources emitting numerous organics, the time and expense of this approach will be formidable.

2.0 Summary of Method

2.1 An emission sample is withdrawn from the stack at a constant rate through a heated filter and a chilled condensate trap by means of an evacuated sample tank. After sampling is completed, the TGNMO are determined by independently analyzing the condensate trap and sample tank fractions and combining the analytical results. The organic content of the condensate trap fraction is determined by oxidizing the NMO to carbon dioxide (CO_2) and quantitatively collecting in the effluent in an evacuated vessel; then a portion of the CO_2 is reduced to CH_4 and measured by an FID. The organic content of the sample tank fraction is measured by injecting a portion of the sample into a gas chromatographic column to separate the NMO from carbon monoxide (CO), CO_2, and CH_4; the NMO are oxidized to CO_2, reduced to CH_4, and measured by an FID. In this manner, the variable response of the FID associated with different types of organics is eliminated.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Carbon Dioxide and Water Vapor. When carbon dioxide (CO_2) and water vapor are present together in the stack, they can produce a positive bias in the sample. The magnitude of the bias depends on the concentrations of CO_2 and water vapor. As a guideline, multiply the CO_2 concentration, expressed as volume percent, times the water vapor concentration. If this product does not exceed 100, the bias can be considered insignificant. For example, the bias is not significant for a source having 10 percent CO_2 and 10 percent water vapor, but it might be significant for a source having 10 percent CO_2 and 20 percent water vapor.

4.2. Particulate Matter. Collection of organic particulate matter in the condensate trap would produce a positive bias. A filter is included in the sampling equipment to minimize this bias.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling system consists of a heated probe, heated filter, condensate trap, flow control system, and sample tank (see Figure 25–1). The TGNMO sampling equipment can be constructed from commercially available components and components fabricated in a machine shop. The following equipment is required:

6.1.1 Heated Probe. 6.4-mm (¼-in.) OD stainless steel tubing with a heating system capable of maintaining a gas temperature at the exit end of at least 129 °C (265 °F). The probe shall be equipped with a temperature sensor at the exit end to monitor the gas temperature. A suitable probe is shown in Figure 25–1. The nozzle is an elbow fitting attached to the front end of the probe while the temperature sensor is inserted in the side arm of a tee fitting attached to the rear of the probe. The probe is wrapped with a suitable length of high temperature heating tape, and then covered with two layers of glass cloth insulation and one layer of aluminum foil or an equivalent wrapping.

NOTE: If it is not possible to use a heating system for safety reasons, an unheated system with an in-stack filter is a suitable alternative.

6.1.2 Filter Holder. 25-mm (15/16-in.) ID Gelman filter holder with 303 stainless steel body and 316 stainless steel support screen with the Viton O-ring replaced by a Teflon O-ring.

6.1.3 Filter Heating System.

6.1.3.1 A metal box consisting of an inner and an outer shell separated by insulating material with a heating element in the inner shell capable of maintaining a gas temperature at the filter of 121 ±3 °C (250 ±5 °F). The heating box shall include temperature sensors to monitor the gas temperature immediately upstream and immediately downstream of the filter.

6.1.3.2 A suitable heating box is shown in Figure 25–2. The outer shell is a metal box that measures 102 mm × 280 mm × 292 mm (4 in. × 11 in. × 11½ in.), while the inner shell is a metal box measuring 76 mm × 229 mm × 241 mm (3 in. × 9 in. × 9½ in.). The inner box is supported by 13-mm (½-in.) phenolic rods. The void space between the boxes is filled with ceramic fiber insulation which is sealed in place by means of a silicon rubber bead around the upper sides of the box. A removable lid made in a similar manner, with a 25-mm (1-in.) gap between the parts is used to cover the heating chamber. The inner box is heated with a 250-watt cartridge heater, shielded by a stainless steel shroud. The heater is regulated by a thermostatic temperature controller which is set to maintain a gas temperature of 121 °C (250 °F) as measured by the temperature sensor upstream of the filter.

NOTE: If it is not possible to use a heating system for safety reasons, an unheated system with an in-stack filter is a suitable alternative.

6.1.4 Condensate Trap. 9.5-mm (⅜-in.) OD 316 stainless steel tubing bent into a U-shape. Exact dimensions are shown in Figure

25–3. The tubing shall be packed with coarse quartz wool, to a density of approximately 0.11 g/cm^3 before bending. While the condensate trap is packed with dry ice in the Dewar, an ice bridge may form between the arms of the condensate trap making it difficult to remove the condensate trap. This problem can be prevented by attaching a steel plate between the arms of the condensate trap in the same plane as the arms to completely fill the intervening space.

6.1.5 Valve. Stainless steel control valve for starting and stopping sample flow.

6.1.6 Metering Valve. Stainless steel valve for regulating the sample flow rate through the sample train.

6.1.7 Rate Meter. Rotameter, or equivalent, capable of measuring sample flow in the range of 60 to 100 cm^3/min (0.13 to 0.21 ft^3/hr).

6.1.8 Sample Tank. Stainless steel or aluminum tank with a minimum volume of 4 liters (0.14 ft^3).

NOTE: Sample volumes greater than 4 liters may be required for sources with low organic concentrations.

6.1.9 Mercury Manometer. U-tube manometer or absolute pressure gauge capable of measuring pressure to within 1 mm Hg in the range of 0 to 900 mm.

6.1.10 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

6.2 Condensate Recovery. The system for the recovery of the organics captured in the condensate trap consists of a heat source, an oxidation catalyst, a nondispersive infrared (NDIR) analyzer, and an intermediate collection vessel (ICV). Figure 25–4 is a schematic of a typical system. The system shall be capable of proper oxidation and recovery, as specified in section 10.1.1. The following major components are required:

6.2.1 Heat Source. Sufficient to heat the condensate trap (including probe) to a temperature of 200 °C (390 °F). A system using both a heat gun and an electric tube furnace is recommended.

6.2.2 Heat Tape. Sufficient to heat the connecting tubing between the water trap and the oxidation catalyst to 100 °C (212 °F).

6.2.3 Oxidation Catalyst. A suitable length of 9.5 mm (3/8-in.) OD Inconel 600 tubing packed with 15 cm (6 in.) of 3.2 mm (3/8-in.) diameter 19 percent chromia on alumina pellets. The catalyst material is packed in the center of the catalyst tube with quartz wool packed on either end to hold it in place.

6.2.4 Water Trap. Leak-proof, capable of removing moisture from the gas stream.

6.2.5 Syringe Port. A 6.4-mm (1/4-in.) OD stainless steel tee fitting with a rubber septum placed in the side arm.

6.2.6 NDIR Detector. Capable of indicating CO_2 concentration in the range of zero to 5 percent, to monitor the progress of combustion of the organic compounds from the condensate trap.

6.2.7 Flow-Control Valve. Stainless steel, to maintain the trap conditioning system near atmospheric pressure.

6.2.8 Intermediate Collection Vessel. Stainless steel or aluminum, equipped with a female quick connect. Tanks with nominal volumes of at least 6 liters (0.2 ft^3) are recommended.

6.2.9 Mercury Manometer. Same as described in section 6.1.9.

6.2.10 Syringe. 10-ml gas-tight glass syringe equipped with an appropriate needle.

6.2.11 Syringes. 10-µl and 50-µl liquid injection syringes.

6.2.12 Liquid Sample Injection Unit. 316 Stainless steel U-tube fitted with an injection septum (see Figure 25–7).

6.3 Analysis.

6.3.1 NMO Analyzer. The NMO analyzer is a gas chromatograph (GC) with backflush capability for NMO analysis and is equipped with an oxidation catalyst, reduction catalyst, and FID. Figures 25–5 and 25–6 are schematics of a typical NMO analyzer. This semicontinuous GC/FID analyzer shall be capable of: (1) Separating CO, CO_2, and CH_4 from NMO, (2) reducing the CO_2 to CH_4 and quantifying as CH_4, and (3) oxidizing the NMO to CO_2, reducing the CO_2 to CH_4 and quantifying as CH_4, according to section 10.1.2. The analyzer consists of the following major components:

6.3.1.1 Oxidation Catalyst. A suitable length of 9.5-mm (3/8-in.) OD Inconel 600 tubing packed with 5.1 cm (2 in.) of 19 percent chromia on 3.2-mm (1/8-in.) alumina pellets. The catalyst material is packed in the center of the tube supported on either side by quartz wool. The catalyst tube must be mounted vertically in a 650 °C (1200 °F) furnace. Longer catalysts mounted horizontally may be used, provided they can meet the specifications of section 10.1.2.1.

6.3.1.2 Reduction Catalyst. A 7.6-cm (3-in.) length of 6.4-mm (1/4-in.) OD Inconel tubing fully packed with 100-mesh pure nickel powder. The catalyst tube must be mounted vertically in a 400 °C (750 °F) furnace.

6.3.1.3 Separation Column(s). A 30-cm (1-ft) length of 3.2-mm (1/8-in.) OD stainless steel tubing packed with 60/80 mesh Unibeads 1S followed by a 61-cm (2-ft) length of 3.2-mm (1/8-in.) OD stainless steel tubing packed with 60/80 mesh Carbosieve G. The Carbosieve and Unibeads columns must be baked separately at 200 °C (390 °F) with carrier gas flowing through them for 24 hours before initial use.

6.3.1.4 Sample Injection System. A single 10-port GC sample injection valve or a group of valves with sufficient ports fitted with a sample loop properly sized to interface with the NMO analyzer (1-cc loop recommended).

6.3.1.5 FID. An FID meeting the following specifications is required:

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6.3.1.5.1 Linearity. A linear response (±5 percent) over the operating range as demonstrated by the procedures established in section 10.1.2.3.

6.3.1.5.2 Range. A full scale range of 10 to 50,000 ppm CH_4. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.3.1.6 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the analytical results.

6.3.2 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm Hg.

6.3.3 Temperature Sensor. Capable of measuring the laboratory temperature within 1 °C (2 °F).

6.3.4 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

7.0 Reagents and Standards

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Dry Ice. Solid CO2, crushed.

7.1.2 Coarse Quartz Wool. 8 to 15 um.

7.1.3 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Method D2986–71, 78, or 95a (incorporated by reference—see §60.17). Test data from the supplier's quality control program are sufficient for this purpose.

7.2 NMO Analysis. The following gases are required for NMO analysis:

7.2.1 Carrier Gases. Helium (He) and oxygen (O_2) containing less than 1 ppm CO_2 and less than 0.1 ppm hydrocarbon.

7.2.2 Fuel Gas. Hydrogen (H_2), at least 99.999 percent pure.

7.2.3 Combustion Gas. Either air (less than 0.1 ppm total hydrocarbon content) or O_2 (purity 99.99 percent or greater), as required by the detector.

7.3 Condensate Analysis. The following are required for condensate analysis:

7.3.1 Gases. Containing less than 1 ppm carbon.

7.3.1.1 Air.

7.3.1.2 Oxygen.

7.3.2 Liquids. To conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society.

7.3.2.1 Hexane.

7.3.2.2 Decane.

7.4 Calibration. For all calibration gases, the manufacturer must recommend a maximum shelf life for each cylinder (i.e., the length of time the gas concentration is not expected to change more than ±5 percent from its certified value). The date of gas cylinder preparation, certified organic concentration, and recommended maximum shelf life must be affixed to each cylinder before shipment from the gas manufacturer to the buyer. The following calibration gases are required:

7.4.1 Oxidation Catalyst Efficiency Check Calibration Gas. Gas mixture standard with nominal concentration of 1 percent methane in air.

7.4.2 FID Linearity and NMO Calibration Gases. Three gas mixture standards with nominal propane concentrations of 20 ppm, 200 ppm, and 3000 ppm, in air.

7.4.3 CO_2 Calibration Gases. Three gas mixture standards with nominal CO_2 concentrations of 50 ppm, 500 ppm, and 1 percent, in air.

NOTE: Total NMO less than 1 ppm required for 1 percent mixture.

7.4.4 NMO Analyzer System Check Calibration Gases. Four calibration gases are needed as follows:

7.4.4.1 Propane Mixture. Gas mixture standard containing (nominal) 50 ppm CO, 50 ppm CH_4, 1 percent CO_2, and 20 ppm C_3H_8, prepared in air.

7.4.4.2 Hexane. Gas mixture standard containing (nominal) 50 ppm hexane in air.

7.4.4.3 Toluene. Gas mixture standard containing (nominal) 20 ppm toluene in air.

7.4.4.4 Methanol. Gas mixture standard containing (nominal) 100 ppm methanol in air.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Sampling Equipment Preparation.

8.1.1 Condensate Trap Cleaning. Before its initial use and after each use, a condensate trap should be thoroughly cleaned and checked to ensure that it is not contaminated. Both cleaning and checking can be accomplished by installing the trap in the condensate recovery system and treating it as if it were a sample. The trap should be heated as described in section 11.1.3. A trap may be considered clean when the CO_2 concentration in its effluent gas drops below 10 ppm. This check is optional for traps that most recently have been used to collect samples which were then recovered according to the procedure in section 11.1.3.

8.1.2 Sample Tank Evacuation and Leak-Check. Evacuate the sample tank to 10 mm Hg absolute pressure or less. Then close the sample tank valve, and allow the tank to sit for 60 minutes. The tank is acceptable if a change in tank vacuum of less than 1 mm Hg is noted. The evacuation and leak-check may be conducted either in the laboratory or the field.

8.1.3 Sampling Train Assembly. Just before assembly, measure the tank vacuum using a mercury manometer. Record this vacuum, the ambient temperature, and the barometric pressure at this time. Close the sample tank valve and assemble the sampling

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system as shown in Figure 25–1. Immerse the condensate trap body in dry ice at least 30 minutes before commencing sampling to improve collection efficiency. The point where the inlet tube joins the trap body should be 2.5 to 5 cm (1 to 2 in.) above the top of the dry ice.

8.1.4 Pretest Leak-Check. A pretest leak-check is required. Calculate or measure the approximate volume of the sampling train from the probe tip to the sample tank valve. After assembling the sampling train, plug the probe tip, and make certain that the sample tank valve is closed. Turn on the vacuum pump, and evacuate the sampling system from the probe tip to the sample tank valve to an absolute pressure of 10 mm Hg or less. Close the purge valve, turn off the pump, wait a minimum period of 10 minutes, and recheck the indicated vacuum. Calculate the maximum allowable pressure change based on a leak rate of 1 percent of the sampling rate using Equation 25–1, section 12.2. If the measured pressure change exceeds the allowable, correct the problem and repeat the leak-check before beginning sampling.

8.2 Sample Collection.

8.2.1 Unplug the probe tip, and place the probe into the stack such that the probe is perpendicular to the duct or stack axis; locate the probe tip at a single preselected point of average velocity facing away from the direction of gas flow. For stacks having a negative static pressure, seal the sample port sufficiently to prevent air in-leakage around the probe. Set the probe temperature controller to 129 °C (265 °F) and the filter temperature controller to 121 °C (250 °F). Allow the probe and filter to heat for about 30 minutes before purging the sample train.

8.2.2 Close the sample valve, open the purge valve, and start the vacuum pump. Set the flow rate between 60 and 100 cm^3/min (0.13 and 0.21 ft^3/hr), and purge the train with stack gas for at least 10 minutes.

8.2.3 When the temperatures at the exit ends of the probe and filter are within the corresponding specified ranges, check the dry ice level around the condensate trap, and add dry ice if necessary. Record the clock time. To begin sampling, close the purge valve and stop the pump. Open the sample valve and the sample tank valve. Using the flow control valve, set the flow through the sample train to the proper rate. Adjust the flow rate as necessary to maintain a constant rate (±10 percent) throughout the duration of the sampling period. Record the sample tank vacuum and flowmeter setting at 5-minute intervals. (See Figure 25–8.) Select a total sample time greater than or equal to the minimum sampling time specified in the applicable subpart of the regulations; end the sampling when this time period is reached or when a constant flow rate can no longer be maintained because of reduced sample tank vacuum.

NOTE: If sampling had to be stopped before obtaining the minimum sampling time (specified in the applicable subpart) because a constant flow rate could not be maintained, proceed as follows: After closing the sample tank valve, remove the used sample tank from the sampling train (without disconnecting other portions of the sampling train). Take another evacuated and leak-checked sample tank, measure and record the tank vacuum, and attach the new tank to the sampling train. After the new tank is attached to the sample train, proceed with the sampling until the required minimum sampling time has been exceeded.

8.3 Sample Recovery. After sampling is completed, close the flow control valve, and record the final tank vacuum; then record the tank temperature and barometric pressure. Close the sample tank valve, and disconnect the sample tank from the sample system. Disconnect the condensate trap at the inlet to the rate meter, and tightly seal both ends of the condensate trap. Do not include the probe from the stack to the filter as part of the condensate sample.

8.4 Sample Storage and Transport. Keep the trap packed in dry ice until the samples are returned to the laboratory for analysis. Ensure that run numbers are identified on the condensate trap and the sample tank(s).

9.0 Quality Control

Section	Quality control measure	Effect
10.1.1	Initial performance check of condensate recovery apparatus.	Ensure acceptable condensate recovery efficiency.
10.1.2, 10.2	NMO analyzer initial and daily performance checks.	Ensure precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Initial Performance Checks.

10.1.1 Condensate Recovery Apparatus. Perform these tests before the system is first placed in operation, after any shutdown of 6 months or more, and after any major modification of the system, or at the frequency recommended by the manufacturer.

10.1.1.1 Carrier Gas and Auxiliary O_2 Blank Check. Analyze each new tank of carrier gas or auxiliary O_2 with the NMO analyzer to

check for contamination. Treat the gas cylinders as noncondensible gas samples, and analyze according to the procedure in section 11.2.3. Add together any measured CH_4, CO, CO_2, or NMO. The total concentration must be less than 5 ppm.

10.1.1.2 Oxidation Catalyst Efficiency Check.

10.1.1.2.1 With a clean condensate trap installed in the recovery system or a ⅛″ stainless steel connector tube, replace the carrier gas cylinder with the high level methane standard gas cylinder (Section 7.4.1). Set the four-port valve to the recovery position, and attach an ICV to the recovery system. With the sample recovery valve in vent position and the flow-control and ICV valves fully open, evacuate the manometer or gauge, the connecting tubing, and the ICV to 10 mm Hg absolute pressure. Close the flow-control and vacuum pump valves.

10.1.1.2.2 After the NDIR response has stabilized, switch the sample recovery valve from vent to collect. When the manometer or pressure gauge begins to register a slight positive pressure, open the flow-control valve. Keep the flow adjusted such that the pressure in the system is maintained within 10 percent of atmospheric pressure. Continue collecting the sample in a normal manner until the ICV is filled to a nominal gauge pressure of 300 mm Hg. Close the ICV valve, and remove the ICV from the system. Place the sample recovery valve in the vent position, and return the recovery system to its normal carrier gas and normal operating conditions. Analyze the ICV for CO_2 using the NMO analyzer; the catalyst efficiency is acceptable if the CO_2 concentration is within 2 percent of the methane standard concentration.

10.1.1.3 System Performance Check. Construct a liquid sample injection unit similar in design to the unit shown in Figure 25–7. Insert this unit into the condensate recovery and conditioning system in place of a condensate trap, and set the carrier gas and auxiliary O_2 flow rates to normal operating levels. Attach an evacuated ICV to the system, and switch from system vent to collect. With the carrier gas routed through the injection unit and the oxidation catalyst, inject a liquid sample (see sections 10.1.1.3.1 to 10.1.1.3.4) into the injection port. Operate the trap recovery system as described in section 11.1.3. Measure the final ICV pressure, and then analyze the vessel to determine the CO_2 concentration. For each injection, calculate the percent recovery according to section 12.7. Calculate the relative standard deviation for each set of triplicate injections according to section 12.8. The performance test is acceptable if the average percent recovery is 100 ±5 percent and the relative standard deviation is less than 2 percent for each set of triplicate injections.

10.1.1.3.1 50 µl hexane.

10.1.1.3.2 10 µl hexane.

10.1.1.3.3 50 µl decane.

10.1.1.3.4 10 µl decane.

10.1.2 NMO Analyzer. Perform these tests before the system is first placed in operation, after any shutdown longer than 6 months, and after any major modification of the system.

10.1.2.1 Oxidation Catalyst Efficiency Check. Turn off or bypass the NMO analyzer reduction catalyst. Make triplicate injections of the high level methane standard (Section 7.4.1). The oxidation catalyst operation is acceptable if the FID response is less than 1 percent of the injected methane concentration.

10.1.2.2 Reduction Catalyst Efficiency Check. With the oxidation catalyst unheated or bypassed and the heated reduction catalyst bypassed, make triplicate injections of the high level methane standard (Section 7.4.1). Repeat this procedure with both catalysts operative. The reduction catalyst operation is acceptable if the responses under both conditions agree within 5 percent of their average.

10.1.2.3 NMO Analyzer Linearity Check Calibration. While operating both the oxidation and reduction catalysts, conduct a linearity check of the analyzer using the propane standards specified in section 7.4.2. Make triplicate injections of each calibration gas. For each gas (*i.e.*, each set of triplicate injections), calculate the average response factor (area/ppm C) for each gas, as well as and the relative standard deviation (according to section 12.8). Then calculate the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within 2.5 percent of the overall mean value and if the relative standard deviation gas is less than 2 percent of the overall mean value. Record the overall mean of the propane response factor values as the NMO calibration response factor (RF_{NMO}). Repeat the linearity check using the CO_2 standards specified in section 7.4.3. Make triplicate injections of each gas, and then calculate the average response factor (area/ppm C) for each gas, as well as the overall mean of the response factor values. Record the overall mean of the response factor values as the CO_2 calibration response factor (RF_{CO2}). The RF_{CO2} must be within 10 percent of the RF_{NMO}.

10.1.2.4 System Performance Check. Check the column separation and overall performance of the analyzer by making triplicate injections of the calibration gases listed in section 7.4.4. The analyzer performance is acceptable if the measured NMO value for each gas (average of triplicate injections) is within 5 percent of the expected value.

10.2 NMO Analyzer Daily Calibration. The following calibration procedures shall be performed before and immediately after the

analysis of each set of samples, or on a daily basis, whichever is more stringent:

10.2.1 CO_2 Response Factor. Inject triplicate samples of the high level CO_2 calibration gas (Section 7.4.3), and calculate the average response factor. The system operation is adequate if the calculated response factor is within 5 percent of the RF_{CO2} calculated during the initial performance test (Section 10.1.2.3). Use the daily response factor (DRF_{CO2}) for analyzer calibration and the calculation of measured CO_2 concentrations in the ICV samples.

10.2.2 NMO Response Factors. Inject triplicate samples of the mixed propane calibration cylinder gas (Section 7.4.4.1), and calculate the average NMO response factor. The system operation is adequate if the calculated response factor is within 10 percent of the RF_{NMO} calculated during the initial performance test (Section 10.1.2.4). Use the daily response factor (DRF_{NMO}) for analyzer calibration and calculation of NMO concentrations in the sample tanks.

10.3 Sample Tank and ICV Volume. The volume of the gas sampling tanks used must be determined. Determine the tank and ICV volumes by weighing them empty and then filled with deionized distilled water; weigh to the nearest 5 g, and record the results. Alternatively, measure the volume of water used to fill them to the nearest 5 ml.

11.0 Analytical Procedure

11.1 Condensate Recovery. See Figure 25–9. Set the carrier gas flow rate, and heat the catalyst to its operating temperature to condition the apparatus.

11.1.1 Daily Performance Checks. Each day before analyzing any samples, perform the following tests:

11.1.1.1 Leak-Check. With the carrier gas inlets and the sample recovery valve closed, install a clean condensate trap in the system, and evacuate the system to 10 mm Hg absolute pressure or less. Monitor the system pressure for 10 minutes. The system is acceptable if the pressure change is less than 2 mm Hg.

11.1.1.2 System Background Test. Adjust the carrier gas and auxiliary oxygen flow rate to their normal values of 100 cc/min and 150 cc/min, respectively, with the sample recovery valve in vent position. Using a 10-ml syringe, withdraw a sample from the system effluent through the syringe port. Inject this sample into the NMO analyzer, and measure the CO_2 content. The system background is acceptable if the CO_2 concentration is less than 10 ppm.

11.1.1.3 Oxidation Catalyst Efficiency Check. Conduct a catalyst efficiency test as specified in section 10.1.1.2. If the criterion of this test cannot be met, make the necessary repairs to the system before proceeding.

11.1.2 Condensate Trap CO_2 Purge and Sample Tank Pressurization.

11.1.2.1 After sampling is completed, the condensate trap will contain condensed water and organics and a small volume of sampled gas. This gas from the stack may contain a significant amount of CO_2 which must be removed from the condensate trap before the sample is recovered. This is accomplished by purging the condensate trap with zero air and collecting the purged gas in the original sample tank.

11.1.2.2 Begin with the sample tank and condensate trap from the test run to be analyzed. Set the four-port valve of the condensate recovery system in the CO_2 purge position as shown in Figure 25–9. With the sample tank valve closed, attach the sample tank to the sample recovery system. With the sample recovery valve in the vent position and the flow control valve fully open, evacuate the manometer or pressure gauge to the vacuum of the sample tank. Next, close the vacuum pump valve, open the sample tank valve, and record the tank pressure.

11.1.2.3 Attach the dry ice-cooled condensate trap to the recovery system, and initiate the purge by switching the sample recovery valve from vent to collect position. Adjust the flow control valve to maintain atmospheric pressure in the recovery system. Continue the purge until the CO_2 concentration of the trap effluent is less than 5 ppm. CO_2 concentration in the trap effluent should be measured by extracting syringe samples from the recovery system and analyzing the samples with the NMO analyzer. This procedure should be used only after the NDIR response has reached a minimum level. Using a 10-ml syringe, extract a sample from the syringe port prior to the NDIR, and inject this sample into the NMO analyzer.

11.1.2.4 After the completion of the CO_2 purge, use the carrier gas bypass valve to pressurize the sample tank to approximately 1,060 mm Hg absolute pressure with zero air.

11.1.3 Recovery of the Condensate Trap Sample (See Figure 25–10).

11.1.3.1 Attach the ICV to the sample recovery system. With the sample recovery valve in a closed position, between vent and collect, and the flow control and ICV valves fully open, evacuate the manometer or gauge, the connecting tubing, and the ICV to 10 mm Hg absolute pressure. Close the flow-control and vacuum pump valves.

11.1.3.2 Begin auxiliary oxygen flow to the oxidation catalyst at a rate of 150 cc/min, then switch the four-way valve to the trap recovery position and the sample recovery valve to collect position. The system should now be set up to operate as indicated in Figure 25–10. After the manometer or pressure gauge begins to register a slight positive pressure, open the flow control valve. Adjust the flow-control valve to maintain atmospheric pressure in the system within 10 percent.

11.1.3.3 Remove the condensate trap from the dry ice, and allow it to warm to ambient temperature while monitoring the NDIR response. If, after 5 minutes, the CO_2 concentration of the catalyst effluent is below 10,000 ppm, discontinue the auxiliary oxygen flow to the oxidation catalyst. Begin heating the trap by placing it in a furnace preheated to 200 °C (390 °F). Once heating has begun, carefully monitor the NDIR response to ensure that the catalyst effluent concentration does not exceed 50,000 ppm. Whenever the CO_2 concentration exceeds 50,000 ppm, supply auxiliary oxygen to the catalyst at the rate of 150 cc/min. Begin heating the tubing that connected the heated sample box to the condensate trap only after the CO_2 concentration falls below 10,000 ppm. This tubing may be heated in the same oven as the condensate trap or with an auxiliary heat source such as a heat gun. Heating temperature must not exceed 200 °C (390 °F). If a heat gun is used, heat the tubing slowly along its entire length from the upstream end to the downstream end, and repeat the pattern for a total of three times. Continue the recovery until the CO_2 concentration drops to less than 10 ppm as determined by syringe injection as described under the condensate trap CO_2 purge procedure (Section 11.1.2).

11.1.3.4 After the sample recovery is completed, use the carrier gas bypass valve to pressurize the ICV to approximately 1060 mm Hg absolute pressure with zero air.

11.2 Analysis. Once the initial performance test of the NMO analyzer has been successfully completed (see section 10.1.2) and the daily CO_2 and NMO response factors have been determined (see section 10.2), proceed with sample analysis as follows:

11.2.1 Operating Conditions. The carrier gas flow rate is 29.5 cc/min He and 2.2 cc/min O_2. The column oven is heated to 85 °C (185 °F). The order of elution for the sample from the column is CO, CH_4, CO_2, and NMO.

11.2.2 Analysis of Recovered Condensate Sample. Purge the sample loop with sample, and then inject the sample. Under the specified operating conditions, the CO_2 in the sample will elute in approximately 100 seconds. As soon as the detector response returns to baseline following the CO_2 peak, switch the carrier gas flow to backflush, and raise the column oven temperature to 195 °C (380 °F) as rapidly as possible. A rate of 30 °C/min (90 °F) has been shown to be adequate. Record the value obtained for the condensible organic material (C_{cm}) measured as CO_2 and any measured NMO. Return the column oven temperature to 85 °C (185 °F) in preparation for the next analysis. Analyze each sample in triplicate, and report the average C_{cm}.

11.2.3 Analysis of Sample Tank. Perform the analysis as described in section 11.2.2, but record only the value measured for NMO (C_{tm}).

12.0 Data Analysis and Calculations

Carry out the calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculations. All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge or manometer pressure.

12.1 Nomenclature.

C = TGNMO concentration of the effluent, ppm C equivalent.
C_c = Calculated condensible organic (condensate trap) concentration of the effluent, ppm C equivalent.
C_{cm} = Measured concentration (NMO analyzer) for the condensate trap ICV, ppm CO_2.
C_t = Calculated noncondensible organic concentration (sample tank) of the effluent, ppm C equivalent.
C_{tm} = Measured concentration (NMO analyzer) for the sample tank, ppm NMO.
F = Sampling flow rate, cc/min.
L = Volume of liquid injected, µl.
M = Molecular weight of the liquid injected, g/g-mole.
M_c = TGNMO mass concentration of the effluent, mg C/dsm³.
N = Carbon number of the liquid compound injected (N = 12 for decane, N = 6 for hexane).
n = Number of data points.
P_f = Final pressure of the intermediate collection vessel, mm Hg absolute.
P_b = Barometric pressure, cm Hg.
P_{ti} = Gas sample tank pressure before sampling, mm Hg absolute.
P_t = Gas sample tank pressure after sampling, but before pressurizing, mm Hg absolute.
P_{tf} = Final gas sample tank pressure after pressurizing, mm Hg absolute.
q = Total number of analyzer injections of intermediate collection vessel during analysis (where k = injection number, 1 * * * q).
r = Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 * * * r).
r = Density of liquid injected, g/cc.
T_f = Final temperature of intermediate collection vessel, °K.
T_{ti} = Sample tank temperature before sampling, °K.
T_t = Sample tank temperature at completion of sampling, °K.
T_{tf} = Sample tank temperature after pressurizing, °K.
V = Sample tank volume, m³.
V_t = Sample train volume, cc.
V_v = Intermediate collection vessel volume, m³.
V_s = Gas volume sampled, dsm³.
x_i = Individual measurements.
$\bar{x}$ = Mean value.

ΔP = Allowable pressure change, cm Hg.
Θ = Leak-check period, min.

12.2 Allowable Pressure Change. For the pretest leak-check, calculate the allowable pressure change using Equation 25–1:

$$\Delta P = 0.01 \frac{F P_b \Theta}{V_t} \qquad \text{Eq. 25-1}$$

12.3 Sample Volume. For each test run, calculate the gas volume sampled using Equation 25–2:

$$V_s = 0.3857\, V \left(\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}} \right) \qquad \text{Eq. 25-2}$$

12.4 Noncondensible Organics. For each sample tank, determine the concentration of nonmethane organics (ppm C) using Equation 25–3:

$$C_t = \left(\frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}} \right) \left(\frac{1}{r} \sum_{j=1}^{r} C_{tm_j} \right) \qquad \text{Eq. 25-3}$$

12.5 Condensible Organics. For each condensate trap determine the concentration of organics (ppm C) using Equation 25–4:

$$C_c = 0.3857 \frac{V_v P_f}{V_s T_f} \left(\frac{1}{q} \sum_{k=1}^{q} C_{cm_k} \right) \qquad \text{Eq. 25-4}$$

12.6 TGNMO Mass Concentration. Determine the TGNMO mass concentration as carbon for each test run, using Equation 25–5:

$$M_c = 0.4993 \left(C_t + C_c \right) \qquad \text{Eq. 25-5}$$

12.7 Percent Recovery. Calculate the percent recovery for the liquid injections to the condensate recovery and conditioning system using Equation 25–6:

$$\text{Percent Recovery} = K \frac{M V_v P_t C_{cm}}{L P T_f N} \qquad \text{Eq. 25-6}$$

where K = 1.604 (°K)(g-mole)(%)/(mm Hg)(ml)(m^3)(ppm).

12.8 Relative Standard Deviation. Use Equation 25–7 to calculate the relative standard deviation (RSD) of percent recovery and analyzer linearity.

$$RSD = \frac{100}{\bar{x}} \left[\frac{\sum_{i=1}^{n} \left(x_i - \bar{x} \right)^2}{n-1} \right]^{\frac{1}{2}} \qquad \text{Eq. 25-7}$$

13.0 Method Performance

13.1 Range. The minimum detectable limit of the method has been determined to be 50 parts per million by volume (ppm). No upper limit has been established.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, A.E., S. Witz, and R.D. MacPhee. Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, MA. June 15–20, 1975.) 14 p.

2. Salo, A.E., W.L. Oaks, and R.D. MacPhee. Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, CO. June 9–13, 1974.) 25 p.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

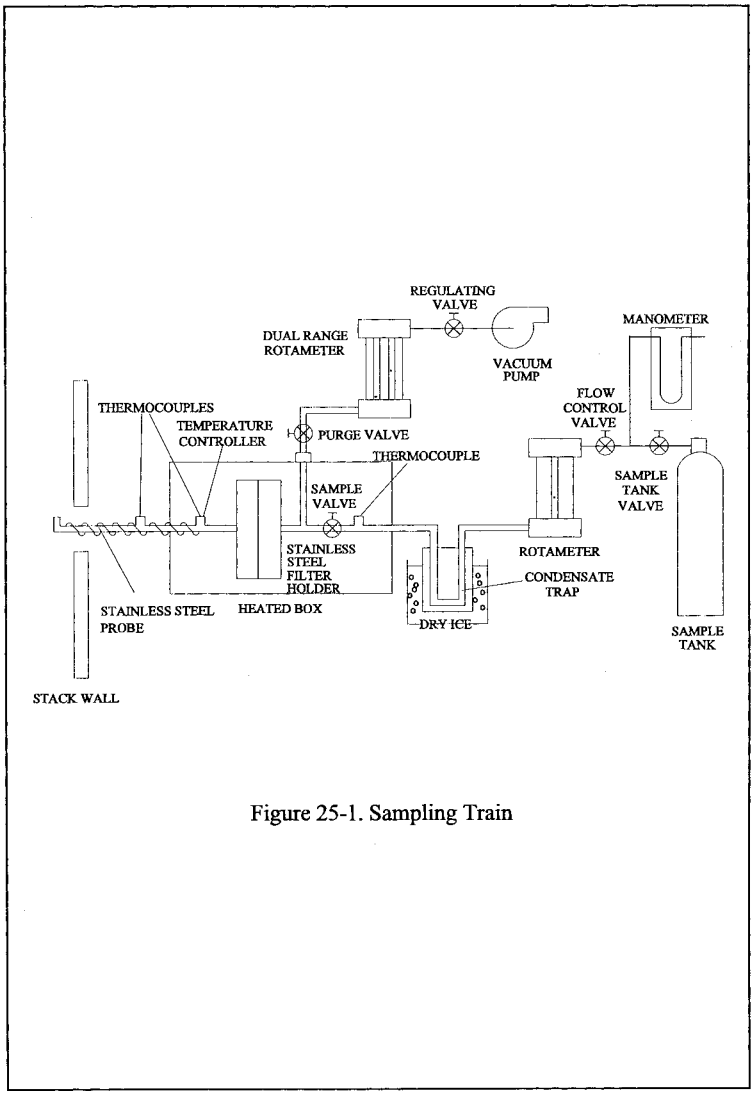


Figure 25-1. Sampling Train

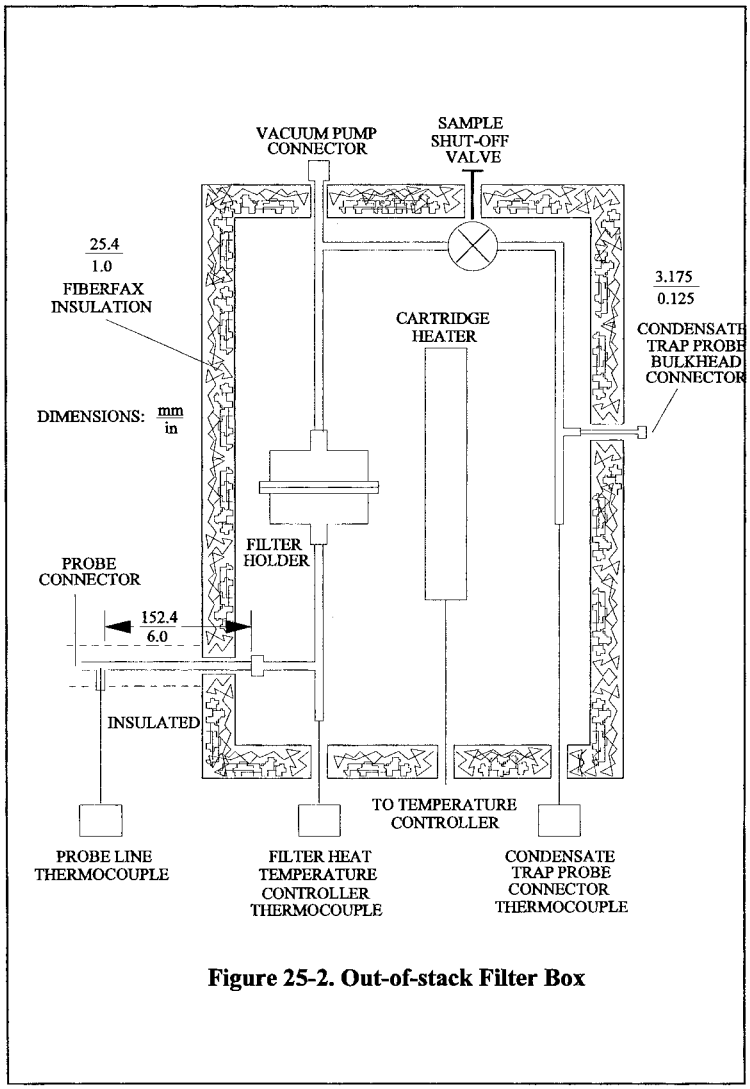


Figure 25-2. Out-of-stack Filter Box

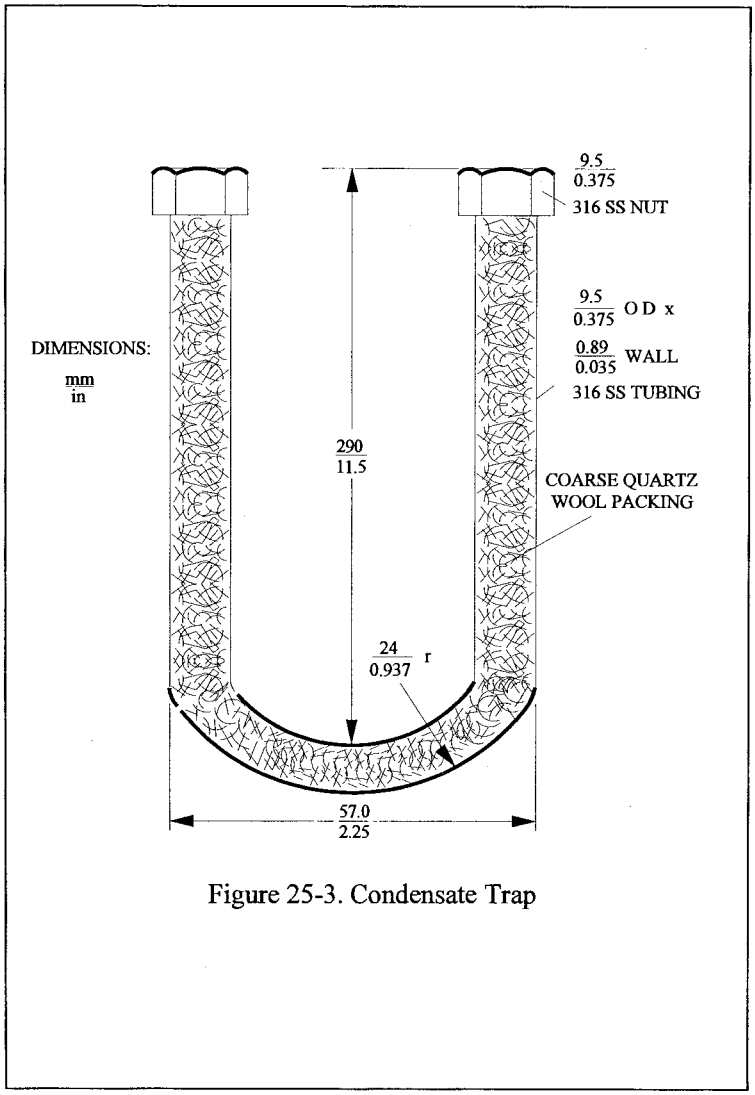


Figure 25-3. Condensate Trap

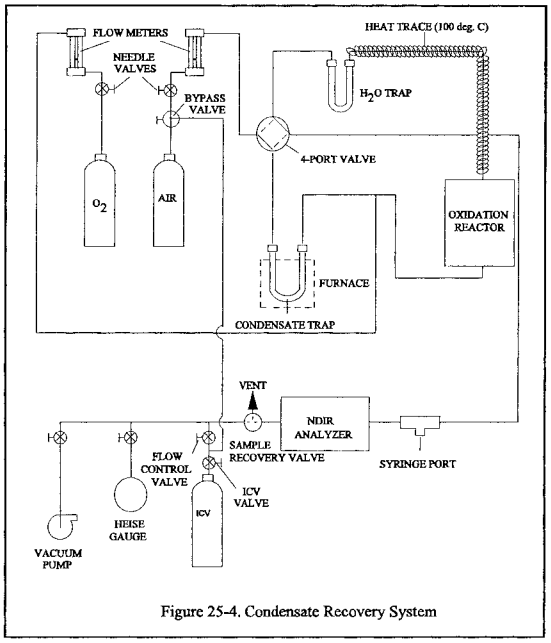


Figure 25-4. Condensate Recovery System

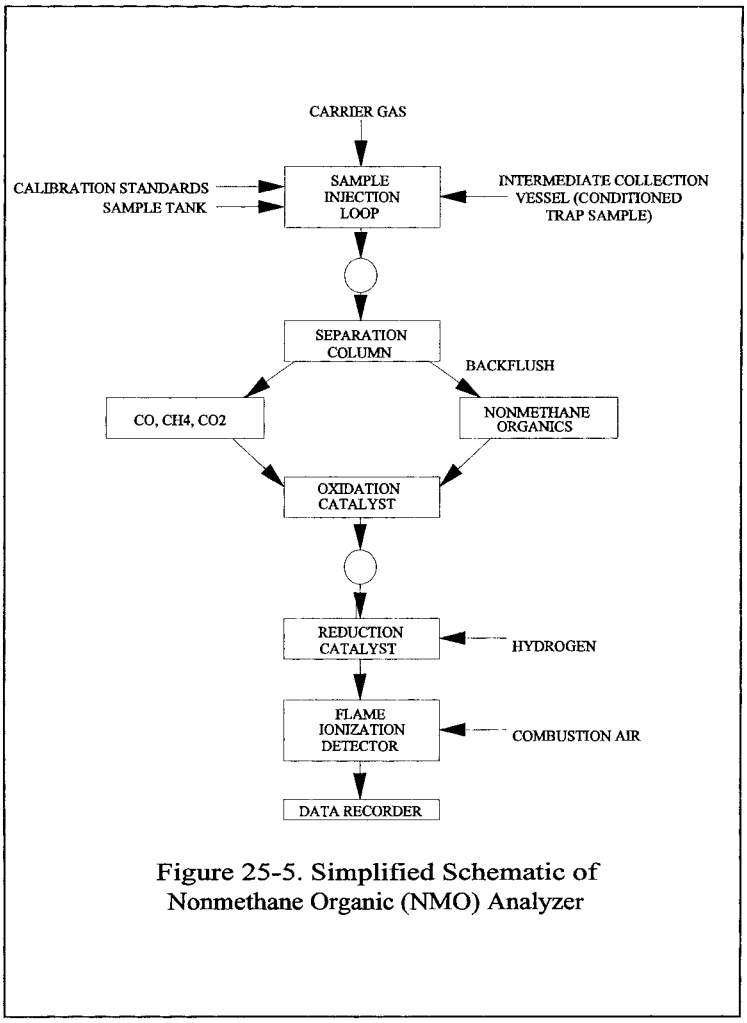


Figure 25-5. Simplified Schematic of Nonmethane Organic (NMO) Analyzer

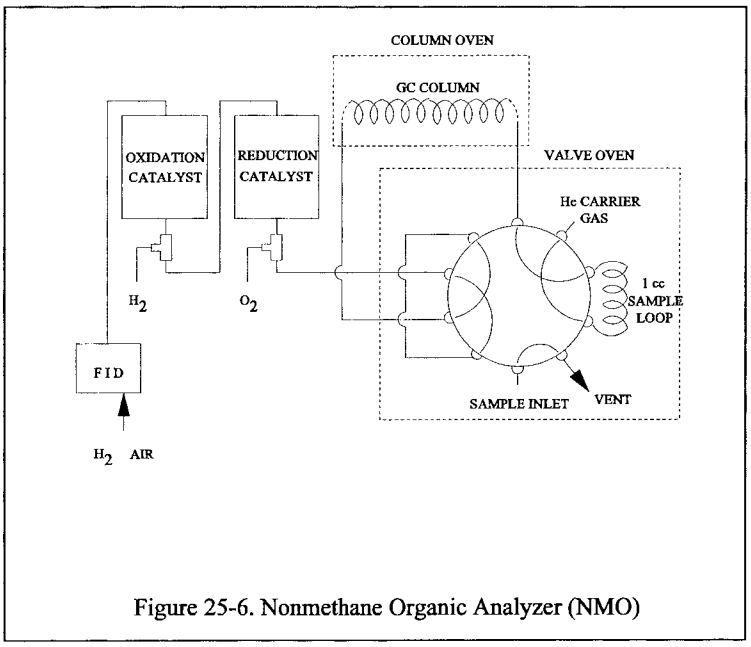


Figure 25-6. Nonmethane Organic Analyzer (NMO)

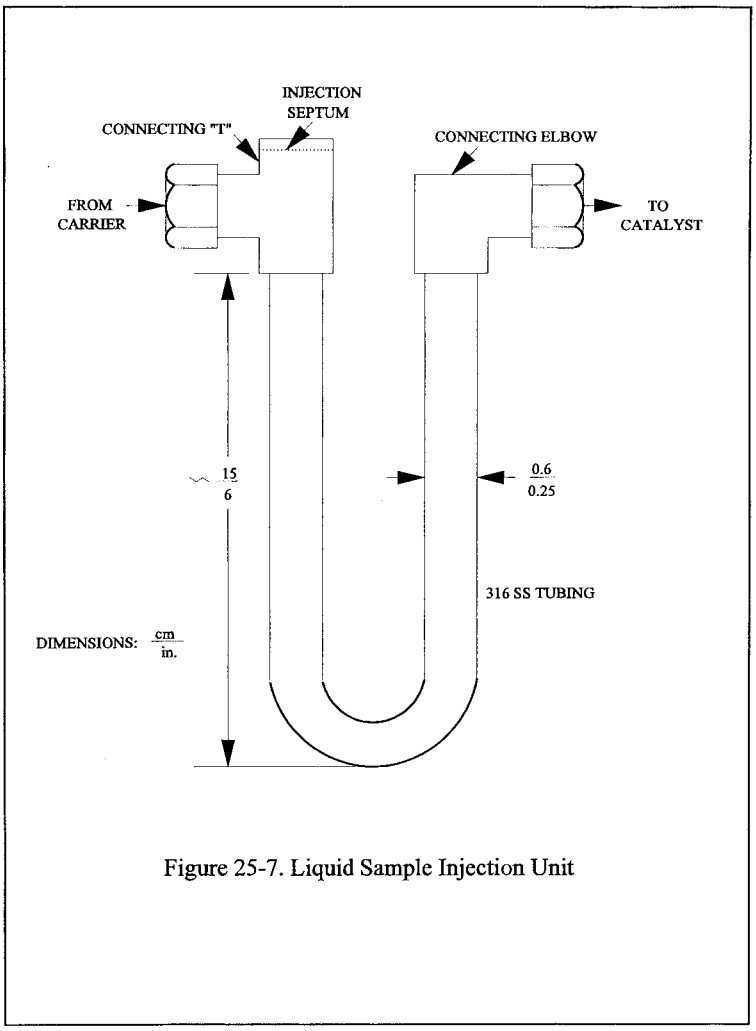


Figure 25-7. Liquid Sample Injection Unit

VOLATILE ORGANIC CARBON

FACILITY _____ SAMPLE LOCATION _____

LOCATION _____ OPERATOR _____

DATE _____ RUN NUMBER _____

TANK NUMBER _____ TRAP NUMBER _____ SAMPLE ID NUMBER _____

TANK VACUUM mm HG	TANK VACUUM cm Hg	BAROMETRIC PRESSURE mm Hg	AMBIENT TEMPERATURE °C
PRETEST (MANOMETER)	(GAUGE)		
POST-TEST (MANOMETER)	(GAUGE)		

LEAK RATE _____ cm Hg / l.0 min

PRETEST _____

TIME CLOCK/SAMPLE	VACUUM cm Hg	FLOWMETER SETTINGS	COMMENTS

Figure 25-8. Example Field Data Form

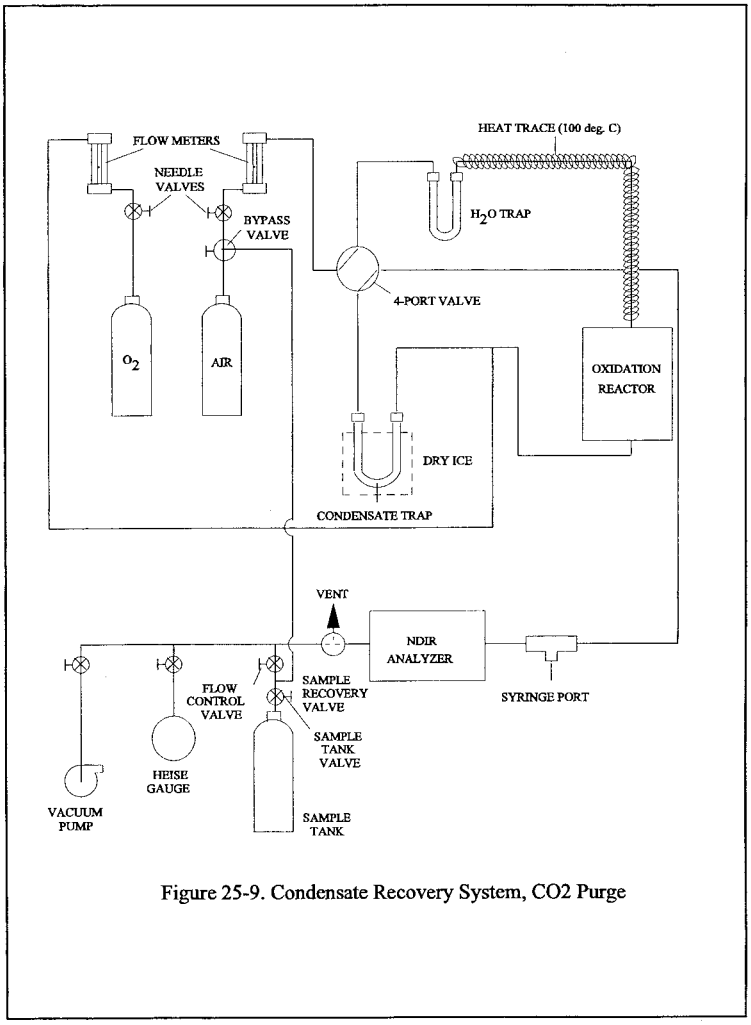


Figure 25-9. Condensate Recovery System, CO2 Purge

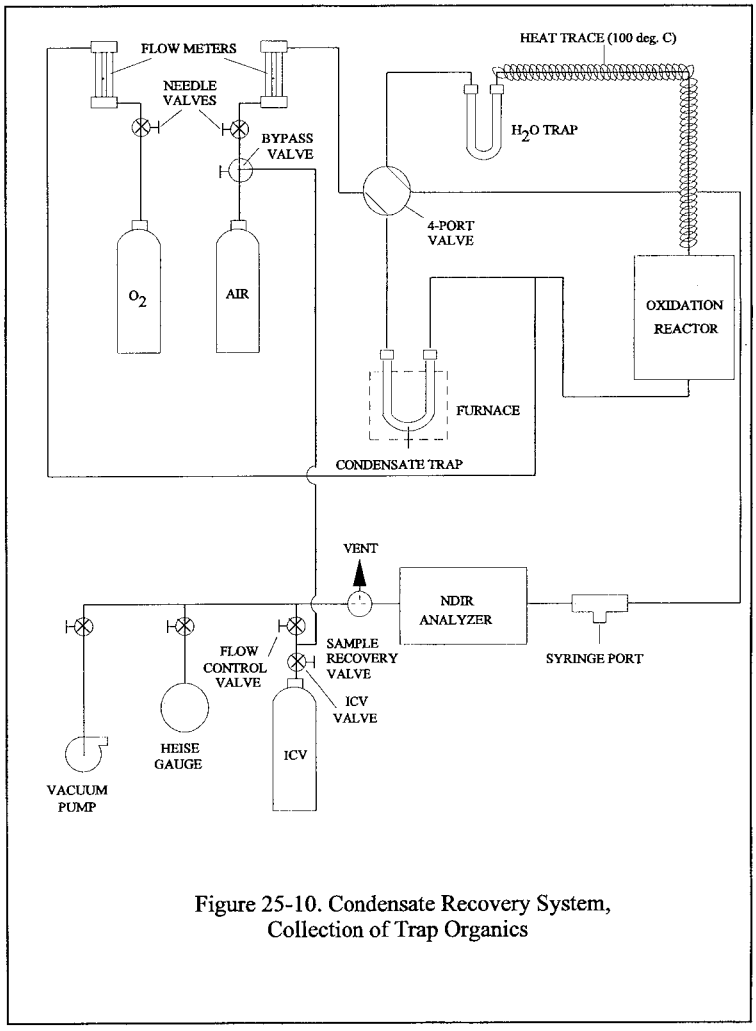


Figure 25-10. Condensate Recovery System, Collection of Trap Organics

METHOD 25A—DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A FLAME IONIZATION ANALYZER

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total Organic Compounds	N/A	<2% of span.

1.2 Applicability. This method is applicable for the determination of total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the source through a heated sample line and glass fiber filter to a flame ionization analyzer (FIA). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

3.0 Definitions

3.1 *Calibration drift* means the difference in the measurement system response to a mid-level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

3.2 *Calibration error* means the difference between the gas concentration indicated by the measurement system and the know concentration of the calibration gas.

3.3 *Calibration gas* means a known concentration of a gas in an appropriate diluent gas.

3.4 *Measurement system* means the total equipment required for the determination of the gas concentration. The system consists of the following major subsystems:

3.4.1 *Sample interface* means that portion of a system used for one or more of the following: sample acquisition, sample transportation, sample conditioning, or protection of the analyzer(s) from the effects of the stack effluent.

3.4.2 *Organic analyzer* means that portion of the measurement system that senses the gas to be measured and generates an output proportional to its concentration.

3.5 *Response time* means the time interval from a step change in pollutant concentration at the inlet to the emission measurement system to the time at which 95 percent of the corresponding final value is reached as displayed on the recorder.

3.6 *Span Value* means the upper limit of a gas concentration measurement range that is specified for affected source categories in the applicable part of the regulations. The span value is established in the applicable regulation and is usually 1.5 to 2.5 times the applicable emission limit. If no span value is provided, use a span value equivalent to 1.5 to 2.5 times the expected concentration. For convenience, the span value should correspond to 100 percent of the recorder scale.

3.7 *Zero drift* means the difference in the measurement system response to a zero level calibration gas before or after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

5.2 Explosive Atmosphere. This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

6.0 Equipment and Supplies

6.1 Measurement System. Any measurement system for total organic concentration that meets the specifications of this method. A schematic of an acceptable measurement system is shown in Figure 25A–1. All sampling components leading to the analyzer shall be heated ≥110 °C (220 °F) throughout the sampling period, unless safety reasons are cited (Section 5.2) The essential components of the measurement system are described below:

6.1.1 Organic Concentration Analyzer. A flame ionization analyzer (FIA) capable of meeting or exceeding the specifications of this method. The flame ionization detector block shall be heated >120 °C (250 °F).

6.1.2 Sample Probe. Stainless steel, or equivalent, three-hole rake type. Sample holes shall be 4 mm (0.16-in.) in diameter or smaller and located at 16.7, 50, and 83.3 percent of the equivalent stack diameter. Alternatively, a single opening probe may be used so that a gas sample is collected from the centrally located 10 percent area of the stack cross-section.

6.1.3 Heated Sample Line. Stainless steel or Teflon'' tubing to transport the sample gas

to the analyzer. The sample line should be heated (≥110 °C) to prevent any condensation.

6.1.4 Calibration Valve Assembly. A three-way valve assembly to direct the zero and calibration gases to the analyzers is recommended. Other methods, such as quick-connect lines, to route calibration gas to the analyzers are applicable.

6.1.5 Particulate Filter. An in-stack or an out-of-stack glass fiber filter is recommended if exhaust gas particulate loading is significant. An out-of-stack filter should be heated to prevent any condensation.

6.1.6 Recorder. A strip-chart recorder, analog computer, or digital recorder for recording measurement data. The minimum data recording requirement is one measurement value per minute.

7.0 Reagents and Standards

7.1 Calibration Gases. The calibration gases for the gas analyzer shall be propane in air or propane in nitrogen. Alternatively, organic compounds other than propane can be used; the appropriate corrections for response factor must be made. Calibration gases shall be prepared in accordance with the procedure listed in Citation 2 of section 16. Additionally, the manufacturer of the cylinder should provide a recommended shelf life for each calibration gas cylinder over which the concentration does not change more than ±2 percent from the certified value. For calibration gas values not generally available (*i.e.*, organics between 1 and 10 percent by volume), alternative methods for preparing calibration gas mixtures, such as dilution systems (Test Method 205, 40 CFR Part 51, Appendix M), may be used with prior approval of the Administrator.

7.1.1 Fuel. A 40 percent H_2/60 percent N_2 gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value.

7.1.2 Zero Gas. High purity air with less than 0.1 part per million by volume (ppmv) of organic material (propane or carbon equivalent) or less than 0.1 percent of the span value, whichever is greater.

7.1.3 Low-level Calibration Gas. An organic calibration gas with a concentration equivalent to 25 to 35 percent of the applicable span value.

7.1.4 Mid-level Calibration Gas. An organic calibration gas with a concentration equivalent to 45 to 55 percent of the applicable span value.

7.1.5 High-level Calibration Gas. An organic calibration gas with a concentration equivalent to 80 to 90 percent of the applicable span value.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Selection of Sampling Site. The location of the sampling site is generally specified by the applicable regulation or purpose of the test (*i.e.*, exhaust stack, inlet line, etc.). The sample port shall be located to meet the testing requirements of Method 1.

8.2 Location of Sample Probe. Install the sample probe so that the probe is centrally located in the stack, pipe, or duct and is sealed tightly at the stack port connection.

8.3 Measurement System Preparation. Prior to the emission test, assemble the measurement system by following the manufacturer's written instructions for preparing sample interface and the organic analyzer. Make the system operable (Section 10.1).

8.4 Calibration Error Test. Immediately prior to the test series (within 2 hours of the start of the test), introduce zero gas and high-level calibration gas at the calibration valve assembly. Adjust the analyzer output to the appropriate levels, if necessary. Calculate the predicted response for the low-level and mid-level gases based on a linear response line between the zero and high-level response. Then introduce low-level and mid-level calibration gases successively to the measurement system. Record the analyzer responses for low-level and mid-level calibration gases and determine the differences between the measurement system responses and the predicted responses. These differences must be less than 5 percent of the respective calibration gas value. If not, the measurement system is not acceptable and must be replaced or repaired prior to testing. No adjustments to the measurement system shall be conducted after the calibration and before the drift check (Section 8.6.2). If adjustments are necessary before the completion of the test series, perform the drift checks prior to the required adjustments and repeat the calibration following the adjustments. If multiple electronic ranges are to be used, each additional range must be checked with a mid-level calibration gas to verify the multiplication factor.

8.5 Response Time Test. Introduce zero gas into the measurement system at the calibration valve assembly. When the system output has stabilized, switch quickly to the high-level calibration gas. Record the time from the concentration change to the measurement system response equivalent to 95 percent of the step change. Repeat the test three times and average the results.

8.6 Emission Measurement Test Procedure.

8.6.1 Organic Measurement. Begin sampling at the start of the test period, recording time and any required process information as appropriate. In particulate, note on the recording chart, periods of process interruption or cyclic operation.

8.6.2 Drift Determination. Immediately following the completion of the test period and hourly during the test period, reintroduce the zero and mid-level calibration gases, one at a time, to the measurement system at the calibration valve assembly. (Make no adjustments to the measurement system until both the zero and calibration drift checks are made.) Record the analyzer response. If the drift values exceed the specified limits, invalidate the test results preceding the check and repeat the test following corrections to the measurement system. Alternatively, recalibrate the test measurement system as in section 8.4 and report the results using both sets of calibration data (i.e., data determined prior to the test period and data determined following the test period).

NOTE: Note on the recording chart periods of process interruption or cyclic operation.

9.0 Quality Control

Method section	Quality control measure	Effect
8.4	Zero and calibration drift tests	Ensures that bias introduced by drift in the measurement system output during the run is no greater than 3 percent of span.

10.0 Calibration and Standardization

10.1 FIA equipment can be calibrated for almost any range of total organic concentrations. For high concentrations of organics (>1.0 percent by volume as propane), modifications to most commonly available analyzers are necessary. One accepted method of equipment modification is to decrease the size of the sample to the analyzer through the use of a smaller diameter sample capillary. Direct and continuous measurement of organic concentration is a necessary consideration when determining any modification design.

11.0 Analytical Procedure

The sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Calculations and Data Analysis

12.1 Determine the average organic concentration in terms of ppmv as propane or other calibration gas. The average shall be determined by integration of the output recording over the period specified in the applicable regulation. If results are required in terms of ppmv as carbon, adjust measured concentrations using Equation 25A–1.

$$C_c = K C_{meas} \qquad \text{Eq. 25A-1}$$

Where:

C_c = Organic concentration as carbon, ppmv.
C_{meas} = Organic concentration as measured, ppmv.
K = Carbon equivalent correction factor.
= 2 for ethane.
= 3 for propane.
= 4 for butane.
= Appropriate response factor for other organic calibration gases.

13.0 Method Performance

13.1 Measurement System Performance Specifications.

13.1.1 Zero Drift. Less than ±3 percent of the span value.

13.1.2 Calibration Drift. Less than ±3 percent of span value.

13.1.3 Calibration Error. Less than ±5 percent of the calibration gas value.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Measurement of Volatile Organic Compounds—Guideline Series. U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA–450/2–78–041. June 1978. p. 46–54.

2. EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards. U.S. Environmental Protection Agency, Quality Assurance and Technical Support Division. Research Triangle Park, N.C. September 1993.

3. Gasoline Vapor Emission Laboratory Evaluation—Part 2. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, NC. EMB Report No. 75–GAS–6. August 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

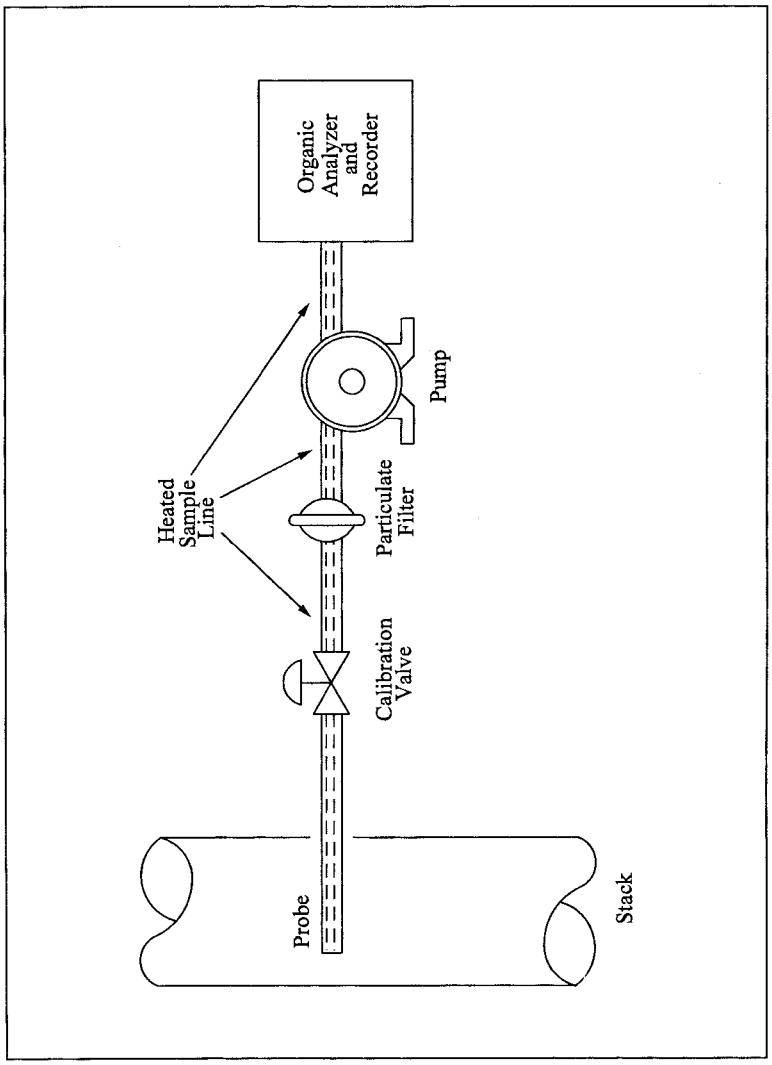


Figure 25A-1. Organic Concentration Measurement System.

METHOD 25B—DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A NONDISPERSIVE INFRARED ANALYZER

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 6C, and Method 25A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total Organic Compounds	N/A	<2% of span.

1.2 Applicability. This method is applicable for the determination of total gaseous organic concentration of vapors consisting primarily of alkanes. Other organic materials may be measured using the general procedure in this method, the appropriate calibration gas, and an analyzer set to the appropriate absorption band.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

A gas sample is extracted from the source through a heated sample line, if necessary, and glass fiber filter to a nondispersive infrared analyzer (NDIR). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

3.0 Definitions

Same as Method 25A, section 3.0.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

5.2 Explosive Atmosphere. This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

6.0 Equipment and Supplies

Same as Method 25A, section 6.0, with the exception of the following:

6.1 Organic Concentration Analyzer. A nondispersive infrared analyzer designed to measure alkane organics and capable of meeting or exceeding the specifications in this method.

7.0 Reagents and Standards

Same as Method 25A, section 7.1. No fuel gas is required for an NDIR.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as Method 25A, section 8.0.

9.0 Quality Control

Same as Method 25A, section 9.0.

10.0 Calibration and Standardization

Same as Method 25A, section 10.0.

11.0 Analytical Procedure

The sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Calculations and Data Analysis

Same as Method 25A, section 12.0.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 25A, section 16.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 25C—DETERMINATION OF NONMETHANE ORGANIC COMPOUNDS (NMOC) IN LANDFILL GASES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should also have a thorough knowledge of EPA Method 25.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Nonmethane organic compounds (NMOC).	No CAS number assigned.

1.2 Applicability. This method is applicable to the sampling and measurement of NMOC as carbon in landfill gases (LFG).

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A sample probe that has been perforated at one end is driven or augured to a depth of 0.9 m (3 ft) below the bottom of the landfill cover. A sample of the landfill gas is extracted with an evacuated cylinder. The NMOC content of the gas is determined by

injecting a portion of the gas into a gas chromatographic column to separate the NMOC from carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4); the NMOC are oxidized to CO_2, reduced to CH_4, and measured by a flame ionization detector (FID). In this manner, the variable response of the FID associated with different types of organics is eliminated.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Since this method is complex, only experienced personnel should perform this test. LFG contains methane, therefore explosive mixtures may exist on or near the landfill. It is advisable to take appropriate safety precautions when testing landfills, such as refraining from smoking and installing explosion-proof equipment.

6.0 Equipment and Supplies

6.1 Sample Probe. Stainless steel, with the bottom third perforated. Teflon probe liners and sampling lines are also allowed. Non-perforated probes are allowed as long as they are withdrawn to create a gap equivalent to having the bottom third perforated. The sample probe must be capped at the bottom and must have a threaded cap with a sampling attachment at the top. The sample probe must be long enough to go through and extend no less than 0.9 m (3 ft) below the landfill cover. If the sample probe is to be driven into the landfill, the bottom cap should be designed to facilitate driving the probe into the landfill.

6.2 Sampling Train.

6.2.1 Rotameter with Flow Control Valve. Capable of measuring a sample flow rate of 100 ±10 ml/min. The control valve must be made of stainless steel.

6.2.2 Sampling Valve. Stainless steel.

6.2.3 Pressure Gauge. U-tube mercury manometer, or equivalent, capable of measuring pressure to within 1 mm Hg (0.5 in H_2O) in the range of 0 to 1,100 mm Hg (0 to 590 in H_2O).

6.2.4 Sample Tank. Stainless steel or aluminum cylinder, equipped with a stainless steel sample tank valve.

6.3 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg (5.4 in H_2O).

6.4 Purging Pump. Portable, explosion proof, and suitable for sampling NMOC.

6.5 Pilot Probe Procedure. The following are needed only if the tester chooses to use the procedure described in section 8.2.1.

6.5.1 Pilot Probe. Tubing of sufficient strength to withstand being driven into the landfill by a post driver and an outside diameter of at least 6 mm (0.25 in.) smaller than the sample probe. The pilot probe shall be capped on both ends and long enough to go through the landfill cover and extend no less than 0.9 m (3 ft) into the landfill.

6.5.2 Post Driver and Compressor. Capable of driving the pilot probe and the sampling probe into the landfill. The Kitty Hawk portable post driver has been found to be acceptable.

6.6 Auger Procedure. The following are needed only if the tester chooses to use the procedure described in section 8.2.2.

6.6.1 Auger. Capable of drilling through the landfill cover and to a depth of no less than 0.9 m (3 ft) into the landfill.

6.6.2 Pea Gravel.

6.6.3 Bentonite.

6.7 NMOC Analyzer, Barometer, Thermometer, and Syringes. Same as in sections 6.3.1, 6.3.2, 6.33, and 6.2.10, respectively, of Method 25.

7.0 Reagents and Standards

7.1 NMOC Analysis. Same as in Method 25, section 7.2.

7.2 Calibration. Same as in Method 25, section 7.4, except omit section 7.4.3.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sample Tank Evacuation and Leak-Check. Conduct the sample tank evacuation and leak-check either in the laboratory or the field. Connect the pressure gauge and sampling valve to the sample tank. Evacuate the sample tank to 10 mm Hg (5.4 in H_2O) absolute pressure or less. Close the sampling valve, and allow the tank to sit for 30 minutes. The tank is acceptable if no change more than ±2 mm is noted. Include the results of the leak-check in the test report.

8.2 Sample Probe Installation. The tester may use the procedure in section 8.2.1 or 8.2.2.

8.2.1 Pilot Probe Procedure. Use the post driver to drive the pilot probe at least 0.9 m (3 ft) below the landfill cover. Alternative procedures to drive the probe into the landfill may be used subject to the approval of the Administrator's designated representative.

8.2.1.1 Remove the pilot probe and drive the sample probe into the hole left by the pilot probe. The sample probe shall extend at least 0.9 m (3 ft) below the landfill cover and shall protrude about 0.3 m (1 ft) above the landfill cover. Seal around the sampling probe with bentonite and cap the sampling probe with the sampling probe cap.

8.2.2 Auger Procedure. Use an auger to drill a hole to at least 0.9 m (3 ft) below the landfill cover. Place the sample probe in the hole and backfill with pea gravel to a level 0.6 m (2 ft) from the surface. The sample probe shall protrude at least 0.3 m (1 ft) above the landfill cover. Seal the remaining area around the probe with bentonite. Allow 24

hours for the landfill gases to equilibrate inside the augured probe before sampling.

8.2.3 Driven Probes. Closed-point probes may be driven directly into the landfill in a single step. This method may not require backfilling if the probe is adequately sealed by its insertion. Unperforated probes that are inserted in this manner and withdrawn at a distance from a detachable tip to create an open space are also acceptable.

8.3 Sample Train Assembly. Just before assembling the sample train, measure the sample tank vacuum using the pressure gauge. Record the vacuum, the ambient temperature, and the barometric pressure at this time. Assemble the sampling probe purging system as shown in Figure 25C–1.

8.4 Sampling Procedure. Open the sampling valve and use the purge pump and the flow control valve to evacuate at least two sample probe volumes from the system at a flow rate of 500 ml/min or less. Close the sampling valve and replace the purge pump with the sample tank apparatus as shown in Figure 25C–2. Open the sampling valve and the sample tank valve and, using the flow control valve, sample at a flow rate of 500 ml/min or less until either a constant flow rate can no longer be maintained because of reduced sample tank vacuum or the appropriate composite volume is attained. Disconnect the sampling tank apparatus and pressurize the sample cylinder to approximately 1,060 mm Hg (567 in. H_2O) absolute pressure with helium, and record the final pressure. Alternatively, the sample tank may be pressurized in the lab.

8.4.1 The following restrictions apply to compositing samples from different probe sites into a single cylinder: (1) Individual composite samples per cylinder must be of equal volume; this must be verified by recording the flow rate, sampling time, vacuum readings, or other appropriate volume measuring data, (2) individual composite samples must have a minimum volume of 1 liter unless data is provided showing smaller volumes can be accurately measured, and (3) composite samples must not be collected using the final cylinder vacuum as it diminishes to ambient pressure.

8.4.2 Use Method 3C to determine the percent N_2 in each cylinder. The presence of N_2 indicates either infiltration of ambient air into the landfill gas sample or an inappropriate testing site has been chosen where anaerobic decomposition has not begun. The landfill gas sample is acceptable if the concentration of N_2 is less than 20 percent. Alternatively, Method 3C may be used to determine the oxygen content of each cylinder as an air infiltration test. With this option, the oxygen content of each cylinder must be less than 5 percent.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4.2	Verify that landfill gas sample contains less than 20 percent N_2 or 5 percent O_2.	Ensures that ambient air was not drawn into the landfill gas sample and gas was sampled from an appropriate location.
10.1, 10.2	NMOC analyzer initial and daily performance checks.	Ensures precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Initial NMOC Analyzer Performance Test. Same as in Method 25, section 10.1, except omit the linearity checks for CO_2 standards.

10.2 NMOC Analyzer Daily Calibration.

10.2.1 NMOC Response Factors. Same as in Method 25, section 10.2.2.

10.3 Sample Tank Volume. The volume of the gas sampling tanks must be determined. Determine the tank volumes by weighing them empty and then filled with deionized water; weigh to the nearest 5 g, and record the results. Alternatively, measure the volume of water used to fill them to the nearest 5 ml.

11.0 Analytical Procedures

11.1 The oxidation, reduction, and measurement of NMOC's is similar to Method 25. Before putting the NMOC analyzer into routine operation, conduct an initial performance test. Start the analyzer, and perform all the necessary functions in order to put the analyzer into proper working order. Conduct the performance test according to the procedures established in section 10.1. Once the performance test has been successfully completed and the NMOC calibration response factor has been determined, proceed with sample analysis as follows:

11.1.1 Daily Operations and Calibration Checks. Before and immediately after the analysis of each set of samples or on a daily basis (whichever occurs first), conduct a calibration test according to the procedures established in section 10.2. If the criteria of the daily calibration test cannot be met, repeat

the NMOC analyzer performance test (Section 10.1) before proceeding.

11.1.2 Operating Conditions. Same as in Method 25, section 11.2.1.

11.1.3 Analysis of Sample Tank. Purge the sample loop with sample, and then inject the sample. Under the specified operating conditions, the CO_2 in the sample will elute in approximately 100 seconds. As soon as the detector response returns to baseline following the CO_2 peak, switch the carrier gas flow to backflush, and raise the column oven temperature to 195 °C (383 °F) as rapidly as possible. A rate of 30 °C/min (54 °F/min) has been shown to be adequate. Record the value obtained for any measured NMOC. Return the column oven temperature to 85 °C (185 °F) in preparation for the next analysis. Analyze each sample in triplicate, and report the average as C_{tm}.

12.0 Data Analysis and Calculations

NOTE: All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge or manometer pressure.

12.1 Nomenclature

B_w = Moisture content in the sample, fraction.
C_{N2} = N_2 concentration in the diluted sample gas.
C_{mN2} = Measured N_2 concentration, fraction in landfill gas.
C_{mOx} = Measured Oxygen concentration, fraction in landfill gas.
C_{Ox} = Oxygen concentration in the diluted sample gas.
C_t = Calculated NMOC concentration, ppmv C equivalent.
C_{tm} = Measured NMOC concentration, ppmv C equivalent.
P_b = Barometric pressure, mm Hg.
P_t = Gas sample tank pressure after sampling, but before pressurizing, mm Hg absolute.
P_{tf} = Final gas sample tank pressure after pressurizing, mm Hg absolute.
P_{ti} = Gas sample tank pressure after evacuation, mm Hg absolute.
P_w = Vapor pressure of H_2O (from Table 25C–1), mm Hg.
r = Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 . . . r).
T_t = Sample tank temperature at completion of sampling, °K.
T_{ti} = Sample tank temperature before sampling, °K.
T_{tf} = Sample tank temperature after pressuring, °K.

12.2 Water Correction. Use Table 25C–1 (Section 17.0), the LFG temperature, and barometric pressure at the sampling site to calculate B_w.

$$B_w = \frac{P_w}{P_b} \qquad \text{Eq. 25C-1}$$

12.3 Nitrogen Concentration in the landfill gas. Use equation 25C–2 to calculate the measured concentration of nitrogen in the original landfill gas.

$$C_{N2} = \left[\frac{\left(\frac{P_{tf}}{T_{tf}}\right)}{\left(\left(\frac{P_t}{T_t}\right)-\left(\frac{P_{ti}}{T_{ti}}\right)\right)}\right] C_{mN2} \qquad \text{Eq.25C-2}$$

12.4 Oxygen Concentration in the landfill gas. Use equation 25C–3 to calculate the measured concentration of oxygen in the original landfill gas.

$$C_{Ox} = \left[\frac{\left(\frac{P_{tf}}{T_{tf}}\right)}{\left(\left(\frac{P_t}{T_t}\right)-\left(\frac{P_{ti}}{T_{ti}}\right)\right)}\right] C_{mOx} \qquad \text{Eq.25C-3}$$

12.5 You must correct the NMOC Concentration for the concentration of nitrogen or oxygen based on which gas or gases passes the requirements in section 9.1.

12.5.1 NMOC Concentration with nitrogen correction. Use Equation 25C–4 to calculate the concentration of NMOC for each sample tank when the nitrogen concentration is less than 20 percent.

$$C_t = \frac{\frac{P_{tf}}{T_{tf}}}{\left(\frac{P_t}{T_t}-\frac{P_{ti}}{T_{ti}}\right)\left(1-\frac{99}{78}C_{N2}\right)-B_w}\frac{1}{r}\sum_{j=1}^{r} C_{tm(j)} \qquad \text{Eq. 25C-4}$$

12.5.2 NMOC Concentration with oxygen correction. Use Equation 25C–5 to calculate the concentration of NMOC for each sample tank if the landfill gas oxygen is less than 5 percent and the landfill gas nitrogen concentration is greater than 20 percent.

$$C_t = \frac{\frac{P_{tf}}{T_{tf}}}{\left(\frac{P_t}{T_t}-\frac{P_{ti}}{T_{ti}}\right)\left(1-\frac{99}{21}C_{Ox}\right)-B_w}\frac{1}{r}\sum_{j=1}^{r} C_{tm(j)} \qquad \text{Eq. 25C-5}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, Albert E., Samuel Witz, and Robert D. MacPhee. Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, Massachusetts. June 15–20, 1975.) 14 p.

2. Salo, Albert E., William L. Oaks, and Robert D. MacPhee. Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, Colorado. June 9–13, 1974.) 25 p.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

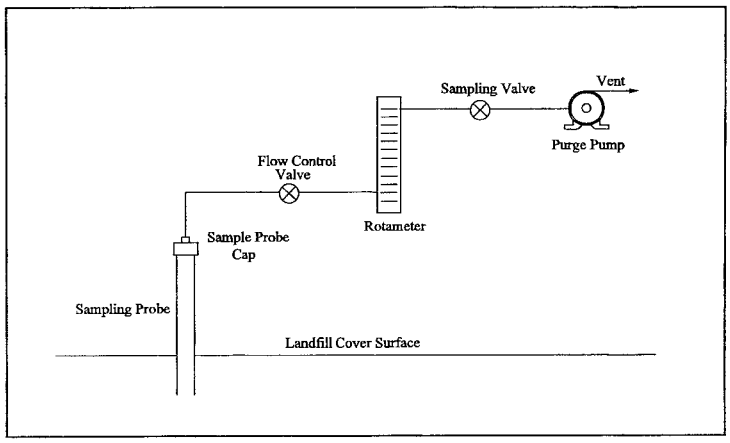


Figure 25C-1. Schematic of Sampling Probe Purging System

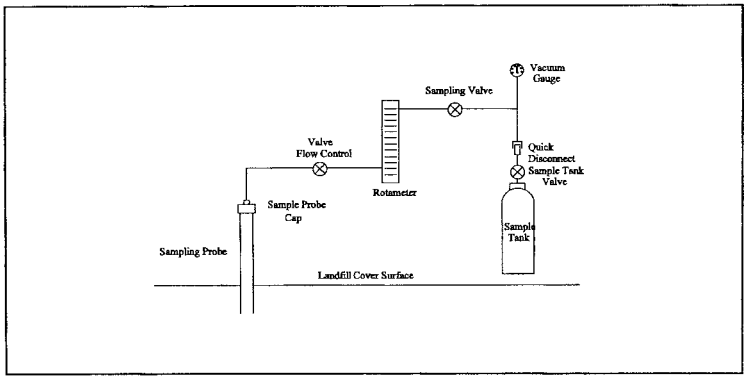


Figure 25C-2. Schematic of Sampling Train.

TABLE 25C–1—MOISTURE CORRECTION

Temperature, °C	Vapor Pressure of H_2O, mm Hg	Temperature, °C	Vapor Pressure of H_2O, mm Hg
4	6.1	18	15.5
6	7.0	20	17.5
8	8.0	22	19.8
10	9.2	24	22.4
12	10.5	26	25.2
14	12.0	28	28.3

TABLE 25C–1—MOISTURE CORRECTION—Continued

Temperature, °C	Vapor Pressure of H_2O, mm Hg	Temperature, °C	Vapor Pressure of H_2O, mm Hg
16	13.6	30	31.8

METHOD 25D—DETERMINATION OF THE VOLATILE ORGANIC CONCENTRATION OF WASTE SAMPLES

NOTE: Performance of this method should not be attempted by persons unfamiliar with the operation of a flame ionization detector (FID) or an electrolytic conductivity detector (ELCD) because knowledge beyond the scope of this presentation is required.

1.0 Scope and Application

1.1 Analyte. Volatile Organic Compounds. No CAS No. assigned.

1.2 Applicability. This method is applicable for determining the volatile organic (VO) concentration of a waste sample.

2.0 Summary of Method

2.1 Principle. A sample of waste is obtained at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to the atmosphere). The sample is suspended in an organic/aqueous matrix, then heated and purged with nitrogen for 30 min. in order to separate certain organic compounds. Part of the sample is analyzed for carbon concentration, as methane, with an FID, and part of the sample is analyzed for chlorine concentration, as chloride, with an ELCD. The VO concentration is the sum of the carbon and chlorine content of the sample.

3.0 Definitions

3.1 *Well-mixed* in the context of this method refers to turbulent flow which results in multiple-phase waste in effect behaving as single-phase waste due to good mixing.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1 Sampling. The following equipment is required:

6.1.1 Sampling Tube. Flexible Teflon, 0.25 in. ID (6.35 mm).

6.1.2 Sample Container. Borosilicate glass, 40-mL, and a Teflon-lined screw cap capable of forming an air tight seal.

6.1.3 Cooling Coil. Fabricated from 0.25 in (6.35 mm). ID 304 stainless steel tubing with a thermocouple at the coil outlet.

6.2 Analysis. The following equipment is required.

6.2.1 Purging Apparatus. For separating the VO from the waste sample. A schematic of the system is shown in Figure 25D–1. The purging apparatus consists of the following major components.

6.2.1.1 Purging Flask. A glass container to hold the sample while it is heated and purged with dry nitrogen. The cap of the purging flask is equipped with three fittings: one for a purging lance (fitting with the #7 Ace-thread), one for the Teflon exit tubing (side fitting, also a #7 Ace-thread), and a third (a 50-mm Ace-thread) to attach the base of the purging flask as shown in Figure 25D–2. The base of the purging flask is a 50-mm ID (2 in) cylindrical glass tube. One end of the tube is open while the other end is sealed. Exact dimensions are shown in Figure 25D–2.

6.2.1.2 Purging Lance. Glass tube, 6-mm OD (0.2 in) by 30 cm (12 in) long. The purging end of the tube is fitted with a four-arm bubbler with each tip drawn to an opening 1 mm (0.04 in) in diameter. Details and exact dimensions are shown in Figure 25D–2.

6.2.1.3 Coalescing Filter. Porous fritted disc incorporated into a container with the same dimensions as the purging flask. The details of the design are shown in Figure 25D–3.

6.2.1.4 Constant Temperature Chamber. A forced draft oven capable of maintaining a uniform temperature around the purging flask and coalescing filter of 75 ±2 °C (167 ±3.6 °F).

6.2.1.5 Three-way Valve. Manually operated, stainless steel. To introduce calibration gas into system.

6.2.1.6 Flow Controllers. Two, adjustable. One capable of maintaining a purge gas flow rate of 6 ±0.06 L/min (0.2 ±0.002 ft^3/min) The other capable of maintaining a calibration gas flow rate of 1–100 mL/min (0.00004–0.004 ft^3/min).

6.2.1.7 Rotameter. For monitoring the air flow through the purging system (0–10 L/min)(0–0.4 ft^3/min).

6.2.1.8 Sample Splitters. Two heated flow restrictors (placed inside oven or heated to 120 ±10 °C (248 ±18 °F)). At a purge rate of 6 L/min (0.2 ft^3/min), one will supply a constant flow to the first detector (the rest of the flow will be directed to the second sample splitter). The second splitter will split the analytical flow between the second detector and the flow restrictor. The approximate flow to the FID will be 40 mL/min (0.0014 ft^3/min) and to the ELCD will be 15 mL/min (0.0005 ft^3/min), but the exact flow must be adjusted to be compatible with the individual detector and to meet its linearity requirement. The two sample splitters will be connected to each other by 1/8″ OD (3.175 mm) stainless steel tubing.

6.2.1.9 Flow Restrictor. Stainless steel tubing, 1/8″ OD (3.175 mm), connecting the second sample splitter to the ice bath. Length is determined by the resulting pressure in the purging flask (as measured by the pressure gauge). The resulting pressure from the use of the flow restrictor shall be 6–7 psig.

6.2.1.10 Filter Flask. With one-hole stopper. Used to hold ice bath. Excess purge gas is vented through the flask to prevent condensation in the flowmeter and to trap volatile organic compounds.

6.2.1.11 Four-way Valve. Manually operated, stainless steel. Placed inside oven, used to bypass purging flask.

6.2.1.12 On/Off Valves. Two, stainless steel. One heat resistant up to 130 °C (266 °F) and placed between oven and ELCD. The other a toggle valve used to control purge gas flow.

6.2.1.13 Pressure Gauge. Range 0–40 psi. To monitor pressure in purging flask and coalescing filter.

6.2.1.14 Sample Lines. Teflon, 1/4″ OD (6.35 mm), used inside the oven to carry purge gas to and from purging chamber and to and from coalescing filter to four-way valve. Also used to carry sample from four-way valve to first sample splitter.

6.2.1.15 Detector Tubing. Stainless steel, 1/8″ OD (3.175 mm), heated to 120 ±10 °C (248 ±18 °F) . Used to carry sample gas from each sample splitter to a detector. Each piece of tubing must be wrapped with heat tape and insulating tape in order to insure that no cold spots exist. The tubing leading to the ELCD will also contain a heat-resistant on-off valve (Section 6.2.1.12) which shall also be wrapped with heat-tape and insulation.

6.2.2 Volatile Organic Measurement System. Consisting of an FID to measure the carbon concentration of the sample and an ELCD to measure the chlorine concentration.

6.2.2.1 FID. A heated FID meeting the following specifications is required.

6.2.2.1.1 Linearity. A linear response (±5 percent) over the operating range as demonstrated by the procedures established in section 10.1.1.

6.2.2.1.2 Range. A full scale range of 50 pg carbon/sec to 50 µg carbon/sec. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.2.2.1.3 Data Recording System. A digital integration system compatible with the FID for permanently recording the output of the detector. The recorder shall have the capability to start and stop integration at points selected by the operator or it shall be capable of the ''integration by slices'' technique (this technique involves breaking down the chromatogram into smaller increments, integrating the area under the curve for each portion, subtracting the background for each portion, and then adding all of the areas together for the final area count).

6.2.2.2 ELCD. An ELCD meeting the following specifications is required. 1-propanol must be used as the electrolyte. The electrolyte flow through the conductivity cell shall be 1 to 2 mL/min (0.00004 to 0.00007 ft^3/min).

NOTE: A ¼-in. ID (6.35 mm) quartz reactor tube is strongly recommended to reduce carbon buildup and the resulting detector maintenance.

6.2.2.2.1 Linearity. A linear response (±10 percent) over the response range as demonstrated by the procedures in section 10.1.2.

6.2.2.2.2 Range. A full scale range of 5.0 pg/sec to 500 ng/sec chloride. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.2.2.2.3 Data Recording System. A digital integration system compatible with the output voltage range of the ELCD. The recorder must have the capability to start and stop integration at points selected by the operator or it shall be capable of performing the ''integration by slices'' technique.

7.0 Reagents and Standards

7.1 Sampling.

7.1.1 Polyethylene Glycol (PEG). Ninety-eight percent pure with an average molecular weight of 400. Before using the PEG, remove any organic compounds that might be detected as volatile organics by heating it to 120 °C (248 °F) and purging it with nitrogen at a flow rate of 1 to 2 L/min (0.04 to 0.07 ft^3/min) for 2 hours. The cleaned PEG must be stored under a 1 to 2 L/min (0.04 to 0.07 ft^3/min) nitrogen purge until use. The purge apparatus is shown in Figure 25D–4.

7.2 Analysis.

7.2.1 Sample Separation. The following are required for the sample purging step.

7.2.1.1 PEG. Same as section 7.1.1.

7.2.1.2 Purge Gas. Zero grade nitrogen (N_2), containing less than 1 ppm carbon.

7.2.2 Volatile Organics Measurement. The following are required for measuring the VO concentration.

7.2.2.1 Hydrogen (H_2). Zero grade H_2, 99.999 percent pure.

7.2.2.2 Combustion Gas. Zero grade air or oxygen as required by the FID.

7.2.2.3 Calibration Gas. Pressurized gas cylinder containing 10 percent propane and 1 percent 1,1-dichloroethylene by volume in nitrogen.

7.2.2.4 Water. Deionized distilled water that conforms to American Society for Testing and Materials Specification D 1193–74, Type 3, is required for analysis. At the option of the analyst, the $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations are not expected to be present.

7.2.2.5 1-Propanol. ACS grade or better. Electrolyte Solution. For use in the ELCD.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling.

8.1.1 Sampling Plan Design and Development. Use the procedures in chapter nine of Reference 1 in section 16 as guidance in developing a sampling plan.

8.1.2 Single Phase or Well-mixed Waste.

8.1.2.1 Install a sampling tap to obtain the sample at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to the atmosphere). Assemble the sampling apparatus as shown in Figure 25D–5.

8.1.2.2 Prepare the sampling containers as follows: Pour 30 mL of clean PEG into the container. PEG will reduce but not eliminate the loss of organics during sample collection. Weigh the sample container with the screw cap, the PEG, and any labels to the nearest 0.01 g and record the weight (m_{st}). Store the containers in an ice bath until 1 hour before sampling (PEG will solidify at ice bath temperatures; allow the containers to reach room temperature before sampling).

8.1.2.3 Begin sampling by purging the sample lines and cooling coil with at least four volumes of waste. Collect the purged material in a separate container and dispose of it properly.

8.1.2.4 After purging, stop the sample flow and direct the sampling tube to a preweighed sample container, prepared as described in section 8.1.2.2. Keep the tip of the tube below the surface of the PEG during sampling to minimize contact with the atmosphere. Sample at a flow rate such that the temperature of the waste is less than 10 °C (50 °F). Fill the sample container and immediately cap it (within 5 seconds) so that a minimum headspace exists in the container. Store immediately in a cooler and cover with ice.

8.1.3 Multiple-phase Waste. Collect a 10 g sample of each phase of waste generated using the procedures described in section 8.1.2 or 8.1.5. Each phase of the waste shall be analyzed as a separate sample. Calculate the weighted average VO concentration of the waste using Equation 25D–13 (Section 12.14).

8.1.4 Solid waste. Add approximately 10 g of the solid waste to a container prepared in the manner described in section 8.1.2.2, minimizing headspace. Cap and chill immediately.

8.1.5 Alternative to Tap Installation. If tap installation is impractical or impossible, fill a large, clean, empty container by submerging the container into the waste below the surface of the waste. Immediately fill a container prepared in the manner described in section 8.1.2.2 with approximately 10 g of the waste collected in the large container. Minimize headspace, cap and chill immediately.

8.1.6 Alternative sampling techniques may be used upon the approval of the Administrator.

8.2 Sample Recovery.

8.2.1 Assemble the purging apparatus as shown in Figures 25D–1 and 25D–2. The oven shall be heated to 75 ±2 °C (167 ±3.6 °F). The sampling lines leading from the oven to the detectors shall be heated to 120 ±10 °C (248 ±18 °F) with no cold spots. The flame ionization detector shall be operated with a heated block. Adjust the purging lance so that it reaches the bottom of the chamber.

8.2.2 Remove the sample container from the cooler, and wipe the exterior of the container to remove any extraneous ice, water, or other debris. Reweigh the sample container to the nearest 0.01 g, and record the weight (m_{sf}). Pour the contents of the sample container into the purging flask, rinse the sample container three times with a total of 20 mL of PEG (since the sample container originally held 30 mL of PEG, the total volume of PEG added to the purging flask will be 50 mL), transferring the rinsings to the purging flask after each rinse. Cap purging flask between rinses. The total volume of PEG in the purging flask shall be 50 mL. Add 50 mL of water to the purging flask.

9.0 Quality Control

9.1 Quality Control Samples. If audit samples are not available, prepare and analyze the two types of quality control samples (QCS) listed in Sections 9.1.1 and 9.1.2. Before placing the system in operation, after a shutdown of greater than six months, and after any major modifications, analyze each QCS in triplicate. For each detector, calculate the percent recovery by dividing measured concentration by theoretical concentration and multiplying by 100. Determine the mean percent recovery for each detector for each QCS triplicate analysis. The RSD for any triplicate analysis shall be ≤10 percent. For QCS 1 (methylene chloride), the percent recovery shall be ≥90 percent for carbon as methane, and ≥55 percent for chlorine as chloride. For QCS 2 (1,3-dichloro-2-propanol), the percent recovery shall be ≤15 percent for carbon as methane, and ≤6 percent for chlorine as chloride. If the analytical system does not meet the above-mentioned criteria for both detectors, check the system parameters (temperature, system pressure, purge rate, etc.), correct the problem, and repeat the triplicate analysis of each QCS.

9.1.1 QCS 1, Methylene Chloride. Prepare a stock solution by weighing, to the nearest 0.1 mg, 55 µL of HPLC grade methylene chloride in a tared 5 mL volumetric flask. Record the weight in milligrams, dilute to 5 mL with cleaned PEG, and inject 100 µL of the stock solution into a sample prepared as a water blank (50 mL of cleaned PEG and 60 mL of water in the purging flask). Analyze

the QCS according to the procedures described in sections 10.2 and 10.3, excluding section 10.2.2. To calculate the theoretical carbon concentration (in mg) in QCS 1, multiply mg of methylene chloride in the stock solution by 3.777×10^{-3}. To calculate the theoretical chlorine concentration (in mg) in QCS 1, multiply mg of methylene chloride in the stock solution by 1.670×10^{-2}.

9.1.2 QCS 2, 1,3-dichloro-2-propanol. Prepare a stock solution by weighing, to the nearest 0.1 mg, 60 μL of high purity grade 1,3-dichloro-2-propanol in a tared 5 mL volumetric flask. Record the weight in milligrams, dilute to 5 mL with cleaned PEG, and inject 100 μL of the stock solution into a sample prepared as a water blank (50 mL of cleaned PEG and 60 mL of water in the purging flask). Analyze the QCS according to the procedures described in sections 10.2 and 10.3, excluding section 10.2.2. To calculate the theoretical carbon concentration (in mg) in QCS 2, multiply mg of 1,3-dichloro-2-propanol in the stock solution by 7.461×10^{-3}. To calculate the theoretical chlorine concentration (in mg) in QCS 2, multiply mg of 1,3-dichloro-2-propanol in the stock solution by 1.099×10^{-2}.

9.1.3 Routine QCS Analysis. For each set of compliance samples (in this context, set is per facility, per compliance test), analyze one QCS 1 and one QCS 2 sample. The percent recovery for each sample for each detector shall be ±13 percent of the mean recovery established for the most recent set of QCS triplicate analysis (Section 9.4). If the sample does not meet this criteria, check the system components and analyze another QCS 1 and 2 until a single set of QCS meet the ±13 percent criteria.

10.0 Calibration and Standardization

10.1 Initial Performance Check of Purging System. Before placing the system in operation, after a shutdown of greater than six months, after any major modifications, and at least once per month during continuous operation, conduct the linearity checks described in sections 10.1.1 and 10.1.2. Install calibration gas at the three-way calibration gas valve. See Figure 25D–1.

10.1.1 Linearity Check Procedure. Using the calibration standard described in section 7.2.2.3 and by varying the injection time, it is possible to calibrate at multiple concentration levels. Use Equation 25D–3 to calculate three sets of calibration gas flow rates and run times needed to introduce a total mass of carbon, as methane, (m_c) of 1, 5, and 10 mg into the system (low, medium and high FID calibration, respectively). Use Equation 25D–4 to calculate three sets of calibration gas flow rates and run times needed to introduce a total chloride mass (m_{ch}) of 1, 5, and 10 mg into the system (low, medium and high ELCD calibration, respectively). With the system operating in standby mode, allow the FID and the ELCD to establish a stable baseline. Set the secondary pressure regulator of the calibration gas cylinder to the same pressure as the purge gas cylinder and set the proper flow rate with the calibration flow controller (see Figure 25D–1). The calibration gas flow rate can be measured with a flowmeter attached to the vent position of the calibration gas valve. Set the four-way bypass valve to standby position so that the calibration gas flows through the coalescing filter only. Inject the calibration gas by turning the calibration gas valve from vent position to inject position. Continue the calibration gas flow for the appropriate period of time before switching the calibration valve to vent position. Continue recording the response of the FID and the ELCD for 5 min after switching off calibration gas flow. Make triplicate injections of all six levels of calibration.

10.1.2 Linearity Criteria. Calculate the average response factor (Equations 25D–5 and 25D–6) and the relative standard deviation (RSD) (Equation 25D–10) at each level of the calibration curve for both detectors. Calculate the overall mean of the three response factor averages for each detector. The FID linearity is acceptable if each response factor is within 5 percent of the overall mean and if the RSD for each set of triplicate injections is less than 5 percent. The ELCD linearity is acceptable if each response factor is within 10 percent of the overall mean and if the RSD for each set of triplicate injections is less than 10 percent. Record the overall mean value of the response factors for the FID and the ELCD. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat sections 10.1.1 and 10.1.2.

10.2 Daily Calibrations.

10.2.1 Daily Linearity Check. Follow the procedures outlined in section 10.1.1 to analyze the medium level calibration for both the FID and the ELCD in duplicate at the start of the day. Calculate the response factors and the RSDs for each detector. For the FID, the calibration is acceptable if the average response factor is within 5 percent of the overall mean response factor (Section 10.1.2) and if the RSD for the duplicate injection is less than 5 percent. For the ELCD, the calibration is acceptable if the average response factor is within 10 percent of the overall mean response factor (Section 10.1.2) and if the RSD for the duplicate injection is less than 10 percent. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat sections 10.1.1 and 10.1.2.

10.2.2 Calibration Range Check.

10.2.2.1 If the waste concentration for either detector falls below the range of calibration for that detector, use the procedure outlined in section 10.1.1 to choose two calibration points that bracket the new target

concentration. Analyze each of these points in triplicate (as outlined in section 10.1.1) and use the criteria in section 10.1.2 to determine the linearity of the detector in this ''mini-calibration'' range.

10.2.2.2 After the initial linearity check of the mini-calibration curve, it is only necessary to test one of the points in duplicate for the daily calibration check (in addition to the points specified in section 10.2.1). The average daily mini-calibration point should fit the linearity criteria specified in section 10.2.1. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat the calibration procedure mentioned in the first paragraph of section 10.2.2. A mini-calibration curve for waste concentrations above the calibration curve for either detector is optional.

10.3 Analytical Balance. Calibrate against standard weights.

11.0 Analysis

11.1 Sample Analysis.

11.1.1 Turn on the constant temperature chamber and allow the temperature to equilibrate at 75 ±2 °C (167 ±3.6 °F). Turn the four-way valve so that the purge gas bypasses the purging flask, the purge gas flowing through the coalescing filter and to the detectors (standby mode). Turn on the purge gas. Allow both the FID and the ELCD to warm up until a stable baseline is achieved on each detector. Pack the filter flask with ice. Replace ice after each run and dispose of the waste water properly. When the temperature of the oven reaches 75 ±2 °C (167 ±3.6 °F), start both integrators and record baseline. After 1 min, turn the four-way valve so that the purge gas flows through the purging flask, to the coalescing filter and to the sample splitters (purge mode). Continue recording the response of the FID and the ELCD. Monitor the readings of the pressure gauge and the rotameter. If the readings fall below established setpoints, stop the purging, determine the source of the leak, and resolve the problem before resuming. Leaks detected during a sampling period invalidate that sample.

11.1.2 As the purging continues, monitor the output of the detectors to make certain that the analysis is proceeding correctly and that the results are being properly recorded. Every 10 minutes read and record the purge flow rate, the pressure and the chamber temperature. Continue the purging for 30 minutes.

11.1.3 For each detector output, integrate over the entire area of the peak starting at 1 minute and continuing until the end of the run. Subtract the established baseline area from the peak area. Record the corrected area of the peak. See Figure 25D–6 for an example integration.

11.2 Water Blank. A water blank shall be analyzed for each batch of cleaned PEG prepared. Transfer about 60 mL of water into the purging flask. Add 50 mL of the cleaned PEG to the purging flask. Treat the blank as described in sections 8.2 and 8.3, excluding section 8.2.2. Calculate the concentration of carbon and chlorine in the blank sample (assume 10 g of waste as the mass). A VO concentration equivalent to ≤10 percent of the applicable standard may be subtracted from the measured VO concentration of the waste samples. Include all blank results and documentation in the test report.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

A_b = Area under the water blank response curve, counts.

A_c = Area under the calibration response curve, counts.

A_s = Area under the sample response curve, counts.

C = Concentration of volatile organics in the sample, ppmw.

C_c = Concentration of carbon, as methane, in the calibration gas, mg/L.

C_{ch} = Concentration of chloride in the calibration gas, mg/L.

C_j = VO concentration of phase j, ppmw.

DR_t = Average daily response factor of the FID, mg CH_4/counts.

Dr_{th} = Average daily response factor of the ELCD, mg Cl^-/counts.

F_j = Weight fraction of phase j present in the waste.

m_c = Mass of carbon, as methane, in a calibration run, mg.

m_{ch} = Mass of chloride in a calibration run, mg.

m_s = Mass of the waste sample, g.

m_{sc} = Mass of carbon, as methane, in the sample, mg.

m_{sf} = Mass of sample container and waste sample, g.

m_{sh} = Mass of chloride in the sample, mg.

m_{st} = Mass of sample container prior to sampling, g.

m_{VO} = Mass of volatile organics in the sample, mg.

n = Total number of phases present in the waste.

P_p = Percent propane in calibration gas (L/L).

P_{vc} = Percent 1,1-dichloroethylene in calibration gas (L/L).

Q_c = Flow rate of calibration gas, L/min.

t_c = Length of time standard gas is delivered to the analyzer, min.

W = Weighted average VO concentration, ppmw.

12.2 Concentration of Carbon, as Methane, in the Calibration Gas.

$$C_c = (19.681 \times P_p) + (13.121 \times P_{vc}) \qquad \text{Eq. 25D-1}$$

12.3 Concentration of Chloride in the Calibration Gas.

$$C_{ch} = 28.998 \times P_{vc} \qquad \text{Eq. 25D-2}$$

12.4 Mass of Carbon, as Methane, in a Calibration Run.

$$M_c = C_c \times Q_c \times t_c \qquad \text{Eq. 25D-3}$$

12.5 Mass of Chloride in a Calibration Run.

$$m_{ch} = C_{ch} \times Q_c \times t_c \qquad \text{Eq. 25D-4}$$

12.6 FID Response Factor, mg/counts.

$$DR_t = \frac{m_c}{A_c} \qquad \text{Eq. 25D-5}$$

12.7 ELCD Response Factor, mg/counts.

$$DR_{th} = \frac{m_{ch}}{A_c} \qquad \text{Eq. 25D-6}$$

12.8 Mass of Carbon in the Sample.

$$m_{sc} = DR_t(A_s - A_b) \qquad \text{Eq. 25D-7}$$

12.9 Mass of Chloride in the Sample.

$$m_{sh} = DR_{th}(A_s - A_b) \qquad \text{Eq. 25D-8}$$

12.10 Mass of Volatile Organics in the Sample.

$$m_{vo} = m_{sc} + m_{sh} \qquad \text{Eq. 25D-9}$$

12.11 Relative Standard Deviation.

$$RSD = \frac{100}{\bar{x}} \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}} \qquad \text{Eq. 25D-10}$$

12.12 Mass of Sample.

$$m_s = m_{sf} - m_{st} \qquad \text{Eq. 25D-11}$$

12.13 Concentration of Volatile Organics in Waste.

$$C = \frac{(m_{vo} \times 1000)}{m_s} \qquad \text{Eq. 25D-12}$$

12.14 Weighted Average VO Concentration of Multi-phase Waste.

$$W = \sum_{j=1}^{n} F_j x \overline{C}_j \qquad \text{Eq. 25D-13}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. ''Test Methods for Evaluating Solid Waste, Physical/Chemistry Methods'', U.S. Environmental Protection Agency. Publication SW–846, 3rd Edition, November 1986 as amended by Update I, November 1990.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

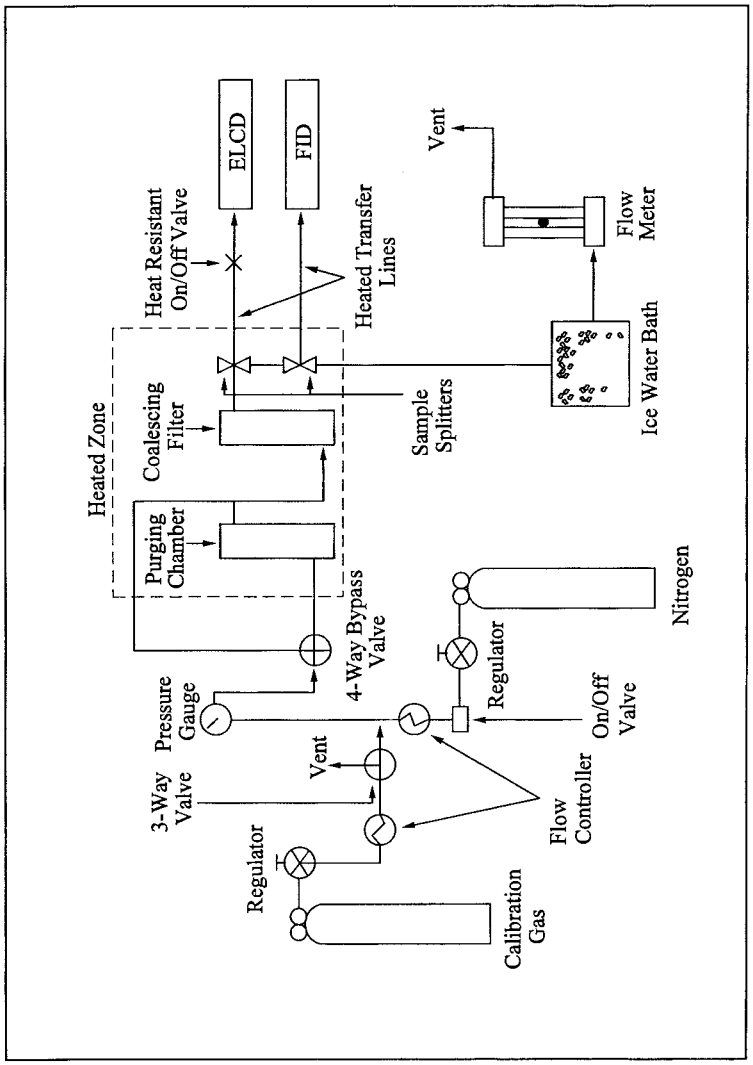


Figure 25D-1. Schematic of Purging Apparatus.

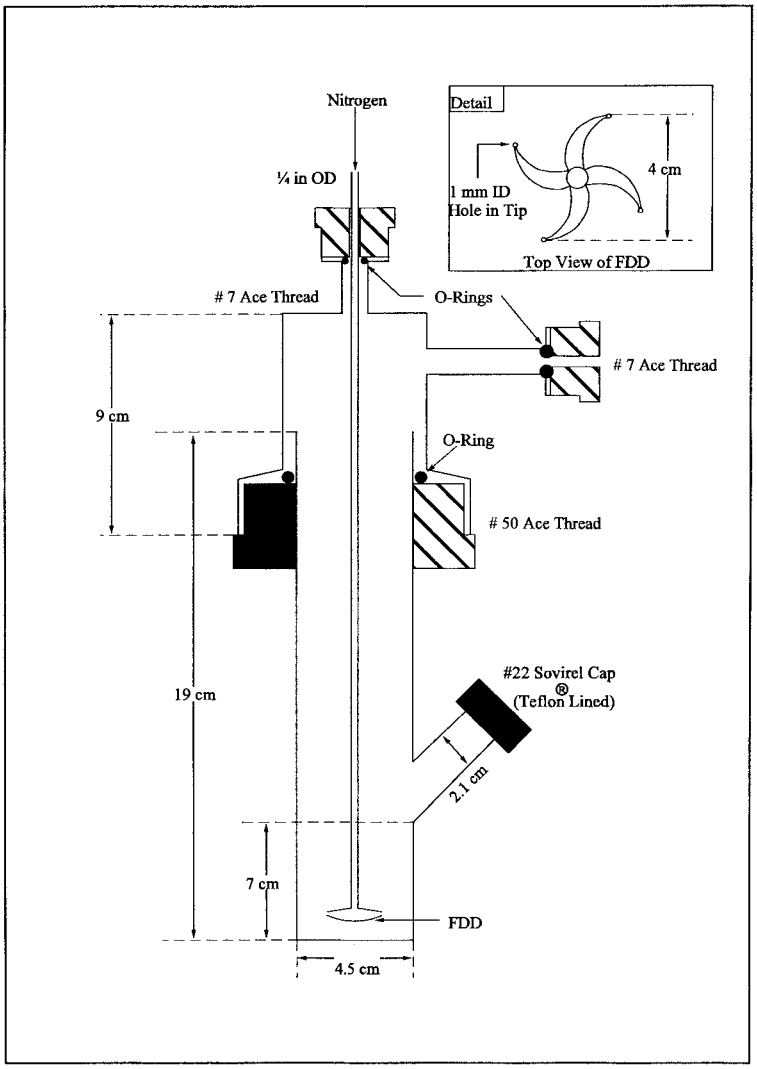
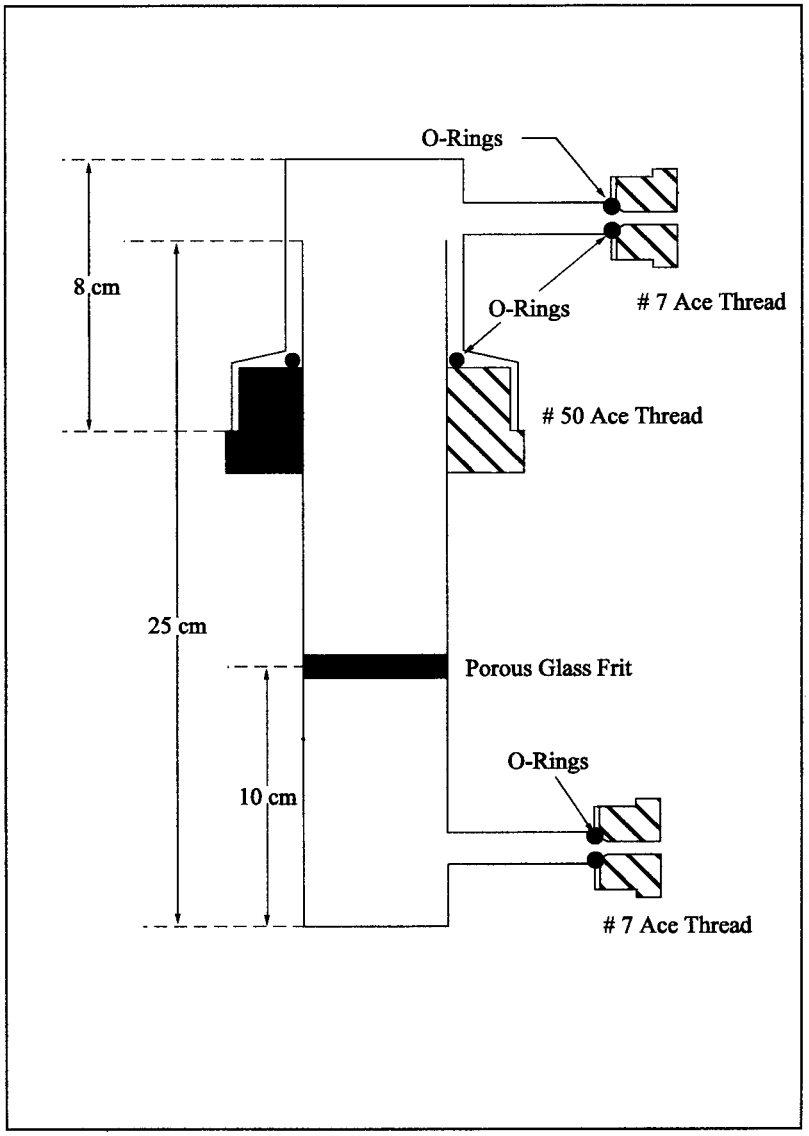


Figure 25D-2. Purging Lance.


O-Rings
8 cm
O-Rings
7 Ace Thread
50 Ace Thread
25 cm
Porous Glass Frit
O-Rings
10 cm
7 Ace Thread

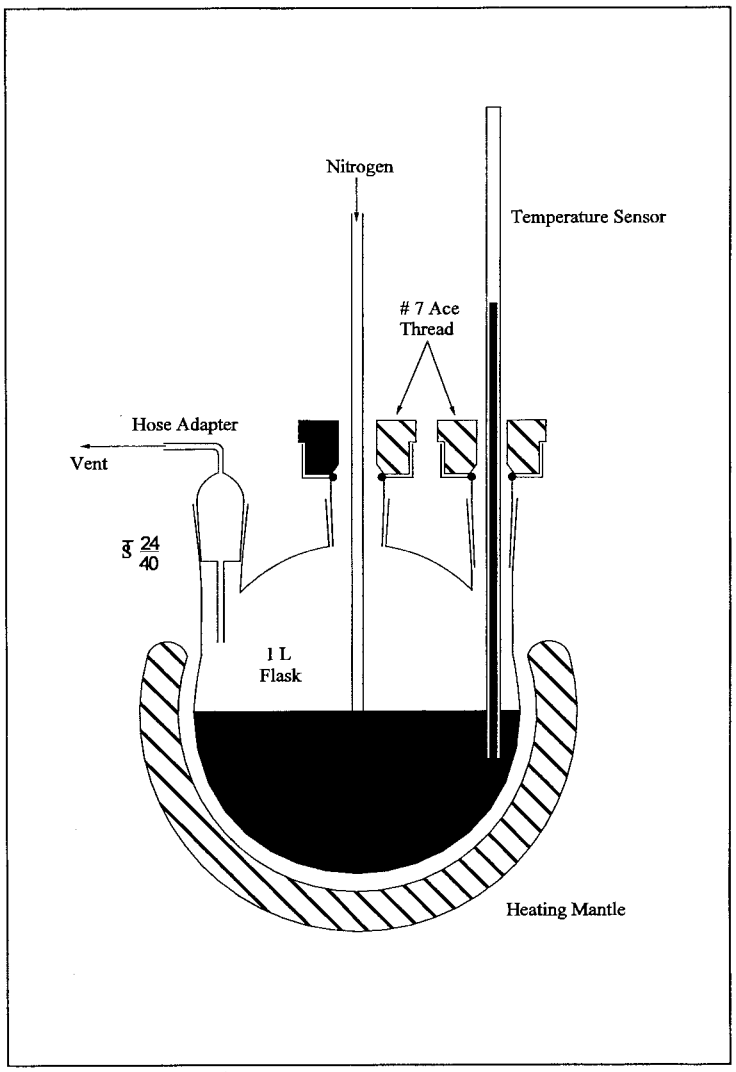


Figure 25D-4. Schematic of PEG Cleaning System.

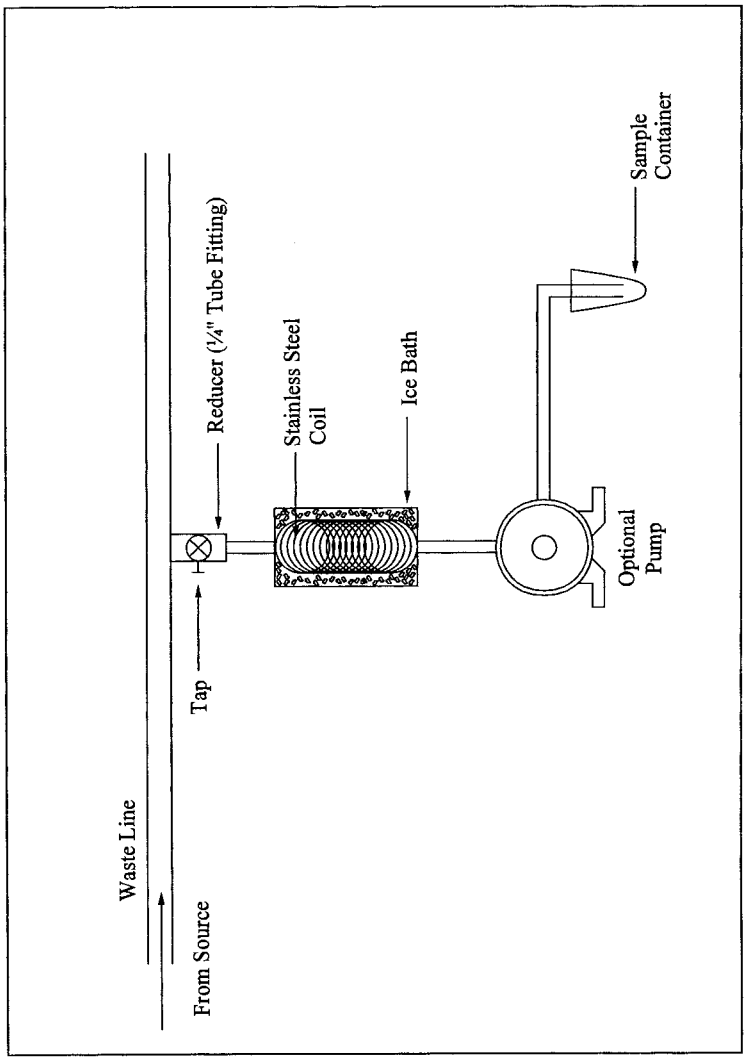


Figure 25D-5. Schematic of Sampling Apparatus.

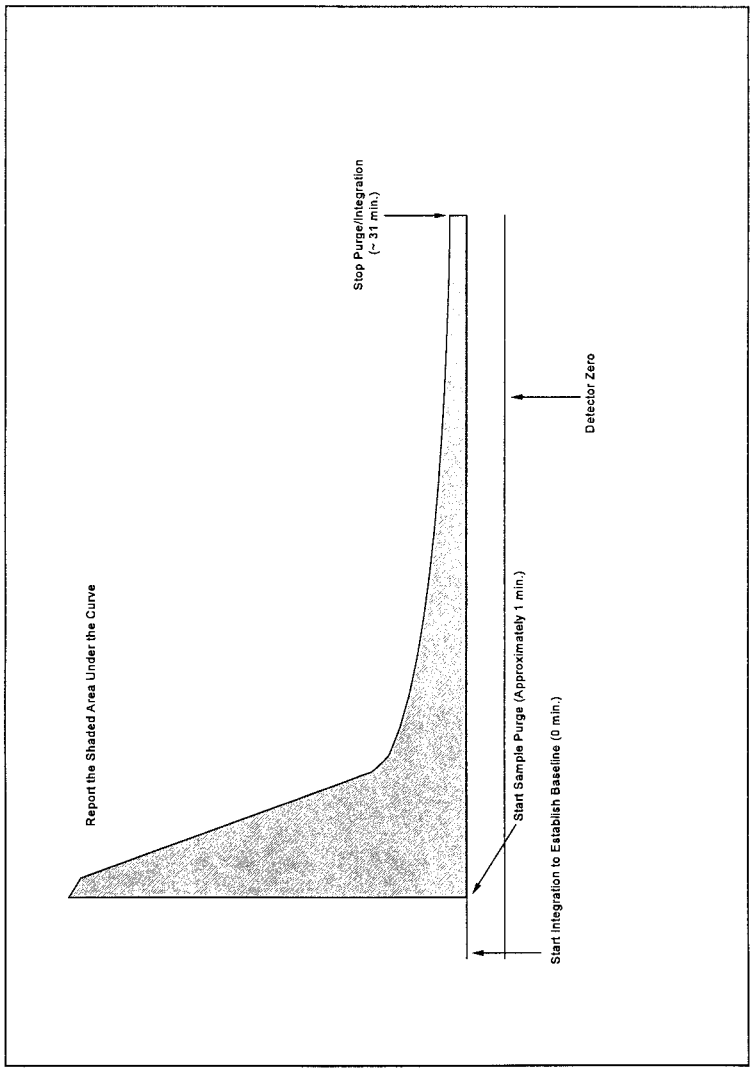


Figure 25D-6. Example Integration of Either Detector.

METHOD 25E—DETERMINATION OF VAPOR PHASE ORGANIC CONCENTRATION IN WASTE SAMPLES

NOTE: Performance of this method should not be attempted by persons unfamiliar with the operation of a flame ionization detector (FID) nor by those who are unfamiliar with source sampling because knowledge beyond the scope of this presentation is required. This method is not inclusive with respect to specifications (*e.g.*, reagents and standards) and calibration procedures. Some material is incorporated by reference from other methods. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 106, part 61, Appendix B, and Method 18, part 60, Appendix A.

1.0 Scope and Application

1.1 Applicability. This method is applicable for determining the vapor pressure of waste cited by an applicable regulation.

1.2 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 The headspace vapor of the sample is analyzed for carbon content by a headspace analyzer, which uses an FID.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 The analyst shall select the operating parameters best suited to the requirements for a particular analysis. The analyst shall produce confirming data through an adequate supplemental analytical technique and have the data available for review by the Administrator.

5.0 Safety [Reserved]

6.0 Equipment and Supplies

6.1 Sampling. The following equipment is required:

6.1.1 Sample Containers. Vials, glass, with butyl rubber septa, Perkin-Elmer Corporation Numbers 0105–0129 (glass vials), B001–0728 (gray butyl rubber septum, plug style), 0105–0131 (butyl rubber septa), or equivalent. The seal must be made from butyl rubber. Silicone rubber seals are not acceptable.

6.1.2 Vial Sealer. Perkin-Elmer Number 105–0106, or equivalent.

6.1.3 Gas-Tight Syringe. Perkin-Elmer Number 00230117, or equivalent.

6.1.4 The following equipment is required for sampling.

6.1.4.1 Tap.

6.1.4.2 Tubing. Teflon, 0.25-in. ID.

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1.4.3 Cooling Coil. Stainless steel (304), 0.25 in.-ID, equipped with a thermocouple at the coil outlet.

6.2 Analysis. The following equipment is required.

6.2.1 Balanced Pressure Headspace Sampler. Perkin-Elmer HS–6, HS–100, or equivalent, equipped with a glass bead column instead of a chromatographic column.

6.2.2 FID. An FID meeting the following specifications is required.

6.2.2.1 Linearity. A linear response (±5 percent) over the operating range as demonstrated by the procedures established in section 10.2.

6.2.2.2 Range. A full scale range of 1 to 10,000 parts per million (ppm) propane (C_3H_8). Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.2.3 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the output of the detector.

6.2.4 Temperature Sensor. Capable of reading temperatures in the range of 30 to 60 °C (86 to 140 °F) with an accuracy of ±0.1 °C (±0.2 °F).

7.0 Reagents and Standards

7.1 Analysis. The following items are required for analysis.

7.1.1 Hydrogen (H_2). Zero grade hydrogen, as required by the FID.

7.1.2 Carrier Gas. Zero grade nitrogen, containing less than 1 ppm carbon (C) and less than 1 ppm carbon dioxide.

7.1.3 Combustion Gas. Zero grade air or oxygen as required by the FID.

7.2 Calibration and Linearity Check.

7.2.1 Stock Cylinder Gas Standard. 100 percent propane. The manufacturer shall: (a) Certify the gas composition to be accurate to ±3 percent or better (see section 7.2.1.1); (b) recommend a maximum shelf life over which the gas concentration does not change by greater than ±5 percent from the certified value; and (c) affix the date of gas cylinder preparation, certified propane concentration, and recommended maximum shelf life to the cylinder before shipment to the buyer.

7.2.1.1 Cylinder Standards Certification. The manufacturer shall certify the concentration of the calibration gas in the cylinder by (a) directly analyzing the cylinder and (b) calibrating his analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use, as a minimum, a three-point calibration curve.

7.2.1.2 Verification of Manufacturer's Calibration Standards. Before using, the manufacturer shall verify each calibration standard by (a) comparing it to gas mixtures prepared in accordance with the procedure described in section 7.1 of Method 106 of Part 61, Appendix B, or by (b) calibrating it against Standard Reference Materials (SRM's) prepared by the National Bureau of Standards, if such SRM's are available. The agreement between the initially determined concentration value and the verification concentration value must be within ±5 percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

8.0 Sampling Collection, Preservation, Storage, and Transport

8.1 Install a sampling tap to obtain a sample at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to

the atmosphere). Assemble the sampling apparatus as shown in Figure 25E–1.

8.2 Begin sampling by purging the sample lines and cooling coil with at least four volumes of waste. Collect the purged material in a separate container and dispose of it properly.

8.3 After purging, stop the sample flow and transfer the Teflon sampling tube to a sample container. Sample at a flow rate such that the temperature of the waste is <10 °C (<50 °F). Fill the sample container halfway (±5 percent) and cap it within 5 seconds. Store immediately in a cooler and cover with ice.

8.4 Alternative sampling techniques may be used upon the approval of the Administrator.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
10.2, 10.3	FID calibration and response check	Ensure precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Use the procedures in sections 10.2 to calibrate the headspace analyzer and FID and check for linearity before the system is first placed in operation, after any shutdown longer than 6 months, and after any modification of the system.

10.2 Calibration and Linearity. Use the procedures in section 10 of Method 18 of Part 60, Appendix A, to prepare the standards and calibrate the flowmeters, using propane as the standard gas. Fill the calibration standard vials halfway (±5 percent) with deionized water. Purge and fill the airspace with calibration standard. Prepare a minimum of three concentrations of calibration standards in triplicate at concentrations that will bracket the applicable cutoff. For a cutoff of 5.2 kPa (0.75 psi), prepare nominal concentrations of 30,000, 50,000, and 70,000 ppm as propane. For a cutoff of 27.6 kPa (4.0 psi), prepare nominal concentrations of 200,000, 300,000, and 400,000 ppm as propane.

10.2.1 Use the procedures in section 11.3 to measure the FID response of each standard. Use a linear regression analysis to calculate the values for the slope (k) and the y-intercept (b). Use the procedures in sections 12.3 and 12.2 to test the calibration and the linearity.

10.3 Daily FID Calibration Check. Check the calibration at the beginning and at the end of the daily runs by using the following procedures. Prepare 2 calibration standards at the nominal cutoff concentration using the procedures in section 10.2. Place one at the beginning and one at the end of the daily run. Measure the FID response of the daily calibration standard and use the values for k and b from the most recent calibration to calculate the concentration of the daily standard. Use an equation similar to 25E–2 to calculate the percent difference between the daily standard and C_s. If the difference is within 5 percent, then the previous values for k and b can be used. Otherwise, use the procedures in section 10.2 to recalibrate the FID.

11.0 Analytical Procedures

11.1 Allow one hour for the headspace vials to equilibrate at the temperature specified in the regulation. Allow the FID to warm up until a stable baseline is achieved on the detector.

11.2 Check the calibration of the FID daily using the procedures in section 10.3.

11.3 Follow the manufacturer's recommended procedures for the normal operation of the headspace sampler and FID.

11.4 Use the procedures in sections 12.4 and 12.5 to calculate the vapor phase organic vapor pressure in the samples.

11.5 Monitor the output of the detector to make certain that the results are being properly recorded.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

A = Measurement of the area under the response curve, counts.
b = y-intercept of the linear regression line.
C_a = Measured vapor phase organic concentration of sample, ppm as propane.
C_{ma} = Average measured vapor phase organic concentration of standard, ppm as propane.
C_m = Measured vapor phase organic concentration of standard, ppm as propane.
C_s = Calculated standard concentration, ppm as propane.
k = Slope of the linear regression line.
P_{bar} = Atmospheric pressure at analysis conditions, mm Hg (in. Hg).
P* = Organic vapor pressure in the sample, kPa (psi).
PD = Percent difference between the average measured vapor phase organic concentration (C_m) and the calculated standard concentration (C_s).
RSD = Relative standard deviation.
$\beta = 1.333 \times 10^{-7}$ kPa/[(mm Hg)(ppm)], $(4.91 \times 10^{-7}$ psi/[(in. Hg)(ppm)])

12.2 Linearity. Use the following equation to calculate the measured standard concentration for each standard vial.

$$C_m = kA + b \qquad \text{Eq. 25E-1}$$

12.2.1 Calculate the average measured standard concentration (C_{ma}) for each set of triplicate standards and use the following equation to calculate PD between C_{ma} and C_s. The instrument linearity is acceptable if the PD is within five for each standard.

$$PD = \frac{C_s - C_{ma}}{C_s} \times 100 \qquad \text{Eq. 25E-2}$$

12.3. Relative Standard Deviation (RSD). Use the following equation to calculate the RSD for each triplicate set of standards.

$$RSD = \frac{100}{C_{ma}} \sqrt{\frac{\sum (C_m - C_{ma})^2}{2}} \qquad \text{Eq. 25E-3}$$

The calibration is acceptable if the RSD is within five for each standard concentration.

12.4 Concentration of organics in the headspace. Use the following equation to calculate the concentration of vapor phase organics in each sample.

$$C_a = kA + b \qquad \text{Eq. 25E-4}$$

12.5 Vapor Pressure of Organics in the Headspace Sample. Use the following equation to calculate the vapor pressure of organics in the sample.

$$P^* = \beta P_{bar} C_a \qquad \text{Eq. 25E-5}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, Albert E., Samuel Witz, and Robert D. MacPhee. ''Determination of Solvent Vapor Concentrations by Total Combustion Analysis: a Comparison of Infared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, Massachusetts.

2. Salo, Albert E., William L. Oaks, and Robert D. MacPhee. ''Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, Colorado. June 9–13, 1974.) p. 25.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

12.2 Linearity. Use the following equation to calculate the measured standard concentration for each standard vial.

$$C_m = kA + b \qquad \text{Eq. 25E-1}$$

12.2.1 Calculate the average measured standard concentration (C_{ma}) for each set of triplicate standards and use the following equation to calculate PD between C_{ma} and C_s. The instrument linearity is acceptable if the PD is within five for each standard.

$$PD = \frac{C_s - C_{ma}}{C_s} \times 100 \qquad \text{Eq. 25E-2}$$

12.3. Relative Standard Deviation (RSD). Use the following equation to calculate the RSD for each triplicate set of standards.

$$RSD = \frac{100}{C_{ma}} \sqrt{\frac{\sum (C_m - C_{ma})^2}{2}} \qquad \text{Eq. 25E-3}$$

The calibration is acceptable if the RSD is within five for each standard concentration.

12.4 Concentration of organics in the headspace. Use the following equation to calculate the concentration of vapor phase organics in each sample.

$$C_a = kA + b \qquad \text{Eq. 25E-4}$$

12.5 Vapor Pressure of Organics in the Headspace Sample. Use the following equation to calculate the vapor pressure of organics in the sample.

$$P^* = \beta P_{bar} C_a \qquad \text{Eq. 25E-5}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, Albert E., Samuel Witz, and Robert D. MacPhee. ''Determination of Solvent Vapor Concentrations by Total Combustion Analysis: a Comparison of Infared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, Massachusetts.

2. Salo, Albert E., William L. Oaks, and Robert D. MacPhee. ''Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, Colorado. June 9–13, 1974.) p. 25.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

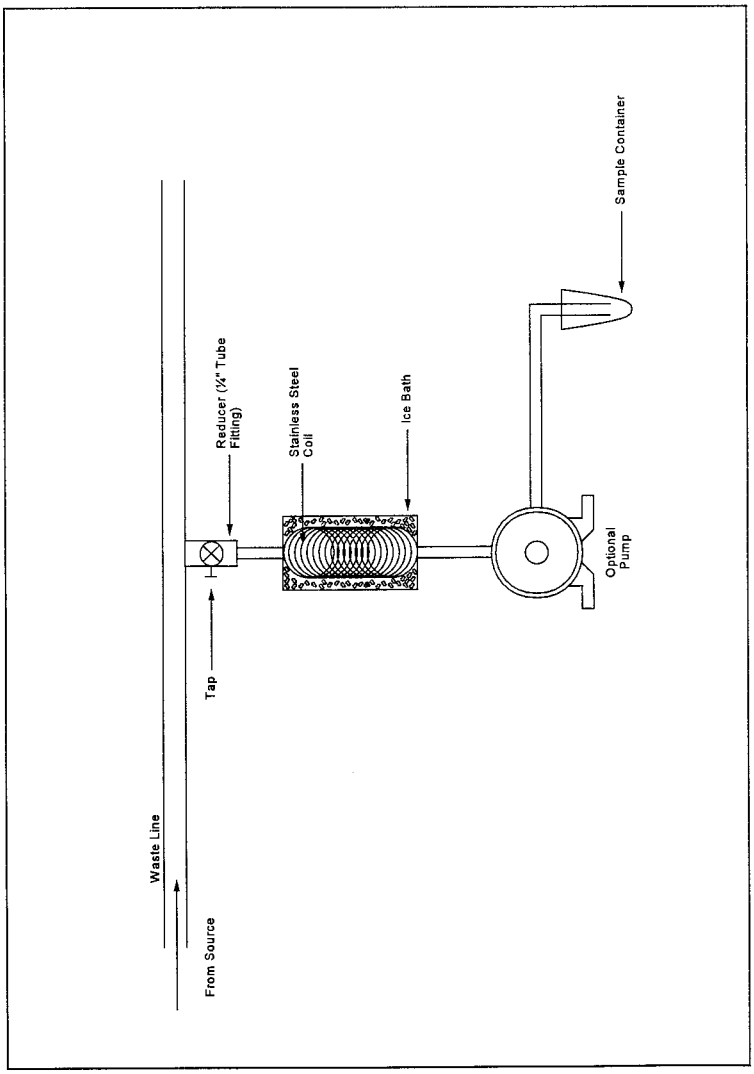


Figure 25E-1. Schematic of Sampling Apparatus

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–7 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

APPENDIX A–8 TO PART 60—TEST METHODS 26 THROUGH 30B

Method 26—Determination of Hydrogen Chloride Emissions From Stationary Sources

Method 26A—Determination of hydrogen halide and halogen emissions from stationary sources—isokinetic method

Method 27—Determination of vapor tightness of gasoline delivery tank using pressure-vacuum test
Method 28—Certification and auditing of wood heaters
Method 28A—Measurement of air to fuel ratio and minimum achievable burn rates for wood-fired appliances
Method 29—Determination of metals emissions from stationary sources

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

Method 26—Determination of Hydrogen Halide and Halogen Emissions From Stationary Sources Non-Isokinetic Method

1.0 Scope and Application

1.1 Analytes.

Analytes	CAS No.
Hydrogen Chloride (HCl)	7647–01–0
Hydrogen Bromide (HBr)	10035–10–6
Hydrogen Fluoride (HF)	7664–39–3
Chlorine (Cl_2)	7882–50–5
Bromine (Br_2)	7726–95–6

1.2 Applicability. This method is applicable for determining emissions of hydrogen halides (HX) (HCl, HBr, and HF) and halogens (X_2) (Cl_2 and Br_2) from stationary sources when specified by the applicable subpart. Sources, such as those controlled by wet scrubbers, that emit acid particulate matter must be sampled using Method 26A.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 An integrated sample is extracted from the source and passed through a prepurged heated probe and filter into dilute sulfuric acid and dilute sodium hydroxide solutions which collect the gaseous hydrogen halides and halogens, respectively. The filter collects particulate matter including halide salts but is not routinely recovered and analyzed. The hydrogen halides are solubilized in the acidic solution and form chloride (Cl^-), bromide (Br^-), and fluoride (F^-) ions. The halogens have a very low solubility in the acidic solution and pass through to the alkaline solution where they are hydrolyzed to form a proton (H^+), the halide ion, and the hypohalous acid (HClO or HBrO). Sodium thiosulfate is added in excess to the alkaline solution to assure reaction with the hypohalous acid to form a second halide ion such that 2 halide ions are formed for each molecule of halogen gas. The halide ions in the separate solutions are measured by ion chromatography (IC).

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Volatile materials, such as chlorine dioxide (ClO_2) and ammonium chloride (NH_4Cl), which produce halide ions upon dissolution during sampling are potential interferents. Interferents for the halide measurements are the halogen gases which disproportionate to a hydrogen halide and a hydrohalous acid upon dissolution in water. However, the use of acidic rather than neutral or basic solutions for collection of the hydrogen halides greatly reduces the dissolution of any halogens passing through this solution.

4.2 The simultaneous presence of HBr and CL_2 may cause a positive bias in the HCL result with a corresponding negative bias in the Cl_2 result as well as affecting the HBr/Br_2 split.

4.3 High concentrations of nitrogen oxides (NO_X) may produce sufficient nitrate (NO_3^- to interfere with measurements of very low Br^- levels.

4.4 A glass wool plug should *not* be used to remove particulate matter since a negative bias in the data could result.

4.5 There is anecdotal evidence that HF may be outgassed from new teflon components. If HF is a target analyte, then preconditioning of new teflon components, by heating should be considered.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations before performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.2 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1 Sampling. The sampling train is shown in Figure 26–1, and component parts are discussed below.

6.1.1 Probe. Borosilicate glass, approximately 3/8-in. (9-mm) I.D. with a heating system capable of maintaining a probe gas temperature during sampling between 120 and 134 °C (248 and 273 °F) to prevent moisture condensation; or Teflon where stack probes are below 210 °C. If HF is a target analyte, then preconditioning of new teflon components by heating should be considered to prevent potential HF outgassing. A Teflon-glass filter in a mat configuration should be installed to remove particulate matter from the gas stream.

6.1.2 Three-way Stopcock. A borosilicate-glass three-way stopcock with a heating system to prevent moisture condensation. The heated stopcock should connect to the outlet of the heated filter and the inlet of the first impinger. The heating system should be capable of preventing condensation up to the inlet of the first impinger. Silicone grease may be used, if necessary, to prevent leakage.

6.1.3 Impingers. Four 30-ml midget impingers with leak-free glass connectors. Silicone grease may be used, if necessary, to prevent leakage. For sampling at high moisture sources or for sampling times greater than one hour, a midget impinger with a shortened stem (such that the gas sample does not bubble through the collected condensate) should be used in front of the first impinger.

6.1.4 Drying Tube or Impinger. Tube or impinger, of Mae West design, filled with 6- to 16-mesh indicating type silica gel, or equivalent, to dry the gas sample and to protect the dry gas meter and pump. If the silica gel has been used previously, dry at 175 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used.

6.1.5 Heating System. Any heating system capable of maintaining a temperature around the probe and filter holder between 120 and 134 °C (248 and 273 °F) during sampling, or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application.

6.1.6 Filter Holder and Support. The filter holder shall be made of Teflon or quartz. The filter support shall be made of Teflon. All Teflon filter holders and supports are available from Savillex Corp., 5325 Hwy 101, Minnetonka, MN 55345.

6.1.7 Sample Line. Leak-free, with compatible fittings to connect the last impinger to the needle valve.

6.1.8 Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of the selected flow rate of 2 liters/min (0.07 ft^3/min).

6.1.9 Purge Pump, Purge Line, Drying Tube, Needle Valve, and Rate Meter. Pump capable of purging the sampling probe at 2 liters/min, with drying tube, filled with silica gel or equivalent, to protect pump, and a rate meter capable of measuring 0 to 5 liters/min (0.2 ft^3/min).

6.1.10 Stopcock Grease, Valve, Pump, Volume Meter, Barometer, and Vacuum Gauge. Same as in Method 6, sections 6.1.1.4, 6.1.1.7, 6.1.1.8, 6.1.1.10, 6.1.2, and 6.1.3.

6.1.11 Temperature Measuring Devices. Temperature sensors to monitor the temperature of the probe and to monitor the temperature of the sampling system from the outlet of the probe to the inlet of the first impinger.

6.1.12 Ice Water Bath. To minimize loss of absorbing solution.

6.2 Sample Recovery.

6.2.1 Wash Bottles. Polyethylene or glass, 500-ml or larger, two.

6.2.2 Storage Bottles. 100- or 250-ml, high-density polyethylene bottles with Teflon screw cap liners to store impinger samples.

6.3 Sample Preparation and Analysis. The materials required for volumetric dilution and chromatographic analysis of samples are described below.

6.3.1 Volumetric Flasks. Class A, 100-ml size.

6.3.2 Volumetric Pipets. Class A, assortment. To dilute samples to the calibration range of the ion chromatograph.

6.3.3 Ion Chromatograph (IC). Suppressed or non-suppressed, with a conductivity detector and electronic integrator operating in the peak area mode. Other detectors, strip chart recorders, and peak height measurements may be used.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society (ACS reagent grade). When such specifications are not available, the best available grade shall be used.

7.1 Sampling.

7.1.1 Filter. A 25-mm (1 in) (or other size) Teflon glass mat, Pallflex TX40HI75 (Pallflex Inc., 125 Kennedy Drive, Putnam, CT 06260). This filter is in a mat configuration to prevent fine particulate matter from entering the sampling train. Its composition is 75% Teflon/25% borosilicate glass. Other filters may be used, but they must be in a mat (as opposed to a laminate) configuration and contain at least 75% Teflon. For practical rather than scientific reasons, when the stack gas temperature exceeds 210 °C (410 °F) and the HCl concentration is greater than 20 ppm, a quartz-fiber filter may be used since Teflon becomes unstable above this temperature.

7.1.2 Water. Deionized, distilled water that conforms to American Society of Testing and Materials (ASTM) Specification D 1193–77 or 91, Type 3 (incorporated by reference—see §60.17).

7.1.3 Acidic Absorbing Solution, 0.1 N Sulfuric Acid (H_2SO_4). To prepare 100 ml of the absorbing solution for the front impinger pair, slowly add 0.28 ml of concentrated H_2SO_4 to about 90 ml of water while stirring, and adjust the final volume to 100 ml using additional water. Shake well to mix the solution.

7.1.4 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 180 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants may be used, subject to the approval of the Administrator.

7.1.5 Alkaline Adsorbing Solution, 0.1 N Sodium Hydroxide (NaOH). To prepare 100 ml of the scrubber solution for the third and fourth impinger, dissolve 0.40 g of solid NaOH in about 90 ml of water, and adjust the final

solution volume to 100 ml using additional water. Shake well to mix the solution.

7.1.6 Sodium Thiosulfate ($Na_2S_2O_3$ 5 H_2O)

7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in section 7.1.2.

7.2.2 Absorbing Solution Blanks. A separate blank solution of each absorbing reagent should be prepared for analysis with the field samples. Dilute 30 ml of each absorbing solution to approximately the same final volume as the field samples using the blank sample of rinse water.

7.2.3 Halide Salt Stock Standard Solutions. Prepare concentrated stock solutions from reagent grade sodium chloride (NaCl), sodium bromide (NaBr), and sodium fluoride (NaF). Each must be dried at 110 °C (230 °F) for two or more hours and then cooled to room temperature in a desiccator immediately before weighing. Accurately weigh 1.6 to 1.7 g of the dried NaCl to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact Cl^- concentration using Equation 26–1 in section 12.2. In a similar manner, accurately weigh and solubilize 1.2 to 1.3 g of dried NaBr and 2.2 to 2.3 g of NaF to make 1-liter solutions. Use Equations 26–2 and 26–3 in section 12.2, to calculate the Br^- and F^- concentrations. Alternately, solutions containing a nominal certified concentration of 1000 mg/l NaCl are commercially available as convenient stock solutions from which standards can be made by appropriate volumetric dilution. Refrigerate the stock standard solutions and store no longer than one month.

7.2.4 Chromatographic Eluent. Effective eluents for nonsuppressed IC using a resin-or silica-based weak ion exchange column are a 4 mM potassium hydrogen phthalate solution, adjusted to pH 4.0 using a saturated sodium borate solution, and a 4 mM 4-hydroxy benzoate solution, adjusted to pH 8.6 using 1 N NaOH. An effective eluent for suppressed ion chromatography is a solution containing 3 mM sodium bicarbonate and 2.4 mM sodium carbonate. Other dilute solutions buffered to a similar pH and containing no interfering ions may be used. When using suppressed ion chromatography, if the ''water dip'' resulting from sample injection interferes with the chloride peak, use a 2 mM NaOH/2.4 mM sodium bicarbonate eluent.

8.0 Sample Collection, Preservation, Storage, and Transport

NOTE: Because of the complexity of this method, testers and analyst should be trained and experienced with the procedure to ensure reliable results.

8.1 Sampling.

8.1.1 Preparation of Collection Train. Prepare the sampling train as follows: Pour 15 ml of the acidic absorbing solution into each one of the first pair of impingers, and 15 ml of the alkaline absorbing solution into each one of the second pair of impingers. Connect the impingers in series with the knockout impinger first, if used, followed by the two impingers containing the acidic absorbing solution and the two impingers containing the alkaline absorbing solution. Place a fresh charge of silica gel, or equivalent, in the drying tube or impinger at the end of the impinger train.

8.1.2 Adjust the probe temperature and the temperature of the filter and the stopcock (*i.e.*, the heated area in Figure 26–1) to a temperature sufficient to prevent water condensation. This temperature must be maintained between 120 and 134 °C (248 and 273 °F). The temperature should be monitored throughout a sampling run to ensure that the desired temperature is maintained. It is important to maintain a temperature around the probe and filter in this range since it is extremely difficult to purge acid gases off these components. (These components are not quantitatively recovered and, hence, any collection of acid gases on these components would result in potential undereporting of these emissions. The applicable subparts may specify alternative higher temperatures.)

8.1.3 Leak-Check Procedure.

8.1.3.1 Sampling Train. A leak-check prior to the sampling run is optional; however, a leak-check after the sampling run is mandatory. The leak-check procedure is as follows: Temporarily attach a suitable [*e.g.*, 0–40 cc/min (0–2.4 in^3/min)] rotameter to the outlet of the dry gas meter and place a vacuum gauge at or near the probe inlet. Plug the probe inlet, pull a vacuum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter. A leakage rate not in excess of 2 percent of the average sampling rate is acceptable.

NOTE: Carefully release the probe inlet plug before turning off the pump.

8.1.3.2 Pump. It is suggested (not mandatory) that the pump be leak-checked separately, either prior to or after the sampling run. If done prior to the sampling run, the pump leak-check shall precede the leak-check of the sampling train described immediately above; if done after the sampling run, the pump leak-check shall follow the train leak-check. To leak-check the pump, proceed as follows: Disconnect the drying tube from the probe-impinger assembly. Place a vacuum gauge at the inlet to either the drying tube or pump, pull a vacuum of 250 mm (10 in) Hg, plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum should remain stable for at least 30 sec. Other leak-check procedures may be used, subject to the approval of the Administrator, U.S. Environmental Protection Agency.

8.1.4 Purge Procedure. Immediately before sampling, connect the purge line to the stopcock, and turn the stopcock to permit the purge pump to purge the probe (see Figure 1A of Figure 26–1). Turn on the purge pump, and adjust the purge rate to 2 liters/min (0.07 ft^3/min). Purge for at least 5 minutes before sampling.

8.1.5 Sample Collection. Turn on the sampling pump, pull a slight vacuum of approximately 25 mm Hg (1 in Hg) on the impinger train, and turn the stopcock to permit stack gas to be pulled through the impinger train (see Figure 1C of Figure 26–1). Adjust the sampling rate to 2 liters/min, as indicated by the rate meter, and maintain this rate to within 10 percent during the entire sampling run. Take readings of the dry gas meter volume and temperature, rate meter, and vacuum gauge at least once every five minutes during the run. A sampling time of one hour is recommended. Shorter sampling times may introduce a significant negative bias in the HCl concentration. At the conclusion of the sampling run, remove the train from the stack, cool, and perform a leak-check as described in section 8.1.3.1.

8.2 Sample Recovery.

8.2.1 Disconnect the impingers after sampling. Quantitatively transfer the contents of the acid impingers and the knockout impinger, if used, to a leak-free storage bottle. Add the water rinses of each of these impingers and connecting glassware to the storage bottle.

8.2.2 Repeat this procedure for the alkaline impingers and connecting glassware using a separate storage bottle. Add 25 mg of sodium thiosulfate per the product of ppm of halogen anticipated to be in the stack gas times the volume (dscm) of stack gas sampled (0.7 mg per ppm-dscf).

NOTE: This amount of sodium thiosulfate includes a safety factor of approximately 5 to assure complete reaction with the hypohalous acid to form a second Cl^- ion in the alkaline solution.

8.2.3 Save portions of the absorbing reagents (0.1 N H_2SO_4 and 0.1 N NaOH) equivalent to the amount used in the sampling train (these are the absorbing solution blanks described in section 7.2.2); dilute to the approximate volume of the corresponding samples using rinse water directly from the wash bottle being used. Add the same amount of sodium thiosulfate solution to the 0.1 N NaOH absorbing solution blank. Also, save a portion of the rinse water used to rinse the sampling train. Place each in a separate, prelabeled storage bottle. The sample storage bottles should be sealed, shaken to mix, and labeled. Mark the fluid level.

8.3 Sample Preparation for Analysis. Note the liquid levels in the storage bottles and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Quantitatively transfer the sample solutions to 100-ml volumetric flasks, and dilute to 100 ml with water.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Volume Metering System, Temperature Sensors, Rate Meter, and Barometer. Same as in Method 6, sections 10.1, 10.2, 10.3, and 10.4.

10.2 Ion Chromatograph.

10.2.1 To prepare the calibration standards, dilute given amounts (1.0 ml or greater) of the stock standard solutions to convenient volumes, using 0.1 N H_2SO_4 or 0.1 N NaOH, as appropriate. Prepare at least four calibration standards for each absorbing reagent containing the appropriate stock solutions such that they are within the linear range of the field samples.

10.2.2 Using one of the standards in each series, ensure adequate baseline separation for the peaks of interest.

10.2.3 Inject the appropriate series of calibration standards, starting with the lowest concentration standard first both before and after injection of the quality control check sample, reagent blanks, and field samples. This allows compensation for any instrument drift occurring during sample analysis. The values from duplicate injections of these calibration samples should agree within 5 percent of their mean for the analysis to be valid.

10.2.4 Determine the peak areas, or heights, for the standards and plot individual values versus halide ion concentrations in µg/ml.

10.2.5 Draw a smooth curve through the points. Use linear regression to calculate a formula describing the resulting linear curve.

11.0 Analytical Procedures

11.1 Sample Analysis.

11.1.1 The IC conditions will depend upon analytical column type and whether suppressed or non-suppressed IC is used. An example chromatogram from a non-suppressed system using a 150-mm Hamilton PRP-X100 anion column, a 2 ml/min flow rate of a 4 mM 4-hydroxy benzoate solution adjusted to a pH of 8.6 using 1 N NaOH, a 50 µl sample loop, and a conductivity detector set on 1.0 µS full scale is shown in Figure 26–2.

11.1.2 Before sample analysis, establish a stable baseline. Next, inject a sample of water, and determine if any Cl^-, Br^-, or F^- appears in the chromatogram. If any of these ions are present, repeat the load/injection

procedure until they are no longer present. Analysis of the acid and alkaline absorbing solution samples requires separate standard calibration curves; prepare each according to section 10.2. Ensure adequate baseline separation of the analyses.

11.1.3 Between injections of the appropriate series of calibration standards, inject in duplicate the reagent blanks, quality control sample, and the field samples. Measure the areas or heights of the Cl^-, Br^-, and F^- peaks. Use the mean response of the duplicate injections to determine the concentrations of the field samples and reagent blanks using the linear calibration curve. The values from duplicate injections should agree within 5 percent of their mean for the analysis to be valid. If the values of duplicate injections are not within 5 percent of the mean, the duplicate injections shall be repeated and all four values used to determine the average response. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

12.0 Data Analysis and Calculations

NOTE: Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

12.1 Nomenclature.

B_X^- = Mass concentration of applicable absorbing solution blank, µg halide ion (Cl^-, Br^-, F^-) /ml, not to exceed 1 µg/ml which is 10 times the published analytical detection limit of 0.1 µg/ml.

C = Concentration of hydrogen halide (HX) or halogen (X_2), dry basis, mg/dscm.

K = 10^{-3} mg/µg.

K_{HCl} = 1.028 (µg HCl/µg-mole)/(µg Cl^-/µg-mole).

K_{HBr} = 1.013 (µg HBr/µg-mole)/(µg Br^-/µg-mole).

K_{HF} = 1.053 (µg HF/µg-mole)/(µg F^-/µg-mole).

m_{HX} = Mass of HCl, HBr, or HF in sample, µg.

m_{X2} = Mass of Cl_2 or Br_2 in sample, µg.

S_X^- = Analysis of sample, µg halide ion (Cl^-, Br^-, F^-)/ml.

$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm.

V_s = Volume of filtered and diluted sample, ml.

12.2 Calculate the exact Cl^-, Br^-, and F^- concentration in the halide salt stock standard solutions using the following equations.

$$\mu g\ Cl^-/ml = g\ of\ NaCl \times 10^3 \times 35.453/58.44 \qquad \text{Eq. 26-1}$$

$$\mu g\ Br^-/ml = g\ of\ NaBr \times 10^3 \times 79.904/102.90 \qquad \text{Eq. 26-2}$$

$$\mu g\ F^-/ml = g\ of\ NaF \times 10^3 \times 18.998/41.99 \qquad \text{Eq. 26-3}$$

12.3 Sample Volume, Dry Basis, Corrected to Standard Conditions. Calculate the sample volume using Eq. 6–1 of Method 6.

12.4 Total µg HCl, HBr, or HF Per Sample.

$$m_{HX} = K_{HC1,Hbr,HF} V_s \left(S_x^- - B_x^-\right) \qquad \text{Eq. 26-4}$$

12.5 Total µg Cl_2 or Br_2 Per Sample.

$$M_{x2} = V_s \left(S_X^- - B_X^-\right) \qquad \text{Eq. 26-5}$$

12.6 Concentration of Hydrogen Halide or Halogen in Flue Gas.

$$C = K m_{XH,X2} / V_{m(std)} \qquad \text{Eq. 26-6}$$

13.0 Method Performance

13.1 Precision and Bias. The within-laboratory relative standard deviations are 6.2 and 3.2 percent at HCl concentrations of 3.9 and 15.3 ppm, respectively. The method does not

exhibit a bias to Cl_2 when sampling at concentrations less than 50 ppm.

13.2 Sample Stability. The collected Cl^- samples can be stored for up to 4 weeks.

13.3 Detection Limit. A typical IC instrumental detection limit for Cl^- is 0.2 µg/ml. Detection limits for the other analyses should be similar. Assuming 50 ml liquid recovered from both the acidified impingers, and the basic impingers, and 0.12 dscm (4.24 dscf) of stack gas sampled, then the analytical detection limit in the stack gas would be about 0.05 ppm for HCl and Cl_2, respectively.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

Method 26A. Method 26A, which uses isokinetic sampling equipment, is an acceptable alternative to Method 26.

17.0 References

1. Steinsberger, S. C. and J. H. Margeson, ''Laboratory and Field Evaluation of a Methodology for Determination of Hydrogen Chloride Emissions from Municipal and Hazardous Waste Incinerators,'' U.S. Environmental Protection Agency, Office of Research and Development, Report No. 600/3–89/064, April 1989. Available from the National Technical Information Service, Springfield, VA 22161 as PB89220586/AS.

2. State of California, Air Resources Board, Method 421, ''Determination of Hydrochloric Acid Emissions from Stationary Sources,'' March 18, 1987.

3. Cheney, J.L. and C.R. Fortune. Improvements in the Methodology for Measuring Hydrochloric Acid in Combustion Source Emissions. J. Environ. Sci. Health. *A19*(3): 337–350. 1984.

4. Stern, D. A., B. M. Myatt, J. F. Lachowski, and K. T. McGregor. Speciation of Halogen and Hydrogen Halide Compounds in Gaseous Emissions. In: Incineration and Treatment of Hazardous Waste: Proceedings of the 9th Annual Research Symposium, Cincinnati, Ohio, May 2–4, 1983. Publication No. 600/9–84–015. July 1984. Available from National Technical Information Service, Springfield, VA 22161 as PB84–234525.

5. Holm, R. D. and S. A. Barksdale. Analysis of Anions in Combustion Products. In: Ion Chromatographic Analysis of Environmental Pollutants. E. Sawicki, J. D. Mulik, and E. Wittgenstein (eds.). Ann Arbor, Michigan, Ann Arbor Science Publishers. 1978. pp. 99–110.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

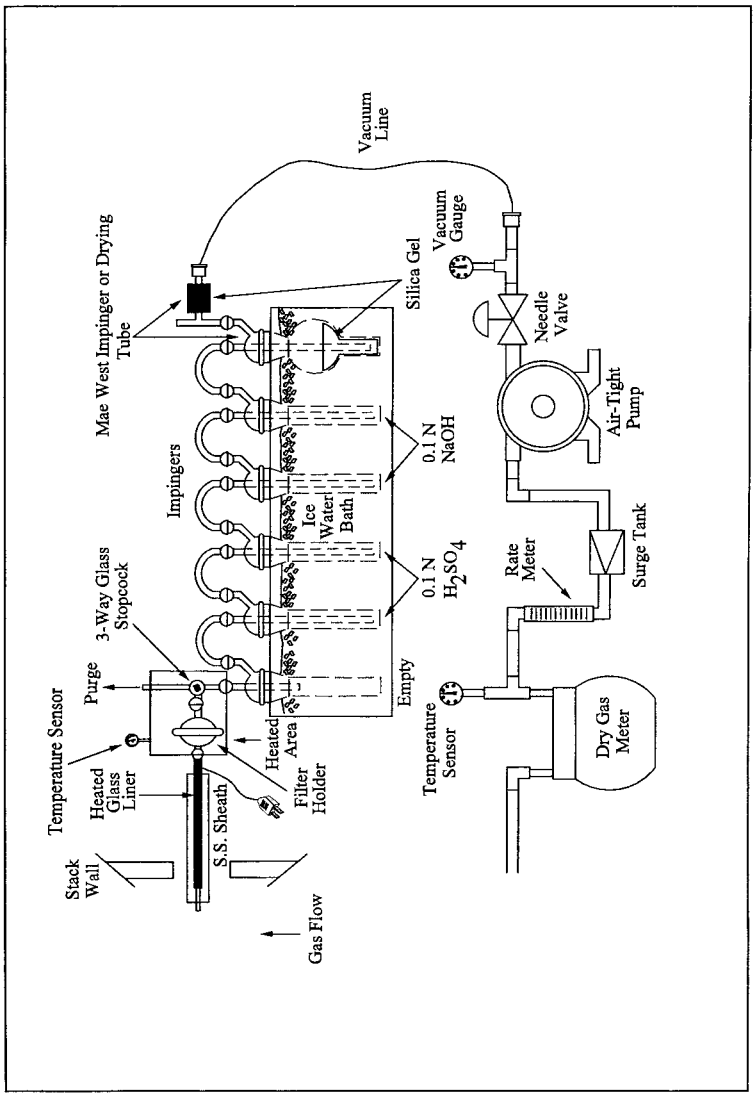


Figure 26-1. Sampling Train.

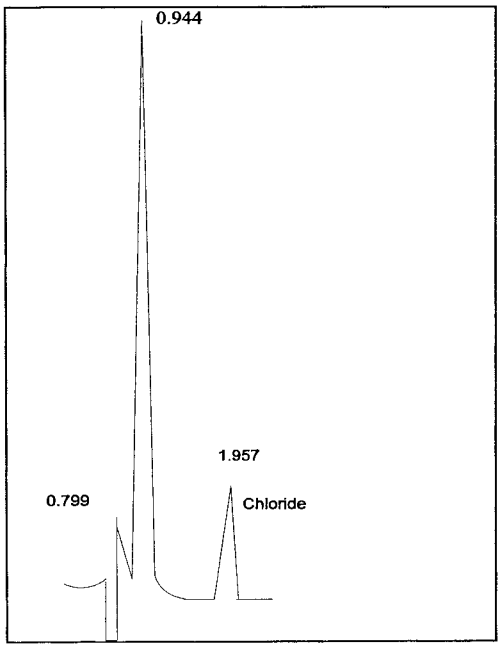


Figure 26-2. Example Chromatogram.

METHOD 26A—DETERMINATION OF HYDROGEN HALIDE AND HALOGEN EMISSIONS FROM STATIONARY SOURCES ISOKINETIC METHOD

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 2, Method 5, and Method 26.

1.0 Scope and Application

1.1 Analytes.

Analytes	CAS No.
Hydrogen Chloride (HCl)	7647–01–0
Hydrogen Bromide (HBr)	10035–10–6
Hydrogen Fluoride (HF)	7664–39–3
Chlorine (Cl_2)	7882–50–5
Bromine (Br_2)	7726–95–6

1.2 This method is applicable for determining emissions of hydrogen halides (HX) [HCl, HBr, and HF] and halogens (X_2) [Cl_2 and Br_2] from stationary sources when specified by the applicable subpart. This method collects the emission sample isokinetically and is therefore particularly suited for sampling at sources, such as those controlled by wet scrubbers, emitting acid particulate matter (*e.g.*, hydrogen halides dissolved in water droplets).

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Principle. Gaseous and particulate pollutants are withdrawn isokinetically from the source and collected in an optional cyclone, on a filter, and in absorbing solutions. The cyclone collects any liquid droplets and is not necessary if the source emissions do not contain them; however, it is preferable to include the cyclone in the sampling train to protect the filter from any liquid present. The filter collects particulate matter including halide salts but is not routinely recovered or analyzed. Acidic and alkaline absorbing solutions collect the gaseous hydrogen halides and halogens, respectively. Following sampling of emissions containing liquid droplets, any halides/halogens dissolved in the liquid in the cyclone and on the filter are vaporized to gas and collected in the impingers by pulling conditioned ambient air through the sampling train. The hydrogen halides are solubilized in the acidic solution and form chloride (Cl^-), bromide (Br^-),

and fluoride (F^-) ions. The halogens have a very low solubility in the acidic solution and pass through to the alkaline solution where they are hydrolyzed to form a proton (H^+), the halide ion, and the hypohalous acid (HClO or HBrO). Sodium thiosulfate is added to the alkaline solution to assure reaction with the hypohalous acid to form a second halide ion such that 2 halide ions are formed for each molecule of halogen gas. The halide ions in the separate solutions are measured by ion chromatography (IC). If desired, the particulate matter recovered from the filter and the probe is analyzed following the procedures in Method 5.

NOTE: If the tester intends to use this sampling arrangement to sample concurrently for particulate matter, the alternative Teflon probe liner, cyclone, and filter holder should not be used. The Teflon filter support must be used. The tester must also meet the probe and filter temperature requirements of both sampling trains.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Volatile materials, such as chlorine dioxide (ClO_2) and ammonium chloride (NH_4Cl), which produce halide ions upon dissolution during sampling are potential interferents. Interferents for the halide measurements are the halogen gases which disproportionate to a hydrogen halide and a hypohalous acid upon dissolution in water. The use of acidic rather than neutral or basic solutions for collection of the hydrogen halides greatly reduces the dissolution of any halogens passing through this solution.

4.2 The simultaneous presence of both HBr and Cl_2 may cause a positive bias in the HCl result with a corresponding negative bias in the Cl_2 result as well as affecting the HBr/Br_2 split.

4.3 High concentrations of nitrogen oxides (NO_X) may produce sufficient nitrate (NO_3^-) to interfere with measurements of very low Br^- levels. Dissociating chloride salts (*e.g.*, ammonium chloride) at elevated temperatures interfere with halogen acid measurement in this method. Maintaining particulate probe/filter temperatures between 120 °C and 134 °C (248 °F and 273 °F) minimizes this interference.

4.4 There is anecdotal evidence that HF may be outgassed from new Teflon components. If HF is a target analyte then preconditioning of new Teflon components, by heating, should be considered.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations before performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.2 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0. Equipment and Supplies

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1 Sampling. The sampling train is shown in Figure 26A–1; the apparatus is similar to the Method 5 train where noted as follows:

6.1.1 Probe Nozzle. Borosilicate or quartz glass; constructed and calibrated according to Method 5, sections 6.1.1.1 and 10.1, and coupled to the probe liner using a Teflon union; a stainless steel nut is recommended for this union. When the stack temperature exceeds 210 °C (410 °F), a one-piece glass nozzle/liner assembly must be used.

6.1.2 Probe Liner. Same as Method 5, section 6.1.1.2, except metal liners shall not be used. Water-cooling of the stainless steel sheath is recommended at temperatures exceeding 500 °C (932 °F). Teflon may be used in limited applications where the minimum stack temperature exceeds 120 °C (250 °F) but never exceeds the temperature where Teflon is estimated to become unstable [approximately 210 °C (410 °F)].

6.1.3 Pitot Tube, Differential Pressure Gauge, Filter Heating System, Metering System, Barometer, Gas Density Determination Equipment. Same as Method 5, sections 6.1.1.3, 6.1.1.4, 6.1.1.6, 6.1.1.9, 6.1.2, and 6.1.3.

6.1.4 Cyclone (Optional). Glass or Teflon. Use of the cyclone is required only when the sample gas stream is saturated with moisture; however, the cyclone is recommended to protect the filter from any liquid droplets present.

6.1.5 Filter Holder. Borosilicate or quartz glass, or Teflon filter holder, with a Teflon filter support and a sealing gasket. The sealing gasket shall be constructed of Teflon or equivalent materials. The holder design shall provide a positive seal against leakage at any point along the filter circumference. The holder shall be attached immediately to the outlet of the cyclone.

6.1.6 Impinger Train. The following system shall be used to determine the stack gas moisture content and to collect the hydrogen halides and halogens: five or six impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. The first impinger shown in Figure 26A–1 (knockout or condensate impinger) is optional and is recommended as a water knockout trap for use under high moisture conditions. If used, this impinger should be constructed as described below for the alkaline impingers, but with a shortened stem, and should contain 50 ml of 0.1 N H_2SO_4. The following two impingers (acid impingers which each contain 100 ml of 0.1 N H_2SO_4) shall be of the Greenburg-Smith design with the standard tip (Method 5, section 6.1.1.8). The next two impingers (alkaline impingers which each contain 100 ml of 0.1 N NaOH) and the last impinger (containing silica gel) shall be of the modified Greenburg-Smith design (Method 5, section 6.1.1.8). The condensate, acid, and alkaline impingers shall contain known quantities of the appropriate absorbing reagents. The last impinger shall contain a known weight of silica gel or equivalent desiccant. Teflon impingers are an acceptable alternative.

6.1.7 Heating System. Any heating system capable of maintaining a temperature around the probe and filter holder between 120 and 134 °C (248 to 273 °F) during sampling, or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application.

6.1.8 Ambient Air Conditioning Tube (Optional). Tube tightly packed with approximately 150 g of fresh 8 to 20 mesh sodium hydroxide-coated silica, or equivalent, (Ascarite II has been found suitable) to dry and remove acid gases from the ambient air used to remove moisture from the filter and cyclone, when the cyclone is used. The inlet and outlet ends of the tube should be packed with at least 1-cm thickness of glass wool or filter material suitable to prevent escape of fines. Fit one end with flexible tubing, etc. to allow connection to probe nozzle following the test run.

6.2 Sample Recovery.

6.2.1 Probe-Liner and Probe-Nozzle Brushes, Wash Bottles, Glass Sample Storage Containers, Petri Dishes, Graduated Cylinder and/or Balance, and Rubber Policeman. Same as Method 5, sections 6.2.1, 6.2.2, 6.2.3, 6.2.4, 6.2.5, and 6.2.7.

6.2.2 Plastic Storage Containers. Screw-cap polypropylene or polyethylene containers to store silica gel. High-density polyethylene bottles with Teflon screw cap liners to store impinger reagents, 1-liter.

6.2.3 Funnels. Glass or high-density polyethylene, to aid in sample recovery.

6.3 Sample Preparation and Analysis.

6.3.1 Volumetric Flasks. Class A, various sizes.

6.3.2 Volumetric Pipettes. Class A, assortment. To dilute samples to calibration range of the ion chromatograph (IC).

6.3.3 Ion Chromatograph (IC). Suppressed or nonsuppressed, with a conductivity detector and electronic integrator operating in the peak area mode. Other detectors, a strip chart recorder, and peak heights may be used.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society (ACS reagent grade). When such specifications are not available, the best available grade shall be used.

7.1 Sampling.

7.1.1 Filter. Teflon mat (*e.g.*, Pallflex TX40HI45) filter. When the stack gas temperature exceeds 210 °C (410 °F) a quartz fiber filter may be used.

7.1.2 Water. Deionized, distilled water that conforms to American Society of Testing and Materials (ASTM) Specification D 1193–77 or 91, Type 3 (incorporated by reference—see §60.17).

7.1.3 Acidic Absorbing Solution, 0.1 N Sulfuric Acid (H_2SO_4). To prepare 1 L, slowly add 2.80 ml of concentrated 17.9 M H2SO4 to about 900 ml of water while stirring, and adjust the final volume to 1 L using additional water. Shake well to mix the solution.

7.1.4 Silica Gel, Crushed Ice, and Stopcock Grease. Same as Method 5, sections 7.1.2, 7.1.4, and 7.1.5, respectively.

7.1.5 Alkaline Absorbing Solution, 0.1 N Sodium Hydroxide (NaOH). To prepare 1 L, dissolve 4.00 g of solid NaOH in about 900 ml of water and adjust the final volume to 1 L using additional water. Shake well to mix the solution.

7.1.6 Sodium Thiosulfate, ($Na_2S_2O_3$3.5 H_2O).

7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in section 7.1.2.

7.2.2 Absorbing Solution Blanks. A separate blank solution of each absorbing reagent should be prepared for analysis with the field samples. Dilute 200 ml of each absorbing solution (250 ml of the acidic absorbing solution, if a condensate impinger is used) to the same final volume as the field samples using the blank sample of rinse water. If a particulate determination is conducted, collect a blank sample of acetone.

7.2.3 Halide Salt Stock Standard Solutions. Prepare concentrated stock solutions from reagent grade sodium chloride (NaCl), sodium bromide (NaBr), and sodium fluoride (NaF). Each must be dried at 110 °C (230 °F) for two or more hours and then cooled to room temperature in a desiccator immediately before weighing. Accurately weigh 1.6 to 1.7 g of the dried NaCl to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact Cl^- concentration using Equation 26A–1 in section 12.2. In a similar manner, accurately weigh and solubilize 1.2 to 1.3 g of dried NaBr and 2.2 to 2.3 g of NaF to make 1-liter solutions. Use Equations 26A–2 and 26A–3 in section 12.2, to calculate the Br^- and F^- concentrations. Alternately, solutions containing a nominal certified concentration of 1000 mg/L NaCl are commercially available as convenient stock solutions from which standards can be made by appropriate volumetric dilution. Refrigerate the stock standard solutions and store no longer than one month.

7.2.4 Chromatographic Eluent. Same as Method 26, section 7.2.4.

7.2.5 Water. Same as section 7.1.1.

7.2.6 Acetone. Same as Method 5, section 7.2.

8.0 Sample Collection, Preservation, Storage, and Transport

NOTE: Because of the complexity of this method, testers and analysts should be trained and experienced with the procedures to ensure reliable results.

8.1 Sampling.

8.1.1 Pretest Preparation. Follow the general procedure given in Method 5, section 8.1, except the filter need only be desiccated and weighed if a particulate determination will be conducted.

8.1.2 Preliminary Determinations. Same as Method 5, section 8.2.

8.1.3 Preparation of Sampling Train. Follow the general procedure given in Method 5, section 8.1.3, except for the following variations: Add 50 ml of 0.1 N H_2SO_4 to the condensate impinger, if used. Place 100 ml of 0.1 N H_2SO_4 in each of the next two impingers. Place 100 ml of 0.1 N NaOH in each of the following two impingers. Finally, transfer approximately 200–300 g of preweighed silica gel from its container to the last impinger. Set up the train as in Figure 26A–1. When used, the optional cyclone is inserted between the probe liner and filter holder and located in the heated filter box.

8.1.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, sections 8.4.2 (Pretest Leak-Check), 8.4.3 (Leak-Checks During the Sample Run), and 8.4.4 (Post-Test Leak-Check).

8.1.5 Sampling Train Operation. Follow the general procedure given in Method 5, Section 8.5. It is important to maintain a temperature around the probe, filter (and cyclone, if used) between 120 and 134 °C (248 and 273 °F) since it is extremely difficult to purge acid gases off these components. (These components are not quantitatively recovered and hence any collection of acid gases on these components would result in potential undereporting these emissions. The applicable subparts may specify alternative higher temperatures.) For each run, record the data required on a data sheet such as the one shown in Method 5, Figure 5–3. If the condensate impinger becomes too full, it may be emptied, recharged with 50 ml of 0.1 N H2SO4, and replaced during the sample run. The condensate emptied must be saved and included in the measurement of the volume of moisture collected and included in the sample for analysis. The additional 50 ml of absorbing reagent must also be considered in calculating the moisture. Before the sampling train integrity is compromised by removing the impinger, conduct a leak-check as described in Method 5, Section 8.4.2.

8.1.6 Post-Test Moisture Removal (Optional). When the optional cyclone is included in the sampling train or when liquid is visible on the filter at the end of a sample run even in the absence of a cyclone, perform the following procedure. Upon completion of the test run, connect the ambient air conditioning tube at the probe inlet and operate the train with the filter heating system between 120 and 134 °C (248 and 273 °F) at a low flow rate (*e.g.*, ΔH = 1 in. H_2O) to vaporize any liquid and hydrogen halides in the cyclone or on the filter and pull them through the train into the impingers. After 30 minutes, turn off the flow, remove the conditioning tube, and examine the cyclone and filter for any visible liquid. If liquid is visible, repeat this step for 15 minutes and observe again. Keep repeating until the cyclone is dry.

NOTE: It is critical that this procedure is repeated until the cyclone is completely dry.

8.2 Sample Recovery. Allow the probe to cool. When the probe can be handled safely, wipe off all the external surfaces of the tip of the probe nozzle and place a cap loosely over the tip to prevent gaining or losing particulate matter. Do not cap the probe tip tightly while the sampling train is cooling down because this will create a vacuum in the filter holder, drawing water from the impingers into the holder. Before moving the sampling train to the cleanup site, remove the probe from the sample train, wipe off any silicone grease, and cap the open outlet of the impinger train, being careful not to lose any condensate that might be present. Wipe off any silicone grease and cap the filter or cyclone inlet. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger and the filter holder, disconnect it at

the filter holder and let any condensed water drain into the first impinger. Wipe off any silicone grease and cap the filter holder outlet and the impinger inlet. Ground glass stoppers, plastic caps, serum caps, Teflon tape, Parafilm, or aluminum foil may be used to close these openings. Transfer the probe and filter/impinger assembly to the cleanup area. This area should be clean and protected from the weather to minimize sample contamination or loss. Inspect the train prior to and during disassembly and note any abnormal conditions. Treat samples as follows:

8.2.1 Container No. 1 (Optional; Filter Catch for Particulate Determination). Same as Method 5, section 8.7.6.1, Container No. 1.

8.2.2 Container No. 2 (Optional; Front-Half Rinse for Particulate Determination). Same as Method 5, section 8.7.6.2, Container No. 2.

8.2.3 Container No. 3 (Knockout and Acid Impinger Catch for Moisture and Hydrogen Halide Determination). Disconnect the impingers. Measure the liquid in the acid and knockout impingers to ±1 ml by using a graduated cylinder or by weighing it to ±0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas. Quantitatively transfer this liquid to a leak-free sample storage container. Rinse these impingers and connecting glassware including the back portion of the filter holder (and flexible tubing, if used) with water and add these rinses to the storage container. Seal the container, shake to mix, and label. The fluid level should be marked so that if any sample is lost during transport, a correction proportional to the lost volume can be applied. Retain rinse water and acidic absorbing solution blanks to be analyzed with the samples.

8.2.4 Container No. 4 (Alkaline Impinger Catch for Halogen and Moisture Determination). Measure and record the liquid in the alkaline impingers as described in section 8.2.3. Quantitatively transfer this liquid to a leak-free sample storage container. Rinse these two impingers and connecting glassware with water and add these rinses to the container. Add 25 mg of sodium thiosulfate per ppm halogen anticipated to be in the stack gas multiplied by the volume (dscm) of stack gas sampled (0.7 mg/ppm-dscf). Seal the container, shake to mix, and label; mark the fluid level. Retain alkaline absorbing solution blank to be analyzed with the samples.

NOTE: 25 mg per sodium thiosulfate per ppm halogen anticipated to be in the stack includes a safety factor of approximately 5 to assure complete reaction with the hypohalous acid to form a second Cl^- ion in the alkaline solution.

8.2.5 Container No. 5 (Silica Gel for Moisture Determination). Same as Method 5, section 8.7.6.3, Container No. 3.

8.2.6 Container Nos. 6 through 9 (Reagent Blanks). Save portions of the absorbing reagents (0.1 N H_2SO_4 and 0.1 N NaOH) equivalent to the amount used in the sampling train; dilute to the approximate volume of the corresponding samples using rinse water directly from the wash bottle being used. Add the same ratio of sodium thiosulfate solution used in container No. 4 to the 0.1 N NaOH absorbing reagent blank. Also, save a portion of the rinse water alone and a portion of the acetone equivalent to the amount used to rinse the front half of the sampling train. Place each in a separate, prelabeled sample container.

8.2.7 Prior to shipment, recheck all sample containers to ensure that the caps are well-secured. Seal the lids of all containers around the circumference with Teflon tape. Ship all liquid samples upright and all particulate filters with the particulate catch facing upward.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.1.4, 10.1	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Probe Nozzle, Pitot Tube Assembly, Dry Gas Metering System, Probe Heater, Temperature Sensors, Leak-Check of Metering System, and Barometer. Same as Method 5, sections 10.1, 10.2, 10.3, 10.4, 10.5, 8.4.1, and 10.6, respectively.

10.2 Ion Chromatograph.

10.2.1 To prepare the calibration standards, dilute given amounts (1.0 ml or greater) of the stock standard solutions to convenient volumes, using 0.1 N H_2SO_4 or 0.1 N NaOH, as appropriate. Prepare at least four calibration standards for each absorbing reagent containing the three stock solutions such that they are within the linear range of the field samples.

10.2.2 Using one of the standards in each series, ensure adequate baseline separation for the peaks of interest.

10.2.3 Inject the appropriate series of calibration standards, starting with the lowest concentration standard first both before and after injection of the quality control check sample, reagent blanks, and field samples. This allows compensation for any instrument drift occurring during sample analysis. The values from duplicate injections of these calibration samples should agree within 5 percent of their mean for the analysis to be valid.

10.2.4 Determine the peak areas, or height, of the standards and plot individual values versus halide ion concentrations in µg/ml.

10.2.5 Draw a smooth curve through the points. Use linear regression to calculate a formula describing the resulting linear curve.

11.0 Analytical Procedures

NOTE: The liquid levels in the sample containers and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.1 Sample Analysis.

11.1.1 The IC conditions will depend upon analytical column type and whether suppressed or non-suppressed IC is used. An example chromatogram from a non-suppressed system using a 150-mm Hamilton PRP-X100 anion column, a 2 ml/min flow rate of a 4 mM 4-hydroxy benzoate solution adjusted to a pH of 8.6 using 1 N NaOH, a 50 µl sample loop, and a conductivity detector set on 1.0 µS full scale is shown in Figure 26–2.

11.1.2 Before sample analysis, establish a stable baseline. Next, inject a sample of water, and determine if any Cl^-, Br^-, or F^- appears in the chromatogram. If any of these ions are present, repeat the load/injection procedure until they are no longer present. Analysis of the acid and alkaline absorbing solution samples requires separate standard calibration curves; prepare each according to section 10.2. Ensure adequate baseline separation of the analyses.

11.1.3 Between injections of the appropriate series of calibration standards, inject in duplicate the reagent blanks, quality control sample, and the field samples. Measure the areas or heights of the Cl^-, Br^-, and F^- peaks. Use the mean response of the duplicate injections to determine the concentrations of the field samples and reagent blanks using the linear calibration curve. The values from duplicate injections should agree within 5 percent of their mean for the analysis to be valid. If the values of duplicate injections are not within 5 percent of the mean, the duplicator injections shall be repeated and all four values used to determine the average response. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

11.2 Container Nos. 1 and 2 and Acetone Blank (Optional; Particulate Determination). Same as Method 5, sections 11.2.1 and 11.2.2, respectively.

11.3 Container No. 5. Same as Method 5, section 11.2.3 for silica gel.

12.0 Data Analysis and Calculations

NOTE: Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

12.1 Nomenclature. Same as Method 5, section 12.1. In addition:

B_{X-} = Mass concentration of applicable absorbing solution blank, µg halide ion (Cl^-, Br^-, F^-)/ml, not to exceed 1 µg/ml which is 10 times the published analytical detection limit of 0.1 µg/ml. (It is also approximately 5 percent of the mass concentration anticipated to result from a one hour sample at 10 ppmv HCl.)

C = Concentration of hydrogen halide (HX) or halogen (X_2), dry basis, mg/dscm.

$K = 10^{-3}$ mg/µg.

K_{HCl} = 1.028 (µg HCl/µg-mole)/(µg Cl^-/µg-mole).

K_{HBr} = 1.013 (µg HBr/µg-mole)/(µg Br^-/µg-mole).

K_{HF} = 1.053 (µg HF/µg-mole)/(µg F^-/µg-mole).

m_{HX} = Mass of HCl, HBr, or HF in sample, ug.

m_{X2} = Mass of Cl_2 or Br_2 in sample, ug.

S_{X-} = Analysis of sample, ug halide ion (Cl^-, Br^-, F^-)/ml.

V_s = Volume of filtered and diluted sample, ml.

12.2 Calculate the exact Cl^-, Br^-, and F^- concentration in the halide salt stock standard solutions using the following equations.

$$\mu g\ Cl^-/ml = g\ of\ NaCl \times 10^3 \times 35.453/58.44 \qquad \text{Eq. 26A-1}$$

$$\mu g\ Br^-/ml = g\ of\ NaBr \times 10^3 \times 79.904/102.90 \qquad \text{Eq. 26A-2}$$

$$\mu g\ F^-/ml = g\ of\ NaF \times 10^3 \times 18.998/41.99 \qquad \text{Eq. 26A-3}$$

12.3 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 5–3 of Method 5).

12.4 Dry Gas Volume. Calculate $V_{m(std)}$ and adjust for leakage, if necessary, using the equation in section 12.3 of Method 5.

12.5 Volume of Water Vapor and Moisture Content. Calculate the volume of water vapor $V_{w(std)}$ and moisture content B_{ws} from the data obtained in this method (Figure 5–3 of Method 5); use Equations 5–2 and 5–3 of Method 5.

12.6 Isokinetic Variation and Acceptable Results. Use Method 5, section 12.11.

12.7 Acetone Blank Concentration, Acetone Wash Blank Residue Weight, Particulate Weight, and Particulate Concentration. For particulate determination.

12.8 Total μg HCl, HBr, or HF Per Sample.

$$m_{HX} = K_{HC1,Hbr,HF} V_s \left(S_{X^-} - B_{X^-} \right) \qquad \text{Eq. 26A-4}$$

12.9 Total μg Cl_2 or Br_2 Per Sample.

$$m_{X2} = V_s \left(S_{X^-} - B_{X^-} \right) \qquad \text{Eq. 26A-5}$$

12.10 Concentration of Hydrogen Halide or Halogen in Flue Gas.

$$C = K\, m_{HX,X2} / V_{m(std)} \qquad \text{Eq. 26A-6}$$

12.11 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate, if needed, using data obtained in this method and the equations in sections 12.3 and 12.4 of Method 2.

13.0 Method Performance

13.1 Precision and Bias. The method has a possible measurable negative bias below 20 ppm HCl perhaps due to reaction with small amounts of moisture in the probe and filter. Similar bias for the other hydrogen halides is possible.

13.2 Sample Stability. The collected Cl-samples can be stored for up to 4 weeks for analysis for HCl and Cl2.

13.3 Detection Limit. A typical analytical detection limit for HCl is 0.2 μg/ml. Detection limits for the other analyses should be similar. Assuming 300 ml of liquid recovered for the acidified impingers and a similar amounts recovered from the basic impingers, and 1 dscm of stack gas sampled, the analytical detection limits in the stack gas would be about 0.04 ppm for HCl and Cl2, respectively.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

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4. Stern, D.A., B.M. Myatt, J.F. Lachowski, and K.T. McGregor. Speciation of Halogen and Hydrogen Halide Compounds in Gaseous Emissions. In: Incineration and Treatment of Hazardous Waste: Proceedings of the 9th Annual Research Symposium, Cincinnati, Ohio, May 2–4, 1983. Publication No. 600/9–84–015. July 1984. Available from National Technical Information Service, Springfield, VA 22161 as PB84–234525.

5. Holm, R.D. and S.A. Barksdale. Analysis of Anions in Combustion Products. In: Ion Chromatographic Analysis of Environmental Pollutants, E. Sawicki, J.D. Mulik, and E. Wittgenstein (eds.). Ann Arbor, Michigan, Ann Arbor Science Publishers. 1978. pp. 99–110.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

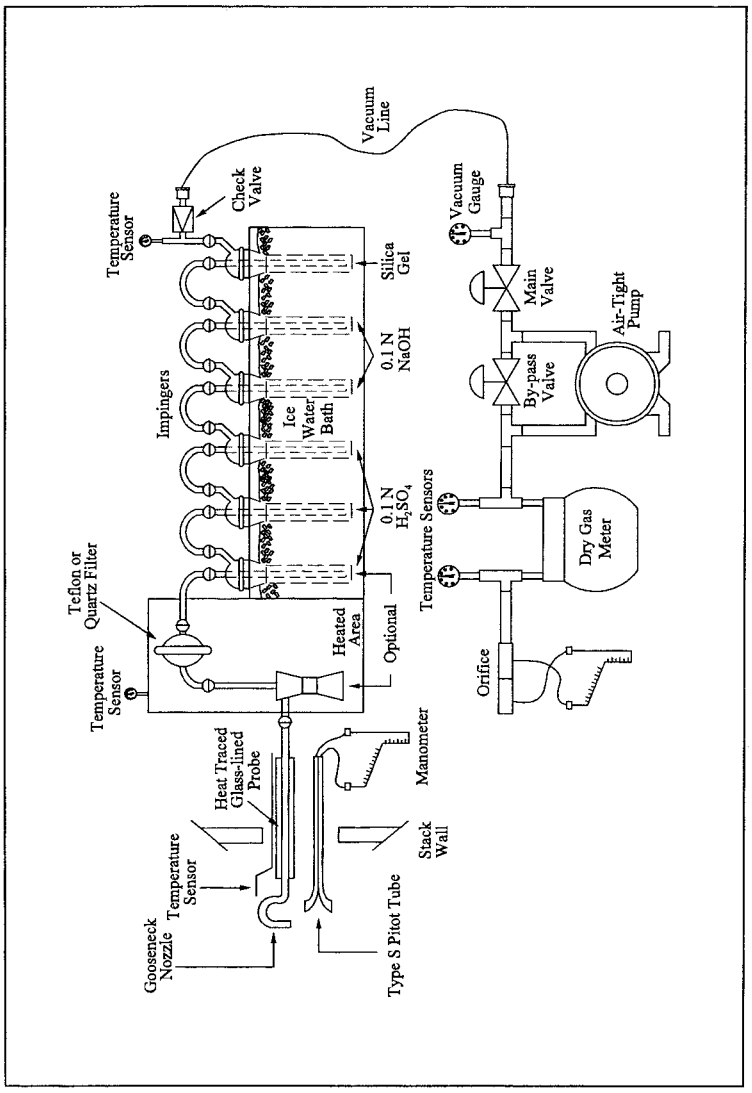


Figure 26A-1. Sampling Train

METHOD 27—DETERMINATION OF VAPOR TIGHTNESS OF GASOLINE DELIVERY TANK USING PRESSURE VACUUM TEST

1.0 Scope and Application

1.1 Applicability. This method is applicable for the determination of vapor tightness of a gasoline delivery collection equipment.

2.0 Summary of Method

2.1 Pressure and vacuum are applied alternately to the compartments of a gasoline delivery tank and the change in pressure or vacuum is recorded after a specified period of time.

3.0 Definitions

3.1 *Allowable pressure change (Δp)* means the allowable amount of decrease in pressure during the static pressure test, within the time period t, as specified in the appropriate regulation, in mm H_2O.

3.2 *Allowable vacuum change (Δv)* means the allowable amount of decrease in vacuum during the static vacuum test, within the time period t, as specified in the appropriate regulation, in mm H_2O.

3.3 *Compartment* means a liquid-tight division of a delivery tank.

3.4 *Delivery tank* means a container, including associated pipes and fittings, that is attached to or forms a part of any truck, trailer, or railcar used for the transport of gasoline.

3.5 *Delivery tank vapor collection equipment* means any piping, hoses, and devices on the delivery tank used to collect and route gasoline vapors either from the tank to a bulk terminal vapor control system or from a bulk plant or service station into the tank.

3.6 *Gasoline* means a petroleum distillate or petroleum distillate/alcohol blend having a Reid vapor pressure of 27.6 kilopascals or greater which is used as a fuel for internal combustion engines.

3.7 *Initial pressure (P_i)* means the pressure applied to the delivery tank at the beginning of the static pressure test, as specified in the appropriate regulation, in mm H_2O.

3.8 *Initial vacuum (V_i)* means the vacuum applied to the delivery tank at the beginning of the static vacuum test, as specified in the appropriate regulation, in mm H_3.

3.9 *Time period of the pressure or vacuum test (t)* means the time period of the test, as specified in the appropriate regulation, during which the change in pressure or vacuum is monitored, in minutes.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Gasoline contains several volatile organic compounds (*e.g.*, benzene and hexane) which presents a potential for fire and/or explosions. It is advisable to take appropriate precautions when testing a gasoline vessel's vapor tightness, such as refraining from smoking and using explosion-proof equipment.

5.2 This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method

6.0 Equipment and Supplies

The following equipment and supplies are required for testing:

6.1 Pressure Source. Pump or compressed gas cylinder of air or inert gas sufficient to pressurize the delivery tank to 500 mm (20 in.) H_2O above atmospheric pressure.

6.2 Regulator. Low pressure regulator for controlling pressurization of the delivery tank.

6.3 Vacuum Source. Vacuum pump capable of evacuating the delivery tank to 250 mm (10 in.) H_2O below atmospheric pressure.

6.4 Pressure-Vacuum Supply Hose.

6.5 Manometer. Liquid manometer, or equivalent instrument, capable of measuring up to 500 mm (20 in.) H_2O gauge pressure with ±2.5 mm (0.1 in.) H_2O precision.

6.6 Pressure-Vacuum Relief Valves. The test apparatus shall be equipped with an inline pressure-vacuum relief valve set to activate at 675 mm (26.6 in.) H_2O above atmospheric pressure or 250 mm (10 in.) H2O below atmospheric pressure, with a capacity equal to the pressurizing or evacuating pumps.

6.7 Test Cap for Vapor Recovery Hose. This cap shall have a tap for manometer connection and a fitting with shut-off valve for connection to the pressure-vacuum supply hose.

6.8 Caps for Liquid Delivery Hoses.

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparations.

8.1.1 Summary. Testing problems may occur due to the presence of volatile vapors and/or temperature fluctuations inside the delivery tank. Under these conditions, it is often difficult to obtain a stable initial pressure at the beginning of a test, and erroneous test results may occur. To help prevent this, it is recommended that prior to testing, volatile vapors be removed from the tank and the temperature inside the tank be allowed to stabilize. Because it is not always possible to completely attain these pretest conditions, a provision to ensure reproducible results is included. The difference in results for two consecutive runs must meet the criteria in sections 8.2.2.5 and 8.2.3.5.

8.1.2 Emptying of Tank. The delivery tank shall be emptied of all liquid.

8.1.3 Purging of Vapor. As much as possible the delivery tank shall be purged of all volatile vapors by any safe, acceptable method. One method is to carry a load of non-volatile liquid fuel, such as diesel or heating oil, immediately prior to the test, thus flushing out all the volatile gasoline vapors. A second method is to remove the volatile vapors by blowing ambient air into each tank compartment for at least 20 minutes. This second method is usually not as effective and often causes stabilization problems, requiring a

much longer time for stabilization during the testing.

8.1.4 Temperature Stabilization. As much as possible, the test shall be conducted under isothermal conditions. The temperature of the delivery tank should be allowed to equilibrate in the test environment. During the test, the tank should be protected from extreme environmental and temperature variability, such as direct sunlight.

8.2 Test Procedure.

8.2.1 Preparations.

8.2.1.1 Open and close each dome cover.

8.2.1.2 Connect static electrical ground connections to the tank. Attach the liquid delivery and vapor return hoses, remove the liquid delivery elbows, and plug the liquid delivery fittings.

NOTE: The purpose of testing the liquid delivery hoses is to detect tears or holes that would allow liquid leakage during a delivery. Liquid delivery hoses are not considered to be possible sources of vapor leakage, and thus, do not have to be attached for a vapor leakage test. Instead, a liquid delivery hose could be either visually inspected, or filled with water to detect any liquid leakage.

8.2.1.3 Attach the test cap to the end of the vapor recovery hose.

8.2.1.4 Connect the pressure-vacuum supply hose and the pressure-vacuum relief valve to the shut-off valve. Attach a manometer to the pressure tap.

8.2.1.5 Connect compartments of the tank internally to each other if possible. If not possible, each compartment must be tested separately, as if it were an individual delivery tank.

8.2.2 Pressure Test.

8.2.2.1 Connect the pressure source to the pressure-vacuum supply hose.

8.2.2.2 Open the shut-off valve in the vapor recovery hose cap. Apply air pressure slowly, pressurize the tank to P_i, the initial pressure specified in the regulation.

8.2.2.3 Close the shut-off and allow the pressure in the tank to stabilize, adjusting the pressure if necessary to maintain pressure of P_i. When the pressure stabilizes, record the time and initial pressure.

8.2.2.4 At the end of the time period (t) specified in the regulation, record the time and final pressure.

8.2.2.5 Repeat steps 8.2.2.2 through 8.2.2.4 until the change in pressure for two consecutive runs agrees within 12.5 mm (0.5 in.) H_2O. Calculate the arithmetic average of the two results.

8.2.2.6 Compare the average measured change in pressure to the allowable pressure change, Δp, specified in the regulation. If the delivery tank does not satisfy the vapor tightness criterion specified in the regulation, repair the sources of leakage, and repeat the pressure test until the criterion is met.

8.2.2.7 Disconnect the pressure source from the pressure-vacuum supply hose, and slowly open the shut-off valve to bring the tank to atmospheric pressure.

8.2.3 Vacuum Test.

8.2.3.1 Connect the vacuum source to the pressure-vacuum supply hose.

8.2.3.2 Open the shut-off valve in the vapor recovery hose cap. Slowly evacuate the tank to V_i, the initial vacuum specified in the regulation.

8.2.3.3 Close the shut-off valve and allow the pressure in the tank to stabilize, adjusting the pressure if necessary to maintain a vacuum of V_i. When the pressure stabilizes, record the time and initial vacuum.

8.2.3.4 At the end of the time period specified in the regulation (t), record the time and final vacuum.

8.2.3.5 Repeat steps 8.2.3.2 through 8.2.3.4 until the change in vacuum for two consecutive runs agrees within 12.5 mm (0.5 in.) H_2O. Calculate the arithmetic average of the two results.

8.2.3.6 Compare the average measured change in vacuum to the allowable vacuum change, Δv, as specified in the regulation. If the delivery tank does not satisfy the vapor tightness criterion specified in the regulation, repair the sources of leakage, and repeat the vacuum test until the criterion is met.

8.2.3.7 Disconnect the vacuum source from the pressure-vacuum supply hose, and slowly open the shut-off valve to bring the tank to atmospheric pressure.

8.2.4 Post-Test Clean-up. Disconnect all test equipment and return the delivery tank to its pretest condition.

9.0 Quality Control

Section(s)	Quality control measure	Effect
8.2.2.5, 8.3.3.5	Repeat test procedures until change in pressure or vacuum for two consecutive runs agrees within ±12.5 mm (0.5 in.) H_2O.	Ensures data precision.

10.0 Calibration and Standardization
[Reserved]

11.0 Analytical Procedures [Reserved]

12.0 Data Analysis and Calculations [Reserved]

13.0 Method Performance

13.1 Precision. The vapor tightness of a gasoline delivery tank under positive or negative pressure, as measured by this method, is precise within 12.5 mm (0.5 in.) H_2O

13.2 Bias. No bias has been identified.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 The pumping of water into the bottom of a delivery tank is an acceptable alternative to the pressure source described above. Likewise, the draining of water out of the bottom of a delivery tank may be substituted for the vacuum source. Note that some of the specific step-by-step procedures in the method must be altered slightly to accommodate these different pressure and vacuum sources.

16.2 Techniques other than specified above may be used for purging and pressurizing a delivery tank, if prior approval is obtained from the Administrator. Such approval will be based upon demonstrated equivalency with the above method.

17.0 References [Reserved]

18.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 28—CERTIFICATION AND AUDITING OF WOOD HEATERS

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 4, Method 5, Method 5G, Method 5H, Method 6, Method 6C, and Method 16A.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the certification and auditing of wood heaters, including pellet burning wood heaters.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Particulate matter emissions are measured from a wood heater burning a prepared test fuel crib in a test facility maintained at a set of prescribed conditions. Procedures for determining burn rates and particulate emission rates and for reducing data are provided.

3.0 Definitions

3.1 *2 × 4 or 4 × 4* means two inches by four inches or four inches by four inches (50 mm by 100 mm or 100 mm by 100 mm), as nominal dimensions for lumber.

3.2 *Burn rate* means the rate at which test fuel is consumed in a wood heater. Measured in kilograms or lbs of wood (dry basis) per hour (kg/hr or lb/hr).

3.3 *Certification or audit test* means a series of at least four test runs conducted for certification or audit purposes that meets the burn rate specifications in section 8.4.

3.4 *Firebox* means the chamber in the wood heater in which the test fuel charge is placed and combusted.

3.5 *Height* means the vertical distance extending above the loading door, if fuel could reasonably occupy that space, but not more than 2 inches above the top (peak height) of the loading door, to the floor of the firebox (*i.e.*, below a permanent grate) if the grate allows a 1-inch diameter piece of wood to pass through the grate, or, if not, to the top of the grate. Firebox height is not necessarily uniform but must account for variations caused by internal baffles, air channels, or other permanent obstructions.

3.6 *Length* means the longest horizontal fire chamber dimension that is parallel to a wall of the chamber.

3.7 *Pellet burning wood heater* means a wood heater which meets the following criteria: (1) The manufacturer makes no reference to burning cord wood in advertising or other literature, (2) the unit is safety listed for pellet fuel only, (3) the unit operating and instruction manual must state that the use of cordwood is prohibited by law, and (4) the unit must be manufactured and sold including the hopper and auger combination as integral parts.

3.8 *Secondary air supply* means an air supply that introduces air to the wood heater such that the burn rate is not altered by more than 25 percent when the secondary air supply is adjusted during the test run. The wood heater manufacturer can document this through design drawings that show the secondary air is introduced only into a mixing chamber or secondary chamber outside the firebox.

3.9 *Test facility* means the area in which the wood heater is installed, operated, and sampled for emissions.

3.10 *Test fuel charge* means the collection of test fuel pieces placed in the wood heater at the start of the emission test run.

3.11 *Test fuel crib* means the arrangement of the test fuel charge with the proper spacing requirements between adjacent fuel pieces.

3.12 *Test fuel loading density* means the weight of the as-fired test fuel charge per unit volume of usable firebox.

3.13 *Test fuel piece* means the 2 × 4 or 4 × 4 wood piece cut to the length required for the test fuel charge and used to construct the test fuel crib.

3.14 *Test run* means an individual emission test which encompasses the time required to consume the mass of the test fuel charge.

3.15 *Usable firebox volume* means the volume of the firebox determined using its height, length, and width as defined in this section.

3.16 *Width* means the shortest horizontal fire chamber dimension that is parallel to a wall of the chamber.

3.17 *Wood heater* means an enclosed, woodburning appliance capable of and intended for space heating or domestic water heating, as defined in the applicable regulation.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

Same as section 6.0 of either Method 5G or Method 5H, with the addition of the following:

6.1 Insulated Solid Pack Chimney. For installation of wood heaters. Solid pack insulated chimneys shall have a minimum of 2.5 cm (1 in.) solid pack insulating material surrounding the entire flue and possess a label demonstrating conformance to U.L. 103 (incorporated by reference—see §60.17).

6.2 Platform Scale and Monitor. For monitoring of fuel load weight change. The scale shall be capable of measuring weight to within 0.05 kg (0.1 lb) or 1 percent of the initial test fuel charge weight, whichever is greater.

6.3 Wood Heater Temperature Monitors. Seven, each capable of measuring temperature to within 1.5 percent of expected absolute temperatures.

6.4 Test Facility Temperature Monitor. A thermocouple located centrally in a vertically oriented 150 mm (6 in.) long, 50 mm (2 in.) diameter pipe shield that is open at both ends, capable of measuring temperature to within 1.5 percent of expected temperatures.

6.5 Balance (optional). Balance capable of weighing the test fuel charge to within 0.05 kg (0.1 lb).

6.6 Moisture Meter. Calibrated electrical resistance meter for measuring test fuel moisture to within 1 percent moisture content.

6.7 Anemometer. Device capable of detecting air velocities less than 0.10 m/sec (20 ft/min), for measuring air velocities near the test appliance.

6.8 Barometer. Mercury, aneroid or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg).

6.9 Draft Gauge. Electromanometer or other device for the determination of flue draft or static pressure readable to within 0.50 Pa (0.002 in. H_2O).

6.10 Humidity Gauge. Psychrometer or hygrometer for measuring room humidity.

6.11 Wood Heater Flue.

6.11.1 Steel flue pipe extending to 2.6 ±0.15 m (8.5 ±0.5 ft) above the top of the platform scale, and above this level, insulated solid pack type chimney extending to 4.6 ±0.3 m (15 ±1 ft) above the platform scale, and of the size specified by the wood heater manufacturer. This applies to both freestanding and insert type wood heaters.

6.11.2 Other chimney types (*e.g.*, solid pack insulated pipe) may be used in place of the steel flue pipe if the wood heater manufacturer's written appliance specifications require such chimney for home installation (*e.g.*, zero clearance wood heater inserts). Such alternative chimney or flue pipe must remain and be sealed with the wood heater following the certification test.

6.12 Test Facility. The test facility shall meet the following requirements during testing:

6.12.1 The test facility temperature shall be maintained between 18 and 32 °C (65 and 90 °F) during each test run.

6.12.2 Air velocities within 0.6 m (2 ft) of the test appliance and exhaust system shall be less than 0.25 m/sec (50 ft/min) without fire in the unit.

6.12.3 The flue shall discharge into the same space or into a space freely communicating with the test facility. Any hood or similar device used to vent combustion products shall not induce a draft greater than 1.25 Pa (0.005 in. H_2O) on the wood heater measured when the wood heater is not operating.

6.12.4 For test facilities with artificially induced barometric pressures (*e.g.*, pressurized chambers), the barometric pressure in the test facility shall not exceed 775 mm Hg (30.5 in. Hg) during any test run.

7.0 Reagents and Standards

Same as section 6.0 of either Method 5G or Method 5H, with the addition of the following:

7.1 Test Fuel. The test fuel shall conform to the following requirements:

7.1.1 Fuel Species. Untreated, air-dried, Douglas fir lumber. Kiln-dried lumber is not permitted. The lumber shall be certified C grade (standard) or better Douglas fir by a lumber grader at the mill of origin as specified in the West Coast Lumber Inspection Bureau Standard No. 16 (incorporated by reference—see §60.17).

7.1.2 Fuel Moisture. The test fuel shall have a moisture content range between 16 to 20 percent on a wet basis (19 to 25 percent dry basis). Addition of moisture to previously dried wood is not allowed. It is recommended that the test fuel be stored in a temperature and humidity-controlled room.

7.1.3 Fuel Temperature. The test fuel shall be at the test facility temperature of 18 to 32 °C (65 to 90 °F).

7.1.4 Fuel Dimensions. The dimensions of each test fuel piece shall conform to the nominal measurements of 2×4 and 4×4 lumber. Each piece of test fuel (not including spacers) shall be of equal length, except as necessary to meet requirements in section 8.8, and shall closely approximate ⅝ the dimensions of the length of the usable firebox. The fuel piece dimensions shall be determined in relation to the appliance's firebox volume according to guidelines listed below:

7.1.4.1 If the usable firebox volume is less than or equal to 0.043 m^3 (1.5 ft^3), use 2×4 lumber.

7.1.4.2 If the usable firebox volume is greater than 0.043 m^3 (1.5 ft^3) and less than or equal to 0.085 m^3 (3.0 ft^3), use 2×4 and 4×4 lumber. About half the weight of the test fuel charge shall be 2×4 lumber, and the remainder shall be 4×4 lumber.

7.1.4.3 If the usable firebox volume is greater than 0.085 m^3 (3.0 ft^3), use 4×4 lumber.

7.2 Test Fuel Spacers. Air-dried, Douglas fir lumber meeting the requirements outlined in sections 7.1.1 through 7.1.3. The spacers shall be $130 \times 40 \times 20$ mm ($5 \times 1.5 \times 0.75$ in.).

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Test Run Requirements.

8.1.1 Burn Rate Categories. One emission test run is required in each of the following burn rate categories:

BURN RATE CATEGORIES

[Average kg/hr (lb/hr), dry basis]

Category 1	Category 2	Category 3	Category 4
<0.80 (<1.76)	0.80 to 1.25 (1.76 to 2.76)	1.25 to 1.90 (2.76 to 4.19)	Maximum. burn rate.

8.1.1.1 Maximum Burn Rate. For Category 4, the wood heater shall be operated with the primary air supply inlet controls fully open (or, if thermostatically controlled, the thermostat shall be set at maximum heat output) during the entire test run, or the maximum burn rate setting specified by the manufacturer's written instructions.

8.1.1.2 Other Burn Rate Categories. For burn rates in Categories 1 through 3, the wood heater shall be operated with the primary air supply inlet control, or other mechanical control device, set at a predetermined position necessary to obtain the average burn rate required for the category.

8.1.1.3 Alternative Burn Rates for Burn Rate Categories 1 and 2.

8.1.1.3.1 If a wood heater cannot be operated at a burn rate below 0.80 kg/hr (1.76 lb/hr), two test runs shall be conducted with burn rates within Category 2. If a wood heater cannot be operated at a burn rate below 1.25 kg/hr (2.76 lb/hr), the flue shall be dampered or the air supply otherwise controlled in order to achieve two test runs within Category 2.

8.1.1.3.2 Evidence that a wood heater cannot be operated at a burn rate less than 0.80 kg/hr shall include documentation of two or more attempts to operate the wood heater in burn rate Category 1 and fuel combustion has stopped, or results of two or more test runs demonstrating that the burn rates were greater than 0.80 kg/hr when the air supply controls were adjusted to the lowest possible position or settings. Stopped fuel combustion is evidenced when an elapsed time of 30 minutes or more has occurred without a measurable (<0.05 kg (0.1 lb) or 1.0 percent, whichever is greater) weight change in the test fuel charge. See also section 8.8.3. Report the evidence and the reasoning used to determine that a test in burn rate Category 1 cannot be achieved; for example, two unsuccessful attempts to operate at a burn rate of 0.4 kg/hr are not sufficient evidence that burn rate Category 1 cannot be achieved.

NOTE: After July 1, 1990, if a wood heater cannot be operated at a burn rate less than 0.80 kg/hr, at least one test run with an average burn rate of 1.00 kg/hr or less shall be conducted. Additionally, if flue dampering must be used to achieve burn rates below 1.25

kg/hr (or 1.0 kg/hr), results from a test run conducted at burn rates below 0.90 kg/hr need not be reported or included in the test run average provided that such results are replaced with results from a test run meeting the criteria above.

8.2 Catalytic Combustor and Wood Heater Aging. The catalyst-equipped wood heater or a wood heater of any type shall be aged before the certification test begins. The aging procedure shall be conducted and documented by a testing laboratory accredited according to procedures in §60.535 of 40 CFR part 60.

8.2.1 Catalyst-equipped Wood Heater. Operate the catalyst-equipped wood heater using fuel meeting the specifications outlined in sections 7.1.1 through 7.1.3, or cordwood with a moisture content between 15 and 25 percent on a wet basis. Operate the wood heater at a medium burn rate (Category 2 or 3) with a new catalytic combustor in place and in operation for at least 50 hours. Record and report hourly catalyst exit temperature data (Section 8.6.2) and the hours of operation.

8.2.2 Non-Catalyst Wood Heater. Operate the wood heater using the fuel described in section 8.4.1 at a medium burn rate for at least 10 hours. Record and report the hours of operation.

8.3 Pretest Recordkeeping. Record the test fuel charge dimensions and weights, and wood heater and catalyst descriptions as shown in the example in Figure 28–1.

8.4 Wood Heater Installation. Assemble the wood heater appliance and parts in conformance with the manufacturer's written installation instructions. Place the wood heater centrally on the platform scale and connect the wood heater to the flue described in section 6.11. Clean the flue with an appropriately sized, wire chimney brush before each certification test.

8.5 Wood Heater Temperature Monitors.

8.5.1 For catalyst-equipped wood heaters, locate a temperature monitor (optional) about 25 mm (1 in.) upstream of the catalyst at the centroid of the catalyst face area, and locate a temperature monitor (mandatory) that will indicate the catalyst exhaust temperature. This temperature monitor is centrally located within 25 mm (1 in.) downstream at the centroid of catalyst face area. Record these locations.

8.5.2 Locate wood heater surface temperature monitors at five locations on the wood heater firebox exterior surface. Position the temperature monitors centrally on the top surface, on two sidewall surfaces, and on the bottom and back surfaces. Position the monitor sensing tip on the firebox exterior surface inside of any heat shield, air circulation walls, or other wall or shield separated from the firebox exterior surface. Surface temperature locations for unusual design shapes (*e.g.*, spherical, etc.) shall be positioned so that there are four surface temperature monitors in both the vertical and horizontal planes passing at right angles through the centroid of the firebox, not including the fuel loading door (total of five temperature monitors).

8.6 Test Facility Conditions.

8.6.1 Locate the test facility temperature monitor on the horizontal plane that includes the primary air intake opening for the wood heater. Locate the temperature monitor 1 to 2 m (3 to 6 ft) from the front of the wood heater in the 90° sector in front of the wood heater.

8.6.2 Use an anemometer to measure the air velocity. Measure and record the room air velocity before the pretest ignition period (Section 8.7) and once immediately following the test run completion.

8.6.3 Measure and record the test facility's ambient relative humidity, barometric pressure, and temperature before and after each test run.

8.6.4 Measure and record the flue draft or static pressure in the flue at a location no greater than 0.3 m (1 ft) above the flue connector at the wood heater exhaust during the test run at the recording intervals (Section 8.8.2).

8.7 Wood Heater Firebox Volume.

8.7.1 Determine the firebox volume using the definitions for height, width, and length in section 3. Volume adjustments due to presence of firebrick and other permanent fixtures may be necessary. Adjust width and length dimensions to extend to the metal wall of the wood heater above the firebrick or permanent obstruction if the firebrick or obstruction extending the length of the side(s) or back wall extends less than one-third of the usable firebox height. Use the width or length dimensions inside the firebrick if the firebrick extends more than one-third of the usable firebox height. If a log retainer or grate is a permanent fixture and the manufacturer recommends that no fuel be placed outside the retainer, the area outside of the retainer is excluded from the firebox volume calculations.

8.7.2 In general, exclude the area above the ash lip if that area is less than 10 percent of the usable firebox volume. Otherwise, take into account consumer loading practices. For instance, if fuel is to be loaded front-to-back, an ash lip may be considered usable firebox volume.

8.7.3 Include areas adjacent to and above a baffle (up to two inches above the fuel loading opening) if four inches or more horizontal space exist between the edge of the baffle and a vertical obstruction (*e.g.*, sidewalls or air channels).

8.8 Test Fuel Charge.

8.8.1 Prepare the test fuel pieces in accordance with the specifications outlined in sections 7.1 and 7.2. Determine the test fuel moisture content with a calibrated electrical

resistance meter or other equivalent performance meter. If necessary, convert fuel moisture content values from dry basis ($\%M_d$) to wet basis ($\%M_w$) in section 12.2 using Equation 28–1. Determine fuel moisture for each fuel piece (not including spacers) by averaging at least three moisture meter readings, one from each of three sides, measured parallel to the wood grain. Average all the readings for all the fuel pieces in the test fuel charge. If an electrical resistance type meter is used, penetration of insulated electrodes shall be one-fourth the thickness of the test fuel piece or 19 mm (0.75 in.), whichever is greater. Measure the moisture content within a 4-hour period prior to the test run. Determine the fuel temperature by measuring the temperature of the room where the wood has been stored for at least 24 hours prior to the moisture determination.

8.8.2 Attach the spacers to the test fuel pieces with uncoated, ungalvanized nails or staples as illustrated in Figure 28–2. Attachment of spacers to the top of the test fuel piece(s) on top of the test fuel charge is optional.

8.8.3 To avoid stacking difficulties, or when a whole number of test fuel pieces does not result, all piece lengths shall be adjusted uniformly to remain within the specified loading density. The shape of the test fuel crib shall be geometrically similar to the shape of the firebox volume without resorting to special angular or round cuts on the individual fuel pieces.

8.8.4 The test fuel loading density shall be 112 ±11.2 kg/m³ (7 ±0.7 lb/ft³) of usable firebox volume on a wet basis.

8.9 Sampling Equipment. Prepare the sampling equipment as defined by the selected method (*i.e.*, either Method 5G or Method 5H). Collect one particulate emission sample for each test run.

8.10 Secondary Air Adjustment Validation.

8.10.1 If design drawings do not show the introduction of secondary air into a chamber outside the firebox (see ''secondary air supply'' under section 3.0, Definitions), conduct a separate test of the wood heater's secondary air supply. Operate the wood heater at a burn rate in Category 1 (Section 8.1.1) with the secondary air supply operated following the manufacturer's written instructions. Start the secondary air validation test run as described in section 8.8.1, except no emission sampling is necessary and burn rate data shall be recorded at 5-minute intervals.

8.10.2 After the start of the test run, operate the wood heater with the secondary air supply set as per the manufacturer's instructions, but with no adjustments to this setting. After 25 percent of the test fuel has been consumed, adjust the secondary air supply controls to another setting, as per the manufacturer's instructions. Record the burn rate data (5-minute intervals) for 20 minutes following the air supply adjustment.

8.10.3 Adjust the air supply control(s) to the original position(s), operate at this condition for at least 20 minutes, and repeat the air supply adjustment procedure above. Repeat the procedure three times at equal intervals over the entire burn period as defined in section 8.8. If the secondary air adjustment results in a burn rate change of more than an average of 25 percent between the 20-minute periods before and after the secondary adjustments, the secondary air supply shall be considered a primary air supply, and no adjustment to this air supply is allowed during the test run.

8.10.4 The example sequence below describes a typical secondary air adjustment validation check. The first cycle begins after at least 25 percent of the test fuel charge has been consumed.

Cycle 1
- Part 1, sec air adjusted to final position—20 min
- Part 2, sec air adjusted to final position—20 min
- Part 3, sec air adjusted to final position—20 min

Cycle 2
- Part 1, sec air adjusted to final position—20 min
- Part 2, sec air adjusted to final position—20 min
- Part 3, sec air adjusted to final position—20 min

Cycle 3
- Part 1, sec air adjusted to final position—20 min
- Part 2, sec air adjusted to final position—20 min
- Part 3, sec air adjusted to final position—20 min

Note that the cycles may overlap; that is, Part 3 of Cycle 1 may coincide in part or in total with Part 1 of Cycle 2. The calculation of the secondary air percent effect for this example is as follows:

$$\%BR_{sec} = \frac{\left|\overline{BR_{1,3}} - \overline{BR_2}\right|}{\overline{BR_{1,3}}} \times 100 \qquad \text{Eq. 28-1}$$

8.11 Pretest Ignition. Build a fire in the wood heater in accordance with the manufacturer's written instructions.

8.11.1 Pretest Fuel Charge. Crumpled newspaper loaded with kindling may be used to help ignite the pretest fuel. The pretest fuel, used to sustain the fire, shall meet the same fuel requirements prescribed in section 7.1. The pretest fuel charge shall consist of whole 2 × 4's that are no less than ⅓ the length of the test fuel pieces. Pieces of 4 × 4 lumber in approximately the same weight ratio as for the test fuel charge may be added to the pretest fuel charge.

8.11.2 Wood Heater Operation and Adjustments. Set the air inlet supply controls at any position that will maintain combustion of the pretest fuel load. At least one hour before the start of the test run, set the air supply controls at the approximate positions necessary to achieve the burn rate desired for the test run. Adjustment of the air supply controls, fuel addition or subtractions, and coalbed raking shall be kept to a minimum but are allowed up to 15 minutes prior to the start of the test run. For the purposes of this method, coalbed raking is the use of a metal tool (poker) to stir coals, break burning fuel into smaller pieces, dislodge fuel pieces from positions of poor combustion, and check for the condition of uniform charcoalization. Record all adjustments made to the air supply controls, adjustments to and additions or subtractions of fuel, and any other changes to wood heater operations that occur during pretest ignition period. Record fuel weight data and wood heater temperature measurements at 10-minute intervals during the hour of the pretest ignition period preceding the start of the test run. During the 15-minute period prior to the start of the test run, the wood heater loading door shall not be open more than a total of 1 minute. Coalbed raking is the only adjustment allowed during this period.

NOTE: One purpose of the pretest ignition period is to achieve uniform charcoalization of the test fuel bed prior to loading the test fuel charge. Uniform charcoalization is a general condition of the test fuel bed evidenced by an absence of large pieces of burning wood in the coal bed and the remaining fuel pieces being brittle enough to be broken into smaller charcoal pieces with a metal poker. Manipulations to the fuel bed prior to the start of the test run should be done to achieve uniform charcoalization while maintaining the desired burn rate. In addition, some wood heaters (*e.g.*, high mass units) may require extended pretest burn time and fuel additions to reach an initial average surface temperature sufficient to meet the thermal equilibrium criteria in section 8.3.

8.11.3 The weight of pretest fuel remaining at the start of the test run is determined as the difference between the weight of the wood heater with the remaining pretest fuel and the tare weight of the cleaned, dry wood heater with or without dry ash or sand added consistent with the manufacturer's instructions and the owner's manual. The tare weight of the wood heater must be determined with the wood heater (and ash, if added) in a dry condition.

8.12 Test Run. Complete a test run in each burn rate category, as follows:

8.12.1 Test Run Start.

8.12.1.1 When the kindling and pretest fuel have been consumed to leave a fuel weight between 20 and 25 percent of the weight of the test fuel charge, record the weight of the fuel remaining and start the test run. Record and report any other criteria, in addition to those specified in this section, used to determine the moment of the test run start (*e.g.*, firebox or catalyst temperature), whether such criteria are specified by the wood heater manufacturer or the testing laboratory. Record all wood heater individual surface temperatures, catalyst temperatures, any initial sampling method measurement values, and begin the particulate emission sampling. Within 1 minute following the start of the test run, open the wood heater door, load the test fuel charge, and record the test fuel charge weight. Recording of average, rather than individual, surface temperatures is acceptable for tests conducted in accordance with §60.533(o)(3)(i) of 40 CFR part 60.

8.12.1.2 Position the fuel charge so that the spacers are parallel to the floor of the firebox, with the spacer edges abutting each other. If loading difficulties result, some fuel pieces may be placed on edge. If the usable firebox volume is between 0.043 and 0.085 m^3 (1.5 and 3.0 ft^3), alternate the piece sizes in vertical stacking layers to the extent possible. For example, place 2 × 4's on the bottom layer in direct contact with the coal bed and 4 × 4's on the next layer, etc. (See Figure 28–3). Position the fuel pieces parallel to each other and parallel to the longest wall of the firebox to the extent possible within the specifications in section 8.8.

8.12.1.3 Load the test fuel in appliances having unusual or unconventional firebox design maintaining air space intervals between the test fuel pieces and in conformance with the manufacturer's written instructions. For any appliance that will not accommodate the loading arrangement specified in the paragraph above, the test facility personnel shall contact the Administrator for an alternative loading arrangement.

8.12.1.4 The wood heater door may remain open and the air supply controls adjusted up to five minutes after the start of the test run in order to make adjustments to the test fuel charge and to ensure ignition of the test fuel charge has occurred. Within the five minutes after the start of the test run, close the wood heater door and adjust the air supply controls to the position determined to produce

the desired burn rate. No other adjustments to the air supply controls or the test fuel charge are allowed (except as specified in sections 8.12.3 and 8.12.4) after the first five minutes of the test run. Record the length of time the wood heater door remains open, the adjustments to the air supply controls, and any other operational adjustments.

8.12.2 Data Recording. Record on a data sheet similar to that shown in Figure 28–4, at intervals no greater than 10 minutes, fuel weight data, wood heater individual surface and catalyst temperature measurements, other wood heater operational data (*e.g.*, draft), test facility temperature and sampling method data.

8.12.3 Test Fuel Charge Adjustment. The test fuel charge may be adjusted (*i.e.*, repositioned) once during a test run if more than 60 percent of the initial test fuel charge weight has been consumed and more than 10 minutes have elapsed without a measurable (<0.05 kg (0.1 lb) or 1.0 percent, whichever is greater) weight change. The time used to make this adjustment shall be less than 15 seconds.

8.12.4 Air Supply Adjustment. Secondary air supply controls may be adjusted once during the test run following the manufacturer's written instructions (see section 8.10). No other air supply adjustments are allowed during the test run. Recording of wood heater flue draft during the test run is optional for tests conducted in accordance with § 60.533(o)(3)(i) of 40 CFR part 60.

8.12.5 Auxiliary Wood Heater Equipment Operation. Heat exchange blowers sold with the wood heater shall be operated during the test run following the manufacturer's written instructions. If no manufacturer's written instructions are available, operate the heat exchange blower in the ''high'' position. (Automatically operated blowers shall be operated as designed.) Shaker grates, by-pass controls, or other auxiliary equipment may be adjusted only one time during the test run following the manufacturer's written instructions.

Record all adjustments on a wood heater operational written record.

NOTE: If the wood heater is sold with a heat exchange blower as an option, test the wood heater with the heat exchange blower operating as described in sections 8.1 through 8.12 and report the results. As an alternative to repeating all test runs without the heat exchange blower operating, one additional test run may be without the blower operating as described in section 8.12.5 at a burn rate in Category 2 (Section 8.1.1). If the emission rate resulting from this test run without the blower operating is equal to or less than the emission rate plus 1.0 g/hr (0.0022 lb/hr) for the test run in burn rate Category 2 with the blower operating, the wood heater may be considered to have the same average emission rate with or without the blower operating. Additional test runs without the blower operating are unnecessary.

8.13 Test Run Completion. Continue emission sampling and wood heater operation for 2 hours. The test run is completed when the remaining weight of the test fuel charge is 0.00 kg (0.0 lb). End the test run when the scale has indicated a test fuel charge weight of 0.00 kg (0.0 lb) or less for 30 seconds. At the end of the test run, stop the particulate sampling, and record the final fuel weight, the run time, and all final measurement values.

8.14 Wood Heater Thermal Equilibrium. The average of the wood heater surface temperatures at the end of the test run shall agree with the average surface temperature at the start of the test run to within 70 °C (126 °F).

8.15 Consecutive Test Runs. Test runs on a wood heater may be conducted consecutively provided that a minimum one-hour interval occurs between test runs.

8.16 Additional Test Runs. The testing laboratory may conduct more than one test run in each of the burn rate categories specified in section 8.1.1. If more than one test run is conducted at a specified burn rate, the results from at least two-thirds of the test runs in that burn rate category shall be used in calculating the weighted average emission rate (see section 12.2). The measurement data and results of all test runs shall be reported regardless of which values are used in calculating the weighted average emission rate (see note in section 8.1).

9.0 Quality Control

Same as section 9.0 of either Method 5G or Method 5H.

10.0 Calibration and Standardizations

Same as section 10.0 of either Method 5G or Method 5H, with the addition of the following:

10.1 Platform Scale. Perform a multi-point calibration (at least five points spanning the operational range) of the platform scale before its initial use. The scale manufacturer's calibration results are sufficient for this purpose. Before each certification test, audit the scale with the wood heater in place by weighing at least one calibration weight (Class F) that corresponds to between 20 percent and 80 percent of the expected test fuel charge weight. If the scale cannot reproduce the value of the calibration weight within 0.05 kg (0.1 lb) or 1 percent of the expected test fuel charge weight, whichever is greater, recalibrate the scale before use with at least five calibration weights spanning the operational range of the scale.

10.2 Balance (optional). Calibrate as described in section 10.1.

10.3 Temperature Monitor. Calibrate as in Method 2, section 4.3, before the first certification test and semiannually thereafter.

10.4 Moisture Meter. Calibrate as per the manufacturer's instructions before each certification test.

10.5 Anemometer. Calibrate the anemometer as specified by the manufacturer's instructions before the first certification test and semiannually thereafter.

10.6 Barometer. Calibrate against a mercury barometer before the first certification test and semiannually thereafter.

10.7 Draft Gauge. Calibrate as per the manufacturer's instructions; a liquid manometer does not require calibration.

10.8 Humidity Gauge. Calibrate as per the manufacturer's instructions before the first certification test and semiannually thereafter.

11.0 Analytical Procedures

Same as section 11.0 of either Method 5G or Method 5H.

12.0 Data Analysis and Calculations

Same as section 12.0 of either Method 5G or Method 5H, with the addition of the following:

12.1 Nomenclature.

BR = Dry wood burn rate, kg/hr (lb/hr)

E_i = Emission rate for test run, i, from Method 5G or 5H, g/hr (lb/hr)

E_w = Weighted average emission rate, g/hr (lb/hr)

k_i = Test run weighting factor = $P_{i+1} - P_{i-1}$

$\%M_d$ = Fuel moisture content, dry basis, percent.

$\%M_w$ = Average moisture in test fuel charge, wet basis, percent.

n = Total number of test runs.

P_i = Probability for burn rate during test run, i, obtained from Table 28–1. Use linear interpolation to determine probability values for burn rates between those listed on the table.

W_{wd} = Total mass of wood burned during the test run, kg (lb).

12.2 Wet Basis Fuel Moisture Content.

$$\%M_w = \frac{100(\%M_d)}{100 + \%M_d} \qquad \text{Eq. 28-2}$$

12.3 Weighted Average Emission Rate. Calculate the weighted average emission rate (E_w) using Equation 28–1:

$$E_w = \frac{\sum_{i=1}^{n}(K_i E_i)}{\sum_{i=1}^{n} K_i} \qquad \text{Eq. 28-3}$$

NOTE: P_o always equals 0, $P_{(n+1)}$ always equals 1, P_1 corresponds to the probability of the lowest recorded burn rate, P_2 corresponds to the probability of the next lowest burn rate, etc. An example calculation is in section 12.3.1.

12.3.1 Example Calculation of Weighted Average Emission Rate.

Burn rate category	Test No.	Burn rate (Dry-kg/hr)	Emissions (g/hr)
1	1	0.65	5.0
2[1]	2	0.85	6.7
2	3	0.90	4.7
2	4	1.00	5.3
3	5	1.45	3.8
4	6	2.00	5.1

[1] As permitted in section 6.6, this test run may be omitted from the calculation of the weighted average emission rate because three runs were conducted for this burn rate category.

Test No.	Burn rate	P_i	E_i	K_i
0	.....	0.000	.....	.....
1	0.65	0.121	5.0	0.300
2	0.90	0.300	4.7	0.259
3	1.00	0.380	5.3	0.422
4	1.45	0.722	3.8	0.532
5	2.00	0.912	5.1	0.278
6	.....	1.000	.....	.....

$K_1 = P_2 - P_0 = 0.300 - 0 = 0.300$
$K_2 = P_3 - P_1 = 0.381 - 0.121 = 0.259$
$K_3 = P_4 - P_2 = 0.722 - 0.300 = 0.422$
$K_4 = P_5 - P_3 = 0.912 - 0.380 = 0.532$
$K_5 = P_6 - P_4 = 1.000 - 0.722 = 0.278$

Weighted Average Emission Rate, E_w, Calculation

$$E_w = \frac{\sum(K_i E_i)}{\sum K_i}$$

$$= \frac{(0.3)(5.0)+(0.259)(4.7)+(0.422)(5.3)+(0.532)(3.8)+(0.278)(5.1)}{1.791}$$

$$= 4.69\,g/hr$$

12.4 Average Wood Heater Surface Temperatures. Calculate the average of the wood heater surface temperatures for the start of the test run (Section 8.12.1) and for the test run completion (Section 8.13). If the two average temperatures do not agree within 70 °C (125 °F), report the test run results, but do not include the test run results in the test average. Replace such test run results with results from another test run in the same burn rate category.

12.5 Burn Rate. Calculate the burn rate (BR) using Equation 28–3:

$$BR = \frac{60 W_{wd}}{\theta} \times \frac{100 - \%M_w}{100} \qquad \text{Eq. 28-3}$$

12.6 Reporting Criteria. Submit both raw and reduced test data for wood heater tests.

12.6.1 Suggested Test Report Format.

12.6.1.1 Introduction.

12.6.1.1.1 Purpose of test-certification, audit, efficiency, research and development.

12.6.1.1.2 Wood heater identification-manufacturer, model number, catalytic/noncatalytic, options.

12.6.1.1.3 Laboratory-name, location (altitude), participants.

12.6.1.1.4 Test information-date wood heater received, date of tests, sampling methods used, number of test runs.

12.6.1.2 Summary and Discussion of Results

12.6.1.2.1 Table of results (in order of increasing burn rate)-test run number, burn rate, particulate emission rate, efficiency (if determined), averages (indicate which test runs are used).

12.6.1.2.2 Summary of other data-test facility conditions, surface temperature averages, catalyst temperature averages, pretest fuel weights, test fuel charge weights, run times.

12.6.1.2.3 Discussion-Burn rate categories achieved, test run result selection, specific test run problems and solutions.

12.6.1.3 Process Description.

12.6.1.3.1 Wood heater dimensions-volume, height, width, lengths (or other linear dimensions), weight, volume adjustments.

12.6.1.3.2 Firebox configuration-air supply locations and operation, air supply introduction location, refractory location and dimensions, catalyst location, baffle and by-pass location and operation (include line drawings or photographs).

12.6.1.3.3 Process operation during test-air supply settings and adjustments, fuel bed adjustments, draft.

12.6.1.3.4 Test fuel-test fuel properties (moisture and temperature), test fuel crib description (include line drawing or photograph), test fuel loading density.

12.6.1.4 Sampling Locations.

12.6.1.4.1 Describe sampling location relative to wood heater. Include drawing or photograph.

12.6.1.5 Sampling and Analytical Procedures

12.6.1.5.1 Sampling methods-brief reference to operational and sampling procedures and optional and alternative procedures used.

12.6.1.5.2 Analytical methods-brief description of sample recovery and analysis procedures.

12.6.1.6 Quality Control and Assurance Procedures and Results

12.6.1.6.1 Calibration procedures and results-certification procedures, sampling and analysis procedures.

12.6.1.6.2 Test method quality control procedures-leak-checks, volume meter checks, stratification (velocity) checks, proportionality results.

12.6.1.7 Appendices

12.6.1.7.1 Results and Example Calculations. Complete summary tables and accompanying examples of all calculations.

12.6.1.7.2 Raw Data. Copies of all uncorrected data sheets for sampling measurements, temperature records and sample recovery data. Copies of all pretest burn rate and wood heater temperature data.

12.6.1.7.3 Sampling and Analytical Procedures. Detailed description of procedures followed by laboratory personnel in conducting the certification test, emphasizing particular parts of the procedures differing from the methods (*e.g.*, approved alternatives).

12.6.1.7.4 Calibration Results. Summary of all calibrations, checks, and audits pertinent to certification test results with dates.

12.6.1.7.5 Participants. Test personnel, manufacturer representatives, and regulatory observers.

12.6.1.7.6 Sampling and Operation Records. Copies of uncorrected records of activities not included on raw data sheets (*e.g.*, wood heater door open times and durations).

12.6.1.7.7 Additional Information. Wood heater manufacturer's written instructions for operation during the certification test.

12.6.2.1 Wood Heater Identification. Report wood heater identification information. An example data form is shown in Figure 28–4.

12.6.2.2 Test Facility Information. Report test facility temperature, air velocity, and humidity information. An example data form is shown on Figure 28–4.

12.6.2.3 Test Equipment Calibration and Audit Information. Report calibration and audit results for the platform scale, test fuel balance, test fuel moisture meter, and sampling equipment including volume metering systems and gaseous analyzers.

12.6.2.4 Pretest Procedure Description. Report all pretest procedures including pretest fuel weight, burn rates, wood heater temperatures, and air supply settings. An example data form is shown on Figure 28–4.

12.6.2.5 Particulate Emission Data. Report a summary of test results for all test runs and the weighted average emission rate. Submit copies of all data sheets and other records collected during the testing. Submit examples of all calculations.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Pellet Burning Heaters. Certification testing requirements and procedures for pellet burning wood heaters are identical to those for other wood heaters, with the following exceptions:

16.1.1 Test Fuel Properties. The test fuel shall be all wood pellets with a moisture content no greater than 20 percent on a wet basis (25 percent on a dry basis). Determine the wood moisture content with either ASTM D 2016–74 or 83, (Method A), ASTM D 4444–92, or ASTM D 4442–84 or 92 (all noted ASTM standards are incorporated by reference—see §60.17).

16.1.2 Test Fuel Charge Specifications. The test fuel charge size shall be as per the manufacturer's written instructions for maintaining the desired burn rate.

16.1.3 Wood Heater Firebox Volume. The firebox volume need not be measured or determined for establishing the test fuel charge size. The firebox dimensions and other heater specifications needed to identify the heater for certification purposes shall be reported.

16.1.4 Heater Installation. Arrange the heater with the fuel supply hopper on the platform scale as described in section 8.6.1.

16.1.5 Pretest Ignition. Start a fire in the heater as directed by the manufacturer's written instructions, and adjust the heater controls to achieve the desired burn rate. Operate the heater at the desired burn rate for at least 1 hour before the start of the test run.

16.1.6 Test Run. Complete a test run in each burn rate category as follows:

16.1.6.1 Test Run Start. When the wood heater has operated for at least 1 hour at the desired burn rate, add fuel to the supply hopper as necessary to complete the test run, record the weight of the fuel in the supply hopper (the wood heater weight), and start the test run. Add no additional fuel to the hopper during the test run.

Record all the wood heater surface temperatures, the initial sampling method measurement values, the time at the start of the test, and begin the emission sampling. Make no adjustments to the wood heater air supply or wood supply rate during the test run.

16.1.6.2 Data Recording. Record the fuel (wood heater) weight data, wood heater temperature and operational data, and emission sampling data as described in section 8.12.2.

16.1.6.3 Test Run Completion. Continue emission sampling and wood heater operation for 2 hours. At the end of the test run, stop the particulate sampling, and record the final fuel weight, the run time, and all final measurement values, including all wood heater individual surface temperatures.

16.1.7 Calculations. Determine the burn rate using the difference between the initial and final fuel (wood heater) weights and the procedures described in section 12.4. Complete the other calculations as described in section 12.0.

17.0 References

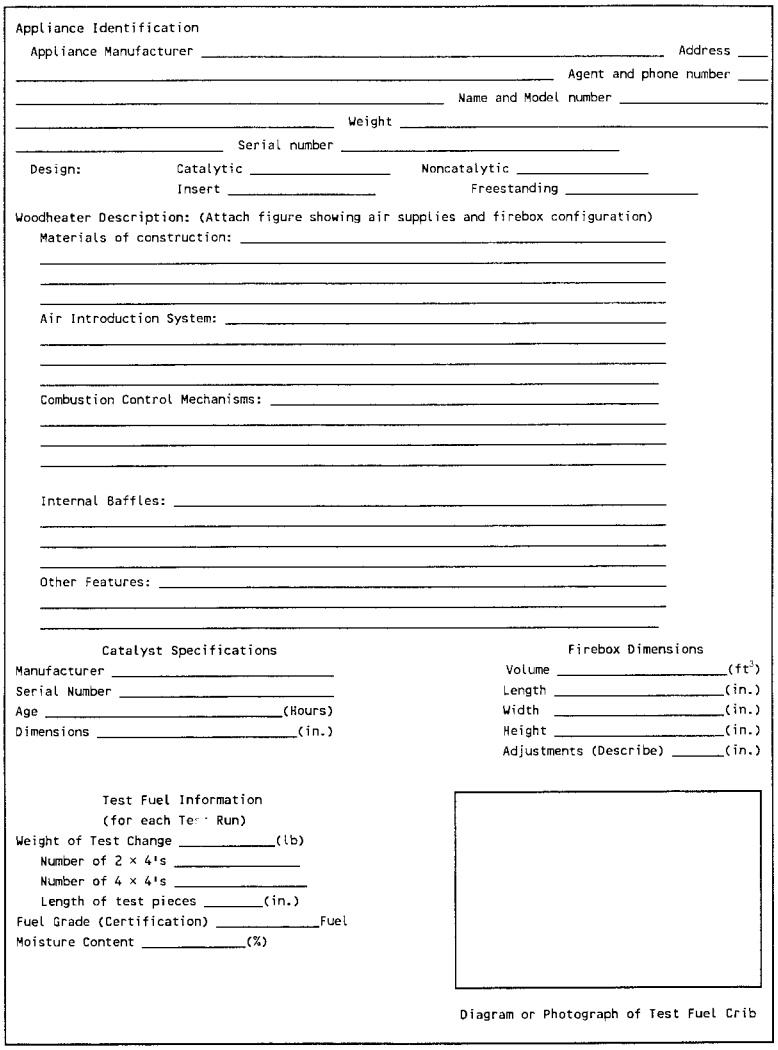
Same as Method 5G, with the addition of the following:

1. Radian Corporation. OMNI Environmental Services, Inc., Cumulative Probability for a Given Burn Rate Based on Data Generated in the CONEG and BPA Studies. Package of materials submitted to the Fifth Session of the Regulatory Negotiation Committee, July 16–17, 1986.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 28–1—BURN RATE WEIGHTED PROBABILITIES FOR CALCULATING WEIGHTED AVERAGE EMISSION RATES

Burn rate (kg/hr-dry)	Cumulative probability (P)	Burn rate (kg/hr-dry)	Cumulative probability (P)	Burn rate (kg/hr-dry)	Cumulative probability (P)
0.00	0.000	1.70	0.840	3.40	0.989
0.05	0.002	1.75	0.857	3.45	0.989
0.10	0.007	1.80	0.875	3.50	0.990
0.15	0.012	1.85	0.882	3.55	0.991
0.20	0.016	1.90	0.895	3.60	0.991
0.25	0.021	1.95	0.906	3.65	0.992
0.30	0.028	2.00	0.912	3.70	0.992
0.35	0.033	2.05	0.920	3.75	0.992
0.40	0.041	2.10	0.925	3.80	0.993
0.45	0.054	2.15	0.932	3.85	0.994
0.50	0.065	2.20	0.936	3.90	0.994
0.55	0.086	2.25	0.940	3.95	0.994
0.60	0.100	2.30	0.945	4.00	0.994
0.65	0.121	2.35	0.951	4.05	0.995
0.70	0.150	2.40	0.956	4.10	0.995
0.75	0.185	2.45	0.959	4.15	0.995
0.80	0.220	2.50	0.964	4.20	0.995
0.85	0.254	2.55	0.968	4.25	0.995
0.90	0.300	2.60	0.972	4.30	0.996
0.95	0.328	2.65	0.975	4.35	0.996
1.00	0.380	2.70	0.977	4.40	0.996
1.05	0.407	2.75	0.979	4.45	0.996
1.10	0.460	2.80	0.980	4.50	0.996
1.15	0.490	2.85	0.981	4.55	0.996
1.20	0.550	2.90	0.982	4.60	0.996
1.25	0.572	2.95	0.984	4.65	0.996
1.30	0.620	3.00	0.984	4.70	0.996
1.35	0.654	3.05	0.985	4.75	0.997
1.40	0.695	3.10	0.986	4.80	0.997
1.45	0.722	3.15	0.987	4.85	0.997
1.50	0.750	3.20	0.987	4.90	0.997
1.55	0.779	3.25	0.988	4.95	0.997
1.60	0.800	3.30	0.988	≥5.00	1.000
1.65	0.825	3.35	0.989		



Appliance Identification

Appliance Manufacturer _____ Address ____

_____ Agent and phone number ____

_____ Name and Model number _____

_____ Weight _____

_____ Serial number _____

Design: Catalytic _____ Noncatalytic _____

Insert _____ Freestanding _____

Woodheater Description: (Attach figure showing air supplies and firebox configuration)

Materials of construction: _____

_____

_____

_____

Air Introduction System: _____

_____

_____

_____

Combustion Control Mechanisms: _____

_____

_____

_____

Internal Baffles: _____

_____

_____

_____

Other Features: _____

_____

_____

Catalyst Specifications

Manufacturer _____

Serial Number _____

Age _____(Hours)

Dimensions _____(in.)

Firebox Dimensions

Volume _____(ft^3)

Length _____(in.)

Width _____(in.)

Height _____(in.)

Adjustments (Describe) _____(in.)

Test Fuel Information
(for each Test Run)

Weight of Test Change _____(lb)

Number of 2 × 4's _____

Number of 4 × 4's _____

Length of test pieces _____(in.)

Fuel Grade (Certification) _____Fuel

Moisture Content _____(%)

Diagram or Photograph of Test Fuel Crib

Figure 28-1. Wood Heater and Test Fuel Information.

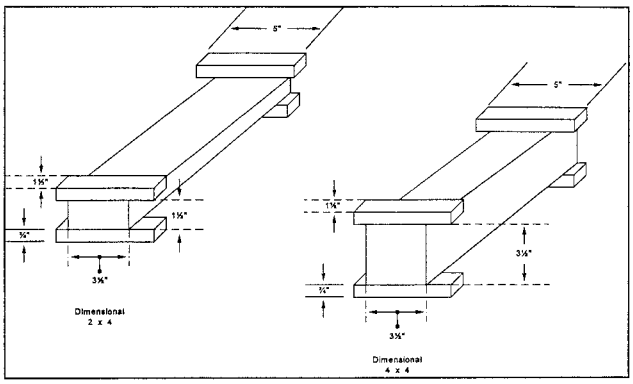


Figure 28-2. Test Fuel Spacer Dimensions.

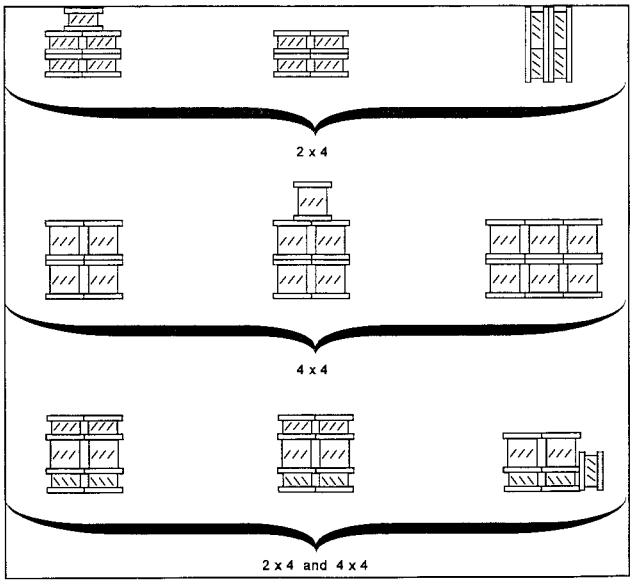


Figure 28-3. Test Fuel Crib Arrangements.

Sheet _____ of _____

Date _____

Operator _____

Sampling Method _____

Wood Heater Information

Manufacturer _____

Model _____

Primary Air Setting _____

Secondary Air Setting _____

Thermostat Setting _____

Other Settings _____

Test Run Information

Test Run No. _____

Burn Rate _____

Room Temperature before/after _____/_____

Barometric Pressure before/after _____/_____

Relative Humidity before/after _____/_____

Room Air Velocity before/after _____/_____

Surface Temp Average Pretest _____ end _____

Test Run Time (minutes)	Test Fuel Scale Reading (lb)	Surface Temperature					Catalyst Temperature		Flue Draft (in. H_2O)
							Inlet (°F)	Outlet (°F)	
(Pretest Period)									
(Test Run Start)									

Figure 28-4. Test Run Wood Heater Operation Data Sheet.

METHOD 28A—MEASUREMENT OF AIR- TO-FUEL RATIO AND MINIMUM ACHIEVABLE BURN RATES FOR WOOD-FIRED APPLIANCES

NOTE: This method does not include all or the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should also have a thorough knowledge of at least the following additional test methods: Method 3, Method 3A, Method 5H, Method 6C, and Method 28.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the measurement of air-to-fuel ratios and minimum achievable burn rates, for determining whether a wood-fired appliance is an affected facility, as specified in 40 CFR 60.530.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from a location in the stack of a wood-fired appliance while the appliance is operating at a prescribed set of conditions. The gas sample is analyzed for carbon dioxide (CO_2), oxygen (O_2), and carbon monoxide (CO). These stack gas components are measured for determining the dry molecular weight of the exhaust gas. Total moles of exhaust gas are determined stoichiometrically. Air-to-fuel ratio is determined by relating the mass of dry combustion air to the mass of dry fuel consumed.

3.0 Definitions

Same as Method 28, section 3.0, with the addition of the following:

3.1 Air-to-fuel ratio means the ratio of the mass of dry combustion air introduced into the firebox to the mass of dry fuel consumed (grams of dry air per gram of dry wood burned).

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Test Facility. Insulated Solid Pack Chimney, Platform Scale and Monitor, Test Facility Temperature Monitor, Balance, Moisture Meter, Anemometer, Barometer, Draft Gauge, Humidity Gauge, Wood Heater Flue, and Test Facility. Same as Method 28, sections 6.1, 6.2, and 6.4 to 6.12, respectively.

6.2 Sampling System. Probe, Condenser, Valve, Pump, Rate Meter, Flexible Bag, Pressure Gauge, and Vacuum Gauge. Same as Method 3, sections 6.2.1 to 6.2.8, respectively. Alternatively, the sampling system described in Method 5H, section 6.1 may be used.

6.3 Exhaust Gas Analysis. Use one or both of the following:

6.3.1 Orsat Analyzer. Same as Method 3, section 6.1.3

6.3.2 Instrumental Analyzers. Same as Method 5H, sections 6.1.3.4 and 6.1.3.5, for CO_2 and CO analyzers, except use a CO analyzer with a range of 0 to 5 percent and use a CO_2 analyzer with a range of 0 to 5 percent. Use an O_2 analyzer capable of providing a measure of O_2 in the range of 0 to 25 percent by volume at least once every 10 minutes.

7.0 Reagents and Standards

7.1 Test Fuel and Test Fuel Spacers. Same as Method 28, sections 7.1 and 7.2, respectively.

7.2 Cylinder Gases. For each of the three analyzers, use the same concentration as specified in sections 7.2.1, 7.2.2, and 7.2.3 of Method 6C.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Wood Heater Air Supply Adjustments.

8.1.1 This section describes how dampers are to be set or adjusted and air inlet ports closed or sealed during Method 28A tests. The specifications in this section are intended to ensure that affected facility determinations are made on the facility configurations that could reasonably be expected to be employed by the user. They are also intended to prevent circumvention of the standard through the addition of an air port that would often be blocked off in actual use. These specifications are based on the assumption that consumers will remove such items as dampers or other closure mechanism stops if this can be done readily with household tools; that consumers will block air inlet passages not visible during normal operation of the appliance using aluminum tape or parts generally available at retail stores; and that consumers will cap off any threaded or flanged air inlets. They also assume that air leakage around glass doors, sheet metal joints or through inlet grilles visible during normal operation of the appliance would not be further blocked or taped off by a consumer.

8.1.2 It is not the intention of this section to cause an appliance that is clearly designed, intended, and, in most normal installations, used as a fireplace to be converted into a wood heater for purposes of applicability testing. Such a fireplace would be identifiable by such features as large or multiple glass doors or panels that are not gasketed, relatively unrestricted air inlets intended, in large part, to limit smoking and fogging of glass surfaces, and other aesthetic features not normally included in wood heaters.

8.1.3 Adjustable Air Supply Mechanisms. Any commercially available flue damper, other adjustment mechanism or other air

inlet port that is designed, intended or otherwise reasonably expected to be adjusted or closed by consumers, installers, or dealers and which could restrict air into the firebox shall be set so as to achieve minimum air into the firebox (*i.e.*, closed off or set in the most closed position).

8.1.3.1 Flue dampers, mechanisms and air inlet ports which could reasonably be expected to be adjusted or closed would include:

8.1.3.1.1 All internal or externally adjustable mechanisms (including adjustments that affect the tightness of door fittings) that are accessible either before and/or after installation.

8.1.3.1.2 All mechanisms, other inlet ports, or inlet port stops that are identified in the owner's manual or in any dealer literature as being adjustable or alterable. For example, an inlet port that could be used to provide access to an outside air duct but which is identified as being closable through use of additional materials whether or not they are supplied with the facility.

8.1.3.1.3 Any combustion air inlet port or commercially available flue damper or mechanism stop, which would readily lend itself to closure by consumers who are handy with household tools by the removal of parts or the addition of parts generally available at retail stores (*e.g.*, addition of a pipe cap or plug, addition of a small metal plate to an inlet hole on a nondecorative sheet metal surface, or removal of riveted or screwed damper stops).

8.1.3.1.4 Any flue damper, other adjustment mechanisms or other air inlet ports that are found and documented in several (*e.g.*, a number sufficient to reasonably conclude that the practice is not unique or uncommon) actual installations as having been adjusted to a more closed position, or closed by consumers, installers, or dealers.

8.1.4 Air Supply Adjustments During Test. The test shall be performed with all air inlets identified under this section in the closed or most closed position or in the configuration which otherwise achieves the lowest air inlet (*i.e.*, greatest blockage).

NOTE: For the purposes of this section, air flow shall not be minimized beyond the point necessary to maintain combustion or beyond the point that forces smoke into the room.

8.1.5 Notwithstanding section 8.1.1, any flue damper, adjustment mechanism, or air inlet port (whether or not equipped with flue dampers or adjusting mechanisms) that is visible during normal operation of the appliance and which could not reasonably be closed further or blocked except through means that would significantly degrade the aesthetics of the facility (*e.g.*, through use of duct tape) will not be closed further or blocked.

8.2 Sampling System.

8.2.1 Sampling Location. Same as Method 5H, section 8.1.2.

8.2.2 Sampling System Set Up. Set up the sampling equipment as described in Method 3, section 8.1.

8.3 Wood Heater Installation, Test Facility Conditions, Wood Heater Firebox Volume, and Test Fuel Charge. Same as Method 28, sections 8.4 and 8.6 to 8.8, respectively.

8.4 Pretest Ignition. Same as Method 28, section 8.11. Set the wood heater air supply settings to achieve a burn rate in Category 1 or the lowest achievable burn rate (see section 8.1).

8.5 Test Run. Same as Method 28, section 8.12. Begin sample collection at the start of the test run as defined in Method 28, section 8.12.1.

8.5.1 Gas Analysis.

8.5.1.1 If Method 3 is used, collect a minimum of two bag samples simultaneously at a constant sampling rate for the duration of the test run. A minimum sample volume of 30 liters (1.1 ft^3) per bag is recommended.

8.5.1.2 If instrumental gas concentration measurement procedures are used, conduct the gas measurement system performance tests, analyzer calibration, and analyzer calibration error check outlined in Method 6C, sections 8.2.3, 8.2.4, 8.5, and 10.0, respectively. Sample at a constant rate for the duration of the test run.

8.5.2 Data Recording. Record wood heater operational data, test facility temperature, sample train flow rate, and fuel weight data at intervals of no greater than 10 minutes.

8.5.3 Test Run Completion. Same as Method 28, section 8.13.

9.0 Quality Control

9.1 Data Validation. The following quality control procedure is suggested to provide a check on the quality of the data.

9.1.1 Calculate a fuel factor, F_o, using Equation 28A–1 in section 12.2.

9.1.2 If CO is present in quantities measurable by this method, adjust the O_2 and CO_2 values before performing the calculation for F_o as shown in section 12.3 and 12.4.

9.1.3 Compare the calculated F_o factor with the expected F_o range for wood (1.000–1.120). Calculated F_o values beyond this acceptable range should be investigated before accepting the test results. For example, the strength of the solutions in the gas analyzer and the analyzing technique should be checked by sampling and analyzing a known concentration, such as air. If no detectable or correctable measurement error can be identified, the test should be repeated. Alternatively, determine a range of air-to-fuel ratio results that could include the correct value by using an F_o value of 1.05 and calculating a potential range of CO_2 and O_2 values. Acceptance of such results will be based on whether the calculated range includes the

exemption limit and the judgment of the Administrator.

9.2 Method 3 Analyses. Compare the results of the analyses of the two bag samples. If all the gas components (O_2, CO, and CO_2) values for the two analyses agree within 0.5 percent (*e.g.*, 6.0 percent O_2 for bag 1 and 6.5 percent O_2 for bag 2, agree within 0.5 percent), the results of the bag analyses may be averaged for the calculations in section 12. If the analysis results do not agree within 0.5 percent for each component, calculate the air-to-fuel ratio using both sets of analyses and report the results.

10.0 Calibration and Standardization

[Reserved]

11.0 Analytical Procedures

11.1 Method 3 Integrated Bag Samples. Within 4 hours after the sample collection, analyze each bag sample for percent CO_2, O_2, and CO using an Orsat analyzer as described in Method 3, section 11.0.

11.2 Instrumental Analyzers. Average the percent CO_2, CO, and O_2 values for the test run.

12.0 Data Analyses and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figure after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

12.1 Nomenclature.

M_d = Dry molecular weight, g/g-mole (lb/lb-mole).

N_T = Total gram-moles of dry exhaust gas per kg of wood burned (lb-moles/lb).

$\%CO_2$ = Percent CO_2 by volume (dry basis).

%CO = Percent CO by volume (dry basis).

$\%N_2$ = Percent N_2 by volume (dry basis).

$\%O_2$ = Percent O2 by volume (dry basis).

Y_{HC} = Assumed mole fraction of HC (dry as CH_4) = 0.0088 for catalytic wood heaters; = 0.0132 for noncatalytic wood heaters. = 0.0080 for pellet-fired wood heaters.

Y_{CO} = Measured mole fraction of CO (*e.g.*, 1 percent CO = .01 mole fraction), g/g-mole (lb/lb-mole).

Y_{CO2} = Measured mole fraction of CO_{CO2} (*e.g.*, 10 percent CO_2 = .10 mole fraction), g/g-mole (lb/lb-mole).

0.280 = Molecular weight of N_2 or CO, divided by 100.

0.320 = Molecular weight of O_2 divided by 100.

0.440 = Molecular weight of CO_2 divided by 100.

20.9 = Percent O_2 by volume in ambient air.

42.5 = Gram-moles of carbon in 1 kg of dry wood assuming 51 percent carbon by weight dry basis (.0425 lb/lb-mole).

510 = Grams of carbon in exhaust gas per kg of wood burned.

1,000 = Grams in 1 kg.

12.2 Fuel Factor. Use Equation 28A–1 to calculate the fuel factor.

$$F_o = \frac{20.9 - \%O_2}{\%CO_2} \qquad \text{Eq. 28A-1}$$

12. 3 Adjusted $\%CO_2$. Use Equation 28A–2 to adjust CO_2 values if measurable CO is present.

$$\%CO_{2(adj)} = \%CO_2 + \%CO \qquad \text{Eq. 28A-2}$$

12.4 Adjusted $\%O_2$. Use Equation 28A–3 to adjust O_2 value if measurable CO is present.

$$\%O_{2(adj)} = \%O_2 - 0.5\%CO \qquad \text{Eq. 28A-3}$$

12.5 Dry Molecular Weight. Use Equation 28A–4 to calculate the dry molecular weight of the stack gas.

$$M_d = 0.440(\%CO_2) + 0.320(\%O_2) + 0.280(\%N_2 + \%CO) \qquad \text{Eq. 28A-4}$$

NOTE: The above equation does not consider argon in air (about 0.9 percent, molecular weight of 39.9). A negative error of about 0.4 percent is introduced. Argon may

be included in the analysis using procedures subject to approval of the Administrator.

12.6 Dry Moles of Exhaust Gas. Use Equation 28A–5 to calculate the total moles of dry exhaust gas produced per kilogram of dry wood burned.

$$N_T = \frac{42.5}{\left(Y_{CO_2} + Y_{CO} + Y_{HC}\right)} \qquad \text{Eq. 28A-5}$$

12.7 Air-to-Fuel Ratio. Use Equation 28A–6 to calculate the air-to-fuel ratio on a dry mass basis.

$$A/F = \frac{\left(N_T \times M_d\right) - 510}{1{,}000} \qquad \text{Eq. 28A-6}$$

12.8 Burn Rate. Calculate the fuel burn rate as in Method 28, section 12.4.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as section 16.0 of Method 3 and section 17 of Method 5G.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

Test Method 28R for Certification and Auditing of Wood Heaters

1.0 Scope and Application

1.1 This test method applies to certification and auditing of wood-fired room heaters and fireplace inserts.

1.2 The test method covers the fueling and operating protocol for measuring particulate emissions, as well as determining burn rates, heat output and efficiency.

1.3 Particulate emissions are measured by the dilution tunnel method as specified in ASTM E2515–11 *Standard Test Method for Determination of Particulate Matter Emissions Collected in a Dilution Tunnel* (IBR, see §60.17). Upon request, four-inch filters may be used. Upon request, Teflon membrane filters or Teflon-coated glass fiber filters may be used.

2.0 Procedures

2.1 This method incorporates the provisions of ASTM E2780–10 (IBR, see §60.17) except as follows:

2.1.1 The burn rate categories, low burn rate requirement, and weightings in Method 28 shall be used.

2.1.2 The startup procedures shall be the same as in Method 28.

2.1.3 Manufacturers shall not specify a smaller volume of the firebox for testing than the full usable firebox.

2.1.4 Prior to testing, the heater must be operated for a minimum of 50 hours using a medium burn rate. The conditioning may be at the manufacturer's facility prior to the certification test. If the conditioning is at the certification test laboratory, the preburn for the first test can be included as part of the conditioning requirement.

2.2 Manufacturers may use ASTM E871–82 (reapproved 2013) (IBR, see §60.17) as an alternative to the procedures in Method 5H or Method 28 for determining total weight basis moisture in the analysis sample of particulate wood fuel.

Test Method 28WHH for Measurement of Particulate Emissions and Heating Efficiency of Wood-Fired Hydronic Heating Appliances

1.0 Scope and Application

1.1 This test method applies to wood-fired hydronic heating appliances. The units typically transfer heat through circulation of a liquid heat exchange media such as water or a water-antifreeze mixture.

1.2 The test method measures particulate emissions and delivered heating efficiency at specified heat output rates based on the appliance's rated heating capacity.

1.3 Particulate emissions are measured by the dilution tunnel method as specified in ASTM E2515–11 *Standard Test Method for Determination of Particulate Matter Emissions Collected in a Dilution Tunnel* (IBR, see §60.17). Upon request, four-inch filters may be used. Upon request, Teflon membrane filters or Teflon-coated glass fiber filters may be used. Delivered efficiency is measured by determining the heat output through measurement of the flow rate and temperature change of water circulated through a heat exchanger external to the appliance and determining the input from the mass of dry wood fuel and its higher heating value. Delivered efficiency does not attempt to account for pipeline loss.

1.4 Products covered by this test method include both pressurized and non-pressurized heating appliances intended to be fired with wood. These products are wood-fired hydronic heating appliances that the manufacturer specifies for indoor or outdoor installation. They are often connected to a heat exchanger by insulated pipes and normally include a pump to circulate heated liquid. They are used to heat structures such as homes, barns and greenhouses and can heat domestic hot water, spas or swimming pools.

1.5 Distinguishing features of products covered by this standard include:

1.5.1 Manufacturer specifies for indoor or outdoor installation.

1.5.2 A firebox with an access door for hand loading of fuel.

1.5.3 Typically, an aquastat that controls combustion air supply to maintain the liquid in the appliance within a predetermined temperature range provided sufficient fuel is available in the firebox.

1.5.4 A chimney or vent that exhausts combustion products from the appliance.

1.6 The values stated are to be regarded as the standard whether in I–P or SI units. The values given in parentheses are for information only.

2.0 Summary of Method and References

2.1 Particulate matter emissions are measured from a wood-fired hydronic heating appliance burning a prepared test fuel crib in a test facility maintained at a set of prescribed conditions. Procedures for determining burn rates, and particulate emissions rates and for reducing data are provided.

2.2 Referenced Documents

2.2.1 EPA Standards

2.2.1.1 Method 28 Certification and Auditing of Wood Heaters

2.2.2 Other Standards

2.2.2.1 ASTM E2515–11—*Standard Test Method for Determination of Particulate Matter Emissions Collected in a Dilution Tunnel* (IBR, see §60.17).

2.2.2.2 CSA–B415.1–10 *Performance Testing of Solid-Fuel-Burning Heating Appliances* (IBR, see §60.17).

3.0 Terminology

3.1 Definitions.

3.1.1 Hydronic Heating—A heating system in which a heat source supplies energy to a liquid heat exchange media such as water that is circulated to a heating load and returned to the heat source through pipes.

3.1.2 Aquastat—A control device that opens or closes a circuit to control the rate of fuel consumption in response to the temperature of the heating media in the heating appliance.

3.1.3 Delivered Efficiency—The percentage of heat available in a test fuel charge that is delivered to a simulated heating load as specified in this test method.

3.1.4 Manufacturer's Rated Heat Output Capacity—The value in Btu/hr (MJ/hr) that the manufacturer specifies that a particular model of hydronic heating appliance is capable of supplying at its design capacity as verified by testing, in accordance with Section 13.

3.1.5 Burn Rate—The rate at which test fuel is consumed in an appliance. Measured in pounds (lbs) or kilograms of wood (dry basis) per hour (lb/hr or kg/hr).

3.1.6 Firebox—The chamber in the appliance in which the test fuel charge is placed and combusted.

3.1.7 Test Fuel Charge—The collection of test fuel layers placed in the appliance at the start of the emission test run.

3.1.8 Test Fuel Layer—Horizontal arrangement of test fuel units.

3.1.9 Test Fuel Unit—One or more test fuel pieces with ¾ inch (19 mm) spacers attached to the bottom and to one side. If composed of multiple test fuel pieces, the bottom spacer may be one continuous piece.

3.1.10 Test Fuel Piece—A single 4 × 4 (4 ±0.25 inches by 4 ±0.25 inches) [100 ±6 mm by 100 ±6 mm] white or red oak wood piece cut to the length required.

3.1.11 Test Run—An individual emission test that encompasses the time required to consume the mass of the test fuel charge.

3.1.12 Overall Efficiency (SLM)—The efficiency for each test run as determined using the CSA B415.1–10 (IBR, see §60.17) stack loss method.

3.1.13 Thermopile—A device consisting of a number of thermocouples connected in series, used for measuring differential temperature.

4.0 Summary of Test Method

4.1 Dilution Tunnel. Emissions are determined using the ''dilution tunnel'' method specified in ASTM E2515–11 *Standard Test Method for Determination of Particulate Matter Emissions Collected in a Dilution Tunnel* (IBR, see §60.17). The flow rate in the dilution tunnel is maintained at a constant level throughout the test cycle and accurately measured. Samples of the dilution tunnel flow stream are extracted at a constant flow rate and drawn through high efficiency filters. The filters are dried and weighed before and after the test to determine the emissions catch and this value is multiplied by the ratio of tunnel flow to filter flow to determine the total particulate emissions produced in the test cycle.

4.2 Efficiency. The efficiency test procedure takes advantage of the fact that this type of appliance delivers heat through circulation of the heated liquid (water) from the appliance to a remote heat exchanger and back to the appliance. Measurements of the water temperature difference as it enters and exits the heat exchanger along with the measured flow rate allow for an accurate determination of the useful heat output of the appliance. The input is determined by weight of the test fuel charge, adjusted for moisture content, multiplied by the higher heating value. Additional measurements of the appliance weight and temperature at the beginning and end of a test cycle are used to correct for heat stored in the appliance. Overall efficiency (SLM) is determined using the CSA B415.1–10 (IBR, see §60.17) stack loss method for data quality assurance purposes.

4.3 Operation. Appliance operation is conducted on a hot-to-hot test cycle meaning that the appliance is brought to operating

temperature and a coal bed is established prior to the addition of the test fuel charge and measurements are made for each test fuel charge cycle. The measurements are made under constant heat draw conditions within predetermined ranges. No attempt is made to modulate the heat demand to simulate an indoor thermostat cycling on and off in response to changes in the indoor environment. Four test categories are used. These are:

4.3.1 Category I: A heat output of 15 percent or less of manufacturer's rated heat output capacity.

4.3.2 Category II: A heat output of 16 percent to 24 percent of manufacturer's rated heat output capacity.

4.3.3 Category III: A heat output of 25 percent to 50 percent of manufacturer's rated heat output capacity.

4.3.4 Category IV: Manufacturer's rated heat output capacity.

5.0 Significance and Use

5.1 The measurement of particulate matter emission rates is an important test method widely used in the practice of air pollution control.

5.1.1 These measurements, when approved by state or federal agencies, are often required for the purpose of determining compliance with regulations and statutes.

5.1.2 The measurements made before and after design modifications are necessary to demonstrate the effectiveness of design changes in reducing emissions and make this standard an important tool in manufacturers' research and development programs.

5.2 Measurement of heating efficiency provides a uniform basis for comparison of product performance that is useful to the consumer. It is also required to relate emissions produced to the useful heat production.

5.3 This is a laboratory method and is not intended to be fully representative of all actual field use. It is recognized that users of hand-fired, wood-burning equipment have a great deal of influence over the performance of any wood-burning appliance. Some compromises in realism have been made in the interest of providing a reliable and repeatable test method.

6.0 Test Equipment

6.1 Scale. A platform scale capable of weighing the appliance under test and associated parts and accessories when completely filled with water to an accuracy of ±1.0 pound (±0.5 kg).

6.2 Heat Exchanger. A water-to-water heat exchanger capable of dissipating the expected heat output from the system under test.

6.3 Water Temperature Difference Measurement. A Type—T 'special limits' thermopile with a minimum of 5 pairs of junctions shall be used to measure the temperature difference in water entering and leaving the heat exchanger. The temperature difference measurement uncertainty of this type of thermopile is equal to or less than ±0.50 °F (±0.25 °C). Other temperature measurement methods may be used if the temperature difference measurement uncertainty is equal to or less than ±0.50 °F (±0.25 °C).

6.4 Water Flow Meter. A water flow meter shall be installed in the inlet to the load side of the heat exchanger. The flow meter shall have an accuracy of ±1 percent of measured flow.

6.4.1 Optional—Appliance Side Water Flow Meter. A water flow meter with an accuracy of ±1 percent of the flow rate is recommended to monitor supply side water flow rate.

6.5 Optional Recirculation Pump. Circulating pump used during test to prevent stratification of liquid being heated.

6.6 Water Temperature Measurement—Thermocouples or other temperature sensors to measure the water temperature at the inlet and outlet of the load side of the heat exchanger. Must meet the calibration requirements specified in section 10.1.

6.7 Wood Moisture Meter—Calibrated electrical resistance meter capable of measuring test fuel moisture to within 1 percent moisture content. Must meet the calibration requirements specified in section 10.4.

6.8 Flue Gas Temperature Measurement—Must meet the requirements of CSA B415.1–10 (IBR, see §60.17), clause 6.2.2.

6.9 Test Room Temperature Measurement—Must meet the requirements of CSA B415.1–10 (IBR, see §60.17), clause 6.2.1.

6.10 Flue Gas Composition Measurement—Must meet the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 6.3.1 through 6.3.3.

7.0 Safety

7.1 These tests involve combustion of wood fuel and substantial release of heat and products of combustion. The heating system also produces large quantities of very hot water and the potential for steam production and system pressurization. Appropriate precautions must be taken to protect personnel from burn hazards and respiration of products of combustion.

8.0 Sampling, Test Specimens and Test Appliances

8.1 Test specimens shall be supplied as complete appliances including all controls and accessories necessary for installation in the test facility. A full set of specifications and design and assembly drawings shall be provided when the product is to be placed under certification of a third-party agency. The manufacturer's written installation and operating instructions are to be used as a

guide in the set-up and testing of the appliance.

9.0 Preparation of Test Equipment

9.1 The appliance is to be placed on a scale capable of weighing the appliance fully loaded with a resolution of ±1.0 lb (0.5 kg).

9.2 The appliance shall be fitted with the type of chimney recommended or provided by the manufacturer and extending to 15 ±0.5 feet (4.6 ±0.15 m) from the upper surface of the scale. If no flue or chimney system is recommended or provided by the manufacturer, connect the appliance to a flue of a diameter equal to the flue outlet of the appliance. The flue section from the appliance flue collar to 8 ±0.5 feet above the scale shall be single wall stove pipe and the remainder of the flue shall be double wall insulated class A chimney.

9.3 Optional Equipment Use

9.3.1 A recirculation pump may be installed between connections at the top and bottom of the appliance to minimize thermal stratification if specified by the manufacturer. The pump shall not be installed in such a way as to change or affect the flow rate between the appliance and the heat exchanger.

9.3.2 If the manufacturer specifies that a thermal control valve or other device be installed and set to control the return water temperature to a specific set point, the valve or other device shall be installed and set per the manufacturer's written instructions.

9.4 Prior to filling the tank, weigh and record the appliance mass.

9.5 Heat Exchanger

9.5.1 Plumb the unit to a water-to-water heat exchanger with sufficient capacity to draw off heat at the maximum rate anticipated. Route hoses, electrical cables, and instrument wires in a manner that does not influence the weighing accuracy of the scale as indicated by placing dead weights on the platform and verifying the scale's accuracy.

9.5.2 Locate thermocouples to measure the water temperature at the inlet and outlet of the load side of the heat exchanger.

9.5.3 Install a thermopile meeting the requirements of section 6.3 to measure the water temperature difference between the inlet and outlet of the load side of the heat exchanger.

9.5.4 Install a calibrated water flow meter in the heat exchanger load side supply line. The water flow meter is to be installed on the cooling water inlet side of the heat exchanger so that it will operate at the temperature at which it is calibrated.

9.5.5 Place the heat exchanger in a box with 2 in. (50 mm) of expanded polystyrene (EPS) foam insulation surrounding it to minimize heat losses from the heat exchanger.

9.5.6 The reported efficiency and heat output rate shall be based on measurements made on the load side of the heat exchanger.

9.5.7 Temperature instrumentation per section 6.6 shall be installed in the appliance outlet and return lines. The average of the outlet and return water temperature on the supply side of the system shall be considered the average appliance temperature for calculation of heat storage in the appliance (TF_{avg} and TI_{avg}). Installation of a water flow meter in the supply side of the system is optional.

9.6 Fill the system with water. Determine the total weight of the water in the appliance when the water is circulating. Verify that the scale indicates a stable weight under operating conditions. Make sure air is purged properly.

10.0 Calibration and Standardization

10.1 Water Temperature Sensors. Temperature measuring equipment shall be calibrated before initial use and at least semi-annually thereafter. Calibrations shall be in compliance with National Institute of Standards and Technology (NIST) Monograph 175, Standard Limits of Error.

10.2 Heat Exchanger Load Side Water Flow Meter.

10.2.1 The heat exchanger load side water flow meter shall be calibrated within the flow range used for the test run using NIST traceable methods. Verify the calibration of the water flow meter before and after each test run and at least once during each test run by comparing the water flow rate indicated by the flow meter to the mass of water collected from the outlet of the heat exchanger over a timed interval. Volume of the collected water shall be determined based on the water density calculated from section 13, Eq. 8, using the water temperature measured at the flow meter. The uncertainty in the verification procedure used shall be 1 percent or less. The water flow rate determined by the collection and weighing method shall be within 1 percent of the flow rate indicated by the water flow meter.

10.3 Scales. The scales used to weigh the appliance and test fuel charge shall be calibrated using NIST traceable methods at least once every 6 months.

10.4 Moisture Meter. The moisture meter shall be calibrated per the manufacturer's instructions and checked before each use.

10.5 Flue Gas Analyzers—In accordance with CSA B415.1–10 (IBR, see §60.17), clause 6.8.

11.0 Conditioning

11.1 Prior to testing, the appliance is to be operated for a minimum of 50 hours using a medium heat draw rate. The conditioning may be at the manufacturer's facility prior to the certification test. If the conditioning is at the certification test laboratory, the pre-burn for the first test can be included as

part of the conditioning requirement. If conditioning is included in pre-burn, then the appliance shall be aged with fuel meeting the specifications outlined in sections 12.2 with a moisture content between 19 and 25 percent on a dry basis. Operate the appliance at a medium burn rate (Category II or III) for at least 10 hours for noncatalytic appliances and 50 hours for catalytic appliances. Record and report hourly flue gas exit temperature data and the hours of operation. The aging procedure shall be conducted and documented by a testing laboratory.

12.0 Procedure

12.1 Appliance Installation. Assemble the appliance and parts in conformance with the manufacturer's written installation instructions. Clean the flue with an appropriately sized, wire chimney brush before each certification test series.

12.2 Fuel. Test fuel charge fuel shall be red (*Quercus ruba L.*) or white (*Quercus alba*) oak 19 to 25 percent moisture content on a dry basis. Piece length shall be 80 percent of the firebox depth rounded down to the nearest 1 inch (25mm) increment. For example, if the firebox depth is 46 inches (1168mm) the 4 × 4 piece length would be 36 inches (46 inches × 0.8 = 36.8 inches rounded down to 36 inches). Pieces are to be placed in the firebox parallel to the longest firebox dimension. For fireboxes with sloped surfaces that create a non-uniform firebox length, the piece length shall be adjusted for each layer based on 80 percent of the length at the level where the layer is placed. Pieces are to be spaced ¾ inches (19 mm) apart on all faces. The first fuel layer may be assembled using fuel units consisting of multiple 4 × 4s consisting of single pieces with bottom and side spacers of 3 or more pieces if needed for a stable layer. The second layer may consist of fuel units consisting of no more than two pieces with spacers attached on the bottom and side. The top two layers of the fuel charge must consist of single pieces unless the fuel charge is only three layers. In that instance only the top layer must consist of single units. Three-quarter inch (19 mm) by 1.5 inch (38 mm) spacers shall be attached to the bottom of piece to maintain a ¾ inch (19 mm) separation. When a layer consists of two or more units of 4 × 4s an additional ¾ inch (19 mm) thick by 1.5 inch (38 mm) wide spacer shall be attached to the vertical face of each end of one 4 × 4, such that the ¾ inch (19 mm) space will be maintained when two 4 × 4 units or pieces are loaded side by side. In cases where a layer contains an odd number of 4 × 4s one piece shall not be attached, but shall have spacers attached in a manner that will provide for the ¾ inch (19 mm) space to be maintained (See Figure 1). Spacers shall be attached perpendicular to the length of the 4 × 4s such that the edge of the spacer is 1 ±0.25 inch from the end of the 4 × 4s in the previous layers. Spacers shall be red or white oak and will be attached with either nails (non-galvanized), brads or oak dowels. The use of kiln-dried wood is not allowed.

12.2.1 Using a fuel moisture meter as specified in section 6.7 of the test method, determine the fuel moisture for each test fuel piece used for the test fuel load by averaging at least five fuel moisture meter readings measured parallel to the wood grain. Penetration of the moisture meter insulated electrodes for all readings shall be ¼ the thickness of the fuel piece or 19 mm (¾ in.), whichever is lesser. One measurement from each of three sides shall be made at approximately 3 inches from each end and the center. Two additional measurements shall be made centered between the other three locations. Each individual moisture content reading shall be in the range of 18 to 28 percent on a dry basis. The average moisture content of each piece of test fuel shall be in the range of 19 to 25 percent. It is not required to measure the moisture content of the spacers. Moisture shall not be added to previously dried fuel pieces except by storage under high humidity conditions and temperature up to 100 °F. Fuel moisture shall be measured within 4 hours of using the fuel for a test.

12.2.2 Firebox Volume. Determine the firebox volume in cubic feet. Firebox volume shall include all areas accessible through the fuel loading door where firewood could reasonably be placed up to the horizontal plane defined by the top of the loading door. A drawing of the firebox showing front, side and plan views or an isometric view with interior dimensions shall be provided by the manufacturer and verified by the laboratory. Calculations for firebox volume from computer aided design (CAD) software programs are acceptable and shall be included in the test report if used. If the firebox volume is calculated by the laboratory the firebox drawings and calculations shall be included in the test report.

12.2.3 Test Fuel Charge. Test fuel charges shall be determined by multiplying the firebox volume by 10 pounds (4.54 kg) per ft^3 (28L), or a higher load density as recommended by the manufacturer's printed operating instructions, of wood (as used wet weight). Select the number of pieces of standard fuel that most nearly match this target weight. This is the standard fuel charge for all tests. For example, if the firebox loading area volume is 10 ft^3 (280L) and the firebox depth is 46 inches (1168 mm), test fuel charge target is 100 lbs (45 kg) minimum and the piece length is 36 inches (914 mm). If eight 4 × 4s, 36 inches long weigh 105 lbs (48 kg), use 8 pieces for each test fuel charge. All test fuel charges will be of the same configuration.

12.3 Sampling Equipment. Prepare the particulate emission sampling equipment as defined by ASTM E2515–11 *Standard Test Method for Determination of Particulate Matter Emissions Collected in a Dilution Tunnel* (IBR, see §60.17). Upon request, four-inch filters may be used. Upon request, Teflon membrane filters or Teflon-coated glass fiber filters may be used.

12.4 Appliance Startup. The appliance shall be fired with wood fuel of any species, size and moisture content at the laboratories' discretion to bring it up to operating temperature. Operate the appliance until the water is heated to the upper operating control limit and has cycled at least two times. Then remove all unburned fuel, zero the scale and verify the scales accuracy using dead weights.

12.4.1 Pretest Burn Cycle. Reload appliance with oak wood and allow it to burn down to the specified coal bed weight. The pretest burn cycle fuel charge weight shall be within ±10 percent of the test fuel charge weight. Piece size and length shall be selected such that charcoalization is achieved by the time the fuel charge has burned down to the required coal bed weight. Pieces with a maximum thickness of approximately 2 inches have been found to be suitable. Charcoalization is a general condition of the test fuel bed evidenced by an absence of large pieces of burning wood in the coal bed and the remaining fuel pieces being brittle enough to be broken into smaller charcoal pieces with a metal poker. Manipulations to the fuel bed prior to the start of the test run are to be done to achieve charcoalization while maintaining the desired heat output rate. During the pre-test burn cycle and at least one hour prior to starting the test run, adjust water flow to the heat exchanger to establish the target heat draw for the test. For the first test run the heat draw rate shall be equal to the manufacturer's rated heat output capacity.

12.4.1.1 Allowable Adjustments. Fuel addition or subtractions, and coal bed raking shall be kept to a minimum but are allowed up to 15 minutes prior to the start of the test run. For the purposes of this method, coal bed raking is the use of a metal tool (poker) to stir coals, break burning fuel into smaller pieces, dislodge fuel pieces from positions of poor combustion, and check for the condition of charcoalization. Record all adjustments to and additions or subtractions of fuel, and any other changes to the appliance operations that occur during pretest ignition period. During the 15-minute period prior to the start of the test run, the wood heater loading door shall not be open more than a total of 1 minute. Coal bed raking is the only adjustment allowed during this period.

12.4.2 Coal Bed Weight. The appliance is to be loaded with the test fuel charge when the coal bed weight is between 10 percent and 20 percent of the test fuel charge weight. Coals may be raked as necessary to level the coal bed but may only be raked and stirred once between 15 to 20 minutes prior to the addition of the test fuel charge.

12.5 Test Runs. For all test runs, the return water temperature to the hydronic heater must be equal to or greater than 120 °F. Aquastat or other heater output control device settings that are adjustable shall be set using manufacturer specifications, either as factory set or in accordance with the owner's manual, and shall remain the same for all burn categories.

Complete a test run in each heat output rate category, as follows:

12.5.1 Test Run Start. Once the appliance is operating normally and the pretest coal bed weight has reached the target value per section 12.4.2, tare the scale and load the full test charge into the appliance. Time for loading shall not exceed 5 minutes. The actual weight of the test fuel charge shall be measured and recorded within 30 minutes prior to loading. Start all sampling systems.

12.5.1.1 Record all water temperatures, differential water temperatures and water flow rates at time intervals of one minute or less.

12.5.1.2 Record particulate emissions data per the requirements of ASTM E2515 (IBR, see §60.17).

12.5.1.3 Record data needed to determine overall efficiency (SLM) per the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 6.2.1, 6.2.2, 6.3, 8.5.7, 10.4.3 (a), 10.4.3(f), and 13.7.9.3

12.5.1.3.1 Measure and record the test room air temperature in accordance with the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 6.2.1, 8.5.7 and 10.4.3 (g).

12.5.1.3.2 Measure and record the flue gas temperature in accordance with the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 6.2.2, 8.5.7 and 10.4.3 (f).

12.5.1.3.3 Determine and record the carbon monoxide (CO) and carbon dioxide (CO_2) concentrations in the flue gas in accordance with CSA B415.1–10 (IBR, see §60.17), clauses 6.3, 8.5.7 and 10.4.3 (i) and (j).

12.5.1.3.4 Measure and record the test fuel weight per the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 8.5.7 and 10.4.3 (h).

12.5.1.3.5 Record the test run time per the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 10.4.3 (a).

12.5.1.4 Monitor the average heat output rate on the load side of the heat exchanger. If the heat output rate gets close to the upper or lower limit of the target range (±5 percent) adjust the water flow through the heat exchanger to compensate. Make changes as infrequently as possible while maintaining the target heat output rate. The first test run shall be conducted at the Category IV heat output rate to validate that

the appliance is capable of producing the manufacturer's rated heat output capacity.

12.5.2 Test Fuel Charge Adjustment. It is acceptable to adjust the test fuel charge (*i.e.*, reposition) once during a test run if more than 60 percent of the initial test fuel charge weight has been consumed and more than 10 minutes have elapsed without a measurable (1 lb or 0. 5 kg) weight change while the operating control is in the demand mode. The time used to make this adjustment shall be less than 60 seconds.

12.5.3 Test Run Completion. The test run is completed when the remaining weight of the test fuel charge is 0.0 lb (0.0 kg). End the test run when the scale has indicated a test fuel charge weight of 0.0 lb (0.0 kg) or less for 30 seconds.

12.5.3.1 At the end of the test run, stop the particulate sampling train and overall efficiency (SLM) measurements, and record the run time, and all final measurement values.

12.5.4 Heat Output Capacity Validation. The first test run must produce a heat output rate that is within 10 percent of the manufacturer's rated heat output capacity (Category IV) throughout the test run and an average heat output rate within 5 percent of the manufacturer's rated heat output capacity. If the appliance is not capable of producing a heat output within these limits, the manufacturer's rated heat output capacity is considered not validated and testing is to be terminated. In such cases, the tests may be restarted using a lower heat output capacity if requested by the manufacturer.

12.5.5 Additional Test Runs. Using the manufacturer's rated heat output capacity as a basis, conduct a test for additional heat output categories as specified in section 4.3. It is not required to run these tests in any particular order.

12.5.6 Alternative Heat Output Rate for Category I. If an appliance cannot be operated in the Category I heat output range due to stopped combustion, two test runs shall be conducted at heat output rates within Category II, provided that the completed test run burn rate is no greater than the burn rate expected in home use. If this rate cannot be achieved, the test is not valid.

When the alternative heat output rate is used, the weightings for the weighted averages indicated in Table 2 shall be the average of the Category I and II weightings and shall be applied to both Category II results. The two completed runs in Category II will be deemed to meet the requirement for runs completed in both Category I and Category II. Appliances that are not capable of operation within Category II (<25 percent of maximum) cannot be evaluated by this test method. The test report must include full documentation and discussion of the attempted runs, completed rums and calculations.

12.5.6.1 Stopped Fuel Combustion. Evidence that an appliance cannot be operated at a Category I heat output rate due to stopped fuel combustion shall include documentation of two or more attempts to operate the appliance in burn rate Category I and fuel combustion has stopped prior to complete consumption of the test fuel charge. Stopped fuel combustion is evidenced when an elapsed time of 60 minutes or more has occurred without a measurable (1 lb or 0.5 kg) weight change in the test fuel charge while the appliance operating control is in the demand mode. Report the evidence and the reasoning used to determine that a test in burn rate Category I cannot be achieved. For example, two unsuccessful attempts to operate at an output rate of 10 percent of the rated output capacity are not sufficient evidence that burn rate Category I cannot be achieved. Note that section 12.5.6 requires that the completed test run burn rate can be no greater than the burn rate expected in home use. If this rate cannot be achieved, the test is not valid.

12.5.7 Appliance Overheating. Appliances shall be capable of operating in all heat output categories without overheating to be rated by this test method. Appliance overheating occurs when the rate of heat withdrawal from the appliance is lower than the rate of heat production when the unit control is in the idle mode. This condition results in the water in the appliance continuing to increase in temperature well above the upper limit setting of the operating control. Evidence of overheating includes: 1 hour or more of appliance water temperature increase above the upper temperature set-point of the operating control, exceeding the temperature limit of a safety control device (independent from the operating control), boiling water in a non-pressurized system or activation of a pressure or temperature relief valve in a pressurized system.

12.6 Additional Test Runs. The testing laboratory may conduct more than one test run in each of the heat output categories specified in section 4.3.1. If more than one test run is conducted at a specified heat output rate, the results from at least two-thirds of the test runs in that heat output rate category shall be used in calculating the weighted average emission rate (See section 14.1.14). The measurement data and results of all test runs shall be reported regardless of which values are used in calculating the weighted average emission rate.

13.0 Calculation of Results

13.1 Nomenclature

E_T—Total particulate emissions for the full test run as determined per ASTM E2515–11 (IBR, see §60.17) in grams

$E_{g/MJ}$—Emissions rate in grams per megajoule of heat output
$E_{lb/mmBtu}$ output—Emissions rate in pounds per million Btu of heat output
$E_{g/kg}$—Emissions factor in grams per kilogram of dry fuel burned
$E_{g/hr}$—Emissions factor in grams per hour
HHV—Higher heating value of fuel = 8600 Btu/lb (19.990 MJ/kg)
LHV—Lower heating value of fuel = 7988 Btu/lb (18.567 MJ/kg)
ΔT—Temperature difference between water entering and exiting the heat exchanger
Q_{out}—Total heat output in BTU's (megajoules)
Q_{in}—Total heat input available in test fuel charge in BTU (megajoules)
M—Mass flow rate of water in lb/min (kg/min)
V_i—Volume of water indicated by a totalizing flow meter at the ith reading in gallons (liters)
V_f—Volumetric flow rate of water in heat exchange system in gallons per minute (liters/min)
Θ—Total length of test run in hours
ti—Data sampling interval in minutes
η_{del}—Delivered heating efficiency in percent
Fi—Weighting factor for heat output category i (See Table 2)
T1—Temperature of water at the inlet on the supply side of the heat exchanger
T2—Temperature of the water at the outlet on the supply side of the heat exchanger
T3—Temperature of water at the inlet to the load side of the heat exchanger
TIavg—Average temperature of the appliance and water at start of the test

$$TI_{avg} - (T1 + T2)/2 \text{ at the start of the test, °F} \quad \text{Eq.1}$$

TF_{avg}—Average temperature of the appliance and water at the end of the test

$$TF_{avg} - (T1 + T2)/2 \text{ at the end of the test, °F} \quad \text{Eq.2}$$

MC—Fuel moisture content in percent dry basis
MC_i—Average moisture content of individual 4 × 4 fuel pieces in percent dry basis
MC_{sp}—Moisture content of spacers assumed to be 10 percent dry basis
σ—Density of water in pounds per gallon
C_p—Specific heat of water in Btu/lb, °F
C_{steel}—Specific heat of steel (0.1 Btu/lb, °F)
W_{fuel}—Fuel charge weight in pounds (kg)
W_i—Weight of individual fuel 4 × 4 pieces in pounds (kg)
W_{sp}—Weight of all spacers used in a fuel load in pounds (kg)
W_{app}—Weight of empty appliance in pounds
W_{wa}—Weight of water in supply side of the system in pounds

13.2 After the test is completed, determine the particulate emissions E_T in accordance with ASTM E2515–11 (IBR, see §60.17).

13.3 Determine Average Fuel Load Moisture Content

$$MC_{Ave} = [[\ \Sigma\ W_i \text{ x } MC_i\ ] + [\ W_{sp} \text{ x } MC_{sp}\ ]] \div W_{fuel}, \% \quad \text{Eq. 3}$$

13.4 Determine heat input

$$Q_{in} = (W_{fuel}/(1+(MC/100))) \text{ x HHV, BTU} \quad \text{Eq. 4}$$

$$Q_{in\ LHV} = (W_{fuel}/(1+(MC/100))) \text{ x LHV, BTU} \quad \text{Eq. 5}$$

13.5 Determine Heat Output and Efficiency

13.5.1 Determine heat output as:

Q_{out} = Σ [Heat output determined for each sampling time interval] + Change in heat stored in the appliance.

$$Q_{out} = \left[\sum (C_{pi} \bullet \Delta T_i \bullet \dot{M}_i \bullet t_i)\right] + (W_{app} \bullet C_{Steel} + C_{pa} W_{water}) \bullet (TF_{avg} - TI_{avg}), \text{ BTU} \quad \text{Eq. 6}$$

NOTE: The subscript (i) indicates the parameter value for sampling time interval t_i.

M_i = Mass flow rate = gal/min × density of water (lb/gal) = lb/min

$$M_i = V_{fi} \cdot \sigma_i, \text{ lb/min} \quad \text{Eq. 7}$$

$$\Sigma_i = (62.56 + (-.0003413 \text{ x } T3_i) + (-.00006225 \text{ x } T3_i^2)) \, 0.1337, \text{ lbs/gal} \quad \text{Eq. 8}$$

$$C_p = 1.0014 + (-.000003485 \text{ x } T3_i) \text{ Btu/lb, } ^oF \quad \text{Eq. 9}$$

C_{steel} = 0.1 Btu/lb, ° F

$$C_{pa} = 1.0014 + (-.000003485 \text{ X } (TI_{avg} + TF_{avg})/2), \text{ Btu/lb-}^oF \quad \text{Eq. 10}$$

$$V_{fi} = (V_i - V_{i-1})/(t_i - t_{i-1}), \text{ gal/min} \quad \text{Eq. 11}$$

NOTE: Vi is the total water volume at the end of interval i and Vi-1 is the total water volume at the beginning of the time interval. This calculation is necessary when a totalizing type water meter is used.

13.5.2 Determine heat output rate as:

$$\text{Heat Output Rate} = Q_{out}/\Theta, \text{ BTU/hr} \quad \text{Eq. 12}$$

13.5.3 Determine emission rates and emission factors as:

$$E_{g/MJ} = E_T/(Q_{out} \text{ x } 0.001055), \text{ g/MJ} \quad \text{Eq. 13}$$

$$E_{lb/MM \text{ BTU output}} = (E_T/453.59)/(Q_{output} \text{ x } 10^{-6}), \text{ lb/mmBtu Out} \quad \text{Eq. 14}$$

$$E_{g/kg} = E_T/(W_{fuel}/(1+MC/100)), \text{ g/dry kg} \quad \text{Eq, 15}$$

$$E_{g/hr} = E_T/\Theta, \text{ g/hr} \quad \text{Eq. 16}$$

13.5.4 Determine delivered efficiency as:

$$\eta_{del} = (Q_{out}/Q_{in}) \times 100, \% \quad \text{Eq. 17}$$

$$\eta_{del\ LHV} = (Q_{out}/Q_{in\ LHV}) \times 100, \% \quad \text{Eq. 18}$$

13.5.5 Determine η_{SLM}—Overall Efficiency (SLM) using Stack Loss

For determination of the average overall thermal efficiency (η_{SLM}) for the test run, use the data collected over the full test run and the calculations in accordance with CSA B415.1–10 (IBR, see §60.17), clause 13.7 except for 13.7.2 (e), (f), (g), and (h), use the following average fuel properties for oak: percent C = 50.0, percent H = 6.6, percent O = 43.2, percent ash = 0.2 percent. The averaging period for determination of efficiency by the stack loss method allows averaging over 10 minute time periods for flue gas temperature, flue gas CO_2, and flue gas CO for the determination of the efficiency. However, under some cycling conditions the ''on'' period may be short relative to this 10 minute period. For this reason, during cycling operation the averaging period for these parameters may not be longer than the burner on period divided by 10. The averaging period need not be shorter than one minute. During the off period, under cycling operation, the averaging periods specified may be used. Where short averaging times are used, however, the averaging period for fuel consumption may still be at 10 minutes. This average wood consumption rate shall be applied to all of the smaller time intervals included.

13.5.5.1 Whenever the CSA B415.1–10 (IBR, see §60.17) overall efficiency is found to be lower than the overall efficiency based on load side measurements, as determined by Eq. 16 of this method, section 14.1.7 of the test report must include a discussion of the reasons for this result.

13.6 Weighted Average Emissions and Efficiency

13.6.1 Determine the weighted average emission rate and delivered efficiency from the individual tests in the specified heat output categories. The weighting factors (Fi) are derived from an analysis of ASHRAE bin data which provides details of normal building heating requirements in terms of percent of design capacity and time in a particular capacity range—or ''bin''—over the course of a heating season. The values used in this method represent an average of data from several cities located in the northern United States.

$$\text{Weighted average delivered efficiency: } \eta_{avg} = \Sigma\, \eta_i \times F_i, \% \quad \text{Eq. 19}$$

$$\text{Weighted average emissions: } E_{avg} = \Sigma E_i \times F_i, \% \quad \text{Eq. 20}$$

13.7 Average Heat Output ($Q_{out\text{-}8hr}$) and Efficiency (($\eta_{avg\text{-}8hr}$) for 8 hour burn time.

13.7.1 Units tested under this standard typically require infrequent fuelling, 8 to 12 hours intervals being typical. Rating unit's based on an average output sustainable over an 8 hour duration will assist consumers in appropriately sizing units to match the theoretical heat demand of their application.

13.7.2 Calculations:

$$Q_{out\text{-}8hr} = X1 + \{ (8 - Y1) \times [(X2 - X1) / (Y2 - Y1)] \}, \% \quad \text{Eq. 21}$$

$$\eta_{avg\text{-}8hr} = \eta_{del1} + \{ (8 - Y1) \times [(\eta_{del2} - \eta_{del1}) / (Y2 - Y1)] \}, \% \quad \text{Eq. 22}$$

Where:

Y1 = Test duration just above 8 hrs
Y2 = Test duration just below 8 hrs
X1 = Actual load for duration Y1
X2 = Actual load for duration Y2
η_{del1} = Average delivered efficiency for duration Y1
η_{del2} = Average delivered efficiency for duration Y2

13.7.2.1 Determine the test durations and actual load for each category as recorded in Table 1A.

13.7.2.2 Determine the data point that has the nearest duration greater than 8 hrs.

X1 = Actual load,
Y1 = Test duration, and
η_{del1} = Average delivered efficiency for this data point

13.7.2.3 Determine the data point that has the nearest duration less than 8 hours.

X2 = Actual load,
Y2 = Test duration, and
η_{del2} = Average delivered efficiency for this data point

13.7.2.4 Example:

CATEGORY ACTUAL LOAD DURATION
[Category Actual Load Duration ηdel]

	(Btu/Hr)	(Hr)	(%)
1	15,000	10.2	70.0
2	26,000	8.4	75.5
3	50,000	6.4	80.1
4	100,000	4.7	80.9

Category 2 duration is just above 8 hours, therefore: X1 = 26,000 Btu/hr, η_{del1} = 75.5% and Y1 = 8.4 hrs

Category 3 duration is just below 8 hours, therefore: X2 = 50,000 Btu/hr, η_{del2} = 80.1% and Y2 = 6.4 hrs

$Q_{out\text{-}8hr}$ = 26,000 + {(8—8.4) × [(50,000—26,000)/(6.4—8.4)]} = 30,800 BTU/hr

$\eta_{avg\text{-}8hr}$ = 75.5 + {(8—8.4) × [(80.1—75.5)/(6.4—8.4)]} = 76.4%

13.8 Carbon Monoxide Emissions

For each minute of the test period, the carbon monoxide emission rate shall be calculated as:

$$CO_{g/min} = Q_{std} \cdot CO_s \cdot 3.30\text{x}10^{-5} \qquad \text{Eq. 23}$$

Total CO emissions for each of the three test periods (CO_{-1}, CO_{-2}, CO_{-3}) shall be calculated as the sum of the emission rates for each of the 1 minute intervals.

Total CO emission for the test run, CO_T, shall be calculated as the sum of CO_{-1}, CO_{-2}, and CO_{-3}.

14.0 Report

14.1.1 The report shall include the following.

14.1.2 Name and location of the laboratory conducting the test.

14.1.3 A description of the appliance tested and its condition, date of receipt and dates of tests.

14.1.4 A statement that the test results apply only to the specific appliance tested.

14.1.5 A statement that the test report shall not be reproduced except in full, without the written approval of the laboratory.

14.1.6 A description of the test procedures and test equipment including a schematic or other drawing showing the location of all required test equipment. Also, a description of test fuel sourcing, handling and storage practices shall be included.

14.1.7 Details of deviations from, additions to or exclusions from the test method, and their data quality implications on the test results (if any), as well as information on specific test conditions, such as environmental conditions.

14.1.8 A list of participants and observers present for the tests.

14.1.9 Data and drawings indicating the fire box size and location of the fuel charge.

14.1.10 Drawings and calculations used to determine firebox volume.

14.1.11 Information for each test run fuel charge including piece size, moisture content, and weight.

14.1.12 All required data for each test run shall be provided in spreadsheet format. Formulae used for all calculations shall be accessible for review.

14.1.13 Test run duration for each test.

14.1.14 Calculated results for delivered efficiency at each burn rate and the weighted average emissions reported as total emissions in grams, pounds per mm Btu of delivered heat, grams per MJ of delivered heat, grams per kilogram of dry fuel and grams per hour. Results shall be reported for each heat output category and the weighted average.

14.1.15 Tables 1A, 1B, 1C and Table 2 must be used for presentation of results in test reports.

14.1.16 A statement of the estimated uncertainty of measurement of the emissions and efficiency test results.

14.1.17 Raw data, calibration records, and other relevant documentation shall be retained by the laboratory for a minimum of 7 years.

15.0 Precision and Bias

15.1 Precision—It is not possible to specify the precision of the procedure in Method 28WHH because the appliance operation and

fueling protocols and the appliances themselves produce variable amounts of emissions and cannot be used to determine reproducibility or repeatability of this measurement method.

15.2 Bias—No definitive information can be presented on the bias of the procedure in Method 28WHH for measuring solid fuel burning hydronic heater emissions because no material having an accepted reference value is available.

16.0 Keywords

16.1 Solid fuel, hydronic heating appliances, wood-burning hydronic heaters.

Table 1A. Data Summary Part A

						O	W_{fuel}	MC_{ave}	Q_{in}	Q_{out}
Category	Run No	Load % Capacity	Target Load	Actual Load	Act Load	Test Duration	Wood Wt	Wood Moisture	Heat Input	Heat Output
			BTU/hr	BTU/hr	% of max	hrs	lb	% DB	BTU	BTU
I		< 15% of max								
II		16-24% of max								
III		25-50% of max								
IV		Max capacity								

Table 1B. Data Summary Part B

			T2 Min	E-	E	E	$E_{g/hr}$	$E_{g/kg}$	η_{del}	η_{SLM}
Category	Run No	Load % Capacity	Min Return Water Temp	Total PM Emissions	PM Output Based	PM Output Based	PM Rate	PM Factor	Delivered Efficiency	Stack Loss Efficiency
			°F	g	$lb_{MMBTU\ Out}$	g/MJ	g/hr	g/kg	%	%
I		< 15% of max								
II		16-24% of max								
III		25-50% of max								
IV		Max capacity								

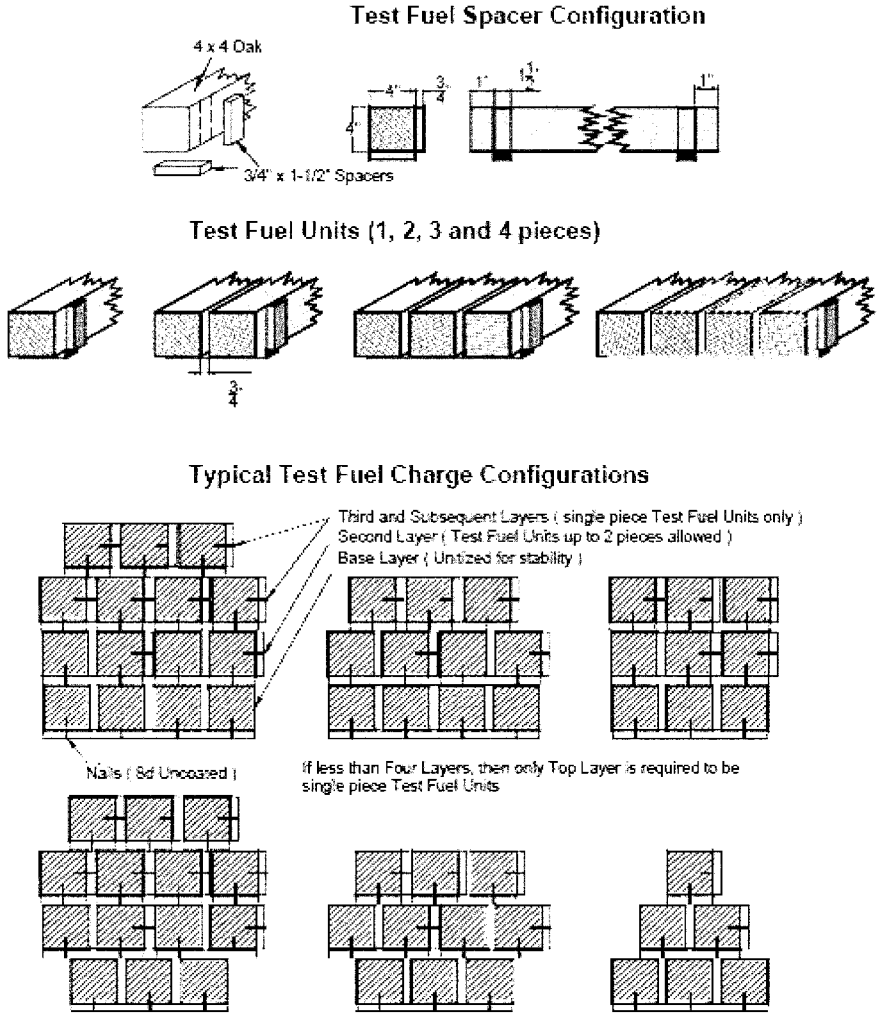
Table 1C: Hangtag Information (optional)

MANUFACTURER:			
MODEL NUMBER:			
MAXIMUM OUTPUT RATING:	Qmax		BTU/HR
ANNUAL EFFICIENCY RATING:	N_{avg}		(Using higher heating value)
PARTICLE EMISSIONS:	E_{avg}		GRAMS/HR (average)
			LBS/MILLION BTU OUTPUT
CARBON MONOXIDE:	COg/MIN		GRAMS/MINUTE

Table 2. Annual Weighting

Category	Weighting Factor (F_i)	$\eta_{del,i} \times F_i$	$E_{g/MJ,i} \times F_i$	$E_{g/kg,i} \times F_i$	$E_{lb/mmBtu\ Out,i} \times F_i$	$E_{g/hr,i} \times F_i$
I	0.437					
II	0.238					
III	0.275					
IV	0.050					
Totals	1.000					

Figure 1. Typical Test Fuel Piece



TEST METHOD 28WHH FOR CERTIFICATION OF CORD WOOD-FIRED HYDRONIC HEATING APPLIANCES WITH PARTIAL THERMAL STORAGE: MEASUREMENT OF PARTICULATE MATTER (PM) AND CARBON MONOXIDE (CO) EMISSIONS AND HEATING EFFICIENCY OF WOOD-FIRED HYDRONIC HEATING APPLIANCES WITH PARTIAL THERMAL STORAGE

1.0 Scope and Application

1.1 This test method applies to wood-fired hydronic heating appliances with heat storage external to the appliance. The units typically transfer heat through circulation of a liquid heat exchange media such as water or a water-antifreeze mixture. Throughout this document, the term ''water'' will be used to denote any of the heat transfer liquids approved for use by the manufacturer.

1.2 The test method measures PM and CO emissions and delivered heating efficiency at specified heat output rates referenced against the appliance's rated heating capacity as specified by the manufacturer and verified under this test method.

1.3 PM emissions are measured by the dilution tunnel method as specified in the EPA Method 28WHH and the standards referenced therein with the exceptions noted in section 12.5.9. Delivered efficiency is measured by determining the fuel energy input and appliance output. Heat output is determined through measurement of the flow rate and temperature change of water circulated through a heat exchanger external to the appliance and the increase in energy of the external storage. Heat input is determined from the mass of dry wood fuel and its higher heating value (HHV). Delivered efficiency does not attempt to account for pipeline loss.

1.4 Products covered by this test method include both pressurized and non-pressurized hydronic heating appliances intended to be fired with wood and for which the manufacturer specifies for indoor or outdoor installation. The system, which includes the heating appliance and external storage, is commonly connected to a heat exchanger by insulated pipes and normally includes a pump to circulate heated liquid. These systems are used to heat structures such as homes, barns and greenhouses. They also provide heat for domestic hot water, spas and swimming pools.

1.5 Distinguishing features of products covered by this standard include:

1.5.1 The manufacturer specifies the application for either indoor or outdoor installation.

1.5.2 A firebox with an access door for hand loading of fuel.

1.5.3 Typically an aquastat mounted as part of the appliance that controls combustion air supply to maintain the liquid in the appliance within a predetermined temperature range provided sufficient fuel is available in the firebox. The appliance may be equipped with other devices to control combustion.

1.5.4 A chimney or vent that exhausts combustion products from the appliance.

1.5.5 A liquid storage system, typically water, which is not large enough to accept all of the heat produced when a full load of wood is burned and the storage system starts a burn cycle at 125 °F.

1.5.6 The heating appliances require external thermal storage and these units will only be installed as part of a system which includes thermal storage. The manufacturer specifies the minimum amount of thermal storage required. However, the storage system shall be large enough to ensure that the boiler (heater) does not cycle, slumber, or go into an off-mode when operated in a Category III load condition (See section 4.3).

1.6 The values stated are to be regarded as the standard whether in I–P or SI units. The values given in parentheses are for information only.

2.0 Summary of Method and References

2.1 PM and CO emissions are measured from a wood–fired hydronic heating appliance burning a prepared test fuel charge in a test facility maintained at a set of prescribed conditions. Procedures for determining heat output rates, PM and CO emissions, and efficiency and for reducing data are provided.

2.2 Referenced Documents

2.2.1 EPA Standards

2.2.1.1 Method 28 Certification and Auditing of Wood Heaters

2.2.1.2 Method 28WHH Measurement of Particulate Emissions and Heating Efficiency of Wood-Fired Hydronic Heating Appliances and the Standards Referenced therein.

2.2.2 Other Standards

2.2.2.1 CSA–B415.1–10 *Performance Testing of Solid-Fuel-Burning Heating Appliances*

3.0 Terminology

3.1 Definitions

3.1.1 Hydronic Heating—A heating system in which a heat source supplies energy to a liquid heat exchange media such as water that is circulated to a heating load and returned to the heat source through pipes.

3.1.2 Aquastat—A control device that opens or closes a circuit to control the rate of fuel consumption in response to the temperature of the heating media in the heating appliance.

3.1.3 Delivered Efficiency—The percentage of heat available in a test fuel charge that is delivered to a simulated heating load or the storage system as specified in this test method.

3.1.4 Emission Factor—The emission of a pollutant expressed in mass per unit of energy (typically) output from the boiler/heater.

3.1.5 Emission Index—The emission of a pollutant expressed in mass per unit mass of fuel used.

3.1.6 Emission Rate—The emission of a pollutant expressed in mass per unit time

3.1.7 Manufacturer's Rated Heat Output Capacity—The value in Btu/hr (MJ/hr) that the manufacturer specifies that a particular model of hydronic heating appliance is capable of supplying at its design capacity as verified by testing, in accordance with section 12.5.4.

3.1.8 Heat Output Rate—The average rate of energy output from the appliance during a specific test period in Btu/hr (MJ/hr).

3.1.9 Firebox—The chamber in the appliance in which the test fuel charge is placed and combusted.

3.1.10 NIST—National Institute of Standards and Technology.

3.1.11 Test Fuel Charge—The collection of test fuel placed in the appliance at the start of the emission test run.

3.1.12 Test Run—An individual emission test which encompasses the time required to consume the mass of the test fuel charge. The time of the test run also considers the time for the energy to be drawn from the thermal storage.

3.1.13 Test Run Under ''Cold-to-Cold'' Condition—Under this test condition the test fuel is added into an empty chamber along with kindling and ignition materials (paper). The boiler/heater at the start of this test is typically 125° to 130 °F.

3.1.14 Test Run Under ''Hot-to-Hot'' Condition—Under this test condition the test fuel is added onto a still-burning bed of charcoals produced in a pre-burn period. The boiler/heater water is near its operating control limit at the start of the test.

3.1.15 Overall Efficiency, also known as Stack Loss Efficiency—The efficiency for each test run as determined using the CSA B415.1–10 (IBR, see §60.17) stack loss method (SLM).

3.1.16 Phases of a Burn Cycle—The ''startup phase'' is defined as the period from the start of the test until 15 percent of the test fuel charge is consumed. The ''steady-state phase'' is defined as the period from the end of the startup phase to a point at which 80 percent of the test fuel charge is consumed. The ''end phase'' is defined as the time from the end of the steady-state period to the end of the test.

3.1.17 Thermopile—A device consisting of a number of thermocouples connected in series, used for measuring differential temperature.

3.1.18 Slumber Mode—This is a mode in which the temperature of the water in the boiler/heater has exceeded the operating control limit and the control has changed the boiler/heater fan speed, dampers, and/or other operating parameters to minimize the heat output of the boiler/heater.

4.0 Summary of Test Method

4.1 Dilution Tunnel. Emissions are determined using the ''dilution tunnel'' method specified in EPA Method 28WHH and the standards referenced therein. The flow rate in the dilution tunnel is maintained at a constant level throughout the test cycle and accurately measured. Samples of the dilution tunnel flow stream are extracted at a constant flow rate and drawn through high efficiency filters. The filters are dried and weighed before and after the test to determine the emissions collected and this value is multiplied by the ratio of tunnel flow to filter flow to determine the total particulate emissions produced in the test cycle.

4.2 Efficiency. The efficiency test procedure takes advantage of the fact that this type of system delivers heat through circulation of the heated liquid (water) from the system to a remote heat exchanger (*e.g.* baseboard radiators in a room) and back to the system. Measurements of the cooling water temperature difference as it enters and exits the test system heat exchanger along with the measured flow rate allow for an accurate determination of the useful heat output of the appliance. Also included in the heat output is the change in the energy content in the storage system during a test run. Energy input to the appliance during the test run is determined by weight of the test fuel charge, adjusted for moisture content, multiplied by the higher heating value. Additional measurements of the appliance weight and temperature at the beginning and end of a test cycle are used to correct for heat stored in the appliance. Overall efficiency (SLM) is determined using the CSA B415.1–10 (IBR, see §60.17) stack loss method for data quality assurance purposes.

4.3 Operation. Four test categories are defined for use in this method. These are:

4.3.1 Category I: A heat output of 15 percent or less of manufacturer's rated heat output capacity.

4.3.2 Category II: A heat output of 16 percent to 24 percent of manufacturer's rated heat output capacity.

4.3.3 Category III: A heat output of 25 percent to 50 percent of manufacturer's rated heat output capacity.

4.3.4 Category IV: Manufacturer's Rated Heat Output Capacity. These heat output categories refer to the output from the system by way of the load heat exchanger installed for the test. The output from just the boiler/heater part of the system may be higher for all or part of a test, as part of this boiler/heater output goes to storage.

For the Category III and IV runs, appliance operation is conducted on a hot-to-hot test

cycle meaning that the appliance is brought to operating temperature and a coal bed is established prior to the addition of the test fuel charge and measurements are made for each test fuel charge cycle. The measurements are made under constant heat draw conditions within pre-determined ranges. No attempt is made to modulate the heat demand to simulate an indoor thermostat cycling on and off in response to changes in the indoor environment.

For the Category I and II runs, the unit is tested with a ''cold start.'' At the manufacturer's option, the Category II and III runs may be waived and it may be assumed that the particulate emission values and efficiency values determined in the startup, steady-state, and end phases of Category I are applicable in Categories II and III for the purpose of determining the annual averages in lb/mmBtu and g/MJ (See section 13). For the annual average in g/hr, the length of time for stored heat to be drawn from thermal storage shall be determined for the test load requirements of the respective category.

All test operations and measurements shall be conducted by personnel of the laboratory responsible for the submission of the test report.

5.0 Significance and Use

5.1 The measurement of particulate matter emission and CO rates is an important test method widely used in the practice of air pollution control.

5.1.1 These measurements, when approved by state or federal agencies, are often required for the purpose of determining compliance with regulations and statutes.

5.1.2 The measurements made before and after design modifications are necessary to demonstrate the effectiveness of design changes in reducing emissions and make this standard an important tool in manufacturers' research and development programs.

5.2 Measurement of heating efficiency provides a uniform basis for comparison of product performance that is useful to the consumer. It is also required to relate emissions produced to the useful heat production.

5.3 This is a laboratory method and is not intended to be fully representative of all actual field use. It is recognized that users of hand-fired, wood-burning equipment have a great deal of influence over the performance of any wood-burning appliance. Some compromises in realism have been made in the interest of providing a reliable and repeatable test method.

6.0 Test Equipment

6.1 Scale. A platform scale capable of weighing the boiler/heater under test and associated parts and accessories when completely filled with water to an accuracy of ±1.0 pound (±0.5 kg) and a readout resolution of ±0.2 pound (±0.1 kg).

6.2 Heat Exchanger. A water-to-water heat exchanger capable of dissipating the expected heat output from the system under test.

6.3 Water Temperature Difference Measurement. A Type—T 'special limits' thermopile with a minimum of 5 pairs of junctions shall be used to measure the temperature difference in water entering and leaving the heat exchanger. The temperature difference measurement uncertainty of this type of thermopile is equal to or less than ±0.50 °F (±0.25 °C). Other temperature measurement methods may be used if the temperature difference measurement uncertainty is equal to or less than ±0.50 °F (±0.25 °C). This measurement uncertainty shall include the temperature sensor, sensor well arrangement, piping arrangements, lead wire, and measurement/recording system. The response time of the temperature measurement system shall be less than half of the time interval at which temperature measurements are recorded.

6.4 Water Flow Meter. A water flow meter shall be installed in the inlet to the load side of the heat exchanger. The flow meter shall have an accuracy of ±1 percent of measured flow.

6.4.1 Optional—Appliance Side Water Flow Meter. A water flow meter with an accuracy of ±1 percent of the flow rate is recommended to monitor supply side water flow rate.

6.5 Optional Recirculation Pump. Circulating pump used during test to prevent stratification, in the boiler/heater, of liquid being heated.

6.6 Water Temperature Measurement. Thermocouples or other temperature sensors to measure the water temperature at the inlet and outlet of the load side of the heat exchanger must meet the calibration requirements specified in 10.1 of this method.

6.7 Lab Scale. For measuring the moisture content of wood slices as part of the overall wood moisture determination. Accuracy of ±0.01 pounds.

6.8 Flue Gas Temperature Measurement. Must meet the requirements of CSA B415.1–10 (IBR, see §60.17), clause 6.2.2.

6.9 Test Room Temperature Measurement. Must meet the requirements of CSA B415.1–10 (IBR, see §60.17), clause 6.2.1.

6.10 Flue Gas Composition Measurement. Must meet the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 6.3.1 through 6.3.3.

6.11 Dilution Tunnel CO Measurement. In parallel with the flue gas composition measurements, the CO concentration in the dilution tunnel shall also be measured and reported at time intervals not to exceed one minute. This analyzer shall meet the zero and span drift requirements of CSA B415.1–10 (IBR, see §60.17). In addition the measurement repeatability shall be better than ±15

ppm over the range of CO levels observed in the dilution tunnel.

7.0 Safety

7.1 These tests involve combustion of wood fuel and substantial release of heat and products of combustion. The heating system also produces large quantities of very hot water and the potential for steam production and system pressurization. Appropriate precautions must be taken to protect personnel from burn hazards and respiration of products of combustion.

8.0 Sampling, Test Specimens and Test Appliances

8.1 Test specimens shall be supplied as complete appliances, as described in marketing materials, including all controls and accessories necessary for installation in the test facility. A full set of specifications, installation and operating instructions, and design and assembly drawings shall be provided when the product is to be placed under certification of a third-party agency. The manufacturer's written installation and operating instructions are to be used as a guide in the set-up and testing of the appliance and shall be part of the test record.

8.2 The size, connection arrangement, and control arrangement for the thermal storage shall be as specified in the manufacturer's documentation. It is not necessary to use the specific storage system that the boiler/heater will be marketed with. However, the capacity of the system used in the test cannot be greater than that specified as the minimum allowable for the boiler/heater.

8.3 All system control settings shall be the as-shipped, default settings. These default settings shall be the same as those communicated in a document to the installer or end user. These control settings and the documentation of the control settings as to be provided to the installer or end user shall be part of the test record.

8.4 Where the manufacturer defines several alternatives for the connection and loading arrangement, one shall be defined in the appliance documentation as the default or standard installation. It is expected that this will be the configuration for use with a simple baseboard heating system. This is the configuration to be followed for these tests. The manufacturer's documentation shall define the other arrangements as optional or alternative arrangements.

9.0 Preparation of Test Equipment

9.1 The appliance is to be placed on a scale capable of weighing the appliance fully loaded with a resolution of ±0.2 lb (0.1 kg).

9.2 The appliance shall be fitted with the type of chimney recommended or provided by the manufacturer and extending to 15 ±0.5 feet (4.6 ±0.15 m) from the upper surface of the scale. If no flue or chimney system is recommended or provided by the manufacturer, connect the appliance to a flue of a diameter equal to the flue outlet of the appliance. The flue section from the appliance flue collar to 8 ±0.5 feet above the scale shall be single wall stove pipe and the remainder of the flue shall be double wall insulated class A chimney.

9.3 Optional Equipment Use

9.3.1 A recirculation pump may be installed between connections at the top and bottom of the appliance to minimize thermal stratification if specified by the manufacturer. The pump shall not be installed in such a way as to change or affect the flow rate between the appliance and the heat exchanger.

9.3.2 If the manufacturer specifies that a thermal control valve or other device be installed and set to control the return water temperature to a specific set point, the valve or other device shall be installed and set per the manufacturer's written instructions.

9.4 Prior to filling the boiler/heater with water, weigh and record the appliance mass.

9.5 Heat Exchanger

9.5.1 Plumb the unit to a water-to-water heat exchanger with sufficient capacity to draw off heat at the maximum rate anticipated. Route hoses and electrical cables and instrument wires in a manner that does not influence the weighing accuracy of the scale as indicated by placing dead weights on the platform and verifying the scale's accuracy.

9.5.2 Locate thermocouples to measure the water temperature at the inlet and outlet of the load side of the heat exchanger.

9.5.3 Install a thermopile (or equivalent instrumentation) meeting the requirements of section 6.3 to measure the water temperature difference between the inlet and outlet of the load side of the heat exchanger

9.5.4 Install a calibrated water flow meter in the heat exchanger load side supply line. The water flow meter is to be installed on the cooling water inlet side of the heat exchanger so that it will operate at the temperature at which it is calibrated.

9.5.5 Place the heat exchanger in a box with 2 in. (50 mm) of expanded polystyrene (EPS) foam insulation surrounding it to minimize heat losses from the heat exchanger.

9.5.6 The reported efficiency and heat output rate shall be based on measurements made on the load side of the heat exchanger.

9.5.7 Temperature instrumentation per section 6.6 shall be installed in the appliance outlet and return lines. The average of the outlet and return water temperature on the supply side of the system shall be considered the average appliance temperature for calculation of heat storage in the appliance (TF_{avg} and TI_{avg}). Installation of a water flow meter in the supply side of the system is optional.

9.6 Storage Tank. The storage tank shall include a destratification pump as illustrated in Figure 1. The pump will draw from the bottom of the tank and return to the top as illustrated. Temperature sensors (TS1 and TS2 in Figure 1) shall be included to measure the temperature in the recirculation loop. The valve plan in Figure 1 allows the tank recirculation loop to operate and the boiler/heater-to-heat exchanger loop to operate at the same time but in isolation. This would typically be done before the start of a test or following completion of a test to determine the end of test average tank temperature. The nominal flow rate in the storage tank recirculation loop can be estimated based on pump manufacturers' performance curves and any significant restriction in the recirculation loop.

9.7 Fill the system with water. Determine the total weight of the water in the appliance when the water is circulating. Verify that the scale indicates a stable weight under operating conditions. Make sure air is purged properly.

10.0 Calibration and Standardization

10.1 Water Temperature Sensors. Temperature measuring equipment shall be calibrated before initial use and at least semiannually thereafter. Calibrations shall be in compliance with National Institute of Standards and Technology (NIST) Monograph 175, Standard Limits of Error.

10.2 Heat Exchanger Load Side Water Flow Meter.

10.2.1 The heat exchanger load side water flow meter shall be calibrated within the flow range used for the test run using NIST-traceable methods. Verify the calibration of the water flow meter before and after each test run and at least once during each test run by comparing the water flow rate indicated by the flow meter to the mass of water collected from the outlet of the heat exchanger over a timed interval. Volume of the collected water shall be determined based on the water density calculated from section 13, Eq. 12, using the water temperature measured at the flow meter. The uncertainty in the verification procedure used shall be 1 percent or less. The water flow rate determined by the collection and weighing method shall be within 1 percent of the flow rate indicated by the water flow meter.

10.3 Scales. The scales used to weigh the appliance and test fuel charge shall be calibrated using NIST-traceable methods at least once every 6 months.

10.4 Flue Gas Analyzers—In accordance with CSA B415.1–10 (IBR, see §60.17), clause 6.8.

11.0 Conditioning

11.1 Prior to testing, an appliance is to be operated for a minimum of 50 hours using a medium heat draw rate. The conditioning may be at the manufacturer's facility prior to the certification test. If the conditioning is at the certification test laboratory, the pre-burn for the first test can be included as part of the conditioning requirement. If conditioning is included in pre-burn, then the appliance shall be aged with fuel meeting the specifications outlined in section 12.2 with a moisture content between 19 and 25 percent on a dry basis. Operate the appliance at a medium heat output rate (Category II or III) for at least 10 hours for non-catalytic appliances and 50 hours for catalytic appliances. Record and report hourly flue gas exit temperature data and the hours of operation. The aging procedure shall be conducted and documented by a testing laboratory.

12.0 Procedure

12.1 Appliance Installation. Assemble the appliance and parts in conformance with the manufacturer's written installation instructions. Clean the flue with an appropriately sized, wire chimney brush before each certification test series.

12.2 Fuel. Test fuel charge fuel shall be red (*Quercus ruba L.*) or white (*Quercus Alba*) oak 19 to 25 percent moisture content on a dry basis. Piece length shall be 80 percent of the firebox depth rounded down to the nearest 1 inch (25mm) increment. For example, if the firebox depth is 46 inches (1168mm) the piece length would be 36 inches (46 inches × 0.8 = 36.8 inches, rounded down to 36 inches). Pieces are to be placed in the firebox parallel to the longest firebox dimension. For fireboxes with sloped surfaces that create a non-uniform firebox length, the piece length shall be adjusted for each layer based on 80 percent of the length at the level where the layer is placed. The test fuel shall be cord wood with cross section dimensions and weight limits as defined in CSA B415.1–10 (IBR, see §60.17), section 8.3, Table 4. The use of dimensional lumber is not allowed.

12.2.1 Select three pieces of cord wood from the same batch of wood as the test fuel and the same weight as the average weight of the pieces in the test load ±1.0 lb. From each of these three pieces, cut three slices. Each slice shall be ½ inch to ¾ inch thick. One slice shall be cut across the center of the length of the piece. The other two slices shall be cut half way between the center and the end. Immediately measure the mass of each piece in pounds. Dry each slice in an oven at 220 °F for 24 hours or until no further weight change occurs. The slices shall be arranged in the oven so as to provide separation between faces. Remove from the oven and measure the mass of each piece again as soon as practical, in pounds.

The moisture content of each slice, on a dry basis, shall be calculated as:

$$MC_{slice} = 100 \cdot \frac{(W_{SliceWet} - W_{SliceDry})}{W_{SliceDry}}$$

Where:

$W_{SliceWet}$ = weight of the slice before drying in pounds

$W_{SliceDry}$ = weight of the slice after drying in pounds

MC_{Slice} = moisture content of the slice in % dry basis

The average moisture content of the entire test load (MC) shall be determined using Eq. 6. Each individual slice shall have a moisture content in the range of 18 percent to 28 percent on a dry basis. The average moisture content for the test fuel load shall be in the range of 19 percent to 25 percent. Moisture shall not be added to previously dried fuel pieces except by storage under high humidity conditions and temperature up to 100 °F. Fuel moisture measurement shall begin within 4 hours of using the fuel batch for a test. Use of a pin-type meter to estimate the moisture content prior to a test is recommended.

12.2.2 Firebox Volume. Determine the firebox volume in cubic feet. Firebox volume shall include all areas accessible through the fuel loading door where firewood could reasonably be placed up to the horizontal plane defined by the top of the loading door. A drawing of the firebox showing front, side and plan views or an isometric view with interior dimensions shall be provided by the manufacturer and verified by the laboratory. Calculations for firebox volume from computer aided design (CAD) software programs are acceptable and shall be included in the test report if used. If the firebox volume is calculated by the laboratory the firebox drawings and calculations shall be included in the test report.

12.2.3 Test Fuel charge. Test fuel charges shall be determined by multiplying the firebox volume by 10 pounds (4.54 kg) per ft^3 (28L), or a higher load density as recommended by the manufacturer's printed operating instructions, of wood (as used wet weight). Select the number of pieces of cord wood that most nearly match this target weight. However, the test fuel charge cannot be less than the target of 10 pounds (4.54 kg) per ft^3 (28L).

12.3 Sampling Equipment. Prepare the particulate emission sampling equipment as defined by EPA Method 28WHH and the standards referenced therein.

12.4 Appliance Startup. The appliance shall be fired with wood fuel of any species, size and moisture content, at the laboratory's discretion, to bring it up to operating temperature. Operate the appliance until the water is heated to the upper operating control limit and has cycled at least two times. Then remove all unburned fuel, zero the scale and verify the scales accuracy using dead weights.

12.4.1 Startup Procedure for Category III and IV Test Runs, ''Hot-to-Hot.''

12.4.1.1 Pretest t Burn Cycle. Following appliance startup (section 12.4), reload appliance with oak cord wood and allow it to burn down to the specified coal bed weight. The pre-test burn cycle fuel charge weight shall be within ±10 percent of the test fuel charge weight. Piece size and length shall be selected such that charcoalization is achieved by the time the fuel charge has burned down to the required coal bed weight. Pieces with a maximum thickness of approximately 2 inches have been found to be suitable. Charcoalization is a general condition of the test fuel bed evidenced by an absence of large pieces of burning wood in the coal bed and the remaining fuel pieces being brittle enough to be broken into smaller charcoal pieces with a metal poker. Manipulations to the fuel bed prior to the start of the test run are to be done to achieve charcoalization while maintaining the desired heat output rate. During the pre-test burn cycle and at least one hour prior to starting the test run, adjust water flow to the heat exchanger to establish the target heat draw for the test. For the first test run the heat draw rate shall be equal to the manufacturer's rated heat output capacity.

12.4.1.2 Allowable Adjustments. Fuel addition or subtractions, and coal bed raking shall be kept to a minimum but are allowed up to 15 minutes prior to the start of the test run. For the purposes of this method, coal bed raking is the use of a metal tool (poker) to stir coals, break burning fuel into smaller pieces, dislodge fuel pieces from positions of poor combustion, and check for the condition of charcoalization. Record all adjustments to and additions or subtractions of fuel, and any other changes to the appliance operations that occur during pretest ignition period. During the 15-minute period prior to the start of the test run, the wood heater loading door shall not be open more than a total of 1 minute. Coal bed raking is the only adjustment allowed during this period.

12.4.1.3 Coal Bed Weight. The appliance is to be loaded with the test fuel charge when the coal bed weight is between 10 percent and 20 percent of the test fuel charge weight. Coals may be raked as necessary to level the coal bed but may only be raked and stirred

once between 15 to 20 minutes prior to the addition of the test fuel charge.

12.4.1.4 Storage. The Category III and IV test runs may be done either with or without the thermal storage. If thermal storage is used, the initial temperature of the storage must be 125 °F or greater at the start of the test. The storage may be heated during the pre-test burn cycle or it may be heated by external means. If thermal storage is used, prior to the start of the test run, the storage tank destratification pump, shown in Figure 1, shall be operated until the total volume pumped exceeds 1.5 times the tank volume and the difference between the temperature at the top and bottom of the storage tank (TS_1 and TS_2) is less than 1 °F. These two temperatures shall then be recorded to determine the starting average tank temperature. The total volume pumped may be based on the nominal flow rate of the destratification pump (See section 9.6). If the Category III and IV runs are done with storage, it is recognized that during the last hour of the pre-burn cycle the storage tank must be mixed to achieve a uniform starting temperature and cannot receive heat from the boiler/heater during this time. During this time period, the boiler/heater might cycle or go into a steady reduced output mode. (Note—this would happen, for example, in a Category IV run if the actual maximum output of the boiler/heater exceed the manufacturer's rated output.) A second storage tank may be used temporarily to enable the boiler/heater to operate during this last hour of the pre-burn period as it will during the test period. The temperature of this second storage tank is not used in the calculations but the return water to the boiler/heater (after mixing device if used) must be 125 °F or greater.

12.4.2 Startup Procedure for Category I and II Test Runs, ''Cold-to-Cold.''

12.4.2.1 Initial Temperatures. This test shall be started with both the boiler/heater and the storage at a minimum temperature of 125 °F. The boiler/heater maximum temperature at the start of this test shall be 135 °F. The boiler/heater and storage may be heated through a pre-burn or it may be heated by external means.

12.4.2.2 Firebox Condition at Test Start. Prior to the start of this test remove all ash and charcoal from the combustion chamber(s). The loading of the test fuel and kindling should follow the manufacturer's recommendations, subject to the following constraints: Up to 10 percent kindling and paper may be used which is in addition to the fuel load. Further, up to 10 percent of the fuel load (*i.e.*, included in the 10 lb/ft^3) may be smaller than the main fuel. This startup fuel shall still be larger than 2 inches.

12.4.2.3 Storage. The Category I and II test runs shall be done with thermal storage. The initial temperature of the storage must be 125 °F or greater at the start of the test. The storage may be heated during the pre-test burn cycle or it may be heated by external means. Prior to the start of the test run, the storage tank destratification pump, shown in Figure 1, shall be operated until the total volume pumped exceeds 1.5 times the tank volume and the difference between the temperature at the top and bottom of the storage tank (TS_1 and TS_2) is less than 1 °F. These two temperatures shall then be recorded to determine the starting average tank temperature. The total volume pumped may be based on the nominal flow rate of the destratification pump (See section 9.6).

12.5 Test Runs. For all test runs, the return water temperature to the hydronic heater must be equal to or greater than 120 °F (this is lower than the initial tank temperature to allow for any pipeline losses). Where the storage system is used, flow of water from the boiler/heater shall be divided between the storage tank and the heat exchanger such that the temperature change of the circulating water across the heat exchanger shall be 30 ±5 °F, averaged over the entire test run. This is typically adjusted using the system valves.

Complete a test run in each heat output rate category, as follows:

12.5.1 Test Run Start. For Category III and IV runs: Once the appliance is operating normally and the pretest coal bed weight has reached the target value per section 12.4.1, tare the scale and load the full test charge into the appliance. Time for loading shall not exceed 5 minutes. The actual weight of the test fuel charge shall be measured and recorded within 30 minutes prior to loading. Start all sampling systems.

For Category I and II runs: Once the appliance has reached the starting temperature, tare the scale and load the full test charge, including kindling into the appliance. The actual weight of the test fuel charge shall be measured and recorded within 30 minutes prior to loading. Light the fire following the manufacturer's written normal startup procedure. Start all sampling systems.

12.5.1.1 Record all water temperatures, differential water temperatures and water flow rates at time intervals of one minute or less.

12.5.1.2 Record particulate emissions data per the requirements of EPA Method 28WHH and the standards referenced therein.

12.5.1.3 Record data needed to determine overall efficiency (SLM) per the requirements of CSA B415.1–10 (IBR, see §60.17) clauses 6.2.1, 6.2.2, 6.3, 8.5.7, 10.4.3(a), 10.4.3(f), and 13.7.9.3

12.5.1.3.1 Measure and record the test room air temperature in accordance with the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 6.2.1, 8.5.7 and 10.4.3(g).

12.5.1.3.2 Measure and record the flue gas temperature in accordance with the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 6.2.2, 8.5.7 and 10.4.3(f).

12.5.1.3.3 Determine and record the carbon monoxide (CO) and carbon dioxide (CO_2) concentrations in the flue gas in accordance with CSA B415.1–10 (IBR, see §60.17), clauses 6.3, 8.5.7 and 10.4.3(i) and (j).

12.5.1.3.4 Measure and record the test fuel weight per the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 8.5.7 and 10.4.3(h).

12.5.1.3.5 Record the test run time per the requirements of CSA B415.1–10 (IBR, see §60.17), clause 10.4.3(a).

12.5.1.3.6 Record and document all settings and adjustments, if any, made to the boiler/heater as recommended/required by manufacturer's instruction manual for different combustion conditions or heat loads. These may include temperature setpoints, under and over-fire air adjustment, or other adjustments that could be made by an operator to optimize or alter combustion. All such settings shall be included in the report for each test run.

12.5.1.4 Monitor the average heat output rate on the load side of the heat exchanger based on water temperatures and flow. If the heat output rate over a 10 minute averaging period gets close to the upper or lower limit of the target range (±5 percent), adjust the water flow through the heat exchanger to compensate. Make changes as infrequently as possible while maintaining the target heat output rate. The first test run shall be conducted at the Category IV heat output rate to validate that the appliance is capable of producing the manufacturer's rated heat output capacity.

12.5.2 Test Fuel Charge Adjustment. It is acceptable to adjust the test fuel charge (*i.e.*, reposition) once during a test run if more than 60 percent of the initial test fuel charge weight has been consumed and more than 10 minutes have elapsed without a measurable (1 lb or 0.5 kg) weight change while the operating control is in the demand mode. The time used to make this adjustment shall be less than 60 seconds.

12.5.3 Test Run Completion. For the Category III and IV, ''hot-to-hot'' test runs, the test run is completed when the remaining weight of the test fuel charge is 0.0 lb (0.0 kg). ($W_{FuelBurned} = W_{fuel}$) End the test run when the scale has indicated a test fuel charge weight of 0.0 lb (0.0 kg) or less for 30 seconds.

For the Category I and II ''cold-to-cold'' test runs, the test run is completed; and the end of a test is defined at the first occurrence of any one of the following:

(a) The remaining weight of the test fuel charge is less than 1 percent of the total test fuel weight ($W_{FuelBurned} > 0.99 \cdot W_{fuel}$);

(b) The automatic control system on the boiler/heater switches to an off mode. In this case, the boiler/heater fan (if used) is typically stopped and all air flow dampers are closed by the control system. Note that this off mode cannot be an ''overheat'' or emergency shutdown which typically requires a manual reset; or

(c) If the boiler/heater does not have an automatic off mode: After 90 percent of the fuel load has been consumed and the scale has indicated a rate of change of the test fuel charge of less than 1.0 lb/hr for a period of 10 minutes or longer. Note—this is not considered ''stopped fuel combustion,'' See section 12.5.6.1.

12.5.3.1 At the end of the test run, stop the particulate sampling train and overall efficiency (SLM) measurements, and record the run time, and all final measurement values.

12.5.3.2 At the end of the test run, continue to operate the storage tank destratification pump until the total volume pumped exceeds 1.5 times the tank volume. The maximum average of the top and bottom temperatures measured after this time may be taken as the average tank temperature at the end of the tests (TFSavg, See section 13.1). The total volume pumped may be based on the nominal flow rate of the destratification pump (See section 9.6).

12.5.3.3 For the Category I and II test runs, there is a need to determine the energy content of the unburned fuel remaining in the chamber if the remaining mass in the chamber is greater than 1 percent of the test fuel weight. Following the completion of the test, as soon as safely practical, this remaining fuel is removed from the chamber, separated from the remaining ash and weighed. This separation could be implemented with a slotted ''scoop'' or similar tool. A ¼ inch opening size in the separation tool shall be used to separate the ash and charcoal. This separated char is assigned a heating value of 12,500 Btu/lb.

12.5.4 Heat Output Capacity Validation. The first test run must produce a heat output rate that is within 10 percent of the manufacturer's rated heat output capacity (Category IV) throughout the test run and an average heat output rate within 5 percent of the manufacturer's rated heat output capacity. If the appliance is not capable of producing a heat output within these limits, the manufacturer's rated heat output capacity is considered not validated and testing is to be terminated. In such cases, the tests may be restarted using a lower heat output capacity if requested by the manufacturer. Alternatively, during the Category IV run, if the rated output cannot be maintained for a 15 minute interval, the manufacturer may elect to reduce the rated output to match the test and complete the Category IV run on this basis. The target outputs for Categories I, II, and III shall then be recalculated based on this change in rated output capacity.

12.5.5 Additional Test Runs. Using the manufacturer's rated heat output capacity

as a basis, conduct a test for additional heat output categories as specified in section 4.3. It is not required to run these tests in any particular order.

12.5.6 Alternative Heat Output Rate for Category I. If an appliance cannot be operated in the Category I heat output range due to stopped combustion, two test runs shall be conducted at heat output rates within Category II. When this is the case, the weightings for the weighted averages indicated in section 14.1.15 shall be the average of the Category I and II weighting's and shall be applied to both Category II results. Appliances that are not capable of operation within Category II (<25 percent of maximum) cannot be evaluated by this test method.

12.5.6.1 Stopped Fuel Combustion. Evidence that an appliance cannot be operated at a Category I heat output rate due to stopped fuel combustion shall include documentation of two or more attempts to operate the appliance in heat output rate Category I and fuel combustion has stopped prior to complete consumption of the test fuel charge. Stopped fuel combustion is evidenced when an elapsed time of 60 minutes or more has occurred without a measurable (1 lb or 0.5 kg) weight change in the test fuel charge while the appliance operating control is in the demand mode. Report the evidence and the reasoning used to determine that a test in heat output rate Category I cannot be achieved. For example, two unsuccessful attempts to operate at an output rate of 10 percent of the rated output capacity are not sufficient evidence that heat output rate Category I cannot be achieved.

12.5.7 Appliance Overheating. Appliances with their associated thermal storage shall be capable of operating in all heat output categories without overheating to be rated by this test method. Appliance overheating occurs when the rate of heat withdrawal from the appliance is lower than the rate of heat production when the unit control is in the idle mode. This condition results in the water in the appliance continuing to increase in temperature well above the upper limit setting of the operating control. Evidence of overheating includes: 1 hour or more of appliance water temperature increase above the upper temperature set-point of the operating control, exceeding the temperature limit of a safety control device (independent from the operating control—typically requires manual reset), boiling water in a non-pressurized system or activation of a pressure or temperature relief valve in a pressurized system.

12.5.8 Option to Eliminate Tests in Category II and III. Following successful completion of a test run in Category I, the manufacturer may eliminate the Category II and III tests. For the purpose of calculating the annual averages for particulates and efficiency, the values obtained in the Category I run shall be assumed to apply also to Category II and Category III. It is envisioned that this option would be applicable to systems which have sufficient thermal storage such that the fuel load in the Category I test can be completely consumed without the system reaching its upper operating temperature limit. In this case, the boiler/heater would likely be operating at maximum thermal output during the entire test and this output rate may be higher than the manufacturer's rated heat output capacity. The Category II and III runs would then be the same as the Category I run. It may be assumed that the particulate emission values and efficiency values determined in the startup, steady-state, and end phases of Category I are applicable in Categories II and III, for the purpose of determining the annual averages in lb/mmBtu and g/MJ (See section 13). For the annual average in g/hr, the length of time for stored heat to be drawn from thermal storage shall be determined for the test load requirements of the respective category.

12.5.9 Modification to Measurement Procedure in EPA Method 28WHH to Determine Emissions Separately During the Startup, Steady-State and End Phases. With one of the two particulate sampling trains used, filter changes shall be made at the end of the startup phase and the steady-state phase (See section 3.0). This shall be done to determine the particulate emission rate and particulate emission index for the startup, steady-state, and end phases individually. For this one train, the particulates measured during each of these three phases shall be added together to also determine the particulate emissions for the whole run.

12.5.10 Modification to Measurement Procedure in EPA Method 28WHH and the Standards Referenced therein on Averaging Period for Determination of Efficiency by the Stack Loss Method. The methods currently defined in Method 28WHH allow averaging over 10-minute time periods for flue gas temperature, flue gas CO_2, and flue gas CO for the determination of the efficiency with the stack loss method. However, under some cycling conditions the ''on'' period may be short relative to this 10-minute period. For this reason, during cycling operation the averaging period for these parameters may not be longer than the burner on period divided by 10. The averaging period need not be shorter than one minute. During the off period, under cycling operation, averaging periods as specified in EPA Method 28WHH and the standards referenced therein, may be used. Where short averaging times are used, however, the averaging period for fuel consumption may still be at 10 minutes. This average wood consumption rate shall be applied to all of the smaller time intervals included.

12.6 Additional Test Runs. The testing laboratory may conduct more than one test run in each of the heat output categories specified in section 4.3. If more than one test run is conducted at a specified heat output rate, the results from at least two-thirds of the test runs in that heat output rate category shall be used in calculating the weighted average emission rate. The measurement data and results of all test runs shall be reported regardless of which values are used in calculating the weighted average emission rate.

13.0 Calculation of Results

13.1 Nomenclature

CO_s—Carbon monoxide measured in the dilution tunnel at arbitrary time in ppm dry basis.

$CO_{g/min}$—Carbon monoxide emission rate in g/min.

CO_T—Total carbon monoxide emission for the full test run in grams.

CO_{-1}—Startup period carbon monoxide emissions in grams.

CO_{-2}—Steady-state period carbon monoxide emission in grams.

CO_{-3}—End period carbon monoxide emission in grams.

E_T—Total particulate emissions for the full test run as determined per EPA Method 28WHH and the standards referenced therein in grams.

E_1—Startup period particulate emissions in grams.

E_2—Steady-state period particulate emissions in grams.

E_3—End period particulate emissions in grams.

$E_{1-g/kg}$—Startup period particulate emission index in grams per kg fuel.

$E_{2-g/kg}$—Steady-state period particulate emission index in grams per kg fuel.

$E_{3-g/kg}$—End period particulate emission index in grams per kg fuel.

$E_{1-g/hr}$—Startup period particulate emission rate in grams per hour.

$E_{2-g/hr}$—Steady-state period particulate emission rate in grams per hour.

$E_{3-g/hr}$—End period particulate emission rate in grams per hour.

$E_{g/MJ}$—Emission rate in grams per MJ of heat output.

$E_{lb/mmBtu\ output}$—Emissions rate in pounds per million Btu of heat output.

$E_{g/kg}$—Emissions factor in grams per kilogram of dry fuel burned.

$E_{g/hr}$—Emission factor in grams per hour.

HHV—Higher heating value of fuel = 8600 Btu/lb (19.990 MJ/kg).

LHV—Lower heating value of fuel = 7988 Btu/lb (18.567 MJ/kg).

ΔT—Temperature difference between cooling water entering and exiting the heat exchanger.

Q_{out}—Total heat output in Btu (MJ).

Q_{in}—Total heat input available in test fuel charge in Btu's (MJ).

Q_{std}—Volumetric flow rate in dilution tunnel in dscfm.

M—Mass flow rate of water in lb/min (kg/min).

V_i—Volume of water indicated by a totalizing flow meter at the i_{th} reading in gallons (liters).

V_f—Volumetric flow rate of water in heat exchange system in gallons per minute (liters/min).

Θ—Total length of burn period in hours ($\Theta_1 + \Theta_2 + \Theta_3$).

Θ_1—Length of time of the startup period in hours.

Θ_2—Length of time of the steady-state period in hours.

Θ_3—Length of time of the end period in hours.

Θ_4—Length of time for stored heat to be used following a burn period in hours.

t_i—Data sampling interval in minutes.

η_{del}—Delivered heating efficiency in percent.

F_i—Weighting factor for heat output category i. (See Table 2.)

T1—Temperature of water at the inlet on the supply side of the heat exchanger, °F.

T2—Temperature of the water at the outlet on the supply side of the heat exchanger, °F.

T3—Temperature of cooling water at the inlet to the load side of the heat exchanger, °F.

T4—Temperature of cooling water at the outlet of the load side of the heat exchanger, °F.

T5—Temperature of the hot water supply as it leaves the boiler/heater, °F.

T6—Temperature of return water as it enters the boiler/heater, °F.

T7—Temperature in the boiler/heater optional destratification loop at the top of the boiler/heater, °F.

T8—Temperature in the boiler/heater optional destratification loop at the bottom of the boiler/heater, °F.

TI_{avg}—Average temperature of the appliance and water at start of the test.

$TI_{avg} - (T5 + T6)/2$ at the start of the test, °F. Eq. 1

TF_{avg}—Average temperature of the appliance and water at the end of the test.

TF_{avg} – (T5 + T6)/2 at the end of the test, °F. Eq. 2

TIS_1—Temperature at the inlet to the storage system at the start of the test.
TIS_2—Temperature at the outlet from the storage system at the start of the test.
TFS_1—Temperature at the inlet to the storage system at the end of the test.
TFS_2—Temperature at the outlet from the storage system at the end of the test.
TIS_{avg}—Average temperature of the storage system at the start of the test.

TIS_{avg} – $(TIS_1 + TIS_2)/2$ at the end of the test. Eq. 3

TFS_{avg}—Average temperature of the storage system at the end of the test.

TFS_{avg} – $(TFS_1 + TFS_2)/2$. Eq. 4

MC—Fuel moisture content in percent dry basis.
σ—Density of water in pounds per gallon.
$\sigma_{Initial}$—Density of water in the boiler/heater system at the start of the test in pounds per gallons.
$\sigma_{boiler/heater}$—Density of water in the boiler/heater system at an arbitrary time during the test in pounds per gallon.
C_p—Specific heat of water in Btu/lb, °F.
C_{steel}—Specific heat of steel (0.1 Btu/lb, °F).
$V_{boiler/heater}$—total volume of water in the boiler/heater system on the weight scale in gallons.
W_{fuel}—Fuel charge weight, as-fired or ''wet'', in pounds (kg).
$W_{fuel—1}$—Fuel consumed during the startup period in pounds (kg).
$W_{fuel—2}$—Fuel consumed during the steady state period in pounds (kg).
$W_{fuel—3}$—Fuel consumed during the end period in pounds (kg).
$W_{FuelBurned}$—Weight of fuel that has been burned from the start of the test to an arbitrary time, including the needed correction for the change in density and weight of the water in the boiler/heater system on the scale in pounds (kg).
$W_{RemainingFuel}$—Weight of unburned fuel separated from the ash at the end of a test. Useful only for Category I and Category II tests.
W_{app}—Weight of empty appliance in pounds (kg).
W_{wat}—Weight of water in supply side of the system in pounds (kg).
$W_{ScaleInitial}$—Weight reading on the scale at the start of the test, just after the test load has been added in pounds (kg).
W_{Scale}—Reading of the weight scale at an arbitrary time during the test run in pounds (kg).
$W_{StorageTank}$—Weight of the storage tank empty in pounds (kg).
$W_{WaterStorage}$—Weight of the water in the storage tank at TIS_{avg} in pounds (kg).

13.2 After the test is completed, determine the particulate emissions E_T in accordance with EPA Method 28WHH and the standards referenced therein.

13.3 Determination of the weight of fuel that has been burned at an arbitrary time.

For the purpose of tracking the consumption of the test fuel load during a test run the following may be used to calculate the weight of fuel that burned since the start of the test:

$$W_{FuelBurned} = (W_{ScaleInitial} - W_{Scale}) + V_{Boiler/heater} \cdot (\sigma_{Initial} - \sigma_{boiler/heater}) \quad \text{Eq. 5}$$

Water density, σ, is calculated using Equation 12.

13.4 Determine Average Fuel Load Moisture Content.

$$MC = \frac{\sum W_{SliceWet_i} - MC_{Slice_i}}{\sum W_{SliceWet_i}} \quad \text{Eq. 6}$$

13.5 Determine Heat Input.

$$Q_{in} = (W_{fuel}/(1+(MC/100))) \text{ x HHV, Btu (MJ).} \quad \text{Eq. 7}$$

$$Q_{in\ LHV} = (W_{fuel}/(1+(MC/100))) \text{ x LHV, Btu (MJ).} \quad \text{Eq. 8}$$

13.5.1 Correction to Q_{in} for the Category I and II tests, where there is greater than 1 percent of the test fuel charge in the chamber at the end of the test period.

$$Q_{lnCorrected} = Q_{in} - W_{Remaining} \cdot 12{,}500\ \underline{Btu} \quad \text{Eq. 9}$$

13.6 Determine Heat Output, Efficiency, and Emissions.

13.6.1 Determine heat output as:

Q_{out} = Σ [Heat output determined for each sampling time interval] + Change in heat stored in the appliance + Change in heat in storage tank.

$$Qout = \Sigma[C_{pi} \cdot \Delta T_i \cdot M_i \cdot t_i] + (W_{app} \cdot C_{steel} + W_{water} \cdot C_{pa}) \cdot (TF_{avg} - TI_{avg})$$
$$+ (W_{StorageTank} \cdot C_{steel} + W_{WaterStorage} \cdot C_{pa}) \cdot (TFS_{avg} - TIS_{avg}) \text{ Btu (MJ)} \quad \text{Eq. 10}$$

NOTE: The subscript (i) indicates the parameter value for sampling time interval t_i.M_i = Mass flow rate = gal/min × density of water (lb/gal) = lb/min.

$$M_i = V_{fi} \cdot \sigma_i, \text{ lb/min.} \quad \text{Eq. 11}$$

$$\sigma_i = (62.56 + (-.0003413 \text{ x } T3_i) + (-.00006225 \text{ x } T3_i^2)) 0.1337, \text{ lb/gal.} \quad \text{Eq. 12}$$

$$C_p = 1.0014 + (-.000003485 \text{ x } T3_i) \text{ Btu/lb, -°F.} \quad \text{Eq. 13}$$

C_{steel} = 0.1 Btu/lb, -° F.

$$C_{pa} = 1.0014 + (-.000003485 \text{ X } (TI_{avg} + TF_{avg})/2), \text{ Btu/lb, °F.} \quad \text{Eq. 14}$$

$$V_{fi} = (V_i - V_{i-1})/(t_i - t_{i-1}), \text{ gal/min.} \quad \text{Eq. 15}$$

NOTE: V_i is the total water volume at the end of interval i and V_{i-1} is the total water volume at the beginning of the time interval. This calculation is necessary when a totalizing type water meter is used.

13.6.2 Determine Heat Output Rate Over Burn Period ($\Theta_1 + \Theta_2 + \Theta_3$) as:

Heat Output Rate = Q_{out}/Θ, Btu/hr (MJ/hr). Eq. 16

13.6.3 Determine Emission Rates and Emission Factors as:

$$E_{g/MJ} = E_T/(Q_{out} \times 0.001055), \text{ g/MJ}. \quad \text{Eq. 17}$$

$$E_{lb/MM\ Btu\ output} = (E_T/453.59)/(Q_{out} \times 10^{-6}), \text{ lb/mmBtu out}. \quad \text{Eq. 18}$$

$$E_{g/kg} = E_T/(W_{fuel}/(1+MC/100)), \text{ g/dry kg}. \quad \text{Eq. 19}$$

$$E_{g/hr} = E_T/(\Theta_1+ \Theta_2+ \Theta_3+ \Theta_4), \text{ g/hr}. \quad \text{Eq. 20}$$

$$\Theta_4 = (W_{StorageTank} \cdot C_{steel} + W_{WaterStorage} \cdot C_{pa}) \cdot (TFS_{avg} - TIS_{avg})/(Q_{out}/\Theta) \quad \text{Eq. 21}$$

If thermal storage is not used in a Category III or IV run, then $\Theta_4 = 0$.

$E_{1—g/kg} = E_1/(W_{fuel—1}/(1 + MC/100))$, g/dry kg.
$E_{2—g/kg} = E_2/(W_{fuel—2}/(1 + MC/100))$, g/dry kg.
$E_{3—g/kg} = E_3/(W_{fuel—3}/(1 + MC/100))$, g/dry kg.
$E_{1—g/hr} = E_1/\Theta_1$, g/hr.
$E_{2—g/hr} = E_2/\Theta_2$, g/hr.
$E_{3—g/hr} = E_3/\Theta_3$, g/hr.

13.6.4 Determine delivered efficiency as:

$$\eta_{del} = (Q_{out}/Q_{InCorrected}) \times 100, \%. \quad \text{Eq. 22}$$

$$\eta_{del\ LHV} = (Q_{out}/Q_{in\ LHV}) \times 100, \%. \quad \text{Eq. 23}$$

13.6.5 Determine η_{SLM}—Overall Efficiency, also known as Stack Loss Efficiency, using stack loss method (SLM).

For determination of the average overall thermal efficiency (η_{SLM}) for the test run, use the data collected over the full test run and the calculations in accordance with CSA B415.1–10 (IBR, see §60.17), clause 13.7 except for 13.7.2(e), (f), (g), and (h), use the following average fuel properties for oak: %C = 50.0, %H = 6.6, %O = 43.2, %Ash = 0.2.

13.6.5.1 Whenever the CSA B415.1–10 (IBR, see §60.17) overall efficiency is found to be lower than the overall efficiency based on load side measurements, as determined by Eq. 22 of this method, section 14.1.7 of the test report must include a discussion of the reasons for this result. For a test where the CSA B415.1–10 overall efficiency SLM is less than 2 percentage points lower than the overall efficiency based on load side measurements, the efficiency based on load side measurements shall be considered invalid. [Note on the rationale for the 2 percentage points limit. The SLM method does not include boiler/heater jacket losses and, for this reason, should provide an efficiency which is actually higher than the efficiency based on the energy input and output measurements or ''delivered efficiency.'' A delivered efficiency that is higher than the efficiency based on the SLM could be considered suspect. A delivered efficiency greater than 2 percentage points higher than the efficiency based on the SLM, then, clearly indicates a measurement error.]

13.6.6 Carbon Monoxide Emissions

For each minute of the test period, the carbon monoxide emission rate shall be calculated as:

$$CO_{g/min} = Q_{std} \cdot CO_s \cdot 3.30 \times 10^{-5} \quad \text{Eq. 24}$$

Total CO emissions for each of the three test periods ($CO_{—1}$, $CO_{—2}$, $CO_{—3}$) shall be calculated as the sum of the emission rates for each of the 1-minute intervals. Total CO emission for the test run, CO_T, shall be calculated as the sum of $CO_{—1}$, $CO_{—2}$, and $CO_{—3}$.

13.7 Weighted Average Emissions and Efficiency.

13.7.1 Determine the weighted average emission rate and delivered efficiency from the individual tests in the specified heat output categories. The weighting factors (F_i) are derived from an analysis of ASHRAE bin data which provides details of normal building heating requirements in terms of percent of design capacity and time in a particular capacity range—or ''bin''—over the course of a heating season. The values used in this method represent an average of data from several cities located in the northern United States.

Weighted average delivered efficiency: $\eta_{avg} = \Sigma\ \eta_i \times F_i$, %. Eq. 25

Weighted average emissions: $E_{avg} = \Sigma\ E_i \times F_i$, % Eq. 26

If, as discussed in section 12.5.8, the option to eliminate tests in Category II and III is elected, the values of efficiency and particulate emission rate as measured in Category I, shall be assigned also to Category II and III for the purpose of determining the annual averages.

14.0 Report

14.1.1 The report shall include the following:

14.1.2 Name and location of the laboratory conducting the test.

14.1.3 A description of the appliance tested and its condition, date of receipt and dates of tests.

14.1.4 A description of the minimum amount of external thermal storage that is required for use with this system. This shall be specified both in terms of volume in gallons and stored energy content in Btu with a storage temperature ranging from 125 °F to the manufacturer's specified setpoint temperature.

14.1.5 A statement that the test results apply only to the specific appliance tested.

14.1.6 A statement that the test report shall not be reproduced except in full, without the written approval of the laboratory.

14.1.7 A description of the test procedures and test equipment including a schematic or other drawing showing the location of all required test equipment. Also, a description of test fuel sourcing, handling and storage practices shall be included.

14.1.8 Details of deviations from, additions to or exclusions from the test method, and their data quality implications on the test results (if any), as well as information on specific test conditions, such as environmental conditions.

14.1.9 A list of participants and their roles and observers present for the tests.

14.1.10 Data and drawings indicating the fire box size and location of the fuel charge.

14.1.11 Drawings and calculations used to determine firebox volume.

14.1.12 Information for each test run fuel charge including piece size, moisture content and weight.

14.1.13 All required data and applicable blanks for each test run shall be provided in spreadsheet format both in the printed report and in a computer file such that the data can be easily analyzed and calculations easily verified. Formulas used for all calculations shall be accessible for review.

14.1.14 For each test run, Θ_1,Θ_2, Θ_3, the total CO and particulate emission for each of these three periods, and Θ_4.

14.1.15 Calculated results for delivered efficiency at each heat output rate and the weighted average emissions reported as total emissions in grams, pounds per mm Btu of delivered heat, grams per MJ of delivered heat, grams per kilogram of dry fuel and grams per hour. Results shall be reported for each heat output category and the weighted average.

14.1.16 Tables 1A, 1B, 1C, 1D, 1E and Table 2 must be used for presentation of results in test reports.

14.1.17 A statement of the estimated uncertainty of measurement of the emissions and efficiency test results.

14.1.18 A plot of CO emission rate in grams/minute vs. time, based on 1 minute averages, for the entire test period, for each run.

14.1.19 A plot of estimated boiler/heater energy release rate in Btu/hr based on 10 minute averages, for the entire test period, for each run. This will be calculated from the fuel used, the wood heating value and moisture content, and the SLM efficiency during each 10 minute period.

14.1.20 Raw data, calibration records, and other relevant documentation shall be retained by the laboratory for a minimum of 7 years.

15.0 Precision and Bias

15.1 Precision—It is not possible to specify the precision of the procedure in this test method because the appliance operation and

fueling protocols and the appliances themselves produce variable amounts of emissions and cannot be used to determine reproducibility or repeatability of this test method.

15.2 Bias—No definitive information can be presented on the bias of the procedure in this test method for measuring solid fuel burning hydronic heater emissions because no material having an accepted reference value is available.

16.0 Keywords

16.1 Solid fuel, hydronic heating appliances, wood-burning hydronic heaters, partial thermal storage.

Table 1A. Data Summary Part A

						Θ	W_{fuel}	MC_{ave}	Q_{in}	Q_{out}
Category	Run No	Load % Capacity	Target Load	Actual Load	Actual Load	Test Duration	Wood Weight as-fired	Wood Moisture	Heat Input	Heat Output
		Btu/hr	Btu/ hr	Btu/ hr	% of max	hrs	lb	%DB	Btu	Btu
I		< 15% of max								
II		16-24% of max								
III		25-50% of max								
IV		Max capacity								

Table 1B. Data Summary Part B

			T2 Min	E_T	E	E	$E_{g/hr}$	$E_{g/kg}$	η_{del}	H_{SLM}
Category	Run No	Load % Capacity	Min Return Water Temp.	Total PM Emissions	PM Output Based	PM Output Based	PM Rate	PM Factor	Delivered Efficiency	Stack Loss Efficiency
			°F	g	lb/mm Btu Out	g/MJ	g/hr	g/kg	%	%
I		< 15% of max								
II		16-24% of max								
III		25-50% of max								
IV		Max capacity								

Table 1C. Data Summary Part C

			Θ_1	Θ_2	Θ_3	$CO_{_1}$	$CO_{_2}$	$CO_{_3}$	CO_T
Category	Run No	Load % Capacity	Startup Time.	Steady State Time	End Time	Startup CO emission	Steady State CO emission	End CO emission	Total CO emission
			min	min	min	g	g	g	g
I		< 15% of max							
II		16-24% of max							
III		25-50% of max							
IV		Max capacity							

Table 1D. Data Summary Part D

			E_1	E_2	E_3	$E_{1_g/kg}$	$E_{2_g/kg}$	$E_{3_g/kg}$
Category	Run No	Load % Capacity	Startup PM	Steady State PM	End PM	Startup PM emission index	Steady State PM emission index	End PM emission index
			g	g	g	g/kg fuel	g/kg fuel	g/kg fuel
I		< 15% of max						
II		16-24% of max						
III		25-50% of max						
IV		Max capacity						

Table 1E: Label Summary Information

MANUFACTURER:			
MODEL NUMBER:			
ANNUAL EFFICIENCY RATING:	η_{avg}		**(Using higher heating value)**
PARTICLE EMISSIONS:	E_{avg}		grams/hr (Average)
			lbs/mmBtu/hr Output

Table 2. Annual Weighting

Category	Weighting Factor (F_i)	$\eta_{del,i} \times F_i$	$E_{g/MJ,i} \times F_i$	$E_{g/kg,i} \times F_i$	$E_{lb/mmBtu\ Out,i} \times F_i$	$E_{g/hr,i} \times F_i$
I	0.437					
II	0.238					
III	0.275					
IV	0.050					
Totals	1.000					

Figure 1. Schematic of Equipment Test Setup

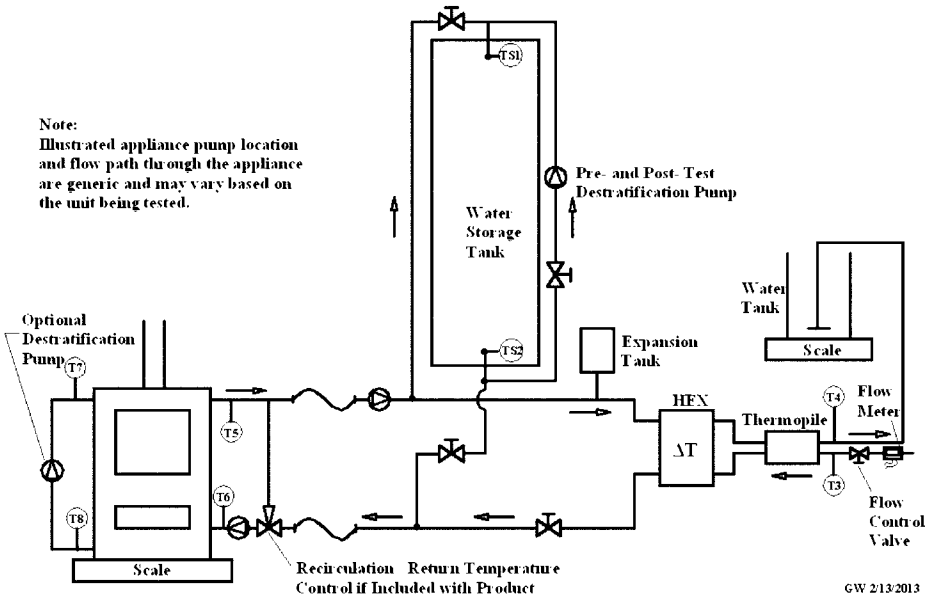
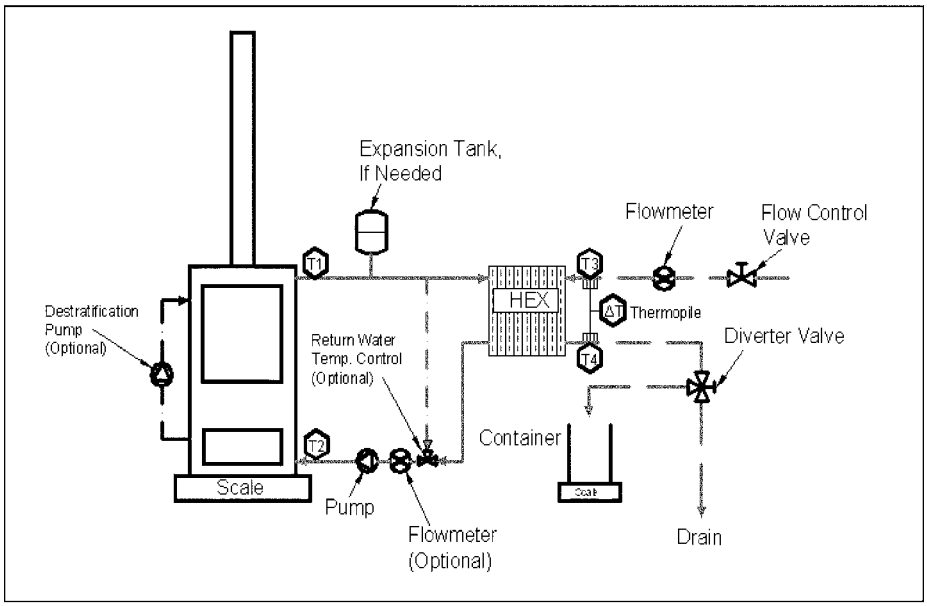


Figure 2. Schematic of Test Equipment Set-up



Note: Illustrated appliance pump location and flow path through the appliance.

METHOD 29—DETERMINATION OF METALS EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 5 and Method 12.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Antimony (Sb)	7440–36–0
Arsenic (As)	7440–38–2
Barium (Ba)	7440–39–3
Beryllium (Be)	7440–41–7
Cadmium (Cd)	7440–43–9
Chromium (Cr)	7440–47–3
Cobalt (Co)	7440–48–4
Copper (Cu)	7440–50–8
Lead (Pb)	7439–92–1
Manganese (Mn)	7439–96–5
Mercury (Hg)	7439–97–6
Nickel (Ni)	7440–02–0
Phosphorus (P)	7723–14–0
Selenium (Se)	7782–49–2
Silver (Ag)	7440–22–4
Thallium (Tl)	7440–28–0
Zinc (Zn)	7440–66–6

1.2 Applicability. This method is applicable to the determination of metals emissions from stationary sources. This method may be used to determine particulate emissions in addition to the metals emissions if the prescribed procedures and precautions are followed.

1.2.1 Hg emissions can be measured, alternatively, using EPA Method 101A of Appendix B, 40 CFR Part 61. Method 101-A measures only Hg but it can be of special interest to sources which need to measure both Hg and Mn emissions.

2.0 Summary of Method

2.1 Principle. A stack sample is withdrawn isokinetically from the source, particulate emissions are collected in the probe and on a heated filter, and gaseous emissions are then collected in an aqueous acidic solution of hydrogen peroxide (analyzed for all metals including Hg) and an aqueous acidic solution of potassium permanganate (analyzed only for Hg). The recovered samples are digested, and appropriate fractions are analyzed for Hg by cold vapor atomic absorption spectroscopy

(CVAAS) and for Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, P, Se, Ag, Tl, and Zn by inductively coupled argon plasma emission spectroscopy (ICAP) or atomic absorption spectroscopy (AAS). Graphite furnace atomic absorption spectroscopy (GFAAS) is used for analysis of Sb, As, Cd, Co, Pb, Se, and Tl if these elements require greater analytical sensitivity than can be obtained by ICAP. If one so chooses, AAS may be used for analysis of all listed metals if the resulting in-stack method detection limits meet the goal of the testing program. Similarly, inductively coupled plasma-mass spectroscopy (ICP-MS) may be used for analysis of Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Ag, Tl and Zn.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Iron (Fe) can be a spectral interference during the analysis of As, Cr, and Cd by ICAP. Aluminum (Al) can be a spectral interference during the analysis of As and Pb by ICAP. Generally, these interferences can be reduced by diluting the analytical sample, but such dilution raises the in-stack detection limits. Background and overlap corrections may be used to adjust for spectral interferences. Refer to Method 6010 of Reference 2 in section 16.0 or the other analytical methods used for details on potential interferences to this method. For all GFAAS analyses, use matrix modifiers to limit interferences, and matrix match all standards.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Nitric Acid (HNO_3). Highly corrosive to eyes, skin, nose, and lungs. Vapors cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

5.2.2 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

5.2.3 Hydrochloric Acid (HC1). Highly corrosive liquid with toxic vapors. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.4 Hydrofluoric Acid (HF). Highly corrosive to eyes, skin, nose, throat, and lungs. Reaction to exposure may be delayed by 24 hours or more. Provide ventilation to limit exposure.

5.2.5 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs. 30% H_2O_2 is a strong oxidizing agent. Avoid contact with skin, eyes, and combustible material. Wear gloves when handling.

5.2.6 Potassium Permanganate ($KMnO_4$). Caustic, strong oxidizer. Avoid bodily contact with.

5.2.7 Potassium Persulfate. Strong oxidizer. Avoid bodily contact with. Keep containers well closed and in a cool place.

5.3 Reaction Pressure. Due to the potential reaction of the potassium permanganate with the acid, there could be pressure buildup in the acidic $KMnO_4$ absorbing solution storage bottle. Therefore these bottles shall not be fully filled and shall be vented to relieve excess pressure and prevent explosion potentials. Venting is required, but not in a manner that will allow contamination of the solution. A No. 70–72 hole drilled in the container cap and Teflon liner has been used.

6.0 Equipment and Supplies

6.1 Sampling. A schematic of the sampling train is shown in Figure 29–1. It has general similarities to the Method 5 train.

6.1.1 Probe Nozzle (Probe Tip) and Borosilicate or Quartz Glass Probe Liner. Same as Method 5, sections 6.1.1.1 and 6.1.1.2, except that glass nozzles are required unless alternate tips are constructed of materials that are free from contamination and will not interfere with the sample. If a probe tip other than glass is used, no correction to the sample test results to compensate for the nozzle's effect on the sample is allowed. Probe fittings of plastic such as Teflon, polypropylene, etc. are recommended instead of metal fittings to prevent contamination. If one chooses to do so, a single glass piece consisting of a combined probe tip and probe liner may be used.

6.1.2 Pitot Tube and Differential Pressure Gauge. Same as Method 2, sections 6.1 and 6.2, respectively.

6.1.3 Filter Holder. Glass, same as Method 5, section 6.1.1.5, except use a Teflon filter support or other non-metallic, non-contaminating support in place of the glass frit.

6.1.4 Filter Heating System. Same as Method 5, section 6.1.1.6.

6.1.5 Condenser. Use the following system for condensing and collecting gaseous metals and determining the moisture content of the stack gas. The condensing system shall consist of four to seven impingers connected in series with leak-free ground glass fittings or other leak-free, non-contaminating fittings. Use the first impinger as a moisture trap. The second impinger (which is the first HNO_3/H_2O_2 impinger) shall be identical to the first impinger in Method 5. The third impinger (which is the second HNO_3/H_2O_2 impinger) shall be a Greenburg Smith impinger with the standard tip as described for the second impinger in Method 5, section 6.1.1.8. The fourth (empty) impinger and the fifth and sixth (both acidified $KMnO_4$) impingers are the same as the first impinger in Method 5. Place a temperature sensor capable of measuring to within 1 °C (2 °F) at the outlet of the last impinger. If no Hg analysis is planned, then the fourth, fifth, and sixth impingers are not used.

6.1.6 Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, sections 6.1.1.9, 6.1.2, and 6.1.3, respectively.

6.1.7 Teflon Tape. For capping openings and sealing connections, if necessary, on the sampling train.

6.2 Sample Recovery. Same as Method 5, sections 6.2.1 through 6.2.8 (Probe-Liner and Probe-Nozzle Brushes or Swabs, Wash Bottles, Sample Storage Containers, Petri Dishes, Glass Graduated Cylinder, Plastic Storage Containers, Funnel and Rubber Policeman, and Glass Funnel), respectively, with the following exceptions and additions:

6.2.1 Non-metallic Probe-Liner and Probe-Nozzle Brushes or Swabs. Use non-metallic probe-liner and probe-nozzle brushes or swabs for quantitative recovery of materials collected in the front-half of the sampling train.

6.2.2 Sample Storage Containers. Use glass bottles (see section 8.1 of this Method) with Teflon-lined caps that are non-reactive to the oxidizing solutions, with capacities of 1000- and 500-ml, for storage of acidified $KMnO_4$—containing samples and blanks. Glass or polyethylene bottles may be used for other sample types.

6.2.3 Graduated Cylinder. Glass or equivalent.

6.2.4 Funnel. Glass or equivalent.

6.2.5 Labels. For identifying samples.

6.2.6 Polypropylene Tweezers and/or Plastic Gloves. For recovery of the filter from the sampling train filter holder.

6.3 Sample Preparation and Analysis.

6.3.1 Volumetric Flasks, 100-ml, 250-ml, and 1000-ml. For preparation of standards and sample dilutions.

6.3.2 Graduated Cylinders. For preparation of reagents.

6.3.3 Parr Bombs or Microwave Pressure Relief Vessels with Capping Station (CEM Corporation model or equivalent). For sample digestion.

6.3.4 Beakers and Watch Glasses. 250-ml beakers, with watch glass covers, for sample digestion.

6.3.5 Ring Stands and Clamps. For securing equipment such as filtration apparatus.

6.3.6 Filter Funnels. For holding filter paper.

6.3.7 Disposable Pasteur Pipets and Bulbs.

6.3.8 Volumetric Pipets.

6.3.9 Analytical Balance. Accurate to within 0.1 mg.

6.3.10 Microwave or Conventional Oven. For heating samples at fixed power levels or temperatures, respectively.

6.3.11 Hot Plates.

6.3.12 Atomic Absorption Spectrometer (AAS). Equipped with a background corrector.

6.3.12.1 Graphite Furnace Attachment. With Sb, As, Cd, Co, Pb, Se, and Tl hollow cathode lamps (HCLs) or electrodeless discharge lamps (EDLs). Same as Reference 2 in section 16.0. Methods 7041 (Sb), 7060 (As), 7131 (Cd), 7201 (Co), 7421 (Pb), 7740 (Se), and 7841 (Tl).

6.3.12.2 Cold Vapor Mercury Attachment. With a mercury HCL or EDL, an air recirculation pump, a quartz cell, an aerator apparatus, and a heat lamp or desiccator tube. The heat lamp shall be capable of raising the temperature at the quartz cell by 10 °C above ambient, so that no condensation forms on the wall of the quartz cell. Same as Method 7470 in Reference 2 in section 16.0. See note 2: section 11.1.3 for other acceptable approaches for analysis of Hg in which analytical detection limits of 0.002 ng/ml were obtained.

6.3.13 Inductively Coupled Argon Plasma Spectrometer. With either a direct or sequential reader and an alumina torch. Same as EPA Method 6010 in Reference 2 in section 16.0.

6.3.14 Inductively Coupled Plasma-Mass Spectrometer.

Same as EPA Method 6020 in Reference 2 in section 16.0.

7.0 Reagents and Standards

7.1 Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are

available. Otherwise, use the best available grade.

7.2 Sampling Reagents.

7.2.1 Sample Filters. Without organic binders. The filters shall contain less than 1.3 μg/in.^{2} of each of the metals to be measured. Analytical results provided by filter manufacturers stating metals content of the filters are acceptable. However, if no such results are available, analyze filter blanks for each target metal prior to emission testing. Quartz fiber filters meeting these requirements are recommended. However, if glass fiber filters become available which meet these requirements, they may be used. Filter efficiencies and unreactiveness to sulfur dioxide (SO_2) or sulfur trioxide (SO_3) shall be as described in section 7.1.1 of Method 5.

7.2.2 Water. To conform to ASTM Specification D1193–77 or 91, Type II (incorporated by reference—see §60.17). If necessary, analyze the water for all target metals prior to field use. All target metals should be less than 1 ng/ml.

7.2.3 HNO_3, Concentrated. Baker Instra-analyzed or equivalent.

7.2.4 HCl, Concentrated. Baker Instra-analyzed or equivalent.

7.2.5 H_2O_2, 30 Percent (V/V).

7.2.6 $KMnO_4$.

7.2.7 H_2SO_4, Concentrated.

7.2.8 Silica Gel and Crushed Ice. Same as Method 5, sections 7.1.2 and 7.1.4, respectively.

7.3 Pretest Preparation of Sampling Reagents.

7.3.1 HNO_3/H_2O_2 Absorbing Solution, 5 Percent HNO_3/10 Percent H_2O_2. Add carefully with stirring 50 ml of concentrated HNO_3 to a 1000-ml volumetric flask containing approximately 500 ml of water, and then add carefully with stirring 333 ml of 30 percent H_2O_2. Dilute to volume with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.3.2 Acidic $KMnO_4$ Absorbing Solution, 4 Percent $KMnO_4$ (W/V), 10 Percent H_2SO_4 (V/V). Prepare fresh daily. Mix carefully, with stirring, 100 ml of concentrated H_2SO_4 into approximately 800 ml of water, and add water with stirring to make a volume of 1 liter: this solution is 10 percent H_2SO_4 (V/V). Dissolve, with stirring, 40 g of $KMnO_4$ into 10 percent H_2SO_4 (V/V) and add 10 percent H_2SO_4 (V/V) with stirring to make a volume of 1 liter. Prepare and store in glass bottles to prevent degradation. This reagent shall contain less than 2 ng/ml of Hg.

Precaution: To prevent autocatalytic decomposition of the permanganate solution, filter the solution through Whatman 541 filter paper.

7.3.3 HNO_3, 0.1 N. Add with stirring 6.3 ml of concentrated HNO_3 (70 percent) to a flask containing approximately 900 ml of water. Dilute to 1000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.3.4 HCl, 8 N. Carefully add with stirring 690 ml of concentrated HCl to a flask containing 250 ml of water. Dilute to 1000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of Hg.

7.4 Glassware Cleaning Reagents.

7.4.1 HNO_3, Concentrated. Fisher ACS grade or equivalent.

7.4.2 Water. To conform to ASTM Specifications D1193, Type II.

7.4.3 HNO_3, 10 Percent (V/V). Add with stirring 500 ml of concentrated HNO_3 to a flask containing approximately 4000 ml of water. Dilute to 5000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.5 Sample Digestion and Analysis Reagents. The metals standards, except Hg, may also be made from solid chemicals as described in Reference 3 in section 16.0. Refer to References 1, 2, or 5 in section 16.0 for additional information on Hg standards. The 1000 μg/ml Hg stock solution standard may be made according to section 7.2.7 of Method 101A.

7.5.1 HCl, Concentrated.

7.5.2 HF, Concentrated.

7.5.3 HNO_3, Concentrated. Baker Instra-analyzed or equivalent.

7.5.4 HNO_3, 50 Percent (V/V). Add with stirring 125 ml of concentrated HNO_3 to 100 ml of water. Dilute to 250 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.5.5 HNO_3, 5 Percent (V/V). Add with stirring 50 ml of concentrated HNO_3 to 800 ml of water. Dilute to 1000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.5.6 Water. To conform to ASTM Specifications D1193, Type II.

7.5.7 Hydroxylamine Hydrochloride and Sodium Chloride Solution. See Reference 2 In section 16.0 for preparation.

7.5.8 Stannous Chloride. See Reference 2 in section 16.0 for preparation.

7.5.9 $KMnO_4$, 5 Percent (W/V). See Reference 2 in section 16.0 for preparation.

7.5.10 H_2SO_4, Concentrated.

7.5.11 Potassium Persulfate, 5 Percent (W/V). See Reference 2 in section 16.0 for preparation.

7.5.12 Nickel Nitrate, $Ni(N0_3)_2 6H_20$.

7.5.13 Lanthanum Oxide, La_20_3.

7.5.14 Hg Standard (AAS Grade), 1000 μg/ml.

7.5.15 Pb Standard (AAS Grade), 1000 μg/ml.

7.5.16 As Standard (AAS Grade), 1000 μg/ml.

7.5.17 Cd Standard (AAS Grade), 1000 μg/ml.

7.5.18 Cr Standard (AAS Grade), 1000 μg/ml.

7.5.19 Sb Standard (AAS Grade), 1000 μg/ml.

7.5.20 Ba Standard (AAS Grade), 1000 μg/ml.

7.5.21 Be Standard (AAS Grade), 1000 μg/ml.

7.5.22 Co Standard (AAS Grade), 1000 μg/ml.

7.5.23 Cu Standard (AAS Grade), 1000 μg/ml.

7.5.24 Mn Standard (AAS Grade), 1000 µg/ml.
7.5.25 Ni Standard (AAS Grade), 1000 µg/ml.
7.5.26 P Standard (AAS Grade), 1000 µg/ml.
7.5.27 Se Standard (AAS Grade), 1000 µg/ml.
7.5.28 Ag Standard (AAS Grade), 1000 µg/ml.
7.5.29 Tl Standard (AAS Grade), 1000 µg/ml.
7.5.30 Zn Standard (AAS Grade), 1000 µg/ml.
7.5.31 Al Standard (AAS Grade), 1000 µg/ml.
7.5.32 Fe Standard (AAS Grade), 1000 µg/ml.

7.5.33 Hg Standards and Quality Control Samples. Prepare fresh weekly a 10 µg/ml intermediate Hg standard by adding 5 ml of 1000 µg/ml Hg stock solution prepared according to Method 101A to a 500-ml volumetric flask; dilute with stirring to 500 ml by first carefully adding 20 ml of 15 percent HNO_3 and then adding water to the 500-ml volume. Mix well. Prepare a 200 ng/ml working Hg standard solution fresh daily: add 5 ml of the 10 µg/ml intermediate standard to a 250-ml volumetric flask, and dilute to 250 ml with 5 ml of 4 percent $KMnO_4$, 5 ml of 15 percent HNO_3, and then water. Mix well. Use at least five separate aliquots of the working Hg standard solution and a blank to prepare the standard curve. These aliquots and blank shall contain 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml of the working standard solution containing 0, 200, 400, 600, 800, and 1000 ng Hg, respectively. Prepare quality control samples by making a separate 10 µg/ml standard and diluting until in the calibration range.

7.5.34 ICAP Standards and Quality Control Samples. Calibration standards for ICAP analysis can be combined into four different mixed standard solutions as follows:

MIXED STANDARD SOLUTIONS FOR ICAP ANALYSIS

Solution	Elements
I	As, Be, Cd, Mn, Pb, Se, Zn.
II	Ba, Co, Cu, Fe.
III	Al, Cr, Ni.
IV	Ag, P, Sb, Tl.

Prepare these standards by combining and diluting the appropriate volumes of the 1000 µg/ml solutions with 5 percent HNO_3. A minimum of one standard and a blank can be used to form each calibration curve. However, prepare a separate quality control sample spiked with known amounts of the target metals in quantities in the mid-range of the calibration curve. Suggested standard levels are 25 µg/ml for Al, Cr and Pb, 15 µg/ml for Fe, and 10 µg/ml for the remaining elements. Prepare any standards containing less than 1 µg/ml of metal on a daily basis. Standards containing greater than 1 µg/ml of metal should be stable for a minimum of 1 to 2 weeks. For ICP-MS, follow Method 6020 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i).

7.5.35 GFAAS Standards. Sb, As, Cd, Co, Pb, Se, and Tl. Prepare a 10 µg/ml standard by adding 1 ml of 1000 µg/ml standard to a 100-ml volumetric flask. Dilute with stirring to 100 ml with 10 percent HNO_3. For GFAAS, matrix match the standards. Prepare a 100 ng/ml standard by adding 1 ml of the 10 µg/ml standard to a 100-ml volumetric flask, and dilute to 100 ml with the appropriate matrix solution. Prepare other standards by diluting the 100 ng/ml standards. Use at least five standards to make up the standard curve. Suggested levels are 0, 10, 50, 75, and 100 ng/ml. Prepare quality control samples by making a separate 10 µg/ml standard and diluting until it is in the range of the samples. Prepare any standards containing less than 1 µg/ml of metal on a daily basis. Standards containing greater than 1 µg/ml of metal should be stable for a minimum of 1 to 2 weeks.

7.5.36 Matrix Modifiers.

7.5.36.1 Nickel Nitrate, 1 Percent (V/V). Dissolve 4.956 g of $Ni(N0_3)_2{\cdot}6H_20$ or other nickel compound suitable for preparation of this matrix modifier in approximately 50 ml of water in a 100-ml volumetric flask. Dilute to 100 ml with water.

7.5.36.2 Nickel Nitrate, 0.1 Percent (V/V). Dilute 10 ml of 1 percent nickel nitrate solution to 100 ml with water. Inject an equal amount of sample and this modifier into the graphite furnace during GFAAS analysis for As.

7.5.36.3 Lanthanum. Carefully dissolve 0.5864 g of La_20_3 in 10 ml of concentrated $HN0_3$, and dilute the solution by adding it with stirring to approximately 50 ml of water. Dilute to 100 ml with water, and mix well. Inject an equal amount of sample and this modifier into the graphite furnace during GFAAS analysis for Pb.

7.5.37 Whatman 40 and 541 Filter Papers (or equivalent). For filtration of digested samples.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Sampling. The complexity of this method is such that, to obtain reliable results, both testers and analysts must be trained and experienced with the test procedures, including source sampling; reagent preparation and handling; sample handling; safety equipment and procedures; analytical calculations; reporting; and the specific procedural descriptions throughout this method.

8.1.1 Pretest Preparation. Follow the same general procedure given in Method 5, section 8.1, except that, unless particulate emissions are to be determined, the filter need not be desiccated or weighed. First, rinse all sampling train glassware with hot tap water and then wash in hot soapy water. Next, rinse glassware three times with tap water, followed by three additional rinses with water. Then soak all glassware in a 10 percent (V/V) nitric acid solution for a minimum of 4

hours, rinse three times with water, rinse a final time with acetone, and allow to air dry. Cover all glassware openings where contamination can occur until the sampling train is assembled for sampling.

8.1.2 Preliminary Determinations. Same as Method 5, section 8.1.2.

8.1.3 Preparation of Sampling Train.

8.1.3.1 Set up the sampling train as shown in Figure 29–1. Follow the same general procedures given in Method 5, section 8.3, except place 100 ml of the HNO_3/H_2O_2 solution (Section 7.3.1 of this method) in each of the second and third impingers as shown in Figure 29–1. Place 100 ml of the acidic $KMnO_4$ absorbing solution (Section 7.3.2 of this method) in each of the fifth and sixth impingers as shown in Figure 29–1, and transfer approximately 200 to 300 g of pre-weighed silica gel from its container to the last impinger. Alternatively, the silica gel may be weighed directly in the impinger just prior to final train assembly.

8.1.3.2 Based on the specific source sampling conditions, the use of an empty first impinger can be eliminated if the moisture to be collected in the impingers will be less than approximately 100 ml.

8.1.3.3 If Hg analysis will not be performed, the fourth, fifth, and sixth impingers as shown in Figure 29–1 are not required.

8.1.3.4 To insure leak-free sampling train connections and to prevent possible sample contamination problems, use Teflon tape or other non-contaminating material instead of silicone grease.

Precaution: Exercise extreme care to prevent contamination within the train. Prevent the acidic $KMnO_4$ from contacting any glassware that contains sample material to be analyzed for Mn. Prevent acidic H_2O_2 from mixing with the acidic $KMnO_4$.

8.1.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, section 8.4.2 (Pretest Leak-Check), section 8.4.3 (Leak-Checks During the Sample Run), and section 8.4.4 (Post-Test Leak-Checks).

8.1.5 Sampling Train Operation. Follow the procedures given in Method 5, section 8.5. When sampling for Hg, use a procedure analogous to that described in section 8.1 of Method 101A, 40 CFR Part 61, Appendix B, if necessary to maintain the desired color in the last acidified permanganate impinger. For each run, record the data required on a data sheet such as the one shown in Figure 5–3 of Method 5.

8.1.6 Calculation of Percent Isokinetic. Same as Method 5, section 12.11.

8.2 Sample Recovery.

8.2.1 Begin cleanup procedures as soon as the probe is removed from the stack at the end of a sampling period. The probe should be allowed to cool prior to sample recovery. When it can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a rinsed, non-contaminating cap over the probe nozzle to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling; a vacuum can form in the filter holder with the undesired result of drawing liquid from the impingers onto the filter.

8.2.2 Before moving the sampling train to the cleanup site, remove the probe from the sampling train and cap the open outlet. Be careful not to lose any condensate that might be present. Cap the filter inlet where the probe was fastened. Remove the umbilical cord from the last impinger and cap the impinger. Cap the filter holder outlet and impinger inlet. Use non-contaminating caps, whether ground-glass stoppers, plastic caps, serum caps, or Teflon® tape to close these openings.

8.2.3 Alternatively, the following procedure may be used to disassemble the train before the probe and filter holder/oven are completely cooled: Initially disconnect the filter holder outlet/impinger inlet and loosely cap the open ends. Then disconnect the probe from the filter holder or cyclone inlet and loosely cap the open ends. Cap the probe tip and remove the umbilical cord as previously described.

8.2.4 Transfer the probe and filter-impinger assembly to a cleanup area that is clean and protected from the wind and other potential causes of contamination or loss of sample. Inspect the train before and during disassembly and note any abnormal conditions. Take special precautions to assure that all the items necessary for recovery do not contaminate the samples. The sample is recovered and treated as follows (see schematic in Figures 29–2a and 29–2b):

8.2.5 Container No. 1 (Sample Filter). Carefully remove the filter from the filter holder and place it in its labeled petri dish container. To handle the filter, use either acid-washed polypropylene or Teflon coated tweezers or clean, disposable surgical gloves rinsed with water and dried. If it is necessary to fold the filter, make certain the particulate cake is inside the fold. Carefully transfer the filter and any particulate matter or filter fibers that adhere to the filter holder gasket to the petri dish by using a dry (acid-cleaned) nylon bristle brush. Do not use any metal-containing materials when recovering this train. Seal the labeled petri dish.

8.2.6 Container No. 2 (Acetone Rinse). Perform this procedure only if a determination of particulate emissions is to be made. Quantitatively recover particulate matter and any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with a total of 100 ml of acetone, while simultaneously taking great care to see that no dust on the outside of the probe or other surfaces gets in the sample. The use of exactly 100 ml

is necessary for the subsequent blank correction procedures. Distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator; in these cases, save a water blank and follow the Administrator's directions on analysis.

8.2.6.1 Carefully remove the probe nozzle, and clean the inside surface by rinsing with acetone from a wash bottle while brushing with a non-metallic brush. Brush until the acetone rinse shows no visible particles, then make a final rinse of the inside surface with acetone.

8.2.6.2 Brush and rinse the sample exposed inside parts of the probe fitting with acetone in a similar way until no visible particles remain. Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Allow the acetone to drain from the lower end into the sample container. A funnel may be used to aid in transferring liquid washings to the container. Follow the acetone rinse with a non-metallic probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action three times through the probe. Hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed through the probe until no visible particulate matter is carried out with the acetone or until none remains in the probe liner on visual inspection. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

8.2.6.3 It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination. Clean the inside of the front-half of the filter holder by rubbing the surfaces with a non-metallic brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. After all acetone washings and particulate matter have been collected in the sample container, tighten the lid so that acetone will not leak out when shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Clearly label the container to identify its contents.

8.2.7 Container No. 3 (Probe Rinse). Keep the probe assembly clean and free from contamination during the probe rinse. Rinse the probe nozzle and fitting, probe liner, and front-half of the filter holder thoroughly with a total of 100 ml of 0.1 N HNO_3, and place the wash into a sample storage container. Perform the rinses as applicable and generally as described in Method 12, section 8.7.1. Record the volume of the rinses. Mark the height of the fluid level on the outside of the storage container and use this mark to determine if leakage occurs during transport. Seal the container, and clearly label the contents. Finally, rinse the nozzle, probe liner, and front-half of the filter holder with water followed by acetone, and discard these rinses.

NOTE: The use of a total of exactly 100 ml is necessary for the subsequent blank correction procedures.

8.2.8 Container No. 4 (Impingers 1 through 3, Moisture Knockout Impinger, when used, HNO_3/H_2O_2 Impingers Contents and Rinses). Due to the potentially large quantity of liquid involved, the tester may place the impinger solutions from impingers 1 through 3 in more than one container, if necessary. Measure the liquid in the first three impingers to within 0.5 ml using a graduated cylinder. Record the volume. This information is required to calculate the moisture content of the sampled flue gas. Clean each of the first three impingers, the filter support, the back half of the filter housing, and connecting glassware by thoroughly rinsing with 100 ml of 0.1 N HNO_3 using the procedure as applicable in Method 12, section 8.7.3.

NOTE: The use of exactly 100 ml of 0.1 N HNO_3 rinse is necessary for the subsequent blank correction procedures. Combine the rinses and impinger solutions, measure and record the final total volume. Mark the height of the fluid level, seal the container, and clearly label the contents.

8.2.9 Container Nos. 5A (0.1 N HNO_3), 5B ($KMnO_4/H_2SO_4$ absorbing solution), and 5C (8 N HCl rinse and dilution).

8.2.9.1 When sampling for Hg, pour all the liquid from the impinger (normally impinger No. 4) that immediately preceded the two permanganate impingers into a graduated cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Place the liquid in Container No. 5A. Rinse the impinger with exactly 100 ml of 0.1 N HNO_3 and place this rinse in Container No. 5A.

8.2.9.2 Pour all the liquid from the two permanganate impingers into a graduated cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Place this acidic $KMnO_4$ solution into Container No. 5B. Using a total of exactly 100 ml of fresh acidified $KMnO_4$ solution for all rinses (approximately 33 ml per rinse), rinse the two permanganate impingers and connecting glassware a minimum of three times. Pour the rinses into Container No. 5B, carefully assuring transfer of all loose precipitated materials from the two impingers. Similarly, using 100 ml total of water, rinse the permanganate impingers and connecting

glass a minimum of three times, and pour the rinses into Container 5B, carefully assuring transfer of any loose precipitated material. Mark the height of the fluid level, and clearly label the contents. Read the *Precaution:* in section 7.3.2.

NOTE: Due to the potential reaction of $KMnO_4$ with acid, pressure buildup can occur in the sample storage bottles. Do not fill these bottles completely and take precautions to relieve excess pressure. A No. 70–72 hole drilled in the container cap and Teflon liner has been used successfully.

8.2.9.3 Wash the two permanganate impingers with 25 ml of 8 N HCl, and place the wash in a separate sample container labeled No. 5C containing 200 ml of water. First, place 200 ml of water in the container. Then wash the impinger walls and stem with the 8 N HCl by turning the impinger on its side and rotating it so that the HCl contacts all inside surfaces. Use a total of only 25 ml of 8 N HCl for rinsing *both permanganate impingers combined*. Rinse the first impinger, then pour the actual rinse used for the first impinger into the second impinger for its rinse. Finally, pour the 25 ml of 8 N HCl rinse carefully into the container with the 200 ml of water. Mark the height of the fluid level on the outside of the container in order to determine if leakage occurs during transport.

8.2.10 Container No. 6 (Silica Gel). Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container and seal it. The tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. The small amount of particles that might adhere to the impinger wall need not be removed. Do not use water or other liquids to transfer the silica gel since weight gained in the silica gel impinger is used for moisture calculations. Alternatively, if a balance is available in the field, record the weight of the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g.

8.2.11 Container No. 7 (Acetone Blank). If particulate emissions are to be determined, at least once during each field test, place a 100-ml portion of the acetone used in the sample recovery process into a container labeled No. 7. Seal the container.

8.2.12 Container No. 8A (0.1 N HNO_3 Blank). At least once during each field test, place 300 ml of the 0.1 N HNO_3 solution used in the sample recovery process into a container labeled No. 8A. Seal the container.

8.2.13 Container No. 8B (Water Blank). At least once during each field test, place 100 ml of the water used in the sample recovery process into a container labeled No. 8B. Seal the container.

8.2.14 Container No. 9 (5 Percent HNO_3/10 Percent H_2O_2 Blank). At least once during each field test, place 200 ml of the 5 Percent HNO_3/10 Percent H_2O_2 solution used as the nitric acid impinger reagent into a container labeled No. 9. Seal the container.

8.2.15 Container No. 10 (Acidified $KMnO_4$ Blank). At least once during each field test, place 100 ml of the acidified $KMnO_4$ solution used as the impinger solution and in the sample recovery process into a container labeled No. 10. Prepare the container as described in section 8.2.9.2. Read the *Precaution*: in section 7.3.2 and read the note in section 8.2.9.2.

8.2.16 Container No. 11 (8 N HCl Blank). At least once during each field test, place 200 ml of water into a sample container labeled No. 11. Then carefully add with stirring 25 ml of 8 N HCl. Mix well and seal the container.

8.2.17 Container No. 12 (Sample Filter Blank). Once during each field test, place into a petri dish labeled No. 12 three unused blank filters from the same lot as the sampling filters. Seal the petri dish.

8.3 Sample Preparation. Note the level of the liquid in each of the containers and determine if any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. A diagram illustrating sample preparation and analysis procedures for each of the sample train components is shown in Figure 29–3.

8.3.1 Container No. 1 (Sample Filter).

8.3.1.1 If particulate emissions are being determined, first desiccate the filter and filter catch without added heat (do not heat the filters to speed the drying) and weigh to a constant weight as described in section 11.2.1 of Method 5.

8.3.1.2 Following this procedure, or initially, if particulate emissions are not being determined in addition to metals analysis, divide the filter with its filter catch into portions containing approximately 0.5 g each. Place the pieces in the analyst's choice of either individual microwave pressure relief vessels or Parr Bombs. Add 6 ml of concentrated HNO_3 and 4 ml of concentrated HF to each vessel. For microwave heating, microwave the samples for approximately 12 to 15 minutes total heating time as follows: heat for 2 to 3 minutes, then turn off the microwave for 2 to 3 minutes, then heat for 2 to 3 minutes, etc., continue this alternation until the 12 to 15 minutes total heating time are completed (this procedure should comprise approximately 24 to 30 minutes at 600 watts). Microwave heating times are approximate and are dependent upon the number of samples being digested simultaneously. Sufficient heating is evidenced by sorbent reflux within the vessel. For conventional heating, heat the Parr Bombs at 140 °C (285 °F) for 6 hours. Then cool the samples to

room temperature, and combine with the acid digested probe rinse as required in section 8.3.3.

8.3.1.3 If the sampling train includes an optional glass cyclone in front of the filter, prepare and digest the cyclone catch by the procedures described in section 8.3.1.2 and then combine the digestate with the digested filter sample.

8.3.2 Container No. 2 (Acetone Rinse). Note the level of liquid in the container and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically within 1 ml or gravimetrically within 0.5 g. Transfer the contents to an acid-cleaned, tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. If particulate emissions are being determined, desiccate for 24 hours without added heat, weigh to a constant weight according to the procedures described in section 11.2.1 of Method 5, and report the results to the nearest 0.1 mg. Redissolve the residue with 10 ml of concentrated HNO_3. Quantitatively combine the resultant sample, including all liquid and any particulate matter, with Container No. 3 before beginning section 8.3.3.

8.3.3 Container No. 3 (Probe Rinse). Verify that the pH of this sample is 2 or lower. If it is not, acidify the sample by careful addition with stirring of concentrated HNO_3 to pH 2. Use water to rinse the sample into a beaker, and cover the beaker with a ribbed watch glass. Reduce the sample volume to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Digest the sample in microwave vessels or Parr Bombs by quantitatively transferring the sample to the vessel or bomb, carefully adding the 6 ml of concentrated HNO_3, 4 ml of concentrated HF, and then continuing to follow the procedures described in section 8.3.1.2. Then combine the resultant sample directly with the acid digested portions of the filter prepared previously in section 8.3.1.2. The resultant combined sample is referred to as *''Sample Fraction 1''*. Filter the combined sample using Whatman 541 filter paper. Dilute to 300 ml (or the appropriate volume for the expected metals concentration) with water. This diluted sample is *''Analytical Fraction 1''*. Measure and record the volume of Analytical Fraction 1 to within 0.1 ml. Quantitatively remove a 50-ml aliquot and label as *''Analytical Fraction 1B''*. Label the remaining 250-ml portion as *''Analytical Fraction 1A''*. Analytical Fraction 1A is used for ICAP or AAS analysis for all desired metals except Hg. Analytical Fraction 1B is used for the determination of front-half Hg.

8.3.4 Container No. 4 (Impingers 1–3). Measure and record the total volume of this sample to within 0.5 ml and label it *''Sample Fraction 2''*. Remove a 75- to 100-ml aliquot for Hg analysis and label the aliquot *''Analytical Fraction 2B''*. Label the remaining portion of Container No. 4 as *''Sample Fraction 2A''*. Sample Fraction 2A defines the volume of Analytical Fraction 2A *prior* to digestion. All of Sample Fraction 2A is digested to produce *''Analytical Fraction 2A''*. Analytical Fraction 2A defines the volume of Sample Fraction 2A *after* its digestion and the volume of Analytical Fraction 2A is normally 150 ml. Analytical Fraction 2A is analyzed for all metals except Hg. Verify that the pH of Sample Fraction 2A is 2 or lower. If necessary, use concentrated HNO_3 by careful addition and stirring to lower Sample Fraction 2A to pH 2. Use water to rinse Sample Fraction 2A into a beaker and then cover the beaker with a ribbed watchglass. Reduce Sample Fraction 2A to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Then follow either of the digestion procedures described in sections 8.3.4.1 or 8.3.4.2.

8.3.4.1 Conventional Digestion Procedure. Add 30 ml of 50 percent HNO_3, and heat for 30 minutes on a hot plate to just below boiling. Add 10 ml of 3 percent H_2O_2 and heat for 10 more minutes. Add 50 ml of hot water, and heat the sample for an additional 20 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water. This dilution produces Analytical Fraction 2A. Measure and record the volume to within 0.1 ml.

8.3.4.2 Microwave Digestion Procedure. Add 10 ml of 50 percent HNO_3 and heat for 6 minutes total *heating* time in alternations of 1 to 2 minutes at 600 Watts followed by 1 to 2 minutes with no power, etc., similar to the procedure described in section 8.3.1. Allow the sample to cool. Add 10 ml of 3 percent H_2O_2 and heat for 2 more minutes. Add 50 ml of hot water, and heat for an additional 5 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water. This dilution produces Analytical Fraction 2A. Measure and record the volume to within 0.1 ml.

NOTE: All microwave heating times given are approximate and are dependent upon the number of samples being digested at a time. Heating times as given above have been found acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by solvent reflux within the vessel.

8.3.5 Container No. 5A (Impinger 4), Container Nos. 5B and 5C (Impingers 5 and 6). Keep the samples in Containers Nos. 5A, 5B, and 5C separate from each other. Measure and record the volume of 5A to within 0.5 ml. Label the contents of Container No. 5A to be

Analytical Fraction 3A. To remove any brown MnO_2 precipitate from the contents of Container No. 5B, filter its contents through Whatman 40 filter paper into a 500 ml volumetric flask and dilute to volume with water. Save the filter for digestion of the brown MnO_2 precipitate. Label the 500 ml filtrate from Container No. 5B to be Analytical Fraction 3B. Analyze Analytical Fraction 3B for Hg within 48 hours of the filtration step. Place the saved filter, which was used to remove the brown MnO_2 precipitate, into an appropriately sized *vented* container, which will allow release of any gases including chlorine formed when the filter is digested. In a laboratory hood which will remove any gas produced by the digestion of the MnO_2, add 25 ml of 8 N HCl to the filter and allow to digest for a minimum of 24 hours at room temperature. Filter the contents of Container No. 5C through a Whatman 40 filter into a 500-ml volumetric flask. Then filter the result of the digestion of the brown MnO_2 from Container No. 5B through a Whatman 40 filter into the same 500-ml volumetric flask, and dilute and mix well to volume with water. Discard the Whatman 40 filter. Mark this combined 500-ml dilute HCl solution as Analytical Fraction 3C.

8.3.6 Container No. 6 (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance.

9.0 Quality Control

9.1 Field Reagent Blanks, if analyzed. Perform the digestion and analysis of the blanks in Container Nos. 7 through 12 that were produced in sections 8.2.11 through 8.2.17, respectively. For Hg field reagent blanks, use a 10 ml aliquot for digestion and analysis.

9.1.1 Digest and analyze one of the filters from Container No. 12 per section 8.3.1, 100 ml from Container No. 7 per section 8.3.2, and 100 ml from Container No. 8A per section 8.3.3. This step produces blanks for Analytical Fractions 1A and 1B.

9.1.2 Combine 100 ml of Container No. 8A with 200 ml from Container No. 9, and digest and analyze the resultant volume per section 8.3.4. This step produces blanks for Analytical Fractions 2A and 2B.

9.1.3 Digest and analyze a 100-ml portion of Container No. 8A to produce a blank for Analytical Fraction 3A.

9.1.4 Combine 100 ml from Container No. 10 with 33 ml from Container No. 8B to produce a blank for Analytical Fraction 3B. Filter the resultant 133 ml as described for Container No. 5B in section 8.3.5, except do not dilute the 133 ml. Analyze this blank for Hg within 48 hr of the filtration step, and use 400 ml as the blank volume when calculating the blank mass value. Use the actual volumes of the other analytical blanks when calculating their mass values.

9.1.5 Digest the filter that was used to remove any brown MnO_2 precipitate from the blank for Analytical Fraction 3B by the same procedure as described in section 8.3.5 for the similar sample filter. Filter the digestate and the contents of Container No. 11 through Whatman 40 paper into a 500-ml volumetric flask, and dilute to volume with water. These steps produce a blank for Analytical Fraction 3C.

9.1.6 Analyze the blanks for Analytical Fraction Blanks 1A and 2A per section 11.1.1 and/or section 11.1.2. Analyze the blanks for Analytical Fractions 1B, 2B, 3A, 3B, and 3C per section 11.1.3. Analysis of the blank for Analytical Fraction 1A produces the front-half reagent blank correction values for the desired metals except for Hg; Analysis of the blank for Analytical Fraction 1B produces the front-half reagent blank correction value for Hg. Analysis of the blank for Analytical Fraction 2A produces the back-half reagent blank correction values for all of the desired metals except for Hg, while separate analyses of the blanks for Analytical Fractions 2B, 3A, 3B, and 3C produce the back-half reagent blank correction value for Hg.

9.2 Quality Control Samples. Analyze the following quality control samples.

9.2.1 ICAP and ICP-MS Analysis. Follow the respective quality control descriptions in section 8 of Methods 6010 and 6020 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i). For the purposes of a source test that consists of three sample runs, modify those requirements to include the following: two instrument check standard runs, two calibration blank runs, one interference check sample at the beginning of the analysis (analyze by Method of Standard Additions unless within 25 percent), one quality control sample to check the accuracy of the calibration standards (required to be within 25 percent of calibration), and one duplicate analysis (required to be within 20 percent of average or repeat all analyses).

9.2.2 Direct Aspiration AAS and/or GFAAS Analysis for Sb, As, Ba, Be, Cd, Cu, Cr, Co, Pb, Ni, Mn, Hg, P, Se, Ag, Tl, and Zn. Analyze all samples in duplicate. Perform a matrix spike on at least one front-half sample and one back-half sample, or one combined sample. If recoveries of less than 75 percent or greater than 125 percent are obtained for the matrix spike, analyze each sample by the Method of Standard Additions. Analyze a quality control sample to check the accuracy of the calibration standards. If the results are not within 20 percent, repeat the calibration.

9.2.3 CVAAS Analysis for Hg. Analyze all samples in duplicate. Analyze a quality control sample to check the accuracy of the calibration standards (if not within 15 percent, repeat calibration). Perform a matrix spike on one sample (if not within 25 percent,

analyze all samples by the Method of Standard Additions). Additional information on quality control can be obtained from Method 7470 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i), or in *Standard Methods for Water and Wastewater* Method 303F.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Sampling Train Calibration. Calibrate the sampling train components according to the indicated sections of Method 5: Probe Nozzle (Section 10.1); Pitot Tube (Section 10.2); Metering System (Section 10.3); Probe Heater (Section 10.4); Temperature Sensors (Section 10.5); Leak-Check of the Metering System (Section 8.4.1); and Barometer (Section 10.6).

10.2 Inductively Coupled Argon Plasma Spectrometer Calibration. Prepare standards as outlined in section 7.5. Profile and calibrate the instrument according to the manufacturer's recommended procedures using those standards. Check the calibration once per hour. If the instrument does not reproduce the standard concentrations within 10 percent, perform the complete calibration procedures. Perform ICP-MS analysis by following Method 6020 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i).

10.3 Atomic Absorption Spectrometer—Direct Aspiration AAS, GFAAS, and CVAAS analyses. Prepare the standards as outlined in section 7.5 and use them to calibrate the spectrometer. Calibration procedures are also outlined in the EPA methods referred to in Table 29–2 and in Method 7470 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i), or in *Standard Methods for Water and Wastewater* Method 303F (for Hg). Run each standard curve in duplicate and use the mean values to calculate the calibration line. Recalibrate the instrument approximately once every 10 to 12 samples.

10.4 Field Balance Calibration Check. Check the calibration of the balance used to weigh impingers with a weight that is at least 500g or within 50g of a loaded impinger. The weight must be ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference-see 40 CFR 60.17) Class 6 (or better). Daily before use, the field balance must measure the weight within ±0.5g of the certified mass. If the daily balance calibration check fails, perform corrective measures and repeat the check before using balance.

10.5 Analytical Balance Calibration. Perform a multipoint calibration (at least five points spanning the operational range) of the analytical balance before the first use, and semiannually thereafter. The calibration of the analytical balance must be conducted using ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 2 (or better) tolerance weights. Audit the balance each day it is used for gravimetric measurements by weighing at least one ASTM E617–13 Class 2 tolerance (or better) calibration weight that corresponds to 50 to 150 percent of the weight of one filter or between 1g and 5g. If the scale cannot reproduce the value of the calibration weight to within 0.5 mg of the certified mass, perform corrective measures, and conduct the multipoint calibration before use.

11.0 Analytical Procedure

11.1 Sample Analysis. For each sampling train sample run, seven individual analytical samples are generated; two for all desired metals except Hg, and five for Hg. A schematic identifying each sample container and the prescribed analytical preparation and analysis scheme is shown in Figure 29–3. The first two analytical samples, labeled Analytical Fractions 1A and 1B, consist of the digested samples from the front-half of the train. Analytical Fraction 1A is for ICAP, ICP-MS or AAS analysis as described in sections 11.1.1 and 11.1.2, respectively. Analytical Fraction 1B is for front-half Hg analysis as described in section 11.1.3. The contents of the back-half of the train are used to prepare the third through seventh analytical samples. The third and fourth analytical samples, labeled Analytical Fractions 2A and 2B, contain the samples from the moisture removal impinger No. 1, if used, and HNO_3/H_2O_2 impingers Nos. 2 and 3. Analytical Fraction 2A is for ICAP, ICP-MS or AAS analysis for target metals, except Hg. Analytical Fraction 2B is for analysis for Hg. The fifth through seventh analytical samples, labeled Analytical Fractions 3A, 3B, and 3C, consist of the impinger contents and rinses from the empty impinger No. 4 and the $H_2SO_4/KMnO_4$ Impingers Nos. 5 and 6. These analytical samples are for analysis for Hg as described in section 11.1.3. The total back-half Hg catch is determined from the sum of Analytical Fractions 2B, 3A, 3B, and 3C. Analytical Fractions 1A and 2A can be combined proportionally prior to analysis.

11.1.1 ICAP and ICP-MS Analysis. Analyze Analytical Fractions 1A and 2A by ICAP using Method 6010 or Method 200.7 (40 CFR 136, Appendix C). Calibrate the ICAP, and set up an analysis program as described in Method 6010 or Method 200.7. Follow the quality control procedures described in section 9.2.1. Recommended wavelengths for analysis are as shown in Table 29–2. These wavelengths represent the best combination of specificity

and potential detection limit. Other wavelengths may be substituted if they can provide the needed specificity and detection limit, and are treated with the same corrective techniques for spectral interference. Initially, analyze all samples for the target metals (except Hg) plus Fe and Al. If Fe and Al are present, the sample might have to be diluted so that each of these elements is at a concentration of less than 50 ppm so as to reduce their spectral interferences on As, Cd, Cr, and Pb. Perform ICP-MS analysis by following Method 6020 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i).

NOTE: When analyzing samples in a HF matrix, an alumina torch should be used; since all front-half samples will contain HF, use an alumina torch.

11.1.2 AAS by Direct Aspiration and/or GFAAS. If analysis of metals in Analytical Fractions 1A and 2A by using GFAAS or direct aspiration AAS is needed, use Table 29–3 to determine which techniques and procedures to apply for each target metal. Use Table 29–3, if necessary, to determine techniques for minimization of interferences. Calibrate the instrument according to section 10.3 and follow the quality control procedures specified in section 9.2.2.

11.1.3 CVAAS Hg analysis. Analyze Analytical Fractions 1B, 2B, 3A, 3B, and 3C separately for Hg using CVAAS following the method outlined in Method 7470 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i), or in *Standard Methods for Water and Wastewater Analysis*, 15th Edition, Method 303F, or, optionally using note no. 2 at the end of this section. Set up the calibration curve (zero to 1000 ng) as described in Method 7470 or similar to Method 303F using 300-ml BOD bottles instead of Erlenmeyers. Perform the following for each Hg analysis. From each original sample, select and record an aliquot in the size range from 1 ml to 10 ml. If no prior knowledge of the expected amount of Hg in the sample exists, a 5 ml aliquot is suggested for the first dilution to 100 ml (see note no. 1 at end of this section). The total amount of Hg in the aliquot shall be less than 1 μg and within the range (zero to 1000 ng) of the calibration curve. Place the sample aliquot into a separate 300-ml BOD bottle, and add enough water to make a total volume of 100 ml. Next add to it sequentially the sample digestion solutions and perform the sample preparation described in the procedures of Method 7470 or Method 303F. (See note no. 2 at the end of this section). If the maximum readings are off-scale (because Hg in the aliquot exceeded the calibration range; including the situation where only a 1-ml aliquot of the original sample was digested), then dilute the original sample (or a portion of it) with 0.15 percent HNO_3 (1.5 ml concentrated HNO_3 per liter aqueous solution) so that when a 1- to 10-ml aliquot of the ''0.15 HNO_3 percent dilution of the original sample'' is digested and analyzed by the procedures described above, it will yield an analysis within the range of the calibration curve.

NOTE NO. 1: When Hg levels in the sample fractions are below the in-stack detection limit given in Table 29–1, select a 10 ml aliquot for digestion and analysis as described.

NOTE NO. 2: Optionally, Hg can be analyzed by using the CVAAS analytical procedures given by some instrument manufacturer's directions. These include calibration and quality control procedures for the Leeman Model PS200, the Perkin Elmer FIAS systems, and similar models, if available, of other instrument manufacturers. For digestion and analyses by these instruments, perform the following two steps: (1), Digest the sample aliquot through the addition of the aqueous hydroxylamine hydrochloride/sodium chloride solution the same as described in this section: (*The Leeman, Perkin Elmer, and similar instruments described in this note add automatically the necessary stannous chloride solution during the automated analysis of Hg.)*; (2), Upon completion of the digestion described in (1), analyze the sample according to the instrument manufacturer's directions. This approach allows multiple (including duplicate) automated analyses of a digested sample aliquot.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

A = Analytical detection limit, μg/ml.
B = Liquid volume of digested sample prior to aliquotting for analysis, ml.
C = Stack sample gas volume, dsm^3.
C_{a1} = Concentration of metal in Analytical Fraction 1A as read from the standard curve, μg/ml.
C_{a2} = Concentration of metal in Analytical Fraction 2A as read from the standard curve, (μg/ml).
C_s = Concentration of a metal in the stack gas, mg/dscm.
D = In-stack detection limit, $\mu g/m^3$.
F_a = Aliquot factor, volume of Sample Fraction 2 divided by volume of Sample Fraction 2A (see section 8.3.4.)
F_d = Dilution factor (F_d = the inverse of the fractional portion of the concentrated sample in the solution actually used in the instrument to produce the reading C_{a1}. For example, if a 2 ml aliquot of Analytical Fraction 1A is diluted to 10 ml to place it in the calibration range, $F_d = 5$).
Hg_{bh} = Total mass of Hg collected in the back-half of the sampling train, μg.
Hg_{bh2} = Total mass of Hg collected in Sample Fraction 2, μg.

$Hg_{bh3(A,B,C)}$ = Total mass of Hg collected separately in Fraction 3A, 3B, or 3C, µg.

Hg_{bhb} = Blank correction value for mass of Hg detected in back-half field reagent blanks, µg.

Hg_{fh} = Total mass of Hg collected in the front-half of the sampling train (Sample Fraction 1), µg.

Hg_{fhb} = Blank correction value for mass of Hg detected in front-half field reagent blank, µg.

Hg_t = Total mass of Hg collected in the sampling train, µg.

M_{bh} = Total mass of each metal (except Hg) collected in the back-half of the sampling train (Sample Fraction 2), µg.

M_{bhb} = Blank correction value for mass of metal detected in back-half field reagent blank, µg.

M_{fh} = Total mass of each metal (except Hg) collected in the front half of the sampling train (Sample Fraction 1), µg.

M_{fhb} = Blank correction value for mass of metal detected in front-half field reagent blank, µg.

M_t = Total mass of each metal (separately stated for each metal) collected in the sampling train, µg.

M_t = Total mass of that metal collected in the sampling train, µg; (substitute Hg_t for M_t for the H_g calculation).

Q_{bh2} = Quantity of Hg, µg, TOTAL in the ALIQUOT of Analytical Fraction 2B selected for digestion and analysis .

NOTE: For example, if a 10 ml aliquot of Analytical Fraction 2B is taken and digested and analyzed (according to section 11.1.3 and its notes nos. 1 and 2), then calculate and use the total amount of Hg in the 10 ml aliquot for Q_{bh2}.

$Q_{bh3(A,B,C)}$ = Quantity of Hg, µg, *TOTAL, separately, in the ALIQUOT of Analytical Fraction 3A, 3B, or 3C selected for digestion and analysis* (see notes in sections 12.7.1 and 12.7.2 describing the quantity ''Q'' and calculate similarly).

Q_{fh} = Quantity of Hg, µg, *TOTAL in the ALIQUOT of Analytical Fraction 1B selected for digestion and analysis.*

NOTE: For example, if a 10 ml aliquot of Analytical Fraction 1B is taken and digested and analyzed (according to section 11.1.3 and its notes nos. 1 and 2), then calculate and use the total amount of Hg in the 10 ml aliquot for Q_{fh}.

V_a = Total volume of digested sample solution (Analytical Fraction 2A), ml (see section 8.3.4.1 or 8.3.4.2, as applicable).

V_{f1B} = Volume of aliquot of Analytical Fraction 1B analyzed, ml.

NOTE: For example, if a 1 ml aliquot of Analytical Fraction 1B was diluted to 50 ml with 0.15 percent HNO_3 as described in section 11.1.3 to bring it into the proper analytical range, and then 1 ml of that 50-ml was digested according to section 11.1.3 and analyzed, V_{f1B} would be 0.02 ml.

V_{f2B} = Volume of Analytical Fraction 2B analyzed, ml.

NOTE: For example, if 1 ml of Analytical Fraction 2B was diluted to 10 ml with 0.15 percent HNO_3 as described in section 11.1.3 to bring it into the proper analytical range, and then 5 ml of that 10 ml was analyzed, V_{f2B} would be 0.5 ml.

$V_{f3(A,B,C)}$ = Volume, separately, of Analytical Fraction 3A, 3B, or 3C analyzed, ml (see previous notes in sections 12.7.1 and 12.7.2, describing the quantity ''V'' and calculate similarly).

$V_{m(std)}$ = Volume of gas sample as measured by the dry gas meter, corrected to dry standard conditions, dscm.

$V_{soln,1}$ = Total volume of digested sample solution (Analytical Fraction 1), ml.

$V_{soln,1}$ = Total volume of Analytical Fraction 1, ml.

$V_{soln,2}$ = Total volume of Sample Fraction 2, ml.

$V_{soln,3(A,B,C)}$ = Total volume, separately, of Analytical Fraction 3A, 3B, or 3C, ml.

$K_4 = 10^{-3}$ mg/µg.

12.2 Dry Gas Volume. Using the data from this test, calculate $V_{m(std)}$, the dry gas sample volume at standard conditions as outlined in section 12.3 of Method 5.

12.3 Volume of Water Vapor and Moisture Content. Using the total volume of condensate collected during the source sampling, calculate the volume of water vapor $V_{w(std)}$ and the moisture content B_{ws} of the stack gas. Use Equations 5–2 and 5–3 of Method 5.

12.4 Stack Gas Velocity. Using the data from this test and Equation 2–9 of Method 2, calculate the average stack gas velocity.

12.5 In-Stack Detection Limits. Calculate the in-stack method detection limits shown in Table 29–4 using the conditions described in section 13.3.1 as follows:

$$A \times \frac{B}{C} = D \qquad \text{Eq. 29-1}$$

12.6 Metals (Except Hg) in Source Sample.

12.6.1 Analytical Fraction 1A, Front-Half, Metals (except Hg). Calculate separately the amount of each metal collected in Sample Fraction 1 of the sampling train using the following equation:

$$M_{fh} = C_{al} F_d V_{soln,1} \qquad \text{Eq. 29-2}$$

NOTE: If Analytical Fractions 1A and 2A are combined, use proportional aliquots. Then make appropriate changes in Equations 29–2 through 29–4 to reflect this approach.

12.6.2 Analytical Fraction 2A, Back-Half, Metals (except Hg). Calculate separately the amount of each metal collected in Fraction 2 of the sampling train using the following equation:

$$M_{bh} = C_{a2} F_a V_a \qquad \text{Eq. 29-3}$$

12.6.3 Total Train, Metals (except Hg). Calculate the total amount of each of the quantified metals collected in the sampling train as follows:

$$M_t = \left(M_{fh} - M_{fhb}\right) + \left(M_{bh} - M_{bhb}\right) \qquad \text{Eq. 29-4}$$

NOTE: If the measured blank value for the front half (M_{fhb}) is in the range 0.0 to ''A'' µg (where ''A'' µg equals the value determined by multiplying 1.4 µg/in.^{2} times the actual area in in.^{2} of the sample filter), use M_{fhb} to correct the emission sample value (M_{fh}); if M_{fhb} exceeds ''A'' µg, use the greater of I or II:

I. ''A'' µg.

II. The lesser of (a) M_{fhb}, or (b) 5 percent of M_{fh}. If the measured blank value for the back-half (M_{bhb}) is in the range 0.0 to 1 µg, use M_{bhb} to correct the emission sample value (M_{bh}); if M_{bhb} exceeds 1 µg, use the greater of I or II:

I. 1 µg.

II. The lesser of (a) M_{bhb}, or (b) 5 percent of M_{bh}.

12.7 Hg in Source Sample.

12.7.1 Analytical Fraction 1B; Front-Half Hg. Calculate the amount ofHg collected in the front-half, Sample Fraction 1, of the sampling train by using Equation 29–5:

$$Hg_{fh} = \frac{Q_{fh}}{V_{flB}}\left(V_{soln,1}\right) \qquad \text{Eq. 29-5}$$

12.7.2 Analytical Fractions 2B, 3A, 3B, and 3C; Back Half Hg.

12.7.2.1 Calculate the amount of Hg collected in Sample Fraction 2 by using Equation 29–6:

$$Hg_{bh2} = \frac{Q_{bh2}}{V_{f2B}}\left(V_{soln,2}\right) \qquad \text{Eq. 29-6}$$

12.7.2.2 Calculate each of the back-half Hg values for Analytical Fractions 3A, 3B, and 3C by using Equation 29–7:

$$Hg_{bh3(A,B,C)} = \frac{Q_{bh3(A,B,C)}}{V_{f3(A,B,C)}}\left(V_{soln,3(A,B,C)}\right) \qquad \text{Eq. 29-7}$$

12.7.2.3 Calculate the total amount of Hg collected in the back-half of the sampling train by using Equation 29–8:

$$Hg_{bh} = Hg_{bh2} + Hg_{bh3A} + Hg_{bh3B} + Hg_{bh3C} \qquad \text{Eq. 29-8}$$

12.7.3 Total Train Hg Catch. Calculate the total amount of Hg collected in the sampling train by using Equation 29–9:

$$Hg_t = \left(Hg_{fh} - Hg_{fhb}\right) + \left(Hg_{bh} - Hg_{bhb}\right) \qquad \text{Eq. 29-9}$$

NOTE: If the total of the measured blank values (Hg_{fhb} + Hg_{bhb}) is in the range of 0.0 to 0.6 µg, then use the total to correct the sample value (Hg_{fh} + Hg_{bh}); if it exceeds 0.6 µg, use the greater of I. or II:

I. 0.6 µg.

II. The lesser of (a) (Hg_{fhb} + Hg_{bhb}), or (b) 5 percent of the sample value (Hg_{fh} + Hg_{bh}).

12.8 Individual Metal Concentrations in Stack Gas. Calculate the concentration of

each metal in the stack gas (dry basis, adjusted to standard conditions) by using Equation 29–10:

$$C_s = \frac{K_4 M_t}{V_{m(std)}} \qquad \text{Eq. 29-10}$$

12.9 Isokinetic Variation and Acceptable Results. Same as Method 5, sections 12.11 and 12.12, respectively.

13.0 Method Performance

13.1 Range. For the analysis described and for similar analyses, the ICAP response is linear over several orders of magnitude. Samples containing metal concentrations in the nanograms per ml (ng/ml) to micrograms per ml (μg/ml) range in the final analytical solution can be analyzed using this method. Samples containing greater than approximately 50 μg/ml As, Cr, or Pb should be diluted to that level or lower for final analysis. Samples containing greater than approximately 20 μg/ml of Cd should be diluted to that level before analysis.

13.2 Analytical Detection Limits.

NOTE: See section 13.3 for the description of in-stack detection limits.

13.2.1 ICAP analytical detection limits for the sample solutions (based on *SW–846*, Method 6010) are approximately as follows: Sb (32 ng/ml), As (53 ng/ml), Ba (2 ng/ml), Be (0.3 ng/ml), Cd (4 ng/ml), Cr (7 ng/ml), Co (7 ng/ml), Cu (6 ng/ml), Pb (42 ng/ml), Mn (2 ng/ml), Ni (15 ng/ml), P (75 ng/ml), Se (75 ng/ml), Ag (7 ng/ml), Tl (40 ng/ml), and Zn (2 ng/ml). ICP-MS analytical detection limits (based on *SW–846*, Method 6020) are lower generally by a factor of ten or more. Be is lower by a factor of three. The actual sample analytical detection limits are sample dependent and may vary due to the sample matrix.

13.2.2 The analytical detection limits for analysis by direct aspiration AAS (based on *SW–846*, Method 7000 series) are approximately as follows: Sb (200 ng/ml), As (2 ng/ml), Ba (100 ng/ml), Be (5 ng/ml), Cd (5 ng/ml), Cr (50 ng/ml), Co (50 ng/ml), Cu (20 ng/ml), Pb (100 ng/ml), Mn (10 ng/ml), Ni (40 ng/ml), Se (2 ng/ml), Ag (10 ng/ml), Tl (100 ng/ml), and Zn (5 ng/ml).

13.2.3 The detection limit for Hg by CVAAS (on the resultant volume of the *digestion* of the aliquots taken for Hg analyses) can be approximately 0.02 to 0.2 ng/ml, depending upon the type of CVAAS analytical instrument used. 13.2.4 The use of GFAAS can enhance the detection limits compared to direct aspiration AAS as follows: Sb (3 ng/ml), As (1 ng/ml), Be (0.2 ng/ml), Cd (0.1 ng/ml), Cr (1 ng/ml), Co (1 ng/ml), Pb (1 ng/ml), Se (2 ng/ml), and Tl (1 ng/ml).

13.3 In-stack Detection Limits.

13.3.1 For test planning purposes in-stack detection limits can be developed by using the following information: (1) The procedures described in this method, (2) the analytical detection limits described in section 13.2 and in *SW–846*,(3) the normal volumes of 300 ml (Analytical Fraction 1) for the front-half and 150 ml (Analytical Fraction 2A) for the back-half samples, and (4) a stack gas sample volume of 1.25 m^3. The resultant in-stack method detection limits for the above set of conditions are presented in Table 29–1 and were calculated by using Eq. 29–1 shown in section 12.5.

13.3.2 To ensure optimum precision/resolution in the analyses, the target concentrations of metals in the analytical solutions should be at least ten times their respective analytical detection limits. Under certain conditions, and with greater care in the analytical procedure, these concentrations can be as low as approximately three times the respective analytical detection limits without seriously impairing the precision of the analyses. On at least one sample run in the source test, and for each metal analyzed, perform either repetitive analyses, Method of Standard Additions, serial dilution, or matrix spike addition, etc., to document the quality of the data.

13.3.3 Actual in-stack method detection limits are based on actual source sampling parameters and analytical results as described above. If required, the method in-stack detection limits can be improved over those shown in Table 29–1 for a specific test by either increasing the sampled stack gas volume, reducing the total volume of the digested samples, improving the analytical detection limits, or any combination of the three. For extremely low levels of *Hg only*, the aliquot size selected for digestion and analysis can be increased to as much as 10 ml, thus improving the in-stack detection limit by a factor of ten compared to a 1 ml aliquot size.

13.3.3.1 A nominal one hour sampling run will collect a stack gas sampling volume of about 1.25 m^3. If the sampling time is increased to four hours and 5 m^3 are collected, the in-stack method detection limits would be improved by a factor of four compared to the values shown in Table 29–1.

13.3.3.2 The in-stack detection limits assume that all of the sample is digested and the final liquid volumes for analysis are the normal values of 300 ml for Analytical Fraction 1, and 150 ml for Analytical Fraction 2A. If the volume of Analytical Fraction 1 is reduced from 300 to 30 ml, the in-stack detection limits for that fraction of the sample would be improved by a factor of ten. If the volume of Analytical Fraction 2A is reduced from 150 to 25 ml, the in-stack detection limits for that fraction of the sample would be improved by a factor of six. Matrix effect checks are necessary on sample analyses and typically are of much greater significance for samples that have been concentrated to

less than the normal original sample volume. Reduction of Analytical Fractions 1 and 2A to volumes of less than 30 and 25 ml, respectively, could interfere with the redissolving of the residue and could increase interference by other compounds to an intolerable level.

13.3.3.3 When both of the modifications described in sections 13.3.3.1 and 13.3.3.2 are used simultaneously on one sample, the resultant improvements are multiplicative. For example, an increase in stack gas volume by a factor of four and a reduction in the total liquid sample digested volume of both Analytical Fractions 1 and 2A by a factor of six would result in an improvement by a factor of twenty-four of the in-stack method detection limit.

13.4 Precision. The precision (relative standard deviation) for each metal detected in a method development test performed at a sewage sludge incinerator were found to be as follows:

Sb (12.7 percent), As (13.5 percent), Ba (20.6 percent), Cd (11.5 percent), Cr (11.2 percent), Cu (11.5 percent), Pb (11.6 percent), P (14.6 percent), Se (15.3 percent), Tl (12.3 percent), and Zn (11.8 percent). The precision for Ni was 7.7 percent for another test conducted at a source simulator. Be, Mn, and Ag were not detected in the tests. However, based on the analytical detection limits of the ICAP for these metals, their precisions could be similar to those for the other metals when detected at similar levels.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Alternative Analyzer. Samples may also be analyzed by cold vapor atomic fluorescence spectrometry.

16.2 [Reserved]

17.0 References

1. Method 303F in *Standard Methods for the Examination of Water Wastewater*, 15th Edition, 1980. Available from the American Public Health Association, 1015 18th Street N.W., Washington, D.C. 20036.

2. EPA Methods 6010, 6020, 7000, 7041, 7060, 7131, 7421, 7470, 7740, and 7841, *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*. SW–846, Third Edition, November 1986, with updates I, II, IIA, IIB and III. Office of Solid Waste and Emergency Response, U. S. Environmental Protection Agency, Washington, DC 20460.

3. EPA Method 200.7, Code of Federal Regulations, Title 40, Part 136, Appendix C. July 1, 1987.

4. EPA Methods 1 through 5, Code of Federal Regulations, Title 40, Part 60, Appendix A, July 1, 1991.

5. EPA Method 101A, Code of Federal Regulations, Title 40, Part 61, Appendix B, July 1, 1991.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 29–1—IN STACK METHOD DETECTION LIMITS (UG/M^3) FOR THE FRONT-HALF, THE BACK HALF, AND THE TOTAL SAMPLING TRAIN USING ICAP, GFAAS, AND CVAAS

Metal	Front-half: probe and filter	Back-half: impinters 1–3	Back-half: impringers 4–6 [a]	Total train
Antimony	[1] 7.7 (0.7)	[1] 3.8 (0.4)	.....	[1] 11.5 (1.1)
Arsenic	[1] 12.7 (0.3)	[1] 6.4 (0.1)	.....	[1] 19.1 (0.4)
Barium	0.5	0.3	.....	0.8
Beryllium	[1] 0.07 (0.05)	[1] 0.04 (0.03)	.....	[1] 0.11 (0.08)
Cadmium	[1] 1.0 (0.02)	[1] 0.5 (0.01)	.....	[1] 1.5 (0.03)
Chromium	[1] 1.7 (0.2)	[1] 0.8 (0.1)	.....	[1] 2.5 (0.3)
Cobalt	[1] 1.7 (0.2)	[1] 0.8 (0.1)	.....	[1] 2.5 (0.3)
Copper	1.4	0.7	.....	2.1
Lead	[1] 10.1 (0.2)	[1] 5.0 (0.1)	.....	[1] 15.1 (0.3)
Manganese	[1] 0.5 (0.2)	[1] 0.2 (0.1)	.....	[1] 0.7 (0.3)
Mercury	[2] 0.06	[2] 0.3	[2] 0.2	[2] 0.56
Nickel	3.6	1.8	.....	5.4
Phosphorus	18	9	.....	27
Selenium	[1] 18 (0.5)	[1] 9 (0.3)	.....	[1] 27 (0.8)
Silver	1.7	0.9 (0.7)	.....	2.6
Thallium	[1] 9.6 (0.2)	[1] 4.8 (0.1)	.....	[1] 14.4 (0.3)
Zinc	0.5	0.3	.....	0.8

[a] Mercury analysis only.
[1] Detection limit when analyzed by ICAP or GFAAS as shown in parentheses (see section 11.1.2).
[2] Detection limit when anaylzed by CVAAS, estimated for Back-half and Total Train. See sections 13.2 and 11.1.3. Note: Actual method in-stack detection limits may vary from these values, as described in section 13.3.3.

TABLE 29–2—RECOMMENDED WAVELENGTHS FOR ICAP ANALYSIS

Analyte	Wavelength (nm)
Aluminum (Al)	308.215
Antimony (Sb)	206.833
Arsenic (As)	193.696
Barium (Ba)	455.403
Beryllium (Be)	313.042
Cadmium (Cd)	226.502
Chromium (Cr)	267.716
Cobalt (Co)	228.616
Copper (Cu)	328.754
Iron (Fe)	259.940

TABLE 29–2—RECOMMENDED WAVELENGTHS FOR ICAP ANALYSIS—Continued

Analyte	Wavelength (nm)
Lead (Pb)	220.353
Manganese (Mn)	257.610
Nickel (Ni)	231.604
Phosphorus (P)	214.914
Selenium (Se)	196.026
Silver (Ag)	328.068
Thallium (T_1)	190,864
Zinc (Zn)	213,856

TABLE 29–3—APPLICABLE TECHNIQUES, METHODS AND MINIMIZATION OF INTERFERENCES FOR AAS ANALYSIS

Metal	Technique	SW–846 [1] Methods No.	Wavelength (nm)	Interferences	
				Cause	Minimization
Fe	Aspiration	7380	248.3	Contamination	Great care taken to avoid contamination.
Pb	Aspiration	7420	283.3	217.0 nm alternate	Background correction required.
Pb	Furnace	7421	283.3	Poor recoveries	Matrix modifier, add 10 μl of phosphorus acid to 1 ml of prepared sample in sampler cup.
Mn	Aspiration	7460	279.5	403.1 nm alternate	Background correction required.
Ni	Aspiration	7520	232.0	352.4 nm alternate Fe, Co, and Cr.	Background correction required. Matrix matching or nitrous-oxide/acetylene flame
				Nonlinear response	Sample dilution or use 352.3 nm line
Se	Furnace	7740	196.0	Volatility	Spike samples and reference materials and add nickel nitrate to minimize volatilization.
				Adsorption & scatter	Background correction is required and Zeeman background correction can be useful.
Ag	Aspiration	7760	328.1	Adsorption & scatter AgCl insoluble.	Background correction is required. Avoid hydrochloric acid unless silver is in solution as a chloride complex. Sample and standards monitored for aspiration rate.
Tl	Aspiration	7840	276.8		Background correction is required. Hydrochloric acid should not be used.
Tl	Furnace	7841	276.8	Hydrochloric acid or chloride.	Background correction is required. Verify that losses are not occurring for volatilization by spiked samples or standard addition; Palladium is a suitable matrix modifier.
Zn	Aspiration	7950	213.9	High Si, Cu, & P Contamination.	Strontium removes Cu and phosphate. Great care taken to avoid contamination.
Sb	Aspiration	7040	217.6	1000 mg/ml Pb, Ni, Cu, or acid.	Use secondary wavelength of 231.1 nm; match sample & standards acid concentration or use nitrous oxide/acetylene flame.
Sb	Furnace	7041	217.6	High Pb	Secondary wavelength or Zeeman correction.
As	Furnace	7060	193.7	Arsenic Volatilization Aluminum.	Spike samples and add nickel nitrate solution to digestates prior to analysis. Use Zeeman background correction.
Ba	Aspiration	7080	553.6		
				Calcium.	
				Barium Ionization	High hollow cathode current and narrow band set.
					2 ml of KCl per 100 m1 of sample.
Be	Aspiration	7090	234.9	500 ppm Al. High Mg and Si.	Add 0.1% fluoride.
Be	Furnace	7091	234.9	Be in optical path	Optimize parameters to minimize effects.
Cd	Aspiration	7130	228.8	Absorption and light scattering.	Background correction is required.

TABLE 29–3—APPLICABLE TECHNIQUES, METHODS AND MINIMIZATION OF INTERFERENCES FOR AAS ANALYSIS—Continued

Metal	Technique	SW–846 [1] Methods No.	Wavelength (nm)	Interferences	
				Cause	Minimization
Cd	Furnace	7131	228.8	As above	As above.
				Excess Chloride	Ammonium phosphate used as a matrix modifier.
				Pipet Tips	Use cadmium-free tips.
Cr	Aspiration	7190	357.9	Alkali metal	KCl ionization suppressant in samples and standards—Consult mfgs' literature.
Co	Furnace	7201	240.7	Excess chloride	Use Method of Standard Additions.
Cr	Furnace	7191	357.9	200 mg/L Ca and P	All calcium nitrate for a know constant effect and to eliminate effect of phosphate.
Cu	Aspiration	7210	324.7	Absorption and Scatter	Consult manufacturer's manual.

[1] Refer to EPA publication SW–846 (Reference 2 in section 16.0).

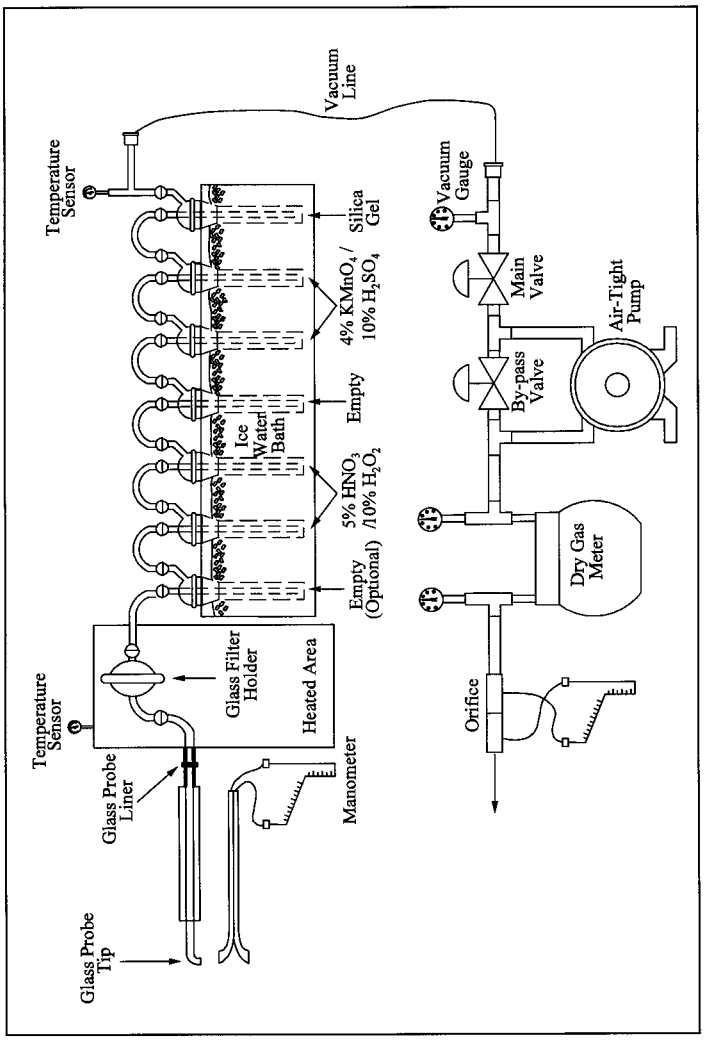


Figure 29-1. Sampling Train.

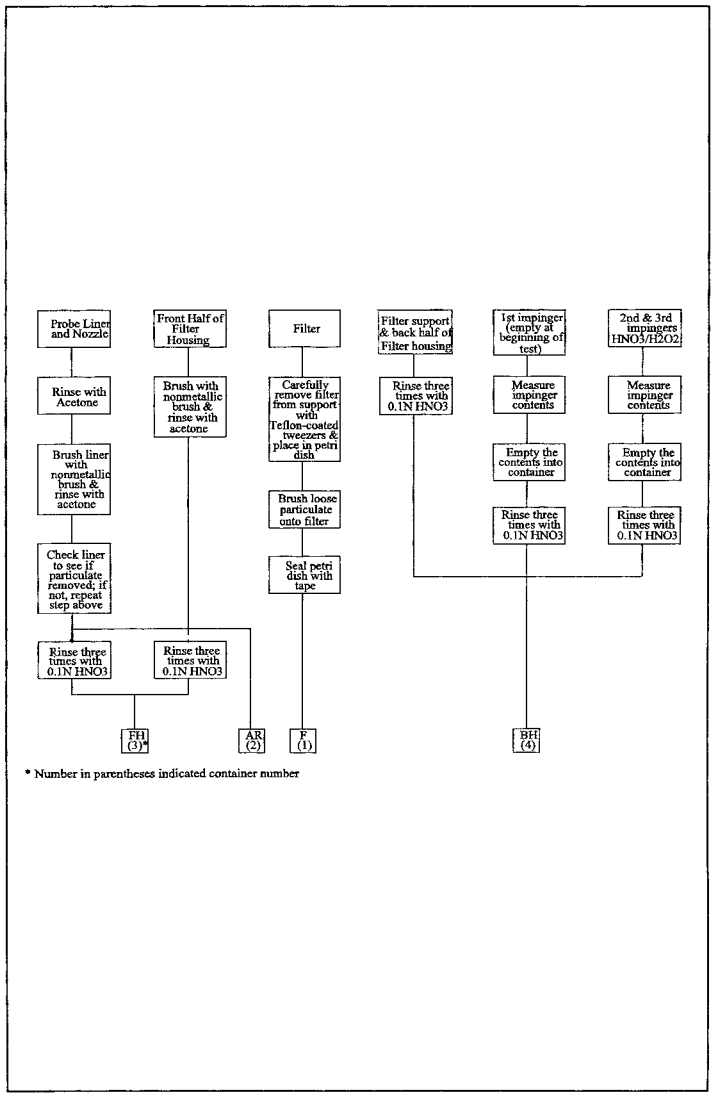


Figure 29-2a. Sample Recovery Scheme.

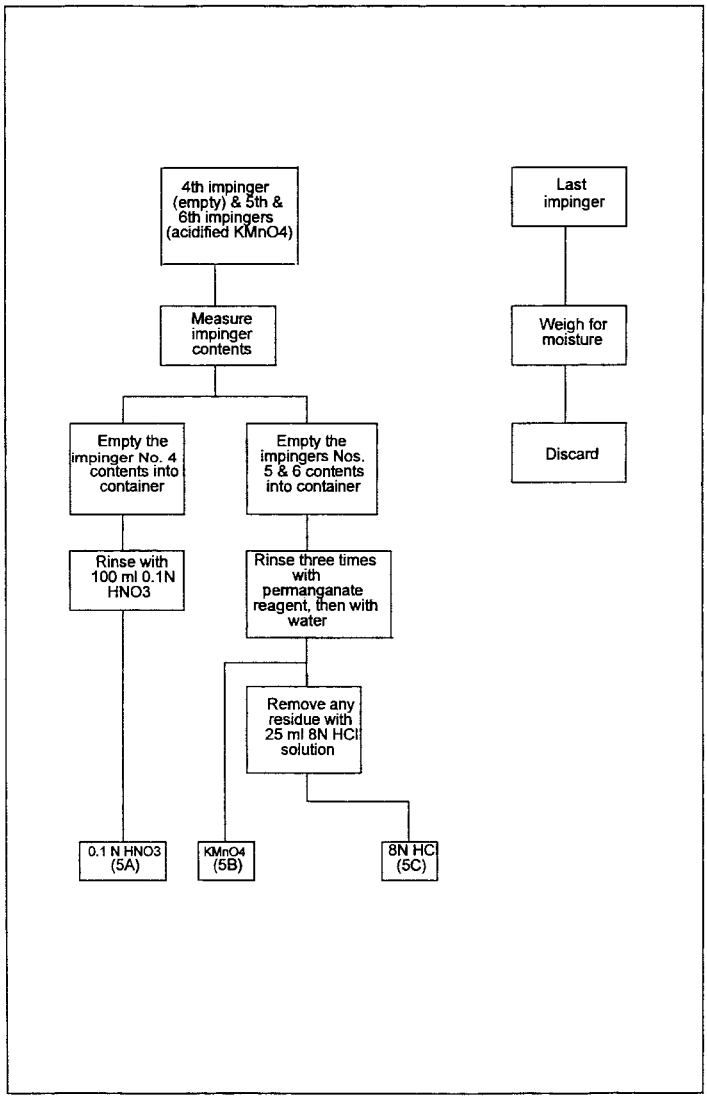


Figure 29-2b. Sample Recovery Scheme.

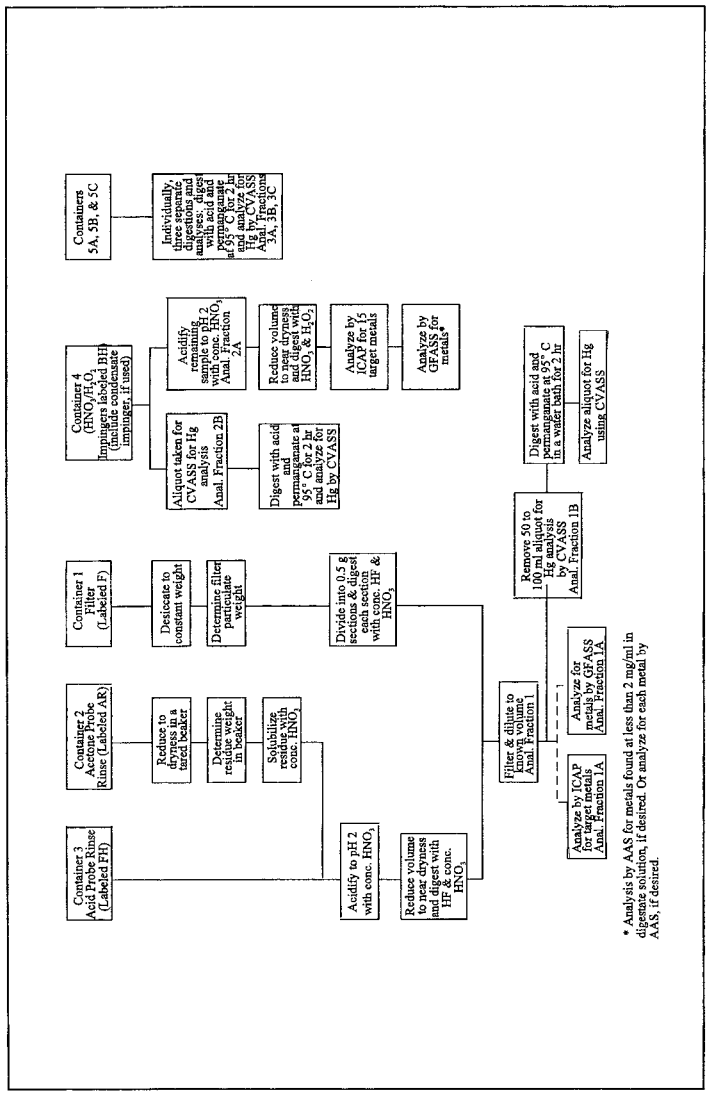


Figure 29-3. Sample Preparation and Analysis Scheme.

METHOD 30A—DETERMINATION OF TOTAL VAPOR PHASE MERCURY EMISSIONS FROM STATIONARY SOURCES (INSTRUMENTAL ANALYZER PROCEDURE)

1.0 Scope and Application

What Is Method 30A?

Method 30A is a procedure for measuring total vapor phase mercury (Hg) emissions from stationary sources using an instrumental analyzer. This method is particularly appropriate for performing emissions testing and for conducting relative accuracy test audits (RATAs) of mercury continuous emissions monitoring systems (Hg CEMS) and sorbent trap monitoring systems at coal-fired combustion sources. Quality assurance and quality control requirements are included to assure that you, the tester, collect

data of known and acceptable quality for each testing site. This method does not completely describe all equipment, supplies, and sampling procedures and analytical procedures you will need but refers to other test methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional methods which are also found in appendices A–1 and A–3 to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 4—Determination of Moisture Content in Stack Gases.

1.1 Analytes. What does this method determine? This method is designed to measure the mass concentration of total vapor phase Hg in flue gas, which represents the sum of elemental Hg (Hg^0) and oxidized forms of Hg (Hg^{+2}), in mass concentration units of micrograms per cubic meter ($\mu g/m^3$).

Analyte	CAS No.	Sensitivity
Elemental Hg (Hg^0) ..	7439–97–6	Typically <2% of Calibration Span.
Oxidized Hg (Hg^{+2})		(Same).

1.2 Applicability. When is this method required? Method 30A is offered as a reference method for emission testing and for RATAs of Hg CEMS and sorbent trap monitoring systems at coal-fired boilers. Method 30A may also be specified for other source categories in the future, either by New Source Performance Standards (NSPS), National Emission Standards for Hazardous Air Pollutants (NESHAP), emissions trading programs, State Implementation Plans (SIP), or operating permits that require measurement of Hg concentrations in stationary source emissions to determine compliance with an applicable emission standard or limit, or to conduct RATAs of Hg CEMS and sorbent trap monitoring systems.

1.3 Data Quality Objectives (DQO). How good must my collected data be? Method 30A has been designed to provide data of high and known quality for Hg emission testing and for relative accuracy testing of Hg monitoring systems including Hg CEMS and sorbent trap monitoring systems. In these and other applications, the principle objective is to ensure the accuracy of the data at the actual emission levels encountered. To meet this objective, calibration standards prepared according to an EPA traceability protocol must be used and measurement system performance tests are required.

2.0 Summary of Method

In this method, a sample of the effluent gas is continuously extracted and conveyed to an analyzer capable of measuring the total vapor phase Hg concentration. Elemental and oxidized mercury (i.e., Hg^0 and Hg^{+2}) may be measured separately or simultaneously but, for purposes of this method, total vapor phase Hg is the sum of Hg^0 and Hg^{+2}. You must meet the performance requirements of this method (i.e., system calibration, interference testing, dynamic spiking, and system integrity/drift checks) to validate your data. The dynamic spiking requirement is deferred until January 1, 2009.

3.0 Definitions

3.1 *Calibration Curve* means the relationship between an analyzer's response to the injection of a series of calibration gases and the actual concentrations of those gases.

3.2 *Calibration Gas* means a gas standard containing Hg^0 or $HgCl_2$ at a known concentration that is produced and certified in accordance with an EPA traceability protocol for certification of Hg calibration standards.

3.2.1 *Zero Gas* means a calibration gas with a concentration that is below the level detectable by the measurement system.

3.2.2 *Low-Level Gas* means a calibration gas with a concentration that is 10 to 30 percent of the calibration span.

3.2.3 *Mid-Level Gas* means a calibration gas with a concentration that is 40 to 60 percent of the calibration span.

3.2.4 *High-Level Gas* means a calibration gas whose concentration is equal to the calibration span.

3.3 *Converter* means a device that reduces oxidized mercury (Hg^{+2}) to elemental mercury (Hg^0).

3.4 *Calibration Span* means the upper limit of valid instrument response during sampling. To the extent practicable the measured emissions are to be between 10 and 100 percent of the selected calibration span (*i.e.*, the measured emissions should be within the calibrated range determined by the Low- and High-Level gas standards). It is recommended that the calibration span be at least twice the native concentration to accommodate the dynamic spiking procedure.

3.5 *Centroidal Area* means the central area that has the same shape as the stack or duct cross section and is no greater than one percent of the stack or duct total cross-sectional area.

3.6 *Data Recorder* means the equipment that permanently records the concentrations reported by the analyzer.

3.7 *Drift Check* means the test to determine the difference between the measurement system readings obtained in a post-run system integrity check and the prior pre-run system integrity check at a specific calibration gas concentration level (*i.e.*, zero, mid-level, or high-level).

3.8 *Dynamic Spiking* means a procedure in which a known mass or concentration of vapor phase $HgCl_2$ is injected into the probe sample gas stream at a known flow rate, in

order to assess the effects of the flue gas matrix on the accuracy of the measurement system.

3.9 *Gas Analyzer* means the equipment that detects the total vapor phase Hg being measured and generates an output proportional to its concentration.

3.10 *Interference Test* means the test to detect analyzer responses to compounds other than Hg, usually gases present in the measured gas stream, that are not adequately accounted for in the calibration procedure and may cause measurement bias.

3.11 *Measurement System* means all of the equipment used to determine the Hg concentration. The measurement system may generally include the following major subsystems: sample acquisition, Hg^{+2} to Hg^0 converter, sample transport, sample conditioning, flow control/gas manifold, gas analyzer, and data recorder.

3.12 *Native Concentration* means the total vapor phase Hg concentration in the effluent gas stream.

3.13 *NIST* means the National Institute of Standards and Technology, located in Gaithersburg, Maryland.

3.14 *Response Time* means the time it takes for the measurement system, while operating normally at its target sample flow rate or dilution ratio, to respond to a known step change in gas concentration (from a low-level to a high-level gas) and to read within 5 percent of the stable high-level gas response.

3.15 *Run* means a series of gas samples taken successively from the stack or duct. A test normally consists of a specific number of runs.

3.16 *System Calibration Error* means the difference between the measured concentration of a low-, mid-, or high-level Hg^0 calibration gas and the certified concentration of the gas when it is introduced in system calibration mode.

3.17 *System Calibration Mode* means introducing the calibration gases into the measurement system at the probe, upstream of all sample conditioning components.

3.18 *Test* refers to the series of runs required by the applicable regulation.

4.0 Interferences

Interferences will vary among instruments and potential instrument-specific spectral and matrix interferences must be evaluated through the interference test and the dynamic spiking tests.

5.0 Safety

What safety measures should I consider when using this method?

This method may require you to work with hazardous materials and in hazardous conditions. You are encouraged to establish safety procedures before using the method. Among other precautions, you should become familiar with the safety recommendations in the gas analyzer user's manual. Occupational Safety and Health Administration (OSHA) regulations concerning use of compressed gas cylinders and noxious gases may apply.

6.0 Equipment and Supplies

6.1 What do I need for the measurement system? This method is intended to be applicable to multiple instrumental technologies. You may use any equipment and supplies that meet the following specifications.

6.1.1 All wetted sampling system components, including probe components prior to the point at which the calibration gas is introduced, must be chemically inert to all Hg species. Materials such as perfluoroalkoxy (PFA) Teflon™, quartz, treated stainless steel (SS) are examples of such materials. [NOTE: These materials of construction are required because components prior to the calibration gas injection point are not included in the system calibration error, system integrity, and interference tests.]

6.1.2 The interference, system calibration error, system integrity, drift and dynamic spiking test criteria must all be met by the system used.

6.1.3 The system must be capable of measuring and controlling sample flow rate.

6.1.4 All system components prior to the Hg^{+2} to Hg^0 converter must be maintained at a sample temperature above the acid gas dew point.

6.2 Measurement System Components. Figure 30A–1 in section 17.0 is an example schematic of a Method 30A measurement system.

6.2.1 Sample Probe. The probe must be made of the appropriate materials as noted in section 6.1.1, heated when necessary (see section 6.1.4), configured with ports for introduction of calibration and spiking gases, and of sufficient length to traverse all of the sample points.

6.2.2 Filter or Other Particulate Removal Device. The filter or other particulate removal device is considered to be a part of the measurement system, must be made of appropriate materials as noted in section 6.1.1, and must be included in all system tests.

6.2.3 Sample Line. The sample line that connects the probe to the converter, conditioning system and analyzer must be made of appropriate materials as noted in section 6.1.1.

6.2.4 Conditioning Equipment. For dry basis measurements, a condenser, dryer or other suitable device is required to remove moisture continuously from the sample gas. Any equipment needed to heat the probe, or sample line to avoid condensation prior to the moisture removal component is also required. For wet basis systems, you must keep the sample above its dew point either by: (1) Heating the sample line and all sample transport components up to the inlet of

the analyzer (and, for hot-wet extractive systems, also heating the analyzer) or (2) by diluting the sample prior to analysis using a dilution probe system. The components required to do either of the above are considered to be conditioning equipment.

6.2.5 Sampling Pump. A pump is needed to push or pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system. If a mechanical sample pump is used and its surfaces are in contact with the sample gas prior to detection, the pump must be leak free and must be constructed of a material that is non-reactive to the gas being sampled (see section 6.1.1). For dilution-type measurement systems, an ejector pump (eductor) may be used to create a sufficient vacuum that sample gas will be drawn through a critical orifice at a constant rate. The ejector pump may be constructed of any material that is non-reactive to the gas being sampled.

6.2.6 Calibration Gas System(s). One or more systems may be needed to introduce calibration gases into the measurement system. A system should be able to flood the sampling probe sufficiently to prevent entry of gas from the effluent stream.

6.2.7 Dynamic Spiking Port. For the purposes of the dynamic spiking procedure described in section 8.2.7, the measurement system must be equipped with a port to allow introduction of the dynamic spike gas stream with the sample gas stream, at a point as close as possible to the inlet of the probe so as to ensure adequate mixing. The same port used for system calibrations and calibration error checks may be used for dynamic spiking purposes.

6.2.8 Sample Gas Delivery. The sample line may feed directly to a converter, to a bypass valve (for speciating systems), or to a sample manifold. All valve and/or manifold components must be made of material that is non-reactive to the gas sampled and the calibration gas, and must be configured to safely discharge any excess gas.

6.2.9 Hg Analyzer. An instrument is required that continuously measures the total vapor phase Hg in the gas stream and meets the applicable specifications in section 13.0.

6.2.10 Data Recorder. A recorder, such as a computerized data acquisition and handling system (DAHS), digital recorder, strip chart, or data logger, is required for recording measurement data.

6.3 Moisture Measurement System. If correction of the measured Hg emissions for moisture is required (see section 8.5), either Method 4 in appendix A–3 to this part or other moisture measurement methods approved by the Administrator will be needed to measure stack gas moisture content.

7.0 Reagents and Standards

7.1 Calibration Gases. What calibration gases do I need? You will need calibration gases of known concentrations of Hg^0 and $HgCl_2$. Special reagents and equipment may be required to prepare the $HgCl^2$ gas standards (e.g., a NIST-traceable solution of $HgCl_2$ and a gas generator equipped with mass flow controllers).

The following calibration gas concentrations are required:

7.1.1 High-Level Gas. Equal to the selected calibration span.

7.1.2 Mid-Level Gas. 40 to 60 percent of the calibration span.

7.1.3 Low-Level Gas. 10 to 30 percent of the calibration span.

7.1.4 Zero Gas. No detectable Hg.

7.1.5 Dynamic Spike Gas. The exact concentration of the $HgCl_2$ calibration gas used to perform the pre-test dynamic spiking procedure described in section 8.2.7 depends on the native Hg concentration in the stack The spike gas must produce a spiked sample concentration above the native concentration, as specified in section 8.2.7.2.2.

7.2 Interference Test. What reagents do I need for the interference test? Use the appropriate test gases listed in Table 30A–3 in section 17.0 (i.e., the potential interferents for the source to be tested, as identified by the instrument manufacturer) to conduct the interference check. These gases need not be of protocol gas quality.

8.0 Sample Collection

Emission Test Procedure

Figure 30A–2 in section 17.0 presents an overview of the test procedures required by this method. Since you may choose different options to comply with certain performance criteria, you must identify the specific options and associated frequencies you select and document your results in regard to the performance criteria.

8.1 Selection of Sampling Sites and Sampling Points. What sampling site and sampling points do I select?

8.1.1 When this method is used solely for Hg emission testing (e.g., to determine compliance with an emission standard or limit), use twelve sampling points located according to Table 1–1 or Table 1–2 of Method 1 in appendix A–1 to this part. Alternatively, you may conduct a stratification test as described in section 8.1.3 to determine the number and location of the sampling points.

8.1.2 When this method is used for relative accuracy testing of a Hg CEMS or sorbent trap monitoring system, follow the sampling

site selection and sampling point layout procedures for gas monitor RATA testing described in the appropriate performance specification or applicable regulation (e.g., Performance Specification 2, section 8.1.3 of appendix B to this part or section 6.5.6 of appendix A to part 75 of this chapter), with one exception. If you elect to perform stratification testing as part of the sampling point selection process, perform the testing in accordance with section 8.1.3 of this method (see also ''Summary Table of QA/QC Requirements'' in section 9.0).

8.1.3 Determination of Stratification. If you elect to perform stratification testing as part of the sampling point selection process and the test results show your effluent gas stream to be unstratified or minimally stratified, you may be allowed to sample at fewer points or at different points than would otherwise be required.

8.1.3.1 Test Procedure. To test for stratification, use a probe of appropriate length to measure the total vapor phase Hg concentration at twelve traverse points located according to Table 1–1 or Table 1–2 of Method 1 in appendix A–1 to this part. Alternatively, for a sampling location where stratification is expected (e.g., after a wet scrubber or at a point where dissimilar gas streams are combined together), if a 12-point Hg stratification test has been previously performed at that location and the results of the test showed the location to be minimally stratified or unstratified according to the criteria in section 8.1.3.2, you may perform an abbreviated 3-point or 6-point Hg stratification test at the points specified in section 6.5.6.2(a) of appendix A to part 75 of this chapter in lieu of performing the 12-point test. Sample for a minimum of twice the system response time (see section 8.2.6) at each traverse point. Calculate the individual point and mean Hg concentrations.

8.1.3.2 Acceptance Criteria and Sampling Point Location.

8.1.3.2.1 If the Hg concentration at each traverse point differs from the mean concentration for all traverse points by no more than: (a) ±5 percent of the mean concentration; or (b) ±0.2 μg/m^3 (whichever is less restrictive), the gas stream is considered to be unstratified and you may collect samples from a single point that most closely matches the mean.

8.1.3.2.2 If the 5 percent or 0.2 μg/m^3 criterion in section 8.1.3.2.1 is not met, but the Hg concentration at each traverse point differs from the mean concentration for all traverse points by no more than: (a)±10 percent of the mean; or (b)±0.5 μg/m^3 (whichever is less restrictive), the gas stream is considered to be minimally stratified, and you may take samples from three points, provided the points are located on the measurement line exhibiting the highest average Hg concentration during the stratification test. If the stack diameter (or equivalent diameter, for a rectangular stack or duct) is greater than 2.4 meters (7.8 ft), locate the three sampling points at 0.4, 1.0, and 2.0 meters from the stack or duct wall. Alternatively, if a RATA required by part 75 of this chapter is being conducted, you may locate the three points at 4.4, 14.6, and 29.6 percent of the duct diameter, in accordance with Method 1 in appendix A–1 to this part. For stack or duct diameters of 2.4 meters (7.8 ft) or less, locate the three sampling points at 16.7, 50.0, and 83.3 percent of the measurement line.

8.1.3.2.3 If the gas stream is found to be stratified because the 10 percent or 0.5 μg/m^3 criterion in section 8.1.3.2.2 is not met, then either locate three sampling points at 16.7, 50.0, and 83.3 percent of the measurement line that exhibited the highest average Hg concentration during the stratification test, or locate twelve traverse points for the test in accordance with Table 1–1 or Table 1–2 of Method 1 in appendix A–1 to this part; or, if a RATA required by part 75 of this chapter is being conducted, locate six Method 1 points along the measurement line that exhibited the highest average Hg concentration.

8.1.3.3 Temporal Variations. Temporal variations in the source Hg concentration during a stratification test may complicate the determination of stratification. If temporal variations are a concern, you may use the following procedure to normalize the stratification test data. A second Hg measurement system, i.e., either an installed Hg CEMS or another Method 30A system, is required to perform this procedure. Position the sampling probe of the second Hg measurement system at a fixed point in the stack or duct, at least one meter from the stack or duct wall. Then, each time that the Hg concentration is measured at one of the stratification test points, make a concurrent measurement of Hg concentration at the fixed point. Normalize the Hg concentration measured at each traverse point, by multiplying it by the ratio of $C_{F,avg}$ to C_F, where C_F is the corresponding fixed-point Hg concentration measurement, and $C_{F,avg}$ is the average of all of the fixed-point measurements over the duration of the stratification test. Evaluate the results of the stratification test according to section 8.1.3.2, using the normalized Hg concentrations.

8.1.3.4 Stratification Testing Exemption. Stratification testing need not be performed at a test location where it would otherwise be required to justify using fewer sample points or different sample points, if the owner or operator documents that the Hg concentration in the stack gas is expected to be 3 μg/m^3 or less at the time of a Hg monitoring system RATA or an Hg emissions test. To demonstrate that a particular test location qualifies for the stratification testing exemption, representative Hg emissions data must be collected just prior to the RATA or

emissions test. At least one hour of Hg concentration data is required for the demonstration. The data used for the demonstration shall be recorded at process operating conditions that closely approximate the operating conditions that will exist during the RATA or emissions test. It is recommended that collection of the demonstration data be integrated with the on-site pretest procedures required by the reference method being used for the RATA or emissions test (whether this method or another approved Hg reference method is used). Quality-assured data from an installed Hg monitoring system may also be used for the demonstration. If a particular test location qualifies for the stratification testing exemption, sampling shall be performed at three points, as described in section 8.1.3.2.2 of this method. The owner or operator shall fully document the method used to collect the demonstration data and shall keep this documentation on file with the data from the associated RATA or Hg emissions test.

8.1.3.5 Interim Alternative Stratification Test Procedures. In the time period between the effective date of this method and January 1, 2009, you may follow one of the following two procedures. Substitute a stratification test for sulfur dioxide (SO_2) for the Hg stratification test described in section 8.1.3.1. If this option is chosen, follow the test procedures in section 6.5.6.1 of appendix A to part 75 of this chapter. Evaluate the test results and determine the sampling point locations according to section 6.5.6.3 of appendix A to part 75 of this chapter. If the sampling location is found to be minimally stratified or unstratified for SO_2, it shall be considered minimally stratified or unstratified for Hg. Alternatively, you may forgo stratification testing, assume the gas stream is minimally stratified, and sample at three points as described in section 8.1.3.2.2 of this method.

8.2 Initial Measurement System Performance Tests. What initial performance criteria must my system meet before I begin sampling? Before measuring emissions, perform the following procedures:

(a) Interference Test;

(b) Calibration Gas Verification;

(c) Measurement System Preparation;

(d) 3-Point System Calibration Error Test;

(e) System Integrity Check;

(f) Measurement System Response Time Test; and

(g) Dynamic Spiking Test.

8.2.1 Interference Test (Optional). Your measurement system should be free of known interferences. It is recommended that you conduct this interference test of your measurement system prior to its initial use in the field to verify that the candidate test instrument is free from inherent biases or interferences resulting from common combustion emission constituents. If you have multiple measurement systems with components of the same make and model numbers, you need only perform this interference check on one system and you may also rely on an interference test conducted by the manufacturer on a system having components of the same make and model(s) of the system that you use. The interference test procedure is found in section 8.6 of this method.

8.2.2 Calibration Gas Verification. How must I verify the concentrations of my calibration gases?

8.2.2.1 Cylinder Gas Standards. When cylinder gas standards are used for Hg^0, obtain a certificate from the gas manufacturer and confirm that the documentation includes all information required by an EPA traceability protocol (see section 16). Confirm that the manufacturer certification is complete and current. Ensure that the calibration gas certifications have not expired.

8.2.2.2 Other Calibration Standards. All other calibration standards for $HgCl_2$ and Hg^0, such as gas generators, must meet the requirements of an EPA traceability protocol (see section 16), and the certification procedures must be fully documented in the test report.

8.2.2.3 Calibration Span. Select the calibration span (i.e., high-level gas concentration) so that the measured source emissions are 10 to 100 percent of the calibration span. This requirement is waived for applications in which the Hg concentrations are consistently below 1 $\mu g/m^3$; however, the calibration span for these low-concentration applications shall not exceed 5 $\mu g/m^3$.

8.2.3 Measurement System Preparation. How do I prepare my measurement system for use? Assemble, prepare, and precondition the measurement system according to your standard operating procedure. Adjust the system to achieve the correct sampling rate or dilution ratio (as applicable). Then, conduct a 3-point system calibration error test using Hg^0 as described in section 8.2.4, an initial system integrity check using $HgCl_2$ and a zero gas as described in section 8.2.5, and a pre-test dynamic spiking test as described in section 8.2.7.

8.2.4 System Calibration Error Test. Conduct a 3-point system calibration error test before the first test run. Use Hg^0 standards for this test. Introduce the low-, mid-, and high-level calibration gases in any order, in system calibration mode, unless you desire to determine the system response time during this test, in which case, inject the gases such that the high-level injection directly follows the low-level injection. For non-dilution systems, you may adjust the system to maintain the correct flow rate at the analyzer during the test, but you may not make adjustments for any other purpose. For dilution systems, you must operate the measurement system at the appropriate dilution

ratio during all system calibration error checks, and you may make only the adjustments necessary to maintain the proper ratio. After each gas injection, wait until a stable response has been obtained. Record the analyzer's final, stable response to each calibration gas on a form similar to Table 30A–1 in section 17.0. For each calibration gas, calculate the system calibration error using Equation 30A–1 in section 12.2. The calibration error specification in section 13.1 must be met for the low-, mid-, and high-level gases. If the calibration error specification is not met for all three gases, take corrective action and repeat the test until an acceptable 3-point calibration is achieved.

8.2.5 System Integrity Check. Perform a two-point system integrity check before the first test run. Use the zero gas and either the mid- or high-level $HgCl_2$ calibration gas for the check, whichever one best represents the total vapor phase Hg concentration levels in the stack. Record the data on a form similar to Table 30A–2 in section 17.0. The system integrity check specification in section 13.2 must be met for both the zero gas and the mid- or high-level gas. If the system integrity specification is not met for both gases, take corrective action and repeat the test until an acceptable system integrity check is achieved.

8.2.6 Measurement System Response Time. The measurement system response time is used to determine the minimum sampling time for each sampling point and is equal to the time that is required for the measured Hg concentration to increase from the stable low-level calibration gas response to a value within 5 percent of the stable high-level calibration gas response during the system calibration error test in section 8.2.4. Round off the measured system response time to the nearest minute.

8.2.7 Dynamic Spiking Test. You must perform dynamic spiking prior to the first test run to validate your test data. The purpose of this procedure is to demonstrate that the site-specific flue gas matrix does not adversely affect the accuracy of the measurement system. The specifications in section 13.5 must be met to validate your data. If these specifications are not met for the pretest dynamic spiking, you may not proceed with the test until satisfactory results are obtained. For the time period between the effective date of this method and January 1, 2009, the dynamic spiking requirement is waived.

8.2.7.1 How do I perform dynamic spiking? Dynamic spiking is a gas phase application of the method of standard additions, which involves injecting a known quantity of Hg into the measurement system upstream of all sample conditioning components, similar to system calibration mode, except the probe is not flooded and the resulting sample stream includes both effluent gas and the spike gas. You must follow a written procedure that details how the spike is added to the system, how the spike dilution factor (DF) is measured, and how the Hg concentration data are collected and processed.

8.2.7.2 Spiking Procedure Requirements.

8.2.7.2.1 Spiking Gas Requirements. The spike gas must also be a $HgCl_2$ calibration gas certified by an EPA traceability protocol. You must choose concentrations that can produce the target levels while being injected at a volumetric flow rate that is ≤20 percent of the total volumetric flow rate through the measurement system (i.e., sample flow rate plus spike gas flow rate).

8.2.7.2.2 Target Spiking Level. The target level for spiking must be 150 to 200 percent of the native Hg concentration; however, if the native Hg concentration is <1 μg/m³, set the target level to add between 1 and 4 μg/m³ Hg^{+2} to the native concentration. Use Equation 30A–5 in section 12.5 to calculate the acceptable range of spike gas concentrations at the target level. Then select a spike gas concentration in that range.

8.2.7.2.3 Spike Injections. You must inject spikes in such a manner that the spiking does not alter the total volumetric sample system flow rate and dilution ratio (if applicable). You must collect at least 3 data points, and the relative standard deviation (RSD) specification in section 13.5 must be met. Each data point represents a single spike injection, and pre- and post-injection measurements of the native Hg concentration (or diluted native concentration, as applicable) are required for each spike injection.

8.2.7.2.4 Spike Dilution Factor (DF). For each spike injection, DF, the dilution factor must be determined. DF is the ratio of the total volumetric flow rate of gas through the measurement system to the spike gas flow rate. This factor must be ≥5. The spiking mass balance calculation is directly dependent on the accuracy of the DF determination. As a result, high accuracy total volumetric flow rate and spike gas flowrate measurements are required. These flow rates may be determined by direct or indirect measurement. Calibrated flow meters, venturies, orifices or tracer gas measurements are examples of potential flow measurement techniques.

8.2.7.2.5 Concentrations. The measurement system must record total vapor phase Hg concentrations continuously during the dynamic spiking procedure. It is possible that dynamic spiking at a level close to 200 percent of the native Hg concentration may cause the measured Hg concentration to exceed the calibration span value. Avoid this by choosing a lower spiking level or by recalibration at a higher span. The measurements shall not exceed 120 percent of the calibration span. The ''baseline'' measurements made between spikes may represent

the native Hg concentration (if spike gas flow is stopped between injections) or the native Hg concentration diluted by blank or carrier gas flowing at the same rate as the spike gas (if gas flow cannot be stopped between injections). Each baseline measurement must include at least 4 readings or 1 minute (whichever is greater) of stable responses. Use Equation 30A–10 or 30A–11 in section 12.10 (as applicable) to convert baseline measurements to native concentration.

8.2.7.2.6 Recovery. Calculate spike recoveries using Equation 30A–7 in section 12.7. Mass recoveries may be calculated from stable responses based on injected mass flows or from integrated response peaks based on total mass injected. Calculate the mean and RSD for the three (or more) spike injections and compare to the specifications in section 13.5.

8.2.7.2.7 Error Adjustment Option. You may adjust the measurement data collected during dynamic spiking for the system calibration error using Equation 30A–3 in section 12. To do this, perform the initial system integrity check prior to the dynamic spiking test, and perform another system integrity check following the dynamic spiking test and before the first test run. If you choose this option, you must apply Equation 30A–3 to both the spiked sample concentration measurement (C_{ss}) and the baseline or native concentration measurement (C_{native}), each substituted in place of C_{avg} in the equation.

8.2.7.3 Example Spiking Procedure Using a Hot Vapor Calibration Source Generator.

(a) Introduce the spike gas into the probe using a hot vapor calibration source generator and a solution of $HgCl_2$ in dilute HC1 and HNO_3. The calibrator uses a mass flow controller (accurate within 2 percent) to measure the gas flow, and the solution feed is measured using a top-loading balance accurate to 0.01g. The challenges of injecting oxidized Hg may make it impractical to stop the flow of gas between spike injections. In this case, operate the hot vapor calibration source generator continuously during the spiking procedure, swapping blank solutions for $HgCl_2$ solutions when switching between spiking and baseline measurements.

(b) If applicable, monitor the measurement system to make sure the total sampling system flow rate and the sample dilution ratio do not change during this procedure. Record all data on a data sheet similar to Table 30A–5 in section 17.0. If the Hg measurement system design makes it impractical to measure the total volumetric flow rate through the system, use a spike gas that includes a tracer for measuring the dilution factor, DF (see Equation 30A–9 in section 12.9). Allow the measurements to stabilize between each spike injection, average the pre- and post-injection baseline measurements, and calculate the native concentration. If this measurement shifts by more than 5 percent during any injection, it may be necessary to discard that data point and repeat the injection to achieve the required RSD among the injections. If the spikes persistently show poor repeatability, or if the recoveries are not within the range specified in section 13.5, take corrective action.

8.2.8 Run Validation. How do I confirm that each run I conduct is valid?

8.2.8.1 System Integrity Checks.

(a) Before and after each test run, perform a two-point system integrity check using the same procedure as the initial system integrity check described in section 8.2.5. You may use data from that initial system integrity check as the pre-run data for the first test run, provided it is the most recent system integrity check done before the first run. You may also use the results of a successful post-run system integrity check as the pre-run data for the next test run. Do not make any adjustments to the measurement system during these checks, other than to maintain the target calibration gas flow rate and the proper dilution ratio.

(b) As a time-saving alternative, you may, at the risk of invalidating multiple test runs, skip one or more integrity checks during a test day. Provided there have been no auto-calibrations or other instrument alterations, a single integrity check may suffice as a post-run check to validate (or invalidate) as many consecutive test runs as can be completed during a single test day. All subsequent test days must begin with a pre-run system integrity check subject to the same performance criteria and corrective action requirements as a post-run system integrity check.

(c) Each system integrity check must meet the criteria for system integrity checks in section 13.2. If a post-run system integrity check is failed, all test runs since the last passed system integrity check are invalid. If a post-run or a pre-run system integrity check is failed, you must take corrective action and pass another 3-point Hg^0 system calibration error test (Section 8.2.4) followed by another system integrity check before conducting any additional test runs. Record the results of the pre- and post-run system integrity checks on a form similar to Table 30A–2 in section 17.0.

8.2.8.2 Drift Check. Using the data from the successful pre- and post-run system integrity checks, calculate the zero and upscale drift, using Equation 30A–2 in section 12.3. Exceeding the section 13.3 specification does not invalidate the run, but corrective action must be taken and a new 3-point Hg^0 system calibration error test and a system integrity check must be passed before any more runs are made.

8.3 Dilution-Type Systems—Special Considerations. When a dilution-type measurement system is used, there are three important considerations that must be taken into

account to ensure the quality of the emissions data. First, the critical orifice size and dilution ratio must be selected properly so that the sample dew point will be below the sample line and analyzer temperatures. Second, a high-quality, accurate dilution controller must be used to maintain the correct dilution ratio during sampling. The dilution controller should be capable of monitoring the dilution air pressure, orifice upstream pressure, eductor vacuum, and sample flow rates. Third, differences between the molecular weight of calibration gas mixtures, dilution air, and the stack gas molecular weight must be considered because these can affect the dilution ratio and introduce measurement bias.

8.4 Sampling.

(a) Position the probe at the first sampling point. Allow the system to flush and equilibrate for at least two times the measurement system response time before recording any data. Then, traverse and record measurements at all required sampling points. Sample at each traverse point for an equal length of time, maintaining the appropriate sample flow rate or dilution ratio (as applicable). For all Hg instrumental method systems, the minimum sampling time at each sampling point must be at least two times the system response time, but not less than 10 minutes. For concentrating systems, the minimum sampling time must also include at least 4 concentration measurement cycles.

(b) After recording data for the appropriate period of time at the first traverse point, you may move the sample probe to the next point and continue recording, omitting the requirement to allow the system to equilibrate for two times the system response time before recording data at the subsequent traverse points. You must, however, sample at this and all subsequent traverse points for the required minimum amount of time specified in this section. If you must remove the probe from the stack for any reason, you must again allow the sampling system to equilibrate for at least two times the system response time prior to resuming data recording.

(c) If at any point the measured Hg concentration exceeds the calibration span value, you must at a minimum identify and report this as a deviation from the method. Depending on the data quality objectives of the test, this event may require corrective action before proceeding. If the average Hg concentration for any run exceeds the calibration span value, the run is invalidated.

8.5 Moisture Correction. If the moisture basis (wet or dry) of the measurements made with this method is different from the moisture basis of either: (1) The applicable emission limit; or (2) a Hg CEMS or sorbent trap monitoring system being evaluated for relative accuracy, you must determine the moisture content of the flue gas and correct the measured gas concentrations to a dry basis using Method 4 in appendix A–3 of this part or other appropriate methods, subject to the approval of the Administrator.

8.6 Optional Interference Test Procedure.

(a) Select an appropriate calibration span that reflects the source(s) to be tested and perform the interference check at 40 percent of the lowest calibration span value anticipated, e.g., 10 $\mu g/m^3$. Alternatively, successfully conducting the interference test at an absolute Hg concentration of 2 $\mu g/m^3$ will demonstrate performance for an equivalent calibration span of 5 $\mu g/m^3$, the lowest calibration span allowed for Method 30A testing. Therefore, performing the interference test at the 2 μ/m^3 level will serve to demonstrate acceptable performance for all calibration spans greater than or equal to 5 $\mu g/m^3$.

(b) Introduce the interference test gases listed in Table 30A–3 in section 17.0 into the measurement system separately or as a mixture. The interference test gases HCl and NO must be introduced as a mixture. The interference test gases must be introduced into the sampling system at the probe such that the interference gas mixtures pass through all filters, scrubbers, conditioners, and other components as would be configured for normal sampling.

(c) The interference test must be performed using $HgCl_2$, and each interference test gas (or gas mixture) must be evaluated in triplicate. This is accomplished by measuring the Hg response first with only the $HgCl_2$ gas present and then when adding the interference test gas(es) while maintaining the $HgCl_2$ concentration of the test stream constant. It is important that the equipment used to conduct the interference test be of sufficient quality so as to be capable of blending the $HgCl_2$ and interference gases while maintaining the Hg concentration constant. Gas blending system or manifolds may be used.

(d) The duration of each test should be for a sufficient period of time to ensure the Hg measurement system surfaces are conditioned and a stable output is obtained. Measure the Hg response of the analyzer to these gases in µg/m3. Record the responses and determine the overall interference response using Table 30A–4 in section 17.0 and the equations presented in section 12.11. The specification in section 13.4 must be met.

(e) A copy of these data, including the date completed and a signed certification, must be included with each test report. The intent of this test is that the interference test results are intended to be valid for the life of the system. As a result, the Hg measurement system should be operated and tested in a configuration consistent with the configuration that will be used for field applications. However, if the system used for field testing is not consistent with the system that was interference-tested, the interference test

must be repeated before it is used for any field applications. Examples of such conditions include, but are not limited to: major changes in dilution ratio (for dilution based systems), changes in catalyst materials, changes in filtering device design or materials, changes in probe design or configuration, and changes in gas conditioning materials or approaches.

9.0 Quality Control

What quality control measures must I take?

The table which follows is a summary of the mandatory, suggested, and alternative quality assurance and quality control measures and the associated frequency and acceptance criteria. All of the QC data, along with the run data, must be documented and included in the test report.

SUMMARY TABLE OF QA/QC REQUIREMENTS

Status [1]	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
S	Identify Data User	Regulatory Agency or other primary end user of data.	Before designing test..	
M	Analyzer Design	Analyzer range	Sufficiently >high-level gas to allow determination of system calibration error.	
S	Analyzer resolution or sensitivity.	<2.0 % of full-scale range.	Manufacturer design..	
S	Interference response.	Overall response ≤3% of calibration span. Alternatively, overall response ≤0.3 μg/m³.		
M	Calibration Gases	Traceability protocol	Validation of concentration required.	
M	High-level Hg^0 gas	Equal to the calibration span.	Each calibration error test..	
M	Mid-level Hg^0 gas	40 to 60% of calibration span.	Each calibration error test..	
M	Low-level Hg^0 gas	10 to 30% of calibration span.	Each calibration error test..	
M	High-level $HgCl_2$ gas	Equal to the calibration span.	Each system integrity check (if it better represents C_{native} than the mid level gas)..	
M	Mid-level $HgCl_2$	40 to 60% of calibration span.	Each system gas integrity check (if it better represents C_{native} than the high level gas)..	
M	Zero gas	Each system integrity check..		
M	Dynamic spike gas (C_{native} ≥1 μg/m³).	A high-concentration $HgCl_2$ gas, used to produce a spiked sample concentration that is 150 to 200% of the native concentration.	Pre-test; dynamic spiking not required until 1/1/09..	
M	Dynamic spike gas (C_{native} <1 μg/m³).	A high-concentration $HgCl_2$ gas, used to produce a spiked sample concentration that is 1 to 2 μg/m³ above the native concentration.	Pre-test; dynamic spiking not required until 1/1/09..	
S	Data Recorder Design.	Data resolution	≤0.5% of full-scale	Manufacturer design.
M	Sample Extraction	Probe material	Inert to sample constituents (e.g., PFA Teflon, or quartz if stack >500 °F).	Each run.
M	Sample Extraction	Probe, filter and sample line temperature.	For dry-basis analyzers, keep sample above the dew point, by heating prior to moisture removal. For wet-basis analyzers, keep sample above dew point at all times, by heating or dilution.	Each run.
M	Sample Extraction	Calibration valve material.	Inert to sample constituents (e.g., PFA Teflon or PFA Teflon coated).	Each test.
S	Sample Extraction	Sample pump material.	Inert to sample constituents	Each test.
M	Sample Extraction	Manifold material	Inert to sample constituents	Each test.

SUMMARY TABLE OF QA/QC REQUIREMENTS—Continued

Status [1]	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
M	Particulate Removal	Filter inertness	Pass calibration error check	Each calibration error check.
M	System Calibration Performance.	System calibration error (CE) test.	CE ≤5.0 % of the calibration span for the low-, mid-or high-level Hg^0 calibration gas. Alternative specification: ≤0.5 µg/m³ absolute difference between system response and reference value.	Before initial run and after a failed system integrity check or drift test.
M	System Calibration Performance.	System integrity check.	Error ≤5.0% of the calibration span for the zero and mid- or high-level $HgCl_2$ calibration gas. Alternative specification: ≤0.5 µg/m³ absolute difference between system response and reference value.	Before initial run, after each run, at the beginning of subsequent test days, and after a failed system integrity check or drift test.
M	System Performance	System response time.	Used to determine minimum sampling time per point.	During initial 3-point system calibration error test.
M	System Performance	Drift	≤3.0% of calibration span for the zero and mid- or high-level gas. Alternative specification: ≤0.3 µg/m³ absolute difference between pre- and post-run system calibration error percentages..	At least once per test day.
M	System Performance	Minimum sampling time.	The greater of two times the system response time or 10 minutes. Concentrating systems must also include at least 4 cycles.	Each sampling point.
M	System Performance	Percentage spike recovery and relative standard deviation.	Percentage spike recovery, at the target level: 100 ±10%. Relative standard deviation: ≤5 percent ... Alternative specification: absolute difference between calculated and measured spike values ≤0.5 µg/m³.	Before initial run; dynamic spiking not required until 1/1/09.
M	Sample Point Selection. For Part 60 RATAs, follow the procedures in Performance Specification 2, section 8.1.3, and for Part 75 RATAs, follow the procedures in section 6.5.6 of appendix A to Part 75. That is: • At *any* test location, you may use 3 sample points located at 16.7, 50.0, and 83.3% of a ''long'' measurement line passing through the centroidal area; or • At *any* test location, you may use 6 sample points along a diameter, located according to Method 1 (Part 75 RATAs, only); or	Number and Location of Sample Points.	For emission testing applications, use 12 points, located according to Method 1 in appendix A–1 to this part, unless the results of a stratification test allow fewer points to be used.	Prior to first run.

SUMMARY TABLE OF QA/QC REQUIREMENTS—Continued

Status [1]	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
	• At a location where stratification is not expected and the measurement line is >2.4 m (7.8 ft), you may use 3 sample points located along a ''short'' measurement line at 0.4, 1.0, and 2.0 m from the stack or duct wall or, for Part 75 only, sample points may be located at 4.4, 14.6, and 29.6% of the measurement line; or • After a wet scrubber or at a point where dissimilar gas streams are combined, either locate 3 sample points along the ''long'' measurement line or locate 6 Method 1 points along a diameter (Part 75, only), unless the results of a stratification test allow you to use a ''short'' 3-point measurement line or to sample at a single point. • If it can be demonstrated that stack gas concentration is ≤3 µg/m³, then the test site is exempted from stratification testing. Use the 3-point ''short'' measurement line if the stack diameter is >2.4 m (7.8 ft) and the 3-point ''long'' line for stack diameters ≤2.4 m (7.8 ft).			

SUMMARY TABLE OF QA/QC REQUIREMENTS—Continued

Status[1]	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
A	Sample Point Selection	Stratification Test (See section 8.1.3)..	If the Hg concentration[2] at each traverse point during the stratification test is: • Within ±5% of mean, use 1-point sampling (at the point closest to the mean); or. • Not within ±5% of mean, but is within ±10% of mean, use 3-point sampling. Locate points according to section 8.1.3.2.2 of this method.. Alternatively, if the Hg concentration at each point is:. • Within ±0.2 μg/m³ of mean, use 1-point sampling (at the point closest to the mean); or. • Not within ±0.2 μg/m³ of mean, but is within ±0.5 μg/m³ of mean, use 3-point sampling. Locate points according to section 8.1.3.2.2 of this method..	Prior to first run. Prior to 1/1/09, you may (1) forgo stratification testing and use 3 sampling points (as per section 8.1.3.2.2) or (2) perform a SO_2 stratification test (see sections 6.5.6.1 and 6.5.6.3 of appendix A to part 75), in lieu of a Hg stratification test. If the test location is unstratified or minimally stratified for SO_2, it can be considered unstratified or minimally stratified for Hg also.
M	Data Recording	Frequency	Once per cycle	During run.
S	Data Parameters	Sample concentration and calibration span.	All analyzer readings during each run within calibration span.	Each run.
M	Data Parameters	Sample concentration and calibration span.	All analyzer readings during dynamic spiking tests within 120% of calibration span.	Each spike injection.
M	Data Parameters	Sample concentration and calibration span.	Average Hg concentration for the run ≤calibration span.	Each run.

[1] M = Mandatory; S = Suggested; A = Alternative.
[2] These may either be the unadjusted Hg concentrations or concentrations normalized to account for temporal variations.

10.0 Calibration and Standardization

What measurement system calibrations are required?

Your analyzer must be calibrated with Hg° standards. The initial 3-point system calibration error test described in section 8.2.4 is required before you start the test. Also, prior to and following test runs, the two-point system integrity checks described in sections 8.2.5 and 8.2.8 are required. On and after January 1, 2009, the pre-test dynamic spiking procedure described in section 8.2.7 is also required to verify that the accuracy of the measurement system is suitable and not adversely affected by the flue gas matrix.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the procedures for calculations and data analysis listed in this section.

12.1 Nomenclature. The terms used in the equations are defined as follows:

B_{ws} = Moisture content of sample gas as measured by Method 4 in Appendix A–3 to this part, percent/100.

C_{avg} = Average unadjusted Hg concentration for the test run, as indicated by the data recorder μg/m³.

$\bar{C}_{baseline}$ = Average Hg concentration measured before and after dynamic spiking injections, μg/m³.

C_d = Hg concentration, dry basis, μg/m³.

C_{dif} = Absolute value of the difference between the measured Hg concentrations of the reference $HgCl_2$ calibration gas, with and without the individual or combined interference gases, μg/m³.

$C_{dif\ avg}$ = Average of the 3 absolute values of the difference between the measured Hg concentrations of the reference $HgCl_2$ calibration gas, with and without the individual or combined interference gases, μg/m³.

C_{gas} = Average Hg concentration in the effluent gas for the test run, adjusted for system calibration error, μg/m³.

C_{int} = Measured Hg concentration of the reference $HgCl_2$ calibration gas plus the individual or combined interference gases, µg/m³.
C_m = Average of pre- and post-run system integrity check responses for the upscale (i.e., mid- or high-level) calibration gas, µg/m³.
C_{ma} = Actual concentration of the upscale (i.e., mid- or high-level) calibration gas used for the system integrity checks, µg/m³.
C_0 = Average of pre- and post-run system integrity check responses from the zero gas, µg/m³.
C_{native} = Vapor phase Hg concentration in the source effluent, µg/m³.
C_{ref} = Measured Hg concentration of the reference $HgCl_2$ calibration gas alone, in the interference test, µg/m³.
C_s = Measured concentration of a calibration gas (zero-, low-, mid-, or high-level), when introduced in system calibration mode, µg/m³.
C_{spike} = Actual Hg concentration of the spike gas, µg/m³.
C^*_{spike} = Hg concentration of the spike gas required to achieve a certain target value for the spiked sample Hg concentration, µg/m³.
C_{ss} = Measured Hg concentration of the spiked sample at the target level, µg/m³.
C^*_{ss} = Expected Hg concentration of the spiked sample at the target level, µg/m³.
C_{target} = Target Hg concentration of the spiked sample, µg/m³.
$C_{Tnative}$ = Measured tracer gas concentration present in native effluent gas, ppm.
C_{Tdir} = Tracer gas concentration injected with spike gas, ppm.
C_{Tv} = Diluted tracer gas concentration measured in a spiked sample, ppm.
C_v = Certified Hg° or $HgCl_2$ concentration of a calibration gas (zero, low, mid, or high), µg/m³.
C_w = Hg concentration measured under moist sample conditions, wet basis, µg/m³.
CS = Calibration span, µg/m³.
D = Zero or upscale drift, percent of calibration span.
DF = Dilution factor of the spike gas, dimensionless.
I = Interference response, percent of calibration span.
Q_{probe} = Total flow rate of the stack gas sample plus the spike gas, liters/min.
Q_{spike} = Flow rate of the spike gas, liters/min.
R_i = Individual injection spike recovery, %.
$\bar{R}$ = Mean value of spike recoveries at a particular target level, %.
RSD = Relative standard deviation, %;.
SCE = System calibration error, percent of calibration span.
SCE_i = Pre-run system calibration error during the two-point system integrity check, percent of calibration span.
SCE_f = Post-run system calibration error during the two-point system integrity check, percent of calibration span.

12.2 System Calibration Error. Use Equation 30A–1 to calculate the system calibration error. Equation 30A–1 applies to: 3–point system calibration error tests performed with Hg° standards; and pre- and post-run two-point system integrity checks performed with $HgCl_2$.

$$SCE = \frac{C_s - C_v}{CS} \times 100 \qquad \text{Eq. 30A-1}$$

12.3 Drift Assessment. Use Equation 30A–2 to separately calculate the zero and upscale drift for each test run.

$$D = \left|SCE_f - SCE_i\right| \qquad \text{Eq. 30A-2}$$

12.3 Effluent Hg Concentration. For each test run, calculate C_{avg}, the arithmetic average of all valid Hg concentration values recorded during the run. Then, adjust the value of C_{avg} for system calibration error, using Equation 30A–3.

$$C_{gas} = (C_{avg} - C_0)\,\frac{C_{ma}}{C_m - C_0} \qquad \text{Eq. 30A-3}$$

12.4 Moisture Correction. Use Equation 30A–4a if your measurements need to be corrected to a dry basis.

$$C_d = \frac{C_w}{1 - B_{ws}} \qquad \text{Eq. 30A-4a}$$

Use Equation 30A–4b if your measurements need to be corrected to a wet basis.

$$C_w = C_d \times (1 - B_{ws}) \qquad \text{Eq. 30A-4b}$$

12.5 Dynamic Spike Gas Concentrations. Use Equation 30A–5 to determine the spike gas concentration needed to produce a spiked sample with a certain ''target'' Hg concentration.

$$C^{*}_{spike} = DF(C_{target} - C_{native}) + C_{native} \qquad \text{Eq. 30A-5}$$

12.6 Spiked Sample Concentration. Use Equation 30A–6 to determine the expected or theoretical Hg concentration of a spiked sample.

$$C^{*}_{ss} = C_{native} + \frac{(C_{spike} - C_{native})}{DF} \qquad \text{Eq. 30A-6}$$

12.7 Spike Recovery. Use Equation 30A–7 to calculate the percentage recovery of each spike.

$$R = \frac{DF\,(C_{ss} - C_{native}) + C_{native}}{C_{spike}} \times 100\% \qquad \text{Eq. 30A-7}$$

12.8 Relative Standard Deviation. Use Equation 30A–8 to calculate the relative standard deviation of the individual percentage spike recovery values from the mean.

$$RSD = \frac{100\%}{\bar{R}} \sqrt{\frac{\sum_{i=1}^{n} (R_i - \bar{R})^2}{n-1}} \qquad \text{Eq. 30A-8}$$

12.9 Spike Dilution Factor. Use Equation 30A–9 to calculate the spike dilution factor, using either direct flow measurements or tracer gas measurements.

$$DF = \frac{Q_{probe}}{Q_{spike}} = \frac{C_{Tdir} - C_{Tnative}}{C_{Ttv} - C_{Tnative}} \qquad \text{Eq. 30A-9}$$

12.10 Native Concentration. For spiking procedures that inject blank or carrier gases (at the spiking flow rate, Q_{spike}) between spikes, use Equation 30A–10 to calculate the native concentration.

$$C_{native} = \frac{\bar{C}_{baseline} DF}{DF - 1} \qquad \text{Eq. 30A-10}$$

For spiking procedures that halt all injections between spikes, the native concentration equals the average baseline concentration (see Equation 30A–11).

$$C_{native} = \bar{C}_{baseline} \qquad \text{Eq. 30A-11}$$

12.11 Overall Interference Response. Use equation 30A–12 to calculate the overall interference response.

$$I = \frac{\sum C_{difavg}}{CS} \times 100 \qquad \text{Eq. 30A-12}$$

Where, for each interference gas (or mixture):

$$C_{difavg} = \frac{\sum_{1}^{3} C_{dif}}{3} \qquad \text{Eq. 30A-13}$$

$$C_{dif} = \left| C_{ref} - C_{int} \right| \qquad \text{Eq. 30A-14}$$

13.0 Method Performance

13.1 System Calibration Error Test. This specification applies to the 3-point system calibration error tests using Hg^0. At each calibration gas level tested (low-, mid-, or high-level), the calibration error must be within ±5.0 percent of the calibration span. Alternatively, the results are acceptable if $|C_s - C_v| \leq 0.5$ µg/m³.

13.2 System Integrity Checks. This specification applies to all pre- and post-run 2-point system integrity checks using $HgCl_2$ and zero gas. At each calibration gas level tested (zero and mid- or high-level), the error must be within ±5.0 percent of the calibration span. Alternatively, the results are acceptable if $|C_s - C_v| \leq 0.5$ µg/m³.

13.3 Drift. For each run, the low-level and upscale drift must be less than or equal to 3.0 percent of the calibration span. The drift is also acceptable if the pre- and post-run system integrity check responses do not differ by more than 0.3 µg/m³ (i.e., $|C_{s\ post\text{-}run} - C_{s\ pre\text{-}run}| \leq 0.3$ µg/m³).

13.4 Interference Test. Summarize the results following the format contained in Table 30A–4. For each interference gas (or mixture), calculate the mean difference between the measurement system responses with and without the interference test gas(es). The overall interference response for the analyzer that was used for the test (calculated according to Equation 30A–12), must not be greater than 3.0 percent of the calibration span used for the test (see section 8.6). The results of the interference test are also acceptable if the sum of the absolute average differences for all interference gases (i.e., $\Sigma\ C_{dif\ avg}$) does not exceed 0.3 µg/m³.

13.5 Dynamic Spiking Test. For the pretest dynamic spiking, the mean value of the percentage spike recovery must be 100 ±10 percent. In addition, the relative standard deviation (RSD) of the individual percentage spike recovery values from the mean must be ≤5.0 percent. Alternatively, if the mean percentage recovery is not met, the results are acceptable if the absolute difference between the theoretical spiked sample concentration (see section 12.6) and the actual average value of the spiked sample concentration is ≤0.5 µg/m³.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. EPA Traceability Protocol for Qualification and Certification of Elemental Mercury Gas Generators, expected publication date December 2008, see *www.epa.gov/ttn/emc*.

2. EPA Traceability Protocol for Qualification and Certification of Oxidized Mercury Gas Generators, expected publication date December 2008, see *www.epa.gov/ttn/emc*.

3. EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards, expected revision publication date December 2008, see *www.epa.gov/ttn/emc*.

17.0 Figures and Tables

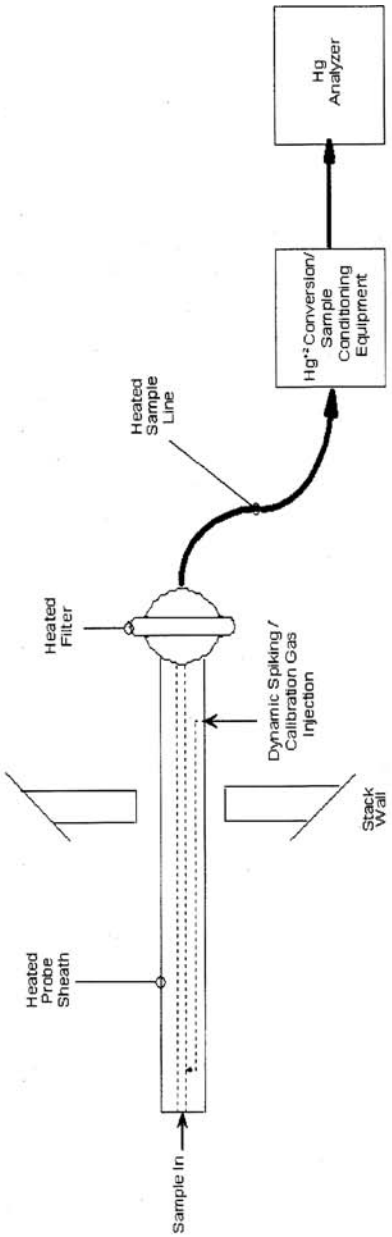


Figure 30A-1: Example Hg Measurement System

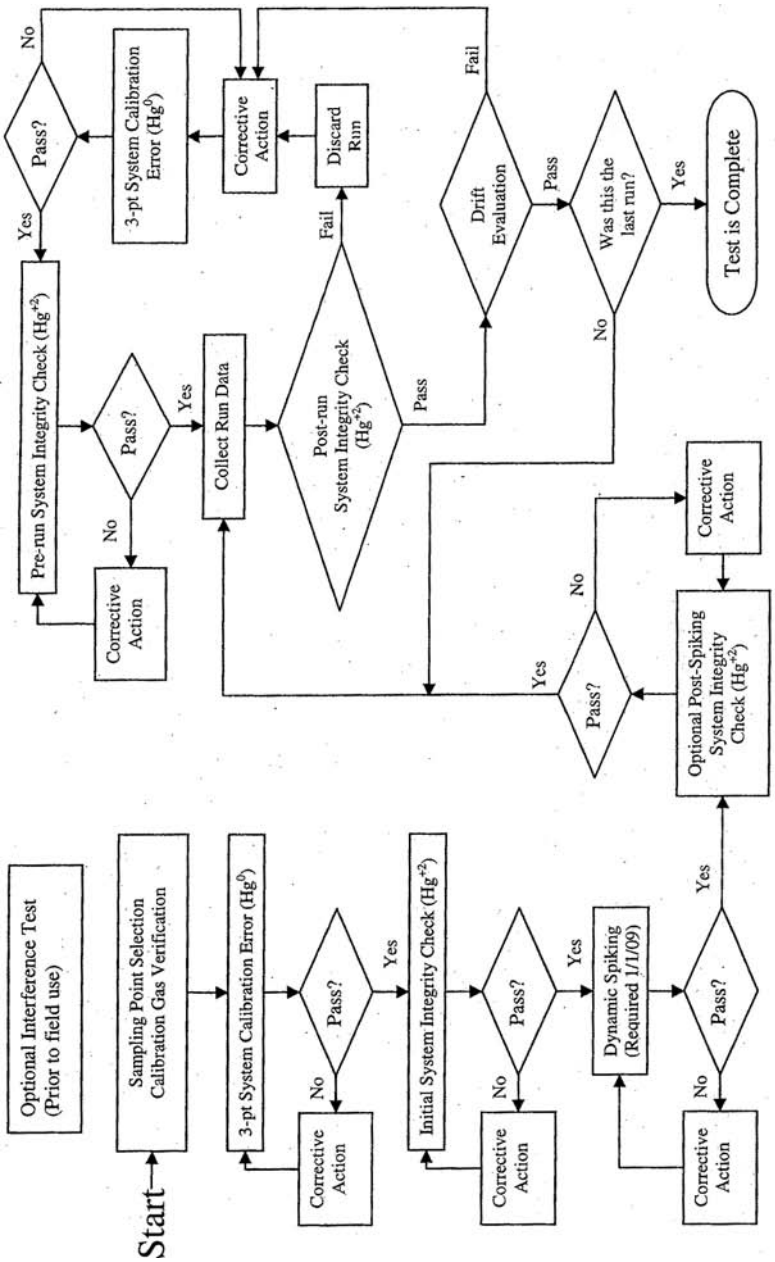


Figure 30A-2. Testing Flow Chart

Table 30A-1: 3-Point System Calibration Error Tests

Facility name: _____ Unit(s) tested: _____ Test personnel: _____ Date: _____ Time: _____	Test Runs Covered: _____ Analyzer make & model no. _____ Serial no. _____ Calibration span (CS): _____ System response time: _____

Calibration Gas Level	Certified Gas Concentration ($\mu g/m^3$) A	System Response ($\mu g/m^3$) B	Absolute Difference |A-B|	Calibration Error (% of calibration span) $\frac{[\|A-B\|]*100}{CS}$
Low				
Mid				
High				

Table 30A-2: System Integrity Check and Drift Data

Facility name:_____ Analyzer make & model: _____

Unit(s) tested: _____ Serial number: _____

Test personnel: _____ Run number(s) covered:_____

Date(s): _____ Calibration span: _____

Calibration Gas Level (zero, mid, or high)	Certified Calibration Gas Value ($\mu g/m^3$)	Initial System Response ($\mu g/m^3$)	Final System Response ($\mu g/m^3$)	Absolute Difference ($\mu g/m^3$)	Drift (% of calibration span)

TABLE 30A–3—INTERFERENCE CHECK GAS CONCENTRATIONS

Potential interferent gas [1]	Concentration, tentative—(balance N_2)
CO_2	15% ±1% CO_2
CO	100 ±20 ppm
HCl [2]	100 ±20 ppm
NO [2]	250 ±50 ppm
SO_2	200 ±20 ppm
O_2	3% ±1% O_2
H_2O	10% ±1% H_2O
Nitrogen	Balance

TABLE 30A–3—INTERFERENCE CHECK GAS CONCENTRATIONS—Continued

Potential interferent gas [1]	Concentration, tentative—(balance N_2)
Other.	

[1] Any of these specific gases can be tested at a lower level if the manufacturer has provided reliable means for limiting or scrubbing that gas to a specified level.

[2] HCl and NO must be tested as a mixture.

Table 30A-4: Example Interference Test Data Sheet

Date of Test: _____
Analyzer Type: _____
Model No.: _____
Serial No.: _____
Calibration Span: _____
Test Organization: _____
Test Personnel: _____

Interference Gas	Hg Concentration ($\mu g/m^3$)	Hg Concentration ($\mu g/m^3$) w/Interference Gas	Absolute Difference ($\mu g/m^3$)	Average Absolute Difference ($\mu g/m^3$)
			Sum of Responses	
			% of Calibration Span	

Table 30A-5: Example Dynamic Spiking Data Sheet

Facility name: _____ Date: _____ Time: _____

Unit(s) tested: _____ Test personnel: _____

Analyzer make & model: _____ Estimated native Hg concentration: _____ $\mu g/m^3$

Serial number: _____ Estimated unspiked sample flow rate: _____ lpm

Calibration span: _____ $\mu g/m^3$ Estimated spike gas flow rate: _____ lpm

Q_{probe} (lpm)	Q_{spike} (lpm)	DF[1]	Target Level[2]		C_{native} ($\mu g/m^3$)			Actual Values		% Spike Recovery
			C^*_{spike} ($\mu g/m^3$)	C^*_{ss} ($\mu g/m^3$)	Pre	Post	Avg.	C_{spike} ($\mu g/m^3$)	C_{ss} ($\mu g/m^3$)	
									Avg. RSD	

1 DF must be ≥ 5

2 C^*_{ss}/C_{native} must be ≥ 1.5 and ≤ 2.0, where C_{native} and C^*_{ss} are estimated values

METHOD 30B—DETERMINATION OF TOTAL VAPOR PHASE MERCURY EMISSIONS FROM COAL-FIRED COMBUSTION SOURCES USING CARBON SORBENT TRAPS

1.0 Scope and Application

What is Method 30B?

Method 30B is a procedure for measuring total vapor phase mercury (Hg) emissions from coal-fired combustion sources using sorbent trap sampling and an extractive or thermal analytical technique. This method is only intended for use only under relatively low particulate conditions (e.g., sampling after all pollution control devices). Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known and acceptable quality for each testing program. This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need, but instead refers to other test methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional methods which are found in Appendices A–1 and A–3 to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 4—Determination of Moisture Content in Stack Gases.

(c) Method 5—Determination of Particulate Matter Emissions from Stationary Sources

1.1 Analytes. What does this method determine? This method is designed to measure the mass concentration of total vapor phase Hg in flue gas, including elemental Hg (Hg^0) and oxidized forms of Hg (Hg^{+2}), in micrograms per dry standard cubic meter (µg/dscm).

Analyte	CAS No.	Analytical range and sensitivity
Elemental Hg (Hg^0) ..	7439–97–6	Typically 0.1 µg/dscm to >50 µg/dscm.
Oxidized Hg (Hg^{+2}) ...	.....	(Same)

1.2 Applicability. When is this method required? Method 30B is a reference method for relative accuracy test audits (RATAs) of vapor phase Hg CEMS and sorbent trap monitoring systems installed at coal-fired boilers and is also appropriate for Hg emissions testing at such boilers. It is intended for use only under relatively low particulate conditions (i.e., sampling after all pollution control devices); in cases where significant amounts of particle-bound Hg may be present, an isokinetic sampling method for Hg should be used. Method 30B may also be specified by New Source Performance Standards (NSPS), National Emission Standards for Hazardous Air Pollutants (NESHAP), emissions trading programs, State Implementation Plans (SIPs), and operating permits that require measurement of Hg concentrations in stationary source emissions, either to determine compliance with an applicable emission standard or limit, or to conduct RATAs of Hg CEMS and sorbent trap monitoring systems.

1.3 Data Quality Objectives (DQO). How good must my collected data be? Method 30B has been designed to provide data of high and known quality for Hg emissions testing and for RATA testing of Hg monitoring systems, including CEMS and sorbent trap monitors. In these and other applications, the principal objective is to ensure the accuracy of the data at the actual emissions levels and in the actual emissions matrix encountered. To meet this objective, NIST-traceable calibration standards must be used and method performance tests are required.

2.0 Summary of Method

Known volumes of flue gas are extracted from a stack or duct through paired, in-stack sorbent media traps at an appropriate flow rate. Collection of mercury on the sorbent media in the stack mitigates potential loss of mercury during transport through a probe/sample line. For each test run, paired train sampling is required to determine measurement precision and verify acceptability of the measured emissions data. A field recovery test which assesses recovery of an elemental Hg spike to determine measurement bias is also used to verify data acceptability. The sorbent traps are recovered from the sampling system, prepared for analysis as needed, and analyzed by any suitable determinative technique that can meet the performance criteria.

3.0 Definitions

3.1 *Analytical System* is the combined equipment and apparatus used to perform sample analyses. This includes any associated sample preparation apparatus e.g., digestion equipment, spiking systems, reduction devices, etc., as well as analytical instrumentation such as UV AA and UV AF cold vapor analyzers.

3.2 *Calibration Standards* are the Hg containing solutions prepared from NIST traceable standards and are used to directly calibrate analytical systems.

3.3 *Independent Calibration Standard* is a NIST traceable standard obtained from a source or supplier independent of that for the calibration standards and is used to confirm the integrity of the calibration standards used.

3.4 *Method Detection Limit (MDL)* is the lowest mass of Hg greater than zero that can be estimated and reported by your candidate analytical technique. The MDL is statistically derived from replicate low level measurements near your analytical instrument's detection level.

3.5 *NIST* means the National Institute of Standards and Technology, located in Gaithersburg, Maryland.

3.6 *Run* means a series of gas samples taken successively from the stack or duct. A test normally consists of a specific number of runs.

3.7 *Sorbent Trap* means a cartridge or sleeve containing a sorbent media (typically activated carbon treated with iodine or some other halogen) with multiple sections separated by an inert material such as glass wool. These sorbent traps are optimized for the quantitative capture of elemental and oxidized forms of Hg and can be analyzed by multiple techniques.

3.8 *Test* refers to the series of runs required by the applicable regulation.

3.9 *Thermal Analysis* means an analytical technique where the contents of the sorbent traps are analyzed using a thermal technique (desorption or combustion) to release the captured Hg in a detectable form for quantification.

3.10 *Wet Analysis* means an analytical technique where the contents of the sorbent tube are first leached or digested to quantitatively transfer the captured Hg to liquid solution for subsequent analysis.

4.0 Interferences

Interferences may result from the sorbent trap material used as well as from the measurement environment itself. The iodine present on some sorbent traps may impart a negative measurement bias. High levels of sulfur trioxide (SO_3) are also suspected to compromise the performance of sorbent trap Hg capture. These, and other, potential interferences are assessed by performing the analytical matrix interference, Hg^0 and $HgCl_2$ analytical bias and field recovery tests.

5.0 Safety

What safety measures should I consider when using this method? This method may require you to work with hazardous materials and in hazardous conditions. You are encouraged to establish safety procedures before using the method. Among other precautions, you should become familiar with the safety recommendations in the gas analyzer user's manual. Occupational Safety and Health Administration (OSHA) regulations concerning use of compressed gas cylinders and noxious gases may apply.

5.1 Site Hazards. Prior to applying these procedures/specifications in the field, the potential hazards at the test site should be considered; advance coordination with the site is critical to understand the conditions and applicable safety policies. At a minimum, portions of the sampling system will be hot, requiring appropriate gloves, long sleeves, and caution in handling this equipment.

5.2 Laboratory Safety. Policies should be in place to minimize risk of chemical exposure and to properly handle waste disposal in the laboratory. Personnel shall wear appropriate laboratory attire according to a Chemical Hygiene Plan established by the laboratory.

5.3 Reagent Toxicity/Carcinogenicity. The toxicity and carcinogenicity of any reagents used must be considered. Depending upon the sampling and analytical technologies selected, this measurement may involve hazardous materials, operations, and equipment and this method does not address all of the safety problems associated with implementing this approach. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicable regulatory limitations prior to performance. Any chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized. Chemists should refer to the Material Safety Data Sheet (MSDS) for each chemical used.

5.4 Waste Disposal. Any waste generated by this procedure must be disposed of according to a hazardous materials management plan that details and tracks various waste streams and disposal procedures.

6.0 Equipment and Supplies

The following list is presented as an example of key equipment and supplies likely required to measure vapor-phase Hg using a sorbent trap sampling system. It is recognized that additional equipment and supplies may be needed. Collection of paired samples is required.

6.1 Sorbent Trap Sampling System. A typical sorbent trap sampling system is shown in Figure 30B–1 in section 17.0. The sorbent trap sampling system shall include the following components:

6.1.1 Sorbent Traps. The sorbent media used to collect Hg must be configured in a trap with at least two distinct segments or sections, connected in series, that are amenable to separate analyses. section 1 is designated for primary capture of gaseous Hg. section 2 is designated as a backup section for determination of vapor phase Hg breakthrough. Each sorbent trap must be inscribed or otherwise permanently marked with a unique identification number, for tracking purposes. The sorbent media may be any collection material (e.g., carbon, chemically-treated filter, etc.) capable of quantitatively capturing and recovering for subsequent analysis, all gaseous forms of Hg in the emissions from the intended application. Selection of the sorbent media shall be based on the material's ability to achieve the performance criteria contained in this method as well as the sorbent's vapor phase

Hg capture efficiency for the emissions matrix and the expected sampling duration at the test site. The sorbent media must be obtained from a source that can demonstrate their quality assurance and quality control (see section 7.2). The paired sorbent traps are supported on a probe (or probes) and inserted directly into the flue gas stream.

6.1.2 Sampling Probe Assembly. Each probe assembly shall have a leak-free attachment to the sorbent trap(s). Each sorbent trap must be mounted at the entrance of or within the probe such that the gas sampled enters the trap directly. Each probe/sorbent trap assembly must be heated to a temperature sufficient to prevent liquid condensation in the sorbent trap(s). Auxiliary heating is required only where the stack temperature is too low to prevent condensation. Use a calibrated thermocouple to monitor the stack temperature. A single probe capable of operating the paired sorbent traps may be used. Alternatively, individual probe/sorbent trap assemblies may be used, provided that the individual sorbent traps are co-located to ensure representative Hg monitoring.

6.1.3 Moisture Removal Device. A moisture removal device or system shall be used to remove water vapor from the gas stream prior to entering dry gas flow metering devices.

6.1.4 Vacuum Pump. Use a leak-tight, vacuum pump capable of operating within the system's flow range.

6.1.5 Gas Flow Meter. A gas flow meter (such as a dry gas meter, thermal mass flow meter, or other suitable measurement device) shall be used to determine the total sample volume on a dry basis, in units of standard cubic meters. The meter must be sufficiently accurate to measure the total sample volume to within 2 percent and must be calibrated at selected flow rates across the range of sample flow rates at which the sampling train will be operated. The gas flow meter shall be equipped with any necessary auxiliary measurement devices (e.g., temperature sensors, pressure measurement devices) needed to correct the sample volume to standard conditions.

6.1.6 Sample Flow Rate Meter and Controller. Use a flow rate indicator and controller for maintaining necessary sampling flow rates.

6.1.7 Temperature Sensor. Same as section 6.1.1.7 of Method 5 in Appendix A–3 to this part.

6.1.8 Barometer. Same as section 6.1.2 of Method 5 in Appendix A–3 to this part.

6.1.9 Data Logger (optional). Device for recording associated and necessary ancillary information (e.g., temperatures, pressures, flow, time, etc.).

6.2 Gaseous Hg^0 Sorbent Trap Spiking System. A known mass of gaseous Hg^0 must be either present on or spiked onto the first section of sorbent traps in order to perform the Hg^0 and $HgCl_2$ analytical bias test and the field recovery study. Any approach capable of quantitatively delivering known masses of Hg^0 onto sorbent traps is acceptable. Several spiking technologies or devices are available to meet this objective. Their practicality is a function of Hg mass spike levels. For low levels, NIST-certified or NIST-traceable gas generators or tanks may be suitable. An alternative system, capable of delivering almost any mass required, makes use of NIST-certified or NIST-traceable Hg salt solutions (e.g., $HgCl_2$, $Hg(NO_3)_2$). With this system, an aliquot of known volume and concentration is added to a reaction vessel containing a reducing agent (e.g., stannous chloride); the Hg salt solution is reduced to Hg^0 and purged onto the sorbent trap using an impinger sparging system. When available, information on example spiking systems will be posted at *http://www.epa.gov/ttn/emc*.

6.3 Sample Analysis Equipment. Any analytical system capable of quantitatively recovering and quantifying total Hg from the sorbent media selected is acceptable provided that the analysis can meet the performance criteria described in this method. Example recovery techniques include acid leaching, digestion, and thermal desorption/direct combustion. Example analytical techniques include, but are not limited to, ultraviolet atomic fluorescence (UV AF), ultraviolet atomic absorption (UV AA) with and without gold trapping, and X-ray fluorescence (XRF) analysis.

6.3 Moisture Measurement System. If correction of the measured Hg emissions for moisture is required (see section 8.3.3.7), either Method 4 in Appendix A–3 to this part or other moisture measurement methods approved by the Administrator will be needed to measure stack gas moisture content.

7.0 Reagents and Standards

7.1 Reagents and Standards. Only NIST-certified or NIST-traceable calibration standards, standard reference materials, and reagents shall be used for the tests and procedures required by this method.

7.2 Sorbent Trap Media. The sorbent trap media shall be prepared such that the material used for testing is of known and acceptable quality. Sorbent supplier quality assurance/quality control measures to ensure appropriate and consistent performance such as sorptive capacity, uniformity of preparation treatments, and background levels shall be considered.

8.0 Sample Collection and Handling

This section presents the sample collection and handling procedures along with the pretest and on-site performance tests required by this method. Since you may choose different options to comply with certain performance criteria, each test report must identify the specific options selected and

document the results with respect to the performance criteria of this method.

8.1 Selection of Sampling Sites and Sampling Points. What sampling site and sampling points do I select? Same as section 8.1 of Method 30A of this appendix.

8.2 Measurement System Performance Tests. What performance criteria must my measurement system meet? The following laboratory and field procedures and associated criteria of this section are designed to ensure (1) selection of a sorbent and analytical technique combination capable of quantitative collection and analysis of gaseous Hg, (2) collection of an adequate amount of Hg on each sorbent trap during field tests, and (3) adequate performance of the method for each test program: The primary objectives of these performance tests are to characterize and verify the performance of your intended analytical system and associated sampling and analytical procedures, and to define the minimum amount of Hg (as the sample collection target) that can be quantified reliably.

(a) Analytical Matrix Interference Test;

(b) Determination of Minimum Sample Mass;

(c) Hg^0 and $HgCl_2$ Analytical Bias Test;

(d) Determination of Nominal Sample Volume;

(e) Field Recovery Test.

8.2.1 Analytical Matrix Interference Test and Minimum Sample Dilution.

(a) The analytical matrix interference test is a laboratory procedure. It is required only if you elect to use a liquid digestion analytical approach and needs to be performed only once for each sorbent material used. The purpose of the test is to verify the presence or absence of known and potential analytical matrix interferences, including the potential negative bias associated with iodine common to many sorbent trap materials. The analytical matrix interference test determines the minimum dilution (if any) necessary to mitigate matrix effects on the sample digestate solutions.

(b) The result of the analytical matrix interference test, i.e., the minimum sample dilution required (if any) for all sample analyses, is used to establish the minimum sample mass needed for the Hg^0 and $HgCl_2$ analytical bias test and to determine the nominal sample volume for a test run. The analytical matrix interference test is sorbent material-specific and shall be performed for each sorbent material you intend to use for field sampling and analysis. The test shall be performed using a mass of sorbent material comparable to the sorbent mass typically used in the first section of the trap for sampling. Similar sorbent materials from different sources of supply are considered to be different materials and must be tested individually. You must conduct the analytical matrix interference test for each sorbent material prior to the analysis of field samples.

8.2.1.1 Analytical Matrix Interference Test Procedures. Digest and prepare for analysis a representative mass of sorbent material (unsampled) according to your intended laboratory techniques for field samples. Analyze the digestate according to your intended analytical conditions at the least diluted level you intend to use for sample analysis (e.g., undiluted, 1 in 10 dilution, etc.). Determine the Hg concentration of the undiluted digestate solution. Prepare a series of solutions with a fixed final volume containing graduated aliquots of the sample digestate and, a fixed aliquot of a calibration standard (with the balance being Hg-free reagent or H_20) to establish solutions of varied digestate dilution ratio (e.g., 1:2, 1:5, 1:10, 1:100, etc.—see example in section 8.2.1.3, below). One of these solutions should contain only the aliquot of the calibration standard in Hg-free reagent or H_2O. This will result in a series of solutions where the amount of Hg is held relatively constant and only the volume of digestate diluted is varied. Analyze each of these solutions following intended sample analytical procedures and conditions, determining the concentration for each solution.

8.2.1.2 Analytical Matrix Interference Test Acceptance Criteria. Compare the measured concentration of each solution containing digestate to the measured concentration of the digestate-free solution. The lowest dilution ratio of any solution having a Hg concentration within ±5 percent of the digestate-free solution is the minimum dilution ratio required for analysis of all samples. If you desire to measure the digestate without dilution, the ±5 percent criterion must be met at a dilution ratio of at least 9:10 (i.e., ≥90% digestate).

8.2.1.3 Example Analytical Matrix Interference Test. An example analytical matrix interference test is presented below. Additional information on the conduct of the analytical matrix interference test will be posted at *http://www.epa.gov/ttn/emc*. Determine the most sensitive working range for the analyzer to be used. This will be a narrow range of concentrations. Digest and prepare for analysis a representative mass of sorbent material (unsampled) according to your intended laboratory techniques for sample preparation and analysis. Prepare a calibration curve for the most sensitive analytical region, e.g., 0.0, 0.5, 1.0, 3.0, 5.0, 10 ppb. Using the highest calibration standard, e.g., 10.0 ppb, prepare a series of solutions by adding successively smaller increments of the digestate to a fixed volume of the calibration standard and bringing each solution to a final fixed volume with mercury-free deionized water (diH_2O). To 2.0 ml of the calibration standard add 18.0, 10.0, 4.0, 2.0, 1.0, 0.2, and 0.0 ml of the digestate. Bring the final volume of each solution to a total volume of

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20 ml by adding 0.0, 8.0, 14.0, 16.0, 17.0, 17.8, and 18.0 ml of diH_2O. This will yield solutions with dilution ratios of 9:10, 1:2, 1:5, 1:10, 1:20, 1:100, and 0:10, respectively. Determine the Hg concentration of each solution. The dilution ratio of any solution having a concentration that is within ±5 percent of the concentration of the solution containing 0.0 ml of digestate is an acceptable dilution ratio for analyzing field samples. If more than one solution meets this criterion, the one with the lowest dilution ratio is the minimum dilution required for analysis of field samples. If the 9:10 dilution meets this criterion, then no sample dilution is required.

8.2.2 Determination of Minimum Sample Mass. The minimum mass of Hg that must be collected per sample must be determined. This information is necessary in order to effectively perform the Hg^0 and $HgCl_2$ Analytical Bias Test, to estimate target sample volumes/sample times for test runs, and to ensure the quality of the measurements. The determination of minimum sample mass is a direct function of analytical technique, measurement sensitivity, dilutions, etc. This determination is required for all analytical techniques. Based on the analytical approach you employ, you should determine the most sensitive calibration range. Based on a calibration point within that range, you must consider all sample treatments (e.g., dilutions) to determine the mass of sample that needs to be collected to ensure that all sample analyses fall within your calibration curve.

8.2.2.1 Determination of Minimum Calibration Concentration or Mass. Based on your instrument's sensitivity and linearity, determine the calibration concentrations or masses that make up a representative low level calibration range. Verify that you are able to meet the multipoint calibration performance criteria in section 11.0 of this method. Select a calibration concentration or mass that is no less than 2 times the lowest concentration or mass in your calibration curve. The lowest point in your calibration curve must be at least 5, and preferably 10, times the Method Detection Limit (MDL), which is the minimum amount of the analyte that can be detected and reported. The MDL must be determined at least once for the analytical system using an MDL study such as that found in section 15.0 to Method 301 of appendix A to part 63 of this chapter.

NOTE TO SECTION 8.2.2.1: While it might be desirable to base the minimum calibration concentration or mass on the lowest point in the calibration curve, selecting a higher concentration or mass is necessary to ensure that all analyses of the field samples will fall within the calibration curve. Therefore, it is strongly recommended that you select a minimum calibration concentration or mass that is sufficiently above the lowest point of the calibration curve (see examples in sections 8.2.2.2.1 and 8.2.2.2.2 below).

8.2.2.2 Determination of Minimum Sample Mass. Based on your minimum calibration concentration or mass and other sample treatments including, but not limited to, final digestate volume and minimum sample dilution, determine the minimum sample mass. Consideration should also be given to the Hg levels expected to be measured in section 2 of the sorbent traps and to the breakthrough criteria presented in Table 9–1.

8.2.2.2.1 Example Determination of Minimum Sample Mass for Thermal Desorption Analysis. A thermal analysis system has been calibrated at five Hg mass levels: 10 ng, 20 ng, 50 ng, 100 ng, 200 ng, and shown to meet the calibration performance criteria in this method. Based on 2 times the lowest point in the calibration curve, 20 ng is selected as the minimum calibration mass. Because the entire sample is analyzed and there are no dilutions involved, the minimum sample mass is also 20 ng.

NOTE: In this example, if the typical background (blank) Hg levels in section 2 were relatively high (e.g., 3 to 5 ng), a sample mass of 20 ng might not have been sufficient to ensure that the breakthrough criteria in Table 9–1 would be met, thereby necessitating the use of a higher point on the calibration curve (e.g., 50 ng) as the minimum calibration and sample mass.

8.2.2.2.2 Example Determination of Minimum Sample Mass for Acid Leachate/Digestate Analysis. A cold vapor analysis system has been calibrated at four Hg concentration levels: 2 ng/L, 5 ng, 10 ng/L, 20 ng/L, and shown to meet the calibration performance criteria in this method. Based on 2 times the lowest point in the calibration curve, 4 ng/L was selected as the minimum calibration concentration. The final sample volume of a digestate is nominally 50 ml (0.05 L) and the minimum dilution necessary was determined to be 1:100 by the Analytical Matrix Interference Test of section 8.2.1. The following calculation would be used to determine the minimum sample mass.

$$\text{Minimum sample mass} = (4\ \text{ng/L}) \times (0.05\ \text{L}) \times (100) = 20\ \text{ng}$$

NOTE: In this example, if the typical background (blank) Hg levels in section 2 were relatively high (e.g., 3 to 5 ng), a sample mass of 20 ng might not have been sufficient to ensure that the breakthrough criterion in Table 9–1 would be met, thereby necessitating the use of a higher point on the calibration curve (e.g., 10 ng/L) as the minimum calibration concentration.

8.2.3 Hg^0 and $HgCl_2$ Analytical Bias Test. Before analyzing any field samples, the laboratory must demonstrate the ability to recover and accurately quantify Hg^0 and $HgCl_2$

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from the chosen sorbent media by performing the following analytical bias test for sorbent traps spiked with Hg^0 and $HgCl_2$. The analytical bias test is performed at a minimum of two distinct sorbent trap Hg loadings that will: (1) Represent the lower and upper bound of sample Hg loadings for application of the analytical technique to the field samples, and (2) be used for data validation.

8.2.3.1 Hg^0 and $HgCl_2$ Analytical Bias Test Procedures. Determine the lower and upper bound mass loadings. The minimum sample mass established in section 8.2.2.2 can be used for the lower bound Hg mass loading although lower Hg loading levels are acceptable. The upper bound Hg loading level should be an estimate of the greatest mass loading that may result as a function of stack concentration and volume sampled. As previously noted, this test defines the bounds that actual field samples must be within in order to be valid.

8.2.3.1.1 Hg^0 Analytical Bias Test. Analyze the front section of three sorbent traps containing Hg^0 at the lower bound mass loading level and the front section of three sorbent traps containing Hg^0 at the upper bound mass loading level. In other words, analyze each mass loading level in triplicate. You may refer to section 6.2 for spiking guidance. Prepare and analyze each spiked trap, using the same techniques that will be used to prepare and analyze the field samples. The average recovery for the three traps at each mass loading level must be between 90 and 110 percent. If multiple types of sorbent media are to be analyzed, a separate analytical bias test is required for each sorbent material.

8.2.3.1.2 $HgCl_2$ Analytical Bias Test. Analyze the front section of three sorbent traps containing $HgCl_2$ at the lower bound mass loading level and the front section of three traps containing $HgCl_2$ at the upper bound mass loading level. $HgCl_2$ can be spiked as a gas, or as a liquid solution containing $HgCl_2$. However the liquid volume spiked must be <100 µL. Prepare and analyze each spiked trap, using the techniques that will be used to prepare and analyze the field samples. The average recovery for three traps at each spike concentration must be between 90 and 110 percent. Again, if multiple types of sorbent media are to be analyzed, a separate analytical bias test is required for each sorbent material.

8.2.4 Determination of Target Sample Volume. The target sample volume is an estimate of the sample volume needed to ensure that valid emissions data are collected (i.e., that sample mass Hg loadings fall within the analytical calibration curve and are within the upper and lower bounds set by the analytical bias tests). The target sample volume and minimum sample mass can also be determined by performing a diagnostic test run prior to initiation of formal testing.

Example: If the minimum sample mass is 50 ng and the concentration of mercury in the stack gas is estimated to be 2 µg/m^3 (ng/L) then the following calculation would be used to determine the target sample volume:

Target Sample Volume = (50 ng) / (2 ng/L) = 25 L

NOTE TO SECTION 8.2.4: For the purposes of relative accuracy testing of Hg monitoring systems under subpart UUUUU of part 63 of this chapter and Performance Specifications 12A and 12B in appendix B to this part, when the stack gas Hg concentration is expected to be very low (<0.5 µg/dscm), you may estimate the Hg concentration at 0.5 µg/dscm.

8.2.5 Determination of Sample Run Time. Sample run time will be a function of minimum sample mass (see section 8.2.2), target sample volume and nominal equipment sample flow rate. The minimum sample run time for conducting relative accuracy test audits of Hg monitoring systems is 30 minutes and for emissions testing to characterize an emission source is 1 hour. The target sample run time can be calculated using the following example.

Example: If the target sample volume has been determined to be 25 L, then the following formula would be used to determine the sampling time necessary to acquire 25 L of gas when sampling at a rate of 0.4 L/min.

Sampling time (min) = 25 L / 0.4 L/min = 63 minutes

8.2.6 Field Recovery Test. The field recovery test provides a test program-specific verification of the performance of the combined sampling and analytical approach. Three sets of paired samples, one of each pair which is spiked with a known level of Hg, are collected and analyzed and the average recovery of the spiked samples is used to verify performance of the measurement system under field conditions during that test program. The conduct of this test requires an estimate or confirmation of the stack Hg concentrations at the time of testing.

8.2.6.1 Calculation of Pre-sampling Spiking Level. Determine the sorbent trap spiking level for the field recovery test using estimates of the stack Hg concentration, the target sample flow rate, and the planned sample duration. First, determine the Hg mass expected to be collected in section 1 of the sorbent trap. The pre-sampling spike must be within 50 to 150 percent of this expected mass.

Example calculation: For an expected stack Hg concentration of 5 ug/m^3 (ng/L) a target sample rate of 0.40 liters/min, and a sample duration of 1 hour:

(0.40 L/min) * (60 min) * (5ng/L) = 120 ng

A Hg spike of 60 to 180 ng (50–150% of 120 ng) would be appropriate.

8.2.6.2 Procedures. Set up two identical sampling trains. One of the sampling trains

shall be designated the spiked train and the other the unspiked train. Spike Hg^0 onto the front section of the sorbent trap in the spiked train before sampling. The mass of Hg spiked shall be 50 to 150 percent of the mass expected to be collected with the unspiked train. Sample the stack gas with the two trains simultaneously using the same procedures as for the field samples (see section 8.3). The total sample volume must be within ±20 percent of the target sample volume for the field sample test runs. Analyze the sorbent traps from the two trains utilizing the same analytical procedures and instrumentation as for the field samples (see section 11.0). Determine the fraction of spiked Hg recovered (R) using the equations in section 12.7. Repeat this procedure for a total of three runs. Report the individual R values in the test report; the average of the three R values must be between 85 and 115 percent.

NOTE TO SECTION 8.2.6.2: It is acceptable to perform the field recovery test concurrent with actual test runs (e.g., through the use of a quad probe). It is also acceptable to use the field recovery test runs as test runs for emissions testing or for the RATA of a Hg monitoring system under subpart UUUUU of part 63 of this chapter and Performance Specifications 12A and 12B in appendix B to this part, if certain conditions are met. To determine whether a particular field recovery test run may be used as a RATA run, subtract the mass of the Hg^0 spike from the total Hg mass collected in sections 1 and 2 of the spiked trap. The difference represents the mass of Hg in the stack gas sample. Divide this mass by the sample volume to obtain the Hg concentration in the effluent gas stream, as measured with the spiked trap. Compare this concentration to the corresponding Hg concentration measured with the unspiked trap. If the paired trains meet the relative deviation and other applicable data validation criteria in Table 9–1, then the average of the two Hg concentrations may be used as an emissions test run value or as the reference method value for a RATA run.

8.3 Sampling. This section describes the procedures and criteria for collecting the field samples for analysis. As noted in section 8.2.6, the field recovery test samples are also collected using these procedures.

8.3.1 Pre-test leak check. Perform a leak check of the sampling system with the sorbent traps in place. For each of the paired sampling trains, draw a vacuum in the train, and adjust the vacuum to ~15″ Hg; and, using the gas flow meter, determine leak rate. The leak rate for an individual train must not exceed 4 percent of the target sampling rate. Once the leak check passes this criterion, carefully release the vacuum in the sample train, then seal the sorbent trap inlet until the probe is ready for insertion into the stack or duct.

8.3.2 Determination of Flue Gas Characteristics. Determine or measure the flue gas measurement environment characteristics (gas temperature, static pressure, gas velocity, stack moisture, etc.) in order to determine ancillary requirements such as probe heating requirements (if any), initial sampling rate, moisture management, etc.

8.3.3 Sample Collection

8.3.3.1 Remove the plug from the end of each sorbent trap and store each plug in a clean sorbent trap storage container. Remove the stack or duct port cap and insert the probe(s). Secure the probe(s) and ensure that no leakage occurs between the duct and environment.

8.3.3.2 Record initial data including the sorbent trap ID, date, and the run start time.

8.3.3.3 Record the initial gas flow meter reading, stack temperature, meter temperatures (if needed), and any other appropriate information, before beginning sampling. Begin sampling and target a sampling flow rate similar to that for the field recovery test. Then, at regular intervals (≤5 minutes) during the sampling period, record the date and time, the sample flow rate, the gas meter reading, the stack temperature, the flow meter temperatures (if using a dry gas meter), temperatures of heated equipment such as the vacuum lines and the probes (if heated), and the sampling system vacuum readings. Adjust the sampling flow rate as necessary to maintain the initial sample flow rate. Ensure that the total volume sampled for each run is within 20 percent of the total volume sampled for the field recovery test.

8.3.3.4 Data Recording. Obtain and record any essential operating data for the facility during the test period, e.g., the barometric pressure must be obtained for correcting sample volume to standard conditions when using a dry gas meter. At the end of the data collection period, record the final gas flow meter reading and the final values of all other essential parameters.

8.3.3.5 Post-Test Leak Check. When sampling is completed, turn off the sample pump, remove the probe(s) with sorbent traps from the port, and carefully seal the end of each sorbent trap. Perform another leak check of each sampling train with the sorbent trap in place, at the maximum vacuum reached during the sampling period. Record the leakage rates and vacuums. The leakage rate for each train must not exceed 4 percent of the average sampling rate for the data collection period. Following each leak check, carefully release the vacuum in the sample train.

8.3.3.6 Sample Recovery. Recover each sampled sorbent trap by removing it from the probe and sealing both ends. Wipe any deposited material from the outside of the sorbent

trap. Place the sorbent trap into an appropriate sample storage container and store/preserve in appropriate manner (see section 8.3.3.8).

8.3.3.7 Stack Gas Moisture Determination. If the moisture basis of the measurements made with this method (dry) is different from the moisture basis of either: (1) the applicable emission limit; or (2) a Hg CEMS being evaluated for relative accuracy, you must determine the moisture content of the flue gas and correct for moisture using Method 4 in appendix A–3 to this part. If correction of the measured Hg concentrations for moisture is required, at least one Method 4 moisture determination shall be made during each test run.

8.3.3.8 Sample Handling, Preservation, Storage, and Transport. While the performance criteria of this approach provides for verification of appropriate sample handling, it is still important that the user consider, determine and plan for suitable sample preservation, storage, transport, and holding times for these measurements. Therefore, procedures in ASTM D6911–15 ''Standard Guide for Packaging and Shipping Environmental Samples for Laboratory Analysis'' (incorporated by reference-see 40 CFR 60.17) shall be followed for all samples, where appropriate. To avoid Hg contamination of the samples, special attention should be paid to cleanliness during transport, field handling, sampling, recovery, and laboratory analysis, as well as during preparation of the sorbent cartridges. Collection and analysis of blank samples (*e.g.*, reagent, sorbent, field, etc.) is useful in verifying the absence or source of contaminant Hg.

8.3.3.9 Sample Custody. Proper procedures and documentation for sample chain of custody are critical to ensuring data integrity. The chain of custody procedures in ASTM D4840–99 ''Standard Guide for Sampling Chain-of-Custody Procedures'' shall be followed for all samples (including field samples and blanks).

9.0 Quality Assurance and Quality Control

Table 9–1 summarizes the QA/QC performance criteria that are used to validate the Hg emissions data from Method 30B sorbent trap measurement systems.

TABLE 9–1—QUALITY ASSURANCE/QUALITY CONTROL CRITERIA FOR METHOD 30B

QA/QC test or specification	Acceptance criteria	Frequency	Consequences if not met
Gas flow meter calibration (At 3 settings or points).	Calibration factor (Y_i) at each flow rate must be within ±2% of the average value (Y).	Prior to initial use and when post-test check is not within ±5% of Y.	Recalibrate at 3 points until the acceptance criteria are met.
Gas flow meter post-test calibration check (Single-point).	Calibration factor (Y_i) must be within ±5% of the Y value from the most recent 3-point calibration.	After each field test. For mass flow meters, must be done on-site, using stack gas.	Recalibrate gas flow meter at 3 points to determine a new value of Y. For mass flow meters, must be done on-site, using stack gas. Apply the new Y value to the field test data.
Temperature sensor calibration	Absolute temperature measures by sensor within ±1.5% of a reference sensor.	Prior to initial use and before each test thereafter.	Recalibrate; sensor may not be used until specification is met.
Barometer calibration	Absolute pressure measured by instrument within ±10 mm Hg of reading with a mercury barometer or NIST traceable barometer.	Prior to initial use and before each test thereafter.	Recalibrate; instrument may not be used until specification is met.
Pre-test leak check	≤4% of target sampling rate ..	Prior to sampling	Sampling shall not commence until the leak check is passed.
Post-test leak check	≤4% of average sampling rate	After sampling	Sample invalidated.*
Analytical matrix interference test (wet chemical analysis, only).	Establish minimum dilution (if any) needed to eliminate sorbent matrix interferences.	Prior to analyzing any field samples; repeat for each type of sorbent used.	Field sample results not validated.
Analytical bias test	Average recovery between 90% and 110% for Hg^0 and $HgCl_2$ at each of the 2 spike concentration levels.	Prior to analyzing field samples and prior to use of new sorbent media.	Field samples shall not be analyzed until the percent recovery criteria has been met.
Multipoint analyzer calibration	Each analyzer reading within ±10% of true value *and* $r^2 \geq 0.99$.	On the day of analysis, before analyzing any samples.	Recalibrate until successful.
Analysis of independent calibration standard.	Within ±10% of true value	Following daily calibration, prior to analyzing field samples.	Recalibrate and repeat independent standard analysis until successful.

TABLE 9–1—QUALITY ASSURANCE/QUALITY CONTROL CRITERIA FOR METHOD 30B—Continued

QA/QC test or specification	Acceptance criteria	Frequency	Consequences if not met
Analysis of continuing calibration verification standard (CCVS).	Within ±10% of true value	Following daily calibration, after analyzing ≤10 field samples, and at end of each set of analyses.	Recalibrate and repeat independent standard analysis, reanalyze samples until successful, if possible; for destructive techniques, samples invalidated.
Test run total sample volume ..	Within ±20% of total volume sampled during field recovery test.	Each individual sample	Sample invalidated.
Sorbent trap section 2 breakthrough.	For compliance/emissions testing: ≤10% of section 1 Hg mass for Hg concentrations >1 μg/dscm;. ≤20% of section 1 Hg mass for Hg concentrations ≤1 μg/dscm. ≤50% of section 1 Hg mass if the stack Hg concentration is ≤30% of the Hg concentration that is equivalent to the applicable emission limit. For relative accuracy testing: ≤10% of section 1 Hg mass for Hg concentrations >1 μg/dscm;. ≤20% of section 1 Hg mass for Hg concentrations ≤1 μg/dscm and >0.5 μg/dscm;. ≤50% of section 1 Hg mass for Hg concentrations ≤0.5 μg/dscm >0.1 μg/dscm;. no criterion for Hg concentrations ≤0.1 μg/dscm (must meet all other QA/QC specifications).	Every sample	Sample invalidated.*
Paired sorbent trap agreement	≤10% Relative Deviation (RD) mass for Hg concentrations >1 μg/dscm; ≤20% RD or ≤0.2 μg/dscm absolute difference for Hg concentrations ≤1 μg/dscm.	Every run	Run invalidated.*
Sample analysis	Within valid calibration range (within calibration curve).	All Section 1 samples where stack Hg concentration is ≥0.02 μg/dscm except in case where stack Hg concentration is ≤30% of the applicable emission limit.	Reanalyze at more concentrated level if possible, samples invalidated if not within calibrated range.
Sample analysis	Within bounds of Hg^0 and $HgCl_2$ Analytical Bias Test.	All Section 1 samples where stack Hg concentration is ≥0.5 μg/dscm.	Expand bounds of Hg^0 and $HgCl_2$ Analytical Bias Test; if not successful, samples invalidated.
Field recovery test	Average recovery between 85% and 115% for Hg^0.	Once per field test	Field sample runs not validated without successful field recovery test.

*And data from the pair of sorbent traps are also invalidated.

10.0 Calibration and Standardization

10.1 Only NIST-certified and NIST-traceable calibration standards (i.e., calibration gases, solutions, etc.) shall be used for the spiking and analytical procedures in this method.

10.2 Gas Flow Meter Calibration.

10.2.1 Preliminaries. The manufacturer or equipment supplier of the gas flow meter should perform all necessary set-up, testing, programming, etc., and should provide the end user with any necessary instructions, to

ensure that the meter will give an accurate readout of dry gas volume in standard cubic meters for this method.

10.2.2 Initial Calibration. Prior to its initial use, a calibration of the gas flow meter shall be performed. The initial calibration may be done by the manufacturer, by the equipment supplier, or by the end user. If the flow meter is volumetric in nature (*e.g.*, a dry gas meter), the manufacturer or end user may perform a direct volumetric calibration using any gas. For a mass flow meter, the manufacturer, equipment supplier, or end user may calibrate the meter using either: (1) A bottled gas mixture containing 12 ±0.5% CO_2, 7 ±0.5% O_2, and balance N_2 (when this method is applied to coal-fired boilers); (2) a bottled gas mixture containing CO_2, O_2, and N_2 in proportions representative of the expected stack gas composition; or (3) the actual stack gas.

10.2.2.1 Initial Calibration Procedures. Determine an average calibration factor (Y) for the gas flow meter by calibrating it at three sample flow rate settings covering the range of sample flow rates at which the sampling system will be operated. You may either follow the procedures in section 10.3.1 of Method 5 in appendix A–3 to this part or in section 16 of Method 5 in appendix A–3 to this part. If a dry gas meter is being calibrated, use at least five revolutions of the meter at each flow rate.

10.2.2.2 Alternative Initial Calibration Procedures. Alternatively, you may perform the initial calibration of the gas flow meter using a reference gas flow meter (RGFM). The RGFM may be: (1) A wet test meter calibrated according to section 10.3.1 of Method 5 in appendix A–3 to this part; (2) a gas flow metering device calibrated at multiple flow rates using the procedures in section 16 of Method 5 in appendix A–3 to this part; or (3) a NIST-traceable calibration device capable of measuring volumetric flow to an accuracy of 1 percent. To calibrate the gas flow meter using the RGFM, proceed as follows: While the Method 30B sampling system is sampling the actual stack gas or a compressed gas mixture that simulates the stack gas composition (as applicable), connect the RGFM to the discharge of the system. Care should be taken to minimize the dead volume between the gas flow meter being tested and the RGFM. Concurrently measure dry stack gas volume with the RGFM and the flow meter being calibrated for at least 10 minutes at each of three flow rates covering the typical range of operation of the sampling system. For each set of concurrent measurements, record the total sample volume, in units of dry standard cubic meters (dscm), measured by the RGFM and the gas flow meter being tested.

10.2.2.3 Initial Calibration Factor. Calculate an individual calibration factor Y_i at each tested flow rate from section 10.2.2.1 or 10.2.2.2 of this method (as applicable) by taking the ratio of the reference sample volume to the sample volume recorded by the gas flow meter. Average the three Y_i values, to determine Y, the calibration factor for the flow meter. Each of the three individual values of Y_i must be within ±0.02 of Y. Except as otherwise provided in sections 10.2.2.4 and 10.2.2.5 of this method, use the average Y value from the initial 3-point calibration to adjust subsequent gas volume measurements made with the gas flow meter.

10.2.2.4 Pretest On-Site Calibration Check (Optional). For a mass flow meter, if the most recent 3-point calibration of the flow meter was performed using a compressed gas mixture, you may want to conduct the following on-site calibration check prior to testing, to ensure that the flow meter will accurately measure the volume of the stack gas: While sampling stack gas, check the calibration of the flow meter at one intermediate flow rate setting representative of normal operation of the sampling system. If the pretest calibration check shows that the value of Y_i, the calibration factor at the tested flow rate, differs from the current value of Y by more than 5 percent, perform a full 3-point recalibration of the meter using stack gas to determine a new value of Y, and (except as otherwise provided in section 10.2.2.5 of this method) apply the new Y value to the data recorded during the field test.

10.2.2.5 Post-Test Calibration Check. Check the calibration of the gas flow meter following each field test at one intermediate flow rate setting, either at, or in close proximity to, the average sample flow rate during the field test. For dry gas meters, ensure at least three revolutions of the meter during the calibration check. For mass flow meters, this check must be performed before leaving the test site, while sampling stack gas. If a one-point calibration check shows that the value of Y_i at the tested flow rate differs by more than 5 percent from the current value of Y, repeat the full 3-point calibration procedure to determine a new value of Y, and apply the new Y value to the gas volume measurements made with the gas flow meter during the field test that was just completed. For mass flow meters, perform the 3-point recalibration while sampling stack gas.

10.3 Thermocouples and Other Temperature Sensors. Use the procedures and criteria in Section 10.3 of Method 2 in appendix A–1 to this part to calibrate in-stack temperature sensors and thermocouples. Dial thermometers shall be calibrated against mercury-in-glass thermometers or equivalent. Calibrations must be performed prior to initial use and before each field test thereafter. At each calibration point, the absolute temperature measured by the temperature sensor must agree to within ±1.5 percent of the temperature measured with the reference

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sensor, otherwise the sensor may not continue to be used.

10.4 Barometer. Calibrate against a mercury barometer or other NIST-traceable barometer as per Section 10.6 of Method 5 in appendix A–3 to this part. Calibration must be performed prior to initial use and before each test program, and the absolute pressure measured by the barometer must agree to within ±10 mm Hg of the pressure measured by the mercury or other NIST-traceable barometer, otherwise the barometer may not continue to be used.

10.5 Other Sensors and Gauges. Calibrate all other sensors and gauges according to the procedures specified by the instrument manufacturer(s).

10.6 Analytical System Calibration. See section 11.1 of this method.

11.0 Analytical Procedures

The analysis of Hg in the field and quality control samples may be conducted using any instrument or technology capable of quantifying total Hg from the sorbent media and meeting the performance criteria in this method. Because multiple analytical approaches, equipment and techniques are appropriate for the analysis of sorbent traps, it is not possible to provide detailed, technique-specific analytical procedures. As they become available, detailed procedures for a variety of candidate analytical approaches will be posted at *http://www.epa.gov/ttn/emc.*

11.1 Analytical System Calibration. Perform a multipoint calibration of the analyzer at three or more upscale points over the desired quantitative range (multiple calibration ranges shall be calibrated, if necessary). The field samples analyzed must fall within a calibrated, quantitative range and meet the performance criteria specified below. For samples suitable for aliquotting, a series of dilutions may be needed to ensure that the samples fall within a calibrated range. However, for sorbent media samples consumed during analysis (e.g., when using thermal desorption techniques), extra care must be taken to ensure that the analytical system is appropriately calibrated prior to sample analysis. The calibration curve range(s) should be determined such that the levels of Hg mass expected to be collected and measured will fall within the calibrated range. The calibration curve may be generated by directly introducing standard solutions into the analyzer or by spiking the standards onto the sorbent media and then introducing into the analyzer after preparing the sorbent/standard according to the particular analytical technique. For each calibration curve, the value of the square of the linear correlation coefficient, i.e., r^2, must be ≥0.99, and the analyzer response must be within ±10 percent of the reference value at each upscale calibration point. Calibrations must be performed on the day of the analysis, before analyzing any of the samples. Following calibration, an independent standard shall be analyzed. The measured value of the independently prepared standard must be within ±10 percent of the expected value.

11.2 Sample Preparation. Carefully separate the sections of each sorbent trap. Combine for analysis all materials associated with each section; any supporting substrate that the sample gas passes through prior to entering a media section (e.g., glass wool separators, acid gas traps, etc.) must be analyzed with that segment.

11.3 Field Sample Analyses. Analyze the sorbent trap samples following the same procedures that were used for conducting the Hg^0 and $HgCl_2$ analytical bias tests. The individual sections of the sorbent trap and their respective components must be analyzed separately (*i.e.*, section 1 and its components, then section 2 and its components). All sorbent trap section 1 sample analyses must be within the calibrated range of the analytical system as specified in Table 9–1. For wet analyses, the sample can simply be diluted to fall within the calibrated range. However, for the destructive thermal analyses, samples that are not within the calibrated range cannot be re-analyzed. As a result, the sample cannot be validated, and another sample must be collected. It is strongly suggested that the analytical system be calibrated over multiple ranges so that thermally analyzed samples fall within the calibrated range. The total mass of Hg measured in each sorbent trap section 1 must also fall within the lower and upper mass limits established during the initial Hg^0 and $HgCl_2$ analytical bias test. If a sample is analyzed and found to fall outside of these limits, it is acceptable for an additional Hg^0 and $HgCl_2$ analytical bias test to be performed that now includes this level. However, some samples (e.g., the mass collected in trap section 2), may have Hg levels so low that it may not be possible to quantify them in the analytical system's calibrated range. Because a reliable estimate of these low-level Hg measurements is necessary to fully validate the emissions data, the MDL (see section 8.2.2.1 of this method) is used to establish the minimum amount that can be detected and reported. If the measured mass or concentration is below the lowest point in the calibration curve and above the MDL, the analyst must estimate the mass or concentration of the sample based on the analytical instrument response relative to an additional calibration standard at a concentration or mass between the MDL and the lowest point in the calibration curve. This is accomplished by establishing a response factor (e.g., area counts per Hg mass or concentration) and estimating the amount of Hg present in the sample based on the analytical response and this response factor.

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Example: The analysis of a particular sample results in a measured mass above the MDL, but below the lowest point in the calibration curve which is 10 ng. An MDL of 1.3 ng Hg has been established by the MDL study. A calibration standard containing 5 ng of Hg is analyzed and gives an analytical response of 6,170 area counts, which equates to a response factor of 1,234 area counts/ng Hg. The analytical response for the sample is 4,840 area counts. Dividing the analytical response for the sample (4,840 area counts) by the response factor gives 3.9 ng Hg, which is the estimated mass of Hg in the sample.

11.4 Analysis of Continuing Calibration Verification Standard (CCVS). After no more than 10 samples and at the end of each set of analyses, a continuing calibration verification standard must be analyzed. The measured value of the continuing calibration standard must be within ±10 percent of the expected value.

11.5 Blanks. The analysis of blanks is optional. The analysis of blanks is useful to verify the absence of, or an acceptable level of, Hg contamination. Blank levels should be considered when quantifying low Hg levels and their potential contribution to meeting the sorbent trap section 2 breakthrough requirements; however, correcting sorbent trap results for blank levels is prohibited.

12.0 Calculations and Data Analysis

You must follow the procedures for calculation and data analysis listed in this section.

12.1 Nomenclature. The terms used in the equations are defined as follows:

B = Breakthrough (%).
B_{ws} = Moisture content of sample gas as measured by Method 4, percent/100.
C_a = Concentration of Hg for the sample collection period, for sorbent trap ''a'' (µg/dscm).
C_b = Concentration of Hg for the sample collection period, for sorbent trap ''b'' (µg/dscm).
C_d = Hg concentration, dry basis (µg/dscm).
C_{rec} = Concentration of spiked compound measured (µg/m^3).
C_w = Hg concentration, wet basis (µg/m^3).
m_1 = Mass of Hg measured on sorbent trap section 1 (µg).
m_2 = Mass of Hg measured on sorbent trap section 2 (µg).
$m_{recovered}$ = Mass of spiked Hg recovered in Analytical Bias or Field Recovery Test (µg).
m_s = Total mass of Hg measured on spiked trap in Field Recovery Test (µg).
m_{spiked} = Mass of Hg spiked in Analytical Bias or Field Recovery Test (µg).
m_u = Total mass of Hg measured on unspiked trap in Field Recovery Test (µg).
R = Percentage of spiked mass recovered (%).
RD = Relative deviation between the Hg concentrations from traps ''a'' and ''b'' (%).
v_s = Volume of gas sampled, spiked trap in Field Recovery Test (dscm).
V_t = Total volume of dry gas metered during the collection period (dscm); for the purposes of this method, standard temperature and pressure are defined as 20 °C and 760 mm Hg, respectively.
v_u = Volume of gas sampled, unspiked trap in Field Recovery Test (dscm).

12.2 Calculation of Spike Recovery (Analytical Bias Test). Calculate the percent recovery of Hg^0 and $HgCl_2$ using Equation 30B–1.

$$R = \frac{m_{recovered}}{m_{spiked}} \times 100 \qquad \text{Eq. 30B-1}$$

12.3 Calculation of Breakthrough. Use Equation 30B–2 to calculate the percent breakthrough to the second section of the sorbent trap.

$$B = \frac{m_2}{m_1} \times 100 \qquad \text{Eq. 30B-2}$$

12.4 Calculation of Hg Concentration. Calculate the Hg concentration measured with sorbent trap ''a'', using Equation 30B–3.

$$C_a = \frac{(m_1 + m_2)}{V_t} \qquad \text{Eq. 30B-3}$$

For sorbent trap ''b'', replace ''C_a '' with ''C_b '' in Equation 30B–3. Report the average concentration, i.e., ½ (C_a + C_b).

12.5 Moisture Correction. Use Equation 30B–4 if your measurements need to be corrected to a wet basis.

$$C_w = C_d \times (1 - B_{ws}) \qquad \text{Eq. 30B-4}$$

12.6 Calculation of Paired Trap Agreement. Calculate the relative deviation (RD) between the Hg concentrations measured with the paired sorbent traps using Equation 30B–5.

$$RD = \frac{|C_a - C_b|}{C_a + C_b} \times 100 \qquad \text{Eq. 30B-5}$$

12.7 Calculation of Measured Spike Hg Concentration (Field Recovery Test). Calculate the measured spike concentration using Equation 30B–6.

$$C_{rec} = \frac{m_s}{v_s} - \frac{m_u}{v_u} \qquad \text{Eq. 30B-6}$$

Then calculate the spiked Hg recovery, R, using Equation 30B–7.

State of Oregon Department of Environmental Quality

OAR 340-232-0100 Attachments

California Environmental Protection Agency

Air Resources Board

Vapor Recovery Test Procedure

TP-204.1

Determination of Five Minute Static Pressure Performance of Vapor Recovery Systems of Cargo Tanks

Adopted: April 12, 1996
Amended: March 17, 1999
Amended: November 7, 2014

California Environmental Protection Agency
Air Resources Board

Vapor Recovery Test Procedure

TP-204.1

Determination of Five Minute Static Pressure Performance of Vapor Recovery Systems of Cargo Tanks

1 APPLICABILITY

Definitions common to all certification and test procedures are in:

D-200 Definitions for Vapor Recovery Procedures

For the purpose of this procedure, the term "ARB" or “CARB” refers to the California Air Resources Board, and the term "Executive Officer" refers to the Executive Officer of the ARB or his or her authorized representative or designee.

1.1 General Applicability

This procedure is used to determine compliance with the five minute static pressure performance standard referenced in Vapor Recovery Certification Procedure 204 (CP-204), “Certification Procedure for Vapor Recovery Systems of Cargo Tanks.” This procedure may be used to determine the five minute static pressure associated with the dispensing of any fluid, although it is written to reflect application to the hydrocarbon vapors associated with the dispensing of gasoline.

2 PRINCIPLE AND SUMMARY OF TEST PROCEDURE

The cargo tank, mounted on either the truck or trailer, is pressurized to 18 inches water column (WC) and the pressure in the system is then allowed to decay for five (5) minutes. Similarly in a separate test, the cargo tank is evacuated to negative six (-6) inches WC and the pressure in the system is then allow to decay for five (5) minutes. The acceptability of the final pressure or vacuum level is based on the capacity of the cargo tank and is listed in CP-204. The performance of the cargo tank internal vapor valve can be determined by pressurizing the cargo tank to 18 inches WC and then closing the internal vapor valves. The system is then allowed to decay for five (5) minutes. The acceptability of final pressure level for the internal

vapor valve is listed in CP-204.

3 BIASES AND INTERFERENCES

Thermal expansion due to direct sunlight on an exposed cargo tank can bias the results of this test procedure. Keep 100 percent of the length of the vapor space of a cargo tank in shade during testing.

4 EQUIPMENT

4.1 Source of air or inert gas capable of pressurizing tanks to 27.7 inches of water (1 psi) above atmospheric pressure.

4.2 Low pressure (5 psi divisions) regulator for controlling pressurization of tank.

4.3 Water manometer, or equivalent, with 0 to 25 inch range, with scale readings of 0.1 inch.

4.4 Test cap for vapor line with a shut-off valve for connection to the pressure and vacuum supply hoses. The test cap is to be equipped with a tap for connecting the manometer.

4.5 Caps for liquid delivery line.

4.6 Vacuum pump of sufficient capacity to evacuate tank to ten inches of water.

4.7 Pressure and vacuum supply hose of 1/4 inch internal diameter.

4.8 In-line, pressure vacuum relief valve set to activate at one (1) psi and with a capacity equal to the pressurizing or evacuating pumps.

5 PRE-TEST PROTOCOL

5.1 The requirement that each compartment shall have its own internal vapor valve must be met to conduct this test.

5.2 The following shall be performed for all cargo tanks subject to testing in accordance with this test procedure:

5.2.1 Cargo tank and trailers shall be empty of gasoline or product to conduct this test.

Warning: Under no circumstances shall the vapors in any cargo tank be purged or vented directly to the atmosphere.

5.2.2 Cargo tank shall be purged by one of the following methods:

(a) Air from the purged cargo tank shall be routed to an incinerator that is certified by ARB and permitted by a district.

(b) Cargo tank vapors shall be routed to an ARB certified vapor recovery system at a bulk plant or terminal when water is used to purge the cargo tank. The water can be reused. If the water is disposed of, it shall conform to all applicable federal, state, and local regulations.

(c) Cargo tank vapors shall be routed to an ARB certified vapor recovery system at a bulk plant or terminal when a liquid with a vapor pressure of less than four pounds Reid Vapor Pressure (<4 psi RVP) is used to purge the cargo tank.

(d) Any purging method or system must be approved in writing by the Executive Officer.

6 TEST PROCEDURE

This test shall be conducted with product hoses and vapor hoses connected and exposed to the pressurized cargo tanks or compartments. The cargo tank shall meet the standards for all three tests in consecutive runs.

6.1 Static Pressure Performance, Positive Pressurization

6.1.1 Open and close the dome covers.

6.1.2 Connect static electrical ground connections to tank. Attach the delivery and vapor hoses, remove the delivery elbows and plug the liquid delivery fittings.

6.1.3 Attach the test cap to the vapor recovery line of the cargo tank.

6.1.4 Connect the vacuum and pressure supply hose and the pressure-vacuum relief valve to the shut-off valve. Attach the pressure source to the hose. Attach a manometer to the pressure tap.

6.1.5 Connect compartments of the tank internally to each other if possible.

6.1.6 Applying air pressure slowly, pressurize the tank, or alternatively the first compartment, to 18 inches WC.

6.1.7 Close the shut-off valve, allow the pressure in the cargo tank to stabilize (adjust the pressure if necessary to maintain 18 inches WC), record the time and initial pressure.

6.1.8 At the end of five minutes, record the final time and pressure.

6.1.9 Calculate and record the pressure change (inches WC) between initial pressure of+18 inches WC and the final pressure.

6.1.10 Repeat sections 6.1.6 through 6.1.9 for each compartment if they are not interconnected.

6.2 Static Pressure Performance, Vacuum Test (Negative Pressurization)

6.2.1 Connect vacuum source to pressure and vacuum supply hose referenced in section 6.1.4.

6.2.2 Slowly evacuate the tank, or alternatively the first compartment, to six (6) inches WC vacuum. Close the shut-off valve, allow the pressure in the cargo tank to stabilize (adjust the pressure if necessary to maintain a vacuum or negative six (-6) inches WC), and record the initial pressure and time. At the end of five (5) minutes, record the final pressure and time.

6.2.3 Calculate and record the pressure change (inches WC) from the initial 6 inches of WC and the final pressure. If pressurized air lines or other equipment penetrate the cargo tank headspace, record and report the value of the pressure change as zero.

6.2.4 Repeat sections 6.2.2 to 6.2.3 for each compartment if they are not interconnected.

6.3 Internal Vapor Valve Performance, Positive Pressurization

6.3.1 After completing the vacuum and pressure tests (section 6.1 and 6.2), pressurize the tank as in section 6.1.6 18 inches WC.

6.3.2 Close the cargo tank's internal valve(s) thereby isolating the vapor return line and manifold from the cargo tank.

6.3.3 Relieve the pressure in the vapor return line to atmospheric pressure.

6.3.4 Seal the vapor return line and after five (5) minutes record the final gauge pressure existing in the vapor return line and manifold.

6.3.5 Calculate the pressure change (inches WC) from + 18 inches WC to the final pressure.

7 REQUIREMENTS AT CONCLUSION OF PRESSURE TESTING

The entire cargo tank, including tank, domes, dome vents, piping hose connections, adaptors, couplings, hoses and delivery elbows shall be inspected for evidence of wear, damage, or maladjustment that could be a potential leak source. Any part found to be defective shall be adjusted, repaired or replaced as necessary.

8 REPORTING RESULTS

Results for a given cargo tank shall be reported by the company responsible for testing as listed on the 48 hour test notification that was submitted to the Board. Results can be submitted through the ARB Online Cargo Tank Vapor Recovery Certification Program that can be accessed through the ARB webpage at www.arb.ca.gov/enf/cargotanks/cargotanks.htm.

9 ALTERNATE TEST PROCEDURES

9.1 U.S. EPA Method 27

U.S. EPA Method 27 referenced in the Code of Federal Regulations – Title 40, Chapter I, Subchapter C, Part 63, Subpart R, section 63.425(e), (as last amended on December 19, 2003) may be used an alternate to the procedure described in Section 6 with the following exceptions:

a. The purging of vapor from cargo tanks and compartments shall be conducted in accordance with section 5.

b. Results of each test conducted shall comply with the performance standards reference in section 3.1 CP-204 without taking the arithmetic

mean of two successive results as allowed by section 40 CFR 63.425(e)

c. Results from three consecutive tests (pressure, vacuum, and internal vapor valve) run in any sequence shall comply with performance standards reference in section 3.1 of CP-204.

9.2 Other Alternate Test Procedures

This test procedure shall be conducted as specified. Modifications to this test procedure shall not be used to determine compliance unless prior written approval has been obtained from the Executive Officer, pursuant to section 5 of Certification Procedure 204 (CP-204).

State of Oregon Department of Environmental Quality

OAR 340-232-0140
EPA Reference Method 21

While we have taken steps to ensure the accuracy of this Internet version of the document, it is not the official version. To see a complete version including any recent edits, visit: https://www.ecfr.gov/cgi-bin/ECFR?page=browse and search under Title 40, Protection of Environment.

METHOD 21 - DETERMINATION OF VOLATILE ORGANIC COMPOUND LEAKS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile Organic Compounds (VOC)	No CAS number assigned.

1.2 Scope. This method is applicable for the determination of VOC leaks from process equipment. These sources include, but are not limited to, valves, flanges and other connections, pumps and compressors, pressure relief devices, process drains, open-ended valves, pump and compressor seal system degassing vents, accumulator vessel vents, agitator seals, and access door seals.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A portable instrument is used to detect VOC leaks from individual sources. The instrument detector type is not specified, but it must meet the specifications and performance criteria contained in Section 6.0. A leak definition concentration based on a reference compound is specified in each applicable regulation. This method is intended to locate and classify leaks only, and is not to be used as a direct measure of mass emission rate from individual sources.

3.0 Definitions

3.1 *Calibration gas* means the VOC compound used to adjust the instrument meter reading to a known value. The calibration gas is usually the reference compound at a known concentration approximately equal to the leak definition concentration.

3.2 *Calibration precision* means the degree of agreement between measurements of the same known value, expressed as the relative percentage of the average difference between the meter readings and the known concentration to the known concentration.

3.3 *Leak definition concentration* means the local VOC concentration at the surface of a leak source that indicates that a VOC emission (leak) is present. The leak definition is an instrument meter reading based on a reference compound.

3.4 *No detectable emission* means a local VOC concentration at the surface of a leak source, adjusted for local VOC ambient concentration, that is less than 2.5 percent of the specified leak definition concentration. that indicates that a VOC emission (leak) is not present.

3.5 *Reference compound* means the VOC species selected as the instrument calibration basis for specification of the leak definition concentration. (For example, if a leak definition concentration is 10,000 ppm as methane, then any source emission that results in a local concentration that yields a meter reading of 10,000 on an instrument meter calibrated with methane would be classified as a leak. In this example, the leak definition concentration is 10,000 ppm and the reference compound is methane.)

3.6 *Response factor* means the ratio of the known concentration of a VOC compound to the observed meter reading when measured using an instrument calibrated with the reference compound specified in the applicable regulation.

3.7 *Response time* means the time interval from a step change in VOC concentration at the input of the sampling system to the time at which 90 percent of the corresponding final value is reached as displayed on the instrument readout meter.

4.0 Interferences[Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Pollutants. Several of the compounds, leaks of which may be determined by this method, may be irritating or corrosive to tissues (*e.g.*, heptane) or may be toxic (*e.g.*, benzene, methyl alcohol). Nearly all are fire hazards. Compounds in emissions should be determined through familiarity with the source. Appropriate precautions can be found in reference documents, such as reference No. 4 in Section 16.0.

6.0 Equipment and Supplies

A VOC monitoring instrument meeting the following specifications is required:

6.1 The VOC instrument detector shall respond to the compounds being processed. Detector types that may meet this requirement include, but are not limited to, catalytic oxidation, flame ionization, infrared absorption, and photoionization.

6.2 The instrument shall be capable of measuring the leak definition concentration specified in the regulation.

6.3 The scale of the instrument meter shall be readable to ±2.5 percent of the specified leak definition concentration.

6.4 The instrument shall be equipped with an electrically driven pump to ensure that a sample is provided to the detector at a constant flow rate. The nominal sample flow rate, as measured at the sample probe tip, shall be 0.10 to 3.0 l/min (0.004 to 0.1 ft^3 /min) when the probe is fitted with a glass wool plug or filter that may be used to prevent plugging of the instrument.

6.5 The instrument shall be equipped with a probe or probe extension or sampling not to exceed 6.4 mm (1/4in) in outside diameter, with a single end opening for admission of sample.

6.6 The instrument shall be intrinsically safe for operation in explosive atmospheres as defined by the National Electrical Code by the National Fire Prevention Association or other applicable regulatory code for operation in any explosive atmospheres that may be encountered in its use. The instrument shall, at a minimum, be intrinsically safe for Class 1, Division 1 conditions, and/or Class 2, Division 1 conditions, as appropriate, as defined by the example code. The instrument shall not be operated with any safety device, such as an exhaust flame arrestor, removed.

7.0 Reagents and Standards

7.1 Two gas mixtures are required for instrument calibration and performance evaluation:

7.1.1 Zero Gas. Air, less than 10 parts per million by volume (ppmv) VOC.

7.1.2 Calibration Gas. For each organic species that is to be measured during individual source surveys, obtain or prepare a known standard in air at a concentration approximately equal to the applicable leak definition specified in the regulation.

7.2 Cylinder Gases. If cylinder calibration gas mixtures are used, they must be analyzed and certified by the manufacturer to be within 2 percent accuracy, and a shelf life must be specified. Cylinder standards must be either reanalyzed or replaced at the end of the specified shelf life.

7.3 Prepared Gases. Calibration gases may be prepared by the user according to any accepted gaseous preparation procedure that will yield a mixture accurate to within 2 percent. Prepared standards must be replaced each day of use unless it is demonstrated that degradation does not occur during storage.

7.4 Mixtures with non-Reference Compound Gases. Calibrations may be performed using a compound other than the reference compound. In this case, a conversion factor must be determined for the alternative compound such that the resulting meter readings during source surveys can be converted to reference compound results.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Instrument Performance Evaluation. Assemble and start up the instrument according to the manufacturer's instructions for recommended warm-up period and preliminary adjustments.

8.1.1 Response Factor. A response factor must be determined for each compound that is to be measured, either by testing or from reference sources. The response factor tests are required before placing the analyzer into service, but do not have to be repeated at subsequent intervals.

8.1.1.1 Calibrate the instrument with the reference compound as specified in the applicable regulation. Introduce the calibration gas mixture to the analyzer and record the observed meter reading. Introduce zero gas until a stable reading is obtained. Make a total of three measurements by alternating between the calibration gas and zero gas. Calculate the response factor for each repetition and the average response factor.

8.1.1.2 The instrument response factors for each of the individual VOC to be measured shall be less than 10 unless otherwise specified in the applicable regulation. When no instrument is available that meets this specification when calibrated with the reference VOC specified in the applicable regulation, the available instrument may be calibrated with one of the VOC to be measured, or any other VOC, so long as the instrument then has a response factor of less than 10 for each of the individual VOC to be measured.

8.1.1.3 Alternatively, if response factors have been published for the compounds of interest for the instrument or detector type, the response factor determination is not required, and existing results may be referenced. Examples of published response factors for flame ionization and catalytic oxidation detectors are included in References 1–3 of Section 17.0.

8.1.2 Calibration Precision. The calibration precision test must be completed prior to placing the analyzer into service and at subsequent 3-month intervals or at the next use, whichever is later.

8.1.2.1 Make a total of three measurements by alternately using zero gas and the specified calibration gas. Record the meter readings. Calculate the average algebraic difference between the meter readings and the known value. Divide this average difference by the known calibration value and multiply by 100 to express the resulting calibration precision as a percentage.

8.1.2.2 The calibration precision shall be equal to or less than 10 percent of the calibration gas value.

8.1.3 Response Time. The response time test is required before placing the instrument into service. If a modification to the sample pumping system or flow configuration is made that would change the response time, a new test is required before further use.

8.1.3.1 Introduce zero gas into the instrument sample probe. When the meter reading has stabilized, switch quickly to the specified calibration gas. After switching, measure the time required to attain 90 percent of the final stable reading. Perform this test sequence three times and record the results. Calculate the average response time.

8.1.3.2 The instrument response time shall be equal to or less than 30 seconds. The instrument pump, dilution probe (if any), sample probe, and probe filter that will be used during testing shall all be in place during the response time determination.

8.2 Instrument Calibration. Calibrate the VOC monitoring instrument according to Section 10.0.

8.3 Individual Source Surveys.

8.3.1 Type I—Leak Definition Based on Concentration. Place the probe inlet at the surface of the component interface where leakage could occur. Move the probe along the interface periphery while observing the instrument readout. If an increased meter reading is observed, slowly sample the interface where leakage is indicated until the maximum meter reading is obtained. Leave the probe inlet at this maximum reading location for approximately two times the instrument response time. If the maximum observed meter reading is greater than the leak definition in the applicable regulation, record and report the results as specified in the regulation reporting requirements. Examples of the application of this general technique to specific equipment types are:

8.3.1.1 Valves. The most common source of leaks from valves is the seal between the stem and housing. Place the probe at the interface where the stem exits the packing gland and sample the stem circumference. Also, place the probe at the interface of the packing gland take-up flange seat and sample

the periphery. In addition, survey valve housings of multipart assembly at the surface of all interfaces where a leak could occur.

8.3.1.2 Flanges and Other Connections. For welded flanges, place the probe at the outer edge of the flange-gasket interface and sample the circumference of the flange. Sample other types of nonpermanent joints (such as threaded connections) with a similar traverse.

8.3.1.3 Pumps and Compressors. Conduct a circumferential traverse at the outer surface of the pump or compressor shaft and seal interface. If the source is a rotating shaft, position the probe inlet within 1 cm of the shaft-seal interface for the survey. If the housing configuration prevents a complete traverse of the shaft periphery, sample all accessible portions. Sample all other joints on the pump or compressor housing where leakage could occur.

8.3.1.4 Pressure Relief Devices. The configuration of most pressure relief devices prevents sampling at the sealing seat interface. For those devices equipped with an enclosed extension, or horn, place the probe inlet at approximately the center of the exhaust area to the atmosphere.

8.3.1.5 Process Drains. For open drains, place the probe inlet at approximately the center of the area open to the atmosphere. For covered drains, place the probe at the surface of the cover interface and conduct a peripheral traverse.

8.3.1.6 Open-ended Lines or Valves. Place the probe inlet at approximately the center of the opening to the atmosphere.

8.3.1.7 Seal System Degassing Vents and Accumulator Vents. Place the probe inlet at approximately the center of the opening to the atmosphere.

8.3.1.8 Access door seals. Place the probe inlet at the surface of the door seal interface and conduct a peripheral traverse.

8.3.2 Type II—"No Detectable Emission". Determine the local ambient VOC concentration around the source by moving the probe randomly upwind and downwind at a distance of one to two meters from the source. If an interference exists with this determination due to a nearby emission or leak, the local ambient concentration may be determined at distances closer to the source, but in no case shall the distance be less than 25 centimeters. Then move the probe inlet to the surface of the source and determine the concentration as outlined in Section 8.3.1. The difference between these concentrations determines whether there are no detectable emissions. Record and report the results as specified by the regulation. For those cases where the regulation requires a specific device installation, or that specified vents be ducted or piped to a control device, the existence of these conditions shall be visually confirmed. When the regulation also requires that no detectable emissions exist, visual observations and sampling surveys are required. Examples of this technique are:

8.3.2.1 Pump or Compressor Seals. If applicable, determine the type of shaft seal. Perform a survey of the local area ambient VOC concentration and determine if detectable emissions exist as described in Section 8.3.2.

8.3.2.2 Seal System Degassing Vents, Accumulator Vessel Vents, Pressure Relief Devices. If applicable, observe whether or not the applicable ducting or piping exists. Also, determine if any sources exist in the ducting or piping where emissions could occur upstream of the control device. If the required ducting or piping exists and there are no sources where the emissions could be vented to the atmosphere upstream of

the control device, then it is presumed that no detectable emissions are present. If there are sources in the ducting or piping where emissions could be vented or sources where leaks could occur, the sampling surveys described in Section 8.3.2 shall be used to determine if detectable emissions exist.

8.3.3 Alternative Screening Procedure.

8.3.3.1 A screening procedure based on the formation of bubbles in a soap solution that is sprayed on a potential leak source may be used for those sources that do not have continuously moving parts, that do not have surface temperatures greater than the boiling point or less than the freezing point of the soap solution, that do not have open areas to the atmosphere that the soap solution cannot bridge, or that do not exhibit evidence of liquid leakage. Sources that have these conditions present must be surveyed using the instrument technique of Section 8.3.1 or 8.3.2.

8.3.3.2 Spray a soap solution over all potential leak sources. The soap solution may be a commercially available leak detection solution or may be prepared using concentrated detergent and water. A pressure sprayer or squeeze bottle may be used to dispense the solution. Observe the potential leak sites to determine if any bubbles are formed. If no bubbles are observed, the source is presumed to have no detectable emissions or leaks as applicable. If any bubbles are observed, the instrument techniques of Section 8.3.1 or 8.3.2 shall be used to determine if a leak exists, or if the source has detectable emissions, as applicable.

9.0 Quality Control

Section	Quality control measure	Effect
8.1.2	Instrument calibration precision check	Ensure precision and accuracy, respectively, of instrument response to standard.
10.0	Instrument calibration	

10.0 Calibration and Standardization

10.1 Calibrate the VOC monitoring instrument as follows. After the appropriate warm-up period and zero internal calibration procedure, introduce the calibration gas into the instrument sample probe. Adjust the instrument meter readout to correspond to the calibration gas value.

Note: If the meter readout cannot be adjusted to the proper value, a malfunction of the analyzer is indicated and corrective actions are necessary before use.

11.0 Analytical Procedures[Reserved]

12.0 Data Analyses and Calculations[Reserved]

13.0 Method Performance[Reserved]

14.0 Pollution Prevention[Reserved]

15.0 Waste Management[Reserved]

16.0 References

1. Dubose, D.A., and G.E. Harris. Response Factors of VOC Analyzers at a Meter Reading of 10,000 ppmv for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81051. September 1981.

2. Brown, G.E., *et al.* Response Factors of VOC Analyzers Calibrated with Methane for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81–022. May 1981.

3. DuBose, D.A. *et al.* Response of Portable VOC Analyzers to Chemical Mixtures. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81–110. September 1981.

4. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data[Reserved]

State of Oregon Department of Environmental Quality

OAR 340-232-0170 Attachments

SOURCE TEST PROCEDURE **ST-7**

ORGANIC COMPOUNDS

REF: Regulation 8

1. APPLICABILITY

1.1 This procedure is used to quantify emissions of organic compounds. It is applicable to the determination of compliance with Regulation 8.

1.2 The combustion technique detailed in ST-7 is not applicable when carbon dioxide constitutes over 85%, on a molar basis, of the total carbon (organic plus inorganic, as C_1), in the sample.

1.3 The use of a flame ionization detector (FID) for direct measurement of organic compounds may be used when carbon dioxide constitues over 85%, on a molar basis, of the total carbon in the sample.

2. PRINCIPLE

2.1 Combustion Technique: A continuous sample of effluent is passed through a combustion tube. The combusted sample is conditioned to remove water and particulate. The continuously combusted sample is analyzed for Total Carbon (TC) using a non-dispersive infrared (NDIR) CO_2 analyzer. At the same time, a continuous sample of effluent is conditioned to remove water and particulate material. This sample which has bypassed the combustion tube is analyzed to determine the background CO_2, CO, and methane concentrations which are subtracted from the TC value to determine the non-methane organic carbon (NMOC) concentration. The background CO_2 concentration is measured using the same NDIR as that used to measure TC.

2.2 FID Direct Measurement: A continuous sample of effluent is conditioned to remove water and particulate material. The conditioned sample is analyzed for total hydrocarbons (THC) by FID. NMOC concentration is calculated by subtracting the methane concentration from the THC concentration.

2.3 The methane content of the sample is determined either (A) by filling an evacuated cylinder with sample for subsequent gas chromatographic analysis or (B) by directing a portion of the conditioned sample through a bed of activated carbon to remove NMOC and then into a FID.

3. RANGE AND SENSITIVITY

3.1 The minimum measurable concentration of carbon dioxide is 10 ppm if the appropriate NDIR cell is used.

3.2 The maximum concentration of organic compounds for which the combustion technique in this procedure is applicable is 5% when the appropriate NDIR cell is used.

3.3 The minimum sensitivity of the NDIR is 2% of full scale.

3.4 Use of the combustion technique requires a molar concentration ratio of oxygen to VOC of 5:1 or greater.

3.5 The minimum measurable concentration of THC by FID is 5 ppmv when interferences are not present.

3.6 The minimum sensitivity of the FID is 2% of full scale.

4. INTERFERENCES

4.1 Combustion Technique:Negative bias may occur due to reaction of highly reactive organics (e.g., aldehydes or acids) with internal surfaces or if the condensation point of the sample is above the condenser temperature. Combustion at the emission point, prior to condenser and the use of the minimum probe to combustor tubing length, greatly reduces this bias.

4.2 Combustion Technique: High concentrations or widely varying concentrations of methane, carbon monoxide or carbon dioxide may adversely affect the accuracy of this procedure for the measurement of the organic compounds present. Alternate methods may be used upon prior approval by the Source Test Section Manager.

4.3 FID Direct Measurement: Response factors vary be tween hydrocarbons. Propane used as a span gas minimizes this variability. The measurement of chlorinated hydrocarbons, in some instances, may require the use of an alternative span gas. Use of an alternative span gas must be approved by the Source Test Manager.

4.4 FID Methane Measurement: The activated charcoal scrubber adsorbs non-methane hydrocarbons from sample gas before its subsequent analysis by FID. Previous contamination or unclean activated charcoal in this scrubber can lead to the determination of erroneously high levels of methane. This problem is obviated by establishing a zero methane base-line response. Methane determination requires that the response time must be sufficient to allow for the residence time of sample gas in the carbon adsorber.

5. APPARATUS

5.1 Carbon dioxide analyzer. Use a non-dispersive infrared gas analyzer (in accordance with ST-5).

5.2 Carbon monoxide analyzer. Use a non-dispersive infrared gas analyzer (in accordance with ST-6).

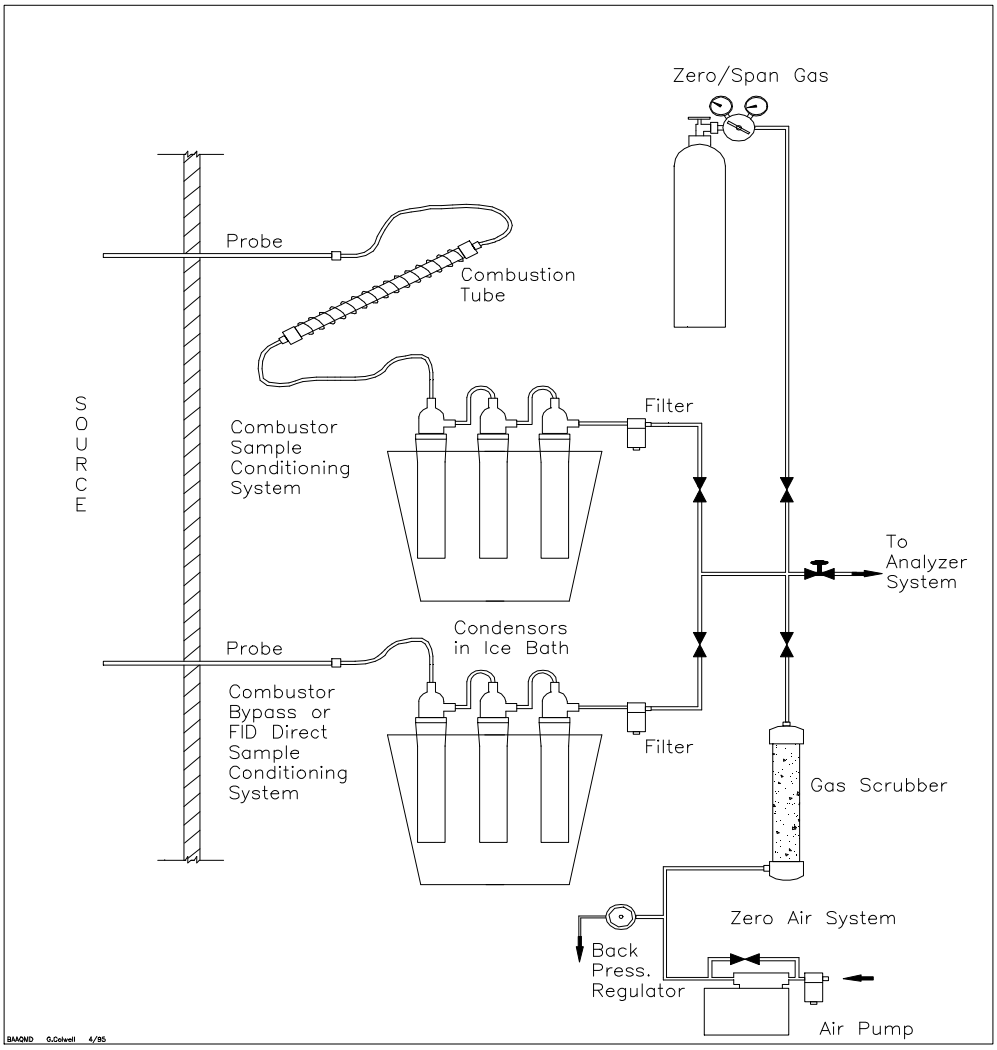
5.3 Flame ionization detector.

5.4 Chart recorder. Record the continuous output from each analyzer.

5.5 Sample conditioning, zero air, and span gas system. Assemble this system as shown in Figure 7-1. Sample conditioning system shall provide a dry, particulate-free gas flow to the instrument. The zero-air system shall provide clean, dry CO_2 free air for instrument calibration. The span-gas system shall provide known concentration of the appropriate gas for use in calibrating the analyzers. Except as specified, all materials which come in contact with either the sample or span gases must be constructed of Teflon or stainless steel.

Figure 7-1

Sample Conditioning, Zero Air, Zero/Span Gas Systems



5.7 Sample probe. Use a tube of inert material and sufficient length to traverse the stack being tested. If the stack temperature exceeds 425C (800F), use a quartz probe. Other probes are acceptable subject to approval by the Source Test Section.

5.8 Condensers. Use modified Greenberg-Smith impingers with the im paction plates removed and the inlet tubes shortened to a length of 10 CM (4 inches).

5.9 Cooling system. Immerse the impingers in an ice bath during the test.

5.10 Particulate filter. Use a Balston type 95 holder with a grade B filter, or equivalent, in the sample system.

5.11 Pumps. Use leak-free, Teflon-lined, diaphragm pumps in the sample and zero air system. The pumps shall have a free-flow capacity of at least 28 liters/min. (1.0 CFM).

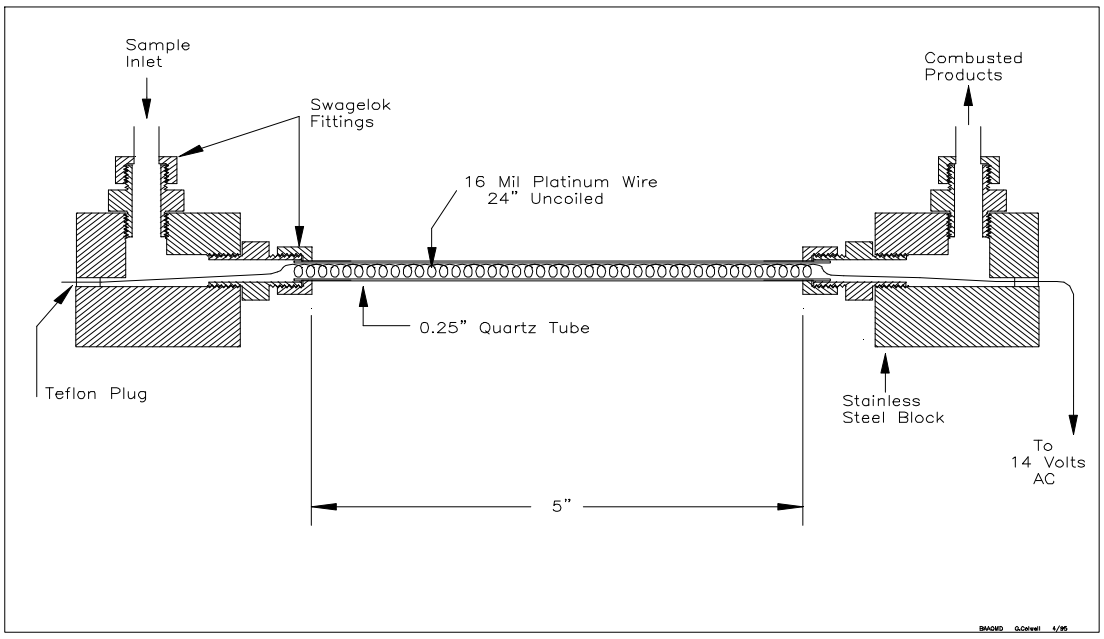
5.12 Gas scrubber. Use a bed of silica gel, Ascarite (or soda-lime), and charcoal to remove moisture, carbon dioxide, and hydrocarbons from the zero air system.

5.13 Span gas. Use a high-pressure cylinder containing a known concentration of propane in air or nitrogen. A cylinder containing a known concentration of solvent, where applicable, may also be used. This option may only be used with prior approval of the Source Test Section.

5.14 Combustor. Use a system to oxidize all organics in the sample including methane. Examples of acceptable combustion tubes found adequate by the BAAQMD are described in Figures 7-2 and 7-3.

Figure 7-2

Internally Heated Combustion Tube



6. PRE-TEST PROCEDURES

6.1 Warm-up the instruments according to manufacturers' instructions.

6.2 Assemble the sampling system as shown in Figure 7-4 or 7-5.

6.3 Leak-test the sampling system by starting the pump, plugging the probe, and assuring that the pressure to the analyzer falls to zero.

6.4 Introduce zero-air into the analyzers and calibrate the instruments ac cording to manufacturers' instructions.

6.5 Introduce span-gas into the analyzers and calibrate the instruments according to manufacturers' instruction.

6.6 Conduct a preliminary concentration traverse (in accordance with ST-18) to determine if stratification of the stack gases exists. If the hydrocarbon concentration at any point differs from the average concentration by more than 10%, traverse the stack during the test; if not, sample at any single point.

Figure 7-3

Externally Heated Combustion Tube

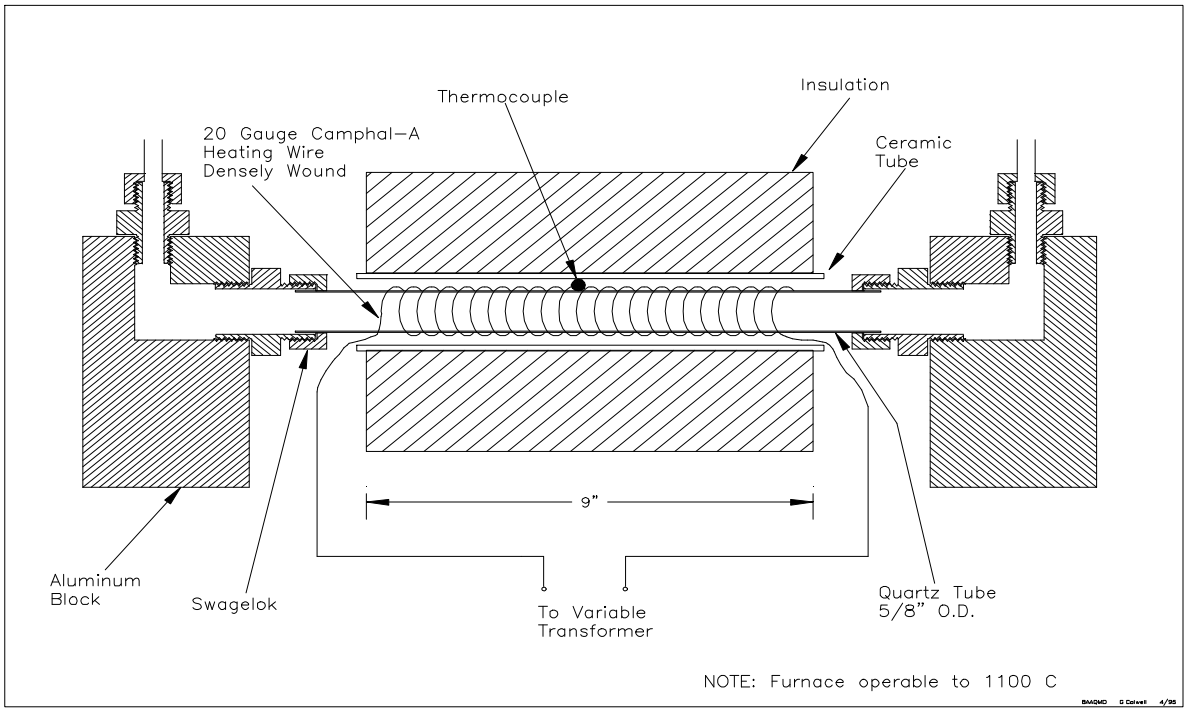


Figure 7-4

Analyzer Manifold for ST-7

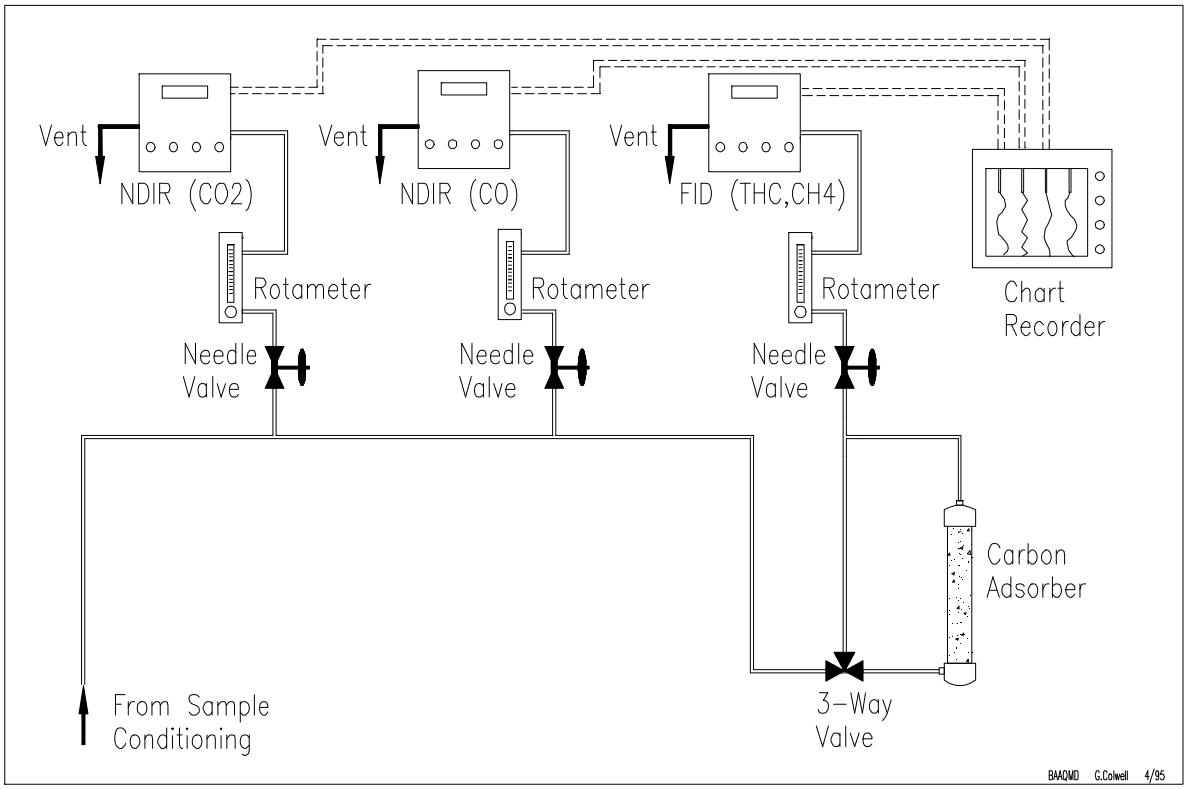
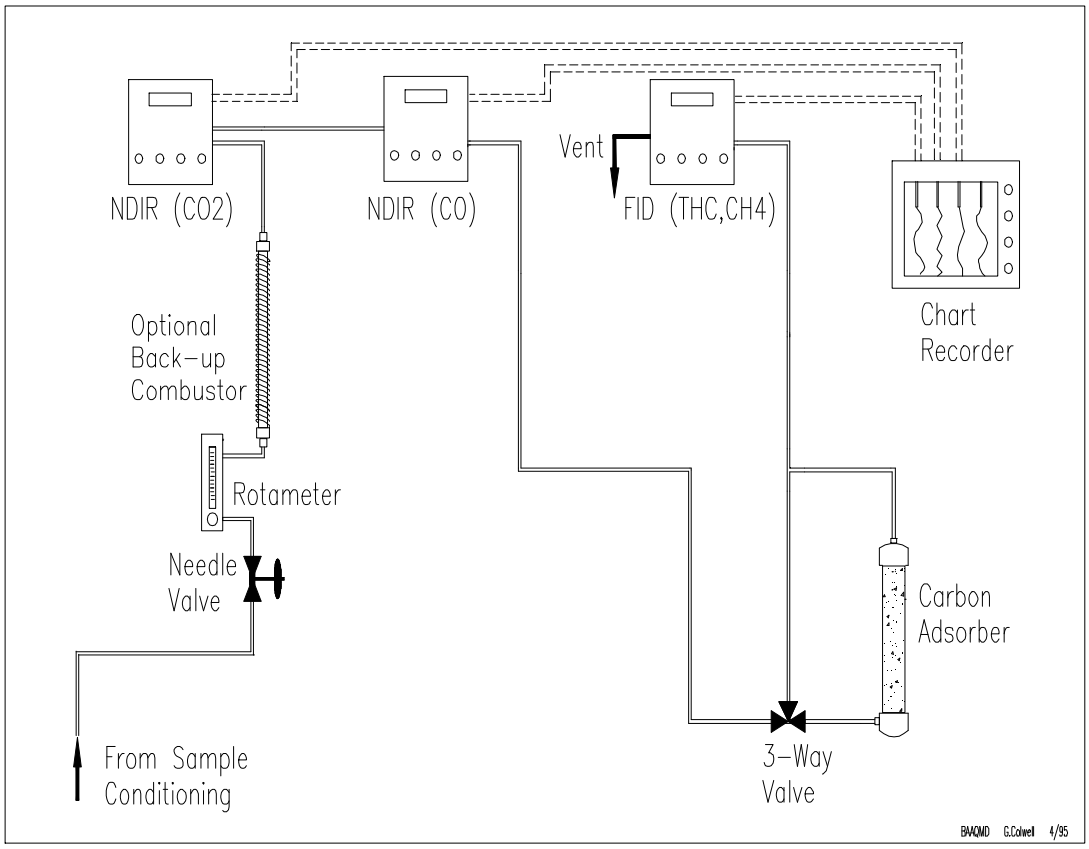


Figure 7-5

Analyzer Manifold for Combustor of Less Than 100% Efficiency



6.7 Prepare the chart recorder according to manufacturer's instructions.

6.8 Set the voltage to the combustor to at least 14 volts A.C. for the combustor illustrated in Figure 7-2. Efficiency of this combustor will be a function of the platinum wire, voltage, sample flow-rate and sample composition. All voltages will be combustor specific and efficiency data may be requested by the Source Test Section.

6.9 Set the temperature of the combustor to 870 ^{O}C ±10^{O}C (1598^{O}F ±18^{O}F) for the combustor in Figure 7-3. The residence time of sample through this combustor must be greater than 2 seconds. Efficiency data may be required by the Source Test Section.

7. SAMPLING

7.1 Each test run shall be of 30 minute duration when testing from continuous operations. Each test run of a batch operation shall be for 90% of the batch time or thirty minutes, whichever is less.

7.2 At sources requiring both inlet and outlet tests on a control device (e.g., afterburners), the test times may be adjusted to aid in obtaining representative results.

7.3 Introduce sample gas into the analytical system at the same flow rate used to calibrate the analyzers.

7.4 By-pass the combustion tube (at approximately ten minute intervals), to measure the background CO_2, CO, and methane in the sample stream.

7.5 Verify that the CO and THC concentrations from the combustor ar e zero. Non-zero concentrations of these parameters must be continuously monitored during all combustion technique testing.

7.6 Determine the methane concentration by either passing a portion of the sample stream through an activated carbon scrubber to remove non-methane hydrocarbons and then through a flame ionization detector or by obtaining a grab sample for analysis by Lab 17.

7.7 Maintain ice in the cooling system throughout the test.

7.8 Calibrate the analyzers before and after each test run. Rec ord each step of the process on the chart recording.

7.9 Conduct three consecutive test runs.

8. AUXILIARY TESTS

8.1 Stack gas flow rate. Use ST-17 to determine the stack gas flow rate after each test run.

8.2 Moisture content. Use ST-23 to determine the moisture content of the stack gases.

9. CALCULATIONS

9.1 Use Equations 1 and 2 to calculate Non-Methane Organic Compound concentrations from Combustion Technique data.

$$C_{TC} = (C_{TC})_{Comb} + (C_{CO})_{Comb} + (C_{THC})_{Comb} \quad (1)$$

$$C_{NMOC} = C_{TC} - C_{CO_2} - C_{CO} - C_M \quad (2)$$

9.2 Use Equation 3 to calculate Non-Methane Organic Compound concentrations from FID Direct Measurement data:

$$C_{NMOC} = C_{THC} - C_M \quad (3)$$

9.3 Mass flow rate of the non-methane organic compounds, as carbon are calculated according to equation 4.

$$M_{NMOC} = \frac{12(\text{lb C/lb-mole } C_1) \times Q_0 \times C_{NMOC} \times 60 \text{ (min/hr)}}{386.9 \text{ (SDCF/lb-mole)} \times 10^6 \text{(ppm)}} \quad (4)$$

9.4 Mass flow rate of Volatile Organic Compounds are calculated according to equation 5:

$$M_{VOC} = \frac{X_{VOC} \times Q_o \times C_{NMOC} \times 60 \text{ (min/hr)}}{386.9 \text{ (SDCF/lb-mole)} \times 10^6 \text{(ppm)}} \quad (5)$$

9.5 Molecular weight and VOC Density Calculations. If organic mass rate emissions are subject to rules requiring the determination of precusor organic compounds or volatile organic compounds, then the average molecular weight of VOC per carbon (X_{VOC})must be determined. If it is not practicable to determine or estimate X_{VOC}, then a value of 14 lb/lb-mol shall be used. Calculations of exhaust emission rates shall be based upon the same X_{VOC} as that determined for the inlet. Use the worksheet shown in Figure 7-6 to correctly calculate or estimate the average molecular weight.

9.6 Mass flow rate of carbon monoxide is calculated according to equation 6:

$$M_{CO} = \frac{28\text{(lb CO/lb-mole)} \times Q_o \times C_{CO} \times 60 \text{ (min/hr)}}{386.9 \text{ (SDCF/lb-mole)} \times 10^6 \text{(ppm)}} \quad (6)$$

9.7 The VOC Emission Factor, $(m_{Ctg})_{overall}$, from coating operations, will be calculated according to equation 7. If organic emissions are subject to equivalent control (for example: Regulation 8 Rule 11, Section 302), the Equivalent Coatings Emission Factor, $(m_{EQCtg})_{overall}$, shall be calculated using worksheet shown in Figure 7-7. Fugitive emissions shall be added to measured emission rates by calculating solvent usage rate (lb/hr), subtracting control device inlet VOC rate and adding the result to the control device outlet VOC rate.

$$(m_{Ctg})_{overall} = \frac{(M_{VOC})_{overall}}{\text{Application Rate (gal/hr)}} \quad (7)$$

9.8 If organic emissions are controlled by incineration, the efficiency of oxidation to carbon dioxide for the determination of exemption in Regulation 8, Rule 1, Section 110.3, shall be calculated using equations 8 or 9. Operations whose emissions are not controlled by incineration or are not subject to the exemption, shall be calculated using equations 10 or 11.

9.8.1 If the control device is an incinerator and $(M_{CO})_{out}$ is greater than $(M_{CO})_{in}$, then control efficiency will be calculated using equation 8 or 9:

$$E_{device} = \frac{(M_{NMOC})_{in} - (M_{NMOC})_{out} - (^{12}/_{28}) \times \{(M_{CO})_{out} - (M_{CO})_{in}\}}{(M_{NMOC})_{in}} \times 100\% \quad (8)$$

$$E_{device} = \frac{(M_{VOC})_{in} - (M_{VOC})_{out} - (^{X_{VOC}}/_{28}) \times \{(M_{CO})_{out} - (M_{CO})_{in}\}}{(M_{VOC})_{in}} \times 100\% \quad (9)$$

9.8.2 In all other situations, the control efficiency will be calculated using equation 10 or 11:

$$E_{device} = \frac{(M_{NMOC})_{in} - (M_{NMOC})_{out}}{(M_{NMOC})_{in}} \times 100\% \quad (10)$$

$$E_{device} = \frac{(M_{VOC})_{in} - (M_{VOC})_{out}}{(M_{VOC})_{in}} \times 100\% \quad (11)$$

9.9 Overall mass rate emissions shall include fugitive emissions according to equations 12 through 15.

9.9.1 Overall mass rate emissions of Non-Methane Organic Carbon shall include fugitive emissions as given by equations 12 and 13:

$$(M_{NMOC})_{fugitive} = (M_{NMOC})_{process} - (M_{NMOC})_{in} \quad (12)$$

$$(M_{NMOC})_{overall} = (M_{NMOC})_{out} + (M_{NMOC})_{fugitive} \quad (13)$$

9.9.2 Overall mass rate emissions of Volatile Organic Compounds shal l include fugitive emissions as given by equations 14 and 15:

$$(M_{VOC})_{fugitive} = (M_{VOC})_{process} - (M_{VOC})_{in} \quad (14)$$

$$(M_{VOC})_{overall} = (M_{VOC})_{out} + (M_{VOC})_{fugitive} \quad (15)$$

9.10 Sample calculations.

Example 1: Incinerator Abating Cyclohexanone

Given:

Process data shows coating applied at a rate of 8 gallons per hour. Laboratory analysis of the coating indicates it contains 5 pounds VOC per

gallon. The VOC is pure Cyclohexanone ($C_6H_{10}O$). The Incinerator outlet flow is virtually the same as the inlet flow.

Inlet measurements to the Afterburner:

$$\begin{aligned} Q_o &= 1{,}000 \text{ SDCFM} \\ (C_{TC})_{comb} &= 22{,}400 \text{ ppm} \\ (C_{CO})_{comb} &< 10 \text{ ppm} \\ (C_{THC})_{comb} &< 5 \text{ ppm} \\ C_{CO} &= 250 \text{ ppm} \\ C_M &= 150 \text{ ppm} \\ C_{CO2} &= 10{,}000 \text{ ppm} \end{aligned}$$

Outlet measurements from the Afterburner:

$$\begin{aligned} C_{THC} &= 200 \text{ ppm} \\ C_M &= 100 \text{ ppm} \\ C_{CO} &= 50 \text{ ppm} \end{aligned}$$

Calculation of Afterburner Inlet parameters:

$$C_{TC} = (C_{TC})_{Comb} + (C_{CO})_{Comb} + (C_{THC})_{Comb} \quad (1)$$

$$= 22400 - (<10) - (<5)$$

$$C_{TC} = 22400 \text{ ppm}$$

$$C_{NMOC} = C_{TC} - C_{CO2} - C_{CO} - C_M \quad (2)$$

$$= 22400 - 10000 - 250 - 150$$

$$C_{NMOC} = 12000 \text{ ppm}$$

$$M_{NMOC} = \frac{12(\text{lb C/lb-mole } C_1) \times Q_o \times C_{NMOC} \times 60 \text{ (min/hr)}}{386.9 \text{ (SDCF/lb-mole)} \times 10^6 \text{(ppm)}} \quad (4)$$

$$= (12 \times 1000 \times 12000 \times 60)/(386.9 \times 10^6)$$

$$M_{NMOC} = 22.3 \text{ lbs NMOC/hr}$$

$$X_{VOC} = 16.33 \text{ lb VOC/lb-mol } C_1 \quad \text{(From Worksheet IV-22)}$$

$$M_{VOC} = \frac{X_{VOC} \times Q_o \times C_{NMOC} \times 60 \text{ (min/hr)}}{386.9 \text{ (SDCF/lb-mole)} \times 10^6 \text{(ppm)}} \quad (5)$$

$$= (16.33 \times 1000 \times 12000 \times 60)/(386.9 \times 10^6)$$

M_{VOC} = 30.39 lb VOC/hr

Calculation of Afterburner Outlet parameters:

$$C_{NMOC} = C_{THC} - C_M \quad (3)$$

$$= 200 - 100$$

C_{NMOC} = 100 ppmv

$$M_{NMOC} = \frac{12(\text{lb C/lb-mole } C_1) \times Q_o \times C_{NMOC} \times 60 \text{ (min/hr)}}{386.9 \text{ (SDCF/lb-mole)} \times 10^6 \text{(ppm)}} \quad (4)$$

$$= (12 \times 1000 \times 100 \times 60)/(386.9 \times 10^6)$$

M_{NMOC} = 0.19 lb NMOC/hr

$$M_{VOC} = \frac{X_{VOC} \times Q_o \times C_{NMOC} \times 60 \text{ (min/hr)}}{386.9 \text{ (SDCF/lb-mole)} \times 10^6 \text{(ppm)}} \quad (5)$$

$$= (16.33 \times 1000 \times 100 \times 60)/(386.9 \times 10^6)$$

M_{VOC} = .25 lb VOC/hr

Calculation of Afterburner and Process parameters:

$$E_{device} = \frac{(M_{VOC})_{in} - (M_{VOC})_{out}}{(M_{VOC})_{in}} \times 100\% \quad (11)$$

$$= ((30.39 - .25)/30.39) \times 100\ \%$$

E_{device} = 99.1 %

$$(M_{NMOC})_{fugitive} = (M_{NMOC})_{process} - (M_{NMOC})_{in} \quad (12)$$

$$= (12/16.33) \times 40 - 22.3$$

$(M_{NMOC})_{fugitive}$ = 7.09 lb NMOC/hr

$$(M_{NMOC})_{overall} = (M_{NMOC})_{out} + (M_{NMOC})_{fugitive} \quad (13)$$

$$= 0.19 + 7.09$$

$(M_{NMOC})_{overall}$ = 7.28 lb NMOC/hr

$$(M_{VOC})_{fugitive} = (M_{VOC})_{process} - (M_{VOC})_{in} \quad (14)$$

$$= 40 - 30.39$$

$(M_{VOC})_{fugitive}$ = 9.61 lb VOC/hr

$(M_{VOC})_{overall} = (M_{VOC})_{out} + (M_{VOC})_{fugitive}$ (15)

= .25 + 9.61

$(M_{VOC})_{overall}$ = 9.86 lb VOC/hr

$$(m_{Ctg})_{overall} = \frac{(M_{VOC})_{overall}}{\text{Application Rate (gal/hr)}}$$ (7)

$$= \frac{9.86}{8.0}$$

= 1.23 lb VOC/gallon coating applied

Example 2:

Given:

A source subject to Regulation 8, Rule 2, uses incineration to control non-methane organic carbon emissions. The process operates 20 hours per day.

Inlet Measurements to the Afterburner:

Q_o = 100 SDCFM
C_{TC} = 10300 ppmv
C_{CO_2} = 500 ppmv
C_{CO} = 800 ppmv
C_M < 5 ppmv

Outlet Measurements from the Afterburner:

Q_o = 500 SDCFM
C_{THC} = 500 ppmv
C_{CO} = 400 ppmv
C_M = 100 ppmv

Calculation of Afterburner Inlet parameters:

$C_{NMOC} = C_{TC} - C_{CO2} - C_{CO} - C_M$ (2)

= 10300 - 500 - 800 - (<5)

C_{NMOC} = 9000 ppmv

$$M_{NMOC} = \frac{12(\text{lb C/lb-mole } C_1) \times Q_o \times C_{NMOC} \times 60 \text{ (min/hr)}}{386.9 \text{ (SDCF/lb-mole)} \times 10^6 \text{ (ppm)}}$$ (4)

$$= (12 \times 100 \times 9000 \times 60)/386.9 \times 10^6)$$

M_{NMOC} = 1.675 lb NMOC/hr

$$M_{CO} = \frac{28(\text{lb CO/lb-mole}) \times Q_o \times C_{CO} \times 60\ (\text{min/hr})}{386.9\ (\text{SDCF/lb-mole}) \times 10^6\ (\text{ppm})} \quad (6)$$

$$= (28 \times 100 \times 800 \times 60)/(386.9 \times 10^6)$$

M_{CO} = 0.347 lb CO/hr

Calculation of Afterburner Outlet parameters:

$$C_{NMOC} = C_{THC} - C_M \quad (3)$$

$$= 500 - 100$$

C_{NMOC} = 400 ppmv

$$M_{NMOC} = \frac{12(\text{lb C/lb-mole } C_1) \times Q_o \times C_{NMOC} \times 60\ (\text{min/hr})}{386.9\ (\text{SDCF/lb-mole}) \times 10^6\ (\text{ppm})} \quad (4)$$

$$= (12 \times 500 \times 400 \times 60)/386.9 \times 10^6)$$

M_{NMOC} = 0.372 lb NMOC/hr

$$M_{CO} = \frac{28(\text{lb CO/lb-mole}) \times Q_o \times C_{CO} \times 60\ (\text{min/hr})}{386.9\ (\text{SDCF/lb-mole}) \times 10^6\ (\text{ppm})} \quad (6)$$

$$= (28 \times 500 \times 400 \times 60)/(386.9 \times 10^6)$$

M_{CO} = 0.868 lb CO/hr

Calculation of Afterburner Efficiency:

$$E_{device} = \frac{(M_{NMOC})_{in} - (M_{NMOC})_{out} - (^{12}/_{28}) \times \{(M_{CO})_{out} - (M_{CO})_{in}\}}{(M_{NMOC})_{in}} \times 100\% \quad (8)$$

$$= \frac{(1.675 - 0.372 - (^{12}/_{28}) \times \{(0.868 - 0.347))}{1.675} \times 100\%$$

E_{device} = 64.5 %

Emission Rate (lb/day) = Emission Rate (lb/hr) x Operating Time (hr/day)

= 0.372 lb NMOC / hr x 20 hr / day

= 7.44 lb NMOC/day

Example 3: Paint spray booth abated by a Charcoal Adsorber

Given:

Solvent fumes to the adsorber are primarily from methyl ethyl ketone (MEK). Material and Safety Data Sheets (MSDS) indicate that other solvents are also present, but plant operating data show their contribution is unknown and less than 10 % of the total. The coating is 5.2 lb VOC/gal and 3.0 lb solids/gal. Regulations do not allow the use of a coating with a solvent content in excess of 3.5 lb VOC/gal unless emissions are controlled to an extent equivalent to that of a compliant coating. There is no water in the coating. No dilution of gas occurs through the adsorber bed.

Estimate:

X_{VOC} = 18 lb/lb-mol (ref. sect 9.5 and Fig. 7-6)

Process Measurements:

Paint is drawn out of a one foot diameter drum at a rate of 3.0 inches per hour. 100 pieces per hour at 400 in^2 per piece are coated with paint. Quality assurance data indicate that there are 0.20 grams of solids per 4 in^2.

Inlet Measurements:

Q_o = 1000 SDCFM
C_{TC} = 2350 ppm
C_{CO} < 10 ppm
C_{CO2} = 350 ppm
C_M < 5 ppm

Outlet Measurements:

C_{THC} = 40 ppm
C_M < 5 ppm

Calculation of process parameters:

One way to calculate the volume of paint used is:
Paint Used = 3/12 ft/hr x π (1 ft^2)/4 x 7.48 gal/ft^3
Paint Used = 1.469 gph

An alternative way to calculate paint usage would be:

Paint Used = (0.2 g solids/4 in^2)x(lb/453.6 g)x(100 pieces/hr)x(400 in^2/piece)x(gal/3 lb solids)
Paint Used = 1.469 gph

$(M_{VOC})_{process}$ = 1.469 gph x 5.2 lb VOC/gal
$(M_{VOC})_{process}$ = 7.638 lb VOC/hr

Calculation of Adsorber Inlet parameters:

C_{NMOC} = 2000 ppmv

$$M_{VOC} = \frac{X_{VOC} \times Q_o \times C_{NMOC} \times 60 \text{ (min/hr)}}{386.9 \text{ (SDCF/lb-mole)} \times 10^6 \text{ (ppm)}} \quad (5)$$

$$= (18 \times 1000 \times 2000 \times 60)/(386.9 \times 10^6)$$

M_{VOC} = 5.582 lb VOC/hr

Calculation of Adsorber Outlet parameters:

$$C_{NMOC} = C_{THC} - C_M \quad (3)$$

C_{NMOC} = 40 ppmv

$$M_{VOC} = \frac{X_{VOC} \times Q_o \times C_{NMOC} \times 60 \text{ (min/hr)}}{386.9 \text{ (SDCF/lb-mole)} \times 10^6 \text{ (ppm)}} \quad (5)$$

$$= (18 \times 1000 \times 40 \times 60)/(386.9 \times 10^6)$$

M_{VOC} = .112 lb VOC/hr

$$(M_{VOC})_{fugitive} = (M_{VOC})_{process} - (M_{VOC})_{in} \quad (16)$$

$$= 7.638 - 5.582$$

$(M_{VOC})_{fugitive}$ = 1.056

Calculation of Adsorber Bed parameters:

$$E_{device} = \frac{(M_{VOC})_{in} - (M_{VOC})_{out}}{(M_{VOC})_{in}} \times 100\% \quad (11)$$

$$= (5.582 - 0.112)/5.582 \times 100\ \%$$

E_{device} = 98.0 %

Calculation of Emissions per gallon equivalent coating: (ref. Fig. 7-7)

Line A	= 0	There is no water in this coating
Line B	= 0	There are no exempt volatiles in this coating
Line C		Leave blank. This is not listed on the MSDS cited in this example
Line D	= 0	No water
Line E	= 0	No exempt volatiles
Line F	= 0.671	5.2 lb VOC per 8.2 lb Coating
Line G	= 7.36	There is no PNRS, therefore assign it this default value
Line H	= 6.885	MEK has a known density
Line I	= 8.2	Specified operating condition
Line J	= 5.2	F/(1/I - D/8.34 - E/G)
Line K	= 1.168	Exhaust of .112 plus fugitive of 1.056 From source test data and calculations
Line L	= 3.5	Specified in this example. Actual value will depend on which regulation applies
Line M	= 0.245	1 - J/H
Line N	= 1.469	Calculated above
Line P	= 1.469	(1 - A - B) $\times$ N
Line Q	= 0.492	1 - L/H
Line R	= 0.359	P x M
Line S	= 0.731	R/Q
Line T	= 1.60	K/S

$(m_{EQCtg})_{overall}$ = 1.60 lb VOC/gal Equivalent Coating

Example 4 Petroleum Dry Cleaner

Given:

Petroleum Dry Cleaner washes two 10 lb loads per hour. The solvent used has an average molecular weight per carbon of 14. Gases are vented to a solvent recovery dryer.

Outlet Measurements:

Q_o = 1000 SDCFM
C_{THC} = 100 ppm
C_M < 5 ppm

Calculation of Recovery Dryer Exhaust:

$$M_{VOC} = \frac{X_{VOC} \times Q_o \times C_{NMOC} \times 60 \text{ (min/hr)}}{386.9 \text{ (SDCF/lb-mole)} \times 10^6 \text{ (ppm)}} \quad (5)$$

$$= (14 \times 1000 \times 100 \times 60)/(386.9 \times 10^6)$$

M_{VOC} = 0.217 lb VOC/hr

M_{VOC} /100 kg clothes = M_{VOC}/(2 load/hr x 10 lb/load) x (5/5) x ($^{Kg/lb}/_{Kg/lb}$)

= 5 x M_{VOC} ($^{Kg}/_{lb}$)(hr) 100 Kg Clothes

M_{VOC} /100 kg clothes = 1.085 kg VOC/100 kg clothes

10. Reporting

10.1 Results shall be reported as shown in Figure 7-8.

11. Nomenclature

C_{CO}	[=]	Concentration of Carbon Monoxide, ppmv
C_{CO2}	[=]	Concentration of Carbon Dioxide, ppmv
C_M	[=]	Concentration of Methane, ppmv
C_{NMOC}	[=]	Concentration of Non-Methane Organic Carbon, ppmv
C_{TC}	[=]	Concentration of Total Carbon, ppmv
C_{THC}	[=]	Concentration of Total Hydorcarbons, ppmv
E_{device}	[=]	Efficiency with which NMOC or VOC emissions are abated by the Control Device on a mass basis, %
M_{CO}	[=]	Mass flow rate of CO, lbs/hr
M_{NMOC}	[=]	Mass flow rate of NMOC, lbs/hr
M_{VOC}	[=]	Mass flow rate of VOC, lbs/hr
Q_o	[=]	Volumetric Flowrate, SDCFM
X_{VOC}	[=]	Molecular weight of VOC per Carbon, lb VOC/lb-mol C_1
$(C_{CO})_{comb}$	[=]	Apparent CO concentration measured at combustor. Non-zero only when combustor is less than 100% efficient, ppmv
$(C_{TC})_{comb}$	[=]	Apparent CO_2 (Total Carbon) measured at combustor. $(C_{TC})_{Comb}$ is less than C_{TC} only when combustor is less than 100% efficient, ppmv
$(C_{THC})_{comb}$	[=]	Apparent THC measured at combustor. Non-zero only when combustor is less than 100% efficient, ppmv

$(m_{Ctg})_{overall}$	[=]	Mass flow rate of VOC, including fugitives, exhausted from a coating operation relative to the quantity of coating applied, lb/gal
$(m_{EQCtg})_{overall}$	[=]	Mass flow rate of VOC, including fugitives, exhausted from a coating operation relative the quantity of equivalent coating used had a compliant coating been used in place of the actual coating, lb/gal
$(M_{CO})_{in}$	[=]	Mass flow rate of CO at the inlet of a given abatement device, lb/hr
$(M_{CO})_{out}$	[=]	Mass flow rate of CO at the outlet of a given abatement device, lb/hr
$(M_{NMOC})_{fugitives}$	[=]	Mass flow rate of NMOC attributed to fugitive emissions from a given process, lb NMOC/hr
$(M_{NMOC})_{in}$	[=]	Mass flow rate of NMOC at the inlet of a given abatement device, lb NMOC/hr
$(M_{NMOC})_{out}$	[=]	Mass flow rate of NMOC at the outlet of a given abatement device, lb NMOC/hr
$(M_{NMOC})_{overall}$	[=]	Mass flow rate of NMOC attributed to fugitive and exhausted emissions from abatement devices associated with a given process, lb NMOC/hr
$(M_{NMOC})_{process}$	[=]	The calculated usage rate of NMOC based on process data, lb NMOC/hr
$(M_{VOC})_{fugitives}$	[=]	Mass flow rate of organics as VOC attributed to fugitive emissions, lb VOC/hr
$(M_{VOC})_{in}$	[=]	Mass flow rate of organics as VOC at the inlet of a given abatement device, lb VOC/hr
$(M_{VOC})_{out}$	[=]	Mass flow rate of organics as VOC at the exhaust of a given abatement device, lb VOC/hr
$(M_{VOC})_{overall}$	[=]	Mass flow rate of organics as VOC attributed to fugitive and exhausted emissions from abatement devices associated with a given process, lb VOC/hr
$(M_{VOC})_{process}$	[=]	The calculated usage rate of organic compounds based on process data, lb VOC/hr

Figure 7-6: Molecular Weight and VOC Density Calculation Worksheet

	a	b	c	d	e	f	g	h
	Weight of Solvent	Weight fraction of each Component	Molecular Weight of each Component	Number of Carbons Per Component	Molecular Weight Per Carbon	Molecular Weight Fraction for each Component	VOC Density (lb/gal)	VOC Density Per Component
	*	a / a_{total}	**	**	c / d	b x e	**	b x g
A								
B								
C								
D								
E								
etc.								
Total		1.000						

Average Molecular Weight per Carbon (from total sum f) _____

Average Solvent Density (from total sum h) _____

* From Laboratory Analysis or Coating Data Sheet
** From Reference Material

Figure 7-7 Equivalent Coatings Worksheet

A) Volume fraction H_2O*, gal H_2O/gal CTG _____

B) Volume fraction PNRS*, gal PNRS/gal CTG _____

C) Volume fraction VOC*, gal VOC/gal NECTG _____

D) Weight fraction H_2O*, lb H_2O/lb CTG _____

E) Weight fraction PNRS*, lb PNRS/lb CTG _____

F) Weight fraction VOC*, lb VOC/lb CTG _____

G) Density of PNRS*, lb PNRS/gal PNRS _____
If unknown use 7.36

H) Assumed solvent density, lb VOC/gal VOC _____
If unknown use 7.36

I) Coating density*, lb CTG/gal CTG _____

J) Lb VOC/gal NECTG _____

$$J = \frac{H \times C}{1 - A - B}$$

or

$$J = \frac{F}{\frac{1}{I} - \frac{D}{8.34} - \frac{E}{G}}$$

K) Emission rate **, lb VOC/hr, includes fugitives _____

L) Regulation limit, lb VOC/gal EQCTG _____

M) Gal solids/gal NECTG $M = 1 - J/H$ _____

N) Application Rate **, gal CTG/hr _____

P) Gal NECTG/hr $P = N(1 - A - B)$ _____

Q) Gal solids/gal EQCTG $Q = 1 - L/H$ _____

R) Gal solids/hr $R = P \times M$ _____

S) Gal EQCTG/hr $S = R/Q$ _____

T) Lb VOC emitted/gal EQCTG, $(m_{EQCtg})_{overall}$ $T = K/S$ _____

CTG - Coating as applied

PNRS - photochemically non-reactive solvent

NECTG - non-exempt coating (excludes water and PNRS)

EQCTG - equivalent coating

* From coating data

** From source test data

Figure 7-8

Report No.: _____ Test Date: _____	**BAY AREA AIR QUALITY MANAGEMENT DISTRICT** **Summary of Source Test Results**	**Test Times:** Run A: _____ Run B: _____ Run C: _____

Source Information		**Test Representatives**
Firm Name and Address	Firm Representative and Title Phone No. ( )	
Permit Conditions:	Source: Plant No. Permit No. Operates Hr/Day & Day/Yr.	Operating Parameters
Applicable Regulations:		

Source Test Results and Comments:

METHOD:	TEST	RUN A IN*	RUN A OUT*	RUN B IN	RUN B OUT	RUN C IN	RUN C OUT	AVERAGE IN	AVERAGE OUT
	Run Time,minutes								
	Sample point temperature, F								
ST-17	Stack Volume Flowrate,SDCFM								
ST-14	O_2 , percent								
ST-5	CO_2, percent								
ST-6	CO, PPM								
ST-23	H_2O, percent								
ST-7	Non-methane organic carbon, as C_1								
	a) PPM								
	b) lb/hr								
ST-7	Volatile Organic Compounds, as C_1								
	a) PPM								
	b) lb/hr								
ST-7	Abatement Efficiency, %								

* Control device inlet
** Control device outlet

Test Team Leader Date	Reviewed by Date	Approved By Date

State of Oregon Department of Environmental Quality

OAR 340-232-0230 Attachments

SOURCE TEST PROCEDURE **ST-7**

ORGANIC COMPOUNDS

REF: Regulation 8

1. APPLICABILITY

1.1 This procedure is used to quantify emissions of organic compounds. It is applicable to the determination of compliance with Regulation 8.

1.2 The combustion technique detailed in ST-7 is not applicable when carbon dioxide constitutes over 85%, on a molar basis, of the total carbon (organic plus inorganic, as C_1), in the sample.

1.3 The use of a flame ionization detector (FID) for direct measurement of organic compounds may be used when carbon dioxide constitues over 85%, on a molar basis, of the total carbon in the sample.

2. PRINCIPLE

2.1 Combustion Technique: A continuous sample of effluent is passed through a combustion tube. The combusted sample is conditioned to remove water and particulate. The continuously combusted sample is analyzed for Total Carbon (TC) using a non-dispersive infrared (NDIR) CO_2 analyzer. At the same time, a continuous sample of effluent is conditioned to remove water and particulate material. This sample which has bypassed the combustion tube is analyzed to determine the background CO_2, CO, and methane concentrations which are subtracted from the TC value to determine the non-methane organic carbon (NMOC) concentration. The background CO_2 concentration is measured using the same NDIR as that used to measure TC.

2.2 FID Direct Measurement: A continuous sample of effluent is conditioned to remove water and particulate material. The conditioned sample is analyzed for total hydrocarbons (THC) by FID. NMOC concentration is calculated by subtracting the methane concentration from the THC concentration.

2.3 The methane content of the sample is determined either (A) by filling an evacuated cylinder with sample for subsequent gas chromatographic analysis or (B) by directing a portion of the conditioned sample through a bed of activated carbon to remove NMOC and then into a FID.

3. RANGE AND SENSITIVITY

3.1 The minimum measurable concentration of carbon dioxide is 10 ppm if the appropriate NDIR cell is used.

3.2 The maximum concentration of organic compounds for which the combustion technique in this procedure is applicable is 5% when the appropriate NDIR cell is used.

3.3 The minimum sensitivity of the NDIR is 2% of full scale.

3.4 Use of the combustion technique requires a molar concentration ratio of oxygen to VOC of 5:1 or greater.

3.5 The minimum measurable concentration of THC by FID is 5 ppmv when interferences are not present.

3.6 The minimum sensitivity of the FID is 2% of full scale.

4. INTERFERENCES

4.1 Combustion Technique:Negative bias may occur due to reaction of highly reactive organics (e.g., aldehydes or acids) with internal surfaces or if the condensation point of the sample is above the condenser temperature. Combustion at the emission point, prior to condenser and the use of the minimum probe to combustor tubing length, greatly reduces this bias.

4.2 Combustion Technique: High concentrations or widely varying concentrations of methane, carbon monoxide or carbon dioxide may adversely affect the accuracy of this procedure for the measurement of the organic compounds present. Alternate methods may be used upon prior approval by the Source Test Section Manager.

4.3 FID Direct Measurement: Response factors vary be tween hydrocarbons. Propane used as a span gas minimizes this variability. The measurement of chlorinated hydrocarbons, in some instances, may require the use of an alternative span gas. Use of an alternative span gas must be approved by the Source Test Manager.

4.4 FID Methane Measurement: The activated charcoal scrubber adsorbs non-methane hydrocarbons from sample gas before its subsequent analysis by FID. Previous contamination or unclean activated charcoal in this scrubber can lead to the determination of erroneously high levels of methane. This problem is obviated by establishing a zero methane base-line response. Methane determination requires that the response time must be sufficient to allow for the residence time of sample gas in the carbon adsorber.

5. APPARATUS

5.1 Carbon dioxide analyzer. Use a non-dispersive infrared gas analyzer (in accordance with ST-5).

5.2 Carbon monoxide analyzer. Use a non-dispersive infrared gas analyzer (in accordance with ST-6).

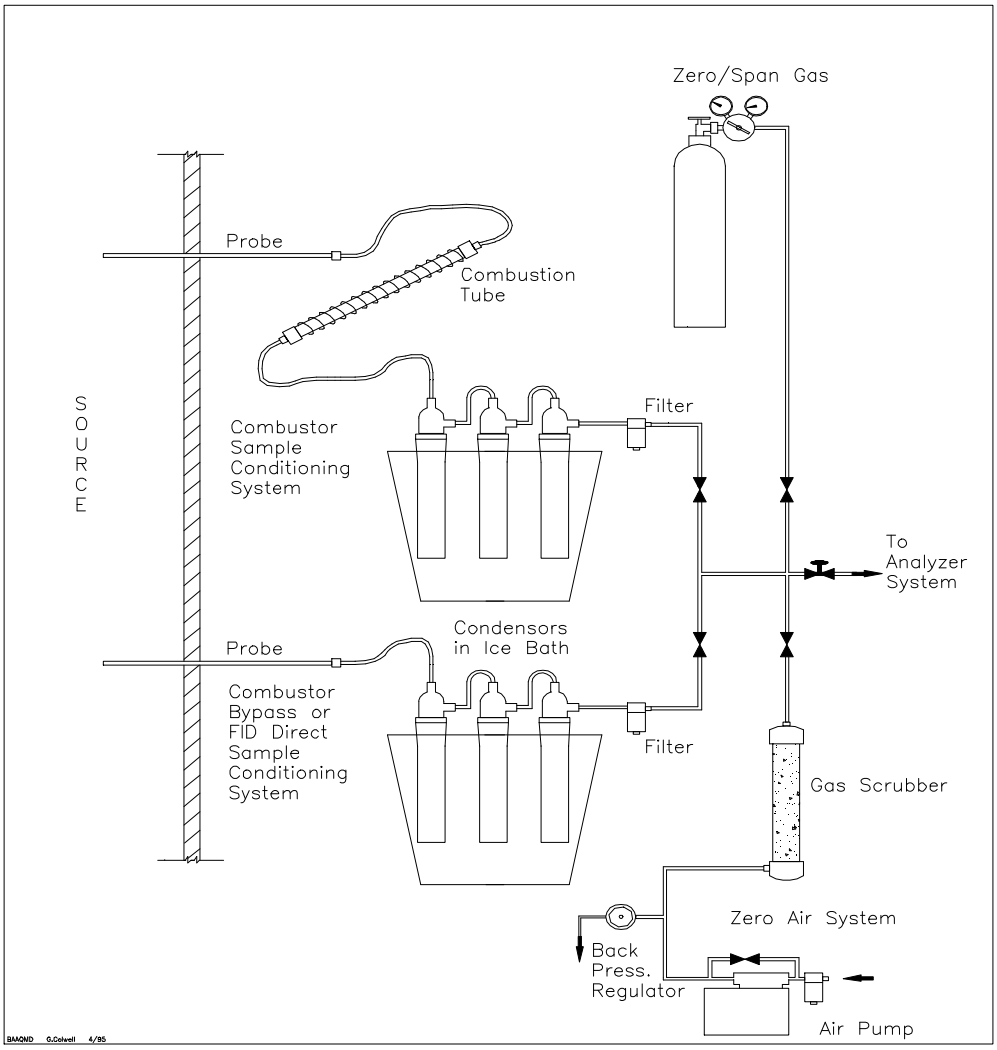
5.3 Flame ionization detector.

5.4 Chart recorder. Record the continuous output from each analyzer.

5.5 Sample conditioning, zero air, and span gas system. Assemble this system as shown in Figure 7-1. Sample conditioning system shall provide a dry, particulate-free gas flow to the instrument. The zero-air system shall provide clean, dry CO_2 free air for instrument calibration. The span-gas system shall provide known concentration of the appropriate gas for use in calibrating the analyzers. Except as specified, all materials which come in contact with either the sample or span gases must be constructed of Teflon or stainless steel.

Figure 7-1

Sample Conditioning, Zero Air, Zero/Span Gas Systems



5.7 Sample probe. Use a tube of inert material and sufficient length to traverse the stack being tested. If the stack temperature exceeds 425C (800F), use a quartz probe. Other probes are acceptable subject to approval by the Source Test Section.

5.8 Condensers. Use modified Greenberg-Smith impingers with the im paction plates removed and the inlet tubes shortened to a length of 10 CM (4 inches).

5.9 Cooling system. Immerse the impingers in an ice bath during the test.

5.10 Particulate filter. Use a Balston type 95 holder with a grade B filter, or equivalent, in the sample system.

5.11 Pumps. Use leak-free, Teflon-lined, diaphragm pumps in the sample and zero air system. The pumps shall have a free-flow capacity of at least 28 liters/min. (1.0 CFM).

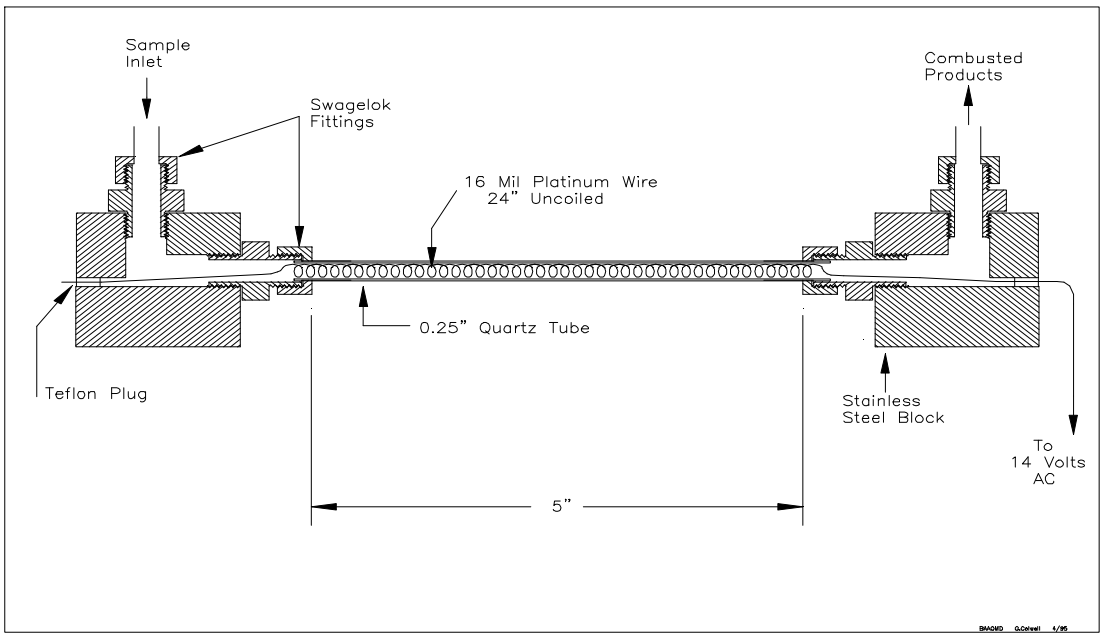
5.12 Gas scrubber. Use a bed of silica gel, Ascarite (or soda-lime), and charcoal to remove moisture, carbon dioxide, and hydrocarbons from the zero air system.

5.13 Span gas. Use a high-pressure cylinder containing a known concentration of propane in air or nitrogen. A cylinder containing a known concentration of solvent, where applicable, may also be used. This option may only be used with prior approval of the Source Test Section.

5.14 Combustor. Use a system to oxidize all organics in the sample including methane. Examples of acceptable combustion tubes found adequate by the BAAQMD are described in Figures 7-2 and 7-3.

Figure 7-2

Internally Heated Combustion Tube



6. PRE-TEST PROCEDURES

6.1 Warm-up the instruments according to manufacturers' instructions.

6.2 Assemble the sampling system as shown in Figure 7-4 or 7-5.

6.3 Leak-test the sampling system by starting the pump, plugging the probe, and assuring that the pressure to the analyzer falls to zero.

6.4 Introduce zero-air into the analyzers and calibrate the instruments ac cording to manufacturers' instructions.

6.5 Introduce span-gas into the analyzers and calibrate the instruments according to manufacturers' instruction.

6.6 Conduct a preliminary concentration traverse (in accordance with ST-18) to determine if stratification of the stack gases exists. If the hydrocarbon concentration at any point differs from the average concentration by more than 10%, traverse the stack during the test; if not, sample at any single point.

Figure 7-3

Externally Heated Combustion Tube

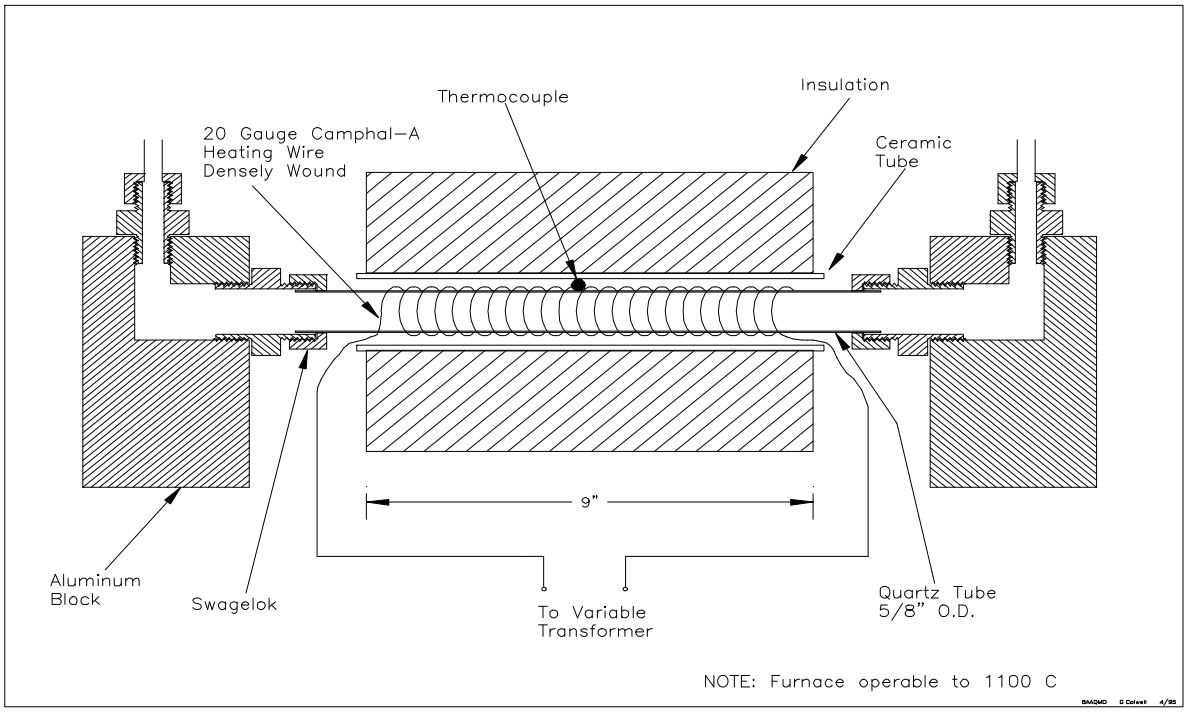


Figure 7-4

Analyzer Manifold for ST-7

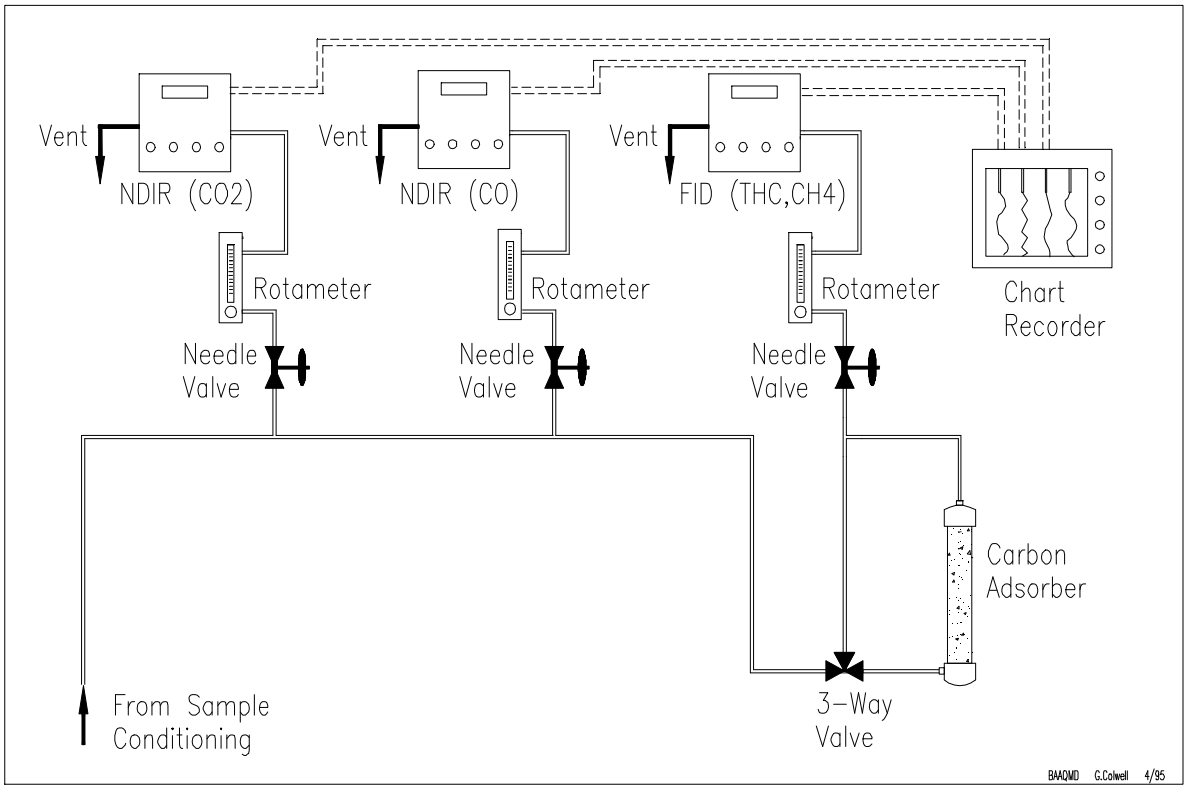
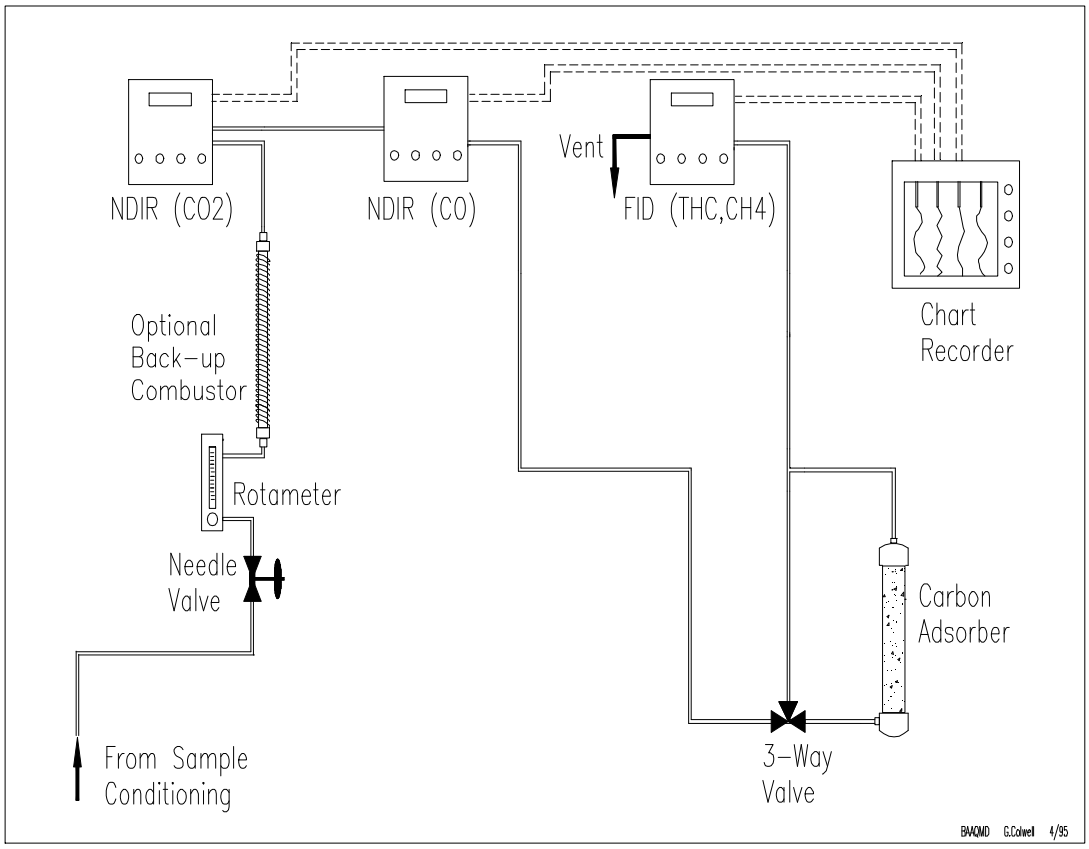


Figure 7-5

Analyzer Manifold for Combustor of Less Than 100% Efficiency



6.7 Prepare the chart recorder according to manufacturer's instructions.

6.8 Set the voltage to the combustor to at least 14 volts A.C. for the combustor illustrated in Figure 7-2. Efficiency of this combustor will be a function of the platinum wire, voltage, sample flow-rate and sample composition. All voltages will be combustor specific and efficiency data may be requested by the Source Test Section.

6.9 Set the temperature of the combustor to 870 ^{O}C ±10^{O}C (1598^{O}F ±18^{O}F) for the combustor in Figure 7-3. The residence time of sample through this combustor must be greater than 2 seconds. Efficiency data may be required by the Source Test Section.

7. SAMPLING

7.1 Each test run shall be of 30 minute duration when testing from continuous operations. Each test run of a batch operation shall be for 90% of the batch time or thirty minutes, whichever is less.

7.2 At sources requiring both inlet and outlet tests on a control device (e.g., afterburners), the test times may be adjusted to aid in obtaining representative results.

7.3 Introduce sample gas into the analytical system at the same flow rate used to calibrate the analyzers.

7.4 By-pass the combustion tube (at approximately ten minute intervals), to measure the background CO_2, CO, and methane in the sample stream.

7.5 Verify that the CO and THC concentrations from the combustor ar e zero. Non-zero concentrations of these parameters must be continuously monitored during all combustion technique testing.

7.6 Determine the methane concentration by either passing a portion of the sample stream through an activated carbon scrubber to remove non-methane hydrocarbons and then through a flame ionization detector or by obtaining a grab sample for analysis by Lab 17.

7.7 Maintain ice in the cooling system throughout the test.

7.8 Calibrate the analyzers before and after each test run. Rec ord each step of the process on the chart recording.

7.9 Conduct three consecutive test runs.

8. AUXILIARY TESTS

8.1 Stack gas flow rate. Use ST-17 to determine the stack gas flow rate after each test run.

8.2 Moisture content. Use ST-23 to determine the moisture content of the stack gases.

9. CALCULATIONS

9.1 Use Equations 1 and 2 to calculate Non-Methane Organic Compound concentrations from Combustion Technique data.

$$C_{TC} = (C_{TC})_{Comb} + (C_{CO})_{Comb} + (C_{THC})_{Comb} \quad (1)$$

$$C_{NMOC} = C_{TC} - C_{CO_2} - C_{CO} - C_M \quad (2)$$

9.2 Use Equation 3 to calculate Non-Methane Organic Compound concentrations from FID Direct Measurement data:

$$C_{NMOC} = C_{THC} - C_M \quad (3)$$

9.3 Mass flow rate of the non-methane organic compounds, as carbon are calculated according to equation 4.

$$M_{NMOC} = \frac{12(\text{lb C/lb-mole } C_1) \times Q_0 \times C_{NMOC} \times 60 \text{ (min/hr)}}{386.9 \text{ (SDCF/lb-mole)} \times 10^6 \text{(ppm)}} \quad (4)$$

9.4 Mass flow rate of Volatile Organic Compounds are calculated according to equation 5:

$$M_{VOC} = \frac{X_{VOC} \times Q_o \times C_{NMOC} \times 60 \text{ (min/hr)}}{386.9 \text{ (SDCF/lb-mole)} \times 10^6 \text{(ppm)}} \quad (5)$$

9.5 Molecular weight and VOC Density Calculations. If organic mass rate emissions are subject to rules requiring the determination of precusor organic compounds or volatile organic compounds, then the average molecular weight of VOC per carbon (X_{VOC})must be determined. If it is not practicable to determine or estimate X_{VOC}, then a value of 14 lb/lb-mol shall be used. Calculations of exhaust emission rates shall be based upon the same X_{VOC} as that determined for the inlet. Use the worksheet shown in Figure 7-6 to correctly calculate or estimate the average molecular weight.

9.6 Mass flow rate of carbon monoxide is calculated according to equation 6:

$$M_{CO} = \frac{28\text{(lb CO/lb-mole)} \times Q_o \times C_{CO} \times 60 \text{ (min/hr)}}{386.9 \text{ (SDCF/lb-mole)} \times 10^6 \text{(ppm)}} \quad (6)$$

9.7 The VOC Emission Factor, $(m_{Ctg})_{overall}$, from coating operations, will be calculated according to equation 7. If organic emissions are subject to equivalent control (for example: Regulation 8 Rule 11, Section 302), the Equivalent Coatings Emission Factor, $(m_{EQCtg})_{overall}$, shall be calculated using worksheet shown in Figure 7-7. Fugitive emissions shall be added to measured emission rates by calculating solvent usage rate (lb/hr), subtracting control device inlet VOC rate and adding the result to the control device outlet VOC rate.

$$(m_{Ctg})_{overall} = \frac{(M_{VOC})_{overall}}{\text{Application Rate (gal/hr)}} \quad (7)$$

9.8 If organic emissions are controlled by incineration, the efficiency of oxidation to carbon dioxide for the determination of exemption in Regulation 8, Rule 1, Section 110.3, shall be calculated using equations 8 or 9. Operations whose emissions are not controlled by incineration or are not subject to the exemption, shall be calculated using equations 10 or 11.

9.8.1 If the control device is an incinerator and $(M_{CO})_{out}$ is greater than $(M_{CO})_{in}$, then control efficiency will be calculated using equation 8 or 9:

$$E_{device} = \frac{(M_{NMOC})_{in} - (M_{NMOC})_{out} - (^{12}/_{28}) \times \{(M_{CO})_{out} - (M_{CO})_{in}\}}{(M_{NMOC})_{in}} \times 100\% \quad (8)$$

$$E_{device} = \frac{(M_{VOC})_{in} - (M_{VOC})_{out} - (^{X_{VOC}}/_{28}) \times \{(M_{CO})_{out} - (M_{CO})_{in}\}}{(M_{VOC})_{in}} \times 100\% \quad (9)$$

9.8.2 In all other situations, the control efficiency will be calculated using equation 10 or 11:

$$E_{device} = \frac{(M_{NMOC})_{in} - (M_{NMOC})_{out}}{(M_{NMOC})_{in}} \times 100\% \quad (10)$$

$$E_{device} = \frac{(M_{VOC})_{in} - (M_{VOC})_{out}}{(M_{VOC})_{in}} \times 100\% \quad (11)$$

9.9 Overall mass rate emissions shall include fugitive emissions according to equations 12 through 15.

9.9.1 Overall mass rate emissions of Non-Methane Organic Carbon shall include fugitive emissions as given by equations 12 and 13:

$$(M_{NMOC})_{fugitive} = (M_{NMOC})_{process} - (M_{NMOC})_{in} \quad (12)$$

$$(M_{NMOC})_{overall} = (M_{NMOC})_{out} + (M_{NMOC})_{fugitive} \quad (13)$$

9.9.2 Overall mass rate emissions of Volatile Organic Compounds shal l include fugitive emissions as given by equations 14 and 15:

$$(M_{VOC})_{fugitive} = (M_{VOC})_{process} - (M_{VOC})_{in} \quad (14)$$

$$(M_{VOC})_{overall} = (M_{VOC})_{out} + (M_{VOC})_{fugitive} \quad (15)$$

9.10 Sample calculations.

Example 1: Incinerator Abating Cyclohexanone

Given:

Process data shows coating applied at a rate of 8 gallons per hour. Laboratory analysis of the coating indicates it contains 5 pounds VOC per

gallon. The VOC is pure Cyclohexanone ($C_6H_{10}O$). The Incinerator outlet flow is virtually the same as the inlet flow.

Inlet measurements to the Afterburner:

$$\begin{aligned} Q_o &= 1{,}000 \text{ SDCFM} \\ (C_{TC})_{comb} &= 22{,}400 \text{ ppm} \\ (C_{CO})_{comb} &< 10 \text{ ppm} \\ (C_{THC})_{comb} &< 5 \text{ ppm} \\ C_{CO} &= 250 \text{ ppm} \\ C_M &= 150 \text{ ppm} \\ C_{CO2} &= 10{,}000 \text{ ppm} \end{aligned}$$

Outlet measurements from the Afterburner:

$$\begin{aligned} C_{THC} &= 200 \text{ ppm} \\ C_M &= 100 \text{ ppm} \\ C_{CO} &= 50 \text{ ppm} \end{aligned}$$

Calculation of Afterburner Inlet parameters:

$$C_{TC} = (C_{TC})_{Comb} + (C_{CO})_{Comb} + (C_{THC})_{Comb} \quad (1)$$

$$= 22400 - (<10) - (<5)$$

$$C_{TC} = 22400 \text{ ppm}$$

$$C_{NMOC} = C_{TC} - C_{CO2} - C_{CO} - C_M \quad (2)$$

$$= 22400 - 10000 - 250 - 150$$

$$C_{NMOC} = 12000 \text{ ppm}$$

$$M_{NMOC} = \frac{12(\text{lb C/lb-mole } C_1) \times Q_o \times C_{NMOC} \times 60 \text{ (min/hr)}}{386.9 \text{ (SDCF/lb-mole)} \times 10^6 \text{(ppm)}} \quad (4)$$

$$= (12 \times 1000 \times 12000 \times 60)/(386.9 \times 10^6)$$

$$M_{NMOC} = 22.3 \text{ lbs NMOC/hr}$$

$$X_{VOC} = 16.33 \text{ lb VOC/lb-mol } C_1 \quad \text{(From Worksheet IV-22)}$$

$$M_{VOC} = \frac{X_{VOC} \times Q_o \times C_{NMOC} \times 60 \text{ (min/hr)}}{386.9 \text{ (SDCF/lb-mole)} \times 10^6 \text{(ppm)}} \quad (5)$$

$$= (16.33 \times 1000 \times 12000 \times 60)/(386.9 \times 10^6)$$

M_{VOC} = 30.39 lb VOC/hr

Calculation of Afterburner Outlet parameters:

$$C_{NMOC} = C_{THC} - C_M \quad (3)$$

= 200 - 100

C_{NMOC} = 100 ppmv

$$M_{NMOC} = \frac{12(\text{lb C/lb-mole } C_1) \times Q_o \times C_{NMOC} \times 60 \text{ (min/hr)}}{386.9 \text{ (SDCF/lb-mole)} \times 10^6 \text{(ppm)}} \quad (4)$$

= (12 x 1000 x 100 x 60)/(386.9 x 10^6)

M_{NMOC} = 0.19 lb NMOC/hr

$$M_{VOC} = \frac{X_{VOC} \times Q_o \times C_{NMOC} \times 60 \text{ (min/hr)}}{386.9 \text{ (SDCF/lb-mole)} \times 10^6 \text{(ppm)}} \quad (5)$$

= (16.33 x 1000 x 100 x 60)/(386.9 x 10^6)

M_{VOC} = .25 lb VOC/hr

Calculation of Afterburner and Process parameters:

$$E_{device} = \frac{(M_{VOC})_{in} - (M_{VOC})_{out}}{(M_{VOC})_{in}} \times 100\% \quad (11)$$

= ((30.39 - .25)/30.39) x 100 %

E_{device} = 99.1 %

$$(M_{NMOC})_{fugitive} = (M_{NMOC})_{process} - (M_{NMOC})_{in} \quad (12)$$

= (12/16.33) x 40 - 22.3

$(M_{NMOC})_{fugitive}$ = 7.09 lb NMOC/hr

$$(M_{NMOC})_{overall} = (M_{NMOC})_{out} + (M_{NMOC})_{fugitive} \quad (13)$$

= 0.19 + 7.09

$(M_{NMOC})_{overall}$ = 7.28 lb NMOC/hr

$$(M_{VOC})_{fugitive} = (M_{VOC})_{process} - (M_{VOC})_{in} \quad (14)$$

= 40 - 30.39

$(M_{VOC})_{fugitive}$ = 9.61 lb VOC/hr

$(M_{VOC})_{overall} = (M_{VOC})_{out} + (M_{VOC})_{fugitive}$ (15)

$= .25 + 9.61$

$(M_{VOC})_{overall}$ = 9.86 lb VOC/hr

$$(m_{Ctg})_{overall} = \frac{(M_{VOC})_{overall}}{\text{Application Rate (gal/hr)}}$$ (7)

$$= \frac{9.86}{8.0}$$

= 1.23 lb VOC/gallon coating applied

Example 2:

Given:

A source subject to Regulation 8, Rule 2, uses incineration to control non-methane organic carbon emissions. The process operates 20 hours per day.

Inlet Measurements to the Afterburner:

Q_o = 100 SDCFM
C_{TC} = 10300 ppmv
C_{CO_2} = 500 ppmv
C_{CO} = 800 ppmv
C_M < 5 ppmv

Outlet Measurements from the Afterburner:

Q_o = 500 SDCFM
C_{THC} = 500 ppmv
C_{CO} = 400 ppmv
C_M = 100 ppmv

Calculation of Afterburner Inlet parameters:

$C_{NMOC} = C_{TC} - C_{CO2} - C_{CO} - C_M$ (2)

$= 10300 - 500 - 800 - (<5)$

C_{NMOC} = 9000 ppmv

$$M_{NMOC} = \frac{12(\text{lb C/lb-mole } C_1) \times Q_o \times C_{NMOC} \times 60 \text{ (min/hr)}}{386.9 \text{ (SDCF/lb-mole)} \times 10^6 \text{ (ppm)}}$$ (4)

$= (12 \times 100 \times 9000 \times 60)/386.9 \times 10^6)$

$M_{NMOC} = 1.675$ lb NMOC/hr

$$M_{CO} = \frac{28(\text{lb CO/lb-mole}) \times Q_o \times C_{CO} \times 60 \text{ (min/hr)}}{386.9 \text{ (SDCF/lb-mole)} \times 10^6 \text{ (ppm)}} \quad (6)$$

$= (28 \times 100 \times 800 \times 60)/(386.9 \times 10^6)$

$M_{CO} = 0.347$ lb CO/hr

Calculation of Afterburner Outlet parameters:

$$C_{NMOC} = C_{THC} - C_M \quad (3)$$

$= 500 - 100$

$C_{NMOC} = 400$ ppmv

$$M_{NMOC} = \frac{12(\text{lb C/lb-mole } C_1) \times Q_o \times C_{NMOC} \times 60 \text{ (min/hr)}}{386.9 \text{ (SDCF/lb-mole)} \times 10^6 \text{ (ppm)}} \quad (4)$$

$= (12 \times 500 \times 400 \times 60)/386.9 \times 10^6)$

$M_{NMOC} = 0.372$ lb NMOC/hr

$$M_{CO} = \frac{28(\text{lb CO/lb-mole}) \times Q_o \times C_{CO} \times 60 \text{ (min/hr)}}{386.9 \text{ (SDCF/lb-mole)} \times 10^6 \text{ (ppm)}} \quad (6)$$

$= (28 \times 500 \times 400 \times 60)/(386.9 \times 10^6)$

$M_{CO} = 0.868$ lb CO/hr

Calculation of Afterburner Efficiency:

$$E_{device} = \frac{(M_{NMOC})_{in} - (M_{NMOC})_{out} - (^{12}/_{28}) \times \{(M_{CO})_{out} - (M_{CO})_{in}\}}{(M_{NMOC})_{in}} \times 100\% \quad (8)$$

$$= \frac{(1.675 - 0.372 - (^{12}/_{28}) \times \{(0.868 - 0.347))}{1.675} \times 100\%$$

$E_{device} = 64.5$ %

Emission Rate (lb/day) = Emission Rate (lb/hr) x Operating Time (hr/day)

= 0.372 lb NMOC / hr x 20 hr / day

= 7.44 lb NMOC/day

Example 3: Paint spray booth abated by a Charcoal Adsorber

Given:

Solvent fumes to the adsorber are primarily from methyl ethyl ketone (MEK). Material and Safety Data Sheets (MSDS) indicate that other solvents are also present, but plant operating data show their contribution is unknown and less than 10 % of the total. The coating is 5.2 lb VOC/gal and 3.0 lb solids/gal. Regulations do not allow the use of a coating with a solvent content in excess of 3.5 lb VOC/gal unless emissions are controlled to an extent equivalent to that of a compliant coating. There is no water in the coating. No dilution of gas occurs through the adsorber bed.

Estimate:

X_{VOC} = 18 lb/lb-mol (ref. sect 9.5 and Fig. 7-6)

Process Measurements:

Paint is drawn out of a one foot diameter drum at a rate of 3.0 inches per hour. 100 pieces per hour at 400 in^2 per piece are coated with paint. Quality assurance data indicate that there are 0.20 grams of solids per 4 in^2.

Inlet Measurements:

Q_o = 1000 SDCFM
C_{TC} = 2350 ppm
C_{CO} < 10 ppm
C_{CO2} = 350 ppm
C_M < 5 ppm

Outlet Measurements:

C_{THC} = 40 ppm
C_M < 5 ppm

Calculation of process parameters:

One way to calculate the volume of paint used is:
Paint Used = 3/12 ft/hr x π (1 ft^2)/4 x 7.48 gal/ft^3
Paint Used = 1.469 gph

An alternative way to calculate paint usage would be:

Paint Used = (0.2 g solids/4 in^2)x(lb/453.6 g)x(100 pieces/hr)x(400 in^2/piece)x(gal/3 lb solids)
Paint Used = 1.469 gph

$(M_{VOC})_{process}$ = 1.469 gph x 5.2 lb VOC/gal
$(M_{VOC})_{process}$ = 7.638 lb VOC/hr

Calculation of Adsorber Inlet parameters:

C_{NMOC} = 2000 ppmv

$$M_{VOC} = \frac{X_{VOC} \times Q_o \times C_{NMOC} \times 60 \text{ (min/hr)}}{386.9 \text{ (SDCF/lb-mole)} \times 10^6 \text{ (ppm)}} \quad (5)$$

$$= (18 \times 1000 \times 2000 \times 60)/(386.9 \times 10^6)$$

M_{VOC} = 5.582 lb VOC/hr

Calculation of Adsorber Outlet parameters:

$$C_{NMOC} = C_{THC} - C_M \quad (3)$$

C_{NMOC} = 40 ppmv

$$M_{VOC} = \frac{X_{VOC} \times Q_o \times C_{NMOC} \times 60 \text{ (min/hr)}}{386.9 \text{ (SDCF/lb-mole)} \times 10^6 \text{ (ppm)}} \quad (5)$$

$$= (18 \times 1000 \times 40 \times 60)/(386.9 \times 10^6)$$

M_{VOC} = .112 lb VOC/hr

$$(M_{VOC})_{fugitive} = (M_{VOC})_{process} - (M_{VOC})_{in} \quad (16)$$

$$= 7.638 - 5.582$$

$(M_{VOC})_{fugitive}$ = 1.056

Calculation of Adsorber Bed parameters:

$$E_{device} = \frac{(M_{VOC})_{in} - (M_{VOC})_{out}}{(M_{VOC})_{in}} \times 100\% \quad (11)$$

$$= (5.582 - 0.112)/5.582 \times 100\ \%$$

E_{device} = 98.0 %

Calculation of Emissions per gallon equivalent coating: (ref. Fig. 7-7)

Line A	= 0	There is no water in this coating
Line B	= 0	There are no exempt volatiles in this coating
Line C		Leave blank. This is not listed on the MSDS cited in this example
Line D	= 0	No water
Line E	= 0	No exempt volatiles
Line F	= 0.671	5.2 lb VOC per 8.2 lb Coating
Line G	= 7.36	There is no PNRS, therefore assign it this default value
Line H	= 6.885	MEK has a known density
Line I	= 8.2	Specified operating condition
Line J	= 5.2	F/(1/I - D/8.34 - E/G)
Line K	= 1.168	Exhaust of .112 plus fugitive of 1.056 From source test data and calculations
Line L	= 3.5	Specified in this example. Actual value will depend on which regulation applies
Line M	= 0.245	1 - J/H
Line N	= 1.469	Calculated above
Line P	= 1.469	(1 - A - B) $\times$ N
Line Q	= 0.492	1 - L/H
Line R	= 0.359	P x M
Line S	= 0.731	R/Q
Line T	= 1.60	K/S

$(m_{EQCtg})_{overall}$ = 1.60 lb VOC/gal Equivalent Coating

Example 4 Petroleum Dry Cleaner

Given:

Petroleum Dry Cleaner washes two 10 lb loads per hour. The solvent used has an average molecular weight per carbon of 14. Gases are vented to a solvent recovery dryer.

Outlet Measurements:

Q_o = 1000 SDCFM
C_{THC} = 100 ppm
C_M < 5 ppm

Calculation of Recovery Dryer Exhaust:

$$M_{VOC} = \frac{X_{VOC} \times Q_o \times C_{NMOC} \times 60 \text{ (min/hr)}}{386.9 \text{ (SDCF/lb-mole)} \times 10^6 \text{ (ppm)}} \quad (5)$$

$$= (14 \times 1000 \times 100 \times 60)/(386.9 \times 10^6)$$

M_{VOC} = 0.217 lb VOC/hr

M_{VOC} /100 kg clothes = M_{VOC}/(2 load/hr x 10 lb/load) x (5/5) x ($^{Kg/lb}/_{Kg/lb}$)

= 5 x M_{VOC} ($^{Kg}/_{lb}$)(hr) 100 Kg Clothes

M_{VOC} /100 kg clothes = 1.085 kg VOC/100 kg clothes

10. Reporting

10.1 Results shall be reported as shown in Figure 7-8.

11. Nomenclature

C_{CO}	[=]	Concentration of Carbon Monoxide, ppmv
C_{CO2}	[=]	Concentration of Carbon Dioxide, ppmv
C_M	[=]	Concentration of Methane, ppmv
C_{NMOC}	[=]	Concentration of Non-Methane Organic Carbon, ppmv
C_{TC}	[=]	Concentration of Total Carbon, ppmv
C_{THC}	[=]	Concentration of Total Hydorcarbons, ppmv
E_{device}	[=]	Efficiency with which NMOC or VOC emissions are abated by the Control Device on a mass basis, %
M_{CO}	[=]	Mass flow rate of CO, lbs/hr
M_{NMOC}	[=]	Mass flow rate of NMOC, lbs/hr
M_{VOC}	[=]	Mass flow rate of VOC, lbs/hr
Q_o	[=]	Volumetric Flowrate, SDCFM
X_{VOC}	[=]	Molecular weight of VOC per Carbon, lb VOC/lb-mol C_1
$(C_{CO})_{comb}$	[=]	Apparent CO concentration measured at combustor. Non-zero only when combustor is less than 100% efficient, ppmv
$(C_{TC})_{comb}$	[=]	Apparent CO_2 (Total Carbon) measured at combustor. $(C_{TC})_{Comb}$ is less than C_{TC} only when combustor is less than 100% efficient, ppmv
$(C_{THC})_{comb}$	[=]	Apparent THC measured at combustor. Non-zero only when combustor is less than 100% efficient, ppmv

$(m_{Ctg})_{overall}$	[=]	Mass flow rate of VOC, including fugitives, exhausted from a coating operation relative to the quantity of coating applied, lb/gal
$(m_{EQCtg})_{overall}$	[=]	Mass flow rate of VOC, including fugitives, exhausted from a coating operation relative the quantity of equivalent coating used had a compliant coating been used in place of the actual coating, lb/gal
$(M_{CO})_{in}$	[=]	Mass flow rate of CO at the inlet of a given abatement device, lb/hr
$(M_{CO})_{out}$	[=]	Mass flow rate of CO at the outlet of a given abatement device, lb/hr
$(M_{NMOC})_{fugitives}$	[=]	Mass flow rate of NMOC attributed to fugitive emissions from a given process, lb NMOC/hr
$(M_{NMOC})_{in}$	[=]	Mass flow rate of NMOC at the inlet of a given abatement device, lb NMOC/hr
$(M_{NMOC})_{out}$	[=]	Mass flow rate of NMOC at the outlet of a given abatement device, lb NMOC/hr
$(M_{NMOC})_{overall}$	[=]	Mass flow rate of NMOC attributed to fugitive and exhausted emissions from abatement devices associated with a given process, lb NMOC/hr
$(M_{NMOC})_{process}$	[=]	The calculated usage rate of NMOC based on process data, lb NMOC/hr
$(M_{VOC})_{fugitives}$	[=]	Mass flow rate of organics as VOC attributed to fugitive emissions, lb VOC/hr
$(M_{VOC})_{in}$	[=]	Mass flow rate of organics as VOC at the inlet of a given abatement device, lb VOC/hr
$(M_{VOC})_{out}$	[=]	Mass flow rate of organics as VOC at the exhaust of a given abatement device, lb VOC/hr
$(M_{VOC})_{overall}$	[=]	Mass flow rate of organics as VOC attributed to fugitive and exhausted emissions from abatement devices associated with a given process, lb VOC/hr
$(M_{VOC})_{process}$	[=]	The calculated usage rate of organic compounds based on process data, lb VOC/hr

Figure 7-6: Molecular Weight and VOC Density Calculation Worksheet

	a	b	c	d	e	f	g	h
	Weight of Solvent	Weight fraction of each Component	Molecular Weight of each Component	Number of Carbons Per Component	Molecular Weight Per Carbon	Molecular Weight Fraction for each Component	VOC Density (lb/gal)	VOC Density Per Component
	*	a / a_{total}	**	**	c / d	b x e	**	b x g
A								
B								
C								
D								
E								
etc.								
Total		1.000						

Average Molecular Weight per Carbon (from total sum f) _____

Average Solvent Density (from total sum h) _____

* From Laboratory Analysis or Coating Data Sheet
** From Reference Material

Figure 7-7 Equivalent Coatings Worksheet

A) Volume fraction H_2O*, gal H_2O/gal CTG _____

B) Volume fraction PNRS*, gal PNRS/gal CTG _____

C) Volume fraction VOC*, gal VOC/gal NECTG _____

D) Weight fraction H_2O*, lb H_2O/lb CTG _____

E) Weight fraction PNRS*, lb PNRS/lb CTG _____

F) Weight fraction VOC*, lb VOC/lb CTG _____

G) Density of PNRS*, lb PNRS/gal PNRS _____
If unknown use 7.36

H) Assumed solvent density, lb VOC/gal VOC _____
If unknown use 7.36

I) Coating density*, lb CTG/gal CTG _____

J) Lb VOC/gal NECTG _____

$$J = \frac{H \times C}{1 - A - B}$$

or

$$J = \frac{F}{\frac{1}{I} - \frac{D}{8.34} - \frac{E}{G}}$$

K) Emission rate **, lb VOC/hr, includes fugitives _____

L) Regulation limit, lb VOC/gal EQCTG _____

M) Gal solids/gal NECTG $M = 1 - J/H$ _____

N) Application Rate **, gal CTG/hr _____

P) Gal NECTG/hr $P = N(1 - A - B)$ _____

Q) Gal solids/gal EQCTG $Q = 1 - L/H$ _____

R) Gal solids/hr $R = P \times M$ _____

S) Gal EQCTG/hr $S = R/Q$ _____

T) Lb VOC emitted/gal EQCTG, $(m_{EQCtg})_{overall}$ $T = K/S$ _____

CTG - Coating as applied

PNRS - photochemically non-reactive solvent

NECTG - non-exempt coating (excludes water and PNRS)

EQCTG - equivalent coating

* From coating data

** From source test data

Figure 7-8

Report No.: _____ Test Date: _____	**BAY AREA AIR QUALITY MANAGEMENT DISTRICT** **Summary of Source Test Results**	**Test Times:** Run A: _____ Run B: _____ Run C: _____

Source Information		**Test Representatives**
Firm Name and Address	Firm Representative and Title Phone No. ( )	
Permit Conditions:	Source: Plant No. Permit No. Operates Hr/Day & Day/Yr.	Operating Parameters
Applicable Regulations:		

Source Test Results and Comments:

METHOD:	TEST	RUN A IN*	RUN A OUT*	RUN B IN	RUN B OUT	RUN C IN	RUN C OUT	AVERAGE IN	AVERAGE OUT
	Run Time,minutes								
	Sample point temperature, F								
ST-17	Stack Volume Flowrate,SDCFM								
ST-14	O_2 , percent								
ST-5	CO_2, percent								
ST-6	CO, PPM								
ST-23	H_2O, percent								
ST-7	Non-methane organic carbon, as C_1								
	a) PPM								
	b) lb/hr								
ST-7	Volatile Organic Compounds, as C_1								
	a) PPM								
	b) lb/hr								
ST-7	Abatement Efficiency, %								

* Control device inlet
** Control device outlet

Test Team Leader Date	Reviewed by Date	Approved By Date

State of Oregon Department of Environmental Quality

OAR 340-232-8010
Division 232 Attachments

APPENDIX A–6 TO PART 60—TEST METHODS 16 THROUGH 18

Method 16—Semicontinuous determination of sulfur emissions from stationary sources
Method 16A—Determination of total reduced sulfur emissions from stationary sources (impinger technique)
Method 16B—Determination of total reduced sulfur emissions from stationary sources
Method 16C—Determination of Total Reduced Sulfur Emissions From Stationary Sources
Method 17—Determination of particulate emissions from stationary sources (instack filtration method)
Method 18—Measurement of gaseous organic compound emissions by gas chromatography

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

METHOD 16—SEMICONTINUOUS DETERMINATION OF SULFUR EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of

at least the following additional test methods: Method 1, Method 4, Method 15, and Method 16A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Dimethyl disulfide [$(CH_3)_2S_2$]	62–49–20	50 ppb.
Dimethyl sulfide [$(CH_3)_2S$]	75–18–3	50 ppb.
Hydrogen sulfide [H_2S]	7783–06–4	50 ppb.
Methyl mercaptan [CH_4S]	74–93–1	50 ppb.

1.2 Applicability. This method is applicable for the determination of total reduced sulfur (TRS) compounds from recovery furnaces, lime kilns, and smelt dissolving tanks at kraft pulp mills and fuel gas combustion devices at petroleum refineries.

NOTE: The method described below uses the principle of gas chromatographic (GC) separation and flame photometric detection (FPD). Since there are many systems or sets of operating conditions that represent useable methods of determining sulfur emissions, all systems which employ this principle, but differ only in details of equipment and operation, may be used as alternative methods, provided that the calibration precision and sample line loss criteria are met.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the emission source and an aliquot is analyzed for hydrogen sulfide (H_2S), methyl mercaptan (MeSH), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS) by GC/FPD. These four compounds are known collectively as TRS.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Moisture. Moisture condensation in the sample delivery system, the analytical column, or the FPD burner block can cause losses or interferences. This is prevented by maintaining the probe, filter box, and connections at a temperature of at least 120 °C (248 °F). Moisture is removed in the SO_2 scrubber and heating the sample beyond this point is not necessary when the ambient temperature is above 0 °C (32 °F). Alternatively, moisture may be eliminated by heating the sample line, and by conditioning the sample with dry dilution air to lower its dew point below the operating temperature of the GC/FPD analytical system prior to analysis.

4.2 Carbon Monoxide (CO) and Carbon Dioxide (CO_2). CO and CO_2 have a substantial desensitizing effect on the flame photometric detector even after dilution. Acceptable systems must demonstrate that they have eliminated this interference by some procedure such as eluting these compounds before any of the compounds to be measured. Compliance with this requirement can be demonstrated by submitting chromatograms of calibration gases with and without CO_2 in the diluent gas. The CO_2 level should be approximately 10 percent for the case with CO_2 present. The two chromatograms should show agreement within the precision limits of section 10.2.

4.3 Particulate Matter. Particulate matter in gas samples can cause interference by eventual clogging of the analytical system. This interference is eliminated by using the Teflon filter after the probe.

4.4 Sulfur Dioxide (SO_2). Sulfur dioxide is not a specific interferant but may be present in such large amounts that it cannot effectively be separated from the other compounds of interest. The SO_2 scrubber described in section 6.1.3 will effectively remove SO_2 from the sample.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hydrogen Sulfide. A flammable, poisonous gas with the odor of rotten eggs. H_2S is extremely hazardous and can cause collapse, coma, and death within a few seconds of one or two inhalations at sufficient concentrations. Low concentrations irritate the mucous membranes and may cause nausea, dizziness, and headache after exposure.

6.0 Equipment and Supplies

6.1. Sample Collection. The following items are needed for sample collection.

6.1.1 Probe. Teflon or Teflon-lined stainless steel. The probe must be heated to prevent moisture condensation. It must be designed to allow calibration gas to enter the probe at or near the sample point entry. Any portion of the probe that contacts the stack gas

must be heated to prevent moisture condensation. Figure 16–1 illustrates the probe used in lime kilns and other sources where significant amounts of particulate matter are present. The probe is designed with the deflector shield placed between the sample and the gas inlet holes to reduce clogging of the filter and possible adsorption of sample gas. As an alternative, the probe described in section 6.1.1 of Method 16A having a nozzle directed away from the gas stream may be used at sources having significant amounts of particulate matter.

6.1.2 Particulate Filter. 50–mm Teflon filter holder and a 1- to 2-micron porosity Teflon filter (available through Savillex Corporation, 5325 Highway 101, Minnetonka, Minnesota 55343). The filter holder must be maintained in a hot box at a temperature of at least 120 °C (248 °F).

6.1.3 SO_2 Scrubber. Three 300-ml Teflon segmented impingers connected in series with flexible, thick-walled, Teflon tubing. (Impinger parts and tubing available through Savillex.) The first two impingers contain 100 ml of citrate buffer and the third impinger is initially dry. The tip of the tube inserted into the solution should be constricted to less than 3 mm (⅛ in.) ID and should be immersed to a depth of at least 5 cm (2 in.). Immerse the impingers in an ice water bath and maintain near 0 °C (32 °F). The scrubber solution will normally last for a 3-hour run before needing replacement. This will depend upon the effects of moisture and particulate matter on the solution strength and pH. Connections between the probe, particulate filter, and SO_2 scrubber must be made of Teflon and as short in length as possible. All portions of the probe, particulate filter, and connections prior to the SO_2 scrubber (or alternative point of moisture removal) must be maintained at a temperature of at least 120 °C (248 °F).

6.1.4 Sample Line. Teflon, no greater than 1.3 cm (½ in.) ID. Alternative materials, such as virgin Nylon, may be used provided the line loss test is acceptable.

6.1.5 Sample Pump. The sample pump must be a leakless Teflon-coated diaphragm type or equivalent.

6.2 Analysis. The following items are needed for sample analysis:

6.2.1 Dilution System. Needed only for high sample concentrations. The dilution system must be constructed such that all sample contacts are made of Teflon, glass, or stainless steel.

6.2.2 Gas Chromatograph. The gas chromatograph must have at least the following components:

6.2.2.1 Oven. Capable of maintaining the separation column at the proper operating temperature ±1 °C (2 °F).

6.2.2.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperature ±1 °C (2 °F).

6.2.2.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

6.2.2.4 Flame Photometric Detector.

6.2.2.4.1 Electrometer. Capable of full scale amplification of linear ranges of 10^{-9} to 10^{-4} amperes full scale.

6.2.2.4.2 Power Supply. Capable of delivering up to 750 volts.

6.2.2.4.3 Recorder. Compatible with the output voltage range of the electrometer.

6.2.2.4.4 Rotary Gas Valves. Multiport Teflon-lined valves equipped with sample loop. Sample loop volumes must be chosen to provide the needed analytical range. Teflon tubing and fittings must be used throughout to present an inert surface for sample gas. The gas chromatograph must be calibrated with the sample loop used for sample analysis.

6.2.3 Gas Chromatogram Columns. The column system must be demonstrated to be capable of resolving the four major reduced sulfur compounds: H_2S, MeSH, DMS, and DMDS. It must also demonstrate freedom from known interferences. To demonstrate that adequate resolution has been achieved, submit a chromatogram of a calibration gas containing all four of the TRS compounds in the concentration range of the applicable standard. Adequate resolution will be defined as base line separation of adjacent peaks when the amplifier attenuation is set so that the smaller peak is at least 50 percent of full scale. Baseline separation is defined as a return to zero ±5 percent in the interval between peaks. Systems not meeting this criteria may be considered alternate methods subject to the approval of the Administrator.

6.3 Calibration. A calibration system, containing the following components, is required (see Figure 16–2).

6.3.1 Tube Chamber. Chamber of glass or Teflon of sufficient dimensions to house permeation tubes.

6.3.2 Flow System. To measure air flow over permeation tubes at ±2 percent. Flow over the permeation device may also be determined using a soap bubble flowmeter.

6.3.3 Constant Temperature Bath. Device capable of maintaining the permeation tubes at the calibration temperature within 0.1 °C (0.2 °F).

6.3.4 Temperature Gauge. Thermometer or equivalent to monitor bath temperature within 1 °C (2 °F).

7.0 Reagents and Standards

7.1 Fuel. Hydrogen (H_2), prepurified grade or better.

7.2 Combustion Gas. Oxygen (O_2) or air, research purity or better.

7.3 Carrier Gas. Prepurified grade or better.

7.4 Diluent (if required). Air containing less than 50 ppb total sulfur compounds and less than 10 ppmv each of moisture and total hydrocarbons.

7.5 Calibration Gases

7.5.1 Permeation tubes, one each of H_2S, MeSH, DMS, and DMDS, gravimetrically calibrated and certified at some convenient operating temperature. These tubes consist of hermetically sealed FEP Teflon tubing in which a liquified gaseous substance is enclosed. The enclosed gas permeates through the tubing wall at a constant rate. When the temperature is constant, calibration gases covering a wide range of known concentrations can be generated by varying and accurately measuring the flow rate of diluent gas passing over the tubes. These calibration gases are used to calibrate the GC/FPD system and the dilution system.

7.5.2 Cylinder Gases. Cylinder gases may be used as alternatives to permeation devices. The gases must be traceable to a primary standard (such as permeation tubes) and not used beyond the certification expiration date.

7.6 Citrate Buffer and Sample Line Loss Gas. Same as Method 15, sections 7.6 and 7.7.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as Method 15, section 8.0, except that the references to the dilution system may not be applicable.

9.0 Quality Control

Section	Quality control measure	Effect
8.0	Sample line loss check	Ensures that uncorrected negative bias introduced by sample loss is no greater than 20 percent, and provides for correction of bias of 20 percent or less.
8.0	Calibration drift test	Ensures that bias introduced by drift in the measurement system output during the run is no greater than 5 percent.
10.0	Analytical calibration	Ensures precision of analytical results within 5 percent.

10.0 Calibration and Standardization

Same as Method 15, section 10.0, with the following addition and exceptions:

10.1 Use the four compounds that comprise TRS instead of the three reduced sulfur compounds measured by Method 15.

10.2 Flow Meter. Calibration before each test run is recommended, but not required; calibration following each test series is mandatory. Calibrate each flow meter after each complete test series with a wet-test meter. If the flow measuring device differs from the wet-test meter by 5 percent or more, the completed test runs must be voided. Alternatively, the flow data that yield the lower flow measurement may be used. Flow over the permeation device may also be determined using a soap bubble flowmeter.

11.0 Analytical Procedure

Sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Data Analysis and Calculations

12.1 Concentration of Reduced Sulfur Compounds. Calculate the average concentration of each of the four analytes (*i.e.*, DMDS, DMS, H_2S, and MeSH) over the sample run (specified in section 8.2 of Method 15 as 16 injections).

$$C = \frac{\sum_{i=1}^{N} S_i}{N} \qquad \text{Eq. 16-1}$$

Where:

S_i = Concentration of any reduced sulfur compound from the i^{th} sample injection, ppm.

C = Average concentration of any one of the reduced sulfur compounds for the entire run, ppm.

N = Number of injections in any run period.

12.2 TRS Concentration. Using Equation 16–2, calculate the TRS concentration for each sample run.

$$C_{TRS} = d\sum\left(C_{H_2S} + C_{MeSH} + C_{DMS} + 2C_{DMDS}\right) \qquad \text{Eq. 16-2}$$

Where:

C_{TRS} = TRS concentration, ppmv.

C_{H2S} = Hydrogen sulfide concentration, ppmv.

C_{MeSH} = Methyl mercaptan concentration, ppmv.

C_{DMS} = Dimethyl sulfide concentration, ppmv.

C_{DMDS} = Dimethyl disulfide concentration, ppmv.

d = Dilution factor, dimensionless.

12.3 Average TRS Concentration. Calculate the average TRS concentration for all sample runs performed.

$$\text{Average TRS} = \frac{\sum_{i=1}^{n} TRS_i}{N(1 - B_{wo})} \qquad \text{Eq. 16-3}$$

Where:

Average TRS = Average total reduced sulfur in ppm.

TRS_i = Total reduced sulfur in ppm as determined by Equation 16–2.

N = Number of samples.

B_{wo} = Fraction of volume of water vapor in the gas stream as determined by Method 4—Determination of Moisture in Stack Gases.

13.0 Method Performance

13.1 Analytical Range. The analytical range will vary with the sample loop size. Typically, the analytical range may extend from 0.1 to 100 ppmv using 10- to 0.1-ml sample loop sizes. This eliminates the need for sample dilution in most cases.

13.2 Sensitivity. Using the 10-ml sample size, the minimum detectable concentration is approximately 50 ppb.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. O'Keeffe, A.E., and G.C. Ortman. ''Primary Standards for Trace Gas Analysis.'' Analytical Chemical Journal, 38,76. 1966.

2. Stevens, R.K., A.E. O'Keeffe, and G.C. Ortman. ''Absolute Calibration of a Flame Photometric Detector to Volatile Sulfur Compounds at Sub-Part-Per-Million Levels.'' Environmental Science and Technology, 3:7. July 1969.

3. Mulik, J.D., R.K. Stevens, and R. Baumgardner. ''An Analytical System Designed to Measure Multiple Malodorous Compounds Related to Kraft Mill Activities.'' Presented at the 12th Conference on Methods in Air Pollution and Industrial Hygiene Studies, University of Southern California, Los Angeles, CA. April 6–8, 1971.

4. Devonald, R.H., R.S. Serenius, and A.D. McIntyre. ''Evaluation of the Flame Photometric Detector for Analysis of Sulfur Compounds.'' Pulp and Paper Magazine of Canada, 73,3. March 1972.

5. Grimley, K.W., W.S. Smith, and R.M. Martin. ''The Use of a Dynamic Dilution System in the Conditioning of Stack Gases for Automated Analysis by a Mobile Sampling Van.'' Presented at the 63rd Annual APCA Meeting, St. Louis, MO. June 14–19, 1970.

6. General Reference. Standard Methods of Chemical Analysis, Volumes III-A and III-B Instrumental Methods. Sixth Edition. Van Nostrand Reinhold Co.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

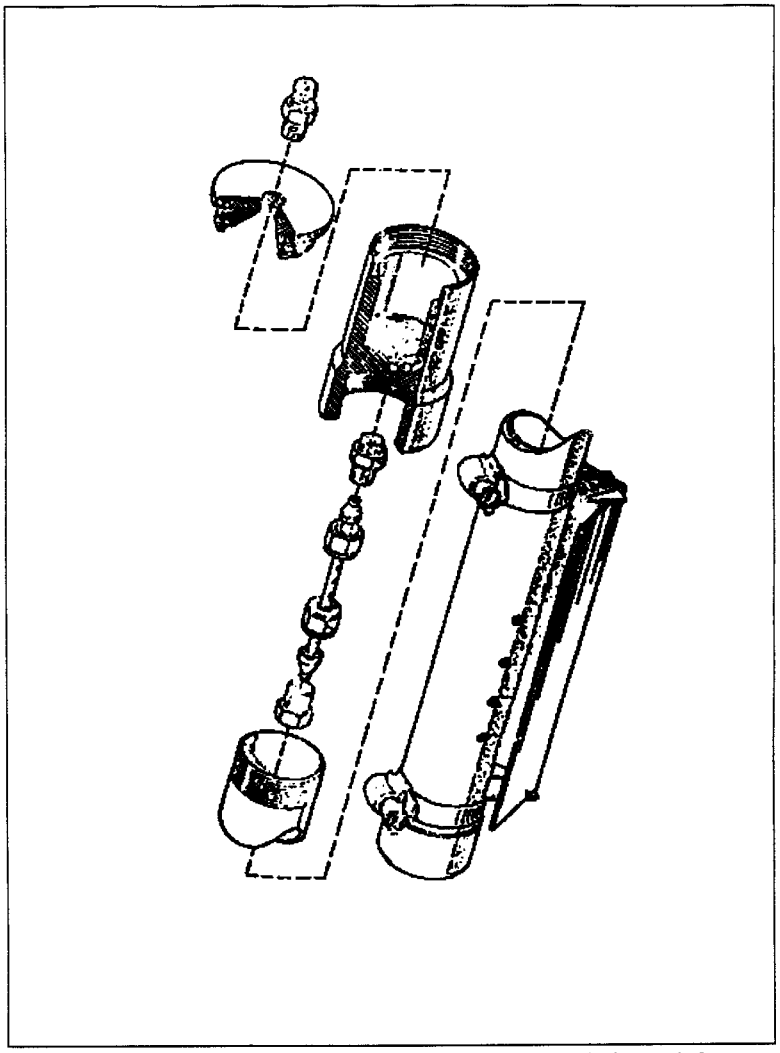


Figure 16-1. Probe used for Sample Gas Containing High Particulate Matter Loading.

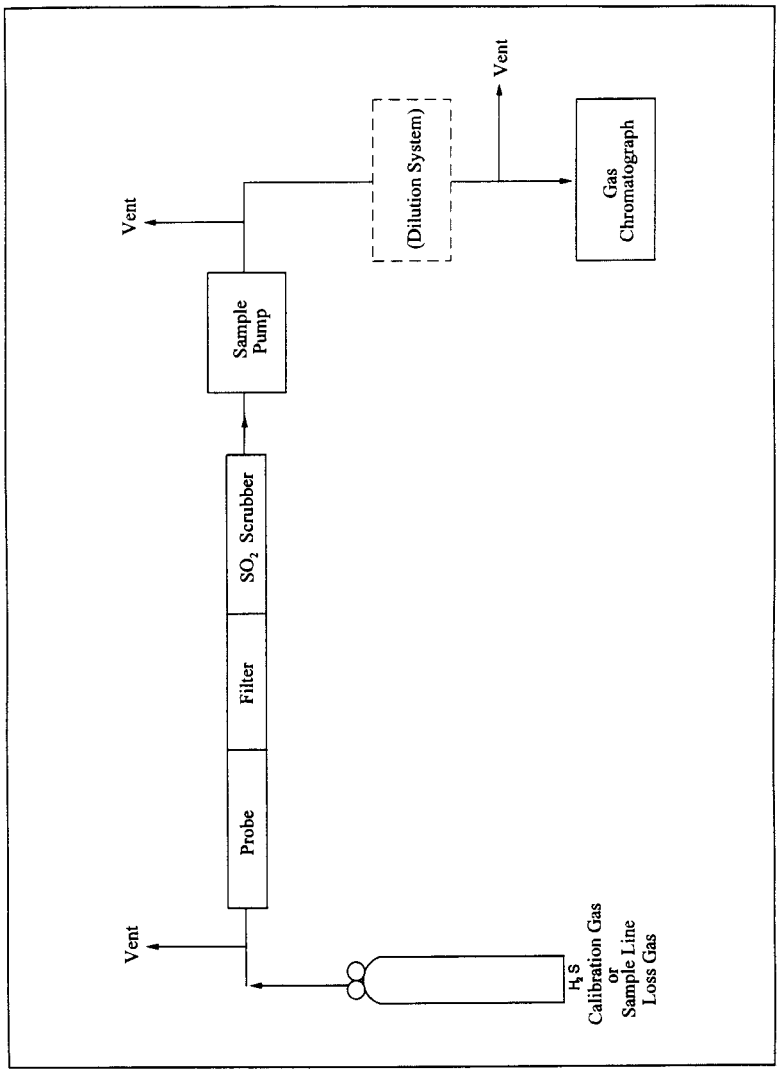


Figure 16-2. Calibration System.

METHOD 16A—DETERMINATION OF TOTAL REDUCED SULFUR EMISSIONS FROM STATIONARY SOURCES (IMPINGER TECHNIQUE)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 6, and Method 16.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total reduced sulfur (TRS) including:	N/A	See section 13.1.
Dimethyl disulfide [$(CH_3)_2S_2$]	62–49–20	
Dimethyl sulfide [$(CH_3)_2S$]	75–18–3	
Hydrogen sulfide [H_2S]	7783–06–4	
Methyl mercaptan [CH_4S]	74–93–1	
Reduced sulfur (RS) including:	N/A	
H_2S	7783–06–4	
Carbonyl sulfide [COS]	463–58–1	
Carbon disulfide [CS_2]	75–15–0	
Reported as: Sulfur dioxide (SO_2)	7449–09–5	

1.2 Applicability. This method is applicable for the determination of TRS emissions from recovery boilers, lime kilns, and smelt dissolving tanks at kraft pulp mills, reduced sulfur compounds (H_2S, carbonyl sulfide, and carbon disulfide) from sulfur recovery units at onshore natural gas processing facilities, and from other sources when specified in an applicable subpart of the regulations. The flue gas must contain at least 1 percent oxygen for complete oxidation of all TRS to SO_2. Note: If sources other than kraft pulp mills experience low oxygen levels in the emissions, the method results may be biased low.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 An integrated gas sample is extracted from the stack. SO_2 is removed selectively from the sample using a citrate buffer solution. TRS compounds are then thermally oxidized to SO_2, collected in hydrogen peroxide as sulfate, and analyzed by the Method 6 barium-thorin titration procedure.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Reduced sulfur compounds other than those regulated by the emission standards, if present, may be measured by this method. Therefore, carbonyl sulfide, which is partially oxidized to SO_2 and may be present in a lime kiln exit stack, would be a positive interferant.

4.2 Particulate matter from the lime kiln stack gas (primarily calcium carbonate) can cause a negative bias if it is allowed to enter the citrate scrubber; the particulate matter will cause the pH to rise and H_2S to be absorbed prior to oxidation. Furthermore, if the calcium carbonate enters the hydrogen peroxide impingers, the calcium will precipitate sulfate ion. Proper use of the particulate filter described in section 6.1.3 will eliminate this interference.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m^3 will cause lung damage in uninitiated. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

5.3 Hydrogen Sulfide (H_2S). A flammable, poisonous gas with the odor of rotten eggs. H_2S is extremely hazardous and can cause collapse, coma, and death within a few seconds of one or two inhalations at sufficient concentrations. Low concentrations irritate the mucous membranes and may cause nausea, dizziness, and headache after exposure.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling train is shown in Figure 16A–1 and component parts are discussed below. Modifications to this sampling train are acceptable provided the system performance check is met (see section 8.5).

6.1.1 Probe. Teflon tubing, 6.4-mm (¼-in.) diameter, sequentially wrapped with heat-resistant fiber strips, a rubberized heat tape

(plug at one end), and heat-resistant adhesive tape. A flexible thermocouple or other suitable temperature measuring device should be placed between the Teflon tubing and the fiber strips so that the temperature can be monitored to prevent softening of the probe. The probe should be sheathed in stainless steel to provide in-stack rigidity. A series of bored-out stainless steel fittings placed at the front of the sheath will prevent moisture and particulate from entering between the probe and sheath. A 6.4-mm (¼-in.) Teflon elbow (bored out) should be attached to the inlet of the probe, and a 2.54 cm (1 in.) piece of Teflon tubing should be attached at the open end of the elbow to permit the opening of the probe to be turned away from the particulate stream; this will reduce the amount of particulate drawn into the sampling train. The probe is depicted in Figure 16A–2.

6.1.2 Probe Brush. Nylon bristle brush with handle inserted into a 3.2-mm (⅛-in.) Teflon tubing. The Teflon tubing should be long enough to pass the brush through the length of the probe.

6.1.3 Particulate Filter. 50-mm Teflon filter holder and a 1- to 2-μm porosity, Teflon filter (available through Savillex Corporation, 5325 Highway 101, Minnetonka, Minnesota 55343). The filter holder must be maintained in a hot box at a temperature sufficient to prevent moisture condensation. A temperature of 121 °C (250 °F) was found to be sufficient when testing a lime kiln under sub-freezing ambient conditions.

6.1.4 SO_2 Scrubber. Three 300-ml Teflon segmented impingers connected in series with flexible, thick-walled, Teflon tubing. (Impinger parts and tubing available through Savillex.) The first two impingers contain 100 ml of citrate buffer and the third impinger is initially dry. The tip of the tube inserted into the solution should be constricted to less than 3 mm (⅛-in.) ID and should be immersed to a depth of at least 5 cm (2 in.).

6.1.5 Combustion Tube. Quartz glass tubing with an expanded combustion chamber 2.54 cm (1 in.) in diameter and at least 30.5 cm (12 in.) long. The tube ends should have an outside diameter of 0.6 cm (¼ in.) and be at least 15.3 cm (6 in.) long. This length is necessary to maintain the quartz-glass connector near ambient temperature and thereby avoid leaks. Alternatively, the outlet may be constructed with a 90-degree glass elbow and socket that would fit directly onto the inlet of the first peroxide impinger.

6.1.6 Furnace. A furnace of sufficient size to enclose the combustion chamber of the combustion tube with a temperature regulator capable of maintaining the temperature at 800 ±100 °C (1472 ±180 °F). The furnace operating temperature should be checked with a thermocouple to ensure accuracy.

6.1.7 Peroxide Impingers, Stopcock Grease, Temperature Sensor, Drying Tube, Valve, Pump, and Barometer. Same as Method 6, sections 6.1.1.2, 6.1.1.4, 6.1.1.5, 6.1.1.6, 6.1.1.7, 6.1.1.8, and 6.1.2, respectively, except that the midget bubbler of Method 6, section 6.1.1.2 is not required.

6.1.8 Vacuum Gauge. At least 760 mm Hg (30 in. Hg) gauge.

6.1.9 Rate Meter. Rotameter, or equivalent, accurate to within 5 percent at the selected flow rate of approximately 2 liters/min (4.2 ft^3/hr).

6.1.10 Volume Meter. Dry gas meter capable of measuring the sample volume under the sampling conditions of 2 liters/min (4.2 ft^3/hr) with an accuracy of 2 percent.

6.2 Sample Recovery. Polyethylene Bottles, 250-ml (one per sample).

6.3 Sample Preparation and Analysis. Same as Method 6, section 6.3, except a 10-ml buret with 0.05-ml graduations is required, and the spectrophotometer is not needed.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. When such specifications are not available, the best available grade must be used.

7.1 Sample Collection. The following reagents are required for sample analysis:

7.1.1 Water. Same as in Method 6, section 7.1.1.

7.1.2 Citrate Buffer. Dissolve 300 g of potassium citrate (or 284 g of sodium citrate) and 41 g of anhydrous citric acid in 1 liter of water (200 ml is needed per test). Adjust the pH to between 5.4 and 5.6 with potassium citrate or citric acid, as required.

7.1.3 Hydrogen Peroxide, 3 percent. Same as in Method 6, section 7.1.3 (40 ml is needed per sample).

7.1.4 Recovery Check Gas. Hydrogen sulfide (100 ppmv or less) in nitrogen, stored in aluminum cylinders. Verify the concentration by Method 11 or by gas chromatography where the instrument is calibrated with an H_2S permeation tube as described below. For Method 11, the relative standard deviation should not exceed 5 percent on at least three 20-minute runs.

NOTE: Alternatively, hydrogen sulfide recovery gas generated from a permeation device gravimetrically calibrated and certified at some convenient operating temperature may be used. The permeation rate of the device must be such that at a dilution gas flow rate of 3 liters/min (6.4 ft^3/hr), an H_2S concentration in the range of the stack gas or within 20 percent of the standard can be generated.

7.1.5 Combustion Gas. Gas containing less than 50 ppb reduced sulfur compounds and less than 10 ppmv total hydrocarbons. The

gas may be generated from a clean-air system that purifies ambient air and consists of the following components: Diaphragm pump, silica gel drying tube, activated charcoal tube, and flow rate measuring device. Flow from a compressed air cylinder is also acceptable.

7.2 Sample Recovery and Analysis. Same as Method 6, sections 7.2.1 and 7.3, respectively.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Preparation of Sampling Train.

8.1.1 For the SO_2 scrubber, measure 100 ml of citrate buffer into the first and second impingers; leave the third impinger empty. Immerse the impingers in an ice bath, and locate them as close as possible to the filter heat box. The connecting tubing should be free of loops. Maintain the probe and filter temperatures sufficiently high to prevent moisture condensation, and monitor with a suitable temperature sensor.

8.1.2 For the Method 6 part of the train, measure 20 ml of 3 percent hydrogen peroxide into the first and second midget impingers. Leave the third midget impinger empty, and place silica gel in the fourth midget impinger. Alternatively, a silica gel drying tube may be used in place of the fourth impinger. Maintain the oxidation furnace at 800 ±100 °C (1472 ±180 °F). Place crushed ice and water around all impingers.

8.2 Citrate Scrubber Conditioning Procedure. Condition the citrate buffer scrubbing solution by pulling stack gas through the Teflon impingers and bypassing all other sampling train components. A purge rate of 2 liters/min for 10 minutes has been found to be sufficient to obtain equilibrium. After the citrate scrubber has been conditioned, assemble the sampling train, and conduct (optional) a leak-check as described in Method 6, section 8.2.

8.3 Sample Collection. Same as in Method 6, section 8.3, except the sampling rate is 2 liters/min (±10 percent) for 1 or 3 hours. After the sample is collected, remove the probe from the stack, and conduct (mandatory) a post-test leak-check as described in Method 6, section 8.2. The 15-minute purge of the train following collection should not be performed. After each 3-hour test run (or after three 1-hour samples), conduct one system performance check (see section 8.5) to determine the reduced sulfur recovery efficiency through the sampling train. After this system performance check and before the next test run, rinse and brush the probe with water, replace the filter, and change the citrate scrubber (optional but recommended).

NOTE: In Method 16, a test run is composed of 16 individual analyses (injects) performed over a period of not less than 3 hours or more than 6 hours. For Method 16A to be consistent with Method 16, the following may be used to obtain a test run: (1) collect three 60-minute samples or (2) collect one 3-hour sample. (Three test runs constitute a test.)

8.4 Sample Recovery. Disconnect the impingers. Quantitatively transfer the contents of the midget impingers of the Method 6 part of the train into a leak-free polyethylene bottle for shipment. Rinse the three midget impingers and the connecting tubes with water and add the washings to the same storage container. Mark the fluid level. Seal and identify the sample container.

8.5 System Performance Check.

8.5.1 A system performance check is done (1) to validate the sampling train components and procedure (prior to testing; optional) and (2) to validate a test run (after a run). Perform a check in the field prior to testing consisting of at least two samples (optional), and perform an additional check after each 3 hour run or after three 1-hour samples (mandatory).

8.5.2 The checks involve sampling a known concentration of H_2S and comparing the analyzed concentration with the known concentration. Mix the H_2S recovery check gas (Section 7.1.4) and combustion gas in a dilution system such as that shown in Figure 16A–3. Adjust the flow rates to generate an H_2S concentration in the range of the stack gas or within 20 percent of the applicable standard and an oxygen concentration greater than 1 percent at a total flow rate of at least 2.5 liters/min (5.3 ft^3/hr). Use Equation 16A–3 to calculate the concentration of recovery gas generated. Calibrate the flow rate from both sources with a soap bubble flow meter so that the diluted concentration of H_2S can be accurately calculated.

8.5.3 Collect 30-minute samples, and analyze in the same manner as the emission samples. Collect the sample through the probe of the sampling train using a manifold or some other suitable device that will ensure extraction of a representative sample.

8.5.4 The recovery check must be performed in the field prior to replacing the SO_2 scrubber and particulate filter and before the probe is cleaned. Use Equation 16A–4 (see section 12.5) to calculate the recovery efficiency. Report the recovery efficiency with the emission data; do not correct the emission data for the recovery efficiency. A sample recovery of 100 ±20 percent must be obtained for the emission data to be valid. However, if the recovery efficiency is not in the 100 ±20 percent range but the results do not affect the compliance or noncompliance status of the affected facility, the Administrator may decide to accept the results of the compliance test.

9.0 Quality Control

Section	Quality control measure	Effect
8.5	System performance check	Ensure validity of sampling train components and analytical procedure.
8.2, 10.0	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.
10.0	Barium standard solution standardization	Ensure precision of normality determination.
11.1	Replicate titrations	Ensure precision of titration determinations.

10.0 Calibration

Same as Method 6, section 10.0.

11.0 Analytical Procedure

11.1 Sample Loss Check and Sample Analysis. Same as Method 6, sections 11.1 and 11.2, respectively, with the following exception: for 1-hour sampling, take a 40-ml aliquot, add 160 ml of 100 percent isopropanol and four drops of thorin.

12.0 Data Analysis and Calculations

In the calculations, at least one extra decimal figure should be retained beyond that of the acquired data. Figures should be rounded off after final calculations.

12.1 Nomenclature.

C_{TRS} = Concentration of TRS as SO_2, dry basis corrected to standard conditions, ppmv.

$C_{RG(act)}$ = Actual concentration of recovery check gas (after dilution), ppm.

$C_{RG(m)}$ = Measured concentration of recovery check gas generated, ppm.

C_{H2S} = Verified concentration of H_2S recovery gas.

N = Normality of barium perchlorate titrant, milliequivalents/ml.

P_{bar} = Barometric pressure at exit orifice of the dry gas meter, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

Q_{H2S} = Calibrated flow rate of H_2S recovery gas, liters/min.

Q_{CG} = Calibrated flow rate of combustion gas, liters/min.

R = Recovery efficiency for the system performance check, percent.

T_m = Average dry gas meter absolute temperature, °K (°R).

T_{std} = Standard absolute temperature, 293 °K (528 °R).

V_a = Volume of sample aliquot titrated, ml.

V_m = Dry gas volume as measured by the dry gas meter, liters (dcf).

$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, liters (dscf).

V_{soln} = Total volume of solution in which the sulfur dioxide sample is contained, 100 ml.

V_t = Volume of barium perchlorate titrant used for the sample, ml (average of replicate titrations).

V_{tb} = Volume of barium perchlorate titrant used for the blank, ml.

Y = Dry gas meter calibration factor.

32.03 = Equivalent weight of sulfur dioxide, mg/meq.

12.2 Dry Sample Gas Volume, Corrected to Standard Conditions.

$$V_{m(std)} = V_m Y \frac{T_{std} P_{bar}}{T_m P_{std}} \qquad \text{Eq. 16A-1}$$

$$= K_1 Y \frac{V_m P_{bar}}{T_m}$$

Where:

K_1 = 0.3855 °K/mm Hg for metric units,
= 17.65 °R/in. Hg for English units.

12.3 Concentration of TRS as ppm SO_2.

$$C_{TRS} = K_2 N \frac{(V_t - V_{tb})(V_{soln}/V_a)}{V_{m(std)}} \qquad \text{Eq. 16A-2}$$

Where:

$$K_2 = 32.03 \frac{mg}{meq} \frac{24.05 L}{mole} \frac{1 mole}{64.06 g} \frac{1 g}{10^3 mg} \frac{10^3 mL}{L} \frac{10^3 \mu L}{lmL}$$
$$= \frac{12025 \mu L}{meq}$$

12.4 Concentration of Recovery Gas Generated in the System Performance Check.

$$C_{RG} = \frac{Q_{H_2S} C_{H_2S}}{Q_{H_2S} + Q_{CG}} \qquad \text{Eq. 16A-3}$$

12.5 Recovery Efficiency for the System Performance Check.

$$R = \frac{C_{RG(m)}}{C_{RG(act)}} \times 100 \qquad \text{Eq. 16A-4}$$

13.0 Method Performance

13.1 Analytical Range. The lower detectable limit is 0.1 ppmv SO_2 when sampling at 2 liters/min (4.2 ft^3/hr) for 3 hours or 0.3 ppmv when sampling at 2 liters/min (4.2 ft^3/hr) for 1 hour. The upper concentration limit of the method exceeds the TRS levels generally encountered at kraft pulp mills.

13.2 Precision. Relative standard deviations of 2.0 and 2.6 percent were obtained when sampling a recovery boiler for 1 and 3 hours, respectively.

13.3 Bias.

13.3.1 No bias was found in Method 16A relative to Method 16 in a separate study at a recovery boiler.

13.3.2 Comparison of Method 16A with Method 16 at a lime kiln indicated that there was no bias in Method 16A. However, instability of the source emissions adversely affected the comparison. The precision of Method 16A at the lime kiln was similar to that obtained at the recovery boiler (Section 13.2.1).

13.3.3 Relative standard deviations of 2.7 and 7.7 percent have been obtained for system performance checks.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

As an alternative to the procedures specified in section 7.1.4, the following procedure may be used to verify the H_2S concentration of the recovery check gas.

16.1 Summary. The H_2S is collected from the calibration gas cylinder and is absorbed in zinc acetate solution to form zinc sulfide. The latter compound is then measured iodometrically.

16.2 Range. The procedure has been examined in the range of 5 to 1500 ppmv.

16.3 Interferences. There are no known interferences to this procedure when used to analyze cylinder gases containing H_2S in nitrogen.

16.4 Precision and Bias. Laboratory tests have shown a relative standard deviation of less than 3 percent. The procedure showed no bias when compared to a gas chromatographic method that used gravimetrically certified permeation tubes for calibration.

16.5 Equipment and Supplies.

16.5.1 Sampling Apparatus. The sampling train is shown in Figure 16A–4. Its component parts are discussed in sections 16.5.1.1 through 16.5.2.

16.5.1.1 Sampling Line. Teflon tubing (¼-in.) to connect the cylinder regulator to the sampling valve.

16.5.1.2 Needle Valve. Stainless steel or Teflon needle valve to control the flow rate of gases to the impingers.

16.5.1.3 Impingers. Three impingers of approximately 100-ml capacity, constructed to permit the addition of reagents through the gas inlet stem. The impingers shall be connected in series with leak-free glass or Teflon connectors. The impinger bottoms have a standard 24/25 ground-glass fitting. The stems are from standard 6.4-mm (¼-in.) ball joint midget impingers, custom lengthened by about 1 in. When fitted together, the stem end should be approximately 1.27 cm (½ in.) from the bottom (Southern Scientific, Inc., Micanopy, Florida: Set Number S6962–048). The third in-line impinger acts as a drop-out bottle.

16.5.1.4 Drying Tube, Rate Meter, and Barometer. Same as Method 11, sections 6.1.5, 6.1.8, and 6.1.10, respectively.

16.5.1.5 Cylinder Gas Regulator. Stainless steel, to reduce the pressure of the gas stream entering the Teflon sampling line to a safe level.

16.5.1.6 Soap Bubble Meter. Calibrated for 100 and 500 ml, or two separate bubble meters.

16.5.1.7 Critical Orifice. For volume and rate measurements. The critical orifice may be fabricated according to section 16.7.3 and must be calibrated as specified in section 16.12.4.

16.5.1.8 Graduated Cylinder. 50-ml size.

16.5.1.9 Volumetric Flask. 1-liter size.

16.5.1.10 Volumetric Pipette. 15-ml size.

16.5.1.11 Vacuum Gauge. Minimum 20 in. Hg capacity.

16.5.1.12 Stopwatch.

16.5.2 Sample Recovery and Analysis.

16.5.2.1 Erlenmeyer Flasks. 125- and 250-ml sizes.

16.5.2.2 Pipettes. 2-, 10-, 20-, and 100-ml volumetric.

16.5.2.3 Burette. 50-ml size.

16.5.2.4 Volumetric Flask. 1-liter size.

16.5.2.5 Graduated Cylinder. 50-ml size.

16.5.2.6 Wash Bottle.

16.5.2.7 Stirring Plate and Bars.

16.6 Reagents and Standards. Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

16.6.1 Water. Same as Method 11, section 7.1.3.

16.6.2 Zinc Acetate Absorbing Solution. Dissolve 20 g zinc acetate in water, and dilute to 1 liter.

16.6.3 Potassium Bi-iodate [$KH(IO_3)_2$] Solution, Standard 0.100 N. Dissolve 3.249 g anhydrous $KH(IO_3)_2$ in water, and dilute to 1 liter.

16.6.4 Sodium Thiosulfate ($Na_2S_2O_3$) Solution, Standard 0.1 N. Same as Method 11, section 7.3.2. Standardize according to section 16.12.2.

16.6.5 $Na_2S_2O_3$ Solution, Standard 0.01 N. Pipette 100.0 ml of 0.1 N $Na_2S_2O_3$ solution into a 1-liter volumetric flask, and dilute to the mark with water.

16.6.6 Iodine Solution, 0.1 N. Same as Method 11, section 7.2.3.

16.6.7 Standard Iodine Solution, 0.01 N. Same as in Method 11, section 7.2.4. Standardize according to section 16.12.3.

16.6.8 Hydrochloric Acid (HCl) Solution, 10 Percent by Weight. Add 230 ml concentrated HCl (specific gravity 1.19) to 770 ml water.

16.6.9 Starch Indicator Solution. To 5 g starch (potato, arrowroot, or soluble), add a little cold water, and grind in a mortar to a thin paste. Pour into 1 liter of boiling water, stir, and let settle overnight. Use the clear supernatant. Preserve with 1.25 g salicylic acid, 4 g zinc chloride, or a combination of 4 g sodium propionate and 2 g sodium azide per liter of starch solution. Some commercial starch substitutes are satisfactory.

16.7 Pre-test Procedures.

16.7.1 Selection of Gas Sample Volumes. This procedure has been validated for estimating the volume of cylinder gas sample needed when the H_2S concentration is in the range of 5 to 1500 ppmv. The sample volume ranges were selected in order to ensure a 35 to 60 percent consumption of the 20 ml of 0.01 N iodine (thus ensuring a 0.01 N $Na_2S_2O_3$ titer of approximately 7 to 12 ml). The sample volumes for various H_2S concentrations can be estimated by dividing the approximate ppm-liters desired for a given concentration range by the H_2S concentration stated by the manufacturer. For example, for analyzing a cylinder gas containing approximately 10 ppmv H_2S, the optimum sample volume is 65 liters (650 ppm-liters/10 ppmv). For analyzing a cylinder gas containing approximately 1000 ppmv H_2S, the optimum sample volume is 1 liter (1000 ppm-liters/1000 ppmv).

Approximate cylinder gas H_2S concentration (ppmv)	Approximate ppm-liters desired
5 to <30	650
30 to <500	800
500 to <1500	1000

16.7.2 Critical Orifice Flow Rate Selection. The following table shows the ranges of sample flow rates that are desirable in order to ensure capture of H_2S in the impinger solution. Slight deviations from these ranges will not have an impact on measured concentrations.

Cylinder gas H_2S concentration (ppmv)	Critical orifice flow rate (ml/min)
5 to 50 ppmv	1500 ±500
50 to 250 ppmv	500 ±250
250 to <1000 ppmv	200 ±50
>1000 ppmv	75 ±25

16.7.3 Critical Orifice Fabrication. Critical orifice of desired flow rates may be fabricated by selecting an orifice tube of desired length and connecting 1/16-in. × 1/4-in. (0.16 cm × 0.64 cm) reducing fittings to both ends. The inside diameters and lengths of orifice tubes needed to obtain specific flow rates are shown below.

Tube (in. OD)	Tube (in. ID)	Length (in.)	Flowrate (ml/min)	Altech Catalog No.
1/16	0.007	1.2	85	301430
1/16	0.01	3.2	215	300530
1/16	0.01	1.2	350	300530
1/16	0.02	1.2	1400	300230

16.7.4 Determination of Critical Orifice Approximate Flow Rate. Connect the critical orifice to the sampling system as shown in Figure 16A–4 but without the H_2S cylinder. Connect a rotameter in the line to the first impinger. Turn on the pump, and adjust the

valve to give a reading of about half atmospheric pressure. Observe the rotameter reading. Slowly increase the vacuum until a stable flow rate is reached, and record this as the critical vacuum. The measured flow rate indicates the expected critical flow rate of the orifice. If this flow rate is in the range shown in section 16.7.2, proceed with the critical orifice calibration according to section 16.12.4.

16.7.5 Determination of Approximate Sampling Time. Determine the approximate sampling time for a cylinder of known concentration. Use the optimum sample volume obtained in section 16.7.1.

$$\text{Approximate sampling time} = \frac{\text{Optimum volume}}{\text{Critical orifice flow rate}}$$

16.8 Sample Collection.

16.8.1 Connect the Teflon tubing, Teflon tee, and rotameter to the flow control needle valve as shown in Figure 16A–4. Vent the rotameter to an exhaust hood. Plug the open end of the tee. Five to 10 minutes prior to sampling, open the cylinder valve while keeping the flow control needle valve closed. Adjust the delivery pressure to 20 psi. Open the needle valve slowly until the rotameter shows a flow rate approximately 50 to 100 ml above the flow rate of the critical orifice being used in the system.

16.8.2 Place 50 ml of zinc acetate solution in two of the impingers, connect them and the empty third impinger (dropout bottle) and the rest of the equipment as shown in Figure 16A–4. Make sure the ground-glass fittings are tight. The impingers can be easily stabilized by using a small cardboard box in which three holes have been cut, to act as a holder. Connect the Teflon sample line to the first impinger. Cover the impingers with a dark cloth or piece of plastic to protect the absorbing solution from light during sampling.

16.8.3 Record the temperature and barometric pressure. Note the gas flow rate through the rotameter. Open the closed end of the tee. Connect the sampling tube to the tee, ensuring a tight connection. Start the sampling pump and stopwatch simultaneously. Note the decrease in flow rate through the excess flow rotameter. This decrease should equal the known flow rate of the critical orifice being used. Continue sampling for the period determined in section 16.7.5.

16.8.4 When sampling is complete, turn off the pump and stopwatch. Disconnect the sampling line from the tee and plug it. Close the needle valve followed by the cylinder valve. Record the sampling time.

16.9 Blank Analysis. While the sample is being collected, run a blank as follows: To a 250-ml Erlenmeyer flask, add 100 ml of zinc acetate solution, 20.0 ml of 0.01 N iodine solution, and 2 ml HCl solution. Titrate, while stirring, with 0.01 N $Na_2S_2O_3$ until the solution is light yellow. Add starch, and continue titrating until the blue color disappears. Analyze a blank with each sample, as the blank titer has been observed to change over the course of a day.

NOTE: Iodine titration of zinc acetate solutions is difficult to perform because the solution turns slightly white in color near the end point, and the disappearance of the blue color is hard to recognize. In addition, a blue color may reappear in the solution about 30 to 45 seconds after the titration endpoint is reached. This should not be taken to mean the original endpoint was in error. It is recommended that persons conducting this test perform several titrations to be able to correctly identify the endpoint. The importance of this should be recognized because the results of this analytical procedure are extremely sensitive to errors in titration.

16.10 Sample Analysis. Sample treatment is similar to the blank treatment. Before detaching the stems from the bottoms of the impingers, add 20.0 ml of 0.01 N iodine solution through the stems of the impingers holding the zinc acetate solution, dividing it between the two (add about 15 ml to the first impinger and the rest to the second). Add 2 ml HCl solution through the stems, dividing it as with the iodine. Disconnect the sampling line, and store the impingers for 30 minutes. At the end of 30 minutes, rinse the impinger stems into the impinger bottoms. Titrate the impinger contents with 0.01 N $Na_2S_2O_3$. Do not transfer the contents of the impinger to a flask because this may result in a loss of iodine and cause a positive bias.

16.11 Post-test Orifice Calibration. Conduct a post-test critical orifice calibration run using the calibration procedures outlined in section 16.12.4. If the Q_{std} obtained before and after the test differs by more than 5 percent, void the sample; if not, proceed to perform the calculations.

16.12 Calibrations and Standardizations.

16.12.1 Rotameter and Barometer. Same as Method 11, sections 10.1.3 and 10.1.4.

16.12.2 $Na_2S_2O_3$ Solution, 0.1 N. Standardize the 0.1 N $Na_2S_2O_3$ solution as follows: To 80 ml water, stirring constantly, add 1 ml concentrated H_2SO_4, 10.0 ml of 0.100 N $KH(IO_3)_2$

and 1 g potassium iodide. Titrate immediately with 0.1 N $Na_2S_2O_3$ until the solution is light yellow. Add 3 ml starch solution, and titrate until the blue color just disappears. Repeat the titration until replicate analyses agree within 0.05 ml. Take the average volume of $Na_2S_2O_3$ consumed to calculate the normality to three decimal figures using Equation 16A–5.

16.12.3 Iodine Solution, 0.01 N. Standardize the 0.01 N iodine solution as follows: Pipet 20.0 ml of 0.01 N iodine solution into a 125-ml Erlenmeyer flask. Titrate with standard 0.01 N $Na_2S_2O_3$ solution until the solution is light yellow. Add 3 ml starch solution, and continue titrating until the blue color just disappears. If the normality of the iodine tested is not 0.010, add a few ml of 0.1 N iodine solution if it is low, or a few ml of water if it is high, and standardize again. Repeat the titration until replicate values agree within 0.05 ml. Take the average volume to calculate the normality to three decimal figures using Equation 16A–6.

16.12.4 Critical Orifice. Calibrate the critical orifice using the sampling train shown in Figure 16A–4 but without the H_2S cylinder and vent rotameter. Connect the soap bubble meter to the Teflon line that is connected to the first impinger. Turn on the pump, and adjust the needle valve until the vacuum is higher than the critical vacuum determined in section 16.7.4. Record the time required for gas flow to equal the soap bubble meter volume (use the 100-ml soap bubble meter for gas flow rates below 100 ml/min, otherwise use the 500-ml soap bubble meter). Make three runs, and record the data listed in Table 16A–1. Use these data to calculate the volumetric flow rate of the orifice.

16.13 Calculations.

16.13.1 Nomenclature.

B_{wa} = Fraction of water vapor in ambient air during orifice calibration.

C_{H_2S} = H_2S concentration in cylinder gas, ppmv.

$$K_2 = 32.03 \frac{\text{mg}}{\text{meq}} \frac{24.05\text{L}}{\text{mole}} \frac{1\text{mole}}{64.06\text{g}} \frac{1\text{g}}{10^3\text{mg}} \frac{10^3\text{mL}}{\text{L}} \frac{10^3\mu\text{L}}{1\text{mL}}$$

$$= \frac{12025\mu\text{L}}{\text{meq}}$$

M_a = Molecular weight of ambient air saturated at impinger temperature, g/g-mole.

M_s = Molecular weight of sample gas (nitrogen) saturated at impinger temperature, g/g-mole.

NOTE: (For tests carried out in a laboratory where the impinger temperature is 25 °C, M_a = 28.5 g/g-mole and M_s = 27.7 g/g-mole.)

N_I = Normality of standard iodine solution (0.01 N), g-eq/liter.

N_T = Normality of standard $Na_2S_2O_3$ solution (0.01 N), g-eq/liter.

P_{bar} = Barometric pressure, mm Hg.

P_{std} = Standard absolute pressure, 760 mm Hg.

Q_{std} = Average volumetric flow rate through critical orifice, liters/min.

T_{amb} = Absolute ambient temperature, °K.

T_{std} = Standard absolute temperature, 293 °K.

θ_s = Sampling time, min.

θ_{sb} = Time for soap bubble meter flow rate measurement, min.

$V_{m(std)}$ = Sample gas volume measured by the critical orifice, corrected to standard conditions, liters.

V_{sb} = Volume of gas as measured by the soap bubble meter, ml.

$V_{sb(std)}$ = Volume of gas as measured by the soap bubble meter, corrected to standard conditions, liters.

V_I = Volume of standard iodine solution (0.01 N) used, ml.

V_T = Volume of standard $Na_2S_2O_3$ solution (0.01 N) used, ml.

V_{TB} = Volume of standard $Na_2S_2O_3$ solution (0.01 N) used for the blank, ml.

16.13.2 Normality of Standard $Na_2S_2O_3$ Solution (0.1 N).

$$N_T = \frac{1}{\text{mL } Na_2S_2O_3 \text{ consumed}} \qquad \text{Eq. 16A-5}$$

16.13.3 Normality of Standard Iodine Solution (0.01 N).

$$N_I = \frac{N_T V_T}{V_I} \qquad \text{Eq. 16A-6}$$

16.13.4 Sample Gas Volume.

$$V_{m(std)} = \overline{Q}_{std}\Theta_s\left(1 - B_{wa}\right)\frac{M_a}{M_b} \qquad \text{Eq. 16A-7}$$

16.13.5 Concentration of H_2S in the Gas Cylinder.

17.0 References

$$C_{H_2S} = \frac{K N_T \left(V_{TB} - V_T\right)}{V_{m(std)}} \qquad \text{Eq. 16A-8}$$

1. American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater. Washington, DC. American Public Health Association. 1975. pp. 316–317.

2. American Society for Testing and Materials. Annual Book of ASTM Standards. Part 31: Water, Atmospheric Analysis. Philadelphia, PA. 1974. pp. 40–42.

3. Blosser, R.O. A Study of TRS Measurement Methods. National Council of the Paper Industry for Air and Stream Improvement, Inc., New York, NY. Technical Bulletin No. 434. May 1984. 14 pp.

4. Blosser, R.O., H.S. Oglesby, and A.K. Jain. A Study of Alternate SO_2 Scrubber Designs Used for TRS Monitoring. A Special Report by the National Council of the Paper Industry for Air and Stream Improvement, Inc., New York, NY. July 1977.

5. Curtis, F., and G.D. McAlister. Development and Evaluation of an Oxidation/Method 6 TRS Emission Sampling Procedure. Emission Measurement Branch, Emission Standards and Engineering Division, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711. February 1980.

6. Gellman, I. A Laboratory and Field Study of Reduced Sulfur Sampling and Monitoring Systems. National Council of the Paper Industry for Air and Stream Improvement, Inc., New York, NY. Atmospheric Quality Improvement Technical Bulletin No. 81. October 1975.

7. Margeson, J.H., J.E. Knoll, and M.R. Midgett. A Manual Method for TRS Determination. Source Branch, Quality Assurance Division, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

8. National Council of the Paper Industry for Air and Stream Improvement. An Investigation of H_2S and SO_2. Calibration Cylinder Gas Stability and Their Standardization Using Wet Chemical Techniques. Special Report 76–06. New York, NY. August 1976.

9. National Council of the Paper Industry for Air and Stream Improvement. Wet Chemical Method for Determining the H_2S Concentration of Calibration Cylinder Gases. Technical Bulletin Number 450. New York, NY. January 1985. 23 pp.

10. National Council of the Paper Industry for Air and Stream Improvement. Modified Wet Chemical Method for Determining the H_2S Concentration of Calibration Cylinder Gases. Draft Report. New York, NY. March 1987. 29 pp.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

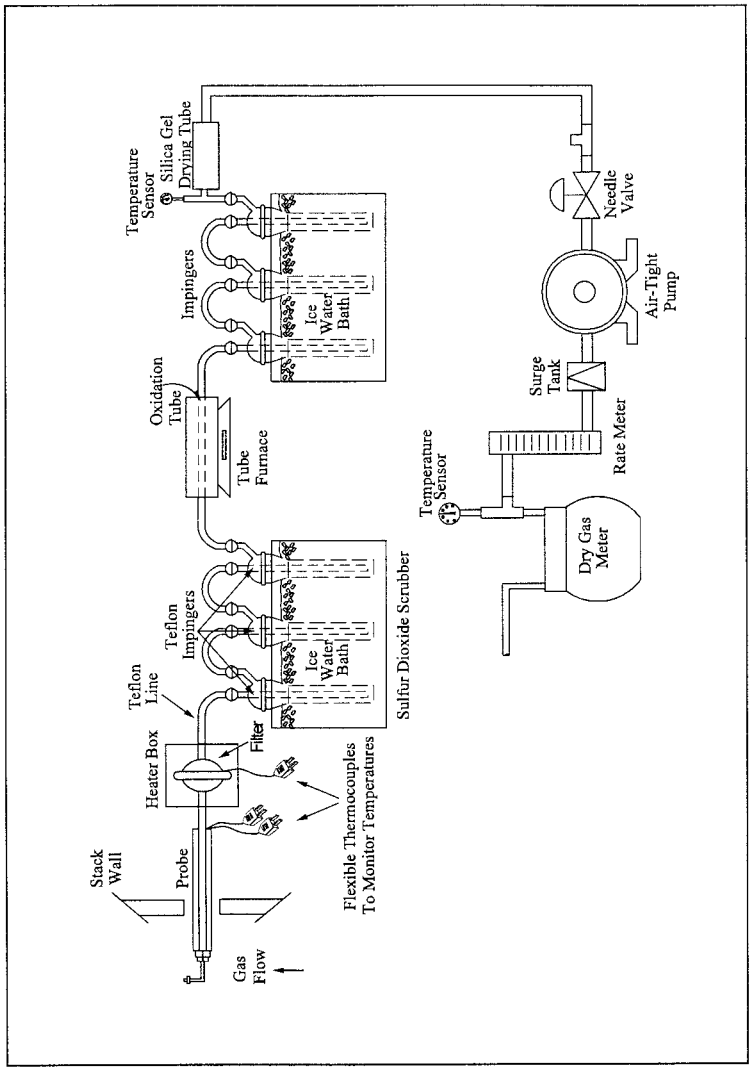


Figure 16A-1. Sampling Train.

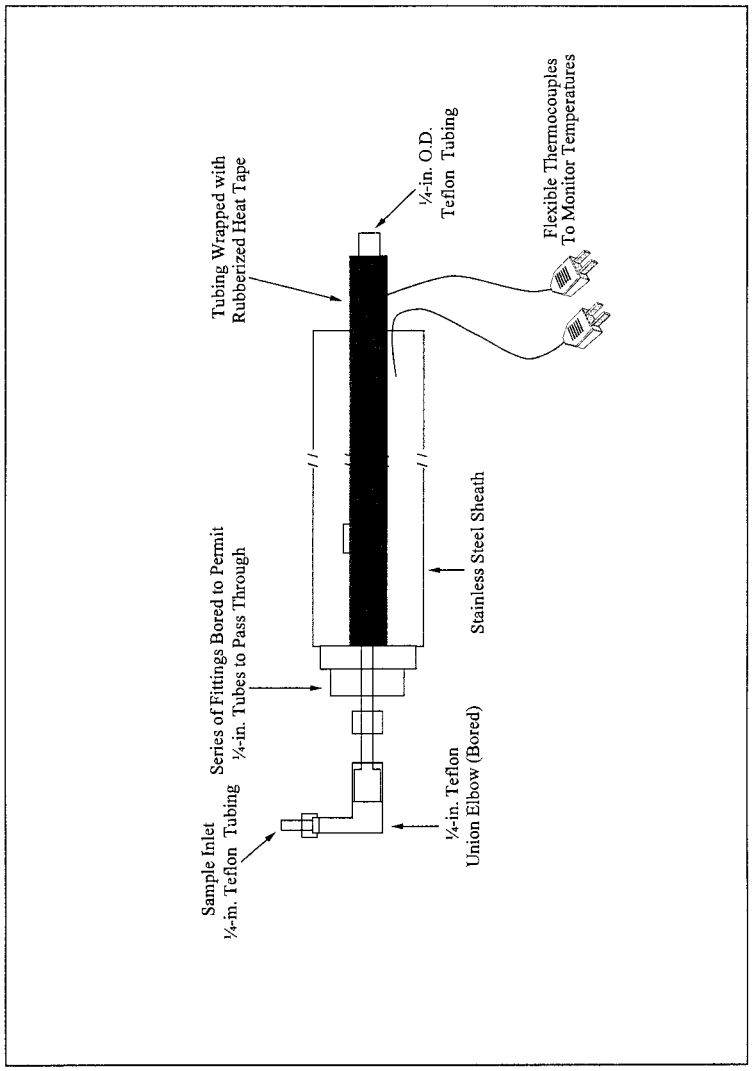


Figure 16A-2. Angled Sampling Probe.

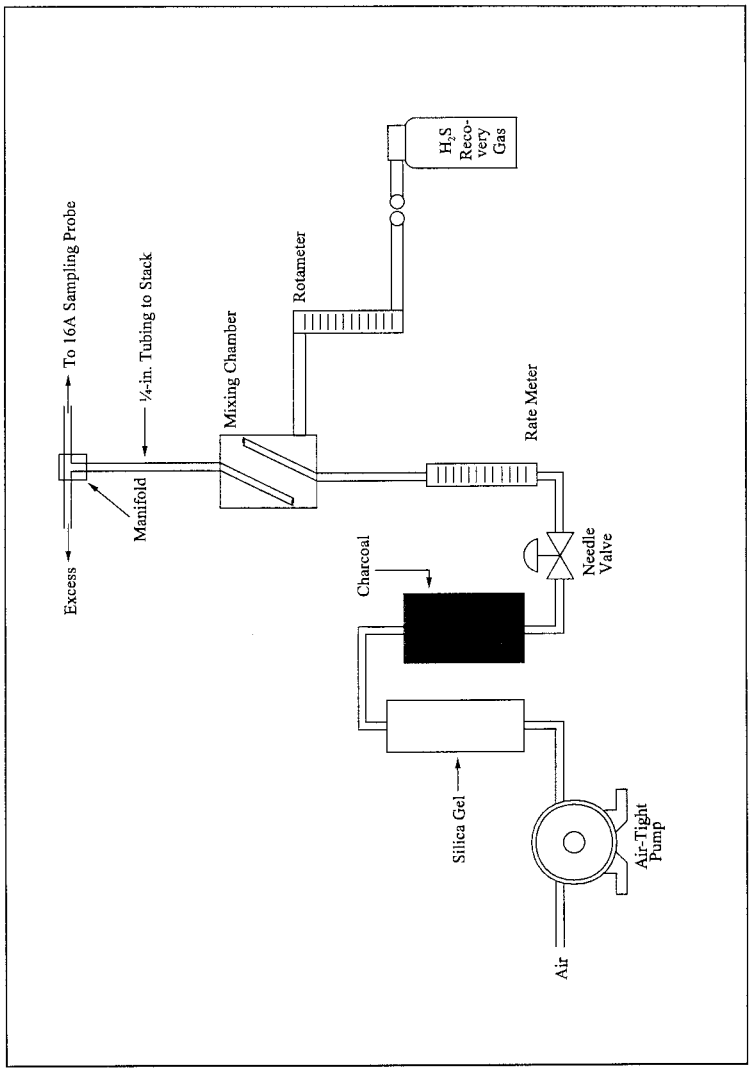


Figure 16A-3. Recovery Gas Dilution System.

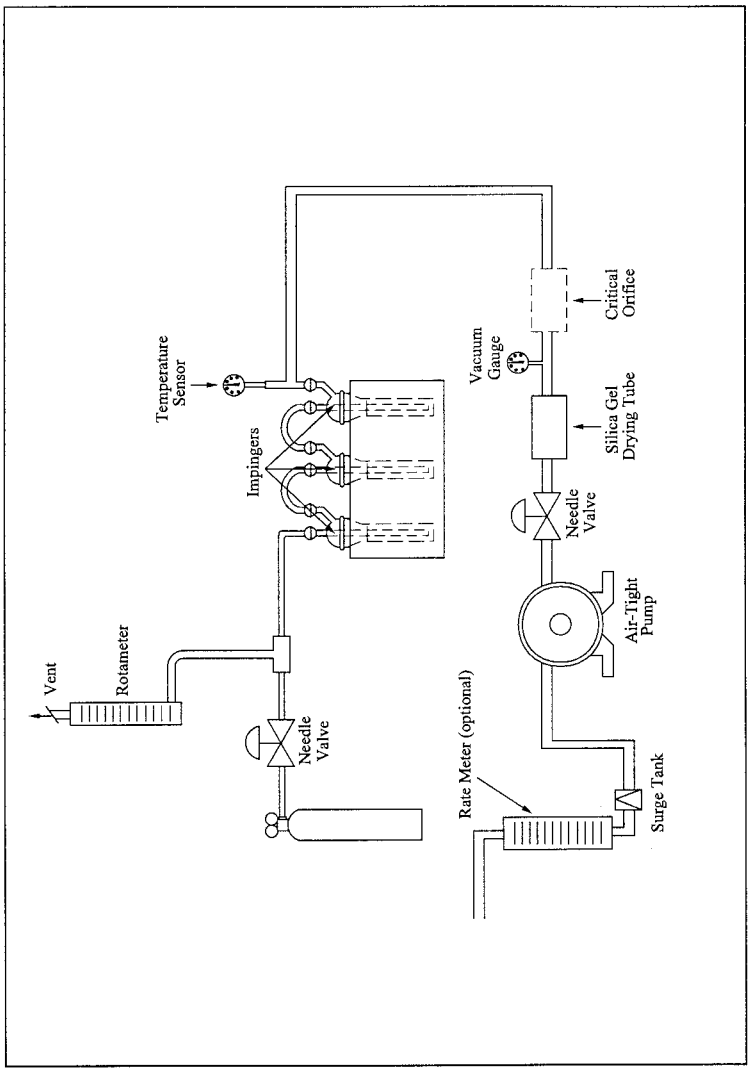


Figure 16A-4. Recovery Check Gas Sampling Train.

Date _____
Critical orifice ID _____
Soap bubble meter volume, Vsb___ liters
Time, θsb
Run no. 1 ____ min ____ sec
Run no. 2 ____ min ____ sec
Run no. 3 ____ min ____ sec
Average ____ min ____ sec
Covert the seconds to fraction of minute:
Time=____ min + ____ Sec/60=____ min

Barometric pressure, P_{bar}=____ mm Hg
Ambient temperature, t_{amb} = 273 + ____ °C=____ °K=____ mm Hg. (This should be approximately 0.4 times barometric pressure.)
Pump vacuum,

$$V_{sb(std)} = \frac{V_{sb} T_{std} P_{bar} (10^{-3})}{T_{amb} P_{std}}$$

$$= ---------- \text{ liters}$$

$$Q_{std} = \frac{V_{sb(std)}}{\Theta_{sb}}$$

$$= ---------- \text{ liters/min}$$

Table 16A–1. Critical Orifice Calibration Data

METHOD 16B—DETERMINATION OF TOTAL REDUCED SULFUR EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a knowledge of at least the following additional test methods: Method 6C, Method 16, and Method 16A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Total reduced sulfur (TRS) including:	N/A
Dimethyl disulfide (DMDS), [$(CH_3)_2S_2$]	62–49–20
Dimethyl sulfide (DMS), [$(CH_3)_2S$]	75–18–3
Hydrogen sulfide (H_2S)	7783–06–4
Methyl mercaptan (MeSH), [CH_4S]	74–93–1
Reported as: Sulfur dioxide (SO_2)	7449–09–5

1.2 Applicability. This method is applicable for determining TRS emissions from recovery furnaces (boilers), lime kilns, and smelt dissolving tanks at kraft pulp mills, and from other sources when specified in an applicable subpart of the regulations. The flue gas must contain at least 1 percent oxygen for complete oxidation of all TRS to SO_2.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 An integrated gas sample is extracted from the stack. The SO_2 is removed selectively from the sample using a citrate buffer solution. The TRS compounds are then thermally oxidized to SO_2 and analyzed as SO_2 by gas chromatography (GC) using flame photometric detection (FPD).

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Reduced sulfur compounds other than those regulated by the emission standards, if present, may be measured by this method. Therefore, carbonyl sulfide, which is partially oxidized to SO_2 and may be present in a lime kiln exit stack, would be a positive interferant.

4.2 Particulate matter from the lime kiln stack gas (primarily calcium carbonate) can cause a negative bias if it is allowed to enter the citrate scrubber; the particulate matter will cause the pH to rise and H_2S to be absorbed before oxidation. Proper use of the particulate filter, described in section 6.1.3 of Method 16A, will eliminate this interference.

4.3 Carbon monoxide (CO) and carbon dioxide (CO_2) have substantial desensitizing effects on the FPD even after dilution. Acceptable systems must demonstrate that they have eliminated this interference by some procedure such as eluting these compounds before the SO_2. Compliance with this requirement can be demonstrated by submitting chromatograms of calibration gases with and without CO_2 in diluent gas. The CO_2 level should be approximately 10 percent for the case with CO_2 present. The two chromatograms should show agreement within the precision limits of section 13.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hydrogen Sulfide (H_2S). A flammable, poisonous gas with the odor of rotten eggs. H_2S is extremely hazardous and can cause collapse, coma, and death within a few seconds of one or two inhalations at sufficient concentrations. Low concentrations irritate the mucous membranes and may cause nausea, dizziness, and headache after exposure.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling train is shown in Figure 16B–1. Modifications to the apparatus are accepted provided the system performance check in section 8.4.1 is met.

6.1.1 Probe, Probe Brush, Particulate Filter, SO_2 Scrubber, Combustion Tube, and Furnace. Same as in Method 16A, sections 6.1.1 to 6.1.6.

6.1.2 Sampling Pump. Leakless Teflon-coated diaphragm type or equivalent.

6.2 Analysis.

6.2.1 Dilution System (optional), Gas Chromatograph, Oven, Temperature Gauges, Flow System, Flame Photometric Detector, Electrometer, Power Supply, Recorder, Calibration System, Tube Chamber, Flow System, and Constant Temperature Bath. Same as in Method 16, sections 6.2.1, 6.2.2, and 6.3.

6.2.2 Gas Chromatograph Columns. Same as in Method 16, section 6.2.3. Other columns with demonstrated ability to resolve SO_2 and be free from known interferences are acceptable alternatives. Single column systems such as a 7-ft Carbsorb B HT 100 column have been found satisfactory in resolving SO_2 from CO_2.

7.0 Reagents and Standards

Same as in Method 16, section 7.0, except for the following:

7.1 Calibration Gas. SO_2 permeation tube gravimetrically calibrated and certified at some convenient operating temperature. These tubes consist of hermetically sealed FEP Teflon tubing in which a liquefied gaseous substance is enclosed. The enclosed gas permeates through the tubing wall at a constant rate. When the temperature is constant, calibration gases covering a wide range of known concentrations can be generated by varying and accurately measuring the flow rate of diluent gas passing over the tubes. In place of SO_2 permeation tubes, cylinder gases containing SO_2 in nitrogen may be used for calibration. The cylinder gas concentration must be verified according to section 8.2.1 of Method 6C. The calibration gas is used to calibrate the GC/FPD system and the dilution system.

7.2 Recovery Check Gas.

7.2.1 Hydrogen sulfide [100 parts per million by volume (ppmv) or less] in nitrogen, stored in aluminum cylinders. Verify the concentration by Method 11, the procedure discussed in section 16.0 of Method 16A, or gas chromatography where the instrument is calibrated with an H_2S permeation tube as described below. For the wet-chemical methods, the standard deviation should not exceed 5 percent on at least three 20-minute runs.

7.2.2 Hydrogen sulfide recovery gas generated from a permeation device gravimetrically calibrated and certified at some convenient operation temperature may be used. The permeation rate of the device must be such that at a dilution gas flow rate of 3 liters/min (64 ft^3/hr), an H_2S concentration in the range of the stack gas or within 20 percent of the emission standard can be generated.

7.3 Combustion Gas. Gas containing less than 50 ppbv reduced sulfur compounds and less than 10 ppmv total hydrocarbons. The gas may be generated from a clean-air system that purifies ambient air and consists of the following components: diaphragm pump, silica gel drying tube, activated charcoal tube, and flow rate measuring device. Gas from a compressed air cylinder is also acceptable.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Procedures. Same as in Method 15, section 8.1.

8.2 Sample Collection. Before any source sampling is performed, conduct a system performance check as detailed in section 8.4.1 to validate the sampling train components and procedures. Although this test is optional, it would significantly reduce the possibility of rejecting tests as a result of failing the post-test performance check. At the completion of the pretest system performance check, insert the sampling probe into the test port making certain that no dilution air enters the stack though the port. Condition the entire system with sample for a minimum of 15 minutes before beginning analysis. If the sample is diluted, determine the dilution factor as in section 10.4 of Method 15.

8.3 Analysis. Inject aliquots of the sample into the GC/FPD analyzer for analysis. Determine the concentration of SO_2 directly from the calibration curves or from the equation for the least-squares line.

8.4. Post-Test Procedures

8.4.1 System Performance Check. Same as in Method 16A, section 8.5. A sufficient number of sample injections should be made so that the precision requirements of section 13.2 are satisfied.

8.4.2 Determination of Calibration Drift. Same as in Method 15, section 8.3.2.

9.0 Quality Control

Section	Quality control measure	Effect
8.2, 8.3	System performance check	Ensure validity of sampling train components and analytical procedure.
8.1	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.
10.0	Analytical calibration	Ensure precision of analytical results within 5 percent.

10.0 Calibration

Same as in Method 16, section 10, except SO_2 is used instead of H_2S.

11.0 Analytical Procedure

11.1 Sample collection and analysis are concurrent for this method (see section 8.3).

12.0 Data Analysis and Calculations

12.1 Nomenclature.

C_{SO2} = Sulfur dioxide concentration, ppmv.
C_{TRS} = Total reduced sulfur concentration as determined by Equation 16B–1, ppmv.
d = Dilution factor, dimensionless.
N = Number of samples.

12.2 SO_2 Concentration. Determine the concentration of SO_2, C_{SO2}, directly from the calibration curves. Alternatively, the concentration may be calculated using the equation for the least-squares line.

12.3 TRS Concentration.

$$C_{TRS} = C_{SO_2} d \qquad \text{Eq. 16B-1}$$

12.4 Average TRS Concentration

$$\text{Avg.}\, C_{TRS} = \frac{\sum_{i=1}^{n} C_{TRS}}{N} \qquad \text{Eq. 16B-2}$$

13.0 Method Performance.

13.1 Range and Sensitivity. Coupled with a GC using a 1-ml sample size, the maximum limit of the FPD for SO_2 is approximately 10 ppmv. This limit is extended by diluting the sample gas before analysis or by reducing the sample aliquot size. For sources with emission levels between 10 and 100 ppm, the measuring range can be best extended by reducing the sample size.

13.2 GC/FPD Calibration and Precision. A series of three consecutive injections of the sample calibration gas, at any dilution, must produce results which do not vary by more than 5 percent from the mean of the three injections.

13.3 Calibration Drift. The calibration drift determined from the mean of the three injections made at the beginning and end of any run or series of runs within a 24-hour period must not exceed 5 percent.

13.4 System Calibration Accuracy. Losses through the sample transport system must be measured and a correction factor developed to adjust the calibration accuracy to 100 percent.

13.5 Field tests between this method and Method 16A showed an average difference of less than 4.0 percent. This difference was not determined to be significant.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Same as in Method 16, section 16.0.

2. National Council of the Paper Industry for Air and Stream Improvement, Inc, A Study of TRS Measurement Methods. Technical Bulletin No. 434. New York, NY. May 1984. 12p.

3. Margeson, J.H., J.E. Knoll, and M.R. Midgett. A Manual Method for TRS Determination. Draft available from the authors. Source Branch, Quality Assurance Division, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

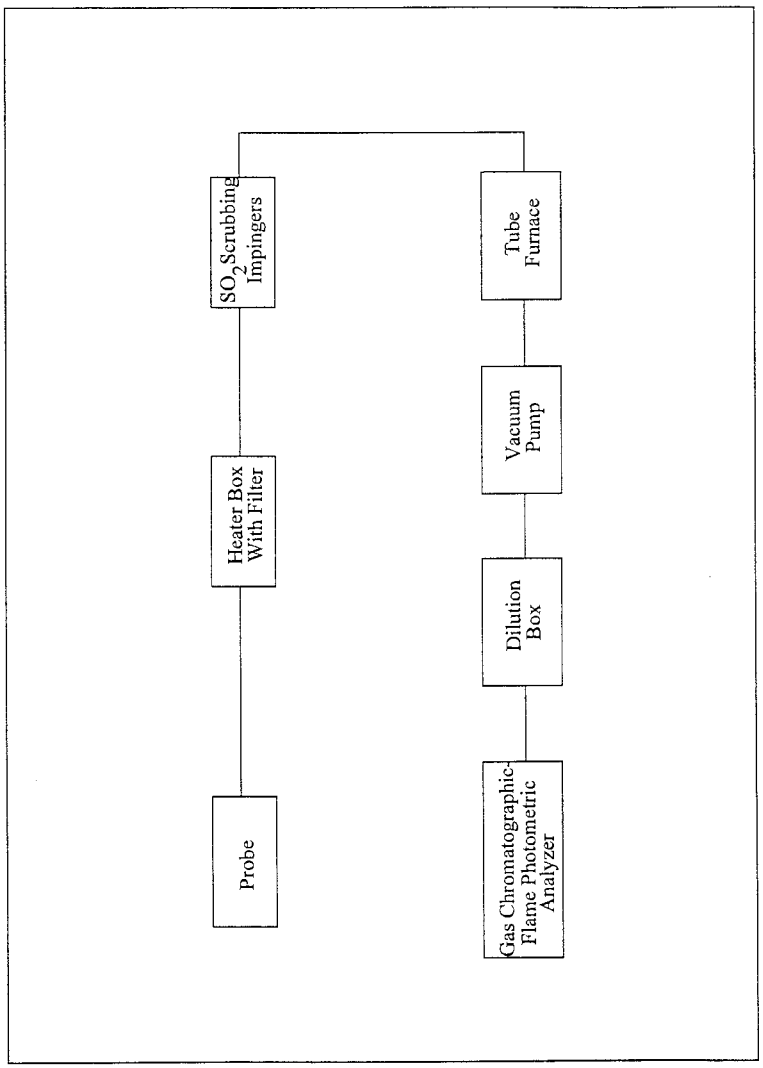


Figure 16B-1. Method 16B Sampling Train.

METHOD 16C—DETERMINATION OF TOTAL REDUCED SULFUR EMISSIONS FROM STATIONARY SOURCES

1.0 Scope and Application

What is Method 16C?

Method 16C is a procedure for measuring total reduced sulfur (TRS) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis. This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to

other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

(a) Method 6C—Determination of Sulfur Dioxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)

(b) Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure)

(c) Method 16A—Determination of Total Reduced Sulfur Emissions from Stationary Sources (Impinger Technique)

1.1 Analytes. What does Method 16C determine?

Analyte	CAS No.
Total reduced sulfur including:	N/A
Dimethyl disulfide (DMDS), [$(CH_3)_2S_2$]	62–49–20
Dimethyl sulfide (DMS), [$(CH_3)_2S$]	75–18–3
Hydrogen sulfide (H_2S)	7783–06–4
Methyl mercaptan (MeSH), (CH_4S)	74–93–1
Reported as: Sulfur dioxide (SO_2)	7449–09–5

1.2 Applicability. This method is applicable for determining TRS emissions from recovery furnaces (boilers), lime kilns, and smelt dissolving tanks at kraft pulp mills, and from other sources when specified in an applicable subpart of the regulations.

1.3 Data Quality Objectives. Adherence to the requirements described in Method 16C will enhance the quality of the data obtained.

2.0 Summary of Method

2.1 An integrated gas sample is extracted from the stack. The SO_2 is removed selectively from the sample using a citrate buffer solution. The TRS compounds are then thermally oxidized to SO_2 and determined as SO_2 by an instrumental analyzer. This method is a combination of the sampling procedures of Method 16A and the analytical procedures of Method 6C (referenced in Method 7E), with minor modifications to facilitate their use together.

3.0 Definitions

Analyzer calibration error, *Calibration curve*, *Calibration gas*, *Low-level gas*, *Mid-level gas*, *High-level gas*, *Calibration drift*, *Calibration span*, *Data recorder*, *Direct calibration mode*, *Gas analyzer*, *Interference check*, *Measurement system*, *Response time*, *Run*, *System calibration mode*, *System performance check*, and *Test* are the same as used in Methods 16A and 6C.

4.0 Interferences

4.1 Reduced sulfur compounds other than those defined as TRS, if present, may be measured by this method. Compounds like carbonyl sulfide, which is partially oxidized to SO_2 and may be present in a lime kiln exit stack, would be a positive interferent. Interferences may vary among instruments, and instrument-specific interferences must be evaluated through the interference check.

4.2 Particulate matter from the lime kiln stack gas (primarily calcium carbonate) can cause a negative bias if it is allowed to enter the citrate scrubber; the particulate matter will cause the pH to rise and H_2S to be absorbed before oxidation. Proper use of the particulate filter, described in section 6.1.3 of Method 16A, will eliminate this interference.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices before performing this test method.

5.2 Hydrogen Sulfide. Hydrogen sulfide is a flammable, poisonous gas with the odor of rotten eggs. Hydrogen sulfide is extremely hazardous and can cause collapse, coma, and death within a few seconds of one or two inhalations at sufficient concentrations. Low concentrations irritate the mucous membranes and may cause nausea, dizziness, and headache after exposure. It is the responsibility of the user of this test method to establish appropriate safety and health practices.

6.0 Equipment and Supplies

What do I need for the measurement system?

The measurement system is similar to those applicable components in Methods 16A and 6C. Modifications to the apparatus are accepted provided the performance criteria in section 13.0 are met.

6.1 Probe. Teflon tubing, 6.4-mm (¼ in.) diameter, sequentially wrapped with heat-resistant fiber strips, a rubberized heat tape (plug at one end), and heat-resistant adhesive tape. A flexible thermocouple or other suitable temperature measuring device must be placed between the Teflon tubing and the fiber strips so that the temperature can be monitored to prevent softening of the probe. The probe must be sheathed in stainless steel to provide in-stack rigidity. A series of bored-out stainless steel fittings placed at the front of the sheath will prevent moisture and particulate from entering between the probe and sheath. A 6.4-mm (¼ in.) Teflon elbow (bored out) must be attached to the inlet of the probe, and a 2.54 cm (1 in.) piece of Teflon tubing must be attached at the open end of the elbow to permit the opening of the probe to be turned away from the particulate stream; this will reduce the amount of particulate drawn into the sampling train. The probe is depicted in Figure 16A–2 of Method 16A.

6.2 Probe Brush. Nylon bristle brush with handle inserted into a 3.2-mm (⅛ in.) Teflon

tubing. The Teflon tubing should be long enough to pass the brush through the length of the probe.

6.3 Particulate Filter. 50-mm Teflon filter holder and a 1- to 2-μm porosity, Teflon filter (may be available through Savillex Corporation, 5325 Highway 101, Minnetonka, Minnesota 55343, or other suppliers of filters). The filter holder must be maintained in a hot box at a temperature sufficient to prevent moisture condensation. A temperature of 121 °C (250 °F) was found to be sufficient when testing a lime kiln under sub-freezing ambient conditions.

6.4 SO_2 Scrubber. Three 300-ml Teflon segmented impingers connected in series with flexible, thick-walled, Teflon tubing. (Impinger parts and tubing may be available through Savillex or other suppliers.) The first two impingers contain 100 ml of citrate buffer, and the third impinger is initially dry. The tip of the tube inserted into the solution should be constricted to less than 3 mm (⅛ in.) ID and should be immersed to a depth of at least 5 cm (2 in.).

6.5 Combustion Tube. Quartz glass tubing with an expanded combustion chamber 2.54 cm (1 in.) in diameter and at least 30.5 cm (12 in.) long. The tube ends should have an outside diameter of 0.6 cm (¼ in.) and be at least 15.3 cm (6 in.) long. This length is necessary to maintain the quartz-glass connector near ambient temperature and thereby avoid leaks. Alternative combustion tubes are acceptable provided they are shown to combust TRS at concentrations encountered during tests.

6.6 Furnace. A furnace of sufficient size to enclose the combustion chamber of the combustion tube with a temperature regulator capable of maintaining the temperature at 800 ±100 °C (1472 ±180 °F). The furnace operating temperature should be checked with a thermocouple to ensure accuracy.

6.7 Sampling Pump. A leak-free pump is required to pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system and must be constructed of material that is non-reactive to the gas it contacts. For dilution-type measurement systems, an eductor pump may be used to create a vacuum that draws the sample through a critical orifice at a constant rate.

6.8 Calibration Gas Manifold. The calibration gas manifold must allow the introduction of calibration gases either directly to the gas analyzer in direct calibration mode or into the measurement system, at the probe, in system calibration mode, or both, depending upon the type of system used. In system calibration mode, the system must be able to flood the sampling probe and vent excess gas. Alternatively, calibration gases may be introduced at the calibration valve following the probe. Maintain a constant pressure in the gas manifold. For in-stack dilution-type systems, a gas dilution subsystem is required to transport large volumes of purified air to the sample probe, and a probe controller is needed to maintain the proper dilution ratio.

6.9 Sample Gas Manifold. The sample gas manifold diverts a portion of the sample to the analyzer, delivering the remainder to the by-pass discharge vent. The manifold should also be able to introduce calibration gases directly to the analyzer. The manifold must be made of material that is non-reactive to SO_2 and be configured to safely discharge the bypass gas.

6.10 SO_2 Analyzer. You must use an instrument that uses an ultraviolet, non-dispersive infrared, fluorescence, or other detection principle to continuously measure SO_2 in the gas stream provided it meets the performance specifications in section 13.0.

6.11 Data Recording. A strip chart recorder, computerized data acquisition system, digital recorder, or data logger for recording measurement data must be used.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. When such specifications are not available, the best available grade must be used.

7.1 Water. Deionized distilled water must conform to ASTM Specification D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17). The $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.2 Citrate Buffer. Dissolve 300 g of potassium citrate (or 284 g of sodium citrate) and 41 g of anhydrous citric acid in 1 liter of water (200 ml is needed per test). Adjust the pH to between 5.4 and 5.6 with potassium citrate or citric acid, as required.

7.3 Calibration Gas. Refer to section 7.1 of Method 7E (as applicable) for the calibration gas requirements. Example calibration gas mixtures are listed below.

(a) SO_2 in nitrogen (N_2).
(b) SO_2 in air.
(c) SO_2 and carbon dioxide (CO_2) in N_2.
(d) SO_2 and oxygen (O_2) in N_2.
(e) $SO_2/CO_2/O_2$ gas mixture in N_2.
(f) CO_2/NO_X gas mixture in N_2.
(g) $CO_2/SO_2/NO_X$ gas mixture in N_2.

For fluorescence-based analyzers, the O_2 and CO_2 concentrations of the calibration gases as introduced to the analyzer must be within 1.0 percent (absolute) O_2 and 1.0 percent (absolute) CO_2 of the O_2 and CO_2 concentrations of the effluent samples as introduced to the analyzer. Alternatively, for fluorescence-based analyzers, use calibration blends of SO_2 in air and the nomographs provided by

the vendor to determine the quenching correction factor (the effluent O_2 and CO_2 concentrations must be known). This requirement does not apply to ambient-level fluorescence analyzers that are used in conjunction with sample dilution systems. Alternatively, H_2S in O_2 or air may be used to calibrate the analyzer through the tube furnace.

7.4 System Performance Check Gas. You must use H_2S (100 ppmv or less) stored in aluminum cylinders with the concentration certified by the manufacturer. Hydrogen sulfide in nitrogen is more stable than H_2S in air, but air may be used as the balance gas.

NOTE: Alternatively, H_2S recovery gas generated from a permeation device gravimetrically calibrated and certified at some convenient operating temperature may be used. The permeation rate of the device must be such that at the appropriate dilution gas flow rate, an H_2S concentration can be generated in the range of the stack gas or within 20 percent of the emission standard.

7.5 Interference Check. Examples of test gases for the interference check are listed in Table 7E–3 of Method 7E.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pre-sampling Tests. Before measuring emissions, perform the following procedures:

(a) Calibration gas verification,

(b) Calibration error test,

(c) System performance check,

(d) Verification that the interference check has been satisfied.

8.1.1 Calibration Gas Verification. Obtain a certificate from the gas manufacturer documenting the quality of the gas. Confirm that the manufacturer certification is complete and current. Ensure that your calibration gas certifications have not expired. This documentation should be available on-site for inspection. To the extent practicable, select a high-level gas concentration that will result in the measured emissions being between 20 and 100 percent of the calibration span.

8.1.2 Analyzer Calibration Error Test. After you have assembled, prepared, and calibrated your sampling system and analyzer, you must conduct a 3-point analyzer calibration error test before the first run and again after any failed system performance check or failed drift test to ensure the calibration is acceptable. Introduce the low-, mid-, and high-level calibration gases sequentially to the analyzer in direct calibration mode. For each calibration gas, calculate the analyzer calibration error using Equation 16C–1 in section 12.2. The calibration error for the low-, mid-, and high-level gases must not exceed 5.0 percent or 0.5 ppmv. If the calibration error specification is not met, take corrective action and repeat the test until an acceptable 3-point calibration is achieved.

8.1.3 System Performance Check. A system performance check is done (1) to validate the sampling train components and procedure (prior to testing), and (2) to validate a test run (after a run). You must conduct a performance check in the field prior to testing, and after each 3-hour run or after three 1-hour runs. A performance check consists of sampling and analyzing a known concentration of H_2S (system performance check gas) and comparing the analyzed concentration to the known concentration. To conduct the system performance check, mix the system performance check gas (Section 7.4) and ambient air, that has been conditioned to remove moisture and sulfur-containing gases, in a dilution system such as that shown in Figure 16A–3 of Method 16A. Alternatively, ultra-high purity (UHP) grade air may be used. Adjust the gas flow rates to generate an H_2S concentration in the range of the stack gas or within 20 percent of the applicable standard and an oxygen concentration greater than 1 percent at a total flow rate of at least 2.5 liters/min (5.3 ft3/hr). Use Equation 16A–3 from Method 16A to calculate the concentration of system performance check gas generated. Calibrate the flow rate from both gas sources with a soap bubble flow meter so that the diluted concentration of H_2S can be accurately calculated. Alternatively, mass flow controllers with documented calibrations may be used if UHP grade air is being used. Sample duration should be sufficiently long to ensure a stable response from the analyzer. Analyze in the same manner as the emission samples. Collect the sample through the probe of the sampling train using a manifold or other suitable device that will ensure extraction of a representative sample. The TRS sample concentration measured between system performance checks is corrected by the average of the pre- and post-system performance checks.

8.1.4 Interference Check. Same as in Method 7E, section 8.2.7.

8.2 Measurement System Preparation.

8.2.1 For the SO_2 scrubber, measure 100 ml of citrate buffer into the first and second impingers; leave the third impinger empty. Immerse the impingers in an ice bath, and locate them as close as possible to the filter heat box. The connecting tubing should be free of loops. Maintain the probe and filter temperatures sufficiently high to prevent moisture condensation, and monitor with a suitable temperature sensor. Prepare the oxidation furnace and maintain at 800 ±100 °C (1472 ±180 °F).

8.2.2 Citrate Scrubber Conditioning Procedure. Condition the citrate buffer scrubbing solution by pulling stack gas through the Teflon impingers as described in section 8.4.1.

8.3 Pretest Procedures. After the complete measurement system has been set up at the site and deemed to be operational, the following procedures must be completed before sampling is initiated.

8.3.1 Leak-Check. Appropriate leak-check procedures must be employed to verify the integrity of all components, sample lines, and connections. For components upstream of the sample pump, attach the probe end of the sample line to a manometer or vacuum gauge, start the pump and pull a vacuum greater than 50 mm (2 in.) Hg, close off the pump outlet, and then stop the pump and ascertain that there is no leak for 1 minute. For components after the pump, apply a slight positive pressure and check for leaks by applying a liquid (detergent in water, for example) at each joint. Bubbling indicates the presence of a leak.

8.3.2 Initial System Performance Check. A system performance check using the test gas (Section 7.4) is performed prior to testing to validate the sampling train components and procedure.

8.4 Sample Collection and Analysis.

8.4.1 After performing the required pretest procedures described in section 8.1, insert the sampling probe into the test port ensuring that no dilution air enters the stack through the port. Condition the sampling system and citrate buffer solution for a minimum of 15 minutes before beginning analysis. Begin sampling and analysis. A source test consists of three test runs. A test run shall consist of a single sample collected over a 3-hour period or three separate 1-hour samples collected over a period not to exceed six hours.

8.5 Post-Run Evaluations.

8.5.1 System Performance Check. Perform a post-run system performance check before replacing the citrate buffer solution and particulate filter and before the probe is cleaned. The check results must not exceed the 100 ±20 percent limit set forth in section 13.2. If this limit is exceeded, the intervening run is considered invalid. However, if the recovery efficiency is not in the 100 ±20 percent range, but the results do not affect the compliance or noncompliance status of the affected facility, the Administrator may decide to accept the results of the compliance test.

8.5.2 Calibration Drift. After a run or series of runs, not to exceed a 24-hour period after initial calibration, perform a calibration drift test using a calibration gas (preferably the level that best approximates the sample concentration) in direct calibration mode. This drift must not differ from the initial calibration error percent by more than 3.0 percent or 0.5 ppm. If the drift exceeds this limit, the intervening run or runs are considered valid, but a new analyzer calibration error test must be performed and passed before continuing sampling.

9.0 Quality Control

Section	Quality control measure	Effect
8.1.2	Analyzer calibration error test	Establishes initial calibration accuracy within 5.0%.
8.1.3, 8.5.1	System performance check	Ensures accuracy of sampling/analytical procedure to 100 ±20%.
8.5.2	Calibration drift test	Ensures calibration drift is within 3.0%.
8.1.4	Interference check	Checks for analytical interferences.
8.3	Sampling equipment leak-check	Ensures accurate measurement of sample gas flow rate, sample volume.

10.0 Calibration

10.1 Calibrate the system using the gases described in section 7.3. Perform the initial 3-point calibration error test as described in section 8.1.2 before you start the test. The specification in section 13 must be met. Conduct an initial system performance test described in section 8.1.3 as well before the test to validate the sampling components and procedures before sampling. After the test commences, a system performance check is required after each run. You must include a copy of the manufacturer's certification of the calibration gases used in the testing as part of the test report. This certification must include the 13 documentation requirements in the EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards, September 1997, as amended August 25, 1999.

11.0 Analytical Procedure

Because sample collection and analysis are performed together (see section 8.0), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

12.1 Nomenclature.

ACE = Analyzer calibration error, percent of calibration span.

CD = Calibration drift, percent.

C_{Dir} = Measured concentration of a calibration gas (low, mid, or high) when introduced in direct calibration mode, ppmv.

C_{H2S} = Concentration of the system performance check gas, ppmv H_2S.

C_S = Measured concentration of the system performance gas when introduced in system calibration mode, ppmv H_2S.
C_V = Manufacturer certified concentration of a calibration gas (low, mid, or high), ppmv SO_2.
C_{SO2} = Unadjusted sample SO_2 concentration, ppmv.
C_{TRS} = Total reduced sulfur concentration corrected for system performance, ppmv.
CS = Calibration span, ppmv.
DF = Dilution system (if used) dilution factor, dimensionless.
SP = System performance, percent.

12.2 Analyzer Calibration Error. For nondilution systems, use Equation 16C–1 to calculate the analyzer calibration error for the low-, mid-, and high-level calibration gases.

$$ACE = \frac{C_{Dir} - C_v}{CS} X\ 100 \qquad \text{Eq. 16C-1}$$

12.3 System Performance Check. Use Equation 16C–2 to calculate the system performance.

$$SP = \frac{C_S - C_{H2S}}{C_{H2S}} x\ 100 \qquad \text{Eq. 16C-2}$$

12.4 Calibration Drift. Use Equation 16C–3 to calculate the calibration drift at a single concentration level after a run or series of runs (not to exceed a 24-hr period) from initial calibration. Compare the single-level calibration gas error (ACE_n) to the original error obtained for that gas in the initial analyzer calibration error test (ACE_i).

$$CD = \left| ACE_i - ACE_n \right| \qquad \text{Eq. 16C-3}$$

12.5 TRS Concentration as SO_2. For each sample or test run, calculate the arithmetic average of SO_2 concentration values (e.g., 1-minute averages). Then calculate the sample TRS concentration by adjusting the average value of C_{SO2} for system performance using Equation 16C–4.

$$C_{TRS} = \frac{\overline{C_{SO2}}}{1 - \left| \overline{SP} \right|} \qquad \text{Eq. 16C-4}$$

13.0 Method Performance

13.1 Analyzer Calibration Error. At each calibration gas level (low, mid, and high), the calibration error must either not exceed 5.0 percent of the calibration gas concentration or $|C_{Dir} - C_v|$ must be ≤0.5 ppmv.

13.2 System Performance. Each system performance check must not deviate from the system performance gas concentration by more than 20 percent. Alternatively, the results are acceptable if $|C_s - C_{H2S}|$ is ≤0.5 ppmv.

13.3 Calibration Drift. The calibration drift at the end of any run or series of runs within a 24-hour period must not differ by more than 3.0 percent from the original ACE at the test concentration level or $|ACEi - ACE_n|$ must not exceed 0.5 ppmv.

13.4 Interference Check. For the analyzer, the total interference response (i.e., the sum of the interference responses of all tested gaseous components) must not be greater than 2.5 percent of the calibration span. Any interference is also acceptable if the sum of the responses does not exceed 0.5 ppmv for a

calibration span of 5 to 10 ppmv, or 0.2 ppmv for a calibration span <5 ppmv.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. The references are the same as in section 16.0 of Method 16, section 17.0 of Method 16A, and section 17.0 of Method 6C.
2. National Council of the Paper Industry for Air and Stream Improvement, Inc,. A Study of TRS Measurement Methods. Technical Bulletin No. 434. New York, NY. May 1984. 12p.
3. Margeson, J.H., J.E. Knoll, and M.R. Midgett. A Manual Method for TRS Determination. Draft available from the authors. Source Branch, Quality Assurance Division, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 17—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

NOTE: Particulate matter is not an absolute quantity. It is a function of temperature and pressure. Therefore, to prevent variability in PM emission regulations and/or associated test methods, the temperature and pressure at which PM is to be measured must be carefully defined. Of the two variables (*i.e.*, temperature and pressure), temperature has the greater effect upon the amount of PM in an effluent gas stream; in most stationary source categories, the effect of pressure appears to be negligible. In Method 5, 120 °C (248 °F) is established as a nominal reference temperature. Thus, where Method 5 is specified in an applicable subpart of the standard, PM is defined with respect to temperature. In order to maintain a collection temperature of 120 °C (248 °F), Method 5 employs a heated glass sample probe and a heated filter holder. This equipment is somewhat cumbersome and requires care in its operation. Therefore, where PM concentrations (over the normal range of temperature associated with a specified source category) are known to be independent of temperature, it is desirable to eliminate the glass probe and the heating systems, and to sample at stack temperature.

1.2 Applicability. This method is applicable for the determination of PM emissions, where PM concentrations are known to be independent of temperature over the normal range of temperatures characteristic of emissions from a specified source category. It is intended to be used only when specified by an applicable subpart of the standards, and only within the applicable temperature limits (if specified), or when otherwise approved by the Administrator. This method is not applicable to stacks that contain liquid droplets or are saturated with water vapor. In addition, this method shall not be used as written if the projected cross-sectional area of the probe extension-filter holder assembly covers more than 5 percent of the stack cross-sectional area (see section 8.1.2).

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at stack temperature. The PM mass is determined gravimetrically after the removal of uncombined water.

3.0 Definitions

Same as Method 5, section 3.0.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 17–1. The sampling train components and operation and maintenance are very similar to Method 5, which should be consulted for details.

6.1.1 Probe Nozzle, Differential Pressure Gauge, Metering System, Barometer, Gas Density Determination Equipment. Same as in Method 5, sections 6.1.1, 6.1.4, 6.1.8, 6.1.9, and 6.1.10, respectively.

6.1.2 Filter Holder. The in-stack filter holder shall be constructed of borosilicate or

quartz glass, or stainless steel. If a gasket is used, it shall be made of silicone rubber, Teflon, or stainless steel. Other holder and gasket materials may be used, subject to the approval of the Administrator. The filter holder shall be designed to provide a positive seal against leakage from the outside or around the filter.

6.1.3 Probe Extension. Any suitable rigid probe extension may be used after the filter holder.

6.1.4 Pitot Tube. Same as in Method 5, section 6.1.3.

6.1.4.1 It is recommended (1) that the pitot tube have a known baseline coefficient, determined as outlined in section 10 of Method 2; and (2) that this known coefficient be preserved by placing the pitot tube in an interference-free arrangement with respect to the sampling nozzle, filter holder, and temperature sensor (see Figure 17–1). Note that the 1.9 cm (¾-in.) free-space between the nozzle and pitot tube shown in Figure 17–1, is based on a 1.3 cm (½-in.) ID nozzle. If the sampling train is designed for sampling at higher flow rates than that described in APTD-0581, thus necessitating the use of larger sized nozzles, the free-space shall be 1.9 cm (¾-in.) with the largest sized nozzle in place.

6.1.4.2 Source-sampling assemblies that do not meet the minimum spacing requirements of Figure 17–1 (or the equivalent of these requirements, *e.g.*, Figure 2–4 of Method 2) may be used; however, the pitot tube coefficients of such assemblies shall be determined by calibration, using methods subject to the approval of the Administrator.

6.1.5 Condenser. It is recommended that the impinger system or alternatives described in Method 5 be used to determine the moisture content of the stack gas. Flexible tubing may be used between the probe extension and condenser. Long tubing lengths may affect the moisture determination.

6.2 Sample Recovery. Probe-liner and probe-nozzle brushes, wash bottles, glass sample storage containers, petri dishes, graduated cylinder and/or balance, plastic storage containers, funnel and rubber policeman, funnel. Same as in Method 5, sections 6.2.1 through 6.2.8, respectively.

6.3 Sample Analysis. Glass weighing dishes, desiccator, analytical balance, balance, beakers, hygrometer, temperature sensor. Same as in Method 5, sections 6.3.1 through 6.3.7, respectively.

7.0 Reagents and Standards

7.1 Sampling. Filters, silica gel, water, crushed ice, stopcock grease. Same as in Method 5, sections 7.1.1, 7.1.2, 7.1.3, 7.1.4, and 7.1.5, respectively. Thimble glass fiber filters may also be used.

7.2 Sample Recovery. Acetone (reagent grade). Same as in Method 5, section 7.2.

7.3 Sample Analysis. Acetone and Desiccant. Same as in Method 5, sections 7.3.1 and 7.3.2, respectively.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling.

8.1.1 Pretest Preparation. Same as in Method 5, section 8.1.1.

8.1.2 Preliminary Determinations. Same as in Method 5, section 8.1.2, except as follows: Make a projected-area model of the probe extension-filter holder assembly, with the pitot tube face openings positioned along the centerline of the stack, as shown in Figure 17–2. Calculate the estimated cross-section blockage, as shown in Figure 17–2. If the blockage exceeds 5 percent of the duct cross sectional area, the tester has the following options exist: (1) a suitable out-of-stack filtration method may be used instead of in-stack filtration; or (2) a special in-stack arrangement, in which the sampling and velocity measurement sites are separate, may be used; for details concerning this approach, consult with the Administrator (see also Reference 1 in section 17.0). Select a probe extension length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probes.

8.1.3 Preparation of Sampling Train. Same as in Method 5, section 8.1.3, except the following: Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as not to allow the sample gas stream to circumvent the filter. Check filter for tears after assembly is completed. Mark the probe extension with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point. Assemble the train as in Figure 17–1, using a very light coat of silicone grease on all ground glass joints and greasing only the outer portion (see APTD–0576) to avoid possibility of contamination by the silicone grease. Place crushed ice around the impingers.

8.1.4 Leak-Check Procedures. Same as in Method 5, section 8.1.4, except that the filter holder is inserted into the stack during the sampling train leak-check. To do this, plug the inlet to the probe nozzle with a material that will be able to withstand the stack temperature. Insert the filter holder into the stack and wait approximately 5 minutes (or longer, if necessary) to allow the system to come to equilibrium with the temperature of the stack gas stream.

8.1.5 Sampling Train Operation. The operation is the same as in Method 5. Use a data sheet such as the one shown in Figure 5–3 of Method 5, except that the filter holder temperature is not recorded.

8.1.6 Calculation of Percent Isokinetic. Same as in Method 5, section 12.11.

8.2 Sample Recovery.

8.2.1 Proper cleanup procedure begins as soon as the probe extension assembly is removed from the stack at the end of the sampling period. Allow the assembly to cool.

8.2.2 When the assembly can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to prevent losing or gaining particulate matter. Do not cap off the probe tip tightly while the sampling train is cooling down as this would create a vacuum in the filter holder, forcing condenser water backward.

8.2.3 Before moving the sample train to the cleanup site, disconnect the filter holder-probe nozzle assembly from the probe extension; cap the open inlet of the probe extension. Be careful not to lose any condensate, if present. Remove the umbilical cord from the condenser outlet and cap the outlet. If a flexible line is used between the first impinger (or condenser) and the probe extension, disconnect the line at the probe extension and let any condensed water or liquid drain into the impingers or condenser. Disconnect the probe extension from the condenser; cap the probe extension outlet. After wiping off the silicone grease, cap off the condenser inlet. Ground glass stoppers, plastic caps, or serum caps (whichever are appropriate) may be used to close these openings.

8.2.4 Transfer both the filter holder-probe nozzle assembly and the condenser to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

8.2.5 Save a portion of the acetone used for cleanup as a blank. Take 200 ml of this acetone from the wash bottle being used and place it in a glass sample container labeled ''acetone blank.'' Inspect the train prior to and during disassembly and not any abnormal conditions. Treat the sample as discussed in Method 5, section 8.2.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization

The calibrations of the probe nozzle, pitot tube, metering system, temperature sensors, and barometer are the same as in Method 5, sections 10.1 through 10.3, 10.5, and 10.6, respectively.

11.0 Analytical Procedure

Same as in Method 5, section 11.0. Analytical data should be recorded on a form similar to that shown in Figure 5–6 of Method 5.

12.0 Data Analysis and Calculations.

Same as in Method 5, section 12.0.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

Same as in Method 5, section 16.0.

17.0 References

Same as in Method 5, section 17.0, with the addition of the following:

1. Vollaro, R.F. Recommended Procedure for Sample Traverses in Ducts Smaller than 12 Inches in Diameter. U.S. Environmental Protection Agency, Emission Measurement Branch. Research Triangle Park, NC. November 1976.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

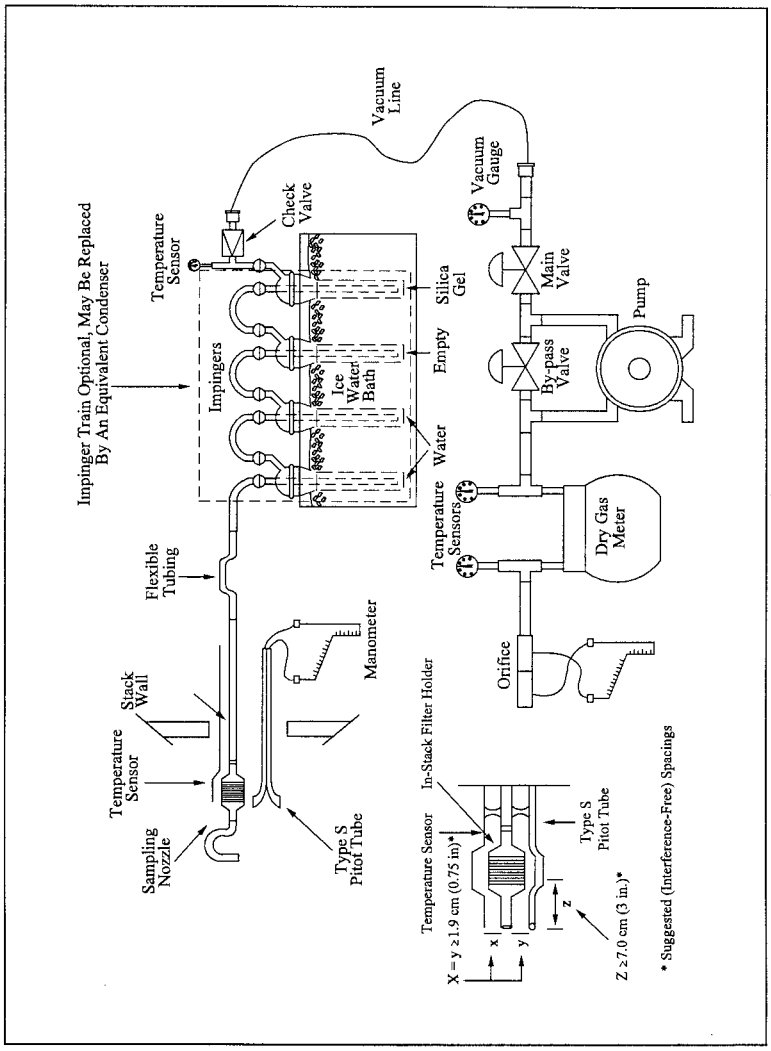


Figure 17-1. Particulate Matter Sampling Train with In-Stack Filter.

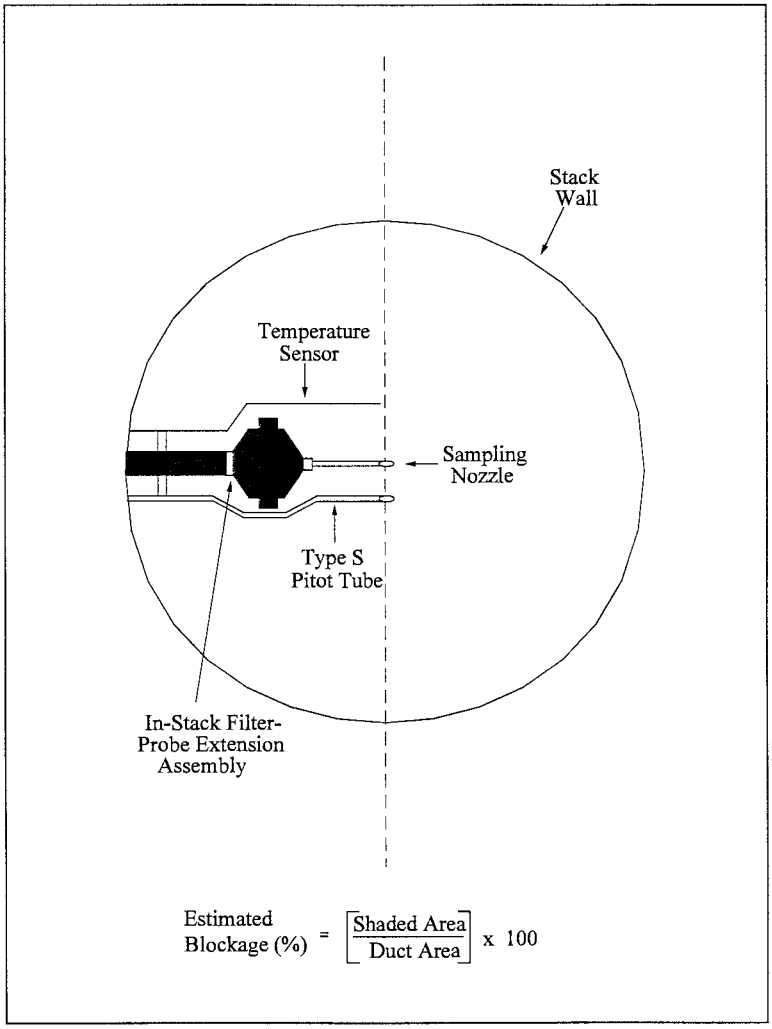


Figure 17-2. Projected-Area Model of Cross-Section Blockage (approximate average for a sample traverse) Caused by an In-Stack Filter Holder-Probe Extension Assembly.

METHOD 18—MEASUREMENT OF GASEOUS ORGANIC COMPOUND EMISSIONS BY GAS CHROMATOGRAPHY

NOTE: This method is not inclusive with respect to specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3.

NOTE: This method should not be attempted by persons unfamiliar with the performance characteristics of gas chromatography, nor by those persons who are unfamiliar with source sampling. Particular care

should be exercised in the area of safety concerning choice of equipment and operation in potentially explosive atmospheres.

1.0 Scope and Application

1.1 Analyte. Total gaseous organic compounds.

1.2 Applicability.

1.2.1 This method is designed to measure gaseous organics emitted from an industrial source. While designed for ppm level sources, some detectors are quite capable of detecting compounds at ambient levels, *e.g.*, ECD, ELCD, and helium ionization detectors. Some other types of detectors are evolving such that the sensitivity and applicability may well be in the ppb range in only a few years.

1.2.2 This method will not determine compounds that (1) are polymeric (high molecular weight), (2) can polymerize before analysis, or (3) have very low vapor pressures at stack or instrument conditions.

1.3 Range. The lower range of this method is determined by the sampling system; adsorbents may be used to concentrate the sample, thus lowering the limit of detection below the 1 part per million (ppm) typically achievable with direct interface or bag sampling. The upper limit is governed by GC detector saturation or column overloading; the upper range can be extended by dilution of sample with an inert gas or by using smaller volume gas sampling loops. The upper limit can also be governed by condensation of higher boiling compounds.

1.4 Sensitivity. The sensitivity limit for a compound is defined as the minimum detectable concentration of that compound, or the concentration that produces a signal-to-noise ratio of three to one. The minimum detectable concentration is determined during the presurvey calibration for each compound.

2.0 Summary of Method

The major organic components of a gas mixture are separated by gas chromatography (GC) and individually quantified by flame ionization, photoionization, electron capture, or other appropriate detection principles. The retention times of each separated component are compared with those of known compounds under identical conditions. Therefore, the analyst confirms the identity and approximate concentrations of the organic emission components beforehand. With this information, the analyst then prepares or purchases commercially available standard mixtures to calibrate the GC under conditions identical to those of the samples. The analyst also determines the need for sample dilution to avoid detector saturation, gas stream filtration to eliminate particulate matter, and prevention of moisture condensation.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Resolution interferences that may occur can be eliminated by appropriate GC column and detector choice or by shifting the retention times through changes in the column flow rate and the use of temperature programming.

4.2 The analytical system is demonstrated to be essentially free from contaminants by periodically analyzing blanks that consist of hydrocarbon-free air or nitrogen.

4.3 Sample cross-contamination that occurs when high-level and low-level samples or standards are analyzed alternately is best dealt with by thorough purging of the GC sample loop between samples.

4.4 To assure consistent detector response, calibration gases are contained in dry air. To adjust gaseous organic concentrations when water vapor is present in the sample, water vapor concentrations are determined for those samples, and a correction factor is applied.

4.5 The gas chromatograph run time must be sufficient to clear all eluting peaks from the column before proceeding to the next run (in order to prevent sample carryover).

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

6.0 Equipment and Supplies

6.1 Equipment needed for the presurvey sampling procedure can be found in section 16.1.1.

6.2 Equipment needed for the integrated bag sampling and analysis procedure can be found in section 8.2.1.1.1.

6.3 Equipment needed for direct interface sampling and analysis can be found in section 8.2.2.1.

6.4 Equipment needed for the dilution interface sampling and analysis can be found in section 8.2.3.1.

6.5 Equipment needed for adsorbent tube sampling and analysis can be found in section 8.2.4.1.

7.0 Reagents and Standards

7.1 Reagents needed for the presurvey sampling procedure can be found in section 16.1.2.

8.0 Sample Collection, Preservation, Storage, and Transport

8.2 Final Sampling and Analysis Procedure. Considering safety (flame hazards) and the source conditions, select an appropriate sampling and analysis procedure (Section 8.2.1, 8.2.2, 8.2.3 or 8.2.4). In situations where a hydrogen flame is a hazard and no intrinsically safe GC is suitable, use the flexible bag collection technique or an adsorption technique.

8.2.1 Integrated Bag Sampling and Analysis.

8.2.1.1 Evacuated Container Sampling Procedure. In this procedure, the bags are filled by evacuating the rigid air-tight container holding the bags. Use a field sample data sheet as shown in Figure 18–10. Collect triplicate samples from each sample location.

8.2.1.1.1 Apparatus.

8.2.1.1.1.1 Probe. Stainless steel, Pyrex glass, or Teflon tubing probe, according to the duct temperature, with Teflon tubing of sufficient length to connect to the sample bag. Use stainless steel or Teflon unions to connect probe and sample line.

8.2.1.1.1.2 Quick Connects. Male (2) and female (2) of stainless steel construction.

8.2.1.1.1.3 Needle Valve. To control gas flow.

8.2.1.1.1.4 Pump. Leakless Teflon-coated diaphragm-type pump or equivalent. To deliver at least 1 liter/min.

8.2.1.1.1.5 Charcoal Adsorption Tube. Tube filled with activated charcoal, with glass wool plugs at each end, to adsorb organic vapors.

8.2.1.1.1.6 Flowmeter. 0 to 500-ml flow range; with manufacturer's calibration curve.

8.2.1.1.2 Sampling Procedure. To obtain a sample, assemble the sample train as shown in Figure 18–9. Leak-check both the bag and the container. Connect the vacuum line from the needle valve to the Teflon sample line from the probe. Place the end of the probe at the centroid of the stack or at a point no closer to the walls than 1 in., and start the pump. Set the flow rate so that the final volume of the sample is approximately 80 percent of the bag capacity. After allowing sufficient time to purge the line several times, connect the vacuum line to the bag, and evacuate until the rotameter indicates no flow. Then position the sample and vacuum lines for sampling, and begin the actual sampling, keeping the rate proportional to the stack velocity. As a precaution, direct the gas exiting the rotameter away from sampling personnel. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Record the source temperature, barometric pressure, ambient temperature, sampling flow rate, and initial and final sampling time on the data sheet shown in Figure 18–10. Protect the bag and its container from sunlight. Record the time lapsed between sample collection and analysis, and then conduct the recovery procedure in Section 8.4.2.

8.2.1.2 Direct Pump Sampling Procedure. Follow 8.2.1.1, except place the pump and needle valve between the probe and the bag. Use a pump and needle valve constructed of inert material not affected by the stack gas. Leak-check the system, and then purge with stack gas before connecting to the previously evacuated bag.

8.2.1.3 Explosion Risk Area Bag Sampling Procedure. Follow 8.2.1.1 except replace the pump with another evacuated can (see Figure 18–9a). Use this method whenever there is a possibility of an explosion due to pumps, heated probes, or other flame producing equipment.

8.2.1.4 Other Modified Bag Sampling Procedures. In the event that condensation is observed in the bag while collecting the sample and a direct interface system cannot be used, heat the bag during collection and maintain it at a suitably elevated temperature during all subsequent operations. (Note: Take care to leak-check the system prior to the dilutions so as not to create a potentially explosive atmosphere.) As an alternative, collect the sample gas, and simultaneously dilute it in the bag.

8.2.1.4.1 First Alternative Procedure. Heat the box containing the sample bag to 120 °C (±5 °C). Then transport the bag as rapidly as possible to the analytical area while maintaining the heating, or cover the box with an insulating blanket. In the analytical area, keep the box heated to 120 °C (±5 °C) until analysis. Be sure that the method of heating the box and the control for the heating circuit are compatible with the safety restrictions required in each area.

8.2.1.4.2 Second Alternative Procedure. Prefill the bag with a known quantity of inert gas. Meter the inert gas into the bag according to the procedure for the preparation of gas concentration standards of volatile liquid materials (Section 10.1.2.2), but eliminate the midget impinger section. Take the partly filled bag to the source, and meter the source gas into the bag through heated sampling lines and a heated flowmeter, or Teflon positive displacement pump. Verify the dilution factors before sampling each bag through dilution and analysis of gases of known concentration.

8.2.1.5 Analysis of Bag Samples.

8.2.1.5.1 Apparatus. Same as section 8.1. A minimum of three gas standards are required.

8.2.1.5.2 Procedure.

8.2.1.5.2.1 Establish proper GC operating conditions as described in section 10.2, and record all data listed in Figure 18–7. Prepare the GC so that gas can be drawn through the sample valve. Flush the sample loop with

calibration gas mixture, and activate the valve (sample pressure at the inlet to the GC introduction valve should be similar during calibration as during actual sample analysis). Obtain at least three chromatograms for the mixture. The results are acceptable when the peak areas for the three injections agree to within 5 percent of their average. If they do not agree, run additional samples or correct the analytical techniques until this requirement is met. Then analyze the other two calibration mixtures in the same manner. Prepare a calibration curve as described in section 10.2.

8.2.1.5.2.2 Analyze the three source gas samples by connecting each bag to the sampling valve with a piece of Teflon tubing identified with that bag. Analyze each bag sample three times. Record the data in Figure 18–11. If certain items do not apply, use the notation ''N.A.'' If the bag has been maintained at an elevated temperature as described in section 8.2.1.4, determine the stack gas water content by Method 4. After all samples have been analyzed, repeat the analysis of the mid-level calibration gas for each compound. Compare the average response factor of the pre- and post-test analysis for each compound. If they differ by >5percent, analyze the other calibration gas levels for that compound, and prepare a calibration curve using all the pre- and post-test calibration gas mixture values. If the two response factor averages (pre-and post-test) differ by less than 5 percent from their mean value, the tester has the option of using only the pre-test calibration curve to generate the concentration values.

8.2.1.6 Determination of Bag Water Vapor Content. Measure the ambient temperature and barometric pressure near the bag. From a water saturation vapor pressure table, determine and record the water vapor content of the bag as a decimal figure. (Assume the relative humidity to be 100 percent unless a lesser value is known.) If the bag has been maintained at an elevated temperature as described in section 8.2.1.4, determine the stack gas water content by Method 4.

8.2.1.8 Emission Calculations. From the calibration curve described in section 8.2.1.5, select the value of C_s that corresponds to the peak area. Calculate the concentration C_c in ppm, dry basis, of each organic in the sample using Equation 18–5 in section 12.6.

8.2.2 Direct Interface Sampling and Analysis Procedure. The direct interface procedure can be used provided that the moisture content of the gas does not interfere with the analysis procedure, the physical requirements of the equipment can be met at the site, and the source gas concentration falls within the linear range of the detector. Adhere to all safety requirements with this method.

8.2.2.1 Apparatus.

8.2.2.1.1 Probe. Constructed of stainless steel, Pyrex glass, or Teflon tubing as dictated by duct temperature and reactivity of target compounds. A filter or glass wool plug may be needed if particulate is present in the stack gas. If necessary, heat the probe with heating tape or a special heating unit capable of maintaining a temperature greater than 110 °C.

8.2.2.1.2 Sample Lines. 6.4-mm OD (or other diameter as needed) Teflon lines, heat-traced to prevent condensation of material (greater than 110 °C).

8.2.2.1.3 Quick Connects. To connect sample line to gas sampling valve on GC instrument and to pump unit used to withdraw source gas. Use a quick connect or equivalent on the cylinder or bag containing calibration gas to allow connection of the calibration gas to the gas sampling valve.

8.2.2.1.4 Thermocouple Readout Device. Potentiometer or digital thermometer, to measure source temperature and probe temperature.

8.2.2.1.5 Heated Gas Sampling Valve. Of two-position, six-port design, to allow sample loop to be purged with source gas or to direct source gas into the GC instrument.

8.2.2.1.6 Needle Valve. To control gas sampling rate from the source.

8.2.2.1.7 Pump. Leakless Teflon-coated diaphragm-type pump or equivalent, capable of at least 1 liter/minute sampling rate.

8.2.2.1.8 Flowmeter. Of suitable range to measure sampling rate.

8.2.2.1.9 Charcoal Adsorber. To adsorb organic vapor vented from the source to prevent exposure of personnel to source gas.

8.2.2.1.10 Gas Cylinders. Carrier gas, oxygen and fuel as needed to run GC and detector.

8.2.2.1.11 Gas Chromatograph. Capable of being moved into the field, with detector, heated gas sampling valve, column required to complete separation of desired components, and option for temperature programming.

8.2.2.1.12 Recorder/Integrator. To record results.

8.2.2.2 Procedure. Calibrate the GC using the procedures in section 8.2.1.5.2.1. To obtain a stack gas sample, assemble the sampling system as shown in Figure 18–12. Make sure all connections are tight. Turn on the probe and sample line heaters. As the temperature of the probe and heated line approaches the target temperature as indicated on the thermocouple readout device, control the heating to maintain a temperature greater than 110 °C. Conduct a 3-point calibration of the GC by analyzing each gas mixture in triplicate. Generate a calibration curve. Place the inlet of the probe at the centroid of the duct, or at a point no closer to the walls than 1 m, and draw source gas into the probe, heated line, and sample loop. After thorough flushing, analyze the stack gas sample using the same conditions as for

the calibration gas mixture. For each run, sample, analyze, and record five consecutive samples. A test consists of three runs (five samples per run times three runs, for a total of fifteen samples). After all samples have been analyzed, repeat the analysis of the mid-level calibration gas for each compound. For each calibration standard, compare the pre- and post-test average response factors (RF) for each compound. If the two calibration RF values (pre- and post-analysis) differ by more than 5 percent from their mean value, then analyze the other calibration gas levels for that compound and determine the stack gas sample concentrations by comparison to both calibration curves (this is done by preparing a calibration curve using all the pre- and post-test calibration gas mixture values.) If the two calibration RF values differ by less than 5 percent from their mean value, the tester has the option of using only the pre-test calibration curve to generate the concentration values. Record this calibration data and the other required data on the data sheet shown in Figure 18–11, deleting the dilution gas information.

NOTE: Take care to draw all samples and calibration mixtures through the sample loop at the same pressure.

8.2.2.3 Determination of Stack Gas Moisture Content. Use Method 4 to measure the stack gas moisture content.

8.2.2.5 Emission Calculations. Same as section 8.2.1.8.

8.2.3 Dilution Interface Sampling and Analysis Procedure. Source samples that contain a high concentration of organic materials may require dilution prior to analysis to prevent saturating the GC detector. The apparatus required for this direct interface procedure is basically the same as that described in the section 8.2.2, except a dilution system is added between the heated sample line and the gas sampling valve. The apparatus is arranged so that either a 10:1 or 100:1 dilution of the source gas can be directed to the chromatograph. A pump of larger capacity is also required, and this pump must be heated and placed in the system between the sample line and the dilution apparatus.

8.2.3.1 Apparatus. The equipment required in addition to that specified for the direct interface system is as follows:

8.2.3.1.1 Sample Pump. Leakless Teflon-coated diaphragm-type that can withstand being heated to 120 °C and deliver 1.5 liters/minute.

8.2.3.1.2 Dilution Pumps. Two Model A–150 Komhyr Teflon positive displacement type delivering 150 cc/minute, or equivalent. As an option, calibrated flowmeters can be used in conjunction with Teflon-coated diaphragm pumps.

8.2.3.1.3 Valves. Two Teflon three-way valves, suitable for connecting to Teflon tubing.

8.2.3.1.4 Flowmeters. Two, for measurement of diluent gas.

8.2.3.1.5 Diluent Gas with Cylinders and Regulators. Gas can be nitrogen or clean dry air, depending on the nature of the source gases.

8.2.3.1.6 Heated Box. Suitable for being heated to 120 °C, to contain the three pumps, three-way valves, and associated connections. The box should be equipped with quick connect fittings to facilitate connection of: (1) the heated sample line from the probe, (2) the gas sampling valve, (3) the calibration gas mixtures, and (4) diluent gas lines. A schematic diagram of the components and connections is shown in Figure 18–13. The heated box shown in Figure 18–13 is designed to receive a heated line from the probe. An optional design is to build a probe unit that attaches directly to the heated box. In this way, the heated box contains the controls for the probe heaters, or, if the box is placed against the duct being sampled, it may be possible to eliminate the probe heaters. In either case, a heated Teflon line is used to connect the heated box to the gas sampling valve on the chromatograph.

NOTE: Care must be taken to leak-check the system prior to the dilutions so as not to create a potentially explosive atmosphere.

8.2.3.2 Procedure.

8.2.3.2.1 Assemble the apparatus by connecting the heated box, shown in Figure 18–13, between the heated sample line from the probe and the gas sampling valve on the chromatograph. Vent the source gas from the gas sampling valve directly to the charcoal filter, eliminating the pump and rotameter. Heat the sample probe, sample line, and heated box. Insert the probe and source thermocouple at the centroid of the duct, or to a point no closer to the walls than 1 m. Measure the source temperature, and adjust all heating units to a temperature 0 to 3 °C above this temperature. If this temperature is above the safe operating temperature of the Teflon components, adjust the heating to maintain a temperature high enough to prevent condensation of water and organic compounds (greater than 110 °C). Calibrate the GC through the dilution system by following the procedures in section 8.2.1.5.2.1. Determine the concentration of the diluted calibration gas using the dilution factor and the certified concentration of the calibration gas. Record the pertinent data on the data sheet shown in Figure 18–11.

8.2.3.2.2 Once the dilution system and GC operations are satisfactory, proceed with the analysis of source gas, maintaining the same dilution settings as used for the standards.

8.2.3.2.3 Analyze the audit samples using either the dilution system, or directly connect to the gas sampling valve as required. Record all data and report the results to the audit supervisor.

8.2.3.3 Determination of Stack Gas Moisture Content. Same as section 8.2.2.3.

8.2.3.4 Quality Assurance. Same as section 8.2.2.4.

8.2.3.5 Emission Calculations. Same as section 8.2.2.5, with the dilution factor applied.

8.2.4 Adsorption Tube Procedure. Any commercially available adsorbent is allowed for the purposes of this method, as long as the recovery study criteria in section 8.4.3 are met. Help in choosing the adsorbent may be found by calling the distributor, or the tester may refer to National Institute for Occupational Safety and Health (NIOSH) methods for the particular organics to be sampled. For some adsorbents, the principal interferent will be water vapor. If water vapor is thought to be a problem, the tester may place a midget impinger in an ice bath before the adsorbent tubes. If this option is chosen, the water catch in the midget impinger shall be analyzed for the target compounds. Also, the spike for the recovery study (in section 8.4.3) shall be conducted in both the midget impinger and the adsorbent tubes. The combined recovery (add the recovered amount in the impinger and the adsorbent tubes to calculate R) shall then meet the criteria in section 8.4.3.

NOTE: Post-test leak-checks are not allowed for this technique since this can result in sample contamination.

8.2.4.1 Additional Apparatus. The following items (or equivalent) are suggested.

8.2.4.1.1 Probe. Borosilicate glass or stainless steel, approximately 6-mm ID, with a heating system if water condensation is a problem, and a filter (either in-stack or out-of-stack, heated to stack temperature) to remove particulate matter. In most instances, a plug of glass wool is a satisfactory filter.

8.2.4.1.2 Flexible Tubing. To connect probe to adsorption tubes. Use a material that exhibits minimal sample adsorption.

8.2.4.1.3 Leakless Sample Pump. Flow controlled, constant rate pump, with a set of limiting (sonic) orifices.

8.2.4.1.4 Bubble-Tube Flowmeter. Volume accuracy within 1 percent, to calibrate pump.

8.2.4.1.5 Stopwatch. To time sampling and pump rate calibration.

8.2.4.1.6 Adsorption Tubes. Precleaned adsorbent, with mass of adsorbent to be determined by calculating breakthrough volume and expected concentration in the stack.

8.2.4.1.7 Barometer. Accurate to 5 mm Hg, to measure atmospheric pressure during sampling and pump calibration.

8.2.4.1.8 Rotameter. O to 100 cc/min, to detect changes in flow rate during sampling.

8.2.4.2 Sampling and Analysis.

8.2.4.2.1 Calibrate the pump and limiting orifice flow rate through adsorption tubes with the bubble tube flowmeter before sampling. The sample system can be operated as a ''recirculating loop'' for this operation. Record the ambient temperature and barometric pressure. Then, during sampling, use the rotameter to verify that the pump and orifice sampling rate remains constant.

8.2.4.2.2 Use a sample probe, if required, to obtain the sample at the centroid of the duct or at a point no closer to the walls than 1 m. Minimize the length of flexible tubing between the probe and adsorption tubes. Several adsorption tubes can be connected in series, if the extra adsorptive capacity is needed. Adsorption tubes should be maintained vertically during the test in order to prevent channeling. Provide the gas sample to the sample system at a pressure sufficient for the limiting orifice to function as a sonic orifice. Record the total time and sample flow rate (or the number of pump strokes), the barometric pressure, and ambient temperature. Obtain a total sample volume commensurate with the expected concentration(s) of the volatile organic(s) present and recommended sample loading factors (weight sample per weight adsorption media). Laboratory tests prior to actual sampling may be necessary to predetermine this volume. If water vapor is present in the sample at concentrations above 2 to 3 percent, the adsorptive capacity may be severely reduced. Operate the gas chromatograph according to the manufacturer's instructions. After establishing optimum conditions, verify and document these conditions during all operations. Calibrate the instrument and then analyze the emission samples.

8.2.4.3 Standards and Calibration. If using thermal desorption, obtain calibration gases using the procedures in section 10.1. If using solvent extraction, prepare liquid standards in the desorption solvent. Use a minimum of three different standards; select the concentrations to bracket the expected average sample concentration. Perform the calibration before and after each day's sample analyses using the procedures in section 8.2.1.5.2.1.

8.2.4.4 Quality Assurance.

8.2.4.4.1 Determine the recovery efficiency of the pollutants of interest according to section 8.4.3.

8.2.4.4.2 Determination of Sample Collection Efficiency (Optional). If sample breakthrough is thought to be a problem, a routine procedure for determining breakthrough is to analyze the primary and backup portions of the adsorption tubes separately. If the backup portion exceeds 10 percent of the total amount (primary and back-up), it is usually a sign of sample breakthrough. For the purposes of this method, only the recovery efficiency value (Section 8.4.3) is used to determine the appropriateness of the sampling and analytical procedure.

8.2.4.4.3 Volume Flow Rate Checks. Perform this check immediately after sampling with all sampling train components in place.

Use the bubble-tube flowmeter to measure the pump volume flow rate with the orifice used in the test sampling, and record the result. If it has changed by more than 5 but less than 20 percent, calculate an average flow rate for the test. If the flow rate has changed by more than 20 percent, recalibrate the pump and repeat the sampling.

8.2.4.4.4 Calculations. Correct all sample volumes to standard conditions. If a sample dilution system has been used, multiply the results by the appropriate dilution ratio. Correct all results according to the applicable procedure in section 8.4.3. Report results as ppm by volume, dry basis.

8.3 Reporting of Results. At the completion of the field analysis portion of the study, ensure that the data sheets shown in Figure 18–11 have been completed. Summarize this data on the data sheets shown in Figure 18–15.

8.4 Recovery Study. After conducting the presurvey and identifying all of the pollutants of interest, conduct the appropriate recovery study during the test based on the sampling system chosen for the compounds of interest.

8.4.1 Recovery Study for Direct Interface or Dilution Interface Sampling. If the procedures in section 8.2.2 or 8.2.3 are to be used to analyze the stack gas, conduct the calibration procedure as stated in section 8.2.2.2 or 8.2.3.2, as appropriate. Upon successful completion of the appropriate calibration procedure, attach the mid-level calibration gas for at least one target compound to the inlet of the probe or as close as possible to the inlet of the probe, but before the filter. Repeat the calibration procedure by sampling and analyzing the mid-level calibration gas through the entire sampling and analytical system in triplicate. The mean of the calibration gas response sampled through the probe shall be within 10 percent of the analyzer response. If the difference in the two means is greater than 10 percent, check for leaks throughout the sampling system and repeat the analysis of the standard through the sampling system until this criterion is met.

8.4.2 Recovery Study for Bag Sampling.

8.4.2.1 Follow the procedures for the bag sampling and analysis in section 8.2.1. After analyzing all three bag samples, choose one of the bag samples and tag this bag as the spiked bag. Spike the chosen bag sample with a known mixture (gaseous or liquid) of all of the target pollutants. The theoretical concentration, in ppm, of each spiked compound in the bag shall be 40 to 60 percent of the average concentration measured in the three bag samples. If a target compound was not detected in the bag samples, the concentration of that compound to be spiked shall be 5 times the limit of detection for that compound. Store the spiked bag for the same period of time as the bag samples collected in the field. After the appropriate storage time has passed, analyze the spiked bag three times. Calculate the average fraction recovered (R) of each spiked target compound with the equation in section 12.7.

8.4.2.2 For the bag sampling technique to be considered valid for a compound, $0.70 \leq R \leq 1.30$. If the R value does not meet this criterion for a target compound, the sampling technique is not acceptable for that compound, and therefore another sampling technique shall be evaluated for acceptance (by repeating the recovery study with another sampling technique). Report the R value in the test report and correct all field measurements with the calculated R value for that compound by using the equation in section 12.8.

8.4.3 Recovery Study for Adsorption Tube Sampling. If following the adsorption tube procedure in section 8.2.4, conduct a recovery study of the compounds of interest during the actual field test. Set up two identical sampling trains. Collocate the two sampling probes in the stack. The probes shall be placed in the same horizontal plane, where the first probe tip is 2.5 cm from the outside edge of the other. One of the sampling trains shall be designated the spiked train and the other the unspiked train. Spike all of the compounds of interest (in gaseous or liquid form) onto the adsorbent tube(s) in the spiked train before sampling. The mass of each spiked compound shall be 40 to 60 percent of the mass expected to be collected with the unspiked train. Sample the stack gas into the two trains simultaneously. Analyze the adsorbents from the two trains utilizing identical analytical procedures and instrumentation. Determine the fraction of spiked compound recovered (R) using the equations in section 12.9.

8.4.3.1 Repeat the procedure in section 8.4.3 twice more, for a total of three runs. In order for the adsorbent tube sampling and analytical procedure to be acceptable for a compound, $0.70 \leq R \leq 1.30$ (R in this case is the average of three runs). If the average R value does not meet this criterion for a target compound, the sampling technique is not acceptable for that compound, and therefore another sampling technique shall be evaluated for acceptance (by repeating the recovery study with another sampling technique). Report the R value in the test report and correct all field measurements with the calculated R value for that compound by using the equation in section 12.8.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures

Section	Quality control measure	Effect
8.4.1	Recovery study for direct interface or dilution interface sampling.	Ensure that there are no significant leaks in the sampling system.
8.4.2	Recovery study for bag sampling	Demonstrate that proper sampling/analysis procedures were selected.
8.4.3	Recovery study for adsorption tube sampling.	Demonstrate that proper sampling/analysis procedures were selected.

10.0 Calibration and Standardization.

10.1 Calibration Standards. Obtain calibration gas standards for each target compound to be analyzed. Commercial cylinder gases certified by the manufacturer to be accurate to within 1 percent of the certified label value are preferable, although cylinder gases certified by the manufacturer to 2 percent accuracy are allowed. Another option allowed by this method is for the tester to obtain high concentration certified cylinder gases and then use a dilution system meeting the requirements of Test Method 205, 40 CFR Part 51, Appendix M to make multilevel calibration gas standards. Prepare or obtain enough calibration standards so that there are three different concentrations of each organic compound expected to be measured in the source sample. For each organic compound, select those concentrations that bracket the concentrations expected in the source samples. A calibration standard may contain more than one organic compound. If samples are collected in adsorbent tubes and extracted using solvent extraction, prepare or obtain standards in the same solvent used for the sample extraction procedure. Verify the stability of all standards for the time periods they are used.

10.2 Preparation of Calibration Curves.

10.2.1 Establish proper GC conditions, then flush the sampling loop for 30 seconds. Allow the sample loop pressure to equilibrate to atmospheric pressure, and activate the injection valve. Record the standard concentration, attenuator factor, injection time, chart speed, retention time, peak area, sample loop temperature, column temperature, and carrier gas flow rate. Analyze each standard in triplicate.

10.2.2 Repeat this procedure for each standard. Prepare a graphical plot of concentration (C_s) versus the calibration area values. Perform a regression analysis, and draw the least square line.

11.0 Analytical Procedures

11.1 Analysis Development

11.1.1 Selection of GC Parameters

11.1.1.1 Column Choice. Based on the initial contact with plant personnel concerning the plant process and the anticipated emissions, choose a column that provides good resolution and rapid analysis time. The choice of an appropriate column can be aided by a literature search, contact with manufacturers of GC columns, and discussion with personnel at the emission source.

NOTE: Most column manufacturers keep excellent records on their products. Their technical service departments may be able to recommend appropriate columns and detector type for separating the anticipated compounds, and they may be able to provide information on interferences, optimum operating conditions, and column limitations. Plants with analytical laboratories may be able to provide information on their analytical procedures.

11.1.1.2 Preliminary GC Adjustment. Using the standards and column obtained in section 11.1.1.1, perform initial tests to determine appropriate GC conditions that provide good resolution and minimum analysis time for the compounds of interest.

11.1.1.3 Preparation of Presurvey Samples. If the samples were collected on an adsorbent, extract the sample as recommended by the manufacturer for removal of the compounds with a solvent suitable to the type of GC analysis. Prepare other samples in an appropriate manner.

11.1.1.4 Presurvey Sample Analysis.

11.1.1.4.1 Before analysis, heat the presurvey sample to the duct temperature to vaporize any condensed material. Analyze the samples by the GC procedure, and compare the retention times against those of the calibration samples that contain the components expected to be in the stream. If any compounds cannot be identified with certainty by this procedure, identify them by other means such as GC/mass spectroscopy (GC/MS) or GC/infrared techniques. A GC/MS system is recommended.

11.1.1.4.2 Use the GC conditions determined by the procedure of section 11.1.1.2 for the first injection. Vary the GC parameters during subsequent injections to determine the optimum settings. Once the optimum settings have been determined, perform repeat injections of the sample to determine the retention time of each compound. To inject a sample, draw sample through the loop at a constant rate (100 ml/min for 30 seconds). Be careful not to pressurize the gas in the loop. Turn off the pump and allow the gas in the sample loop to come to ambient pressure. Activate the sample valve, and record injection time, loop temperature, column temperature, carrier flow rate, chart speed, and attenuator setting. Calculate the retention

time of each peak using the distance from injection to the peak maximum divided by the chart speed. Retention times should be repeatable within 0.5 seconds.

11.1.1.4.3 If the concentrations are too high for appropriate detector response, a smaller sample loop or dilutions may be used for gas samples, and, for liquid samples, dilution with solvent is appropriate. Use the standard curves (Section 10.2) to obtain an estimate of the concentrations.

11.1.1.4.4 Identify all peaks by comparing the known retention times of compounds expected to be in the retention times of peaks in the sample. Identify any remaining unidentified peaks which have areas larger than 5 percent of the total using a GC/MS, or estimation of possible compounds by their retention times compared to known compounds, with confirmation by further GC analysis.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

B_{ws} = Water vapor content of the bag sample or stack gas, proportion by volume.
C_s = Concentration of the organic from the calibration curve, ppm.
G_v = Gas volume or organic compound injected, ml.
L_v = Liquid volume of organic injected, µl.
M = Molecular weight of organic, g/g-mole.
m_s = Total mass of compound measured on adsorbent with spiked train (µg).
m_u = Total mass of compound measured on adsorbent with unspiked train (µg).
m_v = Mass per volume of spiked compound measured (µg/L).
P_i = Barometric or absolute sample loop pressure at time of sample analysis, mm Hg.
P_m = Absolute pressure of dry gas meter, mm Hg.
P_r = Reference pressure, the barometric pressure or absolute sample loop pressure recorded during calibration, mm Hg.
P_s = Absolute pressure of syringe before injection, mm Hg.
q_c = Flow rate of the calibration gas to be diluted.
q_{c1} = Flow rate of the calibration gas to be diluted in stage 1.
q_{c2} = Flow rate of the calibration gas to be diluted in stage 2.
q_d = Diluent gas flow rate.
q_{d1} = Flow rate of diluent gas in stage 1.
q_{d2} = Flow rate of diluent gas in stage 2.
s = Theoretical concentration (ppm) of spiked target compound in the bag.
S = Theoretical mass of compound spiked onto adsorbent in spiked train (µg).
t = Measured average concentration (ppm) of target compound and source sample (analysis results subsequent to bag spiking)
T_i = Sample loop temperature at the time of sample analysis, °K.
T_m = Absolute temperature of dry gas meter, °K.
T_s = Absolute temperature of syringe before injection, °K.
u = Source sample average concentration (ppm) of target compound in the bag (analysis results before bag spiking).
V_m = Gas volume indicated by dry gas meter, liters.
v_s = volume of stack gas sampled with spiked train (L).
v_u = volume of stack gas sampled with unspiked train (L).
X = Mole or volume fraction of the organic in the calibration gas to be diluted.
Y = Dry gas meter calibration factor, dimensionless.
µl = Liquid organic density as determined, g/ml.
24.055 = Ideal gas molar volume at 293 °K and 760 mm Hg, liters/g-mole.
1000 = Conversion factor, ml/liter.
10^6 = Conversion to ppm.

12.2 Calculate the concentration, C_s, in ppm using the following equation:

$$C_s = \frac{10^6\left(\overline{X}q_c\right)}{q_c + q_d} \qquad \text{Eq. 18-1}$$

12.3 Calculate the concentration, C_s, in ppm of the organic in the final gas mixture using the following equation:

$$C_s = 10^6\,\overline{X}\left(\frac{q_{c1}}{q_{c1}+q_{d1}}\right)\left(\frac{q_{c2}}{q_{c2}+q_{d2}}\right) \qquad \text{Eq. 18-2}$$

12.4 Calculate each organic standard concentration, C_s, in ppm using the following equation:

$$C_s = \frac{G_v \times 10^6 \frac{293}{T_s} \frac{P_s}{760}}{V_m Y \frac{293}{T_m} \frac{P_m}{760} 1000} = \frac{G_v \times 10^3 \frac{P_s}{T_s} \frac{T_m}{P_m}}{V_m Y} \quad \text{Eq. 18-3}$$

12.5 Calculate each organic standard concentration, C_s, in ppm using the following equation:

$$C_s = \frac{\frac{L_v}{M}\rho\left(24.055 \times 10^6\right)}{V_m Y \frac{293}{T_m} \frac{P_m}{760} 1000} = 6.24 \times 10^4 \frac{L_v \rho T_m}{M V_m Y P_m} \quad \text{Eq. 18-4}$$

12.6 Calculate the concentration, C_c, in ppm, dry basis, of each organic is the sample using the following equation:

$$C_c = \frac{C_s P_r T_i F_r}{P_i T_r \left(1 - B_{ws}\right)} \quad \text{Eq. 18-5}$$

12.7 Calculate the average fraction recovered (R) of each spiked target compound using the following equation:

$$R = \frac{t - u}{s} \quad \text{Eq. 18-6}$$

12.8 Correct all field measurements with the calculated R value for that compound using the following equation:

$$\text{Reported Result} = \frac{\text{Measured Concentration (ppm)}}{R} \quad \text{Eq. 18-7}$$

12.9 Determine the mass per volume of spiked compound measured using the following equation:

$$m_v = \frac{m_s}{V_s} - \frac{m_u}{V_u} \qquad \text{Eq. 18-8}$$

12.10 Calculate the fraction of spiked compound recovered, R, using the following equation:

$$R = \frac{m_v \times v_s}{S} \qquad \text{Eq. 18-9}$$

13.0 Method Performance

13.1 Since a potential sample may contain a variety of compounds from various sources, a specific precision limit for the analysis of field samples is impractical. Precision in the range of 5 to 10 percent relative standard deviation (RSD) is typical for gas chromatographic techniques, but an experienced GC operator with a reliable instrument can readily achieve 5 percent RSD. For this method, the following combined GC/operator values are required.

(a) Precision. Triplicate analyses of calibration standards fall within 5 percent of their mean value.

(c) Recovery. After developing an appropriate sampling and analytical system for the pollutants of interest, conduct the procedure in section 8.4. Conduct the appropriate recovery study in section 8.4 at each sampling point where the method is being applied. Submit the data and results of the recovery procedure with the reporting of results under section 8.3.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Optional Presurvey and Presurvey Sampling.

NOTE: Presurvey screening is optional. Presurvey sampling should be conducted for sources where the target pollutants are not known from previous tests and/or process knowledge.

Perform a presurvey for each source to be tested. Refer to Figure 18–1. Some of the information can be collected from literature surveys and source personnel. Collect gas samples that can be analyzed to confirm the identities and approximate concentrations of the organic emissions.

16.1.1 Apparatus. This apparatus list also applies to sections 8.2 and 11.

16.1.1.1 Teflon Tubing. (Mention of trade names or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.) Diameter and length determined by connection requirements of cylinder regulators and the GC. Additional tubing is necessary to connect the GC sample loop to the sample.

16.1.1.2 Gas Chromatograph. GC with suitable detector, columns, temperature-controlled sample loop and valve assembly, and temperature programmable oven, if necessary. The GC shall achieve sensitivity requirements for the compounds under study.

16.1.1.3 Pump. Capable of pumping 100 ml/min. For flushing sample loop.

16.1.1.4 Flow Meter. To measure flow rates.

16.1.1.5 Regulators. Used on gas cylinders for GC and for cylinder standards.

16.1.1.6 Recorder. Recorder with linear strip chart is minimum acceptable. Integrator (optional) is recommended.

16.1.1.7 Syringes. 0.5-ml, 1.0- and 10-microliter size, calibrated, maximum accuracy (gas tight) for preparing calibration standards. Other appropriate sizes can be used.

16.1.1.8 Tubing Fittings. To plumb GC and gas cylinders.

16.1.1.9 Septa. For syringe injections.

16.1.1.10 Glass Jars. If necessary, clean, colored glass jars with Teflon-lined lids for condensate sample collection. Size depends on volume of condensate.

16.1.1.11 Soap Film Flowmeter. To determine flow rates.

16.1.1.12 Flexible Bags. Tedlar or equivalent, 10- and 50-liter capacity, for preparation of standards. (Verify through the manufacturer that the Tedlar alternative is suitable for the compound of interest and make this verifying information available for inspection.)

16.1.1.13 Dry Gas Meter with Temperature and Pressure Gauges. Accurate to ±2 percent, for preparation of gas standards.

16.1.1.14 Midget Impinger/Hot Plate Assembly. For preparation of gas standards.

16.1.1.15 Sample Flasks. For presurvey samples, must have gas-tight seals.

16.1.1.16 Adsorption Tubes. If necessary, blank tubes filled with necessary adsorbent (charcoal, Tenax, XAD–2, etc.) for presurvey samples.

16.1.1.17 Personnel Sampling Pump. Calibrated, for collecting adsorbent tube presurvey samples.

16.1.1.18 Dilution System. Calibrated, the dilution system is to be constructed following the specifications of an acceptable method.

16.1.1.19 Sample Probes. Pyrex or stainless steel, of sufficient length to reach centroid of stack, or a point no closer to the walls than 1 m.

16.1.1.20 Barometer. To measure barometric pressure.

16.1.2 Reagents.

16.1.2.1 Water. Deionized distilled.

16.1.2.2 Methylene chloride.

16.1.2.3 Calibration Gases. A series of standards prepared for every compound of interest.

16.1.2.4 Organic Compound Solutions. Pure (99.9 percent), or as pure as can reasonably be obtained, liquid samples of all the organic compounds needed to prepare calibration standards.

16.1.2.5 Extraction Solvents. For extraction of adsorbent tube samples in preparation for analysis.

16.1.2.6 Fuel. As recommended by the manufacturer for operation of the GC.

16.1.2.7 Carrier Gas. Hydrocarbon free, as recommended by the manufacturer for operation of the detector and compatibility with the column.

16.1.2.8 Zero Gas. Hydrocarbon free air or nitrogen, to be used for dilutions, blank preparation, and standard preparation.

16.1.3 Sampling.

16.1.3.1 Collection of Samples with Glass Sampling Flasks. Presurvey samples may be collected in precleaned 250-ml double-ended glass sampling flasks. Teflon stopcocks, without grease, are preferred. Flasks should be cleaned as follows: Remove the stopcocks from both ends of the flasks, and wipe the parts to remove any grease. Clean the stopcocks, barrels, and receivers with methylene chloride (or other non-target pollutant solvent, or heat and humidified air). Clean all glass ports with a soap solution, then rinse with tap and deionized distilled water. Place the flask in a cool glass annealing furnace, and apply heat up to 500 °C. Maintain at this temperature for 1 hour. After this time period, shut off and open the furnace to allow the flask to cool. Return the stopcocks to the flask receivers. Purge the assembly with high-purity nitrogen for 2 to 5 minutes. Close off the stopcocks after purging to maintain a slight positive nitrogen pressure. Secure the stopcocks with tape. Presurvey samples can be obtained either by drawing the gases into the previously evacuated flask or by drawing the gases into and purging the flask with a rubber suction bulb.

16.1.3.1.1 Evacuated Flask Procedure. Use a high-vacuum pump to evacuate the flask to the capacity of the pump; then close off the stopcock leading to the pump. Attach a 6-mm outside diameter (OD) glass tee to the flask inlet with a short piece of Teflon tubing. Select a 6-mm OD borosilicate sampling probe, enlarged at one end to a 12-mm OD and of sufficient length to reach the centroid of the duct to be sampled. Insert a glass wool plug in the enlarged end of the probe to remove particulate matter. Attach the other end of the probe to the tee with a short piece of Teflon tubing. Connect a rubber suction bulb to the third leg of the tee. Place the filter end of the probe at the centroid of the duct, and purge the probe with the rubber suction bulb. After the probe is completely purged and filled with duct gases, open the stopcock to the grab flask until the pressure in the flask reaches duct pressure. Close off the stopcock, and remove the probe from the duct. Remove the tee from the flask and tape the stopcocks to prevent leaks during shipment. Measure and record the duct temperature and pressure.

16.1.3.1.2 Purged Flask Procedure. Attach one end of the sampling flask to a rubber suction bulb. Attach the other end to a 6-mm OD glass probe as described in section 8.3.3.1.1. Place the filter end of the probe at the centroid of the duct, or at a point no closer to the walls than 1 m, and apply suction with the bulb to completely purge the probe and flask. After the flask has been purged, close off the stopcock near the suction bulb, and then close off the stopcock near the probe. Remove the probe from the duct, and disconnect both the probe and suction bulb. Tape the stopcocks to prevent leakage during shipment. Measure and record the duct temperature and pressure.

16.1.3.2 Flexible Bag Procedure. Any leak-free plastic (e.g., Tedlar, Mylar, Teflon) or plastic-coated aluminum (e.g., aluminized Mylar) bag, or equivalent, can be used to obtain the pre-survey sample. Use new bags, and leak-check them before field use. In addition, check the bag before use for contamination by filling it with nitrogen or air and analyzing the gas by GC at high sensitivity. Experience indicates that it is desirable to allow the inert gas to remain in the bag about 24 hours or longer to check for desorption of organics from the bag. Follow the leak-check and sample collection procedures given in Section 8.2.1.

16.1.3.3 Determination of Moisture Content. For combustion or water-controlled processes, obtain the moisture content from plant personnel or by measurement during the presurvey. If the source is below 59 °C, measure the wet bulb and dry bulb temperatures, and calculate the moisture content using a psychrometric chart. At higher temperatures, use Method 4 to determine the moisture content.

16.1.4 Determination of Static Pressure. Obtain the static pressure from the plant personnel or measurement. If a type S pitot tube and an inclined manometer are used, take care to align the pitot tube 90° from the direction of the flow. Disconnect one of the tubes to the manometer, and read the static pressure; note whether the reading is positive or negative.

16.1.5 Collection of Presurvey Samples with Adsorption Tube. Follow section 8.2.4 for presurvey sampling.

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Volume 1—O17–033–00267–3/$13
Volume 2—O17–033–00260–6/$11
Volume 3—O17–033–00261–4/$14
Volume 4—O17–033–00317–3/$7.25
Volume 5—O17–033–00349–1/$10
Volume 6—O17–033–00369–6/$9
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18.0 Tables, Diagrams, Flowcharts, and Validation Data

I. Name of company _____
Date _____
Address _____
_____
Contracts _____
Phone _____
Process to be sampled _____
_____
_____
Duct or vent to be sampled _____
_____
II. Process description _____
_____
_____
_____
_____
Raw material _____
_____
_____
Products _____
_____
_____
Operating cycle
Check: Batch _____ Continuous _____
Cyclic _____
Timing of batch or cycle _____
Best time to test _____
III. Sampling site _____
A. Description _____
Site decription _____
Duct shape and size _____

Material _____
Wall thickness _____ inches
Upstream distance _____ inches _____ diameter
Downstream distance _____ inches _____ diameter
Size of port _____
Size of access area _____
Hazards _____ Ambient temp. _____ °F

B. Properties of gas stream
Temperature _____ °C _____ °F, Data source _____
Velocity _____, Data source _____
Static pressure _____ inches H_2O, Data source _____
Moisture content _____%, Data source _____
Particulate content _____, Data source_____

Gaseous components
N_2 _____ % Hydrocarbons _____ ppm
O_2 _____% _____
CO _____ % _____ _____
CO_2 _____ % _____ _____
SO_2 _____ % _____ _____

Hydrocarbon components
_____ _____ ppm
_____ _____ ppm
_____ _____ ppm
_____ _____ ppm
_____ _____ ppm
_____ _____ ppm

C. Sampling considerations
Location to set up GC _____
_____
Special hazards to be considered _____
_____
Power available at duct _____
Power available for GC _____
Plant safety requirements _____
_____
Vehicle traffic rules _____
_____
Plant entry requirements _____
_____
Security agreements _____
_____
Potential problems _____
_____

D. Site diagrams. (Attach additional sheets if required).

Figure 18–1. Preliminary Survey Data Sheet

Components to be analyzed and Expected concentration

_____
_____
_____
_____
_____
_____
Suggested chromatographic column _____
_____
Column flow rate __ ml/min
Head pressure _____ mm Hg
Column temperature: Isothermal _____ °C, Programmed from _____ °C to _____ °C at _____ °C/min
Injection port/sample loop temperature _____ °C
Detector temperature _____ °C
Detector flow rates: Hydrogen _____ ml/min., head pressure _____ mm Hg, Air/Oxygen _____ ml/min., head pressure _____ mm Hg.
Chart speed _____ inches/minute
Compound data:
Compound and Retention time and Attenuation
_____
_____
_____
_____
_____

Figure 18–2. Chromatographic Conditions Data Sheet

FIGURE 18–3. PREPARATION OF STANDARDS IN TEDLAR OR TEDLAR-EQULIVALENT BAGS AND CALIBRATION CURVE

	Standards		
	Mixture #1	Mixture #2	Mixture #3
Standards Preparation Data:			
Organic:			
Bag number or identification.			
Dry gas meter calibration factor.			
Final meter reading (liters).			
Initial meter reading (liters).			
Metered volume (liters).			
Average meter temperature (°K).			
Average meter pressure, gauge (mm Hg).			
Average atmospheric perssure (mm Hg).			
Average meter pressure, absolute (mm Hg).			
Syringe temperature (°K) (see section 10.1.2.1).			
Syringe pressure, absolute (mm Hg) (see section 10.1.2.1).			
Volume of gas in syringe (ml) (Section 10.1.2.1).			
Density of liquid organic (g/ml) (Section 10.1.2.1).			
Volume of liquid in syringe (ml) (Section 10.1.2.1).			

FIGURE 18–3. PREPARATION OF STANDARDS IN TEDLAR OR TEDLAR-EQULIVALENT BAGS AND CALIBRATION CURVE—Continued

	Standards		
	Mixture #1	Mixture #2	Mixture #3
GC Operating Conditions:			
Sample loop volume (ml).			
Sample loop temperature (°C).			
Carrier gas flow rate (ml/min).			
Column temperature:			
Initial (°C).			
Rate change (°C/min).			
Final (°C).			
Organic Peak Identification and Calculated Concentrations:			
Injection time (24 hour clock).			
Distance to peak (cm).			
Chart speed (cm/min).			
Organic retention time (min).			
Attenuation factor.			
Peak height (mm).			
Peak area (mm_2).			
Peak area * attenuation factor (mm_2).			
Calculated concentration (ppm) (Equation 18–3 or 18–4).			

Plot peak area * attenuation factor against calculated concentration to obtain calibration curve.

Flowmeter number or identification _____
Flowmeter Type _____
Method: Bubble meter____ Spirometer____
Wet test meter ____
Readings at laboratory conditions:

Laboratory temperature (T_{lab}) ____ °K
Laboratory barometric pressure (P_{lab})____ mm Hg
Flow data:

FLOWMETER

Reading (as marked)	Temp. (°K)	Pressure (absolute)

CALIBRATION DEVICE

Time (min)	Gas volume [a]	Flow rate [b]

[a] Vol. of gas may be measured in milliliters, liters or cubic feet.
[b] Convert to standard conditions (20 °C and 760 mm Hg). Plot flowmeter reading against flow rate (standard conditions), and draw a smooth curve. If the flowmeter being calibrated is a rotameter or other flow device that is viscosity dependent, it may be necessary to generate a ''family'' of calibration curves that cover the operating pressure and temperature ranges of the flowmeter. While the following technique should be verified before application, it may be possible to calculate flow rate reading for rotameters at standard conditions Q_{std} as follows:

$$Q_{std} = Q_{lab}\left(\frac{760 \times T_{lab}}{P_{lab} \times 293}\right)^{1/2}$$

Flow rate (laboratory conditions)	Flow rate (STD conditions)

Figure 18–4. Flowmeter Calibration

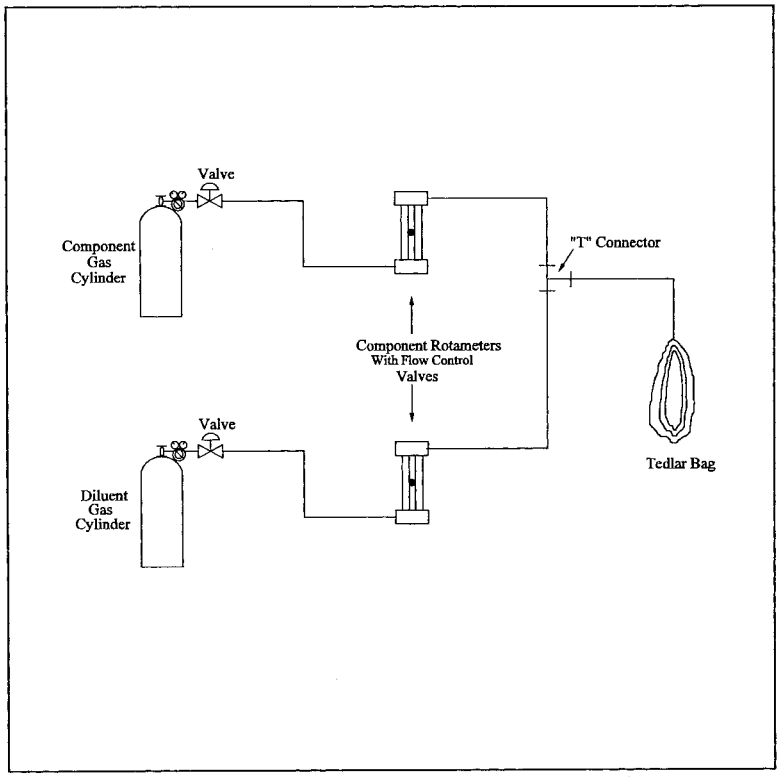

Figure 18-5. Single-Stage Calibration Gas Dilution System.

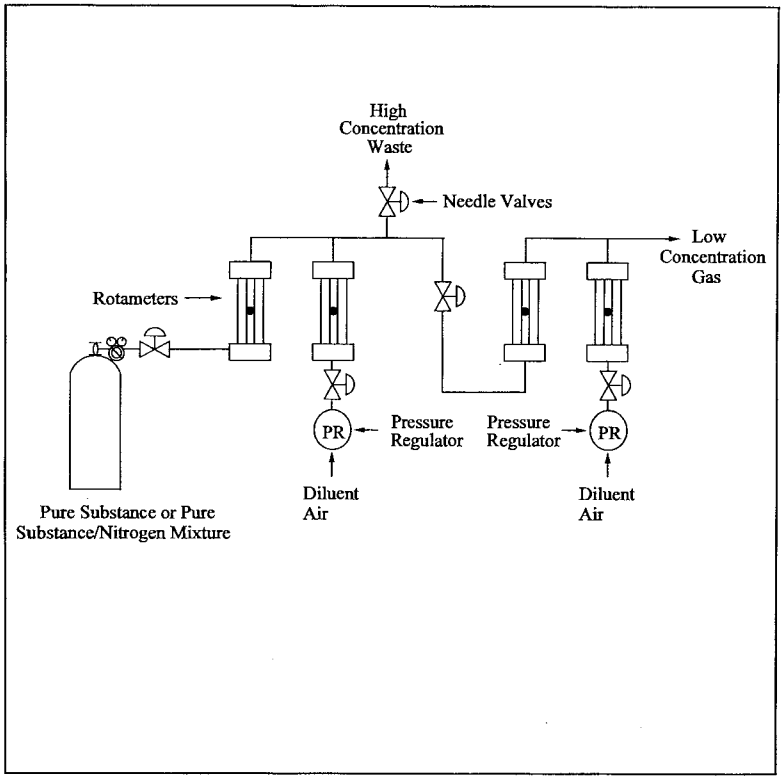

Figure 18-6. Two-Stage Dilution Apparatus.

PREPARATION OF STANDARDS BY DILUTION OF CYLINDER STANDARD

[Cylinder Standard: Organic _____ Certified Concentration _____ ppm]

Standards preparation data:	Date:		
	Mixture 1	Mixture 2	Mixture 3
Stage 1:			
Standard gas flowmeter reading.			
Diluent gas flowmeter reading			
Laboratory temperature (°K)			
Barometric pressure (mm Hg)			
Flowmeter gage pressure (mm Hg)			
Flow rate cylinder gas at standard conditions (ml/min)			
Flow rate diluent gas at standard conditions (ml/min)			
Calculated concentration (ppm)			
Stage 2 (if used):			
Standard gas flowmeter reading			
Diluent gas flowmeter reading			
Flow rate Stage 1 gas at standard conditions (ml/min)			
Flow rate diluent gas at standard conditions			
Calculated concentration (ppm)			
GC Operating Conditions:			
Sample loop volume (ml)			
Sample loop temperature (°C)			
Carrier gas flow rate (ml/min)			
Column temperature:			
Initial (°C)			

PREPARATION OF STANDARDS BY DILUTION OF CYLINDER STANDARD—Continued

[Cylinder Standard: Organic _____ Certified Concentration _____ ppm]

Standards preparation data:	Date:		
	Mixture 1	Mixture 2	Mixture 3
Program rate (°C/min)			
Final (°C)			
Organic Peak Identification and Calculated Concentrations:			
Injection time (24-hour clock)			
Distance to peak (cm)			
Chart speed (cm/min)			
Retention time (min)			
Attenuation factor			
Peak area (mm^2)			
Peak area *attenuation factor			

Plot peak area *attenuation factor against calculated concentration to obtain calibration curve.

Figure 18–7. Standards Prepared by Dilution of Cylinder Standard

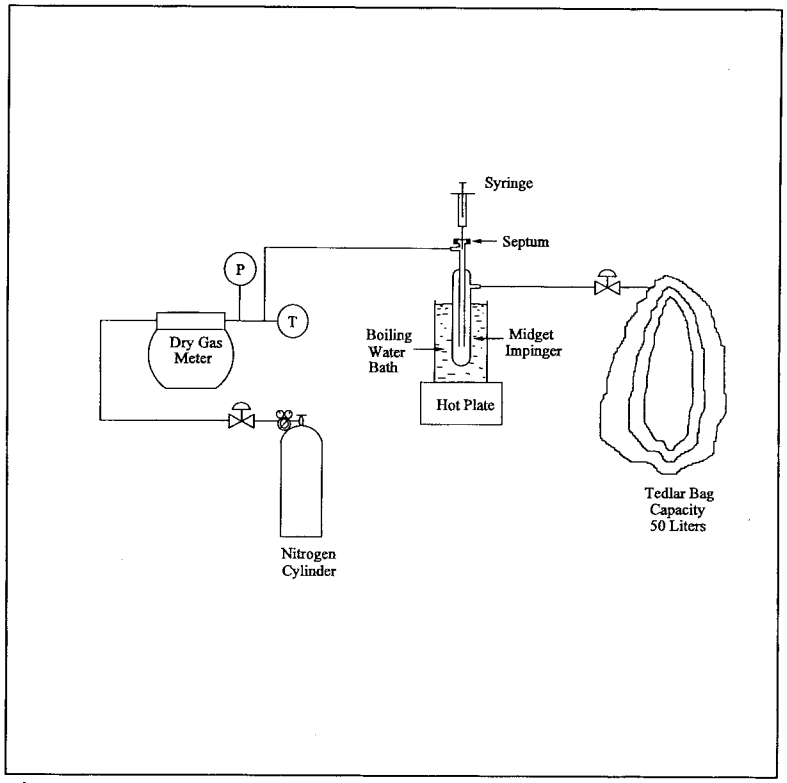

Figure 18-8. Apparatus for Preparation of Liquid Materials.

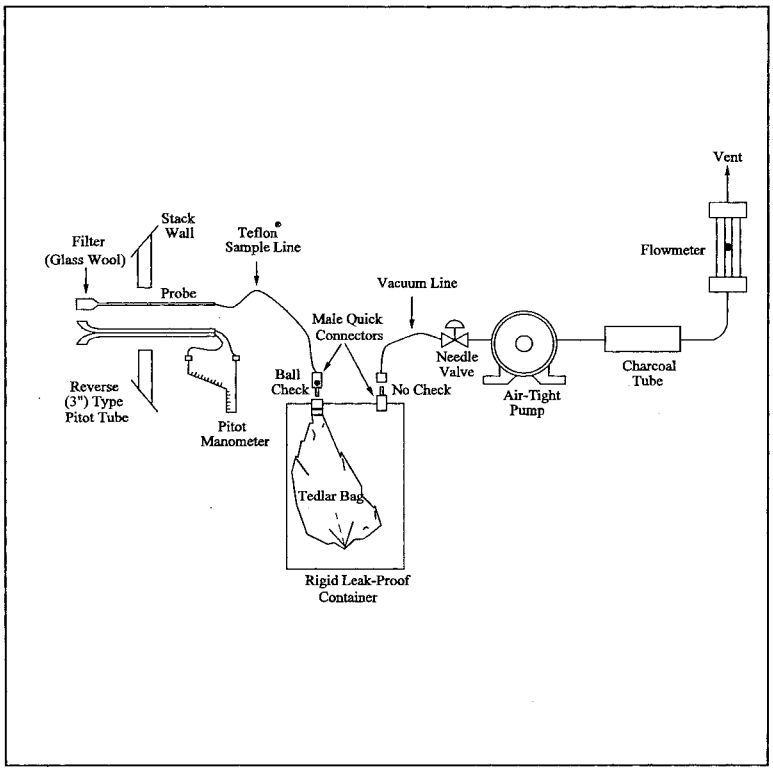

Figure 18-9. Integrated Bag Sampling Train.

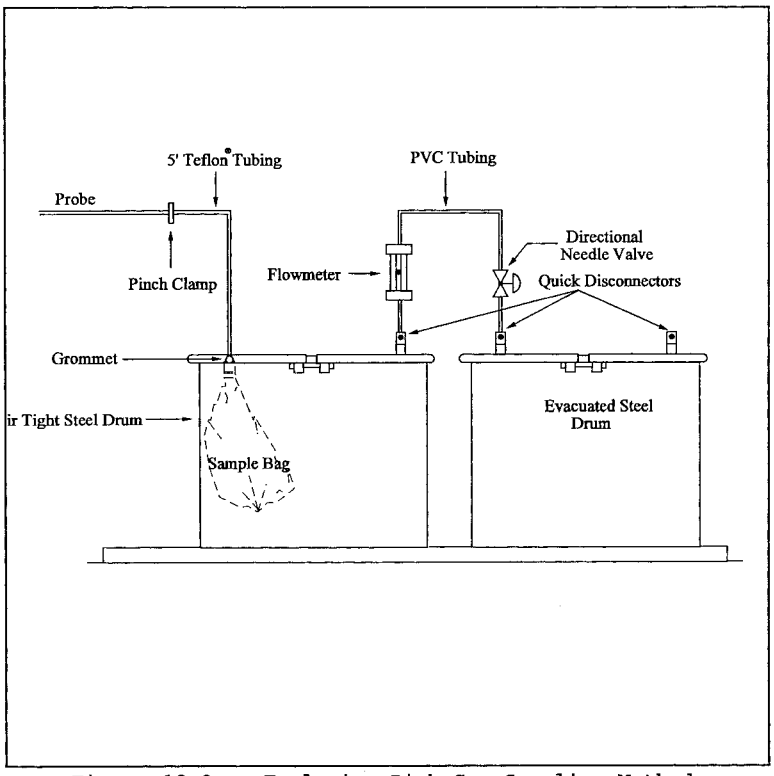

Figure 18-9a. Explosion Risk Gas Sampling Method.

PLANT_____ DATE_____ SITE_____

	Sample 1	Sample 2	Sample 3
Source temperature (°C)			
Barometric pressure (mm Hg)			
Ambient temperature (°C)			
Sample flow rate (appr.)			
Bag number			
Start time			
Finish time			

Figure 18–10. Field Sample Data Sheet—Tedlar or Tedlar-Equivalent Bag Collection Method

PLANT _____ DATE _____ LOCATION _____

1. General information:
- Source temperature (°C) .....
- Probe temperature (°C) .....
- Ambient temperature (°C) .....
- Atmospheric pressure (mm) .....
- Source pressure ('Hg) .....
- Absolute source pressure (mm) .....
- Sampling rate (liter/min) .....
- Sample loop volume (ml) .....
- Sample loop temperature (°C) .....
- Columnar temperature:
  - Initial (°C) time (min) .....
  - Program rate (°C/min) .....
  - Final (°C)/time (min) .....
- Carrier gas flow rate (ml/min) .....

PLANT _____ DATE _____ LOCATION _____—

Continued

Detector temperature (°C) .....
Injection time (24-hour basis) .....
Chart Speed (mm/min) .....
Dilution gas flow rate (ml/min) .....
Dilution gas used (symbol) .....
Dilution ratio .....

2. FIELD ANALYSIS DATA—CALIBRATION GAS

2. [Run No. _____ Time _____]

Components	Area	Attenuation	A × A Factor	Conc.__ (ppm)

Figure 18–11. Field Analysis Data Sheets

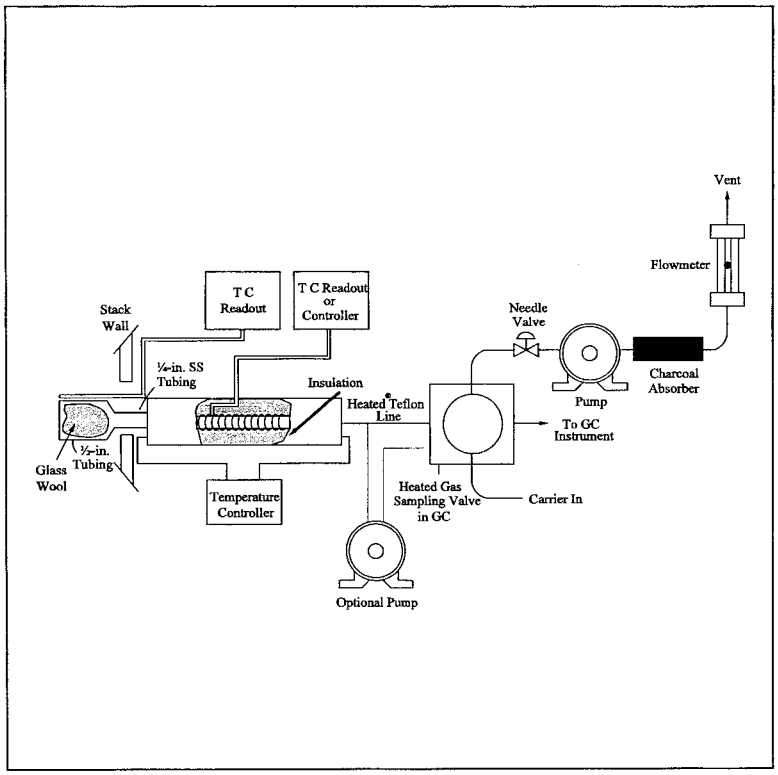

Figure 18-12. Direct Interface Sampling System.

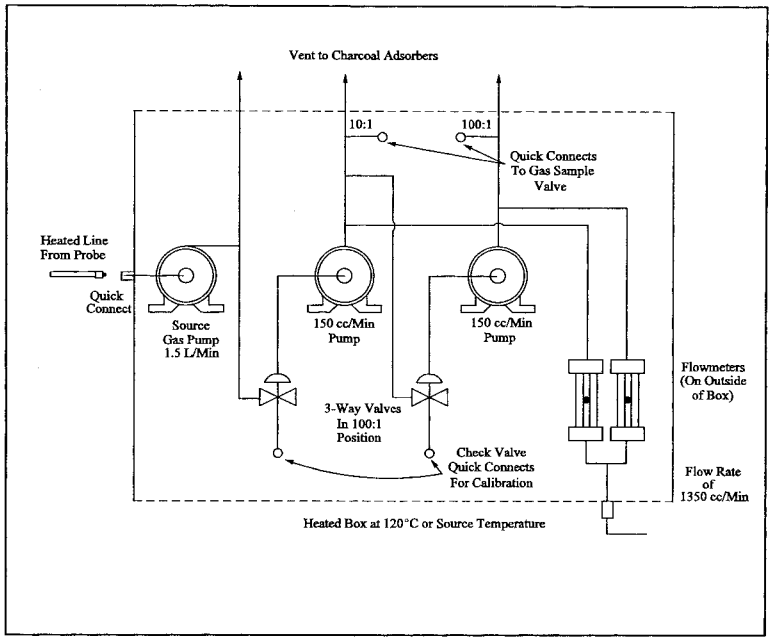

Figure 18-13. Schematic Diagram of the Heated Box Required for Dilution of Sample Gas.

GASEOUS ORGANIC SAMPLING AND ANALYSIS CHECK LIST

[Respond with initials or number as appropriate]

1. Presurvey data:		
A. Grab sample collected	☐	_____
B. Grab sample analyzed for composition	☐	_____
Method GC	☐	_____
GC/MS	☐	_____
Other	☐	_____
C. GC-FID analysis performed	☐	_____
2. Laboratory calibration data:		
A. Calibration curves prepared	☐	_____
Number of components	☐	_____
Number of concentrations/component (3 required).	☐	_____
B. Audit samples (optional):		
Analysis completed	☐	_____
Verified for concentration	☐	_____
OK obtained for field work	☐	_____
3. Sampling procedures:		
A. Method:		
Bag sample	☐	_____
Direct interface	☐	_____
Dilution interface	☐	_____
B. Number of samples collected	☐	_____
4. Field Analysis:		
A. Total hydrocarbon analysis performed	☐	_____
B. Calibration curve prepared	☐	_____
Number of components	☐	_____
Number of concentrations per component (3 required).	☐	_____

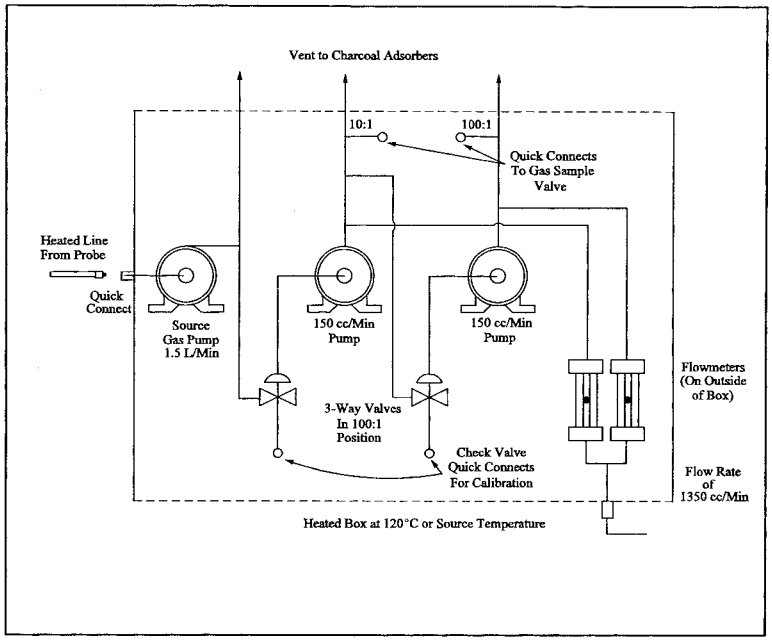

Figure 18-13. Schematic Diagram of the Heated Box Required for Dilution of Sample Gas.

GASEOUS ORGANIC SAMPLING AND ANALYSIS CHECK LIST

[Respond with initials or number as appropriate]

1. Presurvey data:		
A. Grab sample collected	☐	_____
B. Grab sample analyzed for composition	☐	_____
Method GC	☐	_____
GC/MS	☐	_____
Other	☐	_____
C. GC-FID analysis performed	☐	_____
2. Laboratory calibration data:		
A. Calibration curves prepared	☐	_____
Number of components	☐	_____
Number of concentrations/component (3 required).	☐	_____
B. Audit samples (optional):		
Analysis completed	☐	_____
Verified for concentration	☐	_____
OK obtained for field work	☐	_____
3. Sampling procedures:		
A. Method:		
Bag sample	☐	_____
Direct interface	☐	_____
Dilution interface	☐	_____
B. Number of samples collected	☐	_____
4. Field Analysis:		
A. Total hydrocarbon analysis performed	☐	_____
B. Calibration curve prepared	☐	_____
Number of components	☐	_____
Number of concentrations per component (3 required).	☐	_____

Gaseous Organic Sampling and Analysis Data

Date _____
Location _____

Plant _____

GASEOUS ORGANIC SAMPLING AND ANALYSIS CHECK LIST (RESPOND WITH INITIALS OR NUMBER AS APPROPRIATE)

	Date
1. Pre-survey data	
A. Grab sample collected	_____
B. Grab sample analyzed for composition	_____
Method GC	_____
GC/MS	_____
Other_____	_____
C. GC–FID analysis performed	_____
2. Laboratory calibration curves prepared	_____
A. Number of components	_____
B. Number of concentrations per component (3 required)	_____
C. OK obtained for field work	_____
3. Sampling procedures.	
A. Method.	
Bag sample	_____
Direct interface	_____
Dilution interface	_____
B. Number of samples collected	_____
4. Field Analysis.	
A. Total hydrocarbon analysis performed	_____
B. Calibration curve prepared	_____
Number of components	_____
Number of concentrations per component (3 required)	_____

Figure 18–14. Sampling and Analysis Sheet

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–6 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

APPENDIX A–7 TO PART 60—TEST METHODS 19 THROUGH 25E

Method 19—Determination of sulfur dioxide removal efficiency and particulate, sulfur dioxide and nitrogen oxides emission rates
Method 20—Determination of nitrogen oxides, sulfur dioxide, and diluent emissions from stationary gas turbines
Method 21—Determination of volatile organic compound leaks
Method 22—Visual determination of fugitive emissions from material sources and smoke emissions from flares
Method 23—Determination of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans From Stationary Sources
Method 24—Determination of volatile matter content, water content, density, volume solids, and weight solids of surface coatings
Method 24A—Determination of volatile matter content and density of printing inks and related coatings
Method 25—Determination of total gaseous nonmethane organic emissions as carbon
Method 25A—Determination of total gaseous organic concentration using a flame ionization analyzer
Method 25B—Determination of total gaseous organic concentration using a nondispersive infrared analyzer
Method 25C—Determination of nonmethane organic compounds (NMOC) in MSW landfill gases
Method 25D—Determination of the Volatile Organic Concentration of Waste Samples
Method 25E—Determination of Vapor Phase Organic Concentration in Waste Samples

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

Method 19—Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates

1.0 Scope and Application

1.1 Analytes. This method provides data reduction procedures relating to the following pollutants, but does not include any sample collection or analysis procedures.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), including:		
Nitric oxide (NO)	10102–43–9	N/A
Nitrogen dioxide (NO_2)	10102–44–0.	
Particulate matter (PM)	None assigned	N/A
Sulfur dioxide (SO_2)	7499–09–05	N/A

1.2 Applicability. Where specified by an applicable subpart of the regulations, this method is applicable for the determination of (a) PM, SO_2, and NO_X emission rates; (b) sulfur removal efficiencies of fuel pretreatment and SO_2 control devices; and (c) overall reduction of potential SO_2 emissions.

2.0 Summary of Method

2.1 Emission Rates. Oxygen (O_2) or carbon dioxide (CO_2) concentrations and appropriate F factors (ratios of combustion gas volumes to heat inputs) are used to calculate pollutant emission rates from pollutant concentrations.

2.2 Sulfur Reduction Efficiency and SO_2 Removal Efficiency. An overall SO_2 emission reduction efficiency is computed from the efficiency of fuel pretreatment systems, where applicable, and the efficiency of SO_2 control devices.

2.2.1 The sulfur removal efficiency of a fuel pretreatment system is determined by fuel sampling and analysis of the sulfur and heat contents of the fuel before and after the pretreatment system.

2.2.2 The SO_2 removal efficiency of a control device is determined by measuring the SO_2 rates before and after the control device.

2.2.2.1 The inlet rates to SO_2 control systems (or, when SO_2 control systems are not used, SO_2 emission rates to the atmosphere) are determined by fuel sampling and analysis.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety [Reserved]

6.0 Equipment and Supplies [Reserved]

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transport [Reserved]

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedures [Reserved]

12.0 Data Analysis and Calculations

12.1 Nomenclature

B_{wa} = Moisture fraction of ambient air, percent.

B_{ws} = Moisture fraction of effluent gas, percent.

%C = Concentration of carbon from an ultimate analysis of fuel, weight percent.

C_d = Pollutant concentration, dry basis, ng/scm (lb/scf)

$\%CO_{2d}$,$\%CO_{2w}$ = Concentration of carbon dioxide on a dry and wet basis, respectively, percent.

C_w = Pollutant concentration, wet basis, ng/scm (lb/scf).

D = Number of sampling periods during the performance test period.

E = Pollutant emission rate, ng/J (lb/million Btu).

E_a = Average pollutant rate for the specified performance test period, ng/J (lb/million Btu).

E_{ao}, E_{ai} = Average pollutant rate of the control device, outlet and inlet, respectively, for the performance test period, ng/J (lb/million Btu).

E_{bi} = Pollutant rate from the steam generating unit, ng/J (lb/million Btu)

E_{bo} = Pollutant emission rate from the steam generating unit, ng/J (lb/million Btu).

E_{ci} = Pollutant rate in combined effluent, ng/J (lb/million Btu).

E_{co} = Pollutant emission rate in combined effluent, ng/J (lb/million Btu).

E_d = Average pollutant rate for each sampling period (*e.g.*, 24-hr Method 6B sample or 24-hr fuel sample) or for each fuel lot (*e.g.*, amount of fuel bunkered), ng/J (lb/million Btu).

E_{di} = Average inlet SO_2 rate for each sampling period d, ng/J (lb/million Btu)

E_g = Pollutant rate from gas turbine, ng/J (lb/million Btu).

E_{ga} = Daily geometric average pollutant rate, ng/J (lbs/million Btu) or ppm corrected to 7 percent O_2.

E_{jo},E_{ji} = Matched pair hourly arithmetic average pollutant rate, outlet and inlet, respectively, ng/J (lb/million Btu) or ppm corrected to 7 percent O_2.

E_h = Hourly average pollutant, ng/J (lb/million Btu).

E_{hj} = Hourly arithmetic average pollutant rate for hour ''j,'' ng/J (lb/million Btu) or ppm corrected to 7 percent O_2.

EXP = Natural logarithmic base (2.718) raised to the value enclosed by brackets.

F_d, F_w, F_c = Volumes of combustion components per unit of heat content, scm/J (scf/million Btu).

GCV = Gross calorific value of the fuel consistent with the ultimate analysis, kJ/kg (Btu/lb).

GCV_p, GCV_r = Gross calorific value for the product and raw fuel lots, respectively, dry basis, kJ/kg (Btu/lb).

%H = Concentration of hydrogen from an ultimate analysis of fuel, weight percent.

H = Total number of operating hours for which pollutant rates are determined in the performance test period.

H_b = Heat input rate to the steam generating unit from fuels fired in the steam generating unit, J/hr (million Btu/hr).

H_g = Heat input rate to gas turbine from all fuels fired in the gas turbine, J/hr (million Btu/hr).

$\%H_2O$ = Concentration of water from an ultimate analysis of fuel, weight percent.
H_r = Total numbers of hours in the performance test period (*e.g.*, 720 hours for 30-day performance test period).
K = Conversion factor, 10^{-5} (kJ/J)/(%) [10^6 Btu/million Btu].
K_c = (9.57 scm/kg)/% [(1.53 scf/lb)/%].
K_{cc} = (2.0 scm/kg)/% [(0.321 scf/lb)/%].
K_{hd} = (22.7 scm/kg)/% [(3.64 scf/lb)/%].
K_{hw} = (34.74 scm/kg)/% [(5.57 scf/lb)/%].
K_n = (0.86 scm/kg)/% [(0.14 scf/lb)/%].
K_o = (2.85 scm/kg)/% [(0.46 scf/lb)/%].
K_s = (3.54 scm/kg)/% [(0.57 scf/lb)/%].
K_w = (1.30 scm/kg)/% [(0.21 scf/lb)/%].
ln = Natural log of indicated value.
L_p,L_r = Weight of the product and raw fuel lots, respectively, metric ton (ton).
%N = Concentration of nitrogen from an ultimate analysis of fuel, weight percent.
N = Number of fuel lots during the averaging period.
n = Number of fuels being burned in combination.
n_d = Number of operating hours of the affected facility within the performance test period for each E_d determined.
n_t = Total number of hourly averages for which paired inlet and outlet pollutant rates are available within the 24-hr midnight to midnight daily period.
%O = Concentration of oxygen from an ultimate analysis of fuel, weight percent.
$\%O_{2d}$, $\%O_{2w}$ = Concentration of oxygen on a dry and wet basis, respectively, percent.
P_s = Potential SO_2 emissions, percent.
$\%R_f$ = SO_2 removal efficiency from fuel pretreatment, percent.
$\%R_g$ = SO_2 removal efficiency of the control device, percent.
$\%R_{ga}$ = Daily geometric average percent reduction.
$\%R_o$ = Overall SO_2 reduction, percent.
%S = Sulfur content of as-fired fuel lot, dry basis, weight percent.
S_e = Standard deviation of the hourly average pollutant rates for each performance test period, ng/J (lb/million Btu).
$\%S_f$ = Concentration of sulfur from an ultimate analysis of fuel, weight percent.
S_i = Standard deviation of the hourly average inlet pollutant rates for each performance test period, ng/J (lb/million Btu).
S_o = Standard deviation of the hourly average emission rates for each performance test period, ng/J (lb/million Btu).
$\%S_p$, $\%S_r$ = Sulfur content of the product and raw fuel lots respectively, dry basis, weight percent.
$t_{0.95}$ = Values shown in Table 19–3 for the indicated number of data points n.
X_k = Fraction of total heat input from each type of fuel k.

12.2 Emission Rates of PM, SO_2, and NO_X. Select from the following sections the applicable procedure to compute the PM, S_{O2}, or NO_X emission rate (E) in ng/J (lb/million Btu). The pollutant concentration must be in ng/scm (lb/scf) and the F factor must be in scm/J (scf/million Btu). If the pollutant concentration (C) is not in the appropriate units, use Table 19–1 in section 17.0 to make the proper conversion. An F factor is the ratio of the gas volume of the products of combustion to the heat content of the fuel. The dry F factor (F_d) includes all components of combustion less water, the wet F factor (F_w) includes all components of combustion, and the carbon F factor (F_c) includes only carbon dioxide.

NOTE: Since F_w factors include water resulting only from the combustion of hydrogen in the fuel, the procedures using F_w factors are not applicable for computing E from steam generating units with wet scrubbers or with other processes that add water (*e.g.*, steam injection).

12.2.1 Oxygen-Based F Factor, Dry Basis. When measurements are on a dry basis for both O ($\%O_{2d}$) and pollutant (C_d) concentrations, use the following equation:

$$E = C_d F_d \frac{20.9}{(20.9 - \%O_{2d})} \qquad \text{Eq. 19-1}$$

12.2.2 Oxygen-Based F Factor, Wet Basis. When measurements are on a wet basis for both O_2 ($\%O_{2w}$) and pollutant (C_w) concentrations, use either of the following:

12.2.2.1 If the moisture fraction of ambient air (B_{wa}) is measured:

$$E = C_w F_w \frac{20.9}{\left[20.9(1 - B_{wa}) - \%O_{2w}\right]} \qquad \text{Eq. 19-2}$$

Instead of actual measurement, B_{wa} may be estimated according to the procedure below.

NOTE: The estimates are selected to ensure that negative errors will not be larger than −1.5 percent. However, positive errors, or over-estimation of emissions by as much as 5 percent may be introduced depending upon the geographic location of the facility and the associated range of ambient moisture.

12.2.2.1.1 B_{wa} = 0.027. This value may be used at any location at all times.

12.2.2.1.2 B_{wa} = Highest monthly average of B_{wa} that occurred within the previous calendar year at the nearest Weather Service Station. This value shall be determined annually and may be used as an estimate for the entire current calendar year.

12.2.2.1.3 B_{wa} = Highest daily average of Bwa that occurred within a calendar month at the nearest Weather Service Station, calculated from the data from the past 3 years. This value shall be computed for each month and may be used as an estimate for the current respective calendar month.

12.2.2.2 If the moisture fraction (B_{ws}) of the effluent gas is measured:

$$E = C_w F_d \frac{20.9}{\left[20.9\left(1-B_{ws}\right)-\%O_{2w}\right]} \qquad \text{Eq. 19-3}$$

12.2.3 Oxygen-Based F Factor, Dry/Wet Basis.

12.2.3.1 When the pollutant concentration is measured on a wet basis (C_w) and O_2 concentration is measured on a dry basis ($\%O_{2d}$), use the following equation:

$$E = \frac{\left(C_w F_d\right)(20.9)}{\left(1-B_{ws}\right)\left(20.9-\%O_{2d}\right)} \qquad \text{Eq. 19-4}$$

12.2.3.2 When the pollutant concentration is measured on a dry basis (C_d) and the O_2 concentration is measured on a wet basis ($\%O_{2w}$), use the following equation:

$$E = \frac{C_d F_d 20.9}{\frac{\left(20.9-\%O_{2w}\right)}{\left(1-B_{ws}\right)}} \qquad \text{Eq. 19-5}$$

12.2.4 Carbon Dioxide-Based F Factor, Dry Basis. When measurements are on a dry basis for both CO_2 ($\%CO_{2d}$) and pollutant (C_d) concentrations, use the following equation:

$$E = C_d F_c \frac{100}{\%CO_{2d}} \qquad \text{Eq. 19-6}$$

12.2.5 Carbon Dioxide-Based F Factor, Wet Basis. When measurements are on a wet basis for both CO_2 ($\%CO_{2w}$) and pollutant (C_w) concentrations, use the following equation:

$$E = C_w F_c \frac{100}{\%CO_{2w}} \qquad \text{Eq. 19-7}$$

12.2.6 Carbon Dioxide-Based F Factor, Dry/Wet Basis.

12.2.6.1 When the pollutant concentration is measured on a wet basis (C_w) and CO_2 concentration is measured on a dry basis ($\%CO_{2d}$), use the following equation:

$$E = \frac{C_w F_c}{\left(1-B_{ws}\right)} \frac{100}{\%CO_{2d}} \qquad \text{Eq. 19-8}$$

12.2.6.2 When the pollutant concentration is measured on a dry basis (C_d) and CO_2 concentration is measured on a wet basis ($\%CO_{2w}$), use the following equation:

$$E = C_d F_c \left(1-B_{ws}\right) \frac{100}{\%CO_{2w}} \qquad \text{Eq. 19-9}$$

12.2.7 Direct-Fired Reheat Fuel Burning. The effect of direct-fired reheat fuel burning (for the purpose of raising the temperature of the exhaust effluent from wet scrubbers to above the moisture dew-point) on emission rates will be less than 1.0 percent and, therefore, may be ignored.

12.2.8 Combined Cycle-Gas Turbine Systems. For gas turbine-steam generator combined cycle systems, determine the emissions from the steam generating unit or the percent reduction in potential SO_2 emissions as follows:

12.2.8.1 Compute the emission rate from the steam generating unit using the following equation:

$$E_{bo} = E_{co} + \frac{H_g}{H_b}\left(E_{co} - E_g\right) \qquad \text{Eq. 19-10}$$

12.2.8.1.1 Use the test methods and procedures section of 40 CFR Part 60, Subpart GG to obtain E_{co} and E_g. Do not use F_w factors for determining E_g or E_{co}. If an SO_2 control device is used, measure E_{co} after the control device.

12.2.8.1.2 Suitable methods shall be used to determine the heat input rates to the steam generating units (H_b) and the gas turbine (H_g).

12.2.8.2 If a control device is used, compute the percent of potential SO_2 emissions (P_s) using the following equations:

$$E_{bi} = E_{ci} - \frac{H_g}{H_b}\left(E_{ci} - E_g\right) \qquad \text{Eq. 19-11}$$

$$P_s = 100\left(1 - \frac{E_{bo}}{E_{bi}}\right) \qquad \text{Eq. 19-12}$$

NOTE: Use the test methods and procedures section of Subpart GG to obtain E_{ci} and E_g. Do not use F_w factors for determining E_g or E_{ci}.

12.3 F Factors. Use an average F factor according to section 12.3.1 or determine an applicable F factor according to section 12.3.2. If combined fuels are fired, prorate the applicable F factors using the procedure in section 12.3.3.

12.3.1 Average F Factors. Average F factors (F_d, F_w, or F_c) from Table 19–2 in section 17.0 may be used.

12.3.2 Determined F Factors. If the fuel burned is not listed in Table 19–2 or if the owner or operator chooses to determine an F factor rather than use the values in Table 19–2, use the procedure below:

12.3.2.1 Equations. Use the equations below, as appropriate, to compute the F factors:

$$F_d = \frac{K\left(K_{hd}\%H + K_c\%C + K_s\%S + K_n\%N - K_o\%O\right)}{GCV} \qquad \text{Eq. 19-13}$$

$$F_w = \frac{K\left[K_{hw}\%H + K_c\%C + K_s\%S + K_n\%N - K_o\%O + K_w\%H_2O\right]}{GCV_w} \qquad \text{Eq. 19-14}$$

$$F_c = \frac{K\left(K_{cc}\%C\right)}{GCV} \qquad \text{Eq. 19-15}$$

NOTE: Omit the $\%H_2O$ term in the equations for F_w if %H and %O include the unavailable hydrogen and oxygen in the form of H_2O.)

12.3.2.2 Use applicable sampling procedures in section 12.5.2.1 or 12.5.2.2 to obtain samples for analyses.

12.3.2.3 Use ASTM D 3176–74 or 89 (all cited ASTM standards are incorporated by reference—see §60.17) for ultimate analysis of the fuel.

12.3.2.4 Use applicable methods in section 12.5.2.1 or 12.5.2.2 to determine the heat content of solid or liquid fuels. For gaseous fuels, use ASTM D 1826–77 or 94 (incorporated by reference—see §60.17) to determine the heat content.

12.3.3 F Factors for Combination of Fuels. If combinations of fuels are burned, use the following equations, as applicable unless otherwise specified in an applicable subpart:

$$F_d = \sum_{k=1}^{n}\left(X_k F_{dk}\right) \qquad \text{Eq. 19-16}$$

$$F_w = \sum_{k=1}^{n}\left(X_k F_{wk}\right) \qquad \text{Eq. 19-17}$$

$$F_c = \sum_{k=1}^{n}\left(X_k F_{ck}\right) \qquad \text{Eq. 19-18}$$

12.4 Determination of Average Pollutant Rates.

12.4.1 Average Pollutant Rates from Hourly Values. When hourly average pollutant rates (E_h), inlet or outlet, are obtained (*e.g.*, CEMS values), compute the average pollutant rate (E_a) for the performance test period (*e.g.*, 30 days) specified in the applicable regulation using the following equation:

$$E_a = \frac{1}{H}\sum_{j=1}^{n} E_{hj} \qquad \text{Eq. 19-19}$$

12.4.2 Average Pollutant Rates from Other than Hourly Averages. When pollutant rates are determined from measured values representing longer than 1-hour periods (*e.g.*, daily fuel sampling and analyses or Method 6B values), or when pollutant rates are determined from combinations of 1-hour and longer than 1-hour periods (*e.g.*, CEMS and Method 6B values), compute the average pollutant rate (E_a) for the performance test period (*e.g.*, 30 days) specified in the applicable regulation using the following equation:

$$E_a = \frac{\sum_{j=1}^{D}\left(n_d E_d\right)_j}{\sum_{j=1}^{D} n_{dj}} \qquad \text{Eq. 19-20}$$

12.4.3 Daily Geometric Average Pollutant Rates from Hourly Values. The geometric average pollutant rate (E_{ga}) is computed using the following equation:

$$E_{ga} = \exp\left[\frac{1}{n_t}\sum_{j=1}^{n_t}\left[\ln\left(E_{hj}\right)\right]\right] \quad \text{Eq. 19-21}$$

12.5 Determination of Overall Reduction in Potential Sulfur Dioxide Emission.

12.5.1 Overall Percent Reduction. Compute the overall percent SO_2 reduction ($\%R_o$) using the following equation:

$$\%R_o = 100\left[1.0 - \left(1.0 - \frac{\%R_f}{100}\right)\left(1.0 - \frac{\%R_g}{100}\right)\right] \quad \text{Eq. 19-22}$$

12.5.2 Pretreatment Removal Efficiency (Optional). Compute the SO_2 removal efficiency from fuel pretreatment ($\%R_f$) for the averaging period (*e.g.*, 90 days) as specified in the applicable regulation using the following equation:

$$\%R_f = 100\left[1.0 - \frac{\sum_{j=1}^{N}\left(\frac{\%S_{pj}}{GCV_{pj}}\right)L_{pj}}{\sum_{j=1}^{N}\left(\frac{\%S_{rj}}{GCV_{rj}}\right)L_{rj}}\right] \quad \text{Eq. 19-23}$$

NOTE: In calculating $\%R_f$, include %S and GCV values for all fuel lots that are not pretreated and are used during the averaging period.

12.5.2.1 Solid Fossil (Including Waste) Fuel/Sampling and Analysis.

NOTE: For the purposes of this method, raw fuel (coal or oil) is the fuel delivered to the desulfurization (pretreatment) facility. For oil, the input oil to the oil desulfurization process (*e.g.*, hydrotreatment) is considered to be the raw fuel.

12.5.2.1.1 Sample Increment Collection. Use ASTM D 2234–76, 96, 97a, or 98 (incorporated by reference—see §60.17), Type I, Conditions A, B, or C, and systematic spacing. As used in this method, systematic spacing is intended to include evenly spaced increments in time or increments based on equal weights of coal passing the collection area. As a minimum, determine the number and weight of increments required per gross sample representing each coal lot according to Table 2 or Paragraph 7.1.5.2 of ASTM D 2234. Collect one gross sample for each lot of raw coal and one gross sample for each lot of product coal.

12.5.2.1.2 ASTM Lot Size. For the purpose of section 12.5.2 (fuel pretreatment), the lot size of product coal is the weight of product coal from one type of raw coal. The lot size of raw coal is the weight of raw coal used to produce one lot of product coal. Typically, the lot size is the weight of coal processed in a 1-day (24-hour) period. If more than one type of coal is treated and produced in 1 day, then gross samples must be collected and analyzed for each type of coal. A coal lot size equaling the 90-day quarterly fuel quantity for a steam generating unit may be used if representative sampling can be conducted for each raw coal and product coal.

NOTE: Alternative definitions of lot sizes may be used, subject to prior approval of the Administrator.

12.5.2.1.3 Gross Sample Analysis. Use ASTM D 2013–72 or 86 to prepare the sample, ASTM D 3177–75 or 89 or ASTM D 4239–85, 94, or 97 to determine sulfur content (%S), ASTM D 3173–73 or 87 to determine moisture content, and ASTM D 2015–77 (Reapproved 1978) or 96, D 3286–85 or 96, or D 5865–98 or 10 to determine gross calorific value (GCV) (all standards cited are incorporated by reference—see §60.17 for acceptable versions of the standards) on a dry basis for each gross sample.

12.5.2.2 Liquid Fossil Fuel-Sampling and Analysis. See Note under section 12.5.2.1.

12.5.2.2.1 Sample Collection. Follow the procedures for continuous sampling in ASTM D 270 or D 4177–95 (incorporated by reference—see §60.17) for each gross sample from each fuel lot.

12.5.2.2.2 Lot Size. For the purpose of section 12.5.2 (fuel pretreatment), the lot size of a product oil is the weight of product oil from one pretreatment facility and intended as one shipment (ship load, barge load, etc.). The lot size of raw oil is the weight of each crude liquid fuel type used to produce a lot of product oil.

NOTE: Alternative definitions of lot sizes may be used, subject to prior approval of the Administrator.

12.5.2.2.3 Sample Analysis. Use ASTM D 129–64, 78, or 95, ASTM D 1552–83 or 95, or ASTM D 4057–81 or 95 to determine the sulfur content (%S) and ASTM D 240–76 or 92 (all standards cited are incorporated by reference—see §60.17) to determine the GCV of each gross sample. These values may be assumed to be on a dry basis. The owner or operator of an affected facility may elect to determine the GCV by sampling the oil combusted on the first steam generating unit operating day of each calendar month and then using the lowest GCV value of the three GCV values per quarter for the GCV of all oil combusted in that calendar quarter.

12.5.2.3 Use appropriate procedures, subject to the approval of the Administrator, to determine the fraction of total mass input derived from each type of fuel.

12.5.3 Control Device Removal Efficiency. Compute the percent removal efficiency ($\%R_g$) of the control device using the following equation:

$$\%R_g = 100\left(1.0 - \frac{E_{ao}}{E_{ai}}\right) \qquad \text{Eq. 19-24}$$

12.5.3.1 Use continuous emission monitoring systems or test methods, as appropriate, to determine the outlet SO_2 rates and, if appropriate, the inlet SO_2 rates. The rates may be determined as hourly (E_h) or other sampling period averages (E_d). Then, compute the average pollutant rates for the performance test period (E_{ao} and E_{ai}) using the procedures in section 12.4.

12.5.3.2 As an alternative, as-fired fuel sampling and analysis may be used to determine inlet SO_2 rates as follows:

12.5.3.2.1 Compute the average inlet SO_2 rate (E_{di}) for each sampling period using the following equation:

$$E_{di} = K\frac{\%S}{GCV} \qquad \text{Eq. 19-25}$$

Where:

$$K = 2\times10^7\left(\frac{\text{ng SO}_2}{\%S}\right)\left(\frac{(\text{kJ})}{\text{J}}\right)\left(\frac{1}{\text{kg coal}}\right)\left[2\times10^4\left(\frac{\text{lb SO}_2}{\%S}\right)\left(\frac{\text{Btu}}{\text{million Btu}}\right)\left(\frac{1}{\text{lb coal}}\right)\right]$$

After calculating E_{di}, use the procedures in section 12.4 to determine the average inlet SO_2 rate for the performance test period (E_{ai}).

12.5.3.2.2 Collect the fuel samples from a location in the fuel handling system that provides a sample representative of the fuel bunkered or consumed during a steam generating unit operating day. For the purpose of as-fired fuel sampling under section 12.5.3.2 or section 12.6, the lot size for coal is the weight of coal bunkered or consumed during each steam generating unit operating day. The lot size for oil is the weight of oil supplied to the ''day'' tank or consumed during each steam generating unit operating day. For reporting and calculation purposes, the gross sample shall be identified with the calendar day on which sampling began. For steam generating unit operating days when a coal-fired steam generating unit is operated without coal being added to the bunkers, the coal analysis from the previous ''as bunkered'' coal sample shall be used until coal is bunkered again. For steam generating unit operating days when an oil-fired steam generating unit is operated without oil being added to the oil ''day'' tank, the oil analysis from the previous day shall be used until the ''day'' tank is filled again. Alternative definitions of fuel lot size may be used, subject to prior approval of the Administrator.

12.5.3.2.3 Use ASTM procedures specified in section 12.5.2.1 or 12.5.2.2 to determine %S and GCV.

12.5.4 Daily Geometric Average Percent Reduction from Hourly Values. The geometric average percent reduction ($\%R_{ga}$) is computed using the following equation:

$$\%R_{ga} = 100\left[1 - EXP\left(\frac{1}{n_t}\sum_{j=1}^{n_t} 1n\frac{E_{jo}}{E_{ji}}\right)\right] \qquad \text{Eq. 19-26}$$

NOTE: The calculation includes only paired data sets (hourly average) for the inlet and outlet pollutant measurements.

12.6 Sulfur Retention Credit for Compliance Fuel. If fuel sampling and analysis procedures in section 12.5.2.1 are being used to determine average SO_2 emission rates (E_{as}) to the atmosphere from a coal-fired steam generating unit when there is no SO_2 control device, the following equation may be used to adjust the emission rate for sulfur retention credits (no credits are allowed for oil-fired systems) (E_{di}) for each sampling period using the following equation:

$$E_{di} = 0.97K\ \frac{\%S}{GDV} \qquad \text{Eq. 19-27}$$

Where:

$$K = 2\times10^{7}\left(\frac{\text{ng } SO_2}{\%S}\right)\left(\frac{kJ}{J}\right)\left(\frac{1}{\text{kg coal}}\right)\left[2\times10^{4}\left(\frac{\text{lb } SO_2}{\%S}\right)\left(\frac{\text{Btu}}{\text{million Btu}}\right)\left(\frac{1}{\text{lb coal}}\right)\right]$$

After calculating E_{di}, use the procedures in section 12.4.2 to determine the average SO_2 emission rate to the atmosphere for the performance test period (E_{ao}).

12.7 Determination of Compliance When Minimum Data Requirement Is Not Met.

12.7.1 Adjusted Emission Rates and Control Device Removal Efficiency. When the minimum data requirement is not met, the Administrator may use the following adjusted emission rates or control device removal efficiencies to determine compliance with the applicable standards.

12.7.1.1 Emission Rate. Compliance with the emission rate standard may be determined by using the lower confidence limit of the emission rate (E_{ao}*) as follows:

$$E^{*}_{ao} = E_{ao} - t_{0.95}S_o \qquad \text{Eq. 19-28}$$

12.7.1.2 Control Device Removal Efficiency. Compliance with the overall emission reduction ($\%R_o$) may be determined by using the lower confidence limit of the emission rate (E_{ao}*) and the upper confidence limit of the inlet pollutant rate (E_{ai}*) in calculating the control device removal efficiency ($\%R_g$) as follows:

$$\%R_g = 100\left(1.0 - \frac{E^{*}_{ao}}{E^{*}_{ai}}\right) \qquad \text{Eq. 19-29}$$

$$E^{*}_{ai} = E_{ai} + t_{0.95}S_i \qquad \text{Eq. 19-30}$$

12.7.2 Standard Deviation of Hourly Average Pollutant Rates. Compute the standard deviation (S_e) of the hourly average pollutant rates using the following equation:

$$S_e = \sqrt{\frac{1}{H} - \frac{1}{H_r}}\ \sqrt{\frac{\sum_{j=1}^{H}\left(E_{hj} - E_a\right)^2}{H-1}} \qquad \text{Eq. 19-31}$$

Equation 19–19 through 19–31 may be used to compute the standard deviation for both the outlet (S_o) and, if applicable, inlet (S_i) pollutant rates.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References [Reserved]

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 19–1—CONVERSION FACTORS FOR CONCENTRATION

From	To	Multiply by
g/scm	ng/scm	10^9
mg/scm	ng/scm	10^6
lb/scf	ng/scm	1.602×10^{13}

TABLE 19–1—CONVERSION FACTORS FOR CONCENTRATION—Continued

From	To	Multiply by
ppm SO_2	ng/scm	2.66×10^6
ppm NO_X	ng/scm	1.912×10^6
ppm SO_2	lb/scf	1.660×10^{-7}
ppm NO_X	lb/scf	1.194×10^{-7}

TABLE 19–2—F FACTORS FOR VARIOUS FUELS[1]

Fuel Type	F_d		F_w		F_c	
	dscm/J	dscf/10^6 Btu	wscm/J	wscf/10^6 Btu	scm/J	scf/10^6 Btu
Coal:						
Anthracite[2]	2.71×10^{-7}	10,100	2.83×10^{-7}	10,540	0.530×10^{-7}	1,970
Bituminus[2]	2.63×10^{-7}	9,780	2.86×10^{-7}	10,640	0.484×10^{-7}	1,800
Lignite	2.65×10^{-7}	9,860	3.21×10^{-7}	11,950	0.513×10^{-7}	1,910
Oil[3]	2.47×10^{-7}	9,190	2.77×10^{-7}	10,320	0.383×10^{-7}	1,420
Gas:.						
Natural	2.34×10^{-7}	8,710	2.85×10^{-7}	10,610	0.287×10^{-7}	1,040
Propane	2.34×10^{-7}	8,710	2.74×10^{-7}	10,200	0.321×10^{-7}	1,190
Butane	2.34×10^{-7}	8,710	2.79×10^{-7}	10,390	0.337×10^{-7}	1,250
Wood	2.48×10^{-7}	9,240			0.492×10^{-7}	1,830
Wood Bark	2.58×10^{-7}	9,600			0.516×10^{-7}	1,920
Municipal	2.57×10^{-7}	9,570			0.488×10^{-7}	1,820
Solid Waste						

[1] Determined at standard conditions: 20 °C (68 °F) and 760 mm Hg (29.92 in Hg)
[2] As classified according to ASTM D 388.
[3] Crude, residual, or distillate.

TABLE 19–3—VALUES FOR $T_{0.95*}$

n[1]	$t_{0.95}$	n[1]	$t_{0.95}$	n[1]	$t_{0.95}$
2	6.31	8	1.89	22–26	1.71
3	2.42	9	1.86	27–31	1.70
4	2.35	10	1.83	32–51	1.68
5	2.13	11	1.81	52–91	1.67
6	2.02	12–16	1.77	92–151	1.66
7	1.94	17–21	1.73	152 or more	1.65

[1]The values of this table are corrected for n-1 degrees of freedom. Use n equal to the number (H) of hourly average data points.

METHOD 20—DETERMINATION OF NITROGEN OXIDES, SULFUR DIOXIDE, AND DILUENT EMISSIONS FROM STATIONARY GAS TURBINES

1.0 Scope and Application

What is Method 20?

Method 20 contains the details you must follow when using an instrumental analyzer to determine concentrations of nitrogen oxides, oxygen, carbon dioxide, and sulfur dioxide in the emissions from stationary gas turbines. This method follows the specific instructions for equipment and performance requirements, supplies, sample collection and analysis, calculations, and data analysis in the methods listed in section 2.0.

1.1 Analytes. What does this method determine?

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X) as nitrogen dioxide:	10102–43–9	Typically <2% of Calibration Span.
Nitric oxide (NO)	10102–44–0	
Nitrogen dioxide NO_2.		
Diluent oxygen (O_2) or carbon dioxide (CO_2)		Typically <2% of Calibration Span.
Sulfur dioxide (SO_X)	7446–09–5	Typically <2% of Calibration Span.

1.2 Applicability. When is this method required? The use of Method 20 may be required by specific New Source Performance Standards, Clean Air Marketing rules, and State Implementation Plans and permits where

measuring SO_2, NO_X, CO_2, and/or O_2 concentrations in stationary gas turbines emissions are required. Other regulations may also require its use.

1.3 Data Quality Objectives. How good must my collected data be? Refer to section 1.3 of Method 7E.

2.0 Summary of Method

In this method, NO_X, O_2 (or CO_2), and SO_X are measured using the following methods found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 3A—Determination of Oxygen and Carbon Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(c) Method 6C—Determination of Sulfur Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(d) Method 7E—Determination of Nitrogen Oxides Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(e) Method 19—Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates.

3.0 Definitions

Refer to section 3.0 of Method 7E for the applicable definitions.

4.0 Interferences

Refer to section 4.0 of Methods 3A, 6C, and 7E as applicable.

5.0 Safety

Refer to section 5.0 of Method 7E.

6.0 Equipment and Supplies

The measurement system design is shown in Figure 7E–1 of Method 7E. Refer to the appropriate methods listed in section 2.0 for equipment and supplies.

7.0 Reagents and Standards

Refer to the appropriate methods listed in section 2.0 for reagents and standards.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling Site and Sampling Points. Follow the procedures of section 8.1 of Method 7E. For the stratification test in section 8.1.2, determine the diluent-corrected pollutant concentration at each traverse point.

8.2 Initial Measurement System Performance Tests. You must refer to the appropriate methods listed in section 2.0 for the measurement system performance tests as applicable.

8.3 Interference Check. You must follow the procedures in section 8.3 of Method 3A or 6C, or section 8.2.7 of Method 7E (as appropriate).

8.4 Sample Collection. You must follow the procedures of section 8.4 of the appropriate methods listed in section 2.0. A test run must have a duration of at least 21 minutes.

8.5 Post-Run System Bias Check, Drift Assessment, and Alternative Dynamic Spike Procedure. You must follow the procedures of sections 8.5 and 8.6 of the appropriate methods listed in section 2.0. A test run must have a duration of at least 21 minutes.

9.0 Quality Control

Follow quality control procedures in section 9.0 of Method 7E.

10.0 Calibration and Standardization

Follow the procedures for calibration and standardization in section 10.0 of Method 7E.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the procedures for calculations and data analysis in section 12.0 of the appropriate method listed in section 2.0. Follow the procedures in section 12.0 of Method 19 for calculating fuel-specific F factors, diluent-corrected pollutant concentrations, and emission rates.

13.0 Method Performance

The specifications for the applicable performance checks are the same as in section 13.0 of Method 7E.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

Refer to section 16.0 of the appropriate method listed in section 2.0 for alternative procedures.

17.0 References

Refer to section 17.0 of the appropriate method listed in section 2.0 for references.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

Refer to section 18.0 of the appropriate method listed in section 2.0 for tables, diagrams, flowcharts, and validation data.

METHOD 21—DETERMINATION OF VOLATILE ORGANIC COMPOUND LEAKS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile Organic Compounds (VOC).	No CAS number assigned.

1.2 Scope. This method is applicable for the determination of VOC leaks from process equipment. These sources include, but are not limited to, valves, flanges and other connections, pumps and compressors, pressure relief devices, process drains, open-ended valves, pump and compressor seal system degassing vents, accumulator vessel vents, agitator seals, and access door seals.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A portable instrument is used to detect VOC leaks from individual sources. The instrument detector type is not specified, but it must meet the specifications and performance criteria contained in section 6.0. A leak definition concentration based on a reference compound is specified in each applicable regulation. This method is intended to locate and classify leaks only, and is not to be used as a direct measure of mass emission rate from individual sources.

3.0 Definitions

3.1 *Calibration gas* means the VOC compound used to adjust the instrument meter reading to a known value. The calibration gas is usually the reference compound at a known concentration approximately equal to the leak definition concentration.

3.2 *Calibration precision* means the degree of agreement between measurements of the same known value, expressed as the relative percentage of the average difference between the meter readings and the known concentration to the known concentration.

3.3 *Leak definition concentration* means the local VOC concentration at the surface of a leak source that indicates that a VOC emission (leak) is present. The leak definition is an instrument meter reading based on a reference compound.

3.4 *No detectable emission* means a local VOC concentration at the surface of a leak source, adjusted for local VOC ambient concentration, that is less than 2.5 percent of the specified leak definition concentration. that indicates that a VOC emission (leak) is not present.

3.5 *Reference compound* means the VOC species selected as the instrument calibration basis for specification of the leak definition concentration. (For example, if a leak definition concentration is 10,000 ppm as methane, then any source emission that results in a local concentration that yields a meter reading of 10,000 on an instrument meter calibrated with methane would be classified as a leak. In this example, the leak definition concentration is 10,000 ppm and the reference compound is methane.)

3.6 *Response factor* means the ratio of the known concentration of a VOC compound to the observed meter reading when measured using an instrument calibrated with the reference compound specified in the applicable regulation.

3.7 *Response time* means the time interval from a step change in VOC concentration at the input of the sampling system to the time at which 90 percent of the corresponding final value is reached as displayed on the instrument readout meter.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Pollutants. Several of the compounds, leaks of which may be determined by this method, may be irritating or corrosive to tissues (*e.g.*, heptane) or may be toxic (*e.g.*, benzene, methyl alcohol). Nearly all are fire hazards. Compounds in emissions should be determined through familiarity with the source. Appropriate precautions can be found in reference documents, such as reference No. 4 in section 16.0.

6.0 Equipment and Supplies

A VOC monitoring instrument meeting the following specifications is required:

6.1 The VOC instrument detector shall respond to the compounds being processed. Detector types that may meet this requirement include, but are not limited to, catalytic oxidation, flame ionization, infrared absorption, and photoionization.

6.2 The instrument shall be capable of measuring the leak definition concentration specified in the regulation.

6.3 The scale of the instrument meter shall be readable to ±2.5 percent of the specified leak definition concentration.

6.4 The instrument shall be equipped with an electrically driven pump to ensure that a sample is provided to the detector at a constant flow rate. The nominal sample flow rate, as measured at the sample probe tip, shall be 0.10 to 3.0 l/min (0.004 to 0.1 ft^3/min) when the probe is fitted with a glass wool plug or filter that may be used to prevent plugging of the instrument.

6.5 The instrument shall be equipped with a probe or probe extension or sampling not to exceed 6.4 mm (¼ in) in outside diameter,

with a single end opening for admission of sample.

6.6 The instrument shall be intrinsically safe for operation in explosive atmospheres as defined by the National Electrical Code by the National Fire Prevention Association or other applicable regulatory code for operation in any explosive atmospheres that may be encountered in its use. The instrument shall, at a minimum, be intrinsically safe for Class 1, Division 1 conditions, and/or Class 2, Division 1 conditions, as appropriate, as defined by the example code. The instrument shall not be operated with any safety device, such as an exhaust flame arrestor, removed.

7.0 Reagents and Standards

7.1 Two gas mixtures are required for instrument calibration and performance evaluation:

7.1.1 Zero Gas. Air, less than 10 parts per million by volume (ppmv) VOC.

7.1.2 Calibration Gas. For each organic species that is to be measured during individual source surveys, obtain or prepare a known standard in air at a concentration approximately equal to the applicable leak definition specified in the regulation.

7.2 Cylinder Gases. If cylinder calibration gas mixtures are used, they must be analyzed and certified by the manufacturer to be within 2 percent accuracy, and a shelf life must be specified. Cylinder standards must be either reanalyzed or replaced at the end of the specified shelf life.

7.3 Prepared Gases. Calibration gases may be prepared by the user according to any accepted gaseous preparation procedure that will yield a mixture accurate to within 2 percent. Prepared standards must be replaced each day of use unless it is demonstrated that degradation does not occur during storage.

7.4 Mixtures with non-Reference Compound Gases. Calibrations may be performed using a compound other than the reference compound. In this case, a conversion factor must be determined for the alternative compound such that the resulting meter readings during source surveys can be converted to reference compound results.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Instrument Performance Evaluation. Assemble and start up the instrument according to the manufacturer's instructions for recommended warmup period and preliminary adjustments.

8.1.1 Response Factor. A response factor must be determined for each compound that is to be measured, either by testing or from reference sources. The response factor tests are required before placing the analyzer into service, but do not have to be repeated at subsequent intervals.

8.1.1.1 Calibrate the instrument with the reference compound as specified in the applicable regulation. Introduce the calibration gas mixture to the analyzer and record the observed meter reading. Introduce zero gas until a stable reading is obtained. Make a total of three measurements by alternating between the calibration gas and zero gas. Calculate the response factor for each repetition and the average response factor.

8.1.1.2 The instrument response factors for each of the individual VOC to be measured shall be less than 10 unless otherwise specified in the applicable regulation. When no instrument is available that meets this specification when calibrated with the reference VOC specified in the applicable regulation, the available instrument may be calibrated with one of the VOC to be measured, or any other VOC, so long as the instrument then has a response factor of less than 10 for each of the individual VOC to be measured.

8.1.1.3 Alternatively, if response factors have been published for the compounds of interest for the instrument or detector type, the response factor determination is not required, and existing results may be referenced. Examples of published response factors for flame ionization and catalytic oxidation detectors are included in References 1–3 of section 17.0.

8.1.2 Calibration Precision. The calibration precision test must be completed prior to placing the analyzer into service and at subsequent 3-month intervals or at the next use, whichever is later.

8.1.2.1 Make a total of three measurements by alternately using zero gas and the specified calibration gas. Record the meter readings. Calculate the average algebraic difference between the meter readings and the known value. Divide this average difference by the known calibration value and multiply by 100 to express the resulting calibration precision as a percentage.

8.1.2.2 The calibration precision shall be equal to or less than 10 percent of the calibration gas value.

8.1.3 Response Time. The response time test is required before placing the instrument into service. If a modification to the sample pumping system or flow configuration is made that would change the response time, a new test is required before further use.

8.1.3.1 Introduce zero gas into the instrument sample probe. When the meter reading has stabilized, switch quickly to the specified calibration gas. After switching, measure the time required to attain 90 percent of the final stable reading. Perform this test sequence three times and record the results. Calculate the average response time.

8.1.3.2 The instrument response time shall be equal to or less than 30 seconds. The instrument pump, dilution probe (if any), sample probe, and probe filter that will be used

during testing shall all be in place during the response time determination.

8.2 Instrument Calibration. Calibrate the VOC monitoring instrument according to section 10.0.

8.3 Individual Source Surveys.

8.3.1 Type I—Leak Definition Based on Concentration. Place the probe inlet at the surface of the component interface where leakage could occur. Move the probe along the interface periphery while observing the instrument readout. If an increased meter reading is observed, slowly sample the interface where leakage is indicated until the maximum meter reading is obtained. Leave the probe inlet at this maximum reading location for approximately two times the instrument response time. If the maximum observed meter reading is greater than the leak definition in the applicable regulation, record and report the results as specified in the regulation reporting requirements. Examples of the application of this general technique to specific equipment types are:

8.3.1.1 Valves. The most common source of leaks from valves is the seal between the stem and housing. Place the probe at the interface where the stem exits the packing gland and sample the stem circumference. Also, place the probe at the interface of the packing gland take-up flange seat and sample the periphery. In addition, survey valve housings of multipart assembly at the surface of all interfaces where a leak could occur.

8.3.1.2 Flanges and Other Connections. For welded flanges, place the probe at the outer edge of the flange-gasket interface and sample the circumference of the flange. Sample other types of nonpermanent joints (such as threaded connections) with a similar traverse.

8.3.1.3 Pumps and Compressors. Conduct a circumferential traverse at the outer surface of the pump or compressor shaft and seal interface. If the source is a rotating shaft, position the probe inlet within 1 cm of the shaft-seal interface for the survey. If the housing configuration prevents a complete traverse of the shaft periphery, sample all accessible portions. Sample all other joints on the pump or compressor housing where leakage could occur.

8.3.1.4 Pressure Relief Devices. The configuration of most pressure relief devices prevents sampling at the sealing seat interface. For those devices equipped with an enclosed extension, or horn, place the probe inlet at approximately the center of the exhaust area to the atmosphere.

8.3.1.5 Process Drains. For open drains, place the probe inlet at approximately the center of the area open to the atmosphere. For covered drains, place the probe at the surface of the cover interface and conduct a peripheral traverse.

8.3.1.6 Open-ended Lines or Valves. Place the probe inlet at approximately the center of the opening to the atmosphere.

8.3.1.7 Seal System Degassing Vents and Accumulator Vents. Place the probe inlet at approximately the center of the opening to the atmosphere.

8.3.1.8 Access door seals. Place the probe inlet at the surface of the door seal interface and conduct a peripheral traverse.

8.3.2 Type II—''No Detectable Emission''. Determine the local ambient VOC concentration around the source by moving the probe randomly upwind and downwind at a distance of one to two meters from the source. If an interference exists with this determination due to a nearby emission or leak, the local ambient concentration may be determined at distances closer to the source, but in no case shall the distance be less than 25 centimeters. Then move the probe inlet to the surface of the source and determine the concentration as outlined in section 8.3.1. The difference between these concentrations determines whether there are no detectable emissions. Record and report the results as specified by the regulation. For those cases where the regulation requires a specific device installation, or that specified vents be ducted or piped to a control device, the existence of these conditions shall be visually confirmed. When the regulation also requires that no detectable emissions exist, visual observations and sampling surveys are required. Examples of this technique are:

8.3.2.1 Pump or Compressor Seals. If applicable, determine the type of shaft seal. Perform a survey of the local area ambient VOC concentration and determine if detectable emissions exist as described in section 8.3.2.

8.3.2.2 Seal System Degassing Vents, Accumulator Vessel Vents, Pressure Relief Devices. If applicable, observe whether or not the applicable ducting or piping exists. Also, determine if any sources exist in the ducting or piping where emissions could occur upstream of the control device. If the required ducting or piping exists and there are no sources where the emissions could be vented to the atmosphere upstream of the control device, then it is presumed that no detectable emissions are present. If there are sources in the ducting or piping where emissions could be vented or sources where leaks could occur, the sampling surveys described in section 8.3.2 shall be used to determine if detectable emissions exist.

8.3.3 Alternative Screening Procedure.

8.3.3.1 A screening procedure based on the formation of bubbles in a soap solution that is sprayed on a potential leak source may be used for those sources that do not have continuously moving parts, that do not have surface temperatures greater than the boiling point or less than the freezing point of the soap solution, that do not have open

areas to the atmosphere that the soap solution cannot bridge, or that do not exhibit evidence of liquid leakage. Sources that have these conditions present must be surveyed using the instrument technique of section 8.3.1 or 8.3.2.

8.3.3.2 Spray a soap solution over all potential leak sources. The soap solution may be a commercially available leak detection solution or may be prepared using concentrated detergent and water. A pressure sprayer or squeeze bottle may be used to dispense the solution. Observe the potential leak sites to determine if any bubbles are formed. If no bubbles are observed, the source is presumed to have no detectable emissions or leaks as applicable. If any bubbles are observed, the instrument techniques of section 8.3.1 or 8.3.2 shall be used to determine if a leak exists, or if the source has detectable emissions, as applicable.

9.0 Quality Control

Section	Quality control measure	Effect
8.1.2	Instrument calibration precision check	Ensure precision and accuracy, respectively, of instrument response to standard.
10.0	Instrument calibration.	

10.0 Calibration and Standardization

10.1 Calibrate the VOC monitoring instrument as follows. After the appropriate warmup period and zero internal calibration procedure, introduce the calibration gas into the instrument sample probe. Adjust the instrument meter readout to correspond to the calibration gas value.

NOTE: If the meter readout cannot be adjusted to the proper value, a malfunction of the analyzer is indicated and corrective actions are necessary before use.

11.0 Analytical Procedures [Reserved]

12.0 Data Analyses and Calculations [Reserved]

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Dubose, D.A., and G.E. Harris. Response Factors of VOC Analyzers at a Meter Reading of 10,000 ppmv for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81051. September 1981.

2. Brown, G.E., *et al.* Response Factors of VOC Analyzers Calibrated with Methane for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81–022. May 1981.

3. DuBose, D.A. *et al.* Response of Portable VOC Analyzers to Chemical Mixtures. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81–110. September 1981.

4. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 22—VISUAL DETERMINATION OF FUGITIVE EMISSIONS FROM MATERIAL SOURCES AND SMOKE EMISSIONS FROM FLARES

NOTE: This method is not inclusive with respect to observer certification. Some material is incorporated by reference from Method 9.

1.0 Scope and Application

This method is applicable for the determination of the frequency of fugitive emissions from stationary sources, only as specified in an applicable subpart of the regulations. This method also is applicable for the determination of the frequency of visible smoke emissions from flares.

2.0 Summary of Method

2.1 Fugitive emissions produced during material processing, handling, and transfer operations or smoke emissions from flares are visually determined by an observer without the aid of instruments.

2.2 This method is used also to determine visible smoke emissions from flares used for combustion of waste process materials.

2.3 This method determines the amount of time that visible emissions occur during the observation period (*i.e.*, the accumulated emission time). This method does not require that the opacity of emissions be determined. Since this procedure requires only the determination of whether visible emissions occur and does not require the determination of opacity levels, observer certification according to the procedures of Method 9 is not required. However, it is necessary that the observer is knowledgeable with respect to the general procedures for determining the presence of visible emissions. At a minimum, the observer must be trained and knowledgeable regarding the effects of background contrast, ambient lighting, observer position relative

to lighting, wind, and the presence of uncombined water (condensing water vapor) on the visibility of emissions. This training is to be obtained from written materials found in References 1 and 2 or from the lecture portion of the Method 9 certification course.

3.0 Definitions

3.1 *Emission frequency* means the percentage of time that emissions are visible during the observation period.

3.2 *Emission time* means the accumulated amount of time that emissions are visible during the observation period.

3.3 *Fugitive emissions* means emissions generated by an affected facility which is not collected by a capture system and is released to the atmosphere. This includes emissions that (1) escape capture by process equipment exhaust hoods; (2) are emitted during material transfer; (3) are emitted from buildings housing material processing or handling equipment; or (4) are emitted directly from process equipment.

3.4 *Observation period* means the accumulated time period during which observations are conducted, not to be less than the period specified in the applicable regulation.

3.5 *Smoke emissions* means a pollutant generated by combustion in a flare and occurring immediately downstream of the flame. Smoke occurring within the flame, but not downstream of the flame, is not considered a smoke emission.

4.0 Interferences

4.1 Occasionally, fugitive emissions from sources other than the affected facility (*e.g.*, road dust) may prevent a clear view of the affected facility. This may particularly be a problem during periods of high wind. If the view of the potential emission points is obscured to such a degree that the observer questions the validity of continuing observations, then the observations shall be terminated, and the observer shall clearly note this fact on the data form.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment

6.1 Stopwatches (two). Accumulative type with unit divisions of at least 0.5 seconds.

6.2 Light Meter. Light meter capable of measuring illuminance in the 50 to 200 lux range, required for indoor observations only.

7.0 Reagents and Supplies [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transfer [Reserved]

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

11.1 Selection of Observation Location. Survey the affected facility, or the building or structure housing the process to be observed, and determine the locations of potential emissions. If the affected facility is located inside a building, determine an observation location that is consistent with the requirements of the applicable regulation (*i.e.*, outside observation of emissions escaping the building/structure or inside observation of emissions directly emitted from the affected facility process unit). Then select a position that enables a clear view of the potential emission point(s) of the affected facility or of the building or structure housing the affected facility, as appropriate for the applicable subpart. A position at least 4.6 m (15 feet), but not more than 400 m (0.25 miles), from the emission source is recommended. For outdoor locations, select a position where the sunlight is not shining directly in the observer's eyes.

11.2 Field Records.

11.2.1 Outdoor Location. Record the following information on the field data sheet (Figure 22–1): Company name, industry, process unit, observer's name, observer's affiliation, and date. Record also the estimated wind speed, wind direction, and sky condition. Sketch the process unit being observed, and note the observer location relative to the source and the sun. Indicate the potential and actual emission points on the sketch.

11.2.2 Indoor Location. Record the following information on the field data sheet (Figure 22–2): Company name, industry, process unit, observer's name, observer's affiliation, and date. Record as appropriate the type, location, and intensity of lighting on the data sheet. Sketch the process unit being observed, and note the observer location relative to the source. Indicate the potential and actual fugitive emission points on the sketch.

11.3 Indoor Lighting Requirements. For indoor locations, use a light meter to measure the level of illumination at a location as close to the emission source(s) as is feasible. An illumination of greater than 100 lux (10 foot candles) is considered necessary for proper application of this method.

11.4 Observations.

11.4.1 Procedure. Record the clock time when observations begin. Use one stopwatch to monitor the duration of the observation

period. Start this stopwatch when the observation period begins. If the observation period is divided into two or more segments by process shutdowns or observer rest breaks (see section 11.4.3), stop the stopwatch when a break begins and restart the stopwatch without resetting it when the break ends. Stop the stopwatch at the end of the observation period. The accumulated time indicated by this stopwatch is the duration of observation period. When the observation period is completed, record the clock time. During the observation period, continuously watch the emission source. Upon observing an emission (condensed water vapor is not considered an emission), start the second accumulative stopwatch; stop the watch when the emission stops. Continue this procedure for the entire observation period. The accumulated elapsed time on this stopwatch is the total time emissions were visible during the observation period (*i.e.*, the emission time.)

11.4.2 Observation Period. Choose an observation period of sufficient length to meet the requirements for determining compliance with the emission standard in the applicable subpart of the regulations. When the length of the observation period is specifically stated in the applicable subpart, it may not be necessary to observe the source for this entire period if the emission time required to indicate noncompliance (based on the specified observation period) is observed in a shorter time period. In other words, if the regulation prohibits emissions for more than 6 minutes in any hour, then observations may (optional) be stopped after an emission time of 6 minutes is exceeded. Similarly, when the regulation is expressed as an emission frequency and the regulation prohibits emissions for greater than 10 percent of the time in any hour, then observations may (optional) be terminated after 6 minutes of emission are observed since 6 minutes is 10 percent of an hour. In any case, the observation period shall not be less than 6 minutes in duration. In some cases, the process operation may be intermittent or cyclic. In such cases, it may be convenient for the observation period to coincide with the length of the process cycle.

11.4.3 Observer Rest Breaks. Do not observe emissions continuously for a period of more than 15 to 20 minutes without taking a rest break. For sources requiring observation periods of greater than 20 minutes, the observer shall take a break of not less than 5 minutes and not more than 10 minutes after every 15 to 20 minutes of observation. If continuous observations are desired for extended time periods, two observers can alternate between making observations and taking breaks.

11.5 Recording Observations. Record the accumulated time of the observation period on the data sheet as the observation period duration. Record the accumulated time emissions were observed on the data sheet as the emission time. Record the clock time the observation period began and ended, as well as the clock time any observer breaks began and ended.

12.0 Data Analysis and Calculations

If the applicable subpart requires that the emission rate be expressed as an emission frequency (in percent), determine this value as follows: Divide the accumulated emission time (in seconds) by the duration of the observation period (in seconds) or by any minimum observation period required in the applicable subpart, if the actual observation period is less than the required period, and multiply this quotient by 100.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Missan, R., and A. Stein. Guidelines for Evaluation of Visible Emissions Certification, Field Procedures, Legal Aspects, and Background Material. EPA Publication No. EPA–340/1–75–007. April 1975.

2. Wohlschlegel, P., and D.E. Wagoner. Guideline for Development of a Quality Assurance Program: Volume IX—Visual Determination of Opacity Emissions from Stationary Sources. EPA Publication No. EPA–650/4–74–005i. November 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

FUGITIVE OR SMOKE EMISSION INSPECTION
OUTDOOR LOCATION

Company Location Company Rep.	Observer Affiliation Date
Sky Conditions Precipitation	Wind Direction Wind Speed
Industry	Process Unit

Sketch process unit: indicate observer position relative to source; indicate potential emission points and/or actual emission points.

OBSERVATIONS	Clock Time	Observation period duration, min:sec	Accumulated emission time, min:sec
Begin Observation			
End Observation			

Figure 22-1

FUGITIVE OR SMOKE EMISSION INSPECTION
INDOOR LOCATION

Company Location Company Rep.	Observer Affiliation Date
Industry	Process Unit

Light type (fluorescent, incandescent, natural)
Light location (overhead, behind observer, etc.)
Illuminance (lux or footcandles)
Sketch process unit: indicate observer position relative to source; indicate potential emission points and/or actual emission points.

OBSERVATIONS	Clock Time	Observation period duration, min:sec	Accumulated emission time, min:sec
Begin			
End Observation			

Figure 22-2

METHOD 23—DETERMINATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS FROM STATIONARY SOURCES

1. Applicability and Principle

1.1 Applicability. This method is applicable to the determination of polychlorinated dibenzo-p-dioxins (PCDD's) and polychlorinated dibenzofurans (PCDF's) from stationary sources.

1.2 Principle. A sample is withdrawn from the gas stream isokinetically and collected in the sample probe, on a glass fiber filter, and on a packed column of adsorbent material. The sample cannot be separated into a particle vapor fraction. The PCDD's and

PCDF's are extracted from the sample, separated by high resolution gas chromatography, and measured by high resolution mass spectrometry.

2. Apparatus

2.1 Sampling. A schematic of the sampling train used in this method is shown in Figure 23–1. Sealing greases may not be used in assembling the train. The train is identical to that described in section 2.1 of Method 5 of this appendix with the following additions:

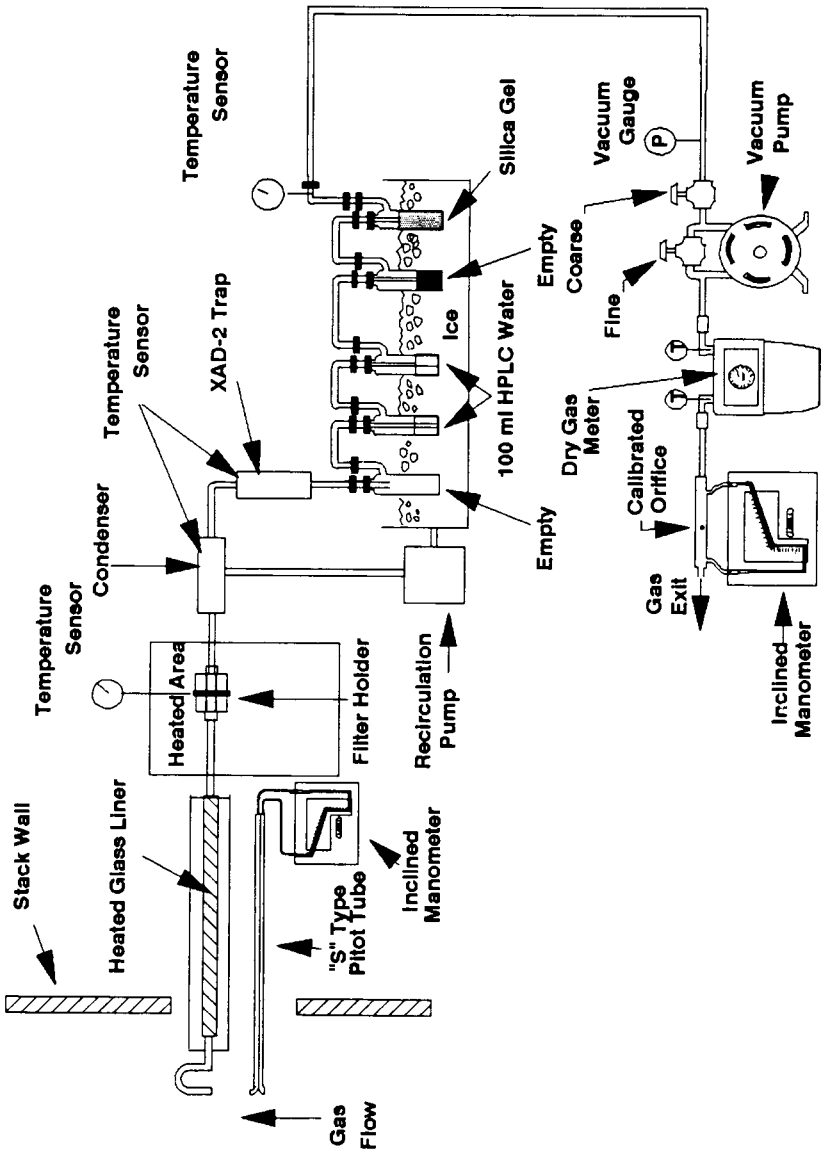

Figure 23.1 Sampling train

2.1.1 Nozzle. The nozzle shall be made of nickel, nickel-plated stainless steel, quartz, or borosilicate glass.

2.1.2 Sample Transfer Lines. The sample transfer lines, if needed, shall be heat traced, heavy walled TFE (½ in. OD with ⅛ in. wall) with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases. The line shall be as short as possible and must be maintained at 120 °C.

2.1.1 Filter Support. Teflon or Teflon-coated wire.

2.1.2 Condenser. Glass, coil type with compatible fittings. A schematic diagram is shown in Figure 23–2.

2.1.3 Water Bath. Thermostatically controlled to maintain the gas temperature exiting the condenser at <20 °C (68 °F).

2.1.4 Adsorbent Module. Glass container to hold the solid adsorbent. A shematic diagram is shown in Figure 23–2. Other physical configurations of the resin trap/condenser assembly are acceptable. The connecting fittings shall form leak-free, vacuum tight seals. No sealant greases shall be used in the sampling train. A coarse glass frit is included to retain the adsorbent.

2.2 Sample Recovery.

2.2.1 Fitting Caps. Ground glass, Teflon tape, or aluminum foil (Section 2.2.6) to cap off the sample exposed sections of the train.

2.2.2 Wash Bottles. Teflon, 500-ml.

2.2.3 Probe-Liner Probe-Nozzle, and Filter-Holder Brushes. Inert bristle brushes with precleaned stainless steel or Teflon handles. The probe brush shall have extensions of stainless steel or Teflon, at least as long as the probe. The brushes shall be properly sized and shaped to brush out the nozzle, probe liner, and transfer line, if used.

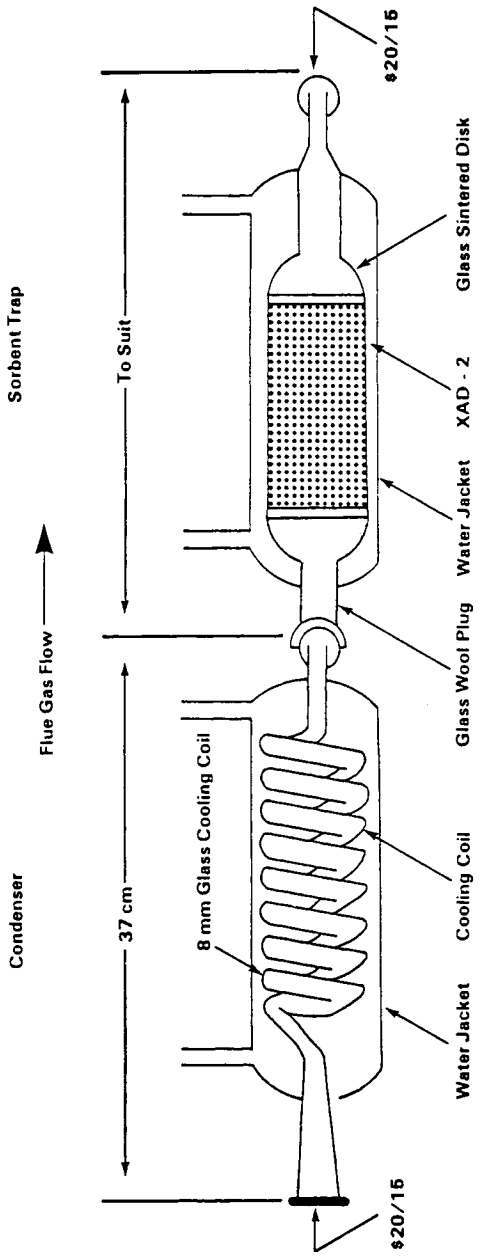

Figure 23.2. Condenser and adsorbent trap

2.2.4 Filter Storage Container. Sealed filter holder, wide-mouth amber glass jar with Teflon-lined cap, or glass petri dish.

2.2.5 Balance. Triple beam.

2.2.6 Aluminum Foil. Heavy duty, hexane-rinsed.

2.2.7 Storage Container. Air-tight container to store silica gel.

2.2.8 Graduated Cylinder. Glass, 250-ml with 2-ml graduation.

2.2.9 Glass Sample Storage Container. Amber glass bottle for sample glassware washes, 500- or 1000-ml, with leak free Teflon-lined caps.

2.3 Analysis.

2.3.1 Sample Container. 125- and 250-ml flint glass bottles with Teflon-lined caps.

2.3.2 Test Tube. Glass.

2.3.3 Soxhlet Extraction Apparatus. Capable of holding 43 × 123 mm extraction thimbles.

2.3.4 Extraction Thimble. Glass, precleaned cellulosic, or glass fiber.

2.3.5 Pasteur Pipettes. For preparing liquid chromatographic columns.

2.3.6 Reacti-vials. Amber glass, 2-ml, silanized prior to use.

2.3.7 Rotary Evaporator. Buchi/Brinkman RF–121 or equivalent.

2.3.8 Nitrogen Evaporative Concentrator. N-Evap Analytical Evaporator Model III or equivalent.

2.3.9 Separatory Funnels. Glass, 2-liter.

2.3.10 Gas Chromatograph. Consisting of the following components:

2.3.10.1 Oven. Capable of maintaining the separation column at the proper operating temperature ±°C and performing programmed increases in temperature at rates of at least 40 °C/min.

2.3.10.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperatures ±1 °C.

2.3.10.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

2.3.10.4 Capillary Columns. A fused silica column, 60 × 0.25 mm inside diameter (ID), coated with DB–5 and a fused silica column, 30 m × 0.25 mm ID coated with DB–225. Other column systems may be used provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of section 6.1.2.2.

2.3.11 Mass Spectrometer. Capable of routine operation at a resolution of 1:10000 with a stability of ±5 ppm.

2.3.12 Data System. Compatible with the mass spectrometer and capable of monitoring at least five groups of 25 ions.

2.3.13 Analytical Balance. To measure within 0.1 mg.

3. Reagents

3.1 Sampling.

3.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D 2986–71 (Reapproved 1978) (incorporated by reference—see §60.17).

3.1.1.1 Precleaning. All filters shall be cleaned before their initial use. Place a glass extraction thimble and 1 g of silica gel and a plug of glass wool into a Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Place no more than 50 filters in the thimble onto the silica gel bed and top with the cleaned glass wool. Charge the Soxhlet with toluene and reflux for 16 hours. After extraction, allow the Soxhlet to cool, remove the filters, and dry them under a clean N_2 stream. Store the filters in a glass petri dish sealed with Teflon tape.

3.1.2 Adsorbent Resin. Amberlite XAD–2 resin. Thoroughly cleaned before initial use.

3.1.2.1 Cleaning Procedure. This procedure may be carried out in a giant Soxhlet extractor. An all-glass filter thimble containing an extra-course frit is used for extraction of XAD–2. The frit is recessed 10–15 mm above a crenelated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass wool plug and a stainless steel ring because it floats on methylene chloride. This process involves sequential extraction in the following order.

Solvent	Procedure
Water	Initial rinse: Place resin in a beaker, rinse once with water, and discard. Fill with water a second time, let stand overnight, and discard.
Water	Extract with water for 8 hours.
Methanol	Extract for 22 hours.
Methylene Chloride	Extract for 22 hours.
Toluene	Extract for 22 hours.

3.1.2.2 Drying.

3.1.2.2.1 Drying Column. Pyrex pipe, 10.2 cm ID by 0.6 m long, with suitable retainers.

3.1.2.2.2 Procedure. The adsorbent must be dried with clean inert gas. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has proven to be a reliable source of large volumes of gas free from organic contaminants. Connect the liquid nitrogen cylinder to the column by a length of cleaned copper tubing, 0.95 cm ID, coiled to pass through a heat source. A convenient heat source is a water-bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40 °C. Continue flowing nitrogen through the adsorbent until all the residual solvent is removed. The flow rate should be sufficient to gently agitate the particles but not so excessive as the cause the particles to fracture.

3.1.2.3 Quality Control Check. The adsorbent must be checked for residual toluene.

3.1.2.3.1 Extraction. Weigh 1.0 g sample of dried resin into a small vial, add 3 ml of toluene, cap the vial, and shake it well.

3.1.2.3.2 Analysis. Inject a 2 µl sample of the extract into a gas chromatograph operated under the following conditions:

Column: 6 ft × ⅛ in stainless steel containing 10 percent OV–101 on 100/120 Supelcoport.
Carrier Gas: Helium at a rate of 30 ml/min.
Detector: Flame ionization detector operated at a sensitivity of 4×10^{-11} A/mV.
Injection Port Temperature: 250 °C.
Detector Temperature: 305 °C.
Oven Temperature: 30 °C for 4 min; programmed to rise at 40 °C/min until it reaches 250 °C; return to 30 °C after 17 minutes.

Compare the results of the analysis to the results from the reference solution. Prepare the reference solution by injection 2.5 µl of methylene chloride into 100 ml of toluene. This corresponds to 100 µg of methylene chloride per g of adsorbent. The maximum acceptable concentration is 1000 µg/g of adsorbent. If the adsorbent exceeds this level, drying must be continued until the excess methylene chloride is removed.

3.1.2.4 Storage. The adsorbent must be used within 4 weeks of cleaning. After cleaning, it may be stored in a wide mouth amber glass container with a Teflon-lined cap or placed in one of the glass adsorbent modules tightly sealed with glass stoppers. If precleaned adsorbent is purchased in sealed containers, it must be used within 4 weeks after the seal is broken.

3.1.3 Glass Wool. Cleaned by sequential immersion in three aliquots of methylene chloride, dried in a 110 °C oven, and stored in a methylene chloride-washed glass jar with a Teflon-lined screw cap.

3.1.4 Water. Deionized distilled and stored in a methylene chloride-rinsed glass container with a Teflon-lined screw cap.

3.1.5 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175 °C (350 °F) for two hours. New silica gel may be used as received. Alternately other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

3.1.6 Chromic Acid Cleaning Solution. Dissolve 20 g of sodium dichromate in 15 ml of water, and then carefully add 400 ml of concentrated sulfuric acid.

3.2 Sample Recovery.

3.2.2 Acetone. Pesticide quality.

3.2.2 Methylene Chloride. Pesticide qualtity.

3.2.3 Toluene. Pesticide quality.

3.3 Analysis.

3.3.1 Potassium Hydroxide. ACS grade, 2-percent (weight/volume) in water.

3.3.2 Sodium Sulfate. Granulated, reagent grade. Purify prior to use by rinsing with methylene chloride and oven drying. Store the cleaned material in a glass container with a Teflon-lined screw cap.

3.3.3 Sulfuric Acid. Reagent grade.

3.3.4 Sodium Hydroxide. 1.0 N. Weigh 40 g of sodium hydroxide into a 1-liter volumetric flask. Dilute to 1 liter with water.

3.3.5 Hexane. Pesticide grade.

3.3.6 Methylene Chloride. Pesticide grade.

3.3.7 Benzene. Pesticide Grade.

3.3.8 Ethyl Acetate.

3.3.9 Methanol. Pesticide Grade.

3.3.10 Toluene. Pesticide Grade.

3.3.11 Nonane. Pesticide Grade.

3.3.12 Cyclohexane. Pesticide Grade.

3.3.13 Basic Alumina. Activity grade 1, 100–200 mesh. Prior to use, activate the alumina by heating for 16 hours at 130 °C before use. Store in a desiccator. Pre-activated alumina may be purchased from a supplier and may be used as received.

3.3.14 Silica Gel. Bio-Sil A, 100–200 mesh. Prior to use, activate the silica gel by heating for at least 30 minutes at 180 °C. After cooling, rinse the silica gel sequentially with methanol and methylene chloride. Heat the rinsed silica gel at 50 °C for 10 minutes, then increase the temperature gradually to 180 °C over 25 minutes and maintain it at this temperature for 90 minutes. Cool at room temperature and store in a glass container with a Teflon-lined screw cap.

3.3.15 Silica Gel Impregnated with Sulfuric Acid. Combine 100 g of silica gel with 44 g of concentrated sulfuric acid in a screw capped glass bottle and agitate thoroughly. Disperse the solids with a stirring rod until a uniform mixture is obtained. Store the mixture in a glass container with a Teflon-lined screw cap.

3.3.16 Silica Gel Impregnated with Sodium Hydroxide. Combine 39 g of 1 N sodium hydroxide with 100 g of silica gel in a screw capped glass bottle and agitate thoroughly. Disperse solids with a stirring rod until a uniform mixture is obtained. Store the mixture in glass container with a Teflon-lined screw cap.

3.3.17 Carbon/Celite. Combine 10.7 g of AX–21 carbon with 124 g of Celite 545 in a 250-ml glass bottle with a Teflon-lined screw cap. Agitate the mixture thoroughly until a uniform mixture is obtained. Store in the glass container.

3.3.18 Nitrogen. Ultra high purity.

3.3.19 Hydrogen. Ultra high purity.

3.3.20 Internal Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Internal Standards'' in 10 ml of nonane.

3.3.21 Surrogate Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Surrogate Standards'' in 10 ml of nonane.

3.3.22 Recovery Standard Solution. Prepare a stock standard solution containing the

isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Recovery Standards'' in 10 ml of nonane.

4. Procedure

4.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, testers should be trained and experienced with the test procedures.

4.1.1 Pretest Preparation.

4.1.1.1 Cleaning Glassware. All glass components of the train upstream of and including the adsorbent module, shall be cleaned as described in section 3A of the ''Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples.'' Special care shall be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. Any residue shall be removed by soaking the glassware for several hours in a chromic acid cleaning solution prior to cleaning as described above.

4.1.1.2 Adsorbent Trap. The traps must be loaded in a clean area to avoid contamination. They may not be loaded in the field. Fill a trap with 20 to 40 g of XAD–2. Follow the XAD–2 with glass wool and tightly cap both ends of the trap. Add 100 μl of the surrogate standard solution (section 3.3.21) to each trap.

4.1.1.3 Sample Train. It is suggested that all components be maintained according to the procedure described in APTD–0576. Alternative mercury-free thermometers may be used if the thermometers are, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

4.1.1.4 Silica Gel. Weigh several 200 to 300 g portions of silica gel in an air tight container to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel may be weighed directly in its impinger or sampling holder just prior to sampling.

4.1.1.5 Filter. Check each filter against light for irregularities and flaws or pinhole leaks. Pack the filters flat in a clean glass container.

4.1.2 Preliminary Determinations. Same as section 4.1.2 of Method 5.

4.1.3 Preparation of Collection Train.

4.1.3.1 During preparation and assembly of the sampling train, keep all train openings where contamination can enter, sealed until just prior to assembly or until sampling is about to begin.

NOTE: Do not use sealant grease in assembling the train.

4.1.3.2 Place approximately 100 ml of water in the second and third impingers, leave the first and fourth impingers empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fifth impinger.

4.1.3.3 Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

4.1.3.4 Assemble the train as shown in Figure 23–1.

4.1.3.5 Turn on the adsorbent module and condenser coil recirculating pump and begin monitoring the adsorbent module gas entry temperature. Ensure proper sorbent temperature gas entry temperature before proceeding and before sampling is initiated. It is extremely important that the XAD–2 adsorbent resin temperature never exceed 50 °C because thermal decomposition will occur. During testing, the XAD–2 temperature must not exceed 20 °C for efficient capture of the PCDD's and PCDF's.

4.1.4 Leak-Check Procedure. Same as Method 5, section 4.1.4.

4.1.5 Sample Train Operation. Same as Method 5, section 4.1.5.

4.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Seal the nozzle end of the sampling probe with Teflon tape or aluminum foil.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe. Remove the probe from the train and close off both ends with aluminum foil. Seal off the inlet to the train with Teflon tape, a ground glass cap, or aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area shall be clean and enclosed so that the chances of losing or contaminating the sample are minimized. Smoking, which could contaminate the sample, shall not be allowed in the cleanup area.

Inspect the train prior to and during disassembly and note any abnormal conditions, e.g., broken filters, colored impinger liquid, etc. Treat the samples as follows:

4.2.1 Container No. 1. Either seal the filter holder or carefully remove the filter from the filter holder and place it in its identified container. Use a pair of cleaned tweezers to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and filter fibers which adhere to the filter holder gasket, by using a dry inert bristle brush and a sharp-edged blade. Seal the container.

4.2.2 Adsorbent Module. Remove the module from the train, tightly cap both ends, label it, cover with aluminum foil, and store it on ice for transport to the laboratory.

4.2.3 Container No. 2. Quantitatively recover material deposited in the nozzle, probe transfer lines, the front half of the filter holder, and the cyclone, if used, first, by

brushing while rinsing three times each with acetone and then, by rinsing the probe three times with methylene chloride. Collect all the rinses in Container No. 2.

Rinse the back half of the filter holder three times with acetone. Rinse the connecting line between the filter and the condenser three times with acetone. Soak the connecting line with three separate portions of methylene chloride for 5 minutes each. If using a separate condenser and adsorbent trap, rinse the condenser in the same manner as the connecting line. Collect all the rinses in Container No. 2 and mark the level of the liquid on the container.

4.2.4 Container No. 3. Repeat the methylene chloride-rinsing described in section 4.2.3 using toluene as the rinse solvent. Collect the rinses in Container No. 3 and mark the level of the liquid on the container.

4.2.5 Impinger Water. Measure the liquid in the first three impingers to within ±1 ml by using a graduated cylinder or by weighing it to within ±0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

Discard the liquid after measuring and recording the volume or weight.

4.2.7 Silica Gel. Note the color of the indicating silica gel to determine if it has been completely spent and make a mention of its condition. Transfer the silica gel from the fifth impinger to its original container and seal. If a moisture determination is made, follow the applicable procedures in sections 8.7.6.3 and 11.2.3 of Method 5 to handle and weigh the silica gel. If moisture is not measured, the silica gel may be disposed.

5. Analysis

All glassware shall be cleaned as described in section 3A of the ''Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples.'' All samples must be extracted within 30 days of collection and analyzed within 45 days of extraction.

5.1 Sample Extraction.

5.1.1 Extraction System. Place an extraction thimble (section 2.3.4), 1 g of silica gel, and a plug of glass wool into the Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Remove the extraction thimble from the extraction system and place it in a glass beaker to catch the solvent rinses.

5.1.2 Container No. 1 (Filter). Transfer the contents directly to the glass thimble of the extraction system and extract them simultaneously with the XAD–2 resin.

5.1.3 Adsorbent Cartridge. Suspend the adsorbent module directly over the extraction thimble in the beaker (See section 5.1.1). The glass frit of the module should be in the up position. Using a Teflon squeeze bottle containing toluene, flush the XAD–2 into the thimble onto the bed of cleaned silica gel. Thoroughly rinse the glass module catching the rinsings in the beaker containing the thimble. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. Add the XAD–2 glass wool plug into the thimble.

5.1.4 Container No. 2 (Acetone and Methylene Chloride). Concentrate the sample to a volume of about 1–5 ml using the rotary evaporator apparatus, at a temperature of less than 37 °C. Rinse the sample container three times with small portions of methylene chloride and add these to the concentrated solution and concentrate further to near dryness. This residue contains particulate matter removed in the rinse of the train probe and nozzle. Add the concentrate to the filter and the XAD–2 resin in the Soxhlet apparatus described in section 5.1.1.

5.1.5 Extraction. Add 100 µl of the internal standard solution (Section 3.3.20) to the extraction thimble containing the contents of the adsorbent cartridge, the contents of Container No. 1, and the concentrate from section 5.1.4. Cover the contents of the extraction thimble with the cleaned glass wool plug to prevent the XAD–2 resin from floating into the solvent reservoir of the extractor. Place the thimble in the extractor, and add the toluene contained in the beaker to the solvent reservoir. Pour additional toluene to fill the reservoir approximately ⅔ full. Add Teflon boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle three times per hour. Extract the sample for 16 hours. After extraction, allow the Soxhlet to cool. Transfer the toluene extract and three 10-ml rinses to the rotary evaporator. Concentrate the extract to approximately 10 ml. At this point the analyst may choose to split the sample in half. If so, split the sample, store one half for future use, and analyze the other according to the procedures in sections 5.2 and 5.3. In either case, use a nitrogen evaporative concentrator to reduce the volume of the sample being analyzed to near dryness. Dissolve the residue in 5 ml of hexane.

5.1.6 Container No. 3 (Toluene Rinse). Add 100 µl of the Internal Standard solution (section 3.3.2) to the contents of the container. Concentrate the sample to a volume of about 1–5 ml using the rotary evaporator apparatus at a temperature of less than 37 °C. Rinse the sample container apparatus at a temperature of less than 37 °C. Rinse the sample container three times with small portions of toluene and add these to the concentrated solution and concentrate further to near dryness. Analyze the extract separately according to the procedures in sections 5.2 and 5.3, but concentrate the solution in a rotary evaporator apparatus rather than a nitrogen evaporative concentrator.

5.2 Sample Cleanup and Fractionation.

5.2.1 Silica Gel Column. Pack one end of a glass column, 20 mm × 230 mm, with glass wool. Add in sequence, 1 g silica gel, 2 g of sodium hydroxide impregnated silica gel, 1 g silica gel, 4 g of acid-modified silica gel, and 1 g of silica gel. Wash the column with 30 ml of hexane and discard it. Add the sample extract, dissolved in 5 ml of hexane to the column with two additional 5-ml rinses. Elute the column with an additional 90 ml of hexane and retain the entire eluate. Concentrate this solution to a volume of about 1 ml using the nitrogen evaporative concentrator (section 2.3.7).

5.2.2 Basic Alumina Column. Shorten a 25-ml disposable Pasteur pipette to about 16 ml. Pack the lower section with glass wool and 12 g of basic alumina. Transfer the concentrated extract from the silica gel column to the top of the basic alumina column and elute the column sequentially with 120 ml of 0.5 percent methylene chloride in hexane followed by 120 ml of 35 percent methylene chloride in hexane. Discard the first 120 ml of eluate. Collect the second 120 ml of eluate and concentrate it to about 0.5 ml using the nitrogen evaporative concentrator.

5.2.3 AX–21 Carbon/Celite 545 Column. Remove the botton 0.5 in. from the tip of a 9-ml disposable Pasteur pipette. Insert a glass fiber filter disk in the top of the pipette 2.5 cm from the constriction. Add sufficient carbon/celite mixture to form a 2 cm column. Top with a glass wool plug. In some cases AX–21 carbon fines may wash through the glass wool plug and enter the sample. This may be prevented by adding a celite plug to the exit end of the column. Rinse the column in sequence with 2 ml of 50 percent benzene in ethyl acetate, 1 ml of 50 percent methylene chloride in cyclohexane, and 2 ml of hexane. Discard these rinses. Transfer the concentrate in 1 ml of hexane from the basic alumina column to the carbon/celite column along with 1 ml of hexane rinse. Elute the column sequentially with 2 ml of 50 percent methylene chloride in hexane and 2 ml of 50 percent benzene in ethyl acetate and discard these eluates. Invert the column and elute in the reverse direction with 13 ml of toluene. Collect this eluate. Concentrate the eluate in a rotary evaporator at 50 °C to about 1 ml. Transfer the concentrate to a Reacti-vial using a toluene rinse and concentrate to a volume of 200 µl using a stream of N_2. Store extracts at room temperature, shielded from light, until the analysis is performed.

5.3 Analysis. Analyze the sample with a gas chromatograph coupled to a mass spectrometer (GC/MS) using the instrumental parameters in sections 5.3.1 and 5.3.2. Immediately prior to analysis, add a 20 µl aliquot of the Recovery Standard solution from Table 1 to each sample. A 2 µl aliquot of the extract is injected into the GC. Sample extracts are first analyzed using the DB–5 capillary column to determine the concentration of each isomer of PCDD's and PCDF's (tetra-through octa-). If tetra-chlorinated dibenzofurans are detected in this analysis, then analyze another aliquot of the sample in a separate run, using the DB–225 column to measure the 2,3,7,8 tetra-chloro dibenzofuran isomer. Other column systems may be used, provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of section 6.1.2.2.

5.3.1 Gas Chromatograph Operating Conditions.

5.3.1.1 Injector. Configured for capillary column, splitless, 250 °C.

5.3.1.2 Carrier Gas. Helium, 1–2 ml/min.

5.3.1.3 Oven. Initially at 150 °C. Raise by at least 40 °C/min to 190 °C and then at 3 °C/min up to 300 °C.

5.3.2 High Resolution Mass Spectrometer.

5.3.2.1 Resolution. 10000 m/e.

5.3.2.2 Ionization Mode. Electron impact.

5.3.2.3 Source Temperature 250 °C.

5.3.2.4 Monitoring Mode. Selected ion monitoring. A list of the various ions to be monitored is summarized in Table 3.

5.3.2.5 Identification Criteria. The following identification criteria shall be used for the characterization of polychlorinated dibenzodioxins and dibenzofurans.

1. The integrated ion-abundance ratio (M/M + 2 or M + 2/M + 4) shall be within 15 percent of the theoretical value. The acceptable ion-abundance ratio ranges for the identification of chlorine-containing compounds are given in Table 4.

2. The retention time for the analytes must be within 3 seconds of the corresponding ^{13}C-labeled internal standard, surrogate or alternate standard.

3. The monitored ions, shown in Table 3 for a given analyte, shall reach their maximum within 2 seconds of each other.

4. The identification of specific isomers that do not have corresponding ^{13}C-labeled standards is done by comparison of the relative retention time (RRT) of the analyte to the nearest internal standard retention time with reference (i.e., within 0.005 RRT units) to the comparable RRT's found in the continuing calibration.

5. The signal to noise ratio for all monitored ions must be greater than 2.5.

6. The confirmation of 2, 3, 7, 8–TCDD and 2, 3, 7, 8–TCDF shall satisfy all of the above identification criteria.

7. For the identification of PCDF's, no signal may be found in the corresponding PCDPE channels.

5.3.2.6 Quantification. The peak areas for the two ions monitored for each analyte are summed to yield the total response for each analyte. Each internal standard is used to quantify the indigenous PCDD's or PCDF's in its homologous series. For example, the $^{13}C_{12}$–2,3,7,8-tetra chlorinated dibenzodioxin is used to calculate the concentrations of all

other tetra chlorinated isomers. Recoveries of the tetra- and penta- internal standards are calculated using the $^{13}C_{12}$–1,2,3,4–TCDD. Recoveries of the hexa- through octa- internal standards are calculated using $^{13}C_{12}$–1,2,3,7,8,9–HxCDD. Recoveries of the surrogate standards are calculated using the corresponding homolog from the internal standard.

6. Calibration

Same as Method 5 with the following additions.

6.1 GC/MS System.

6.1.1 Initial Calibration. Calibrate the GC/MS system using the set of five standards shown in Table 2. The relative standard deviation for the mean response factor from each of the unlabeled analytes (Table 2) and of the internal, surrogate, and alternate standards shall be less than or equal to the values in Table 5. The signal to noise ratio for the GC signal present in every selected ion current profile shall be greater than or equal to 2.5. The ion abundance ratios shall be within the control limits in Table 4.

6.1.2 Daily Performance Check.

6.1.2.1 Calibration Check. Inject on µl of solution Number 3 from Table 2. Calculate the relative response factor (RRF) for each compound and compare each RRF to the corresponding mean RRF obtained during the initial calibration. The analyzer performance is acceptable if the measured RRF's for the labeled and unlabeled compounds for the daily run are within the limits of the mean values shown in Table 5. In addition, the ion-abundance ratios shall be within the allowable control limits shown in Table 4.

6.1.2.2 Column Separation Check. Inject a solution of a mixture of PCDD's and PCDF's that documents resolution between 2,3,7,8–TCDD and other TCDD isomers. Resolution is defined as a valley between peaks that is less than 25 percent of the lower of the two peaks. Identify and record the retention time windows for each homologous series.

Perform a similar resolution check on the confirmation column to document the resolution between 2,3,7,8 TCDF and other TCDF isomers.

6.2 Lock Channels. Set mass spectrometer lock channels as specified in Table 3. Monitor the quality control check channels specified in Table 3 to verify instrument stability during the analysis.

7. Quality Control

7.1 Sampling Train Collection Efficiency Check. Add 100 µl of the surrogate standards in Table 1 to the absorbent cartridge of each train before collecting the field samples.

7.2 Internal Standard Percent Recoveries. A group of nine carbon labeled PCDD's and PCDF's representing, the tetra-through octachlorinated homologues, is added to every sample prior to extraction. The role of the internal standards is to quantify the native PCDD's and PCDF's present in the sample as well as to determine the overall method efficiency. Recoveries of the internal standards must be between 40 to 130 percent for the tetra-through hexachlorinated compounds while the range is 25 to 130 percent for the higher hepta- and octachlorinated homologues.

7.3 Surrogate Recoveries. The five surrogate compounds in Table 2 are added to the resin in the adsorbent sampling cartridge before the sample is collected. The surrogate recoveries are measured relative to the internal standards and are a measure of collection efficiency. They are not used to measure native PCDD's and PCDF's. All recoveries shall be between 70 and 130 percent. Poor recoveries for all the surrogates may be an indication of breakthrough in the sampling train. If the recovery of all standards is below 70 percent, the sampling runs must be repeated. As an alternative, the sampling runs do not have to be repeated if the final results are divided by the fraction of surrogate recovery. Poor recoveries of isolated surrogate compounds should not be grounds for rejecting an entire set of the samples.

7.4 Toluene QA Rinse. Report the results of the toluene QA rinse separately from the total sample catch. Do not add it to the total sample.

8.0 [Reserved]

9. Calculations

Same as Method 5, section 6 with the following additions.

9.1 Nomenclature.

A_{ai} = Integrated ion current of the noise at the retention time of the analyte.

A^*_{ci} = Integrated ion current of the two ions characteristic of the internal standard i in the calibration standard.

A_{cij} = Integrated ion current of the two ions characteristic of compound i in the jth calibration standard.

A^*_{cij} = Integrated ion current of the two ions characteristic of the internal standard i in the jth calibration standard.

A_{csi} = Integrated ion current of the two ions characteristic of surrogate compound i in the calibration standard.

A_i = Integrated ion current of the two ions characteristic of compound i in the sample.

A^*_i = Integrated ion current of the two ions characteristic of internal standard i in the sample.

A_{rs} = Integrated ion current of the two ions characteristic of the recovery standard.

A_{si} = Integrated ion current of the two ions characteristic of surrogate compound i in the sample.

C_i = Concentration of PCDD or PCDF i in the sample, pg/M^3.

C_T = Total concentration of PCDD's or PCDF's in the sample, pg/M^3.
m_{ci} = Mass of compound i in the calibration standard injected into the analyzer, pg.
m_{rs} = Mass of recovery standard in the calibration standard injected into the analyzer, pg.
m_{si} = Mass of surrogate compound in the calibration standard, pg.
RRF_i = Relative response factor.
RRF_{rs} = Recovery standard response factor.
RRF_s = Surrogate compound response factor.

9.2 Average Relative Response Factor.

$$RRF_i = \frac{1}{n}\sum_{j=1}^{n}\frac{A_{cij}\,m^*_{ci}}{A^*_{cij}\,m_{ci}} \qquad \text{Eq. 23-1}$$

9.3 Concentration of the PCDD's and PCDF's.

$$C_i = \frac{m_i^* A_i}{A_i^* RRF_i V_{mstd}} \qquad \text{Eq. 23-2}$$

9.4 Recovery Standard Response Factor.

$$RRF_{rs} = \frac{A_{ci}^* m_{rs}}{A_{rs} m_{ci}^*} \qquad \text{Eq. 23-3}$$

9.5 Recovery of Internal Standards (R*).

$$R^* = \frac{A_i^* m_{rs}}{A_{rs} RF_{rs} m_i^*} \times 100\% \qquad \text{Eq. 23-4}$$

9.6 Surrogate Compound Response Factor.

$$RRF_s = \frac{A_{ci}^* m_s}{A_{cis} m_{ci}^*} \qquad \text{Eq. 23-5}$$

9.7 Recovery of Surrogate Compounds (R_s).

$$R_s = \frac{A_s m_i^*}{A_i^* RRF_s m_s} \times 100\% \qquad \text{Eq. 23-6}$$

9.8 Minimum Detectable Limit (MDL).

$$MDL = \frac{2.5\, A_{ai} m_i^*}{A_{ci}^* RRF_i} \qquad \text{Eq. 23-7}$$

9.9 Total Concentration of PCDD's and PCDF's in the Sample.

$$C_{Tr} = \sum_{i=1}^{n} C_i \qquad \text{Eq. 23-8}$$

Any PCDD's or PCDF's that are reported as nondetected (below the MDL) shall be counted as zero for the purpose of calculating the total concentration of PCDD's and PCDF's in the sample.

10. Bibliography

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TABLE 1—COMPOSITION OF THE SAMPLE FORTIFICATION AND RECOVERY STANDARDS SOLUTIONS

Analyte	Concentration (pg/µl)
Internal Standards:	
$^{13}C_{12}$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100
$^{13}C_{12}$-OCDD	100
$^{13}C_{12}$-2,3,7,8-TCDF	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100
Surrogate Standards:	
$^{37}Cl_4$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100
Recovery Standards:	
$^{13}C_{12}$-1,2,3,4-TCDD	500
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	500

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS

Compound	Concentrations (pg/µL)				
	Solution No.				
	1	2	3	4	5
Alternate Standard:					
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	2.5	5	25	250	500

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS—Continued

Compound	Concentrations (pg/μL)				
	Solution No.				
	1	2	3	4	5
Recovery Standards:					
$^{13}C_{12}$-1,2,3,4-TCDD ..	100	100	100	100	100

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS—Continued

Compound	Concentrations (pg/μL)				
	Solution No.				
	1	2	3	4	5
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

TABLE 3—ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HIGH RESOLUTION MASS SPECTROMETRY FOR PCDD'S AND PCDF'S

Descriptor No.	Accurate mass	Ion type	Elemental composition	Analyte
2	292.9825	LOCK	C_7F_{11}	PFK
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M + 2	$C_{12}H_4{}^{35}Cl^{37}O$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M + 2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}ClO_2$	TCDD
	321.8936	M + 2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD (S)
	330.9792	QC	C_7F_{13}	PFK
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9339	M + 2	$^{13}C_{12}H_4{}^{35}Cl^{37}ClO_2$	TCDD (S)
	339.8597	M + 2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PECDF
	341.8567	M + 4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M + 2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M + 4	$^{13}C_{12}H_3{}^{35}Cl^{3537}Cl_2O$	PeCDF (S)
	355.8546	M + 2	$C_{12}H_3{}^{35}Cl_3 37ClO_2$	PeCDD
	357.8516	M + 4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M + 2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M + 4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}\ Cl_2O_2$	PeCDD (S)
	375.8364	M + 2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
	409.7974	M + 2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCPDE
3	373.8208	M + 2	$C_{12}H_2 35Cl_5{}^{37}ClO$	HxCDF
	375.8178	M + 4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M + 2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8157	M + 2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M + 4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	392.9760	LOCK	C_9F_{15}	PFK
	401.8559	M + 2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M + 4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDD (S)
	445.7555	M + 4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	430.9729	QC	C_9F_{17}	PFK
4	407.7818	M + 2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M + 4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8253	M	$^{13}C_{12}H^{35}Cl_7O$	HpCDF (S)
	419.8220	M + 2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF (S)
	423.7766	M + 2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M + 4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M + 2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M + 4	$^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S)
	479.7165	M + 4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCPDE
	430.9729	LOCK	C_9F_{17}	PFK
	441.7428	M + 2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M + 4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M + 2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M + 4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M + 2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M + 4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S)
	513.6775	M + 4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O_2$	DCDPE
	442.9728	QC	$C_{10}F_{17}$	PFK

(a) The following nuclidic masses were used:
H = 1.007825
C = 12.000000
^{13}C = 13.003355
F = 18.9984
O = 15.994915
^{35}Cl = 34.968853
^{37}Cl = 36.965903

S = Labeled Standard
QC = Ion selected for monitoring instrument stability during the GC/MS analysis.

TABLE 4—ACCEPTABLE RANGES FOR ION-ABUNDANCE RATIOS OF PCDD'S AND PCDF'S

No. of chlorine atoms	Ion type	Theoretical ratio	Control limits	
			Lower	Upper
4	M/M + 2	0.77	0.65	0.89
5	M + 2/M + 4	1.55	1.32	1.78
6	M + 2/M + 4	1.24	1.05	1.43
6[a]	M/M + 2	0.51	0.43	0.59
7[b]	M/M + 2	0.44	0.37	0.51
7	M + 2/M + 4	1.04	0.88	1.20
8	M + 2/M + 4	0.89	0.76	1.02

[a] Used only for ^{13}C-HxCDF.
[b] Used only for ^{13}C-HpCDF.

TABLE 5—MINIMUM REQUIREMENTS FOR INITIAL AND DAILY CALIBRATION RESPONSE FACTORS

Compound	Relative response factors	
	Initial calibration RSD	Daily calibration % difference
Unlabeled Analytes:		
2,3,7,8-TCDD	25	25
2,3,7,8-TCDF	25	25
1,2,3,7,8-PeCDD	25	25
1,2,3,7,8-PeCDF	25	25
2,3,4,7,8-PeCDF	25	25
1,2,4,5,7,8-HxCDD	25	25
1,2,3,6,7,8-HxCDD	25	25
1,2,3,7,8,9-HxCDD	25	25
1,2,3,4,7,8-HxCDF	25	25
1,2,3,6,7,8-HxCDF	25	25
1,2,3,7,8,9-HxCDF	25	25
2,3,4,6,7,8-HxCDF	25	25
1,2,3,4,6,7,8-HpCDD	25	25
1,2,3,4,6,7,8-HpCDF	25	25
OCDD	25	25
OCDF	30	30
Internal Standards:		
$^{13}C_{12}$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-1,2,3,7,8-PeCDD	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	30	30
$^{13}C_{12}$-OCDD	30	30
$^{13}C_{12}$-2,3,7,8-TCDF	30	30
$^{13}C_{12}$-1,2,3,7,8-PeCDF	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	30	30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	30	30
Surrogate Standards:		
$^{37}Cl_4$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-2,3,4,7,8-PeCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	25	25
Alternate Standard:		
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	25	25

METHOD 24—DETERMINATION OF VOLATILE MATTER CONTENT, WATER CONTENT, DENSITY, VOLUME SOLIDS, AND WEIGHT SOLIDS OF SURFACE COATINGS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile organic compounds	No CAS Number assigned
Water.	7732–18–5

1.2 Applicability. This method is applicable for the determination of volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or other related surface coatings.

1.3 Precision and Bias. Intra-and inter-laboratory analytical precision statements are presented in section 13.1. No bias has been identified.

2.0 Summary of Method

2.1 Standard methods are used to determine the volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or other related surface coatings.

3.0 Definitions

3.1 *Waterborne coating* means any coating which contains more than 5 percent water by weight in its volatile fraction.

3.2 *Multicomponent coatings* are coatings that are packaged in two or more parts, which are combined before application. Upon combination a coreactant from one part of the coating chemically reacts, at ambient conditions, with a coreactant from another part of the coating.

3.3 *Ultraviolet (UV) radiation-cured coatings* are coatings which contain unreacted monomers that are polymerized by exposure to ultraviolet light.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Components. Several of the compounds that may be contained in the coatings analyzed by this method may be irritating or corrosive to tissues (e.g., heptane) or may be toxic (e.g., benzene, methyl alcohol). Nearly all are fire hazards.

Appropriate precautions can be found in reference documents, such as Reference 3 of section 16.0.

6.0 Equipment and Supplies

The equipment and supplies specified in the ASTM methods listed in sections 6.1 through 6.6 (incorporated by reference—see §60.17 for acceptable versions of the methods) are required:

6.1 ASTM D 1475–60, 80, or 90, Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products.

6.2 ASTM D 2369–81, 87, 90, 92, 93, or 95, Standard Test Method for Volatile Content of Coatings.

6.3 ASTM D 3792–79 or 91, Standard Test Method for Water Content of Water Reducible Paints by Direct Injection into a Gas Chromatograph.

6.4 ASTM D 4017–81, 90, or 96a, Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Titration Method.

6.5 ASTM 4457–85 91, Standard Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph.

6.6 ASTM D 5403–93, Standard Test Methods for Volatile Content of Radiation Curable Materials.

6.7 ASTM D 6419–00, Test Method for Volatile Content of Sheet-Fed and Coldset Web Offset Printing Inks.

7.0 Reagents and Standards

7.1 The reagents and standards specified in the ASTM methods listed in sections 6.1 through 6.6 are required.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Follow the sample collection, preservation, storage, and transport procedures described in Reference 1 of section 16.0.

9.0 Quality Control

9.1 Reproducibility

NOTE: Not applicable to UV radiation-cured coatings). The variety of coatings that may be subject to analysis makes it necessary to verify the ability of the analyst and the analytical procedures to obtain reproducible results for the coatings tested. Verification is accomplished by running duplicate analyses on each sample tested (Sections 11.2 through 11.4) and comparing the results with the intra-laboratory precision statements (Section 13.1) for each parameter.

9.2 Confidence Limits for Waterborne Coatings. Because of the inherent increased imprecision in the determination of the VOC content of waterborne coatings as the weight percent of water increases, measured parameters for waterborne coatings are replaced with appropriate confidence limits (Section 12.6). These confidence limits are based on measured parameters and inter-laboratory precision statements.

10.0 Calibration and Standardization

10.1 Perform the calibration and standardization procedures specified in the ASTM methods listed in sections 6.1 through 6.6.

11.0 Analytical Procedure

Additional guidance can be found in Reference 2 of section 16.0.

11.1 Non Thin-film Ultraviolet Radiation-cured (UV radiation-cured) Coatings.

11.1.1 Volatile Content. Use the procedure in ASTM D 5403 to determine the volatile matter content of the coating except the curing test described in NOTE 2 of ASTM D 5403 is required.

11.1.2 Water Content. To determine water content, follow section 11.3.2.

11.1.3 Coating Density. To determine coating density, follow section 11.3.3.

11.1.4 Solids Content. To determine solids content, follow section 11.3.4.

11.1.5 To determine if a coating or ink can be classified as a thin-film UV cured coating or ink, use the equation in section 12.2. If C is less than 0.2 g and A is greater than or equal to 225 cm^2 (35 in^2) then the coating or ink is considered a thin-film UV radiation-cured coating and ASTM D 5403 is not applicable.

NOTE: As noted in section 1.4 of ASTM D 5403, this method may not be applicable to radiation curable materials wherein the volatile material is water.

11.2 Multi-component Coatings.

11.2.1 Sample Preparation.

11.2.1.1 Prepare about 100 ml of sample by mixing the components in a storage container, such as a glass jar with a screw top or a metal can with a cap. The storage container should be just large enough to hold the mixture. Combine the components (by weight or volume) in the ratio recommended by the manufacturer. Tightly close the container between additions and during mixing to prevent loss of volatile materials. However, most manufacturers mixing instructions are by volume. Because of possible error caused by expansion of the liquid when measuring the volume, it is recommended that the components be combined by weight. When weight is used to combine the components and the manufacturer's recommended ratio is by volume, the density must be determined by section 11.3.3.

11.2.1.2 Immediately after mixing, take aliquots from this 100 ml sample for determination of the total volatile content, water content, and density.

11.2.2 Volatile Content. To determine total volatile content, use the apparatus and

reagents described in ASTM D2369 (incorporated by reference; see §60.17 for the approved versions of the standard), respectively, and use the following procedures:

11.2.2.1 Weigh and record the weight of an aluminum foil weighing dish. Add 3 ±1 ml of suitable solvent as specified in ASTM D2369 to the weighing dish. Using a syringe as specified in ASTM D2369, weigh to 1 mg, by difference, a sample of coating into the weighing dish. For coatings believed to have a volatile content less than 40 weight percent, a suitable size is 0.3 + 0.10 g, but for coatings believed to have a volatile content greater than 40 weight percent, a suitable size is 0.5 ±0.1 g.

NOTE: If the volatile content determined pursuant to section 12.4 is not in the range corresponding to the sample size chosen repeat the test with the appropriate sample size. Add the specimen dropwise, shaking (swirling) the dish to disperse the specimen completely in the solvent. If the material forms a lump that cannot be dispersed, discard the specimen and prepare a new one. Similarly, prepare a duplicate. The sample shall stand for a minimum of 1 hour, but no more than 24 hours prior to being oven cured at 110 ±5 °C (230 ±9 °F) for 1 hour.

11.2.2.2 Heat the aluminum foil dishes containing the dispersed specimens in the forced draft oven for 60 min at 110 ±5 °C (230 ±9 °F). Caution—provide adequate ventilation, consistent with accepted laboratory practice, to prevent solvent vapors from accumulating to a dangerous level.

11.2.2.3 Remove the dishes from the oven, place immediately in a desiccator, cool to ambient temperature, and weigh to within 1 mg.

11.2.2.4 Run analyses in pairs (duplicate sets) for each coating mixture until the criterion in section 11.4 is met. Calculate W_v following Equation 24–2 and record the arithmetic average.

11.2.3 Water Content. To determine water content, follow section 11.3.2.

11.2.4 Coating Density. To determine coating density, follow section 11.3.3.

11.2.5 Solids Content. To determine solids content, follow section 11.3.4.

11.2.6 Exempt Solvent Content. To determine the exempt solvent content, follow section 11.3.5.

NOTE: For all other coatings (*i.e.*, water-or solvent-borne coatings) not covered by multicomponent or UV radiation-cured coatings, analyze as shown below:

11.3 Water-or Solvent-borne coatings.

11.3.1 Volatile Content. Use the procedure in ASTM D 2369 to determine the volatile matter content (may include water) of the coating.

11.3.1.1 Record the following information:

W_1 = weight of dish and sample before heating, g

W_2 = weight of dish and sample after heating, g

W_3 = sample weight, g.

11.3.1.2 Calculate the weight fraction of the volatile matter (W_v) for each analysis as shown in section 12.3.

11.3.1.3 Run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement in section 13.1.

11.3.1.4 Record the arithmetic average (W_v).

11.3.2 Water Content. For waterborne coatings only, determine the weight fraction of water (W_w) using either ASTM D 3792 or ASTM D 4017.

11.3.2.1 Run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement in section 13.1.

11.3.2.2 Record the arithmetic average (w_w).

11.3.3 Coating Density. Determine the density (Dc, kg/l) of the surface coating using the procedure in ASTM D 1475.

11.3.3.1 Run duplicate analyses until each value in a set deviates from the mean of the set by no more than the intra-laboratory precision statement in section 13.1.

11.3.3.2 Record the arithmetic average (D_c).

11.3.4 Solids Content. Determine the volume fraction (V_s) solids of the coating by calculation using the manufacturer's formulation.

11.3.5 Exempt Solvent Content. Determine the weight fraction of exempt solvents (W_E) by using ASTM Method D4457. Run a duplicate set of determinations and record the arithmetic average (W_E).

11.4 Sample Analysis Criteria. For W_v and W_w, run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement for that parameter. For D_c, run duplicate analyses until each value in a set deviates from the mean of the set by no more than the intra-laboratory precision statement. If, after several attempts, it is concluded that the ASTM procedures cannot be used for the specific coating with the established intra-laboratory precision (excluding UV radiation-cured coatings), the U.S. Environmental Protection Agency (EPA) will assume responsibility for providing the necessary procedures for revising the method or precision statements upon written request to: Director, Emissions, Monitoring, and Analysis Division, MD–14, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

12.0 Calculations and Data Analysis

12.1 Nomenclature.

A = Area of substrate, cm^2, (in^2).

C = Amount of coating or ink added to the substrate, g.

D_c = Density of coating or ink, g/cm^3 (g/in^3).

F = Manufacturer's recommended film thickness, cm (in).
W_o = Weight fraction of nonaqueous volatile matter, g/g.
W_s = Weight fraction of solids, g/g.
W_v = Weight fraction of the volatile matter, g/g.
W_w = Weight fraction of the water, g/g.

12.2 To determine if a coating or ink can be classified as a thin-film UV cured coating or ink, use the following equation:

$$C = F A D_c \qquad \text{Eq. 24-1}$$

12.3 Calculate W_v for each analysis as shown below:

$$W_v = \frac{W_1 - W_2}{W_3} \qquad \text{Eq. 24-2}$$

12.4 Nonaqueous Volatile Matter.
12.4.1 Solvent-borne Coatings.

$$W_o = W_v \qquad \text{Eq. 24-3}$$

12.4.2 Waterborne Coatings.

$$W_o = W_v - W_w \qquad \text{Eq. 24-4}$$

12.4.3 Coatings Containing Exempt Solvents.

$$W_o = W_v - W_E - W_w \qquad \text{Eq. 24-5}$$

12.5 Weight Fraction Solids.

$$W_s = 1 - W_v \qquad \text{Eq. 24-6}$$

12.6 Confidence Limit Calculations for Waterborne Coatings. To calculate the lower confidence limit, subtract the appropriate inter-laboratory precision value from the measured mean value for that parameter. To calculate the upper confidence limit, add the appropriate inter-laboratory precision value to the measured mean value for that parameter. For W_v and D_c, use the lower confidence limits; for W_w, use the upper confidence limit. Because W_s is calculated, there is no adjustment for this parameter.

13.0 Method Performance

13.1 Analytical Precision Statements. The intra-and inter-laboratory precision statements are given in Table 24–1 in section 17.0.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as specified in section 6.0, with the addition of the following:

1. Standard Procedure for Collection of Coating and Ink Samples for Analysis by Reference Methods 24 and 24A. EPA–340/1–91–010. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

2. Standard Operating Procedure for Analysis of Coating and Ink Samples by Reference Methods 24 and 24A.

EPA–340/1–91–011. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

3. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 24–1—ANALYTICAL PRECISION STATEMENTS

	Intra-laboratory	Inter-laboratory
Volatile matter content, W_v	±0.015 $\overline{W}_v$	±0.047 $\overline{W}_v$
Water content, W_w	±0.029 $\overline{W}_w$	±0.075 $\overline{W}_w$
Density, D_c	±0.001 kg/l	±0.002 kg/l

METHOD 24A—DETERMINATION OF VOLATILE MATTER CONTENT AND DENSITY OF PUBLICATION ROTOGRAVURE INKS AND RELATED PUBLICATION ROTOGRAVURE COATINGS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile organic compounds (VOC).	No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of the VOC content and density of solvent-borne (solvent-reducible) publication rotogravure inks and related publication rotogravure coatings.

2.0 Summary of Method

2.1 Separate procedures are used to determine the VOC weight fraction and density of the ink or related coating and the density of the solvent in the ink or related coating. The VOC weight fraction is determined by measuring the weight loss of a known sample quantity which has been heated for a specified length of time at a specified temperature. The density of both the ink or related coating and solvent are measured by a standard procedure. From this information, the VOC volume fraction is calculated.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Components. Some of the compounds that may be contained in the inks or related coatings analyzed by this method may be irritating or corrosive to tissues or may be toxic. Nearly all are fire hazards. Appropriate precautions can be found in reference documents, such as Reference 6 of section 16.0.

6.0 Equipment and Supplies

The following equipment and supplies are required for sample analysis:

6.1 Weighing Dishes. Aluminum foil, 58 mm (2.3 in.) in diameter by 18 mm (0.7 in.) high, with a flat bottom. There must be at least three weighing dishes per sample.

6.2 Disposable Syringe. 5 ml.

6.3 Analytical Balance. To measure to within 0.1 mg.

6.4 Oven. Vacuum oven capable of maintaining a temperature of 120 ±2 °C (248 ±4 °F) and an absolute pressure of 510 ±51 mm Hg (20 ±2 in. Hg) for 4 hours. Alternatively, a forced draft oven capable of maintaining a temperature of 120 ±2 °C (248 ±4 °F) for 24 hours.

6.5 The equipment and supplies specified in ASTM D 1475–60, 80, or 90 (incorporated by reference—see §60.17).

7.0 Reagents and Standards

7.1 The reagents and standards specified in ASTM D 1475–60, 80, or 90 are required.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Follow the sample collection, preservation, storage, and transport procedures described in Reference 4 of section 16.0.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

Additional guidance can be found in Reference 5 of section 16.0.

11.1 VOC Weight Fraction. Shake or mix the ink or related coating sample thoroughly to assure that all the solids are completely suspended. Label and weigh to the nearest 0.1 mg a weighing dish and record this weight (M_{x1}). Using a 5 ml syringe, without a needle, extract an aliquot from the ink or related coating sample. Weigh the syringe and aliquot to the nearest 0.1 mg and record this weight (M_{cy1}). Transfer 1 to 3 g of the aliquot to the tared weighing dish. Reweigh the syringe and remaining aliquot to the nearest 0.1 mg and record this weight (M_{cy2}). Heat the weighing dish with the transferred aliquot in a vacuum oven at an absolute pressure of 510 ±51 mm Hg (20 ±2 in. Hg) and a temperature of 120 ±2 °C (248 ±4 °F) for 4 hours. Alternatively, heat the weighing dish with the transferred aliquot in a forced draft oven at a temperature of 120 ±2 °C for 24 hours. After the weighing dish has cooled, reweigh it to the nearest 0.1 mg and record the weight (M_{x2}). Repeat this procedure two times for each ink or related coating sample, for a total of three samples.

11.2 Ink or Related Coating Density. Determine the density of the ink or related coating (D_c) according to the procedure outlined in ASTM D 1475. Make a total of three determinations for each ink or related coating sample. Report the ink or related coating density as the arithmetic average (D_c) of the three determinations.

11.3 Solvent Density. Determine the density of the solvent (D_o) according to the procedure outlined in ASTM D 1475. Make a total of three determinations for each ink or related coating sample. Report the solvent density as the arithmetic average (D_o) of the three determinations.

12.0 Calculations and Data Analysis

12.1 VOC Weight Fraction. For each determination, calculate the volatile organic content weight fraction (W_o) using the following equation:

$$W_o = \frac{M_{x1} + M_{cy1} - M_{cy2} - M_{x2}}{M_{cy1} - M_{cy2}} \qquad \text{Eq. 24A-1}$$

Make a total of three determinations. Report the VOC weight fraction as the arithmetic average ($\bar{W}_o$) of the three determinations.

12.2 VOC Volume Fraction. Calculate the volume fraction volatile organic content (V_o) using the following equation:

$$V_o = \frac{\overline{W}_o \overline{D}_c}{\overline{D}_o} \qquad \text{Eq. 24A-2}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products. ASTM Designation D 1475.

2. Teleconversation. Wright, Chuck, Inmont Corporation with Reich, R., A., Radian Corporation. September 25, 1979, Gravure Ink Analysis.

3. Teleconversation. Oppenheimer, Robert, Gravure Research Institute with Burt, Rick, Radian Corporation, November 5, 1979, Gravure Ink Analysis.

4. Standard Procedure for Collection of Coating and Ink Samples for Analysis by Reference Methods 24 and 24A. EPA–340/1–91–010. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

5. Standard Operating Procedure for Analysis of Coating and Ink Samples by Reference Methods 24 and 24A. EPA–340/1–91–011. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

6. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

Method 25—Determination of Total Gaseous Nonmethane Organic Emissions as Carbon

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total gaseous nonmethane organic compounds (TGNMO)	N/A	Dependent upon analytical equipment.

1.2 Applicability.

1.2.1 This method is applicable for the determination of volatile organic compounds (VOC) (measured as total gaseous nonmethane organics (TGNMO) and reported as carbon) in stationary source emissions. This method is not applicable for the determination of organic particulate matter.

1.2.2 This method is not the only method that applies to the measurement of VOC. Costs, logistics, and other practicalities of source testing may make other test methods more desirable for measuring VOC contents of certain effluent streams. Proper judgment is required in determining the most applicable VOC test method. For example, depending upon the molecular composition of the organics in the effluent stream, a totally automated semicontinuous nonmethane organics (NMO) analyzer interfaced directly to the source may yield accurate results. This approach has the advantage of providing emission data semicontinuously over an extended time period.

1.2.3 Direct measurement of an effluent with a flame ionization detector (FID) analyzer may be appropriate with prior characterization of the gas stream and knowledge that the detector responds predictably to the organic compounds in the stream. If present, methane (CH_4) will, of course, also be measured. The FID can be used under any of the following limited conditions: (1) Where only one compound is known to exist; (2) when the organic compounds consist of only hydrogen and carbon; (3) where the relative percentages of the compounds are known or can be determined, and the FID responses to the compounds are known; (4) where a consistent mixture of the compounds exists before and after emission control and only the relative concentrations are to be assessed; or (5) where the FID can be calibrated against mass standards of the compounds emitted (solvent emissions, for example).

1.2.4 Another example of the use of a direct FID is as a screening method. If there is enough information available to provide a rough estimate of the analyzer accuracy, the FID analyzer can be used to determine the VOC content of an uncharacterized gas stream. With a sufficient buffer to account for possible inaccuracies, the direct FID can be a useful tool to obtain the desired results without costly exact determination.

1.2.5 In situations where a qualitative/quantitative analysis of an effluent stream is desired or required, a gas chromatographic FID system may apply. However, for sources emitting numerous organics, the time and expense of this approach will be formidable.

2.0 Summary of Method

2.1 An emission sample is withdrawn from the stack at a constant rate through a heated filter and a chilled condensate trap by means of an evacuated sample tank. After sampling is completed, the TGNMO are determined by independently analyzing the condensate trap and sample tank fractions and combining the analytical results. The organic content of the condensate trap fraction is determined by oxidizing the NMO to carbon dioxide (CO_2) and quantitatively collecting in the effluent in an evacuated vessel; then a portion of the CO_2 is reduced to CH_4 and measured by an FID. The organic content of the sample tank fraction is measured by injecting a portion of the sample into a gas chromatographic column to separate the NMO from carbon monoxide (CO), CO_2, and CH_4; the NMO are oxidized to CO_2, reduced to CH_4, and measured by an FID. In this manner, the variable response of the FID associated with different types of organics is eliminated.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Carbon Dioxide and Water Vapor. When carbon dioxide (CO_2) and water vapor are present together in the stack, they can produce a positive bias in the sample. The magnitude of the bias depends on the concentrations of CO_2 and water vapor. As a guideline, multiply the CO_2 concentration, expressed as volume percent, times the water vapor concentration. If this product does not exceed 100, the bias can be considered insignificant. For example, the bias is not significant for a source having 10 percent CO_2 and 10 percent water vapor, but it might be significant for a source having 10 percent CO_2 and 20 percent water vapor.

4.2. Particulate Matter. Collection of organic particulate matter in the condensate trap would produce a positive bias. A filter is included in the sampling equipment to minimize this bias.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling system consists of a heated probe, heated filter, condensate trap, flow control system, and sample tank (see Figure 25–1). The TGNMO sampling equipment can be constructed from commercially available components and components fabricated in a machine shop. The following equipment is required:

6.1.1 Heated Probe. 6.4-mm (¼-in.) OD stainless steel tubing with a heating system capable of maintaining a gas temperature at the exit end of at least 129 °C (265 °F). The probe shall be equipped with a temperature sensor at the exit end to monitor the gas temperature. A suitable probe is shown in Figure 25–1. The nozzle is an elbow fitting attached to the front end of the probe while the temperature sensor is inserted in the side arm of a tee fitting attached to the rear of the probe. The probe is wrapped with a suitable length of high temperature heating tape, and then covered with two layers of glass cloth insulation and one layer of aluminum foil or an equivalent wrapping.

NOTE: If it is not possible to use a heating system for safety reasons, an unheated system with an in-stack filter is a suitable alternative.

6.1.2 Filter Holder. 25-mm (15/16-in.) ID Gelman filter holder with 303 stainless steel body and 316 stainless steel support screen with the Viton O-ring replaced by a Teflon O-ring.

6.1.3 Filter Heating System.

6.1.3.1 A metal box consisting of an inner and an outer shell separated by insulating material with a heating element in the inner shell capable of maintaining a gas temperature at the filter of 121 ±3 °C (250 ±5 °F). The heating box shall include temperature sensors to monitor the gas temperature immediately upstream and immediately downstream of the filter.

6.1.3.2 A suitable heating box is shown in Figure 25–2. The outer shell is a metal box that measures 102 mm × 280 mm × 292 mm (4 in. × 11 in. × 11½ in.), while the inner shell is a metal box measuring 76 mm × 229 mm × 241 mm (3 in. × 9 in. × 9½ in.). The inner box is supported by 13-mm (½-in.) phenolic rods. The void space between the boxes is filled with ceramic fiber insulation which is sealed in place by means of a silicon rubber bead around the upper sides of the box. A removable lid made in a similar manner, with a 25-mm (1-in.) gap between the parts is used to cover the heating chamber. The inner box is heated with a 250-watt cartridge heater, shielded by a stainless steel shroud. The heater is regulated by a thermostatic temperature controller which is set to maintain a gas temperature of 121 °C (250 °F) as measured by the temperature sensor upstream of the filter.

NOTE: If it is not possible to use a heating system for safety reasons, an unheated system with an in-stack filter is a suitable alternative.

6.1.4 Condensate Trap. 9.5-mm (⅜-in.) OD 316 stainless steel tubing bent into a U-shape. Exact dimensions are shown in Figure

25–3. The tubing shall be packed with coarse quartz wool, to a density of approximately 0.11 g/cm^3 before bending. While the condensate trap is packed with dry ice in the Dewar, an ice bridge may form between the arms of the condensate trap making it difficult to remove the condensate trap. This problem can be prevented by attaching a steel plate between the arms of the condensate trap in the same plane as the arms to completely fill the intervening space.

6.1.5 Valve. Stainless steel control valve for starting and stopping sample flow.

6.1.6 Metering Valve. Stainless steel valve for regulating the sample flow rate through the sample train.

6.1.7 Rate Meter. Rotameter, or equivalent, capable of measuring sample flow in the range of 60 to 100 cm^3/min (0.13 to 0.21 ft^3/hr).

6.1.8 Sample Tank. Stainless steel or aluminum tank with a minimum volume of 4 liters (0.14 ft^3).

NOTE: Sample volumes greater than 4 liters may be required for sources with low organic concentrations.

6.1.9 Mercury Manometer. U-tube manometer or absolute pressure gauge capable of measuring pressure to within 1 mm Hg in the range of 0 to 900 mm.

6.1.10 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

6.2 Condensate Recovery. The system for the recovery of the organics captured in the condensate trap consists of a heat source, an oxidation catalyst, a nondispersive infrared (NDIR) analyzer, and an intermediate collection vessel (ICV). Figure 25–4 is a schematic of a typical system. The system shall be capable of proper oxidation and recovery, as specified in section 10.1.1. The following major components are required:

6.2.1 Heat Source. Sufficient to heat the condensate trap (including probe) to a temperature of 200 °C (390 °F). A system using both a heat gun and an electric tube furnace is recommended.

6.2.2 Heat Tape. Sufficient to heat the connecting tubing between the water trap and the oxidation catalyst to 100 °C (212 °F).

6.2.3 Oxidation Catalyst. A suitable length of 9.5 mm (3/8-in.) OD Inconel 600 tubing packed with 15 cm (6 in.) of 3.2 mm (3/8-in.) diameter 19 percent chromia on alumina pellets. The catalyst material is packed in the center of the catalyst tube with quartz wool packed on either end to hold it in place.

6.2.4 Water Trap. Leak-proof, capable of removing moisture from the gas stream.

6.2.5 Syringe Port. A 6.4-mm (1/4-in.) OD stainless steel tee fitting with a rubber septum placed in the side arm.

6.2.6 NDIR Detector. Capable of indicating CO_2 concentration in the range of zero to 5 percent, to monitor the progress of combustion of the organic compounds from the condensate trap.

6.2.7 Flow-Control Valve. Stainless steel, to maintain the trap conditioning system near atmospheric pressure.

6.2.8 Intermediate Collection Vessel. Stainless steel or aluminum, equipped with a female quick connect. Tanks with nominal volumes of at least 6 liters (0.2 ft^3) are recommended.

6.2.9 Mercury Manometer. Same as described in section 6.1.9.

6.2.10 Syringe. 10-ml gas-tight glass syringe equipped with an appropriate needle.

6.2.11 Syringes. 10-µl and 50-µl liquid injection syringes.

6.2.12 Liquid Sample Injection Unit. 316 Stainless steel U-tube fitted with an injection septum (see Figure 25–7).

6.3 Analysis.

6.3.1 NMO Analyzer. The NMO analyzer is a gas chromatograph (GC) with backflush capability for NMO analysis and is equipped with an oxidation catalyst, reduction catalyst, and FID. Figures 25–5 and 25–6 are schematics of a typical NMO analyzer. This semicontinuous GC/FID analyzer shall be capable of: (1) Separating CO, CO_2, and CH_4 from NMO, (2) reducing the CO_2 to CH_4 and quantifying as CH_4, and (3) oxidizing the NMO to CO_2, reducing the CO_2 to CH_4 and quantifying as CH_4, according to section 10.1.2. The analyzer consists of the following major components:

6.3.1.1 Oxidation Catalyst. A suitable length of 9.5-mm (3/8-in.) OD Inconel 600 tubing packed with 5.1 cm (2 in.) of 19 percent chromia on 3.2-mm (1/8-in.) alumina pellets. The catalyst material is packed in the center of the tube supported on either side by quartz wool. The catalyst tube must be mounted vertically in a 650 °C (1200 °F) furnace. Longer catalysts mounted horizontally may be used, provided they can meet the specifications of section 10.1.2.1.

6.3.1.2 Reduction Catalyst. A 7.6-cm (3-in.) length of 6.4-mm (1/4-in.) OD Inconel tubing fully packed with 100-mesh pure nickel powder. The catalyst tube must be mounted vertically in a 400 °C (750 °F) furnace.

6.3.1.3 Separation Column(s). A 30-cm (1-ft) length of 3.2-mm (1/8-in.) OD stainless steel tubing packed with 60/80 mesh Unibeads 1S followed by a 61-cm (2-ft) length of 3.2-mm (1/8-in.) OD stainless steel tubing packed with 60/80 mesh Carbosieve G. The Carbosieve and Unibeads columns must be baked separately at 200 °C (390 °F) with carrier gas flowing through them for 24 hours before initial use.

6.3.1.4 Sample Injection System. A single 10-port GC sample injection valve or a group of valves with sufficient ports fitted with a sample loop properly sized to interface with the NMO analyzer (1-cc loop recommended).

6.3.1.5 FID. An FID meeting the following specifications is required:

6.3.1.5.1 Linearity. A linear response (±5 percent) over the operating range as demonstrated by the procedures established in section 10.1.2.3.

6.3.1.5.2 Range. A full scale range of 10 to 50,000 ppm CH_4. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.3.1.6 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the analytical results.

6.3.2 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm Hg.

6.3.3 Temperature Sensor. Capable of measuring the laboratory temperature within 1 °C (2 °F).

6.3.4 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

7.0 Reagents and Standards

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Dry Ice. Solid CO2, crushed.

7.1.2 Coarse Quartz Wool. 8 to 15 um.

7.1.3 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Method D2986–71, 78, or 95a (incorporated by reference—see §60.17). Test data from the supplier's quality control program are sufficient for this purpose.

7.2 NMO Analysis. The following gases are required for NMO analysis:

7.2.1 Carrier Gases. Helium (He) and oxygen (O_2) containing less than 1 ppm CO_2 and less than 0.1 ppm hydrocarbon.

7.2.2 Fuel Gas. Hydrogen (H_2), at least 99.999 percent pure.

7.2.3 Combustion Gas. Either air (less than 0.1 ppm total hydrocarbon content) or O_2 (purity 99.99 percent or greater), as required by the detector.

7.3 Condensate Analysis. The following are required for condensate analysis:

7.3.1 Gases. Containing less than 1 ppm carbon.

7.3.1.1 Air.

7.3.1.2 Oxygen.

7.3.2 Liquids. To conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society.

7.3.2.1 Hexane.

7.3.2.2 Decane.

7.4 Calibration. For all calibration gases, the manufacturer must recommend a maximum shelf life for each cylinder (i.e., the length of time the gas concentration is not expected to change more than ±5 percent from its certified value). The date of gas cylinder preparation, certified organic concentration, and recommended maximum shelf life must be affixed to each cylinder before shipment from the gas manufacturer to the buyer. The following calibration gases are required:

7.4.1 Oxidation Catalyst Efficiency Check Calibration Gas. Gas mixture standard with nominal concentration of 1 percent methane in air.

7.4.2 FID Linearity and NMO Calibration Gases. Three gas mixture standards with nominal propane concentrations of 20 ppm, 200 ppm, and 3000 ppm, in air.

7.4.3 CO_2 Calibration Gases. Three gas mixture standards with nominal CO_2 concentrations of 50 ppm, 500 ppm, and 1 percent, in air.

NOTE: Total NMO less than 1 ppm required for 1 percent mixture.

7.4.4 NMO Analyzer System Check Calibration Gases. Four calibration gases are needed as follows:

7.4.4.1 Propane Mixture. Gas mixture standard containing (nominal) 50 ppm CO, 50 ppm CH_4, 1 percent CO_2, and 20 ppm C_3H_8, prepared in air.

7.4.4.2 Hexane. Gas mixture standard containing (nominal) 50 ppm hexane in air.

7.4.4.3 Toluene. Gas mixture standard containing (nominal) 20 ppm toluene in air.

7.4.4.4 Methanol. Gas mixture standard containing (nominal) 100 ppm methanol in air.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Sampling Equipment Preparation.

8.1.1 Condensate Trap Cleaning. Before its initial use and after each use, a condensate trap should be thoroughly cleaned and checked to ensure that it is not contaminated. Both cleaning and checking can be accomplished by installing the trap in the condensate recovery system and treating it as if it were a sample. The trap should be heated as described in section 11.1.3. A trap may be considered clean when the CO_2 concentration in its effluent gas drops below 10 ppm. This check is optional for traps that most recently have been used to collect samples which were then recovered according to the procedure in section 11.1.3.

8.1.2 Sample Tank Evacuation and Leak-Check. Evacuate the sample tank to 10 mm Hg absolute pressure or less. Then close the sample tank valve, and allow the tank to sit for 60 minutes. The tank is acceptable if a change in tank vacuum of less than 1 mm Hg is noted. The evacuation and leak-check may be conducted either in the laboratory or the field.

8.1.3 Sampling Train Assembly. Just before assembly, measure the tank vacuum using a mercury manometer. Record this vacuum, the ambient temperature, and the barometric pressure at this time. Close the sample tank valve and assemble the sampling

system as shown in Figure 25–1. Immerse the condensate trap body in dry ice at least 30 minutes before commencing sampling to improve collection efficiency. The point where the inlet tube joins the trap body should be 2.5 to 5 cm (1 to 2 in.) above the top of the dry ice.

8.1.4 Pretest Leak-Check. A pretest leak-check is required. Calculate or measure the approximate volume of the sampling train from the probe tip to the sample tank valve. After assembling the sampling train, plug the probe tip, and make certain that the sample tank valve is closed. Turn on the vacuum pump, and evacuate the sampling system from the probe tip to the sample tank valve to an absolute pressure of 10 mm Hg or less. Close the purge valve, turn off the pump, wait a minimum period of 10 minutes, and recheck the indicated vacuum. Calculate the maximum allowable pressure change based on a leak rate of 1 percent of the sampling rate using Equation 25–1, section 12.2. If the measured pressure change exceeds the allowable, correct the problem and repeat the leak-check before beginning sampling.

8.2 Sample Collection.

8.2.1 Unplug the probe tip, and place the probe into the stack such that the probe is perpendicular to the duct or stack axis; locate the probe tip at a single preselected point of average velocity facing away from the direction of gas flow. For stacks having a negative static pressure, seal the sample port sufficiently to prevent air in-leakage around the probe. Set the probe temperature controller to 129 °C (265 °F) and the filter temperature controller to 121 °C (250 °F). Allow the probe and filter to heat for about 30 minutes before purging the sample train.

8.2.2 Close the sample valve, open the purge valve, and start the vacuum pump. Set the flow rate between 60 and 100 cm^3/min (0.13 and 0.21 ft^3/hr), and purge the train with stack gas for at least 10 minutes.

8.2.3 When the temperatures at the exit ends of the probe and filter are within the corresponding specified ranges, check the dry ice level around the condensate trap, and add dry ice if necessary. Record the clock time. To begin sampling, close the purge valve and stop the pump. Open the sample valve and the sample tank valve. Using the flow control valve, set the flow through the sample train to the proper rate. Adjust the flow rate as necessary to maintain a constant rate (±10 percent) throughout the duration of the sampling period. Record the sample tank vacuum and flowmeter setting at 5-minute intervals. (See Figure 25–8.) Select a total sample time greater than or equal to the minimum sampling time specified in the applicable subpart of the regulations; end the sampling when this time period is reached or when a constant flow rate can no longer be maintained because of reduced sample tank vacuum.

NOTE: If sampling had to be stopped before obtaining the minimum sampling time (specified in the applicable subpart) because a constant flow rate could not be maintained, proceed as follows: After closing the sample tank valve, remove the used sample tank from the sampling train (without disconnecting other portions of the sampling train). Take another evacuated and leak-checked sample tank, measure and record the tank vacuum, and attach the new tank to the sampling train. After the new tank is attached to the sample train, proceed with the sampling until the required minimum sampling time has been exceeded.

8.3 Sample Recovery. After sampling is completed, close the flow control valve, and record the final tank vacuum; then record the tank temperature and barometric pressure. Close the sample tank valve, and disconnect the sample tank from the sample system. Disconnect the condensate trap at the inlet to the rate meter, and tightly seal both ends of the condensate trap. Do not include the probe from the stack to the filter as part of the condensate sample.

8.4 Sample Storage and Transport. Keep the trap packed in dry ice until the samples are returned to the laboratory for analysis. Ensure that run numbers are identified on the condensate trap and the sample tank(s).

9.0 Quality Control

Section	Quality control measure	Effect
10.1.1	Initial performance check of condensate recovery apparatus.	Ensure acceptable condensate recovery efficiency.
10.1.2, 10.2	NMO analyzer initial and daily performance checks.	Ensure precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Initial Performance Checks.

10.1.1 Condensate Recovery Apparatus. Perform these tests before the system is first placed in operation, after any shutdown of 6 months or more, and after any major modification of the system, or at the frequency recommended by the manufacturer.

10.1.1.1 Carrier Gas and Auxiliary O_2 Blank Check. Analyze each new tank of carrier gas or auxiliary O_2 with the NMO analyzer to

check for contamination. Treat the gas cylinders as noncondensible gas samples, and analyze according to the procedure in section 11.2.3. Add together any measured CH_4, CO, CO_2, or NMO. The total concentration must be less than 5 ppm.

10.1.1.2 Oxidation Catalyst Efficiency Check.

10.1.1.2.1 With a clean condensate trap installed in the recovery system or a ⅛″ stainless steel connector tube, replace the carrier gas cylinder with the high level methane standard gas cylinder (Section 7.4.1). Set the four-port valve to the recovery position, and attach an ICV to the recovery system. With the sample recovery valve in vent position and the flow-control and ICV valves fully open, evacuate the manometer or gauge, the connecting tubing, and the ICV to 10 mm Hg absolute pressure. Close the flow-control and vacuum pump valves.

10.1.1.2.2 After the NDIR response has stabilized, switch the sample recovery valve from vent to collect. When the manometer or pressure gauge begins to register a slight positive pressure, open the flow-control valve. Keep the flow adjusted such that the pressure in the system is maintained within 10 percent of atmospheric pressure. Continue collecting the sample in a normal manner until the ICV is filled to a nominal gauge pressure of 300 mm Hg. Close the ICV valve, and remove the ICV from the system. Place the sample recovery valve in the vent position, and return the recovery system to its normal carrier gas and normal operating conditions. Analyze the ICV for CO_2 using the NMO analyzer; the catalyst efficiency is acceptable if the CO_2 concentration is within 2 percent of the methane standard concentration.

10.1.1.3 System Performance Check. Construct a liquid sample injection unit similar in design to the unit shown in Figure 25–7. Insert this unit into the condensate recovery and conditioning system in place of a condensate trap, and set the carrier gas and auxiliary O_2 flow rates to normal operating levels. Attach an evacuated ICV to the system, and switch from system vent to collect. With the carrier gas routed through the injection unit and the oxidation catalyst, inject a liquid sample (see sections 10.1.1.3.1 to 10.1.1.3.4) into the injection port. Operate the trap recovery system as described in section 11.1.3. Measure the final ICV pressure, and then analyze the vessel to determine the CO_2 concentration. For each injection, calculate the percent recovery according to section 12.7. Calculate the relative standard deviation for each set of triplicate injections according to section 12.8. The performance test is acceptable if the average percent recovery is 100 ±5 percent and the relative standard deviation is less than 2 percent for each set of triplicate injections.

10.1.1.3.1 50 µl hexane.

10.1.1.3.2 10 µl hexane.

10.1.1.3.3 50 µl decane.

10.1.1.3.4 10 µl decane.

10.1.2 NMO Analyzer. Perform these tests before the system is first placed in operation, after any shutdown longer than 6 months, and after any major modification of the system.

10.1.2.1 Oxidation Catalyst Efficiency Check. Turn off or bypass the NMO analyzer reduction catalyst. Make triplicate injections of the high level methane standard (Section 7.4.1). The oxidation catalyst operation is acceptable if the FID response is less than 1 percent of the injected methane concentration.

10.1.2.2 Reduction Catalyst Efficiency Check. With the oxidation catalyst unheated or bypassed and the heated reduction catalyst bypassed, make triplicate injections of the high level methane standard (Section 7.4.1). Repeat this procedure with both catalysts operative. The reduction catalyst operation is acceptable if the responses under both conditions agree within 5 percent of their average.

10.1.2.3 NMO Analyzer Linearity Check Calibration. While operating both the oxidation and reduction catalysts, conduct a linearity check of the analyzer using the propane standards specified in section 7.4.2. Make triplicate injections of each calibration gas. For each gas (*i.e.*, each set of triplicate injections), calculate the average response factor (area/ppm C) for each gas, as well as and the relative standard deviation (according to section 12.8). Then calculate the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within 2.5 percent of the overall mean value and if the relative standard deviation gas is less than 2 percent of the overall mean value. Record the overall mean of the propane response factor values as the NMO calibration response factor (RF_{NMO}). Repeat the linearity check using the CO_2 standards specified in section 7.4.3. Make triplicate injections of each gas, and then calculate the average response factor (area/ppm C) for each gas, as well as the overall mean of the response factor values. Record the overall mean of the response factor values as the CO_2 calibration response factor (RF_{CO2}). The RF_{CO2} must be within 10 percent of the RF_{NMO}.

10.1.2.4 System Performance Check. Check the column separation and overall performance of the analyzer by making triplicate injections of the calibration gases listed in section 7.4.4. The analyzer performance is acceptable if the measured NMO value for each gas (average of triplicate injections) is within 5 percent of the expected value.

10.2 NMO Analyzer Daily Calibration. The following calibration procedures shall be performed before and immediately after the

analysis of each set of samples, or on a daily basis, whichever is more stringent:

10.2.1 CO_2 Response Factor. Inject triplicate samples of the high level CO_2 calibration gas (Section 7.4.3), and calculate the average response factor. The system operation is adequate if the calculated response factor is within 5 percent of the RF_{CO2} calculated during the initial performance test (Section 10.1.2.3). Use the daily response factor (DRF_{CO2}) for analyzer calibration and the calculation of measured CO_2 concentrations in the ICV samples.

10.2.2 NMO Response Factors. Inject triplicate samples of the mixed propane calibration cylinder gas (Section 7.4.4.1), and calculate the average NMO response factor. The system operation is adequate if the calculated response factor is within 10 percent of the RF_{NMO} calculated during the initial performance test (Section 10.1.2.4). Use the daily response factor (DRF_{NMO}) for analyzer calibration and calculation of NMO concentrations in the sample tanks.

10.3 Sample Tank and ICV Volume. The volume of the gas sampling tanks used must be determined. Determine the tank and ICV volumes by weighing them empty and then filled with deionized distilled water; weigh to the nearest 5 g, and record the results. Alternatively, measure the volume of water used to fill them to the nearest 5 ml.

11.0 Analytical Procedure

11.1 Condensate Recovery. See Figure 25–9. Set the carrier gas flow rate, and heat the catalyst to its operating temperature to condition the apparatus.

11.1.1 Daily Performance Checks. Each day before analyzing any samples, perform the following tests:

11.1.1.1 Leak-Check. With the carrier gas inlets and the sample recovery valve closed, install a clean condensate trap in the system, and evacuate the system to 10 mm Hg absolute pressure or less. Monitor the system pressure for 10 minutes. The system is acceptable if the pressure change is less than 2 mm Hg.

11.1.1.2 System Background Test. Adjust the carrier gas and auxiliary oxygen flow rate to their normal values of 100 cc/min and 150 cc/min, respectively, with the sample recovery valve in vent position. Using a 10-ml syringe, withdraw a sample from the system effluent through the syringe port. Inject this sample into the NMO analyzer, and measure the CO_2 content. The system background is acceptable if the CO_2 concentration is less than 10 ppm.

11.1.1.3 Oxidation Catalyst Efficiency Check. Conduct a catalyst efficiency test as specified in section 10.1.1.2. If the criterion of this test cannot be met, make the necessary repairs to the system before proceeding.

11.1.2 Condensate Trap CO_2 Purge and Sample Tank Pressurization.

11.1.2.1 After sampling is completed, the condensate trap will contain condensed water and organics and a small volume of sampled gas. This gas from the stack may contain a significant amount of CO_2 which must be removed from the condensate trap before the sample is recovered. This is accomplished by purging the condensate trap with zero air and collecting the purged gas in the original sample tank.

11.1.2.2 Begin with the sample tank and condensate trap from the test run to be analyzed. Set the four-port valve of the condensate recovery system in the CO_2 purge position as shown in Figure 25–9. With the sample tank valve closed, attach the sample tank to the sample recovery system. With the sample recovery valve in the vent position and the flow control valve fully open, evacuate the manometer or pressure gauge to the vacuum of the sample tank. Next, close the vacuum pump valve, open the sample tank valve, and record the tank pressure.

11.1.2.3 Attach the dry ice-cooled condensate trap to the recovery system, and initiate the purge by switching the sample recovery valve from vent to collect position. Adjust the flow control valve to maintain atmospheric pressure in the recovery system. Continue the purge until the CO_2 concentration of the trap effluent is less than 5 ppm. CO_2 concentration in the trap effluent should be measured by extracting syringe samples from the recovery system and analyzing the samples with the NMO analyzer. This procedure should be used only after the NDIR response has reached a minimum level. Using a 10-ml syringe, extract a sample from the syringe port prior to the NDIR, and inject this sample into the NMO analyzer.

11.1.2.4 After the completion of the CO_2 purge, use the carrier gas bypass valve to pressurize the sample tank to approximately 1,060 mm Hg absolute pressure with zero air.

11.1.3 Recovery of the Condensate Trap Sample (See Figure 25–10).

11.1.3.1 Attach the ICV to the sample recovery system. With the sample recovery valve in a closed position, between vent and collect, and the flow control and ICV valves fully open, evacuate the manometer or gauge, the connecting tubing, and the ICV to 10 mm Hg absolute pressure. Close the flow-control and vacuum pump valves.

11.1.3.2 Begin auxiliary oxygen flow to the oxidation catalyst at a rate of 150 cc/min, then switch the four-way valve to the trap recovery position and the sample recovery valve to collect position. The system should now be set up to operate as indicated in Figure 25–10. After the manometer or pressure gauge begins to register a slight positive pressure, open the flow control valve. Adjust the flow-control valve to maintain atmospheric pressure in the system within 10 percent.

11.1.3.3 Remove the condensate trap from the dry ice, and allow it to warm to ambient temperature while monitoring the NDIR response. If, after 5 minutes, the CO_2 concentration of the catalyst effluent is below 10,000 ppm, discontinue the auxiliary oxygen flow to the oxidation catalyst. Begin heating the trap by placing it in a furnace preheated to 200 °C (390 °F). Once heating has begun, carefully monitor the NDIR response to ensure that the catalyst effluent concentration does not exceed 50,000 ppm. Whenever the CO_2 concentration exceeds 50,000 ppm, supply auxiliary oxygen to the catalyst at the rate of 150 cc/min. Begin heating the tubing that connected the heated sample box to the condensate trap only after the CO_2 concentration falls below 10,000 ppm. This tubing may be heated in the same oven as the condensate trap or with an auxiliary heat source such as a heat gun. Heating temperature must not exceed 200 °C (390 °F). If a heat gun is used, heat the tubing slowly along its entire length from the upstream end to the downstream end, and repeat the pattern for a total of three times. Continue the recovery until the CO_2 concentration drops to less than 10 ppm as determined by syringe injection as described under the condensate trap CO_2 purge procedure (Section 11.1.2).

11.1.3.4 After the sample recovery is completed, use the carrier gas bypass valve to pressurize the ICV to approximately 1060 mm Hg absolute pressure with zero air.

11.2 Analysis. Once the initial performance test of the NMO analyzer has been successfully completed (see section 10.1.2) and the daily CO_2 and NMO response factors have been determined (see section 10.2), proceed with sample analysis as follows:

11.2.1 Operating Conditions. The carrier gas flow rate is 29.5 cc/min He and 2.2 cc/min O_2. The column oven is heated to 85 °C (185 °F). The order of elution for the sample from the column is CO, CH_4, CO_2, and NMO.

11.2.2 Analysis of Recovered Condensate Sample. Purge the sample loop with sample, and then inject the sample. Under the specified operating conditions, the CO_2 in the sample will elute in approximately 100 seconds. As soon as the detector response returns to baseline following the CO_2 peak, switch the carrier gas flow to backflush, and raise the column oven temperature to 195 °C (380 °F) as rapidly as possible. A rate of 30 °C/min (90 °F) has been shown to be adequate. Record the value obtained for the condensible organic material (C_{cm}) measured as CO_2 and any measured NMO. Return the column oven temperature to 85 °C (185 °F) in preparation for the next analysis. Analyze each sample in triplicate, and report the average C_{cm}.

11.2.3 Analysis of Sample Tank. Perform the analysis as described in section 11.2.2, but record only the value measured for NMO (C_{tm}).

12.0 Data Analysis and Calculations

Carry out the calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculations. All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge or manometer pressure.

12.1 Nomenclature.

C = TGNMO concentration of the effluent, ppm C equivalent.
C_c = Calculated condensible organic (condensate trap) concentration of the effluent, ppm C equivalent.
C_{cm} = Measured concentration (NMO analyzer) for the condensate trap ICV, ppm CO_2.
C_t = Calculated noncondensible organic concentration (sample tank) of the effluent, ppm C equivalent.
C_{tm} = Measured concentration (NMO analyzer) for the sample tank, ppm NMO.
F = Sampling flow rate, cc/min.
L = Volume of liquid injected, µl.
M = Molecular weight of the liquid injected, g/g-mole.
M_c = TGNMO mass concentration of the effluent, mg C/dsm³.
N = Carbon number of the liquid compound injected (N = 12 for decane, N = 6 for hexane).
n = Number of data points.
P_f = Final pressure of the intermediate collection vessel, mm Hg absolute.
P_b = Barometric pressure, cm Hg.
P_{ti} = Gas sample tank pressure before sampling, mm Hg absolute.
P_t = Gas sample tank pressure after sampling, but before pressurizing, mm Hg absolute.
P_{tf} = Final gas sample tank pressure after pressurizing, mm Hg absolute.
q = Total number of analyzer injections of intermediate collection vessel during analysis (where k = injection number, 1 * * * q).
r = Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 * * * r).
r = Density of liquid injected, g/cc.
T_f = Final temperature of intermediate collection vessel, °K.
T_{ti} = Sample tank temperature before sampling, °K.
T_t = Sample tank temperature at completion of sampling, °K.
T_{tf} = Sample tank temperature after pressurizing, °K.
V = Sample tank volume, m³.
V_t = Sample train volume, cc.
V_v = Intermediate collection vessel volume, m³.
V_s = Gas volume sampled, dsm³.
x_i = Individual measurements.
$\bar{x}$ = Mean value.

ΔP = Allowable pressure change, cm Hg.
Θ = Leak-check period, min.

12.2 Allowable Pressure Change. For the pretest leak-check, calculate the allowable pressure change using Equation 25–1:

$$\Delta P = 0.01 \frac{F P_b \Theta}{V_t} \qquad \text{Eq. 25-1}$$

12.3 Sample Volume. For each test run, calculate the gas volume sampled using Equation 25–2:

$$V_s = 0.3857\, V \left(\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}} \right) \qquad \text{Eq. 25-2}$$

12.4 Noncondensible Organics. For each sample tank, determine the concentration of nonmethane organics (ppm C) using Equation 25–3:

$$C_t = \left(\frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}} \right) \left(\frac{1}{r} \sum_{j=1}^{r} C_{tm_j} \right) \qquad \text{Eq. 25-3}$$

12.5 Condensible Organics. For each condensate trap determine the concentration of organics (ppm C) using Equation 25–4:

$$C_c = 0.3857 \frac{V_v P_f}{V_s T_f} \left(\frac{1}{q} \sum_{k=1}^{q} C_{cm_k} \right) \qquad \text{Eq. 25-4}$$

12.6 TGNMO Mass Concentration. Determine the TGNMO mass concentration as carbon for each test run, using Equation 25–5:

$$M_c = 0.4993 \left(C_t + C_c \right) \qquad \text{Eq. 25-5}$$

12.7 Percent Recovery. Calculate the percent recovery for the liquid injections to the condensate recovery and conditioning system using Equation 25–6:

$$\text{Percent Recovery} = K \frac{M V_v P_t C_{cm}}{L P T_f N} \qquad \text{Eq. 25-6}$$

where K = 1.604 (°K)(g-mole)(%)/(mm Hg)(ml)(m^3)(ppm).

12.8 Relative Standard Deviation. Use Equation 25–7 to calculate the relative standard deviation (RSD) of percent recovery and analyzer linearity.

$$RSD = \frac{100}{\bar{x}} \left[\frac{\sum_{i=1}^{n} \left(x_i - \bar{x} \right)^2}{n-1} \right]^{\frac{1}{2}} \qquad \text{Eq. 25-7}$$

13.0 Method Performance

13.1 Range. The minimum detectable limit of the method has been determined to be 50 parts per million by volume (ppm). No upper limit has been established.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, A.E., S. Witz, and R.D. MacPhee. Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, MA. June 15–20, 1975.) 14 p.

2. Salo, A.E., W.L. Oaks, and R.D. MacPhee. Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, CO. June 9–13, 1974.) 25 p.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

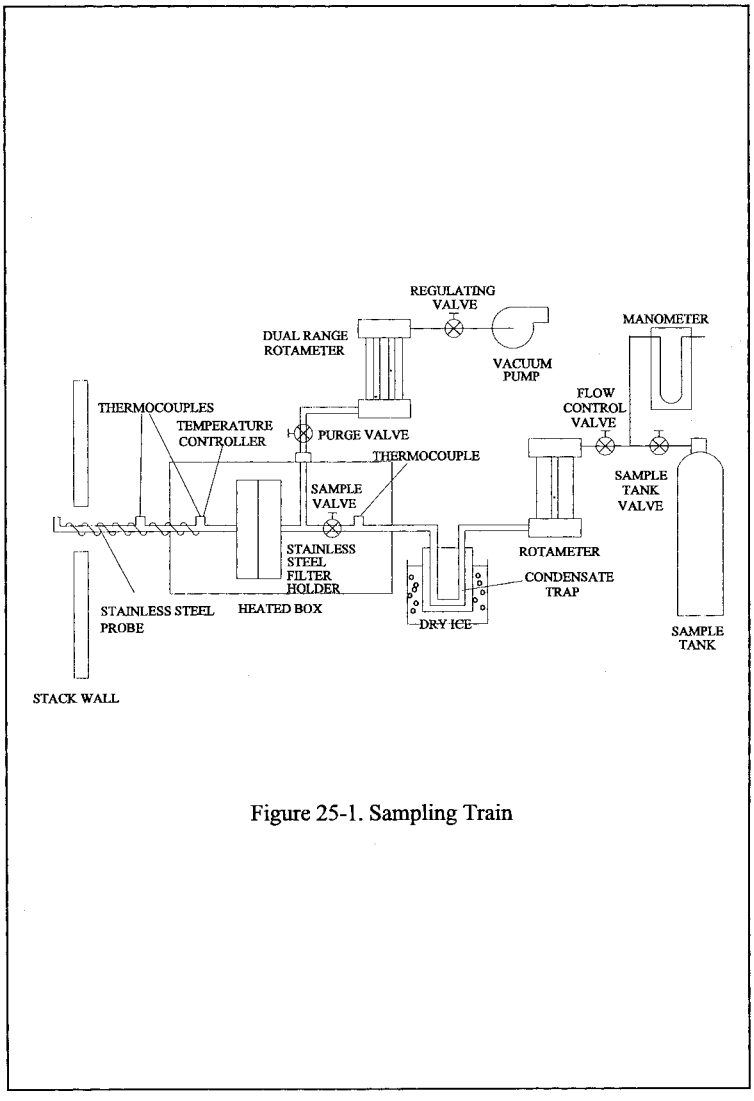


Figure 25-1. Sampling Train

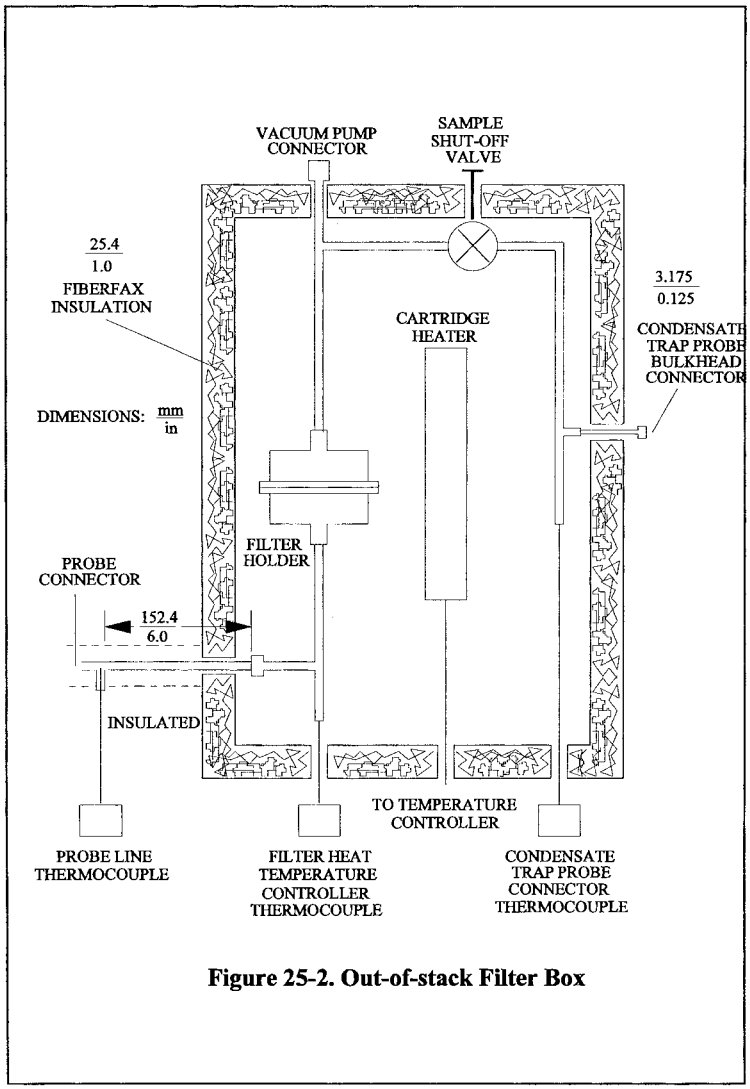


Figure 25-2. Out-of-stack Filter Box

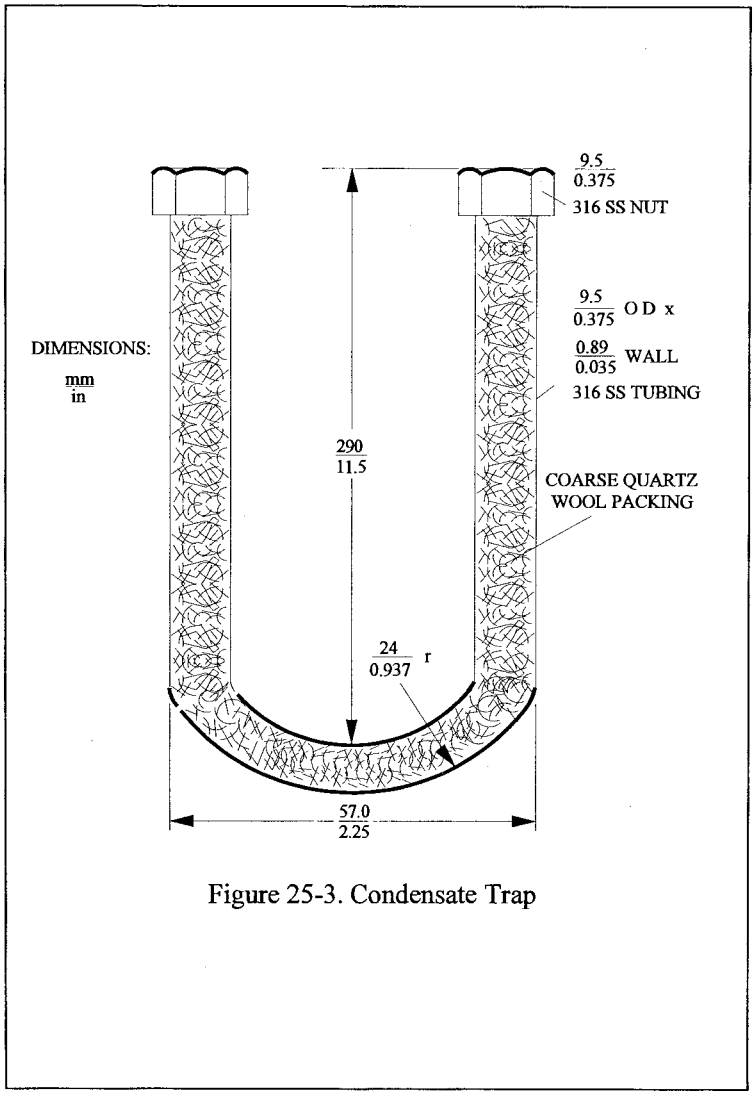


Figure 25-3. Condensate Trap

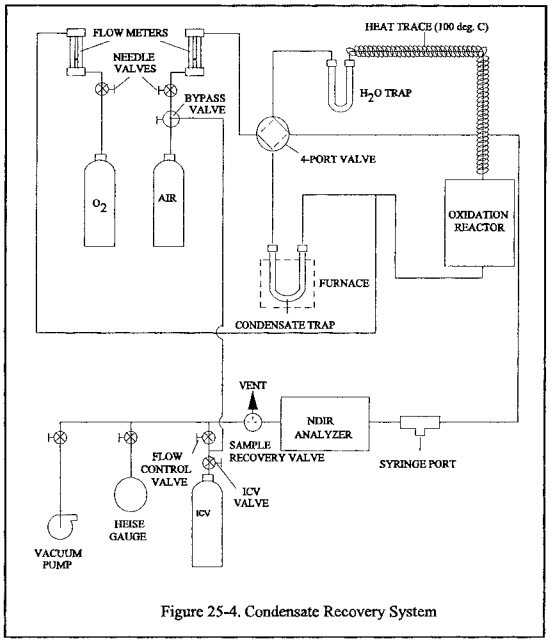


Figure 25-4. Condensate Recovery System

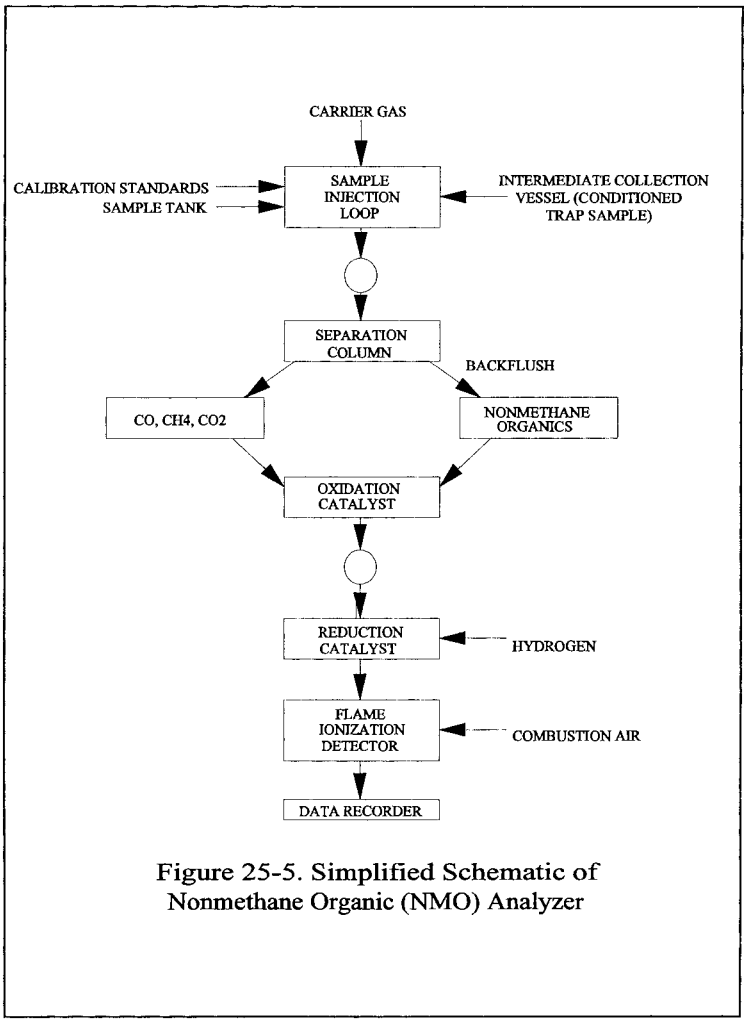


Figure 25-5. Simplified Schematic of Nonmethane Organic (NMO) Analyzer

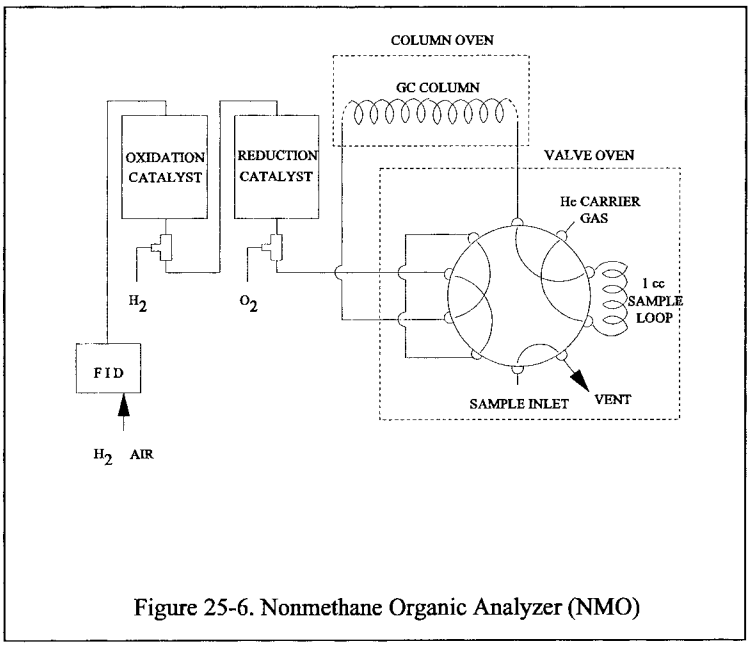


Figure 25-6. Nonmethane Organic Analyzer (NMO)

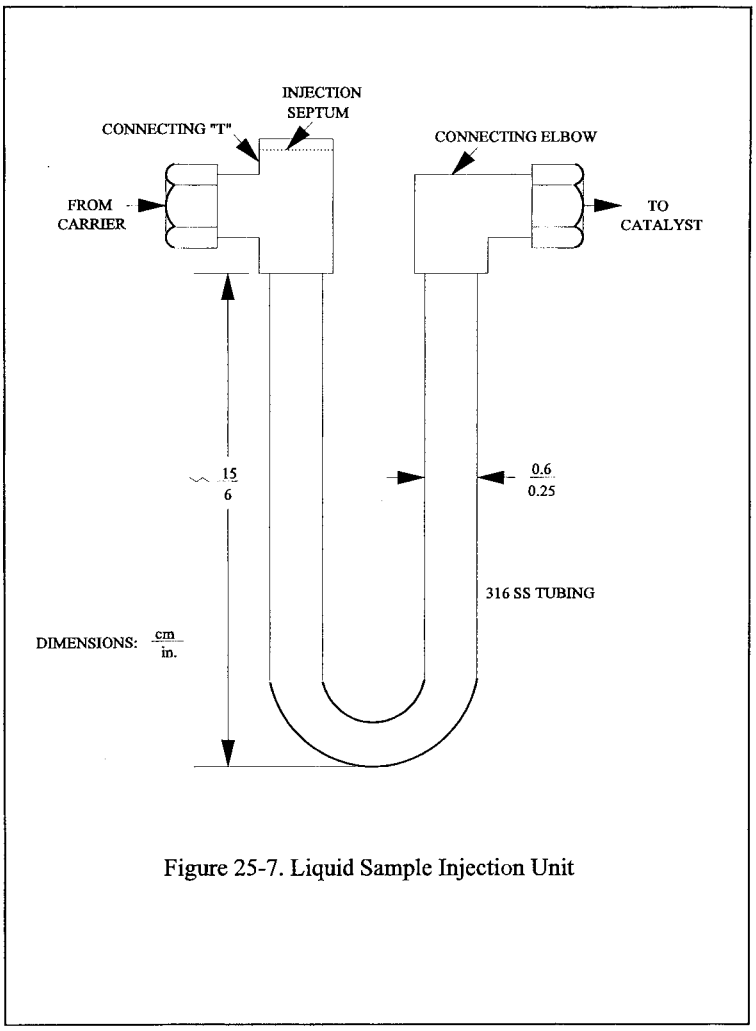


Figure 25-7. Liquid Sample Injection Unit

VOLATILE ORGANIC CARBON

FACILITY _____ SAMPLE LOCATION _____

LOCATION _____ OPERATOR _____

DATE _____ RUN NUMBER _____

TANK NUMBER _____ TRAP NUMBER _____ SAMPLE ID NUMBER _____

TANK VACUUM mm HG	TANK VACUUM cm Hg	BAROMETRIC PRESSURE mm Hg	AMBIENT TEMPERATURE °C
PRETEST (MANOMETER)	(GAUGE)		
POST-TEST (MANOMETER)	(GAUGE)		

LEAK RATE _____ cm Hg / l fl min _____

PRETEST _____

TIME CLOCK/SAMPLE	VACUUM cm Hg	FLOWMETER SETTINGS	COMMENTS

Figure 25-8. Example Field Data Form

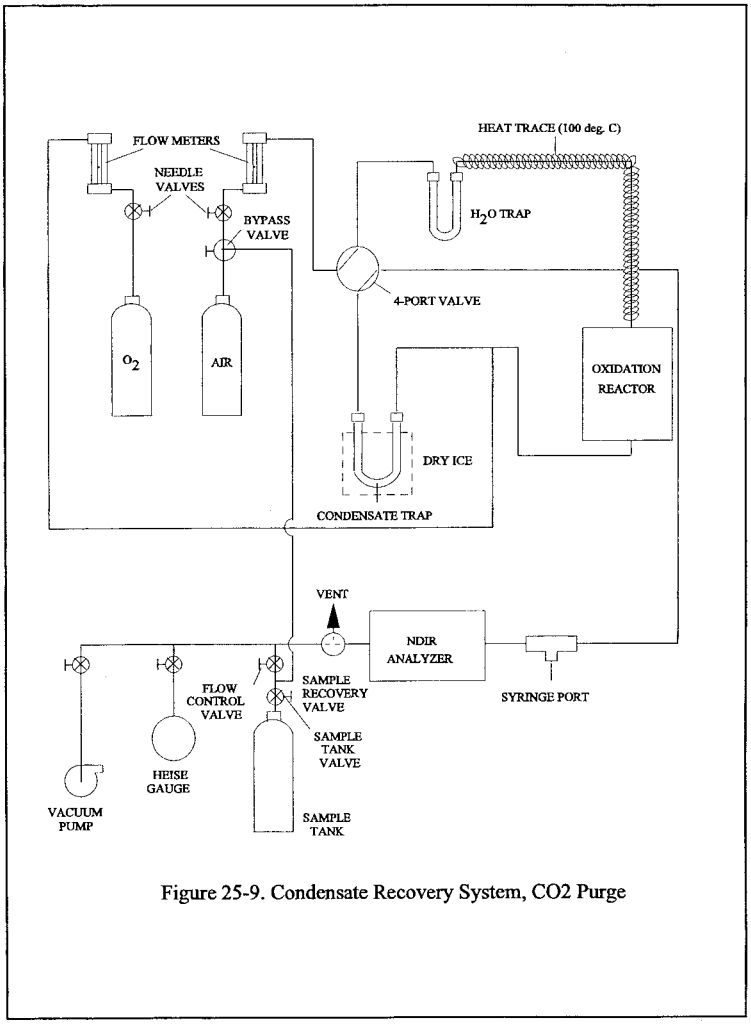


Figure 25-9. Condensate Recovery System, CO2 Purge

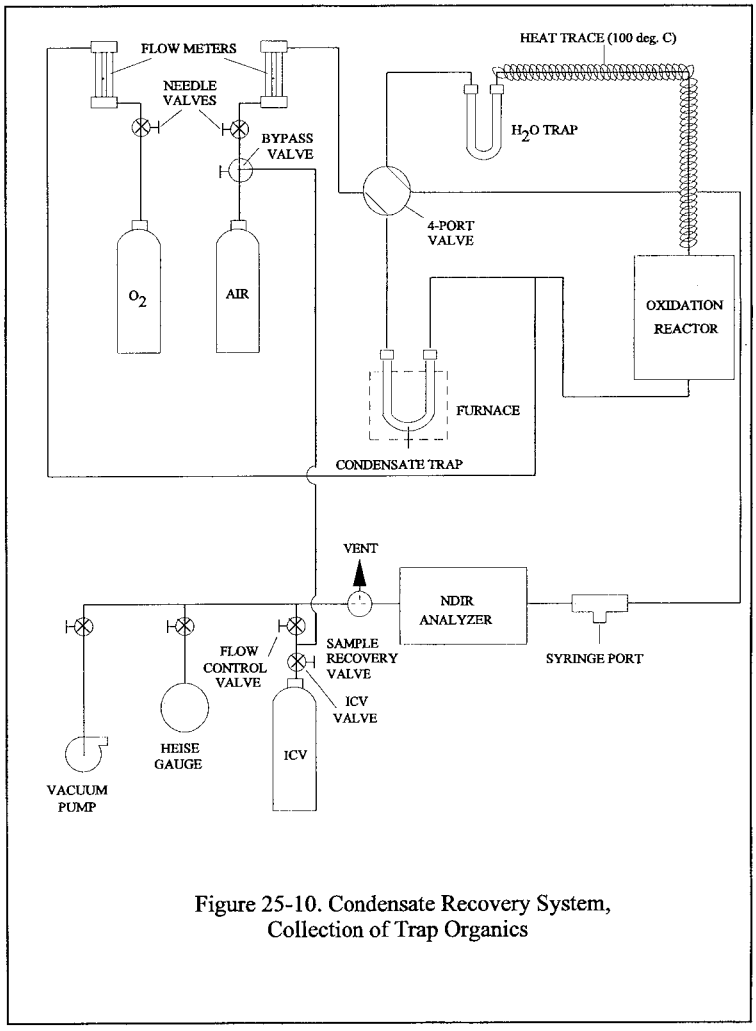


Figure 25-10. Condensate Recovery System, Collection of Trap Organics

METHOD 25A—DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A FLAME IONIZATION ANALYZER

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total Organic Compounds	N/A	<2% of span.

1.2 Applicability. This method is applicable for the determination of total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the source through a heated sample line and glass fiber filter to a flame ionization analyzer (FIA). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

3.0 Definitions

3.1 *Calibration drift* means the difference in the measurement system response to a mid-level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

3.2 *Calibration error* means the difference between the gas concentration indicated by the measurement system and the know concentration of the calibration gas.

3.3 *Calibration gas* means a known concentration of a gas in an appropriate diluent gas.

3.4 *Measurement system* means the total equipment required for the determination of the gas concentration. The system consists of the following major subsystems:

3.4.1 *Sample interface* means that portion of a system used for one or more of the following: sample acquisition, sample transportation, sample conditioning, or protection of the analyzer(s) from the effects of the stack effluent.

3.4.2 *Organic analyzer* means that portion of the measurement system that senses the gas to be measured and generates an output proportional to its concentration.

3.5 *Response time* means the time interval from a step change in pollutant concentration at the inlet to the emission measurement system to the time at which 95 percent of the corresponding final value is reached as displayed on the recorder.

3.6 *Span Value* means the upper limit of a gas concentration measurement range that is specified for affected source categories in the applicable part of the regulations. The span value is established in the applicable regulation and is usually 1.5 to 2.5 times the applicable emission limit. If no span value is provided, use a span value equivalent to 1.5 to 2.5 times the expected concentration. For convenience, the span value should correspond to 100 percent of the recorder scale.

3.7 *Zero drift* means the difference in the measurement system response to a zero level calibration gas before or after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

5.2 Explosive Atmosphere. This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

6.0 Equipment and Supplies

6.1 Measurement System. Any measurement system for total organic concentration that meets the specifications of this method. A schematic of an acceptable measurement system is shown in Figure 25A–1. All sampling components leading to the analyzer shall be heated ≥110 °C (220 °F) throughout the sampling period, unless safety reasons are cited (Section 5.2) The essential components of the measurement system are described below:

6.1.1 Organic Concentration Analyzer. A flame ionization analyzer (FIA) capable of meeting or exceeding the specifications of this method. The flame ionization detector block shall be heated >120 °C (250 °F).

6.1.2 Sample Probe. Stainless steel, or equivalent, three-hole rake type. Sample holes shall be 4 mm (0.16-in.) in diameter or smaller and located at 16.7, 50, and 83.3 percent of the equivalent stack diameter. Alternatively, a single opening probe may be used so that a gas sample is collected from the centrally located 10 percent area of the stack cross-section.

6.1.3 Heated Sample Line. Stainless steel or Teflon'' tubing to transport the sample gas

to the analyzer. The sample line should be heated (≥110 °C) to prevent any condensation.

6.1.4 Calibration Valve Assembly. A three-way valve assembly to direct the zero and calibration gases to the analyzers is recommended. Other methods, such as quick-connect lines, to route calibration gas to the analyzers are applicable.

6.1.5 Particulate Filter. An in-stack or an out-of-stack glass fiber filter is recommended if exhaust gas particulate loading is significant. An out-of-stack filter should be heated to prevent any condensation.

6.1.6 Recorder. A strip-chart recorder, analog computer, or digital recorder for recording measurement data. The minimum data recording requirement is one measurement value per minute.

7.0 Reagents and Standards

7.1 Calibration Gases. The calibration gases for the gas analyzer shall be propane in air or propane in nitrogen. Alternatively, organic compounds other than propane can be used; the appropriate corrections for response factor must be made. Calibration gases shall be prepared in accordance with the procedure listed in Citation 2 of section 16. Additionally, the manufacturer of the cylinder should provide a recommended shelf life for each calibration gas cylinder over which the concentration does not change more than ±2 percent from the certified value. For calibration gas values not generally available (*i.e.*, organics between 1 and 10 percent by volume), alternative methods for preparing calibration gas mixtures, such as dilution systems (Test Method 205, 40 CFR Part 51, Appendix M), may be used with prior approval of the Administrator.

7.1.1 Fuel. A 40 percent H_2/60 percent N_2 gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value.

7.1.2 Zero Gas. High purity air with less than 0.1 part per million by volume (ppmv) of organic material (propane or carbon equivalent) or less than 0.1 percent of the span value, whichever is greater.

7.1.3 Low-level Calibration Gas. An organic calibration gas with a concentration equivalent to 25 to 35 percent of the applicable span value.

7.1.4 Mid-level Calibration Gas. An organic calibration gas with a concentration equivalent to 45 to 55 percent of the applicable span value.

7.1.5 High-level Calibration Gas. An organic calibration gas with a concentration equivalent to 80 to 90 percent of the applicable span value.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Selection of Sampling Site. The location of the sampling site is generally specified by the applicable regulation or purpose of the test (*i.e.*, exhaust stack, inlet line, etc.). The sample port shall be located to meet the testing requirements of Method 1.

8.2 Location of Sample Probe. Install the sample probe so that the probe is centrally located in the stack, pipe, or duct and is sealed tightly at the stack port connection.

8.3 Measurement System Preparation. Prior to the emission test, assemble the measurement system by following the manufacturer's written instructions for preparing sample interface and the organic analyzer. Make the system operable (Section 10.1).

8.4 Calibration Error Test. Immediately prior to the test series (within 2 hours of the start of the test), introduce zero gas and high-level calibration gas at the calibration valve assembly. Adjust the analyzer output to the appropriate levels, if necessary. Calculate the predicted response for the low-level and mid-level gases based on a linear response line between the zero and high-level response. Then introduce low-level and mid-level calibration gases successively to the measurement system. Record the analyzer responses for low-level and mid-level calibration gases and determine the differences between the measurement system responses and the predicted responses. These differences must be less than 5 percent of the respective calibration gas value. If not, the measurement system is not acceptable and must be replaced or repaired prior to testing. No adjustments to the measurement system shall be conducted after the calibration and before the drift check (Section 8.6.2). If adjustments are necessary before the completion of the test series, perform the drift checks prior to the required adjustments and repeat the calibration following the adjustments. If multiple electronic ranges are to be used, each additional range must be checked with a mid-level calibration gas to verify the multiplication factor.

8.5 Response Time Test. Introduce zero gas into the measurement system at the calibration valve assembly. When the system output has stabilized, switch quickly to the high-level calibration gas. Record the time from the concentration change to the measurement system response equivalent to 95 percent of the step change. Repeat the test three times and average the results.

8.6 Emission Measurement Test Procedure.

8.6.1 Organic Measurement. Begin sampling at the start of the test period, recording time and any required process information as appropriate. In particulate, note on the recording chart, periods of process interruption or cyclic operation.

8.6.2 Drift Determination. Immediately following the completion of the test period and hourly during the test period, reintroduce the zero and mid-level calibration gases, one at a time, to the measurement system at the calibration valve assembly. (Make no adjustments to the measurement system until both the zero and calibration drift checks are made.) Record the analyzer response. If the drift values exceed the specified limits, invalidate the test results preceding the check and repeat the test following corrections to the measurement system. Alternatively, recalibrate the test measurement system as in section 8.4 and report the results using both sets of calibration data (i.e., data determined prior to the test period and data determined following the test period).

NOTE: Note on the recording chart periods of process interruption or cyclic operation.

9.0 Quality Control

Method section	Quality control measure	Effect
8.4	Zero and calibration drift tests	Ensures that bias introduced by drift in the measurement system output during the run is no greater than 3 percent of span.

10.0 Calibration and Standardization

10.1 FIA equipment can be calibrated for almost any range of total organic concentrations. For high concentrations of organics (>1.0 percent by volume as propane), modifications to most commonly available analyzers are necessary. One accepted method of equipment modification is to decrease the size of the sample to the analyzer through the use of a smaller diameter sample capillary. Direct and continuous measurement of organic concentration is a necessary consideration when determining any modification design.

11.0 Analytical Procedure

The sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Calculations and Data Analysis

12.1 Determine the average organic concentration in terms of ppmv as propane or other calibration gas. The average shall be determined by integration of the output recording over the period specified in the applicable regulation. If results are required in terms of ppmv as carbon, adjust measured concentrations using Equation 25A–1.

$$C_c = K C_{meas} \qquad \text{Eq. 25A-1}$$

Where:

C_c = Organic concentration as carbon, ppmv.
C_{meas} = Organic concentration as measured, ppmv.
K = Carbon equivalent correction factor.
= 2 for ethane.
= 3 for propane.
= 4 for butane.
= Appropriate response factor for other organic calibration gases.

13.0 Method Performance

13.1 Measurement System Performance Specifications.

13.1.1 Zero Drift. Less than ±3 percent of the span value.

13.1.2 Calibration Drift. Less than ±3 percent of span value.

13.1.3 Calibration Error. Less than ±5 percent of the calibration gas value.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Measurement of Volatile Organic Compounds—Guideline Series. U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA–450/2–78–041. June 1978. p. 46–54.

2. EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards. U.S. Environmental Protection Agency, Quality Assurance and Technical Support Division. Research Triangle Park, N.C. September 1993.

3. Gasoline Vapor Emission Laboratory Evaluation—Part 2. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, NC. EMB Report No. 75–GAS–6. August 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

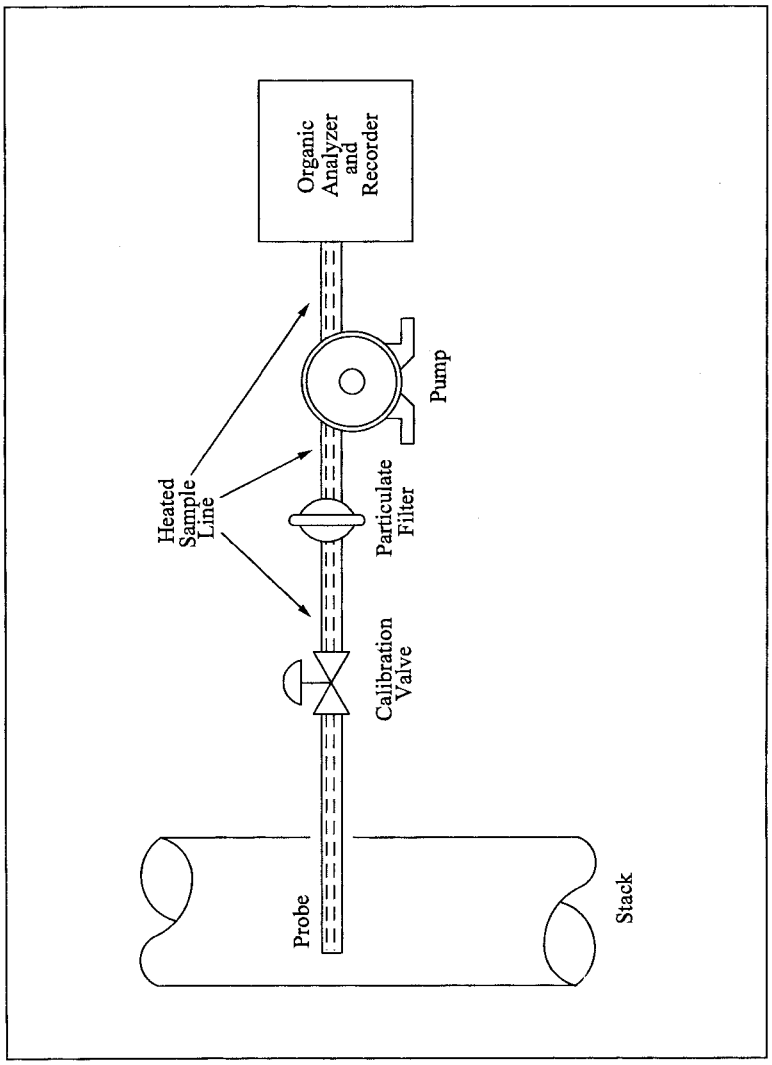


Figure 25A-1. Organic Concentration Measurement System.

METHOD 25B—DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A NONDISPERSIVE INFRARED ANALYZER

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 6C, and Method 25A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total Organic Compounds	N/A	<2% of span.

1.2 Applicability. This method is applicable for the determination of total gaseous organic concentration of vapors consisting primarily of alkanes. Other organic materials may be measured using the general procedure in this method, the appropriate calibration gas, and an analyzer set to the appropriate absorption band.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

A gas sample is extracted from the source through a heated sample line, if necessary, and glass fiber filter to a nondispersive infrared analyzer (NDIR). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

3.0 Definitions

Same as Method 25A, section 3.0.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

5.2 Explosive Atmosphere. This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

6.0 Equipment and Supplies

Same as Method 25A, section 6.0, with the exception of the following:

6.1 Organic Concentration Analyzer. A nondispersive infrared analyzer designed to measure alkane organics and capable of meeting or exceeding the specifications in this method.

7.0 Reagents and Standards

Same as Method 25A, section 7.1. No fuel gas is required for an NDIR.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as Method 25A, section 8.0.

9.0 Quality Control

Same as Method 25A, section 9.0.

10.0 Calibration and Standardization

Same as Method 25A, section 10.0.

11.0 Analytical Procedure

The sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Calculations and Data Analysis

Same as Method 25A, section 12.0.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 25A, section 16.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 25C—DETERMINATION OF NONMETHANE ORGANIC COMPOUNDS (NMOC) IN LANDFILL GASES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should also have a thorough knowledge of EPA Method 25.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Nonmethane organic compounds (NMOC).	No CAS number assigned.

1.2 Applicability. This method is applicable to the sampling and measurement of NMOC as carbon in landfill gases (LFG).

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A sample probe that has been perforated at one end is driven or augured to a depth of 0.9 m (3 ft) below the bottom of the landfill cover. A sample of the landfill gas is extracted with an evacuated cylinder. The NMOC content of the gas is determined by

injecting a portion of the gas into a gas chromatographic column to separate the NMOC from carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4); the NMOC are oxidized to CO_2, reduced to CH_4, and measured by a flame ionization detector (FID). In this manner, the variable response of the FID associated with different types of organics is eliminated.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Since this method is complex, only experienced personnel should perform this test. LFG contains methane, therefore explosive mixtures may exist on or near the landfill. It is advisable to take appropriate safety precautions when testing landfills, such as refraining from smoking and installing explosion-proof equipment.

6.0 Equipment and Supplies

6.1 Sample Probe. Stainless steel, with the bottom third perforated. Teflon probe liners and sampling lines are also allowed. Non-perforated probes are allowed as long as they are withdrawn to create a gap equivalent to having the bottom third perforated. The sample probe must be capped at the bottom and must have a threaded cap with a sampling attachment at the top. The sample probe must be long enough to go through and extend no less than 0.9 m (3 ft) below the landfill cover. If the sample probe is to be driven into the landfill, the bottom cap should be designed to facilitate driving the probe into the landfill.

6.2 Sampling Train.

6.2.1 Rotameter with Flow Control Valve. Capable of measuring a sample flow rate of 100 ±10 ml/min. The control valve must be made of stainless steel.

6.2.2 Sampling Valve. Stainless steel.

6.2.3 Pressure Gauge. U-tube mercury manometer, or equivalent, capable of measuring pressure to within 1 mm Hg (0.5 in H_2O) in the range of 0 to 1,100 mm Hg (0 to 590 in H_2O).

6.2.4 Sample Tank. Stainless steel or aluminum cylinder, equipped with a stainless steel sample tank valve.

6.3 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg (5.4 in H_2O).

6.4 Purging Pump. Portable, explosion proof, and suitable for sampling NMOC.

6.5 Pilot Probe Procedure. The following are needed only if the tester chooses to use the procedure described in section 8.2.1.

6.5.1 Pilot Probe. Tubing of sufficient strength to withstand being driven into the landfill by a post driver and an outside diameter of at least 6 mm (0.25 in.) smaller than the sample probe. The pilot probe shall be capped on both ends and long enough to go through the landfill cover and extend no less than 0.9 m (3 ft) into the landfill.

6.5.2 Post Driver and Compressor. Capable of driving the pilot probe and the sampling probe into the landfill. The Kitty Hawk portable post driver has been found to be acceptable.

6.6 Auger Procedure. The following are needed only if the tester chooses to use the procedure described in section 8.2.2.

6.6.1 Auger. Capable of drilling through the landfill cover and to a depth of no less than 0.9 m (3 ft) into the landfill.

6.6.2 Pea Gravel.

6.6.3 Bentonite.

6.7 NMOC Analyzer, Barometer, Thermometer, and Syringes. Same as in sections 6.3.1, 6.3.2, 6.33, and 6.2.10, respectively, of Method 25.

7.0 Reagents and Standards

7.1 NMOC Analysis. Same as in Method 25, section 7.2.

7.2 Calibration. Same as in Method 25, section 7.4, except omit section 7.4.3.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sample Tank Evacuation and Leak-Check. Conduct the sample tank evacuation and leak-check either in the laboratory or the field. Connect the pressure gauge and sampling valve to the sample tank. Evacuate the sample tank to 10 mm Hg (5.4 in H_2O) absolute pressure or less. Close the sampling valve, and allow the tank to sit for 30 minutes. The tank is acceptable if no change more than ±2 mm is noted. Include the results of the leak-check in the test report.

8.2 Sample Probe Installation. The tester may use the procedure in section 8.2.1 or 8.2.2.

8.2.1 Pilot Probe Procedure. Use the post driver to drive the pilot probe at least 0.9 m (3 ft) below the landfill cover. Alternative procedures to drive the probe into the landfill may be used subject to the approval of the Administrator's designated representative.

8.2.1.1 Remove the pilot probe and drive the sample probe into the hole left by the pilot probe. The sample probe shall extend at least 0.9 m (3 ft) below the landfill cover and shall protrude about 0.3 m (1 ft) above the landfill cover. Seal around the sampling probe with bentonite and cap the sampling probe with the sampling probe cap.

8.2.2 Auger Procedure. Use an auger to drill a hole to at least 0.9 m (3 ft) below the landfill cover. Place the sample probe in the hole and backfill with pea gravel to a level 0.6 m (2 ft) from the surface. The sample probe shall protrude at least 0.3 m (1 ft) above the landfill cover. Seal the remaining area around the probe with bentonite. Allow 24

hours for the landfill gases to equilibrate inside the augured probe before sampling.

8.2.3 Driven Probes. Closed-point probes may be driven directly into the landfill in a single step. This method may not require backfilling if the probe is adequately sealed by its insertion. Unperforated probes that are inserted in this manner and withdrawn at a distance from a detachable tip to create an open space are also acceptable.

8.3 Sample Train Assembly. Just before assembling the sample train, measure the sample tank vacuum using the pressure gauge. Record the vacuum, the ambient temperature, and the barometric pressure at this time. Assemble the sampling probe purging system as shown in Figure 25C–1.

8.4 Sampling Procedure. Open the sampling valve and use the purge pump and the flow control valve to evacuate at least two sample probe volumes from the system at a flow rate of 500 ml/min or less. Close the sampling valve and replace the purge pump with the sample tank apparatus as shown in Figure 25C–2. Open the sampling valve and the sample tank valve and, using the flow control valve, sample at a flow rate of 500 ml/min or less until either a constant flow rate can no longer be maintained because of reduced sample tank vacuum or the appropriate composite volume is attained. Disconnect the sampling tank apparatus and pressurize the sample cylinder to approximately 1,060 mm Hg (567 in. H_2O) absolute pressure with helium, and record the final pressure. Alternatively, the sample tank may be pressurized in the lab.

8.4.1 The following restrictions apply to compositing samples from different probe sites into a single cylinder: (1) Individual composite samples per cylinder must be of equal volume; this must be verified by recording the flow rate, sampling time, vacuum readings, or other appropriate volume measuring data, (2) individual composite samples must have a minimum volume of 1 liter unless data is provided showing smaller volumes can be accurately measured, and (3) composite samples must not be collected using the final cylinder vacuum as it diminishes to ambient pressure.

8.4.2 Use Method 3C to determine the percent N_2 in each cylinder. The presence of N_2 indicates either infiltration of ambient air into the landfill gas sample or an inappropriate testing site has been chosen where anaerobic decomposition has not begun. The landfill gas sample is acceptable if the concentration of N_2 is less than 20 percent. Alternatively, Method 3C may be used to determine the oxygen content of each cylinder as an air infiltration test. With this option, the oxygen content of each cylinder must be less than 5 percent.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4.2	Verify that landfill gas sample contains less than 20 percent N_2 or 5 percent O_2.	Ensures that ambient air was not drawn into the landfill gas sample and gas was sampled from an appropriate location.
10.1, 10.2	NMOC analyzer initial and daily performance checks.	Ensures precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Initial NMOC Analyzer Performance Test. Same as in Method 25, section 10.1, except omit the linearity checks for CO_2 standards.

10.2 NMOC Analyzer Daily Calibration.

10.2.1 NMOC Response Factors. Same as in Method 25, section 10.2.2.

10.3 Sample Tank Volume. The volume of the gas sampling tanks must be determined. Determine the tank volumes by weighing them empty and then filled with deionized water; weigh to the nearest 5 g, and record the results. Alternatively, measure the volume of water used to fill them to the nearest 5 ml.

11.0 Analytical Procedures

11.1 The oxidation, reduction, and measurement of NMOC's is similar to Method 25. Before putting the NMOC analyzer into routine operation, conduct an initial performance test. Start the analyzer, and perform all the necessary functions in order to put the analyzer into proper working order. Conduct the performance test according to the procedures established in section 10.1. Once the performance test has been successfully completed and the NMOC calibration response factor has been determined, proceed with sample analysis as follows:

11.1.1 Daily Operations and Calibration Checks. Before and immediately after the analysis of each set of samples or on a daily basis (whichever occurs first), conduct a calibration test according to the procedures established in section 10.2. If the criteria of the daily calibration test cannot be met, repeat

the NMOC analyzer performance test (Section 10.1) before proceeding.

11.1.2 Operating Conditions. Same as in Method 25, section 11.2.1.

11.1.3 Analysis of Sample Tank. Purge the sample loop with sample, and then inject the sample. Under the specified operating conditions, the CO_2 in the sample will elute in approximately 100 seconds. As soon as the detector response returns to baseline following the CO_2 peak, switch the carrier gas flow to backflush, and raise the column oven temperature to 195 °C (383 °F) as rapidly as possible. A rate of 30 °C/min (54 °F/min) has been shown to be adequate. Record the value obtained for any measured NMOC. Return the column oven temperature to 85 °C (185 °F) in preparation for the next analysis. Analyze each sample in triplicate, and report the average as C_{tm}.

12.0 Data Analysis and Calculations

NOTE: All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge or manometer pressure.

12.1 Nomenclature

B_w = Moisture content in the sample, fraction.
C_{N2} = N_2 concentration in the diluted sample gas.
C_{mN2} = Measured N_2 concentration, fraction in landfill gas.
C_{mOx} = Measured Oxygen concentration, fraction in landfill gas.
C_{Ox} = Oxygen concentration in the diluted sample gas.
C_t = Calculated NMOC concentration, ppmv C equivalent.
C_{tm} = Measured NMOC concentration, ppmv C equivalent.
P_b = Barometric pressure, mm Hg.
P_t = Gas sample tank pressure after sampling, but before pressurizing, mm Hg absolute.
P_{tf} = Final gas sample tank pressure after pressurizing, mm Hg absolute.
P_{ti} = Gas sample tank pressure after evacuation, mm Hg absolute.
P_w = Vapor pressure of H_2O (from Table 25C–1), mm Hg.
r = Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 . . . r).
T_t = Sample tank temperature at completion of sampling, °K.
T_{ti} = Sample tank temperature before sampling, °K.
T_{tf} = Sample tank temperature after pressuring, °K.

12.2 Water Correction. Use Table 25C–1 (Section 17.0), the LFG temperature, and barometric pressure at the sampling site to calculate B_w.

$$B_w = \frac{P_w}{P_b} \qquad \text{Eq. 25C-1}$$

12.3 Nitrogen Concentration in the landfill gas. Use equation 25C–2 to calculate the measured concentration of nitrogen in the original landfill gas.

$$C_{N2} = \left[\frac{\left(\frac{P_{tf}}{T_{tf}}\right)}{\left(\left(\frac{P_t}{T_t}\right)-\left(\frac{P_{ti}}{T_{ti}}\right)\right)}\right] C_{mN2} \qquad \text{Eq.25C-2}$$

12.4 Oxygen Concentration in the landfill gas. Use equation 25C–3 to calculate the measured concentration of oxygen in the original landfill gas.

$$C_{Ox} = \left[\frac{\left(\frac{P_{tf}}{T_{tf}}\right)}{\left(\left(\frac{P_t}{T_t}\right)-\left(\frac{P_{ti}}{T_{ti}}\right)\right)}\right] C_{mOx} \qquad \text{Eq.25C-3}$$

12.5 You must correct the NMOC Concentration for the concentration of nitrogen or oxygen based on which gas or gases passes the requirements in section 9.1.

12.5.1 NMOC Concentration with nitrogen correction. Use Equation 25C–4 to calculate the concentration of NMOC for each sample tank when the nitrogen concentration is less than 20 percent.

$$C_t = \frac{\frac{P_{tf}}{T_{tf}}}{\left(\frac{P_t}{T_t}-\frac{P_{ti}}{T_{ti}}\right)\left(1-\frac{99}{78}C_{N2}\right)-B_w}\frac{1}{r}\sum_{j=1}^{r} C_{tm(j)} \qquad \text{Eq. 25C-4}$$

12.5.2 NMOC Concentration with oxygen correction. Use Equation 25C–5 to calculate the concentration of NMOC for each sample tank if the landfill gas oxygen is less than 5 percent and the landfill gas nitrogen concentration is greater than 20 percent.

$$C_t = \frac{\frac{P_{tf}}{T_{tf}}}{\left(\frac{P_t}{T_t}-\frac{P_{ti}}{T_{ti}}\right)\left(1-\frac{99}{21}C_{Ox}\right)-B_w}\frac{1}{r}\sum_{j=1}^{r} C_{tm(j)} \qquad \text{Eq. 25C-5}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, Albert E., Samuel Witz, and Robert D. MacPhee. Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, Massachusetts. June 15–20, 1975.) 14 p.

2. Salo, Albert E., William L. Oaks, and Robert D. MacPhee. Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, Colorado. June 9–13, 1974.) 25 p.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

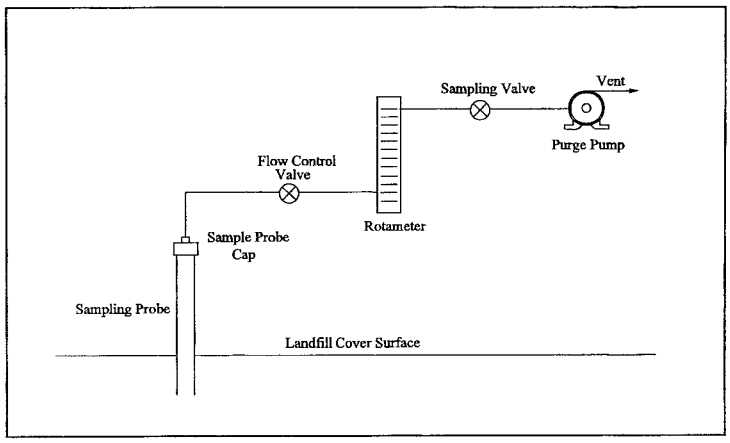


Figure 25C-1. Schematic of Sampling Probe Purging System

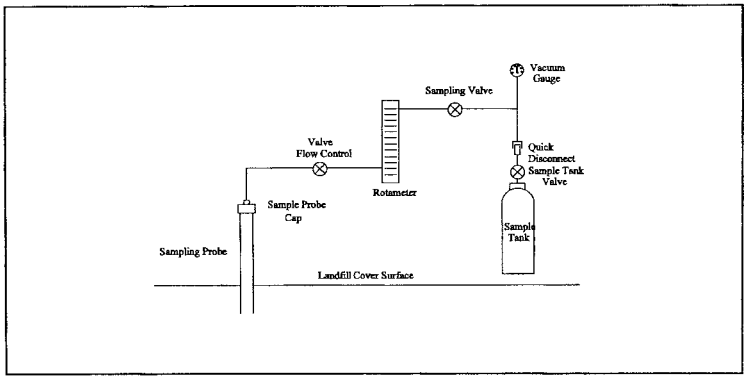


Figure 25C-2. Schematic of Sampling Train.

TABLE 25C–1—MOISTURE CORRECTION

Temperature, °C	Vapor Pressure of H_2O, mm Hg	Temperature, °C	Vapor Pressure of H_2O, mm Hg
4	6.1	18	15.5
6	7.0	20	17.5
8	8.0	22	19.8
10	9.2	24	22.4
12	10.5	26	25.2
14	12.0	28	28.3

TABLE 25C–1—MOISTURE CORRECTION—Continued

Temperature, °C	Vapor Pressure of H_2O, mm Hg	Temperature, °C	Vapor Pressure of H_2O, mm Hg
16	13.6	30	31.8

METHOD 25D—DETERMINATION OF THE VOLATILE ORGANIC CONCENTRATION OF WASTE SAMPLES

NOTE: Performance of this method should not be attempted by persons unfamiliar with the operation of a flame ionization detector (FID) or an electrolytic conductivity detector (ELCD) because knowledge beyond the scope of this presentation is required.

1.0 Scope and Application

1.1 Analyte. Volatile Organic Compounds. No CAS No. assigned.

1.2 Applicability. This method is applicable for determining the volatile organic (VO) concentration of a waste sample.

2.0 Summary of Method

2.1 Principle. A sample of waste is obtained at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to the atmosphere). The sample is suspended in an organic/aqueous matrix, then heated and purged with nitrogen for 30 min. in order to separate certain organic compounds. Part of the sample is analyzed for carbon concentration, as methane, with an FID, and part of the sample is analyzed for chlorine concentration, as chloride, with an ELCD. The VO concentration is the sum of the carbon and chlorine content of the sample.

3.0 Definitions

3.1 *Well-mixed* in the context of this method refers to turbulent flow which results in multiple-phase waste in effect behaving as single-phase waste due to good mixing.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1 Sampling. The following equipment is required:

6.1.1 Sampling Tube. Flexible Teflon, 0.25 in. ID (6.35 mm).

6.1.2 Sample Container. Borosilicate glass, 40-mL, and a Teflon-lined screw cap capable of forming an air tight seal.

6.1.3 Cooling Coil. Fabricated from 0.25 in (6.35 mm). ID 304 stainless steel tubing with a thermocouple at the coil outlet.

6.2 Analysis. The following equipment is required.

6.2.1 Purging Apparatus. For separating the VO from the waste sample. A schematic of the system is shown in Figure 25D–1. The purging apparatus consists of the following major components.

6.2.1.1 Purging Flask. A glass container to hold the sample while it is heated and purged with dry nitrogen. The cap of the purging flask is equipped with three fittings: one for a purging lance (fitting with the #7 Ace-thread), one for the Teflon exit tubing (side fitting, also a #7 Ace-thread), and a third (a 50-mm Ace-thread) to attach the base of the purging flask as shown in Figure 25D–2. The base of the purging flask is a 50-mm ID (2 in) cylindrical glass tube. One end of the tube is open while the other end is sealed. Exact dimensions are shown in Figure 25D–2.

6.2.1.2 Purging Lance. Glass tube, 6-mm OD (0.2 in) by 30 cm (12 in) long. The purging end of the tube is fitted with a four-arm bubbler with each tip drawn to an opening 1 mm (0.04 in) in diameter. Details and exact dimensions are shown in Figure 25D–2.

6.2.1.3 Coalescing Filter. Porous fritted disc incorporated into a container with the same dimensions as the purging flask. The details of the design are shown in Figure 25D–3.

6.2.1.4 Constant Temperature Chamber. A forced draft oven capable of maintaining a uniform temperature around the purging flask and coalescing filter of 75 ±2 °C (167 ±3.6 °F).

6.2.1.5 Three-way Valve. Manually operated, stainless steel. To introduce calibration gas into system.

6.2.1.6 Flow Controllers. Two, adjustable. One capable of maintaining a purge gas flow rate of 6 ±0.06 L/min (0.2 ±0.002 ft^3/min) The other capable of maintaining a calibration gas flow rate of 1–100 mL/min (0.00004–0.004 ft^3/min).

6.2.1.7 Rotameter. For monitoring the air flow through the purging system (0–10 L/min)(0–0.4 ft^3/min).

6.2.1.8 Sample Splitters. Two heated flow restrictors (placed inside oven or heated to 120 ±10 °C (248 ±18 °F)). At a purge rate of 6 L/min (0.2 ft^3/min), one will supply a constant flow to the first detector (the rest of the flow will be directed to the second sample splitter). The second splitter will split the analytical flow between the second detector and the flow restrictor. The approximate flow to the FID will be 40 mL/min (0.0014 ft^3/min) and to the ELCD will be 15 mL/min (0.0005 ft^3/min), but the exact flow must be adjusted to be compatible with the individual detector and to meet its linearity requirement. The two sample splitters will be connected to each other by 1/8″ OD (3.175 mm) stainless steel tubing.

6.2.1.9 Flow Restrictor. Stainless steel tubing, 1/8″ OD (3.175 mm), connecting the second sample splitter to the ice bath. Length is determined by the resulting pressure in the purging flask (as measured by the pressure gauge). The resulting pressure from the use of the flow restrictor shall be 6–7 psig.

6.2.1.10 Filter Flask. With one-hole stopper. Used to hold ice bath. Excess purge gas is vented through the flask to prevent condensation in the flowmeter and to trap volatile organic compounds.

6.2.1.11 Four-way Valve. Manually operated, stainless steel. Placed inside oven, used to bypass purging flask.

6.2.1.12 On/Off Valves. Two, stainless steel. One heat resistant up to 130 °C (266 °F) and placed between oven and ELCD. The other a toggle valve used to control purge gas flow.

6.2.1.13 Pressure Gauge. Range 0–40 psi. To monitor pressure in purging flask and coalescing filter.

6.2.1.14 Sample Lines. Teflon, 1/4″ OD (6.35 mm), used inside the oven to carry purge gas to and from purging chamber and to and from coalescing filter to four-way valve. Also used to carry sample from four-way valve to first sample splitter.

6.2.1.15 Detector Tubing. Stainless steel, 1/8″ OD (3.175 mm), heated to 120 ±10 °C (248 ±18 °F) . Used to carry sample gas from each sample splitter to a detector. Each piece of tubing must be wrapped with heat tape and insulating tape in order to insure that no cold spots exist. The tubing leading to the ELCD will also contain a heat-resistant on-off valve (Section 6.2.1.12) which shall also be wrapped with heat-tape and insulation.

6.2.2 Volatile Organic Measurement System. Consisting of an FID to measure the carbon concentration of the sample and an ELCD to measure the chlorine concentration.

6.2.2.1 FID. A heated FID meeting the following specifications is required.

6.2.2.1.1 Linearity. A linear response (±5 percent) over the operating range as demonstrated by the procedures established in section 10.1.1.

6.2.2.1.2 Range. A full scale range of 50 pg carbon/sec to 50 µg carbon/sec. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.2.2.1.3 Data Recording System. A digital integration system compatible with the FID for permanently recording the output of the detector. The recorder shall have the capability to start and stop integration at points selected by the operator or it shall be capable of the ''integration by slices'' technique (this technique involves breaking down the chromatogram into smaller increments, integrating the area under the curve for each portion, subtracting the background for each portion, and then adding all of the areas together for the final area count).

6.2.2.2 ELCD. An ELCD meeting the following specifications is required. 1-propanol must be used as the electrolyte. The electrolyte flow through the conductivity cell shall be 1 to 2 mL/min (0.00004 to 0.00007 ft^3/min).

NOTE: A ¼-in. ID (6.35 mm) quartz reactor tube is strongly recommended to reduce carbon buildup and the resulting detector maintenance.

6.2.2.2.1 Linearity. A linear response (±10 percent) over the response range as demonstrated by the procedures in section 10.1.2.

6.2.2.2.2 Range. A full scale range of 5.0 pg/sec to 500 ng/sec chloride. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.2.2.2.3 Data Recording System. A digital integration system compatible with the output voltage range of the ELCD. The recorder must have the capability to start and stop integration at points selected by the operator or it shall be capable of performing the ''integration by slices'' technique.

7.0 Reagents and Standards

7.1 Sampling.

7.1.1 Polyethylene Glycol (PEG). Ninety-eight percent pure with an average molecular weight of 400. Before using the PEG, remove any organic compounds that might be detected as volatile organics by heating it to 120 °C (248 °F) and purging it with nitrogen at a flow rate of 1 to 2 L/min (0.04 to 0.07 ft^3/min) for 2 hours. The cleaned PEG must be stored under a 1 to 2 L/min (0.04 to 0.07 ft^3/min) nitrogen purge until use. The purge apparatus is shown in Figure 25D–4.

7.2 Analysis.

7.2.1 Sample Separation. The following are required for the sample purging step.

7.2.1.1 PEG. Same as section 7.1.1.

7.2.1.2 Purge Gas. Zero grade nitrogen (N_2), containing less than 1 ppm carbon.

7.2.2 Volatile Organics Measurement. The following are required for measuring the VO concentration.

7.2.2.1 Hydrogen (H_2). Zero grade H_2, 99.999 percent pure.

7.2.2.2 Combustion Gas. Zero grade air or oxygen as required by the FID.

7.2.2.3 Calibration Gas. Pressurized gas cylinder containing 10 percent propane and 1 percent 1,1-dichloroethylene by volume in nitrogen.

7.2.2.4 Water. Deionized distilled water that conforms to American Society for Testing and Materials Specification D 1193–74, Type 3, is required for analysis. At the option of the analyst, the $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations are not expected to be present.

7.2.2.5 1-Propanol. ACS grade or better. Electrolyte Solution. For use in the ELCD.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling.

8.1.1 Sampling Plan Design and Development. Use the procedures in chapter nine of Reference 1 in section 16 as guidance in developing a sampling plan.

8.1.2 Single Phase or Well-mixed Waste.

8.1.2.1 Install a sampling tap to obtain the sample at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to the atmosphere). Assemble the sampling apparatus as shown in Figure 25D–5.

8.1.2.2 Prepare the sampling containers as follows: Pour 30 mL of clean PEG into the container. PEG will reduce but not eliminate the loss of organics during sample collection. Weigh the sample container with the screw cap, the PEG, and any labels to the nearest 0.01 g and record the weight (m_{st}). Store the containers in an ice bath until 1 hour before sampling (PEG will solidify at ice bath temperatures; allow the containers to reach room temperature before sampling).

8.1.2.3 Begin sampling by purging the sample lines and cooling coil with at least four volumes of waste. Collect the purged material in a separate container and dispose of it properly.

8.1.2.4 After purging, stop the sample flow and direct the sampling tube to a preweighed sample container, prepared as described in section 8.1.2.2. Keep the tip of the tube below the surface of the PEG during sampling to minimize contact with the atmosphere. Sample at a flow rate such that the temperature of the waste is less than 10 °C (50 °F). Fill the sample container and immediately cap it (within 5 seconds) so that a minimum headspace exists in the container. Store immediately in a cooler and cover with ice.

8.1.3 Multiple-phase Waste. Collect a 10 g sample of each phase of waste generated using the procedures described in section 8.1.2 or 8.1.5. Each phase of the waste shall be analyzed as a separate sample. Calculate the weighted average VO concentration of the waste using Equation 25D–13 (Section 12.14).

8.1.4 Solid waste. Add approximately 10 g of the solid waste to a container prepared in the manner described in section 8.1.2.2, minimizing headspace. Cap and chill immediately.

8.1.5 Alternative to Tap Installation. If tap installation is impractical or impossible, fill a large, clean, empty container by submerging the container into the waste below the surface of the waste. Immediately fill a container prepared in the manner described in section 8.1.2.2 with approximately 10 g of the waste collected in the large container. Minimize headspace, cap and chill immediately.

8.1.6 Alternative sampling techniques may be used upon the approval of the Administrator.

8.2 Sample Recovery.

8.2.1 Assemble the purging apparatus as shown in Figures 25D–1 and 25D–2. The oven shall be heated to 75 ±2 °C (167 ±3.6 °F). The sampling lines leading from the oven to the detectors shall be heated to 120 ±10 °C (248 ±18 °F) with no cold spots. The flame ionization detector shall be operated with a heated block. Adjust the purging lance so that it reaches the bottom of the chamber.

8.2.2 Remove the sample container from the cooler, and wipe the exterior of the container to remove any extraneous ice, water, or other debris. Reweigh the sample container to the nearest 0.01 g, and record the weight (m_{sf}). Pour the contents of the sample container into the purging flask, rinse the sample container three times with a total of 20 mL of PEG (since the sample container originally held 30 mL of PEG, the total volume of PEG added to the purging flask will be 50 mL), transferring the rinsings to the purging flask after each rinse. Cap purging flask between rinses. The total volume of PEG in the purging flask shall be 50 mL. Add 50 mL of water to the purging flask.

9.0 Quality Control

9.1 Quality Control Samples. If audit samples are not available, prepare and analyze the two types of quality control samples (QCS) listed in Sections 9.1.1 and 9.1.2. Before placing the system in operation, after a shutdown of greater than six months, and after any major modifications, analyze each QCS in triplicate. For each detector, calculate the percent recovery by dividing measured concentration by theoretical concentration and multiplying by 100. Determine the mean percent recovery for each detector for each QCS triplicate analysis. The RSD for any triplicate analysis shall be ≤10 percent. For QCS 1 (methylene chloride), the percent recovery shall be ≥90 percent for carbon as methane, and ≥55 percent for chlorine as chloride. For QCS 2 (1,3-dichloro-2-propanol), the percent recovery shall be ≤15 percent for carbon as methane, and ≤6 percent for chlorine as chloride. If the analytical system does not meet the above-mentioned criteria for both detectors, check the system parameters (temperature, system pressure, purge rate, etc.), correct the problem, and repeat the triplicate analysis of each QCS.

9.1.1 QCS 1, Methylene Chloride. Prepare a stock solution by weighing, to the nearest 0.1 mg, 55 µL of HPLC grade methylene chloride in a tared 5 mL volumetric flask. Record the weight in milligrams, dilute to 5 mL with cleaned PEG, and inject 100 µL of the stock solution into a sample prepared as a water blank (50 mL of cleaned PEG and 60 mL of water in the purging flask). Analyze

the QCS according to the procedures described in sections 10.2 and 10.3, excluding section 10.2.2. To calculate the theoretical carbon concentration (in mg) in QCS 1, multiply mg of methylene chloride in the stock solution by 3.777×10^{-3}. To calculate the theoretical chlorine concentration (in mg) in QCS 1, multiply mg of methylene chloride in the stock solution by 1.670×10^{-2}.

9.1.2 QCS 2, 1,3-dichloro-2-propanol. Prepare a stock solution by weighing, to the nearest 0.1 mg, 60 μL of high purity grade 1,3-dichloro-2-propanol in a tared 5 mL volumetric flask. Record the weight in milligrams, dilute to 5 mL with cleaned PEG, and inject 100 μL of the stock solution into a sample prepared as a water blank (50 mL of cleaned PEG and 60 mL of water in the purging flask). Analyze the QCS according to the procedures described in sections 10.2 and 10.3, excluding section 10.2.2. To calculate the theoretical carbon concentration (in mg) in QCS 2, multiply mg of 1,3-dichloro-2-propanol in the stock solution by 7.461×10^{-3}. To calculate the theoretical chlorine concentration (in mg) in QCS 2, multiply mg of 1,3-dichloro-2-propanol in the stock solution by 1.099×10^{-2}.

9.1.3 Routine QCS Analysis. For each set of compliance samples (in this context, set is per facility, per compliance test), analyze one QCS 1 and one QCS 2 sample. The percent recovery for each sample for each detector shall be ±13 percent of the mean recovery established for the most recent set of QCS triplicate analysis (Section 9.4). If the sample does not meet this criteria, check the system components and analyze another QCS 1 and 2 until a single set of QCS meet the ±13 percent criteria.

10.0 Calibration and Standardization

10.1 Initial Performance Check of Purging System. Before placing the system in operation, after a shutdown of greater than six months, after any major modifications, and at least once per month during continuous operation, conduct the linearity checks described in sections 10.1.1 and 10.1.2. Install calibration gas at the three-way calibration gas valve. See Figure 25D–1.

10.1.1 Linearity Check Procedure. Using the calibration standard described in section 7.2.2.3 and by varying the injection time, it is possible to calibrate at multiple concentration levels. Use Equation 25D–3 to calculate three sets of calibration gas flow rates and run times needed to introduce a total mass of carbon, as methane, (m_c) of 1, 5, and 10 mg into the system (low, medium and high FID calibration, respectively). Use Equation 25D–4 to calculate three sets of calibration gas flow rates and run times needed to introduce a total chloride mass (m_{ch}) of 1, 5, and 10 mg into the system (low, medium and high ELCD calibration, respectively). With the system operating in standby mode, allow the FID and the ELCD to establish a stable baseline. Set the secondary pressure regulator of the calibration gas cylinder to the same pressure as the purge gas cylinder and set the proper flow rate with the calibration flow controller (see Figure 25D–1). The calibration gas flow rate can be measured with a flowmeter attached to the vent position of the calibration gas valve. Set the four-way bypass valve to standby position so that the calibration gas flows through the coalescing filter only. Inject the calibration gas by turning the calibration gas valve from vent position to inject position. Continue the calibration gas flow for the appropriate period of time before switching the calibration valve to vent position. Continue recording the response of the FID and the ELCD for 5 min after switching off calibration gas flow. Make triplicate injections of all six levels of calibration.

10.1.2 Linearity Criteria. Calculate the average response factor (Equations 25D–5 and 25D–6) and the relative standard deviation (RSD) (Equation 25D–10) at each level of the calibration curve for both detectors. Calculate the overall mean of the three response factor averages for each detector. The FID linearity is acceptable if each response factor is within 5 percent of the overall mean and if the RSD for each set of triplicate injections is less than 5 percent. The ELCD linearity is acceptable if each response factor is within 10 percent of the overall mean and if the RSD for each set of triplicate injections is less than 10 percent. Record the overall mean value of the response factors for the FID and the ELCD. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat sections 10.1.1 and 10.1.2.

10.2 Daily Calibrations.

10.2.1 Daily Linearity Check. Follow the procedures outlined in section 10.1.1 to analyze the medium level calibration for both the FID and the ELCD in duplicate at the start of the day. Calculate the response factors and the RSDs for each detector. For the FID, the calibration is acceptable if the average response factor is within 5 percent of the overall mean response factor (Section 10.1.2) and if the RSD for the duplicate injection is less than 5 percent. For the ELCD, the calibration is acceptable if the average response factor is within 10 percent of the overall mean response factor (Section 10.1.2) and if the RSD for the duplicate injection is less than 10 percent. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat sections 10.1.1 and 10.1.2.

10.2.2 Calibration Range Check.

10.2.2.1 If the waste concentration for either detector falls below the range of calibration for that detector, use the procedure outlined in section 10.1.1 to choose two calibration points that bracket the new target

concentration. Analyze each of these points in triplicate (as outlined in section 10.1.1) and use the criteria in section 10.1.2 to determine the linearity of the detector in this ''mini-calibration'' range.

10.2.2.2 After the initial linearity check of the mini-calibration curve, it is only necessary to test one of the points in duplicate for the daily calibration check (in addition to the points specified in section 10.2.1). The average daily mini-calibration point should fit the linearity criteria specified in section 10.2.1. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat the calibration procedure mentioned in the first paragraph of section 10.2.2. A mini-calibration curve for waste concentrations above the calibration curve for either detector is optional.

10.3 Analytical Balance. Calibrate against standard weights.

11.0 Analysis

11.1 Sample Analysis.

11.1.1 Turn on the constant temperature chamber and allow the temperature to equilibrate at 75 ±2 °C (167 ±3.6 °F). Turn the four-way valve so that the purge gas bypasses the purging flask, the purge gas flowing through the coalescing filter and to the detectors (standby mode). Turn on the purge gas. Allow both the FID and the ELCD to warm up until a stable baseline is achieved on each detector. Pack the filter flask with ice. Replace ice after each run and dispose of the waste water properly. When the temperature of the oven reaches 75 ±2 °C (167 ±3.6 °F), start both integrators and record baseline. After 1 min, turn the four-way valve so that the purge gas flows through the purging flask, to the coalescing filter and to the sample splitters (purge mode). Continue recording the response of the FID and the ELCD. Monitor the readings of the pressure gauge and the rotameter. If the readings fall below established setpoints, stop the purging, determine the source of the leak, and resolve the problem before resuming. Leaks detected during a sampling period invalidate that sample.

11.1.2 As the purging continues, monitor the output of the detectors to make certain that the analysis is proceeding correctly and that the results are being properly recorded. Every 10 minutes read and record the purge flow rate, the pressure and the chamber temperature. Continue the purging for 30 minutes.

11.1.3 For each detector output, integrate over the entire area of the peak starting at 1 minute and continuing until the end of the run. Subtract the established baseline area from the peak area. Record the corrected area of the peak. See Figure 25D–6 for an example integration.

11.2 Water Blank. A water blank shall be analyzed for each batch of cleaned PEG prepared. Transfer about 60 mL of water into the purging flask. Add 50 mL of the cleaned PEG to the purging flask. Treat the blank as described in sections 8.2 and 8.3, excluding section 8.2.2. Calculate the concentration of carbon and chlorine in the blank sample (assume 10 g of waste as the mass). A VO concentration equivalent to ≤10 percent of the applicable standard may be subtracted from the measured VO concentration of the waste samples. Include all blank results and documentation in the test report.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

A_b = Area under the water blank response curve, counts.
A_c = Area under the calibration response curve, counts.
A_s = Area under the sample response curve, counts.
C = Concentration of volatile organics in the sample, ppmw.
C_c = Concentration of carbon, as methane, in the calibration gas, mg/L.
C_{ch} = Concentration of chloride in the calibration gas, mg/L.
C_j = VO concentration of phase j, ppmw.
DR_t = Average daily response factor of the FID, mg CH_4/counts.
Dr_{th} = Average daily response factor of the ELCD, mg Cl^-/counts.
F_j = Weight fraction of phase j present in the waste.
m_c = Mass of carbon, as methane, in a calibration run, mg.
m_{ch} = Mass of chloride in a calibration run, mg.
m_s = Mass of the waste sample, g.
m_{sc} = Mass of carbon, as methane, in the sample, mg.
m_{sf} = Mass of sample container and waste sample, g.
m_{sh} = Mass of chloride in the sample, mg.
m_{st} = Mass of sample container prior to sampling, g.
m_{VO} = Mass of volatile organics in the sample, mg.
n = Total number of phases present in the waste.
P_p = Percent propane in calibration gas (L/L).
P_{vc} = Percent 1,1-dichloroethylene in calibration gas (L/L).
Q_c = Flow rate of calibration gas, L/min.
t_c = Length of time standard gas is delivered to the analyzer, min.
W = Weighted average VO concentration, ppmw.

12.2 Concentration of Carbon, as Methane, in the Calibration Gas.

$$C_c = \left(19.681 \times P_p\right) + \left(13.121 \times P_{vc}\right) \qquad \text{Eq. 25D-1}$$

12.3 Concentration of Chloride in the Calibration Gas.

$$C_{ch} = 28.998 \times P_{vc} \qquad \text{Eq. 25D-2}$$

12.4 Mass of Carbon, as Methane, in a Calibration Run.

$$M_c = C_c \times Q_c \times t_c \qquad \text{Eq. 25D-3}$$

12.5 Mass of Chloride in a Calibration Run.

$$m_{ch} = C_{ch} \times Q_c \times t_c \qquad \text{Eq. 25D-4}$$

12.6 FID Response Factor, mg/counts.

$$DR_t = \frac{m_c}{A_c} \qquad \text{Eq. 25D-5}$$

12.7 ELCD Response Factor, mg/counts.

$$DR_{th} = \frac{m_{ch}}{A_c} \qquad \text{Eq. 25D-6}$$

12.8 Mass of Carbon in the Sample.

$$m_{sc} = DR_t\left(A_s - A_b\right) \qquad \text{Eq. 25D-7}$$

12.9 Mass of Chloride in the Sample.

$$m_{sh} = DR_{th}\left(A_s - A_b\right) \qquad \text{Eq. 25D-8}$$

12.10 Mass of Volatile Organics in the Sample.

$$m_{vo} = m_{sc} + m_{sh} \qquad \text{Eq. 25D-9}$$

12.11 Relative Standard Deviation.

$$RSD = \frac{100}{\bar{x}} \sqrt{\frac{\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2}{n-1}} \qquad \text{Eq. 25D-10}$$

12.12 Mass of Sample.

$$m_s = m_{sf} - m_{st} \qquad \text{Eq. 25D-11}$$

12.13 Concentration of Volatile Organics in Waste.

$$C = \frac{\left(m_{vo} \times 1000\right)}{m_s} \qquad \text{Eq. 25D-12}$$

12.14 Weighted Average VO Concentration of Multi-phase Waste.

$$W = \sum_{j=1}^{n} F_j x \overline{C}_j \qquad \text{Eq. 25D-13}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. ''Test Methods for Evaluating Solid Waste, Physical/Chemistry Methods'', U.S. Environmental Protection Agency. Publication SW–846, 3rd Edition, November 1986 as amended by Update I, November 1990.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

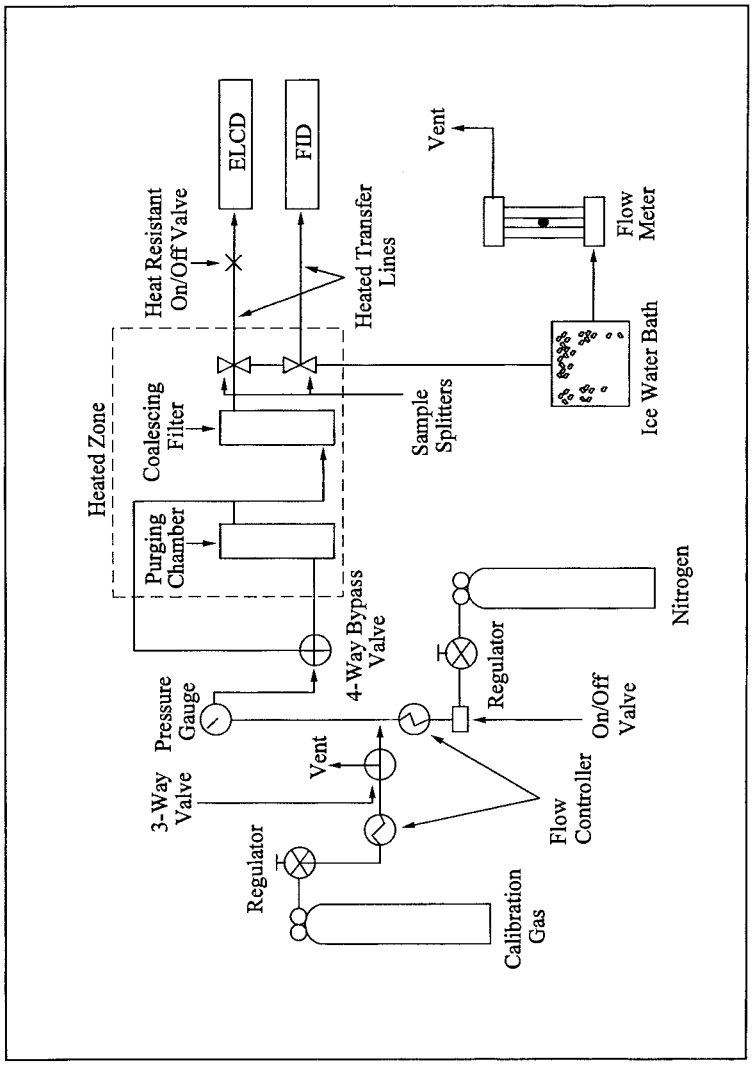


Figure 25D-1. Schematic of Purging Apparatus.

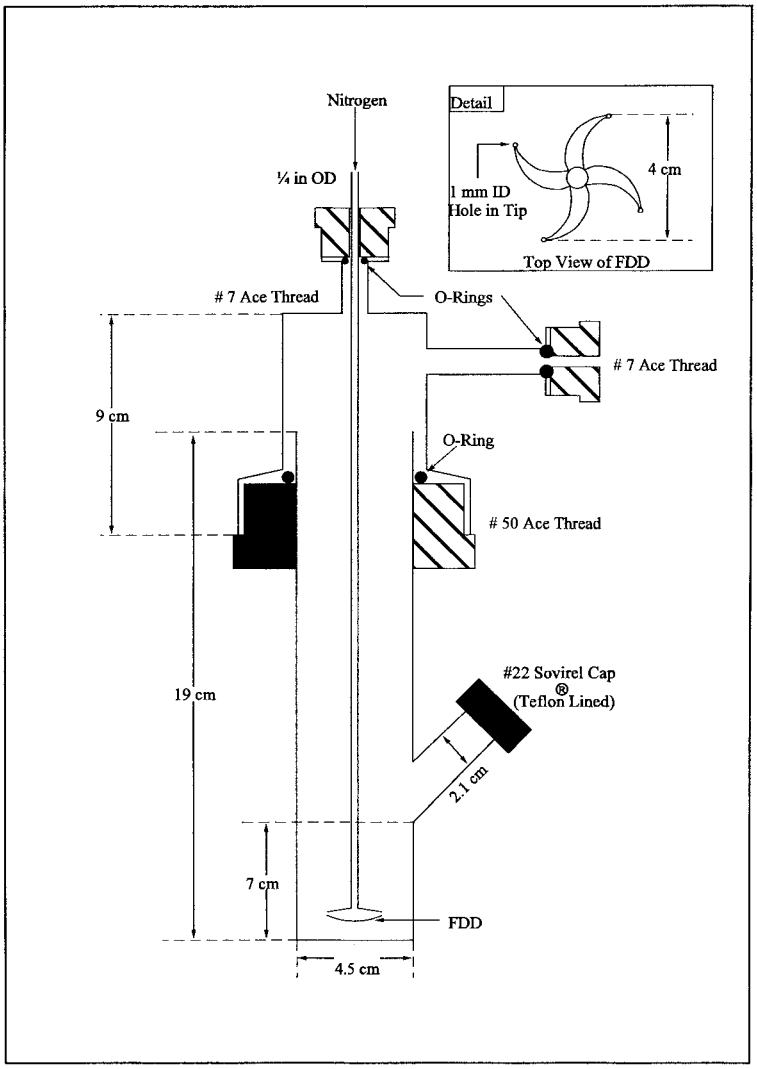
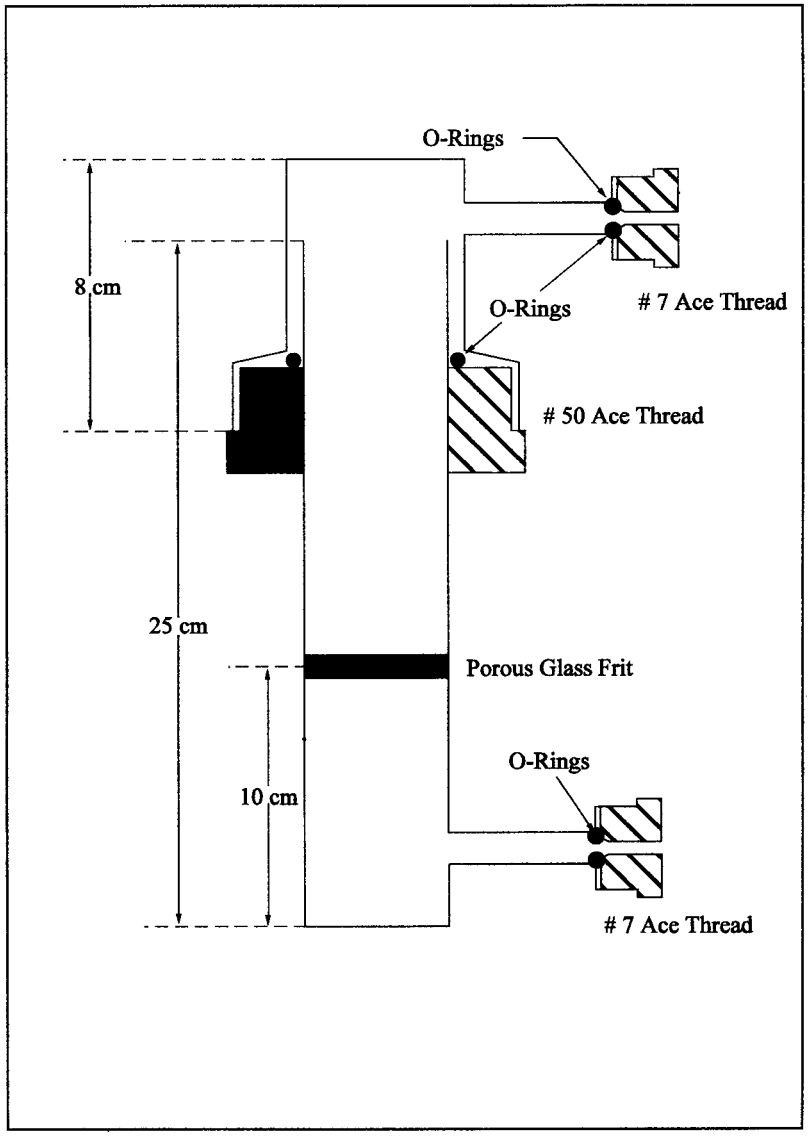


Figure 25D-2. Purging Lance.


O-Rings
8 cm
O-Rings
7 Ace Thread
50 Ace Thread
25 cm
Porous Glass Frit
O-Rings
10 cm
7 Ace Thread

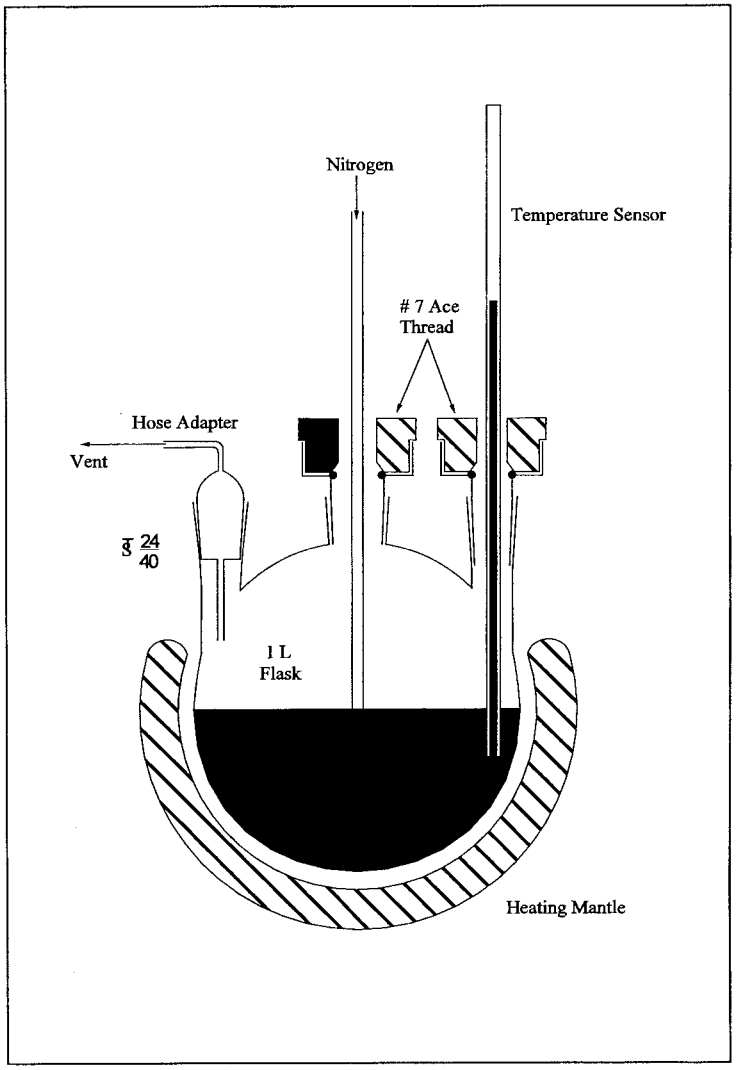


Figure 25D-4. Schematic of PEG Cleaning System.

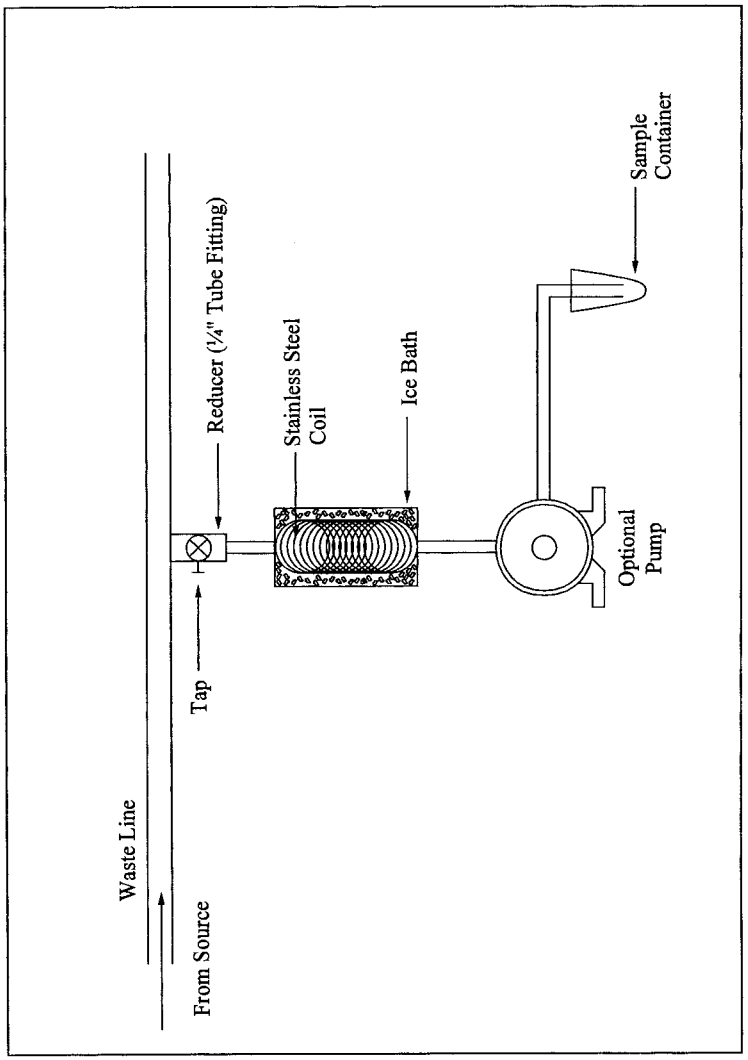


Figure 25D-5. Schematic of Sampling Apparatus.

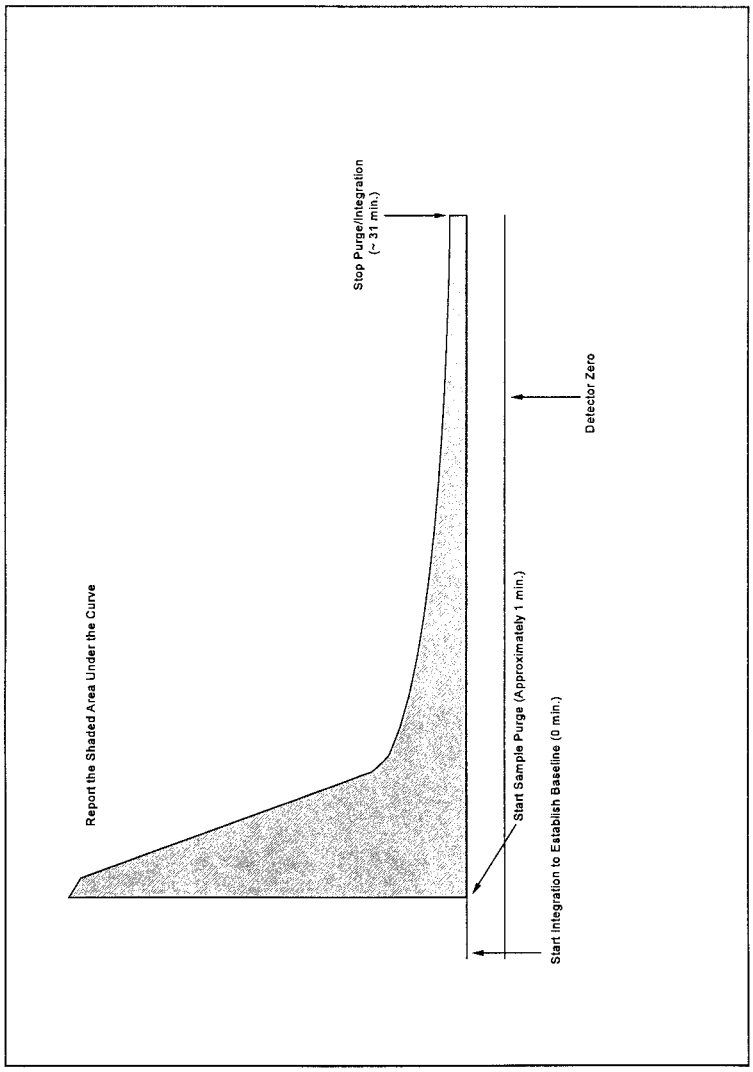


Figure 25D-6. Example Integration of Either Detector.

METHOD 25E—DETERMINATION OF VAPOR PHASE ORGANIC CONCENTRATION IN WASTE SAMPLES

NOTE: Performance of this method should not be attempted by persons unfamiliar with the operation of a flame ionization detector (FID) nor by those who are unfamiliar with source sampling because knowledge beyond the scope of this presentation is required. This method is not inclusive with respect to specifications (*e.g.*, reagents and standards) and calibration procedures. Some material is incorporated by reference from other methods. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 106, part 61, Appendix B, and Method 18, part 60, Appendix A.

1.0 Scope and Application

1.1 Applicability. This method is applicable for determining the vapor pressure of waste cited by an applicable regulation.

1.2 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 The headspace vapor of the sample is analyzed for carbon content by a headspace analyzer, which uses an FID.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 The analyst shall select the operating parameters best suited to the requirements for a particular analysis. The analyst shall produce confirming data through an adequate supplemental analytical technique and have the data available for review by the Administrator.

5.0 Safety [Reserved]

6.0 Equipment and Supplies

6.1 Sampling. The following equipment is required:

6.1.1 Sample Containers. Vials, glass, with butyl rubber septa, Perkin-Elmer Corporation Numbers 0105–0129 (glass vials), B001–0728 (gray butyl rubber septum, plug style), 0105–0131 (butyl rubber septa), or equivalent. The seal must be made from butyl rubber. Silicone rubber seals are not acceptable.

6.1.2 Vial Sealer. Perkin-Elmer Number 105–0106, or equivalent.

6.1.3 Gas-Tight Syringe. Perkin-Elmer Number 00230117, or equivalent.

6.1.4 The following equipment is required for sampling.

6.1.4.1 Tap.

6.1.4.2 Tubing. Teflon, 0.25-in. ID.

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1.4.3 Cooling Coil. Stainless steel (304), 0.25 in.-ID, equipped with a thermocouple at the coil outlet.

6.2 Analysis. The following equipment is required.

6.2.1 Balanced Pressure Headspace Sampler. Perkin-Elmer HS–6, HS–100, or equivalent, equipped with a glass bead column instead of a chromatographic column.

6.2.2 FID. An FID meeting the following specifications is required.

6.2.2.1 Linearity. A linear response (±5 percent) over the operating range as demonstrated by the procedures established in section 10.2.

6.2.2.2 Range. A full scale range of 1 to 10,000 parts per million (ppm) propane (C_3H_8). Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.2.3 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the output of the detector.

6.2.4 Temperature Sensor. Capable of reading temperatures in the range of 30 to 60 °C (86 to 140 °F) with an accuracy of ±0.1 °C (±0.2 °F).

7.0 Reagents and Standards

7.1 Analysis. The following items are required for analysis.

7.1.1 Hydrogen (H_2). Zero grade hydrogen, as required by the FID.

7.1.2 Carrier Gas. Zero grade nitrogen, containing less than 1 ppm carbon (C) and less than 1 ppm carbon dioxide.

7.1.3 Combustion Gas. Zero grade air or oxygen as required by the FID.

7.2 Calibration and Linearity Check.

7.2.1 Stock Cylinder Gas Standard. 100 percent propane. The manufacturer shall: (a) Certify the gas composition to be accurate to ±3 percent or better (see section 7.2.1.1); (b) recommend a maximum shelf life over which the gas concentration does not change by greater than ±5 percent from the certified value; and (c) affix the date of gas cylinder preparation, certified propane concentration, and recommended maximum shelf life to the cylinder before shipment to the buyer.

7.2.1.1 Cylinder Standards Certification. The manufacturer shall certify the concentration of the calibration gas in the cylinder by (a) directly analyzing the cylinder and (b) calibrating his analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use, as a minimum, a three-point calibration curve.

7.2.1.2 Verification of Manufacturer's Calibration Standards. Before using, the manufacturer shall verify each calibration standard by (a) comparing it to gas mixtures prepared in accordance with the procedure described in section 7.1 of Method 106 of Part 61, Appendix B, or by (b) calibrating it against Standard Reference Materials (SRM's) prepared by the National Bureau of Standards, if such SRM's are available. The agreement between the initially determined concentration value and the verification concentration value must be within ±5 percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

8.0 Sampling Collection, Preservation, Storage, and Transport

8.1 Install a sampling tap to obtain a sample at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to

the atmosphere). Assemble the sampling apparatus as shown in Figure 25E–1.

8.2 Begin sampling by purging the sample lines and cooling coil with at least four volumes of waste. Collect the purged material in a separate container and dispose of it properly.

8.3 After purging, stop the sample flow and transfer the Teflon sampling tube to a sample container. Sample at a flow rate such that the temperature of the waste is <10 °C (<50 °F). Fill the sample container halfway (±5 percent) and cap it within 5 seconds. Store immediately in a cooler and cover with ice.

8.4 Alternative sampling techniques may be used upon the approval of the Administrator.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
10.2, 10.3	FID calibration and response check	Ensure precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Use the procedures in sections 10.2 to calibrate the headspace analyzer and FID and check for linearity before the system is first placed in operation, after any shutdown longer than 6 months, and after any modification of the system.

10.2 Calibration and Linearity. Use the procedures in section 10 of Method 18 of Part 60, Appendix A, to prepare the standards and calibrate the flowmeters, using propane as the standard gas. Fill the calibration standard vials halfway (±5 percent) with deionized water. Purge and fill the airspace with calibration standard. Prepare a minimum of three concentrations of calibration standards in triplicate at concentrations that will bracket the applicable cutoff. For a cutoff of 5.2 kPa (0.75 psi), prepare nominal concentrations of 30,000, 50,000, and 70,000 ppm as propane. For a cutoff of 27.6 kPa (4.0 psi), prepare nominal concentrations of 200,000, 300,000, and 400,000 ppm as propane.

10.2.1 Use the procedures in section 11.3 to measure the FID response of each standard. Use a linear regression analysis to calculate the values for the slope (k) and the y-intercept (b). Use the procedures in sections 12.3 and 12.2 to test the calibration and the linearity.

10.3 Daily FID Calibration Check. Check the calibration at the beginning and at the end of the daily runs by using the following procedures. Prepare 2 calibration standards at the nominal cutoff concentration using the procedures in section 10.2. Place one at the beginning and one at the end of the daily run. Measure the FID response of the daily calibration standard and use the values for k and b from the most recent calibration to calculate the concentration of the daily standard. Use an equation similar to 25E–2 to calculate the percent difference between the daily standard and C_s. If the difference is within 5 percent, then the previous values for k and b can be used. Otherwise, use the procedures in section 10.2 to recalibrate the FID.

11.0 Analytical Procedures

11.1 Allow one hour for the headspace vials to equilibrate at the temperature specified in the regulation. Allow the FID to warm up until a stable baseline is achieved on the detector.

11.2 Check the calibration of the FID daily using the procedures in section 10.3.

11.3 Follow the manufacturer's recommended procedures for the normal operation of the headspace sampler and FID.

11.4 Use the procedures in sections 12.4 and 12.5 to calculate the vapor phase organic vapor pressure in the samples.

11.5 Monitor the output of the detector to make certain that the results are being properly recorded.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

A = Measurement of the area under the response curve, counts.
b = y-intercept of the linear regression line.
C_a = Measured vapor phase organic concentration of sample, ppm as propane.
C_{ma} = Average measured vapor phase organic concentration of standard, ppm as propane.
C_m = Measured vapor phase organic concentration of standard, ppm as propane.
C_s = Calculated standard concentration, ppm as propane.
k = Slope of the linear regression line.
P_{bar} = Atmospheric pressure at analysis conditions, mm Hg (in. Hg).
P* = Organic vapor pressure in the sample, kPa (psi).
PD = Percent difference between the average measured vapor phase organic concentration (C_m) and the calculated standard concentration (C_s).
RSD = Relative standard deviation.
$\beta = 1.333 \times 10^{-7}$ kPa/[(mm Hg)(ppm)], $(4.91 \times 10^{-7}$ psi/[(in. Hg)(ppm)])

12.2 Linearity. Use the following equation to calculate the measured standard concentration for each standard vial.

$$C_m = kA + b \qquad \text{Eq. 25E-1}$$

12.2.1 Calculate the average measured standard concentration (C_{ma}) for each set of triplicate standards and use the following equation to calculate PD between C_{ma} and C_s. The instrument linearity is acceptable if the PD is within five for each standard.

$$PD = \frac{C_s - C_{ma}}{C_s} \times 100 \qquad \text{Eq. 25E-2}$$

12.3. Relative Standard Deviation (RSD). Use the following equation to calculate the RSD for each triplicate set of standards.

$$RSD = \frac{100}{C_{ma}} \sqrt{\frac{\sum (C_m - C_{ma})^2}{2}} \qquad \text{Eq. 25E-3}$$

The calibration is acceptable if the RSD is within five for each standard concentration.

12.4 Concentration of organics in the headspace. Use the following equation to calculate the concentration of vapor phase organics in each sample.

$$C_a = kA + b \qquad \text{Eq. 25E-4}$$

12.5 Vapor Pressure of Organics in the Headspace Sample. Use the following equation to calculate the vapor pressure of organics in the sample.

$$P^* = \beta P_{bar} C_a \qquad \text{Eq. 25E-5}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, Albert E., Samuel Witz, and Robert D. MacPhee. ''Determination of Solvent Vapor Concentrations by Total Combustion Analysis: a Comparison of Infared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, Massachusetts.

2. Salo, Albert E., William L. Oaks, and Robert D. MacPhee. ''Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, Colorado. June 9–13, 1974.) p. 25.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

12.2 Linearity. Use the following equation to calculate the measured standard concentration for each standard vial.

$$C_m = kA + b \qquad \text{Eq. 25E-1}$$

12.2.1 Calculate the average measured standard concentration (C_{ma}) for each set of triplicate standards and use the following equation to calculate PD between C_{ma} and C_s. The instrument linearity is acceptable if the PD is within five for each standard.

$$PD = \frac{C_s - C_{ma}}{C_s} \times 100 \qquad \text{Eq. 25E-2}$$

12.3. Relative Standard Deviation (RSD). Use the following equation to calculate the RSD for each triplicate set of standards.

$$RSD = \frac{100}{C_{ma}} \sqrt{\frac{\sum (C_m - C_{ma})^2}{2}} \qquad \text{Eq. 25E-3}$$

The calibration is acceptable if the RSD is within five for each standard concentration.

12.4 Concentration of organics in the headspace. Use the following equation to calculate the concentration of vapor phase organics in each sample.

$$C_a = kA + b \qquad \text{Eq. 25E-4}$$

12.5 Vapor Pressure of Organics in the Headspace Sample. Use the following equation to calculate the vapor pressure of organics in the sample.

$$P^* = \beta P_{bar} C_a \qquad \text{Eq. 25E-5}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, Albert E., Samuel Witz, and Robert D. MacPhee. ''Determination of Solvent Vapor Concentrations by Total Combustion Analysis: a Comparison of Infared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, Massachusetts.

2. Salo, Albert E., William L. Oaks, and Robert D. MacPhee. ''Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, Colorado. June 9–13, 1974.) p. 25.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

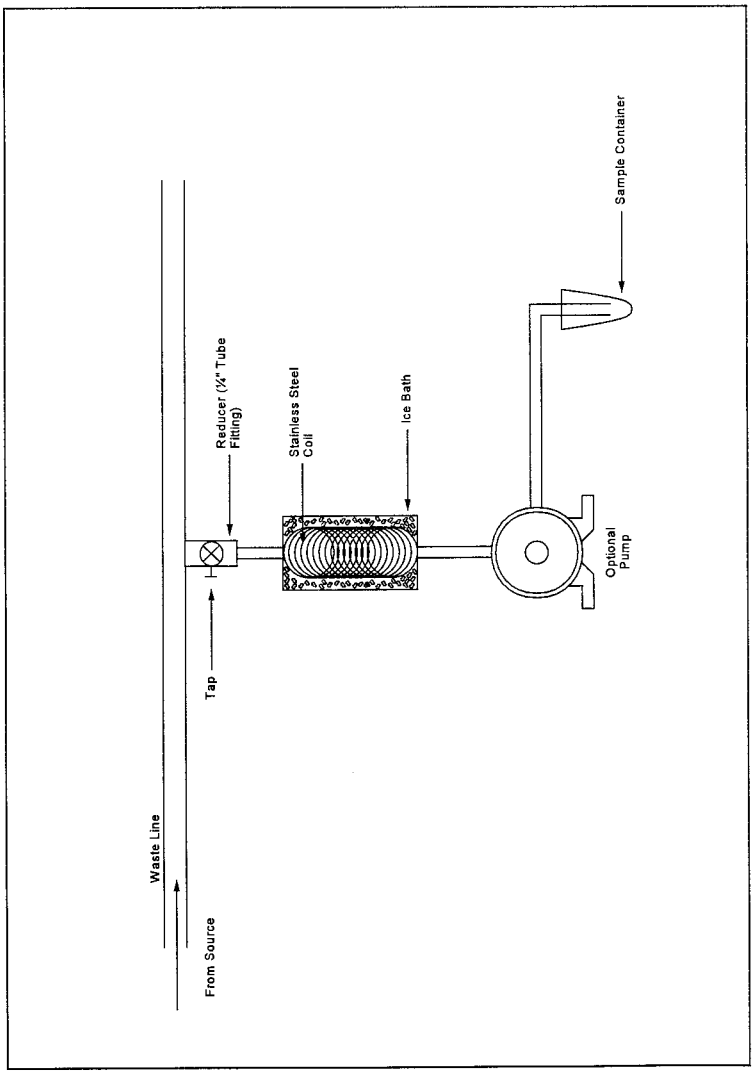


Figure 25E-1. Schematic of Sampling Apparatus

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–7 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

APPENDIX A–8 TO PART 60—TEST METHODS 26 THROUGH 30B

Method 26—Determination of Hydrogen Chloride Emissions From Stationary Sources

Method 26A—Determination of hydrogen halide and halogen emissions from stationary sources—isokinetic method

Method 27—Determination of vapor tightness of gasoline delivery tank using pressure-vacuum test
Method 28—Certification and auditing of wood heaters
Method 28A—Measurement of air to fuel ratio and minimum achievable burn rates for wood-fired appliances
Method 29—Determination of metals emissions from stationary sources

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

Method 26—Determination of Hydrogen Halide and Halogen Emissions From Stationary Sources Non-Isokinetic Method

1.0 Scope and Application

1.1 Analytes.

Analytes	CAS No.
Hydrogen Chloride (HCl)	7647–01–0
Hydrogen Bromide (HBr)	10035–10–6
Hydrogen Fluoride (HF)	7664–39–3
Chlorine (Cl_2)	7882–50–5
Bromine (Br_2)	7726–95–6

1.2 Applicability. This method is applicable for determining emissions of hydrogen halides (HX) (HCl, HBr, and HF) and halogens (X_2) (Cl_2 and Br_2) from stationary sources when specified by the applicable subpart. Sources, such as those controlled by wet scrubbers, that emit acid particulate matter must be sampled using Method 26A.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 An integrated sample is extracted from the source and passed through a prepurged heated probe and filter into dilute sulfuric acid and dilute sodium hydroxide solutions which collect the gaseous hydrogen halides and halogens, respectively. The filter collects particulate matter including halide salts but is not routinely recovered and analyzed. The hydrogen halides are solubilized in the acidic solution and form chloride (Cl^-), bromide (Br^-), and fluoride (F^-) ions. The halogens have a very low solubility in the acidic solution and pass through to the alkaline solution where they are hydrolyzed to form a proton (H^+), the halide ion, and the hypohalous acid (HClO or HBrO). Sodium thiosulfate is added in excess to the alkaline solution to assure reaction with the hypohalous acid to form a second halide ion such that 2 halide ions are formed for each molecule of halogen gas. The halide ions in the separate solutions are measured by ion chromatography (IC).

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Volatile materials, such as chlorine dioxide (ClO_2) and ammonium chloride (NH_4Cl), which produce halide ions upon dissolution during sampling are potential interferents. Interferents for the halide measurements are the halogen gases which disproportionate to a hydrogen halide and a hydrohalous acid upon dissolution in water. However, the use of acidic rather than neutral or basic solutions for collection of the hydrogen halides greatly reduces the dissolution of any halogens passing through this solution.

4.2 The simultaneous presence of HBr and CL_2 may cause a positive bias in the HCL result with a corresponding negative bias in the Cl_2 result as well as affecting the HBr/Br_2 split.

4.3 High concentrations of nitrogen oxides (NO_X) may produce sufficient nitrate (NO_3^- to interfere with measurements of very low Br^- levels.

4.4 A glass wool plug should *not* be used to remove particulate matter since a negative bias in the data could result.

4.5 There is anecdotal evidence that HF may be outgassed from new teflon components. If HF is a target analyte, then preconditioning of new teflon components, by heating should be considered.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations before performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.2 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1 Sampling. The sampling train is shown in Figure 26–1, and component parts are discussed below.

6.1.1 Probe. Borosilicate glass, approximately 3/8-in. (9-mm) I.D. with a heating system capable of maintaining a probe gas temperature during sampling between 120 and 134 °C (248 and 273 °F) to prevent moisture condensation; or Teflon where stack probes are below 210 °C. If HF is a target analyte, then preconditioning of new teflon components by heating should be considered to prevent potential HF outgassing. A Teflon-glass filter in a mat configuration should be installed to remove particulate matter from the gas stream.

6.1.2 Three-way Stopcock. A borosilicate-glass three-way stopcock with a heating system to prevent moisture condensation. The heated stopcock should connect to the outlet of the heated filter and the inlet of the first impinger. The heating system should be capable of preventing condensation up to the inlet of the first impinger. Silicone grease may be used, if necessary, to prevent leakage.

6.1.3 Impingers. Four 30-ml midget impingers with leak-free glass connectors. Silicone grease may be used, if necessary, to prevent leakage. For sampling at high moisture sources or for sampling times greater than one hour, a midget impinger with a shortened stem (such that the gas sample does not bubble through the collected condensate) should be used in front of the first impinger.

6.1.4 Drying Tube or Impinger. Tube or impinger, of Mae West design, filled with 6- to 16-mesh indicating type silica gel, or equivalent, to dry the gas sample and to protect the dry gas meter and pump. If the silica gel has been used previously, dry at 175 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used.

6.1.5 Heating System. Any heating system capable of maintaining a temperature around the probe and filter holder between 120 and 134 °C (248 and 273 °F) during sampling, or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application.

6.1.6 Filter Holder and Support. The filter holder shall be made of Teflon or quartz. The filter support shall be made of Teflon. All Teflon filter holders and supports are available from Savillex Corp., 5325 Hwy 101, Minnetonka, MN 55345.

6.1.7 Sample Line. Leak-free, with compatible fittings to connect the last impinger to the needle valve.

6.1.8 Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of the selected flow rate of 2 liters/min (0.07 ft^3/min).

6.1.9 Purge Pump, Purge Line, Drying Tube, Needle Valve, and Rate Meter. Pump capable of purging the sampling probe at 2 liters/min, with drying tube, filled with silica gel or equivalent, to protect pump, and a rate meter capable of measuring 0 to 5 liters/min (0.2 ft^3/min).

6.1.10 Stopcock Grease, Valve, Pump, Volume Meter, Barometer, and Vacuum Gauge. Same as in Method 6, sections 6.1.1.4, 6.1.1.7, 6.1.1.8, 6.1.1.10, 6.1.2, and 6.1.3.

6.1.11 Temperature Measuring Devices. Temperature sensors to monitor the temperature of the probe and to monitor the temperature of the sampling system from the outlet of the probe to the inlet of the first impinger.

6.1.12 Ice Water Bath. To minimize loss of absorbing solution.

6.2 Sample Recovery.

6.2.1 Wash Bottles. Polyethylene or glass, 500-ml or larger, two.

6.2.2 Storage Bottles. 100- or 250-ml, high-density polyethylene bottles with Teflon screw cap liners to store impinger samples.

6.3 Sample Preparation and Analysis. The materials required for volumetric dilution and chromatographic analysis of samples are described below.

6.3.1 Volumetric Flasks. Class A, 100-ml size.

6.3.2 Volumetric Pipets. Class A, assortment. To dilute samples to the calibration range of the ion chromatograph.

6.3.3 Ion Chromatograph (IC). Suppressed or non-suppressed, with a conductivity detector and electronic integrator operating in the peak area mode. Other detectors, strip chart recorders, and peak height measurements may be used.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society (ACS reagent grade). When such specifications are not available, the best available grade shall be used.

7.1 Sampling.

7.1.1 Filter. A 25-mm (1 in) (or other size) Teflon glass mat, Pallflex TX40HI75 (Pallflex Inc., 125 Kennedy Drive, Putnam, CT 06260). This filter is in a mat configuration to prevent fine particulate matter from entering the sampling train. Its composition is 75% Teflon/25% borosilicate glass. Other filters may be used, but they must be in a mat (as opposed to a laminate) configuration and contain at least 75% Teflon. For practical rather than scientific reasons, when the stack gas temperature exceeds 210 °C (410 °F) and the HCl concentration is greater than 20 ppm, a quartz-fiber filter may be used since Teflon becomes unstable above this temperature.

7.1.2 Water. Deionized, distilled water that conforms to American Society of Testing and Materials (ASTM) Specification D 1193–77 or 91, Type 3 (incorporated by reference—see §60.17).

7.1.3 Acidic Absorbing Solution, 0.1 N Sulfuric Acid (H_2SO_4). To prepare 100 ml of the absorbing solution for the front impinger pair, slowly add 0.28 ml of concentrated H_2SO_4 to about 90 ml of water while stirring, and adjust the final volume to 100 ml using additional water. Shake well to mix the solution.

7.1.4 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 180 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants may be used, subject to the approval of the Administrator.

7.1.5 Alkaline Adsorbing Solution, 0.1 N Sodium Hydroxide (NaOH). To prepare 100 ml of the scrubber solution for the third and fourth impinger, dissolve 0.40 g of solid NaOH in about 90 ml of water, and adjust the final

solution volume to 100 ml using additional water. Shake well to mix the solution.

7.1.6 Sodium Thiosulfate ($Na_2S_2O_3$ 5 H_2O)

7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in section 7.1.2.

7.2.2 Absorbing Solution Blanks. A separate blank solution of each absorbing reagent should be prepared for analysis with the field samples. Dilute 30 ml of each absorbing solution to approximately the same final volume as the field samples using the blank sample of rinse water.

7.2.3 Halide Salt Stock Standard Solutions. Prepare concentrated stock solutions from reagent grade sodium chloride (NaCl), sodium bromide (NaBr), and sodium fluoride (NaF). Each must be dried at 110 °C (230 °F) for two or more hours and then cooled to room temperature in a desiccator immediately before weighing. Accurately weigh 1.6 to 1.7 g of the dried NaCl to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact Cl^- concentration using Equation 26–1 in section 12.2. In a similar manner, accurately weigh and solubilize 1.2 to 1.3 g of dried NaBr and 2.2 to 2.3 g of NaF to make 1-liter solutions. Use Equations 26–2 and 26–3 in section 12.2, to calculate the Br^- and F^- concentrations. Alternately, solutions containing a nominal certified concentration of 1000 mg/l NaCl are commercially available as convenient stock solutions from which standards can be made by appropriate volumetric dilution. Refrigerate the stock standard solutions and store no longer than one month.

7.2.4 Chromatographic Eluent. Effective eluents for nonsuppressed IC using a resin-or silica-based weak ion exchange column are a 4 mM potassium hydrogen phthalate solution, adjusted to pH 4.0 using a saturated sodium borate solution, and a 4 mM 4-hydroxy benzoate solution, adjusted to pH 8.6 using 1 N NaOH. An effective eluent for suppressed ion chromatography is a solution containing 3 mM sodium bicarbonate and 2.4 mM sodium carbonate. Other dilute solutions buffered to a similar pH and containing no interfering ions may be used. When using suppressed ion chromatography, if the ''water dip'' resulting from sample injection interferes with the chloride peak, use a 2 mM NaOH/2.4 mM sodium bicarbonate eluent.

8.0 Sample Collection, Preservation, Storage, and Transport

NOTE: Because of the complexity of this method, testers and analyst should be trained and experienced with the procedure to ensure reliable results.

8.1 Sampling.

8.1.1 Preparation of Collection Train. Prepare the sampling train as follows: Pour 15 ml of the acidic absorbing solution into each one of the first pair of impingers, and 15 ml of the alkaline absorbing solution into each one of the second pair of impingers. Connect the impingers in series with the knockout impinger first, if used, followed by the two impingers containing the acidic absorbing solution and the two impingers containing the alkaline absorbing solution. Place a fresh charge of silica gel, or equivalent, in the drying tube or impinger at the end of the impinger train.

8.1.2 Adjust the probe temperature and the temperature of the filter and the stopcock (*i.e.*, the heated area in Figure 26–1) to a temperature sufficient to prevent water condensation. This temperature must be maintained between 120 and 134 °C (248 and 273 °F). The temperature should be monitored throughout a sampling run to ensure that the desired temperature is maintained. It is important to maintain a temperature around the probe and filter in this range since it is extremely difficult to purge acid gases off these components. (These components are not quantitatively recovered and, hence, any collection of acid gases on these components would result in potential undereporting of these emissions. The applicable subparts may specify alternative higher temperatures.)

8.1.3 Leak-Check Procedure.

8.1.3.1 Sampling Train. A leak-check prior to the sampling run is optional; however, a leak-check after the sampling run is mandatory. The leak-check procedure is as follows: Temporarily attach a suitable [*e.g.*, 0–40 cc/min (0–2.4 in^3/min)] rotameter to the outlet of the dry gas meter and place a vacuum gauge at or near the probe inlet. Plug the probe inlet, pull a vacuum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter. A leakage rate not in excess of 2 percent of the average sampling rate is acceptable.

NOTE: Carefully release the probe inlet plug before turning off the pump.

8.1.3.2 Pump. It is suggested (not mandatory) that the pump be leak-checked separately, either prior to or after the sampling run. If done prior to the sampling run, the pump leak-check shall precede the leak-check of the sampling train described immediately above; if done after the sampling run, the pump leak-check shall follow the train leak-check. To leak-check the pump, proceed as follows: Disconnect the drying tube from the probe-impinger assembly. Place a vacuum gauge at the inlet to either the drying tube or pump, pull a vacuum of 250 mm (10 in) Hg, plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum should remain stable for at least 30 sec. Other leak-check procedures may be used, subject to the approval of the Administrator, U.S. Environmental Protection Agency.

8.1.4 Purge Procedure. Immediately before sampling, connect the purge line to the stopcock, and turn the stopcock to permit the purge pump to purge the probe (see Figure 1A of Figure 26–1). Turn on the purge pump, and adjust the purge rate to 2 liters/min (0.07 ft^3/min). Purge for at least 5 minutes before sampling.

8.1.5 Sample Collection. Turn on the sampling pump, pull a slight vacuum of approximately 25 mm Hg (1 in Hg) on the impinger train, and turn the stopcock to permit stack gas to be pulled through the impinger train (see Figure 1C of Figure 26–1). Adjust the sampling rate to 2 liters/min, as indicated by the rate meter, and maintain this rate to within 10 percent during the entire sampling run. Take readings of the dry gas meter volume and temperature, rate meter, and vacuum gauge at least once every five minutes during the run. A sampling time of one hour is recommended. Shorter sampling times may introduce a significant negative bias in the HCl concentration. At the conclusion of the sampling run, remove the train from the stack, cool, and perform a leak-check as described in section 8.1.3.1.

8.2 Sample Recovery.

8.2.1 Disconnect the impingers after sampling. Quantitatively transfer the contents of the acid impingers and the knockout impinger, if used, to a leak-free storage bottle. Add the water rinses of each of these impingers and connecting glassware to the storage bottle.

8.2.2 Repeat this procedure for the alkaline impingers and connecting glassware using a separate storage bottle. Add 25 mg of sodium thiosulfate per the product of ppm of halogen anticipated to be in the stack gas times the volume (dscm) of stack gas sampled (0.7 mg per ppm-dscf).

NOTE: This amount of sodium thiosulfate includes a safety factor of approximately 5 to assure complete reaction with the hypohalous acid to form a second Cl^- ion in the alkaline solution.

8.2.3 Save portions of the absorbing reagents (0.1 N H_2SO_4 and 0.1 N NaOH) equivalent to the amount used in the sampling train (these are the absorbing solution blanks described in section 7.2.2); dilute to the approximate volume of the corresponding samples using rinse water directly from the wash bottle being used. Add the same amount of sodium thiosulfate solution to the 0.1 N NaOH absorbing solution blank. Also, save a portion of the rinse water used to rinse the sampling train. Place each in a separate, prelabeled storage bottle. The sample storage bottles should be sealed, shaken to mix, and labeled. Mark the fluid level.

8.3 Sample Preparation for Analysis. Note the liquid levels in the storage bottles and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Quantitatively transfer the sample solutions to 100-ml volumetric flasks, and dilute to 100 ml with water.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Volume Metering System, Temperature Sensors, Rate Meter, and Barometer. Same as in Method 6, sections 10.1, 10.2, 10.3, and 10.4.

10.2 Ion Chromatograph.

10.2.1 To prepare the calibration standards, dilute given amounts (1.0 ml or greater) of the stock standard solutions to convenient volumes, using 0.1 N H_2SO_4 or 0.1 N NaOH, as appropriate. Prepare at least four calibration standards for each absorbing reagent containing the appropriate stock solutions such that they are within the linear range of the field samples.

10.2.2 Using one of the standards in each series, ensure adequate baseline separation for the peaks of interest.

10.2.3 Inject the appropriate series of calibration standards, starting with the lowest concentration standard first both before and after injection of the quality control check sample, reagent blanks, and field samples. This allows compensation for any instrument drift occurring during sample analysis. The values from duplicate injections of these calibration samples should agree within 5 percent of their mean for the analysis to be valid.

10.2.4 Determine the peak areas, or heights, for the standards and plot individual values versus halide ion concentrations in µg/ml.

10.2.5 Draw a smooth curve through the points. Use linear regression to calculate a formula describing the resulting linear curve.

11.0 Analytical Procedures

11.1 Sample Analysis.

11.1.1 The IC conditions will depend upon analytical column type and whether suppressed or non-suppressed IC is used. An example chromatogram from a non-suppressed system using a 150-mm Hamilton PRP-X100 anion column, a 2 ml/min flow rate of a 4 mM 4-hydroxy benzoate solution adjusted to a pH of 8.6 using 1 N NaOH, a 50 µl sample loop, and a conductivity detector set on 1.0 µS full scale is shown in Figure 26–2.

11.1.2 Before sample analysis, establish a stable baseline. Next, inject a sample of water, and determine if any Cl^-, Br^-, or F^- appears in the chromatogram. If any of these ions are present, repeat the load/injection

procedure until they are no longer present. Analysis of the acid and alkaline absorbing solution samples requires separate standard calibration curves; prepare each according to section 10.2. Ensure adequate baseline separation of the analyses.

11.1.3 Between injections of the appropriate series of calibration standards, inject in duplicate the reagent blanks, quality control sample, and the field samples. Measure the areas or heights of the Cl^-, Br^-, and F^- peaks. Use the mean response of the duplicate injections to determine the concentrations of the field samples and reagent blanks using the linear calibration curve. The values from duplicate injections should agree within 5 percent of their mean for the analysis to be valid. If the values of duplicate injections are not within 5 percent of the mean, the duplicate injections shall be repeated and all four values used to determine the average response. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

12.0 Data Analysis and Calculations

NOTE: Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

12.1 Nomenclature.

B_X^- = Mass concentration of applicable absorbing solution blank, µg halide ion (Cl^-, Br^-, F^-) /ml, not to exceed 1 µg/ml which is 10 times the published analytical detection limit of 0.1 µg/ml.

C = Concentration of hydrogen halide (HX) or halogen (X_2), dry basis, mg/dscm.

K = 10^{-3} mg/µg.

K_{HCl} = 1.028 (µg HCl/µg-mole)/(µg Cl^-/µg-mole).

K_{HBr} = 1.013 (µg HBr/µg-mole)/(µg Br^-/µg-mole).

K_{HF} = 1.053 (µg HF/µg-mole)/(µg F^-/µg-mole).

m_{HX} = Mass of HCl, HBr, or HF in sample, µg.

m_{X2} = Mass of Cl_2 or Br_2 in sample, µg.

S_X^- = Analysis of sample, µg halide ion (Cl^-, Br^-, F^-)/ml.

$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm.

V_s = Volume of filtered and diluted sample, ml.

12.2 Calculate the exact Cl^-, Br^-, and F^- concentration in the halide salt stock standard solutions using the following equations.

$$\mu g\ Cl^-/ml = g\ of\ NaCl \times 10^3 \times 35.453/58.44 \qquad \text{Eq. 26-1}$$

$$\mu g\ Br^-/ml = g\ of\ NaBr \times 10^3 \times 79.904/102.90 \qquad \text{Eq. 26-2}$$

$$\mu g\ F^-/ml = g\ of\ NaF \times 10^3 \times 18.998/41.99 \qquad \text{Eq. 26-3}$$

12.3 Sample Volume, Dry Basis, Corrected to Standard Conditions. Calculate the sample volume using Eq. 6–1 of Method 6.

12.4 Total µg HCl, HBr, or HF Per Sample.

$$m_{HX} = K_{HC1,Hbr,HF} V_s \left(S_x^- - B_x^-\right) \qquad \text{Eq. 26-4}$$

12.5 Total µg Cl_2 or Br_2 Per Sample.

$$M_{x2} = V_s \left(S_X^- - B_X^-\right) \qquad \text{Eq. 26-5}$$

12.6 Concentration of Hydrogen Halide or Halogen in Flue Gas.

$$C = K m_{XH,X2} / V_{m(std)} \qquad \text{Eq. 26-6}$$

13.0 Method Performance

13.1 Precision and Bias. The within-laboratory relative standard deviations are 6.2 and 3.2 percent at HCl concentrations of 3.9 and 15.3 ppm, respectively. The method does not

exhibit a bias to Cl_2 when sampling at concentrations less than 50 ppm.

13.2 Sample Stability. The collected Cl^- samples can be stored for up to 4 weeks.

13.3 Detection Limit. A typical IC instrumental detection limit for Cl^- is 0.2 μg/ml. Detection limits for the other analyses should be similar. Assuming 50 ml liquid recovered from both the acidified impingers, and the basic impingers, and 0.12 dscm (4.24 dscf) of stack gas sampled, then the analytical detection limit in the stack gas would be about 0.05 ppm for HCl and Cl_2, respectively.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

Method 26A. Method 26A, which uses isokinetic sampling equipment, is an acceptable alternative to Method 26.

17.0 References

1. Steinsberger, S. C. and J. H. Margeson, ''Laboratory and Field Evaluation of a Methodology for Determination of Hydrogen Chloride Emissions from Municipal and Hazardous Waste Incinerators,'' U.S. Environmental Protection Agency, Office of Research and Development, Report No. 600/3–89/064, April 1989. Available from the National Technical Information Service, Springfield, VA 22161 as PB89220586/AS.

2. State of California, Air Resources Board, Method 421, ''Determination of Hydrochloric Acid Emissions from Stationary Sources,'' March 18, 1987.

3. Cheney, J.L. and C.R. Fortune. Improvements in the Methodology for Measuring Hydrochloric Acid in Combustion Source Emissions. J. Environ. Sci. Health. *A19*(3): 337–350. 1984.

4. Stern, D. A., B. M. Myatt, J. F. Lachowski, and K. T. McGregor. Speciation of Halogen and Hydrogen Halide Compounds in Gaseous Emissions. In: Incineration and Treatment of Hazardous Waste: Proceedings of the 9th Annual Research Symposium, Cincinnati, Ohio, May 2–4, 1983. Publication No. 600/9–84–015. July 1984. Available from National Technical Information Service, Springfield, VA 22161 as PB84–234525.

5. Holm, R. D. and S. A. Barksdale. Analysis of Anions in Combustion Products. In: Ion Chromatographic Analysis of Environmental Pollutants. E. Sawicki, J. D. Mulik, and E. Wittgenstein (eds.). Ann Arbor, Michigan, Ann Arbor Science Publishers. 1978. pp. 99–110.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

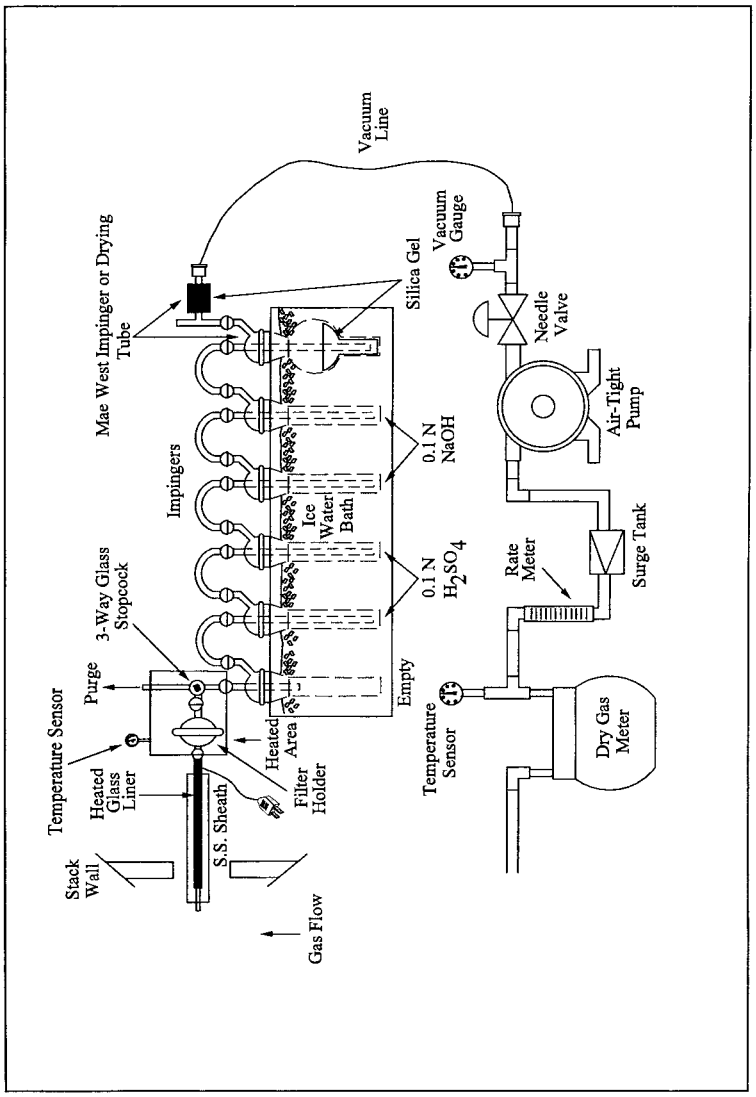


Figure 26-1. Sampling Train.

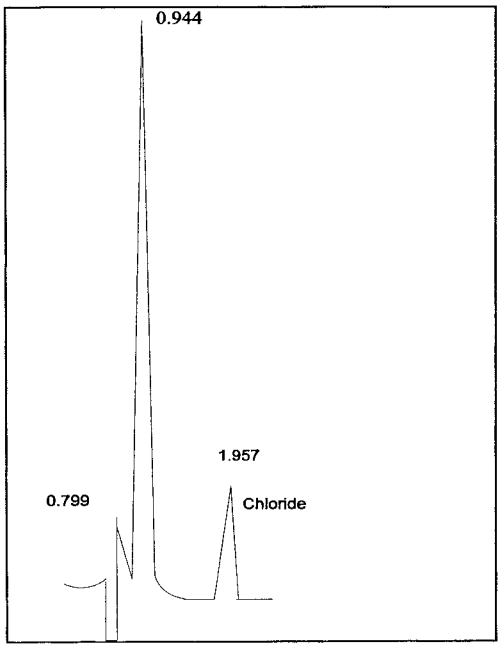


Figure 26-2. Example Chromatogram.

METHOD 26A—DETERMINATION OF HYDROGEN HALIDE AND HALOGEN EMISSIONS FROM STATIONARY SOURCES ISOKINETIC METHOD

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 2, Method 5, and Method 26.

1.0 Scope and Application

1.1 Analytes.

Analytes	CAS No.
Hydrogen Chloride (HCl)	7647–01–0
Hydrogen Bromide (HBr)	10035–10–6
Hydrogen Fluoride (HF)	7664–39–3
Chlorine (Cl_2)	7882–50–5
Bromine (Br_2)	7726–95–6

1.2 This method is applicable for determining emissions of hydrogen halides (HX) [HCl, HBr, and HF] and halogens (X_2) [Cl_2 and Br_2] from stationary sources when specified by the applicable subpart. This method collects the emission sample isokinetically and is therefore particularly suited for sampling at sources, such as those controlled by wet scrubbers, emitting acid particulate matter (*e.g.*, hydrogen halides dissolved in water droplets).

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Principle. Gaseous and particulate pollutants are withdrawn isokinetically from the source and collected in an optional cyclone, on a filter, and in absorbing solutions. The cyclone collects any liquid droplets and is not necessary if the source emissions do not contain them; however, it is preferable to include the cyclone in the sampling train to protect the filter from any liquid present. The filter collects particulate matter including halide salts but is not routinely recovered or analyzed. Acidic and alkaline absorbing solutions collect the gaseous hydrogen halides and halogens, respectively. Following sampling of emissions containing liquid droplets, any halides/halogens dissolved in the liquid in the cyclone and on the filter are vaporized to gas and collected in the impingers by pulling conditioned ambient air through the sampling train. The hydrogen halides are solubilized in the acidic solution and form chloride (Cl^-), bromide (Br^-),

and fluoride (F^-) ions. The halogens have a very low solubility in the acidic solution and pass through to the alkaline solution where they are hydrolyzed to form a proton (H^+), the halide ion, and the hypohalous acid (HClO or HBrO). Sodium thiosulfate is added to the alkaline solution to assure reaction with the hypohalous acid to form a second halide ion such that 2 halide ions are formed for each molecule of halogen gas. The halide ions in the separate solutions are measured by ion chromatography (IC). If desired, the particulate matter recovered from the filter and the probe is analyzed following the procedures in Method 5.

NOTE: If the tester intends to use this sampling arrangement to sample concurrently for particulate matter, the alternative Teflon probe liner, cyclone, and filter holder should not be used. The Teflon filter support must be used. The tester must also meet the probe and filter temperature requirements of both sampling trains.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Volatile materials, such as chlorine dioxide (ClO_2) and ammonium chloride (NH_4Cl), which produce halide ions upon dissolution during sampling are potential interferents. Interferents for the halide measurements are the halogen gases which disproportionate to a hydrogen halide and a hypohalous acid upon dissolution in water. The use of acidic rather than neutral or basic solutions for collection of the hydrogen halides greatly reduces the dissolution of any halogens passing through this solution.

4.2 The simultaneous presence of both HBr and Cl_2 may cause a positive bias in the HCl result with a corresponding negative bias in the Cl_2 result as well as affecting the HBr/Br_2 split.

4.3 High concentrations of nitrogen oxides (NO_X) may produce sufficient nitrate (NO_3^-) to interfere with measurements of very low Br^- levels. Dissociating chloride salts (*e.g.*, ammonium chloride) at elevated temperatures interfere with halogen acid measurement in this method. Maintaining particulate probe/filter temperatures between 120 °C and 134 °C (248 °F and 273 °F) minimizes this interference.

4.4 There is anecdotal evidence that HF may be outgassed from new Teflon components. If HF is a target analyte then preconditioning of new Teflon components, by heating, should be considered.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations before performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.2 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0. Equipment and Supplies

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1 Sampling. The sampling train is shown in Figure 26A–1; the apparatus is similar to the Method 5 train where noted as follows:

6.1.1 Probe Nozzle. Borosilicate or quartz glass; constructed and calibrated according to Method 5, sections 6.1.1.1 and 10.1, and coupled to the probe liner using a Teflon union; a stainless steel nut is recommended for this union. When the stack temperature exceeds 210 °C (410 °F), a one-piece glass nozzle/liner assembly must be used.

6.1.2 Probe Liner. Same as Method 5, section 6.1.1.2, except metal liners shall not be used. Water-cooling of the stainless steel sheath is recommended at temperatures exceeding 500 °C (932 °F). Teflon may be used in limited applications where the minimum stack temperature exceeds 120 °C (250 °F) but never exceeds the temperature where Teflon is estimated to become unstable [approximately 210 °C (410 °F)].

6.1.3 Pitot Tube, Differential Pressure Gauge, Filter Heating System, Metering System, Barometer, Gas Density Determination Equipment. Same as Method 5, sections 6.1.1.3, 6.1.1.4, 6.1.1.6, 6.1.1.9, 6.1.2, and 6.1.3.

6.1.4 Cyclone (Optional). Glass or Teflon. Use of the cyclone is required only when the sample gas stream is saturated with moisture; however, the cyclone is recommended to protect the filter from any liquid droplets present.

6.1.5 Filter Holder. Borosilicate or quartz glass, or Teflon filter holder, with a Teflon filter support and a sealing gasket. The sealing gasket shall be constructed of Teflon or equivalent materials. The holder design shall provide a positive seal against leakage at any point along the filter circumference. The holder shall be attached immediately to the outlet of the cyclone.

6.1.6 Impinger Train. The following system shall be used to determine the stack gas moisture content and to collect the hydrogen halides and halogens: five or six impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. The first impinger shown in Figure 26A–1 (knockout or condensate impinger) is optional and is recommended as a water knockout trap for use under high moisture conditions. If used, this impinger should be constructed as described below for the alkaline impingers, but with a shortened stem, and should contain 50 ml of 0.1 N H_2SO_4. The following two impingers (acid impingers which each contain 100 ml of 0.1 N H_2SO_4) shall be of the Greenburg-Smith design with the standard tip (Method 5, section 6.1.1.8). The next two impingers (alkaline impingers which each contain 100 ml of 0.1 N NaOH) and the last impinger (containing silica gel) shall be of the modified Greenburg-Smith design (Method 5, section 6.1.1.8). The condensate, acid, and alkaline impingers shall contain known quantities of the appropriate absorbing reagents. The last impinger shall contain a known weight of silica gel or equivalent desiccant. Teflon impingers are an acceptable alternative.

6.1.7 Heating System. Any heating system capable of maintaining a temperature around the probe and filter holder between 120 and 134 °C (248 to 273 °F) during sampling, or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application.

6.1.8 Ambient Air Conditioning Tube (Optional). Tube tightly packed with approximately 150 g of fresh 8 to 20 mesh sodium hydroxide-coated silica, or equivalent, (Ascarite II has been found suitable) to dry and remove acid gases from the ambient air used to remove moisture from the filter and cyclone, when the cyclone is used. The inlet and outlet ends of the tube should be packed with at least 1-cm thickness of glass wool or filter material suitable to prevent escape of fines. Fit one end with flexible tubing, etc. to allow connection to probe nozzle following the test run.

6.2 Sample Recovery.

6.2.1 Probe-Liner and Probe-Nozzle Brushes, Wash Bottles, Glass Sample Storage Containers, Petri Dishes, Graduated Cylinder and/or Balance, and Rubber Policeman. Same as Method 5, sections 6.2.1, 6.2.2, 6.2.3, 6.2.4, 6.2.5, and 6.2.7.

6.2.2 Plastic Storage Containers. Screw-cap polypropylene or polyethylene containers to store silica gel. High-density polyethylene bottles with Teflon screw cap liners to store impinger reagents, 1-liter.

6.2.3 Funnels. Glass or high-density polyethylene, to aid in sample recovery.

6.3 Sample Preparation and Analysis.

6.3.1 Volumetric Flasks. Class A, various sizes.

6.3.2 Volumetric Pipettes. Class A, assortment. To dilute samples to calibration range of the ion chromatograph (IC).

6.3.3 Ion Chromatograph (IC). Suppressed or nonsuppressed, with a conductivity detector and electronic integrator operating in the peak area mode. Other detectors, a strip chart recorder, and peak heights may be used.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society (ACS reagent grade). When such specifications are not available, the best available grade shall be used.

7.1 Sampling.

7.1.1 Filter. Teflon mat (*e.g.*, Pallflex TX40HI45) filter. When the stack gas temperature exceeds 210 °C (410 °F) a quartz fiber filter may be used.

7.1.2 Water. Deionized, distilled water that conforms to American Society of Testing and Materials (ASTM) Specification D 1193–77 or 91, Type 3 (incorporated by reference—see §60.17).

7.1.3 Acidic Absorbing Solution, 0.1 N Sulfuric Acid (H_2SO_4). To prepare 1 L, slowly add 2.80 ml of concentrated 17.9 M H2SO4 to about 900 ml of water while stirring, and adjust the final volume to 1 L using additional water. Shake well to mix the solution.

7.1.4 Silica Gel, Crushed Ice, and Stopcock Grease. Same as Method 5, sections 7.1.2, 7.1.4, and 7.1.5, respectively.

7.1.5 Alkaline Absorbing Solution, 0.1 N Sodium Hydroxide (NaOH). To prepare 1 L, dissolve 4.00 g of solid NaOH in about 900 ml of water and adjust the final volume to 1 L using additional water. Shake well to mix the solution.

7.1.6 Sodium Thiosulfate, ($Na_2S_2O_3$3.5 H_2O).

7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in section 7.1.2.

7.2.2 Absorbing Solution Blanks. A separate blank solution of each absorbing reagent should be prepared for analysis with the field samples. Dilute 200 ml of each absorbing solution (250 ml of the acidic absorbing solution, if a condensate impinger is used) to the same final volume as the field samples using the blank sample of rinse water. If a particulate determination is conducted, collect a blank sample of acetone.

7.2.3 Halide Salt Stock Standard Solutions. Prepare concentrated stock solutions from reagent grade sodium chloride (NaCl), sodium bromide (NaBr), and sodium fluoride (NaF). Each must be dried at 110 °C (230 °F) for two or more hours and then cooled to room temperature in a desiccator immediately before weighing. Accurately weigh 1.6 to 1.7 g of the dried NaCl to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact Cl^- concentration using Equation 26A–1 in section 12.2. In a similar manner, accurately weigh and solubilize 1.2 to 1.3 g of dried NaBr and 2.2 to 2.3 g of NaF to make 1-liter solutions. Use Equations 26A–2 and 26A–3 in section 12.2, to calculate the Br^- and F^- concentrations. Alternately, solutions containing a nominal certified concentration of 1000 mg/L NaCl are commercially available as convenient stock solutions from which standards can be made by appropriate volumetric dilution. Refrigerate the stock standard solutions and store no longer than one month.

7.2.4 Chromatographic Eluent. Same as Method 26, section 7.2.4.

7.2.5 Water. Same as section 7.1.1.

7.2.6 Acetone. Same as Method 5, section 7.2.

8.0 Sample Collection, Preservation, Storage, and Transport

NOTE: Because of the complexity of this method, testers and analysts should be trained and experienced with the procedures to ensure reliable results.

8.1 Sampling.

8.1.1 Pretest Preparation. Follow the general procedure given in Method 5, section 8.1, except the filter need only be desiccated and weighed if a particulate determination will be conducted.

8.1.2 Preliminary Determinations. Same as Method 5, section 8.2.

8.1.3 Preparation of Sampling Train. Follow the general procedure given in Method 5, section 8.1.3, except for the following variations: Add 50 ml of 0.1 N H_2SO_4 to the condensate impinger, if used. Place 100 ml of 0.1 N H_2SO_4 in each of the next two impingers. Place 100 ml of 0.1 N NaOH in each of the following two impingers. Finally, transfer approximately 200–300 g of preweighed silica gel from its container to the last impinger. Set up the train as in Figure 26A–1. When used, the optional cyclone is inserted between the probe liner and filter holder and located in the heated filter box.

8.1.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, sections 8.4.2 (Pretest Leak-Check), 8.4.3 (Leak-Checks During the Sample Run), and 8.4.4 (Post-Test Leak-Check).

8.1.5 Sampling Train Operation. Follow the general procedure given in Method 5, Section 8.5. It is important to maintain a temperature around the probe, filter (and cyclone, if used) between 120 and 134 °C (248 and 273 °F) since it is extremely difficult to purge acid gases off these components. (These components are not quantitatively recovered and hence any collection of acid gases on these components would result in potential undereporting these emissions. The applicable subparts may specify alternative higher temperatures.) For each run, record the data required on a data sheet such as the one shown in Method 5, Figure 5–3. If the condensate impinger becomes too full, it may be emptied, recharged with 50 ml of 0.1 N H2SO4, and replaced during the sample run. The condensate emptied must be saved and included in the measurement of the volume of moisture collected and included in the sample for analysis. The additional 50 ml of absorbing reagent must also be considered in calculating the moisture. Before the sampling train integrity is compromised by removing the impinger, conduct a leak-check as described in Method 5, Section 8.4.2.

8.1.6 Post-Test Moisture Removal (Optional). When the optional cyclone is included in the sampling train or when liquid is visible on the filter at the end of a sample run even in the absence of a cyclone, perform the following procedure. Upon completion of the test run, connect the ambient air conditioning tube at the probe inlet and operate the train with the filter heating system between 120 and 134 °C (248 and 273 °F) at a low flow rate (*e.g.*, ΔH = 1 in. H_2O) to vaporize any liquid and hydrogen halides in the cyclone or on the filter and pull them through the train into the impingers. After 30 minutes, turn off the flow, remove the conditioning tube, and examine the cyclone and filter for any visible liquid. If liquid is visible, repeat this step for 15 minutes and observe again. Keep repeating until the cyclone is dry.

NOTE: It is critical that this procedure is repeated until the cyclone is completely dry.

8.2 Sample Recovery. Allow the probe to cool. When the probe can be handled safely, wipe off all the external surfaces of the tip of the probe nozzle and place a cap loosely over the tip to prevent gaining or losing particulate matter. Do not cap the probe tip tightly while the sampling train is cooling down because this will create a vacuum in the filter holder, drawing water from the impingers into the holder. Before moving the sampling train to the cleanup site, remove the probe from the sample train, wipe off any silicone grease, and cap the open outlet of the impinger train, being careful not to lose any condensate that might be present. Wipe off any silicone grease and cap the filter or cyclone inlet. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger and the filter holder, disconnect it at

the filter holder and let any condensed water drain into the first impinger. Wipe off any silicone grease and cap the filter holder outlet and the impinger inlet. Ground glass stoppers, plastic caps, serum caps, Teflon tape, Parafilm, or aluminum foil may be used to close these openings. Transfer the probe and filter/impinger assembly to the cleanup area. This area should be clean and protected from the weather to minimize sample contamination or loss. Inspect the train prior to and during disassembly and note any abnormal conditions. Treat samples as follows:

8.2.1 Container No. 1 (Optional; Filter Catch for Particulate Determination). Same as Method 5, section 8.7.6.1, Container No. 1.

8.2.2 Container No. 2 (Optional; Front-Half Rinse for Particulate Determination). Same as Method 5, section 8.7.6.2, Container No. 2.

8.2.3 Container No. 3 (Knockout and Acid Impinger Catch for Moisture and Hydrogen Halide Determination). Disconnect the impingers. Measure the liquid in the acid and knockout impingers to ±1 ml by using a graduated cylinder or by weighing it to ±0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas. Quantitatively transfer this liquid to a leak-free sample storage container. Rinse these impingers and connecting glassware including the back portion of the filter holder (and flexible tubing, if used) with water and add these rinses to the storage container. Seal the container, shake to mix, and label. The fluid level should be marked so that if any sample is lost during transport, a correction proportional to the lost volume can be applied. Retain rinse water and acidic absorbing solution blanks to be analyzed with the samples.

8.2.4 Container No. 4 (Alkaline Impinger Catch for Halogen and Moisture Determination). Measure and record the liquid in the alkaline impingers as described in section 8.2.3. Quantitatively transfer this liquid to a leak-free sample storage container. Rinse these two impingers and connecting glassware with water and add these rinses to the container. Add 25 mg of sodium thiosulfate per ppm halogen anticipated to be in the stack gas multiplied by the volume (dscm) of stack gas sampled (0.7 mg/ppm-dscf). Seal the container, shake to mix, and label; mark the fluid level. Retain alkaline absorbing solution blank to be analyzed with the samples.

NOTE: 25 mg per sodium thiosulfate per ppm halogen anticipated to be in the stack includes a safety factor of approximately 5 to assure complete reaction with the hypohalous acid to form a second Cl^- ion in the alkaline solution.

8.2.5 Container No. 5 (Silica Gel for Moisture Determination). Same as Method 5, section 8.7.6.3, Container No. 3.

8.2.6 Container Nos. 6 through 9 (Reagent Blanks). Save portions of the absorbing reagents (0.1 N H_2SO_4 and 0.1 N NaOH) equivalent to the amount used in the sampling train; dilute to the approximate volume of the corresponding samples using rinse water directly from the wash bottle being used. Add the same ratio of sodium thiosulfate solution used in container No. 4 to the 0.1 N NaOH absorbing reagent blank. Also, save a portion of the rinse water alone and a portion of the acetone equivalent to the amount used to rinse the front half of the sampling train. Place each in a separate, prelabeled sample container.

8.2.7 Prior to shipment, recheck all sample containers to ensure that the caps are well-secured. Seal the lids of all containers around the circumference with Teflon tape. Ship all liquid samples upright and all particulate filters with the particulate catch facing upward.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.1.4, 10.1	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Probe Nozzle, Pitot Tube Assembly, Dry Gas Metering System, Probe Heater, Temperature Sensors, Leak-Check of Metering System, and Barometer. Same as Method 5, sections 10.1, 10.2, 10.3, 10.4, 10.5, 8.4.1, and 10.6, respectively.

10.2 Ion Chromatograph.

10.2.1 To prepare the calibration standards, dilute given amounts (1.0 ml or greater) of the stock standard solutions to convenient volumes, using 0.1 N H_2SO_4 or 0.1 N NaOH, as appropriate. Prepare at least four calibration standards for each absorbing reagent containing the three stock solutions such that they are within the linear range of the field samples.

10.2.2 Using one of the standards in each series, ensure adequate baseline separation for the peaks of interest.

10.2.3 Inject the appropriate series of calibration standards, starting with the lowest concentration standard first both before and after injection of the quality control check sample, reagent blanks, and field samples. This allows compensation for any instrument drift occurring during sample analysis. The values from duplicate injections of these calibration samples should agree within 5 percent of their mean for the analysis to be valid.

10.2.4 Determine the peak areas, or height, of the standards and plot individual values versus halide ion concentrations in µg/ml.

10.2.5 Draw a smooth curve through the points. Use linear regression to calculate a formula describing the resulting linear curve.

11.0 Analytical Procedures

NOTE: The liquid levels in the sample containers and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.1 Sample Analysis.

11.1.1 The IC conditions will depend upon analytical column type and whether suppressed or non-suppressed IC is used. An example chromatogram from a non-suppressed system using a 150-mm Hamilton PRP-X100 anion column, a 2 ml/min flow rate of a 4 mM 4-hydroxy benzoate solution adjusted to a pH of 8.6 using 1 N NaOH, a 50 µl sample loop, and a conductivity detector set on 1.0 µS full scale is shown in Figure 26–2.

11.1.2 Before sample analysis, establish a stable baseline. Next, inject a sample of water, and determine if any Cl^-, Br^-, or F^- appears in the chromatogram. If any of these ions are present, repeat the load/injection procedure until they are no longer present. Analysis of the acid and alkaline absorbing solution samples requires separate standard calibration curves; prepare each according to section 10.2. Ensure adequate baseline separation of the analyses.

11.1.3 Between injections of the appropriate series of calibration standards, inject in duplicate the reagent blanks, quality control sample, and the field samples. Measure the areas or heights of the Cl^-, Br^-, and F^- peaks. Use the mean response of the duplicate injections to determine the concentrations of the field samples and reagent blanks using the linear calibration curve. The values from duplicate injections should agree within 5 percent of their mean for the analysis to be valid. If the values of duplicate injections are not within 5 percent of the mean, the duplicator injections shall be repeated and all four values used to determine the average response. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

11.2 Container Nos. 1 and 2 and Acetone Blank (Optional; Particulate Determination). Same as Method 5, sections 11.2.1 and 11.2.2, respectively.

11.3 Container No. 5. Same as Method 5, section 11.2.3 for silica gel.

12.0 Data Analysis and Calculations

NOTE: Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

12.1 Nomenclature. Same as Method 5, section 12.1. In addition:

B_{X-} = Mass concentration of applicable absorbing solution blank, µg halide ion (Cl^-, Br^-, F^-)/ml, not to exceed 1 µg/ml which is 10 times the published analytical detection limit of 0.1 µg/ml. (It is also approximately 5 percent of the mass concentration anticipated to result from a one hour sample at 10 ppmv HCl.)

C = Concentration of hydrogen halide (HX) or halogen (X_2), dry basis, mg/dscm.

$K = 10^{-3}$ mg/µg.

K_{HCl} = 1.028 (µg HCl/µg-mole)/(µg Cl^-/µg-mole).

K_{HBr} = 1.013 (µg HBr/µg-mole)/(µg Br^-/µg-mole).

K_{HF} = 1.053 (µg HF/µg-mole)/(µg F^-/µg-mole).

m_{HX} = Mass of HCl, HBr, or HF in sample, ug.

m_{X2} = Mass of Cl_2 or Br_2 in sample, ug.

S_{X-} = Analysis of sample, ug halide ion (Cl^-, Br^-, F^-)/ml.

V_s = Volume of filtered and diluted sample, ml.

12.2 Calculate the exact Cl^-, Br^-, and F^- concentration in the halide salt stock standard solutions using the following equations.

$$\mu g\ Cl^-/ml = g\ of\ NaCl \times 10^3 \times 35.453/58.44 \qquad \text{Eq. 26A-1}$$

$$\mu g\ Br^-/ml = g\ of\ NaBr \times 10^3 \times 79.904/102.90 \qquad \text{Eq. 26A-2}$$

$$\mu g\ F^-/ml = g\ of\ NaF \times 10^3 \times 18.998/41.99 \qquad \text{Eq. 26A-3}$$

12.3 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 5–3 of Method 5).

12.4 Dry Gas Volume. Calculate $V_{m(std)}$ and adjust for leakage, if necessary, using the equation in section 12.3 of Method 5.

12.5 Volume of Water Vapor and Moisture Content. Calculate the volume of water vapor $V_{w(std)}$ and moisture content B_{ws} from the data obtained in this method (Figure 5–3 of Method 5); use Equations 5–2 and 5–3 of Method 5.

12.6 Isokinetic Variation and Acceptable Results. Use Method 5, section 12.11.

12.7 Acetone Blank Concentration, Acetone Wash Blank Residue Weight, Particulate Weight, and Particulate Concentration. For particulate determination.

12.8 Total μg HCl, HBr, or HF Per Sample.

$$m_{HX} = K_{HC1,Hbr,HF} V_s \left(S_{X^-} - B_{X^-} \right) \qquad \text{Eq. 26A-4}$$

12.9 Total μg Cl_2 or Br_2 Per Sample.

$$m_{X2} = V_s \left(S_{X^-} - B_{X^-} \right) \qquad \text{Eq. 26A-5}$$

12.10 Concentration of Hydrogen Halide or Halogen in Flue Gas.

$$C = K\, m_{HX,X2} / V_{m(std)} \qquad \text{Eq. 26A-6}$$

12.11 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate, if needed, using data obtained in this method and the equations in sections 12.3 and 12.4 of Method 2.

13.0 Method Performance

13.1 Precision and Bias. The method has a possible measurable negative bias below 20 ppm HCl perhaps due to reaction with small amounts of moisture in the probe and filter. Similar bias for the other hydrogen halides is possible.

13.2 Sample Stability. The collected Cl- samples can be stored for up to 4 weeks for analysis for HCl and Cl2.

13.3 Detection Limit. A typical analytical detection limit for HCl is 0.2 μg/ml. Detection limits for the other analyses should be similar. Assuming 300 ml of liquid recovered for the acidified impingers and a similar amounts recovered from the basic impingers, and 1 dscm of stack gas sampled, the analytical detection limits in the stack gas would be about 0.04 ppm for HCl and Cl2, respectively.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

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3. Cheney, J.L. and C.R. Fortune. Improvements in the Methodology for Measuring Hydrochloric Acid in Combustion Source Emissions. J. Environ. Sci. Health. *A19*(3): 337–350. 1984.

4. Stern, D.A., B.M. Myatt, J.F. Lachowski, and K.T. McGregor. Speciation of Halogen and Hydrogen Halide Compounds in Gaseous Emissions. In: Incineration and Treatment of Hazardous Waste: Proceedings of the 9th Annual Research Symposium, Cincinnati, Ohio, May 2–4, 1983. Publication No. 600/9–84–015. July 1984. Available from National Technical Information Service, Springfield, VA 22161 as PB84–234525.

5. Holm, R.D. and S.A. Barksdale. Analysis of Anions in Combustion Products. In: Ion Chromatographic Analysis of Environmental Pollutants, E. Sawicki, J.D. Mulik, and E. Wittgenstein (eds.). Ann Arbor, Michigan, Ann Arbor Science Publishers. 1978. pp. 99–110.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

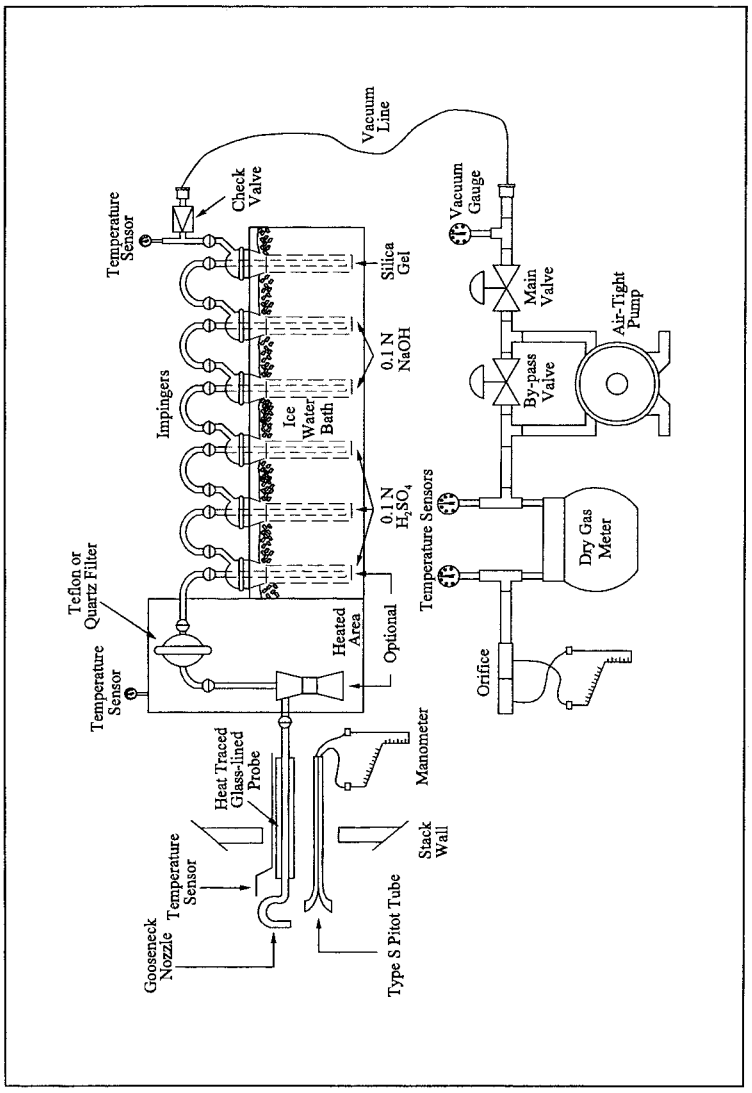


Figure 26A-1. Sampling Train

METHOD 27—DETERMINATION OF VAPOR TIGHTNESS OF GASOLINE DELIVERY TANK USING PRESSURE VACUUM TEST

1.0 Scope and Application

1.1 Applicability. This method is applicable for the determination of vapor tightness of a gasoline delivery collection equipment.

2.0 Summary of Method

2.1 Pressure and vacuum are applied alternately to the compartments of a gasoline delivery tank and the change in pressure or vacuum is recorded after a specified period of time.

3.0 Definitions

3.1 *Allowable pressure change (Δp)* means the allowable amount of decrease in pressure during the static pressure test, within the time period t, as specified in the appropriate regulation, in mm H_2O.

3.2 *Allowable vacuum change (Δv)* means the allowable amount of decrease in vacuum during the static vacuum test, within the time period t, as specified in the appropriate regulation, in mm H_2O.

3.3 *Compartment* means a liquid-tight division of a delivery tank.

3.4 *Delivery tank* means a container, including associated pipes and fittings, that is attached to or forms a part of any truck, trailer, or railcar used for the transport of gasoline.

3.5 *Delivery tank vapor collection equipment* means any piping, hoses, and devices on the delivery tank used to collect and route gasoline vapors either from the tank to a bulk terminal vapor control system or from a bulk plant or service station into the tank.

3.6 *Gasoline* means a petroleum distillate or petroleum distillate/alcohol blend having a Reid vapor pressure of 27.6 kilopascals or greater which is used as a fuel for internal combustion engines.

3.7 *Initial pressure (P_i)* means the pressure applied to the delivery tank at the beginning of the static pressure test, as specified in the appropriate regulation, in mm H_2O.

3.8 *Initial vacuum (V_i)* means the vacuum applied to the delivery tank at the beginning of the static vacuum test, as specified in the appropriate regulation, in mm H_3.

3.9 *Time period of the pressure or vacuum test (t)* means the time period of the test, as specified in the appropriate regulation, during which the change in pressure or vacuum is monitored, in minutes.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Gasoline contains several volatile organic compounds (*e.g.*, benzene and hexane) which presents a potential for fire and/or explosions. It is advisable to take appropriate precautions when testing a gasoline vessel's vapor tightness, such as refraining from smoking and using explosion-proof equipment.

5.2 This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method

6.0 Equipment and Supplies

The following equipment and supplies are required for testing:

6.1 Pressure Source. Pump or compressed gas cylinder of air or inert gas sufficient to pressurize the delivery tank to 500 mm (20 in.) H_2O above atmospheric pressure.

6.2 Regulator. Low pressure regulator for controlling pressurization of the delivery tank.

6.3 Vacuum Source. Vacuum pump capable of evacuating the delivery tank to 250 mm (10 in.) H_2O below atmospheric pressure.

6.4 Pressure-Vacuum Supply Hose.

6.5 Manometer. Liquid manometer, or equivalent instrument, capable of measuring up to 500 mm (20 in.) H_2O gauge pressure with ±2.5 mm (0.1 in.) H_2O precision.

6.6 Pressure-Vacuum Relief Valves. The test apparatus shall be equipped with an inline pressure-vacuum relief valve set to activate at 675 mm (26.6 in.) H_2O above atmospheric pressure or 250 mm (10 in.) H2O below atmospheric pressure, with a capacity equal to the pressurizing or evacuating pumps.

6.7 Test Cap for Vapor Recovery Hose. This cap shall have a tap for manometer connection and a fitting with shut-off valve for connection to the pressure-vacuum supply hose.

6.8 Caps for Liquid Delivery Hoses.

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparations.

8.1.1 Summary. Testing problems may occur due to the presence of volatile vapors and/or temperature fluctuations inside the delivery tank. Under these conditions, it is often difficult to obtain a stable initial pressure at the beginning of a test, and erroneous test results may occur. To help prevent this, it is recommended that prior to testing, volatile vapors be removed from the tank and the temperature inside the tank be allowed to stabilize. Because it is not always possible to completely attain these pretest conditions, a provision to ensure reproducible results is included. The difference in results for two consecutive runs must meet the criteria in sections 8.2.2.5 and 8.2.3.5.

8.1.2 Emptying of Tank. The delivery tank shall be emptied of all liquid.

8.1.3 Purging of Vapor. As much as possible the delivery tank shall be purged of all volatile vapors by any safe, acceptable method. One method is to carry a load of non-volatile liquid fuel, such as diesel or heating oil, immediately prior to the test, thus flushing out all the volatile gasoline vapors. A second method is to remove the volatile vapors by blowing ambient air into each tank compartment for at least 20 minutes. This second method is usually not as effective and often causes stabilization problems, requiring a

much longer time for stabilization during the testing.

8.1.4 Temperature Stabilization. As much as possible, the test shall be conducted under isothermal conditions. The temperature of the delivery tank should be allowed to equilibrate in the test environment. During the test, the tank should be protected from extreme environmental and temperature variability, such as direct sunlight.

8.2 Test Procedure.

8.2.1 Preparations.

8.2.1.1 Open and close each dome cover.

8.2.1.2 Connect static electrical ground connections to the tank. Attach the liquid delivery and vapor return hoses, remove the liquid delivery elbows, and plug the liquid delivery fittings.

NOTE: The purpose of testing the liquid delivery hoses is to detect tears or holes that would allow liquid leakage during a delivery. Liquid delivery hoses are not considered to be possible sources of vapor leakage, and thus, do not have to be attached for a vapor leakage test. Instead, a liquid delivery hose could be either visually inspected, or filled with water to detect any liquid leakage.

8.2.1.3 Attach the test cap to the end of the vapor recovery hose.

8.2.1.4 Connect the pressure-vacuum supply hose and the pressure-vacuum relief valve to the shut-off valve. Attach a manometer to the pressure tap.

8.2.1.5 Connect compartments of the tank internally to each other if possible. If not possible, each compartment must be tested separately, as if it were an individual delivery tank.

8.2.2 Pressure Test.

8.2.2.1 Connect the pressure source to the pressure-vacuum supply hose.

8.2.2.2 Open the shut-off valve in the vapor recovery hose cap. Apply air pressure slowly, pressurize the tank to P_i, the initial pressure specified in the regulation.

8.2.2.3 Close the shut-off and allow the pressure in the tank to stabilize, adjusting the pressure if necessary to maintain pressure of P_i. When the pressure stabilizes, record the time and initial pressure.

8.2.2.4 At the end of the time period (t) specified in the regulation, record the time and final pressure.

8.2.2.5 Repeat steps 8.2.2.2 through 8.2.2.4 until the change in pressure for two consecutive runs agrees within 12.5 mm (0.5 in.) H_2O. Calculate the arithmetic average of the two results.

8.2.2.6 Compare the average measured change in pressure to the allowable pressure change, Δp, specified in the regulation. If the delivery tank does not satisfy the vapor tightness criterion specified in the regulation, repair the sources of leakage, and repeat the pressure test until the criterion is met.

8.2.2.7 Disconnect the pressure source from the pressure-vacuum supply hose, and slowly open the shut-off valve to bring the tank to atmospheric pressure.

8.2.3 Vacuum Test.

8.2.3.1 Connect the vacuum source to the pressure-vacuum supply hose.

8.2.3.2 Open the shut-off valve in the vapor recovery hose cap. Slowly evacuate the tank to V_i, the initial vacuum specified in the regulation.

8.2.3.3 Close the shut-off valve and allow the pressure in the tank to stabilize, adjusting the pressure if necessary to maintain a vacuum of V_i. When the pressure stabilizes, record the time and initial vacuum.

8.2.3.4 At the end of the time period specified in the regulation (t), record the time and final vacuum.

8.2.3.5 Repeat steps 8.2.3.2 through 8.2.3.4 until the change in vacuum for two consecutive runs agrees within 12.5 mm (0.5 in.) H_2O. Calculate the arithmetic average of the two results.

8.2.3.6 Compare the average measured change in vacuum to the allowable vacuum change, Δv, as specified in the regulation. If the delivery tank does not satisfy the vapor tightness criterion specified in the regulation, repair the sources of leakage, and repeat the vacuum test until the criterion is met.

8.2.3.7 Disconnect the vacuum source from the pressure-vacuum supply hose, and slowly open the shut-off valve to bring the tank to atmospheric pressure.

8.2.4 Post-Test Clean-up. Disconnect all test equipment and return the delivery tank to its pretest condition.

9.0 Quality Control

Section(s)	Quality control measure	Effect
8.2.2.5, 8.3.3.5	Repeat test procedures until change in pressure or vacuum for two consecutive runs agrees within ±12.5 mm (0.5 in.) H_2O.	Ensures data precision.

10.0 Calibration and Standardization
[Reserved]

11.0 Analytical Procedures [Reserved]

12.0 Data Analysis and Calculations [Reserved]

13.0 Method Performance

13.1 Precision. The vapor tightness of a gasoline delivery tank under positive or negative pressure, as measured by this method, is precise within 12.5 mm (0.5 in.) H_2O

13.2 Bias. No bias has been identified.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 The pumping of water into the bottom of a delivery tank is an acceptable alternative to the pressure source described above. Likewise, the draining of water out of the bottom of a delivery tank may be substituted for the vacuum source. Note that some of the specific step-by-step procedures in the method must be altered slightly to accommodate these different pressure and vacuum sources.

16.2 Techniques other than specified above may be used for purging and pressurizing a delivery tank, if prior approval is obtained from the Administrator. Such approval will be based upon demonstrated equivalency with the above method.

17.0 References [Reserved]

18.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 28—CERTIFICATION AND AUDITING OF WOOD HEATERS

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 4, Method 5, Method 5G, Method 5H, Method 6, Method 6C, and Method 16A.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the certification and auditing of wood heaters, including pellet burning wood heaters.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Particulate matter emissions are measured from a wood heater burning a prepared test fuel crib in a test facility maintained at a set of prescribed conditions. Procedures for determining burn rates and particulate emission rates and for reducing data are provided.

3.0 Definitions

3.1 *2 × 4 or 4 × 4* means two inches by four inches or four inches by four inches (50 mm by 100 mm or 100 mm by 100 mm), as nominal dimensions for lumber.

3.2 *Burn rate* means the rate at which test fuel is consumed in a wood heater. Measured in kilograms or lbs of wood (dry basis) per hour (kg/hr or lb/hr).

3.3 *Certification or audit test* means a series of at least four test runs conducted for certification or audit purposes that meets the burn rate specifications in section 8.4.

3.4 *Firebox* means the chamber in the wood heater in which the test fuel charge is placed and combusted.

3.5 *Height* means the vertical distance extending above the loading door, if fuel could reasonably occupy that space, but not more than 2 inches above the top (peak height) of the loading door, to the floor of the firebox (*i.e.*, below a permanent grate) if the grate allows a 1-inch diameter piece of wood to pass through the grate, or, if not, to the top of the grate. Firebox height is not necessarily uniform but must account for variations caused by internal baffles, air channels, or other permanent obstructions.

3.6 *Length* means the longest horizontal fire chamber dimension that is parallel to a wall of the chamber.

3.7 *Pellet burning wood heater* means a wood heater which meets the following criteria: (1) The manufacturer makes no reference to burning cord wood in advertising or other literature, (2) the unit is safety listed for pellet fuel only, (3) the unit operating and instruction manual must state that the use of cordwood is prohibited by law, and (4) the unit must be manufactured and sold including the hopper and auger combination as integral parts.

3.8 *Secondary air supply* means an air supply that introduces air to the wood heater such that the burn rate is not altered by more than 25 percent when the secondary air supply is adjusted during the test run. The wood heater manufacturer can document this through design drawings that show the secondary air is introduced only into a mixing chamber or secondary chamber outside the firebox.

3.9 *Test facility* means the area in which the wood heater is installed, operated, and sampled for emissions.

3.10 *Test fuel charge* means the collection of test fuel pieces placed in the wood heater at the start of the emission test run.

3.11 *Test fuel crib* means the arrangement of the test fuel charge with the proper spacing requirements between adjacent fuel pieces.

3.12 *Test fuel loading density* means the weight of the as-fired test fuel charge per unit volume of usable firebox.

3.13 *Test fuel piece* means the 2 × 4 or 4 × 4 wood piece cut to the length required for the test fuel charge and used to construct the test fuel crib.

3.14 *Test run* means an individual emission test which encompasses the time required to consume the mass of the test fuel charge.

3.15 *Usable firebox volume* means the volume of the firebox determined using its height, length, and width as defined in this section.

3.16 *Width* means the shortest horizontal fire chamber dimension that is parallel to a wall of the chamber.

3.17 *Wood heater* means an enclosed, woodburning appliance capable of and intended for space heating or domestic water heating, as defined in the applicable regulation.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

Same as section 6.0 of either Method 5G or Method 5H, with the addition of the following:

6.1 Insulated Solid Pack Chimney. For installation of wood heaters. Solid pack insulated chimneys shall have a minimum of 2.5 cm (1 in.) solid pack insulating material surrounding the entire flue and possess a label demonstrating conformance to U.L. 103 (incorporated by reference—see §60.17).

6.2 Platform Scale and Monitor. For monitoring of fuel load weight change. The scale shall be capable of measuring weight to within 0.05 kg (0.1 lb) or 1 percent of the initial test fuel charge weight, whichever is greater.

6.3 Wood Heater Temperature Monitors. Seven, each capable of measuring temperature to within 1.5 percent of expected absolute temperatures.

6.4 Test Facility Temperature Monitor. A thermocouple located centrally in a vertically oriented 150 mm (6 in.) long, 50 mm (2 in.) diameter pipe shield that is open at both ends, capable of measuring temperature to within 1.5 percent of expected temperatures.

6.5 Balance (optional). Balance capable of weighing the test fuel charge to within 0.05 kg (0.1 lb).

6.6 Moisture Meter. Calibrated electrical resistance meter for measuring test fuel moisture to within 1 percent moisture content.

6.7 Anemometer. Device capable of detecting air velocities less than 0.10 m/sec (20 ft/min), for measuring air velocities near the test appliance.

6.8 Barometer. Mercury, aneroid or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg).

6.9 Draft Gauge. Electromanometer or other device for the determination of flue draft or static pressure readable to within 0.50 Pa (0.002 in. H_2O).

6.10 Humidity Gauge. Psychrometer or hygrometer for measuring room humidity.

6.11 Wood Heater Flue.

6.11.1 Steel flue pipe extending to 2.6 ±0.15 m (8.5 ±0.5 ft) above the top of the platform scale, and above this level, insulated solid pack type chimney extending to 4.6 ±0.3 m (15 ±1 ft) above the platform scale, and of the size specified by the wood heater manufacturer. This applies to both freestanding and insert type wood heaters.

6.11.2 Other chimney types (*e.g.*, solid pack insulated pipe) may be used in place of the steel flue pipe if the wood heater manufacturer's written appliance specifications require such chimney for home installation (*e.g.*, zero clearance wood heater inserts). Such alternative chimney or flue pipe must remain and be sealed with the wood heater following the certification test.

6.12 Test Facility. The test facility shall meet the following requirements during testing:

6.12.1 The test facility temperature shall be maintained between 18 and 32 °C (65 and 90 °F) during each test run.

6.12.2 Air velocities within 0.6 m (2 ft) of the test appliance and exhaust system shall be less than 0.25 m/sec (50 ft/min) without fire in the unit.

6.12.3 The flue shall discharge into the same space or into a space freely communicating with the test facility. Any hood or similar device used to vent combustion products shall not induce a draft greater than 1.25 Pa (0.005 in. H_2O) on the wood heater measured when the wood heater is not operating.

6.12.4 For test facilities with artificially induced barometric pressures (*e.g.*, pressurized chambers), the barometric pressure in the test facility shall not exceed 775 mm Hg (30.5 in. Hg) during any test run.

7.0 Reagents and Standards

Same as section 6.0 of either Method 5G or Method 5H, with the addition of the following:

7.1 Test Fuel. The test fuel shall conform to the following requirements:

7.1.1 Fuel Species. Untreated, air-dried, Douglas fir lumber. Kiln-dried lumber is not permitted. The lumber shall be certified C grade (standard) or better Douglas fir by a lumber grader at the mill of origin as specified in the West Coast Lumber Inspection Bureau Standard No. 16 (incorporated by reference—see §60.17).

7.1.2 Fuel Moisture. The test fuel shall have a moisture content range between 16 to 20 percent on a wet basis (19 to 25 percent dry basis). Addition of moisture to previously dried wood is not allowed. It is recommended that the test fuel be stored in a temperature and humidity-controlled room.

7.1.3 Fuel Temperature. The test fuel shall be at the test facility temperature of 18 to 32 °C (65 to 90 °F).

7.1.4 Fuel Dimensions. The dimensions of each test fuel piece shall conform to the nominal measurements of 2×4 and 4×4 lumber. Each piece of test fuel (not including spacers) shall be of equal length, except as necessary to meet requirements in section 8.8, and shall closely approximate ⅝ the dimensions of the length of the usable firebox. The fuel piece dimensions shall be determined in relation to the appliance's firebox volume according to guidelines listed below:

7.1.4.1 If the usable firebox volume is less than or equal to 0.043 m^3 (1.5 ft^3), use 2×4 lumber.

7.1.4.2 If the usable firebox volume is greater than 0.043 m^3 (1.5 ft^3) and less than or equal to 0.085 m^3 (3.0 ft^3), use 2×4 and 4×4 lumber. About half the weight of the test fuel charge shall be 2×4 lumber, and the remainder shall be 4×4 lumber.

7.1.4.3 If the usable firebox volume is greater than 0.085 m^3 (3.0 ft^3), use 4×4 lumber.

7.2 Test Fuel Spacers. Air-dried, Douglas fir lumber meeting the requirements outlined in sections 7.1.1 through 7.1.3. The spacers shall be $130 \times 40 \times 20$ mm ($5 \times 1.5 \times 0.75$ in.).

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Test Run Requirements.

8.1.1 Burn Rate Categories. One emission test run is required in each of the following burn rate categories:

BURN RATE CATEGORIES

[Average kg/hr (lb/hr), dry basis]

Category 1	Category 2	Category 3	Category 4
<0.80 (<1.76)	0.80 to 1.25 (1.76 to 2.76)	1.25 to 1.90 (2.76 to 4.19)	Maximum. burn rate.

8.1.1.1 Maximum Burn Rate. For Category 4, the wood heater shall be operated with the primary air supply inlet controls fully open (or, if thermostatically controlled, the thermostat shall be set at maximum heat output) during the entire test run, or the maximum burn rate setting specified by the manufacturer's written instructions.

8.1.1.2 Other Burn Rate Categories. For burn rates in Categories 1 through 3, the wood heater shall be operated with the primary air supply inlet control, or other mechanical control device, set at a predetermined position necessary to obtain the average burn rate required for the category.

8.1.1.3 Alternative Burn Rates for Burn Rate Categories 1 and 2.

8.1.1.3.1 If a wood heater cannot be operated at a burn rate below 0.80 kg/hr (1.76 lb/hr), two test runs shall be conducted with burn rates within Category 2. If a wood heater cannot be operated at a burn rate below 1.25 kg/hr (2.76 lb/hr), the flue shall be dampered or the air supply otherwise controlled in order to achieve two test runs within Category 2.

8.1.1.3.2 Evidence that a wood heater cannot be operated at a burn rate less than 0.80 kg/hr shall include documentation of two or more attempts to operate the wood heater in burn rate Category 1 and fuel combustion has stopped, or results of two or more test runs demonstrating that the burn rates were greater than 0.80 kg/hr when the air supply controls were adjusted to the lowest possible position or settings. Stopped fuel combustion is evidenced when an elapsed time of 30 minutes or more has occurred without a measurable (<0.05 kg (0.1 lb) or 1.0 percent, whichever is greater) weight change in the test fuel charge. See also section 8.8.3. Report the evidence and the reasoning used to determine that a test in burn rate Category 1 cannot be achieved; for example, two unsuccessful attempts to operate at a burn rate of 0.4 kg/hr are not sufficient evidence that burn rate Category 1 cannot be achieved.

NOTE: After July 1, 1990, if a wood heater cannot be operated at a burn rate less than 0.80 kg/hr, at least one test run with an average burn rate of 1.00 kg/hr or less shall be conducted. Additionally, if flue dampering must be used to achieve burn rates below 1.25

kg/hr (or 1.0 kg/hr), results from a test run conducted at burn rates below 0.90 kg/hr need not be reported or included in the test run average provided that such results are replaced with results from a test run meeting the criteria above.

8.2 Catalytic Combustor and Wood Heater Aging. The catalyst-equipped wood heater or a wood heater of any type shall be aged before the certification test begins. The aging procedure shall be conducted and documented by a testing laboratory accredited according to procedures in §60.535 of 40 CFR part 60.

8.2.1 Catalyst-equipped Wood Heater. Operate the catalyst-equipped wood heater using fuel meeting the specifications outlined in sections 7.1.1 through 7.1.3, or cordwood with a moisture content between 15 and 25 percent on a wet basis. Operate the wood heater at a medium burn rate (Category 2 or 3) with a new catalytic combustor in place and in operation for at least 50 hours. Record and report hourly catalyst exit temperature data (Section 8.6.2) and the hours of operation.

8.2.2 Non-Catalyst Wood Heater. Operate the wood heater using the fuel described in section 8.4.1 at a medium burn rate for at least 10 hours. Record and report the hours of operation.

8.3 Pretest Recordkeeping. Record the test fuel charge dimensions and weights, and wood heater and catalyst descriptions as shown in the example in Figure 28–1.

8.4 Wood Heater Installation. Assemble the wood heater appliance and parts in conformance with the manufacturer's written installation instructions. Place the wood heater centrally on the platform scale and connect the wood heater to the flue described in section 6.11. Clean the flue with an appropriately sized, wire chimney brush before each certification test.

8.5 Wood Heater Temperature Monitors.

8.5.1 For catalyst-equipped wood heaters, locate a temperature monitor (optional) about 25 mm (1 in.) upstream of the catalyst at the centroid of the catalyst face area, and locate a temperature monitor (mandatory) that will indicate the catalyst exhaust temperature. This temperature monitor is centrally located within 25 mm (1 in.) downstream at the centroid of catalyst face area. Record these locations.

8.5.2 Locate wood heater surface temperature monitors at five locations on the wood heater firebox exterior surface. Position the temperature monitors centrally on the top surface, on two sidewall surfaces, and on the bottom and back surfaces. Position the monitor sensing tip on the firebox exterior surface inside of any heat shield, air circulation walls, or other wall or shield separated from the firebox exterior surface. Surface temperature locations for unusual design shapes (*e.g.*, spherical, etc.) shall be positioned so that there are four surface temperature monitors in both the vertical and horizontal planes passing at right angles through the centroid of the firebox, not including the fuel loading door (total of five temperature monitors).

8.6 Test Facility Conditions.

8.6.1 Locate the test facility temperature monitor on the horizontal plane that includes the primary air intake opening for the wood heater. Locate the temperature monitor 1 to 2 m (3 to 6 ft) from the front of the wood heater in the 90° sector in front of the wood heater.

8.6.2 Use an anemometer to measure the air velocity. Measure and record the room air velocity before the pretest ignition period (Section 8.7) and once immediately following the test run completion.

8.6.3 Measure and record the test facility's ambient relative humidity, barometric pressure, and temperature before and after each test run.

8.6.4 Measure and record the flue draft or static pressure in the flue at a location no greater than 0.3 m (1 ft) above the flue connector at the wood heater exhaust during the test run at the recording intervals (Section 8.8.2).

8.7 Wood Heater Firebox Volume.

8.7.1 Determine the firebox volume using the definitions for height, width, and length in section 3. Volume adjustments due to presence of firebrick and other permanent fixtures may be necessary. Adjust width and length dimensions to extend to the metal wall of the wood heater above the firebrick or permanent obstruction if the firebrick or obstruction extending the length of the side(s) or back wall extends less than one-third of the usable firebox height. Use the width or length dimensions inside the firebrick if the firebrick extends more than one-third of the usable firebox height. If a log retainer or grate is a permanent fixture and the manufacturer recommends that no fuel be placed outside the retainer, the area outside of the retainer is excluded from the firebox volume calculations.

8.7.2 In general, exclude the area above the ash lip if that area is less than 10 percent of the usable firebox volume. Otherwise, take into account consumer loading practices. For instance, if fuel is to be loaded front-to-back, an ash lip may be considered usable firebox volume.

8.7.3 Include areas adjacent to and above a baffle (up to two inches above the fuel loading opening) if four inches or more horizontal space exist between the edge of the baffle and a vertical obstruction (*e.g.*, sidewalls or air channels).

8.8 Test Fuel Charge.

8.8.1 Prepare the test fuel pieces in accordance with the specifications outlined in sections 7.1 and 7.2. Determine the test fuel moisture content with a calibrated electrical

resistance meter or other equivalent performance meter. If necessary, convert fuel moisture content values from dry basis ($\%M_d$) to wet basis ($\%M_w$) in section 12.2 using Equation 28–1. Determine fuel moisture for each fuel piece (not including spacers) by averaging at least three moisture meter readings, one from each of three sides, measured parallel to the wood grain. Average all the readings for all the fuel pieces in the test fuel charge. If an electrical resistance type meter is used, penetration of insulated electrodes shall be one-fourth the thickness of the test fuel piece or 19 mm (0.75 in.), whichever is greater. Measure the moisture content within a 4-hour period prior to the test run. Determine the fuel temperature by measuring the temperature of the room where the wood has been stored for at least 24 hours prior to the moisture determination.

8.8.2 Attach the spacers to the test fuel pieces with uncoated, ungalvanized nails or staples as illustrated in Figure 28–2. Attachment of spacers to the top of the test fuel piece(s) on top of the test fuel charge is optional.

8.8.3 To avoid stacking difficulties, or when a whole number of test fuel pieces does not result, all piece lengths shall be adjusted uniformly to remain within the specified loading density. The shape of the test fuel crib shall be geometrically similar to the shape of the firebox volume without resorting to special angular or round cuts on the individual fuel pieces.

8.8.4 The test fuel loading density shall be 112 ±11.2 kg/m³ (7 ±0.7 lb/ft³) of usable firebox volume on a wet basis.

8.9 Sampling Equipment. Prepare the sampling equipment as defined by the selected method (*i.e.*, either Method 5G or Method 5H). Collect one particulate emission sample for each test run.

8.10 Secondary Air Adjustment Validation.

8.10.1 If design drawings do not show the introduction of secondary air into a chamber outside the firebox (see ''secondary air supply'' under section 3.0, Definitions), conduct a separate test of the wood heater's secondary air supply. Operate the wood heater at a burn rate in Category 1 (Section 8.1.1) with the secondary air supply operated following the manufacturer's written instructions. Start the secondary air validation test run as described in section 8.8.1, except no emission sampling is necessary and burn rate data shall be recorded at 5-minute intervals.

8.10.2 After the start of the test run, operate the wood heater with the secondary air supply set as per the manufacturer's instructions, but with no adjustments to this setting. After 25 percent of the test fuel has been consumed, adjust the secondary air supply controls to another setting, as per the manufacturer's instructions. Record the burn rate data (5-minute intervals) for 20 minutes following the air supply adjustment.

8.10.3 Adjust the air supply control(s) to the original position(s), operate at this condition for at least 20 minutes, and repeat the air supply adjustment procedure above. Repeat the procedure three times at equal intervals over the entire burn period as defined in section 8.8. If the secondary air adjustment results in a burn rate change of more than an average of 25 percent between the 20-minute periods before and after the secondary adjustments, the secondary air supply shall be considered a primary air supply, and no adjustment to this air supply is allowed during the test run.

8.10.4 The example sequence below describes a typical secondary air adjustment validation check. The first cycle begins after at least 25 percent of the test fuel charge has been consumed.

Cycle 1
- Part 1, sec air adjusted to final position—20 min
- Part 2, sec air adjusted to final position—20 min
- Part 3, sec air adjusted to final position—20 min

Cycle 2
- Part 1, sec air adjusted to final position—20 min
- Part 2, sec air adjusted to final position—20 min
- Part 3, sec air adjusted to final position—20 min

Cycle 3
- Part 1, sec air adjusted to final position—20 min
- Part 2, sec air adjusted to final position—20 min
- Part 3, sec air adjusted to final position—20 min

Note that the cycles may overlap; that is, Part 3 of Cycle 1 may coincide in part or in total with Part 1 of Cycle 2. The calculation of the secondary air percent effect for this example is as follows:

$$\%BR_{sec} = \frac{\left|\overline{BR_{1,3}} - \overline{BR_2}\right|}{\overline{BR_{1,3}}} \times 100 \qquad \text{Eq. 28-1}$$

8.11 Pretest Ignition. Build a fire in the wood heater in accordance with the manufacturer's written instructions.

8.11.1 Pretest Fuel Charge. Crumpled newspaper loaded with kindling may be used to help ignite the pretest fuel. The pretest fuel, used to sustain the fire, shall meet the same fuel requirements prescribed in section 7.1. The pretest fuel charge shall consist of whole 2 × 4's that are no less than ⅓ the length of the test fuel pieces. Pieces of 4 × 4 lumber in approximately the same weight ratio as for the test fuel charge may be added to the pretest fuel charge.

8.11.2 Wood Heater Operation and Adjustments. Set the air inlet supply controls at any position that will maintain combustion of the pretest fuel load. At least one hour before the start of the test run, set the air supply controls at the approximate positions necessary to achieve the burn rate desired for the test run. Adjustment of the air supply controls, fuel addition or subtractions, and coalbed raking shall be kept to a minimum but are allowed up to 15 minutes prior to the start of the test run. For the purposes of this method, coalbed raking is the use of a metal tool (poker) to stir coals, break burning fuel into smaller pieces, dislodge fuel pieces from positions of poor combustion, and check for the condition of uniform charcoalization. Record all adjustments made to the air supply controls, adjustments to and additions or subtractions of fuel, and any other changes to wood heater operations that occur during pretest ignition period. Record fuel weight data and wood heater temperature measurements at 10-minute intervals during the hour of the pretest ignition period preceding the start of the test run. During the 15-minute period prior to the start of the test run, the wood heater loading door shall not be open more than a total of 1 minute. Coalbed raking is the only adjustment allowed during this period.

NOTE: One purpose of the pretest ignition period is to achieve uniform charcoalization of the test fuel bed prior to loading the test fuel charge. Uniform charcoalization is a general condition of the test fuel bed evidenced by an absence of large pieces of burning wood in the coal bed and the remaining fuel pieces being brittle enough to be broken into smaller charcoal pieces with a metal poker. Manipulations to the fuel bed prior to the start of the test run should be done to achieve uniform charcoalization while maintaining the desired burn rate. In addition, some wood heaters (*e.g.*, high mass units) may require extended pretest burn time and fuel additions to reach an initial average surface temperature sufficient to meet the thermal equilibrium criteria in section 8.3.

8.11.3 The weight of pretest fuel remaining at the start of the test run is determined as the difference between the weight of the wood heater with the remaining pretest fuel and the tare weight of the cleaned, dry wood heater with or without dry ash or sand added consistent with the manufacturer's instructions and the owner's manual. The tare weight of the wood heater must be determined with the wood heater (and ash, if added) in a dry condition.

8.12 Test Run. Complete a test run in each burn rate category, as follows:

8.12.1 Test Run Start.

8.12.1.1 When the kindling and pretest fuel have been consumed to leave a fuel weight between 20 and 25 percent of the weight of the test fuel charge, record the weight of the fuel remaining and start the test run. Record and report any other criteria, in addition to those specified in this section, used to determine the moment of the test run start (*e.g.*, firebox or catalyst temperature), whether such criteria are specified by the wood heater manufacturer or the testing laboratory. Record all wood heater individual surface temperatures, catalyst temperatures, any initial sampling method measurement values, and begin the particulate emission sampling. Within 1 minute following the start of the test run, open the wood heater door, load the test fuel charge, and record the test fuel charge weight. Recording of average, rather than individual, surface temperatures is acceptable for tests conducted in accordance with §60.533(o)(3)(i) of 40 CFR part 60.

8.12.1.2 Position the fuel charge so that the spacers are parallel to the floor of the firebox, with the spacer edges abutting each other. If loading difficulties result, some fuel pieces may be placed on edge. If the usable firebox volume is between 0.043 and 0.085 m^3 (1.5 and 3.0 ft^3), alternate the piece sizes in vertical stacking layers to the extent possible. For example, place 2 × 4's on the bottom layer in direct contact with the coal bed and 4 × 4's on the next layer, etc. (See Figure 28–3). Position the fuel pieces parallel to each other and parallel to the longest wall of the firebox to the extent possible within the specifications in section 8.8.

8.12.1.3 Load the test fuel in appliances having unusual or unconventional firebox design maintaining air space intervals between the test fuel pieces and in conformance with the manufacturer's written instructions. For any appliance that will not accommodate the loading arrangement specified in the paragraph above, the test facility personnel shall contact the Administrator for an alternative loading arrangement.

8.12.1.4 The wood heater door may remain open and the air supply controls adjusted up to five minutes after the start of the test run in order to make adjustments to the test fuel charge and to ensure ignition of the test fuel charge has occurred. Within the five minutes after the start of the test run, close the wood heater door and adjust the air supply controls to the position determined to produce

the desired burn rate. No other adjustments to the air supply controls or the test fuel charge are allowed (except as specified in sections 8.12.3 and 8.12.4) after the first five minutes of the test run. Record the length of time the wood heater door remains open, the adjustments to the air supply controls, and any other operational adjustments.

8.12.2 Data Recording. Record on a data sheet similar to that shown in Figure 28–4, at intervals no greater than 10 minutes, fuel weight data, wood heater individual surface and catalyst temperature measurements, other wood heater operational data (*e.g.*, draft), test facility temperature and sampling method data.

8.12.3 Test Fuel Charge Adjustment. The test fuel charge may be adjusted (*i.e.*, repositioned) once during a test run if more than 60 percent of the initial test fuel charge weight has been consumed and more than 10 minutes have elapsed without a measurable (<0.05 kg (0.1 lb) or 1.0 percent, whichever is greater) weight change. The time used to make this adjustment shall be less than 15 seconds.

8.12.4 Air Supply Adjustment. Secondary air supply controls may be adjusted once during the test run following the manufacturer's written instructions (see section 8.10). No other air supply adjustments are allowed during the test run. Recording of wood heater flue draft during the test run is optional for tests conducted in accordance with § 60.533(o)(3)(i) of 40 CFR part 60.

8.12.5 Auxiliary Wood Heater Equipment Operation. Heat exchange blowers sold with the wood heater shall be operated during the test run following the manufacturer's written instructions. If no manufacturer's written instructions are available, operate the heat exchange blower in the ''high'' position. (Automatically operated blowers shall be operated as designed.) Shaker grates, by-pass controls, or other auxiliary equipment may be adjusted only one time during the test run following the manufacturer's written instructions.

Record all adjustments on a wood heater operational written record.

NOTE: If the wood heater is sold with a heat exchange blower as an option, test the wood heater with the heat exchange blower operating as described in sections 8.1 through 8.12 and report the results. As an alternative to repeating all test runs without the heat exchange blower operating, one additional test run may be without the blower operating as described in section 8.12.5 at a burn rate in Category 2 (Section 8.1.1). If the emission rate resulting from this test run without the blower operating is equal to or less than the emission rate plus 1.0 g/hr (0.0022 lb/hr) for the test run in burn rate Category 2 with the blower operating, the wood heater may be considered to have the same average emission rate with or without the blower operating. Additional test runs without the blower operating are unnecessary.

8.13 Test Run Completion. Continue emission sampling and wood heater operation for 2 hours. The test run is completed when the remaining weight of the test fuel charge is 0.00 kg (0.0 lb). End the test run when the scale has indicated a test fuel charge weight of 0.00 kg (0.0 lb) or less for 30 seconds. At the end of the test run, stop the particulate sampling, and record the final fuel weight, the run time, and all final measurement values.

8.14 Wood Heater Thermal Equilibrium. The average of the wood heater surface temperatures at the end of the test run shall agree with the average surface temperature at the start of the test run to within 70 °C (126 °F).

8.15 Consecutive Test Runs. Test runs on a wood heater may be conducted consecutively provided that a minimum one-hour interval occurs between test runs.

8.16 Additional Test Runs. The testing laboratory may conduct more than one test run in each of the burn rate categories specified in section 8.1.1. If more than one test run is conducted at a specified burn rate, the results from at least two-thirds of the test runs in that burn rate category shall be used in calculating the weighted average emission rate (see section 12.2). The measurement data and results of all test runs shall be reported regardless of which values are used in calculating the weighted average emission rate (see note in section 8.1).

9.0 Quality Control

Same as section 9.0 of either Method 5G or Method 5H.

10.0 Calibration and Standardizations

Same as section 10.0 of either Method 5G or Method 5H, with the addition of the following:

10.1 Platform Scale. Perform a multi-point calibration (at least five points spanning the operational range) of the platform scale before its initial use. The scale manufacturer's calibration results are sufficient for this purpose. Before each certification test, audit the scale with the wood heater in place by weighing at least one calibration weight (Class F) that corresponds to between 20 percent and 80 percent of the expected test fuel charge weight. If the scale cannot reproduce the value of the calibration weight within 0.05 kg (0.1 lb) or 1 percent of the expected test fuel charge weight, whichever is greater, recalibrate the scale before use with at least five calibration weights spanning the operational range of the scale.

10.2 Balance (optional). Calibrate as described in section 10.1.

10.3 Temperature Monitor. Calibrate as in Method 2, section 4.3, before the first certification test and semiannually thereafter.

10.4 Moisture Meter. Calibrate as per the manufacturer's instructions before each certification test.

10.5 Anemometer. Calibrate the anemometer as specified by the manufacturer's instructions before the first certification test and semiannually thereafter.

10.6 Barometer. Calibrate against a mercury barometer before the first certification test and semiannually thereafter.

10.7 Draft Gauge. Calibrate as per the manufacturer's instructions; a liquid manometer does not require calibration.

10.8 Humidity Gauge. Calibrate as per the manufacturer's instructions before the first certification test and semiannually thereafter.

11.0 Analytical Procedures

Same as section 11.0 of either Method 5G or Method 5H.

12.0 Data Analysis and Calculations

Same as section 12.0 of either Method 5G or Method 5H, with the addition of the following:

12.1 Nomenclature.

BR = Dry wood burn rate, kg/hr (lb/hr)

E_i = Emission rate for test run, i, from Method 5G or 5H, g/hr (lb/hr)

E_w = Weighted average emission rate, g/hr (lb/hr)

k_i = Test run weighting factor = $P_{i+1} - P_{i-1}$

$\%M_d$ = Fuel moisture content, dry basis, percent.

$\%M_w$ = Average moisture in test fuel charge, wet basis, percent.

n = Total number of test runs.

P_i = Probability for burn rate during test run, i, obtained from Table 28–1. Use linear interpolation to determine probability values for burn rates between those listed on the table.

W_{wd} = Total mass of wood burned during the test run, kg (lb).

12.2 Wet Basis Fuel Moisture Content.

$$\%M_w = \frac{100(\%M_d)}{100 + \%M_d} \qquad \text{Eq. 28-2}$$

12.3 Weighted Average Emission Rate. Calculate the weighted average emission rate (E_w) using Equation 28–1:

$$E_w = \frac{\sum_{i=1}^{n}(K_i E_i)}{\sum_{i=1}^{n} K_i} \qquad \text{Eq. 28-3}$$

NOTE: P_o always equals 0, $P_{(n+1)}$ always equals 1, P_1 corresponds to the probability of the lowest recorded burn rate, P_2 corresponds to the probability of the next lowest burn rate, etc. An example calculation is in section 12.3.1.

12.3.1 Example Calculation of Weighted Average Emission Rate.

Burn rate category	Test No.	Burn rate (Dry-kg/hr)	Emissions (g/hr)
1	1	0.65	5.0
2[1]	2	0.85	6.7
2	3	0.90	4.7
2	4	1.00	5.3
3	5	1.45	3.8
4	6	2.00	5.1

[1] As permitted in section 6.6, this test run may be omitted from the calculation of the weighted average emission rate because three runs were conducted for this burn rate category.

Test No.	Burn rate	P_i	E_i	K_i
0	.....	0.000	.....	.....
1	0.65	0.121	5.0	0.300
2	0.90	0.300	4.7	0.259
3	1.00	0.380	5.3	0.422
4	1.45	0.722	3.8	0.532
5	2.00	0.912	5.1	0.278
6	.....	1.000	.....	.....

$K_1 = P_2 - P_0 = 0.300 - 0 = 0.300$
$K_2 = P_3 - P_1 = 0.381 - 0.121 = 0.259$
$K_3 = P_4 - P_2 = 0.722 - 0.300 = 0.422$
$K_4 = P_5 - P_3 = 0.912 - 0.380 = 0.532$
$K_5 = P_6 - P_4 = 1.000 - 0.722 = 0.278$

Weighted Average Emission Rate, E_w, Calculation

$$E_w = \frac{\sum(K_i E_i)}{\sum K_i}$$

$$= \frac{(0.3)(5.0)+(0.259)(4.7)+(0.422)(5.3)+(0.532)(3.8)+(0.278)(5.1)}{1.791}$$

$$= 4.69\,g/hr$$

12.4 Average Wood Heater Surface Temperatures. Calculate the average of the wood heater surface temperatures for the start of the test run (Section 8.12.1) and for the test run completion (Section 8.13). If the two average temperatures do not agree within 70 °C (125 °F), report the test run results, but do not include the test run results in the test average. Replace such test run results with results from another test run in the same burn rate category.

12.5 Burn Rate. Calculate the burn rate (BR) using Equation 28–3:

$$BR = \frac{60 W_{wd}}{\theta} \times \frac{100 - \%M_w}{100} \qquad \text{Eq. 28-3}$$

12.6 Reporting Criteria. Submit both raw and reduced test data for wood heater tests.

12.6.1 Suggested Test Report Format.

12.6.1.1 Introduction.

12.6.1.1.1 Purpose of test-certification, audit, efficiency, research and development.

12.6.1.1.2 Wood heater identification-manufacturer, model number, catalytic/noncatalytic, options.

12.6.1.1.3 Laboratory-name, location (altitude), participants.

12.6.1.1.4 Test information-date wood heater received, date of tests, sampling methods used, number of test runs.

12.6.1.2 Summary and Discussion of Results

12.6.1.2.1 Table of results (in order of increasing burn rate)-test run number, burn rate, particulate emission rate, efficiency (if determined), averages (indicate which test runs are used).

12.6.1.2.2 Summary of other data-test facility conditions, surface temperature averages, catalyst temperature averages, pretest fuel weights, test fuel charge weights, run times.

12.6.1.2.3 Discussion-Burn rate categories achieved, test run result selection, specific test run problems and solutions.

12.6.1.3 Process Description.

12.6.1.3.1 Wood heater dimensions-volume, height, width, lengths (or other linear dimensions), weight, volume adjustments.

12.6.1.3.2 Firebox configuration-air supply locations and operation, air supply introduction location, refractory location and dimensions, catalyst location, baffle and by-pass location and operation (include line drawings or photographs).

12.6.1.3.3 Process operation during test-air supply settings and adjustments, fuel bed adjustments, draft.

12.6.1.3.4 Test fuel-test fuel properties (moisture and temperature), test fuel crib description (include line drawing or photograph), test fuel loading density.

12.6.1.4 Sampling Locations.

12.6.1.4.1 Describe sampling location relative to wood heater. Include drawing or photograph.

12.6.1.5 Sampling and Analytical Procedures

12.6.1.5.1 Sampling methods-brief reference to operational and sampling procedures and optional and alternative procedures used.

12.6.1.5.2 Analytical methods-brief description of sample recovery and analysis procedures.

12.6.1.6 Quality Control and Assurance Procedures and Results

12.6.1.6.1 Calibration procedures and results-certification procedures, sampling and analysis procedures.

12.6.1.6.2 Test method quality control procedures-leak-checks, volume meter checks, stratification (velocity) checks, proportionality results.

12.6.1.7 Appendices

12.6.1.7.1 Results and Example Calculations. Complete summary tables and accompanying examples of all calculations.

12.6.1.7.2 Raw Data. Copies of all uncorrected data sheets for sampling measurements, temperature records and sample recovery data. Copies of all pretest burn rate and wood heater temperature data.

12.6.1.7.3 Sampling and Analytical Procedures. Detailed description of procedures followed by laboratory personnel in conducting the certification test, emphasizing particular parts of the procedures differing from the methods (*e.g.*, approved alternatives).

12.6.1.7.4 Calibration Results. Summary of all calibrations, checks, and audits pertinent to certification test results with dates.

12.6.1.7.5 Participants. Test personnel, manufacturer representatives, and regulatory observers.

12.6.1.7.6 Sampling and Operation Records. Copies of uncorrected records of activities not included on raw data sheets (*e.g.*, wood heater door open times and durations).

12.6.1.7.7 Additional Information. Wood heater manufacturer's written instructions for operation during the certification test.

12.6.2.1 Wood Heater Identification. Report wood heater identification information. An example data form is shown in Figure 28–4.

12.6.2.2 Test Facility Information. Report test facility temperature, air velocity, and humidity information. An example data form is shown on Figure 28–4.

12.6.2.3 Test Equipment Calibration and Audit Information. Report calibration and audit results for the platform scale, test fuel balance, test fuel moisture meter, and sampling equipment including volume metering systems and gaseous analyzers.

12.6.2.4 Pretest Procedure Description. Report all pretest procedures including pretest fuel weight, burn rates, wood heater temperatures, and air supply settings. An example data form is shown on Figure 28–4.

12.6.2.5 Particulate Emission Data. Report a summary of test results for all test runs and the weighted average emission rate. Submit copies of all data sheets and other records collected during the testing. Submit examples of all calculations.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Pellet Burning Heaters. Certification testing requirements and procedures for pellet burning wood heaters are identical to those for other wood heaters, with the following exceptions:

16.1.1 Test Fuel Properties. The test fuel shall be all wood pellets with a moisture content no greater than 20 percent on a wet basis (25 percent on a dry basis). Determine the wood moisture content with either ASTM D 2016–74 or 83, (Method A), ASTM D 4444–92, or ASTM D 4442–84 or 92 (all noted ASTM standards are incorporated by reference—see §60.17).

16.1.2 Test Fuel Charge Specifications. The test fuel charge size shall be as per the manufacturer's written instructions for maintaining the desired burn rate.

16.1.3 Wood Heater Firebox Volume. The firebox volume need not be measured or determined for establishing the test fuel charge size. The firebox dimensions and other heater specifications needed to identify the heater for certification purposes shall be reported.

16.1.4 Heater Installation. Arrange the heater with the fuel supply hopper on the platform scale as described in section 8.6.1.

16.1.5 Pretest Ignition. Start a fire in the heater as directed by the manufacturer's written instructions, and adjust the heater controls to achieve the desired burn rate. Operate the heater at the desired burn rate for at least 1 hour before the start of the test run.

16.1.6 Test Run. Complete a test run in each burn rate category as follows:

16.1.6.1 Test Run Start. When the wood heater has operated for at least 1 hour at the desired burn rate, add fuel to the supply hopper as necessary to complete the test run, record the weight of the fuel in the supply hopper (the wood heater weight), and start the test run. Add no additional fuel to the hopper during the test run.

Record all the wood heater surface temperatures, the initial sampling method measurement values, the time at the start of the test, and begin the emission sampling. Make no adjustments to the wood heater air supply or wood supply rate during the test run.

16.1.6.2 Data Recording. Record the fuel (wood heater) weight data, wood heater temperature and operational data, and emission sampling data as described in section 8.12.2.

16.1.6.3 Test Run Completion. Continue emission sampling and wood heater operation for 2 hours. At the end of the test run, stop the particulate sampling, and record the final fuel weight, the run time, and all final measurement values, including all wood heater individual surface temperatures.

16.1.7 Calculations. Determine the burn rate using the difference between the initial and final fuel (wood heater) weights and the procedures described in section 12.4. Complete the other calculations as described in section 12.0.

17.0 References

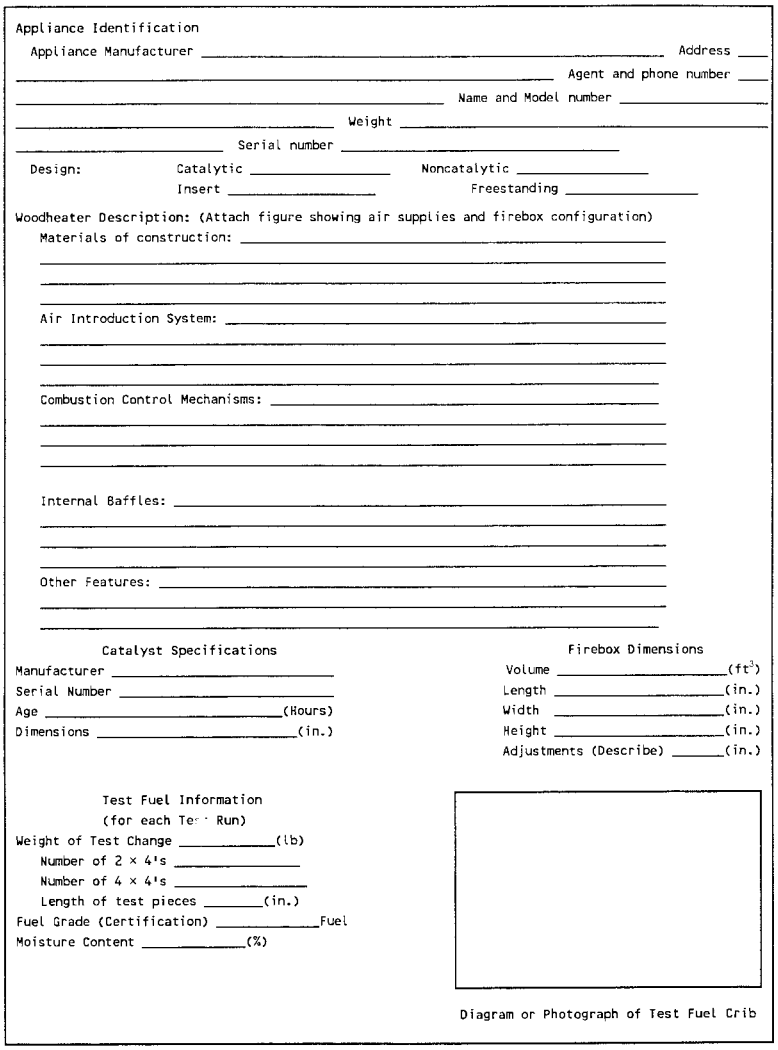
Same as Method 5G, with the addition of the following:

1. Radian Corporation. OMNI Environmental Services, Inc., Cumulative Probability for a Given Burn Rate Based on Data Generated in the CONEG and BPA Studies. Package of materials submitted to the Fifth Session of the Regulatory Negotiation Committee, July 16–17, 1986.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 28–1—BURN RATE WEIGHTED PROBABILITIES FOR CALCULATING WEIGHTED AVERAGE EMISSION RATES

Burn rate (kg/hr-dry)	Cumulative probability (P)	Burn rate (kg/hr-dry)	Cumulative probability (P)	Burn rate (kg/hr-dry)	Cumulative probability (P)
0.00	0.000	1.70	0.840	3.40	0.989
0.05	0.002	1.75	0.857	3.45	0.989
0.10	0.007	1.80	0.875	3.50	0.990
0.15	0.012	1.85	0.882	3.55	0.991
0.20	0.016	1.90	0.895	3.60	0.991
0.25	0.021	1.95	0.906	3.65	0.992
0.30	0.028	2.00	0.912	3.70	0.992
0.35	0.033	2.05	0.920	3.75	0.992
0.40	0.041	2.10	0.925	3.80	0.993
0.45	0.054	2.15	0.932	3.85	0.994
0.50	0.065	2.20	0.936	3.90	0.994
0.55	0.086	2.25	0.940	3.95	0.994
0.60	0.100	2.30	0.945	4.00	0.994
0.65	0.121	2.35	0.951	4.05	0.995
0.70	0.150	2.40	0.956	4.10	0.995
0.75	0.185	2.45	0.959	4.15	0.995
0.80	0.220	2.50	0.964	4.20	0.995
0.85	0.254	2.55	0.968	4.25	0.995
0.90	0.300	2.60	0.972	4.30	0.996
0.95	0.328	2.65	0.975	4.35	0.996
1.00	0.380	2.70	0.977	4.40	0.996
1.05	0.407	2.75	0.979	4.45	0.996
1.10	0.460	2.80	0.980	4.50	0.996
1.15	0.490	2.85	0.981	4.55	0.996
1.20	0.550	2.90	0.982	4.60	0.996
1.25	0.572	2.95	0.984	4.65	0.996
1.30	0.620	3.00	0.984	4.70	0.996
1.35	0.654	3.05	0.985	4.75	0.997
1.40	0.695	3.10	0.986	4.80	0.997
1.45	0.722	3.15	0.987	4.85	0.997
1.50	0.750	3.20	0.987	4.90	0.997
1.55	0.779	3.25	0.988	4.95	0.997
1.60	0.800	3.30	0.988	≥5.00	1.000
1.65	0.825	3.35	0.989	.....	.....



Appliance Identification

Appliance Manufacturer _____ Address ____

_____ Agent and phone number ____

_____ Name and Model number _____

_____ Weight _____

_____ Serial number _____

Design: Catalytic _____ Noncatalytic _____

Insert _____ Freestanding _____

Woodheater Description: (Attach figure showing air supplies and firebox configuration)

Materials of construction: _____

_____

_____

_____

Air Introduction System: _____

_____

_____

_____

Combustion Control Mechanisms: _____

_____

_____

_____

Internal Baffles: _____

_____

_____

_____

Other Features: _____

_____

_____

Catalyst Specifications

Manufacturer _____

Serial Number _____

Age _____(Hours)

Dimensions _____(in.)

Firebox Dimensions

Volume _____(ft^3)

Length _____(in.)

Width _____(in.)

Height _____(in.)

Adjustments (Describe) _____(in.)

Test Fuel Information
(for each Test Run)

Weight of Test Charge _____(lb)

Number of 2 × 4's _____

Number of 4 × 4's _____

Length of test pieces _____(in.)

Fuel Grade (Certification) _____Fuel

Moisture Content _____(%)

Diagram or Photograph of Test Fuel Crib

Figure 28-1. Wood Heater and Test Fuel Information.

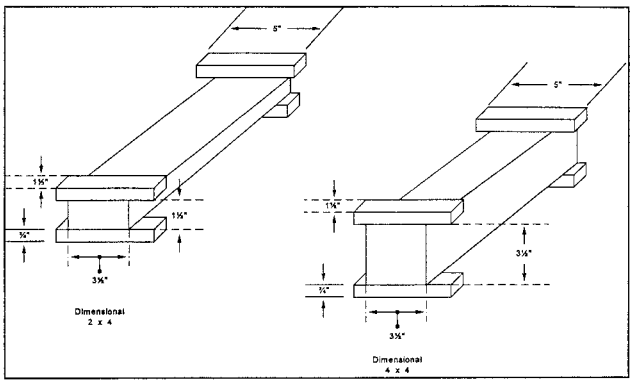


Figure 28-2. Test Fuel Spacer Dimensions.

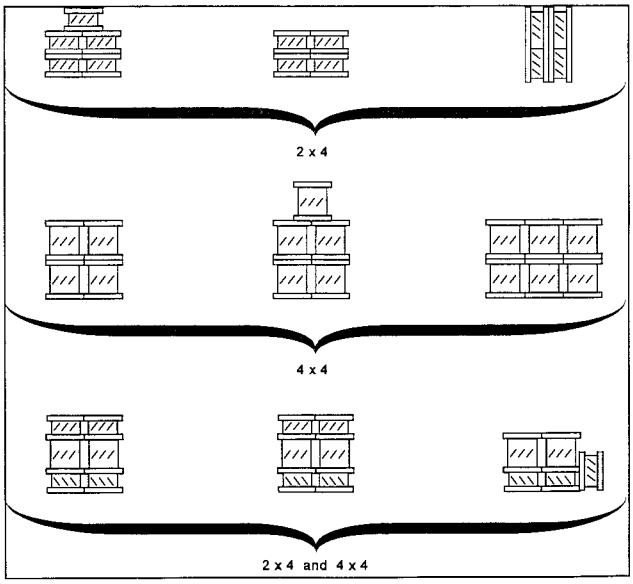


Figure 28-3. Test Fuel Crib Arrangements.

Sheet _____ of _____

Date _____

Operator _____

Sampling Method _____

Wood Heater Information

Manufacturer _____

Model _____

Primary Air Setting _____

Secondary Air Setting _____

Thermostat Setting _____

Other Settings _____

Test Run Information

Test Run No. _____

Burn Rate _____

Room Temperature before/after _____/_____

Barometric Pressure before/after _____/_____

Relative Humidity before/after _____/_____

Room Air Velocity before/after _____/_____

Surface Temp Average Pretest _____ end _____

Test Run Time (minutes)	Test Fuel Scale Reading (lb)	Surface Temperature					Catalyst Temperature		Flue Draft (in. H_2O)
							Inlet (°F)	Outlet (°F)	
(Pretest Period)									
(Test Run Start)									

Figure 28-4. Test Run Wood Heater Operation Data Sheet.

METHOD 28A—MEASUREMENT OF AIR- TO-FUEL RATIO AND MINIMUM ACHIEVABLE BURN RATES FOR WOOD-FIRED APPLIANCES

NOTE: This method does not include all or the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should also have a thorough knowledge of at least the following additional test methods: Method 3, Method 3A, Method 5H, Method 6C, and Method 28.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the measurement of air-to-fuel ratios and minimum achievable burn rates, for determining whether a wood-fired appliance is an affected facility, as specified in 40 CFR 60.530.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from a location in the stack of a wood-fired appliance while the appliance is operating at a prescribed set of conditions. The gas sample is analyzed for carbon dioxide (CO_2), oxygen (O_2), and carbon monoxide (CO). These stack gas components are measured for determining the dry molecular weight of the exhaust gas. Total moles of exhaust gas are determined stoichiometrically. Air-to-fuel ratio is determined by relating the mass of dry combustion air to the mass of dry fuel consumed.

3.0 Definitions

Same as Method 28, section 3.0, with the addition of the following:

3.1 Air-to-fuel ratio means the ratio of the mass of dry combustion air introduced into the firebox to the mass of dry fuel consumed (grams of dry air per gram of dry wood burned).

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Test Facility. Insulated Solid Pack Chimney, Platform Scale and Monitor, Test Facility Temperature Monitor, Balance, Moisture Meter, Anemometer, Barometer, Draft Gauge, Humidity Gauge, Wood Heater Flue, and Test Facility. Same as Method 28, sections 6.1, 6.2, and 6.4 to 6.12, respectively.

6.2 Sampling System. Probe, Condenser, Valve, Pump, Rate Meter, Flexible Bag, Pressure Gauge, and Vacuum Gauge. Same as Method 3, sections 6.2.1 to 6.2.8, respectively. Alternatively, the sampling system described in Method 5H, section 6.1 may be used.

6.3 Exhaust Gas Analysis. Use one or both of the following:

6.3.1 Orsat Analyzer. Same as Method 3, section 6.1.3

6.3.2 Instrumental Analyzers. Same as Method 5H, sections 6.1.3.4 and 6.1.3.5, for CO_2 and CO analyzers, except use a CO analyzer with a range of 0 to 5 percent and use a CO_2 analyzer with a range of 0 to 5 percent. Use an O_2 analyzer capable of providing a measure of O_2 in the range of 0 to 25 percent by volume at least once every 10 minutes.

7.0 Reagents and Standards

7.1 Test Fuel and Test Fuel Spacers. Same as Method 28, sections 7.1 and 7.2, respectively.

7.2 Cylinder Gases. For each of the three analyzers, use the same concentration as specified in sections 7.2.1, 7.2.2, and 7.2.3 of Method 6C.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Wood Heater Air Supply Adjustments.

8.1.1 This section describes how dampers are to be set or adjusted and air inlet ports closed or sealed during Method 28A tests. The specifications in this section are intended to ensure that affected facility determinations are made on the facility configurations that could reasonably be expected to be employed by the user. They are also intended to prevent circumvention of the standard through the addition of an air port that would often be blocked off in actual use. These specifications are based on the assumption that consumers will remove such items as dampers or other closure mechanism stops if this can be done readily with household tools; that consumers will block air inlet passages not visible during normal operation of the appliance using aluminum tape or parts generally available at retail stores; and that consumers will cap off any threaded or flanged air inlets. They also assume that air leakage around glass doors, sheet metal joints or through inlet grilles visible during normal operation of the appliance would not be further blocked or taped off by a consumer.

8.1.2 It is not the intention of this section to cause an appliance that is clearly designed, intended, and, in most normal installations, used as a fireplace to be converted into a wood heater for purposes of applicability testing. Such a fireplace would be identifiable by such features as large or multiple glass doors or panels that are not gasketed, relatively unrestricted air inlets intended, in large part, to limit smoking and fogging of glass surfaces, and other aesthetic features not normally included in wood heaters.

8.1.3 Adjustable Air Supply Mechanisms. Any commercially available flue damper, other adjustment mechanism or other air

inlet port that is designed, intended or otherwise reasonably expected to be adjusted or closed by consumers, installers, or dealers and which could restrict air into the firebox shall be set so as to achieve minimum air into the firebox (*i.e.*, closed off or set in the most closed position).

8.1.3.1 Flue dampers, mechanisms and air inlet ports which could reasonably be expected to be adjusted or closed would include:

8.1.3.1.1 All internal or externally adjustable mechanisms (including adjustments that affect the tightness of door fittings) that are accessible either before and/or after installation.

8.1.3.1.2 All mechanisms, other inlet ports, or inlet port stops that are identified in the owner's manual or in any dealer literature as being adjustable or alterable. For example, an inlet port that could be used to provide access to an outside air duct but which is identified as being closable through use of additional materials whether or not they are supplied with the facility.

8.1.3.1.3 Any combustion air inlet port or commercially available flue damper or mechanism stop, which would readily lend itself to closure by consumers who are handy with household tools by the removal of parts or the addition of parts generally available at retail stores (*e.g.*, addition of a pipe cap or plug, addition of a small metal plate to an inlet hole on a nondecorative sheet metal surface, or removal of riveted or screwed damper stops).

8.1.3.1.4 Any flue damper, other adjustment mechanisms or other air inlet ports that are found and documented in several (*e.g.*, a number sufficient to reasonably conclude that the practice is not unique or uncommon) actual installations as having been adjusted to a more closed position, or closed by consumers, installers, or dealers.

8.1.4 Air Supply Adjustments During Test. The test shall be performed with all air inlets identified under this section in the closed or most closed position or in the configuration which otherwise achieves the lowest air inlet (*i.e.*, greatest blockage).

NOTE: For the purposes of this section, air flow shall not be minimized beyond the point necessary to maintain combustion or beyond the point that forces smoke into the room.

8.1.5 Notwithstanding section 8.1.1, any flue damper, adjustment mechanism, or air inlet port (whether or not equipped with flue dampers or adjusting mechanisms) that is visible during normal operation of the appliance and which could not reasonably be closed further or blocked except through means that would significantly degrade the aesthetics of the facility (*e.g.*, through use of duct tape) will not be closed further or blocked.

8.2 Sampling System.

8.2.1 Sampling Location. Same as Method 5H, section 8.1.2.

8.2.2 Sampling System Set Up. Set up the sampling equipment as described in Method 3, section 8.1.

8.3 Wood Heater Installation, Test Facility Conditions, Wood Heater Firebox Volume, and Test Fuel Charge. Same as Method 28, sections 8.4 and 8.6 to 8.8, respectively.

8.4 Pretest Ignition. Same as Method 28, section 8.11. Set the wood heater air supply settings to achieve a burn rate in Category 1 or the lowest achievable burn rate (see section 8.1).

8.5 Test Run. Same as Method 28, section 8.12. Begin sample collection at the start of the test run as defined in Method 28, section 8.12.1.

8.5.1 Gas Analysis.

8.5.1.1 If Method 3 is used, collect a minimum of two bag samples simultaneously at a constant sampling rate for the duration of the test run. A minimum sample volume of 30 liters (1.1 ft^3) per bag is recommended.

8.5.1.2 If instrumental gas concentration measurement procedures are used, conduct the gas measurement system performance tests, analyzer calibration, and analyzer calibration error check outlined in Method 6C, sections 8.2.3, 8.2.4, 8.5, and 10.0, respectively. Sample at a constant rate for the duration of the test run.

8.5.2 Data Recording. Record wood heater operational data, test facility temperature, sample train flow rate, and fuel weight data at intervals of no greater than 10 minutes.

8.5.3 Test Run Completion. Same as Method 28, section 8.13.

9.0 Quality Control

9.1 Data Validation. The following quality control procedure is suggested to provide a check on the quality of the data.

9.1.1 Calculate a fuel factor, F_o, using Equation 28A–1 in section 12.2.

9.1.2 If CO is present in quantities measurable by this method, adjust the O_2 and CO_2 values before performing the calculation for F_o as shown in section 12.3 and 12.4.

9.1.3 Compare the calculated F_o factor with the expected F_o range for wood (1.000–1.120). Calculated F_o values beyond this acceptable range should be investigated before accepting the test results. For example, the strength of the solutions in the gas analyzer and the analyzing technique should be checked by sampling and analyzing a known concentration, such as air. If no detectable or correctable measurement error can be identified, the test should be repeated. Alternatively, determine a range of air-to-fuel ratio results that could include the correct value by using an F_o value of 1.05 and calculating a potential range of CO_2 and O_2 values. Acceptance of such results will be based on whether the calculated range includes the

exemption limit and the judgment of the Administrator.

9.2 Method 3 Analyses. Compare the results of the analyses of the two bag samples. If all the gas components (O_2, CO, and CO_2) values for the two analyses agree within 0.5 percent (*e.g.*, 6.0 percent O_2 for bag 1 and 6.5 percent O_2 for bag 2, agree within 0.5 percent), the results of the bag analyses may be averaged for the calculations in section 12. If the analysis results do not agree within 0.5 percent for each component, calculate the air-to-fuel ratio using both sets of analyses and report the results.

10.0 Calibration and Standardization

[Reserved]

11.0 Analytical Procedures

11.1 Method 3 Integrated Bag Samples. Within 4 hours after the sample collection, analyze each bag sample for percent CO_2, O_2, and CO using an Orsat analyzer as described in Method 3, section 11.0.

11.2 Instrumental Analyzers. Average the percent CO_2, CO, and O_2 values for the test run.

12.0 Data Analyses and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figure after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

12.1 Nomenclature.

M_d = Dry molecular weight, g/g-mole (lb/lb-mole).

N_T = Total gram-moles of dry exhaust gas per kg of wood burned (lb-moles/lb).

$\%CO_2$ = Percent CO_2 by volume (dry basis).

%CO = Percent CO by volume (dry basis).

$\%N_2$ = Percent N_2 by volume (dry basis).

$\%O_2$ = Percent O2 by volume (dry basis).

Y_{HC} = Assumed mole fraction of HC (dry as CH_4) = 0.0088 for catalytic wood heaters; = 0.0132 for noncatalytic wood heaters. = 0.0080 for pellet-fired wood heaters.

Y_{CO} = Measured mole fraction of CO (*e.g.*, 1 percent CO = .01 mole fraction), g/g-mole (lb/lb-mole).

Y_{CO2} = Measured mole fraction of CO_{CO2} (*e.g.*, 10 percent CO_2 = .10 mole fraction), g/g-mole (lb/lb-mole).

0.280 = Molecular weight of N_2 or CO, divided by 100.

0.320 = Molecular weight of O_2 divided by 100.

0.440 = Molecular weight of CO_2 divided by 100.

20.9 = Percent O_2 by volume in ambient air.

42.5 = Gram-moles of carbon in 1 kg of dry wood assuming 51 percent carbon by weight dry basis (.0425 lb/lb-mole).

510 = Grams of carbon in exhaust gas per kg of wood burned.

1,000 = Grams in 1 kg.

12.2 Fuel Factor. Use Equation 28A–1 to calculate the fuel factor.

$$F_o = \frac{20.9 - \%O_2}{\%CO_2} \qquad \text{Eq. 28A-1}$$

12. 3 Adjusted $\%CO_2$. Use Equation 28A–2 to adjust CO_2 values if measurable CO is present.

$$\%CO_{2(adj)} = \%CO_2 + \%CO \qquad \text{Eq. 28A-2}$$

12.4 Adjusted $\%O_2$. Use Equation 28A–3 to adjust O_2 value if measurable CO is present.

$$\%O_{2(adj)} = \%O_2 - 0.5\%CO \qquad \text{Eq. 28A-3}$$

12.5 Dry Molecular Weight. Use Equation 28A–4 to calculate the dry molecular weight of the stack gas.

$$M_d = 0.440(\%CO_2) + 0.320(\%O_2) + 0.280(\%N_2 + \%CO) \qquad \text{Eq. 28A-4}$$

NOTE: The above equation does not consider argon in air (about 0.9 percent, molecular weight of 39.9). A negative error of about 0.4 percent is introduced. Argon may

be included in the analysis using procedures subject to approval of the Administrator.

12.6 Dry Moles of Exhaust Gas. Use Equation 28A–5 to calculate the total moles of dry exhaust gas produced per kilogram of dry wood burned.

$$N_T = \frac{42.5}{\left(Y_{CO_2} + Y_{CO} + Y_{HC}\right)} \qquad \text{Eq. 28A-5}$$

12.7 Air-to-Fuel Ratio. Use Equation 28A–6 to calculate the air-to-fuel ratio on a dry mass basis.

$$A/F = \frac{\left(N_T \times M_d\right) - 510}{1{,}000} \qquad \text{Eq. 28A-6}$$

12.8 Burn Rate. Calculate the fuel burn rate as in Method 28, section 12.4.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as section 16.0 of Method 3 and section 17 of Method 5G.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

Test Method 28R for Certification and Auditing of Wood Heaters

1.0 Scope and Application

1.1 This test method applies to certification and auditing of wood-fired room heaters and fireplace inserts.

1.2 The test method covers the fueling and operating protocol for measuring particulate emissions, as well as determining burn rates, heat output and efficiency.

1.3 Particulate emissions are measured by the dilution tunnel method as specified in ASTM E2515–11 *Standard Test Method for Determination of Particulate Matter Emissions Collected in a Dilution Tunnel* (IBR, see §60.17). Upon request, four-inch filters may be used. Upon request, Teflon membrane filters or Teflon-coated glass fiber filters may be used.

2.0 Procedures

2.1 This method incorporates the provisions of ASTM E2780–10 (IBR, see §60.17) except as follows:

2.1.1 The burn rate categories, low burn rate requirement, and weightings in Method 28 shall be used.

2.1.2 The startup procedures shall be the same as in Method 28.

2.1.3 Manufacturers shall not specify a smaller volume of the firebox for testing than the full usable firebox.

2.1.4 Prior to testing, the heater must be operated for a minimum of 50 hours using a medium burn rate. The conditioning may be at the manufacturer's facility prior to the certification test. If the conditioning is at the certification test laboratory, the preburn for the first test can be included as part of the conditioning requirement.

2.2 Manufacturers may use ASTM E871–82 (reapproved 2013) (IBR, see §60.17) as an alternative to the procedures in Method 5H or Method 28 for determining total weight basis moisture in the analysis sample of particulate wood fuel.

Test Method 28WHH for Measurement of Particulate Emissions and Heating Efficiency of Wood-Fired Hydronic Heating Appliances

1.0 Scope and Application

1.1 This test method applies to wood-fired hydronic heating appliances. The units typically transfer heat through circulation of a liquid heat exchange media such as water or a water-antifreeze mixture.

1.2 The test method measures particulate emissions and delivered heating efficiency at specified heat output rates based on the appliance's rated heating capacity.

1.3 Particulate emissions are measured by the dilution tunnel method as specified in ASTM E2515–11 *Standard Test Method for Determination of Particulate Matter Emissions Collected in a Dilution Tunnel* (IBR, see §60.17). Upon request, four-inch filters may be used. Upon request, Teflon membrane filters or Teflon-coated glass fiber filters may be used. Delivered efficiency is measured by determining the heat output through measurement of the flow rate and temperature change of water circulated through a heat exchanger external to the appliance and determining the input from the mass of dry wood fuel and its higher heating value. Delivered efficiency does not attempt to account for pipeline loss.

1.4 Products covered by this test method include both pressurized and non-pressurized heating appliances intended to be fired with wood. These products are wood-fired hydronic heating appliances that the manufacturer specifies for indoor or outdoor installation. They are often connected to a heat exchanger by insulated pipes and normally include a pump to circulate heated liquid. They are used to heat structures such as homes, barns and greenhouses and can heat domestic hot water, spas or swimming pools.

1.5 Distinguishing features of products covered by this standard include:

1.5.1 Manufacturer specifies for indoor or outdoor installation.

1.5.2 A firebox with an access door for hand loading of fuel.

1.5.3 Typically, an aquastat that controls combustion air supply to maintain the liquid in the appliance within a predetermined temperature range provided sufficient fuel is available in the firebox.

1.5.4 A chimney or vent that exhausts combustion products from the appliance.

1.6 The values stated are to be regarded as the standard whether in I–P or SI units. The values given in parentheses are for information only.

2.0 Summary of Method and References

2.1 Particulate matter emissions are measured from a wood-fired hydronic heating appliance burning a prepared test fuel crib in a test facility maintained at a set of prescribed conditions. Procedures for determining burn rates, and particulate emissions rates and for reducing data are provided.

2.2 Referenced Documents

2.2.1 EPA Standards

2.2.1.1 Method 28 Certification and Auditing of Wood Heaters

2.2.2 Other Standards

2.2.2.1 ASTM E2515–11—*Standard Test Method for Determination of Particulate Matter Emissions Collected in a Dilution Tunnel* (IBR, see §60.17).

2.2.2.2 CSA–B415.1–10 *Performance Testing of Solid-Fuel-Burning Heating Appliances* (IBR, see §60.17).

3.0 Terminology

3.1 Definitions.

3.1.1 Hydronic Heating—A heating system in which a heat source supplies energy to a liquid heat exchange media such as water that is circulated to a heating load and returned to the heat source through pipes.

3.1.2 Aquastat—A control device that opens or closes a circuit to control the rate of fuel consumption in response to the temperature of the heating media in the heating appliance.

3.1.3 Delivered Efficiency—The percentage of heat available in a test fuel charge that is delivered to a simulated heating load as specified in this test method.

3.1.4 Manufacturer's Rated Heat Output Capacity—The value in Btu/hr (MJ/hr) that the manufacturer specifies that a particular model of hydronic heating appliance is capable of supplying at its design capacity as verified by testing, in accordance with Section 13.

3.1.5 Burn Rate—The rate at which test fuel is consumed in an appliance. Measured in pounds (lbs) or kilograms of wood (dry basis) per hour (lb/hr or kg/hr).

3.1.6 Firebox—The chamber in the appliance in which the test fuel charge is placed and combusted.

3.1.7 Test Fuel Charge—The collection of test fuel layers placed in the appliance at the start of the emission test run.

3.1.8 Test Fuel Layer—Horizontal arrangement of test fuel units.

3.1.9 Test Fuel Unit—One or more test fuel pieces with ¾ inch (19 mm) spacers attached to the bottom and to one side. If composed of multiple test fuel pieces, the bottom spacer may be one continuous piece.

3.1.10 Test Fuel Piece—A single 4 × 4 (4 ±0.25 inches by 4 ±0.25 inches) [100 ±6 mm by 100 ±6 mm] white or red oak wood piece cut to the length required.

3.1.11 Test Run—An individual emission test that encompasses the time required to consume the mass of the test fuel charge.

3.1.12 Overall Efficiency (SLM)—The efficiency for each test run as determined using the CSA B415.1–10 (IBR, see §60.17) stack loss method.

3.1.13 Thermopile—A device consisting of a number of thermocouples connected in series, used for measuring differential temperature.

4.0 Summary of Test Method

4.1 Dilution Tunnel. Emissions are determined using the ''dilution tunnel'' method specified in ASTM E2515–11 *Standard Test Method for Determination of Particulate Matter Emissions Collected in a Dilution Tunnel* (IBR, see §60.17). The flow rate in the dilution tunnel is maintained at a constant level throughout the test cycle and accurately measured. Samples of the dilution tunnel flow stream are extracted at a constant flow rate and drawn through high efficiency filters. The filters are dried and weighed before and after the test to determine the emissions catch and this value is multiplied by the ratio of tunnel flow to filter flow to determine the total particulate emissions produced in the test cycle.

4.2 Efficiency. The efficiency test procedure takes advantage of the fact that this type of appliance delivers heat through circulation of the heated liquid (water) from the appliance to a remote heat exchanger and back to the appliance. Measurements of the water temperature difference as it enters and exits the heat exchanger along with the measured flow rate allow for an accurate determination of the useful heat output of the appliance. The input is determined by weight of the test fuel charge, adjusted for moisture content, multiplied by the higher heating value. Additional measurements of the appliance weight and temperature at the beginning and end of a test cycle are used to correct for heat stored in the appliance. Overall efficiency (SLM) is determined using the CSA B415.1–10 (IBR, see §60.17) stack loss method for data quality assurance purposes.

4.3 Operation. Appliance operation is conducted on a hot-to-hot test cycle meaning that the appliance is brought to operating

temperature and a coal bed is established prior to the addition of the test fuel charge and measurements are made for each test fuel charge cycle. The measurements are made under constant heat draw conditions within predetermined ranges. No attempt is made to modulate the heat demand to simulate an indoor thermostat cycling on and off in response to changes in the indoor environment. Four test categories are used. These are:

4.3.1 Category I: A heat output of 15 percent or less of manufacturer's rated heat output capacity.

4.3.2 Category II: A heat output of 16 percent to 24 percent of manufacturer's rated heat output capacity.

4.3.3 Category III: A heat output of 25 percent to 50 percent of manufacturer's rated heat output capacity.

4.3.4 Category IV: Manufacturer's rated heat output capacity.

5.0 Significance and Use

5.1 The measurement of particulate matter emission rates is an important test method widely used in the practice of air pollution control.

5.1.1 These measurements, when approved by state or federal agencies, are often required for the purpose of determining compliance with regulations and statutes.

5.1.2 The measurements made before and after design modifications are necessary to demonstrate the effectiveness of design changes in reducing emissions and make this standard an important tool in manufacturers' research and development programs.

5.2 Measurement of heating efficiency provides a uniform basis for comparison of product performance that is useful to the consumer. It is also required to relate emissions produced to the useful heat production.

5.3 This is a laboratory method and is not intended to be fully representative of all actual field use. It is recognized that users of hand-fired, wood-burning equipment have a great deal of influence over the performance of any wood-burning appliance. Some compromises in realism have been made in the interest of providing a reliable and repeatable test method.

6.0 Test Equipment

6.1 Scale. A platform scale capable of weighing the appliance under test and associated parts and accessories when completely filled with water to an accuracy of ±1.0 pound (±0.5 kg).

6.2 Heat Exchanger. A water-to-water heat exchanger capable of dissipating the expected heat output from the system under test.

6.3 Water Temperature Difference Measurement. A Type—T 'special limits' thermopile with a minimum of 5 pairs of junctions shall be used to measure the temperature difference in water entering and leaving the heat exchanger. The temperature difference measurement uncertainty of this type of thermopile is equal to or less than ±0.50 °F (±0.25 °C). Other temperature measurement methods may be used if the temperature difference measurement uncertainty is equal to or less than ±0.50 °F (±0.25 °C).

6.4 Water Flow Meter. A water flow meter shall be installed in the inlet to the load side of the heat exchanger. The flow meter shall have an accuracy of ±1 percent of measured flow.

6.4.1 Optional—Appliance Side Water Flow Meter. A water flow meter with an accuracy of ±1 percent of the flow rate is recommended to monitor supply side water flow rate.

6.5 Optional Recirculation Pump. Circulating pump used during test to prevent stratification of liquid being heated.

6.6 Water Temperature Measurement—Thermocouples or other temperature sensors to measure the water temperature at the inlet and outlet of the load side of the heat exchanger. Must meet the calibration requirements specified in section 10.1.

6.7 Wood Moisture Meter—Calibrated electrical resistance meter capable of measuring test fuel moisture to within 1 percent moisture content. Must meet the calibration requirements specified in section 10.4.

6.8 Flue Gas Temperature Measurement—Must meet the requirements of CSA B415.1–10 (IBR, see §60.17), clause 6.2.2.

6.9 Test Room Temperature Measurement—Must meet the requirements of CSA B415.1–10 (IBR, see §60.17), clause 6.2.1.

6.10 Flue Gas Composition Measurement—Must meet the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 6.3.1 through 6.3.3.

7.0 Safety

7.1 These tests involve combustion of wood fuel and substantial release of heat and products of combustion. The heating system also produces large quantities of very hot water and the potential for steam production and system pressurization. Appropriate precautions must be taken to protect personnel from burn hazards and respiration of products of combustion.

8.0 Sampling, Test Specimens and Test Appliances

8.1 Test specimens shall be supplied as complete appliances including all controls and accessories necessary for installation in the test facility. A full set of specifications and design and assembly drawings shall be provided when the product is to be placed under certification of a third-party agency. The manufacturer's written installation and operating instructions are to be used as a

guide in the set-up and testing of the appliance.

9.0 Preparation of Test Equipment

9.1 The appliance is to be placed on a scale capable of weighing the appliance fully loaded with a resolution of ±1.0 lb (0.5 kg).

9.2 The appliance shall be fitted with the type of chimney recommended or provided by the manufacturer and extending to 15 ±0.5 feet (4.6 ±0.15 m) from the upper surface of the scale. If no flue or chimney system is recommended or provided by the manufacturer, connect the appliance to a flue of a diameter equal to the flue outlet of the appliance. The flue section from the appliance flue collar to 8 ±0.5 feet above the scale shall be single wall stove pipe and the remainder of the flue shall be double wall insulated class A chimney.

9.3 Optional Equipment Use

9.3.1 A recirculation pump may be installed between connections at the top and bottom of the appliance to minimize thermal stratification if specified by the manufacturer. The pump shall not be installed in such a way as to change or affect the flow rate between the appliance and the heat exchanger.

9.3.2 If the manufacturer specifies that a thermal control valve or other device be installed and set to control the return water temperature to a specific set point, the valve or other device shall be installed and set per the manufacturer's written instructions.

9.4 Prior to filling the tank, weigh and record the appliance mass.

9.5 Heat Exchanger

9.5.1 Plumb the unit to a water-to-water heat exchanger with sufficient capacity to draw off heat at the maximum rate anticipated. Route hoses, electrical cables, and instrument wires in a manner that does not influence the weighing accuracy of the scale as indicated by placing dead weights on the platform and verifying the scale's accuracy.

9.5.2 Locate thermocouples to measure the water temperature at the inlet and outlet of the load side of the heat exchanger.

9.5.3 Install a thermopile meeting the requirements of section 6.3 to measure the water temperature difference between the inlet and outlet of the load side of the heat exchanger.

9.5.4 Install a calibrated water flow meter in the heat exchanger load side supply line. The water flow meter is to be installed on the cooling water inlet side of the heat exchanger so that it will operate at the temperature at which it is calibrated.

9.5.5 Place the heat exchanger in a box with 2 in. (50 mm) of expanded polystyrene (EPS) foam insulation surrounding it to minimize heat losses from the heat exchanger.

9.5.6 The reported efficiency and heat output rate shall be based on measurements made on the load side of the heat exchanger.

9.5.7 Temperature instrumentation per section 6.6 shall be installed in the appliance outlet and return lines. The average of the outlet and return water temperature on the supply side of the system shall be considered the average appliance temperature for calculation of heat storage in the appliance (TF_{avg} and TI_{avg}). Installation of a water flow meter in the supply side of the system is optional.

9.6 Fill the system with water. Determine the total weight of the water in the appliance when the water is circulating. Verify that the scale indicates a stable weight under operating conditions. Make sure air is purged properly.

10.0 Calibration and Standardization

10.1 Water Temperature Sensors. Temperature measuring equipment shall be calibrated before initial use and at least semi-annually thereafter. Calibrations shall be in compliance with National Institute of Standards and Technology (NIST) Monograph 175, Standard Limits of Error.

10.2 Heat Exchanger Load Side Water Flow Meter.

10.2.1 The heat exchanger load side water flow meter shall be calibrated within the flow range used for the test run using NIST traceable methods. Verify the calibration of the water flow meter before and after each test run and at least once during each test run by comparing the water flow rate indicated by the flow meter to the mass of water collected from the outlet of the heat exchanger over a timed interval. Volume of the collected water shall be determined based on the water density calculated from section 13, Eq. 8, using the water temperature measured at the flow meter. The uncertainty in the verification procedure used shall be 1 percent or less. The water flow rate determined by the collection and weighing method shall be within 1 percent of the flow rate indicated by the water flow meter.

10.3 Scales. The scales used to weigh the appliance and test fuel charge shall be calibrated using NIST traceable methods at least once every 6 months.

10.4 Moisture Meter. The moisture meter shall be calibrated per the manufacturer's instructions and checked before each use.

10.5 Flue Gas Analyzers—In accordance with CSA B415.1–10 (IBR, see §60.17), clause 6.8.

11.0 Conditioning

11.1 Prior to testing, the appliance is to be operated for a minimum of 50 hours using a medium heat draw rate. The conditioning may be at the manufacturer's facility prior to the certification test. If the conditioning is at the certification test laboratory, the pre-burn for the first test can be included as

part of the conditioning requirement. If conditioning is included in pre-burn, then the appliance shall be aged with fuel meeting the specifications outlined in sections 12.2 with a moisture content between 19 and 25 percent on a dry basis. Operate the appliance at a medium burn rate (Category II or III) for at least 10 hours for noncatalytic appliances and 50 hours for catalytic appliances. Record and report hourly flue gas exit temperature data and the hours of operation. The aging procedure shall be conducted and documented by a testing laboratory.

12.0 Procedure

12.1 Appliance Installation. Assemble the appliance and parts in conformance with the manufacturer's written installation instructions. Clean the flue with an appropriately sized, wire chimney brush before each certification test series.

12.2 Fuel. Test fuel charge fuel shall be red (*Quercus ruba L.*) or white (*Quercus alba*) oak 19 to 25 percent moisture content on a dry basis. Piece length shall be 80 percent of the firebox depth rounded down to the nearest 1 inch (25mm) increment. For example, if the firebox depth is 46 inches (1168mm) the 4 × 4 piece length would be 36 inches (46 inches × 0.8 = 36.8 inches rounded down to 36 inches). Pieces are to be placed in the firebox parallel to the longest firebox dimension. For fireboxes with sloped surfaces that create a non-uniform firebox length, the piece length shall be adjusted for each layer based on 80 percent of the length at the level where the layer is placed. Pieces are to be spaced ¾ inches (19 mm) apart on all faces. The first fuel layer may be assembled using fuel units consisting of multiple 4 × 4s consisting of single pieces with bottom and side spacers of 3 or more pieces if needed for a stable layer. The second layer may consist of fuel units consisting of no more than two pieces with spacers attached on the bottom and side. The top two layers of the fuel charge must consist of single pieces unless the fuel charge is only three layers. In that instance only the top layer must consist of single units. Three-quarter inch (19 mm) by 1.5 inch (38 mm) spacers shall be attached to the bottom of piece to maintain a ¾ inch (19 mm) separation. When a layer consists of two or more units of 4 × 4s an additional ¾ inch (19 mm) thick by 1.5 inch (38 mm) wide spacer shall be attached to the vertical face of each end of one 4 × 4, such that the ¾ inch (19 mm) space will be maintained when two 4 × 4 units or pieces are loaded side by side. In cases where a layer contains an odd number of 4 × 4s one piece shall not be attached, but shall have spacers attached in a manner that will provide for the ¾ inch (19 mm) space to be maintained (See Figure 1). Spacers shall be attached perpendicular to the length of the 4 × 4s such that the edge of the spacer is 1 ±0.25 inch from the end of the 4 × 4s in the previous layers. Spacers shall be red or white oak and will be attached with either nails (non-galvanized), brads or oak dowels. The use of kiln-dried wood is not allowed.

12.2.1 Using a fuel moisture meter as specified in section 6.7 of the test method, determine the fuel moisture for each test fuel piece used for the test fuel load by averaging at least five fuel moisture meter readings measured parallel to the wood grain. Penetration of the moisture meter insulated electrodes for all readings shall be ¼ the thickness of the fuel piece or 19 mm (¾ in.), whichever is lesser. One measurement from each of three sides shall be made at approximately 3 inches from each end and the center. Two additional measurements shall be made centered between the other three locations. Each individual moisture content reading shall be in the range of 18 to 28 percent on a dry basis. The average moisture content of each piece of test fuel shall be in the range of 19 to 25 percent. It is not required to measure the moisture content of the spacers. Moisture shall not be added to previously dried fuel pieces except by storage under high humidity conditions and temperature up to 100 °F. Fuel moisture shall be measured within 4 hours of using the fuel for a test.

12.2.2 Firebox Volume. Determine the firebox volume in cubic feet. Firebox volume shall include all areas accessible through the fuel loading door where firewood could reasonably be placed up to the horizontal plane defined by the top of the loading door. A drawing of the firebox showing front, side and plan views or an isometric view with interior dimensions shall be provided by the manufacturer and verified by the laboratory. Calculations for firebox volume from computer aided design (CAD) software programs are acceptable and shall be included in the test report if used. If the firebox volume is calculated by the laboratory the firebox drawings and calculations shall be included in the test report.

12.2.3 Test Fuel Charge. Test fuel charges shall be determined by multiplying the firebox volume by 10 pounds (4.54 kg) per ft^3 (28L), or a higher load density as recommended by the manufacturer's printed operating instructions, of wood (as used wet weight). Select the number of pieces of standard fuel that most nearly match this target weight. This is the standard fuel charge for all tests. For example, if the firebox loading area volume is 10 ft^3 (280L) and the firebox depth is 46 inches (1168 mm), test fuel charge target is 100 lbs (45 kg) minimum and the piece length is 36 inches (914 mm). If eight 4 × 4s, 36 inches long weigh 105 lbs (48 kg), use 8 pieces for each test fuel charge. All test fuel charges will be of the same configuration.

12.3 Sampling Equipment. Prepare the particulate emission sampling equipment as defined by ASTM E2515–11 *Standard Test Method for Determination of Particulate Matter Emissions Collected in a Dilution Tunnel* (IBR, see §60.17). Upon request, four-inch filters may be used. Upon request, Teflon membrane filters or Teflon-coated glass fiber filters may be used.

12.4 Appliance Startup. The appliance shall be fired with wood fuel of any species, size and moisture content at the laboratories' discretion to bring it up to operating temperature. Operate the appliance until the water is heated to the upper operating control limit and has cycled at least two times. Then remove all unburned fuel, zero the scale and verify the scales accuracy using dead weights.

12.4.1 Pretest Burn Cycle. Reload appliance with oak wood and allow it to burn down to the specified coal bed weight. The pretest burn cycle fuel charge weight shall be within ±10 percent of the test fuel charge weight. Piece size and length shall be selected such that charcoalization is achieved by the time the fuel charge has burned down to the required coal bed weight. Pieces with a maximum thickness of approximately 2 inches have been found to be suitable. Charcoalization is a general condition of the test fuel bed evidenced by an absence of large pieces of burning wood in the coal bed and the remaining fuel pieces being brittle enough to be broken into smaller charcoal pieces with a metal poker. Manipulations to the fuel bed prior to the start of the test run are to be done to achieve charcoalization while maintaining the desired heat output rate. During the pre-test burn cycle and at least one hour prior to starting the test run, adjust water flow to the heat exchanger to establish the target heat draw for the test. For the first test run the heat draw rate shall be equal to the manufacturer's rated heat output capacity.

12.4.1.1 Allowable Adjustments. Fuel addition or subtractions, and coal bed raking shall be kept to a minimum but are allowed up to 15 minutes prior to the start of the test run. For the purposes of this method, coal bed raking is the use of a metal tool (poker) to stir coals, break burning fuel into smaller pieces, dislodge fuel pieces from positions of poor combustion, and check for the condition of charcoalization. Record all adjustments to and additions or subtractions of fuel, and any other changes to the appliance operations that occur during pretest ignition period. During the 15-minute period prior to the start of the test run, the wood heater loading door shall not be open more than a total of 1 minute. Coal bed raking is the only adjustment allowed during this period.

12.4.2 Coal Bed Weight. The appliance is to be loaded with the test fuel charge when the coal bed weight is between 10 percent and 20 percent of the test fuel charge weight. Coals may be raked as necessary to level the coal bed but may only be raked and stirred once between 15 to 20 minutes prior to the addition of the test fuel charge.

12.5 Test Runs. For all test runs, the return water temperature to the hydronic heater must be equal to or greater than 120 °F. Aquastat or other heater output control device settings that are adjustable shall be set using manufacturer specifications, either as factory set or in accordance with the owner's manual, and shall remain the same for all burn categories.

Complete a test run in each heat output rate category, as follows:

12.5.1 Test Run Start. Once the appliance is operating normally and the pretest coal bed weight has reached the target value per section 12.4.2, tare the scale and load the full test charge into the appliance. Time for loading shall not exceed 5 minutes. The actual weight of the test fuel charge shall be measured and recorded within 30 minutes prior to loading. Start all sampling systems.

12.5.1.1 Record all water temperatures, differential water temperatures and water flow rates at time intervals of one minute or less.

12.5.1.2 Record particulate emissions data per the requirements of ASTM E2515 (IBR, see §60.17).

12.5.1.3 Record data needed to determine overall efficiency (SLM) per the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 6.2.1, 6.2.2, 6.3, 8.5.7, 10.4.3 (a), 10.4.3(f), and 13.7.9.3

12.5.1.3.1 Measure and record the test room air temperature in accordance with the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 6.2.1, 8.5.7 and 10.4.3 (g).

12.5.1.3.2 Measure and record the flue gas temperature in accordance with the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 6.2.2, 8.5.7 and 10.4.3 (f).

12.5.1.3.3 Determine and record the carbon monoxide (CO) and carbon dioxide (CO_2) concentrations in the flue gas in accordance with CSA B415.1–10 (IBR, see §60.17), clauses 6.3, 8.5.7 and 10.4.3 (i) and (j).

12.5.1.3.4 Measure and record the test fuel weight per the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 8.5.7 and 10.4.3 (h).

12.5.1.3.5 Record the test run time per the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 10.4.3 (a).

12.5.1.4 Monitor the average heat output rate on the load side of the heat exchanger. If the heat output rate gets close to the upper or lower limit of the target range (±5 percent) adjust the water flow through the heat exchanger to compensate. Make changes as infrequently as possible while maintaining the target heat output rate. The first test run shall be conducted at the Category IV heat output rate to validate that

the appliance is capable of producing the manufacturer's rated heat output capacity.

12.5.2 Test Fuel Charge Adjustment. It is acceptable to adjust the test fuel charge (*i.e.*, reposition) once during a test run if more than 60 percent of the initial test fuel charge weight has been consumed and more than 10 minutes have elapsed without a measurable (1 lb or 0. 5 kg) weight change while the operating control is in the demand mode. The time used to make this adjustment shall be less than 60 seconds.

12.5.3 Test Run Completion. The test run is completed when the remaining weight of the test fuel charge is 0.0 lb (0.0 kg). End the test run when the scale has indicated a test fuel charge weight of 0.0 lb (0.0 kg) or less for 30 seconds.

12.5.3.1 At the end of the test run, stop the particulate sampling train and overall efficiency (SLM) measurements, and record the run time, and all final measurement values.

12.5.4 Heat Output Capacity Validation. The first test run must produce a heat output rate that is within 10 percent of the manufacturer's rated heat output capacity (Category IV) throughout the test run and an average heat output rate within 5 percent of the manufacturer's rated heat output capacity. If the appliance is not capable of producing a heat output within these limits, the manufacturer's rated heat output capacity is considered not validated and testing is to be terminated. In such cases, the tests may be restarted using a lower heat output capacity if requested by the manufacturer.

12.5.5 Additional Test Runs. Using the manufacturer's rated heat output capacity as a basis, conduct a test for additional heat output categories as specified in section 4.3. It is not required to run these tests in any particular order.

12.5.6 Alternative Heat Output Rate for Category I. If an appliance cannot be operated in the Category I heat output range due to stopped combustion, two test runs shall be conducted at heat output rates within Category II, provided that the completed test run burn rate is no greater than the burn rate expected in home use. If this rate cannot be achieved, the test is not valid.

When the alternative heat output rate is used, the weightings for the weighted averages indicated in Table 2 shall be the average of the Category I and II weightings and shall be applied to both Category II results. The two completed runs in Category II will be deemed to meet the requirement for runs completed in both Category I and Category II. Appliances that are not capable of operation within Category II (<25 percent of maximum) cannot be evaluated by this test method. The test report must include full documentation and discussion of the attempted runs, completed rums and calculations.

12.5.6.1 Stopped Fuel Combustion. Evidence that an appliance cannot be operated at a Category I heat output rate due to stopped fuel combustion shall include documentation of two or more attempts to operate the appliance in burn rate Category I and fuel combustion has stopped prior to complete consumption of the test fuel charge. Stopped fuel combustion is evidenced when an elapsed time of 60 minutes or more has occurred without a measurable (1 lb or 0.5 kg) weight change in the test fuel charge while the appliance operating control is in the demand mode. Report the evidence and the reasoning used to determine that a test in burn rate Category I cannot be achieved. For example, two unsuccessful attempts to operate at an output rate of 10 percent of the rated output capacity are not sufficient evidence that burn rate Category I cannot be achieved. Note that section 12.5.6 requires that the completed test run burn rate can be no greater than the burn rate expected in home use. If this rate cannot be achieved, the test is not valid.

12.5.7 Appliance Overheating. Appliances shall be capable of operating in all heat output categories without overheating to be rated by this test method. Appliance overheating occurs when the rate of heat withdrawal from the appliance is lower than the rate of heat production when the unit control is in the idle mode. This condition results in the water in the appliance continuing to increase in temperature well above the upper limit setting of the operating control. Evidence of overheating includes: 1 hour or more of appliance water temperature increase above the upper temperature set-point of the operating control, exceeding the temperature limit of a safety control device (independent from the operating control), boiling water in a non-pressurized system or activation of a pressure or temperature relief valve in a pressurized system.

12.6 Additional Test Runs. The testing laboratory may conduct more than one test run in each of the heat output categories specified in section 4.3.1. If more than one test run is conducted at a specified heat output rate, the results from at least two-thirds of the test runs in that heat output rate category shall be used in calculating the weighted average emission rate (See section 14.1.14). The measurement data and results of all test runs shall be reported regardless of which values are used in calculating the weighted average emission rate.

13.0 Calculation of Results

13.1 Nomenclature

E_T—Total particulate emissions for the full test run as determined per ASTM E2515–11 (IBR, see §60.17) in grams

$E_{g/MJ}$—Emissions rate in grams per megajoule of heat output
$E_{lb/mmBtu}$ output—Emissions rate in pounds per million Btu of heat output
$E_{g/kg}$—Emissions factor in grams per kilogram of dry fuel burned
$E_{g/hr}$—Emissions factor in grams per hour
HHV—Higher heating value of fuel = 8600 Btu/lb (19.990 MJ/kg)
LHV—Lower heating value of fuel = 7988 Btu/lb (18.567 MJ/kg)
ΔT—Temperature difference between water entering and exiting the heat exchanger
Q_{out}—Total heat output in BTU's (megajoules)
Q_{in}—Total heat input available in test fuel charge in BTU (megajoules)
M—Mass flow rate of water in lb/min (kg/min)
V_i—Volume of water indicated by a totalizing flow meter at the ith reading in gallons (liters)
V_f—Volumetric flow rate of water in heat exchange system in gallons per minute (liters/min)
Θ—Total length of test run in hours
ti—Data sampling interval in minutes
η_{del}—Delivered heating efficiency in percent
Fi—Weighting factor for heat output category i (See Table 2)
T1—Temperature of water at the inlet on the supply side of the heat exchanger
T2—Temperature of the water at the outlet on the supply side of the heat exchanger
T3—Temperature of water at the inlet to the load side of the heat exchanger
TIavg—Average temperature of the appliance and water at start of the test

$$TI_{avg} - (T1 + T2)/2 \text{ at the start of the test, °F} \quad \text{Eq.1}$$

TF_{avg}—Average temperature of the appliance and water at the end of the test

$$TF_{avg} - (T1 + T2)/2 \text{ at the end of the test, °F} \quad \text{Eq.2}$$

MC—Fuel moisture content in percent dry basis
MC_i—Average moisture content of individual 4 × 4 fuel pieces in percent dry basis
MC_{sp}—Moisture content of spacers assumed to be 10 percent dry basis
σ—Density of water in pounds per gallon
C_p—Specific heat of water in Btu/lb, °F
C_{steel}—Specific heat of steel (0.1 Btu/lb, °F)
W_{fuel}—Fuel charge weight in pounds (kg)
W_i—Weight of individual fuel 4 × 4 pieces in pounds (kg)
W_{sp}—Weight of all spacers used in a fuel load in pounds (kg)
W_{app}—Weight of empty appliance in pounds
W_{wa}—Weight of water in supply side of the system in pounds

13.2 After the test is completed, determine the particulate emissions E_T in accordance with ASTM E2515–11 (IBR, see §60.17).

13.3 Determine Average Fuel Load Moisture Content

$$MC_{Ave} = [[\ \Sigma\ W_i \text{ x } MC_i\ ] + [\ W_{sp} \text{ x } MC_{sp}\ ]] \div W_{fuel}, \% \quad \text{Eq. 3}$$

13.4 Determine heat input

$$Q_{in} = (W_{fuel}/(1+(MC/100))) \text{ x HHV, BTU} \quad \text{Eq. 4}$$

$$Q_{in\ LHV} = (W_{fuel}/(1+(MC/100))) \text{ x LHV, BTU} \quad \text{Eq. 5}$$

13.5 Determine Heat Output and Efficiency

13.5.1 Determine heat output as:

Q_{out} = Σ [Heat output determined for each sampling time interval] + Change in heat stored in the appliance.

$$Q_{out} = \left[\sum (C_{pi} \bullet \Delta T_i \bullet \dot{M}_i \bullet t_i)\right] + (W_{app} \bullet C_{Steel} + C_{pa} W_{water}) \bullet (TF_{avg} - TI_{avg}), \text{ BTU} \quad \text{Eq. 6}$$

NOTE: The subscript (i) indicates the parameter value for sampling time interval t_i.

M_i = Mass flow rate = gal/min × density of water (lb/gal) = lb/min

$$M_i = V_{fi} \cdot \sigma_i, \text{ lb/min} \quad \text{Eq. 7}$$

$$\Sigma_i = (62.56 + (-.0003413 \text{ x } T3_i) + (-.00006225 \text{ x } T3_i^2)) \, 0.1337, \text{ lbs/gal} \quad \text{Eq. 8}$$

$$C_p = 1.0014 + (-.000003485 \text{ x } T3_i) \text{ Btu/lb, } ^oF \quad \text{Eq. 9}$$

C_{steel} = 0.1 Btu/lb, ° F

$$C_{pa} = 1.0014 + (-.000003485 \text{ X } (TI_{avg} + TF_{avg})/2), \text{ Btu/lb-}^oF \quad \text{Eq. 10}$$

$$V_{fi} = (V_i - V_{i-1})/(t_i - t_{i-1}), \text{ gal/min} \quad \text{Eq. 11}$$

NOTE: Vi is the total water volume at the end of interval i and Vi-1 is the total water volume at the beginning of the time interval. This calculation is necessary when a totalizing type water meter is used.

13.5.2 Determine heat output rate as:

$$\text{Heat Output Rate} = Q_{out}/\Theta, \text{ BTU/hr} \quad \text{Eq. 12}$$

13.5.3 Determine emission rates and emission factors as:

$$E_{g/MJ} = E_T/(Q_{out} \text{ x } 0.001055), \text{ g/MJ} \quad \text{Eq. 13}$$

$$E_{lb/MM \text{ BTU output}} = (E_T/453.59)/(Q_{output} \text{ x } 10^{-6}), \text{ lb/mmBtu Out} \quad \text{Eq. 14}$$

$$E_{g/kg} = E_T/(W_{fuel}/(1+MC/100)), \text{ g/dry kg} \quad \text{Eq, 15}$$

$$E_{g/hr} = E_T/\Theta, \text{ g/hr} \quad \text{Eq. 16}$$

13.5.4 Determine delivered efficiency as:

$$\eta_{del} = (Q_{out}/Q_{in}) \times 100, \% \quad \text{Eq. 17}$$

$$\eta_{del\ LHV} = (Q_{out}/Q_{in\ LHV}) \times 100, \% \quad \text{Eq. 18}$$

13.5.5 Determine η_{SLM}—Overall Efficiency (SLM) using Stack Loss

For determination of the average overall thermal efficiency (η_{SLM}) for the test run, use the data collected over the full test run and the calculations in accordance with CSA B415.1–10 (IBR, see §60.17), clause 13.7 except for 13.7.2 (e), (f), (g), and (h), use the following average fuel properties for oak: percent C = 50.0, percent H = 6.6, percent O = 43.2, percent ash = 0.2 percent. The averaging period for determination of efficiency by the stack loss method allows averaging over 10 minute time periods for flue gas temperature, flue gas CO_2, and flue gas CO for the determination of the efficiency. However, under some cycling conditions the ''on'' period may be short relative to this 10 minute period. For this reason, during cycling operation the averaging period for these parameters may not be longer than the burner on period divided by 10. The averaging period need not be shorter than one minute. During the off period, under cycling operation, the averaging periods specified may be used. Where short averaging times are used, however, the averaging period for fuel consumption may still be at 10 minutes. This average wood consumption rate shall be applied to all of the smaller time intervals included.

13.5.5.1 Whenever the CSA B415.1–10 (IBR, see §60.17) overall efficiency is found to be lower than the overall efficiency based on load side measurements, as determined by Eq. 16 of this method, section 14.1.7 of the test report must include a discussion of the reasons for this result.

13.6 Weighted Average Emissions and Efficiency

13.6.1 Determine the weighted average emission rate and delivered efficiency from the individual tests in the specified heat output categories. The weighting factors (Fi) are derived from an analysis of ASHRAE bin data which provides details of normal building heating requirements in terms of percent of design capacity and time in a particular capacity range—or ''bin''—over the course of a heating season. The values used in this method represent an average of data from several cities located in the northern United States.

$$\text{Weighted average delivered efficiency: } \eta_{avg} = \Sigma\, \eta_i \times F_i, \% \quad \text{Eq. 19}$$

$$\text{Weighted average emissions: } E_{avg} = \Sigma E_i \times F_i, \% \quad \text{Eq. 20}$$

13.7 Average Heat Output ($Q_{out\text{-}8hr}$) and Efficiency (($\eta_{avg\text{-}8hr}$) for 8 hour burn time.

13.7.1 Units tested under this standard typically require infrequent fuelling, 8 to 12 hours intervals being typical. Rating unit's based on an average output sustainable over an 8 hour duration will assist consumers in appropriately sizing units to match the theoretical heat demand of their application.

13.7.2 Calculations:

$$Q_{out\text{-}8hr} = X1 + \{ (8 - Y1) \times [(X2 - X1) / (Y2 - Y1)] \}, \% \quad \text{Eq. 21}$$

$$\eta_{avg\text{-}8hr} = \eta_{del1} + \{ (8 - Y1) \times [(\eta_{del2} - \eta_{del1}) / (Y2 - Y1)] \}, \% \quad \text{Eq. 22}$$

Where:

Y1 = Test duration just above 8 hrs
Y2 = Test duration just below 8 hrs
X1 = Actual load for duration Y1
X2 = Actual load for duration Y2
η_{del1} = Average delivered efficiency for duration Y1
η_{del2} = Average delivered efficiency for duration Y2

13.7.2.1 Determine the test durations and actual load for each category as recorded in Table 1A.

13.7.2.2 Determine the data point that has the nearest duration greater than 8 hrs.

X1 = Actual load,
Y1 = Test duration, and
η_{del1} = Average delivered efficiency for this data point

13.7.2.3 Determine the data point that has the nearest duration less than 8 hours.

X2 = Actual load,
Y2 = Test duration, and
η_{del2} = Average delivered efficiency for this data point

13.7.2.4 Example:

CATEGORY ACTUAL LOAD DURATION
[Category Actual Load Duration ηdel]

	(Btu/Hr)	(Hr)	(%)
1	15,000	10.2	70.0
2	26,000	8.4	75.5
3	50,000	6.4	80.1
4	100,000	4.7	80.9

Category 2 duration is just above 8 hours, therefore: X1 = 26,000 Btu/hr, η_{del1} = 75.5% and Y1 = 8.4 hrs

Category 3 duration is just below 8 hours, therefore: X2 = 50,000 Btu/hr, η_{del2} = 80.1% and Y2 = 6.4 hrs

$Q_{out\text{-}8hr}$ = 26,000 + {(8—8.4) × [(50,000—26,000)/(6.4—8.4)]} = 30,800 BTU/hr

$\eta_{avg\text{-}8hr}$ = 75.5 + {(8—8.4) × [(80.1—75.5)/(6.4—8.4)]} = 76.4%

13.8 Carbon Monoxide Emissions

For each minute of the test period, the carbon monoxide emission rate shall be calculated as:

$$CO_{g/min} = Q_{std} \cdot CO_s \cdot 3.30\text{x}10^{-5} \qquad \text{Eq. 23}$$

Total CO emissions for each of the three test periods (CO_{-1}, CO_{-2}, CO_{-3}) shall be calculated as the sum of the emission rates for each of the 1 minute intervals.

Total CO emission for the test run, CO_T, shall be calculated as the sum of CO_{-1}, CO_{-2}, and CO_{-3}.

14.0 Report

14.1.1 The report shall include the following.

14.1.2 Name and location of the laboratory conducting the test.

14.1.3 A description of the appliance tested and its condition, date of receipt and dates of tests.

14.1.4 A statement that the test results apply only to the specific appliance tested.

14.1.5 A statement that the test report shall not be reproduced except in full, without the written approval of the laboratory.

14.1.6 A description of the test procedures and test equipment including a schematic or other drawing showing the location of all required test equipment. Also, a description of test fuel sourcing, handling and storage practices shall be included.

14.1.7 Details of deviations from, additions to or exclusions from the test method, and their data quality implications on the test results (if any), as well as information on specific test conditions, such as environmental conditions.

14.1.8 A list of participants and observers present for the tests.

14.1.9 Data and drawings indicating the fire box size and location of the fuel charge.

14.1.10 Drawings and calculations used to determine firebox volume.

14.1.11 Information for each test run fuel charge including piece size, moisture content, and weight.

14.1.12 All required data for each test run shall be provided in spreadsheet format. Formulae used for all calculations shall be accessible for review.

14.1.13 Test run duration for each test.

14.1.14 Calculated results for delivered efficiency at each burn rate and the weighted average emissions reported as total emissions in grams, pounds per mm Btu of delivered heat, grams per MJ of delivered heat, grams per kilogram of dry fuel and grams per hour. Results shall be reported for each heat output category and the weighted average.

14.1.15 Tables 1A, 1B, 1C and Table 2 must be used for presentation of results in test reports.

14.1.16 A statement of the estimated uncertainty of measurement of the emissions and efficiency test results.

14.1.17 Raw data, calibration records, and other relevant documentation shall be retained by the laboratory for a minimum of 7 years.

15.0 Precision and Bias

15.1 Precision—It is not possible to specify the precision of the procedure in Method 28WHH because the appliance operation and

fueling protocols and the appliances themselves produce variable amounts of emissions and cannot be used to determine reproducibility or repeatability of this measurement method.

15.2 Bias—No definitive information can be presented on the bias of the procedure in Method 28WHH for measuring solid fuel burning hydronic heater emissions because no material having an accepted reference value is available.

16.0 Keywords

16.1 Solid fuel, hydronic heating appliances, wood-burning hydronic heaters.

Table 1A. Data Summary Part A

						O	W_{fuel}	MC_{ave}	Q_{in}	Q_{out}
Category	Run No	Load % Capacity	Target Load	Actual Load	Act Load	Test Duration	Wood Wt	Wood Moisture	Heat Input	Heat Output
			BTU/hr	BTU/hr	% of max	hrs	lb	% DB	BTU	BTU
I		< 15% of max								
II		16-24% of max								
III		25-50% of max								
IV		Max capacity								

Table 1B. Data Summary Part B

			T2 Min	E-	E	E	$E_{g/hr}$	$E_{g/kg}$	η_{del}	η_{SLM}
Category	Run No	Load % Capacity	Min Return Water Temp	Total PM Emissions	PM Output Based	PM Output Based	PM Rate	PM Factor	Delivered Efficiency	Stack Loss Efficiency
			°F	g	$lb_{MMBTU\ Out}$	g/MJ	g/hr	g/kg	%	%
I		< 15% of max								
II		16-24% of max								
III		25-50% of max								
IV		Max capacity								

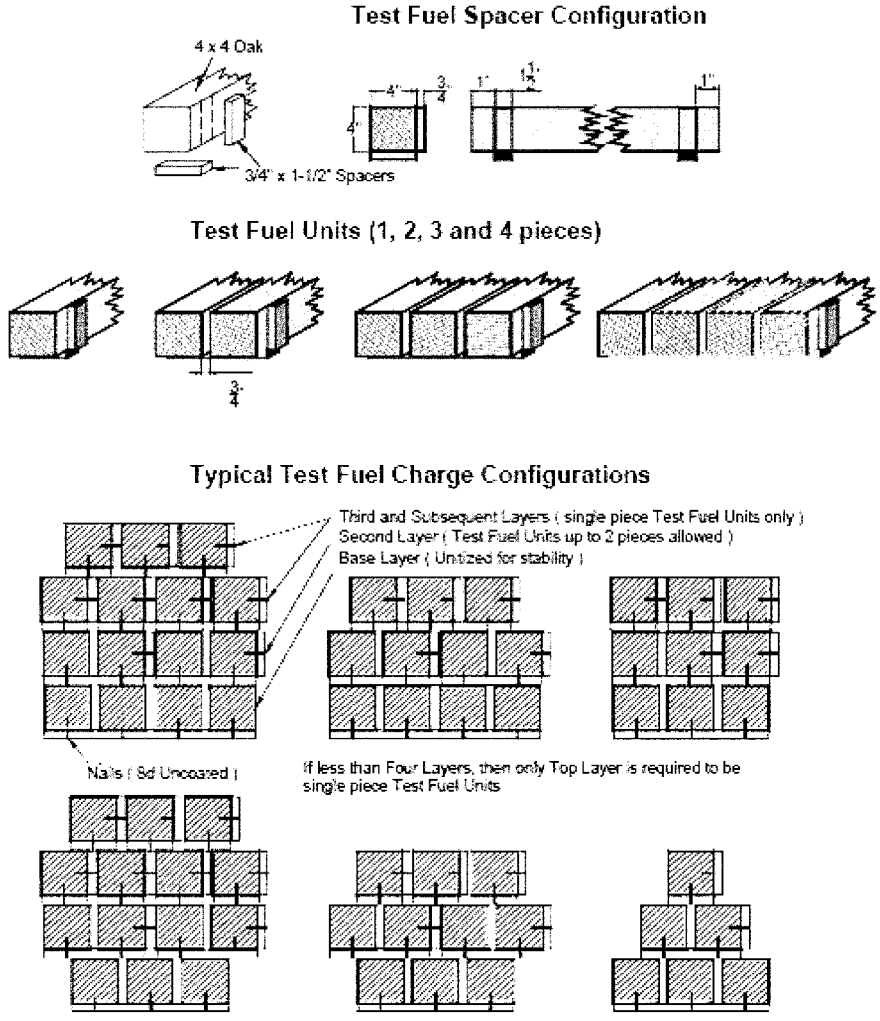
Table 1C: Hangtag Information (optional)

MANUFACTURER:			
MODEL NUMBER:			
MAXIMUM OUTPUT RATING:	Qmax		BTU/HR
ANNUAL EFFICIENCY RATING:	N_{avg}		(Using higher heating value)
PARTICLE EMISSIONS:	E_{avg}		GRAMS/HR (average)
			LBS/MILLION BTU OUTPUT
CARBON MONOXIDE:	COg/MIN		GRAMS/MINUTE

Table 2. Annual Weighting

Category	Weighting Factor (F_i)	$\eta_{del,i} \times F_i$	$E_{g/MJ,i} \times F_i$	$E_{g/kg,i} \times F_i$	$E_{lb/mmBtu\ Out,i} \times F_i$	$E_{g/hr,i} \times F_i$
I	0.437					
II	0.238					
III	0.275					
IV	0.050					
Totals	1.000					

Figure 1. Typical Test Fuel Piece



TEST METHOD 28WHH FOR CERTIFICATION OF CORD WOOD-FIRED HYDRONIC HEATING APPLIANCES WITH PARTIAL THERMAL STORAGE: MEASUREMENT OF PARTICULATE MATTER (PM) AND CARBON MONOXIDE (CO) EMISSIONS AND HEATING EFFICIENCY OF WOOD-FIRED HYDRONIC HEATING APPLIANCES WITH PARTIAL THERMAL STORAGE

1.0 Scope and Application

1.1 This test method applies to wood-fired hydronic heating appliances with heat storage external to the appliance. The units typically transfer heat through circulation of a liquid heat exchange media such as water or a water-antifreeze mixture. Throughout this document, the term ''water'' will be used to denote any of the heat transfer liquids approved for use by the manufacturer.

1.2 The test method measures PM and CO emissions and delivered heating efficiency at specified heat output rates referenced against the appliance's rated heating capacity as specified by the manufacturer and verified under this test method.

1.3 PM emissions are measured by the dilution tunnel method as specified in the EPA Method 28WHH and the standards referenced therein with the exceptions noted in section 12.5.9. Delivered efficiency is measured by determining the fuel energy input and appliance output. Heat output is determined through measurement of the flow rate and temperature change of water circulated through a heat exchanger external to the appliance and the increase in energy of the external storage. Heat input is determined from the mass of dry wood fuel and its higher heating value (HHV). Delivered efficiency does not attempt to account for pipeline loss.

1.4 Products covered by this test method include both pressurized and non-pressurized hydronic heating appliances intended to be fired with wood and for which the manufacturer specifies for indoor or outdoor installation. The system, which includes the heating appliance and external storage, is commonly connected to a heat exchanger by insulated pipes and normally includes a pump to circulate heated liquid. These systems are used to heat structures such as homes, barns and greenhouses. They also provide heat for domestic hot water, spas and swimming pools.

1.5 Distinguishing features of products covered by this standard include:

1.5.1 The manufacturer specifies the application for either indoor or outdoor installation.

1.5.2 A firebox with an access door for hand loading of fuel.

1.5.3 Typically an aquastat mounted as part of the appliance that controls combustion air supply to maintain the liquid in the appliance within a predetermined temperature range provided sufficient fuel is available in the firebox. The appliance may be equipped with other devices to control combustion.

1.5.4 A chimney or vent that exhausts combustion products from the appliance.

1.5.5 A liquid storage system, typically water, which is not large enough to accept all of the heat produced when a full load of wood is burned and the storage system starts a burn cycle at 125 °F.

1.5.6 The heating appliances require external thermal storage and these units will only be installed as part of a system which includes thermal storage. The manufacturer specifies the minimum amount of thermal storage required. However, the storage system shall be large enough to ensure that the boiler (heater) does not cycle, slumber, or go into an off-mode when operated in a Category III load condition (See section 4.3).

1.6 The values stated are to be regarded as the standard whether in I–P or SI units. The values given in parentheses are for information only.

2.0 Summary of Method and References

2.1 PM and CO emissions are measured from a wood–fired hydronic heating appliance burning a prepared test fuel charge in a test facility maintained at a set of prescribed conditions. Procedures for determining heat output rates, PM and CO emissions, and efficiency and for reducing data are provided.

2.2 Referenced Documents

2.2.1 EPA Standards

2.2.1.1 Method 28 Certification and Auditing of Wood Heaters

2.2.1.2 Method 28WHH Measurement of Particulate Emissions and Heating Efficiency of Wood-Fired Hydronic Heating Appliances and the Standards Referenced therein.

2.2.2 Other Standards

2.2.2.1 CSA–B415.1–10 *Performance Testing of Solid-Fuel-Burning Heating Appliances*

3.0 Terminology

3.1 Definitions

3.1.1 Hydronic Heating—A heating system in which a heat source supplies energy to a liquid heat exchange media such as water that is circulated to a heating load and returned to the heat source through pipes.

3.1.2 Aquastat—A control device that opens or closes a circuit to control the rate of fuel consumption in response to the temperature of the heating media in the heating appliance.

3.1.3 Delivered Efficiency—The percentage of heat available in a test fuel charge that is delivered to a simulated heating load or the storage system as specified in this test method.

3.1.4 Emission Factor—The emission of a pollutant expressed in mass per unit of energy (typically) output from the boiler/heater.

3.1.5 Emission Index—The emission of a pollutant expressed in mass per unit mass of fuel used.

3.1.6 Emission Rate—The emission of a pollutant expressed in mass per unit time

3.1.7 Manufacturer's Rated Heat Output Capacity—The value in Btu/hr (MJ/hr) that the manufacturer specifies that a particular model of hydronic heating appliance is capable of supplying at its design capacity as verified by testing, in accordance with section 12.5.4.

3.1.8 Heat Output Rate—The average rate of energy output from the appliance during a specific test period in Btu/hr (MJ/hr).

3.1.9 Firebox—The chamber in the appliance in which the test fuel charge is placed and combusted.

3.1.10 NIST—National Institute of Standards and Technology.

3.1.11 Test Fuel Charge—The collection of test fuel placed in the appliance at the start of the emission test run.

3.1.12 Test Run—An individual emission test which encompasses the time required to consume the mass of the test fuel charge. The time of the test run also considers the time for the energy to be drawn from the thermal storage.

3.1.13 Test Run Under ''Cold-to-Cold'' Condition—Under this test condition the test fuel is added into an empty chamber along with kindling and ignition materials (paper). The boiler/heater at the start of this test is typically 125° to 130 °F.

3.1.14 Test Run Under ''Hot-to-Hot'' Condition—Under this test condition the test fuel is added onto a still-burning bed of charcoals produced in a pre-burn period. The boiler/heater water is near its operating control limit at the start of the test.

3.1.15 Overall Efficiency, also known as Stack Loss Efficiency—The efficiency for each test run as determined using the CSA B415.1–10 (IBR, see §60.17) stack loss method (SLM).

3.1.16 Phases of a Burn Cycle—The ''startup phase'' is defined as the period from the start of the test until 15 percent of the test fuel charge is consumed. The ''steady-state phase'' is defined as the period from the end of the startup phase to a point at which 80 percent of the test fuel charge is consumed. The ''end phase'' is defined as the time from the end of the steady-state period to the end of the test.

3.1.17 Thermopile—A device consisting of a number of thermocouples connected in series, used for measuring differential temperature.

3.1.18 Slumber Mode—This is a mode in which the temperature of the water in the boiler/heater has exceeded the operating control limit and the control has changed the boiler/heater fan speed, dampers, and/or other operating parameters to minimize the heat output of the boiler/heater.

4.0 Summary of Test Method

4.1 Dilution Tunnel. Emissions are determined using the ''dilution tunnel'' method specified in EPA Method 28WHH and the standards referenced therein. The flow rate in the dilution tunnel is maintained at a constant level throughout the test cycle and accurately measured. Samples of the dilution tunnel flow stream are extracted at a constant flow rate and drawn through high efficiency filters. The filters are dried and weighed before and after the test to determine the emissions collected and this value is multiplied by the ratio of tunnel flow to filter flow to determine the total particulate emissions produced in the test cycle.

4.2 Efficiency. The efficiency test procedure takes advantage of the fact that this type of system delivers heat through circulation of the heated liquid (water) from the system to a remote heat exchanger (*e.g.* baseboard radiators in a room) and back to the system. Measurements of the cooling water temperature difference as it enters and exits the test system heat exchanger along with the measured flow rate allow for an accurate determination of the useful heat output of the appliance. Also included in the heat output is the change in the energy content in the storage system during a test run. Energy input to the appliance during the test run is determined by weight of the test fuel charge, adjusted for moisture content, multiplied by the higher heating value. Additional measurements of the appliance weight and temperature at the beginning and end of a test cycle are used to correct for heat stored in the appliance. Overall efficiency (SLM) is determined using the CSA B415.1–10 (IBR, see §60.17) stack loss method for data quality assurance purposes.

4.3 Operation. Four test categories are defined for use in this method. These are:

4.3.1 Category I: A heat output of 15 percent or less of manufacturer's rated heat output capacity.

4.3.2 Category II: A heat output of 16 percent to 24 percent of manufacturer's rated heat output capacity.

4.3.3 Category III: A heat output of 25 percent to 50 percent of manufacturer's rated heat output capacity.

4.3.4 Category IV: Manufacturer's Rated Heat Output Capacity. These heat output categories refer to the output from the system by way of the load heat exchanger installed for the test. The output from just the boiler/heater part of the system may be higher for all or part of a test, as part of this boiler/heater output goes to storage.

For the Category III and IV runs, appliance operation is conducted on a hot-to-hot test

cycle meaning that the appliance is brought to operating temperature and a coal bed is established prior to the addition of the test fuel charge and measurements are made for each test fuel charge cycle. The measurements are made under constant heat draw conditions within pre-determined ranges. No attempt is made to modulate the heat demand to simulate an indoor thermostat cycling on and off in response to changes in the indoor environment.

For the Category I and II runs, the unit is tested with a ''cold start.'' At the manufacturer's option, the Category II and III runs may be waived and it may be assumed that the particulate emission values and efficiency values determined in the startup, steady-state, and end phases of Category I are applicable in Categories II and III for the purpose of determining the annual averages in lb/mmBtu and g/MJ (See section 13). For the annual average in g/hr, the length of time for stored heat to be drawn from thermal storage shall be determined for the test load requirements of the respective category.

All test operations and measurements shall be conducted by personnel of the laboratory responsible for the submission of the test report.

5.0 Significance and Use

5.1 The measurement of particulate matter emission and CO rates is an important test method widely used in the practice of air pollution control.

5.1.1 These measurements, when approved by state or federal agencies, are often required for the purpose of determining compliance with regulations and statutes.

5.1.2 The measurements made before and after design modifications are necessary to demonstrate the effectiveness of design changes in reducing emissions and make this standard an important tool in manufacturers' research and development programs.

5.2 Measurement of heating efficiency provides a uniform basis for comparison of product performance that is useful to the consumer. It is also required to relate emissions produced to the useful heat production.

5.3 This is a laboratory method and is not intended to be fully representative of all actual field use. It is recognized that users of hand-fired, wood-burning equipment have a great deal of influence over the performance of any wood-burning appliance. Some compromises in realism have been made in the interest of providing a reliable and repeatable test method.

6.0 Test Equipment

6.1 Scale. A platform scale capable of weighing the boiler/heater under test and associated parts and accessories when completely filled with water to an accuracy of ±1.0 pound (±0.5 kg) and a readout resolution of ±0.2 pound (±0.1 kg).

6.2 Heat Exchanger. A water-to-water heat exchanger capable of dissipating the expected heat output from the system under test.

6.3 Water Temperature Difference Measurement. A Type—T 'special limits' thermopile with a minimum of 5 pairs of junctions shall be used to measure the temperature difference in water entering and leaving the heat exchanger. The temperature difference measurement uncertainty of this type of thermopile is equal to or less than ±0.50 °F (±0.25 °C). Other temperature measurement methods may be used if the temperature difference measurement uncertainty is equal to or less than ±0.50 °F (±0.25 °C). This measurement uncertainty shall include the temperature sensor, sensor well arrangement, piping arrangements, lead wire, and measurement/recording system. The response time of the temperature measurement system shall be less than half of the time interval at which temperature measurements are recorded.

6.4 Water Flow Meter. A water flow meter shall be installed in the inlet to the load side of the heat exchanger. The flow meter shall have an accuracy of ±1 percent of measured flow.

6.4.1 Optional—Appliance Side Water Flow Meter. A water flow meter with an accuracy of ±1 percent of the flow rate is recommended to monitor supply side water flow rate.

6.5 Optional Recirculation Pump. Circulating pump used during test to prevent stratification, in the boiler/heater, of liquid being heated.

6.6 Water Temperature Measurement. Thermocouples or other temperature sensors to measure the water temperature at the inlet and outlet of the load side of the heat exchanger must meet the calibration requirements specified in 10.1 of this method.

6.7 Lab Scale. For measuring the moisture content of wood slices as part of the overall wood moisture determination. Accuracy of ±0.01 pounds.

6.8 Flue Gas Temperature Measurement. Must meet the requirements of CSA B415.1–10 (IBR, see §60.17), clause 6.2.2.

6.9 Test Room Temperature Measurement. Must meet the requirements of CSA B415.1–10 (IBR, see §60.17), clause 6.2.1.

6.10 Flue Gas Composition Measurement. Must meet the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 6.3.1 through 6.3.3.

6.11 Dilution Tunnel CO Measurement. In parallel with the flue gas composition measurements, the CO concentration in the dilution tunnel shall also be measured and reported at time intervals not to exceed one minute. This analyzer shall meet the zero and span drift requirements of CSA B415.1–10 (IBR, see §60.17). In addition the measurement repeatability shall be better than ±15

ppm over the range of CO levels observed in the dilution tunnel.

7.0 Safety

7.1 These tests involve combustion of wood fuel and substantial release of heat and products of combustion. The heating system also produces large quantities of very hot water and the potential for steam production and system pressurization. Appropriate precautions must be taken to protect personnel from burn hazards and respiration of products of combustion.

8.0 Sampling, Test Specimens and Test Appliances

8.1 Test specimens shall be supplied as complete appliances, as described in marketing materials, including all controls and accessories necessary for installation in the test facility. A full set of specifications, installation and operating instructions, and design and assembly drawings shall be provided when the product is to be placed under certification of a third-party agency. The manufacturer's written installation and operating instructions are to be used as a guide in the set-up and testing of the appliance and shall be part of the test record.

8.2 The size, connection arrangement, and control arrangement for the thermal storage shall be as specified in the manufacturer's documentation. It is not necessary to use the specific storage system that the boiler/heater will be marketed with. However, the capacity of the system used in the test cannot be greater than that specified as the minimum allowable for the boiler/heater.

8.3 All system control settings shall be the as-shipped, default settings. These default settings shall be the same as those communicated in a document to the installer or end user. These control settings and the documentation of the control settings as to be provided to the installer or end user shall be part of the test record.

8.4 Where the manufacturer defines several alternatives for the connection and loading arrangement, one shall be defined in the appliance documentation as the default or standard installation. It is expected that this will be the configuration for use with a simple baseboard heating system. This is the configuration to be followed for these tests. The manufacturer's documentation shall define the other arrangements as optional or alternative arrangements.

9.0 Preparation of Test Equipment

9.1 The appliance is to be placed on a scale capable of weighing the appliance fully loaded with a resolution of ±0.2 lb (0.1 kg).

9.2 The appliance shall be fitted with the type of chimney recommended or provided by the manufacturer and extending to 15 ±0.5 feet (4.6 ±0.15 m) from the upper surface of the scale. If no flue or chimney system is recommended or provided by the manufacturer, connect the appliance to a flue of a diameter equal to the flue outlet of the appliance. The flue section from the appliance flue collar to 8 ±0.5 feet above the scale shall be single wall stove pipe and the remainder of the flue shall be double wall insulated class A chimney.

9.3 Optional Equipment Use

9.3.1 A recirculation pump may be installed between connections at the top and bottom of the appliance to minimize thermal stratification if specified by the manufacturer. The pump shall not be installed in such a way as to change or affect the flow rate between the appliance and the heat exchanger.

9.3.2 If the manufacturer specifies that a thermal control valve or other device be installed and set to control the return water temperature to a specific set point, the valve or other device shall be installed and set per the manufacturer's written instructions.

9.4 Prior to filling the boiler/heater with water, weigh and record the appliance mass.

9.5 Heat Exchanger

9.5.1 Plumb the unit to a water-to-water heat exchanger with sufficient capacity to draw off heat at the maximum rate anticipated. Route hoses and electrical cables and instrument wires in a manner that does not influence the weighing accuracy of the scale as indicated by placing dead weights on the platform and verifying the scale's accuracy.

9.5.2 Locate thermocouples to measure the water temperature at the inlet and outlet of the load side of the heat exchanger.

9.5.3 Install a thermopile (or equivalent instrumentation) meeting the requirements of section 6.3 to measure the water temperature difference between the inlet and outlet of the load side of the heat exchanger

9.5.4 Install a calibrated water flow meter in the heat exchanger load side supply line. The water flow meter is to be installed on the cooling water inlet side of the heat exchanger so that it will operate at the temperature at which it is calibrated.

9.5.5 Place the heat exchanger in a box with 2 in. (50 mm) of expanded polystyrene (EPS) foam insulation surrounding it to minimize heat losses from the heat exchanger.

9.5.6 The reported efficiency and heat output rate shall be based on measurements made on the load side of the heat exchanger.

9.5.7 Temperature instrumentation per section 6.6 shall be installed in the appliance outlet and return lines. The average of the outlet and return water temperature on the supply side of the system shall be considered the average appliance temperature for calculation of heat storage in the appliance (TF_{avg} and TI_{avg}). Installation of a water flow meter in the supply side of the system is optional.

9.6 Storage Tank. The storage tank shall include a destratification pump as illustrated in Figure 1. The pump will draw from the bottom of the tank and return to the top as illustrated. Temperature sensors (TS1 and TS2 in Figure 1) shall be included to measure the temperature in the recirculation loop. The valve plan in Figure 1 allows the tank recirculation loop to operate and the boiler/heater-to-heat exchanger loop to operate at the same time but in isolation. This would typically be done before the start of a test or following completion of a test to determine the end of test average tank temperature. The nominal flow rate in the storage tank recirculation loop can be estimated based on pump manufacturers' performance curves and any significant restriction in the recirculation loop.

9.7 Fill the system with water. Determine the total weight of the water in the appliance when the water is circulating. Verify that the scale indicates a stable weight under operating conditions. Make sure air is purged properly.

10.0 Calibration and Standardization

10.1 Water Temperature Sensors. Temperature measuring equipment shall be calibrated before initial use and at least semiannually thereafter. Calibrations shall be in compliance with National Institute of Standards and Technology (NIST) Monograph 175, Standard Limits of Error.

10.2 Heat Exchanger Load Side Water Flow Meter.

10.2.1 The heat exchanger load side water flow meter shall be calibrated within the flow range used for the test run using NIST-traceable methods. Verify the calibration of the water flow meter before and after each test run and at least once during each test run by comparing the water flow rate indicated by the flow meter to the mass of water collected from the outlet of the heat exchanger over a timed interval. Volume of the collected water shall be determined based on the water density calculated from section 13, Eq. 12, using the water temperature measured at the flow meter. The uncertainty in the verification procedure used shall be 1 percent or less. The water flow rate determined by the collection and weighing method shall be within 1 percent of the flow rate indicated by the water flow meter.

10.3 Scales. The scales used to weigh the appliance and test fuel charge shall be calibrated using NIST-traceable methods at least once every 6 months.

10.4 Flue Gas Analyzers—In accordance with CSA B415.1–10 (IBR, see §60.17), clause 6.8.

11.0 Conditioning

11.1 Prior to testing, an appliance is to be operated for a minimum of 50 hours using a medium heat draw rate. The conditioning may be at the manufacturer's facility prior to the certification test. If the conditioning is at the certification test laboratory, the pre-burn for the first test can be included as part of the conditioning requirement. If conditioning is included in pre-burn, then the appliance shall be aged with fuel meeting the specifications outlined in section 12.2 with a moisture content between 19 and 25 percent on a dry basis. Operate the appliance at a medium heat output rate (Category II or III) for at least 10 hours for non-catalytic appliances and 50 hours for catalytic appliances. Record and report hourly flue gas exit temperature data and the hours of operation. The aging procedure shall be conducted and documented by a testing laboratory.

12.0 Procedure

12.1 Appliance Installation. Assemble the appliance and parts in conformance with the manufacturer's written installation instructions. Clean the flue with an appropriately sized, wire chimney brush before each certification test series.

12.2 Fuel. Test fuel charge fuel shall be red (*Quercus ruba L.*) or white (*Quercus Alba*) oak 19 to 25 percent moisture content on a dry basis. Piece length shall be 80 percent of the firebox depth rounded down to the nearest 1 inch (25mm) increment. For example, if the firebox depth is 46 inches (1168mm) the piece length would be 36 inches (46 inches × 0.8 = 36.8 inches, rounded down to 36 inches). Pieces are to be placed in the firebox parallel to the longest firebox dimension. For fireboxes with sloped surfaces that create a non-uniform firebox length, the piece length shall be adjusted for each layer based on 80 percent of the length at the level where the layer is placed. The test fuel shall be cord wood with cross section dimensions and weight limits as defined in CSA B415.1–10 (IBR, see §60.17), section 8.3, Table 4. The use of dimensional lumber is not allowed.

12.2.1 Select three pieces of cord wood from the same batch of wood as the test fuel and the same weight as the average weight of the pieces in the test load ±1.0 lb. From each of these three pieces, cut three slices. Each slice shall be ½ inch to ¾ inch thick. One slice shall be cut across the center of the length of the piece. The other two slices shall be cut half way between the center and the end. Immediately measure the mass of each piece in pounds. Dry each slice in an oven at 220 °F for 24 hours or until no further weight change occurs. The slices shall be arranged in the oven so as to provide separation between faces. Remove from the oven and measure the mass of each piece again as soon as practical, in pounds.

The moisture content of each slice, on a dry basis, shall be calculated as:

$$MC_{slice} = 100 \cdot \frac{(W_{SliceWet} - W_{SliceDry})}{W_{SliceDry}}$$

Where:

$W_{SliceWet}$ = weight of the slice before drying in pounds

$W_{SliceDry}$ = weight of the slice after drying in pounds

MC_{Slice} = moisture content of the slice in % dry basis

The average moisture content of the entire test load (MC) shall be determined using Eq. 6. Each individual slice shall have a moisture content in the range of 18 percent to 28 percent on a dry basis. The average moisture content for the test fuel load shall be in the range of 19 percent to 25 percent. Moisture shall not be added to previously dried fuel pieces except by storage under high humidity conditions and temperature up to 100 °F. Fuel moisture measurement shall begin within 4 hours of using the fuel batch for a test. Use of a pin-type meter to estimate the moisture content prior to a test is recommended.

12.2.2 Firebox Volume. Determine the firebox volume in cubic feet. Firebox volume shall include all areas accessible through the fuel loading door where firewood could reasonably be placed up to the horizontal plane defined by the top of the loading door. A drawing of the firebox showing front, side and plan views or an isometric view with interior dimensions shall be provided by the manufacturer and verified by the laboratory. Calculations for firebox volume from computer aided design (CAD) software programs are acceptable and shall be included in the test report if used. If the firebox volume is calculated by the laboratory the firebox drawings and calculations shall be included in the test report.

12.2.3 Test Fuel charge. Test fuel charges shall be determined by multiplying the firebox volume by 10 pounds (4.54 kg) per ft^3 (28L), or a higher load density as recommended by the manufacturer's printed operating instructions, of wood (as used wet weight). Select the number of pieces of cord wood that most nearly match this target weight. However, the test fuel charge cannot be less than the target of 10 pounds (4.54 kg) per ft^3 (28L).

12.3 Sampling Equipment. Prepare the particulate emission sampling equipment as defined by EPA Method 28WHH and the standards referenced therein.

12.4 Appliance Startup. The appliance shall be fired with wood fuel of any species, size and moisture content, at the laboratory's discretion, to bring it up to operating temperature. Operate the appliance until the water is heated to the upper operating control limit and has cycled at least two times. Then remove all unburned fuel, zero the scale and verify the scales accuracy using dead weights.

12.4.1 Startup Procedure for Category III and IV Test Runs, ''Hot-to-Hot.''

12.4.1.1 Pretest t Burn Cycle. Following appliance startup (section 12.4), reload appliance with oak cord wood and allow it to burn down to the specified coal bed weight. The pre-test burn cycle fuel charge weight shall be within ±10 percent of the test fuel charge weight. Piece size and length shall be selected such that charcoalization is achieved by the time the fuel charge has burned down to the required coal bed weight. Pieces with a maximum thickness of approximately 2 inches have been found to be suitable. Charcoalization is a general condition of the test fuel bed evidenced by an absence of large pieces of burning wood in the coal bed and the remaining fuel pieces being brittle enough to be broken into smaller charcoal pieces with a metal poker. Manipulations to the fuel bed prior to the start of the test run are to be done to achieve charcoalization while maintaining the desired heat output rate. During the pre-test burn cycle and at least one hour prior to starting the test run, adjust water flow to the heat exchanger to establish the target heat draw for the test. For the first test run the heat draw rate shall be equal to the manufacturer's rated heat output capacity.

12.4.1.2 Allowable Adjustments. Fuel addition or subtractions, and coal bed raking shall be kept to a minimum but are allowed up to 15 minutes prior to the start of the test run. For the purposes of this method, coal bed raking is the use of a metal tool (poker) to stir coals, break burning fuel into smaller pieces, dislodge fuel pieces from positions of poor combustion, and check for the condition of charcoalization. Record all adjustments to and additions or subtractions of fuel, and any other changes to the appliance operations that occur during pretest ignition period. During the 15-minute period prior to the start of the test run, the wood heater loading door shall not be open more than a total of 1 minute. Coal bed raking is the only adjustment allowed during this period.

12.4.1.3 Coal Bed Weight. The appliance is to be loaded with the test fuel charge when the coal bed weight is between 10 percent and 20 percent of the test fuel charge weight. Coals may be raked as necessary to level the coal bed but may only be raked and stirred

once between 15 to 20 minutes prior to the addition of the test fuel charge.

12.4.1.4 Storage. The Category III and IV test runs may be done either with or without the thermal storage. If thermal storage is used, the initial temperature of the storage must be 125 °F or greater at the start of the test. The storage may be heated during the pre-test burn cycle or it may be heated by external means. If thermal storage is used, prior to the start of the test run, the storage tank destratification pump, shown in Figure 1, shall be operated until the total volume pumped exceeds 1.5 times the tank volume and the difference between the temperature at the top and bottom of the storage tank (TS_1 and TS_2) is less than 1 °F. These two temperatures shall then be recorded to determine the starting average tank temperature. The total volume pumped may be based on the nominal flow rate of the destratification pump (See section 9.6). If the Category III and IV runs are done with storage, it is recognized that during the last hour of the pre-burn cycle the storage tank must be mixed to achieve a uniform starting temperature and cannot receive heat from the boiler/heater during this time. During this time period, the boiler/heater might cycle or go into a steady reduced output mode. (Note—this would happen, for example, in a Category IV run if the actual maximum output of the boiler/heater exceed the manufacturer's rated output.) A second storage tank may be used temporarily to enable the boiler/heater to operate during this last hour of the pre-burn period as it will during the test period. The temperature of this second storage tank is not used in the calculations but the return water to the boiler/heater (after mixing device if used) must be 125 °F or greater.

12.4.2 Startup Procedure for Category I and II Test Runs, ''Cold-to-Cold.''

12.4.2.1 Initial Temperatures. This test shall be started with both the boiler/heater and the storage at a minimum temperature of 125 °F. The boiler/heater maximum temperature at the start of this test shall be 135 °F. The boiler/heater and storage may be heated through a pre-burn or it may be heated by external means.

12.4.2.2 Firebox Condition at Test Start. Prior to the start of this test remove all ash and charcoal from the combustion chamber(s). The loading of the test fuel and kindling should follow the manufacturer's recommendations, subject to the following constraints: Up to 10 percent kindling and paper may be used which is in addition to the fuel load. Further, up to 10 percent of the fuel load (*i.e.*, included in the 10 lb/ft^3) may be smaller than the main fuel. This startup fuel shall still be larger than 2 inches.

12.4.2.3 Storage. The Category I and II test runs shall be done with thermal storage. The initial temperature of the storage must be 125 °F or greater at the start of the test. The storage may be heated during the pre-test burn cycle or it may be heated by external means. Prior to the start of the test run, the storage tank destratification pump, shown in Figure 1, shall be operated until the total volume pumped exceeds 1.5 times the tank volume and the difference between the temperature at the top and bottom of the storage tank (TS_1 and TS_2) is less than 1 °F. These two temperatures shall then be recorded to determine the starting average tank temperature. The total volume pumped may be based on the nominal flow rate of the destratification pump (See section 9.6).

12.5 Test Runs. For all test runs, the return water temperature to the hydronic heater must be equal to or greater than 120 °F (this is lower than the initial tank temperature to allow for any pipeline losses). Where the storage system is used, flow of water from the boiler/heater shall be divided between the storage tank and the heat exchanger such that the temperature change of the circulating water across the heat exchanger shall be 30 ±5 °F, averaged over the entire test run. This is typically adjusted using the system valves.

Complete a test run in each heat output rate category, as follows:

12.5.1 Test Run Start. For Category III and IV runs: Once the appliance is operating normally and the pretest coal bed weight has reached the target value per section 12.4.1, tare the scale and load the full test charge into the appliance. Time for loading shall not exceed 5 minutes. The actual weight of the test fuel charge shall be measured and recorded within 30 minutes prior to loading. Start all sampling systems.

For Category I and II runs: Once the appliance has reached the starting temperature, tare the scale and load the full test charge, including kindling into the appliance. The actual weight of the test fuel charge shall be measured and recorded within 30 minutes prior to loading. Light the fire following the manufacturer's written normal startup procedure. Start all sampling systems.

12.5.1.1 Record all water temperatures, differential water temperatures and water flow rates at time intervals of one minute or less.

12.5.1.2 Record particulate emissions data per the requirements of EPA Method 28WHH and the standards referenced therein.

12.5.1.3 Record data needed to determine overall efficiency (SLM) per the requirements of CSA B415.1–10 (IBR, see §60.17) clauses 6.2.1, 6.2.2, 6.3, 8.5.7, 10.4.3(a), 10.4.3(f), and 13.7.9.3

12.5.1.3.1 Measure and record the test room air temperature in accordance with the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 6.2.1, 8.5.7 and 10.4.3(g).

12.5.1.3.2 Measure and record the flue gas temperature in accordance with the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 6.2.2, 8.5.7 and 10.4.3(f).

12.5.1.3.3 Determine and record the carbon monoxide (CO) and carbon dioxide (CO_2) concentrations in the flue gas in accordance with CSA B415.1–10 (IBR, see §60.17), clauses 6.3, 8.5.7 and 10.4.3(i) and (j).

12.5.1.3.4 Measure and record the test fuel weight per the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 8.5.7 and 10.4.3(h).

12.5.1.3.5 Record the test run time per the requirements of CSA B415.1–10 (IBR, see §60.17), clause 10.4.3(a).

12.5.1.3.6 Record and document all settings and adjustments, if any, made to the boiler/heater as recommended/required by manufacturer's instruction manual for different combustion conditions or heat loads. These may include temperature setpoints, under and over-fire air adjustment, or other adjustments that could be made by an operator to optimize or alter combustion. All such settings shall be included in the report for each test run.

12.5.1.4 Monitor the average heat output rate on the load side of the heat exchanger based on water temperatures and flow. If the heat output rate over a 10 minute averaging period gets close to the upper or lower limit of the target range (±5 percent), adjust the water flow through the heat exchanger to compensate. Make changes as infrequently as possible while maintaining the target heat output rate. The first test run shall be conducted at the Category IV heat output rate to validate that the appliance is capable of producing the manufacturer's rated heat output capacity.

12.5.2 Test Fuel Charge Adjustment. It is acceptable to adjust the test fuel charge (*i.e.*, reposition) once during a test run if more than 60 percent of the initial test fuel charge weight has been consumed and more than 10 minutes have elapsed without a measurable (1 lb or 0.5 kg) weight change while the operating control is in the demand mode. The time used to make this adjustment shall be less than 60 seconds.

12.5.3 Test Run Completion. For the Category III and IV, ''hot-to-hot'' test runs, the test run is completed when the remaining weight of the test fuel charge is 0.0 lb (0.0 kg). ($W_{FuelBurned} = W_{fuel}$) End the test run when the scale has indicated a test fuel charge weight of 0.0 lb (0.0 kg) or less for 30 seconds.

For the Category I and II ''cold-to-cold'' test runs, the test run is completed; and the end of a test is defined at the first occurrence of any one of the following:

(a) The remaining weight of the test fuel charge is less than 1 percent of the total test fuel weight ($W_{FuelBurned} > 0.99 \cdot W_{fuel}$);

(b) The automatic control system on the boiler/heater switches to an off mode. In this case, the boiler/heater fan (if used) is typically stopped and all air flow dampers are closed by the control system. Note that this off mode cannot be an ''overheat'' or emergency shutdown which typically requires a manual reset; or

(c) If the boiler/heater does not have an automatic off mode: After 90 percent of the fuel load has been consumed and the scale has indicated a rate of change of the test fuel charge of less than 1.0 lb/hr for a period of 10 minutes or longer. Note—this is not considered ''stopped fuel combustion,'' See section 12.5.6.1.

12.5.3.1 At the end of the test run, stop the particulate sampling train and overall efficiency (SLM) measurements, and record the run time, and all final measurement values.

12.5.3.2 At the end of the test run, continue to operate the storage tank destratification pump until the total volume pumped exceeds 1.5 times the tank volume. The maximum average of the top and bottom temperatures measured after this time may be taken as the average tank temperature at the end of the tests (TFSavg, See section 13.1). The total volume pumped may be based on the nominal flow rate of the destratification pump (See section 9.6).

12.5.3.3 For the Category I and II test runs, there is a need to determine the energy content of the unburned fuel remaining in the chamber if the remaining mass in the chamber is greater than 1 percent of the test fuel weight. Following the completion of the test, as soon as safely practical, this remaining fuel is removed from the chamber, separated from the remaining ash and weighed. This separation could be implemented with a slotted ''scoop'' or similar tool. A ¼ inch opening size in the separation tool shall be used to separate the ash and charcoal. This separated char is assigned a heating value of 12,500 Btu/lb.

12.5.4 Heat Output Capacity Validation. The first test run must produce a heat output rate that is within 10 percent of the manufacturer's rated heat output capacity (Category IV) throughout the test run and an average heat output rate within 5 percent of the manufacturer's rated heat output capacity. If the appliance is not capable of producing a heat output within these limits, the manufacturer's rated heat output capacity is considered not validated and testing is to be terminated. In such cases, the tests may be restarted using a lower heat output capacity if requested by the manufacturer. Alternatively, during the Category IV run, if the rated output cannot be maintained for a 15 minute interval, the manufacturer may elect to reduce the rated output to match the test and complete the Category IV run on this basis. The target outputs for Categories I, II, and III shall then be recalculated based on this change in rated output capacity.

12.5.5 Additional Test Runs. Using the manufacturer's rated heat output capacity

as a basis, conduct a test for additional heat output categories as specified in section 4.3. It is not required to run these tests in any particular order.

12.5.6 Alternative Heat Output Rate for Category I. If an appliance cannot be operated in the Category I heat output range due to stopped combustion, two test runs shall be conducted at heat output rates within Category II. When this is the case, the weightings for the weighted averages indicated in section 14.1.15 shall be the average of the Category I and II weighting's and shall be applied to both Category II results. Appliances that are not capable of operation within Category II (<25 percent of maximum) cannot be evaluated by this test method.

12.5.6.1 Stopped Fuel Combustion. Evidence that an appliance cannot be operated at a Category I heat output rate due to stopped fuel combustion shall include documentation of two or more attempts to operate the appliance in heat output rate Category I and fuel combustion has stopped prior to complete consumption of the test fuel charge. Stopped fuel combustion is evidenced when an elapsed time of 60 minutes or more has occurred without a measurable (1 lb or 0.5 kg) weight change in the test fuel charge while the appliance operating control is in the demand mode. Report the evidence and the reasoning used to determine that a test in heat output rate Category I cannot be achieved. For example, two unsuccessful attempts to operate at an output rate of 10 percent of the rated output capacity are not sufficient evidence that heat output rate Category I cannot be achieved.

12.5.7 Appliance Overheating. Appliances with their associated thermal storage shall be capable of operating in all heat output categories without overheating to be rated by this test method. Appliance overheating occurs when the rate of heat withdrawal from the appliance is lower than the rate of heat production when the unit control is in the idle mode. This condition results in the water in the appliance continuing to increase in temperature well above the upper limit setting of the operating control. Evidence of overheating includes: 1 hour or more of appliance water temperature increase above the upper temperature set-point of the operating control, exceeding the temperature limit of a safety control device (independent from the operating control—typically requires manual reset), boiling water in a non-pressurized system or activation of a pressure or temperature relief valve in a pressurized system.

12.5.8 Option to Eliminate Tests in Category II and III. Following successful completion of a test run in Category I, the manufacturer may eliminate the Category II and III tests. For the purpose of calculating the annual averages for particulates and efficiency, the values obtained in the Category I run shall be assumed to apply also to Category II and Category III. It is envisioned that this option would be applicable to systems which have sufficient thermal storage such that the fuel load in the Category I test can be completely consumed without the system reaching its upper operating temperature limit. In this case, the boiler/heater would likely be operating at maximum thermal output during the entire test and this output rate may be higher than the manufacturer's rated heat output capacity. The Category II and III runs would then be the same as the Category I run. It may be assumed that the particulate emission values and efficiency values determined in the startup, steady-state, and end phases of Category I are applicable in Categories II and III, for the purpose of determining the annual averages in lb/mmBtu and g/MJ (See section 13). For the annual average in g/hr, the length of time for stored heat to be drawn from thermal storage shall be determined for the test load requirements of the respective category.

12.5.9 Modification to Measurement Procedure in EPA Method 28WHH to Determine Emissions Separately During the Startup, Steady-State and End Phases. With one of the two particulate sampling trains used, filter changes shall be made at the end of the startup phase and the steady-state phase (See section 3.0). This shall be done to determine the particulate emission rate and particulate emission index for the startup, steady-state, and end phases individually. For this one train, the particulates measured during each of these three phases shall be added together to also determine the particulate emissions for the whole run.

12.5.10 Modification to Measurement Procedure in EPA Method 28WHH and the Standards Referenced therein on Averaging Period for Determination of Efficiency by the Stack Loss Method. The methods currently defined in Method 28WHH allow averaging over 10-minute time periods for flue gas temperature, flue gas CO_2, and flue gas CO for the determination of the efficiency with the stack loss method. However, under some cycling conditions the ''on'' period may be short relative to this 10-minute period. For this reason, during cycling operation the averaging period for these parameters may not be longer than the burner on period divided by 10. The averaging period need not be shorter than one minute. During the off period, under cycling operation, averaging periods as specified in EPA Method 28WHH and the standards referenced therein, may be used. Where short averaging times are used, however, the averaging period for fuel consumption may still be at 10 minutes. This average wood consumption rate shall be applied to all of the smaller time intervals included.

12.6 Additional Test Runs. The testing laboratory may conduct more than one test run in each of the heat output categories specified in section 4.3. If more than one test run is conducted at a specified heat output rate, the results from at least two-thirds of the test runs in that heat output rate category shall be used in calculating the weighted average emission rate. The measurement data and results of all test runs shall be reported regardless of which values are used in calculating the weighted average emission rate.

13.0 Calculation of Results

13.1 Nomenclature

CO_s—Carbon monoxide measured in the dilution tunnel at arbitrary time in ppm dry basis.

$CO_{g/min}$—Carbon monoxide emission rate in g/min.

CO_T—Total carbon monoxide emission for the full test run in grams.

CO_{-1}—Startup period carbon monoxide emissions in grams.

CO_{-2}—Steady-state period carbon monoxide emission in grams.

CO_{-3}—End period carbon monoxide emission in grams.

E_T—Total particulate emissions for the full test run as determined per EPA Method 28WHH and the standards referenced therein in grams.

E_1—Startup period particulate emissions in grams.

E_2—Steady-state period particulate emissions in grams.

E_3—End period particulate emissions in grams.

$E_{1-g/kg}$—Startup period particulate emission index in grams per kg fuel.

$E_{2-g/kg}$—Steady-state period particulate emission index in grams per kg fuel.

$E_{3-g/kg}$—End period particulate emission index in grams per kg fuel.

$E_{1-g/hr}$—Startup period particulate emission rate in grams per hour.

$E_{2-g/hr}$—Steady-state period particulate emission rate in grams per hour.

$E_{3-g/hr}$—End period particulate emission rate in grams per hour.

$E_{g/MJ}$—Emission rate in grams per MJ of heat output.

$E_{lb/mmBtu\ output}$—Emissions rate in pounds per million Btu of heat output.

$E_{g/kg}$—Emissions factor in grams per kilogram of dry fuel burned.

$E_{g/hr}$—Emission factor in grams per hour.

HHV—Higher heating value of fuel = 8600 Btu/lb (19.990 MJ/kg).

LHV—Lower heating value of fuel = 7988 Btu/lb (18.567 MJ/kg).

ΔT—Temperature difference between cooling water entering and exiting the heat exchanger.

Q_{out}—Total heat output in Btu (MJ).

Q_{in}—Total heat input available in test fuel charge in Btu's (MJ).

Q_{std}—Volumetric flow rate in dilution tunnel in dscfm.

M—Mass flow rate of water in lb/min (kg/min).

V_i—Volume of water indicated by a totalizing flow meter at the i_{th} reading in gallons (liters).

V_f—Volumetric flow rate of water in heat exchange system in gallons per minute (liters/min).

Θ—Total length of burn period in hours ($\Theta_1 + \Theta_2 + \Theta_3$).

Θ_1—Length of time of the startup period in hours.

Θ_2—Length of time of the steady-state period in hours.

Θ_3—Length of time of the end period in hours.

Θ_4—Length of time for stored heat to be used following a burn period in hours.

t_i—Data sampling interval in minutes.

η_{del}—Delivered heating efficiency in percent.

F_i—Weighting factor for heat output category i. (See Table 2.)

T1—Temperature of water at the inlet on the supply side of the heat exchanger, °F.

T2—Temperature of the water at the outlet on the supply side of the heat exchanger, °F.

T3—Temperature of cooling water at the inlet to the load side of the heat exchanger, °F.

T4—Temperature of cooling water at the outlet of the load side of the heat exchanger, °F.

T5—Temperature of the hot water supply as it leaves the boiler/heater, °F.

T6—Temperature of return water as it enters the boiler/heater, °F.

T7—Temperature in the boiler/heater optional destratification loop at the top of the boiler/heater, °F.

T8—Temperature in the boiler/heater optional destratification loop at the bottom of the boiler/heater, °F.

TI_{avg}—Average temperature of the appliance and water at start of the test.

$TI_{avg} - (T5 + T6)/2$ at the start of the test, °F. Eq. 1

TF_{avg}—Average temperature of the appliance and water at the end of the test.

TF_{avg} – (T5 + T6)/2 at the end of the test, °F. Eq. 2

TIS_1—Temperature at the inlet to the storage system at the start of the test.
TIS_2—Temperature at the outlet from the storage system at the start of the test.
TFS_1—Temperature at the inlet to the storage system at the end of the test.
TFS_2—Temperature at the outlet from the storage system at the end of the test.
TIS_{avg}—Average temperature of the storage system at the start of the test.

TIS_{avg} – $(TIS_1 + TIS_2)/2$ at the end of the test. Eq. 3

TFS_{avg}—Average temperature of the storage system at the end of the test.

TFS_{avg} – $(TFS_1 + TFS_2)/2$. Eq. 4

MC—Fuel moisture content in percent dry basis.
σ—Density of water in pounds per gallon.
$\sigma_{Initial}$—Density of water in the boiler/heater system at the start of the test in pounds per gallons.
$\sigma_{boiler/heater}$—Density of water in the boiler/heater system at an arbitrary time during the test in pounds per gallon.
C_p—Specific heat of water in Btu/lb, °F.
C_{steel}—Specific heat of steel (0.1 Btu/lb, °F).
$V_{boiler/heater}$—total volume of water in the boiler/heater system on the weight scale in gallons.
W_{fuel}—Fuel charge weight, as-fired or ''wet'', in pounds (kg).
$W_{fuel—1}$—Fuel consumed during the startup period in pounds (kg).
$W_{fuel—2}$—Fuel consumed during the steady state period in pounds (kg).
$W_{fuel—3}$—Fuel consumed during the end period in pounds (kg).
$W_{FuelBurned}$—Weight of fuel that has been burned from the start of the test to an arbitrary time, including the needed correction for the change in density and weight of the water in the boiler/heater system on the scale in pounds (kg).
$W_{RemainingFuel}$—Weight of unburned fuel separated from the ash at the end of a test. Useful only for Category I and Category II tests.
W_{app}—Weight of empty appliance in pounds (kg).
W_{wat}—Weight of water in supply side of the system in pounds (kg).
$W_{ScaleInitial}$—Weight reading on the scale at the start of the test, just after the test load has been added in pounds (kg).
W_{Scale}—Reading of the weight scale at an arbitrary time during the test run in pounds (kg).
$W_{StorageTank}$—Weight of the storage tank empty in pounds (kg).
$W_{WaterStorage}$—Weight of the water in the storage tank at TIS_{avg} in pounds (kg).

13.2 After the test is completed, determine the particulate emissions E_T in accordance with EPA Method 28WHH and the standards referenced therein.

13.3 Determination of the weight of fuel that has been burned at an arbitrary time.

For the purpose of tracking the consumption of the test fuel load during a test run the following may be used to calculate the weight of fuel that burned since the start of the test:

$$W_{FuelBurned} = (W_{ScaleInitial} - W_{Scale}) + V_{Boiler/heater} \cdot (\sigma_{Initial} - \sigma_{boiler/heater}) \quad \text{Eq. 5}$$

Water density, σ, is calculated using Equation 12.

13.4 Determine Average Fuel Load Moisture Content.

$$MC = \frac{\sum W_{SliceWet_i} - MC_{Slice_i}}{\sum W_{SliceWet_i}} \quad \text{Eq. 6}$$

13.5 Determine Heat Input.

$$Q_{in} = (W_{fuel}/(1+(MC/100))) \text{ x HHV, Btu (MJ).} \quad \text{Eq. 7}$$

$$Q_{in\ LHV} = (W_{fuel}/(1+(MC/100))) \text{ x LHV, Btu (MJ).} \quad \text{Eq. 8}$$

13.5.1 Correction to Q_{in} for the Category I and II tests, where there is greater than 1 percent of the test fuel charge in the chamber at the end of the test period.

$$Q_{lnCorrected} = Q_{in} - W_{Remaining} \cdot 12{,}500\ \underline{Btu} \quad \text{Eq. 9}$$

13.6 Determine Heat Output, Efficiency, and Emissions.

13.6.1 Determine heat output as:

Q_{out} = Σ [Heat output determined for each sampling time interval] + Change in heat stored in the appliance + Change in heat in storage tank.

$$Qout = \Sigma[C_{pi} \cdot \Delta T_i \cdot M_i \cdot t_i] + (W_{app} \cdot C_{steel} + W_{water} \cdot C_{pa}) \cdot (TF_{avg} - TI_{avg})$$
$$+ (W_{StorageTank} \cdot C_{steel} + W_{WaterStorage} \cdot C_{pa}) \cdot (TFS_{avg} - TIS_{avg}) \text{ Btu (MJ)} \quad \text{Eq. 10}$$

NOTE: The subscript (i) indicates the parameter value for sampling time interval t_i.M_i = Mass flow rate = gal/min × density of water (lb/gal) = lb/min.

$$M_i = V_{fi} \cdot \sigma_i, \text{ lb/min.} \quad \text{Eq. 11}$$

$$\sigma_i = (62.56 + (-.0003413 \text{ x } T3_i) + (-.00006225 \text{ x } T3_i^2)) 0.1337, \text{ lb/gal.} \quad \text{Eq. 12}$$

$$C_p = 1.0014 + (-.000003485 \text{ x } T3_i) \text{ Btu/lb, -°F.} \quad \text{Eq. 13}$$

C_{steel} = 0.1 Btu/lb, -° F.

$$C_{pa} = 1.0014 + (-.000003485 \text{ X } (TI_{avg} + TF_{avg})/2), \text{ Btu/lb, °F.} \quad \text{Eq. 14}$$

$$V_{fi} = (V_i - V_{i-1})/(t_i - t_{i-1}), \text{ gal/min.} \quad \text{Eq. 15}$$

NOTE: V_i is the total water volume at the end of interval i and V_{i-1} is the total water volume at the beginning of the time interval. This calculation is necessary when a totalizing type water meter is used.

13.6.2 Determine Heat Output Rate Over Burn Period ($\Theta_1 + \Theta_2 + \Theta_3$) as:

Heat Output Rate = Q_{out}/Θ, Btu/hr (MJ/hr). Eq. 16

13.6.3 Determine Emission Rates and Emission Factors as:

$E_{g/MJ} = E_T/(Q_{out} \times 0.001055)$, g/MJ. Eq. 17

$E_{lb/MM\ Btu\ output} = (E_T/453.59)/(Q_{out} \times 10^{-6})$, lb/mmBtu out. Eq. 18

$E_{g/kg} = E_T/(W_{fuel}/(1+MC/100))$, g/dry kg. Eq. 19

$E_{g/hr} = E_T/(\Theta_1+ \Theta_2+ \Theta_3+ \Theta_4)$, g/hr. Eq. 20

$\Theta_4 = (W_{StorageTank} \cdot C_{steel} + W_{WaterStorage} \cdot C_{pa}) \cdot (TFS_{avg} - TIS_{avg})/(Q_{out}/\Theta)$ Eq. 21

If thermal storage is not used in a Category III or IV run, then $\Theta_4 = 0$.

$E_{1—g/kg} = E_1/(W_{fuel—1}/(1 + MC/100))$, g/dry kg.
$E_{2—g/kg} = E_2/(W_{fuel—2}/(1 + MC/100))$, g/dry kg.
$E_{3—g/kg} = E_3/(W_{fuel—3}/(1 + MC/100))$, g/dry kg.
$E_{1—g/hr} = E_1/\Theta_1$, g/hr.
$E_{2—g/hr} = E_2/\Theta_2$, g/hr.
$E_{3—g/hr} = E_3/\Theta_3$, g/hr.

13.6.4 Determine delivered efficiency as:

$\eta_{del} = (Q_{out}/Q_{InCorrected}) \times 100$, %. Eq. 22

$\eta_{del\ LHV} = (Q_{out}/Q_{in\ LHV}) \times 100$, %. Eq. 23

13.6.5 Determine η_{SLM}—Overall Efficiency, also known as Stack Loss Efficiency, using stack loss method (SLM).

For determination of the average overall thermal efficiency (η_{SLM}) for the test run, use the data collected over the full test run and the calculations in accordance with CSA B415.1–10 (IBR, see §60.17), clause 13.7 except for 13.7.2(e), (f), (g), and (h), use the following average fuel properties for oak: %C = 50.0, %H = 6.6, %O = 43.2, %Ash = 0.2.

13.6.5.1 Whenever the CSA B415.1–10 (IBR, see §60.17) overall efficiency is found to be lower than the overall efficiency based on load side measurements, as determined by Eq. 22 of this method, section 14.1.7 of the test report must include a discussion of the reasons for this result. For a test where the CSA B415.1–10 overall efficiency SLM is less than 2 percentage points lower than the overall efficiency based on load side measurements, the efficiency based on load side measurements shall be considered invalid. [Note on the rationale for the 2 percentage points limit. The SLM method does not include boiler/heater jacket losses and, for this reason, should provide an efficiency which is actually higher than the efficiency based on the energy input and output measurements or ''delivered efficiency.'' A delivered efficiency that is higher than the efficiency based on the SLM could be considered suspect. A delivered efficiency greater than 2 percentage points higher than the efficiency based on the SLM, then, clearly indicates a measurement error.]

13.6.6 Carbon Monoxide Emissions

For each minute of the test period, the carbon monoxide emission rate shall be calculated as:

$$CO_{g/min} = Q_{std} \cdot CO_s \cdot 3.30 \times 10^{-5} \quad \text{Eq. 24}$$

Total CO emissions for each of the three test periods ($CO_{—1}$, $CO_{—2}$, $CO_{—3}$) shall be calculated as the sum of the emission rates for each of the 1-minute intervals. Total CO emission for the test run, CO_T, shall be calculated as the sum of $CO_{—1}$, $CO_{—2}$, and $CO_{—3}$.

13.7 Weighted Average Emissions and Efficiency.

13.7.1 Determine the weighted average emission rate and delivered efficiency from the individual tests in the specified heat output categories. The weighting factors (F_i) are derived from an analysis of ASHRAE bin data which provides details of normal building heating requirements in terms of percent of design capacity and time in a particular capacity range—or ''bin''—over the course of a heating season. The values used in this method represent an average of data from several cities located in the northern United States.

Weighted average delivered efficiency: $\eta_{avg} = \Sigma\ \eta_i \times F_i$, %. Eq. 25

Weighted average emissions: $E_{avg} = \Sigma\ E_i \times F_i$, % Eq. 26

If, as discussed in section 12.5.8, the option to eliminate tests in Category II and III is elected, the values of efficiency and particulate emission rate as measured in Category I, shall be assigned also to Category II and III for the purpose of determining the annual averages.

14.0 Report

14.1.1 The report shall include the following:

14.1.2 Name and location of the laboratory conducting the test.

14.1.3 A description of the appliance tested and its condition, date of receipt and dates of tests.

14.1.4 A description of the minimum amount of external thermal storage that is required for use with this system. This shall be specified both in terms of volume in gallons and stored energy content in Btu with a storage temperature ranging from 125 °F to the manufacturer's specified setpoint temperature.

14.1.5 A statement that the test results apply only to the specific appliance tested.

14.1.6 A statement that the test report shall not be reproduced except in full, without the written approval of the laboratory.

14.1.7 A description of the test procedures and test equipment including a schematic or other drawing showing the location of all required test equipment. Also, a description of test fuel sourcing, handling and storage practices shall be included.

14.1.8 Details of deviations from, additions to or exclusions from the test method, and their data quality implications on the test results (if any), as well as information on specific test conditions, such as environmental conditions.

14.1.9 A list of participants and their roles and observers present for the tests.

14.1.10 Data and drawings indicating the fire box size and location of the fuel charge.

14.1.11 Drawings and calculations used to determine firebox volume.

14.1.12 Information for each test run fuel charge including piece size, moisture content and weight.

14.1.13 All required data and applicable blanks for each test run shall be provided in spreadsheet format both in the printed report and in a computer file such that the data can be easily analyzed and calculations easily verified. Formulas used for all calculations shall be accessible for review.

14.1.14 For each test run, Θ_1,Θ_2, Θ_3, the total CO and particulate emission for each of these three periods, and Θ_4.

14.1.15 Calculated results for delivered efficiency at each heat output rate and the weighted average emissions reported as total emissions in grams, pounds per mm Btu of delivered heat, grams per MJ of delivered heat, grams per kilogram of dry fuel and grams per hour. Results shall be reported for each heat output category and the weighted average.

14.1.16 Tables 1A, 1B, 1C, 1D, 1E and Table 2 must be used for presentation of results in test reports.

14.1.17 A statement of the estimated uncertainty of measurement of the emissions and efficiency test results.

14.1.18 A plot of CO emission rate in grams/minute vs. time, based on 1 minute averages, for the entire test period, for each run.

14.1.19 A plot of estimated boiler/heater energy release rate in Btu/hr based on 10 minute averages, for the entire test period, for each run. This will be calculated from the fuel used, the wood heating value and moisture content, and the SLM efficiency during each 10 minute period.

14.1.20 Raw data, calibration records, and other relevant documentation shall be retained by the laboratory for a minimum of 7 years.

15.0 Precision and Bias

15.1 Precision—It is not possible to specify the precision of the procedure in this test method because the appliance operation and

fueling protocols and the appliances themselves produce variable amounts of emissions and cannot be used to determine reproducibility or repeatability of this test method.

15.2 Bias—No definitive information can be presented on the bias of the procedure in this test method for measuring solid fuel burning hydronic heater emissions because no material having an accepted reference value is available.

16.0 Keywords

16.1 Solid fuel, hydronic heating appliances, wood-burning hydronic heaters, partial thermal storage.

Table 1A. Data Summary Part A

						Θ	W_{fuel}	MC_{ave}	Q_{in}	Q_{out}
Category	Run No	Load % Capacity	Target Load	Actual Load	Actual Load	Test Duration	Wood Weight as-fired	Wood Moisture	Heat Input	Heat Output
		Btu/hr	Btu/ hr	Btu/ hr	% of max	hrs	lb	%DB	Btu	Btu
I		< 15% of max								
II		16-24% of max								
III		25-50% of max								
IV		Max capacity								

Table 1B. Data Summary Part B

			T2 Min	E_T	E	E	$E_{g/hr}$	$E_{g/kg}$	η_{del}	H_{SLM}
Category	Run No	Load % Capacity	Min Return Water Temp.	Total PM Emissions	PM Output Based	PM Output Based	PM Rate	PM Factor	Delivered Efficiency	Stack Loss Efficiency
			°F	g	lb/mm Btu Out	g/MJ	g/hr	g/kg	%	%
I		< 15% of max								
II		16-24% of max								
III		25-50% of max								
IV		Max capacity								

Table 1C. Data Summary Part C

			Θ_1	Θ_2	Θ_3	$CO_{_1}$	$CO_{_2}$	$CO_{_3}$	CO_T
Category	Run No	Load % Capacity	Startup Time.	Steady State Time	End Time	Startup CO emission	Steady State CO emission	End CO emission	Total CO emission
			min	min	min	g	g	g	g
I		< 15% of max							
II		16-24% of max							
III		25-50% of max							
IV		Max capacity							

Table 1D. Data Summary Part D

			E_1	E_2	E_3	$E_{1_g/kg}$	$E_{2_g/kg}$	$E_{3_g/kg}$
Category	Run No	Load % Capacity	Startup PM	Steady State PM	End PM	Startup PM emission index	Steady State PM emission index	End PM emission index
			g	g	g	g/kg fuel	g/kg fuel	g/kg fuel
I		< 15% of max						
II		16-24% of max						
III		25-50% of max						
IV		Max capacity						

Table 1E: Label Summary Information

MANUFACTURER:			
MODEL NUMBER:			
ANNUAL EFFICIENCY RATING:	η_{avg}		**(Using higher heating value)**
PARTICLE EMISSIONS:	E_{avg}		grams/hr (Average)
			lbs/mmBtu/hr Output

Table 2. Annual Weighting

Category	Weighting Factor (F_i)	$\eta_{del,i} \times F_i$	$E_{g/MJ,i} \times F_i$	$E_{g/kg,i} \times F_i$	$E_{lb/mmBtu\ Out,i} \times F_i$	$E_{g/hr,i} \times F_i$
I	0.437					
II	0.238					
III	0.275					
IV	0.050					
Totals	1.000					

Figure 1. Schematic of Equipment Test Setup

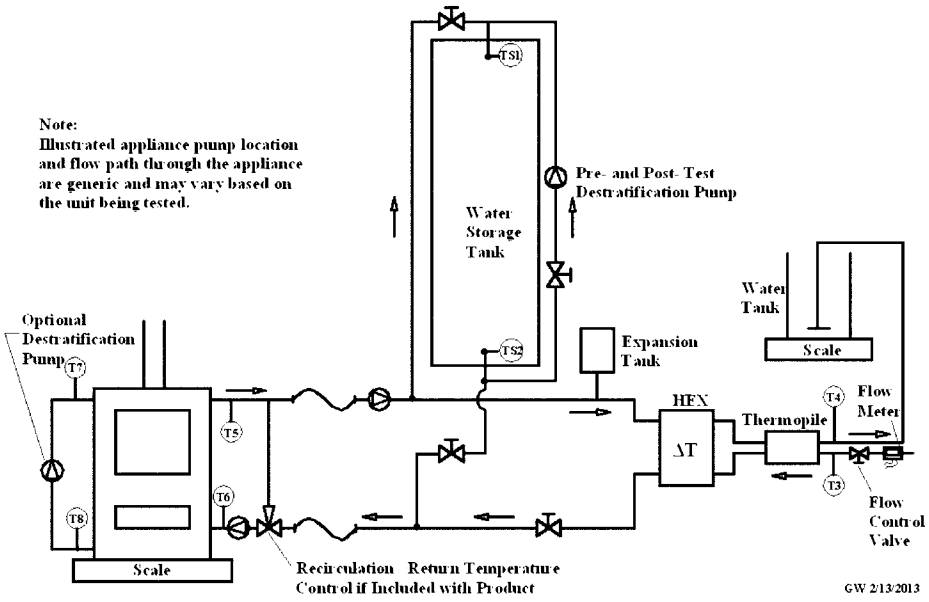
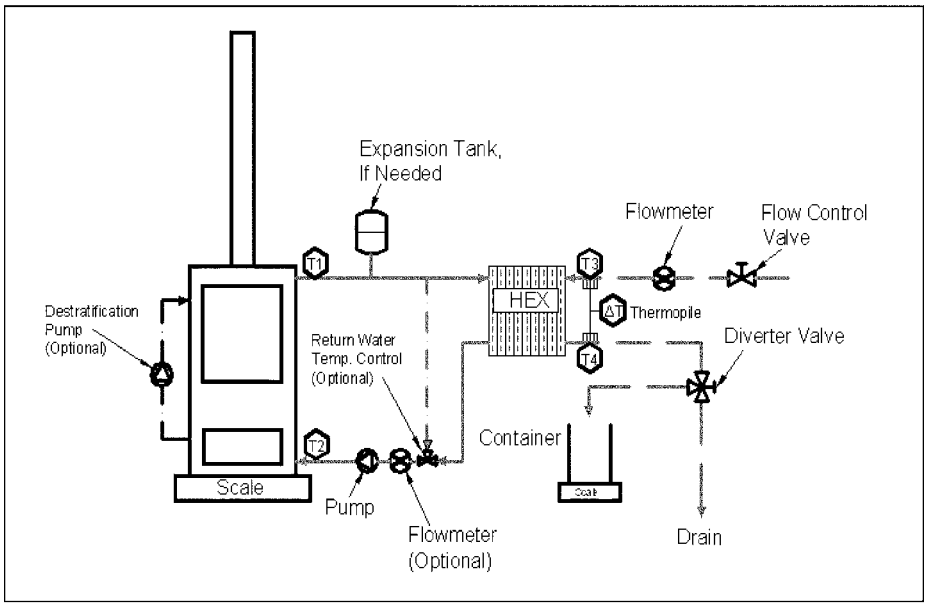


Figure 2. Schematic of Test Equipment Set-up



Note: Illustrated appliance pump location and flow path through the appliance.

METHOD 29—DETERMINATION OF METALS EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 5 and Method 12.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Antimony (Sb)	7440–36–0
Arsenic (As)	7440–38–2
Barium (Ba)	7440–39–3
Beryllium (Be)	7440–41–7
Cadmium (Cd)	7440–43–9
Chromium (Cr)	7440–47–3
Cobalt (Co)	7440–48–4
Copper (Cu)	7440–50–8
Lead (Pb)	7439–92–1
Manganese (Mn)	7439–96–5
Mercury (Hg)	7439–97–6
Nickel (Ni)	7440–02–0
Phosphorus (P)	7723–14–0
Selenium (Se)	7782–49–2
Silver (Ag)	7440–22–4
Thallium (Tl)	7440–28–0
Zinc (Zn)	7440–66–6

1.2 Applicability. This method is applicable to the determination of metals emissions from stationary sources. This method may be used to determine particulate emissions in addition to the metals emissions if the prescribed procedures and precautions are followed.

1.2.1 Hg emissions can be measured, alternatively, using EPA Method 101A of Appendix B, 40 CFR Part 61. Method 101-A measures only Hg but it can be of special interest to sources which need to measure both Hg and Mn emissions.

2.0 Summary of Method

2.1 Principle. A stack sample is withdrawn isokinetically from the source, particulate emissions are collected in the probe and on a heated filter, and gaseous emissions are then collected in an aqueous acidic solution of hydrogen peroxide (analyzed for all metals including Hg) and an aqueous acidic solution of potassium permanganate (analyzed only for Hg). The recovered samples are digested, and appropriate fractions are analyzed for Hg by cold vapor atomic absorption spectroscopy

(CVAAS) and for Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, P, Se, Ag, Tl, and Zn by inductively coupled argon plasma emission spectroscopy (ICAP) or atomic absorption spectroscopy (AAS). Graphite furnace atomic absorption spectroscopy (GFAAS) is used for analysis of Sb, As, Cd, Co, Pb, Se, and Tl if these elements require greater analytical sensitivity than can be obtained by ICAP. If one so chooses, AAS may be used for analysis of all listed metals if the resulting in-stack method detection limits meet the goal of the testing program. Similarly, inductively coupled plasma-mass spectroscopy (ICP-MS) may be used for analysis of Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Ag, Tl and Zn.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Iron (Fe) can be a spectral interference during the analysis of As, Cr, and Cd by ICAP. Aluminum (Al) can be a spectral interference during the analysis of As and Pb by ICAP. Generally, these interferences can be reduced by diluting the analytical sample, but such dilution raises the in-stack detection limits. Background and overlap corrections may be used to adjust for spectral interferences. Refer to Method 6010 of Reference 2 in section 16.0 or the other analytical methods used for details on potential interferences to this method. For all GFAAS analyses, use matrix modifiers to limit interferences, and matrix match all standards.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Nitric Acid (HNO_3). Highly corrosive to eyes, skin, nose, and lungs. Vapors cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

5.2.2 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

5.2.3 Hydrochloric Acid (HC1). Highly corrosive liquid with toxic vapors. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.4 Hydrofluoric Acid (HF). Highly corrosive to eyes, skin, nose, throat, and lungs. Reaction to exposure may be delayed by 24 hours or more. Provide ventilation to limit exposure.

5.2.5 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs. 30% H_2O_2 is a strong oxidizing agent. Avoid contact with skin, eyes, and combustible material. Wear gloves when handling.

5.2.6 Potassium Permanganate ($KMnO_4$). Caustic, strong oxidizer. Avoid bodily contact with.

5.2.7 Potassium Persulfate. Strong oxidizer. Avoid bodily contact with. Keep containers well closed and in a cool place.

5.3 Reaction Pressure. Due to the potential reaction of the potassium permanganate with the acid, there could be pressure buildup in the acidic $KMnO_4$ absorbing solution storage bottle. Therefore these bottles shall not be fully filled and shall be vented to relieve excess pressure and prevent explosion potentials. Venting is required, but not in a manner that will allow contamination of the solution. A No. 70–72 hole drilled in the container cap and Teflon liner has been used.

6.0 Equipment and Supplies

6.1 Sampling. A schematic of the sampling train is shown in Figure 29–1. It has general similarities to the Method 5 train.

6.1.1 Probe Nozzle (Probe Tip) and Borosilicate or Quartz Glass Probe Liner. Same as Method 5, sections 6.1.1.1 and 6.1.1.2, except that glass nozzles are required unless alternate tips are constructed of materials that are free from contamination and will not interfere with the sample. If a probe tip other than glass is used, no correction to the sample test results to compensate for the nozzle's effect on the sample is allowed. Probe fittings of plastic such as Teflon, polypropylene, etc. are recommended instead of metal fittings to prevent contamination. If one chooses to do so, a single glass piece consisting of a combined probe tip and probe liner may be used.

6.1.2 Pitot Tube and Differential Pressure Gauge. Same as Method 2, sections 6.1 and 6.2, respectively.

6.1.3 Filter Holder. Glass, same as Method 5, section 6.1.1.5, except use a Teflon filter support or other non-metallic, non-contaminating support in place of the glass frit.

6.1.4 Filter Heating System. Same as Method 5, section 6.1.1.6.

6.1.5 Condenser. Use the following system for condensing and collecting gaseous metals and determining the moisture content of the stack gas. The condensing system shall consist of four to seven impingers connected in series with leak-free ground glass fittings or other leak-free, non-contaminating fittings. Use the first impinger as a moisture trap. The second impinger (which is the first HNO_3/H_2O_2 impinger) shall be identical to the first impinger in Method 5. The third impinger (which is the second HNO_3/H_2O_2 impinger) shall be a Greenburg Smith impinger with the standard tip as described for the second impinger in Method 5, section 6.1.1.8. The fourth (empty) impinger and the fifth and sixth (both acidified $KMnO_4$) impingers are the same as the first impinger in Method 5. Place a temperature sensor capable of measuring to within 1 °C (2 °F) at the outlet of the last impinger. If no Hg analysis is planned, then the fourth, fifth, and sixth impingers are not used.

6.1.6 Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, sections 6.1.1.9, 6.1.2, and 6.1.3, respectively.

6.1.7 Teflon Tape. For capping openings and sealing connections, if necessary, on the sampling train.

6.2 Sample Recovery. Same as Method 5, sections 6.2.1 through 6.2.8 (Probe-Liner and Probe-Nozzle Brushes or Swabs, Wash Bottles, Sample Storage Containers, Petri Dishes, Glass Graduated Cylinder, Plastic Storage Containers, Funnel and Rubber Policeman, and Glass Funnel), respectively, with the following exceptions and additions:

6.2.1 Non-metallic Probe-Liner and Probe-Nozzle Brushes or Swabs. Use non-metallic probe-liner and probe-nozzle brushes or swabs for quantitative recovery of materials collected in the front-half of the sampling train.

6.2.2 Sample Storage Containers. Use glass bottles (see section 8.1 of this Method) with Teflon-lined caps that are non-reactive to the oxidizing solutions, with capacities of 1000- and 500-ml, for storage of acidified $KMnO_4$—containing samples and blanks. Glass or polyethylene bottles may be used for other sample types.

6.2.3 Graduated Cylinder. Glass or equivalent.

6.2.4 Funnel. Glass or equivalent.

6.2.5 Labels. For identifying samples.

6.2.6 Polypropylene Tweezers and/or Plastic Gloves. For recovery of the filter from the sampling train filter holder.

6.3 Sample Preparation and Analysis.

6.3.1 Volumetric Flasks, 100-ml, 250-ml, and 1000-ml. For preparation of standards and sample dilutions.

6.3.2 Graduated Cylinders. For preparation of reagents.

6.3.3 Parr Bombs or Microwave Pressure Relief Vessels with Capping Station (CEM Corporation model or equivalent). For sample digestion.

6.3.4 Beakers and Watch Glasses. 250-ml beakers, with watch glass covers, for sample digestion.

6.3.5 Ring Stands and Clamps. For securing equipment such as filtration apparatus.

6.3.6 Filter Funnels. For holding filter paper.

6.3.7 Disposable Pasteur Pipets and Bulbs.

6.3.8 Volumetric Pipets.

6.3.9 Analytical Balance. Accurate to within 0.1 mg.

6.3.10 Microwave or Conventional Oven. For heating samples at fixed power levels or temperatures, respectively.

6.3.11 Hot Plates.

6.3.12 Atomic Absorption Spectrometer (AAS). Equipped with a background corrector.

6.3.12.1 Graphite Furnace Attachment. With Sb, As, Cd, Co, Pb, Se, and Tl hollow cathode lamps (HCLs) or electrodeless discharge lamps (EDLs). Same as Reference 2 in section 16.0. Methods 7041 (Sb), 7060 (As), 7131 (Cd), 7201 (Co), 7421 (Pb), 7740 (Se), and 7841 (Tl).

6.3.12.2 Cold Vapor Mercury Attachment. With a mercury HCL or EDL, an air recirculation pump, a quartz cell, an aerator apparatus, and a heat lamp or desiccator tube. The heat lamp shall be capable of raising the temperature at the quartz cell by 10 °C above ambient, so that no condensation forms on the wall of the quartz cell. Same as Method 7470 in Reference 2 in section 16.0. See note 2: section 11.1.3 for other acceptable approaches for analysis of Hg in which analytical detection limits of 0.002 ng/ml were obtained.

6.3.13 Inductively Coupled Argon Plasma Spectrometer. With either a direct or sequential reader and an alumina torch. Same as EPA Method 6010 in Reference 2 in section 16.0.

6.3.14 Inductively Coupled Plasma-Mass Spectrometer.

Same as EPA Method 6020 in Reference 2 in section 16.0.

7.0 Reagents and Standards

7.1 Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are

available. Otherwise, use the best available grade.

7.2 Sampling Reagents.

7.2.1 Sample Filters. Without organic binders. The filters shall contain less than 1.3 μg/in.^{2} of each of the metals to be measured. Analytical results provided by filter manufacturers stating metals content of the filters are acceptable. However, if no such results are available, analyze filter blanks for each target metal prior to emission testing. Quartz fiber filters meeting these requirements are recommended. However, if glass fiber filters become available which meet these requirements, they may be used. Filter efficiencies and unreactiveness to sulfur dioxide (SO_2) or sulfur trioxide (SO_3) shall be as described in section 7.1.1 of Method 5.

7.2.2 Water. To conform to ASTM Specification D1193–77 or 91, Type II (incorporated by reference—see §60.17). If necessary, analyze the water for all target metals prior to field use. All target metals should be less than 1 ng/ml.

7.2.3 HNO_3, Concentrated. Baker Instra-analyzed or equivalent.

7.2.4 HCl, Concentrated. Baker Instra-analyzed or equivalent.

7.2.5 H_2O_2, 30 Percent (V/V).

7.2.6 $KMnO_4$.

7.2.7 H_2SO_4, Concentrated.

7.2.8 Silica Gel and Crushed Ice. Same as Method 5, sections 7.1.2 and 7.1.4, respectively.

7.3 Pretest Preparation of Sampling Reagents.

7.3.1 HNO_3/H_2O_2 Absorbing Solution, 5 Percent HNO_3/10 Percent H_2O_2. Add carefully with stirring 50 ml of concentrated HNO_3 to a 1000-ml volumetric flask containing approximately 500 ml of water, and then add carefully with stirring 333 ml of 30 percent H_2O_2. Dilute to volume with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.3.2 Acidic $KMnO_4$ Absorbing Solution, 4 Percent $KMnO_4$ (W/V), 10 Percent H_2SO_4 (V/V). Prepare fresh daily. Mix carefully, with stirring, 100 ml of concentrated H_2SO_4 into approximately 800 ml of water, and add water with stirring to make a volume of 1 liter: this solution is 10 percent H_2SO_4 (V/V). Dissolve, with stirring, 40 g of $KMnO_4$ into 10 percent H_2SO_4 (V/V) and add 10 percent H_2SO_4 (V/V) with stirring to make a volume of 1 liter. Prepare and store in glass bottles to prevent degradation. This reagent shall contain less than 2 ng/ml of Hg.

Precaution: To prevent autocatalytic decomposition of the permanganate solution, filter the solution through Whatman 541 filter paper.

7.3.3 HNO_3, 0.1 N. Add with stirring 6.3 ml of concentrated HNO_3 (70 percent) to a flask containing approximately 900 ml of water. Dilute to 1000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.3.4 HCl, 8 N. Carefully add with stirring 690 ml of concentrated HCl to a flask containing 250 ml of water. Dilute to 1000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of Hg.

7.4 Glassware Cleaning Reagents.

7.4.1 HNO_3, Concentrated. Fisher ACS grade or equivalent.

7.4.2 Water. To conform to ASTM Specifications D1193, Type II.

7.4.3 HNO_3, 10 Percent (V/V). Add with stirring 500 ml of concentrated HNO_3 to a flask containing approximately 4000 ml of water. Dilute to 5000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.5 Sample Digestion and Analysis Reagents. The metals standards, except Hg, may also be made from solid chemicals as described in Reference 3 in section 16.0. Refer to References 1, 2, or 5 in section 16.0 for additional information on Hg standards. The 1000 μg/ml Hg stock solution standard may be made according to section 7.2.7 of Method 101A.

7.5.1 HCl, Concentrated.

7.5.2 HF, Concentrated.

7.5.3 HNO_3, Concentrated. Baker Instra-analyzed or equivalent.

7.5.4 HNO_3, 50 Percent (V/V). Add with stirring 125 ml of concentrated HNO_3 to 100 ml of water. Dilute to 250 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.5.5 HNO_3, 5 Percent (V/V). Add with stirring 50 ml of concentrated HNO_3 to 800 ml of water. Dilute to 1000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.5.6 Water. To conform to ASTM Specifications D1193, Type II.

7.5.7 Hydroxylamine Hydrochloride and Sodium Chloride Solution. See Reference 2 In section 16.0 for preparation.

7.5.8 Stannous Chloride. See Reference 2 in section 16.0 for preparation.

7.5.9 $KMnO_4$, 5 Percent (W/V). See Reference 2 in section 16.0 for preparation.

7.5.10 H_2SO_4, Concentrated.

7.5.11 Potassium Persulfate, 5 Percent (W/V). See Reference 2 in section 16.0 for preparation.

7.5.12 Nickel Nitrate, $Ni(N0_3)_2 6H_20$.

7.5.13 Lanthanum Oxide, La_20_3.

7.5.14 Hg Standard (AAS Grade), 1000 μg/ml.

7.5.15 Pb Standard (AAS Grade), 1000 μg/ml.

7.5.16 As Standard (AAS Grade), 1000 μg/ml.

7.5.17 Cd Standard (AAS Grade), 1000 μg/ml.

7.5.18 Cr Standard (AAS Grade), 1000 μg/ml.

7.5.19 Sb Standard (AAS Grade), 1000 μg/ml.

7.5.20 Ba Standard (AAS Grade), 1000 μg/ml.

7.5.21 Be Standard (AAS Grade), 1000 μg/ml.

7.5.22 Co Standard (AAS Grade), 1000 μg/ml.

7.5.23 Cu Standard (AAS Grade), 1000 μg/ml.

7.5.24 Mn Standard (AAS Grade), 1000 µg/ml.
7.5.25 Ni Standard (AAS Grade), 1000 µg/ml.
7.5.26 P Standard (AAS Grade), 1000 µg/ml.
7.5.27 Se Standard (AAS Grade), 1000 µg/ml.
7.5.28 Ag Standard (AAS Grade), 1000 µg/ml.
7.5.29 Tl Standard (AAS Grade), 1000 µg/ml.
7.5.30 Zn Standard (AAS Grade), 1000 µg/ml.
7.5.31 Al Standard (AAS Grade), 1000 µg/ml.
7.5.32 Fe Standard (AAS Grade), 1000 µg/ml.

7.5.33 Hg Standards and Quality Control Samples. Prepare fresh weekly a 10 µg/ml intermediate Hg standard by adding 5 ml of 1000 µg/ml Hg stock solution prepared according to Method 101A to a 500-ml volumetric flask; dilute with stirring to 500 ml by first carefully adding 20 ml of 15 percent HNO_3 and then adding water to the 500-ml volume. Mix well. Prepare a 200 ng/ml working Hg standard solution fresh daily: add 5 ml of the 10 µg/ml intermediate standard to a 250-ml volumetric flask, and dilute to 250 ml with 5 ml of 4 percent $KMnO_4$, 5 ml of 15 percent HNO_3, and then water. Mix well. Use at least five separate aliquots of the working Hg standard solution and a blank to prepare the standard curve. These aliquots and blank shall contain 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml of the working standard solution containing 0, 200, 400, 600, 800, and 1000 ng Hg, respectively. Prepare quality control samples by making a separate 10 µg/ml standard and diluting until in the calibration range.

7.5.34 ICAP Standards and Quality Control Samples. Calibration standards for ICAP analysis can be combined into four different mixed standard solutions as follows:

MIXED STANDARD SOLUTIONS FOR ICAP ANALYSIS

Solution	Elements
I	As, Be, Cd, Mn, Pb, Se, Zn.
II	Ba, Co, Cu, Fe.
III	Al, Cr, Ni.
IV	Ag, P, Sb, Tl.

Prepare these standards by combining and diluting the appropriate volumes of the 1000 µg/ml solutions with 5 percent HNO_3. A minimum of one standard and a blank can be used to form each calibration curve. However, prepare a separate quality control sample spiked with known amounts of the target metals in quantities in the mid-range of the calibration curve. Suggested standard levels are 25 µg/ml for Al, Cr and Pb, 15 µg/ml for Fe, and 10 µg/ml for the remaining elements. Prepare any standards containing less than 1 µg/ml of metal on a daily basis. Standards containing greater than 1 µg/ml of metal should be stable for a minimum of 1 to 2 weeks. For ICP-MS, follow Method 6020 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i).

7.5.35 GFAAS Standards. Sb, As, Cd, Co, Pb, Se, and Tl. Prepare a 10 µg/ml standard by adding 1 ml of 1000 µg/ml standard to a 100-ml volumetric flask. Dilute with stirring to 100 ml with 10 percent HNO_3. For GFAAS, matrix match the standards. Prepare a 100 ng/ml standard by adding 1 ml of the 10 µg/ml standard to a 100-ml volumetric flask, and dilute to 100 ml with the appropriate matrix solution. Prepare other standards by diluting the 100 ng/ml standards. Use at least five standards to make up the standard curve. Suggested levels are 0, 10, 50, 75, and 100 ng/ml. Prepare quality control samples by making a separate 10 µg/ml standard and diluting until it is in the range of the samples. Prepare any standards containing less than 1 µg/ml of metal on a daily basis. Standards containing greater than 1 µg/ml of metal should be stable for a minimum of 1 to 2 weeks.

7.5.36 Matrix Modifiers.

7.5.36.1 Nickel Nitrate, 1 Percent (V/V). Dissolve 4.956 g of $Ni(N0_3)_2{\cdot}6H_20$ or other nickel compound suitable for preparation of this matrix modifier in approximately 50 ml of water in a 100-ml volumetric flask. Dilute to 100 ml with water.

7.5.36.2 Nickel Nitrate, 0.1 Percent (V/V). Dilute 10 ml of 1 percent nickel nitrate solution to 100 ml with water. Inject an equal amount of sample and this modifier into the graphite furnace during GFAAS analysis for As.

7.5.36.3 Lanthanum. Carefully dissolve 0.5864 g of La_20_3 in 10 ml of concentrated $HN0_3$, and dilute the solution by adding it with stirring to approximately 50 ml of water. Dilute to 100 ml with water, and mix well. Inject an equal amount of sample and this modifier into the graphite furnace during GFAAS analysis for Pb.

7.5.37 Whatman 40 and 541 Filter Papers (or equivalent). For filtration of digested samples.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Sampling. The complexity of this method is such that, to obtain reliable results, both testers and analysts must be trained and experienced with the test procedures, including source sampling; reagent preparation and handling; sample handling; safety equipment and procedures; analytical calculations; reporting; and the specific procedural descriptions throughout this method.

8.1.1 Pretest Preparation. Follow the same general procedure given in Method 5, section 8.1, except that, unless particulate emissions are to be determined, the filter need not be desiccated or weighed. First, rinse all sampling train glassware with hot tap water and then wash in hot soapy water. Next, rinse glassware three times with tap water, followed by three additional rinses with water. Then soak all glassware in a 10 percent (V/V) nitric acid solution for a minimum of 4

hours, rinse three times with water, rinse a final time with acetone, and allow to air dry. Cover all glassware openings where contamination can occur until the sampling train is assembled for sampling.

8.1.2 Preliminary Determinations. Same as Method 5, section 8.1.2.

8.1.3 Preparation of Sampling Train.

8.1.3.1 Set up the sampling train as shown in Figure 29–1. Follow the same general procedures given in Method 5, section 8.3, except place 100 ml of the HNO_3/H_2O_2 solution (Section 7.3.1 of this method) in each of the second and third impingers as shown in Figure 29–1. Place 100 ml of the acidic $KMnO_4$ absorbing solution (Section 7.3.2 of this method) in each of the fifth and sixth impingers as shown in Figure 29–1, and transfer approximately 200 to 300 g of pre-weighed silica gel from its container to the last impinger. Alternatively, the silica gel may be weighed directly in the impinger just prior to final train assembly.

8.1.3.2 Based on the specific source sampling conditions, the use of an empty first impinger can be eliminated if the moisture to be collected in the impingers will be less than approximately 100 ml.

8.1.3.3 If Hg analysis will not be performed, the fourth, fifth, and sixth impingers as shown in Figure 29–1 are not required.

8.1.3.4 To insure leak-free sampling train connections and to prevent possible sample contamination problems, use Teflon tape or other non-contaminating material instead of silicone grease.

Precaution: Exercise extreme care to prevent contamination within the train. Prevent the acidic $KMnO_4$ from contacting any glassware that contains sample material to be analyzed for Mn. Prevent acidic H_2O_2 from mixing with the acidic $KMnO_4$.

8.1.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, section 8.4.2 (Pretest Leak-Check), section 8.4.3 (Leak-Checks During the Sample Run), and section 8.4.4 (Post-Test Leak-Checks).

8.1.5 Sampling Train Operation. Follow the procedures given in Method 5, section 8.5. When sampling for Hg, use a procedure analogous to that described in section 8.1 of Method 101A, 40 CFR Part 61, Appendix B, if necessary to maintain the desired color in the last acidified permanganate impinger. For each run, record the data required on a data sheet such as the one shown in Figure 5–3 of Method 5.

8.1.6 Calculation of Percent Isokinetic. Same as Method 5, section 12.11.

8.2 Sample Recovery.

8.2.1 Begin cleanup procedures as soon as the probe is removed from the stack at the end of a sampling period. The probe should be allowed to cool prior to sample recovery. When it can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a rinsed, non-contaminating cap over the probe nozzle to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling; a vacuum can form in the filter holder with the undesired result of drawing liquid from the impingers onto the filter.

8.2.2 Before moving the sampling train to the cleanup site, remove the probe from the sampling train and cap the open outlet. Be careful not to lose any condensate that might be present. Cap the filter inlet where the probe was fastened. Remove the umbilical cord from the last impinger and cap the impinger. Cap the filter holder outlet and impinger inlet. Use non-contaminating caps, whether ground-glass stoppers, plastic caps, serum caps, or Teflon® tape to close these openings.

8.2.3 Alternatively, the following procedure may be used to disassemble the train before the probe and filter holder/oven are completely cooled: Initially disconnect the filter holder outlet/impinger inlet and loosely cap the open ends. Then disconnect the probe from the filter holder or cyclone inlet and loosely cap the open ends. Cap the probe tip and remove the umbilical cord as previously described.

8.2.4 Transfer the probe and filter-impinger assembly to a cleanup area that is clean and protected from the wind and other potential causes of contamination or loss of sample. Inspect the train before and during disassembly and note any abnormal conditions. Take special precautions to assure that all the items necessary for recovery do not contaminate the samples. The sample is recovered and treated as follows (see schematic in Figures 29–2a and 29–2b):

8.2.5 Container No. 1 (Sample Filter). Carefully remove the filter from the filter holder and place it in its labeled petri dish container. To handle the filter, use either acid-washed polypropylene or Teflon coated tweezers or clean, disposable surgical gloves rinsed with water and dried. If it is necessary to fold the filter, make certain the particulate cake is inside the fold. Carefully transfer the filter and any particulate matter or filter fibers that adhere to the filter holder gasket to the petri dish by using a dry (acid-cleaned) nylon bristle brush. Do not use any metal-containing materials when recovering this train. Seal the labeled petri dish.

8.2.6 Container No. 2 (Acetone Rinse). Perform this procedure only if a determination of particulate emissions is to be made. Quantitatively recover particulate matter and any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with a total of 100 ml of acetone, while simultaneously taking great care to see that no dust on the outside of the probe or other surfaces gets in the sample. The use of exactly 100 ml

is necessary for the subsequent blank correction procedures. Distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator; in these cases, save a water blank and follow the Administrator's directions on analysis.

8.2.6.1 Carefully remove the probe nozzle, and clean the inside surface by rinsing with acetone from a wash bottle while brushing with a non-metallic brush. Brush until the acetone rinse shows no visible particles, then make a final rinse of the inside surface with acetone.

8.2.6.2 Brush and rinse the sample exposed inside parts of the probe fitting with acetone in a similar way until no visible particles remain. Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Allow the acetone to drain from the lower end into the sample container. A funnel may be used to aid in transferring liquid washings to the container. Follow the acetone rinse with a non-metallic probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action three times through the probe. Hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed through the probe until no visible particulate matter is carried out with the acetone or until none remains in the probe liner on visual inspection. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

8.2.6.3 It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination. Clean the inside of the front-half of the filter holder by rubbing the surfaces with a non-metallic brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. After all acetone washings and particulate matter have been collected in the sample container, tighten the lid so that acetone will not leak out when shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Clearly label the container to identify its contents.

8.2.7 Container No. 3 (Probe Rinse). Keep the probe assembly clean and free from contamination during the probe rinse. Rinse the probe nozzle and fitting, probe liner, and front-half of the filter holder thoroughly with a total of 100 ml of 0.1 N HNO_3, and place the wash into a sample storage container. Perform the rinses as applicable and generally as described in Method 12, section 8.7.1. Record the volume of the rinses. Mark the height of the fluid level on the outside of the storage container and use this mark to determine if leakage occurs during transport. Seal the container, and clearly label the contents. Finally, rinse the nozzle, probe liner, and front-half of the filter holder with water followed by acetone, and discard these rinses.

NOTE: The use of a total of exactly 100 ml is necessary for the subsequent blank correction procedures.

8.2.8 Container No. 4 (Impingers 1 through 3, Moisture Knockout Impinger, when used, HNO_3/H_2O_2 Impingers Contents and Rinses). Due to the potentially large quantity of liquid involved, the tester may place the impinger solutions from impingers 1 through 3 in more than one container, if necessary. Measure the liquid in the first three impingers to within 0.5 ml using a graduated cylinder. Record the volume. This information is required to calculate the moisture content of the sampled flue gas. Clean each of the first three impingers, the filter support, the back half of the filter housing, and connecting glassware by thoroughly rinsing with 100 ml of 0.1 N HNO_3 using the procedure as applicable in Method 12, section 8.7.3.

NOTE: The use of exactly 100 ml of 0.1 N HNO_3 rinse is necessary for the subsequent blank correction procedures. Combine the rinses and impinger solutions, measure and record the final total volume. Mark the height of the fluid level, seal the container, and clearly label the contents.

8.2.9 Container Nos. 5A (0.1 N HNO_3), 5B ($KMnO_4/H_2SO_4$ absorbing solution), and 5C (8 N HCl rinse and dilution).

8.2.9.1 When sampling for Hg, pour all the liquid from the impinger (normally impinger No. 4) that immediately preceded the two permanganate impingers into a graduated cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Place the liquid in Container No. 5A. Rinse the impinger with exactly 100 ml of 0.1 N HNO_3 and place this rinse in Container No. 5A.

8.2.9.2 Pour all the liquid from the two permanganate impingers into a graduated cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Place this acidic $KMnO_4$ solution into Container No. 5B. Using a total of exactly 100 ml of fresh acidified $KMnO_4$ solution for all rinses (approximately 33 ml per rinse), rinse the two permanganate impingers and connecting glassware a minimum of three times. Pour the rinses into Container No. 5B, carefully assuring transfer of all loose precipitated materials from the two impingers. Similarly, using 100 ml total of water, rinse the permanganate impingers and connecting

glass a minimum of three times, and pour the rinses into Container 5B, carefully assuring transfer of any loose precipitated material. Mark the height of the fluid level, and clearly label the contents. Read the *Precaution:* in section 7.3.2.

NOTE: Due to the potential reaction of $KMnO_4$ with acid, pressure buildup can occur in the sample storage bottles. Do not fill these bottles completely and take precautions to relieve excess pressure. A No. 70–72 hole drilled in the container cap and Teflon liner has been used successfully.

8.2.9.3 Wash the two permanganate impingers with 25 ml of 8 N HCl, and place the wash in a separate sample container labeled No. 5C containing 200 ml of water. First, place 200 ml of water in the container. Then wash the impinger walls and stem with the 8 N HCl by turning the impinger on its side and rotating it so that the HCl contacts all inside surfaces. Use a total of only 25 ml of 8 N HCl for rinsing *both permanganate impingers combined*. Rinse the first impinger, then pour the actual rinse used for the first impinger into the second impinger for its rinse. Finally, pour the 25 ml of 8 N HCl rinse carefully into the container with the 200 ml of water. Mark the height of the fluid level on the outside of the container in order to determine if leakage occurs during transport.

8.2.10 Container No. 6 (Silica Gel). Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container and seal it. The tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. The small amount of particles that might adhere to the impinger wall need not be removed. Do not use water or other liquids to transfer the silica gel since weight gained in the silica gel impinger is used for moisture calculations. Alternatively, if a balance is available in the field, record the weight of the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g.

8.2.11 Container No. 7 (Acetone Blank). If particulate emissions are to be determined, at least once during each field test, place a 100-ml portion of the acetone used in the sample recovery process into a container labeled No. 7. Seal the container.

8.2.12 Container No. 8A (0.1 N HNO_3 Blank). At least once during each field test, place 300 ml of the 0.1 N HNO_3 solution used in the sample recovery process into a container labeled No. 8A. Seal the container.

8.2.13 Container No. 8B (Water Blank). At least once during each field test, place 100 ml of the water used in the sample recovery process into a container labeled No. 8B. Seal the container.

8.2.14 Container No. 9 (5 Percent HNO_3/10 Percent H_2O_2 Blank). At least once during each field test, place 200 ml of the 5 Percent HNO_3/10 Percent H_2O_2 solution used as the nitric acid impinger reagent into a container labeled No. 9. Seal the container.

8.2.15 Container No. 10 (Acidified $KMnO_4$ Blank). At least once during each field test, place 100 ml of the acidified $KMnO_4$ solution used as the impinger solution and in the sample recovery process into a container labeled No. 10. Prepare the container as described in section 8.2.9.2. Read the *Precaution*: in section 7.3.2 and read the note in section 8.2.9.2.

8.2.16 Container No. 11 (8 N HCl Blank). At least once during each field test, place 200 ml of water into a sample container labeled No. 11. Then carefully add with stirring 25 ml of 8 N HCl. Mix well and seal the container.

8.2.17 Container No. 12 (Sample Filter Blank). Once during each field test, place into a petri dish labeled No. 12 three unused blank filters from the same lot as the sampling filters. Seal the petri dish.

8.3 Sample Preparation. Note the level of the liquid in each of the containers and determine if any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. A diagram illustrating sample preparation and analysis procedures for each of the sample train components is shown in Figure 29–3.

8.3.1 Container No. 1 (Sample Filter).

8.3.1.1 If particulate emissions are being determined, first desiccate the filter and filter catch without added heat (do not heat the filters to speed the drying) and weigh to a constant weight as described in section 11.2.1 of Method 5.

8.3.1.2 Following this procedure, or initially, if particulate emissions are not being determined in addition to metals analysis, divide the filter with its filter catch into portions containing approximately 0.5 g each. Place the pieces in the analyst's choice of either individual microwave pressure relief vessels or Parr Bombs. Add 6 ml of concentrated HNO_3 and 4 ml of concentrated HF to each vessel. For microwave heating, microwave the samples for approximately 12 to 15 minutes total heating time as follows: heat for 2 to 3 minutes, then turn off the microwave for 2 to 3 minutes, then heat for 2 to 3 minutes, etc., continue this alternation until the 12 to 15 minutes total heating time are completed (this procedure should comprise approximately 24 to 30 minutes at 600 watts). Microwave heating times are approximate and are dependent upon the number of samples being digested simultaneously. Sufficient heating is evidenced by sorbent reflux within the vessel. For conventional heating, heat the Parr Bombs at 140 °C (285 °F) for 6 hours. Then cool the samples to

room temperature, and combine with the acid digested probe rinse as required in section 8.3.3.

8.3.1.3 If the sampling train includes an optional glass cyclone in front of the filter, prepare and digest the cyclone catch by the procedures described in section 8.3.1.2 and then combine the digestate with the digested filter sample.

8.3.2 Container No. 2 (Acetone Rinse). Note the level of liquid in the container and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically within 1 ml or gravimetrically within 0.5 g. Transfer the contents to an acid-cleaned, tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. If particulate emissions are being determined, desiccate for 24 hours without added heat, weigh to a constant weight according to the procedures described in section 11.2.1 of Method 5, and report the results to the nearest 0.1 mg. Redissolve the residue with 10 ml of concentrated HNO_3. Quantitatively combine the resultant sample, including all liquid and any particulate matter, with Container No. 3 before beginning section 8.3.3.

8.3.3 Container No. 3 (Probe Rinse). Verify that the pH of this sample is 2 or lower. If it is not, acidify the sample by careful addition with stirring of concentrated HNO_3 to pH 2. Use water to rinse the sample into a beaker, and cover the beaker with a ribbed watch glass. Reduce the sample volume to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Digest the sample in microwave vessels or Parr Bombs by quantitatively transferring the sample to the vessel or bomb, carefully adding the 6 ml of concentrated HNO_3, 4 ml of concentrated HF, and then continuing to follow the procedures described in section 8.3.1.2. Then combine the resultant sample directly with the acid digested portions of the filter prepared previously in section 8.3.1.2. The resultant combined sample is referred to as *''Sample Fraction 1''*. Filter the combined sample using Whatman 541 filter paper. Dilute to 300 ml (or the appropriate volume for the expected metals concentration) with water. This diluted sample is *''Analytical Fraction 1''*. Measure and record the volume of Analytical Fraction 1 to within 0.1 ml. Quantitatively remove a 50-ml aliquot and label as *''Analytical Fraction 1B''*. Label the remaining 250-ml portion as *''Analytical Fraction 1A''*. Analytical Fraction 1A is used for ICAP or AAS analysis for all desired metals except Hg. Analytical Fraction 1B is used for the determination of front-half Hg.

8.3.4 Container No. 4 (Impingers 1–3). Measure and record the total volume of this sample to within 0.5 ml and label it *''Sample Fraction 2''*. Remove a 75- to 100-ml aliquot for Hg analysis and label the aliquot *''Analytical Fraction 2B''*. Label the remaining portion of Container No. 4 as *''Sample Fraction 2A''*. Sample Fraction 2A defines the volume of Analytical Fraction 2A *prior* to digestion. All of Sample Fraction 2A is digested to produce *''Analytical Fraction 2A''*. Analytical Fraction 2A defines the volume of Sample Fraction 2A *after* its digestion and the volume of Analytical Fraction 2A is normally 150 ml. Analytical Fraction 2A is analyzed for all metals except Hg. Verify that the pH of Sample Fraction 2A is 2 or lower. If necessary, use concentrated HNO_3 by careful addition and stirring to lower Sample Fraction 2A to pH 2. Use water to rinse Sample Fraction 2A into a beaker and then cover the beaker with a ribbed watchglass. Reduce Sample Fraction 2A to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Then follow either of the digestion procedures described in sections 8.3.4.1 or 8.3.4.2.

8.3.4.1 Conventional Digestion Procedure. Add 30 ml of 50 percent HNO_3, and heat for 30 minutes on a hot plate to just below boiling. Add 10 ml of 3 percent H_2O_2 and heat for 10 more minutes. Add 50 ml of hot water, and heat the sample for an additional 20 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water. This dilution produces Analytical Fraction 2A. Measure and record the volume to within 0.1 ml.

8.3.4.2 Microwave Digestion Procedure. Add 10 ml of 50 percent HNO_3 and heat for 6 minutes total *heating* time in alternations of 1 to 2 minutes at 600 Watts followed by 1 to 2 minutes with no power, etc., similar to the procedure described in section 8.3.1. Allow the sample to cool. Add 10 ml of 3 percent H_2O_2 and heat for 2 more minutes. Add 50 ml of hot water, and heat for an additional 5 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water. This dilution produces Analytical Fraction 2A. Measure and record the volume to within 0.1 ml.

NOTE: All microwave heating times given are approximate and are dependent upon the number of samples being digested at a time. Heating times as given above have been found acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by solvent reflux within the vessel.

8.3.5 Container No. 5A (Impinger 4), Container Nos. 5B and 5C (Impingers 5 and 6). Keep the samples in Containers Nos. 5A, 5B, and 5C separate from each other. Measure and record the volume of 5A to within 0.5 ml. Label the contents of Container No. 5A to be

Analytical Fraction 3A. To remove any brown MnO_2 precipitate from the contents of Container No. 5B, filter its contents through Whatman 40 filter paper into a 500 ml volumetric flask and dilute to volume with water. Save the filter for digestion of the brown MnO_2 precipitate. Label the 500 ml filtrate from Container No. 5B to be Analytical Fraction 3B. Analyze Analytical Fraction 3B for Hg within 48 hours of the filtration step. Place the saved filter, which was used to remove the brown MnO_2 precipitate, into an appropriately sized *vented* container, which will allow release of any gases including chlorine formed when the filter is digested. In a laboratory hood which will remove any gas produced by the digestion of the MnO_2, add 25 ml of 8 N HCl to the filter and allow to digest for a minimum of 24 hours at room temperature. Filter the contents of Container No. 5C through a Whatman 40 filter into a 500-ml volumetric flask. Then filter the result of the digestion of the brown MnO_2 from Container No. 5B through a Whatman 40 filter into the same 500-ml volumetric flask, and dilute and mix well to volume with water. Discard the Whatman 40 filter. Mark this combined 500-ml dilute HCl solution as Analytical Fraction 3C.

8.3.6 Container No. 6 (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance.

9.0 Quality Control

9.1 Field Reagent Blanks, if analyzed. Perform the digestion and analysis of the blanks in Container Nos. 7 through 12 that were produced in sections 8.2.11 through 8.2.17, respectively. For Hg field reagent blanks, use a 10 ml aliquot for digestion and analysis.

9.1.1 Digest and analyze one of the filters from Container No. 12 per section 8.3.1, 100 ml from Container No. 7 per section 8.3.2, and 100 ml from Container No. 8A per section 8.3.3. This step produces blanks for Analytical Fractions 1A and 1B.

9.1.2 Combine 100 ml of Container No. 8A with 200 ml from Container No. 9, and digest and analyze the resultant volume per section 8.3.4. This step produces blanks for Analytical Fractions 2A and 2B.

9.1.3 Digest and analyze a 100-ml portion of Container No. 8A to produce a blank for Analytical Fraction 3A.

9.1.4 Combine 100 ml from Container No. 10 with 33 ml from Container No. 8B to produce a blank for Analytical Fraction 3B. Filter the resultant 133 ml as described for Container No. 5B in section 8.3.5, except do not dilute the 133 ml. Analyze this blank for Hg within 48 hr of the filtration step, and use 400 ml as the blank volume when calculating the blank mass value. Use the actual volumes of the other analytical blanks when calculating their mass values.

9.1.5 Digest the filter that was used to remove any brown MnO_2 precipitate from the blank for Analytical Fraction 3B by the same procedure as described in section 8.3.5 for the similar sample filter. Filter the digestate and the contents of Container No. 11 through Whatman 40 paper into a 500-ml volumetric flask, and dilute to volume with water. These steps produce a blank for Analytical Fraction 3C.

9.1.6 Analyze the blanks for Analytical Fraction Blanks 1A and 2A per section 11.1.1 and/or section 11.1.2. Analyze the blanks for Analytical Fractions 1B, 2B, 3A, 3B, and 3C per section 11.1.3. Analysis of the blank for Analytical Fraction 1A produces the front-half reagent blank correction values for the desired metals except for Hg; Analysis of the blank for Analytical Fraction 1B produces the front-half reagent blank correction value for Hg. Analysis of the blank for Analytical Fraction 2A produces the back-half reagent blank correction values for all of the desired metals except for Hg, while separate analyses of the blanks for Analytical Fractions 2B, 3A, 3B, and 3C produce the back-half reagent blank correction value for Hg.

9.2 Quality Control Samples. Analyze the following quality control samples.

9.2.1 ICAP and ICP-MS Analysis. Follow the respective quality control descriptions in section 8 of Methods 6010 and 6020 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i). For the purposes of a source test that consists of three sample runs, modify those requirements to include the following: two instrument check standard runs, two calibration blank runs, one interference check sample at the beginning of the analysis (analyze by Method of Standard Additions unless within 25 percent), one quality control sample to check the accuracy of the calibration standards (required to be within 25 percent of calibration), and one duplicate analysis (required to be within 20 percent of average or repeat all analyses).

9.2.2 Direct Aspiration AAS and/or GFAAS Analysis for Sb, As, Ba, Be, Cd, Cu, Cr, Co, Pb, Ni, Mn, Hg, P, Se, Ag, Tl, and Zn. Analyze all samples in duplicate. Perform a matrix spike on at least one front-half sample and one back-half sample, or one combined sample. If recoveries of less than 75 percent or greater than 125 percent are obtained for the matrix spike, analyze each sample by the Method of Standard Additions. Analyze a quality control sample to check the accuracy of the calibration standards. If the results are not within 20 percent, repeat the calibration.

9.2.3 CVAAS Analysis for Hg. Analyze all samples in duplicate. Analyze a quality control sample to check the accuracy of the calibration standards (if not within 15 percent, repeat calibration). Perform a matrix spike on one sample (if not within 25 percent,

analyze all samples by the Method of Standard Additions). Additional information on quality control can be obtained from Method 7470 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i), or in *Standard Methods for Water and Wastewater* Method 303F.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Sampling Train Calibration. Calibrate the sampling train components according to the indicated sections of Method 5: Probe Nozzle (Section 10.1); Pitot Tube (Section 10.2); Metering System (Section 10.3); Probe Heater (Section 10.4); Temperature Sensors (Section 10.5); Leak-Check of the Metering System (Section 8.4.1); and Barometer (Section 10.6).

10.2 Inductively Coupled Argon Plasma Spectrometer Calibration. Prepare standards as outlined in section 7.5. Profile and calibrate the instrument according to the manufacturer's recommended procedures using those standards. Check the calibration once per hour. If the instrument does not reproduce the standard concentrations within 10 percent, perform the complete calibration procedures. Perform ICP-MS analysis by following Method 6020 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i).

10.3 Atomic Absorption Spectrometer—Direct Aspiration AAS, GFAAS, and CVAAS analyses. Prepare the standards as outlined in section 7.5 and use them to calibrate the spectrometer. Calibration procedures are also outlined in the EPA methods referred to in Table 29–2 and in Method 7470 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i), or in *Standard Methods for Water and Wastewater* Method 303F (for Hg). Run each standard curve in duplicate and use the mean values to calculate the calibration line. Recalibrate the instrument approximately once every 10 to 12 samples.

10.4 Field Balance Calibration Check. Check the calibration of the balance used to weigh impingers with a weight that is at least 500g or within 50g of a loaded impinger. The weight must be ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference-see 40 CFR 60.17) Class 6 (or better). Daily before use, the field balance must measure the weight within ±0.5g of the certified mass. If the daily balance calibration check fails, perform corrective measures and repeat the check before using balance.

10.5 Analytical Balance Calibration. Perform a multipoint calibration (at least five points spanning the operational range) of the analytical balance before the first use, and semiannually thereafter. The calibration of the analytical balance must be conducted using ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 2 (or better) tolerance weights. Audit the balance each day it is used for gravimetric measurements by weighing at least one ASTM E617–13 Class 2 tolerance (or better) calibration weight that corresponds to 50 to 150 percent of the weight of one filter or between 1g and 5g. If the scale cannot reproduce the value of the calibration weight to within 0.5 mg of the certified mass, perform corrective measures, and conduct the multipoint calibration before use.

11.0 Analytical Procedure

11.1 Sample Analysis. For each sampling train sample run, seven individual analytical samples are generated; two for all desired metals except Hg, and five for Hg. A schematic identifying each sample container and the prescribed analytical preparation and analysis scheme is shown in Figure 29–3. The first two analytical samples, labeled Analytical Fractions 1A and 1B, consist of the digested samples from the front-half of the train. Analytical Fraction 1A is for ICAP, ICP-MS or AAS analysis as described in sections 11.1.1 and 11.1.2, respectively. Analytical Fraction 1B is for front-half Hg analysis as described in section 11.1.3. The contents of the back-half of the train are used to prepare the third through seventh analytical samples. The third and fourth analytical samples, labeled Analytical Fractions 2A and 2B, contain the samples from the moisture removal impinger No. 1, if used, and HNO_3/H_2O_2 impingers Nos. 2 and 3. Analytical Fraction 2A is for ICAP, ICP-MS or AAS analysis for target metals, except Hg. Analytical Fraction 2B is for analysis for Hg. The fifth through seventh analytical samples, labeled Analytical Fractions 3A, 3B, and 3C, consist of the impinger contents and rinses from the empty impinger No. 4 and the $H_2SO_4/KMnO_4$ Impingers Nos. 5 and 6. These analytical samples are for analysis for Hg as described in section 11.1.3. The total back-half Hg catch is determined from the sum of Analytical Fractions 2B, 3A, 3B, and 3C. Analytical Fractions 1A and 2A can be combined proportionally prior to analysis.

11.1.1 ICAP and ICP-MS Analysis. Analyze Analytical Fractions 1A and 2A by ICAP using Method 6010 or Method 200.7 (40 CFR 136, Appendix C). Calibrate the ICAP, and set up an analysis program as described in Method 6010 or Method 200.7. Follow the quality control procedures described in section 9.2.1. Recommended wavelengths for analysis are as shown in Table 29–2. These wavelengths represent the best combination of specificity

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and potential detection limit. Other wavelengths may be substituted if they can provide the needed specificity and detection limit, and are treated with the same corrective techniques for spectral interference. Initially, analyze all samples for the target metals (except Hg) plus Fe and Al. If Fe and Al are present, the sample might have to be diluted so that each of these elements is at a concentration of less than 50 ppm so as to reduce their spectral interferences on As, Cd, Cr, and Pb. Perform ICP-MS analysis by following Method 6020 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i).

NOTE: When analyzing samples in a HF matrix, an alumina torch should be used; since all front-half samples will contain HF, use an alumina torch.

11.1.2 AAS by Direct Aspiration and/or GFAAS. If analysis of metals in Analytical Fractions 1A and 2A by using GFAAS or direct aspiration AAS is needed, use Table 29–3 to determine which techniques and procedures to apply for each target metal. Use Table 29–3, if necessary, to determine techniques for minimization of interferences. Calibrate the instrument according to section 10.3 and follow the quality control procedures specified in section 9.2.2.

11.1.3 CVAAS Hg analysis. Analyze Analytical Fractions 1B, 2B, 3A, 3B, and 3C separately for Hg using CVAAS following the method outlined in Method 7470 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i), or in *Standard Methods for Water and Wastewater Analysis*, 15th Edition, Method 303F, or, optionally using note no. 2 at the end of this section. Set up the calibration curve (zero to 1000 ng) as described in Method 7470 or similar to Method 303F using 300-ml BOD bottles instead of Erlenmeyers. Perform the following for each Hg analysis. From each original sample, select and record an aliquot in the size range from 1 ml to 10 ml. If no prior knowledge of the expected amount of Hg in the sample exists, a 5 ml aliquot is suggested for the first dilution to 100 ml (see note no. 1 at end of this section). The total amount of Hg in the aliquot shall be less than 1 μg and within the range (zero to 1000 ng) of the calibration curve. Place the sample aliquot into a separate 300-ml BOD bottle, and add enough water to make a total volume of 100 ml. Next add to it sequentially the sample digestion solutions and perform the sample preparation described in the procedures of Method 7470 or Method 303F. (See note no. 2 at the end of this section). If the maximum readings are off-scale (because Hg in the aliquot exceeded the calibration range; including the situation where only a 1-ml aliquot of the original sample was digested), then dilute the original sample (or a portion of it) with 0.15 percent HNO_3 (1.5 ml concentrated HNO_3 per liter aqueous solution) so that when a 1- to 10-ml aliquot of the ''0.15 HNO_3 percent dilution of the original sample'' is digested and analyzed by the procedures described above, it will yield an analysis within the range of the calibration curve.

NOTE NO. 1: When Hg levels in the sample fractions are below the in-stack detection limit given in Table 29–1, select a 10 ml aliquot for digestion and analysis as described.

NOTE NO. 2: Optionally, Hg can be analyzed by using the CVAAS analytical procedures given by some instrument manufacturer's directions. These include calibration and quality control procedures for the Leeman Model PS200, the Perkin Elmer FIAS systems, and similar models, if available, of other instrument manufacturers. For digestion and analyses by these instruments, perform the following two steps: (1), Digest the sample aliquot through the addition of the aqueous hydroxylamine hydrochloride/sodium chloride solution the same as described in this section: (*The Leeman, Perkin Elmer, and similar instruments described in this note add automatically the necessary stannous chloride solution during the automated analysis of Hg.)*; (2), Upon completion of the digestion described in (1), analyze the sample according to the instrument manufacturer's directions. This approach allows multiple (including duplicate) automated analyses of a digested sample aliquot.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

A = Analytical detection limit, μg/ml.
B = Liquid volume of digested sample prior to aliquotting for analysis, ml.
C = Stack sample gas volume, dsm^3.
C_{a1} = Concentration of metal in Analytical Fraction 1A as read from the standard curve, μg/ml.
C_{a2} = Concentration of metal in Analytical Fraction 2A as read from the standard curve, (μg/ml).
C_s = Concentration of a metal in the stack gas, mg/dscm.
D = In-stack detection limit, $\mu g/m^3$.
F_a = Aliquot factor, volume of Sample Fraction 2 divided by volume of Sample Fraction 2A (see section 8.3.4.)
F_d = Dilution factor (F_d = the inverse of the fractional portion of the concentrated sample in the solution actually used in the instrument to produce the reading C_{a1}. For example, if a 2 ml aliquot of Analytical Fraction 1A is diluted to 10 ml to place it in the calibration range, $F_d = 5$).
Hg_{bh} = Total mass of Hg collected in the back-half of the sampling train, μg.
Hg_{bh2} = Total mass of Hg collected in Sample Fraction 2, μg.

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$Hg_{bh3(A,B,C)}$ = Total mass of Hg collected separately in Fraction 3A, 3B, or 3C, µg.

Hg_{bhb} = Blank correction value for mass of Hg detected in back-half field reagent blanks, µg.

Hg_{fh} = Total mass of Hg collected in the front-half of the sampling train (Sample Fraction 1), µg.

Hg_{fhb} = Blank correction value for mass of Hg detected in front-half field reagent blank, µg.

Hg_t = Total mass of Hg collected in the sampling train, µg.

M_{bh} = Total mass of each metal (except Hg) collected in the back-half of the sampling train (Sample Fraction 2), µg.

M_{bhb} = Blank correction value for mass of metal detected in back-half field reagent blank, µg.

M_{fh} = Total mass of each metal (except Hg) collected in the front half of the sampling train (Sample Fraction 1), µg.

M_{fhb} = Blank correction value for mass of metal detected in front-half field reagent blank, µg.

M_t = Total mass of each metal (separately stated for each metal) collected in the sampling train, µg.

M_t = Total mass of that metal collected in the sampling train, µg; (substitute Hg_t for M_t for the H_g calculation).

Q_{bh2} = Quantity of Hg, µg, TOTAL in the ALIQUOT of Analytical Fraction 2B selected for digestion and analysis .

NOTE: For example, if a 10 ml aliquot of Analytical Fraction 2B is taken and digested and analyzed (according to section 11.1.3 and its notes nos. 1 and 2), then calculate and use the total amount of Hg in the 10 ml aliquot for Q_{bh2}.

$Q_{bh3(A,B,C)}$ = Quantity of Hg, µg, *TOTAL, separately, in the ALIQUOT of Analytical Fraction 3A, 3B, or 3C selected for digestion and analysis* (see notes in sections 12.7.1 and 12.7.2 describing the quantity ''Q'' and calculate similarly).

Q_{fh} = Quantity of Hg, µg, *TOTAL in the ALIQUOT of Analytical Fraction 1B selected for digestion and analysis.*

NOTE: For example, if a 10 ml aliquot of Analytical Fraction 1B is taken and digested and analyzed (according to section 11.1.3 and its notes nos. 1 and 2), then calculate and use the total amount of Hg in the 10 ml aliquot for Q_{fh}.

V_a = Total volume of digested sample solution (Analytical Fraction 2A), ml (see section 8.3.4.1 or 8.3.4.2, as applicable).

V_{f1B} = Volume of aliquot of Analytical Fraction 1B analyzed, ml.

NOTE: For example, if a 1 ml aliquot of Analytical Fraction 1B was diluted to 50 ml with 0.15 percent HNO_3 as described in section 11.1.3 to bring it into the proper analytical range, and then 1 ml of that 50-ml was digested according to section 11.1.3 and analyzed, V_{f1B} would be 0.02 ml.

V_{f2B} = Volume of Analytical Fraction 2B analyzed, ml.

NOTE: For example, if 1 ml of Analytical Fraction 2B was diluted to 10 ml with 0.15 percent HNO_3 as described in section 11.1.3 to bring it into the proper analytical range, and then 5 ml of that 10 ml was analyzed, V_{f2B} would be 0.5 ml.

$V_{f3(A,B,C)}$ = Volume, separately, of Analytical Fraction 3A, 3B, or 3C analyzed, ml (see previous notes in sections 12.7.1 and 12.7.2, describing the quantity ''V'' and calculate similarly).

$V_{m(std)}$ = Volume of gas sample as measured by the dry gas meter, corrected to dry standard conditions, dscm.

$V_{soln,1}$ = Total volume of digested sample solution (Analytical Fraction 1), ml.

$V_{soln,1}$ = Total volume of Analytical Fraction 1, ml.

$V_{soln,2}$ = Total volume of Sample Fraction 2, ml.

$V_{soln,3(A,B,C)}$ = Total volume, separately, of Analytical Fraction 3A, 3B, or 3C, ml.

$K_4 = 10^{-3}$ mg/µg.

12.2 Dry Gas Volume. Using the data from this test, calculate $V_{m(std)}$, the dry gas sample volume at standard conditions as outlined in section 12.3 of Method 5.

12.3 Volume of Water Vapor and Moisture Content. Using the total volume of condensate collected during the source sampling, calculate the volume of water vapor $V_{w(std)}$ and the moisture content B_{ws} of the stack gas. Use Equations 5–2 and 5–3 of Method 5.

12.4 Stack Gas Velocity. Using the data from this test and Equation 2–9 of Method 2, calculate the average stack gas velocity.

12.5 In-Stack Detection Limits. Calculate the in-stack method detection limits shown in Table 29–4 using the conditions described in section 13.3.1 as follows:

$$A \times \frac{B}{C} = D \qquad \text{Eq. 29-1}$$

12.6 Metals (Except Hg) in Source Sample.

12.6.1 Analytical Fraction 1A, Front-Half, Metals (except Hg). Calculate separately the amount of each metal collected in Sample Fraction 1 of the sampling train using the following equation:

$$M_{fh} = C_{al} F_d V_{soln,1} \qquad \text{Eq. 29-2}$$

NOTE: If Analytical Fractions 1A and 2A are combined, use proportional aliquots. Then make appropriate changes in Equations 29–2 through 29–4 to reflect this approach.

12.6.2 Analytical Fraction 2A, Back-Half, Metals (except Hg). Calculate separately the amount of each metal collected in Fraction 2 of the sampling train using the following equation:

$$M_{bh} = C_{a2} F_a V_a \qquad \text{Eq. 29-3}$$

12.6.3 Total Train, Metals (except Hg). Calculate the total amount of each of the quantified metals collected in the sampling train as follows:

$$M_t = \left(M_{fh} - M_{fhb}\right) + \left(M_{bh} - M_{bhb}\right) \qquad \text{Eq. 29-4}$$

NOTE: If the measured blank value for the front half (M_{fhb}) is in the range 0.0 to ''A'' µg (where ''A'' µg equals the value determined by multiplying 1.4 µg/in.^{2} times the actual area in in.^{2} of the sample filter), use M_{fhb} to correct the emission sample value (M_{fh}); if M_{fhb} exceeds ''A'' µg, use the greater of I or II:

I. ''A'' µg.

II. The lesser of (a) M_{fhb}, or (b) 5 percent of M_{fh}. If the measured blank value for the back-half (M_{bhb}) is in the range 0.0 to 1 µg, use M_{bhb} to correct the emission sample value (M_{bh}); if M_{bhb} exceeds 1 µg, use the greater of I or II:

I. 1 µg.

II. The lesser of (a) M_{bhb}, or (b) 5 percent of M_{bh}.

12.7 Hg in Source Sample.

12.7.1 Analytical Fraction 1B; Front-Half Hg. Calculate the amount ofHg collected in the front-half, Sample Fraction 1, of the sampling train by using Equation 29–5:

$$Hg_{fh} = \frac{Q_{fh}}{V_{flB}}\left(V_{soln,1}\right) \qquad \text{Eq. 29-5}$$

12.7.2 Analytical Fractions 2B, 3A, 3B, and 3C; Back Half Hg.

12.7.2.1 Calculate the amount of Hg collected in Sample Fraction 2 by using Equation 29–6:

$$Hg_{bh2} = \frac{Q_{bh2}}{V_{f2B}}\left(V_{soln,2}\right) \qquad \text{Eq. 29-6}$$

12.7.2.2 Calculate each of the back-half Hg values for Analytical Fractions 3A, 3B, and 3C by using Equation 29–7:

$$Hg_{bh3(A,B,C)} = \frac{Q_{bh3(A,B,C)}}{V_{f3(A,B,C)}}\left(V_{soln,3(A,B,C)}\right) \qquad \text{Eq. 29-7}$$

12.7.2.3 Calculate the total amount of Hg collected in the back-half of the sampling train by using Equation 29–8:

$$Hg_{bh} = Hg_{bh2} + Hg_{bh3A} + Hg_{bh3B} + Hg_{bh3C} \qquad \text{Eq. 29-8}$$

12.7.3 Total Train Hg Catch. Calculate the total amount of Hg collected in the sampling train by using Equation 29–9:

$$Hg_t = \left(Hg_{fh} - Hg_{fhb}\right) + \left(Hg_{bh} - Hg_{bhb}\right) \qquad \text{Eq. 29-9}$$

NOTE: If the total of the measured blank values (Hg_{fhb} + Hg_{bhb}) is in the range of 0.0 to 0.6 µg, then use the total to correct the sample value (Hg_{fh} + Hg_{bh}); if it exceeds 0.6 µg, use the greater of I. or II:

I. 0.6 µg.

II. The lesser of (a) (Hg_{fhb} + Hg_{bhb}), or (b) 5 percent of the sample value (Hg_{fh} + Hg_{bh}).

12.8 Individual Metal Concentrations in Stack Gas. Calculate the concentration of

each metal in the stack gas (dry basis, adjusted to standard conditions) by using Equation 29–10:

$$C_s = \frac{K_4 M_t}{V_{m(std)}} \qquad \text{Eq. 29-10}$$

12.9 Isokinetic Variation and Acceptable Results. Same as Method 5, sections 12.11 and 12.12, respectively.

13.0 Method Performance

13.1 Range. For the analysis described and for similar analyses, the ICAP response is linear over several orders of magnitude. Samples containing metal concentrations in the nanograms per ml (ng/ml) to micrograms per ml (μg/ml) range in the final analytical solution can be analyzed using this method. Samples containing greater than approximately 50 μg/ml As, Cr, or Pb should be diluted to that level or lower for final analysis. Samples containing greater than approximately 20 μg/ml of Cd should be diluted to that level before analysis.

13.2 Analytical Detection Limits.

NOTE: See section 13.3 for the description of in-stack detection limits.

13.2.1 ICAP analytical detection limits for the sample solutions (based on *SW–846*, Method 6010) are approximately as follows: Sb (32 ng/ml), As (53 ng/ml), Ba (2 ng/ml), Be (0.3 ng/ml), Cd (4 ng/ml), Cr (7 ng/ml), Co (7 ng/ml), Cu (6 ng/ml), Pb (42 ng/ml), Mn (2 ng/ml), Ni (15 ng/ml), P (75 ng/ml), Se (75 ng/ml), Ag (7 ng/ml), Tl (40 ng/ml), and Zn (2 ng/ml). ICP-MS analytical detection limits (based on *SW–846*, Method 6020) are lower generally by a factor of ten or more. Be is lower by a factor of three. The actual sample analytical detection limits are sample dependent and may vary due to the sample matrix.

13.2.2 The analytical detection limits for analysis by direct aspiration AAS (based on *SW–846*, Method 7000 series) are approximately as follows: Sb (200 ng/ml), As (2 ng/ml), Ba (100 ng/ml), Be (5 ng/ml), Cd (5 ng/ml), Cr (50 ng/ml), Co (50 ng/ml), Cu (20 ng/ml), Pb (100 ng/ml), Mn (10 ng/ml), Ni (40 ng/ml), Se (2 ng/ml), Ag (10 ng/ml), Tl (100 ng/ml), and Zn (5 ng/ml).

13.2.3 The detection limit for Hg by CVAAS (on the resultant volume of the *digestion* of the aliquots taken for Hg analyses) can be approximately 0.02 to 0.2 ng/ml, depending upon the type of CVAAS analytical instrument used. 13.2.4 The use of GFAAS can enhance the detection limits compared to direct aspiration AAS as follows: Sb (3 ng/ml), As (1 ng/ml), Be (0.2 ng/ml), Cd (0.1 ng/ml), Cr (1 ng/ml), Co (1 ng/ml), Pb (1 ng/ml), Se (2 ng/ml), and Tl (1 ng/ml).

13.3 In-stack Detection Limits.

13.3.1 For test planning purposes in-stack detection limits can be developed by using the following information: (1) The procedures described in this method, (2) the analytical detection limits described in section 13.2 and in *SW–846*,(3) the normal volumes of 300 ml (Analytical Fraction 1) for the front-half and 150 ml (Analytical Fraction 2A) for the back-half samples, and (4) a stack gas sample volume of 1.25 m^3. The resultant in-stack method detection limits for the above set of conditions are presented in Table 29–1 and were calculated by using Eq. 29–1 shown in section 12.5.

13.3.2 To ensure optimum precision/resolution in the analyses, the target concentrations of metals in the analytical solutions should be at least ten times their respective analytical detection limits. Under certain conditions, and with greater care in the analytical procedure, these concentrations can be as low as approximately three times the respective analytical detection limits without seriously impairing the precision of the analyses. On at least one sample run in the source test, and for each metal analyzed, perform either repetitive analyses, Method of Standard Additions, serial dilution, or matrix spike addition, etc., to document the quality of the data.

13.3.3 Actual in-stack method detection limits are based on actual source sampling parameters and analytical results as described above. If required, the method in-stack detection limits can be improved over those shown in Table 29–1 for a specific test by either increasing the sampled stack gas volume, reducing the total volume of the digested samples, improving the analytical detection limits, or any combination of the three. For extremely low levels of *Hg only*, the aliquot size selected for digestion and analysis can be increased to as much as 10 ml, thus improving the in-stack detection limit by a factor of ten compared to a 1 ml aliquot size.

13.3.3.1 A nominal one hour sampling run will collect a stack gas sampling volume of about 1.25 m^3. If the sampling time is increased to four hours and 5 m^3 are collected, the in-stack method detection limits would be improved by a factor of four compared to the values shown in Table 29–1.

13.3.3.2 The in-stack detection limits assume that all of the sample is digested and the final liquid volumes for analysis are the normal values of 300 ml for Analytical Fraction 1, and 150 ml for Analytical Fraction 2A. If the volume of Analytical Fraction 1 is reduced from 300 to 30 ml, the in-stack detection limits for that fraction of the sample would be improved by a factor of ten. If the volume of Analytical Fraction 2A is reduced from 150 to 25 ml, the in-stack detection limits for that fraction of the sample would be improved by a factor of six. Matrix effect checks are necessary on sample analyses and typically are of much greater significance for samples that have been concentrated to

less than the normal original sample volume. Reduction of Analytical Fractions 1 and 2A to volumes of less than 30 and 25 ml, respectively, could interfere with the redissolving of the residue and could increase interference by other compounds to an intolerable level.

13.3.3.3 When both of the modifications described in sections 13.3.3.1 and 13.3.3.2 are used simultaneously on one sample, the resultant improvements are multiplicative. For example, an increase in stack gas volume by a factor of four and a reduction in the total liquid sample digested volume of both Analytical Fractions 1 and 2A by a factor of six would result in an improvement by a factor of twenty-four of the in-stack method detection limit.

13.4 Precision. The precision (relative standard deviation) for each metal detected in a method development test performed at a sewage sludge incinerator were found to be as follows:

Sb (12.7 percent), As (13.5 percent), Ba (20.6 percent), Cd (11.5 percent), Cr (11.2 percent), Cu (11.5 percent), Pb (11.6 percent), P (14.6 percent), Se (15.3 percent), Tl (12.3 percent), and Zn (11.8 percent). The precision for Ni was 7.7 percent for another test conducted at a source simulator. Be, Mn, and Ag were not detected in the tests. However, based on the analytical detection limits of the ICAP for these metals, their precisions could be similar to those for the other metals when detected at similar levels.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Alternative Analyzer. Samples may also be analyzed by cold vapor atomic fluorescence spectrometry.

16.2 [Reserved]

17.0 References

1. Method 303F in *Standard Methods for the Examination of Water Wastewater*, 15th Edition, 1980. Available from the American Public Health Association, 1015 18th Street N.W., Washington, D.C. 20036.

2. EPA Methods 6010, 6020, 7000, 7041, 7060, 7131, 7421, 7470, 7740, and 7841, *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*. SW–846, Third Edition, November 1986, with updates I, II, IIA, IIB and III. Office of Solid Waste and Emergency Response, U. S. Environmental Protection Agency, Washington, DC 20460.

3. EPA Method 200.7, Code of Federal Regulations, Title 40, Part 136, Appendix C. July 1, 1987.

4. EPA Methods 1 through 5, Code of Federal Regulations, Title 40, Part 60, Appendix A, July 1, 1991.

5. EPA Method 101A, Code of Federal Regulations, Title 40, Part 61, Appendix B, July 1, 1991.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 29–1—IN STACK METHOD DETECTION LIMITS (UG/M^3) FOR THE FRONT-HALF, THE BACK HALF, AND THE TOTAL SAMPLING TRAIN USING ICAP, GFAAS, AND CVAAS

Metal	Front-half: probe and filter	Back-half: impinters 1–3	Back-half: impringers 4–6 [a]	Total train
Antimony	[1] 7.7 (0.7)	[1] 3.8 (0.4)	.....	[1] 11.5 (1.1)
Arsenic	[1] 12.7 (0.3)	[1] 6.4 (0.1)	.....	[1] 19.1 (0.4)
Barium	0.5	0.3	.....	0.8
Beryllium	[1] 0.07 (0.05)	[1] 0.04 (0.03)	.....	[1] 0.11 (0.08)
Cadmium	[1] 1.0 (0.02)	[1] 0.5 (0.01)	.....	[1] 1.5 (0.03)
Chromium	[1] 1.7 (0.2)	[1] 0.8 (0.1)	.....	[1] 2.5 (0.3)
Cobalt	[1] 1.7 (0.2)	[1] 0.8 (0.1)	.....	[1] 2.5 (0.3)
Copper	1.4	0.7	.....	2.1
Lead	[1] 10.1 (0.2)	[1] 5.0 (0.1)	.....	[1] 15.1 (0.3)
Manganese	[1] 0.5 (0.2)	[1] 0.2 (0.1)	.....	[1] 0.7 (0.3)
Mercury	[2] 0.06	[2] 0.3	[2] 0.2	[2] 0.56
Nickel	3.6	1.8	.....	5.4
Phosphorus	18	9	.....	27
Selenium	[1] 18 (0.5)	[1] 9 (0.3)	.....	[1] 27 (0.8)
Silver	1.7	0.9 (0.7)	.....	2.6
Thallium	[1] 9.6 (0.2)	[1] 4.8 (0.1)	.....	[1] 14.4 (0.3)
Zinc	0.5	0.3	.....	0.8

[a] Mercury analysis only.
[1] Detection limit when analyzed by ICAP or GFAAS as shown in parentheses (see section 11.1.2).
[2] Detection limit when anaylzed by CVAAS, estimated for Back-half and Total Train. See sections 13.2 and 11.1.3. Note: Actual method in-stack detection limits may vary from these values, as described in section 13.3.3.

TABLE 29–2—RECOMMENDED WAVELENGTHS FOR ICAP ANALYSIS

Analyte	Wavelength (nm)
Aluminum (Al)	308.215
Antimony (Sb)	206.833
Arsenic (As)	193.696
Barium (Ba)	455.403
Beryllium (Be)	313.042
Cadmium (Cd)	226.502
Chromium (Cr)	267.716
Cobalt (Co)	228.616
Copper (Cu)	328.754
Iron (Fe)	259.940

TABLE 29–2—RECOMMENDED WAVELENGTHS FOR ICAP ANALYSIS—Continued

Analyte	Wavelength (nm)
Lead (Pb)	220.353
Manganese (Mn)	257.610
Nickel (Ni)	231.604
Phosphorus (P)	214.914
Selenium (Se)	196.026
Silver (Ag)	328.068
Thallium (T_1)	190,864
Zinc (Zn)	213,856

TABLE 29–3—APPLICABLE TECHNIQUES, METHODS AND MINIMIZATION OF INTERFERENCES FOR AAS ANALYSIS

Metal	Technique	SW–846 [1] Methods No.	Wavelength (nm)	Interferences	
				Cause	Minimization
Fe	Aspiration	7380	248.3	Contamination	Great care taken to avoid contamination.
Pb	Aspiration	7420	283.3	217.0 nm alternate	Background correction required.
Pb	Furnace	7421	283.3	Poor recoveries	Matrix modifier, add 10 μl of phosphorus acid to 1 ml of prepared sample in sampler cup.
Mn	Aspiration	7460	279.5	403.1 nm alternate	Background correction required.
Ni	Aspiration	7520	232.0	352.4 nm alternate Fe, Co, and Cr.	Background correction required. Matrix matching or nitrous-oxide/acetylene flame
				Nonlinear response	Sample dilution or use 352.3 nm line
Se	Furnace	7740	196.0	Volatility	Spike samples and reference materials and add nickel nitrate to minimize volatilization.
				Adsorption & scatter	Background correction is required and Zeeman background correction can be useful.
Ag	Aspiration	7760	328.1	Adsorption & scatter AgCl insoluble.	Background correction is required. Avoid hydrochloric acid unless silver is in solution as a chloride complex. Sample and standards monitored for aspiration rate.
Tl	Aspiration	7840	276.8		Background correction is required. Hydrochloric acid should not be used.
Tl	Furnace	7841	276.8	Hydrochloric acid or chloride.	Background correction is required. Verify that losses are not occurring for volatilization by spiked samples or standard addition; Palladium is a suitable matrix modifier.
Zn	Aspiration	7950	213.9	High Si, Cu, & P Contamination.	Strontium removes Cu and phosphate. Great care taken to avoid contamination.
Sb	Aspiration	7040	217.6	1000 mg/ml Pb, Ni, Cu, or acid.	Use secondary wavelength of 231.1 nm; match sample & standards acid concentration or use nitrous oxide/acetylene flame.
Sb	Furnace	7041	217.6	High Pb	Secondary wavelength or Zeeman correction.
As	Furnace	7060	193.7	Arsenic Volatilization Aluminum.	Spike samples and add nickel nitrate solution to digestates prior to analysis. Use Zeeman background correction.
Ba	Aspiration	7080	553.6		
				Calcium.	
				Barium Ionization	High hollow cathode current and narrow band set.
					2 ml of KCl per 100 m1 of sample.
Be	Aspiration	7090	234.9	500 ppm Al. High Mg and Si.	Add 0.1% fluoride.
Be	Furnace	7091	234.9	Be in optical path	Optimize parameters to minimize effects.
Cd	Aspiration	7130	228.8	Absorption and light scattering.	Background correction is required.

TABLE 29–3—APPLICABLE TECHNIQUES, METHODS AND MINIMIZATION OF INTERFERENCES FOR AAS ANALYSIS—Continued

Metal	Technique	SW–846 [1] Methods No.	Wavelength (nm)	Interferences	
				Cause	Minimization
Cd	Furnace	7131	228.8	As above	As above.
				Excess Chloride	Ammonium phosphate used as a matrix modifier.
				Pipet Tips	Use cadmium-free tips.
Cr	Aspiration	7190	357.9	Alkali metal	KCl ionization suppressant in samples and standards—Consult mfgs' literature.
Co	Furnace	7201	240.7	Excess chloride	Use Method of Standard Additions.
Cr	Furnace	7191	357.9	200 mg/L Ca and P	All calcium nitrate for a know constant effect and to eliminate effect of phosphate.
Cu	Aspiration	7210	324.7	Absorption and Scatter	Consult manufacturer's manual.

[1] Refer to EPA publication SW–846 (Reference 2 in section 16.0).

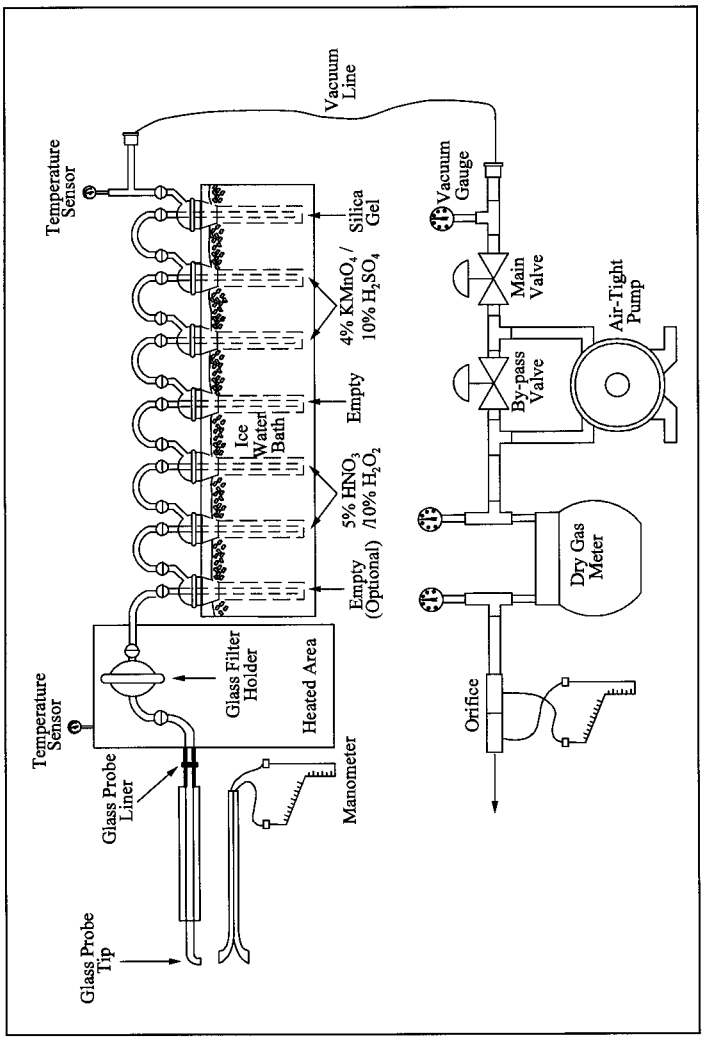

Figure 29-1. Sampling Train.

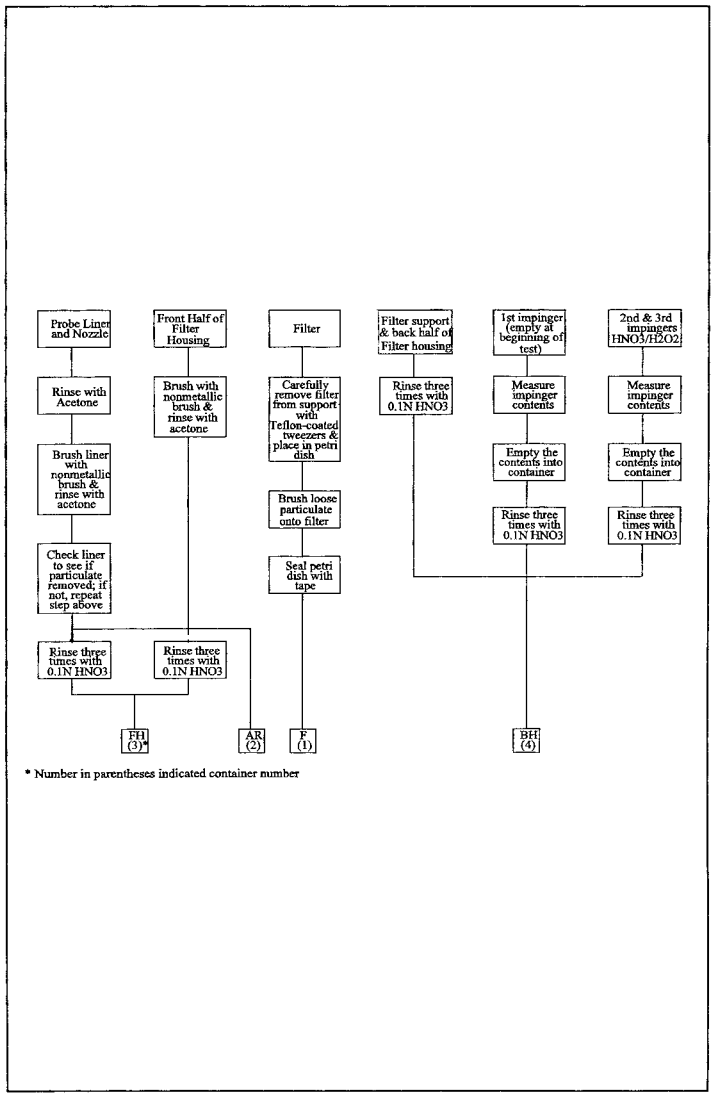

Figure 29-2a. Sample Recovery Scheme.

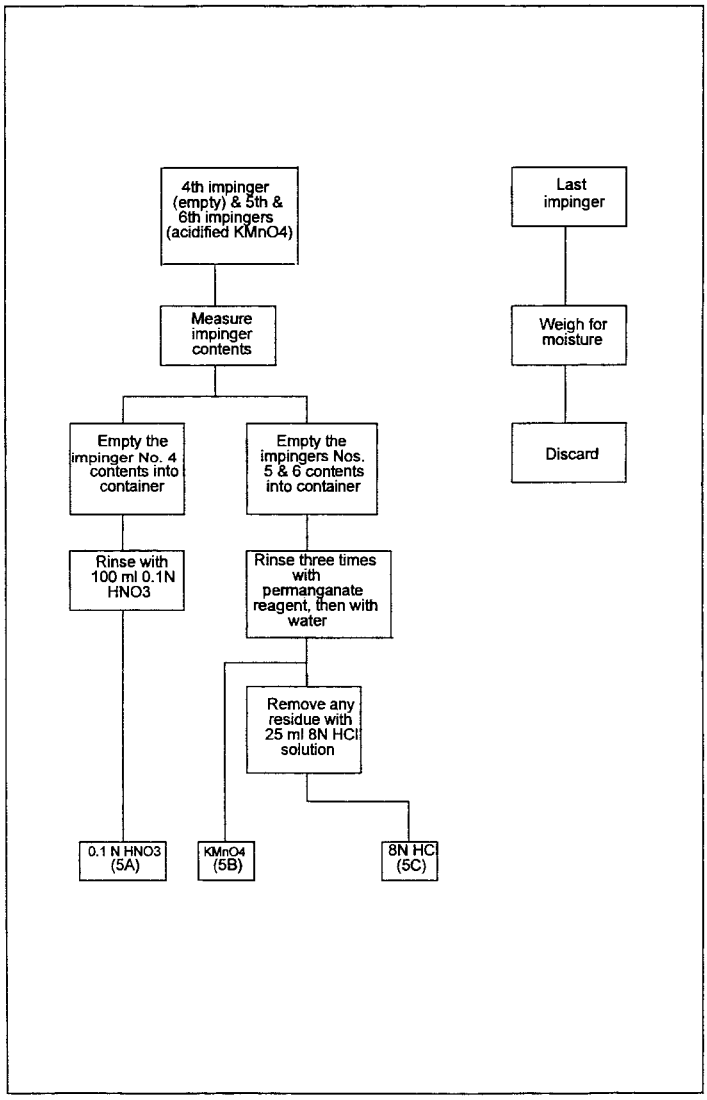

Figure 29-2b. Sample Recovery Scheme.

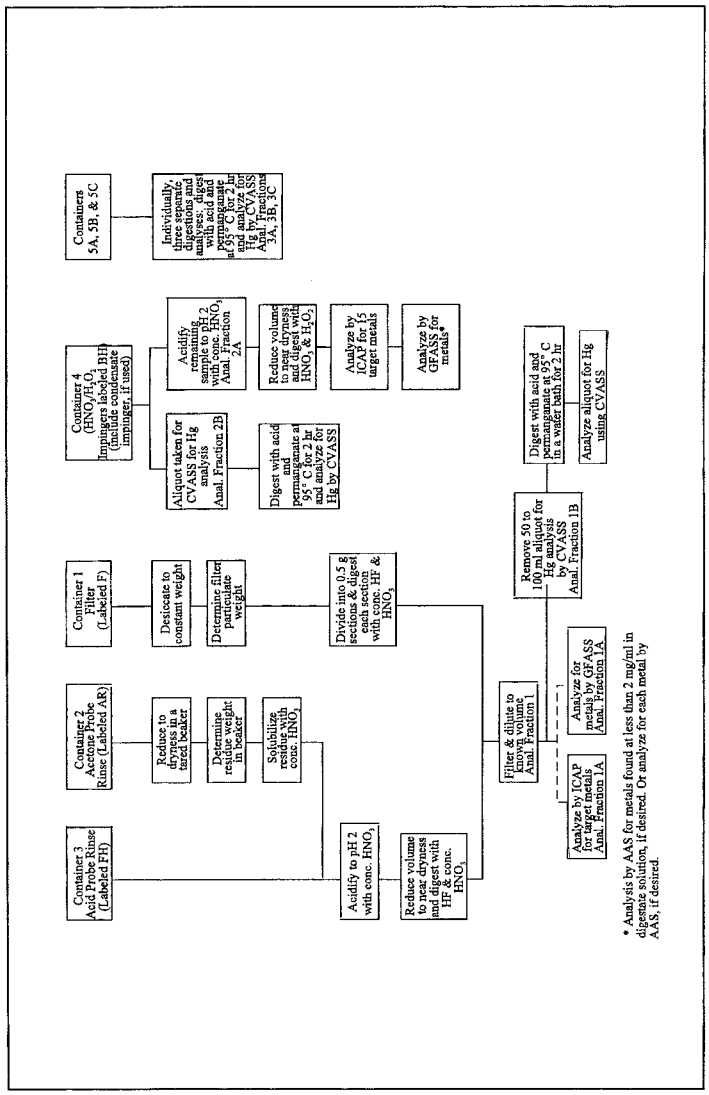

Figure 29-3. Sample Preparation and Analysis Scheme.

METHOD 30A—DETERMINATION OF TOTAL VAPOR PHASE MERCURY EMISSIONS FROM STATIONARY SOURCES (INSTRUMENTAL ANALYZER PROCEDURE)

1.0 Scope and Application

What Is Method 30A?

Method 30A is a procedure for measuring total vapor phase mercury (Hg) emissions from stationary sources using an instrumental analyzer. This method is particularly appropriate for performing emissions testing and for conducting relative accuracy test audits (RATAs) of mercury continuous emissions monitoring systems (Hg CEMS) and sorbent trap monitoring systems at coal-fired combustion sources. Quality assurance and quality control requirements are included to assure that you, the tester, collect

data of known and acceptable quality for each testing site. This method does not completely describe all equipment, supplies, and sampling procedures and analytical procedures you will need but refers to other test methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional methods which are also found in appendices A–1 and A–3 to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 4—Determination of Moisture Content in Stack Gases.

1.1 Analytes. What does this method determine? This method is designed to measure the mass concentration of total vapor phase Hg in flue gas, which represents the sum of elemental Hg (Hg^0) and oxidized forms of Hg (Hg^{+2}), in mass concentration units of micrograms per cubic meter ($\mu g/m^3$).

Analyte	CAS No.	Sensitivity
Elemental Hg (Hg^0) ..	7439–97–6	Typically <2% of Calibration Span.
Oxidized Hg (Hg^{+2})		(Same).

1.2 Applicability. When is this method required? Method 30A is offered as a reference method for emission testing and for RATAs of Hg CEMS and sorbent trap monitoring systems at coal-fired boilers. Method 30A may also be specified for other source categories in the future, either by New Source Performance Standards (NSPS), National Emission Standards for Hazardous Air Pollutants (NESHAP), emissions trading programs, State Implementation Plans (SIP), or operating permits that require measurement of Hg concentrations in stationary source emissions to determine compliance with an applicable emission standard or limit, or to conduct RATAs of Hg CEMS and sorbent trap monitoring systems.

1.3 Data Quality Objectives (DQO). How good must my collected data be? Method 30A has been designed to provide data of high and known quality for Hg emission testing and for relative accuracy testing of Hg monitoring systems including Hg CEMS and sorbent trap monitoring systems. In these and other applications, the principle objective is to ensure the accuracy of the data at the actual emission levels encountered. To meet this objective, calibration standards prepared according to an EPA traceability protocol must be used and measurement system performance tests are required.

2.0 Summary of Method

In this method, a sample of the effluent gas is continuously extracted and conveyed to an analyzer capable of measuring the total vapor phase Hg concentration. Elemental and oxidized mercury (i.e., Hg^0 and Hg^{+2}) may be measured separately or simultaneously but, for purposes of this method, total vapor phase Hg is the sum of Hg^0 and Hg^{+2}. You must meet the performance requirements of this method (i.e., system calibration, interference testing, dynamic spiking, and system integrity/drift checks) to validate your data. The dynamic spiking requirement is deferred until January 1, 2009.

3.0 Definitions

3.1 *Calibration Curve* means the relationship between an analyzer's response to the injection of a series of calibration gases and the actual concentrations of those gases.

3.2 *Calibration Gas* means a gas standard containing Hg^0 or $HgCl_2$ at a known concentration that is produced and certified in accordance with an EPA traceability protocol for certification of Hg calibration standards.

3.2.1 *Zero Gas* means a calibration gas with a concentration that is below the level detectable by the measurement system.

3.2.2 *Low-Level Gas* means a calibration gas with a concentration that is 10 to 30 percent of the calibration span.

3.2.3 *Mid-Level Gas* means a calibration gas with a concentration that is 40 to 60 percent of the calibration span.

3.2.4 *High-Level Gas* means a calibration gas whose concentration is equal to the calibration span.

3.3 *Converter* means a device that reduces oxidized mercury (Hg^{+2}) to elemental mercury (Hg^0).

3.4 *Calibration Span* means the upper limit of valid instrument response during sampling. To the extent practicable the measured emissions are to be between 10 and 100 percent of the selected calibration span (*i.e.*, the measured emissions should be within the calibrated range determined by the Low- and High-Level gas standards). It is recommended that the calibration span be at least twice the native concentration to accommodate the dynamic spiking procedure.

3.5 *Centroidal Area* means the central area that has the same shape as the stack or duct cross section and is no greater than one percent of the stack or duct total cross-sectional area.

3.6 *Data Recorder* means the equipment that permanently records the concentrations reported by the analyzer.

3.7 *Drift Check* means the test to determine the difference between the measurement system readings obtained in a post-run system integrity check and the prior pre-run system integrity check at a specific calibration gas concentration level (*i.e.*, zero, mid-level, or high-level).

3.8 *Dynamic Spiking* means a procedure in which a known mass or concentration of vapor phase $HgCl_2$ is injected into the probe sample gas stream at a known flow rate, in

order to assess the effects of the flue gas matrix on the accuracy of the measurement system.

3.9 *Gas Analyzer* means the equipment that detects the total vapor phase Hg being measured and generates an output proportional to its concentration.

3.10 *Interference Test* means the test to detect analyzer responses to compounds other than Hg, usually gases present in the measured gas stream, that are not adequately accounted for in the calibration procedure and may cause measurement bias.

3.11 *Measurement System* means all of the equipment used to determine the Hg concentration. The measurement system may generally include the following major subsystems: sample acquisition, Hg^{+2} to Hg^0 converter, sample transport, sample conditioning, flow control/gas manifold, gas analyzer, and data recorder.

3.12 *Native Concentration* means the total vapor phase Hg concentration in the effluent gas stream.

3.13 *NIST* means the National Institute of Standards and Technology, located in Gaithersburg, Maryland.

3.14 *Response Time* means the time it takes for the measurement system, while operating normally at its target sample flow rate or dilution ratio, to respond to a known step change in gas concentration (from a low-level to a high-level gas) and to read within 5 percent of the stable high-level gas response.

3.15 *Run* means a series of gas samples taken successively from the stack or duct. A test normally consists of a specific number of runs.

3.16 *System Calibration Error* means the difference between the measured concentration of a low-, mid-, or high-level Hg^0 calibration gas and the certified concentration of the gas when it is introduced in system calibration mode.

3.17 *System Calibration Mode* means introducing the calibration gases into the measurement system at the probe, upstream of all sample conditioning components.

3.18 *Test* refers to the series of runs required by the applicable regulation.

4.0 Interferences

Interferences will vary among instruments and potential instrument-specific spectral and matrix interferences must be evaluated through the interference test and the dynamic spiking tests.

5.0 Safety

What safety measures should I consider when using this method?

This method may require you to work with hazardous materials and in hazardous conditions. You are encouraged to establish safety procedures before using the method. Among other precautions, you should become familiar with the safety recommendations in the gas analyzer user's manual. Occupational Safety and Health Administration (OSHA) regulations concerning use of compressed gas cylinders and noxious gases may apply.

6.0 Equipment and Supplies

6.1 What do I need for the measurement system? This method is intended to be applicable to multiple instrumental technologies. You may use any equipment and supplies that meet the following specifications.

6.1.1 All wetted sampling system components, including probe components prior to the point at which the calibration gas is introduced, must be chemically inert to all Hg species. Materials such as perfluoroalkoxy (PFA) Teflon™, quartz, treated stainless steel (SS) are examples of such materials. [NOTE: These materials of construction are required because components prior to the calibration gas injection point are not included in the system calibration error, system integrity, and interference tests.]

6.1.2 The interference, system calibration error, system integrity, drift and dynamic spiking test criteria must all be met by the system used.

6.1.3 The system must be capable of measuring and controlling sample flow rate.

6.1.4 All system components prior to the Hg^{+2} to Hg^0 converter must be maintained at a sample temperature above the acid gas dew point.

6.2 Measurement System Components. Figure 30A–1 in section 17.0 is an example schematic of a Method 30A measurement system.

6.2.1 Sample Probe. The probe must be made of the appropriate materials as noted in section 6.1.1, heated when necessary (see section 6.1.4), configured with ports for introduction of calibration and spiking gases, and of sufficient length to traverse all of the sample points.

6.2.2 Filter or Other Particulate Removal Device. The filter or other particulate removal device is considered to be a part of the measurement system, must be made of appropriate materials as noted in section 6.1.1, and must be included in all system tests.

6.2.3 Sample Line. The sample line that connects the probe to the converter, conditioning system and analyzer must be made of appropriate materials as noted in section 6.1.1.

6.2.4 Conditioning Equipment. For dry basis measurements, a condenser, dryer or other suitable device is required to remove moisture continuously from the sample gas. Any equipment needed to heat the probe, or sample line to avoid condensation prior to the moisture removal component is also required. For wet basis systems, you must keep the sample above its dew point either by: (1) Heating the sample line and all sample transport components up to the inlet of

the analyzer (and, for hot-wet extractive systems, also heating the analyzer) or (2) by diluting the sample prior to analysis using a dilution probe system. The components required to do either of the above are considered to be conditioning equipment.

6.2.5 Sampling Pump. A pump is needed to push or pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system. If a mechanical sample pump is used and its surfaces are in contact with the sample gas prior to detection, the pump must be leak free and must be constructed of a material that is non-reactive to the gas being sampled (see section 6.1.1). For dilution-type measurement systems, an ejector pump (eductor) may be used to create a sufficient vacuum that sample gas will be drawn through a critical orifice at a constant rate. The ejector pump may be constructed of any material that is non-reactive to the gas being sampled.

6.2.6 Calibration Gas System(s). One or more systems may be needed to introduce calibration gases into the measurement system. A system should be able to flood the sampling probe sufficiently to prevent entry of gas from the effluent stream.

6.2.7 Dynamic Spiking Port. For the purposes of the dynamic spiking procedure described in section 8.2.7, the measurement system must be equipped with a port to allow introduction of the dynamic spike gas stream with the sample gas stream, at a point as close as possible to the inlet of the probe so as to ensure adequate mixing. The same port used for system calibrations and calibration error checks may be used for dynamic spiking purposes.

6.2.8 Sample Gas Delivery. The sample line may feed directly to a converter, to a bypass valve (for speciating systems), or to a sample manifold. All valve and/or manifold components must be made of material that is non-reactive to the gas sampled and the calibration gas, and must be configured to safely discharge any excess gas.

6.2.9 Hg Analyzer. An instrument is required that continuously measures the total vapor phase Hg in the gas stream and meets the applicable specifications in section 13.0.

6.2.10 Data Recorder. A recorder, such as a computerized data acquisition and handling system (DAHS), digital recorder, strip chart, or data logger, is required for recording measurement data.

6.3 Moisture Measurement System. If correction of the measured Hg emissions for moisture is required (see section 8.5), either Method 4 in appendix A–3 to this part or other moisture measurement methods approved by the Administrator will be needed to measure stack gas moisture content.

7.0 Reagents and Standards

7.1 Calibration Gases. What calibration gases do I need? You will need calibration gases of known concentrations of Hg^0 and $HgCl_2$. Special reagents and equipment may be required to prepare the $HgCl^2$ gas standards (e.g., a NIST-traceable solution of $HgCl_2$ and a gas generator equipped with mass flow controllers).

The following calibration gas concentrations are required:

7.1.1 High-Level Gas. Equal to the selected calibration span.

7.1.2 Mid-Level Gas. 40 to 60 percent of the calibration span.

7.1.3 Low-Level Gas. 10 to 30 percent of the calibration span.

7.1.4 Zero Gas. No detectable Hg.

7.1.5 Dynamic Spike Gas. The exact concentration of the $HgCl_2$ calibration gas used to perform the pre-test dynamic spiking procedure described in section 8.2.7 depends on the native Hg concentration in the stack The spike gas must produce a spiked sample concentration above the native concentration, as specified in section 8.2.7.2.2.

7.2 Interference Test. What reagents do I need for the interference test? Use the appropriate test gases listed in Table 30A–3 in section 17.0 (i.e., the potential interferents for the source to be tested, as identified by the instrument manufacturer) to conduct the interference check. These gases need not be of protocol gas quality.

8.0 Sample Collection

Emission Test Procedure

Figure 30A–2 in section 17.0 presents an overview of the test procedures required by this method. Since you may choose different options to comply with certain performance criteria, you must identify the specific options and associated frequencies you select and document your results in regard to the performance criteria.

8.1 Selection of Sampling Sites and Sampling Points. What sampling site and sampling points do I select?

8.1.1 When this method is used solely for Hg emission testing (e.g., to determine compliance with an emission standard or limit), use twelve sampling points located according to Table 1–1 or Table 1–2 of Method 1 in appendix A–1 to this part. Alternatively, you may conduct a stratification test as described in section 8.1.3 to determine the number and location of the sampling points.

8.1.2 When this method is used for relative accuracy testing of a Hg CEMS or sorbent trap monitoring system, follow the sampling

site selection and sampling point layout procedures for gas monitor RATA testing described in the appropriate performance specification or applicable regulation (e.g., Performance Specification 2, section 8.1.3 of appendix B to this part or section 6.5.6 of appendix A to part 75 of this chapter), with one exception. If you elect to perform stratification testing as part of the sampling point selection process, perform the testing in accordance with section 8.1.3 of this method (see also ''Summary Table of QA/QC Requirements'' in section 9.0).

8.1.3 Determination of Stratification. If you elect to perform stratification testing as part of the sampling point selection process and the test results show your effluent gas stream to be unstratified or minimally stratified, you may be allowed to sample at fewer points or at different points than would otherwise be required.

8.1.3.1 Test Procedure. To test for stratification, use a probe of appropriate length to measure the total vapor phase Hg concentration at twelve traverse points located according to Table 1–1 or Table 1–2 of Method 1 in appendix A–1 to this part. Alternatively, for a sampling location where stratification is expected (e.g., after a wet scrubber or at a point where dissimilar gas streams are combined together), if a 12-point Hg stratification test has been previously performed at that location and the results of the test showed the location to be minimally stratified or unstratified according to the criteria in section 8.1.3.2, you may perform an abbreviated 3-point or 6-point Hg stratification test at the points specified in section 6.5.6.2(a) of appendix A to part 75 of this chapter in lieu of performing the 12-point test. Sample for a minimum of twice the system response time (see section 8.2.6) at each traverse point. Calculate the individual point and mean Hg concentrations.

8.1.3.2 Acceptance Criteria and Sampling Point Location.

8.1.3.2.1 If the Hg concentration at each traverse point differs from the mean concentration for all traverse points by no more than: (a) ±5 percent of the mean concentration; or (b) ±0.2 μg/m^3 (whichever is less restrictive), the gas stream is considered to be unstratified and you may collect samples from a single point that most closely matches the mean.

8.1.3.2.2 If the 5 percent or 0.2 μg/m^3 criterion in section 8.1.3.2.1 is not met, but the Hg concentration at each traverse point differs from the mean concentration for all traverse points by no more than: (a)±10 percent of the mean; or (b)±0.5 μg/m^3 (whichever is less restrictive), the gas stream is considered to be minimally stratified, and you may take samples from three points, provided the points are located on the measurement line exhibiting the highest average Hg concentration during the stratification test. If the stack diameter (or equivalent diameter, for a rectangular stack or duct) is greater than 2.4 meters (7.8 ft), locate the three sampling points at 0.4, 1.0, and 2.0 meters from the stack or duct wall. Alternatively, if a RATA required by part 75 of this chapter is being conducted, you may locate the three points at 4.4, 14.6, and 29.6 percent of the duct diameter, in accordance with Method 1 in appendix A–1 to this part. For stack or duct diameters of 2.4 meters (7.8 ft) or less, locate the three sampling points at 16.7, 50.0, and 83.3 percent of the measurement line.

8.1.3.2.3 If the gas stream is found to be stratified because the 10 percent or 0.5 μg/m^3 criterion in section 8.1.3.2.2 is not met, then either locate three sampling points at 16.7, 50.0, and 83.3 percent of the measurement line that exhibited the highest average Hg concentration during the stratification test, or locate twelve traverse points for the test in accordance with Table 1–1 or Table 1–2 of Method 1 in appendix A–1 to this part; or, if a RATA required by part 75 of this chapter is being conducted, locate six Method 1 points along the measurement line that exhibited the highest average Hg concentration.

8.1.3.3 Temporal Variations. Temporal variations in the source Hg concentration during a stratification test may complicate the determination of stratification. If temporal variations are a concern, you may use the following procedure to normalize the stratification test data. A second Hg measurement system, i.e., either an installed Hg CEMS or another Method 30A system, is required to perform this procedure. Position the sampling probe of the second Hg measurement system at a fixed point in the stack or duct, at least one meter from the stack or duct wall. Then, each time that the Hg concentration is measured at one of the stratification test points, make a concurrent measurement of Hg concentration at the fixed point. Normalize the Hg concentration measured at each traverse point, by multiplying it by the ratio of $C_{F,avg}$ to C_F, where C_F is the corresponding fixed-point Hg concentration measurement, and $C_{F,avg}$ is the average of all of the fixed-point measurements over the duration of the stratification test. Evaluate the results of the stratification test according to section 8.1.3.2, using the normalized Hg concentrations.

8.1.3.4 Stratification Testing Exemption. Stratification testing need not be performed at a test location where it would otherwise be required to justify using fewer sample points or different sample points, if the owner or operator documents that the Hg concentration in the stack gas is expected to be 3 μg/m^3 or less at the time of a Hg monitoring system RATA or an Hg emissions test. To demonstrate that a particular test location qualifies for the stratification testing exemption, representative Hg emissions data must be collected just prior to the RATA or

emissions test. At least one hour of Hg concentration data is required for the demonstration. The data used for the demonstration shall be recorded at process operating conditions that closely approximate the operating conditions that will exist during the RATA or emissions test. It is recommended that collection of the demonstration data be integrated with the on-site pretest procedures required by the reference method being used for the RATA or emissions test (whether this method or another approved Hg reference method is used). Quality-assured data from an installed Hg monitoring system may also be used for the demonstration. If a particular test location qualifies for the stratification testing exemption, sampling shall be performed at three points, as described in section 8.1.3.2.2 of this method. The owner or operator shall fully document the method used to collect the demonstration data and shall keep this documentation on file with the data from the associated RATA or Hg emissions test.

8.1.3.5 Interim Alternative Stratification Test Procedures. In the time period between the effective date of this method and January 1, 2009, you may follow one of the following two procedures. Substitute a stratification test for sulfur dioxide (SO_2) for the Hg stratification test described in section 8.1.3.1. If this option is chosen, follow the test procedures in section 6.5.6.1 of appendix A to part 75 of this chapter. Evaluate the test results and determine the sampling point locations according to section 6.5.6.3 of appendix A to part 75 of this chapter. If the sampling location is found to be minimally stratified or unstratified for SO_2, it shall be considered minimally stratified or unstratified for Hg. Alternatively, you may forgo stratification testing, assume the gas stream is minimally stratified, and sample at three points as described in section 8.1.3.2.2 of this method.

8.2 Initial Measurement System Performance Tests. What initial performance criteria must my system meet before I begin sampling? Before measuring emissions, perform the following procedures:

(a) Interference Test;

(b) Calibration Gas Verification;

(c) Measurement System Preparation;

(d) 3-Point System Calibration Error Test;

(e) System Integrity Check;

(f) Measurement System Response Time Test; and

(g) Dynamic Spiking Test.

8.2.1 Interference Test (Optional). Your measurement system should be free of known interferences. It is recommended that you conduct this interference test of your measurement system prior to its initial use in the field to verify that the candidate test instrument is free from inherent biases or interferences resulting from common combustion emission constituents. If you have multiple measurement systems with components of the same make and model numbers, you need only perform this interference check on one system and you may also rely on an interference test conducted by the manufacturer on a system having components of the same make and model(s) of the system that you use. The interference test procedure is found in section 8.6 of this method.

8.2.2 Calibration Gas Verification. How must I verify the concentrations of my calibration gases?

8.2.2.1 Cylinder Gas Standards. When cylinder gas standards are used for Hg^0, obtain a certificate from the gas manufacturer and confirm that the documentation includes all information required by an EPA traceability protocol (see section 16). Confirm that the manufacturer certification is complete and current. Ensure that the calibration gas certifications have not expired.

8.2.2.2 Other Calibration Standards. All other calibration standards for $HgCl_2$ and Hg^0, such as gas generators, must meet the requirements of an EPA traceability protocol (see section 16), and the certification procedures must be fully documented in the test report.

8.2.2.3 Calibration Span. Select the calibration span (i.e., high-level gas concentration) so that the measured source emissions are 10 to 100 percent of the calibration span. This requirement is waived for applications in which the Hg concentrations are consistently below 1 $\mu g/m^3$; however, the calibration span for these low-concentration applications shall not exceed 5 $\mu g/m^3$.

8.2.3 Measurement System Preparation. How do I prepare my measurement system for use? Assemble, prepare, and precondition the measurement system according to your standard operating procedure. Adjust the system to achieve the correct sampling rate or dilution ratio (as applicable). Then, conduct a 3-point system calibration error test using Hg^0 as described in section 8.2.4, an initial system integrity check using $HgCl_2$ and a zero gas as described in section 8.2.5, and a pre-test dynamic spiking test as described in section 8.2.7.

8.2.4 System Calibration Error Test. Conduct a 3-point system calibration error test before the first test run. Use Hg^0 standards for this test. Introduce the low-, mid-, and high-level calibration gases in any order, in system calibration mode, unless you desire to determine the system response time during this test, in which case, inject the gases such that the high-level injection directly follows the low-level injection. For non-dilution systems, you may adjust the system to maintain the correct flow rate at the analyzer during the test, but you may not make adjustments for any other purpose. For dilution systems, you must operate the measurement system at the appropriate dilution

ratio during all system calibration error checks, and you may make only the adjustments necessary to maintain the proper ratio. After each gas injection, wait until a stable response has been obtained. Record the analyzer's final, stable response to each calibration gas on a form similar to Table 30A–1 in section 17.0. For each calibration gas, calculate the system calibration error using Equation 30A–1 in section 12.2. The calibration error specification in section 13.1 must be met for the low-, mid-, and high-level gases. If the calibration error specification is not met for all three gases, take corrective action and repeat the test until an acceptable 3-point calibration is achieved.

8.2.5 System Integrity Check. Perform a two-point system integrity check before the first test run. Use the zero gas and either the mid- or high-level $HgCl_2$ calibration gas for the check, whichever one best represents the total vapor phase Hg concentration levels in the stack. Record the data on a form similar to Table 30A–2 in section 17.0. The system integrity check specification in section 13.2 must be met for both the zero gas and the mid- or high-level gas. If the system integrity specification is not met for both gases, take corrective action and repeat the test until an acceptable system integrity check is achieved.

8.2.6 Measurement System Response Time. The measurement system response time is used to determine the minimum sampling time for each sampling point and is equal to the time that is required for the measured Hg concentration to increase from the stable low-level calibration gas response to a value within 5 percent of the stable high-level calibration gas response during the system calibration error test in section 8.2.4. Round off the measured system response time to the nearest minute.

8.2.7 Dynamic Spiking Test. You must perform dynamic spiking prior to the first test run to validate your test data. The purpose of this procedure is to demonstrate that the site-specific flue gas matrix does not adversely affect the accuracy of the measurement system. The specifications in section 13.5 must be met to validate your data. If these specifications are not met for the pretest dynamic spiking, you may not proceed with the test until satisfactory results are obtained. For the time period between the effective date of this method and January 1, 2009, the dynamic spiking requirement is waived.

8.2.7.1 How do I perform dynamic spiking? Dynamic spiking is a gas phase application of the method of standard additions, which involves injecting a known quantity of Hg into the measurement system upstream of all sample conditioning components, similar to system calibration mode, except the probe is not flooded and the resulting sample stream includes both effluent gas and the spike gas. You must follow a written procedure that details how the spike is added to the system, how the spike dilution factor (DF) is measured, and how the Hg concentration data are collected and processed.

8.2.7.2 Spiking Procedure Requirements.

8.2.7.2.1 Spiking Gas Requirements. The spike gas must also be a $HgCl_2$ calibration gas certified by an EPA traceability protocol. You must choose concentrations that can produce the target levels while being injected at a volumetric flow rate that is ≤20 percent of the total volumetric flow rate through the measurement system (i.e., sample flow rate plus spike gas flow rate).

8.2.7.2.2 Target Spiking Level. The target level for spiking must be 150 to 200 percent of the native Hg concentration; however, if the native Hg concentration is <1 μg/m³, set the target level to add between 1 and 4 μg/m³ Hg^{+2} to the native concentration. Use Equation 30A–5 in section 12.5 to calculate the acceptable range of spike gas concentrations at the target level. Then select a spike gas concentration in that range.

8.2.7.2.3 Spike Injections. You must inject spikes in such a manner that the spiking does not alter the total volumetric sample system flow rate and dilution ratio (if applicable). You must collect at least 3 data points, and the relative standard deviation (RSD) specification in section 13.5 must be met. Each data point represents a single spike injection, and pre- and post-injection measurements of the native Hg concentration (or diluted native concentration, as applicable) are required for each spike injection.

8.2.7.2.4 Spike Dilution Factor (DF). For each spike injection, DF, the dilution factor must be determined. DF is the ratio of the total volumetric flow rate of gas through the measurement system to the spike gas flow rate. This factor must be ≥5. The spiking mass balance calculation is directly dependent on the accuracy of the DF determination. As a result, high accuracy total volumetric flow rate and spike gas flowrate measurements are required. These flow rates may be determined by direct or indirect measurement. Calibrated flow meters, venturies, orifices or tracer gas measurements are examples of potential flow measurement techniques.

8.2.7.2.5 Concentrations. The measurement system must record total vapor phase Hg concentrations continuously during the dynamic spiking procedure. It is possible that dynamic spiking at a level close to 200 percent of the native Hg concentration may cause the measured Hg concentration to exceed the calibration span value. Avoid this by choosing a lower spiking level or by recalibration at a higher span. The measurements shall not exceed 120 percent of the calibration span. The ''baseline'' measurements made between spikes may represent

the native Hg concentration (if spike gas flow is stopped between injections) or the native Hg concentration diluted by blank or carrier gas flowing at the same rate as the spike gas (if gas flow cannot be stopped between injections). Each baseline measurement must include at least 4 readings or 1 minute (whichever is greater) of stable responses. Use Equation 30A–10 or 30A–11 in section 12.10 (as applicable) to convert baseline measurements to native concentration.

8.2.7.2.6 Recovery. Calculate spike recoveries using Equation 30A–7 in section 12.7. Mass recoveries may be calculated from stable responses based on injected mass flows or from integrated response peaks based on total mass injected. Calculate the mean and RSD for the three (or more) spike injections and compare to the specifications in section 13.5.

8.2.7.2.7 Error Adjustment Option. You may adjust the measurement data collected during dynamic spiking for the system calibration error using Equation 30A–3 in section 12. To do this, perform the initial system integrity check prior to the dynamic spiking test, and perform another system integrity check following the dynamic spiking test and before the first test run. If you choose this option, you must apply Equation 30A–3 to both the spiked sample concentration measurement (C_{ss}) and the baseline or native concentration measurement (C_{native}), each substituted in place of C_{avg} in the equation.

8.2.7.3 Example Spiking Procedure Using a Hot Vapor Calibration Source Generator.

(a) Introduce the spike gas into the probe using a hot vapor calibration source generator and a solution of $HgCl_2$ in dilute HC1 and HNO_3. The calibrator uses a mass flow controller (accurate within 2 percent) to measure the gas flow, and the solution feed is measured using a top-loading balance accurate to 0.01g. The challenges of injecting oxidized Hg may make it impractical to stop the flow of gas between spike injections. In this case, operate the hot vapor calibration source generator continuously during the spiking procedure, swapping blank solutions for $HgCl_2$ solutions when switching between spiking and baseline measurements.

(b) If applicable, monitor the measurement system to make sure the total sampling system flow rate and the sample dilution ratio do not change during this procedure. Record all data on a data sheet similar to Table 30A–5 in section 17.0. If the Hg measurement system design makes it impractical to measure the total volumetric flow rate through the system, use a spike gas that includes a tracer for measuring the dilution factor, DF (see Equation 30A–9 in section 12.9). Allow the measurements to stabilize between each spike injection, average the pre- and post-injection baseline measurements, and calculate the native concentration. If this measurement shifts by more than 5 percent during any injection, it may be necessary to discard that data point and repeat the injection to achieve the required RSD among the injections. If the spikes persistently show poor repeatability, or if the recoveries are not within the range specified in section 13.5, take corrective action.

8.2.8 Run Validation. How do I confirm that each run I conduct is valid?

8.2.8.1 System Integrity Checks.

(a) Before and after each test run, perform a two-point system integrity check using the same procedure as the initial system integrity check described in section 8.2.5. You may use data from that initial system integrity check as the pre-run data for the first test run, provided it is the most recent system integrity check done before the first run. You may also use the results of a successful post-run system integrity check as the pre-run data for the next test run. Do not make any adjustments to the measurement system during these checks, other than to maintain the target calibration gas flow rate and the proper dilution ratio.

(b) As a time-saving alternative, you may, at the risk of invalidating multiple test runs, skip one or more integrity checks during a test day. Provided there have been no auto-calibrations or other instrument alterations, a single integrity check may suffice as a post-run check to validate (or invalidate) as many consecutive test runs as can be completed during a single test day. All subsequent test days must begin with a pre-run system integrity check subject to the same performance criteria and corrective action requirements as a post-run system integrity check.

(c) Each system integrity check must meet the criteria for system integrity checks in section 13.2. If a post-run system integrity check is failed, all test runs since the last passed system integrity check are invalid. If a post-run or a pre-run system integrity check is failed, you must take corrective action and pass another 3-point Hg^0 system calibration error test (Section 8.2.4) followed by another system integrity check before conducting any additional test runs. Record the results of the pre- and post-run system integrity checks on a form similar to Table 30A–2 in section 17.0.

8.2.8.2 Drift Check. Using the data from the successful pre- and post-run system integrity checks, calculate the zero and upscale drift, using Equation 30A–2 in section 12.3. Exceeding the section 13.3 specification does not invalidate the run, but corrective action must be taken and a new 3-point Hg^0 system calibration error test and a system integrity check must be passed before any more runs are made.

8.3 Dilution-Type Systems—Special Considerations. When a dilution-type measurement system is used, there are three important considerations that must be taken into

account to ensure the quality of the emissions data. First, the critical orifice size and dilution ratio must be selected properly so that the sample dew point will be below the sample line and analyzer temperatures. Second, a high-quality, accurate dilution controller must be used to maintain the correct dilution ratio during sampling. The dilution controller should be capable of monitoring the dilution air pressure, orifice upstream pressure, eductor vacuum, and sample flow rates. Third, differences between the molecular weight of calibration gas mixtures, dilution air, and the stack gas molecular weight must be considered because these can affect the dilution ratio and introduce measurement bias.

8.4 Sampling.

(a) Position the probe at the first sampling point. Allow the system to flush and equilibrate for at least two times the measurement system response time before recording any data. Then, traverse and record measurements at all required sampling points. Sample at each traverse point for an equal length of time, maintaining the appropriate sample flow rate or dilution ratio (as applicable). For all Hg instrumental method systems, the minimum sampling time at each sampling point must be at least two times the system response time, but not less than 10 minutes. For concentrating systems, the minimum sampling time must also include at least 4 concentration measurement cycles.

(b) After recording data for the appropriate period of time at the first traverse point, you may move the sample probe to the next point and continue recording, omitting the requirement to allow the system to equilibrate for two times the system response time before recording data at the subsequent traverse points. You must, however, sample at this and all subsequent traverse points for the required minimum amount of time specified in this section. If you must remove the probe from the stack for any reason, you must again allow the sampling system to equilibrate for at least two times the system response time prior to resuming data recording.

(c) If at any point the measured Hg concentration exceeds the calibration span value, you must at a minimum identify and report this as a deviation from the method. Depending on the data quality objectives of the test, this event may require corrective action before proceeding. If the average Hg concentration for any run exceeds the calibration span value, the run is invalidated.

8.5 Moisture Correction. If the moisture basis (wet or dry) of the measurements made with this method is different from the moisture basis of either: (1) The applicable emission limit; or (2) a Hg CEMS or sorbent trap monitoring system being evaluated for relative accuracy, you must determine the moisture content of the flue gas and correct the measured gas concentrations to a dry basis using Method 4 in appendix A–3 of this part or other appropriate methods, subject to the approval of the Administrator.

8.6 Optional Interference Test Procedure.

(a) Select an appropriate calibration span that reflects the source(s) to be tested and perform the interference check at 40 percent of the lowest calibration span value anticipated, e.g., 10 $\mu g/m^3$. Alternatively, successfully conducting the interference test at an absolute Hg concentration of 2 $\mu g/m^3$ will demonstrate performance for an equivalent calibration span of 5 $\mu g/m^3$, the lowest calibration span allowed for Method 30A testing. Therefore, performing the interference test at the 2 μ/m^3 level will serve to demonstrate acceptable performance for all calibration spans greater than or equal to 5 $\mu g/m^3$.

(b) Introduce the interference test gases listed in Table 30A–3 in section 17.0 into the measurement system separately or as a mixture. The interference test gases HCl and NO must be introduced as a mixture. The interference test gases must be introduced into the sampling system at the probe such that the interference gas mixtures pass through all filters, scrubbers, conditioners, and other components as would be configured for normal sampling.

(c) The interference test must be performed using $HgCl_2$, and each interference test gas (or gas mixture) must be evaluated in triplicate. This is accomplished by measuring the Hg response first with only the $HgCl_2$ gas present and then when adding the interference test gas(es) while maintaining the $HgCl_2$ concentration of the test stream constant. It is important that the equipment used to conduct the interference test be of sufficient quality so as to be capable of blending the $HgCl_2$ and interference gases while maintaining the Hg concentration constant. Gas blending system or manifolds may be used.

(d) The duration of each test should be for a sufficient period of time to ensure the Hg measurement system surfaces are conditioned and a stable output is obtained. Measure the Hg response of the analyzer to these gases in µg/m3. Record the responses and determine the overall interference response using Table 30A–4 in section 17.0 and the equations presented in section 12.11. The specification in section 13.4 must be met.

(e) A copy of these data, including the date completed and a signed certification, must be included with each test report. The intent of this test is that the interference test results are intended to be valid for the life of the system. As a result, the Hg measurement system should be operated and tested in a configuration consistent with the configuration that will be used for field applications. However, if the system used for field testing is not consistent with the system that was interference-tested, the interference test

must be repeated before it is used for any field applications. Examples of such conditions include, but are not limited to: major changes in dilution ratio (for dilution based systems), changes in catalyst materials, changes in filtering device design or materials, changes in probe design or configuration, and changes in gas conditioning materials or approaches.

9.0 Quality Control

What quality control measures must I take?

The table which follows is a summary of the mandatory, suggested, and alternative quality assurance and quality control measures and the associated frequency and acceptance criteria. All of the QC data, along with the run data, must be documented and included in the test report.

SUMMARY TABLE OF QA/QC REQUIREMENTS

Status [1]	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
S	Identify Data User	Regulatory Agency or other primary end user of data.	Before designing test..	
M	Analyzer Design	Analyzer range	Sufficiently >high-level gas to allow determination of system calibration error.	
S	Analyzer resolution or sensitivity.	<2.0 % of full-scale range.	Manufacturer design..	
S	Interference response.	Overall response ≤3% of calibration span. Alternatively, overall response ≤0.3 µg/m³.		
M	Calibration Gases	Traceability protocol	Validation of concentration required.	
M	High-level Hg^0 gas	Equal to the calibration span.	Each calibration error test..	
M	Mid-level Hg^0 gas	40 to 60% of calibration span.	Each calibration error test..	
M	Low-level Hg^0 gas	10 to 30% of calibration span.	Each calibration error test..	
M	High-level $HgCl_2$ gas	Equal to the calibration span.	Each system integrity check (if it better represents C_{native} than the mid level gas)..	
M	Mid-level $HgCl_2$	40 to 60% of calibration span.	Each system gas integrity check (if it better represents C_{native} than the high level gas)..	
M	Zero gas	Each system integrity check..		
M	Dynamic spike gas (C_{native} ≥1 µg/m³).	A high-concentration $HgCl_2$ gas, used to produce a spiked sample concentration that is 150 to 200% of the native concentration.	Pre-test; dynamic spiking not required until 1/1/09..	
M	Dynamic spike gas (C_{native} <1 µg/m³).	A high-concentration $HgCl_2$ gas, used to produce a spiked sample concentration that is 1 to 2 µg/m³ above the native concentration.	Pre-test; dynamic spiking not required until 1/1/09..	
S	Data Recorder Design.	Data resolution	≤0.5% of full-scale	Manufacturer design.
M	Sample Extraction	Probe material	Inert to sample constituents (e.g., PFA Teflon, or quartz if stack >500 °F).	Each run.
M	Sample Extraction	Probe, filter and sample line temperature.	For dry-basis analyzers, keep sample above the dew point, by heating prior to moisture removal. For wet-basis analyzers, keep sample above dew point at all times, by heating or dilution.	Each run.
M	Sample Extraction	Calibration valve material.	Inert to sample constituents (e.g., PFA Teflon or PFA Teflon coated).	Each test.
S	Sample Extraction	Sample pump material.	Inert to sample constituents	Each test.
M	Sample Extraction	Manifold material	Inert to sample constituents	Each test.

SUMMARY TABLE OF QA/QC REQUIREMENTS—Continued

Status [1]	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
M	Particulate Removal	Filter inertness	Pass calibration error check	Each calibration error check.
M	System Calibration Performance.	System calibration error (CE) test.	CE ≤5.0 % of the calibration span for the low-, mid-or high-level Hg^0 calibration gas. Alternative specification: ≤0.5 µg/m³ absolute difference between system response and reference value.	Before initial run and after a failed system integrity check or drift test.
M	System Calibration Performance.	System integrity check.	Error ≤5.0% of the calibration span for the zero and mid- or high-level $HgCl_2$ calibration gas. Alternative specification: ≤0.5 µg/m³ absolute difference between system response and reference value.	Before initial run, after each run, at the beginning of subsequent test days, and after a failed system integrity check or drift test.
M	System Performance	System response time.	Used to determine minimum sampling time per point.	During initial 3-point system calibration error test.
M	System Performance	Drift	≤3.0% of calibration span for the zero and mid- or high-level gas. Alternative specification: ≤0.3 µg/m³ absolute difference between pre- and post-run system calibration error percentages..	At least once per test day.
M	System Performance	Minimum sampling time.	The greater of two times the system response time or 10 minutes. Concentrating systems must also include at least 4 cycles.	Each sampling point.
M	System Performance	Percentage spike recovery and relative standard deviation.	Percentage spike recovery, at the target level: 100 ±10%. Relative standard deviation: ≤5 percent ... Alternative specification: absolute difference between calculated and measured spike values ≤0.5 µg/m³.	Before initial run; dynamic spiking not required until 1/1/09.
M	Sample Point Selection. For Part 60 RATAs, follow the procedures in Performance Specification 2, section 8.1.3, and for Part 75 RATAs, follow the procedures in section 6.5.6 of appendix A to Part 75. That is: • At *any* test location, you may use 3 sample points located at 16.7, 50.0, and 83.3% of a ''long'' measurement line passing through the centroidal area; or • At *any* test location, you may use 6 sample points along a diameter, located according to Method 1 (Part 75 RATAs, only); or	Number and Location of Sample Points.	For emission testing applications, use 12 points, located according to Method 1 in appendix A–1 to this part, unless the results of a stratification test allow fewer points to be used.	Prior to first run.

SUMMARY TABLE OF QA/QC REQUIREMENTS—Continued

Status [1]	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
	• At a location where stratification is not expected and the measurement line is >2.4 m (7.8 ft), you may use 3 sample points located along a ''short'' measurement line at 0.4, 1.0, and 2.0 m from the stack or duct wall or, for Part 75 only, sample points may be located at 4.4, 14.6, and 29.6% of the measurement line; or • After a wet scrubber or at a point where dissimilar gas streams are combined, either locate 3 sample points along the ''long'' measurement line or locate 6 Method 1 points along a diameter (Part 75, only), unless the results of a stratification test allow you to use a ''short'' 3-point measurement line or to sample at a single point. • If it can be demonstrated that stack gas concentration is ≤3 µg/m^3, then the test site is exempted from stratification testing. Use the 3-point ''short'' measurement line if the stack diameter is >2.4 m (7.8 ft) and the 3-point ''long'' line for stack diameters ≤2.4 m (7.8 ft).			

SUMMARY TABLE OF QA/QC REQUIREMENTS—Continued

Status[1]	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
A	Sample Point Selection	Stratification Test (See section 8.1.3)..	If the Hg concentration[2] at each traverse point during the stratification test is: • Within ±5% of mean, use 1-point sampling (at the point closest to the mean); or. • Not within ±5% of mean, but is within ±10% of mean, use 3-point sampling. Locate points according to section 8.1.3.2.2 of this method.. Alternatively, if the Hg concentration at each point is:. • Within ±0.2 μg/m³ of mean, use 1-point sampling (at the point closest to the mean); or. • Not within ±0.2 μg/m³ of mean, but is within ±0.5 μg/m³ of mean, use 3-point sampling. Locate points according to section 8.1.3.2.2 of this method..	Prior to first run. Prior to 1/1/09, you may (1) forgo stratification testing and use 3 sampling points (as per section 8.1.3.2.2) or (2) perform a SO_2 stratification test (see sections 6.5.6.1 and 6.5.6.3 of appendix A to part 75), in lieu of a Hg stratification test. If the test location is unstratified or minimally stratified for SO_2, it can be considered unstratified or minimally stratified for Hg also.
M	Data Recording	Frequency	Once per cycle	During run.
S	Data Parameters	Sample concentration and calibration span.	All analyzer readings during each run within calibration span.	Each run.
M	Data Parameters	Sample concentration and calibration span.	All analyzer readings during dynamic spiking tests within 120% of calibration span.	Each spike injection.
M	Data Parameters	Sample concentration and calibration span.	Average Hg concentration for the run ≤calibration span.	Each run.

[1] M = Mandatory; S = Suggested; A = Alternative.
[2] These may either be the unadjusted Hg concentrations or concentrations normalized to account for temporal variations.

10.0 Calibration and Standardization

What measurement system calibrations are required?

Your analyzer must be calibrated with Hg° standards. The initial 3-point system calibration error test described in section 8.2.4 is required before you start the test. Also, prior to and following test runs, the two-point system integrity checks described in sections 8.2.5 and 8.2.8 are required. On and after January 1, 2009, the pre-test dynamic spiking procedure described in section 8.2.7 is also required to verify that the accuracy of the measurement system is suitable and not adversely affected by the flue gas matrix.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the procedures for calculations and data analysis listed in this section.

12.1 Nomenclature. The terms used in the equations are defined as follows:

B_{ws} = Moisture content of sample gas as measured by Method 4 in Appendix A–3 to this part, percent/100.

C_{avg} = Average unadjusted Hg concentration for the test run, as indicated by the data recorder μg/m³.

$\bar{C}_{baseline}$ = Average Hg concentration measured before and after dynamic spiking injections, μg/m³.

C_d = Hg concentration, dry basis, μg/m³.

C_{dif} = Absolute value of the difference between the measured Hg concentrations of the reference $HgCl_2$ calibration gas, with and without the individual or combined interference gases, μg/m³.

$C_{dif\ avg}$ = Average of the 3 absolute values of the difference between the measured Hg concentrations of the reference $HgCl_2$ calibration gas, with and without the individual or combined interference gases, μg/m³.

C_{gas} = Average Hg concentration in the effluent gas for the test run, adjusted for system calibration error, μg/m³.

C_{int} = Measured Hg concentration of the reference $HgCl_2$ calibration gas plus the individual or combined interference gases, µg/m³.
C_m = Average of pre- and post-run system integrity check responses for the upscale (i.e., mid- or high-level) calibration gas, µg/m³.
C_{ma} = Actual concentration of the upscale (i.e., mid- or high-level) calibration gas used for the system integrity checks, µg/m³.
C_0 = Average of pre- and post-run system integrity check responses from the zero gas, µg/m³.
C_{native} = Vapor phase Hg concentration in the source effluent, µg/m³.
C_{ref} = Measured Hg concentration of the reference $HgCl_2$ calibration gas alone, in the interference test, µg/m³.
C_s = Measured concentration of a calibration gas (zero-, low-, mid-, or high-level), when introduced in system calibration mode, µg/m³.
C_{spike} = Actual Hg concentration of the spike gas, µg/m³.
C^*_{spike} = Hg concentration of the spike gas required to achieve a certain target value for the spiked sample Hg concentration, µg/m³.
C_{ss} = Measured Hg concentration of the spiked sample at the target level, µg/m³.
C^*_{ss} = Expected Hg concentration of the spiked sample at the target level, µg/m³.
C_{target} = Target Hg concentration of the spiked sample, µg/m³.
$C_{Tnative}$ = Measured tracer gas concentration present in native effluent gas, ppm.
C_{Tdir} = Tracer gas concentration injected with spike gas, ppm.
C_{Tv} = Diluted tracer gas concentration measured in a spiked sample, ppm.
C_v = Certified Hg° or $HgCl_2$ concentration of a calibration gas (zero, low, mid, or high), µg/m³.
C_w = Hg concentration measured under moist sample conditions, wet basis, µg/m³.
CS = Calibration span, µg/m³.
D = Zero or upscale drift, percent of calibration span.
DF = Dilution factor of the spike gas, dimensionless.
I = Interference response, percent of calibration span.
Q_{probe} = Total flow rate of the stack gas sample plus the spike gas, liters/min.
Q_{spike} = Flow rate of the spike gas, liters/min.
R_i = Individual injection spike recovery, %.
$\bar{R}$ = Mean value of spike recoveries at a particular target level, %.
RSD = Relative standard deviation, %;.
SCE = System calibration error, percent of calibration span.
SCE_i = Pre-run system calibration error during the two-point system integrity check, percent of calibration span.
SCE_f = Post-run system calibration error during the two-point system integrity check, percent of calibration span.

12.2 System Calibration Error. Use Equation 30A–1 to calculate the system calibration error. Equation 30A–1 applies to: 3–point system calibration error tests performed with Hg° standards; and pre- and post-run two-point system integrity checks performed with $HgCl_2$.

$$SCE = \frac{C_s - C_v}{CS} \times 100 \qquad \text{Eq. 30A-1}$$

12.3 Drift Assessment. Use Equation 30A–2 to separately calculate the zero and upscale drift for each test run.

$$D = \left|SCE_f - SCE_i\right| \qquad \text{Eq. 30A-2}$$

12.3 Effluent Hg Concentration. For each test run, calculate C_{avg}, the arithmetic average of all valid Hg concentration values recorded during the run. Then, adjust the value of C_{avg} for system calibration error, using Equation 30A–3.

$$C_{gas} = (C_{avg} - C_0)\,\frac{C_{ma}}{C_m - C_0} \qquad \text{Eq. 30A-3}$$

12.4 Moisture Correction. Use Equation 30A–4a if your measurements need to be corrected to a dry basis.

$$C_d = \frac{C_w}{1 - B_{ws}} \qquad \text{Eq. 30A-4a}$$

Use Equation 30A–4b if your measurements need to be corrected to a wet basis.

$$C_w = C_d \times (1 - B_{ws}) \qquad \text{Eq. 30A-4b}$$

12.5 Dynamic Spike Gas Concentrations. Use Equation 30A–5 to determine the spike gas concentration needed to produce a spiked sample with a certain ''target'' Hg concentration.

$$C^{*}_{spike} = DF(C_{target} - C_{native}) + C_{native} \qquad \text{Eq. 30A-5}$$

12.6 Spiked Sample Concentration. Use Equation 30A–6 to determine the expected or theoretical Hg concentration of a spiked sample.

$$C^{*}_{ss} = C_{native} + \frac{(C_{spike} - C_{native})}{DF} \qquad \text{Eq. 30A-6}$$

12.7 Spike Recovery. Use Equation 30A–7 to calculate the percentage recovery of each spike.

$$R = \frac{DF\,(C_{ss} - C_{native}) + C_{native}}{C_{spike}} \times 100\% \qquad \text{Eq. 30A-7}$$

12.8 Relative Standard Deviation. Use Equation 30A–8 to calculate the relative standard deviation of the individual percentage spike recovery values from the mean.

$$RSD = \frac{100\%}{\bar{R}} \sqrt{\frac{\sum_{i=1}^{n} (R_i - \bar{R})^2}{n-1}} \qquad \text{Eq. 30A-8}$$

12.9 Spike Dilution Factor. Use Equation 30A–9 to calculate the spike dilution factor, using either direct flow measurements or tracer gas measurements.

$$DF = \frac{Q_{probe}}{Q_{spike}} = \frac{C_{Tdir} - C_{Tnative}}{C_{Ttv} - C_{Tnative}} \qquad \text{Eq. 30A-9}$$

12.10 Native Concentration. For spiking procedures that inject blank or carrier gases (at the spiking flow rate, Q_{spike}) between spikes, use Equation 30A–10 to calculate the native concentration.

$$C_{native} = \frac{\bar{C}_{baseline} DF}{DF - 1} \qquad \text{Eq. 30A-10}$$

For spiking procedures that halt all injections between spikes, the native concentration equals the average baseline concentration (see Equation 30A–11).

$$C_{native} = \bar{C}_{baseline} \qquad \text{Eq. 30A-11}$$

12.11 Overall Interference Response. Use equation 30A–12 to calculate the overall interference response.

$$I = \frac{\sum C_{difavg}}{CS} \times 100 \qquad \text{Eq. 30A-12}$$

Where, for each interference gas (or mixture):

$$C_{difavg} = \frac{\sum_{1}^{3} C_{dif}}{3} \qquad \text{Eq. 30A-13}$$

$$C_{dif} = \left| C_{ref} - C_{int} \right| \qquad \text{Eq. 30A-14}$$

13.0 Method Performance

13.1 System Calibration Error Test. This specification applies to the 3-point system calibration error tests using Hg^0. At each calibration gas level tested (low-, mid-, or high-level), the calibration error must be within ±5.0 percent of the calibration span. Alternatively, the results are acceptable if $|C_s - C_v| \leq 0.5$ µg/m³.

13.2 System Integrity Checks. This specification applies to all pre- and post-run 2-point system integrity checks using $HgCl_2$ and zero gas. At each calibration gas level tested (zero and mid- or high-level), the error must be within ±5.0 percent of the calibration span. Alternatively, the results are acceptable if $|C_s - C_v| \leq 0.5$ µg/m³.

13.3 Drift. For each run, the low-level and upscale drift must be less than or equal to 3.0 percent of the calibration span. The drift is also acceptable if the pre- and post-run system integrity check responses do not differ by more than 0.3 µg/m³ (i.e., $|C_{s\ post\text{-}run} - C_{s\ pre\text{-}run}| \leq 0.3$ µg/m³).

13.4 Interference Test. Summarize the results following the format contained in Table 30A–4. For each interference gas (or mixture), calculate the mean difference between the measurement system responses with and without the interference test gas(es). The overall interference response for the analyzer that was used for the test (calculated according to Equation 30A–12), must not be greater than 3.0 percent of the calibration span used for the test (see section 8.6). The results of the interference test are also acceptable if the sum of the absolute average differences for all interference gases (i.e., $\Sigma\ C_{dif\ avg}$) does not exceed 0.3 µg/m³.

13.5 Dynamic Spiking Test. For the pretest dynamic spiking, the mean value of the percentage spike recovery must be 100 ±10 percent. In addition, the relative standard deviation (RSD) of the individual percentage spike recovery values from the mean must be ≤5.0 percent. Alternatively, if the mean percentage recovery is not met, the results are acceptable if the absolute difference between the theoretical spiked sample concentration (see section 12.6) and the actual average value of the spiked sample concentration is ≤0.5 µg/m³.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. EPA Traceability Protocol for Qualification and Certification of Elemental Mercury Gas Generators, expected publication date December 2008, see *www.epa.gov/ttn/emc*.

2. EPA Traceability Protocol for Qualification and Certification of Oxidized Mercury Gas Generators, expected publication date December 2008, see *www.epa.gov/ttn/emc*.

3. EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards, expected revision publication date December 2008, see *www.epa.gov/ttn/emc*.

17.0 Figures and Tables

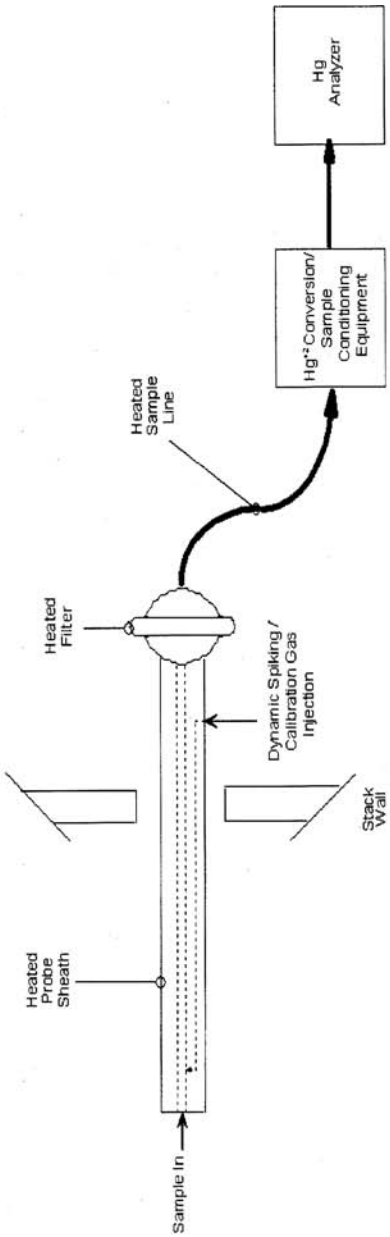

Figure 30A-1: Example Hg Measurement System

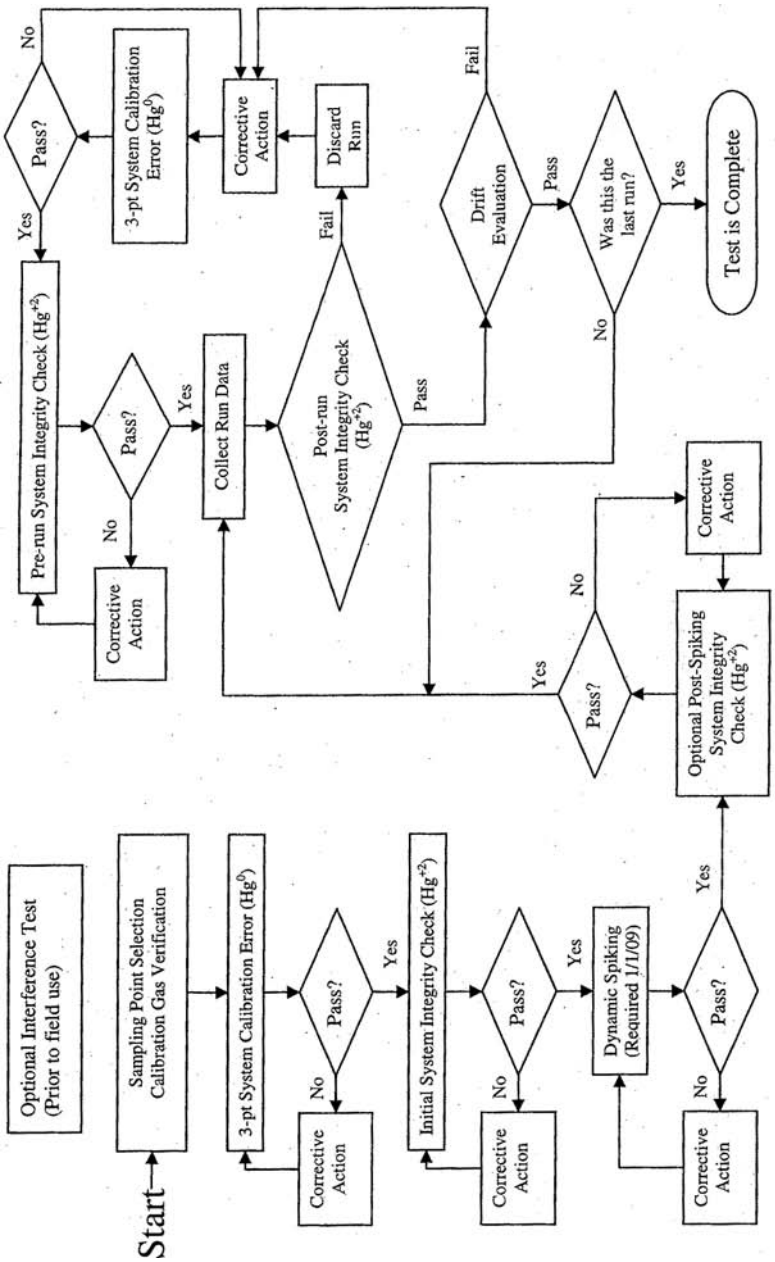

Figure 30A-2. Testing Flow Chart

Table 30A-1: 3-Point System Calibration Error Tests

Facility name: _____ Unit(s) tested: _____ Test personnel: _____ Date: _____ Time: _____	Test Runs Covered: _____ Analyzer make & model no. _____ Serial no. _____ Calibration span (CS): _____ System response time: _____

Calibration Gas Level	Certified Gas Concentration ($\mu g/m^3$) A	System Response ($\mu g/m^3$) B	Absolute Difference |A-B|	Calibration Error (% of calibration span) $\frac{[\|A-B\|]*100}{CS}$
Low				
Mid				
High				

Table 30A-2: System Integrity Check and Drift Data

Facility name:_____ Analyzer make & model: _____

Unit(s) tested: _____ Serial number: _____

Test personnel: _____ Run number(s) covered:_____

Date(s): _____ Calibration span: _____

Calibration Gas Level (zero, mid, or high)	Certified Calibration Gas Value ($\mu g/m^3$)	Initial System Response ($\mu g/m^3$)	Final System Response ($\mu g/m^3$)	Absolute Difference ($\mu g/m^3$)	Drift (% of calibration span)

TABLE 30A–3—INTERFERENCE CHECK GAS CONCENTRATIONS

Potential interferent gas [1]	Concentration, tentative—(balance N_2)
CO_2	15% ±1% CO_2
CO	100 ±20 ppm
HCl [2]	100 ±20 ppm
NO [2]	250 ±50 ppm
SO_2	200 ±20 ppm
O_2	3% ±1% O_2
H_2O	10% ±1% H_2O
Nitrogen	Balance

TABLE 30A–3—INTERFERENCE CHECK GAS CONCENTRATIONS—Continued

Potential interferent gas [1]	Concentration, tentative—(balance N_2)
Other.	

[1] Any of these specific gases can be tested at a lower level if the manufacturer has provided reliable means for limiting or scrubbing that gas to a specified level.

[2] HCl and NO must be tested as a mixture.

Table 30A-4: Example Interference Test Data Sheet

Date of Test: _____
Analyzer Type: _____
Model No.: _____
Serial No.: _____
Calibration Span: _____
Test Organization: _____
Test Personnel: _____

Interference Gas	Hg Concentration ($\mu g/m^3$)	Hg Concentration ($\mu g/m^3$) w/Interference Gas	Absolute Difference ($\mu g/m^3$)	Average Absolute Difference ($\mu g/m^3$)
			Sum of Responses	
			% of Calibration Span	

Table 30A-5: Example Dynamic Spiking Data Sheet

Facility name: _____ Date: _____ Time: _____
Unit(s) tested: _____ Test personnel: _____
Analyzer make & model: _____ Estimated native Hg concentration: _____ µg/m^3
Serial number: _____ Estimated unspiked sample flow rate: _____ lpm
Calibration span: _____ µg/m^3 Estimated spike gas flow rate: _____ lpm

Q_{probe} (lpm)	Q_{spike} (lpm)	DF[1]	Target Level[2]		C_{native} (µg/m^3)			Actual Values		% Spike Recovery
			C^*_{spike} (µg/m^3)	C^*_{ss} (µg/m^3)	Pre	Post	Avg.	C_{spike} (µg/m^3)	C_{ss} (µg/m^3)	
									Avg. RSD	

1 DF must be ≥ 5
2 C^*_{ss}/C_{native} must be ≥ 1.5 and ≤ 2.0, where C_{native} and C^*_{ss} are estimated values

METHOD 30B—DETERMINATION OF TOTAL VAPOR PHASE MERCURY EMISSIONS FROM COAL-FIRED COMBUSTION SOURCES USING CARBON SORBENT TRAPS

1.0 Scope and Application

What is Method 30B?

Method 30B is a procedure for measuring total vapor phase mercury (Hg) emissions from coal-fired combustion sources using sorbent trap sampling and an extractive or thermal analytical technique. This method is only intended for use only under relatively low particulate conditions (e.g., sampling after all pollution control devices). Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known and acceptable quality for each testing program. This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need, but instead refers to other test methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional methods which are found in Appendices A–1 and A–3 to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 4—Determination of Moisture Content in Stack Gases.

(c) Method 5—Determination of Particulate Matter Emissions from Stationary Sources

1.1 Analytes. What does this method determine? This method is designed to measure the mass concentration of total vapor phase Hg in flue gas, including elemental Hg (Hg^0) and oxidized forms of Hg (Hg^{+2}), in micrograms per dry standard cubic meter (µg/dscm).

Analyte	CAS No.	Analytical range and sensitivity
Elemental Hg (Hg^0) ..	7439–97–6	Typically 0.1 µg/dscm to >50 µg/dscm.
Oxidized Hg (Hg^{+2}) ...	.....	(Same)

1.2 Applicability. When is this method required? Method 30B is a reference method for relative accuracy test audits (RATAs) of vapor phase Hg CEMS and sorbent trap monitoring systems installed at coal-fired boilers and is also appropriate for Hg emissions testing at such boilers. It is intended for use only under relatively low particulate conditions (i.e., sampling after all pollution control devices); in cases where significant amounts of particle-bound Hg may be present, an isokinetic sampling method for Hg should be used. Method 30B may also be specified by New Source Performance Standards (NSPS), National Emission Standards for Hazardous Air Pollutants (NESHAP), emissions trading programs, State Implementation Plans (SIPs), and operating permits that require measurement of Hg concentrations in stationary source emissions, either to determine compliance with an applicable emission standard or limit, or to conduct RATAs of Hg CEMS and sorbent trap monitoring systems.

1.3 Data Quality Objectives (DQO). How good must my collected data be? Method 30B has been designed to provide data of high and known quality for Hg emissions testing and for RATA testing of Hg monitoring systems, including CEMS and sorbent trap monitors. In these and other applications, the principal objective is to ensure the accuracy of the data at the actual emissions levels and in the actual emissions matrix encountered. To meet this objective, NIST-traceable calibration standards must be used and method performance tests are required.

2.0 Summary of Method

Known volumes of flue gas are extracted from a stack or duct through paired, in-stack sorbent media traps at an appropriate flow rate. Collection of mercury on the sorbent media in the stack mitigates potential loss of mercury during transport through a probe/sample line. For each test run, paired train sampling is required to determine measurement precision and verify acceptability of the measured emissions data. A field recovery test which assesses recovery of an elemental Hg spike to determine measurement bias is also used to verify data acceptability. The sorbent traps are recovered from the sampling system, prepared for analysis as needed, and analyzed by any suitable determinative technique that can meet the performance criteria.

3.0 Definitions

3.1 *Analytical System* is the combined equipment and apparatus used to perform sample analyses. This includes any associated sample preparation apparatus e.g., digestion equipment, spiking systems, reduction devices, etc., as well as analytical instrumentation such as UV AA and UV AF cold vapor analyzers.

3.2 *Calibration Standards* are the Hg containing solutions prepared from NIST traceable standards and are used to directly calibrate analytical systems.

3.3 *Independent Calibration Standard* is a NIST traceable standard obtained from a source or supplier independent of that for the calibration standards and is used to confirm the integrity of the calibration standards used.

3.4 *Method Detection Limit (MDL)* is the lowest mass of Hg greater than zero that can be estimated and reported by your candidate analytical technique. The MDL is statistically derived from replicate low level measurements near your analytical instrument's detection level.

3.5 *NIST* means the National Institute of Standards and Technology, located in Gaithersburg, Maryland.

3.6 *Run* means a series of gas samples taken successively from the stack or duct. A test normally consists of a specific number of runs.

3.7 *Sorbent Trap* means a cartridge or sleeve containing a sorbent media (typically activated carbon treated with iodine or some other halogen) with multiple sections separated by an inert material such as glass wool. These sorbent traps are optimized for the quantitative capture of elemental and oxidized forms of Hg and can be analyzed by multiple techniques.

3.8 *Test* refers to the series of runs required by the applicable regulation.

3.9 *Thermal Analysis* means an analytical technique where the contents of the sorbent traps are analyzed using a thermal technique (desorption or combustion) to release the captured Hg in a detectable form for quantification.

3.10 *Wet Analysis* means an analytical technique where the contents of the sorbent tube are first leached or digested to quantitatively transfer the captured Hg to liquid solution for subsequent analysis.

4.0 Interferences

Interferences may result from the sorbent trap material used as well as from the measurement environment itself. The iodine present on some sorbent traps may impart a negative measurement bias. High levels of sulfur trioxide (SO_3) are also suspected to compromise the performance of sorbent trap Hg capture. These, and other, potential interferences are assessed by performing the analytical matrix interference, Hg^0 and $HgCl_2$ analytical bias and field recovery tests.

5.0 Safety

What safety measures should I consider when using this method? This method may require you to work with hazardous materials and in hazardous conditions. You are encouraged to establish safety procedures before using the method. Among other precautions, you should become familiar with the safety recommendations in the gas analyzer user's manual. Occupational Safety and Health Administration (OSHA) regulations concerning use of compressed gas cylinders and noxious gases may apply.

5.1 Site Hazards. Prior to applying these procedures/specifications in the field, the potential hazards at the test site should be considered; advance coordination with the site is critical to understand the conditions and applicable safety policies. At a minimum, portions of the sampling system will be hot, requiring appropriate gloves, long sleeves, and caution in handling this equipment.

5.2 Laboratory Safety. Policies should be in place to minimize risk of chemical exposure and to properly handle waste disposal in the laboratory. Personnel shall wear appropriate laboratory attire according to a Chemical Hygiene Plan established by the laboratory.

5.3 Reagent Toxicity/Carcinogenicity. The toxicity and carcinogenicity of any reagents used must be considered. Depending upon the sampling and analytical technologies selected, this measurement may involve hazardous materials, operations, and equipment and this method does not address all of the safety problems associated with implementing this approach. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicable regulatory limitations prior to performance. Any chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized. Chemists should refer to the Material Safety Data Sheet (MSDS) for each chemical used.

5.4 Waste Disposal. Any waste generated by this procedure must be disposed of according to a hazardous materials management plan that details and tracks various waste streams and disposal procedures.

6.0 Equipment and Supplies

The following list is presented as an example of key equipment and supplies likely required to measure vapor-phase Hg using a sorbent trap sampling system. It is recognized that additional equipment and supplies may be needed. Collection of paired samples is required.

6.1 Sorbent Trap Sampling System. A typical sorbent trap sampling system is shown in Figure 30B–1 in section 17.0. The sorbent trap sampling system shall include the following components:

6.1.1 Sorbent Traps. The sorbent media used to collect Hg must be configured in a trap with at least two distinct segments or sections, connected in series, that are amenable to separate analyses. section 1 is designated for primary capture of gaseous Hg. section 2 is designated as a backup section for determination of vapor phase Hg breakthrough. Each sorbent trap must be inscribed or otherwise permanently marked with a unique identification number, for tracking purposes. The sorbent media may be any collection material (e.g., carbon, chemically-treated filter, etc.) capable of quantitatively capturing and recovering for subsequent analysis, all gaseous forms of Hg in the emissions from the intended application. Selection of the sorbent media shall be based on the material's ability to achieve the performance criteria contained in this method as well as the sorbent's vapor phase

Hg capture efficiency for the emissions matrix and the expected sampling duration at the test site. The sorbent media must be obtained from a source that can demonstrate their quality assurance and quality control (see section 7.2). The paired sorbent traps are supported on a probe (or probes) and inserted directly into the flue gas stream.

6.1.2 Sampling Probe Assembly. Each probe assembly shall have a leak-free attachment to the sorbent trap(s). Each sorbent trap must be mounted at the entrance of or within the probe such that the gas sampled enters the trap directly. Each probe/sorbent trap assembly must be heated to a temperature sufficient to prevent liquid condensation in the sorbent trap(s). Auxiliary heating is required only where the stack temperature is too low to prevent condensation. Use a calibrated thermocouple to monitor the stack temperature. A single probe capable of operating the paired sorbent traps may be used. Alternatively, individual probe/sorbent trap assemblies may be used, provided that the individual sorbent traps are co-located to ensure representative Hg monitoring.

6.1.3 Moisture Removal Device. A moisture removal device or system shall be used to remove water vapor from the gas stream prior to entering dry gas flow metering devices.

6.1.4 Vacuum Pump. Use a leak-tight, vacuum pump capable of operating within the system's flow range.

6.1.5 Gas Flow Meter. A gas flow meter (such as a dry gas meter, thermal mass flow meter, or other suitable measurement device) shall be used to determine the total sample volume on a dry basis, in units of standard cubic meters. The meter must be sufficiently accurate to measure the total sample volume to within 2 percent and must be calibrated at selected flow rates across the range of sample flow rates at which the sampling train will be operated. The gas flow meter shall be equipped with any necessary auxiliary measurement devices (e.g., temperature sensors, pressure measurement devices) needed to correct the sample volume to standard conditions.

6.1.6 Sample Flow Rate Meter and Controller. Use a flow rate indicator and controller for maintaining necessary sampling flow rates.

6.1.7 Temperature Sensor. Same as section 6.1.1.7 of Method 5 in Appendix A–3 to this part.

6.1.8 Barometer. Same as section 6.1.2 of Method 5 in Appendix A–3 to this part.

6.1.9 Data Logger (optional). Device for recording associated and necessary ancillary information (e.g., temperatures, pressures, flow, time, etc.).

6.2 Gaseous Hg^0 Sorbent Trap Spiking System. A known mass of gaseous Hg^0 must be either present on or spiked onto the first section of sorbent traps in order to perform the Hg^0 and $HgCl_2$ analytical bias test and the field recovery study. Any approach capable of quantitatively delivering known masses of Hg^0 onto sorbent traps is acceptable. Several spiking technologies or devices are available to meet this objective. Their practicality is a function of Hg mass spike levels. For low levels, NIST-certified or NIST-traceable gas generators or tanks may be suitable. An alternative system, capable of delivering almost any mass required, makes use of NIST-certified or NIST-traceable Hg salt solutions (e.g., $HgCl_2$, $Hg(NO_3)_2$). With this system, an aliquot of known volume and concentration is added to a reaction vessel containing a reducing agent (e.g., stannous chloride); the Hg salt solution is reduced to Hg^0 and purged onto the sorbent trap using an impinger sparging system. When available, information on example spiking systems will be posted at *http://www.epa.gov/ttn/emc*.

6.3 Sample Analysis Equipment. Any analytical system capable of quantitatively recovering and quantifying total Hg from the sorbent media selected is acceptable provided that the analysis can meet the performance criteria described in this method. Example recovery techniques include acid leaching, digestion, and thermal desorption/direct combustion. Example analytical techniques include, but are not limited to, ultraviolet atomic fluorescence (UV AF), ultraviolet atomic absorption (UV AA) with and without gold trapping, and X-ray fluorescence (XRF) analysis.

6.3 Moisture Measurement System. If correction of the measured Hg emissions for moisture is required (see section 8.3.3.7), either Method 4 in Appendix A–3 to this part or other moisture measurement methods approved by the Administrator will be needed to measure stack gas moisture content.

7.0 Reagents and Standards

7.1 Reagents and Standards. Only NIST-certified or NIST-traceable calibration standards, standard reference materials, and reagents shall be used for the tests and procedures required by this method.

7.2 Sorbent Trap Media. The sorbent trap media shall be prepared such that the material used for testing is of known and acceptable quality. Sorbent supplier quality assurance/quality control measures to ensure appropriate and consistent performance such as sorptive capacity, uniformity of preparation treatments, and background levels shall be considered.

8.0 Sample Collection and Handling

This section presents the sample collection and handling procedures along with the pretest and on-site performance tests required by this method. Since you may choose different options to comply with certain performance criteria, each test report must identify the specific options selected and

document the results with respect to the performance criteria of this method.

8.1 Selection of Sampling Sites and Sampling Points. What sampling site and sampling points do I select? Same as section 8.1 of Method 30A of this appendix.

8.2 Measurement System Performance Tests. What performance criteria must my measurement system meet? The following laboratory and field procedures and associated criteria of this section are designed to ensure (1) selection of a sorbent and analytical technique combination capable of quantitative collection and analysis of gaseous Hg, (2) collection of an adequate amount of Hg on each sorbent trap during field tests, and (3) adequate performance of the method for each test program: The primary objectives of these performance tests are to characterize and verify the performance of your intended analytical system and associated sampling and analytical procedures, and to define the minimum amount of Hg (as the sample collection target) that can be quantified reliably.

(a) Analytical Matrix Interference Test;

(b) Determination of Minimum Sample Mass;

(c) Hg^0 and $HgCl_2$ Analytical Bias Test;

(d) Determination of Nominal Sample Volume;

(e) Field Recovery Test.

8.2.1 Analytical Matrix Interference Test and Minimum Sample Dilution.

(a) The analytical matrix interference test is a laboratory procedure. It is required only if you elect to use a liquid digestion analytical approach and needs to be performed only once for each sorbent material used. The purpose of the test is to verify the presence or absence of known and potential analytical matrix interferences, including the potential negative bias associated with iodine common to many sorbent trap materials. The analytical matrix interference test determines the minimum dilution (if any) necessary to mitigate matrix effects on the sample digestate solutions.

(b) The result of the analytical matrix interference test, i.e., the minimum sample dilution required (if any) for all sample analyses, is used to establish the minimum sample mass needed for the Hg^0 and $HgCl_2$ analytical bias test and to determine the nominal sample volume for a test run. The analytical matrix interference test is sorbent material-specific and shall be performed for each sorbent material you intend to use for field sampling and analysis. The test shall be performed using a mass of sorbent material comparable to the sorbent mass typically used in the first section of the trap for sampling. Similar sorbent materials from different sources of supply are considered to be different materials and must be tested individually. You must conduct the analytical matrix interference test for each sorbent material prior to the analysis of field samples.

8.2.1.1 Analytical Matrix Interference Test Procedures. Digest and prepare for analysis a representative mass of sorbent material (unsampled) according to your intended laboratory techniques for field samples. Analyze the digestate according to your intended analytical conditions at the least diluted level you intend to use for sample analysis (e.g., undiluted, 1 in 10 dilution, etc.). Determine the Hg concentration of the undiluted digestate solution. Prepare a series of solutions with a fixed final volume containing graduated aliquots of the sample digestate and, a fixed aliquot of a calibration standard (with the balance being Hg-free reagent or H_20) to establish solutions of varied digestate dilution ratio (e.g., 1:2, 1:5, 1:10, 1:100, etc.—see example in section 8.2.1.3, below). One of these solutions should contain only the aliquot of the calibration standard in Hg-free reagent or H_2O. This will result in a series of solutions where the amount of Hg is held relatively constant and only the volume of digestate diluted is varied. Analyze each of these solutions following intended sample analytical procedures and conditions, determining the concentration for each solution.

8.2.1.2 Analytical Matrix Interference Test Acceptance Criteria. Compare the measured concentration of each solution containing digestate to the measured concentration of the digestate-free solution. The lowest dilution ratio of any solution having a Hg concentration within ±5 percent of the digestate-free solution is the minimum dilution ratio required for analysis of all samples. If you desire to measure the digestate without dilution, the ±5 percent criterion must be met at a dilution ratio of at least 9:10 (i.e., ≥90% digestate).

8.2.1.3 Example Analytical Matrix Interference Test. An example analytical matrix interference test is presented below. Additional information on the conduct of the analytical matrix interference test will be posted at *http://www.epa.gov/ttn/emc*. Determine the most sensitive working range for the analyzer to be used. This will be a narrow range of concentrations. Digest and prepare for analysis a representative mass of sorbent material (unsampled) according to your intended laboratory techniques for sample preparation and analysis. Prepare a calibration curve for the most sensitive analytical region, e.g., 0.0, 0.5, 1.0, 3.0, 5.0, 10 ppb. Using the highest calibration standard, e.g., 10.0 ppb, prepare a series of solutions by adding successively smaller increments of the digestate to a fixed volume of the calibration standard and bringing each solution to a final fixed volume with mercury-free deionized water (diH_2O). To 2.0 ml of the calibration standard add 18.0, 10.0, 4.0, 2.0, 1.0, 0.2, and 0.0 ml of the digestate. Bring the final volume of each solution to a total volume of

20 ml by adding 0.0, 8.0, 14.0, 16.0, 17.0, 17.8, and 18.0 ml of diH_2O. This will yield solutions with dilution ratios of 9:10, 1:2, 1:5, 1:10, 1:20, 1:100, and 0:10, respectively. Determine the Hg concentration of each solution. The dilution ratio of any solution having a concentration that is within ±5 percent of the concentration of the solution containing 0.0 ml of digestate is an acceptable dilution ratio for analyzing field samples. If more than one solution meets this criterion, the one with the lowest dilution ratio is the minimum dilution required for analysis of field samples. If the 9:10 dilution meets this criterion, then no sample dilution is required.

8.2.2 Determination of Minimum Sample Mass. The minimum mass of Hg that must be collected per sample must be determined. This information is necessary in order to effectively perform the Hg^0 and $HgCl_2$ Analytical Bias Test, to estimate target sample volumes/sample times for test runs, and to ensure the quality of the measurements. The determination of minimum sample mass is a direct function of analytical technique, measurement sensitivity, dilutions, etc. This determination is required for all analytical techniques. Based on the analytical approach you employ, you should determine the most sensitive calibration range. Based on a calibration point within that range, you must consider all sample treatments (e.g., dilutions) to determine the mass of sample that needs to be collected to ensure that all sample analyses fall within your calibration curve.

8.2.2.1 Determination of Minimum Calibration Concentration or Mass. Based on your instrument's sensitivity and linearity, determine the calibration concentrations or masses that make up a representative low level calibration range. Verify that you are able to meet the multipoint calibration performance criteria in section 11.0 of this method. Select a calibration concentration or mass that is no less than 2 times the lowest concentration or mass in your calibration curve. The lowest point in your calibration curve must be at least 5, and preferably 10, times the Method Detection Limit (MDL), which is the minimum amount of the analyte that can be detected and reported. The MDL must be determined at least once for the analytical system using an MDL study such as that found in section 15.0 to Method 301 of appendix A to part 63 of this chapter.

NOTE TO SECTION 8.2.2.1: While it might be desirable to base the minimum calibration concentration or mass on the lowest point in the calibration curve, selecting a higher concentration or mass is necessary to ensure that all analyses of the field samples will fall within the calibration curve. Therefore, it is strongly recommended that you select a minimum calibration concentration or mass that is sufficiently above the lowest point of the calibration curve (see examples in sections 8.2.2.2.1 and 8.2.2.2.2 below).

8.2.2.2 Determination of Minimum Sample Mass. Based on your minimum calibration concentration or mass and other sample treatments including, but not limited to, final digestate volume and minimum sample dilution, determine the minimum sample mass. Consideration should also be given to the Hg levels expected to be measured in section 2 of the sorbent traps and to the breakthrough criteria presented in Table 9–1.

8.2.2.2.1 Example Determination of Minimum Sample Mass for Thermal Desorption Analysis. A thermal analysis system has been calibrated at five Hg mass levels: 10 ng, 20 ng, 50 ng, 100 ng, 200 ng, and shown to meet the calibration performance criteria in this method. Based on 2 times the lowest point in the calibration curve, 20 ng is selected as the minimum calibration mass. Because the entire sample is analyzed and there are no dilutions involved, the minimum sample mass is also 20 ng.

NOTE: In this example, if the typical background (blank) Hg levels in section 2 were relatively high (e.g., 3 to 5 ng), a sample mass of 20 ng might not have been sufficient to ensure that the breakthrough criteria in Table 9–1 would be met, thereby necessitating the use of a higher point on the calibration curve (e.g., 50 ng) as the minimum calibration and sample mass.

8.2.2.2.2 Example Determination of Minimum Sample Mass for Acid Leachate/Digestate Analysis. A cold vapor analysis system has been calibrated at four Hg concentration levels: 2 ng/L, 5 ng, 10 ng/L, 20 ng/L, and shown to meet the calibration performance criteria in this method. Based on 2 times the lowest point in the calibration curve, 4 ng/L was selected as the minimum calibration concentration. The final sample volume of a digestate is nominally 50 ml (0.05 L) and the minimum dilution necessary was determined to be 1:100 by the Analytical Matrix Interference Test of section 8.2.1. The following calculation would be used to determine the minimum sample mass.

$$\text{Minimum sample mass} = (4\ \text{ng/L}) \times (0.05\ \text{L}) \times (100) = 20\ \text{ng}$$

NOTE: In this example, if the typical background (blank) Hg levels in section 2 were relatively high (e.g., 3 to 5 ng), a sample mass of 20 ng might not have been sufficient to ensure that the breakthrough criterion in Table 9–1 would be met, thereby necessitating the use of a higher point on the calibration curve (e.g., 10 ng/L) as the minimum calibration concentration.

8.2.3 Hg^0 and $HgCl_2$ Analytical Bias Test. Before analyzing any field samples, the laboratory must demonstrate the ability to recover and accurately quantify Hg^0 and $HgCl_2$

from the chosen sorbent media by performing the following analytical bias test for sorbent traps spiked with Hg^0 and $HgCl_2$. The analytical bias test is performed at a minimum of two distinct sorbent trap Hg loadings that will: (1) Represent the lower and upper bound of sample Hg loadings for application of the analytical technique to the field samples, and (2) be used for data validation.

8.2.3.1 Hg^0 and $HgCl_2$ Analytical Bias Test Procedures. Determine the lower and upper bound mass loadings. The minimum sample mass established in section 8.2.2.2 can be used for the lower bound Hg mass loading although lower Hg loading levels are acceptable. The upper bound Hg loading level should be an estimate of the greatest mass loading that may result as a function of stack concentration and volume sampled. As previously noted, this test defines the bounds that actual field samples must be within in order to be valid.

8.2.3.1.1 Hg^0 Analytical Bias Test. Analyze the front section of three sorbent traps containing Hg^0 at the lower bound mass loading level and the front section of three sorbent traps containing Hg^0 at the upper bound mass loading level. In other words, analyze each mass loading level in triplicate. You may refer to section 6.2 for spiking guidance. Prepare and analyze each spiked trap, using the same techniques that will be used to prepare and analyze the field samples. The average recovery for the three traps at each mass loading level must be between 90 and 110 percent. If multiple types of sorbent media are to be analyzed, a separate analytical bias test is required for each sorbent material.

8.2.3.1.2 $HgCl_2$ Analytical Bias Test. Analyze the front section of three sorbent traps containing $HgCl_2$ at the lower bound mass loading level and the front section of three traps containing $HgCl_2$ at the upper bound mass loading level. $HgCl_2$ can be spiked as a gas, or as a liquid solution containing $HgCl_2$. However the liquid volume spiked must be <100 μL. Prepare and analyze each spiked trap, using the techniques that will be used to prepare and analyze the field samples. The average recovery for three traps at each spike concentration must be between 90 and 110 percent. Again, if multiple types of sorbent media are to be analyzed, a separate analytical bias test is required for each sorbent material.

8.2.4 Determination of Target Sample Volume. The target sample volume is an estimate of the sample volume needed to ensure that valid emissions data are collected (i.e., that sample mass Hg loadings fall within the analytical calibration curve and are within the upper and lower bounds set by the analytical bias tests). The target sample volume and minimum sample mass can also be determined by performing a diagnostic test run prior to initiation of formal testing.

Example: If the minimum sample mass is 50 ng and the concentration of mercury in the stack gas is estimated to be 2 $\mu g/m^3$ (ng/L) then the following calculation would be used to determine the target sample volume:

Target Sample Volume = (50 ng) / (2 ng/L) = 25 L

NOTE TO SECTION 8.2.4: For the purposes of relative accuracy testing of Hg monitoring systems under subpart UUUUU of part 63 of this chapter and Performance Specifications 12A and 12B in appendix B to this part, when the stack gas Hg concentration is expected to be very low (<0.5 μg/dscm), you may estimate the Hg concentration at 0.5 μg/dscm.

8.2.5 Determination of Sample Run Time. Sample run time will be a function of minimum sample mass (see section 8.2.2), target sample volume and nominal equipment sample flow rate. The minimum sample run time for conducting relative accuracy test audits of Hg monitoring systems is 30 minutes and for emissions testing to characterize an emission source is 1 hour. The target sample run time can be calculated using the following example.

Example: If the target sample volume has been determined to be 25 L, then the following formula would be used to determine the sampling time necessary to acquire 25 L of gas when sampling at a rate of 0.4 L/min.

Sampling time (min) = 25 L / 0.4 L/min = 63 minutes

8.2.6 Field Recovery Test. The field recovery test provides a test program-specific verification of the performance of the combined sampling and analytical approach. Three sets of paired samples, one of each pair which is spiked with a known level of Hg, are collected and analyzed and the average recovery of the spiked samples is used to verify performance of the measurement system under field conditions during that test program. The conduct of this test requires an estimate or confirmation of the stack Hg concentrations at the time of testing.

8.2.6.1 Calculation of Pre-sampling Spiking Level. Determine the sorbent trap spiking level for the field recovery test using estimates of the stack Hg concentration, the target sample flow rate, and the planned sample duration. First, determine the Hg mass expected to be collected in section 1 of the sorbent trap. The pre-sampling spike must be within 50 to 150 percent of this expected mass.

Example calculation: For an expected stack Hg concentration of 5 ug/m^3 (ng/L) a target sample rate of 0.40 liters/min, and a sample duration of 1 hour:

(0.40 L/min) * (60 min) * (5ng/L) = 120 ng

A Hg spike of 60 to 180 ng (50–150% of 120 ng) would be appropriate.

8.2.6.2 Procedures. Set up two identical sampling trains. One of the sampling trains

shall be designated the spiked train and the other the unspiked train. Spike Hg^0 onto the front section of the sorbent trap in the spiked train before sampling. The mass of Hg spiked shall be 50 to 150 percent of the mass expected to be collected with the unspiked train. Sample the stack gas with the two trains simultaneously using the same procedures as for the field samples (see section 8.3). The total sample volume must be within ±20 percent of the target sample volume for the field sample test runs. Analyze the sorbent traps from the two trains utilizing the same analytical procedures and instrumentation as for the field samples (see section 11.0). Determine the fraction of spiked Hg recovered (R) using the equations in section 12.7. Repeat this procedure for a total of three runs. Report the individual R values in the test report; the average of the three R values must be between 85 and 115 percent.

NOTE TO SECTION 8.2.6.2: It is acceptable to perform the field recovery test concurrent with actual test runs (e.g., through the use of a quad probe). It is also acceptable to use the field recovery test runs as test runs for emissions testing or for the RATA of a Hg monitoring system under subpart UUUUU of part 63 of this chapter and Performance Specifications 12A and 12B in appendix B to this part, if certain conditions are met. To determine whether a particular field recovery test run may be used as a RATA run, subtract the mass of the Hg^0 spike from the total Hg mass collected in sections 1 and 2 of the spiked trap. The difference represents the mass of Hg in the stack gas sample. Divide this mass by the sample volume to obtain the Hg concentration in the effluent gas stream, as measured with the spiked trap. Compare this concentration to the corresponding Hg concentration measured with the unspiked trap. If the paired trains meet the relative deviation and other applicable data validation criteria in Table 9–1, then the average of the two Hg concentrations may be used as an emissions test run value or as the reference method value for a RATA run.

8.3 Sampling. This section describes the procedures and criteria for collecting the field samples for analysis. As noted in section 8.2.6, the field recovery test samples are also collected using these procedures.

8.3.1 Pre-test leak check. Perform a leak check of the sampling system with the sorbent traps in place. For each of the paired sampling trains, draw a vacuum in the train, and adjust the vacuum to ~15″ Hg; and, using the gas flow meter, determine leak rate. The leak rate for an individual train must not exceed 4 percent of the target sampling rate. Once the leak check passes this criterion, carefully release the vacuum in the sample train, then seal the sorbent trap inlet until the probe is ready for insertion into the stack or duct.

8.3.2 Determination of Flue Gas Characteristics. Determine or measure the flue gas measurement environment characteristics (gas temperature, static pressure, gas velocity, stack moisture, etc.) in order to determine ancillary requirements such as probe heating requirements (if any), initial sampling rate, moisture management, etc.

8.3.3 Sample Collection

8.3.3.1 Remove the plug from the end of each sorbent trap and store each plug in a clean sorbent trap storage container. Remove the stack or duct port cap and insert the probe(s). Secure the probe(s) and ensure that no leakage occurs between the duct and environment.

8.3.3.2 Record initial data including the sorbent trap ID, date, and the run start time.

8.3.3.3 Record the initial gas flow meter reading, stack temperature, meter temperatures (if needed), and any other appropriate information, before beginning sampling. Begin sampling and target a sampling flow rate similar to that for the field recovery test. Then, at regular intervals (≤5 minutes) during the sampling period, record the date and time, the sample flow rate, the gas meter reading, the stack temperature, the flow meter temperatures (if using a dry gas meter), temperatures of heated equipment such as the vacuum lines and the probes (if heated), and the sampling system vacuum readings. Adjust the sampling flow rate as necessary to maintain the initial sample flow rate. Ensure that the total volume sampled for each run is within 20 percent of the total volume sampled for the field recovery test.

8.3.3.4 Data Recording. Obtain and record any essential operating data for the facility during the test period, e.g., the barometric pressure must be obtained for correcting sample volume to standard conditions when using a dry gas meter. At the end of the data collection period, record the final gas flow meter reading and the final values of all other essential parameters.

8.3.3.5 Post-Test Leak Check. When sampling is completed, turn off the sample pump, remove the probe(s) with sorbent traps from the port, and carefully seal the end of each sorbent trap. Perform another leak check of each sampling train with the sorbent trap in place, at the maximum vacuum reached during the sampling period. Record the leakage rates and vacuums. The leakage rate for each train must not exceed 4 percent of the average sampling rate for the data collection period. Following each leak check, carefully release the vacuum in the sample train.

8.3.3.6 Sample Recovery. Recover each sampled sorbent trap by removing it from the probe and sealing both ends. Wipe any deposited material from the outside of the sorbent

trap. Place the sorbent trap into an appropriate sample storage container and store/preserve in appropriate manner (see section 8.3.3.8).

8.3.3.7 Stack Gas Moisture Determination. If the moisture basis of the measurements made with this method (dry) is different from the moisture basis of either: (1) the applicable emission limit; or (2) a Hg CEMS being evaluated for relative accuracy, you must determine the moisture content of the flue gas and correct for moisture using Method 4 in appendix A–3 to this part. If correction of the measured Hg concentrations for moisture is required, at least one Method 4 moisture determination shall be made during each test run.

8.3.3.8 Sample Handling, Preservation, Storage, and Transport. While the performance criteria of this approach provides for verification of appropriate sample handling, it is still important that the user consider, determine and plan for suitable sample preservation, storage, transport, and holding times for these measurements. Therefore, procedures in ASTM D6911–15 ''Standard Guide for Packaging and Shipping Environmental Samples for Laboratory Analysis'' (incorporated by reference-see 40 CFR 60.17) shall be followed for all samples, where appropriate. To avoid Hg contamination of the samples, special attention should be paid to cleanliness during transport, field handling, sampling, recovery, and laboratory analysis, as well as during preparation of the sorbent cartridges. Collection and analysis of blank samples (*e.g.*, reagent, sorbent, field, etc.) is useful in verifying the absence or source of contaminant Hg.

8.3.3.9 Sample Custody. Proper procedures and documentation for sample chain of custody are critical to ensuring data integrity. The chain of custody procedures in ASTM D4840–99 ''Standard Guide for Sampling Chain-of-Custody Procedures'' shall be followed for all samples (including field samples and blanks).

9.0 Quality Assurance and Quality Control

Table 9–1 summarizes the QA/QC performance criteria that are used to validate the Hg emissions data from Method 30B sorbent trap measurement systems.

TABLE 9–1—QUALITY ASSURANCE/QUALITY CONTROL CRITERIA FOR METHOD 30B

QA/QC test or specification	Acceptance criteria	Frequency	Consequences if not met
Gas flow meter calibration (At 3 settings or points).	Calibration factor (Y_i) at each flow rate must be within ±2% of the average value (Y).	Prior to initial use and when post-test check is not within ±5% of Y.	Recalibrate at 3 points until the acceptance criteria are met.
Gas flow meter post-test calibration check (Single-point).	Calibration factor (Y_i) must be within ±5% of the Y value from the most recent 3-point calibration.	After each field test. For mass flow meters, must be done on-site, using stack gas.	Recalibrate gas flow meter at 3 points to determine a new value of Y. For mass flow meters, must be done on-site, using stack gas. Apply the new Y value to the field test data.
Temperature sensor calibration	Absolute temperature measures by sensor within ±1.5% of a reference sensor.	Prior to initial use and before each test thereafter.	Recalibrate; sensor may not be used until specification is met.
Barometer calibration	Absolute pressure measured by instrument within ±10 mm Hg of reading with a mercury barometer or NIST traceable barometer.	Prior to initial use and before each test thereafter.	Recalibrate; instrument may not be used until specification is met.
Pre-test leak check	≤4% of target sampling rate ..	Prior to sampling	Sampling shall not commence until the leak check is passed.
Post-test leak check	≤4% of average sampling rate	After sampling	Sample invalidated.*
Analytical matrix interference test (wet chemical analysis, only).	Establish minimum dilution (if any) needed to eliminate sorbent matrix interferences.	Prior to analyzing any field samples; repeat for each type of sorbent used.	Field sample results not validated.
Analytical bias test	Average recovery between 90% and 110% for Hg^0 and $HgCl_2$ at each of the 2 spike concentration levels.	Prior to analyzing field samples and prior to use of new sorbent media.	Field samples shall not be analyzed until the percent recovery criteria has been met.
Multipoint analyzer calibration	Each analyzer reading within ±10% of true value *and* $r^2 \geq 0.99$.	On the day of analysis, before analyzing any samples.	Recalibrate until successful.
Analysis of independent calibration standard.	Within ±10% of true value	Following daily calibration, prior to analyzing field samples.	Recalibrate and repeat independent standard analysis until successful.

TABLE 9–1—QUALITY ASSURANCE/QUALITY CONTROL CRITERIA FOR METHOD 30B—Continued

QA/QC test or specification	Acceptance criteria	Frequency	Consequences if not met
Analysis of continuing calibration verification standard (CCVS).	Within ±10% of true value	Following daily calibration, after analyzing ≤10 field samples, and at end of each set of analyses.	Recalibrate and repeat independent standard analysis, reanalyze samples until successful, if possible; for destructive techniques, samples invalidated.
Test run total sample volume ..	Within ±20% of total volume sampled during field recovery test.	Each individual sample	Sample invalidated.
Sorbent trap section 2 breakthrough.	For compliance/emissions testing: ≤10% of section 1 Hg mass for Hg concentrations >1 μg/dscm;. ≤20% of section 1 Hg mass for Hg concentrations ≤1 μg/dscm. ≤50% of section 1 Hg mass if the stack Hg concentration is ≤30% of the Hg concentration that is equivalent to the applicable emission limit. For relative accuracy testing: ≤10% of section 1 Hg mass for Hg concentrations >1 μg/dscm;. ≤20% of section 1 Hg mass for Hg concentrations ≤1 μg/dscm and >0.5 μg/dscm;. ≤50% of section 1 Hg mass for Hg concentrations ≤0.5 μg/dscm >0.1 μg/dscm;. no criterion for Hg concentrations ≤0.1 μg/dscm (must meet all other QA/QC specifications).	Every sample	Sample invalidated.*
Paired sorbent trap agreement	≤10% Relative Deviation (RD) mass for Hg concentrations >1 μg/dscm; ≤20% RD or ≤0.2 μg/dscm absolute difference for Hg concentrations ≤1 μg/dscm.	Every run	Run invalidated.*
Sample analysis	Within valid calibration range (within calibration curve).	All Section 1 samples where stack Hg concentration is ≥0.02 μg/dscm except in case where stack Hg concentration is ≤30% of the applicable emission limit.	Reanalyze at more concentrated level if possible, samples invalidated if not within calibrated range.
Sample analysis	Within bounds of Hg^0 and $HgCl_2$ Analytical Bias Test.	All Section 1 samples where stack Hg concentration is ≥0.5 μg/dscm.	Expand bounds of Hg^0 and $HgCl_2$ Analytical Bias Test; if not successful, samples invalidated.
Field recovery test	Average recovery between 85% and 115% for Hg^0.	Once per field test	Field sample runs not validated without successful field recovery test.

*And data from the pair of sorbent traps are also invalidated.

10.0 Calibration and Standardization

10.1 Only NIST-certified and NIST-traceable calibration standards (i.e., calibration gases, solutions, etc.) shall be used for the spiking and analytical procedures in this method.

10.2 Gas Flow Meter Calibration.

10.2.1 Preliminaries. The manufacturer or equipment supplier of the gas flow meter should perform all necessary set-up, testing, programming, etc., and should provide the end user with any necessary instructions, to

ensure that the meter will give an accurate readout of dry gas volume in standard cubic meters for this method.

10.2.2 Initial Calibration. Prior to its initial use, a calibration of the gas flow meter shall be performed. The initial calibration may be done by the manufacturer, by the equipment supplier, or by the end user. If the flow meter is volumetric in nature (*e.g.*, a dry gas meter), the manufacturer or end user may perform a direct volumetric calibration using any gas. For a mass flow meter, the manufacturer, equipment supplier, or end user may calibrate the meter using either: (1) A bottled gas mixture containing 12 ±0.5% CO_2, 7 ±0.5% O_2, and balance N_2 (when this method is applied to coal-fired boilers); (2) a bottled gas mixture containing CO_2, O_2, and N_2 in proportions representative of the expected stack gas composition; or (3) the actual stack gas.

10.2.2.1 Initial Calibration Procedures. Determine an average calibration factor (Y) for the gas flow meter by calibrating it at three sample flow rate settings covering the range of sample flow rates at which the sampling system will be operated. You may either follow the procedures in section 10.3.1 of Method 5 in appendix A–3 to this part or in section 16 of Method 5 in appendix A–3 to this part. If a dry gas meter is being calibrated, use at least five revolutions of the meter at each flow rate.

10.2.2.2 Alternative Initial Calibration Procedures. Alternatively, you may perform the initial calibration of the gas flow meter using a reference gas flow meter (RGFM). The RGFM may be: (1) A wet test meter calibrated according to section 10.3.1 of Method 5 in appendix A–3 to this part; (2) a gas flow metering device calibrated at multiple flow rates using the procedures in section 16 of Method 5 in appendix A–3 to this part; or (3) a NIST-traceable calibration device capable of measuring volumetric flow to an accuracy of 1 percent. To calibrate the gas flow meter using the RGFM, proceed as follows: While the Method 30B sampling system is sampling the actual stack gas or a compressed gas mixture that simulates the stack gas composition (as applicable), connect the RGFM to the discharge of the system. Care should be taken to minimize the dead volume between the gas flow meter being tested and the RGFM. Concurrently measure dry stack gas volume with the RGFM and the flow meter being calibrated for at least 10 minutes at each of three flow rates covering the typical range of operation of the sampling system. For each set of concurrent measurements, record the total sample volume, in units of dry standard cubic meters (dscm), measured by the RGFM and the gas flow meter being tested.

10.2.2.3 Initial Calibration Factor. Calculate an individual calibration factor Y_i at each tested flow rate from section 10.2.2.1 or 10.2.2.2 of this method (as applicable) by taking the ratio of the reference sample volume to the sample volume recorded by the gas flow meter. Average the three Y_i values, to determine Y, the calibration factor for the flow meter. Each of the three individual values of Y_i must be within ±0.02 of Y. Except as otherwise provided in sections 10.2.2.4 and 10.2.2.5 of this method, use the average Y value from the initial 3-point calibration to adjust subsequent gas volume measurements made with the gas flow meter.

10.2.2.4 Pretest On-Site Calibration Check (Optional). For a mass flow meter, if the most recent 3-point calibration of the flow meter was performed using a compressed gas mixture, you may want to conduct the following on-site calibration check prior to testing, to ensure that the flow meter will accurately measure the volume of the stack gas: While sampling stack gas, check the calibration of the flow meter at one intermediate flow rate setting representative of normal operation of the sampling system. If the pretest calibration check shows that the value of Y_i, the calibration factor at the tested flow rate, differs from the current value of Y by more than 5 percent, perform a full 3-point recalibration of the meter using stack gas to determine a new value of Y, and (except as otherwise provided in section 10.2.2.5 of this method) apply the new Y value to the data recorded during the field test.

10.2.2.5 Post-Test Calibration Check. Check the calibration of the gas flow meter following each field test at one intermediate flow rate setting, either at, or in close proximity to, the average sample flow rate during the field test. For dry gas meters, ensure at least three revolutions of the meter during the calibration check. For mass flow meters, this check must be performed before leaving the test site, while sampling stack gas. If a one-point calibration check shows that the value of Y_i at the tested flow rate differs by more than 5 percent from the current value of Y, repeat the full 3-point calibration procedure to determine a new value of Y, and apply the new Y value to the gas volume measurements made with the gas flow meter during the field test that was just completed. For mass flow meters, perform the 3-point recalibration while sampling stack gas.

10.3 Thermocouples and Other Temperature Sensors. Use the procedures and criteria in Section 10.3 of Method 2 in appendix A–1 to this part to calibrate in-stack temperature sensors and thermocouples. Dial thermometers shall be calibrated against mercury-in-glass thermometers or equivalent. Calibrations must be performed prior to initial use and before each field test thereafter. At each calibration point, the absolute temperature measured by the temperature sensor must agree to within ±1.5 percent of the temperature measured with the reference

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sensor, otherwise the sensor may not continue to be used.

10.4 Barometer. Calibrate against a mercury barometer or other NIST-traceable barometer as per Section 10.6 of Method 5 in appendix A–3 to this part. Calibration must be performed prior to initial use and before each test program, and the absolute pressure measured by the barometer must agree to within ±10 mm Hg of the pressure measured by the mercury or other NIST-traceable barometer, otherwise the barometer may not continue to be used.

10.5 Other Sensors and Gauges. Calibrate all other sensors and gauges according to the procedures specified by the instrument manufacturer(s).

10.6 Analytical System Calibration. See section 11.1 of this method.

11.0 Analytical Procedures

The analysis of Hg in the field and quality control samples may be conducted using any instrument or technology capable of quantifying total Hg from the sorbent media and meeting the performance criteria in this method. Because multiple analytical approaches, equipment and techniques are appropriate for the analysis of sorbent traps, it is not possible to provide detailed, technique-specific analytical procedures. As they become available, detailed procedures for a variety of candidate analytical approaches will be posted at *http://www.epa.gov/ttn/emc.*

11.1 Analytical System Calibration. Perform a multipoint calibration of the analyzer at three or more upscale points over the desired quantitative range (multiple calibration ranges shall be calibrated, if necessary). The field samples analyzed must fall within a calibrated, quantitative range and meet the performance criteria specified below. For samples suitable for aliquotting, a series of dilutions may be needed to ensure that the samples fall within a calibrated range. However, for sorbent media samples consumed during analysis (e.g., when using thermal desorption techniques), extra care must be taken to ensure that the analytical system is appropriately calibrated prior to sample analysis. The calibration curve range(s) should be determined such that the levels of Hg mass expected to be collected and measured will fall within the calibrated range. The calibration curve may be generated by directly introducing standard solutions into the analyzer or by spiking the standards onto the sorbent media and then introducing into the analyzer after preparing the sorbent/standard according to the particular analytical technique. For each calibration curve, the value of the square of the linear correlation coefficient, i.e., r^2, must be ≥0.99, and the analyzer response must be within ±10 percent of the reference value at each upscale calibration point. Calibrations must be performed on the day of the analysis, before analyzing any of the samples. Following calibration, an independent standard shall be analyzed. The measured value of the independently prepared standard must be within ±10 percent of the expected value.

11.2 Sample Preparation. Carefully separate the sections of each sorbent trap. Combine for analysis all materials associated with each section; any supporting substrate that the sample gas passes through prior to entering a media section (e.g., glass wool separators, acid gas traps, etc.) must be analyzed with that segment.

11.3 Field Sample Analyses. Analyze the sorbent trap samples following the same procedures that were used for conducting the Hg^0 and $HgCl_2$ analytical bias tests. The individual sections of the sorbent trap and their respective components must be analyzed separately (*i.e.*, section 1 and its components, then section 2 and its components). All sorbent trap section 1 sample analyses must be within the calibrated range of the analytical system as specified in Table 9–1. For wet analyses, the sample can simply be diluted to fall within the calibrated range. However, for the destructive thermal analyses, samples that are not within the calibrated range cannot be re-analyzed. As a result, the sample cannot be validated, and another sample must be collected. It is strongly suggested that the analytical system be calibrated over multiple ranges so that thermally analyzed samples fall within the calibrated range. The total mass of Hg measured in each sorbent trap section 1 must also fall within the lower and upper mass limits established during the initial Hg^0 and $HgCl_2$ analytical bias test. If a sample is analyzed and found to fall outside of these limits, it is acceptable for an additional Hg^0 and $HgCl_2$ analytical bias test to be performed that now includes this level. However, some samples (e.g., the mass collected in trap section 2), may have Hg levels so low that it may not be possible to quantify them in the analytical system's calibrated range. Because a reliable estimate of these low-level Hg measurements is necessary to fully validate the emissions data, the MDL (see section 8.2.2.1 of this method) is used to establish the minimum amount that can be detected and reported. If the measured mass or concentration is below the lowest point in the calibration curve and above the MDL, the analyst must estimate the mass or concentration of the sample based on the analytical instrument response relative to an additional calibration standard at a concentration or mass between the MDL and the lowest point in the calibration curve. This is accomplished by establishing a response factor (e.g., area counts per Hg mass or concentration) and estimating the amount of Hg present in the sample based on the analytical response and this response factor.

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Example: The analysis of a particular sample results in a measured mass above the MDL, but below the lowest point in the calibration curve which is 10 ng. An MDL of 1.3 ng Hg has been established by the MDL study. A calibration standard containing 5 ng of Hg is analyzed and gives an analytical response of 6,170 area counts, which equates to a response factor of 1,234 area counts/ng Hg. The analytical response for the sample is 4,840 area counts. Dividing the analytical response for the sample (4,840 area counts) by the response factor gives 3.9 ng Hg, which is the estimated mass of Hg in the sample.

11.4 Analysis of Continuing Calibration Verification Standard (CCVS). After no more than 10 samples and at the end of each set of analyses, a continuing calibration verification standard must be analyzed. The measured value of the continuing calibration standard must be within ±10 percent of the expected value.

11.5 Blanks. The analysis of blanks is optional. The analysis of blanks is useful to verify the absence of, or an acceptable level of, Hg contamination. Blank levels should be considered when quantifying low Hg levels and their potential contribution to meeting the sorbent trap section 2 breakthrough requirements; however, correcting sorbent trap results for blank levels is prohibited.

12.0 Calculations and Data Analysis

You must follow the procedures for calculation and data analysis listed in this section.

12.1 Nomenclature. The terms used in the equations are defined as follows:

B = Breakthrough (%).
B_{ws} = Moisture content of sample gas as measured by Method 4, percent/100.
C_a = Concentration of Hg for the sample collection period, for sorbent trap ''a'' (µg/dscm).
C_b = Concentration of Hg for the sample collection period, for sorbent trap ''b'' (µg/dscm).
C_d = Hg concentration, dry basis (µg/dscm).
C_{rec} = Concentration of spiked compound measured (µg/m^3).
C_w = Hg concentration, wet basis (µg/m^3).
m_1 = Mass of Hg measured on sorbent trap section 1 (µg).
m_2 = Mass of Hg measured on sorbent trap section 2 (µg).
$m_{recovered}$ = Mass of spiked Hg recovered in Analytical Bias or Field Recovery Test (µg).
m_s = Total mass of Hg measured on spiked trap in Field Recovery Test (µg).
m_{spiked} = Mass of Hg spiked in Analytical Bias or Field Recovery Test (µg).
m_u = Total mass of Hg measured on unspiked trap in Field Recovery Test (µg).
R = Percentage of spiked mass recovered (%).
RD = Relative deviation between the Hg concentrations from traps ''a'' and ''b'' (%).
v_s = Volume of gas sampled, spiked trap in Field Recovery Test (dscm).
V_t = Total volume of dry gas metered during the collection period (dscm); for the purposes of this method, standard temperature and pressure are defined as 20 °C and 760 mm Hg, respectively.
v_u = Volume of gas sampled, unspiked trap in Field Recovery Test (dscm).

12.2 Calculation of Spike Recovery (Analytical Bias Test). Calculate the percent recovery of Hg^0 and $HgCl_2$ using Equation 30B–1.

$$R = \frac{m_{recovered}}{m_{spiked}} \times 100 \qquad \text{Eq. 30B-1}$$

12.3 Calculation of Breakthrough. Use Equation 30B–2 to calculate the percent breakthrough to the second section of the sorbent trap.

$$B = \frac{m_2}{m_1} \times 100 \qquad \text{Eq. 30B-2}$$

12.4 Calculation of Hg Concentration. Calculate the Hg concentration measured with sorbent trap ''a'', using Equation 30B–3.

$$C_a = \frac{(m_1 + m_2)}{V_t} \qquad \text{Eq. 30B-3}$$

For sorbent trap ''b'', replace ''C_a '' with ''C_b '' in Equation 30B–3. Report the average concentration, i.e., ½ (C_a + C_b).

12.5 Moisture Correction. Use Equation 30B–4 if your measurements need to be corrected to a wet basis.

$$C_w = C_d \times (1 - B_{ws}) \qquad \text{Eq. 30B-4}$$

12.6 Calculation of Paired Trap Agreement. Calculate the relative deviation (RD) between the Hg concentrations measured with the paired sorbent traps using Equation 30B–5.

$$RD = \frac{|C_a - C_b|}{C_a + C_b} \times 100 \qquad \text{Eq. 30B-5}$$

12.7 Calculation of Measured Spike Hg Concentration (Field Recovery Test). Calculate the measured spike concentration using Equation 30B–6.

$$C_{rec} = \frac{m_s}{v_s} - \frac{m_u}{v_u} \qquad \text{Eq. 30B-6}$$

Then calculate the spiked Hg recovery, R, using Equation 30B–7.

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$$B_w = \frac{P_w}{P_{bar}} \qquad 3C\text{-}1$$

$$C = \frac{A}{R(1-B_w)} \qquad 3C\text{-}2$$

$$C = \frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}} \quad \frac{A}{R(1-B_w)} \qquad 3C\text{-}3$$

7.3 Measured N_2 Concentration Correction. Calculate the reported N_2 correction for Method 25–C using Eq. 3C–4. If oxygen is determined in place of N_2, substitute the oxygen concentration for the nitrogen concentration in the equation.

$$C_{N_2 Corr} = \frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}}(C_{N_2}) \quad Eq.\ 3C-4$$

8. Bibliography

1. McNair, H.M., and E.J. Bonnelli. Basic Gas Chromatography. Consolidated Printers, Berkeley, CA. 1969.

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–2 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

APPENDIX A–3 TO PART 60—TEST METHODS 4 THROUGH 5I

Method 4—Determination of moisture content in stack gases
Method 5—Determination of particulate matter emissions from stationary sources
Method 5A—Determination of particulate matter emissions from the asphalt processing and asphalt roofing industry
Method 5B—Determination of nonsulfuric acid particulate matter emissions from stationary sources
Method 5C [Reserved]
Method 5D—Determination of particulate matter emissions from positive pressure fabric filters
Method 5E—Determination of particulate matter emissions from the wool fiberglass insulation manufacturing industry
Method 5F—Determination of nonsulfate particulate matter emissions from stationary sources
Method 5G—Determination of particulate matter emissions from wood heaters (dilution tunnel sampling location)
Method 5H—Determination of particulate emissions from wood heaters from a stack location
Method 5I—Determination of Low Level Particulate Matter Emissions From Stationary Sources

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference

method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

METHOD 4—DETERMINATION OF MOISTURE CONTENT IN STACK GASES

NOTE: This method does not include all the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 5, and Method 6.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Water vapor (H_2O) ...	7732–18–5	N/A

1.2 Applicability. This method is applicable for the determination of the moisture content of stack gas.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted at a constant rate from the source; moisture is removed from the sample stream and determined either volumetrically or gravimetrically.

2.2 The method contains two possible procedures: a reference method and an approximation method.

2.2.1 The reference method is used for accurate determinations of moisture content (such as are needed to calculate emission data). The approximation method, provides estimates of percent moisture to aid in setting isokinetic sampling rates prior to a pollutant emission measurement run. The approximation method described herein is only a suggested approach; alternative means for approximating the moisture content (*e.g.*, drying tubes, wet bulb-dry bulb techniques, condensation techniques, stoichiometric calculations, previous experience, etc.) are also acceptable.

2.2.2 The reference method is often conducted simultaneously with a pollutant emission measurement run. When it is, calculation of percent isokinetic, pollutant emission rate, etc., for the run shall be based upon the results of the reference method or its equivalent. These calculations shall not

be based upon the results of the approximation method, unless the approximation method is shown, to the satisfaction of the Administrator, to be capable of yielding results within one percent H_2O of the reference method.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 The moisture content of saturated gas streams or streams that contain water droplets, as measured by the reference method, may be positively biased. Therefore, when these conditions exist or are suspected, a second determination of the moisture content shall be made simultaneously with the reference method, as follows: Assume that the gas stream is saturated. Attach a temperature sensor [capable of measuring to ±1 °C (2 °F)] to the reference method probe. Measure the stack gas temperature at each traverse point (see section 8.1.1.1) during the reference method traverse, and calculate the average stack gas temperature. Next, determine the moisture percentage, either by: (1) Using a psychrometric chart and making appropriate corrections if the stack pressure is different from that of the chart, or (2) using saturation vapor pressure tables. In cases where the psychrometric chart or the saturation vapor pressure tables are not applicable (based on evaluation of the process), alternative methods, subject to the approval of the Administrator, shall be used.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Reference Method. A schematic of the sampling train used in this reference method is shown in Figure 4–1.

6.1.1 Probe. Stainless steel or glass tubing, sufficiently heated to prevent water condensation, and equipped with a filter, either in-stack (*e.g.*, a plug of glass wool inserted into the end of the probe) or heated out-of-stack (*e.g.*, as described in Method 5), to remove particulate matter. When stack conditions permit, other metals or plastic tubing may be used for the probe, subject to the approval of the Administrator.

6.1.2 Condenser. Same as Method 5, section 6.1.1.8.

6.1.3 Cooling System. An ice bath container, crushed ice, and water (or equivalent), to aid in condensing moisture.

6.1.4 Metering System. Same as in Method 5, section 6.1.1.9, except do not use sampling systems designed for flow rates higher than 0.0283 m^3/min (1.0 cfm). Other metering systems, capable of maintaining a constant sampling rate to within 10 percent and determining sample gas volume to within 2 percent, may be used, subject to the approval of the Administrator.

6.1.5 Barometer and Graduated Cylinder and/or Balance. Same as Method 5, sections 6.1.2 and 6.2.5, respectively.

6.2. Approximation Method. A schematic of the sampling train used in this approximation method is shown in Figure 4–2.

6.2.1 Probe. Same as section 6.1.1.

6.2.2 Condenser. Two midget impingers, each with 30-ml capacity, or equivalent.

6.2.3 Cooling System. Ice bath container, crushed ice, and water, to aid in condensing moisture in impingers.

6.2.4 Drying Tube. Tube packed with new or regenerated 6- to 16-mesh indicating-type silica gel (or equivalent desiccant), to dry the sample gas and to protect the meter and pump.

6.2.5 Valve. Needle valve, to regulate the sample gas flow rate.

6.2.6 Pump. Leak-free, diaphragm type, or equivalent, to pull the gas sample through the train.

6.2.7 Volume Meter. Dry gas meter, sufficiently accurate to measure the sample volume to within 2 percent, and calibrated over the range of flow rates and conditions actually encountered during sampling.

6.2.8 Rate Meter. Rotameter, or equivalent, to measure the flow range from 0 to 3 liters/min (0 to 0.11 cfm).

6.2.9 Graduated Cylinder. 25-ml.

6.2.10 Barometer. Same as Method 5, section 6.1.2.

6.2.11 Vacuum Gauge. At least 760-mm (30-in.) Hg gauge, to be used for the sampling leak check.

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Reference Method. The following procedure is intended for a condenser system (such as the impinger system described in section 6.1.1.8 of Method 5) incorporating volumetric analysis to measure the condensed moisture, and silica gel and gravimetric analysis to measure the moisture leaving the condenser.

8.1.1 Preliminary Determinations.

8.1.1.1 Unless otherwise specified by the Administrator, a minimum of eight traverse points shall be used for circular stacks having diameters less than 0.61 m (24 in.), a minimum of nine points shall be used for rectangular stacks having equivalent diameters less than 0.61 m (24 in.), and a minimum of twelve traverse points shall be used in all

other cases. The traverse points shall be located according to Method 1. The use of fewer points is subject to the approval of the Administrator. Select a suitable probe and probe length such that all traverse points can be sampled. Consider sampling from opposite sides of the stack (four total sampling ports) for large stacks, to permit use of shorter probe lengths. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

8.1.1.2 Select a total sampling time such that a minimum total gas volume of 0.60 scm (21 scf) will be collected, at a rate no greater than 0.021 m^3/min (0.75 cfm). When both moisture content and pollutant emission rate are to be determined, the moisture determination shall be simultaneous with, and for the same total length of time as, the pollutant emission rate run, unless otherwise specified in an applicable subpart of the standards.

8.1.2 Preparation of Sampling Train.

8.1.2.1 Place known volumes of water in the first two impingers; alternatively, transfer water into the first two impingers and record the weight of each impinger (plus water) to the nearest 0.5 g. Weigh and record the weight of the silica gel to the nearest 0.5 g, and transfer the silica gel to the fourth impinger; alternatively, the silica gel may first be transferred to the impinger, and the weight of the silica gel plus impinger recorded.

8.1.2.2 Set up the sampling train as shown in Figure 4–1. Turn on the probe heater and (if applicable) the filter heating system to temperatures of approximately 120 °C (248 °F), to prevent water condensation ahead of the condenser. Allow time for the temperatures to stabilize. Place crushed ice and water in the ice bath container.

8.1.3 Leak Check Procedures. It is recommended, but not required, that the volume metering system and sampling train be leak-checked as follows:

8.1.3.1 Metering System. Same as Method 5, section 8.4.1.

8.1.3.2 Sampling Train. Disconnect the probe from the first impinger or (if applicable) from the filter holder. Plug the inlet to the first impinger (or filter holder), and pull a 380 mm (15 in.) Hg vacuum. A lower vacuum may be used, provided that it is not exceeded during the test. A leakage rate in excess of 4 percent of the average sampling rate or 0.00057 m^3/min (0.020 cfm), whichever is less, is unacceptable. Following the leak check, reconnect the probe to the sampling train.

8.1.4 Sampling Train Operation. During the sampling run, maintain a sampling rate within 10 percent of constant rate, or as specified by the Administrator. For each run, record the data required on a data sheet similar to that shown in Figure 4–3. Be sure to record the dry gas meter reading at the beginning and end of each sampling time increment and whenever sampling is halted. Take other appropriate readings at each sample point at least once during each time increment.

NOTE: When Method 4 is used concurrently with an isokinetic method (*e.g.*, Method 5) the sampling rate should be maintained at isokinetic conditions rather than 10 percent of constant rate.

8.1.4.1 To begin sampling, position the probe tip at the first traverse point. Immediately start the pump, and adjust the flow to the desired rate. Traverse the cross section, sampling at each traverse point for an equal length of time. Add more ice and, if necessary, salt to maintain a temperature of less than 20 °C (68 °F) at the silica gel outlet.

8.1.4.2 After collecting the sample, disconnect the probe from the first impinger (or from the filter holder), and conduct a leak check (mandatory) of the sampling train as described in section 8.1.3.2. Record the leak rate. If the leakage rate exceeds the allowable rate, either reject the test results or correct the sample volume as in section 12.3 of Method 5.

8.2 Approximation Method.

NOTE: The approximation method described below is presented only as a suggested method (see section 2.0).

8.2.1 Place exactly 5 ml water in each impinger. Leak check the sampling train as follows: Temporarily insert a vacuum gauge at or near the probe inlet. Then, plug the probe inlet and pull a vacuum of at least 250 mm (10 in.) Hg. Note the time rate of change of the dry gas meter dial; alternatively, a rotameter (0 to 40 ml/min) may be temporarily attached to the dry gas meter outlet to determine the leakage rate. A leak rate not in excess of 2 percent of the average sampling rate is acceptable.

NOTE: Release the probe inlet plug slowly before turning off the pump.

8.2.2 Connect the probe, insert it into the stack, and sample at a constant rate of 2 liters/min (0.071 cfm). Continue sampling until the dry gas meter registers about 30 liters (1.1 ft^3) or until visible liquid droplets are carried over from the first impinger to the second. Record temperature, pressure, and dry gas meter readings as indicated by Figure 4–4.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
Section 8.1.1.4	Leak rate of the sampling system cannot exceed four percent of the average sampling rate or 0.00057 m^3/min (0.020 cfm).	Ensures the accuracy of the volume of gas sampled. (Reference Method).
Section 8.2.1	Leak rate of the sampling system cannot exceed two percent of the average sampling rate.	Ensures the accuracy of the volume of gas sampled. (Approximation Method).

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Reference Method. Calibrate the metering system, temperature sensors, and barometer according to Method 5, sections 10.3, 10.5, and 10.6, respectively.

10.2 Approximation Method. Calibrate the metering system and the barometer according to Method 6, section 10.1 and Method 5, section 10.6, respectively.

10.3 Field Balance Calibration Check. Check the calibration of the balance used to weigh impingers with a weight that is at least 500g or within 50g of a loaded impinger. The weight must be ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference-see 40 CFR 60.17) Class 6 (or better). Daily, before use, the field balance must measure the weight within ± 0.5g of the certified mass. If the daily balance calibration check fails, perform corrective measures and repeat the check before using balance.

11.0 Analytical Procedure

11.1 Reference Method. Measure the volume of the moisture condensed in each of the impingers to the nearest ml. Alternatively, if the impingers were weighed prior to sampling, weigh the impingers after sampling and record the difference in weight to the nearest 0.5 g. Determine the increase in weight of the silica gel (or silica gel plus impinger) to the nearest 0.5 g. Record this information (see example data sheet, Figure 4–5), and calculate the moisture content, as described in section 12.0.

11.2 Approximation Method. Combine the contents of the two impingers, and measure the volume to the nearest 0.5 ml.

12.0 Data Analysis and Calculations

Carry out the following calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Reference Method.

12.1.1 Nomenclature.

B_{ws} = Proportion of water vapor, by volume, in the gas stream.

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P_m = Absolute pressure (for this method, same as barometric pressure) at the dry gas meter, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 (mm Hg)(m^3)/(g-mole)(°K) for metric units and 21.85 (in. Hg)(ft^3)/(lb-mole)(°R) for English units.

T_m = Absolute temperature at meter, °K (°R).

T_{std} = Standard absolute temperature, 293 °K (528 °R).

V_f = Final volume of condenser water, ml.

V_i = Initial volume, if any, of condenser water, ml.

V_m = Dry gas volume measured by dry gas meter, dcm (dcf).

$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

$V_{wc(std)}$ = Volume of water vapor condensed, corrected to standard conditions, scm (scf).

$V_{wsg(std)}$ = Volume of water vapor collected in silica gel, corrected to standard conditions, scm (scf).

W_f = Final weight of silica gel or silica gel plus impinger, g.

W_i = Initial weight of silica gel or silica gel plus impinger, g.

Y = Dry gas meter calibration factor.

ΔV_m = Incremental dry gas volume measured by dry gas meter at each traverse point, dcm (dcf).

ρ_w = Density of water, 0.9982 g/ml (0.002201 lb/ml).

12.1.2 Volume of Water Vapor Condensed.

$$V_{wc(std)} = \frac{(V_f - V_i)\,\rho_w R\,T_{std}}{P_{std} M_W} = K_1 (V_f - V_i) \qquad \text{Eq. 4-1}$$

Where:

K_1 = 0.001333 m^3/ml for metric units,
= 0.04706 ft^3/ml for English units.

12.1.3 Volume of Water Collected in Silica Gel.

$$V_{wsg(std)} = \frac{(W_f - W_i)\,R\,T_{std}}{P_{std} M_W K_2} = K_3 (W_f - W_i) \qquad \text{Eq. 4-2}$$

Where:

K_2 = 1.0 g/g for metric units,
= 453.6 g/lb for English units.
K_3 = 0.001335 m^3/g for metric units,
= 0.04715 ft^3/g for English units.

12.1.4 Sample Gas Volume.

$$V_{m(std)} = \frac{V_m\ Y\ P_m T_{std}}{P_{std} T_m} \qquad \text{Eq. 4-3}$$

$$= K_4 Y \frac{V_m P_m}{T_m}$$

Where:

K_4 = 0.3855 °K/mm Hg for metric units,
= 17.64 °R/in. Hg for English units.

NOTE: If the post-test leak rate (Section 8.1.4.2) exceeds the allowable rate, correct the value of Vm in Equation 4–3, as described in section 12.3 of Method 5.

12.1.5 Moisture Content.

$$B_{ws} = \frac{V_{wc(std)} + V_{wsg(std)}}{V_{wc(std)} + V_{wsg(std)} + V_{m(std)}} \qquad \text{Eq. 4-4}$$

12.1.6 Verification of Constant Sampling Rate. For each time increment, determine the ΔV_m. Calculate the average. If the value for any time increment differs from the average by more than 10 percent, reject the results, and repeat the run.

12.1.7 In saturated or moisture droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one using a value based upon the saturated conditions (see section 4.1), and another based upon the results of the impinger analysis. The lower of these two values of B_{ws} shall be considered correct.

12.2 Approximation Method. The approximation method presented is designed to estimate the moisture in the stack gas; therefore, other data, which are only necessary for accurate moisture determinations, are not collected. The following equations adequately estimate the moisture content for the purpose of determining isokinetic sampling rate settings.

12.2.1 Nomenclature.

B_{wm} = Approximate proportion by volume of water vapor in the gas stream leaving the second impinger, 0.025.
B_{ws} = Water vapor in the gas stream, proportion by volume.
M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
P_m = Absolute pressure (for this method, same as barometric pressure) at the dry gas meter, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
R = Ideal gas constant, 0.06236 [(mm Hg)(m^3)]/[(g-mole)(K)] for metric units and 21.85 [(in. Hg)(ft^3)]/[(lb-mole)(°R)] for English units.
T_m = Absolute temperature at meter, °K (°R).
T_{std} = Standard absolute temperature, 293 °K (528 °R).
V_f = Final volume of impinger contents, ml.
V_i = Initial volume of impinger contents, ml.
V_m = Dry gas volume measured by dry gas meter, dcm (dcf).
$V_{m(std)}$ = Dry gas volume measured by dry gas meter, corrected to standard conditions, dscm (dscf).
$V_{wc(std)}$ = Volume of water vapor condensed, corrected to standard conditions, scm (scf).
Y = Dry gas meter calibration factor.
ρ_w = Density of water, 0.09982 g/ml (0.002201 lb/ml).

12.2.2 Volume of Water Vapor Collected.

$$V_{wc(std)} = \frac{\left(V_f - V_i\right) \rho_w R\ T_{std}}{P_{std} M_W} \qquad \text{Eq. 4-5}$$

$$= K_5\left(V_f - V_i\right)$$

Where:

K_5 = 0.001333 m^3/ml for metric units,
= 0.04706 ft^3/ml for English units.

12.2.3 Sample Gas Volume.

$$V_{m(std)} = \frac{V_m\ Y\ P_m T_{std}}{P_{std} T_m} \qquad \text{Eq. 4-6}$$

$$= K_6 Y \frac{V_m P_m}{T_m}$$

Where:

K_6 = 0.3855 °K/mm Hg for metric units,
= 17.64 °R/in. Hg for English units.

12.2.4 Approximate Moisture Content.

$$B_{ws} = \frac{V_{wc(std)}}{V_{wc(std)} + V_{m(std)}} + B_{wm} \qquad \text{Eq. 4-7}$$

$$= \frac{V_{wc(std)}}{V_{wc(std)} + V_{m(std)}} + (0.025)$$

12.2.5 Using F-factors to determine approximate moisture for estimating moisture content where no wet scrubber is being used, for the purpose of determining isokinetic sampling rate settings with no fuel sample, is acceptable using the average F_c or F_d factor from Method 19 (see Method 19, section 12.3.1). If this option is selected, calculate the approximate moisture as follows:

$B_{ws} = B_H + B_A + B_F$

Where:

B_A = Mole Fraction of moisture in the ambient air.

$$B_A = \frac{\%RH}{100 * P_{Bar}} * 10^{\left[6.6912 - \left(\frac{3144}{T+390.86}\right)\right]}$$

B_F = Mole fraction of moisture from free water in the fuel.

$$B_F = \left[\frac{0.0036W^2 + 0.075W}{100}\right]\left[\frac{20.9 - O_2}{20.9}\right]$$

B_H = Mole fraction of moisture from the hydrogen in the fuel.

$$B_H = \left[1 - \frac{F_d}{F_w}\right]\frac{(20.9 - O_2)}{20.9}$$

B_{ws} = Mole fraction of moisture in the stack gas.
F_d = Volume of dry combustion components per unit of heat content at 0 percent oxygen, dscf/10^6.
Btu (scm/J). See Table 19–2 in Method 19.
F_w = Volume of wet combustion components per unit of heat content at 0 percent oxygen, wet.
scf/10^6 Btu (scm/J). See Table 19–2 in Method 19.
%RH = Percent relative humidity (calibrated hygrometer acceptable), percent.
P_{Bar} = Barometric pressure, in. Hg.
T = Ambient temperature, °F.
W = Percent free water by weight, percent.
O_2 = Percent oxygen in stack gas, dry basis, percent.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 The procedure described in Method 5 for determining moisture content is an acceptable alternative to Method 4.

16.2 The procedures in Method 6A for determining moisture is an acceptable alternative to Method 4.

16.3 Method 320 is an acceptable alternative to Method 4 for determining moisture.

16.4 Using F-factors to determine moisture is an acceptable alternative to Method 4 for a combustion stack not using a scrubber, and where a fuel sample is taken during the test run and analyzed for development of an F_d factor (see Method 19, section 12.3.2), and where stack O_2 content is measured by Method 3A or 3B during each test run. If this option is selected, calculate the moisture content as follows:

$B_{ws} = B_H + B_A + B_F$

Where:

B_A = Mole fraction of moisture in the ambient air.

$$B_A = \frac{\%RH}{100\ P_{Bar}}\left[10^{\left[6.6912-\left(\frac{3144}{T+390.86}\right)\right]}\right]$$

NOTE: Values of B_A should be between 0.00 and 0.06 with common values being about 0.015.

B_F = Mole fraction of moisture from free water in the fuel.

$$B_F = \left[\frac{0.0036\ W^2 + 0.075\ W}{100}\right]\left[\frac{20.9 - O_2}{20.9}\right]$$

NOTE: Free water in fuel is minimal for distillate oil and gases, such as propane and natural gas, so this step may be omitted for those fuels.

B_H = Mole fraction of moisture from the hydrogen in the fuel.

$$B_H = \left(1 - \frac{F_d}{F_w}\right)\frac{(20.9 - O_2)}{20.9}$$

B_{ws} = Mole fraction of moisture in the stack gas.
F_d = Volume of dry combustion components per unit of heat content at 0 percent oxygen, dscf/10^6 Btu (scm/J). Develop a test specific F_d value using an integrated fuel sample from each test run and Equation 19–13 in section 12.3.2 of Method 19.
F_w = Volume of wet combustion components per unit of heat content at 0 percent oxygen, wet scf/10^6 Btu (scm/J). Develop a test specific F_w value using an integrated fuel sample from each test run and Equation 19–14 in section 12.3.2 of Method 19.
%RH = Percent relative humidity (calibrated hygrometer acceptable), percent.
P_{Bar} = Barometric pressure, in. Hg.
T = Ambient temperature, °F.
W = Percent free water by weight, percent.
O_2 = Percent oxygen in stack gas, dry basis, percent.

17.0 References

1. Air Pollution Engineering Manual (Second Edition). Danielson, J.A. (ed.). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, NC. Publication No. AP–40. 1973.

2. Devorkin, Howard, et al. Air Pollution Source Testing Manual. Air Pollution Control District, Los Angeles, CA. November 1963.

3. Methods for Determination of Velocity, Volume, Dust and Mist Content of Gases. Western Precipitation Division of Joy Manufacturing Co. Los Angeles, CA. Bulletin WP–50. 1968.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

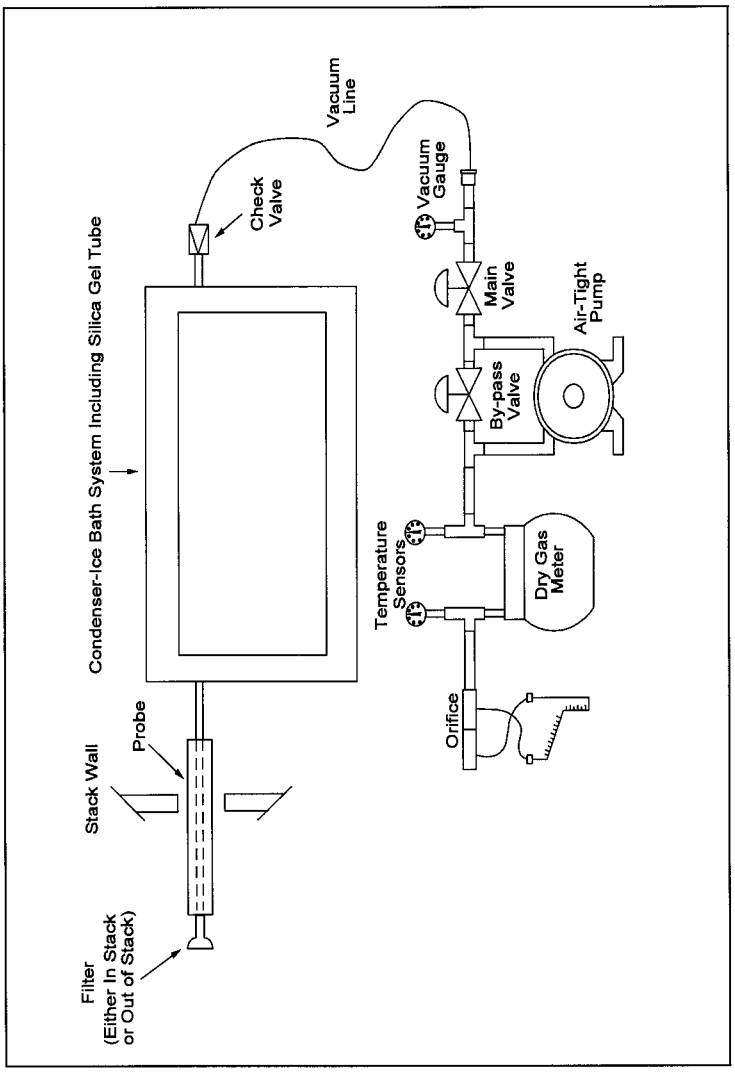

Figure 4-1. Moisture Sampling Train-Reference Method

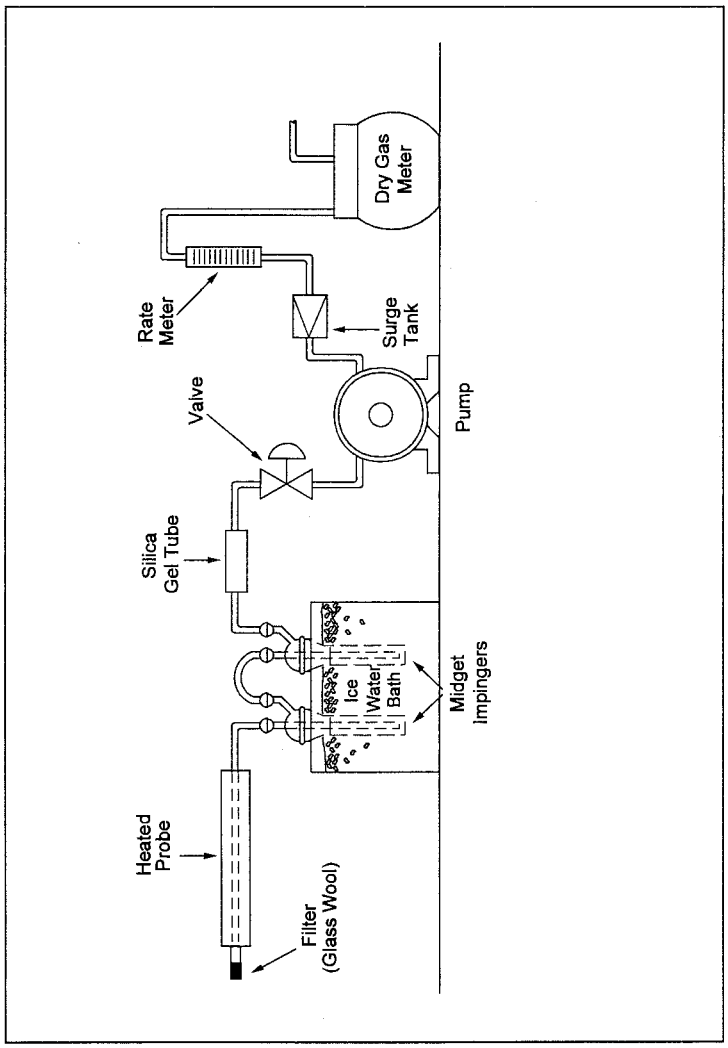

Figure 4-2. Moisture Sampling Train - Approximation Method.

Plant		Run No.	
Location		Ambient temperature	
Operator		Barometric pressure	
Date		Probe Length	

Traverse Pt. No.	Sampling time (Δ), min	Stack temperature °C (°F)	Pressure differential across orifice meter ΔH mm (in.) H_2O	Meter reading gas sample volume m^3 (ft^3)	ΔV_m m^3 (ft^3)	Gas sample temperature at dry gas meter		Temperature of gas leaving condenser or last impinger °C (°F)
						Inlet Tm_{in} °C (°F)	Outlet Tm_{out} °C (°F)	
Average								

Location _____ Barometric pressure _____
Test _____ Comments: _____
Date _____
Operator _____

Figure 4–3. Moisture Determination—Reference Method

Clock time	Gas Volume through meter, (V_m), m^3 (ft^3)	Rate meter setting m^3/min (ft^3/min)	Meter temperature °C (°F)

Figure 4–4. Example Moisture Determination Field Data Sheet—Approximation Method

	Impinger volume, ml	Silica gel weight, g
Final Initial Difference		

Figure 4–5. Analytical Data—Reference Method

METHOD 5—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of PM emissions from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature of 120 ±14 °C (248 ±25 °F) or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. The PM mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after the removal of uncombined water.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. The following items are required for sample collection:

6.1.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 5–1 in section 18.0. Complete construction details are given in APTD–0581 (Reference 2 in section 17.0); commercial models of this train are also available. For

changes from APTD–0581 and for allowable modifications of the train shown in Figure 5–1, see the following subsections.

NOTE: The operating and maintenance procedures for the sampling train are described in APTD–0576 (Reference 3 in section 17.0). Since correct usage is important in obtaining valid results, all users should read APTD–0576 and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein.

6.1.1.1 Probe Nozzle. Stainless steel (316) or glass with a sharp, tapered leading edge. The angle of taper shall be ≤30°, and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. If made of stainless steel, the nozzle shall be constructed from seamless tubing. Other materials of construction may be used, subject to the approval of the Administrator. A range of nozzle sizes suitable for isokinetic sampling should be available. Typical nozzle sizes range from 0.32 to 1.27 cm (⅛ to ½ in) inside diameter (ID) in increments of 0.16 cm (1⁄16 in). Larger nozzles sizes are also available if higher volume sampling trains are used. Each nozzle shall be calibrated, according to the procedures outlined in section 10.1.

6.1.1.2 Probe Liner. Borosilicate or quartz glass tubing with a heating system capable of maintaining a probe gas temperature during sampling of 120 ±14 °C (248 ±25 °F), or such other temperature as specified by an applicable subpart of the standards or as approved by the Administrator for a particular application. Since the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to APTD–0581 and utilizing the calibration curves of APTD–0576 (or calibrated according to the procedure outlined in APTD–0576) will be considered acceptable. Either borosilicate or quartz glass probe liners may be used for stack temperatures up to about 480 °C (900 °F); quartz glass liners shall be used for temperatures between 480 and 900 °C (900 and 1,650 °F). Both types of liners may be used at higher temperatures than specified for short periods of time, subject to the approval of the Administrator. The softening temperature for borosilicate glass is 820 °C (1500 °F), and for quartz glass it is 1500 °C (2700 °F). Whenever practical, every effort should be made to use borosilicate or quartz glass probe liners. Alternatively, metal liners (e.g., 316 stainless steel, Incoloy 825 or other corrosion resistant metals) made of seamless tubing may be used, subject to the approval of the Administrator.

6.1.1.3 Pitot Tube. Type S, as described in section 6.1 of Method 2, or other device approved by the Administrator. The pitot tube shall be attached to the probe (as shown in Figure 5–1) to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see Method 2, Figure 2–7) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in section 10.0 of Method 2.

6.1.1.4 Differential Pressure Gauge. Inclined manometer or equivalent device (two), as described in section 6.2 of Method 2. One manometer shall be used for velocity head (Δp) readings, and the other, for orifice differential pressure readings.

6.1.1.5 Filter Holder. Borosilicate glass, with a glass or Teflon frit filter support and a silicone rubber gasket. Other materials of construction (e.g., stainless steel or Viton) may be used, subject to the approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe (or cyclone, if used).

6.1.1.6 Filter Heating System. Any heating system capable of monitoring and maintaining temperature around the filter shall be used to ensure the sample gas temperature exiting the filter of 120 ±14 °C (248 ±25 °F) during sampling or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. The monitoring and regulation of the temperature around the filter may be done with the filter temperature sensor or another temperature sensor.

6.1.1.7 Filter Temperature Sensor. A temperature sensor capable of measuring temperature to within ±3 °C (5.4 °F) shall be installed so that the sensing tip of the temperature sensor is in direct contact with the sample gas exiting the filter. The sensing tip of the sensor may be encased in glass, Teflon, or metal and must protrude at least ½ in. into the sample gas exiting the filter. The filter temperature sensor must be monitored and recorded during sampling to ensure a sample gas temperature exiting the filter of 120 ±14 °C (248 ±25 °F), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application.

6.1.1.8 Condenser. The following system shall be used to determine the stack gas moisture content: Four impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with a 1.3 cm (½ in.) ID glass tube extending to about 1.3 cm (½ in.) from the bottom of the flask. The second impinger shall be of the Greenburg-Smith design with the standard

tip. Modifications (e.g., using flexible connections between the impingers, using materials other than glass, or using flexible vacuum lines to connect the filter holder to the condenser) may be used, subject to the approval of the Administrator. The first and second impingers shall contain known quantities of water (Section 8.3.1), the third shall be empty, and the fourth shall contain a known weight of silica gel, or equivalent desiccant. A temperature sensor, capable of measuring temperature to within 1 °C (2 °F) shall be placed at the outlet of the fourth impinger for monitoring purposes. Alternatively, any system that cools the sample gas stream and allows measurement of the water condensed and moisture leaving the condenser, each to within 1 ml or 1 g may be used, subject to the approval of the Administrator. An acceptable technique involves the measurement of condensed water either gravimetrically or volumetrically and the determination of the moisture leaving the condenser by: (1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's law of partial pressures; or (2) passing the sample gas stream through a tared silica gel (or equivalent desiccant) trap with exit gases kept below 20 °C (68 °F) and determining the weight gain. If means other than silica gel are used to determine the amount of moisture leaving the condenser, it is recommended that silica gel (or equivalent) still be used between the condenser system and pump to prevent moisture condensation in the pump and metering devices and to avoid the need to make corrections for moisture in the metered volume.

NOTE: If a determination of the PM collected in the impingers is desired in addition to moisture content, the impinger system described above shall be used, without modification. Individual States or control agencies requiring this information shall be contacted as to the sample recovery and analysis of the impinger contents.

6.1.1.9 Metering System. Vacuum gauge, leak-free pump, calibrated temperature sensors, dry gas meter (DGM) capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 5–1. Other metering systems capable of maintaining sampling rates within 10 percent of isokinetic and of determining sample volumes to within 2 percent may be used, subject to the approval of the Administrator. When the metering system is used in conjunction with a pitot tube, the system shall allow periodic checks of isokinetic rates.

6.1.1.10 Sampling trains utilizing metering systems designed for higher flow rates than that described in APTD–0581 or APTD–0576 may be used provided that the specifications of this method are met.

6.1.2 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in.).

NOTE: The barometric pressure reading may be obtained from a nearby National Weather Service station. In this case, the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be made at a rate of minus 2.5 mm Hg (0.1 in.) per 30 m (100 ft) elevation increase or plus 2.5 mm Hg (0.1 in) per 30 m (100 ft) elevation decrease.

6.1.3 Gas Density Determination Equipment. Temperature sensor and pressure gauge, as described in sections 6.3 and 6.4 of Method 2, and gas analyzer, if necessary, as described in Method 3. The temperature sensor shall, preferably, be permanently attached to the pitot tube or sampling probe in a fixed configuration, such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see Method 2, Figure 2–4). As a second alternative, if a difference of not more than 1 percent in the average velocity measurement is to be introduced, the temperature sensor need not be attached to the probe or pitot tube. (This alternative is subject to the approval of the Administrator.)

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Probe-Liner and Probe-Nozzle Brushes. Nylon bristle brushes with stainless steel wire handles. The probe brush shall have extensions (at least as long as the probe) constructed of stainless steel, Nylon, Teflon, or similarly inert material. The brushes shall be properly sized and shaped to brush out the probe liner and nozzle.

6.2.2 Wash Bottles. Two Glass wash bottles are recommended. Alternatively, polyethylene wash bottles may be used. It is recommended that acetone not be stored in polyethylene bottles for longer than a month.

6.2.3 Glass Sample Storage Containers. Chemically resistant, borosilicate glass bottles, for acetone washes, 500 ml or 1000 ml. Screw cap liners shall either be rubber-backed Teflon or shall be constructed so as to be leak-free and resistant to chemical attack by acetone. (Narrow mouth glass bottles have been found to be less prone to leakage.) Alternatively, polyethylene bottles may be used.

6.2.4 Petri Dishes. For filter samples; glass or polyethylene, unless otherwise specified by the Administrator.

6.2.5 Graduated Cylinder and/or Balance. To measure condensed water to within 1 ml or 0.5 g. Graduated cylinders shall have subdivisions no greater than 2 ml.

6.2.6 Plastic Storage Containers. Air-tight containers to store silica gel.

6.2.7 Funnel and Rubber Policeman. To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

6.2.8 Funnel. Glass or polyethylene, to aid in sample recovery.

6.3 Sample Analysis. The following equipment is required for sample analysis:

6.3.1 Glass Weighing Dishes.

6.3.2 Desiccator.

6.3.3 Analytical Balance. To measure to within 0.1 mg.

6.3.4 Balance. To measure to within 0.5 g.

6.3.5 Beakers. 250 ml.

6.3.6 Hygrometer. To measure the relative humidity of the laboratory environment.

6.3.7 Temperature Sensor. To measure the temperature of the laboratory environment.

7.0 Reagents and Standards

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Method D 2986–71, 78, or 95a (incorporated by reference—see §60.17). Test data from the supplier's quality control program are sufficient for this purpose. In sources containing SO_2 or SO_3, the filter material must be of a type that is unreactive to SO_2 or SO_3. Reference 10 in section 17.0 may be used to select the appropriate filter.

7.1.2 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

7.1.3 Water. When analysis of the material caught in the impingers is required, deionized distilled water [to conform to ASTM D1193–77 or 91 Type 3 (incorporated by reference—see §60.17)] with at least <0.001 percent residue shall be used or as specified in the applicable method requiring analysis of the water. Run reagent blanks prior to field use to eliminate a high blank on test samples.

7.1.4 Crushed Ice.

7.2 Sample Recovery. Acetone, reagent grade, ≤0.001 percent residue, in glass bottles, is required. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers; thus, acetone blanks shall be run prior to field use and only acetone with low blank values (≤0.001 percent) shall be used. In no case shall a blank value of greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight.

7.3 Sample Analysis. The following reagents are required for sample analysis:

7.3.1 Acetone. Same as in section 7.2.

7.3.2 Desiccant. Anhydrous calcium sulfate, indicating type. Alternatively, other types of desiccants may be used, subject to the approval of the Administrator.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation. It is suggested that sampling equipment be maintained according to the procedures described in APTD–0576. Alternative mercury-free thermometers may be used if the thermometers are at a minimum equivalent in terms of performance or suitably effective for the specific temperature measurement application.

8.1.1 Place 200 to 300 g of silica gel in each of several air-tight containers. Weigh each container, including silica gel, to the nearest 0.5 g, and record this weight. As an alternative, the silica gel need not be preweighed, but may be weighed directly in its impinger or sampling holder just prior to train assembly.

8.1.2 Check filters visually against light for irregularities, flaws, or pinhole leaks. Label filters of the proper diameter on the back side near the edge using numbering machine ink. As an alternative, label the shipping containers (glass or polyethylene petri dishes), and keep each filter in its identified container at all times except during sampling.

8.1.3 Desiccate the filters at 20 ±5.6 °C (68 ±10 °F) and ambient pressure for at least 24 hours. Weigh each filter (or filter and shipping container) at intervals of at least 6 hours to a constant weight (*i.e.*, ≤0.5 mg change from previous weighing). Record results to the nearest 0.1 mg. During each weighing, the period for which the filter is exposed to the laboratory atmosphere shall be less than 2 minutes. Alternatively (unless otherwise specified by the Administrator), the filters may be oven dried at 105 °C (220 °F) for 2 to 3 hours, desiccated for 2 hours, and weighed. Procedures other than those described, which account for relative humidity effects, may be used, subject to the approval of the Administrator.

8.2 Preliminary Determinations.

8.2.1 Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and the range of velocity heads using Method 2; it is recommended that a leak check of the pitot lines (see Method 2, section 8.1) be performed. Determine the moisture content using Approximation Method 4 or its alternatives for the purpose

of making isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in Method 2, section 8.6; if integrated Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the particulate sample run.

8.2.2 Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see section 8.3 of Method 2).

8.2.3 Select a suitable probe liner and probe length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the required probe length.

8.2.4 Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that (1) the sampling time per point is not less than 2 minutes (or some greater time interval as specified by the Administrator), and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume. The latter is based on an approximate average sampling rate.

8.2.5 The sampling time at each point shall be the same. It is recommended that the number of minutes sampled at each point be an integer or an integer plus one-half minute, in order to avoid timekeeping errors.

8.2.6 In some circumstances (*e.g.*, batch cycles) it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the Administrator's approval must first be obtained.

8.3 Preparation of Sampling Train.

8.3.1 During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin. Place 100 ml of water in each of the first two impingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

8.3.2 Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly is completed.

8.3.3 When glass probe liners are used, install the selected nozzle using a Viton A O-ring when stack temperatures are less than 260 °C (500 °F) or a heat-resistant string gasket when temperatures are higher. See APTD–0576 for details. Other connecting systems using either 316 stainless steel or Teflon ferrules may be used. When metal liners are used, install the nozzle as discussed above or by a leak-free direct mechanical connection. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

8.3.4 Set up the train as shown in Figure 5–1 ensuring that the connections are leaktight. Subject to the approval of the Administrator, a glass cyclone may be used between the probe and filter holder when the total particulate catch is expected to exceed 100 mg or when water droplets are present in the stack gas.

8.3.5 Place crushed ice around the impingers.

8.4 Leak-Check Procedures.

8.4.1 Leak Check of Metering System Shown in Figure 5–1. That portion of the sampling train from the pump to the orifice meter should be leak-checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The following procedure is suggested (see Figure 5–2): Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 to 18 cm (5 to 7 in.) water column by blowing into the rubber tubing. Pinch off the tubing, and observe the manometer for one minute. A loss of pressure on the manometer indicates a leak in the meter box; leaks, if present, must be corrected.

8.4.2 Pretest Leak Check. A pretest leak check of the sampling train is recommended, but not required. If the pretest leak check is conducted, the following procedure should be used.

8.4.2.1 After the sampling train has been assembled, turn on and set the filter and probe heating systems to the desired operating temperatures. Allow time for the temperatures to stabilize. If a Viton A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 380 mm (15 in.) Hg vacuum.

NOTE: A lower vacuum may be used, provided that it is not exceeded during the test.

8.4.2.2 If a heat-resistant string is used, do not connect the probe to the train during the leak check. Instead, leak-check the train by first plugging the inlet to the filter holder (cyclone, if applicable) and pulling a 380 mm (15 in.) Hg vacuum (see note in section 8.4.2.1). Then connect the probe to the train, and leak-check at approximately 25 mm (1 in.) Hg vacuum; alternatively, the probe may be leak-checked with the rest of the sampling train, in one step, at 380 mm (15 in.) Hg vacuum. Leakage rates in excess of 4 percent of the average sampling rate or 0.00057 m^3/min (0.020 cfm), whichever is less, are unacceptable.

8.4.2.3 The following leak-check instructions for the sampling train described in APTD–0576 and APTD–0581 may be helpful. Start the pump with the bypass valve fully open and the coarse adjust valve completely closed. Partially open the coarse adjust valve, and slowly close the bypass valve until the desired vacuum is reached. Do not reverse the direction of the bypass valve, as this will cause water to back up into the filter holder. If the desired vacuum is exceeded, either leak-check at this higher vacuum, or end the leak check and start over.

8.4.2.4 When the leak check is completed, first slowly remove the plug from the inlet to the probe, filter holder, or cyclone (if applicable), and immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the filter holder and the silica gel from being entrained backward into the third impinger.

8.4.3 Leak Checks During Sample Run. If, during the sampling run, a component (*e.g.*, filter assembly or impinger) change becomes necessary, a leak check shall be conducted immediately before the change is made. The leak check shall be done according to the procedure outlined in section 8.4.2 above, except that it shall be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.020 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered; if, however, a higher leakage rate is obtained, either record the leakage rate and plan to correct the sample volume as shown in section 12.3 of this method, or void the sample run.

NOTE: Immediately after component changes, leak checks are optional. If such leak checks are done, the procedure outlined in section 8.4.2 above should be used.

8.4.4 Post-Test Leak Check. A leak check of the sampling train is mandatory at the conclusion of each sampling run. The leak check shall be performed in accordance with the procedures outlined in section 8.4.2, except that it shall be conducted at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m^3 min (0.020 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, either record the leakage rate and correct the sample volume as shown in section 12.3 of this method, or void the sampling run.

8.5 Sampling Train Operation. During the sampling run, maintain an isokinetic sampling rate (within 10 percent of true isokinetic unless otherwise specified by the Administrator) and a sample gas temperature through the filter of 120 ±14 °C (248 ±25 °F) or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator.

8.5.1 For each run, record the data required on a data sheet such as the one shown in Figure 5–3. Be sure to record the initial DGM reading. Record the DGM readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak check, and when sampling is halted. Take other readings indicated by Figure 5–3 at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

8.5.2 Clean the portholes prior to the test run to minimize the chance of collecting deposited material. To begin sampling, verify that the filter and probe heating systems are up to temperature, remove the nozzle cap, verify that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump, and adjust the flow to isokinetic conditions. Nomographs are available which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pitot tube coefficient (C_p) is 0.85 ±0.02, and the stack gas equivalent density [dry molecular weight (M_d)] is equal to 29 ±4. APTD–0576 details the procedure for using the nomographs. If C_p and M_d are outside the above stated ranges, do not use the nomographs unless appropriate steps (see Reference 7 in section 17.0) are taken to compensate for the deviations.

8.5.3 When the stack is under significant negative pressure (*i.e.*, height of impinger stem), take care to close the coarse adjust valve before inserting the probe into the stack to prevent water from backing into the

filter holder. If necessary, the pump may be turned on with the coarse adjust valve closed.

8.5.4 When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

8.5.5 Traverse the stack cross-section, as required by Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the portholes; this minimizes the chance of extracting deposited material.

8.5.6 During the test run, make periodic adjustments to keep the temperature around the filter holder at the proper level to maintain the sample gas temperature exiting the filter; add more ice and, if necessary, salt to maintain a temperature of less than 20 °C (68 °F) at the condenser/silica gel outlet. Also, periodically check the level and zero of the manometer.

8.5.7 If the pressure drop across the filter becomes too high, making isokinetic sampling difficult to maintain, the filter may be replaced in the midst of the sample run. It is recommended that another complete filter assembly be used rather than attempting to change the filter itself. Before a new filter assembly is installed, conduct a leak check (see section 8.4.3). The total PM weight shall include the summation of the filter assembly catches.

8.5.8 A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator.

NOTE: When two or more trains are used, separate analyses of the front-half and (if applicable) impinger catches from each train shall be performed, unless identical nozzle sizes were used on all trains, in which case, the front-half catches from the individual trains may be combined (as may the impinger catches) and one analysis of front-half catch and one analysis of impinger catch may be performed. Consult with the Administrator for details concerning the calculation of results when two or more trains are used.

8.5.9 At the end of the sample run, close the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final DGM meter reading, and conduct a post-test leak check, as outlined in section 8.4.4. Also, leak-check the pitot lines as described in Method 2, section 8.1. The lines must pass this leak check, in order to validate the velocity head data.

8.6 Calculation of Percent Isokinetic. Calculate percent isokinetic (see Calculations, section 12.11) to determine whether the run was valid or another test run should be made. If there was difficulty in maintaining isokinetic rates because of source conditions, consult with the Administrator for possible variance on the isokinetic rates.

8.7 Sample Recovery.

8.7.1 Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

8.7.2 When the probe can be safely handled, wipe off all external PM near the tip of the probe nozzle, and place a cap over it to prevent losing or gaining PM. Do not cap off the probe tip tightly while the sampling train is cooling down. This would create a vacuum in the filter holder, thereby drawing water from the impingers into the filter holder.

8.7.3 Before moving the sample train to the cleanup site, remove the probe from the sample train and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Cap the filter inlet where the probe was fastened. Remove the umbilical cord from the last impinger, and cap the impinger. If a flexible line is used between the first impinger or condenser and the filter holder, disconnect the line at the filter holder, and let any condensed water or liquid drain into the impingers or condenser. Cap off the filter holder outlet and impinger inlet. Either ground-glass stoppers, plastic caps, or serum caps may be used to close these openings.

8.7.4 Transfer the probe and filter-impinger assembly to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

8.7.5 Save a portion of the acetone used for cleanup as a blank. From each storage container of acetone used for cleanup, save 200 ml and place in a glass sample container labeled ''acetone blank.'' To minimize any particulate contamination, rinse the wash bottle prior to filling from the tested container.

8.7.6 Inspect the train prior to and during disassembly, and note any abnormal conditions. Treat the samples as follows:

8.7.6.1 Container No. 1. Carefully remove the filter from the filter holder, and place it in its identified petri dish container. Use a pair of tweezers and/or clean disposable surgical gloves to handle the filter. If it is necessary to fold the filter, do so such that the PM cake is inside the fold. Using a dry Nylon bristle brush and/or a sharp-edged blade, carefully transfer to the petri dish any PM and/or filter fibers that adhere to the filter holder gasket. Seal the container.

8.7.6.2 Container No. 2. Taking care to see that dust on the outside of the probe or other

exterior surfaces does not get into the sample, quantitatively recover PM or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with acetone and placing the wash in a glass container. Deionized distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator. In these cases, save a water blank, and follow the Administrator's directions on analysis. Perform the acetone rinse as follows:

8.7.6.2.1 Carefully remove the probe nozzle. Clean the inside surface by rinsing with acetone from a wash bottle and brushing with a Nylon bristle brush. Brush until the acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

8.7.6.2.2 Brush and rinse the inside parts of the fitting with acetone in a similar way until no visible particles remain.

8.7.6.2.3 Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Let the acetone drain from the lower end into the sample container. A funnel (glass or polyethylene) may be used to aid in transferring liquid washes to the container. Follow the acetone rinse with a probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action through the probe; hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter that is brushed from the probe. Run the brush through the probe three times or more until no visible PM is carried out with the acetone or until none remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times since metal probes have small crevices in which particulate matter can be entrapped. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe.

8.7.6.2.4 It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

8.7.6.2.5 Clean the inside of the front half of the filter holder by rubbing the surfaces with a Nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone, also (if applicable). After all acetone washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to allow determination of whether leakage occurred during transport. Label the container to clearly identify its contents.

8.7.6.3 Container No. 3. Note the color of the indicating silica gel to determine whether it has been completely spent, and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container, and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, follow the procedure for Container No. 3 in section 11.2.3.

8.7.6.4 Impinger Water. Treat the impingers as follows: Make a notation of any color or film in the liquid catch. Measure the liquid that is in the first three impingers to within 1 ml by using a graduated cylinder or by weighing it to within 0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas. Discard the liquid after measuring and recording the volume or weight, unless analysis of the impinger catch is required (see NOTE, section 6.1.1.8). If a different type of condenser is used, measure the amount of moisture condensed either volumetrically or gravimetrically.

8.8 Sample Transport. Whenever possible, containers should be shipped in such a way that they remain upright at all times.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4, 10.1–10.6	Sampling equipment leak check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.

9.2 Volume Metering System Checks. The following procedures are suggested to check the volume metering system calibration values at the field test site prior to sample collection. These procedures are optional.

9.2.1 Meter Orifice Check. Using the calibration data obtained during the calibration procedure described in section 10.3, determine the ΔH@ for the metering system orifice. The ΔH@ is the orifice pressure differential in units of in. H_2O that correlates to 0.75 cfm of air at 528 °R and 29.92 in. Hg. The ΔH@ is calculated as follows:

$$\Delta H@ = 0.0319\ \Delta H \frac{T_M \theta^2}{P_{bar} Y^2 V_m^2}$$

Where:

ΔH = Average pressure differential across the orifice meter, in. H_2O.
T_m = Absolute average DGM temperature, °R.
P_{bar} = Barometric pressure, in. Hg.
θ = Total sampling time, min.
Y = DGM calibration factor, dimensionless.
V_m = Volume of gas sample as measured by DGM, dcf.
0.0319 = (0.0567 in. Hg/°R) (0.75 cfm)^2

9.2.1.1 Before beginning the field test (a set of three runs usually constitutes a field test), operate the metering system (*i.e.*, pump, volume meter, and orifice) at the ΔH@ pressure differential for 10 minutes. Record the volume collected, the DGM temperature, and the barometric pressure. Calculate a DGM calibration check value, Y_c, as follows:

$$Y_c = \frac{10}{V_m}\left[\frac{0.0319\ T_m}{P_{bar}}\right]^{\frac{1}{2}}$$

where:

Y_c = DGM calibration check value, dimensionless.
10 = Run time, min.

9.2.1.2 Compare the Y_c value with the dry gas meter calibration factor Y to determine that: $0.97Y < Y_c < 1.03Y$. If the Y_c value is not within this range, the volume metering system should be investigated before beginning the test.

9.2.2 Calibrated Critical Orifice. A critical orifice, calibrated against a wet test meter or spirometer and designed to be inserted at the inlet of the sampling meter box, may be used as a check by following the procedure of section 16.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Probe Nozzle. Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the ID of the nozzle to the nearest 0.025 mm (0.001 in.). Make three separate measurements using different diameters each time, and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

10.2 Pitot Tube Assembly. The Type S pitot tube assembly shall be calibrated according to the procedure outlined in section 10.1 of Method 2.

10.3 Metering System.

10.3.1 Calibration Prior to Use. Before its initial use in the field, the metering system shall be calibrated as follows: Connect the metering system inlet to the outlet of a wet test meter that is accurate to within 1 percent. Refer to Figure 5–4. The wet test meter should have a capacity of 30 liters/rev (1 ft^3/rev). A spirometer of 400 liters (14 ft^3) or more capacity, or equivalent, may be used for this calibration, although a wet test meter is usually more practical. The wet test meter should be periodically calibrated with a spirometer or a liquid displacement meter to ensure the accuracy of the wet test meter. Spirometers or wet test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained. Run the metering system pump for about 15 minutes with the orifice manometer indicating a median reading as expected in field use to allow the pump to warm up and to permit the interior surface of the wet test meter to be thoroughly wetted. Then, at each of a minimum of three orifice manometer settings, pass an exact quantity of gas through the wet test meter and note the gas volume indicated by the DGM. Also note the barometric pressure and the temperatures of the wet test meter, the inlet of the DGM, and the outlet of the DGM. Select the highest and lowest orifice settings to bracket the expected field operating range of the orifice. Use a minimum volume of 0.14 m^3 (5 ft^3) at all orifice settings. Record all the data on a form similar to Figure 5–5 and calculate Y, the DGM calibration factor, and ΔH , the orifice calibration factor, at each orifice setting as shown on Figure 5–5. Allowable tolerances for individual Y and ΔH values are given in Figure 5–5. Use the average of the Y values in the calculations in section 12.0.

10.3.1.1 Before calibrating the metering system, it is suggested that a leak check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. For these cases the following leak-check procedure is suggested: make a 10-minute calibration run at 0.00057 m^3/min (0.020 cfm). At the end of the run, take the difference of the measured wet test meter and DGM volumes. Divide the difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 m^3/min (0.020 cfm).

10.3.2 Calibration After Use. After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single, intermediate

orifice setting (based on the previous field test), with the vacuum set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet test meter and the inlet of the metering system. Calculate the average value of the DGM calibration factor. If the value has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as detailed in section 10.3.1.

NOTE: Alternative procedures (*e.g.*, rechecking the orifice meter coefficient) may be used, subject to the approval of the Administrator.

10.3.3 Acceptable Variation in Calibration Check. If the DGM coefficient values obtained before and after a test series differ by more than 5 percent, the test series shall either be voided, or calculations for the test series shall be performed using whichever meter coefficient value (*i.e.*, before or after) gives the lower value of total sample volume.

10.4 Probe Heater Calibration. Use a heat source to generate air heated to selected temperatures that approximate those expected to occur in the sources to be sampled. Pass this air through the probe at a typical sample flow rate while measuring the probe inlet and outlet temperatures at various probe heater settings. For each air temperature generated, construct a graph of probe heating system setting versus probe outlet temperature. The procedure outlined in APTD–0576 can also be used. Probes constructed according to APTD–0581 need not be calibrated if the calibration curves in APTD–0576 are used. Also, probes with outlet temperature monitoring capabilities do not require calibration.

NOTE: The probe heating system shall be calibrated before its initial use in the field.

10.5 Temperature Sensors. Use the procedure in Section 10.3 of Method 2 to calibrate in-stack temperature sensors. Dial thermometers, such as are used for the DGM and condenser outlet, shall be calibrated against mercury-in-glass thermometers. An alternative mercury-free NIST-traceable thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application. As an alternative, the following single-point calibration procedure may be used. After each test run series, check the accuracy (and, hence, the calibration) of each thermocouple system at ambient temperature, or any other temperature, within the range specified by the manufacturer, using a reference thermometer (either ASTM reference thermometer or a thermometer that has been calibrated against an ASTM reference thermometer). The temperatures of the thermocouple and reference thermometers shall agree to within ±2 °F.

10.6 Barometer. Calibrate against a mercury barometer or NIST-traceable barometer prior to the field test. Alternatively, barometric pressure may be obtained from a weather report that has been adjusted for the test point (on the stack) elevation.

10.7 Field Balance Calibration Check. Check the calibration of the balance used to weigh impingers with a weight that is at least 500g or within 50g of a loaded impinger. The weight must be ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 6 (or better). Daily before use, the field balance must measure the weight within ±0.5g of the certified mass. If the daily balance calibration check fails, perform corrective measures and repeat the check before using balance.

10.8 Analytical Balance Calibration. Perform a multipoint calibration (at least five points spanning the operational range) of the analytical balance before the first use, and semiannually thereafter. The calibration of the analytical balance must be conducted using ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 2 (or better) tolerance weights. Audit the balance each day it is used for gravimetric measurements by weighing at least one ASTM E617–13 Class 2 tolerance (or better) calibration weight that corresponds to 50 to 150 percent of the weight of one filter or between 1g and 5g. If the scale cannot reproduce the value of the calibration weight to within 0.5 mg of the certified mass, perform corrective measures, and conduct the multipoint calibration before use.

11.0 Analytical Procedure

11.1 Record the data required on a sheet such as the one shown in Figure 5–6.

11.2 Handle each sample container as follows:

11.2.1 Container No. 1. Leave the contents in the shipping container or transfer the filter and any loose PM from the sample container to a tared glass weighing dish. Desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh to a constant weight, and report the results to the nearest 0.1 mg. For the purposes of this section, the term ''constant weight'' means a difference of no more than 0.5 mg or 1 percent of total weight less tare weight, whichever is greater, between two consecutive weighings, with no less than 6 hours of desiccation time between weighings. Alternatively, the sample may be oven dried at 104 °C (220 °F) for 2 to 3 hours, cooled in the desiccator, and weighed to a constant weight, unless otherwise specified by the Administrator. The sample may be oven dried at 104 °C (220 °F) for 2 to 3 hours. Once the

sample has cooled, weigh the sample, and use this weight as a final weight.

11.2.2 Container No. 2. Note the level of liquid in the container, and confirm on the analysis sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to ±1 ml or gravimetrically to ±0.5 g. Transfer the contents to a tared 250 ml beaker, and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours, and weigh to a constant weight. Report the results to the nearest 0.1 mg.

11.2.3 Container No. 3. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. This step may be conducted in the field.

11.2.4 Acetone Blank Container. Measure the acetone in this container either volumetrically or gravimetrically. Transfer the acetone to a tared 250 ml beaker, and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours, and weigh to a constant weight. Report the results to the nearest 0.1 mg.

NOTE: The contents of Container No. 2 as well as the acetone blank container may be evaporated at temperatures higher than ambient. If evaporation is done at an elevated temperature, the temperature must be below the boiling point of the solvent; also, to prevent ''bumping,'' the evaporation process must be closely supervised, and the contents of the beaker must be swirled occasionally to maintain an even temperature. Use extreme care, as acetone is highly flammable and has a low flash point.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used, provided that they give equivalent results.

12.1 Nomenclature.

A_n = Cross-sectional area of nozzle, m^2 (ft^2).
B_{ws} = Water vapor in the gas stream, proportion by volume.
C_a = Acetone blank residue concentration, mg/mg.
c_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (gr/dscf).
I = Percent of isokinetic sampling.
L_1 = Individual leakage rate observed during the leak-check conducted prior to the first component change, m^3/min (ft^3/min)
L_a = Maximum acceptable leakage rate for either a pretest leak-check or for a leak-check following a component change; equal to 0.00057 m^3/min (0.020 cfm) or 4 percent of the average sampling rate, whichever is less.
L_i = Individual leakage rate observed during the leak-check conducted prior to the ''i^{th}'' component change (i = 1, 2, 3 . . . n), m^3/min (cfm).
L_p = Leakage rate observed during the post-test leak-check, m^3/min (cfm).
m_a = Mass of residue of acetone after evaporation, mg.
m_n = Total amount of particulate matter collected, mg.
M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).
P_s = Absolute stack gas pressure, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
R = Ideal gas constant, 0.06236 ((mm Hg)(m^3))/((K)(g-mole)) {21.85 ((in. Hg) (ft^3))/((°R)(lb-mole))}.
T_m = Absolute average DGM temperature (see Figure 5–3), K (°R).
T_s = Absolute average stack gas temperature (see Figure 5–3), K (°R).
T_{std} = Standard absolute temperature, 293 K (528 °R).
V_a = Volume of acetone blank, ml.
V_{aw} = Volume of acetone used in wash, ml.
V_{1c} = Total volume of liquid collected in impingers and silica gel (see Figure 5–6), ml.
V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).
$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).
$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).
V_s = Stack gas velocity, calculated by Method 2, Equation 2–7, using data obtained from Method 5, m/sec (ft/sec).
W_a = Weight of residue in acetone wash, mg.
Y = Dry gas meter calibration factor.
ΔH = Average pressure differential across the orifice meter (see Figure 5–4), mm H_2O (in. H_2O).
ρ_a = Density of acetone, mg/ml (see label on bottle).
ρ_w = Density of water, 0.9982 g/ml. (0.002201 lb/ml).
θ = Total sampling time, min.
θ_1 = Sampling time interval, from the beginning of a run until the first component change, min.
θ_i = Sampling time interval, between two successive component changes, beginning with the interval between the first and second changes, min.
θ_p = Sampling time interval, from the final (n^{th}) component change until the end of the sampling run, min.
13.6 = Specific gravity of mercury.
60 = Sec/min.

100 = Conversion to percent.

12.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 5–3).

12.3 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (20 °C, 760 mm Hg or 68 °F, 29.92 in. Hg) by using Equation 5–1.

$$V_{m(std)} = V_m Y \frac{T_{std}\left(P_{bar} + \frac{\Delta H}{13.6}\right)}{T_m P_{std}} \qquad \text{Eq. 5-1}$$

$$= K_1 V_m Y \frac{P_{bar} + \left(\frac{\Delta H}{13.6}\right)}{T_m}$$

Where:

K_1 = 0.3858 °K/mm Hg for metric units, = 17.64 °R/in. Hg for English units.

NOTE: Equation 5–1 can be used as written unless the leakage rate observed during any of the mandatory leak checks (*i.e.*, the post-test leak check or leak checks conducted prior to component changes) exceeds L_a. If L_p or L_i exceeds L_a, Equation 5–1 must be modified as follows:

(a) Case I. No component changes made during sampling run. In this case, replace V_m in Equation 5–1 with the expression:

$$\left(V_m - \left(L_p - L_a\right)\theta\right)$$

(b) Case II. One or more component changes made during the sampling run. In this case, replace V_m in Equation 5–1 by the expression:

$$\left[V_m - \left(L_1 - L_a\right)\theta_1 - \sum_{i=2}^{n}\left(L_1 - L_a\right)\theta_i - \left(L_p - L_a\right)\theta_p\right]$$

and substitute only for those leakage rates (L_i or L_p) which exceed L_a.

12.4 Volume of Water Vapor Condensed.

$$V_{w(std)} = V_{1c}\frac{\rho_w R T_{std}}{M_w P_{std}} \qquad \text{Eq. 5-2}$$

$$= K_2 V_{1c}$$

Where:

K_2 = 0.001333 m^3/ml for metric units, = 0.04706 ft^3/ml for English units.

12.5 Moisture Content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad \text{Eq. 5-3}$$

NOTE: In saturated or water droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation 5–3), and a second from the assumption of saturated conditions. The lower of the two values of B_{ws} shall be considered correct. The procedure for determining the moisture content based upon the assumption of saturated conditions is given in section 4.0 of Method 4. For the purposes of this method, the average stack gas temperature from Figure 5–3 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is ±1 °C (2 °F).

12.6 Acetone Blank Concentration.

$$C_a = \frac{m_a}{V_a \rho_a} \qquad \text{Eq. 5-4}$$

12.7 Acetone Wash Blank.

$$W_a = C_a V_{aw} \rho_a \qquad \text{Eq. 5-5}$$

12.8 Total Particulate Weight. Determine the total particulate matter catch from the sum of the weights obtained from Containers 1 and 2 less the acetone blank (see Figure 5–6).

NOTE: In no case shall a blank value of greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight. Refer to section 8.5.8 to assist in calculation of results involving two or more filter assemblies or two or more sampling trains.

12.9 Particulate Concentration.

$$C_s = \frac{K_3 m_n}{V_{m(std)}} \qquad \text{Eq. 5-6}$$

Where:

K_3 = 0.001 g/mg for metric units.
= 0.0154 gr/mg for English units.

12.10 Conversion Factors:

From	To	Multiply by
ft^3	m^3	0.02832
gr	mg	64.80004
gr/ft^3	mg/m^3	2288.4
mg	g	0.001
gr	lb	1.429×10^{-4}

12.11 Isokinetic Variation.

12.11.1 Calculation from Raw Data.

$$I = \frac{100\,T_s\left[K_4 V_{1c} + \frac{(V_m Y)}{T_m}\left(P_{bar} + \frac{\Delta H}{13.6}\right)\right]}{60\,\theta\,v_s\,P_s\,A_n} \qquad \text{Eq. 5-7}$$

Where:

K_4 = 0.003454 ((mm Hg)(m^3))/((ml)(°K)) for metric units,
= 0.002669 ((in. Hg)(ft^3))/((ml)(°R)) for English units.

12.11.2 Calculation from Intermediate Values.

$$I = \frac{T_s V_{m(std)} P_{std} 100}{T_{std} v_s \theta A_n P_s 60\left(1 - B_{ws}\right)} \qquad \text{Eq. 5-8}$$

$$= K_5 \frac{T_s V_{m(std)}}{P_s v_s A_n \theta\left(1 - B_{ws}\right)}$$

Where:

K_5 = 4.320 for metric units,
= 0.09450 for English units.

12.11.3 Acceptable Results. If 90 percent ≤I ≤110 percent, the results are acceptable. If the PM results are low in comparison to the standard, and ''I'' is over 110 percent or less than 90 percent, the Administrator may opt to accept the results. Reference 4 in section 17.0 may be used to make acceptability judgments. If ''I'' is judged to be unacceptable, reject the results, and repeat the sampling run.

12.12 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate, if needed, using data obtained in this method and the equations in sections 12.3 and 12.4 of Method 2.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Dry Gas Meter as a Calibration Standard. A DGM may be used as a calibration standard for volume measurements in place of the wet test meter specified in section 10.3, provided that it is calibrated initially and recalibrated periodically as follows:

16.1.1 Standard Dry Gas Meter Calibration.

16.1.1.1. The DGM to be calibrated and used as a secondary reference meter should be of high quality and have an appropriately sized capacity (*e.g.*, 3 liters/rev (0.1 ft^3/rev)). A spirometer (400 liters (14 ft^3) or more capacity), or equivalent, may be used for this calibration, although a wet test meter is usually more practical. The wet test meter should have a capacity of 30 liters/rev (1 ft^3/rev) and capable of measuring volume to within 1.0 percent. Wet test meters should be checked against a spirometer or a liquid displacement meter to ensure the accuracy of the wet test meter. Spirometers or wet test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained.

16.1.1.2 Set up the components as shown in Figure 5–7. A spirometer, or equivalent, may be used in place of the wet test meter in the system. Run the pump for at least 5 minutes at a flow rate of about 10 liters/min (0.35 cfm) to condition the interior surface of the wet test meter. The pressure drop indicated by the manometer at the inlet side of the DGM should be minimized (no greater than 100 mm

H_2O (4 in. H_2O) at a flow rate of 30 liters/min (1 cfm)). This can be accomplished by using large diameter tubing connections and straight pipe fittings.

16.1.1.3 Collect the data as shown in the example data sheet (see Figure 5–8). Make triplicate runs at each of the flow rates and at no less than five different flow rates. The range of flow rates should be between 10 and 34 liters/min (0.35 and 1.2 cfm) or over the expected operating range.

16.1.1.4 Calculate flow rate, Q, for each run using the wet test meter volume, V_w, and the run time, θ. Calculate the DGM coefficient, Y_{ds}, for each run. These calculations are as follows:

$$Q = K_1 \frac{P_{bar} V_w}{(T_w + T_{std})\theta} \qquad \text{Eq. 5-9}$$

$$Y_{ds} = \frac{V_w (T_{ds} + T_{std}) P_{bar}}{V_{ds} (T_w + T_{std}) \left(P_{bar} + \frac{\Delta p}{13.6} \right)} \qquad \text{Eq. 5-10}$$

Where:

K_1 = 0.3858 °C/mm Hg for metric units = 17.64 °F/in. Hg for English units.
V_W = Wet test meter volume, liter (ft^3).
V_{ds} = Dry gas meter volume, liter (ft^3).
T_{ds} = Average dry gas meter temperature, °C (°F).
T_{adj} = 273 °C for metric units = 460 °F for English units.
T_W = Average wet test meter temperature, °C (°F)
P_{bar} = Barometric pressure, mm Hg (in. Hg).
Δp = Dry gas meter inlet differential pressure, mm H_2O (in. H_2O).
θ = Run time, min.

16.1.1.5 Compare the three Y_{ds} values at each of the flow rates and determine the maximum and minimum values. The difference between the maximum and minimum values at each flow rate should be no greater than 0.030. Extra sets of triplicate runs may be made in order to complete this requirement. In addition, the meter coefficients should be between 0.95 and 1.05. If these specifications cannot be met in three sets of successive triplicate runs, the meter is not suitable as a calibration standard and should not be used as such. If these specifications are met, average the three Y_{ds} values at each flow rate resulting in no less than five average meter coefficients, Y_{ds}.

16.1.1.6 Prepare a curve of meter coefficient, Y_{ds}, versus flow rate, Q, for the DGM. This curve shall be used as a reference when the meter is used to calibrate other DGMs and to determine whether recalibration is required.

16.1.2 Standard Dry Gas Meter Recalibration.

16.1.2.1 Recalibrate the standard DGM against a wet test meter or spirometer annually or after every 200 hours of operation, whichever comes first. This requirement is valid provided the standard DGM is kept in a laboratory and, if transported, cared for as any other laboratory instrument. Abuse to the standard meter may cause a change in the calibration and will require more frequent recalibrations.

16.1.2.2 As an alternative to full recalibration, a two-point calibration check may be made. Follow the same procedure and equipment arrangement as for a full recalibration, but run the meter at only two flow rates [suggested rates are 14 and 30 liters/min (0.5 and 1.0 cfm)]. Calculate the meter coefficients for these two points, and compare the values with the meter calibration curve. If the two coefficients are within 1.5 percent of the calibration curve values at the same flow rates, the meter need not be recalibrated until the next date for a recalibration check.

16.2 Critical Orifices As Calibration Standards. Critical orifices may be used as calibration standards in place of the wet test meter specified in section 16.1, provided that they are selected, calibrated, and used as follows:

16.2.1 Selection of Critical Orifices.

16.2.1.1 The procedure that follows describes the use of hypodermic needles or stainless steel needle tubings which have been found suitable for use as critical orifices. Other materials and critical orifice designs may be used provided the orifices act as true critical orifices (*i.e.,* a critical vacuum can be obtained, as described in section 16.2.2.2.3). Select five critical orifices that are appropriately sized to cover the range of flow rates between 10 and 34 liters/min (0.35 and 1.2 cfm) or the expected operating range. Two of the critical orifices should bracket the expected operating range. A minimum of three critical orifices will be needed to calibrate a Method 5 DGM; the other two critical

orifices can serve as spares and provide better selection for bracketing the range of operating flow rates. The needle sizes and tubing lengths shown in Table 5–1 in section 18.0 give the approximate flow rates.

16.2.1.2 These needles can be adapted to a Method 5 type sampling train as follows: Insert a serum bottle stopper, 13 by 20 mm sleeve type, into a ½-inch Swagelok (or equivalent) quick connect. Insert the needle into the stopper as shown in Figure 5–9.

16.2.2 Critical Orifice Calibration. The procedure described in this section uses the Method 5 meter box configuration with a DGM as described in section 6.1.1.9 to calibrate the critical orifices. Other schemes may be used, subject to the approval of the Administrator.

16.2.2.1 Calibration of Meter Box. The critical orifices must be calibrated in the same configuration as they will be used (*i.e.*, there should be no connections to the inlet of the orifice).

16.2.2.1.1 Before calibrating the meter box, leak check the system as follows: Fully open the coarse adjust valve, and completely close the by-pass valve. Plug the inlet. Then turn on the pump, and determine whether there is any leakage. The leakage rate shall be zero (*i.e.*, no detectable movement of the DGM dial shall be seen for 1 minute).

16.2.2.1.2 Check also for leakages in that portion of the sampling train between the pump and the orifice meter. See section 8.4.1 for the procedure; make any corrections, if necessary. If leakage is detected, check for cracked gaskets, loose fittings, worn O-rings, etc., and make the necessary repairs.

16.2.2.1.3 After determining that the meter box is leakless, calibrate the meter box according to the procedure given in section 10.3. Make sure that the wet test meter meets the requirements stated in section 16.1.1.1. Check the water level in the wet test meter. Record the DGM calibration factor, Y.

16.2.2.2 Calibration of Critical Orifices. Set up the apparatus as shown in Figure 5–10.

16.2.2.2.1 Allow a warm-up time of 15 minutes. This step is important to equilibrate the temperature conditions through the DGM.

16.2.2.2.2 Leak check the system as in section 16.2.2.1.1. The leakage rate shall be zero.

16.2.2.2.3 Before calibrating the critical orifice, determine its suitability and the appropriate operating vacuum as follows: Turn on the pump, fully open the coarse adjust valve, and adjust the by-pass valve to give a vacuum reading corresponding to about half of atmospheric pressure. Observe the meter box orifice manometer reading, ΔH. Slowly increase the vacuum reading until a stable reading is obtained on the meter box orifice manometer. Record the critical vacuum for each orifice. Orifices that do not reach a critical value shall not be used.

16.2.2.2.4 Obtain the barometric pressure using a barometer as described in section 6.1.2. Record the barometric pressure, P_{bar}, in mm Hg (in. Hg).

16.2.2.2.5 Conduct duplicate runs at a vacuum of 25 to 50 mm Hg (1 to 2 in. Hg) above the critical vacuum. The runs shall be at least 5 minutes each. The DGM volume readings shall be in increments of complete revolutions of the DGM. As a guideline, the times should not differ by more than 3.0 seconds (this includes allowance for changes in the DGM temperatures) to achieve ±0.5 percent in K′ (see Eq. 5–11). Record the information listed in Figure 5–11.

16.2.2.2.6 Calculate K′ using Equation 5–11.

$$K' = \frac{K_1 V_m Y \left(P_{bar} + \frac{\Delta H}{13.6} \right) T_{amb}^{1/2}}{P_{bar} T_m \theta} \qquad \text{Eq. 5-11}$$

Where:

K′ = Critical orifice coefficient,
$[m^3)(°K)^{1/2}]/$
$[(mm\ Hg)(min)]\ \{[(ft^3)(°R)^{1/2})]\ [(in.\ Hg)(min)]$.
T_{amb} = Absolute ambient temperature, °K (°R).

Calculate the arithmetic mean of the K′ values. The individual K' values should not differ by more than ±0.5 percent from the mean value.

16.2.3 Using the Critical Orifices as Calibration Standards.

16.2.3.1 Record the barometric pressure.

16.2.3.2 Calibrate the metering system according to the procedure outlined in section 16.2.2. Record the information listed in Figure 5–12.

16.2.3.3 Calculate the standard volumes of air passed through the DGM and the critical orifices, and calculate the DGM calibration factor, Y, using the equations below:

$$V_{m(std)} = \frac{K_1 V_m \left[P_{bar} + \left(\frac{\Delta H}{13.6} \right) \right]}{T_m} \qquad \text{Eq. 5-12}$$

$$V_{cr(std)} = K' \frac{P_{bar}\theta}{\sqrt{T_{amb}}} \qquad \text{Eq. 5-13}$$

$$Y = \frac{V_{cr\ (std)}}{V_{m(std)}} \qquad \text{Eq. 5-14}$$

Where:

$V_{cr(std)}$ = Volume of gas sample passed through the critical orifice, corrected to standard conditions, dscm (dscf).

K_1 = 0.3858 K/mm Hg for metric units
= 17.64 °R/in. Hg for English units.

16.2.3.4 Average the DGM calibration values for each of the flow rates. The calibration factor, Y, at each of the flow rates should not differ by more than ±2 percent from the average.

16.2.3.5 To determine the need for recalibrating the critical orifices, compare the DGM Y factors obtained from two adjacent orifices each time a DGM is calibrated; for example, when checking orifice 13/2.5, use orifices 12/10.2 and 13/5.1. If any critical orifice yields a DGM Y factor differing by more than 2 percent from the others, recalibrate the critical orifice according to section 16.2.2.

16.3 Alternative Post-Test Metering System Calibration. The following procedure may be used as an alternative to the post-test calibration described in Section 10.3.2. This alternative procedure does not detect leakages between the inlet of the metering system and the dry gas meter. Therefore, two steps must be included to make it an equivalent alternative:

(1) The metering system must pass the post-test leak-check from either the inlet of the sampling train or the inlet of the metering system. Therefore, if the train fails the former leak-check, another leak-check from the inlet of the metering system must be conducted;

(2) The metering system must pass the leak-check of that portion of the train from the pump to the orifice meter as described in Section 8.4.1.

16.3.1 After each test run, do the following:

16.3.1.1 Ensure that the metering system has passed the post-test leak-check. If not, conduct a leak-check of the metering system from its inlet.

16.3.1.2 Conduct the leak-check of that portion of the train from the pump to the orifice meter as described in Section 10.3.1.1.

16.3.1.3 Calculate Y_{qa} for each test run using the following equation:

$$Y_{qa} = \frac{\theta}{V_m} \sqrt{\frac{0.0319 T_m}{\Delta H@ \left(P_{bar} + \frac{\Delta H_{avg}}{13.6} \right)} \left(\frac{29}{M_d} \right)} \left(\sqrt{\Delta H} \right)_{avg} \qquad \text{Eq. 5-15}$$

Where:

Y_{qa} = Dry gas meter calibration check value, dimensionless.

0.0319 = (29.92/528) (0.75)^2 (in. Hg/°R) cfm^2.

$\Delta H@$ = Orifice meter calibration coefficient, in. H_2O.

M_d = Dry molecular weight of stack gas, lb/lb-mole.

29 = Dry molecular weight of air, lb/lb-mole.

16.3.2 After each test run series, do the following:

16.3.2.1 Average the three or more Y_{qa}'s obtained from the test run series and compare this average Y_{qa} with the dry gas meter calibration factor Y. The average Y_{qa} must be within 5 percent of Y.

16.3.2.2 If the average Y_{qa} does not meet the 5 percent criterion, recalibrate the meter

over the full range of orifice settings as detailed in Section 10.3.1. Then follow the procedure in Section 10.3.3.

17.0 References.

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13. Shigehara, Roger T., P.G. Royals, and E.W. Steward. ''Alternative Method 5 Post-Test Calibration.'' Entropy Incorporated, Research Triangle Park, NC 27709.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 5–1 FLOR RATES FOR VARIOUS NEEDLE SIZES AND TUBE LENGTHS

Gauge/cm	Flow rate liters/min.	Gauge/cm	Flow rate liters/min.
12/7.6	32.56	14/2.5	19.54
12/10.2	30.02	14/5.1	17.27
13/2.5	25.77	14/7.6	16.14
13/5.1	23.50	15/3.2	14.16
13/7.6	22.37	15/7.6	11.61
13/10.2	20.67	15/10.2	10.48

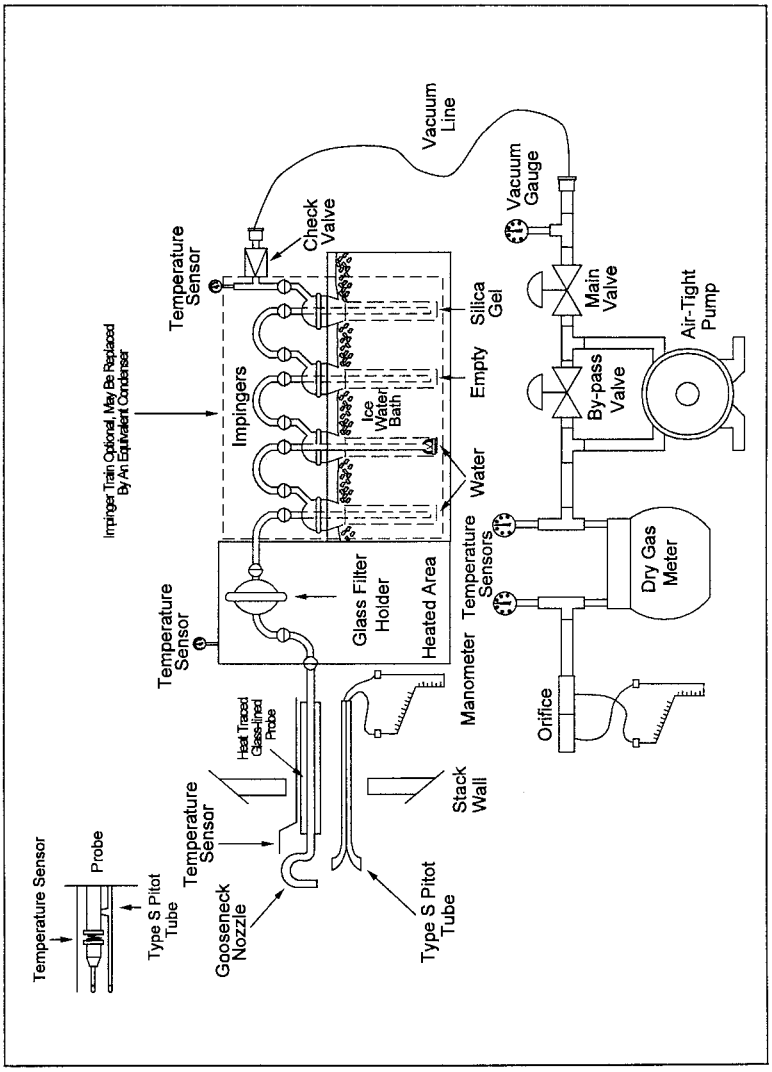


Figure 5-1. Particulate Sampling Train.

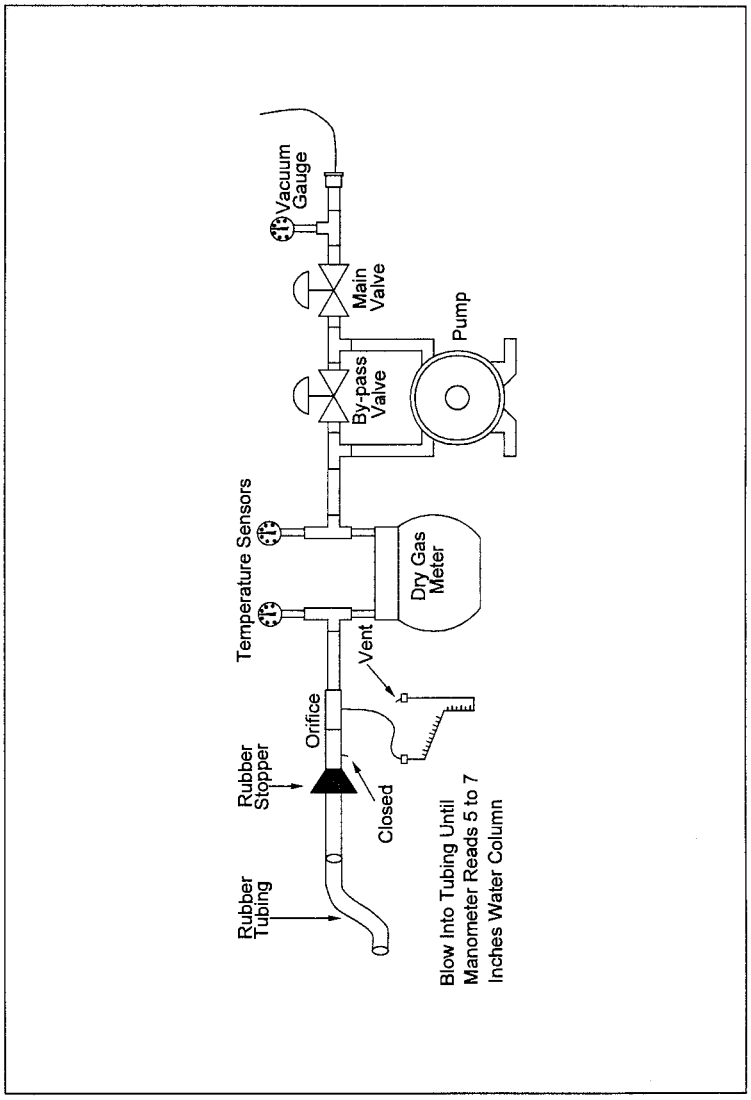


Figure 5-2. Leak Check of Meter Box.

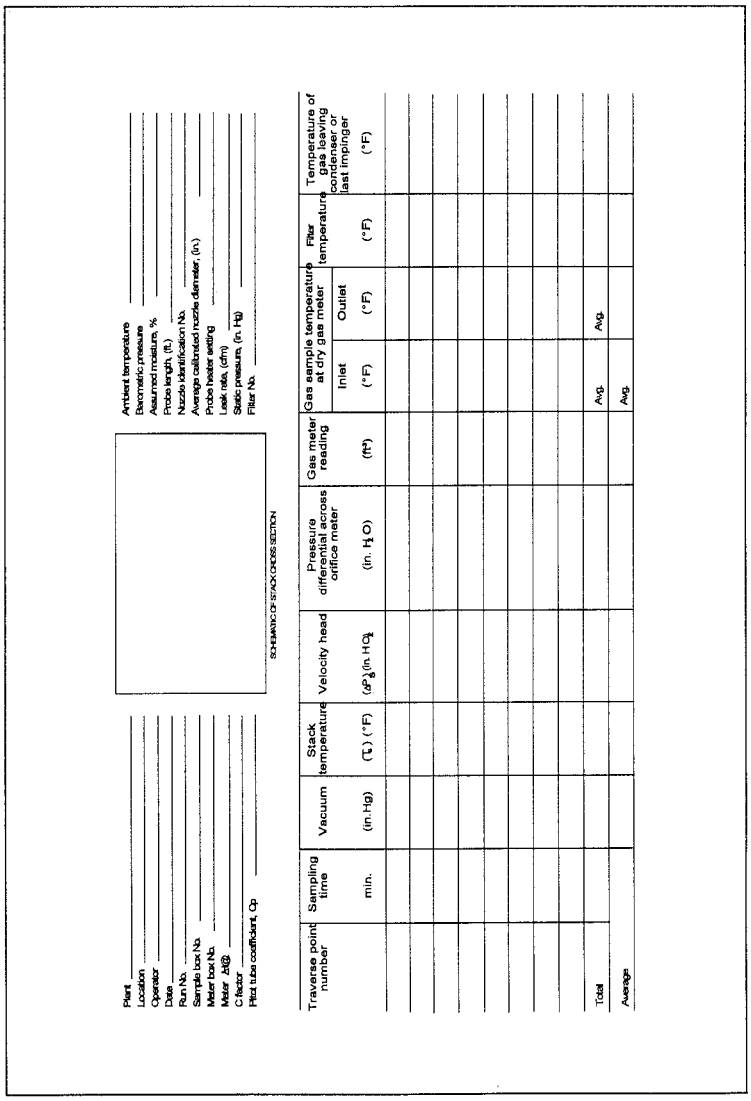


Figure 5-3. Particulate Field Data.

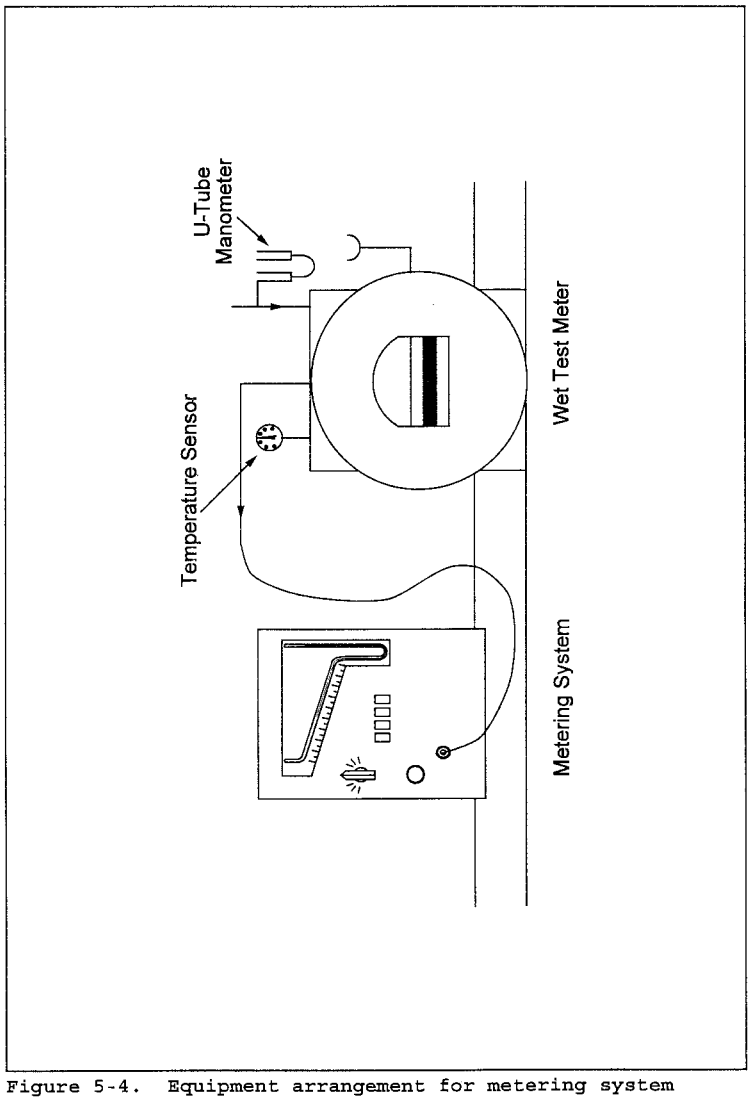
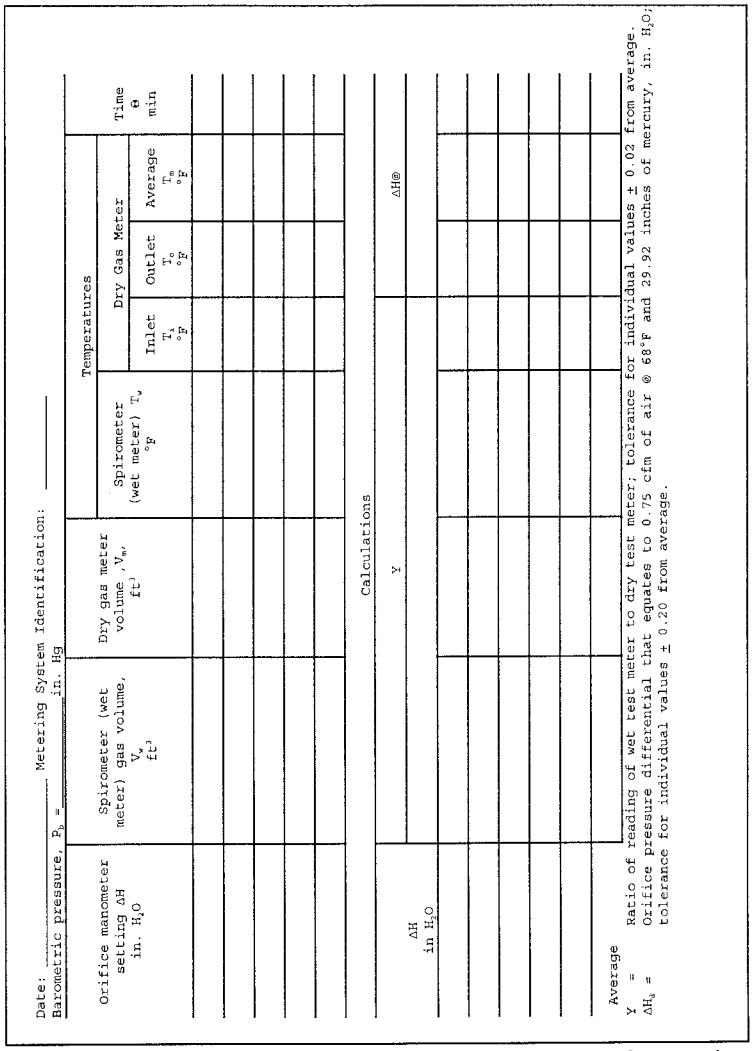


Figure 5-4. Equipment arrangement for metering system calibration.



Date: _____ Metering System Identification: _____
Barometric pressure, P_b = _____ in. Hg

Orifice manometer setting ΔH in. H_2O	Spirometer (wet meter) gas volume, V_w, ft^3	Dry gas meter volume, V_m, ft^3	Temperatures: Spirometer (wet meter) T_w °F	Temperatures: Dry Gas Meter Inlet T_i °F	Temperatures: Dry Gas Meter Outlet T_o °F	Temperatures: Dry Gas Meter Average T_m °F	Time θ min
Average							

Calculations

ΔH in H_2O	Y	ΔH@

Y = Ratio of reading of wet test meter to dry test meter; tolerance for individual values ± 0.02 from average.
$\Delta H_@$ = Orifice pressure differential that equates to 0.75 cfm of air @ 68°F and 29.92 inches of mercury, in. H_2O; tolerance for individual values ± 0.20 from average.

Figure 5-5. Example Data Sheet for Calibration of Metering System (English Units).

Plant _____
Date _____
Run No. _____
Filter No. _____
Amount liquid lost during transport _____

Acetone blank volume, m1 _____
Acetone blank concentration, mg/mg (Equation 5–4) _____
Acetone wash blank, mg (Equation 5–5) ____

Container number	Weight of particulate collected, mg		
	Final weight	Tare weight	Weight gain
1.			
2.			
Total: Less acetone blank. Weight of particulate matter.			

	Volume of liquid water collected	
	Impinger volume, ml	Silica gel weight, g
Final Initial Liquid collected Total volume collected	.....	g* ml

*Convert weight of water to volume by dividing total weight increase by density of water (1 g/ml).

Figure 5–6. Analytical Data Sheet

$$\frac{\text{Increase, g}}{(1\text{g/ml})} = \text{Volume water, ml}$$

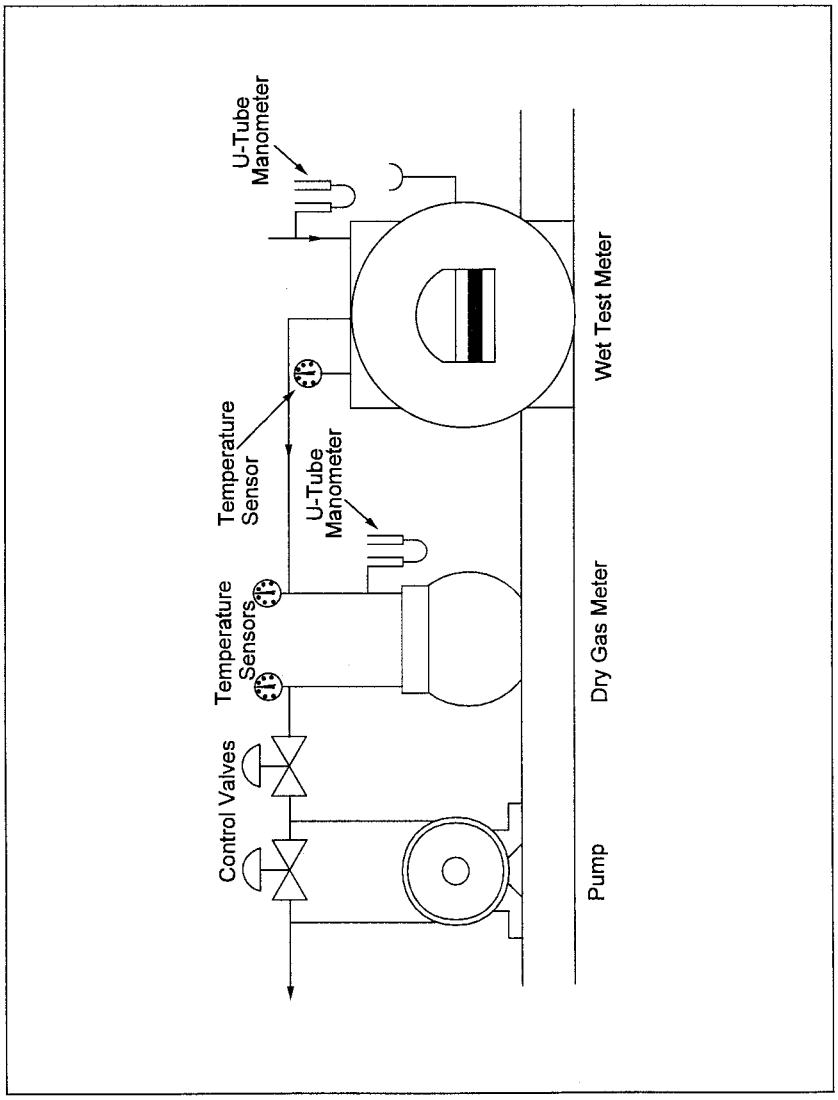


Figure 5-7. Equipment Arrangement for Dry Gas Meter Calibration.

Date: _____

Dry Gas Meter Identification: _____

Barometric Pressure (P): _____ in. Hg

Approximate Flow Rate (Q) cfm	Spirometer (Wet Meter) Gas Volume (V_s) ft³	Dry Gas Meter Volume (V_{dg}) ft³	Temperatures: Spirometer (Wet Meter) (t_g) °F	Temperatures: Dry Gas Meter Inlet (t_i) °F	Temperatures: Dry Gas Meter Outlet (t_o) °F	Temperatures: Dry Gas Meter Average (t_d) °F	Dry Gas Meter Pressure (Δp) in. H_2O	Time (θ) ft³	Flow Rate (Q) cfm	Meter Coefficient (Y_{ds})	Average Meter Coefficient ($\overline{Y}_{ds}$)
0.40											
0.60											
0.80											
1.00											
1.20											

$$Q = K_1 \frac{P_{bar} V_w}{(T_w + T_{std} Q)} \qquad Y_{ds} = \frac{V_w (T_{ds} + T_{std}) P_{bar}}{V_{ds} (T_w + T_{std}) (P_{bar} + \Delta P/13.6)}$$

Figure 5-8. Example Data Sheet for Calibration of a Standard Dry Gas Meter for Method 5 Sampling Equipment (English units).

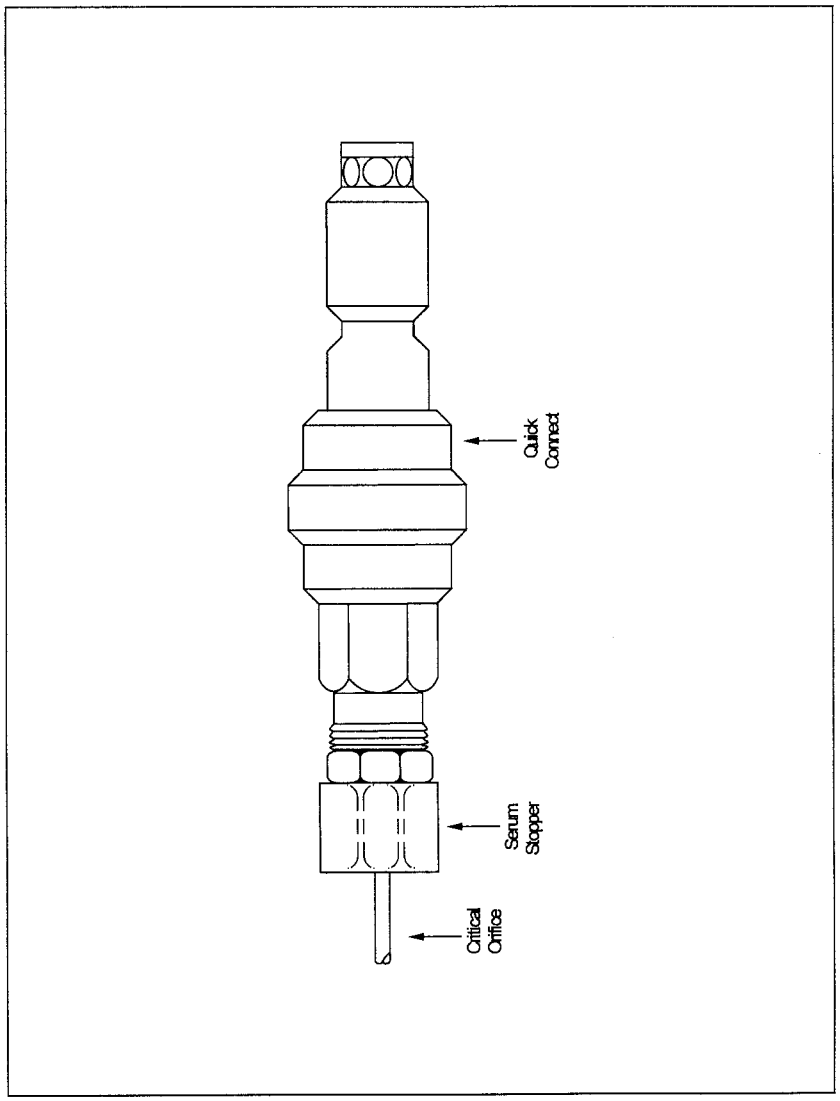


Figure 5-9. Critical Orifice Adaptation to Method 5 Metering System.

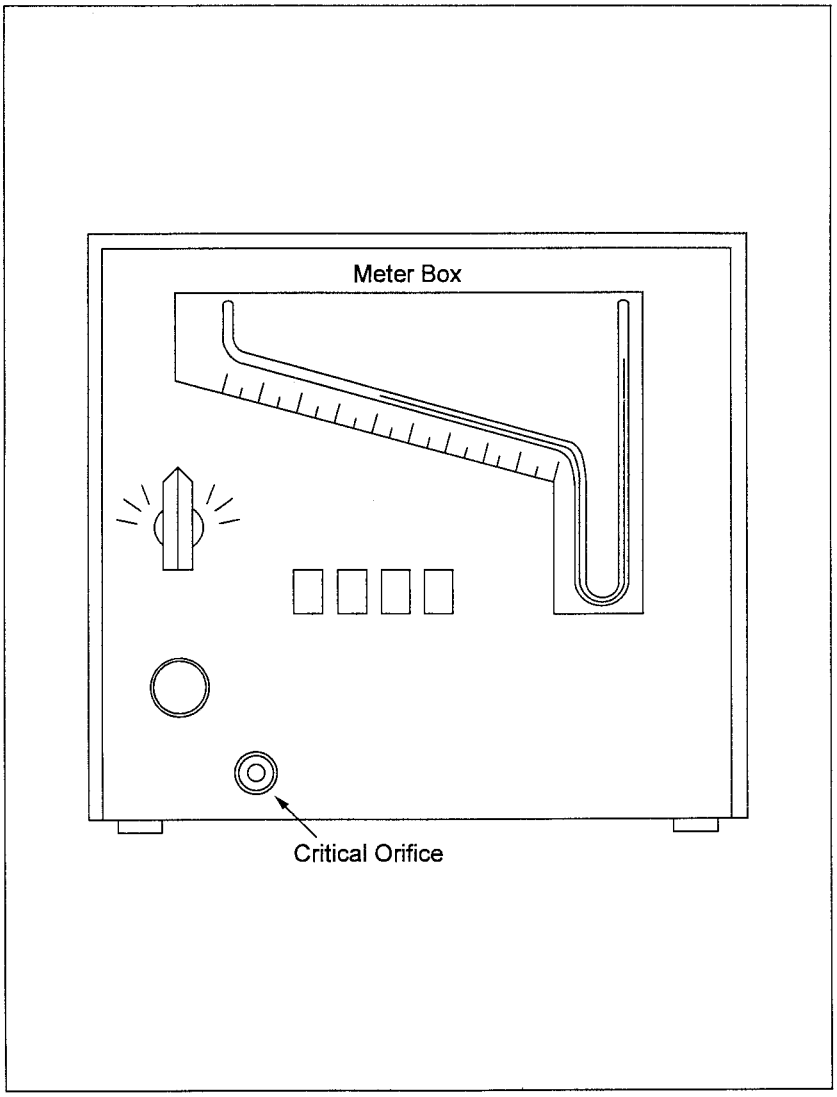


Figure 5-10. Apparatus Setup.

Date _____ DGM cal. factor _____
Train ID _____ Critical orifice ID _____

Dry gas meter		Run No.	
		1	2
Final reading	m^3 (ft^3)		
Initial reading	m^3 (ft^3)		
Difference, V_m	m^3 (ft^3)		
Inlet/Outlet			

Dry gas meter		Run No.	
		1	2
Temperatures:	°C (°F)	/	/
Initial	°C (°F)	/	/
Final	min/sec	/	/
Av. Temeperature, t_m	min		
Time, θ			
Orifice man. rdg., ΔH	mm (in.) H_2		
Bar. pressure, P^{bar}	mm (in.) Hg		
Ambient temperature, t_{amb}	mm (in.) Hg		
Pump vacuum			
K′ factor			
Average			

Figure 5–11. Data sheet of determining K′ factor.

Train ID _____
Critical orifice ID _____
Critical orifice K' factor _____

Date _____

Dry gas meter		Run No.	
		1	2
Final reading	m^3 (ft^3)		
Initial reading	m^3 (ft^3)		
Difference, V_m	m^3 (ft^3)		
Inlet/outlet temperatures	°C (°F)	/	/
Initial	°C (°F)	/	/
Final	°C (°F)		
Avg. Temperature, t_m	min/sec	/	/
Time, θ	min		
Orifice man. rdg., ΔH	min		
Bar. pressure, P_{bar}	mm (in.) H_2O		
Ambient temperature, t_{amb}	mm (in.) Hg		
Pump vacuum	°C (°F)		
$V_{m(std)}$	mm (in.) Hg		
$V_{cr(std)}$	m^3 (ft^3)		
DGM cal. factor, Y	m^3 (ft^3)		

Figure 5–12. Data Sheet for Determining DGM Y Factor

METHOD 5A—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM THE ASPHALT PROCESSING AND ASPHALT ROOFING INDUSTRY

NOTE: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5.

1.0 Scope and Applications

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of PM emissions from asphalt roofing industry process saturators, blowing stills, and other sources as specified in the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature of 42 ±10 °C (108 ±18 °F). The PM mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after the removal of uncombined water.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the

applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 5, section 6.1, with the following exceptions and additions:

6.1.1 Probe Liner. Same as Method 5, section 6.1.1.2, with the note that at high stack gas temperatures greater than 250 °C (480 °F), water-cooled probes may be required to control the probe exit temperature to 42 ±10 °C (108 ±18 °F).

6.1.2 Precollector Cyclone. Borosilicate glass following the construction details shown in Air Pollution Technical Document (APTD)–0581, ''Construction Details of Isokinetic Source-Sampling Equipment'' (Reference 2 in Method 5, section 17.0).

NOTE: The cyclone shall be used when the stack gas moisture is greater than 10 percent, and shall not be used otherwise.

6.1.3 Filter Heating System. Any heating (or cooling) system capable of maintaining a sample gas temperature at the exit end of the filter holder during sampling at 42 ±10 °C (108 ±18 °F).

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Probe-Liner and Probe-Nozzle Brushes, Graduated Cylinder and/or Balance, Plastic Storage Containers, and Funnel and Rubber Policeman. Same as in Method 5, sections 6.2.1, 6.2.5, 6.2.6, and 6.2.7, respectively.

6.2.2 Wash Bottles. Glass.

6.2.3 Sample Storage Containers. Chemically resistant 500-ml or 1,000-ml borosilicate glass bottles, with rubber-backed Teflon screw cap liners or caps that are constructed so as to be leak-free, and resistant to chemical attack by 1,1,1-trichloroethane (TCE). (Narrow-mouth glass bottles have been found to be less prone to leakage.)

6.2.4 Petri Dishes. Glass, unless otherwise specified by the Administrator.

6.2.5 Funnel. Glass.

6.3 Sample Analysis. Same as Method 5, section 6.3, with the following additions:

6.3.1 Beakers. Glass, 250-ml and 500-ml.

6.3.2 Separatory Funnel. 100-ml or greater.

7.0. Reagents and Standards

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Filters, Silica Gel, Water, and Crushed Ice. Same as in Method 5, sections 7.1.1, 7.1.2, 7.1.3, and 7.1.4, respectively.

7.1.2 Stopcock Grease. TCE-insoluble, heat-stable grease (if needed). This is not necessary if screw-on connectors with Teflon sleeves, or similar, are used.

7.2 Sample Recovery. Reagent grade TCE, ≤0.001 percent residue and stored in glass bottles. Run TCE blanks before field use, and use only TCE with low blank values (≤0.001 percent). In no case shall a blank value of greater than 0.001 percent of the weight of TCE used be subtracted from the sample weight.

7.3 Analysis. Two reagents are required for the analysis:

7.3.1 TCE. Same as in section 7.2.

7.3.2 Desiccant. Same as in Method 5, section 7.3.2.

8.0. Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation. Unless otherwise specified, maintain and calibrate all components according to the procedure described in APTD–0576, ''Maintenance, Calibration, and Operation of Isokinetic Source-Sampling Equipment'' (Reference 3 in Method 5, Section 17.0). Alternative mercury-free thermometers may be used if the thermometers are, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

8.1.1 Prepare probe liners and sampling nozzles as needed for use. Thoroughly clean each component with soap and water followed by a minimum of three TCE rinses. Use the probe and nozzle brushes during at least one of the TCE rinses (refer to section 8.7 for rinsing techniques). Cap or seal the open ends of the probe liners and nozzles to prevent contamination during shipping.

8.1.2 Prepare silica gel portions and glass filters as specified in Method 5, section 8.1.

8.2 Preliminary Determinations. Select the sampling site, probe nozzle, and probe length as specified in Method 5, section 8.2. Select a total sampling time greater than or equal to the minimum total sampling time specified in the ''Test Methods and Procedures'' section of the applicable subpart of the regulations. Follow the guidelines outlined in Method 5, section 8.2 for sampling time per point and total sample volume collected.

8.3 Preparation of Sampling Train. Prepare the sampling train as specified in Method 5, section 8.3, with the addition of the precollector cyclone, if used, between the probe and filter holder. The temperature of the precollector cyclone, if used, should be maintained in the same range as that of the filter, *i.e.*, 42 ±10 °C (108 ±18 °F). Use no stopcock grease on ground glass joints unless grease is insoluble in TCE.

8.4 Leak-Check Procedures. Same as Method 5, section 8.4.

8.5 Sampling Train Operation. Operate the sampling train as described in Method 5, section 8.5, except maintain the temperature of the gas exiting the filter holder at 42 ±10 °C (108 ±18 °F).

8.6 Calculation of Percent Isokinetic. Same as Method 5, section 8.6.

8.7 Sample Recovery. Same as Method 5, section 8.7.1 through 8.7.6.1, with the addition of the following:

8.7.1 Container No. 2 (Probe to Filter Holder).

8.7.1.1 Taking care to see that material on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover PM or any condensate from the probe nozzle, probe fitting, probe liner, precollector cyclone and collector flask (if used), and front half of the filter holder by washing these components with TCE and placing the wash in a glass container. Carefully measure the total amount of TCE used in the rinses. Perform the TCE rinses as described in Method 5, section 8.7.6.2, using TCE instead of acetone.

8.7.1.2 Brush and rinse the inside of the cyclone, cyclone collection flask, and the front half of the filter holder. Brush and rinse each surface three times or more, if necessary, to remove visible PM.

8.7.2 Container No. 3 (Silica Gel). Same as in Method 5, section 8.7.6.3.

8.7.3 Impinger Water. Same as Method 5, section 8.7.6.4.

8.8 Blank. Save a portion of the TCE used for cleanup as a blank. Take 200 ml of this TCE directly from the wash bottle being used, and place it in a glass sample container labeled ''TCE Blank.''

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4, 10.0	Sampling equipment leak check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.

9.2 A quality control (QC) check of the volume metering system at the field site is suggested before collecting the sample. Use the procedure outlined in Method 5, section 9.2.

10.0 Calibration and Standardization

Same as Method 5, section 10.0.

11.0 Analytical Procedures

11.1 Analysis. Record the data required on a sheet such as the one shown in Figure 5A–1. Handle each sample container as follows:

11.1.1 Container No. 1 (Filter). Transfer the filter from the sample container to a tared glass weighing dish, and desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Rinse Container No. 1 with a measured amount of TCE, and analyze this rinse with the contents of Container No. 2. Weigh the filter to a constant weight. For the purpose of this analysis, the term ''constant weight'' means a difference of no more than 10 percent of the net filter weight or 2 mg (whichever is greater) between two consecutive weighings made 24 hours apart. Report the ''final weight'' to the nearest 0.1 mg as the average of these two values.

11.1.2 Container No. 2 (Probe to Filter Holder).

11.1.2.1 Before adding the rinse from Container No. 1 to Container No. 2, note the level of liquid in Container No. 2, and confirm on the analysis sheet whether leakage occurred during transport. If noticeable leakage occurred, either void the sample or take steps, subject to the approval of the Administrator, to correct the final results.

11.1.2.2 Add the rinse from Container No. 1 to Container No. 2 and measure the liquid in this container either volumetrically to ±1 ml or gravimetrically to ±0.5 g. Check to see whether there is any appreciable quantity of condensed water present in the TCE rinse (look for a boundary layer or phase separation). If the volume of condensed water appears larger than 5 ml, separate the oil-TCE fraction from the water fraction using a separatory funnel. Measure the volume of the water phase to the nearest ml; adjust the stack gas moisture content, if necessary (see sections 12.3 and 12.4). Next, extract the water phase with several 25-ml portions of TCE until, by visual observation, the TCE does not remove any additional organic material. Transfer the remaining water fraction to a tared beaker and evaporate to dryness at 93 °C (200 °F), desiccate for 24 hours, and weigh to the nearest 0.1 mg.

11.1.2.3 Treat the total TCE fraction (including TCE from the filter container rinse and water phase extractions) as follows: Transfer the TCE and oil to a tared beaker, and evaporate at ambient temperature and pressure. The evaporation of TCE from the solution may take several days. Do not desiccate the sample until the solution reaches an apparent constant volume or until the odor of TCE is not detected. When it appears that the TCE has evaporated, desiccate the sample, and weigh it at 24-hour intervals to obtain a ''constant weight'' (as defined for Container No. 1 above). The ''total weight'' for Container No. 2 is the sum of the evaporated PM weight of the TCE-oil and water phase fractions. Report the results to the nearest 0.1 mg.

11.1.3 Container No. 3 (Silica Gel). This step may be conducted in the field. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance.

11.1.4 ''TCE Blank'' Container. Measure TCE in this container either volumetrically or gravimetrically. Transfer the TCE to a tared 250-ml beaker, and evaporate to dryness at ambient temperature and pressure.

Desiccate for 24 hours, and weigh to a constant weight. Report the results to the nearest 0.1 mg.

NOTE: In order to facilitate the evaporation of TCE liquid samples, these samples may be dried in a controlled temperature oven at temperatures up to 38 °C (100 °F) until the liquid is evaporated.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

12.1 Nomenclature. Same as Method 5, section 12.1, with the following additions:

C_t = TCE blank residue concentration, mg/g.
m_t = Mass of residue of TCE blank after evaporation, mg.
V_{pc} = Volume of water collected in precollector, ml.
V_t = Volume of TCE blank, ml.
V_{tw} = Volume of TCE used in wash, ml.
W_t = Weight of residue in TCE wash, mg.
ρ_t = Density of TCE (see label on bottle), g/ml.

12.2 Dry Gas Meter Temperature, Orifice Pressure Drop, and Dry Gas Volume. Same as Method 5, sections 12.2 and 12.3, except use data obtained in performing this test.

12.3 Volume of Water Vapor.

$$V_{w(std)} = K_2\left(V_{1c} + V_{pc}\right) \qquad \text{Eq. 5A-1}$$

Where:

K_2 = 0.001333 m^3/ml for metric units.
= 0.04706 ft^3/ml for English units.

12.4 Moisture Content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad \text{Eq. 5A-2}$$

NOTE: In saturated or water droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger and precollector analysis (Equations 5A–1 and 5A–2) and a second from the assumption of saturated conditions. The lower of the two values of moisture content shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in section 4.0 of Method 4. For the purpose of this method, the average stack gas temperature from Figure 5–3 of Method 5 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is within 1 °C (2 °F).

12.5 TCE Blank Concentration.

$$C_t = \frac{m_t}{V_t \rho_t} \qquad \text{Eq. 5A-3}$$

NOTE: In no case shall a blank value of greater than 0.001 percent of the weight of TCE used be subtracted from the sample weight.

12.6 TCE Wash Blank.

$$W_t = C_t V_{tw} \rho_t \qquad \text{Eq. 5A-4}$$

12.7 Total PM Weight. Determine the total PM catch from the sum of the weights obtained from Containers 1 and 2, less the TCE blank.

12.8 PM Concentration.

$$c_s = K_3 \frac{m_n}{V_{m(std)}} \qquad \text{Eq. 5A-5}$$

Where:

K_3 = 0.001 g/mg for metric units
= 0.0154 gr/mg for English units

12.9 Isokinetic Variation. Same as in Method 5, section 12.11.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 5, section 17.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

Plant _____
Date _____
Run No. _____
Filter No. _____
Amount liquid lost during transport _____
Acetone blank volume, ml _____
Acetone blank concentration, mg/mg (Equation 5–4) _____
Acetone wash blank, mg (Equation 5–5) _____

Container number	Weight of particulate collected, mg		
	Final weight	Tare weight	Weight gain
1.			
2.			
Total: Less acetone blank.			

Container number	Weight of particulate collected, mg		
	Final weight	Tare weight	Weight gain
Weight of particulate matter.			

	Volume of liquid water collected	
	Impinger volume, ml	Silica gel weight, g
Final		
Initial		
Liquid collected		
Total volume collected		g* ml

*Convert weight of water to volume by dividing total weight increase by density of water (1 g/ml).

$$\frac{\text{Increase, g}}{(1\text{g/ml})} = \text{Volume water, ml}$$

METHOD 5B—DETERMINATION OF NONSULFURIC ACID PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5.

1.0 Scope and Application

1.1 Analyte. Nonsulfuric acid particulate matter. No CAS number assigned.

1.2 Applicability. This method is determining applicable for the determination of nonsulfuric acid particulate matter from stationary sources, only where specified by an applicable subpart of the regulations or where approved by the Administrator for a particular application.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature of 160 ±14 °C (320 ±25 °F). The collected sample is then heated in an oven at 160 °C (320 °F) for 6 hours to volatilize any condensed sulfuric acid that may have been collected, and the nonsulfuric acid particulate mass is determined gravimetrically.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

Same as Method 5, section 6.0, with the following addition and exceptions:

6.1 Sample Collection. The probe liner heating system and filter heating system must be capable of maintaining a sample gas temperature of 160 ±14 °C (320 ±25 °F).

6.2 Sample Preparation. An oven is required for drying the sample.

7.0 Reagents and Standards

Same as Method 5, section 7.0.

8.0 Sample Collection, Preservation, Storage, and Transport.

Same as Method 5, with the exception of the following:

8.1 Initial Filter Tare. Oven dry the filter at 160 ±5 °C (320 ±10 °F) for 2 to 3 hours, cool in a desiccator for 2 hours, and weigh. Desiccate to constant weight to obtain the initial tare weight. Use the applicable specifications and techniques of section 8.1.3 of Method 5 for this determination.

8.2 Probe and Filter Temperatures. Maintain the probe outlet and filter temperatures at 160 ±14 °C (320 ±25 °F).

9.0 Quality Control

Same as Method 5, section 9.0.

10.0 Calibration and Standardization

Same as Method 5, section 10.0.

11.0 Analytical Procedure

Same as Method 5, section 11.0, except replace section

11.2.2 With the following:

11.1 Container No. 2. Note the level of liquid in the container, and confirm on the analysis sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to ±1 ml or gravimetrically to ±0.5 g. Transfer the contents to a tared 250 ml beaker, and evaporate to dryness at ambient temperature and pressure. Then oven dry the probe and filter samples at a temperature of 160 ±5 °C (320 ±10 °F) for 6 hours. Cool in a desiccator for 2 hours, and weigh to constant weight. Report the results to the nearest 0.1 mg.

12.0 Data Analysis and Calculations

Same as in Method 5, section 12.0.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 5, section 17.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 5C [RESERVED]

METHOD 5D—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM POSITIVE PRESSURE FABRIC FILTERS

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, Method 17.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability.

1.2.1 This method is applicable for the determination of PM emissions from positive pressure fabric filters. Emissions are determined in terms of concentration (mg/m^3 or gr/ft^3) and emission rate (kg/hr or lb/hr).

1.2.2 The General Provisions of 40 CFR part 60, §60.8(e), require that the owner or operator of an affected facility shall provide performance testing facilities. Such performance testing facilities include sampling ports, safe sampling platforms, safe access to sampling sites, and utilities for testing. It is intended that affected facilities also provide sampling locations that meet the specification for adequate stack length and minimal flow disturbances as described in Method 1. Provisions for testing are often overlooked factors in designing fabric filters or are extremely costly. The purpose of this procedure is to identify appropriate alternative locations and procedures for sampling the emissions from positive pressure fabric filters. The requirements that the affected facility owner or operator provide adequate access to performance testing facilities remain in effect.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature at or above the exhaust gas temperature up to a nominal 120 °C (248 ±25 °F). The particulate mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after the removal of uncombined water.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

Same as section 6.0 of either Method 5 or Method 17.

7.0 Reagents and Standards

Same as section 7.0 of either Method 5 or Method 17.

8.0 Sample Collection, Preservation, Storage, and Transport

Same section 8.0 of either Method 5 or Method 17, except replace section 8.2.1 of Method 5 with the following:

8.1 Determination of Measurement Site. The configuration of positive pressure fabric filter structures frequently are not amenable

to emission testing according to the requirements of Method 1. Following are several alternatives for determining measurement sites for positive pressure fabric filters.

8.1.1 Stacks Meeting Method 1 Criteria. Use a measurement site as specified in Method 1, section 11.1.

8.1.2 Short Stacks Not Meeting Method 1 Criteria. Use stack extensions and the procedures in Method 1. Alternatively, use flow straightening vanes of the ''egg-crate'' type (see Figure 5D–1). Locate the measurement site downstream of the straightening vanes at a distance equal to or greater than two times the average equivalent diameter of the vane openings and at least one-half of the overall stack diameter upstream of the stack outlet.

8.1.3 Roof Monitor or Monovent. (See Figure 5D–2). For a positive pressure fabric filter equipped with a peaked roof monitor, ridge vent, or other type of monovent, use a measurement site at the base of the monovent. Examples of such locations are shown in Figure 5D–2. The measurement site must be upstream of any exhaust point (*e.g.*, louvered vent).

8.1.4 Compartment Housing. Sample immediately downstream of the filter bags directly above the tops of the bags as shown in the examples in Figure 5D–2. Depending on the housing design, use sampling ports in the housing walls or locate the sampling equipment within the compartment housing.

8.2 Determination of Number and Location of Traverse Points. Locate the traverse points according to Method 1, section 11.3. Because a performance test consists of at least three test runs and because of the varied configurations of positive pressure fabric filters, there are several schemes by which the number of traverse points can be determined and the three test runs can be conducted.

8.2.1 Single Stacks Meeting Method 1 Criteria. Select the number of traverse points according to Method 1. Sample all traverse points for each test run.

8.2.2 Other Single Measurement Sites. For a roof monitor or monovent, single compartment housing, or other stack not meeting Method 1 criteria, use at least 24 traverse points. For example, for a rectangular measurement site, such as a monovent, use a balanced 5×5 traverse point matrix. Sample all traverse points for each test run.

8.2.3 Multiple Measurement Sites. Sampling from two or more stacks or measurement sites may be combined for a test run, provided the following guidelines are met:

8.2.3.1 All measurement sites up to 12 must be sampled. For more than 12 measurement sites, conduct sampling on at least 12 sites or 50 percent of the sites, whichever is greater. The measurement sites sampled should be evenly, or nearly evenly, distributed among the available sites; if not, all sites are to be sampled.

8.2.3.2 The same number of measurement sites must be sampled for each test run.

8.2.3.3 The minimum number of traverse points per test run is 24. An exception to the 24-point minimum would be a test combining the sampling from two stacks meeting Method 1 criteria for acceptable stack length, and Method 1 specifies fewer than 12 points per site.

8.2.3.4 As long as the 24 traverse points per test run criterion is met, the number of traverse points per measurement site may be reduced to eight.

8.2.3.5 Alternatively, conduct a test run for each measurement site individually using the criteria in section 8.2.1 or 8.2.2 to determine the number of traverse points. Each test run shall count toward the total of three required for a performance test. If more than three measurement sites are sampled, the number of traverse points per measurement site may be reduced to eight as long as at least 72 traverse points are sampled for all the tests.

8.2.3.6 The following examples demonstrate the procedures for sampling multiple measurement sites.

8.2.3.6.1 Example 1: A source with nine circular measurement sites of equal areas may be tested as follows: For each test run, traverse three measurement sites using four points per diameter (eight points per measurement site). In this manner, test run number 1 will include sampling from sites 1,2, and 3; run 2 will include samples from sites 4, 5, and 6; and run 3 will include sites 7, 8, and 9. Each test area may consist of a separate test of each measurement site using eight points. Use the results from all nine tests in determining the emission average.

8.2.3.6.2 Example 2: A source with 30 rectangular measurement sites of equal areas may be tested as follows: For each of the three test runs, traverse five measurement sites using a 3×3 matrix of traverse points for each site. In order to distribute the sampling evenly over all the available measurement sites while sampling only 50 percent of the sites, number the sites consecutively from 1 to 30 and sample all the even numbered (or odd numbered) sites. Alternatively, conduct a separate test of each of 15 measurement sites using section 8.2.1 or 8.2.2 to determine the number and location of traverse points, as appropriate.

8.2.3.6.3 Example 3: A source with two measurement sites of equal areas may be tested as follows: For each test of three test runs, traverse both measurement sites, using section 8.2.3 in determining the number of traverse points. Alternatively, conduct two full emission test runs for each measurement site using the criteria in section 8.2.1 or 8.2.2 to determine the number of traverse points.

8.2.3.7 Other test schemes, such as random determination of traverse points for a large number of measurement sites, may be used with prior approval from the Administrator.

8.3 Velocity Determination.

8.3.1 The velocities of exhaust gases from positive pressure baghouses are often too low to measure accurately with the type S pitot tube specified in Method 2 (*i.e.*, velocity head <1.3 mm H_2O (0.05 in. H_2O)). For these conditions, measure the gas flow rate at the fabric filter inlet following the procedures outlined in Method 2. Calculate the average gas velocity at the measurement site as shown in section 12.2 and use this average velocity in determining and maintaining isokinetic sampling rates.

8.3.2 Velocity determinations to determine and maintain isokinetic rates at measurement sites with gas velocities within the range measurable with the type S pitot tube (*i.e.*, velocity head greater than 1.3 mm H_2O (0.05 in. H_2O)) shall be conducted according to the procedures outlined in Method 2.

8.4 Sampling. Follow the procedures specified in sections 8.1 through 8.6 of Method 5 or sections 8.1 through 8.25 in Method 17 with the exceptions as noted above.

8.5 Sample Recovery. Follow the procedures specified in section 8.7 of Method 5 or section 8.2 of Method 17.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.0, 10.0	Sampling equipment leak check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

Same as section 10.0 of either Method 5 or Method 17.

11.0 Analytical Procedure

Same as section 11.0 of either Method 5 or Method 17.

12.0 Data Analysis and Calculations

Same as section 12.0 of either Method 5 or Method 17 with the following exceptions:

12.1 Nomenclature.

A_o = Measurement site(s) total cross-sectional area, m^2 (ft^2).

$\bar{C}$ or C_{avg} = Average concentration of PM for all n runs, mg/scm (gr/scf).

Q_i = Inlet gas volume flow rate, m^3/sec (ft^3/sec).

m_i = Mass collected for run i of n, mg (gr).

T_o = Average temperature of gas at measurement site, °K (°R).

T_i = Average temperature of gas at inlet, °K (°R).

Vol_i = Sample volume collected for run i of n, scm (scf).

$\bar{v}$ = Average gas velocity at the measurement site(s), m/s (ft/s)

Q_o = Total baghouse exhaust volumetric flow rate, m^3/sec (ft^3/sec).

Q_d = Dilution air flow rate, m^3/sec (ft^3/sec).

Tamb = Ambient Temperature, (°K).

12.2 Average Gas Velocity. When following section 8.3.1, calculate the average gas velocity at the measurement site as follows:

$$\bar{v} = \frac{Q_o}{A_o} \qquad \text{Eq. 5D-1}$$

12.3 Volumetric Flow Rate. Total volumetric flow rate may be determined as follows:

$$Q_o = Q_i + Q_d \qquad \text{Eq. 5D-2}$$

12.4 Dilution Air Flow Rate.

$$Q_d = \frac{Q_i\left(T_i - T_o\right)}{T_o - T_{amb}} \qquad \text{Eq. 5D-3}$$

12.5 Average PM Concentration. For multiple measurement sites, calculate the average PM concentration as follows:

$$C_{avg} \text{ or } \overline{C} = \frac{\sum_{i=1}^{n} m_i}{\sum_{i=1}^{n} Vol_i} \qquad \text{Eq. 5D-4}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 5, section 17.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

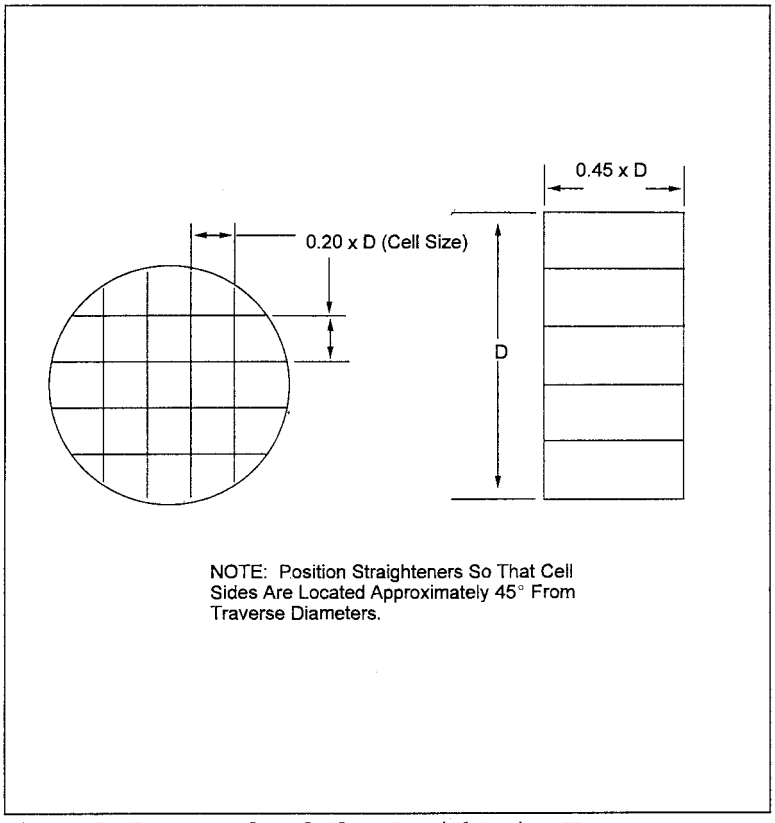


Figure 5D-1. Example of Flow Straightening Vanes.

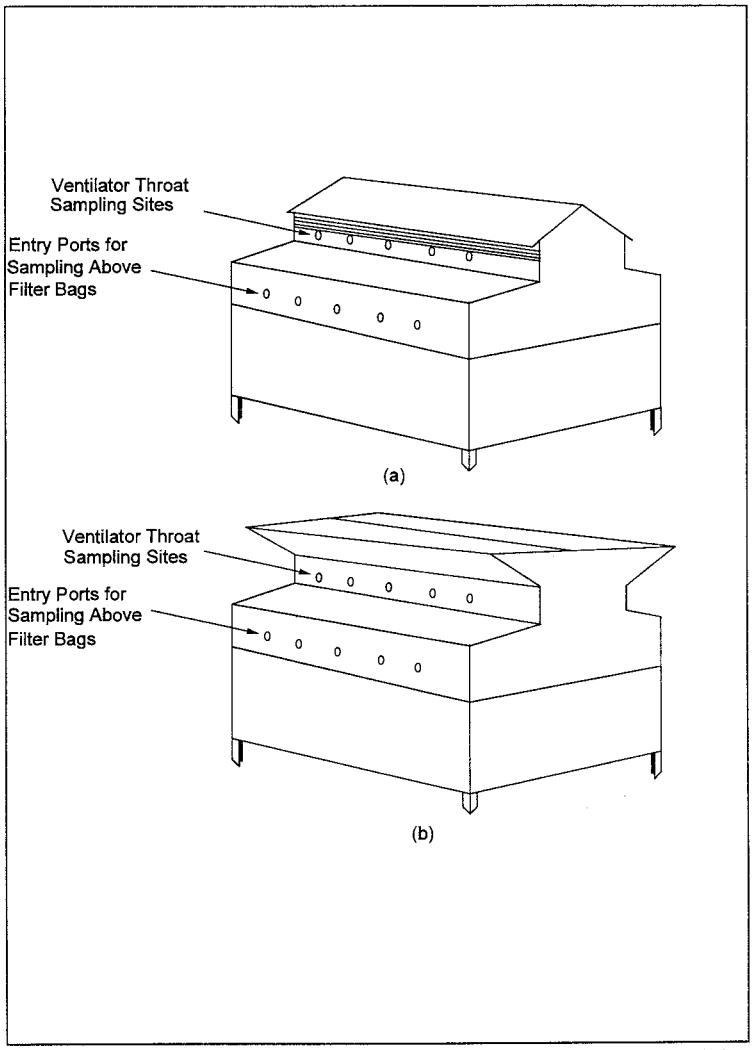


Figure 5D-2. Acceptable Sampling Site Locations for: (a) Peaked Roof; and (b) Ridge Vent Type Fabric Filters

METHOD 5E—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM THE WOOL FIBERGLASS INSULATION MANUFACTURING INDUSTRY

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5.

1.0 Scope and Applications

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of PM emissions from wool fiberglass insulation manufacturing sources.

2.0 Summary of Method

Particulate matter is withdrawn isokinetically from the source and is collected either on a glass fiber filter maintained at a temperature in the range of 120 ±14 °C (248 ±25 °F) and in impingers in solutions of 0.1 N sodium hydroxide (NaOH). The filtered particulate mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after the removal of uncombined water. The condensed PM collected in the impinger solutions is determined as total organic carbon (TOC) using a nondispersive infrared type of analyzer. The sum of the filtered PM mass and the condensed PM is reported as the total PM mass.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Hydrochloric Acid (HCl). Highly toxic. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent in air can be lethal in minutes. Will react with metals, producing hydrogen.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eye tissues and to skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 5, section 6.1, with the exception of the following:

6.1.1 Probe Liner. Same as described in section 6.1.1.2 of Method 5 except use only borosilicate or quartz glass liners.

6.1.2 Filter Holder. Same as described in section 6.1.1.5 of Method 5 with the addition of a leak-tight connection in the rear half of the filter holder designed for insertion of a temperature sensor used for measuring the sample gas exit temperature.

6.2 Sample Recovery. Same as Method 5, section 6.2, except three wash bottles are needed instead of two and only glass storage bottles and funnels may be used.

6.3 Sample Analysis. Same as Method 5, section 6.3, with the additional equipment for TOC analysis as described below:

6.3.1 Sample Blender or Homogenizer. Waring type or ultrasonic.

6.3.2 Magnetic Stirrer.

6.3.3 Hypodermic Syringe. 0- to 100-µl capacity.

6.3.4 Total Organic Carbon Analyzer. Rosemount Model 2100A analyzer or equivalent and a recorder.

6.3.5 Beaker. 30-ml.

6.3.6 Water Bath. Temperature controlled.

6.3.7 Volumetric Flasks. 1000-ml and 500-ml.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 5, section 7.1, with the addition of 0.1 N NaOH (Dissolve 4 g of NaOH in water and dilute to 1 liter).

7.2 Sample Recovery. Same as Method 5, section 7.2, with the addition of the following:

7.2.1 Water. Deionized distilled to conform to ASTM Specification D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17). The potassium permanganate ($KMnO_4$) test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.2.2 Sodium Hydroxide. Same as described in section 7.1.

7.3 Sample Analysis. Same as Method 5, section 7.3, with the addition of the following:

7.3.1 Carbon Dioxide-Free Water. Distilled or deionized water that has been freshly boiled for 15 minutes and cooled to room temperature while preventing exposure to ambient air by using a cover vented with an Ascarite tube.

7.3.2 Hydrochloric Acid. HCl, concentrated, with a dropper.

7.3.3 Organic Carbon Stock Solution. Dissolve 2.1254 g of dried potassium biphthalate ($HOOCC_6H_4COOK$) in CO_2-free water, and dilute to 1 liter in a volumetric flask. This solution contains 1000 mg/L organic carbon.

7.3.4 Inorganic Carbon Stock Solution. Dissolve 4.404 g anhydrous sodium carbonate

(Na_2CO_3.) in about 500 ml of CO_2-free water in a 1-liter volumetric flask. Add 3.497 g anhydrous sodium bicarbonate ($NaHCO_3$) to the flask, and dilute to 1 liter with CO_2 -free water. This solution contains 1000 mg/L inorganic carbon.

7.3.5 Oxygen Gas. CO_2 -free.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation and Preliminary Determinations. Same as Method 5, sections 8.1 and 8.2, respectively.

8.2 Preparation of Sampling Train. Same as Method 5, section 8.3, except that 0.1 N NaOH is used in place of water in the impingers. The volumes of the solutions are the same as in Method 5.

8.3 Leak-Check Procedures, Sampling Train Operation, Calculation of Percent Isokinetic. Same as Method 5, sections 8.4 through 8.6, respectively.

8.4 Sample Recovery. Same as Method 5, sections 8.7.1 through 8.7.4, with the addition of the following:

8.4.1 Save portions of the water, acetone, and 0.1 N NaOH used for cleanup as blanks. Take 200 ml of each liquid directly from the wash bottles being used, and place in glass sample containers labeled ''water blank,'' ''acetone blank,'' and ''NaOH blank,'' respectively.

8.4.2 Inspect the train prior to and during disassembly, and note any abnormal conditions. Treat the samples as follows:

8.4.2.1 Container No. 1. Same as Method 5, section 8.7.6.1.

8.4.2.2 Container No. 2. Use water to rinse the sample nozzle, probe, and front half of the filter holder three times in the manner described in section 8.7.6.2 of Method 5 except that no brushing is done. Put all the water wash in one container, seal, and label.

8.4.2.3 Container No. 3. Rinse and brush the sample nozzle, probe, and front half of the filter holder with acetone as described for Container No. 2 in section 8.7.6.2 of Method 5.

8.4.2.4 Container No. 4. Place the contents of the silica gel impinger in its original container as described for Container No. 3 in section 8.7.6.3 of Method 5.

8.4.2.5 Container No. 5. Measure the liquid in the first three impingers and record the volume or weight as described for the Impinger Water in section 8.7.6.4 of Method 5. Do not discard this liquid, but place it in a sample container using a glass funnel to aid in the transfer from the impingers or graduated cylinder (if used) to the sample container. Rinse each impinger thoroughly with 0.1 N NaOH three times, as well as the graduated cylinder (if used) and the funnel, and put these rinsings in the same sample container. Seal the container and label to clearly identify its contents.

8.5 Sample Transport. Whenever possible, containers should be shipped in such a way that they remain upright at all times.

9.0 Quality Control.

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.3, 10.0	Sampling equipment leak-check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.
10.1.2, 11.2.5.3	Repetitive analyses	Ensures precise measurement of total carbon and inorganic carbon concentration of samples, blank, and standards.
10.1.4	TOC analyzer calibration	Ensures linearity of analyzer response to standards.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

Same as Method 5, section 10.0, with the addition of the following procedures for calibrating the total organic carbon analyzer:

10.1 Preparation of Organic Carbon Standard Curve.

10.1.1 Add 10 ml, 20 ml, 30 ml, 40 ml, and 50 ml of the organic carbon stock solution to a series of five 1000-ml volumetric flasks. Add 30 ml, 40 ml, and 50 ml of the same solution to a series of three 500-ml volumetric flasks. Dilute the contents of each flask to the mark using CO_2-free water. These flasks contain 10, 20, 30, 40, 50, 60, 80, and 100 mg/L organic carbon, respectively.

10.1.2 Use a hypodermic syringe to withdraw a 20- to 50-µl aliquot from the 10 mg/L standard solution and inject it into the total carbon port of the analyzer. Measure the peak height. Repeat the injections until three consecutive peaks are obtained within 10 percent of their arithmetic mean. Repeat this procedure for the remaining organic carbon standard solutions.

10.1.3 Calculate the corrected peak height for each standard by deducting the blank correction (see section 11.2.5.3) as follows:

$$\text{Corrected Peak Height} = A - B \qquad \text{Eq. 5E-1}$$

Where:

A = Peak height of standard or sample, mm or other appropriate unit.

B = Peak height of blank, mm or other appropriate unit.

10.1.4 Prepare a linear regression plot of the arithmetic mean of the three consecutive peak heights obtained for each standard solution against the concentration of that solution. Calculate the calibration factor as the inverse of the slope of this curve. If the product of the arithmetic mean peak height for any standard solution and the calibration factor differs from the actual concentration by more than 5 percent, remake and reanalyze that standard.

10.2 Preparation of Inorganic Carbon Standard Curve. Repeat the procedures outlined in sections 10.1.1 through 10.1.4, substituting the inorganic carbon stock solution for the organic carbon stock solution, and the inorganic carbon port of the analyzer for the total carbon port.

11.0 Analytical Procedure

11.1 Record the data required on a sheet such as the one shown in Figure 5–6 of Method 5.

11.2 Handle each sample container as follows:

11.2.1 Container No. 1. Same as Method 5, section 11.2.1, except that the filters must be dried at 20 ±6 °C (68 ±10 °F) and ambient pressure.

11.2.2 Containers No. 2 and No. 3. Same as Method 5, section 11.2.2, except that evaporation of the samples must be at 20 ±6 °C (68 ±10 °F) and ambient pressure.

11.2.3 Container No. 4. Same as Method 5, section 11.2.3.

11.2.4 ''Water Blank'' and ''Acetone Blank'' Containers. Determine the water and acetone blank values following the procedures for the ''Acetone Blank'' container in section 11.2.4 of Method 5. Evaporate the samples at ambient temperature (20 ±6 °C (68 ±10 °F)) and pressure.

11.2.5 Container No. 5. For the determination of total organic carbon, perform two analyses on successive identical samples, *i.e.*, total carbon and inorganic carbon. The desired quantity is the difference between the two values obtained. Both analyses are based on conversion of sample carbon into carbon dioxide for measurement by a nondispersive infrared analyzer. Results of analyses register as peaks on a strip chart recorder.

11.2.5.1 The principal differences between the operating parameters for the two channels involve the combustion tube packing material and temperature. In the total carbon channel, a high temperature (950 °C (1740 °F)) furnace heats a Hastelloy combustion tube packed with cobalt oxide-impregnated asbestos fiber. The oxygen in the carrier gas, the elevated temperature, and the catalytic effect of the packing result in oxidation of both organic and inorganic carbonaceous material to CO_2, and steam. In the inorganic carbon channel, a low temperature (150 °C (300 °F)) furnace heats a glass tube containing quartz chips wetted with 85 percent phosphoric acid. The acid liberates CO_2 and steam from inorganic carbonates. The operating temperature is below that required to oxidize organic matter. Follow the manufacturer's instructions for assembly, testing, calibration, and operation of the analyzer.

11.2.5.2 As samples collected in 0.1 N NaOH often contain a high measure of inorganic carbon that inhibits repeatable determinations of TOC, sample pretreatment is necessary. Measure and record the liquid volume of each sample (or impinger contents). If the sample contains solids or immiscible liquid matter, homogenize the sample with a blender or ultrasonics until satisfactory repeatability is obtained. Transfer a representative portion of 10 to 15 ml to a 30-ml beaker, and acidify with about 2 drops of concentrated HCl to a pH of 2 or less. Warm the acidified sample at 50 °C (120 °F) in a water bath for 15 minutes.

11.2.5.3 While stirring the sample with a magnetic stirrer, use a hypodermic syringe to withdraw a 20-to 50-µl aliquot from the beaker. Analyze the sample for total carbon and calculate its corrected mean peak height according to the procedures outlined in sections 10.1.2 and 10.1.3. Similarly analyze an aliquot of the sample for inorganic carbon. Repeat the analyses for all the samples and for the 0.1 N NaOH blank.

11.2.5.4 Ascertain the total carbon and inorganic carbon concentrations (C_{TC} and C_{IC}, respectively) of each sample and blank by comparing the corrected mean peak heights for each sample and blank to the appropriate standard curve.

NOTE: If samples must be diluted for analysis, apply an appropriate dilution factor.

12.0 Data Analysis and Calculations

Same as Method 5, section 12.0, with the addition of the following:

12.1 Nomenclature.

C_c = Concentration of condensed particulate matter in stack gas, gas dry basis, corrected to standard conditions, g/dscm (gr/dscf).

C_{IC} = Concentration of condensed TOC in the liquid sample, from section 11.2.5, mg/L.

C_t = Total particulate concentration, dry basis, corrected to standard conditions, g/dscm (gr/dscf).
C_{TC} = Concentration of condensed TOC in the liquid sample, from section 11.2.5, mg/L.
C_{TOC} = Concentration of condensed TOC in the liquid sample, mg/L.
m_{TOC} = Mass of condensed TOC collected in the impingers, mg.
$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, from section 12.3 of Method 5, dscm (dscf).
V_s = Total volume of liquid sample, ml.

12.2 Concentration of Condensed TOC in Liquid Sample.

$$C_{TOC} = C_{TC} - C_{IC} \qquad \text{Eq. 5E-2}$$

12.3 Mass of Condensed TOC Collected.

$$m_{TOC} = 0.001\, C_{TOC} V_s \qquad \text{Eq. 5E-3}$$

Where:

0.001 = Liters per milliliter.

12.4 Concentration of Condensed Particulate Material.

$$C_c = K_4 m_{TOC} / V_{m(std)} \qquad \text{Eq. 5E-4}$$

Where:

K_4 = 0.001 g/mg for metric units.
= 0.0154 gr/mg for English units.

12.5 Total Particulate Concentration.

$$C_t = C_s + C_c \qquad \text{Eq. 5E-4}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Total Organic Carbon Analyzer. Tekmar-Dohrmann analyzers using the single injection technique may be used as an alternative to Rosemount Model 2100A analyzers.

17.0 References.

Same as section 17.0 of Method 5, with the addition of the following:

1. American Public Health Association, American Water Works Association, Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater. Fifteenth Edition. Washington, D.C. 1980.

18.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

Method 5F—Determination of Nonsulfate Particulate Matter Emissions From Stationary Sources

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5.

1.0 Scope and Applications

1.1 Analyte. Nonsulfate particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of nonsulfate PM emissions from stationary sources. Use of this method must be specified by an applicable subpart of the standards, or approved by the Administrator for a particular application.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

Particulate matter is withdrawn isokinetically from the source and collected on a filter maintained at a temperature in the range 160 ±14 °C (320 ±25 °F). The collected sample is extracted with water. A portion of the extract is analyzed for sulfate content by ion chromatography. The remainder is neutralized with ammonium hydroxide (NH_4OH), dried, and weighed. The weight of sulfate in the sample is calculated as ammonium sulfate ($(NH_4)_2SO_4$), and is subtracted from the total particulate weight; the result is reported as nonsulfate particulate matter.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection and Recovery. Same as Method 5, sections 6.1 and 6.2, respectively.

6.2 Sample Analysis. Same as Method 5, section 6.3, with the addition of the following:

6.2.1 Erlenmeyer Flasks. 125-ml, with ground glass joints.

6.2.2 Air Condenser. With ground glass joint compatible with the Erlenmeyer flasks.

6.2.3 Beakers. 600-ml.

6.2.4 Volumetric Flasks. 1-liter, 500-ml (one for each sample), 200-ml, and 50-ml (one for each sample and standard).

6.2.5 Pipet. 5-ml (one for each sample and standard).

6.2.6 Ion Chromatograph. The ion chromatograph should have at least the following components.

6.2.6.1 Columns. An anion separation column or other column capable of resolving the sulfate ion from other species present and a standard anion suppressor column. Suppressor columns are produced as proprietary items; however, one can be produced in the laboratory using the resin available from BioRad Company, 32nd and Griffin Streets, Richmond, California. Other systems which do not use suppressor columns may also be used.

6.2.6.2 Pump. Capable of maintaining a steady flow as required by the system.

6.2.6.3 Flow Gauges. Capable of measuring the specified system flow rate.

6.2.6.4 Conductivity Detector.

6.2.6.5 Recorder. Compatible with the output voltage range of the detector.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 5, section 7.1.

7.2 Sample Recovery. Same as Method 5, section 7.2, with the addition of the following:

7.2.1 Water. Deionized distilled, to conform to ASTM D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17). The potassium permanganate ($KMnO_4$) test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.3 Analysis. Same as Method 5, section 7.3, with the addition of the following:

7.3.1 Water. Same as in section 7.2.1.

7.3.2 Stock Standard Solution, 1 mg $(NH_4)_2SO_4$/ml. Dry an adequate amount of primary standard grade ammonium sulfate ($(NH_4)_2SO_4$) at 105 to 110 °C (220 to 230 °F) for a minimum of 2 hours before preparing the standard solution. Then dissolve exactly 1.000 g of dried $(NH_4)_2SO_4$ in water in a 1-liter volumetric flask, and dilute to 1 liter. Mix well.

7.3.3 Working Standard Solution, 25 µg $(NH_4)_2SO_4$/ml. Pipet 5 ml of the stock standard solution into a 200-ml volumetric flask. Dilute to 200 ml with water.

7.3.4 Eluent Solution. Weigh 1.018 g of sodium carbonate (Na_2CO_3) and 1.008 g of sodium bicarbonate ($NaHCO_3$), and dissolve in 4 liters of water. This solution is 0.0024 M Na_2CO_3/0.003 M $NaHCO_3$. Other eluents appropriate to the column type and capable of resolving sulfate ion from other species present may be used.

7.3.5 Ammonium Hydroxide. Concentrated, 14.8 M.

7.3.6 Phenolphthalein Indicator. 3,3-Bis(4-hydroxyphenyl)-1-(3H)-isobenzo-furanone. Dissolve 0.05 g in 50 ml of ethanol and 50 ml of water.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as Method 5, section 8.0, with the exception of the following:

8.1 Sampling Train Operation. Same as Method 5, section 8.5, except that the probe outlet and filter temperatures shall be maintained at 160 ±14 °C (320 ±25 °F).

8.2 Sample Recovery. Same as Method 5, section 8.7, except that the recovery solvent shall be water instead of acetone, and a clean filter from the same lot as those used during testing shall be saved for analysis as a blank.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures

Section	Quality control measure	Effect
8.3, 10.0	Sampling equipment leak check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.
10.1.2, 11.2.5.3	Repetitive analyses	Ensures precise measurement of total carbon and inorganic carbon concentration of samples, blank, and standards.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

Same as Method 5, section 10.0, with the addition of the following:

10.1 Determination of Ion Chromatograph Calibration Factor S. Prepare a series of five standards by adding 1.0, 2.0, 4.0, 6.0, and 10.0 ml of working standard solution (25 µg/ml) to a series of five 50-ml volumetric flasks. (The standard masses will equal 25, 50, 100, 150, and 250 µg.) Dilute each flask to the mark with water, and mix well. Analyze each standard according to the chromatograph manufacturer's instructions. Take peak height measurements with symmetrical peaks; in all other cases, calculate peak areas. Prepare or calculate a linear regression plot of the standard masses in µg (x-axis) versus their responses (y-axis). From this line, or equation, determine the slope and calculate its reciprocal which is the calibration factor, S. If any point deviates from the line by more than 7 percent of the concentration at that point, remake and reanalyze that standard. This deviation can be determined by multiplying S times the response for each standard. The resultant concentrations must not differ by more than 7 percent from each known standard mass (*i.e.*, 25, 50, 100, 150, and 250 µg).

10.2 Conductivity Detector. Calibrate according to manufacturer's specifications prior to initial use.

11.0 Analytical Procedure

11.1 Sample Extraction.

11.1.1 Note on the analytical data sheet, the level of the liquid in the container, and whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.1.2 Cut the filter into small pieces, and place it in a 125-ml Erlenmeyer flask with a ground glass joint equipped with an air condenser. Rinse the shipping container with water, and pour the rinse into the flask. Add additional water to the flask until it contains about 75 ml, and place the flask on a hot plate. Gently reflux the contents for 6 to 8 hours. Cool the solution, and transfer it to a 500-ml volumetric flask. Rinse the Erlenmeyer flask with water, and transfer the rinsings to the volumetric flask including the pieces of filter.

11.1.3 Transfer the probe rinse to the same 500-ml volumetric flask with the filter sample. Rinse the sample bottle with water, and add the rinsings to the volumetric flask. Dilute the contents of the flask to the mark with water.

11.1.4 Allow the contents of the flask to settle until all solid material is at the bottom of the flask. If necessary, remove and centrifuge a portion of the sample.

11.1.5 Repeat the procedures outlined in sections 11.1.1 through 11.1.4 for each sample and for the filter blank.

11.2 Sulfate (SO_4) Analysis.

11.2.1 Prepare a standard calibration curve according to the procedures outlined in section 10.1.

11.2.2 Pipet 5 ml of the sample into a 50-ml volumetric flask, and dilute to 50 ml with water. (Alternatively, eluent solution may be used instead of water in all sample, standard, and blank dilutions.) Analyze the set of standards followed by the set of samples, including the filter blank, using the same injection volume used for the standards.

11.2.3 Repeat the analyses of the standards and the samples, with the standard set being done last. The two peak height or peak area responses for each sample must agree within 5 percent of their arithmetic mean for the analysis to be valid. Perform this analysis sequence on the same day. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

11.2.4 Document each sample chromatogram by listing the following analytical parameters: injection point, injection volume, sulfate retention time, flow rate, detector sensitivity setting, and recorder chart speed.

11.3 Sample Residue.

11.3.1 Transfer the remaining contents of the volumetric flask to a tared 600-ml beaker or similar container. Rinse the volumetric flask with water, and add the rinsings to the tared beaker. Make certain that all particulate matter is transferred to the beaker. Evaporate the water in an oven at 105 °C (220 °F) until only about 100 ml of water remains. Remove the beakers from the oven, and allow them to cool.

11.3.2 After the beakers have cooled, add five drops of phenolphthalein indicator, and then add concentrated ammonium hydroxide until the solution turns pink. Return the samples to the oven at 105 °C (220 °F), and evaporate the samples to dryness. Cool the samples in a desiccator, and weigh the samples to constant weight.

12.0 Data Analysis and Calculations

Same as Method 5, section 12.0, with the addition of the following:

12.1 Nomenclature.

C_W = Water blank residue concentration, mg/ml.

F = Dilution factor (required only if sample dilution was needed to reduce the concentration into the range of calibration).

H_S = Arithmetic mean response of duplicate sample analyses, mm for height or mm2 for area.

H_b = Arithmetic mean response of duplicate filter blank analyses, mm for height or mm2 for area.
m_b = Mass of beaker used to dry sample, mg.
m_f = Mass of sample filter, mg.
m_n = Mass of nonsulfate particulate matter in the sample as collected, mg.
m_s = Mass of ammonium sulfate in the sample as collected, mg.
m_t = Mass of beaker, filter, and dried sample, mg.
m_w = Mass of residue after evaporation of water blank, mg.
S = Calibration factor, µg/mm.
V_b = Volume of water blank, ml.
V_S = Volume of sample collected, 500 ml.

12.2 Water Blank Concentration.

$$C_w = \frac{m_w}{V_b} \qquad \text{Eq. 5F-1}$$

12.3 Mass of Ammonium Sulfate.

$$m_s = \frac{(99)\, S\, (H_s - H_b)}{(1000)} F \qquad \text{Eq. 5F-2}$$

Where:
100 = Aliquot factor, 495 ml/5 ml
1000 = Constant, µg/mg

12.4 Mass of Nonsulfate Particulate Matter.

$$m_n = m_t - m_b - m_s - m_f - V_s C_w \qquad \text{Eq. 5F-3}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 The following procedure may be used as an alternative to the procedure in section 11.0

16.1.1 Apparatus. Same as for Method 6, sections 6.3.3 to 6.3.6 with the following additions.

16.1.1.1 Beakers. 250-ml, one for each sample, and 600-ml.

16.1.1.2 Oven. Capable of maintaining temperatures of 75 ±5 °C (167 ±9 °F) and 105 ±5 °C (221 ±9 °F).

16.1.1.3 Buchner Funnel.

16.1.1.4 Glass Columns. 25-mm × 305-mm (1-in. × 12-in.) with Teflon stopcock.

16.1.1.5 Volumetric Flasks. 50-ml and 500-ml, one set for each sample, and 100-ml, 200-ml, and 1000-ml.

16.1.1.6 Pipettes. Two 20-ml and one 200-ml, one set for each sample, and 5-ml.

16.1.1.7 Filter Flasks. 500-ml.

16.1.1.8 Polyethylene Bottle. 500-ml, one for each sample.

16.1.2 Reagents. Same as Method 6, sections 7.3.2 to 7.3.5 with the following additions:

16.1.2.1 Water, Ammonium Hydroxide, and Phenolphthalein. Same as sections 7.2.1, 7.3.5, and 7.3.6 of this method, respectively.

16.1.2.2 Filter. Glass fiber to fit Buchner funnel.

16.1.2.3 Hydrochloric Acid (HCl), 1 m. Add 8.3 ml of concentrated HCl (12 M) to 50 ml of water in a 100-ml volumetric flask. Dilute to 100 ml with water.

16.1.2.4 Glass Wool.

16.1.2.5 Ion Exchange Resin. Strong cation exchange resin, hydrogen form, analytical grade.

16.1.2.6 pH Paper. Range of 1 to 7.

16.1.3 Analysis.

16.1.3.1 Ion Exchange Column Preparation. Slurry the resin with 1 M HCl in a 250-ml beaker, and allow to stand overnight. Place 2.5 cm (1 in.) of glass wool in the bottom of the glass column. Rinse the slurried resin twice with water. Resuspend the resin in water, and pour sufficient resin into the column to make a bed 5.1 cm (2 in.) deep. Do not allow air bubbles to become entrapped in the resin or glass wool to avoid channeling, which may produce erratic results. If necessary, stir the resin with a glass rod to remove air bubbles, after the column has been prepared, never let the liquid level fall below the top of the upper glass wool plug. Place a 2.5-cm (1-in.) plug of glass wool on top of the resin. Rinse the column with water until the eluate gives a pH of 5 or greater as measured with pH paper.

16.1.3.2 Sample Extraction. Followup the procedure given in section 11.1.3 except do not dilute the sample to 500 ml.

16.1.3.3 Sample Residue.

16.1.3.3.1 Place at least one clean glass filter for each sample in a Buchner funnel, and rinse the filters with water. Remove the filters from the funnel, and dry them in an oven at 105 ±5 °C (221 ±9 °F); then cool in a desiccator. Weigh each filter to constant weight according to the procedure in Method 5, section 11.0. Record the weight of each filter to the nearest 0.1 mg.

16.1.3.3.2 Assemble the vacuum filter apparatus, and place one of the clean, tared glass fiber filters in the Buchner funnel. Decant the liquid portion of the extracted sample (Section 16.1.3.2) through the tared glass fiber filter into a clean, dry, 500-ml filter flask. Rinse all the particulate matter remaining in the volumetric flask onto the glass fiber filter with water. Rinse the particulate matter with additional water.

Transfer the filtrate to a 500-ml volumetric flask, and dilute to 500 ml with water. Dry the filter overnight at 105 ±5 °C (221 ±9 °F), cool in a desiccator, and weigh to the nearest 0.1 mg.

16.1.3.3.3 Dry a 250-ml beaker at 75 ±5 °C (167 ±9 °F), and cool in a desiccator; then weigh to constant weight to the nearest 0.1 mg. Pipette 200 ml of the filtrate that was saved into a tared 250-ml beaker; add five drops of phenolphthalein indicator and sufficient concentrated ammonium hydroxide to turn the solution pink. Carefully evaporate the contents of the beaker to dryness at 75 ±5 °C (167 ±9 °F). Check for dryness every 30 minutes. Do not continue to bake the sample once it has dried. Cool the sample in a desiccator, and weigh to constant weight to the nearest 0.1 mg.

16.1.3.4 Sulfate Analysis. Adjust the flow rate through the ion exchange column to 3 ml/min. Pipette a 20-ml aliquot of the filtrate onto the top of the ion exchange column, and collect the eluate in a 50-ml volumetric flask. Rinse the column with two 15-ml portions of water. Stop collection of the eluate when the volume in the flask reaches 50-ml. Pipette a 20-ml aliquot of the eluate into a 250-ml Erlenmeyer flask, add 80 ml of 100 percent isopropanol and two to four drops of thorin indicator, and titrate to a pink end point using 0.0100 N barium perchlorate. Repeat and average the titration volumes. Run a blank with each series of samples. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is larger. Perform the ion exchange and titration procedures on duplicate portions of the filtrate. Results should agree within 5 percent. Regenerate or replace the ion exchange resin after 20 sample aliquots have been analyzed or if the end point of the titration becomes unclear.

NOTE: Protect the 0.0100 N barium perchlorate solution from evaporation at all times.

16.1.3.5 Blank Determination. Begin with a sample of water of the same volume as the samples being processed and carry it through the analysis steps described in sections 16.1.3.3 and 16.1.3.4. A blank value larger than 5 mg should not be subtracted from the final particulate matter mass. Causes for large blank values should be investigated and any problems resolved before proceeding with further analyses.

16.1.4 Calibration. Calibrate the barium perchlorate solutions as in Method 6, section 10.5.

16.1.5 Calculations.

16.1.5.1 Nomenclature. Same as section 12.1 with the following additions:

m_a = Mass of clean analytical filter, mg.
m_d = Mass of dissolved particulate matter, mg.
m_e = Mass of beaker and dissolved particulate matter after evaporation of filtrate, mg.
m_p = Mass of insoluble particulate matter, mg.
m_r = Mass of analytical filter, sample filter, and insoluble particulate matter, mg.
m_{bk} = Mass of nonsulfate particulate matter in blank sample, mg.
m_n = Mass of nonsulfate particulate matter, mg.
m_s = Mass of Ammonium sulfate, mg.
N = Normality of $Ba(ClO_4)$ titrant, meq/ml.
V_a = Volume of aliquot taken for titration, 20 ml.
V_c = Volume of titrant used for titration blank, ml.
V_d = Volume of filtrate evaporated, 200 ml.
V_e = Volume of eluate collected, 50 ml.
V_f = Volume of extracted sample, 500 ml.
V_i = Volume of filtrate added to ion exchange column, 20 ml.
V_t = Volume of $Ba(C10_4)_2$ titrant, ml.
W = Equivalent weight of ammonium sulfate, 66.07 mg/meq.

16.1.5.2 Mass of Insoluble Particulate Matter.

$$m_p = m_r - m_a - m_f \qquad \text{Eq. 5F-4}$$

16.1.5.3 Mass of Dissolved Particulate Matter.

$$m_d = \left(m_e - \left(V_f / V_d\right) m_b\right) \qquad \text{Eq. 5F-5}$$

16.1.5.4 Mass of Ammonium Sulfate.

$$m_s = \frac{\left(V_t - V_c\right) N\, W\, V_e V_f}{V_a V_i} \qquad \text{Eq. 5F-6}$$

16.1.5.5 Mass of Nonsulfate Particulate Matter.

$$m_n = m_p + m_d - m_s - m_{bk} \qquad \text{Eq. 5F-7}$$

17.0 References

Same as Method 5, section 17.0, with the addition of the following:

1. Mulik, J.D. and E. Sawicki. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor, Ann Arbor Science Publishers, Inc. Vol. 2, 1979.

2. Sawicki, E., J.D. Mulik, and E. Wittgenstein. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor, Ann Arbor Science Publishers, Inc. Vol. 1. 1978.

3. Siemer, D.D. Separation of Chloride and Bromide from Complex Matrices Prior to Ion Chromatographic Determination. Analytical Chemistry 52(12): 1874–1877. October 1980.

4. Small, H., T.S. Stevens, and W.C. Bauman. Novel Ion Exchange Chromatographic Method Using

Conductimetric Determination. Analytical Chemistry. *47*(11):1801. 1975.

18.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 5G—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM WOOD HEATERS (DILUTION TUNNEL SAMPLING LOCATION)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 4, Method 5, Method 5H, and Method 28.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of PM emissions from wood heaters.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 The exhaust from a wood heater is collected with a total collection hood, and is combined with ambient dilution air. Particulate matter is withdrawn proportionally from a single point in a sampling tunnel, and is collected on two glass fiber filters in series. The filters are maintained at a temperature of no greater than 32 °C (90 °F). The particulate mass is determined gravimetrically after the removal of uncombined water.

2.2 There are three sampling train approaches described in this method: (1) One dual-filter dry sampling train operated at about 0.015 m^3/min (0.5 cfm), (2) One dual-filter plus impingers sampling train operated at about 0.015 m^3/min (0.5 cfm), and (3) two dual-filter dry sampling trains operated simultaneously at any flow rate. Options (2) and (3) are referenced in section 16.0 of this method. The dual-filter dry sampling train equipment and operation, option (1), are described in detail in this method.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. The following items are required for sample collection:

6.1.1 Sampling Train. The sampling train configuration is shown in Figure 5G–1 and consists of the following components:

6.1.1.1 Probe. Stainless steel (*e.g.*, 316 or grade more corrosion resistant) or glass about 9.5 mm (⅜ in.) I.D., 0.6 m (24 in.) in length. If made of stainless steel, the probe shall be constructed from seamless tubing.

6.1.1.2 Pitot Tube. Type S, as described in section 6.1 of Method 2. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Method 2, section 10. Alternatively, a standard pitot may be used as described in Method 2, section 6.1.2.

6.1.1.3 Differential Pressure Gauge. Inclined manometer or equivalent device, as described in Method 2, section 6.2. One manometer shall be used for velocity head (Δp) readings and another (optional) for orifice differential pressure readings (ΔH).

6.1.1.4 Filter Holders. Two each made of borosilicate glass, stainless steel, or Teflon, with a glass frit or stainless steel filter support and a silicone rubber, Teflon, or Viton gasket. The holder design shall provide a positive seal against leakage from the outside or around the filters. The filter holders shall be placed in series with the backup filter holder located 25 to 100 mm (1 to 4 in.) downstream from the primary filter holder. The filter holder shall be capable of holding a filter with a 100 mm (4 in.) diameter, except as noted in section 16.

6.1.1.5 Filter Temperature Monitoring System. A temperature sensor capable of measuring temperature to within ±3 °C (±5 °F). The sensor shall be installed at the exit side of the front filter holder so that the sensing tip of the temperature sensor is in direct contact with the sample gas or in a thermowell as shown in Figure 5G–1. The temperature sensor shall comply with the calibration specifications in Method 2, section 10.3. Alternatively, the sensing tip of the temperature sensor may be installed at the inlet side of the front filter holder.

6.1.1.6 Dryer. Any system capable of removing water from the sample gas to less than 1.5 percent moisture (volume percent) prior to the metering system. The system shall include a temperature sensor for demonstrating that sample gas temperature exiting the dryer is less than 20 °C (68 °F).

6.1.1.7 Metering System. Same as Method 5, section 6.1.1.9.

6.1.2 Barometer. Same as Method 5, section 6.1.2.

6.1.3 Dilution Tunnel Gas Temperature Measurement. A temperature sensor capable

of measuring temperature to within ±3 °C (±5 °F).

6.1.4 Dilution Tunnel. The dilution tunnel apparatus is shown in Figure 5G–2 and consists of the following components:

6.1.4.1 Hood. Constructed of steel with a minimum diameter of 0.3 m (1 ft) on the large end and a standard 0.15 to 0.3 m (0.5 to 1 ft) coupling capable of connecting to standard 0.15 to 0.3 m (0.5 to 1 ft) stove pipe on the small end.

6.1.4.2 90° Elbows. Steel 90° elbows, 0.15 to 0.3 m (0.5 to 1 ft) in diameter for connecting mixing duct, straight duct and optional damper assembly. There shall be at least two 90° elbows upstream of the sampling section (see Figure 5G–2).

6.1.4.3 Straight Duct. Steel, 0.15 to 0.3 m (0.5 to 1 ft) in diameter to provide the ducting for the dilution apparatus upstream of the sampling section. Steel duct, 0.15 m (0.5 ft) in diameter shall be used for the sampling section. In the sampling section, at least 1.2 m (4 ft) downstream of the elbow, shall be two holes (velocity traverse ports) at 90° to each other of sufficient size to allow entry of the pitot for traverse measurements. At least 1.2 m (4 ft) downstream of the velocity traverse ports, shall be one hole (sampling port) of sufficient size to allow entry of the sampling probe. Ducts of larger diameter may be used for the sampling section, provided the specifications for minimum gas velocity and the dilution rate range shown in section 8 are maintained. The length of duct from the hood inlet to the sampling ports shall not exceed 9.1 m (30 ft).

6.1.4.4 Mixing Baffles. Steel semicircles (two) attached at 90° to the duct axis on opposite sides of the duct midway between the two elbows upstream of sampling section. The space between the baffles shall be about 0.3 m (1 ft).

6.1.4.5 Blower. Squirrel cage or other fan capable of extracting gas from the dilution tunnel of sufficient flow to maintain the velocity and dilution rate specifications in section 8 and exhausting the gas to the atmosphere.

6.2 Sample Recovery. The following items are required for sample recovery: probe brushes, wash bottles, sample storage containers, petri dishes, and funnel. Same as Method 5, sections 6.2.1 through 6.2.4, and 6.2.8, respectively.

6.3 Sample Analysis. The following items are required for sample analysis: glass weighing dishes, desiccator, analytical balance, beakers (250-ml or smaller), hygrometer, and temperature sensor. Same as Method 5, sections 6.3.1 through 6.3.3 and 6.3.5 through 6.3.7, respectively.

7.0 Reagents and Standards

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Filters. Glass fiber filters with a minimum diameter of 100 mm (4 in.), without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. Gelman A/E 61631 has been found acceptable for this purpose.

7.1.2 Stopcock Grease. Same as Method 5, section 7.1.5. 7.2 Sample Recovery. Acetone-reagent grade, same as Method 5, section 7.2.

7.3 Sample Analysis. Two reagents are required for the sample analysis:

7.3.1 Acetone. Same as in section 7.2.

7.3.2 Desiccant. Anhydrous calcium sulfate, calcium chloride, or silica gel, indicating type.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Dilution Tunnel Assembly and Cleaning. A schematic of a dilution tunnel is shown in Figure 5G–2. The dilution tunnel dimensions and other features are described in section 6.1.4. Assemble the dilution tunnel, sealing joints and seams to prevent air leakage. Clean the dilution tunnel with an appropriately sized wire chimney brush before each certification test.

8.2 Draft Determination. Prepare the wood heater as in Method 28, section 6.2.1. Locate the dilution tunnel hood centrally over the wood heater stack exhaust. Operate the dilution tunnel blower at the flow rate to be used during the test run. Measure the draft imposed on the wood heater by the dilution tunnel (*i.e.*, the difference in draft measured with and without the dilution tunnel operating) as described in Method 28, section 6.2.3. Adjust the distance between the top of the wood heater stack exhaust and the dilution tunnel hood so that the dilution tunnel induced draft is less than 1.25 Pa (0.005 in. H_2O). Have no fire in the wood heater, close the wood heater doors, and open fully the air supply controls during this check and adjustment.

8.3 Pretest Ignition. Same as Method 28, section 8.7.

8.4 Smoke Capture. During the pretest ignition period, operate the dilution tunnel and visually monitor the wood heater stack exhaust. Operate the wood heater with the doors closed and determine that 100 percent of the exhaust gas is collected by the dilution tunnel hood. If less than 100 percent of the wood heater exhaust gas is collected, adjust the distance between the wood heater stack and the dilution tunnel hood until no visible exhaust gas is escaping. Stop the pretest ignition period, and repeat the draft determination procedure described in section 8.2.

8.5 Velocity Measurements. During the pretest ignition period, conduct a velocity traverse to identify the point of average velocity. This single point shall be used for measuring velocity during the test run.

8.5.1 Velocity Traverse. Measure the diameter of the duct at the velocity traverse port location through both ports. Calculate the duct area using the average of the two diameters. A pretest leak-check of pitot lines as in Method 2, section 8.1, is recommended. Place the calibrated pitot tube at the centroid of the stack in either of the velocity traverse ports. Adjust the damper or similar device on the blower inlet until the velocity indicated by the pitot is approximately 220 m/min (720 ft/min). Continue to read the Δp and temperature until the velocity has remained constant (less than 5 percent change) for 1 minute. Once a constant velocity is obtained at the centroid of the duct, perform a velocity traverse as outlined in Method 2, section 8.3 using four points per traverse as outlined in Method 1. Measure the Δp and tunnel temperature at each traverse point and record the readings. Calculate the total gas flow rate using calculations contained in Method 2, section 12. Verify that the flow rate is 4 ±0.40 dscm/min (140 ±14 dscf/min); if not, readjust the damper, and repeat the velocity traverse. The moisture may be assumed to be 4 percent (100 percent relative humidity at 85 °F). Direct moisture measurements (*e.g.*, according to Method 4) are also permissible.

NOTE: If burn rates exceed 3 kg/hr (6.6 lb/hr), dilution tunnel duct flow rates greater than 4 dscm/min (140 dscfm) and sampling section duct diameters larger than 150 mm (6 in.) are allowed. If larger ducts or flow rates are used, the sampling section velocity shall be at least 220 m/min (720 fpm). In order to ensure measurable particulate mass catch, it is recommended that the ratio of the average mass flow rate in the dilution tunnel to the average fuel burn rate be less than 150:1 if larger duct sizes or flow rates are used.

8.5.2 Testing Velocity Measurements. After obtaining velocity traverse results that meet the flow rate requirements, choose a point of average velocity and place the pitot and temperature sensor at that location in the duct. Alternatively, locate the pitot and the temperature sensor at the duct centroid and calculate a velocity correction factor for the centroidal position. Mount the pitot to ensure no movement during the test run and seal the port holes to prevent any air leakage. Align the pitot opening to be parallel with the duct axis at the measurement point. Check that this condition is maintained during the test run (about 30-minute intervals). Monitor the temperature and velocity during the pretest ignition period to ensure that the proper flow rate is maintained. Make adjustments to the dilution tunnel flow rate as necessary.

8.6 Pretest Preparation. Same as Method 5, section 8.1.

8.7 Preparation of Sampling Train. During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin.

Using a tweezer or clean disposable surgical gloves, place one labeled (identified) and weighed filter in each of the filter holders. Be sure that each filter is properly centered and that the gasket is properly placed so as to prevent the sample gas stream from circumventing the filter. Check each filter for tears after assembly is completed.

Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct. Set up the train as shown in Figure 5G–1.

8.8 Leak-Check Procedures.

8.8.1 Leak-Check of Metering System Shown in Figure 5G–1. That portion of the sampling train from the pump to the orifice meter shall be leak-checked prior to initial use and after each certification or audit test. Leakage after the pump will result in less volume being recorded than is actually sampled. Use the procedure described in Method 5, section 8.4.1. Similar leak-checks shall be conducted for other types of metering systems (*i.e.*, without orifice meters).

8.8.2 Pretest Leak-Check. A pretest leak-check of the sampling train is recommended, but not required. If the pretest leak check is conducted, the procedures outlined in Method 5, section 8.4.2 should be used. A vacuum of 130 mm Hg (5 in. Hg) may be used instead of 380 mm Hg (15 in. Hg).

8.8.3 Post-Test Leak-Check. A leak-check of the sampling train is mandatory at the conclusion of each test run. The leak-check shall be performed in accordance with the procedures outlined in Method 5, section 8.4.2. A vacuum of 130 mm Hg (5 in. Hg) or the highest vacuum measured during the test run, whichever is greater, may be used instead of 380 mm Hg (15 in. Hg).

8.9 Preliminary Determinations. Determine the pressure, temperature and the average velocity of the tunnel gases as in section 8.5. Moisture content of diluted tunnel gases is assumed to be 4 percent for making flow rate calculations; the moisture content may be measured directly as in Method 4.

8.10 Sampling Train Operation. Position the probe inlet at the stack centroid, and block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream. Be careful not to bump the probe into the stack wall when removing or inserting the probe through the porthole; this minimizes the chance of extracting deposited material.

8.10.1 Begin sampling at the start of the test run as defined in Method 28, section 8.8.1. During the test run, maintain a sample flow rate proportional to the dilution tunnel flow rate (within 10 percent of the initial proportionality ratio) and a filter holder temperature of no greater than 32 °C (90 °F).

The initial sample flow rate shall be approximately 0.015 m^3/min (0.5 cfm).

8.10.2 For each test run, record the data required on a data sheet such as the one shown in Figure 5G–3. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment and when sampling is halted. Take other readings as indicated on Figure 5G–3 at least once each 10 minutes during the test run. Since the manometer level and zero may drift because of vibrations and temperature changes, make periodic checks during the test run.

8.10.3 For the purposes of proportional sampling rate determinations, data from calibrated flow rate devices, such as glass rotameters, may be used in lieu of incremental dry gas meter readings. Proportional rate calculation procedures must be revised, but acceptability limits remain the same.

8.10.4 During the test run, make periodic adjustments to keep the temperature between (or upstream of) the filters at the proper level. Do not change sampling trains during the test run.

8.10.5 At the end of the test run (see Method 28, section 6.4.6), turn off the coarse adjust valve, remove the probe from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak-check, as outlined in section 8.8.2. Also, leak-check the pitot lines as described in Method 2, section 8.1; the lines must pass this leak-check in order to validate the velocity head data.

8.11 Calculation of Proportional Sampling Rate. Calculate percent proportionality (see section 12.7) to determine whether the run was valid or another test run should be made.

8.12 Sample Recovery. Same as Method 5, section 8.7, with the exception of the following:

8.12.1 An acetone blank volume of about 50-ml or more may be used.

8.12.2 Treat the samples as follows:

8.12.2.1 Container Nos. 1 and 1A. Treat the two filters according to the procedures outlined in Method 5, section 8.7.6.1. The filters may be stored either in a single container or in separate containers. Use the sum of the filter tare weights to determine the sample mass collected.

8.12.2.3 Container No. 2.

8.12.2.3.1 Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe and filter holders by washing and brushing these components with acetone and placing the wash in a labeled glass container. At least three cycles of brushing and rinsing are required.

8.12.2.3.2 Between sampling runs, keep brushes clean and protected from contamination.

8.12.2.3.3 After all acetone washings and particulate matter have been collected in the sample containers, tighten the lids on the sample containers so that the acetone will not leak out when transferred to the laboratory weighing area. Mark the height of the fluid levels to determine whether leakage occurs during transport. Label the containers clearly to identify contents.

8.13 Sample Transport. Whenever possible, containers should be shipped in such a way that they remain upright at all times.

NOTE: Requirements for capping and transport of sample containers are not applicable if sample recovery and analysis occur in the same room.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.8, 10.1–10.4	Sampling equipment leak check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.
10.5	Analytical balance calibration	Ensure accurate and precise measurement of collected particulate.
16.2.5	Simultaneous, dual-train sample collection.	Ensure precision of measured particulate concentration.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory record of all calibrations.

10.1 Pitot Tube. The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Method 2, section 10.1, prior to the first certification test and checked semiannually, thereafter. A standard pitot need not be calibrated but shall be inspected and cleaned, if necessary, prior to each certification test.

10.2 Volume Metering System.

10.2.1 Initial and Periodic Calibration. Before its initial use and at least semiannually thereafter, calibrate the volume metering system as described in Method 5, section 10.3.1, except that the wet test meter with a capacity of 3.0 liters/rev (0.1 ft^3/rev) may be used. Other liquid displacement systems accurate to within ±1 percent, may be used as calibration standards.

NOTE: Procedures and equipment specified in Method 5, section 16.0, for alternative calibration standards, including calibrated dry gas meters and critical orifices, are allowed for calibrating the dry gas meter in the sampling train. A dry gas meter used as a calibration standard shall be recalibrated at least once annually.

10.2.2 Calibration After Use. After each certification or audit test (four or more test runs conducted on a wood heater at the four burn rates specified in Method 28), check calibration of the metering system by performing three calibration runs at a single, intermediate flow rate as described in Method 5, section 10.3.2.

NOTE: Procedures and equipment specified in Method 5, section 16.0, for alternative calibration standards are allowed for the post-test dry gas meter calibration check.

10.2.3 Acceptable Variation in Calibration. If the dry gas meter coefficient values obtained before and after a certification test differ by more than 5 percent, the certification test shall either be voided and repeated, or calculations for the certification test shall be performed using whichever meter coefficient value (*i.e.*, before or after) gives the lower value of total sample volume.

10.3 Temperature Sensors. Use the procedure in Method 2, section 10.3, to calibrate temperature sensors before the first certification or audit test and at least semiannually, thereafter.

10.4 Barometer. Calibrate against a mercury barometer before the first certification test and at least semiannually, thereafter. If a mercury barometer is used, no calibration is necessary. Follow the manufacturer's instructions for operation.

10.5 Analytical Balance. Perform a multipoint calibration (at least five points spanning the operational range) of the analytical balance before the first certification test and semiannually, thereafter. Before each certification test, audit the balance by weighing at least one calibration weight (class F) that corresponds to 50 to 150 percent of the weight of one filter. If the scale cannot reproduce the value of the calibration weight to within 0.1 mg, conduct the multipoint calibration before use.

11.0 Analytical Procedure

11.1 Record the data required on a sheet such as the one shown in Figure 5G–4. Use the same analytical balance for determining tare weights and final sample weights.

11.2 Handle each sample container as follows:

11.2.1 Container Nos. 1 and 1A. Treat the two filters according to the procedures outlined in Method 5, section 11.2.1.

11.2.2 Container No. 2. Same as Method 5, section 11.2.2, except that the beaker may be smaller than 250 ml.

11.2.3 Acetone Blank Container. Same as Method 5, section 11.2.4, except that the beaker may be smaller than 250 ml.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

12.1 Nomenclature.

B_{ws} = Water vapor in the gas stream, proportion by volume (assumed to be 0.04).
c_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (gr/dscf).
E = Particulate emission rate, g/hr (lb/hr).
E_{adj} = Adjusted particulate emission rate, g/hr (lb/hr).
L_a = Maximum acceptable leakage rate for either a pretest or post-test leak-check, equal to 0.00057 m^3/min (0.020 cfm) or 4 percent of the average sampling rate, whichever is less.
L_p = Leakage rate observed during the post-test leak-check, m^3/min (cfm).
m_a = Mass of residue of acetone blank after evaporation, mg.
m_{aw} = Mass of residue from acetone wash after evaporation, mg.
m_n = Total amount of particulate matter collected, mg.
M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).
PR = Percent of proportional sampling rate.
P_s = Absolute gas pressure in dilution tunnel, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
Q_{sd} = Average gas flow rate in dilution tunnel, calculated as in Method 2, Equation 2–8, dscm/hr (dscf/hr).
T_m = Absolute average dry gas meter temperature (see Figure 5G–3), °K (°R).
T_{mi} = Absolute average dry gas meter temperature during each 10-minute interval, i, of the test run, °K (°R).
T_s = Absolute average gas temperature in the dilution tunnel (see Figure 5G–3), °K (°R).
T_{si} = Absolute average gas temperature in the dilution tunnel during each 10 minute interval, i, of the test run, °K (°R).
T_{std} = Standard absolute temperature, 293 °K (528 °R).
V_a = Volume of acetone blank, ml.
V_{aw} = Volume of acetone used in wash, ml.
V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).

V_{mi} = Volume of gas sample as measured by dry gas meter during each 10-minute interval, i, of the test run, dcm.
$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).
V_s = Average gas velocity in the dilution tunnel, calculated by Method 2, Equation 2–7, m/sec (ft/sec). The dilution tunnel dry gas molecular weight may be assumed to be 29 g/g mole (lb/lb mole).
V_{si} = Average gas velocity in dilution tunnel during each 10-minute interval, i, of the test run, calculated by Method 2, Equation 2–7, m/sec (ft/sec).
Y = Dry gas meter calibration factor.
ΔH = Average pressure differential across the orifice meter, if used (see Figure 5G–2), mm H^2O (in. H^2O).
U = Total sampling time, min.
10 = 10 minutes, length of first sampling period.
13.6 = Specific gravity of mercury.
100 = Conversion to percent.

12.2 Dry Gas Volume. Same as Method 5, section 12.2, except that component changes are not allowable.

12.3 Solvent Wash Blank.

$$m_{aw} = \frac{m_a V_{aw}}{V_a} \qquad \text{Eq. 5G-1}$$

12.4 Total Particulate Weight. Determine the total particulate catch, mn, from the sum of the weights obtained from Container Nos. 1, 1A, and 2, less the acetone blank (see Figure 5G–4).

12.5 Particulate Concentration.

$$c_s = K_2 \frac{m_n}{V_{m(std)}} \qquad \text{Eq. 5G-2}$$

Where:
K_2 = 0.001 g/mg for metric units.
= 0.0154 gr/mg for English units.

12.6 Particulate Emission Rate.

$$E = C_s Q_{sd} \qquad \text{Eq. 5G-3}$$

NOTE: Particulate emission rate results produced using the sampling train described in section 6 and shown in Figure 5G–1 shall be adjusted for reporting purposes by the following method adjustment factor:

$$E_{adj} = K_3 E^{0.83} \qquad \text{Eq. 5G-4}$$

Where:
K_3 = constant, 1.82 for metric units.
= constant, 0.643 for English units.

12.7 Proportional Rate Variation. Calculate PR for each 10-minute interval, i, of the test run.

$$PR = \left(\frac{\theta \left(V_{mi} V_s T_m T_{si} \right)}{10 \left(V_m V_{si} T_s T_{mi} \right)} \right) \times 100 \qquad \text{Eq. 5G-5}$$

Alternate calculation procedures for proportional rate variation may be used if other sample flow rate data (e.g., orifice flow meters or rotameters) are monitored to maintain proportional sampling rates. The proportional rate variations shall be calculated for each 10-minute interval by comparing the stack to nozzle velocity ratio for each 10-minute interval to the average stack to nozzle velocity ratio for the test run. Proportional rate variation may be calculated for intervals shorter than 10 minutes with appropriate revisions to Equation 5G–5. If no more than 10 percent of the PR values for all the intervals exceed 90 percent ≤PR ≤110 percent, and if no PR value for any interval exceeds 80 percent ≤PR ≤120 percent, the results are acceptable. If the PR values for the test run are judged to be unacceptable, report the test run emission results, but do not include the results in calculating the weighted average emission rate, and repeat the test run.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Method 5H Sampling Train. The sampling train and sample collection, recovery, and analysis procedures described in Method 5H, sections 6.1.1, 7.1, 7.2, 8.1, 8.10, 8.11, and 11.0, respectively, may be used in lieu of similar sections in Method 5G. Operation of the Method 5H sampling train in the dilution tunnel is as described in section 8.10 of this method. Filter temperatures and condenser conditions are as described in Method 5H. No adjustment to the measured particulate matter emission rate (Equation 5G–4, section 12.6) is to be applied to the particulate emission rate measured by this alternative method.

16.2 Dual Sampling Trains. Two sampling trains may be operated simultaneously at sample flow rates other than that specified

in section 8.10, provided that the following specifications are met.

16.2.1 Sampling Train. The sampling train configuration shall be the same as specified in section 6.1.1, except the probe, filter, and filter holder need not be the same sizes as specified in the applicable sections. Filter holders of plastic materials such as Nalgene or polycarbonate materials may be used (the Gelman 1119 filter holder has been found suitable for this purpose). With such materials, it is recommended that solvents not be used in sample recovery. The filter face velocity shall not exceed 150 mm/sec (30 ft/min) during the test run. The dry gas meter shall be calibrated for the same flow rate range as encountered during the test runs. Two separate, complete sampling trains are required for each test run.

16.2.2 Probe Location. Locate the two probes in the dilution tunnel at the same level (see section 6.1.4.3). Two sample ports are necessary. Locate the probe inlets within the 50 mm (2 in.) diameter centroidal area of the dilution tunnel no closer than 25 mm (1 in.) apart.

16.2.3 Sampling Train Operation. Operate the sampling trains as specified in section 8.10, maintaining proportional sampling rates and starting and stopping the two sampling trains simultaneously. The pitot values as described in section 8.5.2 shall be used to adjust sampling rates in both sampling trains.

16.2.4 Recovery and Analysis of Sample. Recover and analyze the samples from the two sampling trains separately, as specified in sections 8.12 and 11.0, respectively.

16.2.4.1 For this alternative procedure, the probe and filter holder assembly may be weighed without sample recovery (use no solvents) described above in order to determine the sample weight gains. For this approach, weigh the clean, dry probe and filter holder assembly upstream of the front filter (without filters) to the nearest 0.1 mg to establish the tare weights. The filter holder section between the front and second filter need not be weighed. At the end of the test run, carefully clean the outside of the probe, cap the ends, and identify the sample (label). Remove the filters from the filter holder assemblies as described for container Nos. 1 and 1A in section 8.12.2.1. Reassemble the filter holder assembly, cap the ends, identify the sample (label), and transfer all the samples to the laboratory weighing area for final weighing. Requirements for capping and transport of sample containers are not applicable if sample recovery and analysis occur in the same room.

16.2.4.2 For this alternative procedure, filters may be weighed directly without a petri dish. If the probe and filter holder assembly are to be weighed to determine the sample weight, rinse the probe with acetone to remove moisture before desiccating prior to the test run. Following the test run, transport the probe and filter holder to the desiccator, and uncap the openings of the probe and the filter holder assembly. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

16.2.5 Calculations. Calculate an emission rate (Section 12.6) for the sample from each sampling train separately and determine the average emission rate for the two values. The two emission rates shall not differ by more than 7.5 percent from the average emission rate, or 7.5 percent of the weighted average emission rate limit in the applicable subpart of the regulations, whichever is greater. If this specification is not met, the results are unacceptable. Report the results, but do not include the results in calculating the weighted average emission rate. Repeat the test run until acceptable results are achieved, report the average emission rate for the acceptable test run, and use the average in calculating the weighted average emission rate.

17.0 References

Same as Method 5, section 17.0, References 1 through 11, with the addition of the following:

1. Oregon Department of Environmental Quality. Standard Method for Measuring the Emissions and Efficiencies of Woodstoves. June 8, 1984. Pursuant to Oregon Administrative Rules Chapter 340, Division 21.

2. American Society for Testing and Materials. Proposed Test Methods for Heating Performance and Emissions of Residential Wood-fired Closed Combustion-Chamber Heating Appliances. E–6 Proposal P 180. August 1986.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

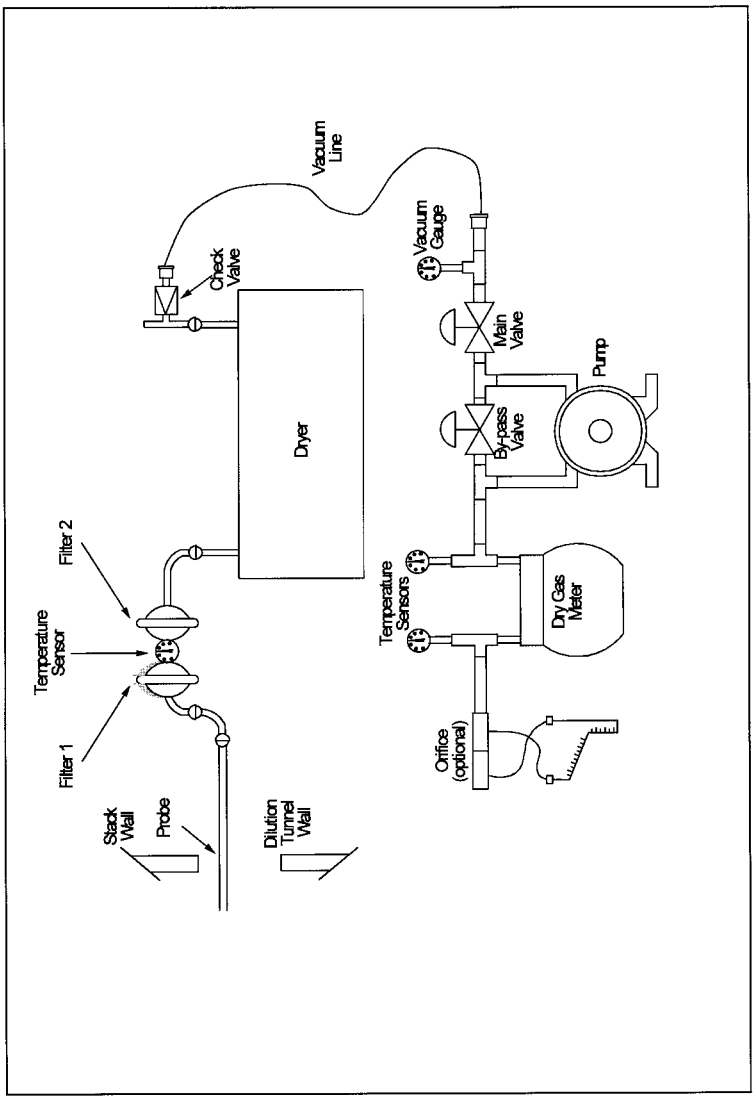


Figure 5G-1. Method 5G Sampling Train.

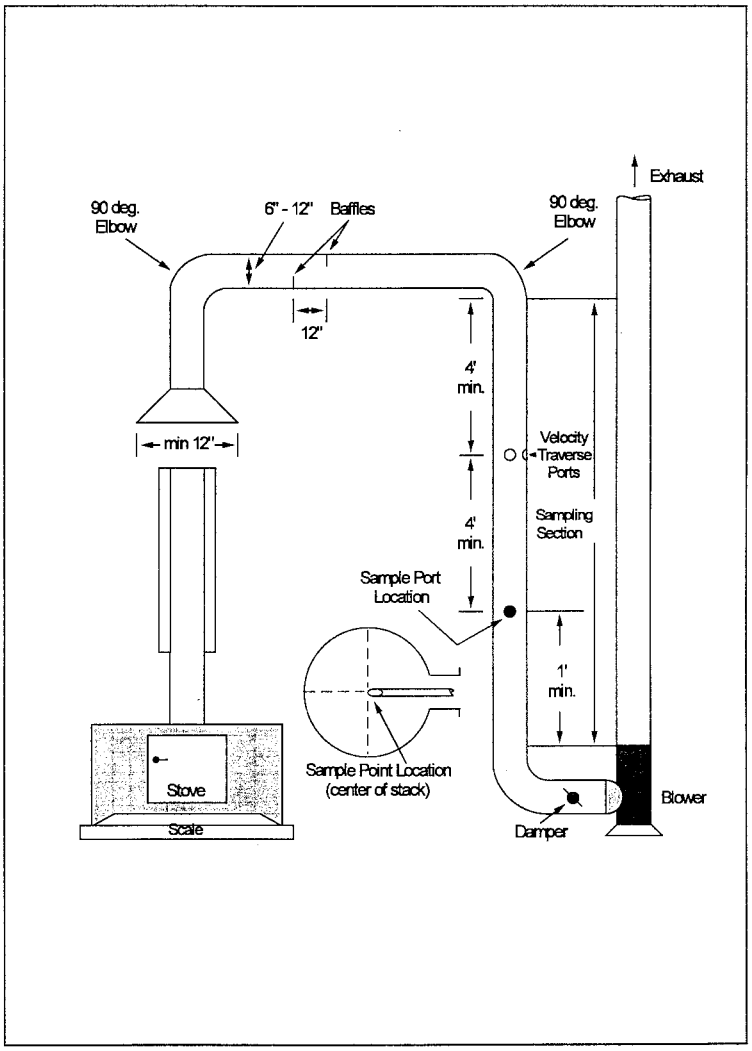


Figure 5G-2. Suggested Construction Details of the Dilution Tunnel.

Stove _____
Test Method _____
Operator _____
Date _____
Run No. _____
Start Time _____
Stop Time _____
Sample Box No. _____
Meter Box No. _____
Meter ΔH @ (optional) _____

Pitot tube coefficient, C_p _____
Room temperature, °C (°F) _____
Barometric pressure mb (in. Hg) _____
Measured or assumed moisture, % _____
Final leak rate, m^3/min, (cfm) _____
Probe liner material _____
Draft or static pressure, mm H_2O (in. H_2O) _____
Filter No. _____

Clock time	Test run time (e) min.	Vacuum mm Hg (in. Hg)	Tunnel temp (T_s) °C (°F)	Velocity head (ΔP_s) mm (in. H_2O)	Sample flow rate indicator (orifice meter optional) mm H_2O (in. H_2O)	Gas meter volume m^3 (ft^3)	Gas sample temp at dry gas meter Inlet °C (°F)	Gas sample temp at dry gas meter Outlet °C (°F)	Filter holder temp °C (°F)	Temperature of gas leaving dryer or last impinger °C (°F)
Total							Avg.	Avg.		
Average							Avg.			

Figure 5G-3. Sampling Data Sheet.

Stove _____
Date _____
Run No. _____
Filter Nos. _____
Liquid lost during transport, ml _____
Acetone blank volume, ml _____
Acetone wash volume, ml _____
Acetone blank concentration, mg/mg _____
Acetone wash blank, mg _____

Container number	Weight of particulate collected, mg	
	Final weight	Tare weight
1		
2		
3		
Total		
Less acetone blank		
Weight of particulate matter		

Stack Moisture Measurement Data
(Optional)

	Volume of liquid water collected	
	Implinger volume, ml	Silica gel weight, g
Final		
Initial		
Liquid collected		
Total volume collected		g[1] or ml

[1]Convert weight of water to volume by dividing total weight increase by density of water (1 g/ml).

$$\frac{\text{Increase, g}}{\text{(1 g/ml)}} = \text{Volume water, ml}$$

Figure 5G-4. Analysis Data Sheet.

METHOD 5H—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM WOOD HEATERS FROM A STACK LOCATION

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 2, Method 3, Method 5, Method 5G, Method 6, Method 6C, Method 16A, and Method 28.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of PM and condensible emissions from wood heaters.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Particulate matter is withdrawn proportionally from the wood heater exhaust and is collected on two glass fiber filters separated by impingers immersed in an ice water bath. The first filter is maintained at a temperature of no greater than 120 °C (248 °F). The second filter and the impinger system are cooled such that the temperature of the gas exiting the second filter is no greater than 20 °C (68 °F). The particulate mass collected in the probe, on the filters, and in the impingers is determined gravimetrically after the removal of uncombined water.

3.0 Definitions

Same as in Method 6C, section 3.0.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. The following items are required for sample collection:

6.1.1 Sampling Train. The sampling train configuration is shown in Figure 5H–1. Same as Method 5, section 6.1.1, with the exception of the following:

6.1.1.1 Probe Nozzle. The nozzle is optional; a straight sampling probe without a nozzle is an acceptable alternative.

6.1.1.2 Probe Liner. Same as Method 5, section 6.1.1.2, except that the maximum length of the sample probe shall be 0.6 m (2 ft) and probe heating is optional.

6.1.1.3 Filter Holders. Two each of borosilicate glass, with a glass frit or stainless steel filter support and a silicone rubber, Teflon, or Viton gasket. The holder design shall provide a positive seal against leakage from the outside or around the filter. The front filter holder shall be attached immediately at the outlet of the probe and prior to the first impinger. The second filter holder shall be attached on the outlet of the third impinger and prior to the inlet of the fourth (silica gel) impinger.

6.1.2 Barometer. Same as Method 5, section 6.2.

6.1.3 Stack Gas Flow Rate Measurement System. A schematic of an example test system is shown in Figure 5H–2. The flow rate measurement system consists of the following components:

6.1.3.1 Sample Probe. A glass or stainless steel sampling probe.

6.1.3.2 Gas Conditioning System. A high density filter to remove particulate matter and a condenser capable of lowering the dew point of the gas to less than 5 °C (40 °F). Desiccant, such as Drierite, may be used to dry the sample gas. Do not use silica gel.

6.1.3.3 Pump. An inert (*e.g.*, Teflon or stainless steel heads) sampling pump capable of delivering more than the total amount of sample required in the manufacturer's instructions for the individual instruments. A means of controlling the analyzer flow rate and a device for determining proper sample flow rate (*e.g.*, precision rotameter, pressure gauge downstream of all flow controls) shall be provided at the analyzer. The requirements for measuring and controlling the analyzer flow rate are not applicable if data are presented that demonstrate that the analyzer is insensitive to flow variations over the range encountered during the test.

6.1.3.4 Carbon Monoxide (CO) Analyzer. Any analyzer capable of providing a measure of CO in the range of 0 to 10 percent by volume at least once every 10 minutes.

6.1.3.5 Carbon Dioxide (CO_2) Analyzer. Any analyzer capable of providing a measure of CO_2 in the range of 0 to 25 percent by volume at least once every 10 minutes.

NOTE: Analyzers with ranges less than those specified above may be used provided actual concentrations do not exceed the range of the analyzer.

6.1.3.6 Manifold. A sampling tube capable of delivering the sample gas to two analyzers and handling an excess of the total amount used by the analyzers. The excess gas is exhausted through a separate port.

6.1.3.7 Recorders (optional). To provide a permanent record of the analyzer outputs.

6.1.4 Proportional Gas Flow Rate System. To monitor stack flow rate changes and provide a measurement that can be used to adjust and maintain particulate sampling flow rates proportional to the stack gas flow rate. A schematic of the proportional flow rate system is shown in Figure 5H–2 and consists of the following components:

6.1.4.1 Tracer Gas Injection System. To inject a known concentration of sulfur dioxide (SO_2) into the flue. The tracer gas injection system consists of a cylinder of SO_2, a gas cylinder regulator, a stainless steel needle valve or flow controller, a nonreactive (stainless steel and glass) rotameter, and an injection loop to disperse the SO_2 evenly in the flue.

6.1.4.2 Sample Probe. A glass or stainless steel sampling probe.

6.1.4.3 Gas Conditioning System. A combustor as described in Method 16A, sections 6.1.5 and 6.1.6, followed by a high density filter to remove particulate matter, and a condenser capable of lowering the dew point of the gas to less than 5 °C (40 °F). Desiccant, such as Drierite, may be used to dry the sample gas. Do not use silica gel.

6.1.4.4 Pump. Same as described in section 6.1.3.3.

6.1.4.5 SO_2 Analyzer. Any analyzer capable of providing a measure of the SO_2 concentration in the range of 0 to 1,000 ppm by volume (or other range necessary to measure the SO_2 concentration) at least once every 10 minutes.

6.1.4.6 Recorder (optional). To provide a permanent record of the analyzer outputs.

NOTE: Other tracer gas systems, including helium gas systems, are acceptable for determination of instantaneous proportional sampling rates.

6.2 Sample Recovery. Same as Method 5, section 6.2.

6.3 Sample Analysis. Same as Method 5, section 6.3, with the addition of the following:

6.3.1 Separatory Funnel. Glass or Teflon, 500-ml or greater.

7.0 Reagents and Standards

7.1 Sample Collection. Same as Method 5, section 7.1, including deionized distilled water.

7.2 Sample Recovery. Same as Method 5, section 7.2.

7.3 Sample Analysis. The following reagents and standards are required for sample analysis:

7.3.1 Acetone. Same as Method 5 section 7.2.

7.3.2 Dichloromethane (Methylene Chloride). Reagent grade, <0.001 percent residue in glass bottles.

7.3.3 Desiccant. Anhydrous calcium sulfate, calcium chloride, or silica gel, indicating type.

7.3.4 Cylinder Gases. For the purposes of this procedure, span value is defined as the upper limit of the range specified for each analyzer as described in section 6.1.3.4 or 6.1.3.5. If an analyzer with a range different from that specified in this method is used, the span value shall be equal to the upper limit of the range for the analyzer used (see note in section 6.1.3.5).

7.3.4.1 Calibration Gases. The calibration gases for the CO_2, CO, and SO_2 analyzers shall be CO_2 in nitrogen (N_2), CO in N_2, and SO_2 in N_2, respectively. CO_2 and CO calibration gases may be combined in a single cylinder. Use three calibration gases as specified in Method 6C, sections 7.2.1 through 7.2.3.

7.3.4.2 SO_2 Injection Gas. A known concentration of SO_2 in N_2. The concentration must be at least 2 percent SO_2 with a maximum of 100 percent SO_2.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Pretest Preparation. Same as Method 5, section 8.1.

8.2 Calibration Gas and SO_2 Injection Gas Concentration Verification, Sampling System Bias Check, Response Time Test, and Zero and Calibration Drift Tests. Same as Method 6C, sections 8.2.1, 8.2.3, 8.2.4, and 8.5, respectively, except that for verification of CO and CO_2 gas concentrations, substitute Method 3 for Method 6.

8.3 Preliminary Determinations.

8.3.1 Sampling Location. The sampling location for the particulate sampling probe shall be 2.45 ±0.15 m (8 ±0.5 ft) above the platform upon which the wood heater is placed (*i.e.*, the top of the scale).

8.3.2 Sampling Probe and Nozzle. Select a nozzle, if used, sized for the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain proportional sampling rates. During the run, do not change the nozzle size. Select a suitable probe liner and probe length to effect minimum blockage.

8.4 Preparation of Particulate Sampling Train. Same as Method 5, section 8.3, with the exception of the following:

8.4.1 The train should be assembled as shown in Figure 5H–1.

8.4.2 A glass cyclone may not be used between the probe and filter holder.

8.5 Leak-Check Procedures.

8.5.1 Leak-Check of Metering System Shown in Figure 5H–1. That portion of the sampling train from the pump to the orifice meter shall be leak-checked after each certification or audit test. Use the procedure described in Method 5, section 8.4.1.

8.5.2 Pretest Leak-Check. A pretest leak-check of the sampling train is recommended, but not required. If the pretest leak-check is conducted, the procedures outlined in Method 5, section 8.5.2 should be used. A vacuum of 130 mm Hg (5 in. Hg) may be used instead of 380 mm Hg (15 in. Hg).

8.5.2 Leak-Checks During Sample Run. If, during the sampling run, a component (*e.g.*, filter assembly or impinger) change becomes necessary, conduct a leak-check as described in Method 5, section 8.4.3.

8.5.3 Post-Test Leak-Check. A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be performed in accordance with the procedures outlined in Method 5, section 8.4.4, except that a vacuum of 130 mm Hg (5 in. Hg) or the greatest vacuum measured during the test run, whichever is greater, may be used instead of 380 mm Hg (15 in. Hg).

8.6 Tracer Gas Procedure. A schematic of the tracer gas injection and sampling systems is shown in Figure 5H–2.

8.6.1 SO_2 Injection Probe. Install the SO_2 injection probe and dispersion loop in the stack at a location 2.9 ±0.15 m (9.5 ±0.5 ft) above the sampling platform.

8.6.2 SO_2 Sampling Probe. Install the SO_2 sampling probe at the centroid of the stack at a location 4.1 ±0.15 m (13.5 ±0.5 ft) above the sampling platform.

8.7 Flow Rate Measurement System. A schematic of the flow rate measurement system is shown in Figure 5H–2. Locate the flow rate measurement sampling probe at the centroid of the stack at a location 2.3 ±0.3 m (7.5 ±1 ft) above the sampling platform.

8.8 Tracer Gas Procedure. Within 1 minute after closing the wood heater door at the start of the test run (as defined in Method 28, section 8.8.1), meter a known concentration of SO_2 tracer gas at a constant flow rate into the wood heater stack. Monitor the SO_2 concentration in the stack, and record the SO_2 concentrations at 10-minute intervals or more often. Adjust the particulate sampling flow rate proportionally to the SO_2 concentration changes using Equation 5H–6 (*e.g.*, the SO_2 concentration at the first 10-minute reading is measured to be 100 ppm; the next 10 minute SO_2 concentration is measured to be 75 ppm: the particulate sample flow rate is adjusted from the initial 0.15 cfm to 0.20 cfm). A check for proportional rate variation shall be made at the completion of the test run using Equation 5H–10.

8.9 Volumetric Flow Rate Procedure. Apply stoichiometric relationships to the wood combustion process in determining the exhaust gas flow rate as follows:

8.9.1 Test Fuel Charge Weight. Record the test fuel charge weight (wet) as specified in Method 28, section 8.8.2. The wood is assumed to have the following weight percent composition: 51 percent carbon, 7.3 percent hydrogen, 41 percent oxygen. Record the wood moisture for each fuel charge as described in Method 28, section 8.6.5. The ash is assumed to have negligible effect on associated C, H, and O concentrations after the test burn.

8.9.2 Measured Values. Record the CO and CO_2 concentrations in the stack on a dry basis every 10 minutes during the test run or more often. Average these values for the test run. Use as a mole fraction (*e.g.*, 10 percent CO_2 is recorded as 0.10) in the calculations to express total flow (see Equation 5H–6).

8.10 Sampling Train Operation.

8.10.1 For each run, record the data required on a data sheet such as the one shown in Figure 5H–3. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak-check, and when sampling is halted. Take other readings as indicated on Figure 5H–3 at least once each 10 minutes during the test run.

8.10.2 Remove the nozzle cap, verify that the filter and probe heating systems are up to temperature, and that the probe is properly positioned. Position the nozzle, if used, facing into gas stream, or the probe tip in the 50 mm (2 in.) centroidal area of the stack.

8.10.3 Be careful not to bump the probe tip into the stack wall when removing or inserting the probe through the porthole; this minimizes the chance of extracting deposited material.

8.10.4 When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

8.10.5 Begin sampling at the start of the test run as defined in Method 28, section 8.8.1, start the sample pump, and adjust the sample flow rate to between 0.003 and 0.014 m^3/min (0.1 and 0.5 cfm). Adjust the sample flow rate proportionally to the stack gas flow during the test run according to the procedures outlined in section 8. Maintain a proportional sampling rate (within 10 percent of the desired value) and a filter holder temperature no greater than 120 °C (248 °F).

8.10.6 During the test run, make periodic adjustments to keep the temperature around the filter holder at the proper level. Add more ice to the impinger box and, if necessary, salt to maintain a temperature of less than 20 °C (68 °F) at the condenser/silica gel outlet.

8.10.7 If the pressure drop across the filter becomes too high, making proportional sampling difficult to maintain, either filter may be replaced during a sample run. It is recommended that another complete filter assembly be used rather than attempting to change the filter itself. Before a new filter assembly is installed, conduct a leak-check (see section 8.5.2). The total particulate weight shall include the summation of all filter assembly catches. The total time for changing sample train components shall not exceed 10 minutes. No more than one component change is allowed for any test run.

8.10.8 At the end of the test run, turn off the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak-check, as outlined in section 8.5.3.

8.11 Sample Recovery. Same as Method 5, section 8.7, with the exception of the following:

8.11.1 Blanks. The volume of the acetone blank may be about 50-ml, rather than 200-ml; a 200-ml water blank shall also be saved for analysis.

8.11.2 Samples.

8.11.2.1 Container Nos. 1 and 1A. Treat the two filters according to the procedures outlined in Method 5, section 8.7.6.1. The filters

may be stored either in a single container or in separate containers.

8.11.2.2 Container No. 2. Same as Method 5, section 8.7.6.2, except that the container should not be sealed until the impinger rinse solution is added (see section 8.10.2.4).

8.11.2.3 Container No. 3. Treat the impingers as follows: Measure the liquid which is in the first three impingers to within 1-ml by using a graduated cylinder or by weighing it to within 0.5 g by using a balance (if one is available). Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas. Transfer the water from the first, second, and third impingers to a glass container. Tighten the lid on the sample container so that water will not leak out.

8.11.2.4 Rinse impingers and graduated cylinder, if used, with acetone three times or more. Avoid direct contact between the acetone and any stopcock grease or collection of any stopcock grease in the rinse solutions. Add these rinse solutions to sample Container No. 2.

8.11.2.5 Container No. 4. Same as Method 5, section 8.7.6.3

8.12 Sample Transport. Whenever possible, containers should be transferred in such a way that they remain upright at all times.

NOTE: Requirements for capping and transport of sample containers are not applicable if sample recovery and analysis occur in the same room.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.2	Sampling system bias check	Ensures that bias introduced by measurement system, minus analyzer, is no greater than 3 percent of span.
8.2	Analyzer zero and calibration drift tests	Ensures that bias introduced by drift in the measurement system output during the run is no greater than 3 percent of span.
8.5, 10.1, 12.13	Sampling equipment leak-check and calibration; proportional sampling rate verification.	Ensures accurate measurement of stack gas flow rate, sample volume.
10.1	Analytical balance calibration	Ensure accurate and precise measurement of collected particulate.
10.3	Analyzer calibration error check	Ensures that bias introduced by analyzer calibration error is no greater than 2 percent of span.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory record of all calibrations.

10.1 Volume Metering System, Temperature Sensors, Barometer, and Analytical Balance. Same as Method 5G, sections 10.2 through 10.5, respectively.

10.2 SO_2 Injection Rotameter. Calibrate the SO_2 injection rotameter system with a soap film flowmeter or similar direct volume measuring device with an accuracy of 2 percent. Operate the rotameter at a single reading for at least three calibration runs for 10 minutes each. When three consecutive calibration flow rates agree within 5 percent, average the three flow rates, mark the rotameter at the calibrated setting, and use the calibration flow rate as the SO_2 injection flow rate during the test run. Repeat the rotameter calibration before the first certification test and semiannually thereafter.

10.3. Gas Analyzers. Same as Method 6C, section 10.0.

10.4 Field Balance Calibration Check. Check the calibration of the balance used to weigh impingers with a weight that is at least 500g or within 50g of a loaded impinger. The weight must be ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 6 (or better). Daily before use, the field balance must measure the weight within ± 0.5g of the certified mass. If the daily balance calibration check fails, perform corrective measures and repeat the check before using balance.

10.5 Analytical Balance Calibration. Perform a multipoint calibration (at least five points spanning the operational range) of the analytical balance before the first use, and semiannually thereafter. The calibration of the analytical balance must be conducted using ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 2 (or better) tolerance weights. Audit the balance each day it is used for gravimetric measurements by weighing at least one ASTM E617–13 Class 2 tolerance (or better) calibration weight that corresponds to 50 to 150 percent of the weight of one filter or between 1g and 5g. If the scale cannot reproduce the value of the calibration weight to within 0.5 mg of the certified mass, perform corrective measures, and conduct the multipoint calibration before use.

11.0 Analytical Procedure

11.1 Record the data required on a sheet such as the one shown in Figure 5H–4.

11.2 Handle each sample container as follows:

11.2.1 Container Nos. 1 and 1A. Treat the two filters according to the procedures outlined in Method 5, section 11.2.1.

11.2.2 Container No. 2. Same as Method 5, section 11.2.2, except that the beaker may be smaller than 250-ml.

11.2.3 Container No. 3. Note the level of liquid in the container and confirm on the analysis sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Determination of sample leakage is not applicable if sample recovery and analysis occur in the same room. Measure the liquid in this container either volumetrically to within 1-ml or gravimetrically to within 0.5 g. Transfer the contents to a 500-ml or larger separatory funnel. Rinse the container with water, and add to the separatory funnel. Add 25-ml of dichloromethane to the separatory funnel, stopper and vigorously shake 1 minute, let separate and transfer the dichloromethane (lower layer) into a tared beaker or evaporating dish. Repeat twice more. It is necessary to rinse Container No. 3 with dichloromethane. This rinse is added to the impinger extract container. Transfer the remaining water from the separatory funnel to a tared beaker or evaporating dish and evaporate to dryness at 104 °C (220 °F). Desiccate and weigh to a constant weight. Evaporate the combined impinger water extracts at ambient temperature and pressure. Desiccate and weigh to a constant weight. Report both results to the nearest 0.1 mg.

11.2.4 Container No. 4. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance.

11.2.5 Acetone Blank Container. Same as Method 5, section 11.2.4, except that the beaker may be smaller than 250 ml.

11.2.6 Dichloromethane Blank Container. Treat the same as the acetone blank.

11.2.7 Water Blank Container. Transfer the water to a tared 250 ml beaker and evaporate to dryness at 104 °C (220 °F). Desiccate and weigh to a constant weight.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

12.1 Nomenclature.

A = Sample flow rate adjustment factor.
BR = Dry wood burn rate, kg/hr (lb/hr), from Method 28, Section 8.3.
B_{ws} = Water vapor in the gas stream, proportion by volume.
C_i = Tracer gas concentration at inlet, ppmv.
C_o = Tracer gas concentration at outlet, ppmv.
C_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (g/dscf).
E = Particulate emission rate, g/hr (lb/hr).
ΔH = Average pressure differential across the orifice meter (see Figure 5H–1), mm H_2O (in. H_2O).
L_a = Maximum acceptable leakage rate for either a post-test leak-check or for a leak-check following a component change; equal to 0.00057 cmm (0.020 cfm) or 4 percent of the average sampling rate, whichever is less.
L_1 = Individual leakage rate observed during the leak-check conducted before a component change, cmm (cfm).
L_p = Leakage rate observed during the post-test leak-check, cmm (cfm).
m_n = Total amount of particulate matter collected, mg.
M_a = Mass of residue of solvent after evaporation, mg.
N_C = Grams of carbon/gram of dry fuel (lb/lb), equal to 0.0425.
N_T = Total dry moles of exhaust gas/kg of dry wood burned, g-moles/kg (lb-moles/lb).
PR = Percent of proportional sampling rate.
P_{bar} = Barometric pressure at the sampling site, mm Hg (in.Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in.Hg).
Q_i = Gas volumetric flow rate at inlet, cfm (l/min).
Q_o = Gas volumetric flow rate at outlet, cfm (l/min).

12.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 5H–3).

12.3 Dry Gas Volume. Same as Method 5, section 12.3.

12.4 Volume of Water Vapor.

$$V_{w(std)} = K_2 V_{1c} \qquad \text{Eq. 5H-1}$$

Where:

K_2 = 0.001333 m^3/ml for metric units.
K_2 = 0.04707 ft^3/ml for English units.

12.5 Moisture Content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad \text{Eq. 5H-2}$$

12.6 Solvent Wash Blank.

$$W_a = \frac{M_a V_{aw}}{V_a} \qquad \text{Eq. 5H-3}$$

12.7 Total Particulate Weight. Determine the total particulate catch from the sum of the weights obtained from containers 1, 2, 3,

and 4 less the appropriate solvent blanks (see Figure 5H–4).

NOTE: Refer to Method 5, section 8.5 to assist in calculation of results involving two filter assemblies.

12.8 Particulate Concentration.

$$C_s = \frac{0.001g}{mg} \frac{m_n}{V_{m(std)}} \qquad \text{Eq. 5H-4}$$

12.9 Sample Flow Rate Adjustment.

$$a = \frac{S_1}{S_i} \qquad \text{Eq. 5H-5}$$

12.10 Carbon Balance for Total Moles of Exhaust Gas (dry)/kg of Wood Burned in the Exhaust Gas.

$$N_T = \frac{K_3 N_C}{Y_{CO_2} + Y_{CO} + Y_{HC}} \qquad \text{Eq. 5H-6}$$

Where:

K_3 = 1000 g/kg for metric units.
K_3 = 1.0 lb/lb for English units.

NOTE: The NO_X/SO_X portion of the gas is assumed to be negligible.

12.11 Total Stack Gas Flow Rate.

$$Q_{sd} = K_4 \, N_T \, BR \qquad \text{Eq. 5H-7}$$

Where:

K_4 = 0.02406 dscm/g-mole for metric units.
K_4 = 384.8 dscf/lb-mole for English units.

12.12 Particulate Emission Rate.

$$E = C_s \, Q_{sd} \qquad \text{Eq. 5H-8}$$

12.13 Proportional Rate Variation. Calculate PR for each 10-minute interval, i, of the test run.

$$PR = \frac{\theta \, S_i V_{mi(std)}}{10 \sum_{i=1}^{N} \left[S_i V_{mi(std)} \right]} \times 100 \qquad \text{Eq. 5H-9}$$

12.14 Acceptable Results. If no more than 15 percent of the PR values for all the intervals fall outside the range 90 percent ≤PR ≤110 percent, and if no PR value for any interval falls outside the range 75 ≤PR ≤125 percent, the results are acceptable. If the PR values for the test runs are judged to be unacceptable, report the test run emission results, but do not include the test run results in calculating the weighted average emission rate, and repeat the test.

12.15 Alternative Tracer Gas Flow Rate Determination.

$$Q_o = \frac{Q_i \times C_i}{C_o} \qquad Eq. 5H - 10$$

NOTE: This gives Q for a single instance only. Repeated multiple determinations are needed to track temporal variations. Very small variations in Q_i, C_i, or C_o may give very large variations in Q_o.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Alternative Stack Gas Volumetric Flow Rate Determination (Tracer Gas).

16.1.1 Apparatus.

16.1.1.1 Tracer Gas Injector System. This is to inject a known concentration of tracer gas into the stack. This system consists of a cylinder of tracer gas, a gas cylinder regulator, a stainless steel needle valve or a flow controller, a nonreactive (stainless steel or glass) rotameter, and an injection loop to disperse the tracer gas evenly in the stack.

16.1.1.2 Tracer Gas Probe. A glass or stainless steel sampling probe.

16.1.1.3 Gas Conditioning System. A gas conditioning system is suitable for delivering a cleaned sample to the analyzer consisting of a filter to remove particulate and a condenser capable of lowering the dew point of the sample gas to less than 5 °C (40 °F). A desiccant such as anhydrous calcium sulfate may be used to dry the sample gas. Desiccants which react or absorb tracer gas or stack gas may not be used, e.g. silica gel absorbs CO_2.

16.1.1.4 Pump. An inert (*i.e.*, stainless steel or Teflon head) pump to deliver more than the total sample required by the manufacturer's specifications for the analyzer used to measure the downstream tracer gas concentration.

16.1.1.5 Gas Analyzer. A gas analyzer is any analyzer capable of measuring the tracer gas concentration in the range necessary at least every 10 minutes. A means of controlling the analyzer flow rate and a device for determining proper sample flow rate shall be provided unless data is provided to show that the analyzer is insensitive to flow variations over the range encountered during the test.

The gas analyzer needs to meet or exceed the following performance specifications:

Linearity	±1 percent of full scale.
Calibration Error	≤2 percent of span.
Response Time	≤10 seconds.
Zero Drift (24 hour)	≤2 percent of full scale.
Span Drift (24 hour)	≤2 percent of full scale.
Resolution	≤0.5 percent of span.

16.1.1.6 Recorder (optional). To provide a permanent record of the analyzer output.

16.1.2 Reagents.

16.1.2.1 Tracer Gas. The tracer gas is sulfur hexafluoride in an appropriate concentration for accurate analyzer measurement or pure sulfur dioxide. The gas used must be nonreactive with the stack effluent and give minimal (<3 percent) interference to measurement by the gas analyzer.

16.1.3 Procedure. Select upstream and downstream locations in the stack or duct for introducing the tracer gas and delivering the sampled gas to the analyzer. The inlet location should be 8 or more duct diameters beyond any upstream flow disturbance. The outlet should be 8 or more undisturbed duct diameters from the inlet and 2 or more duct diameters from the duct exit. After installing the apparatus, meter a known concentration of the tracer gas into the stack at the inlet location. Use the gas sample probe and analyzer to show that no stratification of the tracer gas is found in the stack at the measurement locations. Monitor the tracer gas concentration from the outlet location and record the concentration at 10-minute intervals or more often at the option of the tester. A minimum of three measured intervals is recommended to determine the stack gas volumetric flow rate. Other statistical procedures may be applied for complete flow characterization and additional QA/QC.

17.0 References

Same as Method 5G, section 17.0.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

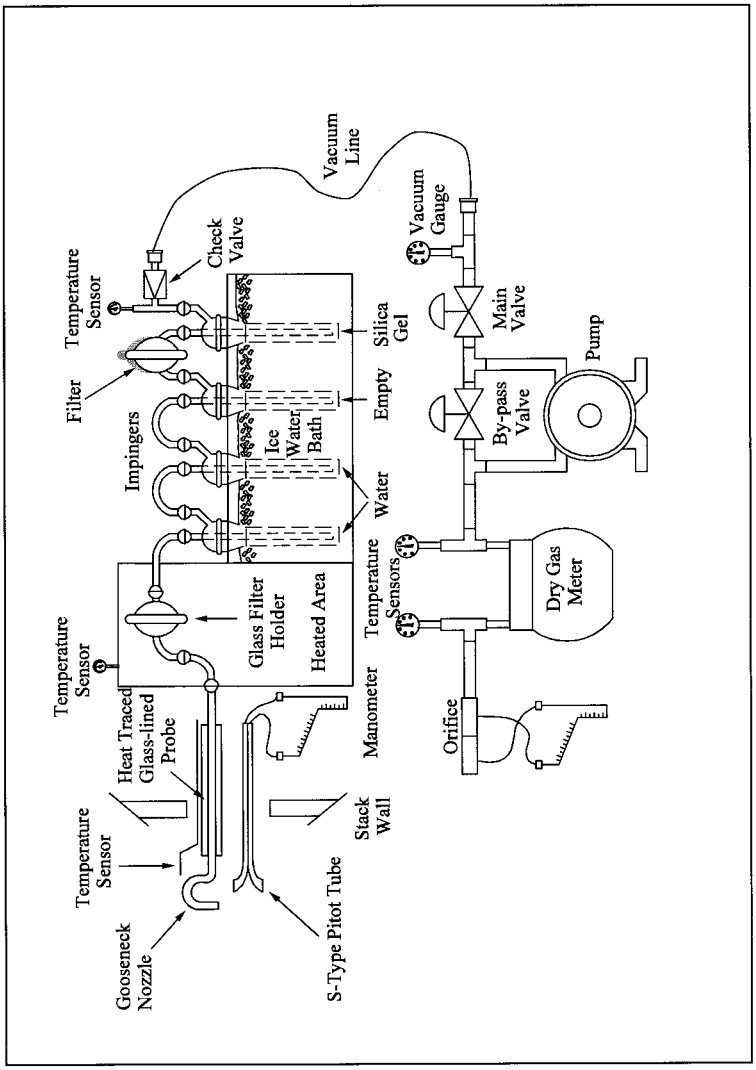


Figure 5H-1. Sampling Train.

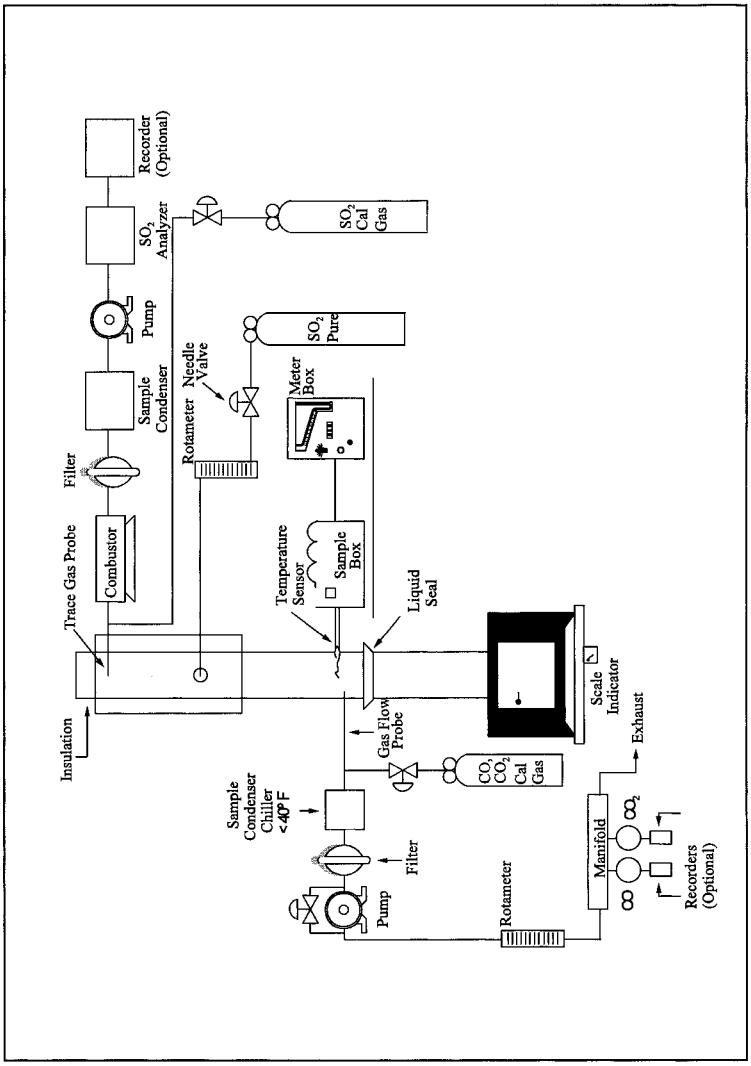
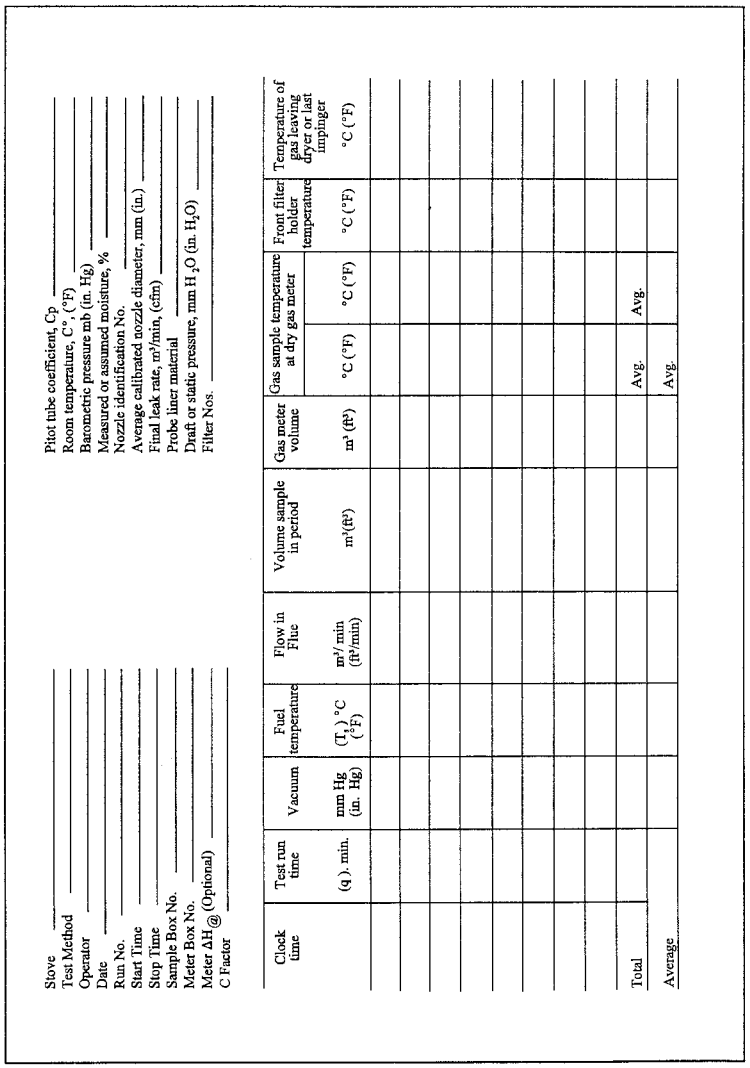


Figure 5H-2. Test System Schematic.



Stove _____
Test Method _____
Operator _____
Date _____
Run No. _____
Start Time _____
Stop Time _____
Sample Box No. _____
Meter Box No. _____
Meter ΔH @ (Optional) _____
C Factor _____

Pitot tube coefficient, Cp _____
Room temperature, C°, (°F) _____
Barometric pressure mb (in. Hg) _____
Measured or assumed moisture, % _____
Nozzle identification No. _____
Average calibrated nozzle diameter, mm (in.) _____
Final leak rate, m³/min, (cfm) _____
Probe liner material _____
Draft or static pressure, mm H_2O (in. H_2O) _____
Filter Nos. _____

Clock time	Test run time (q), min.	Vacuum mm Hg (in. Hg)	Fuel temperature (T_s) °C (°F)	Flow in Flue m³/ min (ft³/min)	Volume sample in period m³(ft³)	Gas meter volume m³ (ft³)	Gas sample temperature at dry gas meter °C (°F)	Gas sample temperature at dry gas meter °C (°F)	Front filter holder temperature °C (°F)	Temperature of gas leaving dryer or last impinger °C (°F)
Total							Avg.	Avg.		
Average							Avg.			

Figure 5H-3. Sampling Data Sheet.

Stove _____
Date _____
Run No. _____
Filter Nos. _____
Amount liquid lost during transport, ml _____
Acetone blank volume, ml _____
Acetone wash volume, ml _____
Acetone blank concentration, mg/ml _____
Acetone wash blank, mg _____

Dichloromethane blank volume, ml _____
Dichloromethane wash volume, ml _____
Dichloromethane blank concentration, mg/ml _____
Dichloromethane wash blank, mg _____
Water blank volume, ml _____
Waster wash volume, ml _____
Water blank concentration, mg/ml _____
Water wash blank, mg _____

Container number	Weight of particulate collected, mg		
	Final weight	Tare weight	Weight gain
1 _____			
2 _____			
3 _____			
4 _____			
5 _____			
Total			
Less acetone blank			
Less dichloromethane blank			
Less water blank			
Weight of particulate matter			

	Volume of liquid water collected	
	Impinger volume, ml	Silica gel weight, g
Final _____		
Initial _____		
Liquid collected _____		
Total volume collected _____		g or ml

* Convert weight of water to volume by dividing total weight increase by density of water (1 g/ml).

$$\frac{\text{Increase, g}}{\text{(1 g/ml)}} = \text{Volume water, ml}$$

Figure 5H-4. Analysis data sheet.

Figure 5H-4. Analysis Data Sheet.

METHOD 5I—DETERMINATION OF LOW LEVEL PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Certain information is contained in other EPA procedures found in this part. Therefore, to obtain reliable results, persons using this method should have experience with and a thorough knowledge of the following Methods: Methods 1, 2, 3, 4 and 5.

1. Scope and Application.

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of low level particulate matter (PM) emissions from stationary sources. The method is most effective for total PM catches of 50 mg or less. This method was initially developed for performing correlation of manual PM measurements to PM continuous emission monitoring systems (CEMS), however it is also useful for other low particulate concentration applications.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods. Method 5I requires the use of paired trains. Acceptance criteria for the identification of data quality outliers from the paired trains are provided in section 12.2 of this Method.

2. Summary of Method.

2.1. Description. The system setup and operation is essentially identical to Method 5. Particulate is withdrawn isokinetically from the source and collected on a 47 mm glass fiber filter maintained at a temperature of 120 ±14 °C (248 ±25 °F). The PM mass is determined by gravimetric analysis after the removal of uncombined water. Specific measures in this procedure designed to improve system performance at low particulate levels include:

1. Improved sample handling procedures
2 Light weight sample filter assembly
3. Use of low residue grade acetone

Accuracy is improved through the minimization of systemic errors associated with sample handling and weighing procedures. High purity reagents, all glass, grease free, sample train components, and light weight filter assemblies and beakers, each contribute to the overall objective of improved precision and accuracy at low particulate concentrations.

2.2 Paired Trains. This method must be performed using a paired train configuration. These trains may be operated as co-located trains (to trains operating collecting from one port) or as simultaneous trains (separate trains operating from different ports at the same time). Procedures for calculating precision of the paired trains are provided in section 12.

2.3 Detection Limit. a. Typical detection limit for manual particulate testing is 0.5 mg. This mass is also cited as the accepted weight variability limit in determination of ''constant weight'' as cited in section 8.1.2 of this Method. EPA has performed studies to provide guidance on minimum PM catch. The minimum detection limit (MDL) is the minimum concentration or amount of an analyte that can be determined with a specified degree of confidence to be different from zero. We have defined the minimum or target catch as a concentration or amount sufficiently larger than the MDL to ensure that the results are reliable and repeatable. The particulate matter catch is the product of the average particulate matter concentration on a mass per volume basis and the volume of gas collected by the sample train. The tester can generally control the volume of gas collected by increasing the sampling time or to a lesser extent by increasing the rate at which sample is collected. If the tester has a reasonable estimate of the PM concentration from the source, the tester can ensure that the target catch is collected by sampling the appropriate gas volume.

b. However, if the source has a very low particulate matter concentration in the stack, the volume of gas sampled may need to be very large which leads to unacceptably long sampling times. When determining compliance with an emission limit, EPA guidance has been that the tester does not always have to collect the target catch. Instead, we have suggested that the tester sample enough stack gas, that if the source were exactly at the level of the emission standard, the sample catch would equal the target catch. Thus, if at the end of the test the catch were smaller than the target, we could still conclude that the source is in compliance though we might not know the exact emission level. This volume of gas becomes a target volume that can be translated into a target sampling time by assuming an average sampling rate. Because the MDL forms the basis for our guidance on target sampling times, EPA has conducted a systematic laboratory study to define what is the MDL for Method 5 and determined the Method to have a calculated practical quantitation limit (PQL) of 3 mg of PM and an MDL of 1 mg.

c. Based on these results, the EPA has concluded that for PM testing, the target catch must be no less than 3 mg. Those sample catches between 1 mg and 3 mg are between the detection limit and the limit of quantitation. If a tester uses the target catch to estimate a target sampling time that results in sample catches that are less than 3 mg, you should not automatically reject the results. If the tester calculated the target sampling time as described above by assuming that the source was at the level of the emission limit, the results would still be valid for determining that the source was in compliance. For purposes other than determining compliance, results should be divided into two categories—those that fall between 3 mg and 1 mg and those that are below 1 mg. A sample catch between 1 and 3 mg may be used for such purposes as calculating emission rates with the understanding that the resulting emission rates can have a high degree of uncertainty. Results of less than 1 mg should not be used for calculating emission rates or pollutant concentrations.

d. When collecting small catches such as 3 mg, bias becomes an important issue. Source testers must use extreme caution to reach the PQL of 3 mg by assuring that sampling

probes are very clean (perhaps confirmed by low blank weights) before use in the field. They should also use low tare weight sample containers, and establish a well-controlled balance room to weigh the samples.

3. Definitions.

3.1 *Light Weight Filter Housing.* A smaller housing that allows the entire filtering system to be weighed before and after sample collection. (See. 6.1.3)

3.2 *Paired Train.* Sample systems trains may be operated as co-located trains (two sample probes attached to each other in the same port) or as simultaneous trains (two separate trains operating from different ports at the same time).

4. Interferences.

a. There are numerous potential interferents that may be encountered during performance of Method 5I sampling and analyses. This Method should be considered more sensitive to the normal interferents typically encountered during particulate testing because of the low level concentrations of the flue gas stream being sampled.

b. Care must be taken to minimize field contamination, especially to the filter housing since the entire unit is weighed (not just the filter media). Care must also be taken to ensure that no sample is lost during the sampling process (such as during port changes, removal of the filter assemblies from the probes, etc.).

c. Balance room conditions are a source of concern for analysis of the low level samples. Relative humidity, ambient temperatures variations, air draft, vibrations and even barometric pressure can affect consistent reproducible measurements of the sample media. Ideally, the same analyst who performs the tare weights should perform the final weights to minimize the effects of procedural differences specific to the analysts.

d. Attention must also be provided to weighing artifacts caused by electrostatic charges which may have to be discharged or neutralized prior to sample analysis. Static charge can affect consistent and reliable gravimetric readings in low humidity environments. Method 5I recommends a relative humidity of less than 50 percent in the weighing room environment used for sample analyses. However, lower humidity may be encountered or required to address sample precision problems. Low humidity conditions can increase the effects of static charge.

e. Other interferences associated with typical Method 5 testing (sulfates, acid gases, etc.) are also applicable to Method 5I.

5. Safety.

Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety concerns associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability and observe all regulatory limitations before using this method.

6. Equipment and Supplies.

6.1 Sample Collection Equipment and Supplies. The sample train is nearly identical in configuration to the train depicted in Figure 5–1 of Method 5. The primary difference in the sample trains is the lightweight Method 5I filter assembly that attaches directly to the exit to the probe. Other exceptions and additions specific to Method 5I include:

6.1.1 Probe Nozzle. Same as Method 5, with the exception that it must be constructed of borosilicate or quartz glass tubing.

6.1.2 Probe Liner. Same as Method 5, with the exception that it must be constructed of borosilicate or quartz glass tubing.

6.1.3 Filter Holder. The filter holder is constructed of borosilicate or quartz glass front cover designed to hold a 47-mm glass fiber filter, with a wafer thin stainless steel (SS) filter support, a silicone rubber or Viton O-ring, and Teflon tape seal. This holder design will provide a positive seal against leakage from the outside or around the filter. The filter holder assembly fits into a SS filter holder and attaches directly to the outlet of the probe. The tare weight of the filter, borosilicate or quartz glass holder, SS filter support, O-ring and Teflon tape seal generally will not exceed approximately 35 grams. The filter holder is designed to use a 47-mm glass fiber filter meeting the quality criteria in of Method 5. These units are commercially available from several source testing equipment vendors. Once the filter holder has been assembled, desiccated and tared, protect it from external sources of contamination by covering the front socket with a ground glass plug. Secure the plug with an impinger clamp or other item that will ensure a leak-free fitting.

6.2 Sample Recovery Equipment and Supplies. Same as Method 5, with the following exceptions:

6.2.1 Probe-Liner and Probe-Nozzle Brushes. Teflon or nylon bristle brushes with stainless steel wire handles, should be used to clean the probe. The probe brush must have extensions (at least as long as the probe) of Teflon, nylon or similarly inert material. The brushes must be properly sized and shaped for brushing out the probe liner and nozzle.

6.2.2 Wash Bottles. Two Teflon wash bottles are recommended however, polyethylene wash bottles may be used at the option of the tester. Acetone should not be stored in polyethylene bottles for longer than one month.

6.2.3 Filter Assembly Transport. A system should be employed to minimize contamination of the filter assemblies during transport to and from the field test location. A carrying case or packet with clean compartments of sufficient size to accommodate each filter assembly can be used. This system should have an air tight seal to further minimize contamination during transport to and from the field.

6.3 Analysis Equipment and Supplies. Same as Method 5, with the following exception:

6.3.1 Lightweight Beaker Liner. Teflon or other lightweight beaker liners are used for the analysis of the probe and nozzle rinses. These light weight liners are used in place of the borosilicate glass beakers typically used for the Method 5 weighings in order to improve sample analytical precision.

6.3.2 Anti-static Treatment. Commercially available gaseous anti-static rinses are recommended for low humidity situations that contribute to static charge problems.

7. Reagents and Standards.

7.1 Sampling Reagents. The reagents used in sampling are the same as Method 5 with the following exceptions:

7.1.1 Filters. The quality specifications for the filters are identical to those cited for Method 5. The only difference is the filter diameter of 47 millimeters.

7.1.2 Stopcock Grease. Stopcock grease cannot be used with this sampling train. We recommend that the sampling train be assembled with glass joints containing O-ring seals or screw-on connectors, or similar.

7.1.3 Acetone. Low residue type acetone, ≤0.001 percent residue, purchased in glass bottles is used for the recovery of particulate matter from the probe and nozzle. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers; thus, acetone blanks must be run prior to field use and only acetone with low blank values (≤0.001 percent residue, as specified by the manufacturer) must be used. Acetone blank correction is not allowed for this method; therefore, it is critical that high purity reagents be purchased and verified prior to use.

7.1.4 Gloves. Disposable, powder-free, latex surgical gloves, or their equivalent are used at all times when handling the filter housings or performing sample recovery.

7.2 Standards. There are no applicable standards commercially available for Method 5I analyses.

8. Sample Collection, Preservation, Storage, and Transport.

8.1 Pretest Preparation. Same as Method 5 with several exceptions specific to filter assembly and weighing.

8.1.1 Filter Assembly. Uniquely identify each filter support before loading filters into the holder assembly. This can be done with an engraving tool or a permanent marker. Use powder free latex surgical gloves whenever handling the filter holder assemblies. Place the O-ring on the back of the filter housing in the O-ring groove. Place a 47 mm glass fiber filter on the O-ring with the face down. Place a stainless steel filter holder against the back of the filter. Carefully wrap 5 mm (¼ inch) wide Teflon'' tape one timearound the outside of the filter holder overlapping the stainless steel filter support by approximately 2.5 mm (⅛ inch). Gently brush the Teflon tape down on the back of the stainless steel filter support. Store the filter assemblies in their transport case until time for weighing or field use.

8.1.2 Filter Weighing Procedures. a. Desiccate the entire filter holder assemblies at 20 ±5.6 °C (68 ±10 °F) and ambient pressure for at least 24 hours. Weigh at intervals of at least 6 hours to a constant weight, *i.e.,* 0.5 mg change from previous weighing. Record the results to the nearest 0.1 mg. During each weighing, the filter holder assemblies must not be exposed to the laboratory atmosphere for a period greater than 2 minutes and a relative humidity above 50 percent. Lower relative humidity may be required in order to improve analytical precision. However, low humidity conditions increase static charge to the sample media.

b. Alternatively (unless otherwise specified by the Administrator), the filters holder assemblies may be oven dried at 105 °C (220 °F) for a minimum of 2 hours, desiccated for 2 hours, and weighed. The procedure used for the tare weigh must also be used for the final weight determination.

c. Experience has shown that weighing uncertainties are not only related to the balance performance but to the entire weighing procedure. Therefore, before performing any measurement, establish and follow standard operating procedures, taking into account the sampling equipment and filters to be used.

8.2 Preliminary Determinations. Select the sampling site, traverse points, probe nozzle, and probe length as specified in Method 5.

8.3 Preparation of Sampling Train. Same as Method 5, section 8.3, with the following exception: During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until justbefore assembly or until sampling is about to begin. Using gloves, place a labeled (identified) and weighed filter holder assembly into the stainless steel holder. Then place this whole unit in the Method 5 hot box, and attach it to the probe. Do not use stopcock grease.

8.4 Leak-Check Procedures. Same as Method 5.

8.5 Sampling Train Operation.

8.5.1. Operation. Operate the sampling train in a manner consistent with those described in Methods 1, 2, 4 and 5 in terms of the number of sample points and minimum time per point. The sample rate and total gas volume should be adjusted based on estimated grain loading of the source being characterized. The total sampling time must be a function of the estimated mass of particulate to be collected for the run. Targeted mass to be collected in a typical Method 5I sample train should be on the order of 10 to 20 mg. Method 5I is most appropriate for total collected masses of less than 50 milligrams, however, there is not an exact particulate loading cutoff, and it is likely that some runs may exceed 50 mg. Exceeding 50 mg (or less than 10 mg) for the sample mass does not necessarily justify invalidating a sample run if all other Method criteria are met.

8.5.2 Paired Train. This Method requires PM samples be collected with paired trains.

8.5.2.1 It is important that the systems be operated truly simultaneously. This implies that both sample systems start and stop at the same times. This also means that if one sample system is stopped during the run, the other sample systems must also be stopped until the cause has been corrected.

8.5.2.2 Care should be taken to maintain the filter box temperature of the paired trains as close as possible to the Method required temperature of 120 ±14 °C (248 ±25 °F). If separate ovens are being used for simultaneously operated trains, it is recommended that the oven temperature of each train be maintained within ±14 °C (±25 °F) of each other.

8.5.2.3 The nozzles for paired trains need not be identically sized.

8.5.2.4 Co-located sample nozzles must be within the same plane perpendicular to the gas flow. Co-located nozzles and pitot assemblies should be within a 6.0 cm × 6.0 cm square (as cited for a quadruple train in Reference Method 301).

8.5.3 Duplicate gas samples for molecular weight determination need not be collected.

8.6 Sample Recovery. Same as Method 5 with several exceptions specific to the filter housing.

8.6.1 Before moving the sampling train to the cleanup site, remove the probe from the train and seal the nozzle inlet and outlet of the probe. Be careful not to lose any condensate that might be present. Cap the filter inlet using a standard ground glass plug and secure the cap with an impinger clamp. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger condenser and the filter holder, disconnect the line at the filter holder and let any condensed water or liquid drain into the impingers or condenser.

8.6.2 Transfer the probe and filter-impinger assembly to the cleanup area. This area must be clean and protected from the wind so that the possibility of losing any of the sample will be minimized.

8.6.3 Inspect the train prior to and during disassembly and note any abnormal conditions such as particulate color, filter loading, impinger liquid color, etc.

8.6.4 Container No. 1, Filter Assembly. Carefully remove the cooled filter holder assembly from the Method 5 hot box and place it in the transport case. Use a pair of clean gloves to handle the filter holder assembly.

8.6.5 Container No. 2, Probe Nozzle and Probe Liner Rinse. Rinse the probe and nozzle components with acetone. Be certain that the probe and nozzle brushes have been thoroughly rinsed prior to use as they can be a source of contamination.

8.6.6 All Other Train Components. (Impingers) Same as Method 5.

8.7 Sample Storage and Transport. Whenever possible, containers should be shipped in such a way that they remain upright at all times. All appropriate dangerous goods shipping requirements must be observed since acetone is a flammable liquid.

9. Quality Control.

9.1 Miscellaneous Field Quality Control Measures.

9.1.1 A quality control (QC) check of the volume metering system at the field site is suggested before collecting the sample using the procedures in Method 5, section 4.4.1.

9.1.2 All other quality control checks outlined in Methods 1, 2, 4 and 5 also apply to Method 5I. This includes procedures such as leak-checks, equipment calibration checks, and independent checks of field data sheets for reasonableness and completeness.

9.2 Quality Control Samples.

9.2.1 Required QC Sample. A laboratory reagent blank must be collected and analyzed for each lot of acetone used for a field program to confirm that it is of suitable purity. The particulate samples cannot be blank corrected.

9.2.2 Recommended QC Samples. These samples may be collected and archived for future analyses.

9.2.2.1 A field reagent blank is a recommended QC sample collected from a portion of the acetone used for cleanup of the probe and nozzle. Take 100 ml of this acetone directly from the wash bottle being used and place it in a glass sample container labeled ''field acetone reagent blank.'' At least one field reagent blank is recommended for every five runs completed. The field reagent blank samples demonstrate the purity of the acetone was maintained throughout the program.

9.2.2.2 A field bias blank train is a recommended QC sample. This sample is collected by recovering a probe and filter assembly that has been assembled, taken to the sample location, leak checked, heated, allowed to sit at the sample location for a similar duration of time as a regular sample run, leak-checked again, and then recovered in the same manner as a regular sample. Field bias blanks are not a Method requirement, however, they are recommended and are very useful for identifying sources of contamination in emission testing samples. Field bias blank train results greater than 5 times the method detection limit may be considered problematic.

10. Calibration and Standardization Same as Method 5, section 5.

10.1 Field Balance Calibration Check. Check the calibration of the balance used to weigh impingers with a weight that is at least 500g or within 50g of a loaded impinger. The weight must be ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 6 (or better). Daily, before use, the field balance must measure the weight within ±0.5g of the certified mass. If the daily balance calibration check fails, perform corrective measures and repeat the check before using balance.

10.2 Analytical Balance Calibration. Perform a multipoint calibration (at least five points spanning the operational range) of the analytical balance before the first use, and semiannually thereafter. The calibration of the analytical balance must be conducted using ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 2 (or better) tolerance weights. Audit the balance each day it is used for gravimetric measurements by weighing at least one ASTM E617–13 Class 2 tolerance (or better) calibration weight that corresponds to 50 to 150 percent of the weight of one filter or between 1g and 5g. If the scale cannot reproduce the value of the calibration weight to within 0.5 mg of the certified mass, perform corrective measures and conduct the multipoint calibration before use.

11. Analytical Procedures.

11.1 Analysis. Same as Method 5, sections 11.1–11.2.4, with the following exceptions:

11.1.1 Container No. 1. Same as Method 5, section 11.2.1, with the following exception: Use disposable gloves to remove each of the filter holder assemblies from the desiccator, transport container, or sample oven (after appropriate cooling).

11.1.2 Container No. 2. Same as Method 5, section 11.2.2, with the following exception: It is recommended that the contents of Container No. 2 be transferred to a 250 ml beaker with a Teflon liner or similar container that has a minimal tare weight before bringing to dryness.

12. Data Analysis and Calculations.

12.1 Particulate Emissions. The analytical results cannot be blank corrected for residual acetone found in any of the blanks. All other sample calculations are identical to Method 5.

12.2 Paired Trains Outliers. a. Outliers are identified through the determination of precision and any systemic bias of the paired trains. Data that do not meet this criteria should be flagged as a data quality problem. The primary reason for performing dual train sampling is to generate information to quantify the precision of the Reference Method data. The relative standard deviation (RSD) of paired data is the parameter used to quantify data precision. RSD for two simultaneously gathered data points is determined according to:

$$RSD = 100\% * \left|\left(C_a - C_b\right)\right| / \left(C_a + C_b\right)$$

where, Ca and Cb are concentration values determined from trains A and B respectively. For RSD calculation, the concentration units are unimportant so long as they are consistent.

b. A minimum precision criteria for Reference Method PM data is that RSD for any data pair must be less than 10% as long as the mean PM concentration is greater than 10 mg/dscm. If the mean PM concentration is less than 10 mg/dscm higher RSD values are acceptable. At mean PM concentration of 1 mg/dscm acceptable RSD for paired trains is 25%. Between 1 and 10 mg/dscm acceptable RSD criteria should be linearly scaled from 25% to 10%. Pairs of manual method data exceeding these RSD criteria should be eliminated from the data set used to develop a PM CEMS correlation or to assess RCA. If the mean PM concentration is less than 1 mg/dscm, RSD does not apply and the mean result is acceptable.

13. Method Performance [Reserved]

14. Pollution Prevention [Reserved]

15. Waste Management [Reserved]

16. Alternative Procedures. Same as Method 5.

17. Bibliography. Same as Method 5.

18. Tables, Diagrams, Flowcharts and Validation Data. Figure 5I–1 is a schematic of the sample train.

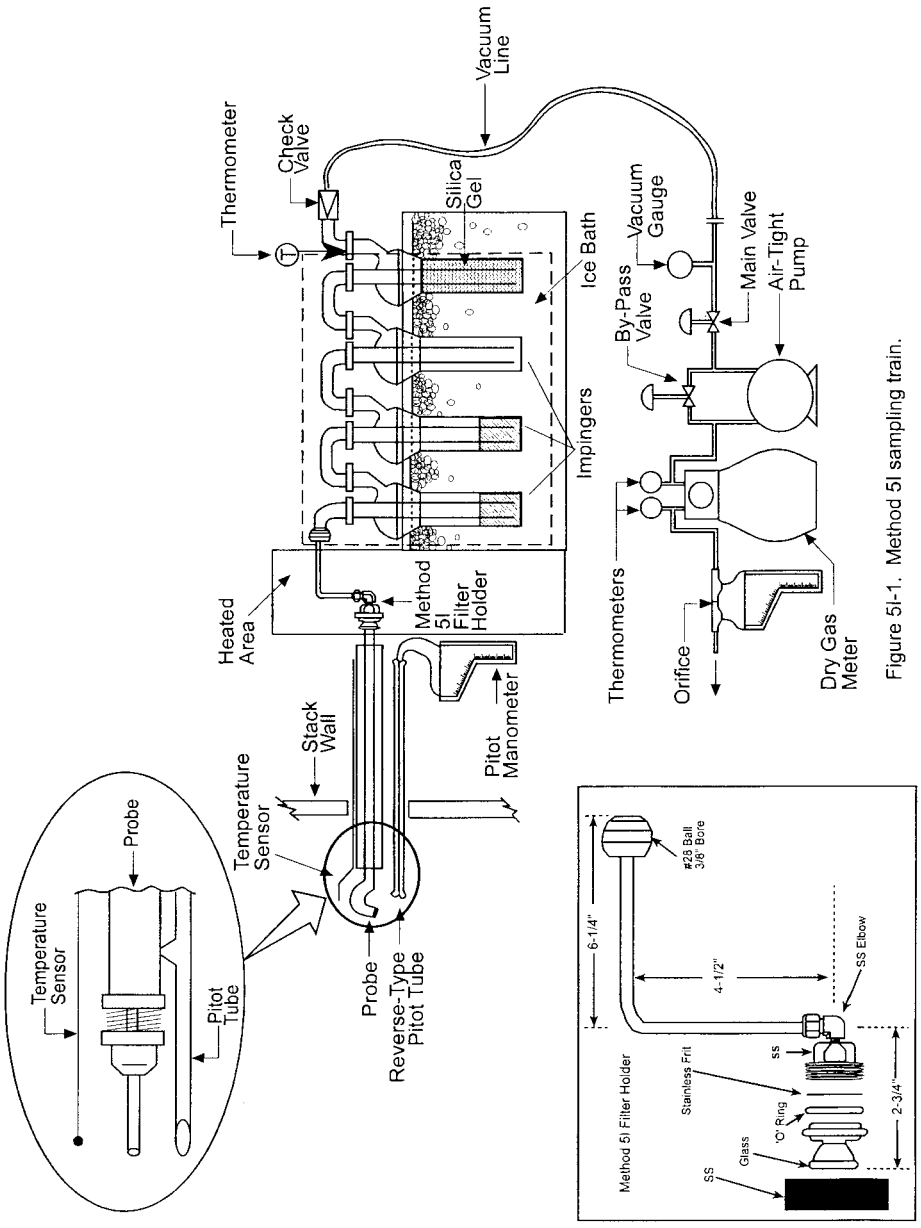


Figure 5I-1. Method 5I sampling train.

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–3 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

APPENDIX A–6 TO PART 60—TEST METHODS 16 THROUGH 18

Method 16—Semicontinuous determination of sulfur emissions from stationary sources
Method 16A—Determination of total reduced sulfur emissions from stationary sources (impinger technique)
Method 16B—Determination of total reduced sulfur emissions from stationary sources
Method 16C—Determination of Total Reduced Sulfur Emissions From Stationary Sources
Method 17—Determination of particulate emissions from stationary sources (in-stack filtration method)
Method 18—Measurement of gaseous organic compound emissions by gas chromatography

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

METHOD 16—SEMICONTINUOUS DETERMINATION OF SULFUR EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of

at least the following additional test methods: Method 1, Method 4, Method 15, and Method 16A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Dimethyl disulfide [$(CH_3)_2S_2$]	62–49–20	50 ppb.
Dimethyl sulfide [$(CH_3)_2S$]	75–18–3	50 ppb.
Hydrogen sulfide [H_2S]	7783–06–4	50 ppb.
Methyl mercaptan [CH_4S]	74–93–1	50 ppb.

1.2 Applicability. This method is applicable for the determination of total reduced sulfur (TRS) compounds from recovery furnaces, lime kilns, and smelt dissolving tanks at kraft pulp mills and fuel gas combustion devices at petroleum refineries.

NOTE: The method described below uses the principle of gas chromatographic (GC) separation and flame photometric detection (FPD). Since there are many systems or sets of operating conditions that represent useable methods of determining sulfur emissions, all systems which employ this principle, but differ only in details of equipment and operation, may be used as alternative methods, provided that the calibration precision and sample line loss criteria are met.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the emission source and an aliquot is analyzed for hydrogen sulfide (H_2S), methyl mercaptan (MeSH), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS) by GC/FPD. These four compounds are known collectively as TRS.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Moisture. Moisture condensation in the sample delivery system, the analytical column, or the FPD burner block can cause losses or interferences. This is prevented by maintaining the probe, filter box, and connections at a temperature of at least 120 °C (248 °F). Moisture is removed in the SO_2 scrubber and heating the sample beyond this point is not necessary when the ambient temperature is above 0 °C (32 °F). Alternatively, moisture may be eliminated by heating the sample line, and by conditioning the sample with dry dilution air to lower its dew point below the operating temperature of the GC/FPD analytical system prior to analysis.

4.2 Carbon Monoxide (CO) and Carbon Dioxide (CO_2). CO and CO_2 have a substantial desensitizing effect on the flame photometric detector even after dilution. Acceptable systems must demonstrate that they have eliminated this interference by some procedure such as eluting these compounds before any of the compounds to be measured. Compliance with this requirement can be demonstrated by submitting chromatograms of calibration gases with and without CO_2 in the diluent gas. The CO_2 level should be approximately 10 percent for the case with CO_2 present. The two chromatograms should show agreement within the precision limits of section 10.2.

4.3 Particulate Matter. Particulate matter in gas samples can cause interference by eventual clogging of the analytical system. This interference is eliminated by using the Teflon filter after the probe.

4.4 Sulfur Dioxide (SO_2). Sulfur dioxide is not a specific interferant but may be present in such large amounts that it cannot effectively be separated from the other compounds of interest. The SO_2 scrubber described in section 6.1.3 will effectively remove SO_2 from the sample.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hydrogen Sulfide. A flammable, poisonous gas with the odor of rotten eggs. H_2S is extremely hazardous and can cause collapse, coma, and death within a few seconds of one or two inhalations at sufficient concentrations. Low concentrations irritate the mucous membranes and may cause nausea, dizziness, and headache after exposure.

6.0 Equipment and Supplies

6.1. Sample Collection. The following items are needed for sample collection.

6.1.1 Probe. Teflon or Teflon-lined stainless steel. The probe must be heated to prevent moisture condensation. It must be designed to allow calibration gas to enter the probe at or near the sample point entry. Any portion of the probe that contacts the stack gas

must be heated to prevent moisture condensation. Figure 16–1 illustrates the probe used in lime kilns and other sources where significant amounts of particulate matter are present. The probe is designed with the deflector shield placed between the sample and the gas inlet holes to reduce clogging of the filter and possible adsorption of sample gas. As an alternative, the probe described in section 6.1.1 of Method 16A having a nozzle directed away from the gas stream may be used at sources having significant amounts of particulate matter.

6.1.2 Particulate Filter. 50–mm Teflon filter holder and a 1- to 2-micron porosity Teflon filter (available through Savillex Corporation, 5325 Highway 101, Minnetonka, Minnesota 55343). The filter holder must be maintained in a hot box at a temperature of at least 120 °C (248 °F).

6.1.3 SO_2 Scrubber. Three 300-ml Teflon segmented impingers connected in series with flexible, thick-walled, Teflon tubing. (Impinger parts and tubing available through Savillex.) The first two impingers contain 100 ml of citrate buffer and the third impinger is initially dry. The tip of the tube inserted into the solution should be constricted to less than 3 mm (⅛ in.) ID and should be immersed to a depth of at least 5 cm (2 in.). Immerse the impingers in an ice water bath and maintain near 0 °C (32 °F). The scrubber solution will normally last for a 3-hour run before needing replacement. This will depend upon the effects of moisture and particulate matter on the solution strength and pH. Connections between the probe, particulate filter, and SO_2 scrubber must be made of Teflon and as short in length as possible. All portions of the probe, particulate filter, and connections prior to the SO_2 scrubber (or alternative point of moisture removal) must be maintained at a temperature of at least 120 °C (248 °F).

6.1.4 Sample Line. Teflon, no greater than 1.3 cm (½ in.) ID. Alternative materials, such as virgin Nylon, may be used provided the line loss test is acceptable.

6.1.5 Sample Pump. The sample pump must be a leakless Teflon-coated diaphragm type or equivalent.

6.2 Analysis. The following items are needed for sample analysis:

6.2.1 Dilution System. Needed only for high sample concentrations. The dilution system must be constructed such that all sample contacts are made of Teflon, glass, or stainless steel.

6.2.2 Gas Chromatograph. The gas chromatograph must have at least the following components:

6.2.2.1 Oven. Capable of maintaining the separation column at the proper operating temperature ±1 °C (2 °F).

6.2.2.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperature ±1 °C (2 °F).

6.2.2.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

6.2.2.4 Flame Photometric Detector.

6.2.2.4.1 Electrometer. Capable of full scale amplification of linear ranges of 10^{-9} to 10^{-4} amperes full scale.

6.2.2.4.2 Power Supply. Capable of delivering up to 750 volts.

6.2.2.4.3 Recorder. Compatible with the output voltage range of the electrometer.

6.2.2.4.4 Rotary Gas Valves. Multiport Teflon-lined valves equipped with sample loop. Sample loop volumes must be chosen to provide the needed analytical range. Teflon tubing and fittings must be used throughout to present an inert surface for sample gas. The gas chromatograph must be calibrated with the sample loop used for sample analysis.

6.2.3 Gas Chromatogram Columns. The column system must be demonstrated to be capable of resolving the four major reduced sulfur compounds: H_2S, MeSH, DMS, and DMDS. It must also demonstrate freedom from known interferences. To demonstrate that adequate resolution has been achieved, submit a chromatogram of a calibration gas containing all four of the TRS compounds in the concentration range of the applicable standard. Adequate resolution will be defined as base line separation of adjacent peaks when the amplifier attenuation is set so that the smaller peak is at least 50 percent of full scale. Baseline separation is defined as a return to zero ±5 percent in the interval between peaks. Systems not meeting this criteria may be considered alternate methods subject to the approval of the Administrator.

6.3 Calibration. A calibration system, containing the following components, is required (see Figure 16–2).

6.3.1 Tube Chamber. Chamber of glass or Teflon of sufficient dimensions to house permeation tubes.

6.3.2 Flow System. To measure air flow over permeation tubes at ±2 percent. Flow over the permeation device may also be determined using a soap bubble flowmeter.

6.3.3 Constant Temperature Bath. Device capable of maintaining the permeation tubes at the calibration temperature within 0.1 °C (0.2 °F).

6.3.4 Temperature Gauge. Thermometer or equivalent to monitor bath temperature within 1 °C (2 °F).

7.0 Reagents and Standards

7.1 Fuel. Hydrogen (H_2), prepurified grade or better.

7.2 Combustion Gas. Oxygen (O_2) or air, research purity or better.

7.3 Carrier Gas. Prepurified grade or better.

7.4 Diluent (if required). Air containing less than 50 ppb total sulfur compounds and less than 10 ppmv each of moisture and total hydrocarbons.

7.5 Calibration Gases

7.5.1 Permeation tubes, one each of H_2S, MeSH, DMS, and DMDS, gravimetrically calibrated and certified at some convenient operating temperature. These tubes consist of hermetically sealed FEP Teflon tubing in which a liquified gaseous substance is enclosed. The enclosed gas permeates through the tubing wall at a constant rate. When the temperature is constant, calibration gases covering a wide range of known concentrations can be generated by varying and accurately measuring the flow rate of diluent gas passing over the tubes. These calibration gases are used to calibrate the GC/FPD system and the dilution system.

7.5.2 Cylinder Gases. Cylinder gases may be used as alternatives to permeation devices. The gases must be traceable to a primary standard (such as permeation tubes) and not used beyond the certification expiration date.

7.6 Citrate Buffer and Sample Line Loss Gas. Same as Method 15, sections 7.6 and 7.7.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as Method 15, section 8.0, except that the references to the dilution system may not be applicable.

9.0 Quality Control

Section	Quality control measure	Effect
8.0	Sample line loss check	Ensures that uncorrected negative bias introduced by sample loss is no greater than 20 percent, and provides for correction of bias of 20 percent or less.
8.0	Calibration drift test	Ensures that bias introduced by drift in the measurement system output during the run is no greater than 5 percent.
10.0	Analytical calibration	Ensures precision of analytical results within 5 percent.

10.0 Calibration and Standardization

Same as Method 15, section 10.0, with the following addition and exceptions:

10.1 Use the four compounds that comprise TRS instead of the three reduced sulfur compounds measured by Method 15.

10.2 Flow Meter. Calibration before each test run is recommended, but not required; calibration following each test series is mandatory. Calibrate each flow meter after each complete test series with a wet-test meter. If the flow measuring device differs from the wet-test meter by 5 percent or more, the completed test runs must be voided. Alternatively, the flow data that yield the lower flow measurement may be used. Flow over the permeation device may also be determined using a soap bubble flowmeter.

11.0 Analytical Procedure

Sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Data Analysis and Calculations

12.1 Concentration of Reduced Sulfur Compounds. Calculate the average concentration of each of the four analytes (*i.e.*, DMDS, DMS, H_2S, and MeSH) over the sample run (specified in section 8.2 of Method 15 as 16 injections).

$$C = \frac{\sum_{i=1}^{N} S_i}{N} \qquad \text{Eq. 16-1}$$

Where:

S_i = Concentration of any reduced sulfur compound from the i^{th} sample injection, ppm.

C = Average concentration of any one of the reduced sulfur compounds for the entire run, ppm.

N = Number of injections in any run period.

12.2 TRS Concentration. Using Equation 16–2, calculate the TRS concentration for each sample run.

$$C_{TRS} = d\sum\left(C_{H_2S} + C_{MeSH} + C_{DMS} + 2C_{DMDS}\right) \qquad \text{Eq. 16-2}$$

Where:

C_{TRS} = TRS concentration, ppmv.

C_{H2S} = Hydrogen sulfide concentration, ppmv.

C_{MeSH} = Methyl mercaptan concentration, ppmv.

C_{DMS} = Dimethyl sulfide concentration, ppmv.

C_{DMDS} = Dimethyl disulfide concentration, ppmv.

d = Dilution factor, dimensionless.

12.3 Average TRS Concentration. Calculate the average TRS concentration for all sample runs performed.

$$\text{Average TRS} = \frac{\sum_{i=1}^{n} TRS_i}{N(1 - B_{wo})} \qquad \text{Eq. 16-3}$$

Where:

Average TRS = Average total reduced sulfur in ppm.

TRS_i = Total reduced sulfur in ppm as determined by Equation 16–2.

N = Number of samples.

B_{wo} = Fraction of volume of water vapor in the gas stream as determined by Method 4—Determination of Moisture in Stack Gases.

13.0 Method Performance

13.1 Analytical Range. The analytical range will vary with the sample loop size. Typically, the analytical range may extend from 0.1 to 100 ppmv using 10- to 0.1-ml sample loop sizes. This eliminates the need for sample dilution in most cases.

13.2 Sensitivity. Using the 10-ml sample size, the minimum detectable concentration is approximately 50 ppb.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. O'Keeffe, A.E., and G.C. Ortman. ''Primary Standards for Trace Gas Analysis.'' Analytical Chemical Journal, 38,76. 1966.

2. Stevens, R.K., A.E. O'Keeffe, and G.C. Ortman. ''Absolute Calibration of a Flame Photometric Detector to Volatile Sulfur Compounds at Sub-Part-Per-Million Levels.'' Environmental Science and Technology, 3:7. July 1969.

3. Mulik, J.D., R.K. Stevens, and R. Baumgardner. ''An Analytical System Designed to Measure Multiple Malodorous Compounds Related to Kraft Mill Activities.'' Presented at the 12th Conference on Methods in Air Pollution and Industrial Hygiene Studies, University of Southern California, Los Angeles, CA. April 6–8, 1971.

4. Devonald, R.H., R.S. Serenius, and A.D. McIntyre. ''Evaluation of the Flame Photometric Detector for Analysis of Sulfur Compounds.'' Pulp and Paper Magazine of Canada, 73,3. March 1972.

5. Grimley, K.W., W.S. Smith, and R.M. Martin. ''The Use of a Dynamic Dilution System in the Conditioning of Stack Gases for Automated Analysis by a Mobile Sampling Van.'' Presented at the 63rd Annual APCA Meeting, St. Louis, MO. June 14–19, 1970.

6. General Reference. Standard Methods of Chemical Analysis, Volumes III-A and III-B Instrumental Methods. Sixth Edition. Van Nostrand Reinhold Co.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

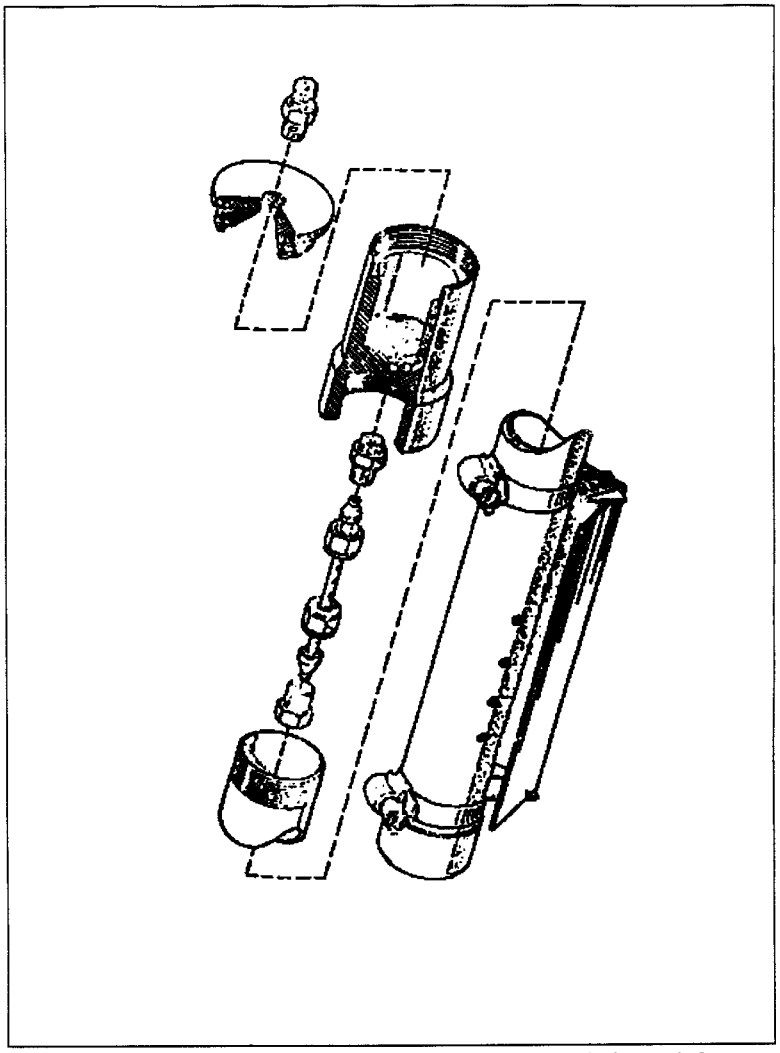


Figure 16-1. Probe used for Sample Gas Containing High Particulate Matter Loading.

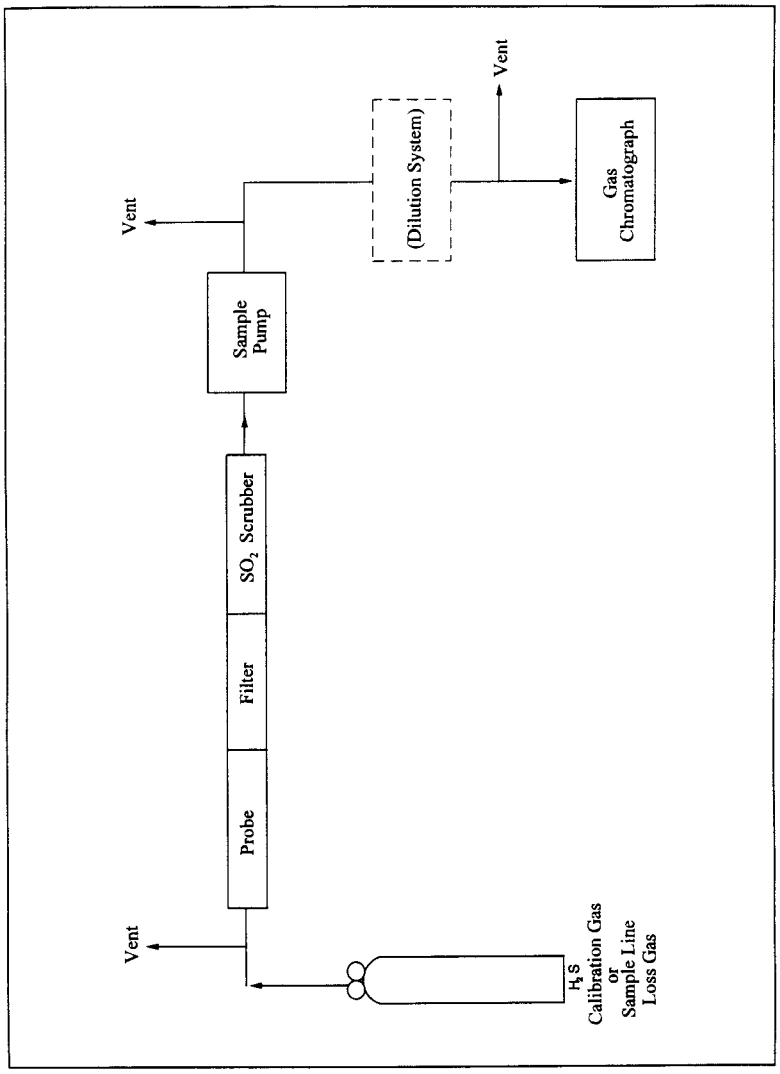


Figure 16-2. Calibration System.

METHOD 16A—DETERMINATION OF TOTAL REDUCED SULFUR EMISSIONS FROM STATIONARY SOURCES (IMPINGER TECHNIQUE)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 6, and Method 16.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total reduced sulfur (TRS) including:	N/A	See section 13.1.
Dimethyl disulfide [$(CH_3)_2S_2$]	62–49–20	
Dimethyl sulfide [$(CH_3)_2S$]	75–18–3	
Hydrogen sulfide [H_2S]	7783–06–4	
Methyl mercaptan [CH_4S]	74–93–1	
Reduced sulfur (RS) including:	N/A	
H_2S	7783–06–4	
Carbonyl sulfide [COS]	463–58–1	
Carbon disulfide [CS_2]	75–15–0	
Reported as: Sulfur dioxide (SO_2)	7449–09–5	

1.2 Applicability. This method is applicable for the determination of TRS emissions from recovery boilers, lime kilns, and smelt dissolving tanks at kraft pulp mills, reduced sulfur compounds (H_2S, carbonyl sulfide, and carbon disulfide) from sulfur recovery units at onshore natural gas processing facilities, and from other sources when specified in an applicable subpart of the regulations. The flue gas must contain at least 1 percent oxygen for complete oxidation of all TRS to SO_2. Note: If sources other than kraft pulp mills experience low oxygen levels in the emissions, the method results may be biased low.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 An integrated gas sample is extracted from the stack. SO_2 is removed selectively from the sample using a citrate buffer solution. TRS compounds are then thermally oxidized to SO_2, collected in hydrogen peroxide as sulfate, and analyzed by the Method 6 barium-thorin titration procedure.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Reduced sulfur compounds other than those regulated by the emission standards, if present, may be measured by this method. Therefore, carbonyl sulfide, which is partially oxidized to SO_2 and may be present in a lime kiln exit stack, would be a positive interferant.

4.2 Particulate matter from the lime kiln stack gas (primarily calcium carbonate) can cause a negative bias if it is allowed to enter the citrate scrubber; the particulate matter will cause the pH to rise and H_2S to be absorbed prior to oxidation. Furthermore, if the calcium carbonate enters the hydrogen peroxide impingers, the calcium will precipitate sulfate ion. Proper use of the particulate filter described in section 6.1.3 will eliminate this interference.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m^3 will cause lung damage in uninitiated. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

5.3 Hydrogen Sulfide (H_2S). A flammable, poisonous gas with the odor of rotten eggs. H_2S is extremely hazardous and can cause collapse, coma, and death within a few seconds of one or two inhalations at sufficient concentrations. Low concentrations irritate the mucous membranes and may cause nausea, dizziness, and headache after exposure.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling train is shown in Figure 16A–1 and component parts are discussed below. Modifications to this sampling train are acceptable provided the system performance check is met (see section 8.5).

6.1.1 Probe. Teflon tubing, 6.4-mm (¼-in.) diameter, sequentially wrapped with heat-resistant fiber strips, a rubberized heat tape

(plug at one end), and heat-resistant adhesive tape. A flexible thermocouple or other suitable temperature measuring device should be placed between the Teflon tubing and the fiber strips so that the temperature can be monitored to prevent softening of the probe. The probe should be sheathed in stainless steel to provide in-stack rigidity. A series of bored-out stainless steel fittings placed at the front of the sheath will prevent moisture and particulate from entering between the probe and sheath. A 6.4-mm (¼-in.) Teflon elbow (bored out) should be attached to the inlet of the probe, and a 2.54 cm (1 in.) piece of Teflon tubing should be attached at the open end of the elbow to permit the opening of the probe to be turned away from the particulate stream; this will reduce the amount of particulate drawn into the sampling train. The probe is depicted in Figure 16A–2.

6.1.2 Probe Brush. Nylon bristle brush with handle inserted into a 3.2-mm (⅛-in.) Teflon tubing. The Teflon tubing should be long enough to pass the brush through the length of the probe.

6.1.3 Particulate Filter. 50-mm Teflon filter holder and a 1- to 2-μm porosity, Teflon filter (available through Savillex Corporation, 5325 Highway 101, Minnetonka, Minnesota 55343). The filter holder must be maintained in a hot box at a temperature sufficient to prevent moisture condensation. A temperature of 121 °C (250 °F) was found to be sufficient when testing a lime kiln under sub-freezing ambient conditions.

6.1.4 SO_2 Scrubber. Three 300-ml Teflon segmented impingers connected in series with flexible, thick-walled, Teflon tubing. (Impinger parts and tubing available through Savillex.) The first two impingers contain 100 ml of citrate buffer and the third impinger is initially dry. The tip of the tube inserted into the solution should be constricted to less than 3 mm (⅛-in.) ID and should be immersed to a depth of at least 5 cm (2 in.).

6.1.5 Combustion Tube. Quartz glass tubing with an expanded combustion chamber 2.54 cm (1 in.) in diameter and at least 30.5 cm (12 in.) long. The tube ends should have an outside diameter of 0.6 cm (¼ in.) and be at least 15.3 cm (6 in.) long. This length is necessary to maintain the quartz-glass connector near ambient temperature and thereby avoid leaks. Alternatively, the outlet may be constructed with a 90-degree glass elbow and socket that would fit directly onto the inlet of the first peroxide impinger.

6.1.6 Furnace. A furnace of sufficient size to enclose the combustion chamber of the combustion tube with a temperature regulator capable of maintaining the temperature at 800 ±100 °C (1472 ±180 °F). The furnace operating temperature should be checked with a thermocouple to ensure accuracy.

6.1.7 Peroxide Impingers, Stopcock Grease, Temperature Sensor, Drying Tube, Valve, Pump, and Barometer. Same as Method 6, sections 6.1.1.2, 6.1.1.4, 6.1.1.5, 6.1.1.6, 6.1.1.7, 6.1.1.8, and 6.1.2, respectively, except that the midget bubbler of Method 6, section 6.1.1.2 is not required.

6.1.8 Vacuum Gauge. At least 760 mm Hg (30 in. Hg) gauge.

6.1.9 Rate Meter. Rotameter, or equivalent, accurate to within 5 percent at the selected flow rate of approximately 2 liters/min (4.2 ft^3/hr).

6.1.10 Volume Meter. Dry gas meter capable of measuring the sample volume under the sampling conditions of 2 liters/min (4.2 ft^3/hr) with an accuracy of 2 percent.

6.2 Sample Recovery. Polyethylene Bottles, 250-ml (one per sample).

6.3 Sample Preparation and Analysis. Same as Method 6, section 6.3, except a 10-ml buret with 0.05-ml graduations is required, and the spectrophotometer is not needed.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. When such specifications are not available, the best available grade must be used.

7.1 Sample Collection. The following reagents are required for sample analysis:

7.1.1 Water. Same as in Method 6, section 7.1.1.

7.1.2 Citrate Buffer. Dissolve 300 g of potassium citrate (or 284 g of sodium citrate) and 41 g of anhydrous citric acid in 1 liter of water (200 ml is needed per test). Adjust the pH to between 5.4 and 5.6 with potassium citrate or citric acid, as required.

7.1.3 Hydrogen Peroxide, 3 percent. Same as in Method 6, section 7.1.3 (40 ml is needed per sample).

7.1.4 Recovery Check Gas. Hydrogen sulfide (100 ppmv or less) in nitrogen, stored in aluminum cylinders. Verify the concentration by Method 11 or by gas chromatography where the instrument is calibrated with an H_2S permeation tube as described below. For Method 11, the relative standard deviation should not exceed 5 percent on at least three 20-minute runs.

NOTE: Alternatively, hydrogen sulfide recovery gas generated from a permeation device gravimetrically calibrated and certified at some convenient operating temperature may be used. The permeation rate of the device must be such that at a dilution gas flow rate of 3 liters/min (6.4 ft^3/hr), an H_2S concentration in the range of the stack gas or within 20 percent of the standard can be generated.

7.1.5 Combustion Gas. Gas containing less than 50 ppb reduced sulfur compounds and less than 10 ppmv total hydrocarbons. The

gas may be generated from a clean-air system that purifies ambient air and consists of the following components: Diaphragm pump, silica gel drying tube, activated charcoal tube, and flow rate measuring device. Flow from a compressed air cylinder is also acceptable.

7.2 Sample Recovery and Analysis. Same as Method 6, sections 7.2.1 and 7.3, respectively.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Preparation of Sampling Train.

8.1.1 For the SO_2 scrubber, measure 100 ml of citrate buffer into the first and second impingers; leave the third impinger empty. Immerse the impingers in an ice bath, and locate them as close as possible to the filter heat box. The connecting tubing should be free of loops. Maintain the probe and filter temperatures sufficiently high to prevent moisture condensation, and monitor with a suitable temperature sensor.

8.1.2 For the Method 6 part of the train, measure 20 ml of 3 percent hydrogen peroxide into the first and second midget impingers. Leave the third midget impinger empty, and place silica gel in the fourth midget impinger. Alternatively, a silica gel drying tube may be used in place of the fourth impinger. Maintain the oxidation furnace at 800 ±100 °C (1472 ±180 °F). Place crushed ice and water around all impingers.

8.2 Citrate Scrubber Conditioning Procedure. Condition the citrate buffer scrubbing solution by pulling stack gas through the Teflon impingers and bypassing all other sampling train components. A purge rate of 2 liters/min for 10 minutes has been found to be sufficient to obtain equilibrium. After the citrate scrubber has been conditioned, assemble the sampling train, and conduct (optional) a leak-check as described in Method 6, section 8.2.

8.3 Sample Collection. Same as in Method 6, section 8.3, except the sampling rate is 2 liters/min (±10 percent) for 1 or 3 hours. After the sample is collected, remove the probe from the stack, and conduct (mandatory) a post-test leak-check as described in Method 6, section 8.2. The 15-minute purge of the train following collection should not be performed. After each 3-hour test run (or after three 1-hour samples), conduct one system performance check (see section 8.5) to determine the reduced sulfur recovery efficiency through the sampling train. After this system performance check and before the next test run, rinse and brush the probe with water, replace the filter, and change the citrate scrubber (optional but recommended).

NOTE: In Method 16, a test run is composed of 16 individual analyses (injects) performed over a period of not less than 3 hours or more than 6 hours. For Method 16A to be consistent with Method 16, the following may be used to obtain a test run: (1) collect three 60-minute samples or (2) collect one 3-hour sample. (Three test runs constitute a test.)

8.4 Sample Recovery. Disconnect the impingers. Quantitatively transfer the contents of the midget impingers of the Method 6 part of the train into a leak-free polyethylene bottle for shipment. Rinse the three midget impingers and the connecting tubes with water and add the washings to the same storage container. Mark the fluid level. Seal and identify the sample container.

8.5 System Performance Check.

8.5.1 A system performance check is done (1) to validate the sampling train components and procedure (prior to testing; optional) and (2) to validate a test run (after a run). Perform a check in the field prior to testing consisting of at least two samples (optional), and perform an additional check after each 3 hour run or after three 1-hour samples (mandatory).

8.5.2 The checks involve sampling a known concentration of H_2S and comparing the analyzed concentration with the known concentration. Mix the H_2S recovery check gas (Section 7.1.4) and combustion gas in a dilution system such as that shown in Figure 16A–3. Adjust the flow rates to generate an H_2S concentration in the range of the stack gas or within 20 percent of the applicable standard and an oxygen concentration greater than 1 percent at a total flow rate of at least 2.5 liters/min (5.3 ft^3/hr). Use Equation 16A–3 to calculate the concentration of recovery gas generated. Calibrate the flow rate from both sources with a soap bubble flow meter so that the diluted concentration of H_2S can be accurately calculated.

8.5.3 Collect 30-minute samples, and analyze in the same manner as the emission samples. Collect the sample through the probe of the sampling train using a manifold or some other suitable device that will ensure extraction of a representative sample.

8.5.4 The recovery check must be performed in the field prior to replacing the SO_2 scrubber and particulate filter and before the probe is cleaned. Use Equation 16A–4 (see section 12.5) to calculate the recovery efficiency. Report the recovery efficiency with the emission data; do not correct the emission data for the recovery efficiency. A sample recovery of 100 ±20 percent must be obtained for the emission data to be valid. However, if the recovery efficiency is not in the 100 ±20 percent range but the results do not affect the compliance or noncompliance status of the affected facility, the Administrator may decide to accept the results of the compliance test.

9.0 Quality Control

Section	Quality control measure	Effect
8.5	System performance check	Ensure validity of sampling train components and analytical procedure.
8.2, 10.0	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.
10.0	Barium standard solution standardization	Ensure precision of normality determination.
11.1	Replicate titrations	Ensure precision of titration determinations.

10.0 Calibration

Same as Method 6, section 10.0.

11.0 Analytical Procedure

11.1 Sample Loss Check and Sample Analysis. Same as Method 6, sections 11.1 and 11.2, respectively, with the following exception: for 1-hour sampling, take a 40-ml aliquot, add 160 ml of 100 percent isopropanol and four drops of thorin.

12.0 Data Analysis and Calculations

In the calculations, at least one extra decimal figure should be retained beyond that of the acquired data. Figures should be rounded off after final calculations.

12.1 Nomenclature.

C_{TRS} = Concentration of TRS as SO_2, dry basis corrected to standard conditions, ppmv.

$C_{RG(act)}$ = Actual concentration of recovery check gas (after dilution), ppm.

$C_{RG(m)}$ = Measured concentration of recovery check gas generated, ppm.

C_{H2S} = Verified concentration of H_2S recovery gas.

N = Normality of barium perchlorate titrant, milliequivalents/ml.

P_{bar} = Barometric pressure at exit orifice of the dry gas meter, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

Q_{H2S} = Calibrated flow rate of H_2S recovery gas, liters/min.

Q_{CG} = Calibrated flow rate of combustion gas, liters/min.

R = Recovery efficiency for the system performance check, percent.

T_m = Average dry gas meter absolute temperature, °K (°R).

T_{std} = Standard absolute temperature, 293 °K (528 °R).

V_a = Volume of sample aliquot titrated, ml.

V_m = Dry gas volume as measured by the dry gas meter, liters (dcf).

$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, liters (dscf).

V_{soln} = Total volume of solution in which the sulfur dioxide sample is contained, 100 ml.

V_t = Volume of barium perchlorate titrant used for the sample, ml (average of replicate titrations).

V_{tb} = Volume of barium perchlorate titrant used for the blank, ml.

Y = Dry gas meter calibration factor.

32.03 = Equivalent weight of sulfur dioxide, mg/meq.

12.2 Dry Sample Gas Volume, Corrected to Standard Conditions.

$$V_{m(std)} = V_m Y \frac{T_{std} P_{bar}}{T_m P_{std}} \qquad \text{Eq. 16A-1}$$

$$= K_1 Y \frac{V_m P_{bar}}{T_m}$$

Where:

K_1 = 0.3855 °K/mm Hg for metric units,
= 17.65 °R/in. Hg for English units.

12.3 Concentration of TRS as ppm SO_2.

$$C_{TRS} = K_2 N \frac{(V_t - V_{tb})(V_{soln}/V_a)}{V_{m(std)}} \qquad \text{Eq. 16A-2}$$

Where:

$$K_2 = 32.03 \frac{mg}{meq} \frac{24.05 L}{mole} \frac{1 mole}{64.06 g} \frac{1 g}{10^3 mg} \frac{10^3 mL}{L} \frac{10^3 \mu L}{lmL}$$
$$= \frac{12025 \mu L}{meq}$$

12.4 Concentration of Recovery Gas Generated in the System Performance Check.

$$C_{RG} = \frac{Q_{H_2S} C_{H_2S}}{Q_{H_2S} + Q_{CG}} \qquad \text{Eq. 16A-3}$$

12.5 Recovery Efficiency for the System Performance Check.

$$R = \frac{C_{RG(m)}}{C_{RG(act)}} \times 100 \qquad \text{Eq. 16A-4}$$

13.0 Method Performance

13.1 Analytical Range. The lower detectable limit is 0.1 ppmv SO_2 when sampling at 2 liters/min (4.2 ft^3/hr) for 3 hours or 0.3 ppmv when sampling at 2 liters/min (4.2 ft^3/hr) for 1 hour. The upper concentration limit of the method exceeds the TRS levels generally encountered at kraft pulp mills.

13.2 Precision. Relative standard deviations of 2.0 and 2.6 percent were obtained when sampling a recovery boiler for 1 and 3 hours, respectively.

13.3 Bias.

13.3.1 No bias was found in Method 16A relative to Method 16 in a separate study at a recovery boiler.

13.3.2 Comparison of Method 16A with Method 16 at a lime kiln indicated that there was no bias in Method 16A. However, instability of the source emissions adversely affected the comparison. The precision of Method 16A at the lime kiln was similar to that obtained at the recovery boiler (Section 13.2.1).

13.3.3 Relative standard deviations of 2.7 and 7.7 percent have been obtained for system performance checks.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

As an alternative to the procedures specified in section 7.1.4, the following procedure may be used to verify the H_2S concentration of the recovery check gas.

16.1 Summary. The H_2S is collected from the calibration gas cylinder and is absorbed in zinc acetate solution to form zinc sulfide. The latter compound is then measured iodometrically.

16.2 Range. The procedure has been examined in the range of 5 to 1500 ppmv.

16.3 Interferences. There are no known interferences to this procedure when used to analyze cylinder gases containing H_2S in nitrogen.

16.4 Precision and Bias. Laboratory tests have shown a relative standard deviation of less than 3 percent. The procedure showed no bias when compared to a gas chromatographic method that used gravimetrically certified permeation tubes for calibration.

16.5 Equipment and Supplies.

16.5.1 Sampling Apparatus. The sampling train is shown in Figure 16A–4. Its component parts are discussed in sections 16.5.1.1 through 16.5.2.

16.5.1.1 Sampling Line. Teflon tubing (¼-in.) to connect the cylinder regulator to the sampling valve.

16.5.1.2 Needle Valve. Stainless steel or Teflon needle valve to control the flow rate of gases to the impingers.

16.5.1.3 Impingers. Three impingers of approximately 100-ml capacity, constructed to permit the addition of reagents through the gas inlet stem. The impingers shall be connected in series with leak-free glass or Teflon connectors. The impinger bottoms have a standard 24/25 ground-glass fitting. The stems are from standard 6.4-mm (¼-in.) ball joint midget impingers, custom lengthened by about 1 in. When fitted together, the stem end should be approximately 1.27 cm (½ in.) from the bottom (Southern Scientific, Inc., Micanopy, Florida: Set Number S6962–048). The third in-line impinger acts as a drop-out bottle.

16.5.1.4 Drying Tube, Rate Meter, and Barometer. Same as Method 11, sections 6.1.5, 6.1.8, and 6.1.10, respectively.

16.5.1.5 Cylinder Gas Regulator. Stainless steel, to reduce the pressure of the gas stream entering the Teflon sampling line to a safe level.

16.5.1.6 Soap Bubble Meter. Calibrated for 100 and 500 ml, or two separate bubble meters.

16.5.1.7 Critical Orifice. For volume and rate measurements. The critical orifice may be fabricated according to section 16.7.3 and must be calibrated as specified in section 16.12.4.

16.5.1.8 Graduated Cylinder. 50-ml size.

16.5.1.9 Volumetric Flask. 1-liter size.

16.5.1.10 Volumetric Pipette. 15-ml size.

16.5.1.11 Vacuum Gauge. Minimum 20 in. Hg capacity.

16.5.1.12 Stopwatch.

16.5.2 Sample Recovery and Analysis.

16.5.2.1 Erlenmeyer Flasks. 125- and 250-ml sizes.

16.5.2.2 Pipettes. 2-, 10-, 20-, and 100-ml volumetric.

16.5.2.3 Burette. 50-ml size.

16.5.2.4 Volumetric Flask. 1-liter size.

16.5.2.5 Graduated Cylinder. 50-ml size.

16.5.2.6 Wash Bottle.

16.5.2.7 Stirring Plate and Bars.

16.6 Reagents and Standards. Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

16.6.1 Water. Same as Method 11, section 7.1.3.

16.6.2 Zinc Acetate Absorbing Solution. Dissolve 20 g zinc acetate in water, and dilute to 1 liter.

16.6.3 Potassium Bi-iodate [$KH(IO_3)_2$] Solution, Standard 0.100 N. Dissolve 3.249 g anhydrous $KH(IO_3)_2$ in water, and dilute to 1 liter.

16.6.4 Sodium Thiosulfate ($Na_2S_2O_3$) Solution, Standard 0.1 N. Same as Method 11, section 7.3.2. Standardize according to section 16.12.2.

16.6.5 $Na_2S_2O_3$ Solution, Standard 0.01 N. Pipette 100.0 ml of 0.1 N $Na_2S_2O_3$ solution into a 1-liter volumetric flask, and dilute to the mark with water.

16.6.6 Iodine Solution, 0.1 N. Same as Method 11, section 7.2.3.

16.6.7 Standard Iodine Solution, 0.01 N. Same as in Method 11, section 7.2.4. Standardize according to section 16.12.3.

16.6.8 Hydrochloric Acid (HCl) Solution, 10 Percent by Weight. Add 230 ml concentrated HCl (specific gravity 1.19) to 770 ml water.

16.6.9 Starch Indicator Solution. To 5 g starch (potato, arrowroot, or soluble), add a little cold water, and grind in a mortar to a thin paste. Pour into 1 liter of boiling water, stir, and let settle overnight. Use the clear supernatant. Preserve with 1.25 g salicylic acid, 4 g zinc chloride, or a combination of 4 g sodium propionate and 2 g sodium azide per liter of starch solution. Some commercial starch substitutes are satisfactory.

16.7 Pre-test Procedures.

16.7.1 Selection of Gas Sample Volumes. This procedure has been validated for estimating the volume of cylinder gas sample needed when the H_2S concentration is in the range of 5 to 1500 ppmv. The sample volume ranges were selected in order to ensure a 35 to 60 percent consumption of the 20 ml of 0.01 N iodine (thus ensuring a 0.01 N $Na_2S_2O_3$ titer of approximately 7 to 12 ml). The sample volumes for various H_2S concentrations can be estimated by dividing the approximate ppm-liters desired for a given concentration range by the H_2S concentration stated by the manufacturer. For example, for analyzing a cylinder gas containing approximately 10 ppmv H_2S, the optimum sample volume is 65 liters (650 ppm-liters/10 ppmv). For analyzing a cylinder gas containing approximately 1000 ppmv H_2S, the optimum sample volume is 1 liter (1000 ppm-liters/1000 ppmv).

Approximate cylinder gas H_2S concentration (ppmv)	Approximate ppm-liters desired
5 to <30	650
30 to <500	800
500 to <1500	1000

16.7.2 Critical Orifice Flow Rate Selection. The following table shows the ranges of sample flow rates that are desirable in order to ensure capture of H_2S in the impinger solution. Slight deviations from these ranges will not have an impact on measured concentrations.

Cylinder gas H_2S concentration (ppmv)	Critical orifice flow rate (ml/min)
5 to 50 ppmv	1500 ±500
50 to 250 ppmv	500 ±250
250 to <1000 ppmv	200 ±50
>1000 ppmv	75 ±25

16.7.3 Critical Orifice Fabrication. Critical orifice of desired flow rates may be fabricated by selecting an orifice tube of desired length and connecting 1/16-in. × 1/4-in. (0.16 cm × 0.64 cm) reducing fittings to both ends. The inside diameters and lengths of orifice tubes needed to obtain specific flow rates are shown below.

Tube (in. OD)	Tube (in. ID)	Length (in.)	Flowrate (ml/min)	Altech Catalog No.
1/16	0.007	1.2	85	301430
1/16	0.01	3.2	215	300530
1/16	0.01	1.2	350	300530
1/16	0.02	1.2	1400	300230

16.7.4 Determination of Critical Orifice Approximate Flow Rate. Connect the critical orifice to the sampling system as shown in Figure 16A–4 but without the H_2S cylinder. Connect a rotameter in the line to the first impinger. Turn on the pump, and adjust the

valve to give a reading of about half atmospheric pressure. Observe the rotameter reading. Slowly increase the vacuum until a stable flow rate is reached, and record this as the critical vacuum. The measured flow rate indicates the expected critical flow rate of the orifice. If this flow rate is in the range shown in section 16.7.2, proceed with the critical orifice calibration according to section 16.12.4.

16.7.5 Determination of Approximate Sampling Time. Determine the approximate sampling time for a cylinder of known concentration. Use the optimum sample volume obtained in section 16.7.1.

$$\text{Approximate sampling time} = \frac{\text{Optimum volume}}{\text{Critical orifice flow rate}}$$

16.8 Sample Collection.

16.8.1 Connect the Teflon tubing, Teflon tee, and rotameter to the flow control needle valve as shown in Figure 16A–4. Vent the rotameter to an exhaust hood. Plug the open end of the tee. Five to 10 minutes prior to sampling, open the cylinder valve while keeping the flow control needle valve closed. Adjust the delivery pressure to 20 psi. Open the needle valve slowly until the rotameter shows a flow rate approximately 50 to 100 ml above the flow rate of the critical orifice being used in the system.

16.8.2 Place 50 ml of zinc acetate solution in two of the impingers, connect them and the empty third impinger (dropout bottle) and the rest of the equipment as shown in Figure 16A–4. Make sure the ground-glass fittings are tight. The impingers can be easily stabilized by using a small cardboard box in which three holes have been cut, to act as a holder. Connect the Teflon sample line to the first impinger. Cover the impingers with a dark cloth or piece of plastic to protect the absorbing solution from light during sampling.

16.8.3 Record the temperature and barometric pressure. Note the gas flow rate through the rotameter. Open the closed end of the tee. Connect the sampling tube to the tee, ensuring a tight connection. Start the sampling pump and stopwatch simultaneously. Note the decrease in flow rate through the excess flow rotameter. This decrease should equal the known flow rate of the critical orifice being used. Continue sampling for the period determined in section 16.7.5.

16.8.4 When sampling is complete, turn off the pump and stopwatch. Disconnect the sampling line from the tee and plug it. Close the needle valve followed by the cylinder valve. Record the sampling time.

16.9 Blank Analysis. While the sample is being collected, run a blank as follows: To a 250-ml Erlenmeyer flask, add 100 ml of zinc acetate solution, 20.0 ml of 0.01 N iodine solution, and 2 ml HCl solution. Titrate, while stirring, with 0.01 N $Na_2S_2O_3$ until the solution is light yellow. Add starch, and continue titrating until the blue color disappears. Analyze a blank with each sample, as the blank titer has been observed to change over the course of a day.

NOTE: Iodine titration of zinc acetate solutions is difficult to perform because the solution turns slightly white in color near the end point, and the disappearance of the blue color is hard to recognize. In addition, a blue color may reappear in the solution about 30 to 45 seconds after the titration endpoint is reached. This should not be taken to mean the original endpoint was in error. It is recommended that persons conducting this test perform several titrations to be able to correctly identify the endpoint. The importance of this should be recognized because the results of this analytical procedure are extremely sensitive to errors in titration.

16.10 Sample Analysis. Sample treatment is similar to the blank treatment. Before detaching the stems from the bottoms of the impingers, add 20.0 ml of 0.01 N iodine solution through the stems of the impingers holding the zinc acetate solution, dividing it between the two (add about 15 ml to the first impinger and the rest to the second). Add 2 ml HCl solution through the stems, dividing it as with the iodine. Disconnect the sampling line, and store the impingers for 30 minutes. At the end of 30 minutes, rinse the impinger stems into the impinger bottoms. Titrate the impinger contents with 0.01 N $Na_2S_2O_3$. Do not transfer the contents of the impinger to a flask because this may result in a loss of iodine and cause a positive bias.

16.11 Post-test Orifice Calibration. Conduct a post-test critical orifice calibration run using the calibration procedures outlined in section 16.12.4. If the Q_{std} obtained before and after the test differs by more than 5 percent, void the sample; if not, proceed to perform the calculations.

16.12 Calibrations and Standardizations.

16.12.1 Rotameter and Barometer. Same as Method 11, sections 10.1.3 and 10.1.4.

16.12.2 $Na_2S_2O_3$ Solution, 0.1 N. Standardize the 0.1 N $Na_2S_2O_3$ solution as follows: To 80 ml water, stirring constantly, add 1 ml concentrated H_2SO_4, 10.0 ml of 0.100 N $KH(IO_3)_2$

and 1 g potassium iodide. Titrate immediately with 0.1 N $Na_2S_2O_3$ until the solution is light yellow. Add 3 ml starch solution, and titrate until the blue color just disappears. Repeat the titration until replicate analyses agree within 0.05 ml. Take the average volume of $Na_2S_2O_3$ consumed to calculate the normality to three decimal figures using Equation 16A–5.

16.12.3 Iodine Solution, 0.01 N. Standardize the 0.01 N iodine solution as follows: Pipet 20.0 ml of 0.01 N iodine solution into a 125-ml Erlenmeyer flask. Titrate with standard 0.01 N $Na_2S_2O_3$ solution until the solution is light yellow. Add 3 ml starch solution, and continue titrating until the blue color just disappears. If the normality of the iodine tested is not 0.010, add a few ml of 0.1 N iodine solution if it is low, or a few ml of water if it is high, and standardize again. Repeat the titration until replicate values agree within 0.05 ml. Take the average volume to calculate the normality to three decimal figures using Equation 16A–6.

16.12.4 Critical Orifice. Calibrate the critical orifice using the sampling train shown in Figure 16A–4 but without the H_2S cylinder and vent rotameter. Connect the soap bubble meter to the Teflon line that is connected to the first impinger. Turn on the pump, and adjust the needle valve until the vacuum is higher than the critical vacuum determined in section 16.7.4. Record the time required for gas flow to equal the soap bubble meter volume (use the 100-ml soap bubble meter for gas flow rates below 100 ml/min, otherwise use the 500-ml soap bubble meter). Make three runs, and record the data listed in Table 16A–1. Use these data to calculate the volumetric flow rate of the orifice.

16.13 Calculations.

16.13.1 Nomenclature.

B_{wa} = Fraction of water vapor in ambient air during orifice calibration.

C_{H_2S} = H_2S concentration in cylinder gas, ppmv.

$$K_2 = 32.03 \frac{\text{mg}}{\text{meq}} \frac{24.05\text{L}}{\text{mole}} \frac{1\text{mole}}{64.06\text{g}} \frac{1\text{g}}{10^3\text{mg}} \frac{10^3\text{mL}}{\text{L}} \frac{10^3\mu\text{L}}{1\text{mL}}$$

$$= \frac{12025\mu\text{L}}{\text{meq}}$$

M_a = Molecular weight of ambient air saturated at impinger temperature, g/g-mole.

M_s = Molecular weight of sample gas (nitrogen) saturated at impinger temperature, g/g-mole.

NOTE: (For tests carried out in a laboratory where the impinger temperature is 25 °C, M_a = 28.5 g/g-mole and M_s = 27.7 g/g-mole.)

N_I = Normality of standard iodine solution (0.01 N), g-eq/liter.

N_T = Normality of standard $Na_2S_2O_3$ solution (0.01 N), g-eq/liter.

P_{bar} = Barometric pressure, mm Hg.

P_{std} = Standard absolute pressure, 760 mm Hg.

Q_{std} = Average volumetric flow rate through critical orifice, liters/min.

T_{amb} = Absolute ambient temperature, °K.

T_{std} = Standard absolute temperature, 293 °K.

θ_s = Sampling time, min.

θ_{sb} = Time for soap bubble meter flow rate measurement, min.

$V_{m(std)}$ = Sample gas volume measured by the critical orifice, corrected to standard conditions, liters.

V_{sb} = Volume of gas as measured by the soap bubble meter, ml.

$V_{sb(std)}$ = Volume of gas as measured by the soap bubble meter, corrected to standard conditions, liters.

V_I = Volume of standard iodine solution (0.01 N) used, ml.

V_T = Volume of standard $Na_2S_2O_3$ solution (0.01 N) used, ml.

V_{TB} = Volume of standard $Na_2S_2O_3$ solution (0.01 N) used for the blank, ml.

16.13.2 Normality of Standard $Na_2S_2O_3$ Solution (0.1 N).

$$N_T = \frac{1}{\text{mL } Na_2S_2O_3 \text{ consumed}} \qquad \text{Eq. 16A-5}$$

16.13.3 Normality of Standard Iodine Solution (0.01 N).

$$N_I = \frac{N_T V_T}{V_I} \qquad \text{Eq. 16A-6}$$

16.13.4 Sample Gas Volume.

$$V_{m(std)} = \overline{Q}_{std}\Theta_s\left(1 - B_{wa}\right)\frac{M_a}{M_b} \qquad \text{Eq. 16A-7}$$

16.13.5 Concentration of H_2S in the Gas Cylinder.

17.0 References

$$C_{H_2S} = \frac{K N_T \left(V_{TB} - V_T\right)}{V_{m(std)}} \qquad \text{Eq. 16A-8}$$

1. American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater. Washington, DC. American Public Health Association. 1975. pp. 316–317.

2. American Society for Testing and Materials. Annual Book of ASTM Standards. Part 31: Water, Atmospheric Analysis. Philadelphia, PA. 1974. pp. 40–42.

3. Blosser, R.O. A Study of TRS Measurement Methods. National Council of the Paper Industry for Air and Stream Improvement, Inc., New York, NY. Technical Bulletin No. 434. May 1984. 14 pp.

4. Blosser, R.O., H.S. Oglesby, and A.K. Jain. A Study of Alternate SO_2 Scrubber Designs Used for TRS Monitoring. A Special Report by the National Council of the Paper Industry for Air and Stream Improvement, Inc., New York, NY. July 1977.

5. Curtis, F., and G.D. McAlister. Development and Evaluation of an Oxidation/Method 6 TRS Emission Sampling Procedure. Emission Measurement Branch, Emission Standards and Engineering Division, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711. February 1980.

6. Gellman, I. A Laboratory and Field Study of Reduced Sulfur Sampling and Monitoring Systems. National Council of the Paper Industry for Air and Stream Improvement, Inc., New York, NY. Atmospheric Quality Improvement Technical Bulletin No. 81. October 1975.

7. Margeson, J.H., J.E. Knoll, and M.R. Midgett. A Manual Method for TRS Determination. Source Branch, Quality Assurance Division, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

8. National Council of the Paper Industry for Air and Stream Improvement. An Investigation of H_2S and SO_2. Calibration Cylinder Gas Stability and Their Standardization Using Wet Chemical Techniques. Special Report 76–06. New York, NY. August 1976.

9. National Council of the Paper Industry for Air and Stream Improvement. Wet Chemical Method for Determining the H_2S Concentration of Calibration Cylinder Gases. Technical Bulletin Number 450. New York, NY. January 1985. 23 pp.

10. National Council of the Paper Industry for Air and Stream Improvement. Modified Wet Chemical Method for Determining the H_2S Concentration of Calibration Cylinder Gases. Draft Report. New York, NY. March 1987. 29 pp.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

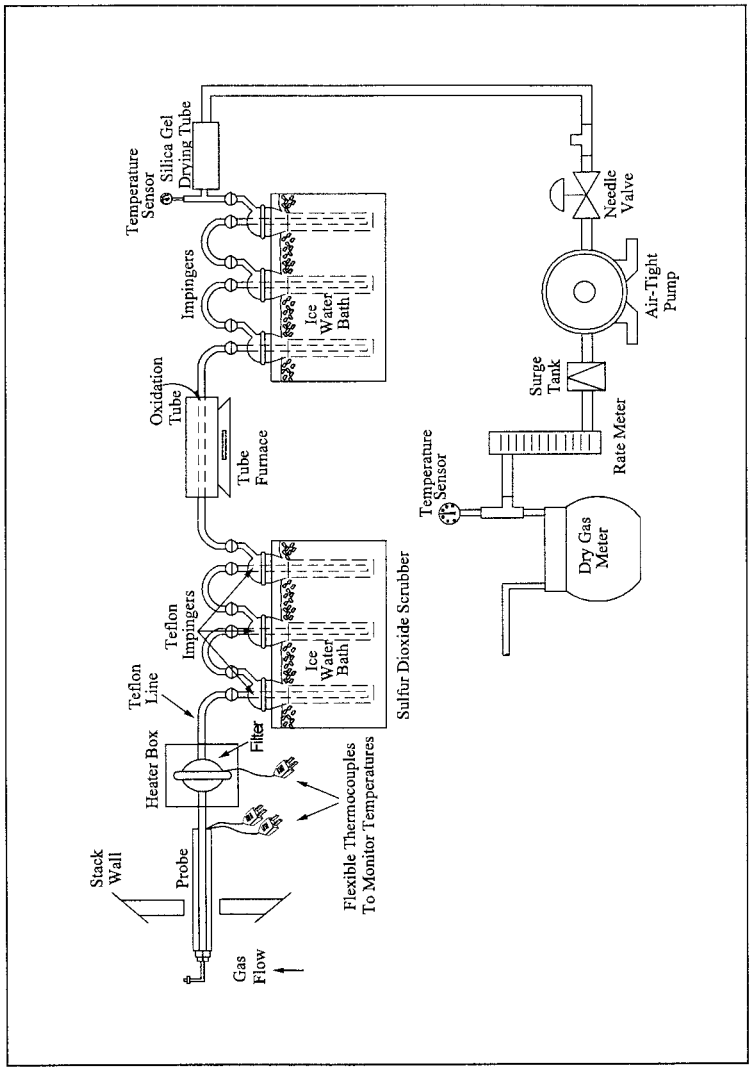


Figure 16A-1. Sampling Train.

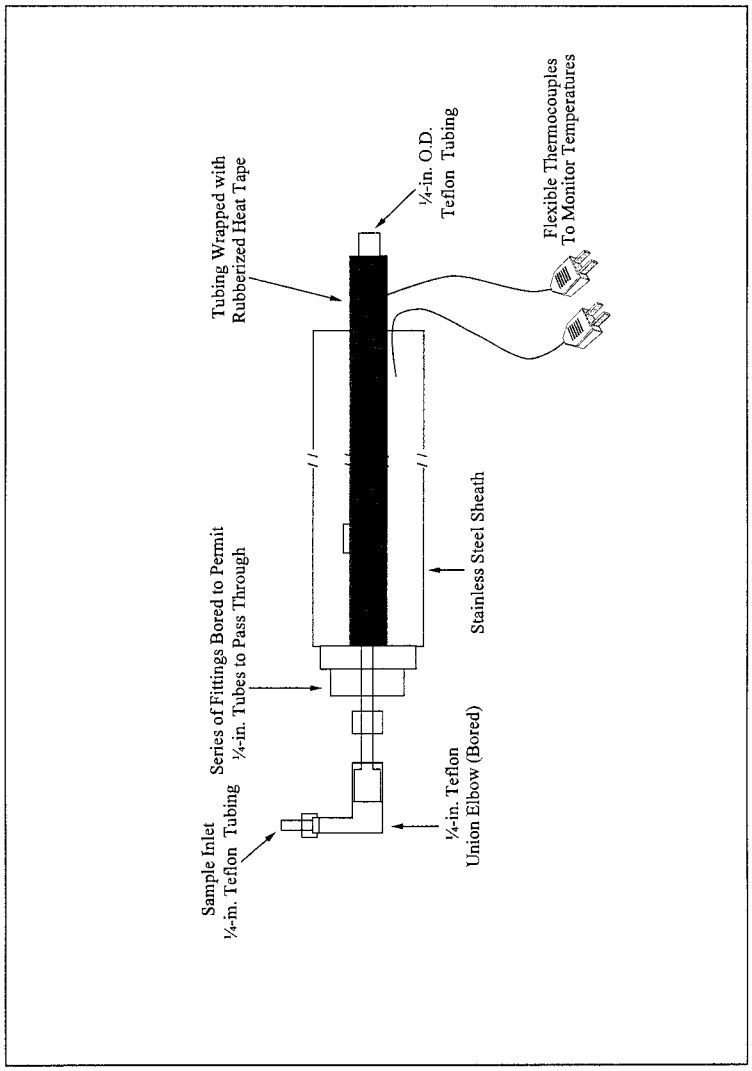


Figure 16A-2. Angled Sampling Probe.

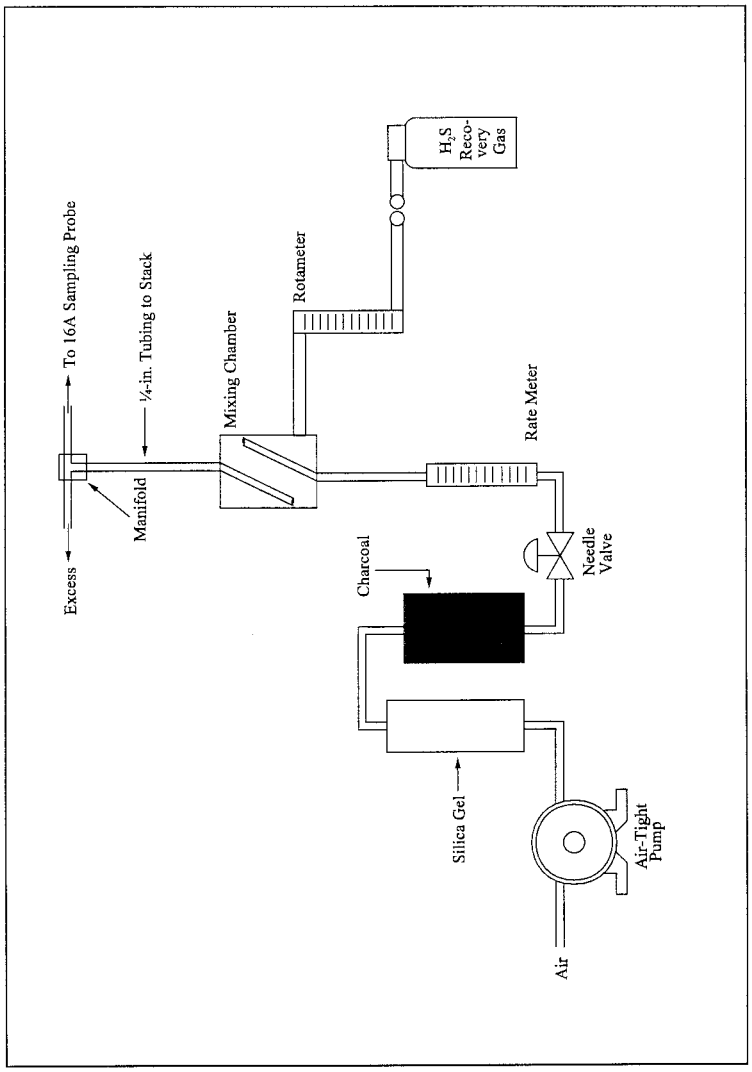


Figure 16A-3. Recovery Gas Dilution System.

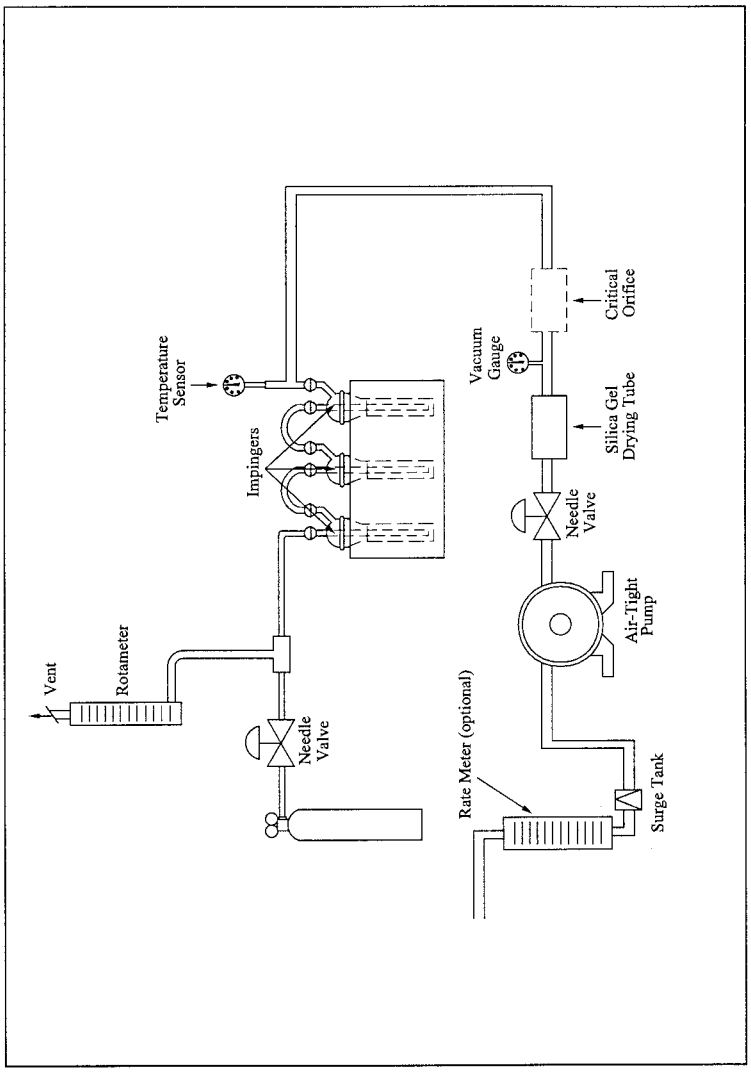


Figure 16A-4. Recovery Check Gas Sampling Train.

Date _____
Critical orifice ID _____
Soap bubble meter volume, Vsb___ liters
Time, θsb
Run no. 1 ____ min ____ sec
Run no. 2 ____ min ____ sec
Run no. 3 ____ min ____ sec
Average ____ min ____ sec
Covert the seconds to fraction of minute:
Time=____ min + ____ Sec/60=____ min

Barometric pressure, P_{bar}=____ mm Hg
Ambient temperature, t_{amb} = 273 + ____ °C=____ °K=____ mm Hg. (This should be approximately 0.4 times barometric pressure.)
Pump vacuum,

$$V_{sb(std)} = \frac{V_{sb} T_{std} P_{bar} \left(10^{-3}\right)}{T_{amb} P_{std}}$$

$$= \text{---------- liters}$$

$$Q_{std} = \frac{V_{sb(std)}}{\Theta_{sb}}$$

$$= \text{---------- liters/min}$$

Table 16A–1. Critical Orifice Calibration Data

METHOD 16B—DETERMINATION OF TOTAL REDUCED SULFUR EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a knowledge of at least the following additional test methods: Method 6C, Method 16, and Method 16A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Total reduced sulfur (TRS) including:	N/A
Dimethyl disulfide (DMDS), [$(CH_3)_2S_2$]	62–49–20
Dimethyl sulfide (DMS), [$(CH_3)_2S$]	75–18–3
Hydrogen sulfide (H_2S)	7783–06–4
Methyl mercaptan (MeSH), [CH_4S]	74–93–1
Reported as: Sulfur dioxide (SO_2)	7449–09–5

1.2 Applicability. This method is applicable for determining TRS emissions from recovery furnaces (boilers), lime kilns, and smelt dissolving tanks at kraft pulp mills, and from other sources when specified in an applicable subpart of the regulations. The flue gas must contain at least 1 percent oxygen for complete oxidation of all TRS to SO_2.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 An integrated gas sample is extracted from the stack. The SO_2 is removed selectively from the sample using a citrate buffer solution. The TRS compounds are then thermally oxidized to SO_2 and analyzed as SO_2 by gas chromatography (GC) using flame photometric detection (FPD).

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Reduced sulfur compounds other than those regulated by the emission standards, if present, may be measured by this method. Therefore, carbonyl sulfide, which is partially oxidized to SO_2 and may be present in a lime kiln exit stack, would be a positive interferant.

4.2 Particulate matter from the lime kiln stack gas (primarily calcium carbonate) can cause a negative bias if it is allowed to enter the citrate scrubber; the particulate matter will cause the pH to rise and H_2S to be absorbed before oxidation. Proper use of the particulate filter, described in section 6.1.3 of Method 16A, will eliminate this interference.

4.3 Carbon monoxide (CO) and carbon dioxide (CO_2) have substantial desensitizing effects on the FPD even after dilution. Acceptable systems must demonstrate that they have eliminated this interference by some procedure such as eluting these compounds before the SO_2. Compliance with this requirement can be demonstrated by submitting chromatograms of calibration gases with and without CO_2 in diluent gas. The CO_2 level should be approximately 10 percent for the case with CO_2 present. The two chromatograms should show agreement within the precision limits of section 13.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hydrogen Sulfide (H_2S). A flammable, poisonous gas with the odor of rotten eggs. H_2S is extremely hazardous and can cause collapse, coma, and death within a few seconds of one or two inhalations at sufficient concentrations. Low concentrations irritate the mucous membranes and may cause nausea, dizziness, and headache after exposure.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling train is shown in Figure 16B–1. Modifications to the apparatus are accepted provided the system performance check in section 8.4.1 is met.

6.1.1 Probe, Probe Brush, Particulate Filter, SO_2 Scrubber, Combustion Tube, and Furnace. Same as in Method 16A, sections 6.1.1 to 6.1.6.

6.1.2 Sampling Pump. Leakless Teflon-coated diaphragm type or equivalent.

6.2 Analysis.

6.2.1 Dilution System (optional), Gas Chromatograph, Oven, Temperature Gauges, Flow System, Flame Photometric Detector, Electrometer, Power Supply, Recorder, Calibration System, Tube Chamber, Flow System, and Constant Temperature Bath. Same as in Method 16, sections 6.2.1, 6.2.2, and 6.3.

6.2.2 Gas Chromatograph Columns. Same as in Method 16, section 6.2.3. Other columns with demonstrated ability to resolve SO_2 and be free from known interferences are acceptable alternatives. Single column systems such as a 7-ft Carbsorb B HT 100 column have been found satisfactory in resolving SO_2 from CO_2.

7.0 Reagents and Standards

Same as in Method 16, section 7.0, except for the following:

7.1 Calibration Gas. SO_2 permeation tube gravimetrically calibrated and certified at some convenient operating temperature. These tubes consist of hermetically sealed FEP Teflon tubing in which a liquefied gaseous substance is enclosed. The enclosed gas permeates through the tubing wall at a constant rate. When the temperature is constant, calibration gases covering a wide range of known concentrations can be generated by varying and accurately measuring the flow rate of diluent gas passing over the tubes. In place of SO_2 permeation tubes, cylinder gases containing SO_2 in nitrogen may be used for calibration. The cylinder gas concentration must be verified according to section 8.2.1 of Method 6C. The calibration gas is used to calibrate the GC/FPD system and the dilution system.

7.2 Recovery Check Gas.

7.2.1 Hydrogen sulfide [100 parts per million by volume (ppmv) or less] in nitrogen, stored in aluminum cylinders. Verify the concentration by Method 11, the procedure discussed in section 16.0 of Method 16A, or gas chromatography where the instrument is calibrated with an H_2S permeation tube as described below. For the wet-chemical methods, the standard deviation should not exceed 5 percent on at least three 20-minute runs.

7.2.2 Hydrogen sulfide recovery gas generated from a permeation device gravimetrically calibrated and certified at some convenient operation temperature may be used. The permeation rate of the device must be such that at a dilution gas flow rate of 3 liters/min (64 ft^3/hr), an H_2S concentration in the range of the stack gas or within 20 percent of the emission standard can be generated.

7.3 Combustion Gas. Gas containing less than 50 ppbv reduced sulfur compounds and less than 10 ppmv total hydrocarbons. The gas may be generated from a clean-air system that purifies ambient air and consists of the following components: diaphragm pump, silica gel drying tube, activated charcoal tube, and flow rate measuring device. Gas from a compressed air cylinder is also acceptable.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Procedures. Same as in Method 15, section 8.1.

8.2 Sample Collection. Before any source sampling is performed, conduct a system performance check as detailed in section 8.4.1 to validate the sampling train components and procedures. Although this test is optional, it would significantly reduce the possibility of rejecting tests as a result of failing the post-test performance check. At the completion of the pretest system performance check, insert the sampling probe into the test port making certain that no dilution air enters the stack though the port. Condition the entire system with sample for a minimum of 15 minutes before beginning analysis. If the sample is diluted, determine the dilution factor as in section 10.4 of Method 15.

8.3 Analysis. Inject aliquots of the sample into the GC/FPD analyzer for analysis. Determine the concentration of SO_2 directly from the calibration curves or from the equation for the least-squares line.

8.4. Post-Test Procedures

8.4.1 System Performance Check. Same as in Method 16A, section 8.5. A sufficient number of sample injections should be made so that the precision requirements of section 13.2 are satisfied.

8.4.2 Determination of Calibration Drift. Same as in Method 15, section 8.3.2.

9.0 Quality Control

Section	Quality control measure	Effect
8.2, 8.3	System performance check	Ensure validity of sampling train components and analytical procedure.
8.1	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.
10.0	Analytical calibration	Ensure precision of analytical results within 5 percent.

10.0 Calibration

Same as in Method 16, section 10, except SO_2 is used instead of H_2S.

11.0 Analytical Procedure

11.1 Sample collection and analysis are concurrent for this method (see section 8.3).

12.0 Data Analysis and Calculations

12.1 Nomenclature.

C_{SO2} = Sulfur dioxide concentration, ppmv.
C_{TRS} = Total reduced sulfur concentration as determined by Equation 16B–1, ppmv.
d = Dilution factor, dimensionless.
N = Number of samples.

12.2 SO_2 Concentration. Determine the concentration of SO_2, C_{SO2}, directly from the calibration curves. Alternatively, the concentration may be calculated using the equation for the least-squares line.

12.3 TRS Concentration.

$$C_{TRS} = C_{SO_2} d \qquad \text{Eq. 16B-1}$$

12.4 Average TRS Concentration

$$\text{Avg.}\, C_{TRS} = \frac{\sum_{i=1}^{n} C_{TRS}}{N} \qquad \text{Eq. 16B-2}$$

13.0 Method Performance.

13.1 Range and Sensitivity. Coupled with a GC using a 1-ml sample size, the maximum limit of the FPD for SO_2 is approximately 10 ppmv. This limit is extended by diluting the sample gas before analysis or by reducing the sample aliquot size. For sources with emission levels between 10 and 100 ppm, the measuring range can be best extended by reducing the sample size.

13.2 GC/FPD Calibration and Precision. A series of three consecutive injections of the sample calibration gas, at any dilution, must produce results which do not vary by more than 5 percent from the mean of the three injections.

13.3 Calibration Drift. The calibration drift determined from the mean of the three injections made at the beginning and end of any run or series of runs within a 24-hour period must not exceed 5 percent.

13.4 System Calibration Accuracy. Losses through the sample transport system must be measured and a correction factor developed to adjust the calibration accuracy to 100 percent.

13.5 Field tests between this method and Method 16A showed an average difference of less than 4.0 percent. This difference was not determined to be significant.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Same as in Method 16, section 16.0.

2. National Council of the Paper Industry for Air and Stream Improvement, Inc, A Study of TRS Measurement Methods. Technical Bulletin No. 434. New York, NY. May 1984. 12p.

3. Margeson, J.H., J.E. Knoll, and M.R. Midgett. A Manual Method for TRS Determination. Draft available from the authors. Source Branch, Quality Assurance Division, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

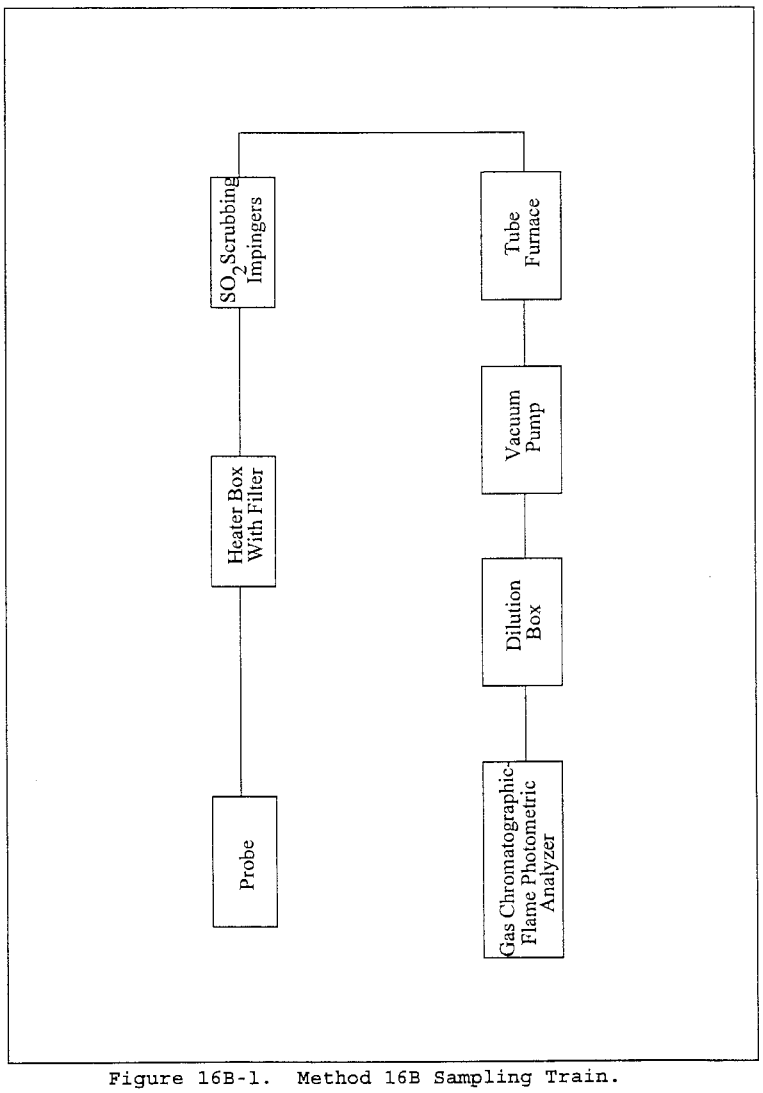


Figure 16B-1. Method 16B Sampling Train.

METHOD 16C—DETERMINATION OF TOTAL REDUCED SULFUR EMISSIONS FROM STATIONARY SOURCES

1.0 Scope and Application

What is Method 16C?

Method 16C is a procedure for measuring total reduced sulfur (TRS) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis. This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to

other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

(a) Method 6C—Determination of Sulfur Dioxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)

(b) Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure)

(c) Method 16A—Determination of Total Reduced Sulfur Emissions from Stationary Sources (Impinger Technique)

1.1 Analytes. What does Method 16C determine?

Analyte	CAS No.
Total reduced sulfur including:	N/A
Dimethyl disulfide (DMDS), [$(CH_3)_2S_2$]	62–49–20
Dimethyl sulfide (DMS), [$(CH_3)_2S$]	75–18–3
Hydrogen sulfide (H_2S)	7783–06–4
Methyl mercaptan (MeSH), (CH_4S)	74–93–1
Reported as: Sulfur dioxide (SO_2)	7449–09–5

1.2 Applicability. This method is applicable for determining TRS emissions from recovery furnaces (boilers), lime kilns, and smelt dissolving tanks at kraft pulp mills, and from other sources when specified in an applicable subpart of the regulations.

1.3 Data Quality Objectives. Adherence to the requirements described in Method 16C will enhance the quality of the data obtained.

2.0 Summary of Method

2.1 An integrated gas sample is extracted from the stack. The SO_2 is removed selectively from the sample using a citrate buffer solution. The TRS compounds are then thermally oxidized to SO_2 and determined as SO_2 by an instrumental analyzer. This method is a combination of the sampling procedures of Method 16A and the analytical procedures of Method 6C (referenced in Method 7E), with minor modifications to facilitate their use together.

3.0 Definitions

Analyzer calibration error, *Calibration curve*, *Calibration gas*, *Low-level gas*, *Mid-level gas*, *High-level gas*, *Calibration drift*, *Calibration span*, *Data recorder*, *Direct calibration mode*, *Gas analyzer*, *Interference check*, *Measurement system*, *Response time*, *Run*, *System calibration mode*, *System performance check*, and *Test* are the same as used in Methods 16A and 6C.

4.0 Interferences

4.1 Reduced sulfur compounds other than those defined as TRS, if present, may be measured by this method. Compounds like carbonyl sulfide, which is partially oxidized to SO_2 and may be present in a lime kiln exit stack, would be a positive interferent. Interferences may vary among instruments, and instrument-specific interferences must be evaluated through the interference check.

4.2 Particulate matter from the lime kiln stack gas (primarily calcium carbonate) can cause a negative bias if it is allowed to enter the citrate scrubber; the particulate matter will cause the pH to rise and H_2S to be absorbed before oxidation. Proper use of the particulate filter, described in section 6.1.3 of Method 16A, will eliminate this interference.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices before performing this test method.

5.2 Hydrogen Sulfide. Hydrogen sulfide is a flammable, poisonous gas with the odor of rotten eggs. Hydrogen sulfide is extremely hazardous and can cause collapse, coma, and death within a few seconds of one or two inhalations at sufficient concentrations. Low concentrations irritate the mucous membranes and may cause nausea, dizziness, and headache after exposure. It is the responsibility of the user of this test method to establish appropriate safety and health practices.

6.0 Equipment and Supplies

What do I need for the measurement system?

The measurement system is similar to those applicable components in Methods 16A and 6C. Modifications to the apparatus are accepted provided the performance criteria in section 13.0 are met.

6.1 Probe. Teflon tubing, 6.4-mm (¼ in.) diameter, sequentially wrapped with heat-resistant fiber strips, a rubberized heat tape (plug at one end), and heat-resistant adhesive tape. A flexible thermocouple or other suitable temperature measuring device must be placed between the Teflon tubing and the fiber strips so that the temperature can be monitored to prevent softening of the probe. The probe must be sheathed in stainless steel to provide in-stack rigidity. A series of bored-out stainless steel fittings placed at the front of the sheath will prevent moisture and particulate from entering between the probe and sheath. A 6.4-mm (¼ in.) Teflon elbow (bored out) must be attached to the inlet of the probe, and a 2.54 cm (1 in.) piece of Teflon tubing must be attached at the open end of the elbow to permit the opening of the probe to be turned away from the particulate stream; this will reduce the amount of particulate drawn into the sampling train. The probe is depicted in Figure 16A–2 of Method 16A.

6.2 Probe Brush. Nylon bristle brush with handle inserted into a 3.2-mm (⅛ in.) Teflon

tubing. The Teflon tubing should be long enough to pass the brush through the length of the probe.

6.3 Particulate Filter. 50-mm Teflon filter holder and a 1- to 2-μm porosity, Teflon filter (may be available through Savillex Corporation, 5325 Highway 101, Minnetonka, Minnesota 55343, or other suppliers of filters). The filter holder must be maintained in a hot box at a temperature sufficient to prevent moisture condensation. A temperature of 121 °C (250 °F) was found to be sufficient when testing a lime kiln under sub-freezing ambient conditions.

6.4 SO_2 Scrubber. Three 300-ml Teflon segmented impingers connected in series with flexible, thick-walled, Teflon tubing. (Impinger parts and tubing may be available through Savillex or other suppliers.) The first two impingers contain 100 ml of citrate buffer, and the third impinger is initially dry. The tip of the tube inserted into the solution should be constricted to less than 3 mm (⅛ in.) ID and should be immersed to a depth of at least 5 cm (2 in.).

6.5 Combustion Tube. Quartz glass tubing with an expanded combustion chamber 2.54 cm (1 in.) in diameter and at least 30.5 cm (12 in.) long. The tube ends should have an outside diameter of 0.6 cm (¼ in.) and be at least 15.3 cm (6 in.) long. This length is necessary to maintain the quartz-glass connector near ambient temperature and thereby avoid leaks. Alternative combustion tubes are acceptable provided they are shown to combust TRS at concentrations encountered during tests.

6.6 Furnace. A furnace of sufficient size to enclose the combustion chamber of the combustion tube with a temperature regulator capable of maintaining the temperature at 800 ±100 °C (1472 ±180 °F). The furnace operating temperature should be checked with a thermocouple to ensure accuracy.

6.7 Sampling Pump. A leak-free pump is required to pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system and must be constructed of material that is non-reactive to the gas it contacts. For dilution-type measurement systems, an eductor pump may be used to create a vacuum that draws the sample through a critical orifice at a constant rate.

6.8 Calibration Gas Manifold. The calibration gas manifold must allow the introduction of calibration gases either directly to the gas analyzer in direct calibration mode or into the measurement system, at the probe, in system calibration mode, or both, depending upon the type of system used. In system calibration mode, the system must be able to flood the sampling probe and vent excess gas. Alternatively, calibration gases may be introduced at the calibration valve following the probe. Maintain a constant pressure in the gas manifold. For in-stack dilution-type systems, a gas dilution subsystem is required to transport large volumes of purified air to the sample probe, and a probe controller is needed to maintain the proper dilution ratio.

6.9 Sample Gas Manifold. The sample gas manifold diverts a portion of the sample to the analyzer, delivering the remainder to the by-pass discharge vent. The manifold should also be able to introduce calibration gases directly to the analyzer. The manifold must be made of material that is non-reactive to SO_2 and be configured to safely discharge the bypass gas.

6.10 SO_2 Analyzer. You must use an instrument that uses an ultraviolet, non-dispersive infrared, fluorescence, or other detection principle to continuously measure SO_2 in the gas stream provided it meets the performance specifications in section 13.0.

6.11 Data Recording. A strip chart recorder, computerized data acquisition system, digital recorder, or data logger for recording measurement data must be used.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. When such specifications are not available, the best available grade must be used.

7.1 Water. Deionized distilled water must conform to ASTM Specification D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17). The $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.2 Citrate Buffer. Dissolve 300 g of potassium citrate (or 284 g of sodium citrate) and 41 g of anhydrous citric acid in 1 liter of water (200 ml is needed per test). Adjust the pH to between 5.4 and 5.6 with potassium citrate or citric acid, as required.

7.3 Calibration Gas. Refer to section 7.1 of Method 7E (as applicable) for the calibration gas requirements. Example calibration gas mixtures are listed below.

(a) SO_2 in nitrogen (N_2).
(b) SO_2 in air.
(c) SO_2 and carbon dioxide (CO_2) in N_2.
(d) SO_2 and oxygen (O_2) in N_2.
(e) $SO_2/CO_2/O_2$ gas mixture in N_2.
(f) CO_2/NO_X gas mixture in N_2.
(g) $CO_2/SO_2/NO_X$ gas mixture in N_2.

For fluorescence-based analyzers, the O_2 and CO_2 concentrations of the calibration gases as introduced to the analyzer must be within 1.0 percent (absolute) O_2 and 1.0 percent (absolute) CO_2 of the O_2 and CO_2 concentrations of the effluent samples as introduced to the analyzer. Alternatively, for fluorescence-based analyzers, use calibration blends of SO_2 in air and the nomographs provided by

the vendor to determine the quenching correction factor (the effluent O_2 and CO_2 concentrations must be known). This requirement does not apply to ambient-level fluorescence analyzers that are used in conjunction with sample dilution systems. Alternatively, H_2S in O_2 or air may be used to calibrate the analyzer through the tube furnace.

7.4 System Performance Check Gas. You must use H_2S (100 ppmv or less) stored in aluminum cylinders with the concentration certified by the manufacturer. Hydrogen sulfide in nitrogen is more stable than H_2S in air, but air may be used as the balance gas.

NOTE: Alternatively, H_2S recovery gas generated from a permeation device gravimetrically calibrated and certified at some convenient operating temperature may be used. The permeation rate of the device must be such that at the appropriate dilution gas flow rate, an H_2S concentration can be generated in the range of the stack gas or within 20 percent of the emission standard.

7.5 Interference Check. Examples of test gases for the interference check are listed in Table 7E–3 of Method 7E.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pre-sampling Tests. Before measuring emissions, perform the following procedures:

(a) Calibration gas verification,

(b) Calibration error test,

(c) System performance check,

(d) Verification that the interference check has been satisfied.

8.1.1 Calibration Gas Verification. Obtain a certificate from the gas manufacturer documenting the quality of the gas. Confirm that the manufacturer certification is complete and current. Ensure that your calibration gas certifications have not expired. This documentation should be available on-site for inspection. To the extent practicable, select a high-level gas concentration that will result in the measured emissions being between 20 and 100 percent of the calibration span.

8.1.2 Analyzer Calibration Error Test. After you have assembled, prepared, and calibrated your sampling system and analyzer, you must conduct a 3-point analyzer calibration error test before the first run and again after any failed system performance check or failed drift test to ensure the calibration is acceptable. Introduce the low-, mid-, and high-level calibration gases sequentially to the analyzer in direct calibration mode. For each calibration gas, calculate the analyzer calibration error using Equation 16C–1 in section 12.2. The calibration error for the low-, mid-, and high-level gases must not exceed 5.0 percent or 0.5 ppmv. If the calibration error specification is not met, take corrective action and repeat the test until an acceptable 3-point calibration is achieved.

8.1.3 System Performance Check. A system performance check is done (1) to validate the sampling train components and procedure (prior to testing), and (2) to validate a test run (after a run). You must conduct a performance check in the field prior to testing, and after each 3-hour run or after three 1-hour runs. A performance check consists of sampling and analyzing a known concentration of H_2S (system performance check gas) and comparing the analyzed concentration to the known concentration. To conduct the system performance check, mix the system performance check gas (Section 7.4) and ambient air, that has been conditioned to remove moisture and sulfur-containing gases, in a dilution system such as that shown in Figure 16A–3 of Method 16A. Alternatively, ultra-high purity (UHP) grade air may be used. Adjust the gas flow rates to generate an H_2S concentration in the range of the stack gas or within 20 percent of the applicable standard and an oxygen concentration greater than 1 percent at a total flow rate of at least 2.5 liters/min (5.3 ft3/hr). Use Equation 16A–3 from Method 16A to calculate the concentration of system performance check gas generated. Calibrate the flow rate from both gas sources with a soap bubble flow meter so that the diluted concentration of H_2S can be accurately calculated. Alternatively, mass flow controllers with documented calibrations may be used if UHP grade air is being used. Sample duration should be sufficiently long to ensure a stable response from the analyzer. Analyze in the same manner as the emission samples. Collect the sample through the probe of the sampling train using a manifold or other suitable device that will ensure extraction of a representative sample. The TRS sample concentration measured between system performance checks is corrected by the average of the pre- and post-system performance checks.

8.1.4 Interference Check. Same as in Method 7E, section 8.2.7.

8.2 Measurement System Preparation.

8.2.1 For the SO_2 scrubber, measure 100 ml of citrate buffer into the first and second impingers; leave the third impinger empty. Immerse the impingers in an ice bath, and locate them as close as possible to the filter heat box. The connecting tubing should be free of loops. Maintain the probe and filter temperatures sufficiently high to prevent moisture condensation, and monitor with a suitable temperature sensor. Prepare the oxidation furnace and maintain at 800 ±100 °C (1472 ±180 °F).

8.2.2 Citrate Scrubber Conditioning Procedure. Condition the citrate buffer scrubbing solution by pulling stack gas through the Teflon impingers as described in section 8.4.1.

8.3 Pretest Procedures. After the complete measurement system has been set up at the site and deemed to be operational, the following procedures must be completed before sampling is initiated.

8.3.1 Leak-Check. Appropriate leak-check procedures must be employed to verify the integrity of all components, sample lines, and connections. For components upstream of the sample pump, attach the probe end of the sample line to a manometer or vacuum gauge, start the pump and pull a vacuum greater than 50 mm (2 in.) Hg, close off the pump outlet, and then stop the pump and ascertain that there is no leak for 1 minute. For components after the pump, apply a slight positive pressure and check for leaks by applying a liquid (detergent in water, for example) at each joint. Bubbling indicates the presence of a leak.

8.3.2 Initial System Performance Check. A system performance check using the test gas (Section 7.4) is performed prior to testing to validate the sampling train components and procedure.

8.4 Sample Collection and Analysis.

8.4.1 After performing the required pretest procedures described in section 8.1, insert the sampling probe into the test port ensuring that no dilution air enters the stack through the port. Condition the sampling system and citrate buffer solution for a minimum of 15 minutes before beginning analysis. Begin sampling and analysis. A source test consists of three test runs. A test run shall consist of a single sample collected over a 3-hour period or three separate 1-hour samples collected over a period not to exceed six hours.

8.5 Post-Run Evaluations.

8.5.1 System Performance Check. Perform a post-run system performance check before replacing the citrate buffer solution and particulate filter and before the probe is cleaned. The check results must not exceed the 100 ±20 percent limit set forth in section 13.2. If this limit is exceeded, the intervening run is considered invalid. However, if the recovery efficiency is not in the 100 ±20 percent range, but the results do not affect the compliance or noncompliance status of the affected facility, the Administrator may decide to accept the results of the compliance test.

8.5.2 Calibration Drift. After a run or series of runs, not to exceed a 24-hour period after initial calibration, perform a calibration drift test using a calibration gas (preferably the level that best approximates the sample concentration) in direct calibration mode. This drift must not differ from the initial calibration error percent by more than 3.0 percent or 0.5 ppm. If the drift exceeds this limit, the intervening run or runs are considered valid, but a new analyzer calibration error test must be performed and passed before continuing sampling.

9.0 Quality Control

Section	Quality control measure	Effect
8.1.2	Analyzer calibration error test	Establishes initial calibration accuracy within 5.0%.
8.1.3, 8.5.1	System performance check	Ensures accuracy of sampling/analytical procedure to 100 ±20%.
8.5.2	Calibration drift test	Ensures calibration drift is within 3.0%.
8.1.4	Interference check	Checks for analytical interferences.
8.3	Sampling equipment leak-check	Ensures accurate measurement of sample gas flow rate, sample volume.

10.0 Calibration

10.1 Calibrate the system using the gases described in section 7.3. Perform the initial 3-point calibration error test as described in section 8.1.2 before you start the test. The specification in section 13 must be met. Conduct an initial system performance test described in section 8.1.3 as well before the test to validate the sampling components and procedures before sampling. After the test commences, a system performance check is required after each run. You must include a copy of the manufacturer's certification of the calibration gases used in the testing as part of the test report. This certification must include the 13 documentation requirements in the EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards, September 1997, as amended August 25, 1999.

11.0 Analytical Procedure

Because sample collection and analysis are performed together (see section 8.0), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

12.1 Nomenclature.

ACE = Analyzer calibration error, percent of calibration span.

CD = Calibration drift, percent.

C_{Dir} = Measured concentration of a calibration gas (low, mid, or high) when introduced in direct calibration mode, ppmv.

C_{H2S} = Concentration of the system performance check gas, ppmv H_2S.

C_S = Measured concentration of the system performance gas when introduced in system calibration mode, ppmv H_2S.
C_V = Manufacturer certified concentration of a calibration gas (low, mid, or high), ppmv SO_2.
C_{SO2} = Unadjusted sample SO_2 concentration, ppmv.
C_{TRS} = Total reduced sulfur concentration corrected for system performance, ppmv.
CS = Calibration span, ppmv.
DF = Dilution system (if used) dilution factor, dimensionless.
SP = System performance, percent.

12.2 Analyzer Calibration Error. For non-dilution systems, use Equation 16C–1 to calculate the analyzer calibration error for the low-, mid-, and high-level calibration gases.

$$ACE = \frac{C_{Dir} - C_v}{CS} X\ 100 \qquad \text{Eq. 16C-1}$$

12.3 System Performance Check. Use Equation 16C–2 to calculate the system performance.

$$SP = \frac{C_S - C_{H2S}}{C_{H2S}} x\ 100 \qquad \text{Eq. 16C-2}$$

12.4 Calibration Drift. Use Equation 16C–3 to calculate the calibration drift at a single concentration level after a run or series of runs (not to exceed a 24-hr period) from initial calibration. Compare the single-level calibration gas error (ACE_n) to the original error obtained for that gas in the initial analyzer calibration error test (ACE_i).

$$CD = \left| ACE_i - ACE_n \right| \qquad \text{Eq. 16C-3}$$

12.5 TRS Concentration as SO_2. For each sample or test run, calculate the arithmetic average of SO_2 concentration values (e.g., 1-minute averages). Then calculate the sample TRS concentration by adjusting the average value of C_{SO2} for system performance using Equation 16C–4.

$$C_{TRS} = \frac{\overline{C_{SO2}}}{1 - \left| \overline{SP} \right|} \qquad \text{Eq. 16C-4}$$

13.0 Method Performance

13.1 Analyzer Calibration Error. At each calibration gas level (low, mid, and high), the calibration error must either not exceed 5.0 percent of the calibration gas concentration or $|C_{Dir} - C_v|$ must be ≤0.5 ppmv.

13.2 System Performance. Each system performance check must not deviate from the system performance gas concentration by more than 20 percent. Alternatively, the results are acceptable if $|C_s - C_{H2S}|$ is ≤0.5 ppmv.

13.3 Calibration Drift. The calibration drift at the end of any run or series of runs within a 24-hour period must not differ by more than 3.0 percent from the original ACE at the test concentration level or $|ACEi - ACE_n|$ must not exceed 0.5 ppmv.

13.4 Interference Check. For the analyzer, the total interference response (i.e., the sum of the interference responses of all tested gaseous components) must not be greater than 2.5 percent of the calibration span. Any interference is also acceptable if the sum of the responses does not exceed 0.5 ppmv for a

calibration span of 5 to 10 ppmv, or 0.2 ppmv for a calibration span <5 ppmv.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. The references are the same as in section 16.0 of Method 16, section 17.0 of Method 16A, and section 17.0 of Method 6C.
2. National Council of the Paper Industry for Air and Stream Improvement, Inc,. A Study of TRS Measurement Methods. Technical Bulletin No. 434. New York, NY. May 1984. 12p.
3. Margeson, J.H., J.E. Knoll, and M.R. Midgett. A Manual Method for TRS Determination. Draft available from the authors. Source Branch, Quality Assurance Division, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

Method 17—Determination of Particulate Matter Emissions From Stationary Sources

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

NOTE: Particulate matter is not an absolute quantity. It is a function of temperature and pressure. Therefore, to prevent variability in PM emission regulations and/or associated test methods, the temperature and pressure at which PM is to be measured must be carefully defined. Of the two variables (*i.e.*, temperature and pressure), temperature has the greater effect upon the amount of PM in an effluent gas stream; in most stationary source categories, the effect of pressure appears to be negligible. In Method 5, 120 °C (248 °F) is established as a nominal reference temperature. Thus, where Method 5 is specified in an applicable subpart of the standard, PM is defined with respect to temperature. In order to maintain a collection temperature of 120 °C (248 °F), Method 5 employs a heated glass sample probe and a heated filter holder. This equipment is somewhat cumbersome and requires care in its operation. Therefore, where PM concentrations (over the normal range of temperature associated with a specified source category) are known to be independent of temperature, it is desirable to eliminate the glass probe and the heating systems, and to sample at stack temperature.

1.2 Applicability. This method is applicable for the determination of PM emissions, where PM concentrations are known to be independent of temperature over the normal range of temperatures characteristic of emissions from a specified source category. It is intended to be used only when specified by an applicable subpart of the standards, and only within the applicable temperature limits (if specified), or when otherwise approved by the Administrator. This method is not applicable to stacks that contain liquid droplets or are saturated with water vapor. In addition, this method shall not be used as written if the projected cross-sectional area of the probe extension-filter holder assembly covers more than 5 percent of the stack cross-sectional area (see section 8.1.2).

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at stack temperature. The PM mass is determined gravimetrically after the removal of uncombined water.

3.0 Definitions

Same as Method 5, section 3.0.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 17–1. The sampling train components and operation and maintenance are very similar to Method 5, which should be consulted for details.

6.1.1 Probe Nozzle, Differential Pressure Gauge, Metering System, Barometer, Gas Density Determination Equipment. Same as in Method 5, sections 6.1.1, 6.1.4, 6.1.8, 6.1.9, and 6.1.10, respectively.

6.1.2 Filter Holder. The in-stack filter holder shall be constructed of borosilicate or

quartz glass, or stainless steel. If a gasket is used, it shall be made of silicone rubber, Teflon, or stainless steel. Other holder and gasket materials may be used, subject to the approval of the Administrator. The filter holder shall be designed to provide a positive seal against leakage from the outside or around the filter.

6.1.3 Probe Extension. Any suitable rigid probe extension may be used after the filter holder.

6.1.4 Pitot Tube. Same as in Method 5, section 6.1.3.

6.1.4.1 It is recommended (1) that the pitot tube have a known baseline coefficient, determined as outlined in section 10 of Method 2; and (2) that this known coefficient be preserved by placing the pitot tube in an interference-free arrangement with respect to the sampling nozzle, filter holder, and temperature sensor (see Figure 17–1). Note that the 1.9 cm (¾-in.) free-space between the nozzle and pitot tube shown in Figure 17–1, is based on a 1.3 cm (½-in.) ID nozzle. If the sampling train is designed for sampling at higher flow rates than that described in APTD-0581, thus necessitating the use of larger sized nozzles, the free-space shall be 1.9 cm (¾-in.) with the largest sized nozzle in place.

6.1.4.2 Source-sampling assemblies that do not meet the minimum spacing requirements of Figure 17–1 (or the equivalent of these requirements, *e.g.*, Figure 2–4 of Method 2) may be used; however, the pitot tube coefficients of such assemblies shall be determined by calibration, using methods subject to the approval of the Administrator.

6.1.5 Condenser. It is recommended that the impinger system or alternatives described in Method 5 be used to determine the moisture content of the stack gas. Flexible tubing may be used between the probe extension and condenser. Long tubing lengths may affect the moisture determination.

6.2 Sample Recovery. Probe-liner and probe-nozzle brushes, wash bottles, glass sample storage containers, petri dishes, graduated cylinder and/or balance, plastic storage containers, funnel and rubber policeman, funnel. Same as in Method 5, sections 6.2.1 through 6.2.8, respectively.

6.3 Sample Analysis. Glass weighing dishes, desiccator, analytical balance, balance, beakers, hygrometer, temperature sensor. Same as in Method 5, sections 6.3.1 through 6.3.7, respectively.

7.0 Reagents and Standards

7.1 Sampling. Filters, silica gel, water, crushed ice, stopcock grease. Same as in Method 5, sections 7.1.1, 7.1.2, 7.1.3, 7.1.4, and 7.1.5, respectively. Thimble glass fiber filters may also be used.

7.2 Sample Recovery. Acetone (reagent grade). Same as in Method 5, section 7.2.

7.3 Sample Analysis. Acetone and Desiccant. Same as in Method 5, sections 7.3.1 and 7.3.2, respectively.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling.

8.1.1 Pretest Preparation. Same as in Method 5, section 8.1.1.

8.1.2 Preliminary Determinations. Same as in Method 5, section 8.1.2, except as follows: Make a projected-area model of the probe extension-filter holder assembly, with the pitot tube face openings positioned along the centerline of the stack, as shown in Figure 17–2. Calculate the estimated cross-section blockage, as shown in Figure 17–2. If the blockage exceeds 5 percent of the duct cross sectional area, the tester has the following options exist: (1) a suitable out-of-stack filtration method may be used instead of in-stack filtration; or (2) a special in-stack arrangement, in which the sampling and velocity measurement sites are separate, may be used; for details concerning this approach, consult with the Administrator (see also Reference 1 in section 17.0). Select a probe extension length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probes.

8.1.3 Preparation of Sampling Train. Same as in Method 5, section 8.1.3, except the following: Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as not to allow the sample gas stream to circumvent the filter. Check filter for tears after assembly is completed. Mark the probe extension with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point. Assemble the train as in Figure 17–1, using a very light coat of silicone grease on all ground glass joints and greasing only the outer portion (see APTD–0576) to avoid possibility of contamination by the silicone grease. Place crushed ice around the impingers.

8.1.4 Leak-Check Procedures. Same as in Method 5, section 8.1.4, except that the filter holder is inserted into the stack during the sampling train leak-check. To do this, plug the inlet to the probe nozzle with a material that will be able to withstand the stack temperature. Insert the filter holder into the stack and wait approximately 5 minutes (or longer, if necessary) to allow the system to come to equilibrium with the temperature of the stack gas stream.

8.1.5 Sampling Train Operation. The operation is the same as in Method 5. Use a data sheet such as the one shown in Figure 5–3 of Method 5, except that the filter holder temperature is not recorded.

8.1.6 Calculation of Percent Isokinetic. Same as in Method 5, section 12.11.

8.2 Sample Recovery.

8.2.1 Proper cleanup procedure begins as soon as the probe extension assembly is removed from the stack at the end of the sampling period. Allow the assembly to cool.

8.2.2 When the assembly can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to prevent losing or gaining particulate matter. Do not cap off the probe tip tightly while the sampling train is cooling down as this would create a vacuum in the filter holder, forcing condenser water backward.

8.2.3 Before moving the sample train to the cleanup site, disconnect the filter holder-probe nozzle assembly from the probe extension; cap the open inlet of the probe extension. Be careful not to lose any condensate, if present. Remove the umbilical cord from the condenser outlet and cap the outlet. If a flexible line is used between the first impinger (or condenser) and the probe extension, disconnect the line at the probe extension and let any condensed water or liquid drain into the impingers or condenser. Disconnect the probe extension from the condenser; cap the probe extension outlet. After wiping off the silicone grease, cap off the condenser inlet. Ground glass stoppers, plastic caps, or serum caps (whichever are appropriate) may be used to close these openings.

8.2.4 Transfer both the filter holder-probe nozzle assembly and the condenser to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

8.2.5 Save a portion of the acetone used for cleanup as a blank. Take 200 ml of this acetone from the wash bottle being used and place it in a glass sample container labeled ''acetone blank.'' Inspect the train prior to and during disassembly and not any abnormal conditions. Treat the sample as discussed in Method 5, section 8.2.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization

The calibrations of the probe nozzle, pitot tube, metering system, temperature sensors, and barometer are the same as in Method 5, sections 10.1 through 10.3, 10.5, and 10.6, respectively.

11.0 Analytical Procedure

Same as in Method 5, section 11.0. Analytical data should be recorded on a form similar to that shown in Figure 5–6 of Method 5.

12.0 Data Analysis and Calculations.

Same as in Method 5, section 12.0.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

Same as in Method 5, section 16.0.

17.0 References

Same as in Method 5, section 17.0, with the addition of the following:

1. Vollaro, R.F. Recommended Procedure for Sample Traverses in Ducts Smaller than 12 Inches in Diameter. U.S. Environmental Protection Agency, Emission Measurement Branch. Research Triangle Park, NC. November 1976.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

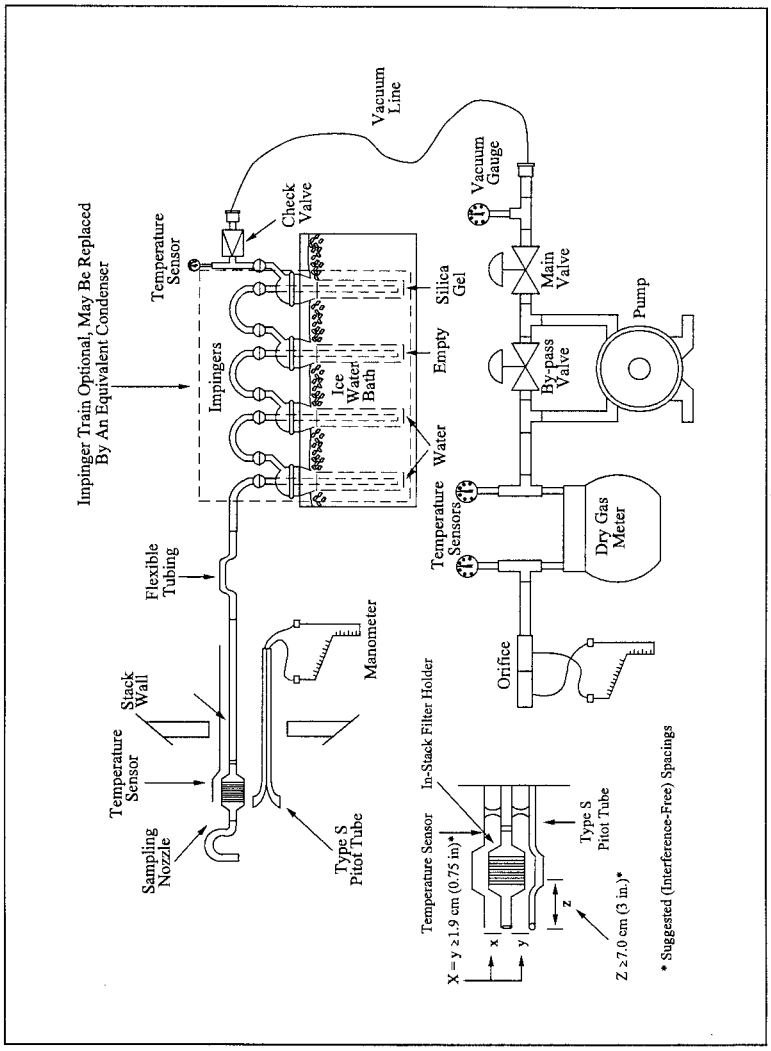


Figure 17-1. Particulate Matter Sampling Train with In-Stack Filter.

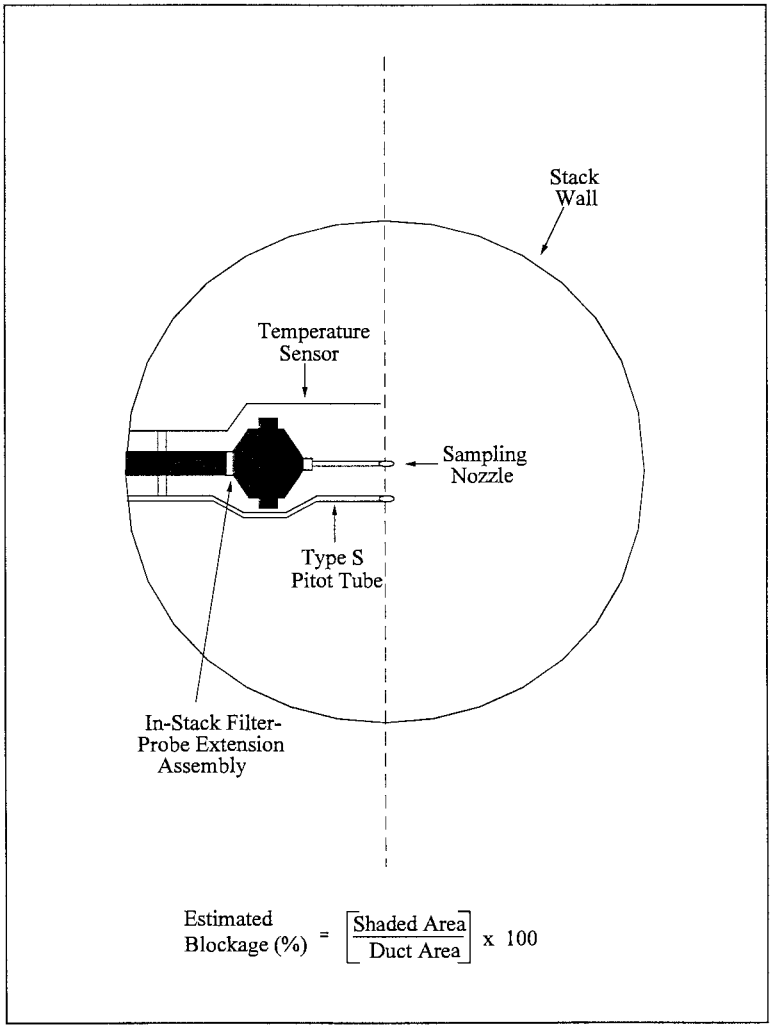


Figure 17-2. Projected-Area Model of Cross-Section Blockage (approximate average for a sample traverse) Caused by an In-Stack Filter Holder-Probe Extension Assembly.

METHOD 18—MEASUREMENT OF GASEOUS ORGANIC COMPOUND EMISSIONS BY GAS CHROMATOGRAPHY

NOTE: This method is not inclusive with respect to specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3.

NOTE: This method should not be attempted by persons unfamiliar with the performance characteristics of gas chromatography, nor by those persons who are unfamiliar with source sampling. Particular care

should be exercised in the area of safety concerning choice of equipment and operation in potentially explosive atmospheres.

1.0 Scope and Application

1.1 Analyte. Total gaseous organic compounds.

1.2 Applicability.

1.2.1 This method is designed to measure gaseous organics emitted from an industrial source. While designed for ppm level sources, some detectors are quite capable of detecting compounds at ambient levels, *e.g.*, ECD, ELCD, and helium ionization detectors. Some other types of detectors are evolving such that the sensitivity and applicability may well be in the ppb range in only a few years.

1.2.2 This method will not determine compounds that (1) are polymeric (high molecular weight), (2) can polymerize before analysis, or (3) have very low vapor pressures at stack or instrument conditions.

1.3 Range. The lower range of this method is determined by the sampling system; adsorbents may be used to concentrate the sample, thus lowering the limit of detection below the 1 part per million (ppm) typically achievable with direct interface or bag sampling. The upper limit is governed by GC detector saturation or column overloading; the upper range can be extended by dilution of sample with an inert gas or by using smaller volume gas sampling loops. The upper limit can also be governed by condensation of higher boiling compounds.

1.4 Sensitivity. The sensitivity limit for a compound is defined as the minimum detectable concentration of that compound, or the concentration that produces a signal-to-noise ratio of three to one. The minimum detectable concentration is determined during the presurvey calibration for each compound.

2.0 Summary of Method

The major organic components of a gas mixture are separated by gas chromatography (GC) and individually quantified by flame ionization, photoionization, electron capture, or other appropriate detection principles. The retention times of each separated component are compared with those of known compounds under identical conditions. Therefore, the analyst confirms the identity and approximate concentrations of the organic emission components beforehand. With this information, the analyst then prepares or purchases commercially available standard mixtures to calibrate the GC under conditions identical to those of the samples. The analyst also determines the need for sample dilution to avoid detector saturation, gas stream filtration to eliminate particulate matter, and prevention of moisture condensation.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Resolution interferences that may occur can be eliminated by appropriate GC column and detector choice or by shifting the retention times through changes in the column flow rate and the use of temperature programming.

4.2 The analytical system is demonstrated to be essentially free from contaminants by periodically analyzing blanks that consist of hydrocarbon-free air or nitrogen.

4.3 Sample cross-contamination that occurs when high-level and low-level samples or standards are analyzed alternately is best dealt with by thorough purging of the GC sample loop between samples.

4.4 To assure consistent detector response, calibration gases are contained in dry air. To adjust gaseous organic concentrations when water vapor is present in the sample, water vapor concentrations are determined for those samples, and a correction factor is applied.

4.5 The gas chromatograph run time must be sufficient to clear all eluting peaks from the column before proceeding to the next run (in order to prevent sample carryover).

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

6.0 Equipment and Supplies

6.1 Equipment needed for the presurvey sampling procedure can be found in section 16.1.1.

6.2 Equipment needed for the integrated bag sampling and analysis procedure can be found in section 8.2.1.1.1.

6.3 Equipment needed for direct interface sampling and analysis can be found in section 8.2.2.1.

6.4 Equipment needed for the dilution interface sampling and analysis can be found in section 8.2.3.1.

6.5 Equipment needed for adsorbent tube sampling and analysis can be found in section 8.2.4.1.

7.0 Reagents and Standards

7.1 Reagents needed for the presurvey sampling procedure can be found in section 16.1.2.

8.0 Sample Collection, Preservation, Storage, and Transport

8.2 Final Sampling and Analysis Procedure. Considering safety (flame hazards) and the source conditions, select an appropriate sampling and analysis procedure (Section 8.2.1, 8.2.2, 8.2.3 or 8.2.4). In situations where a hydrogen flame is a hazard and no intrinsically safe GC is suitable, use the flexible bag collection technique or an adsorption technique.

8.2.1 Integrated Bag Sampling and Analysis.

8.2.1.1 Evacuated Container Sampling Procedure. In this procedure, the bags are filled by evacuating the rigid air-tight container holding the bags. Use a field sample data sheet as shown in Figure 18–10. Collect triplicate samples from each sample location.

8.2.1.1.1 Apparatus.

8.2.1.1.1.1 Probe. Stainless steel, Pyrex glass, or Teflon tubing probe, according to the duct temperature, with Teflon tubing of sufficient length to connect to the sample bag. Use stainless steel or Teflon unions to connect probe and sample line.

8.2.1.1.1.2 Quick Connects. Male (2) and female (2) of stainless steel construction.

8.2.1.1.1.3 Needle Valve. To control gas flow.

8.2.1.1.1.4 Pump. Leakless Teflon-coated diaphragm-type pump or equivalent. To deliver at least 1 liter/min.

8.2.1.1.1.5 Charcoal Adsorption Tube. Tube filled with activated charcoal, with glass wool plugs at each end, to adsorb organic vapors.

8.2.1.1.1.6 Flowmeter. 0 to 500-ml flow range; with manufacturer's calibration curve.

8.2.1.1.2 Sampling Procedure. To obtain a sample, assemble the sample train as shown in Figure 18–9. Leak-check both the bag and the container. Connect the vacuum line from the needle valve to the Teflon sample line from the probe. Place the end of the probe at the centroid of the stack or at a point no closer to the walls than 1 in., and start the pump. Set the flow rate so that the final volume of the sample is approximately 80 percent of the bag capacity. After allowing sufficient time to purge the line several times, connect the vacuum line to the bag, and evacuate until the rotameter indicates no flow. Then position the sample and vacuum lines for sampling, and begin the actual sampling, keeping the rate proportional to the stack velocity. As a precaution, direct the gas exiting the rotameter away from sampling personnel. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Record the source temperature, barometric pressure, ambient temperature, sampling flow rate, and initial and final sampling time on the data sheet shown in Figure 18–10. Protect the bag and its container from sunlight. Record the time lapsed between sample collection and analysis, and then conduct the recovery procedure in Section 8.4.2.

8.2.1.2 Direct Pump Sampling Procedure. Follow 8.2.1.1, except place the pump and needle valve between the probe and the bag. Use a pump and needle valve constructed of inert material not affected by the stack gas. Leak-check the system, and then purge with stack gas before connecting to the previously evacuated bag.

8.2.1.3 Explosion Risk Area Bag Sampling Procedure. Follow 8.2.1.1 except replace the pump with another evacuated can (see Figure 18–9a). Use this method whenever there is a possibility of an explosion due to pumps, heated probes, or other flame producing equipment.

8.2.1.4 Other Modified Bag Sampling Procedures. In the event that condensation is observed in the bag while collecting the sample and a direct interface system cannot be used, heat the bag during collection and maintain it at a suitably elevated temperature during all subsequent operations. (Note: Take care to leak-check the system prior to the dilutions so as not to create a potentially explosive atmosphere.) As an alternative, collect the sample gas, and simultaneously dilute it in the bag.

8.2.1.4.1 First Alternative Procedure. Heat the box containing the sample bag to 120 °C (±5 °C). Then transport the bag as rapidly as possible to the analytical area while maintaining the heating, or cover the box with an insulating blanket. In the analytical area, keep the box heated to 120 °C (±5 °C) until analysis. Be sure that the method of heating the box and the control for the heating circuit are compatible with the safety restrictions required in each area.

8.2.1.4.2 Second Alternative Procedure. Prefill the bag with a known quantity of inert gas. Meter the inert gas into the bag according to the procedure for the preparation of gas concentration standards of volatile liquid materials (Section 10.1.2.2), but eliminate the midget impinger section. Take the partly filled bag to the source, and meter the source gas into the bag through heated sampling lines and a heated flowmeter, or Teflon positive displacement pump. Verify the dilution factors before sampling each bag through dilution and analysis of gases of known concentration.

8.2.1.5 Analysis of Bag Samples.

8.2.1.5.1 Apparatus. Same as section 8.1. A minimum of three gas standards are required.

8.2.1.5.2 Procedure.

8.2.1.5.2.1 Establish proper GC operating conditions as described in section 10.2, and record all data listed in Figure 18–7. Prepare the GC so that gas can be drawn through the sample valve. Flush the sample loop with

calibration gas mixture, and activate the valve (sample pressure at the inlet to the GC introduction valve should be similar during calibration as during actual sample analysis). Obtain at least three chromatograms for the mixture. The results are acceptable when the peak areas for the three injections agree to within 5 percent of their average. If they do not agree, run additional samples or correct the analytical techniques until this requirement is met. Then analyze the other two calibration mixtures in the same manner. Prepare a calibration curve as described in section 10.2.

8.2.1.5.2.2 Analyze the three source gas samples by connecting each bag to the sampling valve with a piece of Teflon tubing identified with that bag. Analyze each bag sample three times. Record the data in Figure 18–11. If certain items do not apply, use the notation ''N.A.'' If the bag has been maintained at an elevated temperature as described in section 8.2.1.4, determine the stack gas water content by Method 4. After all samples have been analyzed, repeat the analysis of the mid-level calibration gas for each compound. Compare the average response factor of the pre- and post-test analysis for each compound. If they differ by >5percent, analyze the other calibration gas levels for that compound, and prepare a calibration curve using all the pre- and post-test calibration gas mixture values. If the two response factor averages (pre-and post-test) differ by less than 5 percent from their mean value, the tester has the option of using only the pre-test calibration curve to generate the concentration values.

8.2.1.6 Determination of Bag Water Vapor Content. Measure the ambient temperature and barometric pressure near the bag. From a water saturation vapor pressure table, determine and record the water vapor content of the bag as a decimal figure. (Assume the relative humidity to be 100 percent unless a lesser value is known.) If the bag has been maintained at an elevated temperature as described in section 8.2.1.4, determine the stack gas water content by Method 4.

8.2.1.8 Emission Calculations. From the calibration curve described in section 8.2.1.5, select the value of C_s that corresponds to the peak area. Calculate the concentration C_c in ppm, dry basis, of each organic in the sample using Equation 18–5 in section 12.6.

8.2.2 Direct Interface Sampling and Analysis Procedure. The direct interface procedure can be used provided that the moisture content of the gas does not interfere with the analysis procedure, the physical requirements of the equipment can be met at the site, and the source gas concentration falls within the linear range of the detector. Adhere to all safety requirements with this method.

8.2.2.1 Apparatus.

8.2.2.1.1 Probe. Constructed of stainless steel, Pyrex glass, or Teflon tubing as dictated by duct temperature and reactivity of target compounds. A filter or glass wool plug may be needed if particulate is present in the stack gas. If necessary, heat the probe with heating tape or a special heating unit capable of maintaining a temperature greater than 110 °C.

8.2.2.1.2 Sample Lines. 6.4-mm OD (or other diameter as needed) Teflon lines, heat-traced to prevent condensation of material (greater than 110 °C).

8.2.2.1.3 Quick Connects. To connect sample line to gas sampling valve on GC instrument and to pump unit used to withdraw source gas. Use a quick connect or equivalent on the cylinder or bag containing calibration gas to allow connection of the calibration gas to the gas sampling valve.

8.2.2.1.4 Thermocouple Readout Device. Potentiometer or digital thermometer, to measure source temperature and probe temperature.

8.2.2.1.5 Heated Gas Sampling Valve. Of two-position, six-port design, to allow sample loop to be purged with source gas or to direct source gas into the GC instrument.

8.2.2.1.6 Needle Valve. To control gas sampling rate from the source.

8.2.2.1.7 Pump. Leakless Teflon-coated diaphragm-type pump or equivalent, capable of at least 1 liter/minute sampling rate.

8.2.2.1.8 Flowmeter. Of suitable range to measure sampling rate.

8.2.2.1.9 Charcoal Adsorber. To adsorb organic vapor vented from the source to prevent exposure of personnel to source gas.

8.2.2.1.10 Gas Cylinders. Carrier gas, oxygen and fuel as needed to run GC and detector.

8.2.2.1.11 Gas Chromatograph. Capable of being moved into the field, with detector, heated gas sampling valve, column required to complete separation of desired components, and option for temperature programming.

8.2.2.1.12 Recorder/Integrator. To record results.

8.2.2.2 Procedure. Calibrate the GC using the procedures in section 8.2.1.5.2.1. To obtain a stack gas sample, assemble the sampling system as shown in Figure 18–12. Make sure all connections are tight. Turn on the probe and sample line heaters. As the temperature of the probe and heated line approaches the target temperature as indicated on the thermocouple readout device, control the heating to maintain a temperature greater than 110 °C. Conduct a 3-point calibration of the GC by analyzing each gas mixture in triplicate. Generate a calibration curve. Place the inlet of the probe at the centroid of the duct, or at a point no closer to the walls than 1 m, and draw source gas into the probe, heated line, and sample loop. After thorough flushing, analyze the stack gas sample using the same conditions as for

the calibration gas mixture. For each run, sample, analyze, and record five consecutive samples. A test consists of three runs (five samples per run times three runs, for a total of fifteen samples). After all samples have been analyzed, repeat the analysis of the mid-level calibration gas for each compound. For each calibration standard, compare the pre- and post-test average response factors (RF) for each compound. If the two calibration RF values (pre- and post-analysis) differ by more than 5 percent from their mean value, then analyze the other calibration gas levels for that compound and determine the stack gas sample concentrations by comparison to both calibration curves (this is done by preparing a calibration curve using all the pre- and post-test calibration gas mixture values.) If the two calibration RF values differ by less than 5 percent from their mean value, the tester has the option of using only the pre-test calibration curve to generate the concentration values. Record this calibration data and the other required data on the data sheet shown in Figure 18–11, deleting the dilution gas information.

NOTE: Take care to draw all samples and calibration mixtures through the sample loop at the same pressure.

8.2.2.3 Determination of Stack Gas Moisture Content. Use Method 4 to measure the stack gas moisture content.

8.2.2.5 Emission Calculations. Same as section 8.2.1.8.

8.2.3 Dilution Interface Sampling and Analysis Procedure. Source samples that contain a high concentration of organic materials may require dilution prior to analysis to prevent saturating the GC detector. The apparatus required for this direct interface procedure is basically the same as that described in the section 8.2.2, except a dilution system is added between the heated sample line and the gas sampling valve. The apparatus is arranged so that either a 10:1 or 100:1 dilution of the source gas can be directed to the chromatograph. A pump of larger capacity is also required, and this pump must be heated and placed in the system between the sample line and the dilution apparatus.

8.2.3.1 Apparatus. The equipment required in addition to that specified for the direct interface system is as follows:

8.2.3.1.1 Sample Pump. Leakless Teflon-coated diaphragm-type that can withstand being heated to 120 °C and deliver 1.5 liters/minute.

8.2.3.1.2 Dilution Pumps. Two Model A–150 Komhyr Teflon positive displacement type delivering 150 cc/minute, or equivalent. As an option, calibrated flowmeters can be used in conjunction with Teflon-coated diaphragm pumps.

8.2.3.1.3 Valves. Two Teflon three-way valves, suitable for connecting to Teflon tubing.

8.2.3.1.4 Flowmeters. Two, for measurement of diluent gas.

8.2.3.1.5 Diluent Gas with Cylinders and Regulators. Gas can be nitrogen or clean dry air, depending on the nature of the source gases.

8.2.3.1.6 Heated Box. Suitable for being heated to 120 °C, to contain the three pumps, three-way valves, and associated connections. The box should be equipped with quick connect fittings to facilitate connection of: (1) the heated sample line from the probe, (2) the gas sampling valve, (3) the calibration gas mixtures, and (4) diluent gas lines. A schematic diagram of the components and connections is shown in Figure 18–13. The heated box shown in Figure 18–13 is designed to receive a heated line from the probe. An optional design is to build a probe unit that attaches directly to the heated box. In this way, the heated box contains the controls for the probe heaters, or, if the box is placed against the duct being sampled, it may be possible to eliminate the probe heaters. In either case, a heated Teflon line is used to connect the heated box to the gas sampling valve on the chromatograph.

NOTE: Care must be taken to leak-check the system prior to the dilutions so as not to create a potentially explosive atmosphere.

8.2.3.2 Procedure.

8.2.3.2.1 Assemble the apparatus by connecting the heated box, shown in Figure 18–13, between the heated sample line from the probe and the gas sampling valve on the chromatograph. Vent the source gas from the gas sampling valve directly to the charcoal filter, eliminating the pump and rotameter. Heat the sample probe, sample line, and heated box. Insert the probe and source thermocouple at the centroid of the duct, or to a point no closer to the walls than 1 m. Measure the source temperature, and adjust all heating units to a temperature 0 to 3 °C above this temperature. If this temperature is above the safe operating temperature of the Teflon components, adjust the heating to maintain a temperature high enough to prevent condensation of water and organic compounds (greater than 110 °C). Calibrate the GC through the dilution system by following the procedures in section 8.2.1.5.2.1. Determine the concentration of the diluted calibration gas using the dilution factor and the certified concentration of the calibration gas. Record the pertinent data on the data sheet shown in Figure 18–11.

8.2.3.2.2 Once the dilution system and GC operations are satisfactory, proceed with the analysis of source gas, maintaining the same dilution settings as used for the standards.

8.2.3.2.3 Analyze the audit samples using either the dilution system, or directly connect to the gas sampling valve as required. Record all data and report the results to the audit supervisor.

8.2.3.3 Determination of Stack Gas Moisture Content. Same as section 8.2.2.3.

8.2.3.4 Quality Assurance. Same as section 8.2.2.4.

8.2.3.5 Emission Calculations. Same as section 8.2.2.5, with the dilution factor applied.

8.2.4 Adsorption Tube Procedure. Any commercially available adsorbent is allowed for the purposes of this method, as long as the recovery study criteria in section 8.4.3 are met. Help in choosing the adsorbent may be found by calling the distributor, or the tester may refer to National Institute for Occupational Safety and Health (NIOSH) methods for the particular organics to be sampled. For some adsorbents, the principal interferent will be water vapor. If water vapor is thought to be a problem, the tester may place a midget impinger in an ice bath before the adsorbent tubes. If this option is chosen, the water catch in the midget impinger shall be analyzed for the target compounds. Also, the spike for the recovery study (in section 8.4.3) shall be conducted in both the midget impinger and the adsorbent tubes. The combined recovery (add the recovered amount in the impinger and the adsorbent tubes to calculate R) shall then meet the criteria in section 8.4.3.

NOTE: Post-test leak-checks are not allowed for this technique since this can result in sample contamination.

8.2.4.1 Additional Apparatus. The following items (or equivalent) are suggested.

8.2.4.1.1 Probe. Borosilicate glass or stainless steel, approximately 6-mm ID, with a heating system if water condensation is a problem, and a filter (either in-stack or out-of-stack, heated to stack temperature) to remove particulate matter. In most instances, a plug of glass wool is a satisfactory filter.

8.2.4.1.2 Flexible Tubing. To connect probe to adsorption tubes. Use a material that exhibits minimal sample adsorption.

8.2.4.1.3 Leakless Sample Pump. Flow controlled, constant rate pump, with a set of limiting (sonic) orifices.

8.2.4.1.4 Bubble-Tube Flowmeter. Volume accuracy within 1 percent, to calibrate pump.

8.2.4.1.5 Stopwatch. To time sampling and pump rate calibration.

8.2.4.1.6 Adsorption Tubes. Precleaned adsorbent, with mass of adsorbent to be determined by calculating breakthrough volume and expected concentration in the stack.

8.2.4.1.7 Barometer. Accurate to 5 mm Hg, to measure atmospheric pressure during sampling and pump calibration.

8.2.4.1.8 Rotameter. O to 100 cc/min, to detect changes in flow rate during sampling.

8.2.4.2 Sampling and Analysis.

8.2.4.2.1 Calibrate the pump and limiting orifice flow rate through adsorption tubes with the bubble tube flowmeter before sampling. The sample system can be operated as a ''recirculating loop'' for this operation. Record the ambient temperature and barometric pressure. Then, during sampling, use the rotameter to verify that the pump and orifice sampling rate remains constant.

8.2.4.2.2 Use a sample probe, if required, to obtain the sample at the centroid of the duct or at a point no closer to the walls than 1 m. Minimize the length of flexible tubing between the probe and adsorption tubes. Several adsorption tubes can be connected in series, if the extra adsorptive capacity is needed. Adsorption tubes should be maintained vertically during the test in order to prevent channeling. Provide the gas sample to the sample system at a pressure sufficient for the limiting orifice to function as a sonic orifice. Record the total time and sample flow rate (or the number of pump strokes), the barometric pressure, and ambient temperature. Obtain a total sample volume commensurate with the expected concentration(s) of the volatile organic(s) present and recommended sample loading factors (weight sample per weight adsorption media). Laboratory tests prior to actual sampling may be necessary to predetermine this volume. If water vapor is present in the sample at concentrations above 2 to 3 percent, the adsorptive capacity may be severely reduced. Operate the gas chromatograph according to the manufacturer's instructions. After establishing optimum conditions, verify and document these conditions during all operations. Calibrate the instrument and then analyze the emission samples.

8.2.4.3 Standards and Calibration. If using thermal desorption, obtain calibration gases using the procedures in section 10.1. If using solvent extraction, prepare liquid standards in the desorption solvent. Use a minimum of three different standards; select the concentrations to bracket the expected average sample concentration. Perform the calibration before and after each day's sample analyses using the procedures in section 8.2.1.5.2.1.

8.2.4.4 Quality Assurance.

8.2.4.4.1 Determine the recovery efficiency of the pollutants of interest according to section 8.4.3.

8.2.4.4.2 Determination of Sample Collection Efficiency (Optional). If sample breakthrough is thought to be a problem, a routine procedure for determining breakthrough is to analyze the primary and backup portions of the adsorption tubes separately. If the backup portion exceeds 10 percent of the total amount (primary and back-up), it is usually a sign of sample breakthrough. For the purposes of this method, only the recovery efficiency value (Section 8.4.3) is used to determine the appropriateness of the sampling and analytical procedure.

8.2.4.4.3 Volume Flow Rate Checks. Perform this check immediately after sampling with all sampling train components in place.

Use the bubble-tube flowmeter to measure the pump volume flow rate with the orifice used in the test sampling, and record the result. If it has changed by more than 5 but less than 20 percent, calculate an average flow rate for the test. If the flow rate has changed by more than 20 percent, recalibrate the pump and repeat the sampling.

8.2.4.4.4 Calculations. Correct all sample volumes to standard conditions. If a sample dilution system has been used, multiply the results by the appropriate dilution ratio. Correct all results according to the applicable procedure in section 8.4.3. Report results as ppm by volume, dry basis.

8.3 Reporting of Results. At the completion of the field analysis portion of the study, ensure that the data sheets shown in Figure 18–11 have been completed. Summarize this data on the data sheets shown in Figure 18–15.

8.4 Recovery Study. After conducting the presurvey and identifying all of the pollutants of interest, conduct the appropriate recovery study during the test based on the sampling system chosen for the compounds of interest.

8.4.1 Recovery Study for Direct Interface or Dilution Interface Sampling. If the procedures in section 8.2.2 or 8.2.3 are to be used to analyze the stack gas, conduct the calibration procedure as stated in section 8.2.2.2 or 8.2.3.2, as appropriate. Upon successful completion of the appropriate calibration procedure, attach the mid-level calibration gas for at least one target compound to the inlet of the probe or as close as possible to the inlet of the probe, but before the filter. Repeat the calibration procedure by sampling and analyzing the mid-level calibration gas through the entire sampling and analytical system in triplicate. The mean of the calibration gas response sampled through the probe shall be within 10 percent of the analyzer response. If the difference in the two means is greater than 10 percent, check for leaks throughout the sampling system and repeat the analysis of the standard through the sampling system until this criterion is met.

8.4.2 Recovery Study for Bag Sampling.

8.4.2.1 Follow the procedures for the bag sampling and analysis in section 8.2.1. After analyzing all three bag samples, choose one of the bag samples and tag this bag as the spiked bag. Spike the chosen bag sample with a known mixture (gaseous or liquid) of all of the target pollutants. The theoretical concentration, in ppm, of each spiked compound in the bag shall be 40 to 60 percent of the average concentration measured in the three bag samples. If a target compound was not detected in the bag samples, the concentration of that compound to be spiked shall be 5 times the limit of detection for that compound. Store the spiked bag for the same period of time as the bag samples collected in the field. After the appropriate storage time has passed, analyze the spiked bag three times. Calculate the average fraction recovered (R) of each spiked target compound with the equation in section 12.7.

8.4.2.2 For the bag sampling technique to be considered valid for a compound, $0.70 \leq R \leq 1.30$. If the R value does not meet this criterion for a target compound, the sampling technique is not acceptable for that compound, and therefore another sampling technique shall be evaluated for acceptance (by repeating the recovery study with another sampling technique). Report the R value in the test report and correct all field measurements with the calculated R value for that compound by using the equation in section 12.8.

8.4.3 Recovery Study for Adsorption Tube Sampling. If following the adsorption tube procedure in section 8.2.4, conduct a recovery study of the compounds of interest during the actual field test. Set up two identical sampling trains. Collocate the two sampling probes in the stack. The probes shall be placed in the same horizontal plane, where the first probe tip is 2.5 cm from the outside edge of the other. One of the sampling trains shall be designated the spiked train and the other the unspiked train. Spike all of the compounds of interest (in gaseous or liquid form) onto the adsorbent tube(s) in the spiked train before sampling. The mass of each spiked compound shall be 40 to 60 percent of the mass expected to be collected with the unspiked train. Sample the stack gas into the two trains simultaneously. Analyze the adsorbents from the two trains utilizing identical analytical procedures and instrumentation. Determine the fraction of spiked compound recovered (R) using the equations in section 12.9.

8.4.3.1 Repeat the procedure in section 8.4.3 twice more, for a total of three runs. In order for the adsorbent tube sampling and analytical procedure to be acceptable for a compound, $0.70 \leq R \leq 1.30$ (R in this case is the average of three runs). If the average R value does not meet this criterion for a target compound, the sampling technique is not acceptable for that compound, and therefore another sampling technique shall be evaluated for acceptance (by repeating the recovery study with another sampling technique). Report the R value in the test report and correct all field measurements with the calculated R value for that compound by using the equation in section 12.8.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures

Section	Quality control measure	Effect
8.4.1	Recovery study for direct interface or dilution interface sampling.	Ensure that there are no significant leaks in the sampling system.
8.4.2	Recovery study for bag sampling	Demonstrate that proper sampling/analysis procedures were selected.
8.4.3	Recovery study for adsorption tube sampling.	Demonstrate that proper sampling/analysis procedures were selected.

10.0 Calibration and Standardization.

10.1 Calibration Standards. Obtain calibration gas standards for each target compound to be analyzed. Commercial cylinder gases certified by the manufacturer to be accurate to within 1 percent of the certified label value are preferable, although cylinder gases certified by the manufacturer to 2 percent accuracy are allowed. Another option allowed by this method is for the tester to obtain high concentration certified cylinder gases and then use a dilution system meeting the requirements of Test Method 205, 40 CFR Part 51, Appendix M to make multilevel calibration gas standards. Prepare or obtain enough calibration standards so that there are three different concentrations of each organic compound expected to be measured in the source sample. For each organic compound, select those concentrations that bracket the concentrations expected in the source samples. A calibration standard may contain more than one organic compound. If samples are collected in adsorbent tubes and extracted using solvent extraction, prepare or obtain standards in the same solvent used for the sample extraction procedure. Verify the stability of all standards for the time periods they are used.

10.2 Preparation of Calibration Curves.

10.2.1 Establish proper GC conditions, then flush the sampling loop for 30 seconds. Allow the sample loop pressure to equilibrate to atmospheric pressure, and activate the injection valve. Record the standard concentration, attenuator factor, injection time, chart speed, retention time, peak area, sample loop temperature, column temperature, and carrier gas flow rate. Analyze each standard in triplicate.

10.2.2 Repeat this procedure for each standard. Prepare a graphical plot of concentration (C_s) versus the calibration area values. Perform a regression analysis, and draw the least square line.

11.0 Analytical Procedures

11.1 Analysis Development

11.1.1 Selection of GC Parameters

11.1.1.1 Column Choice. Based on the initial contact with plant personnel concerning the plant process and the anticipated emissions, choose a column that provides good resolution and rapid analysis time. The choice of an appropriate column can be aided by a literature search, contact with manufacturers of GC columns, and discussion with personnel at the emission source.

NOTE: Most column manufacturers keep excellent records on their products. Their technical service departments may be able to recommend appropriate columns and detector type for separating the anticipated compounds, and they may be able to provide information on interferences, optimum operating conditions, and column limitations. Plants with analytical laboratories may be able to provide information on their analytical procedures.

11.1.1.2 Preliminary GC Adjustment. Using the standards and column obtained in section 11.1.1.1, perform initial tests to determine appropriate GC conditions that provide good resolution and minimum analysis time for the compounds of interest.

11.1.1.3 Preparation of Presurvey Samples. If the samples were collected on an adsorbent, extract the sample as recommended by the manufacturer for removal of the compounds with a solvent suitable to the type of GC analysis. Prepare other samples in an appropriate manner.

11.1.1.4 Presurvey Sample Analysis.

11.1.1.4.1 Before analysis, heat the presurvey sample to the duct temperature to vaporize any condensed material. Analyze the samples by the GC procedure, and compare the retention times against those of the calibration samples that contain the components expected to be in the stream. If any compounds cannot be identified with certainty by this procedure, identify them by other means such as GC/mass spectroscopy (GC/MS) or GC/infrared techniques. A GC/MS system is recommended.

11.1.1.4.2 Use the GC conditions determined by the procedure of section 11.1.1.2 for the first injection. Vary the GC parameters during subsequent injections to determine the optimum settings. Once the optimum settings have been determined, perform repeat injections of the sample to determine the retention time of each compound. To inject a sample, draw sample through the loop at a constant rate (100 ml/min for 30 seconds). Be careful not to pressurize the gas in the loop. Turn off the pump and allow the gas in the sample loop to come to ambient pressure. Activate the sample valve, and record injection time, loop temperature, column temperature, carrier flow rate, chart speed, and attenuator setting. Calculate the retention

time of each peak using the distance from injection to the peak maximum divided by the chart speed. Retention times should be repeatable within 0.5 seconds.

11.1.1.4.3 If the concentrations are too high for appropriate detector response, a smaller sample loop or dilutions may be used for gas samples, and, for liquid samples, dilution with solvent is appropriate. Use the standard curves (Section 10.2) to obtain an estimate of the concentrations.

11.1.1.4.4 Identify all peaks by comparing the known retention times of compounds expected to be in the retention times of peaks in the sample. Identify any remaining unidentified peaks which have areas larger than 5 percent of the total using a GC/MS, or estimation of possible compounds by their retention times compared to known compounds, with confirmation by further GC analysis.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

B_{ws} = Water vapor content of the bag sample or stack gas, proportion by volume.
C_s = Concentration of the organic from the calibration curve, ppm.
G_v = Gas volume or organic compound injected, ml.
L_v = Liquid volume of organic injected, µl.
M = Molecular weight of organic, g/g-mole.
m_s = Total mass of compound measured on adsorbent with spiked train (µg).
m_u = Total mass of compound measured on adsorbent with unspiked train (µg).
m_v = Mass per volume of spiked compound measured (µg/L).
P_i = Barometric or absolute sample loop pressure at time of sample analysis, mm Hg.
P_m = Absolute pressure of dry gas meter, mm Hg.
P_r = Reference pressure, the barometric pressure or absolute sample loop pressure recorded during calibration, mm Hg.
P_s = Absolute pressure of syringe before injection, mm Hg.
q_c = Flow rate of the calibration gas to be diluted.
q_{c1} = Flow rate of the calibration gas to be diluted in stage 1.
q_{c2} = Flow rate of the calibration gas to be diluted in stage 2.
q_d = Diluent gas flow rate.
q_{d1} = Flow rate of diluent gas in stage 1.
q_{d2} = Flow rate of diluent gas in stage 2.
s = Theoretical concentration (ppm) of spiked target compound in the bag.
S = Theoretical mass of compound spiked onto adsorbent in spiked train (µg).
t = Measured average concentration (ppm) of target compound and source sample (analysis results subsequent to bag spiking)
T_i = Sample loop temperature at the time of sample analysis, °K.
T_m = Absolute temperature of dry gas meter, °K.
T_s = Absolute temperature of syringe before injection, °K.
u = Source sample average concentration (ppm) of target compound in the bag (analysis results before bag spiking).
V_m = Gas volume indicated by dry gas meter, liters.
v_s = volume of stack gas sampled with spiked train (L).
v_u = volume of stack gas sampled with unspiked train (L).
X = Mole or volume fraction of the organic in the calibration gas to be diluted.
Y = Dry gas meter calibration factor, dimensionless.
µl = Liquid organic density as determined, g/ml.
24.055 = Ideal gas molar volume at 293 °K and 760 mm Hg, liters/g-mole.
1000 = Conversion factor, ml/liter.
10^6 = Conversion to ppm.

12.2 Calculate the concentration, C_s, in ppm using the following equation:

$$C_s = \frac{10^6\left(\overline{X}q_c\right)}{q_c + q_d} \qquad \text{Eq. 18-1}$$

12.3 Calculate the concentration, C_s, in ppm of the organic in the final gas mixture using the following equation:

$$C_s = 10^6\,\overline{X}\left(\frac{q_{c1}}{q_{c1}+q_{d1}}\right)\left(\frac{q_{c2}}{q_{c2}+q_{d2}}\right) \qquad \text{Eq. 18-2}$$

12.4 Calculate each organic standard concentration, C_s, in ppm using the following equation:

$$C_s = \frac{G_v \times 10^6 \frac{293}{T_s} \frac{P_s}{760}}{V_m Y \frac{293}{T_m} \frac{P_m}{760} 1000} \qquad \text{Eq. 18-3}$$

$$= \frac{G_v \times 10^3 \frac{P_s}{T_s} \frac{T_m}{P_m}}{V_m Y}$$

12.5 Calculate each organic standard concentration, C_s, in ppm using the following equation:

$$C_s = \frac{\frac{L_v}{M} \rho \left(24.055 \times 10^6\right)}{V_m Y \frac{293}{T_m} \frac{P_m}{760} 1000} = 6.24 \times 10^4 \frac{L_v \rho T_m}{M V_m Y P_m} \qquad \text{Eq. 18-4}$$

12.6 Calculate the concentration, C_c, in ppm, dry basis, of each organic is the sample using the following equation:

$$C_c = \frac{C_s P_r T_i F_r}{P_i T_r \left(1 - B_{ws}\right)} \qquad \text{Eq. 18-5}$$

12.7 Calculate the average fraction recovered (R) of each spiked target compound using the following equation:

$$R = \frac{t - u}{s} \qquad \text{Eq. 18-6}$$

12.8 Correct all field measurements with the calculated R value for that compound using the following equation:

$$\text{Reported Result} = \frac{\text{Measured Concentration (ppm)}}{R} \qquad \text{Eq. 18-7}$$

12.9 Determine the mass per volume of spiked compound measured using the following equation:

$$m_v = \frac{m_s}{V_s} - \frac{m_u}{V_u} \qquad \text{Eq. 18-8}$$

12.10 Calculate the fraction of spiked compound recovered, R, using the following equation:

$$R = \frac{m_v \times v_s}{S} \qquad \text{Eq. 18-9}$$

13.0 Method Performance

13.1 Since a potential sample may contain a variety of compounds from various sources, a specific precision limit for the analysis of field samples is impractical. Precision in the range of 5 to 10 percent relative standard deviation (RSD) is typical for gas chromatographic techniques, but an experienced GC operator with a reliable instrument can readily achieve 5 percent RSD. For this method, the following combined GC/operator values are required.

(a) Precision. Triplicate analyses of calibration standards fall within 5 percent of their mean value.

(c) Recovery. After developing an appropriate sampling and analytical system for the pollutants of interest, conduct the procedure in section 8.4. Conduct the appropriate recovery study in section 8.4 at each sampling point where the method is being applied. Submit the data and results of the recovery procedure with the reporting of results under section 8.3.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Optional Presurvey and Presurvey Sampling.

NOTE: Presurvey screening is optional. Presurvey sampling should be conducted for sources where the target pollutants are not known from previous tests and/or process knowledge.

Perform a presurvey for each source to be tested. Refer to Figure 18–1. Some of the information can be collected from literature surveys and source personnel. Collect gas samples that can be analyzed to confirm the identities and approximate concentrations of the organic emissions.

16.1.1 Apparatus. This apparatus list also applies to sections 8.2 and 11.

16.1.1.1 Teflon Tubing. (Mention of trade names or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.) Diameter and length determined by connection requirements of cylinder regulators and the GC. Additional tubing is necessary to connect the GC sample loop to the sample.

16.1.1.2 Gas Chromatograph. GC with suitable detector, columns, temperature-controlled sample loop and valve assembly, and temperature programmable oven, if necessary. The GC shall achieve sensitivity requirements for the compounds under study.

16.1.1.3 Pump. Capable of pumping 100 ml/min. For flushing sample loop.

16.1.1.4 Flow Meter. To measure flow rates.

16.1.1.5 Regulators. Used on gas cylinders for GC and for cylinder standards.

16.1.1.6 Recorder. Recorder with linear strip chart is minimum acceptable. Integrator (optional) is recommended.

16.1.1.7 Syringes. 0.5-ml, 1.0- and 10-microliter size, calibrated, maximum accuracy (gas tight) for preparing calibration standards. Other appropriate sizes can be used.

16.1.1.8 Tubing Fittings. To plumb GC and gas cylinders.

16.1.1.9 Septa. For syringe injections.

16.1.1.10 Glass Jars. If necessary, clean, colored glass jars with Teflon-lined lids for condensate sample collection. Size depends on volume of condensate.

16.1.1.11 Soap Film Flowmeter. To determine flow rates.

16.1.1.12 Flexible Bags. Tedlar or equivalent, 10- and 50-liter capacity, for preparation of standards. (Verify through the manufacturer that the Tedlar alternative is suitable for the compound of interest and make this verifying information available for inspection.)

16.1.1.13 Dry Gas Meter with Temperature and Pressure Gauges. Accurate to ±2 percent, for preparation of gas standards.

16.1.1.14 Midget Impinger/Hot Plate Assembly. For preparation of gas standards.

16.1.1.15 Sample Flasks. For presurvey samples, must have gas-tight seals.

16.1.1.16 Adsorption Tubes. If necessary, blank tubes filled with necessary adsorbent (charcoal, Tenax, XAD–2, etc.) for presurvey samples.

16.1.1.17 Personnel Sampling Pump. Calibrated, for collecting adsorbent tube presurvey samples.

16.1.1.18 Dilution System. Calibrated, the dilution system is to be constructed following the specifications of an acceptable method.

16.1.1.19 Sample Probes. Pyrex or stainless steel, of sufficient length to reach centroid of stack, or a point no closer to the walls than 1 m.

16.1.1.20 Barometer. To measure barometric pressure.

16.1.2 Reagents.

16.1.2.1 Water. Deionized distilled.

16.1.2.2 Methylene chloride.

16.1.2.3 Calibration Gases. A series of standards prepared for every compound of interest.

16.1.2.4 Organic Compound Solutions. Pure (99.9 percent), or as pure as can reasonably be obtained, liquid samples of all the organic compounds needed to prepare calibration standards.

16.1.2.5 Extraction Solvents. For extraction of adsorbent tube samples in preparation for analysis.

16.1.2.6 Fuel. As recommended by the manufacturer for operation of the GC.

16.1.2.7 Carrier Gas. Hydrocarbon free, as recommended by the manufacturer for operation of the detector and compatibility with the column.

16.1.2.8 Zero Gas. Hydrocarbon free air or nitrogen, to be used for dilutions, blank preparation, and standard preparation.

16.1.3 Sampling.

16.1.3.1 Collection of Samples with Glass Sampling Flasks. Presurvey samples may be collected in precleaned 250-ml double-ended glass sampling flasks. Teflon stopcocks, without grease, are preferred. Flasks should be cleaned as follows: Remove the stopcocks from both ends of the flasks, and wipe the parts to remove any grease. Clean the stopcocks, barrels, and receivers with methylene chloride (or other non-target pollutant solvent, or heat and humidified air). Clean all glass ports with a soap solution, then rinse with tap and deionized distilled water. Place the flask in a cool glass annealing furnace, and apply heat up to 500 °C. Maintain at this temperature for 1 hour. After this time period, shut off and open the furnace to allow the flask to cool. Return the stopcocks to the flask receivers. Purge the assembly with high-purity nitrogen for 2 to 5 minutes. Close off the stopcocks after purging to maintain a slight positive nitrogen pressure. Secure the stopcocks with tape. Presurvey samples can be obtained either by drawing the gases into the previously evacuated flask or by drawing the gases into and purging the flask with a rubber suction bulb.

16.1.3.1.1 Evacuated Flask Procedure. Use a high-vacuum pump to evacuate the flask to the capacity of the pump; then close off the stopcock leading to the pump. Attach a 6-mm outside diameter (OD) glass tee to the flask inlet with a short piece of Teflon tubing. Select a 6-mm OD borosilicate sampling probe, enlarged at one end to a 12-mm OD and of sufficient length to reach the centroid of the duct to be sampled. Insert a glass wool plug in the enlarged end of the probe to remove particulate matter. Attach the other end of the probe to the tee with a short piece of Teflon tubing. Connect a rubber suction bulb to the third leg of the tee. Place the filter end of the probe at the centroid of the duct, and purge the probe with the rubber suction bulb. After the probe is completely purged and filled with duct gases, open the stopcock to the grab flask until the pressure in the flask reaches duct pressure. Close off the stopcock, and remove the probe from the duct. Remove the tee from the flask and tape the stopcocks to prevent leaks during shipment. Measure and record the duct temperature and pressure.

16.1.3.1.2 Purged Flask Procedure. Attach one end of the sampling flask to a rubber suction bulb. Attach the other end to a 6-mm OD glass probe as described in section 8.3.3.1.1. Place the filter end of the probe at the centroid of the duct, or at a point no closer to the walls than 1 m, and apply suction with the bulb to completely purge the probe and flask. After the flask has been purged, close off the stopcock near the suction bulb, and then close off the stopcock near the probe. Remove the probe from the duct, and disconnect both the probe and suction bulb. Tape the stopcocks to prevent leakage during shipment. Measure and record the duct temperature and pressure.

16.1.3.2 Flexible Bag Procedure. Any leak-free plastic (e.g., Tedlar, Mylar, Teflon) or plastic-coated aluminum (e.g., aluminized Mylar) bag, or equivalent, can be used to obtain the pre-survey sample. Use new bags, and leak-check them before field use. In addition, check the bag before use for contamination by filling it with nitrogen or air and analyzing the gas by GC at high sensitivity. Experience indicates that it is desirable to allow the inert gas to remain in the bag about 24 hours or longer to check for desorption of organics from the bag. Follow the leak-check and sample collection procedures given in Section 8.2.1.

16.1.3.3 Determination of Moisture Content. For combustion or water-controlled processes, obtain the moisture content from plant personnel or by measurement during the presurvey. If the source is below 59 °C, measure the wet bulb and dry bulb temperatures, and calculate the moisture content using a psychrometric chart. At higher temperatures, use Method 4 to determine the moisture content.

16.1.4 Determination of Static Pressure. Obtain the static pressure from the plant personnel or measurement. If a type S pitot tube and an inclined manometer are used, take care to align the pitot tube 90° from the direction of the flow. Disconnect one of the tubes to the manometer, and read the static pressure; note whether the reading is positive or negative.

16.1.5 Collection of Presurvey Samples with Adsorption Tube. Follow section 8.2.4 for presurvey sampling.

17.0 References

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Volume 1—O17–033–00267–3/$13
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18.0 Tables, Diagrams, Flowcharts, and Validation Data

I. Name of company _____
Date _____
Address _____
_____
Contracts _____
Phone _____
Process to be sampled _____
_____
_____
Duct or vent to be sampled _____
_____
II. Process description _____
_____
_____
_____
_____
Raw material _____
_____
_____
Products _____
_____
_____
Operating cycle
Check: Batch _____ Continuous _____
Cyclic _____
Timing of batch or cycle _____
Best time to test _____
III. Sampling site _____
A. Description _____
Site decription _____
Duct shape and size _____

Material _____
Wall thickness _____ inches
Upstream distance _____ inches _____ diameter
Downstream distance _____ inches _____ diameter
Size of port _____
Size of access area _____
Hazards _____ Ambient temp. _____ °F

B. Properties of gas stream
Temperature _____ °C _____ °F, Data source _____
Velocity _____, Data source _____
Static pressure _____ inches H_2O, Data source _____
Moisture content _____%, Data source _____
Particulate content _____, Data source_____

Gaseous components
N_2 _____ % Hydrocarbons _____ ppm
O_2 _____% _____
CO _____ % _____ _____
CO_2 _____ % _____ _____
SO_2 _____ % _____ _____

Hydrocarbon components
_____ _____ ppm
_____ _____ ppm
_____ _____ ppm
_____ _____ ppm
_____ _____ ppm
_____ _____ ppm

C. Sampling considerations
Location to set up GC _____
_____
Special hazards to be considered _____
_____
Power available at duct _____
Power available for GC _____
Plant safety requirements _____
_____
Vehicle traffic rules _____
_____
Plant entry requirements _____
_____
Security agreements _____
_____
Potential problems _____
_____

D. Site diagrams. (Attach additional sheets if required).

Figure 18–1. Preliminary Survey Data Sheet

Components to be analyzed and Expected concentration

_____
_____
_____
_____
_____
_____

Suggested chromatographic column _____
_____
Column flow rate __ ml/min
Head pressure _____ mm Hg
Column temperature: Isothermal _____ °C, Programmed from _____ °C to _____ °C at _____ °C/min
Injection port/sample loop temperature _____ °C
Detector temperature _____ °C
Detector flow rates: Hydrogen _____ ml/min., head pressure _____ mm Hg, Air/Oxygen _____ ml/min., head pressure _____ mm Hg.
Chart speed _____ inches/minute
Compound data:
Compound and Retention time and Attenuation

_____
_____
_____
_____
_____

Figure 18–2. Chromatographic Conditions Data Sheet

FIGURE 18–3. PREPARATION OF STANDARDS IN TEDLAR OR TEDLAR-EQULIVALENT BAGS AND CALIBRATION CURVE

	Standards		
	Mixture #1	Mixture #2	Mixture #3
Standards Preparation Data:			
Organic:			
Bag number or identification.			
Dry gas meter calibration factor.			
Final meter reading (liters).			
Initial meter reading (liters).			
Metered volume (liters).			
Average meter temperature (°K).			
Average meter pressure, gauge (mm Hg).			
Average atmospheric perssure (mm Hg).			
Average meter pressure, absolute (mm Hg).			
Syringe temperature (°K) (see section 10.1.2.1).			
Syringe pressure, absolute (mm Hg) (see section 10.1.2.1).			
Volume of gas in syringe (ml) (Section 10.1.2.1).			
Density of liquid organic (g/ml) (Section 10.1.2.1).			
Volume of liquid in syringe (ml) (Section 10.1.2.1).			

FIGURE 18–3. PREPARATION OF STANDARDS IN TEDLAR OR TEDLAR-EQULIVALENT BAGS AND CALIBRATION CURVE—Continued

	Standards		
	Mixture #1	Mixture #2	Mixture #3
GC Operating Conditions:			
Sample loop volume (ml).			
Sample loop temperature (°C).			
Carrier gas flow rate (ml/min).			
Column temperature:			
Initial (°C).			
Rate change (°C/min).			
Final (°C).			
Organic Peak Identification and Calculated Concentrations:			
Injection time (24 hour clock).			
Distance to peak (cm).			
Chart speed (cm/min).			
Organic retention time (min).			
Attenuation factor.			
Peak height (mm).			
Peak area (mm_2).			
Peak area * attenuation factor (mm_2).			
Calculated concentration (ppm) (Equation 18–3 or 18–4).			

Plot peak area * attenuation factor against calculated concentration to obtain calibration curve.

Flowmeter number or identification _____
Flowmeter Type _____
Method: Bubble meter____ Spirometer____
Wet test meter ____
Readings at laboratory conditions:

Laboratory temperature (T_{lab}) ____ °K
Laboratory barometric pressure (P_{lab})____ mm Hg
Flow data:

FLOWMETER

Reading (as marked)	Temp. (°K)	Pressure (absolute)

CALIBRATION DEVICE

Time (min)	Gas volume [a]	Flow rate [b]

[a] Vol. of gas may be measured in milliliters, liters or cubic feet.
[b] Convert to standard conditions (20 °C and 760 mm Hg). Plot flowmeter reading against flow rate (standard conditions), and draw a smooth curve. If the flowmeter being calibrated is a rotameter or other flow device that is viscosity dependent, it may be necessary to generate a ''family'' of calibration curves that cover the operating pressure and temperature ranges of the flowmeter. While the following technique should be verified before application, it may be possible to calculate flow rate reading for rotameters at standard conditions Q_{std} as follows:

$$Q_{std} = Q_{lab}\left(\frac{760 \times T_{lab}}{P_{lab} \times 293}\right)^{1/2}$$

Flow rate (laboratory conditions)	Flow rate (STD conditions)

Figure 18–4. Flowmeter Calibration

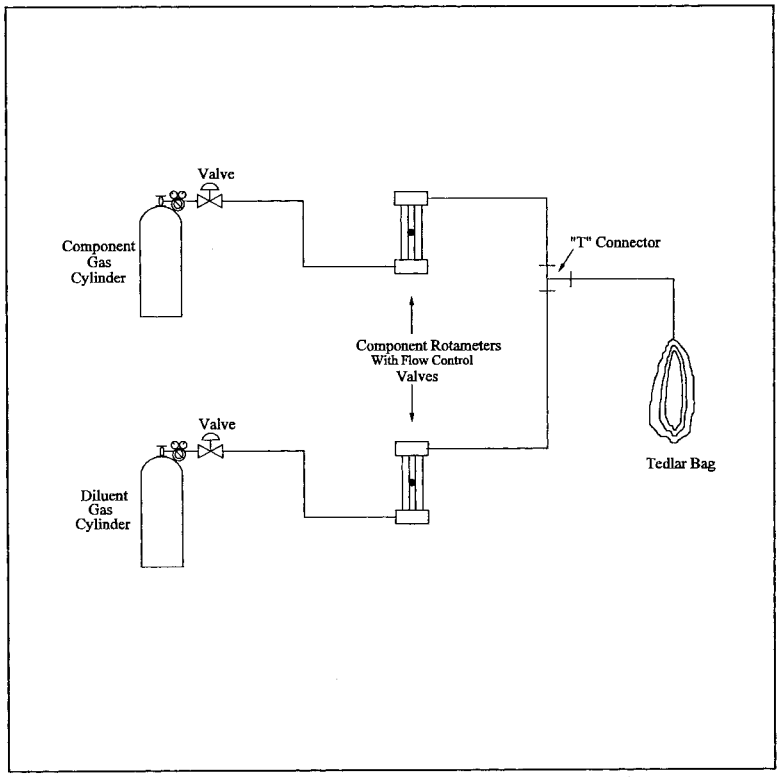

Figure 18-5. Single-Stage Calibration Gas Dilution System.

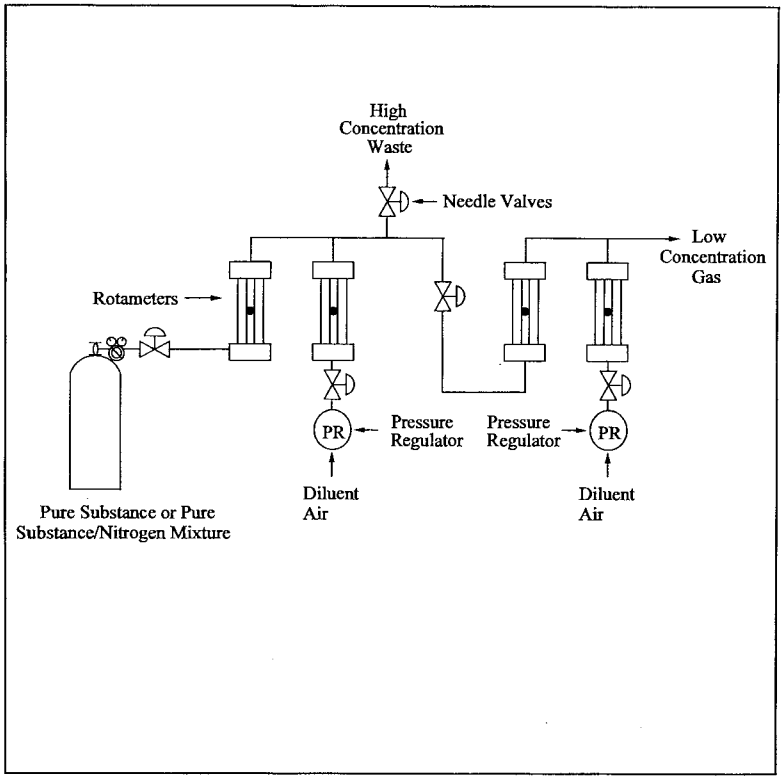

Figure 18-6. Two-Stage Dilution Apparatus.

PREPARATION OF STANDARDS BY DILUTION OF CYLINDER STANDARD

[Cylinder Standard: Organic _____ Certified Concentration _____ ppm]

Standards preparation data:	Date:		
	Mixture 1	Mixture 2	Mixture 3
Stage 1:			
Standard gas flowmeter reading.			
Diluent gas flowmeter reading			
Laboratory temperature (°K)			
Barometric pressure (mm Hg)			
Flowmeter gage pressure (mm Hg)			
Flow rate cylinder gas at standard conditions (ml/min)			
Flow rate diluent gas at standard conditions (ml/min)			
Calculated concentration (ppm)			
Stage 2 (if used):			
Standard gas flowmeter reading			
Diluent gas flowmeter reading			
Flow rate Stage 1 gas at standard conditions (ml/min)			
Flow rate diluent gas at standard conditions			
Calculated concentration (ppm)			
GC Operating Conditions:			
Sample loop volume (ml)			
Sample loop temperature (°C)			
Carrier gas flow rate (ml/min)			
Column temperature:			
Initial (°C)			

PREPARATION OF STANDARDS BY DILUTION OF CYLINDER STANDARD—Continued

[Cylinder Standard: Organic _____ Certified Concentration _____ ppm]

Standards preparation data:	Date:		
	Mixture 1	Mixture 2	Mixture 3
Program rate (°C/min)			
Final (°C)			
Organic Peak Identification and Calculated Concentrations:			
Injection time (24-hour clock)			
Distance to peak (cm)			
Chart speed (cm/min)			
Retention time (min)			
Attenuation factor			
Peak area (mm^2)			
Peak area *attenuation factor			

Plot peak area *attenuation factor against calculated concentration to obtain calibration curve.

Figure 18–7. Standards Prepared by Dilution of Cylinder Standard

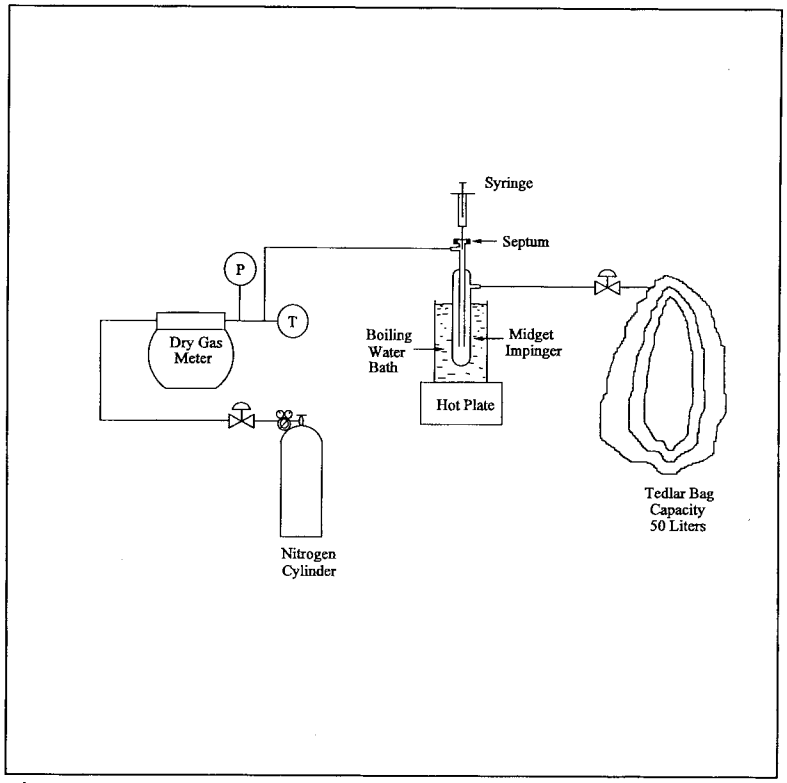

Figure 18-8. Apparatus for Preparation of Liquid Materials.

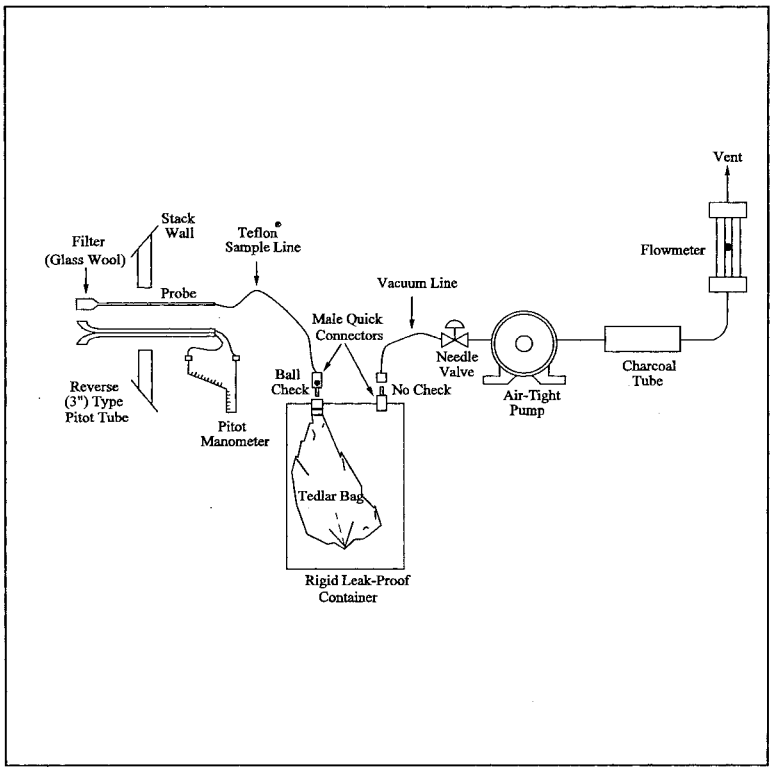

Figure 18-9. Integrated Bag Sampling Train.

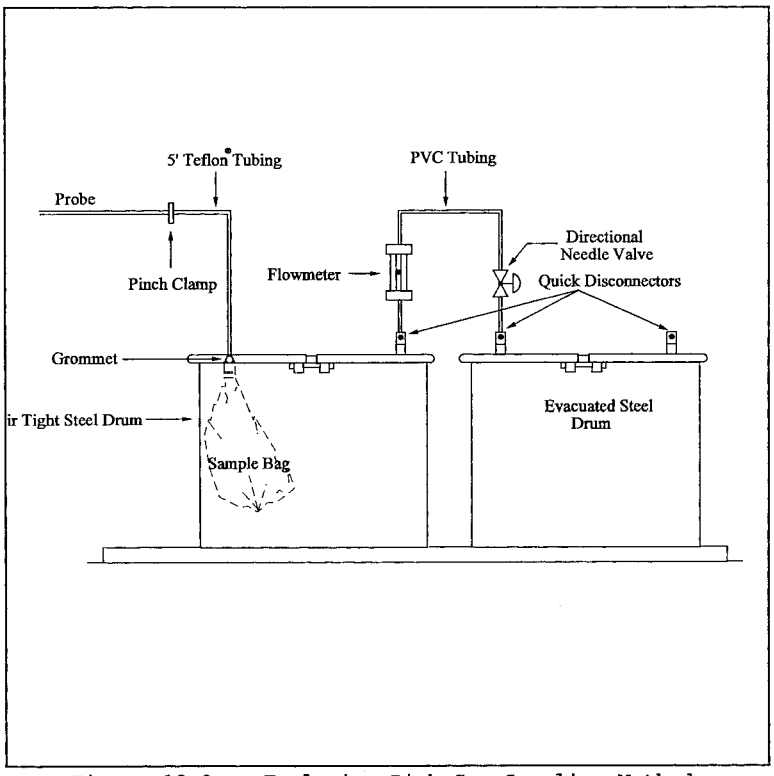

Figure 18-9a. Explosion Risk Gas Sampling Method.

PLANT_____ DATE_____ SITE_____

	Sample 1	Sample 2	Sample 3
Source temperature (°C)			
Barometric pressure (mm Hg)			
Ambient temperature (°C)			
Sample flow rate (appr.)			
Bag number			
Start time			
Finish time			

Figure 18–10. Field Sample Data Sheet—Tedlar or Tedlar-Equivalent Bag Collection Method

PLANT _____ DATE _____ LOCATION _____

1. General information:
- Source temperature (°C) .....
- Probe temperature (°C) .....
- Ambient temperature (°C) .....
- Atmospheric pressure (mm) .....
- Source pressure ('Hg) .....
- Absolute source pressure (mm) .....
- Sampling rate (liter/min) .....
- Sample loop volume (ml) .....
- Sample loop temperature (°C) .....
- Columnar temperature:
  - Initial (°C) time (min) .....
  - Program rate (°C/min) .....
  - Final (°C)/time (min) .....
- Carrier gas flow rate (ml/min) .....

PLANT _____ DATE _____ LOCATION _____—

Continued

Detector temperature (°C) .....
Injection time (24-hour basis) .....
Chart Speed (mm/min) .....
Dilution gas flow rate (ml/min) .....
Dilution gas used (symbol) .....
Dilution ratio .....

2. FIELD ANALYSIS DATA—CALIBRATION GAS

2. [Run No. _____ Time _____]

Components	Area	Attenuation	A × A Factor	Conc.__ (ppm)

Figure 18–11. Field Analysis Data Sheets

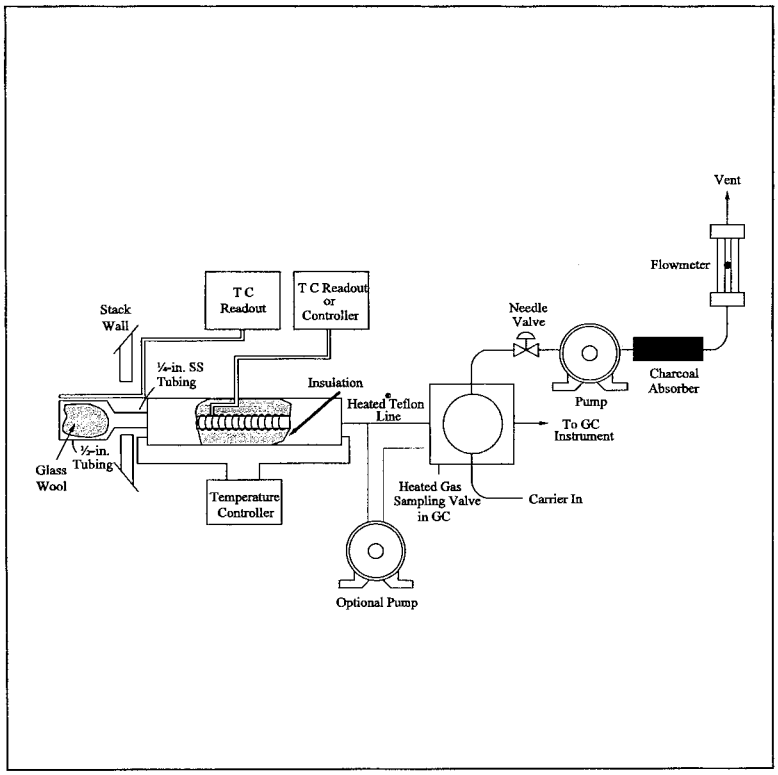

Figure 18-12. Direct Interface Sampling System.

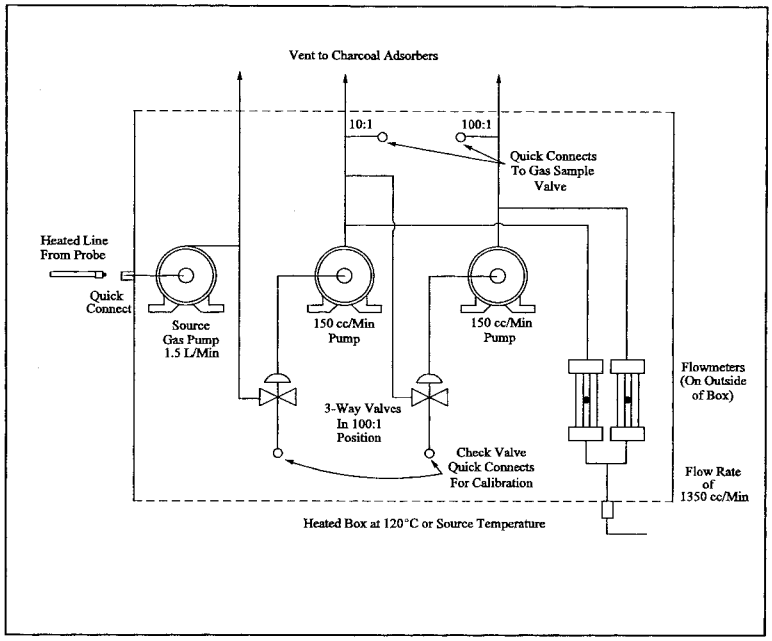

Figure 18-13. Schematic Diagram of the Heated Box Required for Dilution of Sample Gas.

GASEOUS ORGANIC SAMPLING AND ANALYSIS CHECK LIST

[Respond with initials or number as appropriate]

1. Presurvey data:		
A. Grab sample collected	☐	_____
B. Grab sample analyzed for composition	☐	_____
Method GC	☐	_____
GC/MS	☐	_____
Other	☐	_____
C. GC-FID analysis performed	☐	_____
2. Laboratory calibration data:		
A. Calibration curves prepared	☐	_____
Number of components	☐	_____
Number of concentrations/component (3 required).	☐	_____
B. Audit samples (optional):		
Analysis completed	☐	_____
Verified for concentration	☐	_____
OK obtained for field work	☐	_____
3. Sampling procedures:		
A. Method:		
Bag sample	☐	_____
Direct interface	☐	_____
Dilution interface	☐	_____
B. Number of samples collected	☐	_____
4. Field Analysis:		
A. Total hydrocarbon analysis performed	☐	_____
B. Calibration curve prepared	☐	_____
Number of components	☐	_____
Number of concentrations per component (3 required).	☐	_____

State of Oregon Department of Environmental Quality

OAR 340-234-0510 Attachments

APPENDIX A–4 TO PART 60—TEST METHODS 6 THROUGH 10B

Method 6—Determination of sulfur dioxide emissions from stationary sources
Method 6A—Determination of sulfur dioxide, moisture, and carbon dioxide emissions from fossil fuel combustion sources
Method 6B—Determination of sulfur dioxide and carbon dioxide daily average emissions from fossil fuel combustion sources
Method 6C—Determination of Sulfur Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure)
Method 7—Determination of nitrogen oxide emissions from stationary sources
Method 7A—Determination of nitrogen oxide emissions from stationary sources—Ion chromatographic method
Method 7B—Determination of nitrogen oxide emissions from stationary sources (Ultraviolet spectrophotometry)
Method 7C—Determination of nitrogen oxide emissions from stationary sources—Alkaline-permanganate/colorimetric method
Method 7D—Determination of nitrogen oxide emissions from stationary sources—Alkaline-permanganate/ion chromatographic method
Method 7E—Determination of Nitrogen Oxides Emissions From Stationary Sources (Instrumental Analyzer Procedure)
Method 8—Determination of sulfuric acid mist and sulfur dioxide emissions from stationary sources
Method 9—Visual determination of the opacity of emissions from stationary sources
Alternate method 1—Determination of the opacity of emissions from stationary sources remotely by lidar
Method 10—Determination of carbon monoxide emissions from stationary sources
Method 10A—Determination of carbon monoxide emissions in certifying continuous emission monitoring systems at petroleum refineries
Method 10B—Determination of carbon monoxide emissions from stationary sources

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that

the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

METHOD 6—DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, and Method 8.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
SO_2	7449–09–5	3.4 mg SO_2/m^3 $(2.12 \times 10)_{-7}$ lb/ft^3

1.2 Applicability. This method applies to the measurement of sulfur dioxide (SO_2) emissions from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the sampling point in the stack. The SO_2 and the sulfur trioxide, including those fractions in any sulfur acid mist, are separated. The SO_2 fraction is measured by the barium-thorin titration method.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Free Ammonia. Free ammonia interferes with this method by reacting with SO_2 to form particulate sulfite and by reacting with the indicator. If free ammonia is present (this can be determined by knowledge of the process and/or noticing white particulate matter in the probe and isopropanol bubbler), alternative methods, subject to the approval of the Administrator are required. One approved alternative is listed in Reference 13 of section 17.0.

4.2 Water-Soluble Cations and Fluorides. The cations and fluorides are removed by a glass wool filter and an isopropanol bubbler; therefore, they do not affect the SO_2 analysis. When samples are collected from a gas stream with high concentrations of metallic fumes (*i.e.*, very fine cation aerosols) a high-efficiency glass fiber filter must be used in place of the glass wool plug (*i.e.*, the one in the probe) to remove the cation interferent.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations before performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs. 30% H_2O_2 is a strong oxidizing agent. Avoid contact with skin, eyes, and combustible material. Wear gloves when handling.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

6.1 Sample Collection. The following items are required for sample collection:

6.1.1 Sampling Train. A schematic of the sampling train is shown in Figure 6–1. The sampling equipment described in Method 8 may be substituted in place of the midget impinger equipment of Method 6. However, the Method 8 train must be modified to include a heated filter between the probe and isopropanol impinger, and the operation of the sampling train and sample analysis must be at the flow rates and solution volumes defined in Method 8. Alternatively, SO_2 may be determined simultaneously with particulate

matter and moisture determinations by either (1) replacing the water in a Method 5 impinger system with a 3 percent H_2O_2 solution, or (2) replacing the Method 5 water impinger system with a Method 8 isopropanol-filter-H_2O_2 system. The analysis for SO_2 must be consistent with the procedure of Method 8. The Method 6 sampling train consists of the following components:

6.1.1.1 Probe. Borosilicate glass or stainless steel (other materials of construction may be used, subject to the approval of the Administrator), approximately 6 mm (0.25 in.) inside diameter, with a heating system to prevent water condensation and a filter (either in-stack or heated out-of-stack) to remove particulate matter, including sulfuric acid mist. A plug of glass wool is a satisfactory filter.

6.1.1.2 Bubbler and Impingers. One midget bubbler with medium-coarse glass frit and borosilicate or quartz glass wool packed in top (see Figure 6–1) to prevent sulfuric acid mist carryover, and three 30-ml midget impingers. The midget bubbler and midget impingers must be connected in series with leak-free glass connectors. Silicone grease may be used, if necessary, to prevent leakage. A midget impinger may be used in place of the midget bubbler.

NOTE: Other collection absorbers and flow rates may be used, subject to the approval of the Administrator, but the collection efficiency must be shown to be at least 99 percent for each test run and must be documented in the report. If the efficiency is found to be acceptable after a series of three tests, further documentation is not required. To conduct the efficiency test, an extra absorber must be added and analyzed separately. This extra absorber must not contain more than 1 percent of the total SO_2.

6.1.1.3 Glass Wool. Borosilicate or quartz.

6.1.1.4 Stopcock Grease. Acetone-insoluble, heat-stable silicone grease may be used, if necessary.

6.1.1.5 Temperature Sensor. Dial thermometer, or equivalent, to measure temperature of gas leaving impinger train to within 1 °C (2 °F).

6.1.1.6 Drying Tube. Tube packed with 6- to 16- mesh indicating-type silica gel, or equivalent, to dry the gas sample and to protect the meter and pump. If silica gel is previously used, dry at 177 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

6.1.1.7 Valve. Needle valve, to regulate sample gas flow rate.

6.1.1.8 Pump. Leak-free diaphragm pump, or equivalent, to pull gas through the train. Install a small surge tank between the pump and rate meter to negate the pulsation effect of the diaphragm pump on the rate meter.

6.1.1.9 Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of the selected flow rate of about 1 liter/min (0.035 cfm).

6.1.1.10 Volume Meter. Dry gas meter (DGM), sufficiently accurate to measure the sample volume to within 2 percent, calibrated at the selected flow rate and conditions actually encountered during sampling, and equipped with a temperature sensor (dial thermometer, or equivalent) capable of measuring temperature accurately to within 3 °C (5.4 °F). A critical orifice may be used in place of the DGM specified in this section provided that it is selected, calibrated, and used as specified in section 16.0.

6.1.2 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). See the note in Method 5, section 6.1.2.

6.1.3 Vacuum Gauge and Rotameter. At least 760-mm Hg (30-in. Hg) gauge and 0- to 40-ml/min rotameter, to be used for leak-check of the sampling train.

6.2 Sample Recovery. The following items are needed for sample recovery:

6.2.1 Wash Bottles. Two polyethylene or glass bottles, 500-ml.

6.2.2 Storage Bottles. Polyethylene bottles, 100-ml, to store impinger samples (one per sample).

6.3 Sample Analysis. The following equipment is needed for sample analysis:

6.3.1 Pipettes. Volumetric type, 5-ml, 20-ml (one needed per sample), and 25-ml sizes.

6.3.2 Volumetric Flasks. 100-ml size (one per sample) and 1000-ml size.

6.3.3 Burettes. 5- and 50-ml sizes.

6.3.4 Erlenmeyer Flasks. 250-ml size (one for each sample, blank, and standard).

6.3.5 Dropping Bottle. 125-ml size, to add indicator.

6.3.6 Graduated Cylinder. 100-ml size.

6.3.7 Spectrophotometer. To measure absorbance at 352 nm.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Water. Deionized distilled to conform to ASTM Specification D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17). The $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.1.2 Isopropanol, 80 Percent by Volume. Mix 80 ml of isopropanol with 20 ml of water.

7.1.2.1 Check each lot of isopropanol for peroxide impurities as follows: Shake 10 ml of isopropanol with 10 ml of freshly prepared 10 percent potassium iodide solution. Prepare a blank by similarly treating 10 ml of water. After 1 minute, read the absorbance at 352 nm on a spectrophotometer using a 1-cm path length. If absorbance exceeds 0.1, reject alcohol for use.

7.1.2.2 Peroxides may be removed from isopropanol by redistilling or by passage through a column of activated alumina; however, reagent grade isopropanol with suitably low peroxide levels may be obtained from commercial sources. Rejection of contaminated lots may, therefore, be a more efficient procedure.

7.1.3 Hydrogen Peroxide (H_2O_2), 3 Percent by Volume. Add 10 ml of 30 percent H_2O_2 to 90 ml of water. Prepare fresh daily.

7.1.4 Potassium Iodide Solution, 10 Percent Weight by Volume (w/v). Dissolve 10.0 g of KI in water, and dilute to 100 ml. Prepare when needed.

7.2 Sample Recovery. The following reagents are required for sample recovery:

7.2.1 Water. Same as in section 7.1.1.

7.2.2 Isopropanol, 80 Percent by Volume. Same as in section 7.1.2.

7.3 Sample Analysis. The following reagents and standards are required for sample analysis:

7.3.1 Water. Same as in section 7.1.1.

7.3.2 Isopropanol, 100 Percent.

7.3.3 Thorin Indicator. 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, disodium salt, or equivalent. Dissolve 0.20 g in 100 ml of water.

7.3.4 Barium Standard Solution, 0.0100 N. Dissolve 1.95 g of barium perchlorate trihydrate [$Ba(ClO_4)_2$ $3H_2O$] in 200 ml water, and dilute to 1 liter with isopropanol. Alternatively, 1.22 g of barium chloride dihydrate [$BaCl_2$ $2H_2O$] may be used instead of the barium perchlorate trihydrate. Standardize as in section 10.5.

7.3.5 Sulfuric Acid Standard, 0.0100 N. Purchase or standardize to ±0.0002 N against 0.0100 N NaOH which has previously been standardized against potassium acid phthalate (primary standard grade).

8.0 Sample Collection, Preservation, Storage and Transport

8.1 Preparation of Sampling Train. Measure 15 ml of 80 percent isopropanol into the midget bubbler and 15 ml of 3 percent H_2O_2 into each of the first two midget impingers. Leave the final midget impinger dry. Assemble the train as shown in Figure 6–1. Adjust the probe heater to a temperature sufficient to prevent water condensation. Place crushed ice and water around the impingers.

8.2 Sampling Train Leak-Check Procedure. A leak-check prior to the sampling run is recommended, but not required. A leak-check after the sampling run is mandatory. The leak-check procedure is as follows:

8.2.1 Temporarily attach a suitable (*e.g.*, 0- to 40- ml/min) rotameter to the outlet of the DGM, and place a vacuum gauge at or near the probe inlet. Plug the probe inlet, pull a vacuum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter. A leakage rate in excess of 2 percent of the average sampling rate is not acceptable.

NOTE: Carefully (*i.e.*, slowly) release the probe inlet plug before turning off the pump.

8.2.2 It is suggested (not mandatory) that the pump be leak-checked separately, either prior to or after the sampling run. To leak-check the pump, proceed as follows: Disconnect the drying tube from the probe-impinger assembly. Place a vacuum gauge at the inlet to either the drying tube or the pump, pull a vacuum of 250 mm Hg (10 in. Hg), plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum should remain stable for at least 30 seconds.

If performed prior to the sampling run, the pump leak-check shall precede the leak-check of the sampling train described immediately above; if performed after the sampling run, the pump leak-check shall follow the sampling train leak-check.

8.2.3 Other leak-check procedures may be used, subject to the approval of the Administrator.

8.3 Sample Collection.

8.3.1 Record the initial DGM reading and barometric pressure. To begin sampling, position the tip of the probe at the sampling point, connect the probe to the bubbler, and start the pump. Adjust the sample flow to a constant rate of approximately 1.0 liter/min as indicated by the rate meter. Maintain this constant rate (±10 percent) during the entire sampling run.

8.3.2 Take readings (DGM volume, temperatures at DGM and at impinger outlet, and rate meter flow rate) at least every 5 minutes. Add more ice during the run to keep the temperature of the gases leaving the last impinger at 20 °C (68 °F) or less.

8.3.3 At the conclusion of each run, turn off the pump, remove the probe from the stack, and record the final readings. Conduct a leak-check as described in section 8.2. (This leak-check is mandatory.) If a leak is detected, void the test run or use procedures acceptable to the Administrator to adjust the sample volume for the leakage.

8.3.4 Drain the ice bath, and purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at the sampling rate. Clean ambient air can be provided by passing air through a charcoal filter or through an extra midget impinger containing 15 ml of 3 percent H_2O_2. Alternatively, ambient air without purification may be used.

8.4 Sample Recovery. Disconnect the impingers after purging. Discard the contents of the midget bubbler. Pour the contents of the midget impingers into a leak-free polyethylene bottle for shipment. Rinse the three midget impingers and the connecting tubes with water, and add the rinse to the same storage container. Mark the fluid level. Seal and identify the sample container.

9.0 Quality Control

Section	Quality control measure	Effect
7.1.2	Isopropanol check	Ensure acceptable level of peroxide impurities in isopropanol.
8.2, 10.1–10.4	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.
10.5	Barium standard solution standardization	Ensure precision of normality determination
11.2.3	Replicate titrations	Ensure precision of titration determinations.

10.0 Calibration and Standardization

10.1 Volume Metering System.

10.1.1 Initial Calibration.

10.1.1.1 Before its initial use in the field, leak-check the metering system (drying tube, needle valve, pump, rate meter, and DGM) as follows: Place a vacuum gauge at the inlet to the drying tube and pull a vacuum of 250 mm Hg (10 in. Hg). Plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum must remain stable for at least 30 seconds. Carefully release the vacuum gauge before releasing the flow meter end.

10.1.1.2 Remove the drying tube, and calibrate the metering system (at the sampling flow rate specified by the method) as follows: Connect an appropriately sized wet-test meter (*e.g.*, 1 liter per revolution) to the inlet of the needle valve. Make three independent calibration runs, using at least five revolutions of the DGM per run. Calculate the calibration factor Y (wet-test meter calibration volume divided by the DGM volume, both volumes adjusted to the same reference temperature and pressure) for each run, and average the results (Y_i). If any Y-value deviates by more than 2 percent from (Y_i), the metering system is unacceptable for use. If the metering system is acceptable, use (Y_i) as the calibration factor for subsequent test runs.

10.1.2 Post-Test Calibration Check. After each field test series, conduct a calibration check using the procedures outlined in section 10.1.1.2, except that three or more revolutions of the DGM may be used, and only two independent runs need be made. If the average of the two post-test calibration factors does not deviate by more than 5 percent from Y_i, then Y_i is accepted as the DGM calibration factor (Y), which is used in Equation 6–1 to calculate collected sample volume (see section 12.2). If the deviation is more than 5 percent, recalibrate the metering system as in section 10.1.1, and determine a post-test calibration factor (Y_f). Compare Y_i and Y_f; the smaller of the two factors is accepted as the DGM calibration factor. If recalibration indicates that the metering system is unacceptable for use, either void the test run or use methods, subject to the approval of the Administrator, to determine an acceptable value for the collected sample volume.

10.1.3 DGM as a Calibration Standard. A DGM may be used as a calibration standard for volume measurements in place of the wet-test meter specified in section 10.1.1.2, provided that it is calibrated initially and recalibrated periodically according to the same procedures outlined in Method 5, section 10.3 with the following exceptions: (a) the DGM is calibrated against a wet-test meter having a capacity of 1 liter/rev (0.035 ft^3/rev) or 3 liters/rev (0.1 ft^3/rev) and having the capability of measuring volume to within 1 percent; (b) the DGM is calibrated at 1 liter/min (0.035 cfm); and (c) the meter box of the Method 6 sampling train is calibrated at the same flow rate.

10.2 Temperature Sensors. Calibrate against mercury-in-glass thermometers. An alternative mercury-free thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

10.3 Rate Meter. The rate meter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instructions.

10.4 Barometer. Calibrate against a mercury barometer or NIST-traceable barometer prior to the field test.

10.5 Barium Standard Solution. Standardize the barium perchlorate or chloride solution against 25 ml of standard sulfuric acid to which 100 ml of 100 percent isopropanol has been added. Run duplicate analyses. Calculate the normality using the average of duplicate analyses where the titrations agree within 1 percent or 0.2 ml, whichever is larger.

11.0 Analytical Procedure

11.1 Sample Loss Check. Note level of liquid in container and confirm whether any sample was lost during shipment; note this

finding on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Analysis.

11.2.1 Transfer the contents of the storage container to a 100-ml volumetric flask, dilute to exactly 100 ml with water, and mix the diluted sample.

11.2.2 Pipette a 20-ml aliquot of the diluted sample into a 250-ml Erlenmeyer flask and add 80 ml of 100 percent isopropanol plus two to four drops of thorin indicator. While stirring the solution, titrate to a pink endpoint using 0.0100 N barium standard solution.

11.2.3 Repeat the procedures in section 11.2.2, and average the titration volumes. Run a blank with each series of samples. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is larger.

NOTE: Protect the 0.0100 N barium standard solution from evaporation at all times.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 NOMENCLATURE

C_{SO2} = Concentration of SO_2, dry basis, corrected to standard conditions, mg/dscm (lb/dscf).
N = Normality of barium standard titrant, meq/ml.
P_{bar} = Barometric pressure, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
T_m = Average DGM absolute temperature, °K (°R).
T_{std} = Standard absolute temperature, 293 °K (528 °R).
V_a = Volume of sample aliquot titrated, ml.
V_m = Dry gas volume as measured by the DGM, dcm (dcf).
$V_{m(std)}$ = Dry gas volume measured by the DGM, corrected to standard conditions, dscm (dscf).
V_{soln} = Total volume of solution in which the SO_2 sample is contained, 100 ml.
V_t = Volume of barium standard titrant used for the sample (average of replicate titration), ml.
V_{tb} = Volume of barium standard titrant used for the blank, ml.
Y = DGM calibration factor.

12.2 Dry Sample Gas Volume, Corrected to Standard Conditions.

$$V_{m(std)} = \frac{\left(V_m Y T_{std} P_{bar}\right)}{\left(T_m P_{std}\right)} = \frac{K_1 Y V_m P_{bar}}{T_m} \quad \text{Eq. 6-1}$$

Where:

K_1 = 0.3855 °K/mm Hg for metric units,
K_1 = 17.65 °R/in. Hg for English units.

12.3 SO_2 Concentration.

$$C_{so_2} = \frac{K_2 N \left(V_t - V_{tb}\right)\left(V_{soln}/V_a\right)}{V_{m(std)}} \quad \text{Eq. 6-2}$$

Where:

K_2 = 32.03 mg SO_2/meq for metric units,
$K_2 = 7.061 \times 10^{-5}$ lb SO_2/meq for English units.

13.0 Method Performance

13.1 Range. The minimum detectable limit of the method has been determined to be 3.4 mg SO_2/m^3 (2.12×10^{-7} lb/ft³). Although no upper limit has been established, tests have shown that concentrations as high as 80,000 mg/m³ (0.005 lb/ft³) of SO_2 can be collected efficiently at a rate of 1.0 liter/min (0.035 cfm) for 20 minutes in two midget impingers, each containing 15 ml of 3 percent H_2O_2. Based on theoretical calculations, the upper concentration limit in a 20 liter (0.7 ft³) sample is about 93,300 mg/m³ (0.00583 lb/ft³).

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Nomenclature. Same as section 12.1, with the following additions:

B_{wa} = Water vapor in ambient air, proportion by volume.
M_a = Molecular weight of the ambient air saturated at impinger temperature, g/g-mole (lb/lb-mole).
M_s = Molecular weight of the sample gas saturated at impinger temperature, g/g-mole (lb/lb-mole).
P_c = Inlet vacuum reading obtained during the calibration run, mm Hg (in. Hg).
P_{sr} = Inlet vacuum reading obtained during the sampling run, mm Hg (in. Hg).

$\bar{Q}_{std}$ = Volumetric flow rate through critical orifice, scm/min (scf/min).
Q_{std} = Average flow rate of pre-test and post-test calibration runs, scm/min (scf/min).
T_{amb} = Ambient absolute temperature of air, °K (°R).
V_{sb} = Volume of gas as measured by the soap bubble meter, m^3 (ft^3).
$V_{sb(std)}$ = Volume of gas as measured by the soap bubble meter, corrected to standard conditions, scm (scf).
θ = Soap bubble travel time, min.
θ_s = Time, min.

16.2 Critical Orifices for Volume and Rate Measurements. A critical orifice may be used in place of the DGM specified in section 6.1.1.10, provided that it is selected, calibrated, and used as follows:

16.2.1 Preparation of Sampling Train. Assemble the sampling train as shown in Figure 6–2. The rate meter and surge tank are optional but are recommended in order to detect changes in the flow rate.

NOTE: The critical orifices can be adapted to a Method 6 type sampling train as follows: Insert sleeve type, serum bottle stoppers into two reducing unions. Insert the needle into the stoppers as shown in Figure 6–3.

16.2.2 Selection of Critical Orifices.

16.2.2.1 The procedure that follows describes the use of hypodermic needles and stainless steel needle tubings, which have been found suitable for use as critical orifices. Other materials and critical orifice designs may be used provided the orifices act as true critical orifices, (*i.e.*, a critical vacuum can be obtained) as described in this section. Select a critical orifice that is sized to operate at the desired flow rate. The needle sizes and tubing lengths shown in Table 6–1 give the following approximate flow rates.

16.2.2.2 Determine the suitability and the appropriate operating vacuum of the critical orifice as follows: If applicable, temporarily attach a rate meter and surge tank to the outlet of the sampling train, if said equipment is not present (see section 16.2.1). Turn on the pump and adjust the valve to give an outlet vacuum reading corresponding to about half of the atmospheric pressure. Observe the rate meter reading. Slowly increase the vacuum until a stable reading is obtained on the rate meter. Record the critical vacuum, which is the outlet vacuum when the rate meter first reaches a stable value. Orifices that do not reach a critical value must not be used.

16.2.3 Field Procedures.

16.2.3.1 Leak-Check Procedure. A leak-check before the sampling run is recommended, but not required. The leak-check procedure is as follows: Temporarily attach a suitable (*e.g.*, 0–40 ml/min) rotameter and surge tank, or a soap bubble meter and surge tank to the outlet of the pump. Plug the probe inlet, pull an outlet vacuum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter or bubble meter. A leakage rate in excess of 2 percent of the average sampling rate ($\bar{Q}_{std}$) is not acceptable. Carefully release the probe inlet plug before turning off the pump.

16.2.3.2 Moisture Determination. At the sampling location, prior to testing, determine the percent moisture of the ambient air using the wet and dry bulb temperatures or, if appropriate, a relative humidity meter.

16.2.3.3 Critical Orifice Calibration. At the sampling location, prior to testing, calibrate the entire sampling train (*i.e.*, determine the flow rate of the sampling train when operated at critical conditions). Attach a 500-ml soap bubble meter to the inlet of the probe, and operate the sampling train at an outlet vacuum of 25 to 50 mm Hg (1 to 2 in. Hg) above the critical vacuum. Record the information listed in Figure 6–4. Calculate the standard volume of air measured by the soap bubble meter and the volumetric flow rate using the equations below:

$$V_{sb(std)} = V_{sb}\left(T_{std}/T_{amb}\right)\left(P_{bar}/P_{std}\right) \qquad \text{Eq. 6-4}$$

$$Q_{std} = \frac{V_{sb(std)}}{\theta} \qquad \text{Eq. 6-5}$$

16.2.3.4 Sampling.

16.2.3.4.1 Operate the sampling train for sample collection at the same vacuum used during the calibration run. Start the watch and pump simultaneously. Take readings (temperature, rate meter, inlet vacuum, and outlet vacuum) at least every 5 minutes. At the end of the sampling run, stop the watch and pump simultaneously.

16.2.3.4.2 Conduct a post-test calibration run using the calibration procedure outlined in section 16.2.3.3. If the Q_{std} obtained before and after the test differ by more than 5 percent, void the test run; if not, calculate the volume of the gas measured with the critical orifice using Equation 6–6 as follows:

$$V_{m(std)} = \frac{\overline{Q}_{std}\ \theta_s\ (1-B_{wa})(P_{bar}+P_{sr})}{(P_{bar}+P_c)} \quad \text{Eq. 6-6}$$

16.2.3.4.3 If the percent difference between the molecular weight of the ambient air at saturated conditions and the sample gas is more that ±3 percent, then the molecular weight of the gas sample must be considered in the calculations using the following equation:

$$_{(std)} = \frac{\overline{Q}_{std}\ \theta_s\ (1-B_{wa})(P_{bar}+P_{sr})(M_a/M_s)^1}{(P_{bar}+P_c)} \quad \text{Eq. 6-7}$$

NOTE: A post-test leak-check is not necessary because the post-test calibration run results will indicate whether there is any leakage.

16.2.3.4.4 Drain the ice bath, and purge the sampling train using the procedure described in section 8.3.4.

16.3 Elimination of Ammonia Interference. The following alternative procedures must be used in addition to those specified in the method when sampling at sources having ammonia emissions.

16.3.1 Sampling. The probe shall be maintained at 275 °C (527 °F) and equipped with a high-efficiency in-stack filter (glass fiber) to remove particulate matter. The filter material shall be unreactive to SO_2. Whatman 934AH (formerly Reeve Angel 934AH) filters treated as described in Reference 10 in section 17.0 of Method 5 is an example of a filter that has been shown to work. Where alkaline particulate matter and condensed moisture are present in the gas stream, the filter shall be heated above the moisture dew point but below 225 °C (437 °F).

16.3.2 Sample Recovery. Recover the sample according to section 8.4 except for discarding the contents of the midget bubbler. Add the bubbler contents, including the rinsings of the bubbler with water, to a separate polyethylene bottle from the rest of the sample. Under normal testing conditions where sulfur trioxide will not be present significantly, the tester may opt to delete the midget bubbler from the sampling train. If an approximation of the sulfur trioxide concentration is desired, transfer the contents of the midget bubbler to a separate polyethylene bottle.

16.3.3 Sample Analysis. Follow the procedures in sections 11.1 and 11.2, except add 0.5 ml of 0.1 N HCl to the Erlenmeyer flask and mix before adding the indicator. The following analysis procedure may be used for an approximation of the sulfur trioxide concentration. The accuracy of the calculated concentration will depend upon the ammonia to SO_2 ratio and the level of oxygen present in the gas stream. A fraction of the SO_2 will be counted as sulfur trioxide as the ammonia to SO_2 ratio and the sample oxygen content increases. Generally, when this ratio is 1 or less and the oxygen content is in the range of 5 percent, less than 10 percent of the SO_2 will be counted as sulfur trioxide. Analyze the peroxide and isopropanol sample portions separately. Analyze the peroxide portion as described above. Sulfur trioxide is determined by difference using sequential titration of the isopropanol portion of the sample. Transfer the contents of the isopropanol storage container to a 100-ml volumetric flask, and dilute to exactly 100 ml with water. Pipette a 20-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 0.5 ml of 0.1 N HCl, 80 ml of 100 percent isopropanol, and two to four drops of thorin indicator. Titrate to a pink endpoint using 0.0100 N barium perchlorate. Repeat and average the titration volumes that agree within 1 percent or 0.2 ml, whichever is larger. Use this volume in Equation 6–2 to determine the sulfur trioxide concentration. From the flask containing the remainder of the isopropanol sample, determine the fraction of SO_2 collected in the bubbler by pipetting 20-ml aliquots into 250-ml Erlenmeyer flasks. Add 5 ml of 3 percent H_2O_2, 100 ml of 100 percent isopropanol, and two to four drips of thorin indicator, and titrate as before. From this titration volume, subtract the titrant volume determined for sulfur trioxide, and add the titrant volume determined for the peroxide portion. This final volume constitutes V_t, the volume of barium perchlorate used for the SO_2 sample.

17.0 References

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18.0 Tables, Diagrams, Flowcharts and Validation Data

TABLE 6–1—APPROXIMATE FLOW RATES FOR VARIOUS NEEDLE SIZES

Needle size (gauge)	Needle length (cm)	Flow rate (ml/min)
21	7.6	1,100
22	2.9	1,000
22	3.8	900
23	3.8	500
23	5.1	450
24	3.2	400

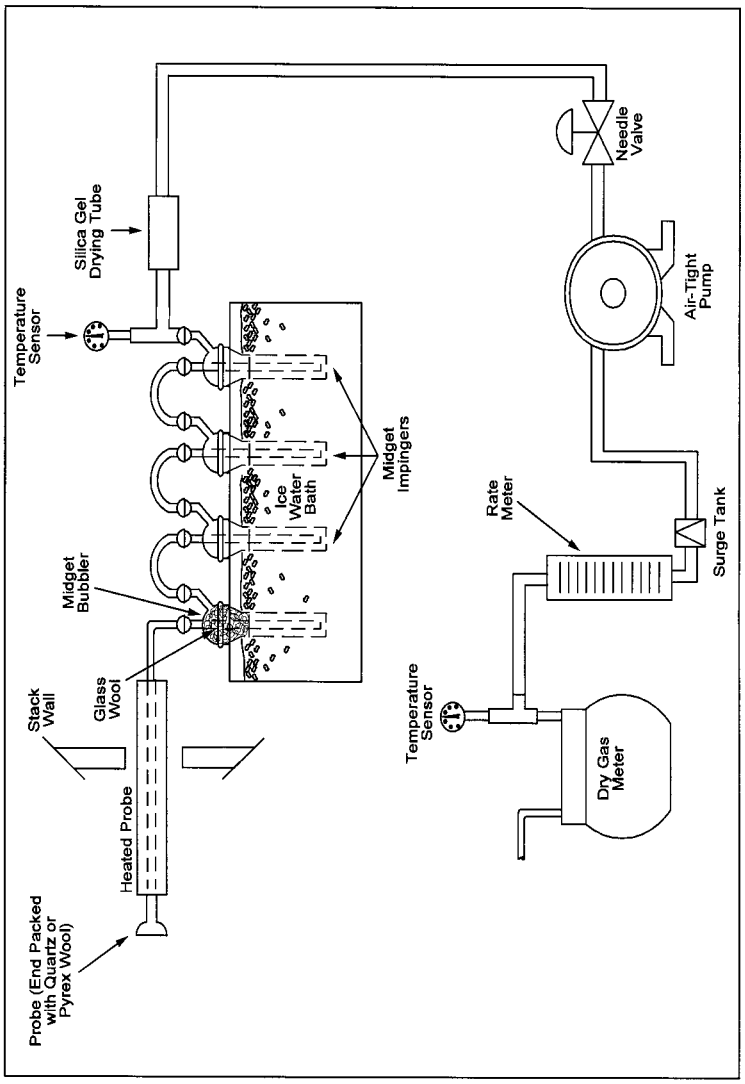

Figure 6-1. Sulfur Dioxide Sampling Train.

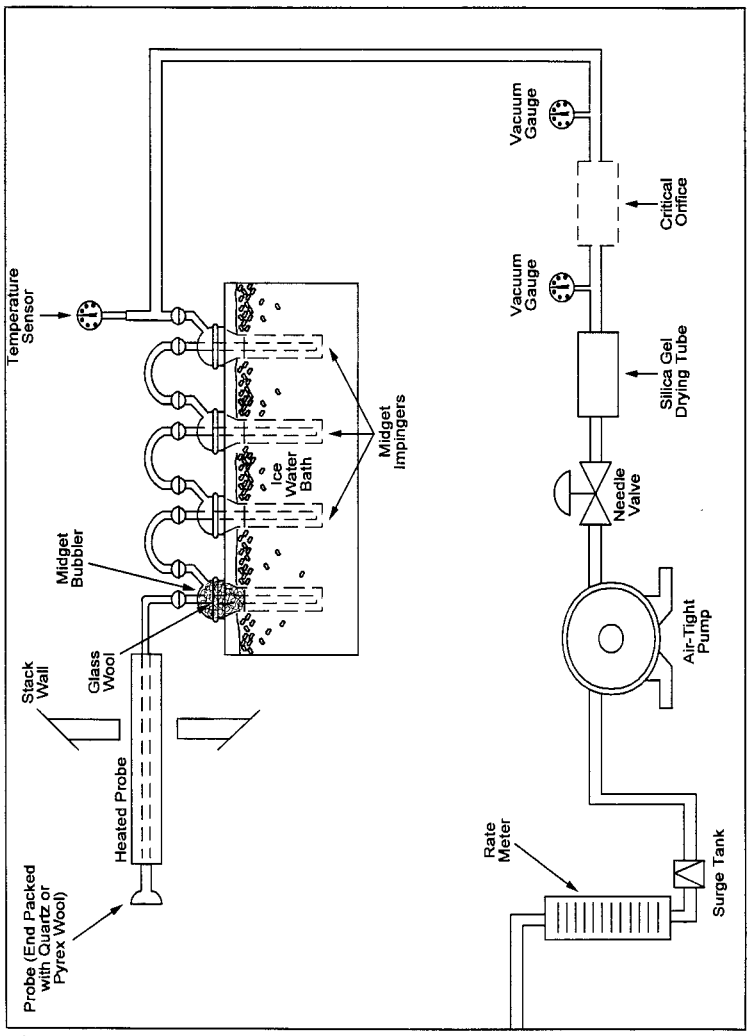

Figure 6-2. Sulfur Dioxide Sampling Train Using a Critical Orifice.

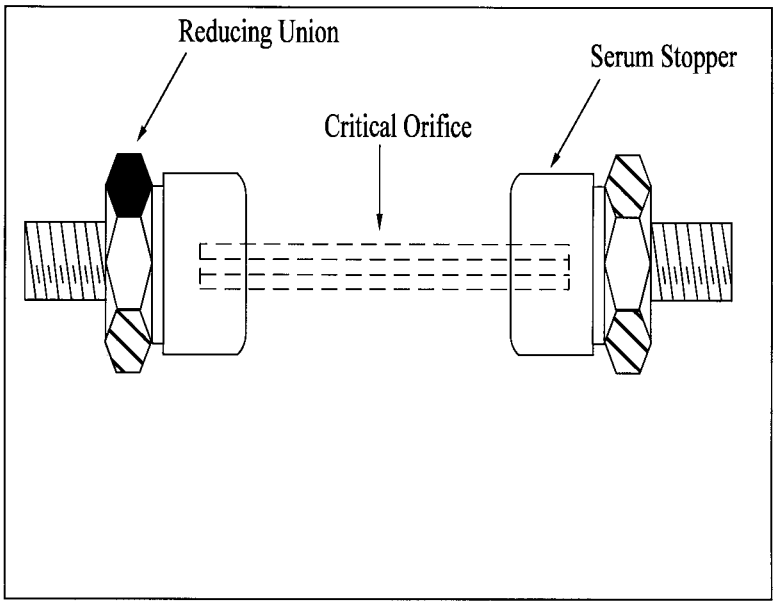

Figure 6-3. Critical Orifice Adaptation for the Method 6 Sampling Train.

Date _____ Train ID _____

Critical orifice size _____ Critical vacuum _____

		Pretest	Post-test
Soap bubble meter volume, V_{sb}	cc		
	m^3 (ft^3)		
Time, θ	sec		
	min		
Barometric pressure, P_{bar}	mm Hg (in. Hg)		
Ambient temperature, t_{amb}	°C (°F)		
Inlet vacuum, P_c	mm Hg (in. Hg)		
Outlet vacuum	mm Hg (in. Hg)		
$V_{sb(std)}$	m^3 (ft^3)		
Flow rate, Q_{std}	$\frac{m^3}{min}\left(\frac{ft^3}{min}\right)$		

Figure 6-4. Critical Orifice Calibration Data Sheet.

METHOD 6A—DETERMINATION OF SULFUR DIOXIDE, MOISTURE, AND CARBON DIOXIDE FROM FOSSIL FUEL COMBUSTION SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, Method 6, and Method 19.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
SO_2	7449–09–05	3.4 mg SO_2/m^3 (2.12×10^{-7} lb/ft^3)
CO_2	124–38–9	N/A
H_2O	7732–18–5	N/A

1.2 Applicability. This method is applicable for the determination of sulfur dioxide (SO_2) emissions from fossil fuel combustion sources in terms of concentration (mg/dscm or lb/dscf) and in terms of emission rate (ng/J or lb/10^6 Btu) and for the determination of carbon dioxide (CO_2) concentration (percent). Moisture content (percent), if desired, may also be determined by this method.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from a sampling point in the stack. The SO_2 and the sulfur trioxide, including those fractions in any sulfur acid mist, are separated. The SO_2 fraction is measured by the barium-thorin titration method. Moisture and CO_2 fractions are collected in the same sampling train, and are determined gravimetrically.

3.0 Definitions [Reserved]

4.0 Interferences

Same as Method 6, section 4.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. Same as Method 6, section 5.2.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 6, section 6.1, with the exception of the following:

6.1.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 6A–1.

6.1.1.1 Impingers and Bubblers. Two 30 = ml midget impingers with a 1 = mm restricted tip and two 30 = ml midget bubblers with unrestricted tips. Other types of impingers and bubblers (*e.g.,* Mae West for SO_2 collection and rigid cylinders containing Drierite for moisture absorbers), may be used with proper attention to reagent volumes and levels, subject to the approval of the Administrator.

6.1.1.2 CO_2 Absorber. A sealable rigid cylinder or bottle with an inside diameter between 30 and 90 mm , a length between 125 and 250 mm, and appropriate connections at both ends. The filter may be a separate heated unit or may be within the heated portion of the probe. If the filter is within the sampling probe, the filter should not be within 15 cm of the probe inlet or any unheated section of the probe, such as the connection to the first bubbler. The probe and filter should be heated to at least 20 °C (68 °F) above the source temperature, but not greater than 120 °C (248 °F). The filter temperature (*i.e.,* the sample gas temperature) should be monitored to assure the desired temperature is maintained. A heated Teflon connector may be used to connect the filter holder or probe to the first impinger.

NOTE: For applications downstream of wet scrubbers, a heated out-of-stack filter (either borosilicate glass wool or glass fiber mat) is necessary.

6.2 Sample Recovery. Same as Method 6, section 6.2.

6.3 Sample Analysis. Same as Method 6, section 6.3, with the addition of a balance to measure within 0.05 g.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

7.1 Sample Collection. Same as Method 6, section 7.1, with the addition of the following:

7.1.1 Drierite. Anhydrous calcium sulfate ($CaSO_4$) desiccant, 8 mesh, indicating type is recommended.

NOTE: Do not use silica gel or similar desiccant in this application.

7.1.2 CO_2 Absorbing Material. Ascarite II. Sodium hydroxide-coated silica, 8- to 20-mesh.

7.2 Sample Recovery and Analysis. Same as Method 6, sections 7.2 and 7.3, respectively.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Preparation of Sampling Train.

8.1.1 Measure 15 ml of 80 percent isopropanol into the first midget bubbler and 15 ml of 3 percent hydrogen peroxide into each of the two midget impingers (the second

and third vessels in the train) as described in Method 6, section 8.1. Insert the glass wool into the top of the isopropanol bubbler as shown in Figure 6A–1. Place about 25 g of Drierite into the second midget bubbler (the fourth vessel in the train). Clean the outside of the bubblers and impingers and allow the vessels to reach room temperature. Weigh the four vessels simultaneously to the nearest 0.1 g, and record this initial weight (m_{wi}).

8.1.2 With one end of the CO_2 absorber sealed, place glass wool into the cylinder to a depth of about 1 cm (0.5 in.). Place about 150 g of CO_2 absorbing material in the cylinder on top of the glass wool, and fill the remaining space in the cylinder with glass wool. Assemble the cylinder as shown in figure 6A–2. With the cylinder in a horizontal position, rotate it around the horizontal axis. The CO_2 absorbing material should remain in position during the rotation, and no open spaces or channels should be formed. If necessary, pack more glass wool into the cylinder to make the CO_2 absorbing material stable. Clean the outside of the cylinder of loose dirt and moisture and allow the cylinder to reach room temperature. Weigh the cylinder to the nearest 0.1 g, and record this initial weight (m_{ai}).

8.1.3 Assemble the train as shown in figure 6A–1. Adjust the probe heater to a temperature sufficient to prevent condensation (see note in section 6.1). Place crushed ice and water around the impingers and bubblers. Mount the CO_2 absorber outside the water bath in a vertical flow position with the sample gas inlet at the bottom. Flexible tubing (*e.g.*, Tygon) may be used to connect the last SO_2 absorbing impinger to the moisture absorber and to connect the moisture absorber to the CO_2 absorber. A second, smaller CO_2 absorber containing Ascarite II may be added in-line downstream of the primary CO_2 absorber as a breakthrough indicator. Ascarite II turns white when CO_2 is absorbed.

8.2 Sampling Train Leak-Check Procedure and Sample Collection. Same as Method 6, sections 8.2 and 8.3, respectively.

8.3 Sample Recovery.

8.3.1 Moisture Measurement. Disconnect the isopropanol bubbler, the SO_2 impingers, and the moisture absorber from the sample train. Allow about 10 minutes for them to reach room temperature, clean the outside of loose dirt and moisture, and weigh them simultaneously in the same manner as in section 8.1. Record this final weight (m_{wf}).

8.3.2 Peroxide Solution. Discard the contents of the isopropanol bubbler and pour the contents of the midget impingers into a leak-free polyethylene bottle for shipping. Rinse the two midget impingers and connecting tubes with water, and add the washing to the same storage container.

8.3.3 CO_2 Absorber. Allow the CO_2 absorber to warm to room temperature (about 10 minutes), clean the outside of loose dirt and moisture, and weigh to the nearest 0.1 g in the same manner as in section 8.1. Record this final weight (m_{af}). Discard used Ascarite II material.

9.0 Quality Control

Same as Method 6, section 9.0.

10.0 Calibration and Standardization

Same as Method 6, section 10.0.

11.0 Analytical Procedure

11.1 Sample Analysis. The sample analysis procedure for SO_2 is the same as that specified in Method 6, section 11.0.

12.0 Data Analysis and Calculations

Same as Method 6, section 12.0, with the addition of the following:

12.1 Nomenclature.

C_w = Concentration of moisture, percent.
C_{CO2} = Concentration of CO_2, dry basis, percent.
E_{SO2} = Emission rate of SO_2, ng/J (lb/10^6 Btu).
F_C = Carbon F-factor from Method 19 for the fuel burned, dscm/J (dscf/10^6 Btu).
m_{wi} = Initial weight of impingers, bubblers, and moisture absorber, g.
m_{wf} = Final weight of impingers, bubblers, and moisture absorber, g.
m_{ai} = Initial weight of CO_2 absorber, g.
m_{af} = Final weight of CO_2 absorber, g.
m_{SO2} = Mass of SO_2 collected, mg.
$V_{CO2(std)}$ = Equivalent volume of CO_2 collected at standard conditions, dscm (dscf).
$V_{w(std)}$ = Equivalent volume of moisture collected at standard conditions, scm (scf).

12.2 CO_2 Volume Collected, Corrected to Standard Conditions.

$$V_{CO_2(std)} = K_3 \left(m_{af} - m_{ai}\right) \qquad \text{Eq. 6A-1}$$

Where:

K_3 = Equivalent volume of gaseous CO_2 at standard conditions, 5.467×10^{-4} dscm/g (1.930×10^{-2} dscf/g).

12.3 Moisture Volume Collected, Corrected to Standard Conditions.

$$V_{w(std)} = K_4 \left(m_{wf} - m_{wi}\right) \qquad \text{Eq. 6A-2}$$

Where:

K_4 = Equivalent volume of water vapor at standard conditions, 1.336×10^{-3} scm/g (4.717×10^{-2} scf/g).

12.4 SO_2 Concentration.

$$C_{so_2} = \frac{K_2 N (V_t - V_{tb})(V_{so\,ln}/V_a)}{V_{m(std)} + V_{co_2(std)}} \qquad \text{Eq. 6A-3}$$

Where:

K_2 = 32.03 mg SO_2/meq. SO_2 (7.061×10^{-5} lb SO_2/meq. SO_2)

12.5 CO_2 Concentration.

$$C_{co_2} = \frac{V_{co_2(std)}}{V_{m(std)} + V_{co_2(std)}} \qquad \text{Eq. 6A-4}$$

12.6 Moisture Concentration.

$$C_w = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)} + V_{co_2(std)}} \qquad \text{Eq. 6A-5}$$

13.0 Method Performance

13.1 Range and Precision. The minimum detectable limit and the upper limit for the measurement of SO_2 are the same as for Method 6. For a 20-liter sample, this method has a precision of ±0.5 percent CO_2 for concentrations between 2.5 and 25 percent CO_2 and ±1.0 percent moisture for moisture concentrations greater than 5 percent.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Methods

If the only emission measurement desired is in terms of emission rate of SO_2 (ng/J or lb/10^6 Btu), an abbreviated procedure may be used. The differences between the above procedure and the abbreviated procedure are described below.

16.1 Sampling Train. The sampling train is the same as that shown in Figure 6A–1 and as described in section 6.1, except that the dry gas meter is not needed.

16.2 Preparation of the Sampling Train. Follow the same procedure as in section 8.1, except do not weigh the isopropanol bubbler, the SO_2 absorbing impingers, or the moisture absorber.

16.3 Sampling Train Leak-Check Procedure and Sample Collection. Leak-check and operate the sampling train as described in section 8.2, except that dry gas meter readings, barometric pressure, and dry gas meter temperatures need not be recorded during sampling.

16.4 Sample Recovery. Follow the procedure in section 8.3, except do not weigh the isopropanol bubbler, the SO_2 absorbing impingers, or the moisture absorber.

16.5 Sample Analysis. Analysis of the peroxide solution is the same as that described in section 11.1.

16.6 Calculations.

16.6.1 SO_2 Collected.

$$m_{SO_2} = K_2 N (V_t - V_{tb})(V_{soln}/V_a) \qquad \text{Eq. 6A-6}$$

Where:

K_2 = 32.03 mg SO_2/meq. SO_2
$K_2 = 7.061 \times 10^{-5}$ lb SO_2/meq. SO_2

16.6.2 Sulfur Dioxide Emission Rate.

$$E_{SO_2} = K_5 F_c m_{so_2} / (m_{af} - m_{ai}) \qquad \text{Eq. 6A-7}$$

Where:

$K_5 = 1.829 \times 10^9$ mg/dscm
$K_2 = 0.1142$ lb/dscf

17.0 References

Same as Method 6, section 17.0, References 1 through 8, with the addition of the following:

1. Stanley, Jon and P.R. Westlin. An Alternate Method for Stack Gas Moisture Determination. Source Evaluation Society Newsletter. *3*(4). November 1978.

2. Whittle, Richard N. and P.R. Westlin. Air Pollution Test Report: Development and Evaluation of an Intermittent Integrated SO_2/CO_2 Emission Sampling Procedure. Environmental Protection Agency, Emission Standard and Engineering Division, Emission Measurement Branch. Research Triangle Park, NC. December 1979. 14 pp.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

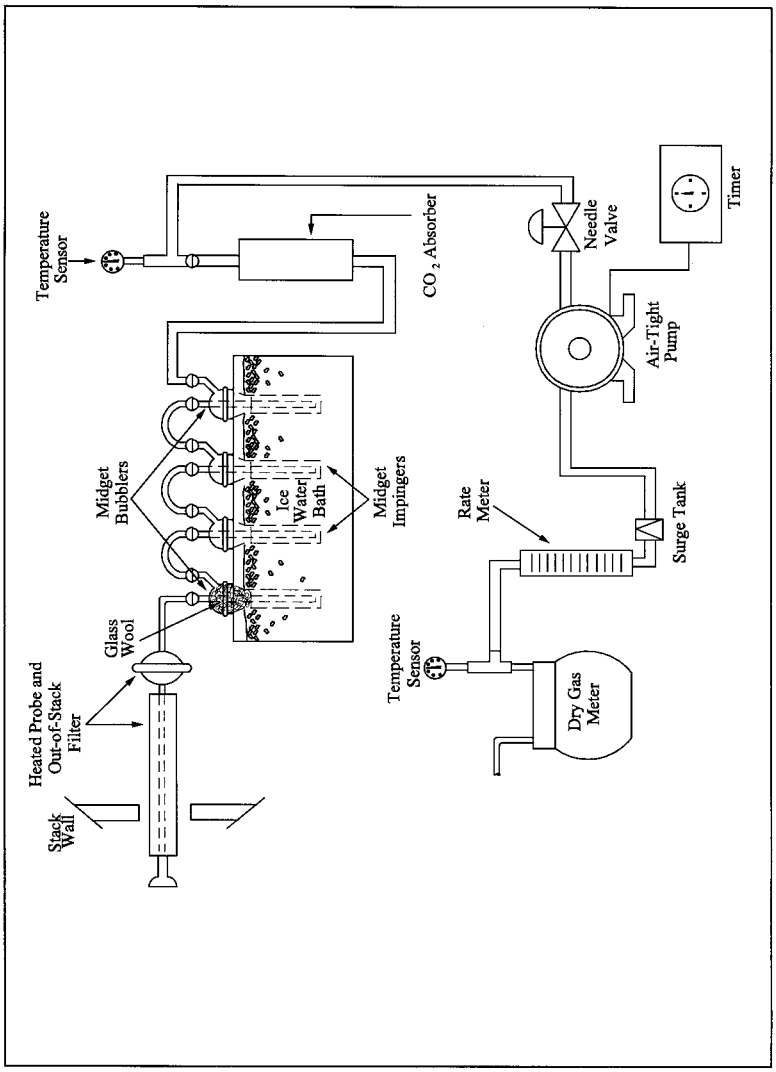

Figure 6A-1. Sampling train.

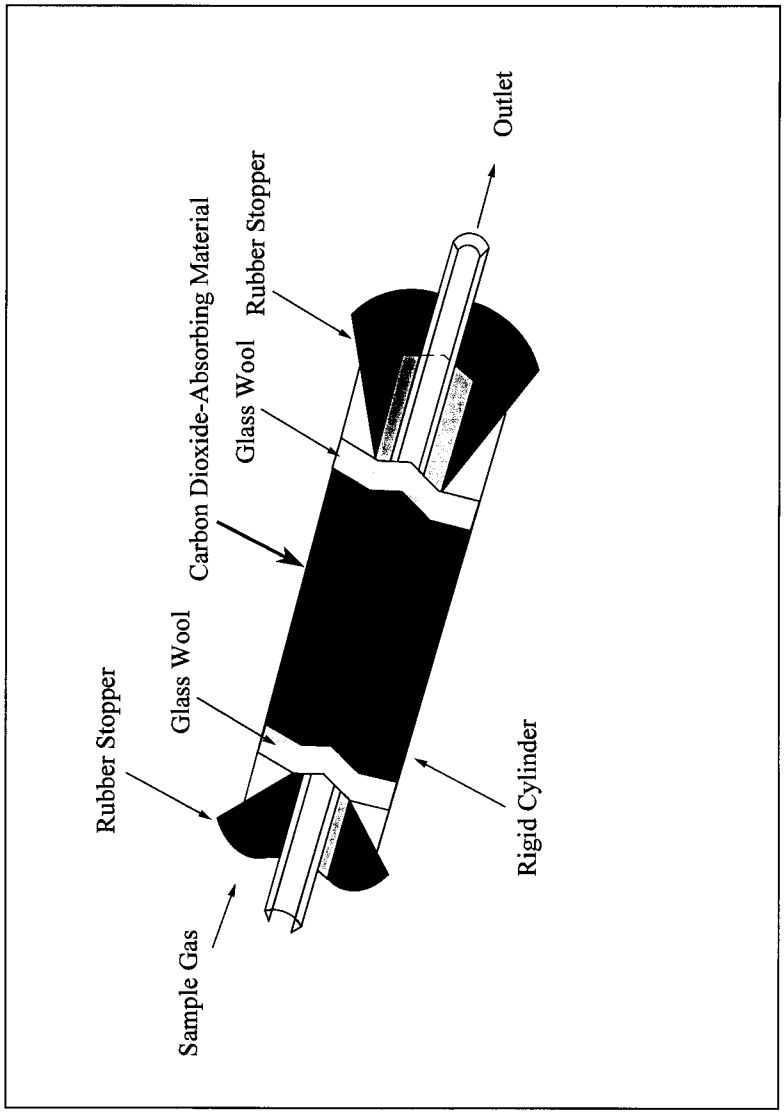

Figure 6A-2. CO_2 Absorber

METHOD 6B—DETERMINATION OF SULFUR DIOXIDE AND CARBON DIOXIDE DAILY AVERAGE EMISSIONS FROM FOSSIL FUEL COMBUSTION SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, Method 6, and Method 6A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Sulfur dioxide (SO_2)	7449–09–05	3.4 mg SO_2/m^3 (2.12×10^{-7} lb/ft^3)
Carbon dioxide (CO_2)	124–38–9	N/A

1.2 Applicability. This method is applicable for the determination of SO_2 emissions from combustion sources in terms of concentration (ng/dscm or lb/dscf) and emission rate (ng/J or lb/10^6 Btu), and for the determination of CO_2 concentration (percent) on a daily (24 hours) basis.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the sampling point in the stack intermittently over a 24-hour or other specified time period. The SO_2 fraction is measured by the barium-thorin titration method. Moisture and CO_2 fractions are collected in the same sampling train, and are determined gravimetrically.

3.0 Definitions [Reserved]

4.0 Interferences

Same as Method 6, section 4.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. Same as Method 6, section 5.2.

6.0 Equipment and Supplies

Same as Method 6A, section 6.0, with the following exceptions and additions:

6.1 The isopropanol bubbler is not used. An empty bubbler for the collection of liquid droplets, that does not allow direct contact between the collected liquid and the gas sample, may be included in the sampling train.

6.2 For intermittent operation, include an industrial timer-switch designed to operate in the ''on'' position at least 2 minutes continuously and ''off'' the remaining period over a repeating cycle. The cycle of operation is designated in the applicable regulation. At a minimum, the sampling operation should include at least 12, equal, evenly-spaced periods per 24 hours.

6.3 Stainless steel sampling probes, type 316, are not recommended for use with Method 6B because of potential sample contamination due to corrosion. Glass probes or other types of stainless steel, *e.g.*, Hasteloy or Carpenter 20, are recommended for long-term use.

NOTE: For applications downstream of wet scrubbers, a heated out-of-stack filter (either borosilicate glass wool or glass fiber mat) is necessary. Probe and filter heating systems capable of maintaining a sample gas temperature of between 20 and 120 °C (68 and 248 °F) at the filter are also required in these cases. The electric supply for these heating systems should be continuous and separate from the timed operation of the sample pump.

7.0 Reagents and Standards

Same as Method 6A, section 7.0, with the following exceptions:

7.1 Isopropanol is not used for sampling.

7.2 The hydrogen peroxide absorbing solution shall be diluted to no less than 6 percent by volume, instead of 3 percent as specified in Methods 6 and 6A.

7.3 If the Method 6B sampling train is to be operated in a low sample flow condition (less than 100 ml/min or 0.21 ft^3/hr), molecular sieve material may be substituted for Ascarite II as the CO_2 absorbing material. The recommended molecular sieve material is Union Carbide 1/16 inch pellets, 5 A°, or equivalent. Molecular sieve material need not be discarded following the sampling run, provided that it is regenerated as per the manufacturer's instruction. Use of molecular sieve material at flow rates higher than 100 ml/min (0.21 ft^3/hr) may cause erroneous CO_2 results.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Preparation of Sampling Train. Same as Method 6A, section 8.1, with the addition of the following:

8.1.1 The sampling train is assembled as shown in Figure 6A–1 of Method 6A, except that the isopropanol bubbler is not included.

8.1.2 Adjust the timer-switch to operate in the ''on'' position from 2 to 4 minutes on a 2-hour repeating cycle or other cycle specified in the applicable regulation. Other timer sequences may be used with the restriction that the total sample volume collected is between 25 and 60 liters (0.9 and 2.1 ft^3) for the amounts of sampling reagents prescribed in this method.

8.1.3 Add cold water to the tank until the impingers and bubblers are covered at least two-thirds of their length. The impingers and bubbler tank must be covered and protected from intense heat and direct sunlight. If freezing conditions exist, the impinger solution and the water bath must be protected.

NOTE: Sampling may be conducted continuously if a low flow-rate sample pump [20

to 40 ml/min (0.04 to 0.08 ft^3/hr) for the reagent volumes described in this method] is used. If sampling is continuous, the timer-switch is not necessary. In addition, if the sample pump is designed for constant rate sampling, the rate meter may be deleted. The total gas volume collected should be between 25 and 60 liters (0.9 and 2.1 ft^3) for the amounts of sampling reagents prescribed in this method.

8.2 Sampling Train Leak-Check Procedure. Same as Method 6, section 8.2.

8.3 Sample Collection.

8.3.1 The probe and filter (either in-stack, out-of-stack, or both) must be heated to a temperature sufficient to prevent water condensation.

8.3.2 Record the initial dry gas meter reading. To begin sampling, position the tip of the probe at the sampling point, connect the probe to the first impinger (or filter), and start the timer and the sample pump. Adjust the sample flow to a constant rate of approximately 1.0 liter/min (0.035 cfm) as indicated by the rotameter. Observe the operation of the timer, and determine that it is operating as intended (*i.e.*, the timer is in the ''on'' position for the desired period, and the cycle repeats as required).

8.3.3 One time between 9 a.m. and 11 a.m. during the 24-hour sampling period, record the dry gas meter temperature (T_m) and the barometric pressure ($P_{(bar)}$).

8.3.4 At the conclusion of the run, turn off the timer and the sample pump, remove the probe from the stack, and record the final gas meter volume reading. Conduct a leak-check as described in section 8.2. If a leak is found, void the test run or use procedures acceptable to the Administrator to adjust the sample volume for leakage. Repeat the steps in sections 8.3.1 to 8.3.4 for successive runs.

8.4 Sample Recovery. The procedures for sample recovery (moisture measurement, peroxide solution, and CO_2 absorber) are the same as those in Method 6A, section 8.3.

9.0 Quality Control

Same as Method 6, section 9.0., with the exception of the isopropanol-check.

10.0 Calibration and Standardization

Same as Method 6, section 10.0, with the addition of the following:

10.1 Periodic Calibration Check. After 30 days of operation of the test train, conduct a calibration check according to the same procedures as the post-test calibration check (Method 6, section 10.1.2). If the deviation between initial and periodic calibration factors exceeds 5 percent, use the smaller of the two factors in calculations for the preceding 30 days of data, but use the most recent calibration factor for succeeding test runs.

11.0 Analytical Procedures

11.1 Sample Loss Check and Analysis. Same as Method 6, sections 11.1 and 11.2, respectively.

12.0 Data Analysis and Calculations

Same as Method 6A, section 12.0, except that P_{bar} and T_m correspond to the values recorded in section 8.3.3 of this method. The values are as follows:

P_{bar} = Initial barometric pressure for the test period, mm Hg.

T_m = Absolute meter temperature for the test period, °K.

13.0 Method Performance

13.1 Range.

13.1.1 Sulfur Dioxide. Same as Method 6.

13.1.2 Carbon Dioxide. Not determined.

13.2 Repeatability and Reproducibility. EPA-sponsored collaborative studies were undertaken to determine the magnitude of repeatability and reproducibility achievable by qualified testers following the procedures in this method. The results of the studies evolve from 145 field tests including comparisons with Methods 3 and 6. For measurements of emission rates from wet, flue gas desulfurization units in (ng/J), the repeatability (intra-laboratory precision) is 8.0 percent and the reproducibility (inter-laboratory precision) is 11.1 percent.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Methods

Same as Method 6A, section 16.0, except that the timer is needed and is operated as outlined in this method.

17.0 References

Same as Method 6A, section 17.0, with the addition of the following:

1. Butler, Frank E., et. al. The Collaborative Test of Method 6B: Twenty-Four-Hour Analysis of SO_2 and CO_2. JAPCA. Vol. 33, No. 10. October 1983.

18.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 6C—DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES (INSTRUMENTAL ANALYZER PROCEDURE)

1.0 Scope and Application

What is Method 6C?

Method 6C is a procedure for measuring sulfur dioxide (SO_2) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that

you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis.

This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 4—Determination of Moisture Content in Stack Gases.

(c) Method 6—Determination of Sulfur Dioxide Emissions from Stationary Sources.

(d) Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure).

1.1 Analytes. What does this method determine? This method measures the concentration of sulfur dioxide.

Analyte	CAS No.	Sensitivity
SO_2	7446–09–5	Typically <2% of Calibration Span.

1.2 Applicability. When is this method required? The use of Method 6C may be required by specific New Source Performance Standards, Clean Air Marketing rules, State Implementation Plans, and permits where SO_2 concentrations in stationary source emissions must be measured, either to determine compliance with an applicable emission standard or to conduct performance testing of a continuous emission monitoring system (CEMS). Other regulations may also require the use of Method 6C.

1.3 Data Quality Objectives. How good must my collected data be? Refer to section 1.3 of Method 7E.

2.0 Summary of Method

In this method, you continuously sample the effluent gas and convey the sample to an analyzer that measures the concentration of SO_2. You must meet the performance requirements of this method to validate your data.

3.0 Definitions

Refer to section 3.0 of Method 7E for the applicable definitions.

4.0 Interferences

Refer to Section 4.0 of Method 7E.

5.0 Safety

Refer to section 5.0 of Method 7E.

6.0 Equipment and Supplies

Figure 7E–1 of Method 7E is a schematic diagram of an acceptable measurement system.

6.1 What do I need for the measurement system? The essential components of the measurement system are the same as those in sections 6.1 and 6.2 of Method 7E, except that the SO_2 analyzer described in section 6.2 of this method must be used instead of the analyzer described in section 6.2 of Method 7E. You must follow the noted specifications in section 6.1 of Method 7E.

6.2 What analyzer must I use? You may use an instrument that uses an ultraviolet, nondispersive infrared, fluorescence, or other detection principle to continuously measure SO_2 in the gas stream and meets the performance specifications in section 13.0. The low-range and dual-range analyzer provisions in sections 6.2.8.1 and 6.2.8.2 of Method 7E apply.

7.0 Reagents and Standards

7.1 Calibration Gas. What calibration gases do I need? Refer to section 7.1 of Method 7E for the calibration gas requirements. Example calibration gas mixtures are listed below.

(a) SO_2 in nitrogen (N_2).

(b) SO_2 in air.

(c) SO_2 and CO_2 in N_2.

(d) SO_2 andO_2 in N_2.

(e) $SO_2/CO_2/O_2$ gas mixture in N_2.

(f) CO_2/NO_X gas mixture in N_2.

(g) $CO_2/SO_2/NO_X$ gas mixture in N_2.

7.2 Interference Check. What additional reagents do I need for the interference check? The test gases for the interference check are listed in Table 7E–3 of Method 7E. For the alternative interference check, you must use the reagents described in section 7.0 of Method 6.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling Site and Sampling Points. You must follow the procedures of section 8.1 of Method 7E.

8.2 Initial Measurement System Performance Tests. You must follow the procedures in section 8.2 of Method 7E. If a dilution-type measurement system is used, the special considerations in section 8.3 of Method 7E also apply.

8.3 Interference Check. You must follow the procedures of section 8.2.7 of Method 7E

to conduct an interference check, substituting SO_2 for NO_X as the method pollutant. For dilution-type measurement systems, you must use the alternative interference check procedure in section 16 and a co-located, unmodified Method 6 sampling train.

8.4 Sample Collection. You must follow the procedures of section 8.4 of Method 7E.

8.5 Post-Run System Bias Check and Drift Assessment. You must follow the procedures of section 8.5 of Method 7E.

9.0 Quality Control

Follow quality control procedures in section 9.0 of Method 7E.

10.0 Calibration and Standardization

Follow the procedures for calibration and standardization in section 10.0 of Method 7E.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the applicable procedures for calculations and data analysis in section 12.0 of Method 7E as applicable, substituting SO_2 for NO_X as appropriate.

13.0 Method Performance

13.1 The specifications for the applicable performance checks are the same as in section 13.0 of Method 7E.

13.2 Alternative Interference Check. The results are acceptable if the difference between the Method 6C result and the modified Method 6 result is less than 7.0 percent of the Method 6 result for each of the three test runs. For the purposes of comparison, the Method 6 and 6C results must be expressed in the same units of measure.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Alternative Interference Check. You may perform an alternative interference check consisting of at least three comparison runs between Method 6C and Method 6. This check validates the Method 6C results at each particular source category (type of facility) where the check is performed. When testing under conditions of low concentrations (<15 ppm), this alternative interference check is not allowed.

NOTE: The procedure described below applies to non-dilution sampling systems only. If this alternative interference check is used for a dilution sampling system, use a standard Method 6 sampling train and extract the sample directly from the exhaust stream at points collocated with the Method 6C sample probe.

a. Build the modified Method 6 sampling train (flow control valve, two midget impingers containing 3 percent hydrogen peroxide, and dry gas meter) shown in Figure 6C–1. Connect the sampling train to the sample bypass discharge vent. Record the dry gas meter reading before you begin sampling. Simultaneously collect modified Method 6 and Method 6C samples. Open the flow control valve in the modified Method 6 train as you begin to sample with Method 6C. Adjust the Method 6 sampling rate to 1 liter per minute (.10 percent). The sampling time per run must be the same as for Method 6 plus twice the average measurement system response time. If your modified Method 6 train does not include a pump, you risk biasing the results high if you over-pressurize the midget impingers and cause a leak. You can reduce this risk by cautiously increasing the flow rate as sampling begins.

b. After completing a run, record the final dry gas meter reading, meter temperature, and barometric pressure. Recover and analyze the contents of the midget impingers using the procedures in Method 6. Determine the average gas concentration reported by Method 6C for the run.

17.0 References

1. ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards'' September 1997 as amended, EPA–600/R–97/121

18.0 Tables, Diagrams, Flowcharts, and Validation Data

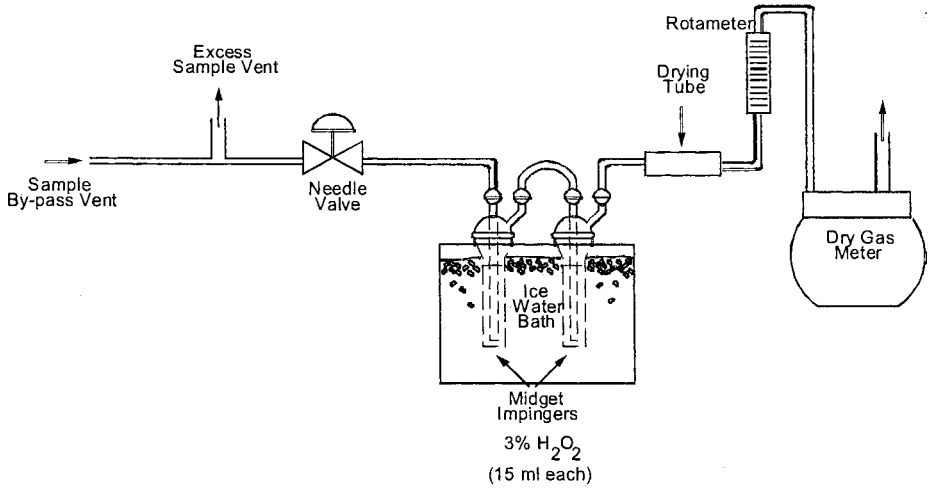

Figure 6C-1. Modified Method 6
Alternative Interference Check Sampling Train

METHOD 7—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1 and Method 5.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–0	2–400 mg/dscm

1.2 Applicability. This method is applicable for the measurement of nitrogen oxides (NO_X) emitted from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sample methods.

2.0 Summary of Method

A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution, and the nitrogen oxides, except nitrous oxide, are measured colorimetrically using the phenoldisulfonic acid (PDS) procedure.

3.0 Definitions [Reserved]

4.0 Interferences

Biased results have been observed when sampling under conditions of high sulfur dioxide concentrations. At or above 2100 ppm SO_2, use five times the H_2O_2 concentration of the Method 7 absorbing solution. Laboratory tests have shown that high concentrations of SO_2 (about 2100 ppm) cause low results in Method 7 and 7A. Increasing the H_2O_2 concentration to five times the original concentration eliminates this bias. However, when no SO_2 is present, increasing the concentration by five times results in a low bias.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs.

5.2.2 Phenoldisulfonic Acid. Irritating to eyes and skin.

5.2.3 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.4 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

5.2.5 Phenol. Poisonous and caustic. Do not handle with bare hands as it is absorbed through the skin.

6.0 Equipment and Supplies

6.1 Sample Collection. A schematic of the sampling train used in performing this method is shown in Figure 7–1. Other grab sampling systems or equipment, capable of measuring sample volume to within 2.0 percent and collecting a sufficient sample volume to allow analytical reproducibility to within 5 percent, will be considered acceptable alternatives, subject to the approval of the Administrator. The following items are required for sample collection:

6.1.1 Probe. Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or heated out-of-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Stainless steel or Teflon tubing may also be used for the probe. Heating is not necessary if the probe remains dry during the purging period.

6.1.2 Collection Flask. Two-liter borosilicate, round bottom flask, with short neck and 24/40 standard taper opening, protected against implosion or breakage.

6.1.3 Flask Valve. T-bore stopcock connected to a 24/40 standard taper joint.

6.1.4 Temperature Gauge. Dial-type thermometer, or other temperature gauge, capable of measuring 1 °C (2 °F) intervals from −5 to 50 °C (23 to 122 °F).

6.1.5 Vacuum Line. Tubing capable of withstanding a vacuum of 75 mm (3 in.) Hg absolute pressure, with ''T'' connection and T-bore stopcock.

6.1.6 Vacuum Gauge. U-tube manometer, 1 meter (39 in.), with 1 mm (0.04 in.) divisions, or other gauge capable of measuring pressure to within 2.5 mm (0.10 in.) Hg.

6.1.7 Pump. Capable of evacuating the collection flask to a pressure equal to or less than 75 mm (3 in.) Hg absolute.

6.1.8 Squeeze Bulb. One-way.

6.1.9 Volumetric Pipette. 25-ml.

6.1.10 Stopcock and Ground Joint Grease. A high-vacuum, high-temperature chlorofluorocarbon grease is required. Halocarbon 25–5S has been found to be effective.

6.1.11 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg. See note in Method 5, section 6.1.2.

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Graduated Cylinder. 50-ml with 1 ml divisions.

6.2.2 Storage Containers. Leak-free polyethylene bottles.

6.2.3 Wash Bottle. Polyethylene or glass.

6.2.4 Glass Stirring Rod.

6.2.5 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

6.3 Analysis. The following items are required for analysis:

6.3.1 Volumetric Pipettes. Two 1-ml, two 2-ml, one 3-ml, one 4-ml, two 10-ml, and one 25-ml for each sample and standard.

6.3.2 Porcelain Evaporating Dishes. 175- to 250-ml capacity with lip for pouring, one for each sample and each standard. The Coors No. 45006 (shallowform, 195-ml) has been found to be satisfactory. Alternatively, polymethyl pentene beakers (Nalge No. 1203, 150-ml), or glass beakers (150-ml) may be used. When glass beakers are used, etching of the beakers may cause solid matter to be present in the analytical step; the solids should be removed by filtration.

6.3.3 Steam Bath. Low-temperature ovens or thermostatically controlled hot plates kept below 70 °C (160 °F) are acceptable alternatives.

6.3.4 Dropping Pipette or Dropper. Three required.

6.3.5 Polyethylene Policeman. One for each sample and each standard.

6.3.6 Graduated Cylinder. 100-ml with 1-ml divisions.

6.3.7 Volumetric Flasks. 50-ml (one for each sample and each standard), 100-ml (one for each sample and each standard, and one for the working standard KNO_3 solution), and 1000-ml (one).

6.3.8 Spectrophotometer. To measure at 410 nm.

6.3.9 Graduated Pipette. 10-ml with 0.1-ml divisions.

6.3.10 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

6.3.11 Analytical Balance. To measure to within 0.1 mg.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. The following reagents are required for sampling:

7.1.1 Water. Deionized distilled to conform to ASTM D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17). The $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.1.2 Absorbing Solution. Cautiously add 2.8 ml concentrated H_2SO_4 to a 1-liter flask partially filled with water. Mix well, and add 6 ml of 3 percent hydrogen peroxide, freshly prepared from 30 percent hydrogen peroxide solution. Dilute to 1 liter of water and mix well. The absorbing solution should be used within 1 week of its preparation. Do not expose to extreme heat or direct sunlight.

7.2 Sample Recovery. The following reagents are required for sample recovery:

7.2.1 Water. Same as in 7.1.1.

7.2.2 Sodium Hydroxide, 1 N. Dissolve 40 g NaOH in water, and dilute to 1 liter.

7.3 Analysis. The following reagents and standards are required for analysis:

7.3.1 Water. Same as in 7.1.1.

7.3.2 Fuming Sulfuric Acid. 15 to 18 percent by weight free sulfur trioxide. HANDLE WITH CAUTION.

7.3.3 Phenol. White solid.

7.3.4 Sulfuric Acid. Concentrated, 95 percent minimum assay.

7.3.5 Potassium Nitrate (KNO_3). Dried at 105 to 110 °C (221 to 230 °F) for a minimum of 2 hours just prior to preparation of standard solution.

7.3.6 Standard KNO_3 Solution. Dissolve exactly 2.198 g of dried KNO_3 in water, and dilute to 1 liter with water in a 1000-ml volumetric flask.

7.3.7 Working Standard KNO_3 Solution. Dilute 10 ml of the standard solution to 100 ml with water. One ml of the working standard solution is equivalent to 100 μg nitrogen dioxide (NO_2).

7.3.8 Phenoldisulfonic Acid Solution. Dissolve 25 g of pure white phenol solid in 150 ml concentrated sulfuric acid on a steam bath. Cool, add 75 ml fuming sulfuric acid (15 to 18 percent by weight free sulfur trioxide—HANDLE WITH CAUTION), and heat at 100 °C (212 °F) for 2 hours. Store in a dark, stoppered bottle.

7.3.9 Concentrated Ammonium Hydroxide.

8.0 Sample Collection, Preservation, Storage and Transport

8.1 Sample Collection.

8.1.1 Flask Volume. The volume of the collection flask and flask valve combination must be known prior to sampling. Assemble the flask and flask valve, and fill with water to the stopcock. Measure the volume of water to ±10 ml. Record this volume on the flask.

8.1.2 Pipette 25 ml of absorbing solution into a sample flask, retaining a sufficient quantity for use in preparing the calibration standards. Insert the flask valve stopper into the flask with the valve in the ''purge'' position. Assemble the sampling train as shown in Figure 7–1, and place the probe at the sampling point. Make sure that all fittings are tight and leak-free, and that all ground glass joints have been greased properly with a high-vacuum, high temperature chlorofluorocarbon-based stopcock grease. Turn the flask valve and the pump valve to their ''evacuate'' positions. Evacuate the flask to 75 mm (3 in.) Hg absolute pressure, or less. Evacuation to a pressure approaching the vapor pressure of water at the existing temperature is desirable. Turn the pump valve to its ''vent'' position, and turn off the pump. Check for leakage by observing the manometer for any pressure fluctuation. (Any variation greater than 10 mm (0.4 in.) Hg over a period of 1 minute is not acceptable, and the flask is not to be used until the leakage problem is corrected. Pressure in the flask is not to exceed 75 mm (3 in.) Hg absolute at the time sampling is commenced.) Record the volume of the flask and valve (V_f), the flask temperature (T_i), and the barometric pressure. Turn the flask valve counterclockwise to its ''purge'' position, and do the same with the pump valve. Purge the probe and the vacuum tube using the squeeze bulb. If condensation occurs in the probe and the flask valve area, heat the probe, and purge until the condensation disappears. Next, turn the pump valve to its ''vent'' position. Turn the flask valve clockwise to its ''evacuate'' position, and record the difference in the mercury levels in the manometer. The absolute internal pressure in the flask (P_i) is equal to the barometric pressure less the manometer reading. Immediately turn the flask valve to the ''sample'' position, and permit the gas to enter the flask until pressures in the flask and sample line (*i.e.*, duct, stack) are equal. This will usually require about 15 seconds; a longer period indicates a plug in the probe, which must be

corrected before sampling is continued. After collecting the sample, turn the flask valve to its ''purge'' position, and disconnect the flask from the sampling train.

8.1.3 Shake the flask for at least 5 minutes.

8.1.4 If the gas being sampled contains insufficient oxygen for the conversion of NO to NO_2 (*e.g.,* an applicable subpart of the standards may require taking a sample of a calibration gas mixture of NO in N_2), then introduce oxygen into the flask to permit this conversion. Oxygen may be introduced into the flask by one of three methods: (1) Before evacuating the sampling flask, flush with pure cylinder oxygen, then evacuate flask to 75 mm (3 in.) Hg absolute pressure or less; or (2) inject oxygen into the flask after sampling; or (3) terminate sampling with a minimum of 50 mm (2 in.) Hg vacuum remaining in the flask, record this final pressure, and then vent the flask to the atmosphere until the flask pressure is almost equal to atmospheric pressure.

8.2 Sample Recovery. Let the flask sit for a minimum of 16 hours, and then shake the contents for 2 minutes.

8.2.1 Connect the flask to a mercury filled U-tube manometer. Open the valve from the flask to the manometer, and record the flask temperature (T_f), the barometric pressure, and the difference between the mercury levels in the manometer. The absolute internal pressure in the flask (P_f) is the barometric pressure less the manometer reading. Transfer the contents of the flask to a leak-free polyethylene bottle. Rinse the flask twice with 5 ml portions of water, and add the rinse water to the bottle. Adjust the pH to between 9 and 12 by adding 1 N NaOH, dropwise (about 25 to 35 drops). Check the pH by dipping a stirring rod into the solution and then touching the rod to the pH test paper. Remove as little material as possible during this step. Mark the height of the liquid level so that the container can be checked for leakage after transport. Label the container to identify clearly its contents. Seal the container for shipping.

9.0 Quality Control

Section	Quality control measure	Effect
10.1	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.

10.0 Calibration and Standardization

10.1 Spectrophotometer.

10.1.1 Optimum Wavelength Determination.

10.1.1.1 Calibrate the wavelength scale of the spectrophotometer every 6 months. The calibration may be accomplished by using an energy source with an intense line emission such as a mercury lamp, or by using a series of glass filters spanning the measuring range of the spectrophotometer. Calibration materials are available commercially and from the National Institute of Standards and Technology. Specific details on the use of such materials should be supplied by the vendor; general information about calibration techniques can be obtained from general reference books on analytical chemistry. The wavelength scale of the spectrophotometer must read correctly within 5 nm at all calibration points; otherwise, repair and recalibrate the spectrophotometer. Once the wavelength scale of the spectrophotometer is in proper calibration, use 410 nm as the optimum wavelength for the measurement of the absorbance of the standards and samples.

10.1.1.2 Alternatively, a scanning procedure may be employed to determine the proper measuring wavelength. If the instrument is a double-beam spectrophotometer, scan the spectrum between 400 and 415 nm using a 200 μg NO_2 standard solution in the sample cell and a blank solution in the reference cell. If a peak does not occur, the spectrophotometer is probably malfunctioning and should be repaired. When a peak is obtained within the 400 to 415 nm range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of absorbance of both the standards and the samples. For a single-beam spectrophotometer, follow the scanning procedure described above, except scan separately the blank and standard solutions. The optimum wavelength shall be the wavelength at which the maximum difference in absorbance between the standard and the blank occurs.

10.1.2 Determination of Spectrophotometer Calibration Factor K_c. Add 0 ml, 2.0 ml, 4.0 ml, 6.0 ml, and 8.0 ml of the KNO_3 working standard solution (1 ml = 100 μg NO_2) to a series of five 50-ml volumetric flasks. To each flask, add 25 ml of absorbing solution and 10 ml water. Add 1 N NaOH to each flask until the pH is between 9 and 12 (about 25 to 35 drops). Dilute to the mark with water. Mix thoroughly, and pipette a 25-ml aliquot of each solution into a separate porcelain evaporating dish. Beginning with the evaporation step, follow the analysis procedure of section 11.2 until the solution has been transferred to the 100-ml volumetric flask and diluted to the mark. Measure the absorbance of each solution at the optimum wavelength as determined in section 10.2.1. This calibration procedure must be repeated on each day that samples are analyzed. Calculate the spectrophotometer calibration factor as shown in section 12.2.

10.1.3 Spectrophotometer Calibration Quality Control. Multiply the absorbance value obtained for each standard by the K_c factor (reciprocal of the least squares slope) to determine the distance each calibration point lies from the theoretical calibration line. The difference between the calculated concentration values and the actual concentrations (*i.e.*, 100, 200, 300, and 400 µg NO_2) should be less than 7 percent for all standards.

10.2 Barometer. Calibrate against a mercury barometer or NIST-traceable barometer prior to the field test.

10.3 Temperature Gauge. Calibrate dial thermometers against mercury-in-glass thermometers. An alternative mercury-free thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

10.4 Vacuum Gauge. Calibrate mechanical gauges, if used, against a mercury manometer such as that specified in section 6.1.6.

10.5 Analytical Balance. Calibrate against standard weights.

11.0 Analytical Procedures

11.1 Sample Loss Check. Note the level of the liquid in the container, and confirm whether any sample was lost during shipment. Note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Preparation. Immediately prior to analysis, transfer the contents of the shipping container to a 50 ml volumetric flask, and rinse the container twice with 5 ml portions of water. Add the rinse water to the flask, and dilute to mark with water; mix thoroughly. Pipette a 25-ml aliquot into the porcelain evaporating dish. Return any unused portion of the sample to the polyethylene storage bottle. Evaporate the 25-ml aliquot to dryness on a steam bath, and allow to cool. Add 2 ml phenoldisulfonic acid solution to the dried residue, and triturate thoroughly with a polyethylene policeman. Make sure the solution contacts all the residue. Add 1 ml water and 4 drops of concentrated sulfuric acid. Heat the solution on a steam bath for 3 minutes with occasional stirring. Allow the solution to cool, add 20 ml water, mix well by stirring, and add concentrated ammonium hydroxide, dropwise, with constant stirring, until the pH is 10 (as determined by pH paper). If the sample contains solids, these must be removed by filtration (centrifugation is an acceptable alternative, subject to the approval of the Administrator) as follows: Filter through Whatman No. 41 filter paper into a 100-ml volumetric flask. Rinse the evaporating dish with three 5-ml portions of water. Filter these three rinses. Wash the filter with at least three 15-ml portions of water. Add the filter washings to the contents of the volumetric flask, and dilute to the mark with water. If solids are absent, the solution can be transferred directly to the 100-ml volumetric flask and diluted to the mark with water.

11.3 Sample Analysis. Mix the contents of the flask thoroughly, and measure the absorbance at the optimum wavelength used for the standards (Section 10.2.1), using the blank solution as a zero reference. Dilute the sample and the blank with equal volumes of water if the absorbance exceeds A_4, the absorbance of the 400-µg NO_2 standard (see section 10.2.2).

12.0 Data Analysis and Calculations

Carry out the calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculations.

12.1 12.1 Nomenclature

A = Absorbance of sample.
A_1 = Absorbance of the 100-µg NO_2 standard.
A_2 = Absorbance of the 200-µg NO_2 standard.
A_3 = Absorbance of the 300-µg NO_2 standard.
A_4 = Absorbance of the 400-µg NO_2 standard.
C = Concentration of NO_X as NO_2, dry basis, corrected to standard conditions, mg/dsm^3 (lb/dscf).
F = Dilution factor (*i.e.*, 25/5, 25/10, *etc.*, required only if sample dilution was needed to reduce the absorbance into the range of the calibration).
K_c = Spectrophotometer calibration factor.
M = Mass of NO_X as NO_2 in gas sample, µg.
P_f = Final absolute pressure of flask, mm Hg (in. Hg).
P_i = Initial absolute pressure of flask, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
T_f = Final absolute temperature of flask, °K (°R).
T_i = Initial absolute temperature of flask, °K (°R).
T_{std} = Standard absolute temperature, 293 °K (528°R).
V_{sc} = Sample volume at standard conditions (dry basis), ml.
V_f = Volume of flask and valve, ml.
V_a = Volume of absorbing solution, 25 ml.

12.2 Spectrophotometer Calibration Factor.

$$K_c = 100\frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^{\,2} + A_2^{\,2} + A_3^{\,2} + A_4^{\,2}} \qquad \text{Eq. 7-1}$$

12.3 Sample Volume, Dry Basis, Corrected to Standard Conditions.

$$V_{sc} = \left(V_f - V_a\right)\frac{T_{std}}{P_{std}}\left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right] \qquad \text{Eq. 7-2}$$

$$= K_1\left(V_f - 25\right)\left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right]$$

Where:

K_1 = 0.3858 °K/mm Hg for metric units,
K_1 = 17.65 °R/in. Hg for English units.

12.4 Total µg NO_2 per sample.

$$m = 2K_c AF \qquad \text{Eq. 7-3}$$

Where:

2 = 50/25, the aliquot factor.

NOTE: If other than a 25-ml aliquot is used for analysis, the factor 2 must be replaced by a corresponding factor.

12.5 Sample Concentration, Dry Basis, Corrected to Standard Conditions.

$$C = K_2\left(m/V_{sc}\right) \qquad \text{Eq. 7-4}$$

Where:

K2 = 10^3 (mg/m^3)/(µg/ml) for metric units,
K_2 = 6.242 × 10^{-5} (lb/scf)/(µg/ml) for English units.

13.0 Method Performance

13.1 Range. The analytical range of the method has been determined to be 2 to 400 milligrams NO_X (as NO_2) per dry standard cubic meter, without having to dilute the sample.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Standard Methods of Chemical Analysis. 6th ed. New York, D. Van Nostrand Co., Inc. 1962. Vol. 1, pp. 329–330.

2. Standard Method of Test for Oxides of Nitrogen in Gaseous Combustion Products (Phenoldisulfonic Acid Procedure). In: 1968 Book of ASTM Standards, Part 26. Philadelphia, PA. 1968. ASTM Designation D 1608–60, pp. 725–729.

3. Jacob, M.B. The Chemical Analysis of Air Pollutants. New York. Interscience Publishers, Inc. 1960. Vol. 10, pp. 351–356.

4. Beatty, R.L., L.B. Berger, and H.H. Schrenk. Determination of Oxides of Nitrogen by the Phenoldisulfonic Acid Method. Bureau of Mines, U.S. Dept. of Interior. R.I. 3687. February 1943.

5. Hamil, H.F. and D.E. Camann. Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Fossil Fuel-Fired Steam Generators). Southwest Research Institute Report for Environmental Protection Agency. Research Triangle Park, NC. October 5, 1973.

6. Hamil, H.F. and R.E. Thomas. Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Nitric Acid Plants). Southwest Research Institute Report for Environmental Protection Agency. Research Triangle Park, NC. May 8, 1974.

7. Stack Sampling Safety Manual (Draft). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC. September 1978.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

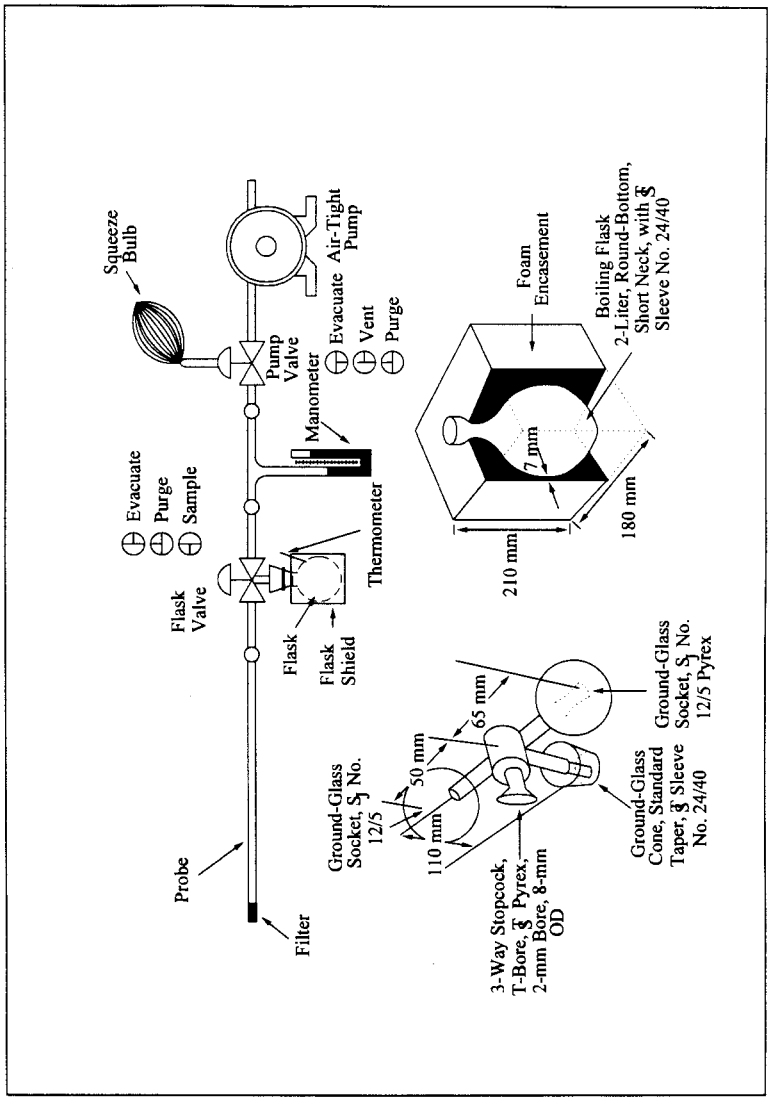

Figure 7-1. Sampling Train, Flask Valve, and Flask.

METHOD 7A—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ION CHROMATOGRAPHIC METHOD)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 3, Method 5, and Method 7.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–0	65–655 ppmv

1.2 Applicability. This method is applicable for the determination of NO_X emissions from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution. The nitrogen oxides, excluding nitrous oxide (N_2O), are oxidized to nitrate and measured by ion chromatography.

3.0 Definitions [Reserved]

4.0 Interferences

Biased results have been observed when sampling under conditions of high sulfur dioxide concentrations. At or above 2100 ppm SO_2, use five times the H_2O_2 concentration of the Method 7 absorbing solution. Laboratory tests have shown that high concentrations of SO_2 (about 2100 ppm) cause low results in Method 7 and 7A. Increasing the H_2O_2 concentration to five times the original concentration eliminates this bias. However, when no SO_2 is present, increasing the concentration by five times results in a low bias.

5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs.

5.2.2 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m^3 will cause lung damage in uninitiated. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as in Method 7, section 6.1.

6.2 Sample Recovery. Same as in Method 7, section 6.2, except the stirring rod and pH paper are not needed.

6.3 Analysis. For the analysis, the following equipment and supplies are required. Alternative instrumentation and procedures will be allowed provided the calibration precision requirement in section 10.1.2 can be met.

6.3.1 Volumetric Pipets. Class A;1-, 2-, 4-, 5-ml (two for the set of standards and one per sample), 6-, 10-, and graduated 5-ml sizes.

6.3.2 Volumetric Flasks. 50-ml (two per sample and one per standard), 200-ml, and 1-liter sizes.

6.3.3 Analytical Balance. To measure to within 0.1 mg.

6.3.4 Ion Chromatograph. The ion chromatograph should have at least the following components:

6.3.4.1 Columns. An anion separation or other column capable of resolving the nitrate ion from sulfate and other species present and a standard anion suppressor column (optional). Suppressor columns are produced as proprietary items; however, one can be produced in the laboratory using the resin available from BioRad Company, 32nd and Griffin Streets, Richmond, California. Peak resolution can be optimized by varying the eluent strength or column flow rate, or by experimenting with alternative columns that may offer more efficient separation. When using guard columns with the stronger reagent to protect the separation column, the analyst should allow rest periods between injection intervals to purge possible sulfate buildup in the guard column.

6.3.4.2 Pump. Capable of maintaining a steady flow as required by the system.

6.3.4.3 Flow Gauges. Capable of measuring the specified system flow rate.

6.3.4.4 Conductivity Detector.

6.3.4.5 Recorder. Compatible with the output voltage range of the detector.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 7, section 7.1.

7.2 Sample Recovery. Same as Method 7, section 7.1.1.

7.3 Analysis. The following reagents and standards are required for analysis:

7.3.1 Water. Same as Method 7, section 7.1.1.

7.3.2 Stock Standard Solution, 1 mg NO_2/ml. Dry an adequate amount of sodium nitrate ($NaNO_3$) at 105 to 110 °C (221 to 230 °F) for a minimum of 2 hours just before preparing the standard solution. Then dissolve exactly 1.847 g of dried $NaNO_3$ in water, and dilute to 1 liter in a volumetric flask. Mix well. This solution is stable for 1 month and should not be used beyond this time.

7.3.3 Working Standard Solution, 25 μg/ml. Dilute 5 ml of the standard solution to 200 ml with water in a volumetric flask, and mix well.

7.3.4 Eluent Solution. Weigh 1.018 g of sodium carbonate (Na_2CO_3) and 1.008 g of sodium bicarbonate ($NaHCO_3$), and dissolve in 4 liters of water. This solution is 0.0024 M Na_2CO_3/0.003 M $NaHCO_3$. Other eluents appropriate to the column type and capable of resolving nitrate ion from sulfate and other species present may be used.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling. Same as in Method 7, section 8.1.

8.2 Sample Recovery. Same as in Method 7, section 8.2, except delete the steps on adjusting and checking the pH of the sample. Do not store the samples more than 4 days between collection and analysis.

9.0 Quality Control

Section	Quality control measure	Effect
10.1	Ion chromatographn calibration	Ensure linearity of ion chromatograph response to standards.

10.0 Calibration and Standardizations

10.1 Ion Chromatograph.

10.1.1 Determination of Ion Chromatograph Calibration Factor S. Prepare a series of five standards by adding 1.0, 2.0, 4.0, 6.0, and 10.0 ml of working standard solution (25 μg/ml) to a series of five 50-ml volumetric flasks. (The standard masses will equal 25, 50, 100, 150, and 250 μg.) Dilute each flask to the mark with water, and mix well. Analyze with the samples as described in section 11.2, and subtract the blank from each value. Prepare or calculate a linear regression plot of the standard masses in μg (x-axis) versus their peak height responses in millimeters (y-axis). (Take peak height measurements with symmetrical peaks; in all other cases, calculate peak areas.) From this curve, or equation, determine the slope, and calculate its reciprocal to denote as the calibration factor, S.

10.1.2 Ion Chromatograph Calibration Quality Control. If any point on the calibration curve deviates from the line by more than 7 percent of the concentration at that point, remake and reanalyze that standard. This deviation can be determined by multiplying S times the peak height response for each standard. The resultant concentrations must not differ by more than 7 percent from each known standard mass (*i.e.*, 25, 50, 100, 150, and 250 μg).

10.2 Conductivity Detector. Calibrate according to manufacturer's specifications prior to initial use.

10.3 Barometer. Calibrate against a mercury barometer.

10.4 Temperature Gauge. Calibrate dial thermometers against mercury-in-glass thermometers. An alternative mercury-free thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

10.5 Vacuum Gauge. Calibrate mechanical gauges, if used, against a mercury manometer such as that specified in section 6.1.6 of Method 7.

10.6 Analytical Balance. Calibrate against standard weights.

11.0 Analytical Procedures

11.1 Sample Preparation.

11.1.1 Note on the analytical data sheet, the level of the liquid in the container, and whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Immediately before analysis, transfer the contents of the shipping container to a 50-ml volumetric flask, and rinse the container twice with 5 ml portions of water. Add the rinse water to the flask, and dilute to the mark with water. Mix thoroughly.

11.1.2 Pipet a 5-ml aliquot of the sample into a 50-ml volumetric flask, and dilute to the mark with water. Mix thoroughly. For each set of determinations, prepare a reagent

blank by diluting 5 ml of absorbing solution to 50 ml with water. (Alternatively, eluent solution may be used instead of water in all sample, standard, and blank dilutions.)

11.2 Analysis.

11.2.1 Prepare a standard calibration curve according to section 10.1.1. Analyze the set of standards followed by the set of samples using the same injection volume for both standards and samples. Repeat this analysis sequence followed by a final analysis of the standard set. Average the results. The two sample values must agree within 5 percent of their mean for the analysis to be valid. Perform this duplicate analysis sequence on the same day. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

11.2.2 Document each sample chromatogram by listing the following analytical parameters: injection point, injection volume, nitrate and sulfate retention times, flow rate, detector sensitivity setting, and recorder chart speed.

12.0 Data Analysis and Calculations

Carry out the calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculations.

12.1 Sample Volume. Calculate the sample volume Vsc (in ml), on a dry basis, corrected to standard conditions, using Equation 7–2 of Method 7.

12.2 Sample Concentration of NO_X as NO_2.

12.2.1 Calculate the sample concentration C (in mg/dscm) as follows:

$$C = (H)(S)(F)\left(10^4\right)/V_{sc} \qquad \text{Eq. 7A-1}$$

Where:

H = Sample peak height, mm.

S = Calibration factor, µg/mm.

F = Dilution factor (required only if sample dilution was needed to reduce the concentration into the range of calibration), dimensionless.

10^4 = 1:10 dilution times conversion factor of: $(mg/10^3\ \mu g)(10^6\ ml/m^3)$.

12.2.2 If desired, the concentration of NO_2 may be calculated as ppm NO_2 at standard conditions as follows:

$$\text{ppm } NO_2 = 0.5228C \qquad \text{Eq. 7A-2}$$

Where:

0.5228 = ml/mg NO_2.

13.0 Method Performance

13.1 Range. The analytical range of the method is from 125 to 1250 mg NO_X/m^3 as NO_2 (65 to 655 ppmv), and higher concentrations may be analyzed by diluting the sample. The lower detection limit is approximately 19 mg/m^3 (10 ppmv), but may vary among instruments.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Mulik, J.D., and E. Sawicki. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor, Ann Arbor Science Publishers, Inc. Vol. 2, 1979.

2. Sawicki, E., J.D. Mulik, and E. Wittgenstein. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor, Ann Arbor Science Publishers, Inc. Vol. 1. 1978.

3. Siemer, D.D. Separation of Chloride and Bromide from Complex Matrices Prior to Ion Chromatographic Determination. Anal. Chem. *52*(12):1874–1877. October 1980.

4. Small, H., T.S. Stevens, and W.C. Bauman. Novel Ion Exchange Chromatographic Method Using Conductimetric Determination. Anal. Chem. *47*(11):1801. 1975.

5. Yu, K.K., and P.R. Westlin. Evaluation of Reference Method 7 Flask Reaction Time. Source Evaluation Society Newsletter. *4*(4). November 1979. 10 pp.

6. Stack Sampling Safety Manual (Draft). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standard, Research Triangle Park, NC. September 1978.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 7B—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ULTRAVIOLET SPECTROPHOTOMETRIC METHOD)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 5, and Method 7.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		

Analyte	CAS No.	Sensitivity
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–0	30–786 ppmv

1.2 Applicability. This method is applicable for the determination of NO_X emissions from nitric acid plants.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution; the NO_X, excluding nitrous oxide (N_2O), are measured by ultraviolet spectrophotometry.

3.0 Definition [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m^3 will cause lung damage in uninitiated. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 7, section 6.1.

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Wash Bottle. Polyethylene or glass.

6.2.2 Volumetric Flasks. 100-ml (one for each sample).

6.3 Analysis. The following items are required for analysis:

6.3.1 Volumetric Pipettes. 5-, 10-, 15-, and 20-ml to make standards and sample dilutions.

6.3.2 Volumetric Flasks. 1000- and 100-ml for preparing standards and dilution of samples.

6.3.3 Spectrophotometer. To measure ultraviolet absorbance at 210 nm.

6.3.4 Analytical Balance. To measure to within 0.1 mg.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents are to conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 7, section 7.1. It is important that the amount of hydrogen peroxide in the absorbing solution not be increased. Higher concentrations of peroxide may interfere with sample analysis.

7.2 Sample Recovery. Same as Method 7, section 7.2.

7.3 Analysis. Same as Method 7, sections 7.3.1, 7.3.3, and 7.3.4, with the addition of the following:

7.3.1 Working Standard KNO_3 Solution. Dilute 10 ml of the standard solution to 1000 ml with water. One milliliter of the working standard is equivalent to 10 μg NO_2.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sample Collection. Same as Method 7, section 8.1.

8.2 Sample Recovery.

8.2.1 Let the flask sit for a minimum of 16 hours, and then shake the contents for 2 minutes.

8.2.2 Connect the flask to a mercury filled U-tube manometer. Open the valve from the flask to the manometer, and record the flask temperature (T_f), the barometric pressure, and the difference between the mercury levels in the manometer. The absolute internal pressure in the flask (P_f) is the barometric pressure less the manometer reading.

8.2.3 Transfer the contents of the flask to a leak-free wash bottle. Rinse the flask three times with 10-ml portions of water, and add

to the bottle. Mark the height of the liquid level so that the container can be checked for leakage after transport. Label the container to identify clearly its contents. Seal the container for shipping.

9.0 Quality Control

Section	Quality control measure	Effect
10.1	Spectrophotometer calibration	Ensures linearity of spectrophotometer response to standards.

10.0 Calibration and Standardizations

Same as Method 7, sections 10.2 through 10.5, with the addition of the following:

10.1 Determination of Spectrophotometer Standard Curve. Add 0 ml, 5 ml, 10 ml, 15 ml, and 20 ml of the KNO_3 working standard solution (1 ml = 10 µg NO_2) to a series of five 100-ml volumetric flasks. To each flask, add 5 ml of absorbing solution. Dilute to the mark with water. The resulting solutions contain 0.0, 50, 100, 150, and 200 µg NO_2, respectively. Measure the absorbance by ultraviolet spectrophotometry at 210 nm, using the blank as a zero reference. Prepare a standard curve plotting absorbance vs. µg NO_2.

NOTE: If other than a 20-ml aliquot of sample is used for analysis, then the amount of absorbing solution in the blank and standards must be adjusted such that the same amount of absorbing solution is in the blank and standards as is in the aliquot of sample used.

10.1.1 Calculate the spectrophotometer calibration factor as follows:

$$K_c = \frac{\sum_{i=1}^{n} M_i A_i}{\sum_{i=1}^{n} A_i^2} \qquad \text{Eq. 7B-1}$$

Where:

Mi = Mass of NO_2 in standard i, µg.
Ai = Absorbance of NO_2 standard i.
n = Total number of calibration standards.

10.1.2 For the set of calibration standards specified here, Equation 7B–1 simplifies to the following:

$$K_c = 50\frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2} \qquad \text{Eq. 7B-2}$$

10.2 Spectrophotometer Calibration Quality Control. Multiply the absorbance value obtained for each standard by the K_c factor (reciprocal of the least squares slope) to determine the distance each calibration point lies from the theoretical calibration line. The difference between the calculated concentration values and the actual concentrations (*i.e.*, 50, 100, 150, and 200 µg NO_2) should be less than 7 percent for all standards.

11.0 Analytical Procedures

11.1 Sample Loss Check. Note the level of the liquid in the container, and confirm whether any sample was lost during shipment. Note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Preparation. Immediately prior to analysis, transfer the contents of the shipping container to a 100-ml volumetric flask, and rinse the container twice with 5-ml portions of water. Add the rinse water to the flask, and dilute to mark with water.

11.3 Sample Analysis. Mix the contents of the flask thoroughly and pipette a 20 ml-aliquot of sample into a 100-ml volumetric flask. Dilute to the mark with water. Using the blank as zero reference, read the absorbance of the sample at 210 nm.

11.4 Audit Sample Analysis. Same as Method 7, section 11.4, except that a set of audit samples must be analyzed with each set of compliance samples or once per analysis day, or once per week when averaging continuous samples.

12.0 Data Analysis and Calculations

Same as Method 7, section 12.0, except replace section 12.3 with the following:

12.1 Total µg NO_2 Per Sample.

$$m = 5\,K_c\,A\,F \qquad \text{Eq. 7B-3}$$

Where:

5 = 100/20, the aliquot factor.

NOTE: If other than a 20-ml aliquot is used for analysis, the factor 5 must be replaced by a corresponding factor.

13.0 Method Performance

13.1 Range. The analytical range of the method as outlined has been determined to be 57 to 1500 milligrams NO_X (as NO_2) per dry standard cubic meter, or 30 to 786 parts per million by volume (ppmv) NO_X.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. National Institute for Occupational Safety and Health. Recommendations for Occupational Exposure to Nitric Acid. In: Occupational Safety and Health Reporter. Washington, D.C. Bureau of National Affairs, Inc. 1976. p. 149.

2. Rennie, P.J., A.M. Sumner, and F.B. Basketter. Determination of Nitrate in Raw, Potable, and Waste Waters by Ultraviolet Spectrophotometry. Analyst. *104*:837. September 1979.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 7C—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ALKALINE PERMANGANATE/COLORIMETRIC METHOD)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 3, Method 6 and Method 7.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS no.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–07	ppmv

1.2 Applicability. This method applies to the measurement of NO_X emissions from fossil-fuel fired steam generators, electric utility plants, nitric acid plants, or other sources as specified in the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

An integrated gas sample is extracted from the stack and passed through impingers containing an alkaline potassium permanganate solution; NO_X (NO + NO_2) emissions are oxidized to NO_2 and NO_3. Then NO_3^- is reduced to NO_2^- with cadmium, and the NO_2^- is analyzed colorimetrically.

3.0 Definitions [Reserved]

4.0 Interferences

Possible interferents are sulfur dioxides (SO_2) and ammonia (NH_3).

4.1 High concentrations of SO_2 could interfere because SO_2 consumes MnO_4 (as does NO_X) and, therefore, could reduce the NO_X collection efficiency. However, when sampling emissions from a coal-fired electric utility plant burning 2.1 percent sulfur coal with no control of SO_2 emissions, collection efficiency was not reduced. In fact, calculations show that sampling 3000 ppm SO_2 will reduce the MnO_4 concentration by only 5 percent if all the SO_2 is consumed in the first impinger.

4.2 Ammonia (NH_3) is slowly oxidized to NO_3^- by the absorbing solution. At 100 ppm NH_3 in the gas stream, an interference of 6 ppm NO_X (11 mg NO_2/m^3) was observed when the sample was analyzed 10 days after collection. Therefore, the method may not be applicable to plants using NH_3 injection to control NO_X emissions unless means are taken to correct the results. An equation has been developed to allow quantification of the interference and is discussed in Reference 5 of section 16.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrochloric Acid (HCl). Highly toxic and corrosive. Causes severe damage to skin. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to vapor concentrations of 0.13 to 0.2 percent can be lethal in minutes. Will react with metals, producing hydrogen.

5.2.2 Oxalic Acid $(COOH)_2$. Poisonous. Irritating to eyes, skin, nose, and throat.

5.2.3 Sodium Hydroxide (NaOH). Causes severe damage to eye tissues and to skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with small amounts of water.

5.2.4 Potassium Permanganate ($KMnO_4$). Caustic, strong oxidizer. Avoid bodily contact with.

6.0 Equipment and Supplies

6.1 Sample Collection and Sample Recovery. A schematic of the Method 7C sampling train is shown in Figure 7C–1, and component parts are discussed below. Alternative apparatus and procedures are allowed provided acceptable accuracy and precision can be demonstrated to the satisfaction of the Administrator.

6.1.1 Probe. Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or heated out-of-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Stainless steel or Teflon tubing may also be used for the probe.

6.1.2 Impingers. Three restricted-orifice glass impingers, having the specifications given in Figure 7C–2, are required for each sampling train. The impingers must be connected in series with leak-free glass connectors. Stopcock grease may be used, if necessary, to prevent leakage. (The impingers can be fabricated by a glass blower if not available commercially.)

6.1.3 Glass Wool, Stopcock Grease, Drying Tube, Valve, Pump, Barometer, and Vacuum Gauge and Rotameter. Same as in Method 6, sections 6.1.1.3, 6.1.1.4, 6.1.1.6, 6.1.1.7, 6.1.1.8, 6.1.2, and 6.1.3, respectively.

6.1.4 Rate Meter. Rotameter, or equivalent, accurate to within 2 percent at the selected flow rate of between 400 and 500 ml/min (0.014 to 0.018 cfm). For rotameters, a range of 0 to 1 liter/min (0 to 0.035 cfm) is recommended.

6.1.5 Volume Meter. Dry gas meter (DGM) capable of measuring the sample volume under the sampling conditions of 400 to 500 ml/min (0.014 to 0.018 cfm) for 60 minutes within an accuracy of 2 percent.

6.1.6 Filter. To remove NO_X from ambient air, prepared by adding 20 g of 5-angstrom molecular sieve to a cylindrical tube (*e.g.*, a polyethylene drying tube).

6.1.7 Polyethylene Bottles. 1-liter, for sample recovery.

6.1.8 Funnel and Stirring Rods. For sample recovery.

6.2 Sample Preparation and Analysis.

6.2.1 Hot Plate. Stirring type with 50- by 10-mm Teflon-coated stirring bars.

6.2.2 Beakers. 400-, 600-, and 1000-ml capacities.

6.2.3 Filtering Flask. 500-ml capacity with side arm.

6.2.4 Buchner Funnel. 75-mm ID, with spout equipped with a 13-mm ID by 90-mm long piece of Teflon tubing to minimize possibility of aspirating sample solution during filtration.

6.2.5 Filter Paper. Whatman GF/C, 7.0-cm diameter.

6.2.6 Stirring Rods.

6.2.7 Volumetric Flasks. 100-, 200- or 250-, 500-, and 1000-ml capacity.

6.2.8 Watch Glasses. To cover 600- and 1000-ml beakers.

6.2.9 Graduated Cylinders. 50- and 250-ml capacities.

6.2.10 Pipettes. Class A.

6.2.11 pH Meter. To measure pH from 0.5 to 12.0.

6.2.12 Burette. 50-ml with a micrometer type stopcock. (The stopcock is Catalog No. 8225–t–05, Ace Glass, Inc., Post Office Box 996, Louisville, Kentucky 50201.) Place a glass wool plug in bottom of burette. Cut off burette at a height of 43 cm (17 in.) from the top of plug, and have a blower attach a glass funnel to top of burette such that the diameter of the burette remains essentially unchanged. Other means of attaching the funnel are acceptable.

6.2.13 Glass Funnel. 75-mm ID at the top.

6.2.14 Spectrophotometer. Capable of measuring absorbance at 540 nm; 1-cm cells are adequate.

6.2.15 Metal Thermometers. Bimetallic thermometers, range 0 to 150 °C (32 to 300 °F).

6.2.16 Culture Tubes. 20-by 150-mm, Kimax No. 45048.

6.2.17 Parafilm ''M.'' Obtained from American Can Company, Greenwich, Connecticut 06830.

6.2.18 CO_2 Measurement Equipment. Same as in Method 3, section 6.0.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection.

7.1.1 Water. Deionized distilled to conform to ASTM Specification D 1193–77 or 91 Type 3 (incorporated by reference—see § 60.17).

7.1.2 Potassium Permanganate, 4.0 Percent (w/w), Sodium Hydroxide, 2.0 Percent (w/w) solution ($KMnO_4$/NaOH solution). Dissolve 40.0 g of $KMnO_4$ and 20.0 g of NaOH in 940 ml of water.

7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in section 7.1.1.

7.2.2 Oxalic Acid Solution. Dissolve 48 g of oxalic acid [$(COOH)_2 \cdot 2H_2O$] in water, and dilute to 500 ml. Do not heat the solution.

7.2.3 Sodium Hydroxide, 0.5 N. Dissolve 20 g of NaOH in water, and dilute to 1 liter.

7.2.4 Sodium Hydroxide, 10 N. Dissolve 40 g of NaOH in water, and dilute to 100 ml.

7.2.5 Ethylenediamine Tetraacetic Acid (EDTA) Solution, 6.5 percent (w/v). Dissolve 6.5 g of EDTA (disodium salt) in water, and dilute to 100 ml. Dissolution is best accomplished by using a magnetic stirrer.

7.2.6 Column Rinse Solution. Add 20 ml of 6.5 percent EDTA solution to 960 ml of water, and adjust the pH to between 11.7 and 12.0 with 0.5 N NaOH.

7.2.7 Hydrochloric Acid (HCl), 2 N. Add 86 ml of concentrated HCl to a 500 ml-volumetric flask containing water, dilute to volume, and mix well. Store in a glass-stoppered bottle.

7.2.8 Sulfanilamide Solution. Add 20 g of sulfanilamide (melting point 165 to 167 °C (329 to 333 °F)) to 700 ml of water. Add, with mixing, 50 ml concentrated phosphoric acid (85 percent), and dilute to 1000 ml. This solution is stable for at least 1 month, if refrigerated.

7.2.9 N-(1-Naphthyl)-Ethylenediamine Dihydrochloride (NEDA) Solution. Dissolve 0.5 g of NEDA in 500 ml of water. An aqueous solution should have one absorption peak at 320 nm over the range of 260 to 400 nm. NEDA that shows more than one absorption peak over this range is impure and should not be used. This solution is stable for at least 1 month if protected from light and refrigerated.

7.2.10 Cadmium. Obtained from Matheson Coleman and Bell, 2909 Highland Avenue, Norwood, Ohio 45212, as EM Laboratories Catalog No. 2001. Prepare by rinsing in 2 N HCl for 5 minutes until the color is silver-grey. Then rinse the cadmium with water until the rinsings are neutral when tested with pH paper. CAUTION: H_2 is liberated during preparation. Prepare in an exhaust hood away from any flame or combustion source.

7.2.11 Sodium Sulfite ($NaNO_2$) Standard Solution, Nominal Concentration, 1000 μg NO_2^-/ml. Desiccate NaNO2 overnight. Accurately weigh 1.4 to 1.6 g of $NaNO_2$ (assay of 97 percent $NaNO_2$ or greater), dissolve in water, and dilute to 1 liter. Calculate the exact NO_2^- concentration using Equation 7C–1 in section 12.2. This solution is stable for at least 6 months under laboratory conditions.

7.2.12 Potassium Nitrate (KNO_3) Standard Solution. Dry KNO_3 at 110 °C (230 °F) for 2 hours, and cool in a desiccator. Accurately weigh 9 to 10 g of KNO_3 to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact NO_3^- concentration using Equation 7C–2 in section 12.3. This solution is stable for 2 months without preservative under laboratory conditions.

7.2.13 Spiking Solution. Pipette 7 ml of the KNO_3 standard into a 100-ml volumetric flask, and dilute to volume.

7.2.14 Blank Solution. Dissolve 2.4 g of $KMnO_4$ and 1.2 g of NaOH in 96 ml of water. Alternatively, dilute 60 ml of $KMnO_4$/NaOH solution to 100 ml.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Preparation of Sampling Train. Add 200 ml of $KMnO_4$/NaOH solution (Section 7.1.2) to each of three impingers, and assemble the train as shown in Figure 7C–1. Adjust the probe heater to a temperature sufficient to prevent water condensation.

8.2 Leak-Checks. Same as in Method 6, section 8.2.

8.3 Sample Collection.

8.3.1 Record the initial DGM reading and barometric pressure. Determine the sampling point or points according to the appropriate regulations (*e.g.*, §60.46(b)(5) of 40 CFR Part 60). Position the tip of the probe at the sampling point, connect the probe to the first impinger, and start the pump. Adjust the sample flow to a value between 400 and 500 ml/min (0.014 and 0.018 cfm). CAUTION: DO NOT EXCEED THESE FLOW RATES. Once adjusted, maintain a constant flow rate during the entire sampling run. Sample for 60 minutes. For relative accuracy (RA) testing of continuous emission monitors, the minimum sampling time is 1 hour, sampling 20 minutes at each traverse point.

NOTE: When the SO_2 concentration is greater than 1200 ppm, the sampling time may have to be reduced to 30 minutes to eliminate plugging of the impinger orifice with MnO_2. For RA tests with SO_2 greater than 1200 ppm, sample for 30 minutes (10 minutes at each point).

8.3.2 Record the DGM temperature, and check the flow rate at least every 5 minutes. At the conclusion of each run, turn off the pump, remove the probe from the stack, and record the final readings. Divide the sample volume by the sampling time to determine the average flow rate. Conduct the mandatory post-test leak-check. If a leak is found, void the test run, or use procedures acceptable to the Administrator to adjust the sample volume for the leakage.

8.4 CO_2 Measurement. During sampling, measure the CO_2 content of the stack gas near the sampling point using Method 3. The single-point grab sampling procedure is adequate, provided the measurements are made at least three times (near the start, midway, and before the end of a run), and the average CO_2 concentration is computed. The Orsat or Fyrite analyzer may be used for this analysis.

8.5 Sample Recovery. Disconnect the impingers. Pour the contents of the impingers into a 1-liter polyethylene bottle

using a funnel and a stirring rod (or other means) to prevent spillage. Complete the quantitative transfer by rinsing the impingers and connecting tubes with water until the rinsings are clear to light pink, and add the rinsings to the bottle. Mix the sample, and mark the solution level. Seal and identify the sample container.

9.0 Quality Control

Section	Quality control measure	Effect
8.2, 10.1–10.3	Sampling equipment leak-check and calibration.	Ensure accurate measurement of sample volume.
10.4	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards
11.3	Spiked sample analysis.	Ensure reduction efficiency of column.

10.0 Calibration and Standardizations

10.1 Volume Metering System. Same as Method 6, section 10.1. For detailed instructions on carrying out these calibrations, it is suggested that section 3.5.2 of Reference 4 of section 16.0 be consulted.

10.2 Temperature Sensors and Barometer. Same as in Method 6, sections 10.2 and 10.4, respectively.

10.3 Check of Rate Meter Calibration Accuracy (Optional). Disconnect the probe from the first impinger, and connect the filter. Start the pump, and adjust the rate meter to read between 400 and 500 ml/min (0.014 and 0.018 cfm). After the flow rate has stabilized, start measuring the volume sampled, as recorded by the dry gas meter and the sampling time. Collect enough volume to measure accurately the flow rate. Then calculate the flow rate. This average flow rate must be less than 500 ml/min (0.018 cfm) for the sample to be valid; therefore, it is recommended that the flow rate be checked as above prior to each test.

10.4 Spectrophotometer.

10.4.1 Dilute 5.0 ml of the $NaNO_2$ standard solution to 200 ml with water. This solution nominally contains 25 μg NO_2^-/ml. Use this solution to prepare calibration standards to cover the range of 0.25 to 3.00 μg NO_2^-/ml. Prepare a minimum of three standards each for the linear and slightly nonlinear (described below) range of the curve. Use pipettes for all additions.

10.4.2 Measure the absorbance of the standards and a water blank as instructed in section 11.5. Plot the net absorbance vs. μg NO_2^-/ml. Draw a smooth curve through the points. The curve should be linear up to an absorbance of approximately 1.2 with a slope of approximately 0.53 absorbance units/μg NO_2^-/ml. The curve should pass through the origin. The curve is slightly nonlinear from an absorbance of 1.2 to 1.6.

11.0 Analytical Procedures

11.1 Sample Stability. Collected samples are stable for at least four weeks; thus, analysis must occur within 4 weeks of collection.

11.2 Sample Preparation.

11.2.1 Prepare a cadmium reduction column as follows: Fill the burette with water. Add freshly prepared cadmium slowly, with tapping, until no further settling occurs. The height of the cadmium column should be 39 cm (15 in). When not in use, store the column under rinse solution.

NOTE: The column should not contain any bands of cadmium fines. This may occur if regenerated cadmium is used and will greatly reduce the column lifetime.

11.2.2 Note the level of liquid in the sample container, and determine whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume lost can be determined from the difference between initial and final solution levels, and this value can then be used to correct the analytical result. Quantitatively transfer the contents to a 1-liter volumetric flask, and dilute to volume.

11.2.3 Take a 100-ml aliquot of the sample and blank (unexposed $KMnO_4$/NaOH) solutions, and transfer to 400-ml beakers containing magnetic stirring bars. Using a pH meter, add concentrated H_2SO_4 with stirring until a pH of 0.7 is obtained. Allow the solutions to stand for 15 minutes. Cover the beakers with watch glasses, and bring the temperature of the solutions to 50 °C (122 °F). Keep the temperature below 60 °C (140 °F). Dissolve 4.8 g of oxalic acid in a minimum volume of water, approximately 50 ml, at room temperature. Do not heat the solution. Add this solution slowly, in increments, until the $KMnO_4$ solution becomes colorless. If the color is not completely removed, prepare some more of the above oxalic acid solution, and add until a colorless solution is obtained. Add an excess of oxalic acid by dissolving 1.6 g of oxalic acid in 50 ml of water, and add 6 ml of this solution to the colorless solution. If suspended matter is present, add concentrated H_2SO_4 until a clear solution is obtained.

11.2.4 Allow the samples to cool to near room temperature, being sure that the samples are still clear. Adjust the pH to between 11.7 and 12.0 with 10 N NaOH. Quantitatively transfer the mixture to a Buchner funnel containing GF/C filter paper, and filter the

precipitate. Filter the mixture into a 500-ml filtering flask. Wash the solid material four times with water. When filtration is complete, wash the Teflon tubing, quantitatively transfer the filtrate to a 500-ml volumetric flask, and dilute to volume. The samples are now ready for cadmium reduction. Pipette a 50-ml aliquot of the sample into a 150-ml beaker, and add a magnetic stirring bar. Pipette in 1.0 ml of 6.5 percent EDTA solution, and mix.

11.3 Determine the correct stopcock setting to establish a flow rate of 7 to 9 ml/min of column rinse solution through the cadmium reduction column. Use a 50-ml graduated cylinder to collect and measure the solution volume. After the last of the rinse solution has passed from the funnel into the burette, but before air entrapment can occur, start adding the sample, and collect it in a 250-ml graduated cylinder. Complete the quantitative transfer of the sample to the column as the sample passes through the column. After the last of the sample has passed from the funnel into the burette, start adding 60 ml of column rinse solution, and collect the rinse solution until the solution just disappears from the funnel. Quantitatively transfer the sample to a 200-ml volumetric flask (a 250-ml flask may be required), and dilute to volume. The samples are now ready for NO_2-analysis.

NOTE: Two spiked samples should be run with every group of samples passed through the column. To do this, prepare two additional 50-ml aliquots of the sample suspected to have the highest NO_2-concentration, and add 1 ml of the spiking solution to these aliquots. If the spike recovery or column efficiency (see section 12.2) is below 95 percent, prepare a new column, and repeat the cadmium reduction.

11.5 Sample Analysis. Pipette 10 ml of sample into a culture tube. Pipette in 10 ml of sulfanilamide solution and 1.4 ml of NEDA solution. Cover the culture tube with parafilm, and mix the solution. Prepare a blank in the same manner using the sample from treatment of the unexposed $KMnO_4$/NaOH solution. Also, prepare a calibration standard to check the slope of the calibration curve. After a 10-minute color development interval, measure the absorbance at 540 nm against water. Read μg NO_2^-/ml from the calibration curve. If the absorbance is greater than that of the highest calibration standard, use less than 10 ml of sample, and repeat the analysis. Determine the NO_2^-concentration using the calibration curve obtained in section 10.4.

NOTE: Some test tubes give a high blank NO_2^- value but culture tubes do not.

11.6 Audit Sample Analysis. Same as in Method 7, section 11.4.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature.

B = Analysis of blank, μg NO_2^-/ml.
C = Concentration of NO_X as NO_2, dry basis, mg/dsm³.
E = Column efficiency, dimensionless
$K_2 = 10^{-3}$ mg/μg.
m = Mass of NO_X, as NO_2, in sample, μg.
P_{bar} = Barometric pressure, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
s = Concentration of spiking solution, μg NO_3/ml.
S = Analysis of sample, μg NO_2^-/ml.
T_m = Average dry gas meter absolute temperature, °K.
T_{std} = Standard absolute temperature, 293 °K (528 °R).
$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).
V_m = Dry gas volume as measured by the dry gas meter, scm (scf).
x = Analysis of spiked sample, μg NO_2^-/ml.
X = Correction factor for CO_2 collection = $100/(100 - \%CO_2(V/V))$.
y = Analysis of unspiked sample, μg NO_2^-/ml.
Y = Dry gas meter calibration factor.
1.0 ppm NO = 1.247 mg NO/m³ at STP.
1.0 ppm NO_2 = 1.912 mg NO_2/m³ at STP.
1 ft³ = 2.832×10^{-2} m³.

12.2 NO_2 Concentration. Calculate the NO_2 concentration of the solution (see section 7.2.11) using the following equation:

$$\frac{\mu g\ NO_2^-}{ml} = g\ NaNO_2 \times \frac{purity,\ \%}{100} \times 10^3 \times \frac{46.01}{69.01} \qquad \text{Eq. 7C-1}$$

12.3 NO_3 Concentration. Calculate the NO_3 concentration of the KNO_3 solution (see section 7.2.12) using the following equation:

$$\frac{\mu g\ NO_3^-}{ml} = g\ KNO_3 \times \left(10^3\right) \times \frac{62.01}{101.10} \qquad \text{Eq. 7C-2}$$

12.4 Sample Volume, Dry Basis, Corrected to Standard Conditions.

$$V_{m(std)} = V_m\ X\ Y \frac{T_{std}}{T_m} \frac{P_{bar}}{P_{std}} \qquad \text{Eq. 7C-3}$$

$$= K_1\ X\ Y\ V_m \frac{P_{bar}}{T_m}$$

Where:

K_1 = 0.3855 °K/mm Hg for metric units.
K_1 = 17.65 °R/in. Hg for English units.

12.5 Efficiency of Cadmium Reduction Column. Calculate this value as follows:

$$E = \frac{200\ (x-y)}{1.0\ s\ \frac{46.01}{62.01}} = \frac{269.6\ (x-y)}{s} \qquad \text{Eq. 7C-4}$$

Where:

200 = Final volume of sample and blank after passing through the column, ml.
1.0 = Volume of spiking solution added, ml.
46.01=μg NO_2^-/μmole.
62.01=μg NO_3^-/μmole.

12.6 Total μg NO_2.

$$m = 200\left(\frac{500}{50}\right)\left(\frac{1000}{100}\right)\left(\frac{(S-B)}{E}\right) = \frac{(2\times10^4)(S-B)}{E} \qquad \text{Eq. 7C-5}$$

Where:

500 = Total volume of prepared sample, ml.
50 = Aliquot of prepared sample processed through cadmium column, ml.
100 = Aliquot of $KMnO_4$/NaOH solution, ml.
1000 = Total volume of $KMnO_4$/NaOH solution, ml.

12.7 Sample Concentration.

$$C = K_2 \frac{m}{V_{m(std)}} \qquad \text{Eq. 7C-6}$$

13.0 Method Performance

13.1 Precision. The intra-laboratory relative standard deviation for a single measurement is 2.8 and 2.9 percent at 201 and 268 ppm NO_X, respectively.

13.2 Bias. The method does not exhibit any bias relative to Method 7.

13.3 Range. The lower detectable limit is 13 mg NO_X/m^3, as NO_2 (7 ppm NO_X) when sampling at 500 ml/min for 1 hour. No upper limit has been established; however, when using the recommended sampling conditions, the method has been found to collect NO_X emissions quantitatively up to 1782 mg NO_X/m^3, as NO_2 (932 ppm NO_X).

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Margeson, J.H., W.J. Mitchell, J.C. Suggs, and M.R. Midgett. Integrated Sampling and Analysis Methods for Determining NO_X Emissions at Electric Utility Plants. U.S. Environmental Protection Agency, Research Triangle Park, NC. Journal of the Air Pollution Control Association. *32*:1210–1215. 1982.

2. Memorandum and attachment from J.H. Margeson, Source Branch, Quality Assurance Division, Environmental Monitoring Systems Laboratory, to The Record, EPA. March 30, 1983. NH_3 Interference in Methods 7C and 7D.

3. Margeson, J.H., J.C. Suggs, and M.R. Midgett. Reduction of Nitrate to Nitrite with Cadmium. Anal. Chem. *52*:1955–57. 1980.

4. Quality Assurance Handbook for Air Pollution Measurement Systems. Volume III—Stationary Source Specific Methods. U.S.

Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA–600/4–77–027b. August 1977.

5. Margeson, J.H., *et al.* An Integrated Method for Determining NO_X Emissions at Nitric Acid Plants. Analytical Chemistry. *47* (11):1801. 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

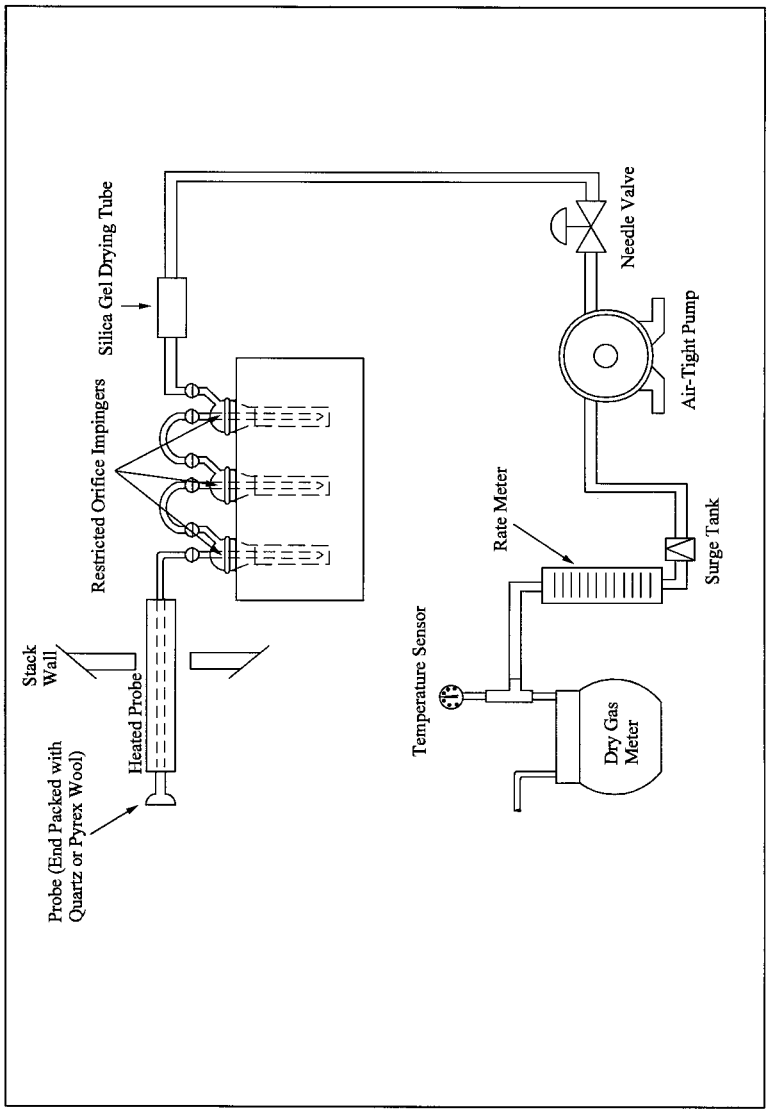

Figure 7C-1. NO_x Sampling Train.

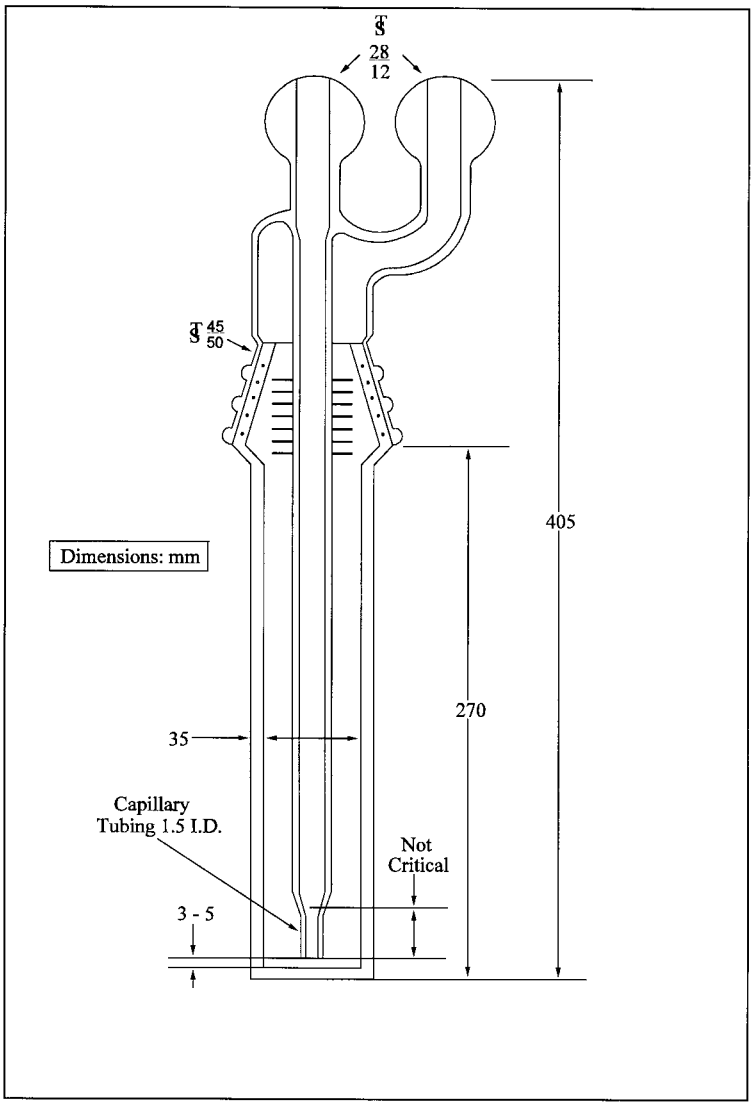

Figure 7C-2. Restricted-Orifice Impinger.

METHOD 7D—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ALKALINE-PERMANGANATE/ION CHROMATOGRAPHIC METHOD)

NOTE: This method is not inclusive with respect to specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 3, Method 6, Method 7, and Method 7C.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–0	7 ppmv

1.2 Applicability. This method applies to the measurement of NO_X emissions from fossil-fuel fired steam generators, electric utility plants, nitric acid plants, or other sources as specified in the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

An integrated gas sample is extracted from the stack and passed through impingers containing an alkaline-potassium permanganate solution; NO_X ($NO + NO_2$) emissions are oxidized to NO_3^-. Then NO_3^- is analyzed by ion chromatography.

3.0 Definitions [Reserved]

4.0 Interferences

Same as in Method 7C, section 4.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs. 30% H_2O_2 is a strong oxidizing agent; avoid contact with skin, eyes, and combustible material. Wear gloves when handling.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eye tissues and to skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Potassium Permanganate ($KMnO_4$). Caustic, strong oxidizer. Avoid bodily contact with.

6.0 Equipment and Supplies

6.1 Sample Collection and Sample Recovery. Same as Method 7C, section 6.1. A schematic of the sampling train used in performing this method is shown in Figure 7C–1 of Method 7C.

6.2 Sample Preparation and Analysis.

6.2.1 Magnetic Stirrer. With 25- by 10-mm Teflon-coated stirring bars.

6.2.2 Filtering Flask. 500-ml capacity with sidearm.

6.2.3 Buchner Funnel. 75-mm ID, with spout equipped with a 13-mm ID by 90-mm long piece of Teflon tubing to minimize possibility of aspirating sample solution during filtration.

6.2.4 Filter Paper. Whatman GF/C, 7.0-cm diameter.

6.2.5 Stirring Rods.

6.2.6 Volumetric Flask. 250-ml.

6.2.7 Pipettes. Class A.

6.2.8 Erlenmeyer Flasks. 250-ml.

6.2.9 Ion Chromatograph. Equipped with an anion separator column to separate NO_3^-, H_3^+ suppressor, and necessary auxiliary equipment. Nonsuppressed and other forms of ion chromatography may also be used provided that adequate resolution of NO_3^- is obtained. The system must also be able to resolve and detect NO_2^-.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection.

7.1.1 Water. Deionized distilled to conform to ASTM specification D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17).

7.1.2 Potassium Permanganate, 4.0 Percent (w/w), Sodium Hydroxide, 2.0 Percent (w/w). Dissolve 40.0 g of $KMnO_4$ and 20.0 g of NaOH in 940 ml of water.

7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in section 7.1.1.

7.2.2 Hydrogen Peroxide (H_2O_2), 5 Percent. Dilute 30 percent H_2O_2 1:5 (v/v) with water.

7.2.3 Blank Solution. Dissolve 2.4 g of $KMnO_4$ and 1.2 g of NaOH in 96 ml of water. Alternatively, dilute 60 ml of $KMnO_4$/NaOH solution to 100 ml.

7.2.4 KNO_3 Standard Solution. Dry KNO_3 at 110 °C for 2 hours, and cool in a desiccator. Accurately weigh 9 to 10 g of KNO_3 to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact NO_3^- concentration using Equation 7D–1 in section 12.2. This

solution is stable for 2 months without preservative under laboratory conditions.

7.2.5 Eluent, 0.003 M $NaHCO_3$/0.0024 M Na_2CO_3. Dissolve 1.008 g $NaHCO_3$ and 1.018 g Na_2CO_3 in water, and dilute to 4 liters. Other eluents capable of resolving nitrate ion from sulfate and other species present may be used.

8.0 Sample Collection, Preservation, Transport, and Storage.

8.1 Sampling. Same as in Method 7C, section 8.1.

8.2 Sample Recovery. Same as in Method 7C, section 8.2.

8.3 Sample Preparation for Analysis.

NOTE: Samples must be analyzed within 28 days of collection.

8.3.1 Note the level of liquid in the sample container, and determine whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume lost can be determined from the difference between initial and final solution levels, and this value can then be used to correct the analytical result. Quantitatively transfer the contents to a 1-liter volumetric flask, and dilute to volume.

8.3.2 Sample preparation can be started 36 hours after collection. This time is necessary to ensure that all NO_2^- is converted to NO_3^- in the collection solution. Take a 50-ml aliquot of the sample and blank, and transfer to 250-ml Erlenmeyer flasks. Add a magnetic stirring bar. Adjust the stirring rate to as fast a rate as possible without loss of solution. Add 5 percent H_2O_2 in increments of approximately 5 ml using a 5-ml pipette. When the $KMnO_4$ color appears to have been removed, allow the precipitate to settle, and examine the supernatant liquid. If the liquid is clear, the H_2O_2 addition is complete. If the $KMnO_4$ color persists, add more H_2O_2, with stirring, until the supernatant liquid is clear.

NOTE: The faster the stirring rate, the less volume of H_2O_2 that will be required to remove the $KMnO_4$.) Quantitatively transfer the mixture to a Buchner funnel containing GF/C filter paper, and filter the precipitate. The spout of the Buchner funnel should be equipped with a 13-mm ID by 90-mm long piece of Teflon tubing. This modification minimizes the possibility of aspirating sample solution during filtration. Filter the mixture into a 500-ml filtering flask. Wash the solid material four times with water. When filtration is complete, wash the Teflon tubing, quantitatively transfer the filtrate to a 250-ml volumetric flask, and dilute to volume. The sample and blank are now ready for NO_3^- analysis.

9.0 Quality Control

Section	Quality control measure	Effect
8.2, 10.1–10.3	Sampling equipment leak-check and calibration.	Ensure accurate measurement of sample volume.
10.4	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.
11.3	Spiked sample analysis	Ensure reduction efficiency of column.

10.0 Calibration and Standardizations

10.1 Dry Gas Meter (DGM) System.

10.1.1 Initial Calibration. Same as in Method 6, section 10.1.1. For detailed instructions on carrying out this calibration, it is suggested that section 3.5.2 of Citation 4 in section 16.0 of Method 7C be consulted.

10.1.2 Post-Test Calibration Check. Same as in Method 6, section 10.1.2.

10.2 Thermometers for DGM and Barometer. Same as in Method 6, sections 10.2 and 10.4, respectively.

10.3 Ion Chromatograph.

10.3.1 Dilute a given volume (1.0 ml or greater) of the KNO_3 standard solution to a convenient volume with water, and use this solution to prepare calibration standards. Prepare at least four standards to cover the range of the samples being analyzed. Use pipettes for all additions. Run standards as instructed in section 11.2. Determine peak height or area, and plot the individual values versus concentration in µg NO_3^-/ml.

10.3.2 Do not force the curve through zero. Draw a smooth curve through the points. The curve should be linear. With the linear curve, use linear regression to determine the calibration equation.

11.0 Analytical Procedures

11.1 The following chromatographic conditions are recommended: 0.003 M $NaHCO_3$/0.0024 Na_2CO_3 eluent solution (Section 7.2.5), full scale range, 3 µMHO; sample loop, 0.5 ml; flow rate, 2.5 ml/min. These conditions should give a NO_3^- retention time of approximately 15 minutes (Figure 7D–1).

11.2 Establish a stable baseline. Inject a sample of water, and determine whether any NO_3^- appears in the chromatogram. If NO_3^- is present, repeat the water load/injection procedure approximately five times; then reinject a water sample and observe the chromatogram. When no NO_3^- is present, the instrument is ready for use. Inject calibration standards. Then inject samples and a blank. Repeat the injection of the calibration

standards (to compensate for any drift in response of the instrument). Measure the NO_3^- peak height or peak area, and determine the sample concentration from the calibration curve.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature. Same as in Method 7C, section 12.1.

12.2 NO_3^- concentration. Calculate the NO_3^- concentration in the KNO_3 standard solution (see section 7.2.4) using the following equation:

$$\frac{\mu g\ NO_3^-}{ml} = g\ of\ KNO_3 \times 10^3 \times \frac{62.01}{101.10} \qquad \text{Eq. 7D-1}$$

12.3 Sample Volume, Dry Basis, Corrected to Standard Conditions. Same as in Method 7C, section 12.4.

12.4 Total μg NO_2 Per Sample.

$$m = 250\left(\frac{1000}{50}\right)\left(\frac{46.01}{62.01}\right)(S-B) \qquad \text{Eq. 7D-2}$$
$$= 3710\ (S-B)$$

Where:

250 = Volume of prepared sample, ml.

1000 = Total volume of $KMnO_4$ solution, ml.

50 = Aliquot of $KMnO_4$/NaOH solution, ml.

46.01 = Molecular weight of NO_3^-.

62.01 = Molecular weight of NO_3^-.

12.5 Sample Concentration. Same as in Method 7C, section 12.7.

13.0 Method Performance

13.1 Precision. The intra-laboratory relative standard deviation for a single measurement is approximately 6 percent at 200 to 270 ppm NO_X.

13.2 Bias. The method does not exhibit any bias relative to Method 7.

13.3 Range. The lower detectable limit is similar to that of Method 7C. No upper limit has been established; however, when using the recommended sampling conditions, the method has been found to collect NO_X emissions quantitatively up to 1782 mg NO_X/m^3, as NO_2 (932 ppm NO_X).

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 7C, section 16.0, References 1, 2, 4, and 5.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

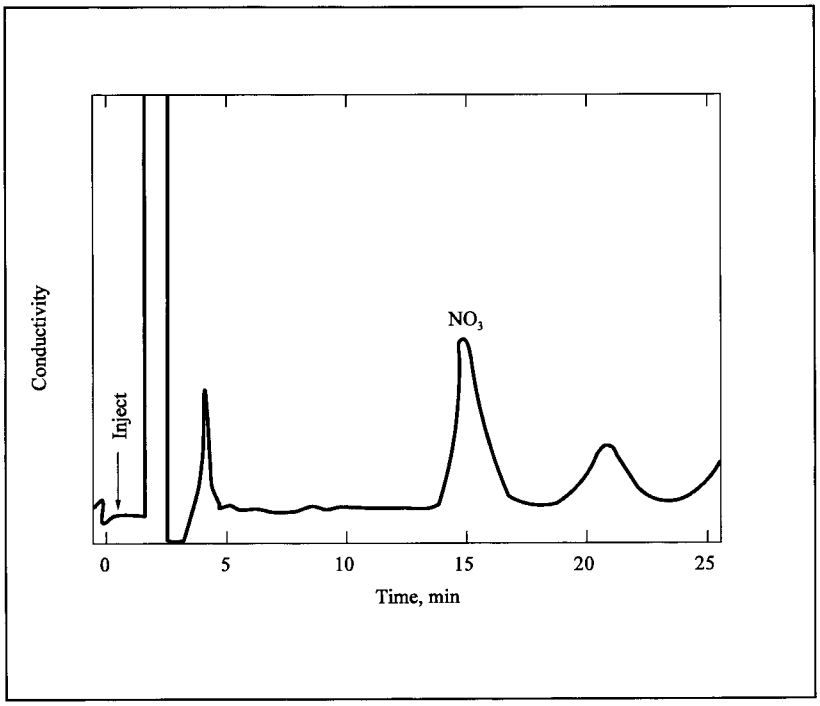

Figure 7D-1. Ion Chromatograph of a Prepared Sample.

METHOD 7E—DETERMINATION OF NITROGEN OXIDES EMISSIONS FROM STATIONARY SOURCES (INSTRUMENTAL ANALYZER PROCEDURE)

1.0 Scope and Application

What is Method 7E?

Method 7E is a procedure for measuring nitrogen oxides (NO_X) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis. This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 4—Determination of Moisture Content in Stack Gases.

1.1 Analytes. What does this method determine? This method measures the concentration of nitrogen oxides as NO_2.

Analyte	CAS No.	Sensitivity
Nitric oxide (NO)	10102–43–9	Typically <2% of
Nitrogen dioxide (NO_2)	10102–44–0	Calibration Span.

1.2 Applicability. When is this method required? The use of Method 7E may be required by specific New Source Performance Standards, Clean Air Marketing rules, State Implementation Plans, and permits where measurement of NO_X concentrations in stationary source emissions is required, either to determine compliance with an applicable

emissions standard or to conduct performance testing of a continuous monitoring system (CEMS). Other regulations may also require the use of Method 7E.

1.3 Data Quality Objectives (DQO). How good must my collected data be? Method 7E is designed to provide high-quality data for determining compliance with Federal and State emission standards and for relative accuracy testing of CEMS. In these and other applications, the principal objective is to ensure the accuracy of the data at the actual emission levels encountered. To meet this objective, the use of EPA traceability protocol calibration gases and measurement system performance tests are required.

1.4 Data Quality Assessment for Low Emitters. Is performance relief granted when testing low-emission units? Yes. For low-emitting sources, there are alternative performance specifications for analyzer calibration error, system bias, drift, and response time. Also, the alternative dynamic spiking procedure in section 16 may provide performance relief for certain low-emitting units.

2.0 Summary of Method

In this method, a sample of the effluent gas is continuously sampled and conveyed to the analyzer for measuring the concentration of NO_X. You may measure NO and NO_2 separately or simultaneously together but, for the purposes of this method, NO_X is the sum of NO and NO_2. You must meet the performance requirements of this method to validate your data.

3.0 Definitions

3.1 Analyzer Calibration Error, for non-dilution systems, means the difference between the manufacturer certified concentration of a calibration gas and the measured concentration of the same gas when it is introduced into the analyzer in direct calibration mode.

3.2 Calibration Curve means the relationship between an analyzer's response to the injection of a series of calibration gases and the actual concentrations of those gases.

3.3 Calibration Gas means the gas mixture containing NO_X at a known concentration and produced and certified in accordance with ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards,'' September 1997, as amended August 25, 1999, EPA–600/R–97/121 or more recent updates. The tests for analyzer calibration error, drift, and system bias require the use of calibration gas prepared according to this protocol. If a zero gas is used for the low-level gas, it must meet the requirements under the definition for ''zero air material'' in 40 CFR 72.2 in place of being prepared by the traceability protocol.

3.3.1 Low-Level Gas means a calibration gas with a concentration that is less than 20 percent of the calibration span and may be a zero gas.

3.3.2 Mid-Level Gas means a calibration gas with a concentration that is 40 to 60 percent of the calibration span.

3.3.3 High-Level Gas means a calibration gas with a concentration that is equal to the calibration span.

3.4 Calibration Span means the upper limit of the analyzer's calibration that is set by the choice of high-level calibration gas. No valid run average concentration may exceed the calibration span. To the extent practicable, the measured emissions should be between 20 to 100 percent of the selected calibration span. This may not be practicable in some cases of low-concentration measurements or testing for compliance with an emission limit when emissions are substantially less than the limit. In such cases, calibration spans that are practicable to achieving the data quality objectives without being excessively high should be chosen.

3.5 Centroidal Area means the central area of the stack or duct that is no greater than 1 percent of the stack or duct cross section. This area has the same geometric shape as the stack or duct.

3.6 Converter Efficiency Gas means a calibration gas with a known NO or NO_2 concentration and of Traceability Protocol quality.

3.7 Data Recorder means the equipment that permanently records the concentrations reported by the analyzer.

3.8 Direct Calibration Mode means introducing the calibration gases directly into the analyzer (or into the assembled measurement system at a point downstream of all sample conditioning equipment) according to manufacturer's recommended calibration procedure. This mode of calibration applies to non-dilution-type measurement systems.

3.9 Drift means the difference between the pre- and post-run system bias (or system calibration error) checks at a specific calibration gas concentration level (*i.e.* low-, mid- or high-).

3.10 Gas Analyzer means the equipment that senses the gas being measured and generates an output proportional to its concentration.

3.11 Interference Check means the test to detect analyzer responses to compounds other than the compound of interest, usually a gas present in the measured gas stream, that is not adequately accounted for in the calibration procedure and may cause measurement bias.

3.12 Low-Concentration Analyzer means any analyzer that operates with a calibration span of 20 ppm NO_X or lower. Each analyzer model used routinely to measure low NO_X concentrations must pass a manufacturer's stability test (MST). An MST subjects the analyzer to a range of line voltages and temperatures that reflect potential field conditions to demonstrate its stability following

procedures similar to those provided in 40 CFR 53.23. Ambient-level analyzers are exempt from the MST requirements of section 16.3. A copy of this information must be included in each test report. Table 7E–5 lists the criteria to be met.

3.13 Measurement System means all of the equipment used to determine the NO_x concentration. The measurement system comprises six major subsystems: Sample acquisition, sample transport, sample conditioning, calibration gas manifold, gas analyzer, and data recorder.

3.14 Response Time means the time it takes the measurement system to respond to a change in gas concentration occurring at the sampling point when the system is operating normally at its target sample flow rate or dilution ratio.

3.15 Run means a series of gas samples taken successively from the stack or duct. A test normally consists of a specific number of runs.

3.16 System Bias means the difference between a calibration gas measured in direct calibration mode and in system calibration mode. System bias is determined before and after each run at the low- and mid- or high-concentration levels. For dilution-type systems, pre- and post-run system calibration error is measured rather than system bias.

3.17 System Calibration Error applies to dilution-type systems and means the difference between the measured concentration of low-, mid-, or high-level calibration gas and the certified concentration for each gas when introduced in system calibration mode. For dilution-type systems, a 3-point system calibration error test is conducted in lieu of the analyzer calibration error test, and 2-point system calibration error tests are conducted in lieu of system bias tests.

3.18 System Calibration Mode means introducing the calibration gases into the measurement system at the probe, upstream of the filter and all sample conditioning components.

3.19 Test refers to the series of runs required by the applicable regulation.

4.0 Interferences

Note that interferences may vary among instruments and that instrument-specific interferences must be evaluated through the interference test.

5.0 Safety

What safety measures should I consider when using this method? This method may require you to work with hazardous materials and in hazardous conditions. We encourage you to establish safety procedures before using the method. Among other precautions, you should become familiar with the safety recommendations in the gas analyzer user's manual. Occupational Safety and Health Administration (OSHA) regulations concerning cylinder and noxious gases may apply. Nitric oxide and NO_2 are toxic and dangerous gases. Nitric oxide is immediately converted to NO_2 upon reaction with air. Nitrogen dioxide is a highly poisonous and insidious gas. Inflammation of the lungs from exposure may cause only slight pain or pass unnoticed, but the resulting edema several days later may cause death. A concentration of 100 ppm is dangerous for even a short exposure, and 200 ppm may be fatal. Calibration gases must be handled with utmost care and with adequate ventilation. Emission-level exposure to these gases should be avoided.

6.0 Equipment and Supplies

The performance criteria in this method will be met or exceeded if you are properly using equipment designed for this application.

6.1 What do I need for the measurement system? You may use any equipment and supplies meeting the following specifications:

(1) Sampling system components that are not evaluated in the system bias or system calibration error test must be glass, Teflon, or stainless steel. Other materials are potentially acceptable, subject to approval by the Administrator.

(2) The interference, calibration error, and system bias criteria must be met.

(3) Sample flow rate must be maintained within 10 percent of the flow rate at which the system response time was measured.

(4) All system components (excluding sample conditioning components, if used) must maintain the sample temperature above the moisture dew point. Ensure minimal contact between any condensate and the sample gas. Section 6.2 provides example equipment specifications for a NO_x measurement system. Figure 7E–1 is a diagram of an example dry-basis measurement system that is likely to meet the method requirements and is provided as guidance. For wet-basis systems, you may use alternative equipment and supplies as needed (some of which are described in Section 6.2), provided that the measurement system meets the applicable performance specifications of this method.

6.2 Measurement System Components

6.2.1 Sample Probe. Glass, stainless steel, or other approved material, of sufficient length to traverse the sample points.

6.2.2 Particulate Filter. An in-stack or out-of-stack filter. The filter must be made of material that is non-reactive to the gas being sampled. The filter media for out-of-stack filters must be included in the system bias test. The particulate filter requirement may be waived in applications where no significant particulate matter is expected (*e.g.*, for emission testing of a combustion turbine firing natural gas).

6.2.3 Sample Line. The sample line from the probe to the conditioning system/sample pump should be made of Teflon or other material that does not absorb or otherwise alter the sample gas. For a dry-basis measurement system (as shown in Figure 7E–1), the temperature of the sample line must be maintained at a sufficiently high level to prevent condensation before the sample conditioning components. For wet-basis measurement systems, the temperature of the sample line must be maintained at a sufficiently high level to prevent condensation before the analyzer.

6.2.4 Conditioning Equipment. For dry basis measurements, a condenser, dryer or other suitable device is required to remove moisture continuously from the sample gas. Any equipment needed to heat the probe or sample line to avoid condensation prior to the sample conditioning component is also required.

For wet basis systems, you must keep the sample above its dew point either by: (1) Heating the sample line and all sample transport components up to the inlet of the analyzer (and, for hot-wet extractive systems, also heating the analyzer) or (2) by diluting the sample prior to analysis using a dilution probe system. The components required to do either of the above are considered to be conditioning equipment.

6.2.5 Sampling Pump. For systems similar to the one shown in Figure 7E–1, a leak-free pump is needed to pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system. The pump may be constructed of any material that is non-reactive to the gas being sampled. For dilution-type measurement systems, an ejector pump (eductor) is used to create a vacuum that draws the sample through a critical orifice at a constant rate.

6.2.6 Calibration Gas Manifold. Prepare a system to allow the introduction of calibration gases either directly to the gas analyzer in direct calibration mode or into the measurement system, at the probe, in system calibration mode, or both, depending upon the type of system used. In system calibration mode, the system should be able to flood the sampling probe and vent excess gas. Alternatively, calibration gases may be introduced at the calibration valve following the probe. Maintain a constant pressure in the gas manifold. For in-stack dilution-type systems, a gas dilution subsystem is required to transport large volumes of purified air to the sample probe and a probe controller is needed to maintain the proper dilution ratio.

6.2.7 Sample Gas Manifold. For the type of system shown in Figure 7E–1, the sample gas manifold diverts a portion of the sample to the analyzer, delivering the remainder to the by-pass discharge vent. The manifold should also be able to introduce calibration gases directly to the analyzer (except for dilution-type systems). The manifold must be made of material that is non-reactive to the gas sampled or the calibration gas and be configured to safely discharge the bypass gas.

6.2.8 NO_X Analyzer. An instrument that continuously measures NO_X in the gas stream and meets the applicable specifications in section 13.0. An analyzer that operates on the principle of chemiluminescence with an NO_2 to NO converter is one example of an analyzer that has been used successfully in the past. Analyzers operating on other principles may also be used provided the performance criteria in section 13.0 are met.

6.2.8.1 Dual Range Analyzers. For certain applications, a wide range of gas concentrations may be encountered, necessitating the use of two measurement ranges. Dual-range analyzers are readily available for these applications. These analyzers are often equipped with automated range-switching capability, so that when readings exceed the full-scale of the low measurement range, they are recorded on the high range. As an alternative to using a dual-range analyzer, you may use two segments of a single, large measurement scale to serve as the low and high ranges. In all cases, when two ranges are used, you must quality-assure both ranges using the proper sets of calibration gases. You must also meet the interference, calibration error, system bias, and drift checks. However, we caution that when you use two segments of a large measurement scale for dual range purposes, it may be difficult to meet the performance specifications on the low range due to signal-to-noise ratio considerations.

6.2.8.2 Low Concentration Analyzer. When an analyzer is routinely calibrated with a calibration span of 20 ppmv or less, the manufacturer's stability test (MST) is required. See Table 7E–5 for test parameters.

6.2.9 Data Recording. A strip chart recorder, computerized data acquisition system, digital recorder, or data logger for recording measurement data may be used.

7.0 Reagents and Standards

7.1 Calibration Gas. What calibration gases do I need? Your calibration gas must be NO in N_2 and certified (or recertified) within an uncertainty of 2.0 percent in accordance with ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards'' September 1997, as amended August 25, 1999, EPA–600/R–97/121. Blended gases meeting the Traceability Protocol are allowed if the additional gas components are shown not to interfere with the analysis. If a zero gas is used for the low-level gas, it must meet the requirements under the definition for ''zero air material'' in 40 CFR 72.2. The calibration gas must not be used after its expiration date. Except for applications under part 75 of

this chapter, it is acceptable to prepare calibration gas mixtures from EPA Traceability Protocol gases in accordance with Method 205 in appendix M to part 51 of this chapter. For part 75 applications, the use of Method 205 is subject to the approval of the Administrator. The goal and recommendation for selecting calibration gases is to bracket the sample concentrations. The following calibration gas concentrations are required:

7.1.1 *High-Level Gas.* This concentration is chosen to set the calibration span as defined in Section 3.4.

7.1.2 Mid-Level Gas. 40 to 60 percent of the calibration span.

7.1.3 Low-Level Gas. Less than 20 percent of the calibration span.

7.1.4 Converter Efficiency Gas. What reagents do I need for the converter efficiency test? The converter efficiency gas is a manufacturer-certified gas with a concentration sufficient to show NO_2 conversion at the concentrations encountered in the source. A test gas concentration in the 40 to 60 ppm range is suggested, but other concentrations may be more appropriate to specific sources. For the test described in section 8.2.4.1, NO_2 is required. For the alternative converter efficiency tests in section 16.2, NO is required.

7.2 Interference Check. What reagents do I need for the interference check? Use the appropriate test gases listed in Table 7E–3 or others not listed that can potentially interfere (as indicated by the test facility type, instrument manufacturer, etc.) to conduct the interference check. These gases should be manufacturer certified but do not have to be prepared by the EPA traceability protocol.

8.0 Sample Collection, Preservation, Storage, and Transport

Emission Test Procedure

Since you are allowed to choose different options to comply with some of the performance criteria, it is your responsibility to identify the specific options you have chosen, to document that the performance criteria for that option have been met, and to identify any deviations from the method.

8.1 What sampling site and sampling points do I select?

8.1.1 Unless otherwise specified in an applicable regulation or by the Administrator, when this method is used to determine compliance with an emission standard, conduct a stratification test as described in section 8.1.2 to determine the sampling traverse points to be used. For performance testing of continuous emission monitoring systems, follow the sampling site selection and traverse point layout procedures described in the appropriate performance specification or applicable regulation (e.g., Performance Specification 2 in appendix B to this part).

8.1.2 Determination of Stratification. Perform a stratification test at each test site to determine the appropriate number of sample traverse points. If testing for multiple pollutants or diluents at the same site, a stratification test using only one pollutant or diluent satisfies this requirement. A stratification test is not required for small stacks that are less than 4 inches in diameter. To test for stratification, use a probe of appropriate length to measure the NO_X (or pollutant of interest) concentration at 12 traverse points located according to Table 1–1 or Table 1–2 of Method 1. Alternatively, you may measure at three points on a line passing through the centroidal area. Space the three points at 16.7, 50.0, and 83.3 percent of the measurement line. Sample for a minimum of twice the system response time (see section 8.2.6) at each traverse point. Calculate the individual point and mean NO_X concentrations. If the concentration at each traverse point differs from the mean concentration for all traverse points by no more than: ±5.0 percent of the mean concentration; or ±0.5 ppm (whichever is less restrictive), the gas stream is considered unstratified, and you may collect samples from a single point that most closely matches the mean. If the 5.0 percent or 0.5 ppm criterion is not met, but the concentration at each traverse point differs from the mean concentration for all traverse points by not more than: ±10.0 percent of the mean concentration; or ±1.0 ppm (whichever is less restrictive), the gas stream is considered to be minimally stratified and you may take samples from three points. Space the three points at 16.7, 50.0, and 83.3 percent of the measurement line. Alternatively, if a 12-point stratification test was performed and the emissions were shown to be minimally stratified (all points within ± 10.0 percent of their mean or within ±1.0 ppm), and if the stack diameter (or equivalent diameter, for a rectangular stack or duct) is greater than 2.4 meters (7.8 ft), then you may use 3-point sampling and locate the three points along the measurement line exhibiting the highest average concentration during the stratification test at 0.4, 1.2 and 2.0 meters from the stack or duct wall. If the gas stream is found to be stratified because the 10.0 percent or 1.0 ppm criterion for a 3-point test is not met, locate 12 traverse points for the test in accordance with Table 1–1 or Table 1–2 of Method 1.

8.2 Initial Measurement System Performance Tests. What initial performance criteria must my system meet before I begin collecting samples? Before measuring emissions, perform the following procedures:

(a) Calibration gas verification,

(b) Measurement system preparation,

(c) Calibration error test,

(d) NO_2 to NO conversion efficiency test, if applicable,

(e) System bias check,

(f) System response time test, and

(g) Interference check

8.2.1 Calibration Gas Verification. How must I verify the concentrations of my calibration gases? Obtain a certificate from the gas manufacturer documenting the quality of the gas. Confirm that the manufacturer certification is complete and current. Ensure that your calibration gas certifications have not expired. This documentation should be available on-site for inspection. To the extent practicable, select a high-level gas concentration that will result in the measured emissions being between 20 and 100 percent of the calibration span.

8.2.2 Measurement System Preparation. How do I prepare my measurement system? Assemble, prepare, and precondition the measurement system according to your standard operating procedure. Adjust the system to achieve the correct sampling rate or dilution ratio (as applicable).

8.2.3 Calibration Error Test. How do I confirm my analyzer calibration is correct? After you have assembled, prepared and calibrated your sampling system and analyzer, you must conduct a 3-point analyzer calibration error test (or a 3-point system calibration error test for dilution systems) before the first run and again after any failed system bias test (or 2-point system calibration error test for dilution systems) or failed drift test. Introduce the low-, mid-, and high-level calibration gases sequentially. For non-dilution-type measurement systems, introduce the gases in direct calibration mode. For dilution-type measurement systems, introduce the gases in system calibration mode.

(1) For non-dilution systems, you may adjust the system to maintain the correct flow rate at the analyzer during the test, but you may not make adjustments for any other purpose. For dilution systems, you must operate the measurement system at the appropriate dilution ratio during all system calibration error checks, and may make only the adjustments necessary to maintain the proper ratio.

(2) Record the analyzer's response to each calibration gas on a form similar to Table 7E–1. For each calibration gas, calculate the analyzer calibration error using Equation 7E–1 in section 12.2 or the system calibration error using Equation 7E–3 in section 12.4 (as applicable). The calibration error specification in section 13.1 must be met for the low-, mid-, and high-level gases. If the calibration error specification is not met, take corrective action and repeat the test until an acceptable 3-point calibration is achieved.

8.2.4 NO_2 to NO Conversion Efficiency Test. Before or after each field test, you must conduct an NO_2 to NO conversion efficiency test if your system converts NO_2 to NO before analyzing for NO_X. You may risk testing multiple facilities before performing this test provided you pass this test at the conclusion of the final facility test. A failed final conversion efficiency test in this case will invalidate all tests performed subsequent to the test in which the converter efficiency test was passed. Follow the procedures in section 8.2.4.1, or 8.2.4.2. If desired, the converter efficiency factor derived from this test may be used to correct the test results for converter efficiency if the NO_2 fraction in the measured test gas is known. Use Equation 7E–8 in section 12.8 for this correction.

8.2.4.1 Introduce NO_2 converter efficiency gas to the analyzer in direct calibration mode and record the NO_X concentration displayed by the analyzer. Calculate the converter efficiency using Equation 7E–7 in section 12.7. The specification for converter efficiency in section 13.5 must be met. The user is cautioned that state-of-the-art NO_2 calibration gases may have limited shelf lives, and this could affect the ability to pass the 90-percent conversion efficiency requirement.

8.2.4.2 Alternatively, either of the procedures for determining conversion efficiency using NO in section 16.2 may be used.

8.2.5 Initial System Bias and System Calibration Error Checks. Before sampling begins, determine whether the high-level or mid-level calibration gas best approximates the emissions and use it as the upscale gas. Introduce the upscale gas at the probe upstream of all sample conditioning components in system calibration mode. Record the time it takes for the measured concentration to increase to a value that is at least 95 percent or within 0.5 ppm (whichever is less restrictive) of a stable response for both the low-level and upscale gases. Continue to observe the gas concentration reading until it has reached a final, stable value. Record this value on a form similar to Table 7E–2.

(1) Next, introduce the low-level gas in system calibration mode and record the time required for the concentration response to decrease to a value that is within 5.0 percent or 0.5 ppm (whichever is less restrictive) of the certified low-range gas concentration. If the low-level gas is a zero gas, use the procedures described above and observe the change in concentration until the response is 0.5 ppm or 5.0 percent of the upscale gas concentration (whichever is less restrictive).

(2) Continue to observe the low-level gas reading until it has reached a final, stable value and record the result on a form similar to Table 7E–2. Operate the measurement system at the normal sampling rate during all system bias checks. Make only the adjustments necessary to achieve proper calibration gas flow rates at the analyzer.

(3) From these data, calculate the measurement system response time (see section 8.2.6) and then calculate the initial system bias using Equation 7E–2 in section 12.3. For dilution systems, calculate the system calibration error in lieu of system bias using

equation 7E–3 in section 12.4. See section 13.2 for acceptable performance criteria for system bias and system calibration error. If the initial system bias (or system calibration error) specification is not met, take corrective action. Then, you must repeat the applicable calibration error test from section 8.2.3 and the initial system bias (or 2-point system calibration error) check until acceptable results are achieved, after which you may begin sampling.

(NOTE: For dilution-type systems, data from the 3-point system calibration error test described in section 8.2.3 may be used to meet the initial 2-point system calibration error test requirement of this section, if the calibration gases were injected as described in this section, and if response time data were recorded).

8.2.6 Measurement System Response Time. As described in section 8.2.5, you must determine the measurement system response time during the initial system bias (or 2-point system calibration error) check. Observe the times required to achieve 95 percent of a stable response for both the low-level and upscale gases. The longer interval is the response time.

8.2.7 Interference Check. Conduct an interference response test of the gas analyzer prior to its initial use in the field. If you have multiple analyzers of the same make and model, you need only perform this alternative interference check on one analyzer. You may also meet the interference check requirement if the instrument manufacturer performs this or a similar check on an analyzer of the same make and model of the analyzer that you use and provides you with documented results.

(1) You may introduce the appropriate interference test gases (that are potentially encountered during a test; see examples in Table 7E–3) into the analyzer separately or as mixtures. Test the analyzer with the interference gas alone at the highest concentration expected at a test source and again with the interference gas and NO_X at a representative NO_X test concentration. For analyzers measuring NO_X greater than 20 ppm, use a calibration gas with a NO_X concentration of 80 to 100 ppm and set this concentration equal to the calibration span. For analyzers measuring less than 20 ppm NO_X, select an NO concentration for the calibration span that reflects the emission levels at the sources to be tested, and perform the interference check at that level. Measure the total interference response of the analyzer to these gases in ppmv. Record the responses and determine the interference using Table 7E–4. The specification in section 13.4 must be met.

(2) A copy of this data, including the date completed and signed certification, must be available for inspection at the test site and included with each test report. This interference test is valid for the life of the instrument unless major analytical components (*e.g.,* the detector) are replaced with different model parts. If major components are replaced with different model parts, the interference gas check must be repeated before returning the analyzer to service. If major components are replaced, the interference gas check must be repeated before returning the analyzer to service. The tester must ensure that any specific technology, equipment, or procedures that are intended to remove interference effects are operating properly during testing.

8.3 Dilution-Type Systems—Special Considerations. When a dilution-type measurement system is used, there are three important considerations that must be taken into account to ensure the quality of the emissions data. First, the critical orifice size and dilution ratio must be selected properly so that the sample dew point will be below the sample line and analyzer temperatures. Second, a high-quality, accurate probe controller must be used to maintain the dilution ratio during the test. The probe controller should be capable of monitoring the dilution air pressure, eductor vacuum, and sample flow rates. Third, differences between the molecular weight of calibration gas mixtures and the stack gas molecular weight must be addressed because these can affect the dilution ratio and introduce measurement bias.

8.4 Sample Collection.

(1) Position the probe at the first sampling point. Purge the system for at least two times the response time before recording any data. Then, traverse all required sampling points, sampling at each point for an equal length of time and maintaining the appropriate sample flow rate or dilution ratio (as applicable). You must record at least one valid data point per minute during the test run.

(2) Each time the probe is removed from the stack and replaced, you must recondition the sampling system for at least two times the system response time prior to your next recording. If the average of any run exceeds the calibration span value, that run is invalid.

(3) You may satisfy the multipoint traverse requirement by sampling sequentially using a single-hole probe or a multi-hole probe designed to sample at the prescribed points with a flow within 10 percent of mean flow rate. Notwithstanding, for applications under part 75 of this chapter, the use of multi-hole probes is subject to the approval of the Administrator.

8.5 Post-Run System Bias Check and Drift Assessment.

How do I confirm that each sample I collect is valid? After each run, repeat the system bias check or 2-point system calibration error check (for dilution systems) to validate

the run. Do not make adjustments to the measurement system (other than to maintain the target sampling rate or dilution ratio) between the end of the run and the completion of the post-run system bias or system calibration error check. Note that for all post-run system bias or 2-point system calibration error checks, you may inject the low-level gas first and the upscale gas last, or vice-versa. You may risk sampling for multiple runs before performing the post-run bias or system calibration error check provided you pass this test at the conclusion of the group of runs. A failed final test in this case will invalidate all runs subsequent to the last passed test.

(1) If you do not pass the post-run system bias (or system calibration error) check, then the run is invalid. You must diagnose and fix the problem and pass another calibration error test (Section 8.2.3) and system bias (or 2-point system calibration error) check (Section 8.2.5) before repeating the run. Record the system bias (or system calibration error) results on a form similar to Table 7E–2.

(2) After each run, calculate the low-level and upscale drift, using Equation 7E–4 in section 12.5. If the post-run low- and upscale bias (or 2-point system calibration error) checks are passed, but the low-or upscale drift exceeds the specification in section 13.3, the run data are valid, but a 3-point calibration error test and a system bias (or 2-point system calibration error) check must be performed and passed before any more test runs are done.

(3) For dilution systems, data from a 3-point system calibration error test may be used to met the pre-run 2-point system calibration error requirement for the first run in a test sequence. Also, the post-run bias (or 2-point calibration error) check data may be used as the pre-run data for the next run in the test sequence at the discretion of the tester.

8.6 Alternative Interference and System Bias Checks (Dynamic Spike Procedure). If I want to use the dynamic spike procedure to validate my data, what procedure should I follow? Except for applications under part 75 of this chapter, you may use the dynamic spiking procedure and requirements provided in section 16.1 during each test as an alternative to the interference check and the pre- and post-run system bias checks. The calibration error test is still required under this option. Use of the dynamic spiking procedure for Part 75 applications is subject to the approval of the Administrator.

8.7 Moisture correction. You must determine the moisture content of the flue gas and correct the measured gas concentrations to a dry basis using Method 4 or other appropriate methods, subject to the approval of the Administrator, when the moisture basis (wet or dry) of the measurements made with this method is different from the moisture basis of either: (1) The applicable emissions limit; or (2) the CEMS being evaluated for relative accuracy. Moisture correction is also required if the applicable limit is in lb/mmBtu and the moisture basis of the Method 7E NO_X analyzer is different from the moisture basis of the Method 3A diluent gas (CO_2 or O_2) analyzer.

9.0 Quality Control

What quality control measures must I take?

The following table is a summary of the mandatory, suggested, and alternative quality assurance and quality control measures and the associated frequency and acceptance criteria. All of the QC data, along with the sample run data, must be documented and included in the test report.

SUMMARY TABLE OF AQ/QC

Status	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
S	Identify Data User		Regulatory Agency or other primary end user of data.	Before designing test.
S	Analyzer Design	Analyzer resolution or sensitivity.	<2.0% of full-scale range	Manufacturer design.
M		Interference gas check.	Sum of responses ≤2.5% of calibration span Alternatively, sum of responses: ≤0.5 ppmv for calibration spans of 5 to 10 ppmv. ≤0.2 ppmv for calibration spans <5 ppmv. See Table 7E-3.	
M	Calibration Gases	Traceability protocol (G1, G2).	Valid certificate required Uncertainty ≤2.0% of tag value.	
M		High-level gas	Equal to the calibration span	Each test.
M		Mid-level gas	40 to 60% of calibration span	Each test.
M		Low-level gas	<20% of calibration span	Each test.
S	Data Recorder Design.	Data resolution	≤0.5% of full-scale range	Manufacturer design.
S	Sample Extraction	Probe material	SS or quartz if stack >500 °F	East test.
M	Sample Extraction	Probe, filter and sample line temperature.	For dry-basis analyzers, keep sample above the dew point by heating, prior to sample conditioning.	Each run.

SUMMARY TABLE OF AQ/QC—Continued

Status	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
			For wet-basis analyzers, keep sample above dew point at all times, by heating or dilution.	
S	Sample Extraction	Calibration valve material.	SS	Each test.
S	Sample Extraction	Sample pump material.	Inert to sample constituents	Each test.
S	Sample Extraction	Manifolding material	Inert to sample constituents	Each test.
S	Moisture Removal	Equipment efficiency	<5% target compound removal	Verified through system bias check.
S	Particulate Removal	Filter inertness	Pass system bias check	Each bias check.
M	Analyzer & Calibration Gas Performance.	Analyzer calibration error (of 3-point system calibration error for dilution systems).	Within ±2.0 percent of the calibration span of the analyzer for the low-, mid-, and high-level calibration gases. Alternative specification: ≤0.5 ppmv absolute difference.	Before initial run and after a failed system bias test or drift test.
M	System Performance	System bias (or pre- and post-run 2-point system calibration error for dilution (Systems).	Within ±5.0% of the analyzer calibration span for low-sacle and upscale calibration gases. Alternative specification: ≤0.5 ppmv absolute difference.	Before and after each run.
M	System Performance	System response time.	Determines minimum sampling time per point.	During initial sampling system bias test.
M	System Performance	Drift	≤3.0% of calibration span for low-level and mid- or high-level gases. Alternative specification: ≤0.5 ppmv absolute difference.	After each test run.
M	System Performance	NO_2-NO conversion efficiency.	≥90% of certified test gas concentration	Before or after each test.
M	System Performance	Purge time	≥2 times system response time	Before starting the first run and when probe is removed from and re-inserted into the stack.
M	System Performance	Minimum sample time at each point.	Two times the system response time	Each sample point.
M	System Performance	Stable sample flow rate (surrogate for maintaining system response time).	Within 10% of flow rate established during system response time check.	Each run.
M	Sample Point Selection.	Stratification test	All points within: ±5% of mean for 1-point sampling. ±10% of mean for 3-point. Alternatively, all points within: ±0.5 ppm of mean for 1-point sampling. ±1.0 ppm of mean for 3-point sampling.	Prior to first run.
A	Multiple sample points simultaneously.	No. of openings in probe.	Multi-hole probe with verifiable constant flow through all holes within 10% of mean flow rate (requires Administrative approval for Part 75).	Each run.
M	Data Recording	Frequency	≤1 minute average	During run.
S	Data Parameters	Sample concentration range.	All 1-minute averages within calibration span.	Each run.
M	Date Parameters	Average concentration for the run.	Run average ≤calibration span	Each run.

S = Suggest.
M = Mandatory.
A = Alternative.
Agency.

10.0 Calibration and Standardization

What measurement system calibrations are required?

(1) The initial 3-point calibration error test as described in section 8.2.3 and the system bias (or system calibration error) checks described in section 8.2.5 are required and must meet the specifications in section 13 before you start the test. Make all necessary adjustments to calibrate the gas analyzer and data recorder. Then, after the test commences, the system bias or system calibration error checks described in section 8.5 are required before and after each run. Your analyzer must be calibrated for all species of NO_X that it detects. Analyzers that measure NO and NO_2 separately without using a converter must be calibrated with both NO and NO_2.

(2) You must include a copy of the manufacturer's certification of the calibration gases used in the testing as part of the test report. This certification must include the 13 documentation requirements in the EPA Traceability Protocol For Assay and Certification of Gaseous Calibration Standards, September 1997, as amended August 25, 1999. When Method 205 is used to produce diluted calibration gases, you must document that the specifications for the gas dilution system are met for the test. You must also include the date of the most recent dilution system calibration against flow standards and the name of the person or manufacturer who carried out the calibration in the test report.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the procedures for calculations and data analysis listed in this section.

12.1 *Nomenclature.* The terms used in the equations are defined as follows:

ACE = Analyzer calibration error, percent of calibration span.

B_{WS} = Moisture content of sample gas as measured by Method 4 or other approved method, percent/100.

C_{Avg} = Average unadjusted gas concentration indicated by data recorder for the test run, ppmv.

C_D = Pollutant concentration adjusted to dry conditions, ppmv.

C_{Dir} = Measured concentration of a calibration gas (low, mid, or high) when introduced in direct calibration mode, ppmv.

C_{Gas} = Average effluent gas concentration adjusted for bias, ppmv.

C_M = Average of initial and final system calibration bias (or 2-point system calibration error) check responses for the upscale calibration gas, ppmv.

C_{MA} = Actual concentration of the upscale calibration gas, ppmv.

C_{Native} = NO_X concentration in the stack gas as calculated in section 12.6, ppmv.

C_O = Average of the initial and final system calibration bias (or 2-point system calibration error) check responses from the low-level (or zero) calibration gas, ppmv.

C_{OA} = Actual concentration of the low-level calibration gas, ppmv.

C_S = Measured concentration of a calibration gas (low, mid, or high) when introduced in system calibration mode, ppmv.

C_{SS} = Concentration of NO_X measured in the spiked sample, ppmv.

C_{Spike} = Concentration of NO_X in the undiluted spike gas, ppmv.

C_{Calc} = Calculated concentration of NO_X in the spike gas diluted in the sample, ppmv.

C_V = Manufacturer certified concentration of a calibration gas (low, mid, or high), ppmv.

C_W = Pollutant concentration measured under moist sample conditions, wet basis, ppmv.

CS = Calibration span, ppmv.

D = Drift assessment, percent of calibration span.

DF = Dilution system dilution factor or spike gas dilution factor, dimensionless.

Eff_{NO2} = NO_2 to NO converter efficiency, percent.

NO_{XCorr} = The NO_X concentration corrected for the converter efficiency, ppmv.

NOX_{Final} = The final NO_X concentration observed during the converter efficiency test in section 16.2.2, ppmv.

NO_{XPeak} = The highest NO_X concentration observed during the converter efficiency test in section 16.2.2, ppmv.

Q_{Spike} = Flow rate of spike gas introduced in system calibration mode, L/min.

Q_{Total} = Total sample flow rate during the spike test, L/min.

R = Spike recovery, percent.

SB = System bias, percent of calibration span.

SB_i = Pre-run system bias, percent of calibration span.

SB_{final} = Post-run system bias, percent of calibration span.

SCE = System calibration error, percent of calibration span.

SCE_i = Pre-run system calibration error, percent of calibration span.

SCE_{Final} = Post-run system calibration error, percent of calibration span.

12.2 Analyzer Calibration Error. For non-dilution systems, use Equation 7E–1 to calculate the analyzer calibration error for the low-, mid-, and high-level calibration gases.

$$ACE = \frac{C_{Dir} - C_v}{CS} \times 100 \qquad \text{Eq. 7E-1}$$

12.3 System Bias. For non-dilution systems, use Equation 7E–2 to calculate the system bias separately for the low-level and upscale calibration gases.

$$SB = \frac{C_S - C_{Dir}}{CS} \times 100 \qquad \text{Eq. 7E-2}$$

12.4 System Calibration Error. Use Equation 7E–3 to calculate the system calibration error for dilution systems. Equation 7E–3 applies to both the initial 3-point system calibration error test and the subsequent 2-point calibration error checks between test runs. In this equation, the term ''C_s'' refers to the diluted calibration gas concentration measured by the analyzer.

$$SCE = \frac{(C_S \quad DF) - C_V}{CS} \times 100 \qquad \text{Eq. 7E-3}$$

12.5 Drift Assessment. Use Equation 7E–4 to separately calculate the low-level and upscale drift over each test run. For dilution systems, replace ''SB_{final}'' and ''SB_i'' with ''SCE_{final}'' and ''SCE_i'', respectively, to calculate and evaluate drift.

$$D = \left|SB_{final} - SB_i\right| \qquad \text{Eq. 7E-4}$$

12.6 Effluent Gas Concentration. For each test run, calculate C_{avg}, the arithmetic average of all valid NO_X concentration values (*e.g.*, 1-minute averages). Then adjust the value of C_{avg} for bias using Equation 7E–5a if you use a non-zero gas as your low-level calibration gas, or Equation 7E–5b if you use a zero gas as your low-level calibration gas.

$$C_{Gas} = \left(C_{Avg} - C_M\right)\frac{C_{MA} - C_{OA}}{C_M - C_O} + C_{MA} \qquad \text{Eq. 7E-5a}$$

$$C_{Gas} = \left(C_{Avg} - C_O\right)\frac{C_{MA}}{C_M - C_O} \qquad \text{Eq. 7E-5b}$$

12.7 NO_2—NO Conversion Efficiency. If the NO_X converter efficiency test described in section 8.2.4.1 is performed, calculate the efficiency using Equation 7E–7.

$$Eff_{NO2} = \frac{C_{Dir}}{C_V} \times 100 \qquad \text{Eq. 7E-7}$$

12.8 NO_2—NO Conversion Efficiency Correction. If desired, calculate the total NO_X concentration with a correction for converter efficiency using Equation 7E–8.

$$NO_{x\,Corr} = NO + \left(\frac{(NO_X - NO)}{Eff_{NO_2}} x\ 100\right) \qquad \text{Eq. 7E-8}$$

12.9 Alternative NO_2 Converter Efficiency. If the alternative procedure of section 16.2.2 is used, determine the NO_X concentration decrease from NO_{XPeak} after the minimum 30-minute test interval using Equation 7E–9.

This decrease from NO_{XPeak} must meet the requirement in section 13.5 for the converter to be acceptable.

$$\%\,Decrease = \frac{NO_{XPeak} - NO_{XFinal}}{NO_{XPeak}} \times 100 \qquad \text{Eq. 7E-9}$$

12.10 Moisture Correction. Use Equation 7E–10 if your measurements need to be corrected to a dry basis.

$$C_D = \frac{C_W}{1 - B_{WS}} \qquad \text{Eq. 7E-10}$$

12.11 Calculated Spike Gas Concentration and Spike Recovery for the Example Alternative Dynamic Spiking Procedure in section 16.1.3. Use Equation 7E–11 to determine the calculated spike gas concentration. Use Equation 7E–12 to calculate the spike recovery.

$$C_{Calc} = \frac{\left(C_{Spike}\right)\left(Q_{Spike}\right)}{Q_{Total}} \qquad \text{Eq. 7E-11}$$

$$R = \frac{DF\left(C_{ss} - C_{native}\right) + C_{native}}{C_{Spike}} \times 100 \qquad \text{Eq. 7E-12}$$

13.0 Method Performance

13.1 Calibration Error. This specification is applicable to both the analyzer calibration error and the 3-point system calibration error tests described in section 8.2.3. At each calibration gas level (low, mid, and high) the calibration error must either be within ±2.0 percent of the calibration span. Alternatively, the results are acceptable if $|C_{dir} - C_v|$ or $|C_s - C_v|$ (as applicable) is ≤0.5 ppmv.

13.2 System Bias. This specification is applicable to both the system bias and 2-point system calibration error tests described in section 8.2.5 and 8.5. The pre- and post-run system bias (or system calibration error) must be within ±5.0 percent of the calibration span for the low-level and upscale calibration gases. Alternatively, the results are acceptable if $|C_s - C_{dir}|$ is ≤0.5 ppmv or if $|C_s - C_v|$ is ≤0.5 ppmv (as applicable).

13.3 Drift. For each run, the low-level and upscale drift must be less than or equal to 3.0 percent of the calibration span. The drift is also acceptable if the pre- and post-run bias (or the pre- and post-run system calibration error) responses do not differ by more than 0.5 ppmv at each gas concentration (i.e. $|C_{s\ post\text{-}run} - C_{s\ pre\text{-}run}| \leq 0.5$ ppmv).

13.4 Interference Check. The total interference response (i.e., the sum of the interference responses of all tested gaseous components) must not be greater than 2.50 percent of the calibration span for the analyzer tested. In summing the interferences, use the larger of the absolute values obtained for the interferent tested with and without the pollutant present. The results are also acceptable if the sum of the responses does not exceed 0.5 ppmv for a calibration span of 5 to 10 ppmv, or 0.2 ppmv for a calibration span <5 ppmv.

13.5 NO_2 to NO Conversion Efficiency Test (as applicable). The NO_2 to NO conversion efficiency, calculated according to Equation 7E–7, must be greater than or equal to 90 percent. The alternative conversion efficiency check, described in section 16.2.2 and calculated according to Equation 7E–9, must not result in a decrease from NO_{XPeak} by more than 2.0 percent.

13.6 Alternative Dynamic Spike Procedure. Recoveries of both pre-test spikes and post-test spikes must be within 100 ±10 percent. If the absolute difference between the calculated spike value and measured spike value is equal to or less than 0.20 ppmv, then the requirements of the ADSC are met.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Dynamic Spike Procedure. Except for applications under part 75 of this chapter, you may use a dynamic spiking procedure to validate your test data for a specific test matrix in place of the interference check and pre- and post-run system bias checks. For part 75 applications, use of this procedure is subject to the approval of the Administrator.

Best results are obtained for this procedure when source emissions are steady and not varying. Fluctuating emissions may render this alternative procedure difficult to pass. To use this alternative, you must meet the following requirements.

16.1.1 Procedure Documentation. You must detail the procedure you followed in the test report, including how the spike was measured, added, verified during the run, and calculated after the test.

16.1.2 Spiking Procedure Requirements. The spikes must be prepared from EPA Traceability Protocol gases. Your procedure must be designed to spike field samples at two target levels both before and after the test. Your target spike levels should bracket the average sample NO_X concentrations. The higher target concentration must be less than the calibration span. You must collect at least 5 data points for each target concentration. The spiking procedure must be performed before the first run and repeated after the last run of the test program.

16.1.3 Example Spiking Procedure. Determine the NO concentration needed to generate concentrations that are 50 and 150 percent of the anticipated NO_X concentration in the stack at the total sampling flow rate while keeping the spike flow rate at or below 10 percent of this total. Use a mass flow meter (accurate within 2.0 percent) to generate these NO spike gas concentrations at a constant flow rate. Use Equation 7E–11 in section 12.11 to determine the calculated spike concentration in the collected sample.

(1) Prepare the measurement system and conduct the analyzer calibration error test as described in sections 8.2.2 and 8.2.3. Following the sampling procedures in section 8.1, determine the stack NO_X concentration and use this concentration as the average stack concentration (C_{avg}) for the first spike level, or if desired, for both pre-test spike levels. Introduce the first level spike gas into the system in system calibration mode and begin sample collection. Wait for at least two times the system response time before measuring the spiked sample concentration. Then record at least five successive 1-minute averages of the spiked sample gas. Monitor the spike gas flow rate and maintain at the determined addition rate. Average the five 1-minute averages and determine the spike recovery using Equation 7E–12. Repeat this procedure for the other pre-test spike level. The recovery at each level must be within the limits in section 13.6 before proceeding with the test.

(2) Conduct the number of runs required for the test. Then repeat the above procedure for the post-test spike evaluation. The last run of the test may serve as the average stack concentration for the post-test spike test calculations. The results of the post-test spikes must meet the limits in section 13.6.

16.2 Alternative NO_2 to NO Conversion Efficiency Procedures. You may use either of the following procedures to determine converter efficiency in place of the procedure in section 8.2.4.1.

16.2.1 The procedure for determining conversion efficiency using NO in 40 CFR 86.123–78.

16.2.2 Bag Procedure. Perform the analyzer calibration error test to document the calibration (both NO and NO_X modes, as applicable). Fill a Tedlar or equivalent bag approximately half full with either ambient air, pure oxygen, or an oxygen standard gas with at least 19.5 percent by volume oxygen content. Fill the remainder of the bag with mid- to high-level NO in N_2 (or other appropriate concentration) calibration gas. (Note that the concentration of the NO standard should be sufficiently high enough for the diluted concentration to be easily and accurately measured on the scale used. The size of the bag should be large enough to accommodate the procedure and time required. Verify through the manufacturer that the Tedlar alternative is suitable for NO and make this verifed information available for inspection.)

(1) Immediately attach the bag to the inlet of the NO_X analyzer (or external converter if used). In the case of a dilution-system, introduce the gas at a point upstream of the dilution assembly. Measure the NO_X concentration for a period of 30 minutes. If the NO_X concentration drops more than 2 percent absolute from the peak value observed, then the NO_2 converter has failed to meet the criteria of this test. Take corrective action. The highest NO_X value observed is considered to be NO_{XPeak}. The final NO_X value observed is considered to be NO_{Xfinal}.

(2) [Reserved]

16.3 Manufacturer's Stability Test. A manufacturer's stability test is required for all analyzers that routinely measure emissions below 20 ppmv and is optional but recommended for other analyzers. This test evaluates each analyzer model by subjecting it to the tests listed in Table 7E–5 following procedures similar to those in 40 CFR 53.23 for thermal stability and insensitivity to supply voltage variations. If the analyzer will be used under temperature conditions that are outside the test conditions in Table B–4 of Part 53.23, alternative test temperatures that better reflect the analyzer field environment should be used. Alternative procedures or documentation that establish the analyzer's stability over the appropriate line voltages and temperatures are acceptable.

17.0 References

1. ''ERA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards'' September 1997 as amended, ERA–600/R–97/121.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

Figure 7E-1. Measurement System

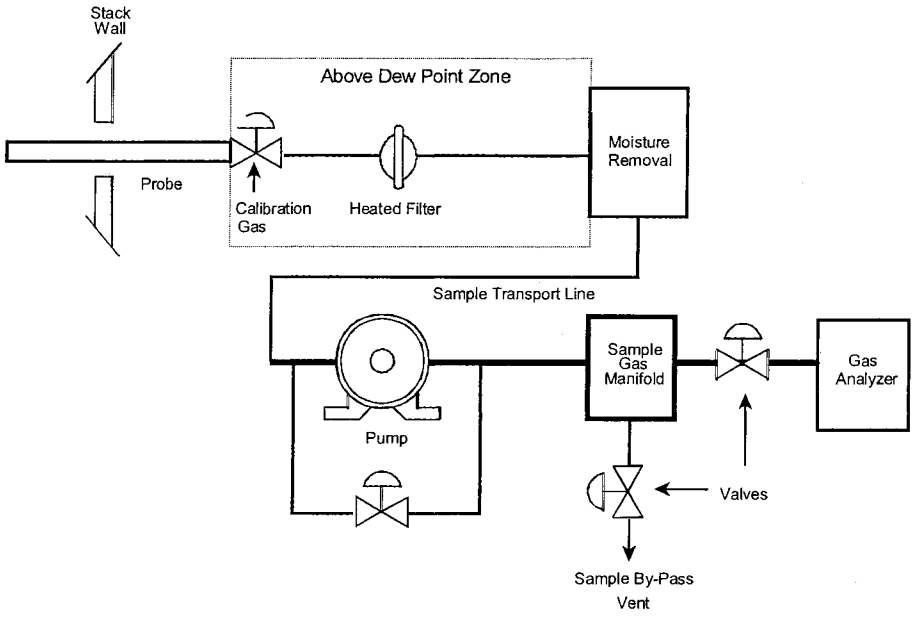

Figure 7E-2. Testing Flow Chart

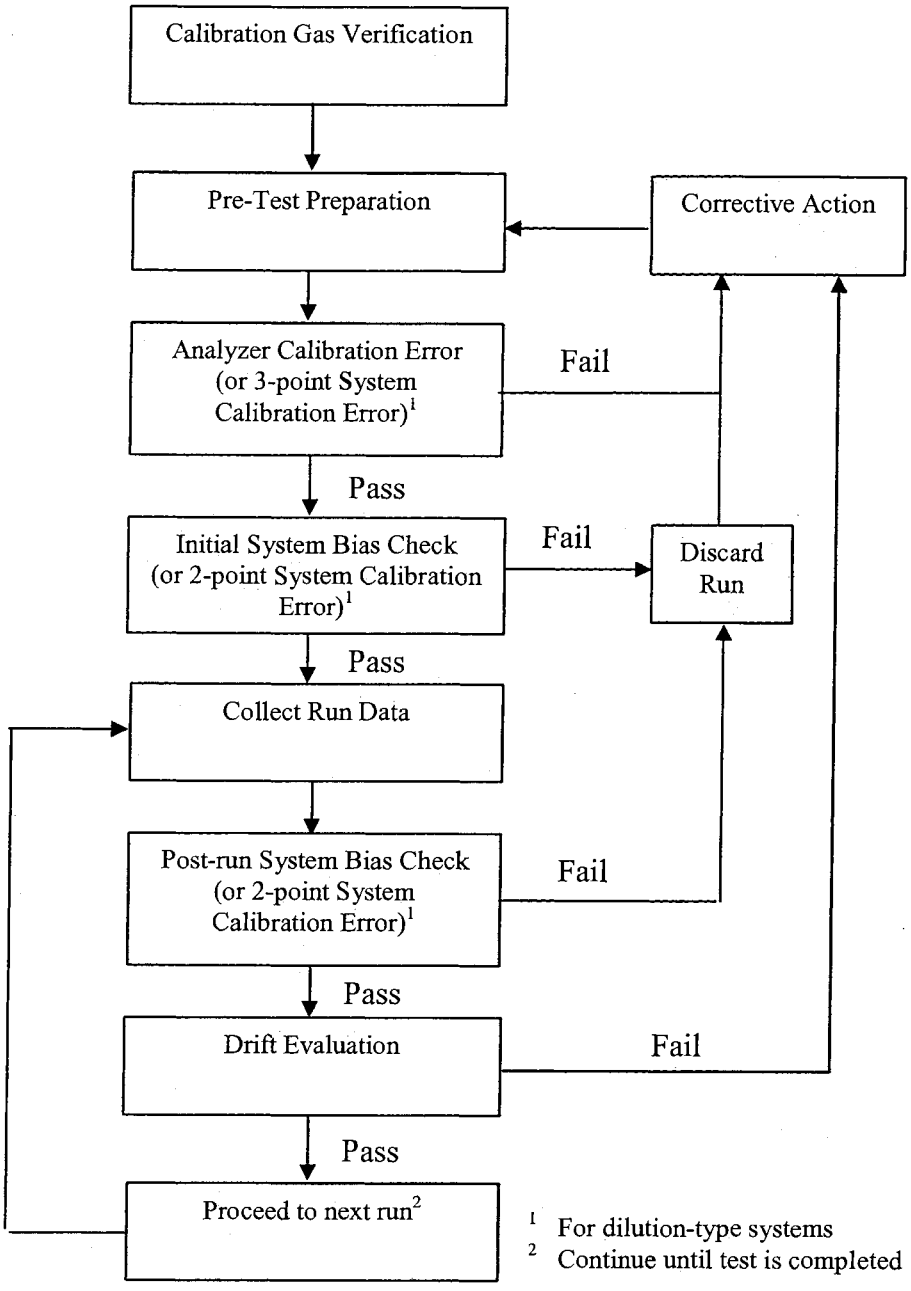

Table 7E-1 - Analyzer (or System) Calibration Error Data

Source Identification: _____ Test personnel: _____ Date: _____ Time: _____		Analyzer[1] or System[2] calibration error data for sampling runs: _____ Analyzer Model No. _____ Serial No. _____ Calibration Span (CS):		
	Manufacturer Certified Cylinder Value (indicate units) A	Analyzer calibration response (indicate units) B	Absolute difference (indicate units) A-B	Calibration Error (percent of calibration span) $\frac{A-B}{CS} \times 100$
Low-level (or zero) calibration gas	.....	.....	.....	.....
Mid-level calibration gas	.....	.....	.....	.....
High-level calibration gas	.....	.....	.....	.....

[1] Refers to data from the analyzer calibration error test of a non-dilution system.
[2] Refers to data from a 3-point system calibration error test of a dilution system.

Table 7E-2 - System Bias (or System Calibration Error) and Drift Data

Source Identification: _____ Run Number: _____
Test personnel: _____ Calibration Span: _____
Date: _____ Response Time: _____
Analyzer Model No. _____ Serial No. _____

	Initial values			Final values		
Calibration Gas Level	Certified Calibration gas value (indicate units)	System Response (indicate units)	System Bias[1] or Calibration Error[2] (% of calibration span)	System response (indicate units)	System Bias[1] or Calibration Error[2] (% of calibration span)	Drift (% of calibration span)
Low-level gas.....	.....	.....	.....	.....	.....	
Upscale (high- or mid-) level gas.....	.....	.....	.....	.....	.....	

[1] Refers to the pre- and post-run system bias checks of a non-dilution system.
[2] Refers to the pre- and post-run system calibration error checks of a dilution system.

TABLE 7E–3—EXAMPLE INTERFERENCE CHECK GAS CONCENTRATIONS

Potential interferent gas [1]	Concentrations [2] sample conditioning type	
	Hot wet	Dried
CO_2	5 and 15%	5 and 15%
H_2O	25%	1%
NO	15 ppmv	15 ppmv
NO_2	15 ppmv	15 ppmv
N_2O	10 ppmv	10 ppmv
CO	50 ppmv	50 ppmv
NH_3	10 ppmv	10 ppmv
CH_4	50 ppmv	50 ppmv
SO_2	20 ppmv	20 ppmv
H_2	50 ppmv	50 ppmv
HCl	10 ppmv	10 ppmv

[1] Any applicable gas may be eliminated or tested at a reduced level if the manufacturer has provided reliable means for limiting or scrubbing that gas to a specified level.
[2] As practicable, gas concentrations should be the highest expected at test sites.

TABLE 7E–4—INTERFERENCE RESPONSE

Date of Test: _____

Analyzer Type: _____
Model No.: _____
Serial No: _____
Calibration Span: _____

Test gas type	Concentration (ppm)	Analyzer response
	Sum of Responses	
	% of Calibration Span	

TABLE 7E–5—MANUFACTURER STABILITY TEST

Test description	Acceptance criteria (note 1)
Thermal Stability	Temperature range when drift does not exceed 3.0% of analyzer range over a 12-hour run when measured with NO_X present @ 80% of calibration span.
Fault Conditions	Identify conditions which, when they occur, result in performance which is not in compliance with the Manufacturer's Stability Test criteria. These are to be indicated visually or electrically to alert the operator of the problem.
Insensitivity to Supply Voltage Variations.	±10.0% (or manufacturers alternative) variation from nominal voltage must produce a drift of ≤2.0% of calibration span for either zero or concentration ≥80% NO_X present.
Analyzer Calibration Error.	For a low-, medium-, and high-calibration gas, the difference between the manufacturer certified value and the analyzer response in direct calibration mode, no more than 2.0% of calibration span.

Note 1: If the instrument is to be used as a Low Range analyzer, all tests must be performed at a calibration span of 20 ppm or less.

METHOD 8—DETERMINATION OF SULFURIC ACID AND SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, and Method 6.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Sulfuric acid, including: Sulfuric acid (H_2SO_4) mist, Sulfur trioxide (SO_3).	7664–93–9, 7449–11–9	0.05 mg/m³ (0.03×10^{-7} lb/ft³).
Sulfur dioxide (SO_2)	7449–09–5	1.2 mg/m³ (3×10^{-9} lb/ft³).

1.2 Applicability. This method is applicable for the determination of H_2SO_4 (including H_2SO_4 mist and SO_3) and gaseous SO_2 emissions from stationary sources.

NOTE: Filterable particulate matter may be determined along with H_2SO_4 and SO_2 (subject to the approval of the Administrator) by inserting a heated glass fiber filter between the probe and isopropanol impinger (see section 6.1.1 of Method 6). If this option is chosen, particulate analysis is gravimetric only; sulfuric acid is not determined separately.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

A gas sample is extracted isokinetically from the stack. The H_2SO_4 and the SO_2 are separated, and both fractions are measured separately by the barium-thorin titration method.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Possible interfering agents of this method are fluorides, free ammonia, and dimethyl aniline. If any of these interfering agents is present (this can be determined by knowledge of the process), alternative methods, subject to the approval of the Administrator, are required.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. Same as Method 6, section 5.2.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 5, section 6.1, with the following additions and exceptions:

6.1.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 8–1; it is similar to the Method 5 sampling train, except that the filter position is different, and the filter holder does not have to be heated. See Method 5, section 6.1.1, for details and guidelines on operation and maintenance.

6.1.1.1 Probe Liner. Borosilicate or quartz glass, with a heating system to prevent visible condensation during sampling. Do not use metal probe liners.

6.1.1.2 Filter Holder. Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other gasket materials (*e.g.*, Teflon or Viton) may be used, subject to the approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The filter holder shall be placed between the first and second impingers. Do not heat the filter holder.

6.1.1.3 Impingers. Four, of the Greenburg-Smith design, as shown in Figure 8–1. The first and third impingers must have standard tips. The second and fourth impingers must be modified by replacing the insert with an approximately 13-mm (½-in.) ID glass tube, having an unconstricted tip located 13 mm (½ in.) from the bottom of the impinger. Similar collection systems, subject to the approval of the Administrator, may be used.

6.1.1.4 Temperature Sensor. Thermometer, or equivalent, to measure the temperature of the gas leaving the impinger train to within 1 °C (2 °F).

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Wash Bottles. Two polyethylene or glass bottles, 500-ml.

6.2.2 Graduated Cylinders. Two graduated cylinders (volumetric flasks may be used), 250-ml, 1-liter.

6.2.3 Storage Bottles. Leak-free polyethylene bottles, 1-liter size (two for each sampling run).

6.2.4 Trip Balance. 500-g capacity, to measure to ±0.5 g (necessary only if a moisture content analysis is to be done).

6.3 Analysis. The following items are required for sample analysis:

6.3.1 Pipettes. Volumetric 10-ml, 100-ml.

6.3.2 Burette. 50-ml.

6.3.3 Erlenmeyer Flask. 250-ml (one for each sample, blank, and standard).

6.3.4 Graduated Cylinder. 100-ml.

6.3.5 Dropping Bottle. To add indicator solution, 125-ml size.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents are to conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Filters and Silica Gel. Same as in Method 5, sections 7.1.1 and 7.1.2, respectively.

7.1.2 Water. Same as in Method 6, section 7.1.1.

7.1.3 Isopropanol, 80 Percent by Volume. Mix 800 ml of isopropanol with 200 ml of water.

NOTE: Check for peroxide impurities using the procedure outlined in Method 6, section 7.1.2.1.

7.1.4 Hydrogen Peroxide (H^2O^2), 3 Percent by Volume. Dilute 100 ml of 30 percent H_2O_2) to 1 liter with water. Prepare fresh daily.

7.1.5 Crushed Ice.

7.2 Sample Recovery. The reagents and standards required for sample recovery are:

7.2.1 Water. Same as in section 7.1.2.

7.2.2 Isopropanol, 80 Percent. Same as in section 7.1.3.

7.3 Sample Analysis. Same as Method 6, section 7.3.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation. Same as Method 5, section 8.1, except that filters should be inspected but need not be desiccated, weighed, or identified. If the effluent gas can be considered dry (i.e., moisture-free), the silica gel need not be weighed.

8.2 Preliminary Determinations. Same as Method 5, section 8.2.

8.3 Preparation of Sampling Train. Same as Method 5, section 8.3, with the following exceptions:

8.3.1 Use Figure 8–1 instead of Figure 5–1.

8.3.2 Replace the second sentence of Method 5, section 8.3.1 with: Place 100 ml of 80 percent isopropanol in the first impinger, 100 ml of 3 percent H_2O_2 in both the second and third impingers; retain a portion of each reagent for use as a blank solution. Place about 200 g of silica gel in the fourth impinger.

8.3.3 Ignore any other statements in section 8.3 of Method 5 that are obviously not applicable to the performance of Method 8.

NOTE: If moisture content is to be determined by impinger analysis, weigh each of the first three impingers (plus absorbing solution) to the nearest 0.5 g, and record these weights. Weigh also the silica gel (or silica gel plus container) to the nearest 0.5 g, and record.)

8.4 Metering System Leak-Check Procedure. Same as Method 5, section 8.4.1.

8.5 Pretest Leak-Check Procedure. Follow the basic procedure in Method 5, section 8.4.2, noting that the probe heater shall be adjusted to the minimum temperature required to prevent condensation, and also that verbage such as ''* * * plugging the inlet to the filter holder * * * '' found in section 8.4.2.2 of Method 5 shall be replaced by '' * * * plugging the inlet to the first impinger * * * ''. The pretest leak-check is recommended, but is not required.

8.6 Sampling Train Operation. Follow the basic procedures in Method 5, section 8.5, in conjunction with the following special instructions:

8.6.1 Record the data on a sheet similar to that shown in Figure 8–2 (alternatively, Figure 5–2 in Method 5 may be used). The sampling rate shall not exceed 0.030 m^3/min (1.0 cfm) during the run. Periodically during the test, observe the connecting line between the probe and first impinger for signs of condensation. If condensation does occur, adjust the probe heater setting upward to the minimum temperature required to prevent condensation. If component changes become necessary during a run, a leak-check shall be performed immediately before each change, according to the procedure outlined in section 8.4.3 of Method 5 (with appropriate modifications, as mentioned in section 8.5 of this method); record all leak rates. If the leakage rate(s) exceeds the specified rate, the tester shall either void the run or plan to correct the sample volume as outlined in section 12.3 of Method 5. Leak-checks immediately after component changes are recommended, but not required. If these leak-checks are performed, the procedure in section 8.4.2 of Method 5 (with appropriate modifications) shall be used.

8.6.2 After turning off the pump and recording the final readings at the conclusion of each run, remove the probe from the stack. Conduct a post-test (mandatory) leak-check as outlined in section 8.4.4 of Method 5 (with appropriate modifications), and record the leak rate. If the post-test leakage rate exceeds the specified acceptable rate, either correct the sample volume, as outlined in section 12.3 of Method 5, or void the run.

8.6.3 Drain the ice bath and, with the probe disconnected, purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at the average flow rate used for sampling.

NOTE: Clean ambient air can be provided by passing air through a charcoal filter. Alternatively, ambient air (without cleaning) may be used.

8.7 Calculation of Percent Isokinetic. Same as Method 5, section 8.6.

8.8 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. Treat the samples as follows:

8.8.1 Container No. 1.

8.8.1.1 If a moisture content analysis is to be performed, clean and weigh the first impinger (plus contents) to the nearest 0.5 g, and record this weight.

8.8.1.2 Transfer the contents of the first impinger to a 250-ml graduated cylinder. Rinse the probe, first impinger, all connecting glassware before the filter, and the front half of the filter holder with 80 percent isopropanol. Add the isopropanol rinse solution to the cylinder. Dilute the contents of the cylinder to 225 ml with 80 percent isopropanol, and transfer the cylinder contents to the storage container. Rinse the cylinder with 25 ml of 80 percent isopropanol, and transfer the rinse to the storage container. Add the filter to the solution in the storage container and mix. Seal the container to protect the solution against evaporation. Mark the level of liquid on the container, and identify the sample container.

8.8.2 Container No. 2.

8.8.2.1 If a moisture content analysis is to be performed, clean and weigh the second and third impingers (plus contents) to the nearest 0.5 g, and record the weights. Also, weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g, and record the weight.

8.8.2.2 Transfer the solutions from the second and third impingers to a 1-liter graduated cylinder. Rinse all connecting glassware (including back half of filter holder) between the filter and silica gel impinger with water, and add this rinse water to the cylinder. Dilute the contents of the cylinder to 950 ml with water. Transfer the solution to a storage container. Rinse the cylinder with 50 ml of water, and transfer the rinse to the storage container. Mark the level of liquid on the container. Seal and identify the sample container.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
7.1.3	Isopropanol check	Ensure acceptable level of peroxide impurities in isopropanol.
8.4, 8.5, 10.1	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.
10.2	Barium standard solution standardization	Ensure normality determination.
11.2	Replicate titrations	Ensure precision of titration determinations.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

10.1 Sampling Equipment. Same as Method 5, section 10.0.

10.2 Barium Standard Solution. Same as Method 6, section 10.5.

11.0 Analytical Procedure

11.1. Sample Loss. Same as Method 6, section 11.1.

11.2. Sample Analysis.

11.2.1 Container No. 1. Shake the container holding the isopropanol solution and the filter. If the filter breaks up, allow the fragments to settle for a few minutes before removing a sample aliquot. Pipette a 100-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 2 to 4 drops of thorin indicator, and titrate to a pink endpoint using 0.0100 N barium standard solution. Repeat the titration with a second aliquot of sample, and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater.

11.2.2 Container No. 2. Thoroughly mix the solution in the container holding the contents of the second and third impingers. Pipette a 10-ml aliquot of sample into a 250-ml Erlenmeyer flask. Add 40 ml of isopropanol, 2 to 4 drops of thorin indicator, and titrate to a pink endpoint using 0.0100 N barium standard solution. Repeat the titration with a second aliquot of sample, and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater.

11.2.3 Blanks. Prepare blanks by adding 2 to 4 drops of thorin indicator to 100 ml of 80 percent isopropanol. Titrate the blanks in the same manner as the samples.

12.0 Data Analysis and Calculations

Carry out calculations retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature. Same as Method 5, section 12.1, with the following additions and exceptions:

$C_{H_2SO_4}$ = Sulfuric acid (including SO_3) concentration, g/dscm (lb/dscf).

C_{SO_2} = Sulfur dioxide concentration, g/dscm (lb/dscf).

N = Normality of barium perchlorate titrant, meq/ml.

V_a = Volume of sample aliquot titrated, 100 ml for H_2SO_4 and 10 ml for SO_2.

V_{soln} = Total volume of solution in which the sample is contained, 1000 ml for the SO_2 sample and 250 ml for the H_2SO_4 sample.

V_t = Volume of barium standard solution titrant used for the sample, ml.

V_{tb} = Volume of barium standard solution titrant used for the blank, ml.

12.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 8–2).

12.3 Dry Gas Volume. Same as Method 5, section 12.3.

12.4 Volume of Water Vapor Condensed and Moisture Content. Calculate the volume of water vapor using Equation 5–2 of Method 5; the weight of water collected in the impingers and silica gel can be converted directly to milliliters (the specific gravity of water is 1 g/ml). Calculate the moisture content of the stack gas (B_{ws}) using Equation 5–3 of Method 5. The note in section 12.5 of Method 5 also applies to this method. Note that if the effluent gas stream can be considered dry, the volume of water vapor and moisture content need not be calculated.

12.5 Sulfuric Acid Mist (Including SO_3) Concentration.

$$C_{H_2SO_4} = K_3\left[N\left(V_t - V_{tb}\right)\left(V_{soln}/V_a\right)\right]/V_{m(std)} \qquad \text{Eq. 8-1}$$

Where:

K_3 = 0.04904 g/meq for metric units,

$K_3 = 1.081 \times 10^{-4}$ lb/meq for English units.

12.6 Sulfur Dioxide Concentration.

$$C_{SO_2} = K_4\left[N\left(V_t - V_{tb}\right)\left(V_{soln}/V_a\right)\right]/V_{m(std)} \qquad \text{Eq. 8-2}$$

Where:

K_4 = 0.03203 g/meq for metric units,

$K_4 = 7.061 \times 10^{-5}$ lb/meq for English units.

12.7 Isokinetic Variation. Same as Method 5, section 12.11.

12.8 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate, if needed, using data obtained in this method and the equations in sections 12.6 and 12.7 of Method 2.

13.0 Method Performance

13.1 Analytical Range. Collaborative tests have shown that the minimum detectable limits of the method are 0.06 mg/m^3 (4×10^{-9} lb/ft^3) for H_2SO_4 and 1.2 mg/m^3 (74×10^{-9} lb/ft^3) for SO_2. No upper limits have been established. Based on theoretical calculations for 200 ml of 3 percent H_2O_2 solution, the upper concentration limit for SO_2 in a 1.0 m^3 (35.3 ft^3) gas sample is about 12,000 mg/m^3 (7.7×10^{-4} lb/ft^3). The upper limit can be extended by increasing the quantity of peroxide solution in the impingers.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as section 17.0 of Methods 5 and 6.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

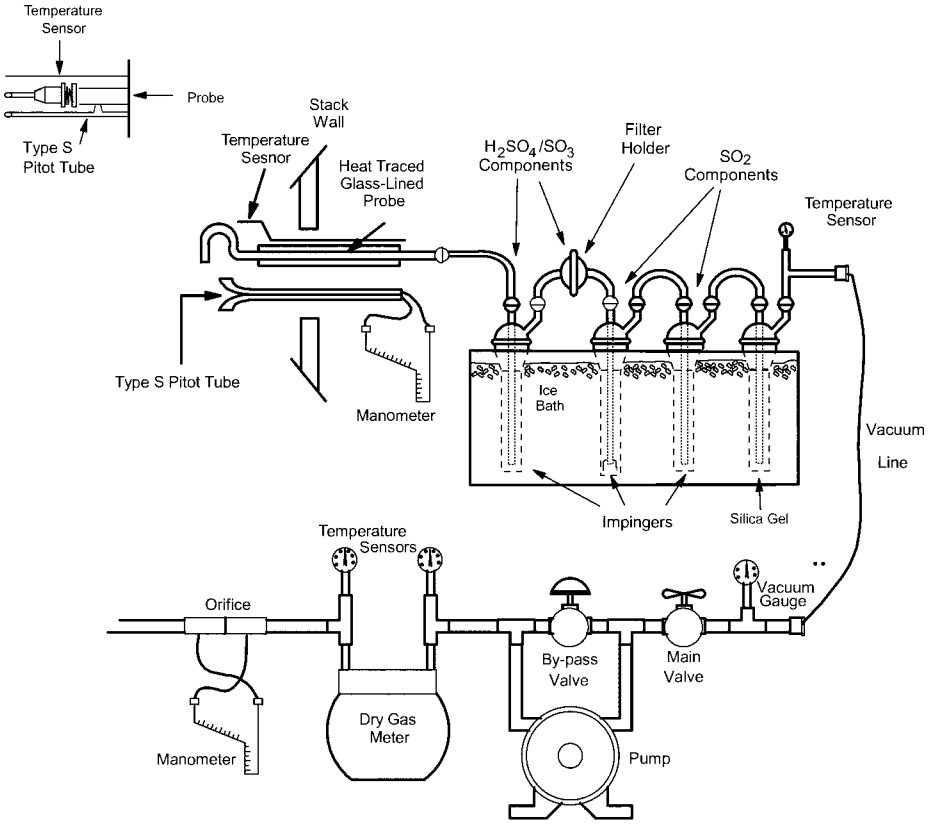

Figure 8-1. Sulfuric Acid Sampling Train

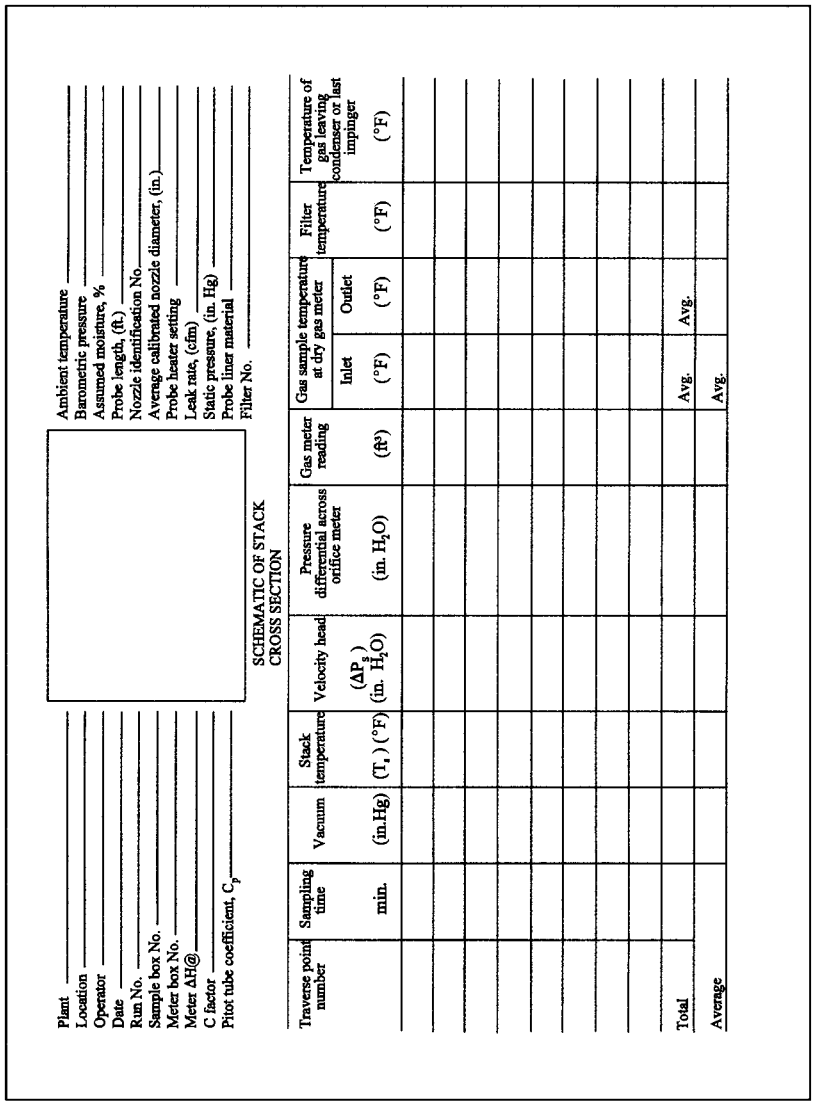

Figure 8-2. Field Data Sheet.

METHOD 9—VISUAL DETERMINATION OF THE OPACITY OF EMISSIONS FROM STATIONARY SOURCES

Many stationary sources discharge visible emissions into the atmosphere; these emissions are usually in the shape of a plume. This method involves the determination of plume opacity by qualified observers. The method includes procedures for the training and certification of observers, and procedures to be used in the field for determination of plume opacity. The appearance of a plume as viewed by an observer depends upon a number of variables, some of which may be controllable and some of which may not be controllable in the field. Variables which can be controlled to an extent to which they no longer exert a significant influence upon

plume appearance include: Angle of the observer with respect to the plume; angle of the observer with respect to the sun; point of observation of attached and detached steam plume; and angle of the observer with respect to a plume emitted from a rectangular stack with a large length to width ratio. The method includes specific criteria applicable to these variables.

Other variables which may not be controllable in the field are luminescence and color contrast between the plume and the background against which the plume is viewed. These variables exert an influence upon the appearance of a plume as viewed by an observer, and can affect the ability of the observer to accurately assign opacity values to the observed plume. Studies of the theory of plume opacity and field studies have demonstrated that a plume is most visible and presents the greatest apparent opacity when viewed against a contrasting background. It follows from this, and is confirmed by field trials, that the opacity of a plume, viewed under conditions where a contrasting background is present can be assigned with the greatest degree of accuracy. However, the potential for a positive error is also the greatest when a plume is viewed under such contrasting conditions. Under conditions presenting a less contrasting background, the apparent opacity of a plume is less and approaches zero as the color and luminescence contrast decrease toward zero. As a result, significant negative bias and negative errors can be made when a plume is viewed under less contrasting conditions. A negative bias decreases rather than increases the possibility that a plant operator will be cited for a violation of opacity standards due to observer error.

Studies have been undertaken to determine the magnitude of positive errors which can be made by qualified observers while reading plumes under contrasting conditions and using the procedures set forth in this method. The results of these studies (field trials) which involve a total of 769 sets of 25 readings each are as follows:

(1) For black plumes (133 sets at a smoke generator), 100 percent of the sets were read with a positive error[1] of less than 7.5 percent opacity; 99 percent were read with a positive error of less than 5 percent opacity.

(2) For white plumes (170 sets at a smoke generator, 168 sets at a coal-fired power plant, 298 sets at a sulfuric acid plant), 99 percent of the sets were read with a positive error of less than 7.5 percent opacity; 95 percent were read with a positive error of less than 5 percent opacity.

[1] For a set, positive error = average opacity determined by observers' 25 observations—average opacity determined from transmissometer's 25 recordings.

The positive observational error associated with an average of twenty-five readings is therefore established. The accuracy of the method must be taken into account when determining possible violations of applicable opacity standards.

1. Principle and Applicability

1.1 Principle. The opacity of emissions from stationary sources is determined visually by a qualified observer.

1.2 Applicability. This method is applicable for the determination of the opacity of emissions from stationary sources pursuant to §60.11(b) and for qualifying observers for visually determining opacity of emissions.

2. Procedures

The observer qualified in accordance with section 3 of this method shall use the following procedures for visually determining the opacity of emissions:

2.1 Position. The qualified observer shall stand at a distance sufficient to provide a clear view of the emissions with the sun oriented in the 140° sector to his back. Consistent with maintaining the above requirement, the observer shall, as much as possible, make his observations from a position such that his line of vision is approximately perpendicular to the plume direction, and when observing opacity of emissions from rectangular outlets (e.g., roof monitors, open baghouses, noncircular stacks), approximately perpendicular to the longer axis of the outlet. The observer's line of sight should not include more than one plume at a time when multiple stacks are involved, and in any case the observer should make his observations with his line of sight perpendicular to the longer axis of such a set of multiple stacks (e.g., stub stacks on baghouses).

2.2 Field Records. The observer shall record the name of the plant, emission location, type facility, observer's name and affiliation, a sketch of the observer's position relative to the source, and the date on a field data sheet (Figure 9–1). The time, estimated distance to the emission location, approximate wind direction, estimated wind speed, description of the sky condition (presence and color of clouds), and plume background are recorded on a field data sheet at the time opacity readings are initiated and completed.

2.3 Observations. Opacity observations shall be made at the point of greatest opacity in that portion of the plume where condensed water vapor is not present. The observer shall not look continuously at the plume, but instead shall observe the plume momentarily at 15-second intervals.

2.3.1 Attached Steam Plumes. When condensed water vapor is present within the

plume as it emerges from the emission outlet, opacity observations shall be made beyond the point in the plume at which condensed water vapor is no longer visible. The observer shall record the approximate distance from the emission outlet to the point in the plume at which the observations are made.

2.3.2 Detached Steam Plume. When water vapor in the plume condenses and becomes visible at a distinct distance from the emission outlet, the opacity of emissions should be evaluated at the emission outlet prior to the condensation of water vapor and the formation of the steam plume.

2.4 Recording Observations. Opacity observations shall be recorded to the nearest 5 percent at 15-second intervals on an observational record sheet. (See Figure 9–2 for an example.) A minimum of 24 observations shall be recorded. Each momentary observation recorded shall be deemed to represent the average opacity of emissions for a 15-second period.

2.5 Data Reduction. Opacity shall be determined as an average of 24 consecutive observations recorded at 15-second intervals. Divide the observations recorded on the record sheet into sets of 24 consecutive observations. A set is composed of any 24 consecutive observations. Sets need not be consecutive in time and in no case shall two sets overlap. For each set of 24 observations, calculate the average by summing the opacity of the 24 observations and dividing this sum by 24. If an applicable standard specifies an averaging time requiring more than 24 observations, calculate the average for all observations made during the specified time period. Record the average opacity on a record sheet. (See Figure 9–1 for an example.)

3. Qualifications and Testing

3.1 Certification Requirements. To receive certification as a qualified observer, a candidate must be tested and demonstrate the ability to assign opacity readings in 5 percent increments to 25 different black plumes and 25 different white plumes, with an error not to exceed 15 percent opacity on any one reading and an average error not to exceed 7.5 percent opacity in each category. Candidates shall be tested according to the procedures described in section 3.2. Smoke generators used pursuant to section 3.2 shall be equipped with a smoke meter which meets the requirements of section 3.3.

The certification shall be valid for a period of 6 months, at which time the qualification procedure must be repeated by any observer in order to retain certification.

3.2 Certification Procedure. The certification test consists of showing the candidate a complete run of 50 plumes—25 black plumes and 25 white plumes—generated by a smoke generator. Plumes within each set of 25 black and 25 white runs shall be presented in random order. The candidate assigns an opacity value to each plume and records his observation on a suitable form. At the completion of each run of 50 readings, the score of the candidate is determined. If a candidate fails to qualify, the complete run of 50 readings must be repeated in any retest. The smoke test may be administered as part of a smoke school or training program, and may be preceded by training or familiarization runs of the smoke generator during which candidates are shown black and white plumes of known opacity.

3.3 Smoke Generator Specifications. Any smoke generator used for the purposes of section 3.2 shall be equipped with a smoke meter installed to measure opacity across the diameter of the smoke generator stack. The smoke meter output shall display instack opacity based upon a pathlength equal to the stack exit diameter, on a full 0 to 100 percent chart recorder scale. The smoke meter optical design and performance shall meet the specifications shown in Table 9–1. The smoke meter shall be calibrated as prescribed in section 3.3.1 prior to the conduct of each smoke reading test. At the completion of each test, the zero and span drift shall be checked and if the drift exceeds ±1 percent opacity, the condition shall be corrected prior to conducting any subsequent test runs. The smoke meter shall be demonstrated, at the time of installation, to meet the specifications listed in Table 9–1. This demonstration shall be repeated following any subsequent repair or replacement of the photocell or associated electronic circuitry including the chart recorder or output meter, or every 6 months, whichever occurs first.

TABLE 9–1—SMOKE METER DESIGN AND PERFORMANCE SPECIFICATIONS

Parameter	Specification
a. Light source	Incandescent lamp operated at nominal rated voltage.
b. Spectral response of photocell.	Photopic (daylight spectral response of the human eye—Citation 3).
c. Angle of view	15° maximum total angle.
d. Angle of projection	15° maximum total angle.
e. Calibration error	±3% opacity, maximum.
f. Zero and span drift	±1% opacity, 30 minutes.
g. Response time	5 seconds.

3.3.1 Calibration. The smoke meter is calibrated after allowing a minimum of 30 minutes warmup by alternately producing simulated opacity of 0 percent and 100 percent. When stable response at 0 percent or 100 percent is noted, the smoke meter is adjusted to produce an output of 0 percent or 100 percent, as appropriate. This calibration shall be repeated until stable 0 percent and 100

percent readings are produced without adjustment. Simulated 0 percent and 100 percent opacity values may be produced by alternately switching the power to the light source on and off while the smoke generator is not producing smoke.

3.3.2 Smoke Meter Evaluation. The smoke meter design and performance are to be evaluated as follows:

3.3.2.1 Light Source. Verify from manufacturer's data and from voltage measurements made at the lamp, as installed, that the lamp is operated within ±5 percent of the nominal rated voltage.

3.3.2.2 Spectral Response of Photocell. Verify from manufacturer's data that the photocell has a photopic response; i.e., the spectral sensitivity of the cell shall closely approximate the standard spectral-luminosity curve for photopic vision which is referenced in (b) of Table 9–1.

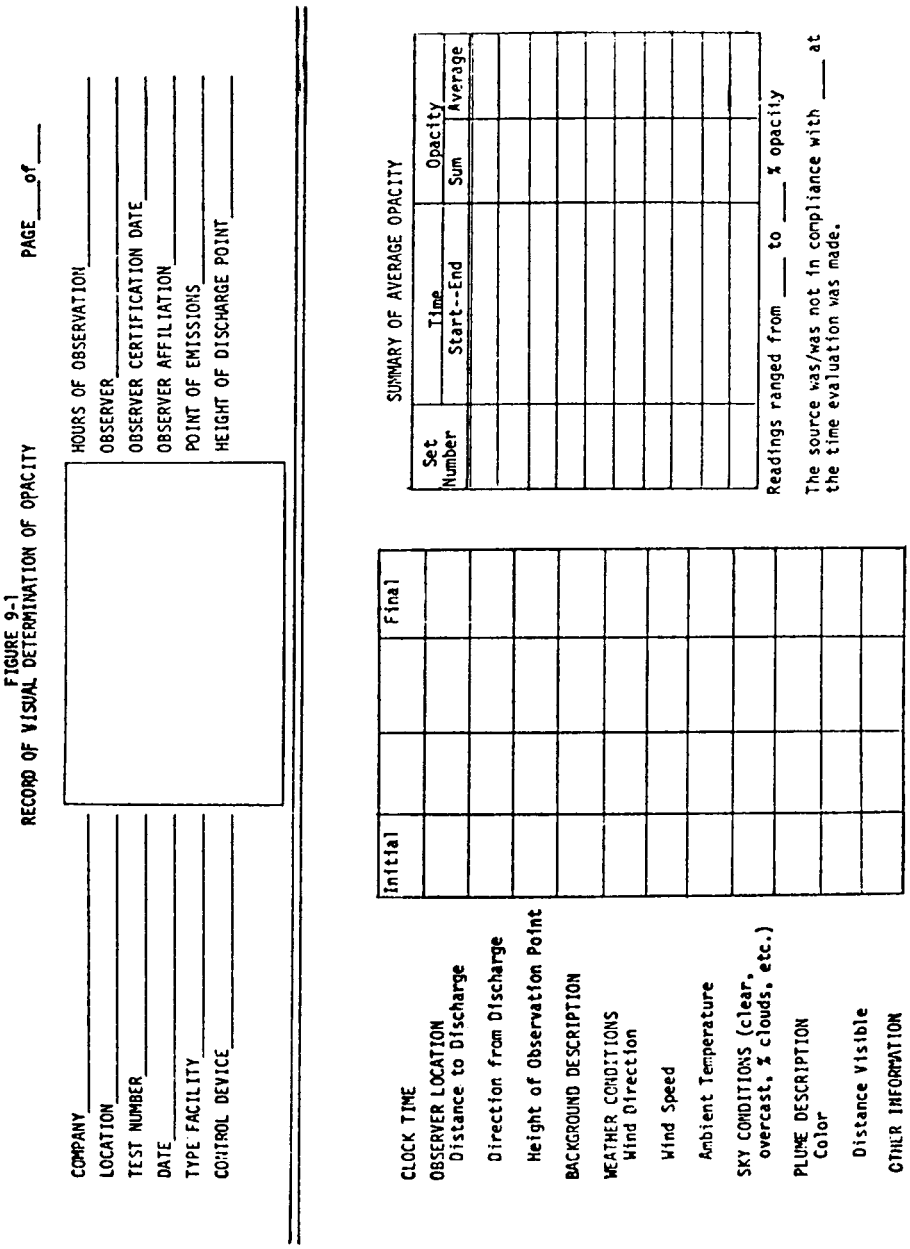

FIGURE 9–2—OBSERVATION RECORD

Page ___ of ___

Company .....
Location .....
Test Number .....
Date.

Observer .....
Type facility .....
Point of emissions .....

Hr.	Min.	Seconds				Steam plume (check if applicable)		Comments
		0	15	30	45	Attached	Detached	
	0							
	1							
	2							
	3							
	4							
	5							
	6							
	7							
	8							
	9							
	10							
	11							
	12							
	13							
	14							
	15							
	16							
	17							
	18							
	19							
	20							
	21							
	22							
	23							
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	25							
	26							
	27							
	28							
	29							

FIGURE 9–2—OBSERVATION RECORD (CONTINUED)

Page ____ of ____

Company .....
Location .....
Test Number .....
Date.

Observer .....
Type facility .....
Point of emissions .....

Hr.	Min.	Seconds				Steam plume (check if applicable)		Comments
		0	15	30	45	Attached	Detached	
	30							

Hr.	Min.	Seconds				Steam plume (check if applicable)		Comments
		0	15	30	45	Attached	Detached	
	31							
	32							
	33							
	34							
	35							
	36							
	37							
	38							
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3.3.2.3 Angle of View. Check construction geometry to ensure that the total angle of view of the smoke plume, as seen by the photocell, does not exceed 15°. The total angle of view may be calculated from: $\theta = 2 \tan^{-1} d/2L$, where θ = total angle of view; d = the sum of the photocell diameter + the diameter of the limiting aperture; and L = the distance from the photocell to the limiting aperture. The limiting aperture is the point in the path between the photocell and the smoke plume where the angle of view is most restricted. In smoke generator smoke meters this is normally an orifice plate.

3.3.2.4 Angle of Projection. Check construction geometry to ensure that the total angle of projection of the lamp on the smoke plume does not exceed 15°. The total angle of projection may be calculated from: $\theta = 2 \tan^{-1} d/2L$, where θ = total angle of projection; d = the sum of the length of the lamp

filament + the diameter of the limiting aperture; and L = the distance from the lamp to the limiting aperture.

3.3.2.5 Calibration Error. Using neutral-density filters of known opacity, check the error between the actual response and the theoretical linear response of the smoke meter. This check is accomplished by first calibrating the smoke meter according to 3.3.1 and then inserting a series of three neutral-density filters of nominal opacity of 20, 50, and 75 percent in the smoke meter pathlength. Filters calibrated within ±2 percent shall be used. Care should be taken when inserting the filters to prevent stray light from affecting the meter. Make a total of five nonconsecutive readings for each filter. The maximum error on any one reading shall be 3 percent opacity.

3.3.2.6 Zero and Span Drift. Determine the zero and span drift by calibrating and operating the smoke generator in a normal manner over a 1-hour period. The drift is measured by checking the zero and span at the end of this period.

3.3.2.7 Response Time. Determine the response time by producing the series of five simulated 0 percent and 100 percent opacity values and observing the time required to reach stable response. Opacity values of 0 percent and 100 percent may be simulated by alternately switching the power to the light source off and on while the smoke generator is not operating.

4. Bibliography

1. Air Pollution Control District Rules and Regulations, Los Angeles County Air Pollution Control District, Regulation IV, Prohibitions, Rule 50.

2. Weisburd, Melvin I., Field Operations and Enforcement Manual for Air, U.S. Environmental Protection Agency, Research Triangle Park, NC. APTD–1100, August 1972, pp. 4.1–4.36.

3. Condon, E.U., and Odishaw, H., Handbook of Physics, McGraw-Hill Co., New York, NY, 1958, Table 3.1, p. 6–52.

Alternate Method 1—Determination of the Opacity of Emissions From Stationary Sources Remotely by Lidar

This alternate method provides the quantitative determination of the opacity of an emissions plume remotely by a mobile lidar system (laser radar; Light Detection and Ranging). The method includes procedures for the calibration of the lidar and procedures to be used in the field for the lidar determination of plume opacity. The lidar is used to measure plume opacity during either day or nighttime hours because it contains its own pulsed light source or transmitter. The operation of the lidar is not dependent upon ambient lighting conditions (light, dark, sunny or cloudy).

The lidar mechanism or technique is applicable to measuring plume opacity at numerous wavelengths of laser radiation. However, the performance evaluation and calibration test results given in support of this method apply only to a lidar that employs a ruby (red light) laser [Reference 5.1].

1. Principle and Applicability

1.1 Principle. The opacity of visible emissions from stationary sources (stacks, roof vents, etc.) is measured remotely by a mobile lidar (laser radar).

1.2 Applicability. This method is applicable for the remote measurement of the opacity of visible emissions from stationary sources during both nighttime and daylight conditions, pursuant to 40 CFR §60.11(b). It is also applicable for the calibration and performance verification of the mobile lidar for the measurement of the opacity of emissions. A performance/design specification for a basic lidar system is also incorporated into this method.

1.3 Definitions.

Azimuth angle: The angle in the horizontal plane that designates where the laser beam is pointed. It is measured from an arbitrary fixed reference line in that plane.

Backscatter: The scattering of laser light in a direction opposite to that of the incident laser beam due to reflection from particulates along the beam's atmospheric path which may include a smoke plume.

Backscatter signal: The general term for the lidar return signal which results from laser light being backscattered by atmospheric and smoke plume particulates.

Convergence distance: The distance from the lidar to the point of overlap of the lidar receiver's field-of-view and the laser beam.

Elevation angle: The angle of inclination of the laser beam referenced to the horizontal plane.

Far region: The region of the atmosphere's path along the lidar line-of-sight beyond or behind the plume being measured.

Lidar: Acronym for Light Detection and Ranging.

Lidar range: The range or distance from the lidar to a point of interest along the lidar line-of-sight.

Near region: The region of the atmospheric path along the lidar line-of-sight between the lidar's convergence distance and the plume being measured.

Opacity: One minus the optical transmittance of a smoke plume, screen target, etc.

Pick interval: The time or range intervals in the lidar backscatter signal whose minimum average amplitude is used to calculate opacity. Two pick intervals are required, one in the near region and one in the far region.

Plume: The plume being measured by lidar.

Plume signal: The backscatter signal resulting from the laser light pulse passing through a plume.

$1/R^2$Correction: The correction made for the systematic decrease in lidar backscatter signal amplitude with range.

Reference signal: The backscatter signal resulting from the laser light pulse passing through ambient air.

Sample interval: The time period between successive samples for a digital signal or between successive measurements for an analog signal.

Signal spike: An abrupt, momentary increase and decrease in signal amplitude.

Source: The source being tested by lidar.

Time reference: The time (t_o) when the laser pulse emerges from the laser, used as the reference in all lidar time or range measurements.

2. Procedures

The mobile lidar calibrated in accordance with Paragraph 3 of this method shall use the following procedures for remotely measuring the opacity of stationary source emissions:

2.1 Lidar Position. The lidar shall be positioned at a distance from the plume sufficient to provide an unobstructed view of the source emissions. The plume must be at a range of at least 50 meters or three consecutive pick intervals (whichever is greater) from the lidar's transmitter/receiver convergence distance along the line-of-sight. The maximum effective opacity measurement distance of the lidar is a function of local atmospheric conditions, laser beam diameter, and plume diameter. The test position of the lidar shall be selected so that the diameter of the laser beam at the measurement point within the plume shall be no larger than three-fourths the plume diameter. The beam diameter is calculated by Equation (AM1–1):

$$D(\text{lidar}) = A + R\varphi \leq 0.75\ D(\text{Plume}) \quad \text{(AM1–1)}$$

Where:

D(Plume) = diameter of the plume (cm),
φ = laser beam divergence measured in radians
R = range from the lidar to the source (cm)
D(Lidar) = diameter of the laser beam at range R (cm),
A = diameter of the laser beam or pulse where it leaves the laser.

The lidar range, R, is obtained by aiming and firing the laser at the emissions source structure immediately below the outlet. The range value is then determined from the backscatter signal which consists of a signal spike (return from source structure) and the atmospheric backscatter signal [Reference 5.1]. This backscatter signal should be recorded.

When there is more than one source of emissions in the immediate vicinity of the plume, the lidar shall be positioned so that the laser beam passes through only a single plume, free from any interference of the other plumes for a minimum of 50 meters or three consecutive pick intervals (whichever is greater) in each region before and beyond the plume along the line-of-sight (determined from the backscatter signals). The lidar shall initially be positioned so that its line-of-sight is approximately perpendicular to the plume.

When measuring the opacity of emissions from rectangular outlets (e.g., roof monitors, open baghouses, noncircular stacks, etc.), the lidar shall be placed in a position so that its line-of-sight is approximately perpendicular to the longer (major) axis of the outlet.

2.2 Lidar Operational Restrictions. The lidar receiver shall not be aimed within an angle of ±15° (cone angle) of the sun.

This method shall not be used to make opacity measurements if thunderstorms, snowstorms, hail storms, high wind, high-ambient dust levels, fog or other atmospheric conditions cause the reference signals to consistently exceed the limits specified in section 2.3.

2.3 Reference Signal Requirements. Once placed in its proper position for opacity measurement, the laser is aimed and fired with the line-of-sight near the outlet height and rotated horizontally to a position clear of the source structure and the associated plume. The backscatter signal obtained from this position is called the ambient-air or reference signal. The lidar operator shall inspect this signal [Section V of Reference 5.1] to: (1) determine if the lidar line-of-sight is free from interference from other plumes and from physical obstructions such as cables, power lines, etc., for a minimum of 50 meters or three consecutive pick intervals (whichever is greater) in each region before and beyond the plume, and (2) obtain a qualitative measure of the homogeneity of the ambient air by noting any signal spikes.

Should there be any signal spikes on the reference signal within a minimum of 50 meters or three consecutive pick intervals (whichever is greater) in each region before and beyond the plume, the laser shall be fired three more times and the operator shall inspect the reference signals on the display. If the spike(s) remains, the azimuth angle shall be changed and the above procedures conducted again. If the spike(s) disappears in all three reference signals, the lidar line-of-sight is acceptable if there is shot-to-shot consistency and there is no interference from other plumes.

Shot-to-shot consistency of a series of reference signals over a period of twenty seconds is verified in either of two ways. (1) The lidar operator shall observe the reference signal amplitudes. For shot-to-shot consistency the ratio of R_f to R_n [amplitudes of the near and far region pick intervals (Section 2.6.1)] shall vary by not more than ±6% between shots; or (2) the lidar operator shall accept any one of the reference signals and

treat the other two as plume signals; then the opacity for each of the subsequent reference signals is calculated (Equation AM1–2). For shot-to-shot consistency, the opacity values shall be within ±3% of 0% opacity and the associated S_o values less than or equal to 8% (full scale) [Section 2.6].

If a set of reference signals fails to meet the requirements of this section, then all plume signals [Section 2.4] from the last set of acceptable reference signals to the failed set shall be discarded.

2.3.1 Initial and Final Reference Signals. Three reference signals shall be obtained within a 90-second time period prior to any data run. A final set of three reference signals shall be obtained within three (3) minutes after the completion of the same data run.

2.3.2 Temporal Criterion for Additional Reference Signals. An additional set of reference signals shall be obtained during a data run if there is a change in wind direction or plume drift of 30° or more from the direction that was prevalent when the last set of reference signals was obtained. An additional set of reference signals shall also be obtained if there is an increase in value of S_{In} (near region standard deviation, Equation AM1–5) or S_{If} (far region standard deviation, Equation AM1–6) that is greater than 6% (full scale) over the respective values calculated from the immediately previous plume signal, and this increase in value remains for 30 seconds or longer. An additional set of reference signals shall also be obtained if there is a change in amplitude in either the near or the far region of the plume signal, that is greater than 6% of the near signal amplitude and this change in amplitude remains for 30 seconds or more.

2.4 Plume Signal Requirements. Once properly aimed, the lidar is placed in operation with the nominal pulse or firing rate of six pulses/minute (1 pulse/10 seconds). The lidar operator shall observe the plume backscatter signals to determine the need for additional reference signals as required by section 2.3.2. The plume signals are recorded from lidar start to stop and are called a data run. The length of a data run is determined by operator discretion. Short-term stops of the lidar to record additional reference signals do not constitute the end of a data run if plume signals are resumed within 90 seconds after the reference signals have been recorded, and the total stop or interrupt time does not exceed 3 minutes.

2.4.1 Non-hydrated Plumes. The laser shall be aimed at the region of the plume which displays the greatest opacity. The lidar operator must visually verify that the laser is aimed clearly above the source exit structure.

2.4.2 Hydrated Plumes. The lidar will be used to measure the opacity of hydrated or so-called steam plumes. As listed in the reference method, there are two types, i.e., attached and detached steam plumes.

2.4.2.1 Attached Steam Plumes. When condensed water vapor is present within a plume, lidar opacity measurements shall be made at a point within the residual plume where the condensed water vapor is no longer visible. The laser shall be aimed into the most dense region (region of highest opacity) of the residual plume.

During daylight hours the lidar operator locates the most dense portion of the residual plume visually. During nighttime hours a high-intensity spotlight, night vision scope, or low light level TV, etc., can be used as an aid to locate the residual plume. If visual determination is ineffective, the lidar may be used to locate the most dense region of the residual plume by repeatedly measuring opacity, along the longitudinal axis or center of the plume from the emissions outlet to a point just beyond the steam plume. The lidar operator should also observe color differences and plume reflectivity to ensure that the lidar is aimed completely within the residual plume. If the operator does not obtain a clear indication of the location of the residual plume, this method shall not be used.

Once the region of highest opacity of the residual plume has been located, aiming adjustments shall be made to the laser line-of-sight to correct for the following: movement to the region of highest opacity out of the lidar line-of-sight (away from the laser beam) for more than 15 seconds, expansion of the steam plume (air temperature lowers and/or relative humidity increases) so that it just begins to encroach on the field-of-view of the lidar's optical telescope receiver, or a decrease in the size of the steam plume (air temperature higher and/or relative humidity decreases) so that regions within the residual plume whose opacity is higher than the one being monitored, are present.

2.4.2.2 Detached Steam Plumes. When the water vapor in a hydrated plume condenses and becomes visible at a finite distance from the stack or source emissions outlet, the opacity of the emissions shall be measured in the region of the plume clearly above the emissions outlet and below condensation of the water vapor.

During daylight hours the lidar operators can visually determine if the steam plume is detached from the stack outlet. During nighttime hours a high-intensity spotlight, night vision scope, low light level TV, etc., can be used as an aid in determining if the steam plume is detached. If visual determination is ineffective, the lidar may be used to determine if the steam plume is detached by repeatedly measuring plume opacity from the outlet to the steam plume along the plume's longitudinal axis or center line. The lidar operator should also observe color differences and plume reflectivity to detect a

detached plume. If the operator does not obtain a clear indication of the location of the detached plume, this method shall not be used to make opacity measurements between the outlet and the detached plume.

Once the determination of a detached steam plume has been confirmed, the laser shall be aimed into the region of highest opacity in the plume between the outlet and the formation of the steam plume. Aiming adjustments shall be made to the lidar's line-of-sight within the plume to correct for changes in the location of the most dense region of the plume due to changes in wind direction and speed or if the detached steam plume moves closer to the source outlet encroaching on the most dense region of the plume. If the detached steam plume should move too close to the source outlet for the lidar to make interference-free opacity measurements, this method shall not be used.

2.5 Field Records. In addition to the recording recommendations listed in other sections of this method the following records should be maintained. Each plume measured should be uniquely identified. The name of the facility, type of facility, emission source type, geographic location of the lidar with respect to the plume, and plume characteristics should be recorded. The date of the test, the time period that a source was monitored, the time (to the nearest second) of each opacity measurement, and the sample interval should also be recorded. The wind speed, wind direction, air temperature, relative humidity, visibility (measured at the lidar's position), and cloud cover should be recorded at the beginning and end of each time period for a given source. A small sketch depicting the location of the laser beam within the plume should be recorded.

If a detached or attached steam plume is present at the emissions source, this fact should be recorded. Figures AM1–I and AM1–II are examples of logbook forms that may be used to record this type of data. Magnetic tape or paper tape may also be used to record data.

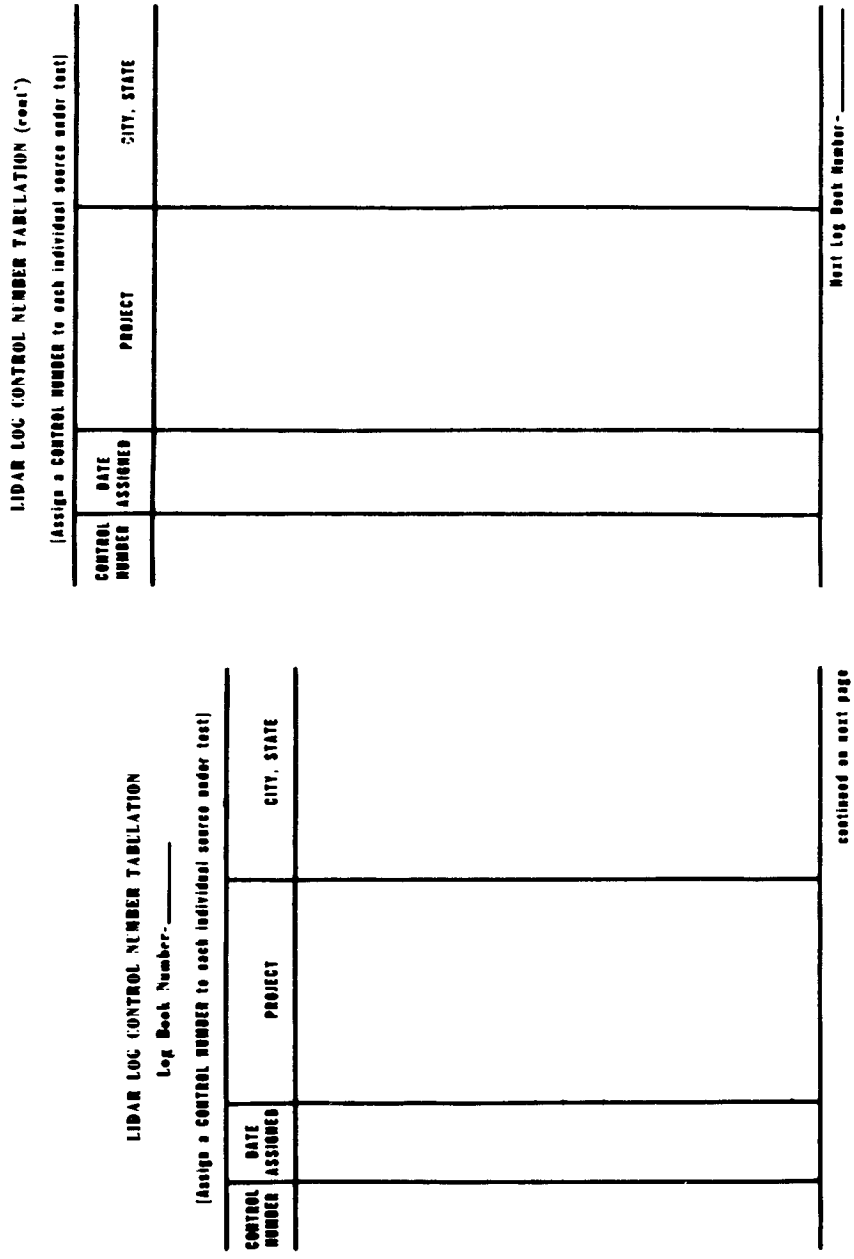


Figure AM1-1 Lidar Log Control Number Tabulation

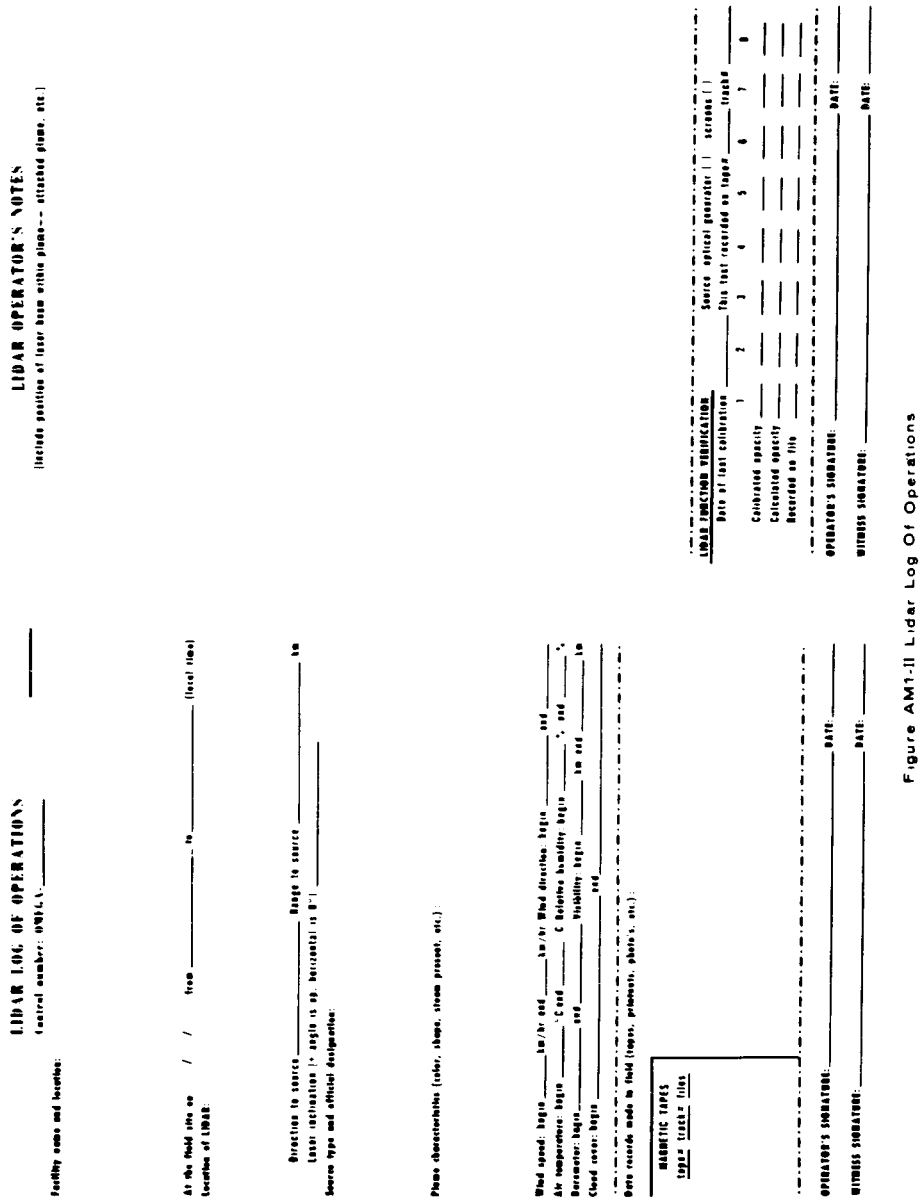
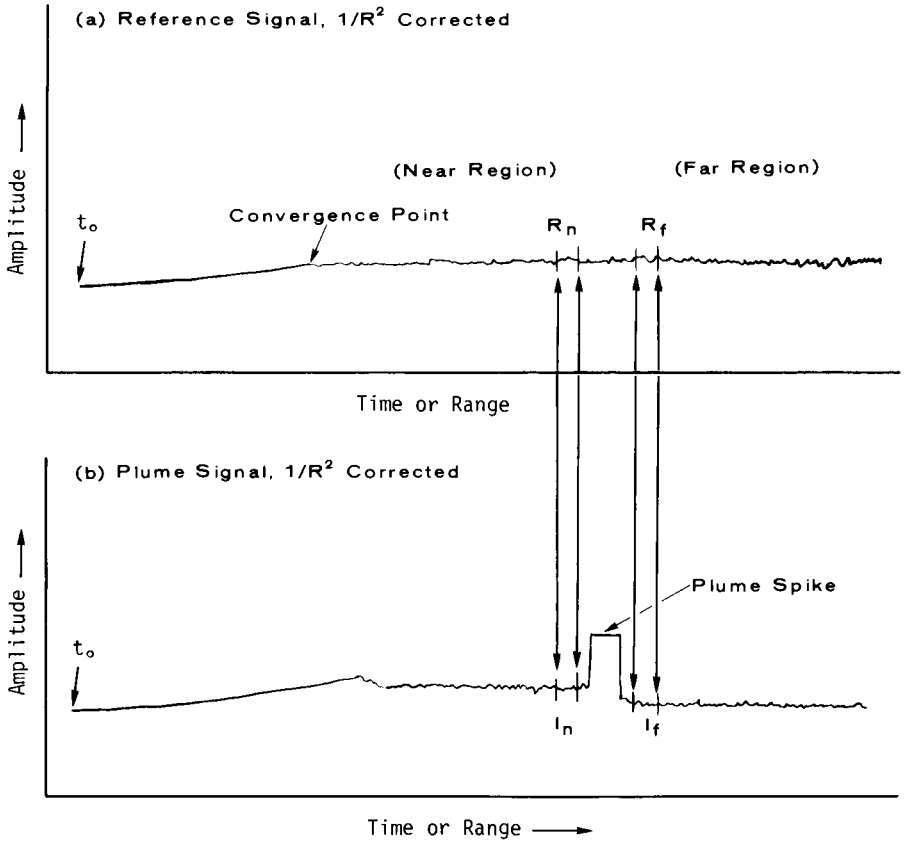


Figure AM1-11 Lidar Log Of Operations



(a) Reference signal, $1/R^2$-corrected. This reference signal is for plume signal (b). R_n, R_f are chosen to coincide with I_n, I_f.

(b) Plume signal, $1/R^2$-corrected. The plume spike and the decrease in the backscatter signal amplitude in the far region are due to the opacity of the plume. I_n, I_f are chosen as indicated in Section 2.6.

Figure AM1-III. Plots of Lidar Backscatter Signals

2.6 Opacity Calculation and Data Analysis. Referring to the reference signal and plume signal in Figure AM1–III, the measured opacity (O_p) in percent for each lidar measurement is calculated using Equation AM1–2. ($O_p = 1 - T_p$; T_p is the plume transmittance.)

$$O_p = (100\%)\left[1 - \left(\frac{I_f}{R_f}\frac{R_n}{I_n}\right)^{\frac{1}{2}}\right], \quad \text{(AM1-2)}$$

Where:

I_n = near-region pick interval signal amplitude, plume signal, $1/R^2$ corrected,

I_f = far-region pick interval signal amplitude, plume signal, $1/R^2$ corrected,

R_n = near-region pick interval signal amplitude, reference signal, $1/R^2$ corrected, and

R_f = far-region pick interval signal amplitude, reference signal, $1/R^2$ corrected.

The $1/R^2$ correction to the plume and reference signal amplitudes is made by multiplying the amplitude for each successive sample interval from the time reference, by the square of the lidar time (or range) associated with that sample interval [Reference 5.1].

The first step in selecting the pick intervals for Equation AM1–2 is to divide the plume signal amplitude by the reference signal amplitude at the same respective ranges to obtain a ''normalized'' signal. The pick intervals selected using this normalized signal, are a minimum of 15 m (100 nanoseconds) in length and consist of at least 5 contiguous sample intervals. In addition, the following criteria, listed in order of importance, govern pick interval selection. (1) The intervals shall be in a region of the normalized signal where the reference signal meets the requirements of section 2.3 and is everywhere greater than zero. (2) The intervals (near and far) with the minimum average amplitude are chosen. (3) If more than one interval with the same minimum average amplitude is found, the interval closest to the plume is chosen. (4) The standard deviation, S_o, for the calculated opacity shall be 8% or less. (S_o is calculated by Equation AM1–7).

If S_o is greater than 8%, then the far pick interval shall be changed to the next interval of minimal average amplitude. If S_o is still greater than 8%, then this procedure is repeated for the far pick interval. This procedure may be repeated once again for the near pick interval, but if S_o remains greater than 8%, the plume signal shall be discarded.

The reference signal pick intervals, R_n and R_f, must be chosen over the same time interval as the plume signal pick intervals, I_n and I_f, respectively [Figure AM1–III]. Other methods of selecting pick intervals may be used if they give equivalent results. Field-oriented examples of pick interval selection are available in Reference 5.1.

The average amplitudes for each of the pick intervals, I_n, I_f, R_n, R_f, shall be calculated by averaging the respective individual amplitudes of the sample intervals from the plume signal and the associated reference signal each corrected for $1/R^2$. The amplitude of I_n shall be calculated according to Equation (AM–3).

$$I_n = \frac{1}{m}\sum_{i=1}^{m} I_{ni}, \quad \text{(AM1-3)}$$

Where:

I_{ni} = the amplitude of the ith sample interval (near-region),

Σ = sum of the individual amplitudes for the sample intervals,

m = number of sample intervals in the pick interval, and

I_n = average amplitude of the near-region pick interval.

Similarly, the amplitudes for I_f, R_n, and R_f are calculated with the three expressions in Equation (AM1–4).

$$I_f = \frac{1}{m}\sum_{i=1}^{m} I_{fi}, \quad R_n = \frac{1}{m}\sum_{i=1}^{m} R_{ni}, \quad R_f = \frac{1}{m}\sum_{i=1}^{m} R_{fi}. \quad \text{(AM1-4)}$$

The standard deviation, S_{In}, of the set of amplitudes for the near-region pick interval, I_n, shall be calculated using Equation (AM1–5).

Similarly, the standard deviations S_{If}, S_{Rn}, and S_{Rf} are calculated with the three expressions in Equation (AM1–6).

$$S_{In} = \left[\sum_{i=1}^{m} \frac{(I_{ni} - I_n)^2}{(m-1)} \right]^{1/2} \qquad S_{If} = \left[\sum_{i=1}^{m} \frac{(I_{fi} - I_f)^2}{(m-1)} \right]^{1/2} \tag{AM1-5}$$

$$S_{Rn} = \left[\sum_{i=1}^{m} \frac{(R_{ni} - R_n)^2}{(m-1)} \right]^{1/2},$$

$$S_{Rf} = \left[\sum_{i=1}^{m} \frac{(R_{fi} - R_f)^2}{(m-1)} \right]^{1/2}. \tag{AM1-6}$$

The standard deviation, S_o, for each associated opacity value, O_p, shall be calculated using Equation (AM1–7).

$$S_o = \frac{(100\%)}{2} \left(\frac{I_f}{R_f} \frac{R_n}{I_n} \right)^{1/2} \left[\frac{S_{In}^2}{I_n^2} + \frac{S_{If}^2}{I_f^2} + \frac{S_{Rn}^2}{R_n^2} + \frac{S_{Rf}^2}{R_f^2} \right]^{1/2} \tag{AM1-7}$$

The calculated values of I_n, I_f, R_n, R_f, S_{In}, S_{If}, S_{Rn}, S_{Rf}, O_p, and S_o should be recorded. Any plume signal with an S_o greater than 8% shall be discarded.

2.6.1 Azimuth Angle Correction. If the azimuth angle correction to opacity specified in this section is performed, then the elevation angle correction specified in section 2.6.2 shall not be performed. When opacity is measured in the residual region of an attached steam plume, and the lidar line-of-sight is not perpendicular to the plume, it may be necessary to correct the opacity measured by the lidar to obtain the opacity that would be measured on a path perpendicular to the plume. The following method, or any other method which produces equivalent results, shall be used to determine the need for a correction, to calculate the correction, and to document the point within the plume at which the opacity was measured.

Figure AM1–IV(b) shows the geometry of the opacity correction. L′ is the path through the plume along which the opacity measurement is made. P′ is the path perpendicular to the plume at the same point. The angle ε is the angle between L′ and the plume center line. The angle (π/2-ε), is the angle between the L′ and P′. The measured opacity, O_p, measured along the path L′ shall be corrected to obtain the corrected opacity, O_{pc}, for the path P′, using Equation (AM1–8).

$$O_{pc} = (100\%) \left[1 - (1 - 0.01\, O_p)^{\mathrm{Cos}\,(\pi/2-\varepsilon)} \right]$$

$$= (100\%) \left[1 - (1 - 0.01\, O_p)^{\mathrm{Sin}\,\varepsilon} \right] \tag{AM1-8}$$

The correction in Equation (AM1–8) shall be performed if the inequality in Equation (AM1–9) is true.

$$\varepsilon \geq \text{Sin}^{-1}\left[\frac{\ln (101 - 0_p)}{\ln (100 - 0_p)}\right] \qquad \text{(AM1-9)}$$

Figure AM1–IV(a) shows the geometry used to calculate ε and the position in the plume at which the lidar measurement is made. This analysis assumes that for a given lidar measurement, the range from the lidar to the plume, the elevation angle of the lidar from the horizontal plane, and the azimuth angle of the lidar from an arbitrary fixed reference in the horizontal plane can all be obtained directly.

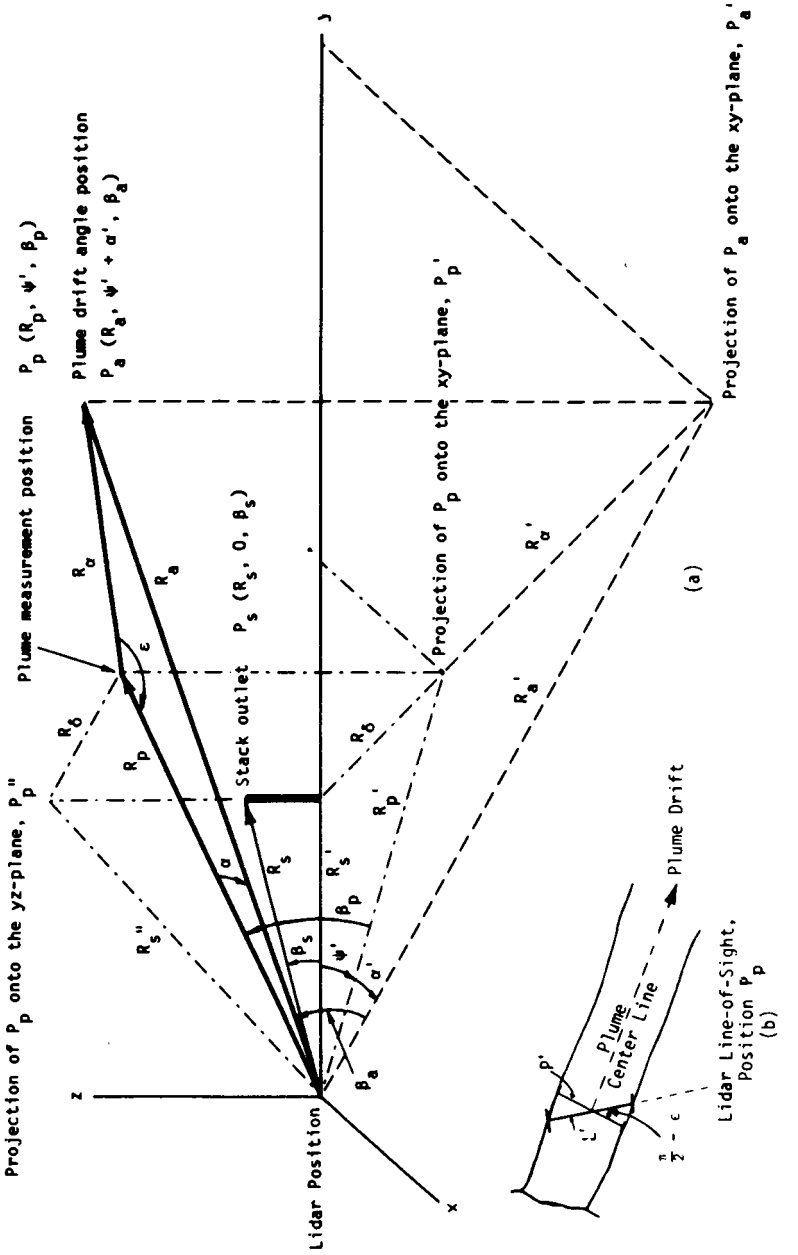


Figure AMI - IV. Correction in Opacity for Drift of the Residual Region of an Attached Steam Plume.

R_s = range from lidar to source*
β_s = elevation angle of R_s*
R_p = range from lidar to plume at the opacity measurement point*
β_p = elevation angle of R_p*
R_a = range from lidar to plume at some arbitrary point, P_a, so the drift angle of the plume can be determined*

β_a = elevation angle of R_a*
α = angle between R_p and R_a
R'_s = projection of R_s in the horizontal plane
R'_p = projection of R_p in the horizontal plane
R'_a = projection of R_a in the horizontal plane
ψ' = angle between R'_s and R'_p*
α' = angle between R'_p and R'_a*
R≤ = distance from the source to the opacity measurement point projected in the horizontal plane
Rθ = distance from opacity measurement point P_p to the point in the plume P_a.

$$O_{pc} = 1 - (1 - O_p)^{\mathrm{Cos}\,(\pi/2-\varepsilon)} = 1 - (1 - O_p)^{\mathrm{Sin}\,\varepsilon} \qquad \text{(AMI-8)}$$

The correction angle ε shall be determined using Equation AM1–10.

Where:

$\alpha = \mathrm{Cos}^{-1}\,(\mathrm{Cos}\beta_p\,\mathrm{Cos}\beta_a\,\mathrm{Cos}\alpha' + \mathrm{Sin}\beta_p\,\mathrm{Sin}\beta_a)$, and

$R\theta = (R_p 2 + R_a 2 - 2\,R_p\,R_a\,\mathrm{Cos}\alpha)^{1/2}$

R≤, the distance from the source to the opacity measurement point projected in the horizontal plane, shall be determined using Equation AM1–11.

$$R_\delta = (R'^2_s + R'^2_p - 2R'_sR'_p\mathrm{Cos}\psi')^{\frac{1}{2}}, \qquad \text{(AM1-11)}$$

Where:

$R'_s = R_s\,\mathrm{Cos}\,\beta_s$, and
$R'_p = R_p\,\mathrm{Cos}\,\beta_p$.

In the special case where the plume centerline at the opacity measurement point is horizontal, parallel to the ground, Equation AM1–12 may be used to determine ε instead of Equation AM1–10.

$$\varepsilon = \mathrm{Cos}^{-1}\left[\frac{R_p^2 + R_\delta^2 - R''^2_s}{2\,R_p\,R_\delta}\right] \qquad \text{(AM1-12)}$$

Where:

$R''_s = (R'^2_s + R_p^2\mathrm{Sin}^2\beta_p)^{1/2}$.

If the angle ε is such that ε≤30° or ε ≥150°, the azimuth angle correction shall not be performed and the associated opacity value shall be discarded.

2.6.2 Elevation Angle Correction. An individual lidar-measured opacity, O_p, shall be corrected for elevation angle if the laser elevation or inclination angle, β_p [Figure AM1–V], is greater than or equal to the value calculated in Equation AM1–13.

$$\beta_p \geq \mathrm{Cos}^{-1}\left[\frac{\ln\,(101 - O_p)}{\ln\,(100 - O_p)}\right] \qquad \text{(AM1-13)}$$

The measured opacity, O_p, along the lidar path L, is adjusted to obtain the corrected opacity, O_{pc}, for the actual plume (horizontal) path, P, by using Equation (AM1–14).

*Obtained directly from lidar. These values should be recorded.

$$O_{pc} = (100\%)\left[1-\left(1-0.01\,O_p\right)^{Cos\beta}p\right], \qquad (AM1\text{-}14)$$

Where:

β_p = lidar elevation or inclination angle,
O_p = measured opacity along path L, and
O_{pc} = corrected opacity for the actual plume thickness P.

The values for β_p, O_p and O_{pc} should be recorded.

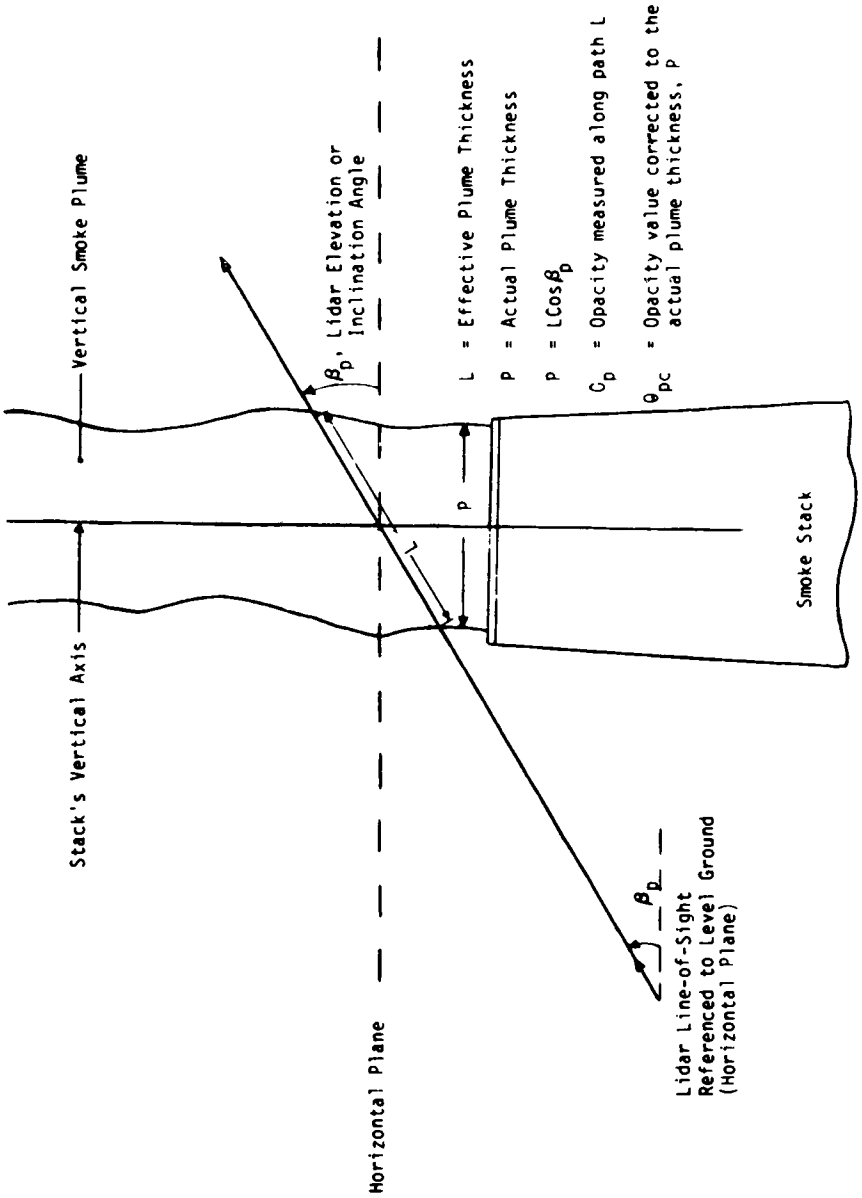


Figure AM1-V. Elevation Angle Correction for Vertical Plumes.

2.6.3 Determination of Actual Plume Opacity. Actual opacity of the plume shall be determined by Equation AM1–15.

$$O_{pa} = O_{pc} - [2\ S_o + 5\%]. \quad \text{(AM1-15)}$$

2.6.4 Calculation of Average Actual Plume Opacity. The average of the actual plume opacity, O_{pa}, shall be calculated as the average of the consecutive individual actual opacity values, O_{pa}, by Equation AM1–16.

$$\bar{O}_{pa} = \frac{1}{n}\sum_{k=1}^{n}(O_{pa})_k \quad , \qquad \text{(AM1-16)}$$

Where:

$(O_{pa})_k$ = the kth actual opacity value in an averaging interval containing n opacity values; k is a summing index.

Σ = the sum of the individual actual opacity values.

n = the number of individual actual opacity values contained in the averaging interval.

O_{pa} = average actual opacity calculated over the averaging interval.

3. Lidar Performance Verification

The lidar shall be subjected to two types of performance verifications that shall be performed in the field. The annual calibration, conducted at least once a year, shall be used to directly verify operation and performance of the entire lidar system. The routine verification, conducted for each emission source measured, shall be used to insure proper performance of the optical receiver and associated electronics.

3.1 Annual Calibration Procedures. Either a plume from a smoke generator or screen targets shall be used to conduct this calibration.

If the screen target method is selected, five screens shall be fabricated by placing an opaque mesh material over a narrow frame (wood, metal extrusion, etc.). The screen shall have a surface area of at least one square meter. The screen material should be chosen for precise optical opacities of about 10, 20, 40, 60, and 80%. Opacity of each target shall be optically determined and should be recorded. If a smoke generator plume is selected, it shall meet the requirements of section 3.3 of Reference Method 9. This calibration shall be performed in the field during calm (as practical) atmospheric conditions. The lidar shall be positioned in accordance with section 2.1.

The screen targets must be placed perpendicular to and coincident with the lidar line-of-sight at sufficient height above the ground (suggest about 30 ft) to avoid ground-level dust contamination. Reference signals shall be obtained just prior to conducting the calibration test.

The lidar shall be aimed through the center of the plume within 1 stack diameter of the exit, or through the geometric center of the screen target selected. The lidar shall be set in operation for a 6-minute data run at a nominal pulse rate of 1 pulse every 10 seconds. Each backscatter return signal and each respective opacity value obtained from the smoke generator transmissometer, shall be obtained in temporal coincidence. The data shall be analyzed and reduced in accordance with section 2.6 of this method. This calibration shall be performed for 0% (clean air), and at least five other opacities (nominally 10, 20, 40, 60, and 80%).

The average of the lidar opacity values obtained during a 6-minute calibration run shall be calculated and should be recorded. Also the average of the opacity values obtained from the smoke generator transmissometer for the same 6-minute run shall be calculated and should be recorded.

Alternate calibration procedures that do not meet the above requirements but produce equivalent results may be used.

3.2 Routine Verification Procedures. Either one of two techniques shall be used to conduct this verification. It shall be performed at least once every 4 hours for each emission source measured. The following parameters shall be directly verified.

1) The opacity value of 0% plus a minimum of 5 (nominally 10, 20, 40, 60, and 80%) opacity values shall be verified through the PMT detector and data processing electronics.

2) The zero-signal level (receiver signal with no optical signal from the source present) shall be inspected to insure that no spurious noise is present in the signal. With the entire lidar receiver and analog/digital electronics turned on and adjusted for normal operating performance, the following procedures shall be used for Techniques 1 and 2, respectively.

3.2.1 Procedure for Technique 1. This test shall be performed with no ambient or stray light reaching the PMT detector. The narrow band filter (694.3 nanometers peak) shall be removed from its position in front of the PMT detector. Neutral density filters of nominal opacities of 10, 20, 40, 60, and 80% shall be used. The recommended test configuration is depicted in Figure AM1–VI.

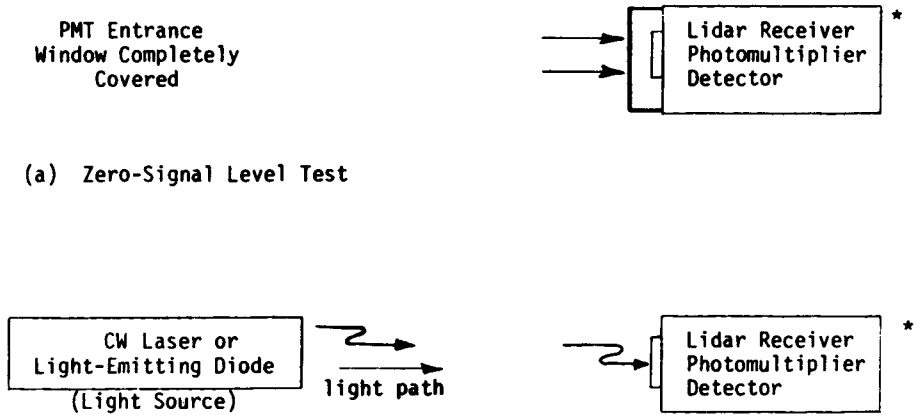


Figure AM1–VI. Test Configuration for Technique 1.

The zero-signal level shall be measured and should be recorded, as indicated in Figure AM1–VI(a). This simulated clear-air or 0% opacity value shall be tested in using the selected light source depicted in Figure AM1–VI(b).

The light source either shall be a continuous wave (CW) laser with the beam mechanically chopped or a light emitting diode controlled with a pulse generator (rectangular pulse). (A laser beam may have to be attenuated so as not to saturate the PMT detector). This signal level shall be measured

and should be recorded. The opacity value is calculated by taking two pick intervals [Section 2.6] about 1 microsecond apart in time and using Equation (AM1–2) setting the ratio $R_n/R_f = 1$. This calculated value should be recorded.

The simulated clear-air signal level is also employed in the optical test using the neutral density filters. Using the test configuration in Figure AM1–VI(c), each neutral density filter shall be separately placed into the light path from the light source to the PMT detector. The signal level shall be measured and should be recorded. The opacity value for each filter is calculated by taking the signal level for that respective filter (I_f), dividing it by the 0% opacity signal level (I_n) and performing the remainder of the calculation by Equation (AM1–2) with $R_n/R_f = 1$. The calculated opacity value for each filter should be recorded.

The neutral density filters used for Technique 1 shall be calibrated for actual opacity with accuracy of ±2% or better. This calibration shall be done monthly while the filters are in use and the calibrated values should be recorded.

3.2.2 Procedure for Technique 2. An optical generator (built-in calibration mechanism) that contains a light-emitting diode (red light for a lidar containing a ruby laser) is used. By injecting an optical signal into the lidar receiver immediately ahead of the PMT detector, a backscatter signal is simulated. With the entire lidar receiver electronics turned on and adjusted for normal operating performance, the optical generator is turned on and the simulation signal (corrected for $1/R^2$) is selected with no plume spike signal and with the opacity value equal to 0%. This simulated clear-air atmospheric return signal is displayed on the system's video display. The lidar operator then makes any fine adjustments that may be necessary to maintain the system's normal operating range.

The opacity values of 0% and the other five values are selected one at a time in any order. The simulated return signal data should be recorded. The opacity value shall be calculated. This measurement/calculation shall be performed at least three times for each selected opacity value. While the order is not important, each of the opacity values from the optical generator shall be verified. The calibrated optical generator opacity value for each selection should be recorded.

The optical generator used for Technique 2 shall be calibrated for actual opacity with an accuracy of ±1% or better. This calibration shall be done monthly while the generator is in use and calibrated value should be recorded.

Alternate verification procedures that do not meet the above requirements but produce equivalent results may be used.

3.3 Deviation. The permissible error for the annual calibration and routine verification are:

3.3.1 Annual Calibration Deviation.

3.3.1.1 Smoke Generator. If the lidar-measured average opacity for each data run is not within ±5% (full scale) of the respective smoke generator's average opacity over the range of 0% through 80%, then the lidar shall be considered out of calibration.

3.3.1.2 Screens. If the lidar-measured average opacity for each data run is not within ±3% (full scale) of the laboratory-determined opacity for each respective simulation screen target over the range of 0% through 80%, then the lidar shall be considered out of calibration.

3.3.2 Routine Verification Error. If the lidar-measured average opacity for each neutral density filter (Technique 1) or optical generator selection (Technique 2) is not within ±3% (full scale) of the respective laboratory calibration value then the lidar shall be considered non-operational.

4. Performance/Design Specification for Basic Lidar System

4.1 Lidar Design Specification. The essential components of the basic lidar system are a pulsed laser (transmitter), optical receiver, detector, signal processor, recorder, and an aiming device that is used in aiming the lidar transmitter and receiver. Figure AM1–VII shows a functional block diagram of a basic lidar system.

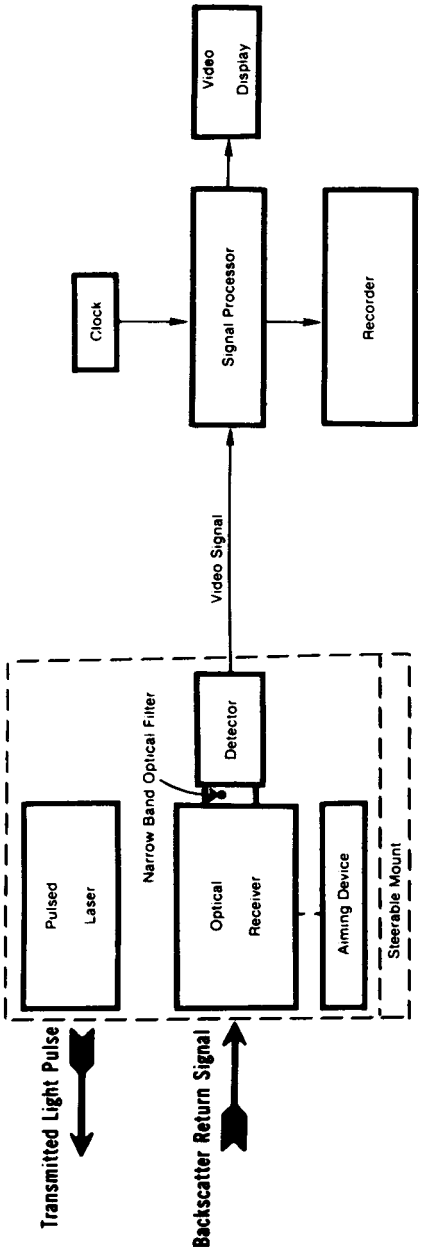


Figure AM1-VII. Functional Block Diagram of a Basic Lidar System

4.2 Performance Evaluation Tests. The owner of a lidar system shall subject such a lidar system to the performance verification tests described in section 3, prior to first use of this method. The annual calibration shall be performed for three separate, complete

runs and the results of each should be recorded. The requirements of section 3.3.1 must be fulfilled for each of the three runs.

Once the conditions of the annual calibration are fulfilled the lidar shall be subjected to the routine verification for three separate complete runs. The requirements of section 3.3.2 must be fulfilled for each of the three runs and the results should be recorded. The Administrator may request that the results of the performance evaluation be submitted for review.

5. References

5.1 The Use of Lidar for Emissions Source Opacity Determination, U.S. Environmental Protection Agency, National Enforcement Investigations Center, Denver, CO. EPA–330/1–79–003–R, Arthur W. Dybdahl, current edition [NTIS No. PB81–246662].

5.2 Field Evaluation of Mobile Lidar for the Measurement of Smoke Plume Opacity, U.S. Environmental Protection Agency, National Enforcement Investigations Center, Denver, CO. EPA/NEIC-TS-128, February 1976.

5.3 Remote Measurement of Smoke Plume Transmittance Using Lidar, C. S. Cook, G. W. Bethke, W. D. Conner (EPA/RTP). Applied Optics 11, pg 1742. August 1972.

5.4 Lidar Studies of Stack Plumes in Rural and Urban Environments, EPA–650/4–73–002, October 1973.

5.5 American National Standard for the Safe Use of Lasers ANSI Z 136.1–176, March 8, 1976.

5.6 U.S. Army Technical Manual TB MED 279, Control of Hazards to Health from Laser Radiation, February 1969.

5.7 Laser Institute of America Laser Safety Manual, 4th Edition.

5.8 U.S. Department of Health, Education and Welfare, Regulations for the Administration and Enforcement of the Radiation Control for Health and Safety Act of 1968, January 1976.

5.9 Laser Safety Handbook, Alex Mallow, Leon Chabot, Van Nostrand Reinhold Co., 1978.

Method 10—Determination of Carbon Monoxide Emissions From Stationary Sources (Instrumental Analyzer Procedure)

1.0 Scope and Application

What is Method 10?

Method 10 is a procedure for measuring carbon monoxide (CO) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis. This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 4—Determination of Moisture Content in Stack Gases.

(c) Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure).

1.1 Analytes. What does this method determine? This method measures the concentration of carbon monoxide.

Analyte	CAS No.	Sensitivity
CO	630–08–0	Typically <2% of Calibration Span.

1.2 Applicability. When is this method required? The use of Method 10 may be required by specific New Source Performance Standards, State Implementation Plans, and permits where CO concentrations in stationary source emissions must be measured, either to determine compliance with an applicable emission standard or to conduct performance testing of a continuous emission monitoring system (CEMS). Other regulations may also require the use of Method 10.

1.3 Data Quality Objectives. Refer to section 1.3 of Method 7E.

2.0 Summary of Method

In this method, you continuously or intermittently sample the effluent gas and convey the sample to an analyzer that measures the concentration of CO. You must meet the performance requirements of this method to validate your data.

3.0 Definitions

Refer to section 3.0 of Method 7E for the applicable definitions.

4.0 Interferences

Substances having a strong absorption of infrared energy may interfere to some extent in some analyzers. Instrumental correction may be used to compensate for the interference. You may also use silica gel and ascarite traps to eliminate the interferences. If this option is used, correct the measured

gas volume for the carbon dioxide (CO_2) removed in the trap.

5.0 Safety

Refer to section 5.0 of Method 7E.

6.0 Equipment and Supplies

What do I need for the measurement system?

6.1 Continuous Sampling. Figure 7E–1 of Method 7E is a schematic diagram of an acceptable measurement system. The components are the same as those in sections 6.1 and 6.2 of Method 7E, except that the CO analyzer described in section 6.2 of this method must be used instead of the analyzer described in section 6.2 of Method 7E. You must follow the noted specifications in section 6.1 of Method 7E except that the requirements to use stainless steel, Teflon, or non-reactive glass filters do not apply. Also, a heated sample line is not required to transport dry gases or for systems that measure the CO concentration on a dry basis.

6.2 Integrated Sampling.

6.2.1 Air-Cooled Condenser or Equivalent. To remove any excess moisture.

6.2.2 Valve. Needle valve, or equivalent, to adjust flow rate.

6.2.3 Pump. Leak-free diaphragm type, or equivalent, to transport gas.

6.2.4 Rate Meter. Rotameter, or equivalent, to measure a flow range from 0 to 1.0 liter per minute (0.035 cfm).

6.2.5 Flexible Bag. Tedlar, or equivalent, with a capacity of 60 to 90 liters (2 to 3 ft^3). (Verify through the manufacturer that the Tedlar alternative is suitable for CO and make this verified information available for inspection.) Leak-test the bag in the laboratory before using by evacuating with a pump followed by a dry gas meter. When the evacuation is complete, there should be no flow through the meter.

6.2.6 Sample Tank. Stainless steel or aluminum tank equipped with a pressure indicator with a minimum volume of 4 liters.

6.3 What analyzer must I use? You must use an instrument that continuously measures CO in the gas stream and meets the specifications in section 13.0. The dual-range analyzer provisions in section 6.2.8.1 of Method 7E apply.

7.0 Reagents and Standards

7.1 Calibration Gas. What calibration gases do I need? Refer to section 7.1 of Method 7E for the calibration gas requirements.

7.2 Interference Check. What additional reagents do I need for the interference check? Use the appropriate test gases listed in Table 7E–3 of Method 7E (i.e., potential interferents, as identified by the instrument manufacturer) to conduct the interference check.

8.0 Sample Collection, Preservation, Storage, and Transport

Emission Test Procedure

8.1 Sampling Site and Sampling Points. You must follow section 8.1 of Method 7E.

8.2 Initial Measurement System Performance Tests. You must follow the procedures in section 8.2 of Method 7E. If a dilution-type measurement system is used, the special considerations in section 8.3 of Method 7E also apply.

8.3 Interference Check. You must follow the procedures of section 8.2.7 of Method 7E.

8.4 Sample Collection.

8.4.1 Continuous Sampling. You must follow the procedures of section 8.4 of Method 7E.

8.4.2 Integrated Sampling. Evacuate the flexible bag or sample tank. Set up the equipment as shown in Figure 10–1 with the bag disconnected. Place the probe in the stack and purge the sampling line. Connect the bag, making sure that all connections are leak-free. Sample at a rate proportional to the stack velocity. If needed, the CO_2 content of the gas may be determined by using the Method 3 integrated sample procedures, or by weighing an ascarite CO_2 removal tube used and computing CO_2 concentration from the gas volume sampled and the weight gain of the tube. Data may be recorded on a form similar to Table 10–1. If a sample tank is used for sample collection, follow procedures similar to those in sections 8.1.2, 8.2.3, 8.3, and 12.4 of Method 25 as appropriate to prepare the tank, conduct the sampling, and correct the measured sample concentration.

8.5 Post-Run System Bias Check, Drift Assessment, and Alternative Dynamic Spike Procedure. You must follow the procedures in sections 8.5 and 8.6 of Method 7E.

9.0 Quality Control

Follow the quality control procedures in section 9.0 of Method 7E.

10.0 Calibration and Standardization

Follow the procedures for calibration and standardization in section 10.0 of Method 7E.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the procedures for calculations and data analysis in section 12.0 of Method 7E, as applicable, substituting CO for NO_X as applicable.

12.1 Concentration Correction for CO_2 Removal. Correct the CO concentration for CO_2 removal (if applicable) using Eq. 10–1.

$$C_{Avg} = C_{CO\ stack}\left(1 - F_{CO2}\right)$$

Where:

C_{Avg} = Average gas concentration for the test run, ppm.

$C_{CO\ stack}$ = Average unadjusted stack gas CO concentration indicated by the data recorder for the test run, ppmv.

F_{CO2} = Volume fraction of CO_2 in the sample, i.e., percent CO_2 from Orsat analysis divided by 100.

13.0 Method Performance

The specifications for analyzer calibration error, system bias, drift, interference check, and alternative dynamic spike procedure are the same as in section 13.0 of Method 7E.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

The dynamic spike procedure and the manufacturer stability test are the same as in sections 16.1 and 16.3 of Method 7E

17.0 References

1. ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards— September 1997 as amended, EPA–600/R–97/121

18.0 Tables, Diagrams, Flowcharts, and Validation Data

Figure 10-1. Integrated Gas Sampling Train.

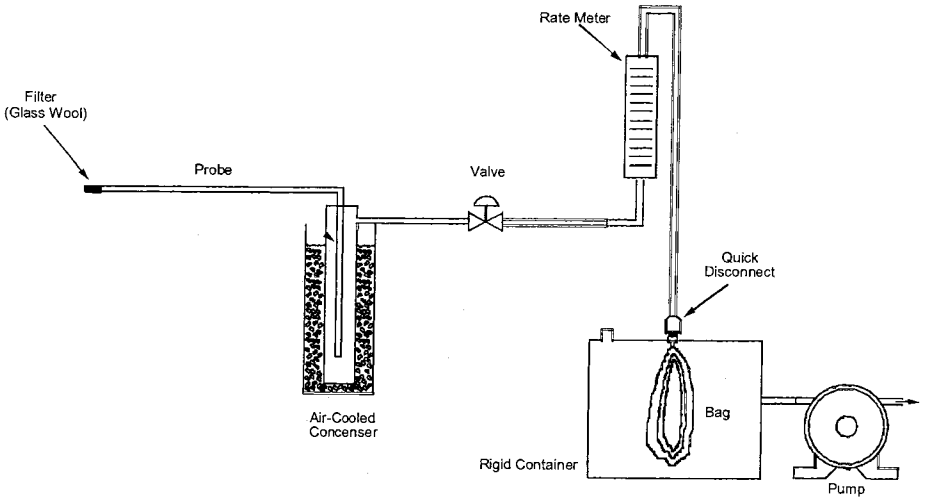


TABLE 10–1—FIELD DATA

[Integrated sampling]

Location:	Date:	
Test:	Operator:	
Clock Time	Rotameter Reading liters/min (cfm)	Comments

TABLE 10–1—FIELD DATA—Continued

[Integrated sampling]

METHOD 10A—DETERMINATION OF CARBON MONOXIDE EMISSIONS IN CERTIFYING CONTINUOUS EMISSION MONITORING SYSTEMS AT PETROLEUM REFINERIES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 4, and Method 5.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Carbon monoxide (CO)	630–08–0	3 ppmv

1.2 Applicability. This method is applicable for the determination of CO emissions at petroleum refineries. This method serves as the reference method in the relative accuracy test for nondispersive infrared (NDIR) CO continuous emission monitoring systems (CEMS) that are required to be installed in petroleum refineries on fluid catalytic cracking unit catalyst regenerators (§60.105(a)(2) of this part).

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

An integrated gas sample is extracted from the stack, passed through an alkaline permanganate solution to remove sulfur oxides and nitrogen oxides, and collected in a Tedlar or equivalent bag. (Verify through the manufacturer that the Tedlar alternative is suitable for NO and make this verified information available for inspection.) The CO concentration in the sample is measured spectrophotometrically using the reaction of CO with *p*-sulfaminobenzoic acid.

3.0 Definitions [Reserved]

4.0 Interferences

Sulfur oxides, nitric oxide, and other acid gases interfere with the colorimetric reaction. They are removed by passing the sampled gas through an alkaline potassium permanganate scrubbing solution. Carbon dioxide (CO_2) does not interfere, but, because it is removed by the scrubbing solution, its concentration must be measured independently and an appropriate volume correction made to the sampled gas.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs.

Reacts exothermically with limited amounts of water.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling train shown in Figure 10A–1 is required for sample collection. Component parts are described below:

6.1.1 Probe. Stainless steel, sheathed Pyrex glass, or equivalent, equipped with a glass wool plug to remove particulate matter.

6.1.2 Sample Conditioning System. Three Greenburg-Smith impingers connected in series with leak-free connections.

6.1.3 Pump. Leak-free pump with stainless steel and Teflon parts to transport sample at a flow rate of 300 ml/min (0.01 ft^3/min) to the flexible bag.

6.1.4 Surge Tank. Installed between the pump and the rate meter to eliminate the pulsation effect of the pump on the rate meter.

6.1.5 Rate Meter. Rotameter, or equivalent, to measure flow rate at 300 ml/min (0.01 ft^3/min). Calibrate according to section 10.2.

6.1.6 Flexible Bag. Tedlar, or equivalent, with a capacity of 10 liters (0.35 ft^3) and equipped with a sealing quick-connect plug. The bag must be leak-free according to section 8.1. For protection, it is recommended that the bag be enclosed within a rigid container.

6.1.7 Sample Tank. Stainless steel or aluminum tank equipped with a pressure indicator with a minimum volume of 10 liters.

6.1.8 Valves. Stainless-steel needle valve to adjust flow rate, and stainless-steel 3-way valve, or equivalent.

6.1.9 CO_2 Analyzer. Fyrite, or equivalent, to measure CO_2 concentration to within 0.5 percent.

6.1.10 Volume Meter. Dry gas meter, capable of measuring the sample volume under calibration conditions of 300 ml/min (0.01 ft^3/min) for 10 minutes.

6.1.11 Pressure Gauge. A water filled U-tube manometer, or equivalent, of about 30 cm (12 in.) to leak-check the flexible bag.

6.2 Sample Analysis.

6.2.1 Spectrophotometer. Single- or double-beam to measure absorbance at 425 and 600 nm. Slit width should not exceed 20 nm.

6.2.2 Spectrophotometer Cells. 1-cm pathlength.

6.2.3 Vacuum Gauge. U-tube mercury manometer, 1 meter (39 in.), with 1-mm divisions, or other gauge capable of measuring pressure to within 1 mm Hg.

6.2.4 Pump. Capable of evacuating the gas reaction bulb to a pressure equal to or less than 40 mm Hg absolute, equipped with coarse and fine flow control valves.

6.2.5 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm Hg.

6.2.6 Reaction Bulbs. Pyrex glass, 100-ml with Teflon stopcock (Figure 10A–2), leak-free at 40 mm Hg, designed so that 10 ml of the colorimetric reagent can be added and removed easily and accurately. Commercially available gas sample bulbs such as Supelco Catalog No. 2–2161 may also be used.

6.2.7 Manifold. Stainless steel, with connections for three reaction bulbs and the appropriate connections for the manometer and sampling bag as shown in Figure 10A–3.

6.2.8 Pipets. Class A, 10–ml size.

6.2.9 Shaker Table. Reciprocating-stroke type such as Eberbach Corporation, Model 6015. A rocking arm or rotary-motion type shaker may also be used. The shaker must be large enough to accommodate at least six gas sample bulbs simultaneously. It may be necessary to construct a table top extension for most commercial shakers to provide sufficient space for the needed bulbs (Figure 10A–4).

6.2.10 Valve. Stainless steel shut-off valve.

6.2.11 Analytical Balance. Capable of weighing to 0.1 mg.

7.0 Reagents and Standards

Unless otherwise indicated, all reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, the best available grade shall be used.

7.1 Sample Collection.

7.1.1 Water. Deionized distilled, to conform to ASTM D 1193–77 or 91, Type 3 (incorporated by reference—see §60.17). If high concentrations of organic matter are not expected to be present, the potassium permanganate test for oxidizable organic matter may be omitted.

7.1.2 Alkaline Permanganate Solution, 0.25 M $KMnO_4$/1.5 M Sodium Hydroxide (NaOH). Dissolve 40 g $KMnO_4$ and 60 g NaOH in approximately 900 ml water, cool, and dilute to 1 liter.

7.2 Sample Analysis.

7.2.1 Water. Same as in section 7.1.1.

7.2.2 1 M Sodium Hydroxide Solution. Dissolve 40 g NaOH in approximately 900 ml of water, cool, and dilute to 1 liter.

7.2.3 0.1 M NaOH Solution. Dilute 50 ml of the 1 M NaOH solution prepared in section 7.2.2 to 500 ml.

7.2.4 0.1 M Silver Nitrate ($AgNO_3$) Solution. Dissolve 8.5 g $AgNO_3$ in water, and dilute to 500 ml.

7.2.5 0.1 M Para-Sulfaminobenzoic Acid (p-SABA) Solution. Dissolve 10.0 g p-SABA in 0.1 M NaOH, and dilute to 500 ml with 0.1 M NaOH.

7.2.6 Colorimetric Solution. To a flask, add 100 ml of 0.1 M p-SABA solution and 100 ml of 0.1 M $AgNO_3$ solution. Mix, and add 50 ml of 1 M NaOH with shaking. The resultant solution should be clear and colorless. This solution is acceptable for use for a period of 2 days.

7.2.7 Standard Gas Mixtures. Traceable to National Institute of Standards and Technology (NIST) standards and containing between 50 and 1000 ppm CO in nitrogen. At least two concentrations are needed to span each calibration range used (Section 10.3). The calibration gases must be certified by the manufacturer to be within 2 percent of the specified concentrations.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sample Bag or Tank Leak-Checks. While a leak-check is required after bag or sample tank use, it should also be done before the bag or sample tank is used for sample collection. The tank should be leak-checked according to the procedure specified in section 8.1.2 of Method 25. The bag should be leak-checked in the inflated and deflated condition according to the following procedure:

8.1.1 Connect the bag to a water manometer, and pressurize the bag to 5 to 10 cm H_2O (2 to 4 in H_2O). Allow the bag to stand for 60 minutes. Any displacement in the water manometer indicates a leak.

8.1.2 Evacuate the bag with a leakless pump that is connected to the downstream side of a flow indicating device such as a 0- to 100-ml/min rotameter or an impinger containing water. When the bag is completely evacuated, no flow should be evident if the bag is leak-free.

8.2 Sample Collection.

8.2.1 Evacuate and leak check the sample bag or tank as specified in section 8.1. Assemble the apparatus as shown in Figure 10A–1. Loosely pack glass wool in the tip of the probe. Place 400 ml of alkaline permanganate solution in the first two impingers and 250 ml in the third. Connect the pump to the third impinger, and follow this with the surge tank, rate meter, and 3-way valve. Do not connect the bag or sample tank to the system at this time.

8.2.2 Leak-check the sampling system by plugging the probe inlet, opening the 3-way valve, and pulling a vacuum of approximately 250 mm Hg on the system while observing the rate meter for flow. If flow is indicated on the rate meter, do not proceed further until the leak is found and corrected.

8.2.3 Purge the system with sample gas by inserting the probe into the stack and drawing the sample gas through the system at 300 ml/min ±10 percent for 5 minutes. Connect the evacuated bag or sample tank to the system, record the starting time, and sample at a rate of 300 ml/min for 30 minutes, or until the bag is nearly full, or the sample tank reaches ambient pressure. Record the sampling time, the barometric pressure, and the ambient temperature. Purge the system as described above immediately before each sample.

8.2.4 The scrubbing solution is adequate for removing sulfur oxides and nitrogen oxides from 50 liters (1.8 ft^3) of stack gas when the concentration of each is less than 1,000 ppm and the CO_2 concentration is less than 15 percent. Replace the scrubber solution after every fifth sample.

8.3 Carbon Dioxide Measurement. Measure the CO_2 content in the stack to the nearest 0.5 percent each time a CO sample is collected. A simultaneous grab sample analyzed by the Fyrite analyzer is acceptable.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.1	Sampling equipment leak-checks and calibration.	Ensure accuracy and precision of sampling measurements.
10.3	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Gas Bulb Calibration. Weigh the empty bulb to the nearest 0.1 g. Fill the bulb to the stopcock with water, and again weigh to the nearest 0.1 g. Subtract the tare weight, and calculate the volume in liters to three significant figures using the density of water at the measurement temperature. Record the volume on the bulb. Alternatively, mark an identification number on the bulb, and record the volume in a notebook.

10.2 Rate Meter Calibration. Assemble the system as shown in Figure 10A–1 (the impingers may be removed), and attach a volume meter to the probe inlet. Set the rotameter at 300 ml/min, record the volume meter reading, start the pump, and pull ambient air through the system for 10 minutes. Record the final volume meter reading. Repeat the procedure and average the results to determine the volume of gas that passed through the system.

10.3 Spectrophotometer Calibration Curve.

10.3.1 Collect the standards as described in section 8.2. Prepare at least two sets of three bulbs as standards to span the 0 to 400 or 400 to 1000 ppm range. If any samples span both

concentration ranges, prepare a calibration curve for each range using separate reagent blanks. Prepare a set of three bulbs containing colorimetric reagent but no CO to serve as a reagent blank. Analyze each standard and blank according to the sample analysis procedure of section 11.0 Reject the standard set where any of the individual bulb absorbances differs from the set mean by more than 10 percent.

10.3.2 Calculate the average absorbance for each set (3 bulbs) of standards using Equation 10A–1 and Table 10A–1. Construct a graph of average absorbance for each standard against its corresponding concentration. Draw a smooth curve through the points. The curve should be linear over the two concentration ranges discussed in section 13.3.

11.0 Analytical Procedure

11.1 Assemble the system shown in Figure 10A–3, and record the information required in Table 10A–1 as it is obtained. Pipet 10.0 ml of the colorimetric reagent into each gas reaction bulb, and attach the bulbs to the system. Open the stopcocks to the reaction bulbs, but leave the valve to the bag closed. Turn on the pump, fully open the coarse-adjust flow valve, and slowly open the fine-adjust valve until the pressure is reduced to at least 40 mm Hg. Now close the coarse adjust valve, and observe the manometer to be certain that the system is leak-free. Wait a minimum of 2 minutes. If the pressure has increased less than 1 mm Hg, proceed as described below. If a leak is present, find and correct it before proceeding further.

11.2 Record the vacuum pressure (P_v) to the nearest 1 mm Hg, and close the reaction bulb stopcocks. Open the bag valve, and allow the system to come to atmospheric pressure. Close the bag valve, open the pump coarse adjust valve, and evacuate the system again. Repeat this fill/evacuation procedure at least twice to flush the manifold completely. Close the pump coarse adjust valve, open the bag valve, and let the system fill to atmospheric pressure. Open the stopcocks to the reaction bulbs, and let the entire system come to atmospheric pressure. Close the bulb stopcocks, remove the bulbs, record the room temperature and barometric pressure (P_{bar}, to nearest mm Hg), and place the bulbs on the shaker table with their main axis either parallel to or perpendicular to the plane of the table top. Purge the bulb-filling system with ambient air for several minutes between samples. Shake the samples for exactly 2 hours.

11.3 Immediately after shaking, measure the absorbance (A) of each bulb sample at 425 nm if the concentration is less than or equal to 400 ppm CO or at 600 nm if the concentration is above 400 ppm.

NOTE: This may be accomplished with multiple bulb sets by sequentially collecting sets and adding to the shaker at staggered intervals, followed by sequentially removing sets from the shaker for absorbance measurement after the two-hour designated intervals have elapsed.

11.4 Use a small portion of the sample to rinse a spectrophotometer cell several times before taking an aliquot for analysis. If one cell is used to analyze multiple samples, rinse the cell with deionized distilled water several times between samples. Prepare and analyze standards and a reagent blank as described in section 10.3. Use water as the reference. Reject the analysis if the blank absorbance is greater than 0.1. All conditions should be the same for analysis of samples and standards. Measure the absorbances as soon as possible after shaking is completed.

11.5 Determine the CO concentration of each bag sample using the calibration curve for the appropriate concentration range as discussed in section 10.3.

12.0 Calculations and Data Analysis

Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature.

A = Sample absorbance, uncorrected for the reagent blank.
A_r = Absorbance of the reagent blank.
A_s = Average sample absorbance per liter, units/liter.
B_w = Moisture content in the bag sample.
C = CO concentration in the stack gas, dry basis, ppm.
C_b = CO concentration of the bag sample, dry basis, ppm.
C_g = CO concentration from the calibration curve, ppm.
F = Volume fraction of CO_2 in the stack.
n = Number of reaction bulbs used per bag sample.
P_b = Barometric pressure, mm Hg.
P_v = Residual pressure in the sample bulb after evacuation, mm Hg.
P_w = Vapor pressure of H_2O in the bag (from Table 10A–2), mm Hg.
V_b = Volume of the sample bulb, liters.
V_r = Volume of reagent added to the sample bulb, 0.0100 liter.

12.2 Average Sample Absorbance per Liter. Calculate A_s for each gas bulb using Equation 10A–1, and record the value in Table 10A–1. Calculate the average A_s for each bag sample, and compare the three values to the average. If any single value differs by more than 10 percent from the average, reject this value, and calculate a new average using the two remaining values.

$$A_s = \frac{(A - A_r)(P_b)}{(V_b - V_r)(P_b - P_v)} \qquad \text{Eq. 10A-1}$$

NOTE: A and A_r must be at the same wavelength.

12.3 CO Concentration in the Bag. Calculate C_b using Equations 10A–2 and 10A–3. If condensate is visible in the bag, calculate B_w using Table 10A–2 and the temperature and barometric pressure in the analysis room. If condensate is not visible, calculate B_w using the temperature and barometric pressure at the sampling site.

$$B_w = \frac{P_w}{P_b} \qquad \text{Eq. 10A-2}$$

$$C_b = \frac{C_g}{(1 - B_w)} \qquad \text{Eq. 10A-3}$$

12.4 CO Concentration in the Stack.

$$C = C_b\,(1 - F) \qquad \text{Eq. 10A-4}$$

13.0 Method Performance

13.1 Precision. The estimated intralaboratory standard deviation of the method is 3 percent of the mean for gas samples analyzed in duplicate in the concentration range of 39 to 412 ppm. The interlaboratory precision has not been established.

13.2 Accuracy. The method contains no significant biases when compared to an NDIR analyzer calibrated with NIST standards.

13.3 Range. Approximately 3 to 1800 ppm CO. Samples having concentrations below 400 ppm are analyzed at 425 nm, and samples having concentrations above 400 ppm are analyzed at 600 nm.

13.4 Sensitivity. The detection limit is 3 ppmv based on a change in concentration equal to three times the standard deviation of the reagent blank solution.

13.5 Stability. The individual components of the colorimetric reagent are stable for at least one month. The colorimetric reagent must be used within two days after preparation to avoid excessive blank correction. The samples in the bag should be stable for at least one week if the bags are leak-free.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Butler, F.E., J.E. Knoll, and M.R. Midgett. Development and Evaluation of Methods for Determining Carbon Monoxide Emissions. U.S. Environmental Protection Agency, Research Triangle Park, N.C. June 1985. 33 pp.

2. Ferguson, B.B., R.E. Lester, and W.J. Mitchell. Field Evaluation of Carbon Monoxide and Hydrogen Sulfide Continuous Emission Monitors at an Oil Refinery. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA–600/4–82–054. August 1982. 100 pp.

3. Lambert, J.L., and R.E. Weins. Induced Colorimetric Method for Carbon Monoxide. Analytical Chemistry. *46*(7):929–930. June 1974.

4. Levaggi, D.A., and M. Feldstein. The Colorimetric Determination of Low Concentrations of Carbon Monoxide. Industrial Hygiene Journal. *25*:64–66. January-February 1964.

5. Repp, M. Evaluation of Continuous Monitors For Carbon Monoxide in Stationary Sources. U.S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA–600/2–77–063. March 1977. 155 pp.

6. Smith, F., D.E. Wagoner, and R.P. Donovan. Guidelines for Development of a Quality Assurance Program: Volume VIII—Determination of CO Emissions from Stationary Sources by NDIR Spectrometry. U.S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA–650/4–74–005–h. February 1975. 96 pp.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 10A–1—DATA RECORDING SHEET FOR SAMPLES ANALYZED IN TRIPLICATE

Sample No./type	Room temp °C	Stack %CO_2	Bulb No.	Bulb vol. liters	Reagent vol. in bulb, liter	Partial pressure of gas in bulb, mm Hg	$P_{b,r}$, mm Hg	Shaking time, min	Abs versus water	A-A_r	A_s	Avg A_s
blank												
Std. 1												
Std. 2												
Sample 1												
Sample 2												
Sample 3												

TABLE 10A–2—MOISTURE CORRECTION

Temperature °C	Vapor pressure of H_2O, mm Hg	Temperature °C	Vapor pressure of H_2, mm Hg
4	6.1	18	15.5
6	7.0	20	17.5
8	8.0	22	19.8
10	9.2	24	22.4
12	10.5	26	25.2
14	12.0	28	28.3
16	13.6	30	31.8

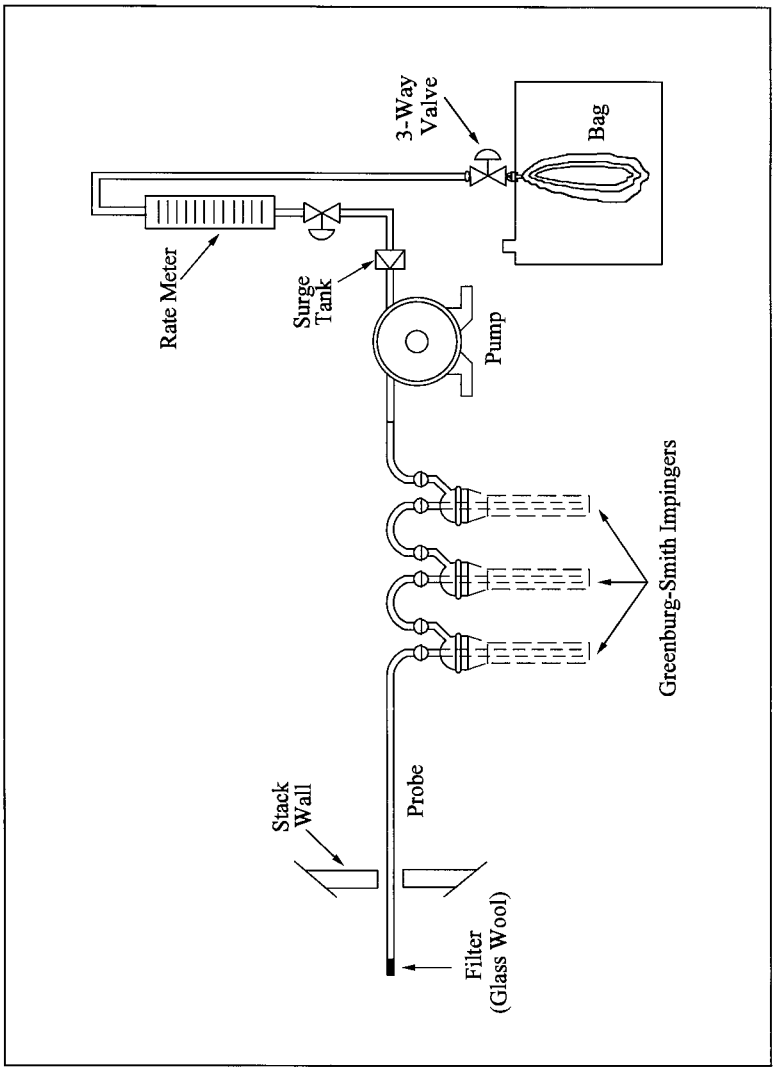


Figure 10A-1. Sampling Train.

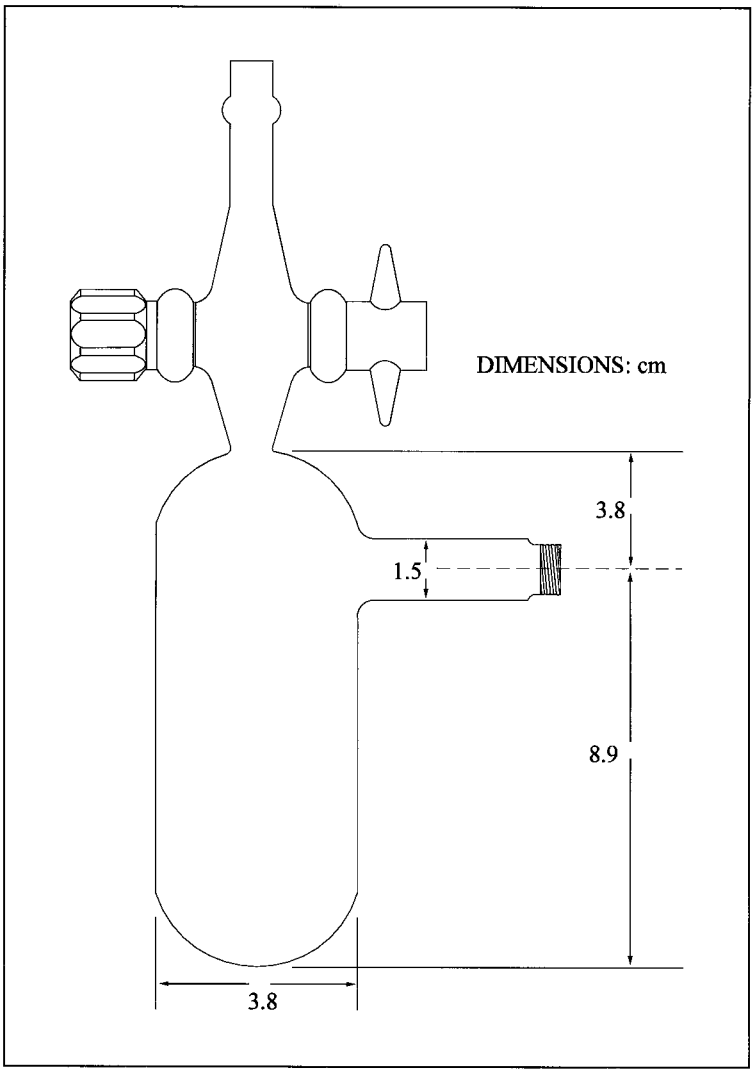


Figure 10A-2. Sample Reaction Bulbs.

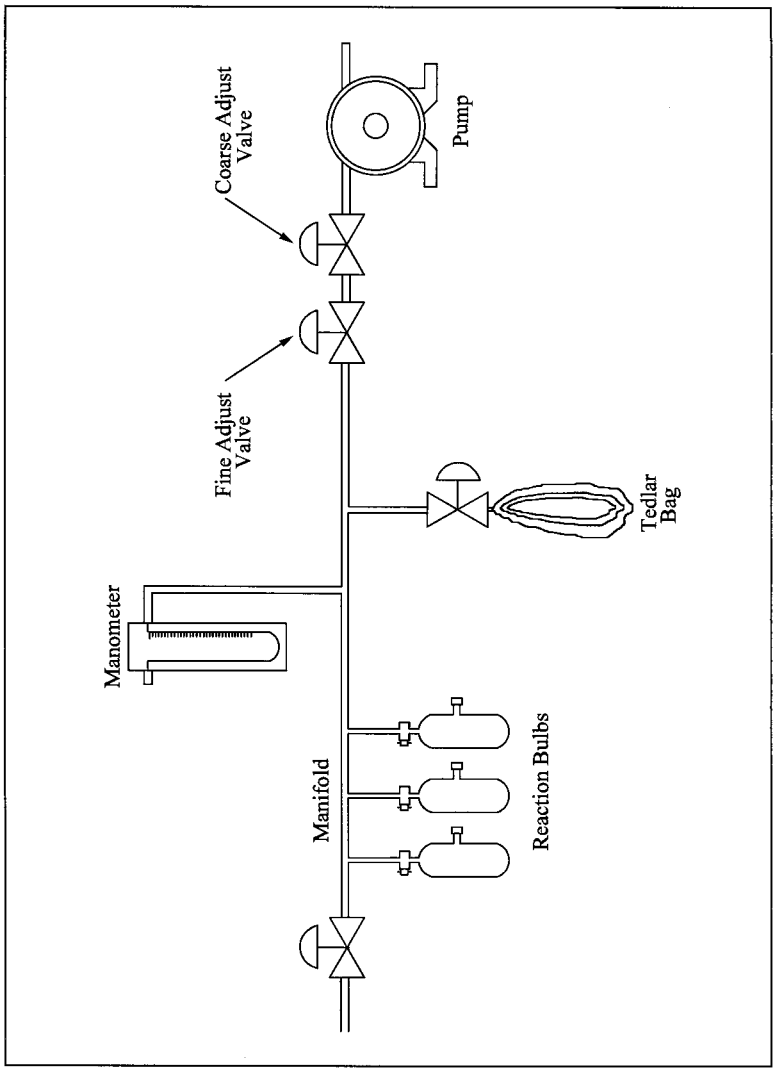


Figure 10A-3. Sample Bulb Filling System.

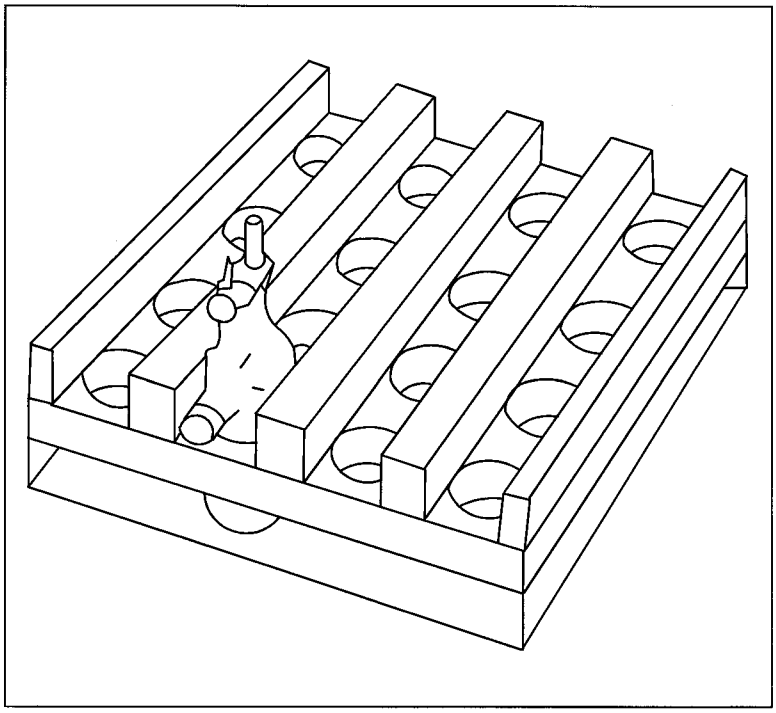


Figure 10A-4. Shaker Table Adapter.

METHOD 10B—DETERMINATION OF CARBON MONOXIDE EMISSIONS FROM STATIONARY SOURCES

NOTE: This method is not inclusive with respect to specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 4, Method 10A, and Method 25.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Carbon monoxide (CO)	630–08–0	Not determined.

1.2 Applicability. This method applies to the measurement of CO emissions at petroleum refineries and from other sources when specified in an applicable subpart of the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 An integrated gas sample is extracted from the sampling point, passed through a conditioning system to remove interferences, and collected in a Tedlar or equivalent bag. (Verify through the manufacturer that the Tedlar alternative is suitable for NO and make this verifying information available for inspection.) The CO is separated from the sample by gas chromatography (GC) and catalytically reduced to methane (CH_4) which is determined by flame ionization detection (FID). The analytical portion of this method is identical to applicable sections in Method 25 detailing CO measurement.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Carbon dioxide (CO_2) and organics potentially can interfere with the analysis. Most of the CO_2 is removed from the sample by the alkaline permanganate conditioning system; any residual CO_2 and organics are separated from the CO by GC.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions concerning the analytical procedure.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as in Method 10A, section 6.1 (paragraphs 6.1.1 through 6.1.11).

6.2 Sample Analysis. A GC/FID analyzer, capable of quantifying CO in the sample and consisting of at least the following major components, is required for sample analysis. [Alternatively, complete Method 25 analytical systems (Method 25, section 6.3) are acceptable alternatives when calibrated for CO and operated in accordance with the Method 25 analytical procedures (Method 25, section 11.0).]

6.2.1 Separation Column. A column capable of separating CO from CO_2 and organic compounds that may be present. A 3.2-mm (⅛-in.) OD stainless steel column packed with 1.7 m (5.5 ft.) of 60/80 mesh Carbosieve S-II (available from Supelco) has been used successfully for this purpose.

6.2.2 Reduction Catalyst. Same as in Method 25, section 6.3.1.2.

6.2.3 Sample Injection System. Same as in Method 25, Section 6.3.1.4, equipped to accept a sample line from the bag.

6.2.4 Flame Ionization Detector. Meeting the linearity specifications of section 10.3 and having a minimal instrument range of 10 to 1,000 ppm CO.

6.2.5 Data Recording System. Analog strip chart recorder or digital integration system, compatible with the FID, for permanently recording the analytical results.

7.0 Reagents and Standards

7.1 Sample Collection. Same as in Method 10A, section 7.1.

7.2 Sample Analysis.

7.2.1 Carrier, Fuel, and Combustion Gases. Same as in Method 25, sections 7.2.1, 7.2.2, and 7.2.3, respectively.

7.2.2 Calibration Gases. Three standard gases with nominal CO concentrations of 20, 200, and 1,000 ppm CO in nitrogen. The calibration gases shall be certified by the manufacturer to be ±2 percent of the specified concentrations.

7.2.3 Reduction Catalyst Efficiency Check Calibration Gas. Standard CH_4 gas with a nominal concentration of 1,000 ppm in air.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as in Method 10A, section 8.0.

9.0 Quality Control

Section	Quality control measure	Effect
8.0	Sample bag/sampling system leak-checks	Ensures that negative bias introduced through leakage is minimized.
10.1	Carrier gas blank check	Ensures that positive bias introduced by contamination of carrier gas is less than 5 ppmv.
10.2	Reduction catalyst efficiency check	Ensures that negative bias introduced by inefficient reduction catalyst is less than 5 percent.
10.3	Analyzer calibration	Ensures linearity of analyzer response to standards.
11.2	Triplicate sample analyses	Ensures precision of analytical results.

10.0 Calibration and Standardization

10.1 Carrier Gas Blank Check. Analyze each new tank of carrier gas with the GC analyzer according to section 11.2 to check for contamination. The corresponding concentration must be less than 5 ppm for the tank to be acceptable for use.

10.2 Reduction Catalyst Efficiency Check. Prior to initial use, the reduction catalyst shall be tested for reduction efficiency. With the heated reduction catalyst bypassed, make triplicate injections of the 1,000 ppm CH_4 gas (Section 7.2.3) to calibrate the analyzer. Repeat the procedure using 1,000 ppm CO gas (Section 7.2.2) with the catalyst in operation. The reduction catalyst operation is acceptable if the CO response is within 5 percent of the certified gas value.

10.3 Analyzer Calibration. Perform this test before the system is first placed into operation. With the reduction catalyst in operation, conduct a linearity check of the analyzer using the standards specified in section 7.2.2. Make triplicate injections of each calibration gas, and then calculate the average

response factor (area/ppm) for each gas, as well as the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within 2.5 percent of the overall mean value and if the relative standard deviation (calculated in section 12.8 of Method 25) for each set of triplicate injections is less than 2 percent. Record the overall mean of the response factor values as the calibration response factor (R).

11.0 Analytical Procedure

11.1 Preparation for Analysis. Before putting the GC analyzer into routine operation, conduct the calibration procedures listed in section 10.0. Establish an appropriate carrier flow rate and detector temperature for the specific instrument used.

11.2 Sample Analysis. Purge the sample loop with sample, and then inject the sample. Analyze each sample in triplicate, and calculate the average sample area (A). Determine the bag CO concentration according to section 12.2.

12.0 Calculations and Data Analysis

Carry out calculations retaining at least one extra significant figure beyond that of the acquired data. Round off results only after the final calculation.

12.1 Nomenclature.

A = Average sample area.
B_w = Moisture content in the bag sample, fraction.
C = CO concentration in the stack gas, dry basis, ppm.
C_b = CO concentration in the bag sample, dry basis, ppm.
F = Volume fraction of CO_2 in the stack, fraction.
P_{bar} = Barometric pressure, mm Hg.
P_w = Vapor pressure of the H_2O in the bag (from Table 10A–2, Method 10A), mm Hg.
R = Mean calibration response factor, area/ppm.

12.2 CO Concentration in the Bag. Calculate C_b using Equations 10B–1 and 10B–2. If condensate is visible in the bag, calculate B_w using Table 10A–2 of Method 10A and the temperature and barometric pressure in the analysis room. If condensate is not visible, calculate B_w using the temperature and barometric pressure at the sampling site.

$$B_w = \frac{P_w}{P_{bar}} \qquad \text{Eq. 10B-1}$$

$$C_b = \frac{A}{R\left(1 - B_w\right)} \qquad \text{Eq. 10B-2}$$

12.3 CO Concentration in the Stack

$$C = C_b\left(1 - F\right) \qquad \text{Eq. 10B-3}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as in Method 25, section 16.0, with the addition of the following:

1. Butler, F.E, J.E. Knoll, and M.R. Midgett. Development and Evaluation of Methods for Determining Carbon Monoxide Emissions. Quality Assurance Division, Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC. June 1985. 33 pp.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–4 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

APPENDIX A–5 TO PART 60—TEST METHODS 11 THROUGH 15A

Method 11—Determination of hydrogen sulfide content of fuel gas streams in petroleum refineries
Method 12—Determination of inorganic lead emissions from stationary sources
Method 13A—Determination of total fluoride emissions from stationary sources—SPADNS zirconium lake method
Method 13B—Determination of total fluoride emissions from stationary sources—Specific ion electrode method
Method 14—Determination of fluoride emissions from potroom roof monitors for primary aluminum plants
Method 14A—Determination of Total Fluoride Emissions from Selected Sources at Primary Aluminum Production Facilities
Method 15—Determination of hydrogen sulfide, carbonyl sulfide, and carbon disulfide emissions from stationary sources
Method 15A—Determination of total reduced sulfur emissions from sulfur recovery plants in petroleum refineries

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods

OAR 340-236-8010
Process Weight Table

Process Wt/hr (lbs)	Maximum Weight Discharge/hr (lbs)	Process Wt/hr (lbs)	Maximum Weight Discharge/hr (lbs)
50	0.24	3400	5.44
100	0.46	3500	5.52
150	0.66	3600	5.61
200	0.85	3700	5.69
250	1.03	3800	5.77
300	1.20	3900	5.85
350	1.35	4000	5.93
400	1.50	4100	6.01
450	1.63	4200	6.08
500	1.77	4300	6.15
550	1.89	4400	6.22
600	2.01	4500	6.30
650	2.12	4600	6.37
700	2.24	4700	6.45
750	2.34	4800	6.52
800	2.43	4900	6.60
850	2.53	5000	6.67
900	2.62	5500	7.03
950	2.72	6000	7.37
1000	2.80	6500	7.71
1100	2.97	7000	8.05
1200	3.12	7500	8.39

OAR 340-236-8010
Process Weight Table

Process Wt/hr (lbs)	Maximum Weight Discharge/hr (lbs)	Process Wt/hr (lbs)	Maximum Weight Discharge/hr (lbs)
1300	3.26	8000	8.71
1400	3.40	8500	9.03
1500	3.54	9000	9.36
1600	3.66	9500	9.67
1700	3.79	10000	10.00
1800	3.91	11000	10.63
1900	4.03	12000	11.28
2000	4.14	13000	11.89
2100	4.24	14000	12.50
2200	4.34	15000	13.13
2300	4.44	16000	13.74
2400	4.55	17000	14.36
2500	4.64	18000	14.97
2600	4.74	19000	15.58
2700	4.84	20000	16.19
2800	4.92	30000	22.22
2900	5.02	40000	28.30
3000	5.10	50000	34.30
3100	5.18	600000	40.00
3200	5.27	Or	
3300	5.36	More	

State of Oregon Department of Environmental Quality

OAR 340-240-0050 Attachments

EDITORIAL NOTE: At 79 FR 11257, Feb. 27, 2014, Figure 1-2 was added to part 60, appendix A-1, method 1, section 17. However, this amendment could not be performed because Figure 1-2 already existed.

APPENDIX A–2 TO PART 60—TEST METHODS 2G THROUGH 3C

Method 2G—Determination of Stack Gas Velocity and Volumetric Flow Rate With Two-Dimensional Probes
Method 2H—Determination of Stack Gas Velocity Taking Into Account Velocity Decay Near the Stack Wall
Method 3—Gas analysis for the determination of dry molecular weight
Method 3A—Determination of Oxygen and Carbon Dioxide Concentrations in Emissions From Stationary Sources (Instrumental Analyzer Procedure)
Method 3B—Gas analysis for the determination of emission rate correction factor or excess air
Method 3C—Determination of carbon dioxide, methane, nitrogen, and oxygen from stationary sources

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

METHOD 2G—DETERMINATION OF STACK GAS VELOCITY AND VOLUMETRIC FLOW RATE WITH TWO-DIMENSIONAL PROBES

NOTE: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling) essential to its performance. Some material has been incorporated from other methods in this part. Therefore, to obtain reliable results, those using this method should have a thorough knowledge of at least the following additional test methods: Methods 1, 2, 3 or 3A, and 4.

1.0 Scope and Application

1.1 This method is applicable for the determination of yaw angle, near-axial velocity, and the volumetric flow rate of a gas stream in a stack or duct using a two-dimensional (2–D) probe.

2.0 Summary of Method

2.1 A 2–D probe is used to measure the velocity pressure and the yaw angle of the flow velocity vector in a stack or duct. Alternatively, these measurements may be made by operating one of the three-dimensional (3–D) probes described in Method 2F, in yaw determination mode only. From these measurements and a determination of the stack gas density, the average near-axial velocity of the stack gas is calculated. The near-axial velocity accounts for the yaw, but not the pitch, component of flow. The average gas volumetric flow rate in the stack or duct is then determined from the average near-axial velocity.

3.0 Definitions

3.1. *Angle-measuring Device Rotational Offset (R_{ADO}).* The rotational position of an angle-measuring device relative to the reference scribe line, as determined during the pre-test rotational position check described in section 8.3.

3.2 *Calibration Pitot Tube.* The standard (Prandtl type) pitot tube used as a reference when calibrating a probe under this method.

3.3 *Field Test.* A set of measurements conducted at a specific unit or exhaust stack/duct to satisfy the applicable regulation (e.g., a three-run boiler performance test, a single-or multiple-load nine-run relative accuracy test).

3.4 *Full Scale of Pressure-measuring Device.* Full scale refers to the upper limit of the measurement range displayed by the device. For bi-directional pressure gauges, full scale includes the entire pressure range from the lowest negative value to the highest positive value on the pressure scale.

3.5 *Main probe.* Refers to the probe head and that section of probe sheath directly attached to the probe head. The main probe sheath is distinguished from probe extensions, which are sections of sheath added onto the main probe to extend its reach.

3.6 *''May,'' ''Must,'' ''Shall,'' ''Should,''* and the imperative form of verbs.

3.6.1 *''May''* is used to indicate that a provision of this method is optional.

3.6.2 *''Must,'' ''Shall,''* and the imperative form of verbs (such as ''record'' or ''enter'') are used to indicate that a provision of this method is mandatory.

3.6.3 *''Should''* is used to indicate that a provision of this method is not mandatory, but is highly recommended as good practice.

3.7 *Method 1.* Refers to 40 CFR part 60, appendix A, ''Method 1—Sample and velocity traverses for stationary sources.''

3.8 *Method 2.* Refers to 40 CFR part 60, appendix A, ''Method 2—Determination of stack gas velocity and volumetric flow rate (Type S pitot tube).''

3.9 *Method 2F.* Refers to 40 CFR part 60, appendix A, ''Method 2F—Determination of stack gas velocity and volumetric flow rate with three-dimensional probes.''

3.10 *Near-axial Velocity.* The velocity vector parallel to the axis of the stack or duct that accounts for the yaw angle component of gas flow. The term ''near-axial'' is used herein to indicate that the velocity and volumetric flow rate results account for the measured yaw angle component of flow at each measurement point.

3.11 *Nominal Velocity.* Refers to a wind tunnel velocity setting that approximates the actual wind tunnel velocity to within ±1.5 m/sec (±5 ft/sec).

3.12 *Pitch Angle.* The angle between the axis of the stack or duct and the pitch component of flow, i.e., the component of the total velocity vector in a plane defined by the traverse line and the axis of the stack or duct. (Figure 2G–1 illustrates the ''pitch plane.'') From the standpoint of a tester facing a test port in a vertical stack, the pitch component of flow is the vector of flow moving from the center of the stack toward or away from that test port. The pitch angle is the angle described by this pitch component of flow and the vertical axis of the stack.

3.13 *Readability.* For the purposes of this method, readability for an analog measurement device is one half of the smallest scale division. For a digital measurement device, it is the number of decimals displayed by the device.

3.14 *Reference Scribe Line.* A line permanently inscribed on the main probe sheath (in accordance with section 6.1.5.1) to serve as a reference mark for determining yaw angles.

3.15 *Reference Scribe Line Rotational Offset (R_{SLO}).* The rotational position of a probe's reference scribe line relative to the probe's yaw-null position, as determined during the yaw angle calibration described in section 10.5.

3.16 *Response Time*. The time required for the measurement system to fully respond to a change from zero differential pressure and ambient temperature to the stable stack or duct pressure and temperature readings at a traverse point.

3.17 *Tested Probe*. A probe that is being calibrated.

3.18 *Three-dimensional (3–D) Probe*. A directional probe used to determine the velocity pressure and the yaw and pitch angles in a flowing gas stream.

3.19 *Two-dimensional (2–D) Probe*. A directional probe used to measure velocity pressure and yaw angle in a flowing gas stream.

3.20 *Traverse Line*. A diameter or axis extending across a stack or duct on which measurements of velocity pressure and flow angles are made.

3.21 *Wind Tunnel Calibration Location*. A point, line, area, or volume within the wind tunnel test section at, along, or within which probes are calibrated. At a particular wind tunnel velocity setting, the average velocity pressures at specified points at, along, or within the calibration location shall vary by no more than 2 percent or 0.3 mm H_20 (0.01 in. H_2O), whichever is less restrictive, from the average velocity pressure at the calibration pitot tube location. Air flow at this location shall be axial, i.e., yaw and pitch angles within ±3° of 0°. Compliance with these flow criteria shall be demonstrated by performing the procedures prescribed in sections 10.1.1 and 10.1.2. For circular tunnels, no part of the calibration location may be closer to the tunnel wall than 10.2 cm (4 in.) or 25 percent of the tunnel diameter, whichever is farther from the wall. For elliptical or rectangular tunnels, no part of the calibration location may be closer to the tunnel wall than 10.2 cm (4 in.) or 25 percent of the applicable cross-sectional axis, whichever is farther from the wall.

3.22 *Wind Tunnel with Documented Axial Flow*. A wind tunnel facility documented as meeting the provisions of sections 10.1.1 (velocity pressure cross-check) and 10.1.2 (axial flow verification) using the procedures described in these sections or alternative procedures determined to be technically equivalent.

3.23 *Yaw Angle*. The angle between the axis of the stack or duct and the yaw component of flow, i.e., the component of the total velocity vector in a plane perpendicular to the traverse line at a particular traverse point. (Figure 2G–1 illustrates the ''yaw plane.'') From the standpoint of a tester facing a test port in a vertical stack, the yaw component of flow is the vector of flow moving to the left or right from the center of the stack as viewed by the tester. (This is sometimes referred to as ''vortex flow,'' i.e., flow around the centerline of a stack or duct.) The yaw angle is the angle described by this yaw component of flow and the vertical axis of the stack. The algebraic sign convention is illustrated in Figure 2G–2.

3.24 *Yaw Nulling*. A procedure in which a Type-S pitot tube or a 3–D probe is rotated about its axis in a stack or duct until a zero differential pressure reading (''yaw null'') is obtained. When a Type S probe is yaw-nulled, the rotational position of its impact port is 90° from the direction of flow in the stack or duct and the ΔP reading is zero. When a 3–D probe is yaw-nulled, its impact pressure port (P_1) faces directly into the direction of flow in the stack or duct and the differential pressure between pressure ports P_2 and P_3 is zero.

4.0 Interferences [Reserved]

5.0 Safety

5.1 This test method may involve hazardous operations and the use of hazardous materials or equipment. This method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user to establish and implement appropriate safety and health practices and to determine the applicability of regulatory limitations before using this test method.

6.0 Equipment and Supplies

6.1 Two-dimensional Probes. Probes that provide both the velocity pressure and the yaw angle of the flow vector in a stack or duct, as listed in sections 6.1.1 and 6.1.2, qualify for use based on comprehensive wind tunnel and field studies involving both inter-and intra-probe comparisons by multiple test teams. Each 2–D probe shall have a unique identification number or code permanently marked on the main probe sheath. Each probe shall be calibrated prior to use according to the procedures in section 10. Manufacturer-supplied calibration data shall be used as example information only, except when the manufacturer calibrates the probe as specified in section 10 and provides complete documentation.

6.1.1 Type S (Stausscheibe or reverse type) pitot tube. This is the same as specified in Method 2, section 2.1, except for the following additional specifications that enable the pitot tube to accurately determine the yaw component of flow. For the purposes of this method, the external diameter of the tubing used to construct the Type S pitot tube (dimension D_t in Figure 2–2 of Method 2) shall be no less than 9.5 mm (3/8 in.). The pitot tube shall also meet the following alignment specifications. The angles α_1, α_2, β_1, and β_2, as shown in Method 2, Figure 2–3, shall not exceed ±2°. The dimensions w and z, shown in Method 2, Figure 2–3 shall not exceed 0.5 mm (0.02 in.).

6.1.1.1 Manual Type S probe. This refers to a Type S probe that is positioned at individual traverse points and yaw nulled manually by an operator.

6.1.1.2 Automated Type S probe. This refers to a system that uses a computer-controlled motorized mechanism to position the Type S pitot head at individual traverse points and perform yaw angle determinations.

6.1.2 Three-dimensional probes used in 2–D mode. A 3–D probe, as specified in sections 6.1.1 through 6.1.3 of Method 2F, may, for the purposes of this method, be used in a two-dimensional mode (i.e., measuring yaw angle, but not pitch angle). When the 3–D probe is used as a 2–D probe, only the velocity pressure and yaw-null pressure are obtained using the pressure taps referred to as P_1, P_2, and P_3. The differential pressure P_1–P_2 is a function of total velocity and corresponds to the ΔP obtained using the Type S probe. The differential pressure P_2–P_3 is used to yaw null the probe and determine the yaw angle. The differential pressure P_4–P_5, which is a function of pitch angle, is not measured when the 3–D probe is used in 2–D mode.

6.1.3 Other probes. [Reserved]

6.1.4 Probe sheath. The probe shaft shall include an outer sheath to: (1) provide a surface for inscribing a permanent reference scribe line, (2) accommodate attachment of an angle-measuring device to the probe shaft, and (3) facilitate precise rotational movement of the probe for determining yaw angles. The sheath shall be rigidly attached to the probe assembly and shall enclose all pressure lines from the probe head to the farthest position away from the probe head where an angle-measuring device may be attached during use in the field. The sheath of the fully assembled probe shall be sufficiently rigid and straight at all rotational positions such that, when one end of the probe shaft is held in a horizontal position, the fully extended probe meets the horizontal straightness specifications indicated in section 8.2 below.

6.1.5 Scribe lines.

6.1.5.1 Reference scribe line. A permanent line, no greater than 1.6 mm (1/16 in.) in width, shall be inscribed on each manual probe that will be used to determine yaw angles of flow. This line shall be placed on the main probe sheath in accordance with the procedures described in section 10.4 and is used as a reference position for installation of the yaw angle-measuring device on the probe. At the discretion of the tester, the scribe line may be a single line segment placed at a particular position on the probe sheath (e.g., near the probe head), multiple line segments placed at various locations along the length of the probe sheath (e.g., at every position where a yaw angle-measuring device may be mounted), or a single continuous line extending along the full length of the probe sheath.

6.1.5.2 Scribe line on probe extensions. A permanent line may also be inscribed on any probe extension that will be attached to the main probe in performing field testing. This allows a yaw angle-measuring device mounted on the extension to be readily aligned with the reference scribe line on the main probe sheath.

6.1.5.3 Alignment specifications. This specification shall be met separately, using the procedures in section 10.4.1, on the main probe and on each probe extension. The rotational position of the scribe line or scribe line segments on the main probe or any probe extension must not vary by more than 2°. That is, the difference between the minimum and maximum of all of the rotational angles that are measured along the full length of the main probe or the probe extension must not exceed 2°.

6.1.6 Probe and system characteristics to ensure horizontal stability.

6.1.6.1 For manual probes, it is recommended that the effective length of the probe (coupled with a probe extension, if necessary) be at least 0.9 m (3 ft.) longer than the farthest traverse point mark on the probe shaft away from the probe head. The operator should maintain the probe's horizontal stability when it is fully inserted into the stack or duct. If a shorter probe is used, the probe should be inserted through a bushing sleeve, similar to the one shown in Figure 2G–3, that is installed on the test port; such a bushing shall fit snugly around the probe and be secured to the stack or duct entry port in such a manner as to maintain the probe's horizontal stability when fully inserted into the stack or duct.

6.1.6.2 An automated system that includes an external probe casing with a transport system shall have a mechanism for maintaining horizontal stability comparable to that obtained by manual probes following the provisions of this method. The automated probe assembly shall also be constructed to maintain the alignment and position of the pressure ports during sampling at each traverse point. The design of the probe casing and transport system shall allow the probe to be removed from the stack or duct and checked through direct physical measurement for angular position and insertion depth.

6.1.7 The tubing that is used to connect the probe and the pressure-measuring device should have an inside diameter of at least 3.2 mm (⅛ in.), to reduce the time required for pressure equilibration, and should be as short as practicable.

6.1.8 If a detachable probe head without a sheath [e.g., a pitot tube, typically 15.2 to 30.5 cm (6 to 12 in.) in length] is coupled with a probe sheath and calibrated in a wind tunnel in accordance with the yaw angle calibration procedure in section 10.5, the probe head shall remain attached to the probe

sheath during field testing in the same configuration and orientation as calibrated. Once the detachable probe head is uncoupled or re-oriented, the yaw angle calibration of the probe is no longer valid and must be repeated before using the probe in subsequent field tests.

6.2 Yaw Angle-measuring Device. One of the following devices shall be used for measurement of the yaw angle of flow.

6.2.1 Digital inclinometer. This refers to a digital device capable of measuring and displaying the rotational position of the probe to within ±1°. The device shall be able to be locked into position on the probe sheath or probe extension, so that it indicates the probe's rotational position throughout the test. A rotational position collar block that can be attached to the probe sheath (similar to the collar shown in Figure 2G–4) may be required to lock the digital inclinometer into position on the probe sheath.

6.2.2 Protractor wheel and pointer assembly. This apparatus, similar to that shown in Figure 2G–5, consists of the following components.

6.2.2.1 A protractor wheel that can be attached to a port opening and set in a fixed rotational position to indicate the yaw angle position of the probe's scribe line relative to the longitudinal axis of the stack or duct. The protractor wheel must have a measurement ring on its face that is no less than 17.8 cm (7 in.) in diameter, shall be able to be rotated to any angle and then locked into position on the stack or duct test port, and shall indicate angles to a resolution of 1°.

6.2.2.2 A pointer assembly that includes an indicator needle mounted on a collar that can slide over the probe sheath and be locked into a fixed rotational position on the probe sheath. The pointer needle shall be of sufficient length, rigidity, and sharpness to allow the tester to determine the probe's angular position to within 1° from the markings on the protractor wheel. Corresponding to the position of the pointer, the collar must have a scribe line to be used in aligning the pointer with the scribe line on the probe sheath.

6.2.3 Other yaw angle-measuring devices. Other angle-measuring devices with a manufacturer's specified precision of 1° or better may be used, if approved by the Administrator.

6.3 Probe Supports and Stabilization Devices. When probes are used for determining flow angles, the probe head should be kept in a stable horizontal position. For probes longer than 3.0 m (10 ft.), the section of the probe that extends outside the test port shall be secured. Three alternative devices are suggested for maintaining the horizontal position and stability of the probe shaft during flow angle determinations and velocity pressure measurements: (1) monorails installed above each port, (2) probe stands on which the probe shaft may be rested, or (3) bushing sleeves of sufficient length secured to the test ports to maintain probes in a horizontal position. Comparable provisions shall be made to ensure that automated systems maintain the horizontal position of the probe in the stack or duct. The physical characteristics of each test platform may dictate the most suitable type of stabilization device. Thus, the choice of a specific stabilization device is left to the judgement of the testers.

6.4 Differential Pressure Gauges. The velocity pressure (ΔP) measuring devices used during wind tunnel calibrations and field testing shall be either electronic manometers (e.g., pressure transducers), fluid manometers, or mechanical pressure gauges (e.g., MagnehelicΔ gauges). Use of electronic manometers is recommended. Under low velocity conditions, use of electronic manometers may be necessary to obtain acceptable measurements.

6.4.1 Differential pressure-measuring device. This refers to a device capable of measuring pressure differentials and having a readability of ±1 percent of full scale. The device shall be capable of accurately measuring the maximum expected pressure differential. Such devices are used to determine the following pressure measurements: velocity pressure, static pressure, and yaw-null pressure. For an inclined-vertical manometer, the readability specification of ±1 percent shall be met separately using the respective full-scale upper limits of the inclined anvertical portions of the scales. To the extent practicable, the device shall be selected such that most of the pressure readings are between 10 and 90 percent of the device's full-scale measurement range (as defined in section 3.4). In addition, pressure-measuring devices should be selected such that the zero does not drift by more than 5 percent of the average expected pressure readings to be encountered during the field test. This is particularly important under low pressure conditions.

6.4.2 Gauge used for yaw nulling. The differential pressure-measuring device chosen for yaw nulling the probe during the wind tunnel calibrations and field testing shall be bi-directional, i.e., capable of reading both positive and negative differential pressures. If a mechanical, bi-directional pressure gauge is chosen, it shall have a full-scale range no greater than 2.6 cm (i.e., −1.3 to + 1.3 cm) [1 in. H_2O (i.e., −0.5 in. to + 0.5 in.)].

6.4.3 Devices for calibrating differential pressure-measuring devices. A precision manometer (e.g., a U-tube, inclined, or inclined-vertical manometer, or micromanometer) or NIST (National Institute of Standards and Technology) traceable pressure source shall be used for calibrating differential pressure-measuring devices. The device shall be maintained under laboratory conditions or in a similar protected environment (e.g., a climate-controlled trailer). It shall not be used

in field tests. The precision manometer shall have a scale gradation of 0.3 mm H_2O (0.01 in. H_2O), or less, in the range of 0 to 5.1 cm H_2O (0 to 2 in. H_2O) and 2.5 mm H_2O (0.1 in. H_2O), or less, in the range of 5.1 to 25.4 cm H_2O (2 to 10 in. H_2O). The manometer shall have manufacturer's documentation that it meets an accuracy specification of at least 0.5 percent of full scale. The NIST-traceable pressure source shall be recertified annually.

6.4.4 Devices used for post-test calibration check. A precision manometer meeting the specifications in section 6.4.3, a pressure-measuring device or pressure source with a documented calibration traceable to NIST, or an equivalent device approved by the Administrator shall be used for the post-test calibration check. The pressure-measuring device shall have a readability equivalent to or greater than the tested device. The pressure source shall be capable of generating pressures between 50 and 90 percent of the range of the tested device and known to within ±1 percent of the full scale of the tested device. The pressure source shall be recertified annually.

6.5 Data Display and Capture Devices. Electronic manometers (if used) shall be coupled with a data display device (such as a digital panel meter, personal computer display, or strip chart) that allows the tester to observe and validate the pressure measurements taken during testing. They shall also be connected to a data recorder (such as a data logger or a personal computer with data capture software) that has the ability to compute and retain the appropriate average value at each traverse point, identified by collection time and traverse point.

6.6 Temperature Gauges. For field tests, a thermocouple or resistance temperature detector (RTD) capable of measuring temperature to within ±3 °C (±5 °F) of the stack or duct temperature shall be used. The thermocouple shall be attached to the probe such that the sensor tip does not touch any metal. The position of the thermocouple relative to the pressure port face openings shall be in the same configuration as used for the probe calibrations in the wind tunnel. Temperature gauges used for wind tunnel calibrations shall be capable of measuring temperature to within ±0.6 °C (±1 °F) of the temperature of the flowing gas stream in the wind tunnel.

6.7 Stack or Duct Static Pressure Measurement. The pressure-measuring device used with the probe shall be as specified in section 6.4 of this method. The static tap of a standard (Prandtl type) pitot tube or one leg of a Type S pitot tube with the face opening planes positioned parallel to the gas flow may be used for this measurement. Also acceptable is the pressure differential reading of P_1-P_{bar} from a five-hole prism-shaped 3–D probe, as specified in section 6.1.1 of Method 2F (such as the Type DA or DAT probe), with the P_1 pressure port face opening positioned parallel to the gas flow in the same manner as the Type S probe. However, the 3–D spherical probe, as specified in section 6.1.2 of Method 2F, is unable to provide this measurement and shall not be used to take static pressure measurements. Static pressure measurement is further described in section 8.11.

6.8 Barometer. Same as Method 2, section 2.5.

6.9 Gas Density Determination Equipment. Method 3 or 3A shall be used to determine the dry molecular weight of the stack or duct gas. Method 4 shall be used for moisture content determination and computation of stack or duct gas wet molecular weight. Other methods may be used, if approved by the Administrator.

6.10 Calibration Pitot Tube. Same as Method 2, section 2.7.

6.11 Wind Tunnel for Probe Calibration. Wind tunnels used to calibrate velocity probes must meet the following design specifications.

6.11.1 Test section cross-sectional area. The flowing gas stream shall be confined within a circular, rectangular, or elliptical duct. The cross-sectional area of the tunnel must be large enough to ensure fully developed flow in the presence of both the calibration pitot tube and the tested probe. The calibration site, or ''test section,'' of the wind tunnel shall have a minimum diameter of 30.5 cm (12 in.) for circular or elliptical duct cross-sections or a minimum width of 30.5 cm (12 in.) on the shorter side for rectangular cross-sections. Wind tunnels shall meet the probe blockage provisions of this section and the qualification requirements prescribed in section 10.1. The projected area of the portion of the probe head, shaft, and attached devices inside the wind tunnel during calibration shall represent no more than 2 percent of the cross-sectional area of the tunnel. If the pitot and/or probe assembly blocks more than 2 percent of the cross-sectional area at an insertion point only 4 inches inside the wind tunnel, the diameter of the wind tunnel must be increased.

6.11.2 Velocity range and stability. The wind tunnel should be capable of achieving and maintaining a constant and steady velocity between 6.1 m/sec and 30.5 m/sec (20 ft/sec and 100 ft/sec) for the entire calibration period for each selected calibration velocity. The wind tunnel shall produce fully developed flow patterns that are stable and parallel to the axis of the duct in the test section.

6.11.3 Flow profile at the calibration location. The wind tunnel shall provide axial flow within the test section calibration location (as defined in section 3.21). Yaw and pitch angles in the calibration location shall be within ±3° of 0°. The procedure for determining that this requirement has been met is described in section 10.1.2.

6.11.4 Entry ports in the wind tunnel test section.

6.11.4.1 Port for tested probe. A port shall be constructed for the tested probe. This port shall be located to allow the head of the tested probe to be positioned within the wind tunnel calibration location (as defined in section 3.21). The tested probe shall be able to be locked into the 0° pitch angle position. To facilitate alignment of the probe during calibration, the test section should include a window constructed of a transparent material to allow the tested probe to be viewed.

6.11.4.2 Port for verification of axial flow. Depending on the equipment selected to conduct the axial flow verification prescribed in section 10.1.2, a second port, located 90° from the entry port for the tested probe, may be needed to allow verification that the gas flow is parallel to the central axis of the test section. This port should be located and constructed so as to allow one of the probes described in section 10.1.2.2 to access the same test point(s) that are accessible from the port described in section 6.11.4.1.

6.11.4.3 Port for calibration pitot tube. The calibration pitot tube shall be used in the port for the tested probe or in a separate entry port. In either case, all measurements with the calibration pitot tube shall be made at the same point within the wind tunnel over the course of a probe calibration. The measurement point for the calibration pitot tube shall meet the same specifications for distance from the wall and for axial flow as described in section 3.21 for the wind tunnel calibration location.

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection and Analysis

8.1 Equipment Inspection and Set Up

8.1.1 All 2–D and 3–D probes, differential pressure-measuring devices, yaw angle-measuring devices, thermocouples, and barometers shall have a current, valid calibration before being used in a field test. (See sections 10.3.3, 10.3.4, and 10.5 through 10.10 for the applicable calibration requirements.)

8.1.2 Before each field use of a Type S probe, perform a visual inspection to verify the physical condition of the pitot tube. Record the results of the inspection. If the face openings are noticeably misaligned or there is visible damage to the face openings, the probe shall not be used until repaired, the dimensional specifications verified (according to the procedures in section 10.2.1), and the probe recalibrated.

8.1.3 Before each field use of a 3–D probe, perform a visual inspection to verify the physical condition of the probe head according to the procedures in section 10.2 of Method 2F. Record the inspection results on a form similar to Table 2F–1 presented in Method 2F. If there is visible damage to the 3–D probe, the probe shall not be used until it is recalibrated.

8.1.4 After verifying that the physical condition of the probe head is acceptable, set up the apparatus using lengths of flexible tubing that are as short as practicable. Surge tanks installed between the probe and pressure-measuring device may be used to dampen pressure fluctuations provided that an adequate measurement system response time (see section 8.8) is maintained.

8.2 Horizontal Straightness Check. A horizontal straightness check shall be performed before the start of each field test, except as otherwise specified in this section. Secure the fully assembled probe (including the probe head and all probe shaft extensions) in a horizontal position using a stationary support at a point along the probe shaft approximating the location of the stack or duct entry port when the probe is sampling at the farthest traverse point from the stack or duct wall. The probe shall be rotated to detect bends. Use an angle-measuring device or trigonometry to determine the bend or sag between the probe head and the secured end. (See Figure 2G–6.) Probes that are bent or sag by more than 5° shall not be used. Although this check does not apply when the probe is used for a vertical traverse, care should be taken to avoid the use of bent probes when conducting vertical traverses. If the probe is constructed of a rigid steel material and consists of a main probe without probe extensions, this check need only be performed before the initial field use of the probe, when the probe is recalibrated, when a change is made to the design or material of the probe assembly, and when the probe becomes bent. With such probes, a visual inspection shall be made of the fully assembled probe before each field test to determine if a bend is visible. The probe shall be rotated to detect bends. The inspection results shall be documented in the field test report. If a bend in the probe is visible, the horizontal straightness check shall be performed before the probe is used.

8.3 Rotational Position Check. Before each field test, and each time an extension is added to the probe during a field test, a rotational position check shall be performed on all manually operated probes (except as noted in section 8.3.5 below) to ensure that, throughout testing, the angle-measuring device is either: aligned to within ±1° of the rotational position of the reference scribe line; or is affixed to the probe such that the rotational offset of the device from the reference scribe line is known to within ±1°. This check shall consist of direct measurements of the rotational positions of the reference scribe line and angle-measuring device sufficient to verify that these specifications are met. Annex A in section 18 of this method gives recommended procedures for performing the rotational position check, and Table 2G–2

gives an example data form. Procedures other than those recommended in Annex A in section 18 may be used, provided they demonstrate whether the alignment specification is met and are explained in detail in the field test report.

8.3.1 Angle-measuring device rotational offset. The tester shall maintain a record of the angle-measuring device rotational offset, R_{ADO}, as defined in section 3.1. Note that R_{ADO} is assigned a value of 0° when the angle-measuring device is aligned to within ±1° of the rotational position of the reference scribe line. The R_{ADO} shall be used to determine the yaw angle of flow in accordance with section 8.9.4.

8.3.2 Sign of angle-measuring device rotational offset. The sign of R_{ADO} is positive when the angle-measuring device (as viewed from the ''tail'' end of the probe) is positioned in a clockwise direction from the reference scribe line and negative when the device is positioned in a counterclockwise direction from the reference scribe line.

8.3.3 Angle-measuring devices that can be independently adjusted (e.g., by means of a set screw), after being locked into position on the probe sheath, may be used. However, the R_{ADO} must also take into account this adjustment.

8.3.4 Post-test check. If probe extensions remain attached to the main probe throughout the field test, the rotational position check shall be repeated, at a minimum, at the completion of the field test to ensure that the angle-measuring device has remained within ±2° of its rotational position established prior to testing. At the discretion of the tester, additional checks may be conducted after completion of testing at any sample port or after any test run. If the ±2° specification is not met, all measurements made since the last successful rotational position check must be repeated. section 18.1.1.3 of Annex A provides an example procedure for performing the post-test check.

8.3.5 Exceptions.

8.3.5.1 A rotational position check need not be performed if, for measurements taken at all velocity traverse points, the yaw angle-measuring device is mounted and aligned directly on the reference scribe line specified in sections 6.1.5.1 and 6.1.5.3 and no independent adjustments, as described in section 8.3.3, are made to device's rotational position.

8.3.5.2 If extensions are detached and re-attached to the probe during a field test, a rotational position check need only be performed the first time an extension is added to the probe, rather than each time the extension is re-attached, if the probe extension is designed to be locked into a mechanically fixed rotational position (e.g., through the use of interlocking grooves), that can re-establish the initial rotational position to within ±1°.

8.4 Leak Checks. A pre-test leak check shall be conducted before each field test. A post-test check shall be performed at the end of the field test, but additional leak checks may be conducted after any test run or group of test runs. The post-test check may also serve as the pre-test check for the next group of test runs. If any leak check is failed, all runs since the last passed leak check are invalid. While performing the leak check procedures, also check each pressure device's responsiveness to changes in pressure.

8.4.1 To perform the leak check on a Type S pitot tube, pressurize the pitot impact opening until at least 7.6 cm H_2O (3 in. H_2O) velocity pressure, or a pressure corresponding to approximately 75 percent of the pressure device's measurement scale, whichever is less, registers on the pressure device; then, close off the impact opening. The pressure shall remain stable (±2.5 mm H_2O, ±0.10 in. H_2O) for at least 15 seconds. Repeat this procedure for the static pressure side, except use suction to obtain the required pressure. Other leak-check procedures may be used, if approved by the Administrator.

8.4.2 To perform the leak check on a 3–D probe, pressurize the probe's impact (P_1) opening until at least 7.6 cm H_2O (3 in. H_2O) velocity pressure, or a pressure corresponding to approximately 75 percent of the pressure device's measurement scale, whichever is less, registers on the pressure device; then, close off the impact opening. The pressure shall remain stable (±2.5 mm H_2O, ±0.10 in. H_2O) for at least 15 seconds. Check the P_2 and P_3 pressure ports in the same fashion. Other leak-check procedures may be used, if approved by the Administrator.

8.5 Zeroing the Differential Pressure-measuring Device. Zero each differential pressure-measuring device, including the device used for yaw nulling, before each field test. At a minimum, check the zero after each field test. A zero check may also be performed after any test run or group of test runs. For fluid manometers and mechanical pressure gauges (e.g., Magnehelic∆ gauges), the zero reading shall not deviate from zero by more than ±0.8 mm H_2O (±0.03 in. H_2O) or one minor scale division, whichever is greater, between checks. For electronic manometers, the zero reading shall not deviate from zero between checks by more than: ±0.3 mm H_2O (±0.01 in. H_2O), for full scales less than or equal to 5.1 cm H_2O (2.0 in. H_2O); or ±0.8 mm H_2O (±0.03 in. H_2O), for full scales greater than 5.1 cm H_2O (2.0 in. H_2O). (NOTE: If negative zero drift is not directly readable, estimate the reading based on the position of the gauge oil in the manometer or of the needle on the pressure gauge.) In addition, for all pressure-measuring devices except those used exclusively for yaw nulling, the zero

reading shall not deviate from zero by more than 5 percent of the average measured differential pressure at any distinct process condition or load level. If any zero check is failed at a specific process condition or load level, all runs conducted at that process condition or load level since the last passed zero check are invalid.

8.6 Traverse Point Verification. The number and location of the traverse points shall be selected based on Method 1 guidelines. The stack or duct diameter and port nipple lengths, including any extension of the port nipples into the stack or duct, shall be verified the first time the test is performed; retain and use this information for subsequent field tests, updating it as required. Physically measure the stack or duct dimensions or use a calibrated laser device; do not use engineering drawings of the stack or duct. The probe length necessary to reach each traverse point shall be recorded to within ±6.4 mm (±¼ in.) and, for manual probes, marked on the probe sheath. In determining these lengths, the tester shall take into account both the distance that the port flange projects outside of the stack and the depth that any port nipple extends into the gas stream. The resulting point positions shall reflect the true distances from the inside wall of the stack or duct, so that when the tester aligns any of the markings with the outside face of the stack port, the probe's impact port shall be located at the appropriate distance from the inside wall for the respective Method 1 traverse point. Before beginning testing at a particular location, an out-of-stack or duct verification shall be performed on each probe that will be used to ensure that these position markings are correct. The distances measured during the verification must agree with the previously calculated distances to within ±¼ in. For manual probes, the traverse point positions shall be verified by measuring the distance of each mark from the probe's impact pressure port (the P_1 port for a 3-D probe). A comparable out-of-stack test shall be performed on automated probe systems. The probe shall be extended to each of the prescribed traverse point positions. Then, the accuracy of the positioning for each traverse point shall be verified by measuring the distance between the port flange and the probe's impact pressure port.

8.7 Probe Installation. Insert the probe into the test port. A solid material shall be used to seal the port.

8.8 System Response Time. Determine the response time of the probe measurement system. Insert and position the ''cold'' probe (at ambient temperature and pressure) at any Method 1 traverse point. Read and record the probe differential pressure, temperature, and elapsed time at 15-second intervals until stable readings for both pressure and temperature are achieved. The response time is the longer of these two elapsed times. Record the response time.

8.9 Sampling.

8.9.1 Yaw angle measurement protocol. With manual probes, yaw angle measurements may be obtained in two alternative ways during the field test, either by using a yaw angle-measuring device (e.g., digital inclinometer) affixed to the probe, or using a protractor wheel and pointer assembly. For horizontal traversing, either approach may be used. For vertical traversing, i.e., when measuring from on top or into the bottom of a horizontal duct, only the protractor wheel and pointer assembly may be used. With automated probes, curve-fitting protocols may be used to obtain yaw-angle measurements.

8.9.1.1 If a yaw angle-measuring device affixed to the probe is to be used, lock the device on the probe sheath, aligning it either on the reference scribe line or in the rotational offset position established under section 8.3.1.

8.9.1.2 If a protractor wheel and pointer assembly is to be used, follow the procedures in Annex B of this method.

8.9.1.3 Curve-fitting procedures. Curve-fitting routines sweep through a range of yaw angles to create curves correlating pressure to yaw position. To find the zero yaw position and the yaw angle of flow, the curve found in the stack is computationally compared to a similar curve that was previously generated under controlled conditions in a wind tunnel. A probe system that uses a curve-fitting routine for determining the yaw-null position of the probe head may be used, provided that it is verified in a wind tunnel to be able to determine the yaw angle of flow to within ±1°.

8.9.1.4 Other yaw angle determination procedures. If approved by the Administrator, other procedures for determining yaw angle may be used, provided that they are verified in a wind tunnel to be able to perform the yaw angle calibration procedure as described in section 10.5.

8.9.2 Sampling strategy. At each traverse point, first yaw-null the probe, as described in section 8.9.3, below. Then, with the probe oriented into the direction of flow, measure and record the yaw angle, the differential pressure and the temperature at the traverse point, after stable readings are achieved, in accordance with sections 8.9.4 and 8.9.5. At the start of testing in each port (i.e., after a probe has been inserted into the flue gas stream), allow at least the response time to elapse before beginning to take measurements at the first traverse point accessed from that port. Provided that the probe is not removed from the flue gas stream, measurements may be taken at subsequent traverse points accessed from the same test port without waiting again for the response time to elapse.

8.9.3 Yaw-nulling procedure. In preparation for yaw angle determination, the probe must first be yaw nulled. After positioning the probe at the appropriate traverse point, perform the following procedures.

8.9.3.1 For Type S probes, rotate the probe until a null differential pressure reading is obtained. The direction of the probe rotation shall be such that the thermocouple is located downstream of the probe pressure ports at the yaw-null position. Rotate the probe 90° back from the yaw-null position to orient the impact pressure port into the direction of flow. Read and record the angle displayed by the angle-measuring device.

8.9.3.2 For 3-D probes, rotate the probe until a null differential pressure reading (the difference in pressures across the P_2 and P_3 pressure ports is zero, i.e., $P_2 = P_3$) is indicated by the yaw angle pressure gauge. Read and record the angle displayed by the angle-measuring device.

8.9.3.3 Sign of the measured angle. The angle displayed on the angle-measuring device is considered positive when the probe's impact pressure port (as viewed from the ''tail'' end of the probe) is oriented in a clockwise rotational position relative to the stack or duct axis and is considered negative when the probe's impact pressure port is oriented in a counterclockwise rotational position (see Figure 2G–7).

8.9.4 Yaw angle determination. After performing the applicable yaw-nulling procedure in section 8.9.3, determine the yaw angle of flow according to one of the following procedures. Special care must be observed to take into account the signs of the recorded angle reading and all offsets.

8.9.4.1 Direct-reading. If all rotational offsets are zero or if the angle-measuring device rotational offset (R_{ADO}) determined in section 8.3 exactly compensates for the scribe line rotational offset (R_{SLO}) determined in section 10.5, then the magnitude of the yaw angle is equal to the displayed angle-measuring device reading from section 8.9.3.1 or 8.9.3.2. The algebraic sign of the yaw angle is determined in accordance with section 8.9.3.3. [NOTE: Under certain circumstances (e.g., testing of horizontal ducts) a 90° adjustment to the angle-measuring device readings may be necessary to obtain the correct yaw angles.]

8.9.4.2 Compensation for rotational offsets during data reduction. When the angle-measuring device rotational offset does not compensate for reference scribe line rotational offset, the following procedure shall be used to determine the yaw angle:

(a) Enter the reading indicated by the angle-measuring device from section 8.9.3.1 or 8.9.3.2.

(b) Associate the proper algebraic sign from section 8.9.3.3 with the reading in step (a).

(c) Subtract the reference scribe line rotational offset, R_{SLO}, from the reading in step (b).

(d) Subtract the angle-measuring device rotational offset, R_{ADO}, if any, from the result obtained in step (c).

(e) The final result obtained in step (d) is the yaw angle of flow.

[NOTE: It may be necessary to first apply a 90° adjustment to the reading in step (a), in order to obtain the correct yaw angle.]

8.9.4.3 Record the yaw angle measurements on a form similar to Table 2G–3.

8.9.5 Impact velocity determination. Maintain the probe rotational position established during the yaw angle determination. Then, begin recording the pressure-measuring device readings. These pressure measurements shall be taken over a sampling period of sufficiently long duration to ensure representative readings at each traverse point. If the pressure measurements are determined from visual readings of the pressure device or display, allow sufficient time to observe the pulsation in the readings to obtain a sight-weighted average, which is then recorded manually. If an automated data acquisition system (e.g., data logger, computer-based data recorder, strip chart recorder) is used to record the pressure measurements, obtain an integrated average of all pressure readings at the traverse point. Stack or duct gas temperature measurements shall be recorded, at a minimum, once at each traverse point. Record all necessary data as shown in the example field data form (Table 2G–3).

8.9.6 Alignment check. For manually operated probes, after the required yaw angle and differential pressure and temperature measurements have been made at each traverse point, verify (e.g., by visual inspection) that the yaw angle-measuring device has remained in proper alignment with the reference scribe line or with the rotational offset position established in section 8.3. If, for a particular traverse point, the angle-measuring device is found to be in proper alignment, proceed to the next traverse point; otherwise, re-align the device and repeat the angle and differential pressure measurements at the traverse point. In the course of a traverse, if a mark used to properly align the angle-measuring device (e.g., as described in section 18.1.1.1) cannot be located, re-establish the alignment mark before proceeding with the traverse.

8.10 Probe Plugging. Periodically check for plugging of the pressure ports by observing the responses on the pressure differential readouts. Plugging causes erratic results or sluggish responses. Rotate the probe to determine whether the readouts respond in the expected direction. If plugging is detected, correct the problem and repeat the affected measurements.

8.11 Static Pressure. Measure the static pressure in the stack or duct using the equipment described in section 6.7.

8.11.1 If a Type S probe is used for this measurement, position the probe at or between any traverse point(s) and rotate the probe until a null differential pressure reading is obtained. Disconnect the tubing from one of the pressure ports; read and record the ΔP. For pressure devices with one-directional scales, if a deflection in the positive direction is noted with the negative side disconnected, then the static pressure is positive. Likewise, if a deflection in the positive direction is noted with the positive side disconnected, then the static pressure is negative.

8.11.2 If a 3–D probe is used for this measurement, position the probe at or between any traverse point(s) and rotate the probe until a null differential pressure reading is obtained at P_2–P_3. Rotate the probe 90°. Disconnect the P_2 pressure side of the probe and read the pressure P_1–P_{bar} and record as the static pressure. (NOTE: The spherical probe, specified in section 6.1.2 of Method 2F, is unable to provide this measurement and shall not be used to take static pressure measurements.)

8.12 Atmospheric Pressure. Determine the atmospheric pressure at the sampling elevation during each test run following the procedure described in section 2.5 of Method 2.

8.13 Molecular Weight. Determine the stack or duct gas dry molecular weight. For combustion processes or processes that emit essentially CO_2, O_2, CO, and N_2, use Method 3 or 3A. For processes emitting essentially air, an analysis need not be conducted; use a dry molecular weight of 29.0. Other methods may be used, if approved by the Administrator.

8.14 Moisture. Determine the moisture content of the stack gas using Method 4 or equivalent.

8.15 Data Recording and Calculations. Record all required data on a form similar to Table 2G–3.

8.15.1 2–D probe calibration coefficient. When a Type S pitot tube is used in the field, the appropriate calibration coefficient as determined in section 10.6 shall be used to perform velocity calculations. For calibrated Type S pitot tubes, the A-side coefficient shall be used when the A-side of the tube faces the flow, and the B-side coefficient shall be used when the B-side faces the flow.

8.15.2 3–D calibration coefficient. When a 3–D probe is used to collect data with this method, follow the provisions for the calibration of 3–D probes in section 10.6 of Method 2F to obtain the appropriate velocity calibration coefficient (F_2 as derived using Equation 2F–2 in Method 2F) corresponding to a pitch angle position of 0°.

8.15.3 Calculations. Calculate the yaw-adjusted velocity at each traverse point using the equations presented in section 12.2. Calculate the test run average stack gas velocity by finding the arithmetic average of the point velocity results in accordance with sections 12.3 and 12.4, and calculate the stack gas volumetric flow rate in accordance with section 12.5 or 12.6, as applicable.

9.0 Quality Control

9.1 Quality Control Activities. In conjunction with the yaw angle determination and the pressure and temperature measurements specified in section 8.9, the following quality control checks should be performed.

9.1.1 Range of the differential pressure gauge. In accordance with the specifications in section 6.4, ensure that the proper differential pressure gauge is being used for the range of ΔP values encountered. If it is necessary to change to a more sensitive gauge, replace the gauge with a gauge calibrated according to section 10.3.3, perform the leak check described in section 8.4 and the zero check described in section 8.5, and repeat the differential pressure and temperature readings at each traverse point.

9.1.2 Horizontal stability check. For horizontal traverses of a stack or duct, visually check that the probe shaft is maintained in a horizontal position prior to taking a pressure reading. Periodically, during a test run, the probe's horizontal stability should be verified by placing a carpenter's level, a digital inclinometer, or other angle-measuring device on the portion of the probe sheath that extends outside of the test port. A comparable check should be performed by automated systems.

10.0 Calibration

10.1 Wind Tunnel Qualification Checks. To qualify for use in calibrating probes, a wind tunnel shall have the design features specified in section 6.11 and satisfy the following qualification criteria. The velocity pressure cross-check in section 10.1.1 and axial flow verification in section 10.1.2 shall be performed before the initial use of the wind tunnel and repeated immediately after any alteration occurs in the wind tunnel's configuration, fans, interior surfaces, straightening vanes, controls, or other properties that could reasonably be expected to alter the flow pattern or velocity stability in the tunnel. The owner or operator of a wind tunnel used to calibrate probes according to this method shall maintain records documenting that the wind tunnel meets the requirements of sections 10.1.1 and 10.1.2 and shall provide these records to the Administrator upon request.

10.1.1 Velocity pressure cross-check. To verify that the wind tunnel produces the same velocity at the tested probe head as at the calibration pitot tube impact port, perform the following cross-check. Take three

differential pressure measurements at the fixed calibration pitot tube location, using the calibration pitot tube specified in section 6.10, and take three measurements with the calibration pitot tube at the wind tunnel calibration location, as defined in section 3.21. Alternate the measurements between the two positions. Perform this procedure at the lowest and highest velocity settings at which the probes will be calibrated. Record the values on a form similar to Table 2G–4. At each velocity setting, the average velocity pressure obtained at the wind tunnel calibration location shall be within ±2 percent or 2.5 mm H_2O (0.01 in. H_2O), whichever is less restrictive, of the average velocity pressure obtained at the fixed calibration pitot tube location. This comparative check shall be performed at 2.5-cm (1-in.), or smaller, intervals across the full length, width, and depth (if applicable) of the wind tunnel calibration location. If the criteria are not met at every tested point, the wind tunnel calibration location must be redefined, so that acceptable results are obtained at every point. Include the results of the velocity pressure cross-check in the calibration data section of the field test report. (See section 16.1.4.)

10.1.2 Axial flow verification. The following procedures shall be performed to demonstrate that there is fully developed axial flow within the wind tunnel calibration location and at the calibration pitot tube location. Two options are available to conduct this check.

10.1.2.1 Using a calibrated 3–D probe. A probe that has been previously calibrated in a wind tunnel with documented axial flow (as defined in section 3.22) may be used to conduct this check. Insert the calibrated 3–D probe into the wind tunnel test section using the tested probe port. Following the procedures in sections 8.9 and 12.2 of Method 2F, determine the yaw and pitch angles at all the point(s) in the test section where the velocity pressure cross-check, as specified in section 10.1.1, is performed. This includes all the points in the calibration location and the point where the calibration pitot tube will be located. Determine the yaw and pitch angles at each point. Repeat these measurements at the highest and lowest velocities at which the probes will be calibrated. Record the values on a form similar to Table 2G–5. Each measured yaw and pitch angle shall be within ±3° of 0°. Exceeding the limits indicates unacceptable flow in the test section. Until the problem is corrected and acceptable flow is verified by repetition of this procedure, the wind tunnel shall not be used for calibration of probes. Include the results of the axial flow verification in the calibration data section of the field test report. (See section 16.1.4.)

10.1.2.2 Using alternative probes. Axial flow verification may be performed using an uncalibrated prism-shaped 3–D probe (e.g., DA or DAT probe) or an uncalibrated wedge probe. (Figure 2G–8 illustrates a typical wedge probe.) This approach requires use of two ports: the tested probe port and a second port located 90° from the tested probe port. Each port shall provide access to all the points within the wind tunnel test section where the velocity pressure cross-check, as specified in section 10.1.1, is conducted. The probe setup shall include establishing a reference yaw-null position on the probe sheath to serve as the location for installing the angle-measuring device. Physical design features of the DA, DAT, and wedge probes are relied on to determine the reference position. For the DA or DAT probe, this reference position can be determined by setting a digital inclinometer on the flat facet where the P_1 pressure port is located and then identifying the rotational position on the probe sheath where a second angle-measuring device would give the same angle reading. The reference position on a wedge probe shaft can be determined either geometrically or by placing a digital inclinometer on each side of the wedge and rotating the probe until equivalent readings are obtained. With the latter approach, the reference position is the rotational position on the probe sheath where an angle-measuring device would give a reading of 0°. After installation of the angle-measuring device in the reference yaw-null position on the probe sheath, determine the yaw angle from the tested port. Repeat this measurement using the 90° offset port, which provides the pitch angle of flow. Determine the yaw and pitch angles at all the point(s) in the test section where the velocity pressure cross-check, as specified in section 10.1.1, is performed. This includes all the points in the wind tunnel calibration location and the point where the calibration pitot tube will be located. Perform this check at the highest and lowest velocities at which the probes will be calibrated. Record the values on a form similar to Table 2G–5. Each measured yaw and pitch angle shall be within ±3° of 0°. Exceeding the limits indicates unacceptable flow in the test section. Until the problem is corrected and acceptable flow is verified by repetition of this procedure, the wind tunnel shall not be used for calibration of probes. Include the results in the probe calibration report.

10.1.3 Wind tunnel audits.

10.1.3.1 Procedure. Upon the request of the Administrator, the owner or operator of a wind tunnel shall calibrate a 2-D audit probe in accordance with the procedures described in sections 10.3 through 10.6. The calibration shall be performed at two velocities that encompass the velocities typically used for this method at the facility. The resulting calibration data shall be submitted to the Agency in an audit test report. These results shall be

compared by the Agency to reference calibrations of the audit probe at the same velocity settings obtained at two different wind tunnels.

10.1.3.2 Acceptance criterion. The audited tunnel's calibration coefficient is acceptable if it is within ±3 percent of the reference calibrations obtained at each velocity setting by one (or both) of the wind tunnels. If the acceptance criterion is not met at each calibration velocity setting, the audited wind tunnel shall not be used to calibrate probes for use under this method until the problems are resolved and acceptable results are obtained upon completion of a subsequent audit.

10.2 Probe Inspection.

10.2.1 Type S probe. Before each calibration of a Type S probe, verify that one leg of the tube is permanently marked A, and the other, B. Carefully examine the pitot tube from the top, side, and ends. Measure the angles (α_1, α_2, β_1, and β_2) and the dimensions (w and z) illustrated in Figures 2–2 and 2–3 in Method 2. Also measure the dimension A, as shown in the diagram in Table 2G–1, and the external tubing diameter (dimension D_t, Figure 2–2b in Method 2). For the purposes of this method, D_t shall be no less than 9.5 mm (3/8 in.). The base-to-opening plane distances P_A and P_B in Figure 2–3 of Method 2 shall be equal, and the dimension A in Table 2G–1 should be between $2.10D_t$ and $3.00D_t$. Record the inspection findings and probe measurements on a form similar to Table CD2–1 of the ''Quality Assurance Handbook for Air Pollution Measurement Systems: Volume III, Stationary Source-Specific Methods'' (EPA/600/R–94/038c, September 1994). For reference, this form is reproduced herein as Table 2G–1. The pitot tube shall not be used under this method if it fails to meet the specifications in this section and the alignment specifications in section 6.1.1. All Type S probes used to collect data with this method shall be calibrated according to the procedures outlined in sections 10.3 through 10.6 below. During calibration, each Type S pitot tube shall be configured in the same manner as used, or planned to be used, during the field test, including all components in the probe assembly (e.g., thermocouple, probe sheath, sampling nozzle). Probe shaft extensions that do not affect flow around the probe head need not be attached during calibration.

10.2.2 3-D probe. If a 3-D probe is used to collect data with this method, perform the pre-calibration inspection according to procedures in Method 2F, section 10.2.

10.3 Pre-Calibration Procedures. Prior to calibration, a scribe line shall have been placed on the probe in accordance with section 10.4. The yaw angle and velocity calibration procedures shall not begin until the pretest requirements in sections 10.3.1 through 10.3.4 have been met.

10.3.1 Perform the horizontal straightness check described in section 8.2 on the probe assembly that will be calibrated in the wind tunnel.

10.3.2 Perform a leak check in accordance with section 8.4.

10.3.3 Except as noted in section 10.3.3.3, calibrate all differential pressure-measuring devices to be used in the probe calibrations, using the following procedures. At a minimum, calibrate these devices on each day that probe calibrations are performed.

10.3.3.1 Procedure. Before each wind tunnel use, all differential pressure-measuring devices shall be calibrated against the reference device specified in section 6.4.3 using a common pressure source. Perform the calibration at three reference pressures representing 30, 60, and 90 percent of the full-scale range of the pressure-measuring device being calibrated. For an inclined-vertical manometer, perform separate calibrations on the inclined and vertical portions of the measurement scale, considering each portion of the scale to be a separate full-scale range. [For example, for a manometer with a 0-to 2.5-cm H_2O (0-to 1-in. H_2O) inclined scale and a 2.5-to 12.7-cm H_2O (1-to 5-in. H_2O) vertical scale, calibrate the inclined portion at 7.6, 15.2, and 22.9 mm H_2O (0.3, 0.6, and 0.9 in. H_2O), and calibrate the vertical portion at 3.8, 7.6, and 11.4 cm H_2O (1.5, 3.0, and 4.5 in. H_2O).] Alternatively, for the vertical portion of the scale, use three evenly spaced reference pressures, one of which is equal to or higher than the highest differential pressure expected in field applications.

10.3.3.2 Acceptance criteria. At each pressure setting, the two pressure readings made using the reference device and the pressure-measuring device being calibrated shall agree to within ±2 percent of full scale of the device being calibrated or 0.5 mm H_2O (0.02 in. H_2O), whichever is less restrictive. For an inclined-vertical manometer, these requirements shall be met separately using the respective full-scale upper limits of the inclined and vertical portions of the scale. Differential pressure-measuring devices not meeting the ±2 percent of full scale or 0.5 mm H_2O (0.02 in. H_2O) calibration requirement shall not be used.

10.3.3.3 Exceptions. Any precision manometer that meets the specifications for a reference device in section 6.4.3 and that is not used for field testing does not require calibration, but must be leveled and zeroed before each wind tunnel use. Any pressure device used exclusively for yaw nulling does not require calibration, but shall be checked for responsiveness to rotation of the probe prior to each wind tunnel use.

10.3.4 Calibrate digital inclinometers on each day of wind tunnel or field testing

(prior to beginning testing) using the following procedures. Calibrate the inclinometer according to the manufacturer's calibration procedures. In addition, use a triangular block (illustrated in Figure 2G–9) with a known angle θ, independently determined using a protractor or equivalent device, between two adjacent sides to verify the inclinometer readings. (NOTE: If other angle-measuring devices meeting the provisions of section 6.2.3 are used in place of a digital inclinometer, comparable calibration procedures shall be performed on such devices.) Secure the triangular block in a fixed position. Place the inclinometer on one side of the block (side A) to measure the angle of inclination (R_1). Repeat this measurement on the adjacent side of the block (side B) using the inclinometer to obtain a second angle reading (R_2). The difference of the sum of the two readings from 180° (i.e., 180°-R_1-R_2) shall be within ±2° of the known angle, θ.

10.4 Placement of Reference Scribe Line. Prior to the first calibration of a probe, a line shall be permanently inscribed on the main probe sheath to serve as a reference mark for determining yaw angles. Annex C in section 18 of this method gives a guideline for placement of the reference scribe line.

10.4.1 This reference scribe line shall meet the specifications in sections 6.1.5.1 and 6.1.5.3 of this method. To verify that the alignment specification in section 6.1.5.3 is met, secure the probe in a horizontal position and measure the rotational angle of each scribe line and scribe line segment using an angle-measuring device that meets the specifications in section 6.2.1 or 6.2.3. For any scribe line that is longer than 30.5 cm (12 in.), check the line's rotational position at 30.5-cm (12-in.) intervals. For each line segment that is 12 in. or less in length, check the rotational position at the two endpoints of the segment. To meet the alignment specification in section 6.1.5.3, the minimum and maximum of all of the rotational angles that are measured along the full length of main probe must not differ by more than 2°. (NOTE: A short reference scribe line segment [e.g., 15.2 cm (6 in.) or less in length] meeting the alignment specifications in section 6.1.5.3 is fully acceptable under this method. See section 18.1.1.1 of Annex A for an example of a probe marking procedure, suitable for use with a short reference scribe line.)

10.4.2 The scribe line should be placed on the probe first and then its offset from the yaw-null position established (as specified in section 10.5). The rotational position of the reference scribe line relative to the yaw-null position of the probe, as determined by the yaw angle calibration procedure in section 10.5, is the reference scribe line rotational offset, R_{SLO}. The reference scribe line rotational offset shall be recorded and retained as part of the probe's calibration record.

10.4.3 Scribe line for automated probes. A scribe line may not be necessary for an automated probe system if a reference rotational position of the probe is built into the probe system design. For such systems, a ''flat'' (or comparable, clearly identifiable physical characteristic) should be provided on the probe casing or flange plate to ensure that the reference position of the probe assembly remains in a vertical or horizontal position. The rotational offset of the flat (or comparable, clearly identifiable physical characteristic) needed to orient the reference position of the probe assembly shall be recorded and maintained as part of the automated probe system's specifications.

10.5 Yaw Angle Calibration Procedure. For each probe used to measure yaw angles with this method, a calibration procedure shall be performed in a wind tunnel meeting the specifications in section 10.1 to determine the rotational position of the reference scribe line relative to the probe's yaw-null position. This procedure shall be performed on the main probe with all devices that will be attached to the main probe in the field [such as thermocouples, resistance temperature detectors (RTDs), or sampling nozzles] that may affect the flow around the probe head. Probe shaft extensions that do not affect flow around the probe head need not be attached during calibration. At a minimum, this procedure shall include the following steps.

10.5.1 Align and lock the angle-measuring device on the reference scribe line. If a marking procedure (such as described in section 18.1.1.1) is used, align the angle-measuring device on a mark within ±1° of the rotational position of the reference scribe line. Lock the angle-measuring device onto the probe sheath at this position.

10.5.2 Zero the pressure-measuring device used for yaw nulling.

10.5.3 Insert the probe assembly into the wind tunnel through the entry port, positioning the probe's impact port at the calibration location. Check the responsiveness of the pressure-measurement device to probe rotation, taking corrective action if the response is unacceptable.

10.5.4 Ensure that the probe is in a horizontal position, using a carpenter's level.

10.5.5 Rotate the probe either clockwise or counterclockwise until a yaw null [zero ΔP for a Type S probe or zero (P_2-P_3) for a 3–D probe] is obtained. If using a Type S probe with an attached thermocouple, the direction of the probe rotation shall be such that the thermocouple is located downstream of the probe pressure ports at the yaw-null position.

10.5.6 Use the reading displayed by the angle-measuring device at the yaw-null position to determine the magnitude of the reference scribe line rotational offset, R_{SLO}, as defined in section 3.15. Annex D in section 18

of this method gives a recommended procedure for determining the magnitude of R_{SLO} with a digital inclinometer and a second procedure for determining the magnitude of R_{SLO} with a protractor wheel and pointer device. Table 2G–6 gives an example data form and Table 2G–7 is a look-up table with the recommended procedure. Procedures other than those recommended in Annex D in section 18 may be used, if they can determine R_{SLO} to within 1° and are explained in detail in the field test report. The algebraic sign of R_{SLO} will either be positive if the rotational position of the reference scribe line (as viewed from the ''tail'' end of the probe) is clockwise, or negative, if counterclockwise with respect to the probe's yaw-null position. (This is illustrated in Figure 2G–10.)

10.5.7 The steps in sections 10.5.3 through 10.5.6 shall be performed twice at each of the velocities at which the probe will be calibrated (in accordance with section 10.6). Record the values of R_{SLO}.

10.5.8 The average of all of the R_{SLO} values shall be documented as the reference scribe line rotational offset for the probe.

10.5.9 Use of reference scribe line offset. The reference scribe line rotational offset shall be used to determine the yaw angle of flow in accordance with section 8.9.4.

10.6 Velocity Calibration Procedure. When a 3–D probe is used under this method, follow the provisions for the calibration of 3–D probes in section 10.6 of Method 2F to obtain the necessary velocity calibration coefficients (F_2 as derived using Equation 2F–2 in Method 2F) corresponding to a pitch angle position of 0°. The following procedure applies to Type S probes. This procedure shall be performed on the main probe and all devices that will be attached to the main probe in the field (e.g., thermocouples, RTDs, sampling nozzles) that may affect the flow around the probe head. Probe shaft extensions that do not affect flow around the probe head need not be attached during calibration. (Note: If a sampling nozzle is part of the assembly, two additional requirements must be satisfied before proceeding. The distance between the nozzle and the pitot tube shall meet the minimum spacing requirement prescribed in Method 2, and a wind tunnel demonstration shall be performed that shows the probe's ability to yaw null is not impaired when the nozzle is drawing sample.) To obtain velocity calibration coefficient(s) for the tested probe, proceed as follows.

10.6.1 Calibration velocities. The tester may calibrate the probe at two nominal wind tunnel velocity settings of 18.3 m/sec and 27.4 m/sec (60 ft/sec and 90 ft/sec) and average the results of these calibrations, as described in sections 10.6.12 through 10.6.14, in order to generate the calibration coefficient, C_p. If this option is selected, this calibration coefficient may be used for all field applications where the velocities are 9.1 m/sec (30 ft/sec) or greater. Alternatively, the tester may customize the probe calibration for a particular field test application (or for a series of applications), based on the expected average velocity(ies) at the test site(s). If this option is selected, generate the calibration coefficients by calibrating the probe at two nominal wind tunnel velocity settings, one of which is less than or equal to and the other greater than or equal to the expected average velocity(ies) for the field application(s), and average the results as described in sections 10.6.12 through 10.6.14. Whichever calibration option is selected, the probe calibration coefficient(s) obtained at the two nominal calibration velocities shall meet the conditions specified in sections 10.6.12 through 10.6.14.

10.6.2 Connect the tested probe and calibration pitot tube to their respective pressure-measuring devices. Zero the pressure-measuring devices. Inspect and leak-check all pitot lines; repair or replace them, if necessary. Turn on the fan, and allow the wind tunnel air flow to stabilize at the first of the selected nominal velocity settings.

10.6.3 Position the calibration pitot tube at its measurement location (determined as outlined in section 6.11.4.3), and align the tube so that its tip is pointed directly into the flow. Ensure that the entry port surrounding the tube is properly sealed. The calibration pitot tube may either remain in the wind tunnel throughout the calibration, or be removed from the wind tunnel while measurements are taken with the probe being calibrated.

10.6.4 Check the zero setting of each pressure-measuring device.

10.6.5 Insert the tested probe into the wind tunnel and align it so that the designated pressure port (e.g., either the A-side or B-side of a Type S probe) is pointed directly into the flow and is positioned within the wind tunnel calibration location (as defined in section 3.21). Secure the probe at the 0° pitch angle position. Ensure that the entry port surrounding the probe is properly sealed.

10.6.6 Read the differential pressure from the calibration pitot tube (ΔP_{std}), and record its value. Read the barometric pressure to within ±2.5 mm Hg (±0.1 in. Hg) and the temperature in the wind tunnel to within 0.6 °C (1 °F). Record these values on a data form similar to Table 2G–8. Record the rotational speed of the fan or indicator of wind tunnel velocity control (damper setting, variac rheostat, etc.) and make no adjustment to fan speed or wind tunnel velocity control between this observation and the Type S probe reading.

10.6.7 After the tested probe's differential pressure gauges have had sufficient time to stabilize, yaw null the probe (and then rotate it back 90° for Type S probes), then obtain the differential pressure reading (ΔP). Record

the yaw angle and differential pressure readings.

10.6.8 Take paired differential pressure measurements with the calibration pitot tube and tested probe (according to sections 10.6.6 and 10.6.7). The paired measurements in each replicate can be made either simultaneously (*i.e.*, with both probes in the wind tunnel) or by alternating the measurements of the two probes (*i.e.*, with only one probe at a time in the wind tunnel). Adjustments made to the fan speed or other changes to the system designed to change the air flow velocity of the wind tunnel between observation of the calibration pitot tube (ΔP_{std}) and the Type S pitot tube invalidates the reading and the observation must be repeated.

10.6.9 Repeat the steps in sections 10.6.6 through 10.6.8 at the same nominal velocity setting until three pairs of ΔP readings have been obtained from the calibration pitot tube and the tested probe.

10.6.10 Repeat the steps in sections 10.6.6 through 10.6.9 above for the A-side and B-side of the Type S pitot tube. For a probe assembly constructed such that its pitot tube is always used in the same orientation, only one side of the pitot tube need be calibrated (the side that will face the flow). However, the pitot tube must still meet the alignment and dimension specifications in section 6.1.1 and must have an average deviation (σ) value of 0.01 or less as provided in section 10.6.12.4.

10.6.11 Repeat the calibration procedures in sections 10.6.6 through 10.6.10 at the second selected nominal wind tunnel velocity setting.

10.6.12 Perform the following calculations separately on the A-side and B-side values.

10.6.12.1 Calculate a C_p value for each of the three replicates performed at the lower velocity setting where the calibrations were performed using Equation 2–2 in section 4.1.4 of Method 2.

10.6.12.2 Calculate the arithmetic average, $C_{p(avg\text{-}low)}$, of the three C_p values.

10.6.12.3 Calculate the deviation of each of the three individual values of C_p from the A-side average $C_{p(avg\text{-}low)}$ value using Equation 2–3 in Method 2.

10.6.12.4 Calculate the average deviation (σ) of the three individual C_p values from $C_{p(avg\text{-}low)}$ using Equation 2–4 in Method 2. Use the Type S pitot tube only if the values of σ (side A) and σ (side B) are less than or equal to 0.01. If both A-side and B-side calibration coefficients are calculated, the absolute value of the difference between $C_{p(avg\text{-}low)}$ (side A) and $C_{p(avg\text{-}low)}$ (side B) must not exceed 0.01.

10.6.13 Repeat the calculations in section 10.6.12 using the data obtained at the higher velocity setting to derive the arithmetic C_p values at the higher velocity setting, $C_{p(avg\text{-}high)}$, and to determine whether the conditions in 10.6.12.4 are met by both the A-side and B-side calibrations at this velocity setting.

10.6.14 Use equation 2G–1 to calculate the percent difference of the averaged C_p values at the two calibration velocities.

$$\%\text{Difference} = \frac{C_{p(avg\text{-}low)} - C_{p(avg\text{-}high)}}{C_{p(avg\text{-}low)}} \times 100\% \quad \text{Eq. 2G-1}$$

The percent difference between the averaged C_p values shall not exceed ±3 percent. If the specification is met, average the A-side values of $C_{p(avg\text{-}low)}$ and $C_{p(avg\text{-}high)}$ to produce a single A-side calibration coefficient, C_p. Repeat for the B-side values if calibrations were performed on that side of the pitot. If the specification is not met, make necessary adjustments in the selected velocity settings and repeat the calibration procedure until acceptable results are obtained.

10.6.15 If the two nominal velocities used in the calibration were 18.3 and 27.4 m/sec (60 and 90 ft/sec), the average C_p from section 10.6.14 is applicable to all velocities 9.1 m/sec (30 ft/sec) or greater. If two other nominal velocities were used in the calibration, the resulting average C_p value shall be applicable only in situations where the velocity calculated using the calibration coefficient is neither less than the lower nominal velocity nor greater than the higher nominal velocity.

10.7 Recalibration. Recalibrate the probe using the procedures in section 10 either within 12 months of its first field use after its most recent calibration or after 10 field tests (as defined in section 3.3), whichever occurs later. In addition, whenever there is visible damage to the probe head, the probe shall be recalibrated before it is used again.

10.8 Calibration of pressure-measuring devices used in the field. Before its initial use in a field test, calibrate each pressure-measuring device (except those used exclusively for yaw nulling) using the three-point calibration procedure described in section 10.3.3. The device shall be recalibrated according to the procedure in section 10.3.3 no later than 90 days after its first field use following its most recent calibration. At the discretion of the tester, more frequent calibrations (e.g.,

after a field test) may be performed. No adjustments, other than adjustments to the zero setting, shall be made to the device between calibrations.

10.8.1 Post-test calibration check. A single-point calibration check shall be performed on each pressure-measuring device after completion of each field test. At the discretion of the tester, more frequent single-point calibration checks (e.g., after one or more field test runs) may be performed. It is recommended that the post-test check be performed before leaving the field test site. The check shall be performed at a pressure between 50 and 90 percent of full scale by taking a common pressure reading with the tested probe and a reference pressure-measuring device (as described in section 6.4.4) or by challenging the tested device with a reference pressure source (as described in section 6.4.4) or by performing an equivalent check using a reference device approved by the Administrator.

10.8.2 Acceptance criterion. At the selected pressure setting, the pressure readings made using the reference device and the tested device shall agree to within ±3 percent of full scale of the tested device or 0.8 mm H_2O (0.03 in. H_2O), whichever is less restrictive. If this specification is met, the test data collected during the field test are valid. If the specification is not met, all test data collected since the last successful calibration or calibration check are invalid and shall be repeated using a pressure-measuring device with a current, valid calibration. Any device that fails the calibration check shall not be used in a field test until a successful recalibration is performed according to the procedures in section 10.3.3.

10.9 Temperature Gauges. Same as Method 2, section 4.3. The alternative thermocouple calibration procedures outlined in Emission Measurement Center (EMC) Approved Alternative Method (ALT–011) ''Alternative Method 2 Thermocouple Calibration Procedure'' may be performed. Temperature gauges shall be calibrated no more than 30 days prior to the start of a field test or series of field tests and recalibrated no more than 30 days after completion of a field test or series of field tests.

10.10 Barometer. Same as Method 2, section 4.4. The barometer shall be calibrated no more than 30 days prior to the start of a field test or series of field tests.

11.0 Analytical Procedure

Sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Data Analysis and Calculations

These calculations use the measured yaw angle and the differential pressure and temperature measurements at individual traverse points to derive the near-axial flue gas velocity ($v_{a(i)}$) at each of those points. The near-axial velocity values at all traverse points that comprise a full stack or duct traverse are then averaged to obtain the average near-axial stack or duct gas velocity ($v_{a(avg)}$).

12.1 Nomenclature

A = Cross-sectional area of stack or duct at the test port location, m^2 (ft^2).

B_{ws} = Water vapor in the gas stream (from Method 4 or alternative), proportion by volume.

C_p = Pitot tube calibration coefficient, dimensionless.

$F_{2(i)}$ = 3-D probe velocity coefficient at 0 pitch, applicable at traverse point i.

K_p = Pitot tube constant,

$$34.97\frac{m}{sec}\left[\frac{(g/g\text{-}mole)(mm\ Hg)}{(^\circ K)(mm\ H_2O)}\right]^{1/2}$$

for the metric system, and

$$85.49\frac{ft}{sec}\left[\frac{(lb/lb\text{-}mole)(in.\ Hg)}{(^\circ R)(in.\ H_2O)}\right]^{1/2}$$

for the English system.

M_d = Molecular weight of stack or duct gas, dry basis (see section 8.13), g/g-mole (lb/lb-mole).

M_s = Molecular weight of stack or duct gas, wet basis, g/g-mole (lb/lb-mole).

$$M_s = M_d(1-B_{ws}) + 18.0B_{ws} \quad \text{Eq. 2G-2}$$

P_{bar} = Barometric pressure at velocity measurement site, mm Hg (in. Hg).

P_g = Stack or duct static pressure, mm H_2O (in. H_2O).

P_s = Absolute stack or duct pressure, mm Hg (in. Hg),

$$P_s = P_{bar} + \frac{P_g}{13.6} \qquad \text{Eq. 2G-3}$$

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

13.6 = Conversion from mm H_2O (in. H_2O) to mm Hg (in. Hg).

Q_{sd} = Average dry-basis volumetric stack or duct gas flow rate corrected to standard conditions, dscm/hr (dscf/hr).

Q_{sw} = Average wet-basis volumetric stack or duct gas flow rate corrected to standard conditions, wscm/hr (wscf/hr).

$t_{s(i)}$ = Stack or duct temperature, °C (°F), at traverse point i.

$T_{s(i)}$ = Absolute stack or duct temperature, °K (°R), at traverse point i.

$$T_{s(i)} = 273 + t_{s(i)} \qquad \text{Eq. 2G-4}$$

for the metric system, and

$$T_{s(i)} = 460 + t_{s(i)} \qquad \text{Eq. 2G-5}$$

for the English system.

$T_{s(avg)}$ = Average absolute stack or duct gas temperature across all traverse points.

T_{std} = Standard absolute temperature, 293 °K (528 °R).

$v_{a(i)}$ = Measured stack or duct gas impact velocity, m/sec (ft/sec), at traverse point i.

$v_{a(avg)}$ = Average near-axial stack or duct gas velocity, m/sec (ft/sec) across all traverse points.

ΔP_i = Velocity head (differential pressure) of stack or duct gas, mm H_2O (in. H_2O), applicable at traverse point i.

$(P_1\text{-}P_2)$ = Velocity head (differential pressure) of stack or duct gas measured by a 3-D probe, mm H_2O (in. H_2O), applicable at traverse point i.

3,600 = Conversion factor, sec/hr.

18.0 = Molecular weight of water, g/g-mole (lb/lb-mole).

$\theta_{y(i)}$ = Yaw angle of the flow velocity vector, at traverse point i.

n = Number of traverse points.

12.2 Traverse Point Velocity Calculations. Perform the following calculations from the measurements obtained at each traverse point.

12.2.1 Selection of calibration coefficient. Select the calibration coefficient as described in section 10.6.1.

12.2.2 Near-axial traverse point velocity. When using a Type S probe, use the following equation to calculate the traverse point near-axial velocity ($v_{a(i)}$) from the differential pressure (ΔP_i), yaw angle ($\theta_{y(i)}$), absolute stack or duct standard temperature ($T_{s(i)}$) measured at traverse point i, the absolute stack or duct pressure (P_s), and molecular weight (M_s).

$$v_{a(i)} = K_p C_p \sqrt{\frac{(\Delta P)_i T_{s(i)}}{P_s M_s}} \left(\cos\theta_{y(i)}\right) \qquad \text{Eq. 2G-6}$$

Use the following equation when using a 3–D probe.

$$v_{a(i)} = K_p F_2 \sqrt{\frac{(P_1 - P_2)_i T_{s(i)}}{P_s M_s}} \left(\cos\theta_{y(i)}\right) \qquad \text{Eq. 2G-7}$$

12.2.3 Handling multiple measurements at a traverse point. For pressure or temperature devices that take multiple measurements at a traverse point, the multiple measurements (or where applicable, their square roots) may first be averaged and the resulting average values used in the equations above. Alternatively, the individual measurements may be used in the equations above and the resulting calculated values may then be averaged to obtain a single traverse point value. With either approach, all of the individual measurements recorded at a traverse point must be used in calculating the applicable traverse point value.

12.3 Average Near-Axial Velocity in Stack or Duct. Use the reported traverse point near-axial velocity in the following equation.

$$v_{a(avg)} = \frac{\sum_{i=1}^{n} v_{a(i)}}{n} \qquad \text{Eq. 2G-8}$$

12.4 Acceptability of Results. The acceptability provisions in section 12.4 of Method 2F apply to 3-D probes used under Method 2G. The following provisions apply to Type S probes. For Type S probes, the test results are acceptable and the calculated value of $v_{a(avg)}$ may be reported as the average near-axial velocity for the test run if the conditions in either section 12.4.1 or 12.4.2 are met.

12.4.1 The average calibration coefficient C_p used in Equation 2G–6 was generated at nominal velocities of 18.3 and 27.4 m/sec (60 and 90 ft/sec) and the value of $v_{a(avg)}$ calculated using Equation 2G–8 is greater than or equal to 9.1 m/sec (30 ft/sec).

12.4.2 The average calibration coefficient C_p used in Equation 2G–6 was generated at nominal velocities other than 18.3 or 27.4 m/

sec (60 or 90 ft/sec) and the value of $v_{a(avg)}$ calculated using Equation 2G–8 is greater than or equal to the lower nominal velocity and less than or equal to the higher nominal velocity used to derive the average C_p.

12.4.3 If the conditions in neither section 12.4.1 nor section 12.4.2 are met, the test results obtained from Equation 2G–8 are not acceptable, and the steps in sections 12.2 and 12.3 must be repeated using an average calibration coefficient C_p that satisfies the conditions in section 12.4.1 or 12.4.2.

12.5 Average Gas Volumetric Flow Rate in Stack or Duct (Wet Basis). Use the following equation to compute the average volumetric flow rate on a wet basis.

$$Q_{sw} = 3{,}600\left(v_{a(avg)}\right)(A)\left(\frac{T_{std}}{T_{s(avg)}}\right)\left(\frac{P_s}{P_{std}}\right) \qquad \text{Eq. 2G-9}$$

12.6 Average Gas Volumetric Flow Rate in Stack or Duct (Dry Basis). Use the following equation to compute the average volumetric flow rate on a dry basis.

$$Q_{sd} = 3{,}600\left(1 - B_{ws}\right)\left(v_{a(avg)}\right)(A)\left(\frac{T_{std}}{T_{s(avg)}}\right)\left(\frac{P_s}{P_{std}}\right) \qquad \text{Eq. 2G-10}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Reporting.

16.1 Field Test Reports. Field test reports shall be submitted to the Agency according to applicable regulatory requirements. Field test reports should, at a minimum, include the following elements.

16.1.1 Description of the source. This should include the name and location of the test site, descriptions of the process tested, a description of the combustion source, an accurate diagram of stack or duct cross-sectional area at the test site showing the dimensions of the stack or duct, the location of the test ports, and traverse point locations and identification numbers or codes. It should also include a description and diagram of the stack or duct layout, showing the distance of the test location from the nearest upstream and downstream disturbances and all structural elements (including breachings, baffles, fans, straighteners, etc.) affecting the flow pattern. If the source and test location descriptions have been previously submitted to the Agency in a document (e.g., a monitoring plan or test plan), referencing the document in lieu of including this information in the field test report is acceptable.

16.1.2 Field test procedures. These should include a description of test equipment and test procedures. Testing conventions, such as traverse point numbering and measurement sequence (e.g., sampling from center to wall, or wall to center), should be clearly stated. Test port identification and directional reference for each test port should be included on the appropriate field test data sheets.

16.1.3 Field test data.

16.1.3.1 Summary of results. This summary should include the dates and times of testing, and the average near-axial gas velocity and the average flue gas volumetric flow results for each run and tested condition.

16.1.3.2 Test data. The following values for each traverse point should be recorded and reported:

(a) Differential pressure at traverse point i (ΔP_i)

(b) Stack or duct temperature at traverse point i ($t_{s(i)}$)

(c) Absolute stack or duct temperature at traverse point i ($T_{s(i)}$)

(d) Yaw angle at traverse point i ($\theta_{y(i)}$)

(e) Stack gas near-axial velocity at traverse point i ($v_{a(i)}$)

16.1.3.3 The following values should be reported once per run:

(a) Water vapor in the gas stream (from Method 4 or alternative), proportion by volume (B_{ws}), measured at the frequency specified in the applicable regulation

(b) Molecular weight of stack or duct gas, dry basis (M_d)

(c) Molecular weight of stack or duct gas, wet basis (M_s)

(d) Stack or duct static pressure (P_g)

(e) Absolute stack or duct pressure (P_s)

(f) Carbon dioxide concentration in the flue gas, dry basis ($\%_d$ CO_2)

(g) Oxygen concentration in the flue gas, dry basis (%$_d$ O_2)

(h) Average near-axial stack or duct gas velocity ($v_{a(avg)}$) across all traverse points

(i) Gas volumetric flow rate corrected to standard conditions, dry or wet basis as required by the applicable regulation (Q_{sd} or Q_{sw})

16.1.3.4 The following should be reported once per complete set of test runs:

(a) Cross-sectional area of stack or duct at the test location (A)

(b) Pitot tube calibration coefficient (C_p)

(c) Measurement system response time (sec)

(d) Barometric pressure at measurement site (P_{bar})

16.1.4 Calibration data. The field test report should include calibration data for all probes and test equipment used in the field test. At a minimum, the probe calibration data reported to the Agency should include the following:

(a) Date of calibration

(b) Probe type

(c) Probe identification number(s) or code(s)

(d) Probe inspection sheets

(e) Pressure measurements and calculations used to obtain calibration coefficients in accordance with section 10.6 of this method

(f) Description and diagram of wind tunnel used for the calibration, including dimensions of cross-sectional area and position and size of the test section

(g) Documentation of wind tunnel qualification tests performed in accordance with section 10.1 of this method

16.1.5 Quality assurance. Specific quality assurance and quality control procedures used during the test should be described.

17.0 Bibliography.

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(3) 40 CFR Part 60, Appendix A, Method 2F—Determination of stack gas velocity and volumetric flow rate with three-dimensional probes.

(4) 40 CFR Part 60, Appendix A, Method 2H—Determination of stack gas velocity taking into account velocity decay near the stack wall.

(5) 40 CFR Part 60, Appendix A, Method 3—Gas analysis for carbon dioxide, oxygen, excess air, and dry molecular weight.

(6) 40 CFR Part 60, Appendix A, Method 3A—Determination of oxygen and carbon dioxide concentrations in emissions from stationary sources (instrumental analyzer procedure).

(7) 40 CFR Part 60, Appendix A, Method 4—Determination of moisture content in stack gases.

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18.0 Annexes

Annex A, C, and D describe recommended procedures for meeting certain provisions in sections 8.3, 10.4, and 10.5 of this method. Annex B describes procedures to be followed when using the protractor wheel and pointer assembly to measure yaw angles, as provided under section 8.9.1.

18.1 Annex A—Rotational Position Check. The following are recommended procedures that may be used to satisfy the rotational position check requirements of section 8.3 of this method and to determine the angle-measuring device rotational offset (R_{ADO}).

18.1.1 Rotational position check with probe outside stack. Where physical constraints at the sampling location allow full assembly of the probe outside the stack and insertion into the test port, the following procedures should be performed before the start of testing. Two angle-measuring devices that meet the specifications in section 6.2.1 or 6.2.3 are required for the rotational position check. An angle measuring device whose position can be independently adjusted (e.g., by means of a set screw) after being locked into position on the probe sheath shall not be used for this check unless the independent adjustment is set so that the device performs exactly like a device without the capability for independent adjustment. That is, when aligned on the probe such a device must give the same reading as a device that does not have the capability of being independently adjusted. With the fully assembled probe (including probe shaft extensions, if any) secured in a horizontal position, affix one yaw angle-measuring device to the probe sheath and lock it into position on the reference scribe line specified in section 6.1.5.1. Position the second angle-measuring device using the procedure in section 18.1.1.1 or 18.1.1.2.

18.1.1.1 Marking procedure. The procedures in this section should be performed at each location on the fully assembled probe where the yaw angle-measuring device will be mounted during the velocity traverse. Place the second yaw angle-measuring device on the main probe sheath (or extension) at the position where a yaw angle will be measured during the velocity traverse. Adjust the position of the second angle-measuring device until it indicates the same angle (±1°) as the reference device, and affix the second device to the probe sheath (or extension). Record the angles indicated by the two angle-measuring devices on a form similar to table 2G–2. In this position, the second angle-measuring device is considered to be properly positioned for yaw angle measurement. Make a mark, no wider than 1.6 mm (1/16 in.), on the probe sheath (or extension), such that the yaw angle-measuring device can be re-affixed at this same properly aligned position during the velocity traverse.

18.1.1.2 Procedure for probe extensions with scribe lines. If, during a velocity traverse the angle-measuring device will be affixed to a probe extension having a scribe line as specified in section 6.1.5.2, the following procedure may be used to align the extension's scribe line with the reference scribe line instead of marking the extension as described in section 18.1.1.1. Attach the probe extension to the main probe. Align and lock the second angle-measuring device on the probe extension's scribe line. Then, rotate the extension until both measuring devices indicate the same angle (±1°). Lock the extension at this rotational position. Record the angles indicated by the two angle-measuring devices on a form similar to table 2G–2. An angle-measuring device may be aligned at any position on this scribe line during the velocity traverse, if the scribe line meets the alignment specification in section 6.1.5.3.

18.1.1.3 Post-test rotational position check. If the fully assembled probe includes one or more extensions, the following check should be performed immediately after the completion of a velocity traverse. At the discretion

of the tester, additional checks may be conducted after completion of testing at any sample port. Without altering the alignment of any of the components of the probe assembly used in the velocity traverse, secure the fully assembled probe in a horizontal position. Affix an angle-measuring device at the reference scribe line specified in section 6.1.5.1. Use the other angle-measuring device to check the angle at each location where the device was checked prior to testing. Record the readings from the two angle-measuring devices.

18.1.2 Rotational position check with probe in stack. This section applies only to probes that, due to physical constraints, cannot be inserted into the test port as fully assembled with all necessary extensions needed to reach the inner-most traverse point(s).

18.1.2.1 Perform the out-of-stack procedure in section 18.1.1 on the main probe and any attached extensions that will be initially inserted into the test port.

18.1.2.2 Use the following procedures to perform additional rotational position check(s) with the probe in the stack, each time a probe extension is added. Two angle-measuring devices are required. The first of these is the device that was used to measure yaw angles at the preceding traverse point, left in its properly aligned measurement position. The second angle-measuring device is positioned on the added probe extension. Use the applicable procedures in section 18.1.1.1 or 18.1.1.2 to align, adjust, lock, and mark (if necessary) the position of the second angle-measuring device to within ±1° of the first device. Record the readings of the two devices on a form similar to Table 2G–2.

18.1.2.3 The procedure in section 18.1.2.2 should be performed at the first port where measurements are taken. The procedure should be repeated each time a probe extension is re-attached at a subsequent port, unless the probe extensions are designed to be locked into a mechanically fixed rotational position (e.g., through use of interlocking grooves), which can be reproduced from port to port as specified in section 8.3.5.2.

18.2 Annex B—Angle Measurement Protocol for Protractor Wheel and Pointer Device. The following procedure shall be used when a protractor wheel and pointer assembly, such as the one described in section 6.2.2 and illustrated in Figure 2G–5 is used to measure the yaw angle of flow. With each move to a new traverse point, unlock, re-align, and re-lock the probe, angle-pointer collar, and protractor wheel to each other. At each such move, particular attention is required to ensure that the scribe line on the angle pointer collar is either aligned with the reference scribe line on the main probe sheath or is at the rotational offset position established under section 8.3.1. The procedure consists of the following steps:

18.2.1 Affix a protractor wheel to the entry port for the test probe in the stack or duct.

18.2.2 Orient the protractor wheel so that the 0° mark corresponds to the longitudinal axis of the stack or duct. For stacks, vertical ducts, or ports on the side of horizontal ducts, use a digital inclinometer meeting the specifications in section 6.2.1 to locate the 0° orientation. For ports on the top or bottom of horizontal ducts, identify the longitudinal axis at each test port and permanently mark the duct to indicate the 0° orientation. Once the protractor wheel is properly aligned, lock it into position on the test port.

18.2.3 Move the pointer assembly along the probe sheath to the position needed to take measurements at the first traverse point. Align the scribe line on the pointer collar with the reference scribe line or at the rotational offset position established under section 8.3.1. Maintaining this rotational alignment, lock the pointer device onto the probe sheath. Insert the probe into the entry port to the depth needed to take measurements at the first traverse point.

18.2.4 Perform the yaw angle determination as specified in sections 8.9.3 and 8.9.4 and record the angle as shown by the pointer on the protractor wheel. Then, take velocity pressure and temperature measurements in accordance with the procedure in section 8.9.5. Perform the alignment check described in section 8.9.6.

18.2.5 After taking velocity pressure measurements at that traverse point, unlock the probe from the collar and slide the probe through the collar to the depth needed to reach the next traverse point.

18.2.6 Align the scribe line on the pointer collar with the reference scribe line on the main probe or at the rotational offset position established under section 8.3.1. Lock the collar onto the probe.

18.2.7 Repeat the steps in sections 18.2.4 through 18.2.6 at the remaining traverse points accessed from the current stack or duct entry port.

18.2.8 After completing the measurement at the last traverse point accessed from a port, verify that the orientation of the protractor wheel on the test port has not changed over the course of the traverse at that port. For stacks, vertical ducts, or ports on the side of horizontal ducts, use a digital inclinometer meeting the specifications in section 6.2.1 to check the rotational position of the 0° mark on the protractor wheel. For ports on the top or bottom of horizontal ducts, observe the alignment of the angle wheel 0° mark relative to the permanent 0° mark on the duct at that test port. If these observed comparisons exceed ±2° of 0°, all angle and pressure measurements taken at that port since the protractor wheel was last locked into position on the port shall be repeated.

18.2.9 Move to the next stack or duct entry port and repeat the steps in sections 18.2.1 through 18.2.8.

18.3 Annex C—Guideline for Reference Scribe Line Placement. Use of the following guideline is recommended to satisfy the requirements of section 10.4 of this method. The rotational position of the reference scribe line should be either 90° or 180° from the probe's impact pressure port. For Type-S probes, place separate scribe lines, on opposite sides of the probe sheath, if both the A and B sides of the pitot tube are to be used for yaw angle measurements.

18.4 Annex D—Determination of Reference Scribe Line Rotational Offset. The following procedures are recommended for determining the magnitude and sign of a probe's reference scribe line rotational offset, R_{SLO}. Separate procedures are provided for two types of angle-measuring devices: digital inclinometers and protractor wheel and pointer assemblies.

18.4.1 Perform the following procedures on the main probe with all devices that will be attached to the main probe in the field [such as thermocouples, resistance temperature detectors (RTDs), or sampling nozzles] that may affect the flow around the probe head. Probe shaft extensions that do not affect flow around the probe head need not be attached during calibration.

18.4.2 The procedures below assume that the wind tunnel duct used for probe calibration is horizontal and that the flow in the calibration wind tunnel is axial as determined by the axial flow verification check described in section 10.1.2. Angle-measuring devices are assumed to display angles in alternating 0° to 90° and 90° to 0° intervals. If angle-measuring devices with other readout conventions are used or if other calibration wind tunnel duct configurations are used, make the appropriate calculational corrections. For Type-S probes, calibrate the A-side and B-sides separately, using the appropriate scribe line (see section 18.3, above), if both the A and B sides of the pitot tube are to be used for yaw angle determinations.

18.4.2.1 Position the angle-measuring device in accordance with one of the following procedures.

18.4.2.1.1 If using a digital inclinometer, affix the calibrated digital inclinometer to the probe. If the digital inclinometer can be independently adjusted after being locked into position on the probe sheath (e.g., by means of a set screw), the independent adjustment must be set so that the device performs exactly like a device without the capability for independent adjustment. That is, when aligned on the probe the device must give the same readings as a device that does not have the capability of being independently adjusted. Either align it directly on the reference scribe line or on a mark aligned with the scribe line determined according to the procedures in section 18.1.1.1. Maintaining this rotational alignment, lock the digital inclinometer onto the probe sheath.

18.4.2.1.2 If using a protractor wheel and pointer device, orient the protractor wheel on the test port so that the 0° mark is aligned with the longitudinal axis of the wind tunnel duct. Maintaining this alignment, lock the wheel into place on the wind tunnel test port. Align the scribe line on the pointer collar with the reference scribe line or with a mark aligned with the reference scribe line, as determined under section 18.1.1.1. Maintaining this rotational alignment, lock the pointer device onto the probe sheath.

18.4.2.2 Zero the pressure-measuring device used for yaw nulling.

18.4.2.3 Insert the probe assembly into the wind tunnel through the entry port, positioning the probe's impact port at the calibration location. Check the responsiveness of the pressure-measuring device to probe rotation, taking corrective action if the response is unacceptable.

18.4.2.4 Ensure that the probe is in a horizontal position using a carpenter's level.

18.4.2.5 Rotate the probe either clockwise or counterclockwise until a yaw null [zero ΔP for a Type S probe or zero (P_2–P_3) for a 3–D probe] is obtained. If using a Type S probe with an attached thermocouple, the direction of the probe rotation shall be such that the thermocouple is located downstream of the probe pressure ports at the yaw-null position.

18.4.2.6 Read and record the value of θ_{null}, the angle indicated by the angle-measuring device at the yaw-null position. Record the angle reading on a form similar to Table 2G–6. Do not associate an algebraic sign with this reading.

18.4.2.7 Determine the magnitude and algebraic sign of the reference scribe line rotational offset, R_{SLO}. The magnitude of R_{SLO} will be equal to either θ_{null} or $(90° - \theta_{null})$, depending on the type of probe being calibrated and the type of angle-measuring device used. (See Table 2G–7 for a summary.) The algebraic sign of R_{SLO} will either be positive if the rotational position of the reference scribe line is clockwise or negative if counterclockwise with respect to the probe's yaw-null position. Figure 2G–10 illustrates how the magnitude and sign of R_{SLO} are determined.

18.4.2.8 Perform the steps in sections 18.3.2.3 through 18.3.2.7 twice at each of the two calibration velocities selected for the probe under section 10.6. Record the values of R_{SLO} in a form similar to Table 2G–6.

18.4.2.9 The average of all R_{SLO} values is the reference scribe line rotational offset for the probe.

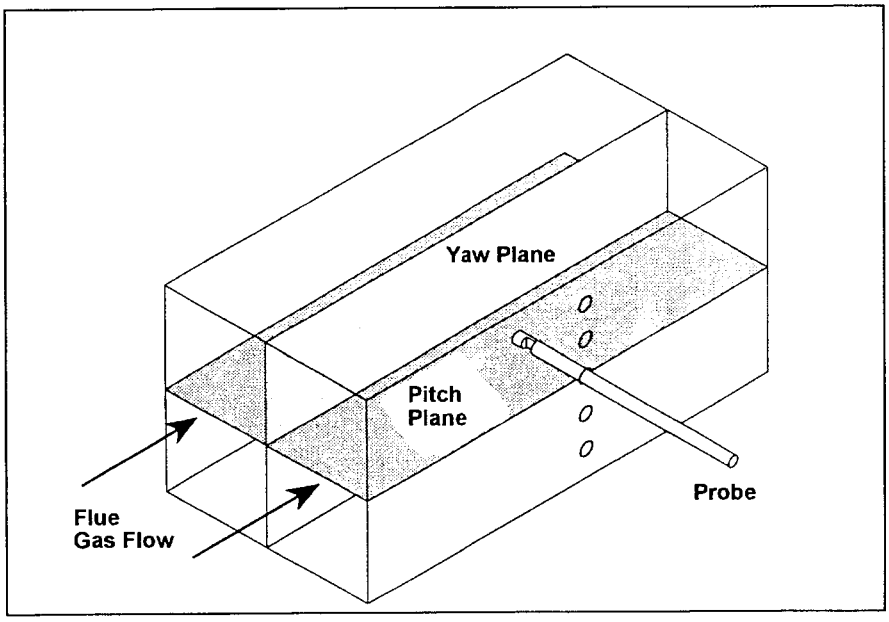


Figure 2G-1. Illustration of yaw and pitch planes in stack or duct.

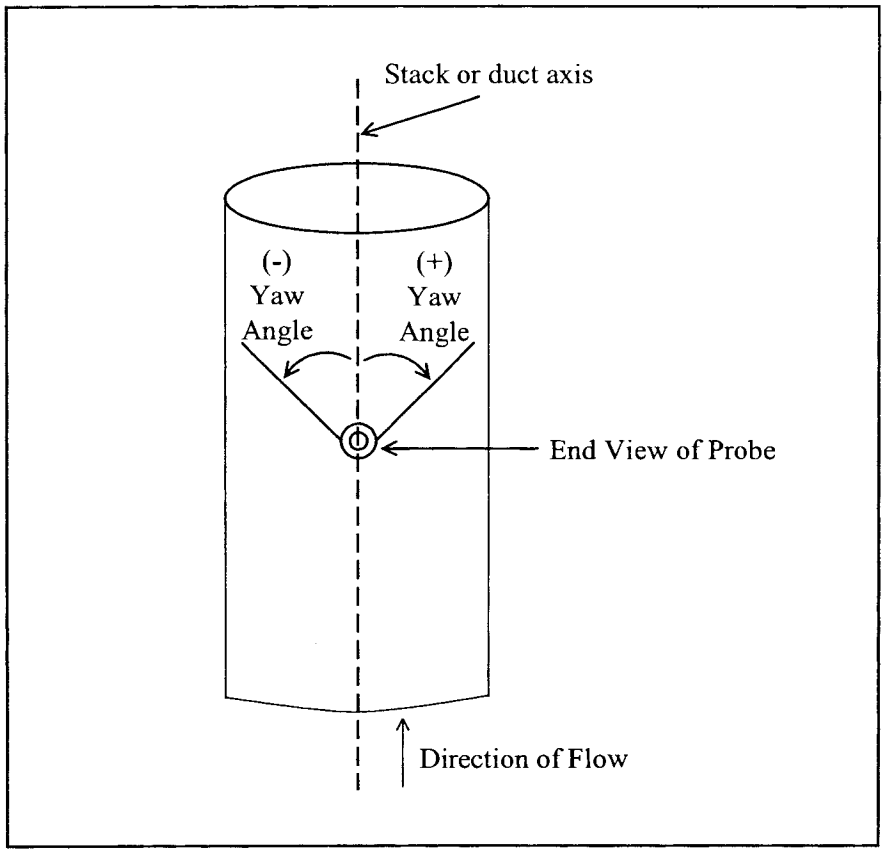


Figure 2G-2. Illustration of probe rotation representing positive and negative yaw angles.

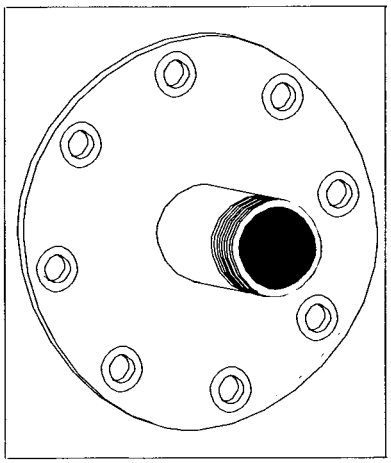


Figure 2G-3. Example bushing sleeve.

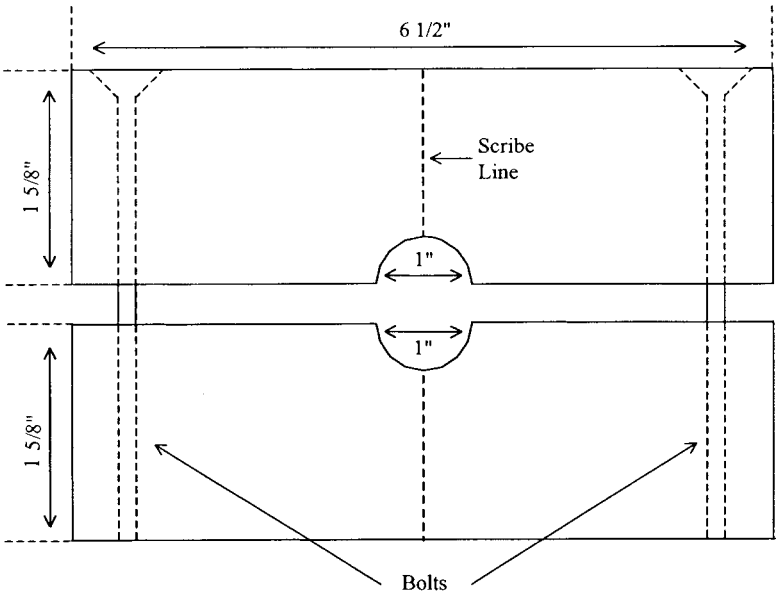


Figure 2G-4. Rotational position collar block.

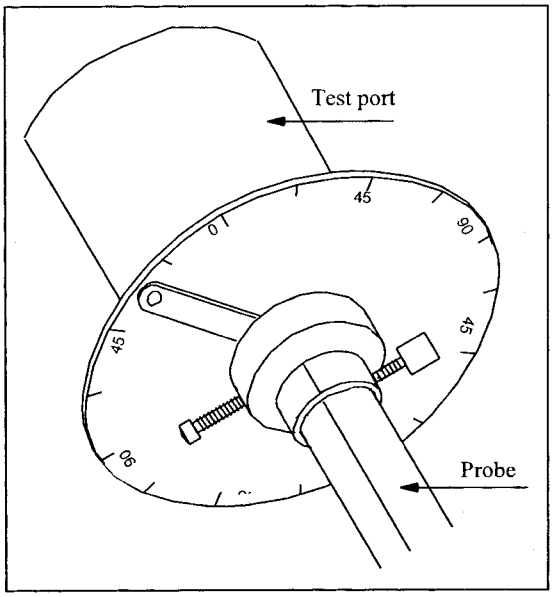


Figure 2G-5. Yaw angle protractor wheel and pointer.

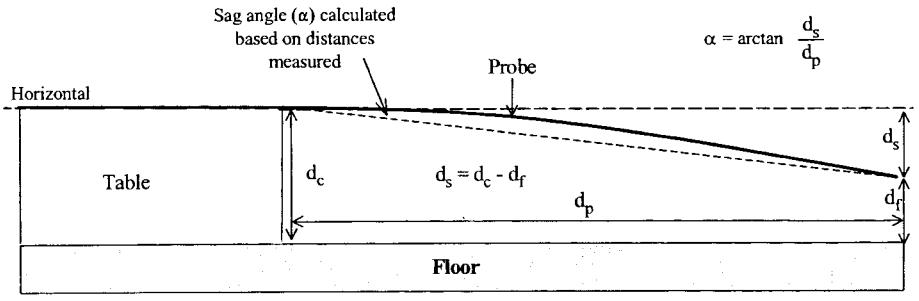


Figure 2G-6. Elements in horizontal straightness test based on trigonometry.

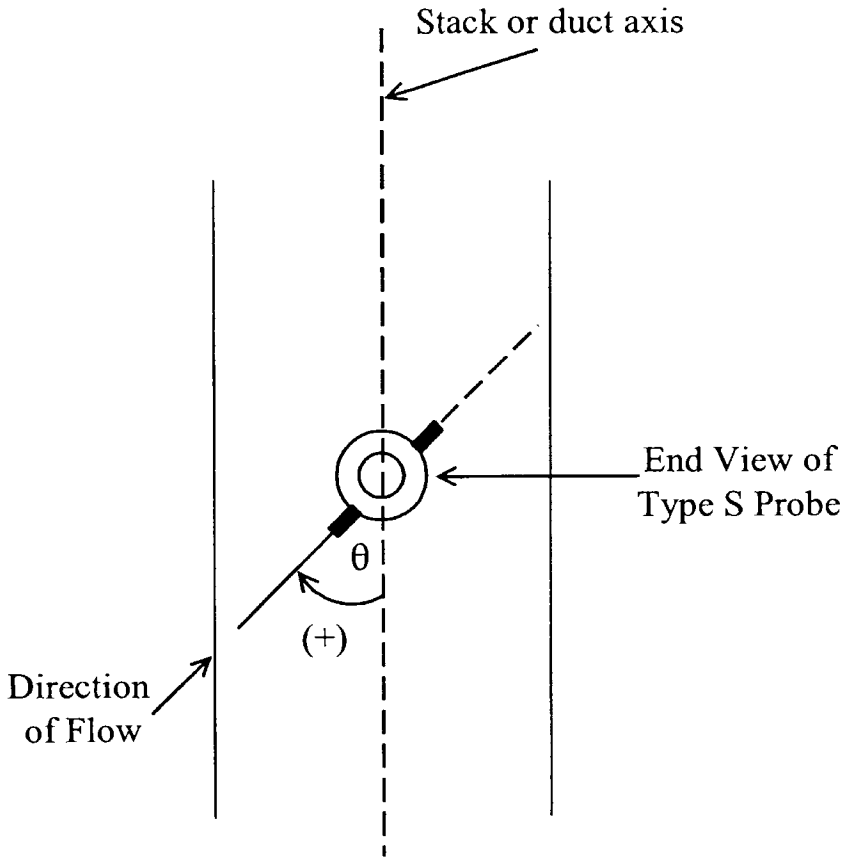


Figure 2G-7. Sign convention for the measured angle (θ) when the probe impact port is pointed directly into the flow. The angle θ is positive when the probe's impact pressure port is oriented in a clockwise rotational position relative to the stack or duct axis, as shown above, and negative for a counter-clockwise orientation.

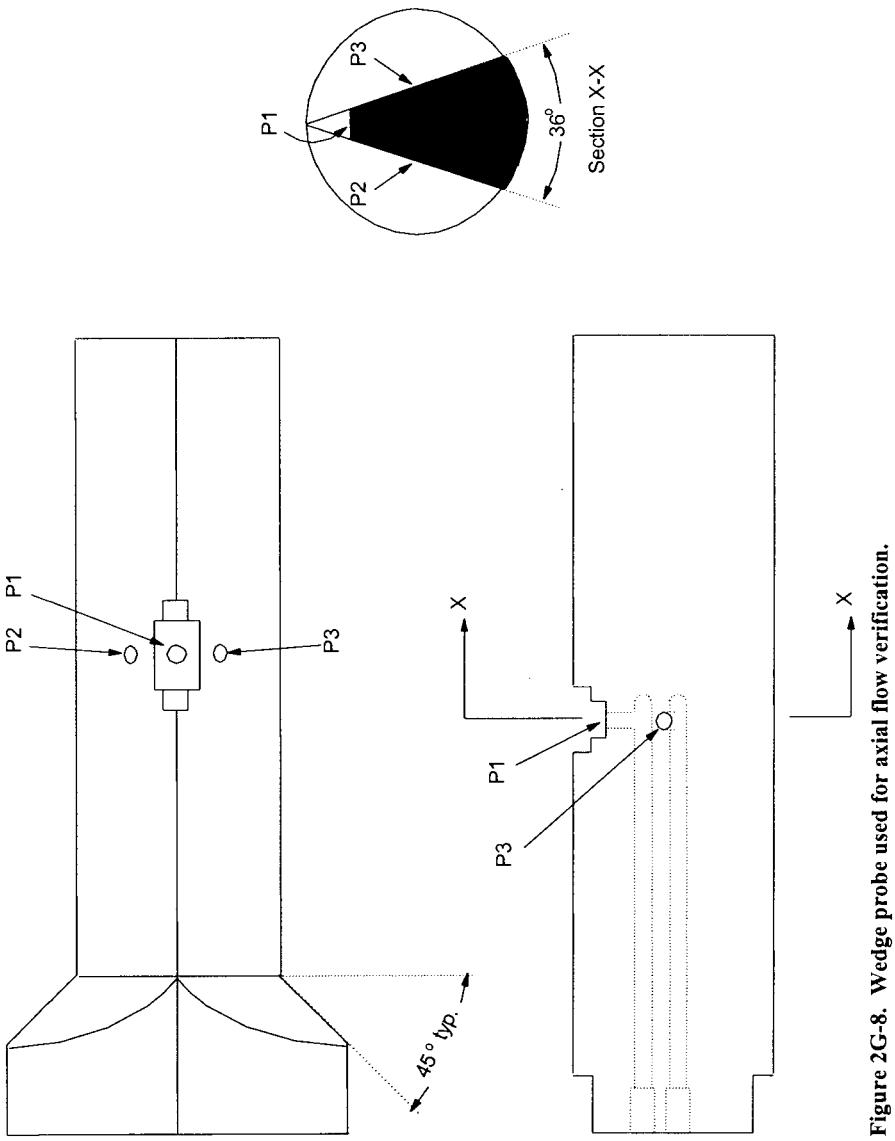


Figure 2G-8. Wedge probe used for axial flow verification.

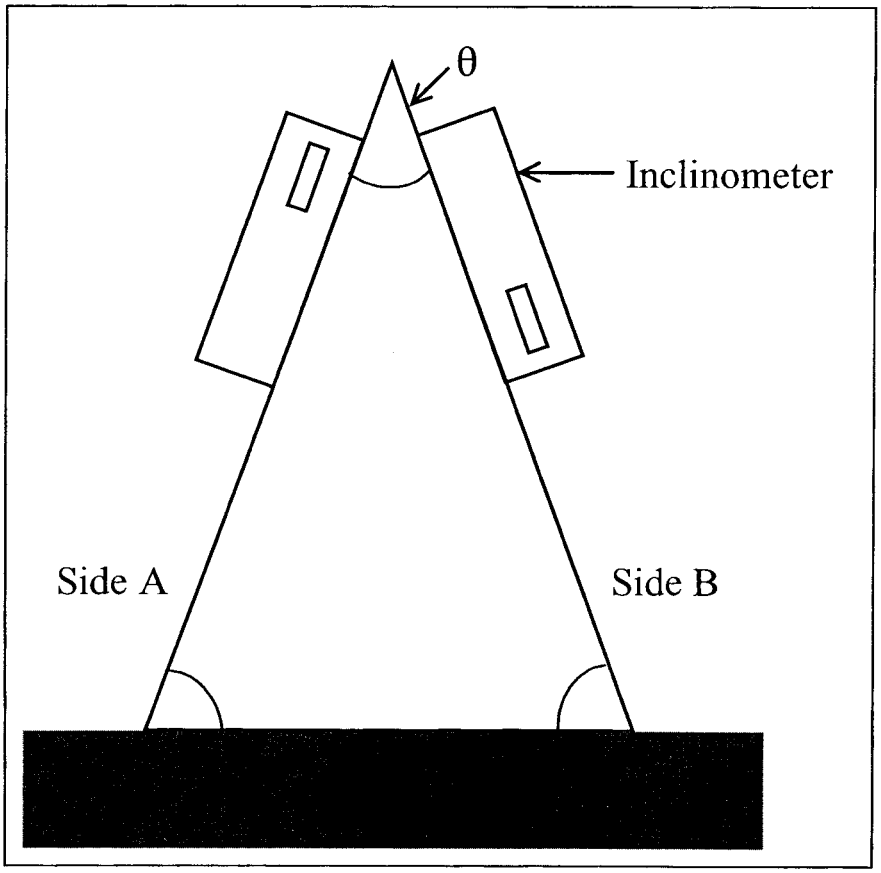


Figure 2G-9. Triangular block used for digital inclinometer calibration.

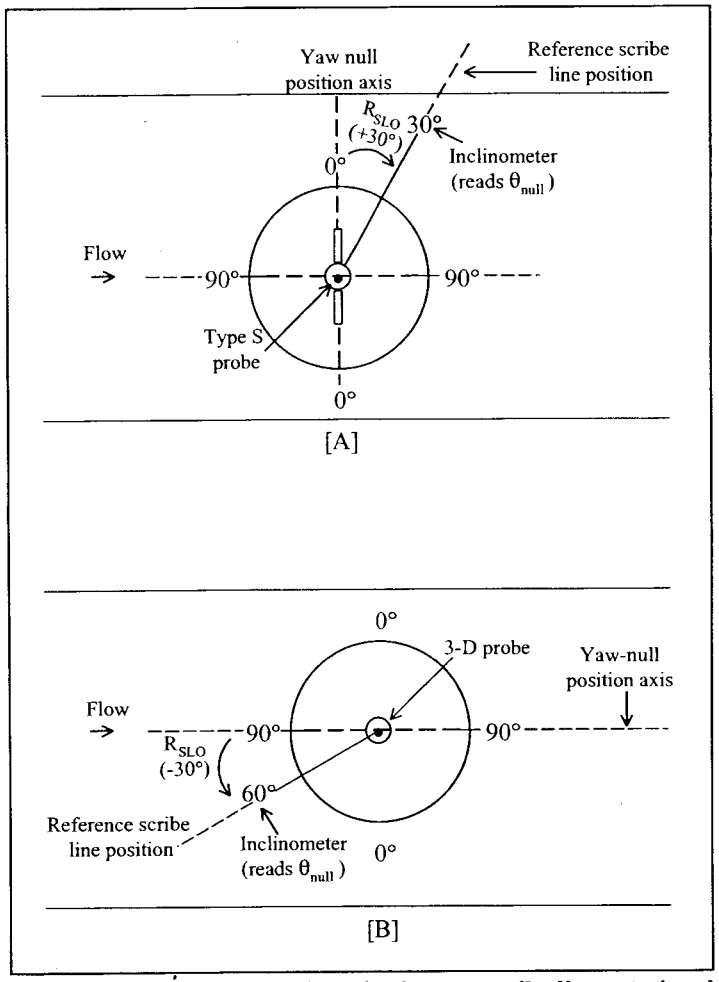
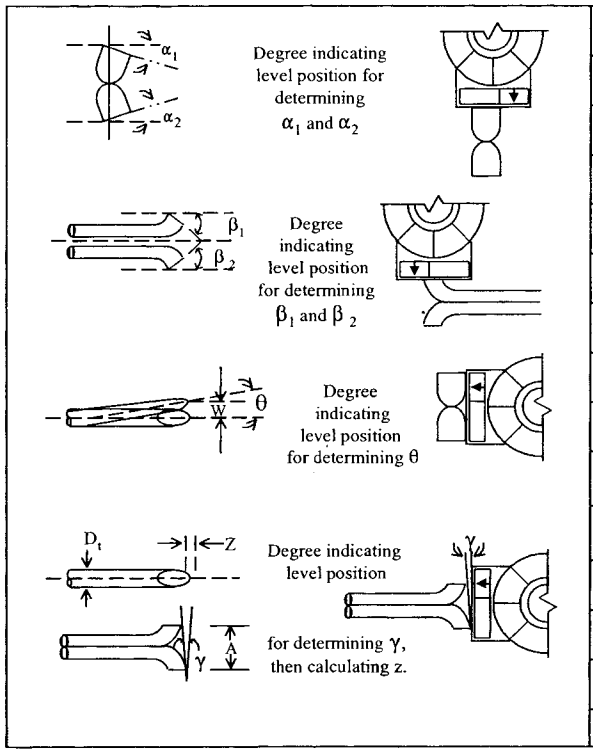


Figure 2G-10. Determination of reference scribe line rotational offset (R_{SLO}) in a horizontal wind tunnel with axial flow for: [A], a Type S probe, and [B], a 3-D probe. In [A] and [B], the probe impact pressure port is aligned with the yaw-null position axis and the inclinometer reads θ_{null}. In [A], the magnitude of R_{SLO} = θ_{null} and the sign is positive (clockwise from yaw-null position axis). In [B], the magnitude of $R_{SLO} = 90° - \theta_{null}$ and the sign is negative (counterclockwise from yaw-null position axis).

Table 2G-1. Type S Probe Inspection Sheet

Note: Method 2 provides the criteria for an acceptably constructed Type S pitot tube. However, the procedure for making the necessary measurements is not specified. One approach is given below.

1. Use a vise with parallel and perpendicular faces. Use an angle-measuring device (analog or digital) for this check.
2. Place the pitot tube in the vise, and level the pitot tube horizontally using the angle-measuring device.
3. Place the angle-measuring device as shown below.
4. Measure distance A, which is P_A plus P_B. Method 2 specifies that $P_A = P_B$, but provides no tolerance for this measurement. Because this measurement is very difficult, it is suggested that $P_A = P_B = A/2$.
5. Measure the external tube diameter (D_t) with a micrometer, machinist's rule, or internal caliper.
6. Record all data as shown on the form below.
7. Calculate dimensions w and z as shown below.



Level and perpendicular?	
Obstruction?	
Damaged?	
α_1 $(-2° \le \alpha_1 \le +2°)$	
α_2 $(-2° \le \alpha_2 \le +2°)$	
β_1 $(-2° \le \beta_1 \le +2°)$	
β_2 $(-2° \le \beta_2 \le +2°)$	
γ	
θ	
$z = A (\tan\gamma)$ [≤ 0.5 mm (0.02 in.)]	
$w = A (\tan\theta)$ [≤ 0.5 mm (0.02 in.)]	
D_t [≥ 9.5 mm (3/8 in.)]	
A	
$A/2D_t$ $(1.05 \le P_A/D_t \le 1.5)$ *	
* Recommended dimensions	

QA/QC Check

Completeness_____ Legibility_____ Accuracy_____

Specifications_____ Reasonableness_____

Certification

I certify that the Type S probe ID _____ meets or exceeds all specifications, criteria, and applicable design features.

Certified by:_____ Date:_____

Table 2G-2. Rotational Position Check

Source:_____ Date:_____

Test Location:_____ Tester(s):_____

Probe Type:_____ Affiliation:_____

Probe ID:_____ Fully-Assembled Probe Length in mm (in.):_____

Position	Angle Comparisons		
Distance of 2nd measurement device from probe head impact port in mm (in.)	1st Device Angle measured by device aligned on the reference scribe line, including algebraic sign (degrees)	2nd Device Angle measured by device mounted at each position to be used during testing, including algebraic sign (degrees)	R_{ADO} Difference between readings by 1st and 2nd angle-measuring devices (degrees)[a]
(Col. A)	(Col. B)	(Col. C)	(Col. C - Col. B)

[a] The algebraic sign must be consistent with section 8.3.2.

Specifications: For the pre-test rotational position check, the value of R_{ADO} at each location along the probe shaft must be determined to within ±1°. In the post-test check, R_{ADO} at each location must remain within ±2° of the value obtained in the pre-test check.

Table 2G-3. Example EPA Method 2G Field Data Form

Source: _____ Date: _____

Source Location: _____ Test Personnel: _____

Measurement Location: _____ Probe Type: _____

Run ID:	
Start Time:	
End Time:	
Pitot Tube ID:	
Pitot Tube Coefficient (C_p):	
Pressure Gauge ID:	
Pressure Gauge Readability:	in. H_2O
Temperature Gauge ID:	
Measurement System Response Time	sec.

Stack Diameter:		
Stack Area:		
Barometric Pressure (P_{bar}):		in. Hg
Static Pressure (P_g):		in. H_2O
R_{SLO}		
R_{ADO}		
	Pre-test	Post-test
Pitot Tube Condition: Damage Noted?		
Leak Check Performed?		

Clock Time	Traverse Point	Yaw Angle, including algebraic sign (degrees)	Differential Pressure (Δ P)	Stack or Duct Gas Temperature (° F)

Table 2G-4. Wind Tunnel Velocity Pressure Cross-Check

Wind Tunnel Facility: _____
Date: _____
Wind Tunnel Temperature: _____
Barometric Pressure: _____
Test Point Locations: _____
Lowest Test Velocity in m/sec (ft/sec): _____
Highest Test Velocity in m/sec (ft/sec): _____

Port		Rep.	Velocity Pressure (ΔP_{std})	
			@ Lowest Test Velocity	@ Highest Test Velocity
Calibration Pitot Tube Location		1		
		2		
		3		
		Average		
Calibration Location Test Points *	1	1		
		2		
		3		
		Average		
		% Difference **		
	2	1		
		2		
		3		
		Average		
		% Difference **		
	..	1		
		2		
		3		
		Average		
		% Difference **		

* Measurements must be taken at all points in the calibration location as specified in section 10.1.1

** Percent Difference = $\frac{(Calibration\ Location\ Test\ Point\ Avg - Cal.\ Pitot\ Tube\ Location\ Avg)}{Cal.\ Pitot\ Tube\ Location\ Avg} \times 100\%$

Specification: At each velocity setting, the average velocity pressure obtained at the calibration location shall be within ±2 percent or 0.01 in. H_2O, whichever is less restrictive, of the average velocity pressure obtained at the fixed calibration pitot tube location.

Table 2G-5. Wind Tunnel Axial Flow Verification

Wind Tunnel Facility: _____
Date: _____
Wind Tunnel Temperature: _____
Barometric Pressure: _____
Probe Type/I.D. Used To Conduct Check: _____
Test Point Locations: _____
Lowest Test Velocity in m/sec (ft/sec): _____
Highest Test Velocity in m/sec (ft/sec): _____

Port		@ Lowest Test Velocity		@ Highest Test Velocity	
		Yaw Angle * (degrees)	Pitch Angle * (degrees)	Yaw Angle * (degrees)	Pitch Angle * (degrees)
Calibration Location Test Points **	1				
	2				
	3				
	..				
Calibration Pitot Tube Location					

* When following the procedures in section 10.1.2.1, both the yaw and pitch angles are obtained from the same port. When following the procedures in section 10.1.2.2, the yaw angle is obtained using the port for the tested probe, and the pitch angle is obtained using the port for verification of axial flow.

** Yaw and pitch angle measurements must be taken at all points that define the calibration location (as per the requirements in section 10.1.1)

Specification: At each velocity setting, each measured yaw and pitch angle shall be within ±3° of 0° in accordance with the requirements in section 10.1.2.

Table 2G-6. Yaw Angle Calibration

Probe Type: _____ **Tester(s):** _____

Probe ID: _____ **Affiliation:** _____

Test Location: _____ **Date:** _____

	Repetition 1		Repetition 2	
Nominal Velocity Setting in m/sec (ft/sec)	**θ_{null} (degrees)**	**R_{SLO} (degrees)***	**θ_{null} (degrees)**	**R_{SLO} (degrees)***

Average of all recorded R_{SLO} values: _____

* Include magnitude and algebraic sign in accordance with section 10.5.6.

Table 2G-7. Determining the Magnitude of Reference Scribe Line Offset

Probe/Angle-Measuring Device	Magnitude of R_{SLO}
Type S probe with inclinometer	θ_{null}
Type S probe with protractor wheel and pointer	$90° - \theta_{null}$
3-D probe with inclinometer	$90° - \theta_{null}$
3-D probe with protractor wheel and pointer	θ_{null}

Table 2G-8. Probe Calibration for Method 2G

Wind Tunnel Facility: _____
Wind Tunnel Location: _____
Probe Type: _____
Probe ID: _____
Probe Calibration Date: _____
Test Point Location: _____
Ambient Temperature (°F): _____
Barometric Pressure (P_{bar}): _____

Repetition	Low Velocity Setting (ft/sec)	Calibration Pitot		Tested Probe		Calculated C_p or F_2
		ΔP_{std} (in. H_2O)	Temp. (°F)	ΔP or P_1-P_2 (in. H_2O)	Yaw Angle (°)	
1						
2						
3						
					Average ($C_{p(avg\text{-}low)}$) =	

Repetition	High Velocity Setting (ft/sec)	Calibration Pitot		Tested Probe		Calculated C_p or F_2
		ΔP_{std} (in. H_2O)	Temp. (°F)	ΔP or P_1-P_2 (in. H_2O)	Yaw Angle (°)	
1						
2						
3						
					Average ($C_{p(avg\text{-}high)}$) =	

$$\% \text{ Difference} = \frac{C_{p(avg\text{-}low)} - C_{p(avg\text{-}high)}}{C_{p(avg\text{-}low)}} \times 100\% = _____\%$$

Note: (1) The percent difference between the low and high velocity setting C_p values shall be within ±3 percent.
(2) If calibrating a 3-D probe for this method, the pitch angle setting must be 0°.

METHOD 2H—DETERMINATION OF STACK GAS VELOCITY TAKING INTO ACCOUNT VELOCITY DECAY NEAR THE STACK WALL

1.0 Scope and Application

1.1 This method is applicable in conjunction with Methods 2, 2F, and 2G (40 CFR Part 60, Appendix A) to account for velocity decay near the wall in circular stacks and ducts.

1.2 This method is not applicable for testing stacks and ducts less than 3.3 ft (1.0 m) in diameter.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A wall effects adjustment factor is determined. It is used to adjust the average stack gas velocity obtained under Method 2, 2F, or 2G of this appendix to take into account velocity decay near the stack or duct wall.

2.2 The method contains two possible procedures: a calculational approach which derives an adjustment factor from velocity measurements and a default procedure which assigns a generic adjustment factor based on the construction of the stack or duct.

2.2.1 The calculational procedure derives a wall effects adjustment factor from velocity measurements taken using Method 2, 2F, or 2G at 16 (or more) traverse points specified under Method 1 of this appendix and a total of eight (or more) wall effects traverse points specified under this method. The calculational procedure based on velocity measurements is not applicable for horizontal circular ducts where build-up of particulate matter or other material in the bottom of the duct is present.

2.2.2 A default wall effects adjustment factor of 0.9900 for brick and mortar stacks and 0.9950 for all other types of stacks and ducts may be used without taking wall effects measurements in a stack or duct.

2.3 When the calculational procedure is conducted as part of a relative accuracy test audit (RATA) or other multiple-run test procedure, the wall effects adjustment factor derived from a single traverse (i.e., single RATA run) may be applied to all runs of the same RATA without repeating the wall effects measurements. Alternatively, wall effects adjustment factors may be derived for several traverses and an average wall effects adjustment factor applied to all runs of the same RATA.

3.0 Definitions.

3.1 *Complete wall effects traverse* means a traverse in which measurements are taken at d_{rem} (see section 3.3) and at 1-in. intervals in each of the four Method 1 equal-area sectors closest to the wall, beginning not farther than 4 in. (10.2 cm) from the wall and extending either (1) across the entire width of the Method 1 equal-area sector or (2) for stacks or ducts where this width exceeds 12 in. (30.5 cm) (i.e., stacks or ducts greater than or equal to 15.6 ft [4.8 m] in diameter), to a distance of not less than 12 in. (30.5 cm) from the wall. Note: Because this method specifies that measurements must be taken at whole number multiples of 1 in. from a stack or duct wall, for clarity numerical quantities in this method are expressed in English units followed by metric units in parentheses. To enhance readability, hyphenated terms such as ''1-in. intervals'' or ''1-in. incremented,'' are expressed in English units only.

3.2 d_{last} Depending on context, d_{last} means either (1) the distance from the wall of the last 1-in. incremented wall effects traverse point or (2) the traverse point located at that distance (see Figure 2H–2).

3.3 d_{rem} Depending on context, d_{rem} means either (1) the distance from the wall of the centroid of the area between d_{last} and the interior edge of the Method 1 equal-area sector closest to the wall or (2) the traverse point located at that distance (see Figure 2H–2).

3.4 ''*May,*'' ''*Must,*'' ''*Shall,*'' ''*Should,*'' and the imperative form of verbs.

3.4.1 ''*May*'' is used to indicate that a provision of this method is optional.

3.4.2 ''*Must,*'' ''*Shall,*'' and the imperative form of verbs (such as ''record'' or ''enter'') are used to indicate that a provision of this method is mandatory.

3.4.3 ''*Should*'' is used to indicate that a provision of this method is not mandatory but is highly recommended as good practice.

3.5 *Method 1* refers to 40 CFR part 60, appendix A, ''Method 1—Sample and velocity traverses for stationary sources.''

3.6 *Method 1 exterior equal-area sector and Method 1 equal-area sector closest to the wall* mean any one of the four equal-area sectors that are closest to the wall for a circular stack or duct laid out in accordance with section 2.3.1 of Method 1 (see Figure 2H–1).

3.7 *Method 1 interior equal-area sector* means any of the equal-area sectors other than the Method 1 exterior equal-area sectors (as defined in section 3.6) for a circular stack or duct laid out in accordance with section 2.3.1 of Method 1 (see Figure 2H–1).

3.8 *Method 1 traverse point and Method 1 equal-area traverse point* mean a traverse point located at the centroid of an equal-area sector of a circular stack laid out in accordance with section 2.3.1 of Method 1.

3.9 *Method 2* refers to 40 CFR part 60, appendix A, ''Method 2—Determination of stack gas velocity and volumetric flow rate (Type S pitot tube).''

3.10 *Method 2F* refers to 40 CFR part 60, appendix A, ''Method 2F—Determination of stack gas velocity and volumetric flow rate with three-dimensional probes.''

3.11 *Method 2G* refers to 40 CFR part 60, appendix A, ''Method 2G—Determination of stack gas velocity and volumetric flow rate with two-dimensional probes.''

3.12 *1-in. incremented wall effects traverse point* means any of the wall effects traverse points that are located at 1-in. intervals, i.e., traverse points d_1 through d_{last} (see Figure 2H–2).

3.13 *Partial wall effects traverse* means a traverse in which measurements are taken at fewer than the number of traverse points required for a ''complete wall effects traverse'' (as defined in section 3.1), but are taken at a minimum of two traverse points in each Method 1 equal-area sector closest to the wall, as specified in section 8.2.2.

3.14 *Relative accuracy test audit (RATA)* is a field test procedure performed in a stack or duct in which a series of concurrent measurements of the same stack gas stream is taken by a reference method and an installed monitoring system. A RATA usually consists of series of 9 to 12 sets of such concurrent measurements, each of which is referred to as a RATA run. In a volumetric flow RATA, each reference method run consists of a complete traverse of the stack or duct.

3.15 *Wall effects-unadjusted average velocity* means the average stack gas velocity, not accounting for velocity decay near the wall, as determined in accordance with Method 2, 2F, or 2G for a Method 1 traverse consisting of 16 or more points.

3.16 *Wall effects-adjusted average velocity* means the average stack gas velocity, taking into account velocity decay near the wall, as calculated from measurements at 16 or more Method 1 traverse points and at the additional wall effects traverse points specified in this method.

3.17 *Wall effects traverse point* means a traverse point located in accordance with sections 8.2.2 or 8.2.3 of this method.

4.0 Interferences [Reserved]

5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This method does not purport to address all of the health and safety considerations associated with its use. It is the responsibility of the user of this method to establish appropriate health and safety practices and to determine the applicability of occupational health and safety regulatory requirements prior to performing this method.

6.0 Equipment and Supplies

6.1 The provisions pertaining to equipment and supplies in the method that is used to take the traverse point measurements (i.e., Method 2, 2F, or 2G) are applicable under this method.

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection and Analysis

8.1 Default Wall Effects Adjustment Factors. A default wall effects adjustment factor of 0.9900 for brick and mortar stacks and 0.9950 for all other types of stacks and ducts may be used without conducting the following procedures.

8.2 Traverse Point Locations. Determine the location of the Method 1 traverse points in accordance with section 8.2.1 and the location of the traverse points for either a partial wall effects traverse in accordance with section 8.2.2 or a complete wall effects traverse in accordance with section 8.2.3.

8.2.1 Method 1 equal-area traverse point locations. Determine the location of the Method 1 equal-area traverse points for a traverse consisting of 16 or more points using Table 1–2 (Location of Traverse Points in Circular Stacks) of Method 1.

8.2.2 Partial wall effects traverse. For a partial wall effects traverse, measurements must be taken at a minimum of the following two wall effects traverse point locations in all four Method 1 equal-area sectors closest to the wall: (1) 1 in. (2.5 cm) from the wall (except as provided in section 8.2.2.1) and (2) d_{rem}, as determined using Equation 2H–1 or 2H–2 (see section 8.2.2.2).

8.2.2.1 If the probe cannot be positioned at 1 in. (2.5 cm) from the wall (e.g., because of insufficient room to withdraw the probe shaft) or if velocity pressure cannot be detected at 1 in. (2.5 cm) from the wall (for any reason other than build-up of particulate matter in the bottom of a duct), take measurements at the 1-in. incremented wall effects traverse point closest to the wall where the probe can be positioned and velocity pressure can be detected.

8.2.2.2 Calculate the distance of d_{rem} from the wall to within ±¼ in. (6.4 mm) using Equation 2H–1 or Equation 2H–2 (for a 16-point traverse).

$$d_{last} \leq d_b \qquad \text{Eq. 2H-3}$$

Where:

r = the stack or duct radius determined from direct measurement of the stack or duct diameter in accordance with section 8.6 of Method 2F or Method 2G, in. (cm);

p = the number of Method 1 equal-area traverse points on a diameter, $p \geq 8$ (e.g., for a 16-point traverse, $p = 8$); d_{last} and d_{rem} are defined in sections 3.2 and 3.3 respectively, in. (cm).

For a 16-point Method 1 traverse, Equation 2H–1 becomes:

$$d_{rem} = r - \sqrt{\frac{7}{8}r^2 - rd_{last} + \frac{1}{2}d_{last}^2} \qquad \text{Eq. 2H-2}$$

8.2.2.3 Measurements may be taken at any number of additional wall effects traverse points, with the following provisions.

(a) d_{last} must not be closer to the center of the stack or duct than the distance of the interior edge (boundary), d_b, of the Method 1 equal-area sector closest to the wall (see Figure 2H–2 or 2H–3). That is,

Where:

$$d_b = r\left(1 - \sqrt{1 - \frac{2}{p}}\right) \qquad \text{Eq. 2H-4}$$

Table 2H–1 shows d_b as a function of the stack or duct radius, r, for traverses ranging from 16 to 48 points (i.e., for values of p ranging from 8 to 24).

(b) Each point must be located at a distance that is a whole number (e.g., 1, 2, 3) multiple of 1 in. (2.5 cm).

(c) Points do not have to be located at consecutive 1-in. intervals. That is, one or more 1-in. incremented points may be skipped. For example, it would be acceptable for points to be located at 1 in. (2.5 cm), 3 in. (7.6 cm), 5 in. (12.7 cm), d_{last}, and d_{rem}; or at 1 in. (2.5 cm), 2 in. (5.1 cm), 4 in. (10.2 cm), 7 in. (17.8 cm), d_{last}, and d_{rem}. Follow the instructions in section 8.7.1.2 of this method for recording results for wall effects traverse points that are skipped. It should be noted that the full extent of velocity decay may not be accounted for if measurements are not taken at all 1-in. incremented points close to the wall.

8.2.3 Complete wall effects traverse. For a complete wall effects traverse, measurements must be taken at the following points in all four Method 1 equal-area sectors closest to the wall.

(a) The 1-in. incremented wall effects traverse point closest to the wall where the probe can be positioned and velocity can be detected, but no farther than 4 in. (10.2 cm) from the wall.

(b) Every subsequent 1-in. incremented wall effects traverse point out to the interior edge of the Method 1 equal-area sector or to 12 in. (30.5 cm) from the wall, whichever comes first. Note: In stacks or ducts with diameters greater than 15.6 ft (4.8 m) the interior edge of the Method 1 equal-area sector is farther from the wall than 12 in. (30.5 cm).

(c) d_{rem}, as determined using Equation 2H–1 or 2H–2 (as applicable). Note: For a complete traverse of a stack or duct with a diameter less than 16.5 ft (5.0 m), the distance between d_{rem} and d_{last} is less than or equal to ½ in. (12.7 mm). As discussed in section 8.2.4.2, when the distance between d_{rem} and d_{last} is less than or equal to ½ in. (12.7 mm), the velocity measured at d_{last} may be used for d_{rem}. Thus, it is not necessary to calculate the distance of d_{rem} or to take measurements at d_{rem} when conducting a complete traverse of a stack or duct with a diameter less than 16.5 ft (5.0 m).

8.2.4 Special considerations. The following special considerations apply when the distance between traverse points is less than or equal to ½ in. (12.7 mm).

8.2.4.1 A wall effects traverse point and the Method 1 traverse point. If the distance between a wall effects traverse point and the Method 1 traverse point is less than or equal to ½ in. (12.7 mm), taking measurements at both points is allowed but not required or recommended; if measurements are taken at only one point, take the measurements at the point that is farther from the wall and use the velocity obtained at that point as the value for both points (see sections 8.2.3 and 9.2 for related requirements).

8.2.4.2 d_{rem} and d_{last}. If the distance between d_{rem} and d_{last} is less than or equal to ½ in. (12.7 mm), taking measurements at d_{rem} is allowed but not required or recommended; if measurements are not taken at d_{rem}, the measured velocity value at d_{last} must be used as the value for both d_{last} and d_{rem}.

8.3 Traverse Point Sampling Order and Probe Selection. Determine the sampling order of the Method 1 and wall effects traverse points and select the appropriate probe for the measurements, taking into account the following considerations.

8.3.1 Traverse points on any radius may be sampled in either direction (i.e., from the wall toward the center of the stack or duct, or vice versa).

8.3.2 To reduce the likelihood of velocity variations during the time of the traverse and the attendant potential impact on the wall effects-adjusted and unadjusted average velocities, the following provisions of this method shall be met.

8.3.2.1 Each complete set of Method 1 and wall effects traverse points accessed from the same port shall be sampled without interruption. Unless traverses are performed simultaneously in all ports using separate probes at each port, this provision disallows first sampling all Method 1 points at all ports and then sampling all the wall effects points.

8.3.2.2 The entire integrated Method 1 and wall effects traverse across all test ports shall be as short as practicable, consistent with the measurement system response time

(see section 8.4.1.1) and sampling (see section 8.4.1.2) provisions of this method.

8.3.3 It is recommended but not required that in each Method 1 equal-area sector closest to the wall, the Method 1 equal-area traverse point should be sampled in sequence between the adjacent wall effects traverse points. For example, for the traverse point configuration shown in Figure 2H–2, it is recommended that the Method 1 equal-area traverse point be sampled between d_{last} and d_{rem}. In this example, if the traverse is conducted from the wall toward the center of the stack or duct, it is recommended that measurements be taken at points in the following order: d_1, d_2, d_{last}, the Method 1 traverse point, d_{rem}, and then at the traverse points in the three Method 1 interior equal-area sectors.

8.3.4 The same type of probe must be used to take measurements at all Method 1 and wall effects traverse points. However, different copies of the same type of probe may be used at different ports (e.g., Type S probe 1 at port A, Type S probe 2 at port B) or at different traverse points accessed from a particular port (e.g., Type S probe 1 for Method 1 interior traverse points accessed from port A, Type S probe 2 for wall effects traverse points and the Method 1 exterior traverse point accessed from port A). The identification number of the probe used to obtain measurements at each traverse point must be recorded.

8.4 Measurements at Method 1 and Wall Effects Traverse Points. Conduct measurements at Method 1 and wall effects traverse points in accordance with Method 2, 2F, or 2G and in accordance with the provisions of the following subsections (some of which are included in Methods 2F and 2G but not in Method 2), which are particularly important for wall effects testing.

8.4.1 Probe residence time at wall effects traverse points. Due to the steep temperature and pressure gradients that can occur close to the wall, it is very important for the probe residence time (i.e., the total time spent at a traverse point) to be long enough to ensure collection of representative temperature and pressure measurements. The provisions of Methods 2F and 2G in the following subsections shall be observed.

8.4.1.1 System response time. Determine the response time of each probe measurement system by inserting and positioning the ''cold'' probe (at ambient temperature and pressure) at any Method 1 traverse point. Read and record the probe differential pressure, temperature, and elapsed time at 15-second intervals until stable readings for both pressure and temperature are achieved. The response time is the longer of these two elapsed times. Record the response time.

8.4.1.2 Sampling. At the start of testing in each port (i.e., after a probe has been inserted into the stack gas stream), allow at least the response time to elapse before beginning to take measurements at the first traverse point accessed from that port. Provided that the probe is not removed from the stack gas stream, measurements may be taken at subsequent traverse points accessed from the same test port without waiting again for the response time to elapse.

8.4.2 Temperature measurement for wall effects traverse points. Either (1) take temperature measurements at each wall effects traverse point in accordance with the applicable provisions of Method 2, 2F, or 2G; or (2) use the temperature measurement at the Method 1 traverse point closest to the wall as the temperature measurement for all the wall effects traverse points in the corresponding equal-area sector.

8.4.3 Non-detectable velocity pressure at wall effects traverse points. If the probe cannot be positioned at a wall effects traverse point or if no velocity pressure can be detected at a wall effects point, measurements shall be taken at the first subsequent wall effects traverse point farther from the wall where velocity can be detected. Follow the instructions in section 8.7.1.2 of this method for recording results for wall effects traverse points where velocity pressure cannot be detected. It should be noted that the full extent of velocity decay may not be accounted for if measurements are not taken at the 1-in. incremented wall effects traverse points closest to the wall.

8.5 Data Recording. For each wall effects and Method 1 traverse point where measurements are taken, record all pressure, temperature, and attendant measurements prescribed in section 3 of Method 2 or section 8.0 of Method 2F or 2G, as applicable.

8.6 Point Velocity Calculation. For each wall effects and Method 1 traverse point, calculate the point velocity value (v_i) in accordance with sections 12.1 and 12.2 of Method 2F for tests using Method 2F and in accordance with sections 12.1 and 12.2 of Method 2G for tests using Method 2 and Method 2G. (Note that the term (v_i) in this method corresponds to the term ($v_{a(i)}$) in Methods 2F and 2G.) When the equations in the indicated sections of Method 2G are used in deriving point velocity values for Method 2 tests, set the value of the yaw angles appearing in the equations to 0°.

8.7 Tabulating Calculated Point Velocity Values for Wall Effects Traverse Points. Enter the following values in a hardcopy or electronic form similar to Form 2H–1 (for 16-point Method 1 traverses) or Form 2H–2 (for Method 1 traverses consisting of more than 16 points). A separate form must be completed for each of the four Method 1 equal-area sectors that are closest to the wall.

(a) Port ID (e.g., A, B, C, or D)

(b) Probe type

(c) Probe ID

(d) Stack or duct diameter in ft (m) (determined in accordance with section 8.6 of Method 2F or Method 2G)

(e) Stack or duct radius in in. (cm)

(f) Distance from the wall of wall effects traverse points at 1-in. intervals, in ascending order starting with 1 in. (2.5 cm) (column A of Form 2H–1 or 2H–2)

(g) Point velocity values (v_d) for 1-in. incremented traverse points (see section 8.7.1), including d_{last} (see section 8.7.2)

(h) Point velocity value (v_{drem}) at d_{rem} (see section 8.7.3).

8.7.1 Point velocity values at wall effects traverse points other than d_{last}. For every 1-in. incremented wall effects traverse point other than d_{last}, enter in column B of Form 2H–1 or 2H–2 either the velocity measured at the point (see section 8.7.1.1) or the velocity measured at the first subsequent traverse point farther from the wall (see section 8.7.1.2). A velocity value must be entered in column B of Form 2H–1 or 2H–2 for every 1-in. incremented traverse point from d_1 (representing the wall effects traverse point 1 in. [2.5 cm] from the wall) to d_{last}.

8.7.1.1 For wall effects traverse points where the probe can be positioned and velocity pressure can be detected, enter the value obtained in accordance with section 8.6.

8.7.1.2 For wall effects traverse points that were skipped [see section 8.2.2.3(c)] and for points where the probe cannot be positioned or where no velocity pressure can be detected, enter the value obtained at the first subsequent traverse point farther from the wall where velocity pressure was detected and measured and follow the entered value with a ''flag,'' such as the notation ''NM,'' to indicate that ''no measurements'' were actually taken at this point.

8.7.2 Point velocity value at d_{last}. For d_{last}, enter in column B of Form 2H–1 or 2H–2 the measured value obtained in accordance with section 8.6.

8.7.3 Point velocity value (v_{drem}) at d_{rem}. Enter the point velocity value obtained at d_{rem} in column G of row 4a in Form 2H–1 or 2H–2. If the distance between d_{rem} and d_{last} is less than or equal to ½ in. (12.7 mm), the measured velocity value at d_{last} may be used as the value at d_{rem} (see section 8.2.4.2).

9.0 Quality Control.

9.1 Particulate Matter Build-up in Horizontal Ducts. Wall effects testing of horizontal circular ducts should be conducted only if build-up of particulate matter or other material in the bottom of the duct is not present.

9.2 Verifying Traverse Point Distances. In taking measurements at wall effects traverse points, it is very important for the probe impact pressure port to be positioned as close as practicable to the traverse point locations in the gas stream. For this reason, before beginning wall effects testing, it is important to calculate and record the traverse point positions that will be marked on each probe for each port, taking into account the distance that each port nipple (or probe mounting flange for automated probes) extends out of the stack and any extension of the port nipple (or mounting flange) into the gas stream. To ensure that traverse point positions are properly identified, the following procedures should be performed on each probe used.

9.2.1 Manual probes. Mark the probe insertion distance of the wall effects and Method 1 traverse points on the probe sheath so that when a mark is aligned with the outside face of the stack port, the probe impact port is located at the calculated distance of the traverse point from the stack inside wall. The use of different colored marks is recommended for designating the wall effects and Method 1 traverse points. Before the first use of each probe, check to ensure that the distance of each mark from the center of the probe impact pressure port agrees with the previously calculated traverse point positions to within ±¼ in. (6.4 mm).

9.2.2 Automated probe systems. For automated probe systems that mechanically position the probe head at prescribed traverse point positions, activate the system with the probe assemblies removed from the test ports and sequentially extend the probes to the programmed location of each wall effects traverse point and the Method 1 traverse points. Measure the distance between the center of the probe impact pressure port and the inside of the probe assembly mounting flange for each traverse point. The measured distances must agree with the previously calculated traverse point positions to within ±¼ in. (6.4 mm).

9.3 Probe Installation. Properly sealing the port area is particularly important in taking measurements at wall effects traverse points. For testing involving manual probes, the area between the probe sheath and the port should be sealed with a tightly fitting flexible seal made of an appropriate material such as heavy cloth so that leakage is minimized. For automated probe systems, the probe assembly mounting flange area should be checked to verify that there is no leakage.

9.4 Velocity Stability. This method should be performed only when the average gas velocity in the stack or duct is relatively constant over the duration of the test. If the average gas velocity changes significantly during the course of a wall effects test, the test results should be discarded.

10.0 Calibration

10.1 The calibration coefficient(s) or curves obtained under Method 2, 2F, or 2G and used to perform the Method 1 traverse are applicable under this method.

11.0 Analytical Procedure

11.1 Sample collection and analysis are concurrent for this method (see section 8).

12.0 Data Analysis and Calculations

12.1 The following calculations shall be performed to obtain a wall effects adjustment factor (*WAF*) from (1) the wall effects-unadjusted average velocity (*T4avg*), (2) the replacement velocity ($\hat{v}e_j$) for each of the four Method 1 sectors closest to the wall, and (3) the average stack gas velocity that accounts for velocity decay near the wall ($\hat{v}_{avg}$).

12.2 Nomenclature. The following terms are listed in the order in which they appear in Equations 2H–5 through 2H–21.

v_{avg} = the average stack gas velocity, unadjusted for wall effects, actual ft/sec (m/sec);

vi_i = stack gas point velocity value at Method 1 interior equal-area sectors, actual ft/sec (m/sec);

ve_j = stack gas point velocity value, unadjusted for wall effects, at Method 1 exterior equal-area sectors, actual ft/sec (m/sec);

i = index of Method 1 interior equal-area traverse points;

j = index of Method 1 exterior equal-area traverse points;

n = total number of traverse points in the Method 1 traverse;

$vdec_d$ = the wall effects decay velocity for a sub-sector located between the traverse points at distances $d-1$ (in metric units, $d-2.5$) and d from the wall, actual ft/sec (m/sec);

v_d = the measured stack gas velocity at distance d from the wall, actual ft/sec (m/sec); Note: $v_0 = 0$;

d = the distance of a 1-in. incremented wall effects traverse point from the wall, for traverse points d_1 through d_{last}, in. (cm);

A_d = the cross-sectional area of a sub-sector located between the traverse points at distances $d-1$ (in metric units, $d-2.5$) and d from the wall, in.^{2} (cm^2) (e.g., sub-sector A_2 shown in Figures 2H–3 and 2H–4);

r = the stack or duct radius, in. (cm);

Q_d = the stack gas volumetric flow rate for a sub-sector located between the traverse points at distances $d-1$ (in metric units, $d-2.5$) and d from the wall, actual ft-in.^{2}/sec (m-cm^2/sec);

$Q_{d_1 \rightarrow d_{last}}$ = the total stack gas volumetric flow rate for all sub-sectors located between the wall and d_{last}, actual ft-in.^{2}/sec (m-cm^2/sec);

d_{last} = the distance from the wall of the last 1-in. incremented wall effects traverse point, in. (cm);

A_{drem} = the cross-sectional area of the sub-sector located between d_{last} and the interior edge of the Method 1 equal-area sector closest to the wall, in.^{2} (cm^2) (see Figure 2H–4);

p = the number of Method 1 traverse points per diameter, $p \geq 8$ (e.g., for a 16-point traverse, $p = 8$);

d_{rem} = the distance from the wall of the centroid of the area between d_{last} and the interior edge of the Method 1 equal-area sector closest to the wall, in. (cm);

Q_{drem} = the total stack gas volumetric flow rate for the sub-sector located between d_{last} and the interior edge of the Method 1 equal-area sector closest to the wall, actual ft-in.^{2}/sec (m-cm^2/sec);

v_{drem} = the measured stack gas velocity at distance d_{rem} from the wall, actual ft/sec (m/sec);

Q_T = the total stack gas volumetric flow rate for the Method 1 equal-area sector closest to the wall, actual ft-in.^{2}/sec (m-cm^2/sec);

$\hat{v}e_j$ = the replacement stack gas velocity for the Method 1 equal-area sector closest to the wall, i.e., the stack gas point velocity value, adjusted for wall effects, for the jth Method 1 equal-area sector closest to the wall, actual ft/sec (m/sec);

$\hat{v}_{avg}$ = the average stack gas velocity that accounts for velocity decay near the wall, actual ft/sec (m/sec);

WAF = the wall effects adjustment factor derived from v_{avg} and $\hat{v}_{avg}$ for a single traverse, dimensionless;

$\hat{v}_{final}$ = the final wall effects-adjusted average stack gas velocity that replaces the unadjusted average stack gas velocity obtained using Method 2, 2F, or 2G for a field test consisting of a single traverse, actual ft/sec (m/sec);

$\bar{W}\bar{A}\bar{F}$ = the wall effects adjustment factor that is applied to the average velocity, unadjusted for wall effects, in order to obtain the final wall effects-adjusted stack gas velocity, $\hat{v}_{final}$ or, $\hat{v}_{final(k)}$, dimensionless;

$\hat{v}_{final(k)}$ = the final wall effects-adjusted average stack gas velocity that replaces the unadjusted average stack gas velocity obtained using Method 2, 2F, or 2G on run k of a RATA or other multiple-run field test procedure, actual ft/sec (m/sec);

$v_{avg(k)}$ = the average stack gas velocity, obtained on run k of a RATA or other multiple-run procedure, unadjusted for velocity decay near the wall, actual ft/sec (m/sec);

k=index of runs in a RATA or other multiple-run procedure.

12.3 Calculate the average stack gas velocity that does not account for velocity decay near the wall (v_{avg}) using Equation 2H–5.

$$v_{avg} = \frac{\left(\sum_{i=1}^{n-4} vi_i + \sum_{j=1}^{4} ve_j\right)}{n} \qquad \text{Eq. 2H-5}$$

(Note that v_{avg} in Equation 2H–5 is the same as $v_{(a)avg}$ in Equations 2F–9 and 2G–8 in Methods 2F and 2G, respectively.)

For a 16-point traverse, Equation 2H–5 may be written as follows:

$$v_{avg} = \frac{\left(\sum_{i=1}^{12} vi_i + \sum_{j=1}^{4} ve_j\right)}{16} \qquad \text{Eq. 2H-6}$$

12.4 Calculate the replacement velocity, $\hat{v}e_j$, for each of the four Method 1 equal-area sectors closest to the wall using the procedures described in sections 12.4.1 through 12.4.8. Forms 2H–1 and 2H–2 provide sample tables that may be used in either hardcopy or spreadsheet format to perform the calculations described in sections 12.4.1 through 12.4.8. Forms 2H–3 and 2H–4 provide examples of Form 2H–1 filled in for partial and complete wall effects traverses.

12.4.1 Calculate the average velocity (designated the ''decay velocity,'' $vdec_d$) for each sub-sector located between the wall and d_{last} (see Figure 2H–3) using Equation 2H–7.

$$vdec_d = \frac{v_{d-1} + v_d}{2} \qquad \text{Eq. 2H-7}$$

For each line in column A of Form 2H–1 or 2H–2 that contains a value of d, enter the corresponding calculated value of $vdec_d$ in column C.

12.4.2 Calculate the cross-sectional area between the wall and the first 1-in. incremented wall effects traverse point and between successive 1-in. incremented wall effects traverse points, from the wall to d_{last} (see Figure 2H–3), using Equation 2H–8.

$$A_d = \frac{1}{4}\pi(r-d+1)^2 - \frac{1}{4}\pi(r-d)^2 \qquad \text{Eq. 2H-8}$$

For each line in column A of Form 2H–1 or 2H–2 that contains a value of d, enter the value of the expression $\frac{1}{4}\pi(r-d+1)^2$ in column D, the value of the expression $\frac{1}{4}\pi(r-d)^2$ in column E, and the value of A_d in column F. Note that Equation 2H–8 is designed for use only with English units (in.). If metric units (cm) are used, the first term, $\frac{1}{4}\pi(r-d+1)^2$, must be changed to $\frac{1}{4}\pi(r-d+2.5)^2$. This change must also be made in column D of Form 2H–1 or 2H–2.

12.4.3 Calculate the volumetric flow through each cross-sectional area derived in section 12.4.2 by multiplying the values of $vdec_d$, derived according to section 12.4.1, by the cross-sectional areas derived in section 12.4.2 using Equation 2H–9.

$$Q_d = vdec_d \times A_d \qquad \text{Eq. 2H-9}$$

For each line in column A of Form 2H–1 or 2H–2 that contains a value of d, enter the corresponding calculated value of Q_d in column G.

12.4.4 Calculate the total volumetric flow through all sub-sectors located between the wall and d_{last}, using Equation 2H–10.

$$Q_{d_1 \rightarrow d_{last}} = \sum_{d=1}^{d_{last}} Q_d \qquad \text{Eq. 2H-10}$$

Enter the calculated value of $Q_{d_1 \rightarrow_c d_{last}}$ in line 3 of column G of Form 2H–1 or 2H–2.

12.4.5 Calculate the cross-sectional area of the sub-sector located between d_{last} and the interior edge of the Method 1 equal-area sector (e.g., sub-sector A_{drem} shown in Figures 2H–3 and 2H–4) using Equation 2H–11.

$$A_{drem} = \frac{1}{4}\pi(r-d_{last})^2 - \frac{p-2}{4p}\pi(r)^2 \qquad \text{Eq. 2H-11}$$

For a 16-point traverse (eight points per diameter), Equation 2H–11 may be written as follows:

$$A_{drem} = \frac{1}{4}\pi\left(r - d_{last}\right)^2 - \frac{3}{16}\pi(r)^2 \qquad \text{Eq. 2H-12}$$

Enter the calculated value of A_{drem} in line 4b of column G of Form 2H–1 or 2H–2.

12.4.6 Calculate the volumetric flow for the sub-sector located between d_{last} and the interior edge of the Method 1 equal-area sector, using Equation 2H–13.

$$Q_{drem} = v_{drem} \times A_{drem} \qquad \text{Eq. 2H-13}$$

In Equation 2H–13, v_{drem} is either (1) the measured velocity value at d_{rem} or (2) the measured velocity at d_{last}, if the distance between d_{rem} and d_{last} is less than or equal to ½ in. (12.7 mm) and no velocity measurement is taken at d_{rem} (see section 8.2.4.2). Enter the calculated value of Q_{drem} in line 4c of column G of Form 2H–1 or 2H–2.

12.4.7 Calculate the total volumetric flow for the Method 1 equal-area sector closest to the wall, using Equation 2H–14.

$$Q_T = Q_{d_1 \rightarrow d_{last}} + Q_{drem} \qquad \text{Eq. 2H-14}$$

Enter the calculated value of Q_T in line 5a of column G of Form 2H–1 or 2H–2.

12.4.8 Calculate the wall effects-adjusted replacement velocity value for the Method 1 equal-area sector closest to the wall, using Equation 2H–15.

$$\hat{v}e_j = \frac{Q_T}{\frac{1}{2p}\pi(r)^2} \qquad \text{Eq. 2H-15}$$

For a 16-point traverse (eight points per diameter), Equation 2H–15 may be written as follows:

$$\hat{v}e_j = \frac{Q_T}{\frac{1}{16}\pi(r)^2} \qquad \text{Eq. 2H-16}$$

Enter the calculated value of $\hat{v}e_j$ in line 5B of column G of Form 2H–1 or 2H–2.

12.5 Calculate the wall effects-adjusted average velocity, $\hat{v}_{avg}$, by replacing the four values of ve_j shown in Equation 2H–5 with the four wall effects-adjusted replacement velocity values,$\hat{v}e_j$, calculated according to section 12.4.8, using Equation 2H–17.

$$\hat{v}_{avg} = \frac{\left(\sum_{i=1}^{n-4} vi_i + \sum_{j=1}^{4} \hat{v}e_j\right)}{n} \qquad \text{Eq. 2H-17}$$

For a 16-point traverse, Equation 2H–17 may be written as follows:

$$\hat{v}_{avg} = \frac{\left(\sum_{i=1}^{12} vi_i + \sum_{j=1}^{4} \hat{v}e_j\right)}{16} \qquad \text{Eq. 2H-18}$$

12.6 Calculate the wall effects adjustment factor, WAF, using Equation 2H–19.

$$WAF = \frac{\hat{v}_{avg}}{v_{avg}} \qquad \text{Eq. 2H-19}$$

12.6.1 Partial wall effects traverse. If a partial wall effects traverse (see section 8.2.2) is conducted, the value obtained from Equation 2H–19 is acceptable and may be reported as the wall effects adjustment factor provided that the value is greater than or equal to 0.9800. If the value is less than 0.9800, it shall not be used and a wall effects adjustment factor of 0.9800 may be used instead.

12.6.2 Complete wall effects traverse. If a complete wall effects traverse (see section 8.2.3) is conducted, the value obtained from Equation 2H–19 is acceptable and may be reported as the wall effects adjustment factor provided that the value is greater than or equal to 0.9700. If the value is less than 0.9700, it shall not be used and a wall effects adjustment factor of 0.9700 may be used instead. If the wall effects adjustment factor for a particular stack or duct is less than 0.9700, the tester may (1) repeat the wall effects test, taking measurements at more Method 1 traverse points and (2) recalculate the wall effects adjustment factor from these measurements, in an attempt to obtain a wall effects adjustment factor that meets the 0.9700 specification and completely characterizes the wall effects.

12.7 Applying a Wall Effects Adjustment Factor. A default wall effects adjustment factor, as specified in section 8.1, or a calculated wall effects adjustment factor meeting the requirements of section 12.6.1 or 12.6.2

may be used to adjust the average stack gas velocity obtained using Methods 2, 2F, or 2G to take into account velocity decay near the wall of circular stacks or ducts. Default wall effects adjustment factors specified in section 8.1 and calculated wall effects adjustment factors that meet the requirements of section 12.6.1 and 12.6.2 are summarized in Table 2H–2.

12.7.1 Single-run tests. Calculate the final wall effects-adjusted average stack gas velocity for field tests consisting of a single traverse using Equation 2H–20.

$$\hat{v}_{final} = \overline{WAF} \times v_{avg} \qquad \text{Eq. 2H-20}$$

The wall effects adjustment factor, WAF, shown in Equation 2H–20, may be (1) a default wall effects adjustment factor, as specified in section 8.1, or (2) a calculated adjustment factor that meets the specifications in sections 12.6.1 or 12.6.2. If a calculated adjustment factor is used in Equation 2H–20, the factor must have been obtained during the same traverse in which v_{avg} was obtained.

12.7.2 RATA or other multiple run test procedure. Calculate the final wall effects-adjusted average stack gas velocity for any run k of a RATA or other multiple-run procedure using Equation 2H–21.

$$\hat{v}_{final(k)} = \overline{WAF} \times v_{avg(k)} \qquad \text{Eq. 2H-21}$$

The wall effects adjustment factor, $\bar{W}\bar{A}\bar{F}$, shown in Equation 2H–21 may be (1) a default wall effects adjustment factor, as specified in section 8.1; (2) a calculated adjustment factor (meeting the specifications in sections 12.6.1 or 12.6.2) obtained from any single run of the RATA that includes run k; or (3) the arithmetic average of more than one WAF (each meeting the specifications in sections 12.6.1 or 12.6.2) obtained through wall effects testing conducted during several runs of the RATA that includes run k. If wall effects adjustment factors (meeting the specifications in sections 12.6.1 or 12.6.2) are determined for more than one RATA run, the arithmetic average of all of the resulting calculated wall effects adjustment factors must be used as the value of $\bar{W}\bar{A}\bar{F}$ and applied to all runs of that RATA. If a calculated, not a default, wall effects adjustment factor is used in Equation 2H–21, the average velocity unadjusted for wall effects, $v_{avg(k)}$ must be obtained from runs in which the number of Method 1 traverse points sampled does not exceed the number of Method 1 traverse points in the runs used to derive the wall effects adjustment factor, $\bar{W}\bar{A}\bar{F}$, shown in Equation 2H–21.

12.8 Calculating Volumetric Flow Using Final Wall Effects-Adjusted Average Velocity Value. To obtain a stack gas flow rate that accounts for velocity decay near the wall of circular stacks or ducts, replace v_s in Equation 2–10 in Method 2, or $v_{a(avg)}$ in Equations 2F–10 and 2F–11 in Method 2F, or $v_{a(avg)}$ in Equations 2G–9 and 2G–10 in Method 2G with one of the following.

12.8.1 For single-run test procedures, use the final wall effects-adjusted average stack gas velocity, $\hat{v}_{final}$, calculated according to Equation 2H–20.

12.8.2 For RATA and other multiple run test procedures, use the final wall effects-adjusted average stack gas velocity, $\hat{v}_{final(k)}$, calculated according to Equation 2H–21.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Reporting

16.1 Field Test Reports. Field test reports shall be submitted to the Agency according to the applicable regulatory requirements. When Method 2H is performed in conjunction with Method 2, 2F, or 2G to derive a wall effects adjustment factor, a single consolidated Method 2H/2F (or 2H/2G) field test report should be prepared. At a minimum, the consolidated field test report should contain (1) all of the general information, and data for Method 1 points, specified in section 16.0 of Method 2F (when Method 2H is used in conjunction with Method 2F) or section 16.0 of Method 2G (when Method 2H is used in conjunction with Method 2 or 2G) and (2) the additional general information, and data for Method 1 points and wall effects points, specified in this section (some of which are included in section 16.0 of Methods 2F and 2G and are repeated in this section to ensure complete reporting for wall effects testing).

16.1.1 Description of the source and site. The field test report should include the descriptive information specified in section 16.1.1 of Method 2F (when using Method 2F) or 2G (when using either Method 2 or 2G). It should also include a description of the stack or duct's construction material along with the diagram showing the dimensions of the stack or duct at the test port elevation prescribed in Methods 2F and 2G. The diagram should indicate the location of all wall effects traverse points where measurements were taken as well as the Method 1 traverse points. The diagram should provide a unique identification number for each wall effects and Method 1 traverse point, its distance from the wall, and its location relative to the probe entry ports.

16.1.2 Field test forms. The field test report should include a copy of Form 2H–1, 2H–2, or an equivalent for each Method 1 exterior equal-area sector.

16.1.3 Field test data. The field test report should include the following data for the Method 1 and wall effects traverse.

16.1.3.1 Data for each traverse point. The field test report should include the values

specified in section 16.1.3.2 of Method 2F (when using Method 2F) or 2G (when using either Method 2 or 2G) for each Method 1 and wall effects traverse point. The provisions of section 8.4.2 of Method 2H apply to the temperature measurements reported for wall effects traverse points. For each wall effects and Method 1 traverse point, the following values should also be included in the field test report.

(a) Traverse point identification number for each Method 1 and wall effects traverse point.

(b) Probe type.

(c) Probe identification number.

(d) Probe velocity calibration coefficient (i.e., C_p when Method 2 or 2G is used; F_2 when Method 2F is used).

For each Method 1 traverse point in an exterior equal-area sector, the following additional value should be included.

(e) Calculated replacement velocity, $\hat{v}e_j$, accounting for wall effects.

16.1.3.2 Data for each run. The values specified in section 16.1.3.3 of Method 2F (when using Method 2F) or 2G (when using either Method 2 or 2G) should be included in the field test report once for each run. The provisions of section 12.8 of Method 2H apply for calculating the reported gas volumetric flow rate. In addition, the following Method 2H run values should also be included in the field test report.

(a) Average velocity for run, accounting for wall effects, $\hat{v}_{avg}$.

(b) Wall effects adjustment factor derived from a test run, WAF.

16.1.3.3 Data for a complete set of runs. The values specified in section 16.1.3.4 of Method 2F (when using Method 2F) or 2G (when using either Method 2 or 2G) should be included in the field test report once for each complete set of runs. In addition, the field test report should include the wall effects adjustment factor, $\bar{W}\bar{A}\bar{F}$, that is applied in accordance with section 12.7.1 or 12.7.2 to obtain the final wall effects-adjusted average stack gas velocity $\hat{v}_{final}$ or $\hat{v}_{final(k)}$.

16.1.4 Quality assurance and control. Quality assurance and control procedures, specifically tailored to wall effects testing, should be described.

16.2 Reporting a Default Wall Effects Adjustment Factor. When a default wall effects adjustment factor is used in accordance with section 8.1 of this method, its value and a description of the stack or duct's construction material should be reported in lieu of submitting a test report.

17.0 References.

(1) 40 CFR Part 60, Appendix A, Method 1—Sample and velocity traverses for stationary sources.

(2) 40 CFR Part 60, Appendix A, Method 2—Determination of stack gas velocity and volumetric flow rate (Type S pitot tube).

(3) 40 CFR Part 60, Appendix A, Method 2F—Determination of stack gas velocity and volumetric flow rate with three-dimensional probes.

(4) 40 CFR Part 60, Appendix A, Method 2G—Determination of stack gas velocity and volumetric flow rate with two-dimensional probes.

(5) 40 CFR Part 60, Appendix A, Method 3—Gas analysis for carbon dioxide, oxygen, excess air, and dry molecular weight.

(6) 40 CFR Part 60, Appendix A, Method 3A—Determination of oxygen and carbon dioxide concentrations in emissions from stationary sources (instrumental analyzer procedure).

(7) 40 CFR Part 60, Appendix A, Method 4—Determination of moisture content in stack gases.

(8) Emission Measurement Center (EMC) Approved Alternative Method (ALT–011) ''Alternative Method 2 Thermocouple Calibration Procedure.''

(9) The Cadmus Group, Inc., 1998, ''EPA Flow Reference Method Testing and Analysis: Data Report, Texas Utilities, DeCordova Steam Electric Station, Volume I: Test Description and Appendix A (Data Distribution Package),'' EPA/430–R–98–015a.

(10) The Cadmus Group, Inc., 1998, ''EPA Flow Reference Method Testing and Analysis: Data Report, Texas Utilities, Lake Hubbard Steam Electric Station, Volume I: Test Description and Appendix A (Data Distribution Package),'' EPA/430–R–98–017a.

(11) The Cadmus Group, Inc., 1998, ''EPA Flow Reference Method Testing and Analysis: Data Report, Pennsylvania Electric Co., G.P.U. Genco Homer City Station: Unit 1, Volume I: Test Description and Appendix A (Data Distribution Package),'' EPA/430–R–98–018a.

(12) The Cadmus Group, Inc., May 1999, ''EPA Flow Reference Method Testing and Analysis: Findings Report,'' EPA/430–R–99–009.

(13) The Cadmus Group, Inc., 1997, ''EPA Flow Reference Method Testing and Analysis: Wind Tunnel Experimental Results,'' EPA/430–R–97–013.

(14) National Institute of Standards and Technology, 1998, ''Report of Special Test of Air Speed Instrumentation, Four Prandtl Probes, Four S-Type Probes, Four French Probes, Four Modified Kiel Probes,'' Prepared for the U.S. Environmental Protection Agency under IAG No. DW13938432–01–0.

(15) National Institute of Standards and Technology, 1998, ''Report of Special Test of Air Speed Instrumentation, Five Autoprobes,'' Prepared for the U.S. Environmental Protection Agency under IAG No. DW13938432–01–0.

(16) National Institute of Standards and Technology, 1998, ''Report of Special Test of Air Speed Instrumentation, Eight Spherical Probes,'' Prepared for the U.S. Environmental Protection Agency under IAG No. DW13938432–01–0.

(17) National Institute of Standards and Technology, 1998, ''Report of Special Test of Air Speed Instrumentation, Four DAT Probes,'' Prepared for the U.S. Environmental Protection Agency under IAG No. DW13938432–01–0.

(18) Massachusetts Institute of Technology (MIT), 1998, ''Calibration of Eight Wind Speed Probes Over a Reynolds Number Range of 46,000 to 725,000 per Foot, Text and Summary Plots,'' Plus Appendices, WBWT-TR–1317, Prepared for The Cadmus Group, Inc., under EPA Contract 68–W6–0050, Work Assignment 0007AA–3.

(19) Fossil Energy Research Corporation, Final Report, ''Velocity Probe Tests in Non-axial Flow Fields,'' November 1998, Prepared for the U.S. Environmental Protection Agency.

(20) Fossil Energy Research Corporation, ''Additional Swirl Tunnel Tests: E-DAT and T-DAT Probes,'' February 24, 1999, Technical Memorandum Prepared for U.S. Environmental Protection Agency, P.O. No. 7W–1193–NALX.

Table 2H-1. Distance from the Wall for the Interior Boundary, d_b, of a Method 1 Exterior Equal-Area Sector as a Function of the Stack or Duct Radius, r, and Number of Method 1 Traverse Points

Number of Method 1 Traverse Points	d_b
16	0.134 × r
20	0.106 × r
24	0.087 × r
28	0.074 × r
32	0.065 × r
36	0.057 × r
40	0.051 × r
44	0.047 × r
48	0.043 × r

Table 2H-2 Default and Minimum Acceptable Calculated Wall Effects Adjustment Factors

		Brick and Mortar Stacks	All Other Stacks and Ducts
Default WAF		0.9900	0.9950
Minimum Acceptable WAF	Partial Traverse	0.9800	
	Complete Traverse	0.9700	

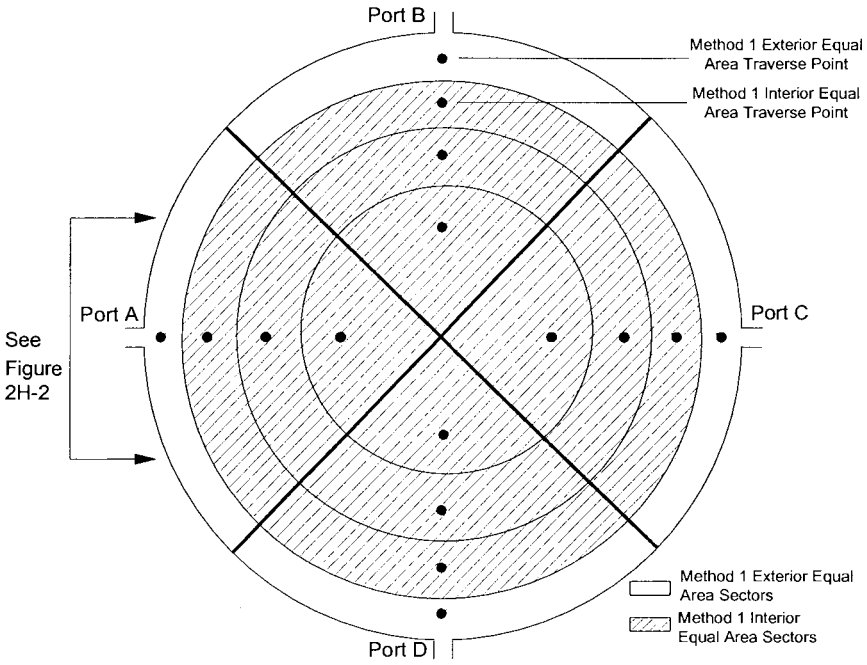


Figure 2H-1. Method 1 exterior and interior equal-area sectors with traverse points indicated.

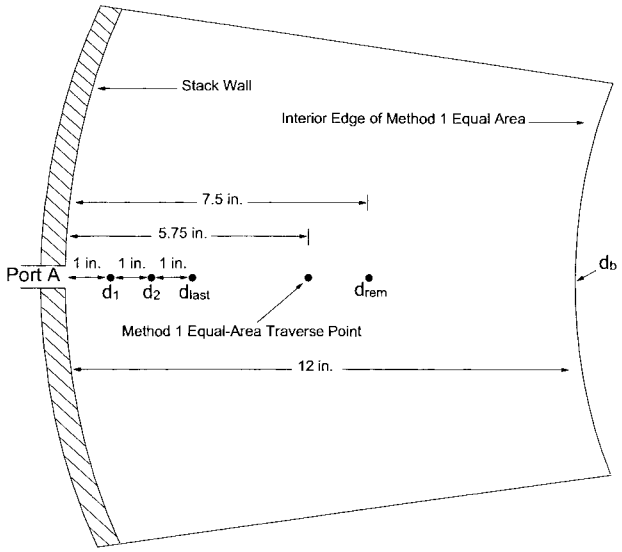


Figure 2H-2. Figure showing part of a Method 1 equal-area sector closest to the stack wall with three illustrative wall effects points at 1 in. intervals, the Method 1 equal-area traverse point, and d_{rem} for a 15 ft diameter stack.[1]

[1] Metric equivalents of English units used in Figure 2H-2 are as follows: 1 in. = 2.5 cm; 5.75 in. = 14.6 cm; 7.5 in. = 19.0 cm; 12 in. = 30.5 cm; and 15 ft = 4.6 m.

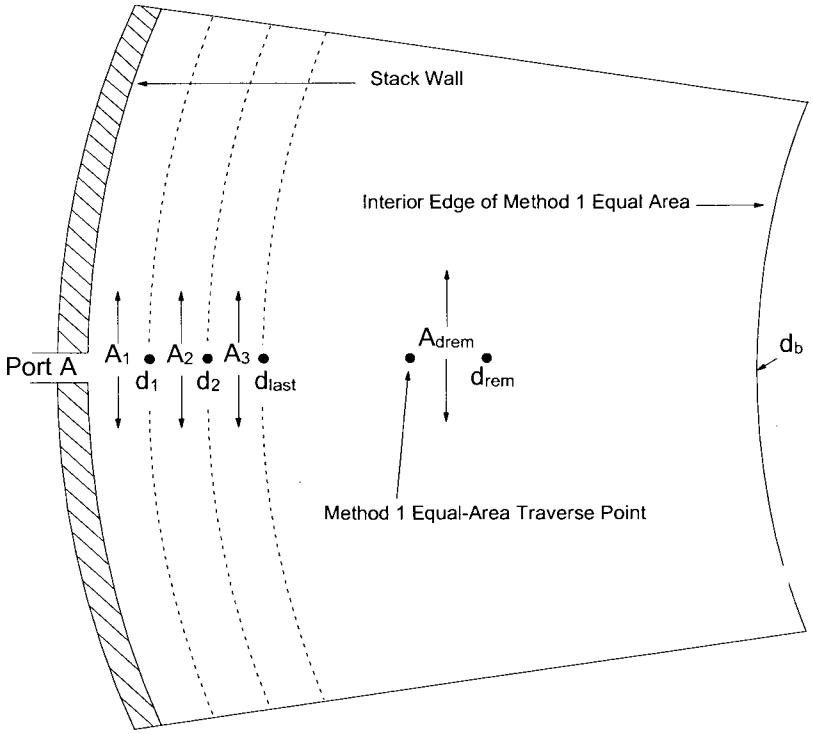


Figure 2H-3. Figure showing part of a Method 1 equal-area sector closest to the stack wall with three illustrative sub-sectors between the stack wall and d_{last} and the sub-sector represented by d_{rem}. A_1 is the area between the stack wall and d_1, A_2 is the area between d_1 and d_2, A_3 is the area between d_2 and d_{last}, and A_{drem} is the area between d_{last} and the interior edge of the Method 1 equal-area sector.

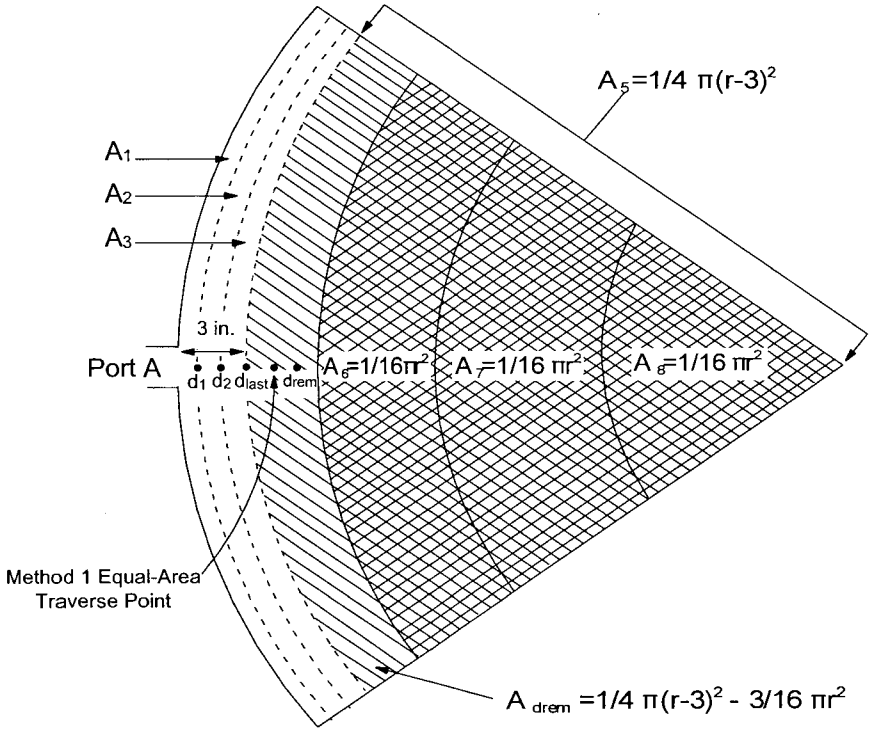


Figure 2H-4. Figure illustrating the calculations in Equation 2H-12 used to calculate the cross sectional area of the sub-sector between d_{last} and the interior edge of the Method 1 sector closest to the stack wall (A_{drem}) for a 16-point Method 1 traverse. The Method 1 equal-area traverse point and four wall effects traverse points (d_1, d_2, d_{last}, and d_{rem}) within the Method 1 sector closest to the stack wall are also shown.[1]

[1] All dimensions are given in in. Metric equivalents (in cm) are as follows: 3 in. = 7.6 cm; A_5 = 1/4 π(r−7.6)²; and A_{drem} = 1/4 π(r−7.6)² − 3/16 πr².

Form 2H-1. Calculation of Wall Effects Replacement Velocity Values (16-Point Method 1 Traverse)

1st Probe Type/ID/Pts. Sampled: _____ Tester(s): _____

2nd Probe Type/ID/Pts. Sampled: _____ Affiliation: _____

Entry Port ID (e.g., A, B, C, or D): _____

1. Diameter of the stack or duct (ft)		Radius, r, of the stack or duct (in.) (= diameter × 6)	

2. Location (column A), measured and decay velocities (columns B and C), and volumetric flow (column G) associated with each successive wall effects traverse point.

(A)	(B)	(C)	(D)	(E)	(F)	(G)
Distance (d) from Wall	Measured Velocity (v_d) at Distance d	Decay Velocity ($vdec_d$)	Intermediate Calculations		Area of Sub-sector (A_d)	Volumetric Flow in Sub-sector (Q_d)
		$\frac{v_{d-1}+v_d}{2}$ Note: $v_0 = 0$	$\frac{1}{4}\pi[r-d+1]^2$	$\frac{1}{4}\pi[r-d]^2$	(Col. D - Col. E)	(Col. C × Col. F)
(*in.*)	(*ft/sec*)	(*ft/sec*)	(*in.*^{2})	(*in.*^{2})	(*in.*^{2})	(*ft-in.*^{2}/*sec*)
$d = 1$						
$d = 2$						
. . .						
d_{last}						

Note: $d_{last} \leq 0.1340\ r$, where r is the radius of the stack or duct. See section 8.2.2.3 of the method.

3. Total volumetric flow for all sub-sectors located between stack wall and d_{last} (total Col. G).	
4. Volumetric flow for remainder of the Method 1 equal-area sector.	
a. Velocity measurement at distance d_{rem} from stack wall (v_{drem}). (If $d_{rem} - d_{last} < ½$ in., then no measurement at d_{rem} is necessary. Enter the velocity at d_{last} on this line.)	
b. Total area in remainder of Method 1 equal-area segment (A_{drem}). Subtract $\frac{3}{16}\pi(r)^2$ from last entry in item 2, column E, and enter the result on this line.	
c. Multiply values on lines 4a and 4b. (Q_{drem})	
5. Wall effects-adjusted velocity in the Method 1 equal-area sector.	
a. Add the values on lines 3 and 4c. (Q_T)	
b. Divide line 5a by $\frac{1}{16}\pi(r)^2$. The resulting value is one of four "replacement" point velocity values adjusted for wall effects, $\hat{v}e_j$, as derived in Equation 2H-16.	
6. Substitute the value shown in 5b for the unadjusted velocity value in the Method 1 sector. (See Eq. 2H-18.)	

Notes: 1. Column B: If no measurement is taken at distance d, enter the velocity value obtained at the first subsequent traverse point where a measurement was taken, followed by the letters "NM". See section 8.7.1.2.

2. For clarity, only English units are shown in this form. Following are metric equivalents of the English units used in the form. In row 2, column A: 1 in. = 2.5 cm; 2 in. = 5.1 cm. In row 2, column D: If metric units (cm) are used, the term $¼\ \pi(r-d+1)^2$ must be changed to $¼\ \pi(r-d+2.5)^2$. In row 4a: ½ in. = 12.7 mm. Throughout the form, the metric equivalents of *in.*, *in.*^{2}, *ft*, *ft/sec*, and *ft-in.*^{2}/*sec* are *cm*, *cm*^{2}, *m*, *m/sec*, and *m-cm*^{2}/*sec*, respectively.

Form 2H-2. Calculation of Wall Effects Replacement Velocity Values (Any Method 1 Traverse ≥16 Points)

1st Probe Type/ID/Pts. Sampled: _____ Tester(s): _____

2nd Probe Type/ID/Pts. Sampled: _____ Affiliation: _____

Entry Port ID (e.g., A, B, C, or D): _____

1. Diameter of the stack or duct (ft)		Radius, r, of the stack or duct (in.) (= diameter × 6)	

2. Location (Column A), measured and decay velocities (Columns B and C), and volumetric flow (Column G) associated with each successive wall effects traverse point.

(A)	(B)	(C)	(D)	(E)	(F)	(G)
Distance (d) from Wall	Measured Velocity (v_d) at Distance d	Decay Velocity ($vdec_d$)	Intermediate Calculations		Area of Sub-sector (A_d)	Volumetric Flow in Sub-sector (Q_d)
		$\frac{v_{d-1}+v_d}{2}$ Note: $v_0 = 0$	$\frac{2}{p}\pi[r-d+1]^2$	$\frac{2}{p}\pi[r-d]^2$	(Col. D - Col. E)	(Col. C × Col. F)
(*in.*)	(*ft/sec*)	(*ft/sec*)	(*in.*^{2})	(*in.*^{2})	(*in.*^{2})	(*ft-in.*^{2}/*sec*)
$d = 1$						
$d = 2$						
. . .						
d_{last}						

Note: $d_{last} \le d_b$, as defined in section 8.2.2.3 of the method.

3. Total volumetric flow for all sub-sectors located between stack wall and d_{last} (total Col. G).	
4. Volumetric flow for remainder of the Method 1 equal-area sector.	
a. Velocity measurement at distance d_{rem} from stack wall (v_{drem}). (If d_{rem}- d_{last} <½ in., then no measurement at d_{rem} is necessary. Enter the velocity at d_{last} on this line.)	
b. Total area in remainder of Method 1 equal-area segment (A_{drem}). Subtract $\left\{\frac{p-2}{4p}\right\}\pi(r)^2$ from last entry in item 2, column E, and enter the result on this line.	
c. Multiply values on lines 4a and 4b. (Q_{drem})	
5. Wall effects-adjusted velocity in the Method 1 near-wall equal-area segment.	
a. Add the values on lines 3 and 4. (Q_T)	
b. Divide line 5a by $\left\{\frac{1}{2p}\right\}\pi(r)^2$. The resulting value is one of four "replacement" point velocity values adjusted for wall effects, $\hat{v}e_j$, as derived in Equation 2H-15.	
6. Substitute the value shown in 5b for the unadjusted velocity value in the Method 1 sector. (See Eq. 2H-17.)	

Notes: 1. Column B: If no measurement is taken at distance d, enter the velocity value obtained at the first subsequent traverse point where a measurement was taken, followed by the letters "NM". See section 8.7.1.2.

2. For clarity, only English units are shown in this form. Following are metric equivalents of the English units used in the form. In row 2, column A: 1 in. = 2.5 cm; 2 in. = 5.1 cm. In row 2, column D: If metric units (cm) are used, the term $¼\,\pi(r-d+1)^2$ must be changed to $¼\,\pi(r-d+2.5)^2$. In row 4a: ½ in. = 12.7 mm. Throughout the form, the metric equivalents of *in.*, *in.*^{2}, *ft*, *ft/sec*, and *ft-in*^{2}*/sec* are *cm*, *cm*^{2}, *m*, *m/sec*, and *m-cm*^{2}*/sec*, respectively.

Form 2H-3. Calculation of Replacement Velocity Values for a Method 1 Equal-Area Sector Closest to the Stack Wall for a 16-Point Method 1 Traverse, Using a Partial Wall Effects Traverse

1st Probe Type/ID/Pts. Sampled: *Type S Straight-up/S-13/All* Tester(s): *Test Team III*

2nd Probe Type/ID/Pts. Sampled: _____ Affiliation: *Contractor III*

Entry Port ID (e.g., A, B, C, or D): *A*

1. Diameter of the stack or duct (ft)	*24*	Radius, r, of the stack or duct (in.) (= diameter × 6)	*144*

2. Location (column A), measured and decay velocities (columns B and C), and volumetric flow (column G) associated with each successive wall effects traverse point.

(A)	(B)	(C)	(D)	(E)	(F)	(G)
Distance (d) from Wall	Measured Velocity (v_d) at Distance d	Decay Velocity ($vdec_d$)	Intermediate Calculations		Area of Sub-sector (A_d)	Volumetric Flow in Sub-sector (Q_d)
		$\frac{v_{d-1}+v_d}{2}$ Note: $v_0 = 0$	$\frac{1}{4}\pi[r-d+1]^2$	$\frac{1}{4}\pi[r-d]^2$	(Col. D - Col. E)	(Col. C × Col. F)
(in.)	(ft/sec)	(ft/sec)	(in.^{2})	(in.^{2})	(in.^{2})	(ft-in.^{2}/sec)
$d = 1$	51.71 NM	25.85	16,286.00	16,060.59	225.41	5,827.47
$d = 2$	51.71 NM	51.71	16,060.59	15,836.76	223.84	11,573.72
$d_{last} = 3$	51.71	51.71	15,836.76	15,614.49	222.27	11,492.51

3. Total volumetric flow for all sub-sectors located between stack wall and d_{last} (total Col. G).	*28,893.70*
4. Volumetric flow for remainder of the Method 1 equal-area sector.	
a. Velocity measurement at distance d_{rem} from stack wall (v_{drem}). (If d_{rem}- d_{last} <½ in., then no measurement at d_{rem} is necessary. Enter the velocity at d_{last} on this line.)	*77.01*
b. Total area in remainder of Method 1 equal-area segment (A_{drem}). Subtract $\frac{3}{16}\pi(r)^2$ from last entry in item 2, column E, and enter the result on this line.	*3,399.99*
c. Multiply values on lines 4a and 4b. (Q_{drem})	*261,832.90*
5. Wall effects-adjusted velocity in the Method 1 equal-area sector.	
a. Add the values on lines 3 and 4c. (Q_T)	*290,726.61*
b. Divide line 5a by $\frac{1}{16}\pi(r)^2$. The resulting value is one of four "replacement" point velocity values adjusted for wall effects, $\hat{v}e_j$, as derived in Equation 2H-16.	*71.41*
6. Substitute the value shown in 5b for the unadjusted velocity value in the Method 1 sector. (See Eq. 2H-18.)	

Form 2H-4 Calculation of Replacement Velocity Values for a Method 1 Equal-Area Sector Closest to the Stack Wall for a 16-Point Method 1 Traverse, Using a Complete Traverse

1st Probe Type/ID/Pts. Sampled: *Type S Straight-up/S-13/All* Tester(s): *Test Team III*

2nd Probe Type/ID/Pts. Sampled: _____ Affiliation: *Contractor III*

Entry Port ID (e.g., A, B, C, or D): *A*

1. Diameter of the stack or duct (ft)	*24*	Radius, r, of the stack or duct (in.) (= diameter × 6)	*144*

2. Location (column A), measured and decay velocities (columns B and C), and volumetric flow (column G) associated with each successive wall effects traverse point.

(A)	(B)	(C)	(D)	(E)	(F)	(G)
Distance (d) from Wall	Measured Velocity (v_d) at Distance d	Decay Velocity ($vdec_d$)	Intermediate Calculations		Area of Sub-sector (A_d)	Volumetric Flow in Sub-sector (Q_s)
		$\frac{v_{d-1}+v_d}{2}$ Note: $v_0 = 0$	$\frac{1}{4}\pi[r-d+1]^2$	$\frac{1}{4}\pi[r-d]^2$	(Col. D - Col. E)	(Col. C × Col. F)
(in.)	(ft/sec)	(ft/sec)	(in.^{2})	(in.^{2})	(in.^{2})	(ft-in.^{2}/sec)
$d = 1$	51.71 NM	25.85	16,286.00	16,060.59	225.41	5,827.47
$d = 2$	51.71 NM	51.71	16,060.59	15,836.76	223.84	11,573.72
$d = 3$	51.71	51.71	15,836.76	15,614.49	222.27	11,492.51
$d = 4$	62.26	56.98	15,614.49	15,393.79	220.70	12,576.24
$d = 5$	67.16	64.71	15,393.79	15,174.67	219.13	14,179.40
$d = 6$	69.44	68.30	15,174.67	14,957.11	217.56	14,858.32
$d = 7$	72.63	71.03	14,957.11	14,741.13	215.98	15,341.75
$d = 8$	71.37	72.00	14,741.13	14,526.71	214.41	15,437.01
$d = 9$	74.37	72.87	14,526.71	14,313.87	212.84	15,510.03
$d = 10$	75.80	75.08	14,313.87	14,102.60	211.27	15,863.30
$d = 11$	77.15	76.47	14,102.60	13,892.90	209.70	16,035.93
$d_{last} = 12$	78.58	77.86	13,892.90	13,684.77	208.13	16,205.92

3. Total volumetric flow for all sub-sectors located between stack wall and d_{last} (total Col. G).	*164,901.59*
4. Volumetric flow for remainder of the Method 1 equal-area sector.	
a. Velocity measurement at distance d_{rem} from stack wall (v_{drem}). (If $d_{rem} - d_{last} < ½$ in., then no measurement at d_{rem} is necessary. Enter the velocity at d_{last} on this line.)	*78.51*
b. Total area in remainder of Method 1 equal-area segment (A_{drem}). Subtract $\frac{3}{16}\pi(r)^2$ from last entry in item 2, column E, and enter the result on this line.	*1,470.26*
c. Multiply values on lines 4a and 4b. (Q_{drem})	*115,430.44*
5. Wall effects-adjusted velocity in the Method 1 equal-area sector.	
a. Add the values on lines 3 and 4c. (Q_T)	*280,332.03*
b. Divide line 5a by $\frac{1}{16}\pi(r)^2$. The resulting value is one of four "replacement" point velocity values adjusted for wall effects, $\hat{v}e_L$, as derived in Equation 2H-16.	*68.85*
6. Substitute the value shown in 5b for the unadjusted velocity value in the Method 1 sector. (See Eq. 2H-18.)	

METHOD 3—GAS ANALYSIS FOR THE DETERMINATION OF DRY MOLECULAR WEIGHT

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should also have a thorough knowledge of Method 1.

1.0 Scope and Application

1.1 Analytes.

Analytes	CAS No.	Sensitivity
Oxygen (O_2)	7782–44–7	2,000 ppmv.
Nitrogen (N_2)	7727–37–9	N/A.
Carbon dioxide (CO_2)	124–38–9	2,000 ppmv.
Carbon monoxide (CO)	630–08–0	N/A.

1.2 Applicability. This method is applicable for the determination of CO_2 and O_2 concentrations and dry molecular weight of a sample from an effluent gas stream of a fossil-fuel combustion process or other process.

1.3 Other methods, as well as modifications to the procedure described herein, are also applicable for all of the above determinations. Examples of specific methods and modifications include: (1) A multi-point grab sampling method using an Orsat analyzer to analyze the individual grab sample obtained at each point; (2) a method for measuring either CO_2 or O_2 and using stoichiometric calculations to determine dry molecular weight; and (3) assigning a value of 30.0 for dry molecular weight, in lieu of actual measurements, for processes burning natural gas, coal, or oil. These methods and modifications may be used, but are subject to the approval of the Administrator. The method may also be applicable to other processes where it has been determined that compounds other than CO_2, O_2, carbon monoxide (CO), and nitrogen (N_2) are not present in concentrations sufficient to affect the results.

1.4 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from a stack by one of the following methods: (1) single-point, grab sampling; (2) single-point, integrated sampling; or (3) multi-point, integrated sampling. The gas sample is analyzed for percent CO_2 and percent O_2. For dry molecular weight determination, either an Orsat or a Fyrite analyzer may be used for the analysis.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Several compounds can interfere, to varying degrees, with the results of Orsat or Fyrite analyses. Compounds that interfere with CO_2 concentration measurement include acid gases (*e.g.*, sulfur dioxide, hydrogen chloride); compounds that interfere with O_2 concentration measurement include unsaturated hydrocarbons (*e.g.*, acetone, acetylene), nitrous oxide, and ammonia. Ammonia reacts chemically with the O_2 absorbing solution, and when present in the effluent gas stream must be removed before analysis.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents.

5.2.1 A typical Orsat analyzer requires four reagents: a gas-confining solution, CO_2 absorbent, O_2 absorbent, and CO absorbent. These reagents may contain potassium hydroxide, sodium hydroxide, cuprous chloride, cuprous sulfate, alkaline pyrogallic acid, and/or chromous chloride. Follow manufacturer's operating instructions and observe all warning labels for reagent use.

5.2.2 A typical Fyrite analyzer contains zinc chloride, hydrochloric acid, and either potassium hydroxide or chromous chloride. Follow manufacturer's operating instructions and observe all warning labels for reagent use.

6.0 Equipment and Supplies

NOTE: As an alternative to the sampling apparatus and systems described herein, other sampling systems (*e.g.*, liquid displacement) may be used, provided such systems are capable of obtaining a representative sample and maintaining a constant sampling rate, and are, otherwise, capable of yielding acceptable results. Use of such systems is subject to the approval of the Administrator.

6.1 Grab Sampling (See Figure 3–1).

6.1.1 Probe. Stainless steel or borosilicate glass tubing equipped with an in-stack or out-of-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Any other materials, resistant to temperature at sampling conditions and inert to all components of the gas stream, may be used for the probe. Examples of such materials may include aluminum, copper, quartz glass, and Teflon.

6.1.2 Pump. A one-way squeeze bulb, or equivalent, to transport the gas sample to the analyzer.

6.2 Integrated Sampling (Figure 3–2).

6.2.1 Probe. Same as in section 6.1.1.

6.2.2 Condenser. An air-cooled or water-cooled condenser, or other condenser no greater than 250 ml that will not remove O_2, CO_2, CO, and N_2, to remove excess moisture which would interfere with the operation of the pump and flowmeter.

6.2.3 Valve. A needle valve, to adjust sample gas flow rate.

6.2.4 Pump. A leak-free, diaphragm-type pump, or equivalent, to transport sample gas to the flexible bag. Install a small surge tank between the pump and rate meter to eliminate the pulsation effect of the diaphragm pump on the rate meter.

6.2.5 Rate Meter. A rotameter, or equivalent, capable of measuring flow rate to ±2 percent of the selected flow rate. A flow rate range of 500 to 1000 ml/min is suggested.

6.2.6 Flexible Bag. Any leak-free plastic (*e.g.*, Tedlar, Mylar, Teflon) or plastic-coated aluminum (*e.g.*, aluminized Mylar) bag, or equivalent, having a capacity consistent with the selected flow rate and duration of the test run. A capacity in the range of 55 to 90 liters (1.9 to 3.2 ft^3) is suggested. To leak-check the bag, connect it to a water manometer, and pressurize the bag to 5 to 10 cm H_2O (2 to 4 in. H_2O). Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak. An alternative leak-check method is to pressurize the bag to 5 to 10 cm (2 to 4 in.) H_2O and allow to stand overnight. A deflated bag indicates a leak.

6.2.7 Pressure Gauge. A water-filled U-tube manometer, or equivalent, of about 30 cm (12 in.), for the flexible bag leak-check.

6.2.8 Vacuum Gauge. A mercury manometer, or equivalent, of at least 760 mm (30 in.) Hg, for the sampling train leak-check.

6.3 Analysis. An Orsat or Fyrite type combustion gas analyzer.

7.0 Reagents and Standards

7.1 Reagents. As specified by the Orsat or Fyrite-type combustion analyzer manufacturer.

7.2 Standards. Two standard gas mixtures, traceable to National Institute of Standards and Technology (NIST) standards, to be used in auditing the accuracy of the analyzer and the analyzer operator technique:

7.2.1. Gas cylinder containing 2 to 4 percent O_2 and 14 to 18 percent CO_2.

7.2.2. Gas cylinder containing 2 to 4 percent CO_2 and about 15 percent O_2.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Single Point, Grab Sampling Procedure.

8.1.1 The sampling point in the duct shall either be at the centroid of the cross section or at a point no closer to the walls than 1.0 m (3.3 ft), unless otherwise specified by the Administrator.

8.1.2 Set up the equipment as shown in Figure 3–1, making sure all connections ahead of the analyzer are tight. If an Orsat analyzer is used, it is recommended that the analyzer be leak-checked by following the procedure in section 11.5; however, the leak-check is optional.

8.1.3 Place the probe in the stack, with the tip of the probe positioned at the sampling point. Purge the sampling line long enough to allow at least five exchanges. Draw a sample into the analyzer, and immediately analyze it for percent CO_2 and percent O_2 according to section 11.2.

8.2 Single-Point, Integrated Sampling Procedure.

8.2.1 The sampling point in the duct shall be located as specified in section 8.1.1.

8.2.2 Leak-check (optional) the flexible bag as in section 6.2.6. Set up the equipment as shown in Figure 3–2. Just before sampling, leak-check (optional) the train by placing a vacuum gauge at the condenser inlet, pulling a vacuum of at least 250 mm Hg (10 in. Hg), plugging the outlet at the quick disconnect, and then turning off the pump. The vacuum should remain stable for at least 0.5 minute. Evacuate the flexible bag. Connect the probe, and place it in the stack, with the tip of the probe positioned at the sampling point. Purge the sampling line. Next, connect the bag, and make sure that all connections are tight.

8.2.3 Sample Collection. Sample at a constant rate (±10 percent). The sampling run should be simultaneous with, and for the same total length of time as, the pollutant emission rate determination. Collection of at least 28 liters (1.0 ft^3) of sample gas is recommended; however, smaller volumes may be collected, if desired.

8.2.4 Obtain one integrated flue gas sample during each pollutant emission rate determination. Within 8 hours after the sample is taken, analyze it for percent CO_2 and percent O_2 using either an Orsat analyzer or a Fyrite type combustion gas analyzer according to section 11.3.

NOTE: When using an Orsat analyzer, periodic Fyrite readings may be taken to verify/confirm the results obtained from the Orsat.

8.3 Multi-Point, Integrated Sampling Procedure.

8.3.1 Unless otherwise specified in an applicable regulation, or by the Administrator, a minimum of eight traverse points shall be used for circular stacks having diameters less than 0.61 m (24 in.), a minimum of nine shall be used for rectangular stacks having equivalent diameters less than 0.61 m (24 in.), and a minimum of 12 traverse points shall be used for all other cases. The traverse points shall be located according to Method 1.

8.3.2 Follow the procedures outlined in sections 8.2.2 through 8.2.4, except for the following: Traverse all sampling points, and sample at each point for an equal length of

time. Record sampling data as shown in Figure 3–3.

9.0 Quality Control

Section	Quality control measure	Effect
8.2	Use of Fyrite to confirm Orsat results	Ensures the accurate measurement of CO_2 and O_2.
10.1	Periodic audit of analyzer and operator technique.	Ensures that the analyzer is operating properly and that the operator performs the sampling procedure correctly and accurately.
11.3	Replicable analyses of integrated samples.	Minimizes experimental error.

10.0 Calibration and Standardization

10.1 Analyzer. The analyzer and analyzer operator's technique should be audited periodically as follows: take a sample from a manifold containing a known mixture of CO_2 and O_2, and analyze according to the procedure in section 11.3. Repeat this procedure until the measured concentration of three consecutive samples agrees with the stated value ±0.5 percent. If necessary, take corrective action, as specified in the analyzer users manual.

10.2 Rotameter. The rotameter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instruction.

11.0 Analytical Procedure

11.1 Maintenance. The Orsat or Fyrite-type analyzer should be maintained and operated according to the manufacturers specifications.

11.2 Grab Sample Analysis. Use either an Orsat analyzer or a Fyrite-type combustion gas analyzer to measure O_2 and CO_2 concentration for dry molecular weight determination, using procedures as specified in the analyzer user's manual. If an Orsat analyzer is used, it is recommended that the Orsat leak-check, described in section 11.5, be performed before this determination; however, the check is optional. Calculate the dry molecular weight as indicated in section 12.0. Repeat the sampling, analysis, and calculation procedures until the dry molecular weights of any three grab samples differ from their mean by no more than 0.3 g/g-mole (0.3 lb/lb-mole). Average these three molecular weights, and report the results to the nearest 0.1 g/g-mole (0.1 lb/lb-mole).

11.3 Integrated Sample Analysis. Use either an Orsat analyzer or a Fyrite-type combustion gas analyzer to measure O_2 and CO_2 concentration for dry molecular weight determination, using procedures as specified in the analyzer user's manual. If an Orsat analyzer is used, it is recommended that the Orsat leak-check, described in section 11.5, be performed before this determination; however, the check is optional. Calculate the dry molecular weight as indicated in section 12.0. Repeat the analysis and calculation procedures until the individual dry molecular weights for any three analyses differ from their mean by no more than 0.3 g/g-mole (0.3 lb/lb-mole). Average these three molecular weights, and report the results to the nearest 0.1 g/g-mole (0.1 lb/lb-mole).

11.4 Standardization. A periodic check of the reagents and of operator technique should be conducted at least once every three series of test runs as outlined in section 10.1.

11.5 Leak-Check Procedure for Orsat Analyzer. Moving an Orsat analyzer frequently causes it to leak. Therefore, an Orsat analyzer should be thoroughly leak-checked on site before the flue gas sample is introduced into it. The procedure for leak-checking an Orsat analyzer is as follows:

11.5.1 Bring the liquid level in each pipette up to the reference mark on the capillary tubing, and then close the pipette stopcock.

11.5.2 Raise the leveling bulb sufficiently to bring the confining liquid meniscus onto the graduated portion of the burette, and then close the manifold stopcock.

11.5.3 Record the meniscus position.

11.5.4 Observe the meniscus in the burette and the liquid level in the pipette for movement over the next 4 minutes.

11.5.5 For the Orsat analyzer to pass the leak-check, two conditions must be met:

11.5.5.1 The liquid level in each pipette must not fall below the bottom of the capillary tubing during this 4-minute interval.

11.5.5.2 The meniscus in the burette must not change by more than 0.2 ml during this 4-minute interval.

11.5.6 If the analyzer fails the leak-check procedure, check all rubber connections and stopcocks to determine whether they might be the cause of the leak. Disassemble, clean, and regrease any leaking stopcocks. Replace leaking rubber connections. After the analyzer is reassembled, repeat the leak-check procedure.

12.0 Calculations and Data Analysis

12.1 Nomenclature.

M_d = Dry molecular weight, g/g-mole (lb/lb-mole).
$\%CO_2$ = Percent CO_2 by volume, dry basis.
$\%O_2$ = Percent O_2 by volume, dry basis.
%CO = Percent CO by volume, dry basis.
$\%N_2$ = Percent N_2 by volume, dry basis.

0.280 = Molecular weight of N_2 or CO, divided by 100.
0.320 = Molecular weight of O_2 divided by 100.
0.440 = Molecular weight of CO_2 divided by 100.

12.2 Nitrogen, Carbon Monoxide Concentration. Determine the percentage of the gas that is N_2 and CO by subtracting the sum of the percent CO_2 and percent O_2 from 100 percent.

12.3 Dry Molecular Weight. Use Equation 3–1 to calculate the dry molecular weight of the stack gas.

$$M_d = 0.440(\%CO_2) + 0.320(\%O_2) + 0.280(\%N_2 + \%CO) \qquad \text{Eq. 3-1}$$

NOTE: The above Equation 3–1 does not consider the effect on calculated dry molecular weight of argon in the effluent gas. The concentration of argon, with a molecular weight of 39.9, in ambient air is about 0.9 percent. A negative error of approximately 0.4 percent is introduced. The tester may choose to include argon in the analysis using procedures subject to approval of the Administrator.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Altshuller, A.P. Storage of Gases and Vapors in Plastic Bags. International Journal of Air and Water Pollution. *6*:75–81. 1963.

2. Conner, William D. and J.S. Nader. Air Sampling with Plastic Bags. Journal of the American Industrial Hygiene Association. *25*:291–297. 1964.

3. Burrell Manual for Gas Analysts, Seventh edition. Burrell Corporation, 2223 Fifth Avenue, Pittsburgh, PA. 15219. 1951.

4. Mitchell, W.J. and M.R. Midgett. Field Reliability of the Orsat Analyzer. Journal of Air Pollution Control Association. *26*:491–495. May 1976.

5. Shigehara, R.T., R.M. Neulicht, and W.S. Smith. Validating Orsat Analysis Data from Fossil Fuel-Fired Units. Stack Sampling News. *4*(2):21–26. August 1976.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

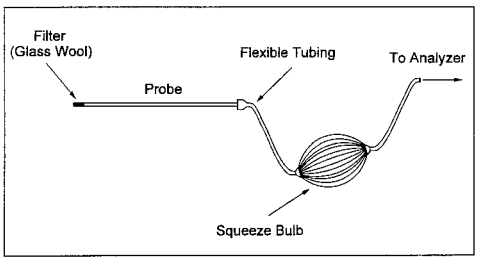


Figure 3-1. Grab-Sampling Train.

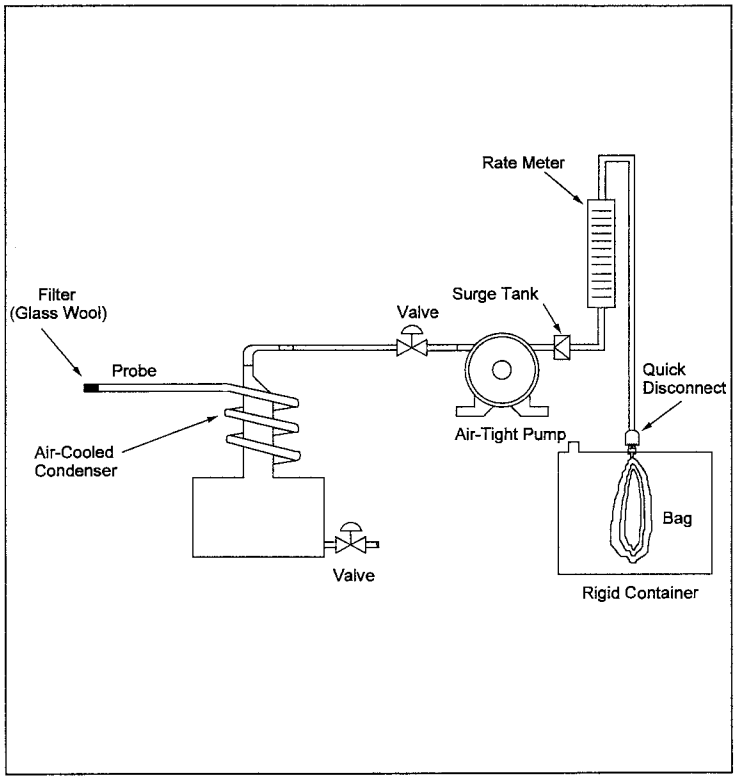


Figure 3-2. Integrated Gas-Sampling Train.

Time	Traverse point	Q (liter/min)	% Deviation [a]
Average			

[a] % Dev.=[(Q − Q_{avg})/Q_{avg}] × 100 (Must be ≤±10%)

Figure 3–3. Sampling Rate Data

METHOD 3A—DETERMINATION OF OXYGEN AND CARBON DIOXIDE CONCENTRATIONS IN EMISSIONS FROM STATIONARY SOURCES (INSTRUMENTAL ANALYZER PROCEDURE)

1.0 Scope and Application

What is Method 3A?

Method 3A is a procedure for measuring oxygen (O_2) and carbon dioxide (CO_2) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis.

This method does not completely describe all equipment, supplies, and sampling and

analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 3—Gas Analysis for the Determination of Molecular Weight.

(c) Method 4—Determination of Moisture Content in Stack Gases.

(d) Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure).

1.1 *Analytes. What does this method determine?* This method measures the concentration of oxygen and carbon dioxide.

Analyte	CAS No.	Sensitivity
Oxygen (O_2)	7782–44–7	Typically <2% of Calibration Span.
Carbon dioxide (CO_2)	124–38–9	Typically <2% of Calibration Span.

1.2 *Applicability. When is this method required?* The use of Method 3A may be required by specific New Source Performance Standards, Clean Air Marketing rules, State Implementation Plans and permits, where measurements of O_2 and CO_2 concentrations in stationary source emissions must be made, either to determine compliance with an applicable emission standard or to conduct performance testing of a continuous emission monitoring system (CEMS). Other regulations may also require the use of Method 3A.

1.3 *Data Quality Objectives. How good must my collected data be?* Refer to section 1.3 of Method 7E.

2.0 Summary of Method

In this method, you continuously or intermittently sample the effluent gas and convey the sample to an analyzer that measures the concentration of O_2 or CO_2. You must meet the performance requirements of this method to validate your data.

3.0 Definitions

Refer to section 3.0 of Method 7E for the applicable definitions.

4.0 Interferences [Reserved]

5.0 Safety

Refer to section 5.0 of Method 7E.

6.0 Equipment and Supplies

Figure 7E–1 in Method 7E is a schematic diagram of an acceptable measurement system.

6.1 What do I need for the measurement system? The components of the measurement system are described (as applicable) in sections 6.1 and 6.2 of Method 7E, except that the analyzer described in section 6.2 of this method must be used instead of the analyzer described in Method 7E. You must follow the noted specifications in section 6.1 of Method 7E except that the requirements to use stainless steel, Teflon, or non-reactive glass filters do not apply. Also, a heated sample line is not required to transport dry gases or for systems that measure the O_2 or CO_2 concentration on a dry basis, provided that the system is not also being used to concurrently measure SO_2 and/or NO_X.

6.2 What analyzer must I use? You must use an analyzer that continuously measures O_2 or CO_2 in the gas stream and meets the specifications in section 13.0.

7.0 Reagents and Standards

7.1 *Calibration Gas.* What calibration gases do I need? Refer to Section 7.1 of Method 7E for the calibration gas requirements. Example calibration gas mixtures are listed below. Pre-cleaned or scrubbed air may be used for the O_2 high-calibration gas provided it does not contain other gases that interfere with the O_2 measurement.

(a) CO_2 in Nitrogen (N_2).

(b) CO_2/SO_2 gas mixture in N_2.

(c) O_2/SO_2 gas mixture in N_2.

(d) $O_2/CO_2/SO_2$ gas mixture in N_2.

(e) CO_2/NO_X gas mixture in N_2.

(f) $CO_2/SO_2/NO_X$ gas mixture in N_2.

The tests for analyzer calibration error and system bias require high-, mid-, and low-level gases.

7.2 Interference Check. What reagents do I need for the interference check? Potential interferences may vary among available analyzers. Table 7E–3 of Method 7E lists a number of gases that should be considered in conducting the interference test.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling Site and Sampling Points. You must follow the procedures of section 8.1 of Method 7E to determine the appropriate sampling points, unless you are using Method 3A only to determine the stack gas molecular weight and for no other purpose. In that case, you may use single-point integrated sampling as described in section 8.2.1 of Method 3. If the stratification test provisions in section 8.1.2 of Method 7E are used to reduce the number of required sampling points, the alternative acceptance criterion for 3-

point sampling will be ±0.5 percent CO_2 or O_2, and the alternative acceptance criterion for single-point sampling will be ±0.3 percent CO_2 or O_2. In that case, you may use single-point integrated sampling as described in section 8.2.1 of Method 3.

8.2 Initial Measurement System Performance Tests. You must follow the procedures in section 8.2 of Method 7E. If a dilution-type measurement system is used, the special considerations in section 8.3 of Method 7E apply.

8.3 Interference Check. The O_2 or CO_2 analyzer must be documented to show that interference effects to not exceed 2.5 percent of the calibration span. The interference test in section 8.2.7 of Method 7E is a procedure that may be used to show this. The effects of all potential interferences at the concentrations encountered during testing must be addressed and documented. This testing and documentation may be done by the instrument manufacturer.

8.4 Sample Collection. You must follow the procedures in section 8.4 of Method 7E.

8.5 Post-Run System Bias Check and Drift Assessment. You must follow the procedures in section 8.5 of Method 7E.

9.0 Quality Control

Follow quality control procedures in section 9.0 of Method 7E.

10.0 Calibration and Standardization

Follow the procedures for calibration and standardization in section 10.0 of Method 7E.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the applicable procedures for calculations and data analysis in section 12.0 of Method 7E, substituting percent O_2 and percent CO_2 for ppmv of NO_X as appropriate.

13.0 Method Performance

The specifications for the applicable performance checks are the same as in section 13.0 of Method 7E except for the alternative specifications for system bias, drift, and calibration error. In these alternative specifications, replace the term ''0.5 ppmv'' with the term ''0.5 percent O_2'' or ''0.5 percent CO_2'' (as applicable).

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures [Reserved]

17.0 References

1. ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards'' September 1997 as amended, EPA–600/R–97/121.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

Refer to section 18.0 of Method 7E.

Method 3B—Gas Analysis for the Determination of Emission Rate Correction Factor or Excess Air

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1 and 3.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Oxygen (O_2)	7782–44–7	2,000 ppmv.
Carbon Dioxide (CO_2)	124–38–9	2,000 ppmv.
Carbon Monoxide (CO)	630–08–0	N/A.

1.2 Applicability. This method is applicable for the determination of O_2, CO_2, and CO concentrations in the effluent from fossil-fuel combustion processes for use in excess air or emission rate correction factor calculations. Where compounds other than CO_2, O_2, CO, and nitrogen (N_2) are present in concentrations sufficient to affect the results, the calculation procedures presented in this method must be modified, subject to the approval of the Administrator.

1.3 Other methods, as well as modifications to the procedure described herein, are also applicable for all of the above determinations. Examples of specific methods and modifications include: (1) A multi-point sampling method using an Orsat analyzer to analyze individual grab samples obtained at each point, and (2) a method using CO_2 or O_2 and stoichiometric calculations to determine excess air. These methods and modifications may be used, but are subject to the approval of the Administrator.

1.4 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from a stack by one of the following methods: (1) Single-point, grab sampling; (2) single-point, integrated sampling; or (3) multi-point, integrated sampling. The gas sample is analyzed for percent CO_2, percent O_2, and, if necessary, percent CO using an Orsat combustion gas analyzer.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Several compounds can interfere, to varying degrees, with the results of Orsat analyses. Compounds that interfere with CO2 concentration measurement include acid gases (*e.g.*, sulfur dioxide, hydrogen chloride); compounds that interfere with O_2 concentration measurement include unsaturated hydrocarbons (*e.g.*, acetone, acetylene), nitrous oxide, and ammonia. Ammonia reacts chemically with the O_2 absorbing solution, and when present in the effluent gas stream must be removed before analysis.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. A typical Orsat analyzer requires four reagents: a gas-confining solution, CO_2 absorbent, O_2 absorbent, and CO absorbent. These reagents may contain potassium hydroxide, sodium hydroxide, cuprous chloride, cuprous sulfate, alkaline pyrogallic acid, and/or chromous chloride. Follow manufacturer's operating instructions and observe all warning labels for reagent use.

6.0 Equipment and Supplies

NOTE: As an alternative to the sampling apparatus and systems described herein, other sampling systems (*e.g.*, liquid displacement) may be used, provided such systems are capable of obtaining a representative sample and maintaining a constant sampling rate, and are, otherwise, capable of yielding acceptable results. Use of such systems is subject to the approval of the Administrator.

6.1 Grab Sampling and Integrated Sampling. Same as in sections 6.1 and 6.2, respectively for Method 3.

6.2 Analysis. An Orsat analyzer only. For low CO_2 (less than 4.0 percent) or high O_2 (greater than 15.0 percent) concentrations, the measuring burette of the Orsat must have at least 0.1 percent subdivisions. For Orsat maintenance and operation procedures, follow the instructions recommended by the manufacturer, unless otherwise specified herein.

7.0 Reagents and Standards

7.1 Reagents. Same as in Method 3, section 7.1.

7.2 Standards. Same as in Method 3, section 7.2.

8.0 Sample Collection, Preservation, Storage, and Transport

NOTE: Each of the three procedures below shall be used only when specified in an applicable subpart of the standards. The use of these procedures for other purposes must have specific prior approval of the Administrator. A Fyrite-type combustion gas analyzer is not acceptable for excess air or emission rate correction factor determinations, unless approved by the Administrator. If both percent CO_2 and percent O_2 are measured, the analytical results of any of the three procedures given below may also be used for calculating the dry molecular weight (see Method 3).

8.1 Single-Point, Grab Sampling and Analytical Procedure.

8.1.1 The sampling point in the duct shall either be at the centroid of the cross section or at a point no closer to the walls than 1.0 m (3.3 ft), unless otherwise specified by the Administrator.

8.1.2 Set up the equipment as shown in Figure 3–1 of Method 3, making sure all connections ahead of the analyzer are tight. Leak-check the Orsat analyzer according to the procedure described in section 11.5 of Method 3. This leak-check is mandatory.

8.1.3 Place the probe in the stack, with the tip of the probe positioned at the sampling point; purge the sampling line long enough to allow at least five exchanges. Draw a sample into the analyzer. For emission rate correction factor determinations, immediately analyze the sample for percent CO_2 or percent O_2, as outlined in section 11.2. For excess air determination, immediately analyze the sample for percent CO_2, O_2, and CO, as outlined in section 11.2, and calculate excess air as outlined in section 12.2.

8.1.4 After the analysis is completed, leak-check (mandatory) the Orsat analyzer once again, as described in section 11.5 of Method 3. For the results of the analysis to be valid, the Orsat analyzer must pass this leak-test before and after the analysis.

8.2 Single-Point, Integrated Sampling and Analytical Procedure.

8.2.1 The sampling point in the duct shall be located as specified in section 8.1.1.

8.2.2 Leak-check (mandatory) the flexible bag as in section 6.2.6 of Method 3. Set up the equipment as shown in Figure 3–2 of Method 3. Just before sampling, leak-check (mandatory) the train by placing a vacuum gauge at the condenser inlet, pulling a vacuum of at least 250 mm Hg (10 in. Hg), plugging the outlet at the quick disconnect, and then turning off the pump. The vacuum should remain stable for at least 0.5 minute. Evacuate the flexible bag. Connect the probe, and place it in the stack, with the tip of the probe positioned at the sampling point; purge the sampling line. Next, connect the bag, and make sure that all connections are tight.

8.2.3 Sample at a constant rate, or as specified by the Administrator. The sampling run must be simultaneous with, and for the same total length of time as, the pollutant emission rate determination. Collect at least 28 liters (1.0 ft^3) of sample gas. Smaller volumes may be collected, subject to approval of the Administrator.

8.2.4 Obtain one integrated flue gas sample during each pollutant emission rate determination. For emission rate correction factor determination, analyze the sample within 4 hours after it is taken for percent CO_2 or percent O_2 (as outlined in section 11.2).

8.3 Multi-Point, Integrated Sampling and Analytical Procedure.

8.3.1 Unless otherwise specified in an applicable regulation, or by the Administrator, a minimum of eight traverse points shall be used for circular stacks having diameters less than 0.61 m (24 in.), a minimum of nine shall be used for rectangular stacks having equivalent diameters less than 0.61 m (24 in.), and a minimum of 12 traverse points shall be used for all other cases. The traverse points shall be located according to Method 1.

8.3.2 Follow the procedures outlined in sections 8.2.2 through 8.2.4, except for the following: Traverse all sampling points, and sample at each point for an equal length of time. Record sampling data as shown in Figure 3–3 of Method 3.

9.0 Quality Control

9.1 Data Validation Using Fuel Factor. Although in most instances, only CO_2 or O_2 measurement is required, it is recommended that both CO_2 and O_2 be measured to provide a check on the quality of the data. The data validation procedure of section 12.3 is suggested.

NOTE: Since this method for validating the CO_2 and O_2 analyses is based on combustion of organic and fossil fuels and dilution of the gas stream with air, this method does not apply to sources that (1) remove CO_2 or O_2 through processes other than combustion, (2) add O_2 (*e.g.*, oxygen enrichment) and N_2 in proportions different from that of air, (3) add CO_2 (*e.g.*, cement or lime kilns), or (4) have no fuel factor, F_O, values obtainable (*e.g.*, extremely variable waste mixtures). This method validates the measured proportions of CO_2 and O_2 for fuel type, but the method does not detect sample dilution resulting from leaks during or after sample collection. The method is applicable for samples collected downstream of most lime or limestone flue-gas desulfurization units as the CO_2 added or removed from the gas stream is not significant in relation to the total CO_2 concentration. The CO_2 concentrations from other types of scrubbers using only water or basic slurry can be significantly affected and would render the fuel factor check minimally useful.

10.0 Calibration and Standardization

10.1 Analyzer. The analyzer and analyzer operator technique should be audited periodically as follows: take a sample from a manifold containing a known mixture of CO_2 and O_2, and analyze according to the procedure in section 11.3. Repeat this procedure until the measured concentration of three consecutive samples agrees with the stated value ±0.5 percent. If necessary, take corrective action, as specified in the analyzer users manual.

10.2 Rotameter. The rotameter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instruction.

11.0 Analytical Procedure

11.1 Maintenance. The Orsat analyzer should be maintained according to the manufacturers specifications.

11.2 Grab Sample Analysis. To ensure complete absorption of the CO_2, O_2, or if applicable, CO, make repeated passes through each absorbing solution until two consecutive readings are the same. Several passes (three or four) should be made between readings. (If constant readings cannot be obtained after three consecutive readings, replace the absorbing solution.) Although in most cases, only CO_2 or O_2 concentration is required, it is recommended that both CO_2 and O_2 be measured, and that the procedure in section 12.3 be used to validate the analytical data.

NOTE: Since this single-point, grab sampling and analytical procedure is normally conducted in conjunction with a single-point, grab sampling and analytical procedure for a pollutant, only one analysis is ordinarily conducted. Therefore, great care must be taken to obtain a valid sample and analysis.

11.3 Integrated Sample Analysis. The Orsat analyzer must be leak-checked (see section 11.5 of Method 3) before the analysis. If excess air is desired, proceed as follows: (1) within 4 hours after the sample is taken, analyze it (as in sections 11.3.1 through

11.3.3) for percent CO_2, O_2, and CO; (2) determine the percentage of the gas that is N_2 by subtracting the sum of the percent CO_2, percent O_2, and percent CO from 100 percent; and (3) calculate percent excess air, as outlined in section 12.2.

11.3.1 To ensure complete absorption of the CO_2, O_2, or if applicable, CO, follow the procedure described in section 11.2.

NOTE: Although in most instances only CO_2 or O_2 is required, it is recommended that both CO_2 and O_2 be measured, and that the procedures in section 12.3 be used to validate the analytical data.

11.3.2 Repeat the analysis until the following criteria are met:

11.3.2.1 For percent CO_2, repeat the analytical procedure until the results of any three analyses differ by no more than (a) 0.3 percent by volume when CO_2 is greater than 4.0 percent or (b) 0.2 percent by volume when CO_2 is less than or equal to 4.0 percent. Average three acceptable values of percent CO_2, and report the results to the nearest 0.2 percent.

11.3.2.2 For percent O_2, repeat the analytical procedure until the results of any three analyses differ by no more than (a) 0.3 percent by volume when O_2 is less than 15.0 percent or (b) 0.2 percent by volume when O_2 is greater than or equal to 15.0 percent. Average the three acceptable values of percent O_2, and report the results to the nearest 0.1 percent.

11.3.2.3 For percent CO, repeat the analytical procedure until the results of any three analyses differ by no more than 0.3 percent. Average the three acceptable values of percent CO, and report the results to the nearest 0.1 percent.

11.3.3 After the analysis is completed, leak-check (mandatory) the Orsat analyzer once again, as described in section 11.5 of Method 3. For the results of the analysis to be valid, the Orsat analyzer must pass this leak-test before and after the analysis.

11.4 Standardization. A periodic check of the reagents and of operator technique should be conducted at least once every three series of test runs as indicated in section 10.1.

12.0 Calculations and Data Analysis

12.1 Nomenclature. Same as section 12.1 of Method 3 with the addition of the following:
%EA = Percent excess air.
0.264 = Ratio of O_2 to N_2 in air, v/v.

12.2 Percent Excess Air. Determine the percentage of the gas that is N_2 by subtracting the sum of the percent CO_2, percent CO, and percent O_2 from 100 percent. Calculate the percent excess air (if applicable) by substituting the appropriate values of percent O_2, CO, and N_2 into Equation 3B–1.

$$\%EA = \frac{\%O_2 - 0.5\ \%CO}{0.264\ \%N_2 - (\%O_2 - 0.5\ \%CO)} \times 100 \qquad \text{Eq. 3B-1}$$

NOTE: The equation above assumes that ambient air is used as the source of O_2 and that the fuel does not contain appreciable amounts of N_2 (as do coke oven or blast furnace gases). For those cases when appreciable amounts of N_2 are present (coal, oil, and natural gas do not contain appreciable amounts of N_2) or when oxygen enrichment is used, alternative methods, subject to approval of the Administrator, are required.

12.3 Data Validation When Both CO_2 and O_2 Are Measured.

12.3.1 Fuel Factor, F_o. Calculate the fuel factor (if applicable) using Equation 3B–2:

$$F_o = \frac{20.9 - \%O_2}{\%CO_2} \qquad \text{Eq. 3B-2}$$

Where:

$\%O_2$ = Percent O_2 by volume, dry basis.
$\%CO_2$ = Percent CO_2 by volume, dry basis.
20.9 = Percent O_2 by volume in ambient air.

If CO is present in quantities measurable by this method, adjust the O_2 and CO_2 values using Equations 3B–3 and 3B–4 before performing the calculation for F_o:

$$\%CO_2(adj) = \%CO_2 + \%CO \qquad \text{Eq. 3B-3}$$

$$\%O_2(adj) = \%O_2 - 0.5\ \%CO \qquad \text{Eq. 3B-4}$$

Where:
%CO = Percent CO by volume, dry basis.

12.3.2 Compare the calculated F_o factor with the expected F_o values. Table 3B–1 in section 17.0 may be used in establishing acceptable ranges for the expected F_o if the fuel being burned is known. When fuels are burned in combinations, calculate the combined fuel F_d and F_c factors (as defined in Method 19, section 12.2) according to the procedure in Method 19, sections 12.2 and 12.3. Then calculate the F_o factor according to Equation 3B–5.

$$F_o = \frac{0.209\ F_d}{F_c} \qquad \text{Eq. 3B-5}$$

12.3.3 Calculated F_o values, beyond the acceptable ranges shown in this table, should be investigated before accepting the test results. For example, the strength of the solutions in the gas analyzer and the analyzing technique should be checked by sampling and analyzing a known concentration, such as air; the fuel factor should be reviewed and verified. An acceptability range of ±12 percent is appropriate for the F_o factor of mixed fuels with variable fuel ratios. The level of the emission rate relative to the compliance level should be considered in determining if a retest is appropriate; i.e., if the measured emissions are much lower or much greater than the compliance limit, repetition of the test would not significantly change the compliance status of the source and would be unnecessarily time consuming and costly.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 3, section 16.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 3B–1—F_o FACTORS FOR SELECTED FUELS

Fuel type	F_o range
Coal:	
Anthracite and lignite	1.016–1.130
Bituminous	1.083–1.230
Oil:	
Distillate	1.260–1.413
Residual	1.210–1.370
Gas:	
Natural	1.600–1.836
Propane	1.434–1.586
Butane	1.405–1.553
Wood	1.000–1.120
Wood bark	1.003–1.130

METHOD 3C—DETERMINATION OF CARBON DIOXIDE, METHANE, NITROGEN, AND OXYGEN FROM STATIONARY SOURCES

1. Applicability and Principle

1.1 Applicability. This method applies to the analysis of carbon dioxide (CO_2), methane (CH_4), nitrogen (N_2), and oxygen (O_2) in samples from municipal solid waste landfills and other sources when specified in an applicable subpart.

1.2 Principle. A portion of the sample is injected into a gas chromatograph (GC) and the CO_2, CH_4, N_2, and O_2 concentrations are determined by using a thermal conductivity detector (TCD) and integrator.

2. Range and Sensitivity

2.1 Range. The range of this method depends upon the concentration of samples. The analytical range of TCD's is generally between approximately 10 ppmv and the upper percent range.

2.2 Sensitivity. The sensitivity limit for a compound is defined as the minimum detectable concentration of that compound, or the concentration that produces a signal-to-noise ratio of three to one. For CO_2, CH_4, N_2, and O_2, the sensitivity limit is in the low ppmv range.

3. Interferences

Since the TCD exhibits universal response and detects all gas components except the carrier, interferences may occur. Choosing the appropriate GC or shifting the retention times by changing the column flow rate may help to eliminate resolution interferences.

To assure consistent detector response, helium is used to prepare calibration gases. Frequent exposure to samples or carrier gas containing oxygen may gradually destroy filaments.

4. Apparatus

4.1 Gas Chromatograph. GC having at least the following components:

4.1.1 Separation Column. Appropriate column(s) to resolve CO_2, CH_4, N_2, O_2, and other gas components that may be present in the sample.

4.1.2 Sample Loop. Teflon or stainless steel tubing of the appropriate diameter.

NOTE: Mention of trade names or specific products does not constitute endorsement or recommendation by the U. S. Environmental Protection Agency.

4.1.3 Conditioning System. To maintain the column and sample loop at constant temperature.

4.1.4 Thermal Conductivity Detector.

4.2 Recorder. Recorder with linear strip chart. Electronic integrator (optional) is recommended.

4.3 Teflon Tubing. Diameter and length determined by connection requirements of cylinder regulators and the GC.

4.4 Regulators. To control gas cylinder pressures and flow rates.

4.5 Adsorption Tubes. Applicable traps to remove any O_2 from the carrier gas.

5. Reagents

5.1 Calibration and Linearity Gases. Standard cylinder gas mixtures for each compound of interest with at least three concentration levels spanning the range of suspected sample concentrations. The calibration gases shall be prepared in helium.

5.2 Carrier Gas. Helium, high-purity.

6. Analysis

6.1 Sample Collection. Use the sample collection procedures described in Methods 3 or 25C to collect a sample of landfill gas (LFG).

6.2 Preparation of GC. Before putting the GC analyzer into routine operation, optimize the operational conditions according to the manufacturer's specifications to provide good resolution and minimum analysis time. Establish the appropriate carrier gas flow and set the detector sample and reference cell flow rates at exactly the same levels. Adjust the column and detector temperatures to the recommended levels. Allow sufficient time for temperature stabilization. This may typically require 1 hour for each change in temperature.

6.3 Analyzer Linearity Check and Calibration. Perform this test before sample analysis.

6.3.1 Using the gas mixtures in section 5.1, verify the detector linearity over the range of suspected sample concentrations with at least three concentrations per compound of interest. This initial check may also serve as the initial instrument calibration.

6.3.2 You may extend the use of the analyzer calibration by performing a single-point calibration verification. Calibration verifications shall be performed by triplicate injections of a single-point standard gas. The concentration of the single-point calibration must either be at the midpoint of the calibration curve or at approximately the source emission concentration measured during operation of the analyzer.

6.3.3 Triplicate injections must agree within 5 percent of their mean, and the average calibration verification point must agree within 10 percent of the initial calibration response factor. If these calibration verification criteria are not met, the initial calibration described in section 6.3.1, using at least three concentrations, must be repeated before analysis of samples can continue.

6.3.4 For each instrument calibration, record the carrier and detector flow rates, detector filament and block temperatures, attenuation factor, injection time, chart speed, sample loop volume, and component concentrations.

6.3.5 Plot a linear regression of the standard concentrations versus area values to obtain the response factor of each compound. Alternatively, response factors of uncorrected component concentrations (wet basis) may be generated using instrumental integration.

NOTE: Peak height may be used instead of peak area throughout this method.

6.4 Sample Analysis. Purge the sample loop with sample, and allow to come to atmospheric pressure before each injection. Analyze each sample in duplicate, and calculate the average sample area (A). The results are acceptable when the peak areas for two consecutive injections agree within 5 percent of their average. If they do not agree, run additional samples until consistent area data are obtained. Determine the tank sample concentrations according to section 7.2.

7. Calculations

Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off results only after the final calculation.

7.1 Nomenclature.

B_w = Moisture content in the sample, fraction.

C_{N2} = Measured N_2 concentration (by Method 3C), fraction.

C_{N2Corr} = Measured N_2 concentration corrected only for dilution, fraction.

C_t = Calculated NMOC concentration, ppmv C equivalent.

C_{tm} = Measured NMOC concentration, ppmv C equivalent.

P_b = Barometric pressure, mm Hg.

P_t = Gas sample tank pressure after sampling, but before pressurizing, mm Hg absolute.

P_{tf} = Final gas sample tank pressure after pressurizing, mm Hg absolute.

P_{ti} = Gas sample tank pressure after evacuation, mm Hg absolute.

P_w = Vapor pressure of H_2O (from Table 25C–1), mm Hg.

r = Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 . . . r).

R = Mean calibration response factor for specific sample component, area/ppm.

T_t = Sample tank temperature at completion of sampling, °K.

T_{ti} = Sample tank temperature before sampling, °K.

T_{tf} = Sample tank temperature after pressurizing, °K.

7.2 Concentration of Sample Components. Calculate C for each compound using Equations 3C–1 and 3C–2. Use the temperature and barometric pressure at the sampling site to calculate Bw. If the sample was diluted with helium using the procedures in Method 25C, use Equation 3C–3 to calculate the concentration.

$$B_w = \frac{P_w}{P_{bar}} \qquad 3C\text{-}1$$

$$C = \frac{A}{R(1-B_w)} \qquad 3C\text{-}2$$

$$C = \frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}} \quad \frac{A}{R(1-B_w)} \qquad 3C\text{-}3$$

7.3 Measured N_2 Concentration Correction. Calculate the reported N_2 correction for Method 25–C using Eq. 3C–4. If oxygen is determined in place of N_2, substitute the oxygen concentration for the nitrogen concentration in the equation.

$$C_{N_2 Corr} = \frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}}(C_{N_2}) \quad Eq.\ 3C-4$$

8. Bibliography

1. McNair, H.M., and E.J. Bonnelli. Basic Gas Chromatography. Consolidated Printers, Berkeley, CA. 1969.

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–2 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

APPENDIX A–3 TO PART 60—TEST METHODS 4 THROUGH 5I

Method 4—Determination of moisture content in stack gases
Method 5—Determination of particulate matter emissions from stationary sources
Method 5A—Determination of particulate matter emissions from the asphalt processing and asphalt roofing industry
Method 5B—Determination of nonsulfuric acid particulate matter emissions from stationary sources
Method 5C [Reserved]
Method 5D—Determination of particulate matter emissions from positive pressure fabric filters
Method 5E—Determination of particulate matter emissions from the wool fiberglass insulation manufacturing industry
Method 5F—Determination of nonsulfate particulate matter emissions from stationary sources
Method 5G—Determination of particulate matter emissions from wood heaters (dilution tunnel sampling location)
Method 5H—Determination of particulate emissions from wood heaters from a stack location
Method 5I—Determination of Low Level Particulate Matter Emissions From Stationary Sources

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference

APPENDIX A–4 TO PART 60—TEST METHODS 6 THROUGH 10B

Method 6—Determination of sulfur dioxide emissions from stationary sources
Method 6A—Determination of sulfur dioxide, moisture, and carbon dioxide emissions from fossil fuel combustion sources
Method 6B—Determination of sulfur dioxide and carbon dioxide daily average emissions from fossil fuel combustion sources
Method 6C—Determination of Sulfur Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure)
Method 7—Determination of nitrogen oxide emissions from stationary sources
Method 7A—Determination of nitrogen oxide emissions from stationary sources—Ion chromatographic method
Method 7B—Determination of nitrogen oxide emissions from stationary sources (Ultraviolet spectrophotometry)
Method 7C—Determination of nitrogen oxide emissions from stationary sources—Alkaline-permanganate/colorimetric method
Method 7D—Determination of nitrogen oxide emissions from stationary sources—Alkaline-permanganate/ion chromatographic method
Method 7E—Determination of Nitrogen Oxides Emissions From Stationary Sources (Instrumental Analyzer Procedure)
Method 8—Determination of sulfuric acid mist and sulfur dioxide emissions from stationary sources
Method 9—Visual determination of the opacity of emissions from stationary sources
Alternate method 1—Determination of the opacity of emissions from stationary sources remotely by lidar
Method 10—Determination of carbon monoxide emissions from stationary sources
Method 10A—Determination of carbon monoxide emissions in certifying continuous emission monitoring systems at petroleum refineries
Method 10B—Determination of carbon monoxide emissions from stationary sources

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that

the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

METHOD 6—DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, and Method 8.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
SO_2	7449–09–5	3.4 mg SO_2/m^3 $(2.12 \times 10)_{-7}$ lb/ft^3

1.2 Applicability. This method applies to the measurement of sulfur dioxide (SO_2) emissions from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the sampling point in the stack. The SO_2 and the sulfur trioxide, including those fractions in any sulfur acid mist, are separated. The SO_2 fraction is measured by the barium-thorin titration method.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Free Ammonia. Free ammonia interferes with this method by reacting with SO_2 to form particulate sulfite and by reacting with the indicator. If free ammonia is present (this can be determined by knowledge of the process and/or noticing white particulate matter in the probe and isopropanol bubbler), alternative methods, subject to the approval of the Administrator are required. One approved alternative is listed in Reference 13 of section 17.0.

4.2 Water-Soluble Cations and Fluorides. The cations and fluorides are removed by a glass wool filter and an isopropanol bubbler; therefore, they do not affect the SO_2 analysis. When samples are collected from a gas stream with high concentrations of metallic fumes (*i.e.*, very fine cation aerosols) a high-efficiency glass fiber filter must be used in place of the glass wool plug (*i.e.*, the one in the probe) to remove the cation interferent.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations before performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs. 30% H_2O_2 is a strong oxidizing agent. Avoid contact with skin, eyes, and combustible material. Wear gloves when handling.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

6.1 Sample Collection. The following items are required for sample collection:

6.1.1 Sampling Train. A schematic of the sampling train is shown in Figure 6–1. The sampling equipment described in Method 8 may be substituted in place of the midget impinger equipment of Method 6. However, the Method 8 train must be modified to include a heated filter between the probe and isopropanol impinger, and the operation of the sampling train and sample analysis must be at the flow rates and solution volumes defined in Method 8. Alternatively, SO_2 may be determined simultaneously with particulate

matter and moisture determinations by either (1) replacing the water in a Method 5 impinger system with a 3 percent H_2O_2 solution, or (2) replacing the Method 5 water impinger system with a Method 8 isopropanol-filter-H_2O_2 system. The analysis for SO_2 must be consistent with the procedure of Method 8. The Method 6 sampling train consists of the following components:

6.1.1.1 Probe. Borosilicate glass or stainless steel (other materials of construction may be used, subject to the approval of the Administrator), approximately 6 mm (0.25 in.) inside diameter, with a heating system to prevent water condensation and a filter (either in-stack or heated out-of-stack) to remove particulate matter, including sulfuric acid mist. A plug of glass wool is a satisfactory filter.

6.1.1.2 Bubbler and Impingers. One midget bubbler with medium-coarse glass frit and borosilicate or quartz glass wool packed in top (see Figure 6–1) to prevent sulfuric acid mist carryover, and three 30-ml midget impingers. The midget bubbler and midget impingers must be connected in series with leak-free glass connectors. Silicone grease may be used, if necessary, to prevent leakage. A midget impinger may be used in place of the midget bubbler.

NOTE: Other collection absorbers and flow rates may be used, subject to the approval of the Administrator, but the collection efficiency must be shown to be at least 99 percent for each test run and must be documented in the report. If the efficiency is found to be acceptable after a series of three tests, further documentation is not required. To conduct the efficiency test, an extra absorber must be added and analyzed separately. This extra absorber must not contain more than 1 percent of the total SO_2.

6.1.1.3 Glass Wool. Borosilicate or quartz.

6.1.1.4 Stopcock Grease. Acetone-insoluble, heat-stable silicone grease may be used, if necessary.

6.1.1.5 Temperature Sensor. Dial thermometer, or equivalent, to measure temperature of gas leaving impinger train to within 1 °C (2 °F).

6.1.1.6 Drying Tube. Tube packed with 6- to 16- mesh indicating-type silica gel, or equivalent, to dry the gas sample and to protect the meter and pump. If silica gel is previously used, dry at 177 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

6.1.1.7 Valve. Needle valve, to regulate sample gas flow rate.

6.1.1.8 Pump. Leak-free diaphragm pump, or equivalent, to pull gas through the train. Install a small surge tank between the pump and rate meter to negate the pulsation effect of the diaphragm pump on the rate meter.

6.1.1.9 Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of the selected flow rate of about 1 liter/min (0.035 cfm).

6.1.1.10 Volume Meter. Dry gas meter (DGM), sufficiently accurate to measure the sample volume to within 2 percent, calibrated at the selected flow rate and conditions actually encountered during sampling, and equipped with a temperature sensor (dial thermometer, or equivalent) capable of measuring temperature accurately to within 3 °C (5.4 °F). A critical orifice may be used in place of the DGM specified in this section provided that it is selected, calibrated, and used as specified in section 16.0.

6.1.2 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). See the note in Method 5, section 6.1.2.

6.1.3 Vacuum Gauge and Rotameter. At least 760-mm Hg (30-in. Hg) gauge and 0- to 40-ml/min rotameter, to be used for leak-check of the sampling train.

6.2 Sample Recovery. The following items are needed for sample recovery:

6.2.1 Wash Bottles. Two polyethylene or glass bottles, 500-ml.

6.2.2 Storage Bottles. Polyethylene bottles, 100-ml, to store impinger samples (one per sample).

6.3 Sample Analysis. The following equipment is needed for sample analysis:

6.3.1 Pipettes. Volumetric type, 5-ml, 20-ml (one needed per sample), and 25-ml sizes.

6.3.2 Volumetric Flasks. 100-ml size (one per sample) and 1000-ml size.

6.3.3 Burettes. 5- and 50-ml sizes.

6.3.4 Erlenmeyer Flasks. 250-ml size (one for each sample, blank, and standard).

6.3.5 Dropping Bottle. 125-ml size, to add indicator.

6.3.6 Graduated Cylinder. 100-ml size.

6.3.7 Spectrophotometer. To measure absorbance at 352 nm.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Water. Deionized distilled to conform to ASTM Specification D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17). The $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.1.2 Isopropanol, 80 Percent by Volume. Mix 80 ml of isopropanol with 20 ml of water.

7.1.2.1 Check each lot of isopropanol for peroxide impurities as follows: Shake 10 ml of isopropanol with 10 ml of freshly prepared 10 percent potassium iodide solution. Prepare a blank by similarly treating 10 ml of water. After 1 minute, read the absorbance at 352 nm on a spectrophotometer using a 1-cm path length. If absorbance exceeds 0.1, reject alcohol for use.

7.1.2.2 Peroxides may be removed from isopropanol by redistilling or by passage through a column of activated alumina; however, reagent grade isopropanol with suitably low peroxide levels may be obtained from commercial sources. Rejection of contaminated lots may, therefore, be a more efficient procedure.

7.1.3 Hydrogen Peroxide (H_2O_2), 3 Percent by Volume. Add 10 ml of 30 percent H_2O_2 to 90 ml of water. Prepare fresh daily.

7.1.4 Potassium Iodide Solution, 10 Percent Weight by Volume (w/v). Dissolve 10.0 g of KI in water, and dilute to 100 ml. Prepare when needed.

7.2 Sample Recovery. The following reagents are required for sample recovery:

7.2.1 Water. Same as in section 7.1.1.

7.2.2 Isopropanol, 80 Percent by Volume. Same as in section 7.1.2.

7.3 Sample Analysis. The following reagents and standards are required for sample analysis:

7.3.1 Water. Same as in section 7.1.1.

7.3.2 Isopropanol, 100 Percent.

7.3.3 Thorin Indicator. 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, disodium salt, or equivalent. Dissolve 0.20 g in 100 ml of water.

7.3.4 Barium Standard Solution, 0.0100 N. Dissolve 1.95 g of barium perchlorate trihydrate [$Ba(ClO_4)_2$ $3H_2O$] in 200 ml water, and dilute to 1 liter with isopropanol. Alternatively, 1.22 g of barium chloride dihydrate [$BaCl_2$ $2H_2O$] may be used instead of the barium perchlorate trihydrate. Standardize as in section 10.5.

7.3.5 Sulfuric Acid Standard, 0.0100 N. Purchase or standardize to ±0.0002 N against 0.0100 N NaOH which has previously been standardized against potassium acid phthalate (primary standard grade).

8.0 Sample Collection, Preservation, Storage and Transport

8.1 Preparation of Sampling Train. Measure 15 ml of 80 percent isopropanol into the midget bubbler and 15 ml of 3 percent H_2O_2 into each of the first two midget impingers. Leave the final midget impinger dry. Assemble the train as shown in Figure 6–1. Adjust the probe heater to a temperature sufficient to prevent water condensation. Place crushed ice and water around the impingers.

8.2 Sampling Train Leak-Check Procedure. A leak-check prior to the sampling run is recommended, but not required. A leak-check after the sampling run is mandatory. The leak-check procedure is as follows:

8.2.1 Temporarily attach a suitable (*e.g.*, 0- to 40- ml/min) rotameter to the outlet of the DGM, and place a vacuum gauge at or near the probe inlet. Plug the probe inlet, pull a vacuum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter. A leakage rate in excess of 2 percent of the average sampling rate is not acceptable.

NOTE: Carefully (*i.e.*, slowly) release the probe inlet plug before turning off the pump.

8.2.2 It is suggested (not mandatory) that the pump be leak-checked separately, either prior to or after the sampling run. To leak-check the pump, proceed as follows: Disconnect the drying tube from the probe-impinger assembly. Place a vacuum gauge at the inlet to either the drying tube or the pump, pull a vacuum of 250 mm Hg (10 in. Hg), plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum should remain stable for at least 30 seconds.

If performed prior to the sampling run, the pump leak-check shall precede the leak-check of the sampling train described immediately above; if performed after the sampling run, the pump leak-check shall follow the sampling train leak-check.

8.2.3 Other leak-check procedures may be used, subject to the approval of the Administrator.

8.3 Sample Collection.

8.3.1 Record the initial DGM reading and barometric pressure. To begin sampling, position the tip of the probe at the sampling point, connect the probe to the bubbler, and start the pump. Adjust the sample flow to a constant rate of approximately 1.0 liter/min as indicated by the rate meter. Maintain this constant rate (±10 percent) during the entire sampling run.

8.3.2 Take readings (DGM volume, temperatures at DGM and at impinger outlet, and rate meter flow rate) at least every 5 minutes. Add more ice during the run to keep the temperature of the gases leaving the last impinger at 20 °C (68 °F) or less.

8.3.3 At the conclusion of each run, turn off the pump, remove the probe from the stack, and record the final readings. Conduct a leak-check as described in section 8.2. (This leak-check is mandatory.) If a leak is detected, void the test run or use procedures acceptable to the Administrator to adjust the sample volume for the leakage.

8.3.4 Drain the ice bath, and purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at the sampling rate. Clean ambient air can be provided by passing air through a charcoal filter or through an extra midget impinger containing 15 ml of 3 percent H_2O_2. Alternatively, ambient air without purification may be used.

8.4 Sample Recovery. Disconnect the impingers after purging. Discard the contents of the midget bubbler. Pour the contents of the midget impingers into a leak-free polyethylene bottle for shipment. Rinse the three midget impingers and the connecting tubes with water, and add the rinse to the same storage container. Mark the fluid level. Seal and identify the sample container.

9.0 Quality Control

Section	Quality control measure	Effect
7.1.2	Isopropanol check	Ensure acceptable level of peroxide impurities in isopropanol.
8.2, 10.1–10.4	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.
10.5	Barium standard solution standardization	Ensure precision of normality determination
11.2.3	Replicate titrations	Ensure precision of titration determinations.

10.0 Calibration and Standardization

10.1 Volume Metering System.

10.1.1 Initial Calibration.

10.1.1.1 Before its initial use in the field, leak-check the metering system (drying tube, needle valve, pump, rate meter, and DGM) as follows: Place a vacuum gauge at the inlet to the drying tube and pull a vacuum of 250 mm Hg (10 in. Hg). Plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum must remain stable for at least 30 seconds. Carefully release the vacuum gauge before releasing the flow meter end.

10.1.1.2 Remove the drying tube, and calibrate the metering system (at the sampling flow rate specified by the method) as follows: Connect an appropriately sized wet-test meter (*e.g.*, 1 liter per revolution) to the inlet of the needle valve. Make three independent calibration runs, using at least five revolutions of the DGM per run. Calculate the calibration factor Y (wet-test meter calibration volume divided by the DGM volume, both volumes adjusted to the same reference temperature and pressure) for each run, and average the results (Y_i). If any Y-value deviates by more than 2 percent from (Y_i), the metering system is unacceptable for use. If the metering system is acceptable, use (Y_i) as the calibration factor for subsequent test runs.

10.1.2 Post-Test Calibration Check. After each field test series, conduct a calibration check using the procedures outlined in section 10.1.1.2, except that three or more revolutions of the DGM may be used, and only two independent runs need be made. If the average of the two post-test calibration factors does not deviate by more than 5 percent from Y_i, then Y_i is accepted as the DGM calibration factor (Y), which is used in Equation 6–1 to calculate collected sample volume (see section 12.2). If the deviation is more than 5 percent, recalibrate the metering system as in section 10.1.1, and determine a post-test calibration factor (Y_f). Compare Y_i and Y_f; the smaller of the two factors is accepted as the DGM calibration factor. If recalibration indicates that the metering system is unacceptable for use, either void the test run or use methods, subject to the approval of the Administrator, to determine an acceptable value for the collected sample volume.

10.1.3 DGM as a Calibration Standard. A DGM may be used as a calibration standard for volume measurements in place of the wet-test meter specified in section 10.1.1.2, provided that it is calibrated initially and recalibrated periodically according to the same procedures outlined in Method 5, section 10.3 with the following exceptions: (a) the DGM is calibrated against a wet-test meter having a capacity of 1 liter/rev (0.035 ft^3/rev) or 3 liters/rev (0.1 ft^3/rev) and having the capability of measuring volume to within 1 percent; (b) the DGM is calibrated at 1 liter/min (0.035 cfm); and (c) the meter box of the Method 6 sampling train is calibrated at the same flow rate.

10.2 Temperature Sensors. Calibrate against mercury-in-glass thermometers. An alternative mercury-free thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

10.3 Rate Meter. The rate meter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instructions.

10.4 Barometer. Calibrate against a mercury barometer or NIST-traceable barometer prior to the field test.

10.5 Barium Standard Solution. Standardize the barium perchlorate or chloride solution against 25 ml of standard sulfuric acid to which 100 ml of 100 percent isopropanol has been added. Run duplicate analyses. Calculate the normality using the average of duplicate analyses where the titrations agree within 1 percent or 0.2 ml, whichever is larger.

11.0 Analytical Procedure

11.1 Sample Loss Check. Note level of liquid in container and confirm whether any sample was lost during shipment; note this

finding on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Analysis.

11.2.1 Transfer the contents of the storage container to a 100-ml volumetric flask, dilute to exactly 100 ml with water, and mix the diluted sample.

11.2.2 Pipette a 20-ml aliquot of the diluted sample into a 250-ml Erlenmeyer flask and add 80 ml of 100 percent isopropanol plus two to four drops of thorin indicator. While stirring the solution, titrate to a pink endpoint using 0.0100 N barium standard solution.

11.2.3 Repeat the procedures in section 11.2.2, and average the titration volumes. Run a blank with each series of samples. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is larger.

NOTE: Protect the 0.0100 N barium standard solution from evaporation at all times.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 NOMENCLATURE

C_{SO2} = Concentration of SO_2, dry basis, corrected to standard conditions, mg/dscm (lb/dscf).
N = Normality of barium standard titrant, meq/ml.
P_{bar} = Barometric pressure, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
T_m = Average DGM absolute temperature, °K (°R).
T_{std} = Standard absolute temperature, 293 °K (528 °R).
V_a = Volume of sample aliquot titrated, ml.
V_m = Dry gas volume as measured by the DGM, dcm (dcf).
$V_{m(std)}$ = Dry gas volume measured by the DGM, corrected to standard conditions, dscm (dscf).
V_{soln} = Total volume of solution in which the SO_2 sample is contained, 100 ml.
V_t = Volume of barium standard titrant used for the sample (average of replicate titration), ml.
V_{tb} = Volume of barium standard titrant used for the blank, ml.
Y = DGM calibration factor.

12.2 Dry Sample Gas Volume, Corrected to Standard Conditions.

$$V_{m(std)} = \frac{\left(V_m Y T_{std} P_{bar}\right)}{\left(T_m P_{std}\right)} = \frac{K_1 Y V_m P_{bar}}{T_m} \quad \text{Eq. 6-1}$$

Where:

K_1 = 0.3855 °K/mm Hg for metric units,
K_1 = 17.65 °R/in. Hg for English units.

12.3 SO_2 Concentration.

$$C_{so_2} = \frac{K_2 N \left(V_t - V_{tb}\right)\left(V_{soln}/V_a\right)}{V_{m(std)}} \quad \text{Eq. 6-2}$$

Where:

K_2 = 32.03 mg SO_2/meq for metric units,
$K_2 = 7.061 \times 10^{-5}$ lb SO_2/meq for English units.

13.0 Method Performance

13.1 Range. The minimum detectable limit of the method has been determined to be 3.4 mg SO_2/m^3 (2.12×10^{-7} lb/ft³). Although no upper limit has been established, tests have shown that concentrations as high as 80,000 mg/m³ (0.005 lb/ft³) of SO_2 can be collected efficiently at a rate of 1.0 liter/min (0.035 cfm) for 20 minutes in two midget impingers, each containing 15 ml of 3 percent H_2O_2. Based on theoretical calculations, the upper concentration limit in a 20 liter (0.7 ft³) sample is about 93,300 mg/m³ (0.00583 lb/ft³).

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Nomenclature. Same as section 12.1, with the following additions:

B_{wa} = Water vapor in ambient air, proportion by volume.
M_a = Molecular weight of the ambient air saturated at impinger temperature, g/g-mole (lb/lb-mole).
M_s = Molecular weight of the sample gas saturated at impinger temperature, g/g-mole (lb/lb-mole).
P_c = Inlet vacuum reading obtained during the calibration run, mm Hg (in. Hg).
P_{sr} = Inlet vacuum reading obtained during the sampling run, mm Hg (in. Hg).

$\bar{Q}_{std}$ = Volumetric flow rate through critical orifice, scm/min (scf/min).
Q_{std} = Average flow rate of pre-test and post-test calibration runs, scm/min (scf/min).
T_{amb} = Ambient absolute temperature of air, °K (°R).
V_{sb} = Volume of gas as measured by the soap bubble meter, m^3 (ft^3).
$V_{sb(std)}$ = Volume of gas as measured by the soap bubble meter, corrected to standard conditions, scm (scf).
θ = Soap bubble travel time, min.
θ_s = Time, min.

16.2 Critical Orifices for Volume and Rate Measurements. A critical orifice may be used in place of the DGM specified in section 6.1.1.10, provided that it is selected, calibrated, and used as follows:

16.2.1 Preparation of Sampling Train. Assemble the sampling train as shown in Figure 6–2. The rate meter and surge tank are optional but are recommended in order to detect changes in the flow rate.

NOTE: The critical orifices can be adapted to a Method 6 type sampling train as follows: Insert sleeve type, serum bottle stoppers into two reducing unions. Insert the needle into the stoppers as shown in Figure 6–3.

16.2.2 Selection of Critical Orifices.

16.2.2.1 The procedure that follows describes the use of hypodermic needles and stainless steel needle tubings, which have been found suitable for use as critical orifices. Other materials and critical orifice designs may be used provided the orifices act as true critical orifices, (*i.e.*, a critical vacuum can be obtained) as described in this section. Select a critical orifice that is sized to operate at the desired flow rate. The needle sizes and tubing lengths shown in Table 6–1 give the following approximate flow rates.

16.2.2.2 Determine the suitability and the appropriate operating vacuum of the critical orifice as follows: If applicable, temporarily attach a rate meter and surge tank to the outlet of the sampling train, if said equipment is not present (see section 16.2.1). Turn on the pump and adjust the valve to give an outlet vacuum reading corresponding to about half of the atmospheric pressure. Observe the rate meter reading. Slowly increase the vacuum until a stable reading is obtained on the rate meter. Record the critical vacuum, which is the outlet vacuum when the rate meter first reaches a stable value. Orifices that do not reach a critical value must not be used.

16.2.3 Field Procedures.

16.2.3.1 Leak-Check Procedure. A leak-check before the sampling run is recommended, but not required. The leak-check procedure is as follows: Temporarily attach a suitable (*e.g.*, 0–40 ml/min) rotameter and surge tank, or a soap bubble meter and surge tank to the outlet of the pump. Plug the probe inlet, pull an outlet vacuum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter or bubble meter. A leakage rate in excess of 2 percent of the average sampling rate ($\bar{Q}_{std}$) is not acceptable. Carefully release the probe inlet plug before turning off the pump.

16.2.3.2 Moisture Determination. At the sampling location, prior to testing, determine the percent moisture of the ambient air using the wet and dry bulb temperatures or, if appropriate, a relative humidity meter.

16.2.3.3 Critical Orifice Calibration. At the sampling location, prior to testing, calibrate the entire sampling train (*i.e.*, determine the flow rate of the sampling train when operated at critical conditions). Attach a 500-ml soap bubble meter to the inlet of the probe, and operate the sampling train at an outlet vacuum of 25 to 50 mm Hg (1 to 2 in. Hg) above the critical vacuum. Record the information listed in Figure 6–4. Calculate the standard volume of air measured by the soap bubble meter and the volumetric flow rate using the equations below:

$$V_{sb(std)} = V_{sb}\left(T_{std}/T_{amb}\right)\left(P_{bar}/P_{std}\right) \qquad \text{Eq. 6-4}$$

$$Q_{std} = \frac{V_{sb(std)}}{\theta} \qquad \text{Eq. 6-5}$$

16.2.3.4 Sampling.

16.2.3.4.1 Operate the sampling train for sample collection at the same vacuum used during the calibration run. Start the watch and pump simultaneously. Take readings (temperature, rate meter, inlet vacuum, and outlet vacuum) at least every 5 minutes. At the end of the sampling run, stop the watch and pump simultaneously.

16.2.3.4.2 Conduct a post-test calibration run using the calibration procedure outlined in section 16.2.3.3. If the Q_{std} obtained before and after the test differ by more than 5 percent, void the test run; if not, calculate the volume of the gas measured with the critical orifice using Equation 6–6 as follows:

$$V_{m(std)} = \frac{\overline{Q}_{std}\ \theta_s\ (1-B_{wa})(P_{bar}+P_{sr})}{(P_{bar}+P_c)} \quad \text{Eq. 6-6}$$

16.2.3.4.3 If the percent difference between the molecular weight of the ambient air at saturated conditions and the sample gas is more that ±3 percent, then the molecular weight of the gas sample must be considered in the calculations using the following equation:

$$_{(std)} = \frac{\overline{Q}_{std}\ \theta_s\ (1-B_{wa})(P_{bar}+P_{sr})(M_a/M_s)^1}{(P_{bar}+P_c)} \quad \text{Eq. 6-7}$$

NOTE: A post-test leak-check is not necessary because the post-test calibration run results will indicate whether there is any leakage.

16.2.3.4.4 Drain the ice bath, and purge the sampling train using the procedure described in section 8.3.4.

16.3 Elimination of Ammonia Interference. The following alternative procedures must be used in addition to those specified in the method when sampling at sources having ammonia emissions.

16.3.1 Sampling. The probe shall be maintained at 275 °C (527 °F) and equipped with a high-efficiency in-stack filter (glass fiber) to remove particulate matter. The filter material shall be unreactive to SO_2. Whatman 934AH (formerly Reeve Angel 934AH) filters treated as described in Reference 10 in section 17.0 of Method 5 is an example of a filter that has been shown to work. Where alkaline particulate matter and condensed moisture are present in the gas stream, the filter shall be heated above the moisture dew point but below 225 °C (437 °F).

16.3.2 Sample Recovery. Recover the sample according to section 8.4 except for discarding the contents of the midget bubbler. Add the bubbler contents, including the rinsings of the bubbler with water, to a separate polyethylene bottle from the rest of the sample. Under normal testing conditions where sulfur trioxide will not be present significantly, the tester may opt to delete the midget bubbler from the sampling train. If an approximation of the sulfur trioxide concentration is desired, transfer the contents of the midget bubbler to a separate polyethylene bottle.

16.3.3 Sample Analysis. Follow the procedures in sections 11.1 and 11.2, except add 0.5 ml of 0.1 N HCl to the Erlenmeyer flask and mix before adding the indicator. The following analysis procedure may be used for an approximation of the sulfur trioxide concentration. The accuracy of the calculated concentration will depend upon the ammonia to SO_2 ratio and the level of oxygen present in the gas stream. A fraction of the SO_2 will be counted as sulfur trioxide as the ammonia to SO_2 ratio and the sample oxygen content increases. Generally, when this ratio is 1 or less and the oxygen content is in the range of 5 percent, less than 10 percent of the SO_2 will be counted as sulfur trioxide. Analyze the peroxide and isopropanol sample portions separately. Analyze the peroxide portion as described above. Sulfur trioxide is determined by difference using sequential titration of the isopropanol portion of the sample. Transfer the contents of the isopropanol storage container to a 100-ml volumetric flask, and dilute to exactly 100 ml with water. Pipette a 20-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 0.5 ml of 0.1 N HCl, 80 ml of 100 percent isopropanol, and two to four drops of thorin indicator. Titrate to a pink endpoint using 0.0100 N barium perchlorate. Repeat and average the titration volumes that agree within 1 percent or 0.2 ml, whichever is larger. Use this volume in Equation 6–2 to determine the sulfur trioxide concentration. From the flask containing the remainder of the isopropanol sample, determine the fraction of SO_2 collected in the bubbler by pipetting 20-ml aliquots into 250-ml Erlenmeyer flasks. Add 5 ml of 3 percent H_2O_2, 100 ml of 100 percent isopropanol, and two to four drips of thorin indicator, and titrate as before. From this titration volume, subtract the titrant volume determined for sulfur trioxide, and add the titrant volume determined for the peroxide portion. This final volume constitutes V_t, the volume of barium perchlorate used for the SO_2 sample.

17.0 References

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18.0 Tables, Diagrams, Flowcharts and Validation Data

TABLE 6–1—APPROXIMATE FLOW RATES FOR VARIOUS NEEDLE SIZES

Needle size (gauge)	Needle length (cm)	Flow rate (ml/min)
21	7.6	1,100
22	2.9	1,000
22	3.8	900
23	3.8	500
23	5.1	450
24	3.2	400

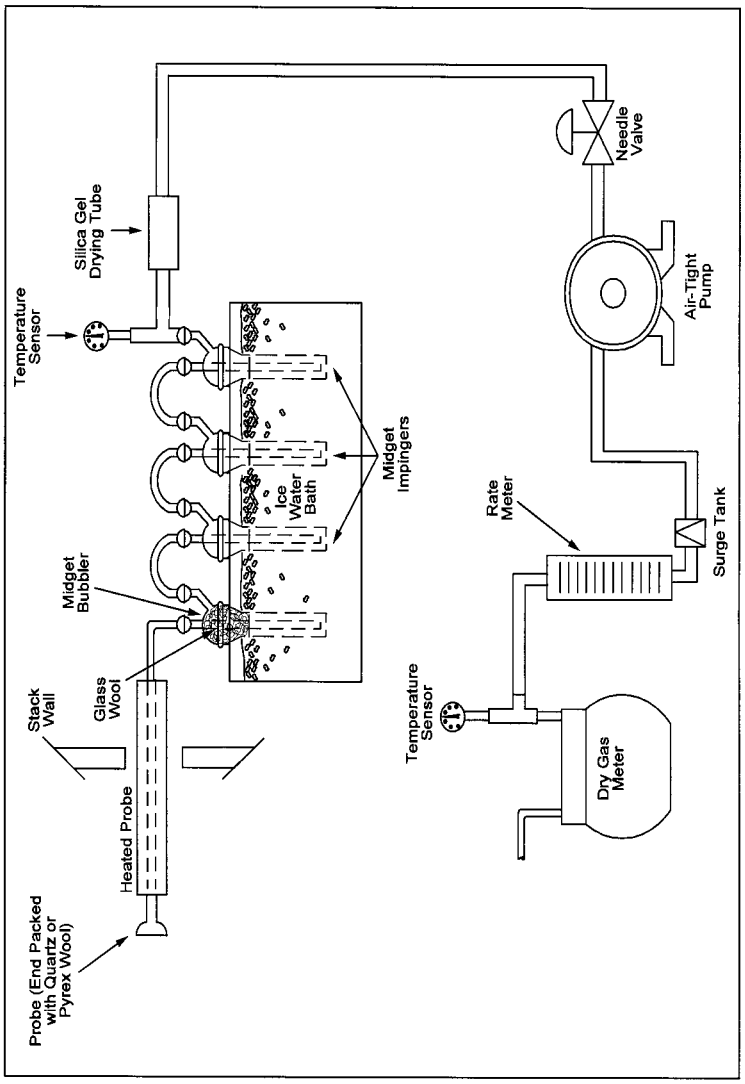

Figure 6-1. Sulfur Dioxide Sampling Train.

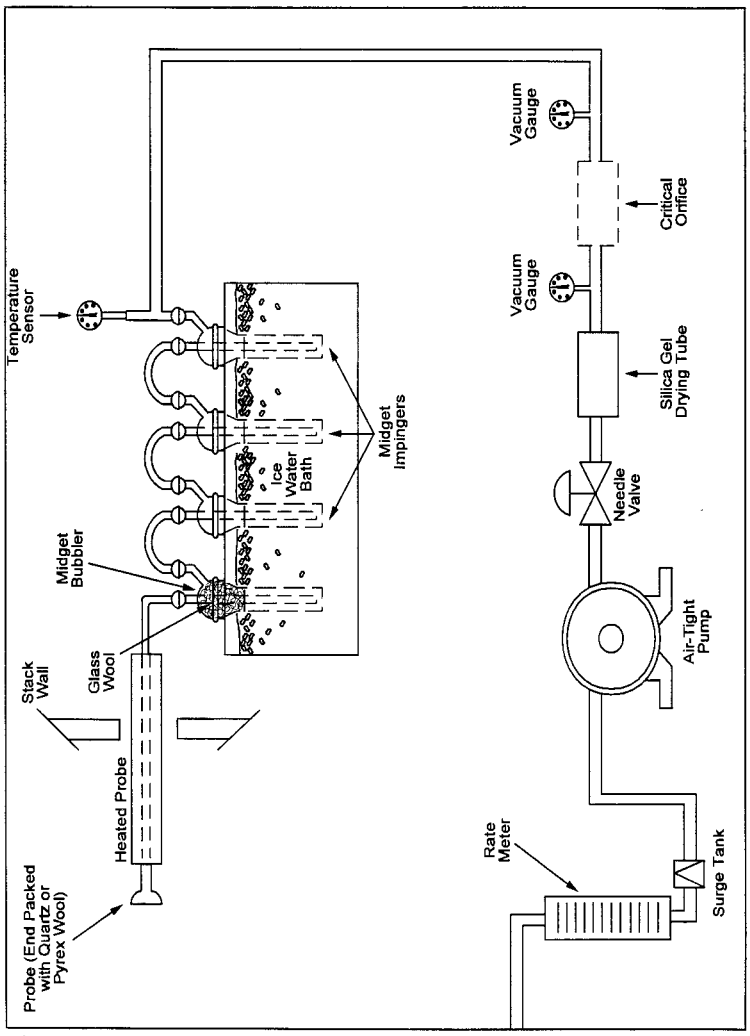

Figure 6-2. Sulfur Dioxide Sampling Train Using a Critical Orifice.

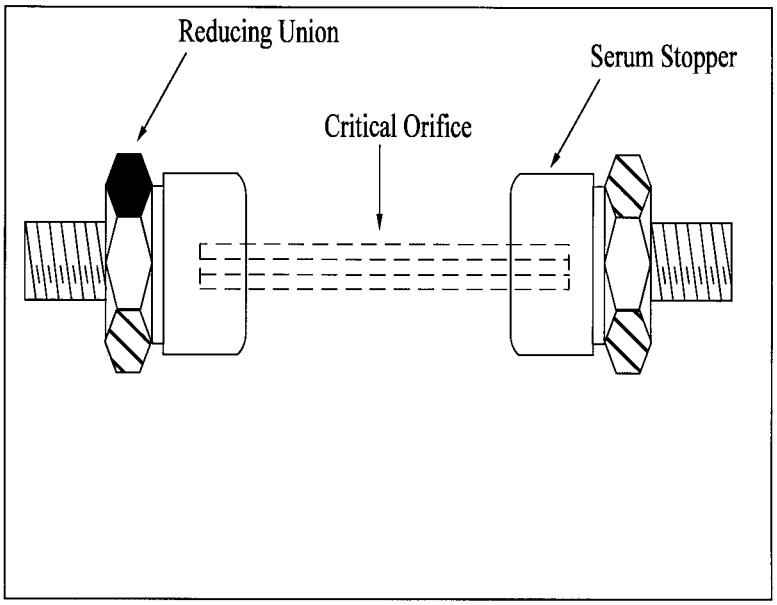

Figure 6-3. Critical Orifice Adaptation for the Method 6 Sampling Train.

Date _____ Train ID _____

Critical orifice size _____ Critical vacuum _____

		Pretest	Post-test
Soap bubble meter volume, V_{sb}	cc		
	m^3 (ft^3)		
Time, θ	sec		
	min		
Barometric pressure, P_{bar}	mm Hg (in. Hg)		
Ambient temperature, t_{amb}	°C (°F)		
Inlet vacuum, P_c	mm Hg (in. Hg)		
Outlet vacuum	mm Hg (in. Hg)		
$V_{sb(std)}$	m^3 (ft^3)		
Flow rate, Q_{std}	$\frac{m^3}{min}\left(\frac{ft^3}{min}\right)$		

Figure 6-4. Critical Orifice Calibration Data Sheet.

METHOD 6A—DETERMINATION OF SULFUR DIOXIDE, MOISTURE, AND CARBON DIOXIDE FROM FOSSIL FUEL COMBUSTION SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, Method 6, and Method 19.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
SO_2	7449–09–05	3.4 mg SO_2/m^3 (2.12×10^{-7} lb/ft^3)
CO_2	124–38–9	N/A
H_2O	7732–18–5	N/A

1.2 Applicability. This method is applicable for the determination of sulfur dioxide (SO_2) emissions from fossil fuel combustion sources in terms of concentration (mg/dscm or lb/dscf) and in terms of emission rate (ng/J or lb/10^6 Btu) and for the determination of carbon dioxide (CO_2) concentration (percent). Moisture content (percent), if desired, may also be determined by this method.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from a sampling point in the stack. The SO_2 and the sulfur trioxide, including those fractions in any sulfur acid mist, are separated. The SO_2 fraction is measured by the barium-thorin titration method. Moisture and CO_2 fractions are collected in the same sampling train, and are determined gravimetrically.

3.0 Definitions [Reserved]

4.0 Interferences

Same as Method 6, section 4.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. Same as Method 6, section 5.2.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 6, section 6.1, with the exception of the following:

6.1.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 6A–1.

6.1.1.1 Impingers and Bubblers. Two 30 = ml midget impingers with a 1 = mm restricted tip and two 30 = ml midget bubblers with unrestricted tips. Other types of impingers and bubblers (*e.g.,* Mae West for SO_2 collection and rigid cylinders containing Drierite for moisture absorbers), may be used with proper attention to reagent volumes and levels, subject to the approval of the Administrator.

6.1.1.2 CO_2 Absorber. A sealable rigid cylinder or bottle with an inside diameter between 30 and 90 mm , a length between 125 and 250 mm, and appropriate connections at both ends. The filter may be a separate heated unit or may be within the heated portion of the probe. If the filter is within the sampling probe, the filter should not be within 15 cm of the probe inlet or any unheated section of the probe, such as the connection to the first bubbler. The probe and filter should be heated to at least 20 °C (68 °F) above the source temperature, but not greater than 120 °C (248 °F). The filter temperature (*i.e.,* the sample gas temperature) should be monitored to assure the desired temperature is maintained. A heated Teflon connector may be used to connect the filter holder or probe to the first impinger.

NOTE: For applications downstream of wet scrubbers, a heated out-of-stack filter (either borosilicate glass wool or glass fiber mat) is necessary.

6.2 Sample Recovery. Same as Method 6, section 6.2.

6.3 Sample Analysis. Same as Method 6, section 6.3, with the addition of a balance to measure within 0.05 g.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

7.1 Sample Collection. Same as Method 6, section 7.1, with the addition of the following:

7.1.1 Drierite. Anhydrous calcium sulfate ($CaSO_4$) desiccant, 8 mesh, indicating type is recommended.

NOTE: Do not use silica gel or similar desiccant in this application.

7.1.2 CO_2 Absorbing Material. Ascarite II. Sodium hydroxide-coated silica, 8- to 20-mesh.

7.2 Sample Recovery and Analysis. Same as Method 6, sections 7.2 and 7.3, respectively.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Preparation of Sampling Train.

8.1.1 Measure 15 ml of 80 percent isopropanol into the first midget bubbler and 15 ml of 3 percent hydrogen peroxide into each of the two midget impingers (the second

and third vessels in the train) as described in Method 6, section 8.1. Insert the glass wool into the top of the isopropanol bubbler as shown in Figure 6A–1. Place about 25 g of Drierite into the second midget bubbler (the fourth vessel in the train). Clean the outside of the bubblers and impingers and allow the vessels to reach room temperature. Weigh the four vessels simultaneously to the nearest 0.1 g, and record this initial weight (m_{wi}).

8.1.2 With one end of the CO_2 absorber sealed, place glass wool into the cylinder to a depth of about 1 cm (0.5 in.). Place about 150 g of CO_2 absorbing material in the cylinder on top of the glass wool, and fill the remaining space in the cylinder with glass wool. Assemble the cylinder as shown in figure 6A–2. With the cylinder in a horizontal position, rotate it around the horizontal axis. The CO_2 absorbing material should remain in position during the rotation, and no open spaces or channels should be formed. If necessary, pack more glass wool into the cylinder to make the CO_2 absorbing material stable. Clean the outside of the cylinder of loose dirt and moisture and allow the cylinder to reach room temperature. Weigh the cylinder to the nearest 0.1 g, and record this initial weight (m_{ai}).

8.1.3 Assemble the train as shown in figure 6A–1. Adjust the probe heater to a temperature sufficient to prevent condensation (see note in section 6.1). Place crushed ice and water around the impingers and bubblers. Mount the CO_2 absorber outside the water bath in a vertical flow position with the sample gas inlet at the bottom. Flexible tubing (*e.g.*, Tygon) may be used to connect the last SO_2 absorbing impinger to the moisture absorber and to connect the moisture absorber to the CO_2 absorber. A second, smaller CO_2 absorber containing Ascarite II may be added in-line downstream of the primary CO_2 absorber as a breakthrough indicator. Ascarite II turns white when CO_2 is absorbed.

8.2 Sampling Train Leak-Check Procedure and Sample Collection. Same as Method 6, sections 8.2 and 8.3, respectively.

8.3 Sample Recovery.

8.3.1 Moisture Measurement. Disconnect the isopropanol bubbler, the SO_2 impingers, and the moisture absorber from the sample train. Allow about 10 minutes for them to reach room temperature, clean the outside of loose dirt and moisture, and weigh them simultaneously in the same manner as in section 8.1. Record this final weight (m_{wf}).

8.3.2 Peroxide Solution. Discard the contents of the isopropanol bubbler and pour the contents of the midget impingers into a leak-free polyethylene bottle for shipping. Rinse the two midget impingers and connecting tubes with water, and add the washing to the same storage container.

8.3.3 CO_2 Absorber. Allow the CO_2 absorber to warm to room temperature (about 10 minutes), clean the outside of loose dirt and moisture, and weigh to the nearest 0.1 g in the same manner as in section 8.1. Record this final weight (m_{af}). Discard used Ascarite II material.

9.0 Quality Control

Same as Method 6, section 9.0.

10.0 Calibration and Standardization

Same as Method 6, section 10.0.

11.0 Analytical Procedure

11.1 Sample Analysis. The sample analysis procedure for SO_2 is the same as that specified in Method 6, section 11.0.

12.0 Data Analysis and Calculations

Same as Method 6, section 12.0, with the addition of the following:

12.1 Nomenclature.

C_w = Concentration of moisture, percent.
C_{CO2} = Concentration of CO_2, dry basis, percent.
E_{SO2} = Emission rate of SO_2, ng/J (lb/10^6 Btu).
F_C = Carbon F-factor from Method 19 for the fuel burned, dscm/J (dscf/10^6 Btu).
m_{wi} = Initial weight of impingers, bubblers, and moisture absorber, g.
m_{wf} = Final weight of impingers, bubblers, and moisture absorber, g.
m_{ai} = Initial weight of CO_2 absorber, g.
m_{af} = Final weight of CO_2 absorber, g.
m_{SO2} = Mass of SO_2 collected, mg.
$V_{CO2(std)}$ = Equivalent volume of CO_2 collected at standard conditions, dscm (dscf).
$V_{w(std)}$ = Equivalent volume of moisture collected at standard conditions, scm (scf).

12.2 CO_2 Volume Collected, Corrected to Standard Conditions.

$$V_{CO_2(std)} = K_3 \left(m_{af} - m_{ai}\right) \qquad \text{Eq. 6A-1}$$

Where:

K_3 = Equivalent volume of gaseous CO_2 at standard conditions, 5.467×10^{-4} dscm/g (1.930×10^{-2} dscf/g).

12.3 Moisture Volume Collected, Corrected to Standard Conditions.

$$V_{w(std)} = K_4 \left(m_{wf} - m_{wi}\right) \qquad \text{Eq. 6A-2}$$

Where:

K_4 = Equivalent volume of water vapor at standard conditions, 1.336×10^{-3} scm/g (4.717×10^{-2} scf/g).

12.4 SO_2 Concentration.

$$C_{so_2} = \frac{K_2 N (V_t - V_{tb})(V_{so\,ln}/V_a)}{V_{m(std)} + V_{co_2(std)}} \qquad \text{Eq. 6A-3}$$

Where:

K_2 = 32.03 mg SO_2/meq. SO_2 (7.061×10^{-5} lb SO_2/meq. SO_2)

12.5 CO_2 Concentration.

$$C_{co_2} = \frac{V_{co_2(std)}}{V_{m(std)} + V_{co_2(std)}} \qquad \text{Eq. 6A-4}$$

12.6 Moisture Concentration.

$$C_w = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)} + V_{co_2(std)}} \qquad \text{Eq. 6A-5}$$

13.0 Method Performance

13.1 Range and Precision. The minimum detectable limit and the upper limit for the measurement of SO_2 are the same as for Method 6. For a 20-liter sample, this method has a precision of ±0.5 percent CO_2 for concentrations between 2.5 and 25 percent CO_2 and ±1.0 percent moisture for moisture concentrations greater than 5 percent.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Methods

If the only emission measurement desired is in terms of emission rate of SO_2 (ng/J or lb/10^6 Btu), an abbreviated procedure may be used. The differences between the above procedure and the abbreviated procedure are described below.

16.1 Sampling Train. The sampling train is the same as that shown in Figure 6A–1 and as described in section 6.1, except that the dry gas meter is not needed.

16.2 Preparation of the Sampling Train. Follow the same procedure as in section 8.1, except do not weigh the isopropanol bubbler, the SO_2 absorbing impingers, or the moisture absorber.

16.3 Sampling Train Leak-Check Procedure and Sample Collection. Leak-check and operate the sampling train as described in section 8.2, except that dry gas meter readings, barometric pressure, and dry gas meter temperatures need not be recorded during sampling.

16.4 Sample Recovery. Follow the procedure in section 8.3, except do not weigh the isopropanol bubbler, the SO_2 absorbing impingers, or the moisture absorber.

16.5 Sample Analysis. Analysis of the peroxide solution is the same as that described in section 11.1.

16.6 Calculations.

16.6.1 SO_2 Collected.

$$m_{SO_2} = K_2 N (V_t - V_{tb})(V_{soln}/V_a) \qquad \text{Eq. 6A-6}$$

Where:

K_2 = 32.03 mg SO_2/meq. SO_2
$K_2 = 7.061 \times 10^{-5}$ lb SO_2/meq. SO_2

16.6.2 Sulfur Dioxide Emission Rate.

$$E_{SO_2} = K_5 F_c m_{so_2} / (m_{af} - m_{ai}) \qquad \text{Eq. 6A-7}$$

Where:

$K_5 = 1.829 \times 10^9$ mg/dscm
$K_2 = 0.1142$ lb/dscf

17.0 References

Same as Method 6, section 17.0, References 1 through 8, with the addition of the following:

1. Stanley, Jon and P.R. Westlin. An Alternate Method for Stack Gas Moisture Determination. Source Evaluation Society Newsletter. *3*(4). November 1978.

2. Whittle, Richard N. and P.R. Westlin. Air Pollution Test Report: Development and Evaluation of an Intermittent Integrated SO_2/CO_2 Emission Sampling Procedure. Environmental Protection Agency, Emission Standard and Engineering Division, Emission Measurement Branch. Research Triangle Park, NC. December 1979. 14 pp.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

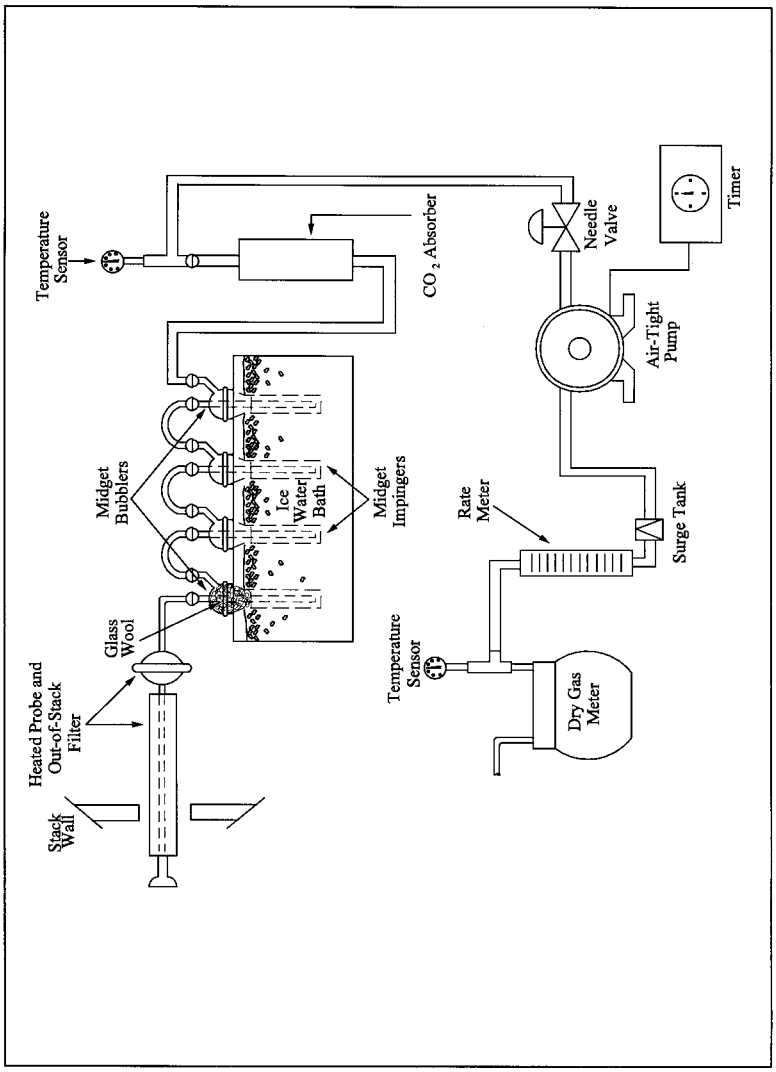

Figure 6A-1. Sampling train.

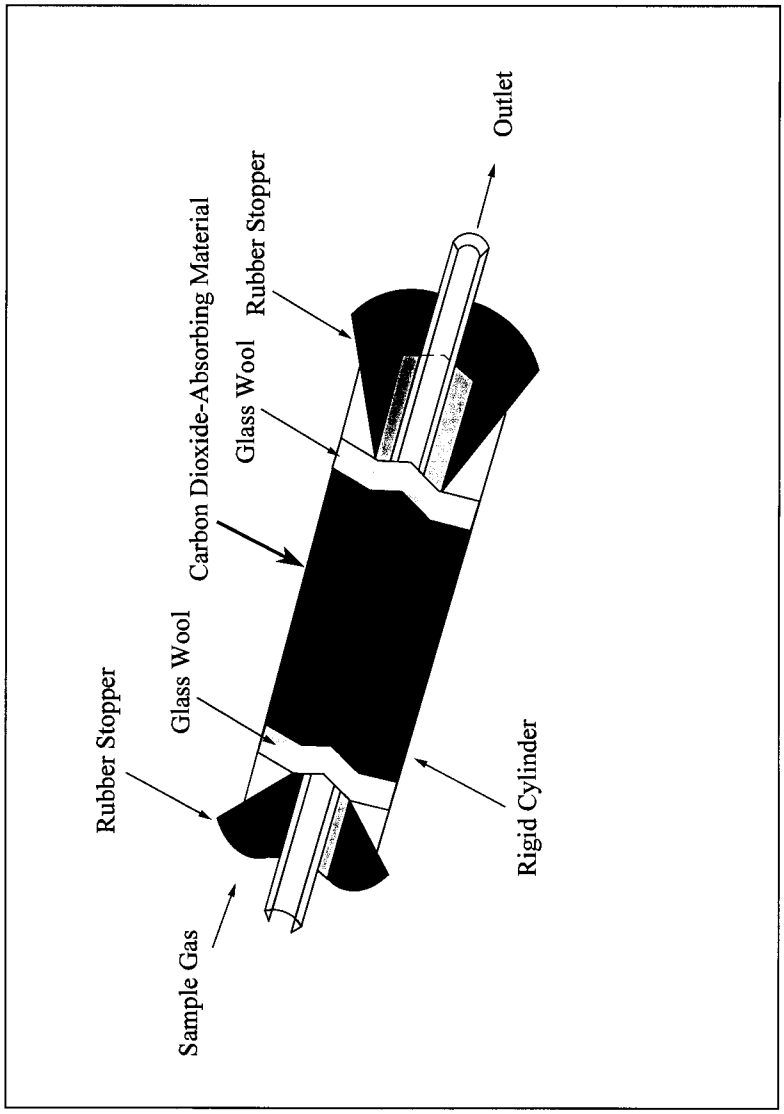

Figure 6A-2. CO_2 Absorber

METHOD 6B—DETERMINATION OF SULFUR DIOXIDE AND CARBON DIOXIDE DAILY AVERAGE EMISSIONS FROM FOSSIL FUEL COMBUSTION SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, Method 6, and Method 6A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Sulfur dioxide (SO_2)	7449–09–05	3.4 mg SO_2/m^3 (2.12×10^{-7} lb/ft^3)
Carbon dioxide (CO_2)	124–38–9	N/A

1.2 Applicability. This method is applicable for the determination of SO_2 emissions from combustion sources in terms of concentration (ng/dscm or lb/dscf) and emission rate (ng/J or lb/10^6 Btu), and for the determination of CO_2 concentration (percent) on a daily (24 hours) basis.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the sampling point in the stack intermittently over a 24-hour or other specified time period. The SO_2 fraction is measured by the barium-thorin titration method. Moisture and CO_2 fractions are collected in the same sampling train, and are determined gravimetrically.

3.0 Definitions [Reserved]

4.0 Interferences

Same as Method 6, section 4.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. Same as Method 6, section 5.2.

6.0 Equipment and Supplies

Same as Method 6A, section 6.0, with the following exceptions and additions:

6.1 The isopropanol bubbler is not used. An empty bubbler for the collection of liquid droplets, that does not allow direct contact between the collected liquid and the gas sample, may be included in the sampling train.

6.2 For intermittent operation, include an industrial timer-switch designed to operate in the ''on'' position at least 2 minutes continuously and ''off'' the remaining period over a repeating cycle. The cycle of operation is designated in the applicable regulation. At a minimum, the sampling operation should include at least 12, equal, evenly-spaced periods per 24 hours.

6.3 Stainless steel sampling probes, type 316, are not recommended for use with Method 6B because of potential sample contamination due to corrosion. Glass probes or other types of stainless steel, *e.g.*, Hasteloy or Carpenter 20, are recommended for long-term use.

NOTE: For applications downstream of wet scrubbers, a heated out-of-stack filter (either borosilicate glass wool or glass fiber mat) is necessary. Probe and filter heating systems capable of maintaining a sample gas temperature of between 20 and 120 °C (68 and 248 °F) at the filter are also required in these cases. The electric supply for these heating systems should be continuous and separate from the timed operation of the sample pump.

7.0 Reagents and Standards

Same as Method 6A, section 7.0, with the following exceptions:

7.1 Isopropanol is not used for sampling.

7.2 The hydrogen peroxide absorbing solution shall be diluted to no less than 6 percent by volume, instead of 3 percent as specified in Methods 6 and 6A.

7.3 If the Method 6B sampling train is to be operated in a low sample flow condition (less than 100 ml/min or 0.21 ft^3/hr), molecular sieve material may be substituted for Ascarite II as the CO_2 absorbing material. The recommended molecular sieve material is Union Carbide 1/16 inch pellets, 5 A°, or equivalent. Molecular sieve material need not be discarded following the sampling run, provided that it is regenerated as per the manufacturer's instruction. Use of molecular sieve material at flow rates higher than 100 ml/min (0.21 ft^3/hr) may cause erroneous CO_2 results.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Preparation of Sampling Train. Same as Method 6A, section 8.1, with the addition of the following:

8.1.1 The sampling train is assembled as shown in Figure 6A–1 of Method 6A, except that the isopropanol bubbler is not included.

8.1.2 Adjust the timer-switch to operate in the ''on'' position from 2 to 4 minutes on a 2-hour repeating cycle or other cycle specified in the applicable regulation. Other timer sequences may be used with the restriction that the total sample volume collected is between 25 and 60 liters (0.9 and 2.1 ft^3) for the amounts of sampling reagents prescribed in this method.

8.1.3 Add cold water to the tank until the impingers and bubblers are covered at least two-thirds of their length. The impingers and bubbler tank must be covered and protected from intense heat and direct sunlight. If freezing conditions exist, the impinger solution and the water bath must be protected.

NOTE: Sampling may be conducted continuously if a low flow-rate sample pump [20

to 40 ml/min (0.04 to 0.08 ft^3/hr) for the reagent volumes described in this method] is used. If sampling is continuous, the timer-switch is not necessary. In addition, if the sample pump is designed for constant rate sampling, the rate meter may be deleted. The total gas volume collected should be between 25 and 60 liters (0.9 and 2.1 ft^3) for the amounts of sampling reagents prescribed in this method.

8.2 Sampling Train Leak-Check Procedure. Same as Method 6, section 8.2.

8.3 Sample Collection.

8.3.1 The probe and filter (either in-stack, out-of-stack, or both) must be heated to a temperature sufficient to prevent water condensation.

8.3.2 Record the initial dry gas meter reading. To begin sampling, position the tip of the probe at the sampling point, connect the probe to the first impinger (or filter), and start the timer and the sample pump. Adjust the sample flow to a constant rate of approximately 1.0 liter/min (0.035 cfm) as indicated by the rotameter. Observe the operation of the timer, and determine that it is operating as intended (*i.e.*, the timer is in the ''on'' position for the desired period, and the cycle repeats as required).

8.3.3 One time between 9 a.m. and 11 a.m. during the 24-hour sampling period, record the dry gas meter temperature (T_m) and the barometric pressure ($P_{(bar)}$).

8.3.4 At the conclusion of the run, turn off the timer and the sample pump, remove the probe from the stack, and record the final gas meter volume reading. Conduct a leak-check as described in section 8.2. If a leak is found, void the test run or use procedures acceptable to the Administrator to adjust the sample volume for leakage. Repeat the steps in sections 8.3.1 to 8.3.4 for successive runs.

8.4 Sample Recovery. The procedures for sample recovery (moisture measurement, peroxide solution, and CO_2 absorber) are the same as those in Method 6A, section 8.3.

9.0 Quality Control

Same as Method 6, section 9.0., with the exception of the isopropanol-check.

10.0 Calibration and Standardization

Same as Method 6, section 10.0, with the addition of the following:

10.1 Periodic Calibration Check. After 30 days of operation of the test train, conduct a calibration check according to the same procedures as the post-test calibration check (Method 6, section 10.1.2). If the deviation between initial and periodic calibration factors exceeds 5 percent, use the smaller of the two factors in calculations for the preceding 30 days of data, but use the most recent calibration factor for succeeding test runs.

11.0 Analytical Procedures

11.1 Sample Loss Check and Analysis. Same as Method 6, sections 11.1 and 11.2, respectively.

12.0 Data Analysis and Calculations

Same as Method 6A, section 12.0, except that P_{bar} and T_m correspond to the values recorded in section 8.3.3 of this method. The values are as follows:

P_{bar} = Initial barometric pressure for the test period, mm Hg.

T_m = Absolute meter temperature for the test period, °K.

13.0 Method Performance

13.1 Range.

13.1.1 Sulfur Dioxide. Same as Method 6.

13.1.2 Carbon Dioxide. Not determined.

13.2 Repeatability and Reproducibility. EPA-sponsored collaborative studies were undertaken to determine the magnitude of repeatability and reproducibility achievable by qualified testers following the procedures in this method. The results of the studies evolve from 145 field tests including comparisons with Methods 3 and 6. For measurements of emission rates from wet, flue gas desulfurization units in (ng/J), the repeatability (intra-laboratory precision) is 8.0 percent and the reproducibility (inter-laboratory precision) is 11.1 percent.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Methods

Same as Method 6A, section 16.0, except that the timer is needed and is operated as outlined in this method.

17.0 References

Same as Method 6A, section 17.0, with the addition of the following:

1. Butler, Frank E., et. al. The Collaborative Test of Method 6B: Twenty-Four-Hour Analysis of SO_2 and CO_2. JAPCA. Vol. 33, No. 10. October 1983.

18.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 6C—DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES (INSTRUMENTAL ANALYZER PROCEDURE)

1.0 Scope and Application

What is Method 6C?

Method 6C is a procedure for measuring sulfur dioxide (SO_2) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that

you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis.

This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 4—Determination of Moisture Content in Stack Gases.

(c) Method 6—Determination of Sulfur Dioxide Emissions from Stationary Sources.

(d) Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure).

1.1 Analytes. What does this method determine? This method measures the concentration of sulfur dioxide.

Analyte	CAS No.	Sensitivity
SO_2	7446–09–5	Typically <2% of Calibration Span.

1.2 Applicability. When is this method required? The use of Method 6C may be required by specific New Source Performance Standards, Clean Air Marketing rules, State Implementation Plans, and permits where SO_2 concentrations in stationary source emissions must be measured, either to determine compliance with an applicable emission standard or to conduct performance testing of a continuous emission monitoring system (CEMS). Other regulations may also require the use of Method 6C.

1.3 Data Quality Objectives. How good must my collected data be? Refer to section 1.3 of Method 7E.

2.0 Summary of Method

In this method, you continuously sample the effluent gas and convey the sample to an analyzer that measures the concentration of SO_2. You must meet the performance requirements of this method to validate your data.

3.0 Definitions

Refer to section 3.0 of Method 7E for the applicable definitions.

4.0 Interferences

Refer to Section 4.0 of Method 7E.

5.0 Safety

Refer to section 5.0 of Method 7E.

6.0 Equipment and Supplies

Figure 7E–1 of Method 7E is a schematic diagram of an acceptable measurement system.

6.1 What do I need for the measurement system? The essential components of the measurement system are the same as those in sections 6.1 and 6.2 of Method 7E, except that the SO_2 analyzer described in section 6.2 of this method must be used instead of the analyzer described in section 6.2 of Method 7E. You must follow the noted specifications in section 6.1 of Method 7E.

6.2 What analyzer must I use? You may use an instrument that uses an ultraviolet, nondispersive infrared, fluorescence, or other detection principle to continuously measure SO_2 in the gas stream and meets the performance specifications in section 13.0. The low-range and dual-range analyzer provisions in sections 6.2.8.1 and 6.2.8.2 of Method 7E apply.

7.0 Reagents and Standards

7.1 Calibration Gas. What calibration gases do I need? Refer to section 7.1 of Method 7E for the calibration gas requirements. Example calibration gas mixtures are listed below.

(a) SO_2 in nitrogen (N_2).

(b) SO_2 in air.

(c) SO_2 and CO_2 in N_2.

(d) SO_2 andO_2 in N_2.

(e) $SO_2/CO_2/O_2$ gas mixture in N_2.

(f) CO_2/NO_X gas mixture in N_2.

(g) $CO_2/SO_2/NO_X$ gas mixture in N_2.

7.2 Interference Check. What additional reagents do I need for the interference check? The test gases for the interference check are listed in Table 7E–3 of Method 7E. For the alternative interference check, you must use the reagents described in section 7.0 of Method 6.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling Site and Sampling Points. You must follow the procedures of section 8.1 of Method 7E.

8.2 Initial Measurement System Performance Tests. You must follow the procedures in section 8.2 of Method 7E. If a dilution-type measurement system is used, the special considerations in section 8.3 of Method 7E also apply.

8.3 Interference Check. You must follow the procedures of section 8.2.7 of Method 7E

to conduct an interference check, substituting SO_2 for NO_X as the method pollutant. For dilution-type measurement systems, you must use the alternative interference check procedure in section 16 and a co-located, unmodified Method 6 sampling train.

8.4 Sample Collection. You must follow the procedures of section 8.4 of Method 7E.

8.5 Post-Run System Bias Check and Drift Assessment. You must follow the procedures of section 8.5 of Method 7E.

9.0 Quality Control

Follow quality control procedures in section 9.0 of Method 7E.

10.0 Calibration and Standardization

Follow the procedures for calibration and standardization in section 10.0 of Method 7E.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the applicable procedures for calculations and data analysis in section 12.0 of Method 7E as applicable, substituting SO_2 for NO_X as appropriate.

13.0 Method Performance

13.1 The specifications for the applicable performance checks are the same as in section 13.0 of Method 7E.

13.2 Alternative Interference Check. The results are acceptable if the difference between the Method 6C result and the modified Method 6 result is less than 7.0 percent of the Method 6 result for each of the three test runs. For the purposes of comparison, the Method 6 and 6C results must be expressed in the same units of measure.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Alternative Interference Check. You may perform an alternative interference check consisting of at least three comparison runs between Method 6C and Method 6. This check validates the Method 6C results at each particular source category (type of facility) where the check is performed. When testing under conditions of low concentrations (<15 ppm), this alternative interference check is not allowed.

NOTE: The procedure described below applies to non-dilution sampling systems only. If this alternative interference check is used for a dilution sampling system, use a standard Method 6 sampling train and extract the sample directly from the exhaust stream at points collocated with the Method 6C sample probe.

a. Build the modified Method 6 sampling train (flow control valve, two midget impingers containing 3 percent hydrogen peroxide, and dry gas meter) shown in Figure 6C–1. Connect the sampling train to the sample bypass discharge vent. Record the dry gas meter reading before you begin sampling. Simultaneously collect modified Method 6 and Method 6C samples. Open the flow control valve in the modified Method 6 train as you begin to sample with Method 6C. Adjust the Method 6 sampling rate to 1 liter per minute (.10 percent). The sampling time per run must be the same as for Method 6 plus twice the average measurement system response time. If your modified Method 6 train does not include a pump, you risk biasing the results high if you over-pressurize the midget impingers and cause a leak. You can reduce this risk by cautiously increasing the flow rate as sampling begins.

b. After completing a run, record the final dry gas meter reading, meter temperature, and barometric pressure. Recover and analyze the contents of the midget impingers using the procedures in Method 6. Determine the average gas concentration reported by Method 6C for the run.

17.0 References

1. ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards'' September 1997 as amended, EPA–600/R–97/121

18.0 Tables, Diagrams, Flowcharts, and Validation Data

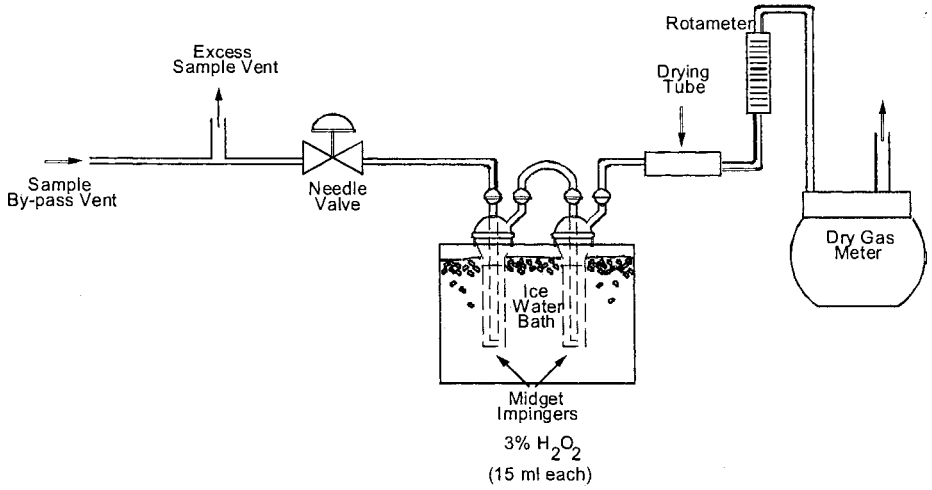

Figure 6C-1. Modified Method 6
Alternative Interference Check Sampling Train

METHOD 7—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1 and Method 5.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–0	2–400 mg/dscm

1.2 Applicability. This method is applicable for the measurement of nitrogen oxides (NO_X) emitted from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sample methods.

2.0 Summary of Method

A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution, and the nitrogen oxides, except nitrous oxide, are measured colorimetrically using the phenoldisulfonic acid (PDS) procedure.

3.0 Definitions [Reserved]

4.0 Interferences

Biased results have been observed when sampling under conditions of high sulfur dioxide concentrations. At or above 2100 ppm SO_2, use five times the H_2O_2 concentration of the Method 7 absorbing solution. Laboratory tests have shown that high concentrations of SO_2 (about 2100 ppm) cause low results in Method 7 and 7A. Increasing the H_2O_2 concentration to five times the original concentration eliminates this bias. However, when no SO_2 is present, increasing the concentration by five times results in a low bias.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs.

5.2.2 Phenoldisulfonic Acid. Irritating to eyes and skin.

5.2.3 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.4 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

5.2.5 Phenol. Poisonous and caustic. Do not handle with bare hands as it is absorbed through the skin.

6.0 Equipment and Supplies

6.1 Sample Collection. A schematic of the sampling train used in performing this method is shown in Figure 7–1. Other grab sampling systems or equipment, capable of measuring sample volume to within 2.0 percent and collecting a sufficient sample volume to allow analytical reproducibility to within 5 percent, will be considered acceptable alternatives, subject to the approval of the Administrator. The following items are required for sample collection:

6.1.1 Probe. Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or heated out-of-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Stainless steel or Teflon tubing may also be used for the probe. Heating is not necessary if the probe remains dry during the purging period.

6.1.2 Collection Flask. Two-liter borosilicate, round bottom flask, with short neck and 24/40 standard taper opening, protected against implosion or breakage.

6.1.3 Flask Valve. T-bore stopcock connected to a 24/40 standard taper joint.

6.1.4 Temperature Gauge. Dial-type thermometer, or other temperature gauge, capable of measuring 1 °C (2 °F) intervals from −5 to 50 °C (23 to 122 °F).

6.1.5 Vacuum Line. Tubing capable of withstanding a vacuum of 75 mm (3 in.) Hg absolute pressure, with ''T'' connection and T-bore stopcock.

6.1.6 Vacuum Gauge. U-tube manometer, 1 meter (39 in.), with 1 mm (0.04 in.) divisions, or other gauge capable of measuring pressure to within 2.5 mm (0.10 in.) Hg.

6.1.7 Pump. Capable of evacuating the collection flask to a pressure equal to or less than 75 mm (3 in.) Hg absolute.

6.1.8 Squeeze Bulb. One-way.

6.1.9 Volumetric Pipette. 25-ml.

6.1.10 Stopcock and Ground Joint Grease. A high-vacuum, high-temperature chlorofluorocarbon grease is required. Halocarbon 25–5S has been found to be effective.

6.1.11 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg. See note in Method 5, section 6.1.2.

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Graduated Cylinder. 50-ml with 1 ml divisions.

6.2.2 Storage Containers. Leak-free polyethylene bottles.

6.2.3 Wash Bottle. Polyethylene or glass.

6.2.4 Glass Stirring Rod.

6.2.5 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

6.3 Analysis. The following items are required for analysis:

6.3.1 Volumetric Pipettes. Two 1-ml, two 2-ml, one 3-ml, one 4-ml, two 10-ml, and one 25-ml for each sample and standard.

6.3.2 Porcelain Evaporating Dishes. 175- to 250-ml capacity with lip for pouring, one for each sample and each standard. The Coors No. 45006 (shallowform, 195-ml) has been found to be satisfactory. Alternatively, polymethyl pentene beakers (Nalge No. 1203, 150-ml), or glass beakers (150-ml) may be used. When glass beakers are used, etching of the beakers may cause solid matter to be present in the analytical step; the solids should be removed by filtration.

6.3.3 Steam Bath. Low-temperature ovens or thermostatically controlled hot plates kept below 70 °C (160 °F) are acceptable alternatives.

6.3.4 Dropping Pipette or Dropper. Three required.

6.3.5 Polyethylene Policeman. One for each sample and each standard.

6.3.6 Graduated Cylinder. 100-ml with 1-ml divisions.

6.3.7 Volumetric Flasks. 50-ml (one for each sample and each standard), 100-ml (one for each sample and each standard, and one for the working standard KNO_3 solution), and 1000-ml (one).

6.3.8 Spectrophotometer. To measure at 410 nm.

6.3.9 Graduated Pipette. 10-ml with 0.1-ml divisions.

6.3.10 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

6.3.11 Analytical Balance. To measure to within 0.1 mg.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. The following reagents are required for sampling:

7.1.1 Water. Deionized distilled to conform to ASTM D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17). The $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.1.2 Absorbing Solution. Cautiously add 2.8 ml concentrated H_2SO_4 to a 1-liter flask partially filled with water. Mix well, and add 6 ml of 3 percent hydrogen peroxide, freshly prepared from 30 percent hydrogen peroxide solution. Dilute to 1 liter of water and mix well. The absorbing solution should be used within 1 week of its preparation. Do not expose to extreme heat or direct sunlight.

7.2 Sample Recovery. The following reagents are required for sample recovery:

7.2.1 Water. Same as in 7.1.1.

7.2.2 Sodium Hydroxide, 1 N. Dissolve 40 g NaOH in water, and dilute to 1 liter.

7.3 Analysis. The following reagents and standards are required for analysis:

7.3.1 Water. Same as in 7.1.1.

7.3.2 Fuming Sulfuric Acid. 15 to 18 percent by weight free sulfur trioxide. HANDLE WITH CAUTION.

7.3.3 Phenol. White solid.

7.3.4 Sulfuric Acid. Concentrated, 95 percent minimum assay.

7.3.5 Potassium Nitrate (KNO_3). Dried at 105 to 110 °C (221 to 230 °F) for a minimum of 2 hours just prior to preparation of standard solution.

7.3.6 Standard KNO_3 Solution. Dissolve exactly 2.198 g of dried KNO_3 in water, and dilute to 1 liter with water in a 1000-ml volumetric flask.

7.3.7 Working Standard KNO_3 Solution. Dilute 10 ml of the standard solution to 100 ml with water. One ml of the working standard solution is equivalent to 100 μg nitrogen dioxide (NO_2).

7.3.8 Phenoldisulfonic Acid Solution. Dissolve 25 g of pure white phenol solid in 150 ml concentrated sulfuric acid on a steam bath. Cool, add 75 ml fuming sulfuric acid (15 to 18 percent by weight free sulfur trioxide—HANDLE WITH CAUTION), and heat at 100 °C (212 °F) for 2 hours. Store in a dark, stoppered bottle.

7.3.9 Concentrated Ammonium Hydroxide.

8.0 Sample Collection, Preservation, Storage and Transport

8.1 Sample Collection.

8.1.1 Flask Volume. The volume of the collection flask and flask valve combination must be known prior to sampling. Assemble the flask and flask valve, and fill with water to the stopcock. Measure the volume of water to ±10 ml. Record this volume on the flask.

8.1.2 Pipette 25 ml of absorbing solution into a sample flask, retaining a sufficient quantity for use in preparing the calibration standards. Insert the flask valve stopper into the flask with the valve in the ''purge'' position. Assemble the sampling train as shown in Figure 7–1, and place the probe at the sampling point. Make sure that all fittings are tight and leak-free, and that all ground glass joints have been greased properly with a high-vacuum, high temperature chlorofluorocarbon-based stopcock grease. Turn the flask valve and the pump valve to their ''evacuate'' positions. Evacuate the flask to 75 mm (3 in.) Hg absolute pressure, or less. Evacuation to a pressure approaching the vapor pressure of water at the existing temperature is desirable. Turn the pump valve to its ''vent'' position, and turn off the pump. Check for leakage by observing the manometer for any pressure fluctuation. (Any variation greater than 10 mm (0.4 in.) Hg over a period of 1 minute is not acceptable, and the flask is not to be used until the leakage problem is corrected. Pressure in the flask is not to exceed 75 mm (3 in.) Hg absolute at the time sampling is commenced.) Record the volume of the flask and valve (V_f), the flask temperature (T_i), and the barometric pressure. Turn the flask valve counterclockwise to its ''purge'' position, and do the same with the pump valve. Purge the probe and the vacuum tube using the squeeze bulb. If condensation occurs in the probe and the flask valve area, heat the probe, and purge until the condensation disappears. Next, turn the pump valve to its ''vent'' position. Turn the flask valve clockwise to its ''evacuate'' position, and record the difference in the mercury levels in the manometer. The absolute internal pressure in the flask (P_i) is equal to the barometric pressure less the manometer reading. Immediately turn the flask valve to the ''sample'' position, and permit the gas to enter the flask until pressures in the flask and sample line (*i.e.*, duct, stack) are equal. This will usually require about 15 seconds; a longer period indicates a plug in the probe, which must be

corrected before sampling is continued. After collecting the sample, turn the flask valve to its ''purge'' position, and disconnect the flask from the sampling train.

8.1.3 Shake the flask for at least 5 minutes.

8.1.4 If the gas being sampled contains insufficient oxygen for the conversion of NO to NO_2 (*e.g.,* an applicable subpart of the standards may require taking a sample of a calibration gas mixture of NO in N_2), then introduce oxygen into the flask to permit this conversion. Oxygen may be introduced into the flask by one of three methods: (1) Before evacuating the sampling flask, flush with pure cylinder oxygen, then evacuate flask to 75 mm (3 in.) Hg absolute pressure or less; or (2) inject oxygen into the flask after sampling; or (3) terminate sampling with a minimum of 50 mm (2 in.) Hg vacuum remaining in the flask, record this final pressure, and then vent the flask to the atmosphere until the flask pressure is almost equal to atmospheric pressure.

8.2 Sample Recovery. Let the flask sit for a minimum of 16 hours, and then shake the contents for 2 minutes.

8.2.1 Connect the flask to a mercury filled U-tube manometer. Open the valve from the flask to the manometer, and record the flask temperature (T_f), the barometric pressure, and the difference between the mercury levels in the manometer. The absolute internal pressure in the flask (P_f) is the barometric pressure less the manometer reading. Transfer the contents of the flask to a leak-free polyethylene bottle. Rinse the flask twice with 5 ml portions of water, and add the rinse water to the bottle. Adjust the pH to between 9 and 12 by adding 1 N NaOH, dropwise (about 25 to 35 drops). Check the pH by dipping a stirring rod into the solution and then touching the rod to the pH test paper. Remove as little material as possible during this step. Mark the height of the liquid level so that the container can be checked for leakage after transport. Label the container to identify clearly its contents. Seal the container for shipping.

9.0 Quality Control

Section	Quality control measure	Effect
10.1	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.

10.0 Calibration and Standardization

10.1 Spectrophotometer.

10.1.1 Optimum Wavelength Determination.

10.1.1.1 Calibrate the wavelength scale of the spectrophotometer every 6 months. The calibration may be accomplished by using an energy source with an intense line emission such as a mercury lamp, or by using a series of glass filters spanning the measuring range of the spectrophotometer. Calibration materials are available commercially and from the National Institute of Standards and Technology. Specific details on the use of such materials should be supplied by the vendor; general information about calibration techniques can be obtained from general reference books on analytical chemistry. The wavelength scale of the spectrophotometer must read correctly within 5 nm at all calibration points; otherwise, repair and recalibrate the spectrophotometer. Once the wavelength scale of the spectrophotometer is in proper calibration, use 410 nm as the optimum wavelength for the measurement of the absorbance of the standards and samples.

10.1.1.2 Alternatively, a scanning procedure may be employed to determine the proper measuring wavelength. If the instrument is a double-beam spectrophotometer, scan the spectrum between 400 and 415 nm using a 200 μg NO_2 standard solution in the sample cell and a blank solution in the reference cell. If a peak does not occur, the spectrophotometer is probably malfunctioning and should be repaired. When a peak is obtained within the 400 to 415 nm range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of absorbance of both the standards and the samples. For a single-beam spectrophotometer, follow the scanning procedure described above, except scan separately the blank and standard solutions. The optimum wavelength shall be the wavelength at which the maximum difference in absorbance between the standard and the blank occurs.

10.1.2 Determination of Spectrophotometer Calibration Factor K_c. Add 0 ml, 2.0 ml, 4.0 ml, 6.0 ml, and 8.0 ml of the KNO_3 working standard solution (1 ml = 100 μg NO_2) to a series of five 50-ml volumetric flasks. To each flask, add 25 ml of absorbing solution and 10 ml water. Add 1 N NaOH to each flask until the pH is between 9 and 12 (about 25 to 35 drops). Dilute to the mark with water. Mix thoroughly, and pipette a 25-ml aliquot of each solution into a separate porcelain evaporating dish. Beginning with the evaporation step, follow the analysis procedure of section 11.2 until the solution has been transferred to the 100-ml volumetric flask and diluted to the mark. Measure the absorbance of each solution at the optimum wavelength as determined in section 10.2.1. This calibration procedure must be repeated on each day that samples are analyzed. Calculate the spectrophotometer calibration factor as shown in section 12.2.

10.1.3 Spectrophotometer Calibration Quality Control. Multiply the absorbance value obtained for each standard by the K_c factor (reciprocal of the least squares slope) to determine the distance each calibration point lies from the theoretical calibration line. The difference between the calculated concentration values and the actual concentrations (*i.e.*, 100, 200, 300, and 400 µg NO_2) should be less than 7 percent for all standards.

10.2 Barometer. Calibrate against a mercury barometer or NIST-traceable barometer prior to the field test.

10.3 Temperature Gauge. Calibrate dial thermometers against mercury-in-glass thermometers. An alternative mercury-free thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

10.4 Vacuum Gauge. Calibrate mechanical gauges, if used, against a mercury manometer such as that specified in section 6.1.6.

10.5 Analytical Balance. Calibrate against standard weights.

11.0 Analytical Procedures

11.1 Sample Loss Check. Note the level of the liquid in the container, and confirm whether any sample was lost during shipment. Note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Preparation. Immediately prior to analysis, transfer the contents of the shipping container to a 50 ml volumetric flask, and rinse the container twice with 5 ml portions of water. Add the rinse water to the flask, and dilute to mark with water; mix thoroughly. Pipette a 25-ml aliquot into the porcelain evaporating dish. Return any unused portion of the sample to the polyethylene storage bottle. Evaporate the 25-ml aliquot to dryness on a steam bath, and allow to cool. Add 2 ml phenoldisulfonic acid solution to the dried residue, and triturate thoroughly with a polyethylene policeman. Make sure the solution contacts all the residue. Add 1 ml water and 4 drops of concentrated sulfuric acid. Heat the solution on a steam bath for 3 minutes with occasional stirring. Allow the solution to cool, add 20 ml water, mix well by stirring, and add concentrated ammonium hydroxide, dropwise, with constant stirring, until the pH is 10 (as determined by pH paper). If the sample contains solids, these must be removed by filtration (centrifugation is an acceptable alternative, subject to the approval of the Administrator) as follows: Filter through Whatman No. 41 filter paper into a 100-ml volumetric flask. Rinse the evaporating dish with three 5-ml portions of water. Filter these three rinses. Wash the filter with at least three 15-ml portions of water. Add the filter washings to the contents of the volumetric flask, and dilute to the mark with water. If solids are absent, the solution can be transferred directly to the 100-ml volumetric flask and diluted to the mark with water.

11.3 Sample Analysis. Mix the contents of the flask thoroughly, and measure the absorbance at the optimum wavelength used for the standards (Section 10.2.1), using the blank solution as a zero reference. Dilute the sample and the blank with equal volumes of water if the absorbance exceeds A_4, the absorbance of the 400-µg NO_2 standard (see section 10.2.2).

12.0 Data Analysis and Calculations

Carry out the calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculations.

12.1 12.1 Nomenclature

A = Absorbance of sample.
A_1 = Absorbance of the 100-µg NO_2 standard.
A_2 = Absorbance of the 200-µg NO_2 standard.
A_3 = Absorbance of the 300-µg NO_2 standard.
A_4 = Absorbance of the 400-µg NO_2 standard.
C = Concentration of NO_X as NO_2, dry basis, corrected to standard conditions, mg/dsm^3 (lb/dscf).
F = Dilution factor (*i.e.*, 25/5, 25/10, *etc.*, required only if sample dilution was needed to reduce the absorbance into the range of the calibration).
K_c = Spectrophotometer calibration factor.
M = Mass of NO_X as NO_2 in gas sample, µg.
P_f = Final absolute pressure of flask, mm Hg (in. Hg).
P_i = Initial absolute pressure of flask, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
T_f = Final absolute temperature of flask, °K (°R).
T_i = Initial absolute temperature of flask, °K (°R).
T_{std} = Standard absolute temperature, 293 °K (528°R).
V_{sc} = Sample volume at standard conditions (dry basis), ml.
V_f = Volume of flask and valve, ml.
V_a = Volume of absorbing solution, 25 ml.

12.2 Spectrophotometer Calibration Factor.

$$K_c = 100\frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^{\,2} + A_2^{\,2} + A_3^{\,2} + A_4^{\,2}} \qquad \text{Eq. 7-1}$$

12.3 Sample Volume, Dry Basis, Corrected to Standard Conditions.

$$V_{sc} = \left(V_f - V_a\right)\frac{T_{std}}{P_{std}}\left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right] \qquad \text{Eq. 7-2}$$

$$= K_1\left(V_f - 25\right)\left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right]$$

Where:

K_1 = 0.3858 °K/mm Hg for metric units,
K_1 = 17.65 °R/in. Hg for English units.

12.4 Total µg NO_2 per sample.

$$m = 2K_c AF \qquad \text{Eq. 7-3}$$

Where:

2 = 50/25, the aliquot factor.

NOTE: If other than a 25-ml aliquot is used for analysis, the factor 2 must be replaced by a corresponding factor.

12.5 Sample Concentration, Dry Basis, Corrected to Standard Conditions.

$$C = K_2\left(m/V_{sc}\right) \qquad \text{Eq. 7-4}$$

Where:

K2 = 10^3 (mg/m^3)/(µg/ml) for metric units,
K_2 = 6.242 × 10^{-5} (lb/scf)/(µg/ml) for English units.

13.0 Method Performance

13.1 Range. The analytical range of the method has been determined to be 2 to 400 milligrams NO_X (as NO_2) per dry standard cubic meter, without having to dilute the sample.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Standard Methods of Chemical Analysis. 6th ed. New York, D. Van Nostrand Co., Inc. 1962. Vol. 1, pp. 329–330.

2. Standard Method of Test for Oxides of Nitrogen in Gaseous Combustion Products (Phenoldisulfonic Acid Procedure). In: 1968 Book of ASTM Standards, Part 26. Philadelphia, PA. 1968. ASTM Designation D 1608–60, pp. 725–729.

3. Jacob, M.B. The Chemical Analysis of Air Pollutants. New York. Interscience Publishers, Inc. 1960. Vol. 10, pp. 351–356.

4. Beatty, R.L., L.B. Berger, and H.H. Schrenk. Determination of Oxides of Nitrogen by the Phenoldisulfonic Acid Method. Bureau of Mines, U.S. Dept. of Interior. R.I. 3687. February 1943.

5. Hamil, H.F. and D.E. Camann. Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Fossil Fuel-Fired Steam Generators). Southwest Research Institute Report for Environmental Protection Agency. Research Triangle Park, NC. October 5, 1973.

6. Hamil, H.F. and R.E. Thomas. Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Nitric Acid Plants). Southwest Research Institute Report for Environmental Protection Agency. Research Triangle Park, NC. May 8, 1974.

7. Stack Sampling Safety Manual (Draft). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC. September 1978.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

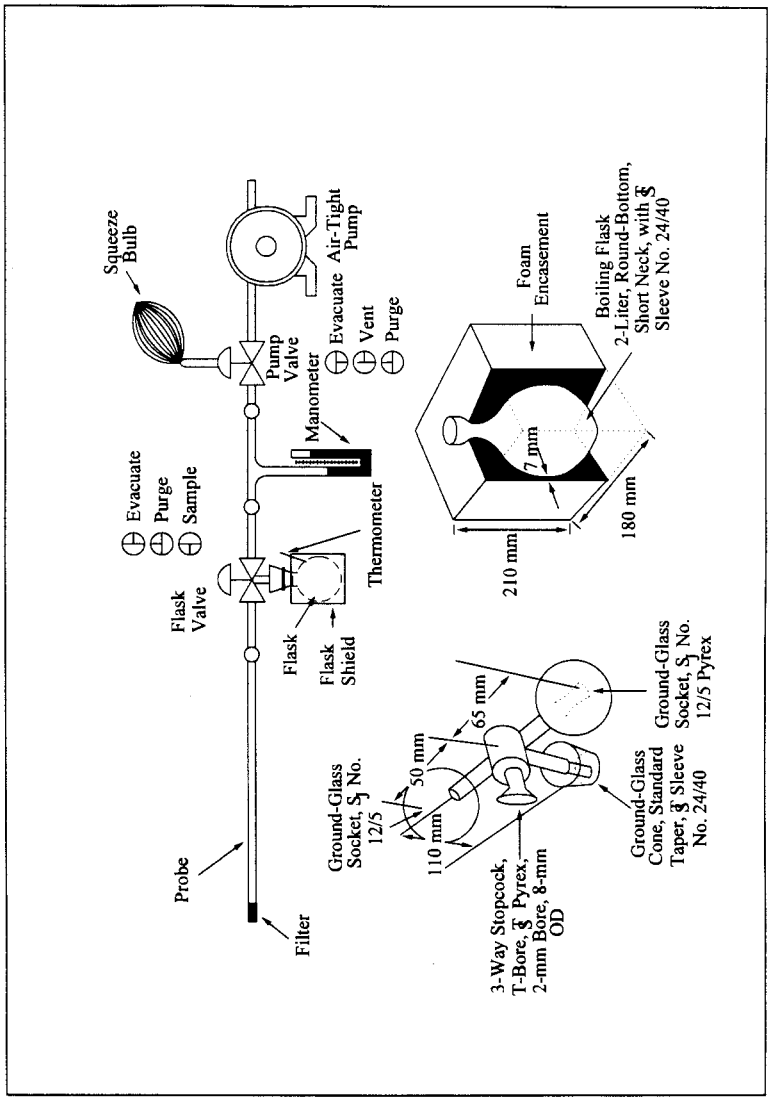

Figure 7-1. Sampling Train, Flask Valve, and Flask.

METHOD 7A—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ION CHROMATOGRAPHIC METHOD)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 3, Method 5, and Method 7.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–0	65–655 ppmv

1.2 Applicability. This method is applicable for the determination of NO_X emissions from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution. The nitrogen oxides, excluding nitrous oxide (N_2O), are oxidized to nitrate and measured by ion chromatography.

3.0 Definitions [Reserved]

4.0 Interferences

Biased results have been observed when sampling under conditions of high sulfur dioxide concentrations. At or above 2100 ppm SO_2, use five times the H_2O_2 concentration of the Method 7 absorbing solution. Laboratory tests have shown that high concentrations of SO_2 (about 2100 ppm) cause low results in Method 7 and 7A. Increasing the H_2O_2 concentration to five times the original concentration eliminates this bias. However, when no SO_2 is present, increasing the concentration by five times results in a low bias.

5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs.

5.2.2 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m^3 will cause lung damage in uninitiated. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as in Method 7, section 6.1.

6.2 Sample Recovery. Same as in Method 7, section 6.2, except the stirring rod and pH paper are not needed.

6.3 Analysis. For the analysis, the following equipment and supplies are required. Alternative instrumentation and procedures will be allowed provided the calibration precision requirement in section 10.1.2 can be met.

6.3.1 Volumetric Pipets. Class A;1-, 2-, 4-, 5-ml (two for the set of standards and one per sample), 6-, 10-, and graduated 5-ml sizes.

6.3.2 Volumetric Flasks. 50-ml (two per sample and one per standard), 200-ml, and 1-liter sizes.

6.3.3 Analytical Balance. To measure to within 0.1 mg.

6.3.4 Ion Chromatograph. The ion chromatograph should have at least the following components:

6.3.4.1 Columns. An anion separation or other column capable of resolving the nitrate ion from sulfate and other species present and a standard anion suppressor column (optional). Suppressor columns are produced as proprietary items; however, one can be produced in the laboratory using the resin available from BioRad Company, 32nd and Griffin Streets, Richmond, California. Peak resolution can be optimized by varying the eluent strength or column flow rate, or by experimenting with alternative columns that may offer more efficient separation. When using guard columns with the stronger reagent to protect the separation column, the analyst should allow rest periods between injection intervals to purge possible sulfate buildup in the guard column.

6.3.4.2 Pump. Capable of maintaining a steady flow as required by the system.

6.3.4.3 Flow Gauges. Capable of measuring the specified system flow rate.

6.3.4.4 Conductivity Detector.

6.3.4.5 Recorder. Compatible with the output voltage range of the detector.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 7, section 7.1.

7.2 Sample Recovery. Same as Method 7, section 7.1.1.

7.3 Analysis. The following reagents and standards are required for analysis:

7.3.1 Water. Same as Method 7, section 7.1.1.

7.3.2 Stock Standard Solution, 1 mg NO_2/ml. Dry an adequate amount of sodium nitrate ($NaNO_3$) at 105 to 110 °C (221 to 230 °F) for a minimum of 2 hours just before preparing the standard solution. Then dissolve exactly 1.847 g of dried $NaNO_3$ in water, and dilute to 1 liter in a volumetric flask. Mix well. This solution is stable for 1 month and should not be used beyond this time.

7.3.3 Working Standard Solution, 25 μg/ml. Dilute 5 ml of the standard solution to 200 ml with water in a volumetric flask, and mix well.

7.3.4 Eluent Solution. Weigh 1.018 g of sodium carbonate (Na_2CO_3) and 1.008 g of sodium bicarbonate ($NaHCO_3$), and dissolve in 4 liters of water. This solution is 0.0024 M Na_2CO_3/0.003 M $NaHCO_3$. Other eluents appropriate to the column type and capable of resolving nitrate ion from sulfate and other species present may be used.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling. Same as in Method 7, section 8.1.

8.2 Sample Recovery. Same as in Method 7, section 8.2, except delete the steps on adjusting and checking the pH of the sample. Do not store the samples more than 4 days between collection and analysis.

9.0 Quality Control

Section	Quality control measure	Effect
10.1	Ion chromatographn calibration	Ensure linearity of ion chromatograph response to standards.

10.0 Calibration and Standardizations

10.1 Ion Chromatograph.

10.1.1 Determination of Ion Chromatograph Calibration Factor S. Prepare a series of five standards by adding 1.0, 2.0, 4.0, 6.0, and 10.0 ml of working standard solution (25 μg/ml) to a series of five 50-ml volumetric flasks. (The standard masses will equal 25, 50, 100, 150, and 250 μg.) Dilute each flask to the mark with water, and mix well. Analyze with the samples as described in section 11.2, and subtract the blank from each value. Prepare or calculate a linear regression plot of the standard masses in μg (x-axis) versus their peak height responses in millimeters (y-axis). (Take peak height measurements with symmetrical peaks; in all other cases, calculate peak areas.) From this curve, or equation, determine the slope, and calculate its reciprocal to denote as the calibration factor, S.

10.1.2 Ion Chromatograph Calibration Quality Control. If any point on the calibration curve deviates from the line by more than 7 percent of the concentration at that point, remake and reanalyze that standard. This deviation can be determined by multiplying S times the peak height response for each standard. The resultant concentrations must not differ by more than 7 percent from each known standard mass (*i.e.*, 25, 50, 100, 150, and 250 μg).

10.2 Conductivity Detector. Calibrate according to manufacturer's specifications prior to initial use.

10.3 Barometer. Calibrate against a mercury barometer.

10.4 Temperature Gauge. Calibrate dial thermometers against mercury-in-glass thermometers. An alternative mercury-free thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

10.5 Vacuum Gauge. Calibrate mechanical gauges, if used, against a mercury manometer such as that specified in section 6.1.6 of Method 7.

10.6 Analytical Balance. Calibrate against standard weights.

11.0 Analytical Procedures

11.1 Sample Preparation.

11.1.1 Note on the analytical data sheet, the level of the liquid in the container, and whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Immediately before analysis, transfer the contents of the shipping container to a 50-ml volumetric flask, and rinse the container twice with 5 ml portions of water. Add the rinse water to the flask, and dilute to the mark with water. Mix thoroughly.

11.1.2 Pipet a 5-ml aliquot of the sample into a 50-ml volumetric flask, and dilute to the mark with water. Mix thoroughly. For each set of determinations, prepare a reagent

blank by diluting 5 ml of absorbing solution to 50 ml with water. (Alternatively, eluent solution may be used instead of water in all sample, standard, and blank dilutions.)

11.2 Analysis.

11.2.1 Prepare a standard calibration curve according to section 10.1.1. Analyze the set of standards followed by the set of samples using the same injection volume for both standards and samples. Repeat this analysis sequence followed by a final analysis of the standard set. Average the results. The two sample values must agree within 5 percent of their mean for the analysis to be valid. Perform this duplicate analysis sequence on the same day. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

11.2.2 Document each sample chromatogram by listing the following analytical parameters: injection point, injection volume, nitrate and sulfate retention times, flow rate, detector sensitivity setting, and recorder chart speed.

12.0 Data Analysis and Calculations

Carry out the calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculations.

12.1 Sample Volume. Calculate the sample volume Vsc (in ml), on a dry basis, corrected to standard conditions, using Equation 7–2 of Method 7.

12.2 Sample Concentration of NO_X as NO_2.

12.2.1 Calculate the sample concentration C (in mg/dscm) as follows:

$$C = (H)(S)(F)\left(10^4\right)/V_{sc} \qquad \text{Eq. 7A-1}$$

Where:

H = Sample peak height, mm.

S = Calibration factor, µg/mm.

F = Dilution factor (required only if sample dilution was needed to reduce the concentration into the range of calibration), dimensionless.

10^4 = 1:10 dilution times conversion factor of: $(mg/10^3\ \mu g)(10^6\ ml/m^3)$.

12.2.2 If desired, the concentration of NO_2 may be calculated as ppm NO_2 at standard conditions as follows:

$$\text{ppm } NO_2 = 0.5228C \qquad \text{Eq. 7A-2}$$

Where:

0.5228 = ml/mg NO_2.

13.0 Method Performance

13.1 Range. The analytical range of the method is from 125 to 1250 mg NO_X/m^3 as NO_2 (65 to 655 ppmv), and higher concentrations may be analyzed by diluting the sample. The lower detection limit is approximately 19 mg/m^3 (10 ppmv), but may vary among instruments.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Mulik, J.D., and E. Sawicki. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor, Ann Arbor Science Publishers, Inc. Vol. 2, 1979.

2. Sawicki, E., J.D. Mulik, and E. Wittgenstein. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor, Ann Arbor Science Publishers, Inc. Vol. 1. 1978.

3. Siemer, D.D. Separation of Chloride and Bromide from Complex Matrices Prior to Ion Chromatographic Determination. Anal. Chem. *52*(12):1874–1877. October 1980.

4. Small, H., T.S. Stevens, and W.C. Bauman. Novel Ion Exchange Chromatographic Method Using Conductimetric Determination. Anal. Chem. *47*(11):1801. 1975.

5. Yu, K.K., and P.R. Westlin. Evaluation of Reference Method 7 Flask Reaction Time. Source Evaluation Society Newsletter. *4*(4). November 1979. 10 pp.

6. Stack Sampling Safety Manual (Draft). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standard, Research Triangle Park, NC. September 1978.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 7B—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ULTRAVIOLET SPECTROPHOTOMETRIC METHOD)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 5, and Method 7.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		

Analyte	CAS No.	Sensitivity
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–0	30–786 ppmv

1.2 Applicability. This method is applicable for the determination of NO_X emissions from nitric acid plants.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution; the NO_X, excluding nitrous oxide (N_2O), are measured by ultraviolet spectrophotometry.

3.0 Definition [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m^3 will cause lung damage in uninitiated. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 7, section 6.1.

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Wash Bottle. Polyethylene or glass.

6.2.2 Volumetric Flasks. 100-ml (one for each sample).

6.3 Analysis. The following items are required for analysis:

6.3.1 Volumetric Pipettes. 5-, 10-, 15-, and 20-ml to make standards and sample dilutions.

6.3.2 Volumetric Flasks. 1000- and 100-ml for preparing standards and dilution of samples.

6.3.3 Spectrophotometer. To measure ultraviolet absorbance at 210 nm.

6.3.4 Analytical Balance. To measure to within 0.1 mg.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents are to conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 7, section 7.1. It is important that the amount of hydrogen peroxide in the absorbing solution not be increased. Higher concentrations of peroxide may interfere with sample analysis.

7.2 Sample Recovery. Same as Method 7, section 7.2.

7.3 Analysis. Same as Method 7, sections 7.3.1, 7.3.3, and 7.3.4, with the addition of the following:

7.3.1 Working Standard KNO_3 Solution. Dilute 10 ml of the standard solution to 1000 ml with water. One milliliter of the working standard is equivalent to 10 μg NO_2.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sample Collection. Same as Method 7, section 8.1.

8.2 Sample Recovery.

8.2.1 Let the flask sit for a minimum of 16 hours, and then shake the contents for 2 minutes.

8.2.2 Connect the flask to a mercury filled U-tube manometer. Open the valve from the flask to the manometer, and record the flask temperature (T_f), the barometric pressure, and the difference between the mercury levels in the manometer. The absolute internal pressure in the flask (P_f) is the barometric pressure less the manometer reading.

8.2.3 Transfer the contents of the flask to a leak-free wash bottle. Rinse the flask three times with 10-ml portions of water, and add

to the bottle. Mark the height of the liquid level so that the container can be checked for leakage after transport. Label the container to identify clearly its contents. Seal the container for shipping.

9.0 Quality Control

Section	Quality control measure	Effect
10.1	Spectrophotometer calibration	Ensures linearity of spectrophotometer response to standards.

10.0 Calibration and Standardizations

Same as Method 7, sections 10.2 through 10.5, with the addition of the following:

10.1 Determination of Spectrophotometer Standard Curve. Add 0 ml, 5 ml, 10 ml, 15 ml, and 20 ml of the KNO_3 working standard solution (1 ml = 10 µg NO_2) to a series of five 100-ml volumetric flasks. To each flask, add 5 ml of absorbing solution. Dilute to the mark with water. The resulting solutions contain 0.0, 50, 100, 150, and 200 µg NO_2, respectively. Measure the absorbance by ultraviolet spectrophotometry at 210 nm, using the blank as a zero reference. Prepare a standard curve plotting absorbance vs. µg NO_2.

NOTE: If other than a 20-ml aliquot of sample is used for analysis, then the amount of absorbing solution in the blank and standards must be adjusted such that the same amount of absorbing solution is in the blank and standards as is in the aliquot of sample used.

10.1.1 Calculate the spectrophotometer calibration factor as follows:

$$K_c = \frac{\sum_{i=1}^{n} M_i A_i}{\sum_{i=1}^{n} A_i^2} \qquad \text{Eq. 7B-1}$$

Where:

Mi = Mass of NO_2 in standard i, µg.
Ai = Absorbance of NO_2 standard i.
n = Total number of calibration standards.

10.1.2 For the set of calibration standards specified here, Equation 7B–1 simplifies to the following:

$$K_c = 50\frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2} \qquad \text{Eq. 7B-2}$$

10.2 Spectrophotometer Calibration Quality Control. Multiply the absorbance value obtained for each standard by the K_c factor (reciprocal of the least squares slope) to determine the distance each calibration point lies from the theoretical calibration line. The difference between the calculated concentration values and the actual concentrations (*i.e.*, 50, 100, 150, and 200 µg NO_2) should be less than 7 percent for all standards.

11.0 Analytical Procedures

11.1 Sample Loss Check. Note the level of the liquid in the container, and confirm whether any sample was lost during shipment. Note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Preparation. Immediately prior to analysis, transfer the contents of the shipping container to a 100-ml volumetric flask, and rinse the container twice with 5-ml portions of water. Add the rinse water to the flask, and dilute to mark with water.

11.3 Sample Analysis. Mix the contents of the flask thoroughly and pipette a 20 ml-aliquot of sample into a 100-ml volumetric flask. Dilute to the mark with water. Using the blank as zero reference, read the absorbance of the sample at 210 nm.

11.4 Audit Sample Analysis. Same as Method 7, section 11.4, except that a set of audit samples must be analyzed with each set of compliance samples or once per analysis day, or once per week when averaging continuous samples.

12.0 Data Analysis and Calculations

Same as Method 7, section 12.0, except replace section 12.3 with the following:

12.1 Total µg NO_2 Per Sample.

$$m = 5\,K_c\,A\,F \qquad \text{Eq. 7B-3}$$

Where:

5 = 100/20, the aliquot factor.

NOTE: If other than a 20-ml aliquot is used for analysis, the factor 5 must be replaced by a corresponding factor.

13.0 Method Performance

13.1 Range. The analytical range of the method as outlined has been determined to be 57 to 1500 milligrams NO_X (as NO_2) per dry standard cubic meter, or 30 to 786 parts per million by volume (ppmv) NO_X.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. National Institute for Occupational Safety and Health. Recommendations for Occupational Exposure to Nitric Acid. In: Occupational Safety and Health Reporter. Washington, D.C. Bureau of National Affairs, Inc. 1976. p. 149.

2. Rennie, P.J., A.M. Sumner, and F.B. Basketter. Determination of Nitrate in Raw, Potable, and Waste Waters by Ultraviolet Spectrophotometry. Analyst. *104*:837. September 1979.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 7C—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ALKALINE PERMANGANATE/COLORIMETRIC METHOD)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 3, Method 6 and Method 7.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS no.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–07	ppmv

1.2 Applicability. This method applies to the measurement of NO_X emissions from fossil-fuel fired steam generators, electric utility plants, nitric acid plants, or other sources as specified in the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

An integrated gas sample is extracted from the stack and passed through impingers containing an alkaline potassium permanganate solution; NO_X (NO + NO_2) emissions are oxidized to NO_2 and NO_3. Then NO_3^- is reduced to NO_2^- with cadmium, and the NO_2^- is analyzed colorimetrically.

3.0 Definitions [Reserved]

4.0 Interferences

Possible interferents are sulfur dioxides (SO_2) and ammonia (NH_3).

4.1 High concentrations of SO_2 could interfere because SO_2 consumes MnO_4 (as does NO_X) and, therefore, could reduce the NO_X collection efficiency. However, when sampling emissions from a coal-fired electric utility plant burning 2.1 percent sulfur coal with no control of SO_2 emissions, collection efficiency was not reduced. In fact, calculations show that sampling 3000 ppm SO_2 will reduce the MnO_4 concentration by only 5 percent if all the SO_2 is consumed in the first impinger.

4.2 Ammonia (NH_3) is slowly oxidized to NO_3^- by the absorbing solution. At 100 ppm NH_3 in the gas stream, an interference of 6 ppm NO_X (11 mg NO_2/m^3) was observed when the sample was analyzed 10 days after collection. Therefore, the method may not be applicable to plants using NH_3 injection to control NO_X emissions unless means are taken to correct the results. An equation has been developed to allow quantification of the interference and is discussed in Reference 5 of section 16.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrochloric Acid (HCl). Highly toxic and corrosive. Causes severe damage to skin. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to vapor concentrations of 0.13 to 0.2 percent can be lethal in minutes. Will react with metals, producing hydrogen.

5.2.2 Oxalic Acid $(COOH)_2$. Poisonous. Irritating to eyes, skin, nose, and throat.

5.2.3 Sodium Hydroxide (NaOH). Causes severe damage to eye tissues and to skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with small amounts of water.

5.2.4 Potassium Permanganate ($KMnO_4$). Caustic, strong oxidizer. Avoid bodily contact with.

6.0 Equipment and Supplies

6.1 Sample Collection and Sample Recovery. A schematic of the Method 7C sampling train is shown in Figure 7C–1, and component parts are discussed below. Alternative apparatus and procedures are allowed provided acceptable accuracy and precision can be demonstrated to the satisfaction of the Administrator.

6.1.1 Probe. Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or heated out-of-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Stainless steel or Teflon tubing may also be used for the probe.

6.1.2 Impingers. Three restricted-orifice glass impingers, having the specifications given in Figure 7C–2, are required for each sampling train. The impingers must be connected in series with leak-free glass connectors. Stopcock grease may be used, if necessary, to prevent leakage. (The impingers can be fabricated by a glass blower if not available commercially.)

6.1.3 Glass Wool, Stopcock Grease, Drying Tube, Valve, Pump, Barometer, and Vacuum Gauge and Rotameter. Same as in Method 6, sections 6.1.1.3, 6.1.1.4, 6.1.1.6, 6.1.1.7, 6.1.1.8, 6.1.2, and 6.1.3, respectively.

6.1.4 Rate Meter. Rotameter, or equivalent, accurate to within 2 percent at the selected flow rate of between 400 and 500 ml/min (0.014 to 0.018 cfm). For rotameters, a range of 0 to 1 liter/min (0 to 0.035 cfm) is recommended.

6.1.5 Volume Meter. Dry gas meter (DGM) capable of measuring the sample volume under the sampling conditions of 400 to 500 ml/min (0.014 to 0.018 cfm) for 60 minutes within an accuracy of 2 percent.

6.1.6 Filter. To remove NO_X from ambient air, prepared by adding 20 g of 5-angstrom molecular sieve to a cylindrical tube (*e.g.*, a polyethylene drying tube).

6.1.7 Polyethylene Bottles. 1-liter, for sample recovery.

6.1.8 Funnel and Stirring Rods. For sample recovery.

6.2 Sample Preparation and Analysis.

6.2.1 Hot Plate. Stirring type with 50- by 10-mm Teflon-coated stirring bars.

6.2.2 Beakers. 400-, 600-, and 1000-ml capacities.

6.2.3 Filtering Flask. 500-ml capacity with side arm.

6.2.4 Buchner Funnel. 75-mm ID, with spout equipped with a 13-mm ID by 90-mm long piece of Teflon tubing to minimize possibility of aspirating sample solution during filtration.

6.2.5 Filter Paper. Whatman GF/C, 7.0-cm diameter.

6.2.6 Stirring Rods.

6.2.7 Volumetric Flasks. 100-, 200- or 250-, 500-, and 1000-ml capacity.

6.2.8 Watch Glasses. To cover 600- and 1000-ml beakers.

6.2.9 Graduated Cylinders. 50- and 250-ml capacities.

6.2.10 Pipettes. Class A.

6.2.11 pH Meter. To measure pH from 0.5 to 12.0.

6.2.12 Burette. 50-ml with a micrometer type stopcock. (The stopcock is Catalog No. 8225–t–05, Ace Glass, Inc., Post Office Box 996, Louisville, Kentucky 50201.) Place a glass wool plug in bottom of burette. Cut off burette at a height of 43 cm (17 in.) from the top of plug, and have a blower attach a glass funnel to top of burette such that the diameter of the burette remains essentially unchanged. Other means of attaching the funnel are acceptable.

6.2.13 Glass Funnel. 75-mm ID at the top.

6.2.14 Spectrophotometer. Capable of measuring absorbance at 540 nm; 1-cm cells are adequate.

6.2.15 Metal Thermometers. Bimetallic thermometers, range 0 to 150 °C (32 to 300 °F).

6.2.16 Culture Tubes. 20-by 150-mm, Kimax No. 45048.

6.2.17 Parafilm ''M.'' Obtained from American Can Company, Greenwich, Connecticut 06830.

6.2.18 CO_2 Measurement Equipment. Same as in Method 3, section 6.0.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection.

7.1.1 Water. Deionized distilled to conform to ASTM Specification D 1193–77 or 91 Type 3 (incorporated by reference—see § 60.17).

7.1.2 Potassium Permanganate, 4.0 Percent (w/w), Sodium Hydroxide, 2.0 Percent (w/w) solution ($KMnO_4$/NaOH solution). Dissolve 40.0 g of $KMnO_4$ and 20.0 g of NaOH in 940 ml of water.

7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in section 7.1.1.

7.2.2 Oxalic Acid Solution. Dissolve 48 g of oxalic acid [$(COOH)_2 \cdot 2H_2O$] in water, and dilute to 500 ml. Do not heat the solution.

7.2.3 Sodium Hydroxide, 0.5 N. Dissolve 20 g of NaOH in water, and dilute to 1 liter.

7.2.4 Sodium Hydroxide, 10 N. Dissolve 40 g of NaOH in water, and dilute to 100 ml.

7.2.5 Ethylenediamine Tetraacetic Acid (EDTA) Solution, 6.5 percent (w/v). Dissolve 6.5 g of EDTA (disodium salt) in water, and dilute to 100 ml. Dissolution is best accomplished by using a magnetic stirrer.

7.2.6 Column Rinse Solution. Add 20 ml of 6.5 percent EDTA solution to 960 ml of water, and adjust the pH to between 11.7 and 12.0 with 0.5 N NaOH.

7.2.7 Hydrochloric Acid (HCl), 2 N. Add 86 ml of concentrated HCl to a 500 ml-volumetric flask containing water, dilute to volume, and mix well. Store in a glass-stoppered bottle.

7.2.8 Sulfanilamide Solution. Add 20 g of sulfanilamide (melting point 165 to 167 °C (329 to 333 °F)) to 700 ml of water. Add, with mixing, 50 ml concentrated phosphoric acid (85 percent), and dilute to 1000 ml. This solution is stable for at least 1 month, if refrigerated.

7.2.9 N-(1-Naphthyl)-Ethylenediamine Dihydrochloride (NEDA) Solution. Dissolve 0.5 g of NEDA in 500 ml of water. An aqueous solution should have one absorption peak at 320 nm over the range of 260 to 400 nm. NEDA that shows more than one absorption peak over this range is impure and should not be used. This solution is stable for at least 1 month if protected from light and refrigerated.

7.2.10 Cadmium. Obtained from Matheson Coleman and Bell, 2909 Highland Avenue, Norwood, Ohio 45212, as EM Laboratories Catalog No. 2001. Prepare by rinsing in 2 N HCl for 5 minutes until the color is silver-grey. Then rinse the cadmium with water until the rinsings are neutral when tested with pH paper. CAUTION: H_2 is liberated during preparation. Prepare in an exhaust hood away from any flame or combustion source.

7.2.11 Sodium Sulfite ($NaNO_2$) Standard Solution, Nominal Concentration, 1000 μg NO_2^-/ml. Desiccate NaNO2 overnight. Accurately weigh 1.4 to 1.6 g of $NaNO_2$ (assay of 97 percent $NaNO_2$ or greater), dissolve in water, and dilute to 1 liter. Calculate the exact NO_2^- concentration using Equation 7C–1 in section 12.2. This solution is stable for at least 6 months under laboratory conditions.

7.2.12 Potassium Nitrate (KNO_3) Standard Solution. Dry KNO_3 at 110 °C (230 °F) for 2 hours, and cool in a desiccator. Accurately weigh 9 to 10 g of KNO_3 to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact NO_3^- concentration using Equation 7C–2 in section 12.3. This solution is stable for 2 months without preservative under laboratory conditions.

7.2.13 Spiking Solution. Pipette 7 ml of the KNO_3 standard into a 100-ml volumetric flask, and dilute to volume.

7.2.14 Blank Solution. Dissolve 2.4 g of $KMnO_4$ and 1.2 g of NaOH in 96 ml of water. Alternatively, dilute 60 ml of $KMnO_4$/NaOH solution to 100 ml.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Preparation of Sampling Train. Add 200 ml of $KMnO_4$/NaOH solution (Section 7.1.2) to each of three impingers, and assemble the train as shown in Figure 7C–1. Adjust the probe heater to a temperature sufficient to prevent water condensation.

8.2 Leak-Checks. Same as in Method 6, section 8.2.

8.3 Sample Collection.

8.3.1 Record the initial DGM reading and barometric pressure. Determine the sampling point or points according to the appropriate regulations (*e.g.*, §60.46(b)(5) of 40 CFR Part 60). Position the tip of the probe at the sampling point, connect the probe to the first impinger, and start the pump. Adjust the sample flow to a value between 400 and 500 ml/min (0.014 and 0.018 cfm). CAUTION: DO NOT EXCEED THESE FLOW RATES. Once adjusted, maintain a constant flow rate during the entire sampling run. Sample for 60 minutes. For relative accuracy (RA) testing of continuous emission monitors, the minimum sampling time is 1 hour, sampling 20 minutes at each traverse point.

NOTE: When the SO_2 concentration is greater than 1200 ppm, the sampling time may have to be reduced to 30 minutes to eliminate plugging of the impinger orifice with MnO_2. For RA tests with SO_2 greater than 1200 ppm, sample for 30 minutes (10 minutes at each point).

8.3.2 Record the DGM temperature, and check the flow rate at least every 5 minutes. At the conclusion of each run, turn off the pump, remove the probe from the stack, and record the final readings. Divide the sample volume by the sampling time to determine the average flow rate. Conduct the mandatory post-test leak-check. If a leak is found, void the test run, or use procedures acceptable to the Administrator to adjust the sample volume for the leakage.

8.4 CO_2 Measurement. During sampling, measure the CO_2 content of the stack gas near the sampling point using Method 3. The single-point grab sampling procedure is adequate, provided the measurements are made at least three times (near the start, midway, and before the end of a run), and the average CO_2 concentration is computed. The Orsat or Fyrite analyzer may be used for this analysis.

8.5 Sample Recovery. Disconnect the impingers. Pour the contents of the impingers into a 1-liter polyethylene bottle

using a funnel and a stirring rod (or other means) to prevent spillage. Complete the quantitative transfer by rinsing the impingers and connecting tubes with water until the rinsings are clear to light pink, and add the rinsings to the bottle. Mix the sample, and mark the solution level. Seal and identify the sample container.

9.0 Quality Control

Section	Quality control measure	Effect
8.2, 10.1–10.3	Sampling equipment leak-check and calibration.	Ensure accurate measurement of sample volume.
10.4	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards
11.3	Spiked sample analysis.	Ensure reduction efficiency of column.

10.0 Calibration and Standardizations

10.1 Volume Metering System. Same as Method 6, section 10.1. For detailed instructions on carrying out these calibrations, it is suggested that section 3.5.2 of Reference 4 of section 16.0 be consulted.

10.2 Temperature Sensors and Barometer. Same as in Method 6, sections 10.2 and 10.4, respectively.

10.3 Check of Rate Meter Calibration Accuracy (Optional). Disconnect the probe from the first impinger, and connect the filter. Start the pump, and adjust the rate meter to read between 400 and 500 ml/min (0.014 and 0.018 cfm). After the flow rate has stabilized, start measuring the volume sampled, as recorded by the dry gas meter and the sampling time. Collect enough volume to measure accurately the flow rate. Then calculate the flow rate. This average flow rate must be less than 500 ml/min (0.018 cfm) for the sample to be valid; therefore, it is recommended that the flow rate be checked as above prior to each test.

10.4 Spectrophotometer.

10.4.1 Dilute 5.0 ml of the $NaNO_2$ standard solution to 200 ml with water. This solution nominally contains 25 μg NO_2^-/ml. Use this solution to prepare calibration standards to cover the range of 0.25 to 3.00 μg NO_2^-/ml. Prepare a minimum of three standards each for the linear and slightly nonlinear (described below) range of the curve. Use pipettes for all additions.

10.4.2 Measure the absorbance of the standards and a water blank as instructed in section 11.5. Plot the net absorbance vs. μg NO_2^-/ml. Draw a smooth curve through the points. The curve should be linear up to an absorbance of approximately 1.2 with a slope of approximately 0.53 absorbance units/μg NO_2^-/ml. The curve should pass through the origin. The curve is slightly nonlinear from an absorbance of 1.2 to 1.6.

11.0 Analytical Procedures

11.1 Sample Stability. Collected samples are stable for at least four weeks; thus, analysis must occur within 4 weeks of collection.

11.2 Sample Preparation.

11.2.1 Prepare a cadmium reduction column as follows: Fill the burette with water. Add freshly prepared cadmium slowly, with tapping, until no further settling occurs. The height of the cadmium column should be 39 cm (15 in). When not in use, store the column under rinse solution.

NOTE: The column should not contain any bands of cadmium fines. This may occur if regenerated cadmium is used and will greatly reduce the column lifetime.

11.2.2 Note the level of liquid in the sample container, and determine whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume lost can be determined from the difference between initial and final solution levels, and this value can then be used to correct the analytical result. Quantitatively transfer the contents to a 1-liter volumetric flask, and dilute to volume.

11.2.3 Take a 100-ml aliquot of the sample and blank (unexposed $KMnO_4$/NaOH) solutions, and transfer to 400-ml beakers containing magnetic stirring bars. Using a pH meter, add concentrated H_2SO_4 with stirring until a pH of 0.7 is obtained. Allow the solutions to stand for 15 minutes. Cover the beakers with watch glasses, and bring the temperature of the solutions to 50 °C (122 °F). Keep the temperature below 60 °C (140 °F). Dissolve 4.8 g of oxalic acid in a minimum volume of water, approximately 50 ml, at room temperature. Do not heat the solution. Add this solution slowly, in increments, until the $KMnO_4$ solution becomes colorless. If the color is not completely removed, prepare some more of the above oxalic acid solution, and add until a colorless solution is obtained. Add an excess of oxalic acid by dissolving 1.6 g of oxalic acid in 50 ml of water, and add 6 ml of this solution to the colorless solution. If suspended matter is present, add concentrated H_2SO_4 until a clear solution is obtained.

11.2.4 Allow the samples to cool to near room temperature, being sure that the samples are still clear. Adjust the pH to between 11.7 and 12.0 with 10 N NaOH. Quantitatively transfer the mixture to a Buchner funnel containing GF/C filter paper, and filter the

precipitate. Filter the mixture into a 500-ml filtering flask. Wash the solid material four times with water. When filtration is complete, wash the Teflon tubing, quantitatively transfer the filtrate to a 500-ml volumetric flask, and dilute to volume. The samples are now ready for cadmium reduction. Pipette a 50-ml aliquot of the sample into a 150-ml beaker, and add a magnetic stirring bar. Pipette in 1.0 ml of 6.5 percent EDTA solution, and mix.

11.3 Determine the correct stopcock setting to establish a flow rate of 7 to 9 ml/min of column rinse solution through the cadmium reduction column. Use a 50-ml graduated cylinder to collect and measure the solution volume. After the last of the rinse solution has passed from the funnel into the burette, but before air entrapment can occur, start adding the sample, and collect it in a 250-ml graduated cylinder. Complete the quantitative transfer of the sample to the column as the sample passes through the column. After the last of the sample has passed from the funnel into the burette, start adding 60 ml of column rinse solution, and collect the rinse solution until the solution just disappears from the funnel. Quantitatively transfer the sample to a 200-ml volumetric flask (a 250-ml flask may be required), and dilute to volume. The samples are now ready for NO_2-analysis.

NOTE: Two spiked samples should be run with every group of samples passed through the column. To do this, prepare two additional 50-ml aliquots of the sample suspected to have the highest NO_2-concentration, and add 1 ml of the spiking solution to these aliquots. If the spike recovery or column efficiency (see section 12.2) is below 95 percent, prepare a new column, and repeat the cadmium reduction.

11.5 Sample Analysis. Pipette 10 ml of sample into a culture tube. Pipette in 10 ml of sulfanilamide solution and 1.4 ml of NEDA solution. Cover the culture tube with parafilm, and mix the solution. Prepare a blank in the same manner using the sample from treatment of the unexposed $KMnO_4$/NaOH solution. Also, prepare a calibration standard to check the slope of the calibration curve. After a 10-minute color development interval, measure the absorbance at 540 nm against water. Read μg NO_2^-/ml from the calibration curve. If the absorbance is greater than that of the highest calibration standard, use less than 10 ml of sample, and repeat the analysis. Determine the NO_2^-concentration using the calibration curve obtained in section 10.4.

NOTE: Some test tubes give a high blank NO_2^- value but culture tubes do not.

11.6 Audit Sample Analysis. Same as in Method 7, section 11.4.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature.

B = Analysis of blank, μg NO_2^-/ml.
C = Concentration of NO_X as NO_2, dry basis, mg/dsm³.
E = Column efficiency, dimensionless
$K_2 = 10^{-3}$ mg/μg.
m = Mass of NO_X, as NO_2, in sample, μg.
P_{bar} = Barometric pressure, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
s = Concentration of spiking solution, μg NO_3/ml.
S = Analysis of sample, μg NO_2^-/ml.
T_m = Average dry gas meter absolute temperature, °K.
T_{std} = Standard absolute temperature, 293 °K (528 °R).
$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).
V_m = Dry gas volume as measured by the dry gas meter, scm (scf).
x = Analysis of spiked sample, μg NO_2^-/ml.
X = Correction factor for CO_2 collection = $100/(100 - \%CO_2(V/V))$.
y = Analysis of unspiked sample, μg NO_2^-/ml.
Y = Dry gas meter calibration factor.
1.0 ppm NO = 1.247 mg NO/m³ at STP.
1.0 ppm NO_2 = 1.912 mg NO_2/m³ at STP.
1 ft³ = 2.832×10^{-2} m³.

12.2 NO_2 Concentration. Calculate the NO_2 concentration of the solution (see section 7.2.11) using the following equation:

$$\frac{\mu g\ NO_2^-}{ml} = g\ NaNO_2 \times \frac{purity,\ \%}{100} \times 10^3 \times \frac{46.01}{69.01} \qquad \text{Eq. 7C-1}$$

12.3 NO_3 Concentration. Calculate the NO_3 concentration of the KNO_3 solution (see section 7.2.12) using the following equation:

$$\frac{\mu g\ NO_3^-}{ml} = g\ KNO_3 \times \left(10^3\right) \times \frac{62.01}{101.10} \qquad \text{Eq. 7C-2}$$

12.4 Sample Volume, Dry Basis, Corrected to Standard Conditions.

$$V_{m(std)} = V_m\ X\ Y \frac{T_{std}}{T_m} \frac{P_{bar}}{P_{std}} \qquad \text{Eq. 7C-3}$$

$$= K_1\ X\ Y\ V_m \frac{P_{bar}}{T_m}$$

Where:

K_1 = 0.3855 °K/mm Hg for metric units.
K_1 = 17.65 °R/in. Hg for English units.

12.5 Efficiency of Cadmium Reduction Column. Calculate this value as follows:

$$E = \frac{200\ (x-y)}{1.0\ s\ \frac{46.01}{62.01}} = \frac{269.6\ (x-y)}{s} \qquad \text{Eq. 7C-4}$$

Where:

200 = Final volume of sample and blank after passing through the column, ml.
1.0 = Volume of spiking solution added, ml.
46.01=μg NO_2^-/μmole.
62.01=μg NO_3^-/μmole.

12.6 Total μg NO_2.

$$m = 200\left(\frac{500}{50}\right)\left(\frac{1000}{100}\right)\left(\frac{(S-B)}{E}\right) = \frac{(2\times10^4)(S-B)}{E} \qquad \text{Eq. 7C-5}$$

Where:

500 = Total volume of prepared sample, ml.
50 = Aliquot of prepared sample processed through cadmium column, ml.
100 = Aliquot of $KMnO_4$/NaOH solution, ml.
1000 = Total volume of $KMnO_4$/NaOH solution, ml.

12.7 Sample Concentration.

$$C = K_2 \frac{m}{V_{m(std)}} \qquad \text{Eq. 7C-6}$$

13.0 Method Performance

13.1 Precision. The intra-laboratory relative standard deviation for a single measurement is 2.8 and 2.9 percent at 201 and 268 ppm NO_X, respectively.

13.2 Bias. The method does not exhibit any bias relative to Method 7.

13.3 Range. The lower detectable limit is 13 mg NO_X/m^3, as NO_2 (7 ppm NO_X) when sampling at 500 ml/min for 1 hour. No upper limit has been established; however, when using the recommended sampling conditions, the method has been found to collect NO_X emissions quantitatively up to 1782 mg NO_X/m^3, as NO_2 (932 ppm NO_X).

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Margeson, J.H., W.J. Mitchell, J.C. Suggs, and M.R. Midgett. Integrated Sampling and Analysis Methods for Determining NO_X Emissions at Electric Utility Plants. U.S. Environmental Protection Agency, Research Triangle Park, NC. Journal of the Air Pollution Control Association. *32*:1210–1215. 1982.

2. Memorandum and attachment from J.H. Margeson, Source Branch, Quality Assurance Division, Environmental Monitoring Systems Laboratory, to The Record, EPA. March 30, 1983. NH_3 Interference in Methods 7C and 7D.

3. Margeson, J.H., J.C. Suggs, and M.R. Midgett. Reduction of Nitrate to Nitrite with Cadmium. Anal. Chem. *52*:1955–57. 1980.

4. Quality Assurance Handbook for Air Pollution Measurement Systems. Volume III—Stationary Source Specific Methods. U.S.

Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA–600/4–77–027b. August 1977.

5. Margeson, J.H., *et al.* An Integrated Method for Determining NO_X Emissions at Nitric Acid Plants. Analytical Chemistry. *47* (11):1801. 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

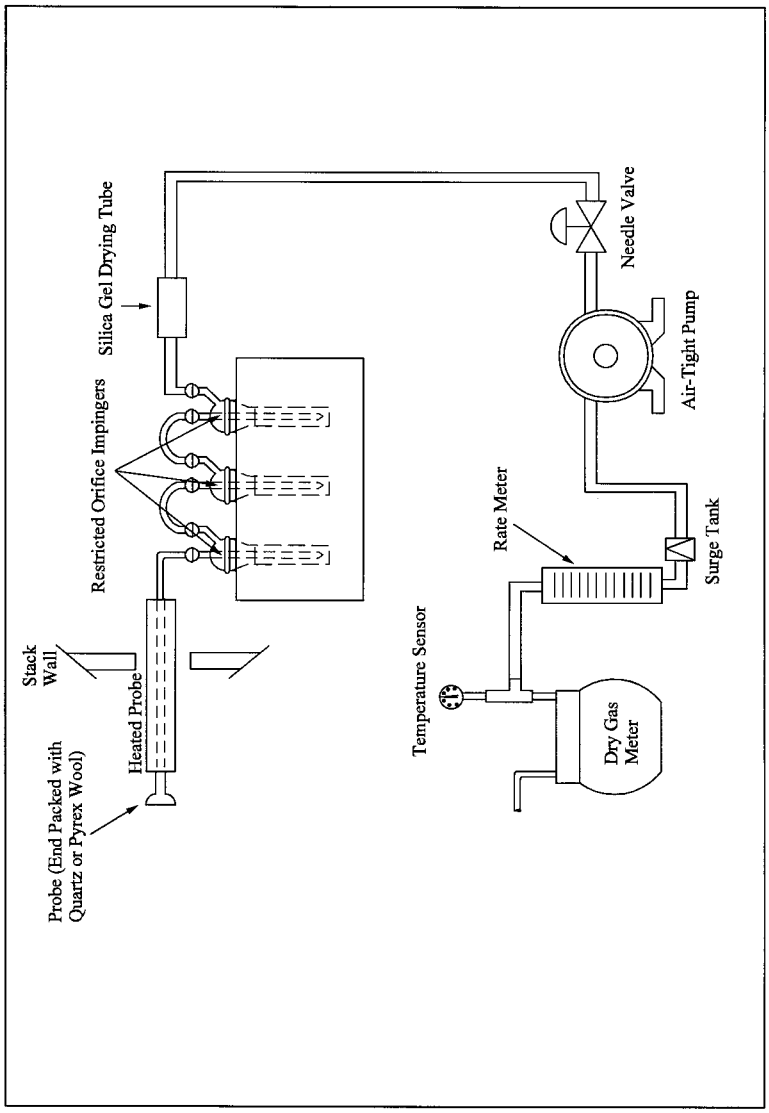

Figure 7C-1. NO_x Sampling Train.

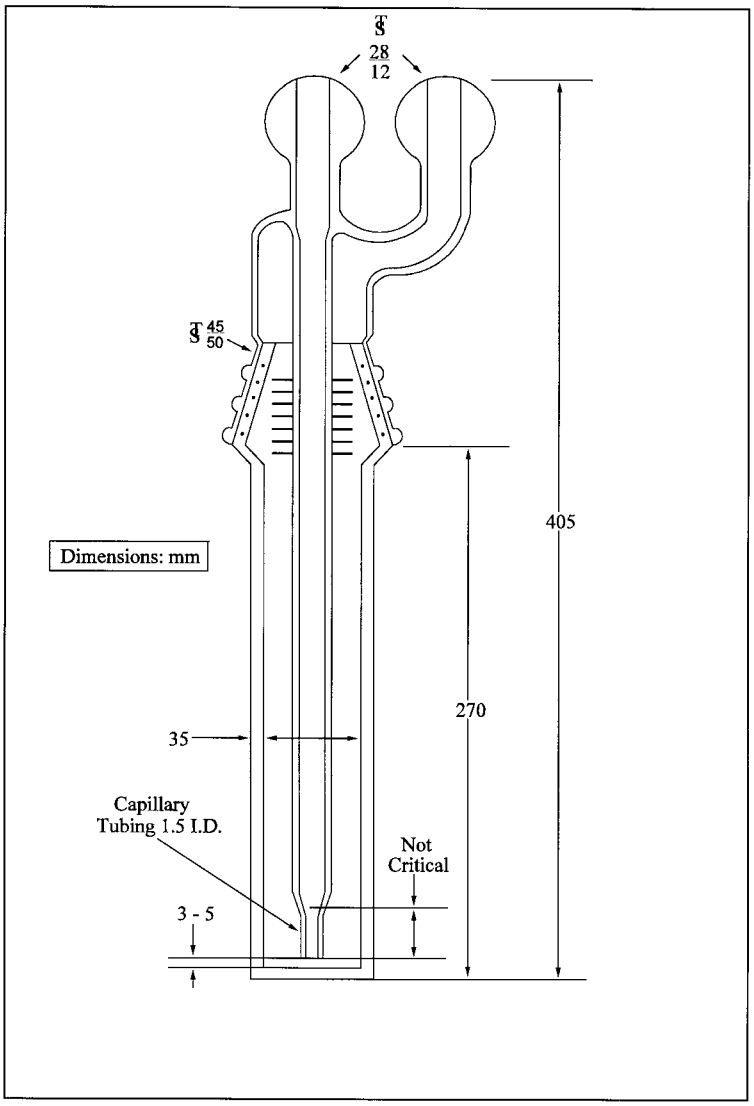

Figure 7C-2. Restricted-Orifice Impinger.

METHOD 7D—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ALKALINE-PERMANGANATE/ION CHROMATOGRAPHIC METHOD)

NOTE: This method is not inclusive with respect to specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 3, Method 6, Method 7, and Method 7C.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–0	7 ppmv

1.2 Applicability. This method applies to the measurement of NO_X emissions from fossil-fuel fired steam generators, electric utility plants, nitric acid plants, or other sources as specified in the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

An integrated gas sample is extracted from the stack and passed through impingers containing an alkaline-potassium permanganate solution; NO_X ($NO + NO_2$) emissions are oxidized to NO_3^-. Then NO_3^- is analyzed by ion chromatography.

3.0 Definitions [Reserved]

4.0 Interferences

Same as in Method 7C, section 4.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs. 30% H_2O_2 is a strong oxidizing agent; avoid contact with skin, eyes, and combustible material. Wear gloves when handling.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eye tissues and to skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Potassium Permanganate ($KMnO_4$). Caustic, strong oxidizer. Avoid bodily contact with.

6.0 Equipment and Supplies

6.1 Sample Collection and Sample Recovery. Same as Method 7C, section 6.1. A schematic of the sampling train used in performing this method is shown in Figure 7C–1 of Method 7C.

6.2 Sample Preparation and Analysis.

6.2.1 Magnetic Stirrer. With 25- by 10-mm Teflon-coated stirring bars.

6.2.2 Filtering Flask. 500-ml capacity with sidearm.

6.2.3 Buchner Funnel. 75-mm ID, with spout equipped with a 13-mm ID by 90-mm long piece of Teflon tubing to minimize possibility of aspirating sample solution during filtration.

6.2.4 Filter Paper. Whatman GF/C, 7.0-cm diameter.

6.2.5 Stirring Rods.

6.2.6 Volumetric Flask. 250-ml.

6.2.7 Pipettes. Class A.

6.2.8 Erlenmeyer Flasks. 250-ml.

6.2.9 Ion Chromatograph. Equipped with an anion separator column to separate NO_3^-, H_3^+ suppressor, and necessary auxiliary equipment. Nonsuppressed and other forms of ion chromatography may also be used provided that adequate resolution of NO_3^- is obtained. The system must also be able to resolve and detect NO_2^-.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection.

7.1.1 Water. Deionized distilled to conform to ASTM specification D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17).

7.1.2 Potassium Permanganate, 4.0 Percent (w/w), Sodium Hydroxide, 2.0 Percent (w/w). Dissolve 40.0 g of $KMnO_4$ and 20.0 g of NaOH in 940 ml of water.

7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in section 7.1.1.

7.2.2 Hydrogen Peroxide (H_2O_2), 5 Percent. Dilute 30 percent H_2O_2 1:5 (v/v) with water.

7.2.3 Blank Solution. Dissolve 2.4 g of $KMnO_4$ and 1.2 g of NaOH in 96 ml of water. Alternatively, dilute 60 ml of $KMnO_4$/NaOH solution to 100 ml.

7.2.4 KNO_3 Standard Solution. Dry KNO_3 at 110 °C for 2 hours, and cool in a desiccator. Accurately weigh 9 to 10 g of KNO_3 to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact NO_3^- concentration using Equation 7D–1 in section 12.2. This

solution is stable for 2 months without preservative under laboratory conditions.

7.2.5 Eluent, 0.003 M $NaHCO_3$/0.0024 M Na_2CO_3. Dissolve 1.008 g $NaHCO_3$ and 1.018 g Na_2CO_3 in water, and dilute to 4 liters. Other eluents capable of resolving nitrate ion from sulfate and other species present may be used.

8.0 Sample Collection, Preservation, Transport, and Storage.

8.1 Sampling. Same as in Method 7C, section 8.1.

8.2 Sample Recovery. Same as in Method 7C, section 8.2.

8.3 Sample Preparation for Analysis.

NOTE: Samples must be analyzed within 28 days of collection.

8.3.1 Note the level of liquid in the sample container, and determine whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume lost can be determined from the difference between initial and final solution levels, and this value can then be used to correct the analytical result. Quantitatively transfer the contents to a 1-liter volumetric flask, and dilute to volume.

8.3.2 Sample preparation can be started 36 hours after collection. This time is necessary to ensure that all NO_2^- is converted to NO_3^- in the collection solution. Take a 50-ml aliquot of the sample and blank, and transfer to 250-ml Erlenmeyer flasks. Add a magnetic stirring bar. Adjust the stirring rate to as fast a rate as possible without loss of solution. Add 5 percent H_2O_2 in increments of approximately 5 ml using a 5-ml pipette. When the $KMnO_4$ color appears to have been removed, allow the precipitate to settle, and examine the supernatant liquid. If the liquid is clear, the H_2O_2 addition is complete. If the $KMnO_4$ color persists, add more H_2O_2, with stirring, until the supernatant liquid is clear.

NOTE: The faster the stirring rate, the less volume of H_2O_2 that will be required to remove the $KMnO_4$.) Quantitatively transfer the mixture to a Buchner funnel containing GF/C filter paper, and filter the precipitate. The spout of the Buchner funnel should be equipped with a 13-mm ID by 90-mm long piece of Teflon tubing. This modification minimizes the possibility of aspirating sample solution during filtration. Filter the mixture into a 500-ml filtering flask. Wash the solid material four times with water. When filtration is complete, wash the Teflon tubing, quantitatively transfer the filtrate to a 250-ml volumetric flask, and dilute to volume. The sample and blank are now ready for NO_3^- analysis.

9.0 Quality Control

Section	Quality control measure	Effect
8.2, 10.1–10.3	Sampling equipment leak-check and calibration.	Ensure accurate measurement of sample volume.
10.4	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.
11.3	Spiked sample analysis	Ensure reduction efficiency of column.

10.0 Calibration and Standardizations

10.1 Dry Gas Meter (DGM) System.

10.1.1 Initial Calibration. Same as in Method 6, section 10.1.1. For detailed instructions on carrying out this calibration, it is suggested that section 3.5.2 of Citation 4 in section 16.0 of Method 7C be consulted.

10.1.2 Post-Test Calibration Check. Same as in Method 6, section 10.1.2.

10.2 Thermometers for DGM and Barometer. Same as in Method 6, sections 10.2 and 10.4, respectively.

10.3 Ion Chromatograph.

10.3.1 Dilute a given volume (1.0 ml or greater) of the KNO_3 standard solution to a convenient volume with water, and use this solution to prepare calibration standards. Prepare at least four standards to cover the range of the samples being analyzed. Use pipettes for all additions. Run standards as instructed in section 11.2. Determine peak height or area, and plot the individual values versus concentration in µg NO_3^-/ml.

10.3.2 Do not force the curve through zero. Draw a smooth curve through the points. The curve should be linear. With the linear curve, use linear regression to determine the calibration equation.

11.0 Analytical Procedures

11.1 The following chromatographic conditions are recommended: 0.003 M $NaHCO_3$/0.0024 Na_2CO_3 eluent solution (Section 7.2.5), full scale range, 3 µMHO; sample loop, 0.5 ml; flow rate, 2.5 ml/min. These conditions should give a NO_3^- retention time of approximately 15 minutes (Figure 7D–1).

11.2 Establish a stable baseline. Inject a sample of water, and determine whether any NO_3^- appears in the chromatogram. If NO_3^- is present, repeat the water load/injection procedure approximately five times; then reinject a water sample and observe the chromatogram. When no NO_3^- is present, the instrument is ready for use. Inject calibration standards. Then inject samples and a blank. Repeat the injection of the calibration

standards (to compensate for any drift in response of the instrument). Measure the NO_3^- peak height or peak area, and determine the sample concentration from the calibration curve.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature. Same as in Method 7C, section 12.1.

12.2 NO_3^- concentration. Calculate the NO_3^- concentration in the KNO_3 standard solution (see section 7.2.4) using the following equation:

$$\frac{\mu g\ NO_3^-}{ml} = g\ of\ KNO_3 \times 10^3 \times \frac{62.01}{101.10} \qquad \text{Eq. 7D-1}$$

12.3 Sample Volume, Dry Basis, Corrected to Standard Conditions. Same as in Method 7C, section 12.4.

12.4 Total μg NO_2 Per Sample.

$$m = 250\left(\frac{1000}{50}\right)\left(\frac{46.01}{62.01}\right)(S-B) \qquad \text{Eq. 7D-2}$$
$$= 3710\ (S-B)$$

Where:

250 = Volume of prepared sample, ml.

1000 = Total volume of $KMnO_4$ solution, ml.

50 = Aliquot of $KMnO_4$/NaOH solution, ml.

46.01 = Molecular weight of NO_3^-.

62.01 = Molecular weight of NO_3^-.

12.5 Sample Concentration. Same as in Method 7C, section 12.7.

13.0 Method Performance

13.1 Precision. The intra-laboratory relative standard deviation for a single measurement is approximately 6 percent at 200 to 270 ppm NO_X.

13.2 Bias. The method does not exhibit any bias relative to Method 7.

13.3 Range. The lower detectable limit is similar to that of Method 7C. No upper limit has been established; however, when using the recommended sampling conditions, the method has been found to collect NO_X emissions quantitatively up to 1782 mg NO_X/m^3, as NO_2 (932 ppm NO_X).

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 7C, section 16.0, References 1, 2, 4, and 5.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

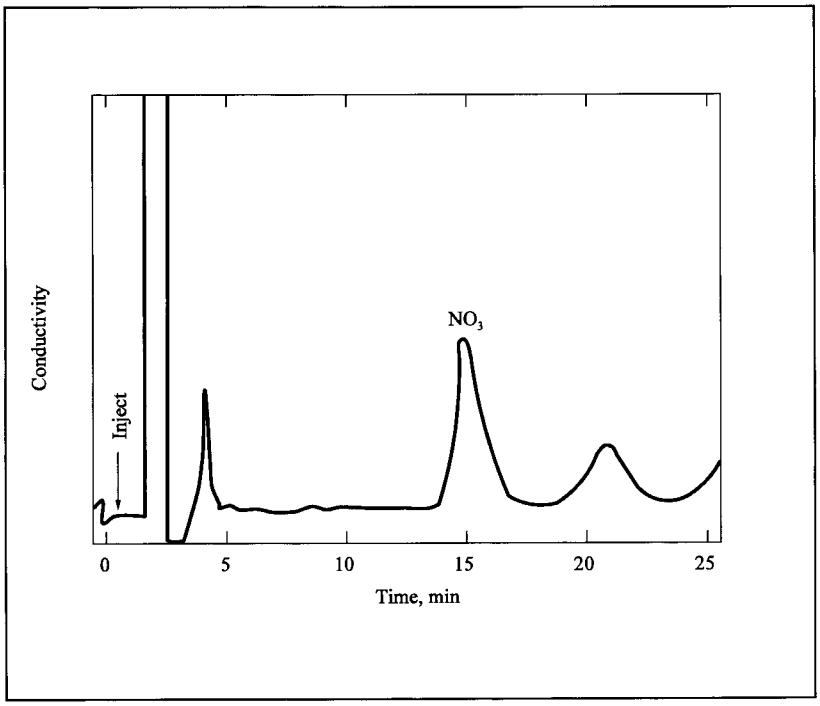

Figure 7D-1. Ion Chromatograph of a Prepared Sample.

METHOD 7E—DETERMINATION OF NITROGEN OXIDES EMISSIONS FROM STATIONARY SOURCES (INSTRUMENTAL ANALYZER PROCEDURE)

1.0 Scope and Application

What is Method 7E?

Method 7E is a procedure for measuring nitrogen oxides (NO_X) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis. This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 4—Determination of Moisture Content in Stack Gases.

1.1 Analytes. What does this method determine? This method measures the concentration of nitrogen oxides as NO_2.

Analyte	CAS No.	Sensitivity
Nitric oxide (NO)	10102–43–9	Typically <2% of
Nitrogen dioxide (NO_2)	10102–44–0	Calibration Span.

1.2 Applicability. When is this method required? The use of Method 7E may be required by specific New Source Performance Standards, Clean Air Marketing rules, State Implementation Plans, and permits where measurement of NO_X concentrations in stationary source emissions is required, either to determine compliance with an applicable

emissions standard or to conduct performance testing of a continuous monitoring system (CEMS). Other regulations may also require the use of Method 7E.

1.3 Data Quality Objectives (DQO). How good must my collected data be? Method 7E is designed to provide high-quality data for determining compliance with Federal and State emission standards and for relative accuracy testing of CEMS. In these and other applications, the principal objective is to ensure the accuracy of the data at the actual emission levels encountered. To meet this objective, the use of EPA traceability protocol calibration gases and measurement system performance tests are required.

1.4 Data Quality Assessment for Low Emitters. Is performance relief granted when testing low-emission units? Yes. For low-emitting sources, there are alternative performance specifications for analyzer calibration error, system bias, drift, and response time. Also, the alternative dynamic spiking procedure in section 16 may provide performance relief for certain low-emitting units.

2.0 Summary of Method

In this method, a sample of the effluent gas is continuously sampled and conveyed to the analyzer for measuring the concentration of NO_X. You may measure NO and NO_2 separately or simultaneously together but, for the purposes of this method, NO_X is the sum of NO and NO_2. You must meet the performance requirements of this method to validate your data.

3.0 Definitions

3.1 Analyzer Calibration Error, for non-dilution systems, means the difference between the manufacturer certified concentration of a calibration gas and the measured concentration of the same gas when it is introduced into the analyzer in direct calibration mode.

3.2 Calibration Curve means the relationship between an analyzer's response to the injection of a series of calibration gases and the actual concentrations of those gases.

3.3 Calibration Gas means the gas mixture containing NO_X at a known concentration and produced and certified in accordance with ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards,'' September 1997, as amended August 25, 1999, EPA–600/R–97/121 or more recent updates. The tests for analyzer calibration error, drift, and system bias require the use of calibration gas prepared according to this protocol. If a zero gas is used for the low-level gas, it must meet the requirements under the definition for ''zero air material'' in 40 CFR 72.2 in place of being prepared by the traceability protocol.

3.3.1 Low-Level Gas means a calibration gas with a concentration that is less than 20 percent of the calibration span and may be a zero gas.

3.3.2 Mid-Level Gas means a calibration gas with a concentration that is 40 to 60 percent of the calibration span.

3.3.3 High-Level Gas means a calibration gas with a concentration that is equal to the calibration span.

3.4 Calibration Span means the upper limit of the analyzer's calibration that is set by the choice of high-level calibration gas. No valid run average concentration may exceed the calibration span. To the extent practicable, the measured emissions should be between 20 to 100 percent of the selected calibration span. This may not be practicable in some cases of low-concentration measurements or testing for compliance with an emission limit when emissions are substantially less than the limit. In such cases, calibration spans that are practicable to achieving the data quality objectives without being excessively high should be chosen.

3.5 Centroidal Area means the central area of the stack or duct that is no greater than 1 percent of the stack or duct cross section. This area has the same geometric shape as the stack or duct.

3.6 Converter Efficiency Gas means a calibration gas with a known NO or NO_2 concentration and of Traceability Protocol quality.

3.7 Data Recorder means the equipment that permanently records the concentrations reported by the analyzer.

3.8 Direct Calibration Mode means introducing the calibration gases directly into the analyzer (or into the assembled measurement system at a point downstream of all sample conditioning equipment) according to manufacturer's recommended calibration procedure. This mode of calibration applies to non-dilution-type measurement systems.

3.9 Drift means the difference between the pre- and post-run system bias (or system calibration error) checks at a specific calibration gas concentration level (*i.e.* low-, mid- or high-).

3.10 Gas Analyzer means the equipment that senses the gas being measured and generates an output proportional to its concentration.

3.11 Interference Check means the test to detect analyzer responses to compounds other than the compound of interest, usually a gas present in the measured gas stream, that is not adequately accounted for in the calibration procedure and may cause measurement bias.

3.12 Low-Concentration Analyzer means any analyzer that operates with a calibration span of 20 ppm NO_X or lower. Each analyzer model used routinely to measure low NO_X concentrations must pass a manufacturer's stability test (MST). An MST subjects the analyzer to a range of line voltages and temperatures that reflect potential field conditions to demonstrate its stability following

procedures similar to those provided in 40 CFR 53.23. Ambient-level analyzers are exempt from the MST requirements of section 16.3. A copy of this information must be included in each test report. Table 7E–5 lists the criteria to be met.

3.13 Measurement System means all of the equipment used to determine the NO_x concentration. The measurement system comprises six major subsystems: Sample acquisition, sample transport, sample conditioning, calibration gas manifold, gas analyzer, and data recorder.

3.14 Response Time means the time it takes the measurement system to respond to a change in gas concentration occurring at the sampling point when the system is operating normally at its target sample flow rate or dilution ratio.

3.15 Run means a series of gas samples taken successively from the stack or duct. A test normally consists of a specific number of runs.

3.16 System Bias means the difference between a calibration gas measured in direct calibration mode and in system calibration mode. System bias is determined before and after each run at the low- and mid- or high-concentration levels. For dilution-type systems, pre- and post-run system calibration error is measured rather than system bias.

3.17 System Calibration Error applies to dilution-type systems and means the difference between the measured concentration of low-, mid-, or high-level calibration gas and the certified concentration for each gas when introduced in system calibration mode. For dilution-type systems, a 3-point system calibration error test is conducted in lieu of the analyzer calibration error test, and 2-point system calibration error tests are conducted in lieu of system bias tests.

3.18 System Calibration Mode means introducing the calibration gases into the measurement system at the probe, upstream of the filter and all sample conditioning components.

3.19 Test refers to the series of runs required by the applicable regulation.

4.0 Interferences

Note that interferences may vary among instruments and that instrument-specific interferences must be evaluated through the interference test.

5.0 Safety

What safety measures should I consider when using this method? This method may require you to work with hazardous materials and in hazardous conditions. We encourage you to establish safety procedures before using the method. Among other precautions, you should become familiar with the safety recommendations in the gas analyzer user's manual. Occupational Safety and Health Administration (OSHA) regulations concerning cylinder and noxious gases may apply. Nitric oxide and NO_2 are toxic and dangerous gases. Nitric oxide is immediately converted to NO_2 upon reaction with air. Nitrogen dioxide is a highly poisonous and insidious gas. Inflammation of the lungs from exposure may cause only slight pain or pass unnoticed, but the resulting edema several days later may cause death. A concentration of 100 ppm is dangerous for even a short exposure, and 200 ppm may be fatal. Calibration gases must be handled with utmost care and with adequate ventilation. Emission-level exposure to these gases should be avoided.

6.0 Equipment and Supplies

The performance criteria in this method will be met or exceeded if you are properly using equipment designed for this application.

6.1 What do I need for the measurement system? You may use any equipment and supplies meeting the following specifications:

(1) Sampling system components that are not evaluated in the system bias or system calibration error test must be glass, Teflon, or stainless steel. Other materials are potentially acceptable, subject to approval by the Administrator.

(2) The interference, calibration error, and system bias criteria must be met.

(3) Sample flow rate must be maintained within 10 percent of the flow rate at which the system response time was measured.

(4) All system components (excluding sample conditioning components, if used) must maintain the sample temperature above the moisture dew point. Ensure minimal contact between any condensate and the sample gas. Section 6.2 provides example equipment specifications for a NO_x measurement system. Figure 7E–1 is a diagram of an example dry-basis measurement system that is likely to meet the method requirements and is provided as guidance. For wet-basis systems, you may use alternative equipment and supplies as needed (some of which are described in Section 6.2), provided that the measurement system meets the applicable performance specifications of this method.

6.2 Measurement System Components

6.2.1 Sample Probe. Glass, stainless steel, or other approved material, of sufficient length to traverse the sample points.

6.2.2 Particulate Filter. An in-stack or out-of-stack filter. The filter must be made of material that is non-reactive to the gas being sampled. The filter media for out-of-stack filters must be included in the system bias test. The particulate filter requirement may be waived in applications where no significant particulate matter is expected (*e.g.*, for emission testing of a combustion turbine firing natural gas).

6.2.3 Sample Line. The sample line from the probe to the conditioning system/sample pump should be made of Teflon or other material that does not absorb or otherwise alter the sample gas. For a dry-basis measurement system (as shown in Figure 7E–1), the temperature of the sample line must be maintained at a sufficiently high level to prevent condensation before the sample conditioning components. For wet-basis measurement systems, the temperature of the sample line must be maintained at a sufficiently high level to prevent condensation before the analyzer.

6.2.4 Conditioning Equipment. For dry basis measurements, a condenser, dryer or other suitable device is required to remove moisture continuously from the sample gas. Any equipment needed to heat the probe or sample line to avoid condensation prior to the sample conditioning component is also required.

For wet basis systems, you must keep the sample above its dew point either by: (1) Heating the sample line and all sample transport components up to the inlet of the analyzer (and, for hot-wet extractive systems, also heating the analyzer) or (2) by diluting the sample prior to analysis using a dilution probe system. The components required to do either of the above are considered to be conditioning equipment.

6.2.5 Sampling Pump. For systems similar to the one shown in Figure 7E–1, a leak-free pump is needed to pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system. The pump may be constructed of any material that is non-reactive to the gas being sampled. For dilution-type measurement systems, an ejector pump (eductor) is used to create a vacuum that draws the sample through a critical orifice at a constant rate.

6.2.6 Calibration Gas Manifold. Prepare a system to allow the introduction of calibration gases either directly to the gas analyzer in direct calibration mode or into the measurement system, at the probe, in system calibration mode, or both, depending upon the type of system used. In system calibration mode, the system should be able to flood the sampling probe and vent excess gas. Alternatively, calibration gases may be introduced at the calibration valve following the probe. Maintain a constant pressure in the gas manifold. For in-stack dilution-type systems, a gas dilution subsystem is required to transport large volumes of purified air to the sample probe and a probe controller is needed to maintain the proper dilution ratio.

6.2.7 Sample Gas Manifold. For the type of system shown in Figure 7E–1, the sample gas manifold diverts a portion of the sample to the analyzer, delivering the remainder to the by-pass discharge vent. The manifold should also be able to introduce calibration gases directly to the analyzer (except for dilution-type systems). The manifold must be made of material that is non-reactive to the gas sampled or the calibration gas and be configured to safely discharge the bypass gas.

6.2.8 NO_X Analyzer. An instrument that continuously measures NO_X in the gas stream and meets the applicable specifications in section 13.0. An analyzer that operates on the principle of chemiluminescence with an NO_2 to NO converter is one example of an analyzer that has been used successfully in the past. Analyzers operating on other principles may also be used provided the performance criteria in section 13.0 are met.

6.2.8.1 Dual Range Analyzers. For certain applications, a wide range of gas concentrations may be encountered, necessitating the use of two measurement ranges. Dual-range analyzers are readily available for these applications. These analyzers are often equipped with automated range-switching capability, so that when readings exceed the full-scale of the low measurement range, they are recorded on the high range. As an alternative to using a dual-range analyzer, you may use two segments of a single, large measurement scale to serve as the low and high ranges. In all cases, when two ranges are used, you must quality-assure both ranges using the proper sets of calibration gases. You must also meet the interference, calibration error, system bias, and drift checks. However, we caution that when you use two segments of a large measurement scale for dual range purposes, it may be difficult to meet the performance specifications on the low range due to signal-to-noise ratio considerations.

6.2.8.2 Low Concentration Analyzer. When an analyzer is routinely calibrated with a calibration span of 20 ppmv or less, the manufacturer's stability test (MST) is required. See Table 7E–5 for test parameters.

6.2.9 Data Recording. A strip chart recorder, computerized data acquisition system, digital recorder, or data logger for recording measurement data may be used.

7.0 Reagents and Standards

7.1 Calibration Gas. What calibration gases do I need? Your calibration gas must be NO in N_2 and certified (or recertified) within an uncertainty of 2.0 percent in accordance with ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards'' September 1997, as amended August 25, 1999, EPA–600/R–97/121. Blended gases meeting the Traceability Protocol are allowed if the additional gas components are shown not to interfere with the analysis. If a zero gas is used for the low-level gas, it must meet the requirements under the definition for ''zero air material'' in 40 CFR 72.2. The calibration gas must not be used after its expiration date. Except for applications under part 75 of

this chapter, it is acceptable to prepare calibration gas mixtures from EPA Traceability Protocol gases in accordance with Method 205 in appendix M to part 51 of this chapter. For part 75 applications, the use of Method 205 is subject to the approval of the Administrator. The goal and recommendation for selecting calibration gases is to bracket the sample concentrations. The following calibration gas concentrations are required:

7.1.1 *High-Level Gas.* This concentration is chosen to set the calibration span as defined in Section 3.4.

7.1.2 Mid-Level Gas. 40 to 60 percent of the calibration span.

7.1.3 Low-Level Gas. Less than 20 percent of the calibration span.

7.1.4 Converter Efficiency Gas. What reagents do I need for the converter efficiency test? The converter efficiency gas is a manufacturer-certified gas with a concentration sufficient to show NO_2 conversion at the concentrations encountered in the source. A test gas concentration in the 40 to 60 ppm range is suggested, but other concentrations may be more appropriate to specific sources. For the test described in section 8.2.4.1, NO_2 is required. For the alternative converter efficiency tests in section 16.2, NO is required.

7.2 Interference Check. What reagents do I need for the interference check? Use the appropriate test gases listed in Table 7E–3 or others not listed that can potentially interfere (as indicated by the test facility type, instrument manufacturer, etc.) to conduct the interference check. These gases should be manufacturer certified but do not have to be prepared by the EPA traceability protocol.

8.0 Sample Collection, Preservation, Storage, and Transport

Emission Test Procedure

Since you are allowed to choose different options to comply with some of the performance criteria, it is your responsibility to identify the specific options you have chosen, to document that the performance criteria for that option have been met, and to identify any deviations from the method.

8.1 What sampling site and sampling points do I select?

8.1.1 Unless otherwise specified in an applicable regulation or by the Administrator, when this method is used to determine compliance with an emission standard, conduct a stratification test as described in section 8.1.2 to determine the sampling traverse points to be used. For performance testing of continuous emission monitoring systems, follow the sampling site selection and traverse point layout procedures described in the appropriate performance specification or applicable regulation (e.g., Performance Specification 2 in appendix B to this part).

8.1.2 Determination of Stratification. Perform a stratification test at each test site to determine the appropriate number of sample traverse points. If testing for multiple pollutants or diluents at the same site, a stratification test using only one pollutant or diluent satisfies this requirement. A stratification test is not required for small stacks that are less than 4 inches in diameter. To test for stratification, use a probe of appropriate length to measure the NO_X (or pollutant of interest) concentration at 12 traverse points located according to Table 1–1 or Table 1–2 of Method 1. Alternatively, you may measure at three points on a line passing through the centroidal area. Space the three points at 16.7, 50.0, and 83.3 percent of the measurement line. Sample for a minimum of twice the system response time (see section 8.2.6) at each traverse point. Calculate the individual point and mean NO_X concentrations. If the concentration at each traverse point differs from the mean concentration for all traverse points by no more than: ±5.0 percent of the mean concentration; or ±0.5 ppm (whichever is less restrictive), the gas stream is considered unstratified, and you may collect samples from a single point that most closely matches the mean. If the 5.0 percent or 0.5 ppm criterion is not met, but the concentration at each traverse point differs from the mean concentration for all traverse points by not more than: ±10.0 percent of the mean concentration; or ±1.0 ppm (whichever is less restrictive), the gas stream is considered to be minimally stratified and you may take samples from three points. Space the three points at 16.7, 50.0, and 83.3 percent of the measurement line. Alternatively, if a 12-point stratification test was performed and the emissions were shown to be minimally stratified (all points within ± 10.0 percent of their mean or within ±1.0 ppm), and if the stack diameter (or equivalent diameter, for a rectangular stack or duct) is greater than 2.4 meters (7.8 ft), then you may use 3-point sampling and locate the three points along the measurement line exhibiting the highest average concentration during the stratification test at 0.4, 1.2 and 2.0 meters from the stack or duct wall. If the gas stream is found to be stratified because the 10.0 percent or 1.0 ppm criterion for a 3-point test is not met, locate 12 traverse points for the test in accordance with Table 1–1 or Table 1–2 of Method 1.

8.2 Initial Measurement System Performance Tests. What initial performance criteria must my system meet before I begin collecting samples? Before measuring emissions, perform the following procedures:

(a) Calibration gas verification,

(b) Measurement system preparation,

(c) Calibration error test,

(d) NO_2 to NO conversion efficiency test, if applicable,

(e) System bias check,

(f) System response time test, and

(g) Interference check

8.2.1 Calibration Gas Verification. How must I verify the concentrations of my calibration gases? Obtain a certificate from the gas manufacturer documenting the quality of the gas. Confirm that the manufacturer certification is complete and current. Ensure that your calibration gas certifications have not expired. This documentation should be available on-site for inspection. To the extent practicable, select a high-level gas concentration that will result in the measured emissions being between 20 and 100 percent of the calibration span.

8.2.2 Measurement System Preparation. How do I prepare my measurement system? Assemble, prepare, and precondition the measurement system according to your standard operating procedure. Adjust the system to achieve the correct sampling rate or dilution ratio (as applicable).

8.2.3 Calibration Error Test. How do I confirm my analyzer calibration is correct? After you have assembled, prepared and calibrated your sampling system and analyzer, you must conduct a 3-point analyzer calibration error test (or a 3-point system calibration error test for dilution systems) before the first run and again after any failed system bias test (or 2-point system calibration error test for dilution systems) or failed drift test. Introduce the low-, mid-, and high-level calibration gases sequentially. For non-dilution-type measurement systems, introduce the gases in direct calibration mode. For dilution-type measurement systems, introduce the gases in system calibration mode.

(1) For non-dilution systems, you may adjust the system to maintain the correct flow rate at the analyzer during the test, but you may not make adjustments for any other purpose. For dilution systems, you must operate the measurement system at the appropriate dilution ratio during all system calibration error checks, and may make only the adjustments necessary to maintain the proper ratio.

(2) Record the analyzer's response to each calibration gas on a form similar to Table 7E–1. For each calibration gas, calculate the analyzer calibration error using Equation 7E–1 in section 12.2 or the system calibration error using Equation 7E–3 in section 12.4 (as applicable). The calibration error specification in section 13.1 must be met for the low-, mid-, and high-level gases. If the calibration error specification is not met, take corrective action and repeat the test until an acceptable 3-point calibration is achieved.

8.2.4 NO_2 to NO Conversion Efficiency Test. Before or after each field test, you must conduct an NO_2 to NO conversion efficiency test if your system converts NO_2 to NO before analyzing for NO_X. You may risk testing multiple facilities before performing this test provided you pass this test at the conclusion of the final facility test. A failed final conversion efficiency test in this case will invalidate all tests performed subsequent to the test in which the converter efficiency test was passed. Follow the procedures in section 8.2.4.1, or 8.2.4.2. If desired, the converter efficiency factor derived from this test may be used to correct the test results for converter efficiency if the NO_2 fraction in the measured test gas is known. Use Equation 7E–8 in section 12.8 for this correction.

8.2.4.1 Introduce NO_2 converter efficiency gas to the analyzer in direct calibration mode and record the NO_X concentration displayed by the analyzer. Calculate the converter efficiency using Equation 7E–7 in section 12.7. The specification for converter efficiency in section 13.5 must be met. The user is cautioned that state-of-the-art NO_2 calibration gases may have limited shelf lives, and this could affect the ability to pass the 90-percent conversion efficiency requirement.

8.2.4.2 Alternatively, either of the procedures for determining conversion efficiency using NO in section 16.2 may be used.

8.2.5 Initial System Bias and System Calibration Error Checks. Before sampling begins, determine whether the high-level or mid-level calibration gas best approximates the emissions and use it as the upscale gas. Introduce the upscale gas at the probe upstream of all sample conditioning components in system calibration mode. Record the time it takes for the measured concentration to increase to a value that is at least 95 percent or within 0.5 ppm (whichever is less restrictive) of a stable response for both the low-level and upscale gases. Continue to observe the gas concentration reading until it has reached a final, stable value. Record this value on a form similar to Table 7E–2.

(1) Next, introduce the low-level gas in system calibration mode and record the time required for the concentration response to decrease to a value that is within 5.0 percent or 0.5 ppm (whichever is less restrictive) of the certified low-range gas concentration. If the low-level gas is a zero gas, use the procedures described above and observe the change in concentration until the response is 0.5 ppm or 5.0 percent of the upscale gas concentration (whichever is less restrictive).

(2) Continue to observe the low-level gas reading until it has reached a final, stable value and record the result on a form similar to Table 7E–2. Operate the measurement system at the normal sampling rate during all system bias checks. Make only the adjustments necessary to achieve proper calibration gas flow rates at the analyzer.

(3) From these data, calculate the measurement system response time (see section 8.2.6) and then calculate the initial system bias using Equation 7E–2 in section 12.3. For dilution systems, calculate the system calibration error in lieu of system bias using

equation 7E–3 in section 12.4. See section 13.2 for acceptable performance criteria for system bias and system calibration error. If the initial system bias (or system calibration error) specification is not met, take corrective action. Then, you must repeat the applicable calibration error test from section 8.2.3 and the initial system bias (or 2-point system calibration error) check until acceptable results are achieved, after which you may begin sampling.

(NOTE: For dilution-type systems, data from the 3-point system calibration error test described in section 8.2.3 may be used to meet the initial 2-point system calibration error test requirement of this section, if the calibration gases were injected as described in this section, and if response time data were recorded).

8.2.6 Measurement System Response Time. As described in section 8.2.5, you must determine the measurement system response time during the initial system bias (or 2-point system calibration error) check. Observe the times required to achieve 95 percent of a stable response for both the low-level and upscale gases. The longer interval is the response time.

8.2.7 Interference Check. Conduct an interference response test of the gas analyzer prior to its initial use in the field. If you have multiple analyzers of the same make and model, you need only perform this alternative interference check on one analyzer. You may also meet the interference check requirement if the instrument manufacturer performs this or a similar check on an analyzer of the same make and model of the analyzer that you use and provides you with documented results.

(1) You may introduce the appropriate interference test gases (that are potentially encountered during a test; see examples in Table 7E–3) into the analyzer separately or as mixtures. Test the analyzer with the interference gas alone at the highest concentration expected at a test source and again with the interference gas and NO_X at a representative NO_X test concentration. For analyzers measuring NO_X greater than 20 ppm, use a calibration gas with a NO_X concentration of 80 to 100 ppm and set this concentration equal to the calibration span. For analyzers measuring less than 20 ppm NO_X, select an NO concentration for the calibration span that reflects the emission levels at the sources to be tested, and perform the interference check at that level. Measure the total interference response of the analyzer to these gases in ppmv. Record the responses and determine the interference using Table 7E–4. The specification in section 13.4 must be met.

(2) A copy of this data, including the date completed and signed certification, must be available for inspection at the test site and included with each test report. This interference test is valid for the life of the instrument unless major analytical components (*e.g.,* the detector) are replaced with different model parts. If major components are replaced with different model parts, the interference gas check must be repeated before returning the analyzer to service. If major components are replaced, the interference gas check must be repeated before returning the analyzer to service. The tester must ensure that any specific technology, equipment, or procedures that are intended to remove interference effects are operating properly during testing.

8.3 Dilution-Type Systems—Special Considerations. When a dilution-type measurement system is used, there are three important considerations that must be taken into account to ensure the quality of the emissions data. First, the critical orifice size and dilution ratio must be selected properly so that the sample dew point will be below the sample line and analyzer temperatures. Second, a high-quality, accurate probe controller must be used to maintain the dilution ratio during the test. The probe controller should be capable of monitoring the dilution air pressure, eductor vacuum, and sample flow rates. Third, differences between the molecular weight of calibration gas mixtures and the stack gas molecular weight must be addressed because these can affect the dilution ratio and introduce measurement bias.

8.4 Sample Collection.

(1) Position the probe at the first sampling point. Purge the system for at least two times the response time before recording any data. Then, traverse all required sampling points, sampling at each point for an equal length of time and maintaining the appropriate sample flow rate or dilution ratio (as applicable). You must record at least one valid data point per minute during the test run.

(2) Each time the probe is removed from the stack and replaced, you must recondition the sampling system for at least two times the system response time prior to your next recording. If the average of any run exceeds the calibration span value, that run is invalid.

(3) You may satisfy the multipoint traverse requirement by sampling sequentially using a single-hole probe or a multi-hole probe designed to sample at the prescribed points with a flow within 10 percent of mean flow rate. Notwithstanding, for applications under part 75 of this chapter, the use of multi-hole probes is subject to the approval of the Administrator.

8.5 Post-Run System Bias Check and Drift Assessment.

How do I confirm that each sample I collect is valid? After each run, repeat the system bias check or 2-point system calibration error check (for dilution systems) to validate

the run. Do not make adjustments to the measurement system (other than to maintain the target sampling rate or dilution ratio) between the end of the run and the completion of the post-run system bias or system calibration error check. Note that for all post-run system bias or 2-point system calibration error checks, you may inject the low-level gas first and the upscale gas last, or vice-versa. You may risk sampling for multiple runs before performing the post-run bias or system calibration error check provided you pass this test at the conclusion of the group of runs. A failed final test in this case will invalidate all runs subsequent to the last passed test.

(1) If you do not pass the post-run system bias (or system calibration error) check, then the run is invalid. You must diagnose and fix the problem and pass another calibration error test (Section 8.2.3) and system bias (or 2-point system calibration error) check (Section 8.2.5) before repeating the run. Record the system bias (or system calibration error) results on a form similar to Table 7E–2.

(2) After each run, calculate the low-level and upscale drift, using Equation 7E–4 in section 12.5. If the post-run low- and upscale bias (or 2-point system calibration error) checks are passed, but the low-or upscale drift exceeds the specification in section 13.3, the run data are valid, but a 3-point calibration error test and a system bias (or 2-point system calibration error) check must be performed and passed before any more test runs are done.

(3) For dilution systems, data from a 3-point system calibration error test may be used to met the pre-run 2-point system calibration error requirement for the first run in a test sequence. Also, the post-run bias (or 2-point calibration error) check data may be used as the pre-run data for the next run in the test sequence at the discretion of the tester.

8.6 Alternative Interference and System Bias Checks (Dynamic Spike Procedure). If I want to use the dynamic spike procedure to validate my data, what procedure should I follow? Except for applications under part 75 of this chapter, you may use the dynamic spiking procedure and requirements provided in section 16.1 during each test as an alternative to the interference check and the pre- and post-run system bias checks. The calibration error test is still required under this option. Use of the dynamic spiking procedure for Part 75 applications is subject to the approval of the Administrator.

8.7 Moisture correction. You must determine the moisture content of the flue gas and correct the measured gas concentrations to a dry basis using Method 4 or other appropriate methods, subject to the approval of the Administrator, when the moisture basis (wet or dry) of the measurements made with this method is different from the moisture basis of either: (1) The applicable emissions limit; or (2) the CEMS being evaluated for relative accuracy. Moisture correction is also required if the applicable limit is in lb/mmBtu and the moisture basis of the Method 7E NO_X analyzer is different from the moisture basis of the Method 3A diluent gas (CO_2 or O_2) analyzer.

9.0 Quality Control

What quality control measures must I take?

The following table is a summary of the mandatory, suggested, and alternative quality assurance and quality control measures and the associated frequency and acceptance criteria. All of the QC data, along with the sample run data, must be documented and included in the test report.

SUMMARY TABLE OF AQ/QC

Status	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
S	Identify Data User		Regulatory Agency or other primary end user of data.	Before designing test.
S	Analyzer Design	Analyzer resolution or sensitivity.	<2.0% of full-scale range	Manufacturer design.
M		Interference gas check.	Sum of responses ≤2.5% of calibration span Alternatively, sum of responses: ≤0.5 ppmv for calibration spans of 5 to 10 ppmv. ≤0.2 ppmv for calibration spans <5 ppmv. See Table 7E-3.	
M	Calibration Gases	Traceability protocol (G1, G2).	Valid certificate required Uncertainty ≤2.0% of tag value.	
M		High-level gas	Equal to the calibration span	Each test.
M		Mid-level gas	40 to 60% of calibration span	Each test.
M		Low-level gas	<20% of calibration span	Each test.
S	Data Recorder Design.	Data resolution	≤0.5% of full-scale range	Manufacturer design.
S	Sample Extraction	Probe material	SS or quartz if stack >500 °F	East test.
M	Sample Extraction	Probe, filter and sample line temperature.	For dry-basis analyzers, keep sample above the dew point by heating, prior to sample conditioning.	Each run.

SUMMARY TABLE OF AQ/QC—Continued

Status	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
			For wet-basis analyzers, keep sample above dew point at all times, by heating or dilution.	
S	Sample Extraction	Calibration valve material.	SS	Each test.
S	Sample Extraction	Sample pump material.	Inert to sample constituents	Each test.
S	Sample Extraction	Manifolding material	Inert to sample constituents	Each test.
S	Moisture Removal	Equipment efficiency	<5% target compound removal	Verified through system bias check.
S	Particulate Removal	Filter inertness	Pass system bias check	Each bias check.
M	Analyzer & Calibration Gas Performance.	Analyzer calibration error (of 3-point system calibration error for dilution systems).	Within ±2.0 percent of the calibration span of the analyzer for the low-, mid-, and high-level calibration gases. Alternative specification: ≤0.5 ppmv absolute difference.	Before initial run and after a failed system bias test or drift test.
M	System Performance	System bias (or pre- and post-run 2-point system calibration error for dilution (Systems).	Within ±5.0% of the analyzer calibration span for low-sacle and upscale calibration gases. Alternative specification: ≤0.5 ppmv absolute difference.	Before and after each run.
M	System Performance	System response time.	Determines minimum sampling time per point.	During initial sampling system bias test.
M	System Performance	Drift	≤3.0% of calibration span for low-level and mid- or high-level gases. Alternative specification: ≤0.5 ppmv absolute difference.	After each test run.
M	System Performance	NO_2-NO conversion efficiency.	≥90% of certified test gas concentration	Before or after each test.
M	System Performance	Purge time	≥2 times system response time	Before starting the first run and when probe is removed from and re-inserted into the stack.
M	System Performance	Minimum sample time at each point.	Two times the system response time	Each sample point.
M	System Performance	Stable sample flow rate (surrogate for maintaining system response time).	Within 10% of flow rate established during system response time check.	Each run.
M	Sample Point Selection.	Stratification test	All points within: ±5% of mean for 1-point sampling. ±10% of mean for 3-point. Alternatively, all points within: ±0.5 ppm of mean for 1-point sampling. ±1.0 ppm of mean for 3-point sampling.	Prior to first run.
A	Multiple sample points simultaneously.	No. of openings in probe.	Multi-hole probe with verifiable constant flow through all holes within 10% of mean flow rate (requires Administrative approval for Part 75).	Each run.
M	Data Recording	Frequency	≤1 minute average	During run.
S	Data Parameters	Sample concentration range.	All 1-minute averages within calibration span.	Each run.
M	Date Parameters	Average concentration for the run.	Run average ≤calibration span	Each run.

S = Suggest.
M = Mandatory.
A = Alternative.
Agency.

10.0 Calibration and Standardization

What measurement system calibrations are required?

(1) The initial 3-point calibration error test as described in section 8.2.3 and the system bias (or system calibration error) checks described in section 8.2.5 are required and must meet the specifications in section 13 before you start the test. Make all necessary adjustments to calibrate the gas analyzer and data recorder. Then, after the test commences, the system bias or system calibration error checks described in section 8.5 are required before and after each run. Your analyzer must be calibrated for all species of NO_X that it detects. Analyzers that measure NO and NO_2 separately without using a converter must be calibrated with both NO and NO_2.

(2) You must include a copy of the manufacturer's certification of the calibration gases used in the testing as part of the test report. This certification must include the 13 documentation requirements in the EPA Traceability Protocol For Assay and Certification of Gaseous Calibration Standards, September 1997, as amended August 25, 1999. When Method 205 is used to produce diluted calibration gases, you must document that the specifications for the gas dilution system are met for the test. You must also include the date of the most recent dilution system calibration against flow standards and the name of the person or manufacturer who carried out the calibration in the test report.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the procedures for calculations and data analysis listed in this section.

12.1 *Nomenclature.* The terms used in the equations are defined as follows:

ACE = Analyzer calibration error, percent of calibration span.

B_{WS} = Moisture content of sample gas as measured by Method 4 or other approved method, percent/100.

C_{Avg} = Average unadjusted gas concentration indicated by data recorder for the test run, ppmv.

C_D = Pollutant concentration adjusted to dry conditions, ppmv.

C_{Dir} = Measured concentration of a calibration gas (low, mid, or high) when introduced in direct calibration mode, ppmv.

C_{Gas} = Average effluent gas concentration adjusted for bias, ppmv.

C_M = Average of initial and final system calibration bias (or 2-point system calibration error) check responses for the upscale calibration gas, ppmv.

C_{MA} = Actual concentration of the upscale calibration gas, ppmv.

C_{Native} = NO_X concentration in the stack gas as calculated in section 12.6, ppmv.

C_O = Average of the initial and final system calibration bias (or 2-point system calibration error) check responses from the low-level (or zero) calibration gas, ppmv.

C_{OA} = Actual concentration of the low-level calibration gas, ppmv.

C_S = Measured concentration of a calibration gas (low, mid, or high) when introduced in system calibration mode, ppmv.

C_{SS} = Concentration of NO_X measured in the spiked sample, ppmv.

C_{Spike} = Concentration of NO_X in the undiluted spike gas, ppmv.

C_{Calc} = Calculated concentration of NO_X in the spike gas diluted in the sample, ppmv.

C_V = Manufacturer certified concentration of a calibration gas (low, mid, or high), ppmv.

C_W = Pollutant concentration measured under moist sample conditions, wet basis, ppmv.

CS = Calibration span, ppmv.

D = Drift assessment, percent of calibration span.

DF = Dilution system dilution factor or spike gas dilution factor, dimensionless.

Eff_{NO2} = NO_2 to NO converter efficiency, percent.

NO_{XCorr} = The NO_X concentration corrected for the converter efficiency, ppmv.

NOX_{Final} = The final NO_X concentration observed during the converter efficiency test in section 16.2.2, ppmv.

NO_{XPeak} = The highest NO_X concentration observed during the converter efficiency test in section 16.2.2, ppmv.

Q_{Spike} = Flow rate of spike gas introduced in system calibration mode, L/min.

Q_{Total} = Total sample flow rate during the spike test, L/min.

R = Spike recovery, percent.

SB = System bias, percent of calibration span.

SB_i = Pre-run system bias, percent of calibration span.

SB_{final} = Post-run system bias, percent of calibration span.

SCE = System calibration error, percent of calibration span.

SCE_i = Pre-run system calibration error, percent of calibration span.

SCE_{Final} = Post-run system calibration error, percent of calibration span.

12.2 Analyzer Calibration Error. For non-dilution systems, use Equation 7E–1 to calculate the analyzer calibration error for the low-, mid-, and high-level calibration gases.

$$ACE = \frac{C_{Dir} - C_v}{CS} \times 100 \qquad \text{Eq. 7E-1}$$

12.3 System Bias. For non-dilution systems, use Equation 7E–2 to calculate the system bias separately for the low-level and upscale calibration gases.

$$SB = \frac{C_S - C_{Dir}}{CS} \times 100 \qquad \text{Eq. 7E-2}$$

12.4 System Calibration Error. Use Equation 7E–3 to calculate the system calibration error for dilution systems. Equation 7E–3 applies to both the initial 3-point system calibration error test and the subsequent 2-point calibration error checks between test runs. In this equation, the term ''C_s'' refers to the diluted calibration gas concentration measured by the analyzer.

$$SCE = \frac{(C_S \quad DF) - C_V}{CS} \times 100 \qquad \text{Eq. 7E-3}$$

12.5 Drift Assessment. Use Equation 7E–4 to separately calculate the low-level and upscale drift over each test run. For dilution systems, replace ''SB_{final}'' and ''SB_i'' with ''SCE_{final}'' and ''SCE_i'', respectively, to calculate and evaluate drift.

$$D = \left|SB_{final} - SB_i\right| \qquad \text{Eq. 7E-4}$$

12.6 Effluent Gas Concentration. For each test run, calculate C_{avg}, the arithmetic average of all valid NO_X concentration values (*e.g.*, 1-minute averages). Then adjust the value of C_{avg} for bias using Equation 7E–5a if you use a non-zero gas as your low-level calibration gas, or Equation 7E–5b if you use a zero gas as your low-level calibration gas.

$$C_{Gas} = \left(C_{Avg} - C_M\right)\frac{C_{MA} - C_{OA}}{C_M - C_O} + C_{MA} \qquad \text{Eq. 7E-5a}$$

$$C_{Gas} = \left(C_{Avg} - C_O\right)\frac{C_{MA}}{C_M - C_O} \qquad \text{Eq. 7E-5b}$$

12.7 NO_2—NO Conversion Efficiency. If the NO_X converter efficiency test described in section 8.2.4.1 is performed, calculate the efficiency using Equation 7E–7.

$$Eff_{NO2} = \frac{C_{Dir}}{C_V} \times 100 \qquad \text{Eq. 7E-7}$$

12.8 NO_2—NO Conversion Efficiency Correction. If desired, calculate the total NO_X concentration with a correction for converter efficiency using Equation 7E–8.

$$NO_{x\,Corr} = NO + \left(\frac{(NO_X - NO)}{Eff_{NO_2}} x\ 100\right) \qquad \text{Eq. 7E-8}$$

12.9 Alternative NO_2 Converter Efficiency. If the alternative procedure of section 16.2.2 is used, determine the NO_X concentration decrease from NO_{XPeak} after the minimum 30-minute test interval using Equation 7E–9.

This decrease from NO_{XPeak} must meet the requirement in section 13.5 for the converter to be acceptable.

$$\%\,Decrease = \frac{NO_{XPeak} - NO_{XFinal}}{NO_{XPeak}} \times 100 \qquad \text{Eq. 7E-9}$$

12.10 Moisture Correction. Use Equation 7E–10 if your measurements need to be corrected to a dry basis.

$$C_D = \frac{C_W}{1 - B_{WS}} \qquad \text{Eq. 7E-10}$$

12.11 Calculated Spike Gas Concentration and Spike Recovery for the Example Alternative Dynamic Spiking Procedure in section 16.1.3. Use Equation 7E–11 to determine the calculated spike gas concentration. Use Equation 7E–12 to calculate the spike recovery.

$$C_{Calc} = \frac{\left(C_{Spike}\right)\left(Q_{Spike}\right)}{Q_{Total}} \qquad \text{Eq. 7E-11}$$

$$R = \frac{DF\left(C_{ss} - C_{native}\right) + C_{native}}{C_{Spike}} \times 100 \qquad \text{Eq. 7E-12}$$

13.0 Method Performance

13.1 Calibration Error. This specification is applicable to both the analyzer calibration error and the 3-point system calibration error tests described in section 8.2.3. At each calibration gas level (low, mid, and high) the calibration error must either be within ±2.0 percent of the calibration span. Alternatively, the results are acceptable if $|C_{dir} - C_v|$ or $|C_s - C_v|$ (as applicable) is ≤0.5 ppmv.

13.2 System Bias. This specification is applicable to both the system bias and 2-point system calibration error tests described in section 8.2.5 and 8.5. The pre- and post-run system bias (or system calibration error) must be within ±5.0 percent of the calibration span for the low-level and upscale calibration gases. Alternatively, the results are acceptable if $|C_s - C_{dir}|$ is ≤0.5 ppmv or if $|C_s - C_v|$ is ≤0.5 ppmv (as applicable).

13.3 Drift. For each run, the low-level and upscale drift must be less than or equal to 3.0 percent of the calibration span. The drift is also acceptable if the pre- and post-run bias (or the pre- and post-run system calibration error) responses do not differ by more than 0.5 ppmv at each gas concentration (i.e. $|C_{s\ post\text{-}run} - C_{s\ pre\text{-}run}| \leq 0.5$ ppmv).

13.4 Interference Check. The total interference response (i.e., the sum of the interference responses of all tested gaseous components) must not be greater than 2.50 percent of the calibration span for the analyzer tested. In summing the interferences, use the larger of the absolute values obtained for the interferent tested with and without the pollutant present. The results are also acceptable if the sum of the responses does not exceed 0.5 ppmv for a calibration span of 5 to 10 ppmv, or 0.2 ppmv for a calibration span <5 ppmv.

13.5 NO_2 to NO Conversion Efficiency Test (as applicable). The NO_2 to NO conversion efficiency, calculated according to Equation 7E–7, must be greater than or equal to 90 percent. The alternative conversion efficiency check, described in section 16.2.2 and calculated according to Equation 7E–9, must not result in a decrease from NO_{XPeak} by more than 2.0 percent.

13.6 Alternative Dynamic Spike Procedure. Recoveries of both pre-test spikes and post-test spikes must be within 100 ±10 percent. If the absolute difference between the calculated spike value and measured spike value is equal to or less than 0.20 ppmv, then the requirements of the ADSC are met.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Dynamic Spike Procedure. Except for applications under part 75 of this chapter, you may use a dynamic spiking procedure to validate your test data for a specific test matrix in place of the interference check and pre- and post-run system bias checks. For part 75 applications, use of this procedure is subject to the approval of the Administrator.

Best results are obtained for this procedure when source emissions are steady and not varying. Fluctuating emissions may render this alternative procedure difficult to pass. To use this alternative, you must meet the following requirements.

16.1.1 Procedure Documentation. You must detail the procedure you followed in the test report, including how the spike was measured, added, verified during the run, and calculated after the test.

16.1.2 Spiking Procedure Requirements. The spikes must be prepared from EPA Traceability Protocol gases. Your procedure must be designed to spike field samples at two target levels both before and after the test. Your target spike levels should bracket the average sample NO_X concentrations. The higher target concentration must be less than the calibration span. You must collect at least 5 data points for each target concentration. The spiking procedure must be performed before the first run and repeated after the last run of the test program.

16.1.3 Example Spiking Procedure. Determine the NO concentration needed to generate concentrations that are 50 and 150 percent of the anticipated NO_X concentration in the stack at the total sampling flow rate while keeping the spike flow rate at or below 10 percent of this total. Use a mass flow meter (accurate within 2.0 percent) to generate these NO spike gas concentrations at a constant flow rate. Use Equation 7E–11 in section 12.11 to determine the calculated spike concentration in the collected sample.

(1) Prepare the measurement system and conduct the analyzer calibration error test as described in sections 8.2.2 and 8.2.3. Following the sampling procedures in section 8.1, determine the stack NO_X concentration and use this concentration as the average stack concentration (C_{avg}) for the first spike level, or if desired, for both pre-test spike levels. Introduce the first level spike gas into the system in system calibration mode and begin sample collection. Wait for at least two times the system response time before measuring the spiked sample concentration. Then record at least five successive 1-minute averages of the spiked sample gas. Monitor the spike gas flow rate and maintain at the determined addition rate. Average the five 1-minute averages and determine the spike recovery using Equation 7E–12. Repeat this procedure for the other pre-test spike level. The recovery at each level must be within the limits in section 13.6 before proceeding with the test.

(2) Conduct the number of runs required for the test. Then repeat the above procedure for the post-test spike evaluation. The last run of the test may serve as the average stack concentration for the post-test spike test calculations. The results of the post-test spikes must meet the limits in section 13.6.

16.2 Alternative NO_2 to NO Conversion Efficiency Procedures. You may use either of the following procedures to determine converter efficiency in place of the procedure in section 8.2.4.1.

16.2.1 The procedure for determining conversion efficiency using NO in 40 CFR 86.123–78.

16.2.2 Bag Procedure. Perform the analyzer calibration error test to document the calibration (both NO and NO_X modes, as applicable). Fill a Tedlar or equivalent bag approximately half full with either ambient air, pure oxygen, or an oxygen standard gas with at least 19.5 percent by volume oxygen content. Fill the remainder of the bag with mid- to high-level NO in N_2 (or other appropriate concentration) calibration gas. (Note that the concentration of the NO standard should be sufficiently high enough for the diluted concentration to be easily and accurately measured on the scale used. The size of the bag should be large enough to accommodate the procedure and time required. Verify through the manufacturer that the Tedlar alternative is suitable for NO and make this verifed information available for inspection.)

(1) Immediately attach the bag to the inlet of the NO_X analyzer (or external converter if used). In the case of a dilution-system, introduce the gas at a point upstream of the dilution assembly. Measure the NO_X concentration for a period of 30 minutes. If the NO_X concentration drops more than 2 percent absolute from the peak value observed, then the NO_2 converter has failed to meet the criteria of this test. Take corrective action. The highest NO_X value observed is considered to be NO_{XPeak}. The final NO_X value observed is considered to be NO_{Xfinal}.

(2) [Reserved]

16.3 Manufacturer's Stability Test. A manufacturer's stability test is required for all analyzers that routinely measure emissions below 20 ppmv and is optional but recommended for other analyzers. This test evaluates each analyzer model by subjecting it to the tests listed in Table 7E–5 following procedures similar to those in 40 CFR 53.23 for thermal stability and insensitivity to supply voltage variations. If the analyzer will be used under temperature conditions that are outside the test conditions in Table B–4 of Part 53.23, alternative test temperatures that better reflect the analyzer field environment should be used. Alternative procedures or documentation that establish the analyzer's stability over the appropriate line voltages and temperatures are acceptable.

17.0 References

1. ''ERA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards'' September 1997 as amended, ERA–600/R–97/121.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

Figure 7E-1. Measurement System

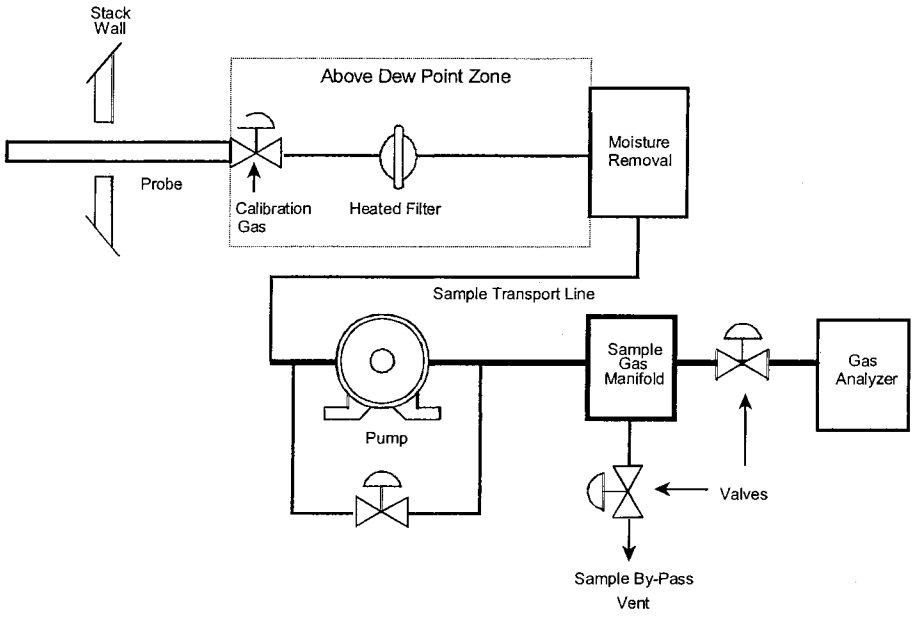

Figure 7E-2. Testing Flow Chart

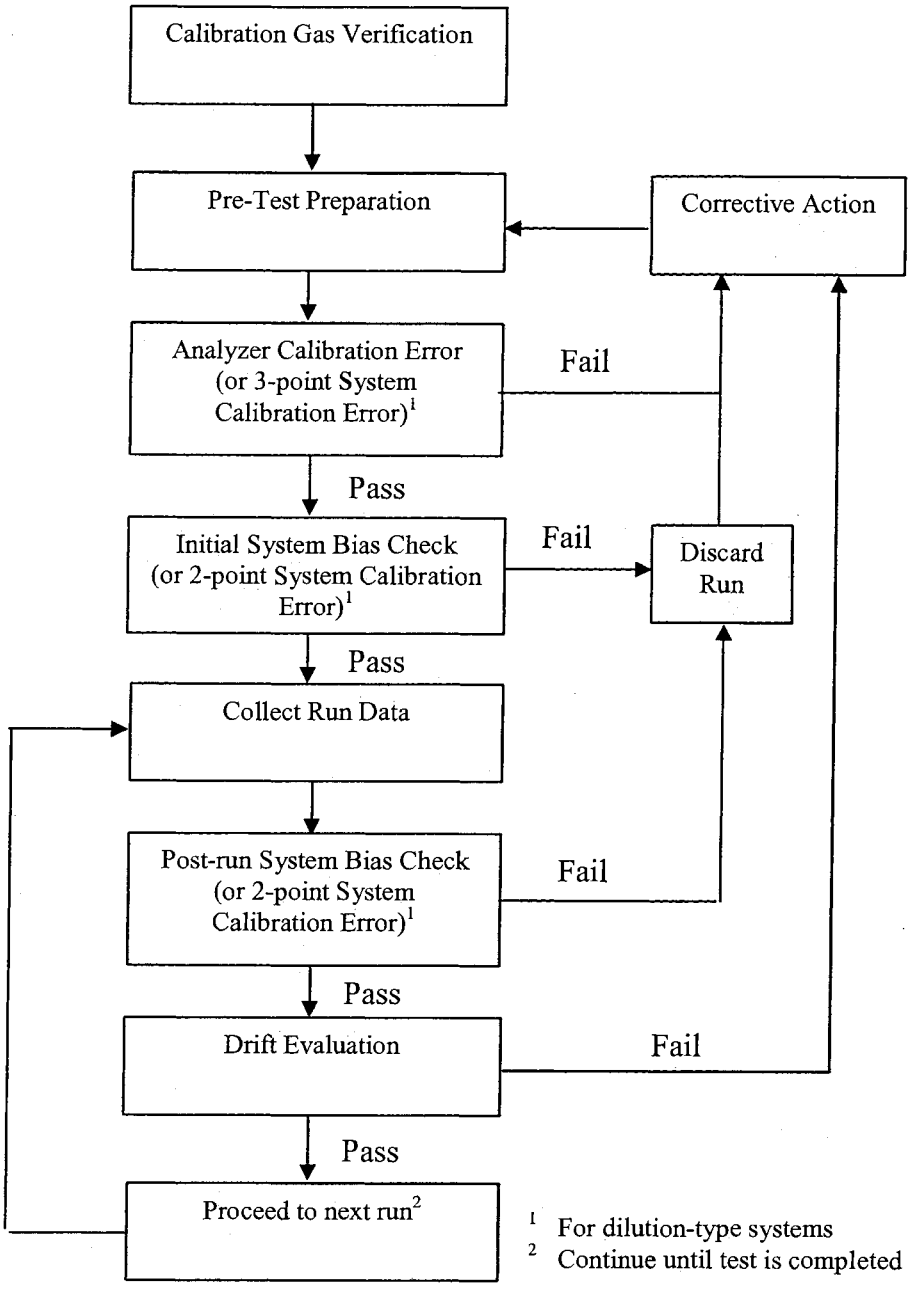

Table 7E-1 - Analyzer (or System) Calibration Error Data

Source Identification: _____ Test personnel: _____ Date: _____ Time: _____		Analyzer[1] or System[2] calibration error data for sampling runs: _____ Analyzer Model No. _____ Serial No. _____ Calibration Span (CS):		
	Manufacturer Certified Cylinder Value (indicate units) A	Analyzer calibration response (indicate units) B	Absolute difference (indicate units) A-B	Calibration Error (percent of calibration span) $\frac{A-B}{CS} \times 100$
Low-level (or zero) calibration gas	.....	.....	.....	.....
Mid-level calibration gas	.....	.....	.....	.....
High-level calibration gas	.....	.....	.....	.....

[1] Refers to data from the analyzer calibration error test of a non-dilution system.
[2] Refers to data from a 3-point system calibration error test of a dilution system.

Table 7E-2 - System Bias (or System Calibration Error) and Drift Data

Source Identification: _____ Run Number: _____
Test personnel: _____ Calibration Span: _____
Date: _____ Response Time: _____
Analyzer Model No. _____ Serial No. _____

	Initial values			Final values		
Calibration Gas Level	Certified Calibration gas value (indicate units)	System Response (indicate units)	System Bias[1] or Calibration Error[2] (% of calibration span)	System response (indicate units)	System Bias[1] or Calibration Error[2] (% of calibration span)	Drift (% of calibration span)
Low-level gas.....	.....	.....	.....	.....	.....	
Upscale (high- or mid-) level gas.....	.....	.....	.....	.....	.....	

[1] Refers to the pre- and post-run system bias checks of a non-dilution system.
[2] Refers to the pre- and post-run system calibration error checks of a dilution system.

TABLE 7E–3—EXAMPLE INTERFERENCE CHECK GAS CONCENTRATIONS

Potential interferent gas[1]	Concentrations[2] sample conditioning type	
	Hot wet	Dried
CO_2	5 and 15%	5 and 15%
H_2O	25%	1%
NO	15 ppmv	15 ppmv
NO_2	15 ppmv	15 ppmv
N_2O	10 ppmv	10 ppmv
CO	50 ppmv	50 ppmv
NH_3	10 ppmv	10 ppmv
CH_4	50 ppmv	50 ppmv
SO_2	20 ppmv	20 ppmv
H_2	50 ppmv	50 ppmv
HCl	10 ppmv	10 ppmv

[1] Any applicable gas may be eliminated or tested at a reduced level if the manufacturer has provided reliable means for limiting or scrubbing that gas to a specified level.
[2] As practicable, gas concentrations should be the highest expected at test sites.

TABLE 7E–4—INTERFERENCE RESPONSE

Date of Test: _____

Analyzer Type: _____
Model No.: _____
Serial No: _____
Calibration Span: _____

Test gas type	Concentration (ppm)	Analyzer response
	Sum of Responses	
	% of Calibration Span	

TABLE 7E–5—MANUFACTURER STABILITY TEST

Test description	Acceptance criteria (note 1)
Thermal Stability	Temperature range when drift does not exceed 3.0% of analyzer range over a 12-hour run when measured with NO_X present @ 80% of calibration span.
Fault Conditions	Identify conditions which, when they occur, result in performance which is not in compliance with the Manufacturer's Stability Test criteria. These are to be indicated visually or electrically to alert the operator of the problem.
Insensitivity to Supply Voltage Variations.	±10.0% (or manufacturers alternative) variation from nominal voltage must produce a drift of ≤2.0% of calibration span for either zero or concentration ≥80% NO_X present.
Analyzer Calibration Error.	For a low-, medium-, and high-calibration gas, the difference between the manufacturer certified value and the analyzer response in direct calibration mode, no more than 2.0% of calibration span.

Note 1: If the instrument is to be used as a Low Range analyzer, all tests must be performed at a calibration span of 20 ppm or less.

METHOD 8—DETERMINATION OF SULFURIC ACID AND SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, and Method 6.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Sulfuric acid, including: Sulfuric acid (H_2SO_4) mist, Sulfur trioxide (SO_3).	7664–93–9, 7449–11–9	0.05 mg/m³ (0.03×10^{-7} lb/ft³).
Sulfur dioxide (SO_2)	7449–09–5	1.2 mg/m³ (3×10^{-9} lb/ft³).

1.2 Applicability. This method is applicable for the determination of H_2SO_4 (including H_2SO_4 mist and SO_3) and gaseous SO_2 emissions from stationary sources.

NOTE: Filterable particulate matter may be determined along with H_2SO_4 and SO_2 (subject to the approval of the Administrator) by inserting a heated glass fiber filter between the probe and isopropanol impinger (see section 6.1.1 of Method 6). If this option is chosen, particulate analysis is gravimetric only; sulfuric acid is not determined separately.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

A gas sample is extracted isokinetically from the stack. The H_2SO_4 and the SO_2 are separated, and both fractions are measured separately by the barium-thorin titration method.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Possible interfering agents of this method are fluorides, free ammonia, and dimethyl aniline. If any of these interfering agents is present (this can be determined by knowledge of the process), alternative methods, subject to the approval of the Administrator, are required.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. Same as Method 6, section 5.2.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 5, section 6.1, with the following additions and exceptions:

6.1.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 8–1; it is similar to the Method 5 sampling train, except that the filter position is different, and the filter holder does not have to be heated. See Method 5, section 6.1.1, for details and guidelines on operation and maintenance.

6.1.1.1 Probe Liner. Borosilicate or quartz glass, with a heating system to prevent visible condensation during sampling. Do not use metal probe liners.

6.1.1.2 Filter Holder. Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other gasket materials (*e.g.*, Teflon or Viton) may be used, subject to the approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The filter holder shall be placed between the first and second impingers. Do not heat the filter holder.

6.1.1.3 Impingers. Four, of the Greenburg-Smith design, as shown in Figure 8–1. The first and third impingers must have standard tips. The second and fourth impingers must be modified by replacing the insert with an approximately 13-mm (½-in.) ID glass tube, having an unconstricted tip located 13 mm (½ in.) from the bottom of the impinger. Similar collection systems, subject to the approval of the Administrator, may be used.

6.1.1.4 Temperature Sensor. Thermometer, or equivalent, to measure the temperature of the gas leaving the impinger train to within 1 °C (2 °F).

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Wash Bottles. Two polyethylene or glass bottles, 500-ml.

6.2.2 Graduated Cylinders. Two graduated cylinders (volumetric flasks may be used), 250-ml, 1-liter.

6.2.3 Storage Bottles. Leak-free polyethylene bottles, 1-liter size (two for each sampling run).

6.2.4 Trip Balance. 500-g capacity, to measure to ±0.5 g (necessary only if a moisture content analysis is to be done).

6.3 Analysis. The following items are required for sample analysis:

6.3.1 Pipettes. Volumetric 10-ml, 100-ml.

6.3.2 Burette. 50-ml.

6.3.3 Erlenmeyer Flask. 250-ml (one for each sample, blank, and standard).

6.3.4 Graduated Cylinder. 100-ml.

6.3.5 Dropping Bottle. To add indicator solution, 125-ml size.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents are to conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Filters and Silica Gel. Same as in Method 5, sections 7.1.1 and 7.1.2, respectively.

7.1.2 Water. Same as in Method 6, section 7.1.1.

7.1.3 Isopropanol, 80 Percent by Volume. Mix 800 ml of isopropanol with 200 ml of water.

NOTE: Check for peroxide impurities using the procedure outlined in Method 6, section 7.1.2.1.

7.1.4 Hydrogen Peroxide (H^2O^2), 3 Percent by Volume. Dilute 100 ml of 30 percent H_2O_2) to 1 liter with water. Prepare fresh daily.

7.1.5 Crushed Ice.

7.2 Sample Recovery. The reagents and standards required for sample recovery are:

7.2.1 Water. Same as in section 7.1.2.

7.2.2 Isopropanol, 80 Percent. Same as in section 7.1.3.

7.3 Sample Analysis. Same as Method 6, section 7.3.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation. Same as Method 5, section 8.1, except that filters should be inspected but need not be desiccated, weighed, or identified. If the effluent gas can be considered dry (i.e., moisture-free), the silica gel need not be weighed.

8.2 Preliminary Determinations. Same as Method 5, section 8.2.

8.3 Preparation of Sampling Train. Same as Method 5, section 8.3, with the following exceptions:

8.3.1 Use Figure 8–1 instead of Figure 5–1.

8.3.2 Replace the second sentence of Method 5, section 8.3.1 with: Place 100 ml of 80 percent isopropanol in the first impinger, 100 ml of 3 percent H_2O_2 in both the second and third impingers; retain a portion of each reagent for use as a blank solution. Place about 200 g of silica gel in the fourth impinger.

8.3.3 Ignore any other statements in section 8.3 of Method 5 that are obviously not applicable to the performance of Method 8.

NOTE: If moisture content is to be determined by impinger analysis, weigh each of the first three impingers (plus absorbing solution) to the nearest 0.5 g, and record these weights. Weigh also the silica gel (or silica gel plus container) to the nearest 0.5 g, and record.)

8.4 Metering System Leak-Check Procedure. Same as Method 5, section 8.4.1.

8.5 Pretest Leak-Check Procedure. Follow the basic procedure in Method 5, section 8.4.2, noting that the probe heater shall be adjusted to the minimum temperature required to prevent condensation, and also that verbage such as ''* * * plugging the inlet to the filter holder * * * '' found in section 8.4.2.2 of Method 5 shall be replaced by '' * * * plugging the inlet to the first impinger * * * ''. The pretest leak-check is recommended, but is not required.

8.6 Sampling Train Operation. Follow the basic procedures in Method 5, section 8.5, in conjunction with the following special instructions:

8.6.1 Record the data on a sheet similar to that shown in Figure 8–2 (alternatively, Figure 5–2 in Method 5 may be used). The sampling rate shall not exceed 0.030 m^3/min (1.0 cfm) during the run. Periodically during the test, observe the connecting line between the probe and first impinger for signs of condensation. If condensation does occur, adjust the probe heater setting upward to the minimum temperature required to prevent condensation. If component changes become necessary during a run, a leak-check shall be performed immediately before each change, according to the procedure outlined in section 8.4.3 of Method 5 (with appropriate modifications, as mentioned in section 8.5 of this method); record all leak rates. If the leakage rate(s) exceeds the specified rate, the tester shall either void the run or plan to correct the sample volume as outlined in section 12.3 of Method 5. Leak-checks immediately after component changes are recommended, but not required. If these leak-checks are performed, the procedure in section 8.4.2 of Method 5 (with appropriate modifications) shall be used.

8.6.2 After turning off the pump and recording the final readings at the conclusion of each run, remove the probe from the stack. Conduct a post-test (mandatory) leak-check as outlined in section 8.4.4 of Method 5 (with appropriate modifications), and record the leak rate. If the post-test leakage rate exceeds the specified acceptable rate, either correct the sample volume, as outlined in section 12.3 of Method 5, or void the run.

8.6.3 Drain the ice bath and, with the probe disconnected, purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at the average flow rate used for sampling.

NOTE: Clean ambient air can be provided by passing air through a charcoal filter. Alternatively, ambient air (without cleaning) may be used.

8.7 Calculation of Percent Isokinetic. Same as Method 5, section 8.6.

8.8 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. Treat the samples as follows:

8.8.1 Container No. 1.

8.8.1.1 If a moisture content analysis is to be performed, clean and weigh the first impinger (plus contents) to the nearest 0.5 g, and record this weight.

8.8.1.2 Transfer the contents of the first impinger to a 250-ml graduated cylinder. Rinse the probe, first impinger, all connecting glassware before the filter, and the front half of the filter holder with 80 percent isopropanol. Add the isopropanol rinse solution to the cylinder. Dilute the contents of the cylinder to 225 ml with 80 percent isopropanol, and transfer the cylinder contents to the storage container. Rinse the cylinder with 25 ml of 80 percent isopropanol, and transfer the rinse to the storage container. Add the filter to the solution in the storage container and mix. Seal the container to protect the solution against evaporation. Mark the level of liquid on the container, and identify the sample container.

8.8.2 Container No. 2.

8.8.2.1 If a moisture content analysis is to be performed, clean and weigh the second and third impingers (plus contents) to the nearest 0.5 g, and record the weights. Also, weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g, and record the weight.

8.8.2.2 Transfer the solutions from the second and third impingers to a 1-liter graduated cylinder. Rinse all connecting glassware (including back half of filter holder) between the filter and silica gel impinger with water, and add this rinse water to the cylinder. Dilute the contents of the cylinder to 950 ml with water. Transfer the solution to a storage container. Rinse the cylinder with 50 ml of water, and transfer the rinse to the storage container. Mark the level of liquid on the container. Seal and identify the sample container.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
7.1.3	Isopropanol check	Ensure acceptable level of peroxide impurities in isopropanol.
8.4, 8.5, 10.1	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.
10.2	Barium standard solution standardization	Ensure normality determination.
11.2	Replicate titrations	Ensure precision of titration determinations.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

10.1 Sampling Equipment. Same as Method 5, section 10.0.

10.2 Barium Standard Solution. Same as Method 6, section 10.5.

11.0 Analytical Procedure

11.1. Sample Loss. Same as Method 6, section 11.1.

11.2. Sample Analysis.

11.2.1 Container No. 1. Shake the container holding the isopropanol solution and the filter. If the filter breaks up, allow the fragments to settle for a few minutes before removing a sample aliquot. Pipette a 100-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 2 to 4 drops of thorin indicator, and titrate to a pink endpoint using 0.0100 N barium standard solution. Repeat the titration with a second aliquot of sample, and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater.

11.2.2 Container No. 2. Thoroughly mix the solution in the container holding the contents of the second and third impingers. Pipette a 10-ml aliquot of sample into a 250-ml Erlenmeyer flask. Add 40 ml of isopropanol, 2 to 4 drops of thorin indicator, and titrate to a pink endpoint using 0.0100 N barium standard solution. Repeat the titration with a second aliquot of sample, and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater.

11.2.3 Blanks. Prepare blanks by adding 2 to 4 drops of thorin indicator to 100 ml of 80 percent isopropanol. Titrate the blanks in the same manner as the samples.

12.0 Data Analysis and Calculations

Carry out calculations retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature. Same as Method 5, section 12.1, with the following additions and exceptions:

$C_{H_2SO_4}$ = Sulfuric acid (including SO_3) concentration, g/dscm (lb/dscf).

C_{SO_2} = Sulfur dioxide concentration, g/dscm (lb/dscf).

N = Normality of barium perchlorate titrant, meq/ml.

V_a = Volume of sample aliquot titrated, 100 ml for H_2SO_4 and 10 ml for SO_2.

V_{soln} = Total volume of solution in which the sample is contained, 1000 ml for the SO_2 sample and 250 ml for the H_2SO_4 sample.

V_t = Volume of barium standard solution titrant used for the sample, ml.

V_{tb} = Volume of barium standard solution titrant used for the blank, ml.

12.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 8–2).

12.3 Dry Gas Volume. Same as Method 5, section 12.3.

12.4 Volume of Water Vapor Condensed and Moisture Content. Calculate the volume of water vapor using Equation 5–2 of Method 5; the weight of water collected in the impingers and silica gel can be converted directly to milliliters (the specific gravity of water is 1 g/ml). Calculate the moisture content of the stack gas (B_{ws}) using Equation 5–3 of Method 5. The note in section 12.5 of Method 5 also applies to this method. Note that if the effluent gas stream can be considered dry, the volume of water vapor and moisture content need not be calculated.

12.5 Sulfuric Acid Mist (Including SO_3) Concentration.

$$C_{H_2SO_4} = K_3\left[N\left(V_t - V_{tb}\right)\left(V_{soln}/V_a\right)\right]/V_{m(std)} \qquad \text{Eq. 8-1}$$

Where:

K_3 = 0.04904 g/meq for metric units,

$K_3 = 1.081 \times 10^{-4}$ lb/meq for English units.

12.6 Sulfur Dioxide Concentration.

$$C_{SO_2} = K_4\left[N\left(V_t - V_{tb}\right)\left(V_{soln}/V_a\right)\right]/V_{m(std)} \qquad \text{Eq. 8-2}$$

Where:

K_4 = 0.03203 g/meq for metric units,

$K_4 = 7.061 \times 10^{-5}$ lb/meq for English units.

12.7 Isokinetic Variation. Same as Method 5, section 12.11.

12.8 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate, if needed, using data obtained in this method and the equations in sections 12.6 and 12.7 of Method 2.

13.0 Method Performance

13.1 Analytical Range. Collaborative tests have shown that the minimum detectable limits of the method are 0.06 mg/m^3 (4×10^{-9} lb/ft^3) for H_2SO_4 and 1.2 mg/m^3 (74×10^{-9} lb/ft^3) for SO_2. No upper limits have been established. Based on theoretical calculations for 200 ml of 3 percent H_2O_2 solution, the upper concentration limit for SO_2 in a 1.0 m^3 (35.3 ft^3) gas sample is about 12,000 mg/m^3 (7.7×10^{-4} lb/ft^3). The upper limit can be extended by increasing the quantity of peroxide solution in the impingers.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as section 17.0 of Methods 5 and 6.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

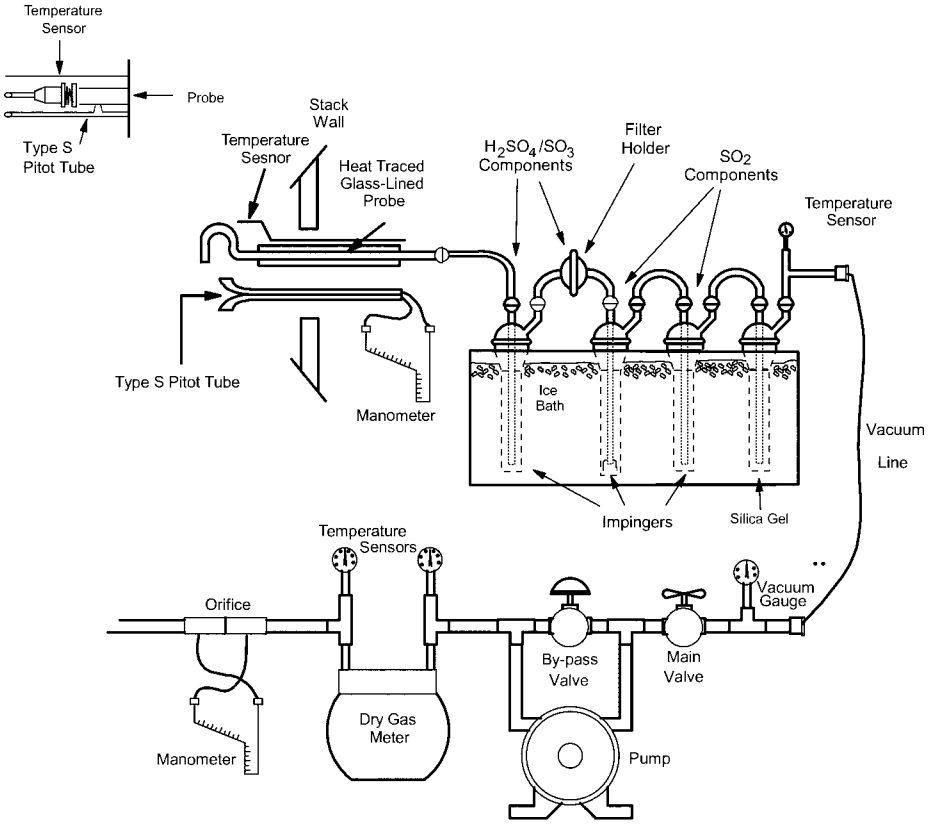

Figure 8-1. Sulfuric Acid Sampling Train

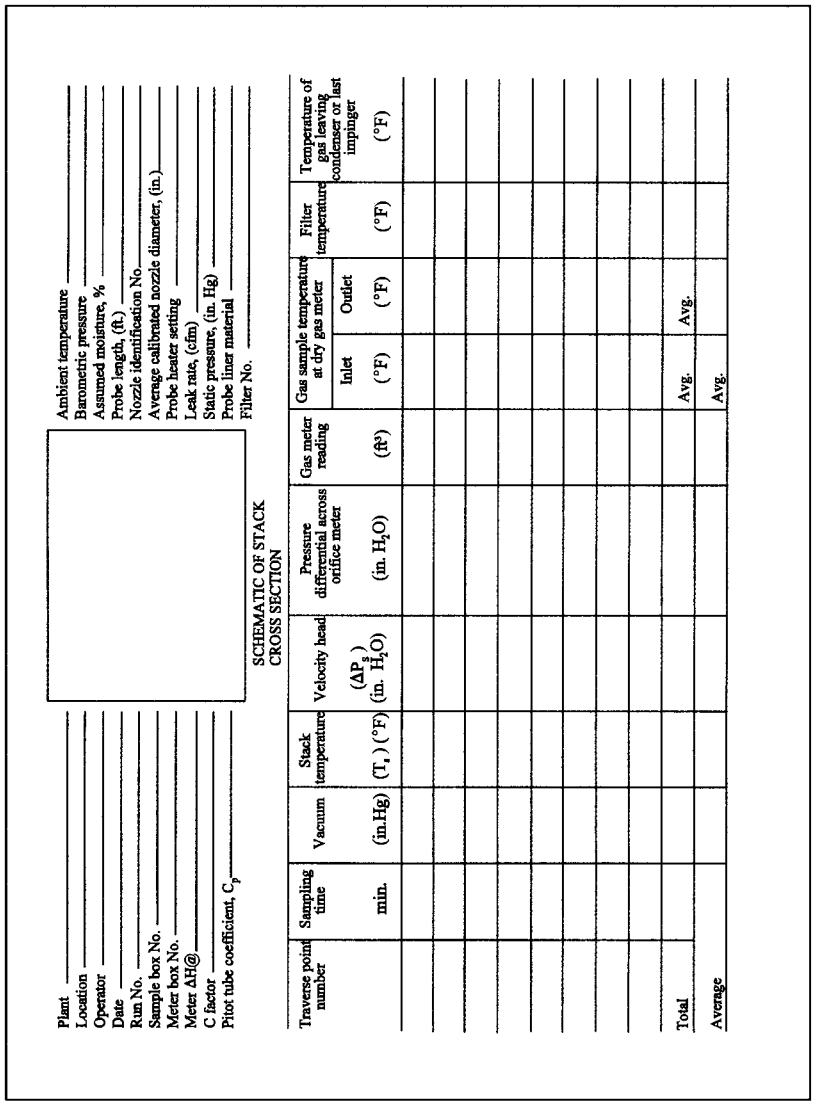

Figure 8-2. Field Data Sheet.

METHOD 9—VISUAL DETERMINATION OF THE OPACITY OF EMISSIONS FROM STATIONARY SOURCES

Many stationary sources discharge visible emissions into the atmosphere; these emissions are usually in the shape of a plume. This method involves the determination of plume opacity by qualified observers. The method includes procedures for the training and certification of observers, and procedures to be used in the field for determination of plume opacity. The appearance of a plume as viewed by an observer depends upon a number of variables, some of which may be controllable and some of which may not be controllable in the field. Variables which can be controlled to an extent to which they no longer exert a significant influence upon

plume appearance include: Angle of the observer with respect to the plume; angle of the observer with respect to the sun; point of observation of attached and detached steam plume; and angle of the observer with respect to a plume emitted from a rectangular stack with a large length to width ratio. The method includes specific criteria applicable to these variables.

Other variables which may not be controllable in the field are luminescence and color contrast between the plume and the background against which the plume is viewed. These variables exert an influence upon the appearance of a plume as viewed by an observer, and can affect the ability of the observer to accurately assign opacity values to the observed plume. Studies of the theory of plume opacity and field studies have demonstrated that a plume is most visible and presents the greatest apparent opacity when viewed against a contrasting background. It follows from this, and is confirmed by field trials, that the opacity of a plume, viewed under conditions where a contrasting background is present can be assigned with the greatest degree of accuracy. However, the potential for a positive error is also the greatest when a plume is viewed under such contrasting conditions. Under conditions presenting a less contrasting background, the apparent opacity of a plume is less and approaches zero as the color and luminescence contrast decrease toward zero. As a result, significant negative bias and negative errors can be made when a plume is viewed under less contrasting conditions. A negative bias decreases rather than increases the possibility that a plant operator will be cited for a violation of opacity standards due to observer error.

Studies have been undertaken to determine the magnitude of positive errors which can be made by qualified observers while reading plumes under contrasting conditions and using the procedures set forth in this method. The results of these studies (field trials) which involve a total of 769 sets of 25 readings each are as follows:

(1) For black plumes (133 sets at a smoke generator), 100 percent of the sets were read with a positive error[1] of less than 7.5 percent opacity; 99 percent were read with a positive error of less than 5 percent opacity.

(2) For white plumes (170 sets at a smoke generator, 168 sets at a coal-fired power plant, 298 sets at a sulfuric acid plant), 99 percent of the sets were read with a positive error of less than 7.5 percent opacity; 95 percent were read with a positive error of less than 5 percent opacity.

[1] For a set, positive error = average opacity determined by observers' 25 observations—average opacity determined from transmissometer's 25 recordings.

The positive observational error associated with an average of twenty-five readings is therefore established. The accuracy of the method must be taken into account when determining possible violations of applicable opacity standards.

1. Principle and Applicability

1.1 Principle. The opacity of emissions from stationary sources is determined visually by a qualified observer.

1.2 Applicability. This method is applicable for the determination of the opacity of emissions from stationary sources pursuant to §60.11(b) and for qualifying observers for visually determining opacity of emissions.

2. Procedures

The observer qualified in accordance with section 3 of this method shall use the following procedures for visually determining the opacity of emissions:

2.1 Position. The qualified observer shall stand at a distance sufficient to provide a clear view of the emissions with the sun oriented in the 140° sector to his back. Consistent with maintaining the above requirement, the observer shall, as much as possible, make his observations from a position such that his line of vision is approximately perpendicular to the plume direction, and when observing opacity of emissions from rectangular outlets (e.g., roof monitors, open baghouses, noncircular stacks), approximately perpendicular to the longer axis of the outlet. The observer's line of sight should not include more than one plume at a time when multiple stacks are involved, and in any case the observer should make his observations with his line of sight perpendicular to the longer axis of such a set of multiple stacks (e.g., stub stacks on baghouses).

2.2 Field Records. The observer shall record the name of the plant, emission location, type facility, observer's name and affiliation, a sketch of the observer's position relative to the source, and the date on a field data sheet (Figure 9–1). The time, estimated distance to the emission location, approximate wind direction, estimated wind speed, description of the sky condition (presence and color of clouds), and plume background are recorded on a field data sheet at the time opacity readings are initiated and completed.

2.3 Observations. Opacity observations shall be made at the point of greatest opacity in that portion of the plume where condensed water vapor is not present. The observer shall not look continuously at the plume, but instead shall observe the plume momentarily at 15-second intervals.

2.3.1 Attached Steam Plumes. When condensed water vapor is present within the

plume as it emerges from the emission outlet, opacity observations shall be made beyond the point in the plume at which condensed water vapor is no longer visible. The observer shall record the approximate distance from the emission outlet to the point in the plume at which the observations are made.

2.3.2 Detached Steam Plume. When water vapor in the plume condenses and becomes visible at a distinct distance from the emission outlet, the opacity of emissions should be evaluated at the emission outlet prior to the condensation of water vapor and the formation of the steam plume.

2.4 Recording Observations. Opacity observations shall be recorded to the nearest 5 percent at 15-second intervals on an observational record sheet. (See Figure 9–2 for an example.) A minimum of 24 observations shall be recorded. Each momentary observation recorded shall be deemed to represent the average opacity of emissions for a 15-second period.

2.5 Data Reduction. Opacity shall be determined as an average of 24 consecutive observations recorded at 15-second intervals. Divide the observations recorded on the record sheet into sets of 24 consecutive observations. A set is composed of any 24 consecutive observations. Sets need not be consecutive in time and in no case shall two sets overlap. For each set of 24 observations, calculate the average by summing the opacity of the 24 observations and dividing this sum by 24. If an applicable standard specifies an averaging time requiring more than 24 observations, calculate the average for all observations made during the specified time period. Record the average opacity on a record sheet. (See Figure 9–1 for an example.)

3. Qualifications and Testing

3.1 Certification Requirements. To receive certification as a qualified observer, a candidate must be tested and demonstrate the ability to assign opacity readings in 5 percent increments to 25 different black plumes and 25 different white plumes, with an error not to exceed 15 percent opacity on any one reading and an average error not to exceed 7.5 percent opacity in each category. Candidates shall be tested according to the procedures described in section 3.2. Smoke generators used pursuant to section 3.2 shall be equipped with a smoke meter which meets the requirements of section 3.3.

The certification shall be valid for a period of 6 months, at which time the qualification procedure must be repeated by any observer in order to retain certification.

3.2 Certification Procedure. The certification test consists of showing the candidate a complete run of 50 plumes—25 black plumes and 25 white plumes—generated by a smoke generator. Plumes within each set of 25 black and 25 white runs shall be presented in random order. The candidate assigns an opacity value to each plume and records his observation on a suitable form. At the completion of each run of 50 readings, the score of the candidate is determined. If a candidate fails to qualify, the complete run of 50 readings must be repeated in any retest. The smoke test may be administered as part of a smoke school or training program, and may be preceded by training or familiarization runs of the smoke generator during which candidates are shown black and white plumes of known opacity.

3.3 Smoke Generator Specifications. Any smoke generator used for the purposes of section 3.2 shall be equipped with a smoke meter installed to measure opacity across the diameter of the smoke generator stack. The smoke meter output shall display instack opacity based upon a pathlength equal to the stack exit diameter, on a full 0 to 100 percent chart recorder scale. The smoke meter optical design and performance shall meet the specifications shown in Table 9–1. The smoke meter shall be calibrated as prescribed in section 3.3.1 prior to the conduct of each smoke reading test. At the completion of each test, the zero and span drift shall be checked and if the drift exceeds ±1 percent opacity, the condition shall be corrected prior to conducting any subsequent test runs. The smoke meter shall be demonstrated, at the time of installation, to meet the specifications listed in Table 9–1. This demonstration shall be repeated following any subsequent repair or replacement of the photocell or associated electronic circuitry including the chart recorder or output meter, or every 6 months, whichever occurs first.

TABLE 9–1—SMOKE METER DESIGN AND PERFORMANCE SPECIFICATIONS

Parameter	Specification
a. Light source	Incandescent lamp operated at nominal rated voltage.
b. Spectral response of photocell.	Photopic (daylight spectral response of the human eye—Citation 3).
c. Angle of view	15° maximum total angle.
d. Angle of projection	15° maximum total angle.
e. Calibration error	±3% opacity, maximum.
f. Zero and span drift	±1% opacity, 30 minutes.
g. Response time	5 seconds.

3.3.1 Calibration. The smoke meter is calibrated after allowing a minimum of 30 minutes warmup by alternately producing simulated opacity of 0 percent and 100 percent. When stable response at 0 percent or 100 percent is noted, the smoke meter is adjusted to produce an output of 0 percent or 100 percent, as appropriate. This calibration shall be repeated until stable 0 percent and 100

percent readings are produced without adjustment. Simulated 0 percent and 100 percent opacity values may be produced by alternately switching the power to the light source on and off while the smoke generator is not producing smoke.

3.3.2 Smoke Meter Evaluation. The smoke meter design and performance are to be evaluated as follows:

3.3.2.1 Light Source. Verify from manufacturer's data and from voltage measurements made at the lamp, as installed, that the lamp is operated within ±5 percent of the nominal rated voltage.

3.3.2.2 Spectral Response of Photocell. Verify from manufacturer's data that the photocell has a photopic response; i.e., the spectral sensitivity of the cell shall closely approximate the standard spectral-luminosity curve for photopic vision which is referenced in (b) of Table 9–1.

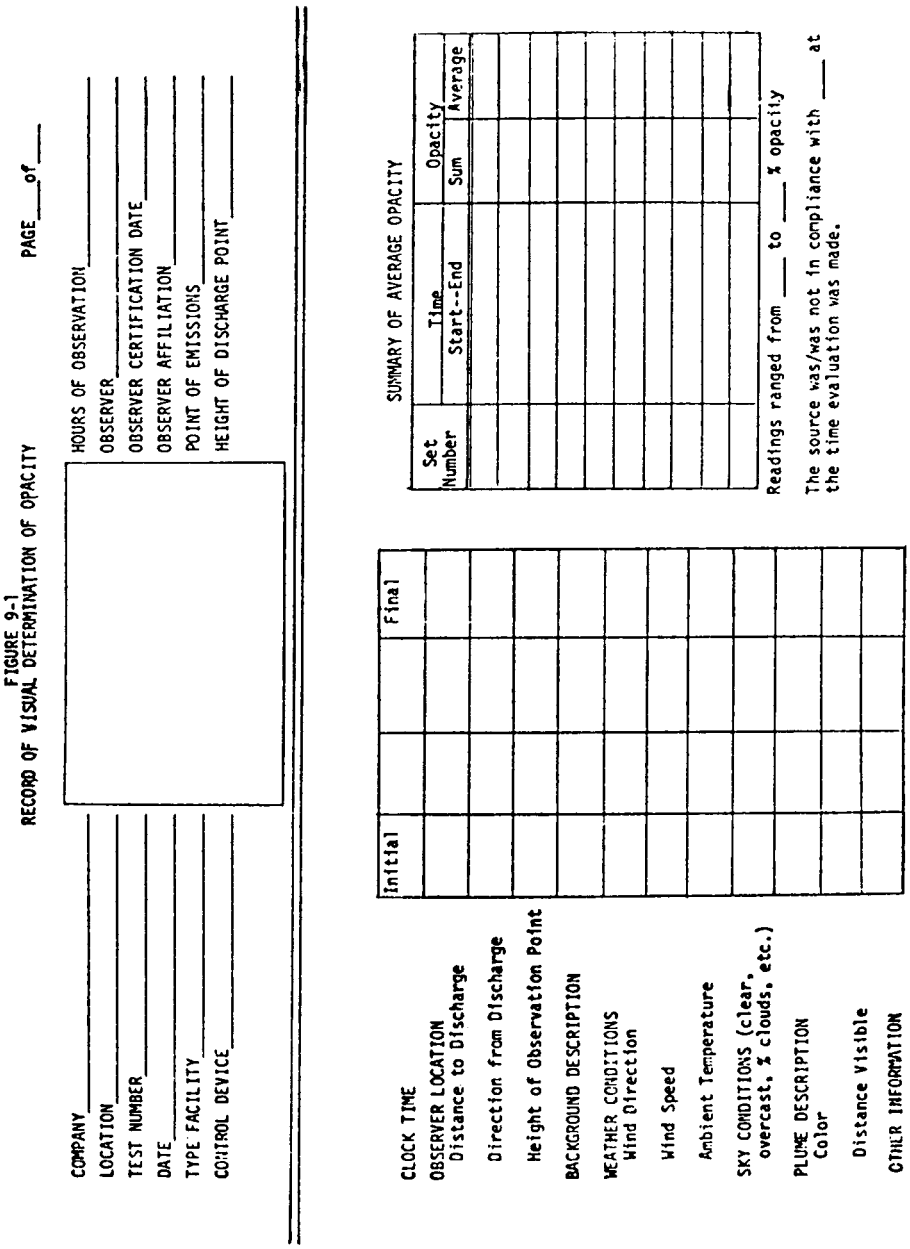

FIGURE 9–2—OBSERVATION RECORD

Page ___ of ___

Company .....
Location .....
Test Number .....
Date.

Observer .....
Type facility .....
Point of emissions .....

Hr.	Min.	Seconds				Steam plume (check if applicable)		Comments
		0	15	30	45	Attached	Detached	
	0							
	1							
	2							
	3							
	4							
	5							
	6							
	7							
	8							
	9							
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FIGURE 9–2—OBSERVATION RECORD (CONTINUED)

Page ____ of ____

Company .....
Location .....
Test Number .....
Date.

Observer .....
Type facility .....
Point of emissions .....

Hr.	Min.	Seconds				Steam plume (check if applicable)		Comments
		0	15	30	45	Attached	Detached	
	30							

Hr.	Min.	Seconds				Steam plume (check if applicable)		Comments
		0	15	30	45	Attached	Detached	
	31							
	32							
	33							
	34							
	35							
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3.3.2.3 Angle of View. Check construction geometry to ensure that the total angle of view of the smoke plume, as seen by the photocell, does not exceed 15°. The total angle of view may be calculated from: $\theta = 2 \tan^{-1} d/2L$, where θ = total angle of view; d = the sum of the photocell diameter + the diameter of the limiting aperture; and L = the distance from the photocell to the limiting aperture. The limiting aperture is the point in the path between the photocell and the smoke plume where the angle of view is most restricted. In smoke generator smoke meters this is normally an orifice plate.

3.3.2.4 Angle of Projection. Check construction geometry to ensure that the total angle of projection of the lamp on the smoke plume does not exceed 15°. The total angle of projection may be calculated from: $\theta = 2 \tan^{-1} d/2L$, where θ = total angle of projection; d = the sum of the length of the lamp

filament + the diameter of the limiting aperture; and L = the distance from the lamp to the limiting aperture.

3.3.2.5 Calibration Error. Using neutral-density filters of known opacity, check the error between the actual response and the theoretical linear response of the smoke meter. This check is accomplished by first calibrating the smoke meter according to 3.3.1 and then inserting a series of three neutral-density filters of nominal opacity of 20, 50, and 75 percent in the smoke meter pathlength. Filters calibrated within ±2 percent shall be used. Care should be taken when inserting the filters to prevent stray light from affecting the meter. Make a total of five nonconsecutive readings for each filter. The maximum error on any one reading shall be 3 percent opacity.

3.3.2.6 Zero and Span Drift. Determine the zero and span drift by calibrating and operating the smoke generator in a normal manner over a 1-hour period. The drift is measured by checking the zero and span at the end of this period.

3.3.2.7 Response Time. Determine the response time by producing the series of five simulated 0 percent and 100 percent opacity values and observing the time required to reach stable response. Opacity values of 0 percent and 100 percent may be simulated by alternately switching the power to the light source off and on while the smoke generator is not operating.

4. Bibliography

1. Air Pollution Control District Rules and Regulations, Los Angeles County Air Pollution Control District, Regulation IV, Prohibitions, Rule 50.

2. Weisburd, Melvin I., Field Operations and Enforcement Manual for Air, U.S. Environmental Protection Agency, Research Triangle Park, NC. APTD–1100, August 1972, pp. 4.1–4.36.

3. Condon, E.U., and Odishaw, H., Handbook of Physics, McGraw-Hill Co., New York, NY, 1958, Table 3.1, p. 6–52.

Alternate Method 1—Determination of the Opacity of Emissions From Stationary Sources Remotely by Lidar

This alternate method provides the quantitative determination of the opacity of an emissions plume remotely by a mobile lidar system (laser radar; Light Detection and Ranging). The method includes procedures for the calibration of the lidar and procedures to be used in the field for the lidar determination of plume opacity. The lidar is used to measure plume opacity during either day or nighttime hours because it contains its own pulsed light source or transmitter. The operation of the lidar is not dependent upon ambient lighting conditions (light, dark, sunny or cloudy).

The lidar mechanism or technique is applicable to measuring plume opacity at numerous wavelengths of laser radiation. However, the performance evaluation and calibration test results given in support of this method apply only to a lidar that employs a ruby (red light) laser [Reference 5.1].

1. Principle and Applicability

1.1 Principle. The opacity of visible emissions from stationary sources (stacks, roof vents, etc.) is measured remotely by a mobile lidar (laser radar).

1.2 Applicability. This method is applicable for the remote measurement of the opacity of visible emissions from stationary sources during both nighttime and daylight conditions, pursuant to 40 CFR §60.11(b). It is also applicable for the calibration and performance verification of the mobile lidar for the measurement of the opacity of emissions. A performance/design specification for a basic lidar system is also incorporated into this method.

1.3 Definitions.

Azimuth angle: The angle in the horizontal plane that designates where the laser beam is pointed. It is measured from an arbitrary fixed reference line in that plane.

Backscatter: The scattering of laser light in a direction opposite to that of the incident laser beam due to reflection from particulates along the beam's atmospheric path which may include a smoke plume.

Backscatter signal: The general term for the lidar return signal which results from laser light being backscattered by atmospheric and smoke plume particulates.

Convergence distance: The distance from the lidar to the point of overlap of the lidar receiver's field-of-view and the laser beam.

Elevation angle: The angle of inclination of the laser beam referenced to the horizontal plane.

Far region: The region of the atmosphere's path along the lidar line-of-sight beyond or behind the plume being measured.

Lidar: Acronym for Light Detection and Ranging.

Lidar range: The range or distance from the lidar to a point of interest along the lidar line-of-sight.

Near region: The region of the atmospheric path along the lidar line-of-sight between the lidar's convergence distance and the plume being measured.

Opacity: One minus the optical transmittance of a smoke plume, screen target, etc.

Pick interval: The time or range intervals in the lidar backscatter signal whose minimum average amplitude is used to calculate opacity. Two pick intervals are required, one in the near region and one in the far region.

Plume: The plume being measured by lidar.

Plume signal: The backscatter signal resulting from the laser light pulse passing through a plume.

$1/R^2$Correction: The correction made for the systematic decrease in lidar backscatter signal amplitude with range.

Reference signal: The backscatter signal resulting from the laser light pulse passing through ambient air.

Sample interval: The time period between successive samples for a digital signal or between successive measurements for an analog signal.

Signal spike: An abrupt, momentary increase and decrease in signal amplitude.

Source: The source being tested by lidar.

Time reference: The time (t_o) when the laser pulse emerges from the laser, used as the reference in all lidar time or range measurements.

2. Procedures

The mobile lidar calibrated in accordance with Paragraph 3 of this method shall use the following procedures for remotely measuring the opacity of stationary source emissions:

2.1 Lidar Position. The lidar shall be positioned at a distance from the plume sufficient to provide an unobstructed view of the source emissions. The plume must be at a range of at least 50 meters or three consecutive pick intervals (whichever is greater) from the lidar's transmitter/receiver convergence distance along the line-of-sight. The maximum effective opacity measurement distance of the lidar is a function of local atmospheric conditions, laser beam diameter, and plume diameter. The test position of the lidar shall be selected so that the diameter of the laser beam at the measurement point within the plume shall be no larger than three-fourths the plume diameter. The beam diameter is calculated by Equation (AM1–1):

$$D(\text{lidar}) = A + R\varphi \leq 0.75\ D(\text{Plume}) \quad \text{(AM1–1)}$$

Where:

D(Plume) = diameter of the plume (cm),
φ = laser beam divergence measured in radians
R = range from the lidar to the source (cm)
D(Lidar) = diameter of the laser beam at range R (cm),
A = diameter of the laser beam or pulse where it leaves the laser.

The lidar range, R, is obtained by aiming and firing the laser at the emissions source structure immediately below the outlet. The range value is then determined from the backscatter signal which consists of a signal spike (return from source structure) and the atmospheric backscatter signal [Reference 5.1]. This backscatter signal should be recorded.

When there is more than one source of emissions in the immediate vicinity of the plume, the lidar shall be positioned so that the laser beam passes through only a single plume, free from any interference of the other plumes for a minimum of 50 meters or three consecutive pick intervals (whichever is greater) in each region before and beyond the plume along the line-of-sight (determined from the backscatter signals). The lidar shall initially be positioned so that its line-of-sight is approximately perpendicular to the plume.

When measuring the opacity of emissions from rectangular outlets (e.g., roof monitors, open baghouses, noncircular stacks, etc.), the lidar shall be placed in a position so that its line-of-sight is approximately perpendicular to the longer (major) axis of the outlet.

2.2 Lidar Operational Restrictions. The lidar receiver shall not be aimed within an angle of ±15° (cone angle) of the sun.

This method shall not be used to make opacity measurements if thunderstorms, snowstorms, hail storms, high wind, high-ambient dust levels, fog or other atmospheric conditions cause the reference signals to consistently exceed the limits specified in section 2.3.

2.3 Reference Signal Requirements. Once placed in its proper position for opacity measurement, the laser is aimed and fired with the line-of-sight near the outlet height and rotated horizontally to a position clear of the source structure and the associated plume. The backscatter signal obtained from this position is called the ambient-air or reference signal. The lidar operator shall inspect this signal [Section V of Reference 5.1] to: (1) determine if the lidar line-of-sight is free from interference from other plumes and from physical obstructions such as cables, power lines, etc., for a minimum of 50 meters or three consecutive pick intervals (whichever is greater) in each region before and beyond the plume, and (2) obtain a qualitative measure of the homogeneity of the ambient air by noting any signal spikes.

Should there be any signal spikes on the reference signal within a minimum of 50 meters or three consecutive pick intervals (whichever is greater) in each region before and beyond the plume, the laser shall be fired three more times and the operator shall inspect the reference signals on the display. If the spike(s) remains, the azimuth angle shall be changed and the above procedures conducted again. If the spike(s) disappears in all three reference signals, the lidar line-of-sight is acceptable if there is shot-to-shot consistency and there is no interference from other plumes.

Shot-to-shot consistency of a series of reference signals over a period of twenty seconds is verified in either of two ways. (1) The lidar operator shall observe the reference signal amplitudes. For shot-to-shot consistency the ratio of R_f to R_n [amplitudes of the near and far region pick intervals (Section 2.6.1)] shall vary by not more than ±6% between shots; or (2) the lidar operator shall accept any one of the reference signals and

treat the other two as plume signals; then the opacity for each of the subsequent reference signals is calculated (Equation AM1–2). For shot-to-shot consistency, the opacity values shall be within ±3% of 0% opacity and the associated S_o values less than or equal to 8% (full scale) [Section 2.6].

If a set of reference signals fails to meet the requirements of this section, then all plume signals [Section 2.4] from the last set of acceptable reference signals to the failed set shall be discarded.

2.3.1 Initial and Final Reference Signals. Three reference signals shall be obtained within a 90-second time period prior to any data run. A final set of three reference signals shall be obtained within three (3) minutes after the completion of the same data run.

2.3.2 Temporal Criterion for Additional Reference Signals. An additional set of reference signals shall be obtained during a data run if there is a change in wind direction or plume drift of 30° or more from the direction that was prevalent when the last set of reference signals was obtained. An additional set of reference signals shall also be obtained if there is an increase in value of S_{In} (near region standard deviation, Equation AM1–5) or S_{If} (far region standard deviation, Equation AM1–6) that is greater than 6% (full scale) over the respective values calculated from the immediately previous plume signal, and this increase in value remains for 30 seconds or longer. An additional set of reference signals shall also be obtained if there is a change in amplitude in either the near or the far region of the plume signal, that is greater than 6% of the near signal amplitude and this change in amplitude remains for 30 seconds or more.

2.4 Plume Signal Requirements. Once properly aimed, the lidar is placed in operation with the nominal pulse or firing rate of six pulses/minute (1 pulse/10 seconds). The lidar operator shall observe the plume backscatter signals to determine the need for additional reference signals as required by section 2.3.2. The plume signals are recorded from lidar start to stop and are called a data run. The length of a data run is determined by operator discretion. Short-term stops of the lidar to record additional reference signals do not constitute the end of a data run if plume signals are resumed within 90 seconds after the reference signals have been recorded, and the total stop or interrupt time does not exceed 3 minutes.

2.4.1 Non-hydrated Plumes. The laser shall be aimed at the region of the plume which displays the greatest opacity. The lidar operator must visually verify that the laser is aimed clearly above the source exit structure.

2.4.2 Hydrated Plumes. The lidar will be used to measure the opacity of hydrated or so-called steam plumes. As listed in the reference method, there are two types, i.e., attached and detached steam plumes.

2.4.2.1 Attached Steam Plumes. When condensed water vapor is present within a plume, lidar opacity measurements shall be made at a point within the residual plume where the condensed water vapor is no longer visible. The laser shall be aimed into the most dense region (region of highest opacity) of the residual plume.

During daylight hours the lidar operator locates the most dense portion of the residual plume visually. During nighttime hours a high-intensity spotlight, night vision scope, or low light level TV, etc., can be used as an aid to locate the residual plume. If visual determination is ineffective, the lidar may be used to locate the most dense region of the residual plume by repeatedly measuring opacity, along the longitudinal axis or center of the plume from the emissions outlet to a point just beyond the steam plume. The lidar operator should also observe color differences and plume reflectivity to ensure that the lidar is aimed completely within the residual plume. If the operator does not obtain a clear indication of the location of the residual plume, this method shall not be used.

Once the region of highest opacity of the residual plume has been located, aiming adjustments shall be made to the laser line-of-sight to correct for the following: movement to the region of highest opacity out of the lidar line-of-sight (away from the laser beam) for more than 15 seconds, expansion of the steam plume (air temperature lowers and/or relative humidity increases) so that it just begins to encroach on the field-of-view of the lidar's optical telescope receiver, or a decrease in the size of the steam plume (air temperature higher and/or relative humidity decreases) so that regions within the residual plume whose opacity is higher than the one being monitored, are present.

2.4.2.2 Detached Steam Plumes. When the water vapor in a hydrated plume condenses and becomes visible at a finite distance from the stack or source emissions outlet, the opacity of the emissions shall be measured in the region of the plume clearly above the emissions outlet and below condensation of the water vapor.

During daylight hours the lidar operators can visually determine if the steam plume is detached from the stack outlet. During nighttime hours a high-intensity spotlight, night vision scope, low light level TV, etc., can be used as an aid in determining if the steam plume is detached. If visual determination is ineffective, the lidar may be used to determine if the steam plume is detached by repeatedly measuring plume opacity from the outlet to the steam plume along the plume's longitudinal axis or center line. The lidar operator should also observe color differences and plume reflectivity to detect a

detached plume. If the operator does not obtain a clear indication of the location of the detached plume, this method shall not be used to make opacity measurements between the outlet and the detached plume.

Once the determination of a detached steam plume has been confirmed, the laser shall be aimed into the region of highest opacity in the plume between the outlet and the formation of the steam plume. Aiming adjustments shall be made to the lidar's line-of-sight within the plume to correct for changes in the location of the most dense region of the plume due to changes in wind direction and speed or if the detached steam plume moves closer to the source outlet encroaching on the most dense region of the plume. If the detached steam plume should move too close to the source outlet for the lidar to make interference-free opacity measurements, this method shall not be used.

2.5 Field Records. In addition to the recording recommendations listed in other sections of this method the following records should be maintained. Each plume measured should be uniquely identified. The name of the facility, type of facility, emission source type, geographic location of the lidar with respect to the plume, and plume characteristics should be recorded. The date of the test, the time period that a source was monitored, the time (to the nearest second) of each opacity measurement, and the sample interval should also be recorded. The wind speed, wind direction, air temperature, relative humidity, visibility (measured at the lidar's position), and cloud cover should be recorded at the beginning and end of each time period for a given source. A small sketch depicting the location of the laser beam within the plume should be recorded.

If a detached or attached steam plume is present at the emissions source, this fact should be recorded. Figures AM1–I and AM1–II are examples of logbook forms that may be used to record this type of data. Magnetic tape or paper tape may also be used to record data.

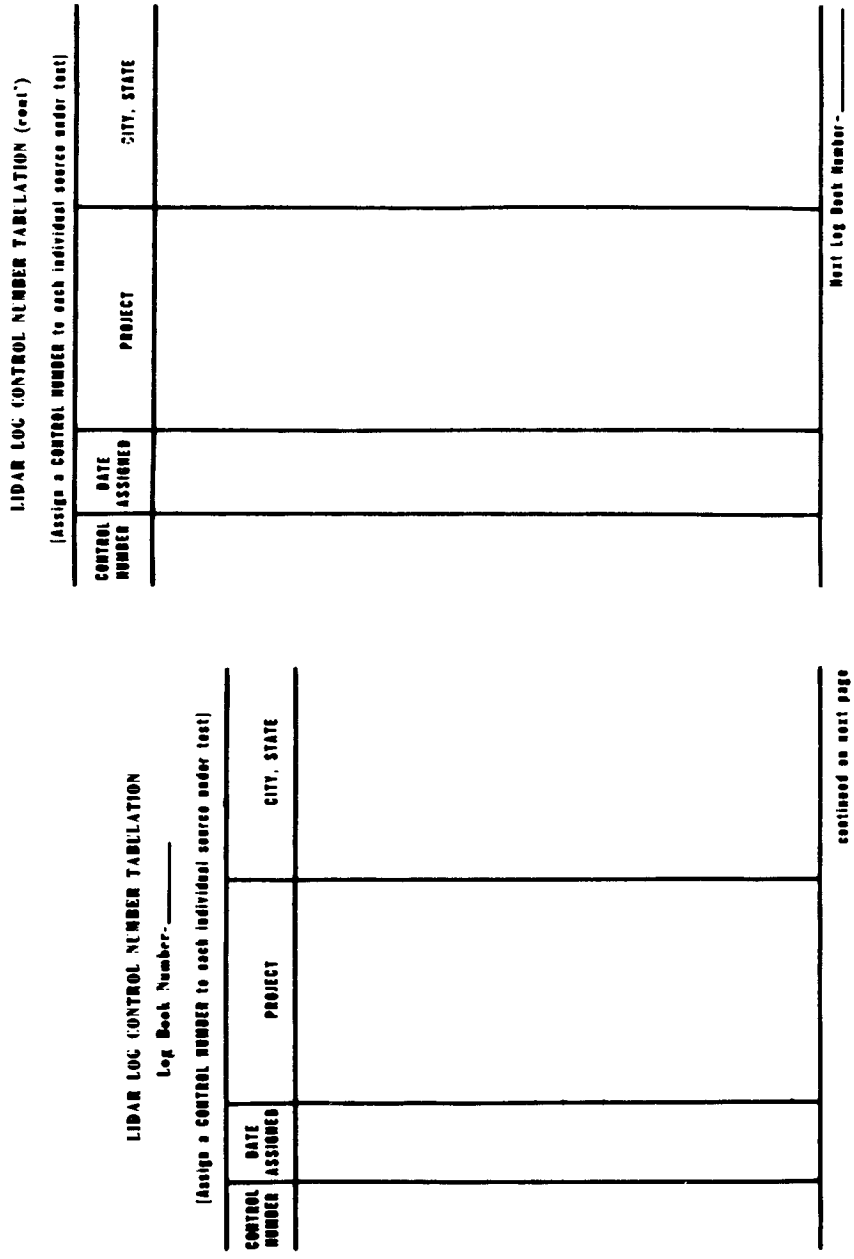


Figure AM1-1 Lidar Log Control Number Tabulation

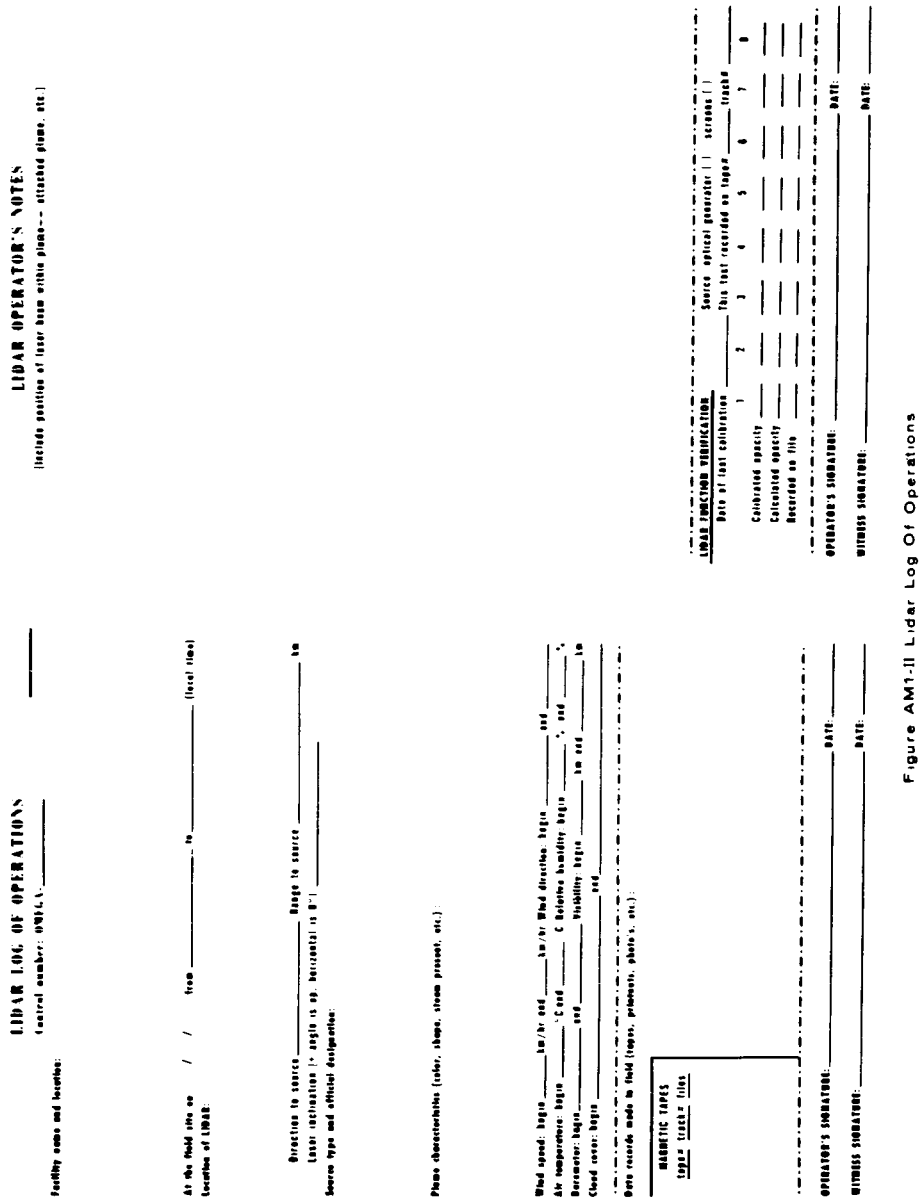
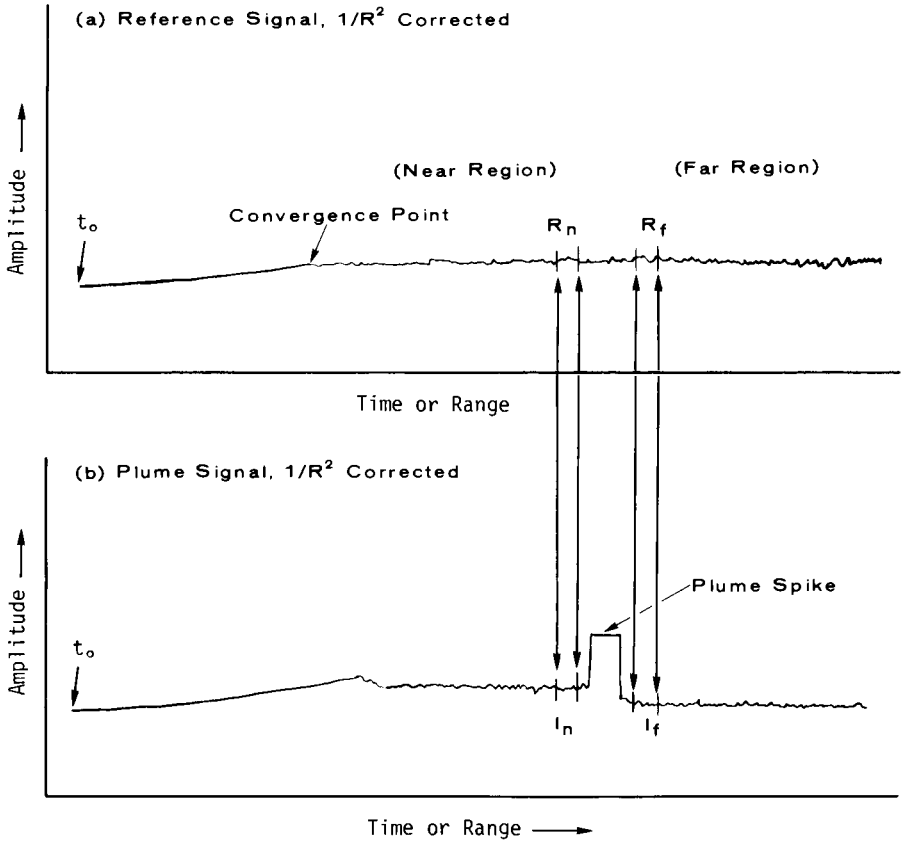


Figure AM1-11 Lidar Log Of Operations



(a) Reference signal, $1/R^2$-corrected. This reference signal is for plume signal (b). R_n, R_f are chosen to coincide with I_n, I_f.

(b) Plume signal, $1/R^2$-corrected. The plume spike and the decrease in the backscatter signal amplitude in the far region are due to the opacity of the plume. I_n, I_f are chosen as indicated in Section 2.6.

Figure AM1-III. Plots of Lidar Backscatter Signals

2.6 Opacity Calculation and Data Analysis. Referring to the reference signal and plume signal in Figure AM1–III, the measured opacity (O_p) in percent for each lidar measurement is calculated using Equation AM1–2. ($O_p = 1 - T_p$; T_p is the plume transmittance.)

$$O_p = (100\%)\left[1 - \left(\frac{I_f}{R_f}\frac{R_n}{I_n}\right)^{\frac{1}{2}}\right], \qquad \text{(AM1-2)}$$

Where:

I_n = near-region pick interval signal amplitude, plume signal, $1/R^2$ corrected,

I_f = far-region pick interval signal amplitude, plume signal, $1/R^2$ corrected,

R_n = near-region pick interval signal amplitude, reference signal, $1/R^2$ corrected, and

R_f = far-region pick interval signal amplitude, reference signal, $1/R^2$ corrected.

The $1/R^2$ correction to the plume and reference signal amplitudes is made by multiplying the amplitude for each successive sample interval from the time reference, by the square of the lidar time (or range) associated with that sample interval [Reference 5.1].

The first step in selecting the pick intervals for Equation AM1–2 is to divide the plume signal amplitude by the reference signal amplitude at the same respective ranges to obtain a ''normalized'' signal. The pick intervals selected using this normalized signal, are a minimum of 15 m (100 nanoseconds) in length and consist of at least 5 contiguous sample intervals. In addition, the following criteria, listed in order of importance, govern pick interval selection. (1) The intervals shall be in a region of the normalized signal where the reference signal meets the requirements of section 2.3 and is everywhere greater than zero. (2) The intervals (near and far) with the minimum average amplitude are chosen. (3) If more than one interval with the same minimum average amplitude is found, the interval closest to the plume is chosen. (4) The standard deviation, S_o, for the calculated opacity shall be 8% or less. (S_o is calculated by Equation AM1–7).

If S_o is greater than 8%, then the far pick interval shall be changed to the next interval of minimal average amplitude. If S_o is still greater than 8%, then this procedure is repeated for the far pick interval. This procedure may be repeated once again for the near pick interval, but if S_o remains greater than 8%, the plume signal shall be discarded.

The reference signal pick intervals, R_n and R_f, must be chosen over the same time interval as the plume signal pick intervals, I_n and I_f, respectively [Figure AM1–III]. Other methods of selecting pick intervals may be used if they give equivalent results. Field-oriented examples of pick interval selection are available in Reference 5.1.

The average amplitudes for each of the pick intervals, I_n, I_f, R_n, R_f, shall be calculated by averaging the respective individual amplitudes of the sample intervals from the plume signal and the associated reference signal each corrected for $1/R^2$. The amplitude of I_n shall be calculated according to Equation (AM–3).

$$I_n = \frac{1}{m}\sum_{i=1}^{m} I_{ni}, \qquad \text{(AM1-3)}$$

Where:

I_{ni} = the amplitude of the ith sample interval (near-region),

Σ = sum of the individual amplitudes for the sample intervals,

m = number of sample intervals in the pick interval, and

I_n = average amplitude of the near-region pick interval.

Similarly, the amplitudes for I_f, R_n, and R_f are calculated with the three expressions in Equation (AM1–4).

$$I_f = \frac{1}{m}\sum_{i=1}^{m} I_{fi}, \quad R_n = \frac{1}{m}\sum_{i=1}^{m} R_{ni}, \quad R_f = \frac{1}{m}\sum_{i=1}^{m} R_{fi}. \qquad \text{(AM1-4)}$$

The standard deviation, S_{In}, of the set of amplitudes for the near-region pick interval, I_n, shall be calculated using Equation (AM1–5).

Similarly, the standard deviations S_{If}, S_{Rn}, and S_{Rf} are calculated with the three expressions in Equation (AM1–6).

$$S_{In} = \left[\sum_{i=1}^{m} \frac{(I_{ni} - I_n)^2}{(m-1)} \right]^{1/2} . \qquad S_{If} = \left[\sum_{i=1}^{m} \frac{(I_{fi} - I_f)^2}{(m-1)} \right]^{1/2} \qquad \text{(AM1-5)}$$

$$S_{Rn} = \left[\sum_{i=1}^{m} \frac{(R_{ni} - R_n)^2}{(m-1)} \right]^{1/2} ,$$

$$S_{Rf} = \left[\sum_{i=1}^{m} \frac{(R_{fi} - R_f)^2}{(m-1)} \right]^{1/2} . \qquad \text{(AM1-6)}$$

The standard deviation, S_o, for each associated opacity value, O_p, shall be calculated using Equation (AM1–7).

$$S_o = \frac{(100\%)}{2} \left(\frac{I_f}{R_f} \frac{R_n}{I_n} \right)^{1/2} \left[\frac{S_{In}^2}{I_n^2} + \frac{S_{If}^2}{I_f^2} + \frac{S_{Rn}^2}{R_n^2} + \frac{S_{Rf}^2}{R_f^2} \right]^{1/2} \qquad \text{(AM1-7)}$$

The calculated values of I_n, I_f, R_n, R_f, S_{In}, S_{If}, S_{Rn}, S_{Rf}, O_p, and S_o should be recorded. Any plume signal with an S_o greater than 8% shall be discarded.

2.6.1 Azimuth Angle Correction. If the azimuth angle correction to opacity specified in this section is performed, then the elevation angle correction specified in section 2.6.2 shall not be performed. When opacity is measured in the residual region of an attached steam plume, and the lidar line-of-sight is not perpendicular to the plume, it may be necessary to correct the opacity measured by the lidar to obtain the opacity that would be measured on a path perpendicular to the plume. The following method, or any other method which produces equivalent results, shall be used to determine the need for a correction, to calculate the correction, and to document the point within the plume at which the opacity was measured.

Figure AM1–IV(b) shows the geometry of the opacity correction. L′ is the path through the plume along which the opacity measurement is made. P′ is the path perpendicular to the plume at the same point. The angle ε is the angle between L′ and the plume center line. The angle (π/2-ε), is the angle between the L′ and P′. The measured opacity, O_p, measured along the path L′ shall be corrected to obtain the corrected opacity, O_{pc}, for the path P′, using Equation (AM1–8).

$$O_{pc} = (100\%) \left[1 - (1 - 0.01\, O_p)^{\text{Cos}\,(\pi/2-\varepsilon)} \right]$$

$$= (100\%) \left[1 - (1 - 0.01\, O_p)^{\text{Sin}\,\varepsilon} \right] \qquad \text{(AM1-8)}$$

The correction in Equation (AM1–8) shall be performed if the inequality in Equation (AM1–9) is true.

$$\varepsilon \geq \text{Sin}^{-1}\left[\frac{\ln (101 - O_p)}{\ln (100 - O_p)}\right] \qquad \text{(AM1-9)}$$

Figure AM1–IV(a) shows the geometry used to calculate ε and the position in the plume at which the lidar measurement is made. This analysis assumes that for a given lidar measurement, the range from the lidar to the plume, the elevation angle of the lidar from the horizontal plane, and the azimuth angle of the lidar from an arbitrary fixed reference in the horizontal plane can all be obtained directly.

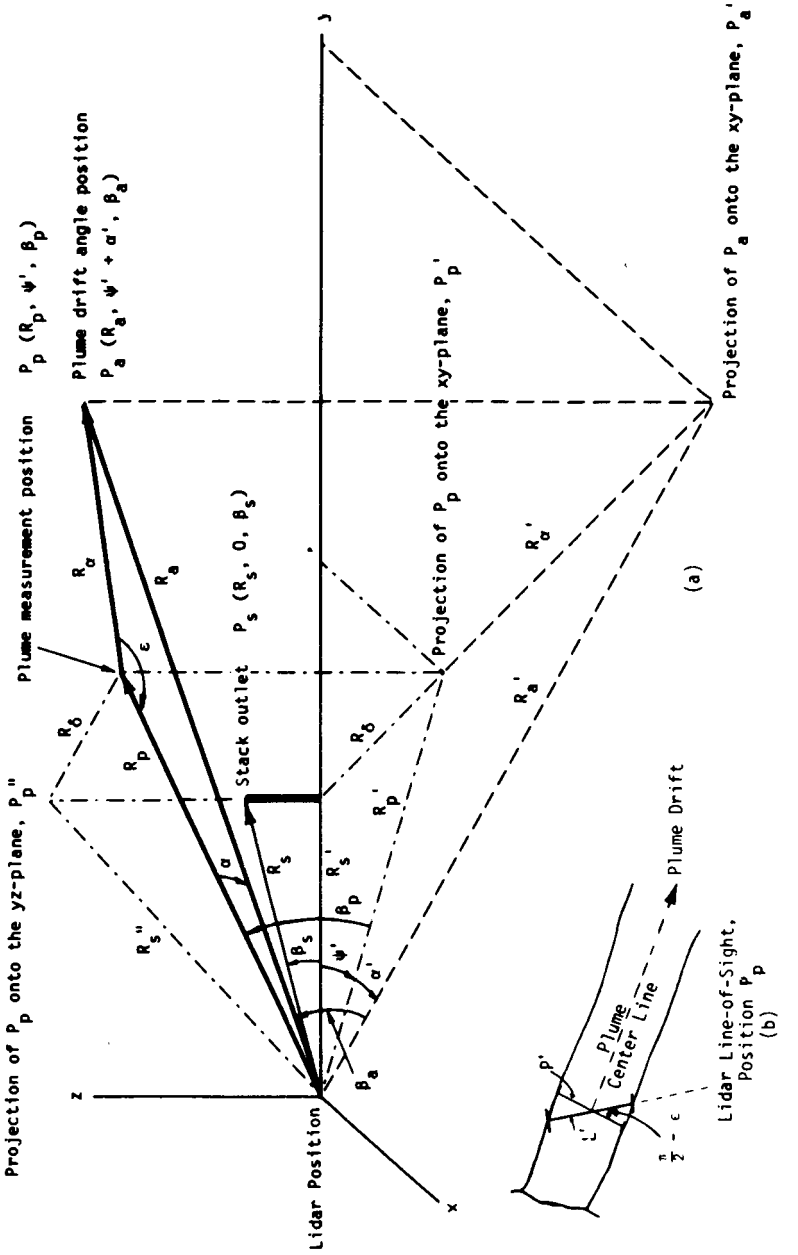


Figure AMI - IV. Correction in Opacity for Drift of the Residual Region of an Attached Steam Plume.

R_s = range from lidar to source*
β_s = elevation angle of R_s*
R_p = range from lidar to plume at the opacity measurement point*
β_p = elevation angle of R_p*
R_a = range from lidar to plume at some arbitrary point, P_a, so the drift angle of the plume can be determined*

β_a = elevation angle of R_a*
α = angle between R_p and R_a
R'_s = projection of R_s in the horizontal plane
R'_p = projection of R_p in the horizontal plane
R'_a = projection of R_a in the horizontal plane
ψ' = angle between R'_s and R'_p*
α' = angle between R'_p and R'_a*
R≤ = distance from the source to the opacity measurement point projected in the horizontal plane
Rθ = distance from opacity measurement point P_p to the point in the plume P_a.

$$O_{pc} = 1 - (1 - O_p)^{\mathrm{Cos}\,(\pi/2-\varepsilon)} = 1 - (1 - O_p)^{\mathrm{Sin}\,\varepsilon} \qquad \text{(AMI-8)}$$

The correction angle ε shall be determined using Equation AM1–10.

Where:

$\alpha = \mathrm{Cos}^{-1}\,(\mathrm{Cos}\beta_p\,\mathrm{Cos}\beta_a\,\mathrm{Cos}\alpha' + \mathrm{Sin}\beta_p\,\mathrm{Sin}\beta_a)$, and

$R\theta = (R_p 2 + R_a 2 - 2\,R_p\,R_a\,\mathrm{Cos}\alpha)^{1/2}$

R≤, the distance from the source to the opacity measurement point projected in the horizontal plane, shall be determined using Equation AM1–11.

$$R_\delta = (R'^2_s + R'^2_p - 2R'_sR'_p\mathrm{Cos}\psi')^{\frac{1}{2}}, \qquad \text{(AM1-11)}$$

Where:

$R'_s = R_s\,\mathrm{Cos}\,\beta_s$, and
$R'_p = R_p\,\mathrm{Cos}\,\beta_p$.

In the special case where the plume centerline at the opacity measurement point is horizontal, parallel to the ground, Equation AM1–12 may be used to determine ε instead of Equation AM1–10.

$$\varepsilon = \mathrm{Cos}^{-1}\left[\frac{R_p^2 + R_\delta^2 - R''^2_s}{2\,R_p\,R_\delta}\right] \qquad \text{(AM1-12)}$$

Where:

$R''_s = (R'^2_s + R_p^2\mathrm{Sin}^2\beta_p)^{1/2}$.

If the angle ε is such that ε≤30° or ε ≥150°, the azimuth angle correction shall not be performed and the associated opacity value shall be discarded.

2.6.2 Elevation Angle Correction. An individual lidar-measured opacity, O_p, shall be corrected for elevation angle if the laser elevation or inclination angle, β_p [Figure AM1–V], is greater than or equal to the value calculated in Equation AM1–13.

$$\beta_p \geq \mathrm{Cos}^{-1}\left[\frac{\ln\,(101 - O_p)}{\ln\,(100 - O_p)}\right] \qquad \text{(AM1-13)}$$

The measured opacity, O_p, along the lidar path L, is adjusted to obtain the corrected opacity, O_{pc}, for the actual plume (horizontal) path, P, by using Equation (AM1–14).

*Obtained directly from lidar. These values should be recorded.

$$O_{pc} = (100\%)\left[1-\left(1-0.01\,O_p\right)^{Cos\beta}p\right], \qquad (AM1\text{-}14)$$

Where:

β_p = lidar elevation or inclination angle,
O_p = measured opacity along path L, and
O_{pc} = corrected opacity for the actual plume thickness P.

The values for β_p, O_p and O_{pc} should be recorded.

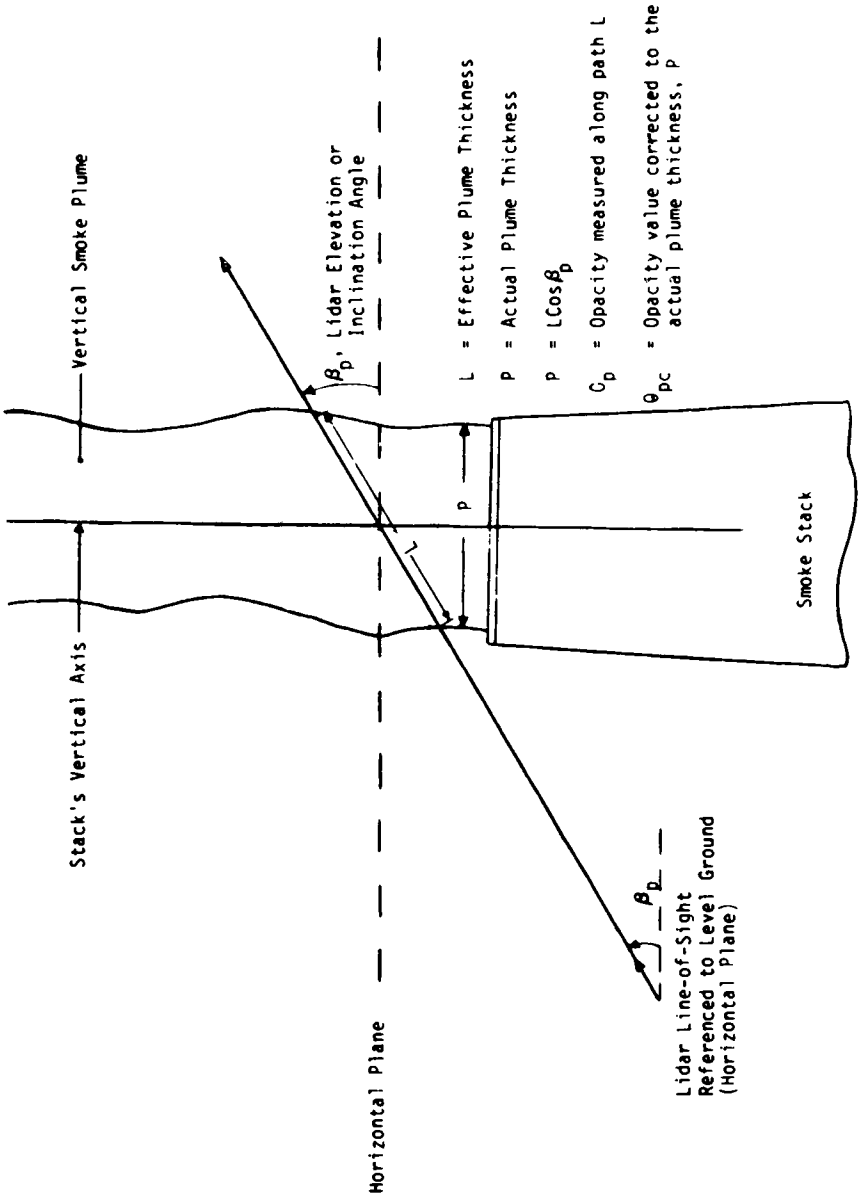


Figure AM1-V. Elevation Angle Correction for Vertical Plumes.

2.6.3 Determination of Actual Plume Opacity. Actual opacity of the plume shall be determined by Equation AM1–15.

$$O_{pa} = O_{pc} - [2\ S_o + 5\%]. \quad \text{(AM1-15)}$$

2.6.4 Calculation of Average Actual Plume Opacity. The average of the actual plume opacity, O_{pa}, shall be calculated as the average of the consecutive individual actual opacity values, O_{pa}, by Equation AM1–16.

$$\bar{O}_{pa} = \frac{1}{n}\sum_{k=1}^{n}(O_{pa})_k \quad , \qquad \text{(AM1-16)}$$

Where:

$(O_{pa})_k$ = the kth actual opacity value in an averaging interval containing n opacity values; k is a summing index.

Σ = the sum of the individual actual opacity values.

n = the number of individual actual opacity values contained in the averaging interval.

O_{pa} = average actual opacity calculated over the averaging interval.

3. Lidar Performance Verification

The lidar shall be subjected to two types of performance verifications that shall be performed in the field. The annual calibration, conducted at least once a year, shall be used to directly verify operation and performance of the entire lidar system. The routine verification, conducted for each emission source measured, shall be used to insure proper performance of the optical receiver and associated electronics.

3.1 Annual Calibration Procedures. Either a plume from a smoke generator or screen targets shall be used to conduct this calibration.

If the screen target method is selected, five screens shall be fabricated by placing an opaque mesh material over a narrow frame (wood, metal extrusion, etc.). The screen shall have a surface area of at least one square meter. The screen material should be chosen for precise optical opacities of about 10, 20, 40, 60, and 80%. Opacity of each target shall be optically determined and should be recorded. If a smoke generator plume is selected, it shall meet the requirements of section 3.3 of Reference Method 9. This calibration shall be performed in the field during calm (as practical) atmospheric conditions. The lidar shall be positioned in accordance with section 2.1.

The screen targets must be placed perpendicular to and coincident with the lidar line-of-sight at sufficient height above the ground (suggest about 30 ft) to avoid ground-level dust contamination. Reference signals shall be obtained just prior to conducting the calibration test.

The lidar shall be aimed through the center of the plume within 1 stack diameter of the exit, or through the geometric center of the screen target selected. The lidar shall be set in operation for a 6-minute data run at a nominal pulse rate of 1 pulse every 10 seconds. Each backscatter return signal and each respective opacity value obtained from the smoke generator transmissometer, shall be obtained in temporal coincidence. The data shall be analyzed and reduced in accordance with section 2.6 of this method. This calibration shall be performed for 0% (clean air), and at least five other opacities (nominally 10, 20, 40, 60, and 80%).

The average of the lidar opacity values obtained during a 6-minute calibration run shall be calculated and should be recorded. Also the average of the opacity values obtained from the smoke generator transmissometer for the same 6-minute run shall be calculated and should be recorded.

Alternate calibration procedures that do not meet the above requirements but produce equivalent results may be used.

3.2 Routine Verification Procedures. Either one of two techniques shall be used to conduct this verification. It shall be performed at least once every 4 hours for each emission source measured. The following parameters shall be directly verified.

1) The opacity value of 0% plus a minimum of 5 (nominally 10, 20, 40, 60, and 80%) opacity values shall be verified through the PMT detector and data processing electronics.

2) The zero-signal level (receiver signal with no optical signal from the source present) shall be inspected to insure that no spurious noise is present in the signal. With the entire lidar receiver and analog/digital electronics turned on and adjusted for normal operating performance, the following procedures shall be used for Techniques 1 and 2, respectively.

3.2.1 Procedure for Technique 1. This test shall be performed with no ambient or stray light reaching the PMT detector. The narrow band filter (694.3 nanometers peak) shall be removed from its position in front of the PMT detector. Neutral density filters of nominal opacities of 10, 20, 40, 60, and 80% shall be used. The recommended test configuration is depicted in Figure AM1–VI.

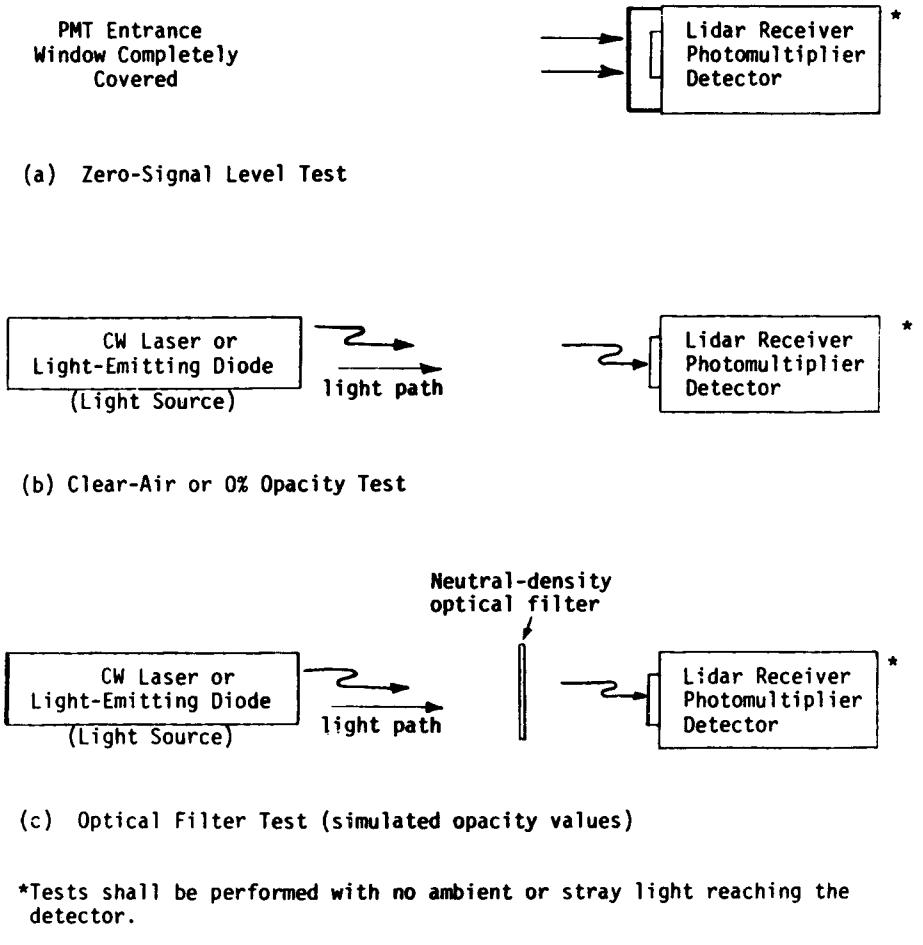


Figure AM1–VI. Test Configuration for Technique 1.

The zero-signal level shall be measured and should be recorded, as indicated in Figure AM1–VI(a). This simulated clear-air or 0% opacity value shall be tested in using the selected light source depicted in Figure AM1–VI(b).

The light source either shall be a continuous wave (CW) laser with the beam mechanically chopped or a light emitting diode controlled with a pulse generator (rectangular pulse). (A laser beam may have to be attenuated so as not to saturate the PMT detector). This signal level shall be measured

and should be recorded. The opacity value is calculated by taking two pick intervals [Section 2.6] about 1 microsecond apart in time and using Equation (AM1–2) setting the ratio $R_n/R_f = 1$. This calculated value should be recorded.

The simulated clear-air signal level is also employed in the optical test using the neutral density filters. Using the test configuration in Figure AM1–VI(c), each neutral density filter shall be separately placed into the light path from the light source to the PMT detector. The signal level shall be measured and should be recorded. The opacity value for each filter is calculated by taking the signal level for that respective filter (I_f), dividing it by the 0% opacity signal level (I_n) and performing the remainder of the calculation by Equation (AM1–2) with $R_n/R_f = 1$. The calculated opacity value for each filter should be recorded.

The neutral density filters used for Technique 1 shall be calibrated for actual opacity with accuracy of ±2% or better. This calibration shall be done monthly while the filters are in use and the calibrated values should be recorded.

3.2.2 Procedure for Technique 2. An optical generator (built-in calibration mechanism) that contains a light-emitting diode (red light for a lidar containing a ruby laser) is used. By injecting an optical signal into the lidar receiver immediately ahead of the PMT detector, a backscatter signal is simulated. With the entire lidar receiver electronics turned on and adjusted for normal operating performance, the optical generator is turned on and the simulation signal (corrected for $1/R^2$) is selected with no plume spike signal and with the opacity value equal to 0%. This simulated clear-air atmospheric return signal is displayed on the system's video display. The lidar operator then makes any fine adjustments that may be necessary to maintain the system's normal operating range.

The opacity values of 0% and the other five values are selected one at a time in any order. The simulated return signal data should be recorded. The opacity value shall be calculated. This measurement/calculation shall be performed at least three times for each selected opacity value. While the order is not important, each of the opacity values from the optical generator shall be verified. The calibrated optical generator opacity value for each selection should be recorded.

The optical generator used for Technique 2 shall be calibrated for actual opacity with an accuracy of ±1% or better. This calibration shall be done monthly while the generator is in use and calibrated value should be recorded.

Alternate verification procedures that do not meet the above requirements but produce equivalent results may be used.

3.3 Deviation. The permissible error for the annual calibration and routine verification are:

3.3.1 Annual Calibration Deviation.

3.3.1.1 Smoke Generator. If the lidar-measured average opacity for each data run is not within ±5% (full scale) of the respective smoke generator's average opacity over the range of 0% through 80%, then the lidar shall be considered out of calibration.

3.3.1.2 Screens. If the lidar-measured average opacity for each data run is not within ±3% (full scale) of the laboratory-determined opacity for each respective simulation screen target over the range of 0% through 80%, then the lidar shall be considered out of calibration.

3.3.2 Routine Verification Error. If the lidar-measured average opacity for each neutral density filter (Technique 1) or optical generator selection (Technique 2) is not within ±3% (full scale) of the respective laboratory calibration value then the lidar shall be considered non-operational.

4. Performance/Design Specification for Basic Lidar System

4.1 Lidar Design Specification. The essential components of the basic lidar system are a pulsed laser (transmitter), optical receiver, detector, signal processor, recorder, and an aiming device that is used in aiming the lidar transmitter and receiver. Figure AM1–VII shows a functional block diagram of a basic lidar system.

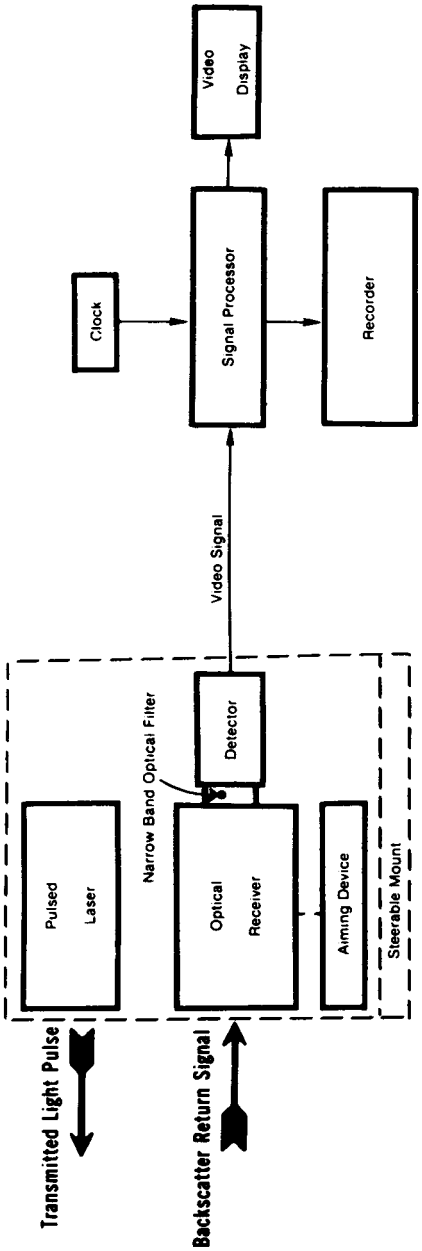


Figure AM1-VII. Functional Block Diagram of a Basic Lidar System

4.2 Performance Evaluation Tests. The owner of a lidar system shall subject such a lidar system to the performance verification tests described in section 3, prior to first use of this method. The annual calibration shall be performed for three separate, complete

runs and the results of each should be recorded. The requirements of section 3.3.1 must be fulfilled for each of the three runs.

Once the conditions of the annual calibration are fulfilled the lidar shall be subjected to the routine verification for three separate complete runs. The requirements of section 3.3.2 must be fulfilled for each of the three runs and the results should be recorded. The Administrator may request that the results of the performance evaluation be submitted for review.

5. References

5.1 The Use of Lidar for Emissions Source Opacity Determination, U.S. Environmental Protection Agency, National Enforcement Investigations Center, Denver, CO. EPA–330/1–79–003–R, Arthur W. Dybdahl, current edition [NTIS No. PB81–246662].

5.2 Field Evaluation of Mobile Lidar for the Measurement of Smoke Plume Opacity, U.S. Environmental Protection Agency, National Enforcement Investigations Center, Denver, CO. EPA/NEIC-TS-128, February 1976.

5.3 Remote Measurement of Smoke Plume Transmittance Using Lidar, C. S. Cook, G. W. Bethke, W. D. Conner (EPA/RTP). Applied Optics 11, pg 1742. August 1972.

5.4 Lidar Studies of Stack Plumes in Rural and Urban Environments, EPA–650/4–73–002, October 1973.

5.5 American National Standard for the Safe Use of Lasers ANSI Z 136.1–176, March 8, 1976.

5.6 U.S. Army Technical Manual TB MED 279, Control of Hazards to Health from Laser Radiation, February 1969.

5.7 Laser Institute of America Laser Safety Manual, 4th Edition.

5.8 U.S. Department of Health, Education and Welfare, Regulations for the Administration and Enforcement of the Radiation Control for Health and Safety Act of 1968, January 1976.

5.9 Laser Safety Handbook, Alex Mallow, Leon Chabot, Van Nostrand Reinhold Co., 1978.

Method 10—Determination of Carbon Monoxide Emissions From Stationary Sources (Instrumental Analyzer Procedure)

1.0 Scope and Application

What is Method 10?

Method 10 is a procedure for measuring carbon monoxide (CO) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis. This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 4—Determination of Moisture Content in Stack Gases.

(c) Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure).

1.1 Analytes. What does this method determine? This method measures the concentration of carbon monoxide.

Analyte	CAS No.	Sensitivity
CO	630–08–0	Typically <2% of Calibration Span.

1.2 Applicability. When is this method required? The use of Method 10 may be required by specific New Source Performance Standards, State Implementation Plans, and permits where CO concentrations in stationary source emissions must be measured, either to determine compliance with an applicable emission standard or to conduct performance testing of a continuous emission monitoring system (CEMS). Other regulations may also require the use of Method 10.

1.3 Data Quality Objectives. Refer to section 1.3 of Method 7E.

2.0 Summary of Method

In this method, you continuously or intermittently sample the effluent gas and convey the sample to an analyzer that measures the concentration of CO. You must meet the performance requirements of this method to validate your data.

3.0 Definitions

Refer to section 3.0 of Method 7E for the applicable definitions.

4.0 Interferences

Substances having a strong absorption of infrared energy may interfere to some extent in some analyzers. Instrumental correction may be used to compensate for the interference. You may also use silica gel and ascarite traps to eliminate the interferences. If this option is used, correct the measured

gas volume for the carbon dioxide (CO_2) removed in the trap.

5.0 Safety

Refer to section 5.0 of Method 7E.

6.0 Equipment and Supplies

What do I need for the measurement system?

6.1 Continuous Sampling. Figure 7E–1 of Method 7E is a schematic diagram of an acceptable measurement system. The components are the same as those in sections 6.1 and 6.2 of Method 7E, except that the CO analyzer described in section 6.2 of this method must be used instead of the analyzer described in section 6.2 of Method 7E. You must follow the noted specifications in section 6.1 of Method 7E except that the requirements to use stainless steel, Teflon, or non-reactive glass filters do not apply. Also, a heated sample line is not required to transport dry gases or for systems that measure the CO concentration on a dry basis.

6.2 Integrated Sampling.

6.2.1 Air-Cooled Condenser or Equivalent. To remove any excess moisture.

6.2.2 Valve. Needle valve, or equivalent, to adjust flow rate.

6.2.3 Pump. Leak-free diaphragm type, or equivalent, to transport gas.

6.2.4 Rate Meter. Rotameter, or equivalent, to measure a flow range from 0 to 1.0 liter per minute (0.035 cfm).

6.2.5 Flexible Bag. Tedlar, or equivalent, with a capacity of 60 to 90 liters (2 to 3 ft^3). (Verify through the manufacturer that the Tedlar alternative is suitable for CO and make this verified information available for inspection.) Leak-test the bag in the laboratory before using by evacuating with a pump followed by a dry gas meter. When the evacuation is complete, there should be no flow through the meter.

6.2.6 Sample Tank. Stainless steel or aluminum tank equipped with a pressure indicator with a minimum volume of 4 liters.

6.3 What analyzer must I use? You must use an instrument that continuously measures CO in the gas stream and meets the specifications in section 13.0. The dual-range analyzer provisions in section 6.2.8.1 of Method 7E apply.

7.0 Reagents and Standards

7.1 Calibration Gas. What calibration gases do I need? Refer to section 7.1 of Method 7E for the calibration gas requirements.

7.2 Interference Check. What additional reagents do I need for the interference check? Use the appropriate test gases listed in Table 7E–3 of Method 7E (i.e., potential interferents, as identified by the instrument manufacturer) to conduct the interference check.

8.0 Sample Collection, Preservation, Storage, and Transport

Emission Test Procedure

8.1 Sampling Site and Sampling Points. You must follow section 8.1 of Method 7E.

8.2 Initial Measurement System Performance Tests. You must follow the procedures in section 8.2 of Method 7E. If a dilution-type measurement system is used, the special considerations in section 8.3 of Method 7E also apply.

8.3 Interference Check. You must follow the procedures of section 8.2.7 of Method 7E.

8.4 Sample Collection.

8.4.1 Continuous Sampling. You must follow the procedures of section 8.4 of Method 7E.

8.4.2 Integrated Sampling. Evacuate the flexible bag or sample tank. Set up the equipment as shown in Figure 10–1 with the bag disconnected. Place the probe in the stack and purge the sampling line. Connect the bag, making sure that all connections are leak-free. Sample at a rate proportional to the stack velocity. If needed, the CO_2 content of the gas may be determined by using the Method 3 integrated sample procedures, or by weighing an ascarite CO_2 removal tube used and computing CO_2 concentration from the gas volume sampled and the weight gain of the tube. Data may be recorded on a form similar to Table 10–1. If a sample tank is used for sample collection, follow procedures similar to those in sections 8.1.2, 8.2.3, 8.3, and 12.4 of Method 25 as appropriate to prepare the tank, conduct the sampling, and correct the measured sample concentration.

8.5 Post-Run System Bias Check, Drift Assessment, and Alternative Dynamic Spike Procedure. You must follow the procedures in sections 8.5 and 8.6 of Method 7E.

9.0 Quality Control

Follow the quality control procedures in section 9.0 of Method 7E.

10.0 Calibration and Standardization

Follow the procedures for calibration and standardization in section 10.0 of Method 7E.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the procedures for calculations and data analysis in section 12.0 of Method 7E, as applicable, substituting CO for NO_X as applicable.

12.1 Concentration Correction for CO_2 Removal. Correct the CO concentration for CO_2 removal (if applicable) using Eq. 10–1.

$$C_{Avg} = C_{CO\ stack}\left(1 - F_{CO2}\right)$$

Where:

C_{Avg} = Average gas concentration for the test run, ppm.

$C_{CO\ stack}$ = Average unadjusted stack gas CO concentration indicated by the data recorder for the test run, ppmv.

F_{CO2} = Volume fraction of CO_2 in the sample, i.e., percent CO_2 from Orsat analysis divided by 100.

13.0 Method Performance

The specifications for analyzer calibration error, system bias, drift, interference check, and alternative dynamic spike procedure are the same as in section 13.0 of Method 7E.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

The dynamic spike procedure and the manufacturer stability test are the same as in sections 16.1 and 16.3 of Method 7E

17.0 References

1. ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards— September 1997 as amended, EPA–600/R–97/121

18.0 Tables, Diagrams, Flowcharts, and Validation Data

Figure 10-1. Integrated Gas Sampling Train.

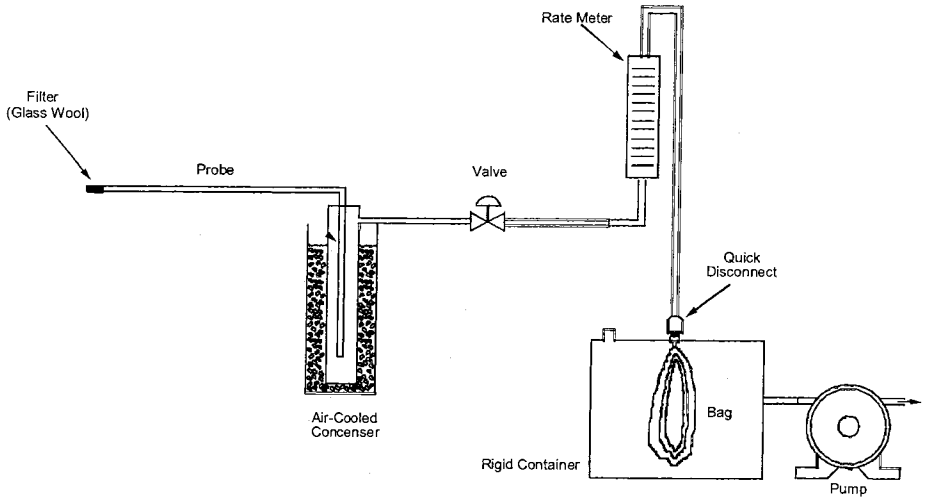


TABLE 10–1—FIELD DATA

[Integrated sampling]

Location:	Date:	
Test:	Operator:	
Clock Time	Rotameter Reading liters/min (cfm)	Comments

TABLE 10–1—FIELD DATA—Continued

[Integrated sampling]

METHOD 10A—DETERMINATION OF CARBON MONOXIDE EMISSIONS IN CERTIFYING CONTINUOUS EMISSION MONITORING SYSTEMS AT PETROLEUM REFINERIES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 4, and Method 5.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Carbon monoxide (CO)	630–08–0	3 ppmv

1.2 Applicability. This method is applicable for the determination of CO emissions at petroleum refineries. This method serves as the reference method in the relative accuracy test for nondispersive infrared (NDIR) CO continuous emission monitoring systems (CEMS) that are required to be installed in petroleum refineries on fluid catalytic cracking unit catalyst regenerators (§60.105(a)(2) of this part).

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

An integrated gas sample is extracted from the stack, passed through an alkaline permanganate solution to remove sulfur oxides and nitrogen oxides, and collected in a Tedlar or equivalent bag. (Verify through the manufacturer that the Tedlar alternative is suitable for NO and make this verified information available for inspection.) The CO concentration in the sample is measured spectrophotometrically using the reaction of CO with *p*-sulfaminobenzoic acid.

3.0 Definitions [Reserved]

4.0 Interferences

Sulfur oxides, nitric oxide, and other acid gases interfere with the colorimetric reaction. They are removed by passing the sampled gas through an alkaline potassium permanganate scrubbing solution. Carbon dioxide (CO_2) does not interfere, but, because it is removed by the scrubbing solution, its concentration must be measured independently and an appropriate volume correction made to the sampled gas.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs.

Reacts exothermically with limited amounts of water.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling train shown in Figure 10A–1 is required for sample collection. Component parts are described below:

6.1.1 Probe. Stainless steel, sheathed Pyrex glass, or equivalent, equipped with a glass wool plug to remove particulate matter.

6.1.2 Sample Conditioning System. Three Greenburg-Smith impingers connected in series with leak-free connections.

6.1.3 Pump. Leak-free pump with stainless steel and Teflon parts to transport sample at a flow rate of 300 ml/min (0.01 ft^3/min) to the flexible bag.

6.1.4 Surge Tank. Installed between the pump and the rate meter to eliminate the pulsation effect of the pump on the rate meter.

6.1.5 Rate Meter. Rotameter, or equivalent, to measure flow rate at 300 ml/min (0.01 ft^3/min). Calibrate according to section 10.2.

6.1.6 Flexible Bag. Tedlar, or equivalent, with a capacity of 10 liters (0.35 ft^3) and equipped with a sealing quick-connect plug. The bag must be leak-free according to section 8.1. For protection, it is recommended that the bag be enclosed within a rigid container.

6.1.7 Sample Tank. Stainless steel or aluminum tank equipped with a pressure indicator with a minimum volume of 10 liters.

6.1.8 Valves. Stainless-steel needle valve to adjust flow rate, and stainless-steel 3-way valve, or equivalent.

6.1.9 CO_2 Analyzer. Fyrite, or equivalent, to measure CO_2 concentration to within 0.5 percent.

6.1.10 Volume Meter. Dry gas meter, capable of measuring the sample volume under calibration conditions of 300 ml/min (0.01 ft^3/min) for 10 minutes.

6.1.11 Pressure Gauge. A water filled U-tube manometer, or equivalent, of about 30 cm (12 in.) to leak-check the flexible bag.

6.2 Sample Analysis.

6.2.1 Spectrophotometer. Single- or double-beam to measure absorbance at 425 and 600 nm. Slit width should not exceed 20 nm.

6.2.2 Spectrophotometer Cells. 1-cm pathlength.

6.2.3 Vacuum Gauge. U-tube mercury manometer, 1 meter (39 in.), with 1-mm divisions, or other gauge capable of measuring pressure to within 1 mm Hg.

6.2.4 Pump. Capable of evacuating the gas reaction bulb to a pressure equal to or less than 40 mm Hg absolute, equipped with coarse and fine flow control valves.

6.2.5 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm Hg.

6.2.6 Reaction Bulbs. Pyrex glass, 100-ml with Teflon stopcock (Figure 10A–2), leak-free at 40 mm Hg, designed so that 10 ml of the colorimetric reagent can be added and removed easily and accurately. Commercially available gas sample bulbs such as Supelco Catalog No. 2–2161 may also be used.

6.2.7 Manifold. Stainless steel, with connections for three reaction bulbs and the appropriate connections for the manometer and sampling bag as shown in Figure 10A–3.

6.2.8 Pipets. Class A, 10–ml size.

6.2.9 Shaker Table. Reciprocating-stroke type such as Eberbach Corporation, Model 6015. A rocking arm or rotary-motion type shaker may also be used. The shaker must be large enough to accommodate at least six gas sample bulbs simultaneously. It may be necessary to construct a table top extension for most commercial shakers to provide sufficient space for the needed bulbs (Figure 10A–4).

6.2.10 Valve. Stainless steel shut-off valve.

6.2.11 Analytical Balance. Capable of weighing to 0.1 mg.

7.0 Reagents and Standards

Unless otherwise indicated, all reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, the best available grade shall be used.

7.1 Sample Collection.

7.1.1 Water. Deionized distilled, to conform to ASTM D 1193–77 or 91, Type 3 (incorporated by reference—see §60.17). If high concentrations of organic matter are not expected to be present, the potassium permanganate test for oxidizable organic matter may be omitted.

7.1.2 Alkaline Permanganate Solution, 0.25 M $KMnO_4$/1.5 M Sodium Hydroxide (NaOH). Dissolve 40 g $KMnO_4$ and 60 g NaOH in approximately 900 ml water, cool, and dilute to 1 liter.

7.2 Sample Analysis.

7.2.1 Water. Same as in section 7.1.1.

7.2.2 1 M Sodium Hydroxide Solution. Dissolve 40 g NaOH in approximately 900 ml of water, cool, and dilute to 1 liter.

7.2.3 0.1 M NaOH Solution. Dilute 50 ml of the 1 M NaOH solution prepared in section 7.2.2 to 500 ml.

7.2.4 0.1 M Silver Nitrate ($AgNO_3$) Solution. Dissolve 8.5 g $AgNO_3$ in water, and dilute to 500 ml.

7.2.5 0.1 M Para-Sulfaminobenzoic Acid (p-SABA) Solution. Dissolve 10.0 g p-SABA in 0.1 M NaOH, and dilute to 500 ml with 0.1 M NaOH.

7.2.6 Colorimetric Solution. To a flask, add 100 ml of 0.1 M p-SABA solution and 100 ml of 0.1 M $AgNO_3$ solution. Mix, and add 50 ml of 1 M NaOH with shaking. The resultant solution should be clear and colorless. This solution is acceptable for use for a period of 2 days.

7.2.7 Standard Gas Mixtures. Traceable to National Institute of Standards and Technology (NIST) standards and containing between 50 and 1000 ppm CO in nitrogen. At least two concentrations are needed to span each calibration range used (Section 10.3). The calibration gases must be certified by the manufacturer to be within 2 percent of the specified concentrations.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sample Bag or Tank Leak-Checks. While a leak-check is required after bag or sample tank use, it should also be done before the bag or sample tank is used for sample collection. The tank should be leak-checked according to the procedure specified in section 8.1.2 of Method 25. The bag should be leak-checked in the inflated and deflated condition according to the following procedure:

8.1.1 Connect the bag to a water manometer, and pressurize the bag to 5 to 10 cm H_2O (2 to 4 in H_2O). Allow the bag to stand for 60 minutes. Any displacement in the water manometer indicates a leak.

8.1.2 Evacuate the bag with a leakless pump that is connected to the downstream side of a flow indicating device such as a 0- to 100-ml/min rotameter or an impinger containing water. When the bag is completely evacuated, no flow should be evident if the bag is leak-free.

8.2 Sample Collection.

8.2.1 Evacuate and leak check the sample bag or tank as specified in section 8.1. Assemble the apparatus as shown in Figure 10A–1. Loosely pack glass wool in the tip of the probe. Place 400 ml of alkaline permanganate solution in the first two impingers and 250 ml in the third. Connect the pump to the third impinger, and follow this with the surge tank, rate meter, and 3-way valve. Do not connect the bag or sample tank to the system at this time.

8.2.2 Leak-check the sampling system by plugging the probe inlet, opening the 3-way valve, and pulling a vacuum of approximately 250 mm Hg on the system while observing the rate meter for flow. If flow is indicated on the rate meter, do not proceed further until the leak is found and corrected.

8.2.3 Purge the system with sample gas by inserting the probe into the stack and drawing the sample gas through the system at 300 ml/min ±10 percent for 5 minutes. Connect the evacuated bag or sample tank to the system, record the starting time, and sample at a rate of 300 ml/min for 30 minutes, or until the bag is nearly full, or the sample tank reaches ambient pressure. Record the sampling time, the barometric pressure, and the ambient temperature. Purge the system as described above immediately before each sample.

8.2.4 The scrubbing solution is adequate for removing sulfur oxides and nitrogen oxides from 50 liters (1.8 ft^3) of stack gas when the concentration of each is less than 1,000 ppm and the CO_2 concentration is less than 15 percent. Replace the scrubber solution after every fifth sample.

8.3 Carbon Dioxide Measurement. Measure the CO_2 content in the stack to the nearest 0.5 percent each time a CO sample is collected. A simultaneous grab sample analyzed by the Fyrite analyzer is acceptable.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.1	Sampling equipment leak-checks and calibration.	Ensure accuracy and precision of sampling measurements.
10.3	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Gas Bulb Calibration. Weigh the empty bulb to the nearest 0.1 g. Fill the bulb to the stopcock with water, and again weigh to the nearest 0.1 g. Subtract the tare weight, and calculate the volume in liters to three significant figures using the density of water at the measurement temperature. Record the volume on the bulb. Alternatively, mark an identification number on the bulb, and record the volume in a notebook.

10.2 Rate Meter Calibration. Assemble the system as shown in Figure 10A–1 (the impingers may be removed), and attach a volume meter to the probe inlet. Set the rotameter at 300 ml/min, record the volume meter reading, start the pump, and pull ambient air through the system for 10 minutes. Record the final volume meter reading. Repeat the procedure and average the results to determine the volume of gas that passed through the system.

10.3 Spectrophotometer Calibration Curve.

10.3.1 Collect the standards as described in section 8.2. Prepare at least two sets of three bulbs as standards to span the 0 to 400 or 400 to 1000 ppm range. If any samples span both

concentration ranges, prepare a calibration curve for each range using separate reagent blanks. Prepare a set of three bulbs containing colorimetric reagent but no CO to serve as a reagent blank. Analyze each standard and blank according to the sample analysis procedure of section 11.0 Reject the standard set where any of the individual bulb absorbances differs from the set mean by more than 10 percent.

10.3.2 Calculate the average absorbance for each set (3 bulbs) of standards using Equation 10A–1 and Table 10A–1. Construct a graph of average absorbance for each standard against its corresponding concentration. Draw a smooth curve through the points. The curve should be linear over the two concentration ranges discussed in section 13.3.

11.0 Analytical Procedure

11.1 Assemble the system shown in Figure 10A–3, and record the information required in Table 10A–1 as it is obtained. Pipet 10.0 ml of the colorimetric reagent into each gas reaction bulb, and attach the bulbs to the system. Open the stopcocks to the reaction bulbs, but leave the valve to the bag closed. Turn on the pump, fully open the coarse-adjust flow valve, and slowly open the fine-adjust valve until the pressure is reduced to at least 40 mm Hg. Now close the coarse adjust valve, and observe the manometer to be certain that the system is leak-free. Wait a minimum of 2 minutes. If the pressure has increased less than 1 mm Hg, proceed as described below. If a leak is present, find and correct it before proceeding further.

11.2 Record the vacuum pressure (P_v) to the nearest 1 mm Hg, and close the reaction bulb stopcocks. Open the bag valve, and allow the system to come to atmospheric pressure. Close the bag valve, open the pump coarse adjust valve, and evacuate the system again. Repeat this fill/evacuation procedure at least twice to flush the manifold completely. Close the pump coarse adjust valve, open the bag valve, and let the system fill to atmospheric pressure. Open the stopcocks to the reaction bulbs, and let the entire system come to atmospheric pressure. Close the bulb stopcocks, remove the bulbs, record the room temperature and barometric pressure (P_{bar}, to nearest mm Hg), and place the bulbs on the shaker table with their main axis either parallel to or perpendicular to the plane of the table top. Purge the bulb-filling system with ambient air for several minutes between samples. Shake the samples for exactly 2 hours.

11.3 Immediately after shaking, measure the absorbance (A) of each bulb sample at 425 nm if the concentration is less than or equal to 400 ppm CO or at 600 nm if the concentration is above 400 ppm.

NOTE: This may be accomplished with multiple bulb sets by sequentially collecting sets and adding to the shaker at staggered intervals, followed by sequentially removing sets from the shaker for absorbance measurement after the two-hour designated intervals have elapsed.

11.4 Use a small portion of the sample to rinse a spectrophotometer cell several times before taking an aliquot for analysis. If one cell is used to analyze multiple samples, rinse the cell with deionized distilled water several times between samples. Prepare and analyze standards and a reagent blank as described in section 10.3. Use water as the reference. Reject the analysis if the blank absorbance is greater than 0.1. All conditions should be the same for analysis of samples and standards. Measure the absorbances as soon as possible after shaking is completed.

11.5 Determine the CO concentration of each bag sample using the calibration curve for the appropriate concentration range as discussed in section 10.3.

12.0 Calculations and Data Analysis

Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature.

A = Sample absorbance, uncorrected for the reagent blank.
A_r = Absorbance of the reagent blank.
A_s = Average sample absorbance per liter, units/liter.
B_w = Moisture content in the bag sample.
C = CO concentration in the stack gas, dry basis, ppm.
C_b = CO concentration of the bag sample, dry basis, ppm.
C_g = CO concentration from the calibration curve, ppm.
F = Volume fraction of CO_2 in the stack.
n = Number of reaction bulbs used per bag sample.
P_b = Barometric pressure, mm Hg.
P_v = Residual pressure in the sample bulb after evacuation, mm Hg.
P_w = Vapor pressure of H_2O in the bag (from Table 10A–2), mm Hg.
V_b = Volume of the sample bulb, liters.
V_r = Volume of reagent added to the sample bulb, 0.0100 liter.

12.2 Average Sample Absorbance per Liter. Calculate A_s for each gas bulb using Equation 10A–1, and record the value in Table 10A–1. Calculate the average A_s for each bag sample, and compare the three values to the average. If any single value differs by more than 10 percent from the average, reject this value, and calculate a new average using the two remaining values.

$$A_s = \frac{(A - A_r)(P_b)}{(V_b - V_r)(P_b - P_v)} \qquad \text{Eq. 10A-1}$$

NOTE: A and A_r must be at the same wavelength.

12.3 CO Concentration in the Bag. Calculate C_b using Equations 10A–2 and 10A–3. If condensate is visible in the bag, calculate B_w using Table 10A–2 and the temperature and barometric pressure in the analysis room. If condensate is not visible, calculate B_w using the temperature and barometric pressure at the sampling site.

$$B_w = \frac{P_w}{P_b} \qquad \text{Eq. 10A-2}$$

$$C_b = \frac{C_g}{(1 - B_w)} \qquad \text{Eq. 10A-3}$$

12.4 CO Concentration in the Stack.

$$C = C_b\,(1 - F) \qquad \text{Eq. 10A-4}$$

13.0 Method Performance

13.1 Precision. The estimated intralaboratory standard deviation of the method is 3 percent of the mean for gas samples analyzed in duplicate in the concentration range of 39 to 412 ppm. The interlaboratory precision has not been established.

13.2 Accuracy. The method contains no significant biases when compared to an NDIR analyzer calibrated with NIST standards.

13.3 Range. Approximately 3 to 1800 ppm CO. Samples having concentrations below 400 ppm are analyzed at 425 nm, and samples having concentrations above 400 ppm are analyzed at 600 nm.

13.4 Sensitivity. The detection limit is 3 ppmv based on a change in concentration equal to three times the standard deviation of the reagent blank solution.

13.5 Stability. The individual components of the colorimetric reagent are stable for at least one month. The colorimetric reagent must be used within two days after preparation to avoid excessive blank correction. The samples in the bag should be stable for at least one week if the bags are leak-free.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Butler, F.E., J.E. Knoll, and M.R. Midgett. Development and Evaluation of Methods for Determining Carbon Monoxide Emissions. U.S. Environmental Protection Agency, Research Triangle Park, N.C. June 1985. 33 pp.

2. Ferguson, B.B., R.E. Lester, and W.J. Mitchell. Field Evaluation of Carbon Monoxide and Hydrogen Sulfide Continuous Emission Monitors at an Oil Refinery. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA–600/4–82–054. August 1982. 100 pp.

3. Lambert, J.L., and R.E. Weins. Induced Colorimetric Method for Carbon Monoxide. Analytical Chemistry. *46*(7):929–930. June 1974.

4. Levaggi, D.A., and M. Feldstein. The Colorimetric Determination of Low Concentrations of Carbon Monoxide. Industrial Hygiene Journal. *25*:64–66. January-February 1964.

5. Repp, M. Evaluation of Continuous Monitors For Carbon Monoxide in Stationary Sources. U.S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA–600/2–77–063. March 1977. 155 pp.

6. Smith, F., D.E. Wagoner, and R.P. Donovan. Guidelines for Development of a Quality Assurance Program: Volume VIII—Determination of CO Emissions from Stationary Sources by NDIR Spectrometry. U.S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA–650/4–74–005–h. February 1975. 96 pp.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 10A–1—DATA RECORDING SHEET FOR SAMPLES ANALYZED IN TRIPLICATE

Sample No./type	Room temp °C	Stack %CO_2	Bulb No.	Bulb vol. liters	Reagent vol. in bulb, liter	Partial pressure of gas in bulb, mm Hg	$P_{b,r}$, mm Hg	Shaking time, min	Abs versus water	A-A_r	A_s	Avg A_s
blank												
Std. 1												
Std. 2												
Sample 1												
Sample 2												
Sample 3												

TABLE 10A–2—MOISTURE CORRECTION

Temperature °C	Vapor pressure of H_2O, mm Hg	Temperature °C	Vapor pressure of H_2, mm Hg
4	6.1	18	15.5
6	7.0	20	17.5
8	8.0	22	19.8
10	9.2	24	22.4
12	10.5	26	25.2
14	12.0	28	28.3
16	13.6	30	31.8

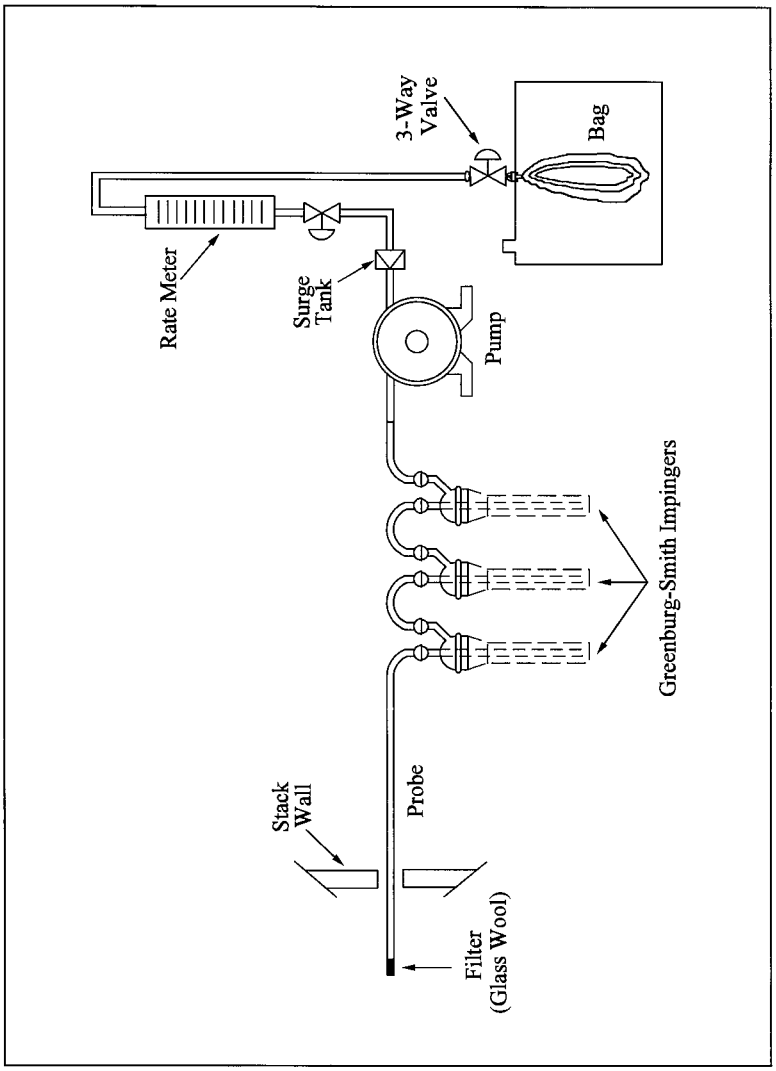


Figure 10A-1. Sampling Train.

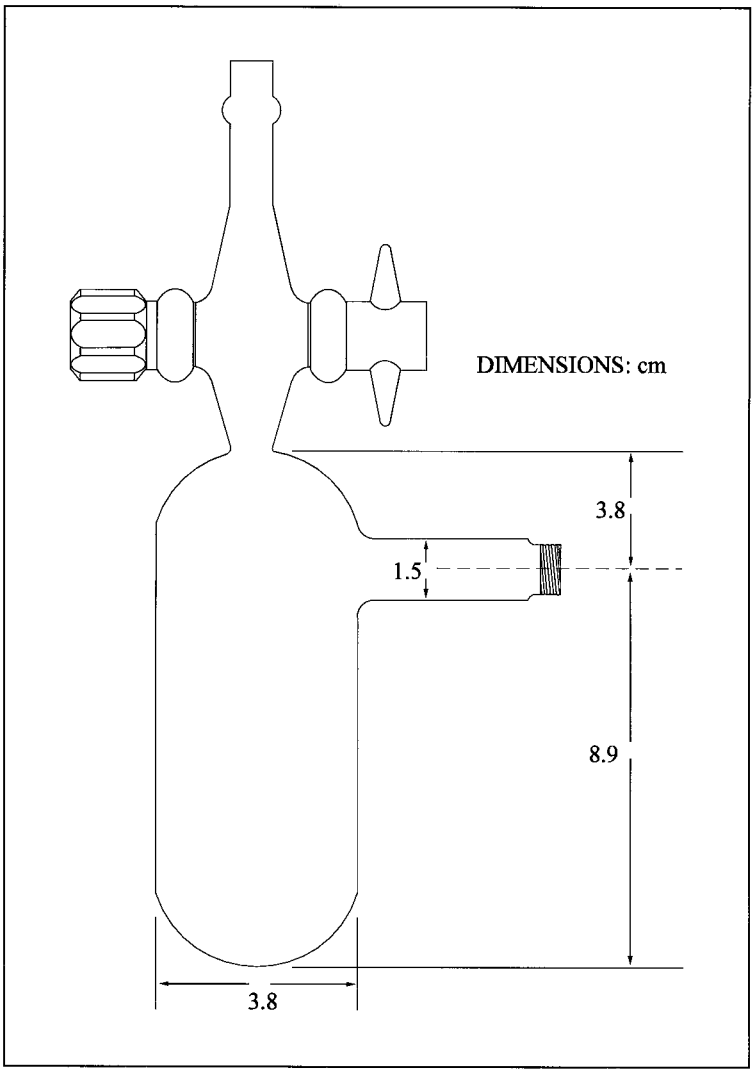


Figure 10A-2. Sample Reaction Bulbs.

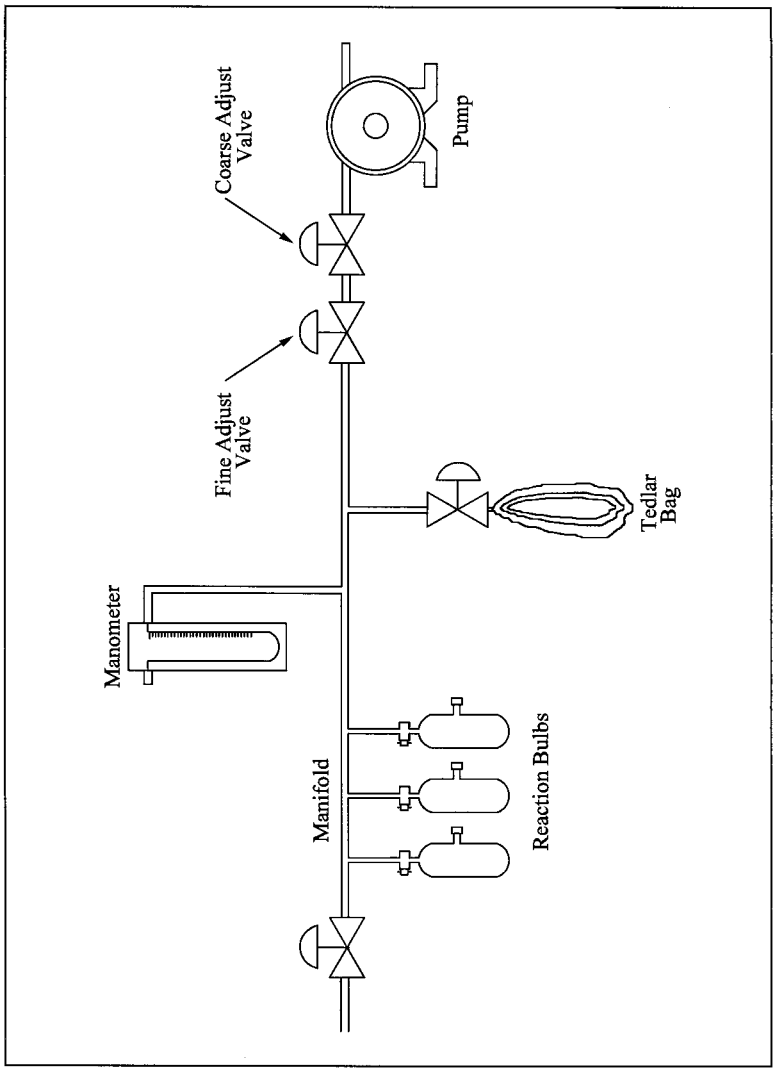


Figure 10A-3. Sample Bulb Filling System.

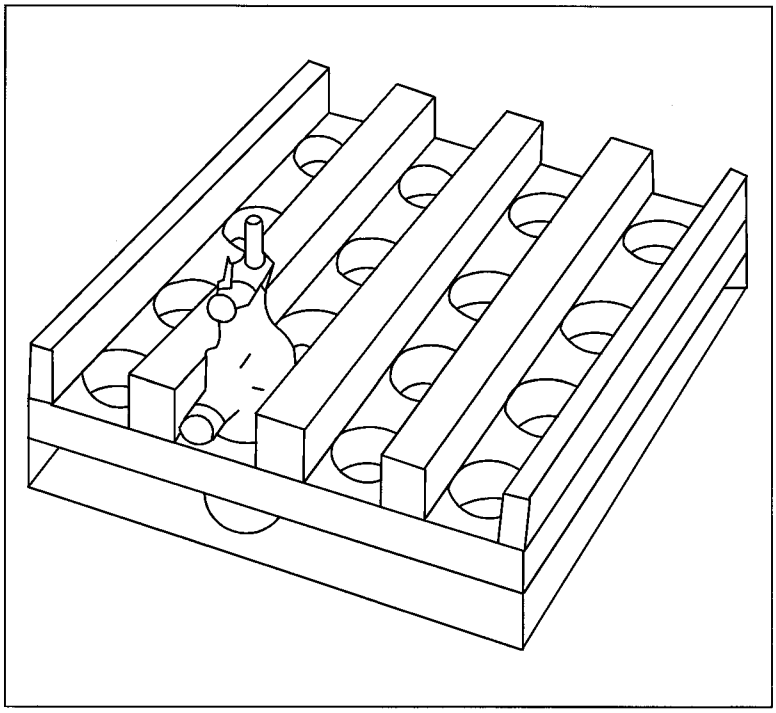


Figure 10A-4. Shaker Table Adapter.

METHOD 10B—DETERMINATION OF CARBON MONOXIDE EMISSIONS FROM STATIONARY SOURCES

NOTE: This method is not inclusive with respect to specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 4, Method 10A, and Method 25.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Carbon monoxide (CO)	630–08–0	Not determined.

1.2 Applicability. This method applies to the measurement of CO emissions at petroleum refineries and from other sources when specified in an applicable subpart of the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 An integrated gas sample is extracted from the sampling point, passed through a conditioning system to remove interferences, and collected in a Tedlar or equivalent bag. (Verify through the manufacturer that the Tedlar alternative is suitable for NO and make this verifying information available for inspection.) The CO is separated from the sample by gas chromatography (GC) and catalytically reduced to methane (CH_4) which is determined by flame ionization detection (FID). The analytical portion of this method is identical to applicable sections in Method 25 detailing CO measurement.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Carbon dioxide (CO_2) and organics potentially can interfere with the analysis. Most of the CO_2 is removed from the sample by the alkaline permanganate conditioning system; any residual CO_2 and organics are separated from the CO by GC.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions concerning the analytical procedure.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as in Method 10A, section 6.1 (paragraphs 6.1.1 through 6.1.11).

6.2 Sample Analysis. A GC/FID analyzer, capable of quantifying CO in the sample and consisting of at least the following major components, is required for sample analysis. [Alternatively, complete Method 25 analytical systems (Method 25, section 6.3) are acceptable alternatives when calibrated for CO and operated in accordance with the Method 25 analytical procedures (Method 25, section 11.0).]

6.2.1 Separation Column. A column capable of separating CO from CO_2 and organic compounds that may be present. A 3.2-mm (⅛-in.) OD stainless steel column packed with 1.7 m (5.5 ft.) of 60/80 mesh Carbosieve S-II (available from Supelco) has been used successfully for this purpose.

6.2.2 Reduction Catalyst. Same as in Method 25, section 6.3.1.2.

6.2.3 Sample Injection System. Same as in Method 25, Section 6.3.1.4, equipped to accept a sample line from the bag.

6.2.4 Flame Ionization Detector. Meeting the linearity specifications of section 10.3 and having a minimal instrument range of 10 to 1,000 ppm CO.

6.2.5 Data Recording System. Analog strip chart recorder or digital integration system, compatible with the FID, for permanently recording the analytical results.

7.0 Reagents and Standards

7.1 Sample Collection. Same as in Method 10A, section 7.1.

7.2 Sample Analysis.

7.2.1 Carrier, Fuel, and Combustion Gases. Same as in Method 25, sections 7.2.1, 7.2.2, and 7.2.3, respectively.

7.2.2 Calibration Gases. Three standard gases with nominal CO concentrations of 20, 200, and 1,000 ppm CO in nitrogen. The calibration gases shall be certified by the manufacturer to be ±2 percent of the specified concentrations.

7.2.3 Reduction Catalyst Efficiency Check Calibration Gas. Standard CH_4 gas with a nominal concentration of 1,000 ppm in air.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as in Method 10A, section 8.0.

9.0 Quality Control

Section	Quality control measure	Effect
8.0	Sample bag/sampling system leak-checks	Ensures that negative bias introduced through leakage is minimized.
10.1	Carrier gas blank check	Ensures that positive bias introduced by contamination of carrier gas is less than 5 ppmv.
10.2	Reduction catalyst efficiency check	Ensures that negative bias introduced by inefficient reduction catalyst is less than 5 percent.
10.3	Analyzer calibration	Ensures linearity of analyzer response to standards.
11.2	Triplicate sample analyses	Ensures precision of analytical results.

10.0 Calibration and Standardization

10.1 Carrier Gas Blank Check. Analyze each new tank of carrier gas with the GC analyzer according to section 11.2 to check for contamination. The corresponding concentration must be less than 5 ppm for the tank to be acceptable for use.

10.2 Reduction Catalyst Efficiency Check. Prior to initial use, the reduction catalyst shall be tested for reduction efficiency. With the heated reduction catalyst bypassed, make triplicate injections of the 1,000 ppm CH_4 gas (Section 7.2.3) to calibrate the analyzer. Repeat the procedure using 1,000 ppm CO gas (Section 7.2.2) with the catalyst in operation. The reduction catalyst operation is acceptable if the CO response is within 5 percent of the certified gas value.

10.3 Analyzer Calibration. Perform this test before the system is first placed into operation. With the reduction catalyst in operation, conduct a linearity check of the analyzer using the standards specified in section 7.2.2. Make triplicate injections of each calibration gas, and then calculate the average

response factor (area/ppm) for each gas, as well as the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within 2.5 percent of the overall mean value and if the relative standard deviation (calculated in section 12.8 of Method 25) for each set of triplicate injections is less than 2 percent. Record the overall mean of the response factor values as the calibration response factor (R).

11.0 Analytical Procedure

11.1 Preparation for Analysis. Before putting the GC analyzer into routine operation, conduct the calibration procedures listed in section 10.0. Establish an appropriate carrier flow rate and detector temperature for the specific instrument used.

11.2 Sample Analysis. Purge the sample loop with sample, and then inject the sample. Analyze each sample in triplicate, and calculate the average sample area (A). Determine the bag CO concentration according to section 12.2.

12.0 Calculations and Data Analysis

Carry out calculations retaining at least one extra significant figure beyond that of the acquired data. Round off results only after the final calculation.

12.1 Nomenclature.

A = Average sample area.
B_w = Moisture content in the bag sample, fraction.
C = CO concentration in the stack gas, dry basis, ppm.
C_b = CO concentration in the bag sample, dry basis, ppm.
F = Volume fraction of CO_2 in the stack, fraction.
P_{bar} = Barometric pressure, mm Hg.
P_w = Vapor pressure of the H_2O in the bag (from Table 10A–2, Method 10A), mm Hg.
R = Mean calibration response factor, area/ppm.

12.2 CO Concentration in the Bag. Calculate C_b using Equations 10B–1 and 10B–2. If condensate is visible in the bag, calculate B_w using Table 10A–2 of Method 10A and the temperature and barometric pressure in the analysis room. If condensate is not visible, calculate B_w using the temperature and barometric pressure at the sampling site.

$$B_w = \frac{P_w}{P_{bar}} \qquad \text{Eq. 10B-1}$$

$$C_b = \frac{A}{R\left(1 - B_w\right)} \qquad \text{Eq. 10B-2}$$

12.3 CO Concentration in the Stack

$$C = C_b\left(1 - F\right) \qquad \text{Eq. 10B-3}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as in Method 25, section 16.0, with the addition of the following:

1. Butler, F.E, J.E. Knoll, and M.R. Midgett. Development and Evaluation of Methods for Determining Carbon Monoxide Emissions. Quality Assurance Division, Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC. June 1985. 33 pp.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–4 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

APPENDIX A–5 TO PART 60—TEST METHODS 11 THROUGH 15A

Method 11—Determination of hydrogen sulfide content of fuel gas streams in petroleum refineries
Method 12—Determination of inorganic lead emissions from stationary sources
Method 13A—Determination of total fluoride emissions from stationary sources—SPADNS zirconium lake method
Method 13B—Determination of total fluoride emissions from stationary sources—Specific ion electrode method
Method 14—Determination of fluoride emissions from potroom roof monitors for primary aluminum plants
Method 14A—Determination of Total Fluoride Emissions from Selected Sources at Primary Aluminum Production Facilities
Method 15—Determination of hydrogen sulfide, carbonyl sulfide, and carbon disulfide emissions from stationary sources
Method 15A—Determination of total reduced sulfur emissions from sulfur recovery plants in petroleum refineries

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods

State of Oregon Department of Environmental Quality

OAR 340-240-0120 Attachments

APPENDIX A–4 TO PART 60—TEST METHODS 6 THROUGH 10B

Method 6—Determination of sulfur dioxide emissions from stationary sources
Method 6A—Determination of sulfur dioxide, moisture, and carbon dioxide emissions from fossil fuel combustion sources
Method 6B—Determination of sulfur dioxide and carbon dioxide daily average emissions from fossil fuel combustion sources
Method 6C—Determination of Sulfur Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure)
Method 7—Determination of nitrogen oxide emissions from stationary sources
Method 7A—Determination of nitrogen oxide emissions from stationary sources—Ion chromatographic method
Method 7B—Determination of nitrogen oxide emissions from stationary sources (Ultraviolet spectrophotometry)
Method 7C—Determination of nitrogen oxide emissions from stationary sources—Alkaline-permanganate/colorimetric method
Method 7D—Determination of nitrogen oxide emissions from stationary sources—Alkaline-permanganate/ion chromatographic method
Method 7E—Determination of Nitrogen Oxides Emissions From Stationary Sources (Instrumental Analyzer Procedure)
Method 8—Determination of sulfuric acid mist and sulfur dioxide emissions from stationary sources
Method 9—Visual determination of the opacity of emissions from stationary sources
Alternate method 1—Determination of the opacity of emissions from stationary sources remotely by lidar
Method 10—Determination of carbon monoxide emissions from stationary sources
Method 10A—Determination of carbon monoxide emissions in certifying continuous emission monitoring systems at petroleum refineries
Method 10B—Determination of carbon monoxide emissions from stationary sources

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that

the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

METHOD 6—DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, and Method 8.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
SO_2	7449–09–5	3.4 mg SO_2/m^3 $(2.12 \times 10)_{-7}$ lb/ft^3

1.2 Applicability. This method applies to the measurement of sulfur dioxide (SO_2) emissions from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the sampling point in the stack. The SO_2 and the sulfur trioxide, including those fractions in any sulfur acid mist, are separated. The SO_2 fraction is measured by the barium-thorin titration method.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Free Ammonia. Free ammonia interferes with this method by reacting with SO_2 to form particulate sulfite and by reacting with the indicator. If free ammonia is present (this can be determined by knowledge of the process and/or noticing white particulate matter in the probe and isopropanol bubbler), alternative methods, subject to the approval of the Administrator are required. One approved alternative is listed in Reference 13 of section 17.0.

4.2 Water-Soluble Cations and Fluorides. The cations and fluorides are removed by a glass wool filter and an isopropanol bubbler; therefore, they do not affect the SO_2 analysis. When samples are collected from a gas stream with high concentrations of metallic fumes (*i.e.*, very fine cation aerosols) a high-efficiency glass fiber filter must be used in place of the glass wool plug (*i.e.*, the one in the probe) to remove the cation interferent.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations before performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs. 30% H_2O_2 is a strong oxidizing agent. Avoid contact with skin, eyes, and combustible material. Wear gloves when handling.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

6.1 Sample Collection. The following items are required for sample collection:

6.1.1 Sampling Train. A schematic of the sampling train is shown in Figure 6–1. The sampling equipment described in Method 8 may be substituted in place of the midget impinger equipment of Method 6. However, the Method 8 train must be modified to include a heated filter between the probe and isopropanol impinger, and the operation of the sampling train and sample analysis must be at the flow rates and solution volumes defined in Method 8. Alternatively, SO_2 may be determined simultaneously with particulate

matter and moisture determinations by either (1) replacing the water in a Method 5 impinger system with a 3 percent H_2O_2 solution, or (2) replacing the Method 5 water impinger system with a Method 8 isopropanol-filter-H_2O_2 system. The analysis for SO_2 must be consistent with the procedure of Method 8. The Method 6 sampling train consists of the following components:

6.1.1.1 Probe. Borosilicate glass or stainless steel (other materials of construction may be used, subject to the approval of the Administrator), approximately 6 mm (0.25 in.) inside diameter, with a heating system to prevent water condensation and a filter (either in-stack or heated out-of-stack) to remove particulate matter, including sulfuric acid mist. A plug of glass wool is a satisfactory filter.

6.1.1.2 Bubbler and Impingers. One midget bubbler with medium-coarse glass frit and borosilicate or quartz glass wool packed in top (see Figure 6–1) to prevent sulfuric acid mist carryover, and three 30-ml midget impingers. The midget bubbler and midget impingers must be connected in series with leak-free glass connectors. Silicone grease may be used, if necessary, to prevent leakage. A midget impinger may be used in place of the midget bubbler.

NOTE: Other collection absorbers and flow rates may be used, subject to the approval of the Administrator, but the collection efficiency must be shown to be at least 99 percent for each test run and must be documented in the report. If the efficiency is found to be acceptable after a series of three tests, further documentation is not required. To conduct the efficiency test, an extra absorber must be added and analyzed separately. This extra absorber must not contain more than 1 percent of the total SO_2.

6.1.1.3 Glass Wool. Borosilicate or quartz.

6.1.1.4 Stopcock Grease. Acetone-insoluble, heat-stable silicone grease may be used, if necessary.

6.1.1.5 Temperature Sensor. Dial thermometer, or equivalent, to measure temperature of gas leaving impinger train to within 1 °C (2 °F).

6.1.1.6 Drying Tube. Tube packed with 6- to 16- mesh indicating-type silica gel, or equivalent, to dry the gas sample and to protect the meter and pump. If silica gel is previously used, dry at 177 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

6.1.1.7 Valve. Needle valve, to regulate sample gas flow rate.

6.1.1.8 Pump. Leak-free diaphragm pump, or equivalent, to pull gas through the train. Install a small surge tank between the pump and rate meter to negate the pulsation effect of the diaphragm pump on the rate meter.

6.1.1.9 Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of the selected flow rate of about 1 liter/min (0.035 cfm).

6.1.1.10 Volume Meter. Dry gas meter (DGM), sufficiently accurate to measure the sample volume to within 2 percent, calibrated at the selected flow rate and conditions actually encountered during sampling, and equipped with a temperature sensor (dial thermometer, or equivalent) capable of measuring temperature accurately to within 3 °C (5.4 °F). A critical orifice may be used in place of the DGM specified in this section provided that it is selected, calibrated, and used as specified in section 16.0.

6.1.2 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). See the note in Method 5, section 6.1.2.

6.1.3 Vacuum Gauge and Rotameter. At least 760-mm Hg (30-in. Hg) gauge and 0- to 40-ml/min rotameter, to be used for leak-check of the sampling train.

6.2 Sample Recovery. The following items are needed for sample recovery:

6.2.1 Wash Bottles. Two polyethylene or glass bottles, 500-ml.

6.2.2 Storage Bottles. Polyethylene bottles, 100-ml, to store impinger samples (one per sample).

6.3 Sample Analysis. The following equipment is needed for sample analysis:

6.3.1 Pipettes. Volumetric type, 5-ml, 20-ml (one needed per sample), and 25-ml sizes.

6.3.2 Volumetric Flasks. 100-ml size (one per sample) and 1000-ml size.

6.3.3 Burettes. 5- and 50-ml sizes.

6.3.4 Erlenmeyer Flasks. 250-ml size (one for each sample, blank, and standard).

6.3.5 Dropping Bottle. 125-ml size, to add indicator.

6.3.6 Graduated Cylinder. 100-ml size.

6.3.7 Spectrophotometer. To measure absorbance at 352 nm.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Water. Deionized distilled to conform to ASTM Specification D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17). The $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.1.2 Isopropanol, 80 Percent by Volume. Mix 80 ml of isopropanol with 20 ml of water.

7.1.2.1 Check each lot of isopropanol for peroxide impurities as follows: Shake 10 ml of isopropanol with 10 ml of freshly prepared 10 percent potassium iodide solution. Prepare a blank by similarly treating 10 ml of water. After 1 minute, read the absorbance at 352 nm on a spectrophotometer using a 1-cm path length. If absorbance exceeds 0.1, reject alcohol for use.

7.1.2.2 Peroxides may be removed from isopropanol by redistilling or by passage through a column of activated alumina; however, reagent grade isopropanol with suitably low peroxide levels may be obtained from commercial sources. Rejection of contaminated lots may, therefore, be a more efficient procedure.

7.1.3 Hydrogen Peroxide (H_2O_2), 3 Percent by Volume. Add 10 ml of 30 percent H_2O_2 to 90 ml of water. Prepare fresh daily.

7.1.4 Potassium Iodide Solution, 10 Percent Weight by Volume (w/v). Dissolve 10.0 g of KI in water, and dilute to 100 ml. Prepare when needed.

7.2 Sample Recovery. The following reagents are required for sample recovery:

7.2.1 Water. Same as in section 7.1.1.

7.2.2 Isopropanol, 80 Percent by Volume. Same as in section 7.1.2.

7.3 Sample Analysis. The following reagents and standards are required for sample analysis:

7.3.1 Water. Same as in section 7.1.1.

7.3.2 Isopropanol, 100 Percent.

7.3.3 Thorin Indicator. 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, disodium salt, or equivalent. Dissolve 0.20 g in 100 ml of water.

7.3.4 Barium Standard Solution, 0.0100 N. Dissolve 1.95 g of barium perchlorate trihydrate [$Ba(ClO_4)_2$ $3H_2O$] in 200 ml water, and dilute to 1 liter with isopropanol. Alternatively, 1.22 g of barium chloride dihydrate [$BaCl_2$ $2H_2O$] may be used instead of the barium perchlorate trihydrate. Standardize as in section 10.5.

7.3.5 Sulfuric Acid Standard, 0.0100 N. Purchase or standardize to ±0.0002 N against 0.0100 N NaOH which has previously been standardized against potassium acid phthalate (primary standard grade).

8.0 Sample Collection, Preservation, Storage and Transport

8.1 Preparation of Sampling Train. Measure 15 ml of 80 percent isopropanol into the midget bubbler and 15 ml of 3 percent H_2O_2 into each of the first two midget impingers. Leave the final midget impinger dry. Assemble the train as shown in Figure 6–1. Adjust the probe heater to a temperature sufficient to prevent water condensation. Place crushed ice and water around the impingers.

8.2 Sampling Train Leak-Check Procedure. A leak-check prior to the sampling run is recommended, but not required. A leak-check after the sampling run is mandatory. The leak-check procedure is as follows:

8.2.1 Temporarily attach a suitable (*e.g.*, 0- to 40- ml/min) rotameter to the outlet of the DGM, and place a vacuum gauge at or near the probe inlet. Plug the probe inlet, pull a vacuum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter. A leakage rate in excess of 2 percent of the average sampling rate is not acceptable.

NOTE: Carefully (*i.e.*, slowly) release the probe inlet plug before turning off the pump.

8.2.2 It is suggested (not mandatory) that the pump be leak-checked separately, either prior to or after the sampling run. To leak-check the pump, proceed as follows: Disconnect the drying tube from the probe-impinger assembly. Place a vacuum gauge at the inlet to either the drying tube or the pump, pull a vacuum of 250 mm Hg (10 in. Hg), plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum should remain stable for at least 30 seconds.

If performed prior to the sampling run, the pump leak-check shall precede the leak-check of the sampling train described immediately above; if performed after the sampling run, the pump leak-check shall follow the sampling train leak-check.

8.2.3 Other leak-check procedures may be used, subject to the approval of the Administrator.

8.3 Sample Collection.

8.3.1 Record the initial DGM reading and barometric pressure. To begin sampling, position the tip of the probe at the sampling point, connect the probe to the bubbler, and start the pump. Adjust the sample flow to a constant rate of approximately 1.0 liter/min as indicated by the rate meter. Maintain this constant rate (±10 percent) during the entire sampling run.

8.3.2 Take readings (DGM volume, temperatures at DGM and at impinger outlet, and rate meter flow rate) at least every 5 minutes. Add more ice during the run to keep the temperature of the gases leaving the last impinger at 20 °C (68 °F) or less.

8.3.3 At the conclusion of each run, turn off the pump, remove the probe from the stack, and record the final readings. Conduct a leak-check as described in section 8.2. (This leak-check is mandatory.) If a leak is detected, void the test run or use procedures acceptable to the Administrator to adjust the sample volume for the leakage.

8.3.4 Drain the ice bath, and purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at the sampling rate. Clean ambient air can be provided by passing air through a charcoal filter or through an extra midget impinger containing 15 ml of 3 percent H_2O_2. Alternatively, ambient air without purification may be used.

8.4 Sample Recovery. Disconnect the impingers after purging. Discard the contents of the midget bubbler. Pour the contents of the midget impingers into a leak-free polyethylene bottle for shipment. Rinse the three midget impingers and the connecting tubes with water, and add the rinse to the same storage container. Mark the fluid level. Seal and identify the sample container.

9.0 Quality Control

Section	Quality control measure	Effect
7.1.2	Isopropanol check	Ensure acceptable level of peroxide impurities in isopropanol.
8.2, 10.1–10.4	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.
10.5	Barium standard solution standardization	Ensure precision of normality determination
11.2.3	Replicate titrations	Ensure precision of titration determinations.

10.0 Calibration and Standardization

10.1 Volume Metering System.

10.1.1 Initial Calibration.

10.1.1.1 Before its initial use in the field, leak-check the metering system (drying tube, needle valve, pump, rate meter, and DGM) as follows: Place a vacuum gauge at the inlet to the drying tube and pull a vacuum of 250 mm Hg (10 in. Hg). Plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum must remain stable for at least 30 seconds. Carefully release the vacuum gauge before releasing the flow meter end.

10.1.1.2 Remove the drying tube, and calibrate the metering system (at the sampling flow rate specified by the method) as follows: Connect an appropriately sized wet-test meter (*e.g.*, 1 liter per revolution) to the inlet of the needle valve. Make three independent calibration runs, using at least five revolutions of the DGM per run. Calculate the calibration factor Y (wet-test meter calibration volume divided by the DGM volume, both volumes adjusted to the same reference temperature and pressure) for each run, and average the results (Y_i). If any Y-value deviates by more than 2 percent from (Y_i), the metering system is unacceptable for use. If the metering system is acceptable, use (Y_i) as the calibration factor for subsequent test runs.

10.1.2 Post-Test Calibration Check. After each field test series, conduct a calibration check using the procedures outlined in section 10.1.1.2, except that three or more revolutions of the DGM may be used, and only two independent runs need be made. If the average of the two post-test calibration factors does not deviate by more than 5 percent from Y_i, then Y_i is accepted as the DGM calibration factor (Y), which is used in Equation 6–1 to calculate collected sample volume (see section 12.2). If the deviation is more than 5 percent, recalibrate the metering system as in section 10.1.1, and determine a post-test calibration factor (Y_f). Compare Y_i and Y_f; the smaller of the two factors is accepted as the DGM calibration factor. If recalibration indicates that the metering system is unacceptable for use, either void the test run or use methods, subject to the approval of the Administrator, to determine an acceptable value for the collected sample volume.

10.1.3 DGM as a Calibration Standard. A DGM may be used as a calibration standard for volume measurements in place of the wet-test meter specified in section 10.1.1.2, provided that it is calibrated initially and recalibrated periodically according to the same procedures outlined in Method 5, section 10.3 with the following exceptions: (a) the DGM is calibrated against a wet-test meter having a capacity of 1 liter/rev (0.035 ft^3/rev) or 3 liters/rev (0.1 ft^3/rev) and having the capability of measuring volume to within 1 percent; (b) the DGM is calibrated at 1 liter/min (0.035 cfm); and (c) the meter box of the Method 6 sampling train is calibrated at the same flow rate.

10.2 Temperature Sensors. Calibrate against mercury-in-glass thermometers. An alternative mercury-free thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

10.3 Rate Meter. The rate meter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instructions.

10.4 Barometer. Calibrate against a mercury barometer or NIST-traceable barometer prior to the field test.

10.5 Barium Standard Solution. Standardize the barium perchlorate or chloride solution against 25 ml of standard sulfuric acid to which 100 ml of 100 percent isopropanol has been added. Run duplicate analyses. Calculate the normality using the average of duplicate analyses where the titrations agree within 1 percent or 0.2 ml, whichever is larger.

11.0 Analytical Procedure

11.1 Sample Loss Check. Note level of liquid in container and confirm whether any sample was lost during shipment; note this

finding on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Analysis.

11.2.1 Transfer the contents of the storage container to a 100-ml volumetric flask, dilute to exactly 100 ml with water, and mix the diluted sample.

11.2.2 Pipette a 20-ml aliquot of the diluted sample into a 250-ml Erlenmeyer flask and add 80 ml of 100 percent isopropanol plus two to four drops of thorin indicator. While stirring the solution, titrate to a pink endpoint using 0.0100 N barium standard solution.

11.2.3 Repeat the procedures in section 11.2.2, and average the titration volumes. Run a blank with each series of samples. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is larger.

NOTE: Protect the 0.0100 N barium standard solution from evaporation at all times.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 NOMENCLATURE

C_{SO2} = Concentration of SO_2, dry basis, corrected to standard conditions, mg/dscm (lb/dscf).

N = Normality of barium standard titrant, meq/ml.

P_{bar} = Barometric pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

T_m = Average DGM absolute temperature, °K (°R).

T_{std} = Standard absolute temperature, 293 °K (528 °R).

V_a = Volume of sample aliquot titrated, ml.

V_m = Dry gas volume as measured by the DGM, dcm (dcf).

$V_{m(std)}$ = Dry gas volume measured by the DGM, corrected to standard conditions, dscm (dscf).

V_{soln} = Total volume of solution in which the SO_2 sample is contained, 100 ml.

V_t = Volume of barium standard titrant used for the sample (average of replicate titration), ml.

V_{tb} = Volume of barium standard titrant used for the blank, ml.

Y = DGM calibration factor.

12.2 Dry Sample Gas Volume, Corrected to Standard Conditions.

$$V_{m(std)} = \frac{\left(V_m Y T_{std} P_{bar}\right)}{\left(T_m P_{std}\right)} = \frac{K_1 Y V_m P_{bar}}{T_m} \quad \text{Eq. 6-1}$$

Where:

K_1 = 0.3855 °K/mm Hg for metric units,

K_1 = 17.65 °R/in. Hg for English units.

12.3 SO_2 Concentration.

$$C_{so_2} = \frac{K_2 N \left(V_t - V_{tb}\right)\left(V_{soln}/V_a\right)}{V_{m(std)}} \quad \text{Eq. 6-2}$$

Where:

K_2 = 32.03 mg SO_2/meq for metric units,

$K_2 = 7.061 \times 10^{-5}$ lb SO_2/meq for English units.

13.0 Method Performance

13.1 Range. The minimum detectable limit of the method has been determined to be 3.4 mg SO_2/m^3 (2.12×10^{-7} lb/ft³). Although no upper limit has been established, tests have shown that concentrations as high as 80,000 mg/m³ (0.005 lb/ft³) of SO_2 can be collected efficiently at a rate of 1.0 liter/min (0.035 cfm) for 20 minutes in two midget impingers, each containing 15 ml of 3 percent H_2O_2. Based on theoretical calculations, the upper concentration limit in a 20 liter (0.7 ft³) sample is about 93,300 mg/m³ (0.00583 lb/ft³).

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Nomenclature. Same as section 12.1, with the following additions:

B_{wa} = Water vapor in ambient air, proportion by volume.

M_a = Molecular weight of the ambient air saturated at impinger temperature, g/g-mole (lb/lb-mole).

M_s = Molecular weight of the sample gas saturated at impinger temperature, g/g-mole (lb/lb-mole).

P_c = Inlet vacuum reading obtained during the calibration run, mm Hg (in. Hg).

P_{sr} = Inlet vacuum reading obtained during the sampling run, mm Hg (in. Hg).

$\bar{Q}_{std}$ = Volumetric flow rate through critical orifice, scm/min (scf/min).
Q_{std} = Average flow rate of pre-test and post-test calibration runs, scm/min (scf/min).
T_{amb} = Ambient absolute temperature of air, °K (°R).
V_{sb} = Volume of gas as measured by the soap bubble meter, m^3 (ft^3).
$V_{sb(std)}$ = Volume of gas as measured by the soap bubble meter, corrected to standard conditions, scm (scf).
θ = Soap bubble travel time, min.
θ_s = Time, min.

16.2 Critical Orifices for Volume and Rate Measurements. A critical orifice may be used in place of the DGM specified in section 6.1.1.10, provided that it is selected, calibrated, and used as follows:

16.2.1 Preparation of Sampling Train. Assemble the sampling train as shown in Figure 6–2. The rate meter and surge tank are optional but are recommended in order to detect changes in the flow rate.

NOTE: The critical orifices can be adapted to a Method 6 type sampling train as follows: Insert sleeve type, serum bottle stoppers into two reducing unions. Insert the needle into the stoppers as shown in Figure 6–3.

16.2.2 Selection of Critical Orifices.

16.2.2.1 The procedure that follows describes the use of hypodermic needles and stainless steel needle tubings, which have been found suitable for use as critical orifices. Other materials and critical orifice designs may be used provided the orifices act as true critical orifices, (*i.e.*, a critical vacuum can be obtained) as described in this section. Select a critical orifice that is sized to operate at the desired flow rate. The needle sizes and tubing lengths shown in Table 6–1 give the following approximate flow rates.

16.2.2.2 Determine the suitability and the appropriate operating vacuum of the critical orifice as follows: If applicable, temporarily attach a rate meter and surge tank to the outlet of the sampling train, if said equipment is not present (see section 16.2.1). Turn on the pump and adjust the valve to give an outlet vacuum reading corresponding to about half of the atmospheric pressure. Observe the rate meter reading. Slowly increase the vacuum until a stable reading is obtained on the rate meter. Record the critical vacuum, which is the outlet vacuum when the rate meter first reaches a stable value. Orifices that do not reach a critical value must not be used.

16.2.3 Field Procedures.

16.2.3.1 Leak-Check Procedure. A leak-check before the sampling run is recommended, but not required. The leak-check procedure is as follows: Temporarily attach a suitable (*e.g.*, 0–40 ml/min) rotameter and surge tank, or a soap bubble meter and surge tank to the outlet of the pump. Plug the probe inlet, pull an outlet vacuum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter or bubble meter. A leakage rate in excess of 2 percent of the average sampling rate ($\bar{Q}_{std}$) is not acceptable. Carefully release the probe inlet plug before turning off the pump.

16.2.3.2 Moisture Determination. At the sampling location, prior to testing, determine the percent moisture of the ambient air using the wet and dry bulb temperatures or, if appropriate, a relative humidity meter.

16.2.3.3 Critical Orifice Calibration. At the sampling location, prior to testing, calibrate the entire sampling train (*i.e.*, determine the flow rate of the sampling train when operated at critical conditions). Attach a 500-ml soap bubble meter to the inlet of the probe, and operate the sampling train at an outlet vacuum of 25 to 50 mm Hg (1 to 2 in. Hg) above the critical vacuum. Record the information listed in Figure 6–4. Calculate the standard volume of air measured by the soap bubble meter and the volumetric flow rate using the equations below:

$$V_{sb(std)} = V_{sb}\left(T_{std}/T_{amb}\right)\left(P_{bar}/P_{std}\right) \qquad \text{Eq. 6-4}$$

$$Q_{std} = \frac{V_{sb(std)}}{\theta} \qquad \text{Eq. 6-5}$$

16.2.3.4 Sampling.

16.2.3.4.1 Operate the sampling train for sample collection at the same vacuum used during the calibration run. Start the watch and pump simultaneously. Take readings (temperature, rate meter, inlet vacuum, and outlet vacuum) at least every 5 minutes. At the end of the sampling run, stop the watch and pump simultaneously.

16.2.3.4.2 Conduct a post-test calibration run using the calibration procedure outlined in section 16.2.3.3. If the Q_{std} obtained before and after the test differ by more than 5 percent, void the test run; if not, calculate the volume of the gas measured with the critical orifice using Equation 6–6 as follows:

$$V_{m(std)} = \frac{\overline{Q}_{std}\ \theta_s\ (1-B_{wa})(P_{bar}+P_{sr})}{(P_{bar}+P_c)} \quad \text{Eq. 6-6}$$

16.2.3.4.3 If the percent difference between the molecular weight of the ambient air at saturated conditions and the sample gas is more that ±3 percent, then the molecular weight of the gas sample must be considered in the calculations using the following equation:

$$_{(std)} = \frac{\overline{Q}_{std}\ \theta_s\ (1-B_{wa})(P_{bar}+P_{sr})(M_a/M_s)^1}{(P_{bar}+P_c)} \quad \text{Eq. 6-7}$$

NOTE: A post-test leak-check is not necessary because the post-test calibration run results will indicate whether there is any leakage.

16.2.3.4.4 Drain the ice bath, and purge the sampling train using the procedure described in section 8.3.4.

16.3 Elimination of Ammonia Interference. The following alternative procedures must be used in addition to those specified in the method when sampling at sources having ammonia emissions.

16.3.1 Sampling. The probe shall be maintained at 275 °C (527 °F) and equipped with a high-efficiency in-stack filter (glass fiber) to remove particulate matter. The filter material shall be unreactive to SO_2. Whatman 934AH (formerly Reeve Angel 934AH) filters treated as described in Reference 10 in section 17.0 of Method 5 is an example of a filter that has been shown to work. Where alkaline particulate matter and condensed moisture are present in the gas stream, the filter shall be heated above the moisture dew point but below 225 °C (437 °F).

16.3.2 Sample Recovery. Recover the sample according to section 8.4 except for discarding the contents of the midget bubbler. Add the bubbler contents, including the rinsings of the bubbler with water, to a separate polyethylene bottle from the rest of the sample. Under normal testing conditions where sulfur trioxide will not be present significantly, the tester may opt to delete the midget bubbler from the sampling train. If an approximation of the sulfur trioxide concentration is desired, transfer the contents of the midget bubbler to a separate polyethylene bottle.

16.3.3 Sample Analysis. Follow the procedures in sections 11.1 and 11.2, except add 0.5 ml of 0.1 N HCl to the Erlenmeyer flask and mix before adding the indicator. The following analysis procedure may be used for an approximation of the sulfur trioxide concentration. The accuracy of the calculated concentration will depend upon the ammonia to SO_2 ratio and the level of oxygen present in the gas stream. A fraction of the SO_2 will be counted as sulfur trioxide as the ammonia to SO_2 ratio and the sample oxygen content increases. Generally, when this ratio is 1 or less and the oxygen content is in the range of 5 percent, less than 10 percent of the SO_2 will be counted as sulfur trioxide. Analyze the peroxide and isopropanol sample portions separately. Analyze the peroxide portion as described above. Sulfur trioxide is determined by difference using sequential titration of the isopropanol portion of the sample. Transfer the contents of the isopropanol storage container to a 100-ml volumetric flask, and dilute to exactly 100 ml with water. Pipette a 20-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 0.5 ml of 0.1 N HCl, 80 ml of 100 percent isopropanol, and two to four drops of thorin indicator. Titrate to a pink endpoint using 0.0100 N barium perchlorate. Repeat and average the titration volumes that agree within 1 percent or 0.2 ml, whichever is larger. Use this volume in Equation 6–2 to determine the sulfur trioxide concentration. From the flask containing the remainder of the isopropanol sample, determine the fraction of SO_2 collected in the bubbler by pipetting 20-ml aliquots into 250-ml Erlenmeyer flasks. Add 5 ml of 3 percent H_2O_2, 100 ml of 100 percent isopropanol, and two to four drips of thorin indicator, and titrate as before. From this titration volume, subtract the titrant volume determined for sulfur trioxide, and add the titrant volume determined for the peroxide portion. This final volume constitutes V_t, the volume of barium perchlorate used for the SO_2 sample.

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18.0 Tables, Diagrams, Flowcharts and Validation Data

TABLE 6–1—APPROXIMATE FLOW RATES FOR VARIOUS NEEDLE SIZES

Needle size (gauge)	Needle length (cm)	Flow rate (ml/min)
21	7.6	1,100
22	2.9	1,000
22	3.8	900
23	3.8	500
23	5.1	450
24	3.2	400

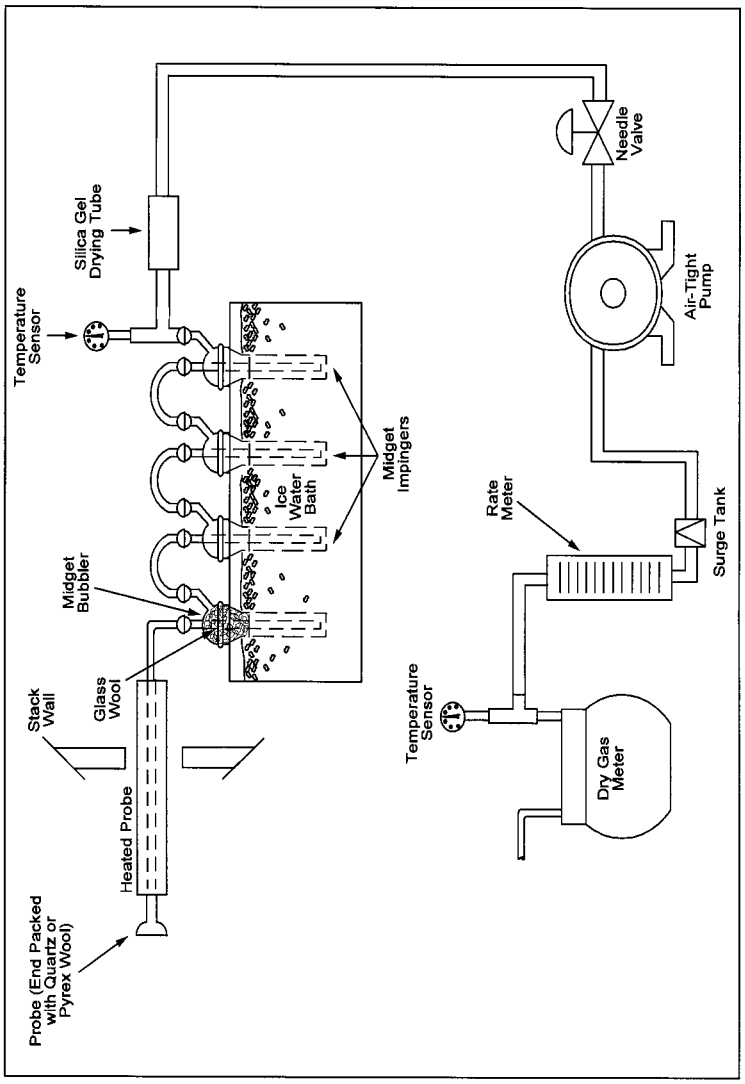

Figure 6-1. Sulfur Dioxide Sampling Train.

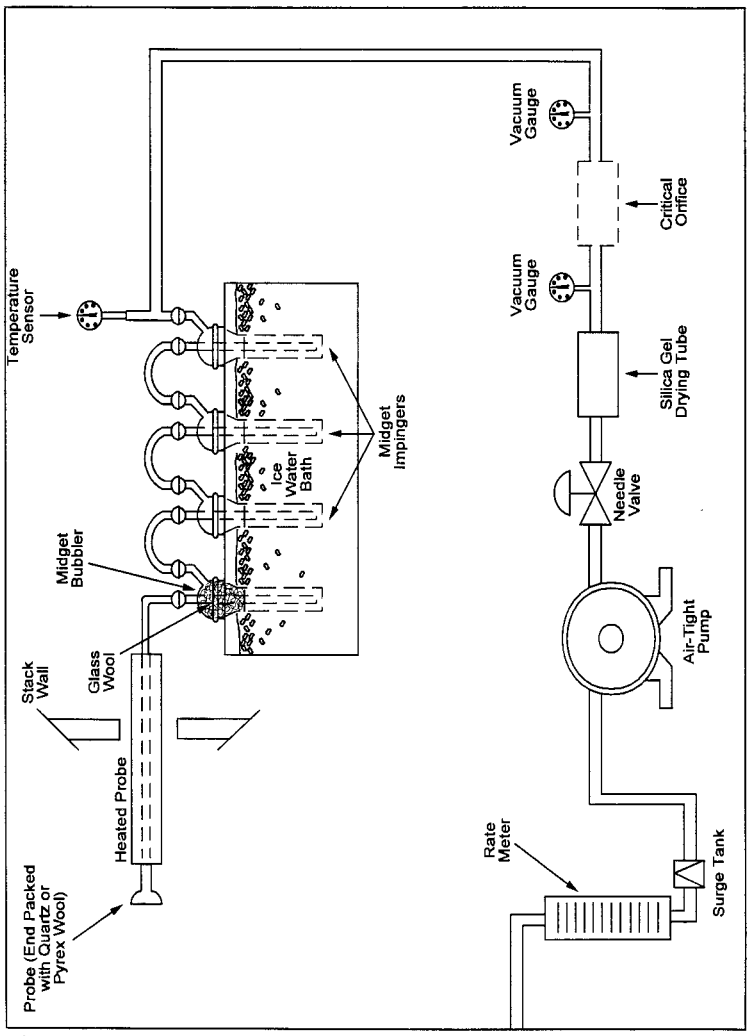

Figure 6-2. Sulfur Dioxide Sampling Train Using a Critical Orifice.

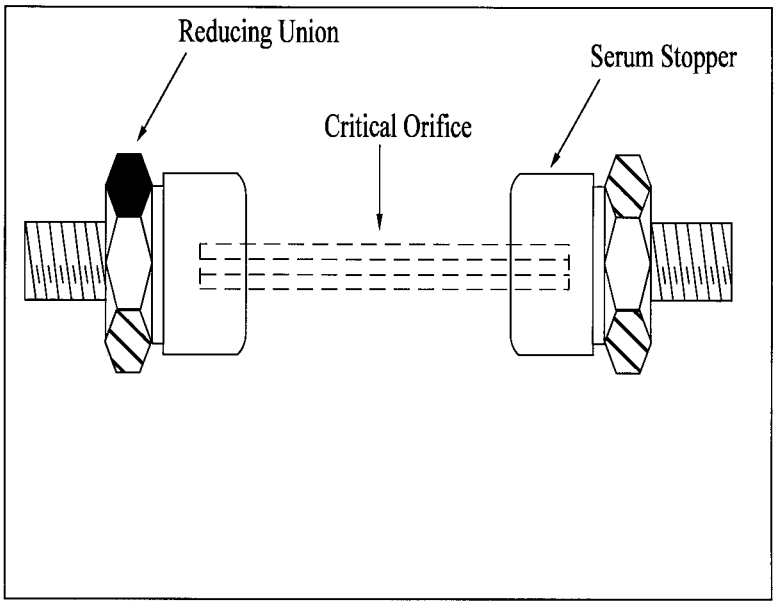

Figure 6-3. Critical Orifice Adaptation for the Method 6 Sampling Train.

Date _____ Train ID _____

Critical orifice size _____ Critical vacuum _____

		Pretest	Post-test
Soap bubble meter volume, V_{sb}	cc		
	m^3 (ft^3)		
Time, θ	sec		
	min		
Barometric pressure, P_{bar}	mm Hg (in. Hg)		
Ambient temperature, t_{amb}	°C (°F)		
Inlet vacuum, P_c	mm Hg (in. Hg)		
Outlet vacuum	mm Hg (in. Hg)		
$V_{sb(std)}$	m^3 (ft^3)		
Flow rate, Q_{std}	$\frac{m^3}{min}\left(\frac{ft^3}{min}\right)$		

Figure 6-4. Critical Orifice Calibration Data Sheet.

METHOD 6A—DETERMINATION OF SULFUR DIOXIDE, MOISTURE, AND CARBON DIOXIDE FROM FOSSIL FUEL COMBUSTION SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, Method 6, and Method 19.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
SO_2	7449–09–05	3.4 mg SO_2/m^3 (2.12×10^{-7} lb/ft^3)
CO_2	124–38–9	N/A
H_2O	7732–18–5	N/A

1.2 Applicability. This method is applicable for the determination of sulfur dioxide (SO_2) emissions from fossil fuel combustion sources in terms of concentration (mg/dscm or lb/dscf) and in terms of emission rate (ng/J or lb/10^6 Btu) and for the determination of carbon dioxide (CO_2) concentration (percent). Moisture content (percent), if desired, may also be determined by this method.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from a sampling point in the stack. The SO_2 and the sulfur trioxide, including those fractions in any sulfur acid mist, are separated. The SO_2 fraction is measured by the barium-thorin titration method. Moisture and CO_2 fractions are collected in the same sampling train, and are determined gravimetrically.

3.0 Definitions [Reserved]

4.0 Interferences

Same as Method 6, section 4.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. Same as Method 6, section 5.2.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 6, section 6.1, with the exception of the following:

6.1.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 6A–1.

6.1.1.1 Impingers and Bubblers. Two 30 = ml midget impingers with a 1 = mm restricted tip and two 30 = ml midget bubblers with unrestricted tips. Other types of impingers and bubblers (*e.g.,* Mae West for SO_2 collection and rigid cylinders containing Drierite for moisture absorbers), may be used with proper attention to reagent volumes and levels, subject to the approval of the Administrator.

6.1.1.2 CO_2 Absorber. A sealable rigid cylinder or bottle with an inside diameter between 30 and 90 mm , a length between 125 and 250 mm, and appropriate connections at both ends. The filter may be a separate heated unit or may be within the heated portion of the probe. If the filter is within the sampling probe, the filter should not be within 15 cm of the probe inlet or any unheated section of the probe, such as the connection to the first bubbler. The probe and filter should be heated to at least 20 °C (68 °F) above the source temperature, but not greater than 120 °C (248 °F). The filter temperature (*i.e.,* the sample gas temperature) should be monitored to assure the desired temperature is maintained. A heated Teflon connector may be used to connect the filter holder or probe to the first impinger.

NOTE: For applications downstream of wet scrubbers, a heated out-of-stack filter (either borosilicate glass wool or glass fiber mat) is necessary.

6.2 Sample Recovery. Same as Method 6, section 6.2.

6.3 Sample Analysis. Same as Method 6, section 6.3, with the addition of a balance to measure within 0.05 g.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

7.1 Sample Collection. Same as Method 6, section 7.1, with the addition of the following:

7.1.1 Drierite. Anhydrous calcium sulfate ($CaSO_4$) desiccant, 8 mesh, indicating type is recommended.

NOTE: Do not use silica gel or similar desiccant in this application.

7.1.2 CO_2 Absorbing Material. Ascarite II. Sodium hydroxide-coated silica, 8- to 20-mesh.

7.2 Sample Recovery and Analysis. Same as Method 6, sections 7.2 and 7.3, respectively.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Preparation of Sampling Train.

8.1.1 Measure 15 ml of 80 percent isopropanol into the first midget bubbler and 15 ml of 3 percent hydrogen peroxide into each of the two midget impingers (the second

and third vessels in the train) as described in Method 6, section 8.1. Insert the glass wool into the top of the isopropanol bubbler as shown in Figure 6A–1. Place about 25 g of Drierite into the second midget bubbler (the fourth vessel in the train). Clean the outside of the bubblers and impingers and allow the vessels to reach room temperature. Weigh the four vessels simultaneously to the nearest 0.1 g, and record this initial weight (m_{wi}).

8.1.2 With one end of the CO_2 absorber sealed, place glass wool into the cylinder to a depth of about 1 cm (0.5 in.). Place about 150 g of CO_2 absorbing material in the cylinder on top of the glass wool, and fill the remaining space in the cylinder with glass wool. Assemble the cylinder as shown in figure 6A–2. With the cylinder in a horizontal position, rotate it around the horizontal axis. The CO_2 absorbing material should remain in position during the rotation, and no open spaces or channels should be formed. If necessary, pack more glass wool into the cylinder to make the CO_2 absorbing material stable. Clean the outside of the cylinder of loose dirt and moisture and allow the cylinder to reach room temperature. Weigh the cylinder to the nearest 0.1 g, and record this initial weight (m_{ai}).

8.1.3 Assemble the train as shown in figure 6A–1. Adjust the probe heater to a temperature sufficient to prevent condensation (see note in section 6.1). Place crushed ice and water around the impingers and bubblers. Mount the CO_2 absorber outside the water bath in a vertical flow position with the sample gas inlet at the bottom. Flexible tubing (*e.g.*, Tygon) may be used to connect the last SO_2 absorbing impinger to the moisture absorber and to connect the moisture absorber to the CO_2 absorber. A second, smaller CO_2 absorber containing Ascarite II may be added in-line downstream of the primary CO_2 absorber as a breakthrough indicator. Ascarite II turns white when CO_2 is absorbed.

8.2 Sampling Train Leak-Check Procedure and Sample Collection. Same as Method 6, sections 8.2 and 8.3, respectively.

8.3 Sample Recovery.

8.3.1 Moisture Measurement. Disconnect the isopropanol bubbler, the SO_2 impingers, and the moisture absorber from the sample train. Allow about 10 minutes for them to reach room temperature, clean the outside of loose dirt and moisture, and weigh them simultaneously in the same manner as in section 8.1. Record this final weight (m_{wf}).

8.3.2 Peroxide Solution. Discard the contents of the isopropanol bubbler and pour the contents of the midget impingers into a leak-free polyethylene bottle for shipping. Rinse the two midget impingers and connecting tubes with water, and add the washing to the same storage container.

8.3.3 CO_2 Absorber. Allow the CO_2 absorber to warm to room temperature (about 10 minutes), clean the outside of loose dirt and moisture, and weigh to the nearest 0.1 g in the same manner as in section 8.1. Record this final weight (m_{af}). Discard used Ascarite II material.

9.0 Quality Control

Same as Method 6, section 9.0.

10.0 Calibration and Standardization

Same as Method 6, section 10.0.

11.0 Analytical Procedure

11.1 Sample Analysis. The sample analysis procedure for SO_2 is the same as that specified in Method 6, section 11.0.

12.0 Data Analysis and Calculations

Same as Method 6, section 12.0, with the addition of the following:

12.1 Nomenclature.

C_w = Concentration of moisture, percent.
C_{CO2} = Concentration of CO_2, dry basis, percent.
E_{SO2} = Emission rate of SO_2, ng/J (lb/10^6 Btu).
F_C = Carbon F-factor from Method 19 for the fuel burned, dscm/J (dscf/10^6 Btu).
m_{wi} = Initial weight of impingers, bubblers, and moisture absorber, g.
m_{wf} = Final weight of impingers, bubblers, and moisture absorber, g.
m_{ai} = Initial weight of CO_2 absorber, g.
m_{af} = Final weight of CO_2 absorber, g.
m_{SO2} = Mass of SO_2 collected, mg.
$V_{CO2(std)}$ = Equivalent volume of CO_2 collected at standard conditions, dscm (dscf).
$V_{w(std)}$ = Equivalent volume of moisture collected at standard conditions, scm (scf).

12.2 CO_2 Volume Collected, Corrected to Standard Conditions.

$$V_{CO_2(std)} = K_3 \left(m_{af} - m_{ai}\right) \qquad \text{Eq. 6A-1}$$

Where:

K_3 = Equivalent volume of gaseous CO_2 at standard conditions, 5.467×10^{-4} dscm/g (1.930×10^{-2} dscf/g).

12.3 Moisture Volume Collected, Corrected to Standard Conditions.

$$V_{w(std)} = K_4 \left(m_{wf} - m_{wi}\right) \qquad \text{Eq. 6A-2}$$

Where:

K_4 = Equivalent volume of water vapor at standard conditions, 1.336×10^{-3} scm/g (4.717×10^{-2} scf/g).

12.4 SO_2 Concentration.

$$C_{so_2} = \frac{K_2 N (V_t - V_{tb})(V_{so\,ln}/V_a)}{V_{m(std)} + V_{co_2(std)}} \qquad \text{Eq. 6A-3}$$

Where:

K_2 = 32.03 mg SO_2/meq. SO_2 (7.061×10^{-5} lb SO_2/meq. SO_2)

12.5 CO_2 Concentration.

$$C_{co_2} = \frac{V_{co_2(std)}}{V_{m(std)} + V_{co_2(std)}} \qquad \text{Eq. 6A-4}$$

12.6 Moisture Concentration.

$$C_w = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)} + V_{co_2(std)}} \qquad \text{Eq. 6A-5}$$

13.0 Method Performance

13.1 Range and Precision. The minimum detectable limit and the upper limit for the measurement of SO_2 are the same as for Method 6. For a 20-liter sample, this method has a precision of ±0.5 percent CO_2 for concentrations between 2.5 and 25 percent CO_2 and ±1.0 percent moisture for moisture concentrations greater than 5 percent.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Methods

If the only emission measurement desired is in terms of emission rate of SO_2 (ng/J or lb/10^6 Btu), an abbreviated procedure may be used. The differences between the above procedure and the abbreviated procedure are described below.

16.1 Sampling Train. The sampling train is the same as that shown in Figure 6A–1 and as described in section 6.1, except that the dry gas meter is not needed.

16.2 Preparation of the Sampling Train. Follow the same procedure as in section 8.1, except do not weigh the isopropanol bubbler, the SO_2 absorbing impingers, or the moisture absorber.

16.3 Sampling Train Leak-Check Procedure and Sample Collection. Leak-check and operate the sampling train as described in section 8.2, except that dry gas meter readings, barometric pressure, and dry gas meter temperatures need not be recorded during sampling.

16.4 Sample Recovery. Follow the procedure in section 8.3, except do not weigh the isopropanol bubbler, the SO_2 absorbing impingers, or the moisture absorber.

16.5 Sample Analysis. Analysis of the peroxide solution is the same as that described in section 11.1.

16.6 Calculations.

16.6.1 SO_2 Collected.

$$m_{SO_2} = K_2 N (V_t - V_{tb})(V_{soln}/V_a) \qquad \text{Eq. 6A-6}$$

Where:

K_2 = 32.03 mg SO_2/meq. SO_2
$K_2 = 7.061 \times 10^{-5}$ lb SO_2/meq. SO_2

16.6.2 Sulfur Dioxide Emission Rate.

$$E_{SO_2} = K_5 F_c m_{so_2} / (m_{af} - m_{ai}) \qquad \text{Eq. 6A-7}$$

Where:

$K_5 = 1.829 \times 10^9$ mg/dscm
$K_2 = 0.1142$ lb/dscf

17.0 References

Same as Method 6, section 17.0, References 1 through 8, with the addition of the following:

1. Stanley, Jon and P.R. Westlin. An Alternate Method for Stack Gas Moisture Determination. Source Evaluation Society Newsletter. *3*(4). November 1978.

2. Whittle, Richard N. and P.R. Westlin. Air Pollution Test Report: Development and Evaluation of an Intermittent Integrated SO_2/CO_2 Emission Sampling Procedure. Environmental Protection Agency, Emission Standard and Engineering Division, Emission Measurement Branch. Research Triangle Park, NC. December 1979. 14 pp.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

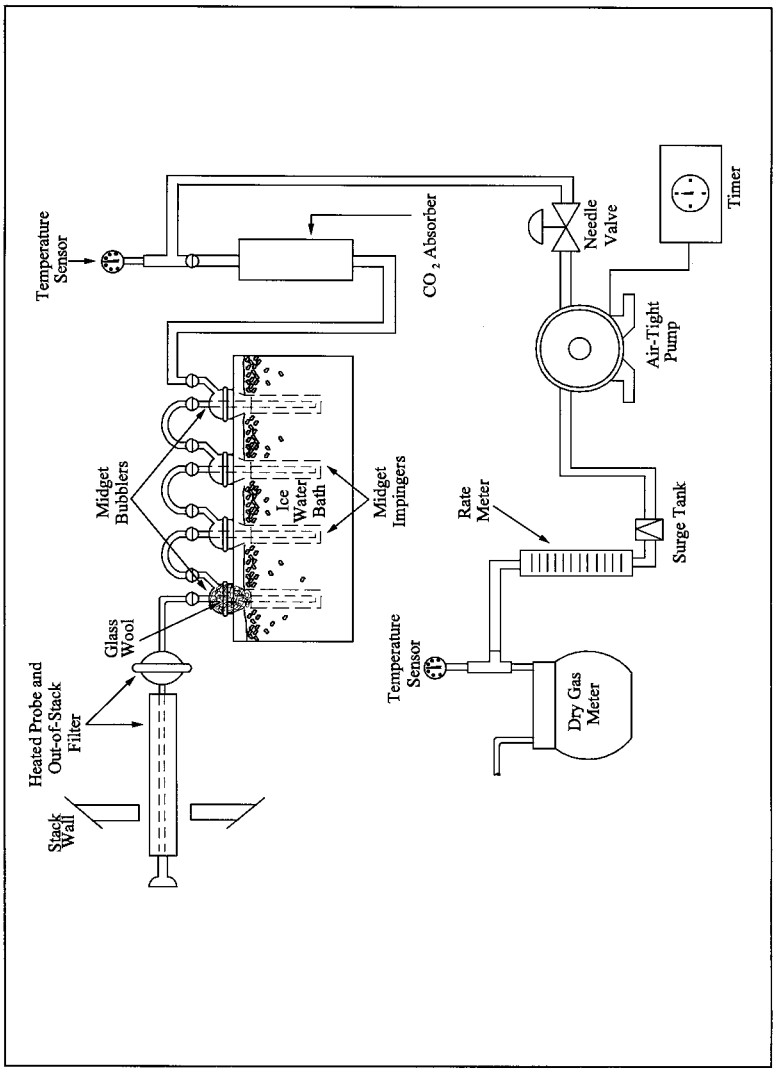

Figure 6A-1. Sampling train.

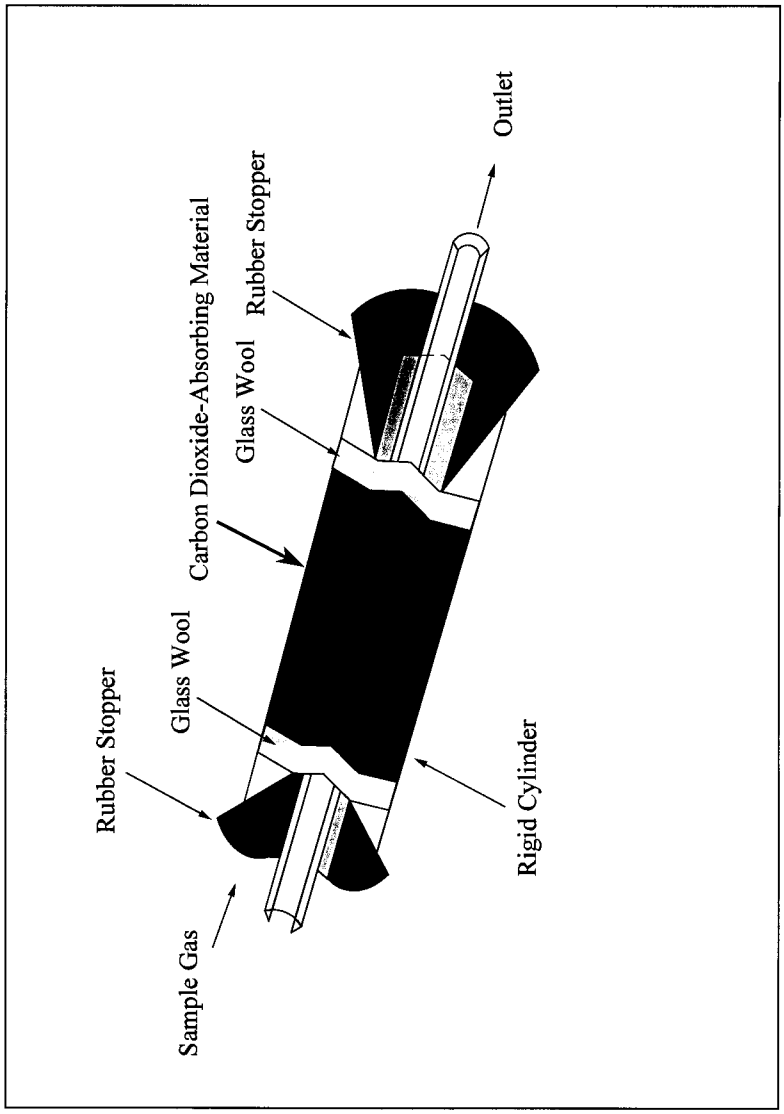

Figure 6A-2. CO_2 Absorber

METHOD 6B—DETERMINATION OF SULFUR DIOXIDE AND CARBON DIOXIDE DAILY AVERAGE EMISSIONS FROM FOSSIL FUEL COMBUSTION SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, Method 6, and Method 6A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Sulfur dioxide (SO_2)	7449–09–05	3.4 mg SO_2/m^3 (2.12×10^{-7} lb/ft^3)
Carbon dioxide (CO_2)	124–38–9	N/A

1.2 Applicability. This method is applicable for the determination of SO_2 emissions from combustion sources in terms of concentration (ng/dscm or lb/dscf) and emission rate (ng/J or lb/10^6 Btu), and for the determination of CO_2 concentration (percent) on a daily (24 hours) basis.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the sampling point in the stack intermittently over a 24-hour or other specified time period. The SO_2 fraction is measured by the barium-thorin titration method. Moisture and CO_2 fractions are collected in the same sampling train, and are determined gravimetrically.

3.0 Definitions [Reserved]

4.0 Interferences

Same as Method 6, section 4.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. Same as Method 6, section 5.2.

6.0 Equipment and Supplies

Same as Method 6A, section 6.0, with the following exceptions and additions:

6.1 The isopropanol bubbler is not used. An empty bubbler for the collection of liquid droplets, that does not allow direct contact between the collected liquid and the gas sample, may be included in the sampling train.

6.2 For intermittent operation, include an industrial timer-switch designed to operate in the ''on'' position at least 2 minutes continuously and ''off'' the remaining period over a repeating cycle. The cycle of operation is designated in the applicable regulation. At a minimum, the sampling operation should include at least 12, equal, evenly-spaced periods per 24 hours.

6.3 Stainless steel sampling probes, type 316, are not recommended for use with Method 6B because of potential sample contamination due to corrosion. Glass probes or other types of stainless steel, *e.g.*, Hasteloy or Carpenter 20, are recommended for long-term use.

NOTE: For applications downstream of wet scrubbers, a heated out-of-stack filter (either borosilicate glass wool or glass fiber mat) is necessary. Probe and filter heating systems capable of maintaining a sample gas temperature of between 20 and 120 °C (68 and 248 °F) at the filter are also required in these cases. The electric supply for these heating systems should be continuous and separate from the timed operation of the sample pump.

7.0 Reagents and Standards

Same as Method 6A, section 7.0, with the following exceptions:

7.1 Isopropanol is not used for sampling.

7.2 The hydrogen peroxide absorbing solution shall be diluted to no less than 6 percent by volume, instead of 3 percent as specified in Methods 6 and 6A.

7.3 If the Method 6B sampling train is to be operated in a low sample flow condition (less than 100 ml/min or 0.21 ft^3/hr), molecular sieve material may be substituted for Ascarite II as the CO_2 absorbing material. The recommended molecular sieve material is Union Carbide 1/16 inch pellets, 5 A°, or equivalent. Molecular sieve material need not be discarded following the sampling run, provided that it is regenerated as per the manufacturer's instruction. Use of molecular sieve material at flow rates higher than 100 ml/min (0.21 ft^3/hr) may cause erroneous CO_2 results.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Preparation of Sampling Train. Same as Method 6A, section 8.1, with the addition of the following:

8.1.1 The sampling train is assembled as shown in Figure 6A–1 of Method 6A, except that the isopropanol bubbler is not included.

8.1.2 Adjust the timer-switch to operate in the ''on'' position from 2 to 4 minutes on a 2-hour repeating cycle or other cycle specified in the applicable regulation. Other timer sequences may be used with the restriction that the total sample volume collected is between 25 and 60 liters (0.9 and 2.1 ft^3) for the amounts of sampling reagents prescribed in this method.

8.1.3 Add cold water to the tank until the impingers and bubblers are covered at least two-thirds of their length. The impingers and bubbler tank must be covered and protected from intense heat and direct sunlight. If freezing conditions exist, the impinger solution and the water bath must be protected.

NOTE: Sampling may be conducted continuously if a low flow-rate sample pump [20

to 40 ml/min (0.04 to 0.08 ft^3/hr) for the reagent volumes described in this method] is used. If sampling is continuous, the timer-switch is not necessary. In addition, if the sample pump is designed for constant rate sampling, the rate meter may be deleted. The total gas volume collected should be between 25 and 60 liters (0.9 and 2.1 ft^3) for the amounts of sampling reagents prescribed in this method.

8.2 Sampling Train Leak-Check Procedure. Same as Method 6, section 8.2.

8.3 Sample Collection.

8.3.1 The probe and filter (either in-stack, out-of-stack, or both) must be heated to a temperature sufficient to prevent water condensation.

8.3.2 Record the initial dry gas meter reading. To begin sampling, position the tip of the probe at the sampling point, connect the probe to the first impinger (or filter), and start the timer and the sample pump. Adjust the sample flow to a constant rate of approximately 1.0 liter/min (0.035 cfm) as indicated by the rotameter. Observe the operation of the timer, and determine that it is operating as intended (*i.e.*, the timer is in the ''on'' position for the desired period, and the cycle repeats as required).

8.3.3 One time between 9 a.m. and 11 a.m. during the 24-hour sampling period, record the dry gas meter temperature (T_m) and the barometric pressure ($P_{(bar)}$).

8.3.4 At the conclusion of the run, turn off the timer and the sample pump, remove the probe from the stack, and record the final gas meter volume reading. Conduct a leak-check as described in section 8.2. If a leak is found, void the test run or use procedures acceptable to the Administrator to adjust the sample volume for leakage. Repeat the steps in sections 8.3.1 to 8.3.4 for successive runs.

8.4 Sample Recovery. The procedures for sample recovery (moisture measurement, peroxide solution, and CO_2 absorber) are the same as those in Method 6A, section 8.3.

9.0 Quality Control

Same as Method 6, section 9.0., with the exception of the isopropanol-check.

10.0 Calibration and Standardization

Same as Method 6, section 10.0, with the addition of the following:

10.1 Periodic Calibration Check. After 30 days of operation of the test train, conduct a calibration check according to the same procedures as the post-test calibration check (Method 6, section 10.1.2). If the deviation between initial and periodic calibration factors exceeds 5 percent, use the smaller of the two factors in calculations for the preceding 30 days of data, but use the most recent calibration factor for succeeding test runs.

11.0 Analytical Procedures

11.1 Sample Loss Check and Analysis. Same as Method 6, sections 11.1 and 11.2, respectively.

12.0 Data Analysis and Calculations

Same as Method 6A, section 12.0, except that P_{bar} and T_m correspond to the values recorded in section 8.3.3 of this method. The values are as follows:

P_{bar} = Initial barometric pressure for the test period, mm Hg.

T_m = Absolute meter temperature for the test period, °K.

13.0 Method Performance

13.1 Range.

13.1.1 Sulfur Dioxide. Same as Method 6.

13.1.2 Carbon Dioxide. Not determined.

13.2 Repeatability and Reproducibility. EPA-sponsored collaborative studies were undertaken to determine the magnitude of repeatability and reproducibility achievable by qualified testers following the procedures in this method. The results of the studies evolve from 145 field tests including comparisons with Methods 3 and 6. For measurements of emission rates from wet, flue gas desulfurization units in (ng/J), the repeatability (intra-laboratory precision) is 8.0 percent and the reproducibility (inter-laboratory precision) is 11.1 percent.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Methods

Same as Method 6A, section 16.0, except that the timer is needed and is operated as outlined in this method.

17.0 References

Same as Method 6A, section 17.0, with the addition of the following:

1. Butler, Frank E., et. al. The Collaborative Test of Method 6B: Twenty-Four-Hour Analysis of SO_2 and CO_2. JAPCA. Vol. 33, No. 10. October 1983.

18.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 6C—DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES (INSTRUMENTAL ANALYZER PROCEDURE)

1.0 Scope and Application

What is Method 6C?

Method 6C is a procedure for measuring sulfur dioxide (SO_2) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that

you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis.

This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 4—Determination of Moisture Content in Stack Gases.

(c) Method 6—Determination of Sulfur Dioxide Emissions from Stationary Sources.

(d) Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure).

1.1 Analytes. What does this method determine? This method measures the concentration of sulfur dioxide.

Analyte	CAS No.	Sensitivity
SO_2	7446–09–5	Typically <2% of Calibration Span.

1.2 Applicability. When is this method required? The use of Method 6C may be required by specific New Source Performance Standards, Clean Air Marketing rules, State Implementation Plans, and permits where SO_2 concentrations in stationary source emissions must be measured, either to determine compliance with an applicable emission standard or to conduct performance testing of a continuous emission monitoring system (CEMS). Other regulations may also require the use of Method 6C.

1.3 Data Quality Objectives. How good must my collected data be? Refer to section 1.3 of Method 7E.

2.0 Summary of Method

In this method, you continuously sample the effluent gas and convey the sample to an analyzer that measures the concentration of SO_2. You must meet the performance requirements of this method to validate your data.

3.0 Definitions

Refer to section 3.0 of Method 7E for the applicable definitions.

4.0 Interferences

Refer to Section 4.0 of Method 7E.

5.0 Safety

Refer to section 5.0 of Method 7E.

6.0 Equipment and Supplies

Figure 7E–1 of Method 7E is a schematic diagram of an acceptable measurement system.

6.1 What do I need for the measurement system? The essential components of the measurement system are the same as those in sections 6.1 and 6.2 of Method 7E, except that the SO_2 analyzer described in section 6.2 of this method must be used instead of the analyzer described in section 6.2 of Method 7E. You must follow the noted specifications in section 6.1 of Method 7E.

6.2 What analyzer must I use? You may use an instrument that uses an ultraviolet, nondispersive infrared, fluorescence, or other detection principle to continuously measure SO_2 in the gas stream and meets the performance specifications in section 13.0. The low-range and dual-range analyzer provisions in sections 6.2.8.1 and 6.2.8.2 of Method 7E apply.

7.0 Reagents and Standards

7.1 Calibration Gas. What calibration gases do I need? Refer to section 7.1 of Method 7E for the calibration gas requirements. Example calibration gas mixtures are listed below.

(a) SO_2 in nitrogen (N_2).

(b) SO_2 in air.

(c) SO_2 and CO_2 in N_2.

(d) SO_2 andO_2 in N_2.

(e) $SO_2/CO_2/O_2$ gas mixture in N_2.

(f) CO_2/NO_X gas mixture in N_2.

(g) $CO_2/SO_2/NO_X$ gas mixture in N_2.

7.2 Interference Check. What additional reagents do I need for the interference check? The test gases for the interference check are listed in Table 7E–3 of Method 7E. For the alternative interference check, you must use the reagents described in section 7.0 of Method 6.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling Site and Sampling Points. You must follow the procedures of section 8.1 of Method 7E.

8.2 Initial Measurement System Performance Tests. You must follow the procedures in section 8.2 of Method 7E. If a dilution-type measurement system is used, the special considerations in section 8.3 of Method 7E also apply.

8.3 Interference Check. You must follow the procedures of section 8.2.7 of Method 7E

to conduct an interference check, substituting SO_2 for NO_X as the method pollutant. For dilution-type measurement systems, you must use the alternative interference check procedure in section 16 and a co-located, unmodified Method 6 sampling train.

8.4 Sample Collection. You must follow the procedures of section 8.4 of Method 7E.

8.5 Post-Run System Bias Check and Drift Assessment. You must follow the procedures of section 8.5 of Method 7E.

9.0 Quality Control

Follow quality control procedures in section 9.0 of Method 7E.

10.0 Calibration and Standardization

Follow the procedures for calibration and standardization in section 10.0 of Method 7E.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the applicable procedures for calculations and data analysis in section 12.0 of Method 7E as applicable, substituting SO_2 for NO_X as appropriate.

13.0 Method Performance

13.1 The specifications for the applicable performance checks are the same as in section 13.0 of Method 7E.

13.2 Alternative Interference Check. The results are acceptable if the difference between the Method 6C result and the modified Method 6 result is less than 7.0 percent of the Method 6 result for each of the three test runs. For the purposes of comparison, the Method 6 and 6C results must be expressed in the same units of measure.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Alternative Interference Check. You may perform an alternative interference check consisting of at least three comparison runs between Method 6C and Method 6. This check validates the Method 6C results at each particular source category (type of facility) where the check is performed. When testing under conditions of low concentrations (<15 ppm), this alternative interference check is not allowed.

NOTE: The procedure described below applies to non-dilution sampling systems only. If this alternative interference check is used for a dilution sampling system, use a standard Method 6 sampling train and extract the sample directly from the exhaust stream at points collocated with the Method 6C sample probe.

a. Build the modified Method 6 sampling train (flow control valve, two midget impingers containing 3 percent hydrogen peroxide, and dry gas meter) shown in Figure 6C–1. Connect the sampling train to the sample bypass discharge vent. Record the dry gas meter reading before you begin sampling. Simultaneously collect modified Method 6 and Method 6C samples. Open the flow control valve in the modified Method 6 train as you begin to sample with Method 6C. Adjust the Method 6 sampling rate to 1 liter per minute (.10 percent). The sampling time per run must be the same as for Method 6 plus twice the average measurement system response time. If your modified Method 6 train does not include a pump, you risk biasing the results high if you over-pressurize the midget impingers and cause a leak. You can reduce this risk by cautiously increasing the flow rate as sampling begins.

b. After completing a run, record the final dry gas meter reading, meter temperature, and barometric pressure. Recover and analyze the contents of the midget impingers using the procedures in Method 6. Determine the average gas concentration reported by Method 6C for the run.

17.0 References

1. ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards'' September 1997 as amended, EPA–600/R–97/121

18.0 Tables, Diagrams, Flowcharts, and Validation Data

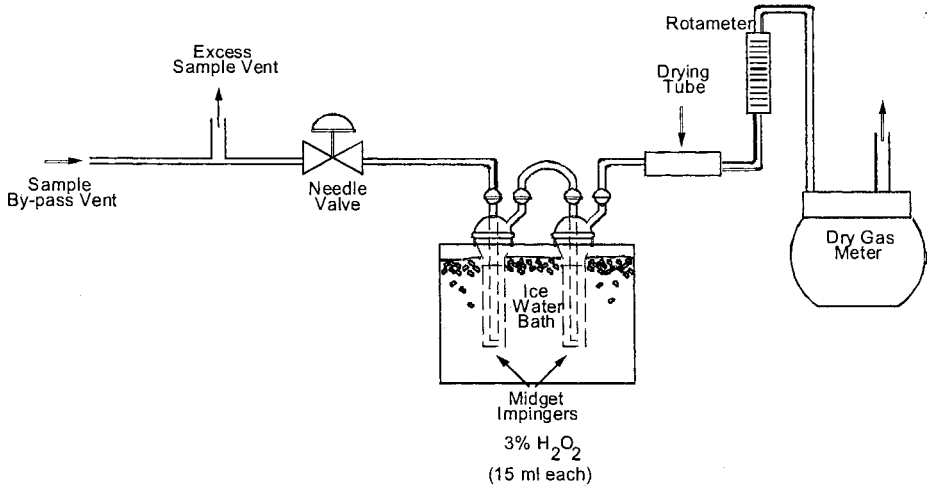

Figure 6C-1. Modified Method 6
Alternative Interference Check Sampling Train

METHOD 7—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1 and Method 5.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–0	2–400 mg/dscm

1.2 Applicability. This method is applicable for the measurement of nitrogen oxides (NO_X) emitted from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sample methods.

2.0 Summary of Method

A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution, and the nitrogen oxides, except nitrous oxide, are measured colorimetrically using the phenoldisulfonic acid (PDS) procedure.

3.0 Definitions [Reserved]

4.0 Interferences

Biased results have been observed when sampling under conditions of high sulfur dioxide concentrations. At or above 2100 ppm SO_2, use five times the H_2O_2 concentration of the Method 7 absorbing solution. Laboratory tests have shown that high concentrations of SO_2 (about 2100 ppm) cause low results in Method 7 and 7A. Increasing the H_2O_2 concentration to five times the original concentration eliminates this bias. However, when no SO_2 is present, increasing the concentration by five times results in a low bias.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs.

5.2.2 Phenoldisulfonic Acid. Irritating to eyes and skin.

5.2.3 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.4 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

5.2.5 Phenol. Poisonous and caustic. Do not handle with bare hands as it is absorbed through the skin.

6.0 Equipment and Supplies

6.1 Sample Collection. A schematic of the sampling train used in performing this method is shown in Figure 7–1. Other grab sampling systems or equipment, capable of measuring sample volume to within 2.0 percent and collecting a sufficient sample volume to allow analytical reproducibility to within 5 percent, will be considered acceptable alternatives, subject to the approval of the Administrator. The following items are required for sample collection:

6.1.1 Probe. Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or heated out-of-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Stainless steel or Teflon tubing may also be used for the probe. Heating is not necessary if the probe remains dry during the purging period.

6.1.2 Collection Flask. Two-liter borosilicate, round bottom flask, with short neck and 24/40 standard taper opening, protected against implosion or breakage.

6.1.3 Flask Valve. T-bore stopcock connected to a 24/40 standard taper joint.

6.1.4 Temperature Gauge. Dial-type thermometer, or other temperature gauge, capable of measuring 1 °C (2 °F) intervals from −5 to 50 °C (23 to 122 °F).

6.1.5 Vacuum Line. Tubing capable of withstanding a vacuum of 75 mm (3 in.) Hg absolute pressure, with ''T'' connection and T-bore stopcock.

6.1.6 Vacuum Gauge. U-tube manometer, 1 meter (39 in.), with 1 mm (0.04 in.) divisions, or other gauge capable of measuring pressure to within 2.5 mm (0.10 in.) Hg.

6.1.7 Pump. Capable of evacuating the collection flask to a pressure equal to or less than 75 mm (3 in.) Hg absolute.

6.1.8 Squeeze Bulb. One-way.

6.1.9 Volumetric Pipette. 25-ml.

6.1.10 Stopcock and Ground Joint Grease. A high-vacuum, high-temperature chlorofluorocarbon grease is required. Halocarbon 25–5S has been found to be effective.

6.1.11 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg. See note in Method 5, section 6.1.2.

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Graduated Cylinder. 50-ml with 1 ml divisions.

6.2.2 Storage Containers. Leak-free polyethylene bottles.

6.2.3 Wash Bottle. Polyethylene or glass.

6.2.4 Glass Stirring Rod.

6.2.5 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

6.3 Analysis. The following items are required for analysis:

6.3.1 Volumetric Pipettes. Two 1-ml, two 2-ml, one 3-ml, one 4-ml, two 10-ml, and one 25-ml for each sample and standard.

6.3.2 Porcelain Evaporating Dishes. 175- to 250-ml capacity with lip for pouring, one for each sample and each standard. The Coors No. 45006 (shallowform, 195-ml) has been found to be satisfactory. Alternatively, polymethyl pentene beakers (Nalge No. 1203, 150-ml), or glass beakers (150-ml) may be used. When glass beakers are used, etching of the beakers may cause solid matter to be present in the analytical step; the solids should be removed by filtration.

6.3.3 Steam Bath. Low-temperature ovens or thermostatically controlled hot plates kept below 70 °C (160 °F) are acceptable alternatives.

6.3.4 Dropping Pipette or Dropper. Three required.

6.3.5 Polyethylene Policeman. One for each sample and each standard.

6.3.6 Graduated Cylinder. 100-ml with 1-ml divisions.

6.3.7 Volumetric Flasks. 50-ml (one for each sample and each standard), 100-ml (one for each sample and each standard, and one for the working standard KNO_3 solution), and 1000-ml (one).

6.3.8 Spectrophotometer. To measure at 410 nm.

6.3.9 Graduated Pipette. 10-ml with 0.1-ml divisions.

6.3.10 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

6.3.11 Analytical Balance. To measure to within 0.1 mg.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. The following reagents are required for sampling:

7.1.1 Water. Deionized distilled to conform to ASTM D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17). The $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.1.2 Absorbing Solution. Cautiously add 2.8 ml concentrated H_2SO_4 to a 1-liter flask partially filled with water. Mix well, and add 6 ml of 3 percent hydrogen peroxide, freshly prepared from 30 percent hydrogen peroxide solution. Dilute to 1 liter of water and mix well. The absorbing solution should be used within 1 week of its preparation. Do not expose to extreme heat or direct sunlight.

7.2 Sample Recovery. The following reagents are required for sample recovery:

7.2.1 Water. Same as in 7.1.1.

7.2.2 Sodium Hydroxide, 1 N. Dissolve 40 g NaOH in water, and dilute to 1 liter.

7.3 Analysis. The following reagents and standards are required for analysis:

7.3.1 Water. Same as in 7.1.1.

7.3.2 Fuming Sulfuric Acid. 15 to 18 percent by weight free sulfur trioxide. HANDLE WITH CAUTION.

7.3.3 Phenol. White solid.

7.3.4 Sulfuric Acid. Concentrated, 95 percent minimum assay.

7.3.5 Potassium Nitrate (KNO_3). Dried at 105 to 110 °C (221 to 230 °F) for a minimum of 2 hours just prior to preparation of standard solution.

7.3.6 Standard KNO_3 Solution. Dissolve exactly 2.198 g of dried KNO_3 in water, and dilute to 1 liter with water in a 1000-ml volumetric flask.

7.3.7 Working Standard KNO_3 Solution. Dilute 10 ml of the standard solution to 100 ml with water. One ml of the working standard solution is equivalent to 100 μg nitrogen dioxide (NO_2).

7.3.8 Phenoldisulfonic Acid Solution. Dissolve 25 g of pure white phenol solid in 150 ml concentrated sulfuric acid on a steam bath. Cool, add 75 ml fuming sulfuric acid (15 to 18 percent by weight free sulfur trioxide—HANDLE WITH CAUTION), and heat at 100 °C (212 °F) for 2 hours. Store in a dark, stoppered bottle.

7.3.9 Concentrated Ammonium Hydroxide.

8.0 Sample Collection, Preservation, Storage and Transport

8.1 Sample Collection.

8.1.1 Flask Volume. The volume of the collection flask and flask valve combination must be known prior to sampling. Assemble the flask and flask valve, and fill with water to the stopcock. Measure the volume of water to ±10 ml. Record this volume on the flask.

8.1.2 Pipette 25 ml of absorbing solution into a sample flask, retaining a sufficient quantity for use in preparing the calibration standards. Insert the flask valve stopper into the flask with the valve in the ''purge'' position. Assemble the sampling train as shown in Figure 7–1, and place the probe at the sampling point. Make sure that all fittings are tight and leak-free, and that all ground glass joints have been greased properly with a high-vacuum, high temperature chlorofluorocarbon-based stopcock grease. Turn the flask valve and the pump valve to their ''evacuate'' positions. Evacuate the flask to 75 mm (3 in.) Hg absolute pressure, or less. Evacuation to a pressure approaching the vapor pressure of water at the existing temperature is desirable. Turn the pump valve to its ''vent'' position, and turn off the pump. Check for leakage by observing the manometer for any pressure fluctuation. (Any variation greater than 10 mm (0.4 in.) Hg over a period of 1 minute is not acceptable, and the flask is not to be used until the leakage problem is corrected. Pressure in the flask is not to exceed 75 mm (3 in.) Hg absolute at the time sampling is commenced.) Record the volume of the flask and valve (V_f), the flask temperature (T_i), and the barometric pressure. Turn the flask valve counterclockwise to its ''purge'' position, and do the same with the pump valve. Purge the probe and the vacuum tube using the squeeze bulb. If condensation occurs in the probe and the flask valve area, heat the probe, and purge until the condensation disappears. Next, turn the pump valve to its ''vent'' position. Turn the flask valve clockwise to its ''evacuate'' position, and record the difference in the mercury levels in the manometer. The absolute internal pressure in the flask (P_i) is equal to the barometric pressure less the manometer reading. Immediately turn the flask valve to the ''sample'' position, and permit the gas to enter the flask until pressures in the flask and sample line (*i.e.*, duct, stack) are equal. This will usually require about 15 seconds; a longer period indicates a plug in the probe, which must be

corrected before sampling is continued. After collecting the sample, turn the flask valve to its ''purge'' position, and disconnect the flask from the sampling train.

8.1.3 Shake the flask for at least 5 minutes.

8.1.4 If the gas being sampled contains insufficient oxygen for the conversion of NO to NO_2 (*e.g.,* an applicable subpart of the standards may require taking a sample of a calibration gas mixture of NO in N_2), then introduce oxygen into the flask to permit this conversion. Oxygen may be introduced into the flask by one of three methods: (1) Before evacuating the sampling flask, flush with pure cylinder oxygen, then evacuate flask to 75 mm (3 in.) Hg absolute pressure or less; or (2) inject oxygen into the flask after sampling; or (3) terminate sampling with a minimum of 50 mm (2 in.) Hg vacuum remaining in the flask, record this final pressure, and then vent the flask to the atmosphere until the flask pressure is almost equal to atmospheric pressure.

8.2 Sample Recovery. Let the flask sit for a minimum of 16 hours, and then shake the contents for 2 minutes.

8.2.1 Connect the flask to a mercury filled U-tube manometer. Open the valve from the flask to the manometer, and record the flask temperature (T_f), the barometric pressure, and the difference between the mercury levels in the manometer. The absolute internal pressure in the flask (P_f) is the barometric pressure less the manometer reading. Transfer the contents of the flask to a leak-free polyethylene bottle. Rinse the flask twice with 5 ml portions of water, and add the rinse water to the bottle. Adjust the pH to between 9 and 12 by adding 1 N NaOH, dropwise (about 25 to 35 drops). Check the pH by dipping a stirring rod into the solution and then touching the rod to the pH test paper. Remove as little material as possible during this step. Mark the height of the liquid level so that the container can be checked for leakage after transport. Label the container to identify clearly its contents. Seal the container for shipping.

9.0 Quality Control

Section	Quality control measure	Effect
10.1	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.

10.0 Calibration and Standardization

10.1 Spectrophotometer.

10.1.1 Optimum Wavelength Determination.

10.1.1.1 Calibrate the wavelength scale of the spectrophotometer every 6 months. The calibration may be accomplished by using an energy source with an intense line emission such as a mercury lamp, or by using a series of glass filters spanning the measuring range of the spectrophotometer. Calibration materials are available commercially and from the National Institute of Standards and Technology. Specific details on the use of such materials should be supplied by the vendor; general information about calibration techniques can be obtained from general reference books on analytical chemistry. The wavelength scale of the spectrophotometer must read correctly within 5 nm at all calibration points; otherwise, repair and recalibrate the spectrophotometer. Once the wavelength scale of the spectrophotometer is in proper calibration, use 410 nm as the optimum wavelength for the measurement of the absorbance of the standards and samples.

10.1.1.2 Alternatively, a scanning procedure may be employed to determine the proper measuring wavelength. If the instrument is a double-beam spectrophotometer, scan the spectrum between 400 and 415 nm using a 200 μg NO_2 standard solution in the sample cell and a blank solution in the reference cell. If a peak does not occur, the spectrophotometer is probably malfunctioning and should be repaired. When a peak is obtained within the 400 to 415 nm range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of absorbance of both the standards and the samples. For a single-beam spectrophotometer, follow the scanning procedure described above, except scan separately the blank and standard solutions. The optimum wavelength shall be the wavelength at which the maximum difference in absorbance between the standard and the blank occurs.

10.1.2 Determination of Spectrophotometer Calibration Factor K_c. Add 0 ml, 2.0 ml, 4.0 ml, 6.0 ml, and 8.0 ml of the KNO_3 working standard solution (1 ml = 100 μg NO_2) to a series of five 50-ml volumetric flasks. To each flask, add 25 ml of absorbing solution and 10 ml water. Add 1 N NaOH to each flask until the pH is between 9 and 12 (about 25 to 35 drops). Dilute to the mark with water. Mix thoroughly, and pipette a 25-ml aliquot of each solution into a separate porcelain evaporating dish. Beginning with the evaporation step, follow the analysis procedure of section 11.2 until the solution has been transferred to the 100-ml volumetric flask and diluted to the mark. Measure the absorbance of each solution at the optimum wavelength as determined in section 10.2.1. This calibration procedure must be repeated on each day that samples are analyzed. Calculate the spectrophotometer calibration factor as shown in section 12.2.

10.1.3 Spectrophotometer Calibration Quality Control. Multiply the absorbance value obtained for each standard by the K_c factor (reciprocal of the least squares slope) to determine the distance each calibration point lies from the theoretical calibration line. The difference between the calculated concentration values and the actual concentrations (*i.e.*, 100, 200, 300, and 400 µg NO_2) should be less than 7 percent for all standards.

10.2 Barometer. Calibrate against a mercury barometer or NIST-traceable barometer prior to the field test.

10.3 Temperature Gauge. Calibrate dial thermometers against mercury-in-glass thermometers. An alternative mercury-free thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

10.4 Vacuum Gauge. Calibrate mechanical gauges, if used, against a mercury manometer such as that specified in section 6.1.6.

10.5 Analytical Balance. Calibrate against standard weights.

11.0 Analytical Procedures

11.1 Sample Loss Check. Note the level of the liquid in the container, and confirm whether any sample was lost during shipment. Note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Preparation. Immediately prior to analysis, transfer the contents of the shipping container to a 50 ml volumetric flask, and rinse the container twice with 5 ml portions of water. Add the rinse water to the flask, and dilute to mark with water; mix thoroughly. Pipette a 25-ml aliquot into the porcelain evaporating dish. Return any unused portion of the sample to the polyethylene storage bottle. Evaporate the 25-ml aliquot to dryness on a steam bath, and allow to cool. Add 2 ml phenoldisulfonic acid solution to the dried residue, and triturate thoroughly with a polyethylene policeman. Make sure the solution contacts all the residue. Add 1 ml water and 4 drops of concentrated sulfuric acid. Heat the solution on a steam bath for 3 minutes with occasional stirring. Allow the solution to cool, add 20 ml water, mix well by stirring, and add concentrated ammonium hydroxide, dropwise, with constant stirring, until the pH is 10 (as determined by pH paper). If the sample contains solids, these must be removed by filtration (centrifugation is an acceptable alternative, subject to the approval of the Administrator) as follows: Filter through Whatman No. 41 filter paper into a 100-ml volumetric flask. Rinse the evaporating dish with three 5-ml portions of water. Filter these three rinses. Wash the filter with at least three 15-ml portions of water. Add the filter washings to the contents of the volumetric flask, and dilute to the mark with water. If solids are absent, the solution can be transferred directly to the 100-ml volumetric flask and diluted to the mark with water.

11.3 Sample Analysis. Mix the contents of the flask thoroughly, and measure the absorbance at the optimum wavelength used for the standards (Section 10.2.1), using the blank solution as a zero reference. Dilute the sample and the blank with equal volumes of water if the absorbance exceeds A_4, the absorbance of the 400-µg NO_2 standard (see section 10.2.2).

12.0 Data Analysis and Calculations

Carry out the calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculations.

12.1 12.1 Nomenclature

A = Absorbance of sample.
A_1 = Absorbance of the 100-µg NO_2 standard.
A_2 = Absorbance of the 200-µg NO_2 standard.
A_3 = Absorbance of the 300-µg NO_2 standard.
A_4 = Absorbance of the 400-µg NO_2 standard.
C = Concentration of NO_X as NO_2, dry basis, corrected to standard conditions, mg/dsm^3 (lb/dscf).
F = Dilution factor (*i.e.*, 25/5, 25/10, *etc.*, required only if sample dilution was needed to reduce the absorbance into the range of the calibration).
K_c = Spectrophotometer calibration factor.
M = Mass of NO_X as NO_2 in gas sample, µg.
P_f = Final absolute pressure of flask, mm Hg (in. Hg).
P_i = Initial absolute pressure of flask, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
T_f = Final absolute temperature of flask, °K (°R).
T_i = Initial absolute temperature of flask, °K (°R).
T_{std} = Standard absolute temperature, 293 °K (528°R).
V_{sc} = Sample volume at standard conditions (dry basis), ml.
V_f = Volume of flask and valve, ml.
V_a = Volume of absorbing solution, 25 ml.

12.2 Spectrophotometer Calibration Factor.

$$K_c = 100\frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^{\,2} + A_2^{\,2} + A_3^{\,2} + A_4^{\,2}} \qquad \text{Eq. 7-1}$$

12.3 Sample Volume, Dry Basis, Corrected to Standard Conditions.

$$V_{sc} = \left(V_f - V_a\right)\frac{T_{std}}{P_{std}}\left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right] \qquad \text{Eq. 7-2}$$

$$= K_1\left(V_f - 25\right)\left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right]$$

Where:

K_1 = 0.3858 °K/mm Hg for metric units,
K_1 = 17.65 °R/in. Hg for English units.

12.4 Total µg NO_2 per sample.

$$m = 2K_c AF \qquad \text{Eq. 7-3}$$

Where:
2 = 50/25, the aliquot factor.

NOTE: If other than a 25-ml aliquot is used for analysis, the factor 2 must be replaced by a corresponding factor.

12.5 Sample Concentration, Dry Basis, Corrected to Standard Conditions.

$$C = K_2\left(m/V_{sc}\right) \qquad \text{Eq. 7-4}$$

Where:

K2 = 10^3 (mg/m^3)/(µg/ml) for metric units,
K_2 = 6.242 × 10^{-5} (lb/scf)/(µg/ml) for English units.

13.0 Method Performance

13.1 Range. The analytical range of the method has been determined to be 2 to 400 milligrams NO_X (as NO_2) per dry standard cubic meter, without having to dilute the sample.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Standard Methods of Chemical Analysis. 6th ed. New York, D. Van Nostrand Co., Inc. 1962. Vol. 1, pp. 329–330.

2. Standard Method of Test for Oxides of Nitrogen in Gaseous Combustion Products (Phenoldisulfonic Acid Procedure). In: 1968 Book of ASTM Standards, Part 26. Philadelphia, PA. 1968. ASTM Designation D 1608–60, pp. 725–729.

3. Jacob, M.B. The Chemical Analysis of Air Pollutants. New York. Interscience Publishers, Inc. 1960. Vol. 10, pp. 351–356.

4. Beatty, R.L., L.B. Berger, and H.H. Schrenk. Determination of Oxides of Nitrogen by the Phenoldisulfonic Acid Method. Bureau of Mines, U.S. Dept. of Interior. R.I. 3687. February 1943.

5. Hamil, H.F. and D.E. Camann. Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Fossil Fuel-Fired Steam Generators). Southwest Research Institute Report for Environmental Protection Agency. Research Triangle Park, NC. October 5, 1973.

6. Hamil, H.F. and R.E. Thomas. Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Nitric Acid Plants). Southwest Research Institute Report for Environmental Protection Agency. Research Triangle Park, NC. May 8, 1974.

7. Stack Sampling Safety Manual (Draft). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC. September 1978.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

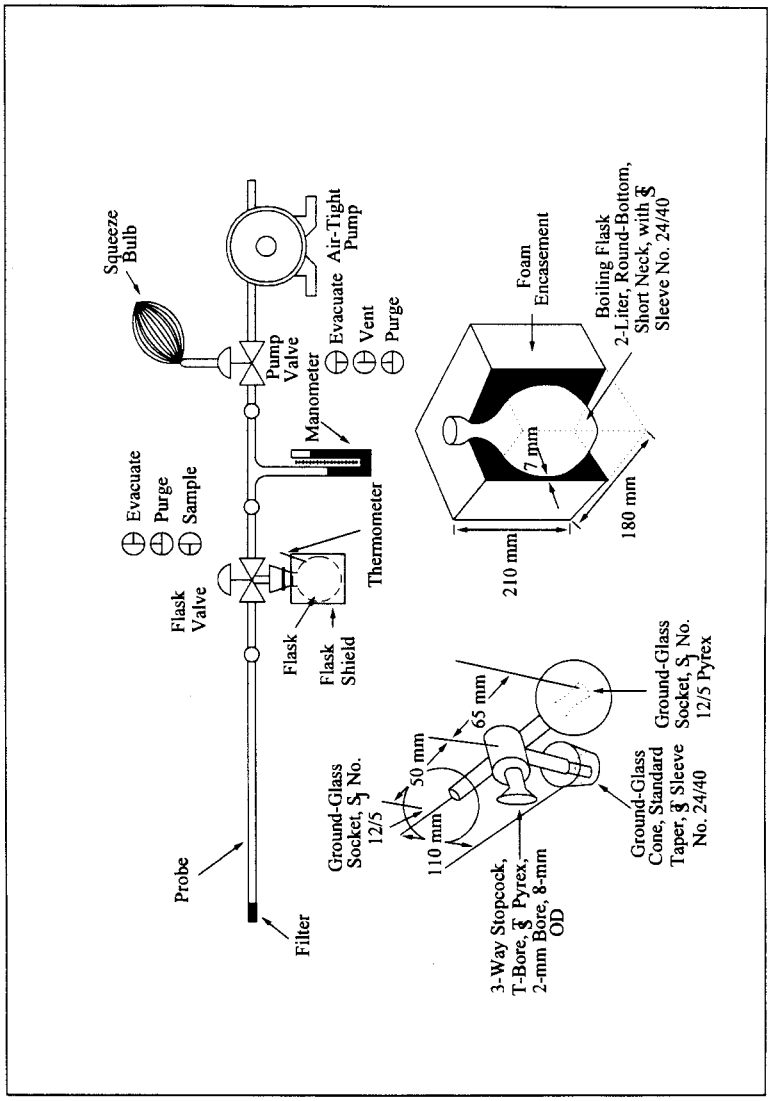

Figure 7-1. Sampling Train, Flask Valve, and Flask.

METHOD 7A—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ION CHROMATOGRAPHIC METHOD)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 3, Method 5, and Method 7.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–0	65–655 ppmv

1.2 Applicability. This method is applicable for the determination of NO_X emissions from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution. The nitrogen oxides, excluding nitrous oxide (N_2O), are oxidized to nitrate and measured by ion chromatography.

3.0 Definitions [Reserved]

4.0 Interferences

Biased results have been observed when sampling under conditions of high sulfur dioxide concentrations. At or above 2100 ppm SO_2, use five times the H_2O_2 concentration of the Method 7 absorbing solution. Laboratory tests have shown that high concentrations of SO_2 (about 2100 ppm) cause low results in Method 7 and 7A. Increasing the H_2O_2 concentration to five times the original concentration eliminates this bias. However, when no SO_2 is present, increasing the concentration by five times results in a low bias.

5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs.

5.2.2 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m^3 will cause lung damage in uninitiated. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as in Method 7, section 6.1.

6.2 Sample Recovery. Same as in Method 7, section 6.2, except the stirring rod and pH paper are not needed.

6.3 Analysis. For the analysis, the following equipment and supplies are required. Alternative instrumentation and procedures will be allowed provided the calibration precision requirement in section 10.1.2 can be met.

6.3.1 Volumetric Pipets. Class A;1-, 2-, 4-, 5-ml (two for the set of standards and one per sample), 6-, 10-, and graduated 5-ml sizes.

6.3.2 Volumetric Flasks. 50-ml (two per sample and one per standard), 200-ml, and 1-liter sizes.

6.3.3 Analytical Balance. To measure to within 0.1 mg.

6.3.4 Ion Chromatograph. The ion chromatograph should have at least the following components:

6.3.4.1 Columns. An anion separation or other column capable of resolving the nitrate ion from sulfate and other species present and a standard anion suppressor column (optional). Suppressor columns are produced as proprietary items; however, one can be produced in the laboratory using the resin available from BioRad Company, 32nd and Griffin Streets, Richmond, California. Peak resolution can be optimized by varying the eluent strength or column flow rate, or by experimenting with alternative columns that may offer more efficient separation. When using guard columns with the stronger reagent to protect the separation column, the analyst should allow rest periods between injection intervals to purge possible sulfate buildup in the guard column.

6.3.4.2 Pump. Capable of maintaining a steady flow as required by the system.

6.3.4.3 Flow Gauges. Capable of measuring the specified system flow rate.

6.3.4.4 Conductivity Detector.

6.3.4.5 Recorder. Compatible with the output voltage range of the detector.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 7, section 7.1.

7.2 Sample Recovery. Same as Method 7, section 7.1.1.

7.3 Analysis. The following reagents and standards are required for analysis:

7.3.1 Water. Same as Method 7, section 7.1.1.

7.3.2 Stock Standard Solution, 1 mg NO_2/ml. Dry an adequate amount of sodium nitrate ($NaNO_3$) at 105 to 110 °C (221 to 230 °F) for a minimum of 2 hours just before preparing the standard solution. Then dissolve exactly 1.847 g of dried $NaNO_3$ in water, and dilute to 1 liter in a volumetric flask. Mix well. This solution is stable for 1 month and should not be used beyond this time.

7.3.3 Working Standard Solution, 25 μg/ml. Dilute 5 ml of the standard solution to 200 ml with water in a volumetric flask, and mix well.

7.3.4 Eluent Solution. Weigh 1.018 g of sodium carbonate (Na_2CO_3) and 1.008 g of sodium bicarbonate ($NaHCO_3$), and dissolve in 4 liters of water. This solution is 0.0024 M Na_2CO_3/0.003 M $NaHCO_3$. Other eluents appropriate to the column type and capable of resolving nitrate ion from sulfate and other species present may be used.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling. Same as in Method 7, section 8.1.

8.2 Sample Recovery. Same as in Method 7, section 8.2, except delete the steps on adjusting and checking the pH of the sample. Do not store the samples more than 4 days between collection and analysis.

9.0 Quality Control

Section	Quality control measure	Effect
10.1	Ion chromatographn calibration	Ensure linearity of ion chromatograph response to standards.

10.0 Calibration and Standardizations

10.1 Ion Chromatograph.

10.1.1 Determination of Ion Chromatograph Calibration Factor S. Prepare a series of five standards by adding 1.0, 2.0, 4.0, 6.0, and 10.0 ml of working standard solution (25 μg/ml) to a series of five 50-ml volumetric flasks. (The standard masses will equal 25, 50, 100, 150, and 250 μg.) Dilute each flask to the mark with water, and mix well. Analyze with the samples as described in section 11.2, and subtract the blank from each value. Prepare or calculate a linear regression plot of the standard masses in μg (x-axis) versus their peak height responses in millimeters (y-axis). (Take peak height measurements with symmetrical peaks; in all other cases, calculate peak areas.) From this curve, or equation, determine the slope, and calculate its reciprocal to denote as the calibration factor, S.

10.1.2 Ion Chromatograph Calibration Quality Control. If any point on the calibration curve deviates from the line by more than 7 percent of the concentration at that point, remake and reanalyze that standard. This deviation can be determined by multiplying S times the peak height response for each standard. The resultant concentrations must not differ by more than 7 percent from each known standard mass (*i.e.*, 25, 50, 100, 150, and 250 μg).

10.2 Conductivity Detector. Calibrate according to manufacturer's specifications prior to initial use.

10.3 Barometer. Calibrate against a mercury barometer.

10.4 Temperature Gauge. Calibrate dial thermometers against mercury-in-glass thermometers. An alternative mercury-free thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

10.5 Vacuum Gauge. Calibrate mechanical gauges, if used, against a mercury manometer such as that specified in section 6.1.6 of Method 7.

10.6 Analytical Balance. Calibrate against standard weights.

11.0 Analytical Procedures

11.1 Sample Preparation.

11.1.1 Note on the analytical data sheet, the level of the liquid in the container, and whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Immediately before analysis, transfer the contents of the shipping container to a 50-ml volumetric flask, and rinse the container twice with 5 ml portions of water. Add the rinse water to the flask, and dilute to the mark with water. Mix thoroughly.

11.1.2 Pipet a 5-ml aliquot of the sample into a 50-ml volumetric flask, and dilute to the mark with water. Mix thoroughly. For each set of determinations, prepare a reagent

blank by diluting 5 ml of absorbing solution to 50 ml with water. (Alternatively, eluent solution may be used instead of water in all sample, standard, and blank dilutions.)

11.2 Analysis.

11.2.1 Prepare a standard calibration curve according to section 10.1.1. Analyze the set of standards followed by the set of samples using the same injection volume for both standards and samples. Repeat this analysis sequence followed by a final analysis of the standard set. Average the results. The two sample values must agree within 5 percent of their mean for the analysis to be valid. Perform this duplicate analysis sequence on the same day. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

11.2.2 Document each sample chromatogram by listing the following analytical parameters: injection point, injection volume, nitrate and sulfate retention times, flow rate, detector sensitivity setting, and recorder chart speed.

12.0 Data Analysis and Calculations

Carry out the calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculations.

12.1 Sample Volume. Calculate the sample volume Vsc (in ml), on a dry basis, corrected to standard conditions, using Equation 7–2 of Method 7.

12.2 Sample Concentration of NO_X as NO_2.

12.2.1 Calculate the sample concentration C (in mg/dscm) as follows:

$$C = (H)(S)(F)\left(10^4\right)/V_{sc} \qquad \text{Eq. 7A-1}$$

Where:

H = Sample peak height, mm.

S = Calibration factor, µg/mm.

F = Dilution factor (required only if sample dilution was needed to reduce the concentration into the range of calibration), dimensionless.

10^4 = 1:10 dilution times conversion factor of: $(mg/10^3\ \mu g)(10^6\ ml/m^3)$.

12.2.2 If desired, the concentration of NO_2 may be calculated as ppm NO_2 at standard conditions as follows:

$$\text{ppm } NO_2 = 0.5228C \qquad \text{Eq. 7A-2}$$

Where:

0.5228 = ml/mg NO_2.

13.0 Method Performance

13.1 Range. The analytical range of the method is from 125 to 1250 mg NO_X/m^3 as NO_2 (65 to 655 ppmv), and higher concentrations may be analyzed by diluting the sample. The lower detection limit is approximately 19 mg/m^3 (10 ppmv), but may vary among instruments.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Mulik, J.D., and E. Sawicki. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor, Ann Arbor Science Publishers, Inc. Vol. 2, 1979.

2. Sawicki, E., J.D. Mulik, and E. Wittgenstein. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor, Ann Arbor Science Publishers, Inc. Vol. 1. 1978.

3. Siemer, D.D. Separation of Chloride and Bromide from Complex Matrices Prior to Ion Chromatographic Determination. Anal. Chem. *52*(12):1874–1877. October 1980.

4. Small, H., T.S. Stevens, and W.C. Bauman. Novel Ion Exchange Chromatographic Method Using Conductimetric Determination. Anal. Chem. *47*(11):1801. 1975.

5. Yu, K.K., and P.R. Westlin. Evaluation of Reference Method 7 Flask Reaction Time. Source Evaluation Society Newsletter. *4*(4). November 1979. 10 pp.

6. Stack Sampling Safety Manual (Draft). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standard, Research Triangle Park, NC. September 1978.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 7B—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ULTRAVIOLET SPECTROPHOTOMETRIC METHOD)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 5, and Method 7.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		

Analyte	CAS No.	Sensitivity
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–0	30–786 ppmv

1.2 Applicability. This method is applicable for the determination of NO_X emissions from nitric acid plants.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution; the NO_X, excluding nitrous oxide (N_2O), are measured by ultraviolet spectrophotometry.

3.0 Definition [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m^3 will cause lung damage in uninitiated. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 7, section 6.1.

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Wash Bottle. Polyethylene or glass.

6.2.2 Volumetric Flasks. 100-ml (one for each sample).

6.3 Analysis. The following items are required for analysis:

6.3.1 Volumetric Pipettes. 5-, 10-, 15-, and 20-ml to make standards and sample dilutions.

6.3.2 Volumetric Flasks. 1000- and 100-ml for preparing standards and dilution of samples.

6.3.3 Spectrophotometer. To measure ultraviolet absorbance at 210 nm.

6.3.4 Analytical Balance. To measure to within 0.1 mg.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents are to conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 7, section 7.1. It is important that the amount of hydrogen peroxide in the absorbing solution not be increased. Higher concentrations of peroxide may interfere with sample analysis.

7.2 Sample Recovery. Same as Method 7, section 7.2.

7.3 Analysis. Same as Method 7, sections 7.3.1, 7.3.3, and 7.3.4, with the addition of the following:

7.3.1 Working Standard KNO_3 Solution. Dilute 10 ml of the standard solution to 1000 ml with water. One milliliter of the working standard is equivalent to 10 μg NO_2.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sample Collection. Same as Method 7, section 8.1.

8.2 Sample Recovery.

8.2.1 Let the flask sit for a minimum of 16 hours, and then shake the contents for 2 minutes.

8.2.2 Connect the flask to a mercury filled U-tube manometer. Open the valve from the flask to the manometer, and record the flask temperature (T_f), the barometric pressure, and the difference between the mercury levels in the manometer. The absolute internal pressure in the flask (P_f) is the barometric pressure less the manometer reading.

8.2.3 Transfer the contents of the flask to a leak-free wash bottle. Rinse the flask three times with 10-ml portions of water, and add

to the bottle. Mark the height of the liquid level so that the container can be checked for leakage after transport. Label the container to identify clearly its contents. Seal the container for shipping.

9.0 Quality Control

Section	Quality control measure	Effect
10.1	Spectrophotometer calibration	Ensures linearity of spectrophotometer response to standards.

10.0 Calibration and Standardizations

Same as Method 7, sections 10.2 through 10.5, with the addition of the following:

10.1 Determination of Spectrophotometer Standard Curve. Add 0 ml, 5 ml, 10 ml, 15 ml, and 20 ml of the KNO_3 working standard solution (1 ml = 10 µg NO_2) to a series of five 100-ml volumetric flasks. To each flask, add 5 ml of absorbing solution. Dilute to the mark with water. The resulting solutions contain 0.0, 50, 100, 150, and 200 µg NO_2, respectively. Measure the absorbance by ultraviolet spectrophotometry at 210 nm, using the blank as a zero reference. Prepare a standard curve plotting absorbance vs. µg NO_2.

NOTE: If other than a 20-ml aliquot of sample is used for analysis, then the amount of absorbing solution in the blank and standards must be adjusted such that the same amount of absorbing solution is in the blank and standards as is in the aliquot of sample used.

10.1.1 Calculate the spectrophotometer calibration factor as follows:

$$K_c = \frac{\sum_{i=1}^{n} M_i A_i}{\sum_{i=1}^{n} A_i^2} \qquad \text{Eq. 7B-1}$$

Where:

Mi = Mass of NO_2 in standard i, µg.
Ai = Absorbance of NO_2 standard i.
n = Total number of calibration standards.

10.1.2 For the set of calibration standards specified here, Equation 7B–1 simplifies to the following:

$$K_c = 50\frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2} \qquad \text{Eq. 7B-2}$$

10.2 Spectrophotometer Calibration Quality Control. Multiply the absorbance value obtained for each standard by the K_c factor (reciprocal of the least squares slope) to determine the distance each calibration point lies from the theoretical calibration line. The difference between the calculated concentration values and the actual concentrations (*i.e.*, 50, 100, 150, and 200 µg NO_2) should be less than 7 percent for all standards.

11.0 Analytical Procedures

11.1 Sample Loss Check. Note the level of the liquid in the container, and confirm whether any sample was lost during shipment. Note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Preparation. Immediately prior to analysis, transfer the contents of the shipping container to a 100-ml volumetric flask, and rinse the container twice with 5-ml portions of water. Add the rinse water to the flask, and dilute to mark with water.

11.3 Sample Analysis. Mix the contents of the flask thoroughly and pipette a 20 ml-aliquot of sample into a 100-ml volumetric flask. Dilute to the mark with water. Using the blank as zero reference, read the absorbance of the sample at 210 nm.

11.4 Audit Sample Analysis. Same as Method 7, section 11.4, except that a set of audit samples must be analyzed with each set of compliance samples or once per analysis day, or once per week when averaging continuous samples.

12.0 Data Analysis and Calculations

Same as Method 7, section 12.0, except replace section 12.3 with the following:

12.1 Total µg NO_2 Per Sample.

$$m = 5\,K_c\,A\,F \qquad \text{Eq. 7B-3}$$

Where:

5 = 100/20, the aliquot factor.

NOTE: If other than a 20-ml aliquot is used for analysis, the factor 5 must be replaced by a corresponding factor.

13.0 Method Performance

13.1 Range. The analytical range of the method as outlined has been determined to be 57 to 1500 milligrams NO_X (as NO_2) per dry standard cubic meter, or 30 to 786 parts per million by volume (ppmv) NO_X.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. National Institute for Occupational Safety and Health. Recommendations for Occupational Exposure to Nitric Acid. In: Occupational Safety and Health Reporter. Washington, D.C. Bureau of National Affairs, Inc. 1976. p. 149.

2. Rennie, P.J., A.M. Sumner, and F.B. Basketter. Determination of Nitrate in Raw, Potable, and Waste Waters by Ultraviolet Spectrophotometry. Analyst. *104*:837. September 1979.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 7C—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ALKALINE PERMANGANATE/COLORIMETRIC METHOD)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 3, Method 6 and Method 7.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS no.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–07	ppmv

1.2 Applicability. This method applies to the measurement of NO_X emissions from fossil-fuel fired steam generators, electric utility plants, nitric acid plants, or other sources as specified in the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

An integrated gas sample is extracted from the stack and passed through impingers containing an alkaline potassium permanganate solution; NO_X (NO + NO_2) emissions are oxidized to NO_2 and NO_3. Then NO_3^- is reduced to NO_2^- with cadmium, and the NO_2^- is analyzed colorimetrically.

3.0 Definitions [Reserved]

4.0 Interferences

Possible interferents are sulfur dioxides (SO_2) and ammonia (NH_3).

4.1 High concentrations of SO_2 could interfere because SO_2 consumes MnO_4 (as does NO_X) and, therefore, could reduce the NO_X collection efficiency. However, when sampling emissions from a coal-fired electric utility plant burning 2.1 percent sulfur coal with no control of SO_2 emissions, collection efficiency was not reduced. In fact, calculations show that sampling 3000 ppm SO_2 will reduce the MnO_4 concentration by only 5 percent if all the SO_2 is consumed in the first impinger.

4.2 Ammonia (NH_3) is slowly oxidized to NO_3^- by the absorbing solution. At 100 ppm NH_3 in the gas stream, an interference of 6 ppm NO_X (11 mg NO_2/m^3) was observed when the sample was analyzed 10 days after collection. Therefore, the method may not be applicable to plants using NH_3 injection to control NO_X emissions unless means are taken to correct the results. An equation has been developed to allow quantification of the interference and is discussed in Reference 5 of section 16.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrochloric Acid (HCl). Highly toxic and corrosive. Causes severe damage to skin. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to vapor concentrations of 0.13 to 0.2 percent can be lethal in minutes. Will react with metals, producing hydrogen.

5.2.2 Oxalic Acid $(COOH)_2$. Poisonous. Irritating to eyes, skin, nose, and throat.

5.2.3 Sodium Hydroxide (NaOH). Causes severe damage to eye tissues and to skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with small amounts of water.

5.2.4 Potassium Permanganate ($KMnO_4$). Caustic, strong oxidizer. Avoid bodily contact with.

6.0 Equipment and Supplies

6.1 Sample Collection and Sample Recovery. A schematic of the Method 7C sampling train is shown in Figure 7C–1, and component parts are discussed below. Alternative apparatus and procedures are allowed provided acceptable accuracy and precision can be demonstrated to the satisfaction of the Administrator.

6.1.1 Probe. Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or heated out-of-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Stainless steel or Teflon tubing may also be used for the probe.

6.1.2 Impingers. Three restricted-orifice glass impingers, having the specifications given in Figure 7C–2, are required for each sampling train. The impingers must be connected in series with leak-free glass connectors. Stopcock grease may be used, if necessary, to prevent leakage. (The impingers can be fabricated by a glass blower if not available commercially.)

6.1.3 Glass Wool, Stopcock Grease, Drying Tube, Valve, Pump, Barometer, and Vacuum Gauge and Rotameter. Same as in Method 6, sections 6.1.1.3, 6.1.1.4, 6.1.1.6, 6.1.1.7, 6.1.1.8, 6.1.2, and 6.1.3, respectively.

6.1.4 Rate Meter. Rotameter, or equivalent, accurate to within 2 percent at the selected flow rate of between 400 and 500 ml/min (0.014 to 0.018 cfm). For rotameters, a range of 0 to 1 liter/min (0 to 0.035 cfm) is recommended.

6.1.5 Volume Meter. Dry gas meter (DGM) capable of measuring the sample volume under the sampling conditions of 400 to 500 ml/min (0.014 to 0.018 cfm) for 60 minutes within an accuracy of 2 percent.

6.1.6 Filter. To remove NO_X from ambient air, prepared by adding 20 g of 5-angstrom molecular sieve to a cylindrical tube (*e.g.*, a polyethylene drying tube).

6.1.7 Polyethylene Bottles. 1-liter, for sample recovery.

6.1.8 Funnel and Stirring Rods. For sample recovery.

6.2 Sample Preparation and Analysis.

6.2.1 Hot Plate. Stirring type with 50- by 10-mm Teflon-coated stirring bars.

6.2.2 Beakers. 400-, 600-, and 1000-ml capacities.

6.2.3 Filtering Flask. 500-ml capacity with side arm.

6.2.4 Buchner Funnel. 75-mm ID, with spout equipped with a 13-mm ID by 90-mm long piece of Teflon tubing to minimize possibility of aspirating sample solution during filtration.

6.2.5 Filter Paper. Whatman GF/C, 7.0-cm diameter.

6.2.6 Stirring Rods.

6.2.7 Volumetric Flasks. 100-, 200- or 250-, 500-, and 1000-ml capacity.

6.2.8 Watch Glasses. To cover 600- and 1000-ml beakers.

6.2.9 Graduated Cylinders. 50- and 250-ml capacities.

6.2.10 Pipettes. Class A.

6.2.11 pH Meter. To measure pH from 0.5 to 12.0.

6.2.12 Burette. 50-ml with a micrometer type stopcock. (The stopcock is Catalog No. 8225–t–05, Ace Glass, Inc., Post Office Box 996, Louisville, Kentucky 50201.) Place a glass wool plug in bottom of burette. Cut off burette at a height of 43 cm (17 in.) from the top of plug, and have a blower attach a glass funnel to top of burette such that the diameter of the burette remains essentially unchanged. Other means of attaching the funnel are acceptable.

6.2.13 Glass Funnel. 75-mm ID at the top.

6.2.14 Spectrophotometer. Capable of measuring absorbance at 540 nm; 1-cm cells are adequate.

6.2.15 Metal Thermometers. Bimetallic thermometers, range 0 to 150 °C (32 to 300 °F).

6.2.16 Culture Tubes. 20-by 150-mm, Kimax No. 45048.

6.2.17 Parafilm ''M.'' Obtained from American Can Company, Greenwich, Connecticut 06830.

6.2.18 CO_2 Measurement Equipment. Same as in Method 3, section 6.0.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection.

7.1.1 Water. Deionized distilled to conform to ASTM Specification D 1193–77 or 91 Type 3 (incorporated by reference—see § 60.17).

7.1.2 Potassium Permanganate, 4.0 Percent (w/w), Sodium Hydroxide, 2.0 Percent (w/w) solution ($KMnO_4$/NaOH solution). Dissolve 40.0 g of $KMnO_4$ and 20.0 g of NaOH in 940 ml of water.

7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in section 7.1.1.

7.2.2 Oxalic Acid Solution. Dissolve 48 g of oxalic acid [$(COOH)_2 \cdot 2H_2O$] in water, and dilute to 500 ml. Do not heat the solution.

7.2.3 Sodium Hydroxide, 0.5 N. Dissolve 20 g of NaOH in water, and dilute to 1 liter.

7.2.4 Sodium Hydroxide, 10 N. Dissolve 40 g of NaOH in water, and dilute to 100 ml.

7.2.5 Ethylenediamine Tetraacetic Acid (EDTA) Solution, 6.5 percent (w/v). Dissolve 6.5 g of EDTA (disodium salt) in water, and dilute to 100 ml. Dissolution is best accomplished by using a magnetic stirrer.

7.2.6 Column Rinse Solution. Add 20 ml of 6.5 percent EDTA solution to 960 ml of water, and adjust the pH to between 11.7 and 12.0 with 0.5 N NaOH.

7.2.7 Hydrochloric Acid (HCl), 2 N. Add 86 ml of concentrated HCl to a 500 ml-volumetric flask containing water, dilute to volume, and mix well. Store in a glass-stoppered bottle.

7.2.8 Sulfanilamide Solution. Add 20 g of sulfanilamide (melting point 165 to 167 °C (329 to 333 °F)) to 700 ml of water. Add, with mixing, 50 ml concentrated phosphoric acid (85 percent), and dilute to 1000 ml. This solution is stable for at least 1 month, if refrigerated.

7.2.9 N-(1-Naphthyl)-Ethylenediamine Dihydrochloride (NEDA) Solution. Dissolve 0.5 g of NEDA in 500 ml of water. An aqueous solution should have one absorption peak at 320 nm over the range of 260 to 400 nm. NEDA that shows more than one absorption peak over this range is impure and should not be used. This solution is stable for at least 1 month if protected from light and refrigerated.

7.2.10 Cadmium. Obtained from Matheson Coleman and Bell, 2909 Highland Avenue, Norwood, Ohio 45212, as EM Laboratories Catalog No. 2001. Prepare by rinsing in 2 N HCl for 5 minutes until the color is silver-grey. Then rinse the cadmium with water until the rinsings are neutral when tested with pH paper. CAUTION: H_2 is liberated during preparation. Prepare in an exhaust hood away from any flame or combustion source.

7.2.11 Sodium Sulfite ($NaNO_2$) Standard Solution, Nominal Concentration, 1000 μg NO_2^-/ml. Desiccate NaNO2 overnight. Accurately weigh 1.4 to 1.6 g of $NaNO_2$ (assay of 97 percent $NaNO_2$ or greater), dissolve in water, and dilute to 1 liter. Calculate the exact NO_2^- concentration using Equation 7C–1 in section 12.2. This solution is stable for at least 6 months under laboratory conditions.

7.2.12 Potassium Nitrate (KNO_3) Standard Solution. Dry KNO_3 at 110 °C (230 °F) for 2 hours, and cool in a desiccator. Accurately weigh 9 to 10 g of KNO_3 to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact NO_3^- concentration using Equation 7C–2 in section 12.3. This solution is stable for 2 months without preservative under laboratory conditions.

7.2.13 Spiking Solution. Pipette 7 ml of the KNO_3 standard into a 100-ml volumetric flask, and dilute to volume.

7.2.14 Blank Solution. Dissolve 2.4 g of $KMnO_4$ and 1.2 g of NaOH in 96 ml of water. Alternatively, dilute 60 ml of $KMnO_4$/NaOH solution to 100 ml.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Preparation of Sampling Train. Add 200 ml of $KMnO_4$/NaOH solution (Section 7.1.2) to each of three impingers, and assemble the train as shown in Figure 7C–1. Adjust the probe heater to a temperature sufficient to prevent water condensation.

8.2 Leak-Checks. Same as in Method 6, section 8.2.

8.3 Sample Collection.

8.3.1 Record the initial DGM reading and barometric pressure. Determine the sampling point or points according to the appropriate regulations (*e.g.*, §60.46(b)(5) of 40 CFR Part 60). Position the tip of the probe at the sampling point, connect the probe to the first impinger, and start the pump. Adjust the sample flow to a value between 400 and 500 ml/min (0.014 and 0.018 cfm). CAUTION: DO NOT EXCEED THESE FLOW RATES. Once adjusted, maintain a constant flow rate during the entire sampling run. Sample for 60 minutes. For relative accuracy (RA) testing of continuous emission monitors, the minimum sampling time is 1 hour, sampling 20 minutes at each traverse point.

NOTE: When the SO_2 concentration is greater than 1200 ppm, the sampling time may have to be reduced to 30 minutes to eliminate plugging of the impinger orifice with MnO_2. For RA tests with SO_2 greater than 1200 ppm, sample for 30 minutes (10 minutes at each point).

8.3.2 Record the DGM temperature, and check the flow rate at least every 5 minutes. At the conclusion of each run, turn off the pump, remove the probe from the stack, and record the final readings. Divide the sample volume by the sampling time to determine the average flow rate. Conduct the mandatory post-test leak-check. If a leak is found, void the test run, or use procedures acceptable to the Administrator to adjust the sample volume for the leakage.

8.4 CO_2 Measurement. During sampling, measure the CO_2 content of the stack gas near the sampling point using Method 3. The single-point grab sampling procedure is adequate, provided the measurements are made at least three times (near the start, midway, and before the end of a run), and the average CO_2 concentration is computed. The Orsat or Fyrite analyzer may be used for this analysis.

8.5 Sample Recovery. Disconnect the impingers. Pour the contents of the impingers into a 1-liter polyethylene bottle

using a funnel and a stirring rod (or other means) to prevent spillage. Complete the quantitative transfer by rinsing the impingers and connecting tubes with water until the rinsings are clear to light pink, and add the rinsings to the bottle. Mix the sample, and mark the solution level. Seal and identify the sample container.

9.0 Quality Control

Section	Quality control measure	Effect
8.2, 10.1–10.3	Sampling equipment leak-check and calibration.	Ensure accurate measurement of sample volume.
10.4	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards
11.3	Spiked sample analysis.	Ensure reduction efficiency of column.

10.0 Calibration and Standardizations

10.1 Volume Metering System. Same as Method 6, section 10.1. For detailed instructions on carrying out these calibrations, it is suggested that section 3.5.2 of Reference 4 of section 16.0 be consulted.

10.2 Temperature Sensors and Barometer. Same as in Method 6, sections 10.2 and 10.4, respectively.

10.3 Check of Rate Meter Calibration Accuracy (Optional). Disconnect the probe from the first impinger, and connect the filter. Start the pump, and adjust the rate meter to read between 400 and 500 ml/min (0.014 and 0.018 cfm). After the flow rate has stabilized, start measuring the volume sampled, as recorded by the dry gas meter and the sampling time. Collect enough volume to measure accurately the flow rate. Then calculate the flow rate. This average flow rate must be less than 500 ml/min (0.018 cfm) for the sample to be valid; therefore, it is recommended that the flow rate be checked as above prior to each test.

10.4 Spectrophotometer.

10.4.1 Dilute 5.0 ml of the $NaNO_2$ standard solution to 200 ml with water. This solution nominally contains 25 μg NO_2^-/ml. Use this solution to prepare calibration standards to cover the range of 0.25 to 3.00 μg NO_2^-/ml. Prepare a minimum of three standards each for the linear and slightly nonlinear (described below) range of the curve. Use pipettes for all additions.

10.4.2 Measure the absorbance of the standards and a water blank as instructed in section 11.5. Plot the net absorbance vs. μg NO_2^-/ml. Draw a smooth curve through the points. The curve should be linear up to an absorbance of approximately 1.2 with a slope of approximately 0.53 absorbance units/μg NO_2^-/ml. The curve should pass through the origin. The curve is slightly nonlinear from an absorbance of 1.2 to 1.6.

11.0 Analytical Procedures

11.1 Sample Stability. Collected samples are stable for at least four weeks; thus, analysis must occur within 4 weeks of collection.

11.2 Sample Preparation.

11.2.1 Prepare a cadmium reduction column as follows: Fill the burette with water. Add freshly prepared cadmium slowly, with tapping, until no further settling occurs. The height of the cadmium column should be 39 cm (15 in). When not in use, store the column under rinse solution.

NOTE: The column should not contain any bands of cadmium fines. This may occur if regenerated cadmium is used and will greatly reduce the column lifetime.

11.2.2 Note the level of liquid in the sample container, and determine whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume lost can be determined from the difference between initial and final solution levels, and this value can then be used to correct the analytical result. Quantitatively transfer the contents to a 1-liter volumetric flask, and dilute to volume.

11.2.3 Take a 100-ml aliquot of the sample and blank (unexposed $KMnO_4$/NaOH) solutions, and transfer to 400-ml beakers containing magnetic stirring bars. Using a pH meter, add concentrated H_2SO_4 with stirring until a pH of 0.7 is obtained. Allow the solutions to stand for 15 minutes. Cover the beakers with watch glasses, and bring the temperature of the solutions to 50 °C (122 °F). Keep the temperature below 60 °C (140 °F). Dissolve 4.8 g of oxalic acid in a minimum volume of water, approximately 50 ml, at room temperature. Do not heat the solution. Add this solution slowly, in increments, until the $KMnO_4$ solution becomes colorless. If the color is not completely removed, prepare some more of the above oxalic acid solution, and add until a colorless solution is obtained. Add an excess of oxalic acid by dissolving 1.6 g of oxalic acid in 50 ml of water, and add 6 ml of this solution to the colorless solution. If suspended matter is present, add concentrated H_2SO_4 until a clear solution is obtained.

11.2.4 Allow the samples to cool to near room temperature, being sure that the samples are still clear. Adjust the pH to between 11.7 and 12.0 with 10 N NaOH. Quantitatively transfer the mixture to a Buchner funnel containing GF/C filter paper, and filter the

precipitate. Filter the mixture into a 500-ml filtering flask. Wash the solid material four times with water. When filtration is complete, wash the Teflon tubing, quantitatively transfer the filtrate to a 500-ml volumetric flask, and dilute to volume. The samples are now ready for cadmium reduction. Pipette a 50-ml aliquot of the sample into a 150-ml beaker, and add a magnetic stirring bar. Pipette in 1.0 ml of 6.5 percent EDTA solution, and mix.

11.3 Determine the correct stopcock setting to establish a flow rate of 7 to 9 ml/min of column rinse solution through the cadmium reduction column. Use a 50-ml graduated cylinder to collect and measure the solution volume. After the last of the rinse solution has passed from the funnel into the burette, but before air entrapment can occur, start adding the sample, and collect it in a 250-ml graduated cylinder. Complete the quantitative transfer of the sample to the column as the sample passes through the column. After the last of the sample has passed from the funnel into the burette, start adding 60 ml of column rinse solution, and collect the rinse solution until the solution just disappears from the funnel. Quantitatively transfer the sample to a 200-ml volumetric flask (a 250-ml flask may be required), and dilute to volume. The samples are now ready for NO_2-analysis.

NOTE: Two spiked samples should be run with every group of samples passed through the column. To do this, prepare two additional 50-ml aliquots of the sample suspected to have the highest NO_2-concentration, and add 1 ml of the spiking solution to these aliquots. If the spike recovery or column efficiency (see section 12.2) is below 95 percent, prepare a new column, and repeat the cadmium reduction.

11.5 Sample Analysis. Pipette 10 ml of sample into a culture tube. Pipette in 10 ml of sulfanilamide solution and 1.4 ml of NEDA solution. Cover the culture tube with parafilm, and mix the solution. Prepare a blank in the same manner using the sample from treatment of the unexposed $KMnO_4$/NaOH solution. Also, prepare a calibration standard to check the slope of the calibration curve. After a 10-minute color development interval, measure the absorbance at 540 nm against water. Read μg NO_2^-/ml from the calibration curve. If the absorbance is greater than that of the highest calibration standard, use less than 10 ml of sample, and repeat the analysis. Determine the NO_2^-concentration using the calibration curve obtained in section 10.4.

NOTE: Some test tubes give a high blank NO_2^- value but culture tubes do not.

11.6 Audit Sample Analysis. Same as in Method 7, section 11.4.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature.

B = Analysis of blank, μg NO_2^-/ml.
C = Concentration of NO_X as NO_2, dry basis, mg/dsm³.
E = Column efficiency, dimensionless
$K_2 = 10^{-3}$ mg/μg.
m = Mass of NO_X, as NO_2, in sample, μg.
P_{bar} = Barometric pressure, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
s = Concentration of spiking solution, μg NO_3/ml.
S = Analysis of sample, μg NO_2^-/ml.
T_m = Average dry gas meter absolute temperature, °K.
T_{std} = Standard absolute temperature, 293 °K (528 °R).
$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).
V_m = Dry gas volume as measured by the dry gas meter, scm (scf).
x = Analysis of spiked sample, μg NO_2^-/ml.
X = Correction factor for CO_2 collection = $100/(100 - \%CO_2(V/V))$.
y = Analysis of unspiked sample, μg NO_2^-/ml.
Y = Dry gas meter calibration factor.
1.0 ppm NO = 1.247 mg NO/m³ at STP.
1.0 ppm NO_2 = 1.912 mg NO_2/m³ at STP.
1 ft³ = 2.832×10^{-2} m³.

12.2 NO_2 Concentration. Calculate the NO_2 concentration of the solution (see section 7.2.11) using the following equation:

$$\frac{\mu g\ NO_2^-}{ml} = g\ NaNO_2 \times \frac{purity,\ \%}{100} \times 10^3 \times \frac{46.01}{69.01} \qquad \text{Eq. 7C-1}$$

12.3 NO_3 Concentration. Calculate the NO_3 concentration of the KNO_3 solution (see section 7.2.12) using the following equation:

$$\frac{\mu g\ NO_3^-}{ml} = g\ KNO_3 \times \left(10^3\right) \times \frac{62.01}{101.10} \qquad \text{Eq. 7C-2}$$

12.4 Sample Volume, Dry Basis, Corrected to Standard Conditions.

$$V_{m(std)} = V_m\ X\ Y \frac{T_{std}}{T_m} \frac{P_{bar}}{P_{std}} \qquad \text{Eq. 7C-3}$$

$$= K_1\ X\ Y\ V_m \frac{P_{bar}}{T_m}$$

Where:

K_1 = 0.3855 °K/mm Hg for metric units.
K_1 = 17.65 °R/in. Hg for English units.

12.5 Efficiency of Cadmium Reduction Column. Calculate this value as follows:

$$E = \frac{200\ (x-y)}{1.0\ s\ \frac{46.01}{62.01}} = \frac{269.6\ (x-y)}{s} \qquad \text{Eq. 7C-4}$$

Where:

200 = Final volume of sample and blank after passing through the column, ml.
1.0 = Volume of spiking solution added, ml.
46.01=μg NO_2^-/μmole.
62.01=μg NO_3^-/μmole.

12.6 Total μg NO_2.

$$m = 200\left(\frac{500}{50}\right)\left(\frac{1000}{100}\right)\left(\frac{(S-B)}{E}\right) = \frac{(2\times10^4)(S-B)}{E} \qquad \text{Eq. 7C-5}$$

Where:

500 = Total volume of prepared sample, ml.
50 = Aliquot of prepared sample processed through cadmium column, ml.
100 = Aliquot of $KMnO_4$/NaOH solution, ml.
1000 = Total volume of $KMnO_4$/NaOH solution, ml.

12.7 Sample Concentration.

$$C = K_2 \frac{m}{V_{m(std)}} \qquad \text{Eq. 7C-6}$$

13.0 Method Performance

13.1 Precision. The intra-laboratory relative standard deviation for a single measurement is 2.8 and 2.9 percent at 201 and 268 ppm NO_X, respectively.

13.2 Bias. The method does not exhibit any bias relative to Method 7.

13.3 Range. The lower detectable limit is 13 mg NO_X/m^3, as NO_2 (7 ppm NO_X) when sampling at 500 ml/min for 1 hour. No upper limit has been established; however, when using the recommended sampling conditions, the method has been found to collect NO_X emissions quantitatively up to 1782 mg NO_X/m^3, as NO_2 (932 ppm NO_X).

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Margeson, J.H., W.J. Mitchell, J.C. Suggs, and M.R. Midgett. Integrated Sampling and Analysis Methods for Determining NO_X Emissions at Electric Utility Plants. U.S. Environmental Protection Agency, Research Triangle Park, NC. Journal of the Air Pollution Control Association. *32*:1210–1215. 1982.

2. Memorandum and attachment from J.H. Margeson, Source Branch, Quality Assurance Division, Environmental Monitoring Systems Laboratory, to The Record, EPA. March 30, 1983. NH_3 Interference in Methods 7C and 7D.

3. Margeson, J.H., J.C. Suggs, and M.R. Midgett. Reduction of Nitrate to Nitrite with Cadmium. Anal. Chem. *52*:1955–57. 1980.

4. Quality Assurance Handbook for Air Pollution Measurement Systems. Volume III—Stationary Source Specific Methods. U.S.

Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA–600/4–77–027b. August 1977.

5. Margeson, J.H., *et al.* An Integrated Method for Determining NO_X Emissions at Nitric Acid Plants. Analytical Chemistry. *47* (11):1801. 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

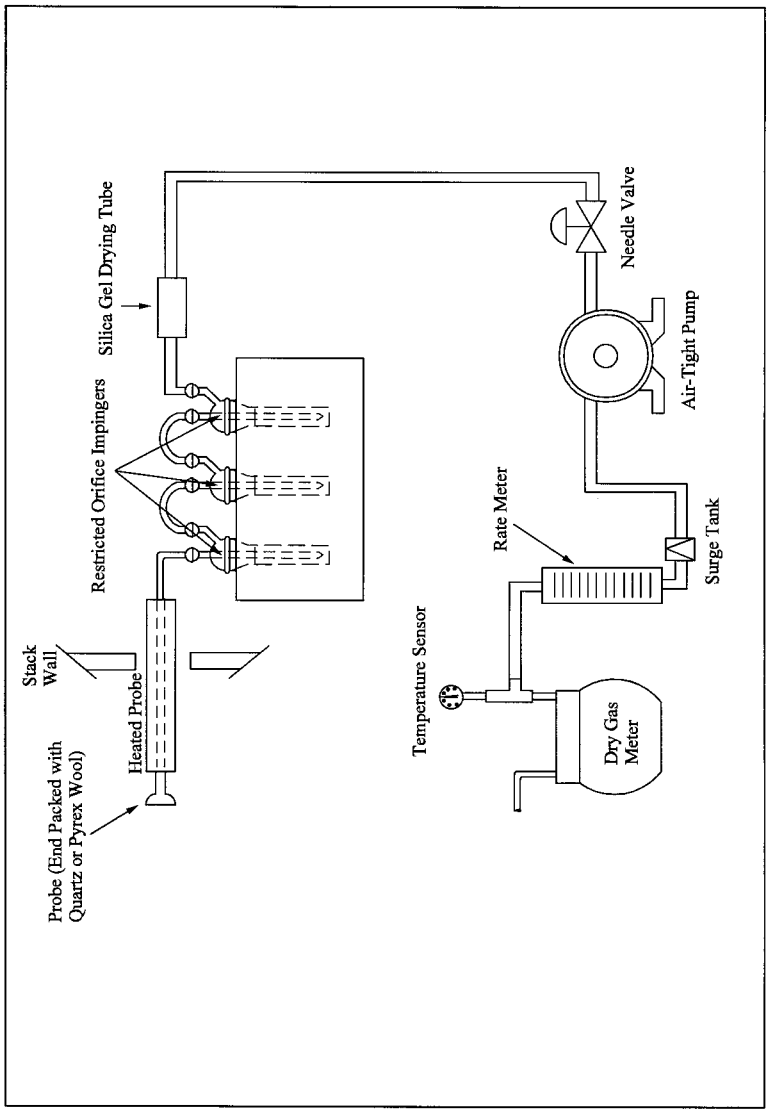

Figure 7C-1. NO_x Sampling Train.

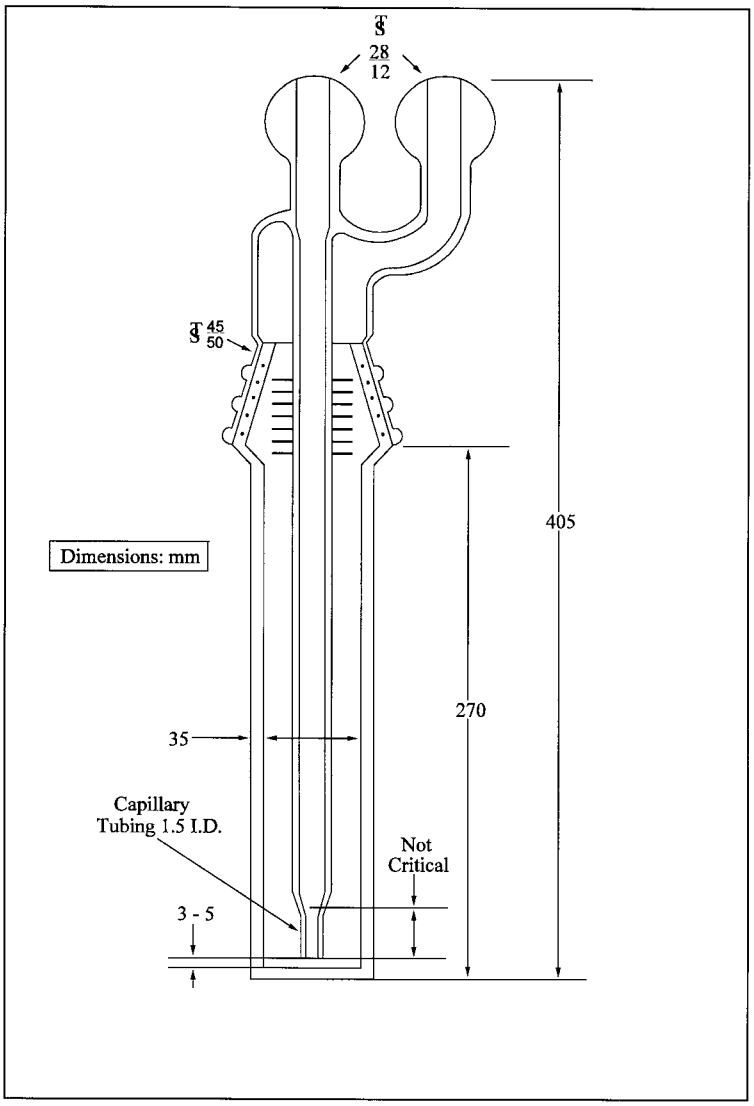

Figure 7C-2. Restricted-Orifice Impinger.

METHOD 7D—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ALKALINE-PERMANGANATE/ION CHROMATOGRAPHIC METHOD)

NOTE: This method is not inclusive with respect to specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 3, Method 6, Method 7, and Method 7C.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), as NO_2, including:		
Nitric oxide (NO)	10102–43–9	
Nitrogen dioxide (NO_2)	10102–44–0	7 ppmv

1.2 Applicability. This method applies to the measurement of NO_X emissions from fossil-fuel fired steam generators, electric utility plants, nitric acid plants, or other sources as specified in the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

An integrated gas sample is extracted from the stack and passed through impingers containing an alkaline-potassium permanganate solution; NO_X ($NO + NO_2$) emissions are oxidized to NO_3^-. Then NO_3^- is analyzed by ion chromatography.

3.0 Definitions [Reserved]

4.0 Interferences

Same as in Method 7C, section 4.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs. 30% H_2O_2 is a strong oxidizing agent; avoid contact with skin, eyes, and combustible material. Wear gloves when handling.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eye tissues and to skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Potassium Permanganate ($KMnO_4$). Caustic, strong oxidizer. Avoid bodily contact with.

6.0 Equipment and Supplies

6.1 Sample Collection and Sample Recovery. Same as Method 7C, section 6.1. A schematic of the sampling train used in performing this method is shown in Figure 7C–1 of Method 7C.

6.2 Sample Preparation and Analysis.

6.2.1 Magnetic Stirrer. With 25- by 10-mm Teflon-coated stirring bars.

6.2.2 Filtering Flask. 500-ml capacity with sidearm.

6.2.3 Buchner Funnel. 75-mm ID, with spout equipped with a 13-mm ID by 90-mm long piece of Teflon tubing to minimize possibility of aspirating sample solution during filtration.

6.2.4 Filter Paper. Whatman GF/C, 7.0-cm diameter.

6.2.5 Stirring Rods.

6.2.6 Volumetric Flask. 250-ml.

6.2.7 Pipettes. Class A.

6.2.8 Erlenmeyer Flasks. 250-ml.

6.2.9 Ion Chromatograph. Equipped with an anion separator column to separate NO_3^-, H_3^+ suppressor, and necessary auxiliary equipment. Nonsuppressed and other forms of ion chromatography may also be used provided that adequate resolution of NO_3^- is obtained. The system must also be able to resolve and detect NO_2^-.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection.

7.1.1 Water. Deionized distilled to conform to ASTM specification D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17).

7.1.2 Potassium Permanganate, 4.0 Percent (w/w), Sodium Hydroxide, 2.0 Percent (w/w). Dissolve 40.0 g of $KMnO_4$ and 20.0 g of NaOH in 940 ml of water.

7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in section 7.1.1.

7.2.2 Hydrogen Peroxide (H_2O_2), 5 Percent. Dilute 30 percent H_2O_2 1:5 (v/v) with water.

7.2.3 Blank Solution. Dissolve 2.4 g of $KMnO_4$ and 1.2 g of NaOH in 96 ml of water. Alternatively, dilute 60 ml of $KMnO_4$/NaOH solution to 100 ml.

7.2.4 KNO_3 Standard Solution. Dry KNO_3 at 110 °C for 2 hours, and cool in a desiccator. Accurately weigh 9 to 10 g of KNO_3 to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact NO_3^- concentration using Equation 7D–1 in section 12.2. This

solution is stable for 2 months without preservative under laboratory conditions.

7.2.5 Eluent, 0.003 M $NaHCO_3$/0.0024 M Na_2CO_3. Dissolve 1.008 g $NaHCO_3$ and 1.018 g Na_2CO_3 in water, and dilute to 4 liters. Other eluents capable of resolving nitrate ion from sulfate and other species present may be used.

8.0 Sample Collection, Preservation, Transport, and Storage.

8.1 Sampling. Same as in Method 7C, section 8.1.

8.2 Sample Recovery. Same as in Method 7C, section 8.2.

8.3 Sample Preparation for Analysis.

NOTE: Samples must be analyzed within 28 days of collection.

8.3.1 Note the level of liquid in the sample container, and determine whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume lost can be determined from the difference between initial and final solution levels, and this value can then be used to correct the analytical result. Quantitatively transfer the contents to a 1-liter volumetric flask, and dilute to volume.

8.3.2 Sample preparation can be started 36 hours after collection. This time is necessary to ensure that all NO_2^- is converted to NO_3^- in the collection solution. Take a 50-ml aliquot of the sample and blank, and transfer to 250-ml Erlenmeyer flasks. Add a magnetic stirring bar. Adjust the stirring rate to as fast a rate as possible without loss of solution. Add 5 percent H_2O_2 in increments of approximately 5 ml using a 5-ml pipette. When the $KMnO_4$ color appears to have been removed, allow the precipitate to settle, and examine the supernatant liquid. If the liquid is clear, the H_2O_2 addition is complete. If the $KMnO_4$ color persists, add more H_2O_2, with stirring, until the supernatant liquid is clear.

NOTE: The faster the stirring rate, the less volume of H_2O_2 that will be required to remove the $KMnO_4$.) Quantitatively transfer the mixture to a Buchner funnel containing GF/C filter paper, and filter the precipitate. The spout of the Buchner funnel should be equipped with a 13-mm ID by 90-mm long piece of Teflon tubing. This modification minimizes the possibility of aspirating sample solution during filtration. Filter the mixture into a 500-ml filtering flask. Wash the solid material four times with water. When filtration is complete, wash the Teflon tubing, quantitatively transfer the filtrate to a 250-ml volumetric flask, and dilute to volume. The sample and blank are now ready for NO_3^- analysis.

9.0 Quality Control

Section	Quality control measure	Effect
8.2, 10.1–10.3	Sampling equipment leak-check and calibration.	Ensure accurate measurement of sample volume.
10.4	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.
11.3	Spiked sample analysis	Ensure reduction efficiency of column.

10.0 Calibration and Standardizations

10.1 Dry Gas Meter (DGM) System.

10.1.1 Initial Calibration. Same as in Method 6, section 10.1.1. For detailed instructions on carrying out this calibration, it is suggested that section 3.5.2 of Citation 4 in section 16.0 of Method 7C be consulted.

10.1.2 Post-Test Calibration Check. Same as in Method 6, section 10.1.2.

10.2 Thermometers for DGM and Barometer. Same as in Method 6, sections 10.2 and 10.4, respectively.

10.3 Ion Chromatograph.

10.3.1 Dilute a given volume (1.0 ml or greater) of the KNO_3 standard solution to a convenient volume with water, and use this solution to prepare calibration standards. Prepare at least four standards to cover the range of the samples being analyzed. Use pipettes for all additions. Run standards as instructed in section 11.2. Determine peak height or area, and plot the individual values versus concentration in µg NO_3^-/ml.

10.3.2 Do not force the curve through zero. Draw a smooth curve through the points. The curve should be linear. With the linear curve, use linear regression to determine the calibration equation.

11.0 Analytical Procedures

11.1 The following chromatographic conditions are recommended: 0.003 M $NaHCO_3$/0.0024 Na_2CO_3 eluent solution (Section 7.2.5), full scale range, 3 µMHO; sample loop, 0.5 ml; flow rate, 2.5 ml/min. These conditions should give a NO_3^- retention time of approximately 15 minutes (Figure 7D–1).

11.2 Establish a stable baseline. Inject a sample of water, and determine whether any NO_3^- appears in the chromatogram. If NO_3^- is present, repeat the water load/injection procedure approximately five times; then reinject a water sample and observe the chromatogram. When no NO_3^- is present, the instrument is ready for use. Inject calibration standards. Then inject samples and a blank. Repeat the injection of the calibration

standards (to compensate for any drift in response of the instrument). Measure the NO_3^- peak height or peak area, and determine the sample concentration from the calibration curve.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature. Same as in Method 7C, section 12.1.

12.2 NO_3^- concentration. Calculate the NO_3^- concentration in the KNO_3 standard solution (see section 7.2.4) using the following equation:

$$\frac{\mu g\ NO_3^-}{ml} = g\ of\ KNO_3 \times 10^3 \times \frac{62.01}{101.10} \qquad \text{Eq. 7D-1}$$

12.3 Sample Volume, Dry Basis, Corrected to Standard Conditions. Same as in Method 7C, section 12.4.

12.4 Total μg NO_2 Per Sample.

$$m = 250\left(\frac{1000}{50}\right)\left(\frac{46.01}{62.01}\right)(S-B) \qquad \text{Eq. 7D-2}$$
$$= 3710\ (S-B)$$

Where:

250 = Volume of prepared sample, ml.

1000 = Total volume of $KMnO_4$ solution, ml.

50 = Aliquot of $KMnO_4$/NaOH solution, ml.

46.01 = Molecular weight of NO_3^-.

62.01 = Molecular weight of NO_3^-.

12.5 Sample Concentration. Same as in Method 7C, section 12.7.

13.0 Method Performance

13.1 Precision. The intra-laboratory relative standard deviation for a single measurement is approximately 6 percent at 200 to 270 ppm NO_X.

13.2 Bias. The method does not exhibit any bias relative to Method 7.

13.3 Range. The lower detectable limit is similar to that of Method 7C. No upper limit has been established; however, when using the recommended sampling conditions, the method has been found to collect NO_X emissions quantitatively up to 1782 mg NO_X/m^3, as NO_2 (932 ppm NO_X).

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 7C, section 16.0, References 1, 2, 4, and 5.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

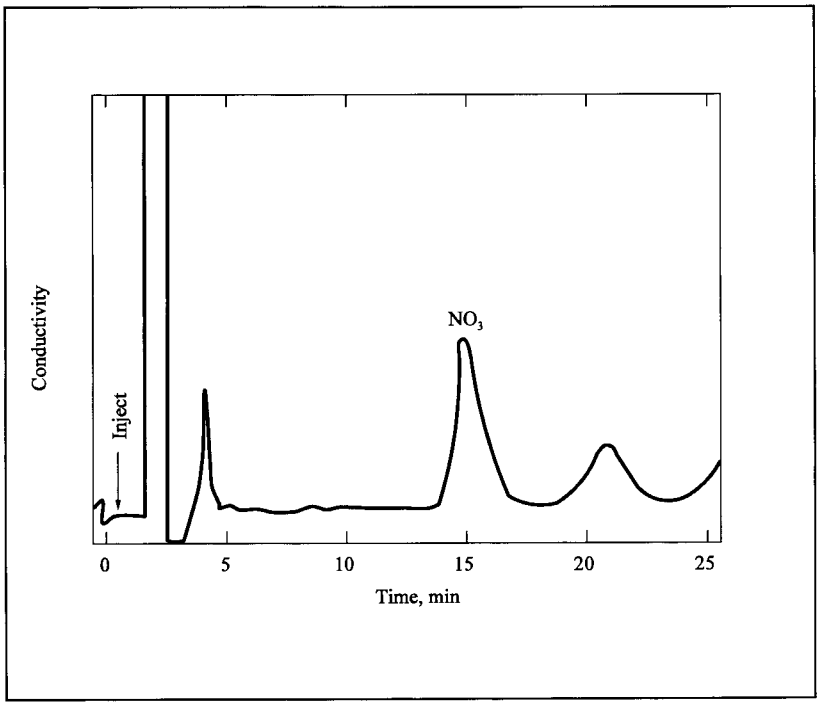

Figure 7D-1. Ion Chromatograph of a Prepared Sample.

METHOD 7E—DETERMINATION OF NITROGEN OXIDES EMISSIONS FROM STATIONARY SOURCES (INSTRUMENTAL ANALYZER PROCEDURE)

1.0 Scope and Application

What is Method 7E?

Method 7E is a procedure for measuring nitrogen oxides (NO_X) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis. This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 4—Determination of Moisture Content in Stack Gases.

1.1 Analytes. What does this method determine? This method measures the concentration of nitrogen oxides as NO_2.

Analyte	CAS No.	Sensitivity
Nitric oxide (NO)	10102–43–9	Typically <2% of
Nitrogen dioxide (NO_2)	10102–44–0	Calibration Span.

1.2 Applicability. When is this method required? The use of Method 7E may be required by specific New Source Performance Standards, Clean Air Marketing rules, State Implementation Plans, and permits where measurement of NO_X concentrations in stationary source emissions is required, either to determine compliance with an applicable

emissions standard or to conduct performance testing of a continuous monitoring system (CEMS). Other regulations may also require the use of Method 7E.

1.3 Data Quality Objectives (DQO). How good must my collected data be? Method 7E is designed to provide high-quality data for determining compliance with Federal and State emission standards and for relative accuracy testing of CEMS. In these and other applications, the principal objective is to ensure the accuracy of the data at the actual emission levels encountered. To meet this objective, the use of EPA traceability protocol calibration gases and measurement system performance tests are required.

1.4 Data Quality Assessment for Low Emitters. Is performance relief granted when testing low-emission units? Yes. For low-emitting sources, there are alternative performance specifications for analyzer calibration error, system bias, drift, and response time. Also, the alternative dynamic spiking procedure in section 16 may provide performance relief for certain low-emitting units.

2.0 Summary of Method

In this method, a sample of the effluent gas is continuously sampled and conveyed to the analyzer for measuring the concentration of NO_X. You may measure NO and NO_2 separately or simultaneously together but, for the purposes of this method, NO_X is the sum of NO and NO_2. You must meet the performance requirements of this method to validate your data.

3.0 Definitions

3.1 Analyzer Calibration Error, for non-dilution systems, means the difference between the manufacturer certified concentration of a calibration gas and the measured concentration of the same gas when it is introduced into the analyzer in direct calibration mode.

3.2 Calibration Curve means the relationship between an analyzer's response to the injection of a series of calibration gases and the actual concentrations of those gases.

3.3 Calibration Gas means the gas mixture containing NO_X at a known concentration and produced and certified in accordance with ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards,'' September 1997, as amended August 25, 1999, EPA–600/R–97/121 or more recent updates. The tests for analyzer calibration error, drift, and system bias require the use of calibration gas prepared according to this protocol. If a zero gas is used for the low-level gas, it must meet the requirements under the definition for ''zero air material'' in 40 CFR 72.2 in place of being prepared by the traceability protocol.

3.3.1 Low-Level Gas means a calibration gas with a concentration that is less than 20 percent of the calibration span and may be a zero gas.

3.3.2 Mid-Level Gas means a calibration gas with a concentration that is 40 to 60 percent of the calibration span.

3.3.3 High-Level Gas means a calibration gas with a concentration that is equal to the calibration span.

3.4 Calibration Span means the upper limit of the analyzer's calibration that is set by the choice of high-level calibration gas. No valid run average concentration may exceed the calibration span. To the extent practicable, the measured emissions should be between 20 to 100 percent of the selected calibration span. This may not be practicable in some cases of low-concentration measurements or testing for compliance with an emission limit when emissions are substantially less than the limit. In such cases, calibration spans that are practicable to achieving the data quality objectives without being excessively high should be chosen.

3.5 Centroidal Area means the central area of the stack or duct that is no greater than 1 percent of the stack or duct cross section. This area has the same geometric shape as the stack or duct.

3.6 Converter Efficiency Gas means a calibration gas with a known NO or NO_2 concentration and of Traceability Protocol quality.

3.7 Data Recorder means the equipment that permanently records the concentrations reported by the analyzer.

3.8 Direct Calibration Mode means introducing the calibration gases directly into the analyzer (or into the assembled measurement system at a point downstream of all sample conditioning equipment) according to manufacturer's recommended calibration procedure. This mode of calibration applies to non-dilution-type measurement systems.

3.9 Drift means the difference between the pre- and post-run system bias (or system calibration error) checks at a specific calibration gas concentration level (*i.e.* low-, mid- or high-).

3.10 Gas Analyzer means the equipment that senses the gas being measured and generates an output proportional to its concentration.

3.11 Interference Check means the test to detect analyzer responses to compounds other than the compound of interest, usually a gas present in the measured gas stream, that is not adequately accounted for in the calibration procedure and may cause measurement bias.

3.12 Low-Concentration Analyzer means any analyzer that operates with a calibration span of 20 ppm NO_X or lower. Each analyzer model used routinely to measure low NO_X concentrations must pass a manufacturer's stability test (MST). An MST subjects the analyzer to a range of line voltages and temperatures that reflect potential field conditions to demonstrate its stability following

procedures similar to those provided in 40 CFR 53.23. Ambient-level analyzers are exempt from the MST requirements of section 16.3. A copy of this information must be included in each test report. Table 7E–5 lists the criteria to be met.

3.13 Measurement System means all of the equipment used to determine the NO_x concentration. The measurement system comprises six major subsystems: Sample acquisition, sample transport, sample conditioning, calibration gas manifold, gas analyzer, and data recorder.

3.14 Response Time means the time it takes the measurement system to respond to a change in gas concentration occurring at the sampling point when the system is operating normally at its target sample flow rate or dilution ratio.

3.15 Run means a series of gas samples taken successively from the stack or duct. A test normally consists of a specific number of runs.

3.16 System Bias means the difference between a calibration gas measured in direct calibration mode and in system calibration mode. System bias is determined before and after each run at the low- and mid- or high-concentration levels. For dilution-type systems, pre- and post-run system calibration error is measured rather than system bias.

3.17 System Calibration Error applies to dilution-type systems and means the difference between the measured concentration of low-, mid-, or high-level calibration gas and the certified concentration for each gas when introduced in system calibration mode. For dilution-type systems, a 3-point system calibration error test is conducted in lieu of the analyzer calibration error test, and 2-point system calibration error tests are conducted in lieu of system bias tests.

3.18 System Calibration Mode means introducing the calibration gases into the measurement system at the probe, upstream of the filter and all sample conditioning components.

3.19 Test refers to the series of runs required by the applicable regulation.

4.0 Interferences

Note that interferences may vary among instruments and that instrument-specific interferences must be evaluated through the interference test.

5.0 Safety

What safety measures should I consider when using this method? This method may require you to work with hazardous materials and in hazardous conditions. We encourage you to establish safety procedures before using the method. Among other precautions, you should become familiar with the safety recommendations in the gas analyzer user's manual. Occupational Safety and Health Administration (OSHA) regulations concerning cylinder and noxious gases may apply. Nitric oxide and NO_2 are toxic and dangerous gases. Nitric oxide is immediately converted to NO_2 upon reaction with air. Nitrogen dioxide is a highly poisonous and insidious gas. Inflammation of the lungs from exposure may cause only slight pain or pass unnoticed, but the resulting edema several days later may cause death. A concentration of 100 ppm is dangerous for even a short exposure, and 200 ppm may be fatal. Calibration gases must be handled with utmost care and with adequate ventilation. Emission-level exposure to these gases should be avoided.

6.0 Equipment and Supplies

The performance criteria in this method will be met or exceeded if you are properly using equipment designed for this application.

6.1 What do I need for the measurement system? You may use any equipment and supplies meeting the following specifications:

(1) Sampling system components that are not evaluated in the system bias or system calibration error test must be glass, Teflon, or stainless steel. Other materials are potentially acceptable, subject to approval by the Administrator.

(2) The interference, calibration error, and system bias criteria must be met.

(3) Sample flow rate must be maintained within 10 percent of the flow rate at which the system response time was measured.

(4) All system components (excluding sample conditioning components, if used) must maintain the sample temperature above the moisture dew point. Ensure minimal contact between any condensate and the sample gas. Section 6.2 provides example equipment specifications for a NO_x measurement system. Figure 7E–1 is a diagram of an example dry-basis measurement system that is likely to meet the method requirements and is provided as guidance. For wet-basis systems, you may use alternative equipment and supplies as needed (some of which are described in Section 6.2), provided that the measurement system meets the applicable performance specifications of this method.

6.2 Measurement System Components

6.2.1 Sample Probe. Glass, stainless steel, or other approved material, of sufficient length to traverse the sample points.

6.2.2 Particulate Filter. An in-stack or out-of-stack filter. The filter must be made of material that is non-reactive to the gas being sampled. The filter media for out-of-stack filters must be included in the system bias test. The particulate filter requirement may be waived in applications where no significant particulate matter is expected (*e.g.*, for emission testing of a combustion turbine firing natural gas).

6.2.3 Sample Line. The sample line from the probe to the conditioning system/sample pump should be made of Teflon or other material that does not absorb or otherwise alter the sample gas. For a dry-basis measurement system (as shown in Figure 7E–1), the temperature of the sample line must be maintained at a sufficiently high level to prevent condensation before the sample conditioning components. For wet-basis measurement systems, the temperature of the sample line must be maintained at a sufficiently high level to prevent condensation before the analyzer.

6.2.4 Conditioning Equipment. For dry basis measurements, a condenser, dryer or other suitable device is required to remove moisture continuously from the sample gas. Any equipment needed to heat the probe or sample line to avoid condensation prior to the sample conditioning component is also required.

For wet basis systems, you must keep the sample above its dew point either by: (1) Heating the sample line and all sample transport components up to the inlet of the analyzer (and, for hot-wet extractive systems, also heating the analyzer) or (2) by diluting the sample prior to analysis using a dilution probe system. The components required to do either of the above are considered to be conditioning equipment.

6.2.5 Sampling Pump. For systems similar to the one shown in Figure 7E–1, a leak-free pump is needed to pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system. The pump may be constructed of any material that is non-reactive to the gas being sampled. For dilution-type measurement systems, an ejector pump (eductor) is used to create a vacuum that draws the sample through a critical orifice at a constant rate.

6.2.6 Calibration Gas Manifold. Prepare a system to allow the introduction of calibration gases either directly to the gas analyzer in direct calibration mode or into the measurement system, at the probe, in system calibration mode, or both, depending upon the type of system used. In system calibration mode, the system should be able to flood the sampling probe and vent excess gas. Alternatively, calibration gases may be introduced at the calibration valve following the probe. Maintain a constant pressure in the gas manifold. For in-stack dilution-type systems, a gas dilution subsystem is required to transport large volumes of purified air to the sample probe and a probe controller is needed to maintain the proper dilution ratio.

6.2.7 Sample Gas Manifold. For the type of system shown in Figure 7E–1, the sample gas manifold diverts a portion of the sample to the analyzer, delivering the remainder to the by-pass discharge vent. The manifold should also be able to introduce calibration gases directly to the analyzer (except for dilution-type systems). The manifold must be made of material that is non-reactive to the gas sampled or the calibration gas and be configured to safely discharge the bypass gas.

6.2.8 NO_X Analyzer. An instrument that continuously measures NO_X in the gas stream and meets the applicable specifications in section 13.0. An analyzer that operates on the principle of chemiluminescence with an NO_2 to NO converter is one example of an analyzer that has been used successfully in the past. Analyzers operating on other principles may also be used provided the performance criteria in section 13.0 are met.

6.2.8.1 Dual Range Analyzers. For certain applications, a wide range of gas concentrations may be encountered, necessitating the use of two measurement ranges. Dual-range analyzers are readily available for these applications. These analyzers are often equipped with automated range-switching capability, so that when readings exceed the full-scale of the low measurement range, they are recorded on the high range. As an alternative to using a dual-range analyzer, you may use two segments of a single, large measurement scale to serve as the low and high ranges. In all cases, when two ranges are used, you must quality-assure both ranges using the proper sets of calibration gases. You must also meet the interference, calibration error, system bias, and drift checks. However, we caution that when you use two segments of a large measurement scale for dual range purposes, it may be difficult to meet the performance specifications on the low range due to signal-to-noise ratio considerations.

6.2.8.2 Low Concentration Analyzer. When an analyzer is routinely calibrated with a calibration span of 20 ppmv or less, the manufacturer's stability test (MST) is required. See Table 7E–5 for test parameters.

6.2.9 Data Recording. A strip chart recorder, computerized data acquisition system, digital recorder, or data logger for recording measurement data may be used.

7.0 Reagents and Standards

7.1 Calibration Gas. What calibration gases do I need? Your calibration gas must be NO in N_2 and certified (or recertified) within an uncertainty of 2.0 percent in accordance with ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards'' September 1997, as amended August 25, 1999, EPA–600/R–97/121. Blended gases meeting the Traceability Protocol are allowed if the additional gas components are shown not to interfere with the analysis. If a zero gas is used for the low-level gas, it must meet the requirements under the definition for ''zero air material'' in 40 CFR 72.2. The calibration gas must not be used after its expiration date. Except for applications under part 75 of

this chapter, it is acceptable to prepare calibration gas mixtures from EPA Traceability Protocol gases in accordance with Method 205 in appendix M to part 51 of this chapter. For part 75 applications, the use of Method 205 is subject to the approval of the Administrator. The goal and recommendation for selecting calibration gases is to bracket the sample concentrations. The following calibration gas concentrations are required:

7.1.1 *High-Level Gas.* This concentration is chosen to set the calibration span as defined in Section 3.4.

7.1.2 Mid-Level Gas. 40 to 60 percent of the calibration span.

7.1.3 Low-Level Gas. Less than 20 percent of the calibration span.

7.1.4 Converter Efficiency Gas. What reagents do I need for the converter efficiency test? The converter efficiency gas is a manufacturer-certified gas with a concentration sufficient to show NO_2 conversion at the concentrations encountered in the source. A test gas concentration in the 40 to 60 ppm range is suggested, but other concentrations may be more appropriate to specific sources. For the test described in section 8.2.4.1, NO_2 is required. For the alternative converter efficiency tests in section 16.2, NO is required.

7.2 Interference Check. What reagents do I need for the interference check? Use the appropriate test gases listed in Table 7E–3 or others not listed that can potentially interfere (as indicated by the test facility type, instrument manufacturer, etc.) to conduct the interference check. These gases should be manufacturer certified but do not have to be prepared by the EPA traceability protocol.

8.0 Sample Collection, Preservation, Storage, and Transport

Emission Test Procedure

Since you are allowed to choose different options to comply with some of the performance criteria, it is your responsibility to identify the specific options you have chosen, to document that the performance criteria for that option have been met, and to identify any deviations from the method.

8.1 What sampling site and sampling points do I select?

8.1.1 Unless otherwise specified in an applicable regulation or by the Administrator, when this method is used to determine compliance with an emission standard, conduct a stratification test as described in section 8.1.2 to determine the sampling traverse points to be used. For performance testing of continuous emission monitoring systems, follow the sampling site selection and traverse point layout procedures described in the appropriate performance specification or applicable regulation (e.g., Performance Specification 2 in appendix B to this part).

8.1.2 Determination of Stratification. Perform a stratification test at each test site to determine the appropriate number of sample traverse points. If testing for multiple pollutants or diluents at the same site, a stratification test using only one pollutant or diluent satisfies this requirement. A stratification test is not required for small stacks that are less than 4 inches in diameter. To test for stratification, use a probe of appropriate length to measure the NO_X (or pollutant of interest) concentration at 12 traverse points located according to Table 1–1 or Table 1–2 of Method 1. Alternatively, you may measure at three points on a line passing through the centroidal area. Space the three points at 16.7, 50.0, and 83.3 percent of the measurement line. Sample for a minimum of twice the system response time (see section 8.2.6) at each traverse point. Calculate the individual point and mean NO_X concentrations. If the concentration at each traverse point differs from the mean concentration for all traverse points by no more than: ±5.0 percent of the mean concentration; or ±0.5 ppm (whichever is less restrictive), the gas stream is considered unstratified, and you may collect samples from a single point that most closely matches the mean. If the 5.0 percent or 0.5 ppm criterion is not met, but the concentration at each traverse point differs from the mean concentration for all traverse points by not more than: ±10.0 percent of the mean concentration; or ±1.0 ppm (whichever is less restrictive), the gas stream is considered to be minimally stratified and you may take samples from three points. Space the three points at 16.7, 50.0, and 83.3 percent of the measurement line. Alternatively, if a 12-point stratification test was performed and the emissions were shown to be minimally stratified (all points within ± 10.0 percent of their mean or within ±1.0 ppm), and if the stack diameter (or equivalent diameter, for a rectangular stack or duct) is greater than 2.4 meters (7.8 ft), then you may use 3-point sampling and locate the three points along the measurement line exhibiting the highest average concentration during the stratification test at 0.4, 1.2 and 2.0 meters from the stack or duct wall. If the gas stream is found to be stratified because the 10.0 percent or 1.0 ppm criterion for a 3-point test is not met, locate 12 traverse points for the test in accordance with Table 1–1 or Table 1–2 of Method 1.

8.2 Initial Measurement System Performance Tests. What initial performance criteria must my system meet before I begin collecting samples? Before measuring emissions, perform the following procedures:

(a) Calibration gas verification,

(b) Measurement system preparation,

(c) Calibration error test,

(d) NO_2 to NO conversion efficiency test, if applicable,

(e) System bias check,

(f) System response time test, and

(g) Interference check

8.2.1 Calibration Gas Verification. How must I verify the concentrations of my calibration gases? Obtain a certificate from the gas manufacturer documenting the quality of the gas. Confirm that the manufacturer certification is complete and current. Ensure that your calibration gas certifications have not expired. This documentation should be available on-site for inspection. To the extent practicable, select a high-level gas concentration that will result in the measured emissions being between 20 and 100 percent of the calibration span.

8.2.2 Measurement System Preparation. How do I prepare my measurement system? Assemble, prepare, and precondition the measurement system according to your standard operating procedure. Adjust the system to achieve the correct sampling rate or dilution ratio (as applicable).

8.2.3 Calibration Error Test. How do I confirm my analyzer calibration is correct? After you have assembled, prepared and calibrated your sampling system and analyzer, you must conduct a 3-point analyzer calibration error test (or a 3-point system calibration error test for dilution systems) before the first run and again after any failed system bias test (or 2-point system calibration error test for dilution systems) or failed drift test. Introduce the low-, mid-, and high-level calibration gases sequentially. For non-dilution-type measurement systems, introduce the gases in direct calibration mode. For dilution-type measurement systems, introduce the gases in system calibration mode.

(1) For non-dilution systems, you may adjust the system to maintain the correct flow rate at the analyzer during the test, but you may not make adjustments for any other purpose. For dilution systems, you must operate the measurement system at the appropriate dilution ratio during all system calibration error checks, and may make only the adjustments necessary to maintain the proper ratio.

(2) Record the analyzer's response to each calibration gas on a form similar to Table 7E–1. For each calibration gas, calculate the analyzer calibration error using Equation 7E–1 in section 12.2 or the system calibration error using Equation 7E–3 in section 12.4 (as applicable). The calibration error specification in section 13.1 must be met for the low-, mid-, and high-level gases. If the calibration error specification is not met, take corrective action and repeat the test until an acceptable 3-point calibration is achieved.

8.2.4 NO_2 to NO Conversion Efficiency Test. Before or after each field test, you must conduct an NO_2 to NO conversion efficiency test if your system converts NO_2 to NO before analyzing for NO_X. You may risk testing multiple facilities before performing this test provided you pass this test at the conclusion of the final facility test. A failed final conversion efficiency test in this case will invalidate all tests performed subsequent to the test in which the converter efficiency test was passed. Follow the procedures in section 8.2.4.1, or 8.2.4.2. If desired, the converter efficiency factor derived from this test may be used to correct the test results for converter efficiency if the NO_2 fraction in the measured test gas is known. Use Equation 7E–8 in section 12.8 for this correction.

8.2.4.1 Introduce NO_2 converter efficiency gas to the analyzer in direct calibration mode and record the NO_X concentration displayed by the analyzer. Calculate the converter efficiency using Equation 7E–7 in section 12.7. The specification for converter efficiency in section 13.5 must be met. The user is cautioned that state-of-the-art NO_2 calibration gases may have limited shelf lives, and this could affect the ability to pass the 90-percent conversion efficiency requirement.

8.2.4.2 Alternatively, either of the procedures for determining conversion efficiency using NO in section 16.2 may be used.

8.2.5 Initial System Bias and System Calibration Error Checks. Before sampling begins, determine whether the high-level or mid-level calibration gas best approximates the emissions and use it as the upscale gas. Introduce the upscale gas at the probe upstream of all sample conditioning components in system calibration mode. Record the time it takes for the measured concentration to increase to a value that is at least 95 percent or within 0.5 ppm (whichever is less restrictive) of a stable response for both the low-level and upscale gases. Continue to observe the gas concentration reading until it has reached a final, stable value. Record this value on a form similar to Table 7E–2.

(1) Next, introduce the low-level gas in system calibration mode and record the time required for the concentration response to decrease to a value that is within 5.0 percent or 0.5 ppm (whichever is less restrictive) of the certified low-range gas concentration. If the low-level gas is a zero gas, use the procedures described above and observe the change in concentration until the response is 0.5 ppm or 5.0 percent of the upscale gas concentration (whichever is less restrictive).

(2) Continue to observe the low-level gas reading until it has reached a final, stable value and record the result on a form similar to Table 7E–2. Operate the measurement system at the normal sampling rate during all system bias checks. Make only the adjustments necessary to achieve proper calibration gas flow rates at the analyzer.

(3) From these data, calculate the measurement system response time (see section 8.2.6) and then calculate the initial system bias using Equation 7E–2 in section 12.3. For dilution systems, calculate the system calibration error in lieu of system bias using

equation 7E–3 in section 12.4. See section 13.2 for acceptable performance criteria for system bias and system calibration error. If the initial system bias (or system calibration error) specification is not met, take corrective action. Then, you must repeat the applicable calibration error test from section 8.2.3 and the initial system bias (or 2-point system calibration error) check until acceptable results are achieved, after which you may begin sampling.

(NOTE: For dilution-type systems, data from the 3-point system calibration error test described in section 8.2.3 may be used to meet the initial 2-point system calibration error test requirement of this section, if the calibration gases were injected as described in this section, and if response time data were recorded).

8.2.6 Measurement System Response Time. As described in section 8.2.5, you must determine the measurement system response time during the initial system bias (or 2-point system calibration error) check. Observe the times required to achieve 95 percent of a stable response for both the low-level and upscale gases. The longer interval is the response time.

8.2.7 Interference Check. Conduct an interference response test of the gas analyzer prior to its initial use in the field. If you have multiple analyzers of the same make and model, you need only perform this alternative interference check on one analyzer. You may also meet the interference check requirement if the instrument manufacturer performs this or a similar check on an analyzer of the same make and model of the analyzer that you use and provides you with documented results.

(1) You may introduce the appropriate interference test gases (that are potentially encountered during a test; see examples in Table 7E–3) into the analyzer separately or as mixtures. Test the analyzer with the interference gas alone at the highest concentration expected at a test source and again with the interference gas and NO_X at a representative NO_X test concentration. For analyzers measuring NO_X greater than 20 ppm, use a calibration gas with a NO_X concentration of 80 to 100 ppm and set this concentration equal to the calibration span. For analyzers measuring less than 20 ppm NO_X, select an NO concentration for the calibration span that reflects the emission levels at the sources to be tested, and perform the interference check at that level. Measure the total interference response of the analyzer to these gases in ppmv. Record the responses and determine the interference using Table 7E–4. The specification in section 13.4 must be met.

(2) A copy of this data, including the date completed and signed certification, must be available for inspection at the test site and included with each test report. This interference test is valid for the life of the instrument unless major analytical components (*e.g.,* the detector) are replaced with different model parts. If major components are replaced with different model parts, the interference gas check must be repeated before returning the analyzer to service. If major components are replaced, the interference gas check must be repeated before returning the analyzer to service. The tester must ensure that any specific technology, equipment, or procedures that are intended to remove interference effects are operating properly during testing.

8.3 Dilution-Type Systems—Special Considerations. When a dilution-type measurement system is used, there are three important considerations that must be taken into account to ensure the quality of the emissions data. First, the critical orifice size and dilution ratio must be selected properly so that the sample dew point will be below the sample line and analyzer temperatures. Second, a high-quality, accurate probe controller must be used to maintain the dilution ratio during the test. The probe controller should be capable of monitoring the dilution air pressure, eductor vacuum, and sample flow rates. Third, differences between the molecular weight of calibration gas mixtures and the stack gas molecular weight must be addressed because these can affect the dilution ratio and introduce measurement bias.

8.4 Sample Collection.

(1) Position the probe at the first sampling point. Purge the system for at least two times the response time before recording any data. Then, traverse all required sampling points, sampling at each point for an equal length of time and maintaining the appropriate sample flow rate or dilution ratio (as applicable). You must record at least one valid data point per minute during the test run.

(2) Each time the probe is removed from the stack and replaced, you must recondition the sampling system for at least two times the system response time prior to your next recording. If the average of any run exceeds the calibration span value, that run is invalid.

(3) You may satisfy the multipoint traverse requirement by sampling sequentially using a single-hole probe or a multi-hole probe designed to sample at the prescribed points with a flow within 10 percent of mean flow rate. Notwithstanding, for applications under part 75 of this chapter, the use of multi-hole probes is subject to the approval of the Administrator.

8.5 Post-Run System Bias Check and Drift Assessment.

How do I confirm that each sample I collect is valid? After each run, repeat the system bias check or 2-point system calibration error check (for dilution systems) to validate

the run. Do not make adjustments to the measurement system (other than to maintain the target sampling rate or dilution ratio) between the end of the run and the completion of the post-run system bias or system calibration error check. Note that for all post-run system bias or 2-point system calibration error checks, you may inject the low-level gas first and the upscale gas last, or vice-versa. You may risk sampling for multiple runs before performing the post-run bias or system calibration error check provided you pass this test at the conclusion of the group of runs. A failed final test in this case will invalidate all runs subsequent to the last passed test.

(1) If you do not pass the post-run system bias (or system calibration error) check, then the run is invalid. You must diagnose and fix the problem and pass another calibration error test (Section 8.2.3) and system bias (or 2-point system calibration error) check (Section 8.2.5) before repeating the run. Record the system bias (or system calibration error) results on a form similar to Table 7E–2.

(2) After each run, calculate the low-level and upscale drift, using Equation 7E–4 in section 12.5. If the post-run low- and upscale bias (or 2-point system calibration error) checks are passed, but the low-or upscale drift exceeds the specification in section 13.3, the run data are valid, but a 3-point calibration error test and a system bias (or 2-point system calibration error) check must be performed and passed before any more test runs are done.

(3) For dilution systems, data from a 3-point system calibration error test may be used to met the pre-run 2-point system calibration error requirement for the first run in a test sequence. Also, the post-run bias (or 2-point calibration error) check data may be used as the pre-run data for the next run in the test sequence at the discretion of the tester.

8.6 Alternative Interference and System Bias Checks (Dynamic Spike Procedure). If I want to use the dynamic spike procedure to validate my data, what procedure should I follow? Except for applications under part 75 of this chapter, you may use the dynamic spiking procedure and requirements provided in section 16.1 during each test as an alternative to the interference check and the pre- and post-run system bias checks. The calibration error test is still required under this option. Use of the dynamic spiking procedure for Part 75 applications is subject to the approval of the Administrator.

8.7 Moisture correction. You must determine the moisture content of the flue gas and correct the measured gas concentrations to a dry basis using Method 4 or other appropriate methods, subject to the approval of the Administrator, when the moisture basis (wet or dry) of the measurements made with this method is different from the moisture basis of either: (1) The applicable emissions limit; or (2) the CEMS being evaluated for relative accuracy. Moisture correction is also required if the applicable limit is in lb/mmBtu and the moisture basis of the Method 7E NO_x analyzer is different from the moisture basis of the Method 3A diluent gas (CO_2 or O_2) analyzer.

9.0 Quality Control

What quality control measures must I take?

The following table is a summary of the mandatory, suggested, and alternative quality assurance and quality control measures and the associated frequency and acceptance criteria. All of the QC data, along with the sample run data, must be documented and included in the test report.

SUMMARY TABLE OF AQ/QC

Status	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
S	Identify Data User		Regulatory Agency or other primary end user of data.	Before designing test.
S	Analyzer Design	Analyzer resolution or sensitivity.	<2.0% of full-scale range	Manufacturer design.
M		Interference gas check.	Sum of responses ≤2.5% of calibration span Alternatively, sum of responses: ≤0.5 ppmv for calibration spans of 5 to 10 ppmv. ≤0.2 ppmv for calibration spans <5 ppmv. See Table 7E-3.	
M	Calibration Gases	Traceability protocol (G1, G2).	Valid certificate required Uncertainty ≤2.0% of tag value.	
M		High-level gas	Equal to the calibration span	Each test.
M		Mid-level gas	40 to 60% of calibration span	Each test.
M		Low-level gas	<20% of calibration span	Each test.
S	Data Recorder Design.	Data resolution	≤0.5% of full-scale range	Manufacturer design.
S	Sample Extraction	Probe material	SS or quartz if stack >500 °F	East test.
M	Sample Extraction	Probe, filter and sample line temperature.	For dry-basis analyzers, keep sample above the dew point by heating, prior to sample conditioning.	Each run.

SUMMARY TABLE OF AQ/QC—Continued

Status	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
			For wet-basis analyzers, keep sample above dew point at all times, by heating or dilution.	
S	Sample Extraction	Calibration valve material.	SS	Each test.
S	Sample Extraction	Sample pump material.	Inert to sample constituents	Each test.
S	Sample Extraction	Manifolding material	Inert to sample constituents	Each test.
S	Moisture Removal	Equipment efficiency	<5% target compound removal	Verified through system bias check.
S	Particulate Removal	Filter inertness	Pass system bias check	Each bias check.
M	Analyzer & Calibration Gas Performance.	Analyzer calibration error (of 3-point system calibration error for dilution systems).	Within ±2.0 percent of the calibration span of the analyzer for the low-, mid-, and high-level calibration gases. Alternative specification: ≤0.5 ppmv absolute difference.	Before initial run and after a failed system bias test or drift test.
M	System Performance	System bias (or pre- and post-run 2-point system calibration error for dilution (Systems).	Within ±5.0% of the analyzer calibration span for low-sacle and upscale calibration gases. Alternative specification: ≤0.5 ppmv absolute difference.	Before and after each run.
M	System Performance	System response time.	Determines minimum sampling time per point.	During initial sampling system bias test.
M	System Performance	Drift	≤3.0% of calibration span for low-level and mid- or high-level gases. Alternative specification: ≤0.5 ppmv absolute difference.	After each test run.
M	System Performance	NO_2-NO conversion efficiency.	≥90% of certified test gas concentration	Before or after each test.
M	System Performance	Purge time	≥2 times system response time	Before starting the first run and when probe is removed from and re-inserted into the stack.
M	System Performance	Minimum sample time at each point.	Two times the system response time	Each sample point.
M	System Performance	Stable sample flow rate (surrogate for maintaining system response time).	Within 10% of flow rate established during system response time check.	Each run.
M	Sample Point Selection.	Stratification test	All points within: ±5% of mean for 1-point sampling. ±10% of mean for 3-point. Alternatively, all points within: ±0.5 ppm of mean for 1-point sampling. ±1.0 ppm of mean for 3-point sampling.	Prior to first run.
A	Multiple sample points simultaneously.	No. of openings in probe.	Multi-hole probe with verifiable constant flow through all holes within 10% of mean flow rate (requires Administrative approval for Part 75).	Each run.
M	Data Recording	Frequency	≤1 minute average	During run.
S	Data Parameters	Sample concentration range.	All 1-minute averages within calibration span.	Each run.
M	Date Parameters	Average concentration for the run.	Run average ≤calibration span	Each run.

S = Suggest.
M = Mandatory.
A = Alternative.
Agency.

10.0 Calibration and Standardization

What measurement system calibrations are required?

(1) The initial 3-point calibration error test as described in section 8.2.3 and the system bias (or system calibration error) checks described in section 8.2.5 are required and must meet the specifications in section 13 before you start the test. Make all necessary adjustments to calibrate the gas analyzer and data recorder. Then, after the test commences, the system bias or system calibration error checks described in section 8.5 are required before and after each run. Your analyzer must be calibrated for all species of NO_X that it detects. Analyzers that measure NO and NO_2 separately without using a converter must be calibrated with both NO and NO_2.

(2) You must include a copy of the manufacturer's certification of the calibration gases used in the testing as part of the test report. This certification must include the 13 documentation requirements in the EPA Traceability Protocol For Assay and Certification of Gaseous Calibration Standards, September 1997, as amended August 25, 1999. When Method 205 is used to produce diluted calibration gases, you must document that the specifications for the gas dilution system are met for the test. You must also include the date of the most recent dilution system calibration against flow standards and the name of the person or manufacturer who carried out the calibration in the test report.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the procedures for calculations and data analysis listed in this section.

12.1 *Nomenclature.* The terms used in the equations are defined as follows:

ACE = Analyzer calibration error, percent of calibration span.

B_{WS} = Moisture content of sample gas as measured by Method 4 or other approved method, percent/100.

C_{Avg} = Average unadjusted gas concentration indicated by data recorder for the test run, ppmv.

C_D = Pollutant concentration adjusted to dry conditions, ppmv.

C_{Dir} = Measured concentration of a calibration gas (low, mid, or high) when introduced in direct calibration mode, ppmv.

C_{Gas} = Average effluent gas concentration adjusted for bias, ppmv.

C_M = Average of initial and final system calibration bias (or 2-point system calibration error) check responses for the upscale calibration gas, ppmv.

C_{MA} = Actual concentration of the upscale calibration gas, ppmv.

C_{Native} = NO_X concentration in the stack gas as calculated in section 12.6, ppmv.

C_O = Average of the initial and final system calibration bias (or 2-point system calibration error) check responses from the low-level (or zero) calibration gas, ppmv.

C_{OA} = Actual concentration of the low-level calibration gas, ppmv.

C_S = Measured concentration of a calibration gas (low, mid, or high) when introduced in system calibration mode, ppmv.

C_{SS} = Concentration of NO_X measured in the spiked sample, ppmv.

C_{Spike} = Concentration of NO_X in the undiluted spike gas, ppmv.

C_{Calc} = Calculated concentration of NO_X in the spike gas diluted in the sample, ppmv.

C_V = Manufacturer certified concentration of a calibration gas (low, mid, or high), ppmv.

C_W = Pollutant concentration measured under moist sample conditions, wet basis, ppmv.

CS = Calibration span, ppmv.

D = Drift assessment, percent of calibration span.

DF = Dilution system dilution factor or spike gas dilution factor, dimensionless.

Eff_{NO2} = NO_2 to NO converter efficiency, percent.

NO_{XCorr} = The NO_X concentration corrected for the converter efficiency, ppmv.

NOX_{Final} = The final NO_X concentration observed during the converter efficiency test in section 16.2.2, ppmv.

NO_{XPeak} = The highest NO_X concentration observed during the converter efficiency test in section 16.2.2, ppmv.

Q_{Spike} = Flow rate of spike gas introduced in system calibration mode, L/min.

Q_{Total} = Total sample flow rate during the spike test, L/min.

R = Spike recovery, percent.

SB = System bias, percent of calibration span.

SB_i = Pre-run system bias, percent of calibration span.

SB_{final} = Post-run system bias, percent of calibration span.

SCE = System calibration error, percent of calibration span.

SCE_i = Pre-run system calibration error, percent of calibration span.

SCE_{Final} = Post-run system calibration error, percent of calibration span.

12.2 Analyzer Calibration Error. For non-dilution systems, use Equation 7E–1 to calculate the analyzer calibration error for the low-, mid-, and high-level calibration gases.

$$ACE = \frac{C_{Dir} - C_v}{CS} \times 100 \qquad \text{Eq. 7E-1}$$

12.3 System Bias. For non-dilution systems, use Equation 7E–2 to calculate the system bias separately for the low-level and upscale calibration gases.

$$SB = \frac{C_S - C_{Dir}}{CS} \times 100 \qquad \text{Eq. 7E-2}$$

12.4 System Calibration Error. Use Equation 7E–3 to calculate the system calibration error for dilution systems. Equation 7E–3 applies to both the initial 3-point system calibration error test and the subsequent 2-point calibration error checks between test runs. In this equation, the term ''C_s'' refers to the diluted calibration gas concentration measured by the analyzer.

$$SCE = \frac{(C_S \quad DF) - C_V}{CS} \times 100 \qquad \text{Eq. 7E-3}$$

12.5 Drift Assessment. Use Equation 7E–4 to separately calculate the low-level and upscale drift over each test run. For dilution systems, replace ''SB_{final}'' and ''SB_i'' with ''SCE_{final}'' and ''SCE_i'', respectively, to calculate and evaluate drift.

$$D = \left|SB_{final} - SB_i\right| \qquad \text{Eq. 7E-4}$$

12.6 Effluent Gas Concentration. For each test run, calculate C_{avg}, the arithmetic average of all valid NO_X concentration values (*e.g.*, 1-minute averages). Then adjust the value of C_{avg} for bias using Equation 7E–5a if you use a non-zero gas as your low-level calibration gas, or Equation 7E–5b if you use a zero gas as your low-level calibration gas.

$$C_{Gas} = \left(C_{Avg} - C_M\right)\frac{C_{MA} - C_{OA}}{C_M - C_O} + C_{MA} \qquad \text{Eq. 7E-5a}$$

$$C_{Gas} = \left(C_{Avg} - C_O\right)\frac{C_{MA}}{C_M - C_O} \qquad \text{Eq. 7E-5b}$$

12.7 NO_2—NO Conversion Efficiency. If the NO_X converter efficiency test described in section 8.2.4.1 is performed, calculate the efficiency using Equation 7E–7.

$$Eff_{NO2} = \frac{C_{Dir}}{C_V} \times 100 \qquad \text{Eq. 7E-7}$$

12.8 NO_2—NO Conversion Efficiency Correction. If desired, calculate the total NO_X concentration with a correction for converter efficiency using Equation 7E–8.

$$NO_{x\,Corr} = NO + \left(\frac{(NO_X - NO)}{Eff_{NO_2}} x\ 100\right) \qquad \text{Eq. 7E-8}$$

12.9 Alternative NO_2 Converter Efficiency. If the alternative procedure of section 16.2.2 is used, determine the NO_X concentration decrease from NO_{XPeak} after the minimum 30-minute test interval using Equation 7E–9.

This decrease from NO_{XPeak} must meet the requirement in section 13.5 for the converter to be acceptable.

$$\%\,Decrease = \frac{NO_{XPeak} - NO_{XFinal}}{NO_{XPeak}} \times 100 \qquad \text{Eq. 7E-9}$$

12.10 Moisture Correction. Use Equation 7E–10 if your measurements need to be corrected to a dry basis.

$$C_D = \frac{C_W}{1 - B_{WS}} \qquad \text{Eq. 7E-10}$$

12.11 Calculated Spike Gas Concentration and Spike Recovery for the Example Alternative Dynamic Spiking Procedure in section 16.1.3. Use Equation 7E–11 to determine the calculated spike gas concentration. Use Equation 7E–12 to calculate the spike recovery.

$$C_{Calc} = \frac{\left(C_{Spike}\right)\left(Q_{Spike}\right)}{Q_{Total}} \qquad \text{Eq. 7E-11}$$

$$R = \frac{DF\left(C_{ss} - C_{native}\right) + C_{native}}{C_{Spike}} \times 100 \qquad \text{Eq. 7E-12}$$

13.0 Method Performance

13.1 Calibration Error. This specification is applicable to both the analyzer calibration error and the 3-point system calibration error tests described in section 8.2.3. At each calibration gas level (low, mid, and high) the calibration error must either be within ±2.0 percent of the calibration span. Alternatively, the results are acceptable if $|C_{dir} - C_v|$ or $|C_s - C_v|$ (as applicable) is ≤0.5 ppmv.

13.2 System Bias. This specification is applicable to both the system bias and 2-point system calibration error tests described in section 8.2.5 and 8.5. The pre- and post-run system bias (or system calibration error) must be within ±5.0 percent of the calibration span for the low-level and upscale calibration gases. Alternatively, the results are acceptable if $|C_s - C_{dir}|$ is ≤0.5 ppmv or if $|C_s - C_v|$ is ≤0.5 ppmv (as applicable).

13.3 Drift. For each run, the low-level and upscale drift must be less than or equal to 3.0 percent of the calibration span. The drift is also acceptable if the pre- and post-run bias (or the pre- and post-run system calibration error) responses do not differ by more than 0.5 ppmv at each gas concentration (i.e. $|C_{s\ post\text{-}run} - C_{s\ pre\text{-}run}| \leq 0.5$ ppmv).

13.4 Interference Check. The total interference response (i.e., the sum of the interference responses of all tested gaseous components) must not be greater than 2.50 percent of the calibration span for the analyzer tested. In summing the interferences, use the larger of the absolute values obtained for the interferent tested with and without the pollutant present. The results are also acceptable if the sum of the responses does not exceed 0.5 ppmv for a calibration span of 5 to 10 ppmv, or 0.2 ppmv for a calibration span <5 ppmv.

13.5 NO_2 to NO Conversion Efficiency Test (as applicable). The NO_2 to NO conversion efficiency, calculated according to Equation 7E–7, must be greater than or equal to 90 percent. The alternative conversion efficiency check, described in section 16.2.2 and calculated according to Equation 7E–9, must not result in a decrease from NO_{XPeak} by more than 2.0 percent.

13.6 Alternative Dynamic Spike Procedure. Recoveries of both pre-test spikes and post-test spikes must be within 100 ±10 percent. If the absolute difference between the calculated spike value and measured spike value is equal to or less than 0.20 ppmv, then the requirements of the ADSC are met.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Dynamic Spike Procedure. Except for applications under part 75 of this chapter, you may use a dynamic spiking procedure to validate your test data for a specific test matrix in place of the interference check and pre- and post-run system bias checks. For part 75 applications, use of this procedure is subject to the approval of the Administrator.

Best results are obtained for this procedure when source emissions are steady and not varying. Fluctuating emissions may render this alternative procedure difficult to pass. To use this alternative, you must meet the following requirements.

16.1.1 Procedure Documentation. You must detail the procedure you followed in the test report, including how the spike was measured, added, verified during the run, and calculated after the test.

16.1.2 Spiking Procedure Requirements. The spikes must be prepared from EPA Traceability Protocol gases. Your procedure must be designed to spike field samples at two target levels both before and after the test. Your target spike levels should bracket the average sample NO_X concentrations. The higher target concentration must be less than the calibration span. You must collect at least 5 data points for each target concentration. The spiking procedure must be performed before the first run and repeated after the last run of the test program.

16.1.3 Example Spiking Procedure. Determine the NO concentration needed to generate concentrations that are 50 and 150 percent of the anticipated NO_X concentration in the stack at the total sampling flow rate while keeping the spike flow rate at or below 10 percent of this total. Use a mass flow meter (accurate within 2.0 percent) to generate these NO spike gas concentrations at a constant flow rate. Use Equation 7E–11 in section 12.11 to determine the calculated spike concentration in the collected sample.

(1) Prepare the measurement system and conduct the analyzer calibration error test as described in sections 8.2.2 and 8.2.3. Following the sampling procedures in section 8.1, determine the stack NO_X concentration and use this concentration as the average stack concentration (C_{avg}) for the first spike level, or if desired, for both pre-test spike levels. Introduce the first level spike gas into the system in system calibration mode and begin sample collection. Wait for at least two times the system response time before measuring the spiked sample concentration. Then record at least five successive 1-minute averages of the spiked sample gas. Monitor the spike gas flow rate and maintain at the determined addition rate. Average the five 1-minute averages and determine the spike recovery using Equation 7E–12. Repeat this procedure for the other pre-test spike level. The recovery at each level must be within the limits in section 13.6 before proceeding with the test.

(2) Conduct the number of runs required for the test. Then repeat the above procedure for the post-test spike evaluation. The last run of the test may serve as the average stack concentration for the post-test spike test calculations. The results of the post-test spikes must meet the limits in section 13.6.

16.2 Alternative NO_2 to NO Conversion Efficiency Procedures. You may use either of the following procedures to determine converter efficiency in place of the procedure in section 8.2.4.1.

16.2.1 The procedure for determining conversion efficiency using NO in 40 CFR 86.123–78.

16.2.2 Bag Procedure. Perform the analyzer calibration error test to document the calibration (both NO and NO_X modes, as applicable). Fill a Tedlar or equivalent bag approximately half full with either ambient air, pure oxygen, or an oxygen standard gas with at least 19.5 percent by volume oxygen content. Fill the remainder of the bag with mid- to high-level NO in N_2 (or other appropriate concentration) calibration gas. (Note that the concentration of the NO standard should be sufficiently high enough for the diluted concentration to be easily and accurately measured on the scale used. The size of the bag should be large enough to accommodate the procedure and time required. Verify through the manufacturer that the Tedlar alternative is suitable for NO and make this verifed information available for inspection.)

(1) Immediately attach the bag to the inlet of the NO_X analyzer (or external converter if used). In the case of a dilution-system, introduce the gas at a point upstream of the dilution assembly. Measure the NO_X concentration for a period of 30 minutes. If the NO_X concentration drops more than 2 percent absolute from the peak value observed, then the NO_2 converter has failed to meet the criteria of this test. Take corrective action. The highest NO_X value observed is considered to be NO_{XPeak}. The final NO_X value observed is considered to be NO_{Xfinal}.

(2) [Reserved]

16.3 Manufacturer's Stability Test. A manufacturer's stability test is required for all analyzers that routinely measure emissions below 20 ppmv and is optional but recommended for other analyzers. This test evaluates each analyzer model by subjecting it to the tests listed in Table 7E–5 following procedures similar to those in 40 CFR 53.23 for thermal stability and insensitivity to supply voltage variations. If the analyzer will be used under temperature conditions that are outside the test conditions in Table B–4 of Part 53.23, alternative test temperatures that better reflect the analyzer field environment should be used. Alternative procedures or documentation that establish the analyzer's stability over the appropriate line voltages and temperatures are acceptable.

17.0 References

1. ''ERA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards'' September 1997 as amended, ERA–600/R–97/121.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

Figure 7E-1. Measurement System

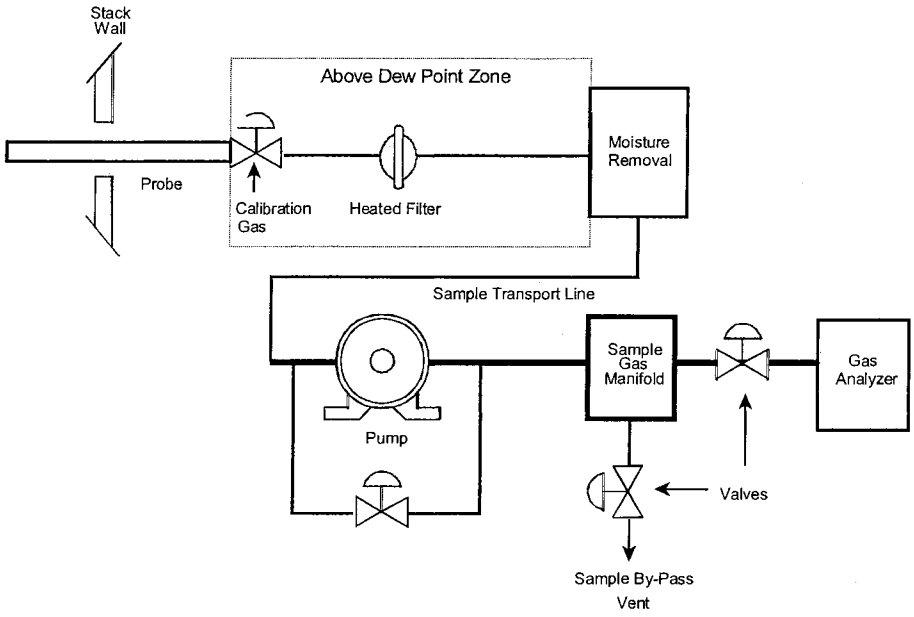

Figure 7E-2. Testing Flow Chart

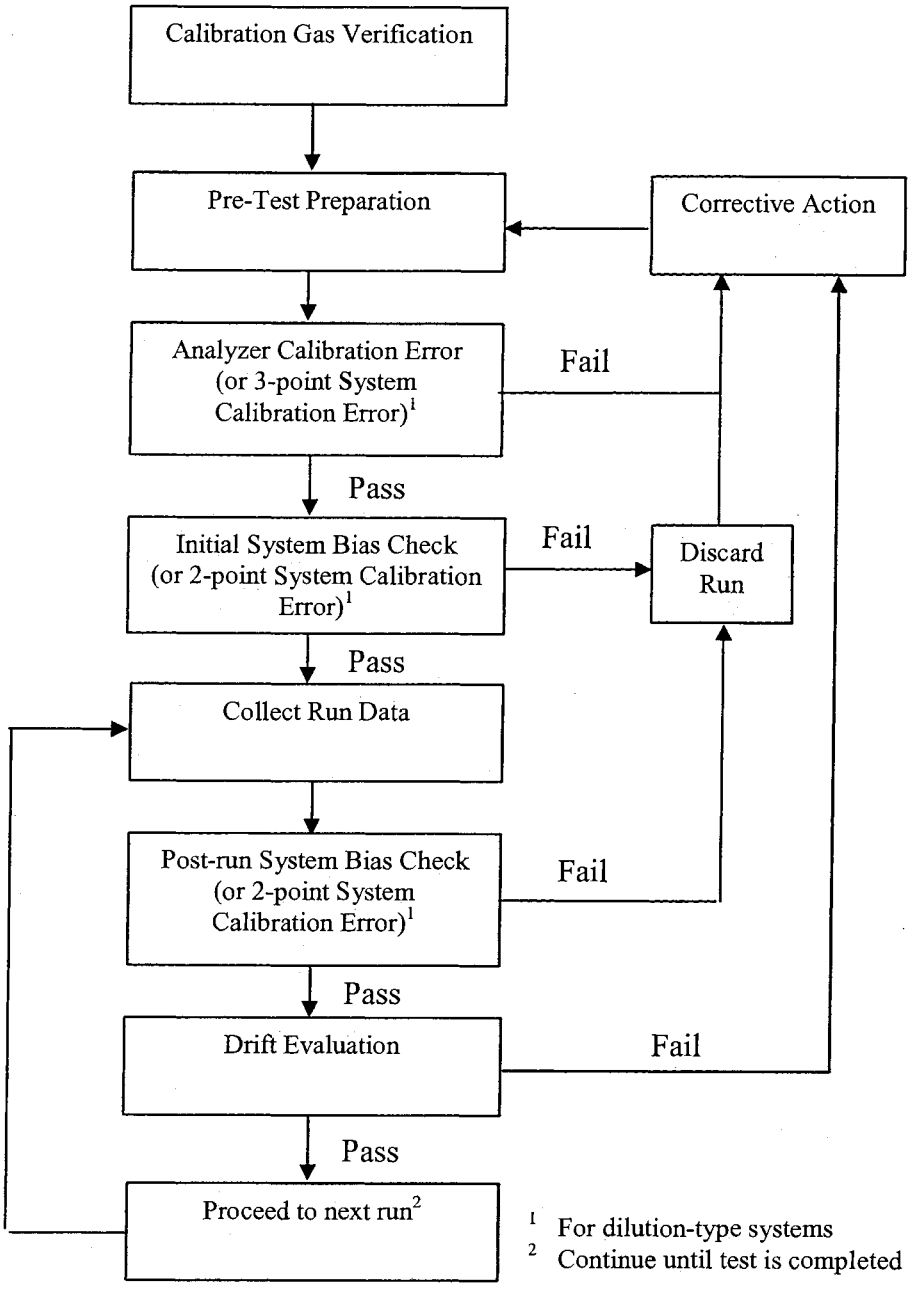

Table 7E-1 - Analyzer (or System) Calibration Error Data

Source Identification: _____ Test personnel: _____ Date: _____ Time: _____		Analyzer[1] or System[2] calibration error data for sampling runs: _____ Analyzer Model No. _____ Serial No. _____ Calibration Span (CS):		
	Manufacturer Certified Cylinder Value (indicate units) A	Analyzer calibration response (indicate units) B	Absolute difference (indicate units) A-B	Calibration Error (percent of calibration span) $\frac{A-B}{CS} \times 100$
Low-level (or zero) calibration gas	.....	.....	.....	.....
Mid-level calibration gas	.....	.....	.....	.....
High-level calibration gas	.....	.....	.....	.....

[1] Refers to data from the analyzer calibration error test of a non-dilution system.
[2] Refers to data from a 3-point system calibration error test of a dilution system.

Table 7E-2 - System Bias (or System Calibration Error) and Drift Data

Source Identification: _____ Run Number: _____
Test personnel: _____ Calibration Span: _____
Date: _____ Response Time: _____
Analyzer Model No. _____ Serial No. _____

	Initial values			Final values		
Calibration Gas Level	Certified Calibration gas value (indicate units)	System Response (indicate units)	System Bias[1] or Calibration Error[2] (% of calibration span)	System response (indicate units)	System Bias[1] or Calibration Error[2] (% of calibration span)	Drift (% of calibration span)
Low-level gas.....	.....	.....	.....	.....	.....	
Upscale (high- or mid-) level gas.....	.....	.....	.....	.....	.....	

[1] Refers to the pre- and post-run system bias checks of a non-dilution system.
[2] Refers to the pre- and post-run system calibration error checks of a dilution system.

TABLE 7E–3—EXAMPLE INTERFERENCE CHECK GAS CONCENTRATIONS

Potential interferent gas[1]	Concentrations[2] sample conditioning type	
	Hot wet	Dried
CO_2	5 and 15%	5 and 15%
H_2O	25%	1%
NO	15 ppmv	15 ppmv
NO_2	15 ppmv	15 ppmv
N_2O	10 ppmv	10 ppmv
CO	50 ppmv	50 ppmv
NH_3	10 ppmv	10 ppmv
CH_4	50 ppmv	50 ppmv
SO_2	20 ppmv	20 ppmv
H_2	50 ppmv	50 ppmv
HCl	10 ppmv	10 ppmv

[1] Any applicable gas may be eliminated or tested at a reduced level if the manufacturer has provided reliable means for limiting or scrubbing that gas to a specified level.
[2] As practicable, gas concentrations should be the highest expected at test sites.

TABLE 7E–4—INTERFERENCE RESPONSE

Date of Test: _____

Analyzer Type: _____
Model No.: _____
Serial No: _____
Calibration Span: _____

Test gas type	Concentration (ppm)	Analyzer response
	Sum of Responses	
	% of Calibration Span	

TABLE 7E–5—MANUFACTURER STABILITY TEST

Test description	Acceptance criteria (note 1)
Thermal Stability	Temperature range when drift does not exceed 3.0% of analyzer range over a 12-hour run when measured with NO_X present @ 80% of calibration span.
Fault Conditions	Identify conditions which, when they occur, result in performance which is not in compliance with the Manufacturer's Stability Test criteria. These are to be indicated visually or electrically to alert the operator of the problem.
Insensitivity to Supply Voltage Variations.	±10.0% (or manufacturers alternative) variation from nominal voltage must produce a drift of ≤2.0% of calibration span for either zero or concentration ≥80% NO_X present.
Analyzer Calibration Error.	For a low-, medium-, and high-calibration gas, the difference between the manufacturer certified value and the analyzer response in direct calibration mode, no more than 2.0% of calibration span.

Note 1: If the instrument is to be used as a Low Range analyzer, all tests must be performed at a calibration span of 20 ppm or less.

METHOD 8—DETERMINATION OF SULFURIC ACID AND SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, and Method 6.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Sulfuric acid, including: Sulfuric acid (H_2SO_4) mist, Sulfur trioxide (SO_3).	7664–93–9, 7449–11–9	0.05 mg/m³ (0.03×10^{-7} lb/ft³).
Sulfur dioxide (SO_2)	7449–09–5	1.2 mg/m³ (3×10^{-9} lb/ft³).

1.2 Applicability. This method is applicable for the determination of H_2SO_4 (including H_2SO_4 mist and SO_3) and gaseous SO_2 emissions from stationary sources.

NOTE: Filterable particulate matter may be determined along with H_2SO_4 and SO_2 (subject to the approval of the Administrator) by inserting a heated glass fiber filter between the probe and isopropanol impinger (see section 6.1.1 of Method 6). If this option is chosen, particulate analysis is gravimetric only; sulfuric acid is not determined separately.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

A gas sample is extracted isokinetically from the stack. The H_2SO_4 and the SO_2 are separated, and both fractions are measured separately by the barium-thorin titration method.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Possible interfering agents of this method are fluorides, free ammonia, and dimethyl aniline. If any of these interfering agents is present (this can be determined by knowledge of the process), alternative methods, subject to the approval of the Administrator, are required.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. Same as Method 6, section 5.2.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 5, section 6.1, with the following additions and exceptions:

6.1.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 8–1; it is similar to the Method 5 sampling train, except that the filter position is different, and the filter holder does not have to be heated. See Method 5, section 6.1.1, for details and guidelines on operation and maintenance.

6.1.1.1 Probe Liner. Borosilicate or quartz glass, with a heating system to prevent visible condensation during sampling. Do not use metal probe liners.

6.1.1.2 Filter Holder. Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other gasket materials (*e.g.*, Teflon or Viton) may be used, subject to the approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The filter holder shall be placed between the first and second impingers. Do not heat the filter holder.

6.1.1.3 Impingers. Four, of the Greenburg-Smith design, as shown in Figure 8–1. The first and third impingers must have standard tips. The second and fourth impingers must be modified by replacing the insert with an approximately 13-mm (½-in.) ID glass tube, having an unconstricted tip located 13 mm (½ in.) from the bottom of the impinger. Similar collection systems, subject to the approval of the Administrator, may be used.

6.1.1.4 Temperature Sensor. Thermometer, or equivalent, to measure the temperature of the gas leaving the impinger train to within 1 °C (2 °F).

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Wash Bottles. Two polyethylene or glass bottles, 500-ml.

6.2.2 Graduated Cylinders. Two graduated cylinders (volumetric flasks may be used), 250-ml, 1-liter.

6.2.3 Storage Bottles. Leak-free polyethylene bottles, 1-liter size (two for each sampling run).

6.2.4 Trip Balance. 500-g capacity, to measure to ±0.5 g (necessary only if a moisture content analysis is to be done).

6.3 Analysis. The following items are required for sample analysis:

6.3.1 Pipettes. Volumetric 10-ml, 100-ml.

6.3.2 Burette. 50-ml.

6.3.3 Erlenmeyer Flask. 250-ml (one for each sample, blank, and standard).

6.3.4 Graduated Cylinder. 100-ml.

6.3.5 Dropping Bottle. To add indicator solution, 125-ml size.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents are to conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Filters and Silica Gel. Same as in Method 5, sections 7.1.1 and 7.1.2, respectively.

7.1.2 Water. Same as in Method 6, section 7.1.1.

7.1.3 Isopropanol, 80 Percent by Volume. Mix 800 ml of isopropanol with 200 ml of water.

NOTE: Check for peroxide impurities using the procedure outlined in Method 6, section 7.1.2.1.

7.1.4 Hydrogen Peroxide (H^2O^2), 3 Percent by Volume. Dilute 100 ml of 30 percent H_2O_2) to 1 liter with water. Prepare fresh daily.

7.1.5 Crushed Ice.

7.2 Sample Recovery. The reagents and standards required for sample recovery are:

7.2.1 Water. Same as in section 7.1.2.

7.2.2 Isopropanol, 80 Percent. Same as in section 7.1.3.

7.3 Sample Analysis. Same as Method 6, section 7.3.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation. Same as Method 5, section 8.1, except that filters should be inspected but need not be desiccated, weighed, or identified. If the effluent gas can be considered dry (i.e., moisture-free), the silica gel need not be weighed.

8.2 Preliminary Determinations. Same as Method 5, section 8.2.

8.3 Preparation of Sampling Train. Same as Method 5, section 8.3, with the following exceptions:

8.3.1 Use Figure 8–1 instead of Figure 5–1.

8.3.2 Replace the second sentence of Method 5, section 8.3.1 with: Place 100 ml of 80 percent isopropanol in the first impinger, 100 ml of 3 percent H_2O_2 in both the second and third impingers; retain a portion of each reagent for use as a blank solution. Place about 200 g of silica gel in the fourth impinger.

8.3.3 Ignore any other statements in section 8.3 of Method 5 that are obviously not applicable to the performance of Method 8.

NOTE: If moisture content is to be determined by impinger analysis, weigh each of the first three impingers (plus absorbing solution) to the nearest 0.5 g, and record these weights. Weigh also the silica gel (or silica gel plus container) to the nearest 0.5 g, and record.)

8.4 Metering System Leak-Check Procedure. Same as Method 5, section 8.4.1.

8.5 Pretest Leak-Check Procedure. Follow the basic procedure in Method 5, section 8.4.2, noting that the probe heater shall be adjusted to the minimum temperature required to prevent condensation, and also that verbage such as ''* * * plugging the inlet to the filter holder * * * '' found in section 8.4.2.2 of Method 5 shall be replaced by '' * * * plugging the inlet to the first impinger * * * ''. The pretest leak-check is recommended, but is not required.

8.6 Sampling Train Operation. Follow the basic procedures in Method 5, section 8.5, in conjunction with the following special instructions:

8.6.1 Record the data on a sheet similar to that shown in Figure 8–2 (alternatively, Figure 5–2 in Method 5 may be used). The sampling rate shall not exceed 0.030 m^3/min (1.0 cfm) during the run. Periodically during the test, observe the connecting line between the probe and first impinger for signs of condensation. If condensation does occur, adjust the probe heater setting upward to the minimum temperature required to prevent condensation. If component changes become necessary during a run, a leak-check shall be performed immediately before each change, according to the procedure outlined in section 8.4.3 of Method 5 (with appropriate modifications, as mentioned in section 8.5 of this method); record all leak rates. If the leakage rate(s) exceeds the specified rate, the tester shall either void the run or plan to correct the sample volume as outlined in section 12.3 of Method 5. Leak-checks immediately after component changes are recommended, but not required. If these leak-checks are performed, the procedure in section 8.4.2 of Method 5 (with appropriate modifications) shall be used.

8.6.2 After turning off the pump and recording the final readings at the conclusion of each run, remove the probe from the stack. Conduct a post-test (mandatory) leak-check as outlined in section 8.4.4 of Method 5 (with appropriate modifications), and record the leak rate. If the post-test leakage rate exceeds the specified acceptable rate, either correct the sample volume, as outlined in section 12.3 of Method 5, or void the run.

8.6.3 Drain the ice bath and, with the probe disconnected, purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at the average flow rate used for sampling.

NOTE: Clean ambient air can be provided by passing air through a charcoal filter. Alternatively, ambient air (without cleaning) may be used.

8.7 Calculation of Percent Isokinetic. Same as Method 5, section 8.6.

8.8 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. Treat the samples as follows:

8.8.1 Container No. 1.

8.8.1.1 If a moisture content analysis is to be performed, clean and weigh the first impinger (plus contents) to the nearest 0.5 g, and record this weight.

8.8.1.2 Transfer the contents of the first impinger to a 250-ml graduated cylinder. Rinse the probe, first impinger, all connecting glassware before the filter, and the front half of the filter holder with 80 percent isopropanol. Add the isopropanol rinse solution to the cylinder. Dilute the contents of the cylinder to 225 ml with 80 percent isopropanol, and transfer the cylinder contents to the storage container. Rinse the cylinder with 25 ml of 80 percent isopropanol, and transfer the rinse to the storage container. Add the filter to the solution in the storage container and mix. Seal the container to protect the solution against evaporation. Mark the level of liquid on the container, and identify the sample container.

8.8.2 Container No. 2.

8.8.2.1 If a moisture content analysis is to be performed, clean and weigh the second and third impingers (plus contents) to the nearest 0.5 g, and record the weights. Also, weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g, and record the weight.

8.8.2.2 Transfer the solutions from the second and third impingers to a 1-liter graduated cylinder. Rinse all connecting glassware (including back half of filter holder) between the filter and silica gel impinger with water, and add this rinse water to the cylinder. Dilute the contents of the cylinder to 950 ml with water. Transfer the solution to a storage container. Rinse the cylinder with 50 ml of water, and transfer the rinse to the storage container. Mark the level of liquid on the container. Seal and identify the sample container.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
7.1.3	Isopropanol check	Ensure acceptable level of peroxide impurities in isopropanol.
8.4, 8.5, 10.1	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.
10.2	Barium standard solution standardization	Ensure normality determination.
11.2	Replicate titrations	Ensure precision of titration determinations.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

10.1 Sampling Equipment. Same as Method 5, section 10.0.

10.2 Barium Standard Solution. Same as Method 6, section 10.5.

11.0 Analytical Procedure

11.1. Sample Loss. Same as Method 6, section 11.1.

11.2. Sample Analysis.

11.2.1 Container No. 1. Shake the container holding the isopropanol solution and the filter. If the filter breaks up, allow the fragments to settle for a few minutes before removing a sample aliquot. Pipette a 100-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 2 to 4 drops of thorin indicator, and titrate to a pink endpoint using 0.0100 N barium standard solution. Repeat the titration with a second aliquot of sample, and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater.

11.2.2 Container No. 2. Thoroughly mix the solution in the container holding the contents of the second and third impingers. Pipette a 10-ml aliquot of sample into a 250-ml Erlenmeyer flask. Add 40 ml of isopropanol, 2 to 4 drops of thorin indicator, and titrate to a pink endpoint using 0.0100 N barium standard solution. Repeat the titration with a second aliquot of sample, and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater.

11.2.3 Blanks. Prepare blanks by adding 2 to 4 drops of thorin indicator to 100 ml of 80 percent isopropanol. Titrate the blanks in the same manner as the samples.

12.0 Data Analysis and Calculations

Carry out calculations retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature. Same as Method 5, section 12.1, with the following additions and exceptions:

$C_{H_2SO_4}$ = Sulfuric acid (including SO_3) concentration, g/dscm (lb/dscf).

C_{SO_2} = Sulfur dioxide concentration, g/dscm (lb/dscf).

N = Normality of barium perchlorate titrant, meq/ml.

V_a = Volume of sample aliquot titrated, 100 ml for H_2SO_4 and 10 ml for SO_2.

V_{soln} = Total volume of solution in which the sample is contained, 1000 ml for the SO_2 sample and 250 ml for the H_2SO_4 sample.

V_t = Volume of barium standard solution titrant used for the sample, ml.

V_{tb} = Volume of barium standard solution titrant used for the blank, ml.

12.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 8–2).

12.3 Dry Gas Volume. Same as Method 5, section 12.3.

12.4 Volume of Water Vapor Condensed and Moisture Content. Calculate the volume of water vapor using Equation 5–2 of Method 5; the weight of water collected in the impingers and silica gel can be converted directly to milliliters (the specific gravity of water is 1 g/ml). Calculate the moisture content of the stack gas (B_{ws}) using Equation 5–3 of Method 5. The note in section 12.5 of Method 5 also applies to this method. Note that if the effluent gas stream can be considered dry, the volume of water vapor and moisture content need not be calculated.

12.5 Sulfuric Acid Mist (Including SO_3) Concentration.

$$C_{H_2SO_4} = K_3\left[N\left(V_t - V_{tb}\right)\left(V_{soln}/V_a\right)\right]/V_{m(std)} \qquad \text{Eq. 8-1}$$

Where:

K_3 = 0.04904 g/meq for metric units,

$K_3 = 1.081 \times 10^{-4}$ lb/meq for English units.

12.6 Sulfur Dioxide Concentration.

$$C_{SO_2} = K_4\left[N\left(V_t - V_{tb}\right)\left(V_{soln}/V_a\right)\right]/V_{m(std)} \qquad \text{Eq. 8-2}$$

Where:

K_4 = 0.03203 g/meq for metric units,

$K_4 = 7.061 \times 10^{-5}$ lb/meq for English units.

12.7 Isokinetic Variation. Same as Method 5, section 12.11.

12.8 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate, if needed, using data obtained in this method and the equations in sections 12.6 and 12.7 of Method 2.

13.0 Method Performance

13.1 Analytical Range. Collaborative tests have shown that the minimum detectable limits of the method are 0.06 mg/m^3 (4×10^{-9} lb/ft^3) for H_2SO_4 and 1.2 mg/m^3 (74×10^{-9} lb/ft^3) for SO_2. No upper limits have been established. Based on theoretical calculations for 200 ml of 3 percent H_2O_2 solution, the upper concentration limit for SO_2 in a 1.0 m^3 (35.3 ft^3) gas sample is about 12,000 mg/m^3 (7.7×10^{-4} lb/ft^3). The upper limit can be extended by increasing the quantity of peroxide solution in the impingers.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as section 17.0 of Methods 5 and 6.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

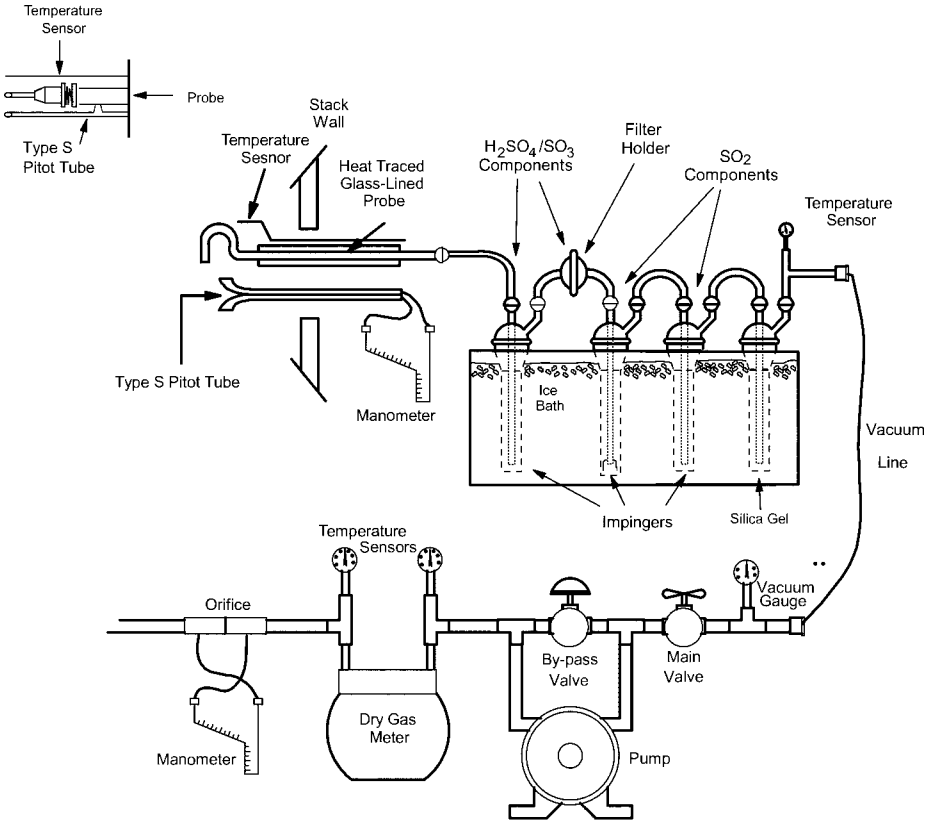

Figure 8-1. Sulfuric Acid Sampling Train

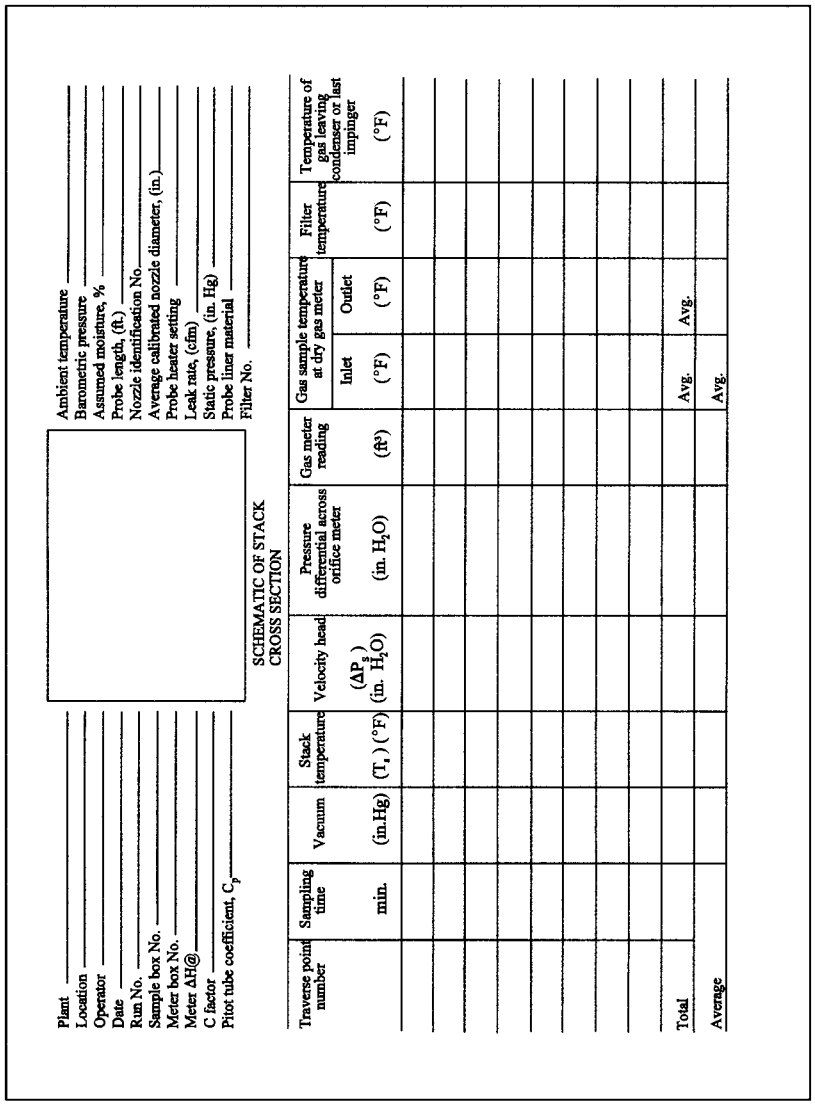

Figure 8-2. Field Data Sheet.

METHOD 9—VISUAL DETERMINATION OF THE OPACITY OF EMISSIONS FROM STATIONARY SOURCES

Many stationary sources discharge visible emissions into the atmosphere; these emissions are usually in the shape of a plume. This method involves the determination of plume opacity by qualified observers. The method includes procedures for the training and certification of observers, and procedures to be used in the field for determination of plume opacity. The appearance of a plume as viewed by an observer depends upon a number of variables, some of which may be controllable and some of which may not be controllable in the field. Variables which can be controlled to an extent to which they no longer exert a significant influence upon

plume appearance include: Angle of the observer with respect to the plume; angle of the observer with respect to the sun; point of observation of attached and detached steam plume; and angle of the observer with respect to a plume emitted from a rectangular stack with a large length to width ratio. The method includes specific criteria applicable to these variables.

Other variables which may not be controllable in the field are luminescence and color contrast between the plume and the background against which the plume is viewed. These variables exert an influence upon the appearance of a plume as viewed by an observer, and can affect the ability of the observer to accurately assign opacity values to the observed plume. Studies of the theory of plume opacity and field studies have demonstrated that a plume is most visible and presents the greatest apparent opacity when viewed against a contrasting background. It follows from this, and is confirmed by field trials, that the opacity of a plume, viewed under conditions where a contrasting background is present can be assigned with the greatest degree of accuracy. However, the potential for a positive error is also the greatest when a plume is viewed under such contrasting conditions. Under conditions presenting a less contrasting background, the apparent opacity of a plume is less and approaches zero as the color and luminescence contrast decrease toward zero. As a result, significant negative bias and negative errors can be made when a plume is viewed under less contrasting conditions. A negative bias decreases rather than increases the possibility that a plant operator will be cited for a violation of opacity standards due to observer error.

Studies have been undertaken to determine the magnitude of positive errors which can be made by qualified observers while reading plumes under contrasting conditions and using the procedures set forth in this method. The results of these studies (field trials) which involve a total of 769 sets of 25 readings each are as follows:

(1) For black plumes (133 sets at a smoke generator), 100 percent of the sets were read with a positive error[1] of less than 7.5 percent opacity; 99 percent were read with a positive error of less than 5 percent opacity.

(2) For white plumes (170 sets at a smoke generator, 168 sets at a coal-fired power plant, 298 sets at a sulfuric acid plant), 99 percent of the sets were read with a positive error of less than 7.5 percent opacity; 95 percent were read with a positive error of less than 5 percent opacity.

[1] For a set, positive error = average opacity determined by observers' 25 observations—average opacity determined from transmissometer's 25 recordings.

The positive observational error associated with an average of twenty-five readings is therefore established. The accuracy of the method must be taken into account when determining possible violations of applicable opacity standards.

1. Principle and Applicability

1.1 Principle. The opacity of emissions from stationary sources is determined visually by a qualified observer.

1.2 Applicability. This method is applicable for the determination of the opacity of emissions from stationary sources pursuant to §60.11(b) and for qualifying observers for visually determining opacity of emissions.

2. Procedures

The observer qualified in accordance with section 3 of this method shall use the following procedures for visually determining the opacity of emissions:

2.1 Position. The qualified observer shall stand at a distance sufficient to provide a clear view of the emissions with the sun oriented in the 140° sector to his back. Consistent with maintaining the above requirement, the observer shall, as much as possible, make his observations from a position such that his line of vision is approximately perpendicular to the plume direction, and when observing opacity of emissions from rectangular outlets (e.g., roof monitors, open baghouses, noncircular stacks), approximately perpendicular to the longer axis of the outlet. The observer's line of sight should not include more than one plume at a time when multiple stacks are involved, and in any case the observer should make his observations with his line of sight perpendicular to the longer axis of such a set of multiple stacks (e.g., stub stacks on baghouses).

2.2 Field Records. The observer shall record the name of the plant, emission location, type facility, observer's name and affiliation, a sketch of the observer's position relative to the source, and the date on a field data sheet (Figure 9–1). The time, estimated distance to the emission location, approximate wind direction, estimated wind speed, description of the sky condition (presence and color of clouds), and plume background are recorded on a field data sheet at the time opacity readings are initiated and completed.

2.3 Observations. Opacity observations shall be made at the point of greatest opacity in that portion of the plume where condensed water vapor is not present. The observer shall not look continuously at the plume, but instead shall observe the plume momentarily at 15-second intervals.

2.3.1 Attached Steam Plumes. When condensed water vapor is present within the

plume as it emerges from the emission outlet, opacity observations shall be made beyond the point in the plume at which condensed water vapor is no longer visible. The observer shall record the approximate distance from the emission outlet to the point in the plume at which the observations are made.

2.3.2 Detached Steam Plume. When water vapor in the plume condenses and becomes visible at a distinct distance from the emission outlet, the opacity of emissions should be evaluated at the emission outlet prior to the condensation of water vapor and the formation of the steam plume.

2.4 Recording Observations. Opacity observations shall be recorded to the nearest 5 percent at 15-second intervals on an observational record sheet. (See Figure 9–2 for an example.) A minimum of 24 observations shall be recorded. Each momentary observation recorded shall be deemed to represent the average opacity of emissions for a 15-second period.

2.5 Data Reduction. Opacity shall be determined as an average of 24 consecutive observations recorded at 15-second intervals. Divide the observations recorded on the record sheet into sets of 24 consecutive observations. A set is composed of any 24 consecutive observations. Sets need not be consecutive in time and in no case shall two sets overlap. For each set of 24 observations, calculate the average by summing the opacity of the 24 observations and dividing this sum by 24. If an applicable standard specifies an averaging time requiring more than 24 observations, calculate the average for all observations made during the specified time period. Record the average opacity on a record sheet. (See Figure 9–1 for an example.)

3. Qualifications and Testing

3.1 Certification Requirements. To receive certification as a qualified observer, a candidate must be tested and demonstrate the ability to assign opacity readings in 5 percent increments to 25 different black plumes and 25 different white plumes, with an error not to exceed 15 percent opacity on any one reading and an average error not to exceed 7.5 percent opacity in each category. Candidates shall be tested according to the procedures described in section 3.2. Smoke generators used pursuant to section 3.2 shall be equipped with a smoke meter which meets the requirements of section 3.3.

The certification shall be valid for a period of 6 months, at which time the qualification procedure must be repeated by any observer in order to retain certification.

3.2 Certification Procedure. The certification test consists of showing the candidate a complete run of 50 plumes—25 black plumes and 25 white plumes—generated by a smoke generator. Plumes within each set of 25 black and 25 white runs shall be presented in random order. The candidate assigns an opacity value to each plume and records his observation on a suitable form. At the completion of each run of 50 readings, the score of the candidate is determined. If a candidate fails to qualify, the complete run of 50 readings must be repeated in any retest. The smoke test may be administered as part of a smoke school or training program, and may be preceded by training or familiarization runs of the smoke generator during which candidates are shown black and white plumes of known opacity.

3.3 Smoke Generator Specifications. Any smoke generator used for the purposes of section 3.2 shall be equipped with a smoke meter installed to measure opacity across the diameter of the smoke generator stack. The smoke meter output shall display instack opacity based upon a pathlength equal to the stack exit diameter, on a full 0 to 100 percent chart recorder scale. The smoke meter optical design and performance shall meet the specifications shown in Table 9–1. The smoke meter shall be calibrated as prescribed in section 3.3.1 prior to the conduct of each smoke reading test. At the completion of each test, the zero and span drift shall be checked and if the drift exceeds ±1 percent opacity, the condition shall be corrected prior to conducting any subsequent test runs. The smoke meter shall be demonstrated, at the time of installation, to meet the specifications listed in Table 9–1. This demonstration shall be repeated following any subsequent repair or replacement of the photocell or associated electronic circuitry including the chart recorder or output meter, or every 6 months, whichever occurs first.

TABLE 9–1—SMOKE METER DESIGN AND PERFORMANCE SPECIFICATIONS

Parameter	Specification
a. Light source	Incandescent lamp operated at nominal rated voltage.
b. Spectral response of photocell.	Photopic (daylight spectral response of the human eye—Citation 3).
c. Angle of view	15° maximum total angle.
d. Angle of projection	15° maximum total angle.
e. Calibration error	±3% opacity, maximum.
f. Zero and span drift	±1% opacity, 30 minutes.
g. Response time	5 seconds.

3.3.1 Calibration. The smoke meter is calibrated after allowing a minimum of 30 minutes warmup by alternately producing simulated opacity of 0 percent and 100 percent. When stable response at 0 percent or 100 percent is noted, the smoke meter is adjusted to produce an output of 0 percent or 100 percent, as appropriate. This calibration shall be repeated until stable 0 percent and 100

percent readings are produced without adjustment. Simulated 0 percent and 100 percent opacity values may be produced by alternately switching the power to the light source on and off while the smoke generator is not producing smoke.

3.3.2 Smoke Meter Evaluation. The smoke meter design and performance are to be evaluated as follows:

3.3.2.1 Light Source. Verify from manufacturer's data and from voltage measurements made at the lamp, as installed, that the lamp is operated within ±5 percent of the nominal rated voltage.

3.3.2.2 Spectral Response of Photocell. Verify from manufacturer's data that the photocell has a photopic response; i.e., the spectral sensitivity of the cell shall closely approximate the standard spectral-luminosity curve for photopic vision which is referenced in (b) of Table 9–1.

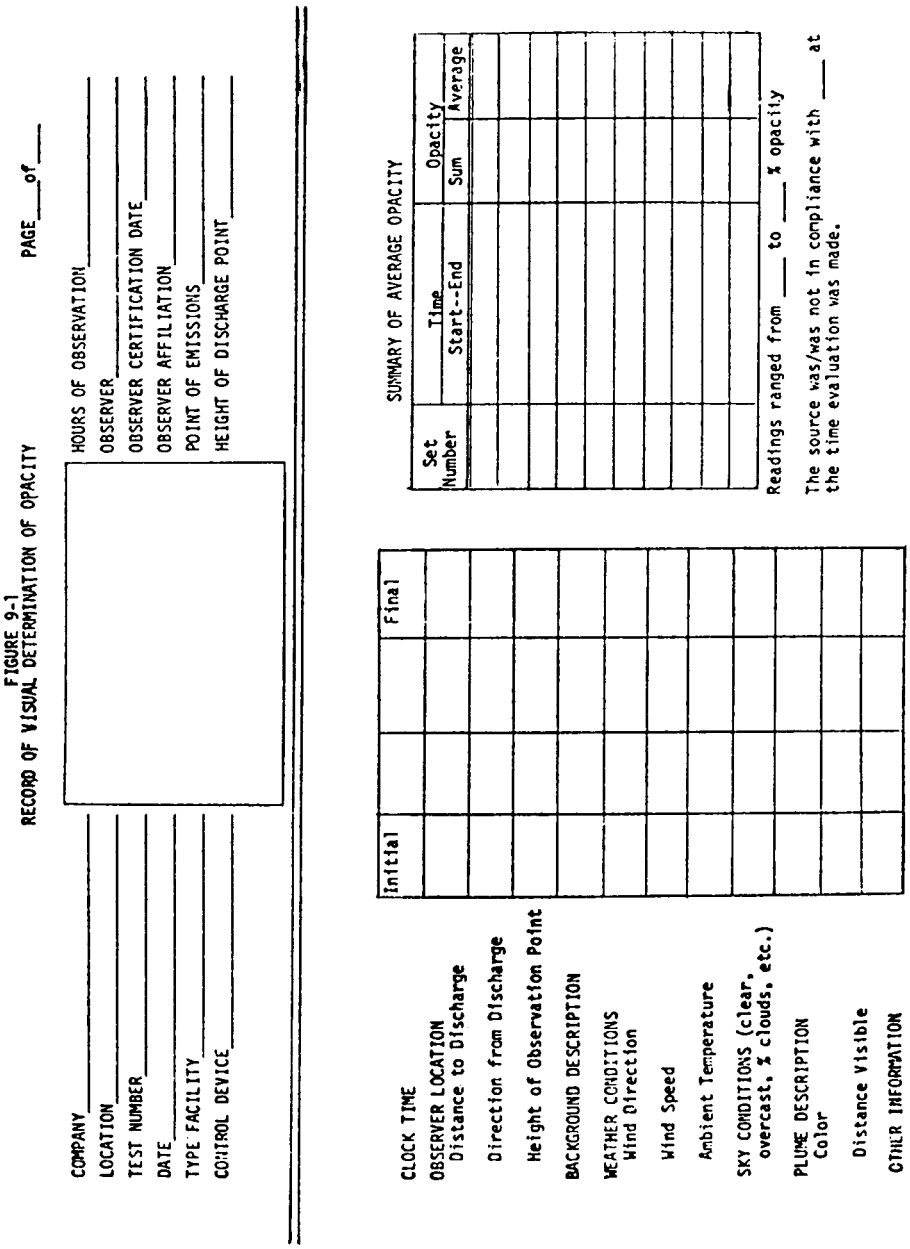

FIGURE 9–2—OBSERVATION RECORD

Page ___ of ___

Company .....
Location .....
Test Number .....
Date.

Observer .....
Type facility .....
Point of emissions .....

Hr.	Min.	Seconds				Steam plume (check if applicable)		Comments
		0	15	30	45	Attached	Detached	
	0							
	1							
	2							
	3							
	4							
	5							
	6							
	7							
	8							
	9							
	10							
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	29							

FIGURE 9–2—OBSERVATION RECORD (CONTINUED)

Page ____ of ____

Company .....
Location .....
Test Number .....
Date.

Observer .....
Type facility .....
Point of emissions .....

Hr.	Min.	Seconds				Steam plume (check if applicable)		Comments
		0	15	30	45	Attached	Detached	
	30							

Hr.	Min.	Seconds				Steam plume (check if applicable)		Comments
		0	15	30	45	Attached	Detached	
	31							
	32							
	33							
	34							
	35							
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3.3.2.3 Angle of View. Check construction geometry to ensure that the total angle of view of the smoke plume, as seen by the photocell, does not exceed 15°. The total angle of view may be calculated from: $\theta = 2 \tan^{-1} d/2L$, where θ = total angle of view; d = the sum of the photocell diameter + the diameter of the limiting aperture; and L = the distance from the photocell to the limiting aperture. The limiting aperture is the point in the path between the photocell and the smoke plume where the angle of view is most restricted. In smoke generator smoke meters this is normally an orifice plate.

3.3.2.4 Angle of Projection. Check construction geometry to ensure that the total angle of projection of the lamp on the smoke plume does not exceed 15°. The total angle of projection may be calculated from: $\theta = 2 \tan^{-1} d/2L$, where θ = total angle of projection; d = the sum of the length of the lamp

filament + the diameter of the limiting aperture; and L = the distance from the lamp to the limiting aperture.

3.3.2.5 Calibration Error. Using neutral-density filters of known opacity, check the error between the actual response and the theoretical linear response of the smoke meter. This check is accomplished by first calibrating the smoke meter according to 3.3.1 and then inserting a series of three neutral-density filters of nominal opacity of 20, 50, and 75 percent in the smoke meter pathlength. Filters calibrated within ±2 percent shall be used. Care should be taken when inserting the filters to prevent stray light from affecting the meter. Make a total of five nonconsecutive readings for each filter. The maximum error on any one reading shall be 3 percent opacity.

3.3.2.6 Zero and Span Drift. Determine the zero and span drift by calibrating and operating the smoke generator in a normal manner over a 1-hour period. The drift is measured by checking the zero and span at the end of this period.

3.3.2.7 Response Time. Determine the response time by producing the series of five simulated 0 percent and 100 percent opacity values and observing the time required to reach stable response. Opacity values of 0 percent and 100 percent may be simulated by alternately switching the power to the light source off and on while the smoke generator is not operating.

4. Bibliography

1. Air Pollution Control District Rules and Regulations, Los Angeles County Air Pollution Control District, Regulation IV, Prohibitions, Rule 50.

2. Weisburd, Melvin I., Field Operations and Enforcement Manual for Air, U.S. Environmental Protection Agency, Research Triangle Park, NC. APTD–1100, August 1972, pp. 4.1–4.36.

3. Condon, E.U., and Odishaw, H., Handbook of Physics, McGraw-Hill Co., New York, NY, 1958, Table 3.1, p. 6–52.

Alternate Method 1—Determination of the Opacity of Emissions From Stationary Sources Remotely by Lidar

This alternate method provides the quantitative determination of the opacity of an emissions plume remotely by a mobile lidar system (laser radar; Light Detection and Ranging). The method includes procedures for the calibration of the lidar and procedures to be used in the field for the lidar determination of plume opacity. The lidar is used to measure plume opacity during either day or nighttime hours because it contains its own pulsed light source or transmitter. The operation of the lidar is not dependent upon ambient lighting conditions (light, dark, sunny or cloudy).

The lidar mechanism or technique is applicable to measuring plume opacity at numerous wavelengths of laser radiation. However, the performance evaluation and calibration test results given in support of this method apply only to a lidar that employs a ruby (red light) laser [Reference 5.1].

1. Principle and Applicability

1.1 Principle. The opacity of visible emissions from stationary sources (stacks, roof vents, etc.) is measured remotely by a mobile lidar (laser radar).

1.2 Applicability. This method is applicable for the remote measurement of the opacity of visible emissions from stationary sources during both nighttime and daylight conditions, pursuant to 40 CFR §60.11(b). It is also applicable for the calibration and performance verification of the mobile lidar for the measurement of the opacity of emissions. A performance/design specification for a basic lidar system is also incorporated into this method.

1.3 Definitions.

Azimuth angle: The angle in the horizontal plane that designates where the laser beam is pointed. It is measured from an arbitrary fixed reference line in that plane.

Backscatter: The scattering of laser light in a direction opposite to that of the incident laser beam due to reflection from particulates along the beam's atmospheric path which may include a smoke plume.

Backscatter signal: The general term for the lidar return signal which results from laser light being backscattered by atmospheric and smoke plume particulates.

Convergence distance: The distance from the lidar to the point of overlap of the lidar receiver's field-of-view and the laser beam.

Elevation angle: The angle of inclination of the laser beam referenced to the horizontal plane.

Far region: The region of the atmosphere's path along the lidar line-of-sight beyond or behind the plume being measured.

Lidar: Acronym for Light Detection and Ranging.

Lidar range: The range or distance from the lidar to a point of interest along the lidar line-of-sight.

Near region: The region of the atmospheric path along the lidar line-of-sight between the lidar's convergence distance and the plume being measured.

Opacity: One minus the optical transmittance of a smoke plume, screen target, etc.

Pick interval: The time or range intervals in the lidar backscatter signal whose minimum average amplitude is used to calculate opacity. Two pick intervals are required, one in the near region and one in the far region.

Plume: The plume being measured by lidar.

Plume signal: The backscatter signal resulting from the laser light pulse passing through a plume.

$1/R^2$Correction: The correction made for the systematic decrease in lidar backscatter signal amplitude with range.

Reference signal: The backscatter signal resulting from the laser light pulse passing through ambient air.

Sample interval: The time period between successive samples for a digital signal or between successive measurements for an analog signal.

Signal spike: An abrupt, momentary increase and decrease in signal amplitude.

Source: The source being tested by lidar.

Time reference: The time (t_o) when the laser pulse emerges from the laser, used as the reference in all lidar time or range measurements.

2. Procedures

The mobile lidar calibrated in accordance with Paragraph 3 of this method shall use the following procedures for remotely measuring the opacity of stationary source emissions:

2.1 Lidar Position. The lidar shall be positioned at a distance from the plume sufficient to provide an unobstructed view of the source emissions. The plume must be at a range of at least 50 meters or three consecutive pick intervals (whichever is greater) from the lidar's transmitter/receiver convergence distance along the line-of-sight. The maximum effective opacity measurement distance of the lidar is a function of local atmospheric conditions, laser beam diameter, and plume diameter. The test position of the lidar shall be selected so that the diameter of the laser beam at the measurement point within the plume shall be no larger than three-fourths the plume diameter. The beam diameter is calculated by Equation (AM1–1):

$$D(\text{lidar}) = A + R\varphi \leq 0.75\ D(\text{Plume}) \quad \text{(AM1–1)}$$

Where:

D(Plume) = diameter of the plume (cm),
φ = laser beam divergence measured in radians
R = range from the lidar to the source (cm)
D(Lidar) = diameter of the laser beam at range R (cm),
A = diameter of the laser beam or pulse where it leaves the laser.

The lidar range, R, is obtained by aiming and firing the laser at the emissions source structure immediately below the outlet. The range value is then determined from the backscatter signal which consists of a signal spike (return from source structure) and the atmospheric backscatter signal [Reference 5.1]. This backscatter signal should be recorded.

When there is more than one source of emissions in the immediate vicinity of the plume, the lidar shall be positioned so that the laser beam passes through only a single plume, free from any interference of the other plumes for a minimum of 50 meters or three consecutive pick intervals (whichever is greater) in each region before and beyond the plume along the line-of-sight (determined from the backscatter signals). The lidar shall initially be positioned so that its line-of-sight is approximately perpendicular to the plume.

When measuring the opacity of emissions from rectangular outlets (e.g., roof monitors, open baghouses, noncircular stacks, etc.), the lidar shall be placed in a position so that its line-of-sight is approximately perpendicular to the longer (major) axis of the outlet.

2.2 Lidar Operational Restrictions. The lidar receiver shall not be aimed within an angle of ±15° (cone angle) of the sun.

This method shall not be used to make opacity measurements if thunderstorms, snowstorms, hail storms, high wind, high-ambient dust levels, fog or other atmospheric conditions cause the reference signals to consistently exceed the limits specified in section 2.3.

2.3 Reference Signal Requirements. Once placed in its proper position for opacity measurement, the laser is aimed and fired with the line-of-sight near the outlet height and rotated horizontally to a position clear of the source structure and the associated plume. The backscatter signal obtained from this position is called the ambient-air or reference signal. The lidar operator shall inspect this signal [Section V of Reference 5.1] to: (1) determine if the lidar line-of-sight is free from interference from other plumes and from physical obstructions such as cables, power lines, etc., for a minimum of 50 meters or three consecutive pick intervals (whichever is greater) in each region before and beyond the plume, and (2) obtain a qualitative measure of the homogeneity of the ambient air by noting any signal spikes.

Should there be any signal spikes on the reference signal within a minimum of 50 meters or three consecutive pick intervals (whichever is greater) in each region before and beyond the plume, the laser shall be fired three more times and the operator shall inspect the reference signals on the display. If the spike(s) remains, the azimuth angle shall be changed and the above procedures conducted again. If the spike(s) disappears in all three reference signals, the lidar line-of-sight is acceptable if there is shot-to-shot consistency and there is no interference from other plumes.

Shot-to-shot consistency of a series of reference signals over a period of twenty seconds is verified in either of two ways. (1) The lidar operator shall observe the reference signal amplitudes. For shot-to-shot consistency the ratio of R_f to R_n [amplitudes of the near and far region pick intervals (Section 2.6.1)] shall vary by not more than ±6% between shots; or (2) the lidar operator shall accept any one of the reference signals and

treat the other two as plume signals; then the opacity for each of the subsequent reference signals is calculated (Equation AM1–2). For shot-to-shot consistency, the opacity values shall be within ±3% of 0% opacity and the associated S_o values less than or equal to 8% (full scale) [Section 2.6].

If a set of reference signals fails to meet the requirements of this section, then all plume signals [Section 2.4] from the last set of acceptable reference signals to the failed set shall be discarded.

2.3.1 Initial and Final Reference Signals. Three reference signals shall be obtained within a 90-second time period prior to any data run. A final set of three reference signals shall be obtained within three (3) minutes after the completion of the same data run.

2.3.2 Temporal Criterion for Additional Reference Signals. An additional set of reference signals shall be obtained during a data run if there is a change in wind direction or plume drift of 30° or more from the direction that was prevalent when the last set of reference signals was obtained. An additional set of reference signals shall also be obtained if there is an increase in value of S_{In} (near region standard deviation, Equation AM1–5) or S_{If} (far region standard deviation, Equation AM1–6) that is greater than 6% (full scale) over the respective values calculated from the immediately previous plume signal, and this increase in value remains for 30 seconds or longer. An additional set of reference signals shall also be obtained if there is a change in amplitude in either the near or the far region of the plume signal, that is greater than 6% of the near signal amplitude and this change in amplitude remains for 30 seconds or more.

2.4 Plume Signal Requirements. Once properly aimed, the lidar is placed in operation with the nominal pulse or firing rate of six pulses/minute (1 pulse/10 seconds). The lidar operator shall observe the plume backscatter signals to determine the need for additional reference signals as required by section 2.3.2. The plume signals are recorded from lidar start to stop and are called a data run. The length of a data run is determined by operator discretion. Short-term stops of the lidar to record additional reference signals do not constitute the end of a data run if plume signals are resumed within 90 seconds after the reference signals have been recorded, and the total stop or interrupt time does not exceed 3 minutes.

2.4.1 Non-hydrated Plumes. The laser shall be aimed at the region of the plume which displays the greatest opacity. The lidar operator must visually verify that the laser is aimed clearly above the source exit structure.

2.4.2 Hydrated Plumes. The lidar will be used to measure the opacity of hydrated or so-called steam plumes. As listed in the reference method, there are two types, i.e., attached and detached steam plumes.

2.4.2.1 Attached Steam Plumes. When condensed water vapor is present within a plume, lidar opacity measurements shall be made at a point within the residual plume where the condensed water vapor is no longer visible. The laser shall be aimed into the most dense region (region of highest opacity) of the residual plume.

During daylight hours the lidar operator locates the most dense portion of the residual plume visually. During nighttime hours a high-intensity spotlight, night vision scope, or low light level TV, etc., can be used as an aid to locate the residual plume. If visual determination is ineffective, the lidar may be used to locate the most dense region of the residual plume by repeatedly measuring opacity, along the longitudinal axis or center of the plume from the emissions outlet to a point just beyond the steam plume. The lidar operator should also observe color differences and plume reflectivity to ensure that the lidar is aimed completely within the residual plume. If the operator does not obtain a clear indication of the location of the residual plume, this method shall not be used.

Once the region of highest opacity of the residual plume has been located, aiming adjustments shall be made to the laser line-of-sight to correct for the following: movement to the region of highest opacity out of the lidar line-of-sight (away from the laser beam) for more than 15 seconds, expansion of the steam plume (air temperature lowers and/or relative humidity increases) so that it just begins to encroach on the field-of-view of the lidar's optical telescope receiver, or a decrease in the size of the steam plume (air temperature higher and/or relative humidity decreases) so that regions within the residual plume whose opacity is higher than the one being monitored, are present.

2.4.2.2 Detached Steam Plumes. When the water vapor in a hydrated plume condenses and becomes visible at a finite distance from the stack or source emissions outlet, the opacity of the emissions shall be measured in the region of the plume clearly above the emissions outlet and below condensation of the water vapor.

During daylight hours the lidar operators can visually determine if the steam plume is detached from the stack outlet. During nighttime hours a high-intensity spotlight, night vision scope, low light level TV, etc., can be used as an aid in determining if the steam plume is detached. If visual determination is ineffective, the lidar may be used to determine if the steam plume is detached by repeatedly measuring plume opacity from the outlet to the steam plume along the plume's longitudinal axis or center line. The lidar operator should also observe color differences and plume reflectivity to detect a

detached plume. If the operator does not obtain a clear indication of the location of the detached plume, this method shall not be used to make opacity measurements between the outlet and the detached plume.

Once the determination of a detached steam plume has been confirmed, the laser shall be aimed into the region of highest opacity in the plume between the outlet and the formation of the steam plume. Aiming adjustments shall be made to the lidar's line-of-sight within the plume to correct for changes in the location of the most dense region of the plume due to changes in wind direction and speed or if the detached steam plume moves closer to the source outlet encroaching on the most dense region of the plume. If the detached steam plume should move too close to the source outlet for the lidar to make interference-free opacity measurements, this method shall not be used.

2.5 Field Records. In addition to the recording recommendations listed in other sections of this method the following records should be maintained. Each plume measured should be uniquely identified. The name of the facility, type of facility, emission source type, geographic location of the lidar with respect to the plume, and plume characteristics should be recorded. The date of the test, the time period that a source was monitored, the time (to the nearest second) of each opacity measurement, and the sample interval should also be recorded. The wind speed, wind direction, air temperature, relative humidity, visibility (measured at the lidar's position), and cloud cover should be recorded at the beginning and end of each time period for a given source. A small sketch depicting the location of the laser beam within the plume should be recorded.

If a detached or attached steam plume is present at the emissions source, this fact should be recorded. Figures AM1–I and AM1–II are examples of logbook forms that may be used to record this type of data. Magnetic tape or paper tape may also be used to record data.

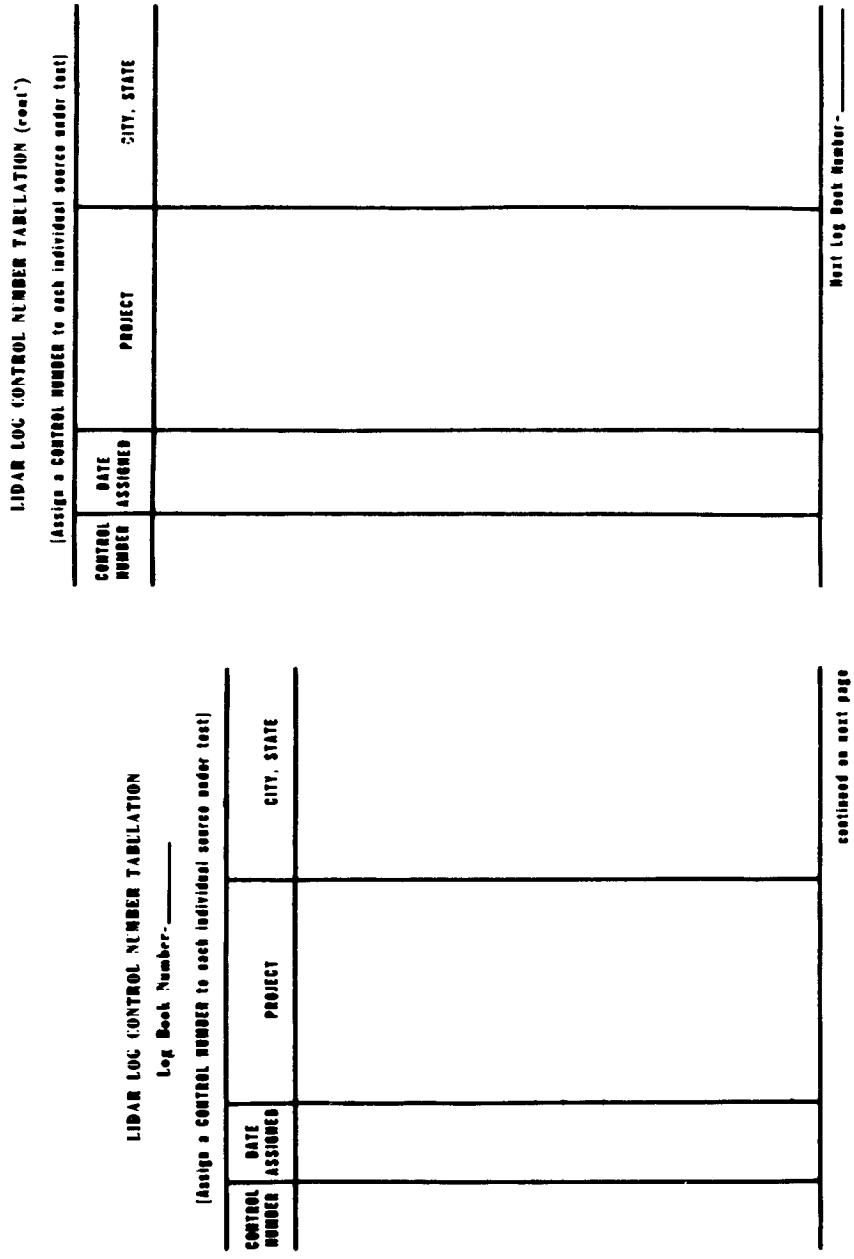


Figure AM1-1 Lidar Log Control Number Tabulation

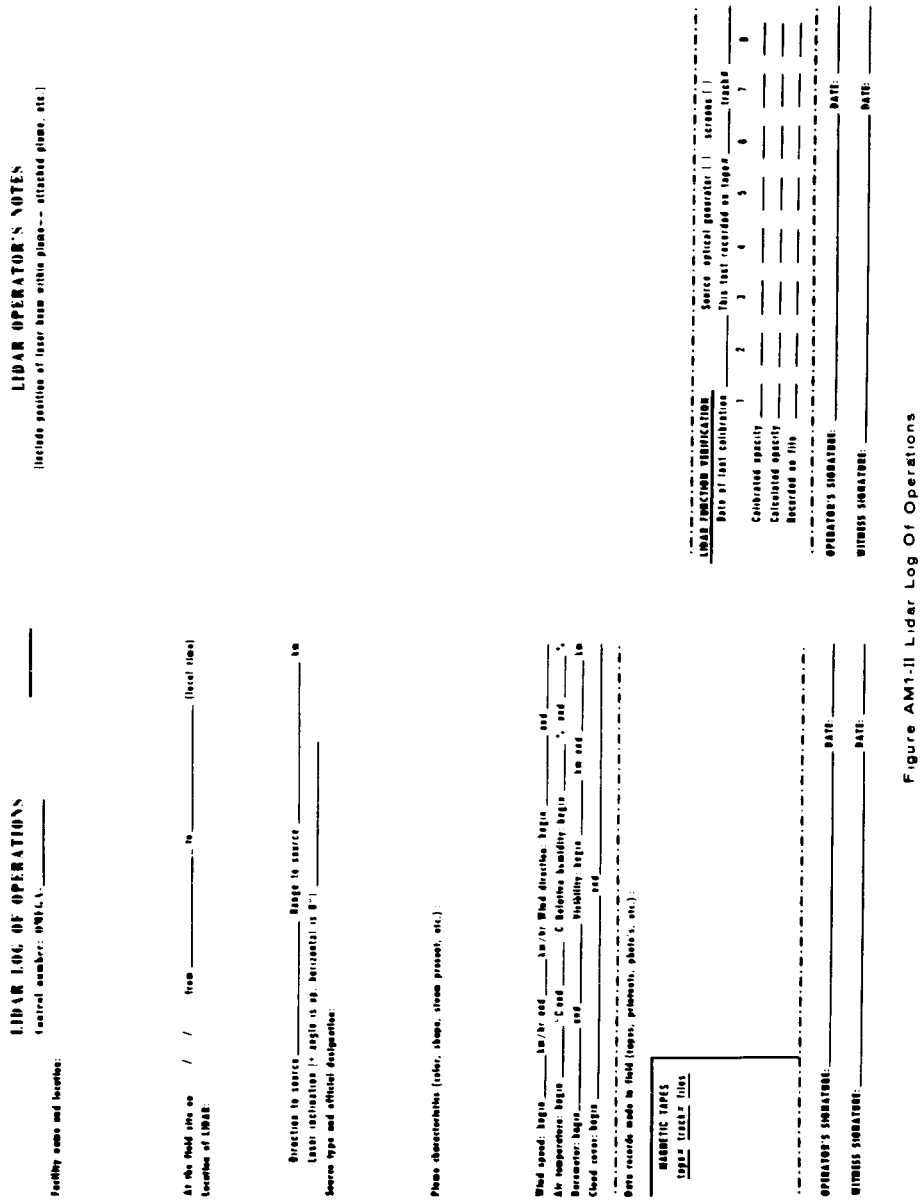
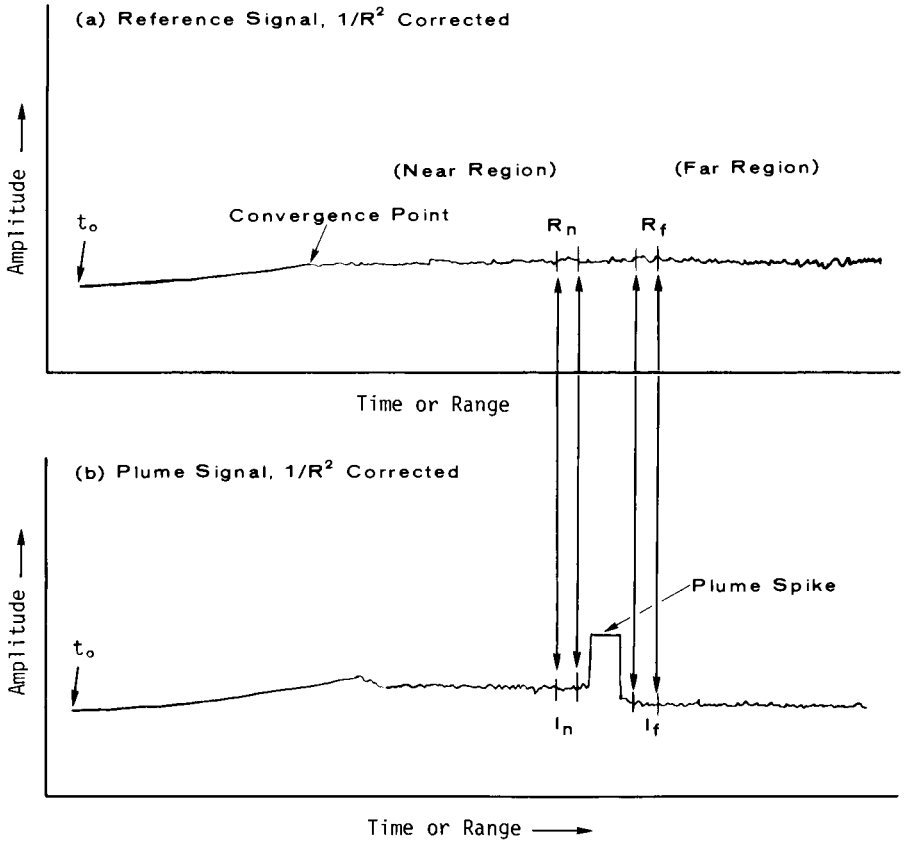


Figure AM1-11 Lidar Log Of Operations



(a) Reference signal, $1/R^2$-corrected. This reference signal is for plume signal (b). R_n, R_f are chosen to coincide with I_n, I_f.

(b) Plume signal, $1/R^2$-corrected. The plume spike and the decrease in the backscatter signal amplitude in the far region are due to the opacity of the plume. I_n, I_f are chosen as indicated in Section 2.6.

Figure AM1-III. Plots of Lidar Backscatter Signals

2.6 Opacity Calculation and Data Analysis. Referring to the reference signal and plume signal in Figure AM1–III, the measured opacity (O_p) in percent for each lidar measurement is calculated using Equation AM1–2. ($O_p = 1 - T_p$; T_p is the plume transmittance.)

$$O_p = (100\%)\left[1 - \left(\frac{I_f}{R_f}\frac{R_n}{I_n}\right)^{\frac{1}{2}}\right], \quad \text{(AM1-2)}$$

Where:

I_n = near-region pick interval signal amplitude, plume signal, $1/R^2$ corrected,

I_f = far-region pick interval signal amplitude, plume signal, $1/R^2$ corrected,

R_n = near-region pick interval signal amplitude, reference signal, $1/R^2$ corrected, and

R_f = far-region pick interval signal amplitude, reference signal, $1/R^2$ corrected.

The $1/R^2$ correction to the plume and reference signal amplitudes is made by multiplying the amplitude for each successive sample interval from the time reference, by the square of the lidar time (or range) associated with that sample interval [Reference 5.1].

The first step in selecting the pick intervals for Equation AM1–2 is to divide the plume signal amplitude by the reference signal amplitude at the same respective ranges to obtain a ''normalized'' signal. The pick intervals selected using this normalized signal, are a minimum of 15 m (100 nanoseconds) in length and consist of at least 5 contiguous sample intervals. In addition, the following criteria, listed in order of importance, govern pick interval selection. (1) The intervals shall be in a region of the normalized signal where the reference signal meets the requirements of section 2.3 and is everywhere greater than zero. (2) The intervals (near and far) with the minimum average amplitude are chosen. (3) If more than one interval with the same minimum average amplitude is found, the interval closest to the plume is chosen. (4) The standard deviation, S_o, for the calculated opacity shall be 8% or less. (S_o is calculated by Equation AM1–7).

If S_o is greater than 8%, then the far pick interval shall be changed to the next interval of minimal average amplitude. If S_o is still greater than 8%, then this procedure is repeated for the far pick interval. This procedure may be repeated once again for the near pick interval, but if S_o remains greater than 8%, the plume signal shall be discarded.

The reference signal pick intervals, R_n and R_f, must be chosen over the same time interval as the plume signal pick intervals, I_n and I_f, respectively [Figure AM1–III]. Other methods of selecting pick intervals may be used if they give equivalent results. Field-oriented examples of pick interval selection are available in Reference 5.1.

The average amplitudes for each of the pick intervals, I_n, I_f, R_n, R_f, shall be calculated by averaging the respective individual amplitudes of the sample intervals from the plume signal and the associated reference signal each corrected for $1/R^2$. The amplitude of I_n shall be calculated according to Equation (AM–3).

$$I_n = \frac{1}{m}\sum_{i=1}^{m} I_{ni}, \quad \text{(AM1-3)}$$

Where:

I_{ni} = the amplitude of the ith sample interval (near-region),

Σ = sum of the individual amplitudes for the sample intervals,

m = number of sample intervals in the pick interval, and

I_n = average amplitude of the near-region pick interval.

Similarly, the amplitudes for I_f, R_n, and R_f are calculated with the three expressions in Equation (AM1–4).

$$I_f = \frac{1}{m}\sum_{i=1}^{m} I_{fi}, \quad R_n = \frac{1}{m}\sum_{i=1}^{m} R_{ni}, \quad R_f = \frac{1}{m}\sum_{i=1}^{m} R_{fi}. \quad \text{(AM1-4)}$$

The standard deviation, S_{In}, of the set of amplitudes for the near-region pick interval, I_n, shall be calculated using Equation (AM1–5).

Similarly, the standard deviations S_{If}, S_{Rn}, and S_{Rf} are calculated with the three expressions in Equation (AM1–6).

$$S_{In} = \left[\sum_{i=1}^{m} \frac{(I_{ni} - I_n)^2}{(m-1)} \right]^{1/2} \qquad S_{If} = \left[\sum_{i=1}^{m} \frac{(I_{fi} - I_f)^2}{(m-1)} \right]^{1/2} \qquad \text{(AM1-5)}$$

$$S_{Rn} = \left[\sum_{i=1}^{m} \frac{(R_{ni} - R_n)^2}{(m-1)} \right]^{1/2},$$

$$S_{Rf} = \left[\sum_{i=1}^{m} \frac{(R_{fi} - R_f)^2}{(m-1)} \right]^{1/2}. \qquad \text{(AM1-6)}$$

The standard deviation, S_o, for each associated opacity value, O_p, shall be calculated using Equation (AM1–7).

$$S_o = \frac{(100\%)}{2} \left(\frac{I_f}{R_f} \frac{R_n}{I_n} \right)^{1/2} \left[\frac{S_{In}^2}{I_n^2} + \frac{S_{If}^2}{I_f^2} + \frac{S_{Rn}^2}{R_n^2} + \frac{S_{Rf}^2}{R_f^2} \right]^{1/2} \qquad \text{(AM1-7)}$$

The calculated values of I_n, I_f, R_n, R_f, S_{In}, S_{If}, S_{Rn}, S_{Rf}, O_p, and S_o should be recorded. Any plume signal with an S_o greater than 8% shall be discarded.

2.6.1 Azimuth Angle Correction. If the azimuth angle correction to opacity specified in this section is performed, then the elevation angle correction specified in section 2.6.2 shall not be performed. When opacity is measured in the residual region of an attached steam plume, and the lidar line-of-sight is not perpendicular to the plume, it may be necessary to correct the opacity measured by the lidar to obtain the opacity that would be measured on a path perpendicular to the plume. The following method, or any other method which produces equivalent results, shall be used to determine the need for a correction, to calculate the correction, and to document the point within the plume at which the opacity was measured.

Figure AM1–IV(b) shows the geometry of the opacity correction. L′ is the path through the plume along which the opacity measurement is made. P′ is the path perpendicular to the plume at the same point. The angle ε is the angle between L′ and the plume center line. The angle (π/2-ε), is the angle between the L′ and P′. The measured opacity, O_p, measured along the path L′ shall be corrected to obtain the corrected opacity, O_{pc}, for the path P′, using Equation (AM1–8).

$$O_{pc} = (100\%)\left[1 - (1 - 0.01\, O_p)^{\text{Cos}\,(\pi/2-\varepsilon)} \right]$$

$$= (100\%)\left[1 - (1 - 0.01\, O_p)^{\text{Sin}\,\varepsilon} \right] \qquad \text{(AM1-8)}$$

The correction in Equation (AM1–8) shall be performed if the inequality in Equation (AM1–9) is true.

$$\varepsilon \geq \text{Sin}^{-1}\left[\frac{\ln(101 - O_p)}{\ln(100 - O_p)}\right] \qquad \text{(AM1-9)}$$

Figure AM1–IV(a) shows the geometry used to calculate ε and the position in the plume at which the lidar measurement is made. This analysis assumes that for a given lidar measurement, the range from the lidar to the plume, the elevation angle of the lidar from the horizontal plane, and the azimuth angle of the lidar from an arbitrary fixed reference in the horizontal plane can all be obtained directly.

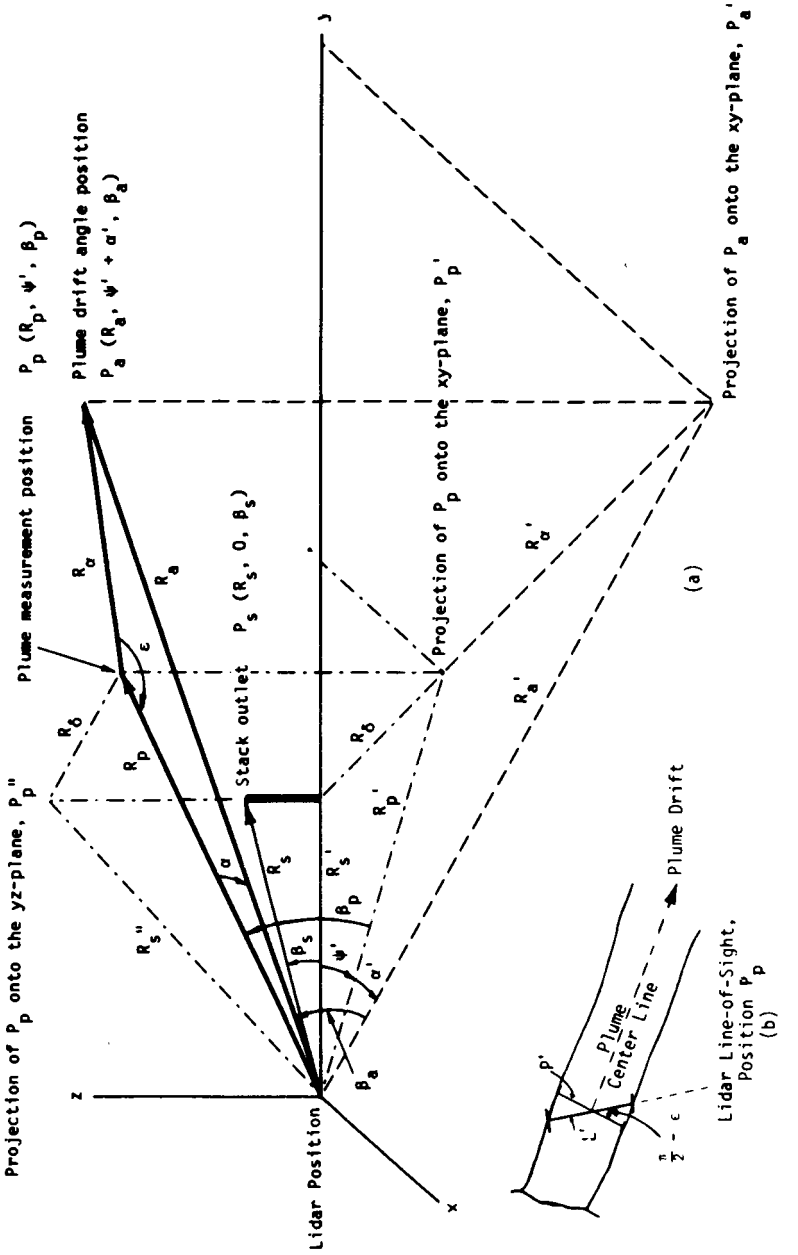


Figure AMI - IV. Correction in Opacity for Drift of the Residual Region of an Attached Steam Plume.

R_s = range from lidar to source*
β_s = elevation angle of R_s*
R_p = range from lidar to plume at the opacity measurement point*
β_p = elevation angle of R_p*
R_a = range from lidar to plume at some arbitrary point, P_a, so the drift angle of the plume can be determined*

β_a = elevation angle of R_a*
α = angle between R_p and R_a
R'_s = projection of R_s in the horizontal plane
R'_p = projection of R_p in the horizontal plane
R'_a = projection of R_a in the horizontal plane
ψ' = angle between R'_s and R'_p*
α' = angle between R'_p and R'_a*
R≤ = distance from the source to the opacity measurement point projected in the horizontal plane
Rθ = distance from opacity measurement point P_p to the point in the plume P_a.

$$O_{pc} = 1 - (1 - O_p)^{\mathrm{Cos}\,(\pi/2-\varepsilon)} = 1 - (1 - O_p)^{\mathrm{Sin}\,\varepsilon} \qquad \text{(AMI-8)}$$

The correction angle ε shall be determined using Equation AM1–10.

Where:

$\alpha = \mathrm{Cos}^{-1}\,(\mathrm{Cos}\beta_p\,\mathrm{Cos}\beta_a\,\mathrm{Cos}\alpha' + \mathrm{Sin}\beta_p\,\mathrm{Sin}\beta_a)$, and

$R\theta = (R_p 2 + R_a 2 - 2\,R_p\,R_a\,\mathrm{Cos}\alpha)^{1/2}$

R≤, the distance from the source to the opacity measurement point projected in the horizontal plane, shall be determined using Equation AM1–11.

$$R_\delta = (R'^2_s + R'^2_p - 2R'_sR'_p\mathrm{Cos}\psi')^{\frac{1}{2}}, \qquad \text{(AM1-11)}$$

Where:

$R'_s = R_s\,\mathrm{Cos}\,\beta_s$, and
$R'_p = R_p\,\mathrm{Cos}\,\beta_p$.

In the special case where the plume centerline at the opacity measurement point is horizontal, parallel to the ground, Equation AM1–12 may be used to determine ε instead of Equation AM1–10.

$$\varepsilon = \mathrm{Cos}^{-1}\left[\frac{R_p^2 + R_\delta^2 - R''^2_s}{2\,R_p\,R_\delta}\right] \qquad \text{(AM1-12)}$$

Where:

$R''_s = (R'^2_s + R_p^2\mathrm{Sin}^2\beta_p)^{1/2}$.

If the angle ε is such that ε≤30° or ε ≥150°, the azimuth angle correction shall not be performed and the associated opacity value shall be discarded.

2.6.2 Elevation Angle Correction. An individual lidar-measured opacity, O_p, shall be corrected for elevation angle if the laser elevation or inclination angle, β_p [Figure AM1–V], is greater than or equal to the value calculated in Equation AM1–13.

$$\beta_p \geq \mathrm{Cos}^{-1}\left[\frac{\ln\,(101 - O_p)}{\ln\,(100 - O_p)}\right] \qquad \text{(AM1-13)}$$

The measured opacity, O_p, along the lidar path L, is adjusted to obtain the corrected opacity, O_{pc}, for the actual plume (horizontal) path, P, by using Equation (AM1–14).

*Obtained directly from lidar. These values should be recorded.

$$O_{pc} = (100\%)\left[1-\left(1-0.01\,O_p\right)^{Cos\beta}p\right], \qquad (AM1\text{-}14)$$

Where:

β_p = lidar elevation or inclination angle,
O_p = measured opacity along path L, and
O_{pc} = corrected opacity for the actual plume thickness P.

The values for β_p, O_p and O_{pc} should be recorded.

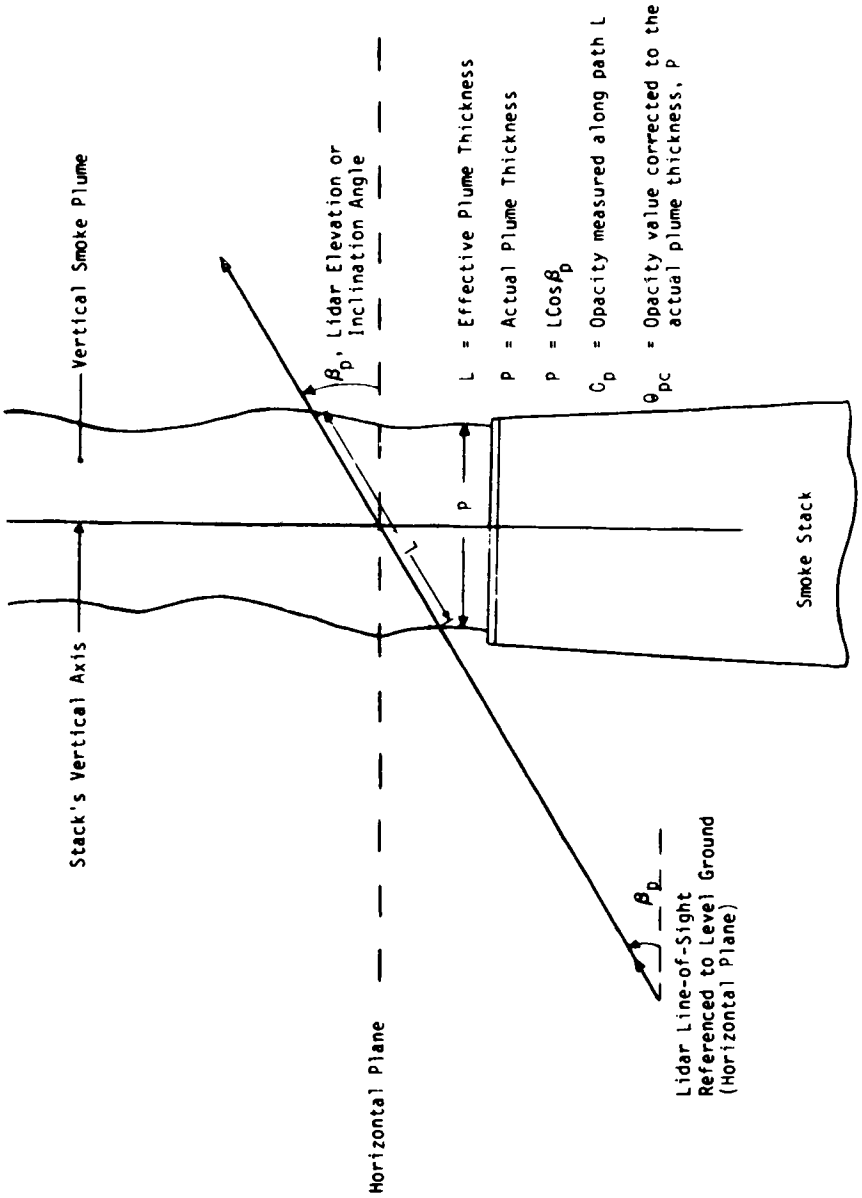


Figure AM1-V. Elevation Angle Correction for Vertical Plumes.

2.6.3 Determination of Actual Plume Opacity. Actual opacity of the plume shall be determined by Equation AM1–15.

$$O_{pa} = O_{pc} - [2\ S_o + 5\%]. \quad \text{(AM1-15)}$$

2.6.4 Calculation of Average Actual Plume Opacity. The average of the actual plume opacity, O_{pa}, shall be calculated as the average of the consecutive individual actual opacity values, O_{pa}, by Equation AM1–16.

$$\bar{O}_{pa} = \frac{1}{n}\sum_{k=1}^{n}(O_{pa})_k \quad , \qquad \text{(AM1-16)}$$

Where:

$(O_{pa})_k$ = the kth actual opacity value in an averaging interval containing n opacity values; k is a summing index.

Σ = the sum of the individual actual opacity values.

n = the number of individual actual opacity values contained in the averaging interval.

O_{pa} = average actual opacity calculated over the averaging interval.

3. Lidar Performance Verification

The lidar shall be subjected to two types of performance verifications that shall be performed in the field. The annual calibration, conducted at least once a year, shall be used to directly verify operation and performance of the entire lidar system. The routine verification, conducted for each emission source measured, shall be used to insure proper performance of the optical receiver and associated electronics.

3.1 Annual Calibration Procedures. Either a plume from a smoke generator or screen targets shall be used to conduct this calibration.

If the screen target method is selected, five screens shall be fabricated by placing an opaque mesh material over a narrow frame (wood, metal extrusion, etc.). The screen shall have a surface area of at least one square meter. The screen material should be chosen for precise optical opacities of about 10, 20, 40, 60, and 80%. Opacity of each target shall be optically determined and should be recorded. If a smoke generator plume is selected, it shall meet the requirements of section 3.3 of Reference Method 9. This calibration shall be performed in the field during calm (as practical) atmospheric conditions. The lidar shall be positioned in accordance with section 2.1.

The screen targets must be placed perpendicular to and coincident with the lidar line-of-sight at sufficient height above the ground (suggest about 30 ft) to avoid ground-level dust contamination. Reference signals shall be obtained just prior to conducting the calibration test.

The lidar shall be aimed through the center of the plume within 1 stack diameter of the exit, or through the geometric center of the screen target selected. The lidar shall be set in operation for a 6-minute data run at a nominal pulse rate of 1 pulse every 10 seconds. Each backscatter return signal and each respective opacity value obtained from the smoke generator transmissometer, shall be obtained in temporal coincidence. The data shall be analyzed and reduced in accordance with section 2.6 of this method. This calibration shall be performed for 0% (clean air), and at least five other opacities (nominally 10, 20, 40, 60, and 80%).

The average of the lidar opacity values obtained during a 6-minute calibration run shall be calculated and should be recorded. Also the average of the opacity values obtained from the smoke generator transmissometer for the same 6-minute run shall be calculated and should be recorded.

Alternate calibration procedures that do not meet the above requirements but produce equivalent results may be used.

3.2 Routine Verification Procedures. Either one of two techniques shall be used to conduct this verification. It shall be performed at least once every 4 hours for each emission source measured. The following parameters shall be directly verified.

1) The opacity value of 0% plus a minimum of 5 (nominally 10, 20, 40, 60, and 80%) opacity values shall be verified through the PMT detector and data processing electronics.

2) The zero-signal level (receiver signal with no optical signal from the source present) shall be inspected to insure that no spurious noise is present in the signal. With the entire lidar receiver and analog/digital electronics turned on and adjusted for normal operating performance, the following procedures shall be used for Techniques 1 and 2, respectively.

3.2.1 Procedure for Technique 1. This test shall be performed with no ambient or stray light reaching the PMT detector. The narrow band filter (694.3 nanometers peak) shall be removed from its position in front of the PMT detector. Neutral density filters of nominal opacities of 10, 20, 40, 60, and 80% shall be used. The recommended test configuration is depicted in Figure AM1–VI.

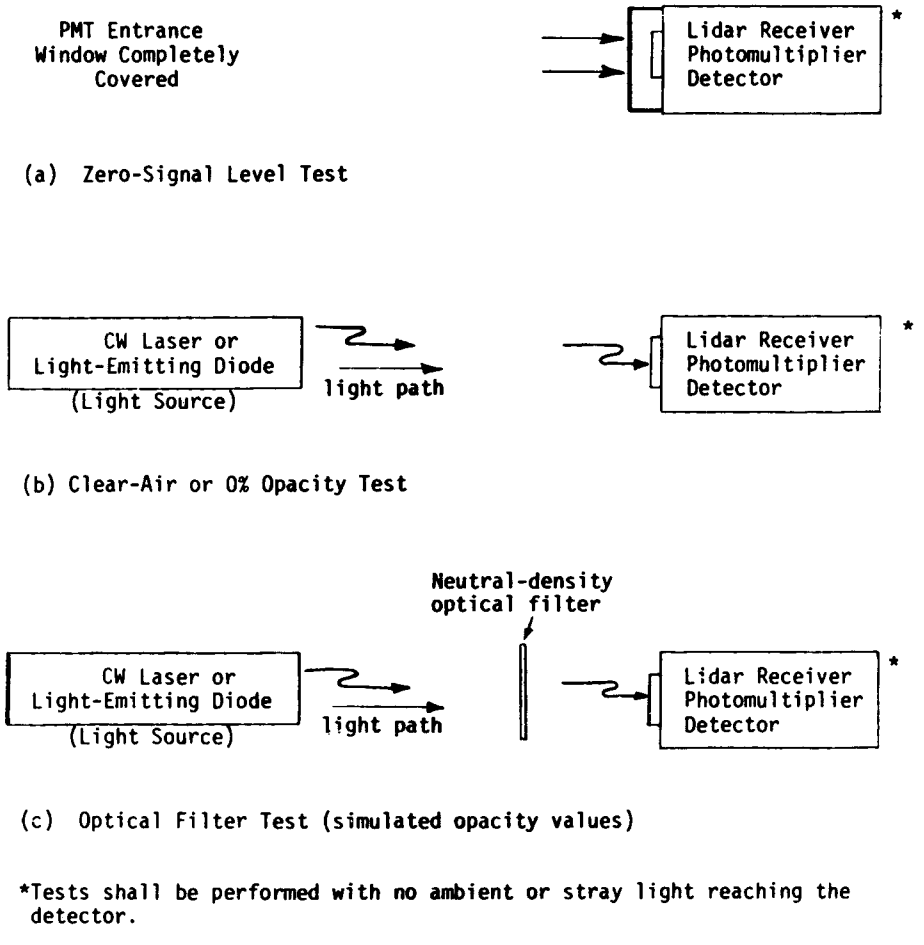


Figure AM1–VI. Test Configuration for Technique 1.

The zero-signal level shall be measured and should be recorded, as indicated in Figure AM1–VI(a). This simulated clear-air or 0% opacity value shall be tested in using the selected light source depicted in Figure AM1–VI(b).

The light source either shall be a continuous wave (CW) laser with the beam mechanically chopped or a light emitting diode controlled with a pulse generator (rectangular pulse). (A laser beam may have to be attenuated so as not to saturate the PMT detector). This signal level shall be measured

and should be recorded. The opacity value is calculated by taking two pick intervals [Section 2.6] about 1 microsecond apart in time and using Equation (AM1–2) setting the ratio $R_n/R_f = 1$. This calculated value should be recorded.

The simulated clear-air signal level is also employed in the optical test using the neutral density filters. Using the test configuration in Figure AM1–VI(c), each neutral density filter shall be separately placed into the light path from the light source to the PMT detector. The signal level shall be measured and should be recorded. The opacity value for each filter is calculated by taking the signal level for that respective filter (I_f), dividing it by the 0% opacity signal level (I_n) and performing the remainder of the calculation by Equation (AM1–2) with $R_n/R_f = 1$. The calculated opacity value for each filter should be recorded.

The neutral density filters used for Technique 1 shall be calibrated for actual opacity with accuracy of ±2% or better. This calibration shall be done monthly while the filters are in use and the calibrated values should be recorded.

3.2.2 Procedure for Technique 2. An optical generator (built-in calibration mechanism) that contains a light-emitting diode (red light for a lidar containing a ruby laser) is used. By injecting an optical signal into the lidar receiver immediately ahead of the PMT detector, a backscatter signal is simulated. With the entire lidar receiver electronics turned on and adjusted for normal operating performance, the optical generator is turned on and the simulation signal (corrected for $1/R^2$) is selected with no plume spike signal and with the opacity value equal to 0%. This simulated clear-air atmospheric return signal is displayed on the system's video display. The lidar operator then makes any fine adjustments that may be necessary to maintain the system's normal operating range.

The opacity values of 0% and the other five values are selected one at a time in any order. The simulated return signal data should be recorded. The opacity value shall be calculated. This measurement/calculation shall be performed at least three times for each selected opacity value. While the order is not important, each of the opacity values from the optical generator shall be verified. The calibrated optical generator opacity value for each selection should be recorded.

The optical generator used for Technique 2 shall be calibrated for actual opacity with an accuracy of ±1% or better. This calibration shall be done monthly while the generator is in use and calibrated value should be recorded.

Alternate verification procedures that do not meet the above requirements but produce equivalent results may be used.

3.3 Deviation. The permissible error for the annual calibration and routine verification are:

3.3.1 Annual Calibration Deviation.

3.3.1.1 Smoke Generator. If the lidar-measured average opacity for each data run is not within ±5% (full scale) of the respective smoke generator's average opacity over the range of 0% through 80%, then the lidar shall be considered out of calibration.

3.3.1.2 Screens. If the lidar-measured average opacity for each data run is not within ±3% (full scale) of the laboratory-determined opacity for each respective simulation screen target over the range of 0% through 80%, then the lidar shall be considered out of calibration.

3.3.2 Routine Verification Error. If the lidar-measured average opacity for each neutral density filter (Technique 1) or optical generator selection (Technique 2) is not within ±3% (full scale) of the respective laboratory calibration value then the lidar shall be considered non-operational.

4. Performance/Design Specification for Basic Lidar System

4.1 Lidar Design Specification. The essential components of the basic lidar system are a pulsed laser (transmitter), optical receiver, detector, signal processor, recorder, and an aiming device that is used in aiming the lidar transmitter and receiver. Figure AM1–VII shows a functional block diagram of a basic lidar system.

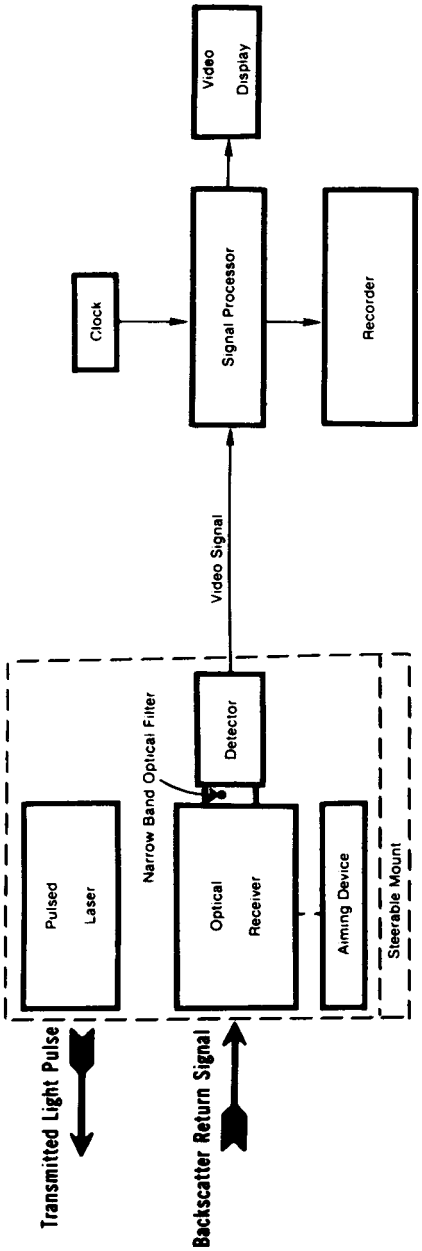


Figure AM1-VII. Functional Block Diagram of a Basic Lidar System

4.2 Performance Evaluation Tests. The owner of a lidar system shall subject such a lidar system to the performance verification tests described in section 3, prior to first use of this method. The annual calibration shall be performed for three separate, complete

runs and the results of each should be recorded. The requirements of section 3.3.1 must be fulfilled for each of the three runs.

Once the conditions of the annual calibration are fulfilled the lidar shall be subjected to the routine verification for three separate complete runs. The requirements of section 3.3.2 must be fulfilled for each of the three runs and the results should be recorded. The Administrator may request that the results of the performance evaluation be submitted for review.

5. References

5.1 The Use of Lidar for Emissions Source Opacity Determination, U.S. Environmental Protection Agency, National Enforcement Investigations Center, Denver, CO. EPA–330/1–79–003–R, Arthur W. Dybdahl, current edition [NTIS No. PB81–246662].

5.2 Field Evaluation of Mobile Lidar for the Measurement of Smoke Plume Opacity, U.S. Environmental Protection Agency, National Enforcement Investigations Center, Denver, CO. EPA/NEIC-TS-128, February 1976.

5.3 Remote Measurement of Smoke Plume Transmittance Using Lidar, C. S. Cook, G. W. Bethke, W. D. Conner (EPA/RTP). Applied Optics 11, pg 1742. August 1972.

5.4 Lidar Studies of Stack Plumes in Rural and Urban Environments, EPA–650/4–73–002, October 1973.

5.5 American National Standard for the Safe Use of Lasers ANSI Z 136.1–176, March 8, 1976.

5.6 U.S. Army Technical Manual TB MED 279, Control of Hazards to Health from Laser Radiation, February 1969.

5.7 Laser Institute of America Laser Safety Manual, 4th Edition.

5.8 U.S. Department of Health, Education and Welfare, Regulations for the Administration and Enforcement of the Radiation Control for Health and Safety Act of 1968, January 1976.

5.9 Laser Safety Handbook, Alex Mallow, Leon Chabot, Van Nostrand Reinhold Co., 1978.

Method 10—Determination of Carbon Monoxide Emissions From Stationary Sources (Instrumental Analyzer Procedure)

1.0 Scope and Application

What is Method 10?

Method 10 is a procedure for measuring carbon monoxide (CO) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis. This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 4—Determination of Moisture Content in Stack Gases.

(c) Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure).

1.1 Analytes. What does this method determine? This method measures the concentration of carbon monoxide.

Analyte	CAS No.	Sensitivity
CO	630–08–0	Typically <2% of Calibration Span.

1.2 Applicability. When is this method required? The use of Method 10 may be required by specific New Source Performance Standards, State Implementation Plans, and permits where CO concentrations in stationary source emissions must be measured, either to determine compliance with an applicable emission standard or to conduct performance testing of a continuous emission monitoring system (CEMS). Other regulations may also require the use of Method 10.

1.3 Data Quality Objectives. Refer to section 1.3 of Method 7E.

2.0 Summary of Method

In this method, you continuously or intermittently sample the effluent gas and convey the sample to an analyzer that measures the concentration of CO. You must meet the performance requirements of this method to validate your data.

3.0 Definitions

Refer to section 3.0 of Method 7E for the applicable definitions.

4.0 Interferences

Substances having a strong absorption of infrared energy may interfere to some extent in some analyzers. Instrumental correction may be used to compensate for the interference. You may also use silica gel and ascarite traps to eliminate the interferences. If this option is used, correct the measured

gas volume for the carbon dioxide (CO_2) removed in the trap.

5.0 Safety

Refer to section 5.0 of Method 7E.

6.0 Equipment and Supplies

What do I need for the measurement system?

6.1 Continuous Sampling. Figure 7E–1 of Method 7E is a schematic diagram of an acceptable measurement system. The components are the same as those in sections 6.1 and 6.2 of Method 7E, except that the CO analyzer described in section 6.2 of this method must be used instead of the analyzer described in section 6.2 of Method 7E. You must follow the noted specifications in section 6.1 of Method 7E except that the requirements to use stainless steel, Teflon, or non-reactive glass filters do not apply. Also, a heated sample line is not required to transport dry gases or for systems that measure the CO concentration on a dry basis.

6.2 Integrated Sampling.

6.2.1 Air-Cooled Condenser or Equivalent. To remove any excess moisture.

6.2.2 Valve. Needle valve, or equivalent, to adjust flow rate.

6.2.3 Pump. Leak-free diaphragm type, or equivalent, to transport gas.

6.2.4 Rate Meter. Rotameter, or equivalent, to measure a flow range from 0 to 1.0 liter per minute (0.035 cfm).

6.2.5 Flexible Bag. Tedlar, or equivalent, with a capacity of 60 to 90 liters (2 to 3 ft^3). (Verify through the manufacturer that the Tedlar alternative is suitable for CO and make this verified information available for inspection.) Leak-test the bag in the laboratory before using by evacuating with a pump followed by a dry gas meter. When the evacuation is complete, there should be no flow through the meter.

6.2.6 Sample Tank. Stainless steel or aluminum tank equipped with a pressure indicator with a minimum volume of 4 liters.

6.3 What analyzer must I use? You must use an instrument that continuously measures CO in the gas stream and meets the specifications in section 13.0. The dual-range analyzer provisions in section 6.2.8.1 of Method 7E apply.

7.0 Reagents and Standards

7.1 Calibration Gas. What calibration gases do I need? Refer to section 7.1 of Method 7E for the calibration gas requirements.

7.2 Interference Check. What additional reagents do I need for the interference check? Use the appropriate test gases listed in Table 7E–3 of Method 7E (i.e., potential interferents, as identified by the instrument manufacturer) to conduct the interference check.

8.0 Sample Collection, Preservation, Storage, and Transport

Emission Test Procedure

8.1 Sampling Site and Sampling Points. You must follow section 8.1 of Method 7E.

8.2 Initial Measurement System Performance Tests. You must follow the procedures in section 8.2 of Method 7E. If a dilution-type measurement system is used, the special considerations in section 8.3 of Method 7E also apply.

8.3 Interference Check. You must follow the procedures of section 8.2.7 of Method 7E.

8.4 Sample Collection.

8.4.1 Continuous Sampling. You must follow the procedures of section 8.4 of Method 7E.

8.4.2 Integrated Sampling. Evacuate the flexible bag or sample tank. Set up the equipment as shown in Figure 10–1 with the bag disconnected. Place the probe in the stack and purge the sampling line. Connect the bag, making sure that all connections are leak-free. Sample at a rate proportional to the stack velocity. If needed, the CO_2 content of the gas may be determined by using the Method 3 integrated sample procedures, or by weighing an ascarite CO_2 removal tube used and computing CO_2 concentration from the gas volume sampled and the weight gain of the tube. Data may be recorded on a form similar to Table 10–1. If a sample tank is used for sample collection, follow procedures similar to those in sections 8.1.2, 8.2.3, 8.3, and 12.4 of Method 25 as appropriate to prepare the tank, conduct the sampling, and correct the measured sample concentration.

8.5 Post-Run System Bias Check, Drift Assessment, and Alternative Dynamic Spike Procedure. You must follow the procedures in sections 8.5 and 8.6 of Method 7E.

9.0 Quality Control

Follow the quality control procedures in section 9.0 of Method 7E.

10.0 Calibration and Standardization

Follow the procedures for calibration and standardization in section 10.0 of Method 7E.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the procedures for calculations and data analysis in section 12.0 of Method 7E, as applicable, substituting CO for NO_X as applicable.

12.1 Concentration Correction for CO_2 Removal. Correct the CO concentration for CO_2 removal (if applicable) using Eq. 10–1.

$$C_{Avg} = C_{CO\ stack}\left(1 - F_{CO2}\right)$$

Where:

C_{Avg} = Average gas concentration for the test run, ppm.

$C_{CO\ stack}$ = Average unadjusted stack gas CO concentration indicated by the data recorder for the test run, ppmv.

F_{CO2} = Volume fraction of CO_2 in the sample, i.e., percent CO_2 from Orsat analysis divided by 100.

13.0 Method Performance

The specifications for analyzer calibration error, system bias, drift, interference check, and alternative dynamic spike procedure are the same as in section 13.0 of Method 7E.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

The dynamic spike procedure and the manufacturer stability test are the same as in sections 16.1 and 16.3 of Method 7E

17.0 References

1. ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards— September 1997 as amended, EPA–600/R–97/121

18.0 Tables, Diagrams, Flowcharts, and Validation Data

Figure 10-1. Integrated Gas Sampling Train.

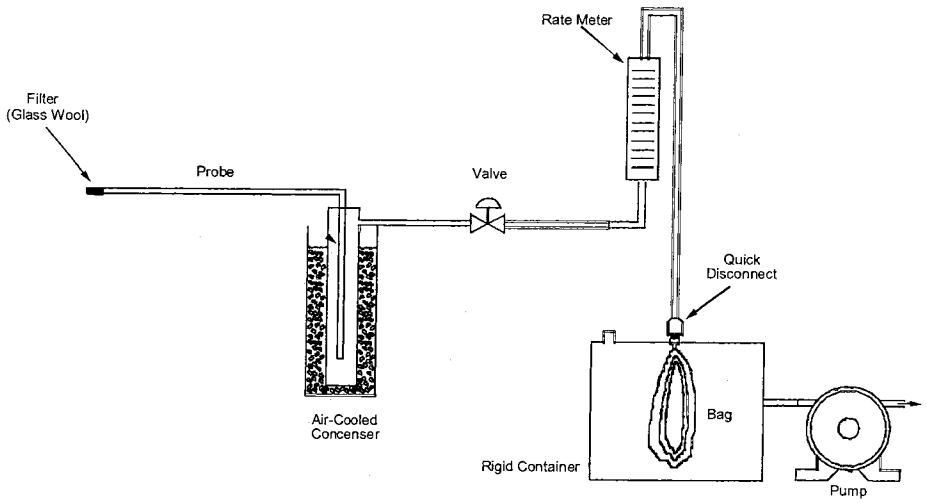


TABLE 10–1—FIELD DATA

[Integrated sampling]

Location:	Date:	
Test:	Operator:	
Clock Time	Rotameter Reading liters/min (cfm)	Comments

TABLE 10–1—FIELD DATA—Continued

[Integrated sampling]

METHOD 10A—DETERMINATION OF CARBON MONOXIDE EMISSIONS IN CERTIFYING CONTINUOUS EMISSION MONITORING SYSTEMS AT PETROLEUM REFINERIES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 4, and Method 5.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Carbon monoxide (CO)	630–08–0	3 ppmv

1.2 Applicability. This method is applicable for the determination of CO emissions at petroleum refineries. This method serves as the reference method in the relative accuracy test for nondispersive infrared (NDIR) CO continuous emission monitoring systems (CEMS) that are required to be installed in petroleum refineries on fluid catalytic cracking unit catalyst regenerators (§60.105(a)(2) of this part).

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

An integrated gas sample is extracted from the stack, passed through an alkaline permanganate solution to remove sulfur oxides and nitrogen oxides, and collected in a Tedlar or equivalent bag. (Verify through the manufacturer that the Tedlar alternative is suitable for NO and make this verified information available for inspection.) The CO concentration in the sample is measured spectrophotometrically using the reaction of CO with *p*-sulfaminobenzoic acid.

3.0 Definitions [Reserved]

4.0 Interferences

Sulfur oxides, nitric oxide, and other acid gases interfere with the colorimetric reaction. They are removed by passing the sampled gas through an alkaline potassium permanganate scrubbing solution. Carbon dioxide (CO_2) does not interfere, but, because it is removed by the scrubbing solution, its concentration must be measured independently and an appropriate volume correction made to the sampled gas.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs.

Reacts exothermically with limited amounts of water.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling train shown in Figure 10A–1 is required for sample collection. Component parts are described below:

6.1.1 Probe. Stainless steel, sheathed Pyrex glass, or equivalent, equipped with a glass wool plug to remove particulate matter.

6.1.2 Sample Conditioning System. Three Greenburg-Smith impingers connected in series with leak-free connections.

6.1.3 Pump. Leak-free pump with stainless steel and Teflon parts to transport sample at a flow rate of 300 ml/min (0.01 ft^3/min) to the flexible bag.

6.1.4 Surge Tank. Installed between the pump and the rate meter to eliminate the pulsation effect of the pump on the rate meter.

6.1.5 Rate Meter. Rotameter, or equivalent, to measure flow rate at 300 ml/min (0.01 ft^3/min). Calibrate according to section 10.2.

6.1.6 Flexible Bag. Tedlar, or equivalent, with a capacity of 10 liters (0.35 ft^3) and equipped with a sealing quick-connect plug. The bag must be leak-free according to section 8.1. For protection, it is recommended that the bag be enclosed within a rigid container.

6.1.7 Sample Tank. Stainless steel or aluminum tank equipped with a pressure indicator with a minimum volume of 10 liters.

6.1.8 Valves. Stainless-steel needle valve to adjust flow rate, and stainless-steel 3-way valve, or equivalent.

6.1.9 CO_2 Analyzer. Fyrite, or equivalent, to measure CO_2 concentration to within 0.5 percent.

6.1.10 Volume Meter. Dry gas meter, capable of measuring the sample volume under calibration conditions of 300 ml/min (0.01 ft^3/min) for 10 minutes.

6.1.11 Pressure Gauge. A water filled U-tube manometer, or equivalent, of about 30 cm (12 in.) to leak-check the flexible bag.

6.2 Sample Analysis.

6.2.1 Spectrophotometer. Single- or double-beam to measure absorbance at 425 and 600 nm. Slit width should not exceed 20 nm.

6.2.2 Spectrophotometer Cells. 1-cm pathlength.

6.2.3 Vacuum Gauge. U-tube mercury manometer, 1 meter (39 in.), with 1-mm divisions, or other gauge capable of measuring pressure to within 1 mm Hg.

6.2.4 Pump. Capable of evacuating the gas reaction bulb to a pressure equal to or less than 40 mm Hg absolute, equipped with coarse and fine flow control valves.

6.2.5 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm Hg.

6.2.6 Reaction Bulbs. Pyrex glass, 100-ml with Teflon stopcock (Figure 10A–2), leak-free at 40 mm Hg, designed so that 10 ml of the colorimetric reagent can be added and removed easily and accurately. Commercially available gas sample bulbs such as Supelco Catalog No. 2–2161 may also be used.

6.2.7 Manifold. Stainless steel, with connections for three reaction bulbs and the appropriate connections for the manometer and sampling bag as shown in Figure 10A–3.

6.2.8 Pipets. Class A, 10–ml size.

6.2.9 Shaker Table. Reciprocating-stroke type such as Eberbach Corporation, Model 6015. A rocking arm or rotary-motion type shaker may also be used. The shaker must be large enough to accommodate at least six gas sample bulbs simultaneously. It may be necessary to construct a table top extension for most commercial shakers to provide sufficient space for the needed bulbs (Figure 10A–4).

6.2.10 Valve. Stainless steel shut-off valve.

6.2.11 Analytical Balance. Capable of weighing to 0.1 mg.

7.0 Reagents and Standards

Unless otherwise indicated, all reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, the best available grade shall be used.

7.1 Sample Collection.

7.1.1 Water. Deionized distilled, to conform to ASTM D 1193–77 or 91, Type 3 (incorporated by reference—see §60.17). If high concentrations of organic matter are not expected to be present, the potassium permanganate test for oxidizable organic matter may be omitted.

7.1.2 Alkaline Permanganate Solution, 0.25 M $KMnO_4$/1.5 M Sodium Hydroxide (NaOH). Dissolve 40 g $KMnO_4$ and 60 g NaOH in approximately 900 ml water, cool, and dilute to 1 liter.

7.2 Sample Analysis.

7.2.1 Water. Same as in section 7.1.1.

7.2.2 1 M Sodium Hydroxide Solution. Dissolve 40 g NaOH in approximately 900 ml of water, cool, and dilute to 1 liter.

7.2.3 0.1 M NaOH Solution. Dilute 50 ml of the 1 M NaOH solution prepared in section 7.2.2 to 500 ml.

7.2.4 0.1 M Silver Nitrate ($AgNO_3$) Solution. Dissolve 8.5 g $AgNO_3$ in water, and dilute to 500 ml.

7.2.5 0.1 M Para-Sulfaminobenzoic Acid (p-SABA) Solution. Dissolve 10.0 g p-SABA in 0.1 M NaOH, and dilute to 500 ml with 0.1 M NaOH.

7.2.6 Colorimetric Solution. To a flask, add 100 ml of 0.1 M p-SABA solution and 100 ml of 0.1 M $AgNO_3$ solution. Mix, and add 50 ml of 1 M NaOH with shaking. The resultant solution should be clear and colorless. This solution is acceptable for use for a period of 2 days.

7.2.7 Standard Gas Mixtures. Traceable to National Institute of Standards and Technology (NIST) standards and containing between 50 and 1000 ppm CO in nitrogen. At least two concentrations are needed to span each calibration range used (Section 10.3). The calibration gases must be certified by the manufacturer to be within 2 percent of the specified concentrations.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sample Bag or Tank Leak-Checks. While a leak-check is required after bag or sample tank use, it should also be done before the bag or sample tank is used for sample collection. The tank should be leak-checked according to the procedure specified in section 8.1.2 of Method 25. The bag should be leak-checked in the inflated and deflated condition according to the following procedure:

8.1.1 Connect the bag to a water manometer, and pressurize the bag to 5 to 10 cm H_2O (2 to 4 in H_2O). Allow the bag to stand for 60 minutes. Any displacement in the water manometer indicates a leak.

8.1.2 Evacuate the bag with a leakless pump that is connected to the downstream side of a flow indicating device such as a 0- to 100-ml/min rotameter or an impinger containing water. When the bag is completely evacuated, no flow should be evident if the bag is leak-free.

8.2 Sample Collection.

8.2.1 Evacuate and leak check the sample bag or tank as specified in section 8.1. Assemble the apparatus as shown in Figure 10A–1. Loosely pack glass wool in the tip of the probe. Place 400 ml of alkaline permanganate solution in the first two impingers and 250 ml in the third. Connect the pump to the third impinger, and follow this with the surge tank, rate meter, and 3-way valve. Do not connect the bag or sample tank to the system at this time.

8.2.2 Leak-check the sampling system by plugging the probe inlet, opening the 3-way valve, and pulling a vacuum of approximately 250 mm Hg on the system while observing the rate meter for flow. If flow is indicated on the rate meter, do not proceed further until the leak is found and corrected.

8.2.3 Purge the system with sample gas by inserting the probe into the stack and drawing the sample gas through the system at 300 ml/min ±10 percent for 5 minutes. Connect the evacuated bag or sample tank to the system, record the starting time, and sample at a rate of 300 ml/min for 30 minutes, or until the bag is nearly full, or the sample tank reaches ambient pressure. Record the sampling time, the barometric pressure, and the ambient temperature. Purge the system as described above immediately before each sample.

8.2.4 The scrubbing solution is adequate for removing sulfur oxides and nitrogen oxides from 50 liters (1.8 ft^3) of stack gas when the concentration of each is less than 1,000 ppm and the CO_2 concentration is less than 15 percent. Replace the scrubber solution after every fifth sample.

8.3 Carbon Dioxide Measurement. Measure the CO_2 content in the stack to the nearest 0.5 percent each time a CO sample is collected. A simultaneous grab sample analyzed by the Fyrite analyzer is acceptable.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.1	Sampling equipment leak-checks and calibration.	Ensure accuracy and precision of sampling measurements.
10.3	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Gas Bulb Calibration. Weigh the empty bulb to the nearest 0.1 g. Fill the bulb to the stopcock with water, and again weigh to the nearest 0.1 g. Subtract the tare weight, and calculate the volume in liters to three significant figures using the density of water at the measurement temperature. Record the volume on the bulb. Alternatively, mark an identification number on the bulb, and record the volume in a notebook.

10.2 Rate Meter Calibration. Assemble the system as shown in Figure 10A–1 (the impingers may be removed), and attach a volume meter to the probe inlet. Set the rotameter at 300 ml/min, record the volume meter reading, start the pump, and pull ambient air through the system for 10 minutes. Record the final volume meter reading. Repeat the procedure and average the results to determine the volume of gas that passed through the system.

10.3 Spectrophotometer Calibration Curve.

10.3.1 Collect the standards as described in section 8.2. Prepare at least two sets of three bulbs as standards to span the 0 to 400 or 400 to 1000 ppm range. If any samples span both

concentration ranges, prepare a calibration curve for each range using separate reagent blanks. Prepare a set of three bulbs containing colorimetric reagent but no CO to serve as a reagent blank. Analyze each standard and blank according to the sample analysis procedure of section 11.0 Reject the standard set where any of the individual bulb absorbances differs from the set mean by more than 10 percent.

10.3.2 Calculate the average absorbance for each set (3 bulbs) of standards using Equation 10A–1 and Table 10A–1. Construct a graph of average absorbance for each standard against its corresponding concentration. Draw a smooth curve through the points. The curve should be linear over the two concentration ranges discussed in section 13.3.

11.0 Analytical Procedure

11.1 Assemble the system shown in Figure 10A–3, and record the information required in Table 10A–1 as it is obtained. Pipet 10.0 ml of the colorimetric reagent into each gas reaction bulb, and attach the bulbs to the system. Open the stopcocks to the reaction bulbs, but leave the valve to the bag closed. Turn on the pump, fully open the coarse-adjust flow valve, and slowly open the fine-adjust valve until the pressure is reduced to at least 40 mm Hg. Now close the coarse adjust valve, and observe the manometer to be certain that the system is leak-free. Wait a minimum of 2 minutes. If the pressure has increased less than 1 mm Hg, proceed as described below. If a leak is present, find and correct it before proceeding further.

11.2 Record the vacuum pressure (P_v) to the nearest 1 mm Hg, and close the reaction bulb stopcocks. Open the bag valve, and allow the system to come to atmospheric pressure. Close the bag valve, open the pump coarse adjust valve, and evacuate the system again. Repeat this fill/evacuation procedure at least twice to flush the manifold completely. Close the pump coarse adjust valve, open the bag valve, and let the system fill to atmospheric pressure. Open the stopcocks to the reaction bulbs, and let the entire system come to atmospheric pressure. Close the bulb stopcocks, remove the bulbs, record the room temperature and barometric pressure (P_{bar}, to nearest mm Hg), and place the bulbs on the shaker table with their main axis either parallel to or perpendicular to the plane of the table top. Purge the bulb-filling system with ambient air for several minutes between samples. Shake the samples for exactly 2 hours.

11.3 Immediately after shaking, measure the absorbance (A) of each bulb sample at 425 nm if the concentration is less than or equal to 400 ppm CO or at 600 nm if the concentration is above 400 ppm.

NOTE: This may be accomplished with multiple bulb sets by sequentially collecting sets and adding to the shaker at staggered intervals, followed by sequentially removing sets from the shaker for absorbance measurement after the two-hour designated intervals have elapsed.

11.4 Use a small portion of the sample to rinse a spectrophotometer cell several times before taking an aliquot for analysis. If one cell is used to analyze multiple samples, rinse the cell with deionized distilled water several times between samples. Prepare and analyze standards and a reagent blank as described in section 10.3. Use water as the reference. Reject the analysis if the blank absorbance is greater than 0.1. All conditions should be the same for analysis of samples and standards. Measure the absorbances as soon as possible after shaking is completed.

11.5 Determine the CO concentration of each bag sample using the calibration curve for the appropriate concentration range as discussed in section 10.3.

12.0 Calculations and Data Analysis

Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature.

A = Sample absorbance, uncorrected for the reagent blank.
A_r = Absorbance of the reagent blank.
A_s = Average sample absorbance per liter, units/liter.
B_w = Moisture content in the bag sample.
C = CO concentration in the stack gas, dry basis, ppm.
C_b = CO concentration of the bag sample, dry basis, ppm.
C_g = CO concentration from the calibration curve, ppm.
F = Volume fraction of CO_2 in the stack.
n = Number of reaction bulbs used per bag sample.
P_b = Barometric pressure, mm Hg.
P_v = Residual pressure in the sample bulb after evacuation, mm Hg.
P_w = Vapor pressure of H_2O in the bag (from Table 10A–2), mm Hg.
V_b = Volume of the sample bulb, liters.
V_r = Volume of reagent added to the sample bulb, 0.0100 liter.

12.2 Average Sample Absorbance per Liter. Calculate A_s for each gas bulb using Equation 10A–1, and record the value in Table 10A–1. Calculate the average A_s for each bag sample, and compare the three values to the average. If any single value differs by more than 10 percent from the average, reject this value, and calculate a new average using the two remaining values.

$$A_s = \frac{(A - A_r)(P_b)}{(V_b - V_r)(P_b - P_v)} \qquad \text{Eq. 10A-1}$$

NOTE: A and A_r must be at the same wavelength.

12.3 CO Concentration in the Bag. Calculate C_b using Equations 10A–2 and 10A–3. If condensate is visible in the bag, calculate B_w using Table 10A–2 and the temperature and barometric pressure in the analysis room. If condensate is not visible, calculate B_w using the temperature and barometric pressure at the sampling site.

$$B_w = \frac{P_w}{P_b} \qquad \text{Eq. 10A-2}$$

$$C_b = \frac{C_g}{(1 - B_w)} \qquad \text{Eq. 10A-3}$$

12.4 CO Concentration in the Stack.

$$C = C_b\,(1 - F) \qquad \text{Eq. 10A-4}$$

13.0 Method Performance

13.1 Precision. The estimated intralaboratory standard deviation of the method is 3 percent of the mean for gas samples analyzed in duplicate in the concentration range of 39 to 412 ppm. The interlaboratory precision has not been established.

13.2 Accuracy. The method contains no significant biases when compared to an NDIR analyzer calibrated with NIST standards.

13.3 Range. Approximately 3 to 1800 ppm CO. Samples having concentrations below 400 ppm are analyzed at 425 nm, and samples having concentrations above 400 ppm are analyzed at 600 nm.

13.4 Sensitivity. The detection limit is 3 ppmv based on a change in concentration equal to three times the standard deviation of the reagent blank solution.

13.5 Stability. The individual components of the colorimetric reagent are stable for at least one month. The colorimetric reagent must be used within two days after preparation to avoid excessive blank correction. The samples in the bag should be stable for at least one week if the bags are leak-free.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Butler, F.E., J.E. Knoll, and M.R. Midgett. Development and Evaluation of Methods for Determining Carbon Monoxide Emissions. U.S. Environmental Protection Agency, Research Triangle Park, N.C. June 1985. 33 pp.

2. Ferguson, B.B., R.E. Lester, and W.J. Mitchell. Field Evaluation of Carbon Monoxide and Hydrogen Sulfide Continuous Emission Monitors at an Oil Refinery. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA–600/4–82–054. August 1982. 100 pp.

3. Lambert, J.L., and R.E. Weins. Induced Colorimetric Method for Carbon Monoxide. Analytical Chemistry. *46*(7):929–930. June 1974.

4. Levaggi, D.A., and M. Feldstein. The Colorimetric Determination of Low Concentrations of Carbon Monoxide. Industrial Hygiene Journal. *25*:64–66. January-February 1964.

5. Repp, M. Evaluation of Continuous Monitors For Carbon Monoxide in Stationary Sources. U.S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA–600/2–77–063. March 1977. 155 pp.

6. Smith, F., D.E. Wagoner, and R.P. Donovan. Guidelines for Development of a Quality Assurance Program: Volume VIII—Determination of CO Emissions from Stationary Sources by NDIR Spectrometry. U.S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA–650/4–74–005–h. February 1975. 96 pp.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 10A–1—DATA RECORDING SHEET FOR SAMPLES ANALYZED IN TRIPLICATE

Sample No./type	Room temp °C	Stack %CO_2	Bulb No.	Bulb vol. liters	Reagent vol. in bulb, liter	Partial pressure of gas in bulb, mm Hg	$P_{b,r}$, mm Hg	Shaking time, min	Abs versus water	A-A_r	A_s	Avg A_s
blank												
Std. 1												
Std. 2												
Sample 1												
Sample 2												
Sample 3												

TABLE 10A–2—MOISTURE CORRECTION

Temperature °C	Vapor pressure of H_2O, mm Hg	Temperature °C	Vapor pressure of H_2, mm Hg
4	6.1	18	15.5
6	7.0	20	17.5
8	8.0	22	19.8
10	9.2	24	22.4
12	10.5	26	25.2
14	12.0	28	28.3
16	13.6	30	31.8

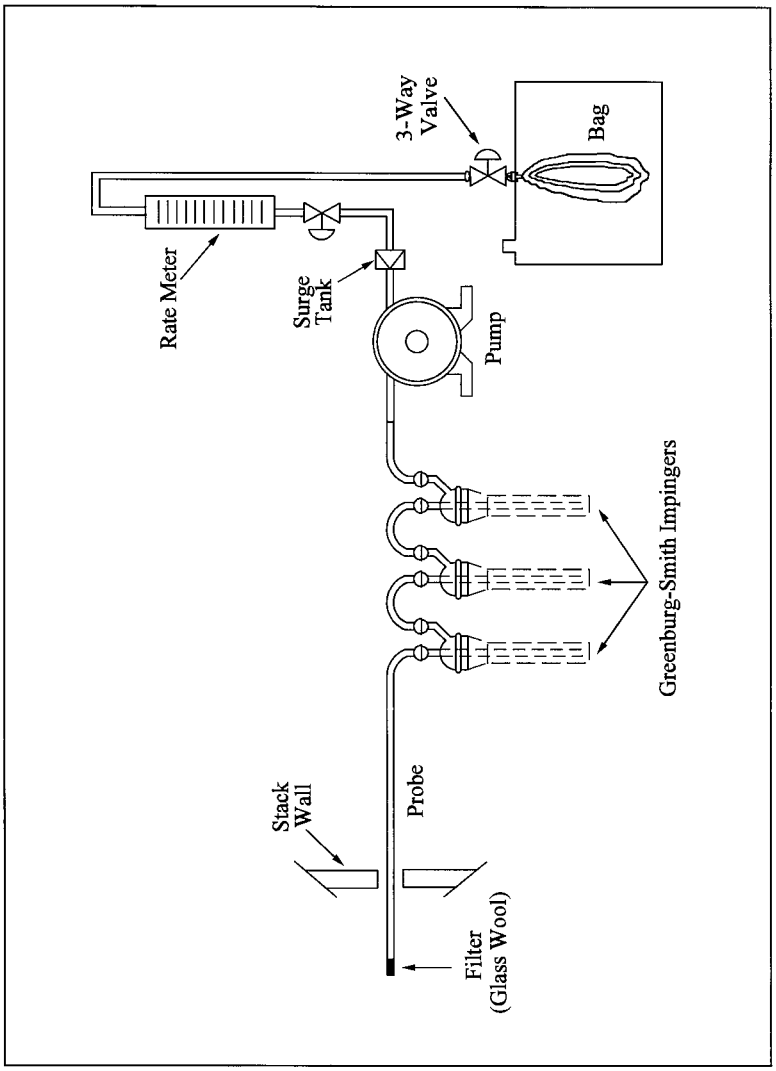


Figure 10A-1. Sampling Train.

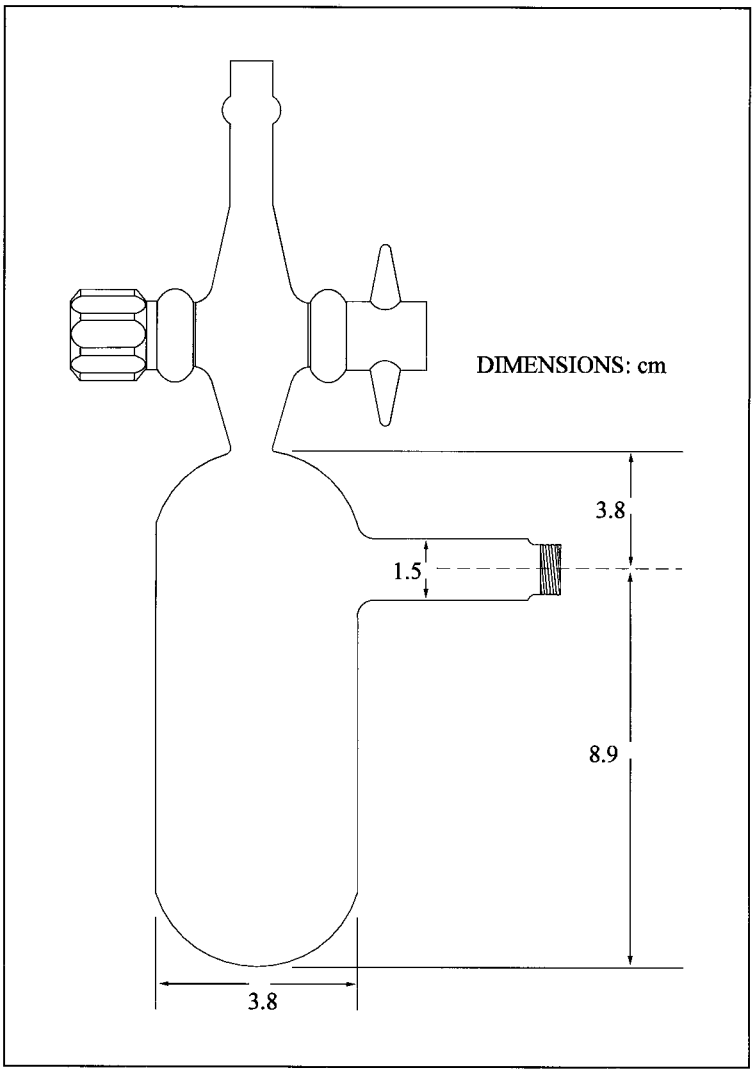


Figure 10A-2. Sample Reaction Bulbs.

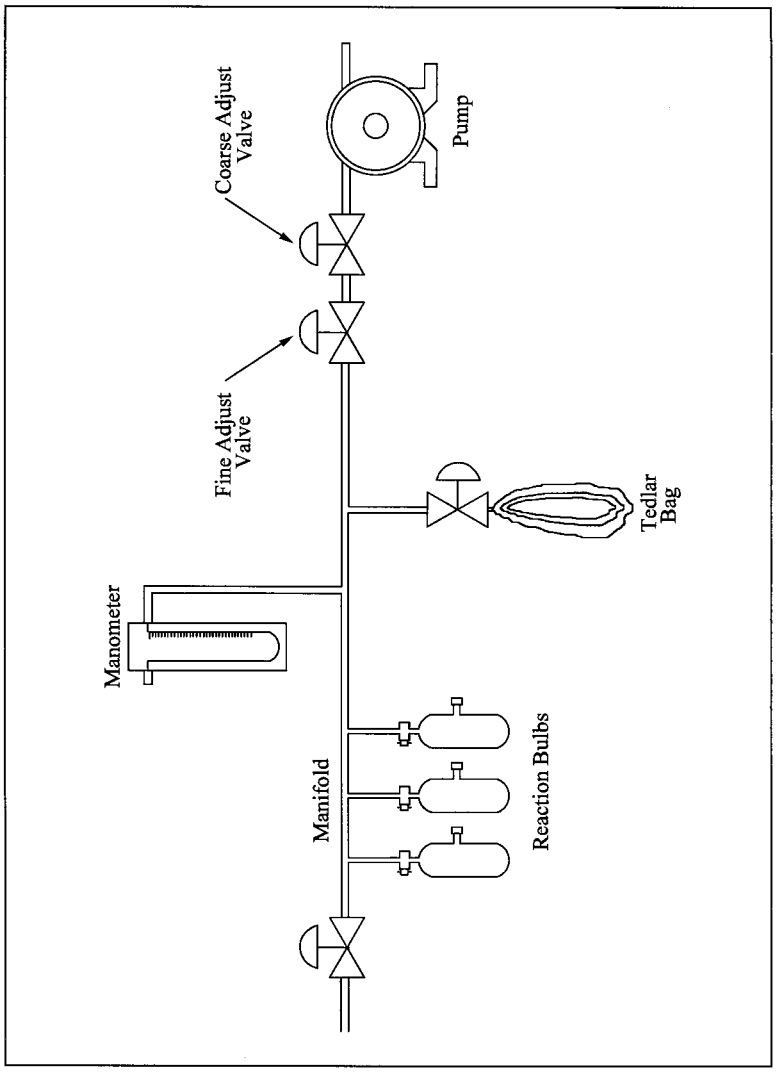


Figure 10A-3. Sample Bulb Filling System.

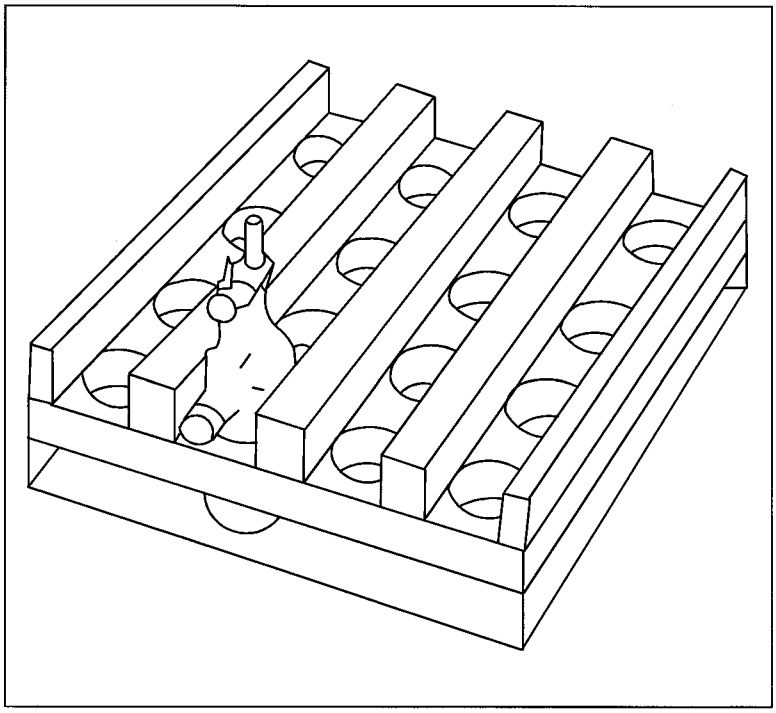


Figure 10A-4. Shaker Table Adapter.

METHOD 10B—DETERMINATION OF CARBON MONOXIDE EMISSIONS FROM STATIONARY SOURCES

NOTE: This method is not inclusive with respect to specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 4, Method 10A, and Method 25.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Carbon monoxide (CO)	630–08–0	Not determined.

1.2 Applicability. This method applies to the measurement of CO emissions at petroleum refineries and from other sources when specified in an applicable subpart of the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 An integrated gas sample is extracted from the sampling point, passed through a conditioning system to remove interferences, and collected in a Tedlar or equivalent bag. (Verify through the manufacturer that the Tedlar alternative is suitable for NO and make this verifying information available for inspection.) The CO is separated from the sample by gas chromatography (GC) and catalytically reduced to methane (CH_4) which is determined by flame ionization detection (FID). The analytical portion of this method is identical to applicable sections in Method 25 detailing CO measurement.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Carbon dioxide (CO_2) and organics potentially can interfere with the analysis. Most of the CO_2 is removed from the sample by the alkaline permanganate conditioning system; any residual CO_2 and organics are separated from the CO by GC.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions concerning the analytical procedure.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as in Method 10A, section 6.1 (paragraphs 6.1.1 through 6.1.11).

6.2 Sample Analysis. A GC/FID analyzer, capable of quantifying CO in the sample and consisting of at least the following major components, is required for sample analysis. [Alternatively, complete Method 25 analytical systems (Method 25, section 6.3) are acceptable alternatives when calibrated for CO and operated in accordance with the Method 25 analytical procedures (Method 25, section 11.0).]

6.2.1 Separation Column. A column capable of separating CO from CO_2 and organic compounds that may be present. A 3.2-mm (⅛-in.) OD stainless steel column packed with 1.7 m (5.5 ft.) of 60/80 mesh Carbosieve S-II (available from Supelco) has been used successfully for this purpose.

6.2.2 Reduction Catalyst. Same as in Method 25, section 6.3.1.2.

6.2.3 Sample Injection System. Same as in Method 25, Section 6.3.1.4, equipped to accept a sample line from the bag.

6.2.4 Flame Ionization Detector. Meeting the linearity specifications of section 10.3 and having a minimal instrument range of 10 to 1,000 ppm CO.

6.2.5 Data Recording System. Analog strip chart recorder or digital integration system, compatible with the FID, for permanently recording the analytical results.

7.0 Reagents and Standards

7.1 Sample Collection. Same as in Method 10A, section 7.1.

7.2 Sample Analysis.

7.2.1 Carrier, Fuel, and Combustion Gases. Same as in Method 25, sections 7.2.1, 7.2.2, and 7.2.3, respectively.

7.2.2 Calibration Gases. Three standard gases with nominal CO concentrations of 20, 200, and 1,000 ppm CO in nitrogen. The calibration gases shall be certified by the manufacturer to be ±2 percent of the specified concentrations.

7.2.3 Reduction Catalyst Efficiency Check Calibration Gas. Standard CH_4 gas with a nominal concentration of 1,000 ppm in air.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as in Method 10A, section 8.0.

9.0 Quality Control

Section	Quality control measure	Effect
8.0	Sample bag/sampling system leak-checks	Ensures that negative bias introduced through leakage is minimized.
10.1	Carrier gas blank check	Ensures that positive bias introduced by contamination of carrier gas is less than 5 ppmv.
10.2	Reduction catalyst efficiency check	Ensures that negative bias introduced by inefficient reduction catalyst is less than 5 percent.
10.3	Analyzer calibration	Ensures linearity of analyzer response to standards.
11.2	Triplicate sample analyses	Ensures precision of analytical results.

10.0 Calibration and Standardization

10.1 Carrier Gas Blank Check. Analyze each new tank of carrier gas with the GC analyzer according to section 11.2 to check for contamination. The corresponding concentration must be less than 5 ppm for the tank to be acceptable for use.

10.2 Reduction Catalyst Efficiency Check. Prior to initial use, the reduction catalyst shall be tested for reduction efficiency. With the heated reduction catalyst bypassed, make triplicate injections of the 1,000 ppm CH_4 gas (Section 7.2.3) to calibrate the analyzer. Repeat the procedure using 1,000 ppm CO gas (Section 7.2.2) with the catalyst in operation. The reduction catalyst operation is acceptable if the CO response is within 5 percent of the certified gas value.

10.3 Analyzer Calibration. Perform this test before the system is first placed into operation. With the reduction catalyst in operation, conduct a linearity check of the analyzer using the standards specified in section 7.2.2. Make triplicate injections of each calibration gas, and then calculate the average

response factor (area/ppm) for each gas, as well as the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within 2.5 percent of the overall mean value and if the relative standard deviation (calculated in section 12.8 of Method 25) for each set of triplicate injections is less than 2 percent. Record the overall mean of the response factor values as the calibration response factor (R).

11.0 Analytical Procedure

11.1 Preparation for Analysis. Before putting the GC analyzer into routine operation, conduct the calibration procedures listed in section 10.0. Establish an appropriate carrier flow rate and detector temperature for the specific instrument used.

11.2 Sample Analysis. Purge the sample loop with sample, and then inject the sample. Analyze each sample in triplicate, and calculate the average sample area (A). Determine the bag CO concentration according to section 12.2.

12.0 Calculations and Data Analysis

Carry out calculations retaining at least one extra significant figure beyond that of the acquired data. Round off results only after the final calculation.

12.1 Nomenclature.

A = Average sample area.
B_w = Moisture content in the bag sample, fraction.
C = CO concentration in the stack gas, dry basis, ppm.
C_b = CO concentration in the bag sample, dry basis, ppm.
F = Volume fraction of CO_2 in the stack, fraction.
P_{bar} = Barometric pressure, mm Hg.
P_w = Vapor pressure of the H_2O in the bag (from Table 10A–2, Method 10A), mm Hg.
R = Mean calibration response factor, area/ppm.

12.2 CO Concentration in the Bag. Calculate C_b using Equations 10B–1 and 10B–2. If condensate is visible in the bag, calculate B_w using Table 10A–2 of Method 10A and the temperature and barometric pressure in the analysis room. If condensate is not visible, calculate B_w using the temperature and barometric pressure at the sampling site.

$$B_w = \frac{P_w}{P_{bar}} \qquad \text{Eq. 10B-1}$$

$$C_b = \frac{A}{R\left(1 - B_w\right)} \qquad \text{Eq. 10B-2}$$

12.3 CO Concentration in the Stack

$$C = C_b\left(1 - F\right) \qquad \text{Eq. 10B-3}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as in Method 25, section 16.0, with the addition of the following:

1. Butler, F.E, J.E. Knoll, and M.R. Midgett. Development and Evaluation of Methods for Determining Carbon Monoxide Emissions. Quality Assurance Division, Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC. June 1985. 33 pp.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–4 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

APPENDIX A–5 TO PART 60—TEST METHODS 11 THROUGH 15A

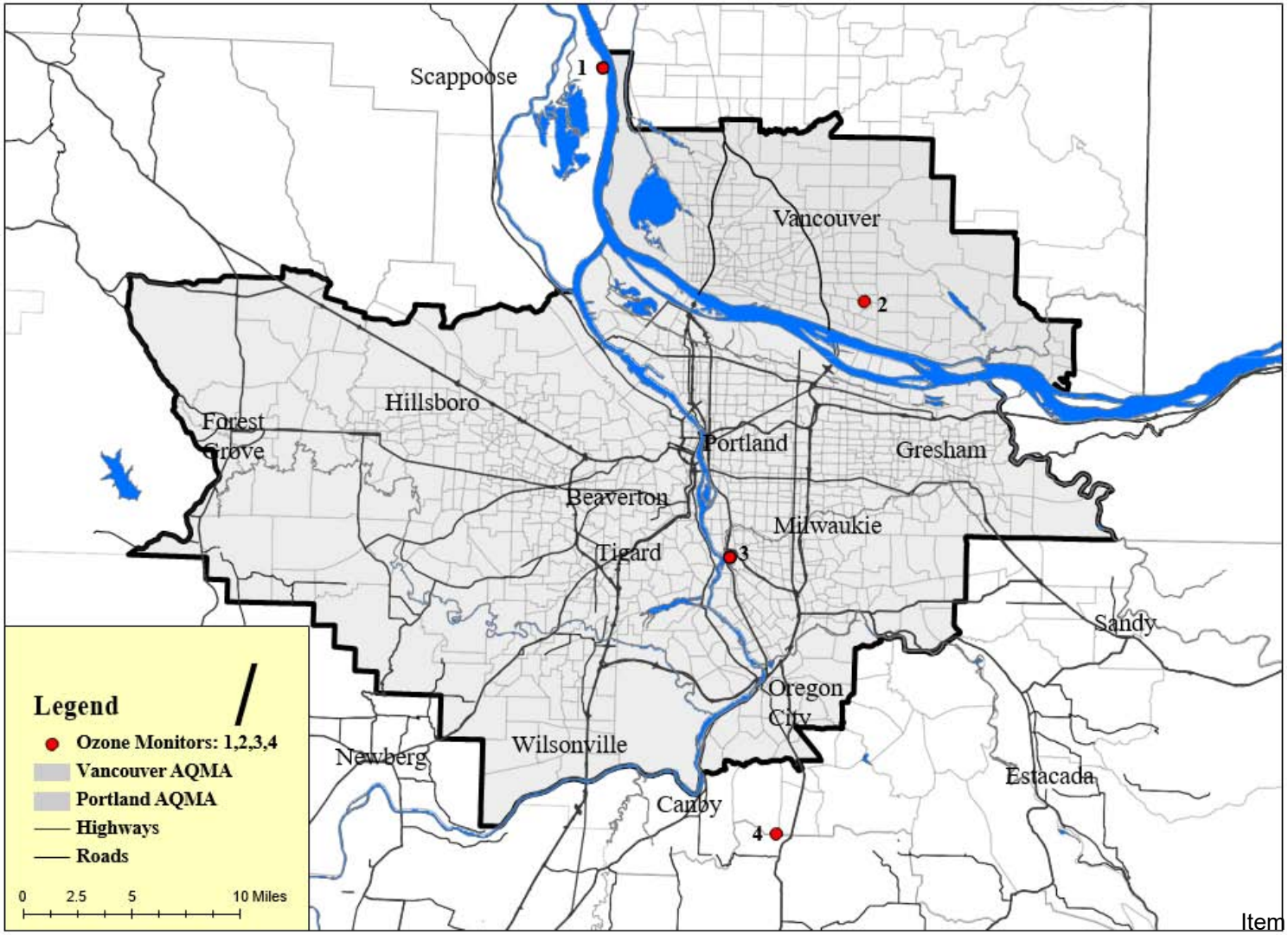
Method 11—Determination of hydrogen sulfide content of fuel gas streams in petroleum refineries
Method 12—Determination of inorganic lead emissions from stationary sources
Method 13A—Determination of total fluoride emissions from stationary sources—SPADNS zirconium lake method
Method 13B—Determination of total fluoride emissions from stationary sources—Specific ion electrode method
Method 14—Determination of fluoride emissions from potroom roof monitors for primary aluminum plants
Method 14A—Determination of Total Fluoride Emissions from Selected Sources at Primary Aluminum Production Facilities
Method 15—Determination of hydrogen sulfide, carbonyl sulfide, and carbon disulfide emissions from stationary sources
Method 15A—Determination of total reduced sulfur emissions from sulfur recovery plants in petroleum refineries

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods

State of Oregon Department of Environmental Quality

OAR 340-242-0020
Figure 1 – Portland Air Quality Maintenance Area



State of Oregon Department of Environmental Quality

OAR 340-242-0390

Table 1 - Voluntary Maximum Parking Ratios for the Portland Area AQMA

Parking ratios are based on spaces per 1,000 sq. ft.
GLA means gross leasable area
GFA means gross floor area

Type of Facility	CCTMP Area			
	Downtown Parking Sectors 1-6, University District and River District Parking Sectors 3-5	Central Eastside Parking Sectors 2 and 3, Goose Hollow and Lloyd	Lower Albina, North Macadam, Central Eastside Parking Sectors 1, 4-6 and River District 1 and 2	Areas outside of CCTMP areas, but inside AQMA boundary
Bank with Drive-In	4.3 GFA Bank with Drive-In is a prohibited land use in Downtown sectors 1-6, University District.	4.3 GLA Bank with Drive-In is a prohibited land use in Goose Hollow.	4.3 GLA	4.3 GLA
Bank with Walk-In	1.0 - 2.0 GFA	4.3 GLA	4.3 GLA	4.3 GLA
Place of Worship	.25* GFA	.5 GFA	.5 GFA	.5 GFA
Commercial Retail**	1.0 – 2.0* GFA	4.1 GFA	4.1 GFA	4.1 GFA
Fast Food with Drive Thru	9.9 GLA Fast Food with Drive Thru is a prohibited land use in Downtown sectors 1 – 6 and University District.	9.9 GLA Fast Food with Drive-Thru is a prohibited land use in Goose Hollow.	9.9 GLA	9.9 GLA
Other Restaurants	1.0 – 2.0* GFA	15.3 GLA	15.3 GLA	15.3 GLA
General Office	.7 – 2.0* GFA	2.0 – 2.5 GFA	2.7 GLA	2.7 GLA
Light Industrial, Industrial Park, Manufacturing	.7 GFA	1.6 GFA	1.6 GFA	1.6 GFA
Medical and Dental	.07 – 2.0* GFA	3.9 GLA	3.9 GLA	3.9 GLA
Movie Theater	.25 GFA	.3 (Spaces per number of seats)	.3 Spaces per number of seats)	.3 (Spaces per number of seats)

Type of Facility	CCTMP Area			
	Downtown Parking Sectors 1-6, University District and River District Parking Sectors 3-5	Central Eastside Parking Sectors 2 and 3, Goose Hollow and Lloyd	Lower Albina, North Macadam, Central Eastside Parking Sectors 1, 4-6 and River District 1 and 2	Areas outside of CCTMP areas, but inside AQMA boundary
Schools	1.0 – 2.0* GFA	.2 (Spaces per number of students and staff)	.2 (Spaces per number of students and staff)	.2 (spaces per number of students and staff)
Sports Club and Recreational Facility	1.0 – 2.8 GFA	4.3 GLA	4.3 GLA	4.3 GLA
Supermarket**	1.0 – 2.0* GFA	2.9 GLA	2.9 GLA	1.0 GLA
Tennis and Racquetball Court	1.0 – 2.0* GFA	1.0 GLA	1.0 GLA	1.0 GLA
Warehouse	.7 This parking ratio applies to all sizes of warehouses	.3 GLA This parking ratio applies to warehouses that are greater than 150,000 sq. ft.	.3 GLA This parking ratio applies to warehouses that are greater than 150,000 sq. ft.	.3 GLA This parking ratio applies to warehouses that are greater than 150,000 sq. ft.

Note: *See parking ratios for specific parking sectors in Central City Transportation Management Plan (CCTMP) adopted by the Portland City Council December 6, 1995.

Note: **See the CCTMP for definition of the land uses Commercial Retail and Supermarket that are located in the CCTMP.

OAR 340-244-0040
Table 1
LIST OF HAZARDOUS AIR POLLUTANTS

CAS Number	Chemical Name
75-07-0	Acetaldehyde
60-35-5	Acetamide
75-05-8	Acetonitrile
98-86-2	Acetophenone
53-96-3	2-Acetylaminofluorene
107-02-8	Acrolein
79-06-1	Acrylamide
79-10-7	Acrylic acid
107-13-1	Acrylonitrile
107-05-1	Allyl chloride
92-67-1	4-Aminobiphenyl
62-53-3	Aniline
90-04-0	o-Anisidine
1332-21-4	Asbestos
71-43-2	Benzene (including benzene from gasoline)
92-87-5	Benzidine
98-07-7	Benzotrichloride
100-44-7	Benzyl chloride
92-52-4	Biphenyl
117-81-7	Bis(2-ethylhexyl) phthalate (DEHP)
542-88-1	Bis(chloromethyl)ether
75-25-2	Bromoform
106-99-0	1,3-Butadiene
156-62-7	Calcium cyanamide
133-06-2	Captan
63-25-2	Carbaryl
75-15-0	Carbon disulfide
56-23-5	Carbon tetrachloride
463-58-1	Carbonyl sulfide
120-80-9	Catechol
133-90-4	Chloramben
57-74-9	Chlordane
7782-50-5	Chlorine
79-11-8	Chloroacetic acid

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Table 1
LIST OF HAZARDOUS AIR POLLUTANTS

CAS Number	Chemical Name
532-27-4	2-Chloroacetophenone
108-90-7	Chlorobenzene
510-15-6	Chlorobenzilate
67-66-3	Chloroform
107-30-2	Chloromethyl methyl ether
126-99-8	Chloroprene
1319-77-3	Cresols/Cresylic acid (isomers and mixture)
95-48-7	o-Cresol
108-39-4	m-Cresol
106-44-5	p-Cresol
98-82-8	Cumene
94-75-7	2,4-D, salts and esters
3547-04-4	DDE
334-88-3	Diazomethane
132-64-9	Dibenzofurans
96-12-8	1,2-Dibromo-3-chloropropane
84-74-2	Dibutylphthalate
106-46-7	1,4-Dichlorobenzene(p)
91-94-1	3,3-Dichlorobenzidene
111-44-4	Dichloroethyl ether (Bis(2-chloroethyl)ether)
542-75-6	1,3-Dichloropropene
62-73-7	Dichlorvos
111-42-2	Diethanolamine
121-69-7	N,N-Diethyl aniline (N,N-Dimethylaniline)
64-67-5	Diethyl sulfate
119-90-4	3,3-Dimethoxybenzidine
60-11-7	Dimethyl aminoazobenzene
119-93-7	3,3’-Dimethyl benzidine
79-44-7	Dimethyl carbamoyl chloride
68-12-2	Dimethyl formamide
57-14-7	1,1-Dimethyl hydrazine
131-11-3	Dimethyl phthalate
77-78-1	Dimethyl sulfate

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Table 1
LIST OF HAZARDOUS AIR POLLUTANTS

CAS Number	Chemical Name
534-52-1	4,6-Dinitro-o-cresol, and salts
51-28-5	2,4-Dinitrophenol
121-14-2	2,4-Dinitrotoluene
123-91-1	1,4-Dioxane (1,4-Diethyleneoxide)
122-66-7	1,2-Diphenylhydrazine
106-89-8	Epichlorohydrin (l-Chloro-2,3-epoxypropane)
106-88-7	1,2-Epoxybutane
140-88-5	Ethyl acrylate
100-41-4	Ethyl benzene
51-79-6	Ethyl carbamate (Urethane)
75-00-3	Ethyl chloride (Chloroethane)
106-93-4	Ethylene dibromide (Dibromoethane)
107-06-2	Ethylene dichloride (1,2-Dichloroethane)
107-21-1	Ethylene glycol
151-56-4	Ethylene imine (Aziridine)
75-21-8	Ethylene oxide
96-45-7	Ethylene thiourea
75-34-3	Ethylidene dichloride (1,1-Dichloroethane)
50-00-0	Formaldehyde
76-44-8	Heptachlor
118-74-1	Hexachlorobenzene
87-68-3	Hexachlorobutadiene
77-47-4	Hexachlorocyclopentadiene
67-72-1	Hexachloroethane
822-06-0	Hexamethylene-1,6-diisocyanate
680-31-9	Hexamethylphosphoramide
110-54-3	Hexane
302-01-2	Hydrazine
7647-01-0	Hydrochloric acid
7664-39-3	Hydrogen fluoride (Hydrofluoric acid)
123-31-9	Hydroquinone
78-59-1	Isophorone
58-89-9	Lindane (all isomers)

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Table 1
LIST OF HAZARDOUS AIR POLLUTANTS

CAS Number	Chemical Name
108-31-6	Maleic anhydride
67-56-1	Methanol
72-43-5	Methoxychlor
74-83-9	Methyl bromide (Bromomethane)
74-87-3	Methyl chloride (Chloromethane)
71-55-6	Methyl chloroform (1,1,1-Trichloroethane)
60-34-4	Methyl hydrazine
74-88-4	Methyl iodide (Iodomethane)
108-10-1	Methyl isobutyl ketone (Hexone)
624-83-9	Methyl isocyanate
80-62-6	Methyl methacrylate
1634-04-4	Methyl tert butyl ether
101-14-4	4,4-Methylene bis(2-chloroaniline)
75-09-2	Methylene chloride (Dichloromethane)
101-68-8	Methylene diphenyl diisocyanate (MDI)
101-77-9	4,4-Methylenedianiline
91-20-3	Naphthalene
98-95-3	Nitrobenzene
92-93-3	4-Nitrobiphenyl
100-02-7	4-Nitrophenol
79-46-9	2-Nitropropane
684-93-5	N-Nitroso-N-methylurea
62-75-9	N-Nitrosodimethylamine
59-89-2	N-Nitrosomorpholine
56-38-2	Parathion
82-68-8	Pentachloronitrobenzene (Quintobenzene)
87-86-5	Pentachlorophenol
108-95-2	Phenol
106-50-3	p-Phenylenediamine
75-44-5	Phosgene
7803-51-2	Phosphine
7723-14-0	Phosphorus

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Table 1
LIST OF HAZARDOUS AIR POLLUTANTS

CAS Number	Chemical Name
85-44-9	Phthalic anhydride
1336-36-3	Polychlorinated biphenyls (Aroclors)
1120-71-4	1,3-Propane sultone
57-57-8	beta-Propiolactone
123-38-6	Propionaldehyde
114-26-1	Propoxur (Baygon)
78-87-5	Propylene dichloride (1,2-Dichloropropane)
75-56-9	Propylene oxide
75-55-8	1,2-Propylenimine (2-Methyl aziridine)
91-22-5	Quinoline
106-51-4	Quinone
100-42-5	Styrene
96-09-3	Styrene oxide
1746-01-6	2,3,7,8-Tetrachlorodibenzo-p-dioxin
79-34-5	1,1,2,2-Tetrachloroethane
127-18-4	Tetrachloroethylene (Perchloroethylene)
7550-45-0	Titanium tetrachloride
108-88-3	Toluene
95-80-7	2,4-Toluene diamine
584-84-9	2,4-Toluene diisocyanate
95-53-4	o-Toluidine
8001-35-2	Toxaphene (chlorinated camphene)
120-82-1	1,2,4-Trichlorobenzene
79-00-5	1,1,2-Trichloroethane
79-01-6	Trichloroethylene
95-95-4	2,4,5-Trichlorophenol
88-06-2	2,4,6-Trichlorophenol
121-44-8	Triethylamine
1582-09-8	Trifluralin
540-84-1	2,2,4-Trimethylpentane
108-05-4	Vinyl acetate
593-60-2	Vinyl bromide
75-01-4	Vinyl chloride

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Table 1
LIST OF HAZARDOUS AIR POLLUTANTS

CAS Number	Chemical Name
75-35-4	Vinylidene chloride (1,1-Dichloroethylene)
1330-20-7	Xylenes (isomers and mixture)
95-47-6	o-Xylenes
108-38-3	m-Xylenes
106-42-3	p-Xylenes
0	Antimony Compounds
0	Arsenic Compounds (inorganic including arsine)
0	Beryllium Compounds
0	Cadmium Compounds
0	Chromium Compounds
0	Cobalt Compounds
0	Coke Oven Emissions
0	Cyanide Compounds[1]
0	Glycol ethers[2]
0	Lead Compounds
0	Manganese Compounds
0	Mercury Compounds
0	Fine mineral fibers[3]
0	Nickel Compounds
0	Polycyclic Organic Matter[4]
0	Radionuclides (including radon)[5]
0	Selenium Compounds

NOTE: *For all listings above that contain the word "compounds" and for glycol ethers, the following applies:* Unless otherwise specified, these listings are defined as including any unique chemical substance that contains the named chemical (i.e., antimony, arsenic, etc.) as part of that chemical's infrastructure.

*1 X'CN where X = H' or any other group where a formal dissociation may occur. For example KCN or $Ca(CN)_2$

*2 Glycol ethers include mono- and di-ethers of ethylene glycol, diethylene glycol, and triethylene glycol $R-(OCH_2CH_2)_n-OR'$.

Where:

n = 1, 2, or 3;

R = alkyl C7 or less; or

R = phenyl or alkyl substituted phenyl;

R' = H, or alkyl C7 or less; or

OR' consisting of carboxylic acid ester, sulfate, phosphate, nitrate, or sulfonate. Does not include ethylene glycol monobutyl ether (EGBE, 2-Butoxyethanol)(CAS No. 111-76-2).

*3 Includes mineral fiber emissions from facilities manufacturing or processing glass, rock, or slag fibers (or other mineral derived fibers) of average diameter 1 micrometer or less.

*4 Includes organic compounds with more than one benzene ring, and which have a boiling point greater than or equal to 100°C.

*5 A type of atom which spontaneously undergoes radioactive decay.

State of Oregon Department of Environmental Quality

OAR 340-244-0242 - Tables

OAR 340-244-0242
Table 2
Management Practices for Gasoline Dispensing Facilities Subject to Stage I Vapor Controls

If owning or operating	The owner or operator must
1. An existing GDF	The permittee must install and operate a vapor balance system on gasoline storage tanks that meets the design criteria in paragraphs (a) through (h). (a) All vapor connections and lines on the storage tank must be equipped with closures that seal upon disconnect. (b) The vapor line from the gasoline storage tank to the gasoline cargo tank must be vapor-tight, as defined in OAR 340-244-0030. (c) The vapor balance system must be designed such that the pressure in the tank truck does not exceed 18 inches water pressure or 5.9 inches water vacuum during product transfer. (d) The vapor recovery and product adaptors, and the method of connection with the delivery elbow, must be designed so as to prevent the over-tightening or loosening of fittings during normal delivery operations. (e) If a gauge well separate from the fill tube is used, it must be provided with a submerged drop tube that extends the same distance from the bottom of the storage tank as specified in OAR 340-244-0240(2). (f) Liquid fill connections for all systems must be equipped with vapor-tight caps.

OAR 340-244-0242
Table 2
Management Practices for Gasoline Dispensing Facilities Subject to Stage I Vapor Controls

If owning or operating	The owner or operator must
	(g) Pressure/vacuum (PV) vent valves must be installed on the storage tank vent pipes. The pressure specifications for PV vent valves must be: a positive pressure setting of 2.5 to 6.0 inches of water and a negative pressure setting of 6.0 to 10.0 inches of water. The total leak rate of all PV vent valves at an affected facility, including connections, must not exceed 0.17 cubic foot per hour at a pressure of 2.0 inches of water and 0.63 cubic foot per hour at a vacuum of 4 inches of water. (h) The vapor balance system must be capable of meeting the static pressure performance requirement of the following equation: $Pf = 2e^{-500.887/v}$ Where: Pf = Minimum allowable final pressure, inches of water. v = Total ullage affected by the test, gallons. e = Dimensionless constant equal to approximately 2.718. 2 = The initial pressure, inches water.
2. For a new or reconstructed GDF with monthly throughput of 100,000 gallons of gasoline or more, or a new storage tank(s) at an existing GDF with monthly throughput of 100,000 gallons of gasoline or more	The permittee must install and operate a dual-point vapor balance system, as defined in OAR 340-244-0030, on each affected gasoline storage tank and comply with the design criteria in item 1 of this Table.

OAR 340-244-0242
Table 3
Management Practices for Gasoline Cargo Tanks Unloading at Gasoline Dispensing Facilities Equipped With Stage I Vapor Controls

The owner or operator of a gasoline cargo tank must:
Not unload gasoline into a storage tank at a GDF with stage I vapor controls unless the following conditions are met: (i) All hoses in the vapor balance system are properly connected, (ii) The adapters or couplers that attach to the vapor line on the storage tank have closures that seal upon disconnect, (iii) All vapor return hoses, couplers, and adapters used in the gasoline delivery are vapor-tight, (iv) All tank truck vapor return equipment is compatible in size and forms a vapor-tight connection with the vapor balance equipment on the GDF storage tank, and (v) All hatches on the tank truck are closed and securely fastened. (vi) The filling of storage tanks at GDF must be limited to unloading by vapor-tight gasoline cargo tanks. Documentation that the cargo tank has met the specifications of EPA Method 27 must be carried on the cargo tank.

State of Oregon Department of Environmental Quality

OAR 340-244-0244 Attachments

California Environmental Protection Agency

Air Resources Board

Vapor Recovery Test Procedure

TP-201.1E

Leak Rate and Cracking Pressure of Pressure/Vacuum Vent Valves

Adopted: October 8, 2003

California Environmental Protection Agency
Air Resources Board

Vapor Recovery Test Procedure

TP-201.1E

Leak Rate and Cracking Pressure of Pressure/Vacuum Vent Valves

Definitions common to all certification and test procedures are in:

D-200 Definitions for Vapor Recovery Procedures

For the purpose of this procedure, the term "CARB" refers to the California Air Resources Board, and the term "Executive Officer" refers to the CARB Executive Officer or his or her authorized representative or designate.

1. PURPOSE AND APPLICABILITY

The purpose of this procedure is to determine the pressure and vacuum at which a Pressure-/Vacuum Vent Valve (P/V Valve) actuates, and to determine the volumetric leak rate at a given pressure as specified in CP-201, Certification Procedure for Vapor Recovery Systems at Gasoline Dispensing Facilities. This procedure is applicable for certification and compliance testing of P/V Valves.

2. PRINCIPLE AND SUMMARY OF TEST PROCEDURE

The volumetric leak rate of a P/V Valve is determined by measuring the positive and negative flow rates at corresponding pressures. The positive and negative cracking pressures of the valve are determined by measuring the pressure at which the P/V Valve opens to atmospheric pressure. With the exception of certification testing performed by the Executive Officer, these measurements are determined by removing the P/V Valve and conducting the test on a test stand. A flow metering device is used to introduce flow while measuring pressure.

3. BIASES AND INTERFERENCES

3.1 Installing a P/V Valve onto the test stand in a manner that is not in accordance with the manufacturer's recommended installation instructions can produce erroneous results.

3.2 Leaks in the test stand or test equipment can produce erroneous results.

4. SENSITIVITY, RANGE, AND PRECISION

4.1 Electronic Pressure Measuring Device. Minimum sensitivity shall be 0.01 inches H_2O with a maximum full-scale range of 20 inches H_2O and minimum accuracy of plus or minus 0.50 percent full-scale range.

4.2 Flow Meter. The measurable leak rate is dependent upon the sensitivity, range and precision of the flow meter used for testing. For electronic flow metering devices, the minimum sensitivity shall be 1.0 ml/min (0.0021 CFH) with a minimum full-scale accuracy of ±1.0 percent. For rotameters, the flow meter minimum sensitivity shall be 12.5 ml/min (.026 CFH) with minimum accuracy of ± 5 percent full-scale. The device scale shall be 150mm (5.91 inches) tall to provide a sufficient number of graduations for readability.

5. EQUIPMENT

5.1 Nitrogen. Use commercial grade gaseous nitrogen in a high-pressure cylinder equipped with a pressure regulator and one (1.00) psig pressure relief valve. As an alternative, compressed air may be used to pressurize to the minimum working pressure required by the Flow Metering device.

5.2 Ballast Tank. If required, use a commercially available tank (2 gallon minimum), capable of being pressurized or evacuated (placed under vacuum) to the minimum working pressure required by the flow-metering device(s).

5.3 Vacuum Pump or Vacuum Generating Device. Use a commercially available vacuum pump or equivalent, capable of evacuating the ballast tank or test stand to the minimum working pressure required by the flow-metering device.

5.4 Electronic Pressure Gauge. Use an electronic pressure gauge or digital manometer that conforms to the minimum requirements listed in section 4 to measure the pressure inside of the test stand.

5.5 Flow Metering Device(s). Use either an electronic flow-metering device or Rotameter as described below to measure or introduce a volumetric flow rate. Although the use of either type of instrument is allowed, electronic flow metering devices provide higher accuracy and precision. For the purpose of certification testing, only electronic flow metering devices shall be used.

5.5.1 Electronic Flow Metering Device. Use a Mass Flow Meter that conforms to the minimum requirements listed in section 4 to introduce nitrogen or compressed air into the test stand. The Mass Flow Meter shall be equipped with a high precision needle valve to accurately adjust the flow settings. The meter may be used for both positive and negative flow rates by reconfiguring the pressure or vacuum lines.

5.5.2 Rotameters. Two (2) devices required. Use two Flow Meters with minimum specifications described in Section 4 to measure or introduce flow rates. One meter shall use a needle valve oriented for introducing positive flow and the other using an inverted needle valve for introducing vacuum.

5.6 Test Stand. If a bench test arrangement is used, use a test stand as shown in Figure 1**,** or equivalent, equipped with a 2-inch NPT threaded pipe on at least one end for attaching the P/V Valve in an upright position. If other than 2-inch NPT is required, use an adaptor to reduce or enlarge the 2 inch pipe. The test stand shall be equipped with at least two (2) ports used for introducing flow and measuring

pressure. Use a bypass valve to enable the tester to set the required flow without pressurizing the P/V Valve. Once the required flow rate is set, the bypass valve shall be closed to route the flow into the stand and pressurize the P/V Valve to check cracking pressure. Test stands may be constructed of various materials or dimensions. For certification testing conducted by Executive Officer only, the P/V valve may be isolated and tested in place at the facility.

6. PRE-TEST PROCEDURES

6.1 All pressure measuring device(s) shall be bench calibrated using a reference gauge, incline manometer or NIST traceable standard at least once every six (6) months. Calibration shall be performed at 20, 50, and 80 percent of full scale. Accuracy shall be within five (5) percent at each of these calibration points.

6.2 Electronic pressure measuring devices shall be calibrated immediately prior to testing using the zero gauge pressure adjustment knob located on the instrument.

6.3 The Flow Metering device(s) shall be calibrated using a reference meter or NIST traceable standard. Calibrations shall be performed at 20, 50, and 80 percent of full-scale range and shall take place at a minimum of once every six (6) months.

6.4 Leak check the test stand or test assembly prior to installing the P/V Valve.

(a) Install a 2-inch cap onto the NPT threads in place of the P/V Valve using pipe sealant or Teflon tape.

(b) Check all fittings for tightness and proper assembly.

(c) Slowly establish a stable gauge pressure in the test stand between 18.00 and 20.00 inches water column and allow pressure to stabilize.

(d) Check for leaks by applying a leak detection solution around all fittings and joints and by observing the pressure for pressure changes that may identify a leak. If no bubbles form, the test stand is leak tight.

(e) If soap bubbles form or the test stand pressure will not stabilize, repeat (a) through (d); it may be necessary to place the test apparatus in an environment that is free from the effects of wind or sunlight.

7. TEST PROCEDURE

7.1 Install the P/V Valve in an upright position following the installation instructions provided by the manufacturer. Incorrectly installing the valve will invalidate any pressure versus flow rate measurement.

7.2 Positive Leak Rate. Slowly open the control valve on the Positive Flow Metering device until the pressure stabilizes at the positive leak rate pressure described in CP-201 section 3. Maintain steady state pressure by using the control valve for at least ten (10) seconds. Steady state flow is indicated by a pressure change of no more than 0.05 inches H_2O on the pressure gauge. Record the final flow rate on the data sheet and close the control valve.

7.3 Positive Cracking Pressure. Open the bypass valve to route the flow outside of the test assembly. Open the control valve on the Positive Flow Metering device to establish a flow rate of 120 ml/min. Once flow is stabilized, close the bypass valve to route the flow into the test assembly. Observe the pressure. The P/V Valve should "crack" at a pressure within the range of positive cracking pressure as described in CP-201 section 3. This is marked by a sudden drop in pressure. Record the cracking pressure (highest pressure achieved***)*** on the data sheet and close the control valve.

7.4 Negative Leak Rate. Open the control valve on the Negative Flow Metering device until the pressure stabilizes at the negative leak rate pressure described in CP-201 section. Maintain steady state pressure by using the control valve for at least ten (10) seconds. Steady state flow is indicated by a pressure change of no more than 0.05 inches H_2O on the pressure gauge. Record the final flow rate on the data sheet and close the control valve.

7.5 Negative Cracking Pressure. Open the bypass valve to route the flow outside of the test assembly. Open the control valve on the Negative Flow Metering device to establish a negative flow rate of 200 ml/min. Once flow is stabilized, close the bypass valve to route the flow into the test assembly. Observe the pressure. The P/V Valve should "crack" at a pressure within the range of negative cracking pressure as described in CP-201 section 3. This is marked by a sudden drop in vacuum. Record the cracking pressure (highest vacuum achieved) on the data sheet and close the control valve.

8. POST-TEST PROCEDURES

8.1 Remove the P/V Valve from the test assembly.

8.2 Disassemble the pressure regulator from the compressed nitrogen cylinder (if used) and place the safety cap back on the cylinder.

8.3 Disassemble all remaining test equipment and store in a protected location.

9. CALCULATING RESULTS

9.1 Commonly used flow rate conversions:

1 CFH = 471.95 ml/min

Example: Convert 0.17 CFH to ml/min***:***

0.17 CFH (471.95) = 80 ml/min

1 ml/min = 0.00212 CFH

Example: Convert 100 ml/min to CFH:

100 ml/min (0.00212) = 0.21 CFH

10. REPORTING RESULTS

10.1 Record the station or location name, address and tester information on Form 1.

10.2 Record the P/V Valve manufacturer's name and model number on Form 1.

10.3 Record the results of the test(s) on Form 1. Use additional copies of Form 1 if needed to record additional P/V Valve tests.

10.4 Alternate data sheets or Forms may be used provided they contain the same parameters as identified on Form 1.

10.5 Use the formulas and example equation provided in Section 9 to convert the flow measurements into units of cubic feet per hour (CFH).

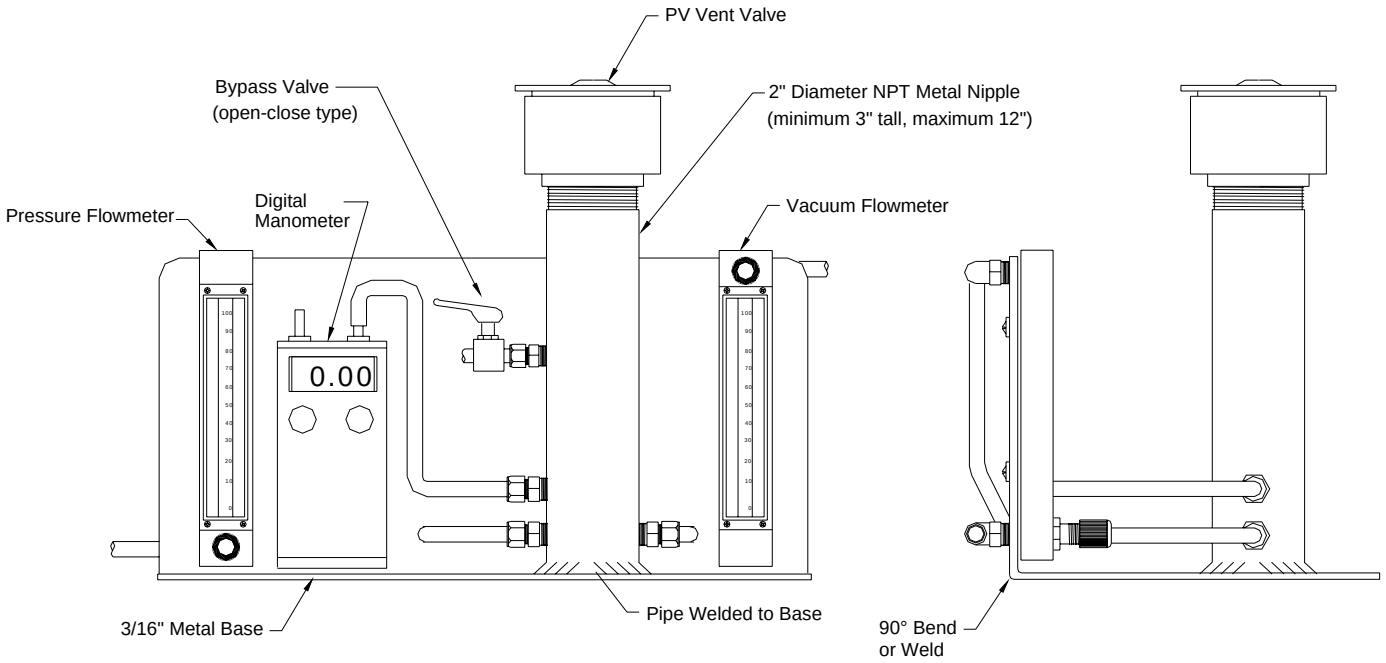
10.6 For certification testing, compare results to the performance standards listed in Table 3-1 of CP-201. For compliance testing, compare the results to the manufacturer's specifications listed on the P/V Valve for both leak rate and cracking pressure. For volumetric leak rates less than the manufacturers specified leakrate and cracking pressures within the manufacturers specified range, circle Pass on the data sheet where provided. If either the volumetric leak rate or cracking pressure exceeds the manufacturers specifications, circle Fail on the data sheet where provided.

11. ALTERNATIVE TEST PROCEDURES

This procedure shall be conducted as specified. Any modifications to this test procedure shall not be used unless prior written approval has been obtained from the Executive Officer pursuant to section 14 of CP-201.

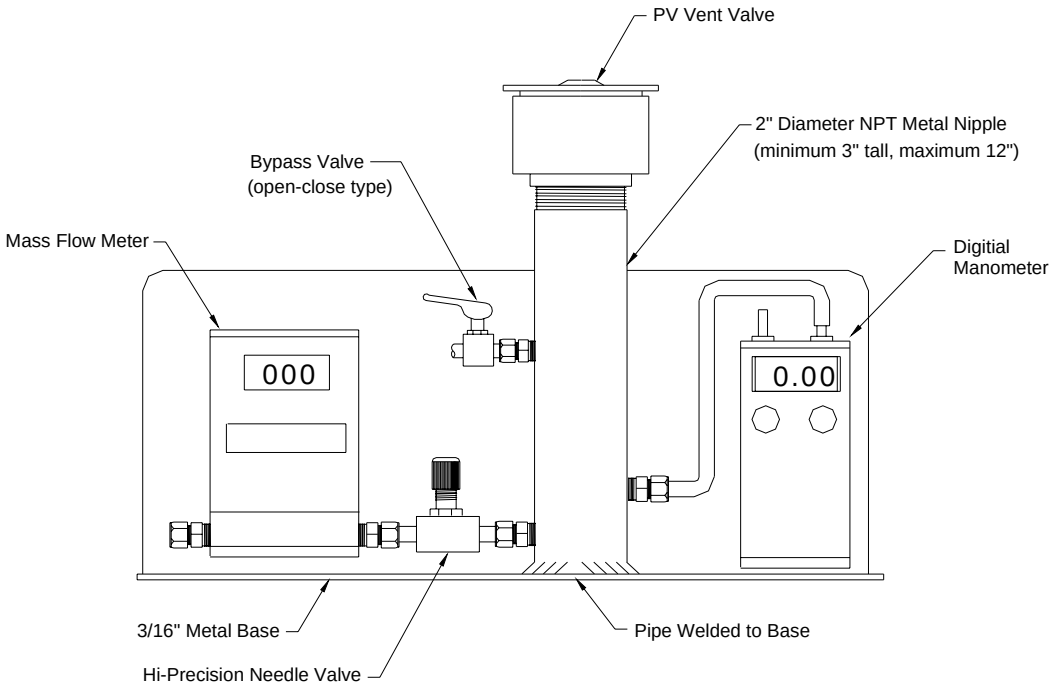
Figure 1

Example of Test Stand



FLOW METER CONFIGURATION

SIDE VIEW



MASS FLOW METER CONFIGURATION

Form 1

Pressure/Vacuum (P/V) Vent Valve Data Sheet

Facility Name:	Test Date:
Address:	Test Company:
City :	Tester Name:

P/V Valve Manufacturer:	**Model Number:**	**Pass**	**Fail**
Manufacturers Specified Positive Leak Rate (CFH):	**Manufacturers Specified Negative Leak Rate (CFH):**		
Measured Positive Leak Rate (CFH):	Measured Negative Leak Rate (CFH):		
Positive Cracking Pressure (in. H_2O):	Negative Cracking Pressure (in. H_2O):		

P/V Valve Manufacturer:	**Model Number:**	**Pass**	**Fail**
Manufacturers Specified Positive Leak Rate (CFH):	**Manufacturers Specified Negative Leak Rate (CFH):**		
Measured Positive Leak Rate (CFH):	Measured Negative Leak Rate (CFH):		
Positive Cracking Pressure (in. H_2O):	Negative Cracking Pressure (in. H_2O):		

P/V Valve Manufacturer:	**Model Number:**	**Pass**	**Fail**
Manufacturers Specified Positive Leak Rate (CFH):	**Manufacturers Specified Negative Leak Rate (CFH):**		
Measured Positive Leak Rate (CFH):	Measured Negative Leak Rate (CFH):		
Positive Cracking Pressure (in. H_2O):	Negative Cracking Pressure (in. H_2O):		

P/V Valve Manufacturer:	**Model Number:**	**Pass**	**Fail**
Manufacturers Specified Positive Leak Rate (CFH):	**Manufacturers Specified Negative Leak Rate (CFH):**		
Measured Positive Leak Rate (CFH):	Measured Negative Leak Rate (CFH):		
Positive Cracking Pressure (in. H_2O):	Negative Cracking Pressure (in. H_2O):		

California Environmental Protection Agency

Air Resources Board

Vapor Recovery Test Procedure

TP-201.3

Determination of 2 Inch WC Static Pressure Performance of Vapor Recovery Systems of Dispensing Facilities

Adopted: April 12, 1996
Amended: March 17, 1999

California Environmental Protection Agency
Air Resources Board
Vapor Recovery Test Procedure

TP-201.3

Determination of 2 Inch WC Static Pressure Performance of Vapor Recovery Systems of Dispensing Facilities

1 APPLICABILITY

Definitions common to all certification and test procedures are in:

D-200 Definitions for Certification Procedures and Test Procedures for Vapor Recovery Systems

For the purpose of this procedure, the term "ARB" refers to the State of California Air Resources Board, and the term "ARB Executive Officer" refers to the Executive Officer of the ARB or his or her authorized representative or designate.

1.1 This test procedure is used to quantify the vapor tightness of vapor recovery systems installed at gasoline dispensing facilities (GDF) equipped with pressure/vacuum (P/V) valves, provided that the designed pressure setting of the P/V valves is a minimum of 2.5 inches of water column (inches H_2O).

1.2 Systems equipped with a P/V valve(s) allowed to have a designed cracking pressure less than 2.5 inches H_2O shall be bagged to eliminate any flow contribution through the valve assembly from the test results. The valve/vent pipe connection, however, shall remain unobstructed during this test.

1.3 At facilities not required to be equipped with a P/V valve(s), the vent pipe(s) shall be capped. For those installations, the test may be conducted at the vent pipe(s).

2 PRINCIPLE AND SUMMARY OF TEST PROCEDURE

2.1 The entire vapor recovery system is pressurized with nitrogen to two (2.0) inches H_2O. The system pressure is then allowed to decay and the pressure after five (5) minutes is compared with an allowable value. The minimum allowable five-minute final pressure is based on the system ullage and pressure decay equations. For the purpose of compliance

determination, this test shall be conducted after all back-filling, paving, and installation of all Phase I and Phase II components, including P/V valves, has been completed.

2.2 For GDF equipped with a coaxial Phase I system, this test shall be conducted at a Phase II vapor riser. For GDF which utilize a two-point Phase I system, this test may be conducted at either a Phase II riser or a Phase I vapor coupler provided that the criteria set forth in Section 6.7 have been met. If the integrity criteria for two-point systems specified in Section 6.7 are met, it is recommended that this test be conducted at the Phase I vapor coupler.

3 RANGE

3.1 If mechanical pressure gauges are employed, the full-scale range of pressure gauges shall be 0-2.0, 0-1.0, and 0-0.50 inches H_2O column. Maximum incremental graduations of the pressure gauge shall be 0.05 inches H_2O and the minimum accuracy of the gauge shall be three percent of full scale. The minimum diameter of the pressure gauge face shall be 4 inches.

3.2 If an electronic pressure measuring device is used, the full-scale range of the device shall not exceed 0-10 inches H_2O with a minimum accuracy of 0.5 percent of full-scale. A 0-20 inches H_2O device may be used, provided the equivalent accuracy is not less than 0.25 percent of full-scale.

3.3 The minimum total ullage, for each individual tank, shall be 1,000 gallons or 25% of the tank capacity, whichever is less. The maximum total ullage, for all manifolded tanks, shall not exceed 25,000 gallons. These values are exclusive of all vapor piping volumes.

3.4 The minimum and maximum nitrogen feed-rates, into the system, shall be one (1) and five (5) CFM, respectively.

4 INTERFERENCES

4.1 Introduction of nitrogen into the system at flowrates exceeding five (5) CFM may bias the results of the test toward non-compliance. Only gaseous nitrogen shall be used to conduct this test. Air, liquefied nitrogen, helium, or any gas other than nitrogen shall not be used for this test procedure.

4.2 For vacuum-assist Phase II systems which utilize an incinerator, power to the collection unit and the processor shall be turned off during testing.

4.3 For vacuum-assist systems, with positive displacement vacuum pumps, which locate the vacuum producing device in-line between the Phase II vapor riser and the storage tank, the following requirements shall apply:

4.3.1 A valve shall be installed at the vacuum producing device. When closed, this valve shall isolate the vapor passage downstream of the vacuum producing device.

4.3.2 The storage tank side of the vacuum producing device shall be tested in accordance with the procedures outlined in Section 7 of this method. Compliance shall be determined by comparing the final five-minute pressure with the allowable minimum five-minute final pressure from the first column (1-6 affected nozzles) in Table IB or use the corresponding equation in Section 9.2.

4.3.3 The upstream vapor passage (nozzle to vacuum producing device) shall also be tested. Methodology for this test shall be submitted to the California Air Resources Board (CARB) for approval prior to submission of test results or shall be conducted in accordance with the procedures set forth in the applicable CARB Executive Order.

4.4 The results of this static pressure integrity test shall not be used to verify compliance if an Air to Liquid Volumetric Ratio Test (TP-201.5 or equivalent) was conducted within 24 hours prior to this test.

4.5 Thermal Bias for Electronic Manometers

Electronic manometers shall have a warm-up period of at least 15 minutes followed by a five minute drift check. If the drift exceeds 0.01 inches water column, the instrument should not be used.

5 APPARATUS

5.1 Nitrogen

Use commercial grade nitrogen in a high pressure cylinder, equipped with a two-stage pressure regulator and a one psig pressure relief valve.

5.2 Pressure Measuring Device

Use 0-2.0, 0-1.0, and 0-0.50 inches H_2O pressure gauges connected in parallel, a 0-2 inches H_2O manometer, or an electronic pressure measuring device to monitor the pressure decay in the vapor recovery system. The pressure measuring device shall, at a minimum, be readable to the nearest 0.05 inches H_2O.

5.3 "T" Connector Assembly

See Figure 1 for example.

5.4 Vapor Coupler Integrity Assembly

Assemble OPW 633-A, 633-B, and 634-A adapters, or equivalent, as shown in Figure 2. If the test is to be conducted at the storage tank Phase I vapor coupler, this assembly shall

be used prior to conducting the static leak test in order to verify the pressure integrity of the vapor poppet. The internal volume of this assembly shall not exceed 0.1 cubic feet.

5.5 Vapor Coupler Test Assembly

Use a compatible OPW 634-B cap, or equivalent, equipped with a center probe to open the poppet, a pressure measuring device to monitor the pressure decay, and a connection for the introduction of nitrogen into the system. See Figure 3 for an example.

5.6 Stopwatch

Use a stopwatch accurate to within 0.2 seconds.

5.7 Flow Meter

Use a Dwyer flowmeter, Model RMC-104, or equivalent, to determine the required pressure setting of the delivery pressure gauge on the nitrogen supply pressure regulator. This pressure shall be set such that the nitrogen flowrate is between 1.0 and 5.0 CFM.

5.8 Combustible Gas Detector

A Bacharach Instrument Company, Model 0023-7356, or equivalent, may be used to verify the pressure integrity of system components during this test.

5.9 Leak Detection Solution

Any liquid solution designed to detect vapor leaks may be used to verify the pressure integrity of system components during this test.

6 PRE-TEST PROCEDURES

6.1 The following safety precautions shall be followed:

6.1.1 Only nitrogen shall be used to pressurize the system.

6.1.2 A one psig relief valve shall be installed to prevent the possible over-pressurizing of the storage tank.

6.1.3 A ground strap should be employed during the introduction of nitrogen into the system.

6.2 Failure to adhere to any or all of the following time and activity restrictions shall invalidate the test results:

6.2.1 There shall be no Phase I bulk product deliveries into or out of the storage tank(s) within the three (3) hours prior to the test or during performance of this test procedure.

6.2.2 There shall be no product dispensing within thirty (30) minutes prior to the test or during performance of this test procedure.

6.2.3 Upon commencement of the thirty minute "no dispensing" portion of this procedure, the headspace pressure in the tank shall be measured. If the pressure exceeds 0.50 inches H_2O, the pressure shall be carefully relieved in accordance with all applicable safety requirements. After the thirty minute "no dispensing" portion of this procedure, and prior to introduction of nitrogen, the headspace pressure shall again be lowered, if necessary, to less than 0.50 inches H_2O.

6.2.4 There shall be no Air to Liquid Volumetric Ratio Test (TP-201.5 or equivalent) conducted within the twenty-four (24) hour period immediately prior to this test.

6.2.5 The test shall be conducted with the station in normal operating mode. This includes all nozzles properly hung up in the dispenser boots and all dispenser cabinet covers in place. The exception to normal operating mode is that dispensing is disallowed as specified.

6.3 Measure the gallons of gasoline present in each underground storage tank and determine the actual capacity of each storage tank from facility records. Calculate the ullage space for each tank by subtracting the gasoline gallonage present from the actual tank capacity. The minimum ullage during the test, for all manifolded tanks, shall be 1,000 gallons or 25 percent of the tank capacity, whichever is less. The total ullage, for all manifolded tanks, shall not exceed 25,000 gallons.

6.4 For two-point Phase I systems, this test shall be conducted with the dust cap removed from both the product and the vapor coupler. This is necessary to determine the vapor tightness of the Phase I vapor poppet. See Section 6.7 if this test is to be conducted at the Phase I vapor coupler.

6.4.1 For coaxial Phase I systems, this test shall be conducted with the dust cap removed from the Phase I coupler. This is necessary to insure the vapor tightness of the Phase I vapor poppet.

6.4.2 Verify that the liquid level in the storage tank is at least four (4) inches above the highest opening at the bottom of the submerged drop tube.

6.5 If the Phase I containment box is equipped with a drain valve, this test shall be conducted with the drain valve installed and the manhole cover removed. If the drain valve is cover-

actuated, the test shall be done once with the cover removed and repeated with the cover installed.

6.6 If the test is to conducted at a Phase II vapor riser, disconnect the dispenser end of one vapor recovery hose and install the "T" connector assembly (see Figure 1). Connect the nitrogen gas supply (do not use air) and the pressure measuring device to the "T" connector.

6.6.1 For those Phase II vapor systems utilizing a dispenser mounted remote vapor check valve, the "T" connector assembly shall be installed on the vapor riser side of the check valve.

6.7 If this test is to be conducted at the Phase I vapor coupler on a two-point Phase I system, the procedures set forth in subsections 6.7.1 and 6.7.2 shall be successfully completed prior to testing. The static pressure integrity test shall not be conducted at the Phase I coupler at facilities equipped with coaxial Phase I systems.

6.7.1 Connect the Vapor Coupler Integrity Assembly to the Phase I vapor coupler. Connect the Vapor Coupler Test Assembly. Connect the nitrogen supply to the assembly and carefully pressurize the internal volume of the assembly to two (2.0) inches H_2O. Start the stopwatch. Record the final pressure after one minute.

6.7.2 If the pressure after one minute is less than 0.25 inches H_2O, the leak rate through the Phase I vapor poppet precludes conducting the static leak test at this location. If the pressure after one minute is greater than or equal to 0.25 inches H_2O, the static leak test may be conducted at this location. This criteria assures a maximum leak rate through the Phase I vapor poppet of less than 0.0004 cubic feet per minute.

6.7.3 Disconnect the Vapor Coupler Integrity Assembly to the Phase I vapor coupler. If the requirements of subsection 6.7.2 were met, connect the Vapor Coupler Test Assembly to the Phase I vapor coupler.

6.7.4 Product may be poured onto the Phase I vapor coupler to check for leaks. This diagnostic procedure shall not be substituted for the procedures set forth in subsections 6.7.1 and 6.7.2.

6.8 All pressure measuring device(s) shall be bench calibrated using either a reference gauge or incline manometer. Calibration shall be performed at 20, 50, and 80 percent of full scale. Accuracy shall be within two percent at each of these calibration points. Calibrations shall be conducted on a frequency not to exceed 90 days.

6.9 Use the flowmeter to determine the nitrogen regulator delivery pressures which correspond to nitrogen flowrates of 1.0 and 5.0 CFM. These pressures define the

allowable range of delivery pressures acceptable for this test procedure. Also record the regulator delivery pressure setting, and the corresponding nitrogen flowrate that will be used during the test. As an alternative, the flowmeter may be connected, in-line between the nitrogen supply regulator and Vapor Coupler Test Assembly, during the test.

6.10 Use Equation 9.3 to calculate the approximate time required to pressurize the system ullage to the initial starting pressure of two (2.0) inches H_2O. This will allow the tester to minimize the quantity of nitrogen introduced into those systems which cannot comply with the static leak standards.

6.11 Attach the Vapor Coupler Test assembly to the Phase I poppet or the "T" connector assembly to the Phase II vapor riser. Read the initial pressure of the storage tank and underground piping. If the initial pressure is greater than 0.5 inches H_2O, carefully bleed off the pressure, in accordance with all applicable safety procedures, in the storage tank and underground piping to less than 0.5 inches H_2O column.

6.12 Any electronic manometers shall be subject to warm-up and drift check before use; see Section 4.5.

7 TESTING

7.1 Open the nitrogen gas supply valve and set the regulator delivery pressure within the allowable range determined in Section 6.9, and start the stopwatch. Pressurize the vapor system (or subsystem for individual vapor return line systems) to **at least 2.2 inches H_2O** initial pressure. It is critical to maintain the nitrogen flow until the pressure stabilizes, indicating temperature and vapor pressure stabilization in the tanks. Check the test equipment using leak detecting solution or a combustible gas detector to verify that all test equipment is leak tight. Note: if a combustible gas detector is used to search for leaks, components which were certified with an allowable leak rate, such as 0.38 CFH at a pressure of two (2) inches, cannot be determined to be faulty solely on the basis of the concentration registered on the instrument.

7.1.1 If the time required to achieve the initial pressure of two (2.0) inches H_2O exceeds twice the time derived from Equation 9.3, stop the test and use liquid leak detector, or a combustible gas detector, to find leak(s) in the system. Failure to achieve the initial starting pressure within twice the time derived from Equation 9.3 demonstrates the inability of the system to meet the performance criteria. Repair or replace the faulty component(s) and restart the test pursuant to Section 7.1.

7.2 Close and disconnect the nitrogen supply. Start the stopwatch when the pressure has decreased to the initial starting pressure of two (2.0) inches H_2O.

7.3 At one-minute intervals during the test, record the system pressure. After five minutes, record the final system pressure. See the applicable of Tables 1A (or Equation 9.1) or 1B (or equation 9.2) to determine the acceptability of the final system static pressure results. For intermediate values of ullage in Tables 1A and 1B, linear interpolation may be employed.

7.4 If the system failed to meet the criteria set forth in Table 1A or 1B (or the appropriate equation in Section 9), repressurize the system and check all accessible vapor connections using leak detector solution or a combustible gas detector. If vapor leaks in the system are encountered, repair or replace the defective component and repeat the test. Potential sources of leaks include nozzle check valves, nozzle vapor paths, pressure/vacuum relief valves, containment box drain valve assemblies, and plumbing connections at the risers.

7.4.1 If the facility fails to comply with the static leak test standards and the two point Phase I system utilizes overfill prevention devices in the drop tubes which were installed before July 1, 1993, and which are unable to pass the test with the dust caps removed from the product and vapor couplers (see Sec. 6.4), the test may be conducted with the caps on the couplers, as an exception.

This exception is not intended to allow bleed holes in drop tubes.

This exception expires on January 1, 2002, after which date all testing shall be conducted with the fill and vapor caps removed from two point systems. Under no circumstances may the test be conducted with the caps on coaxial Phase I couplers.

7.5 After the remaining system pressure has been relieved, remove the "T" connector assembly and reconnect the vapor recovery hose, if applicable.

7.6 If the vapor recovery system utilizes individual vapor return lines, repeat the leak test for each gasoline grade. Avoid leaving any vapor return line open longer than is necessary to install or remove the "T" connector assembly.

7.7 If the applicable CARB Executive Order requires the test to be conducted with and without the containment box cover in place, repeat the test with the cover in place. In these cases clearly specify, on Form 1, which results represent the pressure integrity with and without the cover in place.

8 POST-TEST PROCEDURES

8.1 Use the applicable of Table 1A or 1B, or the applicable of Equations 9.1 or 9.2, to determine the compliance status of the facility by comparing the final five-minute pressure with the minimum allowable final pressure.

8.1.1 For balance Phase II systems use Table 1A or the applicable of Equation 9.1 to determine compliance.

8.1.2 For vacuum-assist Phase II systems use Table 1B or the applicable of Equation 9.2 to determine compliance.

9 CALCULATIONS

9.1 For Phase II Balance Systems, the minimum allowable five-minute final pressure, with an initial pressure of two (2.0) inches H_2O, shall be calculated as follows:

$$P_f = 2e^{\left(\frac{-760.490}{V}\right)} \quad \text{if } N = 1-6 \qquad \text{[Equation 9-1]}$$

$$P_f = 2e^{\left(\frac{-792.196}{V}\right)} \quad \text{if } N = 7-12$$

$$P_f = 2e^{\left(\frac{-824.023}{V}\right)} \quad \text{if } N = 13-18$$

$$P_f = 2e^{\left(\frac{-855.974}{V}\right)} \quad \text{if } N = 19-24$$

$$P_f = 2e^{\left(\frac{-888.047}{V}\right)} \quad \text{if } N > 24$$

where:

N = The number of affected nozzles. For manifolded systems, N equals the total number of nozzles. For dedicated plumbing configurations, N equals the number of nozzles serviced by the tank being tested.

P_f = The minimum allowable five-minute pressure, inches H_2O

V = The total ullage affected by the test, gallons

e = A dimensionless constant approximately equal to 2.718

2 = The initial starting pressure, inches H_2O

9.2 For Phase II Vacuum Assist Systems, the minimum allowable five-minute final pressure, with an initial pressure of two (2.0) inches H_2O, shall be calculated as follows:

$$P_f = 2e^{\left(\frac{-500.887}{V}\right)} \quad \text{if } N = 1-6 \qquad \text{[Equation 9-2]}$$

$$P_f = 2e^{\left(\frac{-531.614}{V}\right)} \quad \text{if } N = 7-12$$

$$P_f = 2e^{\left(\frac{-562.455}{V}\right)} \quad \text{if } N = 13-18$$

$$P_f = 2e^{\left(\frac{-593.412}{V}\right)} \quad \text{if } N = 19-24$$

$$P_f = 2e^{\left(\frac{-624.483}{V}\right)} \quad \text{if } N > 24$$

where:

N = The number of affected nozzles. For manifolded systems, N equals the number of nozzles. For dedicated plumbing configurations, N equals the number of nozzles serviced by the tank being tested.

P_f = The minimum allowable five-minute final pressure, inches H_2O

V = The total ullage affected by the test, gallons

e = A dimensionless constant approximately equal to 2.718

2 = The initial starting pressure, inches H_2O

9.3 The minimum time required to pressurize the system ullage from zero (0) to two (2.0) inches H_2O gauge pressure shall be calculated as follows:

$$t_2 = \frac{V}{[1980]\ F} \qquad \text{[Equation 9-3]}$$

where:

t_2 = The minimum time to pressurize the ullage to two inches H_2O, minutes

V = The total ullage affected by the test, gallons

F = The nitrogen flowrate into the system, CFM

1980 = The conversion factor for pressure and gallons

9.4 If the policy of the local District requires an allowable tolerance for testing error, the minimum allowable five-minute final pressure, including testing error, shall be calculated as follows:

$$P_{f-E} = 2 - \left[1 + \left(\frac{E}{100}\right)\right](408.9 - (P_f + 406.9)) \qquad \text{[Equation 9-4]}$$

where:

P_{f-E} = The minimum allowable five-minute final pressure including allowable testing error, inches H_2O

E = The allowable testing error, percent

P_f = The minimum allowable five-minute final pressure calculated in Equations 9-1 or 9-2, inches H_2O

2 = The initial starting pressure, inches H_2O

408.9 = Atmospheric pressure plus the initial starting pressure, inches H_2O

406.9 = Atmospheric pressure, inches H_2O

10 REPORTING

10.1 The calculated ullage and system pressures for each five-minute vapor recovery system test shall be reported as shown in Form 1. Be sure to include the Phase I system type (two-point or coaxial), the Phase II system type, whether the system is manifolded, and the one-minute pressures during the test.

TABLE 1A

PHASE II **BALANCE** SYSTEMS

PRESSURE DECAY CRITERIA

INITIAL PRESSURE OF 2 INCHES WATER COLUMN (WC)

MINIMUM PRESSURE AFTER 5 MINUTES, INCHES WC

ULLAGE, GALLONS	NUMBER OF AFFECTED NOZZLES				
	01-06	07-12	13-18	19-24	>24
500	0.44	0.41	0.38	0.36	0.34
550	0.50	0.47	0.45	0.42	0.40
600	0.56	0.53	0.51	0.48	0.46
650	0.62	0.59	0.56	0.54	0.51
700	0.67	0.64	0.62	0.59	0.56
750	0.73	0.70	0.67	0.64	0.61
800	0.77	0.74	0.71	0.69	0.66
850	0.82	0.79	0.76	0.73	0.70
900	0.86	0.83	0.80	0.77	0.75
950	0.90	0.87	0.84	0.81	0.79
1,000	0.93	0.91	0.88	0.85	0.82
1,200	1.06	1.03	1.01	0.98	0.95
1,400	1.16	1.14	1.11	1.09	1.06
1,600	1.24	1.22	1.19	1.17	1.15
1,800	1.31	1.29	1.27	1.24	1.22
2,000	1.37	1.35	1.32	1.30	1.28
2,200	1.42	1.40	1.38	1.36	1.34
2,400	1.46	1.44	1.42	1.40	1.38
2,600	1.49	1.47	1.46	1.44	1.42
2,800	1.52	1.51	1.49	1.47	1.46
3,000	1.55	1.54	1.52	1.50	1.49
3,500	1.61	1.59	1.58	1.57	1.55
4,000	1.65	1.64	1.63	1.61	1.60
4,500	1.69	1.68	1.67	1.65	1.64
5,000	1.72	1.71	1.70	1.69	1.67
6,000	1.76	1.75	1.74	1.73	1.72
7,000	1.79	1.79	1.78	1.77	1.76
8,000	1.82	1.81	1.80	1.80	1.79
9,000	1.84	1.83	1.83	1.82	1.81
10,000	1.85	1.85	1.84	1.84	1.83
15,000	1.90	1.90	1.89	1.89	1.89
20,000	1.93	1.91	1.92	1.92	1.91
25,000	1.94	1.94	1.94	1.93	1.93

Note: For manifolded Phase II Balance Systems, the **"Number of Affected Nozzles"** shall be the total of all gasoline nozzles. For dedicated return configurations, the **"Number of Affected Nozzles"** shall be the total of those nozzles served by the tank being tested.

TABLE 1B

PHASE II ASSIST SYSTEMS

PRESSURE DECAY CRITERIA

INITIAL PRESSURE OF 2 INCHES WATER COLUMN (WC)

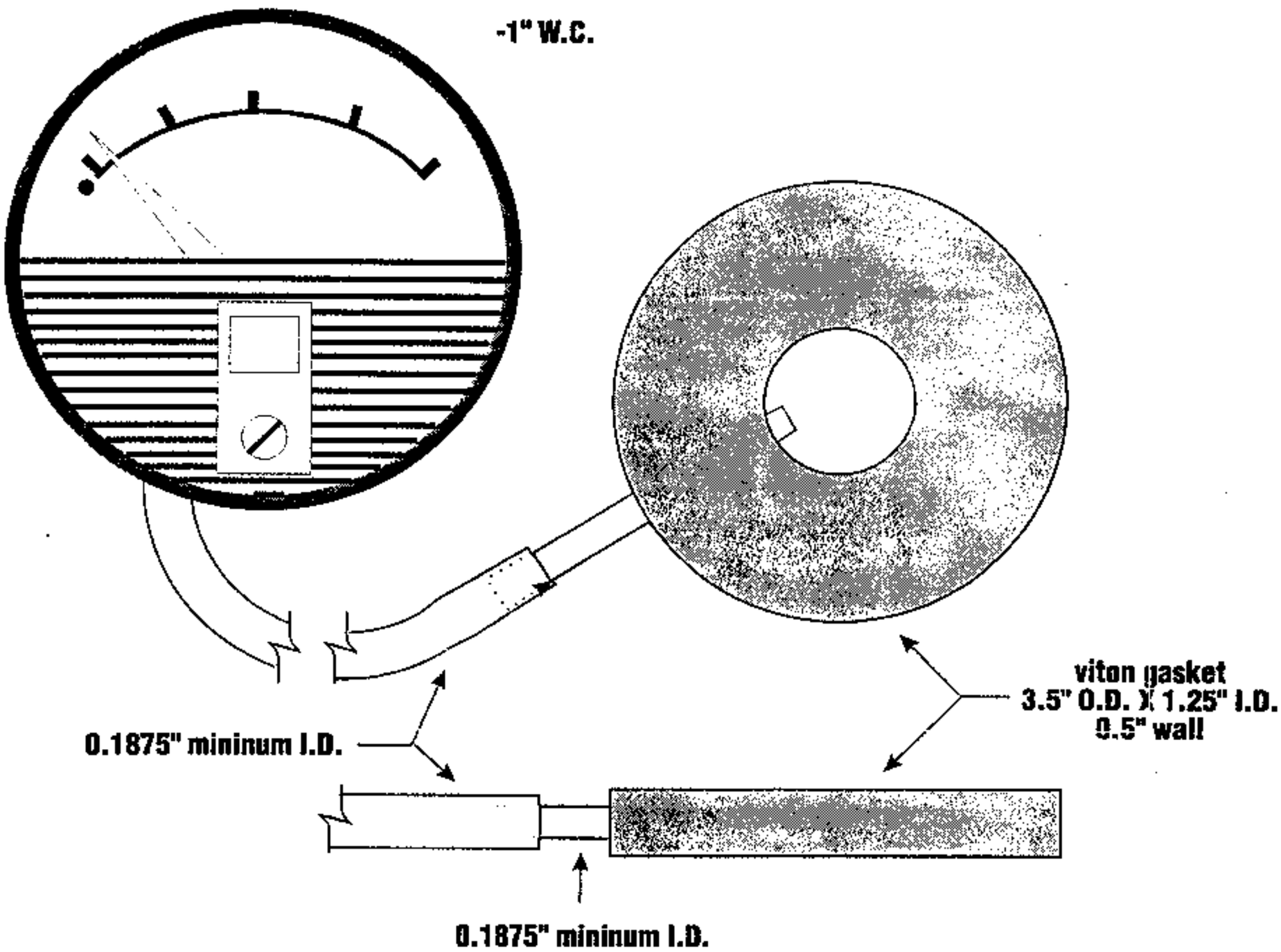
MINIMUM PRESSURE AFTER 5 MINUTES, INCHES WC

ULLAGE, GALLONS	NUMBER OF AFFECTED NOZZLES 01-06	07-12	13-18	19-24	>24
500	**0.73**	**0.69**	**0.65**	0.61	0.57
550	0.80	0.76	0.72	0.68	0.64
600	**0.87**	**0.82**	**0.78**	**0.74**	0.71
650	0.93	0.88	0.84	0.80	0.77
700	**0.98**	**0.94**	**0.90**	**0.86**	**0.82**
750	1.03	0.98	0.94	0.91	0.87
800	**1.07**	**1.03**	**0.99**	**0.95**	**0.92**
850	1.11	1.07	1.03	1.00	0.96
900	**1.15**	**1.11**	**1.07**	**1.03**	**1.00**
950	1.18	1.14	1.11	1.07	1.04
1,000	**1.21**	**1.18**	**1.14**	**1.10**	**1.07**
1,200	1.32	1.28	1.25	1.22	1.19
1,400	**1.40**	**1.37**	**1.34**	**1.31**	**1.28**
1,600	1.46	1.43	1.41	1.38	1.35
1,800	**1.51**	**1.49**	**1.46**	**1.44**	**1.41**
2,000	1.56	1.53	1.51	1.49	1.46
2,200	**1.59**	**1.57**	**1.55**	**1.53**	**1.51**
2,400	1.62	1.60	1.58	1.56	1.54
2,600	**1.65**	**1.63**	**1.61**	**1.59**	**1.57**
2,800	1.67	1.65	1.64	1.62	1.60
3,000	**1.69**	**1.68**	**1.66**	**1.64**	**1.62**
3,500	1.73	1.72	1.70	1.69	1.67
4,000	**1.76**	**1.75**	**1.74**	**1.72**	**1.71**
4,500	1.79	1.78	1.77	1.75	1.74
5,000	**1.81**	**1.80**	**1.79**	**1.78**	**1.77**
6,000	1.84	1.83	1.82	1.81	1.80
7,000	**1.86**	**1.85**	**1.85**	**1.84**	**1.83**
8,000	1.88	1.87	1.86	1.86	1.85
9,000	**1.89**	**1.89**	**1.88**	**1.87**	**1.87**
10,000	1.90	1.90	1.89	1.88	1.88
15,000	**1.93**	**1.93**	**1.93**	**1.92**	**1.92**
20,000	1.95	1.95	1.94	1.94	1.94
25,000	**1.96**	**1.96**	**1.96**	**1.95**	**1.95**

Note: For manifolded Phase II Assist Systems, the **"Number of Affected Nozzles"** shall be the total of all gasoline nozzles. For dedicated return configurations, the **"Number of Affected Nozzles"** shall be t he total of those nozzles served by the tank being tested.

FIGURE 2

Torus Pressure Test Assembly



TP 201.4 F.2/ B. CORDOVA '95

Figure 3 – Fixed Volume Pressure Test Assembly

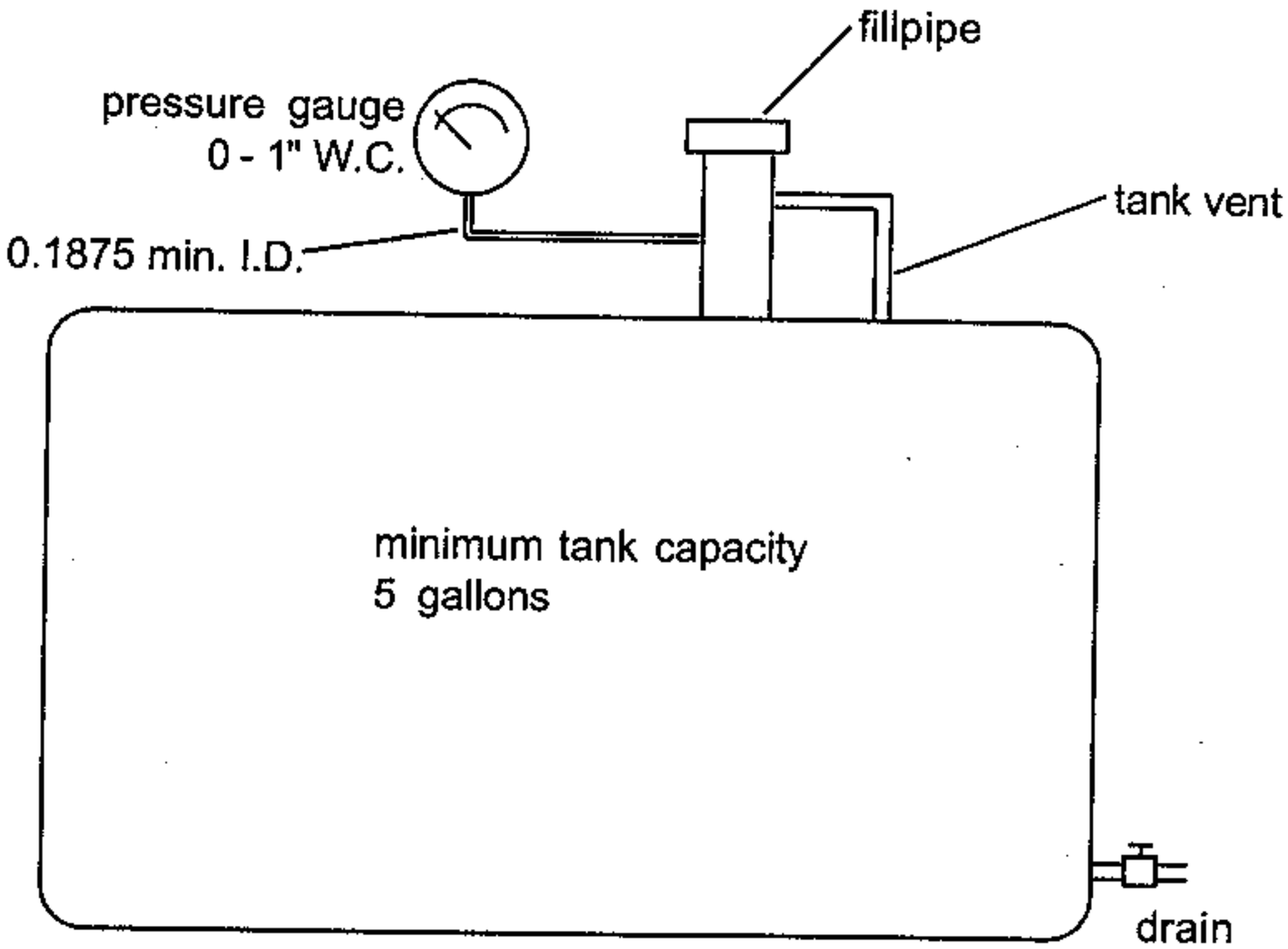


Figure 4 - Field Data Form

Facility Name & Address_____
Inspector_____ Date_____
Vapor Recovery System Type_____
Applicable Air Resources Board Executive Order # _____
Dynamic Pressure Limits from Executive Order: Inches of H_2O CFH Nitrogen

_____ @ _____
_____ @ _____
_____ @ _____

Pump Number	Gasoline Grade	Pressure, Inches of H_2O		Proc. 1 Nitrogen Flow, CFH		Proc. 3 Gallons Dispensed	Proc. 3 Time to Dispense	Proc. 3 Dispensing Rate, CFH

Source Test Procedure ST-30

STATIC PRESSURE INTEGRITY TEST UNDERGROUND STORAGE TANKS

(Adopted November 30, 1983)

REF: Regulation 8-7-301, 302

1. APPLICABILITY

1.1 This test procedure is used to quantify the vapor tightness of vapor recovery systems installed at gasoline dispensing facilities (GDF) equipped with pressure/vacuum (P/V) valves, provided that the designed pressure setting of the P/V valves is a minimum of 2.5 inches of water column (inches H_2O). Excessive leaks in the vapor recovery system will increase the quantity of fugitive hydrocarbon emissions and lower the overall efficiencies of both the Phase I and Phase II vapor recovery systems.

1.2 Systems equipped with a P/V valve(s) allowed to have a designed cracking pressure less than 2.5 inches H_2O shall be bagged to eliminate any flow contribution through the valve assembly from the test results. The valve/vent pipe connection, however, shall remain unobstructed during this test.

1.3 At facilities not required to be equipped with a P/V valve(s), the vent pipe(s) shall be capped. For those installations, the test may be conducted at the vent pipe(s).

2. PRINCIPLE

2.1 The entire vapor recovery system is pressurized with nitrogen to two (2.0) inches H_2O. The system pressure is then allowed to decay and the pressure after five (5) minutes is compared with an allowable value. The minimum allowable five-minute final pressure is based on the system ullage and pressure decay equations. For the purpose of compliance determination, this test shall be conducted after all back-filling, paving, and installation of all Phase I and Phase II components, including P/V valves, has been completed.

2.2 For GDF equipped with a coaxial Phase I system, this test shall be conducted at a Phase II vapor riser. For GDF which utilize a two-point Phase I system, this test may be conducted at either a Phase II riser or a Phase I vapor coupler provided that the criteria set forth in Section 6.7 have been met. If the integrity criteria for two-point systems specified in Section 6.7 are met, it is recommended that this test be conducted at the Phase I vapor coupler.

3. RANGE

3.1 If mechanical pressure gauges are employed, the full-scale range of the pressure gauges shall be 0-2.0, 0-1.0, and 0-0.50 inches H_2O column. Maximum incremental graduations of the pressure gauge shall be 0.05 inches H_2O and the minimum accuracy of the gauge shall be three percent of full scale. The minimum diameter of the pressure gauge face shall be 4 inches.

3.2 If an electronic pressure measuring device is used, the full-scale range of the device shall not exceed 0-10 inches H_2O with a minimum accuracy of 0.5 percent of full-scale. A 0-20 inches H_2O device may be used, provided the equivalent accuracy is not less than 0.25 percent of full scale.

3.3 The minimum and maximum total ullages shall be 500 and 25,000 gallons, respectively. These values are exclusive of all vapor piping volumes.

3.4 The minimum and maximum nitrogen feed-rates, into the system, shall be one (1) and five (5) CFM, respectively.

4. INTERFERENCES

4.1 Introduction of nitrogen into the system at flowrates exceeding five (5) CFM may bias the results of the test toward non-compliance.

4.2 For vacuum-assist Phase II systems which utilize an incinerator, power to the collection unit shall be turned off during testing.

4.3 For vacuum-assist systems which locate the vacuum producing device in-line between the Phase II vapor riser and the storage tank, the following requirements shall apply:

4.3.1 A valve shall be installed at the vacuum producing device. When closed, this valve shall isolate the vapor passage downstream of the vacuum producing device.

4.3.2 The storage tank side of the vacuum producing device shall be tested in accordance with the procedures outlined in Section 7 of this method. Compliance shall be determined by comparing the final five-minute pressure with the allowable minimum five-minute final pressure from the first column (1-6 affected nozzles) in Table 30-IB or use the corresponding equation in Section 9.2.

4.3.3 The upstream vapor passage (nozzle to vacuum producing device) shall also be tested. Methodology for this test shall be submitted to the Source Test Section of the BAAQMD for approval prior to submission of test results or shall be conducted in accordance with the procedures set forth in the applicable California Air Resources Board (CARB) Executive Order.

5. APPARATUS

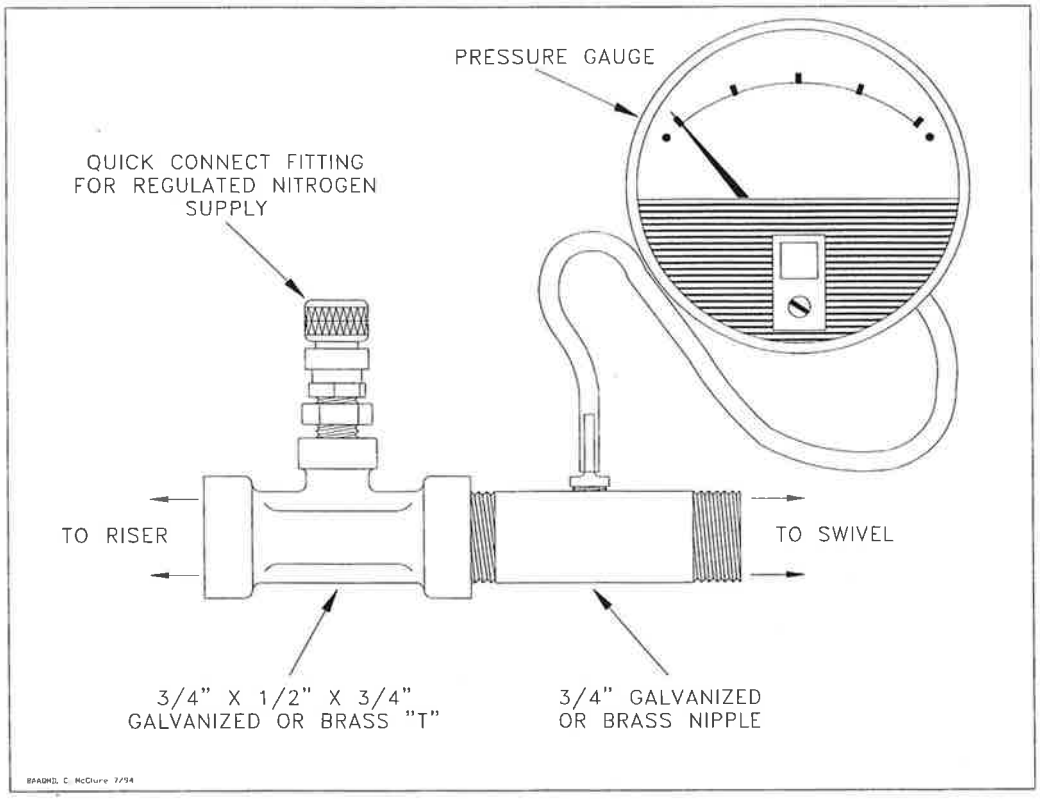
5.1 Nitrogen. Use commercial grade nitrogen in a high pressure cylinder, equipped with a two-stage pressure regulator and a one psig pressure relief valve.

5.2 Pressure Measuring Device. Use 0-2.0, 0-1.0, and 0-0.50 inches H_2O pressure gauges connected in parallel, a 0-2 inches H_2O manometer, or an electronic pressure measuring device to monitor the pressure decay in the vapor recovery system. The pressure measuring device shall, at a minimum, be readable to the nearest 0.05 inches H_2O.

5.3 "T" Connector Assembly. See Figure 30-1 for example.

Figure 30-1

"T" Connector Assembly



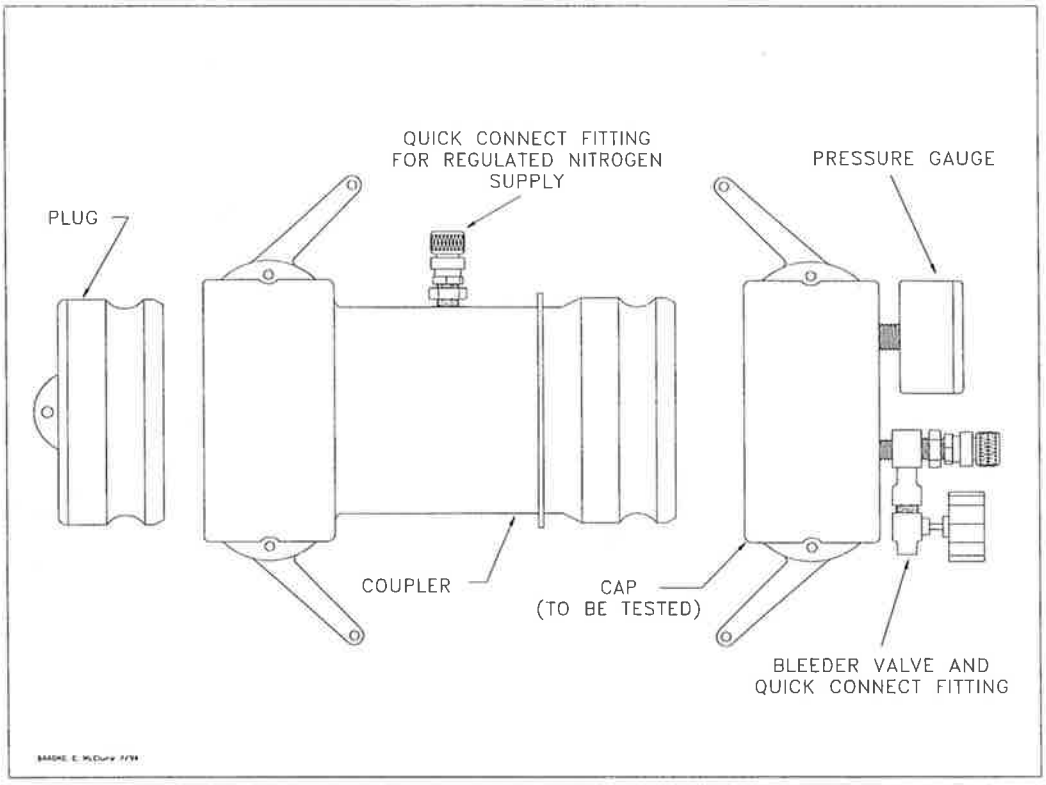
5.4 Vapor Coupler Integrity Assembly. Assemble OPW 633-A, 633-B, and 634-A adapters, or equivalent, as shown in Figure 30-2. If the test is to be conducted at the storage tank Phase I vapor coupler, this assembly shall be used prior to conducting the static leak test in order to verify the pressure integrity of the vapor poppet. The internal volume of this assembly shall not exceed 0.1 cubic feet.

5.5 Vapor Coupler Test Assembly. Use a compatible OPW 634-B cap, or equivalent, equipped with a center probe to open the poppet, a pressure measuring device to monitor the pressure decay, and a connection for the introduction of nitrogen into the system. See Figure 30-3 for an example.

5.6 Stopwatch. Use a stopwatch accurate to within 0.2 seconds.

Figure 30-2

Vapor Coupler Integrity Assembly



5.7 Flowmeter. Use a Dwyer flowmeter, Model RMC-104, or equivalent, to determine the required pressure setting of the delivery pressure gauge on the nitrogen supply pressure regulator. This pressure shall be set such that the nitrogen flowrate is between 1.0 and 5.0 CFM.

5.8 Combustible Gas Detector. A Bacharach Instrument Company, Model 0023-7356, or equivalent, may be used to verify the pressure integrity of system components during this test.

5.9 Leak Detection Solution. Any liquid solution designed to detect vapor leaks may be used to verify the pressure integrity of system components during this test.

6. PRE-TEST PROCEDURES

6.1 The following safety precautions shall be followed:

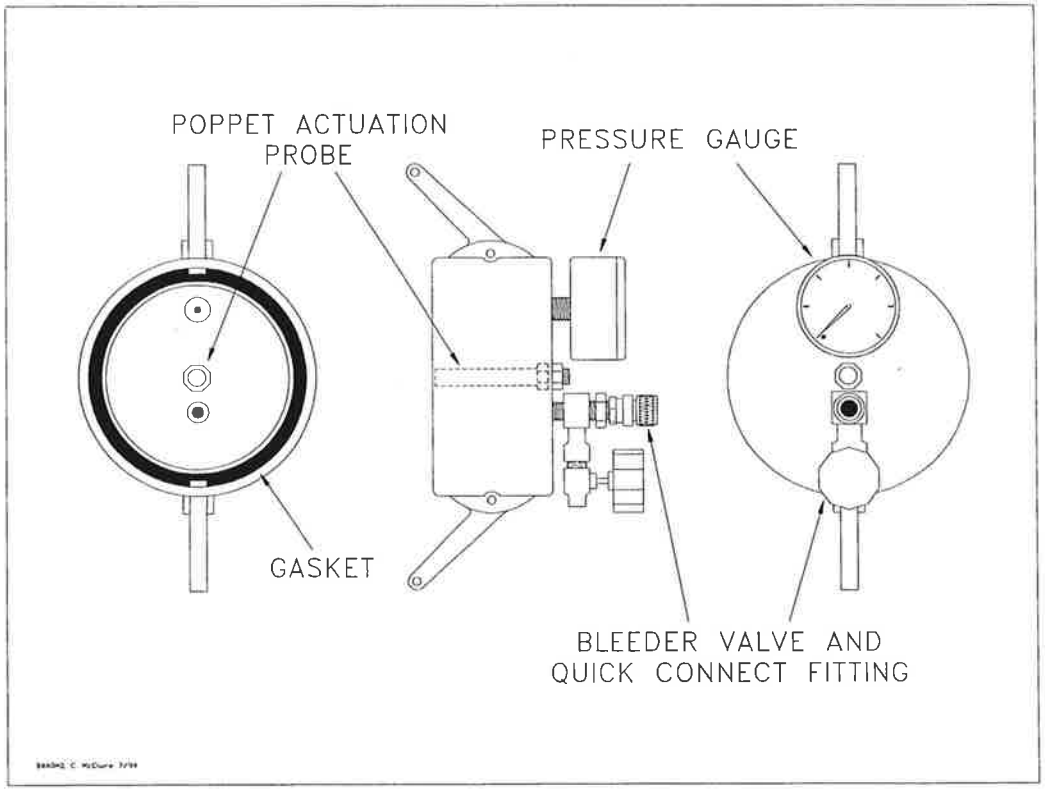
6.1.1 Only nitrogen shall be used to pressurize the system.

6.1.2 A one psig relief valve shall be installed to prevent the possible over-pressurizing of the storage tank.

6.1.3 A ground strap should be employed during the introduction of nitrogen into the system.

Figure 30-3

Vapor Coupler Test Assembly



6.2 Product dispensing shall not occur during the test. There shall have been no Phase I deliveries into or out of the storage tanks within the three hours prior to the test. For vacuum-assist Phase II systems, product dispensing shall not occur during the thirty minutes immediately prior to the test.

6.3 Measure the gallons of gasoline present in each underground storage tank and determine the actual capacity of each storage tank from facility records. Calculate the ullage space for each tank by subtracting the gasoline gallonage present from the actual tank capacity. The minimum ullage during the test shall be 25 percent of the tank capacity or 500 gallons, whichever is greater. The total ullage shall not exceed 25,000 gallons.

6.4 For two-point Phase I systems, this test shall be conducted with the dust cap removed from the vapor coupler. This is necessary to determine the vapor

tightness of the Phase I vapor poppet. See Section 6.7 if this test is to be conducted at the Phase I vapor coupler.

6.4.1 For coaxial Phase I systems, this test shall be conducted with the dust cap removed from the Phase I coupler. This is necessary to insure the vapor tightness of the Phase I vapor poppet.

6.4.2 Verify that the liquid level in the storage tank is at least four (4) inches above the highest opening at the bottom of the submerged drop tube.

6.5 If the Phase I containment box is equipped with a drain valve, the valve assembly may be cleaned and lubricated prior to the test. This test shall, however, be conducted with the drain valve installed and the manhole cover removed. See subsection 7.4.1 for further details regarding containment box drain valves.

6.6 If the test is to be conducted at a Phase II vapor riser, disconnect the dispenser end of one vapor recovery hose and install the "T" connector assembly (see Figure 30-1). Connect the nitrogen gas supply (do not use air) and the pressure measuring device to the "T" connector.

6.6.1 For those Phase II systems utilizing a dispenser mounted remote vapor check valve, the "T" connector assembly shall be installed on the vapor riser side of the check valve.

6.7 If this test is to be conducted at the Phase I vapor coupler on a two-point Phase I system, the procedures set forth in subsections 6.7.1 and 6.7.2 shall be successfully completed prior to testing. The static pressure integrity test shall not be conducted at the Phase I coupler at facilities equipped with coaxial Phase I systems.

6.7.1 Connect the Vapor Coupler Integrity Assembly to the Phase I vapor coupler. Connect the Vapor Coupler Test Assembly. Connect the nitrogen supply to the assembly and carefully pressurize the internal volume of the assembly to two (2.0) inches H_2O. Start the stopwatch. Record the final pressure after one minute.

6.7.2 If the pressure after one minute is less than 0.25 inches H_2O, the leak rate through the Phase I vapor poppet precludes conducting the static leak test at this location. If the pressure after one minute is greater than or equal to 0.25 inches H_2O, the static leak test may be conducted at this location. This criteria assures a maximum leak rate through the Phase I vapor poppet of less than 0.0004 cubic feet per minute.

6.7.3 Disconnect the Vapor Coupler Integrity Assembly from the Phase I vapor coupler. If the requirements of subsection 6.7.2 were met, connect the Vapor Coupler Test Assembly to the Phase I vapor coupler.

6.8 All pressure measuring device(s) shall be bench calibrated using either a reference gauge or incline manometer. Calibration shall be performed at 20, 50, and 80 percent of full scale. Accuracy shall be within two percent at each of these calibration points. Calibrations shall be conducted on a frequency not to exceed 90 days.

6.9 Use the flowmeter to determine the nitrogen regulator delivery pressures which correspond to nitrogen flowrates of 1.0 and 5.0 CFM. These pressures define the allowable range of delivery pressures acceptable for this test procedure. Also record the regulator delivery pressure setting, and the corresponding nitrogen flowrate that will be used during the test. As an alternative, the flowmeter may be connected, in-line between the nitrogen supply regulator and Vapor Coupler Test Assembly, during the test.

6.10 Use Equation 9.3 to calculate the approximate time required to pressurize the system ullage to the initial starting pressure of two (2.0) inches H_2O. This will allow the tester to minimize the quantity of nitrogen introduced into those systems which cannot comply with the static leak standards.

6.11 Attach the Vapor Coupler Test assembly to the Phase I poppet or the "T" connector assembly to the Phase II vapor riser. Read the initial pressure of the storage tank and underground piping. If the initial pressure is greater than 0.5 inches H_2O, carefully bleed off the pressure, in accordance with all applicable safety procedures, in the storage tank and underground piping to less than 0.5 inches H_2O column.

7. TESTING

7.1 Open the nitrogen gas supply valve and set the regulator delivery pressure within the allowable range determined in Section 6.9, and start the stopwatch. Pressurize the vapor system (or subsystem for individual vapor return line systems) to **at least 2.2 inches H_2O** initial pressure. It is critical to maintain the nitrogen flow until the pressure stabilizes, indicating temperature and vapor pressure stabilization in the tanks. Check the test equipment using leak detecting solution or a combustible gas detector to verify that all test equipment is leak tight.

7.1.1 If the time required to achieve the initial pressure of two (2.0) inches H_2O exceeds twice the time derived from Equation 9.3, stop the test and use liquid leak detector, or a combustible gas detector, to find the leak(s) in the system. Failure to achieve the initial starting pressure within twice the time derived from Equation 9.3 demonstrates the inability of the system to meet the performance criteria. Repair or replace the faulty component(s) and restart the test pursuant to Section 7.1.

7.2 Close and disconnect the nitrogen supply. Start the stopwatch when the pressure has decreased to the initial starting pressure of two (2.0) inches H_2O.

7.3 At one-minute intervals during the test, record the system pressure. After five minutes, record the final system pressure. See the applicable of Tables 30-IA (or Equation 9.1) or 30-IB (or Equation 9.2) to determine the acceptability of the final system static pressure results. For intermediate values of ullage in Tables 30-IA and 30-IB, linear interpolation may be employed.

7.4 If the system failed to meet the criteria set forth in Table 30-I (or the appropriate equation in Section 9), repressurize the system and check all accessible vapor connections using leak detector solution or a combustible gas detector. If vapor leaks in the system are encountered, repair or replace the defective component and repeat the test. Potential sources of leaks include nozzle check valves, pressure/vacuum relief valves, containment box drain valve assemblies, and plumbing connections at the risers.

7.4.1 If the facility fails to comply with the static leak test standards and the Phase I system utilizes a non-CARB-certified drain valve equipped containment box, which was installed prior to July 1, 1992, for which a CARB-certified replacement drain valve assembly is not marketed, the following two subsections shall apply:

7.4.1.1 The drain valve may be removed and the port plugged. Reset the system. If the facility complies with the static leak test standards under these conditions, the facility shall be considered complying with the requirements, provided that the manufacturer and model number of the containment box and the date of installation are submitted with the test results.

7.4.1.2 The criteria set forth in subsection 7.4.1.1 shall not apply after July 1, 1996.

7.5 After the remaining system pressure has been relieved, remove the "T" connector assembly and reconnect the vapor recovery hose, if applicable.

7.6 If the vapor recovery system utilizes individual vapor return lines, repeat the leak test for each gasoline grade. Avoid leaving any vapor return line open longer than is necessary to install or remove the "T" connector assembly.

7.7 If the applicable CARB Executive requires the test to be conducted with and without the containment box cover in place, repeat the test with the cover in place. In these cases clearly specify, on Form 30-1, which results represent the pressure integrity with and without the cover in place.

8. POST-TEST PROCEDURES

8.1 Use the applicable of Table 30-IA or 30-IB, or the applicable of Equations 9.1 or 9.2, to determine the compliance status of the facility by comparing the final five-minute pressure with the minimum allowable final pressure.

8.1.1 For balance Phase II systems use Table 30-IA or the applicable of Equation 9.1 to determine compliance.

8.1.2 For vacuum-assist Phase II systems use Table 30-IB or the applicable of Equation 9.2 to determine compliance.

9. CALCULATIONS

9.1 For Phase II Balance Systems, the minimum allowable five-minute final pressure, with an initial pressure of two (2.0) inches H_2O, shall be calculated as follows:

[Equation 9-1]

$$P_f = 2e^{\frac{-760.490}{V}} \quad \text{if N = 1-6}$$

$$P_f = 2e^{\frac{-792.196}{V}} \quad \text{if N = 7-12}$$

$$P_f = 2e^{\frac{-824.023}{V}} \quad \text{if N = 13-18}$$

$$P_f = 2e^{\frac{-855.974}{V}} \quad \text{if N = 19-24}$$

$$P_f = 2e^{\frac{-888.047}{V}} \quad \text{if N > 24}$$

Where:

N = The number of affected nozzles. For manifolded systems, N equals the total number of nozzles. For dedicated plumbing configurations, N equals the number of nozzles serviced by the tank being tested.

P_f = The minimum allowable five-minute final pressure, inches H_2O

V = The total ullage affected by the test, gallons

e = A dimensionless constant approximately equal to 2.718

2 = The initial starting pressure, inches H_2O

9.2 For Phase II Vacuum Assist Systems, the minimum allowable five-minute final pressure, with an initial pressure of two (2.0) inches H_2O, shall be calculated as follows:

[Equation 9-2]

$$P_f = 2e^{\frac{-500.887}{V}} \quad \text{if N = 1-6}$$

$$P_f = 2e^{\frac{-531.614}{V}} \quad \text{if N = 7-12}$$

$$P_f = 2e^{\frac{-562.455}{V}} \quad \text{if N = 13-18}$$

$$P_f = 2e^{\frac{-593.412}{V}} \quad \text{if N = 19-24}$$

$$P_f = 2e^{\frac{-624.483}{V}} \quad \text{if N > 24}$$

Where:

N = The number of affected nozzles. For manifolded systems, N equals the total number of nozzles. For dedicated plumbing configurations, N equals the number of nozzles serviced by the tank being tested.

P_f = The minimum allowable five-minute final pressure, inches H_2O

V = The total ullage affected by the test, gallons

e = A dimensionless constant approximately equal to 2.718

2 = The initial starting pressure, inches H_2O

9.3 The minimum time required to pressurize the system ullage from zero (0) to two (2.0) inches H_2O gauge pressure shall be calculated as follows:

$$t_2 = \frac{V}{[1522]\,F} \qquad \text{[Equation 9-3]}$$

Where:

t_2 = The minimum time to pressurize the ullage to two inches H_2O, minutes

V = The total ullage affected by the test, gallons

F = The nitrogen flowrate into the system, CFM

1522 = The conversion factor for pressure and gallons

9.4 If the policy of the local District requires an allowable tolerance for testing error, the minimum allowable five-minute final pressure, including testing error, shall be calculated as follows:

$$P_{f\text{-}E} = 2 - \left[1 + \left(\frac{E}{100}\right)\right]\left[408.9 - \left(P_f + 406.9\right)\right] \qquad \text{[Equation 9-4]}$$

Where:

$P_{f\text{-}E}$ = The minimum allowable five-minute final pressure including allowable testing error, inches H_2O

E = The allowable testing error, percent

P_f = The minimum allowable five-minute final pressure calculated in Equations 9-1 or 9-2, inches H_2O

2 = The initial starting pressure, inches H_2O

408.9 = Atmospheric pressure plus the initial starting pressure, inches H_2O

406.9 = Atmospheric pressure, inches H_2O

10. REPORTING

10.1 The calculated ullage and system pressures for each five-minute vapor recovery system test shall be reported as shown in Form 30-1. Be sure to include the Phase I system type (two-point or coaxial), the Phase II system type, whether the system is manifolded, and the one-minute pressures during the test.

TABLE 30-1A

PHASE II BALANCE SYSTEMS

PRESSURE DECAY LEAK RATE CRITERIA

INITIAL PRESSURE OF 2 INCHES OF H_2O

MINIMUM PRESSURE AFTER 5 MINUTES, INCHES OF H_2O

ULLAGE, GALLONS	NUMBER OF AFFECTED NOZZLES				
	01-06	07-12	13-18	19-24	> 24
500	**0.44**	**0.41**	**0.38**	**0.36**	**0.34**
550	0.50	0.47	0.45	0.42	0.40
600	**0.56**	**0.53**	**0.51**	**0.48**	**0.46**
650	0.62	0.59	0.56	0.54	0.51
700	**0.67**	**0.64**	**0.62**	**0.59**	**0.56**
750	0.73	0.70	0.67	0.64	0.61
800	**0.77**	**0.74**	**0.71**	**0.69**	**0.66**
850	0.82	0.79	0.76	0.73	0.70
900	**0.86**	**0.83**	**0.80**	**0.77**	**0.75**
950	0.90	0.87	0.84	0.81	0.79
1,000	**0.93**	**0.91**	**0.88**	**0.85**	**0.82**
1,200	1.06	1.03	1.01	0.98	0.95
1,400	**1.16**	**1.14**	**1.11**	**1.09**	**1.06**
1,600	1.24	1.22	1.19	1.17	1.15
1,800	**1.31**	**1.29**	**1.27**	**1.24**	**1.22**
2,000	1.37	1.35	1.32	1.30	1.28
2,200	**1.42**	**1.40**	**1.38**	**1.36**	**1.34**
2,400	1.46	1.44	1.42	1.40	1.38
2,600	**1.49**	**1.47**	**1.46**	**1.44**	**1.42**
2,800	1.52	1.51	1.49	1.47	1.46
3,000	**1.55**	**1.54**	**1.52**	**1.50**	**1.49**
3,500	1.61	1.59	1.58	1.57	1.55
4,000	**1.65**	**1.64**	**1.63**	**1.61**	**1.60**
4,500	1.69	1.68	1.67	1.65	1.64
5,000	**1.72**	**1.71**	**1.70**	**1.69**	**1.67**
6,000	1.76	1.75	1.74	1.73	1.72
7,000	**1.79**	**1.79**	**1.78**	**1.77**	**1.76**
8,000	1.82	1.81	1.80	1.80	1.79
9,000	**1.84**	**1.83**	**1.83**	**1.82**	**1.81**
10,000	1.85	1.85	1.84	1.84	1.83
15,000	**1.90**	**1.90**	**1.89**	**1.89**	**1.89**
20,000	1.93	1.92	1.92	1.92	1.91
25,000	**1.94**	**1.94**	**1.94**	**1.93**	**1.93**

Note: For manifolded Phase II Balance Systems, the **"Number of Affected Nozzles"** shall be the total of all gasoline nozzles. For dedicated return configurations, th **"Number of Affected Nozzles"** shall be the total of those nozzles served by the tank being tested.

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TABLE 30-1B

PHASE II ASSIST SYSTEMS

PRESSURE DECAY LEAK RATE CRITERIA

INITIAL PRESSURE OF 2 INCHES OF H_2O

MINIMUM PRESSURE AFTER 5 MINUTES, INCHES OF H_2O

ULLAGE, GALLONS	NUMBER OF AFFECTED NOZZLES				
	01-06	07-12	13-18	19-24	> 24
500	**0.73**	**0.69**	**0.65**	**0.61**	**0.57**
550	0.80	0.76	0.72	0.68	0.64
600	**0.87**	**0.82**	**0.78**	**0.74**	**0.71**
650	0.93	0.88	0.84	0.80	0.77
700	**0.98**	**0.94**	**0.90**	**0.86**	**0.82**
750	1.03	0.98	0.94	0.91	0.87
800	**1.07**	**1.03**	**0.99**	**0.95**	**0.92**
850	1.11	1.07	1.03	1.00	0.96
900	**1.15**	**1.11**	**1.07**	**1.03**	**1.00**
950	1.18	1.14	1.11	1.07	1.04
1,000	**1.21**	**1.18**	**1.14**	**1.10**	**1.07**
1,200	1.32	1.28	1.25	1.22	1.19
1,400	**1.40**	**1.37**	**1.34**	**1.31**	**1.28**
1,600	1.46	1.43	1.41	1.38	1.35
1,800	**1.51**	**1.49**	**1.46**	**1.44**	**1.41**
2,000	1.56	1.53	1.51	1.49	1.46
2,200	**1.59**	**1.57**	**1.55**	**1.53**	**1.51**
2,400	1.62	1.60	1.58	1.56	1.54
2,600	**1.65**	**1.63**	**1.61**	**1.59**	**1.57**
2,800	1.67	1.65	1.64	1.62	1.60
3,000	**1.69**	**1.68**	**1.66**	**1.64**	**1.62**
3,500	1.73	1.72	1.70	1.69	1.67
4,000	**1.76**	**1.75**	**1.74**	**1.72**	**1.71**
4,500	1.79	1.78	1.77	1.75	1.74
5,000	**1.81**	**1.80**	**1.79**	**1.78**	**1.77**
6,000	1.84	1.83	1.82	1.81	1.80
7,000	**1.86**	**1.85**	**1.85**	**1.84**	**1.83**
8,000	1.88	1.87	1.86	1.86	1.85
9,000	**1.89**	**1.89**	**1.88**	**1.87**	**1.87**
10,000	1.90	1.90	1.89	1.88	1.88
15,000	**1.93**	**1.93**	**1.93**	**1.92**	**1.92**
20,000	1.95	1.95	1.94	1.94	1.94
25,000	**1.96**	**1.96**	**1.96**	**1.95**	**1.95**

Note: For manifolded Phase II Assist Systems, the **"Number of Affected Nozzles"** shall be the total of all gasoline nozzles. For dedicated return configurations, the **"Number of Affected Nozzles"** shall be the total of those nozzles served by the tank being tested.

Item E 004846

Form 30-1

Distribution:

Firm
Permit Services
Enforcement Services
Technical Services
Planning
Requester
DAPCO

BAY AREA
AIR QUALITY MANAGEMENT DISTRICT
939 Ellis Street
San Francisco, California 94109
(415) 771-6000

Summary of Source Test Results

Report No.: _____
Test Date: _____
Test Times:
Run A: _____
Run B: _____
Run C: _____

Source Information

GDF Name and Address

GDF Representative and Title

GDF Phone No. ( )

Source: GDF Vapor Recovery System

BAAQMD GDF # _____

BAAQMD A/C # _____

Permit Conditions

Facility Parameters

PHASE II SYSTEM TYPE (Check One)

Balance ☐

Vapor Assist ☐

Type:

Other ☐

Identify:

Manifolded? Y or N

Operating Parameters:

Number of Nozzles Served by Tank #1 _____
Number of Nozzles Served by Tank #2 _____
Number of Nozzles Served by Tank #3 _____
Total Number of Gas Nozzles at Facility _____

Applicable Regulations: BAAQMD REGULATION 8, RULE 7

FOR OFFICE USE ONLY:

Source Test Results and Comments:

TANK #:	1	2	3	TOTAL
1. Product Grade				
2. Actual Tank Capacity, gallons				
3. Gasoline Volume, Gallons				
4. Ullage, gallons (#2 -#3)				
5. Phase I System Type				
6. Initial Test Pressure, Inches H_2O **(2.0)**				
7. Pressure After 1 Minute, Inches H_2O				
8. Pressure After 2 Minutes, Inches H_2O				
9. Pressure After 3 Minutes, Inches H_2O				
10. Pressure After 4 Minutes, Inches H_2O				
11. **Final Pressure After 5 Minutes, Inches H_2O**				
12. Allowable Final Pressure from Table 30-I				
13. Test Status [**Pass** or **Fail**]				

Test Conducted by:

Test Company
Name _____
Address _____
City _____

Date and Time of Test:

Item E 004847

California Environmental Protection Agency

Air Resources Board

Vapor Recovery Test Procedure

TP-201.1

Volumetric Efficiency for Phase I Vapor Recovery Systems

Adopted: April 12, 1996
Amended: February 1, 2001
Amended: October 8, 2003

California Environmental Protection Agency
Air Resources Board

Vapor Recovery Test Procedure

TP-201.1

Volumetric Efficiency of Phase I Vapor Recovery Systems

Definitions common to all certification and test procedures are in:

D-200 Definitions for Vapor Recovery Procedures

For the purpose of this procedure, the term "CARB" refers to the State of California Air Resources Board, and the term "Executive Officer" refers to the CARB Executive Officer, or his or her authorized representative or designate.

1. PURPOSE AND APPLICABILITY

The purpose of this procedure is to quantify the transfer efficiency when a bulk gasoline delivery between a cargo tank and underground storage tank is made. This procedure is used to determine compliance with Phase I performance standard specified in Certification Procedure 201 (CP-201).

2. PRINCIPLE AND SUMMARY OF TEST PROCEDURE

During a gasoline delivery, the cargo tank and gasoline dispensing facility (GDF) are instrumented with test equipment in order to determine the amount of vapor returned to the cargo tank and the amount of vapor discharged through the GDF vent pipe. From these parameters the Phase I volumetric efficiency is determined. This procedure provides for determining efficiency by way of either direct measurement or calculation.

If a Phase I system fails to meet the volumetric efficiency as required by CP-201, the cargo tank shall be tested for compliance with the daily standards established for cargo tanks as specified in CP-204 to determine if the failure can be attributed to the cargo tank.

3. BIASES AND INTERFERENCES

3.1 Any vapor leaks exceeding 100% of the Lower Explosive Limit (LEL) during the gasoline bulk delivery precludes the use of this method.

3.2 Gasoline cargo tanks exceeding the allowable daily pressure-decay standards as defined in CP-204 preclude the use of this method.

3.3 The presence of vapor leaks in the GDF, greater than the allowable leak decay limits specified in Section 3.2 of CP-201 preclude use of this method.

3.4 Unusually large cargo tank headspace volumes may cause low volumetric efficiency under certain conditions. Conversely, unusually small cargo tank headspace volumes may result in unusually high efficiency. During the Certification Process for a Phase I system, the cargo tank headspace volumes should be between 3.0 and 10.0 percent of the total cargo tank capacity prior to the delivery.

4. SENSITIVITY, PRECISION AND RANGE

4.1 Mechanical Pressure Gauge. The minimum readability shall be 1.00 inches H_2O with a maximum full-scale range of 30 inches H_2O and minimum accuracy of three percent of full scale. Pressure gauges with a higher resolution and higher accuracy may be deemed acceptable with prior approval by the Executive Officer.

4.2 Electronic Pressure Gauge. The maximum full-scale range of the device shall not exceed 20 inches H_2O with minimum sensitivity of 1.00 inches H_2O and minimum accuracy of 0.5 percent of full scale. Electronic pressure gauges shall be calibrated as described in Section 5 of this procedure.

4.3 Volume Meter, Vapor Return. Minimum full-scale range shall be 5,000 CFH with a maximum rated back pressure less than 1.10 in H_2O. The meter shall have an internal diameter of 3 inches, equal to that of a cargo tank vapor return hose.

4.4 Volume Meter, Vent Pipe. Minimum full-scale range shall be 800 CFH with a maximum rated back pressure less than 0.26 in H_2O. The meter shall have an internal diameter of 2 inches, equal to that of a GDF vent pipe.

4.5 Temperature. Maximum range of 0 to 150°F and accurate to within 2°F.

4.6 Barometric Pressure. Minimum accuracy of .08 inches of mercury (1.0 inch H_2O or 2.7 millibar).

5. EQUIPMENT

5.1 Vapor Return Meter(s). Use a volume meter with minimum specifications described in Section 4 to measure the amount of vapor returned to the cargo tank from the underground storage tank. The meter shall be equipped with a pressure gauge and temperature device as described in Section 4 on the inlet side. The meter shall be connected to the GDF in a fashion as to maintain intrinsic safety, see Figure 3.

5.2 Vent Pipe Meter. Use a volume meter with minimum specifications described in Section 4 to measure the amount of vapor discharged through the vent pipe(s). The meter shall be equipped with a pressure gauge and temperature device as described in Section 4 on the inlet side. The meter shall be connected to the GDF in a fashion as to maintain intrinsic safety, see Figure 3.

5.3 Cargo Tank Back Pressure Assembly. When testing Phase I efficiency without the use of volume meters, use OPW® 633-F and 633-D couplers, or equivalent, as shown in Figure 1. The assembly shall be equipped with a pressure gauge capable of measuring up to 30 inches H_2O back pressure at the gasoline cargo tank vapor

coupler. Temperature may be measured at this point as an alternate to, or in addition to 5.1.

5.4 Storage Tank Pressure Assembly. When testing Phase I efficiency with the cargo tank back pressure assembly and the test facility uses a two point Phase I system with storage tanks manifolded underground, use OPW® 634-B cap(s) or equivalent, equipped with a pressure gauge and center probe as shown in Figure 2

5.5 Combustible Gas Detector. Use a Bacharach Instrument Company Model 0023-7356®, or equivalent, to quantify any vapor leaks occurring during the gasoline bulk drop.

5.6 Barometer. Use a mercury, aneroid, or equivalent barometer with minimum specifications described in Section 4 to measure the barometric pressure during testing. The result shall be used to correct the volume of vapor returned or discharged.

5.7 Temperature. Use a minimum of three thermometers, Thermocouples™, or equivalent, to measure the vapor temperature at each meter. The results shall be used to correct the volume of vapor returned or discharged.

5.8 Stopwatch. Use a stopwatch accurate to within 0.1 seconds to time the delivery rate.

6. PRE-TEST PROCEDURES

6.1 The volume meter(s) shall be proofed against a standard reference meter prior to its initial use in the field or at intervals not to exceed 180 days. Calibration shall be performed at a minimum of three flowrates representing 25, 50 and 75 percent of rated capacity. An official statement of proofing is required.

6.2 The GDF shall be pre-tested for leak integrity as described in TP-201.3 at least 24 hours prior, and no longer than 7-days before testing. If a manifold is to be used at the vent pipe, the manifold shall be installed prior to conducting leak integrity testing.

6.3 No product dispensing shall occur for a minimum of 30 minutes prior to testing.

6.4 Taking caution to avoid venting the storage tanks, connect the vent pipe meter(s) to the appropriate storage tank vent pipe(s) with the inlet side attached to the vent pipe. Use a metal ball valve if required to avoid venting. Attach the PV valve(s) to the outlet side of the meter(s) using a threaded nipple or equivalent. A temporary manifold may be constructed of steel where all vent pipes are connected to a single outlet and a single meter is installed.

6.5 Taking caution to avoid venting the storage tanks, connect the vapor return meter(s) to the appropriate Phase I vapor connection(s) using metal fittings in order to maintain intrinsic safety. Use a metal vapor poppet if required to avoid venting. Connect the cargo tank vapor return hose to the outlet side of the meter. The meter will be in line between the Phase I connection and the cargo tank vapor return hose.

6.6 With no product dispensing, record the product grade, tank capacity, tank temperature and ambient conditions on the data sheet where provided.

6.7 If used, connect the Cargo Tank Back Pressure Assembly to the vapor coupler on the cargo tank. This assembly will be in line with the cargo tank vapor recovery hose. If the cargo tank vapor coupler is equipped with a poppet, use a pressure assembly with center probe.

6.8 If the cargo tank back pressure assembly is being used, install a Storage Tank Pressure Assembly on each Phase I vapor connection of those tanks not receiving product. During each bulk drop, record the maximum pressure in those tanks.

6.9 Record the product quantities to be delivered during each bulk drop. Also record the cargo tank CARB decal number and delivery company name on the data sheet where provided.

6.10 Stabilization. Open the corresponding cargo tank internal vapor valve(s) prior to delivering product. Once the vapor valve(s) is opened, wait a period of at least 1-minute to allow for pressure stabilization between the UST and cargo tank.

7. TESTING

7.1 Record the stabilized, vapor return and vent pipe meter reading(s) on the data sheet where provided.

7.2 Start the gasoline bulk drop. Using the stopwatch, time each gasoline drop to determine the delivery rate for each compartment.

7.3 At minimum, record the following parameters for each gasoline bulk drop:

7.3.1 Initial and final meter readings for each vapor return meter

7.3.2 Average vapor return pressure

7.3.3 Average vapor return temperature

7.4 Repeat Sections 7.1 through 7.3 for each gasoline delivery. For deliveries using different Phase I connections (i.e., different storage tanks), relocate the vapor return meter(s) to the appropriate storage as specified in Section 6.7.

7.5 At conclusion of all gasoline deliveries, ensure that each of the cargo tank internal vapor valve is closed prior to disconnecting. Disconnect the vapor return meter(s) from the storage tank(s) taking care to avoid venting pressure. Disconnect the vapor return hose from the outlet side of the vapor return meter.

7.6 Continue to monitor the vent pipe meter for a minimum of 15 minutes. If the UST pressure is less than 1.00 inches H_2O, testing may be concluded. In the event that the station UST pressure is greater than 1.00 inches H_2O, continue to monitor the vent

pipe meter for an additional 45 minutes (1-hour total). These measurements are to be included in the Phase I efficiency calculation.

8. POST TEST PROCEDURES

8.1 At conclusion of the bulk delivery, ensure that each of the cargo tank internal vapor valves is closed prior to removing connections.

8.2 Remove the Cargo Tank Back Pressure Assembly, if used, from the cargo tank vapor return coupler.

8.3 Remove the Storage Tank Pressure Assembly, if used, from each storage tank where installed.

8.4 Remove the temporary manifold (if constructed) and disconnect all instrumentation from the vent pipe area. Replace the PV valve(s) on the vent pipe(s).

8.5 Verify the quantity of gasoline delivered to each storage tank using the facility tank gauge monitor or with use of a tank gauging stick.

9. CALCULATING RESULTS

9.1 The measured volume of vapor passed through the vapor return to the cargo tank and vent pipe shall be corrected to standard conditions as follows:

$$V_{corr} = \frac{(V_{vi})(528)[P_b + \Delta h/13.6]}{(T_{vi})(29.92)} \qquad \textbf{Equation 9.1}$$

Where:

V_{corr} = Volume of vapor, corrected to 68^0F (528^0R) and 29.92" Hg
P_b = Barometric Pressure, inches Hg
V_{vi} = Uncorrected volume of vapor (raw meter reading)
T_{vi} = Average or venting temperature at vent meter, ^{0}R
Δh = Average or venting pressure at vent meter, inches H_2O
13.6 = Inches of water per inch of mercury
528 = Standard ambient temperature, 68^0F converted to degrees Rankine

9.2 If a cargo tank back pressure assembly was used to conduct testing, the volume of vapor returned to the cargo tank shall be calculated to standard conditions as follows:

$$V_t = \left[\frac{(0.1337)(G_t)\left(528\left(P_b + \frac{\Delta h}{13.6}\right)\right)}{(T_t)(29.92)}\right] \qquad \textbf{Equation 9.2}$$

Where:

V_t = Calculated volume of vapor returned to cargo tank corrected to 68^0F (528^0R) and 29.92" Hg
G_t = Volume of gasoline delivered, gallons
Δh = Final gauge pressure at cargo tank, in. H_2O
T_t = Average temperature of vapor returned to cargo tank, ^{o}R
P_b = Barometric pressure, inches Hg
13.6 = Inches of water per inch of mercury
528 = Standard ambient temperature, 68°F converted to degrees Rankine

9.3 The collection efficiency shall be calculated as follows:

$$E = (100)\left[\frac{V_{returned} - V_{vent}}{V_{returned}}\right] \qquad \textbf{Equation 9.3}$$

Where:

E = Phase I Volumetric Efficiency, percent
$V_{returned}$ = Vapor Return: From 9.1(V_{corr}) or 9.2(V_t)
V_{vent} = Corrected Vent Pipe Discharge: From 9.1(V_{corr})

10. REPORTING RESULTS

10.1 Results shall be reported as shown on the data sheets where provided. Districts may require the use of alternate data sheets provided they include, at minimum, the same parameters identified on Form 1.

11. ALTERNATE PROCEDURES

11.1 This procedure shall be conducted as specified. Modifications to this test procedure shall not be used to determine compliance unless prior written approval has been obtained from the ARB Executive Officer, pursuant to Section 14 of Certification Procedure CP-201.

FORM 1
ARB TP-201.1

Test Date: _____ Observations By: _____

Facility Name: _____

Address: _____

System Description: _____

Time: _____ Ambient Temp: _____ deg F Barometric: _____ Hpa

Wind: _____ mph Altitude: _____ ft Other: _____

Cargo Tank Company: _____

Cargo Tank Decal #(s): Truck: _____ Trailer: _____

Compartment #1

Pre-Delivery Observations		Delivery Observations	
		Tank Orientation:	
Initial UST Product Temerature:	deg F	Delivered Product Temperature:	deg F
UST Size:	gal	Avg Vapor Return Pressure:	inWC
Amount To Deliver (BOL):	gal	Avg Vapor Return Temp:	deg F
Grade:	Loading Temp (BOL):	Fuel RVP (BOL):	
Initial Meter Reading:	ft^3	**Final Meter Reading:**	ft^3

Compartment #2

Pre-Delivery Observations		Delivery Observations	
		Tank Orientation:	
Initial UST Product Temerature:	deg F	Delivered Product Temperature:	deg F
UST Size:	gal	Avg Vapor Return Pressure:	inWC
Amount To Deliver (BOL):	gal	Avg Vapor Return Temp:	deg F
Grade:	Loading Temp (BOL):	Fuel RVP (BOL):	
Initial Meter Reading:	ft^3	**Final Meter Reading:**	ft^3

Compartment #3

Pre-Delivery Observations		Delivery Observations	
		Tank Orientation:	
Initial UST Product Temerature:	deg F	Delivered Product Temperature:	deg F
UST Size:	gal	Avg Vapor Return Pressure:	inWC

Compartment #4

Pre-Delivery Observations

Initial UST Product Temerature: _____ deg F
UST Size: _____ gal
Amount To Deliver (BOL): _____ gal
Grade: _____ Loading Temp (BOL): _____
Initial Meter Reading: _____ ft^3

Delivery Observations

Tank Orientation: _____
Delivered Product Temperature: _____ deg F
Avg Vapor Return Pressure: _____ inWC
Avg Vapor Return Temp: _____ deg F
Fuel RVP (BOL): _____
Final Meter Reading: _____ ft^3

Compartment #5

Pre-Delivery Observations

Initial UST Product Temerature: _____ deg F
UST Size: _____ gal
Amount To Deliver (BOL): _____ gal
Grade: _____ Loading Temp (BOL): _____
Initial Meter Reading: _____ ft^3

Delivery Observations

Tank Orientation: _____
Delivered Product Temperature: _____ deg F
Avg Vapor Return Pressure: _____ inWC
Avg Vapor Return Temp: _____ deg F
Fuel RVP (BOL): _____
Final Meter Reading: _____ ft^3

Vent Pipe Discharge

Delivery Observations

Initial Vent Pressure: _____ inWC
Initial Vent Temperature: _____ deg F
Initial Meter Reading: _____ ft^3

Stack Venting Pressure: _____ inWC
Stack Venting Temperature: _____ deg F

Post Delivery Observations

Post Observation Time: _____

Remarks: _____

Final Vent Pressure: _____ inWC
Final Vent Temperature: _____ deg F
Final Meter Reading: _____ ft^3

Figure 1 - Cargo Tank Back Pressure Assembly

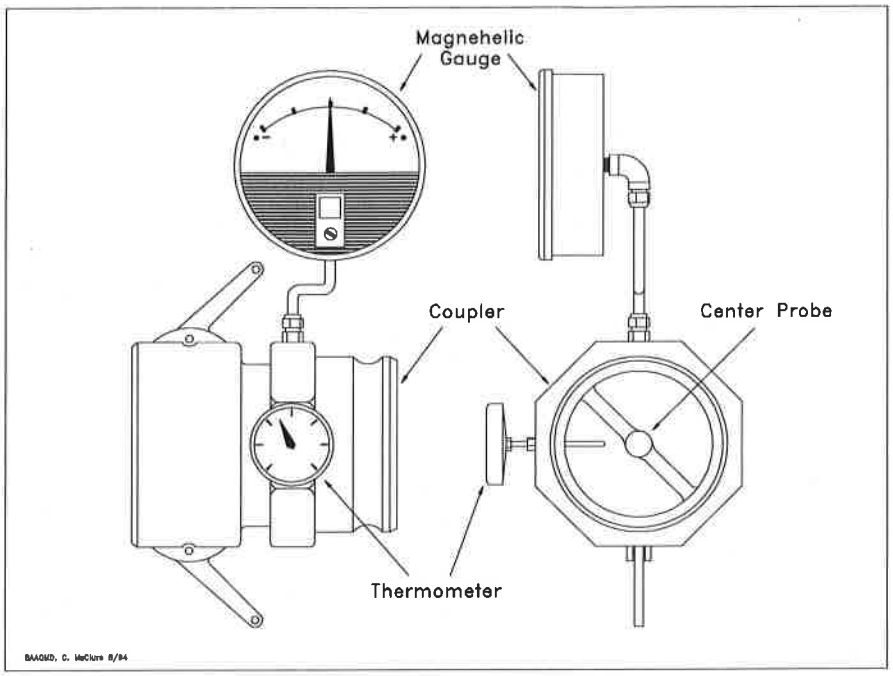


Figure 2 - Storage Tank Pressure Assembly

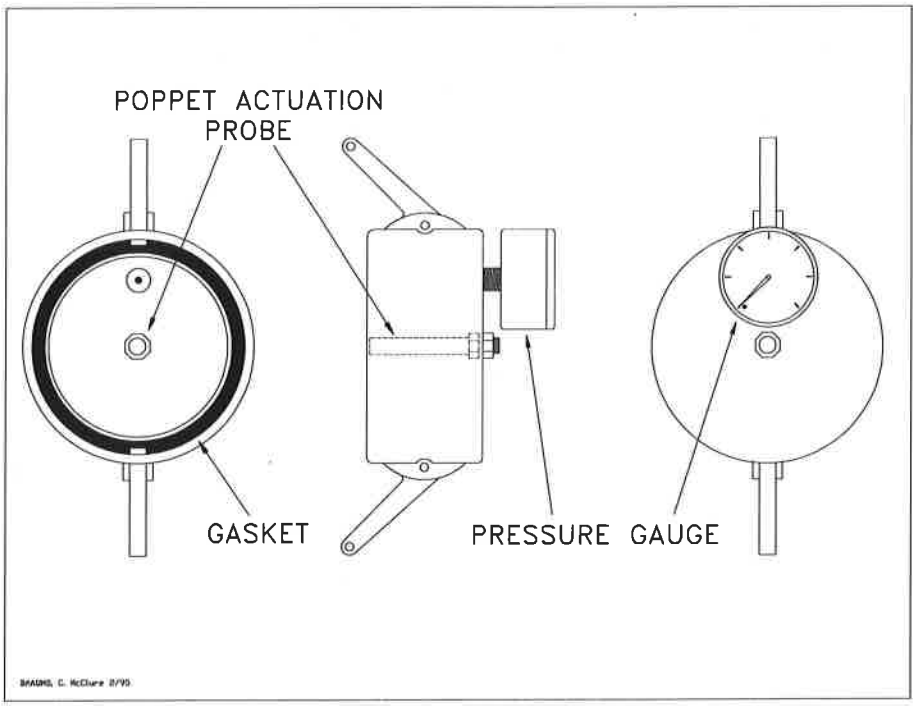


Figure 3 - Vent Pipe and Vapor Return Meter Arrangement

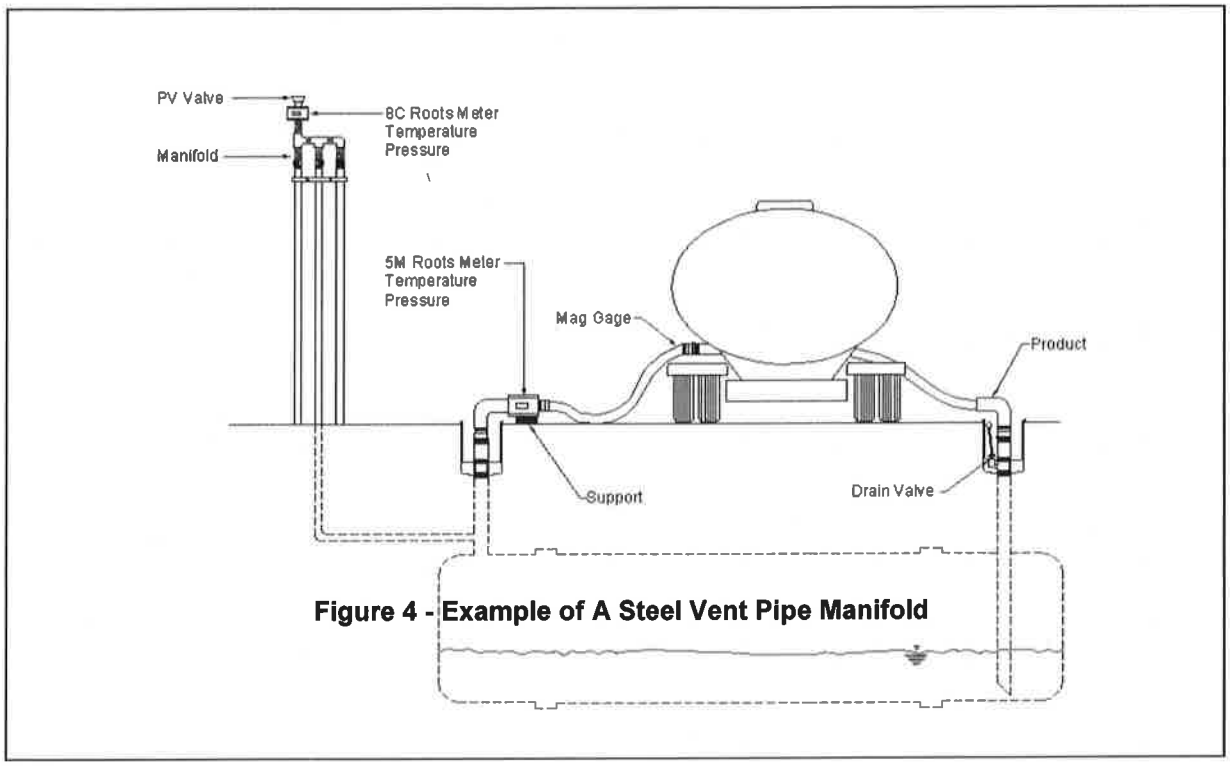
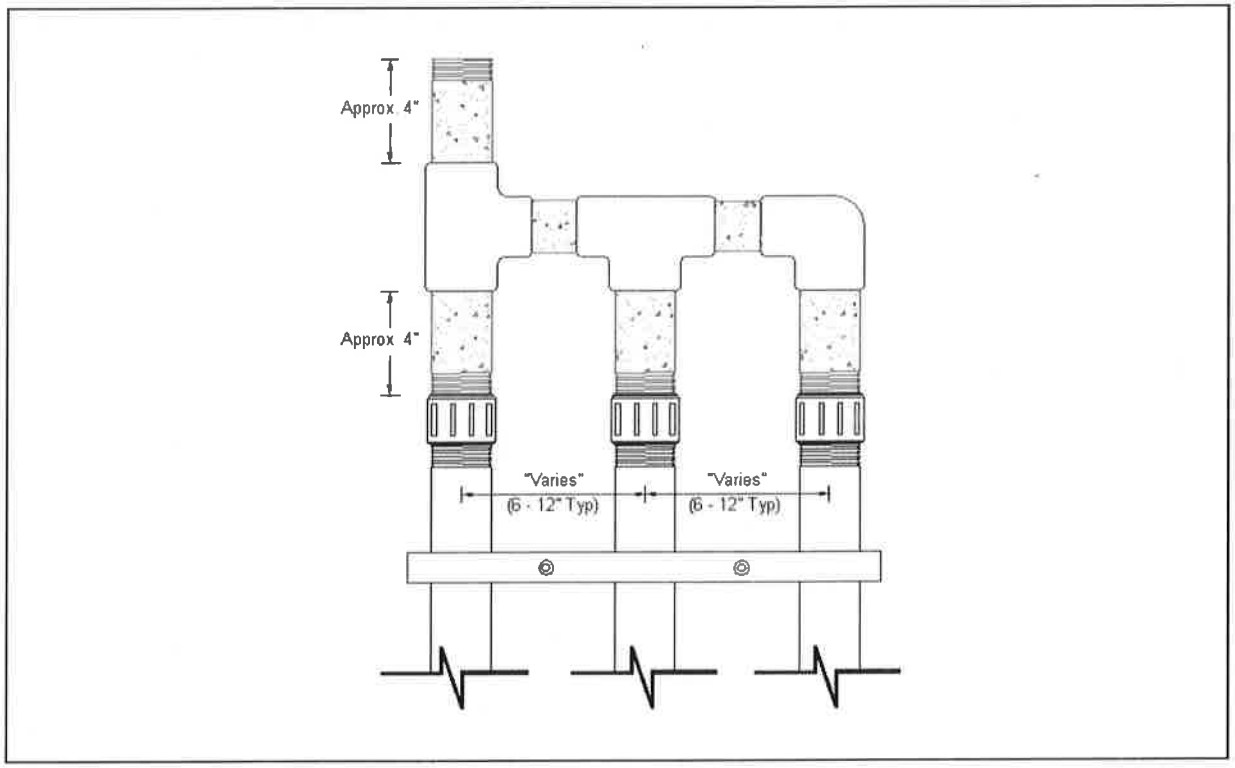


Figure 4 - Example of A Steel Vent Pipe Manifold



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12.2 Linearity. Use the following equation to calculate the measured standard concentration for each standard vial.

$$C_m = kA + b \qquad \text{Eq. 25E-1}$$

12.2.1 Calculate the average measured standard concentration (C_{ma}) for each set of triplicate standards and use the following equation to calculate PD between C_{ma} and C_s. The instrument linearity is acceptable if the PD is within five for each standard.

$$PD = \frac{C_s - C_{ma}}{C_s} \times 100 \qquad \text{Eq. 25E-2}$$

12.3. Relative Standard Deviation (RSD). Use the following equation to calculate the RSD for each triplicate set of standards.

$$RSD = \frac{100}{C_{ma}} \sqrt{\frac{\sum (C_m - C_{ma})^2}{2}} \qquad \text{Eq. 25E-3}$$

The calibration is acceptable if the RSD is within five for each standard concentration.

12.4 Concentration of organics in the headspace. Use the following equation to calculate the concentration of vapor phase organics in each sample.

$$C_a = kA + b \qquad \text{Eq. 25E-4}$$

12.5 Vapor Pressure of Organics in the Headspace Sample. Use the following equation to calculate the vapor pressure of organics in the sample.

$$P^* = \beta P_{bar} C_a \qquad \text{Eq. 25E-5}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, Albert E., Samuel Witz, and Robert D. MacPhee. ''Determination of Solvent Vapor Concentrations by Total Combustion Analysis: a Comparison of Infared with Flame Ionization Detectors. Paper No. 75–33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, Massachusetts.

2. Salo, Albert E., William L. Oaks, and Robert D. MacPhee. ''Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, Colorado. June 9–13, 1974.) p. 25.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

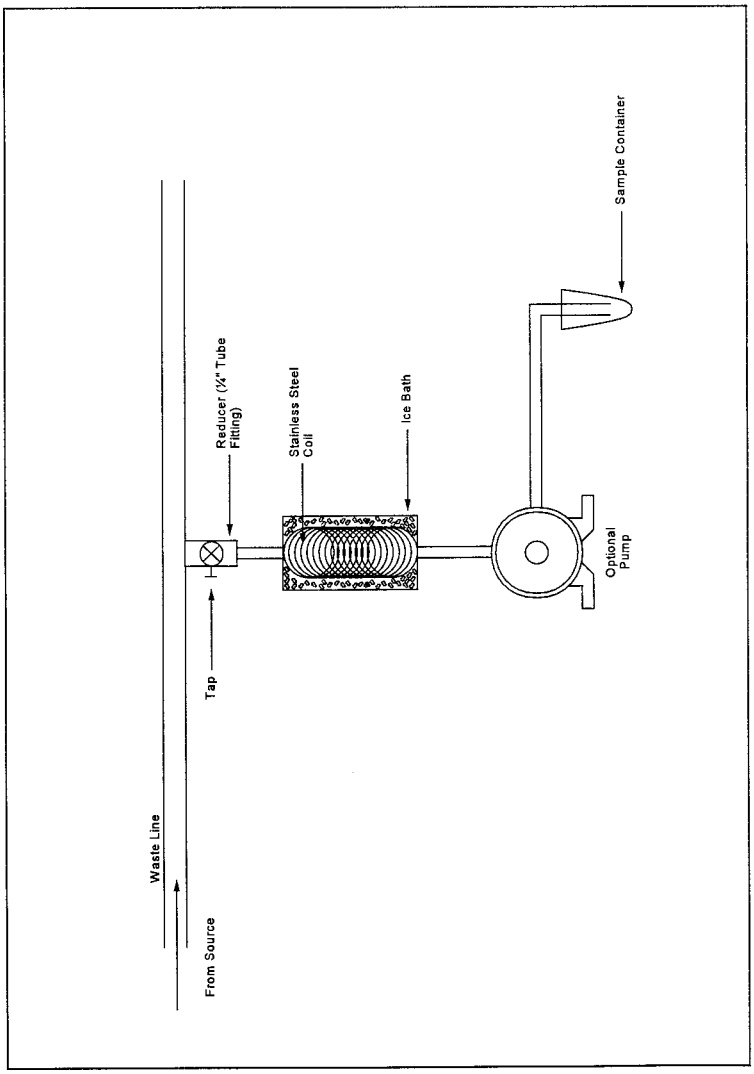


Figure 25E-1. Schematic of Sampling Apparatus

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–7 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

APPENDIX A–8 TO PART 60—TEST METHODS 26 THROUGH 30B

Method 26—Determination of Hydrogen Chloride Emissions From Stationary Sources

Method 26A—Determination of hydrogen halide and halogen emissions from stationary sources—isokinetic method

Method 27—Determination of vapor tightness of gasoline delivery tank using pressure-vacuum test
Method 28—Certification and auditing of wood heaters
Method 28A—Measurement of air to fuel ratio and minimum achievable burn rates for wood-fired appliances
Method 29—Determination of metals emissions from stationary sources

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

METHOD 26—DETERMINATION OF HYDROGEN HALIDE AND HALOGEN EMISSIONS FROM STATIONARY SOURCES NON-ISOKINETIC METHOD

1.0 Scope and Application

1.1 Analytes.

Analytes	CAS No.
Hydrogen Chloride (HCl)	7647–01–0
Hydrogen Bromide (HBr)	10035–10–6
Hydrogen Fluoride (HF)	7664–39–3
Chlorine (Cl_2)	7882–50–5
Bromine (Br_2)	7726–95–6

1.2 Applicability. This method is applicable for determining emissions of hydrogen halides (HX) (HCl, HBr, and HF) and halogens (X_2) (Cl_2 and Br_2) from stationary sources when specified by the applicable subpart. Sources, such as those controlled by wet scrubbers, that emit acid particulate matter must be sampled using Method 26A.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 An integrated sample is extracted from the source and passed through a prepurged heated probe and filter into dilute sulfuric acid and dilute sodium hydroxide solutions which collect the gaseous hydrogen halides and halogens, respectively. The filter collects particulate matter including halide salts but is not routinely recovered and analyzed. The hydrogen halides are solubilized in the acidic solution and form chloride (Cl^-), bromide (Br^-), and fluoride (F^-) ions. The halogens have a very low solubility in the acidic solution and pass through to the alkaline solution where they are hydrolyzed to form a proton (H^+), the halide ion, and the hypohalous acid (HClO or HBrO). Sodium thiosulfate is added in excess to the alkaline solution to assure reaction with the hypohalous acid to form a second halide ion such that 2 halide ions are formed for each molecule of halogen gas. The halide ions in the separate solutions are measured by ion chromatography (IC).

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Volatile materials, such as chlorine dioxide (ClO_2) and ammonium chloride (NH_4Cl), which produce halide ions upon dissolution during sampling are potential interferents. Interferents for the halide measurements are the halogen gases which disproportionate to a hydrogen halide and a hydrohalous acid upon dissolution in water. However, the use of acidic rather than neutral or basic solutions for collection of the hydrogen halides greatly reduces the dissolution of any halogens passing through this solution.

4.2 The simultaneous presence of HBr and CL_2 may cause a positive bias in the HCL result with a corresponding negative bias in the Cl_2 result as well as affecting the HBr/Br_2 split.

4.3 High concentrations of nitrogen oxides (NO_X) may produce sufficient nitrate (NO_3^- to interfere with measurements of very low Br^- levels.

4.4 A glass wool plug should *not* be used to remove particulate matter since a negative bias in the data could result.

4.5 There is anecdotal evidence that HF may be outgassed from new teflon components. If HF is a target analyte, then preconditioning of new teflon components, by heating should be considered.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations before performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.2 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1 Sampling. The sampling train is shown in Figure 26–1, and component parts are discussed below.

6.1.1 Probe. Borosilicate glass, approximately 3/8-in. (9-mm) I.D. with a heating system capable of maintaining a probe gas temperature during sampling between 120 and 134 °C (248 and 273 °F) to prevent moisture condensation; or Teflon where stack probes are below 210 °C. If HF is a target analyte, then preconditioning of new teflon components by heating should be considered to prevent potential HF outgassing. A Teflon-glass filter in a mat configuration should be installed to remove particulate matter from the gas stream.

6.1.2 Three-way Stopcock. A borosilicate-glass three-way stopcock with a heating system to prevent moisture condensation. The heated stopcock should connect to the outlet of the heated filter and the inlet of the first impinger. The heating system should be capable of preventing condensation up to the inlet of the first impinger. Silicone grease may be used, if necessary, to prevent leakage.

6.1.3 Impingers. Four 30-ml midget impingers with leak-free glass connectors. Silicone grease may be used, if necessary, to prevent leakage. For sampling at high moisture sources or for sampling times greater than one hour, a midget impinger with a shortened stem (such that the gas sample does not bubble through the collected condensate) should be used in front of the first impinger.

6.1.4 Drying Tube or Impinger. Tube or impinger, of Mae West design, filled with 6- to 16-mesh indicating type silica gel, or equivalent, to dry the gas sample and to protect the dry gas meter and pump. If the silica gel has been used previously, dry at 175 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used.

6.1.5 Heating System. Any heating system capable of maintaining a temperature around the probe and filter holder between 120 and 134 °C (248 and 273 °F) during sampling, or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application.

6.1.6 Filter Holder and Support. The filter holder shall be made of Teflon or quartz. The filter support shall be made of Teflon. All Teflon filter holders and supports are available from Savillex Corp., 5325 Hwy 101, Minnetonka, MN 55345.

6.1.7 Sample Line. Leak-free, with compatible fittings to connect the last impinger to the needle valve.

6.1.8 Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of the selected flow rate of 2 liters/min (0.07 ft^3/min).

6.1.9 Purge Pump, Purge Line, Drying Tube, Needle Valve, and Rate Meter. Pump capable of purging the sampling probe at 2 liters/min, with drying tube, filled with silica gel or equivalent, to protect pump, and a rate meter capable of measuring 0 to 5 liters/min (0.2 ft^3/min).

6.1.10 Stopcock Grease, Valve, Pump, Volume Meter, Barometer, and Vacuum Gauge. Same as in Method 6, sections 6.1.1.4, 6.1.1.7, 6.1.1.8, 6.1.1.10, 6.1.2, and 6.1.3.

6.1.11 Temperature Measuring Devices. Temperature sensors to monitor the temperature of the probe and to monitor the temperature of the sampling system from the outlet of the probe to the inlet of the first impinger.

6.1.12 Ice Water Bath. To minimize loss of absorbing solution.

6.2 Sample Recovery.

6.2.1 Wash Bottles. Polyethylene or glass, 500-ml or larger, two.

6.2.2 Storage Bottles. 100- or 250-ml, high-density polyethylene bottles with Teflon screw cap liners to store impinger samples.

6.3 Sample Preparation and Analysis. The materials required for volumetric dilution and chromatographic analysis of samples are described below.

6.3.1 Volumetric Flasks. Class A, 100-ml size.

6.3.2 Volumetric Pipets. Class A, assortment. To dilute samples to the calibration range of the ion chromatograph.

6.3.3 Ion Chromatograph (IC). Suppressed or non-suppressed, with a conductivity detector and electronic integrator operating in the peak area mode. Other detectors, strip chart recorders, and peak height measurements may be used.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society (ACS reagent grade). When such specifications are not available, the best available grade shall be used.

7.1 Sampling.

7.1.1 Filter. A 25-mm (1 in) (or other size) Teflon glass mat, Pallflex TX40HI75 (Pallflex Inc., 125 Kennedy Drive, Putnam, CT 06260). This filter is in a mat configuration to prevent fine particulate matter from entering the sampling train. Its composition is 75% Teflon/25% borosilicate glass. Other filters may be used, but they must be in a mat (as opposed to a laminate) configuration and contain at least 75% Teflon. For practical rather than scientific reasons, when the stack gas temperature exceeds 210 °C (410 °F) and the HCl concentration is greater than 20 ppm, a quartz-fiber filter may be used since Teflon becomes unstable above this temperature.

7.1.2 Water. Deionized, distilled water that conforms to American Society of Testing and Materials (ASTM) Specification D 1193–77 or 91, Type 3 (incorporated by reference—see §60.17).

7.1.3 Acidic Absorbing Solution, 0.1 N Sulfuric Acid (H_2SO_4). To prepare 100 ml of the absorbing solution for the front impinger pair, slowly add 0.28 ml of concentrated H_2SO_4 to about 90 ml of water while stirring, and adjust the final volume to 100 ml using additional water. Shake well to mix the solution.

7.1.4 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 180 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants may be used, subject to the approval of the Administrator.

7.1.5 Alkaline Adsorbing Solution, 0.1 N Sodium Hydroxide (NaOH). To prepare 100 ml of the scrubber solution for the third and fourth impinger, dissolve 0.40 g of solid NaOH in about 90 ml of water, and adjust the final

solution volume to 100 ml using additional water. Shake well to mix the solution.

7.1.6 Sodium Thiosulfate ($Na_2S_2O_3$ 5 H_2O)

7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in section 7.1.2.

7.2.2 Absorbing Solution Blanks. A separate blank solution of each absorbing reagent should be prepared for analysis with the field samples. Dilute 30 ml of each absorbing solution to approximately the same final volume as the field samples using the blank sample of rinse water.

7.2.3 Halide Salt Stock Standard Solutions. Prepare concentrated stock solutions from reagent grade sodium chloride (NaCl), sodium bromide (NaBr), and sodium fluoride (NaF). Each must be dried at 110 °C (230 °F) for two or more hours and then cooled to room temperature in a desiccator immediately before weighing. Accurately weigh 1.6 to 1.7 g of the dried NaCl to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact Cl^- concentration using Equation 26–1 in section 12.2. In a similar manner, accurately weigh and solubilize 1.2 to 1.3 g of dried NaBr and 2.2 to 2.3 g of NaF to make 1-liter solutions. Use Equations 26–2 and 26–3 in section 12.2, to calculate the Br^- and F^- concentrations. Alternately, solutions containing a nominal certified concentration of 1000 mg/l NaCl are commercially available as convenient stock solutions from which standards can be made by appropriate volumetric dilution. Refrigerate the stock standard solutions and store no longer than one month.

7.2.4 Chromatographic Eluent. Effective eluents for nonsuppressed IC using a resin-or silica-based weak ion exchange column are a 4 mM potassium hydrogen phthalate solution, adjusted to pH 4.0 using a saturated sodium borate solution, and a 4 mM 4-hydroxy benzoate solution, adjusted to pH 8.6 using 1 N NaOH. An effective eluent for suppressed ion chromatography is a solution containing 3 mM sodium bicarbonate and 2.4 mM sodium carbonate. Other dilute solutions buffered to a similar pH and containing no interfering ions may be used. When using suppressed ion chromatography, if the ''water dip'' resulting from sample injection interferes with the chloride peak, use a 2 mM NaOH/2.4 mM sodium bicarbonate eluent.

8.0 Sample Collection, Preservation, Storage, and Transport

NOTE: Because of the complexity of this method, testers and analyst should be trained and experienced with the procedure to ensure reliable results.

8.1 Sampling.

8.1.1 Preparation of Collection Train. Prepare the sampling train as follows: Pour 15 ml of the acidic absorbing solution into each one of the first pair of impingers, and 15 ml of the alkaline absorbing solution into each one of the second pair of impingers. Connect the impingers in series with the knockout impinger first, if used, followed by the two impingers containing the acidic absorbing solution and the two impingers containing the alkaline absorbing solution. Place a fresh charge of silica gel, or equivalent, in the drying tube or impinger at the end of the impinger train.

8.1.2 Adjust the probe temperature and the temperature of the filter and the stopcock (*i.e.*, the heated area in Figure 26–1) to a temperature sufficient to prevent water condensation. This temperature must be maintained between 120 and 134 °C (248 and 273 °F). The temperature should be monitored throughout a sampling run to ensure that the desired temperature is maintained. It is important to maintain a temperature around the probe and filter in this range since it is extremely difficult to purge acid gases off these components. (These components are not quantitatively recovered and, hence, any collection of acid gases on these components would result in potential undereporting of these emissions. The applicable subparts may specify alternative higher temperatures.)

8.1.3 Leak-Check Procedure.

8.1.3.1 Sampling Train. A leak-check prior to the sampling run is optional; however, a leak-check after the sampling run is mandatory. The leak-check procedure is as follows: Temporarily attach a suitable [*e.g.*, 0–40 cc/min (0–2.4 in^3/min)] rotameter to the outlet of the dry gas meter and place a vacuum gauge at or near the probe inlet. Plug the probe inlet, pull a vacuum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter. A leakage rate not in excess of 2 percent of the average sampling rate is acceptable.

NOTE: Carefully release the probe inlet plug before turning off the pump.

8.1.3.2 Pump. It is suggested (not mandatory) that the pump be leak-checked separately, either prior to or after the sampling run. If done prior to the sampling run, the pump leak-check shall precede the leak-check of the sampling train described immediately above; if done after the sampling run, the pump leak-check shall follow the train leak-check. To leak-check the pump, proceed as follows: Disconnect the drying tube from the probe-impinger assembly. Place a vacuum gauge at the inlet to either the drying tube or pump, pull a vacuum of 250 mm (10 in) Hg, plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum should remain stable for at least 30 sec. Other leak-check procedures may be used, subject to the approval of the Administrator, U.S. Environmental Protection Agency.

8.1.4 Purge Procedure. Immediately before sampling, connect the purge line to the stopcock, and turn the stopcock to permit the purge pump to purge the probe (see Figure 1A of Figure 26–1). Turn on the purge pump, and adjust the purge rate to 2 liters/min (0.07 ft^3/min). Purge for at least 5 minutes before sampling.

8.1.5 Sample Collection. Turn on the sampling pump, pull a slight vacuum of approximately 25 mm Hg (1 in Hg) on the impinger train, and turn the stopcock to permit stack gas to be pulled through the impinger train (see Figure 1C of Figure 26–1). Adjust the sampling rate to 2 liters/min, as indicated by the rate meter, and maintain this rate to within 10 percent during the entire sampling run. Take readings of the dry gas meter volume and temperature, rate meter, and vacuum gauge at least once every five minutes during the run. A sampling time of one hour is recommended. Shorter sampling times may introduce a significant negative bias in the HCl concentration. At the conclusion of the sampling run, remove the train from the stack, cool, and perform a leak-check as described in section 8.1.3.1.

8.2 Sample Recovery.

8.2.1 Disconnect the impingers after sampling. Quantitatively transfer the contents of the acid impingers and the knockout impinger, if used, to a leak-free storage bottle. Add the water rinses of each of these impingers and connecting glassware to the storage bottle.

8.2.2 Repeat this procedure for the alkaline impingers and connecting glassware using a separate storage bottle. Add 25 mg of sodium thiosulfate per the product of ppm of halogen anticipated to be in the stack gas times the volume (dscm) of stack gas sampled (0.7 mg per ppm-dscf).

NOTE: This amount of sodium thiosulfate includes a safety factor of approximately 5 to assure complete reaction with the hypohalous acid to form a second Cl^- ion in the alkaline solution.

8.2.3 Save portions of the absorbing reagents (0.1 N H_2SO_4 and 0.1 N NaOH) equivalent to the amount used in the sampling train (these are the absorbing solution blanks described in section 7.2.2); dilute to the approximate volume of the corresponding samples using rinse water directly from the wash bottle being used. Add the same amount of sodium thiosulfate solution to the 0.1 N NaOH absorbing solution blank. Also, save a portion of the rinse water used to rinse the sampling train. Place each in a separate, prelabeled storage bottle. The sample storage bottles should be sealed, shaken to mix, and labeled. Mark the fluid level.

8.3 Sample Preparation for Analysis. Note the liquid levels in the storage bottles and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Quantitatively transfer the sample solutions to 100-ml volumetric flasks, and dilute to 100 ml with water.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Volume Metering System, Temperature Sensors, Rate Meter, and Barometer. Same as in Method 6, sections 10.1, 10.2, 10.3, and 10.4.

10.2 Ion Chromatograph.

10.2.1 To prepare the calibration standards, dilute given amounts (1.0 ml or greater) of the stock standard solutions to convenient volumes, using 0.1 N H_2SO_4 or 0.1 N NaOH, as appropriate. Prepare at least four calibration standards for each absorbing reagent containing the appropriate stock solutions such that they are within the linear range of the field samples.

10.2.2 Using one of the standards in each series, ensure adequate baseline separation for the peaks of interest.

10.2.3 Inject the appropriate series of calibration standards, starting with the lowest concentration standard first both before and after injection of the quality control check sample, reagent blanks, and field samples. This allows compensation for any instrument drift occurring during sample analysis. The values from duplicate injections of these calibration samples should agree within 5 percent of their mean for the analysis to be valid.

10.2.4 Determine the peak areas, or heights, for the standards and plot individual values versus halide ion concentrations in µg/ml.

10.2.5 Draw a smooth curve through the points. Use linear regression to calculate a formula describing the resulting linear curve.

11.0 Analytical Procedures

11.1 Sample Analysis.

11.1.1 The IC conditions will depend upon analytical column type and whether suppressed or non-suppressed IC is used. An example chromatogram from a non-suppressed system using a 150-mm Hamilton PRP-X100 anion column, a 2 ml/min flow rate of a 4 mM 4-hydroxy benzoate solution adjusted to a pH of 8.6 using 1 N NaOH, a 50 µl sample loop, and a conductivity detector set on 1.0 µS full scale is shown in Figure 26–2.

11.1.2 Before sample analysis, establish a stable baseline. Next, inject a sample of water, and determine if any Cl^-, Br^-, or F^- appears in the chromatogram. If any of these ions are present, repeat the load/injection

procedure until they are no longer present. Analysis of the acid and alkaline absorbing solution samples requires separate standard calibration curves; prepare each according to section 10.2. Ensure adequate baseline separation of the analyses.

11.1.3 Between injections of the appropriate series of calibration standards, inject in duplicate the reagent blanks, quality control sample, and the field samples. Measure the areas or heights of the Cl^-, Br^-, and F^- peaks. Use the mean response of the duplicate injections to determine the concentrations of the field samples and reagent blanks using the linear calibration curve. The values from duplicate injections should agree within 5 percent of their mean for the analysis to be valid. If the values of duplicate injections are not within 5 percent of the mean, the duplicate injections shall be repeated and all four values used to determine the average response. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

12.0 Data Analysis and Calculations

NOTE: Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

12.1 Nomenclature.

B_X^- = Mass concentration of applicable absorbing solution blank, µg halide ion (Cl^-, Br^-, F^-) /ml, not to exceed 1 µg/ml which is 10 times the published analytical detection limit of 0.1 µg/ml.

C = Concentration of hydrogen halide (HX) or halogen (X_2), dry basis, mg/dscm.

K = 10^{-3} mg/µg.

K_{HCl} = 1.028 (µg HCl/µg-mole)/(µg Cl^-/µg-mole).

K_{HBr} = 1.013 (µg HBr/µg-mole)/(µg Br^-/µg-mole).

K_{HF} = 1.053 (µg HF/µg-mole)/(µg F^-/µg-mole).

m_{HX} = Mass of HCl, HBr, or HF in sample, µg.

m_{X2} = Mass of Cl_2 or Br_2 in sample, µg.

S_X^- = Analysis of sample, µg halide ion (Cl^-, Br^-, F^-)/ml.

$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm.

V_s = Volume of filtered and diluted sample, ml.

12.2 Calculate the exact Cl^-, Br^-, and F^- concentration in the halide salt stock standard solutions using the following equations.

$$\mu g\ Cl^-/ml = g\ of\ NaCl \times 10^3 \times 35.453/58.44 \qquad \text{Eq. 26-1}$$

$$\mu g\ Br^-/ml = g\ of\ NaBr \times 10^3 \times 79.904/102.90 \qquad \text{Eq. 26-2}$$

$$\mu g\ F^-/ml = g\ of\ NaF \times 10^3 \times 18.998/41.99 \qquad \text{Eq. 26-3}$$

12.3 Sample Volume, Dry Basis, Corrected to Standard Conditions. Calculate the sample volume using Eq. 6–1 of Method 6.

12.4 Total µg HCl, HBr, or HF Per Sample.

$$m_{HX} = K_{HC1,Hbr,HF} V_s \left(S_x^- - B_x^-\right) \qquad \text{Eq. 26-4}$$

12.5 Total µg Cl_2 or Br_2 Per Sample.

$$M_{x2} = V_s \left(S_X^- - B_X^-\right) \qquad \text{Eq. 26-5}$$

12.6 Concentration of Hydrogen Halide or Halogen in Flue Gas.

$$C = K m_{XH,X2} / V_{m(std)} \qquad \text{Eq. 26-6}$$

13.0 Method Performance

13.1 Precision and Bias. The within-laboratory relative standard deviations are 6.2 and 3.2 percent at HCl concentrations of 3.9 and 15.3 ppm, respectively. The method does not

exhibit a bias to Cl_2 when sampling at concentrations less than 50 ppm.

13.2 Sample Stability. The collected Cl^- samples can be stored for up to 4 weeks.

13.3 Detection Limit. A typical IC instrumental detection limit for Cl^- is 0.2 μg/ml. Detection limits for the other analyses should be similar. Assuming 50 ml liquid recovered from both the acidified impingers, and the basic impingers, and 0.12 dscm (4.24 dscf) of stack gas sampled, then the analytical detection limit in the stack gas would be about 0.05 ppm for HCl and Cl_2, respectively.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

Method 26A. Method 26A, which uses isokinetic sampling equipment, is an acceptable alternative to Method 26.

17.0 References

1. Steinsberger, S. C. and J. H. Margeson, ''Laboratory and Field Evaluation of a Methodology for Determination of Hydrogen Chloride Emissions from Municipal and Hazardous Waste Incinerators,'' U.S. Environmental Protection Agency, Office of Research and Development, Report No. 600/3–89/064, April 1989. Available from the National Technical Information Service, Springfield, VA 22161 as PB89220586/AS.

2. State of California, Air Resources Board, Method 421, ''Determination of Hydrochloric Acid Emissions from Stationary Sources,'' March 18, 1987.

3. Cheney, J.L. and C.R. Fortune. Improvements in the Methodology for Measuring Hydrochloric Acid in Combustion Source Emissions. J. Environ. Sci. Health. *A19*(3): 337–350. 1984.

4. Stern, D. A., B. M. Myatt, J. F. Lachowski, and K. T. McGregor. Speciation of Halogen and Hydrogen Halide Compounds in Gaseous Emissions. In: Incineration and Treatment of Hazardous Waste: Proceedings of the 9th Annual Research Symposium, Cincinnati, Ohio, May 2–4, 1983. Publication No. 600/9–84–015. July 1984. Available from National Technical Information Service, Springfield, VA 22161 as PB84–234525.

5. Holm, R. D. and S. A. Barksdale. Analysis of Anions in Combustion Products. In: Ion Chromatographic Analysis of Environmental Pollutants. E. Sawicki, J. D. Mulik, and E. Wittgenstein (eds.). Ann Arbor, Michigan, Ann Arbor Science Publishers. 1978. pp. 99–110.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

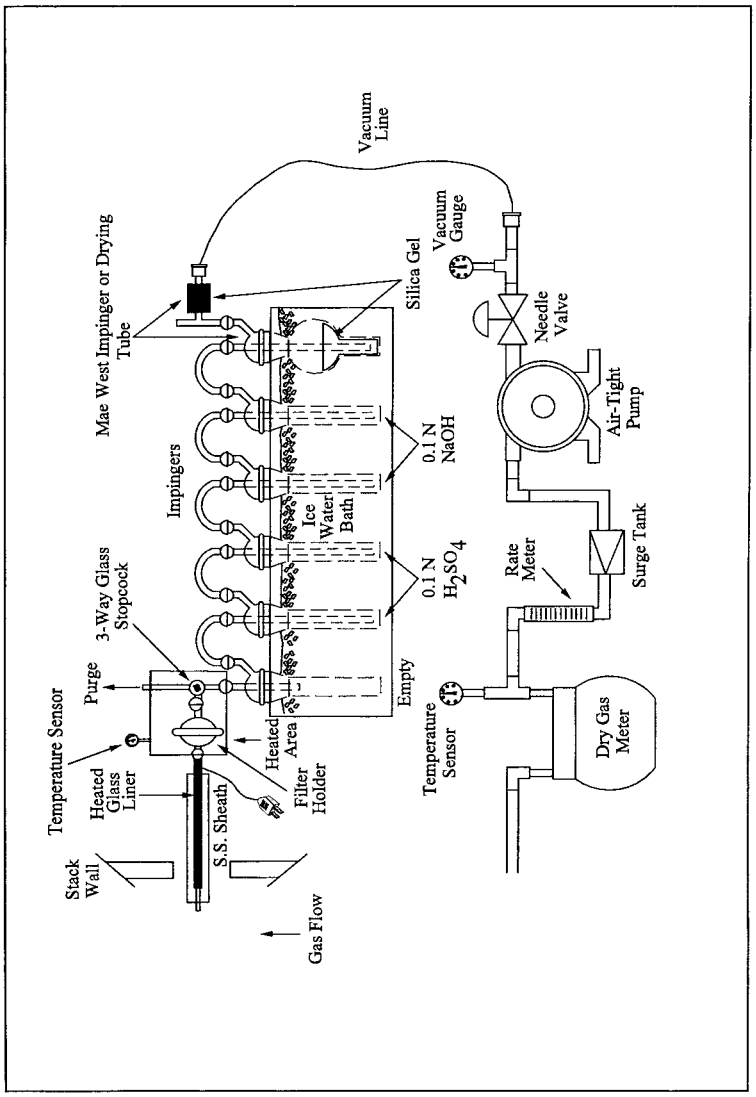


Figure 26-1. Sampling Train.

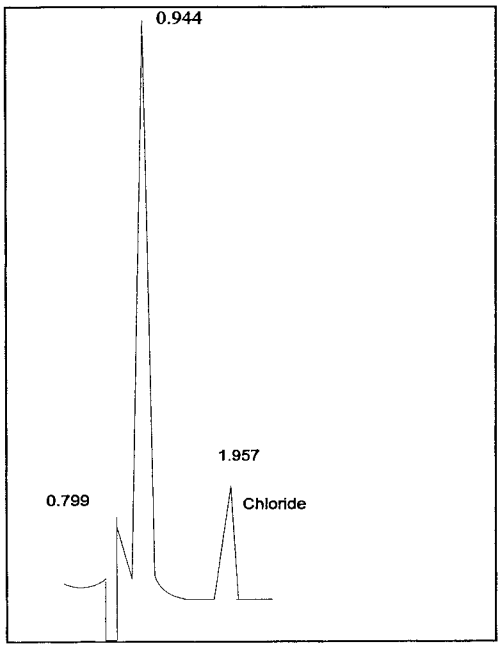


Figure 26-2. Example Chromatogram.

METHOD 26A—DETERMINATION OF HYDROGEN HALIDE AND HALOGEN EMISSIONS FROM STATIONARY SOURCES ISOKINETIC METHOD

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 2, Method 5, and Method 26.

1.0 Scope and Application

1.1 Analytes.

Analytes	CAS No.
Hydrogen Chloride (HCl)	7647–01–0
Hydrogen Bromide (HBr)	10035–10–6
Hydrogen Fluoride (HF)	7664–39–3
Chlorine (Cl_2)	7882–50–5
Bromine (Br_2)	7726–95–6

1.2 This method is applicable for determining emissions of hydrogen halides (HX) [HCl, HBr, and HF] and halogens (X_2) [Cl_2 and Br_2] from stationary sources when specified by the applicable subpart. This method collects the emission sample isokinetically and is therefore particularly suited for sampling at sources, such as those controlled by wet scrubbers, emitting acid particulate matter (*e.g.*, hydrogen halides dissolved in water droplets).

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Principle. Gaseous and particulate pollutants are withdrawn isokinetically from the source and collected in an optional cyclone, on a filter, and in absorbing solutions. The cyclone collects any liquid droplets and is not necessary if the source emissions do not contain them; however, it is preferable to include the cyclone in the sampling train to protect the filter from any liquid present. The filter collects particulate matter including halide salts but is not routinely recovered or analyzed. Acidic and alkaline absorbing solutions collect the gaseous hydrogen halides and halogens, respectively. Following sampling of emissions containing liquid droplets, any halides/halogens dissolved in the liquid in the cyclone and on the filter are vaporized to gas and collected in the impingers by pulling conditioned ambient air through the sampling train. The hydrogen halides are solubilized in the acidic solution and form chloride (Cl^-), bromide (Br^-),

and fluoride (F^-) ions. The halogens have a very low solubility in the acidic solution and pass through to the alkaline solution where they are hydrolyzed to form a proton (H^+), the halide ion, and the hypohalous acid (HClO or HBrO). Sodium thiosulfate is added to the alkaline solution to assure reaction with the hypohalous acid to form a second halide ion such that 2 halide ions are formed for each molecule of halogen gas. The halide ions in the separate solutions are measured by ion chromatography (IC). If desired, the particulate matter recovered from the filter and the probe is analyzed following the procedures in Method 5.

NOTE: If the tester intends to use this sampling arrangement to sample concurrently for particulate matter, the alternative Teflon probe liner, cyclone, and filter holder should not be used. The Teflon filter support must be used. The tester must also meet the probe and filter temperature requirements of both sampling trains.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Volatile materials, such as chlorine dioxide (ClO_2) and ammonium chloride (NH_4Cl), which produce halide ions upon dissolution during sampling are potential interferents. Interferents for the halide measurements are the halogen gases which disproportionate to a hydrogen halide and a hypohalous acid upon dissolution in water. The use of acidic rather than neutral or basic solutions for collection of the hydrogen halides greatly reduces the dissolution of any halogens passing through this solution.

4.2 The simultaneous presence of both HBr and Cl_2 may cause a positive bias in the HCl result with a corresponding negative bias in the Cl_2 result as well as affecting the HBr/Br_2 split.

4.3 High concentrations of nitrogen oxides (NO_X) may produce sufficient nitrate (NO_3^-) to interfere with measurements of very low Br^- levels. Dissociating chloride salts (*e.g.*, ammonium chloride) at elevated temperatures interfere with halogen acid measurement in this method. Maintaining particulate probe/filter temperatures between 120 °C and 134 °C (248 °F and 273 °F) minimizes this interference.

4.4 There is anecdotal evidence that HF may be outgassed from new Teflon components. If HF is a target analyte then preconditioning of new Teflon components, by heating, should be considered.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations before performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.2 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0. Equipment and Supplies

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1 Sampling. The sampling train is shown in Figure 26A–1; the apparatus is similar to the Method 5 train where noted as follows:

6.1.1 Probe Nozzle. Borosilicate or quartz glass; constructed and calibrated according to Method 5, sections 6.1.1.1 and 10.1, and coupled to the probe liner using a Teflon union; a stainless steel nut is recommended for this union. When the stack temperature exceeds 210 °C (410 °F), a one-piece glass nozzle/liner assembly must be used.

6.1.2 Probe Liner. Same as Method 5, section 6.1.1.2, except metal liners shall not be used. Water-cooling of the stainless steel sheath is recommended at temperatures exceeding 500 °C (932 °F). Teflon may be used in limited applications where the minimum stack temperature exceeds 120 °C (250 °F) but never exceeds the temperature where Teflon is estimated to become unstable [approximately 210 °C (410 °F)].

6.1.3 Pitot Tube, Differential Pressure Gauge, Filter Heating System, Metering System, Barometer, Gas Density Determination Equipment. Same as Method 5, sections 6.1.1.3, 6.1.1.4, 6.1.1.6, 6.1.1.9, 6.1.2, and 6.1.3.

6.1.4 Cyclone (Optional). Glass or Teflon. Use of the cyclone is required only when the sample gas stream is saturated with moisture; however, the cyclone is recommended to protect the filter from any liquid droplets present.

6.1.5 Filter Holder. Borosilicate or quartz glass, or Teflon filter holder, with a Teflon filter support and a sealing gasket. The sealing gasket shall be constructed of Teflon or equivalent materials. The holder design shall provide a positive seal against leakage at any point along the filter circumference. The holder shall be attached immediately to the outlet of the cyclone.

6.1.6 Impinger Train. The following system shall be used to determine the stack gas moisture content and to collect the hydrogen halides and halogens: five or six impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. The first impinger shown in Figure 26A–1 (knockout or condensate impinger) is optional and is recommended as a water knockout trap for use under high moisture conditions. If used, this impinger should be constructed as described below for the alkaline impingers, but with a shortened stem, and should contain 50 ml of 0.1 N H_2SO_4. The following two impingers (acid impingers which each contain 100 ml of 0.1 N H_2SO_4) shall be of the Greenburg-Smith design with the standard tip (Method 5, section 6.1.1.8). The next two impingers (alkaline impingers which each contain 100 ml of 0.1 N NaOH) and the last impinger (containing silica gel) shall be of the modified Greenburg-Smith design (Method 5, section 6.1.1.8). The condensate, acid, and alkaline impingers shall contain known quantities of the appropriate absorbing reagents. The last impinger shall contain a known weight of silica gel or equivalent desiccant. Teflon impingers are an acceptable alternative.

6.1.7 Heating System. Any heating system capable of maintaining a temperature around the probe and filter holder between 120 and 134 °C (248 to 273 °F) during sampling, or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application.

6.1.8 Ambient Air Conditioning Tube (Optional). Tube tightly packed with approximately 150 g of fresh 8 to 20 mesh sodium hydroxide-coated silica, or equivalent, (Ascarite II has been found suitable) to dry and remove acid gases from the ambient air used to remove moisture from the filter and cyclone, when the cyclone is used. The inlet and outlet ends of the tube should be packed with at least 1-cm thickness of glass wool or filter material suitable to prevent escape of fines. Fit one end with flexible tubing, etc. to allow connection to probe nozzle following the test run.

6.2 Sample Recovery.

6.2.1 Probe-Liner and Probe-Nozzle Brushes, Wash Bottles, Glass Sample Storage Containers, Petri Dishes, Graduated Cylinder and/or Balance, and Rubber Policeman. Same as Method 5, sections 6.2.1, 6.2.2, 6.2.3, 6.2.4, 6.2.5, and 6.2.7.

6.2.2 Plastic Storage Containers. Screw-cap polypropylene or polyethylene containers to store silica gel. High-density polyethylene bottles with Teflon screw cap liners to store impinger reagents, 1-liter.

6.2.3 Funnels. Glass or high-density polyethylene, to aid in sample recovery.

6.3 Sample Preparation and Analysis.

6.3.1 Volumetric Flasks. Class A, various sizes.

6.3.2 Volumetric Pipettes. Class A, assortment. To dilute samples to calibration range of the ion chromatograph (IC).

6.3.3 Ion Chromatograph (IC). Suppressed or nonsuppressed, with a conductivity detector and electronic integrator operating in the peak area mode. Other detectors, a strip chart recorder, and peak heights may be used.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society (ACS reagent grade). When such specifications are not available, the best available grade shall be used.

7.1 Sampling.

7.1.1 Filter. Teflon mat (*e.g.*, Pallflex TX40HI45) filter. When the stack gas temperature exceeds 210 °C (410 °F) a quartz fiber filter may be used.

7.1.2 Water. Deionized, distilled water that conforms to American Society of Testing and Materials (ASTM) Specification D 1193–77 or 91, Type 3 (incorporated by reference—see §60.17).

7.1.3 Acidic Absorbing Solution, 0.1 N Sulfuric Acid (H_2SO_4). To prepare 1 L, slowly add 2.80 ml of concentrated 17.9 M H2SO4 to about 900 ml of water while stirring, and adjust the final volume to 1 L using additional water. Shake well to mix the solution.

7.1.4 Silica Gel, Crushed Ice, and Stopcock Grease. Same as Method 5, sections 7.1.2, 7.1.4, and 7.1.5, respectively.

7.1.5 Alkaline Absorbing Solution, 0.1 N Sodium Hydroxide (NaOH). To prepare 1 L, dissolve 4.00 g of solid NaOH in about 900 ml of water and adjust the final volume to 1 L using additional water. Shake well to mix the solution.

7.1.6 Sodium Thiosulfate, ($Na_2S_2O_3$3.5 H_2O).

7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in section 7.1.2.

7.2.2 Absorbing Solution Blanks. A separate blank solution of each absorbing reagent should be prepared for analysis with the field samples. Dilute 200 ml of each absorbing solution (250 ml of the acidic absorbing solution, if a condensate impinger is used) to the same final volume as the field samples using the blank sample of rinse water. If a particulate determination is conducted, collect a blank sample of acetone.

7.2.3 Halide Salt Stock Standard Solutions. Prepare concentrated stock solutions from reagent grade sodium chloride (NaCl), sodium bromide (NaBr), and sodium fluoride (NaF). Each must be dried at 110 °C (230 °F) for two or more hours and then cooled to room temperature in a desiccator immediately before weighing. Accurately weigh 1.6 to 1.7 g of the dried NaCl to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact Cl^- concentration using Equation 26A–1 in section 12.2. In a similar manner, accurately weigh and solubilize 1.2 to 1.3 g of dried NaBr and 2.2 to 2.3 g of NaF to make 1-liter solutions. Use Equations 26A–2 and 26A–3 in section 12.2, to calculate the Br^- and F^- concentrations. Alternately, solutions containing a nominal certified concentration of 1000 mg/L NaCl are commercially available as convenient stock solutions from which standards can be made by appropriate volumetric dilution. Refrigerate the stock standard solutions and store no longer than one month.

7.2.4 Chromatographic Eluent. Same as Method 26, section 7.2.4.

7.2.5 Water. Same as section 7.1.1.

7.2.6 Acetone. Same as Method 5, section 7.2.

8.0 Sample Collection, Preservation, Storage, and Transport

NOTE: Because of the complexity of this method, testers and analysts should be trained and experienced with the procedures to ensure reliable results.

8.1 Sampling.

8.1.1 Pretest Preparation. Follow the general procedure given in Method 5, section 8.1, except the filter need only be desiccated and weighed if a particulate determination will be conducted.

8.1.2 Preliminary Determinations. Same as Method 5, section 8.2.

8.1.3 Preparation of Sampling Train. Follow the general procedure given in Method 5, section 8.1.3, except for the following variations: Add 50 ml of 0.1 N H_2SO_4 to the condensate impinger, if used. Place 100 ml of 0.1 N H_2SO_4 in each of the next two impingers. Place 100 ml of 0.1 N NaOH in each of the following two impingers. Finally, transfer approximately 200–300 g of preweighed silica gel from its container to the last impinger. Set up the train as in Figure 26A–1. When used, the optional cyclone is inserted between the probe liner and filter holder and located in the heated filter box.

8.1.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, sections 8.4.2 (Pretest Leak-Check), 8.4.3 (Leak-Checks During the Sample Run), and 8.4.4 (Post-Test Leak-Check).

8.1.5 Sampling Train Operation. Follow the general procedure given in Method 5, Section 8.5. It is important to maintain a temperature around the probe, filter (and cyclone, if used) between 120 and 134 °C (248 and 273 °F) since it is extremely difficult to purge acid gases off these components. (These components are not quantitatively recovered and hence any collection of acid gases on these components would result in potential undereporting these emissions. The applicable subparts may specify alternative higher temperatures.) For each run, record the data required on a data sheet such as the one shown in Method 5, Figure 5–3. If the condensate impinger becomes too full, it may be emptied, recharged with 50 ml of 0.1 N H2SO4, and replaced during the sample run. The condensate emptied must be saved and included in the measurement of the volume of moisture collected and included in the sample for analysis. The additional 50 ml of absorbing reagent must also be considered in calculating the moisture. Before the sampling train integrity is compromised by removing the impinger, conduct a leak-check as described in Method 5, Section 8.4.2.

8.1.6 Post-Test Moisture Removal (Optional). When the optional cyclone is included in the sampling train or when liquid is visible on the filter at the end of a sample run even in the absence of a cyclone, perform the following procedure. Upon completion of the test run, connect the ambient air conditioning tube at the probe inlet and operate the train with the filter heating system between 120 and 134 °C (248 and 273 °F) at a low flow rate (*e.g.*, ΔH = 1 in. H_2O) to vaporize any liquid and hydrogen halides in the cyclone or on the filter and pull them through the train into the impingers. After 30 minutes, turn off the flow, remove the conditioning tube, and examine the cyclone and filter for any visible liquid. If liquid is visible, repeat this step for 15 minutes and observe again. Keep repeating until the cyclone is dry.

NOTE: It is critical that this procedure is repeated until the cyclone is completely dry.

8.2 Sample Recovery. Allow the probe to cool. When the probe can be handled safely, wipe off all the external surfaces of the tip of the probe nozzle and place a cap loosely over the tip to prevent gaining or losing particulate matter. Do not cap the probe tip tightly while the sampling train is cooling down because this will create a vacuum in the filter holder, drawing water from the impingers into the holder. Before moving the sampling train to the cleanup site, remove the probe from the sample train, wipe off any silicone grease, and cap the open outlet of the impinger train, being careful not to lose any condensate that might be present. Wipe off any silicone grease and cap the filter or cyclone inlet. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger and the filter holder, disconnect it at

the filter holder and let any condensed water drain into the first impinger. Wipe off any silicone grease and cap the filter holder outlet and the impinger inlet. Ground glass stoppers, plastic caps, serum caps, Teflon tape, Parafilm, or aluminum foil may be used to close these openings. Transfer the probe and filter/impinger assembly to the cleanup area. This area should be clean and protected from the weather to minimize sample contamination or loss. Inspect the train prior to and during disassembly and note any abnormal conditions. Treat samples as follows:

8.2.1 Container No. 1 (Optional; Filter Catch for Particulate Determination). Same as Method 5, section 8.7.6.1, Container No. 1.

8.2.2 Container No. 2 (Optional; Front-Half Rinse for Particulate Determination). Same as Method 5, section 8.7.6.2, Container No. 2.

8.2.3 Container No. 3 (Knockout and Acid Impinger Catch for Moisture and Hydrogen Halide Determination). Disconnect the impingers. Measure the liquid in the acid and knockout impingers to ±1 ml by using a graduated cylinder or by weighing it to ±0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas. Quantitatively transfer this liquid to a leak-free sample storage container. Rinse these impingers and connecting glassware including the back portion of the filter holder (and flexible tubing, if used) with water and add these rinses to the storage container. Seal the container, shake to mix, and label. The fluid level should be marked so that if any sample is lost during transport, a correction proportional to the lost volume can be applied. Retain rinse water and acidic absorbing solution blanks to be analyzed with the samples.

8.2.4 Container No. 4 (Alkaline Impinger Catch for Halogen and Moisture Determination). Measure and record the liquid in the alkaline impingers as described in section 8.2.3. Quantitatively transfer this liquid to a leak-free sample storage container. Rinse these two impingers and connecting glassware with water and add these rinses to the container. Add 25 mg of sodium thiosulfate per ppm halogen anticipated to be in the stack gas multiplied by the volume (dscm) of stack gas sampled (0.7 mg/ppm-dscf). Seal the container, shake to mix, and label; mark the fluid level. Retain alkaline absorbing solution blank to be analyzed with the samples.

NOTE: 25 mg per sodium thiosulfate per ppm halogen anticipated to be in the stack includes a safety factor of approximately 5 to assure complete reaction with the hypohalous acid to form a second Cl^- ion in the alkaline solution.

8.2.5 Container No. 5 (Silica Gel for Moisture Determination). Same as Method 5, section 8.7.6.3, Container No. 3.

8.2.6 Container Nos. 6 through 9 (Reagent Blanks). Save portions of the absorbing reagents (0.1 N H_2SO_4 and 0.1 N NaOH) equivalent to the amount used in the sampling train; dilute to the approximate volume of the corresponding samples using rinse water directly from the wash bottle being used. Add the same ratio of sodium thiosulfate solution used in container No. 4 to the 0.1 N NaOH absorbing reagent blank. Also, save a portion of the rinse water alone and a portion of the acetone equivalent to the amount used to rinse the front half of the sampling train. Place each in a separate, prelabeled sample container.

8.2.7 Prior to shipment, recheck all sample containers to ensure that the caps are well-secured. Seal the lids of all containers around the circumference with Teflon tape. Ship all liquid samples upright and all particulate filters with the particulate catch facing upward.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.1.4, 10.1	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Probe Nozzle, Pitot Tube Assembly, Dry Gas Metering System, Probe Heater, Temperature Sensors, Leak-Check of Metering System, and Barometer. Same as Method 5, sections 10.1, 10.2, 10.3, 10.4, 10.5, 8.4.1, and 10.6, respectively.

10.2 Ion Chromatograph.

10.2.1 To prepare the calibration standards, dilute given amounts (1.0 ml or greater) of the stock standard solutions to convenient volumes, using 0.1 N H_2SO_4 or 0.1 N NaOH, as appropriate. Prepare at least four calibration standards for each absorbing reagent containing the three stock solutions such that they are within the linear range of the field samples.

10.2.2 Using one of the standards in each series, ensure adequate baseline separation for the peaks of interest.

10.2.3 Inject the appropriate series of calibration standards, starting with the lowest concentration standard first both before and after injection of the quality control check sample, reagent blanks, and field samples. This allows compensation for any instrument drift occurring during sample analysis. The values from duplicate injections of these calibration samples should agree within 5 percent of their mean for the analysis to be valid.

10.2.4 Determine the peak areas, or height, of the standards and plot individual values versus halide ion concentrations in µg/ml.

10.2.5 Draw a smooth curve through the points. Use linear regression to calculate a formula describing the resulting linear curve.

11.0 Analytical Procedures

NOTE: The liquid levels in the sample containers and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.1 Sample Analysis.

11.1.1 The IC conditions will depend upon analytical column type and whether suppressed or non-suppressed IC is used. An example chromatogram from a non-suppressed system using a 150-mm Hamilton PRP-X100 anion column, a 2 ml/min flow rate of a 4 mM 4-hydroxy benzoate solution adjusted to a pH of 8.6 using 1 N NaOH, a 50 µl sample loop, and a conductivity detector set on 1.0 µS full scale is shown in Figure 26–2.

11.1.2 Before sample analysis, establish a stable baseline. Next, inject a sample of water, and determine if any Cl^-, Br^-, or F^- appears in the chromatogram. If any of these ions are present, repeat the load/injection procedure until they are no longer present. Analysis of the acid and alkaline absorbing solution samples requires separate standard calibration curves; prepare each according to section 10.2. Ensure adequate baseline separation of the analyses.

11.1.3 Between injections of the appropriate series of calibration standards, inject in duplicate the reagent blanks, quality control sample, and the field samples. Measure the areas or heights of the Cl^-, Br^-, and F^- peaks. Use the mean response of the duplicate injections to determine the concentrations of the field samples and reagent blanks using the linear calibration curve. The values from duplicate injections should agree within 5 percent of their mean for the analysis to be valid. If the values of duplicate injections are not within 5 percent of the mean, the duplicator injections shall be repeated and all four values used to determine the average response. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

11.2 Container Nos. 1 and 2 and Acetone Blank (Optional; Particulate Determination). Same as Method 5, sections 11.2.1 and 11.2.2, respectively.

11.3 Container No. 5. Same as Method 5, section 11.2.3 for silica gel.

12.0 Data Analysis and Calculations

NOTE: Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

12.1 Nomenclature. Same as Method 5, section 12.1. In addition:

B_{X-} = Mass concentration of applicable absorbing solution blank, µg halide ion (Cl^-, Br^-, F^-)/ml, not to exceed 1 µg/ml which is 10 times the published analytical detection limit of 0.1 µg/ml. (It is also approximately 5 percent of the mass concentration anticipated to result from a one hour sample at 10 ppmv HCl.)

C = Concentration of hydrogen halide (HX) or halogen (X_2), dry basis, mg/dscm.

K = 10^{-3} mg/µg.

K_{HCl} = 1.028 (µg HCl/µg-mole)/(µg Cl^-/µg-mole).

K_{HBr} = 1.013 (µg HBr/µg-mole)/(µg Br^-/µg-mole).

K_{HF} = 1.053 (µg HF/µg-mole)/(µg F^-/µg-mole).

m_{HX} = Mass of HCl, HBr, or HF in sample, ug.

m_{X2} = Mass of Cl_2 or Br_2 in sample, ug.

S_{X-} = Analysis of sample, ug halide ion (Cl^-, Br^-, F^-)/ml.

V_s = Volume of filtered and diluted sample, ml.

12.2 Calculate the exact Cl^-, Br^-, and F^- concentration in the halide salt stock standard solutions using the following equations.

$$\mu g\ Cl^-/ml = g\ of\ NaCl \times 10^3 \times 35.453/58.44 \qquad \text{Eq. 26A-1}$$

$$\mu g\ Br^-/ml = g\ of\ NaBr \times 10^3 \times 79.904/102.90 \qquad \text{Eq. 26A-2}$$

$$\mu g\ F^-/ml = g\ of\ NaF \times 10^3 \times 18.998/41.99 \qquad \text{Eq. 26A-3}$$

12.3 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 5–3 of Method 5).

12.4 Dry Gas Volume. Calculate $V_{m(std)}$ and adjust for leakage, if necessary, using the equation in section 12.3 of Method 5.

12.5 Volume of Water Vapor and Moisture Content. Calculate the volume of water vapor $V_{w(std)}$ and moisture content B_{ws} from the data obtained in this method (Figure 5–3 of Method 5); use Equations 5–2 and 5–3 of Method 5.

12.6 Isokinetic Variation and Acceptable Results. Use Method 5, section 12.11.

12.7 Acetone Blank Concentration, Acetone Wash Blank Residue Weight, Particulate Weight, and Particulate Concentration. For particulate determination.

12.8 Total μg HCl, HBr, or HF Per Sample.

$$m_{HX} = K_{HC1,Hbr,HF} V_s \left(S_{X^-} - B_{X^-} \right) \qquad \text{Eq. 26A-4}$$

12.9 Total μg Cl_2 or Br_2 Per Sample.

$$m_{X2} = V_s \left(S_{X^-} - B_{X^-} \right) \qquad \text{Eq. 26A-5}$$

12.10 Concentration of Hydrogen Halide or Halogen in Flue Gas.

$$C = K\, m_{HX,X2} / V_{m(std)} \qquad \text{Eq. 26A-6}$$

12.11 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate, if needed, using data obtained in this method and the equations in sections 12.3 and 12.4 of Method 2.

13.0 Method Performance

13.1 Precision and Bias. The method has a possible measurable negative bias below 20 ppm HCl perhaps due to reaction with small amounts of moisture in the probe and filter. Similar bias for the other hydrogen halides is possible.

13.2 Sample Stability. The collected Cl- samples can be stored for up to 4 weeks for analysis for HCl and Cl2.

13.3 Detection Limit. A typical analytical detection limit for HCl is 0.2 μg/ml. Detection limits for the other analyses should be similar. Assuming 300 ml of liquid recovered for the acidified impingers and a similar amounts recovered from the basic impingers, and 1 dscm of stack gas sampled, the analytical detection limits in the stack gas would be about 0.04 ppm for HCl and Cl2, respectively.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Steinsberger, S. C. and J. H. Margeson. Laboratory and Field Evaluation of a Methodology for Determination of Hydrogen Chloride Emissions from Municipal and Hazardous Waste Incinerators. U.S. Environmental Protection Agency, Office of Research and Development. Publication No. 600/3–89/064. April 1989. Available from National Technical Information Service, Springfield, VA 22161 as PB89220586/AS.

2. State of California Air Resources Board. Method 421—Determination of Hydrochloric Acid Emissions from Stationary Sources. March 18, 1987.

3. Cheney, J.L. and C.R. Fortune. Improvements in the Methodology for Measuring Hydrochloric Acid in Combustion Source Emissions. J. Environ. Sci. Health. *A19*(3): 337–350. 1984.

4. Stern, D.A., B.M. Myatt, J.F. Lachowski, and K.T. McGregor. Speciation of Halogen and Hydrogen Halide Compounds in Gaseous Emissions. In: Incineration and Treatment of Hazardous Waste: Proceedings of the 9th Annual Research Symposium, Cincinnati, Ohio, May 2–4, 1983. Publication No. 600/9–84–015. July 1984. Available from National Technical Information Service, Springfield, VA 22161 as PB84–234525.

5. Holm, R.D. and S.A. Barksdale. Analysis of Anions in Combustion Products. In: Ion Chromatographic Analysis of Environmental Pollutants, E. Sawicki, J.D. Mulik, and E. Wittgenstein (eds.). Ann Arbor, Michigan, Ann Arbor Science Publishers. 1978. pp. 99–110.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

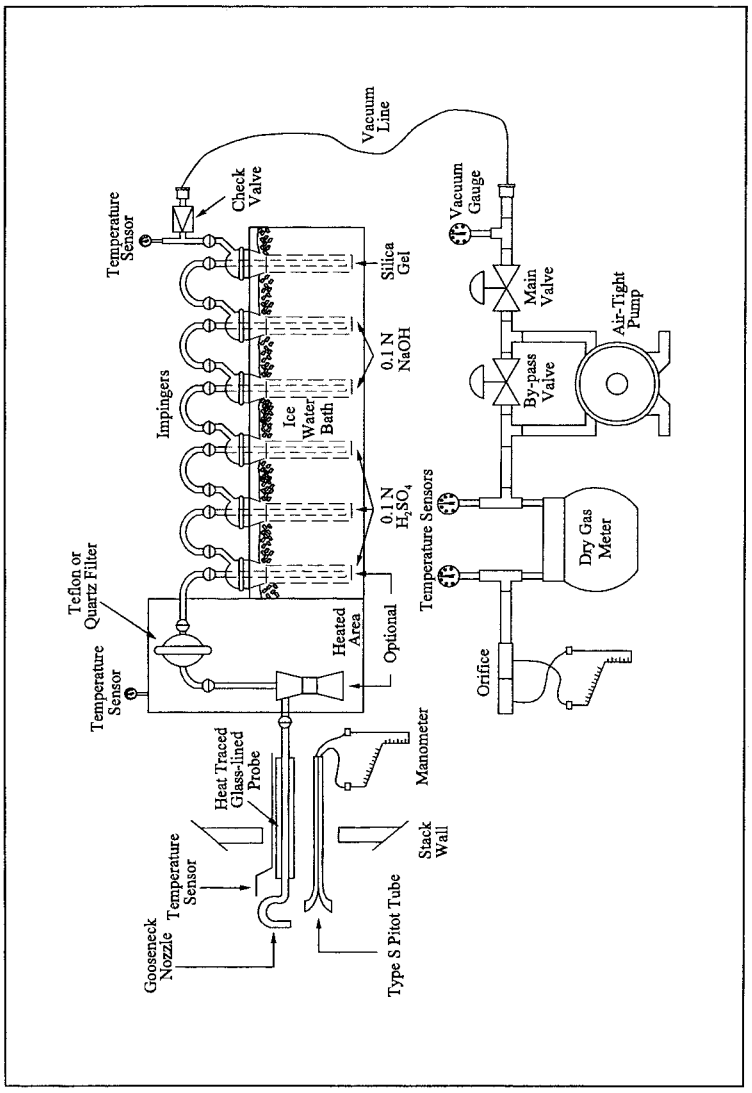


Figure 26A-1. Sampling Train

METHOD 27—DETERMINATION OF VAPOR TIGHTNESS OF GASOLINE DELIVERY TANK USING PRESSURE VACUUM TEST

1.0 Scope and Application

1.1 Applicability. This method is applicable for the determination of vapor tightness of a gasoline delivery collection equipment.

2.0 Summary of Method

2.1 Pressure and vacuum are applied alternately to the compartments of a gasoline delivery tank and the change in pressure or vacuum is recorded after a specified period of time.

3.0 Definitions

3.1 *Allowable pressure change (Δp)* means the allowable amount of decrease in pressure during the static pressure test, within the time period t, as specified in the appropriate regulation, in mm H_2O.

3.2 *Allowable vacuum change (Δv)* means the allowable amount of decrease in vacuum during the static vacuum test, within the time period t, as specified in the appropriate regulation, in mm H_2O.

3.3 *Compartment* means a liquid-tight division of a delivery tank.

3.4 *Delivery tank* means a container, including associated pipes and fittings, that is attached to or forms a part of any truck, trailer, or railcar used for the transport of gasoline.

3.5 *Delivery tank vapor collection equipment* means any piping, hoses, and devices on the delivery tank used to collect and route gasoline vapors either from the tank to a bulk terminal vapor control system or from a bulk plant or service station into the tank.

3.6 *Gasoline* means a petroleum distillate or petroleum distillate/alcohol blend having a Reid vapor pressure of 27.6 kilopascals or greater which is used as a fuel for internal combustion engines.

3.7 *Initial pressure (P_i)* means the pressure applied to the delivery tank at the beginning of the static pressure test, as specified in the appropriate regulation, in mm H_2O.

3.8 *Initial vacuum (V_i)* means the vacuum applied to the delivery tank at the beginning of the static vacuum test, as specified in the appropriate regulation, in mm H_3.

3.9 *Time period of the pressure or vacuum test (t)* means the time period of the test, as specified in the appropriate regulation, during which the change in pressure or vacuum is monitored, in minutes.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Gasoline contains several volatile organic compounds (*e.g.*, benzene and hexane) which presents a potential for fire and/or explosions. It is advisable to take appropriate precautions when testing a gasoline vessel's vapor tightness, such as refraining from smoking and using explosion-proof equipment.

5.2 This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method

6.0 Equipment and Supplies

The following equipment and supplies are required for testing:

6.1 Pressure Source. Pump or compressed gas cylinder of air or inert gas sufficient to pressurize the delivery tank to 500 mm (20 in.) H_2O above atmospheric pressure.

6.2 Regulator. Low pressure regulator for controlling pressurization of the delivery tank.

6.3 Vacuum Source. Vacuum pump capable of evacuating the delivery tank to 250 mm (10 in.) H_2O below atmospheric pressure.

6.4 Pressure-Vacuum Supply Hose.

6.5 Manometer. Liquid manometer, or equivalent instrument, capable of measuring up to 500 mm (20 in.) H_2O gauge pressure with ±2.5 mm (0.1 in.) H_2O precision.

6.6 Pressure-Vacuum Relief Valves. The test apparatus shall be equipped with an inline pressure-vacuum relief valve set to activate at 675 mm (26.6 in.) H_2O above atmospheric pressure or 250 mm (10 in.) H2O below atmospheric pressure, with a capacity equal to the pressurizing or evacuating pumps.

6.7 Test Cap for Vapor Recovery Hose. This cap shall have a tap for manometer connection and a fitting with shut-off valve for connection to the pressure-vacuum supply hose.

6.8 Caps for Liquid Delivery Hoses.

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparations.

8.1.1 Summary. Testing problems may occur due to the presence of volatile vapors and/or temperature fluctuations inside the delivery tank. Under these conditions, it is often difficult to obtain a stable initial pressure at the beginning of a test, and erroneous test results may occur. To help prevent this, it is recommended that prior to testing, volatile vapors be removed from the tank and the temperature inside the tank be allowed to stabilize. Because it is not always possible to completely attain these pretest conditions, a provision to ensure reproducible results is included. The difference in results for two consecutive runs must meet the criteria in sections 8.2.2.5 and 8.2.3.5.

8.1.2 Emptying of Tank. The delivery tank shall be emptied of all liquid.

8.1.3 Purging of Vapor. As much as possible the delivery tank shall be purged of all volatile vapors by any safe, acceptable method. One method is to carry a load of non-volatile liquid fuel, such as diesel or heating oil, immediately prior to the test, thus flushing out all the volatile gasoline vapors. A second method is to remove the volatile vapors by blowing ambient air into each tank compartment for at least 20 minutes. This second method is usually not as effective and often causes stabilization problems, requiring a

much longer time for stabilization during the testing.

8.1.4 Temperature Stabilization. As much as possible, the test shall be conducted under isothermal conditions. The temperature of the delivery tank should be allowed to equilibrate in the test environment. During the test, the tank should be protected from extreme environmental and temperature variability, such as direct sunlight.

8.2 Test Procedure.

8.2.1 Preparations.

8.2.1.1 Open and close each dome cover.

8.2.1.2 Connect static electrical ground connections to the tank. Attach the liquid delivery and vapor return hoses, remove the liquid delivery elbows, and plug the liquid delivery fittings.

NOTE: The purpose of testing the liquid delivery hoses is to detect tears or holes that would allow liquid leakage during a delivery. Liquid delivery hoses are not considered to be possible sources of vapor leakage, and thus, do not have to be attached for a vapor leakage test. Instead, a liquid delivery hose could be either visually inspected, or filled with water to detect any liquid leakage.

8.2.1.3 Attach the test cap to the end of the vapor recovery hose.

8.2.1.4 Connect the pressure-vacuum supply hose and the pressure-vacuum relief valve to the shut-off valve. Attach a manometer to the pressure tap.

8.2.1.5 Connect compartments of the tank internally to each other if possible. If not possible, each compartment must be tested separately, as if it were an individual delivery tank.

8.2.2 Pressure Test.

8.2.2.1 Connect the pressure source to the pressure-vacuum supply hose.

8.2.2.2 Open the shut-off valve in the vapor recovery hose cap. Apply air pressure slowly, pressurize the tank to P_i, the initial pressure specified in the regulation.

8.2.2.3 Close the shut-off and allow the pressure in the tank to stabilize, adjusting the pressure if necessary to maintain pressure of P_i. When the pressure stabilizes, record the time and initial pressure.

8.2.2.4 At the end of the time period (t) specified in the regulation, record the time and final pressure.

8.2.2.5 Repeat steps 8.2.2.2 through 8.2.2.4 until the change in pressure for two consecutive runs agrees within 12.5 mm (0.5 in.) H_2O. Calculate the arithmetic average of the two results.

8.2.2.6 Compare the average measured change in pressure to the allowable pressure change, Δp, specified in the regulation. If the delivery tank does not satisfy the vapor tightness criterion specified in the regulation, repair the sources of leakage, and repeat the pressure test until the criterion is met.

8.2.2.7 Disconnect the pressure source from the pressure-vacuum supply hose, and slowly open the shut-off valve to bring the tank to atmospheric pressure.

8.2.3 Vacuum Test.

8.2.3.1 Connect the vacuum source to the pressure-vacuum supply hose.

8.2.3.2 Open the shut-off valve in the vapor recovery hose cap. Slowly evacuate the tank to V_i, the initial vacuum specified in the regulation.

8.2.3.3 Close the shut-off valve and allow the pressure in the tank to stabilize, adjusting the pressure if necessary to maintain a vacuum of V_i. When the pressure stabilizes, record the time and initial vacuum.

8.2.3.4 At the end of the time period specified in the regulation (t), record the time and final vacuum.

8.2.3.5 Repeat steps 8.2.3.2 through 8.2.3.4 until the change in vacuum for two consecutive runs agrees within 12.5 mm (0.5 in.) H_2O. Calculate the arithmetic average of the two results.

8.2.3.6 Compare the average measured change in vacuum to the allowable vacuum change, Δv, as specified in the regulation. If the delivery tank does not satisfy the vapor tightness criterion specified in the regulation, repair the sources of leakage, and repeat the vacuum test until the criterion is met.

8.2.3.7 Disconnect the vacuum source from the pressure-vacuum supply hose, and slowly open the shut-off valve to bring the tank to atmospheric pressure.

8.2.4 Post-Test Clean-up. Disconnect all test equipment and return the delivery tank to its pretest condition.

9.0 Quality Control

Section(s)	Quality control measure	Effect
8.2.2.5, 8.3.3.5	Repeat test procedures until change in pressure or vacuum for two consecutive runs agrees within ±12.5 mm (0.5 in.) H_2O.	Ensures data precision.

10.0 Calibration and Standardization
[Reserved]

11.0 Analytical Procedures [Reserved]

12.0 Data Analysis and Calculations [Reserved]

13.0 Method Performance

13.1 Precision. The vapor tightness of a gasoline delivery tank under positive or negative pressure, as measured by this method, is precise within 12.5 mm (0.5 in.) H_2O

13.2 Bias. No bias has been identified.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 The pumping of water into the bottom of a delivery tank is an acceptable alternative to the pressure source described above. Likewise, the draining of water out of the bottom of a delivery tank may be substituted for the vacuum source. Note that some of the specific step-by-step procedures in the method must be altered slightly to accommodate these different pressure and vacuum sources.

16.2 Techniques other than specified above may be used for purging and pressurizing a delivery tank, if prior approval is obtained from the Administrator. Such approval will be based upon demonstrated equivalency with the above method.

17.0 References [Reserved]

18.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 28—CERTIFICATION AND AUDITING OF WOOD HEATERS

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 4, Method 5, Method 5G, Method 5H, Method 6, Method 6C, and Method 16A.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the certification and auditing of wood heaters, including pellet burning wood heaters.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Particulate matter emissions are measured from a wood heater burning a prepared test fuel crib in a test facility maintained at a set of prescribed conditions. Procedures for determining burn rates and particulate emission rates and for reducing data are provided.

3.0 Definitions

3.1 *2 × 4 or 4 × 4* means two inches by four inches or four inches by four inches (50 mm by 100 mm or 100 mm by 100 mm), as nominal dimensions for lumber.

3.2 *Burn rate* means the rate at which test fuel is consumed in a wood heater. Measured in kilograms or lbs of wood (dry basis) per hour (kg/hr or lb/hr).

3.3 *Certification or audit test* means a series of at least four test runs conducted for certification or audit purposes that meets the burn rate specifications in section 8.4.

3.4 *Firebox* means the chamber in the wood heater in which the test fuel charge is placed and combusted.

3.5 *Height* means the vertical distance extending above the loading door, if fuel could reasonably occupy that space, but not more than 2 inches above the top (peak height) of the loading door, to the floor of the firebox (*i.e.*, below a permanent grate) if the grate allows a 1-inch diameter piece of wood to pass through the grate, or, if not, to the top of the grate. Firebox height is not necessarily uniform but must account for variations caused by internal baffles, air channels, or other permanent obstructions.

3.6 *Length* means the longest horizontal fire chamber dimension that is parallel to a wall of the chamber.

3.7 *Pellet burning wood heater* means a wood heater which meets the following criteria: (1) The manufacturer makes no reference to burning cord wood in advertising or other literature, (2) the unit is safety listed for pellet fuel only, (3) the unit operating and instruction manual must state that the use of cordwood is prohibited by law, and (4) the unit must be manufactured and sold including the hopper and auger combination as integral parts.

3.8 *Secondary air supply* means an air supply that introduces air to the wood heater such that the burn rate is not altered by more than 25 percent when the secondary air supply is adjusted during the test run. The wood heater manufacturer can document this through design drawings that show the secondary air is introduced only into a mixing chamber or secondary chamber outside the firebox.

3.9 *Test facility* means the area in which the wood heater is installed, operated, and sampled for emissions.

3.10 *Test fuel charge* means the collection of test fuel pieces placed in the wood heater at the start of the emission test run.

3.11 *Test fuel crib* means the arrangement of the test fuel charge with the proper spacing requirements between adjacent fuel pieces.

3.12 *Test fuel loading density* means the weight of the as-fired test fuel charge per unit volume of usable firebox.

3.13 *Test fuel piece* means the 2 × 4 or 4 × 4 wood piece cut to the length required for the test fuel charge and used to construct the test fuel crib.

3.14 *Test run* means an individual emission test which encompasses the time required to consume the mass of the test fuel charge.

3.15 *Usable firebox volume* means the volume of the firebox determined using its height, length, and width as defined in this section.

3.16 *Width* means the shortest horizontal fire chamber dimension that is parallel to a wall of the chamber.

3.17 *Wood heater* means an enclosed, woodburning appliance capable of and intended for space heating or domestic water heating, as defined in the applicable regulation.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

Same as section 6.0 of either Method 5G or Method 5H, with the addition of the following:

6.1 Insulated Solid Pack Chimney. For installation of wood heaters. Solid pack insulated chimneys shall have a minimum of 2.5 cm (1 in.) solid pack insulating material surrounding the entire flue and possess a label demonstrating conformance to U.L. 103 (incorporated by reference—see §60.17).

6.2 Platform Scale and Monitor. For monitoring of fuel load weight change. The scale shall be capable of measuring weight to within 0.05 kg (0.1 lb) or 1 percent of the initial test fuel charge weight, whichever is greater.

6.3 Wood Heater Temperature Monitors. Seven, each capable of measuring temperature to within 1.5 percent of expected absolute temperatures.

6.4 Test Facility Temperature Monitor. A thermocouple located centrally in a vertically oriented 150 mm (6 in.) long, 50 mm (2 in.) diameter pipe shield that is open at both ends, capable of measuring temperature to within 1.5 percent of expected temperatures.

6.5 Balance (optional). Balance capable of weighing the test fuel charge to within 0.05 kg (0.1 lb).

6.6 Moisture Meter. Calibrated electrical resistance meter for measuring test fuel moisture to within 1 percent moisture content.

6.7 Anemometer. Device capable of detecting air velocities less than 0.10 m/sec (20 ft/min), for measuring air velocities near the test appliance.

6.8 Barometer. Mercury, aneroid or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg).

6.9 Draft Gauge. Electromanometer or other device for the determination of flue draft or static pressure readable to within 0.50 Pa (0.002 in. H_2O).

6.10 Humidity Gauge. Psychrometer or hygrometer for measuring room humidity.

6.11 Wood Heater Flue.

6.11.1 Steel flue pipe extending to 2.6 ±0.15 m (8.5 ±0.5 ft) above the top of the platform scale, and above this level, insulated solid pack type chimney extending to 4.6 ±0.3 m (15 ±1 ft) above the platform scale, and of the size specified by the wood heater manufacturer. This applies to both freestanding and insert type wood heaters.

6.11.2 Other chimney types (*e.g.*, solid pack insulated pipe) may be used in place of the steel flue pipe if the wood heater manufacturer's written appliance specifications require such chimney for home installation (*e.g.*, zero clearance wood heater inserts). Such alternative chimney or flue pipe must remain and be sealed with the wood heater following the certification test.

6.12 Test Facility. The test facility shall meet the following requirements during testing:

6.12.1 The test facility temperature shall be maintained between 18 and 32 °C (65 and 90 °F) during each test run.

6.12.2 Air velocities within 0.6 m (2 ft) of the test appliance and exhaust system shall be less than 0.25 m/sec (50 ft/min) without fire in the unit.

6.12.3 The flue shall discharge into the same space or into a space freely communicating with the test facility. Any hood or similar device used to vent combustion products shall not induce a draft greater than 1.25 Pa (0.005 in. H_2O) on the wood heater measured when the wood heater is not operating.

6.12.4 For test facilities with artificially induced barometric pressures (*e.g.*, pressurized chambers), the barometric pressure in the test facility shall not exceed 775 mm Hg (30.5 in. Hg) during any test run.

7.0 Reagents and Standards

Same as section 6.0 of either Method 5G or Method 5H, with the addition of the following:

7.1 Test Fuel. The test fuel shall conform to the following requirements:

7.1.1 Fuel Species. Untreated, air-dried, Douglas fir lumber. Kiln-dried lumber is not permitted. The lumber shall be certified C grade (standard) or better Douglas fir by a lumber grader at the mill of origin as specified in the West Coast Lumber Inspection Bureau Standard No. 16 (incorporated by reference—see §60.17).

7.1.2 Fuel Moisture. The test fuel shall have a moisture content range between 16 to 20 percent on a wet basis (19 to 25 percent dry basis). Addition of moisture to previously dried wood is not allowed. It is recommended that the test fuel be stored in a temperature and humidity-controlled room.

7.1.3 Fuel Temperature. The test fuel shall be at the test facility temperature of 18 to 32 °C (65 to 90 °F).

7.1.4 Fuel Dimensions. The dimensions of each test fuel piece shall conform to the nominal measurements of 2×4 and 4×4 lumber. Each piece of test fuel (not including spacers) shall be of equal length, except as necessary to meet requirements in section 8.8, and shall closely approximate ⅝ the dimensions of the length of the usable firebox. The fuel piece dimensions shall be determined in relation to the appliance's firebox volume according to guidelines listed below:

7.1.4.1 If the usable firebox volume is less than or equal to 0.043 m^3 (1.5 ft^3), use 2×4 lumber.

7.1.4.2 If the usable firebox volume is greater than 0.043 m^3 (1.5 ft^3) and less than or equal to 0.085 m^3 (3.0 ft^3), use 2×4 and 4×4 lumber. About half the weight of the test fuel charge shall be 2×4 lumber, and the remainder shall be 4×4 lumber.

7.1.4.3 If the usable firebox volume is greater than 0.085 m^3 (3.0 ft^3), use 4×4 lumber.

7.2 Test Fuel Spacers. Air-dried, Douglas fir lumber meeting the requirements outlined in sections 7.1.1 through 7.1.3. The spacers shall be $130 \times 40 \times 20$ mm ($5 \times 1.5 \times 0.75$ in.).

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Test Run Requirements.

8.1.1 Burn Rate Categories. One emission test run is required in each of the following burn rate categories:

BURN RATE CATEGORIES

[Average kg/hr (lb/hr), dry basis]

Category 1	Category 2	Category 3	Category 4
<0.80 (<1.76)	0.80 to 1.25 (1.76 to 2.76)	1.25 to 1.90 (2.76 to 4.19)	Maximum. burn rate.

8.1.1.1 Maximum Burn Rate. For Category 4, the wood heater shall be operated with the primary air supply inlet controls fully open (or, if thermostatically controlled, the thermostat shall be set at maximum heat output) during the entire test run, or the maximum burn rate setting specified by the manufacturer's written instructions.

8.1.1.2 Other Burn Rate Categories. For burn rates in Categories 1 through 3, the wood heater shall be operated with the primary air supply inlet control, or other mechanical control device, set at a predetermined position necessary to obtain the average burn rate required for the category.

8.1.1.3 Alternative Burn Rates for Burn Rate Categories 1 and 2.

8.1.1.3.1 If a wood heater cannot be operated at a burn rate below 0.80 kg/hr (1.76 lb/hr), two test runs shall be conducted with burn rates within Category 2. If a wood heater cannot be operated at a burn rate below 1.25 kg/hr (2.76 lb/hr), the flue shall be dampered or the air supply otherwise controlled in order to achieve two test runs within Category 2.

8.1.1.3.2 Evidence that a wood heater cannot be operated at a burn rate less than 0.80 kg/hr shall include documentation of two or more attempts to operate the wood heater in burn rate Category 1 and fuel combustion has stopped, or results of two or more test runs demonstrating that the burn rates were greater than 0.80 kg/hr when the air supply controls were adjusted to the lowest possible position or settings. Stopped fuel combustion is evidenced when an elapsed time of 30 minutes or more has occurred without a measurable (<0.05 kg (0.1 lb) or 1.0 percent, whichever is greater) weight change in the test fuel charge. See also section 8.8.3. Report the evidence and the reasoning used to determine that a test in burn rate Category 1 cannot be achieved; for example, two unsuccessful attempts to operate at a burn rate of 0.4 kg/hr are not sufficient evidence that burn rate Category 1 cannot be achieved.

NOTE: After July 1, 1990, if a wood heater cannot be operated at a burn rate less than 0.80 kg/hr, at least one test run with an average burn rate of 1.00 kg/hr or less shall be conducted. Additionally, if flue dampering must be used to achieve burn rates below 1.25

kg/hr (or 1.0 kg/hr), results from a test run conducted at burn rates below 0.90 kg/hr need not be reported or included in the test run average provided that such results are replaced with results from a test run meeting the criteria above.

8.2 Catalytic Combustor and Wood Heater Aging. The catalyst-equipped wood heater or a wood heater of any type shall be aged before the certification test begins. The aging procedure shall be conducted and documented by a testing laboratory accredited according to procedures in §60.535 of 40 CFR part 60.

8.2.1 Catalyst-equipped Wood Heater. Operate the catalyst-equipped wood heater using fuel meeting the specifications outlined in sections 7.1.1 through 7.1.3, or cordwood with a moisture content between 15 and 25 percent on a wet basis. Operate the wood heater at a medium burn rate (Category 2 or 3) with a new catalytic combustor in place and in operation for at least 50 hours. Record and report hourly catalyst exit temperature data (Section 8.6.2) and the hours of operation.

8.2.2 Non-Catalyst Wood Heater. Operate the wood heater using the fuel described in section 8.4.1 at a medium burn rate for at least 10 hours. Record and report the hours of operation.

8.3 Pretest Recordkeeping. Record the test fuel charge dimensions and weights, and wood heater and catalyst descriptions as shown in the example in Figure 28–1.

8.4 Wood Heater Installation. Assemble the wood heater appliance and parts in conformance with the manufacturer's written installation instructions. Place the wood heater centrally on the platform scale and connect the wood heater to the flue described in section 6.11. Clean the flue with an appropriately sized, wire chimney brush before each certification test.

8.5 Wood Heater Temperature Monitors.

8.5.1 For catalyst-equipped wood heaters, locate a temperature monitor (optional) about 25 mm (1 in.) upstream of the catalyst at the centroid of the catalyst face area, and locate a temperature monitor (mandatory) that will indicate the catalyst exhaust temperature. This temperature monitor is centrally located within 25 mm (1 in.) downstream at the centroid of catalyst face area. Record these locations.

8.5.2 Locate wood heater surface temperature monitors at five locations on the wood heater firebox exterior surface. Position the temperature monitors centrally on the top surface, on two sidewall surfaces, and on the bottom and back surfaces. Position the monitor sensing tip on the firebox exterior surface inside of any heat shield, air circulation walls, or other wall or shield separated from the firebox exterior surface. Surface temperature locations for unusual design shapes (*e.g.*, spherical, etc.) shall be positioned so that there are four surface temperature monitors in both the vertical and horizontal planes passing at right angles through the centroid of the firebox, not including the fuel loading door (total of five temperature monitors).

8.6 Test Facility Conditions.

8.6.1 Locate the test facility temperature monitor on the horizontal plane that includes the primary air intake opening for the wood heater. Locate the temperature monitor 1 to 2 m (3 to 6 ft) from the front of the wood heater in the 90° sector in front of the wood heater.

8.6.2 Use an anemometer to measure the air velocity. Measure and record the room air velocity before the pretest ignition period (Section 8.7) and once immediately following the test run completion.

8.6.3 Measure and record the test facility's ambient relative humidity, barometric pressure, and temperature before and after each test run.

8.6.4 Measure and record the flue draft or static pressure in the flue at a location no greater than 0.3 m (1 ft) above the flue connector at the wood heater exhaust during the test run at the recording intervals (Section 8.8.2).

8.7 Wood Heater Firebox Volume.

8.7.1 Determine the firebox volume using the definitions for height, width, and length in section 3. Volume adjustments due to presence of firebrick and other permanent fixtures may be necessary. Adjust width and length dimensions to extend to the metal wall of the wood heater above the firebrick or permanent obstruction if the firebrick or obstruction extending the length of the side(s) or back wall extends less than one-third of the usable firebox height. Use the width or length dimensions inside the firebrick if the firebrick extends more than one-third of the usable firebox height. If a log retainer or grate is a permanent fixture and the manufacturer recommends that no fuel be placed outside the retainer, the area outside of the retainer is excluded from the firebox volume calculations.

8.7.2 In general, exclude the area above the ash lip if that area is less than 10 percent of the usable firebox volume. Otherwise, take into account consumer loading practices. For instance, if fuel is to be loaded front-to-back, an ash lip may be considered usable firebox volume.

8.7.3 Include areas adjacent to and above a baffle (up to two inches above the fuel loading opening) if four inches or more horizontal space exist between the edge of the baffle and a vertical obstruction (*e.g.*, sidewalls or air channels).

8.8 Test Fuel Charge.

8.8.1 Prepare the test fuel pieces in accordance with the specifications outlined in sections 7.1 and 7.2. Determine the test fuel moisture content with a calibrated electrical

resistance meter or other equivalent performance meter. If necessary, convert fuel moisture content values from dry basis ($\%M_d$) to wet basis ($\%M_w$) in section 12.2 using Equation 28–1. Determine fuel moisture for each fuel piece (not including spacers) by averaging at least three moisture meter readings, one from each of three sides, measured parallel to the wood grain. Average all the readings for all the fuel pieces in the test fuel charge. If an electrical resistance type meter is used, penetration of insulated electrodes shall be one-fourth the thickness of the test fuel piece or 19 mm (0.75 in.), whichever is greater. Measure the moisture content within a 4-hour period prior to the test run. Determine the fuel temperature by measuring the temperature of the room where the wood has been stored for at least 24 hours prior to the moisture determination.

8.8.2 Attach the spacers to the test fuel pieces with uncoated, ungalvanized nails or staples as illustrated in Figure 28–2. Attachment of spacers to the top of the test fuel piece(s) on top of the test fuel charge is optional.

8.8.3 To avoid stacking difficulties, or when a whole number of test fuel pieces does not result, all piece lengths shall be adjusted uniformly to remain within the specified loading density. The shape of the test fuel crib shall be geometrically similar to the shape of the firebox volume without resorting to special angular or round cuts on the individual fuel pieces.

8.8.4 The test fuel loading density shall be 112 ±11.2 kg/m³ (7 ±0.7 lb/ft³) of usable firebox volume on a wet basis.

8.9 Sampling Equipment. Prepare the sampling equipment as defined by the selected method (*i.e.*, either Method 5G or Method 5H). Collect one particulate emission sample for each test run.

8.10 Secondary Air Adjustment Validation.

8.10.1 If design drawings do not show the introduction of secondary air into a chamber outside the firebox (see ''secondary air supply'' under section 3.0, Definitions), conduct a separate test of the wood heater's secondary air supply. Operate the wood heater at a burn rate in Category 1 (Section 8.1.1) with the secondary air supply operated following the manufacturer's written instructions. Start the secondary air validation test run as described in section 8.8.1, except no emission sampling is necessary and burn rate data shall be recorded at 5-minute intervals.

8.10.2 After the start of the test run, operate the wood heater with the secondary air supply set as per the manufacturer's instructions, but with no adjustments to this setting. After 25 percent of the test fuel has been consumed, adjust the secondary air supply controls to another setting, as per the manufacturer's instructions. Record the burn rate data (5-minute intervals) for 20 minutes following the air supply adjustment.

8.10.3 Adjust the air supply control(s) to the original position(s), operate at this condition for at least 20 minutes, and repeat the air supply adjustment procedure above. Repeat the procedure three times at equal intervals over the entire burn period as defined in section 8.8. If the secondary air adjustment results in a burn rate change of more than an average of 25 percent between the 20-minute periods before and after the secondary adjustments, the secondary air supply shall be considered a primary air supply, and no adjustment to this air supply is allowed during the test run.

8.10.4 The example sequence below describes a typical secondary air adjustment validation check. The first cycle begins after at least 25 percent of the test fuel charge has been consumed.

Cycle 1
- Part 1, sec air adjusted to final position—20 min
- Part 2, sec air adjusted to final position—20 min
- Part 3, sec air adjusted to final position—20 min

Cycle 2
- Part 1, sec air adjusted to final position—20 min
- Part 2, sec air adjusted to final position—20 min
- Part 3, sec air adjusted to final position—20 min

Cycle 3
- Part 1, sec air adjusted to final position—20 min
- Part 2, sec air adjusted to final position—20 min
- Part 3, sec air adjusted to final position—20 min

Note that the cycles may overlap; that is, Part 3 of Cycle 1 may coincide in part or in total with Part 1 of Cycle 2. The calculation of the secondary air percent effect for this example is as follows:

$$\%BR_{sec} = \frac{\left|\overline{BR_{1,3}} - \overline{BR_2}\right|}{\overline{BR_{1,3}}} \times 100 \qquad \text{Eq. 28-1}$$

8.11 Pretest Ignition. Build a fire in the wood heater in accordance with the manufacturer's written instructions.

8.11.1 Pretest Fuel Charge. Crumpled newspaper loaded with kindling may be used to help ignite the pretest fuel. The pretest fuel, used to sustain the fire, shall meet the same fuel requirements prescribed in section 7.1. The pretest fuel charge shall consist of whole 2×4's that are no less than ⅓ the length of the test fuel pieces. Pieces of 4×4 lumber in approximately the same weight ratio as for the test fuel charge may be added to the pretest fuel charge.

8.11.2 Wood Heater Operation and Adjustments. Set the air inlet supply controls at any position that will maintain combustion of the pretest fuel load. At least one hour before the start of the test run, set the air supply controls at the approximate positions necessary to achieve the burn rate desired for the test run. Adjustment of the air supply controls, fuel addition or subtractions, and coalbed raking shall be kept to a minimum but are allowed up to 15 minutes prior to the start of the test run. For the purposes of this method, coalbed raking is the use of a metal tool (poker) to stir coals, break burning fuel into smaller pieces, dislodge fuel pieces from positions of poor combustion, and check for the condition of uniform charcoalization. Record all adjustments made to the air supply controls, adjustments to and additions or subtractions of fuel, and any other changes to wood heater operations that occur during pretest ignition period. Record fuel weight data and wood heater temperature measurements at 10-minute intervals during the hour of the pretest ignition period preceding the start of the test run. During the 15-minute period prior to the start of the test run, the wood heater loading door shall not be open more than a total of 1 minute. Coalbed raking is the only adjustment allowed during this period.

NOTE: One purpose of the pretest ignition period is to achieve uniform charcoalization of the test fuel bed prior to loading the test fuel charge. Uniform charcoalization is a general condition of the test fuel bed evidenced by an absence of large pieces of burning wood in the coal bed and the remaining fuel pieces being brittle enough to be broken into smaller charcoal pieces with a metal poker. Manipulations to the fuel bed prior to the start of the test run should be done to achieve uniform charcoalization while maintaining the desired burn rate. In addition, some wood heaters (*e.g.*, high mass units) may require extended pretest burn time and fuel additions to reach an initial average surface temperature sufficient to meet the thermal equilibrium criteria in section 8.3.

8.11.3 The weight of pretest fuel remaining at the start of the test run is determined as the difference between the weight of the wood heater with the remaining pretest fuel and the tare weight of the cleaned, dry wood heater with or without dry ash or sand added consistent with the manufacturer's instructions and the owner's manual. The tare weight of the wood heater must be determined with the wood heater (and ash, if added) in a dry condition.

8.12 Test Run. Complete a test run in each burn rate category, as follows:

8.12.1 Test Run Start.

8.12.1.1 When the kindling and pretest fuel have been consumed to leave a fuel weight between 20 and 25 percent of the weight of the test fuel charge, record the weight of the fuel remaining and start the test run. Record and report any other criteria, in addition to those specified in this section, used to determine the moment of the test run start (*e.g.*, firebox or catalyst temperature), whether such criteria are specified by the wood heater manufacturer or the testing laboratory. Record all wood heater individual surface temperatures, catalyst temperatures, any initial sampling method measurement values, and begin the particulate emission sampling. Within 1 minute following the start of the test run, open the wood heater door, load the test fuel charge, and record the test fuel charge weight. Recording of average, rather than individual, surface temperatures is acceptable for tests conducted in accordance with §60.533(o)(3)(i) of 40 CFR part 60.

8.12.1.2 Position the fuel charge so that the spacers are parallel to the floor of the firebox, with the spacer edges abutting each other. If loading difficulties result, some fuel pieces may be placed on edge. If the usable firebox volume is between 0.043 and 0.085 m^3 (1.5 and 3.0 ft^3), alternate the piece sizes in vertical stacking layers to the extent possible. For example, place 2×4's on the bottom layer in direct contact with the coal bed and 4×4's on the next layer, etc. (See Figure 28–3). Position the fuel pieces parallel to each other and parallel to the longest wall of the firebox to the extent possible within the specifications in section 8.8.

8.12.1.3 Load the test fuel in appliances having unusual or unconventional firebox design maintaining air space intervals between the test fuel pieces and in conformance with the manufacturer's written instructions. For any appliance that will not accommodate the loading arrangement specified in the paragraph above, the test facility personnel shall contact the Administrator for an alternative loading arrangement.

8.12.1.4 The wood heater door may remain open and the air supply controls adjusted up to five minutes after the start of the test run in order to make adjustments to the test fuel charge and to ensure ignition of the test fuel charge has occurred. Within the five minutes after the start of the test run, close the wood heater door and adjust the air supply controls to the position determined to produce

the desired burn rate. No other adjustments to the air supply controls or the test fuel charge are allowed (except as specified in sections 8.12.3 and 8.12.4) after the first five minutes of the test run. Record the length of time the wood heater door remains open, the adjustments to the air supply controls, and any other operational adjustments.

8.12.2 Data Recording. Record on a data sheet similar to that shown in Figure 28–4, at intervals no greater than 10 minutes, fuel weight data, wood heater individual surface and catalyst temperature measurements, other wood heater operational data (*e.g.*, draft), test facility temperature and sampling method data.

8.12.3 Test Fuel Charge Adjustment. The test fuel charge may be adjusted (*i.e.*, repositioned) once during a test run if more than 60 percent of the initial test fuel charge weight has been consumed and more than 10 minutes have elapsed without a measurable (<0.05 kg (0.1 lb) or 1.0 percent, whichever is greater) weight change. The time used to make this adjustment shall be less than 15 seconds.

8.12.4 Air Supply Adjustment. Secondary air supply controls may be adjusted once during the test run following the manufacturer's written instructions (see section 8.10). No other air supply adjustments are allowed during the test run. Recording of wood heater flue draft during the test run is optional for tests conducted in accordance with § 60.533(o)(3)(i) of 40 CFR part 60.

8.12.5 Auxiliary Wood Heater Equipment Operation. Heat exchange blowers sold with the wood heater shall be operated during the test run following the manufacturer's written instructions. If no manufacturer's written instructions are available, operate the heat exchange blower in the ''high'' position. (Automatically operated blowers shall be operated as designed.) Shaker grates, by-pass controls, or other auxiliary equipment may be adjusted only one time during the test run following the manufacturer's written instructions.

Record all adjustments on a wood heater operational written record.

NOTE: If the wood heater is sold with a heat exchange blower as an option, test the wood heater with the heat exchange blower operating as described in sections 8.1 through 8.12 and report the results. As an alternative to repeating all test runs without the heat exchange blower operating, one additional test run may be without the blower operating as described in section 8.12.5 at a burn rate in Category 2 (Section 8.1.1). If the emission rate resulting from this test run without the blower operating is equal to or less than the emission rate plus 1.0 g/hr (0.0022 lb/hr) for the test run in burn rate Category 2 with the blower operating, the wood heater may be considered to have the same average emission rate with or without the blower operating. Additional test runs without the blower operating are unnecessary.

8.13 Test Run Completion. Continue emission sampling and wood heater operation for 2 hours. The test run is completed when the remaining weight of the test fuel charge is 0.00 kg (0.0 lb). End the test run when the scale has indicated a test fuel charge weight of 0.00 kg (0.0 lb) or less for 30 seconds. At the end of the test run, stop the particulate sampling, and record the final fuel weight, the run time, and all final measurement values.

8.14 Wood Heater Thermal Equilibrium. The average of the wood heater surface temperatures at the end of the test run shall agree with the average surface temperature at the start of the test run to within 70 °C (126 °F).

8.15 Consecutive Test Runs. Test runs on a wood heater may be conducted consecutively provided that a minimum one-hour interval occurs between test runs.

8.16 Additional Test Runs. The testing laboratory may conduct more than one test run in each of the burn rate categories specified in section 8.1.1. If more than one test run is conducted at a specified burn rate, the results from at least two-thirds of the test runs in that burn rate category shall be used in calculating the weighted average emission rate (see section 12.2). The measurement data and results of all test runs shall be reported regardless of which values are used in calculating the weighted average emission rate (see note in section 8.1).

9.0 Quality Control

Same as section 9.0 of either Method 5G or Method 5H.

10.0 Calibration and Standardizations

Same as section 10.0 of either Method 5G or Method 5H, with the addition of the following:

10.1 Platform Scale. Perform a multi-point calibration (at least five points spanning the operational range) of the platform scale before its initial use. The scale manufacturer's calibration results are sufficient for this purpose. Before each certification test, audit the scale with the wood heater in place by weighing at least one calibration weight (Class F) that corresponds to between 20 percent and 80 percent of the expected test fuel charge weight. If the scale cannot reproduce the value of the calibration weight within 0.05 kg (0.1 lb) or 1 percent of the expected test fuel charge weight, whichever is greater, recalibrate the scale before use with at least five calibration weights spanning the operational range of the scale.

10.2 Balance (optional). Calibrate as described in section 10.1.

10.3 Temperature Monitor. Calibrate as in Method 2, section 4.3, before the first certification test and semiannually thereafter.

10.4 Moisture Meter. Calibrate as per the manufacturer's instructions before each certification test.

10.5 Anemometer. Calibrate the anemometer as specified by the manufacturer's instructions before the first certification test and semiannually thereafter.

10.6 Barometer. Calibrate against a mercury barometer before the first certification test and semiannually thereafter.

10.7 Draft Gauge. Calibrate as per the manufacturer's instructions; a liquid manometer does not require calibration.

10.8 Humidity Gauge. Calibrate as per the manufacturer's instructions before the first certification test and semiannually thereafter.

11.0 Analytical Procedures

Same as section 11.0 of either Method 5G or Method 5H.

12.0 Data Analysis and Calculations

Same as section 12.0 of either Method 5G or Method 5H, with the addition of the following:

12.1 Nomenclature.

BR = Dry wood burn rate, kg/hr (lb/hr)
E_i = Emission rate for test run, i, from Method 5G or 5H, g/hr (lb/hr)
E_w = Weighted average emission rate, g/hr (lb/hr)
k_i = Test run weighting factor = $P_{i+1} - P_{i-1}$
$\%M_d$ = Fuel moisture content, dry basis, percent.
$\%M_w$ = Average moisture in test fuel charge, wet basis, percent.
n = Total number of test runs.
P_i = Probability for burn rate during test run, i, obtained from Table 28–1. Use linear interpolation to determine probability values for burn rates between those listed on the table.
W_{wd} = Total mass of wood burned during the test run, kg (lb).

12.2 Wet Basis Fuel Moisture Content.

$$\%M_w = \frac{100(\%M_d)}{100 + \%M_d} \qquad \text{Eq. 28-2}$$

12.3 Weighted Average Emission Rate. Calculate the weighted average emission rate (E_w) using Equation 28–1:

$$E_w = \frac{\sum_{i=1}^{n}(K_i E_i)}{\sum_{i=1}^{n} K_i} \qquad \text{Eq. 28-3}$$

NOTE: P_o always equals 0, $P_{(n+1)}$ always equals 1, P_1 corresponds to the probability of the lowest recorded burn rate, P_2 corresponds to the probability of the next lowest burn rate, etc. An example calculation is in section 12.3.1.

12.3.1 Example Calculation of Weighted Average Emission Rate.

Burn rate category	Test No.	Burn rate (Dry-kg/hr)	Emissions (g/hr)
1	1	0.65	5.0
2[1]	2	0.85	6.7
2	3	0.90	4.7
2	4	1.00	5.3
3	5	1.45	3.8
4	6	2.00	5.1

[1] As permitted in section 6.6, this test run may be omitted from the calculation of the weighted average emission rate because three runs were conducted for this burn rate category.

Test No.	Burn rate	P_i	E_i	K_i
0	.....	0.000	.....	.....
1	0.65	0.121	5.0	0.300
2	0.90	0.300	4.7	0.259
3	1.00	0.380	5.3	0.422
4	1.45	0.722	3.8	0.532
5	2.00	0.912	5.1	0.278
6	.....	1.000	.....	.....

$K_1 = P_2 - P_0 = 0.300 - 0 = 0.300$
$K_2 = P_3 - P_1 = 0.381 - 0.121 = 0.259$
$K_3 = P_4 - P_2 = 0.722 - 0.300 = 0.422$
$K_4 = P_5 - P_3 = 0.912 - 0.380 = 0.532$
$K_5 = P_6 - P_4 = 1.000 - 0.722 = 0.278$

Weighted Average Emission Rate, E_w, Calculation

$$E_w = \frac{\sum(K_i E_i)}{\sum K_i}$$

$$= \frac{(0.3)(5.0)+(0.259)(4.7)+(0.422)(5.3)+(0.532)(3.8)+(0.278)(5.1)}{1.791}$$

$$= 4.69\,g/hr$$

12.4 Average Wood Heater Surface Temperatures. Calculate the average of the wood heater surface temperatures for the start of the test run (Section 8.12.1) and for the test run completion (Section 8.13). If the two average temperatures do not agree within 70 °C (125 °F), report the test run results, but do not include the test run results in the test average. Replace such test run results with results from another test run in the same burn rate category.

12.5 Burn Rate. Calculate the burn rate (BR) using Equation 28–3:

$$BR = \frac{60 W_{wd}}{\theta} \times \frac{100 - \%M_w}{100} \qquad \text{Eq. 28-3}$$

12.6 Reporting Criteria. Submit both raw and reduced test data for wood heater tests.

12.6.1 Suggested Test Report Format.

12.6.1.1 Introduction.

12.6.1.1.1 Purpose of test-certification, audit, efficiency, research and development.

12.6.1.1.2 Wood heater identification-manufacturer, model number, catalytic/noncatalytic, options.

12.6.1.1.3 Laboratory-name, location (altitude), participants.

12.6.1.1.4 Test information-date wood heater received, date of tests, sampling methods used, number of test runs.

12.6.1.2 Summary and Discussion of Results

12.6.1.2.1 Table of results (in order of increasing burn rate)-test run number, burn rate, particulate emission rate, efficiency (if determined), averages (indicate which test runs are used).

12.6.1.2.2 Summary of other data-test facility conditions, surface temperature averages, catalyst temperature averages, pretest fuel weights, test fuel charge weights, run times.

12.6.1.2.3 Discussion-Burn rate categories achieved, test run result selection, specific test run problems and solutions.

12.6.1.3 Process Description.

12.6.1.3.1 Wood heater dimensions-volume, height, width, lengths (or other linear dimensions), weight, volume adjustments.

12.6.1.3.2 Firebox configuration-air supply locations and operation, air supply introduction location, refractory location and dimensions, catalyst location, baffle and by-pass location and operation (include line drawings or photographs).

12.6.1.3.3 Process operation during test-air supply settings and adjustments, fuel bed adjustments, draft.

12.6.1.3.4 Test fuel-test fuel properties (moisture and temperature), test fuel crib description (include line drawing or photograph), test fuel loading density.

12.6.1.4 Sampling Locations.

12.6.1.4.1 Describe sampling location relative to wood heater. Include drawing or photograph.

12.6.1.5 Sampling and Analytical Procedures

12.6.1.5.1 Sampling methods-brief reference to operational and sampling procedures and optional and alternative procedures used.

12.6.1.5.2 Analytical methods-brief description of sample recovery and analysis procedures.

12.6.1.6 Quality Control and Assurance Procedures and Results

12.6.1.6.1 Calibration procedures and results-certification procedures, sampling and analysis procedures.

12.6.1.6.2 Test method quality control procedures-leak-checks, volume meter checks, stratification (velocity) checks, proportionality results.

12.6.1.7 Appendices

12.6.1.7.1 Results and Example Calculations. Complete summary tables and accompanying examples of all calculations.

12.6.1.7.2 Raw Data. Copies of all uncorrected data sheets for sampling measurements, temperature records and sample recovery data. Copies of all pretest burn rate and wood heater temperature data.

12.6.1.7.3 Sampling and Analytical Procedures. Detailed description of procedures followed by laboratory personnel in conducting the certification test, emphasizing particular parts of the procedures differing from the methods (*e.g.*, approved alternatives).

12.6.1.7.4 Calibration Results. Summary of all calibrations, checks, and audits pertinent to certification test results with dates.

12.6.1.7.5 Participants. Test personnel, manufacturer representatives, and regulatory observers.

12.6.1.7.6 Sampling and Operation Records. Copies of uncorrected records of activities not included on raw data sheets (*e.g.*, wood heater door open times and durations).

12.6.1.7.7 Additional Information. Wood heater manufacturer's written instructions for operation during the certification test.

12.6.2.1 Wood Heater Identification. Report wood heater identification information. An example data form is shown in Figure 28–4.

12.6.2.2 Test Facility Information. Report test facility temperature, air velocity, and humidity information. An example data form is shown on Figure 28–4.

12.6.2.3 Test Equipment Calibration and Audit Information. Report calibration and audit results for the platform scale, test fuel balance, test fuel moisture meter, and sampling equipment including volume metering systems and gaseous analyzers.

12.6.2.4 Pretest Procedure Description. Report all pretest procedures including pretest fuel weight, burn rates, wood heater temperatures, and air supply settings. An example data form is shown on Figure 28–4.

12.6.2.5 Particulate Emission Data. Report a summary of test results for all test runs and the weighted average emission rate. Submit copies of all data sheets and other records collected during the testing. Submit examples of all calculations.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Pellet Burning Heaters. Certification testing requirements and procedures for pellet burning wood heaters are identical to those for other wood heaters, with the following exceptions:

16.1.1 Test Fuel Properties. The test fuel shall be all wood pellets with a moisture content no greater than 20 percent on a wet basis (25 percent on a dry basis). Determine the wood moisture content with either ASTM D 2016–74 or 83, (Method A), ASTM D 4444–92, or ASTM D 4442–84 or 92 (all noted ASTM standards are incorporated by reference—see §60.17).

16.1.2 Test Fuel Charge Specifications. The test fuel charge size shall be as per the manufacturer's written instructions for maintaining the desired burn rate.

16.1.3 Wood Heater Firebox Volume. The firebox volume need not be measured or determined for establishing the test fuel charge size. The firebox dimensions and other heater specifications needed to identify the heater for certification purposes shall be reported.

16.1.4 Heater Installation. Arrange the heater with the fuel supply hopper on the platform scale as described in section 8.6.1.

16.1.5 Pretest Ignition. Start a fire in the heater as directed by the manufacturer's written instructions, and adjust the heater controls to achieve the desired burn rate. Operate the heater at the desired burn rate for at least 1 hour before the start of the test run.

16.1.6 Test Run. Complete a test run in each burn rate category as follows:

16.1.6.1 Test Run Start. When the wood heater has operated for at least 1 hour at the desired burn rate, add fuel to the supply hopper as necessary to complete the test run, record the weight of the fuel in the supply hopper (the wood heater weight), and start the test run. Add no additional fuel to the hopper during the test run.

Record all the wood heater surface temperatures, the initial sampling method measurement values, the time at the start of the test, and begin the emission sampling. Make no adjustments to the wood heater air supply or wood supply rate during the test run.

16.1.6.2 Data Recording. Record the fuel (wood heater) weight data, wood heater temperature and operational data, and emission sampling data as described in section 8.12.2.

16.1.6.3 Test Run Completion. Continue emission sampling and wood heater operation for 2 hours. At the end of the test run, stop the particulate sampling, and record the final fuel weight, the run time, and all final measurement values, including all wood heater individual surface temperatures.

16.1.7 Calculations. Determine the burn rate using the difference between the initial and final fuel (wood heater) weights and the procedures described in section 12.4. Complete the other calculations as described in section 12.0.

17.0 References

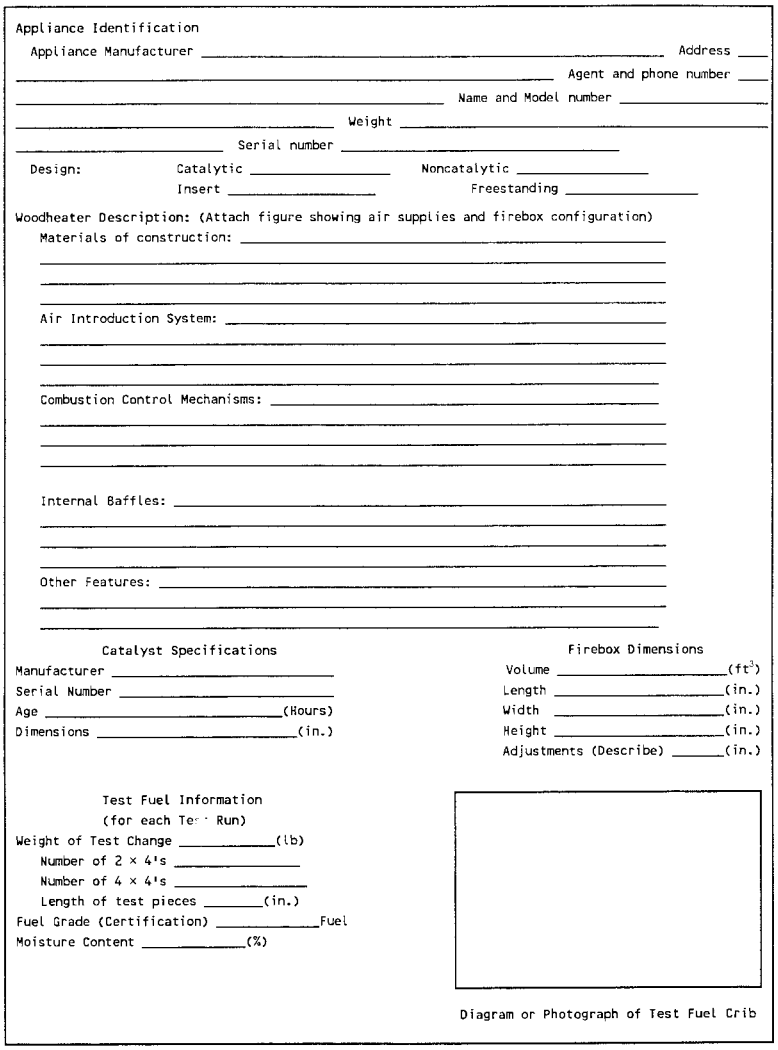
Same as Method 5G, with the addition of the following:

1. Radian Corporation. OMNI Environmental Services, Inc., Cumulative Probability for a Given Burn Rate Based on Data Generated in the CONEG and BPA Studies. Package of materials submitted to the Fifth Session of the Regulatory Negotiation Committee, July 16–17, 1986.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 28–1—BURN RATE WEIGHTED PROBABILITIES FOR CALCULATING WEIGHTED AVERAGE EMISSION RATES

Burn rate (kg/hr-dry)	Cumulative probability (P)	Burn rate (kg/hr-dry)	Cumulative probability (P)	Burn rate (kg/hr-dry)	Cumulative probability (P)
0.00	0.000	1.70	0.840	3.40	0.989
0.05	0.002	1.75	0.857	3.45	0.989
0.10	0.007	1.80	0.875	3.50	0.990
0.15	0.012	1.85	0.882	3.55	0.991
0.20	0.016	1.90	0.895	3.60	0.991
0.25	0.021	1.95	0.906	3.65	0.992
0.30	0.028	2.00	0.912	3.70	0.992
0.35	0.033	2.05	0.920	3.75	0.992
0.40	0.041	2.10	0.925	3.80	0.993
0.45	0.054	2.15	0.932	3.85	0.994
0.50	0.065	2.20	0.936	3.90	0.994
0.55	0.086	2.25	0.940	3.95	0.994
0.60	0.100	2.30	0.945	4.00	0.994
0.65	0.121	2.35	0.951	4.05	0.995
0.70	0.150	2.40	0.956	4.10	0.995
0.75	0.185	2.45	0.959	4.15	0.995
0.80	0.220	2.50	0.964	4.20	0.995
0.85	0.254	2.55	0.968	4.25	0.995
0.90	0.300	2.60	0.972	4.30	0.996
0.95	0.328	2.65	0.975	4.35	0.996
1.00	0.380	2.70	0.977	4.40	0.996
1.05	0.407	2.75	0.979	4.45	0.996
1.10	0.460	2.80	0.980	4.50	0.996
1.15	0.490	2.85	0.981	4.55	0.996
1.20	0.550	2.90	0.982	4.60	0.996
1.25	0.572	2.95	0.984	4.65	0.996
1.30	0.620	3.00	0.984	4.70	0.996
1.35	0.654	3.05	0.985	4.75	0.997
1.40	0.695	3.10	0.986	4.80	0.997
1.45	0.722	3.15	0.987	4.85	0.997
1.50	0.750	3.20	0.987	4.90	0.997
1.55	0.779	3.25	0.988	4.95	0.997
1.60	0.800	3.30	0.988	≥5.00	1.000
1.65	0.825	3.35	0.989		



Appliance Identification

Appliance Manufacturer _____ Address ____

_____ Agent and phone number ____

_____ Name and Model number _____

_____ Weight _____

_____ Serial number _____

Design: Catalytic _____ Noncatalytic _____

Insert _____ Freestanding _____

Woodheater Description: (Attach figure showing air supplies and firebox configuration)

Materials of construction: _____

Air Introduction System: _____

Combustion Control Mechanisms: _____

Internal Baffles: _____

Other Features: _____

Catalyst Specifications

Manufacturer _____

Serial Number _____

Age _____(Hours)

Dimensions _____(in.)

Firebox Dimensions

Volume _____(ft^3)

Length _____(in.)

Width _____(in.)

Height _____(in.)

Adjustments (Describe) _____(in.)

Test Fuel Information
(for each Test Run)

Weight of Test Change _____(lb)

Number of 2 × 4's _____

Number of 4 × 4's _____

Length of test pieces _____(in.)

Fuel Grade (Certification) _____Fuel

Moisture Content _____(%)

Diagram or Photograph of Test Fuel Crib

Figure 28-1. Wood Heater and Test Fuel Information.

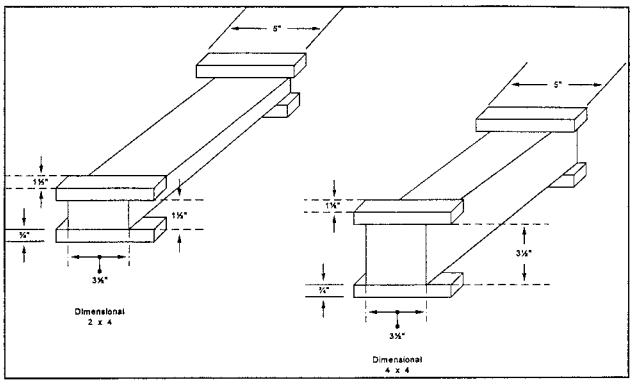


Figure 28-2. Test Fuel Spacer Dimensions.

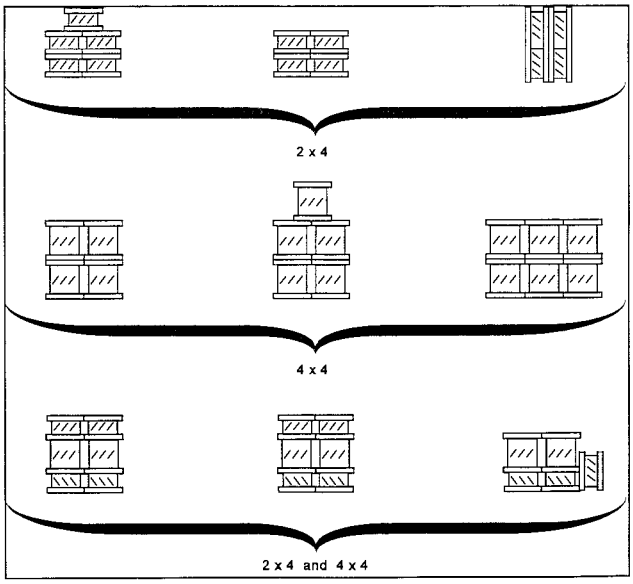


Figure 28-3. Test Fuel Crib Arrangements.

Sheet _____ of _____

Date _____

Operator _____

Sampling Method _____

Wood Heater Information

Manufacturer _____

Model _____

Primary Air Setting _____

Secondary Air Setting _____

Thermostat Setting _____

Other Settings _____

Test Run Information

Test Run No. _____

Burn Rate _____

Room Temperature before/after _____/_____

Barometric Pressure before/after _____/_____

Relative Humidity before/after _____/_____

Room Air Velocity before/after _____/_____

Surface Temp Average Pretest _____ end _____

Test Run Time (minutes)	Test Fuel Scale Reading (lb)	Surface Temperature					Catalyst Temperature		Flue Draft (in. H_2O)
							Inlet (°F)	Outlet (°F)	
(Pretest Period)									
(Test Run Start)									

Figure 28-4. Test Run Wood Heater Operation Data Sheet.

METHOD 28A—MEASUREMENT OF AIR- TO-FUEL RATIO AND MINIMUM ACHIEVABLE BURN RATES FOR WOOD-FIRED APPLIANCES

NOTE: This method does not include all or the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should also have a thorough knowledge of at least the following additional test methods: Method 3, Method 3A, Method 5H, Method 6C, and Method 28.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the measurement of air-to-fuel ratios and minimum achievable burn rates, for determining whether a wood-fired appliance is an affected facility, as specified in 40 CFR 60.530.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from a location in the stack of a wood-fired appliance while the appliance is operating at a prescribed set of conditions. The gas sample is analyzed for carbon dioxide (CO_2), oxygen (O_2), and carbon monoxide (CO). These stack gas components are measured for determining the dry molecular weight of the exhaust gas. Total moles of exhaust gas are determined stoichiometrically. Air-to-fuel ratio is determined by relating the mass of dry combustion air to the mass of dry fuel consumed.

3.0 Definitions

Same as Method 28, section 3.0, with the addition of the following:

3.1 Air-to-fuel ratio means the ratio of the mass of dry combustion air introduced into the firebox to the mass of dry fuel consumed (grams of dry air per gram of dry wood burned).

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Test Facility. Insulated Solid Pack Chimney, Platform Scale and Monitor, Test Facility Temperature Monitor, Balance, Moisture Meter, Anemometer, Barometer, Draft Gauge, Humidity Gauge, Wood Heater Flue, and Test Facility. Same as Method 28, sections 6.1, 6.2, and 6.4 to 6.12, respectively.

6.2 Sampling System. Probe, Condenser, Valve, Pump, Rate Meter, Flexible Bag, Pressure Gauge, and Vacuum Gauge. Same as Method 3, sections 6.2.1 to 6.2.8, respectively. Alternatively, the sampling system described in Method 5H, section 6.1 may be used.

6.3 Exhaust Gas Analysis. Use one or both of the following:

6.3.1 Orsat Analyzer. Same as Method 3, section 6.1.3

6.3.2 Instrumental Analyzers. Same as Method 5H, sections 6.1.3.4 and 6.1.3.5, for CO_2 and CO analyzers, except use a CO analyzer with a range of 0 to 5 percent and use a CO_2 analyzer with a range of 0 to 5 percent. Use an O_2 analyzer capable of providing a measure of O_2 in the range of 0 to 25 percent by volume at least once every 10 minutes.

7.0 Reagents and Standards

7.1 Test Fuel and Test Fuel Spacers. Same as Method 28, sections 7.1 and 7.2, respectively.

7.2 Cylinder Gases. For each of the three analyzers, use the same concentration as specified in sections 7.2.1, 7.2.2, and 7.2.3 of Method 6C.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Wood Heater Air Supply Adjustments.

8.1.1 This section describes how dampers are to be set or adjusted and air inlet ports closed or sealed during Method 28A tests. The specifications in this section are intended to ensure that affected facility determinations are made on the facility configurations that could reasonably be expected to be employed by the user. They are also intended to prevent circumvention of the standard through the addition of an air port that would often be blocked off in actual use. These specifications are based on the assumption that consumers will remove such items as dampers or other closure mechanism stops if this can be done readily with household tools; that consumers will block air inlet passages not visible during normal operation of the appliance using aluminum tape or parts generally available at retail stores; and that consumers will cap off any threaded or flanged air inlets. They also assume that air leakage around glass doors, sheet metal joints or through inlet grilles visible during normal operation of the appliance would not be further blocked or taped off by a consumer.

8.1.2 It is not the intention of this section to cause an appliance that is clearly designed, intended, and, in most normal installations, used as a fireplace to be converted into a wood heater for purposes of applicability testing. Such a fireplace would be identifiable by such features as large or multiple glass doors or panels that are not gasketed, relatively unrestricted air inlets intended, in large part, to limit smoking and fogging of glass surfaces, and other aesthetic features not normally included in wood heaters.

8.1.3 Adjustable Air Supply Mechanisms. Any commercially available flue damper, other adjustment mechanism or other air

inlet port that is designed, intended or otherwise reasonably expected to be adjusted or closed by consumers, installers, or dealers and which could restrict air into the firebox shall be set so as to achieve minimum air into the firebox (*i.e.*, closed off or set in the most closed position).

8.1.3.1 Flue dampers, mechanisms and air inlet ports which could reasonably be expected to be adjusted or closed would include:

8.1.3.1.1 All internal or externally adjustable mechanisms (including adjustments that affect the tightness of door fittings) that are accessible either before and/or after installation.

8.1.3.1.2 All mechanisms, other inlet ports, or inlet port stops that are identified in the owner's manual or in any dealer literature as being adjustable or alterable. For example, an inlet port that could be used to provide access to an outside air duct but which is identified as being closable through use of additional materials whether or not they are supplied with the facility.

8.1.3.1.3 Any combustion air inlet port or commercially available flue damper or mechanism stop, which would readily lend itself to closure by consumers who are handy with household tools by the removal of parts or the addition of parts generally available at retail stores (*e.g.*, addition of a pipe cap or plug, addition of a small metal plate to an inlet hole on a nondecorative sheet metal surface, or removal of riveted or screwed damper stops).

8.1.3.1.4 Any flue damper, other adjustment mechanisms or other air inlet ports that are found and documented in several (*e.g.*, a number sufficient to reasonably conclude that the practice is not unique or uncommon) actual installations as having been adjusted to a more closed position, or closed by consumers, installers, or dealers.

8.1.4 Air Supply Adjustments During Test. The test shall be performed with all air inlets identified under this section in the closed or most closed position or in the configuration which otherwise achieves the lowest air inlet (*i.e.*, greatest blockage).

NOTE: For the purposes of this section, air flow shall not be minimized beyond the point necessary to maintain combustion or beyond the point that forces smoke into the room.

8.1.5 Notwithstanding section 8.1.1, any flue damper, adjustment mechanism, or air inlet port (whether or not equipped with flue dampers or adjusting mechanisms) that is visible during normal operation of the appliance and which could not reasonably be closed further or blocked except through means that would significantly degrade the aesthetics of the facility (*e.g.*, through use of duct tape) will not be closed further or blocked.

8.2 Sampling System.

8.2.1 Sampling Location. Same as Method 5H, section 8.1.2.

8.2.2 Sampling System Set Up. Set up the sampling equipment as described in Method 3, section 8.1.

8.3 Wood Heater Installation, Test Facility Conditions, Wood Heater Firebox Volume, and Test Fuel Charge. Same as Method 28, sections 8.4 and 8.6 to 8.8, respectively.

8.4 Pretest Ignition. Same as Method 28, section 8.11. Set the wood heater air supply settings to achieve a burn rate in Category 1 or the lowest achievable burn rate (see section 8.1).

8.5 Test Run. Same as Method 28, section 8.12. Begin sample collection at the start of the test run as defined in Method 28, section 8.12.1.

8.5.1 Gas Analysis.

8.5.1.1 If Method 3 is used, collect a minimum of two bag samples simultaneously at a constant sampling rate for the duration of the test run. A minimum sample volume of 30 liters (1.1 ft^3) per bag is recommended.

8.5.1.2 If instrumental gas concentration measurement procedures are used, conduct the gas measurement system performance tests, analyzer calibration, and analyzer calibration error check outlined in Method 6C, sections 8.2.3, 8.2.4, 8.5, and 10.0, respectively. Sample at a constant rate for the duration of the test run.

8.5.2 Data Recording. Record wood heater operational data, test facility temperature, sample train flow rate, and fuel weight data at intervals of no greater than 10 minutes.

8.5.3 Test Run Completion. Same as Method 28, section 8.13.

9.0 Quality Control

9.1 Data Validation. The following quality control procedure is suggested to provide a check on the quality of the data.

9.1.1 Calculate a fuel factor, F_o, using Equation 28A–1 in section 12.2.

9.1.2 If CO is present in quantities measurable by this method, adjust the O_2 and CO_2 values before performing the calculation for F_o as shown in section 12.3 and 12.4.

9.1.3 Compare the calculated F_o factor with the expected F_o range for wood (1.000–1.120). Calculated F_o values beyond this acceptable range should be investigated before accepting the test results. For example, the strength of the solutions in the gas analyzer and the analyzing technique should be checked by sampling and analyzing a known concentration, such as air. If no detectable or correctable measurement error can be identified, the test should be repeated. Alternatively, determine a range of air-to-fuel ratio results that could include the correct value by using an F_o value of 1.05 and calculating a potential range of CO_2 and O_2 values. Acceptance of such results will be based on whether the calculated range includes the

exemption limit and the judgment of the Administrator.

9.2 Method 3 Analyses. Compare the results of the analyses of the two bag samples. If all the gas components (O_2, CO, and CO_2) values for the two analyses agree within 0.5 percent (*e.g.*, 6.0 percent O_2 for bag 1 and 6.5 percent O_2 for bag 2, agree within 0.5 percent), the results of the bag analyses may be averaged for the calculations in section 12. If the analysis results do not agree within 0.5 percent for each component, calculate the air-to-fuel ratio using both sets of analyses and report the results.

10.0 Calibration and Standardization

[Reserved]

11.0 Analytical Procedures

11.1 Method 3 Integrated Bag Samples. Within 4 hours after the sample collection, analyze each bag sample for percent CO_2, O_2, and CO using an Orsat analyzer as described in Method 3, section 11.0.

11.2 Instrumental Analyzers. Average the percent CO_2, CO, and O_2 values for the test run.

12.0 Data Analyses and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figure after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

12.1 Nomenclature.

M_d = Dry molecular weight, g/g-mole (lb/lb-mole).

N_T = Total gram-moles of dry exhaust gas per kg of wood burned (lb-moles/lb).

$\%CO_2$ = Percent CO_2 by volume (dry basis).

%CO = Percent CO by volume (dry basis).

$\%N_2$ = Percent N_2 by volume (dry basis).

$\%O_2$ = Percent O2 by volume (dry basis).

Y_{HC} = Assumed mole fraction of HC (dry as CH_4) = 0.0088 for catalytic wood heaters; = 0.0132 for noncatalytic wood heaters. = 0.0080 for pellet-fired wood heaters.

Y_{CO} = Measured mole fraction of CO (*e.g.*, 1 percent CO = .01 mole fraction), g/g-mole (lb/lb-mole).

Y_{CO2} = Measured mole fraction of CO_{CO2} (*e.g.*, 10 percent CO_2 = .10 mole fraction), g/g-mole (lb/lb-mole).

0.280 = Molecular weight of N_2 or CO, divided by 100.

0.320 = Molecular weight of O_2 divided by 100.

0.440 = Molecular weight of CO_2 divided by 100.

20.9 = Percent O_2 by volume in ambient air.

42.5 = Gram-moles of carbon in 1 kg of dry wood assuming 51 percent carbon by weight dry basis (.0425 lb/lb-mole).

510 = Grams of carbon in exhaust gas per kg of wood burned.

1,000 = Grams in 1 kg.

12.2 Fuel Factor. Use Equation 28A–1 to calculate the fuel factor.

$$F_o = \frac{20.9 - \%O_2}{\%CO_2} \qquad \text{Eq. 28A-1}$$

12. 3 Adjusted $\%CO_2$. Use Equation 28A–2 to adjust CO_2 values if measurable CO is present.

$$\%CO_{2(adj)} = \%CO_2 + \%CO \qquad \text{Eq. 28A-2}$$

12.4 Adjusted $\%O_2$. Use Equation 28A–3 to adjust O_2 value if measurable CO is present.

$$\%O_{2(adj)} = \%O_2 - 0.5\%CO \qquad \text{Eq. 28A-3}$$

12.5 Dry Molecular Weight. Use Equation 28A–4 to calculate the dry molecular weight of the stack gas.

$$M_d = 0.440(\%CO_2) + 0.320(\%O_2) + 0.280(\%N_2 + \%CO) \qquad \text{Eq. 28A-4}$$

NOTE: The above equation does not consider argon in air (about 0.9 percent, molecular weight of 39.9). A negative error of about 0.4 percent is introduced. Argon may

be included in the analysis using procedures subject to approval of the Administrator.

12.6 Dry Moles of Exhaust Gas. Use Equation 28A–5 to calculate the total moles of dry exhaust gas produced per kilogram of dry wood burned.

$$N_T = \frac{42.5}{\left(Y_{CO_2} + Y_{CO} + Y_{HC}\right)} \qquad \text{Eq. 28A-5}$$

12.7 Air-to-Fuel Ratio. Use Equation 28A–6 to calculate the air-to-fuel ratio on a dry mass basis.

$$A/F = \frac{\left(N_T \times M_d\right) - 510}{1{,}000} \qquad \text{Eq. 28A-6}$$

12.8 Burn Rate. Calculate the fuel burn rate as in Method 28, section 12.4.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as section 16.0 of Method 3 and section 17 of Method 5G.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

Test Method 28R for Certification and Auditing of Wood Heaters

1.0 Scope and Application

1.1 This test method applies to certification and auditing of wood-fired room heaters and fireplace inserts.

1.2 The test method covers the fueling and operating protocol for measuring particulate emissions, as well as determining burn rates, heat output and efficiency.

1.3 Particulate emissions are measured by the dilution tunnel method as specified in ASTM E2515–11 *Standard Test Method for Determination of Particulate Matter Emissions Collected in a Dilution Tunnel* (IBR, see §60.17). Upon request, four-inch filters may be used. Upon request, Teflon membrane filters or Teflon-coated glass fiber filters may be used.

2.0 Procedures

2.1 This method incorporates the provisions of ASTM E2780–10 (IBR, see §60.17) except as follows:

2.1.1 The burn rate categories, low burn rate requirement, and weightings in Method 28 shall be used.

2.1.2 The startup procedures shall be the same as in Method 28.

2.1.3 Manufacturers shall not specify a smaller volume of the firebox for testing than the full usable firebox.

2.1.4 Prior to testing, the heater must be operated for a minimum of 50 hours using a medium burn rate. The conditioning may be at the manufacturer's facility prior to the certification test. If the conditioning is at the certification test laboratory, the preburn for the first test can be included as part of the conditioning requirement.

2.2 Manufacturers may use ASTM E871–82 (reapproved 2013) (IBR, see §60.17) as an alternative to the procedures in Method 5H or Method 28 for determining total weight basis moisture in the analysis sample of particulate wood fuel.

Test Method 28WHH for Measurement of Particulate Emissions and Heating Efficiency of Wood-Fired Hydronic Heating Appliances

1.0 Scope and Application

1.1 This test method applies to wood-fired hydronic heating appliances. The units typically transfer heat through circulation of a liquid heat exchange media such as water or a water-antifreeze mixture.

1.2 The test method measures particulate emissions and delivered heating efficiency at specified heat output rates based on the appliance's rated heating capacity.

1.3 Particulate emissions are measured by the dilution tunnel method as specified in ASTM E2515–11 *Standard Test Method for Determination of Particulate Matter Emissions Collected in a Dilution Tunnel* (IBR, see §60.17). Upon request, four-inch filters may be used. Upon request, Teflon membrane filters or Teflon-coated glass fiber filters may be used. Delivered efficiency is measured by determining the heat output through measurement of the flow rate and temperature change of water circulated through a heat exchanger external to the appliance and determining the input from the mass of dry wood fuel and its higher heating value. Delivered efficiency does not attempt to account for pipeline loss.

1.4 Products covered by this test method include both pressurized and non-pressurized heating appliances intended to be fired with wood. These products are wood-fired hydronic heating appliances that the manufacturer specifies for indoor or outdoor installation. They are often connected to a heat exchanger by insulated pipes and normally include a pump to circulate heated liquid. They are used to heat structures such as homes, barns and greenhouses and can heat domestic hot water, spas or swimming pools.

1.5 Distinguishing features of products covered by this standard include:

1.5.1 Manufacturer specifies for indoor or outdoor installation.

1.5.2 A firebox with an access door for hand loading of fuel.

1.5.3 Typically, an aquastat that controls combustion air supply to maintain the liquid in the appliance within a predetermined temperature range provided sufficient fuel is available in the firebox.

1.5.4 A chimney or vent that exhausts combustion products from the appliance.

1.6 The values stated are to be regarded as the standard whether in I–P or SI units. The values given in parentheses are for information only.

2.0 Summary of Method and References

2.1 Particulate matter emissions are measured from a wood-fired hydronic heating appliance burning a prepared test fuel crib in a test facility maintained at a set of prescribed conditions. Procedures for determining burn rates, and particulate emissions rates and for reducing data are provided.

2.2 Referenced Documents

2.2.1 EPA Standards

2.2.1.1 Method 28 Certification and Auditing of Wood Heaters

2.2.2 Other Standards

2.2.2.1 ASTM E2515–11—*Standard Test Method for Determination of Particulate Matter Emissions Collected in a Dilution Tunnel* (IBR, see §60.17).

2.2.2.2 CSA–B415.1–10 *Performance Testing of Solid-Fuel-Burning Heating Appliances* (IBR, see §60.17).

3.0 Terminology

3.1 Definitions.

3.1.1 Hydronic Heating—A heating system in which a heat source supplies energy to a liquid heat exchange media such as water that is circulated to a heating load and returned to the heat source through pipes.

3.1.2 Aquastat—A control device that opens or closes a circuit to control the rate of fuel consumption in response to the temperature of the heating media in the heating appliance.

3.1.3 Delivered Efficiency—The percentage of heat available in a test fuel charge that is delivered to a simulated heating load as specified in this test method.

3.1.4 Manufacturer's Rated Heat Output Capacity—The value in Btu/hr (MJ/hr) that the manufacturer specifies that a particular model of hydronic heating appliance is capable of supplying at its design capacity as verified by testing, in accordance with Section 13.

3.1.5 Burn Rate—The rate at which test fuel is consumed in an appliance. Measured in pounds (lbs) or kilograms of wood (dry basis) per hour (lb/hr or kg/hr).

3.1.6 Firebox—The chamber in the appliance in which the test fuel charge is placed and combusted.

3.1.7 Test Fuel Charge—The collection of test fuel layers placed in the appliance at the start of the emission test run.

3.1.8 Test Fuel Layer—Horizontal arrangement of test fuel units.

3.1.9 Test Fuel Unit—One or more test fuel pieces with ¾ inch (19 mm) spacers attached to the bottom and to one side. If composed of multiple test fuel pieces, the bottom spacer may be one continuous piece.

3.1.10 Test Fuel Piece—A single 4 × 4 (4 ±0.25 inches by 4 ±0.25 inches) [100 ±6 mm by 100 ±6 mm] white or red oak wood piece cut to the length required.

3.1.11 Test Run—An individual emission test that encompasses the time required to consume the mass of the test fuel charge.

3.1.12 Overall Efficiency (SLM)—The efficiency for each test run as determined using the CSA B415.1–10 (IBR, see §60.17) stack loss method.

3.1.13 Thermopile—A device consisting of a number of thermocouples connected in series, used for measuring differential temperature.

4.0 Summary of Test Method

4.1 Dilution Tunnel. Emissions are determined using the ''dilution tunnel'' method specified in ASTM E2515–11 *Standard Test Method for Determination of Particulate Matter Emissions Collected in a Dilution Tunnel* (IBR, see §60.17). The flow rate in the dilution tunnel is maintained at a constant level throughout the test cycle and accurately measured. Samples of the dilution tunnel flow stream are extracted at a constant flow rate and drawn through high efficiency filters. The filters are dried and weighed before and after the test to determine the emissions catch and this value is multiplied by the ratio of tunnel flow to filter flow to determine the total particulate emissions produced in the test cycle.

4.2 Efficiency. The efficiency test procedure takes advantage of the fact that this type of appliance delivers heat through circulation of the heated liquid (water) from the appliance to a remote heat exchanger and back to the appliance. Measurements of the water temperature difference as it enters and exits the heat exchanger along with the measured flow rate allow for an accurate determination of the useful heat output of the appliance. The input is determined by weight of the test fuel charge, adjusted for moisture content, multiplied by the higher heating value. Additional measurements of the appliance weight and temperature at the beginning and end of a test cycle are used to correct for heat stored in the appliance. Overall efficiency (SLM) is determined using the CSA B415.1–10 (IBR, see §60.17) stack loss method for data quality assurance purposes.

4.3 Operation. Appliance operation is conducted on a hot-to-hot test cycle meaning that the appliance is brought to operating

temperature and a coal bed is established prior to the addition of the test fuel charge and measurements are made for each test fuel charge cycle. The measurements are made under constant heat draw conditions within predetermined ranges. No attempt is made to modulate the heat demand to simulate an indoor thermostat cycling on and off in response to changes in the indoor environment. Four test categories are used. These are:

4.3.1 Category I: A heat output of 15 percent or less of manufacturer's rated heat output capacity.

4.3.2 Category II: A heat output of 16 percent to 24 percent of manufacturer's rated heat output capacity.

4.3.3 Category III: A heat output of 25 percent to 50 percent of manufacturer's rated heat output capacity.

4.3.4 Category IV: Manufacturer's rated heat output capacity.

5.0 Significance and Use

5.1 The measurement of particulate matter emission rates is an important test method widely used in the practice of air pollution control.

5.1.1 These measurements, when approved by state or federal agencies, are often required for the purpose of determining compliance with regulations and statutes.

5.1.2 The measurements made before and after design modifications are necessary to demonstrate the effectiveness of design changes in reducing emissions and make this standard an important tool in manufacturers' research and development programs.

5.2 Measurement of heating efficiency provides a uniform basis for comparison of product performance that is useful to the consumer. It is also required to relate emissions produced to the useful heat production.

5.3 This is a laboratory method and is not intended to be fully representative of all actual field use. It is recognized that users of hand-fired, wood-burning equipment have a great deal of influence over the performance of any wood-burning appliance. Some compromises in realism have been made in the interest of providing a reliable and repeatable test method.

6.0 Test Equipment

6.1 Scale. A platform scale capable of weighing the appliance under test and associated parts and accessories when completely filled with water to an accuracy of ±1.0 pound (±0.5 kg).

6.2 Heat Exchanger. A water-to-water heat exchanger capable of dissipating the expected heat output from the system under test.

6.3 Water Temperature Difference Measurement. A Type—T 'special limits' thermopile with a minimum of 5 pairs of junctions shall be used to measure the temperature difference in water entering and leaving the heat exchanger. The temperature difference measurement uncertainty of this type of thermopile is equal to or less than ±0.50 °F (±0.25 °C). Other temperature measurement methods may be used if the temperature difference measurement uncertainty is equal to or less than ±0.50 °F (±0.25 °C).

6.4 Water Flow Meter. A water flow meter shall be installed in the inlet to the load side of the heat exchanger. The flow meter shall have an accuracy of ±1 percent of measured flow.

6.4.1 Optional—Appliance Side Water Flow Meter. A water flow meter with an accuracy of ±1 percent of the flow rate is recommended to monitor supply side water flow rate.

6.5 Optional Recirculation Pump. Circulating pump used during test to prevent stratification of liquid being heated.

6.6 Water Temperature Measurement—Thermocouples or other temperature sensors to measure the water temperature at the inlet and outlet of the load side of the heat exchanger. Must meet the calibration requirements specified in section 10.1.

6.7 Wood Moisture Meter—Calibrated electrical resistance meter capable of measuring test fuel moisture to within 1 percent moisture content. Must meet the calibration requirements specified in section 10.4.

6.8 Flue Gas Temperature Measurement—Must meet the requirements of CSA B415.1–10 (IBR, see §60.17), clause 6.2.2.

6.9 Test Room Temperature Measurement—Must meet the requirements of CSA B415.1–10 (IBR, see §60.17), clause 6.2.1.

6.10 Flue Gas Composition Measurement—Must meet the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 6.3.1 through 6.3.3.

7.0 Safety

7.1 These tests involve combustion of wood fuel and substantial release of heat and products of combustion. The heating system also produces large quantities of very hot water and the potential for steam production and system pressurization. Appropriate precautions must be taken to protect personnel from burn hazards and respiration of products of combustion.

8.0 Sampling, Test Specimens and Test Appliances

8.1 Test specimens shall be supplied as complete appliances including all controls and accessories necessary for installation in the test facility. A full set of specifications and design and assembly drawings shall be provided when the product is to be placed under certification of a third-party agency. The manufacturer's written installation and operating instructions are to be used as a

guide in the set-up and testing of the appliance.

9.0 Preparation of Test Equipment

9.1 The appliance is to be placed on a scale capable of weighing the appliance fully loaded with a resolution of ±1.0 lb (0.5 kg).

9.2 The appliance shall be fitted with the type of chimney recommended or provided by the manufacturer and extending to 15 ±0.5 feet (4.6 ±0.15 m) from the upper surface of the scale. If no flue or chimney system is recommended or provided by the manufacturer, connect the appliance to a flue of a diameter equal to the flue outlet of the appliance. The flue section from the appliance flue collar to 8 ±0.5 feet above the scale shall be single wall stove pipe and the remainder of the flue shall be double wall insulated class A chimney.

9.3 Optional Equipment Use

9.3.1 A recirculation pump may be installed between connections at the top and bottom of the appliance to minimize thermal stratification if specified by the manufacturer. The pump shall not be installed in such a way as to change or affect the flow rate between the appliance and the heat exchanger.

9.3.2 If the manufacturer specifies that a thermal control valve or other device be installed and set to control the return water temperature to a specific set point, the valve or other device shall be installed and set per the manufacturer's written instructions.

9.4 Prior to filling the tank, weigh and record the appliance mass.

9.5 Heat Exchanger

9.5.1 Plumb the unit to a water-to-water heat exchanger with sufficient capacity to draw off heat at the maximum rate anticipated. Route hoses, electrical cables, and instrument wires in a manner that does not influence the weighing accuracy of the scale as indicated by placing dead weights on the platform and verifying the scale's accuracy.

9.5.2 Locate thermocouples to measure the water temperature at the inlet and outlet of the load side of the heat exchanger.

9.5.3 Install a thermopile meeting the requirements of section 6.3 to measure the water temperature difference between the inlet and outlet of the load side of the heat exchanger.

9.5.4 Install a calibrated water flow meter in the heat exchanger load side supply line. The water flow meter is to be installed on the cooling water inlet side of the heat exchanger so that it will operate at the temperature at which it is calibrated.

9.5.5 Place the heat exchanger in a box with 2 in. (50 mm) of expanded polystyrene (EPS) foam insulation surrounding it to minimize heat losses from the heat exchanger.

9.5.6 The reported efficiency and heat output rate shall be based on measurements made on the load side of the heat exchanger.

9.5.7 Temperature instrumentation per section 6.6 shall be installed in the appliance outlet and return lines. The average of the outlet and return water temperature on the supply side of the system shall be considered the average appliance temperature for calculation of heat storage in the appliance (TF_{avg} and TI_{avg}). Installation of a water flow meter in the supply side of the system is optional.

9.6 Fill the system with water. Determine the total weight of the water in the appliance when the water is circulating. Verify that the scale indicates a stable weight under operating conditions. Make sure air is purged properly.

10.0 Calibration and Standardization

10.1 Water Temperature Sensors. Temperature measuring equipment shall be calibrated before initial use and at least semi-annually thereafter. Calibrations shall be in compliance with National Institute of Standards and Technology (NIST) Monograph 175, Standard Limits of Error.

10.2 Heat Exchanger Load Side Water Flow Meter.

10.2.1 The heat exchanger load side water flow meter shall be calibrated within the flow range used for the test run using NIST traceable methods. Verify the calibration of the water flow meter before and after each test run and at least once during each test run by comparing the water flow rate indicated by the flow meter to the mass of water collected from the outlet of the heat exchanger over a timed interval. Volume of the collected water shall be determined based on the water density calculated from section 13, Eq. 8, using the water temperature measured at the flow meter. The uncertainty in the verification procedure used shall be 1 percent or less. The water flow rate determined by the collection and weighing method shall be within 1 percent of the flow rate indicated by the water flow meter.

10.3 Scales. The scales used to weigh the appliance and test fuel charge shall be calibrated using NIST traceable methods at least once every 6 months.

10.4 Moisture Meter. The moisture meter shall be calibrated per the manufacturer's instructions and checked before each use.

10.5 Flue Gas Analyzers—In accordance with CSA B415.1–10 (IBR, see §60.17), clause 6.8.

11.0 Conditioning

11.1 Prior to testing, the appliance is to be operated for a minimum of 50 hours using a medium heat draw rate. The conditioning may be at the manufacturer's facility prior to the certification test. If the conditioning is at the certification test laboratory, the pre-burn for the first test can be included as

part of the conditioning requirement. If conditioning is included in pre-burn, then the appliance shall be aged with fuel meeting the specifications outlined in sections 12.2 with a moisture content between 19 and 25 percent on a dry basis. Operate the appliance at a medium burn rate (Category II or III) for at least 10 hours for noncatalytic appliances and 50 hours for catalytic appliances. Record and report hourly flue gas exit temperature data and the hours of operation. The aging procedure shall be conducted and documented by a testing laboratory.

12.0 Procedure

12.1 Appliance Installation. Assemble the appliance and parts in conformance with the manufacturer's written installation instructions. Clean the flue with an appropriately sized, wire chimney brush before each certification test series.

12.2 Fuel. Test fuel charge fuel shall be red (*Quercus ruba L.*) or white (*Quercus alba*) oak 19 to 25 percent moisture content on a dry basis. Piece length shall be 80 percent of the firebox depth rounded down to the nearest 1 inch (25mm) increment. For example, if the firebox depth is 46 inches (1168mm) the 4 × 4 piece length would be 36 inches (46 inches × 0.8 = 36.8 inches rounded down to 36 inches). Pieces are to be placed in the firebox parallel to the longest firebox dimension. For fireboxes with sloped surfaces that create a non-uniform firebox length, the piece length shall be adjusted for each layer based on 80 percent of the length at the level where the layer is placed. Pieces are to be spaced ¾ inches (19 mm) apart on all faces. The first fuel layer may be assembled using fuel units consisting of multiple 4 × 4s consisting of single pieces with bottom and side spacers of 3 or more pieces if needed for a stable layer. The second layer may consist of fuel units consisting of no more than two pieces with spacers attached on the bottom and side. The top two layers of the fuel charge must consist of single pieces unless the fuel charge is only three layers. In that instance only the top layer must consist of single units. Three-quarter inch (19 mm) by 1.5 inch (38 mm) spacers shall be attached to the bottom of piece to maintain a ¾ inch (19 mm) separation. When a layer consists of two or more units of 4 × 4s an additional ¾ inch (19 mm) thick by 1.5 inch (38 mm) wide spacer shall be attached to the vertical face of each end of one 4 × 4, such that the ¾ inch (19 mm) space will be maintained when two 4 × 4 units or pieces are loaded side by side. In cases where a layer contains an odd number of 4 × 4s one piece shall not be attached, but shall have spacers attached in a manner that will provide for the ¾ inch (19 mm) space to be maintained (See Figure 1). Spacers shall be attached perpendicular to the length of the 4 × 4s such that the edge of the spacer is 1 ±0.25 inch from the end of the 4 × 4s in the previous layers. Spacers shall be red or white oak and will be attached with either nails (non-galvanized), brads or oak dowels. The use of kiln-dried wood is not allowed.

12.2.1 Using a fuel moisture meter as specified in section 6.7 of the test method, determine the fuel moisture for each test fuel piece used for the test fuel load by averaging at least five fuel moisture meter readings measured parallel to the wood grain. Penetration of the moisture meter insulated electrodes for all readings shall be ¼ the thickness of the fuel piece or 19 mm (¾ in.), whichever is lesser. One measurement from each of three sides shall be made at approximately 3 inches from each end and the center. Two additional measurements shall be made centered between the other three locations. Each individual moisture content reading shall be in the range of 18 to 28 percent on a dry basis. The average moisture content of each piece of test fuel shall be in the range of 19 to 25 percent. It is not required to measure the moisture content of the spacers. Moisture shall not be added to previously dried fuel pieces except by storage under high humidity conditions and temperature up to 100 °F. Fuel moisture shall be measured within 4 hours of using the fuel for a test.

12.2.2 Firebox Volume. Determine the firebox volume in cubic feet. Firebox volume shall include all areas accessible through the fuel loading door where firewood could reasonably be placed up to the horizontal plane defined by the top of the loading door. A drawing of the firebox showing front, side and plan views or an isometric view with interior dimensions shall be provided by the manufacturer and verified by the laboratory. Calculations for firebox volume from computer aided design (CAD) software programs are acceptable and shall be included in the test report if used. If the firebox volume is calculated by the laboratory the firebox drawings and calculations shall be included in the test report.

12.2.3 Test Fuel Charge. Test fuel charges shall be determined by multiplying the firebox volume by 10 pounds (4.54 kg) per ft^3 (28L), or a higher load density as recommended by the manufacturer's printed operating instructions, of wood (as used wet weight). Select the number of pieces of standard fuel that most nearly match this target weight. This is the standard fuel charge for all tests. For example, if the firebox loading area volume is 10 ft^3 (280L) and the firebox depth is 46 inches (1168 mm), test fuel charge target is 100 lbs (45 kg) minimum and the piece length is 36 inches (914 mm). If eight 4 × 4s, 36 inches long weigh 105 lbs (48 kg), use 8 pieces for each test fuel charge. All test fuel charges will be of the same configuration.

12.3 Sampling Equipment. Prepare the particulate emission sampling equipment as defined by ASTM E2515–11 *Standard Test Method for Determination of Particulate Matter Emissions Collected in a Dilution Tunnel* (IBR, see §60.17). Upon request, four-inch filters may be used. Upon request, Teflon membrane filters or Teflon-coated glass fiber filters may be used.

12.4 Appliance Startup. The appliance shall be fired with wood fuel of any species, size and moisture content at the laboratories' discretion to bring it up to operating temperature. Operate the appliance until the water is heated to the upper operating control limit and has cycled at least two times. Then remove all unburned fuel, zero the scale and verify the scales accuracy using dead weights.

12.4.1 Pretest Burn Cycle. Reload appliance with oak wood and allow it to burn down to the specified coal bed weight. The pretest burn cycle fuel charge weight shall be within ±10 percent of the test fuel charge weight. Piece size and length shall be selected such that charcoalization is achieved by the time the fuel charge has burned down to the required coal bed weight. Pieces with a maximum thickness of approximately 2 inches have been found to be suitable. Charcoalization is a general condition of the test fuel bed evidenced by an absence of large pieces of burning wood in the coal bed and the remaining fuel pieces being brittle enough to be broken into smaller charcoal pieces with a metal poker. Manipulations to the fuel bed prior to the start of the test run are to be done to achieve charcoalization while maintaining the desired heat output rate. During the pre-test burn cycle and at least one hour prior to starting the test run, adjust water flow to the heat exchanger to establish the target heat draw for the test. For the first test run the heat draw rate shall be equal to the manufacturer's rated heat output capacity.

12.4.1.1 Allowable Adjustments. Fuel addition or subtractions, and coal bed raking shall be kept to a minimum but are allowed up to 15 minutes prior to the start of the test run. For the purposes of this method, coal bed raking is the use of a metal tool (poker) to stir coals, break burning fuel into smaller pieces, dislodge fuel pieces from positions of poor combustion, and check for the condition of charcoalization. Record all adjustments to and additions or subtractions of fuel, and any other changes to the appliance operations that occur during pretest ignition period. During the 15-minute period prior to the start of the test run, the wood heater loading door shall not be open more than a total of 1 minute. Coal bed raking is the only adjustment allowed during this period.

12.4.2 Coal Bed Weight. The appliance is to be loaded with the test fuel charge when the coal bed weight is between 10 percent and 20 percent of the test fuel charge weight. Coals may be raked as necessary to level the coal bed but may only be raked and stirred once between 15 to 20 minutes prior to the addition of the test fuel charge.

12.5 Test Runs. For all test runs, the return water temperature to the hydronic heater must be equal to or greater than 120 °F. Aquastat or other heater output control device settings that are adjustable shall be set using manufacturer specifications, either as factory set or in accordance with the owner's manual, and shall remain the same for all burn categories.

Complete a test run in each heat output rate category, as follows:

12.5.1 Test Run Start. Once the appliance is operating normally and the pretest coal bed weight has reached the target value per section 12.4.2, tare the scale and load the full test charge into the appliance. Time for loading shall not exceed 5 minutes. The actual weight of the test fuel charge shall be measured and recorded within 30 minutes prior to loading. Start all sampling systems.

12.5.1.1 Record all water temperatures, differential water temperatures and water flow rates at time intervals of one minute or less.

12.5.1.2 Record particulate emissions data per the requirements of ASTM E2515 (IBR, see §60.17).

12.5.1.3 Record data needed to determine overall efficiency (SLM) per the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 6.2.1, 6.2.2, 6.3, 8.5.7, 10.4.3 (a), 10.4.3(f), and 13.7.9.3

12.5.1.3.1 Measure and record the test room air temperature in accordance with the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 6.2.1, 8.5.7 and 10.4.3 (g).

12.5.1.3.2 Measure and record the flue gas temperature in accordance with the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 6.2.2, 8.5.7 and 10.4.3 (f).

12.5.1.3.3 Determine and record the carbon monoxide (CO) and carbon dioxide (CO_2) concentrations in the flue gas in accordance with CSA B415.1–10 (IBR, see §60.17), clauses 6.3, 8.5.7 and 10.4.3 (i) and (j).

12.5.1.3.4 Measure and record the test fuel weight per the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 8.5.7 and 10.4.3 (h).

12.5.1.3.5 Record the test run time per the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 10.4.3 (a).

12.5.1.4 Monitor the average heat output rate on the load side of the heat exchanger. If the heat output rate gets close to the upper or lower limit of the target range (±5 percent) adjust the water flow through the heat exchanger to compensate. Make changes as infrequently as possible while maintaining the target heat output rate. The first test run shall be conducted at the Category IV heat output rate to validate that

the appliance is capable of producing the manufacturer's rated heat output capacity.

12.5.2 Test Fuel Charge Adjustment. It is acceptable to adjust the test fuel charge (*i.e.*, reposition) once during a test run if more than 60 percent of the initial test fuel charge weight has been consumed and more than 10 minutes have elapsed without a measurable (1 lb or 0. 5 kg) weight change while the operating control is in the demand mode. The time used to make this adjustment shall be less than 60 seconds.

12.5.3 Test Run Completion. The test run is completed when the remaining weight of the test fuel charge is 0.0 lb (0.0 kg). End the test run when the scale has indicated a test fuel charge weight of 0.0 lb (0.0 kg) or less for 30 seconds.

12.5.3.1 At the end of the test run, stop the particulate sampling train and overall efficiency (SLM) measurements, and record the run time, and all final measurement values.

12.5.4 Heat Output Capacity Validation. The first test run must produce a heat output rate that is within 10 percent of the manufacturer's rated heat output capacity (Category IV) throughout the test run and an average heat output rate within 5 percent of the manufacturer's rated heat output capacity. If the appliance is not capable of producing a heat output within these limits, the manufacturer's rated heat output capacity is considered not validated and testing is to be terminated. In such cases, the tests may be restarted using a lower heat output capacity if requested by the manufacturer.

12.5.5 Additional Test Runs. Using the manufacturer's rated heat output capacity as a basis, conduct a test for additional heat output categories as specified in section 4.3. It is not required to run these tests in any particular order.

12.5.6 Alternative Heat Output Rate for Category I. If an appliance cannot be operated in the Category I heat output range due to stopped combustion, two test runs shall be conducted at heat output rates within Category II, provided that the completed test run burn rate is no greater than the burn rate expected in home use. If this rate cannot be achieved, the test is not valid.

When the alternative heat output rate is used, the weightings for the weighted averages indicated in Table 2 shall be the average of the Category I and II weightings and shall be applied to both Category II results. The two completed runs in Category II will be deemed to meet the requirement for runs completed in both Category I and Category II. Appliances that are not capable of operation within Category II (<25 percent of maximum) cannot be evaluated by this test method. The test report must include full documentation and discussion of the attempted runs, completed rums and calculations.

12.5.6.1 Stopped Fuel Combustion. Evidence that an appliance cannot be operated at a Category I heat output rate due to stopped fuel combustion shall include documentation of two or more attempts to operate the appliance in burn rate Category I and fuel combustion has stopped prior to complete consumption of the test fuel charge. Stopped fuel combustion is evidenced when an elapsed time of 60 minutes or more has occurred without a measurable (1 lb or 0.5 kg) weight change in the test fuel charge while the appliance operating control is in the demand mode. Report the evidence and the reasoning used to determine that a test in burn rate Category I cannot be achieved. For example, two unsuccessful attempts to operate at an output rate of 10 percent of the rated output capacity are not sufficient evidence that burn rate Category I cannot be achieved. Note that section 12.5.6 requires that the completed test run burn rate can be no greater than the burn rate expected in home use. If this rate cannot be achieved, the test is not valid.

12.5.7 Appliance Overheating. Appliances shall be capable of operating in all heat output categories without overheating to be rated by this test method. Appliance overheating occurs when the rate of heat withdrawal from the appliance is lower than the rate of heat production when the unit control is in the idle mode. This condition results in the water in the appliance continuing to increase in temperature well above the upper limit setting of the operating control. Evidence of overheating includes: 1 hour or more of appliance water temperature increase above the upper temperature set-point of the operating control, exceeding the temperature limit of a safety control device (independent from the operating control), boiling water in a non-pressurized system or activation of a pressure or temperature relief valve in a pressurized system.

12.6 Additional Test Runs. The testing laboratory may conduct more than one test run in each of the heat output categories specified in section 4.3.1. If more than one test run is conducted at a specified heat output rate, the results from at least two-thirds of the test runs in that heat output rate category shall be used in calculating the weighted average emission rate (See section 14.1.14). The measurement data and results of all test runs shall be reported regardless of which values are used in calculating the weighted average emission rate.

13.0 Calculation of Results

13.1 Nomenclature

E_T—Total particulate emissions for the full test run as determined per ASTM E2515–11 (IBR, see §60.17) in grams

$E_{g/MJ}$—Emissions rate in grams per megajoule of heat output
$E_{lb/mmBtu}$ output—Emissions rate in pounds per million Btu of heat output
$E_{g/kg}$—Emissions factor in grams per kilogram of dry fuel burned
$E_{g/hr}$—Emissions factor in grams per hour
HHV—Higher heating value of fuel = 8600 Btu/lb (19.990 MJ/kg)
LHV—Lower heating value of fuel = 7988 Btu/lb (18.567 MJ/kg)
ΔT—Temperature difference between water entering and exiting the heat exchanger
Q_{out}—Total heat output in BTU's (megajoules)
Q_{in}—Total heat input available in test fuel charge in BTU (megajoules)
M—Mass flow rate of water in lb/min (kg/min)
V_i—Volume of water indicated by a totalizing flow meter at the ith reading in gallons (liters)
V_f—Volumetric flow rate of water in heat exchange system in gallons per minute (liters/min)
Θ—Total length of test run in hours
ti—Data sampling interval in minutes
η_{del}—Delivered heating efficiency in percent
Fi—Weighting factor for heat output category i (See Table 2)
T1—Temperature of water at the inlet on the supply side of the heat exchanger
T2—Temperature of the water at the outlet on the supply side of the heat exchanger
T3—Temperature of water at the inlet to the load side of the heat exchanger
TIavg—Average temperature of the appliance and water at start of the test

$$TI_{avg} - (T1 + T2)/2 \text{ at the start of the test, °F} \quad \text{Eq.1}$$

TF_{avg}—Average temperature of the appliance and water at the end of the test

$$TF_{avg} - (T1 + T2)/2 \text{ at the end of the test, °F} \quad \text{Eq.2}$$

MC—Fuel moisture content in percent dry basis
MC_i—Average moisture content of individual 4 × 4 fuel pieces in percent dry basis
MC_{sp}—Moisture content of spacers assumed to be 10 percent dry basis
σ—Density of water in pounds per gallon
C_p—Specific heat of water in Btu/lb, °F
C_{steel}—Specific heat of steel (0.1 Btu/lb, °F)
W_{fuel}—Fuel charge weight in pounds (kg)
W_i—Weight of individual fuel 4 × 4 pieces in pounds (kg)
W_{sp}—Weight of all spacers used in a fuel load in pounds (kg)
W_{app}—Weight of empty appliance in pounds
W_{wa}—Weight of water in supply side of the system in pounds

13.2 After the test is completed, determine the particulate emissions E_T in accordance with ASTM E2515–11 (IBR, see §60.17).

13.3 Determine Average Fuel Load Moisture Content

$$MC_{Ave} = [[\Sigma W_i \times MC_i] + [W_{sp} \times MC_{sp}]] \div W_{fuel}, \% \quad \text{Eq. 3}$$

13.4 Determine heat input

$$Q_{in} = (W_{fuel}/(1+(MC/100))) \times HHV, BTU \quad \text{Eq. 4}$$

$$Q_{in\ LHV} = (W_{fuel}/(1+(MC/100))) \times LHV, BTU \quad \text{Eq. 5}$$

13.5 Determine Heat Output and Efficiency

13.5.1 Determine heat output as:

Q_{out} = Σ [Heat output determined for each sampling time interval] + Change in heat stored in the appliance.

$$Q_{out} = \left[\sum (C_{pi} \bullet \Delta T_i \bullet \dot{M}_i \bullet t_i)\right] + (W_{app} \bullet C_{Steel} + C_{pa} W_{water}) \bullet (TF_{avg} - TI_{avg}), \text{ BTU} \quad \text{Eq. 6}$$

NOTE: The subscript (i) indicates the parameter value for sampling time interval t_i.

M_i = Mass flow rate = gal/min × density of water (lb/gal) = lb/min

$$M_i = V_{fi} \cdot \sigma_i, \text{ lb/min} \quad \text{Eq. 7}$$

$$\Sigma_i = (62.56 + (-.0003413 \text{ x } T3_i) + (-.00006225 \text{ x } T3_i^2)) \, 0.1337, \text{ lbs/gal} \quad \text{Eq. 8}$$

$$C_p = 1.0014 + (-.000003485 \text{ x } T3_i) \text{ Btu/lb, } ^oF \quad \text{Eq. 9}$$

C_{steel} = 0.1 Btu/lb, ° F

$$C_{pa} = 1.0014 + (-.000003485 \text{ X } (TI_{avg} + TF_{avg})/2), \text{ Btu/lb-}^oF \quad \text{Eq. 10}$$

$$V_{fi} = (V_i - V_{i-1})/(t_i - t_{i-1}), \text{ gal/min} \quad \text{Eq. 11}$$

NOTE: Vi is the total water volume at the end of interval i and Vi-1 is the total water volume at the beginning of the time interval. This calculation is necessary when a totalizing type water meter is used.

13.5.2 Determine heat output rate as:

$$\text{Heat Output Rate} = Q_{out}/\Theta, \text{ BTU/hr} \quad \text{Eq. 12}$$

13.5.3 Determine emission rates and emission factors as:

$$E_{g/MJ} = E_T/(Q_{out} \text{ x } 0.001055), \text{ g/MJ} \quad \text{Eq. 13}$$

$$E_{lb/MM \text{ BTU output}} = (E_T/453.59)/(Q_{output} \text{ x } 10^{-6}), \text{ lb/mmBtu Out} \quad \text{Eq. 14}$$

$$E_{g/kg} = E_T/(W_{fuel}/(1+MC/100)), \text{ g/dry kg} \quad \text{Eq, 15}$$

$$E_{g/hr} = E_T/\Theta, \text{ g/hr} \quad \text{Eq. 16}$$

13.5.4 Determine delivered efficiency as:

$$\eta_{del} = (Q_{out}/Q_{in}) \times 100, \% \quad \text{Eq. 17}$$

$$\eta_{del\ LHV} = (Q_{out}/Q_{in\ LHV}) \times 100, \% \quad \text{Eq. 18}$$

13.5.5 Determine η_{SLM}—Overall Efficiency (SLM) using Stack Loss

For determination of the average overall thermal efficiency (η_{SLM}) for the test run, use the data collected over the full test run and the calculations in accordance with CSA B415.1–10 (IBR, see §60.17), clause 13.7 except for 13.7.2 (e), (f), (g), and (h), use the following average fuel properties for oak: percent C = 50.0, percent H = 6.6, percent O = 43.2, percent ash = 0.2 percent. The averaging period for determination of efficiency by the stack loss method allows averaging over 10 minute time periods for flue gas temperature, flue gas CO_2, and flue gas CO for the determination of the efficiency. However, under some cycling conditions the ''on'' period may be short relative to this 10 minute period. For this reason, during cycling operation the averaging period for these parameters may not be longer than the burner on period divided by 10. The averaging period need not be shorter than one minute. During the off period, under cycling operation, the averaging periods specified may be used. Where short averaging times are used, however, the averaging period for fuel consumption may still be at 10 minutes. This average wood consumption rate shall be applied to all of the smaller time intervals included.

13.5.5.1 Whenever the CSA B415.1–10 (IBR, see §60.17) overall efficiency is found to be lower than the overall efficiency based on load side measurements, as determined by Eq. 16 of this method, section 14.1.7 of the test report must include a discussion of the reasons for this result.

13.6 Weighted Average Emissions and Efficiency

13.6.1 Determine the weighted average emission rate and delivered efficiency from the individual tests in the specified heat output categories. The weighting factors (Fi) are derived from an analysis of ASHRAE bin data which provides details of normal building heating requirements in terms of percent of design capacity and time in a particular capacity range—or ''bin''—over the course of a heating season. The values used in this method represent an average of data from several cities located in the northern United States.

$$\text{Weighted average delivered efficiency: } \eta_{avg} = \Sigma\, \eta_i \times F_i, \% \quad \text{Eq. 19}$$

$$\text{Weighted average emissions: } E_{avg} = \Sigma E_i \times F_i, \% \quad \text{Eq. 20}$$

13.7 Average Heat Output ($Q_{out\text{-}8hr}$) and Efficiency (($\eta_{avg\text{-}8hr}$) for 8 hour burn time.

13.7.1 Units tested under this standard typically require infrequent fuelling, 8 to 12 hours intervals being typical. Rating unit's based on an average output sustainable over an 8 hour duration will assist consumers in appropriately sizing units to match the theoretical heat demand of their application.

13.7.2 Calculations:

$$Q_{out\text{-}8hr} = X1 + \{ (8 - Y1) \times [(X2 - X1) / (Y2 - Y1)] \}, \% \quad \text{Eq. 21}$$

$$\eta_{avg\text{-}8hr} = \eta_{del1} + \{ (8 - Y1) \times [(\eta_{del2} - \eta_{del1}) / (Y2 - Y1)] \}, \% \quad \text{Eq. 22}$$

Where:

Y1 = Test duration just above 8 hrs
Y2 = Test duration just below 8 hrs
X1 = Actual load for duration Y1
X2 = Actual load for duration Y2
η_{del1} = Average delivered efficiency for duration Y1
η_{del2} = Average delivered efficiency for duration Y2

13.7.2.1 Determine the test durations and actual load for each category as recorded in Table 1A.

13.7.2.2 Determine the data point that has the nearest duration greater than 8 hrs.

X1 = Actual load,
Y1 = Test duration, and
η_{del1} = Average delivered efficiency for this data point

13.7.2.3 Determine the data point that has the nearest duration less than 8 hours.

X2 = Actual load,
Y2 = Test duration, and
η_{del2} = Average delivered efficiency for this data point

13.7.2.4 Example:

CATEGORY ACTUAL LOAD DURATION
[Category Actual Load Duration ηdel]

	(Btu/Hr)	(Hr)	(%)
1	15,000	10.2	70.0
2	26,000	8.4	75.5
3	50,000	6.4	80.1
4	100,000	4.7	80.9

Category 2 duration is just above 8 hours, therefore: X1 = 26,000 Btu/hr, η_{del1} = 75.5% and Y1 = 8.4 hrs

Category 3 duration is just below 8 hours, therefore: X2 = 50,000 Btu/hr, η_{del2} = 80.1% and Y2 = 6.4 hrs

$Q_{out\text{-}8hr}$ = 26,000 + {(8—8.4) × [(50,000—26,000)/(6.4—8.4)]} = 30,800 BTU/hr

$\eta_{avg\text{-}8hr}$ = 75.5 + {(8—8.4) × [(80.1—75.5)/(6.4—8.4)]} = 76.4%

13.8 Carbon Monoxide Emissions

For each minute of the test period, the carbon monoxide emission rate shall be calculated as:

$$CO_{g/min} = Q_{std} \cdot CO_s \cdot 3.30\text{x}10^{-5} \qquad \text{Eq. 23}$$

Total CO emissions for each of the three test periods (CO_{-1}, CO_{-2}, CO_{-3}) shall be calculated as the sum of the emission rates for each of the 1 minute intervals.

Total CO emission for the test run, CO_T, shall be calculated as the sum of CO_{-1}, CO_{-2}, and CO_{-3}.

14.0 Report

14.1.1 The report shall include the following.

14.1.2 Name and location of the laboratory conducting the test.

14.1.3 A description of the appliance tested and its condition, date of receipt and dates of tests.

14.1.4 A statement that the test results apply only to the specific appliance tested.

14.1.5 A statement that the test report shall not be reproduced except in full, without the written approval of the laboratory.

14.1.6 A description of the test procedures and test equipment including a schematic or other drawing showing the location of all required test equipment. Also, a description of test fuel sourcing, handling and storage practices shall be included.

14.1.7 Details of deviations from, additions to or exclusions from the test method, and their data quality implications on the test results (if any), as well as information on specific test conditions, such as environmental conditions.

14.1.8 A list of participants and observers present for the tests.

14.1.9 Data and drawings indicating the fire box size and location of the fuel charge.

14.1.10 Drawings and calculations used to determine firebox volume.

14.1.11 Information for each test run fuel charge including piece size, moisture content, and weight.

14.1.12 All required data for each test run shall be provided in spreadsheet format. Formulae used for all calculations shall be accessible for review.

14.1.13 Test run duration for each test.

14.1.14 Calculated results for delivered efficiency at each burn rate and the weighted average emissions reported as total emissions in grams, pounds per mm Btu of delivered heat, grams per MJ of delivered heat, grams per kilogram of dry fuel and grams per hour. Results shall be reported for each heat output category and the weighted average.

14.1.15 Tables 1A, 1B, 1C and Table 2 must be used for presentation of results in test reports.

14.1.16 A statement of the estimated uncertainty of measurement of the emissions and efficiency test results.

14.1.17 Raw data, calibration records, and other relevant documentation shall be retained by the laboratory for a minimum of 7 years.

15.0 Precision and Bias

15.1 Precision—It is not possible to specify the precision of the procedure in Method 28WHH because the appliance operation and

fueling protocols and the appliances themselves produce variable amounts of emissions and cannot be used to determine reproducibility or repeatability of this measurement method.

15.2 Bias—No definitive information can be presented on the bias of the procedure in Method 28WHH for measuring solid fuel burning hydronic heater emissions because no material having an accepted reference value is available.

16.0 Keywords

16.1 Solid fuel, hydronic heating appliances, wood-burning hydronic heaters.

Table 1A. Data Summary Part A

						O	W_{fuel}	MC_{ave}	Q_{in}	Q_{out}
Category	Run No	Load % Capacity	Target Load	Actual Load	Act Load	Test Duration	Wood Wt	Wood Moisture	Heat Input	Heat Output
			BTU/hr	BTU/hr	% of max	hrs	lb	% DB	BTU	BTU
I		< 15% of max								
II		16-24% of max								
III		25-50% of max								
IV		Max capacity								

Table 1B. Data Summary Part B

			T2 Min	E-	E	E	$E_{g/hr}$	$E_{g/kg}$	η_{del}	η_{SLM}
Category	Run No	Load % Capacity	Min Return Water Temp	Total PM Emissions	PM Output Based	PM Output Based	PM Rate	PM Factor	Delivered Efficiency	Stack Loss Efficiency
			°F	g	$lb_{MMBTU\ Out}$	g/MJ	g/hr	g/kg	%	%
I		< 15% of max								
II		16-24% of max								
III		25-50% of max								
IV		Max capacity								

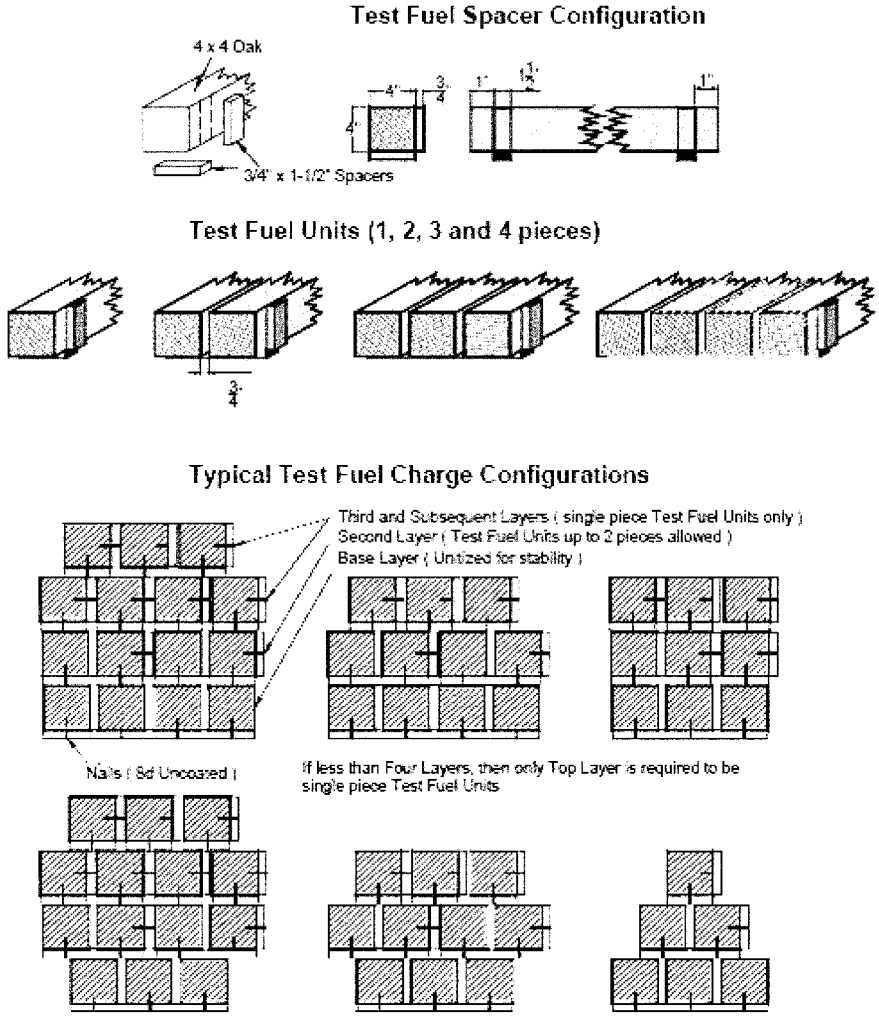
Table 1C: Hangtag Information (optional)

MANUFACTURER:			
MODEL NUMBER:			
MAXIMUM OUTPUT RATING:	Qmax		BTU/HR
ANNUAL EFFICIENCY RATING:	N_{avg}		(Using higher heating value)
PARTICLE EMISSIONS:	E_{avg}		GRAMS/HR (average)
			LBS/MILLION BTU OUTPUT
CARBON MONOXIDE:	COg/MIN		GRAMS/MINUTE

Table 2. Annual Weighting

Category	Weighting Factor (F_i)	$\eta_{del,i} \times F_i$	$E_{g/MJ,i} \times F_i$	$E_{g/kg,i} \times F_i$	$E_{lb/mmBtu\ Out,i} \times F_i$	$E_{g/hr,i} \times F_i$
I	0.437					
II	0.238					
III	0.275					
IV	0.050					
Totals	1.000					

Figure 1. Typical Test Fuel Piece



TEST METHOD 28WHH FOR CERTIFICATION OF CORD WOOD-FIRED HYDRONIC HEATING APPLIANCES WITH PARTIAL THERMAL STORAGE: MEASUREMENT OF PARTICULATE MATTER (PM) AND CARBON MONOXIDE (CO) EMISSIONS AND HEATING EFFICIENCY OF WOOD-FIRED HYDRONIC HEATING APPLIANCES WITH PARTIAL THERMAL STORAGE

1.0 Scope and Application

1.1 This test method applies to wood-fired hydronic heating appliances with heat storage external to the appliance. The units typically transfer heat through circulation of a liquid heat exchange media such as water or a water-antifreeze mixture. Throughout this document, the term ''water'' will be used to denote any of the heat transfer liquids approved for use by the manufacturer.

1.2 The test method measures PM and CO emissions and delivered heating efficiency at specified heat output rates referenced against the appliance's rated heating capacity as specified by the manufacturer and verified under this test method.

1.3 PM emissions are measured by the dilution tunnel method as specified in the EPA Method 28WHH and the standards referenced therein with the exceptions noted in section 12.5.9. Delivered efficiency is measured by determining the fuel energy input and appliance output. Heat output is determined through measurement of the flow rate and temperature change of water circulated through a heat exchanger external to the appliance and the increase in energy of the external storage. Heat input is determined from the mass of dry wood fuel and its higher heating value (HHV). Delivered efficiency does not attempt to account for pipeline loss.

1.4 Products covered by this test method include both pressurized and non-pressurized hydronic heating appliances intended to be fired with wood and for which the manufacturer specifies for indoor or outdoor installation. The system, which includes the heating appliance and external storage, is commonly connected to a heat exchanger by insulated pipes and normally includes a pump to circulate heated liquid. These systems are used to heat structures such as homes, barns and greenhouses. They also provide heat for domestic hot water, spas and swimming pools.

1.5 Distinguishing features of products covered by this standard include:

1.5.1 The manufacturer specifies the application for either indoor or outdoor installation.

1.5.2 A firebox with an access door for hand loading of fuel.

1.5.3 Typically an aquastat mounted as part of the appliance that controls combustion air supply to maintain the liquid in the appliance within a predetermined temperature range provided sufficient fuel is available in the firebox. The appliance may be equipped with other devices to control combustion.

1.5.4 A chimney or vent that exhausts combustion products from the appliance.

1.5.5 A liquid storage system, typically water, which is not large enough to accept all of the heat produced when a full load of wood is burned and the storage system starts a burn cycle at 125 °F.

1.5.6 The heating appliances require external thermal storage and these units will only be installed as part of a system which includes thermal storage. The manufacturer specifies the minimum amount of thermal storage required. However, the storage system shall be large enough to ensure that the boiler (heater) does not cycle, slumber, or go into an off-mode when operated in a Category III load condition (See section 4.3).

1.6 The values stated are to be regarded as the standard whether in I–P or SI units. The values given in parentheses are for information only.

2.0 Summary of Method and References

2.1 PM and CO emissions are measured from a wood–fired hydronic heating appliance burning a prepared test fuel charge in a test facility maintained at a set of prescribed conditions. Procedures for determining heat output rates, PM and CO emissions, and efficiency and for reducing data are provided.

2.2 Referenced Documents

2.2.1 EPA Standards

2.2.1.1 Method 28 Certification and Auditing of Wood Heaters

2.2.1.2 Method 28WHH Measurement of Particulate Emissions and Heating Efficiency of Wood-Fired Hydronic Heating Appliances and the Standards Referenced therein.

2.2.2 Other Standards

2.2.2.1 CSA–B415.1–10 *Performance Testing of Solid-Fuel-Burning Heating Appliances*

3.0 Terminology

3.1 Definitions

3.1.1 Hydronic Heating—A heating system in which a heat source supplies energy to a liquid heat exchange media such as water that is circulated to a heating load and returned to the heat source through pipes.

3.1.2 Aquastat—A control device that opens or closes a circuit to control the rate of fuel consumption in response to the temperature of the heating media in the heating appliance.

3.1.3 Delivered Efficiency—The percentage of heat available in a test fuel charge that is delivered to a simulated heating load or the storage system as specified in this test method.

3.1.4 Emission Factor—The emission of a pollutant expressed in mass per unit of energy (typically) output from the boiler/heater.

3.1.5 Emission Index—The emission of a pollutant expressed in mass per unit mass of fuel used.

3.1.6 Emission Rate—The emission of a pollutant expressed in mass per unit time

3.1.7 Manufacturer's Rated Heat Output Capacity—The value in Btu/hr (MJ/hr) that the manufacturer specifies that a particular model of hydronic heating appliance is capable of supplying at its design capacity as verified by testing, in accordance with section 12.5.4.

3.1.8 Heat Output Rate—The average rate of energy output from the appliance during a specific test period in Btu/hr (MJ/hr).

3.1.9 Firebox—The chamber in the appliance in which the test fuel charge is placed and combusted.

3.1.10 NIST—National Institute of Standards and Technology.

3.1.11 Test Fuel Charge—The collection of test fuel placed in the appliance at the start of the emission test run.

3.1.12 Test Run—An individual emission test which encompasses the time required to consume the mass of the test fuel charge. The time of the test run also considers the time for the energy to be drawn from the thermal storage.

3.1.13 Test Run Under ''Cold-to-Cold'' Condition—Under this test condition the test fuel is added into an empty chamber along with kindling and ignition materials (paper). The boiler/heater at the start of this test is typically 125° to 130 °F.

3.1.14 Test Run Under ''Hot-to-Hot'' Condition—Under this test condition the test fuel is added onto a still-burning bed of charcoals produced in a pre-burn period. The boiler/heater water is near its operating control limit at the start of the test.

3.1.15 Overall Efficiency, also known as Stack Loss Efficiency—The efficiency for each test run as determined using the CSA B415.1–10 (IBR, see §60.17) stack loss method (SLM).

3.1.16 Phases of a Burn Cycle—The ''startup phase'' is defined as the period from the start of the test until 15 percent of the test fuel charge is consumed. The ''steady-state phase'' is defined as the period from the end of the startup phase to a point at which 80 percent of the test fuel charge is consumed. The ''end phase'' is defined as the time from the end of the steady-state period to the end of the test.

3.1.17 Thermopile—A device consisting of a number of thermocouples connected in series, used for measuring differential temperature.

3.1.18 Slumber Mode—This is a mode in which the temperature of the water in the boiler/heater has exceeded the operating control limit and the control has changed the boiler/heater fan speed, dampers, and/or other operating parameters to minimize the heat output of the boiler/heater.

4.0 Summary of Test Method

4.1 Dilution Tunnel. Emissions are determined using the ''dilution tunnel'' method specified in EPA Method 28WHH and the standards referenced therein. The flow rate in the dilution tunnel is maintained at a constant level throughout the test cycle and accurately measured. Samples of the dilution tunnel flow stream are extracted at a constant flow rate and drawn through high efficiency filters. The filters are dried and weighed before and after the test to determine the emissions collected and this value is multiplied by the ratio of tunnel flow to filter flow to determine the total particulate emissions produced in the test cycle.

4.2 Efficiency. The efficiency test procedure takes advantage of the fact that this type of system delivers heat through circulation of the heated liquid (water) from the system to a remote heat exchanger (*e.g.* baseboard radiators in a room) and back to the system. Measurements of the cooling water temperature difference as it enters and exits the test system heat exchanger along with the measured flow rate allow for an accurate determination of the useful heat output of the appliance. Also included in the heat output is the change in the energy content in the storage system during a test run. Energy input to the appliance during the test run is determined by weight of the test fuel charge, adjusted for moisture content, multiplied by the higher heating value. Additional measurements of the appliance weight and temperature at the beginning and end of a test cycle are used to correct for heat stored in the appliance. Overall efficiency (SLM) is determined using the CSA B415.1–10 (IBR, see §60.17) stack loss method for data quality assurance purposes.

4.3 Operation. Four test categories are defined for use in this method. These are:

4.3.1 Category I: A heat output of 15 percent or less of manufacturer's rated heat output capacity.

4.3.2 Category II: A heat output of 16 percent to 24 percent of manufacturer's rated heat output capacity.

4.3.3 Category III: A heat output of 25 percent to 50 percent of manufacturer's rated heat output capacity.

4.3.4 Category IV: Manufacturer's Rated Heat Output Capacity. These heat output categories refer to the output from the system by way of the load heat exchanger installed for the test. The output from just the boiler/heater part of the system may be higher for all or part of a test, as part of this boiler/heater output goes to storage.

For the Category III and IV runs, appliance operation is conducted on a hot-to-hot test

cycle meaning that the appliance is brought to operating temperature and a coal bed is established prior to the addition of the test fuel charge and measurements are made for each test fuel charge cycle. The measurements are made under constant heat draw conditions within pre-determined ranges. No attempt is made to modulate the heat demand to simulate an indoor thermostat cycling on and off in response to changes in the indoor environment.

For the Category I and II runs, the unit is tested with a ''cold start.'' At the manufacturer's option, the Category II and III runs may be waived and it may be assumed that the particulate emission values and efficiency values determined in the startup, steady-state, and end phases of Category I are applicable in Categories II and III for the purpose of determining the annual averages in lb/mmBtu and g/MJ (See section 13). For the annual average in g/hr, the length of time for stored heat to be drawn from thermal storage shall be determined for the test load requirements of the respective category.

All test operations and measurements shall be conducted by personnel of the laboratory responsible for the submission of the test report.

5.0 Significance and Use

5.1 The measurement of particulate matter emission and CO rates is an important test method widely used in the practice of air pollution control.

5.1.1 These measurements, when approved by state or federal agencies, are often required for the purpose of determining compliance with regulations and statutes.

5.1.2 The measurements made before and after design modifications are necessary to demonstrate the effectiveness of design changes in reducing emissions and make this standard an important tool in manufacturers' research and development programs.

5.2 Measurement of heating efficiency provides a uniform basis for comparison of product performance that is useful to the consumer. It is also required to relate emissions produced to the useful heat production.

5.3 This is a laboratory method and is not intended to be fully representative of all actual field use. It is recognized that users of hand-fired, wood-burning equipment have a great deal of influence over the performance of any wood-burning appliance. Some compromises in realism have been made in the interest of providing a reliable and repeatable test method.

6.0 Test Equipment

6.1 Scale. A platform scale capable of weighing the boiler/heater under test and associated parts and accessories when completely filled with water to an accuracy of ±1.0 pound (±0.5 kg) and a readout resolution of ±0.2 pound (±0.1 kg).

6.2 Heat Exchanger. A water-to-water heat exchanger capable of dissipating the expected heat output from the system under test.

6.3 Water Temperature Difference Measurement. A Type—T 'special limits' thermopile with a minimum of 5 pairs of junctions shall be used to measure the temperature difference in water entering and leaving the heat exchanger. The temperature difference measurement uncertainty of this type of thermopile is equal to or less than ±0.50 °F (±0.25 °C). Other temperature measurement methods may be used if the temperature difference measurement uncertainty is equal to or less than ±0.50 °F (±0.25 °C). This measurement uncertainty shall include the temperature sensor, sensor well arrangement, piping arrangements, lead wire, and measurement/recording system. The response time of the temperature measurement system shall be less than half of the time interval at which temperature measurements are recorded.

6.4 Water Flow Meter. A water flow meter shall be installed in the inlet to the load side of the heat exchanger. The flow meter shall have an accuracy of ±1 percent of measured flow.

6.4.1 Optional—Appliance Side Water Flow Meter. A water flow meter with an accuracy of ±1 percent of the flow rate is recommended to monitor supply side water flow rate.

6.5 Optional Recirculation Pump. Circulating pump used during test to prevent stratification, in the boiler/heater, of liquid being heated.

6.6 Water Temperature Measurement. Thermocouples or other temperature sensors to measure the water temperature at the inlet and outlet of the load side of the heat exchanger must meet the calibration requirements specified in 10.1 of this method.

6.7 Lab Scale. For measuring the moisture content of wood slices as part of the overall wood moisture determination. Accuracy of ±0.01 pounds.

6.8 Flue Gas Temperature Measurement. Must meet the requirements of CSA B415.1–10 (IBR, see §60.17), clause 6.2.2.

6.9 Test Room Temperature Measurement. Must meet the requirements of CSA B415.1–10 (IBR, see §60.17), clause 6.2.1.

6.10 Flue Gas Composition Measurement. Must meet the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 6.3.1 through 6.3.3.

6.11 Dilution Tunnel CO Measurement. In parallel with the flue gas composition measurements, the CO concentration in the dilution tunnel shall also be measured and reported at time intervals not to exceed one minute. This analyzer shall meet the zero and span drift requirements of CSA B415.1–10 (IBR, see §60.17). In addition the measurement repeatability shall be better than ±15

ppm over the range of CO levels observed in the dilution tunnel.

7.0 Safety

7.1 These tests involve combustion of wood fuel and substantial release of heat and products of combustion. The heating system also produces large quantities of very hot water and the potential for steam production and system pressurization. Appropriate precautions must be taken to protect personnel from burn hazards and respiration of products of combustion.

8.0 Sampling, Test Specimens and Test Appliances

8.1 Test specimens shall be supplied as complete appliances, as described in marketing materials, including all controls and accessories necessary for installation in the test facility. A full set of specifications, installation and operating instructions, and design and assembly drawings shall be provided when the product is to be placed under certification of a third-party agency. The manufacturer's written installation and operating instructions are to be used as a guide in the set-up and testing of the appliance and shall be part of the test record.

8.2 The size, connection arrangement, and control arrangement for the thermal storage shall be as specified in the manufacturer's documentation. It is not necessary to use the specific storage system that the boiler/heater will be marketed with. However, the capacity of the system used in the test cannot be greater than that specified as the minimum allowable for the boiler/heater.

8.3 All system control settings shall be the as-shipped, default settings. These default settings shall be the same as those communicated in a document to the installer or end user. These control settings and the documentation of the control settings as to be provided to the installer or end user shall be part of the test record.

8.4 Where the manufacturer defines several alternatives for the connection and loading arrangement, one shall be defined in the appliance documentation as the default or standard installation. It is expected that this will be the configuration for use with a simple baseboard heating system. This is the configuration to be followed for these tests. The manufacturer's documentation shall define the other arrangements as optional or alternative arrangements.

9.0 Preparation of Test Equipment

9.1 The appliance is to be placed on a scale capable of weighing the appliance fully loaded with a resolution of ±0.2 lb (0.1 kg).

9.2 The appliance shall be fitted with the type of chimney recommended or provided by the manufacturer and extending to 15 ±0.5 feet (4.6 ±0.15 m) from the upper surface of the scale. If no flue or chimney system is recommended or provided by the manufacturer, connect the appliance to a flue of a diameter equal to the flue outlet of the appliance. The flue section from the appliance flue collar to 8 ±0.5 feet above the scale shall be single wall stove pipe and the remainder of the flue shall be double wall insulated class A chimney.

9.3 Optional Equipment Use

9.3.1 A recirculation pump may be installed between connections at the top and bottom of the appliance to minimize thermal stratification if specified by the manufacturer. The pump shall not be installed in such a way as to change or affect the flow rate between the appliance and the heat exchanger.

9.3.2 If the manufacturer specifies that a thermal control valve or other device be installed and set to control the return water temperature to a specific set point, the valve or other device shall be installed and set per the manufacturer's written instructions.

9.4 Prior to filling the boiler/heater with water, weigh and record the appliance mass.

9.5 Heat Exchanger

9.5.1 Plumb the unit to a water-to-water heat exchanger with sufficient capacity to draw off heat at the maximum rate anticipated. Route hoses and electrical cables and instrument wires in a manner that does not influence the weighing accuracy of the scale as indicated by placing dead weights on the platform and verifying the scale's accuracy.

9.5.2 Locate thermocouples to measure the water temperature at the inlet and outlet of the load side of the heat exchanger.

9.5.3 Install a thermopile (or equivalent instrumentation) meeting the requirements of section 6.3 to measure the water temperature difference between the inlet and outlet of the load side of the heat exchanger

9.5.4 Install a calibrated water flow meter in the heat exchanger load side supply line. The water flow meter is to be installed on the cooling water inlet side of the heat exchanger so that it will operate at the temperature at which it is calibrated.

9.5.5 Place the heat exchanger in a box with 2 in. (50 mm) of expanded polystyrene (EPS) foam insulation surrounding it to minimize heat losses from the heat exchanger.

9.5.6 The reported efficiency and heat output rate shall be based on measurements made on the load side of the heat exchanger.

9.5.7 Temperature instrumentation per section 6.6 shall be installed in the appliance outlet and return lines. The average of the outlet and return water temperature on the supply side of the system shall be considered the average appliance temperature for calculation of heat storage in the appliance (TF_{avg} and TI_{avg}). Installation of a water flow meter in the supply side of the system is optional.

9.6 Storage Tank. The storage tank shall include a destratification pump as illustrated in Figure 1. The pump will draw from the bottom of the tank and return to the top as illustrated. Temperature sensors (TS1 and TS2 in Figure 1) shall be included to measure the temperature in the recirculation loop. The valve plan in Figure 1 allows the tank recirculation loop to operate and the boiler/heater-to-heat exchanger loop to operate at the same time but in isolation. This would typically be done before the start of a test or following completion of a test to determine the end of test average tank temperature. The nominal flow rate in the storage tank recirculation loop can be estimated based on pump manufacturers' performance curves and any significant restriction in the recirculation loop.

9.7 Fill the system with water. Determine the total weight of the water in the appliance when the water is circulating. Verify that the scale indicates a stable weight under operating conditions. Make sure air is purged properly.

10.0 Calibration and Standardization

10.1 Water Temperature Sensors. Temperature measuring equipment shall be calibrated before initial use and at least semiannually thereafter. Calibrations shall be in compliance with National Institute of Standards and Technology (NIST) Monograph 175, Standard Limits of Error.

10.2 Heat Exchanger Load Side Water Flow Meter.

10.2.1 The heat exchanger load side water flow meter shall be calibrated within the flow range used for the test run using NIST-traceable methods. Verify the calibration of the water flow meter before and after each test run and at least once during each test run by comparing the water flow rate indicated by the flow meter to the mass of water collected from the outlet of the heat exchanger over a timed interval. Volume of the collected water shall be determined based on the water density calculated from section 13, Eq. 12, using the water temperature measured at the flow meter. The uncertainty in the verification procedure used shall be 1 percent or less. The water flow rate determined by the collection and weighing method shall be within 1 percent of the flow rate indicated by the water flow meter.

10.3 Scales. The scales used to weigh the appliance and test fuel charge shall be calibrated using NIST-traceable methods at least once every 6 months.

10.4 Flue Gas Analyzers—In accordance with CSA B415.1–10 (IBR, see §60.17), clause 6.8.

11.0 Conditioning

11.1 Prior to testing, an appliance is to be operated for a minimum of 50 hours using a medium heat draw rate. The conditioning may be at the manufacturer's facility prior to the certification test. If the conditioning is at the certification test laboratory, the pre-burn for the first test can be included as part of the conditioning requirement. If conditioning is included in pre-burn, then the appliance shall be aged with fuel meeting the specifications outlined in section 12.2 with a moisture content between 19 and 25 percent on a dry basis. Operate the appliance at a medium heat output rate (Category II or III) for at least 10 hours for non-catalytic appliances and 50 hours for catalytic appliances. Record and report hourly flue gas exit temperature data and the hours of operation. The aging procedure shall be conducted and documented by a testing laboratory.

12.0 Procedure

12.1 Appliance Installation. Assemble the appliance and parts in conformance with the manufacturer's written installation instructions. Clean the flue with an appropriately sized, wire chimney brush before each certification test series.

12.2 Fuel. Test fuel charge fuel shall be red (*Quercus ruba L.*) or white (*Quercus Alba*) oak 19 to 25 percent moisture content on a dry basis. Piece length shall be 80 percent of the firebox depth rounded down to the nearest 1 inch (25mm) increment. For example, if the firebox depth is 46 inches (1168mm) the piece length would be 36 inches (46 inches × 0.8 = 36.8 inches, rounded down to 36 inches). Pieces are to be placed in the firebox parallel to the longest firebox dimension. For fireboxes with sloped surfaces that create a non-uniform firebox length, the piece length shall be adjusted for each layer based on 80 percent of the length at the level where the layer is placed. The test fuel shall be cord wood with cross section dimensions and weight limits as defined in CSA B415.1–10 (IBR, see §60.17), section 8.3, Table 4. The use of dimensional lumber is not allowed.

12.2.1 Select three pieces of cord wood from the same batch of wood as the test fuel and the same weight as the average weight of the pieces in the test load ±1.0 lb. From each of these three pieces, cut three slices. Each slice shall be ½ inch to ¾ inch thick. One slice shall be cut across the center of the length of the piece. The other two slices shall be cut half way between the center and the end. Immediately measure the mass of each piece in pounds. Dry each slice in an oven at 220 °F for 24 hours or until no further weight change occurs. The slices shall be arranged in the oven so as to provide separation between faces. Remove from the oven and measure the mass of each piece again as soon as practical, in pounds.

The moisture content of each slice, on a dry basis, shall be calculated as:

$$MC_{slice} = 100 \cdot \frac{(W_{SliceWet} - W_{SliceDry})}{W_{SliceDry}}$$

Where:

$W_{SliceWet}$ = weight of the slice before drying in pounds

$W_{SliceDry}$ = weight of the slice after drying in pounds

MC_{Slice} = moisture content of the slice in % dry basis

The average moisture content of the entire test load (MC) shall be determined using Eq. 6. Each individual slice shall have a moisture content in the range of 18 percent to 28 percent on a dry basis. The average moisture content for the test fuel load shall be in the range of 19 percent to 25 percent. Moisture shall not be added to previously dried fuel pieces except by storage under high humidity conditions and temperature up to 100 °F. Fuel moisture measurement shall begin within 4 hours of using the fuel batch for a test. Use of a pin-type meter to estimate the moisture content prior to a test is recommended.

12.2.2 Firebox Volume. Determine the firebox volume in cubic feet. Firebox volume shall include all areas accessible through the fuel loading door where firewood could reasonably be placed up to the horizontal plane defined by the top of the loading door. A drawing of the firebox showing front, side and plan views or an isometric view with interior dimensions shall be provided by the manufacturer and verified by the laboratory. Calculations for firebox volume from computer aided design (CAD) software programs are acceptable and shall be included in the test report if used. If the firebox volume is calculated by the laboratory the firebox drawings and calculations shall be included in the test report.

12.2.3 Test Fuel charge. Test fuel charges shall be determined by multiplying the firebox volume by 10 pounds (4.54 kg) per ft^3 (28L), or a higher load density as recommended by the manufacturer's printed operating instructions, of wood (as used wet weight). Select the number of pieces of cord wood that most nearly match this target weight. However, the test fuel charge cannot be less than the target of 10 pounds (4.54 kg) per ft^3 (28L).

12.3 Sampling Equipment. Prepare the particulate emission sampling equipment as defined by EPA Method 28WHH and the standards referenced therein.

12.4 Appliance Startup. The appliance shall be fired with wood fuel of any species, size and moisture content, at the laboratory's discretion, to bring it up to operating temperature. Operate the appliance until the water is heated to the upper operating control limit and has cycled at least two times. Then remove all unburned fuel, zero the scale and verify the scales accuracy using dead weights.

12.4.1 Startup Procedure for Category III and IV Test Runs, ''Hot-to-Hot.''

12.4.1.1 Pretest t Burn Cycle. Following appliance startup (section 12.4), reload appliance with oak cord wood and allow it to burn down to the specified coal bed weight. The pre-test burn cycle fuel charge weight shall be within ±10 percent of the test fuel charge weight. Piece size and length shall be selected such that charcoalization is achieved by the time the fuel charge has burned down to the required coal bed weight. Pieces with a maximum thickness of approximately 2 inches have been found to be suitable. Charcoalization is a general condition of the test fuel bed evidenced by an absence of large pieces of burning wood in the coal bed and the remaining fuel pieces being brittle enough to be broken into smaller charcoal pieces with a metal poker. Manipulations to the fuel bed prior to the start of the test run are to be done to achieve charcoalization while maintaining the desired heat output rate. During the pre-test burn cycle and at least one hour prior to starting the test run, adjust water flow to the heat exchanger to establish the target heat draw for the test. For the first test run the heat draw rate shall be equal to the manufacturer's rated heat output capacity.

12.4.1.2 Allowable Adjustments. Fuel addition or subtractions, and coal bed raking shall be kept to a minimum but are allowed up to 15 minutes prior to the start of the test run. For the purposes of this method, coal bed raking is the use of a metal tool (poker) to stir coals, break burning fuel into smaller pieces, dislodge fuel pieces from positions of poor combustion, and check for the condition of charcoalization. Record all adjustments to and additions or subtractions of fuel, and any other changes to the appliance operations that occur during pretest ignition period. During the 15-minute period prior to the start of the test run, the wood heater loading door shall not be open more than a total of 1 minute. Coal bed raking is the only adjustment allowed during this period.

12.4.1.3 Coal Bed Weight. The appliance is to be loaded with the test fuel charge when the coal bed weight is between 10 percent and 20 percent of the test fuel charge weight. Coals may be raked as necessary to level the coal bed but may only be raked and stirred

once between 15 to 20 minutes prior to the addition of the test fuel charge.

12.4.1.4 Storage. The Category III and IV test runs may be done either with or without the thermal storage. If thermal storage is used, the initial temperature of the storage must be 125 °F or greater at the start of the test. The storage may be heated during the pre-test burn cycle or it may be heated by external means. If thermal storage is used, prior to the start of the test run, the storage tank destratification pump, shown in Figure 1, shall be operated until the total volume pumped exceeds 1.5 times the tank volume and the difference between the temperature at the top and bottom of the storage tank (TS_1 and TS_2) is less than 1 °F. These two temperatures shall then be recorded to determine the starting average tank temperature. The total volume pumped may be based on the nominal flow rate of the destratification pump (See section 9.6). If the Category III and IV runs are done with storage, it is recognized that during the last hour of the preburn cycle the storage tank must be mixed to achieve a uniform starting temperature and cannot receive heat from the boiler/heater during this time. During this time period, the boiler/heater might cycle or go into a steady reduced output mode. (Note—this would happen, for example, in a Category IV run if the actual maximum output of the boiler/heater exceed the manufacturer's rated output.) A second storage tank may be used temporarily to enable the boiler/heater to operate during this last hour of the preburn period as it will during the test period. The temperature of this second storage tank is not used in the calculations but the return water to the boiler/heater (after mixing device if used) must be 125 °F or greater.

12.4.2 Startup Procedure for Category I and II Test Runs, ''Cold-to-Cold.''

12.4.2.1 Initial Temperatures. This test shall be started with both the boiler/heater and the storage at a minimum temperature of 125 °F. The boiler/heater maximum temperature at the start of this test shall be 135 °F. The boiler/heater and storage may be heated through a pre-burn or it may be heated by external means.

12.4.2.2 Firebox Condition at Test Start. Prior to the start of this test remove all ash and charcoal from the combustion chamber(s). The loading of the test fuel and kindling should follow the manufacturer's recommendations, subject to the following constraints: Up to 10 percent kindling and paper may be used which is in addition to the fuel load. Further, up to 10 percent of the fuel load (*i.e.*, included in the 10 lb/ft^3) may be smaller than the main fuel. This startup fuel shall still be larger than 2 inches.

12.4.2.3 Storage. The Category I and II test runs shall be done with thermal storage. The initial temperature of the storage must be 125 °F or greater at the start of the test. The storage may be heated during the pretest burn cycle or it may be heated by external means. Prior to the start of the test run, the storage tank destratification pump, shown in Figure 1, shall be operated until the total volume pumped exceeds 1.5 times the tank volume and the difference between the temperature at the top and bottom of the storage tank (TS_1 and TS_2) is less than 1 °F. These two temperatures shall then be recorded to determine the starting average tank temperature. The total volume pumped may be based on the nominal flow rate of the destratification pump (See section 9.6).

12.5 Test Runs. For all test runs, the return water temperature to the hydronic heater must be equal to or greater than 120 °F (this is lower than the initial tank temperature to allow for any pipeline losses). Where the storage system is used, flow of water from the boiler/heater shall be divided between the storage tank and the heat exchanger such that the temperature change of the circulating water across the heat exchanger shall be 30 ±5 °F, averaged over the entire test run. This is typically adjusted using the system valves.

Complete a test run in each heat output rate category, as follows:

12.5.1 Test Run Start. For Category III and IV runs: Once the appliance is operating normally and the pretest coal bed weight has reached the target value per section 12.4.1, tare the scale and load the full test charge into the appliance. Time for loading shall not exceed 5 minutes. The actual weight of the test fuel charge shall be measured and recorded within 30 minutes prior to loading. Start all sampling systems.

For Category I and II runs: Once the appliance has reached the starting temperature, tare the scale and load the full test charge, including kindling into the appliance. The actual weight of the test fuel charge shall be measured and recorded within 30 minutes prior to loading. Light the fire following the manufacturer's written normal startup procedure. Start all sampling systems.

12.5.1.1 Record all water temperatures, differential water temperatures and water flow rates at time intervals of one minute or less.

12.5.1.2 Record particulate emissions data per the requirements of EPA Method 28WHH and the standards referenced therein.

12.5.1.3 Record data needed to determine overall efficiency (SLM) per the requirements of CSA B415.1–10 (IBR, see §60.17) clauses 6.2.1, 6.2.2, 6.3, 8.5.7, 10.4.3(a), 10.4.3(f), and 13.7.9.3

12.5.1.3.1 Measure and record the test room air temperature in accordance with the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 6.2.1, 8.5.7 and 10.4.3(g).

12.5.1.3.2 Measure and record the flue gas temperature in accordance with the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 6.2.2, 8.5.7 and 10.4.3(f).

12.5.1.3.3 Determine and record the carbon monoxide (CO) and carbon dioxide (CO_2) concentrations in the flue gas in accordance with CSA B415.1–10 (IBR, see §60.17), clauses 6.3, 8.5.7 and 10.4.3(i) and (j).

12.5.1.3.4 Measure and record the test fuel weight per the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 8.5.7 and 10.4.3(h).

12.5.1.3.5 Record the test run time per the requirements of CSA B415.1–10 (IBR, see §60.17), clause 10.4.3(a).

12.5.1.3.6 Record and document all settings and adjustments, if any, made to the boiler/heater as recommended/required by manufacturer's instruction manual for different combustion conditions or heat loads. These may include temperature setpoints, under and over-fire air adjustment, or other adjustments that could be made by an operator to optimize or alter combustion. All such settings shall be included in the report for each test run.

12.5.1.4 Monitor the average heat output rate on the load side of the heat exchanger based on water temperatures and flow. If the heat output rate over a 10 minute averaging period gets close to the upper or lower limit of the target range (±5 percent), adjust the water flow through the heat exchanger to compensate. Make changes as infrequently as possible while maintaining the target heat output rate. The first test run shall be conducted at the Category IV heat output rate to validate that the appliance is capable of producing the manufacturer's rated heat output capacity.

12.5.2 Test Fuel Charge Adjustment. It is acceptable to adjust the test fuel charge (*i.e.*, reposition) once during a test run if more than 60 percent of the initial test fuel charge weight has been consumed and more than 10 minutes have elapsed without a measurable (1 lb or 0.5 kg) weight change while the operating control is in the demand mode. The time used to make this adjustment shall be less than 60 seconds.

12.5.3 Test Run Completion. For the Category III and IV, ''hot-to-hot'' test runs, the test run is completed when the remaining weight of the test fuel charge is 0.0 lb (0.0 kg). ($W_{FuelBurned} = W_{fuel}$) End the test run when the scale has indicated a test fuel charge weight of 0.0 lb (0.0 kg) or less for 30 seconds.

For the Category I and II ''cold-to-cold'' test runs, the test run is completed; and the end of a test is defined at the first occurrence of any one of the following:

(a) The remaining weight of the test fuel charge is less than 1 percent of the total test fuel weight ($W_{FuelBurned} > 0.99 \cdot W_{fuel}$);

(b) The automatic control system on the boiler/heater switches to an off mode. In this case, the boiler/heater fan (if used) is typically stopped and all air flow dampers are closed by the control system. Note that this off mode cannot be an ''overheat'' or emergency shutdown which typically requires a manual reset; or

(c) If the boiler/heater does not have an automatic off mode: After 90 percent of the fuel load has been consumed and the scale has indicated a rate of change of the test fuel charge of less than 1.0 lb/hr for a period of 10 minutes or longer. Note—this is not considered ''stopped fuel combustion,'' See section 12.5.6.1.

12.5.3.1 At the end of the test run, stop the particulate sampling train and overall efficiency (SLM) measurements, and record the run time, and all final measurement values.

12.5.3.2 At the end of the test run, continue to operate the storage tank destratification pump until the total volume pumped exceeds 1.5 times the tank volume. The maximum average of the top and bottom temperatures measured after this time may be taken as the average tank temperature at the end of the tests (TFSavg, See section 13.1). The total volume pumped may be based on the nominal flow rate of the destratification pump (See section 9.6).

12.5.3.3 For the Category I and II test runs, there is a need to determine the energy content of the unburned fuel remaining in the chamber if the remaining mass in the chamber is greater than 1 percent of the test fuel weight. Following the completion of the test, as soon as safely practical, this remaining fuel is removed from the chamber, separated from the remaining ash and weighed. This separation could be implemented with a slotted ''scoop'' or similar tool. A ¼ inch opening size in the separation tool shall be used to separate the ash and charcoal. This separated char is assigned a heating value of 12,500 Btu/lb.

12.5.4 Heat Output Capacity Validation. The first test run must produce a heat output rate that is within 10 percent of the manufacturer's rated heat output capacity (Category IV) throughout the test run and an average heat output rate within 5 percent of the manufacturer's rated heat output capacity. If the appliance is not capable of producing a heat output within these limits, the manufacturer's rated heat output capacity is considered not validated and testing is to be terminated. In such cases, the tests may be restarted using a lower heat output capacity if requested by the manufacturer. Alternatively, during the Category IV run, if the rated output cannot be maintained for a 15 minute interval, the manufacturer may elect to reduce the rated output to match the test and complete the Category IV run on this basis. The target outputs for Categories I, II, and III shall then be recalculated based on this change in rated output capacity.

12.5.5 Additional Test Runs. Using the manufacturer's rated heat output capacity

as a basis, conduct a test for additional heat output categories as specified in section 4.3. It is not required to run these tests in any particular order.

12.5.6 Alternative Heat Output Rate for Category I. If an appliance cannot be operated in the Category I heat output range due to stopped combustion, two test runs shall be conducted at heat output rates within Category II. When this is the case, the weightings for the weighted averages indicated in section 14.1.15 shall be the average of the Category I and II weighting's and shall be applied to both Category II results. Appliances that are not capable of operation within Category II (<25 percent of maximum) cannot be evaluated by this test method.

12.5.6.1 Stopped Fuel Combustion. Evidence that an appliance cannot be operated at a Category I heat output rate due to stopped fuel combustion shall include documentation of two or more attempts to operate the appliance in heat output rate Category I and fuel combustion has stopped prior to complete consumption of the test fuel charge. Stopped fuel combustion is evidenced when an elapsed time of 60 minutes or more has occurred without a measurable (1 lb or 0.5 kg) weight change in the test fuel charge while the appliance operating control is in the demand mode. Report the evidence and the reasoning used to determine that a test in heat output rate Category I cannot be achieved. For example, two unsuccessful attempts to operate at an output rate of 10 percent of the rated output capacity are not sufficient evidence that heat output rate Category I cannot be achieved.

12.5.7 Appliance Overheating. Appliances with their associated thermal storage shall be capable of operating in all heat output categories without overheating to be rated by this test method. Appliance overheating occurs when the rate of heat withdrawal from the appliance is lower than the rate of heat production when the unit control is in the idle mode. This condition results in the water in the appliance continuing to increase in temperature well above the upper limit setting of the operating control. Evidence of overheating includes: 1 hour or more of appliance water temperature increase above the upper temperature set-point of the operating control, exceeding the temperature limit of a safety control device (independent from the operating control—typically requires manual reset), boiling water in a non-pressurized system or activation of a pressure or temperature relief valve in a pressurized system.

12.5.8 Option to Eliminate Tests in Category II and III. Following successful completion of a test run in Category I, the manufacturer may eliminate the Category II and III tests. For the purpose of calculating the annual averages for particulates and efficiency, the values obtained in the Category I run shall be assumed to apply also to Category II and Category III. It is envisioned that this option would be applicable to systems which have sufficient thermal storage such that the fuel load in the Category I test can be completely consumed without the system reaching its upper operating temperature limit. In this case, the boiler/heater would likely be operating at maximum thermal output during the entire test and this output rate may be higher than the manufacturer's rated heat output capacity. The Category II and III runs would then be the same as the Category I run. It may be assumed that the particulate emission values and efficiency values determined in the startup, steady-state, and end phases of Category I are applicable in Categories II and III, for the purpose of determining the annual averages in lb/mmBtu and g/MJ (See section 13). For the annual average in g/hr, the length of time for stored heat to be drawn from thermal storage shall be determined for the test load requirements of the respective category.

12.5.9 Modification to Measurement Procedure in EPA Method 28WHH to Determine Emissions Separately During the Startup, Steady-State and End Phases. With one of the two particulate sampling trains used, filter changes shall be made at the end of the startup phase and the steady-state phase (See section 3.0). This shall be done to determine the particulate emission rate and particulate emission index for the startup, steady-state, and end phases individually. For this one train, the particulates measured during each of these three phases shall be added together to also determine the particulate emissions for the whole run.

12.5.10 Modification to Measurement Procedure in EPA Method 28WHH and the Standards Referenced therein on Averaging Period for Determination of Efficiency by the Stack Loss Method. The methods currently defined in Method 28WHH allow averaging over 10-minute time periods for flue gas temperature, flue gas CO_2, and flue gas CO for the determination of the efficiency with the stack loss method. However, under some cycling conditions the ''on'' period may be short relative to this 10-minute period. For this reason, during cycling operation the averaging period for these parameters may not be longer than the burner on period divided by 10. The averaging period need not be shorter than one minute. During the off period, under cycling operation, averaging periods as specified in EPA Method 28WHH and the standards referenced therein, may be used. Where short averaging times are used, however, the averaging period for fuel consumption may still be at 10 minutes. This average wood consumption rate shall be applied to all of the smaller time intervals included.

12.6 Additional Test Runs. The testing laboratory may conduct more than one test run in each of the heat output categories specified in section 4.3. If more than one test run is conducted at a specified heat output rate, the results from at least two-thirds of the test runs in that heat output rate category shall be used in calculating the weighted average emission rate. The measurement data and results of all test runs shall be reported regardless of which values are used in calculating the weighted average emission rate.

13.0 Calculation of Results

13.1 Nomenclature

CO_s—Carbon monoxide measured in the dilution tunnel at arbitrary time in ppm dry basis.

$CO_{g/min}$—Carbon monoxide emission rate in g/min.

CO_T—Total carbon monoxide emission for the full test run in grams.

CO_{-1}—Startup period carbon monoxide emissions in grams.

CO_{-2}—Steady-state period carbon monoxide emission in grams.

CO_{-3}—End period carbon monoxide emission in grams.

E_T—Total particulate emissions for the full test run as determined per EPA Method 28WHH and the standards referenced therein in grams.

E_1—Startup period particulate emissions in grams.

E_2—Steady-state period particulate emissions in grams.

E_3—End period particulate emissions in grams.

$E_{1-g/kg}$—Startup period particulate emission index in grams per kg fuel.

$E_{2-g/kg}$—Steady-state period particulate emission index in grams per kg fuel.

$E_{3-g/kg}$—End period particulate emission index in grams per kg fuel.

$E_{1-g/hr}$—Startup period particulate emission rate in grams per hour.

$E_{2-g/hr}$—Steady-state period particulate emission rate in grams per hour.

$E_{3-g/hr}$—End period particulate emission rate in grams per hour.

$E_{g/MJ}$—Emission rate in grams per MJ of heat output.

$E_{lb/mmBtu\ output}$—Emissions rate in pounds per million Btu of heat output.

$E_{g/kg}$—Emissions factor in grams per kilogram of dry fuel burned.

$E_{g/hr}$—Emission factor in grams per hour.

HHV—Higher heating value of fuel = 8600 Btu/lb (19.990 MJ/kg).

LHV—Lower heating value of fuel = 7988 Btu/lb (18.567 MJ/kg).

ΔT—Temperature difference between cooling water entering and exiting the heat exchanger.

Q_{out}—Total heat output in Btu (MJ).

Q_{in}—Total heat input available in test fuel charge in Btu's (MJ).

Q_{std}—Volumetric flow rate in dilution tunnel in dscfm.

M—Mass flow rate of water in lb/min (kg/min).

V_i—Volume of water indicated by a totalizing flow meter at the i_{th} reading in gallons (liters).

V_f—Volumetric flow rate of water in heat exchange system in gallons per minute (liters/min).

Θ—Total length of burn period in hours ($\Theta_1 + \Theta_2 + \Theta_3$).

Θ_1—Length of time of the startup period in hours.

Θ_2—Length of time of the steady-state period in hours.

Θ_3—Length of time of the end period in hours.

Θ_4—Length of time for stored heat to be used following a burn period in hours.

t_i—Data sampling interval in minutes.

η_{del}—Delivered heating efficiency in percent.

F_i—Weighting factor for heat output category i. (See Table 2.)

T1—Temperature of water at the inlet on the supply side of the heat exchanger, °F.

T2—Temperature of the water at the outlet on the supply side of the heat exchanger, °F.

T3—Temperature of cooling water at the inlet to the load side of the heat exchanger, °F.

T4—Temperature of cooling water at the outlet of the load side of the heat exchanger, °F.

T5—Temperature of the hot water supply as it leaves the boiler/heater, °F.

T6—Temperature of return water as it enters the boiler/heater, °F.

T7—Temperature in the boiler/heater optional destratification loop at the top of the boiler/heater, °F.

T8—Temperature in the boiler/heater optional destratification loop at the bottom of the boiler/heater, °F.

TI_{avg}—Average temperature of the appliance and water at start of the test.

$TI_{avg} - (T5 + T6)/2$ at the start of the test, °F. Eq. 1

TF_{avg}—Average temperature of the appliance and water at the end of the test.

TF_{avg} – (T5 + T6)/2 at the end of the test, °F. Eq. 2

TIS_1—Temperature at the inlet to the storage system at the start of the test.
TIS_2—Temperature at the outlet from the storage system at the start of the test.
TFS_1—Temperature at the inlet to the storage system at the end of the test.
TFS_2—Temperature at the outlet from the storage system at the end of the test.
TIS_{avg}—Average temperature of the storage system at the start of the test.

TIS_{avg} – $(TIS_1 + TIS_2)/2$ at the end of the test. Eq. 3

TFS_{avg}—Average temperature of the storage system at the end of the test.

TFS_{avg} – $(TFS_1 + TFS_2)/2$. Eq. 4

MC—Fuel moisture content in percent dry basis.
σ—Density of water in pounds per gallon.
$\sigma_{Initial}$—Density of water in the boiler/heater system at the start of the test in pounds per gallons.
$\sigma_{boiler/heater}$—Density of water in the boiler/heater system at an arbitrary time during the test in pounds per gallon.
C_p—Specific heat of water in Btu/lb, °F.
C_{steel}—Specific heat of steel (0.1 Btu/lb, °F).
$V_{boiler/heater}$—total volume of water in the boiler/heater system on the weight scale in gallons.
W_{fuel}—Fuel charge weight, as-fired or ''wet'', in pounds (kg).
$W_{fuel—1}$—Fuel consumed during the startup period in pounds (kg).
$W_{fuel—2}$—Fuel consumed during the steady state period in pounds (kg).
$W_{fuel—3}$—Fuel consumed during the end period in pounds (kg).
$W_{FuelBurned}$—Weight of fuel that has been burned from the start of the test to an arbitrary time, including the needed correction for the change in density and weight of the water in the boiler/heater system on the scale in pounds (kg).
$W_{RemainingFuel}$—Weight of unburned fuel separated from the ash at the end of a test. Useful only for Category I and Category II tests.
W_{app}—Weight of empty appliance in pounds (kg).
W_{wat}—Weight of water in supply side of the system in pounds (kg).
$W_{ScaleInitial}$—Weight reading on the scale at the start of the test, just after the test load has been added in pounds (kg).
W_{Scale}—Reading of the weight scale at an arbitrary time during the test run in pounds (kg).
$W_{StorageTank}$—Weight of the storage tank empty in pounds (kg).
$W_{WaterStorage}$—Weight of the water in the storage tank at TIS_{avg} in pounds (kg).

13.2 After the test is completed, determine the particulate emissions E_T in accordance with EPA Method 28WHH and the standards referenced therein.

13.3 Determination of the weight of fuel that has been burned at an arbitrary time.

For the purpose of tracking the consumption of the test fuel load during a test run the following may be used to calculate the weight of fuel that burned since the start of the test:

$$W_{FuelBurned} = (W_{ScaleInitial} - W_{Scale}) + V_{Boiler/heater} \cdot (\sigma_{Initial} - \sigma_{boiler/heater}) \quad \text{Eq. 5}$$

Water density, σ, is calculated using Equation 12.

13.4 Determine Average Fuel Load Moisture Content.

$$MC = \frac{\sum W_{SliceWet_i} - MC_{Slice_i}}{\sum W_{SliceWet_i}} \quad \text{Eq. 6}$$

13.5 Determine Heat Input.

$$Q_{in} = (W_{fuel}/(1+(MC/100))) \text{ x HHV, Btu (MJ).} \quad \text{Eq. 7}$$

$$Q_{in\ LHV} = (W_{fuel}/(1+(MC/100))) \text{ x LHV, Btu (MJ).} \quad \text{Eq. 8}$$

13.5.1 Correction to Q_{in} for the Category I and II tests, where there is greater than 1 percent of the test fuel charge in the chamber at the end of the test period.

$$Q_{lnCorrected} = Q_{in} - W_{Remaining} \cdot 12{,}500\ \underline{Btu} \quad \text{Eq. 9}$$

13.6 Determine Heat Output, Efficiency, and Emissions.

13.6.1 Determine heat output as:

Q_{out} = Σ [Heat output determined for each sampling time interval] + Change in heat stored in the appliance + Change in heat in storage tank.

$$Qout = \Sigma[C_{pi} \cdot \Delta T_i \cdot M_i \cdot t_i] + (W_{app} \cdot C_{steel} + W_{water} \cdot C_{pa}) \cdot (TF_{avg} - TI_{avg})$$
$$+ (W_{StorageTank} \cdot C_{steel} + W_{WaterStorage} \cdot C_{pa}) \cdot (TFS_{avg} - TIS_{avg}) \text{ Btu (MJ)} \quad \text{Eq. 10}$$

NOTE: The subscript (i) indicates the parameter value for sampling time interval t_i.M_i = Mass flow rate = gal/min × density of water (lb/gal) = lb/min.

$$M_i = V_{fi} \cdot \sigma_i, \text{ lb/min.} \quad \text{Eq. 11}$$

$$\sigma_i = (62.56 + (-.0003413 \text{ x } T3_i) + (-.00006225 \text{ x } T3_i^2)) 0.1337, \text{ lb/gal.} \quad \text{Eq. 12}$$

$$C_p = 1.0014 + (-.000003485 \text{ x } T3_i) \text{ Btu/lb, -°F.} \quad \text{Eq. 13}$$

C_{steel} = 0.1 Btu/lb, -° F.

$$C_{pa} = 1.0014 + (-.000003485 \text{ X } (TI_{avg} + TF_{avg})/2), \text{ Btu/lb, °F.} \quad \text{Eq. 14}$$

$$V_{fi} = (V_i - V_{i-1})/(t_i - t_{i-1}), \text{ gal/min.} \quad \text{Eq. 15}$$

NOTE: V_i is the total water volume at the end of interval i and V_{i-1} is the total water volume at the beginning of the time interval. This calculation is necessary when a totalizing type water meter is used.

13.6.2 Determine Heat Output Rate Over Burn Period ($\Theta_1 + \Theta_2 + \Theta_3$) as:

Heat Output Rate = Q_{out}/Θ, Btu/hr (MJ/hr). Eq. 16

13.6.3 Determine Emission Rates and Emission Factors as:

$E_{g/MJ} = E_T/(Q_{out} \times 0.001055)$, g/MJ. Eq. 17

$E_{lb/MM\ Btu\ output} = (E_T/453.59)/(Q_{out} \times 10^{-6})$, lb/mmBtu out. Eq. 18

$E_{g/kg} = E_T/(W_{fuel}/(1+MC/100))$, g/dry kg. Eq. 19

$E_{g/hr} = E_T/(\Theta_1+ \Theta_2+ \Theta_3+ \Theta_4)$, g/hr. Eq. 20

$\Theta_4 = (W_{StorageTank} \cdot C_{steel} + W_{WaterStorage} \cdot C_{pa}) \cdot (TFS_{avg} - TIS_{avg})/(Q_{out}/\Theta)$ Eq. 21

If thermal storage is not used in a Category III or IV run, then $\Theta_4 = 0$.

$E_{1—g/kg} = E_1/(W_{fuel—1}/(1 + MC/100))$, g/dry kg.
$E_{2—g/kg} = E_2/(W_{fuel—2}/(1 + MC/100))$, g/dry kg.
$E_{3—g/kg} = E_3/(W_{fuel—3}/(1 + MC/100))$, g/dry kg.
$E_{1—g/hr} = E_1/\Theta_1$, g/hr.
$E_{2—g/hr} = E_2/\Theta_2$, g/hr.
$E_{3—g/hr} = E_3/\Theta_3$, g/hr.

13.6.4 Determine delivered efficiency as:

$\eta_{del} = (Q_{out}/Q_{InCorrected}) \times 100$, %. Eq. 22

$\eta_{del\ LHV} = (Q_{out}/Q_{in\ LHV}) \times 100$, %. Eq. 23

13.6.5 Determine η_{SLM}—Overall Efficiency, also known as Stack Loss Efficiency, using stack loss method (SLM).

For determination of the average overall thermal efficiency (η_{SLM}) for the test run, use the data collected over the full test run and the calculations in accordance with CSA B415.1–10 (IBR, see §60.17), clause 13.7 except for 13.7.2(e), (f), (g), and (h), use the following average fuel properties for oak: %C = 50.0, %H = 6.6, %O = 43.2, %Ash = 0.2.

13.6.5.1 Whenever the CSA B415.1–10 (IBR, see §60.17) overall efficiency is found to be lower than the overall efficiency based on load side measurements, as determined by Eq. 22 of this method, section 14.1.7 of the test report must include a discussion of the reasons for this result. For a test where the CSA B415.1–10 overall efficiency SLM is less than 2 percentage points lower than the overall efficiency based on load side measurements, the efficiency based on load side measurements shall be considered invalid. [Note on the rationale for the 2 percentage points limit. The SLM method does not include boiler/heater jacket losses and, for this reason, should provide an efficiency which is actually higher than the efficiency based on the energy input and output measurements or ''delivered efficiency.'' A delivered efficiency that is higher than the efficiency based on the SLM could be considered suspect. A delivered efficiency greater than 2 percentage points higher than the efficiency based on the SLM, then, clearly indicates a measurement error.]

13.6.6 Carbon Monoxide Emissions

For each minute of the test period, the carbon monoxide emission rate shall be calculated as:

$$CO_{g/min} = Q_{std} \cdot CO_s \cdot 3.30 \times 10^{-5} \quad \text{Eq. 24}$$

Total CO emissions for each of the three test periods ($CO_{—1}$, $CO_{—2}$, $CO_{—3}$) shall be calculated as the sum of the emission rates for each of the 1-minute intervals. Total CO emission for the test run, CO_T, shall be calculated as the sum of $CO_{—1}$, $CO_{—2}$, and $CO_{—3}$.

13.7 Weighted Average Emissions and Efficiency.

13.7.1 Determine the weighted average emission rate and delivered efficiency from the individual tests in the specified heat output categories. The weighting factors (F_i) are derived from an analysis of ASHRAE bin data which provides details of normal building heating requirements in terms of percent of design capacity and time in a particular capacity range—or ''bin''—over the course of a heating season. The values used in this method represent an average of data from several cities located in the northern United States.

Weighted average delivered efficiency: $\eta_{avg} = \Sigma\ \eta_i \times F_i$, %. Eq. 25

Weighted average emissions: $E_{avg} = \Sigma\ E_i \times F_i$, % Eq. 26

If, as discussed in section 12.5.8, the option to eliminate tests in Category II and III is elected, the values of efficiency and particulate emission rate as measured in Category I, shall be assigned also to Category II and III for the purpose of determining the annual averages.

14.0 Report

14.1.1 The report shall include the following:

14.1.2 Name and location of the laboratory conducting the test.

14.1.3 A description of the appliance tested and its condition, date of receipt and dates of tests.

14.1.4 A description of the minimum amount of external thermal storage that is required for use with this system. This shall be specified both in terms of volume in gallons and stored energy content in Btu with a storage temperature ranging from 125 °F to the manufacturer's specified setpoint temperature.

14.1.5 A statement that the test results apply only to the specific appliance tested.

14.1.6 A statement that the test report shall not be reproduced except in full, without the written approval of the laboratory.

14.1.7 A description of the test procedures and test equipment including a schematic or other drawing showing the location of all required test equipment. Also, a description of test fuel sourcing, handling and storage practices shall be included.

14.1.8 Details of deviations from, additions to or exclusions from the test method, and their data quality implications on the test results (if any), as well as information on specific test conditions, such as environmental conditions.

14.1.9 A list of participants and their roles and observers present for the tests.

14.1.10 Data and drawings indicating the fire box size and location of the fuel charge.

14.1.11 Drawings and calculations used to determine firebox volume.

14.1.12 Information for each test run fuel charge including piece size, moisture content and weight.

14.1.13 All required data and applicable blanks for each test run shall be provided in spreadsheet format both in the printed report and in a computer file such that the data can be easily analyzed and calculations easily verified. Formulas used for all calculations shall be accessible for review.

14.1.14 For each test run, Θ_1,Θ_2, Θ_3, the total CO and particulate emission for each of these three periods, and Θ_4.

14.1.15 Calculated results for delivered efficiency at each heat output rate and the weighted average emissions reported as total emissions in grams, pounds per mm Btu of delivered heat, grams per MJ of delivered heat, grams per kilogram of dry fuel and grams per hour. Results shall be reported for each heat output category and the weighted average.

14.1.16 Tables 1A, 1B, 1C, 1D, 1E and Table 2 must be used for presentation of results in test reports.

14.1.17 A statement of the estimated uncertainty of measurement of the emissions and efficiency test results.

14.1.18 A plot of CO emission rate in grams/minute vs. time, based on 1 minute averages, for the entire test period, for each run.

14.1.19 A plot of estimated boiler/heater energy release rate in Btu/hr based on 10 minute averages, for the entire test period, for each run. This will be calculated from the fuel used, the wood heating value and moisture content, and the SLM efficiency during each 10 minute period.

14.1.20 Raw data, calibration records, and other relevant documentation shall be retained by the laboratory for a minimum of 7 years.

15.0 Precision and Bias

15.1 Precision—It is not possible to specify the precision of the procedure in this test method because the appliance operation and

fueling protocols and the appliances themselves produce variable amounts of emissions and cannot be used to determine reproducibility or repeatability of this test method.

15.2 Bias—No definitive information can be presented on the bias of the procedure in this test method for measuring solid fuel burning hydronic heater emissions because no material having an accepted reference value is available.

16.0 Keywords

16.1 Solid fuel, hydronic heating appliances, wood-burning hydronic heaters, partial thermal storage.

Table 1A. Data Summary Part A

						Θ	W_{fuel}	MC_{ave}	Q_{in}	Q_{out}
Category	Run No	Load % Capacity	Target Load	Actual Load	Actual Load	Test Duration	Wood Weight as-fired	Wood Moisture	Heat Input	Heat Output
		Btu/hr	Btu/ hr	Btu/ hr	% of max	hrs	lb	%DB	Btu	Btu
I		< 15% of max								
II		16-24% of max								
III		25-50% of max								
IV		Max capacity								

Table 1B. Data Summary Part B

			T2 Min	E_T	E	E	$E_{g/hr}$	$E_{g/kg}$	η_{del}	H_{SLM}
Category	Run No	Load % Capacity	Min Return Water Temp.	Total PM Emissions	PM Output Based	PM Output Based	PM Rate	PM Factor	Delivered Efficiency	Stack Loss Efficiency
			°F	g	lb/mm Btu Out	g/MJ	g/hr	g/kg	%	%
I		< 15% of max								
II		16-24% of max								
III		25-50% of max								
IV		Max capacity								

Table 1C. Data Summary Part C

			Θ_1	Θ_2	Θ_3	$CO_{_1}$	$CO_{_2}$	$CO_{_3}$	CO_T
Category	Run No	Load % Capacity	Startup Time.	Steady State Time	End Time	Startup CO emission	Steady State CO emission	End CO emission	Total CO emission
			min	min	min	g	g	g	g
I		< 15% of max							
II		16-24% of max							
III		25-50% of max							
IV		Max capacity							

Table 1D. Data Summary Part D

			E_1	E_2	E_3	$E_{1_g/kg}$	$E_{2_g/kg}$	$E_{3_g/kg}$
Category	Run No	Load % Capacity	Startup PM	Steady State PM	End PM	Startup PM emission index	Steady State PM emission index	End PM emission index
			g	g	g	g/kg fuel	g/kg fuel	g/kg fuel
I		< 15% of max						
II		16-24% of max						
III		25-50% of max						
IV		Max capacity						

Table 1E: Label Summary Information

MANUFACTURER:			
MODEL NUMBER:			
ANNUAL EFFICIENCY RATING:	η_{avg}		**(Using higher heating value)**
PARTICLE EMISSIONS:	E_{avg}		grams/hr (Average)
			lbs/mmBtu/hr Output

Table 2. Annual Weighting

Category	Weighting Factor (F_i)	$\eta_{del,i} \times F_i$	$E_{g/MJ,i} \times F_i$	$E_{g/kg,i} \times F_i$	$E_{lb/mmBtu\ Out,i} \times F_i$	$E_{g/hr,i} \times F_i$
I	0.437					
II	0.238					
III	0.275					
IV	0.050					
Totals	1.000					

Figure 1. Schematic of Equipment Test Setup

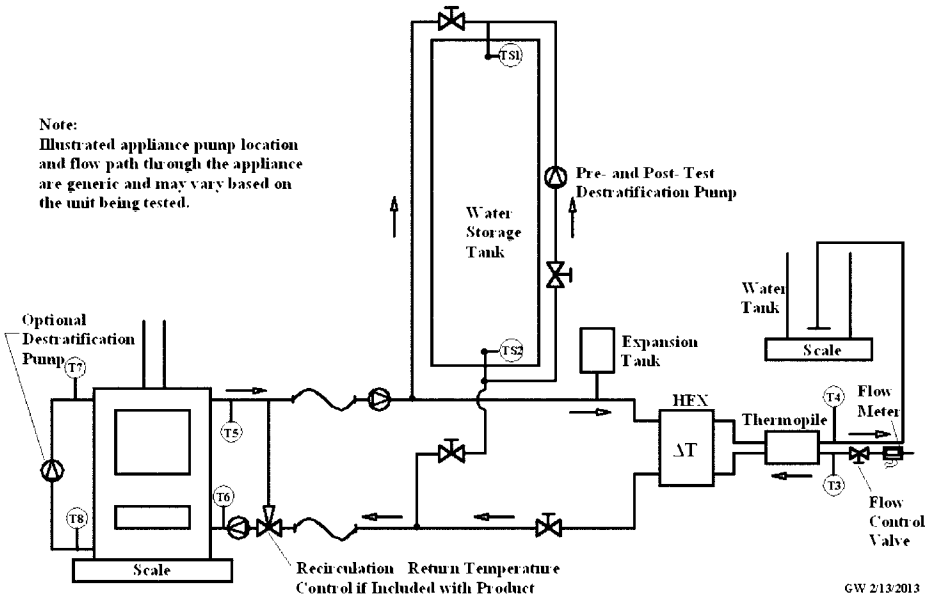
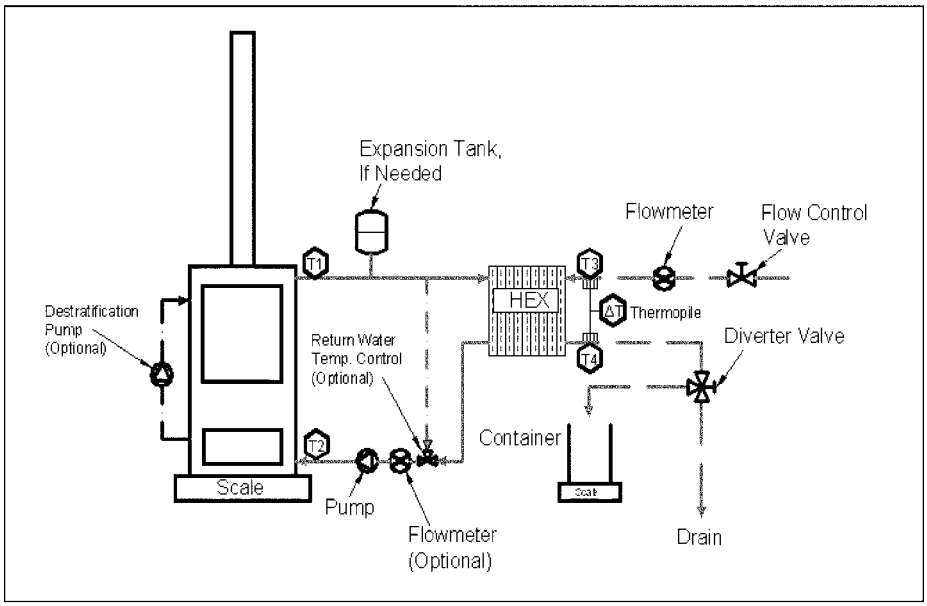


Figure 2. Schematic of Test Equipment Set-up



Note: Illustrated appliance pump location and flow path through the appliance.

METHOD 29—DETERMINATION OF METALS EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 5 and Method 12.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Antimony (Sb)	7440–36–0
Arsenic (As)	7440–38–2
Barium (Ba)	7440–39–3
Beryllium (Be)	7440–41–7
Cadmium (Cd)	7440–43–9
Chromium (Cr)	7440–47–3
Cobalt (Co)	7440–48–4
Copper (Cu)	7440–50–8
Lead (Pb)	7439–92–1
Manganese (Mn)	7439–96–5
Mercury (Hg)	7439–97–6
Nickel (Ni)	7440–02–0
Phosphorus (P)	7723–14–0
Selenium (Se)	7782–49–2
Silver (Ag)	7440–22–4
Thallium (Tl)	7440–28–0
Zinc (Zn)	7440–66–6

1.2 Applicability. This method is applicable to the determination of metals emissions from stationary sources. This method may be used to determine particulate emissions in addition to the metals emissions if the prescribed procedures and precautions are followed.

1.2.1 Hg emissions can be measured, alternatively, using EPA Method 101A of Appendix B, 40 CFR Part 61. Method 101-A measures only Hg but it can be of special interest to sources which need to measure both Hg and Mn emissions.

2.0 Summary of Method

2.1 Principle. A stack sample is withdrawn isokinetically from the source, particulate emissions are collected in the probe and on a heated filter, and gaseous emissions are then collected in an aqueous acidic solution of hydrogen peroxide (analyzed for all metals including Hg) and an aqueous acidic solution of potassium permanganate (analyzed only for Hg). The recovered samples are digested, and appropriate fractions are analyzed for Hg by cold vapor atomic absorption spectroscopy

(CVAAS) and for Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, P, Se, Ag, Tl, and Zn by inductively coupled argon plasma emission spectroscopy (ICAP) or atomic absorption spectroscopy (AAS). Graphite furnace atomic absorption spectroscopy (GFAAS) is used for analysis of Sb, As, Cd, Co, Pb, Se, and Tl if these elements require greater analytical sensitivity than can be obtained by ICAP. If one so chooses, AAS may be used for analysis of all listed metals if the resulting in-stack method detection limits meet the goal of the testing program. Similarly, inductively coupled plasma-mass spectroscopy (ICP-MS) may be used for analysis of Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Ag, Tl and Zn.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Iron (Fe) can be a spectral interference during the analysis of As, Cr, and Cd by ICAP. Aluminum (Al) can be a spectral interference during the analysis of As and Pb by ICAP. Generally, these interferences can be reduced by diluting the analytical sample, but such dilution raises the in-stack detection limits. Background and overlap corrections may be used to adjust for spectral interferences. Refer to Method 6010 of Reference 2 in section 16.0 or the other analytical methods used for details on potential interferences to this method. For all GFAAS analyses, use matrix modifiers to limit interferences, and matrix match all standards.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Nitric Acid (HNO_3). Highly corrosive to eyes, skin, nose, and lungs. Vapors cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

5.2.2 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

5.2.3 Hydrochloric Acid (HC1). Highly corrosive liquid with toxic vapors. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.4 Hydrofluoric Acid (HF). Highly corrosive to eyes, skin, nose, throat, and lungs. Reaction to exposure may be delayed by 24 hours or more. Provide ventilation to limit exposure.

5.2.5 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs. 30% H_2O_2 is a strong oxidizing agent. Avoid contact with skin, eyes, and combustible material. Wear gloves when handling.

5.2.6 Potassium Permanganate ($KMnO_4$). Caustic, strong oxidizer. Avoid bodily contact with.

5.2.7 Potassium Persulfate. Strong oxidizer. Avoid bodily contact with. Keep containers well closed and in a cool place.

5.3 Reaction Pressure. Due to the potential reaction of the potassium permanganate with the acid, there could be pressure build-up in the acidic $KMnO_4$ absorbing solution storage bottle. Therefore these bottles shall not be fully filled and shall be vented to relieve excess pressure and prevent explosion potentials. Venting is required, but not in a manner that will allow contamination of the solution. A No. 70–72 hole drilled in the container cap and Teflon liner has been used.

6.0 Equipment and Supplies

6.1 Sampling. A schematic of the sampling train is shown in Figure 29–1. It has general similarities to the Method 5 train.

6.1.1 Probe Nozzle (Probe Tip) and Borosilicate or Quartz Glass Probe Liner. Same as Method 5, sections 6.1.1.1 and 6.1.1.2, except that glass nozzles are required unless alternate tips are constructed of materials that are free from contamination and will not interfere with the sample. If a probe tip other than glass is used, no correction to the sample test results to compensate for the nozzle's effect on the sample is allowed. Probe fittings of plastic such as Teflon, polypropylene, etc. are recommended instead of metal fittings to prevent contamination. If one chooses to do so, a single glass piece consisting of a combined probe tip and probe liner may be used.

6.1.2 Pitot Tube and Differential Pressure Gauge. Same as Method 2, sections 6.1 and 6.2, respectively.

6.1.3 Filter Holder. Glass, same as Method 5, section 6.1.1.5, except use a Teflon filter support or other non-metallic, non-contaminating support in place of the glass frit.

6.1.4 Filter Heating System. Same as Method 5, section 6.1.1.6.

6.1.5 Condenser. Use the following system for condensing and collecting gaseous metals and determining the moisture content of the stack gas. The condensing system shall consist of four to seven impingers connected in series with leak-free ground glass fittings or other leak-free, non-contaminating fittings. Use the first impinger as a moisture trap. The second impinger (which is the first HNO_3/H_2O_2 impinger) shall be identical to the first impinger in Method 5. The third impinger (which is the second HNO_3/H_2O_2 impinger) shall be a Greenburg Smith impinger with the standard tip as described for the second impinger in Method 5, section 6.1.1.8. The fourth (empty) impinger and the fifth and sixth (both acidified $KMnO_4$) impingers are the same as the first impinger in Method 5. Place a temperature sensor capable of measuring to within 1 °C (2 °F) at the outlet of the last impinger. If no Hg analysis is planned, then the fourth, fifth, and sixth impingers are not used.

6.1.6 Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, sections 6.1.1.9, 6.1.2, and 6.1.3, respectively.

6.1.7 Teflon Tape. For capping openings and sealing connections, if necessary, on the sampling train.

6.2 Sample Recovery. Same as Method 5, sections 6.2.1 through 6.2.8 (Probe-Liner and Probe-Nozzle Brushes or Swabs, Wash Bottles, Sample Storage Containers, Petri Dishes, Glass Graduated Cylinder, Plastic Storage Containers, Funnel and Rubber Policeman, and Glass Funnel), respectively, with the following exceptions and additions:

6.2.1 Non-metallic Probe-Liner and Probe-Nozzle Brushes or Swabs. Use non-metallic probe-liner and probe-nozzle brushes or swabs for quantitative recovery of materials collected in the front-half of the sampling train.

6.2.2 Sample Storage Containers. Use glass bottles (see section 8.1 of this Method) with Teflon-lined caps that are non-reactive to the oxidizing solutions, with capacities of 1000- and 500-ml, for storage of acidified $KMnO_4$—containing samples and blanks. Glass or polyethylene bottles may be used for other sample types.

6.2.3 Graduated Cylinder. Glass or equivalent.

6.2.4 Funnel. Glass or equivalent.

6.2.5 Labels. For identifying samples.

6.2.6 Polypropylene Tweezers and/or Plastic Gloves. For recovery of the filter from the sampling train filter holder.

6.3 Sample Preparation and Analysis.

6.3.1 Volumetric Flasks, 100-ml, 250-ml, and 1000-ml. For preparation of standards and sample dilutions.

6.3.2 Graduated Cylinders. For preparation of reagents.

6.3.3 Parr Bombs or Microwave Pressure Relief Vessels with Capping Station (CEM Corporation model or equivalent). For sample digestion.

6.3.4 Beakers and Watch Glasses. 250-ml beakers, with watch glass covers, for sample digestion.

6.3.5 Ring Stands and Clamps. For securing equipment such as filtration apparatus.

6.3.6 Filter Funnels. For holding filter paper.

6.3.7 Disposable Pasteur Pipets and Bulbs.

6.3.8 Volumetric Pipets.

6.3.9 Analytical Balance. Accurate to within 0.1 mg.

6.3.10 Microwave or Conventional Oven. For heating samples at fixed power levels or temperatures, respectively.

6.3.11 Hot Plates.

6.3.12 Atomic Absorption Spectrometer (AAS). Equipped with a background corrector.

6.3.12.1 Graphite Furnace Attachment. With Sb, As, Cd, Co, Pb, Se, and Tl hollow cathode lamps (HCLs) or electrodeless discharge lamps (EDLs). Same as Reference 2 in section 16.0. Methods 7041 (Sb), 7060 (As), 7131 (Cd), 7201 (Co), 7421 (Pb), 7740 (Se), and 7841 (Tl).

6.3.12.2 Cold Vapor Mercury Attachment. With a mercury HCL or EDL, an air recirculation pump, a quartz cell, an aerator apparatus, and a heat lamp or desiccator tube. The heat lamp shall be capable of raising the temperature at the quartz cell by 10 °C above ambient, so that no condensation forms on the wall of the quartz cell. Same as Method 7470 in Reference 2 in section 16.0. See note 2: section 11.1.3 for other acceptable approaches for analysis of Hg in which analytical detection limits of 0.002 ng/ml were obtained.

6.3.13 Inductively Coupled Argon Plasma Spectrometer. With either a direct or sequential reader and an alumina torch. Same as EPA Method 6010 in Reference 2 in section 16.0.

6.3.14 Inductively Coupled Plasma-Mass Spectrometer.

Same as EPA Method 6020 in Reference 2 in section 16.0.

7.0 Reagents and Standards

7.1 Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are

available. Otherwise, use the best available grade.

7.2 Sampling Reagents.

7.2.1 Sample Filters. Without organic binders. The filters shall contain less than 1.3 μg/in.^{2} of each of the metals to be measured. Analytical results provided by filter manufacturers stating metals content of the filters are acceptable. However, if no such results are available, analyze filter blanks for each target metal prior to emission testing. Quartz fiber filters meeting these requirements are recommended. However, if glass fiber filters become available which meet these requirements, they may be used. Filter efficiencies and unreactiveness to sulfur dioxide (SO_2) or sulfur trioxide (SO_3) shall be as described in section 7.1.1 of Method 5.

7.2.2 Water. To conform to ASTM Specification D1193–77 or 91, Type II (incorporated by reference—see §60.17). If necessary, analyze the water for all target metals prior to field use. All target metals should be less than 1 ng/ml.

7.2.3 HNO_3, Concentrated. Baker Instra-analyzed or equivalent.

7.2.4 HCl, Concentrated. Baker Instra-analyzed or equivalent.

7.2.5 H_2O_2, 30 Percent (V/V).

7.2.6 $KMnO_4$.

7.2.7 H_2SO_4, Concentrated.

7.2.8 Silica Gel and Crushed Ice. Same as Method 5, sections 7.1.2 and 7.1.4, respectively.

7.3 Pretest Preparation of Sampling Reagents.

7.3.1 HNO_3/H_2O_2 Absorbing Solution, 5 Percent HNO_3/10 Percent H_2O_2. Add carefully with stirring 50 ml of concentrated HNO_3 to a 1000-ml volumetric flask containing approximately 500 ml of water, and then add carefully with stirring 333 ml of 30 percent H_2O_2. Dilute to volume with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.3.2 Acidic $KMnO_4$ Absorbing Solution, 4 Percent $KMnO_4$ (W/V), 10 Percent H_2SO_4 (V/V). Prepare fresh daily. Mix carefully, with stirring, 100 ml of concentrated H_2SO_4 into approximately 800 ml of water, and add water with stirring to make a volume of 1 liter: this solution is 10 percent H_2SO_4 (V/V). Dissolve, with stirring, 40 g of $KMnO_4$ into 10 percent H_2SO_4 (V/V) and add 10 percent H_2SO_4 (V/V) with stirring to make a volume of 1 liter. Prepare and store in glass bottles to prevent degradation. This reagent shall contain less than 2 ng/ml of Hg.

Precaution: To prevent autocatalytic decomposition of the permanganate solution, filter the solution through Whatman 541 filter paper.

7.3.3 HNO_3, 0.1 N. Add with stirring 6.3 ml of concentrated HNO_3 (70 percent) to a flask containing approximately 900 ml of water. Dilute to 1000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.3.4 HCl, 8 N. Carefully add with stirring 690 ml of concentrated HCl to a flask containing 250 ml of water. Dilute to 1000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of Hg.

7.4 Glassware Cleaning Reagents.

7.4.1 HNO_3, Concentrated. Fisher ACS grade or equivalent.

7.4.2 Water. To conform to ASTM Specifications D1193, Type II.

7.4.3 HNO_3, 10 Percent (V/V). Add with stirring 500 ml of concentrated HNO_3 to a flask containing approximately 4000 ml of water. Dilute to 5000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.5 Sample Digestion and Analysis Reagents. The metals standards, except Hg, may also be made from solid chemicals as described in Reference 3 in section 16.0. Refer to References 1, 2, or 5 in section 16.0 for additional information on Hg standards. The 1000 μg/ml Hg stock solution standard may be made according to section 7.2.7 of Method 101A.

7.5.1 HCl, Concentrated.

7.5.2 HF, Concentrated.

7.5.3 HNO_3, Concentrated. Baker Instra-analyzed or equivalent.

7.5.4 HNO_3, 50 Percent (V/V). Add with stirring 125 ml of concentrated HNO_3 to 100 ml of water. Dilute to 250 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.5.5 HNO_3, 5 Percent (V/V). Add with stirring 50 ml of concentrated HNO_3 to 800 ml of water. Dilute to 1000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.5.6 Water. To conform to ASTM Specifications D1193, Type II.

7.5.7 Hydroxylamine Hydrochloride and Sodium Chloride Solution. See Reference 2 In section 16.0 for preparation.

7.5.8 Stannous Chloride. See Reference 2 in section 16.0 for preparation.

7.5.9 $KMnO_4$, 5 Percent (W/V). See Reference 2 in section 16.0 for preparation.

7.5.10 H_2SO_4, Concentrated.

7.5.11 Potassium Persulfate, 5 Percent (W/V). See Reference 2 in section 16.0 for preparation.

7.5.12 Nickel Nitrate, $Ni(N0_3)_2 6H_20$.

7.5.13 Lanthanum Oxide, La_20_3.

7.5.14 Hg Standard (AAS Grade), 1000 μg/ml.

7.5.15 Pb Standard (AAS Grade), 1000 μg/ml.

7.5.16 As Standard (AAS Grade), 1000 μg/ml.

7.5.17 Cd Standard (AAS Grade), 1000 μg/ml.

7.5.18 Cr Standard (AAS Grade), 1000 μg/ml.

7.5.19 Sb Standard (AAS Grade), 1000 μg/ml.

7.5.20 Ba Standard (AAS Grade), 1000 μg/ml.

7.5.21 Be Standard (AAS Grade), 1000 μg/ml.

7.5.22 Co Standard (AAS Grade), 1000 μg/ml.

7.5.23 Cu Standard (AAS Grade), 1000 μg/ml.

7.5.24 Mn Standard (AAS Grade), 1000 µg/ml.
7.5.25 Ni Standard (AAS Grade), 1000 µg/ml.
7.5.26 P Standard (AAS Grade), 1000 µg/ml.
7.5.27 Se Standard (AAS Grade), 1000 µg/ml.
7.5.28 Ag Standard (AAS Grade), 1000 µg/ml.
7.5.29 Tl Standard (AAS Grade), 1000 µg/ml.
7.5.30 Zn Standard (AAS Grade), 1000 µg/ml.
7.5.31 Al Standard (AAS Grade), 1000 µg/ml.
7.5.32 Fe Standard (AAS Grade), 1000 µg/ml.

7.5.33 Hg Standards and Quality Control Samples. Prepare fresh weekly a 10 µg/ml intermediate Hg standard by adding 5 ml of 1000 µg/ml Hg stock solution prepared according to Method 101A to a 500-ml volumetric flask; dilute with stirring to 500 ml by first carefully adding 20 ml of 15 percent HNO_3 and then adding water to the 500-ml volume. Mix well. Prepare a 200 ng/ml working Hg standard solution fresh daily: add 5 ml of the 10 µg/ml intermediate standard to a 250-ml volumetric flask, and dilute to 250 ml with 5 ml of 4 percent $KMnO_4$, 5 ml of 15 percent HNO_3, and then water. Mix well. Use at least five separate aliquots of the working Hg standard solution and a blank to prepare the standard curve. These aliquots and blank shall contain 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml of the working standard solution containing 0, 200, 400, 600, 800, and 1000 ng Hg, respectively. Prepare quality control samples by making a separate 10 µg/ml standard and diluting until in the calibration range.

7.5.34 ICAP Standards and Quality Control Samples. Calibration standards for ICAP analysis can be combined into four different mixed standard solutions as follows:

MIXED STANDARD SOLUTIONS FOR ICAP ANALYSIS

Solution	Elements
I	As, Be, Cd, Mn, Pb, Se, Zn.
II	Ba, Co, Cu, Fe.
III	Al, Cr, Ni.
IV	Ag, P, Sb, Tl.

Prepare these standards by combining and diluting the appropriate volumes of the 1000 µg/ml solutions with 5 percent HNO_3. A minimum of one standard and a blank can be used to form each calibration curve. However, prepare a separate quality control sample spiked with known amounts of the target metals in quantities in the mid-range of the calibration curve. Suggested standard levels are 25 µg/ml for Al, Cr and Pb, 15 µg/ml for Fe, and 10 µg/ml for the remaining elements. Prepare any standards containing less than 1 µg/ml of metal on a daily basis. Standards containing greater than 1 µg/ml of metal should be stable for a minimum of 1 to 2 weeks. For ICP-MS, follow Method 6020 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i).

7.5.35 GFAAS Standards. Sb, As, Cd, Co, Pb, Se, and Tl. Prepare a 10 µg/ml standard by adding 1 ml of 1000 µg/ml standard to a 100-ml volumetric flask. Dilute with stirring to 100 ml with 10 percent HNO_3. For GFAAS, matrix match the standards. Prepare a 100 ng/ml standard by adding 1 ml of the 10 µg/ml standard to a 100-ml volumetric flask, and dilute to 100 ml with the appropriate matrix solution. Prepare other standards by diluting the 100 ng/ml standards. Use at least five standards to make up the standard curve. Suggested levels are 0, 10, 50, 75, and 100 ng/ml. Prepare quality control samples by making a separate 10 µg/ml standard and diluting until it is in the range of the samples. Prepare any standards containing less than 1 µg/ml of metal on a daily basis. Standards containing greater than 1 µg/ml of metal should be stable for a minimum of 1 to 2 weeks.

7.5.36 Matrix Modifiers.

7.5.36.1 Nickel Nitrate, 1 Percent (V/V). Dissolve 4.956 g of $Ni(N0_3)_2{\cdot}6H_20$ or other nickel compound suitable for preparation of this matrix modifier in approximately 50 ml of water in a 100-ml volumetric flask. Dilute to 100 ml with water.

7.5.36.2 Nickel Nitrate, 0.1 Percent (V/V). Dilute 10 ml of 1 percent nickel nitrate solution to 100 ml with water. Inject an equal amount of sample and this modifier into the graphite furnace during GFAAS analysis for As.

7.5.36.3 Lanthanum. Carefully dissolve 0.5864 g of La_20_3 in 10 ml of concentrated $HN0_3$, and dilute the solution by adding it with stirring to approximately 50 ml of water. Dilute to 100 ml with water, and mix well. Inject an equal amount of sample and this modifier into the graphite furnace during GFAAS analysis for Pb.

7.5.37 Whatman 40 and 541 Filter Papers (or equivalent). For filtration of digested samples.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Sampling. The complexity of this method is such that, to obtain reliable results, both testers and analysts must be trained and experienced with the test procedures, including source sampling; reagent preparation and handling; sample handling; safety equipment and procedures; analytical calculations; reporting; and the specific procedural descriptions throughout this method.

8.1.1 Pretest Preparation. Follow the same general procedure given in Method 5, section 8.1, except that, unless particulate emissions are to be determined, the filter need not be desiccated or weighed. First, rinse all sampling train glassware with hot tap water and then wash in hot soapy water. Next, rinse glassware three times with tap water, followed by three additional rinses with water. Then soak all glassware in a 10 percent (V/V) nitric acid solution for a minimum of 4

hours, rinse three times with water, rinse a final time with acetone, and allow to air dry. Cover all glassware openings where contamination can occur until the sampling train is assembled for sampling.

8.1.2 Preliminary Determinations. Same as Method 5, section 8.1.2.

8.1.3 Preparation of Sampling Train.

8.1.3.1 Set up the sampling train as shown in Figure 29–1. Follow the same general procedures given in Method 5, section 8.3, except place 100 ml of the HNO_3/H_2O_2 solution (Section 7.3.1 of this method) in each of the second and third impingers as shown in Figure 29–1. Place 100 ml of the acidic $KMnO_4$ absorbing solution (Section 7.3.2 of this method) in each of the fifth and sixth impingers as shown in Figure 29–1, and transfer approximately 200 to 300 g of pre-weighed silica gel from its container to the last impinger. Alternatively, the silica gel may be weighed directly in the impinger just prior to final train assembly.

8.1.3.2 Based on the specific source sampling conditions, the use of an empty first impinger can be eliminated if the moisture to be collected in the impingers will be less than approximately 100 ml.

8.1.3.3 If Hg analysis will not be performed, the fourth, fifth, and sixth impingers as shown in Figure 29–1 are not required.

8.1.3.4 To insure leak-free sampling train connections and to prevent possible sample contamination problems, use Teflon tape or other non-contaminating material instead of silicone grease.

Precaution: Exercise extreme care to prevent contamination within the train. Prevent the acidic $KMnO_4$ from contacting any glassware that contains sample material to be analyzed for Mn. Prevent acidic H_2O_2 from mixing with the acidic $KMnO_4$.

8.1.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, section 8.4.2 (Pretest Leak-Check), section 8.4.3 (Leak-Checks During the Sample Run), and section 8.4.4 (Post-Test Leak-Checks).

8.1.5 Sampling Train Operation. Follow the procedures given in Method 5, section 8.5. When sampling for Hg, use a procedure analogous to that described in section 8.1 of Method 101A, 40 CFR Part 61, Appendix B, if necessary to maintain the desired color in the last acidified permanganate impinger. For each run, record the data required on a data sheet such as the one shown in Figure 5–3 of Method 5.

8.1.6 Calculation of Percent Isokinetic. Same as Method 5, section 12.11.

8.2 Sample Recovery.

8.2.1 Begin cleanup procedures as soon as the probe is removed from the stack at the end of a sampling period. The probe should be allowed to cool prior to sample recovery. When it can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a rinsed, non-contaminating cap over the probe nozzle to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling; a vacuum can form in the filter holder with the undesired result of drawing liquid from the impingers onto the filter.

8.2.2 Before moving the sampling train to the cleanup site, remove the probe from the sampling train and cap the open outlet. Be careful not to lose any condensate that might be present. Cap the filter inlet where the probe was fastened. Remove the umbilical cord from the last impinger and cap the impinger. Cap the filter holder outlet and impinger inlet. Use non-contaminating caps, whether ground-glass stoppers, plastic caps, serum caps, or Teflon® tape to close these openings.

8.2.3 Alternatively, the following procedure may be used to disassemble the train before the probe and filter holder/oven are completely cooled: Initially disconnect the filter holder outlet/impinger inlet and loosely cap the open ends. Then disconnect the probe from the filter holder or cyclone inlet and loosely cap the open ends. Cap the probe tip and remove the umbilical cord as previously described.

8.2.4 Transfer the probe and filter-impinger assembly to a cleanup area that is clean and protected from the wind and other potential causes of contamination or loss of sample. Inspect the train before and during disassembly and note any abnormal conditions. Take special precautions to assure that all the items necessary for recovery do not contaminate the samples. The sample is recovered and treated as follows (see schematic in Figures 29–2a and 29–2b):

8.2.5 Container No. 1 (Sample Filter). Carefully remove the filter from the filter holder and place it in its labeled petri dish container. To handle the filter, use either acid-washed polypropylene or Teflon coated tweezers or clean, disposable surgical gloves rinsed with water and dried. If it is necessary to fold the filter, make certain the particulate cake is inside the fold. Carefully transfer the filter and any particulate matter or filter fibers that adhere to the filter holder gasket to the petri dish by using a dry (acid-cleaned) nylon bristle brush. Do not use any metal-containing materials when recovering this train. Seal the labeled petri dish.

8.2.6 Container No. 2 (Acetone Rinse). Perform this procedure only if a determination of particulate emissions is to be made. Quantitatively recover particulate matter and any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with a total of 100 ml of acetone, while simultaneously taking great care to see that no dust on the outside of the probe or other surfaces gets in the sample. The use of exactly 100 ml

is necessary for the subsequent blank correction procedures. Distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator; in these cases, save a water blank and follow the Administrator's directions on analysis.

8.2.6.1 Carefully remove the probe nozzle, and clean the inside surface by rinsing with acetone from a wash bottle while brushing with a non-metallic brush. Brush until the acetone rinse shows no visible particles, then make a final rinse of the inside surface with acetone.

8.2.6.2 Brush and rinse the sample exposed inside parts of the probe fitting with acetone in a similar way until no visible particles remain. Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Allow the acetone to drain from the lower end into the sample container. A funnel may be used to aid in transferring liquid washings to the container. Follow the acetone rinse with a non-metallic probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action three times through the probe. Hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed through the probe until no visible particulate matter is carried out with the acetone or until none remains in the probe liner on visual inspection. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

8.2.6.3 It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination. Clean the inside of the front-half of the filter holder by rubbing the surfaces with a non-metallic brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. After all acetone washings and particulate matter have been collected in the sample container, tighten the lid so that acetone will not leak out when shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Clearly label the container to identify its contents.

8.2.7 Container No. 3 (Probe Rinse). Keep the probe assembly clean and free from contamination during the probe rinse. Rinse the probe nozzle and fitting, probe liner, and front-half of the filter holder thoroughly with a total of 100 ml of 0.1 N HNO_3, and place the wash into a sample storage container. Perform the rinses as applicable and generally as described in Method 12, section 8.7.1. Record the volume of the rinses. Mark the height of the fluid level on the outside of the storage container and use this mark to determine if leakage occurs during transport. Seal the container, and clearly label the contents. Finally, rinse the nozzle, probe liner, and front-half of the filter holder with water followed by acetone, and discard these rinses.

NOTE: The use of a total of exactly 100 ml is necessary for the subsequent blank correction procedures.

8.2.8 Container No. 4 (Impingers 1 through 3, Moisture Knockout Impinger, when used, HNO_3/H_2O_2 Impingers Contents and Rinses). Due to the potentially large quantity of liquid involved, the tester may place the impinger solutions from impingers 1 through 3 in more than one container, if necessary. Measure the liquid in the first three impingers to within 0.5 ml using a graduated cylinder. Record the volume. This information is required to calculate the moisture content of the sampled flue gas. Clean each of the first three impingers, the filter support, the back half of the filter housing, and connecting glassware by thoroughly rinsing with 100 ml of 0.1 N HNO_3 using the procedure as applicable in Method 12, section 8.7.3.

NOTE: The use of exactly 100 ml of 0.1 N HNO_3 rinse is necessary for the subsequent blank correction procedures. Combine the rinses and impinger solutions, measure and record the final total volume. Mark the height of the fluid level, seal the container, and clearly label the contents.

8.2.9 Container Nos. 5A (0.1 N HNO_3), 5B ($KMnO_4/H_2SO_4$ absorbing solution), and 5C (8 N HCl rinse and dilution).

8.2.9.1 When sampling for Hg, pour all the liquid from the impinger (normally impinger No. 4) that immediately preceded the two permanganate impingers into a graduated cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Place the liquid in Container No. 5A. Rinse the impinger with exactly 100 ml of 0.1 N HNO_3 and place this rinse in Container No. 5A.

8.2.9.2 Pour all the liquid from the two permanganate impingers into a graduated cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Place this acidic $KMnO_4$ solution into Container No. 5B. Using a total of exactly 100 ml of fresh acidified $KMnO_4$ solution for all rinses (approximately 33 ml per rinse), rinse the two permanganate impingers and connecting glassware a minimum of three times. Pour the rinses into Container No. 5B, carefully assuring transfer of all loose precipitated materials from the two impingers. Similarly, using 100 ml total of water, rinse the permanganate impingers and connecting

glass a minimum of three times, and pour the rinses into Container 5B, carefully assuring transfer of any loose precipitated material. Mark the height of the fluid level, and clearly label the contents. Read the *Precaution:* in section 7.3.2.

NOTE: Due to the potential reaction of $KMnO_4$ with acid, pressure buildup can occur in the sample storage bottles. Do not fill these bottles completely and take precautions to relieve excess pressure. A No. 70–72 hole drilled in the container cap and Teflon liner has been used successfully.

8.2.9.3 Wash the two permanganate impingers with 25 ml of 8 N HCl, and place the wash in a separate sample container labeled No. 5C containing 200 ml of water. First, place 200 ml of water in the container. Then wash the impinger walls and stem with the 8 N HCl by turning the impinger on its side and rotating it so that the HCl contacts all inside surfaces. Use a total of only 25 ml of 8 N HCl for rinsing *both permanganate impingers combined*. Rinse the first impinger, then pour the actual rinse used for the first impinger into the second impinger for its rinse. Finally, pour the 25 ml of 8 N HCl rinse carefully into the container with the 200 ml of water. Mark the height of the fluid level on the outside of the container in order to determine if leakage occurs during transport.

8.2.10 Container No. 6 (Silica Gel). Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container and seal it. The tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. The small amount of particles that might adhere to the impinger wall need not be removed. Do not use water or other liquids to transfer the silica gel since weight gained in the silica gel impinger is used for moisture calculations. Alternatively, if a balance is available in the field, record the weight of the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g.

8.2.11 Container No. 7 (Acetone Blank). If particulate emissions are to be determined, at least once during each field test, place a 100-ml portion of the acetone used in the sample recovery process into a container labeled No. 7. Seal the container.

8.2.12 Container No. 8A (0.1 N HNO_3 Blank). At least once during each field test, place 300 ml of the 0.1 N HNO_3 solution used in the sample recovery process into a container labeled No. 8A. Seal the container.

8.2.13 Container No. 8B (Water Blank). At least once during each field test, place 100 ml of the water used in the sample recovery process into a container labeled No. 8B. Seal the container.

8.2.14 Container No. 9 (5 Percent HNO_3/10 Percent H_2O_2 Blank). At least once during each field test, place 200 ml of the 5 Percent HNO_3/10 Percent H_2O_2 solution used as the nitric acid impinger reagent into a container labeled No. 9. Seal the container.

8.2.15 Container No. 10 (Acidified $KMnO_4$ Blank). At least once during each field test, place 100 ml of the acidified $KMnO_4$ solution used as the impinger solution and in the sample recovery process into a container labeled No. 10. Prepare the container as described in section 8.2.9.2. Read the *Precaution*: in section 7.3.2 and read the note in section 8.2.9.2.

8.2.16 Container No. 11 (8 N HCl Blank). At least once during each field test, place 200 ml of water into a sample container labeled No. 11. Then carefully add with stirring 25 ml of 8 N HCl. Mix well and seal the container.

8.2.17 Container No. 12 (Sample Filter Blank). Once during each field test, place into a petri dish labeled No. 12 three unused blank filters from the same lot as the sampling filters. Seal the petri dish.

8.3 Sample Preparation. Note the level of the liquid in each of the containers and determine if any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. A diagram illustrating sample preparation and analysis procedures for each of the sample train components is shown in Figure 29–3.

8.3.1 Container No. 1 (Sample Filter).

8.3.1.1 If particulate emissions are being determined, first desiccate the filter and filter catch without added heat (do not heat the filters to speed the drying) and weigh to a constant weight as described in section 11.2.1 of Method 5.

8.3.1.2 Following this procedure, or initially, if particulate emissions are not being determined in addition to metals analysis, divide the filter with its filter catch into portions containing approximately 0.5 g each. Place the pieces in the analyst's choice of either individual microwave pressure relief vessels or Parr Bombs. Add 6 ml of concentrated HNO_3 and 4 ml of concentrated HF to each vessel. For microwave heating, microwave the samples for approximately 12 to 15 minutes total heating time as follows: heat for 2 to 3 minutes, then turn off the microwave for 2 to 3 minutes, then heat for 2 to 3 minutes, etc., continue this alternation until the 12 to 15 minutes total heating time are completed (this procedure should comprise approximately 24 to 30 minutes at 600 watts). Microwave heating times are approximate and are dependent upon the number of samples being digested simultaneously. Sufficient heating is evidenced by sorbent reflux within the vessel. For conventional heating, heat the Parr Bombs at 140 °C (285 °F) for 6 hours. Then cool the samples to

room temperature, and combine with the acid digested probe rinse as required in section 8.3.3.

8.3.1.3 If the sampling train includes an optional glass cyclone in front of the filter, prepare and digest the cyclone catch by the procedures described in section 8.3.1.2 and then combine the digestate with the digested filter sample.

8.3.2 Container No. 2 (Acetone Rinse). Note the level of liquid in the container and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically within 1 ml or gravimetrically within 0.5 g. Transfer the contents to an acid-cleaned, tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. If particulate emissions are being determined, desiccate for 24 hours without added heat, weigh to a constant weight according to the procedures described in section 11.2.1 of Method 5, and report the results to the nearest 0.1 mg. Redissolve the residue with 10 ml of concentrated HNO_3. Quantitatively combine the resultant sample, including all liquid and any particulate matter, with Container No. 3 before beginning section 8.3.3.

8.3.3 Container No. 3 (Probe Rinse). Verify that the pH of this sample is 2 or lower. If it is not, acidify the sample by careful addition with stirring of concentrated HNO_3 to pH 2. Use water to rinse the sample into a beaker, and cover the beaker with a ribbed watch glass. Reduce the sample volume to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Digest the sample in microwave vessels or Parr Bombs by quantitatively transferring the sample to the vessel or bomb, carefully adding the 6 ml of concentrated HNO_3, 4 ml of concentrated HF, and then continuing to follow the procedures described in section 8.3.1.2. Then combine the resultant sample directly with the acid digested portions of the filter prepared previously in section 8.3.1.2. The resultant combined sample is referred to as *''Sample Fraction 1''*. Filter the combined sample using Whatman 541 filter paper. Dilute to 300 ml (or the appropriate volume for the expected metals concentration) with water. This diluted sample is *''Analytical Fraction 1''*. Measure and record the volume of Analytical Fraction 1 to within 0.1 ml. Quantitatively remove a 50-ml aliquot and label as *''Analytical Fraction 1B''*. Label the remaining 250-ml portion as *''Analytical Fraction 1A''*. Analytical Fraction 1A is used for ICAP or AAS analysis for all desired metals except Hg. Analytical Fraction 1B is used for the determination of front-half Hg.

8.3.4 Container No. 4 (Impingers 1–3). Measure and record the total volume of this sample to within 0.5 ml and label it *''Sample Fraction 2''*. Remove a 75- to 100-ml aliquot for Hg analysis and label the aliquot *''Analytical Fraction 2B''*. Label the remaining portion of Container No. 4 as *''Sample Fraction 2A''*. Sample Fraction 2A defines the volume of Analytical Fraction 2A *prior* to digestion. All of Sample Fraction 2A is digested to produce *''Analytical Fraction 2A''*. Analytical Fraction 2A defines the volume of Sample Fraction 2A *after* its digestion and the volume of Analytical Fraction 2A is normally 150 ml. Analytical Fraction 2A is analyzed for all metals except Hg. Verify that the pH of Sample Fraction 2A is 2 or lower. If necessary, use concentrated HNO_3 by careful addition and stirring to lower Sample Fraction 2A to pH 2. Use water to rinse Sample Fraction 2A into a beaker and then cover the beaker with a ribbed watchglass. Reduce Sample Fraction 2A to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Then follow either of the digestion procedures described in sections 8.3.4.1 or 8.3.4.2.

8.3.4.1 Conventional Digestion Procedure. Add 30 ml of 50 percent HNO_3, and heat for 30 minutes on a hot plate to just below boiling. Add 10 ml of 3 percent H_2O_2 and heat for 10 more minutes. Add 50 ml of hot water, and heat the sample for an additional 20 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water. This dilution produces Analytical Fraction 2A. Measure and record the volume to within 0.1 ml.

8.3.4.2 Microwave Digestion Procedure. Add 10 ml of 50 percent HNO_3 and heat for 6 minutes total *heating* time in alternations of 1 to 2 minutes at 600 Watts followed by 1 to 2 minutes with no power, etc., similar to the procedure described in section 8.3.1. Allow the sample to cool. Add 10 ml of 3 percent H_2O_2 and heat for 2 more minutes. Add 50 ml of hot water, and heat for an additional 5 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water. This dilution produces Analytical Fraction 2A. Measure and record the volume to within 0.1 ml.

NOTE: All microwave heating times given are approximate and are dependent upon the number of samples being digested at a time. Heating times as given above have been found acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by solvent reflux within the vessel.

8.3.5 Container No. 5A (Impinger 4), Container Nos. 5B and 5C (Impingers 5 and 6). Keep the samples in Containers Nos. 5A, 5B, and 5C separate from each other. Measure and record the volume of 5A to within 0.5 ml. Label the contents of Container No. 5A to be

Analytical Fraction 3A. To remove any brown MnO_2 precipitate from the contents of Container No. 5B, filter its contents through Whatman 40 filter paper into a 500 ml volumetric flask and dilute to volume with water. Save the filter for digestion of the brown MnO_2 precipitate. Label the 500 ml filtrate from Container No. 5B to be Analytical Fraction 3B. Analyze Analytical Fraction 3B for Hg within 48 hours of the filtration step. Place the saved filter, which was used to remove the brown MnO_2 precipitate, into an appropriately sized *vented* container, which will allow release of any gases including chlorine formed when the filter is digested. In a laboratory hood which will remove any gas produced by the digestion of the MnO_2, add 25 ml of 8 N HCl to the filter and allow to digest for a minimum of 24 hours at room temperature. Filter the contents of Container No. 5C through a Whatman 40 filter into a 500-ml volumetric flask. Then filter the result of the digestion of the brown MnO_2 from Container No. 5B through a Whatman 40 filter into the same 500-ml volumetric flask, and dilute and mix well to volume with water. Discard the Whatman 40 filter. Mark this combined 500-ml dilute HCl solution as Analytical Fraction 3C.

8.3.6 Container No. 6 (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance.

9.0 Quality Control

9.1 Field Reagent Blanks, if analyzed. Perform the digestion and analysis of the blanks in Container Nos. 7 through 12 that were produced in sections 8.2.11 through 8.2.17, respectively. For Hg field reagent blanks, use a 10 ml aliquot for digestion and analysis.

9.1.1 Digest and analyze one of the filters from Container No. 12 per section 8.3.1, 100 ml from Container No. 7 per section 8.3.2, and 100 ml from Container No. 8A per section 8.3.3. This step produces blanks for Analytical Fractions 1A and 1B.

9.1.2 Combine 100 ml of Container No. 8A with 200 ml from Container No. 9, and digest and analyze the resultant volume per section 8.3.4. This step produces blanks for Analytical Fractions 2A and 2B.

9.1.3 Digest and analyze a 100-ml portion of Container No. 8A to produce a blank for Analytical Fraction 3A.

9.1.4 Combine 100 ml from Container No. 10 with 33 ml from Container No. 8B to produce a blank for Analytical Fraction 3B. Filter the resultant 133 ml as described for Container No. 5B in section 8.3.5, except do not dilute the 133 ml. Analyze this blank for Hg within 48 hr of the filtration step, and use 400 ml as the blank volume when calculating the blank mass value. Use the actual volumes of the other analytical blanks when calculating their mass values.

9.1.5 Digest the filter that was used to remove any brown MnO_2 precipitate from the blank for Analytical Fraction 3B by the same procedure as described in section 8.3.5 for the similar sample filter. Filter the digestate and the contents of Container No. 11 through Whatman 40 paper into a 500-ml volumetric flask, and dilute to volume with water. These steps produce a blank for Analytical Fraction 3C.

9.1.6 Analyze the blanks for Analytical Fraction Blanks 1A and 2A per section 11.1.1 and/or section 11.1.2. Analyze the blanks for Analytical Fractions 1B, 2B, 3A, 3B, and 3C per section 11.1.3. Analysis of the blank for Analytical Fraction 1A produces the front-half reagent blank correction values for the desired metals except for Hg; Analysis of the blank for Analytical Fraction 1B produces the front-half reagent blank correction value for Hg. Analysis of the blank for Analytical Fraction 2A produces the back-half reagent blank correction values for all of the desired metals except for Hg, while separate analyses of the blanks for Analytical Fractions 2B, 3A, 3B, and 3C produce the back-half reagent blank correction value for Hg.

9.2 Quality Control Samples. Analyze the following quality control samples.

9.2.1 ICAP and ICP-MS Analysis. Follow the respective quality control descriptions in section 8 of Methods 6010 and 6020 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i). For the purposes of a source test that consists of three sample runs, modify those requirements to include the following: two instrument check standard runs, two calibration blank runs, one interference check sample at the beginning of the analysis (analyze by Method of Standard Additions unless within 25 percent), one quality control sample to check the accuracy of the calibration standards (required to be within 25 percent of calibration), and one duplicate analysis (required to be within 20 percent of average or repeat all analyses).

9.2.2 Direct Aspiration AAS and/or GFAAS Analysis for Sb, As, Ba, Be, Cd, Cu, Cr, Co, Pb, Ni, Mn, Hg, P, Se, Ag, Tl, and Zn. Analyze all samples in duplicate. Perform a matrix spike on at least one front-half sample and one back-half sample, or one combined sample. If recoveries of less than 75 percent or greater than 125 percent are obtained for the matrix spike, analyze each sample by the Method of Standard Additions. Analyze a quality control sample to check the accuracy of the calibration standards. If the results are not within 20 percent, repeat the calibration.

9.2.3 CVAAS Analysis for Hg. Analyze all samples in duplicate. Analyze a quality control sample to check the accuracy of the calibration standards (if not within 15 percent, repeat calibration). Perform a matrix spike on one sample (if not within 25 percent,

analyze all samples by the Method of Standard Additions). Additional information on quality control can be obtained from Method 7470 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i), or in *Standard Methods for Water and Wastewater* Method 303F.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Sampling Train Calibration. Calibrate the sampling train components according to the indicated sections of Method 5: Probe Nozzle (Section 10.1); Pitot Tube (Section 10.2); Metering System (Section 10.3); Probe Heater (Section 10.4); Temperature Sensors (Section 10.5); Leak-Check of the Metering System (Section 8.4.1); and Barometer (Section 10.6).

10.2 Inductively Coupled Argon Plasma Spectrometer Calibration. Prepare standards as outlined in section 7.5. Profile and calibrate the instrument according to the manufacturer's recommended procedures using those standards. Check the calibration once per hour. If the instrument does not reproduce the standard concentrations within 10 percent, perform the complete calibration procedures. Perform ICP-MS analysis by following Method 6020 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i).

10.3 Atomic Absorption Spectrometer—Direct Aspiration AAS, GFAAS, and CVAAS analyses. Prepare the standards as outlined in section 7.5 and use them to calibrate the spectrometer. Calibration procedures are also outlined in the EPA methods referred to in Table 29–2 and in Method 7470 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i), or in *Standard Methods for Water and Wastewater* Method 303F (for Hg). Run each standard curve in duplicate and use the mean values to calculate the calibration line. Recalibrate the instrument approximately once every 10 to 12 samples.

10.4 Field Balance Calibration Check. Check the calibration of the balance used to weigh impingers with a weight that is at least 500g or within 50g of a loaded impinger. The weight must be ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference-see 40 CFR 60.17) Class 6 (or better). Daily before use, the field balance must measure the weight within ±0.5g of the certified mass. If the daily balance calibration check fails, perform corrective measures and repeat the check before using balance.

10.5 Analytical Balance Calibration. Perform a multipoint calibration (at least five points spanning the operational range) of the analytical balance before the first use, and semiannually thereafter. The calibration of the analytical balance must be conducted using ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 2 (or better) tolerance weights. Audit the balance each day it is used for gravimetric measurements by weighing at least one ASTM E617–13 Class 2 tolerance (or better) calibration weight that corresponds to 50 to 150 percent of the weight of one filter or between 1g and 5g. If the scale cannot reproduce the value of the calibration weight to within 0.5 mg of the certified mass, perform corrective measures, and conduct the multipoint calibration before use.

11.0 Analytical Procedure

11.1 Sample Analysis. For each sampling train sample run, seven individual analytical samples are generated; two for all desired metals except Hg, and five for Hg. A schematic identifying each sample container and the prescribed analytical preparation and analysis scheme is shown in Figure 29–3. The first two analytical samples, labeled Analytical Fractions 1A and 1B, consist of the digested samples from the front-half of the train. Analytical Fraction 1A is for ICAP, ICP-MS or AAS analysis as described in sections 11.1.1 and 11.1.2, respectively. Analytical Fraction 1B is for front-half Hg analysis as described in section 11.1.3. The contents of the back-half of the train are used to prepare the third through seventh analytical samples. The third and fourth analytical samples, labeled Analytical Fractions 2A and 2B, contain the samples from the moisture removal impinger No. 1, if used, and HNO_3/H_2O_2 impingers Nos. 2 and 3. Analytical Fraction 2A is for ICAP, ICP-MS or AAS analysis for target metals, except Hg. Analytical Fraction 2B is for analysis for Hg. The fifth through seventh analytical samples, labeled Analytical Fractions 3A, 3B, and 3C, consist of the impinger contents and rinses from the empty impinger No. 4 and the $H_2SO_4/KMnO_4$ Impingers Nos. 5 and 6. These analytical samples are for analysis for Hg as described in section 11.1.3. The total back-half Hg catch is determined from the sum of Analytical Fractions 2B, 3A, 3B, and 3C. Analytical Fractions 1A and 2A can be combined proportionally prior to analysis.

11.1.1 ICAP and ICP-MS Analysis. Analyze Analytical Fractions 1A and 2A by ICAP using Method 6010 or Method 200.7 (40 CFR 136, Appendix C). Calibrate the ICAP, and set up an analysis program as described in Method 6010 or Method 200.7. Follow the quality control procedures described in section 9.2.1. Recommended wavelengths for analysis are as shown in Table 29–2. These wavelengths represent the best combination of specificity

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and potential detection limit. Other wavelengths may be substituted if they can provide the needed specificity and detection limit, and are treated with the same corrective techniques for spectral interference. Initially, analyze all samples for the target metals (except Hg) plus Fe and Al. If Fe and Al are present, the sample might have to be diluted so that each of these elements is at a concentration of less than 50 ppm so as to reduce their spectral interferences on As, Cd, Cr, and Pb. Perform ICP-MS analysis by following Method 6020 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i).

NOTE: When analyzing samples in a HF matrix, an alumina torch should be used; since all front-half samples will contain HF, use an alumina torch.

11.1.2 AAS by Direct Aspiration and/or GFAAS. If analysis of metals in Analytical Fractions 1A and 2A by using GFAAS or direct aspiration AAS is needed, use Table 29–3 to determine which techniques and procedures to apply for each target metal. Use Table 29–3, if necessary, to determine techniques for minimization of interferences. Calibrate the instrument according to section 10.3 and follow the quality control procedures specified in section 9.2.2.

11.1.3 CVAAS Hg analysis. Analyze Analytical Fractions 1B, 2B, 3A, 3B, and 3C separately for Hg using CVAAS following the method outlined in Method 7470 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i), or in *Standard Methods for Water and Wastewater Analysis*, 15th Edition, Method 303F, or, optionally using note no. 2 at the end of this section. Set up the calibration curve (zero to 1000 ng) as described in Method 7470 or similar to Method 303F using 300-ml BOD bottles instead of Erlenmeyers. Perform the following for each Hg analysis. From each original sample, select and record an aliquot in the size range from 1 ml to 10 ml. If no prior knowledge of the expected amount of Hg in the sample exists, a 5 ml aliquot is suggested for the first dilution to 100 ml (see note no. 1 at end of this section). The total amount of Hg in the aliquot shall be less than 1 μg and within the range (zero to 1000 ng) of the calibration curve. Place the sample aliquot into a separate 300-ml BOD bottle, and add enough water to make a total volume of 100 ml. Next add to it sequentially the sample digestion solutions and perform the sample preparation described in the procedures of Method 7470 or Method 303F. (See note no. 2 at the end of this section). If the maximum readings are off-scale (because Hg in the aliquot exceeded the calibration range; including the situation where only a 1-ml aliquot of the original sample was digested), then dilute the original sample (or a portion of it) with 0.15 percent HNO_3 (1.5 ml concentrated HNO_3 per liter aqueous solution) so that when a 1- to 10-ml aliquot of the ''0.15 HNO_3 percent dilution of the original sample'' is digested and analyzed by the procedures described above, it will yield an analysis within the range of the calibration curve.

NOTE NO. 1: When Hg levels in the sample fractions are below the in-stack detection limit given in Table 29–1, select a 10 ml aliquot for digestion and analysis as described.

NOTE NO. 2: Optionally, Hg can be analyzed by using the CVAAS analytical procedures given by some instrument manufacturer's directions. These include calibration and quality control procedures for the Leeman Model PS200, the Perkin Elmer FIAS systems, and similar models, if available, of other instrument manufacturers. For digestion and analyses by these instruments, perform the following two steps: (1), Digest the sample aliquot through the addition of the aqueous hydroxylamine hydrochloride/sodium chloride solution the same as described in this section: (*The Leeman, Perkin Elmer, and similar instruments described in this note add automatically the necessary stannous chloride solution during the automated analysis of Hg.)*; (2), Upon completion of the digestion described in (1), analyze the sample according to the instrument manufacturer's directions. This approach allows multiple (including duplicate) automated analyses of a digested sample aliquot.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

A = Analytical detection limit, μg/ml.
B = Liquid volume of digested sample prior to aliquotting for analysis, ml.
C = Stack sample gas volume, dsm^3.
C_{a1} = Concentration of metal in Analytical Fraction 1A as read from the standard curve, μg/ml.
C_{a2} = Concentration of metal in Analytical Fraction 2A as read from the standard curve, (μg/ml).
C_s = Concentration of a metal in the stack gas, mg/dscm.
D = In-stack detection limit, $\mu g/m^3$.
F_a = Aliquot factor, volume of Sample Fraction 2 divided by volume of Sample Fraction 2A (see section 8.3.4.)
F_d = Dilution factor (F_d = the inverse of the fractional portion of the concentrated sample in the solution actually used in the instrument to produce the reading C_{a1}. For example, if a 2 ml aliquot of Analytical Fraction 1A is diluted to 10 ml to place it in the calibration range, $F_d = 5$).
Hg_{bh} = Total mass of Hg collected in the back-half of the sampling train, μg.
Hg_{bh2} = Total mass of Hg collected in Sample Fraction 2, μg.

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$Hg_{bh3(A,B,C)}$ = Total mass of Hg collected separately in Fraction 3A, 3B, or 3C, µg.

Hg_{bhb} = Blank correction value for mass of Hg detected in back-half field reagent blanks, µg.

Hg_{fh} = Total mass of Hg collected in the front-half of the sampling train (Sample Fraction 1), µg.

Hg_{fhb} = Blank correction value for mass of Hg detected in front-half field reagent blank, µg.

Hg_t = Total mass of Hg collected in the sampling train, µg.

M_{bh} = Total mass of each metal (except Hg) collected in the back-half of the sampling train (Sample Fraction 2), µg.

M_{bhb} = Blank correction value for mass of metal detected in back-half field reagent blank, µg.

M_{fh} = Total mass of each metal (except Hg) collected in the front half of the sampling train (Sample Fraction 1), µg.

M_{fhb} = Blank correction value for mass of metal detected in front-half field reagent blank, µg.

M_t = Total mass of each metal (separately stated for each metal) collected in the sampling train, µg.

M_t = Total mass of that metal collected in the sampling train, µg; (substitute Hg_t for M_t for the H_g calculation).

Q_{bh2} = Quantity of Hg, µg, TOTAL in the ALIQUOT of Analytical Fraction 2B selected for digestion and analysis .

NOTE: For example, if a 10 ml aliquot of Analytical Fraction 2B is taken and digested and analyzed (according to section 11.1.3 and its notes nos. 1 and 2), then calculate and use the total amount of Hg in the 10 ml aliquot for Q_{bh2}.

$Q_{bh3(A,B,C)}$ = Quantity of Hg, µg, *TOTAL, separately, in the ALIQUOT of Analytical Fraction 3A, 3B, or 3C selected for digestion and analysis* (see notes in sections 12.7.1 and 12.7.2 describing the quantity ''Q'' and calculate similarly).

Q_{fh} = Quantity of Hg, µg, *TOTAL in the ALIQUOT of Analytical Fraction 1B selected for digestion and analysis.*

NOTE: For example, if a 10 ml aliquot of Analytical Fraction 1B is taken and digested and analyzed (according to section 11.1.3 and its notes nos. 1 and 2), then calculate and use the total amount of Hg in the 10 ml aliquot for Q_{fh}.

V_a = Total volume of digested sample solution (Analytical Fraction 2A), ml (see section 8.3.4.1 or 8.3.4.2, as applicable).

V_{f1B} = Volume of aliquot of Analytical Fraction 1B analyzed, ml.

NOTE: For example, if a 1 ml aliquot of Analytical Fraction 1B was diluted to 50 ml with 0.15 percent HNO_3 as described in section 11.1.3 to bring it into the proper analytical range, and then 1 ml of that 50-ml was digested according to section 11.1.3 and analyzed, V_{f1B} would be 0.02 ml.

V_{f2B} = Volume of Analytical Fraction 2B analyzed, ml.

NOTE: For example, if 1 ml of Analytical Fraction 2B was diluted to 10 ml with 0.15 percent HNO_3 as described in section 11.1.3 to bring it into the proper analytical range, and then 5 ml of that 10 ml was analyzed, V_{f2B} would be 0.5 ml.

$V_{f3(A,B,C)}$ = Volume, separately, of Analytical Fraction 3A, 3B, or 3C analyzed, ml (see previous notes in sections 12.7.1 and 12.7.2, describing the quantity ''V'' and calculate similarly).

$V_{m(std)}$ = Volume of gas sample as measured by the dry gas meter, corrected to dry standard conditions, dscm.

$V_{soln,1}$ = Total volume of digested sample solution (Analytical Fraction 1), ml.

$V_{soln,1}$ = Total volume of Analytical Fraction 1, ml.

$V_{soln,2}$ = Total volume of Sample Fraction 2, ml.

$V_{soln,3(A,B,C)}$ = Total volume, separately, of Analytical Fraction 3A, 3B, or 3C, ml.

$K_4 = 10^{-3}$ mg/µg.

12.2 Dry Gas Volume. Using the data from this test, calculate $V_{m(std)}$, the dry gas sample volume at standard conditions as outlined in section 12.3 of Method 5.

12.3 Volume of Water Vapor and Moisture Content. Using the total volume of condensate collected during the source sampling, calculate the volume of water vapor $V_{w(std)}$ and the moisture content B_{ws} of the stack gas. Use Equations 5–2 and 5–3 of Method 5.

12.4 Stack Gas Velocity. Using the data from this test and Equation 2–9 of Method 2, calculate the average stack gas velocity.

12.5 In-Stack Detection Limits. Calculate the in-stack method detection limits shown in Table 29–4 using the conditions described in section 13.3.1 as follows:

$$A \times \frac{B}{C} = D \qquad \text{Eq. 29-1}$$

12.6 Metals (Except Hg) in Source Sample.

12.6.1 Analytical Fraction 1A, Front-Half, Metals (except Hg). Calculate separately the amount of each metal collected in Sample Fraction 1 of the sampling train using the following equation:

$$M_{fh} = C_{al} F_d V_{soln,1} \qquad \text{Eq. 29-2}$$

NOTE: If Analytical Fractions 1A and 2A are combined, use proportional aliquots. Then make appropriate changes in Equations 29–2 through 29–4 to reflect this approach.

12.6.2 Analytical Fraction 2A, Back-Half, Metals (except Hg). Calculate separately the amount of each metal collected in Fraction 2 of the sampling train using the following equation:

$$M_{bh} = C_{a2} F_a V_a \qquad \text{Eq. 29-3}$$

12.6.3 Total Train, Metals (except Hg). Calculate the total amount of each of the quantified metals collected in the sampling train as follows:

$$M_t = \left(M_{fh} - M_{fhb}\right) + \left(M_{bh} - M_{bhb}\right) \qquad \text{Eq. 29-4}$$

NOTE: If the measured blank value for the front half (M_{fhb}) is in the range 0.0 to ''A'' µg (where ''A'' µg equals the value determined by multiplying 1.4 µg/in.^{2} times the actual area in in.^{2} of the sample filter), use M_{fhb} to correct the emission sample value (M_{fh}); if M_{fhb} exceeds ''A'' µg, use the greater of I or II:

I. ''A'' µg.

II. The lesser of (a) M_{fhb}, or (b) 5 percent of M_{fh}. If the measured blank value for the back-half (M_{bhb}) is in the range 0.0 to 1 µg, use M_{bhb} to correct the emission sample value (M_{bh}); if M_{bhb} exceeds 1 µg, use the greater of I or II:

I. 1 µg.

II. The lesser of (a) M_{bhb}, or (b) 5 percent of M_{bh}.

12.7 Hg in Source Sample.

12.7.1 Analytical Fraction 1B; Front-Half Hg. Calculate the amount ofHg collected in the front-half, Sample Fraction 1, of the sampling train by using Equation 29–5:

$$Hg_{fh} = \frac{Q_{fh}}{V_{flB}}\left(V_{soln,1}\right) \qquad \text{Eq. 29-5}$$

12.7.2 Analytical Fractions 2B, 3A, 3B, and 3C; Back Half Hg.

12.7.2.1 Calculate the amount of Hg collected in Sample Fraction 2 by using Equation 29–6:

$$Hg_{bh2} = \frac{Q_{bh2}}{V_{f2B}}\left(V_{soln,2}\right) \qquad \text{Eq. 29-6}$$

12.7.2.2 Calculate each of the back-half Hg values for Analytical Fractions 3A, 3B, and 3C by using Equation 29–7:

$$Hg_{bh3(A,B,C)} = \frac{Q_{bh3(A,B,C)}}{V_{f3(A,B,C)}}\left(V_{soln,3(A,B,C)}\right) \qquad \text{Eq. 29-7}$$

12.7.2.3 Calculate the total amount of Hg collected in the back-half of the sampling train by using Equation 29–8:

$$Hg_{bh} = Hg_{bh2} + Hg_{bh3A} + Hg_{bh3B} + Hg_{bh3C} \qquad \text{Eq. 29-8}$$

12.7.3 Total Train Hg Catch. Calculate the total amount of Hg collected in the sampling train by using Equation 29–9:

$$Hg_t = \left(Hg_{fh} - Hg_{fhb}\right) + \left(Hg_{bh} - Hg_{bhb}\right) \qquad \text{Eq. 29-9}$$

NOTE: If the total of the measured blank values (Hg_{fhb} + Hg_{bhb}) is in the range of 0.0 to 0.6 µg, then use the total to correct the sample value (Hg_{fh} + Hg_{bh}); if it exceeds 0.6 µg, use the greater of I. or II:

I. 0.6 µg.

II. The lesser of (a) (Hg_{fhb} + Hg_{bhb}), or (b) 5 percent of the sample value (Hg_{fh} + Hg_{bh}).

12.8 Individual Metal Concentrations in Stack Gas. Calculate the concentration of

each metal in the stack gas (dry basis, adjusted to standard conditions) by using Equation 29–10:

$$C_s = \frac{K_4 M_t}{V_{m(std)}} \qquad \text{Eq. 29-10}$$

12.9 Isokinetic Variation and Acceptable Results. Same as Method 5, sections 12.11 and 12.12, respectively.

13.0 Method Performance

13.1 Range. For the analysis described and for similar analyses, the ICAP response is linear over several orders of magnitude. Samples containing metal concentrations in the nanograms per ml (ng/ml) to micrograms per ml (μg/ml) range in the final analytical solution can be analyzed using this method. Samples containing greater than approximately 50 μg/ml As, Cr, or Pb should be diluted to that level or lower for final analysis. Samples containing greater than approximately 20 μg/ml of Cd should be diluted to that level before analysis.

13.2 Analytical Detection Limits.

NOTE: See section 13.3 for the description of in-stack detection limits.

13.2.1 ICAP analytical detection limits for the sample solutions (based on *SW–846*, Method 6010) are approximately as follows: Sb (32 ng/ml), As (53 ng/ml), Ba (2 ng/ml), Be (0.3 ng/ml), Cd (4 ng/ml), Cr (7 ng/ml), Co (7 ng/ml), Cu (6 ng/ml), Pb (42 ng/ml), Mn (2 ng/ml), Ni (15 ng/ml), P (75 ng/ml), Se (75 ng/ml), Ag (7 ng/ml), Tl (40 ng/ml), and Zn (2 ng/ml). ICP-MS analytical detection limits (based on *SW–846*, Method 6020) are lower generally by a factor of ten or more. Be is lower by a factor of three. The actual sample analytical detection limits are sample dependent and may vary due to the sample matrix.

13.2.2 The analytical detection limits for analysis by direct aspiration AAS (based on *SW–846*, Method 7000 series) are approximately as follows: Sb (200 ng/ml), As (2 ng/ml), Ba (100 ng/ml), Be (5 ng/ml), Cd (5 ng/ml), Cr (50 ng/ml), Co (50 ng/ml), Cu (20 ng/ml), Pb (100 ng/ml), Mn (10 ng/ml), Ni (40 ng/ml), Se (2 ng/ml), Ag (10 ng/ml), Tl (100 ng/ml), and Zn (5 ng/ml).

13.2.3 The detection limit for Hg by CVAAS (on the resultant volume of the *digestion* of the aliquots taken for Hg analyses) can be approximately 0.02 to 0.2 ng/ml, depending upon the type of CVAAS analytical instrument used. 13.2.4 The use of GFAAS can enhance the detection limits compared to direct aspiration AAS as follows: Sb (3 ng/ml), As (1 ng/ml), Be (0.2 ng/ml), Cd (0.1 ng/ml), Cr (1 ng/ml), Co (1 ng/ml), Pb (1 ng/ml), Se (2 ng/ml), and Tl (1 ng/ml).

13.3 In-stack Detection Limits.

13.3.1 For test planning purposes in-stack detection limits can be developed by using the following information: (1) The procedures described in this method, (2) the analytical detection limits described in section 13.2 and in *SW–846*,(3) the normal volumes of 300 ml (Analytical Fraction 1) for the front-half and 150 ml (Analytical Fraction 2A) for the back-half samples, and (4) a stack gas sample volume of 1.25 m^3. The resultant in-stack method detection limits for the above set of conditions are presented in Table 29–1 and were calculated by using Eq. 29–1 shown in section 12.5.

13.3.2 To ensure optimum precision/resolution in the analyses, the target concentrations of metals in the analytical solutions should be at least ten times their respective analytical detection limits. Under certain conditions, and with greater care in the analytical procedure, these concentrations can be as low as approximately three times the respective analytical detection limits without seriously impairing the precision of the analyses. On at least one sample run in the source test, and for each metal analyzed, perform either repetitive analyses, Method of Standard Additions, serial dilution, or matrix spike addition, etc., to document the quality of the data.

13.3.3 Actual in-stack method detection limits are based on actual source sampling parameters and analytical results as described above. If required, the method in-stack detection limits can be improved over those shown in Table 29–1 for a specific test by either increasing the sampled stack gas volume, reducing the total volume of the digested samples, improving the analytical detection limits, or any combination of the three. For extremely low levels of *Hg only*, the aliquot size selected for digestion and analysis can be increased to as much as 10 ml, thus improving the in-stack detection limit by a factor of ten compared to a 1 ml aliquot size.

13.3.3.1 A nominal one hour sampling run will collect a stack gas sampling volume of about 1.25 m^3. If the sampling time is increased to four hours and 5 m^3 are collected, the in-stack method detection limits would be improved by a factor of four compared to the values shown in Table 29–1.

13.3.3.2 The in-stack detection limits assume that all of the sample is digested and the final liquid volumes for analysis are the normal values of 300 ml for Analytical Fraction 1, and 150 ml for Analytical Fraction 2A. If the volume of Analytical Fraction 1 is reduced from 300 to 30 ml, the in-stack detection limits for that fraction of the sample would be improved by a factor of ten. If the volume of Analytical Fraction 2A is reduced from 150 to 25 ml, the in-stack detection limits for that fraction of the sample would be improved by a factor of six. Matrix effect checks are necessary on sample analyses and typically are of much greater significance for samples that have been concentrated to

less than the normal original sample volume. Reduction of Analytical Fractions 1 and 2A to volumes of less than 30 and 25 ml, respectively, could interfere with the redissolving of the residue and could increase interference by other compounds to an intolerable level.

13.3.3.3 When both of the modifications described in sections 13.3.3.1 and 13.3.3.2 are used simultaneously on one sample, the resultant improvements are multiplicative. For example, an increase in stack gas volume by a factor of four and a reduction in the total liquid sample digested volume of both Analytical Fractions 1 and 2A by a factor of six would result in an improvement by a factor of twenty-four of the in-stack method detection limit.

13.4 Precision. The precision (relative standard deviation) for each metal detected in a method development test performed at a sewage sludge incinerator were found to be as follows:

Sb (12.7 percent), As (13.5 percent), Ba (20.6 percent), Cd (11.5 percent), Cr (11.2 percent), Cu (11.5 percent), Pb (11.6 percent), P (14.6 percent), Se (15.3 percent), Tl (12.3 percent), and Zn (11.8 percent). The precision for Ni was 7.7 percent for another test conducted at a source simulator. Be, Mn, and Ag were not detected in the tests. However, based on the analytical detection limits of the ICAP for these metals, their precisions could be similar to those for the other metals when detected at similar levels.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Alternative Analyzer. Samples may also be analyzed by cold vapor atomic fluorescence spectrometry.

16.2 [Reserved]

17.0 References

1. Method 303F in *Standard Methods for the Examination of Water Wastewater*, 15th Edition, 1980. Available from the American Public Health Association, 1015 18th Street N.W., Washington, D.C. 20036.

2. EPA Methods 6010, 6020, 7000, 7041, 7060, 7131, 7421, 7470, 7740, and 7841, *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*. SW–846, Third Edition, November 1986, with updates I, II, IIA, IIB and III. Office of Solid Waste and Emergency Response, U. S. Environmental Protection Agency, Washington, DC 20460.

3. EPA Method 200.7, Code of Federal Regulations, Title 40, Part 136, Appendix C. July 1, 1987.

4. EPA Methods 1 through 5, Code of Federal Regulations, Title 40, Part 60, Appendix A, July 1, 1991.

5. EPA Method 101A, Code of Federal Regulations, Title 40, Part 61, Appendix B, July 1, 1991.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 29–1—IN STACK METHOD DETECTION LIMITS (UG/M^3) FOR THE FRONT-HALF, THE BACK HALF, AND THE TOTAL SAMPLING TRAIN USING ICAP, GFAAS, AND CVAAS

Metal	Front-half: probe and filter	Back-half: impinters 1–3	Back-half: impringers 4–6 [a]	Total train
Antimony	[1] 7.7 (0.7)	[1] 3.8 (0.4)	.....	[1] 11.5 (1.1)
Arsenic	[1] 12.7 (0.3)	[1] 6.4 (0.1)	.....	[1] 19.1 (0.4)
Barium	0.5	0.3	.....	0.8
Beryllium	[1] 0.07 (0.05)	[1] 0.04 (0.03)	.....	[1] 0.11 (0.08)
Cadmium	[1] 1.0 (0.02)	[1] 0.5 (0.01)	.....	[1] 1.5 (0.03)
Chromium	[1] 1.7 (0.2)	[1] 0.8 (0.1)	.....	[1] 2.5 (0.3)
Cobalt	[1] 1.7 (0.2)	[1] 0.8 (0.1)	.....	[1] 2.5 (0.3)
Copper	1.4	0.7	.....	2.1
Lead	[1] 10.1 (0.2)	[1] 5.0 (0.1)	.....	[1] 15.1 (0.3)
Manganese	[1] 0.5 (0.2)	[1] 0.2 (0.1)	.....	[1] 0.7 (0.3)
Mercury	[2] 0.06	[2] 0.3	[2] 0.2	[2] 0.56
Nickel	3.6	1.8	.....	5.4
Phosphorus	18	9	.....	27
Selenium	[1] 18 (0.5)	[1] 9 (0.3)	.....	[1] 27 (0.8)
Silver	1.7	0.9 (0.7)	.....	2.6
Thallium	[1] 9.6 (0.2)	[1] 4.8 (0.1)	.....	[1] 14.4 (0.3)
Zinc	0.5	0.3	.....	0.8

[a] Mercury analysis only.
[1] Detection limit when analyzed by ICAP or GFAAS as shown in parentheses (see section 11.1.2).
[2] Detection limit when anaylzed by CVAAS, estimated for Back-half and Total Train. See sections 13.2 and 11.1.3. Note: Actual method in-stack detection limits may vary from these values, as described in section 13.3.3.

TABLE 29–2—RECOMMENDED WAVELENGTHS FOR ICAP ANALYSIS

Analyte	Wavelength (nm)
Aluminum (Al)	308.215
Antimony (Sb)	206.833
Arsenic (As)	193.696
Barium (Ba)	455.403
Beryllium (Be)	313.042
Cadmium (Cd)	226.502
Chromium (Cr)	267.716
Cobalt (Co)	228.616
Copper (Cu)	328.754
Iron (Fe)	259.940

TABLE 29–2—RECOMMENDED WAVELENGTHS FOR ICAP ANALYSIS—Continued

Analyte	Wavelength (nm)
Lead (Pb)	220.353
Manganese (Mn)	257.610
Nickel (Ni)	231.604
Phosphorus (P)	214.914
Selenium (Se)	196.026
Silver (Ag)	328.068
Thallium (T_1)	190,864
Zinc (Zn)	213,856

TABLE 29–3—APPLICABLE TECHNIQUES, METHODS AND MINIMIZATION OF INTERFERENCES FOR AAS ANALYSIS

Metal	Technique	SW–846 [1] Methods No.	Wavelength (nm)	Interferences	
				Cause	Minimization
Fe	Aspiration	7380	248.3	Contamination	Great care taken to avoid contamination.
Pb	Aspiration	7420	283.3	217.0 nm alternate	Background correction required.
Pb	Furnace	7421	283.3	Poor recoveries	Matrix modifier, add 10 μl of phosphorus acid to 1 ml of prepared sample in sampler cup.
Mn	Aspiration	7460	279.5	403.1 nm alternate	Background correction required.
Ni	Aspiration	7520	232.0	352.4 nm alternate Fe, Co, and Cr.	Background correction required. Matrix matching or nitrous-oxide/acetylene flame
				Nonlinear response	Sample dilution or use 352.3 nm line
Se	Furnace	7740	196.0	Volatility	Spike samples and reference materials and add nickel nitrate to minimize volatilization.
				Adsorption & scatter	Background correction is required and Zeeman background correction can be useful.
Ag	Aspiration	7760	328.1	Adsorption & scatter AgCl insoluble.	Background correction is required. Avoid hydrochloric acid unless silver is in solution as a chloride complex. Sample and standards monitored for aspiration rate.
Tl	Aspiration	7840	276.8		Background correction is required. Hydrochloric acid should not be used.
Tl	Furnace	7841	276.8	Hydrochloric acid or chloride.	Background correction is required. Verify that losses are not occurring for volatilization by spiked samples or standard addition; Palladium is a suitable matrix modifier.
Zn	Aspiration	7950	213.9	High Si, Cu, & P Contamination.	Strontium removes Cu and phosphate. Great care taken to avoid contamination.
Sb	Aspiration	7040	217.6	1000 mg/ml Pb, Ni, Cu, or acid.	Use secondary wavelength of 231.1 nm; match sample & standards acid concentration or use nitrous oxide/acetylene flame.
Sb	Furnace	7041	217.6	High Pb	Secondary wavelength or Zeeman correction.
As	Furnace	7060	193.7	Arsenic Volatilization Aluminum.	Spike samples and add nickel nitrate solution to digestates prior to analysis. Use Zeeman background correction.
Ba	Aspiration	7080	553.6		
				Calcium.	
				Barium Ionization	High hollow cathode current and narrow band set.
					2 ml of KCl per 100 m1 of sample.
Be	Aspiration	7090	234.9	500 ppm Al. High Mg and Si.	Add 0.1% fluoride.
Be	Furnace	7091	234.9	Be in optical path	Optimize parameters to minimize effects.
Cd	Aspiration	7130	228.8	Absorption and light scattering.	Background correction is required.

TABLE 29–3—APPLICABLE TECHNIQUES, METHODS AND MINIMIZATION OF INTERFERENCES FOR AAS ANALYSIS—Continued

Metal	Technique	SW–846 [1] Methods No.	Wavelength (nm)	Interferences	
				Cause	Minimization
Cd	Furnace	7131	228.8	As above	As above.
				Excess Chloride	Ammonium phosphate used as a matrix modifier.
				Pipet Tips	Use cadmium-free tips.
Cr	Aspiration	7190	357.9	Alkali metal	KCl ionization suppressant in samples and standards—Consult mfgs' literature.
Co	Furnace	7201	240.7	Excess chloride	Use Method of Standard Additions.
Cr	Furnace	7191	357.9	200 mg/L Ca and P	All calcium nitrate for a know constant effect and to eliminate effect of phosphate.
Cu	Aspiration	7210	324.7	Absorption and Scatter	Consult manufacturer's manual.

[1] Refer to EPA publication SW–846 (Reference 2 in section 16.0).

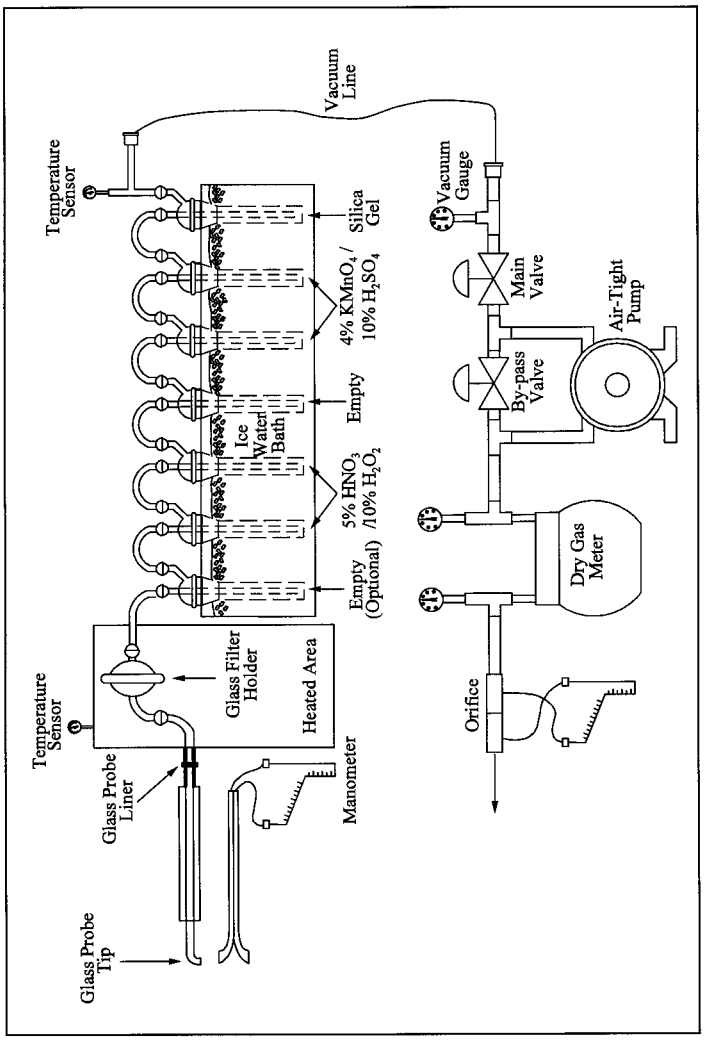

Figure 29-1. Sampling Train.

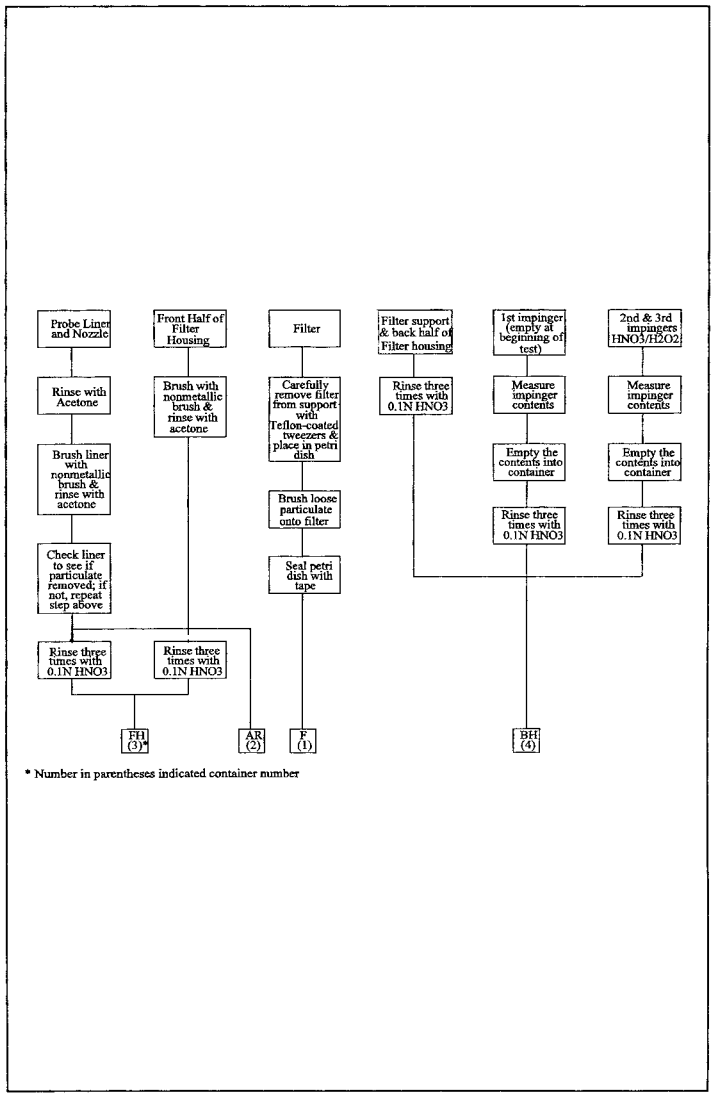

Figure 29-2a. Sample Recovery Scheme.

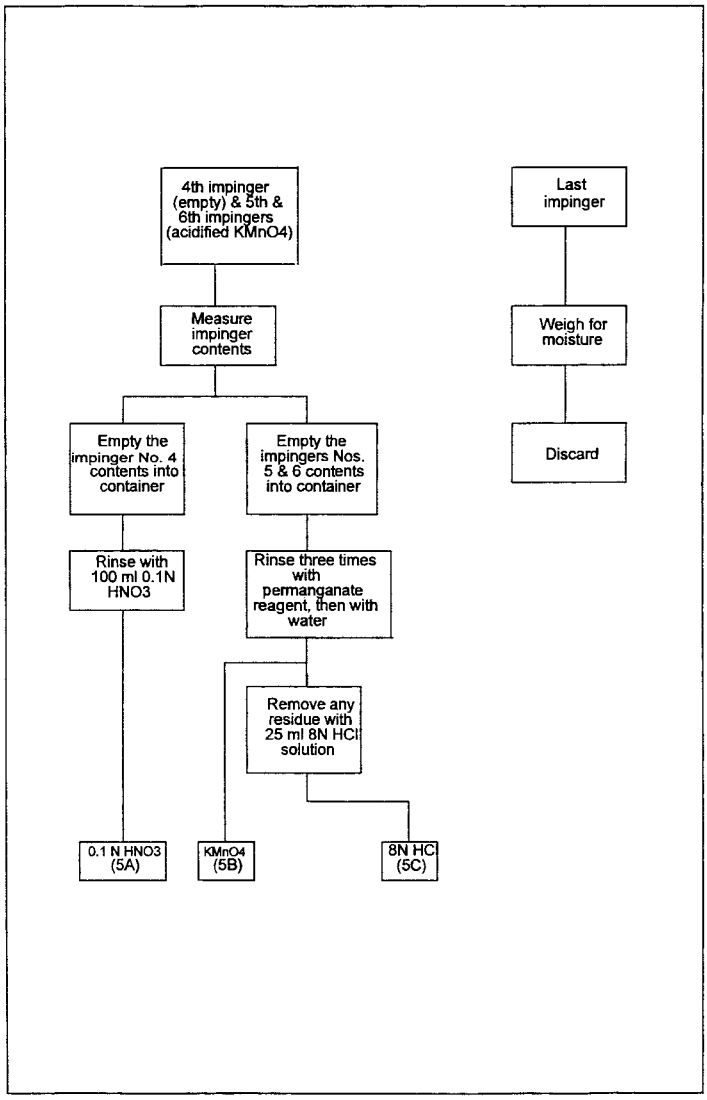

Figure 29-2b. Sample Recovery Scheme.

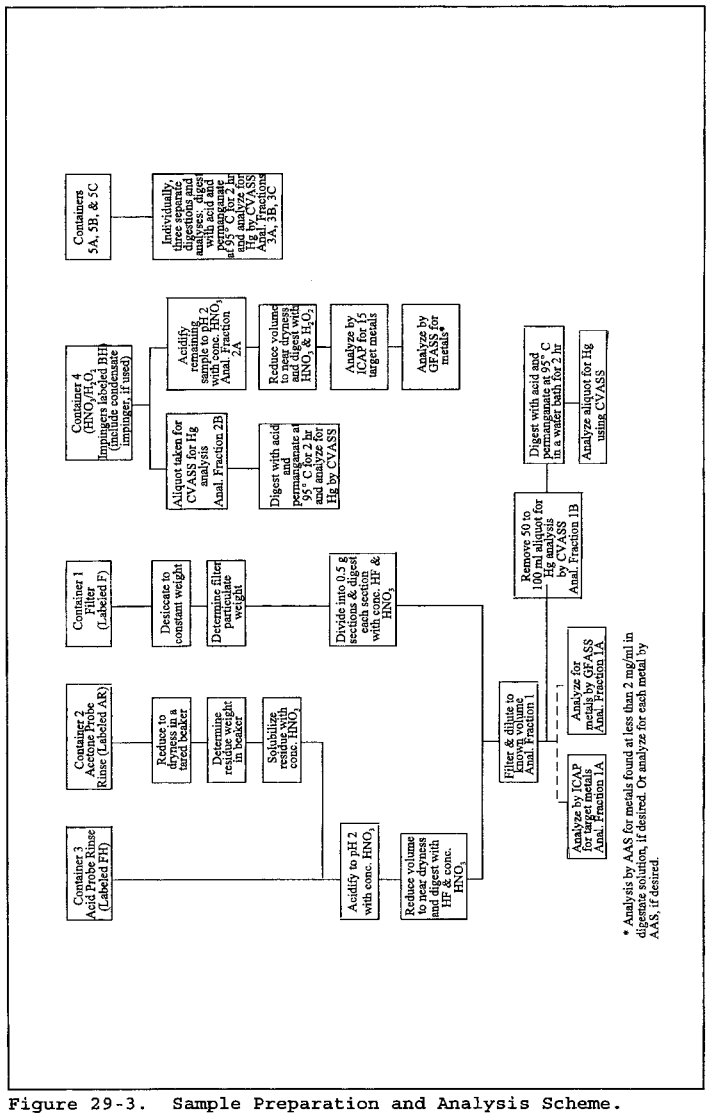

Figure 29-3. Sample Preparation and Analysis Scheme.

METHOD 30A—DETERMINATION OF TOTAL VAPOR PHASE MERCURY EMISSIONS FROM STATIONARY SOURCES (INSTRUMENTAL ANALYZER PROCEDURE)

1.0 Scope and Application

What Is Method 30A?

Method 30A is a procedure for measuring total vapor phase mercury (Hg) emissions from stationary sources using an instrumental analyzer. This method is particularly appropriate for performing emissions testing and for conducting relative accuracy test audits (RATAs) of mercury continuous emissions monitoring systems (Hg CEMS) and sorbent trap monitoring systems at coal-fired combustion sources. Quality assurance and quality control requirements are included to assure that you, the tester, collect

data of known and acceptable quality for each testing site. This method does not completely describe all equipment, supplies, and sampling procedures and analytical procedures you will need but refers to other test methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional methods which are also found in appendices A–1 and A–3 to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 4—Determination of Moisture Content in Stack Gases.

1.1 Analytes. What does this method determine? This method is designed to measure the mass concentration of total vapor phase Hg in flue gas, which represents the sum of elemental Hg (Hg^0) and oxidized forms of Hg (Hg^{+2}), in mass concentration units of micrograms per cubic meter ($\mu g/m^3$).

Analyte	CAS No.	Sensitivity
Elemental Hg (Hg^0) ..	7439–97–6	Typically <2% of Calibration Span.
Oxidized Hg (Hg^{+2})		(Same).

1.2 Applicability. When is this method required? Method 30A is offered as a reference method for emission testing and for RATAs of Hg CEMS and sorbent trap monitoring systems at coal-fired boilers. Method 30A may also be specified for other source categories in the future, either by New Source Performance Standards (NSPS), National Emission Standards for Hazardous Air Pollutants (NESHAP), emissions trading programs, State Implementation Plans (SIP), or operating permits that require measurement of Hg concentrations in stationary source emissions to determine compliance with an applicable emission standard or limit, or to conduct RATAs of Hg CEMS and sorbent trap monitoring systems.

1.3 Data Quality Objectives (DQO). How good must my collected data be? Method 30A has been designed to provide data of high and known quality for Hg emission testing and for relative accuracy testing of Hg monitoring systems including Hg CEMS and sorbent trap monitoring systems. In these and other applications, the principle objective is to ensure the accuracy of the data at the actual emission levels encountered. To meet this objective, calibration standards prepared according to an EPA traceability protocol must be used and measurement system performance tests are required.

2.0 Summary of Method

In this method, a sample of the effluent gas is continuously extracted and conveyed to an analyzer capable of measuring the total vapor phase Hg concentration. Elemental and oxidized mercury (i.e., Hg^0 and Hg^{+2}) may be measured separately or simultaneously but, for purposes of this method, total vapor phase Hg is the sum of Hg^0 and Hg^{+2}. You must meet the performance requirements of this method (i.e., system calibration, interference testing, dynamic spiking, and system integrity/drift checks) to validate your data. The dynamic spiking requirement is deferred until January 1, 2009.

3.0 Definitions

3.1 *Calibration Curve* means the relationship between an analyzer's response to the injection of a series of calibration gases and the actual concentrations of those gases.

3.2 *Calibration Gas* means a gas standard containing Hg^0 or $HgCl_2$ at a known concentration that is produced and certified in accordance with an EPA traceability protocol for certification of Hg calibration standards.

3.2.1 *Zero Gas* means a calibration gas with a concentration that is below the level detectable by the measurement system.

3.2.2 *Low-Level Gas* means a calibration gas with a concentration that is 10 to 30 percent of the calibration span.

3.2.3 *Mid-Level Gas* means a calibration gas with a concentration that is 40 to 60 percent of the calibration span.

3.2.4 *High-Level Gas* means a calibration gas whose concentration is equal to the calibration span.

3.3 *Converter* means a device that reduces oxidized mercury (Hg^{+2}) to elemental mercury (Hg^0).

3.4 *Calibration Span* means the upper limit of valid instrument response during sampling. To the extent practicable the measured emissions are to be between 10 and 100 percent of the selected calibration span (*i.e.*, the measured emissions should be within the calibrated range determined by the Low- and High-Level gas standards). It is recommended that the calibration span be at least twice the native concentration to accommodate the dynamic spiking procedure.

3.5 *Centroidal Area* means the central area that has the same shape as the stack or duct cross section and is no greater than one percent of the stack or duct total cross-sectional area.

3.6 *Data Recorder* means the equipment that permanently records the concentrations reported by the analyzer.

3.7 *Drift Check* means the test to determine the difference between the measurement system readings obtained in a post-run system integrity check and the prior pre-run system integrity check at a specific calibration gas concentration level (*i.e.*, zero, mid-level, or high-level).

3.8 *Dynamic Spiking* means a procedure in which a known mass or concentration of vapor phase $HgCl_2$ is injected into the probe sample gas stream at a known flow rate, in

order to assess the effects of the flue gas matrix on the accuracy of the measurement system.

3.9 *Gas Analyzer* means the equipment that detects the total vapor phase Hg being measured and generates an output proportional to its concentration.

3.10 *Interference Test* means the test to detect analyzer responses to compounds other than Hg, usually gases present in the measured gas stream, that are not adequately accounted for in the calibration procedure and may cause measurement bias.

3.11 *Measurement System* means all of the equipment used to determine the Hg concentration. The measurement system may generally include the following major subsystems: sample acquisition, Hg^{+2} to Hg^0 converter, sample transport, sample conditioning, flow control/gas manifold, gas analyzer, and data recorder.

3.12 *Native Concentration* means the total vapor phase Hg concentration in the effluent gas stream.

3.13 *NIST* means the National Institute of Standards and Technology, located in Gaithersburg, Maryland.

3.14 *Response Time* means the time it takes for the measurement system, while operating normally at its target sample flow rate or dilution ratio, to respond to a known step change in gas concentration (from a low-level to a high-level gas) and to read within 5 percent of the stable high-level gas response.

3.15 *Run* means a series of gas samples taken successively from the stack or duct. A test normally consists of a specific number of runs.

3.16 *System Calibration Error* means the difference between the measured concentration of a low-, mid-, or high-level Hg^0 calibration gas and the certified concentration of the gas when it is introduced in system calibration mode.

3.17 *System Calibration Mode* means introducing the calibration gases into the measurement system at the probe, upstream of all sample conditioning components.

3.18 *Test* refers to the series of runs required by the applicable regulation.

4.0 Interferences

Interferences will vary among instruments and potential instrument-specific spectral and matrix interferences must be evaluated through the interference test and the dynamic spiking tests.

5.0 Safety

What safety measures should I consider when using this method?

This method may require you to work with hazardous materials and in hazardous conditions. You are encouraged to establish safety procedures before using the method. Among other precautions, you should become familiar with the safety recommendations in the gas analyzer user's manual. Occupational Safety and Health Administration (OSHA) regulations concerning use of compressed gas cylinders and noxious gases may apply.

6.0 Equipment and Supplies

6.1 What do I need for the measurement system? This method is intended to be applicable to multiple instrumental technologies. You may use any equipment and supplies that meet the following specifications.

6.1.1 All wetted sampling system components, including probe components prior to the point at which the calibration gas is introduced, must be chemically inert to all Hg species. Materials such as perfluoroalkoxy (PFA) Teflon™, quartz, treated stainless steel (SS) are examples of such materials. [NOTE: These materials of construction are required because components prior to the calibration gas injection point are not included in the system calibration error, system integrity, and interference tests.]

6.1.2 The interference, system calibration error, system integrity, drift and dynamic spiking test criteria must all be met by the system used.

6.1.3 The system must be capable of measuring and controlling sample flow rate.

6.1.4 All system components prior to the Hg^{+2} to Hg^0 converter must be maintained at a sample temperature above the acid gas dew point.

6.2 Measurement System Components. Figure 30A–1 in section 17.0 is an example schematic of a Method 30A measurement system.

6.2.1 Sample Probe. The probe must be made of the appropriate materials as noted in section 6.1.1, heated when necessary (see section 6.1.4), configured with ports for introduction of calibration and spiking gases, and of sufficient length to traverse all of the sample points.

6.2.2 Filter or Other Particulate Removal Device. The filter or other particulate removal device is considered to be a part of the measurement system, must be made of appropriate materials as noted in section 6.1.1, and must be included in all system tests.

6.2.3 Sample Line. The sample line that connects the probe to the converter, conditioning system and analyzer must be made of appropriate materials as noted in section 6.1.1.

6.2.4 Conditioning Equipment. For dry basis measurements, a condenser, dryer or other suitable device is required to remove moisture continuously from the sample gas. Any equipment needed to heat the probe, or sample line to avoid condensation prior to the moisture removal component is also required. For wet basis systems, you must keep the sample above its dew point either by: (1) Heating the sample line and all sample transport components up to the inlet of

the analyzer (and, for hot-wet extractive systems, also heating the analyzer) or (2) by diluting the sample prior to analysis using a dilution probe system. The components required to do either of the above are considered to be conditioning equipment.

6.2.5 Sampling Pump. A pump is needed to push or pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system. If a mechanical sample pump is used and its surfaces are in contact with the sample gas prior to detection, the pump must be leak free and must be constructed of a material that is non-reactive to the gas being sampled (see section 6.1.1). For dilution-type measurement systems, an ejector pump (eductor) may be used to create a sufficient vacuum that sample gas will be drawn through a critical orifice at a constant rate. The ejector pump may be constructed of any material that is non-reactive to the gas being sampled.

6.2.6 Calibration Gas System(s). One or more systems may be needed to introduce calibration gases into the measurement system. A system should be able to flood the sampling probe sufficiently to prevent entry of gas from the effluent stream.

6.2.7 Dynamic Spiking Port. For the purposes of the dynamic spiking procedure described in section 8.2.7, the measurement system must be equipped with a port to allow introduction of the dynamic spike gas stream with the sample gas stream, at a point as close as possible to the inlet of the probe so as to ensure adequate mixing. The same port used for system calibrations and calibration error checks may be used for dynamic spiking purposes.

6.2.8 Sample Gas Delivery. The sample line may feed directly to a converter, to a bypass valve (for speciating systems), or to a sample manifold. All valve and/or manifold components must be made of material that is non-reactive to the gas sampled and the calibration gas, and must be configured to safely discharge any excess gas.

6.2.9 Hg Analyzer. An instrument is required that continuously measures the total vapor phase Hg in the gas stream and meets the applicable specifications in section 13.0.

6.2.10 Data Recorder. A recorder, such as a computerized data acquisition and handling system (DAHS), digital recorder, strip chart, or data logger, is required for recording measurement data.

6.3 Moisture Measurement System. If correction of the measured Hg emissions for moisture is required (see section 8.5), either Method 4 in appendix A–3 to this part or other moisture measurement methods approved by the Administrator will be needed to measure stack gas moisture content.

7.0 Reagents and Standards

7.1 Calibration Gases. What calibration gases do I need? You will need calibration gases of known concentrations of Hg^0 and $HgCl_2$. Special reagents and equipment may be required to prepare the $HgCl^2$ gas standards (e.g., a NIST-traceable solution of $HgCl_2$ and a gas generator equipped with mass flow controllers).

The following calibration gas concentrations are required:

7.1.1 High-Level Gas. Equal to the selected calibration span.

7.1.2 Mid-Level Gas. 40 to 60 percent of the calibration span.

7.1.3 Low-Level Gas. 10 to 30 percent of the calibration span.

7.1.4 Zero Gas. No detectable Hg.

7.1.5 Dynamic Spike Gas. The exact concentration of the $HgCl_2$ calibration gas used to perform the pre-test dynamic spiking procedure described in section 8.2.7 depends on the native Hg concentration in the stack The spike gas must produce a spiked sample concentration above the native concentration, as specified in section 8.2.7.2.2.

7.2 Interference Test. What reagents do I need for the interference test? Use the appropriate test gases listed in Table 30A–3 in section 17.0 (i.e., the potential interferents for the source to be tested, as identified by the instrument manufacturer) to conduct the interference check. These gases need not be of protocol gas quality.

8.0 Sample Collection

Emission Test Procedure

Figure 30A–2 in section 17.0 presents an overview of the test procedures required by this method. Since you may choose different options to comply with certain performance criteria, you must identify the specific options and associated frequencies you select and document your results in regard to the performance criteria.

8.1 Selection of Sampling Sites and Sampling Points. What sampling site and sampling points do I select?

8.1.1 When this method is used solely for Hg emission testing (e.g., to determine compliance with an emission standard or limit), use twelve sampling points located according to Table 1–1 or Table 1–2 of Method 1 in appendix A–1 to this part. Alternatively, you may conduct a stratification test as described in section 8.1.3 to determine the number and location of the sampling points.

8.1.2 When this method is used for relative accuracy testing of a Hg CEMS or sorbent trap monitoring system, follow the sampling

site selection and sampling point layout procedures for gas monitor RATA testing described in the appropriate performance specification or applicable regulation (e.g., Performance Specification 2, section 8.1.3 of appendix B to this part or section 6.5.6 of appendix A to part 75 of this chapter), with one exception. If you elect to perform stratification testing as part of the sampling point selection process, perform the testing in accordance with section 8.1.3 of this method (see also ''Summary Table of QA/QC Requirements'' in section 9.0).

8.1.3 Determination of Stratification. If you elect to perform stratification testing as part of the sampling point selection process and the test results show your effluent gas stream to be unstratified or minimally stratified, you may be allowed to sample at fewer points or at different points than would otherwise be required.

8.1.3.1 Test Procedure. To test for stratification, use a probe of appropriate length to measure the total vapor phase Hg concentration at twelve traverse points located according to Table 1–1 or Table 1–2 of Method 1 in appendix A–1 to this part. Alternatively, for a sampling location where stratification is expected (e.g., after a wet scrubber or at a point where dissimilar gas streams are combined together), if a 12-point Hg stratification test has been previously performed at that location and the results of the test showed the location to be minimally stratified or unstratified according to the criteria in section 8.1.3.2, you may perform an abbreviated 3-point or 6-point Hg stratification test at the points specified in section 6.5.6.2(a) of appendix A to part 75 of this chapter in lieu of performing the 12-point test. Sample for a minimum of twice the system response time (see section 8.2.6) at each traverse point. Calculate the individual point and mean Hg concentrations.

8.1.3.2 Acceptance Criteria and Sampling Point Location.

8.1.3.2.1 If the Hg concentration at each traverse point differs from the mean concentration for all traverse points by no more than: (a) ±5 percent of the mean concentration; or (b) ±0.2 μg/m^3 (whichever is less restrictive), the gas stream is considered to be unstratified and you may collect samples from a single point that most closely matches the mean.

8.1.3.2.2 If the 5 percent or 0.2 μg/m^3 criterion in section 8.1.3.2.1 is not met, but the Hg concentration at each traverse point differs from the mean concentration for all traverse points by no more than: (a)±10 percent of the mean; or (b)±0.5 μg/m^3 (whichever is less restrictive), the gas stream is considered to be minimally stratified, and you may take samples from three points, provided the points are located on the measurement line exhibiting the highest average Hg concentration during the stratification test. If the stack diameter (or equivalent diameter, for a rectangular stack or duct) is greater than 2.4 meters (7.8 ft), locate the three sampling points at 0.4, 1.0, and 2.0 meters from the stack or duct wall. Alternatively, if a RATA required by part 75 of this chapter is being conducted, you may locate the three points at 4.4, 14.6, and 29.6 percent of the duct diameter, in accordance with Method 1 in appendix A–1 to this part. For stack or duct diameters of 2.4 meters (7.8 ft) or less, locate the three sampling points at 16.7, 50.0, and 83.3 percent of the measurement line.

8.1.3.2.3 If the gas stream is found to be stratified because the 10 percent or 0.5 μg/m^3 criterion in section 8.1.3.2.2 is not met, then either locate three sampling points at 16.7, 50.0, and 83.3 percent of the measurement line that exhibited the highest average Hg concentration during the stratification test, or locate twelve traverse points for the test in accordance with Table 1–1 or Table 1–2 of Method 1 in appendix A–1 to this part; or, if a RATA required by part 75 of this chapter is being conducted, locate six Method 1 points along the measurement line that exhibited the highest average Hg concentration.

8.1.3.3 Temporal Variations. Temporal variations in the source Hg concentration during a stratification test may complicate the determination of stratification. If temporal variations are a concern, you may use the following procedure to normalize the stratification test data. A second Hg measurement system, i.e., either an installed Hg CEMS or another Method 30A system, is required to perform this procedure. Position the sampling probe of the second Hg measurement system at a fixed point in the stack or duct, at least one meter from the stack or duct wall. Then, each time that the Hg concentration is measured at one of the stratification test points, make a concurrent measurement of Hg concentration at the fixed point. Normalize the Hg concentration measured at each traverse point, by multiplying it by the ratio of $C_{F,avg}$ to C_F, where C_F is the corresponding fixed-point Hg concentration measurement, and $C_{F,avg}$ is the average of all of the fixed-point measurements over the duration of the stratification test. Evaluate the results of the stratification test according to section 8.1.3.2, using the normalized Hg concentrations.

8.1.3.4 Stratification Testing Exemption. Stratification testing need not be performed at a test location where it would otherwise be required to justify using fewer sample points or different sample points, if the owner or operator documents that the Hg concentration in the stack gas is expected to be 3 μg/m^3 or less at the time of a Hg monitoring system RATA or an Hg emissions test. To demonstrate that a particular test location qualifies for the stratification testing exemption, representative Hg emissions data must be collected just prior to the RATA or

emissions test. At least one hour of Hg concentration data is required for the demonstration. The data used for the demonstration shall be recorded at process operating conditions that closely approximate the operating conditions that will exist during the RATA or emissions test. It is recommended that collection of the demonstration data be integrated with the on-site pretest procedures required by the reference method being used for the RATA or emissions test (whether this method or another approved Hg reference method is used). Quality-assured data from an installed Hg monitoring system may also be used for the demonstration. If a particular test location qualifies for the stratification testing exemption, sampling shall be performed at three points, as described in section 8.1.3.2.2 of this method. The owner or operator shall fully document the method used to collect the demonstration data and shall keep this documentation on file with the data from the associated RATA or Hg emissions test.

8.1.3.5 Interim Alternative Stratification Test Procedures. In the time period between the effective date of this method and January 1, 2009, you may follow one of the following two procedures. Substitute a stratification test for sulfur dioxide (SO_2) for the Hg stratification test described in section 8.1.3.1. If this option is chosen, follow the test procedures in section 6.5.6.1 of appendix A to part 75 of this chapter. Evaluate the test results and determine the sampling point locations according to section 6.5.6.3 of appendix A to part 75 of this chapter. If the sampling location is found to be minimally stratified or unstratified for SO_2, it shall be considered minimally stratified or unstratified for Hg. Alternatively, you may forgo stratification testing, assume the gas stream is minimally stratified, and sample at three points as described in section 8.1.3.2.2 of this method.

8.2 Initial Measurement System Performance Tests. What initial performance criteria must my system meet before I begin sampling? Before measuring emissions, perform the following procedures:

(a) Interference Test;

(b) Calibration Gas Verification;

(c) Measurement System Preparation;

(d) 3-Point System Calibration Error Test;

(e) System Integrity Check;

(f) Measurement System Response Time Test; and

(g) Dynamic Spiking Test.

8.2.1 Interference Test (Optional). Your measurement system should be free of known interferences. It is recommended that you conduct this interference test of your measurement system prior to its initial use in the field to verify that the candidate test instrument is free from inherent biases or interferences resulting from common combustion emission constituents. If you have multiple measurement systems with components of the same make and model numbers, you need only perform this interference check on one system and you may also rely on an interference test conducted by the manufacturer on a system having components of the same make and model(s) of the system that you use. The interference test procedure is found in section 8.6 of this method.

8.2.2 Calibration Gas Verification. How must I verify the concentrations of my calibration gases?

8.2.2.1 Cylinder Gas Standards. When cylinder gas standards are used for Hg^0, obtain a certificate from the gas manufacturer and confirm that the documentation includes all information required by an EPA traceability protocol (see section 16). Confirm that the manufacturer certification is complete and current. Ensure that the calibration gas certifications have not expired.

8.2.2.2 Other Calibration Standards. All other calibration standards for $HgCl_2$ and Hg^0, such as gas generators, must meet the requirements of an EPA traceability protocol (see section 16), and the certification procedures must be fully documented in the test report.

8.2.2.3 Calibration Span. Select the calibration span (i.e., high-level gas concentration) so that the measured source emissions are 10 to 100 percent of the calibration span. This requirement is waived for applications in which the Hg concentrations are consistently below 1 $\mu g/m^3$; however, the calibration span for these low-concentration applications shall not exceed 5 $\mu g/m^3$.

8.2.3 Measurement System Preparation. How do I prepare my measurement system for use? Assemble, prepare, and precondition the measurement system according to your standard operating procedure. Adjust the system to achieve the correct sampling rate or dilution ratio (as applicable). Then, conduct a 3-point system calibration error test using Hg^0 as described in section 8.2.4, an initial system integrity check using $HgCl_2$ and a zero gas as described in section 8.2.5, and a pre-test dynamic spiking test as described in section 8.2.7.

8.2.4 System Calibration Error Test. Conduct a 3-point system calibration error test before the first test run. Use Hg^0 standards for this test. Introduce the low-, mid-, and high-level calibration gases in any order, in system calibration mode, unless you desire to determine the system response time during this test, in which case, inject the gases such that the high-level injection directly follows the low-level injection. For non-dilution systems, you may adjust the system to maintain the correct flow rate at the analyzer during the test, but you may not make adjustments for any other purpose. For dilution systems, you must operate the measurement system at the appropriate dilution

ratio during all system calibration error checks, and you may make only the adjustments necessary to maintain the proper ratio. After each gas injection, wait until a stable response has been obtained. Record the analyzer's final, stable response to each calibration gas on a form similar to Table 30A–1 in section 17.0. For each calibration gas, calculate the system calibration error using Equation 30A–1 in section 12.2. The calibration error specification in section 13.1 must be met for the low-, mid-, and high-level gases. If the calibration error specification is not met for all three gases, take corrective action and repeat the test until an acceptable 3-point calibration is achieved.

8.2.5 System Integrity Check. Perform a two-point system integrity check before the first test run. Use the zero gas and either the mid- or high-level $HgCl_2$ calibration gas for the check, whichever one best represents the total vapor phase Hg concentration levels in the stack. Record the data on a form similar to Table 30A–2 in section 17.0. The system integrity check specification in section 13.2 must be met for both the zero gas and the mid- or high-level gas. If the system integrity specification is not met for both gases, take corrective action and repeat the test until an acceptable system integrity check is achieved.

8.2.6 Measurement System Response Time. The measurement system response time is used to determine the minimum sampling time for each sampling point and is equal to the time that is required for the measured Hg concentration to increase from the stable low-level calibration gas response to a value within 5 percent of the stable high-level calibration gas response during the system calibration error test in section 8.2.4. Round off the measured system response time to the nearest minute.

8.2.7 Dynamic Spiking Test. You must perform dynamic spiking prior to the first test run to validate your test data. The purpose of this procedure is to demonstrate that the site-specific flue gas matrix does not adversely affect the accuracy of the measurement system. The specifications in section 13.5 must be met to validate your data. If these specifications are not met for the pretest dynamic spiking, you may not proceed with the test until satisfactory results are obtained. For the time period between the effective date of this method and January 1, 2009, the dynamic spiking requirement is waived.

8.2.7.1 How do I perform dynamic spiking? Dynamic spiking is a gas phase application of the method of standard additions, which involves injecting a known quantity of Hg into the measurement system upstream of all sample conditioning components, similar to system calibration mode, except the probe is not flooded and the resulting sample stream includes both effluent gas and the spike gas. You must follow a written procedure that details how the spike is added to the system, how the spike dilution factor (DF) is measured, and how the Hg concentration data are collected and processed.

8.2.7.2 Spiking Procedure Requirements.

8.2.7.2.1 Spiking Gas Requirements. The spike gas must also be a $HgCl_2$ calibration gas certified by an EPA traceability protocol. You must choose concentrations that can produce the target levels while being injected at a volumetric flow rate that is ≤20 percent of the total volumetric flow rate through the measurement system (i.e., sample flow rate plus spike gas flow rate).

8.2.7.2.2 Target Spiking Level. The target level for spiking must be 150 to 200 percent of the native Hg concentration; however, if the native Hg concentration is <1 μg/m³, set the target level to add between 1 and 4 μg/m³ Hg^{+2} to the native concentration. Use Equation 30A–5 in section 12.5 to calculate the acceptable range of spike gas concentrations at the target level. Then select a spike gas concentration in that range.

8.2.7.2.3 Spike Injections. You must inject spikes in such a manner that the spiking does not alter the total volumetric sample system flow rate and dilution ratio (if applicable). You must collect at least 3 data points, and the relative standard deviation (RSD) specification in section 13.5 must be met. Each data point represents a single spike injection, and pre- and post-injection measurements of the native Hg concentration (or diluted native concentration, as applicable) are required for each spike injection.

8.2.7.2.4 Spike Dilution Factor (DF). For each spike injection, DF, the dilution factor must be determined. DF is the ratio of the total volumetric flow rate of gas through the measurement system to the spike gas flow rate. This factor must be ≥5. The spiking mass balance calculation is directly dependent on the accuracy of the DF determination. As a result, high accuracy total volumetric flow rate and spike gas flowrate measurements are required. These flow rates may be determined by direct or indirect measurement. Calibrated flow meters, venturies, orifices or tracer gas measurements are examples of potential flow measurement techniques.

8.2.7.2.5 Concentrations. The measurement system must record total vapor phase Hg concentrations continuously during the dynamic spiking procedure. It is possible that dynamic spiking at a level close to 200 percent of the native Hg concentration may cause the measured Hg concentration to exceed the calibration span value. Avoid this by choosing a lower spiking level or by recalibration at a higher span. The measurements shall not exceed 120 percent of the calibration span. The ''baseline'' measurements made between spikes may represent

the native Hg concentration (if spike gas flow is stopped between injections) or the native Hg concentration diluted by blank or carrier gas flowing at the same rate as the spike gas (if gas flow cannot be stopped between injections). Each baseline measurement must include at least 4 readings or 1 minute (whichever is greater) of stable responses. Use Equation 30A–10 or 30A–11 in section 12.10 (as applicable) to convert baseline measurements to native concentration.

8.2.7.2.6 Recovery. Calculate spike recoveries using Equation 30A–7 in section 12.7. Mass recoveries may be calculated from stable responses based on injected mass flows or from integrated response peaks based on total mass injected. Calculate the mean and RSD for the three (or more) spike injections and compare to the specifications in section 13.5.

8.2.7.2.7 Error Adjustment Option. You may adjust the measurement data collected during dynamic spiking for the system calibration error using Equation 30A–3 in section 12. To do this, perform the initial system integrity check prior to the dynamic spiking test, and perform another system integrity check following the dynamic spiking test and before the first test run. If you choose this option, you must apply Equation 30A–3 to both the spiked sample concentration measurement (C_{ss}) and the baseline or native concentration measurement (C_{native}), each substituted in place of C_{avg} in the equation.

8.2.7.3 Example Spiking Procedure Using a Hot Vapor Calibration Source Generator.

(a) Introduce the spike gas into the probe using a hot vapor calibration source generator and a solution of $HgCl_2$ in dilute HC1 and HNO_3. The calibrator uses a mass flow controller (accurate within 2 percent) to measure the gas flow, and the solution feed is measured using a top-loading balance accurate to 0.01g. The challenges of injecting oxidized Hg may make it impractical to stop the flow of gas between spike injections. In this case, operate the hot vapor calibration source generator continuously during the spiking procedure, swapping blank solutions for $HgCl_2$ solutions when switching between spiking and baseline measurements.

(b) If applicable, monitor the measurement system to make sure the total sampling system flow rate and the sample dilution ratio do not change during this procedure. Record all data on a data sheet similar to Table 30A–5 in section 17.0. If the Hg measurement system design makes it impractical to measure the total volumetric flow rate through the system, use a spike gas that includes a tracer for measuring the dilution factor, DF (see Equation 30A–9 in section 12.9). Allow the measurements to stabilize between each spike injection, average the pre- and post-injection baseline measurements, and calculate the native concentration. If this measurement shifts by more than 5 percent during any injection, it may be necessary to discard that data point and repeat the injection to achieve the required RSD among the injections. If the spikes persistently show poor repeatability, or if the recoveries are not within the range specified in section 13.5, take corrective action.

8.2.8 Run Validation. How do I confirm that each run I conduct is valid?

8.2.8.1 System Integrity Checks.

(a) Before and after each test run, perform a two-point system integrity check using the same procedure as the initial system integrity check described in section 8.2.5. You may use data from that initial system integrity check as the pre-run data for the first test run, provided it is the most recent system integrity check done before the first run. You may also use the results of a successful post-run system integrity check as the pre-run data for the next test run. Do not make any adjustments to the measurement system during these checks, other than to maintain the target calibration gas flow rate and the proper dilution ratio.

(b) As a time-saving alternative, you may, at the risk of invalidating multiple test runs, skip one or more integrity checks during a test day. Provided there have been no auto-calibrations or other instrument alterations, a single integrity check may suffice as a post-run check to validate (or invalidate) as many consecutive test runs as can be completed during a single test day. All subsequent test days must begin with a pre-run system integrity check subject to the same performance criteria and corrective action requirements as a post-run system integrity check.

(c) Each system integrity check must meet the criteria for system integrity checks in section 13.2. If a post-run system integrity check is failed, all test runs since the last passed system integrity check are invalid. If a post-run or a pre-run system integrity check is failed, you must take corrective action and pass another 3-point Hg^0 system calibration error test (Section 8.2.4) followed by another system integrity check before conducting any additional test runs. Record the results of the pre- and post-run system integrity checks on a form similar to Table 30A–2 in section 17.0.

8.2.8.2 Drift Check. Using the data from the successful pre- and post-run system integrity checks, calculate the zero and upscale drift, using Equation 30A–2 in section 12.3. Exceeding the section 13.3 specification does not invalidate the run, but corrective action must be taken and a new 3-point Hg^0 system calibration error test and a system integrity check must be passed before any more runs are made.

8.3 Dilution-Type Systems—Special Considerations. When a dilution-type measurement system is used, there are three important considerations that must be taken into

account to ensure the quality of the emissions data. First, the critical orifice size and dilution ratio must be selected properly so that the sample dew point will be below the sample line and analyzer temperatures. Second, a high-quality, accurate dilution controller must be used to maintain the correct dilution ratio during sampling. The dilution controller should be capable of monitoring the dilution air pressure, orifice upstream pressure, eductor vacuum, and sample flow rates. Third, differences between the molecular weight of calibration gas mixtures, dilution air, and the stack gas molecular weight must be considered because these can affect the dilution ratio and introduce measurement bias.

8.4 Sampling.

(a) Position the probe at the first sampling point. Allow the system to flush and equilibrate for at least two times the measurement system response time before recording any data. Then, traverse and record measurements at all required sampling points. Sample at each traverse point for an equal length of time, maintaining the appropriate sample flow rate or dilution ratio (as applicable). For all Hg instrumental method systems, the minimum sampling time at each sampling point must be at least two times the system response time, but not less than 10 minutes. For concentrating systems, the minimum sampling time must also include at least 4 concentration measurement cycles.

(b) After recording data for the appropriate period of time at the first traverse point, you may move the sample probe to the next point and continue recording, omitting the requirement to allow the system to equilibrate for two times the system response time before recording data at the subsequent traverse points. You must, however, sample at this and all subsequent traverse points for the required minimum amount of time specified in this section. If you must remove the probe from the stack for any reason, you must again allow the sampling system to equilibrate for at least two times the system response time prior to resuming data recording.

(c) If at any point the measured Hg concentration exceeds the calibration span value, you must at a minimum identify and report this as a deviation from the method. Depending on the data quality objectives of the test, this event may require corrective action before proceeding. If the average Hg concentration for any run exceeds the calibration span value, the run is invalidated.

8.5 Moisture Correction. If the moisture basis (wet or dry) of the measurements made with this method is different from the moisture basis of either: (1) The applicable emission limit; or (2) a Hg CEMS or sorbent trap monitoring system being evaluated for relative accuracy, you must determine the moisture content of the flue gas and correct the measured gas concentrations to a dry basis using Method 4 in appendix A–3 of this part or other appropriate methods, subject to the approval of the Administrator.

8.6 Optional Interference Test Procedure.

(a) Select an appropriate calibration span that reflects the source(s) to be tested and perform the interference check at 40 percent of the lowest calibration span value anticipated, e.g., 10 $\mu g/m^3$. Alternatively, successfully conducting the interference test at an absolute Hg concentration of 2 $\mu g/m^3$ will demonstrate performance for an equivalent calibration span of 5 $\mu g/m^3$, the lowest calibration span allowed for Method 30A testing. Therefore, performing the interference test at the 2 μ/m^3 level will serve to demonstrate acceptable performance for all calibration spans greater than or equal to 5 $\mu g/m^3$.

(b) Introduce the interference test gases listed in Table 30A–3 in section 17.0 into the measurement system separately or as a mixture. The interference test gases HCl and NO must be introduced as a mixture. The interference test gases must be introduced into the sampling system at the probe such that the interference gas mixtures pass through all filters, scrubbers, conditioners, and other components as would be configured for normal sampling.

(c) The interference test must be performed using $HgCl_2$, and each interference test gas (or gas mixture) must be evaluated in triplicate. This is accomplished by measuring the Hg response first with only the $HgCl_2$ gas present and then when adding the interference test gas(es) while maintaining the $HgCl_2$ concentration of the test stream constant. It is important that the equipment used to conduct the interference test be of sufficient quality so as to be capable of blending the $HgCl_2$ and interference gases while maintaining the Hg concentration constant. Gas blending system or manifolds may be used.

(d) The duration of each test should be for a sufficient period of time to ensure the Hg measurement system surfaces are conditioned and a stable output is obtained. Measure the Hg response of the analyzer to these gases in µg/m3. Record the responses and determine the overall interference response using Table 30A–4 in section 17.0 and the equations presented in section 12.11. The specification in section 13.4 must be met.

(e) A copy of these data, including the date completed and a signed certification, must be included with each test report. The intent of this test is that the interference test results are intended to be valid for the life of the system. As a result, the Hg measurement system should be operated and tested in a configuration consistent with the configuration that will be used for field applications. However, if the system used for field testing is not consistent with the system that was interference-tested, the interference test

must be repeated before it is used for any field applications. Examples of such conditions include, but are not limited to: major changes in dilution ratio (for dilution based systems), changes in catalyst materials, changes in filtering device design or materials, changes in probe design or configuration, and changes in gas conditioning materials or approaches.

9.0 Quality Control

What quality control measures must I take?

The table which follows is a summary of the mandatory, suggested, and alternative quality assurance and quality control measures and the associated frequency and acceptance criteria. All of the QC data, along with the run data, must be documented and included in the test report.

SUMMARY TABLE OF QA/QC REQUIREMENTS

Status [1]	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
S	Identify Data User	Regulatory Agency or other primary end user of data.	Before designing test..	
M	Analyzer Design	Analyzer range	Sufficiently >high-level gas to allow determination of system calibration error.	
S	Analyzer resolution or sensitivity.	<2.0 % of full-scale range.	Manufacturer design..	
S	Interference response.	Overall response ≤3% of calibration span. Alternatively, overall response ≤0.3 μg/m³.		
M	Calibration Gases	Traceability protocol	Validation of concentration required.	
M	High-level Hg^0 gas	Equal to the calibration span.	Each calibration error test..	
M	Mid-level Hg^0 gas	40 to 60% of calibration span.	Each calibration error test..	
M	Low-level Hg^0 gas	10 to 30% of calibration span.	Each calibration error test..	
M	High-level $HgCl_2$ gas	Equal to the calibration span.	Each system integrity check (if it better represents C_{native} than the mid level gas)..	
M	Mid-level $HgCl_2$	40 to 60% of calibration span.	Each system gas integrity check (if it better represents C_{native} than the high level gas)..	
M	Zero gas	Each system integrity check..		
M	Dynamic spike gas (C_{native} ≥1 μg/m³).	A high-concentration $HgCl_2$ gas, used to produce a spiked sample concentration that is 150 to 200% of the native concentration.	Pre-test; dynamic spiking not required until 1/1/09..	
M	Dynamic spike gas (C_{native} <1 μg/m³).	A high-concentration $HgCl_2$ gas, used to produce a spiked sample concentration that is 1 to 2 μg/m³ above the native concentration.	Pre-test; dynamic spiking not required until 1/1/09..	
S	Data Recorder Design.	Data resolution	≤0.5% of full-scale	Manufacturer design.
M	Sample Extraction	Probe material	Inert to sample constituents (e.g., PFA Teflon, or quartz if stack >500 °F).	Each run.
M	Sample Extraction	Probe, filter and sample line temperature.	For dry-basis analyzers, keep sample above the dew point, by heating prior to moisture removal. For wet-basis analyzers, keep sample above dew point at all times, by heating or dilution.	Each run.
M	Sample Extraction	Calibration valve material.	Inert to sample constituents (e.g., PFA Teflon or PFA Teflon coated).	Each test.
S	Sample Extraction	Sample pump material.	Inert to sample constituents	Each test.
M	Sample Extraction	Manifold material	Inert to sample constituents	Each test.

SUMMARY TABLE OF QA/QC REQUIREMENTS—Continued

Status [1]	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
M	Particulate Removal	Filter inertness	Pass calibration error check	Each calibration error check.
M	System Calibration Performance.	System calibration error (CE) test.	CE ≤5.0 % of the calibration span for the low-, mid-or high-level Hg^0 calibration gas. Alternative specification: ≤0.5 µg/m³ absolute difference between system response and reference value.	Before initial run and after a failed system integrity check or drift test.
M	System Calibration Performance.	System integrity check.	Error ≤5.0% of the calibration span for the zero and mid- or high-level $HgCl_2$ calibration gas. Alternative specification: ≤0.5 µg/m³ absolute difference between system response and reference value.	Before initial run, after each run, at the beginning of subsequent test days, and after a failed system integrity check or drift test.
M	System Performance	System response time.	Used to determine minimum sampling time per point.	During initial 3-point system calibration error test.
M	System Performance	Drift	≤3.0% of calibration span for the zero and mid- or high-level gas. Alternative specification: ≤0.3 µg/m³ absolute difference between pre- and post-run system calibration error percentages..	At least once per test day.
M	System Performance	Minimum sampling time.	The greater of two times the system response time or 10 minutes. Concentrating systems must also include at least 4 cycles.	Each sampling point.
M	System Performance	Percentage spike recovery and relative standard deviation.	Percentage spike recovery, at the target level: 100 ±10%. Relative standard deviation: ≤5 percent ... Alternative specification: absolute difference between calculated and measured spike values ≤0.5 µg/m³.	Before initial run; dynamic spiking not required until 1/1/09.
M	Sample Point Selection. For Part 60 RATAs, follow the procedures in Performance Specification 2, section 8.1.3, and for Part 75 RATAs, follow the procedures in section 6.5.6 of appendix A to Part 75. That is: • At *any* test location, you may use 3 sample points located at 16.7, 50.0, and 83.3% of a ''long'' measurement line passing through the centroidal area; or • At *any* test location, you may use 6 sample points along a diameter, located according to Method 1 (Part 75 RATAs, only); or	Number and Location of Sample Points.	For emission testing applications, use 12 points, located according to Method 1 in appendix A–1 to this part, unless the results of a stratification test allow fewer points to be used.	Prior to first run.

SUMMARY TABLE OF QA/QC REQUIREMENTS—Continued

Status [1]	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
	• At a location where stratification is not expected and the measurement line is >2.4 m (7.8 ft), you may use 3 sample points located along a ''short'' measurement line at 0.4, 1.0, and 2.0 m from the stack or duct wall or, for Part 75 only, sample points may be located at 4.4, 14.6, and 29.6% of the measurement line; or • After a wet scrubber or at a point where dissimilar gas streams are combined, either locate 3 sample points along the ''long'' measurement line or locate 6 Method 1 points along a diameter (Part 75, only), unless the results of a stratification test allow you to use a ''short'' 3-point measurement line or to sample at a single point. • If it can be demonstrated that stack gas concentration is ≤3 µg/m³, then the test site is exempted from stratification testing. Use the 3-point ''short'' measurement line if the stack diameter is >2.4 m (7.8 ft) and the 3-point ''long'' line for stack diameters ≤2.4 m (7.8 ft).			

SUMMARY TABLE OF QA/QC REQUIREMENTS—Continued

Status [1]	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
A	Sample Point Selection	Stratification Test (See section 8.1.3)..	If the Hg concentration[2] at each traverse point during the stratification test is: • Within ±5% of mean, use 1-point sampling (at the point closest to the mean); or. • Not within ±5% of mean, but is within ±10% of mean, use 3-point sampling. Locate points according to section 8.1.3.2.2 of this method.. Alternatively, if the Hg concentration at each point is:. • Within ±0.2 μg/m³ of mean, use 1-point sampling (at the point closest to the mean); or. • Not within ±0.2 μg/m³ of mean, but is within ±0.5 μg/m³ of mean, use 3-point sampling. Locate points according to section 8.1.3.2.2 of this method..	Prior to first run. Prior to 1/1/09, you may (1) forgo stratification testing and use 3 sampling points (as per section 8.1.3.2.2) or (2) perform a SO_2 stratification test (see sections 6.5.6.1 and 6.5.6.3 of appendix A to part 75), in lieu of a Hg stratification test. If the test location is unstratified or minimally stratified for SO_2, it can be considered unstratified or minimally stratified for Hg also.
M	Data Recording	Frequency	Once per cycle	During run.
S	Data Parameters	Sample concentration and calibration span.	All analyzer readings during each run within calibration span.	Each run.
M	Data Parameters	Sample concentration and calibration span.	All analyzer readings during dynamic spiking tests within 120% of calibration span.	Each spike injection.
M	Data Parameters	Sample concentration and calibration span.	Average Hg concentration for the run ≤calibration span.	Each run.

[1] M = Mandatory; S = Suggested; A = Alternative.
[2] These may either be the unadjusted Hg concentrations or concentrations normalized to account for temporal variations.

10.0 Calibration and Standardization

What measurement system calibrations are required?

Your analyzer must be calibrated with Hg° standards. The initial 3-point system calibration error test described in section 8.2.4 is required before you start the test. Also, prior to and following test runs, the two-point system integrity checks described in sections 8.2.5 and 8.2.8 are required. On and after January 1, 2009, the pre-test dynamic spiking procedure described in section 8.2.7 is also required to verify that the accuracy of the measurement system is suitable and not adversely affected by the flue gas matrix.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the procedures for calculations and data analysis listed in this section.

12.1 Nomenclature. The terms used in the equations are defined as follows:

B_{ws} = Moisture content of sample gas as measured by Method 4 in Appendix A–3 to this part, percent/100.

C_{avg} = Average unadjusted Hg concentration for the test run, as indicated by the data recorder μg/m³.

$\bar{C}_{baseline}$ = Average Hg concentration measured before and after dynamic spiking injections, μg/m³.

C_d = Hg concentration, dry basis, μg/m³.

C_{dif} = Absolute value of the difference between the measured Hg concentrations of the reference $HgCl_2$ calibration gas, with and without the individual or combined interference gases, μg/m³.

$C_{dif\ avg}$ = Average of the 3 absolute values of the difference between the measured Hg concentrations of the reference $HgCl_2$ calibration gas, with and without the individual or combined interference gases, μg/m³.

C_{gas} = Average Hg concentration in the effluent gas for the test run, adjusted for system calibration error, μg/m³.

C_{int} = Measured Hg concentration of the reference $HgCl_2$ calibration gas plus the individual or combined interference gases, µg/m³.
C_m = Average of pre- and post-run system integrity check responses for the upscale (i.e., mid- or high-level) calibration gas, µg/m³.
C_{ma} = Actual concentration of the upscale (i.e., mid- or high-level) calibration gas used for the system integrity checks, µg/m³.
C_0 = Average of pre- and post-run system integrity check responses from the zero gas, µg/m³.
C_{native} = Vapor phase Hg concentration in the source effluent, µg/m³.
C_{ref} = Measured Hg concentration of the reference $HgCl_2$ calibration gas alone, in the interference test, µg/m³.
C_s = Measured concentration of a calibration gas (zero-, low-, mid-, or high-level), when introduced in system calibration mode, µg/m³.
C_{spike} = Actual Hg concentration of the spike gas, µg/m³.
C^*_{spike} = Hg concentration of the spike gas required to achieve a certain target value for the spiked sample Hg concentration, µg/m³.
C_{ss} = Measured Hg concentration of the spiked sample at the target level, µg/m³.
C^*_{ss} = Expected Hg concentration of the spiked sample at the target level, µg/m³.
C_{target} = Target Hg concentration of the spiked sample, µg/m³.
$C_{Tnative}$ = Measured tracer gas concentration present in native effluent gas, ppm.
C_{Tdir} = Tracer gas concentration injected with spike gas, ppm.
C_{Tv} = Diluted tracer gas concentration measured in a spiked sample, ppm.
C_v = Certified Hg° or $HgCl_2$ concentration of a calibration gas (zero, low, mid, or high), µg/m³.
C_w = Hg concentration measured under moist sample conditions, wet basis, µg/m³.
CS = Calibration span, µg/m³.
D = Zero or upscale drift, percent of calibration span.
DF = Dilution factor of the spike gas, dimensionless.
I = Interference response, percent of calibration span.
Q_{probe} = Total flow rate of the stack gas sample plus the spike gas, liters/min.
Q_{spike} = Flow rate of the spike gas, liters/min.
R_i = Individual injection spike recovery, %.
$\bar{R}$ = Mean value of spike recoveries at a particular target level, %.
RSD = Relative standard deviation, %;.
SCE = System calibration error, percent of calibration span.
SCE_i = Pre-run system calibration error during the two-point system integrity check, percent of calibration span.
SCE_f = Post-run system calibration error during the two-point system integrity check, percent of calibration span.

12.2 System Calibration Error. Use Equation 30A–1 to calculate the system calibration error. Equation 30A–1 applies to: 3–point system calibration error tests performed with Hg° standards; and pre- and post-run two-point system integrity checks performed with $HgCl_2$.

$$SCE = \frac{C_s - C_v}{CS} \times 100 \qquad \text{Eq. 30A-1}$$

12.3 Drift Assessment. Use Equation 30A–2 to separately calculate the zero and upscale drift for each test run.

$$D = \left| SCE_f - SCE_i \right| \qquad \text{Eq. 30A-2}$$

12.3 Effluent Hg Concentration. For each test run, calculate C_{avg}, the arithmetic average of all valid Hg concentration values recorded during the run. Then, adjust the value of C_{avg} for system calibration error, using Equation 30A–3.

$$C_{gas} = (C_{avg} - C_0)\,\frac{C_{ma}}{C_m - C_0} \qquad \text{Eq. 30A-3}$$

12.4 Moisture Correction. Use Equation 30A–4a if your measurements need to be corrected to a dry basis.

$$C_d = \frac{C_w}{1 - B_{ws}} \qquad \text{Eq. 30A-4a}$$

Use Equation 30A–4b if your measurements need to be corrected to a wet basis.

$$C_w = C_d \times (1 - B_{ws}) \qquad \text{Eq. 30A-4b}$$

12.5 Dynamic Spike Gas Concentrations. Use Equation 30A–5 to determine the spike gas concentration needed to produce a spiked sample with a certain ''target'' Hg concentration.

$$C^{*}_{spike} = DF(C_{target} - C_{native}) + C_{native} \qquad \text{Eq. 30A-5}$$

12.6 Spiked Sample Concentration. Use Equation 30A–6 to determine the expected or theoretical Hg concentration of a spiked sample.

$$C^{*}_{ss} = C_{native} + \frac{(C_{spike} - C_{native})}{DF} \qquad \text{Eq. 30A-6}$$

12.7 Spike Recovery. Use Equation 30A–7 to calculate the percentage recovery of each spike.

$$R = \frac{DF\,(C_{ss} - C_{native}) + C_{native}}{C_{spike}} \times 100\% \qquad \text{Eq. 30A-7}$$

12.8 Relative Standard Deviation. Use Equation 30A–8 to calculate the relative standard deviation of the individual percentage spike recovery values from the mean.

$$RSD = \frac{100\%}{\bar{R}} \sqrt{\frac{\sum_{i=1}^{n} (R_i - \bar{R})^2}{n-1}} \qquad \text{Eq. 30A-8}$$

12.9 Spike Dilution Factor. Use Equation 30A–9 to calculate the spike dilution factor, using either direct flow measurements or tracer gas measurements.

$$DF = \frac{Q_{probe}}{Q_{spike}} = \frac{C_{Tdir} - C_{Tnative}}{C_{Ttv} - C_{Tnative}} \qquad \text{Eq. 30A-9}$$

12.10 Native Concentration. For spiking procedures that inject blank or carrier gases (at the spiking flow rate, Q_{spike}) between spikes, use Equation 30A–10 to calculate the native concentration.

$$C_{native} = \frac{\bar{C}_{baseline} DF}{DF - 1} \qquad \text{Eq. 30A-10}$$

For spiking procedures that halt all injections between spikes, the native concentration equals the average baseline concentration (see Equation 30A–11).

$$C_{native} = \bar{C}_{baseline} \qquad \text{Eq. 30A-11}$$

12.11 Overall Interference Response. Use equation 30A–12 to calculate the overall interference response.

$$I = \frac{\sum C_{difavg}}{CS} \times 100 \qquad \text{Eq. 30A-12}$$

Where, for each interference gas (or mixture):

$$C_{difavg} = \frac{\sum_{1}^{3} C_{dif}}{3} \qquad \text{Eq. 30A-13}$$

$$C_{dif} = \left| C_{ref} - C_{int} \right| \qquad \text{Eq. 30A-14}$$

13.0 Method Performance

13.1 System Calibration Error Test. This specification applies to the 3-point system calibration error tests using Hg^0. At each calibration gas level tested (low-, mid-, or high-level), the calibration error must be within ±5.0 percent of the calibration span. Alternatively, the results are acceptable if $|C_s - C_v| \leq 0.5$ µg/m³.

13.2 System Integrity Checks. This specification applies to all pre- and post-run 2-point system integrity checks using $HgCl_2$ and zero gas. At each calibration gas level tested (zero and mid- or high-level), the error must be within ±5.0 percent of the calibration span. Alternatively, the results are acceptable if $|C_s - C_v| \leq 0.5$ µg/m³.

13.3 Drift. For each run, the low-level and upscale drift must be less than or equal to 3.0 percent of the calibration span. The drift is also acceptable if the pre- and post-run system integrity check responses do not differ by more than 0.3 µg/m³ (i.e., $|C_{s\ post\text{-}run} - C_{s\ pre\text{-}run}| \leq 0.3$ µg/m³).

13.4 Interference Test. Summarize the results following the format contained in Table 30A–4. For each interference gas (or mixture), calculate the mean difference between the measurement system responses with and without the interference test gas(es). The overall interference response for the analyzer that was used for the test (calculated according to Equation 30A–12), must not be greater than 3.0 percent of the calibration span used for the test (see section 8.6). The results of the interference test are also acceptable if the sum of the absolute average differences for all interference gases (i.e., $\Sigma\ C_{dif\ avg}$) does not exceed 0.3 µg/m³.

13.5 Dynamic Spiking Test. For the pretest dynamic spiking, the mean value of the percentage spike recovery must be 100 ±10 percent. In addition, the relative standard deviation (RSD) of the individual percentage spike recovery values from the mean must be ≤5.0 percent. Alternatively, if the mean percentage recovery is not met, the results are acceptable if the absolute difference between the theoretical spiked sample concentration (see section 12.6) and the actual average value of the spiked sample concentration is ≤0.5 µg/m³.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. EPA Traceability Protocol for Qualification and Certification of Elemental Mercury Gas Generators, expected publication date December 2008, see *www.epa.gov/ttn/emc*.

2. EPA Traceability Protocol for Qualification and Certification of Oxidized Mercury Gas Generators, expected publication date December 2008, see *www.epa.gov/ttn/emc*.

3. EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards, expected revision publication date December 2008, see *www.epa.gov/ttn/emc*.

17.0 Figures and Tables

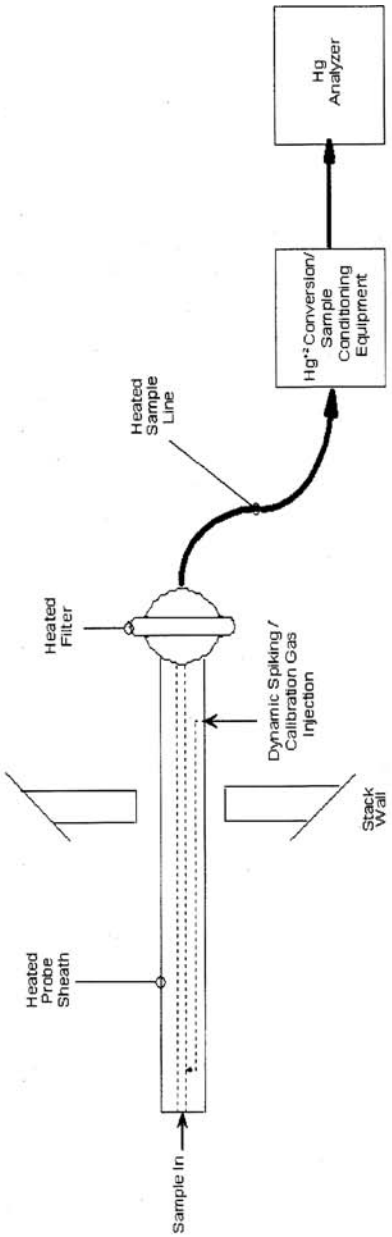

Figure 30A-1: Example Hg Measurement System

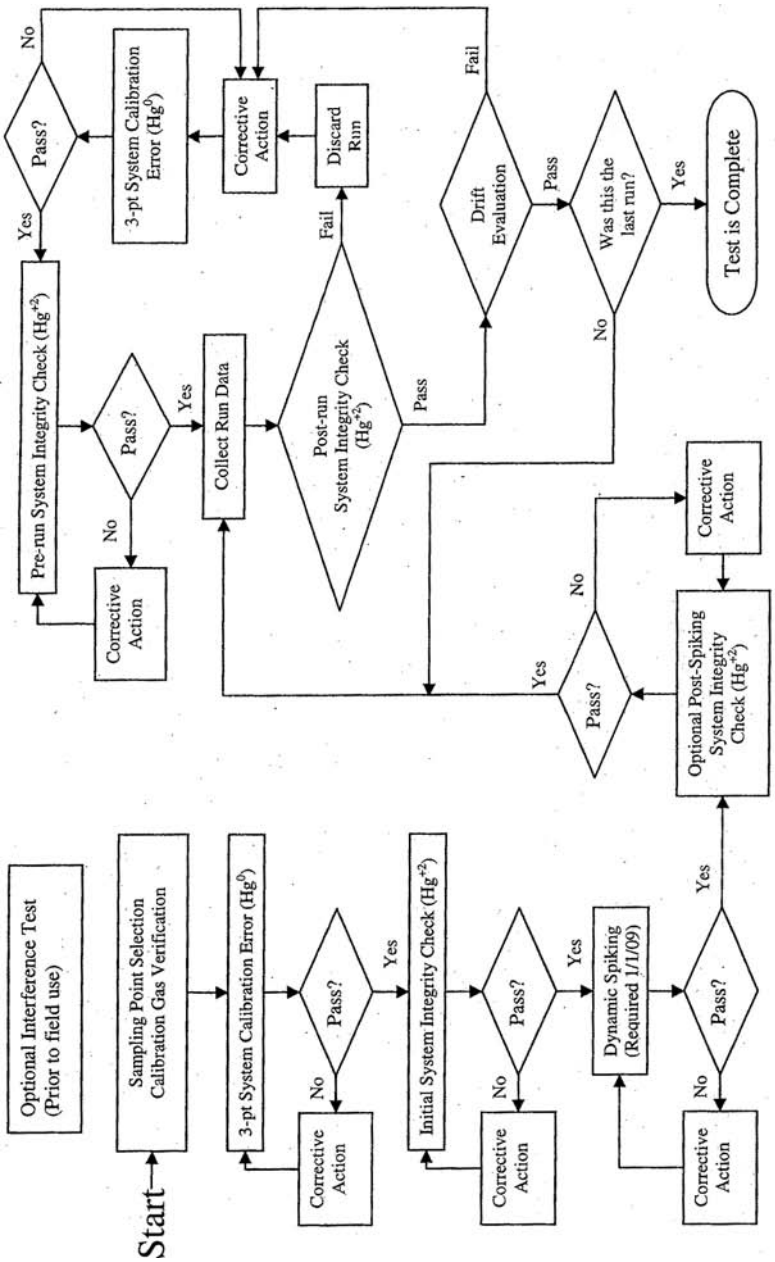

Figure 30A-2. Testing Flow Chart

Table 30A-1: 3-Point System Calibration Error Tests

Facility name: _____ Unit(s) tested: _____ Test personnel: _____ Date: _____ Time: _____	Test Runs Covered: _____ Analyzer make & model no. _____ Serial no. _____ Calibration span (CS): _____ System response time: _____

Calibration Gas Level	Certified Gas Concentration ($\mu g/m^3$) A	System Response ($\mu g/m^3$) B	Absolute Difference |A-B|	Calibration Error (% of calibration span) $\frac{[\|A-B\|]*100}{CS}$
Low				
Mid				
High				

Table 30A-2: System Integrity Check and Drift Data

Facility name:_____ Analyzer make & model: _____

Unit(s) tested: _____ Serial number: _____

Test personnel: _____ Run number(s) covered:_____

Date(s): _____ Calibration span: _____

Calibration Gas Level (zero, mid, or high)	Certified Calibration Gas Value ($\mu g/m^3$)	Initial System Response ($\mu g/m^3$)	Final System Response ($\mu g/m^3$)	Absolute Difference ($\mu g/m^3$)	Drift (% of calibration span)

TABLE 30A–3—INTERFERENCE CHECK GAS CONCENTRATIONS

Potential interferent gas [1]	Concentration, tentative—(balance N_2)
CO_2	15% ±1% CO_2
CO	100 ±20 ppm
HCl [2]	100 ±20 ppm
NO [2]	250 ±50 ppm
SO_2	200 ±20 ppm
O_2	3% ±1% O_2
H_2O	10% ±1% H_2O
Nitrogen	Balance

TABLE 30A–3—INTERFERENCE CHECK GAS CONCENTRATIONS—Continued

Potential interferent gas [1]	Concentration, tentative—(balance N_2)
Other.	

[1] Any of these specific gases can be tested at a lower level if the manufacturer has provided reliable means for limiting or scrubbing that gas to a specified level.

[2] HCl and NO must be tested as a mixture.

Table 30A-4: Example Interference Test Data Sheet

Date of Test: _____
Analyzer Type: _____
Model No.: _____
Serial No.: _____
Calibration Span: _____
Test Organization: _____
Test Personnel: _____

Interference Gas	Hg Concentration ($\mu g/m^3$)	Hg Concentration ($\mu g/m^3$) w/Interference Gas	Absolute Difference ($\mu g/m^3$)	Average Absolute Difference ($\mu g/m^3$)
			Sum of Responses	
			% of Calibration Span	

Table 30A-5: Example Dynamic Spiking Data Sheet

Facility name: _____ Date: _____ Time: _____

Unit(s) tested: _____ Test personnel: _____

Analyzer make & model: _____ Estimated native Hg concentration: _____ µg/m³

Serial number: _____ Estimated unspiked sample flow rate: _____ lpm

Calibration span: _____ µg/m³ Estimated spike gas flow rate: _____ lpm

Q_{probe} (lpm)	Q_{spike} (lpm)	DF[1]	Target Level[2]		C_{native} (µg/m³)			Actual Values		% Spike Recovery
			C^*_{spike} (µg/m³)	C^*_{ss} (µg/m³)	Pre	Post	Avg.	C_{spike} (µg/m³)	C_{ss} (µg/m³)	
									Avg. RSD	

1 DF must be ≥ 5

2 C^*_{ss}/C_{native} must be ≥ 1.5 and ≤ 2.0, where C_{native} and C^*_{ss} are estimated values

METHOD 30B—DETERMINATION OF TOTAL VAPOR PHASE MERCURY EMISSIONS FROM COAL-FIRED COMBUSTION SOURCES USING CARBON SORBENT TRAPS

1.0 Scope and Application

What is Method 30B?

Method 30B is a procedure for measuring total vapor phase mercury (Hg) emissions from coal-fired combustion sources using sorbent trap sampling and an extractive or thermal analytical technique. This method is only intended for use only under relatively low particulate conditions (e.g., sampling after all pollution control devices). Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known and acceptable quality for each testing program. This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need, but instead refers to other test methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional methods which are found in Appendices A–1 and A–3 to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 4—Determination of Moisture Content in Stack Gases.

(c) Method 5—Determination of Particulate Matter Emissions from Stationary Sources

1.1 Analytes. What does this method determine? This method is designed to measure the mass concentration of total vapor phase Hg in flue gas, including elemental Hg (Hg^0) and oxidized forms of Hg (Hg^{+2}), in micrograms per dry standard cubic meter (µg/dscm).

Analyte	CAS No.	Analytical range and sensitivity
Elemental Hg (Hg^0) ..	7439–97–6	Typically 0.1 µg/dscm to >50 µg/dscm.
Oxidized Hg (Hg^{+2}) ...	.....	(Same)

1.2 Applicability. When is this method required? Method 30B is a reference method for relative accuracy test audits (RATAs) of vapor phase Hg CEMS and sorbent trap monitoring systems installed at coal-fired boilers and is also appropriate for Hg emissions testing at such boilers. It is intended for use only under relatively low particulate conditions (i.e., sampling after all pollution control devices); in cases where significant amounts of particle-bound Hg may be present, an isokinetic sampling method for Hg should be used. Method 30B may also be specified by New Source Performance Standards (NSPS), National Emission Standards for Hazardous Air Pollutants (NESHAP), emissions trading programs, State Implementation Plans (SIPs), and operating permits that require measurement of Hg concentrations in stationary source emissions, either to determine compliance with an applicable emission standard or limit, or to conduct RATAs of Hg CEMS and sorbent trap monitoring systems.

1.3 Data Quality Objectives (DQO). How good must my collected data be? Method 30B has been designed to provide data of high and known quality for Hg emissions testing and for RATA testing of Hg monitoring systems, including CEMS and sorbent trap monitors. In these and other applications, the principal objective is to ensure the accuracy of the data at the actual emissions levels and in the actual emissions matrix encountered. To meet this objective, NIST-traceable calibration standards must be used and method performance tests are required.

2.0 Summary of Method

Known volumes of flue gas are extracted from a stack or duct through paired, in-stack sorbent media traps at an appropriate flow rate. Collection of mercury on the sorbent media in the stack mitigates potential loss of mercury during transport through a probe/sample line. For each test run, paired train sampling is required to determine measurement precision and verify acceptability of the measured emissions data. A field recovery test which assesses recovery of an elemental Hg spike to determine measurement bias is also used to verify data acceptability. The sorbent traps are recovered from the sampling system, prepared for analysis as needed, and analyzed by any suitable determinative technique that can meet the performance criteria.

3.0 Definitions

3.1 *Analytical System* is the combined equipment and apparatus used to perform sample analyses. This includes any associated sample preparation apparatus e.g., digestion equipment, spiking systems, reduction devices, etc., as well as analytical instrumentation such as UV AA and UV AF cold vapor analyzers.

3.2 *Calibration Standards* are the Hg containing solutions prepared from NIST traceable standards and are used to directly calibrate analytical systems.

3.3 *Independent Calibration Standard* is a NIST traceable standard obtained from a source or supplier independent of that for the calibration standards and is used to confirm the integrity of the calibration standards used.

3.4 *Method Detection Limit (MDL)* is the lowest mass of Hg greater than zero that can be estimated and reported by your candidate analytical technique. The MDL is statistically derived from replicate low level measurements near your analytical instrument's detection level.

3.5 *NIST* means the National Institute of Standards and Technology, located in Gaithersburg, Maryland.

3.6 *Run* means a series of gas samples taken successively from the stack or duct. A test normally consists of a specific number of runs.

3.7 *Sorbent Trap* means a cartridge or sleeve containing a sorbent media (typically activated carbon treated with iodine or some other halogen) with multiple sections separated by an inert material such as glass wool. These sorbent traps are optimized for the quantitative capture of elemental and oxidized forms of Hg and can be analyzed by multiple techniques.

3.8 *Test* refers to the series of runs required by the applicable regulation.

3.9 *Thermal Analysis* means an analytical technique where the contents of the sorbent traps are analyzed using a thermal technique (desorption or combustion) to release the captured Hg in a detectable form for quantification.

3.10 *Wet Analysis* means an analytical technique where the contents of the sorbent tube are first leached or digested to quantitatively transfer the captured Hg to liquid solution for subsequent analysis.

4.0 Interferences

Interferences may result from the sorbent trap material used as well as from the measurement environment itself. The iodine present on some sorbent traps may impart a negative measurement bias. High levels of sulfur trioxide (SO_3) are also suspected to compromise the performance of sorbent trap Hg capture. These, and other, potential interferences are assessed by performing the analytical matrix interference, Hg^0 and $HgCl_2$ analytical bias and field recovery tests.

5.0 Safety

What safety measures should I consider when using this method? This method may require you to work with hazardous materials and in hazardous conditions. You are encouraged to establish safety procedures before using the method. Among other precautions, you should become familiar with the safety recommendations in the gas analyzer user's manual. Occupational Safety and Health Administration (OSHA) regulations concerning use of compressed gas cylinders and noxious gases may apply.

5.1 Site Hazards. Prior to applying these procedures/specifications in the field, the potential hazards at the test site should be considered; advance coordination with the site is critical to understand the conditions and applicable safety policies. At a minimum, portions of the sampling system will be hot, requiring appropriate gloves, long sleeves, and caution in handling this equipment.

5.2 Laboratory Safety. Policies should be in place to minimize risk of chemical exposure and to properly handle waste disposal in the laboratory. Personnel shall wear appropriate laboratory attire according to a Chemical Hygiene Plan established by the laboratory.

5.3 Reagent Toxicity/Carcinogenicity. The toxicity and carcinogenicity of any reagents used must be considered. Depending upon the sampling and analytical technologies selected, this measurement may involve hazardous materials, operations, and equipment and this method does not address all of the safety problems associated with implementing this approach. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicable regulatory limitations prior to performance. Any chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized. Chemists should refer to the Material Safety Data Sheet (MSDS) for each chemical used.

5.4 Waste Disposal. Any waste generated by this procedure must be disposed of according to a hazardous materials management plan that details and tracks various waste streams and disposal procedures.

6.0 Equipment and Supplies

The following list is presented as an example of key equipment and supplies likely required to measure vapor-phase Hg using a sorbent trap sampling system. It is recognized that additional equipment and supplies may be needed. Collection of paired samples is required.

6.1 Sorbent Trap Sampling System. A typical sorbent trap sampling system is shown in Figure 30B–1 in section 17.0. The sorbent trap sampling system shall include the following components:

6.1.1 Sorbent Traps. The sorbent media used to collect Hg must be configured in a trap with at least two distinct segments or sections, connected in series, that are amenable to separate analyses. section 1 is designated for primary capture of gaseous Hg. section 2 is designated as a backup section for determination of vapor phase Hg breakthrough. Each sorbent trap must be inscribed or otherwise permanently marked with a unique identification number, for tracking purposes. The sorbent media may be any collection material (e.g., carbon, chemically-treated filter, etc.) capable of quantitatively capturing and recovering for subsequent analysis, all gaseous forms of Hg in the emissions from the intended application. Selection of the sorbent media shall be based on the material's ability to achieve the performance criteria contained in this method as well as the sorbent's vapor phase

Hg capture efficiency for the emissions matrix and the expected sampling duration at the test site. The sorbent media must be obtained from a source that can demonstrate their quality assurance and quality control (see section 7.2). The paired sorbent traps are supported on a probe (or probes) and inserted directly into the flue gas stream.

6.1.2 Sampling Probe Assembly. Each probe assembly shall have a leak-free attachment to the sorbent trap(s). Each sorbent trap must be mounted at the entrance of or within the probe such that the gas sampled enters the trap directly. Each probe/sorbent trap assembly must be heated to a temperature sufficient to prevent liquid condensation in the sorbent trap(s). Auxiliary heating is required only where the stack temperature is too low to prevent condensation. Use a calibrated thermocouple to monitor the stack temperature. A single probe capable of operating the paired sorbent traps may be used. Alternatively, individual probe/sorbent trap assemblies may be used, provided that the individual sorbent traps are co-located to ensure representative Hg monitoring.

6.1.3 Moisture Removal Device. A moisture removal device or system shall be used to remove water vapor from the gas stream prior to entering dry gas flow metering devices.

6.1.4 Vacuum Pump. Use a leak-tight, vacuum pump capable of operating within the system's flow range.

6.1.5 Gas Flow Meter. A gas flow meter (such as a dry gas meter, thermal mass flow meter, or other suitable measurement device) shall be used to determine the total sample volume on a dry basis, in units of standard cubic meters. The meter must be sufficiently accurate to measure the total sample volume to within 2 percent and must be calibrated at selected flow rates across the range of sample flow rates at which the sampling train will be operated. The gas flow meter shall be equipped with any necessary auxiliary measurement devices (e.g., temperature sensors, pressure measurement devices) needed to correct the sample volume to standard conditions.

6.1.6 Sample Flow Rate Meter and Controller. Use a flow rate indicator and controller for maintaining necessary sampling flow rates.

6.1.7 Temperature Sensor. Same as section 6.1.1.7 of Method 5 in Appendix A–3 to this part.

6.1.8 Barometer. Same as section 6.1.2 of Method 5 in Appendix A–3 to this part.

6.1.9 Data Logger (optional). Device for recording associated and necessary ancillary information (e.g., temperatures, pressures, flow, time, etc.).

6.2 Gaseous Hg^0 Sorbent Trap Spiking System. A known mass of gaseous Hg^0 must be either present on or spiked onto the first section of sorbent traps in order to perform the Hg^0 and $HgCl_2$ analytical bias test and the field recovery study. Any approach capable of quantitatively delivering known masses of Hg^0 onto sorbent traps is acceptable. Several spiking technologies or devices are available to meet this objective. Their practicality is a function of Hg mass spike levels. For low levels, NIST-certified or NIST-traceable gas generators or tanks may be suitable. An alternative system, capable of delivering almost any mass required, makes use of NIST-certified or NIST-traceable Hg salt solutions (e.g., $HgCl_2$, $Hg(NO_3)_2$). With this system, an aliquot of known volume and concentration is added to a reaction vessel containing a reducing agent (e.g., stannous chloride); the Hg salt solution is reduced to Hg^0 and purged onto the sorbent trap using an impinger sparging system. When available, information on example spiking systems will be posted at *http://www.epa.gov/ttn/emc*.

6.3 Sample Analysis Equipment. Any analytical system capable of quantitatively recovering and quantifying total Hg from the sorbent media selected is acceptable provided that the analysis can meet the performance criteria described in this method. Example recovery techniques include acid leaching, digestion, and thermal desorption/direct combustion. Example analytical techniques include, but are not limited to, ultraviolet atomic fluorescence (UV AF), ultraviolet atomic absorption (UV AA) with and without gold trapping, and X-ray fluorescence (XRF) analysis.

6.3 Moisture Measurement System. If correction of the measured Hg emissions for moisture is required (see section 8.3.3.7), either Method 4 in Appendix A–3 to this part or other moisture measurement methods approved by the Administrator will be needed to measure stack gas moisture content.

7.0 Reagents and Standards

7.1 Reagents and Standards. Only NIST-certified or NIST-traceable calibration standards, standard reference materials, and reagents shall be used for the tests and procedures required by this method.

7.2 Sorbent Trap Media. The sorbent trap media shall be prepared such that the material used for testing is of known and acceptable quality. Sorbent supplier quality assurance/quality control measures to ensure appropriate and consistent performance such as sorptive capacity, uniformity of preparation treatments, and background levels shall be considered.

8.0 Sample Collection and Handling

This section presents the sample collection and handling procedures along with the pretest and on-site performance tests required by this method. Since you may choose different options to comply with certain performance criteria, each test report must identify the specific options selected and

document the results with respect to the performance criteria of this method.

8.1 Selection of Sampling Sites and Sampling Points. What sampling site and sampling points do I select? Same as section 8.1 of Method 30A of this appendix.

8.2 Measurement System Performance Tests. What performance criteria must my measurement system meet? The following laboratory and field procedures and associated criteria of this section are designed to ensure (1) selection of a sorbent and analytical technique combination capable of quantitative collection and analysis of gaseous Hg, (2) collection of an adequate amount of Hg on each sorbent trap during field tests, and (3) adequate performance of the method for each test program: The primary objectives of these performance tests are to characterize and verify the performance of your intended analytical system and associated sampling and analytical procedures, and to define the minimum amount of Hg (as the sample collection target) that can be quantified reliably.

(a) Analytical Matrix Interference Test;

(b) Determination of Minimum Sample Mass;

(c) Hg^0 and $HgCl_2$ Analytical Bias Test;

(d) Determination of Nominal Sample Volume;

(e) Field Recovery Test.

8.2.1 Analytical Matrix Interference Test and Minimum Sample Dilution.

(a) The analytical matrix interference test is a laboratory procedure. It is required only if you elect to use a liquid digestion analytical approach and needs to be performed only once for each sorbent material used. The purpose of the test is to verify the presence or absence of known and potential analytical matrix interferences, including the potential negative bias associated with iodine common to many sorbent trap materials. The analytical matrix interference test determines the minimum dilution (if any) necessary to mitigate matrix effects on the sample digestate solutions.

(b) The result of the analytical matrix interference test, i.e., the minimum sample dilution required (if any) for all sample analyses, is used to establish the minimum sample mass needed for the Hg^0 and $HgCl_2$ analytical bias test and to determine the nominal sample volume for a test run. The analytical matrix interference test is sorbent material-specific and shall be performed for each sorbent material you intend to use for field sampling and analysis. The test shall be performed using a mass of sorbent material comparable to the sorbent mass typically used in the first section of the trap for sampling. Similar sorbent materials from different sources of supply are considered to be different materials and must be tested individually. You must conduct the analytical matrix interference test for each sorbent material prior to the analysis of field samples.

8.2.1.1 Analytical Matrix Interference Test Procedures. Digest and prepare for analysis a representative mass of sorbent material (unsampled) according to your intended laboratory techniques for field samples. Analyze the digestate according to your intended analytical conditions at the least diluted level you intend to use for sample analysis (e.g., undiluted, 1 in 10 dilution, etc.). Determine the Hg concentration of the undiluted digestate solution. Prepare a series of solutions with a fixed final volume containing graduated aliquots of the sample digestate and, a fixed aliquot of a calibration standard (with the balance being Hg-free reagent or H_20) to establish solutions of varied digestate dilution ratio (e.g., 1:2, 1:5, 1:10, 1:100, etc.—see example in section 8.2.1.3, below). One of these solutions should contain only the aliquot of the calibration standard in Hg-free reagent or H_2O. This will result in a series of solutions where the amount of Hg is held relatively constant and only the volume of digestate diluted is varied. Analyze each of these solutions following intended sample analytical procedures and conditions, determining the concentration for each solution.

8.2.1.2 Analytical Matrix Interference Test Acceptance Criteria. Compare the measured concentration of each solution containing digestate to the measured concentration of the digestate-free solution. The lowest dilution ratio of any solution having a Hg concentration within ±5 percent of the digestate-free solution is the minimum dilution ratio required for analysis of all samples. If you desire to measure the digestate without dilution, the ±5 percent criterion must be met at a dilution ratio of at least 9:10 (i.e., ≥90% digestate).

8.2.1.3 Example Analytical Matrix Interference Test. An example analytical matrix interference test is presented below. Additional information on the conduct of the analytical matrix interference test will be posted at *http://www.epa.gov/ttn/emc*. Determine the most sensitive working range for the analyzer to be used. This will be a narrow range of concentrations. Digest and prepare for analysis a representative mass of sorbent material (unsampled) according to your intended laboratory techniques for sample preparation and analysis. Prepare a calibration curve for the most sensitive analytical region, e.g., 0.0, 0.5, 1.0, 3.0, 5.0, 10 ppb. Using the highest calibration standard, e.g., 10.0 ppb, prepare a series of solutions by adding successively smaller increments of the digestate to a fixed volume of the calibration standard and bringing each solution to a final fixed volume with mercury-free deionized water (diH_2O). To 2.0 ml of the calibration standard add 18.0, 10.0, 4.0, 2.0, 1.0, 0.2, and 0.0 ml of the digestate. Bring the final volume of each solution to a total volume of

20 ml by adding 0.0, 8.0, 14.0, 16.0, 17.0, 17.8, and 18.0 ml of diH_2O. This will yield solutions with dilution ratios of 9:10, 1:2, 1:5, 1:10, 1:20, 1:100, and 0:10, respectively. Determine the Hg concentration of each solution. The dilution ratio of any solution having a concentration that is within ±5 percent of the concentration of the solution containing 0.0 ml of digestate is an acceptable dilution ratio for analyzing field samples. If more than one solution meets this criterion, the one with the lowest dilution ratio is the minimum dilution required for analysis of field samples. If the 9:10 dilution meets this criterion, then no sample dilution is required.

8.2.2 Determination of Minimum Sample Mass. The minimum mass of Hg that must be collected per sample must be determined. This information is necessary in order to effectively perform the Hg^0 and $HgCl_2$ Analytical Bias Test, to estimate target sample volumes/sample times for test runs, and to ensure the quality of the measurements. The determination of minimum sample mass is a direct function of analytical technique, measurement sensitivity, dilutions, etc. This determination is required for all analytical techniques. Based on the analytical approach you employ, you should determine the most sensitive calibration range. Based on a calibration point within that range, you must consider all sample treatments (e.g., dilutions) to determine the mass of sample that needs to be collected to ensure that all sample analyses fall within your calibration curve.

8.2.2.1 Determination of Minimum Calibration Concentration or Mass. Based on your instrument's sensitivity and linearity, determine the calibration concentrations or masses that make up a representative low level calibration range. Verify that you are able to meet the multipoint calibration performance criteria in section 11.0 of this method. Select a calibration concentration or mass that is no less than 2 times the lowest concentration or mass in your calibration curve. The lowest point in your calibration curve must be at least 5, and preferably 10, times the Method Detection Limit (MDL), which is the minimum amount of the analyte that can be detected and reported. The MDL must be determined at least once for the analytical system using an MDL study such as that found in section 15.0 to Method 301 of appendix A to part 63 of this chapter.

NOTE TO SECTION 8.2.2.1: While it might be desirable to base the minimum calibration concentration or mass on the lowest point in the calibration curve, selecting a higher concentration or mass is necessary to ensure that all analyses of the field samples will fall within the calibration curve. Therefore, it is strongly recommended that you select a minimum calibration concentration or mass that is sufficiently above the lowest point of the calibration curve (see examples in sections 8.2.2.2.1 and 8.2.2.2.2 below).

8.2.2.2 Determination of Minimum Sample Mass. Based on your minimum calibration concentration or mass and other sample treatments including, but not limited to, final digestate volume and minimum sample dilution, determine the minimum sample mass. Consideration should also be given to the Hg levels expected to be measured in section 2 of the sorbent traps and to the breakthrough criteria presented in Table 9–1.

8.2.2.2.1 Example Determination of Minimum Sample Mass for Thermal Desorption Analysis. A thermal analysis system has been calibrated at five Hg mass levels: 10 ng, 20 ng, 50 ng, 100 ng, 200 ng, and shown to meet the calibration performance criteria in this method. Based on 2 times the lowest point in the calibration curve, 20 ng is selected as the minimum calibration mass. Because the entire sample is analyzed and there are no dilutions involved, the minimum sample mass is also 20 ng.

NOTE: In this example, if the typical background (blank) Hg levels in section 2 were relatively high (e.g., 3 to 5 ng), a sample mass of 20 ng might not have been sufficient to ensure that the breakthrough criteria in Table 9–1 would be met, thereby necessitating the use of a higher point on the calibration curve (e.g., 50 ng) as the minimum calibration and sample mass.

8.2.2.2.2 Example Determination of Minimum Sample Mass for Acid Leachate/Digestate Analysis. A cold vapor analysis system has been calibrated at four Hg concentration levels: 2 ng/L, 5 ng, 10 ng/L, 20 ng/L, and shown to meet the calibration performance criteria in this method. Based on 2 times the lowest point in the calibration curve, 4 ng/L was selected as the minimum calibration concentration. The final sample volume of a digestate is nominally 50 ml (0.05 L) and the minimum dilution necessary was determined to be 1:100 by the Analytical Matrix Interference Test of section 8.2.1. The following calculation would be used to determine the minimum sample mass.

$$\text{Minimum sample mass} = (4\ \text{ng/L}) \times (0.05\ \text{L}) \times (100) = 20\ \text{ng}$$

NOTE: In this example, if the typical background (blank) Hg levels in section 2 were relatively high (e.g., 3 to 5 ng), a sample mass of 20 ng might not have been sufficient to ensure that the breakthrough criterion in Table 9–1 would be met, thereby necessitating the use of a higher point on the calibration curve (e.g., 10 ng/L) as the minimum calibration concentration.

8.2.3 Hg^0 and $HgCl_2$ Analytical Bias Test. Before analyzing any field samples, the laboratory must demonstrate the ability to recover and accurately quantify Hg^0 and $HgCl_2$

from the chosen sorbent media by performing the following analytical bias test for sorbent traps spiked with Hg^0 and $HgCl_2$. The analytical bias test is performed at a minimum of two distinct sorbent trap Hg loadings that will: (1) Represent the lower and upper bound of sample Hg loadings for application of the analytical technique to the field samples, and (2) be used for data validation.

8.2.3.1 Hg^0 and $HgCl_2$ Analytical Bias Test Procedures. Determine the lower and upper bound mass loadings. The minimum sample mass established in section 8.2.2.2 can be used for the lower bound Hg mass loading although lower Hg loading levels are acceptable. The upper bound Hg loading level should be an estimate of the greatest mass loading that may result as a function of stack concentration and volume sampled. As previously noted, this test defines the bounds that actual field samples must be within in order to be valid.

8.2.3.1.1 Hg^0 Analytical Bias Test. Analyze the front section of three sorbent traps containing Hg^0 at the lower bound mass loading level and the front section of three sorbent traps containing Hg^0 at the upper bound mass loading level. In other words, analyze each mass loading level in triplicate. You may refer to section 6.2 for spiking guidance. Prepare and analyze each spiked trap, using the same techniques that will be used to prepare and analyze the field samples. The average recovery for the three traps at each mass loading level must be between 90 and 110 percent. If multiple types of sorbent media are to be analyzed, a separate analytical bias test is required for each sorbent material.

8.2.3.1.2 $HgCl_2$ Analytical Bias Test. Analyze the front section of three sorbent traps containing $HgCl_2$ at the lower bound mass loading level and the front section of three traps containing $HgCl_2$ at the upper bound mass loading level. $HgCl_2$ can be spiked as a gas, or as a liquid solution containing $HgCl_2$. However the liquid volume spiked must be <100 µL. Prepare and analyze each spiked trap, using the techniques that will be used to prepare and analyze the field samples. The average recovery for three traps at each spike concentration must be between 90 and 110 percent. Again, if multiple types of sorbent media are to be analyzed, a separate analytical bias test is required for each sorbent material.

8.2.4 Determination of Target Sample Volume. The target sample volume is an estimate of the sample volume needed to ensure that valid emissions data are collected (i.e., that sample mass Hg loadings fall within the analytical calibration curve and are within the upper and lower bounds set by the analytical bias tests). The target sample volume and minimum sample mass can also be determined by performing a diagnostic test run prior to initiation of formal testing.

Example: If the minimum sample mass is 50 ng and the concentration of mercury in the stack gas is estimated to be 2 µg/m^3 (ng/L) then the following calculation would be used to determine the target sample volume:

Target Sample Volume = (50 ng) / (2 ng/L) = 25 L

NOTE TO SECTION 8.2.4: For the purposes of relative accuracy testing of Hg monitoring systems under subpart UUUUU of part 63 of this chapter and Performance Specifications 12A and 12B in appendix B to this part, when the stack gas Hg concentration is expected to be very low (<0.5 µg/dscm), you may estimate the Hg concentration at 0.5 µg/dscm.

8.2.5 Determination of Sample Run Time. Sample run time will be a function of minimum sample mass (see section 8.2.2), target sample volume and nominal equipment sample flow rate. The minimum sample run time for conducting relative accuracy test audits of Hg monitoring systems is 30 minutes and for emissions testing to characterize an emission source is 1 hour. The target sample run time can be calculated using the following example.

Example: If the target sample volume has been determined to be 25 L, then the following formula would be used to determine the sampling time necessary to acquire 25 L of gas when sampling at a rate of 0.4 L/min.

Sampling time (min) = 25 L / 0.4 L/min = 63 minutes

8.2.6 Field Recovery Test. The field recovery test provides a test program-specific verification of the performance of the combined sampling and analytical approach. Three sets of paired samples, one of each pair which is spiked with a known level of Hg, are collected and analyzed and the average recovery of the spiked samples is used to verify performance of the measurement system under field conditions during that test program. The conduct of this test requires an estimate or confirmation of the stack Hg concentrations at the time of testing.

8.2.6.1 Calculation of Pre-sampling Spiking Level. Determine the sorbent trap spiking level for the field recovery test using estimates of the stack Hg concentration, the target sample flow rate, and the planned sample duration. First, determine the Hg mass expected to be collected in section 1 of the sorbent trap. The pre-sampling spike must be within 50 to 150 percent of this expected mass.

Example calculation: For an expected stack Hg concentration of 5 ug/m^3 (ng/L) a target sample rate of 0.40 liters/min, and a sample duration of 1 hour:

(0.40 L/min) * (60 min) * (5ng/L) = 120 ng

A Hg spike of 60 to 180 ng (50–150% of 120 ng) would be appropriate.

8.2.6.2 Procedures. Set up two identical sampling trains. One of the sampling trains

shall be designated the spiked train and the other the unspiked train. Spike Hg^0 onto the front section of the sorbent trap in the spiked train before sampling. The mass of Hg spiked shall be 50 to 150 percent of the mass expected to be collected with the unspiked train. Sample the stack gas with the two trains simultaneously using the same procedures as for the field samples (see section 8.3). The total sample volume must be within ±20 percent of the target sample volume for the field sample test runs. Analyze the sorbent traps from the two trains utilizing the same analytical procedures and instrumentation as for the field samples (see section 11.0). Determine the fraction of spiked Hg recovered (R) using the equations in section 12.7. Repeat this procedure for a total of three runs. Report the individual R values in the test report; the average of the three R values must be between 85 and 115 percent.

NOTE TO SECTION 8.2.6.2: It is acceptable to perform the field recovery test concurrent with actual test runs (e.g., through the use of a quad probe). It is also acceptable to use the field recovery test runs as test runs for emissions testing or for the RATA of a Hg monitoring system under subpart UUUUU of part 63 of this chapter and Performance Specifications 12A and 12B in appendix B to this part, if certain conditions are met. To determine whether a particular field recovery test run may be used as a RATA run, subtract the mass of the Hg^0 spike from the total Hg mass collected in sections 1 and 2 of the spiked trap. The difference represents the mass of Hg in the stack gas sample. Divide this mass by the sample volume to obtain the Hg concentration in the effluent gas stream, as measured with the spiked trap. Compare this concentration to the corresponding Hg concentration measured with the unspiked trap. If the paired trains meet the relative deviation and other applicable data validation criteria in Table 9–1, then the average of the two Hg concentrations may be used as an emissions test run value or as the reference method value for a RATA run.

8.3 Sampling. This section describes the procedures and criteria for collecting the field samples for analysis. As noted in section 8.2.6, the field recovery test samples are also collected using these procedures.

8.3.1 Pre-test leak check. Perform a leak check of the sampling system with the sorbent traps in place. For each of the paired sampling trains, draw a vacuum in the train, and adjust the vacuum to ~15″ Hg; and, using the gas flow meter, determine leak rate. The leak rate for an individual train must not exceed 4 percent of the target sampling rate. Once the leak check passes this criterion, carefully release the vacuum in the sample train, then seal the sorbent trap inlet until the probe is ready for insertion into the stack or duct.

8.3.2 Determination of Flue Gas Characteristics. Determine or measure the flue gas measurement environment characteristics (gas temperature, static pressure, gas velocity, stack moisture, etc.) in order to determine ancillary requirements such as probe heating requirements (if any), initial sampling rate, moisture management, etc.

8.3.3 Sample Collection

8.3.3.1 Remove the plug from the end of each sorbent trap and store each plug in a clean sorbent trap storage container. Remove the stack or duct port cap and insert the probe(s). Secure the probe(s) and ensure that no leakage occurs between the duct and environment.

8.3.3.2 Record initial data including the sorbent trap ID, date, and the run start time.

8.3.3.3 Record the initial gas flow meter reading, stack temperature, meter temperatures (if needed), and any other appropriate information, before beginning sampling. Begin sampling and target a sampling flow rate similar to that for the field recovery test. Then, at regular intervals (≤5 minutes) during the sampling period, record the date and time, the sample flow rate, the gas meter reading, the stack temperature, the flow meter temperatures (if using a dry gas meter), temperatures of heated equipment such as the vacuum lines and the probes (if heated), and the sampling system vacuum readings. Adjust the sampling flow rate as necessary to maintain the initial sample flow rate. Ensure that the total volume sampled for each run is within 20 percent of the total volume sampled for the field recovery test.

8.3.3.4 Data Recording. Obtain and record any essential operating data for the facility during the test period, e.g., the barometric pressure must be obtained for correcting sample volume to standard conditions when using a dry gas meter. At the end of the data collection period, record the final gas flow meter reading and the final values of all other essential parameters.

8.3.3.5 Post-Test Leak Check. When sampling is completed, turn off the sample pump, remove the probe(s) with sorbent traps from the port, and carefully seal the end of each sorbent trap. Perform another leak check of each sampling train with the sorbent trap in place, at the maximum vacuum reached during the sampling period. Record the leakage rates and vacuums. The leakage rate for each train must not exceed 4 percent of the average sampling rate for the data collection period. Following each leak check, carefully release the vacuum in the sample train.

8.3.3.6 Sample Recovery. Recover each sampled sorbent trap by removing it from the probe and sealing both ends. Wipe any deposited material from the outside of the sorbent

trap. Place the sorbent trap into an appropriate sample storage container and store/preserve in appropriate manner (see section 8.3.3.8).

8.3.3.7 Stack Gas Moisture Determination. If the moisture basis of the measurements made with this method (dry) is different from the moisture basis of either: (1) the applicable emission limit; or (2) a Hg CEMS being evaluated for relative accuracy, you must determine the moisture content of the flue gas and correct for moisture using Method 4 in appendix A–3 to this part. If correction of the measured Hg concentrations for moisture is required, at least one Method 4 moisture determination shall be made during each test run.

8.3.3.8 Sample Handling, Preservation, Storage, and Transport. While the performance criteria of this approach provides for verification of appropriate sample handling, it is still important that the user consider, determine and plan for suitable sample preservation, storage, transport, and holding times for these measurements. Therefore, procedures in ASTM D6911–15 ''Standard Guide for Packaging and Shipping Environmental Samples for Laboratory Analysis'' (incorporated by reference-see 40 CFR 60.17) shall be followed for all samples, where appropriate. To avoid Hg contamination of the samples, special attention should be paid to cleanliness during transport, field handling, sampling, recovery, and laboratory analysis, as well as during preparation of the sorbent cartridges. Collection and analysis of blank samples (*e.g.*, reagent, sorbent, field, etc.) is useful in verifying the absence or source of contaminant Hg.

8.3.3.9 Sample Custody. Proper procedures and documentation for sample chain of custody are critical to ensuring data integrity. The chain of custody procedures in ASTM D4840–99 ''Standard Guide for Sampling Chain-of-Custody Procedures'' shall be followed for all samples (including field samples and blanks).

9.0 Quality Assurance and Quality Control

Table 9–1 summarizes the QA/QC performance criteria that are used to validate the Hg emissions data from Method 30B sorbent trap measurement systems.

TABLE 9–1—QUALITY ASSURANCE/QUALITY CONTROL CRITERIA FOR METHOD 30B

QA/QC test or specification	Acceptance criteria	Frequency	Consequences if not met
Gas flow meter calibration (At 3 settings or points).	Calibration factor (Y_i) at each flow rate must be within ±2% of the average value (Y).	Prior to initial use and when post-test check is not within ±5% of Y.	Recalibrate at 3 points until the acceptance criteria are met.
Gas flow meter post-test calibration check (Single-point).	Calibration factor (Y_i) must be within ±5% of the Y value from the most recent 3-point calibration.	After each field test. For mass flow meters, must be done on-site, using stack gas.	Recalibrate gas flow meter at 3 points to determine a new value of Y. For mass flow meters, must be done on-site, using stack gas. Apply the new Y value to the field test data.
Temperature sensor calibration	Absolute temperature measures by sensor within ±1.5% of a reference sensor.	Prior to initial use and before each test thereafter.	Recalibrate; sensor may not be used until specification is met.
Barometer calibration	Absolute pressure measured by instrument within ±10 mm Hg of reading with a mercury barometer or NIST traceable barometer.	Prior to initial use and before each test thereafter.	Recalibrate; instrument may not be used until specification is met.
Pre-test leak check	≤4% of target sampling rate ..	Prior to sampling	Sampling shall not commence until the leak check is passed.
Post-test leak check	≤4% of average sampling rate	After sampling	Sample invalidated.*
Analytical matrix interference test (wet chemical analysis, only).	Establish minimum dilution (if any) needed to eliminate sorbent matrix interferences.	Prior to analyzing any field samples; repeat for each type of sorbent used.	Field sample results not validated.
Analytical bias test	Average recovery between 90% and 110% for Hg^0 and $HgCl_2$ at each of the 2 spike concentration levels.	Prior to analyzing field samples and prior to use of new sorbent media.	Field samples shall not be analyzed until the percent recovery criteria has been met.
Multipoint analyzer calibration	Each analyzer reading within ±10% of true value *and* $r^2 \geq 0.99$.	On the day of analysis, before analyzing any samples.	Recalibrate until successful.
Analysis of independent calibration standard.	Within ±10% of true value	Following daily calibration, prior to analyzing field samples.	Recalibrate and repeat independent standard analysis until successful.

TABLE 9–1—QUALITY ASSURANCE/QUALITY CONTROL CRITERIA FOR METHOD 30B—Continued

QA/QC test or specification	Acceptance criteria	Frequency	Consequences if not met
Analysis of continuing calibration verification standard (CCVS).	Within ±10% of true value	Following daily calibration, after analyzing ≤10 field samples, and at end of each set of analyses.	Recalibrate and repeat independent standard analysis, reanalyze samples until successful, if possible; for destructive techniques, samples invalidated.
Test run total sample volume ..	Within ±20% of total volume sampled during field recovery test.	Each individual sample	Sample invalidated.
Sorbent trap section 2 breakthrough.	For compliance/emissions testing: ≤10% of section 1 Hg mass for Hg concentrations >1 μg/dscm;. ≤20% of section 1 Hg mass for Hg concentrations ≤1 μg/dscm. ≤50% of section 1 Hg mass if the stack Hg concentration is ≤30% of the Hg concentration that is equivalent to the applicable emission limit. For relative accuracy testing: ≤10% of section 1 Hg mass for Hg concentrations >1 μg/dscm;. ≤20% of section 1 Hg mass for Hg concentrations ≤1 μg/dscm and >0.5 μg/dscm;. ≤50% of section 1 Hg mass for Hg concentrations ≤0.5 μg/dscm >0.1 μg/dscm;. no criterion for Hg concentrations ≤0.1 μg/dscm (must meet all other QA/QC specifications).	Every sample	Sample invalidated.*
Paired sorbent trap agreement	≤10% Relative Deviation (RD) mass for Hg concentrations >1 μg/dscm; ≤20% RD or ≤0.2 μg/dscm absolute difference for Hg concentrations ≤1 μg/dscm.	Every run	Run invalidated.*
Sample analysis	Within valid calibration range (within calibration curve).	All Section 1 samples where stack Hg concentration is ≥0.02 μg/dscm except in case where stack Hg concentration is ≤30% of the applicable emission limit.	Reanalyze at more concentrated level if possible, samples invalidated if not within calibrated range.
Sample analysis	Within bounds of Hg^0 and $HgCl_2$ Analytical Bias Test.	All Section 1 samples where stack Hg concentration is ≥0.5 μg/dscm.	Expand bounds of Hg^0 and $HgCl_2$ Analytical Bias Test; if not successful, samples invalidated.
Field recovery test	Average recovery between 85% and 115% for Hg^0.	Once per field test	Field sample runs not validated without successful field recovery test.

*And data from the pair of sorbent traps are also invalidated.

10.0 Calibration and Standardization

10.1 Only NIST-certified and NIST-traceable calibration standards (i.e., calibration gases, solutions, etc.) shall be used for the spiking and analytical procedures in this method.

10.2 Gas Flow Meter Calibration.

10.2.1 Preliminaries. The manufacturer or equipment supplier of the gas flow meter should perform all necessary set-up, testing, programming, etc., and should provide the end user with any necessary instructions, to

ensure that the meter will give an accurate readout of dry gas volume in standard cubic meters for this method.

10.2.2 Initial Calibration. Prior to its initial use, a calibration of the gas flow meter shall be performed. The initial calibration may be done by the manufacturer, by the equipment supplier, or by the end user. If the flow meter is volumetric in nature (*e.g.*, a dry gas meter), the manufacturer or end user may perform a direct volumetric calibration using any gas. For a mass flow meter, the manufacturer, equipment supplier, or end user may calibrate the meter using either: (1) A bottled gas mixture containing 12 ±0.5% CO_2, 7 ±0.5% O_2, and balance N_2 (when this method is applied to coal-fired boilers); (2) a bottled gas mixture containing CO_2, O_2, and N_2 in proportions representative of the expected stack gas composition; or (3) the actual stack gas.

10.2.2.1 Initial Calibration Procedures. Determine an average calibration factor (Y) for the gas flow meter by calibrating it at three sample flow rate settings covering the range of sample flow rates at which the sampling system will be operated. You may either follow the procedures in section 10.3.1 of Method 5 in appendix A–3 to this part or in section 16 of Method 5 in appendix A–3 to this part. If a dry gas meter is being calibrated, use at least five revolutions of the meter at each flow rate.

10.2.2.2 Alternative Initial Calibration Procedures. Alternatively, you may perform the initial calibration of the gas flow meter using a reference gas flow meter (RGFM). The RGFM may be: (1) A wet test meter calibrated according to section 10.3.1 of Method 5 in appendix A–3 to this part; (2) a gas flow metering device calibrated at multiple flow rates using the procedures in section 16 of Method 5 in appendix A–3 to this part; or (3) a NIST-traceable calibration device capable of measuring volumetric flow to an accuracy of 1 percent. To calibrate the gas flow meter using the RGFM, proceed as follows: While the Method 30B sampling system is sampling the actual stack gas or a compressed gas mixture that simulates the stack gas composition (as applicable), connect the RGFM to the discharge of the system. Care should be taken to minimize the dead volume between the gas flow meter being tested and the RGFM. Concurrently measure dry stack gas volume with the RGFM and the flow meter being calibrated for at least 10 minutes at each of three flow rates covering the typical range of operation of the sampling system. For each set of concurrent measurements, record the total sample volume, in units of dry standard cubic meters (dscm), measured by the RGFM and the gas flow meter being tested.

10.2.2.3 Initial Calibration Factor. Calculate an individual calibration factor Y_i at each tested flow rate from section 10.2.2.1 or 10.2.2.2 of this method (as applicable) by taking the ratio of the reference sample volume to the sample volume recorded by the gas flow meter. Average the three Y_i values, to determine Y, the calibration factor for the flow meter. Each of the three individual values of Y_i must be within ±0.02 of Y. Except as otherwise provided in sections 10.2.2.4 and 10.2.2.5 of this method, use the average Y value from the initial 3-point calibration to adjust subsequent gas volume measurements made with the gas flow meter.

10.2.2.4 Pretest On-Site Calibration Check (Optional). For a mass flow meter, if the most recent 3-point calibration of the flow meter was performed using a compressed gas mixture, you may want to conduct the following on-site calibration check prior to testing, to ensure that the flow meter will accurately measure the volume of the stack gas: While sampling stack gas, check the calibration of the flow meter at one intermediate flow rate setting representative of normal operation of the sampling system. If the pretest calibration check shows that the value of Y_i, the calibration factor at the tested flow rate, differs from the current value of Y by more than 5 percent, perform a full 3-point recalibration of the meter using stack gas to determine a new value of Y, and (except as otherwise provided in section 10.2.2.5 of this method) apply the new Y value to the data recorded during the field test.

10.2.2.5 Post-Test Calibration Check. Check the calibration of the gas flow meter following each field test at one intermediate flow rate setting, either at, or in close proximity to, the average sample flow rate during the field test. For dry gas meters, ensure at least three revolutions of the meter during the calibration check. For mass flow meters, this check must be performed before leaving the test site, while sampling stack gas. If a one-point calibration check shows that the value of Y_i at the tested flow rate differs by more than 5 percent from the current value of Y, repeat the full 3-point calibration procedure to determine a new value of Y, and apply the new Y value to the gas volume measurements made with the gas flow meter during the field test that was just completed. For mass flow meters, perform the 3-point recalibration while sampling stack gas.

10.3 Thermocouples and Other Temperature Sensors. Use the procedures and criteria in Section 10.3 of Method 2 in appendix A–1 to this part to calibrate in-stack temperature sensors and thermocouples. Dial thermometers shall be calibrated against mercury-in-glass thermometers or equivalent. Calibrations must be performed prior to initial use and before each field test thereafter. At each calibration point, the absolute temperature measured by the temperature sensor must agree to within ±1.5 percent of the temperature measured with the reference

sensor, otherwise the sensor may not continue to be used.

10.4 Barometer. Calibrate against a mercury barometer or other NIST-traceable barometer as per Section 10.6 of Method 5 in appendix A–3 to this part. Calibration must be performed prior to initial use and before each test program, and the absolute pressure measured by the barometer must agree to within ±10 mm Hg of the pressure measured by the mercury or other NIST-traceable barometer, otherwise the barometer may not continue to be used.

10.5 Other Sensors and Gauges. Calibrate all other sensors and gauges according to the procedures specified by the instrument manufacturer(s).

10.6 Analytical System Calibration. See section 11.1 of this method.

11.0 Analytical Procedures

The analysis of Hg in the field and quality control samples may be conducted using any instrument or technology capable of quantifying total Hg from the sorbent media and meeting the performance criteria in this method. Because multiple analytical approaches, equipment and techniques are appropriate for the analysis of sorbent traps, it is not possible to provide detailed, technique-specific analytical procedures. As they become available, detailed procedures for a variety of candidate analytical approaches will be posted at *http://www.epa.gov/ttn/emc.*

11.1 Analytical System Calibration. Perform a multipoint calibration of the analyzer at three or more upscale points over the desired quantitative range (multiple calibration ranges shall be calibrated, if necessary). The field samples analyzed must fall within a calibrated, quantitative range and meet the performance criteria specified below. For samples suitable for aliquotting, a series of dilutions may be needed to ensure that the samples fall within a calibrated range. However, for sorbent media samples consumed during analysis (e.g., when using thermal desorption techniques), extra care must be taken to ensure that the analytical system is appropriately calibrated prior to sample analysis. The calibration curve range(s) should be determined such that the levels of Hg mass expected to be collected and measured will fall within the calibrated range. The calibration curve may be generated by directly introducing standard solutions into the analyzer or by spiking the standards onto the sorbent media and then introducing into the analyzer after preparing the sorbent/standard according to the particular analytical technique. For each calibration curve, the value of the square of the linear correlation coefficient, i.e., r^2, must be ≥0.99, and the analyzer response must be within ±10 percent of the reference value at each upscale calibration point. Calibrations must be performed on the day of the analysis, before analyzing any of the samples. Following calibration, an independent standard shall be analyzed. The measured value of the independently prepared standard must be within ±10 percent of the expected value.

11.2 Sample Preparation. Carefully separate the sections of each sorbent trap. Combine for analysis all materials associated with each section; any supporting substrate that the sample gas passes through prior to entering a media section (e.g., glass wool separators, acid gas traps, etc.) must be analyzed with that segment.

11.3 Field Sample Analyses. Analyze the sorbent trap samples following the same procedures that were used for conducting the Hg^0 and $HgCl_2$ analytical bias tests. The individual sections of the sorbent trap and their respective components must be analyzed separately (*i.e.*, section 1 and its components, then section 2 and its components). All sorbent trap section 1 sample analyses must be within the calibrated range of the analytical system as specified in Table 9–1. For wet analyses, the sample can simply be diluted to fall within the calibrated range. However, for the destructive thermal analyses, samples that are not within the calibrated range cannot be re-analyzed. As a result, the sample cannot be validated, and another sample must be collected. It is strongly suggested that the analytical system be calibrated over multiple ranges so that thermally analyzed samples fall within the calibrated range. The total mass of Hg measured in each sorbent trap section 1 must also fall within the lower and upper mass limits established during the initial Hg^0 and $HgCl_2$ analytical bias test. If a sample is analyzed and found to fall outside of these limits, it is acceptable for an additional Hg^0 and $HgCl_2$ analytical bias test to be performed that now includes this level. However, some samples (e.g., the mass collected in trap section 2), may have Hg levels so low that it may not be possible to quantify them in the analytical system's calibrated range. Because a reliable estimate of these low-level Hg measurements is necessary to fully validate the emissions data, the MDL (see section 8.2.2.1 of this method) is used to establish the minimum amount that can be detected and reported. If the measured mass or concentration is below the lowest point in the calibration curve and above the MDL, the analyst must estimate the mass or concentration of the sample based on the analytical instrument response relative to an additional calibration standard at a concentration or mass between the MDL and the lowest point in the calibration curve. This is accomplished by establishing a response factor (e.g., area counts per Hg mass or concentration) and estimating the amount of Hg present in the sample based on the analytical response and this response factor.

Example: The analysis of a particular sample results in a measured mass above the MDL, but below the lowest point in the calibration curve which is 10 ng. An MDL of 1.3 ng Hg has been established by the MDL study. A calibration standard containing 5 ng of Hg is analyzed and gives an analytical response of 6,170 area counts, which equates to a response factor of 1,234 area counts/ng Hg. The analytical response for the sample is 4,840 area counts. Dividing the analytical response for the sample (4,840 area counts) by the response factor gives 3.9 ng Hg, which is the estimated mass of Hg in the sample.

11.4 Analysis of Continuing Calibration Verification Standard (CCVS). After no more than 10 samples and at the end of each set of analyses, a continuing calibration verification standard must be analyzed. The measured value of the continuing calibration standard must be within ±10 percent of the expected value.

11.5 Blanks. The analysis of blanks is optional. The analysis of blanks is useful to verify the absence of, or an acceptable level of, Hg contamination. Blank levels should be considered when quantifying low Hg levels and their potential contribution to meeting the sorbent trap section 2 breakthrough requirements; however, correcting sorbent trap results for blank levels is prohibited.

12.0 Calculations and Data Analysis

You must follow the procedures for calculation and data analysis listed in this section.

12.1 Nomenclature. The terms used in the equations are defined as follows:

B = Breakthrough (%).
B_{ws} = Moisture content of sample gas as measured by Method 4, percent/100.
C_a = Concentration of Hg for the sample collection period, for sorbent trap ''a'' (µg/dscm).
C_b = Concentration of Hg for the sample collection period, for sorbent trap ''b'' (µg/dscm).
C_d = Hg concentration, dry basis (µg/dscm).
C_{rec} = Concentration of spiked compound measured (µg/m^3).
C_w = Hg concentration, wet basis (µg/m^3).
m_1 = Mass of Hg measured on sorbent trap section 1 (µg).
m_2 = Mass of Hg measured on sorbent trap section 2 (µg).
$m_{recovered}$ = Mass of spiked Hg recovered in Analytical Bias or Field Recovery Test (µg).
m_s = Total mass of Hg measured on spiked trap in Field Recovery Test (µg).
m_{spiked} = Mass of Hg spiked in Analytical Bias or Field Recovery Test (µg).
m_u = Total mass of Hg measured on unspiked trap in Field Recovery Test (µg).
R = Percentage of spiked mass recovered (%).
RD = Relative deviation between the Hg concentrations from traps ''a'' and ''b'' (%).
v_s = Volume of gas sampled, spiked trap in Field Recovery Test (dscm).
V_t = Total volume of dry gas metered during the collection period (dscm); for the purposes of this method, standard temperature and pressure are defined as 20 °C and 760 mm Hg, respectively.
v_u = Volume of gas sampled, unspiked trap in Field Recovery Test (dscm).

12.2 Calculation of Spike Recovery (Analytical Bias Test). Calculate the percent recovery of Hg^0 and $HgCl_2$ using Equation 30B–1.

$$R = \frac{m_{recovered}}{m_{spiked}} \times 100 \qquad \text{Eq. 30B-1}$$

12.3 Calculation of Breakthrough. Use Equation 30B–2 to calculate the percent breakthrough to the second section of the sorbent trap.

$$B = \frac{m_2}{m_1} \times 100 \qquad \text{Eq. 30B-2}$$

12.4 Calculation of Hg Concentration. Calculate the Hg concentration measured with sorbent trap ''a'', using Equation 30B–3.

$$C_a = \frac{(m_1 + m_2)}{V_t} \qquad \text{Eq. 30B-3}$$

For sorbent trap ''b'', replace ''C_a '' with ''C_b '' in Equation 30B–3. Report the average concentration, i.e., ½ (C_a + C_b).

12.5 Moisture Correction. Use Equation 30B–4 if your measurements need to be corrected to a wet basis.

$$C_w = C_d \times (1 - B_{ws}) \qquad \text{Eq. 30B-4}$$

12.6 Calculation of Paired Trap Agreement. Calculate the relative deviation (RD) between the Hg concentrations measured with the paired sorbent traps using Equation 30B–5.

$$RD = \frac{|C_a - C_b|}{C_a + C_b} \times 100 \qquad \text{Eq. 30B-5}$$

12.7 Calculation of Measured Spike Hg Concentration (Field Recovery Test). Calculate the measured spike concentration using Equation 30B–6.

$$C_{rec} = \frac{m_s}{v_s} - \frac{m_u}{v_u} \qquad \text{Eq. 30B-6}$$

Then calculate the spiked Hg recovery, R, using Equation 30B–7.

California Environmental Protection Agency

Air Resources Board

Method 436

Determination of Multiple Metals Emissions from Stationary Sources

Adopted: July 28, 1997

Method 436

Determination of Multiple Metals Emissions from Stationary Sources

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Method 436

DETERMINATION OF MULTIPLE METALS EMISSIONS FROM STATIONARY SOURCES

1 INTRODUCTION

1.1 APPLICABILITY

This method applies to the determination of aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), phosphorus (P), selenium (Se), silver (Ag), thallium (Tl), vanadium (Vn) and zinc (Zn) stack emissions from stationary sources. This method is not suitable for the determination of hexavalent chromium or particulate matter emissions.

Any modification of this method shall be subject to approval by the Executive Officer. The term Executive Officer as used in this document shall mean the Executive Officer of the Air Resources Board or his or her authorized representative.

1.2 PRINCIPLE

The stack sample is withdrawn isokinetically from the source, with particulate emissions collected in the probe and on a heated filter and gaseous emissions collected in a series of chilled impingers containing an aqueous solution of dilute nitric acid combined with dilute hydrogen peroxide in two impingers (analyzed for all metals), and acidic potassium permanganate solution in two impingers (analyzed only for Hg).

Sampling train components are recovered into separate front and back half fractions and acid digested using conventional Parr^{R} Bomb or microwave digestion techniques to dissolve inorganics and to remove organic constituents that may create analytical interferences. The analytical sensitivity achieved for a given sample will depend upon the sample matrix, types and concentrations of other chemical compounds in the sample matrix, as well as the original sample mass and instrument sensitivity.

After digestion, portions of the probe, filter and nitric acid/hydrogen peroxide digestion solutions are combined into a single front half composite and analyzed for Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, P, Pb, Sb, Se, Tl, V and Zn by inductively coupled plasma atomic emission spectroscopy (ICPAES), inductively coupled plasma mass spectrometry (ICPMS) or direct aspiration atomic absorption spectroscopy (DAAAS). The acidic potassium permanganate impinger digestion solution, the HCl rinse solution and an aliquot from the front half composite sample are analyzed for mercury (Hg) by cold vapor atomic absorption spectroscopy (CVAAS).

Graphite furnace atomic absorption spectroscopy (GFAAS) is used for analysis of antimony, arsenic, cadmium, cobalt, lead, selenium and thallium, if these elements require greater analytical sensitivity than can be obtained by ICPAES. Additionally, if desired, the tester may use DAAAS for analysis of

all metals if the resulting reporting limits meet the goal of the testing program. Similarly, inductively coupled plasma mass spectroscopy (ICPMS) may be used for analysis of Sb, As, Ba, Be, Cd, Cr, Co, Cu, P, Pb, Mn, Ni, Tl and Zn.

The efficiency of the analytical procedure is quantified by the analysis of spiked quality control samples containing each of the target metals and/or other quality assurance (QA) measures, as necessary, including actual sample matrix effects checks. In all cases, repetitive analyses, method of standard additions (MSA), serial dilution, or matrix spike addition shall be used to establish the quality of the data. The QA requirements of this method are detailed in Section 9.

1.3 DEFINITIONS

1.3.1 End User

For the purposes of this method, the regulating agency or its authorized representative shall be considered the end user if a determination of metals emissions from a stationary source is required as part of a regulatory process. Otherwise the end user shall be the party who defrays the cost of performing this method. The pre-test protocol must identify the end user.

1.3.2 Tester

Usually the tester is a contract engineering firm that performs the sampling procedures and delegates responsibility for specific analytical procedures to an analytical group (usually part of a subcontracting laboratory firm). The tester shall ultimately be responsible for performance of this method whether directly or indirectly through co-ordination of the efforts of the sampling and analytical groups.

1.3.3 Source Target Concentration

This is the target concentration for each emitted metal of interest specified by the end user of the test results. The target concentration shall be expressed in units of target metal mass per volume of emissions; typical units are nanograms per dry standard cubic meter or micrograms per dry standard cubic meter (ng/m^3 or $\mu g/m^3$).

1.3.4 Method Detection Limit

The method detection limit (MDL) is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. It is based on the precision of detection of the analyte concentration near the instrument detection limit.

1.3.5 Reporting Limit

The reporting limit (RL) is a limit for each metal at or below which data must not be reported. It is based on the minimum analyte mass that must be collected in the sampling train to allow detection during routine laboratory operation within the precision established by the MDL determination.

2 RANGE, PRECISION, METHOD DETECTION LIMIT, REPORTING LIMIT AND INTERFERENCES

2.1 ANALYTICAL RANGE

For the analyses described in this methodology and for similar analyses the ICPAES response is linear over several orders of magnitude. Samples containing metal concentrations in the nanograms per milliliter (ng/ml) to micrograms per milliliter (µg/ml) range in the final analytical solution can be analyzed using this technique. Samples containing greater than approximately 50 µg/ml of chromium, lead, or arsenic should be diluted to that level or lower for final analysis. Samples containing greater than approximately 20 µg/ml of cadmium should be diluted to that level before analysis.

2.2 METHOD PRECISION

The precision (relative standard deviation) for each metal detected in an EPA method development test at a sewage sludge incinerator, are as follows: Sb (12.7%), As (13.5%), Ba (20.6%), Cd (11.5%), Cr (11.2%), Cu (11.5%), Pb (11.6%), P (14.6%), Se (15.3%), Tl (12.3%), and Zn (11.8%). The precision for nickel was 7.7% for another test conducted at a source simulator. Beryllium, manganese and silver were not detected in the tests; however, based on the analytical sensitivity of the ICP for these metals, it is assumed that their precisions should be similar to those for the other metals, when detected at similar levels.

2.3 METHOD DETECTION LIMIT (MDL)

Method detection limits for the target metals using the various analytical techniques referenced in this method are estimated in Table 1. The MDLs shown in Table 1 assume complete digestion and a final sample volume of 300 mL. For example, if the sample fraction volume is reduced from 300 mL to 30 mL, the MDL for that fraction is improved by a factor of ten. Actual MDLs are sample dependent and will vary based on the final sample volume, the sample matrix and the skill of the analyst.

ICPAES method detection limits for the sample solutions (based on SW-846, Method 6010-A) are approximately as follows: Sb (32 ng/mL), As (53 ng/mL), Ba (2 ng/mL), Be (0.3 ng/mL), Cd (4 ng/mL), Cr (7 ng/mL), Co (7 ng/mL), Cu (6 ng/mL), Pb (42 ng/mL), Mn (2 ng/mL), Ni (15 ng/mL), P (75 ng/mL), Se (75 ng/mL), Ag (7 ng/mL), Tl (40 ng/mL), and Zn (2 ng/mL). ICPMS method detection limits shown in Table 1 are estimated MDL's and generally are lower by a factor of ten or more. The actual sample method detection limits are sample dependent and may vary due to the sample matrix.

The analytical detection limits for analysis by direct aspiration AAS (based on SW-846, Method 7000-A series) are approximately as follows: Sb (200 ng/mL), As (2 ng/mL), Ba (100 ng/mL), Be (5 ng/mL), Cd (5 ng/mL), Cr (50 ng/mL), Co (50 ng/mL), Cu (20 ng/mL), Pb (100 ng/mL), Mn (10 ng/mL), Ni (40 ng/mL), Se (2 ng/mL), Ag (10 ng/mL), Tl (100 ng/mL), and Zn (5 ng/mL).

The detection limit for Hg by CVAAS (on the resultant volume of the digestion of the aliquots taken for Hg analyses) can be approximately 0.02 to 0.2 ng/mL, depending upon the type of CVAAS analytical instrument used.

The use of GFAAS can enhance the detection limits compared to direct aspiration AAS as follows: Sb (3 ng/mL), As (1 ng/mL), Be (0.2 ng/mL), Cd (0.1 ng/mL), Cr (1 ng/mL), Co (1 ng/mL), Pb (1 ng/mL), Se (2 ng/mL), and Tl (1 ng/mL).

2.4 REPORTING LIMIT (RL)

The tester shall calculate the reporting limits (RLs) for the target metals. This value will be 5 times the MDL determined for the pre-test blank contamination checks or 5 times the field blank sample results if no pre-test analyses are performed. If the field blank analytical results yield unacceptable RLs, then the field reagent blanks may be analyzed to calculate RLs.

The RL is a required parameter for pre-test minimum sample volume and minimum sample time determination. Therefore, when no pre-test contamination checks are performed, the minimum RL for each target metal shall be estimated as 5 times the MDL shown in Table 1 or 5 times the MDL estimated by the laboratory performing sample analysis.

Note: If reagent blanks are not analyzed prior to testing, the RLs are calculated as 5 times the MDL or detection level, whichever is greater, determined for the field blank sample train. If the field blank detection levels yield unacceptable RLs, then the RLs may be established by analysis of the field reagent blank samples.

2.5 INTERFERENCES

2.5.1 ICP

Iron can be a spectral interference during the analysis of arsenic, chromium, and cadmium by ICP. Aluminum can be a spectral interference during the analysis of arsenic and lead by ICP. Generally, these interferences can be reduced by diluting the sample, but this increases the method detection limit. Background and overlap corrections may be used to adjust for spectral interferences. Refer to EPA SW-846, Method 6010-A and Method 6020 for details on potential interferences for this method.

2.5.2 GFAAS

The chemical, physical and spectral interferences associated with GFAAS are described in EPA SW-846, Method 7000-A, Section 3.2. For all GFAAS analyses, matrix modifiers should be used to limit interferences, and standards should be matrix matched.

2.5.3 DAAAS

The chemical, physical and spectral interferences associated with DAAAS are described in EPA SW-846, Method 7000-A, Section 3.1.

2.5.4 CVAAS

The chemical, physical and spectral interferences associated with CVAAS are described in EPA SW-846, Method 7470-A, Section 3.0.

3 RECOMMENDED PRE-TEST PREPARATION

The procedures presented in Section 3.1 through Section 3.5 are recommended procedures only. They are intended to help the tester maximize method performance by providing algorithms for estimating sample volume and times based upon predetermined analytical and process parameters. Failure to perform these procedures should not, by itself, constitute a fatal error when evaluating or auditing Method 436 test results. However, their omission could result in unacceptable test results.

3.1 RESPONSIBILITIES OF THE END USER AND TESTER

3.1.1 The End User

Before testing may begin, the end user of the test results shall specify the source target metals concentrations to be determined by this method using the guidelines of Section 3.2.1.

The end user shall approve the pre-test protocol after reviewing the document and determining that the minimum requirements for the pre-test protocol (Section 3.2) have been met.

3.1.2 The Tester

The tester shall have primary responsibility for the performance of the test method, and shall co-ordinate the efforts of the sampling and analytical groups.

The tester shall plan the test based on the information provided by the end user and the tester's calculations of target source testing parameters.

The tester shall be responsible for selection of an analyst qualified for use of the method. The tester shall make that decision based on information supplied by the analyst.

The tester shall obtain all relevant data that are required for pre-test calculations of sampling parameters. The tester shall develop and write a pre-test protocol before performing this method to help ensure satisfactory results.

The tester shall be responsible for ensuring that all sampling and analytical reporting requirements are met.

3.2 PRE-TEST PROTOCOL

The pre-test protocol should include the test performance criteria of the end user and all assumptions, required data and calculated targets for the following testing parameters:

(1) source target concentration of each emitted metal of interest (3.2.1),

(2) preliminary analytical data (3.3) for each target metal, and

(3) planned sampling parameters (3.5).

The protocol should demonstrate that the testing parameters calculated by the tester will meet the needs of the end user. In addition, the pre-test protocol should include information on equipment, logistics, personnel and other resources necessary for an efficient and coordinated test.

At a minimum, the pre-test protocol shall identify the end user of the results, the tester, the analytical group, and the sampling group, and the protocol shall be approved by the end user of the results and the tester.

The tester should not proceed with the performance of the remainder of this method unless the pre-test protocol is approved by the tester and the end user.

3.2.1 Source Target Concentration (STC)

The tester shall not proceed with the test unless a target concentration has been chosen. The end user shall select a basis for determining each target concentration from: a) regulatory limits, b) environmental risk assessments, and (c) the interests of the end user, the tester, and the stationary source.

3.2.1.1 Regulatory Limits

The regulatory limit shall be the basis for determining a target concentration for stationary source emissions in those cases where the purpose of the emissions test is to demonstrate compliance with the established regulatory limit.

3.2.1.2 Environmental Risk Assessments

In some cases testing is conducted for an environmental risk assessment. A pre-test estimate of the permissible risk shall then be used to determine the target concentration for stationary source emissions.

3.2.1.3 Interests of the End User, the Tester and the Stationary Source

In cases where the emissions test is not being performed to demonstrate compliance with a regulation, nor is it required for a risk assessment, the end user must then provide applicable emissions results if they are available from previous tests of the facility to be tested. Otherwise, an estimate of metals emissions from the source must be obtained from the results of tests performed at similar sources. This target concentration is necessary for the calculation of the target sampling parameters required by Section 3.5.

3.3 PRELIMINARY ANALYTICAL DATA

3.3.1 Results of Blank Contamination Checks

Ideally, the tester should obtain from the analyst the results of pre-test metals contamination checks performed on the filter and reagent batches to be used for sample collection. The analytical report must satisfy the reporting requirements of Section 11.

In some instances, logistical and/or practical considerations may preclude obtaining preliminary contamination checks. In these cases, the tester shall use the analytical results for the field blank sample or the field reagent blank samples to calculate the RL. However, the tester must be aware that calculating the RL in this manner may yield an unacceptable RL resulting in unsatisfactory test data.

3.4 EXPECTED RANGE IN TARGET CONCENTRATIONS

The tester shall calculate the mass or concentration of each target metal expected in the sample that will be submitted for analysis (Section 1.3.3).

Metal analytes in a source test sample can show large differences in concentrations. A sample that might provide sufficient analyte for the detection and quantitation of the lowest concentration metal could contain levels of other metals that exceed the upper limit of the method.

In some cases the solution is two analyses - first with undiluted composite, and then again after appropriate dilution of the composite. With prior notification of expected levels of the target analytes, the analyst can modify the preparation of the samples so that useful results might be obtained.

3.5 SAMPLING RUNS, TIME, AND VOLUME

3.5.1 Sampling Runs

A test shall include at least three sampling runs in series and a blank sampling train.

3.5.2 Minimum Sample Volume (MSV)

This is the minimum sample volume that must be collected in the sampling train to provide the minimum reportable target metal mass for quantitation. It must be based on a) the reporting limit (1.3.5), b) the source target concentration (3.2.1), and c) sampling limitations. Use Equation 436-1 to calculate the target MSV for each target metal analyte.

$$\mathrm{MSV\,(dscm)} = \mathrm{RL} \times \frac{1}{\mathrm{STC}} \qquad \text{Eq. 436-1}$$

Where:

MSV = Minimum sample volume, dscm
RL = The reporting limit, ng/sample (Section 1.3.5)
STC = The source target concentration, ng/dscm (Section 3.2.1)

3.5.3 Minimum Sampling Time (MST)

This is the minimum time required to collect the minimum sample volume at the expected volumetric sampling rate. Use Equation 436-2 to calculate the minimum sampling time. required to collect the minimum sample volume calculated in section 3.5.2. The tester should

use an average volumetric sampling rate (VSR) appropriate for the source to be tested. If the sampling rate (VSR) cannot be achieved in the field (Section 5.1.7), the sampling time shall be revised in Equation 436-2 to achieve the target MSV. The sampling time must be such that the emissions test is conducted during representative operating conditions of the source.

$$\text{MST (hours)} = \frac{\text{MSV}}{\text{VSR}} \times \frac{1}{60} \qquad \text{Eq. 436-2}$$

Where:

MST	=	Minimum sampling time, hours
VSR	=	Expected average volumetric sampling rate, dscmm
60	=	Factor to convert minutes to hours

The end user must decide whether the MSTs are all practically feasible. Based on this decision, the tester must use either Section 3.5.4 (a) or 3.5.4 (b) to calculate a planned sample volume (PSV).

3.5.4 Planned Sample Volume (PSV)

This is the volume of emissions that must be sampled to provide the target analytes at levels between the RL and the limit of linearity. The planned sample volume is the primary sampling target whenever practically feasible. The PSV is calculated according to either (a) or (b). If the end user has decided that the MSTs are practically feasible, the tester must calculate the PSV according to Section 3.5.4 (a) and Equation 436-3.

(a) Calculate the PSV using the largest of the target MSV values calculated in Section 3.5.2 and the largest value for F that will give a practical sample volume. Use this PSV to calculate the planned sampling time (Section 3.5.5) and Equation 436-5.

(b) If the MSTs are not all practical, the tester and the end user must agree on a maximum practical sampling time (Section 3.5.5). This value must then be used for the PST in Equation 436-4 to calculate the PSV. The PST will be less than the MST and the PSV will be less than the MSV. Therefore, the primary reporting objective of the test cannot be achieved for all of the target metals. If the primary reporting objective cannot be achieved for all of the target metals, it must be discussed in the protocol and the alternative reporting objective (section 3.5.6) must be approved by the end user of the results.

$$PSV(dscm) = MSV \times F \qquad \text{Eq. 436-3}$$

$$PSV(dscm) = PST \times VSR \qquad \text{Eq. 436 - 4}$$

Where:

PST = Planned sampling time from Section 2.5.5 (b)
MSV = Minimum sample volume, dscm
F = A safety factor ($\geq$1) that allows for deviation from ideal sampling and analytical conditions

The amount that is actually collected will be determined by practical sampling limitations, the intended use of the data and the level of uncertainty that the end user can tolerate in the measurement of the target concentrations.

3.5.5 Planned Sampling Time (PST)

Two options are available depending on whether the primary objective can be achieved for all of the target metals.

(a) The planned sampling time (PST) shall be long enough to 1) collect the planned sample volume with reportable levels of the target metals and 2) sample representative operating conditions of the source. If the average sampling rate (VSR) used to estimate the planned sampling time cannot be achieved in the field, the sampling time must be recalculated using the actual VSR and the target PSV in equation 436-5.

(b) The planned sampling time shall be a practical maximum approved by the end user and it shall be long enough to sample representative operating conditions of the source.

$$PST = \frac{PSV}{VSR} \times \frac{1}{60} \qquad \text{Eq. 436 - 5}$$

$$F = \frac{PST}{MST} \qquad \text{Eq. 436 - 6}$$

Where:

PST	=	Planned sampling time, hours
PSV	=	Planned sample volume, dscm
VSR	=	Expected average volumetric sampling rate, dscmm
60	=	Factor to convert minutes to hours

3.5.6 Preliminary Estimate of Source Reporting Limit (SRL)

Before the test proceeds, the end user and the tester shall agree on a preliminary estimate of the reporting limit for the source for each target metal. The SRL shall be calculated using Equation 436-7. The planned sample volume will contain reportable levels of a given analyte if that analyte is present in the emissions at a concentration that is equal to or greater than the calculated SRL.

$$SRL = \frac{RL}{PSV} \qquad \text{Eq. 436 - 7}$$

Where:

SRL	=	Preliminary estimate of source reporting limit, ng/dscm
RL	=	Reporting limit, ng/sample
PSV	=	Planned sample volume, dscm

4 APPARATUS

The sampling and recovery apparatus, reagents and analytical equipment necessary for satisfactory performance of this method are described in this section.

The identification and quantitation of target metals in stationary source emissions tests are strongly dependent on the integrity of the samples received and the precision and accuracy of all analytical procedures employed. The QA procedures described in Section 9 are used to monitor the performance of the sampling method, identify problems, and take corrective action.

4.1 SAMPLING TRAIN

The following sampling apparatus is required. The tester may use alternative apparatus only if, after review by the Executive Officer, it is deemed equivalent for the purposes of this test method.

Mention of trade names or specific products does not constitute endorsement by the California Air Resources Board. In all cases, equivalent items from other suppliers may be used.

A schematic of the sampling train is shown in Figure 1. It is similar to the ARB Method 5 Train. The train consists of a nozzle, heated probe, heated filter, a series of five or six impingers emersed in an ice bath and a silica gel impinger or cartridge. A cyclone or similar device in the heated filter box may be used for sampling environments with high particulate matter concentrations.

The optional first impinger is initially dry and strongly recommended for sources with high moisture content. Its purpose is to prevent dilution of impinger reagent contained in the second and third impingers by serving as a moisture trap.

4.1.1 Probe Nozzle

Same as ARB Method 5, Sections 2.1.1 and 2.1.2, constructed of quartz or borosilicate glass with sharp, tapered leading edge. The angle of taper shall be 30^{o} or less and the taper shall be on the outside to preserve a constant internal diameter. The nozzle shall be of the button-hook or elbow design, unless otherwise approved by the Executive Officer.

A range of nozzle sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.27 cm (1/8 to 1/2 in.) - or larger if higher volume sampling trains are used - inside diameter (ID) nozzles in increments of 0.16 cm (1/16 in.). Each nozzle shall be calibrated according to the procedures outlined in ARB Method 5, Section 5.1.

4.1.2 Probe

The probe should be lined or made of quartz, borosilicate glass, or Teflon with a heating system capable of maintaining an exit gas temperature during sampling of $120\pm14^{o}C$ ($248\pm25^{o}F$), or other such temperature as approved by the Executive Officer. For high temperature applications ($\geq 260^{o}C$, $500^{o}F$) a non-heated probe liner or a single glass tube consisting of a combined probe and nozzle may be used.

4.1.3 Preseparator

A cyclone, high capacity impactor or other device may be used if necessary to remove the majority of particles before the gas stream is filtered. This catch must be used for any subsequent analysis. The device shall be constructed of quartz or borosilicate glass. Other materials may be used subject to approval by the Executive Officer.

4.1.4 Filter Holder

The filter holder shall be constructed of borosilicate glass, with a Teflon filter support or other non-metallic, non-contaminating support and glass to glass seal or Teflon gasket. Glass filter supports may be used where stack gas temperatures exceed $260^{o}C$ ($500^{o}F$). Other holder and gasket materials may be used subject to approval by the Executive Officer.

The filter holder shall be contained in a heated enclosure capable of maintaining a temperature of $120\pm14^{o}C$ ($248\pm25^{o}F$) around the filter holder during sampling. A temperature gage capable of measuring temperature to within $3^{o}C$ ($5.4^{o}F$) shall be installed so the temperature around the filter holder can be monitored and regulated during sampling.

4.1.5 Sample Transfer Line

For sample train configurations where the first impinger is not directly connected to the filter holder, a sample transfer line must be used. The sample transfer line shall be Teflon (1/4 in. O.D. x 1/32 in. wall) with connecting fittings capable of forming vacuum tight connections without using sealing greases. The line should be as short as possible.

4.1.6 Impinger Train

The following system shall be used for the condensation and collection of gaseous metals and for determining the moisture content of the stack gas. The impinger train shall consist of five or six

impingers, depending on whether or not a moisture knockout impinger is used. Impingers are connected in series with leak-free ground glass fittings or other leak-free, non-contaminating fittings and immersed in an ice bath. The first impinger is optional and is recommended as a water knockout trap for use during test conditions where high stack gas moisture content might result in considerable dilution of the impinger solutions.

The impingers to be used in the metals train are described as follows. When the first impinger is used as a water knockout, it shall be of the Greenburg-Smith design modified to have either a short or long stem, appropriately sized for the expected moisture catch and installed empty. The second impinger shall be of the Greenburg-Smith design modified to have a long stem as described for the first impinger in ARB Method 5, Section 2.1.7 and contain 100 mL of 5% HNO_3/10% H_2O_2 solution (Section 4.3.1). The third impinger (or the impinger used as the second HNO_3/H_2O_2 impinger) shall be of the Greenburg-Smith design with the standard tip as described for the second impinger in ARB Method 5, Paragraph 2.1.7 and contain 100 mL of 5% HNO_3/10% H_2O_2 solution (Section 4.3.1).

The fourth impinger shall be installed empty and shall be of the Greenburg-Smith design modified to have a short stem. The function of the fourth impinger is to prevent commingling of the solution in the second and third impingers with the solution in the fifth and sixth impingers. The fifth and sixth impingers shall be of the Greenburg-Smith design modified to have a long stem and shall each contain 100 mL of acidic potassium permanganate (4% $KMnO_4$/10% H_2SO_4) solution (Section 4.3.3). A thermometer capable of measuring to within 1^oC (2^oF) shall be placed at the outlet of the last impinger. When the water knock out impinger is not needed, it is removed from the train and the other impingers remain the same. If mercury analysis is not needed, the potassium permanganate impingers and the empty impinger preceding them are removed.

In summary, the optional first impinger is empty, the second and third shall each contain 100 mL of a nitric acid/hydrogen peroxide solution (5% HNO_3/10% H_2O_2, Section 4.3.1), the fourth shall be empty, the fifth and sixth shall each contain 100 mL of acidic potassium permanganate solution (4% $KMnO_4$/10% H_2SO_4, Section 4.3.3). A thermometer capable of measuring to within 1^oC (2^oF) shall be placed at the outlet of the last impinger. When the water knock out (first) impinger is not needed, it is removed from the train and the other impingers remain the same. If mercury analysis is not needed, the potassium permanganate impingers and the empty impinger preceding them are removed.

4.1.7 Silica Gel Cartridge

A silica gel cartridge or impinger shall be placed at the exit of the sixth (last) impinger. The silica gel may be contained in an impinger in the ice bath or an external cartridge if desired. The cartridge or impinger shall contain 200 to 300 grams of silica gel or equivalent desiccant for use in determining stack gas moisture and to prevent damage to the metering system.

4.1.8 Pitot Tube

Type S, as described in Section 2.1 of ARB Method 2 or other devices approved by the Executive Officer. The pitot tube shall be attached to the probe to allow constant monitoring of the stack gas velocity as required by Section 2.1.3 of ARB Method 5. When the pitot tube

occurs as part of an assembly, the configuration must meet the specifications required by Section 4.1.1 of ARB Method 2. Interference-free configurations are illustrated in Figures 2-6 through 2-8 of ARB Method 2 for Type S pitot tubes having external tubing diameters between 0.48 and 0.95 cm (3/16 and 3/8 in.).

4.1.9 Differential Pressure Gauge

Two inclined manometers or equivalent devices, as described in Section 2.2 of ARB Method 2. One manometer shall be used for velocity head (ΔP) readings and the other for orifice differential pressure (ΔH) readings.

4.1.10 Metering System

Vacuum gage, leak-free pump, thermometers accurate to within 3^{o}C (5.4^{o}F), dry gas meter capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 1. Other metering systems must meet the requirements stated in Section 2.1.8 of ARB Method 5.

4.1.11 Barometer

Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and the sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft.) elevation increase or vice versa for elevation decrease.

4.1.12 Gas Density Determination Equipment

Temperature sensor and pressure gage, as described in Section 2.3 and 2.4 of Method 2, and gas analyzer, if necessary, as described in Method 3. The preferred and alternative configurations of the temperature sensor shall be the same as those described in Section 2.1.10 of ARB Method 5.

4.1.13 Teflon Tape

For capping openings and sealing connections on the sampling train. Teflon or other non-contaminating caps, sleeves or seals may also be used.

4.2 SAMPLING MATERIALS AND REAGENTS

A reagents used in performance of this test method shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, unless otherwise approved by the Executive Officer.

4.2.1 Filters

Filters shall contain less than 1.3 $\mu g/in^2$ of each of the metals to be measured. Analytical results provided by filter manufacturers are acceptable. However, if no such results are available, filter blanks should be analyzed for each target metal prior to emission testing. Quartz fiber or glass fiber filters without organic binders such as the Pallflex 2500QAT-UP shall be used. However, if glass fiber filters which meet these requirements become available, they may be used. The

filters should exhibit at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles.

4.2.2 Water

Deionized, distilled. Water conforming to ASTM Specification D1193-77, Type II (incorporated by reference) is recommended. If necessary, analyze the water for all target metals prior to field use (see Sections 7.1 through 7.3). All target metal concentrations shall be less than 1 ng/mL.

4.2.3 Nitric Acid

Concentrated. Baker Instra-analyzed or equivalent.

4.2.4 Hydrochloric Acid

Concentrated. Baker Instra-analyzed or equivalent.

4.2.5 Hydrogen Peroxide

Thirty Percent (V/V).

4.2.6 Potassium Permanganate

4.2.7 Sulfuric Acid

Concentrated.

4.2.8 Silica Gel and Crushed Ice

Same as ARB Method 5, Sections 3.1.2 and 3.1.4 respectively.

4.3 SAMPLING REAGENT PREPARATION

4.3.1 Nitric Acid ($HN0_3$)/Hydrogen Peroxide (H_20_2) Absorbing Solution, 5 Percent $HN0_3$/10 Percent H_20_2

Add carefully with stirring 50 mL of concentrated HNO_3 to a 1000-mL volumetric flask or graduated cylinder containing approximately 500 mL of water, and then add 333 mL of 30 percent H_2O_2. Dilute to volume with water. Mix well. The reagent shall contain less than 2 ng/mL of each target metal.

4.3.2 10 Percent H_2SO_4 (V/V)

Mix carefully, with stirring, 100 mL of concentrated H_2SO_4 into 800 mL of water, and add water with stirring to make a volume of 1 L: this solution is 10 percent H_2SO_4 (V/V).

4.3.3 Acidic Potassium Permanganate ($KMnO_4$) Absorbing Solution, 4 Percent $KMnO_4$ (W/V), 10 Percent H_2SO_4 (V/V)

Prepare fresh daily. Dissolve, with stirring, 40 g of $KMnO_4$ in sufficient 10 percent H_2SO_4 to make 1 liter. Prepare and store in glass bottles to prevent degradation. The reagent shall contain less than 2 ng/mL of Hg.

Precaution: To prevent autocatalytic decomposition of the permanganate solution, filter the solution through Whatman 541 filter paper. Also, due to the potential reaction of $KMnO_4$ with H_2SO_4, there could be pressure buildup in the solution storage bottle. Therefore, these bottles shall not be fully filled and shall be vented to relieve excess pressure and reduce explosion potential. Venting should be performed in a manner that will not allow contamination of the solution. A No. 70-72 hole drilled in the container cap and Teflon liner has been used.

4.3.4 Nitric Acid (HNO_3), 0.1 N

Carefully add, with stirring, 6.3 mL of concentrated HNO_3 (70 percent) to a graduated cylinder containing approximately 900 mL of water. Dilute to 1000 mL with water. Mix well. The reagent shall contain less than 2 ng/mL of each target metal.

4.3.5 Hydrochloric Acid (HCl), 8 N

Carefully add, with stirring, 690 mL of concentrated HCl to a graduated cylinder containing 250 mL of water. Dilute to 1000 mL with water. Mix well. The reagent shall contain less than 2 ng/mL of Hg.

4.4 GLASSWARE CLEANING REAGENTS

4.4.1 Nitric Acid, Concentrated

Fisher ACS grade or equivalent.

4.4.2 Water

As specified in Section 4.2.2.

4.4.3 Nitric Acid, 10 Percent (V/V)

Carefully add, with stirring, 500 mL of concentrated HNO_3 to a graduated cylinder containing approximately 4000 mL of water. Dilute to 5000 mL with water. Mix well. This reagent shall contain less than 2 ng/mL of each target metal.

4.5 SAMPLE DIGESTION AND ANALYSIS REAGENTS

Target metals standards, except Hg, may also be made from solid chemicals as described in EPA Methods 6010-A or 7470-A (SW-846). Refer to Citations 1, 3 or 4 of the Bibliography for additional information on Hg standards. The 1000 µg/mL Hg stock solution standard may be made according to Section 6.2.5 of ARB Method 101A.

4.5.1 Hydrochloric Acid, Concentrated

4.5.2 Hydrofluoric Acid, Concentrated

4.5.3 Nitric Acid, Concentrated

Baker Instra-analyzed or equivalent.

4.5.4 Nitric Acid, 50 Percent (V/V)

Carefully, with stirring, add 125 mL of concentrated HNO_3 to 100 mL of water. Dilute to 250 mL with water. Mix well. Reagent shall contain less than 2 ng/mL of each target metal.

4.5.5 Nitric Acid, 5 Percent (V/V)

Carefully, with stirring, add 50 mL of concentrated HNO_3 to 800 mL of water. Dilute to 1000 mL with water. Reagent shall contain less than 2 ng/mL of each target metal.

4.5.6 Water

As specified in Section 4.1.2.

4.5.7 Hydroxylamine Hydrochloride and Sodium Chloride Solution

See EPA SW 846, Method 7470-A for preparation.

4.5.8 Stannous Chloride

See EPA SW 846, Method 7470-A for preparation.

4.5.9 Potassium Permanganate, 5 Percent (W/V)

See EPA SW 846, Method 7470-A for preparation.

4.5.10 Sulfuric Acid, Concentrated

4.5.11 Potassium Persulfate, 5 Percent (W/V)

See EPA SW 846, Method 7470-A for preparation.

4.5.12 Nickel Nitrate, $Ni(NO_3)_2\ 6H_2O$

4.5.13 Lanthanum Oxide, La_2O_3

4.5.14 Al Standard (AAS Grade), 1000 ug/mL

4.5.15 Ag Standard (AAS Grade), 1000 ug/mL

4.5.16 As Standard (AAS Grade), 1000 ug/mL

4.5.17 Ba Standard (AAS Grade), 1000 ug/mL

4.5.18 Be Standard (AAS Grade), 1000 ug/mL

4.5.19 Cd Standard (AAS Grade), 1000 ug/mL

4.5.20 Co Standard (AAS Grade), 1000 ug/mL

4.5.21 Cr Standard (AAS Grade), 1000 ug/mL

4.5.22 Cu Standard (AAS Grade), 1000 ug/mL

4.5.23 Fe Standard (AAS Grade), 1000 ug/mL

4.5.24 Hg Standard (AAS Grade), 1000 ug/mL

4.5.25 Mn Standard (AAS Grade), 1000 ug/mL

4.5.26 Ni Standard (AAS Grade), 1000 ug/mL

4.5.27 P Standard (AAS Grade), 1000 ug/mL

4.5.28 Pb Standard (AAS Grade), 1000 ug/mL

4.5.29 Sb Standard (AAS Grade), 1000 ug/mL

4.5.30 Se Standard (AAS Grade), 1000 ug/mL

4.5.31 Tl Standard (AAS Grade), 1000 ug/mL

4.5.32 V Standard (AAS Grade), 1000 ug/mL

4.5.33 Zn Standard (AAS Grade), 1000 ug/mL

4.5.34 Mercury Standards and Quality Control Samples

Prepare fresh weekly a 10 µg/mL intermediate mercury standard by adding 5 mL of 1000 µg/mL mercury stock solution (see EPA SW-846 Method 7470-A, Section 5.9 for preparation) to a 500 mL volumetric flask; dilute to 500 mL by first adding 20 mL of 15 percent HNO_3 and then adding water to the 500 mL volume. Prepare a 200 ng/mL working mercury standard solution fresh daily: add 5 mL of the 10 µg/mL intermediate standard to a 250 mL volumetric flask and dilute to 250 mL with 5 mL of 5 percent (w/v) $KMnO_4$ (Section 4.5.9) , 5 mL of 15 percent HNO_3, and then water.

Use at least five separate aliquots of the working mercury standard solution and a blank to prepare the standard curve in the linear range of the instrument. These aliquots and blank shall

contain 0.0, 1.0, 2.0, 3.0, 4.0 and 5.0 mL of the working standard solution containing 0, 200, 400, 600, 800, and 1000 ng Hg, respectively. Prepare quality control samples by making a separate 10 µg/mL standard and diluting until in the calibration range.

4.5.35 ICP Standards and Quality Control Samples

Calibration standards for ICP analysis can be combined into four different mixed standard solutions as follows:

MIXED STANDARD SOLUTIONS FOR ICP ANALYSIS	
Solution	Elements
I	As, Be, Cd, Mn, Pb, Se, Zn
II	Ba, Co, Cu, Fe,
III	Al, Cr, Ni
IV	Ag, P, Sb, Tl

Prepare these standards by combining and diluting the appropriate volumes of the 1000 µg/mL solutions with 5 percent nitric acid. Use a minimum of one standard and a blank to form each calibration curve. Also prepare a separate quality control sample spiked with known amounts of the target metals in quantities in the midrange of the calibration curve. Suggested standard levels are 25 µg/mL for Al, Cr and Pb, 15 µg/mL for Fe, and 10 µg/mL for the remaining elements. Standards containing less than 1 µg/mL of metal should be prepared daily. Standards containing greater than 1 µg/mL of metal are typically stable for a minimum of 1 to 2 weeks. For ICPMS, follow Method 6020 in SW-846.

4.5.36 Graphite Furnace AAS Standards for Antimony, Arsenic, Cadmium, Cobalt, Lead, Selenium, and Thallium

Prepare a 10 µg/mL standard by adding 1 mL of 1000 µg/mL standard to a 100 mL volumetric flask. Dilute to 100 mL with 10 percent nitric acid. For graphite furnace AAS, the standards must be matrix matched; e.g., if the samples contain 6 percent nitric acid and 4 percent hydrofluoric acid, the standards should also be made up with 6 percent nitric acid and 4 percent hydrofluoric acid. Prepare a 100 ng/mL standard by adding 1 mL of the 10 µg mL standard to a 100 mL volumetric flask and dilute to 100 mL with the appropriate matrix solution. Prepare other standards by dilution of the 100 ng/mL standards. At least five standards should be used to make up the standard curve. Suggested levels are 0, 10, 50, 75, and 100 ng/mL. Prepare quality control samples by making a separate 10 µg/mL standard and diluting until it is in the range of the samples. Standards containing less than 1 µg/mL of metal should be prepared daily. Standards containing greater than 1 µg/mL of metal are typically stable for a minimum of 1 to 2 weeks.

4.5.37 Matrix Modifiers

4.5.37.1 Nickel Nitrate, 1 Percent (V/V)

Dissolve 4.956 g of $Ni(NO_3)_2 * 6H_2O$ in approximately 50 mL of water in a 100 mL volumetric flask. Dilute to 100 mL with water.

4.5.37.2 Nickel Nitrate, One tenth (0.1) Percent (V/V)

Dilute 10 mL of 1 percent nickel nitrate solution (Section 4.5.37.1) to 100 mL with water. Inject an equal amount of sample and this modifier into the graphite furnace during GFAAS analysis for As.

4.5.37.3 Lanthanum

Carefully dissolve 0.5864 g of La_2O_3 in 10 mL of concentrated HNO_3 and dilute the solution by adding it with stirring to approximately 50 mL of water and then dilute to 100 mL with water. Mix well. Inject an equal amount of sample and this modifier into the graphite furnace during GFAAS analysis for Pb.

4.5.38 Whatman 40 and 541 Filter Papers (or equivalent)

For filtration of digested samples.

4.6 SAMPLE RECOVERY APPARATUS

Same as ARB Method 5, Sections 2.2.1 through 2.2.8 (Nonmetallic Probe-Liner and Probe-Nozzle Brushes or Swabs, Wash Bottles, Sample Storage Containers, Petri Dishes, Glass Graduated Cylinder, Plastic Storage Containers, Funnel and Rubber Policeman. and Glass Funnel), respectively, with the following exceptions and additions:

4.6.1 Nonmetallic Probe-Liner and Probe-Nozzle Brushes or Swabs

For quantitative recovery of materials collected in the front half of the sampling train.

4.6.2 Sample Storage Containers

Glass bottles (see the precaution in Section 4.3.3 of this Method) with Teflon-lined caps that are non-reactive to the oxidizing solutions, with capacities of 500 mL and 1000 mL, shall be used for storage of acidified $KMnO_4$ containing samples and blanks. Glass or polyethylene bottles may be used for other sample types.

4.6.3 Graduated Cylinder

Glass or equivalent.

4.6.4 Funnel

Glass or equivalent.

4.6.5 Labels

For identification of samples.

4.6.6 Polypropylene Tweezers and/or Plastic Gloves

For recovery of the filter from the sampling train filter holder.

4.7 SAMPLE PREPARATION AND ANALYTICAL EQUIPMENT

4.7.1 Volumetric Flasks, 100 mL, 250 mL, and 1000 mL

For preparation of standards and sample dilution.

4.7.2 Graduated Cylinders

For preparation of reagents.

4.7.3 Parr^{R} Bombs or Microwave Pressure Relief Vessels with Capping Station (CEM Corporation model or equivalent)

For sample digestion.

4.7.4 Beakers and Watchglasses

250 mL beakers for sample digestion with watchglasses to cover the tops.

4.7.5 Ring Stands and Clamps

For securing equipment such as filtration apparatus.

4.7.6 Filter Funnels

For holding filter paper.

4.7.7 Whatman 541 Filter Paper (or equivalent)

For filtration of digested samples.

4.7.8 Disposable Pasteur Pipets and Bulbs

4.7.9 Volumetric Pipets

4.7.10 Analytical Balance

Accurate to within 0.1 mg.

4.7.11 Microwave or Conventional Oven

For heating samples at fixed power levels or temperatures.

4.7.12 Hot Plates

4.7.13 Atomic Absorption Spectrometer (AAS)

Equipped with a background corrector.

4.7.13.1 Graphite Furnace Attachment

With antimony, arsenic, cadmium, lead, selenium, thallium, and hollow cathode lamps (HCLs) or electrodeless discharge lamps (EDLs). Same as EPA SW846, Methods 7041 (antimony), 7060-A (arsenic), 7131-A (cadmium), 7421 (lead), 7740 (selenium), and 7841 (thallium). Pyrolytically-treated graphite platforms and tubes are recommended.

4.7.13.2 Cold Vapor Mercury Attachment

With a mercury hollow cathode lamp or electrodeless discharge lamp. The equipment needed for the cold vapor mercury attachment includes an air recirculation pump, a quartz cell, an aerator apparatus, and a heat lamp or desiccator tube. The heat lamp should be capable of raising the ambient temperature at the quartz cell by 10^{o}C such that no condensation forms on the wall of the quartz cell. Same as EPA SW846, Method 7470-A. See **Note No. 2:** Section 7.3 for other acceptable approaches for analysis of Hg in Which analytical detection limits of 0.02 µg Hg/mL were obtained.

4.7.14 Inductively Coupled Plasma Spectrometer

With either a direct or sequential reader and an alumina torch. Same as EPA Method 6010-A.

5 SAMPLE COLLECTION AND RECOVERY PROCEDURES

The complexity of this method is such that, to obtain reliable results, tester and analyst must be trained and experienced with the test procedures, including source sampling; reagent preparation and handling; sample handling; safety equipment; analytical calculations; reporting and the specific procedural descriptions throughout this method.

5.1 SAMPLING

5.1.1 Number of Sample Runs

The number of sampling runs must be sufficient to provide minimal statistical data and in no case shall be less than three (3).

5.1.2 Sample Train and Sample Recovery Apparatus Preparation

Follow the same general procedure given in ARB Method 5, Section 4.1.1, except that the filter need not be desiccated or weighed. First rinse all sampling train glassware (including filter support), funnels, flasks, beakers and sample storage containers (if previously used) with hot tap water and then wash in hot soapy water. Next, rinse glassware three times with tap water,

followed by three additional rinses with water. Then soak all glassware in a 10 percent (V/V) nitric acid solution for a minimum of 4 hours, rinse three times with water and allow to air dry. Glassware may be dried in oven if desired. Cover all glassware openings where contamination can occur with a non-contaminating material (**do not use aluminum foil**) until the sampling train is assembled for sampling.

5.1.3 Preliminary Determinations

Same as ARB Method 5, Section 4.1.2.

5.1.4 Sample Train Assembly

Assemble the sampling train as shown in Figure 1. Follow the same general procedures given in ARB Method 5, Section 4.1.3 except place 100 mL of HNO_3/H_2O_2 solution (Section 4.3.1) in each of the second and third impingers as shown in Figure 1. Place 100 mL of the acidic $KMnO_4$ absorbing solution (Section 4.3.3) in each of the fifth and sixth impingers as shown in Figure 1, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the last impinger or cartridge. Alternatively, the silica gel may be weighed directly in the impinger or cartridge just prior to train assembly. It is recommended that each impinger also be weighed just prior to train assembly to allow weight difference determinations for moisture calculations. Use the sampling train set-up and recovery sheet shown in Figure 5 or similar data form to record set-up parameters.

5.1.5 Sample Train Configuration Options

Several options are available to the tester based on the source specific sampling requirements and conditions.

5.1.5.1 Elimination of First Impinger

The use of an empty first impinger can be eliminated if the moisture to be collected in the impingers is calculated or determined to be less than 100 mL.

5.1.5.2 Mercury Determination

The tester shall include an empty fourth impinger between the two HNO_3/H_2O_2 impingers and the two impingers containing acidic potassium permanganate solution for all test runs for which mercury is to be determined. Use the procedure described in Section 7.1.1 of ARB Method 101A, if necessary, to maintain the desired color in the last permanganate impinger. Mercury emissions can be measured, alternatively, in a separate train using ARB Method 101A.

Precaution: Take extreme care to prevent contamination within the train. Prevent the mercury collection reagent (acidic potassium permanganate) from contacting any glassware of the train which is washed and analyzed for Mn. Prevent acidic hydrogen peroxide from mixing with the acidic potassium permanganate.

5.1.5.3 Preseparator

Subject to the approval of the Executive Officer, a glass cyclone may be used between the probe and the filter holder when the total particulate catch is expected to exceed 100 mg or

when water droplets are present in the stack gas.

5.1.5.4 Teflon Tape

Teflon tape or seals or other non-contaminating material should be used if necessary to ensure leak-free sampling train connections. The use of silicone grease is prohibited.

5.1.6 Leak-Check Procedures

Follow the leak-check procedures given in ARB Method 5, Section 4.1.4.1 (Pretest Leak-Check), Section 4.1.4.2 (Leak-Checks During the Sample Run), and Section 4.1.4.3 (Post-Test Leak-Checks).

5.1.7 Sampling Train Operation

Follow the procedures given in ARB Method 5, Section 4.1.5. For each run, record the data required on a data sheet such as the one shown in Figure 5-2 of ARB Method 5.

Note: When sampling for Hg, the tester must take steps to maintain the desired color of the acidified permanganate solution in the last impinger, such as described in Section 7.1.1 of ARB Method 101A. Alternatively, the tester may replace the last impinger, as necessary, with an impinger containing 100 mL of fresh acidified permanganate solution to prevent discoloration. If additional permanganate solution is used during a sample run, it must be combined with the original permanganate solution during sample recovery.

5.1.8 Field Blank Train

There shall be at least one field blank train for each series of three tests or fewer. For sources at which emissions are sampled at more than one sampling location, there shall be at least one blank train assembled at each location for each set of three tests or fewer.

Prepare and configure the blank train in a manner identical to the actual sampling trains. The field blank train shall be taken through all of the steps from preparation through leak check without actual sampling. Upon completion of the leak check, the entrance and exit of the blank train shall be sealed with non-contaminating material.

Recover the field blank train in the same manner as described for stack samples in Section 5.2. Follow all subsequent sections for digestion, analysis and data reporting.

5.1.9 Calculation of Percent Isokinetic

Same as ARB Method 5, Section 4.1.6.

5.2 SAMPLE RECOVERY

Begin cleanup procedures as soon as the probe is removed from the stack at the end of a sampling period. Record all post-test sample recovery parameters on the set-up and recovery sheet shown in

Figure 5 or a similar data sheet.

Allow the probe to cool prior to sample recovery. When it can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a rinsed, non-contaminating cap over the probe nozzle to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling. This normally causes a vacuum to form in the filter holder, with the undesired result of drawing liquid from the impingers into the filter or commingling of the impinger contents.

The tester may opt to disassemble the sampling train into components before moving the sampling train from the sampling area to the cleanup site. If so, remove the probe or probe-filter assembly from the sampling train and cap the open outlet. Be careful not to lose any condensate that might be present. Cap the filter inlet where the probe was fastened. Remove the umbilical cord from the last impinger and cap the impinger. Cap off the filter holder outlet and impinger inlet. Use non-contaminating caps, whether ground-glass stoppers, plastic caps, serum caps, or Teflon tape to close these openings.

Alternatively, the train can be disassembled before the probe and filter holder/oven are completely cooled, if this procedure is followed: initially disconnect the filter holder outlet/impinger inlet and loosely cap the open ends, then disconnect the probe from the filter holder or cyclone inlet and loosely cap the open ends. Cap the probe tip and remove the umbilical cord as previously described.

Transfer the probe and filter-impinger assembly to a cleanup area that is clean and protected from the wind and other potential causes of contamination or loss of sample. Inspect the train before and during disassembly and note any abnormal conditions.

The sample is recovered and treated according to the schematic shown in Figure 2. Assure that all items necessary for recovery of the sample do not contaminate the sample. Do not use any metal-containing tools or materials when recovering the train.

Note: Some gloves may contain dust which is high in zinc and may contaminate samples.

5.2.1 Container No. 1 (Filter)

Carefully remove the filter from the filter holder and place it in its labeled petri dish container. Use acid-washed polypropylene or Teflon coated tweezers or clean, single-use surgical gloves rinsed with water to handle the filters. If it is necessary to fold the filter, make certain the particulate cake is inside the fold. Carefully transfer the filter and any particulate matter or filter fibers that adhere to the filter holder gasket to the petri dish by using a dry (acid-cleaned) nylon bristle brush. Do not use any metal-containing materials when recovering the filter. Seal the labeled petri dish.

5.2.2 Container No. 2 (Probe and Filter Holder Front Half Rinses)

Quantitatively recover material deposited in the nozzle, probe liner and front half of the filter holder by thoroughly rinsing and brushing with a measured volume of 0.1 N nitric acid and place the wash into a labeled sample storage container. Perform the rinses as described in ARB Method 5, Section 4.2 using 0.1 N nitric acid in place of acetone. It is recommended that two

people recover the probe to minimize sample losses. Brush until the 0.1 N nitric acid rinse shows no visible particles, after which make a final rinse of the inside surface with 0.1 N nitric acid. Determine the pH of this sample. If the pH is greater than 2, acidify the sample with a measured volume of concentrated nitric acid to pH 2 or less.

Record the volume of the combined rinse and concentrated nitric acid used for pH adjustment (when applicable) to the nearest 2 mL. Mark the height of the fluid level on the outside of the storage container and use this mark to determine if leakage occurs during transport. Seal the container and clearly label the contents. Finally, rinse the nozzle, probe liner, and front half of the filter holder with water and discard these rinses.

5.2.3 Container No. 3 (Impingers 1 through 3, Contents and Rinses)

Due to the large quantity of liquid involved, the tester may place the impinger solutions in more than one container.

Wipe off the outside of each impinger to remove excess water and other material. Record the weight of each impinger or measure the liquid in the first three impingers volumetrically to within 0.5 mL using a graduated cylinder and record the volume of liquid. This information is required to calculate the moisture content of the sampled flue gas. Clean each of the first three impingers, the filter support, the back half of the filter housing, and connecting glassware by thoroughly rinsing with a measured volume of 0.1 N nitric acid. Repeat this rinsing, then inspect the impingers for any abnormal conditions. Rinse each piece of glassware used to connect the impingers twice with a measured volume of 0.1 N HNO_3; transfer this rinse into a labeled Container No. 3. Determine the pH of this sample. If the pH is greater than 2, acidify the sample with a measured volume of concentrated nitric acid to pH 2 or less.

Record the total rinse volume and concentrated nitric acid used for pH adjustment (when applicable). Combine the rinses and impinger solutions, measure and record the final weight or final volume of Container 3. Mark the height of the fluid level on the outside of the container to determine if leakage occurs during transport. Seal the container and clearly label the contents.

5.2.4 Container No. 4 (Impinger 4 - Middle knock-out)

Wipe off the outside of the impinger to remove excess water and other material. Record the weight of the fourth (previously empty) impinger or measure the volume to within 0.5 mL. This information is required to calculate the moisture content of the sampled flue gas. Quantitatively rinse the impinger with a measured volume of 0.1 N HNO_3. Add the rinse and impinger catch to a labeled Container No. 4. Determine the pH of this sample. If the pH is greater than 2, acidify the sample with a measured volume of concentrated nitric acid to pH 2 or less.

Record the total rinse volume and concentrated nitric acid used for pH adjustment (when applicable). Seal the container and mark the fluid level. Record the final weight of the container or record the final volume of its contents.

5.2.5 Container No. 5 (Acidified Potassium Permanganate Solution and Rinses, Impingers No. 5 & 6)

Wipe off the outside of each impinger to remove excess water and other material. Record the

weights of both permanganate impingers (fifth and sixth) or measure the volume to within 0.5 mL. This information is required to calculate the moisture content of the sampled flue gas.

Combine the contents of impingers 5 and 6 into a labeled glass storage bottle identified as container 5. Using measured volumes of fresh $KMnO_4$, rinse impingers 5 and 6 and their connecting glassware a minimum of three times and pour the rinses into container 5. Similarly, using measured volumes of water, rinse impingers 5 and 6 and their connecting glassware a minimum of three times and pour the rinses into container 5, carefully assuring transfer of any loose precipitated material. Record all rinse volumes and the final weight or final volume of container No. 5. Mark the height of the fluid level on the outside of the bottle to determine if leakage occurs during transport. See the following note and the Precaution in Paragraph 4.3.3 and properly seal the bottle and clearly label the contents.

Note: Due to the potential reaction of the potassium permanganate with the acid, there may be pressure buildup in the sample storage bottles. These bottles should not be filled full and should be vented to relieve excess pressure. Venting is highly recommended. A No. 70-72 hole drilled in the container cap and Teflon liner has been found to allow adequate venting without loss of sample.

Do NOT rinse with 8 N HCl if no visible deposits remain after rinsing with the fresh $KMnO_4$.

5.2.6 Container No. 6 (HCl Rinse)

Examine impingers 5 and 6 for sample residue. If residue is observed, rinse these impingers with 25 mL of 8 N HCl. First, place 200 mL of water in the container. Then wash the impinger walls and stem with the HCl by turning the impinger on its side and rotating it so that the HCl contacts all inside surfaces. Use a total of only 25 mL of 8 N HCl for rinsing both permanganate impingers combined. Rinse the first impinger, then pour the actual rinse used for the first impinger into the second impinger for its rinse. Finally, pour the 25 mL of 8 N HCl rinse carefully into the container. Mark the height of the fluid level on the outside of the container to determine if leakage occurs during transport. Properly seal and label container No. 6.

5.2.7 Container No. 7 (Silica Gel)

Observe the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. If a balance is available in the field, record the weight of the spent silica gel (or silica gel plus impinger or cartridge) to the nearest 0.5 g. Alternatively, transfer the silica gel from its impinger to its original container and seal. The tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. The small amount of particles that may adhere to the impinger wall need not be removed. Do not use water or other liquids to transfer the silica gel since weight gained in the silica gel impinger is used for moisture calculations.

5.2.8 Container No. 8 (0.1 N Nitric Acid Field Reagent Blank)

At least once during each field test, place 100 mL of the 0.1 N nitric acid solution used in the sample recovery process into a labeled container for use as a field reagent blank. Seal the container and make the appropriate entries in the reagent blank field data sheet shown in

Figure 6.

5.2.9 Container No. 9 (5% Nitric Acid/10% Hydrogen Peroxide Field Reagent Blank)

At least once during each field test, place 200 mL of 5% nitric acid/10% hydrogen peroxide solution used as the nitric acid impinger reagent into a labeled container for use as a field reagent blank. Seal the container and make the appropriate entries in the reagent blank field data sheet shown in Figure 6.

5.2.10 Container No. 10 (Acidified Potassium Permanganate Field Reagent Blank)

At least once during each field test place 100 mL of the acidified potassium permangante solution used as the impinger solution and in the sample recovery process into a labeled container for use in the back half field reagent blank for mercury analysis. Seal the container and make the appropriate entries in the reagent blank field data sheet shown in Figure 6.

Note: This container should be vented, as described in Section 5.2.4, to relieve excess pressure.

5.2.11 Container No. 11 (8 N HCl Field Reagent Blank)

Collect only if HCl rinse described in Section 5.2.6 was conducted. At least once during each field test, place carefully and with stirring, 25 mL of the 8 N hydrochloric acid used to rinse the acidified potassium permanganate impingers into 200 mL water in a labeled container for use in the back half field reagent blank for mercury and make the appropriate entries in the reagent blank field data sheet shown in Figure 6.

5.2.12 Container No. 12 (Filter Blank)

Once during each field test, place an unused filter from the same lot as the sampling filters in a labeled petri dish. Seal the petri dish and make the appropriate entries in the reagent blank field data sheet shown in Figure 6. Store and transport on wet ice together with the sample filters. This will be used as the field reagent blank.

5.3 SAMPLE STORAGE

5.3.1 Filters

All filters shall be stored in their labelled petri dish away from possible contamination sources. Source filters should be separated from field and reagent blank filters to prevent cross contamination.

5.3.2 Liquid Samples

All liquid samples shall be stored in their respective labelled sample jars away from possible contamination sources. Source samples should be separated from field and reagent blank samples to prevent cross contamination. The tester should also consider separating the acidified $KMnO_4$ samples due to their volatile nature.

6 ANALYTICAL PREPARATION

6.1 FIELD SAMPLES AND REAGENT BLANKS

Note the level of the liquid in each of the containers and determine if any sample was lost during shipment. If leakage has occurred, either void the sample or use methods, subject to the approval of the Executive Officer, to correct the final results. A diagram illustrating sample preparation and analysis procedures for each of the sample train components is shown in Figure 3. Record the data necessary to process, digest and prepare the sample containers for analysis using the data sheets supplied in Figure 7 through Figure 11.

6.1.1 Container No. 1 (Filter)

Divide the filter with its filter catch into portions weighing approximately 0.5 g each. Place the filter pieces into the analyst's choice of either individual microwave pressure relief vessels or Parr^{R} Bombs. Add 6 mL of concentrated nitric acid and 4 mL of concentrated hydrofluoric acid to each vessel. For microwave heating, microwave the sample vessels for approximately 12 to 15 minutes of total heating time at 600 watts in intervals as follows: heat for 2 to 3 minutes, then turn off the microwave for 2 to 3 minutes, then heat for 2 to 3 minutes, etc., continue this alternation until the 12 to 15 minutes total heating time are completed (this procedure should comprise approximately 24 to 30 minutes at 600 watts). For conventional heating, heat the Parr^{R} Bombs at 140^{o}C (285 ^{o}F) for 6 hours. Then cool the samples to room temperature and combine with the acid digested probe rinse as required in Section 5.3.2, below.

Notes: 1. Suggested microwave heating times are approximate and are dependent upon the number of samples being digested. Sufficient heating is evidenced by sorbent reflux within the vessel.

2. If the sampling train uses an optional cyclone, the cyclone catch should be prepared and digested using the same procedures described for the filters and combined with the digested filter samples.

6.1.2 Container No. 2 (Probe Rinse)

Rinse the sample into a beaker with water and cover the beaker with a ribbed watchglass. Reduce the sample volume to approximately 20 mL by heating on a hot plate at a temperature just below boiling. Alternatively, the sample volumes may be reduced by heating the original sample containers covered by a ribbed watchglass on a hot plate. Digest the sample in microwave vessels or Parr^{R} Bombs by carefully adding 6 mL of concentrated nitric acid and 4 mL of concentrated hydrofluoric acid and then continuing to follow the procedures described in Section 6.1.1; then combine the resultant sample directly with the acid digested portions of the filter prepared previously in Section 6.1.1. The resultant combined sample is referred to as Fraction 1. Filter the combined solution of the acid digested filter and probe rinse samples using Whatman 541 filter paper. Dilute to 150 mL (or the appropriate volume for the expected metals concentration) with water. Measure and record the combined volume of the Fraction 1 solution to within 0.1 mL. Quantitatively remove a 15 mL aliquot (or 10% of the Fraction 1 volume) and label as Fraction 1B. Label the remaining 135 mL portion (or 90% of the Fraction 1 volume) as Fraction 1A. Analytical Fraction 1A is analyzed using ICP or AAS for all metals except Hg.

Analytical Fraction 1B is analyzed using CVAAS for front half Hg.

6.1.3 Container No. 3 (Impingers 1-3)

Measure and record the total volume of this sample (Fraction 2) to within 0.5 mL. Remove an aliquot equal in volume to Analytical Fraction 1B for mercury analysis and label as Fraction 2B. Label the remaining portion of Container No. 3 as Fraction 2A.

Rinse the sample into a beaker with water and cover with a ribbed watchglass. Reduce the sample volume to approximately 20 mL by heating on a hot plate at a temperature just below boiling. Alternatively, the sample volumes may be reduced by heating the original sample containers covered by a ribbed watchglass on a hot plate. Then follow either of the digestion procedures described in Sections 6.1.3.1 and 6.1.3.2 below.

Fraction 2A is combined with Fraction 1A to form Analytical Fraction A and analyzed using ICP or AAS for all metals except Hg. Fraction 2B is combined with Fraction 1B to form Analytical Fraction B and analyzed using CVAAS to determine front half mercury.

6.1.3.1 Conventional Digestion Procedure

Add 30 mL of 50 percent nitric acid and heat for 30 minutes on a hot plate to just below boiling. Add 10 mL of 3 percent hydrogen peroxide and heat for 10 more minutes. Add 50 mL of hot water and heat the sample for an additional 20 minutes. Cool, filter the sample, and dilute to 150 mL (or the appropriate volume for the expected metals concentrations) with water.

6.1.3.2 Microwave Digestion Procedure

Add 10 mL of 50 percent nitric acid and heat for 6 minutes total heating time in alternating intervals of 1 to 2 minutes at 600 Watts followed by 1 to 2 minutes with no power, etc., similar to the procedure described in Section 6.1.1. Allow the sample to cool. Add 10 mL of 3 percent hydrogen peroxide and heat for 2 more minutes. Add 50 mL of hot water and heat for an additional 5 minutes. Cool, filter the sample, and dilute to 150 mL (or the appropriate volume for the expected metals concentrations) with water.

Note: All microwave heating times given are approximate and are dependent upon the number of samples being digested at a time. Heating times as given above have been found acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by solvent reflux within the vessel.

6.1.4 Container No. 4 (Impinger 4)

Measure and record the volume of impinger 4 to within 0.5 mL and place in Container No. 4. Label the contents of container No. 4 as Analytical Fraction C. Analytical Fraction C will be separately analyzed for Hg using CVAAS.

6.1.5 Container Nos. 5 and 6 (Impingers 5, 6 and HCl Rinse, If Necessary)

To remove any brown MnO_2 precipitate from the contents of Container No. 5, filter its contents through Whatman 40 filter paper into a 500 mL volumetric flask and dilute to volume with water. Save the filter for digestion of the brown MnO_2 precipitate. Label the 500 mL filtrate from Container No. 5 to be Analytical Fraction D. Analyze Analytical Fraction D for Hg within 48 hours of the filtration step.

Place the saved filter, which was used to remove the brown MnO_2 precipitate, into an appropriately sized vented container, which will allow release of any gases including chlorine formed when the filter is digested. In a laboratory hood which will remove any gas produced by the digestion of the MnO_2, add 25 mL of 8 N HCl to the filter and allow to digest for a minimum of 24 hours at room temperature.

Filter the contents of Container No. 6 through a Whatman 40 filter into a 500-mL volumetric flask. Then filter the result of the digestion of the brown MnO_2 from Container No. 5 through a Whatman 40 filter into the same 500-mL volumetric flask, and dilute and mix well to volume with water. Discard the Whatman 40 filter. Mark this combined 500-mL dilute HCl solution as Analytical Fraction E. Analyze Analytical Fractions C, D and E according to the procedures in Section 7.3.

6.1.6 Container No. 7 (Silica Gel)

Weigh the spent silica gel (or silica gel plus impinger or cartridge) to the nearest 0.5 g using a balance (this step may be conducted in the field).

6.1.7 Field Reagent Blanks

The field reagent blank samples in Container Numbers 8 through 12 produced previously in Sections 5.2.8 through 5.2.12, respectively, are used to correct sample values when authorized by the Executive Officer. These field reagent blanks shall be processed, digested, and analyzed as shown in Figure 4 and described as follows. Digest and process Container No. 12 contents per Section 5.3.1. Combine Container No. 8 with the contents of Container No. 9 and digest and process the resultant volume per Section 5.3.3. Combine the diluted digestates from Containers 8, 9 and 12. Use aliquots as Fractions A and B Blanks. Container No. 10 and Container No. 11 contents are Fraction C Blank and Fraction E Blank respectively. Analyze Fraction C and E Blanks (if applicable) per Section 7.3.

7 SAMPLE ANALYSIS

For each sampling train, four to five individual samples are generated for analysis. Three to four of these samples are specific to mercury, the remaining sample is specific to all other target metals. A schematic identifying each sample and the prescribed sample preparation and analysis scheme is shown in Figure 3.

Fractions A and B consist of the digested samples for the train from the probe rinse through impinger 3. Fraction A is for ICPAES, ICPMS or AAS analysis as described in Sections 7.1 and/or 7.2. Fraction B is for determination of front half mercury as described in Section 7.3. Fraction C consists of the impinger contents and rinses from impinger 4 (middle knockout impinger). Fraction D consists of the impinger

contents and rinses from permanganate Impingers 5 and 6. These samples are analyzed for mercury as described in Section 7.3.

Depending on the test, there may be a separate sample from an HCl rinse of impingers 5 and 6 combined with the digested MnO_2 precipatate from Fraction D. This sample should be analyzed for mercury and included in the total back half mercury catch. The total back half mercury catch is determined from the sum of Fraction C, Fraction D and Fraction E. Report the analytical results on the Laboratory Analytical Results data sheet shown in Figure 12.

7.1 ICPAES AND ICPMS ANALYSIS

Analyze analytical fraction A by ICPAES using Method 6010-A or Method 200.7 (40 CFR 136, Appendix C). Calibrate the ICP, and set up an analysis program as described in Method 6010-A or Method 200.7. Follow the quality control procedures described in Section 9.4.1. Recommended wavelengths for analysis are as follows:

Element	Wavelength (nm)
Aluminum	308.215
Antimony	206.833
Arsenic	193.696
Barium	455.403
Beryllium	313.042
Cadmium	226.502
Chromium	267.716
Cobalt	228.616
Copper	324.754
Iron	259.940
Lead	220.353
Manganese	257.610
Nickel	231.604
Phosphorous	214.914
Selenium	196.026
Silver	328.068
Thallium	190.864
Zinc	213.856

These wavelengths represent the best combination of specificity and potential detection limit. Other wavelengths may be substituted if they can provide the needed specificity and detection limit, and are treated with the same corrective techniques for spectral interference. Initially, analyze all samples for the target metals (except Hg) plus Fe and Al. If Fe and Al are present, the sample might have to be diluted so that each of these elements is at a concentration of less than 50 ppm so as to reduce their spectral interferences on As, Cd, Cr, and Pb. Perform ICPMS analysis by following Method 6020 in SW-846.

NOTE: When analyzing samples in a HF matrix, an alumina torch should be used; since all front-half samples will contain HF, use an alumina torch.

7.2 AAS by Direct Aspiration and/or Graphite Furnace

Analysis of metals in Fraction A using graphite furnace or direct aspiration AAS is often a preferred option. Use Table 2 to determine which techniques and methods should be applied for each target

metal. Table 2 also lists possible interferences and ways to minimize these interferences. Calibrate the instrument according to Section 8.3 and follow the quality control procedures specified in Section 9.4.2.

7.3 Cold Vapor AAS Mercury Analysis

Analyze analytical fractions B, C, D (if applicable) and E (if applicable) separately for Hg using CVAAS following the method outlined in EPA SW-846 Method 7470-A or in Standard Methods for Water and Wastewater Analysis, 15th Edition, Method 245.1 and 245.2, or, optionally using **NOTE No. 2** at the end of this section. Set up the calibration curve (zero to 1000 ng) as described in SW-846 Method 7470-A, Section 4.5.34 of this method or similar to Method 245.1 and 245.2 using 300-mL BOD bottles instead of Erlenmeyers. Perform the following for each Hg analysis. From each original sample, select and record an aliquot in the size range from 1 mL to 10 mL. Dilute the aliquot to 100 mL with water. If no prior knowledge of the expected amount of Hg in the sample exists, a 5 mL aliquot is suggested for the first dilution to 100 mL (see **NOTE No. 1** at end of this Section). The total amount of Hg in the aliquot shall be less than 1 µg and within the range (zero to 1000 ng) of the calibration curve. Place each sample aliquot into a separate 300-mL BOD bottle, and add enough water to make a total volume of 100 mL. Next add to it sequentially the sample digestion solutions and perform the sample preparation described in the procedures of SW-846 Method 7470-A or Method 303F. (See **NOTE No. 2** at the end of this Section). If the maximum readings are off-scale (because Hg in the aliquot exceeded the calibration range; including the situation where only a 1-mL aliquot of the original sample was digested), then dilute the original sample (or a portion of it) with 0.15 percent HNO_3 (1.5 mL concentrated HNO_3 per liter aqueous solution) so that when a 1- to 10-mL aliquot of the "0.15 HNO_3 percent dilution of the original sample" is digested and analyzed by the procedures described above, it will yield an analysis within the range of the calibration curve.

NOTE No. 1: When Hg levels in the sample fractions are below the RLs given in Table 1, select a 10 mL aliquot for digestion and analysis as described.

NOTE No. 2: Optionally, Hg can be analyzed by using the CVAAS analytical procedures given by some instrument manufacturer's directions. These include calibration and quality control procedures for the Leeman Model PS200, the Perkin Elmer FIAS systems, and similar models, if available, of other instrument manufacturers. For digestion and analyses by these instruments, perform the following two steps: (1), Digest the sample aliquot through the addition of the aqueous hydroxylamine hydrochloride/sodium chloride solution the same as described in Section 4.5.7 (The Leeman, Perkin Elmer, and similar instruments described in this note add automatically the necessary stannous chloride solution during the automated analysis of Hg.); (2), Upon completion of the digestion described in (1), analyze the sample according to the instrument manufacturer's directions. This approach allows multiple (including duplicate) automated analyses of a digested sample aliquot.

8 CALIBRATION

Maintain a laboratory log of all calibrations.

8.1 Sampling Train Calibration

Calibrate the sampling train components according to the indicated sections of ARB Method 5: Probe Nozzle (Section 5.1); Pitot Tube (Section 5.2); Metering System (Section 5.3); Probe Heater (Section 5.4); Temperature Gauges (Section 5.5); Leak-Check of the Metering System (Section 5.6); and Barometer (Section 5.7).

8.2 Inductively Coupled Plasma Spectrometer Calibration

Prepare standards as outlined in Section 4.5. Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures using the above standards. Check the instrument calibration once per hour. If the instrument does not reproduce the concentrations of the standard within 10 percent, the complete calibration procedures should be performed. Perform ICPMS calibration by following Method 6020 in SW-846.

8.3 Atomic Absorption Spectrometer - Direct Aspiration, Graphite Furnace and Cold Vapor Mercury Analyses

Prepare the standards as outlined in Section 4.5 and use them to calibrate the spectrometer. Calibration procedures are also outlined in the EPA methods referred to in Table 29-2 and in SW-846 Method 7470-A or in Standard Methods for Water and Wastewater Method 303F (for Hg). Run each standard curve in duplicate and use the mean values to calculate the calibration line. Recalibrate the instrument approximately once every 10 to 12 samples.

9 QUALITY CONTROL

9.1 PRE-TEST DETERMINATIONS (RECOMMENDED)

Determine the linear range and minimum detectable and quantifiable limits of the analytical instrument selected for the respective target metals. Determine the reporting limit, minimum sample volume, planned sample volume and planned sample time according to Section 3 of this method.

9.2 FIELD REAGENT BLANKS (IF ANALYZED)

Follow the steps in Figure 4 of this method.

9.2.1 Filter, Front and Back Half

Combine one filter from the same lot as those used for sample collection (Container No. 12) with the reduced digestate from container 8. Combine 15 mL of this sample with a 15 mL aliquot from Container No. 9 and analyze for Hg. Combine the remainder of this sample with digested portion of Container No. 9 and analyze for multimetals.

9.2.2 Potassium Permanganate and Hydrochloric Acid

Analyze the contents of Container No. 10 and Container No. 11 (if applicable) for Hg.

9.2.3 Reagent Water Check

Analyze a minimum of triplicates of the water described in Section 4.2.2 for concentrations of target metals. All target metal concentrations shall be less than 1 ng/mL.

9.3 SAMPLING

9.3.1 Number of Sample Runs

The number of sampling runs must be sufficient to provide minimal statistical data and in no case shall be less than three (3).

9.3.2 Blank Train

At least one blank train per field test shall be prepared, leak-checked and recovered in the field. The blank train shall be labelled and analyzed as if it were a sample train. The blank train results are used primarily for determining reporting limits (RL's) and as a check for on-site contamination. They also provide information regarding the magnitude of source emissions relative to background.

9.3.3 Dedicated Impingers

Impingers should be coded for easy identification. Impingers used for potassium permanganate should not be used as nitric acid impingers for other tests to avoid contamination.

9.4 SAMPLE HANDLING

9.4.1 Storage and Holding Times

Adjust the pH of all liquid samples in acid solutions to pH 2 or lower during sample recovery. It is recommended that pH paper be used to verify pH 2 or lower condition. All liquid samples should be stored in a secure location immediately after sample train recovery.
Analyze appropriate sample fractions for mercury within 28 days of sample date. Analyze Fraction A for target metals other than mercury within sixty days of sampling date.

9.5 ANALYTICAL QC

Analytical QA/QC requirements for ICP and AA analysis are summarized in Figure 13.

9.5.1 ICPAES and ICPMS Analysis

Follow the respective quality control descriptions in Section 8 of Methods 6010-A and 6020 of SW-846. For the purposes of a three run test series, these requirements have been modified as follows: two instrument check standard runs, two calibration blank runs, one interference check sample at the beginning of the analysis (must be within 25% or analyze by standard addition), one quality control sample to check the accuracy of the calibration standards (must be within 25% of calibration), and one duplicate analysis (must be within 20% of average or repeat all analysis). All reagent blank values shall be reported with sample values to allow project

engineer to calculate blank corrections, when appropriate, or Reporting Limits in instances when no pre-test analyses were performed or field blank analytical results in excess of the Method Detection Limit. Laboratories may make laboratory method blank corrections to sample data, but shall flag each sample value which received a laboratory method blank correction and report the magnitude of the correction applied.

9.5.2 Direct Aspiration and/or Graphite Furnace AAS Analysis for Antimony, Arsenic, Barium, Beryllium, Cadmium, Copper, Chromium, Lead, Nickel, Manganese, Mercury, Phosphorus, Selenium, Silver, Thallium, and Zinc

Analyze all samples in duplicate. Perform a matrix spike on one sample. If recoveries of less than 75 percent or greater than 125 percent are obtained for the matrix spike, analyze each sample by the method of standard additions. Analyze a quality control sample to check the accuracy of the calibration standards. The results must be within 20 percent or the calibration repeated. All reagent blank values shall be reported with sample values to allow project engineer to calculate blank corrections, when appropriate, or Reporting Limits in instances when no pre-test analyses were performed or field blank analytical results in excess of the Method Detection Limit. Laboratories may make laboratory method blank corrections to sample data, but shall flag each sample value which received a laboratory method blank correction and report the magnitude of the correction applied.

9.5.3 Cold Vapor AAS Analysis for Mercury

Analyze all samples in duplicate. Analyze a quality control sample to check the accuracy of the calibration standards (within 15% or repeat calibration). Perform a matrix spike on one sample from the nitric impinger portion (must be within 25% or samples must be analyzed by the method of standard additions). Additional information on quality control can be obtained from EPA SW-846 Method 7470-A or in Standard Methods for Water and Wastewater Method 245.1 and 245.2. Fraction B blank, fraction C blank and fraction E blank (if applicable) values shall be reported with sample values to allow project engineer to calculate blank corrections, when appropriate, or Reporting Limits in instances when no pre-test analyses were performed or field blank analytical results in excess of the Method Detection Limit. Laboratories may make laboratory method blank corrections to sample data, but shall flag each sample value which received a laboratory method blank correction and report the magnitude of the correction applied.

10 CALCULATIONS

10.1 DRY GAS VOLUME

Using the data from this test, calculate $V_{m(std)}$, the dry gas sample volume at standard conditions as outlined in Section 6.3 of ARB Method 5.

10.2 VOLUME OF WATER VAPOR AND MOISTURE CONTENT

Using the total volume of condensate collected during the source sampling, calculate the volume of water vapor $V_{w(std)}$ and the moisture content B_{ws} of the stack gas. Use Equations 5-2 and 5-3 of ARB Method 5.

10.3 STACK GAS VELOCITY

Using the data from this test and Equation 2-9 of ARB Method 2, calculate the average stack gas velocity.

10.4 METALS (Except Hg) IN SOURCE SAMPLE

10.4.1 Total Metals (except Hg); Analytical Fraction A

Calculate separately the amount of each metal collected in Analytical Fraction A of the sampling train using the following equation:

$$M_A = C_{a1} F_d V_{soln,1} \qquad \text{Eq. 436-8}$$

where:

M_A = Total mass of each metal (except Hg) collected in the front half of the sampling train (Analytical Fraction A), µg.

C_{a1} = Concentration of metal in Analytical Fraction A as read from the standard curve, µg/mL.

F_d = Dilution factor (F_d = the inverse of the fractional portion of the concentrated sample in the solution actually used in the instrument to produce the reading C_{a1}. For example, if a 2 mL aliquot of Analytical Fraction A is diluted to 10 mL to place it in the calibration range, $F_d = 5$).

$V_{soln,1}$ = Total volume of digested front half sample solution (sum of Analytical Fractions 1A and 2A), mL.

10.4.2 Total Metals (Fraction A), Method Blank Corrected (except Hg)

In cases when the Executive Officer allows correction of analytical results for method (laboratory) blank metals concentrations, calculate the total amount of each of the quantified metals collected in the sampling train as follows:

$$M_t = (M_A - M_{ab}) \qquad \text{Eq. 436-9}$$

where:

M_t = Total mass of each metal (separately stated for each metal) collected in the sampling train, µg.

M_{ab} = Blank correction value for mass of metal detected in the Fraction A method (laboratory) blank, µg.

10.5 Hg IN SOURCE SAMPLE

10.5.1 Front-Half Hg; Analytical Fraction B

Calculate the amount of Hg collected in the filter and probe rinse combined with impingers 1 through 3 to form Analytical Fraction B of the sampling train by using Equation 436-10:

$$Hg_{fh} = \frac{Q_B}{V_B}\ (V_{soln,B}) \qquad \text{Eq. 436- 10}$$

where:

Hg_{fh} = Total mass of Hg collected in Analytical Fraction B (filter, probe rinse and first three impingers of the sampling train), µg.

Q_B = Quantity of Hg, µg, TOTAL in the ALIQUOT of Analytical Fraction B analyzed . **NOTE**: For example, if a 10 mL aliquot of Analytical Fraction B is digested, but only 1 mL is analyzed (according to Section 7.3 and its NOTES Nos. 1 and 2), then calculate and use the total amount of Hg in the 10 mL aliquot for Q_B.

$V_{soln,B}$ = Total volume of Analytical Fraction B, mL.

V_B = Volume of aliquot of Analytical Fraction B analyzed, mL. **Note**: For example, if the 10 mL aliquot of Analytical Fraction B mentioned above was first diluted to 50 mL with 0.15 percent HNO_3 as described in Section 5.4.3 to bring it into the proper analytical range, and then 1 mL of that 50-mL was digested according to Section 7.3 and analyzed, V_B would be 0.2 mL (10 mL/50 mL).

10.5.2 Back Half Hg; Analytical Fractions C, D and E

10.5.2.1 Calculate the amount of Hg collected in Analytical Fraction C (middle knockout impinger 4), Analytical Fraction D (impingers 5 and 6) and Analytical Fraction E (HCl rinse) by using Equation 436-11:

$$Hg_{C,D,E} = \frac{Q_{C,D,E}}{V_{C,D,E}}\ (V_{soln,C,D,E}) \qquad \text{Eq. 436-11}$$

where:

$Hg_{C,D,E}$ = Total mass of Hg collected in Analytical Fraction C, D or E µg.

$Q_{C,D,E}$ = Quantity of Hg, µg, TOTAL in the ALIQUOT of Analytical Fraction C, D or E analyzed. **NOTE**: For example, if a 10 mL aliquot of Analytical Fraction C is digested, but only 5 mL is analyzed (according to Section 7.3 and its NOTES Nos. 1 and 2), then calculate and use the total amount of Hg in the 5 mL aliquot for Q_C.

$V_{soln,C,D,E}$ = Total volume of Analytical Fraction C, D or E, mL.

$V_{C,D,E}$ = Volume of Analytical Fraction C, D or E analyzed, mL. **Note**: For example, if the 10 mL aliquot of Analytical Fraction C mentioned above was first diluted to 100 mL with 0.15 percent HNO_3 as described in Section 7.3 to bring it into the proper analytical range, and then 5 mL of that 100mL was digested and analyzed, V_C would be 0.1 mL (10 mL/100 mL).

10.5.2.2 Calculate the total amount of Hg collected in the back-half of the sampling train by using Equation 436-13:

$$Hg_{bh} = Hg_C + Hg_D + Hg_E \qquad \text{Eq. 436-12}$$

where:

Hg_{bh} = Total mass of Hg collected in the back-half of the sampling train, µg.

10.5.3 Total Train Hg Catch. Calculate the total amount of Hg collected in the sampling train by using Equation 436-14:

Note: Blank corrections may only be applied with the approval of the Executive Officer or his or her authorized representative.

$$Hg_t = (Hg_{fh} - Hg_{fhb}) + (Hg_{bh} - Hg_{bhb}) \qquad \text{Eq. 436-13}$$

where:

Hg_t = Total mass of Hg collected in the sampling train, µg.

Hg_{fhb} = Blank correction value (if applicable) for mass of Hg detected in front half method blank, µg.

Hg_{bhb} = Blank correction value (if applicable) for mass of Hg detected in back-half method blank, µg.

Note: If the total of the measured blank values ($Hg_{fhb} + Hg_{bhb}$) is in the range of 0.0 to 0.6 µg,

then use the total to correct the sample value (Hg_{fh} + Hg_{bh}); if it exceeds 0.6 µg, use the greater of I. or II:

I. 0.6 µg.

II. the lesser of (a) (Hg_{fhb} + Hg_{bhb}), or (b) 5 percent of the sample value (Hg_{fh} + Hg_{bh}).

10.6 INDIVIDUAL METAL CONCENTRATIONS IN STACK GAS

Calculate the concentration of each metal in the stack gas (dry basis, adjusted to standard conditions) by using Equation 436-15:

$$C_s = \frac{M_t}{V_{m(std)}} \qquad \text{Eq. 436-14}$$

where:

C_s = Concentration of a metal in the stack gas, µg/dscm.

M_t = Total mass of that metal collected in the sampling train, µg; (substitute Hg_t for M_t for the Hg calculation).

$V_{m(std)}$ = Volume of gas sample as measured by the dry gas meter, corrected to dry standard conditions, dscm.

10.7 ISOKINETIC VARIATION AND ACCEPTABLE RESULTS

Same as Method 5, Sections 6.11 and 6.12, respectively.

11 REPORTING REQUIREMENTS

At a minimum, any test report must include all of the calculations described in Section 10 and all of the sampling and laboratory data resulting from Section 5. Example forms for documenting field testing and laboratory work are provided as Figures 5 through 12. The quality assurance data required by Section 9 must be reported in detail (see Figure 13). This test report shall be maintained by the tester for the period of time required by the appropriate Air Pollution Control District (APCD) or Air Quality Management District (AQMD). For all tests required or requested by the local APCD/AQMD, ARB, U.S. EPA or other government agency, these records shall be made available to the Executive Officer upon request.

12 ALTERNATIVE TEST METHODS

Alternative test methods may be used provided that they are equivalent to Method 436 and approved in writing by the Executive Officer of the Air Resources Board. The ARB Executive Officer may require the submittal of test data or other information to demonstrate equivalency.

13 BIBLIOGRAPHY

EPA Methods 6010-A (1992), 6020 (1994), 7000-A (1992), 7041 (1986), 7060-A (1994), 7131-A (1994), 7421 (1986), 7470-A (1994), 7740 (1986), and 7841 (1986), Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846, Third Edition. September 1986. Office of Solid Waste and Emergency Response, U. S. Environmental Protection Agency, Washington, D.C. 20460.

ARB Methods 1 through 5, California Code of Regulations, Title 17, Part III, Chapter 1, Subchapter 8, Article 2.

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EPA Method 29, Code of Federal Regulations, Title 40, Part 60, Appendix B, April 25, 1996.

TABLE 1

**MINIMUM DETECTION AND REPORTING LIMITS (ug/sample)
USING ICP, GFAAS, DAAAS AND CVAAS
ASSUMING INSTRUMENT DETECTION LIMITS PUBLISHED IN EPA SW-846***

ANALYTICAL METHOD	ICPAES		ICPMS		GFAAS		DAAAS		CVAAS	
LEVEL OF SENSITIVITY	MDL	RL	MDL	RL	MDL	RL	MDL	RL	MDL	RL
METAL										
Aluminum (Al)			0.17	0.85					--	--
Antimony (Sb)	9.6	48	0.05	0.25	0.9	4.5	60.	300.	--	--
Arsenic (As)	16	80.	0.62	3.1	0.3	1.5	0.6	3	--	--
Barium (Ba)	0.6	3	0.02	0.10	--	--	30.0	150.	--	--
Beryllium (Be)	0.09	0.45	0.02	0.10	0.06	0.3	1.5	7.5	--	--
Cadmium (Cd)	1.2	6	0.003	0.02	0.03	0.15	1.5	7.5	--	--
Cobalt (Co)	2.1	10.5	0.002	0.01	0.3	1.5	15	75	--	--
Chromium (Cr)	2.1	10.5	0.43	0.22	0.3	1.5	15	75	--	--
Copper (Cu)	1.8	9	0.02	0.10	--	--	6.0	30.	--	--
Lead (Pb)	12.6	63	0.003	0.02	0.3	1.5	30.0	150.	--	--
Manganese (Mn)	0.6	3	0.008	0.04			3.0	15	--	--
Mercury (Hg)	--	--	--	--	--	--	--	--	0.06[@]	0.3[@]

Table 1 (CON'T)

Nickel (Ni)	4.5	22.5	0.02	0.10	--	--	12	60.	--	--
Phosphorous (P)	22.5	112.5	2.9	14.7			--	--	--	--
Selenium (Se)	22.5	112.5	1.27	6.40	0.6	3	0.6	3	--	--
Silver (Ag)	2.1	10.5	0.02	0.10	--		3.0	15	--	--
Thallium (Tl)	12	60.	0.26	1.3	0.3	1.5	30.0	150.	--	--
Vanadium (V)			1.4	7.0					--	--
Zinc (Zn)	0.6	3	0.05	0.3	--	--	1.5	7.5	--	--

* assumes volume of sample from total train = 300 mL prior to aliquot for analysis

@assumes instrument detection limit of 0.2 ng Hg/mL

MDL - Minimum detection limit

RL - Reporting limit = MDL x 5

TABLE 2

APPLICABLE TECHNIQUES, METHODS, AND MINIMIZATION OF INTERFERENCE FOR AAS ANALYSIS

Metal	Technique	Method No.	Wavelength (nm)	Cause	Interference Minimization
Sb	Aspiration	7040	217.6	100 mg/mL Pb, Ni, Cu, or acid	Use secondary wavelength of 231.1 nm. Match sample and standards acid concentration or use nitrous oxide/acetylene flame
Sb	Furnace	7041	217.6	High Pb	Secondary wavelength or Zeeman correction
AS	Furnace	7060-A	193.7	Arsenic volatization	Spiked samples & add nickel nitrate solution to digestates prior to analyses. Use Zeeman background correction
Ba	Aspiration	7080	553.6	Calcium Barium ionization	High hollow cathode current & narrow band set 2 mL of KCI per 100 mL of sample
Be	Aspiration	7090	234.9	500 ppm Al	Add 0.1% fluoride Use method of standard additions
Cd	Aspiration	7130	228.8	Absorption & Light scattering	Background correction is required
Cd	Furnace	7131-A	228.8	As above Excess chloride Pipet tips	As above Ammonium phosphate used as a matrix modifier Use cadmium-free tips
Cr	Aspiration	7191	357.9	Alkali metal Absorption & scatter	KCl ionization suppressant in sample & stand Consult manufacturer's literature
Cr	Furnace	7191	357.9	200 mg/L calcium & phosphate	Add calcium nitrate for a known constant effect and to eliminate effect of phosphate

TABLE 2 (CON'T)

Metal	Technique	Method No.	Wavelength (nm)	Cause	Interference Minimization
Cu	Aspiration	7210	324.7	Absorption & light scattering	Consult manufacturer's manual
Fe	Aspiration	7380	248.3	Contamination	Great care should be taken to avoid contamination
Pb	Aspiration	7420	283.3	217.0 nm alternate	Background correction required
Pb	Furnace	7421	283.3	Poor recoveries	Matrix modifier, add 10 uL of phosphorous acid to 1-mL of prepared sample in sampler cup
Mn	Aspiration	7460	279.5	403.1 nm alternate	Background correction required
Ni	Aspiration	7520	232.0	352.4 nm alternate Fe, Co & Cr Non linear response	Background correction required Matrix matching or a nitrous-oxide/acety flame Sample dilution or use 352.4 nm line
Se	Furnace	7740	196.0	Volatility	Spike samples & reference materials & add nickel nitrate to minimize volatilization. Background correction is required & Zeeman background correction can be useful
Ag	Aspiration	7760	328.1	Absorption & light scattering AgCl insoluble Viscosity	Background correction is required Avoid hydrochloric acid unless silver is in solution as a chloride complex Sample & standards monitored for aspiration rate
Tl	Aspiration	7840	276.8		Background correction is required Hydrochloric acid should not be used

TABLE 2 (CON'T)

Metal	Technique	Method No.	Wavelength (nm)	Cause	Interference Minimization
Tl	Furnace	7841	276.8	Hydrochloric acid or chloride	Background correction is required Verify that losses are not occurring for volatization by spiked samples or standard audit Palladium is a suitable matrix modifier
Zn	Aspiration	7950	213.9	High Si, Cu & P Contamination	Strontium removes Cu and phosphate Care should be taken to avoid contamination

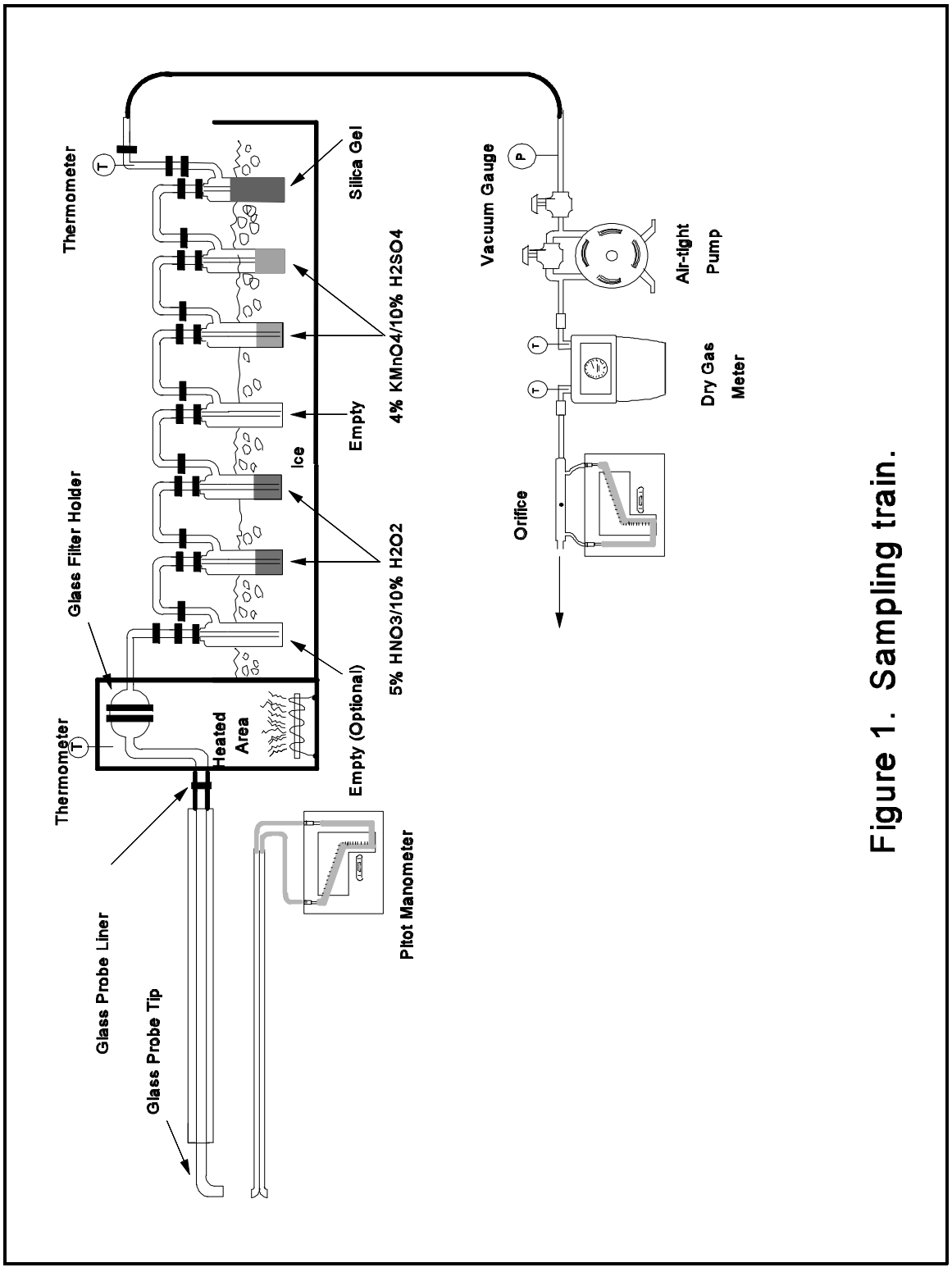
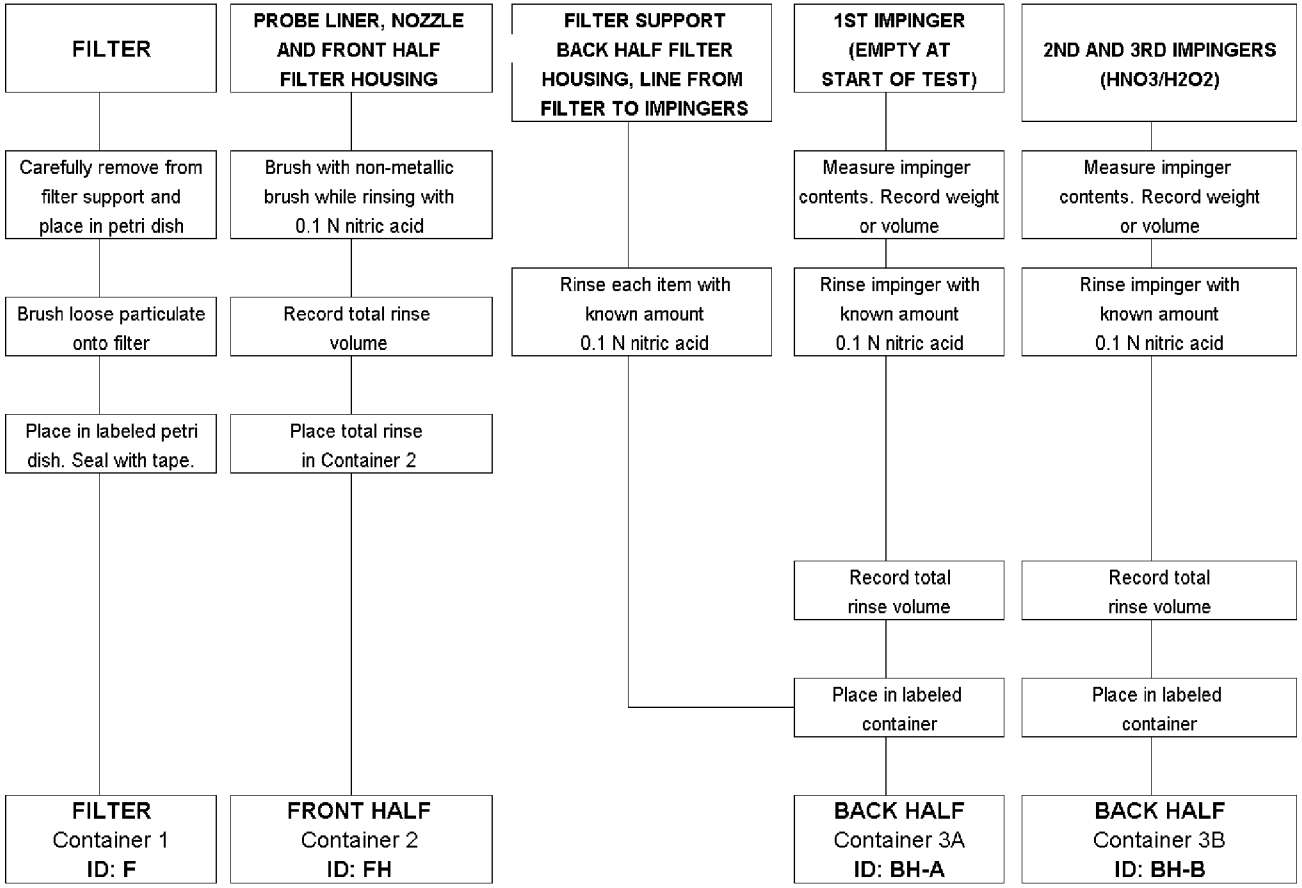


Figure 1. Sampling train.

FIGURE 2
SAMPLE TRAIN RECOVERY



NOTE: Containers 3A and 3B may be combined if desired. Alternatively, more containers may be required.

FIGURE 2 (cont'd)

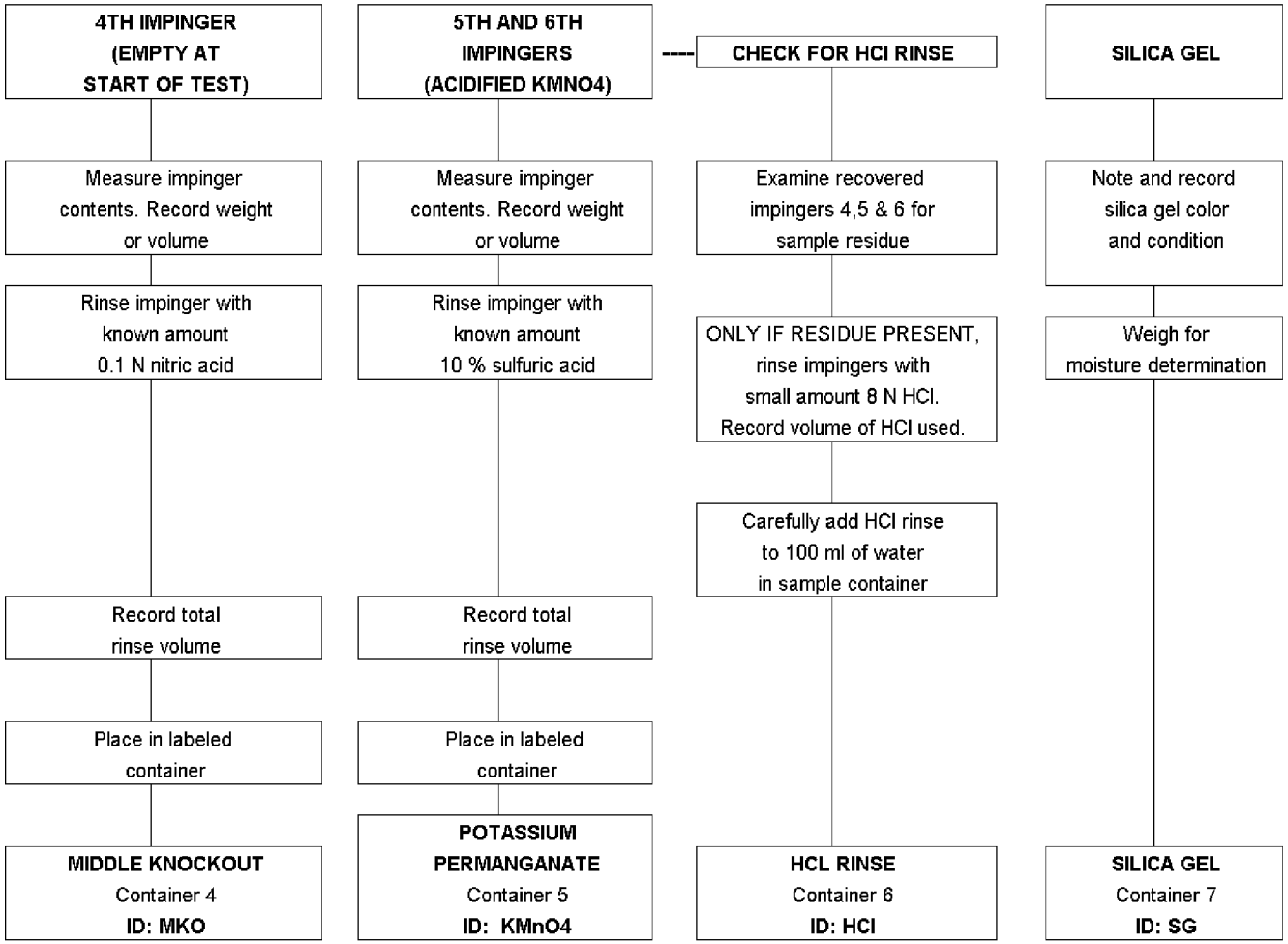


FIGURE 3

Method 436 Sample Analysis Scheme
Sample and Field Blank Preparation and Analysis Flowchart

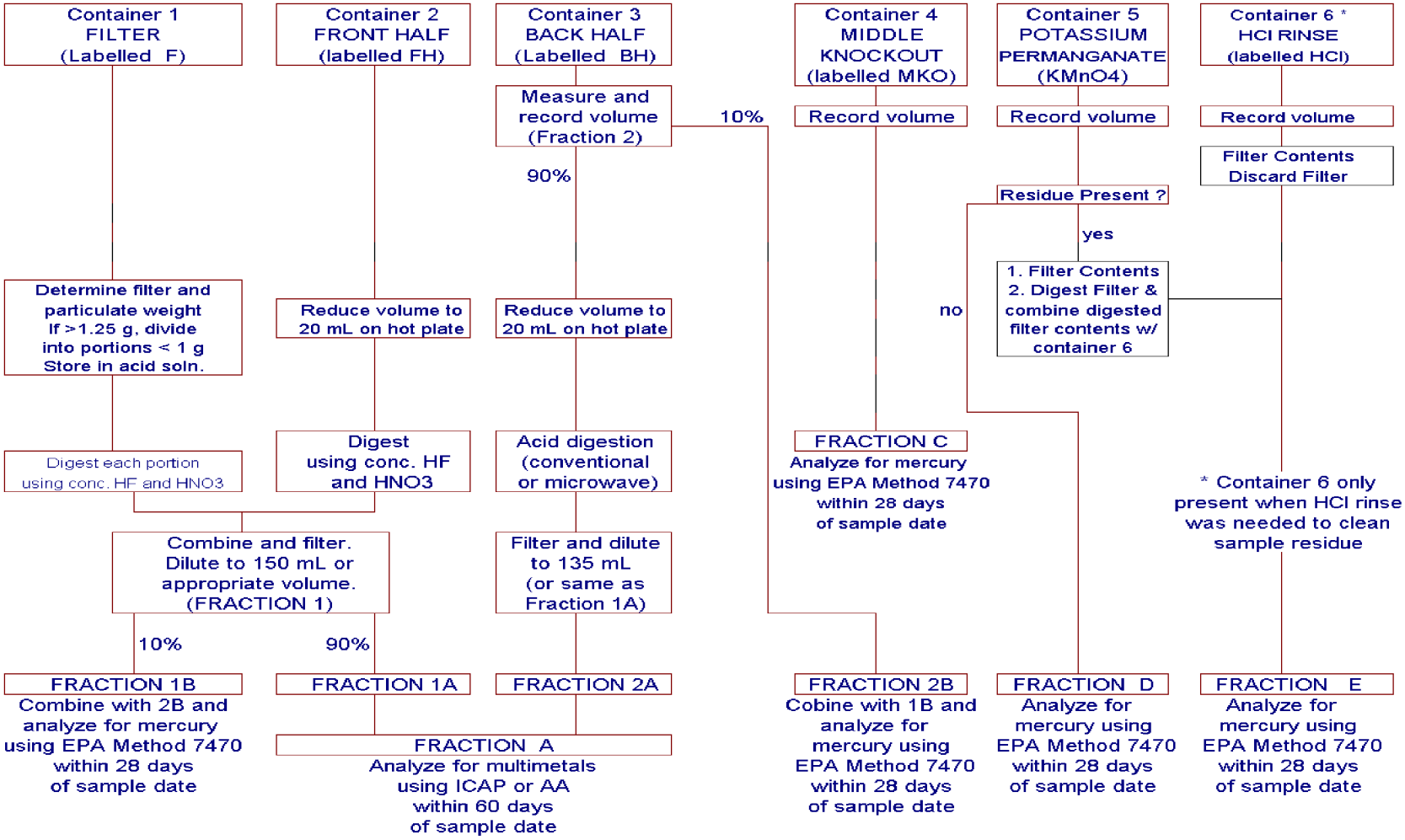


FIGURE 4

METHOD 436 REAGENT BLANK ANALYSIS SCHEME
FIELD REAGENT BLANK SAMPLE PREPARATION AND ANALYSIS FLOWCHART

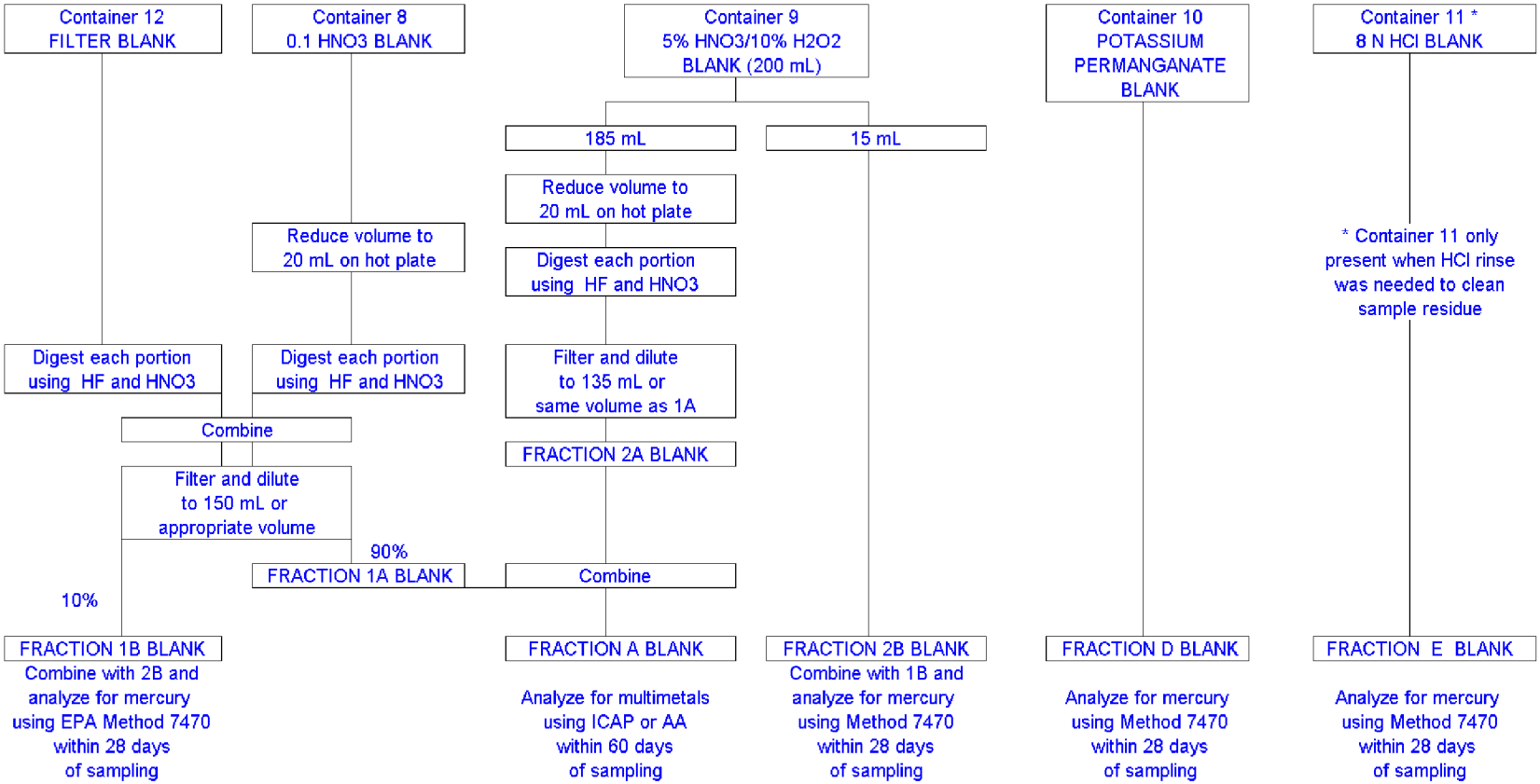


FIGURE 5

METHOD 436 MULTIPLE METALS
RUN SET-UP AND RECOVERY SHEET

PROJECT NO. _____

Method #: _____ Set-up date: _____ Recov. date: _____

Run ID: _____ Set-up time: _____ Recov. time: _____

Set-up by: _____ Recov by: _____

Probe ID: _____ Probe liner material: _____

Filter Box: _____

Filter holder ID: _____

	Filter Brand & Model	Filter Lot No.	Filter Size	Appearance After Sampling	Container ID
Filter					

	Rinse Solution and Amt. (mL)	Appearance	Container ID
Front Half			

	Imp. Type	Imp. Soln.	Initial Vol. (mL)	Initial Wt. (g)	Wt. after Sampling (g)*	Wt. differ. for moisture (g)*	Rinse Soln. and Amt. (mL)	Container ID	Note Appearance
Imp. 1 ID_____									
Imp. 2 ID_____									
Imp. 3 ID_____									
Imp. 4 ID_____									
Imp. 5 ID_____									
Imp. 6 ID_____									
HCI rinse									
Silica gel									
					TOTAL H_2O (g)				

*Can use volume differences
in place of wt. differences if desired

COMMENTS: _____

FIGURE 6

METHOD 436 MULTIPLE METALS
REAGENT BLANKS - FIELD DATA SHEET

PROJECT NO. _____

Container Number	Reagent	Date	Prep. By	Amount (ml)	Sample ID	Notes
8	0.10 HNO_3			(100 ml)		
9	5% HNO_3/ 10% H_2O_2			(200 ml)		
10	$KMnO_4$/ H_2SO_4			(200ml)		vent if necessary
11	8 N HCl			(25 ml in 200 ml H_2O)		only if HCl rinse used
12	Filter					

Reagent blanks must be taken from same lot of reagents used to prepare and recover sampling trains.

FIGURE 7

METHOD 436 MULTIPLE METALS
SAMPLE TRAIN PROCESSING BEFORE DIGESTION

PROJECT NO. _____ **PROJECT LEADER:** _____
SAMPLE DATE: _____
TRAIN ID: _____ **PHONE:** _____

DATE AND TIME	PREPARED BY	SAMPLE ID	CONT-AINER ID	REQUIRED DOCUMENTATION	FINAL SAMPLE ID	TYPE OF CONTAINER	NOTES
			1 FILTER	Filter and particulate weight _____ (If greater than 1.25, divide) Cover with approx. _____ mL 0.10 N HNO_3			HF required for digestion
			2 PROBE WASH	Check pH using _____, pH is _____ (If need, approx. conc. HNO_3 added _____mL) Reduce vol. to ~ 20 mL on hot plate.			HF required for digestion
			3 IMPING. 1 TO 3	Total volume _____mL Remove aliquot for Hg (10%) _____mL Check pH using _____, pH is _____ (If need, approx. conc. HNO_3 added _____mL) Reduce vol. to ~ 20 mL on hot plate.			
			4 MIDDLE KNOCK OUT	Total volume _____mL Add drop of $KMnO_4$ to check for H_2O_2: If rxn - place in container for Hg analysis If no rxn - combine with Container 5			
			5 $KMnO_4$	Check for precipitate formation			
			6 HCl rinse	No pre-analysis processing			

COMMENTS: _____

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FIGURE 8

METHOD 436 MULTIPLE METALS

REAGENT BLANK PROCESSING BEFORE DIGESTION

PROJECT NO._____ **LEADER:** _____

SAMPLE DATE: _____ **PHONE:** _____

DATE AND TIME	PREPARED BY	SAMPLE ID	CONT-AINER ID	REQUIRED DOCUMENTATION	FINAL SAMPLE ID (S)	TYPE OF CONTAINER	NOTES
			8 0.10 N HNO_3	Combine with Container 9			
			9 5% HNO_3/ 10% H_2O_2	Total volume (8+9): _____mL Remove aliquot for Hg (~ 10%) _____mL Check pH using _____, pH is _____ (If need, approx. conc. HNO_3 added _____mL) Reduced vol. to ~ 20 mL on hot plate.			
			10 $KMnO_4$	Check for precipitate formation			vent if necessary
			11 HCl rinse	No pre-analysis processing			
			12 FILTER	Filter and particulate weight _____ Cover with approx. _____mL 0.10 N HNO_3.			HF required

COMMENTS: _____

FIGURE 9

METHOD 436 MULTIPLE METALS
MICROWAVE DIGESTION

PROJECT NO._____ **PROJECT LEADER:** _____

SAMPLE DATE:_____ **PHONE:** _____

DATE	TIME	BY	LAB ID	SAMPLE ID	MICRO VESSEL ID	REAGENTS ADDED (mL)					MICRO POWER (watts)	TOTAL HEATING TIME	NOTES
						FILTERS & PROBE WASH		IMPINGERS					
						CONC. HNO_3	CONC. HF	50% HNO_3	30% H_2O_2	HOT H_2O			

COMMENTS: _____

_____

_____

FIGURE 10

METHOD 436 MULTIPLE METALS
FINAL DIGESTATE VOLUMES

PROJECT NO. _____

SAMPLE DATE: _____

DATE	TIME	INITIALS	LAB ID	SAMPLE ID	MICRO VESSEL ID	FINAL DIGESTATE VOLUME (mL)	FINAL DIGESTATE ID

COMMENTS:_____

FIGURE 11

METHOD 436 MULTIPLE METALS
POST MICROWAVE DIGESTION, PRE-ANALYSIS
SAMPLE TRAIN FLOWCHART

IT IS VERY IMPORTANT THAT CONTAINERS FROM THE SAME SAMPLING TRAIN BE COMBINED FOR ANALYSIS !!!

SAMPLING TRAIN RUN ID: _____

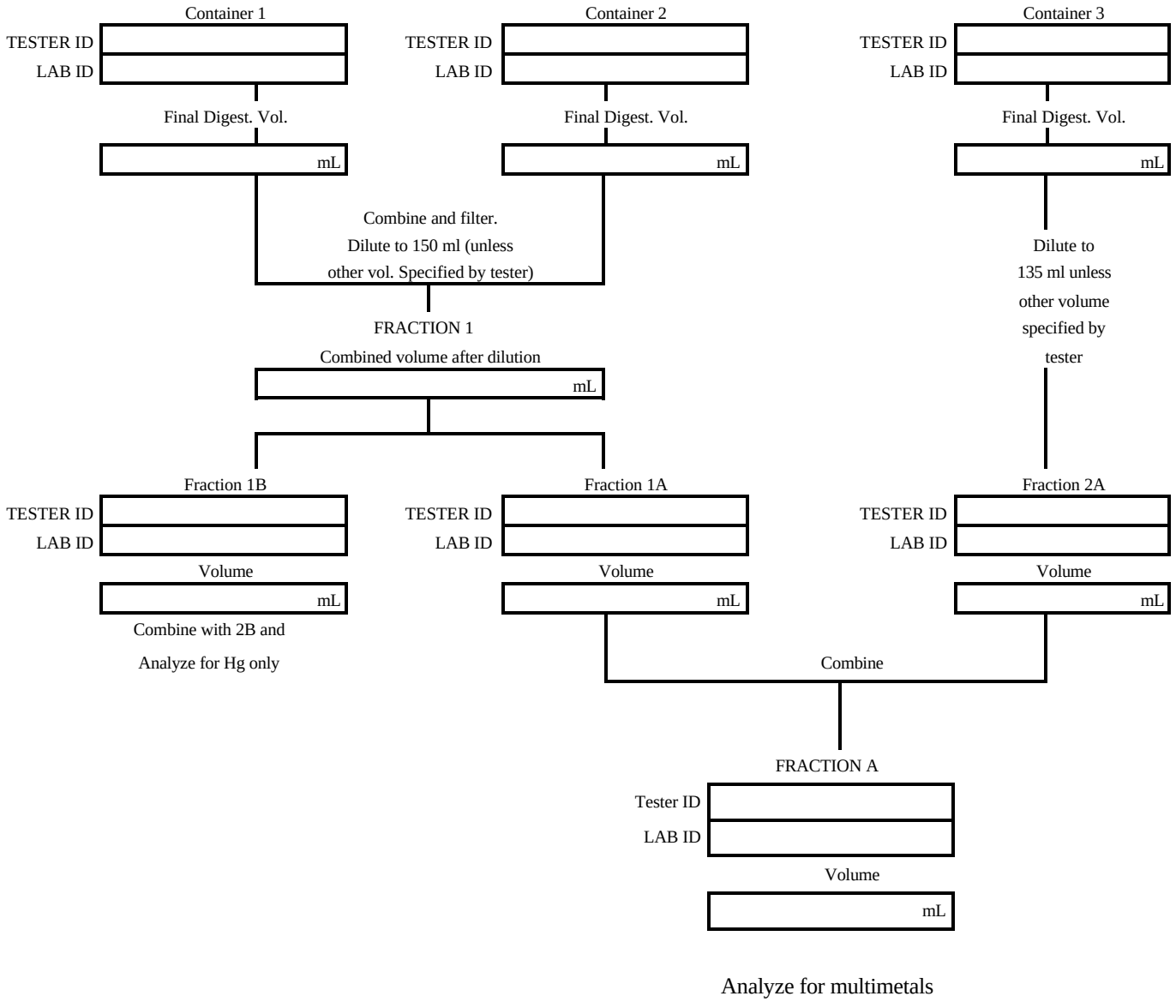

FIGURE 12

METHOD 436 MULTIPLE METALS
LABORATORY ANALYSIS RESULTS

Company name: _____
Report date: _____

Address: _____
_____
_____
Attn: _____

Sample date: _____
Sample Recv. Date: _____
Report #: _____
Page: _____

P.O. Number: _____
Location: _____

Analysis Performed: [ ] ICP/AES [ ] ICP/MS [ ] GFAAS [ ] DAAAS [ ] CVAAS

Sampling Train ID: _____

FIELD COMPOSITE ID									
LAB ID									
Metal	units								
Aluminium	µg/mL								
Antimony	µg/mL								
Arsenic	µg/mL								
Barium	µg/mL								
Beryllium	µg/mL								
Cadmium	µg/mL								
Chromium	µg/mL								
Cobalt	µg/mL								
Copper	µg/mL								
Lead	µg/mL								
Lithium	µg/mL								
Magnesium	µg/mL								
Manganese	µg/mL								
Mercury	µg/mL								
Molybdenum	µg/mL								
Nickel	µg/mL								
Phosphorus	µg/mL								
Potassium	µg/mL								
Selenium	µg/mL								
Silver	µg/mL								
Sodium	µg/mL								
Strontium	µg/mL								
Thallium	µg/mL								
Thorium	µg/mL								
Vanadium	µg/mL								
Zinc	µg/mL								

Data certified by: _____
Report approved by: _____

Item E 005048

FIGURE 13

METHOD 436 MULTIPLE METALS ANALYTICAL QA/QC REQUIREMENTS

ICPAES: (EPA Method 6010)

REQUIREMENT	CRITERIA
2 instrument check standard runs	within 10% or repeat calibration
2 calibration blank runs	within 3 std. Dev. Of mean blank value or repeat calibration
1 interference check sample	within 25% of true value
1 quality control sample	within 25% of calibration curve
1 duplicate analysis	within 20% or repeat all analyses

AA: (EPA Method 7000 series)

REQUIREMENT	CRITERIA
Analyze all samples in duplicate	
1 sample matrix spike	within 25% or method stand. add.
1 quality control sample	within 20% or repeat calibration

ICPMS: (EPA Method 6020)

REQUIREMENT	CRITERIA
Quality Control Sample	Mean Within 10% of True Value
Calibration Blank	Within 20% of the Analyte MDL
Laboratory Control Sample	One per 20 Samples
Calibration Blank Samples	Less than 3 Times Analyte IDL
Calibration Verification Samples	within 10% of calibration standards
Post Digestion Spike Sample	Within 25% of Spike Value
Interference Check Sample	Within 20% of True Value
Mass Calibration Check	Mass Within 0.1 AMU of True Value
Mass Resolution Check	Peak Width 0.9 AMU at 10% Height
Instrument Stability Check	Peak for 4 Replicates Within 5%
Duplicate Sample	RSD Less Then 20%

DEFINITIONS

Instrument check standards: prepared by combining compatible elements at concentrations equivalent to the midpoint of their respective calibration curves.

Calibration blanks: prepared by diluting 2mL of (1:1) HNO_3 and 10 mL (1:) HCI to 100 mL with Type II water.

Interference check sample: prepare to contain known concentrations of interfering elements that will provide an adequate test of correction factors.

Quality control sample: prepared in the same acid matrix as the calibration standards at approximately the calibration mid-point and in accordance with the instructions provided by the supplier.

State of Oregon Department of Environmental Quality

OAR 340-244-9070
EPA Method 5

$$B_w = \frac{P_w}{P_{bar}} \qquad 3C\text{-}1$$

$$C = \frac{A}{R(1-B_w)} \qquad 3C\text{-}2$$

$$C = \frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}} \quad \frac{A}{R(1-B_w)} \qquad 3C\text{-}3$$

7.3 Measured N_2 Concentration Correction. Calculate the reported N_2 correction for Method 25–C using Eq. 3C–4. If oxygen is determined in place of N_2, substitute the oxygen concentration for the nitrogen concentration in the equation.

$$C_{N_2 Corr} = \frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}}(C_{N_2}) \quad Eq.\ 3C-4$$

8. Bibliography

1. McNair, H.M., and E.J. Bonnelli. Basic Gas Chromatography. Consolidated Printers, Berkeley, CA. 1969.

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–2 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

APPENDIX A–3 TO PART 60—TEST METHODS 4 THROUGH 5I

Method 4—Determination of moisture content in stack gases
Method 5—Determination of particulate matter emissions from stationary sources
Method 5A—Determination of particulate matter emissions from the asphalt processing and asphalt roofing industry
Method 5B—Determination of nonsulfuric acid particulate matter emissions from stationary sources
Method 5C [Reserved]
Method 5D—Determination of particulate matter emissions from positive pressure fabric filters
Method 5E—Determination of particulate matter emissions from the wool fiberglass insulation manufacturing industry
Method 5F—Determination of nonsulfate particulate matter emissions from stationary sources
Method 5G—Determination of particulate matter emissions from wood heaters (dilution tunnel sampling location)
Method 5H—Determination of particulate emissions from wood heaters from a stack location
Method 5I—Determination of Low Level Particulate Matter Emissions From Stationary Sources

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference

method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

METHOD 4—DETERMINATION OF MOISTURE CONTENT IN STACK GASES

NOTE: This method does not include all the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 5, and Method 6.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Water vapor (H_2O) ...	7732–18–5	N/A

1.2 Applicability. This method is applicable for the determination of the moisture content of stack gas.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted at a constant rate from the source; moisture is removed from the sample stream and determined either volumetrically or gravimetrically.

2.2 The method contains two possible procedures: a reference method and an approximation method.

2.2.1 The reference method is used for accurate determinations of moisture content (such as are needed to calculate emission data). The approximation method, provides estimates of percent moisture to aid in setting isokinetic sampling rates prior to a pollutant emission measurement run. The approximation method described herein is only a suggested approach; alternative means for approximating the moisture content (*e.g.*, drying tubes, wet bulb-dry bulb techniques, condensation techniques, stoichiometric calculations, previous experience, etc.) are also acceptable.

2.2.2 The reference method is often conducted simultaneously with a pollutant emission measurement run. When it is, calculation of percent isokinetic, pollutant emission rate, etc., for the run shall be based upon the results of the reference method or its equivalent. These calculations shall not

be based upon the results of the approximation method, unless the approximation method is shown, to the satisfaction of the Administrator, to be capable of yielding results within one percent H_2O of the reference method.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 The moisture content of saturated gas streams or streams that contain water droplets, as measured by the reference method, may be positively biased. Therefore, when these conditions exist or are suspected, a second determination of the moisture content shall be made simultaneously with the reference method, as follows: Assume that the gas stream is saturated. Attach a temperature sensor [capable of measuring to ±1 °C (2 °F)] to the reference method probe. Measure the stack gas temperature at each traverse point (see section 8.1.1.1) during the reference method traverse, and calculate the average stack gas temperature. Next, determine the moisture percentage, either by: (1) Using a psychrometric chart and making appropriate corrections if the stack pressure is different from that of the chart, or (2) using saturation vapor pressure tables. In cases where the psychrometric chart or the saturation vapor pressure tables are not applicable (based on evaluation of the process), alternative methods, subject to the approval of the Administrator, shall be used.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Reference Method. A schematic of the sampling train used in this reference method is shown in Figure 4–1.

6.1.1 Probe. Stainless steel or glass tubing, sufficiently heated to prevent water condensation, and equipped with a filter, either in-stack (*e.g.*, a plug of glass wool inserted into the end of the probe) or heated out-of-stack (*e.g.*, as described in Method 5), to remove particulate matter. When stack conditions permit, other metals or plastic tubing may be used for the probe, subject to the approval of the Administrator.

6.1.2 Condenser. Same as Method 5, section 6.1.1.8.

6.1.3 Cooling System. An ice bath container, crushed ice, and water (or equivalent), to aid in condensing moisture.

6.1.4 Metering System. Same as in Method 5, section 6.1.1.9, except do not use sampling systems designed for flow rates higher than 0.0283 m^3/min (1.0 cfm). Other metering systems, capable of maintaining a constant sampling rate to within 10 percent and determining sample gas volume to within 2 percent, may be used, subject to the approval of the Administrator.

6.1.5 Barometer and Graduated Cylinder and/or Balance. Same as Method 5, sections 6.1.2 and 6.2.5, respectively.

6.2. Approximation Method. A schematic of the sampling train used in this approximation method is shown in Figure 4–2.

6.2.1 Probe. Same as section 6.1.1.

6.2.2 Condenser. Two midget impingers, each with 30-ml capacity, or equivalent.

6.2.3 Cooling System. Ice bath container, crushed ice, and water, to aid in condensing moisture in impingers.

6.2.4 Drying Tube. Tube packed with new or regenerated 6- to 16-mesh indicating-type silica gel (or equivalent desiccant), to dry the sample gas and to protect the meter and pump.

6.2.5 Valve. Needle valve, to regulate the sample gas flow rate.

6.2.6 Pump. Leak-free, diaphragm type, or equivalent, to pull the gas sample through the train.

6.2.7 Volume Meter. Dry gas meter, sufficiently accurate to measure the sample volume to within 2 percent, and calibrated over the range of flow rates and conditions actually encountered during sampling.

6.2.8 Rate Meter. Rotameter, or equivalent, to measure the flow range from 0 to 3 liters/min (0 to 0.11 cfm).

6.2.9 Graduated Cylinder. 25-ml.

6.2.10 Barometer. Same as Method 5, section 6.1.2.

6.2.11 Vacuum Gauge. At least 760-mm (30-in.) Hg gauge, to be used for the sampling leak check.

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Reference Method. The following procedure is intended for a condenser system (such as the impinger system described in section 6.1.1.8 of Method 5) incorporating volumetric analysis to measure the condensed moisture, and silica gel and gravimetric analysis to measure the moisture leaving the condenser.

8.1.1 Preliminary Determinations.

8.1.1.1 Unless otherwise specified by the Administrator, a minimum of eight traverse points shall be used for circular stacks having diameters less than 0.61 m (24 in.), a minimum of nine points shall be used for rectangular stacks having equivalent diameters less than 0.61 m (24 in.), and a minimum of twelve traverse points shall be used in all

other cases. The traverse points shall be located according to Method 1. The use of fewer points is subject to the approval of the Administrator. Select a suitable probe and probe length such that all traverse points can be sampled. Consider sampling from opposite sides of the stack (four total sampling ports) for large stacks, to permit use of shorter probe lengths. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

8.1.1.2 Select a total sampling time such that a minimum total gas volume of 0.60 scm (21 scf) will be collected, at a rate no greater than 0.021 m^3/min (0.75 cfm). When both moisture content and pollutant emission rate are to be determined, the moisture determination shall be simultaneous with, and for the same total length of time as, the pollutant emission rate run, unless otherwise specified in an applicable subpart of the standards.

8.1.2 Preparation of Sampling Train.

8.1.2.1 Place known volumes of water in the first two impingers; alternatively, transfer water into the first two impingers and record the weight of each impinger (plus water) to the nearest 0.5 g. Weigh and record the weight of the silica gel to the nearest 0.5 g, and transfer the silica gel to the fourth impinger; alternatively, the silica gel may first be transferred to the impinger, and the weight of the silica gel plus impinger recorded.

8.1.2.2 Set up the sampling train as shown in Figure 4–1. Turn on the probe heater and (if applicable) the filter heating system to temperatures of approximately 120 °C (248 °F), to prevent water condensation ahead of the condenser. Allow time for the temperatures to stabilize. Place crushed ice and water in the ice bath container.

8.1.3 Leak Check Procedures. It is recommended, but not required, that the volume metering system and sampling train be leak-checked as follows:

8.1.3.1 Metering System. Same as Method 5, section 8.4.1.

8.1.3.2 Sampling Train. Disconnect the probe from the first impinger or (if applicable) from the filter holder. Plug the inlet to the first impinger (or filter holder), and pull a 380 mm (15 in.) Hg vacuum. A lower vacuum may be used, provided that it is not exceeded during the test. A leakage rate in excess of 4 percent of the average sampling rate or 0.00057 m^3/min (0.020 cfm), whichever is less, is unacceptable. Following the leak check, reconnect the probe to the sampling train.

8.1.4 Sampling Train Operation. During the sampling run, maintain a sampling rate within 10 percent of constant rate, or as specified by the Administrator. For each run, record the data required on a data sheet similar to that shown in Figure 4–3. Be sure to record the dry gas meter reading at the beginning and end of each sampling time increment and whenever sampling is halted. Take other appropriate readings at each sample point at least once during each time increment.

NOTE: When Method 4 is used concurrently with an isokinetic method (*e.g.*, Method 5) the sampling rate should be maintained at isokinetic conditions rather than 10 percent of constant rate.

8.1.4.1 To begin sampling, position the probe tip at the first traverse point. Immediately start the pump, and adjust the flow to the desired rate. Traverse the cross section, sampling at each traverse point for an equal length of time. Add more ice and, if necessary, salt to maintain a temperature of less than 20 °C (68 °F) at the silica gel outlet.

8.1.4.2 After collecting the sample, disconnect the probe from the first impinger (or from the filter holder), and conduct a leak check (mandatory) of the sampling train as described in section 8.1.3.2. Record the leak rate. If the leakage rate exceeds the allowable rate, either reject the test results or correct the sample volume as in section 12.3 of Method 5.

8.2 Approximation Method.

NOTE: The approximation method described below is presented only as a suggested method (see section 2.0).

8.2.1 Place exactly 5 ml water in each impinger. Leak check the sampling train as follows: Temporarily insert a vacuum gauge at or near the probe inlet. Then, plug the probe inlet and pull a vacuum of at least 250 mm (10 in.) Hg. Note the time rate of change of the dry gas meter dial; alternatively, a rotameter (0 to 40 ml/min) may be temporarily attached to the dry gas meter outlet to determine the leakage rate. A leak rate not in excess of 2 percent of the average sampling rate is acceptable.

NOTE: Release the probe inlet plug slowly before turning off the pump.

8.2.2 Connect the probe, insert it into the stack, and sample at a constant rate of 2 liters/min (0.071 cfm). Continue sampling until the dry gas meter registers about 30 liters (1.1 ft^3) or until visible liquid droplets are carried over from the first impinger to the second. Record temperature, pressure, and dry gas meter readings as indicated by Figure 4–4.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
Section 8.1.1.4	Leak rate of the sampling system cannot exceed four percent of the average sampling rate or 0.00057 m^3/min (0.020 cfm).	Ensures the accuracy of the volume of gas sampled. (Reference Method).
Section 8.2.1	Leak rate of the sampling system cannot exceed two percent of the average sampling rate.	Ensures the accuracy of the volume of gas sampled. (Approximation Method).

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Reference Method. Calibrate the metering system, temperature sensors, and barometer according to Method 5, sections 10.3, 10.5, and 10.6, respectively.

10.2 Approximation Method. Calibrate the metering system and the barometer according to Method 6, section 10.1 and Method 5, section 10.6, respectively.

10.3 Field Balance Calibration Check. Check the calibration of the balance used to weigh impingers with a weight that is at least 500g or within 50g of a loaded impinger. The weight must be ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference-see 40 CFR 60.17) Class 6 (or better). Daily, before use, the field balance must measure the weight within ± 0.5g of the certified mass. If the daily balance calibration check fails, perform corrective measures and repeat the check before using balance.

11.0 Analytical Procedure

11.1 Reference Method. Measure the volume of the moisture condensed in each of the impingers to the nearest ml. Alternatively, if the impingers were weighed prior to sampling, weigh the impingers after sampling and record the difference in weight to the nearest 0.5 g. Determine the increase in weight of the silica gel (or silica gel plus impinger) to the nearest 0.5 g. Record this information (see example data sheet, Figure 4–5), and calculate the moisture content, as described in section 12.0.

11.2 Approximation Method. Combine the contents of the two impingers, and measure the volume to the nearest 0.5 ml.

12.0 Data Analysis and Calculations

Carry out the following calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Reference Method.

12.1.1 Nomenclature.

B_{ws} = Proportion of water vapor, by volume, in the gas stream.

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P_m = Absolute pressure (for this method, same as barometric pressure) at the dry gas meter, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 (mm Hg)(m^3)/(g-mole)(°K) for metric units and 21.85 (in. Hg)(ft^3)/(lb-mole)(°R) for English units.

T_m = Absolute temperature at meter, °K (°R).

T_{std} = Standard absolute temperature, 293 °K (528 °R).

V_f = Final volume of condenser water, ml.

V_i = Initial volume, if any, of condenser water, ml.

V_m = Dry gas volume measured by dry gas meter, dcm (dcf).

$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

$V_{wc(std)}$ = Volume of water vapor condensed, corrected to standard conditions, scm (scf).

$V_{wsg(std)}$ = Volume of water vapor collected in silica gel, corrected to standard conditions, scm (scf).

W_f = Final weight of silica gel or silica gel plus impinger, g.

W_i = Initial weight of silica gel or silica gel plus impinger, g.

Y = Dry gas meter calibration factor.

ΔV_m = Incremental dry gas volume measured by dry gas meter at each traverse point, dcm (dcf).

ρ_w = Density of water, 0.9982 g/ml (0.002201 lb/ml).

12.1.2 Volume of Water Vapor Condensed.

$$V_{wc(std)} = \frac{(V_f - V_i)\,\rho_w R\,T_{std}}{P_{std} M_W} = K_1 (V_f - V_i) \qquad \text{Eq. 4-1}$$

Where:

K_1 = 0.001333 m^3/ml for metric units,
= 0.04706 ft^3/ml for English units.

12.1.3 Volume of Water Collected in Silica Gel.

$$V_{wsg(std)} = \frac{(W_f - W_i)\,R\,T_{std}}{P_{std} M_W K_2} = K_3 (W_f - W_i) \qquad \text{Eq. 4-2}$$

Where:

K_2 = 1.0 g/g for metric units,
= 453.6 g/lb for English units.
K_3 = 0.001335 m^3/g for metric units,
= 0.04715 ft^3/g for English units.

12.1.4 Sample Gas Volume.

$$V_{m(std)} = \frac{V_m\ Y\ P_m T_{std}}{P_{std} T_m} \qquad \text{Eq. 4-3}$$

$$= K_4 Y \frac{V_m P_m}{T_m}$$

Where:

K_4 = 0.3855 °K/mm Hg for metric units,
= 17.64 °R/in. Hg for English units.

NOTE: If the post-test leak rate (Section 8.1.4.2) exceeds the allowable rate, correct the value of Vm in Equation 4–3, as described in section 12.3 of Method 5.

12.1.5 Moisture Content.

$$B_{ws} = \frac{V_{wc(std)} + V_{wsg(std)}}{V_{wc(std)} + V_{wsg(std)} + V_{m(std)}} \qquad \text{Eq. 4-4}$$

12.1.6 Verification of Constant Sampling Rate. For each time increment, determine the ΔV_m. Calculate the average. If the value for any time increment differs from the average by more than 10 percent, reject the results, and repeat the run.

12.1.7 In saturated or moisture droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one using a value based upon the saturated conditions (see section 4.1), and another based upon the results of the impinger analysis. The lower of these two values of B_{ws} shall be considered correct.

12.2 Approximation Method. The approximation method presented is designed to estimate the moisture in the stack gas; therefore, other data, which are only necessary for accurate moisture determinations, are not collected. The following equations adequately estimate the moisture content for the purpose of determining isokinetic sampling rate settings.

12.2.1 Nomenclature.

B_{wm} = Approximate proportion by volume of water vapor in the gas stream leaving the second impinger, 0.025.
B_{ws} = Water vapor in the gas stream, proportion by volume.
M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
P_m = Absolute pressure (for this method, same as barometric pressure) at the dry gas meter, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
R = Ideal gas constant, 0.06236 [(mm Hg)(m^3)]/[(g-mole)(K)] for metric units and 21.85 [(in. Hg)(ft^3)]/[(lb-mole)(°R)] for English units.
T_m = Absolute temperature at meter, °K (°R).
T_{std} = Standard absolute temperature, 293 °K (528 °R).
V_f = Final volume of impinger contents, ml.
V_i = Initial volume of impinger contents, ml.
V_m = Dry gas volume measured by dry gas meter, dcm (dcf).
$V_{m(std)}$ = Dry gas volume measured by dry gas meter, corrected to standard conditions, dscm (dscf).
$V_{wc(std)}$ = Volume of water vapor condensed, corrected to standard conditions, scm (scf).
Y = Dry gas meter calibration factor.
ρ_w = Density of water, 0.09982 g/ml (0.002201 lb/ml).

12.2.2 Volume of Water Vapor Collected.

$$V_{wc(std)} = \frac{\left(V_f - V_i\right) \rho_w R\ T_{std}}{P_{std} M_W} \qquad \text{Eq. 4-5}$$

$$= K_5\left(V_f - V_i\right)$$

Where:

K_5 = 0.001333 m^3/ml for metric units,
= 0.04706 ft^3/ml for English units.

12.2.3 Sample Gas Volume.

$$V_{m(std)} = \frac{V_m\ Y\ P_m T_{std}}{P_{std} T_m} \qquad \text{Eq. 4-6}$$

$$= K_6 Y \frac{V_m P_m}{T_m}$$

Where:

K_6 = 0.3855 °K/mm Hg for metric units,
= 17.64 °R/in. Hg for English units.

12.2.4 Approximate Moisture Content.

$$B_{ws} = \frac{V_{wc(std)}}{V_{wc(std)} + V_{m(std)}} + B_{wm} \qquad \text{Eq. 4-7}$$

$$= \frac{V_{wc(std)}}{V_{wc(std)} + V_{m(std)}} + (0.025)$$

12.2.5 Using F-factors to determine approximate moisture for estimating moisture content where no wet scrubber is being used, for the purpose of determining isokinetic sampling rate settings with no fuel sample, is acceptable using the average F_c or F_d factor from Method 19 (see Method 19, section 12.3.1). If this option is selected, calculate the approximate moisture as follows:

$B_{ws} = B_H + B_A + B_F$

Where:

B_A = Mole Fraction of moisture in the ambient air.

$$B_A = \frac{\%RH}{100 * P_{Bar}} * 10^{\left[6.6912 - \left(\frac{3144}{T+390.86}\right)\right]}$$

B_F = Mole fraction of moisture from free water in the fuel.

$$B_F = \left[\frac{0.0036W^2 + 0.075W}{100}\right]\left[\frac{20.9 - O_2}{20.9}\right]$$

B_H = Mole fraction of moisture from the hydrogen in the fuel.

$$B_H = \left[1 - \frac{F_d}{F_w}\right]\frac{(20.9 - O_2)}{20.9}$$

B_{ws} = Mole fraction of moisture in the stack gas.

F_d = Volume of dry combustion components per unit of heat content at 0 percent oxygen, dscf/10^6.

Btu (scm/J). See Table 19–2 in Method 19.

F_w = Volume of wet combustion components per unit of heat content at 0 percent oxygen, wet.

scf/10^6 Btu (scm/J). See Table 19–2 in Method 19.

%RH = Percent relative humidity (calibrated hygrometer acceptable), percent.

P_{Bar} = Barometric pressure, in. Hg.

T = Ambient temperature, °F.

W = Percent free water by weight, percent.

O_2 = Percent oxygen in stack gas, dry basis, percent.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 The procedure described in Method 5 for determining moisture content is an acceptable alternative to Method 4.

16.2 The procedures in Method 6A for determining moisture is an acceptable alternative to Method 4.

16.3 Method 320 is an acceptable alternative to Method 4 for determining moisture.

16.4 Using F-factors to determine moisture is an acceptable alternative to Method 4 for a combustion stack not using a scrubber, and where a fuel sample is taken during the test run and analyzed for development of an F_d factor (see Method 19, section 12.3.2), and where stack O_2 content is measured by Method 3A or 3B during each test run. If this option is selected, calculate the moisture content as follows:

$B_{ws} = B_H + B_A + B_F$

Where:

B_A = Mole fraction of moisture in the ambient air.

$$B_A = \frac{\%RH}{100\ P_{Bar}}[10^{[6.6912-\left(\frac{3144}{T+390.86}\right)]}]$$

NOTE: Values of B_A should be between 0.00 and 0.06 with common values being about 0.015.

B_F = Mole fraction of moisture from free water in the fuel.

$$B_F = \left[\frac{0.0036\ W^2 + 0.075\ W}{100}\right][\frac{20.9 - O_2}{20.9}]$$

NOTE: Free water in fuel is minimal for distillate oil and gases, such as propane and natural gas, so this step may be omitted for those fuels.

B_H = Mole fraction of moisture from the hydrogen in the fuel.

$$B_H = \left(1 - \frac{F_d}{F_w}\right)\frac{(20.9 - O_2)}{20.9}$$

B_{ws} = Mole fraction of moisture in the stack gas.
F_d = Volume of dry combustion components per unit of heat content at 0 percent oxygen, dscf/10^6 Btu (scm/J). Develop a test specific F_d value using an integrated fuel sample from each test run and Equation 19–13 in section 12.3.2 of Method 19.
F_w = Volume of wet combustion components per unit of heat content at 0 percent oxygen, wet scf/10^6 Btu (scm/J). Develop a test specific F_w value using an integrated fuel sample from each test run and Equation 19–14 in section 12.3.2 of Method 19.
%RH = Percent relative humidity (calibrated hygrometer acceptable), percent.
P_{Bar} = Barometric pressure, in. Hg.
T = Ambient temperature, °F.
W = Percent free water by weight, percent.
O_2 = Percent oxygen in stack gas, dry basis, percent.

17.0 References

1. Air Pollution Engineering Manual (Second Edition). Danielson, J.A. (ed.). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, NC. Publication No. AP–40. 1973.

2. Devorkin, Howard, et al. Air Pollution Source Testing Manual. Air Pollution Control District, Los Angeles, CA. November 1963.

3. Methods for Determination of Velocity, Volume, Dust and Mist Content of Gases. Western Precipitation Division of Joy Manufacturing Co. Los Angeles, CA. Bulletin WP–50. 1968.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

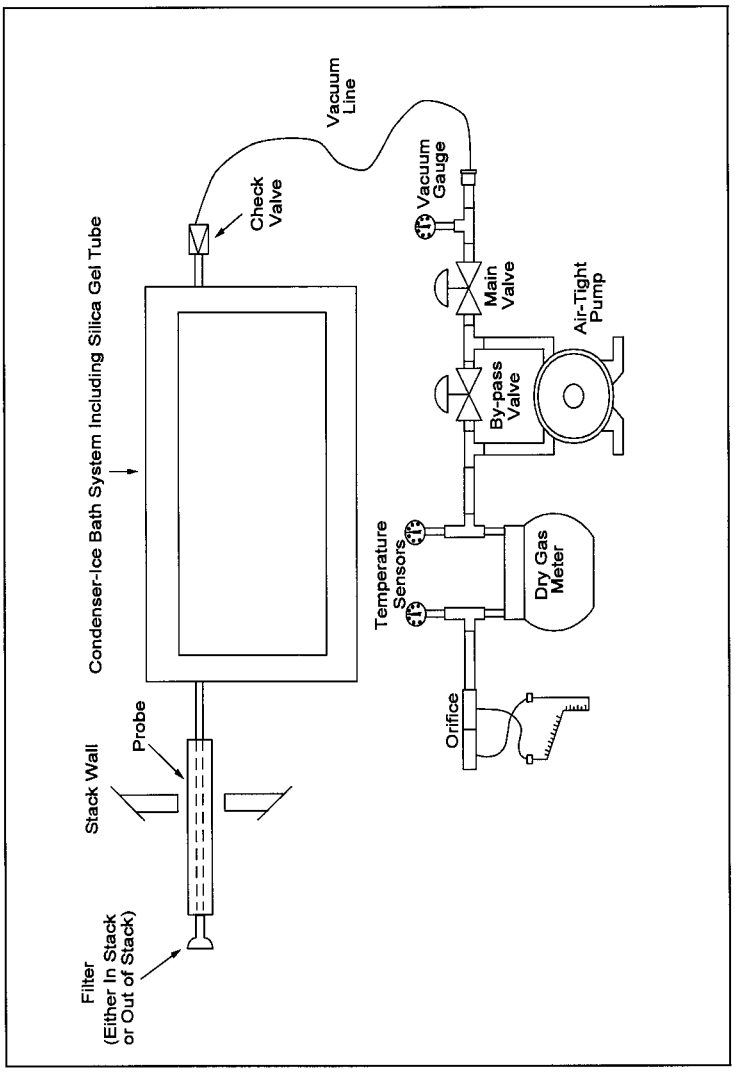

Figure 4-1. Moisture Sampling Train-Reference Method

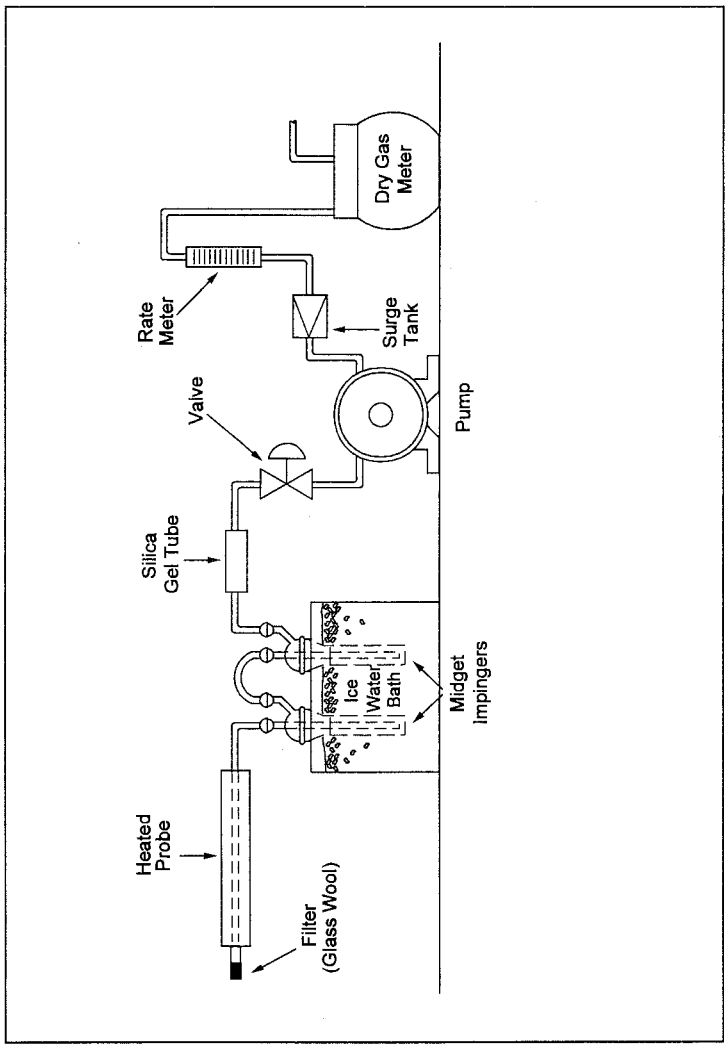

Figure 4-2. Moisture Sampling Train - Approximation Method.

Plant		Run No.	
Location		Ambient temperature	
Operator		Barometric pressure	
Date		Probe Length	

Traverse Pt. No.	Sampling time (Δ), min	Stack temperature °C (°F)	Pressure differential across orifice meter ΔH mm (in.) H_2O	Meter reading gas sample volume m^3 (ft^3)	ΔV_m m^3 (ft^3)	Gas sample temperature at dry gas meter		Temperature of gas leaving condenser or last impinger °C (°F)
						Inlet Tm_{in} °C (°F)	Outlet Tm_{out} °C (°F)	
Average								

Location _____ Barometric pressure _____
Test _____ Comments: _____
Date _____
Operator _____

Figure 4–3. Moisture Determination—Reference Method

Clock time	Gas Volume through meter, (V_m), m^3 (ft^3)	Rate meter setting m^3/min (ft^3/min)	Meter temperature °C (°F)

Figure 4–4. Example Moisture Determination Field Data Sheet—Approximation Method

	Impinger volume, ml	Silica gel weight, g
Final Initial Difference		

Figure 4–5. Analytical Data—Reference Method

METHOD 5—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of PM emissions from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature of 120 ±14 °C (248 ±25 °F) or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. The PM mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after the removal of uncombined water.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. The following items are required for sample collection:

6.1.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 5–1 in section 18.0. Complete construction details are given in APTD–0581 (Reference 2 in section 17.0); commercial models of this train are also available. For

changes from APTD–0581 and for allowable modifications of the train shown in Figure 5–1, see the following subsections.

NOTE: The operating and maintenance procedures for the sampling train are described in APTD–0576 (Reference 3 in section 17.0). Since correct usage is important in obtaining valid results, all users should read APTD–0576 and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein.

6.1.1.1 Probe Nozzle. Stainless steel (316) or glass with a sharp, tapered leading edge. The angle of taper shall be ≤30°, and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. If made of stainless steel, the nozzle shall be constructed from seamless tubing. Other materials of construction may be used, subject to the approval of the Administrator. A range of nozzle sizes suitable for isokinetic sampling should be available. Typical nozzle sizes range from 0.32 to 1.27 cm (⅛ to ½ in) inside diameter (ID) in increments of 0.16 cm (1⁄16 in). Larger nozzles sizes are also available if higher volume sampling trains are used. Each nozzle shall be calibrated, according to the procedures outlined in section 10.1.

6.1.1.2 Probe Liner. Borosilicate or quartz glass tubing with a heating system capable of maintaining a probe gas temperature during sampling of 120 ±14 °C (248 ±25 °F), or such other temperature as specified by an applicable subpart of the standards or as approved by the Administrator for a particular application. Since the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to APTD–0581 and utilizing the calibration curves of APTD–0576 (or calibrated according to the procedure outlined in APTD–0576) will be considered acceptable. Either borosilicate or quartz glass probe liners may be used for stack temperatures up to about 480 °C (900 °F); quartz glass liners shall be used for temperatures between 480 and 900 °C (900 and 1,650 °F). Both types of liners may be used at higher temperatures than specified for short periods of time, subject to the approval of the Administrator. The softening temperature for borosilicate glass is 820 °C (1500 °F), and for quartz glass it is 1500 °C (2700 °F). Whenever practical, every effort should be made to use borosilicate or quartz glass probe liners. Alternatively, metal liners (e.g., 316 stainless steel, Incoloy 825 or other corrosion resistant metals) made of seamless tubing may be used, subject to the approval of the Administrator.

6.1.1.3 Pitot Tube. Type S, as described in section 6.1 of Method 2, or other device approved by the Administrator. The pitot tube shall be attached to the probe (as shown in Figure 5–1) to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see Method 2, Figure 2–7) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in section 10.0 of Method 2.

6.1.1.4 Differential Pressure Gauge. Inclined manometer or equivalent device (two), as described in section 6.2 of Method 2. One manometer shall be used for velocity head (Δp) readings, and the other, for orifice differential pressure readings.

6.1.1.5 Filter Holder. Borosilicate glass, with a glass or Teflon frit filter support and a silicone rubber gasket. Other materials of construction (e.g., stainless steel or Viton) may be used, subject to the approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe (or cyclone, if used).

6.1.1.6 Filter Heating System. Any heating system capable of monitoring and maintaining temperature around the filter shall be used to ensure the sample gas temperature exiting the filter of 120 ±14 °C (248 ±25 °F) during sampling or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. The monitoring and regulation of the temperature around the filter may be done with the filter temperature sensor or another temperature sensor.

6.1.1.7 Filter Temperature Sensor. A temperature sensor capable of measuring temperature to within ±3 °C (5.4 °F) shall be installed so that the sensing tip of the temperature sensor is in direct contact with the sample gas exiting the filter. The sensing tip of the sensor may be encased in glass, Teflon, or metal and must protrude at least ½ in. into the sample gas exiting the filter. The filter temperature sensor must be monitored and recorded during sampling to ensure a sample gas temperature exiting the filter of 120 ±14 °C (248 ±25 °F), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application.

6.1.1.8 Condenser. The following system shall be used to determine the stack gas moisture content: Four impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with a 1.3 cm (½ in.) ID glass tube extending to about 1.3 cm (½ in.) from the bottom of the flask. The second impinger shall be of the Greenburg-Smith design with the standard

tip. Modifications (e.g., using flexible connections between the impingers, using materials other than glass, or using flexible vacuum lines to connect the filter holder to the condenser) may be used, subject to the approval of the Administrator. The first and second impingers shall contain known quantities of water (Section 8.3.1), the third shall be empty, and the fourth shall contain a known weight of silica gel, or equivalent desiccant. A temperature sensor, capable of measuring temperature to within 1 °C (2 °F) shall be placed at the outlet of the fourth impinger for monitoring purposes. Alternatively, any system that cools the sample gas stream and allows measurement of the water condensed and moisture leaving the condenser, each to within 1 ml or 1 g may be used, subject to the approval of the Administrator. An acceptable technique involves the measurement of condensed water either gravimetrically or volumetrically and the determination of the moisture leaving the condenser by: (1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's law of partial pressures; or (2) passing the sample gas stream through a tared silica gel (or equivalent desiccant) trap with exit gases kept below 20 °C (68 °F) and determining the weight gain. If means other than silica gel are used to determine the amount of moisture leaving the condenser, it is recommended that silica gel (or equivalent) still be used between the condenser system and pump to prevent moisture condensation in the pump and metering devices and to avoid the need to make corrections for moisture in the metered volume.

NOTE: If a determination of the PM collected in the impingers is desired in addition to moisture content, the impinger system described above shall be used, without modification. Individual States or control agencies requiring this information shall be contacted as to the sample recovery and analysis of the impinger contents.

6.1.1.9 Metering System. Vacuum gauge, leak-free pump, calibrated temperature sensors, dry gas meter (DGM) capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 5–1. Other metering systems capable of maintaining sampling rates within 10 percent of isokinetic and of determining sample volumes to within 2 percent may be used, subject to the approval of the Administrator. When the metering system is used in conjunction with a pitot tube, the system shall allow periodic checks of isokinetic rates.

6.1.1.10 Sampling trains utilizing metering systems designed for higher flow rates than that described in APTD–0581 or APTD–0576 may be used provided that the specifications of this method are met.

6.1.2 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in.).

NOTE: The barometric pressure reading may be obtained from a nearby National Weather Service station. In this case, the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be made at a rate of minus 2.5 mm Hg (0.1 in.) per 30 m (100 ft) elevation increase or plus 2.5 mm Hg (0.1 in) per 30 m (100 ft) elevation decrease.

6.1.3 Gas Density Determination Equipment. Temperature sensor and pressure gauge, as described in sections 6.3 and 6.4 of Method 2, and gas analyzer, if necessary, as described in Method 3. The temperature sensor shall, preferably, be permanently attached to the pitot tube or sampling probe in a fixed configuration, such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see Method 2, Figure 2–4). As a second alternative, if a difference of not more than 1 percent in the average velocity measurement is to be introduced, the temperature sensor need not be attached to the probe or pitot tube. (This alternative is subject to the approval of the Administrator.)

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Probe-Liner and Probe-Nozzle Brushes. Nylon bristle brushes with stainless steel wire handles. The probe brush shall have extensions (at least as long as the probe) constructed of stainless steel, Nylon, Teflon, or similarly inert material. The brushes shall be properly sized and shaped to brush out the probe liner and nozzle.

6.2.2 Wash Bottles. Two Glass wash bottles are recommended. Alternatively, polyethylene wash bottles may be used. It is recommended that acetone not be stored in polyethylene bottles for longer than a month.

6.2.3 Glass Sample Storage Containers. Chemically resistant, borosilicate glass bottles, for acetone washes, 500 ml or 1000 ml. Screw cap liners shall either be rubber-backed Teflon or shall be constructed so as to be leak-free and resistant to chemical attack by acetone. (Narrow mouth glass bottles have been found to be less prone to leakage.) Alternatively, polyethylene bottles may be used.

6.2.4 Petri Dishes. For filter samples; glass or polyethylene, unless otherwise specified by the Administrator.

6.2.5 Graduated Cylinder and/or Balance. To measure condensed water to within 1 ml or 0.5 g. Graduated cylinders shall have subdivisions no greater than 2 ml.

6.2.6 Plastic Storage Containers. Air-tight containers to store silica gel.

6.2.7 Funnel and Rubber Policeman. To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

6.2.8 Funnel. Glass or polyethylene, to aid in sample recovery.

6.3 Sample Analysis. The following equipment is required for sample analysis:

6.3.1 Glass Weighing Dishes.

6.3.2 Desiccator.

6.3.3 Analytical Balance. To measure to within 0.1 mg.

6.3.4 Balance. To measure to within 0.5 g.

6.3.5 Beakers. 250 ml.

6.3.6 Hygrometer. To measure the relative humidity of the laboratory environment.

6.3.7 Temperature Sensor. To measure the temperature of the laboratory environment.

7.0 Reagents and Standards

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Method D 2986–71, 78, or 95a (incorporated by reference—see §60.17). Test data from the supplier's quality control program are sufficient for this purpose. In sources containing SO_2 or SO_3, the filter material must be of a type that is unreactive to SO_2 or SO_3. Reference 10 in section 17.0 may be used to select the appropriate filter.

7.1.2 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

7.1.3 Water. When analysis of the material caught in the impingers is required, deionized distilled water [to conform to ASTM D1193–77 or 91 Type 3 (incorporated by reference—see §60.17)] with at least <0.001 percent residue shall be used or as specified in the applicable method requiring analysis of the water. Run reagent blanks prior to field use to eliminate a high blank on test samples.

7.1.4 Crushed Ice.

7.2 Sample Recovery. Acetone, reagent grade, ≤0.001 percent residue, in glass bottles, is required. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers; thus, acetone blanks shall be run prior to field use and only acetone with low blank values (≤0.001 percent) shall be used. In no case shall a blank value of greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight.

7.3 Sample Analysis. The following reagents are required for sample analysis:

7.3.1 Acetone. Same as in section 7.2.

7.3.2 Desiccant. Anhydrous calcium sulfate, indicating type. Alternatively, other types of desiccants may be used, subject to the approval of the Administrator.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation. It is suggested that sampling equipment be maintained according to the procedures described in APTD–0576. Alternative mercury-free thermometers may be used if the thermometers are at a minimum equivalent in terms of performance or suitably effective for the specific temperature measurement application.

8.1.1 Place 200 to 300 g of silica gel in each of several air-tight containers. Weigh each container, including silica gel, to the nearest 0.5 g, and record this weight. As an alternative, the silica gel need not be preweighed, but may be weighed directly in its impinger or sampling holder just prior to train assembly.

8.1.2 Check filters visually against light for irregularities, flaws, or pinhole leaks. Label filters of the proper diameter on the back side near the edge using numbering machine ink. As an alternative, label the shipping containers (glass or polyethylene petri dishes), and keep each filter in its identified container at all times except during sampling.

8.1.3 Desiccate the filters at 20 ±5.6 °C (68 ±10 °F) and ambient pressure for at least 24 hours. Weigh each filter (or filter and shipping container) at intervals of at least 6 hours to a constant weight (*i.e.*, ≤0.5 mg change from previous weighing). Record results to the nearest 0.1 mg. During each weighing, the period for which the filter is exposed to the laboratory atmosphere shall be less than 2 minutes. Alternatively (unless otherwise specified by the Administrator), the filters may be oven dried at 105 °C (220 °F) for 2 to 3 hours, desiccated for 2 hours, and weighed. Procedures other than those described, which account for relative humidity effects, may be used, subject to the approval of the Administrator.

8.2 Preliminary Determinations.

8.2.1 Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and the range of velocity heads using Method 2; it is recommended that a leak check of the pitot lines (see Method 2, section 8.1) be performed. Determine the moisture content using Approximation Method 4 or its alternatives for the purpose

of making isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in Method 2, section 8.6; if integrated Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the particulate sample run.

8.2.2 Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see section 8.3 of Method 2).

8.2.3 Select a suitable probe liner and probe length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the required probe length.

8.2.4 Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that (1) the sampling time per point is not less than 2 minutes (or some greater time interval as specified by the Administrator), and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume. The latter is based on an approximate average sampling rate.

8.2.5 The sampling time at each point shall be the same. It is recommended that the number of minutes sampled at each point be an integer or an integer plus one-half minute, in order to avoid timekeeping errors.

8.2.6 In some circumstances (*e.g.*, batch cycles) it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the Administrator's approval must first be obtained.

8.3 Preparation of Sampling Train.

8.3.1 During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin. Place 100 ml of water in each of the first two impingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

8.3.2 Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly is completed.

8.3.3 When glass probe liners are used, install the selected nozzle using a Viton A O-ring when stack temperatures are less than 260 °C (500 °F) or a heat-resistant string gasket when temperatures are higher. See APTD–0576 for details. Other connecting systems using either 316 stainless steel or Teflon ferrules may be used. When metal liners are used, install the nozzle as discussed above or by a leak-free direct mechanical connection. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

8.3.4 Set up the train as shown in Figure 5–1 ensuring that the connections are leaktight. Subject to the approval of the Administrator, a glass cyclone may be used between the probe and filter holder when the total particulate catch is expected to exceed 100 mg or when water droplets are present in the stack gas.

8.3.5 Place crushed ice around the impingers.

8.4 Leak-Check Procedures.

8.4.1 Leak Check of Metering System Shown in Figure 5–1. That portion of the sampling train from the pump to the orifice meter should be leak-checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The following procedure is suggested (see Figure 5–2): Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 to 18 cm (5 to 7 in.) water column by blowing into the rubber tubing. Pinch off the tubing, and observe the manometer for one minute. A loss of pressure on the manometer indicates a leak in the meter box; leaks, if present, must be corrected.

8.4.2 Pretest Leak Check. A pretest leak check of the sampling train is recommended, but not required. If the pretest leak check is conducted, the following procedure should be used.

8.4.2.1 After the sampling train has been assembled, turn on and set the filter and probe heating systems to the desired operating temperatures. Allow time for the temperatures to stabilize. If a Viton A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 380 mm (15 in.) Hg vacuum.

NOTE: A lower vacuum may be used, provided that it is not exceeded during the test.

8.4.2.2 If a heat-resistant string is used, do not connect the probe to the train during the leak check. Instead, leak-check the train by first plugging the inlet to the filter holder (cyclone, if applicable) and pulling a 380 mm (15 in.) Hg vacuum (see note in section 8.4.2.1). Then connect the probe to the train, and leak-check at approximately 25 mm (1 in.) Hg vacuum; alternatively, the probe may be leak-checked with the rest of the sampling train, in one step, at 380 mm (15 in.) Hg vacuum. Leakage rates in excess of 4 percent of the average sampling rate or 0.00057 m^3/min (0.020 cfm), whichever is less, are unacceptable.

8.4.2.3 The following leak-check instructions for the sampling train described in APTD–0576 and APTD–0581 may be helpful. Start the pump with the bypass valve fully open and the coarse adjust valve completely closed. Partially open the coarse adjust valve, and slowly close the bypass valve until the desired vacuum is reached. Do not reverse the direction of the bypass valve, as this will cause water to back up into the filter holder. If the desired vacuum is exceeded, either leak-check at this higher vacuum, or end the leak check and start over.

8.4.2.4 When the leak check is completed, first slowly remove the plug from the inlet to the probe, filter holder, or cyclone (if applicable), and immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the filter holder and the silica gel from being entrained backward into the third impinger.

8.4.3 Leak Checks During Sample Run. If, during the sampling run, a component (*e.g.*, filter assembly or impinger) change becomes necessary, a leak check shall be conducted immediately before the change is made. The leak check shall be done according to the procedure outlined in section 8.4.2 above, except that it shall be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.020 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered; if, however, a higher leakage rate is obtained, either record the leakage rate and plan to correct the sample volume as shown in section 12.3 of this method, or void the sample run.

NOTE: Immediately after component changes, leak checks are optional. If such leak checks are done, the procedure outlined in section 8.4.2 above should be used.

8.4.4 Post-Test Leak Check. A leak check of the sampling train is mandatory at the conclusion of each sampling run. The leak check shall be performed in accordance with the procedures outlined in section 8.4.2, except that it shall be conducted at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m^3 min (0.020 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, either record the leakage rate and correct the sample volume as shown in section 12.3 of this method, or void the sampling run.

8.5 Sampling Train Operation. During the sampling run, maintain an isokinetic sampling rate (within 10 percent of true isokinetic unless otherwise specified by the Administrator) and a sample gas temperature through the filter of 120 ±14 °C (248 ±25 °F) or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator.

8.5.1 For each run, record the data required on a data sheet such as the one shown in Figure 5–3. Be sure to record the initial DGM reading. Record the DGM readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak check, and when sampling is halted. Take other readings indicated by Figure 5–3 at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

8.5.2 Clean the portholes prior to the test run to minimize the chance of collecting deposited material. To begin sampling, verify that the filter and probe heating systems are up to temperature, remove the nozzle cap, verify that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump, and adjust the flow to isokinetic conditions. Nomographs are available which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pitot tube coefficient (C_p) is 0.85 ±0.02, and the stack gas equivalent density [dry molecular weight (M_d)] is equal to 29 ±4. APTD–0576 details the procedure for using the nomographs. If C_p and M_d are outside the above stated ranges, do not use the nomographs unless appropriate steps (see Reference 7 in section 17.0) are taken to compensate for the deviations.

8.5.3 When the stack is under significant negative pressure (*i.e.*, height of impinger stem), take care to close the coarse adjust valve before inserting the probe into the stack to prevent water from backing into the

filter holder. If necessary, the pump may be turned on with the coarse adjust valve closed.

8.5.4 When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

8.5.5 Traverse the stack cross-section, as required by Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the portholes; this minimizes the chance of extracting deposited material.

8.5.6 During the test run, make periodic adjustments to keep the temperature around the filter holder at the proper level to maintain the sample gas temperature exiting the filter; add more ice and, if necessary, salt to maintain a temperature of less than 20 °C (68 °F) at the condenser/silica gel outlet. Also, periodically check the level and zero of the manometer.

8.5.7 If the pressure drop across the filter becomes too high, making isokinetic sampling difficult to maintain, the filter may be replaced in the midst of the sample run. It is recommended that another complete filter assembly be used rather than attempting to change the filter itself. Before a new filter assembly is installed, conduct a leak check (see section 8.4.3). The total PM weight shall include the summation of the filter assembly catches.

8.5.8 A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator.

NOTE: When two or more trains are used, separate analyses of the front-half and (if applicable) impinger catches from each train shall be performed, unless identical nozzle sizes were used on all trains, in which case, the front-half catches from the individual trains may be combined (as may the impinger catches) and one analysis of front-half catch and one analysis of impinger catch may be performed. Consult with the Administrator for details concerning the calculation of results when two or more trains are used.

8.5.9 At the end of the sample run, close the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final DGM meter reading, and conduct a post-test leak check, as outlined in section 8.4.4. Also, leak-check the pitot lines as described in Method 2, section 8.1. The lines must pass this leak check, in order to validate the velocity head data.

8.6 Calculation of Percent Isokinetic. Calculate percent isokinetic (see Calculations, section 12.11) to determine whether the run was valid or another test run should be made. If there was difficulty in maintaining isokinetic rates because of source conditions, consult with the Administrator for possible variance on the isokinetic rates.

8.7 Sample Recovery.

8.7.1 Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

8.7.2 When the probe can be safely handled, wipe off all external PM near the tip of the probe nozzle, and place a cap over it to prevent losing or gaining PM. Do not cap off the probe tip tightly while the sampling train is cooling down. This would create a vacuum in the filter holder, thereby drawing water from the impingers into the filter holder.

8.7.3 Before moving the sample train to the cleanup site, remove the probe from the sample train and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Cap the filter inlet where the probe was fastened. Remove the umbilical cord from the last impinger, and cap the impinger. If a flexible line is used between the first impinger or condenser and the filter holder, disconnect the line at the filter holder, and let any condensed water or liquid drain into the impingers or condenser. Cap off the filter holder outlet and impinger inlet. Either ground-glass stoppers, plastic caps, or serum caps may be used to close these openings.

8.7.4 Transfer the probe and filter-impinger assembly to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

8.7.5 Save a portion of the acetone used for cleanup as a blank. From each storage container of acetone used for cleanup, save 200 ml and place in a glass sample container labeled ''acetone blank.'' To minimize any particulate contamination, rinse the wash bottle prior to filling from the tested container.

8.7.6 Inspect the train prior to and during disassembly, and note any abnormal conditions. Treat the samples as follows:

8.7.6.1 Container No. 1. Carefully remove the filter from the filter holder, and place it in its identified petri dish container. Use a pair of tweezers and/or clean disposable surgical gloves to handle the filter. If it is necessary to fold the filter, do so such that the PM cake is inside the fold. Using a dry Nylon bristle brush and/or a sharp-edged blade, carefully transfer to the petri dish any PM and/or filter fibers that adhere to the filter holder gasket. Seal the container.

8.7.6.2 Container No. 2. Taking care to see that dust on the outside of the probe or other

exterior surfaces does not get into the sample, quantitatively recover PM or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with acetone and placing the wash in a glass container. Deionized distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator. In these cases, save a water blank, and follow the Administrator's directions on analysis. Perform the acetone rinse as follows:

8.7.6.2.1 Carefully remove the probe nozzle. Clean the inside surface by rinsing with acetone from a wash bottle and brushing with a Nylon bristle brush. Brush until the acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

8.7.6.2.2 Brush and rinse the inside parts of the fitting with acetone in a similar way until no visible particles remain.

8.7.6.2.3 Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Let the acetone drain from the lower end into the sample container. A funnel (glass or polyethylene) may be used to aid in transferring liquid washes to the container. Follow the acetone rinse with a probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action through the probe; hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter that is brushed from the probe. Run the brush through the probe three times or more until no visible PM is carried out with the acetone or until none remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times since metal probes have small crevices in which particulate matter can be entrapped. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe.

8.7.6.2.4 It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

8.7.6.2.5 Clean the inside of the front half of the filter holder by rubbing the surfaces with a Nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone, also (if applicable). After all acetone washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to allow determination of whether leakage occurred during transport. Label the container to clearly identify its contents.

8.7.6.3 Container No. 3. Note the color of the indicating silica gel to determine whether it has been completely spent, and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container, and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, follow the procedure for Container No. 3 in section 11.2.3.

8.7.6.4 Impinger Water. Treat the impingers as follows: Make a notation of any color or film in the liquid catch. Measure the liquid that is in the first three impingers to within 1 ml by using a graduated cylinder or by weighing it to within 0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas. Discard the liquid after measuring and recording the volume or weight, unless analysis of the impinger catch is required (see NOTE, section 6.1.1.8). If a different type of condenser is used, measure the amount of moisture condensed either volumetrically or gravimetrically.

8.8 Sample Transport. Whenever possible, containers should be shipped in such a way that they remain upright at all times.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4, 10.1–10.6	Sampling equipment leak check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.

9.2 Volume Metering System Checks. The following procedures are suggested to check the volume metering system calibration values at the field test site prior to sample collection. These procedures are optional.

9.2.1 Meter Orifice Check. Using the calibration data obtained during the calibration procedure described in section 10.3, determine the ΔH@ for the metering system orifice. The ΔH@ is the orifice pressure differential in units of in. H_2O that correlates to 0.75 cfm of air at 528 °R and 29.92 in. Hg. The ΔH@ is calculated as follows:

$$\Delta H@ = 0.0319\ \Delta H \frac{T_M \theta^2}{P_{bar} Y^2 V_m^2}$$

Where:

ΔH = Average pressure differential across the orifice meter, in. H_2O.
T_m = Absolute average DGM temperature, °R.
P_{bar} = Barometric pressure, in. Hg.
θ = Total sampling time, min.
Y = DGM calibration factor, dimensionless.
V_m = Volume of gas sample as measured by DGM, dcf.
0.0319 = (0.0567 in. Hg/°R) (0.75 cfm)²

9.2.1.1 Before beginning the field test (a set of three runs usually constitutes a field test), operate the metering system (*i.e.*, pump, volume meter, and orifice) at the ΔH@ pressure differential for 10 minutes. Record the volume collected, the DGM temperature, and the barometric pressure. Calculate a DGM calibration check value, Y_c, as follows:

$$Y_c = \frac{10}{V_m}\left[\frac{0.0319\ T_m}{P_{bar}}\right]^{\frac{1}{2}}$$

where:

Y_c = DGM calibration check value, dimensionless.
10 = Run time, min.

9.2.1.2 Compare the Y_c value with the dry gas meter calibration factor Y to determine that: $0.97Y < Y_c < 1.03Y$. If the Y_c value is not within this range, the volume metering system should be investigated before beginning the test.

9.2.2 Calibrated Critical Orifice. A critical orifice, calibrated against a wet test meter or spirometer and designed to be inserted at the inlet of the sampling meter box, may be used as a check by following the procedure of section 16.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Probe Nozzle. Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the ID of the nozzle to the nearest 0.025 mm (0.001 in.). Make three separate measurements using different diameters each time, and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

10.2 Pitot Tube Assembly. The Type S pitot tube assembly shall be calibrated according to the procedure outlined in section 10.1 of Method 2.

10.3 Metering System.

10.3.1 Calibration Prior to Use. Before its initial use in the field, the metering system shall be calibrated as follows: Connect the metering system inlet to the outlet of a wet test meter that is accurate to within 1 percent. Refer to Figure 5–4. The wet test meter should have a capacity of 30 liters/rev (1 ft^3/rev). A spirometer of 400 liters (14 ft^3) or more capacity, or equivalent, may be used for this calibration, although a wet test meter is usually more practical. The wet test meter should be periodically calibrated with a spirometer or a liquid displacement meter to ensure the accuracy of the wet test meter. Spirometers or wet test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained. Run the metering system pump for about 15 minutes with the orifice manometer indicating a median reading as expected in field use to allow the pump to warm up and to permit the interior surface of the wet test meter to be thoroughly wetted. Then, at each of a minimum of three orifice manometer settings, pass an exact quantity of gas through the wet test meter and note the gas volume indicated by the DGM. Also note the barometric pressure and the temperatures of the wet test meter, the inlet of the DGM, and the outlet of the DGM. Select the highest and lowest orifice settings to bracket the expected field operating range of the orifice. Use a minimum volume of 0.14 m^3 (5 ft^3) at all orifice settings. Record all the data on a form similar to Figure 5–5 and calculate Y, the DGM calibration factor, and ΔH , the orifice calibration factor, at each orifice setting as shown on Figure 5–5. Allowable tolerances for individual Y and ΔH values are given in Figure 5–5. Use the average of the Y values in the calculations in section 12.0.

10.3.1.1 Before calibrating the metering system, it is suggested that a leak check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. For these cases the following leak-check procedure is suggested: make a 10-minute calibration run at 0.00057 m^3/min (0.020 cfm). At the end of the run, take the difference of the measured wet test meter and DGM volumes. Divide the difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 m^3/min (0.020 cfm).

10.3.2 Calibration After Use. After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single, intermediate

orifice setting (based on the previous field test), with the vacuum set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet test meter and the inlet of the metering system. Calculate the average value of the DGM calibration factor. If the value has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as detailed in section 10.3.1.

NOTE: Alternative procedures (*e.g.*, rechecking the orifice meter coefficient) may be used, subject to the approval of the Administrator.

10.3.3 Acceptable Variation in Calibration Check. If the DGM coefficient values obtained before and after a test series differ by more than 5 percent, the test series shall either be voided, or calculations for the test series shall be performed using whichever meter coefficient value (*i.e.*, before or after) gives the lower value of total sample volume.

10.4 Probe Heater Calibration. Use a heat source to generate air heated to selected temperatures that approximate those expected to occur in the sources to be sampled. Pass this air through the probe at a typical sample flow rate while measuring the probe inlet and outlet temperatures at various probe heater settings. For each air temperature generated, construct a graph of probe heating system setting versus probe outlet temperature. The procedure outlined in APTD–0576 can also be used. Probes constructed according to APTD–0581 need not be calibrated if the calibration curves in APTD–0576 are used. Also, probes with outlet temperature monitoring capabilities do not require calibration.

NOTE: The probe heating system shall be calibrated before its initial use in the field.

10.5 Temperature Sensors. Use the procedure in Section 10.3 of Method 2 to calibrate in-stack temperature sensors. Dial thermometers, such as are used for the DGM and condenser outlet, shall be calibrated against mercury-in-glass thermometers. An alternative mercury-free NIST-traceable thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application. As an alternative, the following single-point calibration procedure may be used. After each test run series, check the accuracy (and, hence, the calibration) of each thermocouple system at ambient temperature, or any other temperature, within the range specified by the manufacturer, using a reference thermometer (either ASTM reference thermometer or a thermometer that has been calibrated against an ASTM reference thermometer). The temperatures of the thermocouple and reference thermometers shall agree to within ±2 °F.

10.6 Barometer. Calibrate against a mercury barometer or NIST-traceable barometer prior to the field test. Alternatively, barometric pressure may be obtained from a weather report that has been adjusted for the test point (on the stack) elevation.

10.7 Field Balance Calibration Check. Check the calibration of the balance used to weigh impingers with a weight that is at least 500g or within 50g of a loaded impinger. The weight must be ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 6 (or better). Daily before use, the field balance must measure the weight within ±0.5g of the certified mass. If the daily balance calibration check fails, perform corrective measures and repeat the check before using balance.

10.8 Analytical Balance Calibration. Perform a multipoint calibration (at least five points spanning the operational range) of the analytical balance before the first use, and semiannually thereafter. The calibration of the analytical balance must be conducted using ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 2 (or better) tolerance weights. Audit the balance each day it is used for gravimetric measurements by weighing at least one ASTM E617–13 Class 2 tolerance (or better) calibration weight that corresponds to 50 to 150 percent of the weight of one filter or between 1g and 5g. If the scale cannot reproduce the value of the calibration weight to within 0.5 mg of the certified mass, perform corrective measures, and conduct the multipoint calibration before use.

11.0 Analytical Procedure

11.1 Record the data required on a sheet such as the one shown in Figure 5–6.

11.2 Handle each sample container as follows:

11.2.1 Container No. 1. Leave the contents in the shipping container or transfer the filter and any loose PM from the sample container to a tared glass weighing dish. Desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh to a constant weight, and report the results to the nearest 0.1 mg. For the purposes of this section, the term ''constant weight'' means a difference of no more than 0.5 mg or 1 percent of total weight less tare weight, whichever is greater, between two consecutive weighings, with no less than 6 hours of desiccation time between weighings. Alternatively, the sample may be oven dried at 104 °C (220 °F) for 2 to 3 hours, cooled in the desiccator, and weighed to a constant weight, unless otherwise specified by the Administrator. The sample may be oven dried at 104 °C (220 °F) for 2 to 3 hours. Once the

sample has cooled, weigh the sample, and use this weight as a final weight.

11.2.2 Container No. 2. Note the level of liquid in the container, and confirm on the analysis sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to ±1 ml or gravimetrically to ±0.5 g. Transfer the contents to a tared 250 ml beaker, and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours, and weigh to a constant weight. Report the results to the nearest 0.1 mg.

11.2.3 Container No. 3. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. This step may be conducted in the field.

11.2.4 Acetone Blank Container. Measure the acetone in this container either volumetrically or gravimetrically. Transfer the acetone to a tared 250 ml beaker, and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours, and weigh to a constant weight. Report the results to the nearest 0.1 mg.

NOTE: The contents of Container No. 2 as well as the acetone blank container may be evaporated at temperatures higher than ambient. If evaporation is done at an elevated temperature, the temperature must be below the boiling point of the solvent; also, to prevent ''bumping,'' the evaporation process must be closely supervised, and the contents of the beaker must be swirled occasionally to maintain an even temperature. Use extreme care, as acetone is highly flammable and has a low flash point.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used, provided that they give equivalent results.

12.1 Nomenclature.

A_n = Cross-sectional area of nozzle, m^2 (ft^2).
B_{ws} = Water vapor in the gas stream, proportion by volume.
C_a = Acetone blank residue concentration, mg/mg.
c_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (gr/dscf).
I = Percent of isokinetic sampling.
L_1 = Individual leakage rate observed during the leak-check conducted prior to the first component change, m^3/min (ft^3/min)
L_a = Maximum acceptable leakage rate for either a pretest leak-check or for a leak-check following a component change; equal to 0.00057 m^3/min (0.020 cfm) or 4 percent of the average sampling rate, whichever is less.
L_i = Individual leakage rate observed during the leak-check conducted prior to the ''i^{th}'' component change (i = 1, 2, 3 . . . n), m^3/min (cfm).
L_p = Leakage rate observed during the post-test leak-check, m^3/min (cfm).
m_a = Mass of residue of acetone after evaporation, mg.
m_n = Total amount of particulate matter collected, mg.
M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).
P_s = Absolute stack gas pressure, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
R = Ideal gas constant, 0.06236 ((mm Hg)(m^3))/((K)(g-mole)) {21.85 ((in. Hg) (ft^3))/((°R)(lb-mole))}.
T_m = Absolute average DGM temperature (see Figure 5–3), K (°R).
T_s = Absolute average stack gas temperature (see Figure 5–3), K (°R).
T_{std} = Standard absolute temperature, 293 K (528 °R).
V_a = Volume of acetone blank, ml.
V_{aw} = Volume of acetone used in wash, ml.
V_{1c} = Total volume of liquid collected in impingers and silica gel (see Figure 5–6), ml.
V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).
$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).
$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).
V_s = Stack gas velocity, calculated by Method 2, Equation 2–7, using data obtained from Method 5, m/sec (ft/sec).
W_a = Weight of residue in acetone wash, mg.
Y = Dry gas meter calibration factor.
ΔH = Average pressure differential across the orifice meter (see Figure 5–4), mm H_2O (in. H_2O).
ρ_a = Density of acetone, mg/ml (see label on bottle).
ρ_w = Density of water, 0.9982 g/ml. (0.002201 lb/ml).
θ = Total sampling time, min.
θ_1 = Sampling time interval, from the beginning of a run until the first component change, min.
θ_i = Sampling time interval, between two successive component changes, beginning with the interval between the first and second changes, min.
θ_p = Sampling time interval, from the final (n^{th}) component change until the end of the sampling run, min.
13.6 = Specific gravity of mercury.
60 = Sec/min.

100 = Conversion to percent.

12.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 5–3).

12.3 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (20 °C, 760 mm Hg or 68 °F, 29.92 in. Hg) by using Equation 5–1.

$$V_{m(std)} = V_m Y \frac{T_{std}\left(P_{bar} + \frac{\Delta H}{13.6}\right)}{T_m P_{std}} \qquad \text{Eq. 5-1}$$

$$= K_1 V_m Y \frac{P_{bar} + \left(\frac{\Delta H}{13.6}\right)}{T_m}$$

Where:

K_1 = 0.3858 °K/mm Hg for metric units, = 17.64 °R/in. Hg for English units.

NOTE: Equation 5–1 can be used as written unless the leakage rate observed during any of the mandatory leak checks (*i.e.*, the post-test leak check or leak checks conducted prior to component changes) exceeds L_a. If L_p or L_i exceeds L_a, Equation 5–1 must be modified as follows:

(a) Case I. No component changes made during sampling run. In this case, replace V_m in Equation 5–1 with the expression:

$$\left(V_m - \left(L_p - L_a\right)\theta\right)$$

(b) Case II. One or more component changes made during the sampling run. In this case, replace V_m in Equation 5–1 by the expression:

$$\left[V_m - \left(L_1 - L_a\right)\theta_1 - \sum_{i=2}^{n}\left(L_1 - L_a\right)\theta_i - \left(L_p - L_a\right)\theta_p\right]$$

and substitute only for those leakage rates (L_i or L_p) which exceed L_a.

12.4 Volume of Water Vapor Condensed.

$$V_{w(std)} = V_{1c}\frac{\rho_w R T_{std}}{M_w P_{std}} \qquad \text{Eq. 5-2}$$

$$= K_2 V_{1c}$$

Where:

K_2 = 0.001333 m^3/ml for metric units, = 0.04706 ft^3/ml for English units.

12.5 Moisture Content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad \text{Eq. 5-3}$$

NOTE: In saturated or water droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation 5–3), and a second from the assumption of saturated conditions. The lower of the two values of B_{ws} shall be considered correct. The procedure for determining the moisture content based upon the assumption of saturated conditions is given in section 4.0 of Method 4. For the purposes of this method, the average stack gas temperature from Figure 5–3 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is ±1 °C (2 °F).

12.6 Acetone Blank Concentration.

$$C_a = \frac{m_a}{V_a \rho_a} \qquad \text{Eq. 5-4}$$

12.7 Acetone Wash Blank.

$$W_a = C_a V_{aw} \rho_a \qquad \text{Eq. 5-5}$$

12.8 Total Particulate Weight. Determine the total particulate matter catch from the sum of the weights obtained from Containers 1 and 2 less the acetone blank (see Figure 5–6).

NOTE: In no case shall a blank value of greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight. Refer to section 8.5.8 to assist in calculation of results involving two or more filter assemblies or two or more sampling trains.

12.9 Particulate Concentration.

$$C_s = \frac{K_3 m_n}{V_{m(std)}} \qquad \text{Eq. 5-6}$$

Where:

K_3 = 0.001 g/mg for metric units.
= 0.0154 gr/mg for English units.

12.10 Conversion Factors:

From	To	Multiply by
ft^3	m^3	0.02832
gr	mg	64.80004
gr/ft^3	mg/m^3	2288.4
mg	g	0.001
gr	lb	1.429×10^{-4}

12.11 Isokinetic Variation.

12.11.1 Calculation from Raw Data.

$$I = \frac{100\,T_s\left[K_4 V_{1c} + \frac{(V_m Y)}{T_m}\left(P_{bar} + \frac{\Delta H}{13.6}\right)\right]}{60\,\theta\,v_s\,P_s\,A_n} \qquad \text{Eq. 5-7}$$

Where:

K_4 = 0.003454 ((mm Hg)(m^3))/((ml)(°K)) for metric units,
= 0.002669 ((in. Hg)(ft^3))/((ml)(°R)) for English units.

12.11.2 Calculation from Intermediate Values.

$$I = \frac{T_s V_{m(std)} P_{std} 100}{T_{std} v_s \theta A_n P_s 60\left(1 - B_{ws}\right)} \qquad \text{Eq. 5-8}$$

$$= K_5 \frac{T_s V_{m(std)}}{P_s v_s A_n \theta\left(1 - B_{ws}\right)}$$

Where:

K_5 = 4.320 for metric units,
= 0.09450 for English units.

12.11.3 Acceptable Results. If 90 percent ≤I ≤110 percent, the results are acceptable. If the PM results are low in comparison to the standard, and ''I'' is over 110 percent or less than 90 percent, the Administrator may opt to accept the results. Reference 4 in section 17.0 may be used to make acceptability judgments. If ''I'' is judged to be unacceptable, reject the results, and repeat the sampling run.

12.12 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate, if needed, using data obtained in this method and the equations in sections 12.3 and 12.4 of Method 2.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Dry Gas Meter as a Calibration Standard. A DGM may be used as a calibration standard for volume measurements in place of the wet test meter specified in section 10.3, provided that it is calibrated initially and recalibrated periodically as follows:

16.1.1 Standard Dry Gas Meter Calibration.

16.1.1.1. The DGM to be calibrated and used as a secondary reference meter should be of high quality and have an appropriately sized capacity (*e.g.*, 3 liters/rev (0.1 ft^3/rev)). A spirometer (400 liters (14 ft^3) or more capacity), or equivalent, may be used for this calibration, although a wet test meter is usually more practical. The wet test meter should have a capacity of 30 liters/rev (1 ft^3/rev) and capable of measuring volume to within 1.0 percent. Wet test meters should be checked against a spirometer or a liquid displacement meter to ensure the accuracy of the wet test meter. Spirometers or wet test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained.

16.1.1.2 Set up the components as shown in Figure 5–7. A spirometer, or equivalent, may be used in place of the wet test meter in the system. Run the pump for at least 5 minutes at a flow rate of about 10 liters/min (0.35 cfm) to condition the interior surface of the wet test meter. The pressure drop indicated by the manometer at the inlet side of the DGM should be minimized (no greater than 100 mm

H_2O (4 in. H_2O) at a flow rate of 30 liters/min (1 cfm)). This can be accomplished by using large diameter tubing connections and straight pipe fittings.

16.1.1.3 Collect the data as shown in the example data sheet (see Figure 5–8). Make triplicate runs at each of the flow rates and at no less than five different flow rates. The range of flow rates should be between 10 and 34 liters/min (0.35 and 1.2 cfm) or over the expected operating range.

16.1.1.4 Calculate flow rate, Q, for each run using the wet test meter volume, V_w, and the run time, θ. Calculate the DGM coefficient, Y_{ds}, for each run. These calculations are as follows:

$$Q = K_1 \frac{P_{bar} V_w}{(T_w + T_{std})\theta} \qquad \text{Eq. 5-9}$$

$$Y_{ds} = \frac{V_w (T_{ds} + T_{std}) P_{bar}}{V_{ds} (T_w + T_{std}) \left(P_{bar} + \frac{\Delta p}{13.6} \right)} \qquad \text{Eq. 5-10}$$

Where:

K_1 = 0.3858 °C/mm Hg for metric units = 17.64 °F/in. Hg for English units.
V_W = Wet test meter volume, liter (ft^3).
V_{ds} = Dry gas meter volume, liter (ft^3).
T_{ds} = Average dry gas meter temperature, °C (°F).
T_{adj} = 273 °C for metric units = 460 °F for English units.
T_W = Average wet test meter temperature, °C (°F)
P_{bar} = Barometric pressure, mm Hg (in. Hg).
Δp = Dry gas meter inlet differential pressure, mm H_2O (in. H_2O).
θ = Run time, min.

16.1.1.5 Compare the three Y_{ds} values at each of the flow rates and determine the maximum and minimum values. The difference between the maximum and minimum values at each flow rate should be no greater than 0.030. Extra sets of triplicate runs may be made in order to complete this requirement. In addition, the meter coefficients should be between 0.95 and 1.05. If these specifications cannot be met in three sets of successive triplicate runs, the meter is not suitable as a calibration standard and should not be used as such. If these specifications are met, average the three Y_{ds} values at each flow rate resulting in no less than five average meter coefficients, Y_{ds}.

16.1.1.6 Prepare a curve of meter coefficient, Y_{ds}, versus flow rate, Q, for the DGM. This curve shall be used as a reference when the meter is used to calibrate other DGMs and to determine whether recalibration is required.

16.1.2 Standard Dry Gas Meter Recalibration.

16.1.2.1 Recalibrate the standard DGM against a wet test meter or spirometer annually or after every 200 hours of operation, whichever comes first. This requirement is valid provided the standard DGM is kept in a laboratory and, if transported, cared for as any other laboratory instrument. Abuse to the standard meter may cause a change in the calibration and will require more frequent recalibrations.

16.1.2.2 As an alternative to full recalibration, a two-point calibration check may be made. Follow the same procedure and equipment arrangement as for a full recalibration, but run the meter at only two flow rates [suggested rates are 14 and 30 liters/min (0.5 and 1.0 cfm)]. Calculate the meter coefficients for these two points, and compare the values with the meter calibration curve. If the two coefficients are within 1.5 percent of the calibration curve values at the same flow rates, the meter need not be recalibrated until the next date for a recalibration check.

16.2 Critical Orifices As Calibration Standards. Critical orifices may be used as calibration standards in place of the wet test meter specified in section 16.1, provided that they are selected, calibrated, and used as follows:

16.2.1 Selection of Critical Orifices.

16.2.1.1 The procedure that follows describes the use of hypodermic needles or stainless steel needle tubings which have been found suitable for use as critical orifices. Other materials and critical orifice designs may be used provided the orifices act as true critical orifices (*i.e.,* a critical vacuum can be obtained, as described in section 16.2.2.2.3). Select five critical orifices that are appropriately sized to cover the range of flow rates between 10 and 34 liters/min (0.35 and 1.2 cfm) or the expected operating range. Two of the critical orifices should bracket the expected operating range. A minimum of three critical orifices will be needed to calibrate a Method 5 DGM; the other two critical

orifices can serve as spares and provide better selection for bracketing the range of operating flow rates. The needle sizes and tubing lengths shown in Table 5–1 in section 18.0 give the approximate flow rates.

16.2.1.2 These needles can be adapted to a Method 5 type sampling train as follows: Insert a serum bottle stopper, 13 by 20 mm sleeve type, into a ½-inch Swagelok (or equivalent) quick connect. Insert the needle into the stopper as shown in Figure 5–9.

16.2.2 Critical Orifice Calibration. The procedure described in this section uses the Method 5 meter box configuration with a DGM as described in section 6.1.1.9 to calibrate the critical orifices. Other schemes may be used, subject to the approval of the Administrator.

16.2.2.1 Calibration of Meter Box. The critical orifices must be calibrated in the same configuration as they will be used (*i.e.*, there should be no connections to the inlet of the orifice).

16.2.2.1.1 Before calibrating the meter box, leak check the system as follows: Fully open the coarse adjust valve, and completely close the by-pass valve. Plug the inlet. Then turn on the pump, and determine whether there is any leakage. The leakage rate shall be zero (*i.e.*, no detectable movement of the DGM dial shall be seen for 1 minute).

16.2.2.1.2 Check also for leakages in that portion of the sampling train between the pump and the orifice meter. See section 8.4.1 for the procedure; make any corrections, if necessary. If leakage is detected, check for cracked gaskets, loose fittings, worn O-rings, etc., and make the necessary repairs.

16.2.2.1.3 After determining that the meter box is leakless, calibrate the meter box according to the procedure given in section 10.3. Make sure that the wet test meter meets the requirements stated in section 16.1.1.1. Check the water level in the wet test meter. Record the DGM calibration factor, Y.

16.2.2.2 Calibration of Critical Orifices. Set up the apparatus as shown in Figure 5–10.

16.2.2.2.1 Allow a warm-up time of 15 minutes. This step is important to equilibrate the temperature conditions through the DGM.

16.2.2.2.2 Leak check the system as in section 16.2.2.1.1. The leakage rate shall be zero.

16.2.2.2.3 Before calibrating the critical orifice, determine its suitability and the appropriate operating vacuum as follows: Turn on the pump, fully open the coarse adjust valve, and adjust the by-pass valve to give a vacuum reading corresponding to about half of atmospheric pressure. Observe the meter box orifice manometer reading, ΔH. Slowly increase the vacuum reading until a stable reading is obtained on the meter box orifice manometer. Record the critical vacuum for each orifice. Orifices that do not reach a critical value shall not be used.

16.2.2.2.4 Obtain the barometric pressure using a barometer as described in section 6.1.2. Record the barometric pressure, P_{bar}, in mm Hg (in. Hg).

16.2.2.2.5 Conduct duplicate runs at a vacuum of 25 to 50 mm Hg (1 to 2 in. Hg) above the critical vacuum. The runs shall be at least 5 minutes each. The DGM volume readings shall be in increments of complete revolutions of the DGM. As a guideline, the times should not differ by more than 3.0 seconds (this includes allowance for changes in the DGM temperatures) to achieve ±0.5 percent in K′ (see Eq. 5–11). Record the information listed in Figure 5–11.

16.2.2.2.6 Calculate K′ using Equation 5–11.

$$K' = \frac{K_1 V_m Y \left(P_{bar} + \frac{\Delta H}{13.6} \right) T_{amb}^{1/2}}{P_{bar} T_m \theta} \qquad \text{Eq. 5-11}$$

Where:

K′ = Critical orifice coefficient,
$[m^3)(°K)^{1/2}]/$
$[(mm\ Hg)(min)]\ \{[(ft^3)(°R)^{1/2})]\ [(in.\ Hg)(min)]$.
T_{amb} = Absolute ambient temperature, °K (°R).

Calculate the arithmetic mean of the K′ values. The individual K' values should not differ by more than ±0.5 percent from the mean value.

16.2.3 Using the Critical Orifices as Calibration Standards.

16.2.3.1 Record the barometric pressure.

16.2.3.2 Calibrate the metering system according to the procedure outlined in section 16.2.2. Record the information listed in Figure 5–12.

16.2.3.3 Calculate the standard volumes of air passed through the DGM and the critical orifices, and calculate the DGM calibration factor, Y, using the equations below:

$$V_{m(std)} = \frac{K_1 V_m \left[P_{bar} + \left(\frac{\Delta H}{13.6} \right) \right]}{T_m} \qquad \text{Eq. 5-12}$$

$$V_{cr(std)} = K' \frac{P_{bar}\theta}{\sqrt{T_{amb}}} \qquad \text{Eq. 5-13}$$

$$Y = \frac{V_{cr\ (std)}}{V_{m(std)}} \qquad \text{Eq. 5-14}$$

Where:

$V_{cr(std)}$ = Volume of gas sample passed through the critical orifice, corrected to standard conditions, dscm (dscf).

K_1 = 0.3858 K/mm Hg for metric units
= 17.64 °R/in. Hg for English units.

16.2.3.4 Average the DGM calibration values for each of the flow rates. The calibration factor, Y, at each of the flow rates should not differ by more than ±2 percent from the average.

16.2.3.5 To determine the need for recalibrating the critical orifices, compare the DGM Y factors obtained from two adjacent orifices each time a DGM is calibrated; for example, when checking orifice 13/2.5, use orifices 12/10.2 and 13/5.1. If any critical orifice yields a DGM Y factor differing by more than 2 percent from the others, recalibrate the critical orifice according to section 16.2.2.

16.3 Alternative Post-Test Metering System Calibration. The following procedure may be used as an alternative to the post-test calibration described in Section 10.3.2. This alternative procedure does not detect leakages between the inlet of the metering system and the dry gas meter. Therefore, two steps must be included to make it an equivalent alternative:

(1) The metering system must pass the post-test leak-check from either the inlet of the sampling train or the inlet of the metering system. Therefore, if the train fails the former leak-check, another leak-check from the inlet of the metering system must be conducted;

(2) The metering system must pass the leak-check of that portion of the train from the pump to the orifice meter as described in Section 8.4.1.

16.3.1 After each test run, do the following:

16.3.1.1 Ensure that the metering system has passed the post-test leak-check. If not, conduct a leak-check of the metering system from its inlet.

16.3.1.2 Conduct the leak-check of that portion of the train from the pump to the orifice meter as described in Section 10.3.1.1.

16.3.1.3 Calculate Y_{qa} for each test run using the following equation:

$$Y_{qa} = \frac{\theta}{V_m} \sqrt{\frac{0.0319 T_m}{\Delta H @ \left(P_{bar} + \frac{\Delta H_{avg}}{13.6} \right)} \left(\frac{29}{M_d} \right)} \left(\sqrt{\Delta H} \right)_{avg} \qquad \text{Eq. 5-15}$$

Where:

Y_{qa} = Dry gas meter calibration check value, dimensionless.

0.0319 = (29.92/528) (0.75)^2 (in. Hg/°R) cfm^2.

$\Delta H@$ = Orifice meter calibration coefficient, in. H_2O.

M_d = Dry molecular weight of stack gas, lb/lb-mole.

29 = Dry molecular weight of air, lb/lb-mole.

16.3.2 After each test run series, do the following:

16.3.2.1 Average the three or more Y_{qa}'s obtained from the test run series and compare this average Y_{qa} with the dry gas meter calibration factor Y. The average Y_{qa} must be within 5 percent of Y.

16.3.2.2 If the average Y_{qa} does not meet the 5 percent criterion, recalibrate the meter

over the full range of orifice settings as detailed in Section 10.3.1. Then follow the procedure in Section 10.3.3.

17.0 References.

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18.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 5–1 FLOR RATES FOR VARIOUS NEEDLE SIZES AND TUBE LENGTHS

Gauge/cm	Flow rate liters/min.	Gauge/cm	Flow rate liters/min.
12/7.6	32.56	14/2.5	19.54
12/10.2	30.02	14/5.1	17.27
13/2.5	25.77	14/7.6	16.14
13/5.1	23.50	15/3.2	14.16
13/7.6	22.37	15/7.6	11.61
13/10.2	20.67	15/10.2	10.48

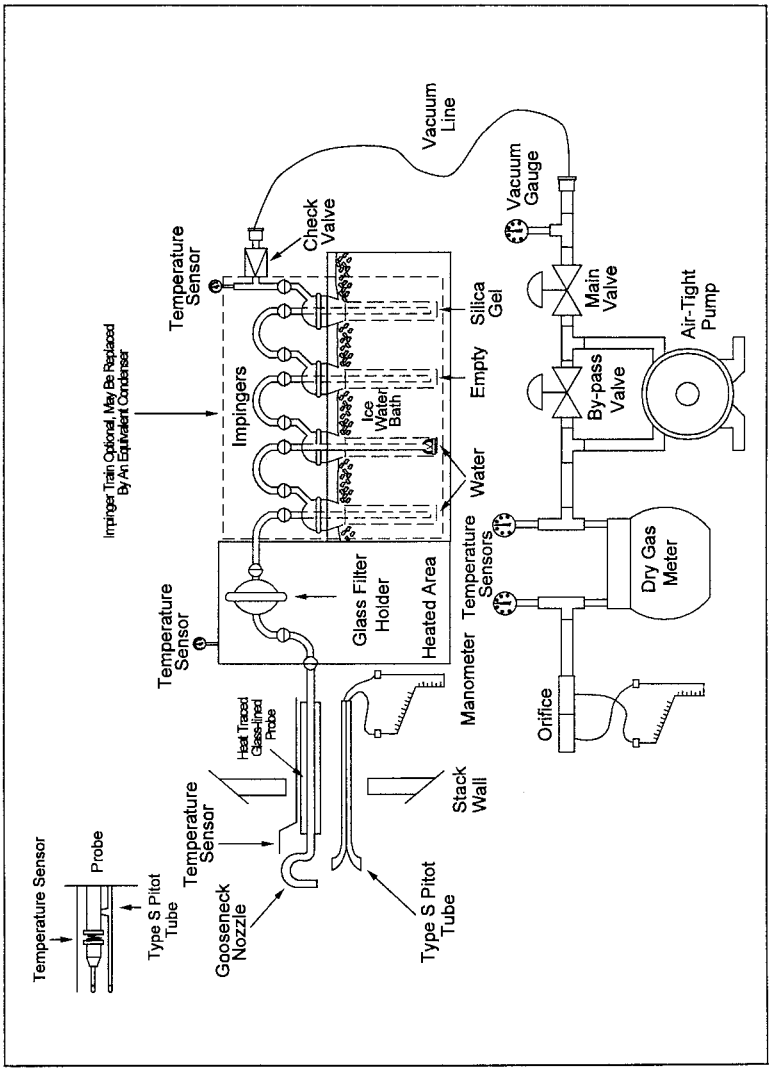


Figure 5-1. Particulate Sampling Train.

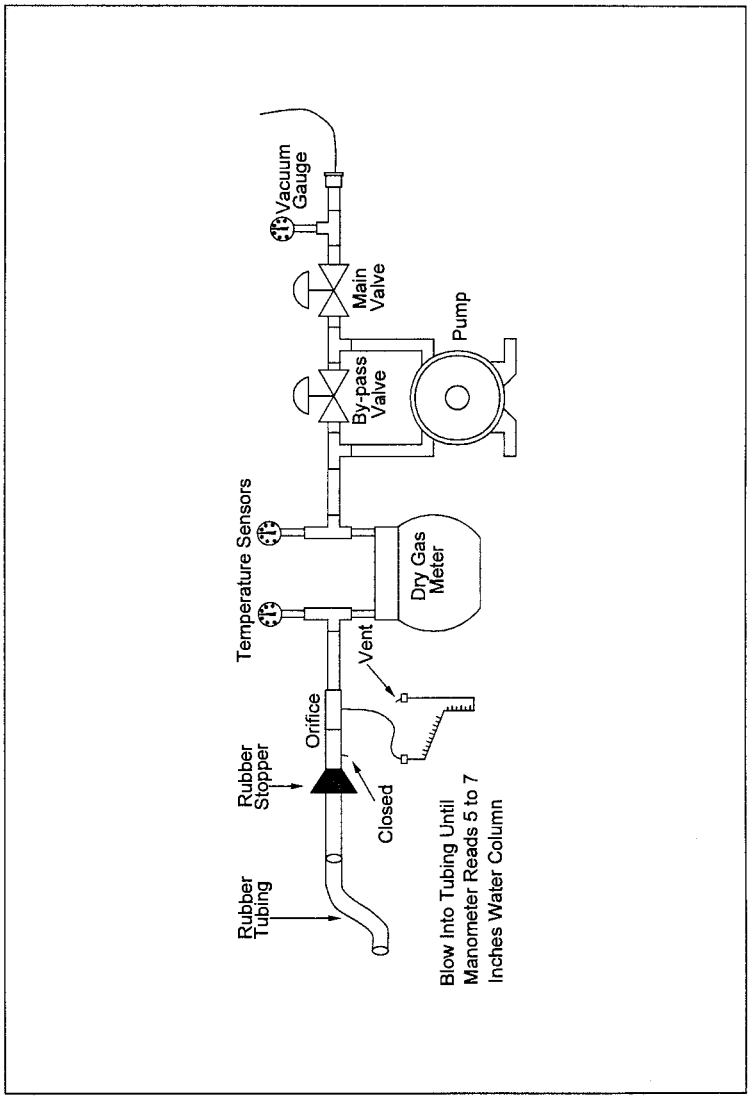


Figure 5-2. Leak Check of Meter Box.

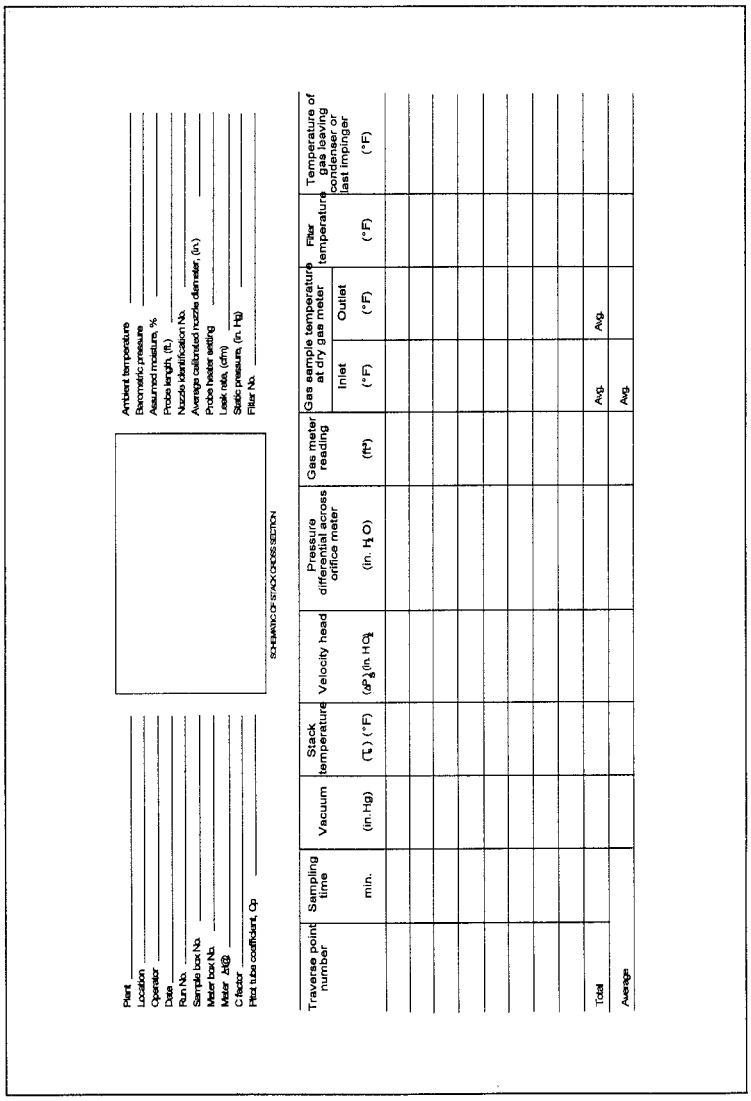


Figure 5-3. Particulate Field Data.

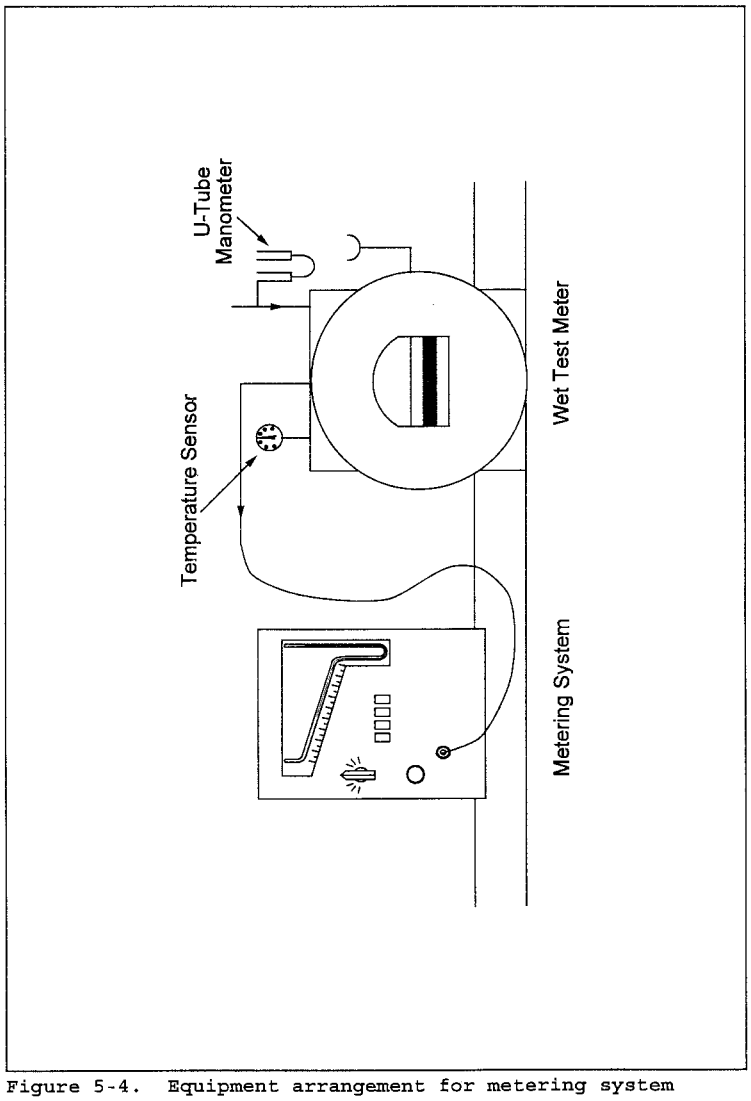
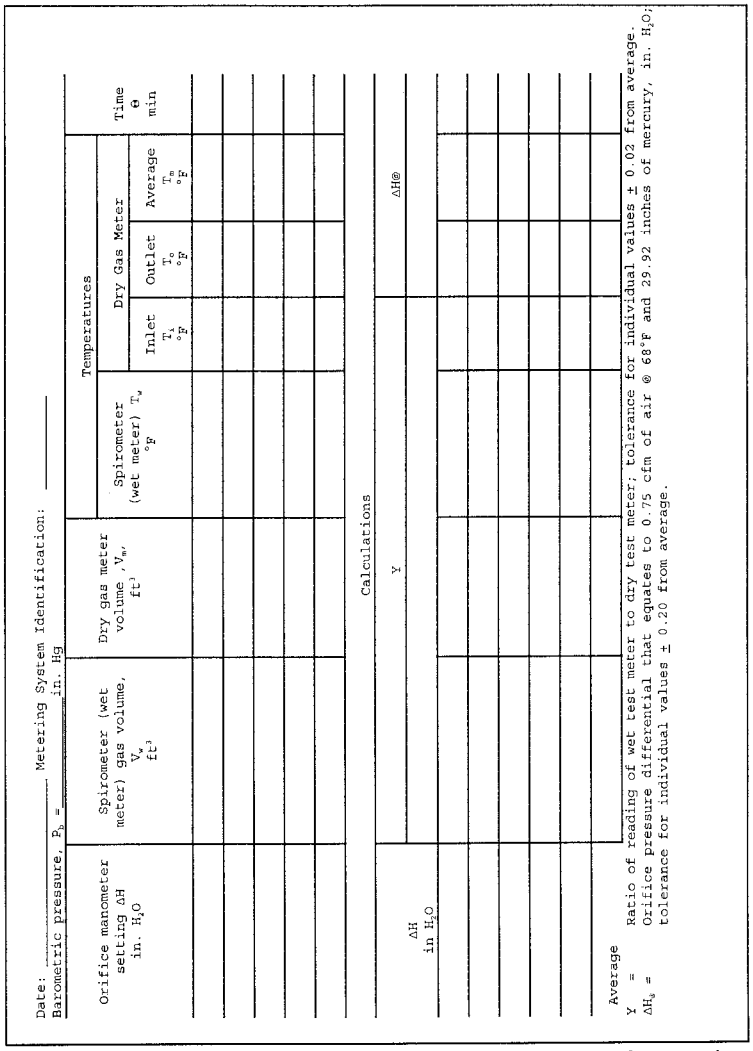


Figure 5-4. Equipment arrangement for metering system calibration.



Date: _____ Metering System Identification: _____
Barometric pressure, P_b = _____ in. Hg

Orifice manometer setting ΔH in. H_2O	Spirometer (wet meter) gas volume, V_w, ft^3	Dry gas meter volume, V_m, ft^3	Temperatures: Spirometer (wet meter) T_w °F	Temperatures: Dry Gas Meter Inlet T_i °F	Temperatures: Dry Gas Meter Outlet T_o °F	Temperatures: Dry Gas Meter Average T_m °F	Time θ min
Average							

Calculations

ΔH in H_2O	Y	ΔH@

Y = Ratio of reading of wet test meter to dry test meter; tolerance for individual values ± 0.02 from average.
$\Delta H_@$ = Orifice pressure differential that equates to 0.75 cfm of air @ 68°F and 29.92 inches of mercury, in. H_2O; tolerance for individual values ± 0.20 from average.

Figure 5-5. Example Data Sheet for Calibration of Metering System (English Units).

Plant _____
Date _____
Run No. _____
Filter No. _____
Amount liquid lost during transport _____

Acetone blank volume, m1 _____
Acetone blank concentration, mg/mg (Equation 5–4) _____
Acetone wash blank, mg (Equation 5–5) ____

Container number	Weight of particulate collected, mg		
	Final weight	Tare weight	Weight gain
1.			
2.			
Total: Less acetone blank. Weight of particulate matter.			

	Volume of liquid water collected	
	Impinger volume, ml	Silica gel weight, g
Final Initial Liquid collected Total volume collected	.....	g* ml

*Convert weight of water to volume by dividing total weight increase by density of water (1 g/ml).

Figure 5–6. Analytical Data Sheet

$$\frac{\text{Increase, g}}{(1\text{g/ml})} = \text{Volume water, ml}$$

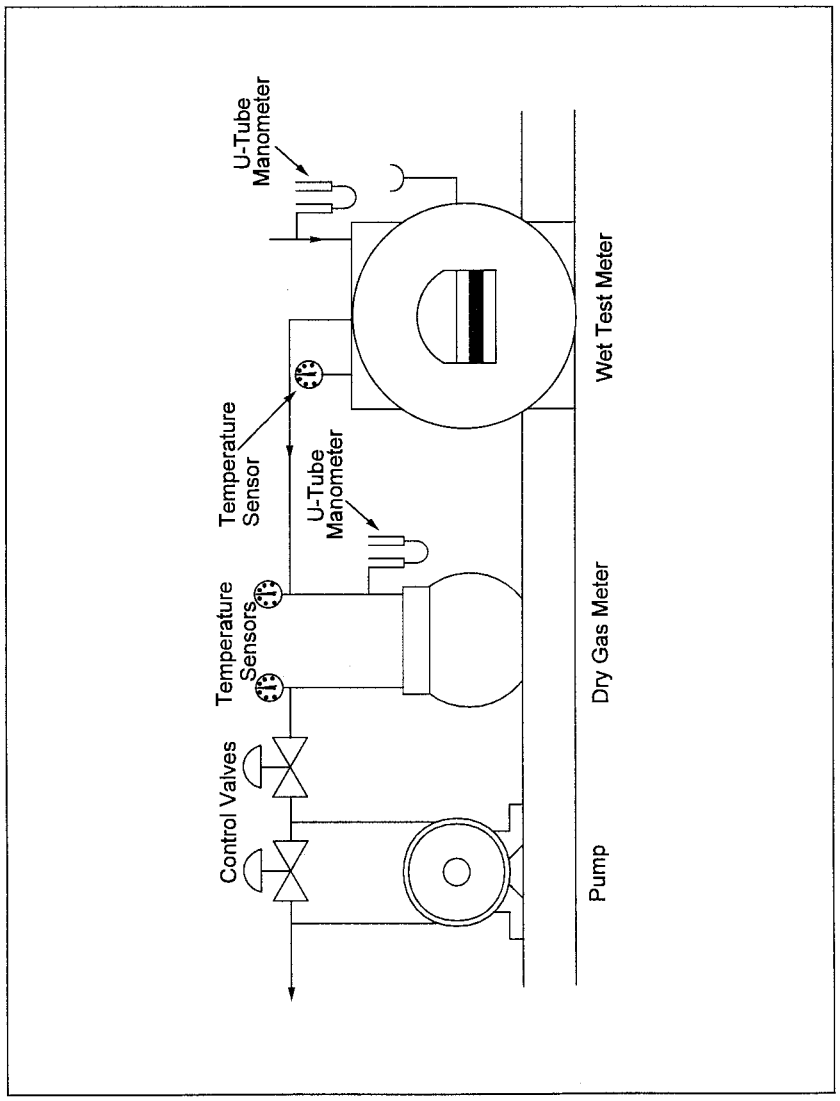


Figure 5-7. Equipment Arrangement for Dry Gas Meter Calibration.

Date: _____

Dry Gas Meter Identification: _____

Barometric Pressure (P): _____ in. Hg

Approximate Flow Rate (Q) cfm	Spirometer (Wet Meter) Gas Volume (V_s) ft³	Dry Gas Meter Volume (V_{dg}) ft³	Temperatures: Spirometer (Wet Meter) (t_g) °F	Temperatures: Dry Gas Meter Inlet (t_i) °F	Temperatures: Dry Gas Meter Outlet (t_o) °F	Temperatures: Dry Gas Meter Average (t_d) °F	Dry Gas Meter Pressure (Δp) in. H_2O	Time (θ) ft³	Flow Rate (Q) cfm	Meter Coefficient (Y_{ds})	Average Meter Coefficient ($\overline{Y}_{ds}$)
0.40											
0.60											
0.80											
1.00											
1.20											

$$Q = K_1 \frac{P_{bar} V_w}{(T_w + T_{std} Q)} \qquad Y_{ds} = \frac{V_w (T_{ds} + T_{std}) P_{bar}}{V_{ds} (T_w + T_{std}) (P_{bar} + \Delta P/13.6)}$$

Figure 5-8. Example Data Sheet for Calibration of a Standard Dry Gas Meter for Method 5 Sampling Equipment (English units).

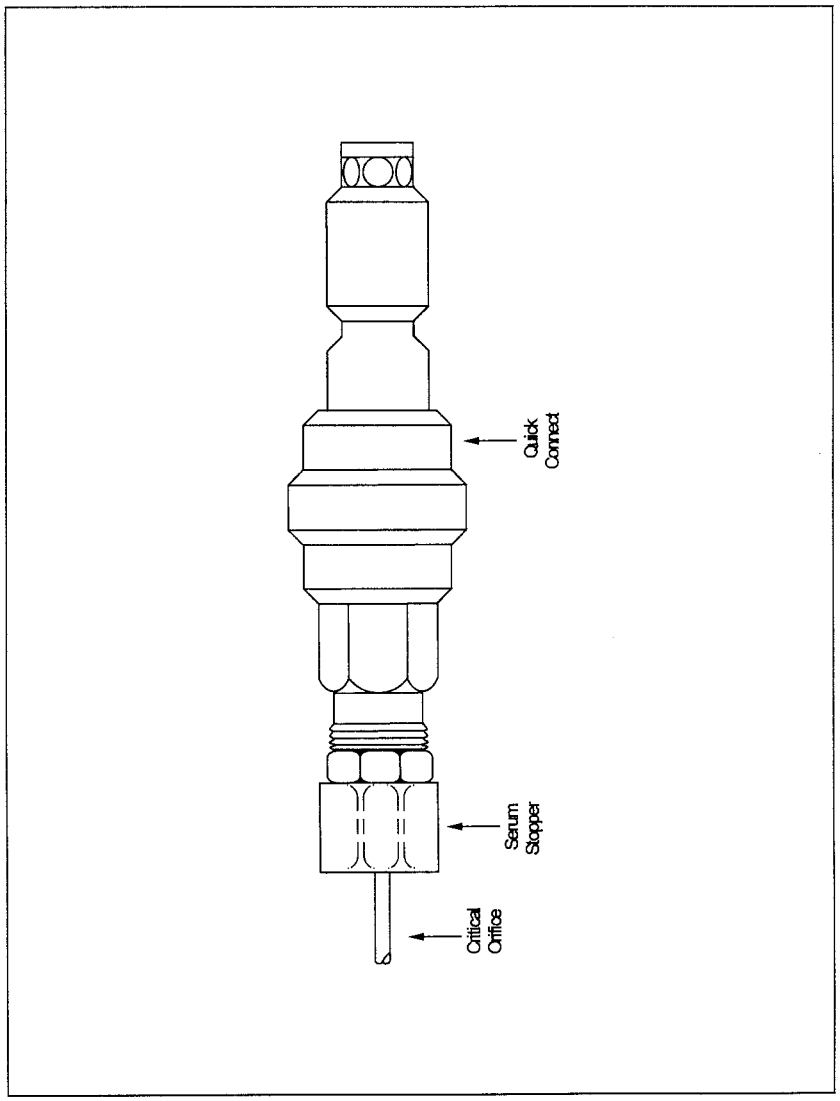


Figure 5-9. Critical Orifice Adaptation to Method 5 Metering System.

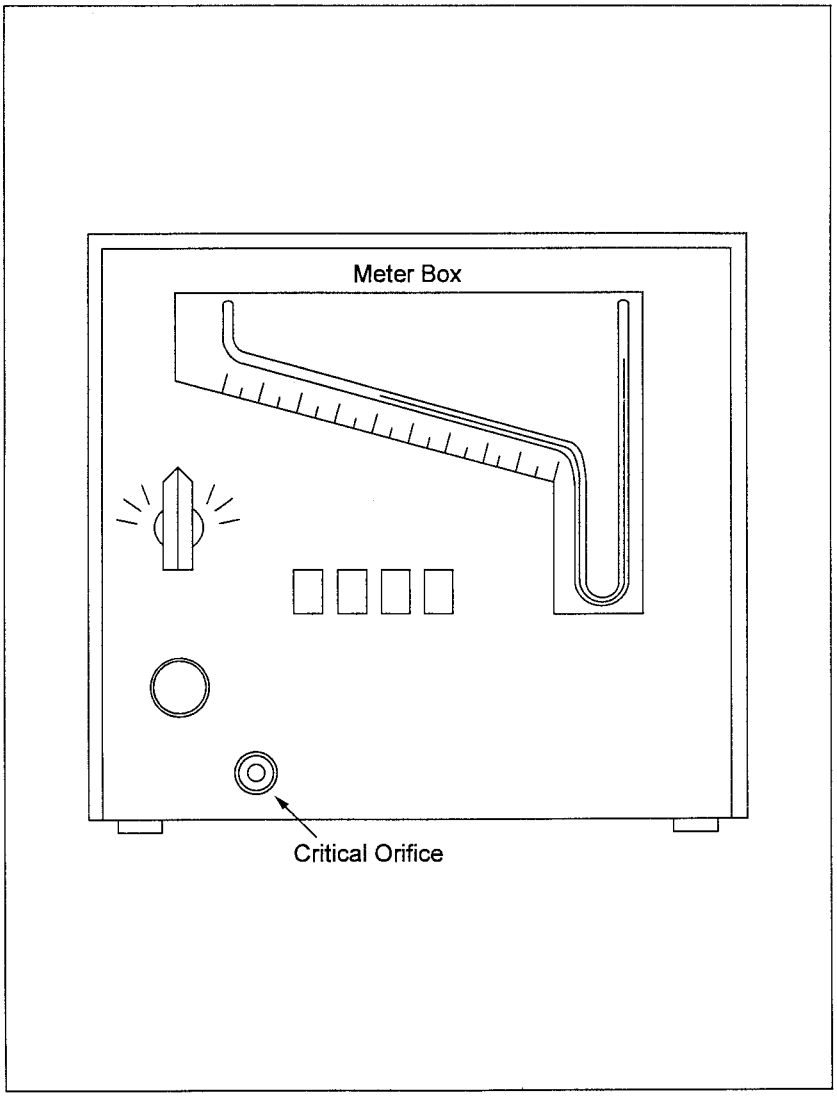


Figure 5-10. Apparatus Setup.

Date _____ DGM cal. factor _____
Train ID _____ Critical orifice ID _____

Dry gas meter		Run No.	
		1	2
Final reading	m^3 (ft^3)		
Initial reading	m^3 (ft^3)		
Difference, V_m	m^3 (ft^3)		
Inlet/Outlet			

Dry gas meter		Run No.	
		1	2
Temperatures:	°C (°F)	/	/
Initial	°C (°F)	/	/
Final	min/sec	/	/
Av. Temeperature, t_m	min		
Time, θ			
Orifice man. rdg., ΔH	mm (in.) H_2		
Bar. pressure, P^{bar}	mm (in.) Hg		
Ambient temperature, t_{amb}	mm (in.) Hg		
Pump vacuum			
K′ factor			
Average			

Figure 5–11. Data sheet of determining K′ factor.

Train ID _____
Critical orifice ID _____
Critical orifice K' factor _____

Date _____

Dry gas meter		Run No.	
		1	2
Final reading	m^3 (ft^3)		
Initial reading	m^3 (ft^3)		
Difference, V_m	m^3 (ft^3)		
Inlet/outlet temperatures	°C (°F)	/	/
Initial	°C (°F)	/	/
Final	°C (°F)		
Avg. Temperature, t_m	min/sec	/	/
Time, θ	min		
Orifice man. rdg., ΔH	min		
Bar. pressure, P_{bar}	mm (in.) H_2O		
Ambient temperature, t_{amb}	mm (in.) Hg		
Pump vacuum	°C (°F)		
$V_{m(std)}$	mm (in.) Hg		
$V_{cr(std)}$	m^3 (ft^3)		
DGM cal. factor, Y	m^3 (ft^3)		

Figure 5–12. Data Sheet for Determining DGM Y Factor

METHOD 5A—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM THE ASPHALT PROCESSING AND ASPHALT ROOFING INDUSTRY

NOTE: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5.

1.0 Scope and Applications

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of PM emissions from asphalt roofing industry process saturators, blowing stills, and other sources as specified in the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature of 42 ±10 °C (108 ±18 °F). The PM mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after the removal of uncombined water.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the

applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 5, section 6.1, with the following exceptions and additions:

6.1.1 Probe Liner. Same as Method 5, section 6.1.1.2, with the note that at high stack gas temperatures greater than 250 °C (480 °F), water-cooled probes may be required to control the probe exit temperature to 42 ±10 °C (108 ±18 °F).

6.1.2 Precollector Cyclone. Borosilicate glass following the construction details shown in Air Pollution Technical Document (APTD)–0581, ''Construction Details of Isokinetic Source-Sampling Equipment'' (Reference 2 in Method 5, section 17.0).

NOTE: The cyclone shall be used when the stack gas moisture is greater than 10 percent, and shall not be used otherwise.

6.1.3 Filter Heating System. Any heating (or cooling) system capable of maintaining a sample gas temperature at the exit end of the filter holder during sampling at 42 ±10 °C (108 ±18 °F).

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Probe-Liner and Probe-Nozzle Brushes, Graduated Cylinder and/or Balance, Plastic Storage Containers, and Funnel and Rubber Policeman. Same as in Method 5, sections 6.2.1, 6.2.5, 6.2.6, and 6.2.7, respectively.

6.2.2 Wash Bottles. Glass.

6.2.3 Sample Storage Containers. Chemically resistant 500-ml or 1,000-ml borosilicate glass bottles, with rubber-backed Teflon screw cap liners or caps that are constructed so as to be leak-free, and resistant to chemical attack by 1,1,1-trichloroethane (TCE). (Narrow-mouth glass bottles have been found to be less prone to leakage.)

6.2.4 Petri Dishes. Glass, unless otherwise specified by the Administrator.

6.2.5 Funnel. Glass.

6.3 Sample Analysis. Same as Method 5, section 6.3, with the following additions:

6.3.1 Beakers. Glass, 250-ml and 500-ml.

6.3.2 Separatory Funnel. 100-ml or greater.

7.0. Reagents and Standards

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Filters, Silica Gel, Water, and Crushed Ice. Same as in Method 5, sections 7.1.1, 7.1.2, 7.1.3, and 7.1.4, respectively.

7.1.2 Stopcock Grease. TCE-insoluble, heat-stable grease (if needed). This is not necessary if screw-on connectors with Teflon sleeves, or similar, are used.

7.2 Sample Recovery. Reagent grade TCE, ≤0.001 percent residue and stored in glass bottles. Run TCE blanks before field use, and use only TCE with low blank values (≤0.001 percent). In no case shall a blank value of greater than 0.001 percent of the weight of TCE used be subtracted from the sample weight.

7.3 Analysis. Two reagents are required for the analysis:

7.3.1 TCE. Same as in section 7.2.

7.3.2 Desiccant. Same as in Method 5, section 7.3.2.

8.0. Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation. Unless otherwise specified, maintain and calibrate all components according to the procedure described in APTD–0576, ''Maintenance, Calibration, and Operation of Isokinetic Source-Sampling Equipment'' (Reference 3 in Method 5, Section 17.0). Alternative mercury-free thermometers may be used if the thermometers are, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

8.1.1 Prepare probe liners and sampling nozzles as needed for use. Thoroughly clean each component with soap and water followed by a minimum of three TCE rinses. Use the probe and nozzle brushes during at least one of the TCE rinses (refer to section 8.7 for rinsing techniques). Cap or seal the open ends of the probe liners and nozzles to prevent contamination during shipping.

8.1.2 Prepare silica gel portions and glass filters as specified in Method 5, section 8.1.

8.2 Preliminary Determinations. Select the sampling site, probe nozzle, and probe length as specified in Method 5, section 8.2. Select a total sampling time greater than or equal to the minimum total sampling time specified in the ''Test Methods and Procedures'' section of the applicable subpart of the regulations. Follow the guidelines outlined in Method 5, section 8.2 for sampling time per point and total sample volume collected.

8.3 Preparation of Sampling Train. Prepare the sampling train as specified in Method 5, section 8.3, with the addition of the precollector cyclone, if used, between the probe and filter holder. The temperature of the precollector cyclone, if used, should be maintained in the same range as that of the filter, *i.e.*, 42 ±10 °C (108 ±18 °F). Use no stopcock grease on ground glass joints unless grease is insoluble in TCE.

8.4 Leak-Check Procedures. Same as Method 5, section 8.4.

8.5 Sampling Train Operation. Operate the sampling train as described in Method 5, section 8.5, except maintain the temperature of the gas exiting the filter holder at 42 ±10 °C (108 ±18 °F).

8.6 Calculation of Percent Isokinetic. Same as Method 5, section 8.6.

8.7 Sample Recovery. Same as Method 5, section 8.7.1 through 8.7.6.1, with the addition of the following:

8.7.1 Container No. 2 (Probe to Filter Holder).

8.7.1.1 Taking care to see that material on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover PM or any condensate from the probe nozzle, probe fitting, probe liner, precollector cyclone and collector flask (if used), and front half of the filter holder by washing these components with TCE and placing the wash in a glass container. Carefully measure the total amount of TCE used in the rinses. Perform the TCE rinses as described in Method 5, section 8.7.6.2, using TCE instead of acetone.

8.7.1.2 Brush and rinse the inside of the cyclone, cyclone collection flask, and the front half of the filter holder. Brush and rinse each surface three times or more, if necessary, to remove visible PM.

8.7.2 Container No. 3 (Silica Gel). Same as in Method 5, section 8.7.6.3.

8.7.3 Impinger Water. Same as Method 5, section 8.7.6.4.

8.8 Blank. Save a portion of the TCE used for cleanup as a blank. Take 200 ml of this TCE directly from the wash bottle being used, and place it in a glass sample container labeled ''TCE Blank.''

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4, 10.0	Sampling equipment leak check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.

9.2 A quality control (QC) check of the volume metering system at the field site is suggested before collecting the sample. Use the procedure outlined in Method 5, section 9.2.

10.0 Calibration and Standardization

Same as Method 5, section 10.0.

11.0 Analytical Procedures

11.1 Analysis. Record the data required on a sheet such as the one shown in Figure 5A–1. Handle each sample container as follows:

11.1.1 Container No. 1 (Filter). Transfer the filter from the sample container to a tared glass weighing dish, and desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Rinse Container No. 1 with a measured amount of TCE, and analyze this rinse with the contents of Container No. 2. Weigh the filter to a constant weight. For the purpose of this analysis, the term ''constant weight'' means a difference of no more than 10 percent of the net filter weight or 2 mg (whichever is greater) between two consecutive weighings made 24 hours apart. Report the ''final weight'' to the nearest 0.1 mg as the average of these two values.

11.1.2 Container No. 2 (Probe to Filter Holder).

11.1.2.1 Before adding the rinse from Container No. 1 to Container No. 2, note the level of liquid in Container No. 2, and confirm on the analysis sheet whether leakage occurred during transport. If noticeable leakage occurred, either void the sample or take steps, subject to the approval of the Administrator, to correct the final results.

11.1.2.2 Add the rinse from Container No. 1 to Container No. 2 and measure the liquid in this container either volumetrically to ±1 ml or gravimetrically to ±0.5 g. Check to see whether there is any appreciable quantity of condensed water present in the TCE rinse (look for a boundary layer or phase separation). If the volume of condensed water appears larger than 5 ml, separate the oil-TCE fraction from the water fraction using a separatory funnel. Measure the volume of the water phase to the nearest ml; adjust the stack gas moisture content, if necessary (see sections 12.3 and 12.4). Next, extract the water phase with several 25-ml portions of TCE until, by visual observation, the TCE does not remove any additional organic material. Transfer the remaining water fraction to a tared beaker and evaporate to dryness at 93 °C (200 °F), desiccate for 24 hours, and weigh to the nearest 0.1 mg.

11.1.2.3 Treat the total TCE fraction (including TCE from the filter container rinse and water phase extractions) as follows: Transfer the TCE and oil to a tared beaker, and evaporate at ambient temperature and pressure. The evaporation of TCE from the solution may take several days. Do not desiccate the sample until the solution reaches an apparent constant volume or until the odor of TCE is not detected. When it appears that the TCE has evaporated, desiccate the sample, and weigh it at 24-hour intervals to obtain a ''constant weight'' (as defined for Container No. 1 above). The ''total weight'' for Container No. 2 is the sum of the evaporated PM weight of the TCE-oil and water phase fractions. Report the results to the nearest 0.1 mg.

11.1.3 Container No. 3 (Silica Gel). This step may be conducted in the field. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance.

11.1.4 ''TCE Blank'' Container. Measure TCE in this container either volumetrically or gravimetrically. Transfer the TCE to a tared 250-ml beaker, and evaporate to dryness at ambient temperature and pressure.

Desiccate for 24 hours, and weigh to a constant weight. Report the results to the nearest 0.1 mg.

NOTE: In order to facilitate the evaporation of TCE liquid samples, these samples may be dried in a controlled temperature oven at temperatures up to 38 °C (100 °F) until the liquid is evaporated.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

12.1 Nomenclature. Same as Method 5, section 12.1, with the following additions:

C_t = TCE blank residue concentration, mg/g.
m_t = Mass of residue of TCE blank after evaporation, mg.
V_{pc} = Volume of water collected in precollector, ml.
V_t = Volume of TCE blank, ml.
V_{tw} = Volume of TCE used in wash, ml.
W_t = Weight of residue in TCE wash, mg.
ρ_t = Density of TCE (see label on bottle), g/ml.

12.2 Dry Gas Meter Temperature, Orifice Pressure Drop, and Dry Gas Volume. Same as Method 5, sections 12.2 and 12.3, except use data obtained in performing this test.

12.3 Volume of Water Vapor.

$$V_{w(std)} = K_2\left(V_{1c} + V_{pc}\right) \qquad \text{Eq. 5A-1}$$

Where:

K_2 = 0.001333 m^3/ml for metric units.
= 0.04706 ft^3/ml for English units.

12.4 Moisture Content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad \text{Eq. 5A-2}$$

NOTE: In saturated or water droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger and precollector analysis (Equations 5A–1 and 5A–2) and a second from the assumption of saturated conditions. The lower of the two values of moisture content shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in section 4.0 of Method 4. For the purpose of this method, the average stack gas temperature from Figure 5–3 of Method 5 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is within 1 °C (2 °F).

12.5 TCE Blank Concentration.

$$C_t = \frac{m_t}{V_t \rho_t} \qquad \text{Eq. 5A-3}$$

NOTE: In no case shall a blank value of greater than 0.001 percent of the weight of TCE used be subtracted from the sample weight.

12.6 TCE Wash Blank.

$$W_t = C_t V_{tw} \rho_t \qquad \text{Eq. 5A-4}$$

12.7 Total PM Weight. Determine the total PM catch from the sum of the weights obtained from Containers 1 and 2, less the TCE blank.

12.8 PM Concentration.

$$c_s = K_3 \frac{m_n}{V_{m(std)}} \qquad \text{Eq. 5A-5}$$

Where:

K_3 = 0.001 g/mg for metric units
= 0.0154 gr/mg for English units

12.9 Isokinetic Variation. Same as in Method 5, section 12.11.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 5, section 17.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

Plant _____
Date _____
Run No. _____
Filter No. _____
Amount liquid lost during transport _____
Acetone blank volume, ml _____
Acetone blank concentration, mg/mg (Equation 5–4) _____
Acetone wash blank, mg (Equation 5–5) _____

Container number	Weight of particulate collected, mg		
	Final weight	Tare weight	Weight gain
1.			
2.			
Total: Less acetone blank.			

Container number	Weight of particulate collected, mg		
	Final weight	Tare weight	Weight gain
Weight of particulate matter.			

	Volume of liquid water collected	
	Impinger volume, ml	Silica gel weight, g
Final		
Initial		
Liquid collected		
Total volume collected		g* ml

*Convert weight of water to volume by dividing total weight increase by density of water (1 g/ml).

$$\frac{\text{Increase, g}}{(1\text{g/ml})} = \text{Volume water, ml}$$

METHOD 5B—DETERMINATION OF NONSULFURIC ACID PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5.

1.0 Scope and Application

1.1 Analyte. Nonsulfuric acid particulate matter. No CAS number assigned.

1.2 Applicability. This method is determining applicable for the determination of nonsulfuric acid particulate matter from stationary sources, only where specified by an applicable subpart of the regulations or where approved by the Administrator for a particular application.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature of 160 ±14 °C (320 ±25 °F). The collected sample is then heated in an oven at 160 °C (320 °F) for 6 hours to volatilize any condensed sulfuric acid that may have been collected, and the nonsulfuric acid particulate mass is determined gravimetrically.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

Same as Method 5, section 6.0, with the following addition and exceptions:

6.1 Sample Collection. The probe liner heating system and filter heating system must be capable of maintaining a sample gas temperature of 160 ±14 °C (320 ±25 °F).

6.2 Sample Preparation. An oven is required for drying the sample.

7.0 Reagents and Standards

Same as Method 5, section 7.0.

8.0 Sample Collection, Preservation, Storage, and Transport.

Same as Method 5, with the exception of the following:

8.1 Initial Filter Tare. Oven dry the filter at 160 ±5 °C (320 ±10 °F) for 2 to 3 hours, cool in a desiccator for 2 hours, and weigh. Desiccate to constant weight to obtain the initial tare weight. Use the applicable specifications and techniques of section 8.1.3 of Method 5 for this determination.

8.2 Probe and Filter Temperatures. Maintain the probe outlet and filter temperatures at 160 ±14 °C (320 ±25 °F).

9.0 Quality Control

Same as Method 5, section 9.0.

10.0 Calibration and Standardization

Same as Method 5, section 10.0.

11.0 Analytical Procedure

Same as Method 5, section 11.0, except replace section

11.2.2 With the following:

11.1 Container No. 2. Note the level of liquid in the container, and confirm on the analysis sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to ±1 ml or gravimetrically to ±0.5 g. Transfer the contents to a tared 250 ml beaker, and evaporate to dryness at ambient temperature and pressure. Then oven dry the probe and filter samples at a temperature of 160 ±5 °C (320 ±10 °F) for 6 hours. Cool in a desiccator for 2 hours, and weigh to constant weight. Report the results to the nearest 0.1 mg.

12.0 Data Analysis and Calculations

Same as in Method 5, section 12.0.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 5, section 17.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 5C [RESERVED]

METHOD 5D—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM POSITIVE PRESSURE FABRIC FILTERS

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, Method 17.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability.

1.2.1 This method is applicable for the determination of PM emissions from positive pressure fabric filters. Emissions are determined in terms of concentration (mg/m^3 or gr/ft^3) and emission rate (kg/hr or lb/hr).

1.2.2 The General Provisions of 40 CFR part 60, §60.8(e), require that the owner or operator of an affected facility shall provide performance testing facilities. Such performance testing facilities include sampling ports, safe sampling platforms, safe access to sampling sites, and utilities for testing. It is intended that affected facilities also provide sampling locations that meet the specification for adequate stack length and minimal flow disturbances as described in Method 1. Provisions for testing are often overlooked factors in designing fabric filters or are extremely costly. The purpose of this procedure is to identify appropriate alternative locations and procedures for sampling the emissions from positive pressure fabric filters. The requirements that the affected facility owner or operator provide adequate access to performance testing facilities remain in effect.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature at or above the exhaust gas temperature up to a nominal 120 °C (248 ±25 °F). The particulate mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after the removal of uncombined water.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

Same as section 6.0 of either Method 5 or Method 17.

7.0 Reagents and Standards

Same as section 7.0 of either Method 5 or Method 17.

8.0 Sample Collection, Preservation, Storage, and Transport

Same section 8.0 of either Method 5 or Method 17, except replace section 8.2.1 of Method 5 with the following:

8.1 Determination of Measurement Site. The configuration of positive pressure fabric filter structures frequently are not amenable

to emission testing according to the requirements of Method 1. Following are several alternatives for determining measurement sites for positive pressure fabric filters.

8.1.1 Stacks Meeting Method 1 Criteria. Use a measurement site as specified in Method 1, section 11.1.

8.1.2 Short Stacks Not Meeting Method 1 Criteria. Use stack extensions and the procedures in Method 1. Alternatively, use flow straightening vanes of the ''egg-crate'' type (see Figure 5D–1). Locate the measurement site downstream of the straightening vanes at a distance equal to or greater than two times the average equivalent diameter of the vane openings and at least one-half of the overall stack diameter upstream of the stack outlet.

8.1.3 Roof Monitor or Monovent. (See Figure 5D–2). For a positive pressure fabric filter equipped with a peaked roof monitor, ridge vent, or other type of monovent, use a measurement site at the base of the monovent. Examples of such locations are shown in Figure 5D–2. The measurement site must be upstream of any exhaust point (*e.g.*, louvered vent).

8.1.4 Compartment Housing. Sample immediately downstream of the filter bags directly above the tops of the bags as shown in the examples in Figure 5D–2. Depending on the housing design, use sampling ports in the housing walls or locate the sampling equipment within the compartment housing.

8.2 Determination of Number and Location of Traverse Points. Locate the traverse points according to Method 1, section 11.3. Because a performance test consists of at least three test runs and because of the varied configurations of positive pressure fabric filters, there are several schemes by which the number of traverse points can be determined and the three test runs can be conducted.

8.2.1 Single Stacks Meeting Method 1 Criteria. Select the number of traverse points according to Method 1. Sample all traverse points for each test run.

8.2.2 Other Single Measurement Sites. For a roof monitor or monovent, single compartment housing, or other stack not meeting Method 1 criteria, use at least 24 traverse points. For example, for a rectangular measurement site, such as a monovent, use a balanced 5×5 traverse point matrix. Sample all traverse points for each test run.

8.2.3 Multiple Measurement Sites. Sampling from two or more stacks or measurement sites may be combined for a test run, provided the following guidelines are met:

8.2.3.1 All measurement sites up to 12 must be sampled. For more than 12 measurement sites, conduct sampling on at least 12 sites or 50 percent of the sites, whichever is greater. The measurement sites sampled should be evenly, or nearly evenly, distributed among the available sites; if not, all sites are to be sampled.

8.2.3.2 The same number of measurement sites must be sampled for each test run.

8.2.3.3 The minimum number of traverse points per test run is 24. An exception to the 24-point minimum would be a test combining the sampling from two stacks meeting Method 1 criteria for acceptable stack length, and Method 1 specifies fewer than 12 points per site.

8.2.3.4 As long as the 24 traverse points per test run criterion is met, the number of traverse points per measurement site may be reduced to eight.

8.2.3.5 Alternatively, conduct a test run for each measurement site individually using the criteria in section 8.2.1 or 8.2.2 to determine the number of traverse points. Each test run shall count toward the total of three required for a performance test. If more than three measurement sites are sampled, the number of traverse points per measurement site may be reduced to eight as long as at least 72 traverse points are sampled for all the tests.

8.2.3.6 The following examples demonstrate the procedures for sampling multiple measurement sites.

8.2.3.6.1 Example 1: A source with nine circular measurement sites of equal areas may be tested as follows: For each test run, traverse three measurement sites using four points per diameter (eight points per measurement site). In this manner, test run number 1 will include sampling from sites 1,2, and 3; run 2 will include samples from sites 4, 5, and 6; and run 3 will include sites 7, 8, and 9. Each test area may consist of a separate test of each measurement site using eight points. Use the results from all nine tests in determining the emission average.

8.2.3.6.2 Example 2: A source with 30 rectangular measurement sites of equal areas may be tested as follows: For each of the three test runs, traverse five measurement sites using a 3×3 matrix of traverse points for each site. In order to distribute the sampling evenly over all the available measurement sites while sampling only 50 percent of the sites, number the sites consecutively from 1 to 30 and sample all the even numbered (or odd numbered) sites. Alternatively, conduct a separate test of each of 15 measurement sites using section 8.2.1 or 8.2.2 to determine the number and location of traverse points, as appropriate.

8.2.3.6.3 Example 3: A source with two measurement sites of equal areas may be tested as follows: For each test of three test runs, traverse both measurement sites, using section 8.2.3 in determining the number of traverse points. Alternatively, conduct two full emission test runs for each measurement site using the criteria in section 8.2.1 or 8.2.2 to determine the number of traverse points.

8.2.3.7 Other test schemes, such as random determination of traverse points for a large number of measurement sites, may be used with prior approval from the Administrator.

8.3 Velocity Determination.

8.3.1 The velocities of exhaust gases from positive pressure baghouses are often too low to measure accurately with the type S pitot tube specified in Method 2 (*i.e.*, velocity head <1.3 mm H_2O (0.05 in. H_2O)). For these conditions, measure the gas flow rate at the fabric filter inlet following the procedures outlined in Method 2. Calculate the average gas velocity at the measurement site as shown in section 12.2 and use this average velocity in determining and maintaining isokinetic sampling rates.

8.3.2 Velocity determinations to determine and maintain isokinetic rates at measurement sites with gas velocities within the range measurable with the type S pitot tube (*i.e.*, velocity head greater than 1.3 mm H_2O (0.05 in. H_2O)) shall be conducted according to the procedures outlined in Method 2.

8.4 Sampling. Follow the procedures specified in sections 8.1 through 8.6 of Method 5 or sections 8.1 through 8.25 in Method 17 with the exceptions as noted above.

8.5 Sample Recovery. Follow the procedures specified in section 8.7 of Method 5 or section 8.2 of Method 17.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.0, 10.0	Sampling equipment leak check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

Same as section 10.0 of either Method 5 or Method 17.

11.0 Analytical Procedure

Same as section 11.0 of either Method 5 or Method 17.

12.0 Data Analysis and Calculations

Same as section 12.0 of either Method 5 or Method 17 with the following exceptions:

12.1 Nomenclature.

A_o = Measurement site(s) total cross-sectional area, m^2 (ft^2).

$\bar{C}$ or C_{avg} = Average concentration of PM for all n runs, mg/scm (gr/scf).

Q_i = Inlet gas volume flow rate, m^3/sec (ft^3/sec).

m_i = Mass collected for run i of n, mg (gr).

T_o = Average temperature of gas at measurement site, °K (°R).

T_i = Average temperature of gas at inlet, °K (°R).

Vol_i = Sample volume collected for run i of n, scm (scf).

$\bar{v}$ = Average gas velocity at the measurement site(s), m/s (ft/s)

Q_o = Total baghouse exhaust volumetric flow rate, m^3/sec (ft^3/sec).

Q_d = Dilution air flow rate, m^3/sec (ft^3/sec).

Tamb = Ambient Temperature, (°K).

12.2 Average Gas Velocity. When following section 8.3.1, calculate the average gas velocity at the measurement site as follows:

$$\bar{v} = \frac{Q_o}{A_o} \qquad \text{Eq. 5D-1}$$

12.3 Volumetric Flow Rate. Total volumetric flow rate may be determined as follows:

$$Q_o = Q_i + Q_d \qquad \text{Eq. 5D-2}$$

12.4 Dilution Air Flow Rate.

$$Q_d = \frac{Q_i\left(T_i - T_o\right)}{T_o - T_{amb}} \qquad \text{Eq. 5D-3}$$

12.5 Average PM Concentration. For multiple measurement sites, calculate the average PM concentration as follows:

$$C_{avg} \text{ or } \overline{C} = \frac{\sum_{i=1}^{n} m_i}{\sum_{i=1}^{n} Vol_i} \qquad \text{Eq. 5D-4}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 5, section 17.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

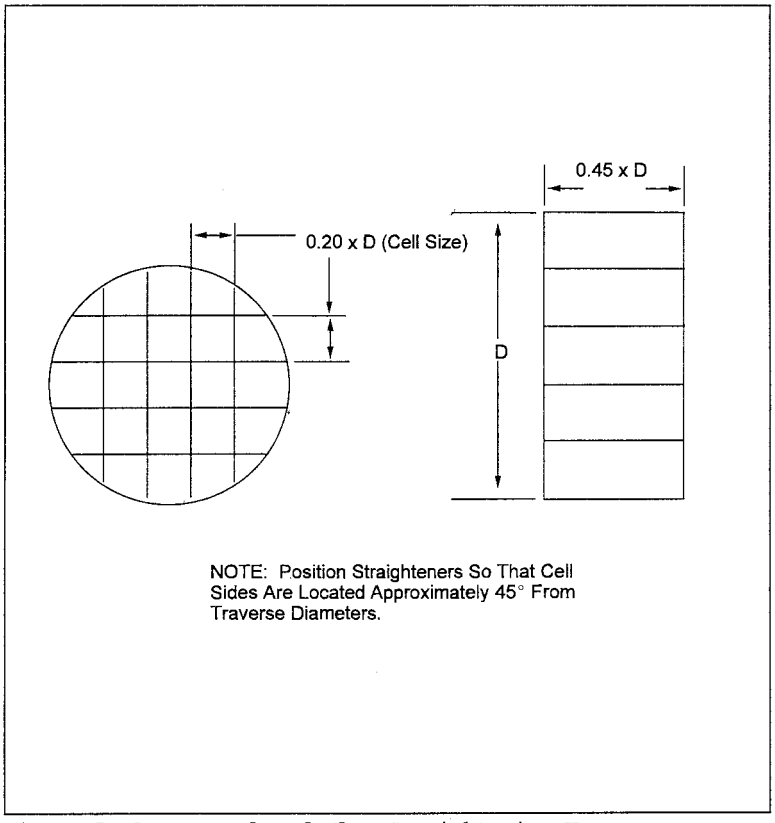


Figure 5D-1. Example of Flow Straightening Vanes.

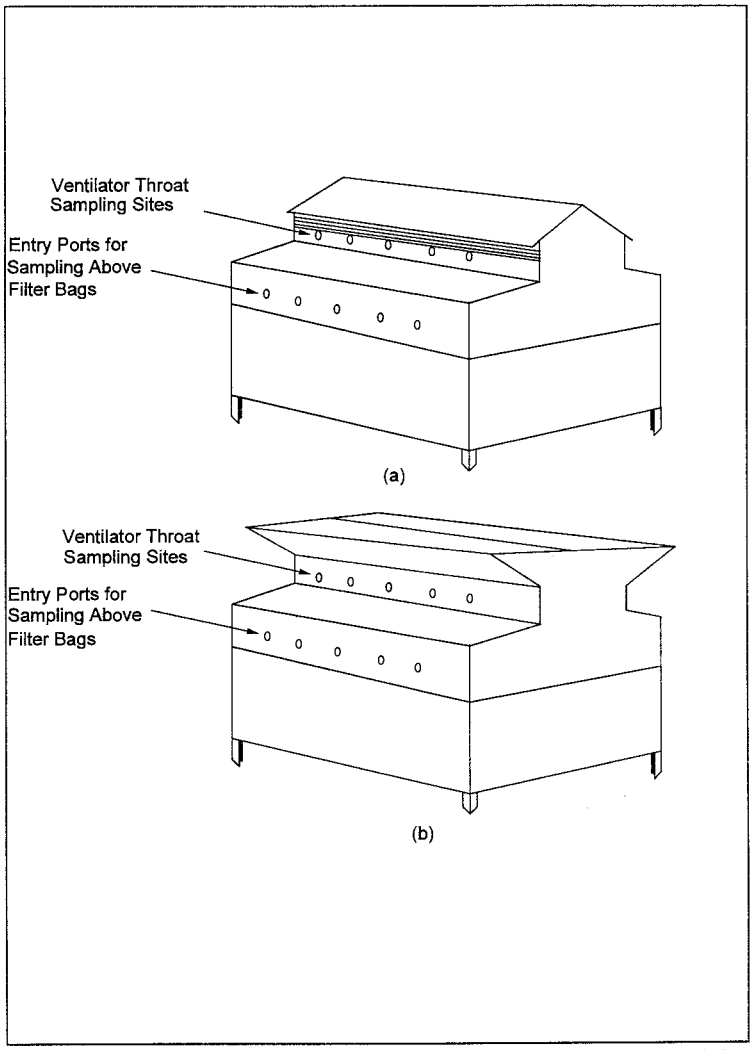


Figure 5D-2. Acceptable Sampling Site Locations for: (a) Peaked Roof; and (b) Ridge Vent Type Fabric Filters

METHOD 5E—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM THE WOOL FIBERGLASS INSULATION MANUFACTURING INDUSTRY

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5.

1.0 Scope and Applications

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of PM emissions from wool fiberglass insulation manufacturing sources.

2.0 Summary of Method

Particulate matter is withdrawn isokinetically from the source and is collected either on a glass fiber filter maintained at a temperature in the range of 120 ±14 °C (248 ±25 °F) and in impingers in solutions of 0.1 N sodium hydroxide (NaOH). The filtered particulate mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after the removal of uncombined water. The condensed PM collected in the impinger solutions is determined as total organic carbon (TOC) using a nondispersive infrared type of analyzer. The sum of the filtered PM mass and the condensed PM is reported as the total PM mass.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Hydrochloric Acid (HCl). Highly toxic. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent in air can be lethal in minutes. Will react with metals, producing hydrogen.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eye tissues and to skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 5, section 6.1, with the exception of the following:

6.1.1 Probe Liner. Same as described in section 6.1.1.2 of Method 5 except use only borosilicate or quartz glass liners.

6.1.2 Filter Holder. Same as described in section 6.1.1.5 of Method 5 with the addition of a leak-tight connection in the rear half of the filter holder designed for insertion of a temperature sensor used for measuring the sample gas exit temperature.

6.2 Sample Recovery. Same as Method 5, section 6.2, except three wash bottles are needed instead of two and only glass storage bottles and funnels may be used.

6.3 Sample Analysis. Same as Method 5, section 6.3, with the additional equipment for TOC analysis as described below:

6.3.1 Sample Blender or Homogenizer. Waring type or ultrasonic.

6.3.2 Magnetic Stirrer.

6.3.3 Hypodermic Syringe. 0- to 100-µl capacity.

6.3.4 Total Organic Carbon Analyzer. Rosemount Model 2100A analyzer or equivalent and a recorder.

6.3.5 Beaker. 30-ml.

6.3.6 Water Bath. Temperature controlled.

6.3.7 Volumetric Flasks. 1000-ml and 500-ml.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 5, section 7.1, with the addition of 0.1 N NaOH (Dissolve 4 g of NaOH in water and dilute to 1 liter).

7.2 Sample Recovery. Same as Method 5, section 7.2, with the addition of the following:

7.2.1 Water. Deionized distilled to conform to ASTM Specification D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17). The potassium permanganate ($KMnO_4$) test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.2.2 Sodium Hydroxide. Same as described in section 7.1.

7.3 Sample Analysis. Same as Method 5, section 7.3, with the addition of the following:

7.3.1 Carbon Dioxide-Free Water. Distilled or deionized water that has been freshly boiled for 15 minutes and cooled to room temperature while preventing exposure to ambient air by using a cover vented with an Ascarite tube.

7.3.2 Hydrochloric Acid. HCl, concentrated, with a dropper.

7.3.3 Organic Carbon Stock Solution. Dissolve 2.1254 g of dried potassium biphthalate ($HOOCC_6H_4COOK$) in CO_2-free water, and dilute to 1 liter in a volumetric flask. This solution contains 1000 mg/L organic carbon.

7.3.4 Inorganic Carbon Stock Solution. Dissolve 4.404 g anhydrous sodium carbonate

(Na_2CO_3.) in about 500 ml of CO_2-free water in a 1-liter volumetric flask. Add 3.497 g anhydrous sodium bicarbonate ($NaHCO_3$) to the flask, and dilute to 1 liter with CO_2 -free water. This solution contains 1000 mg/L inorganic carbon.

7.3.5 Oxygen Gas. CO_2 -free.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation and Preliminary Determinations. Same as Method 5, sections 8.1 and 8.2, respectively.

8.2 Preparation of Sampling Train. Same as Method 5, section 8.3, except that 0.1 N NaOH is used in place of water in the impingers. The volumes of the solutions are the same as in Method 5.

8.3 Leak-Check Procedures, Sampling Train Operation, Calculation of Percent Isokinetic. Same as Method 5, sections 8.4 through 8.6, respectively.

8.4 Sample Recovery. Same as Method 5, sections 8.7.1 through 8.7.4, with the addition of the following:

8.4.1 Save portions of the water, acetone, and 0.1 N NaOH used for cleanup as blanks. Take 200 ml of each liquid directly from the wash bottles being used, and place in glass sample containers labeled ''water blank,'' ''acetone blank,'' and ''NaOH blank,'' respectively.

8.4.2 Inspect the train prior to and during disassembly, and note any abnormal conditions. Treat the samples as follows:

8.4.2.1 Container No. 1. Same as Method 5, section 8.7.6.1.

8.4.2.2 Container No. 2. Use water to rinse the sample nozzle, probe, and front half of the filter holder three times in the manner described in section 8.7.6.2 of Method 5 except that no brushing is done. Put all the water wash in one container, seal, and label.

8.4.2.3 Container No. 3. Rinse and brush the sample nozzle, probe, and front half of the filter holder with acetone as described for Container No. 2 in section 8.7.6.2 of Method 5.

8.4.2.4 Container No. 4. Place the contents of the silica gel impinger in its original container as described for Container No. 3 in section 8.7.6.3 of Method 5.

8.4.2.5 Container No. 5. Measure the liquid in the first three impingers and record the volume or weight as described for the Impinger Water in section 8.7.6.4 of Method 5. Do not discard this liquid, but place it in a sample container using a glass funnel to aid in the transfer from the impingers or graduated cylinder (if used) to the sample container. Rinse each impinger thoroughly with 0.1 N NaOH three times, as well as the graduated cylinder (if used) and the funnel, and put these rinsings in the same sample container. Seal the container and label to clearly identify its contents.

8.5 Sample Transport. Whenever possible, containers should be shipped in such a way that they remain upright at all times.

9.0 Quality Control.

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.3, 10.0	Sampling equipment leak-check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.
10.1.2, 11.2.5.3	Repetitive analyses	Ensures precise measurement of total carbon and inorganic carbon concentration of samples, blank, and standards.
10.1.4	TOC analyzer calibration	Ensures linearity of analyzer response to standards.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

Same as Method 5, section 10.0, with the addition of the following procedures for calibrating the total organic carbon analyzer:

10.1 Preparation of Organic Carbon Standard Curve.

10.1.1 Add 10 ml, 20 ml, 30 ml, 40 ml, and 50 ml of the organic carbon stock solution to a series of five 1000-ml volumetric flasks. Add 30 ml, 40 ml, and 50 ml of the same solution to a series of three 500-ml volumetric flasks. Dilute the contents of each flask to the mark using CO_2-free water. These flasks contain 10, 20, 30, 40, 50, 60, 80, and 100 mg/L organic carbon, respectively.

10.1.2 Use a hypodermic syringe to withdraw a 20- to 50-µl aliquot from the 10 mg/L standard solution and inject it into the total carbon port of the analyzer. Measure the peak height. Repeat the injections until three consecutive peaks are obtained within 10 percent of their arithmetic mean. Repeat this procedure for the remaining organic carbon standard solutions.

10.1.3 Calculate the corrected peak height for each standard by deducting the blank correction (see section 11.2.5.3) as follows:

$$\text{Corrected Peak Height} = A - B \qquad \text{Eq. 5E-1}$$

Where:

A = Peak height of standard or sample, mm or other appropriate unit.

B = Peak height of blank, mm or other appropriate unit.

10.1.4 Prepare a linear regression plot of the arithmetic mean of the three consecutive peak heights obtained for each standard solution against the concentration of that solution. Calculate the calibration factor as the inverse of the slope of this curve. If the product of the arithmetic mean peak height for any standard solution and the calibration factor differs from the actual concentration by more than 5 percent, remake and reanalyze that standard.

10.2 Preparation of Inorganic Carbon Standard Curve. Repeat the procedures outlined in sections 10.1.1 through 10.1.4, substituting the inorganic carbon stock solution for the organic carbon stock solution, and the inorganic carbon port of the analyzer for the total carbon port.

11.0 Analytical Procedure

11.1 Record the data required on a sheet such as the one shown in Figure 5–6 of Method 5.

11.2 Handle each sample container as follows:

11.2.1 Container No. 1. Same as Method 5, section 11.2.1, except that the filters must be dried at 20 ±6 °C (68 ±10 °F) and ambient pressure.

11.2.2 Containers No. 2 and No. 3. Same as Method 5, section 11.2.2, except that evaporation of the samples must be at 20 ±6 °C (68 ±10 °F) and ambient pressure.

11.2.3 Container No. 4. Same as Method 5, section 11.2.3.

11.2.4 ''Water Blank'' and ''Acetone Blank'' Containers. Determine the water and acetone blank values following the procedures for the ''Acetone Blank'' container in section 11.2.4 of Method 5. Evaporate the samples at ambient temperature (20 ±6 °C (68 ±10 °F)) and pressure.

11.2.5 Container No. 5. For the determination of total organic carbon, perform two analyses on successive identical samples, *i.e.*, total carbon and inorganic carbon. The desired quantity is the difference between the two values obtained. Both analyses are based on conversion of sample carbon into carbon dioxide for measurement by a nondispersive infrared analyzer. Results of analyses register as peaks on a strip chart recorder.

11.2.5.1 The principal differences between the operating parameters for the two channels involve the combustion tube packing material and temperature. In the total carbon channel, a high temperature (950 °C (1740 °F)) furnace heats a Hastelloy combustion tube packed with cobalt oxide-impregnated asbestos fiber. The oxygen in the carrier gas, the elevated temperature, and the catalytic effect of the packing result in oxidation of both organic and inorganic carbonaceous material to CO_2, and steam. In the inorganic carbon channel, a low temperature (150 °C (300 °F)) furnace heats a glass tube containing quartz chips wetted with 85 percent phosphoric acid. The acid liberates CO_2 and steam from inorganic carbonates. The operating temperature is below that required to oxidize organic matter. Follow the manufacturer's instructions for assembly, testing, calibration, and operation of the analyzer.

11.2.5.2 As samples collected in 0.1 N NaOH often contain a high measure of inorganic carbon that inhibits repeatable determinations of TOC, sample pretreatment is necessary. Measure and record the liquid volume of each sample (or impinger contents). If the sample contains solids or immiscible liquid matter, homogenize the sample with a blender or ultrasonics until satisfactory repeatability is obtained. Transfer a representative portion of 10 to 15 ml to a 30-ml beaker, and acidify with about 2 drops of concentrated HCl to a pH of 2 or less. Warm the acidified sample at 50 °C (120 °F) in a water bath for 15 minutes.

11.2.5.3 While stirring the sample with a magnetic stirrer, use a hypodermic syringe to withdraw a 20-to 50-µl aliquot from the beaker. Analyze the sample for total carbon and calculate its corrected mean peak height according to the procedures outlined in sections 10.1.2 and 10.1.3. Similarly analyze an aliquot of the sample for inorganic carbon. Repeat the analyses for all the samples and for the 0.1 N NaOH blank.

11.2.5.4 Ascertain the total carbon and inorganic carbon concentrations (C_{TC} and C_{IC}, respectively) of each sample and blank by comparing the corrected mean peak heights for each sample and blank to the appropriate standard curve.

NOTE: If samples must be diluted for analysis, apply an appropriate dilution factor.

12.0 Data Analysis and Calculations

Same as Method 5, section 12.0, with the addition of the following:

12.1 Nomenclature.

C_c = Concentration of condensed particulate matter in stack gas, gas dry basis, corrected to standard conditions, g/dscm (gr/dscf).

C_{IC} = Concentration of condensed TOC in the liquid sample, from section 11.2.5, mg/L.

C_t = Total particulate concentration, dry basis, corrected to standard conditions, g/dscm (gr/dscf).
C_{TC} = Concentration of condensed TOC in the liquid sample, from section 11.2.5, mg/L.
C_{TOC} = Concentration of condensed TOC in the liquid sample, mg/L.
m_{TOC} = Mass of condensed TOC collected in the impingers, mg.
$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, from section 12.3 of Method 5, dscm (dscf).
V_s = Total volume of liquid sample, ml.

12.2 Concentration of Condensed TOC in Liquid Sample.

$$C_{TOC} = C_{TC} - C_{IC} \qquad \text{Eq. 5E-2}$$

12.3 Mass of Condensed TOC Collected.

$$m_{TOC} = 0.001\, C_{TOC} V_s \qquad \text{Eq. 5E-3}$$

Where:

0.001 = Liters per milliliter.

12.4 Concentration of Condensed Particulate Material.

$$C_c = K_4 m_{TOC} / V_{m(std)} \qquad \text{Eq. 5E-4}$$

Where:

K_4 = 0.001 g/mg for metric units.
= 0.0154 gr/mg for English units.

12.5 Total Particulate Concentration.

$$C_t = C_s + C_c \qquad \text{Eq. 5E-4}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Total Organic Carbon Analyzer. Tekmar-Dohrmann analyzers using the single injection technique may be used as an alternative to Rosemount Model 2100A analyzers.

17.0 References.

Same as section 17.0 of Method 5, with the addition of the following:

1. American Public Health Association, American Water Works Association, Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater. Fifteenth Edition. Washington, D.C. 1980.

18.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

Method 5F—Determination of Nonsulfate Particulate Matter Emissions From Stationary Sources

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5.

1.0 Scope and Applications

1.1 Analyte. Nonsulfate particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of nonsulfate PM emissions from stationary sources. Use of this method must be specified by an applicable subpart of the standards, or approved by the Administrator for a particular application.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

Particulate matter is withdrawn isokinetically from the source and collected on a filter maintained at a temperature in the range 160 ±14 °C (320 ±25 °F). The collected sample is extracted with water. A portion of the extract is analyzed for sulfate content by ion chromatography. The remainder is neutralized with ammonium hydroxide (NH_4OH), dried, and weighed. The weight of sulfate in the sample is calculated as ammonium sulfate ($(NH_4)_2SO_4$), and is subtracted from the total particulate weight; the result is reported as nonsulfate particulate matter.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection and Recovery. Same as Method 5, sections 6.1 and 6.2, respectively.

6.2 Sample Analysis. Same as Method 5, section 6.3, with the addition of the following:

6.2.1 Erlenmeyer Flasks. 125-ml, with ground glass joints.

6.2.2 Air Condenser. With ground glass joint compatible with the Erlenmeyer flasks.

6.2.3 Beakers. 600-ml.

6.2.4 Volumetric Flasks. 1-liter, 500-ml (one for each sample), 200-ml, and 50-ml (one for each sample and standard).

6.2.5 Pipet. 5-ml (one for each sample and standard).

6.2.6 Ion Chromatograph. The ion chromatograph should have at least the following components.

6.2.6.1 Columns. An anion separation column or other column capable of resolving the sulfate ion from other species present and a standard anion suppressor column. Suppressor columns are produced as proprietary items; however, one can be produced in the laboratory using the resin available from BioRad Company, 32nd and Griffin Streets, Richmond, California. Other systems which do not use suppressor columns may also be used.

6.2.6.2 Pump. Capable of maintaining a steady flow as required by the system.

6.2.6.3 Flow Gauges. Capable of measuring the specified system flow rate.

6.2.6.4 Conductivity Detector.

6.2.6.5 Recorder. Compatible with the output voltage range of the detector.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 5, section 7.1.

7.2 Sample Recovery. Same as Method 5, section 7.2, with the addition of the following:

7.2.1 Water. Deionized distilled, to conform to ASTM D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17). The potassium permanganate ($KMnO_4$) test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.3 Analysis. Same as Method 5, section 7.3, with the addition of the following:

7.3.1 Water. Same as in section 7.2.1.

7.3.2 Stock Standard Solution, 1 mg $(NH_4)_2SO_4$/ml. Dry an adequate amount of primary standard grade ammonium sulfate ($(NH_4)_2SO_4$) at 105 to 110 °C (220 to 230 °F) for a minimum of 2 hours before preparing the standard solution. Then dissolve exactly 1.000 g of dried $(NH_4)_2SO_4$ in water in a 1-liter volumetric flask, and dilute to 1 liter. Mix well.

7.3.3 Working Standard Solution, 25 µg $(NH_4)_2SO_4$/ml. Pipet 5 ml of the stock standard solution into a 200-ml volumetric flask. Dilute to 200 ml with water.

7.3.4 Eluent Solution. Weigh 1.018 g of sodium carbonate (Na_2CO_3) and 1.008 g of sodium bicarbonate ($NaHCO_3$), and dissolve in 4 liters of water. This solution is 0.0024 M Na_2CO_3/0.003 M $NaHCO_3$. Other eluents appropriate to the column type and capable of resolving sulfate ion from other species present may be used.

7.3.5 Ammonium Hydroxide. Concentrated, 14.8 M.

7.3.6 Phenolphthalein Indicator. 3,3-Bis(4-hydroxyphenyl)-1-(3H)-isobenzo-furanone. Dissolve 0.05 g in 50 ml of ethanol and 50 ml of water.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as Method 5, section 8.0, with the exception of the following:

8.1 Sampling Train Operation. Same as Method 5, section 8.5, except that the probe outlet and filter temperatures shall be maintained at 160 ±14 °C (320 ±25 °F).

8.2 Sample Recovery. Same as Method 5, section 8.7, except that the recovery solvent shall be water instead of acetone, and a clean filter from the same lot as those used during testing shall be saved for analysis as a blank.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures

Section	Quality control measure	Effect
8.3, 10.0	Sampling equipment leak check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.
10.1.2, 11.2.5.3	Repetitive analyses	Ensures precise measurement of total carbon and inorganic carbon concentration of samples, blank, and standards.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

Same as Method 5, section 10.0, with the addition of the following:

10.1 Determination of Ion Chromatograph Calibration Factor S. Prepare a series of five standards by adding 1.0, 2.0, 4.0, 6.0, and 10.0 ml of working standard solution (25 µg/ml) to a series of five 50-ml volumetric flasks. (The standard masses will equal 25, 50, 100, 150, and 250 µg.) Dilute each flask to the mark with water, and mix well. Analyze each standard according to the chromatograph manufacturer's instructions. Take peak height measurements with symmetrical peaks; in all other cases, calculate peak areas. Prepare or calculate a linear regression plot of the standard masses in µg (x-axis) versus their responses (y-axis). From this line, or equation, determine the slope and calculate its reciprocal which is the calibration factor, S. If any point deviates from the line by more than 7 percent of the concentration at that point, remake and reanalyze that standard. This deviation can be determined by multiplying S times the response for each standard. The resultant concentrations must not differ by more than 7 percent from each known standard mass (*i.e.*, 25, 50, 100, 150, and 250 µg).

10.2 Conductivity Detector. Calibrate according to manufacturer's specifications prior to initial use.

11.0 Analytical Procedure

11.1 Sample Extraction.

11.1.1 Note on the analytical data sheet, the level of the liquid in the container, and whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.1.2 Cut the filter into small pieces, and place it in a 125-ml Erlenmeyer flask with a ground glass joint equipped with an air condenser. Rinse the shipping container with water, and pour the rinse into the flask. Add additional water to the flask until it contains about 75 ml, and place the flask on a hot plate. Gently reflux the contents for 6 to 8 hours. Cool the solution, and transfer it to a 500-ml volumetric flask. Rinse the Erlenmeyer flask with water, and transfer the rinsings to the volumetric flask including the pieces of filter.

11.1.3 Transfer the probe rinse to the same 500-ml volumetric flask with the filter sample. Rinse the sample bottle with water, and add the rinsings to the volumetric flask. Dilute the contents of the flask to the mark with water.

11.1.4 Allow the contents of the flask to settle until all solid material is at the bottom of the flask. If necessary, remove and centrifuge a portion of the sample.

11.1.5 Repeat the procedures outlined in sections 11.1.1 through 11.1.4 for each sample and for the filter blank.

11.2 Sulfate (SO_4) Analysis.

11.2.1 Prepare a standard calibration curve according to the procedures outlined in section 10.1.

11.2.2 Pipet 5 ml of the sample into a 50-ml volumetric flask, and dilute to 50 ml with water. (Alternatively, eluent solution may be used instead of water in all sample, standard, and blank dilutions.) Analyze the set of standards followed by the set of samples, including the filter blank, using the same injection volume used for the standards.

11.2.3 Repeat the analyses of the standards and the samples, with the standard set being done last. The two peak height or peak area responses for each sample must agree within 5 percent of their arithmetic mean for the analysis to be valid. Perform this analysis sequence on the same day. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

11.2.4 Document each sample chromatogram by listing the following analytical parameters: injection point, injection volume, sulfate retention time, flow rate, detector sensitivity setting, and recorder chart speed.

11.3 Sample Residue.

11.3.1 Transfer the remaining contents of the volumetric flask to a tared 600-ml beaker or similar container. Rinse the volumetric flask with water, and add the rinsings to the tared beaker. Make certain that all particulate matter is transferred to the beaker. Evaporate the water in an oven at 105 °C (220 °F) until only about 100 ml of water remains. Remove the beakers from the oven, and allow them to cool.

11.3.2 After the beakers have cooled, add five drops of phenolphthalein indicator, and then add concentrated ammonium hydroxide until the solution turns pink. Return the samples to the oven at 105 °C (220 °F), and evaporate the samples to dryness. Cool the samples in a desiccator, and weigh the samples to constant weight.

12.0 Data Analysis and Calculations

Same as Method 5, section 12.0, with the addition of the following:

12.1 Nomenclature.

C_W = Water blank residue concentration, mg/ml.

F = Dilution factor (required only if sample dilution was needed to reduce the concentration into the range of calibration).

H_S = Arithmetic mean response of duplicate sample analyses, mm for height or mm2 for area.

H_b = Arithmetic mean response of duplicate filter blank analyses, mm for height or mm2 for area.
m_b = Mass of beaker used to dry sample, mg.
m_f = Mass of sample filter, mg.
m_n = Mass of nonsulfate particulate matter in the sample as collected, mg.
m_s = Mass of ammonium sulfate in the sample as collected, mg.
m_t = Mass of beaker, filter, and dried sample, mg.
m_w = Mass of residue after evaporation of water blank, mg.
S = Calibration factor, µg/mm.
V_b = Volume of water blank, ml.
V_S = Volume of sample collected, 500 ml.

12.2 Water Blank Concentration.

$$C_w = \frac{m_w}{V_b} \qquad \text{Eq. 5F-1}$$

12.3 Mass of Ammonium Sulfate.

$$m_s = \frac{(99)\, S\, (H_s - H_b)}{(1000)} F \qquad \text{Eq. 5F-2}$$

Where:
100 = Aliquot factor, 495 ml/5 ml
1000 = Constant, µg/mg

12.4 Mass of Nonsulfate Particulate Matter.

$$m_n = m_t - m_b - m_s - m_f - V_s C_w \qquad \text{Eq. 5F-3}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 The following procedure may be used as an alternative to the procedure in section 11.0

16.1.1 Apparatus. Same as for Method 6, sections 6.3.3 to 6.3.6 with the following additions.

16.1.1.1 Beakers. 250-ml, one for each sample, and 600-ml.

16.1.1.2 Oven. Capable of maintaining temperatures of 75 ±5 °C (167 ±9 °F) and 105 ±5 °C (221 ±9 °F).

16.1.1.3 Buchner Funnel.

16.1.1.4 Glass Columns. 25-mm × 305-mm (1-in. × 12-in.) with Teflon stopcock.

16.1.1.5 Volumetric Flasks. 50-ml and 500-ml, one set for each sample, and 100-ml, 200-ml, and 1000-ml.

16.1.1.6 Pipettes. Two 20-ml and one 200-ml, one set for each sample, and 5-ml.

16.1.1.7 Filter Flasks. 500-ml.

16.1.1.8 Polyethylene Bottle. 500-ml, one for each sample.

16.1.2 Reagents. Same as Method 6, sections 7.3.2 to 7.3.5 with the following additions:

16.1.2.1 Water, Ammonium Hydroxide, and Phenolphthalein. Same as sections 7.2.1, 7.3.5, and 7.3.6 of this method, respectively.

16.1.2.2 Filter. Glass fiber to fit Buchner funnel.

16.1.2.3 Hydrochloric Acid (HCl), 1 m. Add 8.3 ml of concentrated HCl (12 M) to 50 ml of water in a 100-ml volumetric flask. Dilute to 100 ml with water.

16.1.2.4 Glass Wool.

16.1.2.5 Ion Exchange Resin. Strong cation exchange resin, hydrogen form, analytical grade.

16.1.2.6 pH Paper. Range of 1 to 7.

16.1.3 Analysis.

16.1.3.1 Ion Exchange Column Preparation. Slurry the resin with 1 M HCl in a 250-ml beaker, and allow to stand overnight. Place 2.5 cm (1 in.) of glass wool in the bottom of the glass column. Rinse the slurried resin twice with water. Resuspend the resin in water, and pour sufficient resin into the column to make a bed 5.1 cm (2 in.) deep. Do not allow air bubbles to become entrapped in the resin or glass wool to avoid channeling, which may produce erratic results. If necessary, stir the resin with a glass rod to remove air bubbles, after the column has been prepared, never let the liquid level fall below the top of the upper glass wool plug. Place a 2.5-cm (1-in.) plug of glass wool on top of the resin. Rinse the column with water until the eluate gives a pH of 5 or greater as measured with pH paper.

16.1.3.2 Sample Extraction. Followup the procedure given in section 11.1.3 except do not dilute the sample to 500 ml.

16.1.3.3 Sample Residue.

16.1.3.3.1 Place at least one clean glass filter for each sample in a Buchner funnel, and rinse the filters with water. Remove the filters from the funnel, and dry them in an oven at 105 ±5 °C (221 ±9 °F); then cool in a desiccator. Weigh each filter to constant weight according to the procedure in Method 5, section 11.0. Record the weight of each filter to the nearest 0.1 mg.

16.1.3.3.2 Assemble the vacuum filter apparatus, and place one of the clean, tared glass fiber filters in the Buchner funnel. Decant the liquid portion of the extracted sample (Section 16.1.3.2) through the tared glass fiber filter into a clean, dry, 500-ml filter flask. Rinse all the particulate matter remaining in the volumetric flask onto the glass fiber filter with water. Rinse the particulate matter with additional water.

Transfer the filtrate to a 500-ml volumetric flask, and dilute to 500 ml with water. Dry the filter overnight at 105 ±5 °C (221 ±9 °F), cool in a desiccator, and weigh to the nearest 0.1 mg.

16.1.3.3.3 Dry a 250-ml beaker at 75 ±5 °C (167 ±9 °F), and cool in a desiccator; then weigh to constant weight to the nearest 0.1 mg. Pipette 200 ml of the filtrate that was saved into a tared 250-ml beaker; add five drops of phenolphthalein indicator and sufficient concentrated ammonium hydroxide to turn the solution pink. Carefully evaporate the contents of the beaker to dryness at 75 ±5 °C (167 ±9 °F). Check for dryness every 30 minutes. Do not continue to bake the sample once it has dried. Cool the sample in a desiccator, and weigh to constant weight to the nearest 0.1 mg.

16.1.3.4 Sulfate Analysis. Adjust the flow rate through the ion exchange column to 3 ml/min. Pipette a 20-ml aliquot of the filtrate onto the top of the ion exchange column, and collect the eluate in a 50-ml volumetric flask. Rinse the column with two 15-ml portions of water. Stop collection of the eluate when the volume in the flask reaches 50-ml. Pipette a 20-ml aliquot of the eluate into a 250-ml Erlenmeyer flask, add 80 ml of 100 percent isopropanol and two to four drops of thorin indicator, and titrate to a pink end point using 0.0100 N barium perchlorate. Repeat and average the titration volumes. Run a blank with each series of samples. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is larger. Perform the ion exchange and titration procedures on duplicate portions of the filtrate. Results should agree within 5 percent. Regenerate or replace the ion exchange resin after 20 sample aliquots have been analyzed or if the end point of the titration becomes unclear.

NOTE: Protect the 0.0100 N barium perchlorate solution from evaporation at all times.

16.1.3.5 Blank Determination. Begin with a sample of water of the same volume as the samples being processed and carry it through the analysis steps described in sections 16.1.3.3 and 16.1.3.4. A blank value larger than 5 mg should not be subtracted from the final particulate matter mass. Causes for large blank values should be investigated and any problems resolved before proceeding with further analyses.

16.1.4 Calibration. Calibrate the barium perchlorate solutions as in Method 6, section 10.5.

16.1.5 Calculations.

16.1.5.1 Nomenclature. Same as section 12.1 with the following additions:

m_a = Mass of clean analytical filter, mg.
m_d = Mass of dissolved particulate matter, mg.
m_e = Mass of beaker and dissolved particulate matter after evaporation of filtrate, mg.
m_p = Mass of insoluble particulate matter, mg.
m_r = Mass of analytical filter, sample filter, and insoluble particulate matter, mg.
m_{bk} = Mass of nonsulfate particulate matter in blank sample, mg.
m_n = Mass of nonsulfate particulate matter, mg.
m_s = Mass of Ammonium sulfate, mg.
N = Normality of $Ba(ClO_4)$ titrant, meq/ml.
V_a = Volume of aliquot taken for titration, 20 ml.
V_c = Volume of titrant used for titration blank, ml.
V_d = Volume of filtrate evaporated, 200 ml.
V_e = Volume of eluate collected, 50 ml.
V_f = Volume of extracted sample, 500 ml.
V_i = Volume of filtrate added to ion exchange column, 20 ml.
V_t = Volume of $Ba(C10_4)_2$ titrant, ml.
W = Equivalent weight of ammonium sulfate, 66.07 mg/meq.

16.1.5.2 Mass of Insoluble Particulate Matter.

$$m_p = m_r - m_a - m_f \qquad \text{Eq. 5F-4}$$

16.1.5.3 Mass of Dissolved Particulate Matter.

$$m_d = \left(m_e - \left(V_f / V_d\right) m_b\right) \qquad \text{Eq. 5F-5}$$

16.1.5.4 Mass of Ammonium Sulfate.

$$m_s = \frac{\left(V_t - V_c\right) N\, W\, V_e V_f}{V_a V_i} \qquad \text{Eq. 5F-6}$$

16.1.5.5 Mass of Nonsulfate Particulate Matter.

$$m_n = m_p + m_d - m_s - m_{bk} \qquad \text{Eq. 5F-7}$$

17.0 References

Same as Method 5, section 17.0, with the addition of the following:

1. Mulik, J.D. and E. Sawicki. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor, Ann Arbor Science Publishers, Inc. Vol. 2, 1979.

2. Sawicki, E., J.D. Mulik, and E. Wittgenstein. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor, Ann Arbor Science Publishers, Inc. Vol. 1. 1978.

3. Siemer, D.D. Separation of Chloride and Bromide from Complex Matrices Prior to Ion Chromatographic Determination. Analytical Chemistry 52(12): 1874–1877. October 1980.

4. Small, H., T.S. Stevens, and W.C. Bauman. Novel Ion Exchange Chromatographic Method Using

Conductimetric Determination. Analytical Chemistry. *47*(11):1801. 1975.

18.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 5G—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM WOOD HEATERS (DILUTION TUNNEL SAMPLING LOCATION)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 4, Method 5, Method 5H, and Method 28.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of PM emissions from wood heaters.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 The exhaust from a wood heater is collected with a total collection hood, and is combined with ambient dilution air. Particulate matter is withdrawn proportionally from a single point in a sampling tunnel, and is collected on two glass fiber filters in series. The filters are maintained at a temperature of no greater than 32 °C (90 °F). The particulate mass is determined gravimetrically after the removal of uncombined water.

2.2 There are three sampling train approaches described in this method: (1) One dual-filter dry sampling train operated at about 0.015 m^3/min (0.5 cfm), (2) One dual-filter plus impingers sampling train operated at about 0.015 m^3/min (0.5 cfm), and (3) two dual-filter dry sampling trains operated simultaneously at any flow rate. Options (2) and (3) are referenced in section 16.0 of this method. The dual-filter dry sampling train equipment and operation, option (1), are described in detail in this method.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. The following items are required for sample collection:

6.1.1 Sampling Train. The sampling train configuration is shown in Figure 5G–1 and consists of the following components:

6.1.1.1 Probe. Stainless steel (*e.g.*, 316 or grade more corrosion resistant) or glass about 9.5 mm (3⁄8 in.) I.D., 0.6 m (24 in.) in length. If made of stainless steel, the probe shall be constructed from seamless tubing.

6.1.1.2 Pitot Tube. Type S, as described in section 6.1 of Method 2. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Method 2, section 10. Alternatively, a standard pitot may be used as described in Method 2, section 6.1.2.

6.1.1.3 Differential Pressure Gauge. Inclined manometer or equivalent device, as described in Method 2, section 6.2. One manometer shall be used for velocity head (Δp) readings and another (optional) for orifice differential pressure readings (ΔH).

6.1.1.4 Filter Holders. Two each made of borosilicate glass, stainless steel, or Teflon, with a glass frit or stainless steel filter support and a silicone rubber, Teflon, or Viton gasket. The holder design shall provide a positive seal against leakage from the outside or around the filters. The filter holders shall be placed in series with the backup filter holder located 25 to 100 mm (1 to 4 in.) downstream from the primary filter holder. The filter holder shall be capable of holding a filter with a 100 mm (4 in.) diameter, except as noted in section 16.

6.1.1.5 Filter Temperature Monitoring System. A temperature sensor capable of measuring temperature to within ±3 °C (±5 °F). The sensor shall be installed at the exit side of the front filter holder so that the sensing tip of the temperature sensor is in direct contact with the sample gas or in a thermowell as shown in Figure 5G–1. The temperature sensor shall comply with the calibration specifications in Method 2, section 10.3. Alternatively, the sensing tip of the temperature sensor may be installed at the inlet side of the front filter holder.

6.1.1.6 Dryer. Any system capable of removing water from the sample gas to less than 1.5 percent moisture (volume percent) prior to the metering system. The system shall include a temperature sensor for demonstrating that sample gas temperature exiting the dryer is less than 20 °C (68 °F).

6.1.1.7 Metering System. Same as Method 5, section 6.1.1.9.

6.1.2 Barometer. Same as Method 5, section 6.1.2.

6.1.3 Dilution Tunnel Gas Temperature Measurement. A temperature sensor capable

of measuring temperature to within ±3 °C (±5 °F).

6.1.4 Dilution Tunnel. The dilution tunnel apparatus is shown in Figure 5G–2 and consists of the following components:

6.1.4.1 Hood. Constructed of steel with a minimum diameter of 0.3 m (1 ft) on the large end and a standard 0.15 to 0.3 m (0.5 to 1 ft) coupling capable of connecting to standard 0.15 to 0.3 m (0.5 to 1 ft) stove pipe on the small end.

6.1.4.2 90° Elbows. Steel 90° elbows, 0.15 to 0.3 m (0.5 to 1 ft) in diameter for connecting mixing duct, straight duct and optional damper assembly. There shall be at least two 90° elbows upstream of the sampling section (see Figure 5G–2).

6.1.4.3 Straight Duct. Steel, 0.15 to 0.3 m (0.5 to 1 ft) in diameter to provide the ducting for the dilution apparatus upstream of the sampling section. Steel duct, 0.15 m (0.5 ft) in diameter shall be used for the sampling section. In the sampling section, at least 1.2 m (4 ft) downstream of the elbow, shall be two holes (velocity traverse ports) at 90° to each other of sufficient size to allow entry of the pitot for traverse measurements. At least 1.2 m (4 ft) downstream of the velocity traverse ports, shall be one hole (sampling port) of sufficient size to allow entry of the sampling probe. Ducts of larger diameter may be used for the sampling section, provided the specifications for minimum gas velocity and the dilution rate range shown in section 8 are maintained. The length of duct from the hood inlet to the sampling ports shall not exceed 9.1 m (30 ft).

6.1.4.4 Mixing Baffles. Steel semicircles (two) attached at 90° to the duct axis on opposite sides of the duct midway between the two elbows upstream of sampling section. The space between the baffles shall be about 0.3 m (1 ft).

6.1.4.5 Blower. Squirrel cage or other fan capable of extracting gas from the dilution tunnel of sufficient flow to maintain the velocity and dilution rate specifications in section 8 and exhausting the gas to the atmosphere.

6.2 Sample Recovery. The following items are required for sample recovery: probe brushes, wash bottles, sample storage containers, petri dishes, and funnel. Same as Method 5, sections 6.2.1 through 6.2.4, and 6.2.8, respectively.

6.3 Sample Analysis. The following items are required for sample analysis: glass weighing dishes, desiccator, analytical balance, beakers (250-ml or smaller), hygrometer, and temperature sensor. Same as Method 5, sections 6.3.1 through 6.3.3 and 6.3.5 through 6.3.7, respectively.

7.0 Reagents and Standards

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Filters. Glass fiber filters with a minimum diameter of 100 mm (4 in.), without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. Gelman A/E 61631 has been found acceptable for this purpose.

7.1.2 Stopcock Grease. Same as Method 5, section 7.1.5. 7.2 Sample Recovery. Acetone-reagent grade, same as Method 5, section 7.2.

7.3 Sample Analysis. Two reagents are required for the sample analysis:

7.3.1 Acetone. Same as in section 7.2.

7.3.2 Desiccant. Anhydrous calcium sulfate, calcium chloride, or silica gel, indicating type.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Dilution Tunnel Assembly and Cleaning. A schematic of a dilution tunnel is shown in Figure 5G–2. The dilution tunnel dimensions and other features are described in section 6.1.4. Assemble the dilution tunnel, sealing joints and seams to prevent air leakage. Clean the dilution tunnel with an appropriately sized wire chimney brush before each certification test.

8.2 Draft Determination. Prepare the wood heater as in Method 28, section 6.2.1. Locate the dilution tunnel hood centrally over the wood heater stack exhaust. Operate the dilution tunnel blower at the flow rate to be used during the test run. Measure the draft imposed on the wood heater by the dilution tunnel (*i.e.*, the difference in draft measured with and without the dilution tunnel operating) as described in Method 28, section 6.2.3. Adjust the distance between the top of the wood heater stack exhaust and the dilution tunnel hood so that the dilution tunnel induced draft is less than 1.25 Pa (0.005 in. H_2O). Have no fire in the wood heater, close the wood heater doors, and open fully the air supply controls during this check and adjustment.

8.3 Pretest Ignition. Same as Method 28, section 8.7.

8.4 Smoke Capture. During the pretest ignition period, operate the dilution tunnel and visually monitor the wood heater stack exhaust. Operate the wood heater with the doors closed and determine that 100 percent of the exhaust gas is collected by the dilution tunnel hood. If less than 100 percent of the wood heater exhaust gas is collected, adjust the distance between the wood heater stack and the dilution tunnel hood until no visible exhaust gas is escaping. Stop the pretest ignition period, and repeat the draft determination procedure described in section 8.2.

8.5 Velocity Measurements. During the pretest ignition period, conduct a velocity traverse to identify the point of average velocity. This single point shall be used for measuring velocity during the test run.

8.5.1 Velocity Traverse. Measure the diameter of the duct at the velocity traverse port location through both ports. Calculate the duct area using the average of the two diameters. A pretest leak-check of pitot lines as in Method 2, section 8.1, is recommended. Place the calibrated pitot tube at the centroid of the stack in either of the velocity traverse ports. Adjust the damper or similar device on the blower inlet until the velocity indicated by the pitot is approximately 220 m/min (720 ft/min). Continue to read the Δp and temperature until the velocity has remained constant (less than 5 percent change) for 1 minute. Once a constant velocity is obtained at the centroid of the duct, perform a velocity traverse as outlined in Method 2, section 8.3 using four points per traverse as outlined in Method 1. Measure the Δp and tunnel temperature at each traverse point and record the readings. Calculate the total gas flow rate using calculations contained in Method 2, section 12. Verify that the flow rate is 4 ±0.40 dscm/min (140 ±14 dscf/min); if not, readjust the damper, and repeat the velocity traverse. The moisture may be assumed to be 4 percent (100 percent relative humidity at 85 °F). Direct moisture measurements (*e.g.*, according to Method 4) are also permissible.

NOTE: If burn rates exceed 3 kg/hr (6.6 lb/hr), dilution tunnel duct flow rates greater than 4 dscm/min (140 dscfm) and sampling section duct diameters larger than 150 mm (6 in.) are allowed. If larger ducts or flow rates are used, the sampling section velocity shall be at least 220 m/min (720 fpm). In order to ensure measurable particulate mass catch, it is recommended that the ratio of the average mass flow rate in the dilution tunnel to the average fuel burn rate be less than 150:1 if larger duct sizes or flow rates are used.

8.5.2 Testing Velocity Measurements. After obtaining velocity traverse results that meet the flow rate requirements, choose a point of average velocity and place the pitot and temperature sensor at that location in the duct. Alternatively, locate the pitot and the temperature sensor at the duct centroid and calculate a velocity correction factor for the centroidal position. Mount the pitot to ensure no movement during the test run and seal the port holes to prevent any air leakage. Align the pitot opening to be parallel with the duct axis at the measurement point. Check that this condition is maintained during the test run (about 30-minute intervals). Monitor the temperature and velocity during the pretest ignition period to ensure that the proper flow rate is maintained. Make adjustments to the dilution tunnel flow rate as necessary.

8.6 Pretest Preparation. Same as Method 5, section 8.1.

8.7 Preparation of Sampling Train. During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin.

Using a tweezer or clean disposable surgical gloves, place one labeled (identified) and weighed filter in each of the filter holders. Be sure that each filter is properly centered and that the gasket is properly placed so as to prevent the sample gas stream from circumventing the filter. Check each filter for tears after assembly is completed.

Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct. Set up the train as shown in Figure 5G–1.

8.8 Leak-Check Procedures.

8.8.1 Leak-Check of Metering System Shown in Figure 5G–1. That portion of the sampling train from the pump to the orifice meter shall be leak-checked prior to initial use and after each certification or audit test. Leakage after the pump will result in less volume being recorded than is actually sampled. Use the procedure described in Method 5, section 8.4.1. Similar leak-checks shall be conducted for other types of metering systems (*i.e.*, without orifice meters).

8.8.2 Pretest Leak-Check. A pretest leak-check of the sampling train is recommended, but not required. If the pretest leak check is conducted, the procedures outlined in Method 5, section 8.4.2 should be used. A vacuum of 130 mm Hg (5 in. Hg) may be used instead of 380 mm Hg (15 in. Hg).

8.8.3 Post-Test Leak-Check. A leak-check of the sampling train is mandatory at the conclusion of each test run. The leak-check shall be performed in accordance with the procedures outlined in Method 5, section 8.4.2. A vacuum of 130 mm Hg (5 in. Hg) or the highest vacuum measured during the test run, whichever is greater, may be used instead of 380 mm Hg (15 in. Hg).

8.9 Preliminary Determinations. Determine the pressure, temperature and the average velocity of the tunnel gases as in section 8.5. Moisture content of diluted tunnel gases is assumed to be 4 percent for making flow rate calculations; the moisture content may be measured directly as in Method 4.

8.10 Sampling Train Operation. Position the probe inlet at the stack centroid, and block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream. Be careful not to bump the probe into the stack wall when removing or inserting the probe through the porthole; this minimizes the chance of extracting deposited material.

8.10.1 Begin sampling at the start of the test run as defined in Method 28, section 8.8.1. During the test run, maintain a sample flow rate proportional to the dilution tunnel flow rate (within 10 percent of the initial proportionality ratio) and a filter holder temperature of no greater than 32 °C (90 °F).

The initial sample flow rate shall be approximately 0.015 m^3/min (0.5 cfm).

8.10.2 For each test run, record the data required on a data sheet such as the one shown in Figure 5G–3. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment and when sampling is halted. Take other readings as indicated on Figure 5G–3 at least once each 10 minutes during the test run. Since the manometer level and zero may drift because of vibrations and temperature changes, make periodic checks during the test run.

8.10.3 For the purposes of proportional sampling rate determinations, data from calibrated flow rate devices, such as glass rotameters, may be used in lieu of incremental dry gas meter readings. Proportional rate calculation procedures must be revised, but acceptability limits remain the same.

8.10.4 During the test run, make periodic adjustments to keep the temperature between (or upstream of) the filters at the proper level. Do not change sampling trains during the test run.

8.10.5 At the end of the test run (see Method 28, section 6.4.6), turn off the coarse adjust valve, remove the probe from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak-check, as outlined in section 8.8.2. Also, leak-check the pitot lines as described in Method 2, section 8.1; the lines must pass this leak-check in order to validate the velocity head data.

8.11 Calculation of Proportional Sampling Rate. Calculate percent proportionality (see section 12.7) to determine whether the run was valid or another test run should be made.

8.12 Sample Recovery. Same as Method 5, section 8.7, with the exception of the following:

8.12.1 An acetone blank volume of about 50-ml or more may be used.

8.12.2 Treat the samples as follows:

8.12.2.1 Container Nos. 1 and 1A. Treat the two filters according to the procedures outlined in Method 5, section 8.7.6.1. The filters may be stored either in a single container or in separate containers. Use the sum of the filter tare weights to determine the sample mass collected.

8.12.2.3 Container No. 2.

8.12.2.3.1 Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe and filter holders by washing and brushing these components with acetone and placing the wash in a labeled glass container. At least three cycles of brushing and rinsing are required.

8.12.2.3.2 Between sampling runs, keep brushes clean and protected from contamination.

8.12.2.3.3 After all acetone washings and particulate matter have been collected in the sample containers, tighten the lids on the sample containers so that the acetone will not leak out when transferred to the laboratory weighing area. Mark the height of the fluid levels to determine whether leakage occurs during transport. Label the containers clearly to identify contents.

8.13 Sample Transport. Whenever possible, containers should be shipped in such a way that they remain upright at all times.

NOTE: Requirements for capping and transport of sample containers are not applicable if sample recovery and analysis occur in the same room.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.8, 10.1–10.4	Sampling equipment leak check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.
10.5	Analytical balance calibration	Ensure accurate and precise measurement of collected particulate.
16.2.5	Simultaneous, dual-train sample collection.	Ensure precision of measured particulate concentration.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory record of all calibrations.

10.1 Pitot Tube. The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Method 2, section 10.1, prior to the first certification test and checked semiannually, thereafter. A standard pitot need not be calibrated but shall be inspected and cleaned, if necessary, prior to each certification test.

10.2 Volume Metering System.

10.2.1 Initial and Periodic Calibration. Before its initial use and at least semiannually thereafter, calibrate the volume metering system as described in Method 5, section 10.3.1, except that the wet test meter with a capacity of 3.0 liters/rev (0.1 ft^3/rev) may be used. Other liquid displacement systems accurate to within ±1 percent, may be used as calibration standards.

NOTE: Procedures and equipment specified in Method 5, section 16.0, for alternative calibration standards, including calibrated dry gas meters and critical orifices, are allowed for calibrating the dry gas meter in the sampling train. A dry gas meter used as a calibration standard shall be recalibrated at least once annually.

10.2.2 Calibration After Use. After each certification or audit test (four or more test runs conducted on a wood heater at the four burn rates specified in Method 28), check calibration of the metering system by performing three calibration runs at a single, intermediate flow rate as described in Method 5, section 10.3.2.

NOTE: Procedures and equipment specified in Method 5, section 16.0, for alternative calibration standards are allowed for the post-test dry gas meter calibration check.

10.2.3 Acceptable Variation in Calibration. If the dry gas meter coefficient values obtained before and after a certification test differ by more than 5 percent, the certification test shall either be voided and repeated, or calculations for the certification test shall be performed using whichever meter coefficient value (*i.e.*, before or after) gives the lower value of total sample volume.

10.3 Temperature Sensors. Use the procedure in Method 2, section 10.3, to calibrate temperature sensors before the first certification or audit test and at least semiannually, thereafter.

10.4 Barometer. Calibrate against a mercury barometer before the first certification test and at least semiannually, thereafter. If a mercury barometer is used, no calibration is necessary. Follow the manufacturer's instructions for operation.

10.5 Analytical Balance. Perform a multipoint calibration (at least five points spanning the operational range) of the analytical balance before the first certification test and semiannually, thereafter. Before each certification test, audit the balance by weighing at least one calibration weight (class F) that corresponds to 50 to 150 percent of the weight of one filter. If the scale cannot reproduce the value of the calibration weight to within 0.1 mg, conduct the multipoint calibration before use.

11.0 Analytical Procedure

11.1 Record the data required on a sheet such as the one shown in Figure 5G–4. Use the same analytical balance for determining tare weights and final sample weights.

11.2 Handle each sample container as follows:

11.2.1 Container Nos. 1 and 1A. Treat the two filters according to the procedures outlined in Method 5, section 11.2.1.

11.2.2 Container No. 2. Same as Method 5, section 11.2.2, except that the beaker may be smaller than 250 ml.

11.2.3 Acetone Blank Container. Same as Method 5, section 11.2.4, except that the beaker may be smaller than 250 ml.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

12.1 Nomenclature.

B_{ws} = Water vapor in the gas stream, proportion by volume (assumed to be 0.04).
c_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (gr/dscf).
E = Particulate emission rate, g/hr (lb/hr).
E_{adj} = Adjusted particulate emission rate, g/hr (lb/hr).
L_a = Maximum acceptable leakage rate for either a pretest or post-test leak-check, equal to 0.00057 m^3/min (0.020 cfm) or 4 percent of the average sampling rate, whichever is less.
L_p = Leakage rate observed during the post-test leak-check, m^3/min (cfm).
m_a = Mass of residue of acetone blank after evaporation, mg.
m_{aw} = Mass of residue from acetone wash after evaporation, mg.
m_n = Total amount of particulate matter collected, mg.
M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).
PR = Percent of proportional sampling rate.
P_s = Absolute gas pressure in dilution tunnel, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
Q_{sd} = Average gas flow rate in dilution tunnel, calculated as in Method 2, Equation 2–8, dscm/hr (dscf/hr).
T_m = Absolute average dry gas meter temperature (see Figure 5G–3), °K (°R).
T_{mi} = Absolute average dry gas meter temperature during each 10-minute interval, i, of the test run, °K (°R).
T_s = Absolute average gas temperature in the dilution tunnel (see Figure 5G–3), °K (°R).
T_{si} = Absolute average gas temperature in the dilution tunnel during each 10 minute interval, i, of the test run, °K (°R).
T_{std} = Standard absolute temperature, 293 °K (528 °R).
V_a = Volume of acetone blank, ml.
V_{aw} = Volume of acetone used in wash, ml.
V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).

V_{mi} = Volume of gas sample as measured by dry gas meter during each 10-minute interval, i, of the test run, dcm.
$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).
V_s = Average gas velocity in the dilution tunnel, calculated by Method 2, Equation 2–7, m/sec (ft/sec). The dilution tunnel dry gas molecular weight may be assumed to be 29 g/g mole (lb/lb mole).
V_{si} = Average gas velocity in dilution tunnel during each 10-minute interval, i, of the test run, calculated by Method 2, Equation 2–7, m/sec (ft/sec).
Y = Dry gas meter calibration factor.
ΔH = Average pressure differential across the orifice meter, if used (see Figure 5G–2), mm H^2O (in. H^2O).
U = Total sampling time, min.
10 = 10 minutes, length of first sampling period.
13.6 = Specific gravity of mercury.
100 = Conversion to percent.

12.2 Dry Gas Volume. Same as Method 5, section 12.2, except that component changes are not allowable.

12.3 Solvent Wash Blank.

$$m_{aw} = \frac{m_a V_{aw}}{V_a} \qquad \text{Eq. 5G-1}$$

12.4 Total Particulate Weight. Determine the total particulate catch, mn, from the sum of the weights obtained from Container Nos. 1, 1A, and 2, less the acetone blank (see Figure 5G–4).

12.5 Particulate Concentration.

$$c_s = K_2 \frac{m_n}{V_{m(std)}} \qquad \text{Eq. 5G-2}$$

Where:
K_2 = 0.001 g/mg for metric units.
= 0.0154 gr/mg for English units.

12.6 Particulate Emission Rate.

$$E = C_s Q_{sd} \qquad \text{Eq. 5G-3}$$

NOTE: Particulate emission rate results produced using the sampling train described in section 6 and shown in Figure 5G–1 shall be adjusted for reporting purposes by the following method adjustment factor:

$$E_{adj} = K_3 E^{0.83} \qquad \text{Eq. 5G-4}$$

Where:
K_3 = constant, 1.82 for metric units.
= constant, 0.643 for English units.

12.7 Proportional Rate Variation. Calculate PR for each 10-minute interval, i, of the test run.

$$PR = \left(\frac{\theta \left(V_{mi} V_s T_m T_{si} \right)}{10 \left(V_m V_{si} T_s T_{mi} \right)} \right) \times 100 \qquad \text{Eq. 5G-5}$$

Alternate calculation procedures for proportional rate variation may be used if other sample flow rate data (e.g., orifice flow meters or rotameters) are monitored to maintain proportional sampling rates. The proportional rate variations shall be calculated for each 10-minute interval by comparing the stack to nozzle velocity ratio for each 10-minute interval to the average stack to nozzle velocity ratio for the test run. Proportional rate variation may be calculated for intervals shorter than 10 minutes with appropriate revisions to Equation 5G–5. If no more than 10 percent of the PR values for all the intervals exceed 90 percent ≤PR ≤110 percent, and if no PR value for any interval exceeds 80 percent ≤PR ≤120 percent, the results are acceptable. If the PR values for the test run are judged to be unacceptable, report the test run emission results, but do not include the results in calculating the weighted average emission rate, and repeat the test run.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Method 5H Sampling Train. The sampling train and sample collection, recovery, and analysis procedures described in Method 5H, sections 6.1.1, 7.1, 7.2, 8.1, 8.10, 8.11, and 11.0, respectively, may be used in lieu of similar sections in Method 5G. Operation of the Method 5H sampling train in the dilution tunnel is as described in section 8.10 of this method. Filter temperatures and condenser conditions are as described in Method 5H. No adjustment to the measured particulate matter emission rate (Equation 5G–4, section 12.6) is to be applied to the particulate emission rate measured by this alternative method.

16.2 Dual Sampling Trains. Two sampling trains may be operated simultaneously at sample flow rates other than that specified

in section 8.10, provided that the following specifications are met.

16.2.1 Sampling Train. The sampling train configuration shall be the same as specified in section 6.1.1, except the probe, filter, and filter holder need not be the same sizes as specified in the applicable sections. Filter holders of plastic materials such as Nalgene or polycarbonate materials may be used (the Gelman 1119 filter holder has been found suitable for this purpose). With such materials, it is recommended that solvents not be used in sample recovery. The filter face velocity shall not exceed 150 mm/sec (30 ft/min) during the test run. The dry gas meter shall be calibrated for the same flow rate range as encountered during the test runs. Two separate, complete sampling trains are required for each test run.

16.2.2 Probe Location. Locate the two probes in the dilution tunnel at the same level (see section 6.1.4.3). Two sample ports are necessary. Locate the probe inlets within the 50 mm (2 in.) diameter centroidal area of the dilution tunnel no closer than 25 mm (1 in.) apart.

16.2.3 Sampling Train Operation. Operate the sampling trains as specified in section 8.10, maintaining proportional sampling rates and starting and stopping the two sampling trains simultaneously. The pitot values as described in section 8.5.2 shall be used to adjust sampling rates in both sampling trains.

16.2.4 Recovery and Analysis of Sample. Recover and analyze the samples from the two sampling trains separately, as specified in sections 8.12 and 11.0, respectively.

16.2.4.1 For this alternative procedure, the probe and filter holder assembly may be weighed without sample recovery (use no solvents) described above in order to determine the sample weight gains. For this approach, weigh the clean, dry probe and filter holder assembly upstream of the front filter (without filters) to the nearest 0.1 mg to establish the tare weights. The filter holder section between the front and second filter need not be weighed. At the end of the test run, carefully clean the outside of the probe, cap the ends, and identify the sample (label). Remove the filters from the filter holder assemblies as described for container Nos. 1 and 1A in section 8.12.2.1. Reassemble the filter holder assembly, cap the ends, identify the sample (label), and transfer all the samples to the laboratory weighing area for final weighing. Requirements for capping and transport of sample containers are not applicable if sample recovery and analysis occur in the same room.

16.2.4.2 For this alternative procedure, filters may be weighed directly without a petri dish. If the probe and filter holder assembly are to be weighed to determine the sample weight, rinse the probe with acetone to remove moisture before desiccating prior to the test run. Following the test run, transport the probe and filter holder to the desiccator, and uncap the openings of the probe and the filter holder assembly. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

16.2.5 Calculations. Calculate an emission rate (Section 12.6) for the sample from each sampling train separately and determine the average emission rate for the two values. The two emission rates shall not differ by more than 7.5 percent from the average emission rate, or 7.5 percent of the weighted average emission rate limit in the applicable subpart of the regulations, whichever is greater. If this specification is not met, the results are unacceptable. Report the results, but do not include the results in calculating the weighted average emission rate. Repeat the test run until acceptable results are achieved, report the average emission rate for the acceptable test run, and use the average in calculating the weighted average emission rate.

17.0 References

Same as Method 5, section 17.0, References 1 through 11, with the addition of the following:

1. Oregon Department of Environmental Quality. Standard Method for Measuring the Emissions and Efficiencies of Woodstoves. June 8, 1984. Pursuant to Oregon Administrative Rules Chapter 340, Division 21.

2. American Society for Testing and Materials. Proposed Test Methods for Heating Performance and Emissions of Residential Wood-fired Closed Combustion-Chamber Heating Appliances. E–6 Proposal P 180. August 1986.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

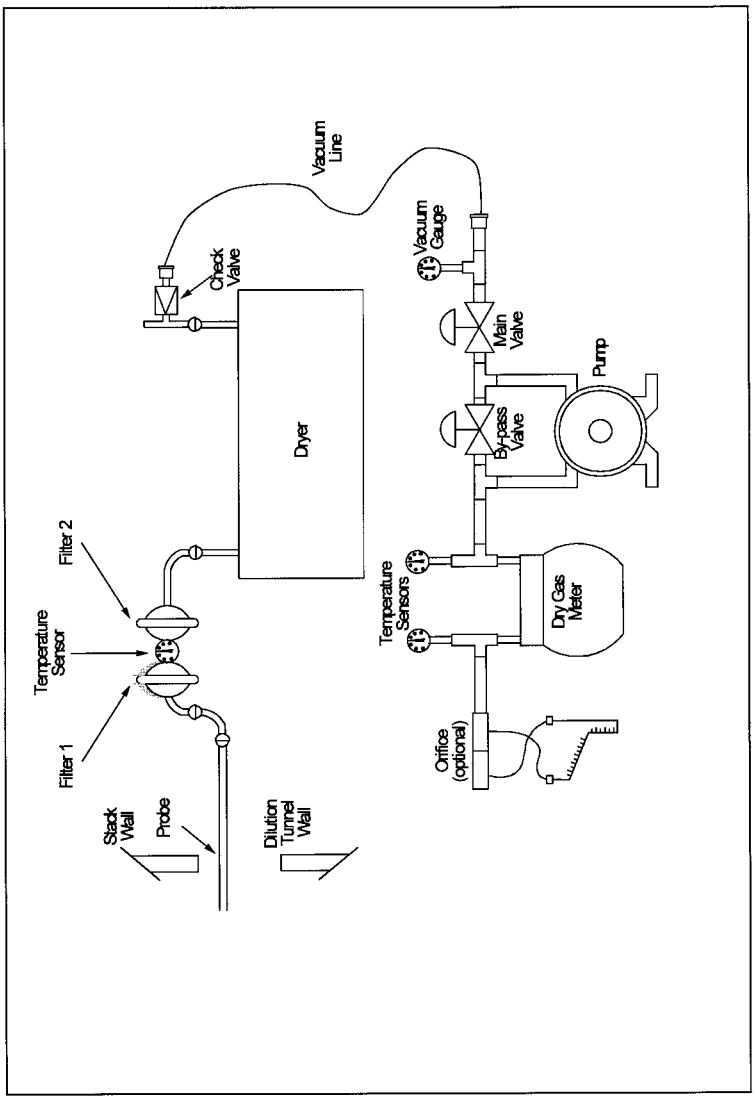


Figure 5G-1. Method 5G Sampling Train.

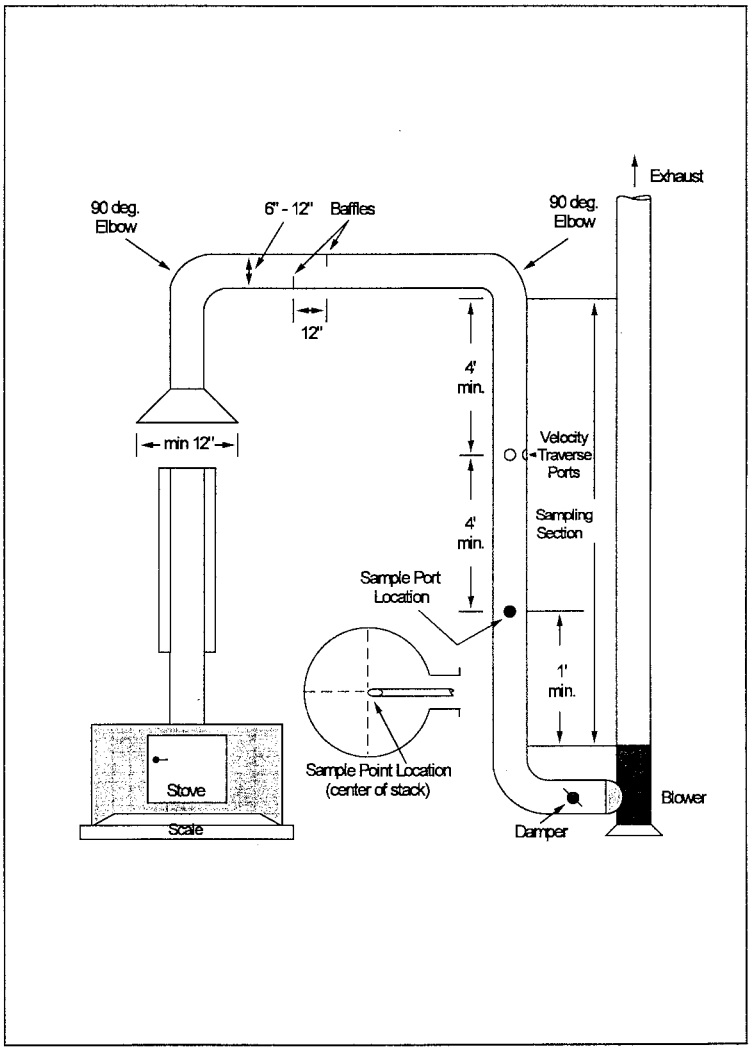


Figure 5G-2. Suggested Construction Details of the Dilution Tunnel.

Stove _____ Pitot tube coefficient, C_p _____
Test Method _____ Room temperature, °C (°F) _____
Operator _____ Barometric pressure mb (in. Hg) _____
Date _____ Measured or assumed moisture, % _____
Run No. _____ Final leak rate, m^3/min, (cfm) _____
Start Time _____ Probe liner material _____
Stop Time _____ Draft or static pressure, mm H_2O (in. H_2O) _____
Sample Box No. _____ Filter No. _____
Meter Box No. _____
Meter ΔH @ (optional) _____

Clock time	Test run time (e) min.	Vacuum mm Hg (in. Hg)	Tunnel temp (T_s) °C (°F)	Velocity head (ΔP_s) mm (in. H_2O)	Sample flow rate indicator (orifice meter optional) mm H_2O (in. H_2O)	Gas meter volume m^3 (ft^3)	Gas sample temp at dry gas meter Inlet °C (°F)	Gas sample temp at dry gas meter Outlet °C (°F)	Filter holder temp °C (°F)	Temperature of gas leaving dryer or last impinger °C (°F)
Total							Avg.	Avg.		
Average							Avg.			

Figure 5G-3. Sampling Data Sheet.

Stove _____
Date _____
Run No. _____
Filter Nos. _____
Liquid lost during transport, ml _____
Acetone blank volume, ml _____
Acetone wash volume, ml _____
Acetone blank concentration, mg/mg _____
Acetone wash blank, mg _____

Container number	Weight of particulate collected, mg	
	Final weight	Tare weight
1		
2		
3		
Total		
Less acetone blank		
Weight of particulate matter		

Stack Moisture Measurement Data
(Optional)

	Volume of liquid water collected	
	Implinger volume, ml	Silica gel weight, g
Final		
Initial		
Liquid collected		
Total volume collected		g[1] or ml

[1]Convert weight of water to volume by dividing total weight increase by density of water (1 g/ml).

$$\frac{\text{Increase, g}}{\text{(1 g/ml)}} = \text{Volume water, ml}$$

Figure 5G-4. Analysis Data Sheet.

METHOD 5H—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM WOOD HEATERS FROM A STACK LOCATION

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 2, Method 3, Method 5, Method 5G, Method 6, Method 6C, Method 16A, and Method 28.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of PM and condensible emissions from wood heaters.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Particulate matter is withdrawn proportionally from the wood heater exhaust and is collected on two glass fiber filters separated by impingers immersed in an ice water bath. The first filter is maintained at a temperature of no greater than 120 °C (248 °F). The second filter and the impinger system are cooled such that the temperature of the gas exiting the second filter is no greater than 20 °C (68 °F). The particulate mass collected in the probe, on the filters, and in the impingers is determined gravimetrically after the removal of uncombined water.

3.0 Definitions

Same as in Method 6C, section 3.0.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Sample Collection. The following items are required for sample collection:

6.1.1 Sampling Train. The sampling train configuration is shown in Figure 5H–1. Same as Method 5, section 6.1.1, with the exception of the following:

6.1.1.1 Probe Nozzle. The nozzle is optional; a straight sampling probe without a nozzle is an acceptable alternative.

6.1.1.2 Probe Liner. Same as Method 5, section 6.1.1.2, except that the maximum length of the sample probe shall be 0.6 m (2 ft) and probe heating is optional.

6.1.1.3 Filter Holders. Two each of borosilicate glass, with a glass frit or stainless steel filter support and a silicone rubber, Teflon, or Viton gasket. The holder design shall provide a positive seal against leakage from the outside or around the filter. The front filter holder shall be attached immediately at the outlet of the probe and prior to the first impinger. The second filter holder shall be attached on the outlet of the third impinger and prior to the inlet of the fourth (silica gel) impinger.

6.1.2 Barometer. Same as Method 5, section 6.2.

6.1.3 Stack Gas Flow Rate Measurement System. A schematic of an example test system is shown in Figure 5H–2. The flow rate measurement system consists of the following components:

6.1.3.1 Sample Probe. A glass or stainless steel sampling probe.

6.1.3.2 Gas Conditioning System. A high density filter to remove particulate matter and a condenser capable of lowering the dew point of the gas to less than 5 °C (40 °F). Desiccant, such as Drierite, may be used to dry the sample gas. Do not use silica gel.

6.1.3.3 Pump. An inert (*e.g.*, Teflon or stainless steel heads) sampling pump capable of delivering more than the total amount of sample required in the manufacturer's instructions for the individual instruments. A means of controlling the analyzer flow rate and a device for determining proper sample flow rate (*e.g.*, precision rotameter, pressure gauge downstream of all flow controls) shall be provided at the analyzer. The requirements for measuring and controlling the analyzer flow rate are not applicable if data are presented that demonstrate that the analyzer is insensitive to flow variations over the range encountered during the test.

6.1.3.4 Carbon Monoxide (CO) Analyzer. Any analyzer capable of providing a measure of CO in the range of 0 to 10 percent by volume at least once every 10 minutes.

6.1.3.5 Carbon Dioxide (CO_2) Analyzer. Any analyzer capable of providing a measure of CO_2 in the range of 0 to 25 percent by volume at least once every 10 minutes.

NOTE: Analyzers with ranges less than those specified above may be used provided actual concentrations do not exceed the range of the analyzer.

6.1.3.6 Manifold. A sampling tube capable of delivering the sample gas to two analyzers and handling an excess of the total amount used by the analyzers. The excess gas is exhausted through a separate port.

6.1.3.7 Recorders (optional). To provide a permanent record of the analyzer outputs.

6.1.4 Proportional Gas Flow Rate System. To monitor stack flow rate changes and provide a measurement that can be used to adjust and maintain particulate sampling flow rates proportional to the stack gas flow rate. A schematic of the proportional flow rate system is shown in Figure 5H–2 and consists of the following components:

6.1.4.1 Tracer Gas Injection System. To inject a known concentration of sulfur dioxide (SO_2) into the flue. The tracer gas injection system consists of a cylinder of SO_2, a gas cylinder regulator, a stainless steel needle valve or flow controller, a nonreactive (stainless steel and glass) rotameter, and an injection loop to disperse the SO_2 evenly in the flue.

6.1.4.2 Sample Probe. A glass or stainless steel sampling probe.

6.1.4.3 Gas Conditioning System. A combustor as described in Method 16A, sections 6.1.5 and 6.1.6, followed by a high density filter to remove particulate matter, and a condenser capable of lowering the dew point of the gas to less than 5 °C (40 °F). Desiccant, such as Drierite, may be used to dry the sample gas. Do not use silica gel.

6.1.4.4 Pump. Same as described in section 6.1.3.3.

6.1.4.5 SO_2 Analyzer. Any analyzer capable of providing a measure of the SO_2 concentration in the range of 0 to 1,000 ppm by volume (or other range necessary to measure the SO_2 concentration) at least once every 10 minutes.

6.1.4.6 Recorder (optional). To provide a permanent record of the analyzer outputs.

NOTE: Other tracer gas systems, including helium gas systems, are acceptable for determination of instantaneous proportional sampling rates.

6.2 Sample Recovery. Same as Method 5, section 6.2.

6.3 Sample Analysis. Same as Method 5, section 6.3, with the addition of the following:

6.3.1 Separatory Funnel. Glass or Teflon, 500-ml or greater.

7.0 Reagents and Standards

7.1 Sample Collection. Same as Method 5, section 7.1, including deionized distilled water.

7.2 Sample Recovery. Same as Method 5, section 7.2.

7.3 Sample Analysis. The following reagents and standards are required for sample analysis:

7.3.1 Acetone. Same as Method 5 section 7.2.

7.3.2 Dichloromethane (Methylene Chloride). Reagent grade, <0.001 percent residue in glass bottles.

7.3.3 Desiccant. Anhydrous calcium sulfate, calcium chloride, or silica gel, indicating type.

7.3.4 Cylinder Gases. For the purposes of this procedure, span value is defined as the upper limit of the range specified for each analyzer as described in section 6.1.3.4 or 6.1.3.5. If an analyzer with a range different from that specified in this method is used, the span value shall be equal to the upper limit of the range for the analyzer used (see note in section 6.1.3.5).

7.3.4.1 Calibration Gases. The calibration gases for the CO_2, CO, and SO_2 analyzers shall be CO_2 in nitrogen (N_2), CO in N_2, and SO_2 in N_2, respectively. CO_2 and CO calibration gases may be combined in a single cylinder. Use three calibration gases as specified in Method 6C, sections 7.2.1 through 7.2.3.

7.3.4.2 SO_2 Injection Gas. A known concentration of SO_2 in N_2. The concentration must be at least 2 percent SO_2 with a maximum of 100 percent SO_2.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Pretest Preparation. Same as Method 5, section 8.1.

8.2 Calibration Gas and SO_2 Injection Gas Concentration Verification, Sampling System Bias Check, Response Time Test, and Zero and Calibration Drift Tests. Same as Method 6C, sections 8.2.1, 8.2.3, 8.2.4, and 8.5, respectively, except that for verification of CO and CO_2 gas concentrations, substitute Method 3 for Method 6.

8.3 Preliminary Determinations.

8.3.1 Sampling Location. The sampling location for the particulate sampling probe shall be 2.45 ±0.15 m (8 ±0.5 ft) above the platform upon which the wood heater is placed (*i.e.*, the top of the scale).

8.3.2 Sampling Probe and Nozzle. Select a nozzle, if used, sized for the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain proportional sampling rates. During the run, do not change the nozzle size. Select a suitable probe liner and probe length to effect minimum blockage.

8.4 Preparation of Particulate Sampling Train. Same as Method 5, section 8.3, with the exception of the following:

8.4.1 The train should be assembled as shown in Figure 5H–1.

8.4.2 A glass cyclone may not be used between the probe and filter holder.

8.5 Leak-Check Procedures.

8.5.1 Leak-Check of Metering System Shown in Figure 5H–1. That portion of the sampling train from the pump to the orifice meter shall be leak-checked after each certification or audit test. Use the procedure described in Method 5, section 8.4.1.

8.5.2 Pretest Leak-Check. A pretest leak-check of the sampling train is recommended, but not required. If the pretest leak-check is conducted, the procedures outlined in Method 5, section 8.5.2 should be used. A vacuum of 130 mm Hg (5 in. Hg) may be used instead of 380 mm Hg (15 in. Hg).

8.5.2 Leak-Checks During Sample Run. If, during the sampling run, a component (*e.g.*, filter assembly or impinger) change becomes necessary, conduct a leak-check as described in Method 5, section 8.4.3.

8.5.3 Post-Test Leak-Check. A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be performed in accordance with the procedures outlined in Method 5, section 8.4.4, except that a vacuum of 130 mm Hg (5 in. Hg) or the greatest vacuum measured during the test run, whichever is greater, may be used instead of 380 mm Hg (15 in. Hg).

8.6 Tracer Gas Procedure. A schematic of the tracer gas injection and sampling systems is shown in Figure 5H–2.

8.6.1 SO_2 Injection Probe. Install the SO_2 injection probe and dispersion loop in the stack at a location 2.9 ±0.15 m (9.5 ±0.5 ft) above the sampling platform.

8.6.2 SO_2 Sampling Probe. Install the SO_2 sampling probe at the centroid of the stack at a location 4.1 ±0.15 m (13.5 ±0.5 ft) above the sampling platform.

8.7 Flow Rate Measurement System. A schematic of the flow rate measurement system is shown in Figure 5H–2. Locate the flow rate measurement sampling probe at the centroid of the stack at a location 2.3 ±0.3 m (7.5 ±1 ft) above the sampling platform.

8.8 Tracer Gas Procedure. Within 1 minute after closing the wood heater door at the start of the test run (as defined in Method 28, section 8.8.1), meter a known concentration of SO_2 tracer gas at a constant flow rate into the wood heater stack. Monitor the SO_2 concentration in the stack, and record the SO_2 concentrations at 10-minute intervals or more often. Adjust the particulate sampling flow rate proportionally to the SO_2 concentration changes using Equation 5H–6 (*e.g.*, the SO_2 concentration at the first 10-minute reading is measured to be 100 ppm; the next 10 minute SO_2 concentration is measured to be 75 ppm: the particulate sample flow rate is adjusted from the initial 0.15 cfm to 0.20 cfm). A check for proportional rate variation shall be made at the completion of the test run using Equation 5H–10.

8.9 Volumetric Flow Rate Procedure. Apply stoichiometric relationships to the wood combustion process in determining the exhaust gas flow rate as follows:

8.9.1 Test Fuel Charge Weight. Record the test fuel charge weight (wet) as specified in Method 28, section 8.8.2. The wood is assumed to have the following weight percent composition: 51 percent carbon, 7.3 percent hydrogen, 41 percent oxygen. Record the wood moisture for each fuel charge as described in Method 28, section 8.6.5. The ash is assumed to have negligible effect on associated C, H, and O concentrations after the test burn.

8.9.2 Measured Values. Record the CO and CO_2 concentrations in the stack on a dry basis every 10 minutes during the test run or more often. Average these values for the test run. Use as a mole fraction (*e.g.*, 10 percent CO_2 is recorded as 0.10) in the calculations to express total flow (see Equation 5H–6).

8.10 Sampling Train Operation.

8.10.1 For each run, record the data required on a data sheet such as the one shown in Figure 5H–3. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak-check, and when sampling is halted. Take other readings as indicated on Figure 5H–3 at least once each 10 minutes during the test run.

8.10.2 Remove the nozzle cap, verify that the filter and probe heating systems are up to temperature, and that the probe is properly positioned. Position the nozzle, if used, facing into gas stream, or the probe tip in the 50 mm (2 in.) centroidal area of the stack.

8.10.3 Be careful not to bump the probe tip into the stack wall when removing or inserting the probe through the porthole; this minimizes the chance of extracting deposited material.

8.10.4 When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

8.10.5 Begin sampling at the start of the test run as defined in Method 28, section 8.8.1, start the sample pump, and adjust the sample flow rate to between 0.003 and 0.014 m^3/min (0.1 and 0.5 cfm). Adjust the sample flow rate proportionally to the stack gas flow during the test run according to the procedures outlined in section 8. Maintain a proportional sampling rate (within 10 percent of the desired value) and a filter holder temperature no greater than 120 °C (248 °F).

8.10.6 During the test run, make periodic adjustments to keep the temperature around the filter holder at the proper level. Add more ice to the impinger box and, if necessary, salt to maintain a temperature of less than 20 °C (68 °F) at the condenser/silica gel outlet.

8.10.7 If the pressure drop across the filter becomes too high, making proportional sampling difficult to maintain, either filter may be replaced during a sample run. It is recommended that another complete filter assembly be used rather than attempting to change the filter itself. Before a new filter assembly is installed, conduct a leak-check (see section 8.5.2). The total particulate weight shall include the summation of all filter assembly catches. The total time for changing sample train components shall not exceed 10 minutes. No more than one component change is allowed for any test run.

8.10.8 At the end of the test run, turn off the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak-check, as outlined in section 8.5.3.

8.11 Sample Recovery. Same as Method 5, section 8.7, with the exception of the following:

8.11.1 Blanks. The volume of the acetone blank may be about 50-ml, rather than 200-ml; a 200-ml water blank shall also be saved for analysis.

8.11.2 Samples.

8.11.2.1 Container Nos. 1 and 1A. Treat the two filters according to the procedures outlined in Method 5, section 8.7.6.1. The filters

may be stored either in a single container or in separate containers.

8.11.2.2 Container No. 2. Same as Method 5, section 8.7.6.2, except that the container should not be sealed until the impinger rinse solution is added (see section 8.10.2.4).

8.11.2.3 Container No. 3. Treat the impingers as follows: Measure the liquid which is in the first three impingers to within 1-ml by using a graduated cylinder or by weighing it to within 0.5 g by using a balance (if one is available). Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas. Transfer the water from the first, second, and third impingers to a glass container. Tighten the lid on the sample container so that water will not leak out.

8.11.2.4 Rinse impingers and graduated cylinder, if used, with acetone three times or more. Avoid direct contact between the acetone and any stopcock grease or collection of any stopcock grease in the rinse solutions. Add these rinse solutions to sample Container No. 2.

8.11.2.5 Container No. 4. Same as Method 5, section 8.7.6.3

8.12 Sample Transport. Whenever possible, containers should be transferred in such a way that they remain upright at all times.

NOTE: Requirements for capping and transport of sample containers are not applicable if sample recovery and analysis occur in the same room.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.2	Sampling system bias check	Ensures that bias introduced by measurement system, minus analyzer, is no greater than 3 percent of span.
8.2	Analyzer zero and calibration drift tests	Ensures that bias introduced by drift in the measurement system output during the run is no greater than 3 percent of span.
8.5, 10.1, 12.13	Sampling equipment leak-check and calibration; proportional sampling rate verification.	Ensures accurate measurement of stack gas flow rate, sample volume.
10.1	Analytical balance calibration	Ensure accurate and precise measurement of collected particulate.
10.3	Analyzer calibration error check	Ensures that bias introduced by analyzer calibration error is no greater than 2 percent of span.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory record of all calibrations.

10.1 Volume Metering System, Temperature Sensors, Barometer, and Analytical Balance. Same as Method 5G, sections 10.2 through 10.5, respectively.

10.2 SO_2 Injection Rotameter. Calibrate the SO_2 injection rotameter system with a soap film flowmeter or similar direct volume measuring device with an accuracy of 2 percent. Operate the rotameter at a single reading for at least three calibration runs for 10 minutes each. When three consecutive calibration flow rates agree within 5 percent, average the three flow rates, mark the rotameter at the calibrated setting, and use the calibration flow rate as the SO_2 injection flow rate during the test run. Repeat the rotameter calibration before the first certification test and semiannually thereafter.

10.3. Gas Analyzers. Same as Method 6C, section 10.0.

10.4 Field Balance Calibration Check. Check the calibration of the balance used to weigh impingers with a weight that is at least 500g or within 50g of a loaded impinger. The weight must be ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 6 (or better). Daily before use, the field balance must measure the weight within ± 0.5g of the certified mass. If the daily balance calibration check fails, perform corrective measures and repeat the check before using balance.

10.5 Analytical Balance Calibration. Perform a multipoint calibration (at least five points spanning the operational range) of the analytical balance before the first use, and semiannually thereafter. The calibration of the analytical balance must be conducted using ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 2 (or better) tolerance weights. Audit the balance each day it is used for gravimetric measurements by weighing at least one ASTM E617–13 Class 2 tolerance (or better) calibration weight that corresponds to 50 to 150 percent of the weight of one filter or between 1g and 5g. If the scale cannot reproduce the value of the calibration weight to within 0.5 mg of the certified mass, perform corrective measures, and conduct the multipoint calibration before use.

11.0 Analytical Procedure

11.1 Record the data required on a sheet such as the one shown in Figure 5H–4.

11.2 Handle each sample container as follows:

11.2.1 Container Nos. 1 and 1A. Treat the two filters according to the procedures outlined in Method 5, section 11.2.1.

11.2.2 Container No. 2. Same as Method 5, section 11.2.2, except that the beaker may be smaller than 250-ml.

11.2.3 Container No. 3. Note the level of liquid in the container and confirm on the analysis sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Determination of sample leakage is not applicable if sample recovery and analysis occur in the same room. Measure the liquid in this container either volumetrically to within 1-ml or gravimetrically to within 0.5 g. Transfer the contents to a 500-ml or larger separatory funnel. Rinse the container with water, and add to the separatory funnel. Add 25-ml of dichloromethane to the separatory funnel, stopper and vigorously shake 1 minute, let separate and transfer the dichloromethane (lower layer) into a tared beaker or evaporating dish. Repeat twice more. It is necessary to rinse Container No. 3 with dichloromethane. This rinse is added to the impinger extract container. Transfer the remaining water from the separatory funnel to a tared beaker or evaporating dish and evaporate to dryness at 104 °C (220 °F). Desiccate and weigh to a constant weight. Evaporate the combined impinger water extracts at ambient temperature and pressure. Desiccate and weigh to a constant weight. Report both results to the nearest 0.1 mg.

11.2.4 Container No. 4. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance.

11.2.5 Acetone Blank Container. Same as Method 5, section 11.2.4, except that the beaker may be smaller than 250 ml.

11.2.6 Dichloromethane Blank Container. Treat the same as the acetone blank.

11.2.7 Water Blank Container. Transfer the water to a tared 250 ml beaker and evaporate to dryness at 104 °C (220 °F). Desiccate and weigh to a constant weight.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

12.1 Nomenclature.

A = Sample flow rate adjustment factor.
BR = Dry wood burn rate, kg/hr (lb/hr), from Method 28, Section 8.3.
B_{ws} = Water vapor in the gas stream, proportion by volume.
C_i = Tracer gas concentration at inlet, ppmv.
C_o = Tracer gas concentration at outlet, ppmv.
C_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (g/dscf).
E = Particulate emission rate, g/hr (lb/hr).
ΔH = Average pressure differential across the orifice meter (see Figure 5H–1), mm H_2O (in. H_2O).
L_a = Maximum acceptable leakage rate for either a post-test leak-check or for a leak-check following a component change; equal to 0.00057 cmm (0.020 cfm) or 4 percent of the average sampling rate, whichever is less.
L_1 = Individual leakage rate observed during the leak-check conducted before a component change, cmm (cfm).
L_p = Leakage rate observed during the post-test leak-check, cmm (cfm).
m_n = Total amount of particulate matter collected, mg.
M_a = Mass of residue of solvent after evaporation, mg.
N_C = Grams of carbon/gram of dry fuel (lb/lb), equal to 0.0425.
N_T = Total dry moles of exhaust gas/kg of dry wood burned, g-moles/kg (lb-moles/lb).
PR = Percent of proportional sampling rate.
P_{bar} = Barometric pressure at the sampling site, mm Hg (in.Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in.Hg).
Q_i = Gas volumetric flow rate at inlet, cfm (l/min).
Q_o = Gas volumetric flow rate at outlet, cfm (l/min).

12.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 5H–3).

12.3 Dry Gas Volume. Same as Method 5, section 12.3.

12.4 Volume of Water Vapor.

$$V_{w(std)} = K_2 V_{1c} \qquad \text{Eq. 5H-1}$$

Where:

K_2 = 0.001333 m^3/ml for metric units.
K_2 = 0.04707 ft^3/ml for English units.

12.5 Moisture Content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad \text{Eq. 5H-2}$$

12.6 Solvent Wash Blank.

$$W_a = \frac{M_a V_{aw}}{V_a} \qquad \text{Eq. 5H-3}$$

12.7 Total Particulate Weight. Determine the total particulate catch from the sum of the weights obtained from containers 1, 2, 3,

and 4 less the appropriate solvent blanks (see Figure 5H–4).

NOTE: Refer to Method 5, section 8.5 to assist in calculation of results involving two filter assemblies.

12.8 Particulate Concentration.

$$C_s = \frac{0.001g}{mg}\ \frac{m_n}{V_{m(std)}} \qquad \text{Eq. 5H-4}$$

12.9 Sample Flow Rate Adjustment.

$$a = \frac{S_1}{S_i} \qquad \text{Eq. 5H-5}$$

12.10 Carbon Balance for Total Moles of Exhaust Gas (dry)/kg of Wood Burned in the Exhaust Gas.

$$N_T = \frac{K_3 N_C}{Y_{CO_2} + Y_{CO} + Y_{HC}} \qquad \text{Eq. 5H-6}$$

Where:

K_3 = 1000 g/kg for metric units.
K_3 = 1.0 lb/lb for English units.

NOTE: The NO_X/SO_X portion of the gas is assumed to be negligible.

12.11 Total Stack Gas Flow Rate.

$$Q_{sd} = K_4\ N_T\ BR \qquad \text{Eq. 5H-7}$$

Where:

K_4 = 0.02406 dscm/g-mole for metric units.
K_4 = 384.8 dscf/lb-mole for English units.

12.12 Particulate Emission Rate.

$$E = C_s\ Q_{sd} \qquad \text{Eq. 5H-8}$$

12.13 Proportional Rate Variation. Calculate PR for each 10-minute interval, i, of the test run.

$$PR = \frac{\theta\ S_i V_{mi(std)}}{10\sum_{i=1}^{N}\left[S_i V_{mi(std)}\right]} \times 100 \qquad \text{Eq. 5H-9}$$

12.14 Acceptable Results. If no more than 15 percent of the PR values for all the intervals fall outside the range 90 percent ≤PR ≤110 percent, and if no PR value for any interval falls outside the range 75 ≤PR ≤125 percent, the results are acceptable. If the PR values for the test runs are judged to be unacceptable, report the test run emission results, but do not include the test run results in calculating the weighted average emission rate, and repeat the test.

12.15 Alternative Tracer Gas Flow Rate Determination.

$$Q_o = \frac{Q_i \times C_i}{C_o} \qquad Eq.\ 5H-10$$

NOTE: This gives Q for a single instance only. Repeated multiple determinations are needed to track temporal variations. Very small variations in Q_i, C_i, or C_o may give very large variations in Q_o.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Alternative Stack Gas Volumetric Flow Rate Determination (Tracer Gas).

16.1.1 Apparatus.

16.1.1.1 Tracer Gas Injector System. This is to inject a known concentration of tracer gas into the stack. This system consists of a cylinder of tracer gas, a gas cylinder regulator, a stainless steel needle valve or a flow controller, a nonreactive (stainless steel or glass) rotameter, and an injection loop to disperse the tracer gas evenly in the stack.

16.1.1.2 Tracer Gas Probe. A glass or stainless steel sampling probe.

16.1.1.3 Gas Conditioning System. A gas conditioning system is suitable for delivering a cleaned sample to the analyzer consisting of a filter to remove particulate and a condenser capable of lowering the dew point of the sample gas to less than 5 °C (40 °F). A desiccant such as anhydrous calcium sulfate may be used to dry the sample gas. Desiccants which react or absorb tracer gas or stack gas may not be used, e.g. silica gel absorbs CO_2.

16.1.1.4 Pump. An inert (*i.e.*, stainless steel or Teflon head) pump to deliver more than the total sample required by the manufacturer's specifications for the analyzer used to measure the downstream tracer gas concentration.

16.1.1.5 Gas Analyzer. A gas analyzer is any analyzer capable of measuring the tracer gas concentration in the range necessary at least every 10 minutes. A means of controlling the analyzer flow rate and a device for determining proper sample flow rate shall be provided unless data is provided to show that the analyzer is insensitive to flow variations over the range encountered during the test.

The gas analyzer needs to meet or exceed the following performance specifications:

Linearity	±1 percent of full scale.
Calibration Error	≤2 percent of span.
Response Time	≤10 seconds.
Zero Drift (24 hour)	≤2 percent of full scale.
Span Drift (24 hour)	≤2 percent of full scale.
Resolution	≤0.5 percent of span.

16.1.1.6 Recorder (optional). To provide a permanent record of the analyzer output.

16.1.2 Reagents.

16.1.2.1 Tracer Gas. The tracer gas is sulfur hexafluoride in an appropriate concentration for accurate analyzer measurement or pure sulfur dioxide. The gas used must be nonreactive with the stack effluent and give minimal (<3 percent) interference to measurement by the gas analyzer.

16.1.3 Procedure. Select upstream and downstream locations in the stack or duct for introducing the tracer gas and delivering the sampled gas to the analyzer. The inlet location should be 8 or more duct diameters beyond any upstream flow disturbance. The outlet should be 8 or more undisturbed duct diameters from the inlet and 2 or more duct diameters from the duct exit. After installing the apparatus, meter a known concentration of the tracer gas into the stack at the inlet location. Use the gas sample probe and analyzer to show that no stratification of the tracer gas is found in the stack at the measurement locations. Monitor the tracer gas concentration from the outlet location and record the concentration at 10-minute intervals or more often at the option of the tester. A minimum of three measured intervals is recommended to determine the stack gas volumetric flow rate. Other statistical procedures may be applied for complete flow characterization and additional QA/QC.

17.0 References

Same as Method 5G, section 17.0.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

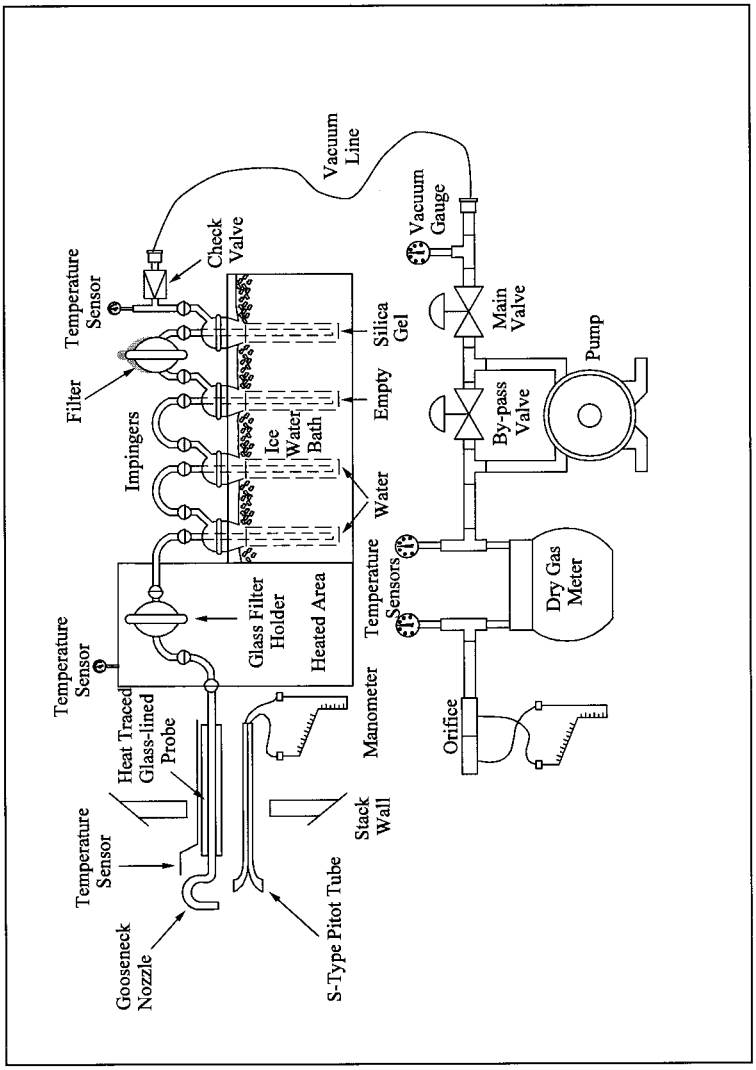


Figure 5H-1. Sampling Train.

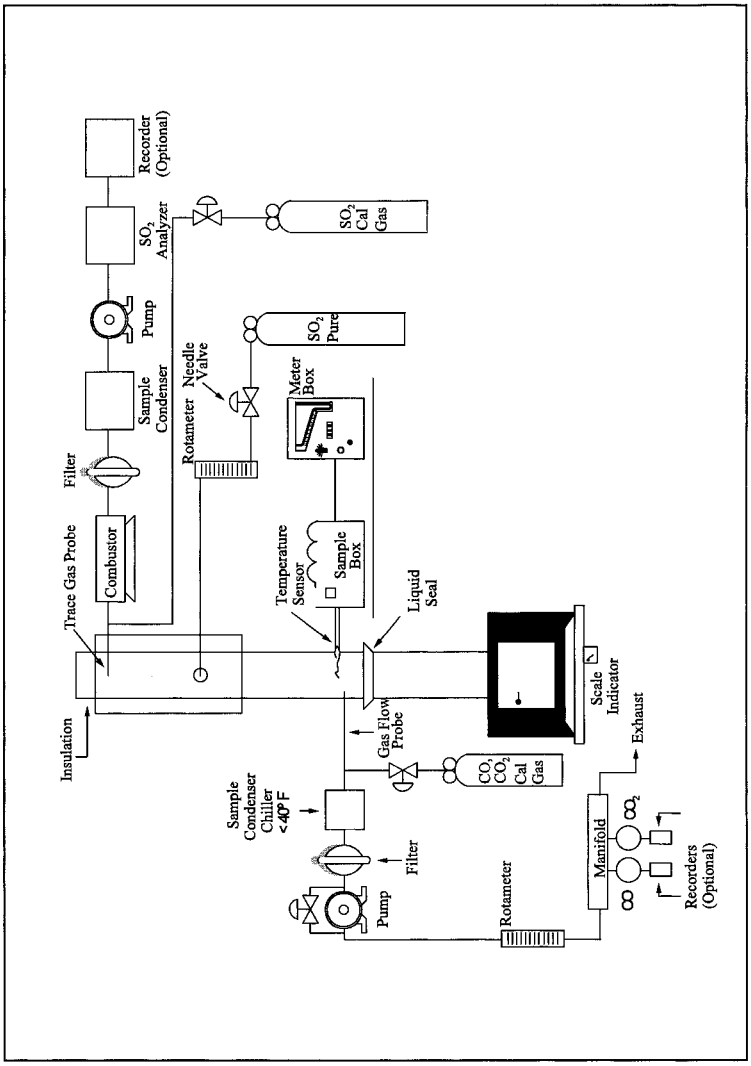


Figure 5H-2. Test System Schematic.

Stove _____ Pitot tube coefficient, Cp _____
Test Method _____ Room temperature, C°, (°F) _____
Operator _____ Barometric pressure mb (in. Hg) _____
Date _____ Measured or assumed moisture, % _____
Run No. _____ Nozzle identification No. _____
Start Time _____ Average calibrated nozzle diameter, mm (in.) _____
Stop Time _____ Final leak rate, m³/min, (cfm) _____
Sample Box No. _____ Probe liner material _____
Meter Box No. _____ Draft or static pressure, mm H_2O (in. H_2O) _____
Meter ΔH @ (Optional) _____ Filter Nos. _____
C Factor _____

Clock time	Test run time (q), min.	Vacuum mm Hg (in. Hg)	Fuel temperature (T_s) °C (°F)	Flow in Flue m³/ min (ft³/min)	Volume sample in period m³(ft³)	Gas meter volume m³ (ft³)	Gas sample temperature at dry gas meter °C (°F)		Front filter holder temperature °C (°F)	Temperature of gas leaving dryer or last impinger °C (°F)
								°C (°F)		
Total							Avg.	Avg.		
Average							Avg.			

Figure 5H-3. Sampling Data Sheet.

Stove _____
Date _____
Run No. _____
Filter Nos. _____
Amount liquid lost during transport, ml _____
Acetone blank volume, ml _____
Acetone wash volume, ml _____
Acetone blank concentration, mg/ml _____
Acetone wash blank, mg _____

Dichloromethane blank volume, ml _____
Dichloromethane wash volume, ml _____
Dichloromethane blank concentration, mg/ml _____
Dichloromethane wash blank, mg _____
Water blank volume, ml _____
Waster wash volume, ml _____
Water blank concentration, mg/ml _____
Water wash blank, mg _____

Container number	Weight of particulate collected, mg		
	Final weight	Tare weight	Weight gain
1 _____			
2 _____			
3 _____			
4 _____			
5 _____			
Total			
Less acetone blank			
Less dichloromethane blank			
Less water blank			
Weight of particulate matter			

	Volume of liquid water collected	
	Impinger volume, ml	Silica gel weight, g
Final _____		
Initial _____		
Liquid collected _____		
Total volume collected _____		g or ml

* Convert weight of water to volume by dividing total weight increase by density of water (1 g/ml).

$$\frac{\text{Increase, g}}{\text{(1 g/ml)}} = \text{Volume water, ml}$$

Figure 5H-4. Analysis data sheet.

Figure 5H-4. Analysis Data Sheet.

METHOD 5I—DETERMINATION OF LOW LEVEL PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Certain information is contained in other EPA procedures found in this part. Therefore, to obtain reliable results, persons using this method should have experience with and a thorough knowledge of the following Methods: Methods 1, 2, 3, 4 and 5.

1. Scope and Application.

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of low level particulate matter (PM) emissions from stationary sources. The method is most effective for total PM catches of 50 mg or less. This method was initially developed for performing correlation of manual PM measurements to PM continuous emission monitoring systems (CEMS), however it is also useful for other low particulate concentration applications.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods. Method 5I requires the use of paired trains. Acceptance criteria for the identification of data quality outliers from the paired trains are provided in section 12.2 of this Method.

2. Summary of Method.

2.1. Description. The system setup and operation is essentially identical to Method 5. Particulate is withdrawn isokinetically from the source and collected on a 47 mm glass fiber filter maintained at a temperature of 120 ±14 °C (248 ±25 °F). The PM mass is determined by gravimetric analysis after the removal of uncombined water. Specific measures in this procedure designed to improve system performance at low particulate levels include:

1. Improved sample handling procedures
2 Light weight sample filter assembly
3. Use of low residue grade acetone

Accuracy is improved through the minimization of systemic errors associated with sample handling and weighing procedures. High purity reagents, all glass, grease free, sample train components, and light weight filter assemblies and beakers, each contribute to the overall objective of improved precision and accuracy at low particulate concentrations.

2.2 Paired Trains. This method must be performed using a paired train configuration. These trains may be operated as co-located trains (to trains operating collecting from one port) or as simultaneous trains (separate trains operating from different ports at the same time). Procedures for calculating precision of the paired trains are provided in section 12.

2.3 Detection Limit. a. Typical detection limit for manual particulate testing is 0.5 mg. This mass is also cited as the accepted weight variability limit in determination of ''constant weight'' as cited in section 8.1.2 of this Method. EPA has performed studies to provide guidance on minimum PM catch. The minimum detection limit (MDL) is the minimum concentration or amount of an analyte that can be determined with a specified degree of confidence to be different from zero. We have defined the minimum or target catch as a concentration or amount sufficiently larger than the MDL to ensure that the results are reliable and repeatable. The particulate matter catch is the product of the average particulate matter concentration on a mass per volume basis and the volume of gas collected by the sample train. The tester can generally control the volume of gas collected by increasing the sampling time or to a lesser extent by increasing the rate at which sample is collected. If the tester has a reasonable estimate of the PM concentration from the source, the tester can ensure that the target catch is collected by sampling the appropriate gas volume.

b. However, if the source has a very low particulate matter concentration in the stack, the volume of gas sampled may need to be very large which leads to unacceptably long sampling times. When determining compliance with an emission limit, EPA guidance has been that the tester does not always have to collect the target catch. Instead, we have suggested that the tester sample enough stack gas, that if the source were exactly at the level of the emission standard, the sample catch would equal the target catch. Thus, if at the end of the test the catch were smaller than the target, we could still conclude that the source is in compliance though we might not know the exact emission level. This volume of gas becomes a target volume that can be translated into a target sampling time by assuming an average sampling rate. Because the MDL forms the basis for our guidance on target sampling times, EPA has conducted a systematic laboratory study to define what is the MDL for Method 5 and determined the Method to have a calculated practical quantitation limit (PQL) of 3 mg of PM and an MDL of 1 mg.

c. Based on these results, the EPA has concluded that for PM testing, the target catch must be no less than 3 mg. Those sample catches between 1 mg and 3 mg are between the detection limit and the limit of quantitation. If a tester uses the target catch to estimate a target sampling time that results in sample catches that are less than 3 mg, you should not automatically reject the results. If the tester calculated the target sampling time as described above by assuming that the source was at the level of the emission limit, the results would still be valid for determining that the source was in compliance. For purposes other than determining compliance, results should be divided into two categories—those that fall between 3 mg and 1 mg and those that are below 1 mg. A sample catch between 1 and 3 mg may be used for such purposes as calculating emission rates with the understanding that the resulting emission rates can have a high degree of uncertainty. Results of less than 1 mg should not be used for calculating emission rates or pollutant concentrations.

d. When collecting small catches such as 3 mg, bias becomes an important issue. Source testers must use extreme caution to reach the PQL of 3 mg by assuring that sampling

probes are very clean (perhaps confirmed by low blank weights) before use in the field. They should also use low tare weight sample containers, and establish a well-controlled balance room to weigh the samples.

3. Definitions.

3.1 *Light Weight Filter Housing.* A smaller housing that allows the entire filtering system to be weighed before and after sample collection. (See. 6.1.3)

3.2 *Paired Train.* Sample systems trains may be operated as co-located trains (two sample probes attached to each other in the same port) or as simultaneous trains (two separate trains operating from different ports at the same time).

4. Interferences.

a. There are numerous potential interferents that may be encountered during performance of Method 5I sampling and analyses. This Method should be considered more sensitive to the normal interferents typically encountered during particulate testing because of the low level concentrations of the flue gas stream being sampled.

b. Care must be taken to minimize field contamination, especially to the filter housing since the entire unit is weighed (not just the filter media). Care must also be taken to ensure that no sample is lost during the sampling process (such as during port changes, removal of the filter assemblies from the probes, etc.).

c. Balance room conditions are a source of concern for analysis of the low level samples. Relative humidity, ambient temperatures variations, air draft, vibrations and even barometric pressure can affect consistent reproducible measurements of the sample media. Ideally, the same analyst who performs the tare weights should perform the final weights to minimize the effects of procedural differences specific to the analysts.

d. Attention must also be provided to weighing artifacts caused by electrostatic charges which may have to be discharged or neutralized prior to sample analysis. Static charge can affect consistent and reliable gravimetric readings in low humidity environments. Method 5I recommends a relative humidity of less than 50 percent in the weighing room environment used for sample analyses. However, lower humidity may be encountered or required to address sample precision problems. Low humidity conditions can increase the effects of static charge.

e. Other interferences associated with typical Method 5 testing (sulfates, acid gases, etc.) are also applicable to Method 5I.

5. Safety.

Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety concerns associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability and observe all regulatory limitations before using this method.

6. Equipment and Supplies.

6.1 Sample Collection Equipment and Supplies. The sample train is nearly identical in configuration to the train depicted in Figure 5–1 of Method 5. The primary difference in the sample trains is the lightweight Method 5I filter assembly that attaches directly to the exit to the probe. Other exceptions and additions specific to Method 5I include:

6.1.1 Probe Nozzle. Same as Method 5, with the exception that it must be constructed of borosilicate or quartz glass tubing.

6.1.2 Probe Liner. Same as Method 5, with the exception that it must be constructed of borosilicate or quartz glass tubing.

6.1.3 Filter Holder. The filter holder is constructed of borosilicate or quartz glass front cover designed to hold a 47-mm glass fiber filter, with a wafer thin stainless steel (SS) filter support, a silicone rubber or Viton O-ring, and Teflon tape seal. This holder design will provide a positive seal against leakage from the outside or around the filter. The filter holder assembly fits into a SS filter holder and attaches directly to the outlet of the probe. The tare weight of the filter, borosilicate or quartz glass holder, SS filter support, O-ring and Teflon tape seal generally will not exceed approximately 35 grams. The filter holder is designed to use a 47-mm glass fiber filter meeting the quality criteria in of Method 5. These units are commercially available from several source testing equipment vendors. Once the filter holder has been assembled, desiccated and tared, protect it from external sources of contamination by covering the front socket with a ground glass plug. Secure the plug with an impinger clamp or other item that will ensure a leak-free fitting.

6.2 Sample Recovery Equipment and Supplies. Same as Method 5, with the following exceptions:

6.2.1 Probe-Liner and Probe-Nozzle Brushes. Teflon or nylon bristle brushes with stainless steel wire handles, should be used to clean the probe. The probe brush must have extensions (at least as long as the probe) of Teflon, nylon or similarly inert material. The brushes must be properly sized and shaped for brushing out the probe liner and nozzle.

6.2.2 Wash Bottles. Two Teflon wash bottles are recommended however, polyethylene wash bottles may be used at the option of the tester. Acetone should not be stored in polyethylene bottles for longer than one month.

6.2.3 Filter Assembly Transport. A system should be employed to minimize contamination of the filter assemblies during transport to and from the field test location. A carrying case or packet with clean compartments of sufficient size to accommodate each filter assembly can be used. This system should have an air tight seal to further minimize contamination during transport to and from the field.

6.3 Analysis Equipment and Supplies. Same as Method 5, with the following exception:

6.3.1 Lightweight Beaker Liner. Teflon or other lightweight beaker liners are used for the analysis of the probe and nozzle rinses. These light weight liners are used in place of the borosilicate glass beakers typically used for the Method 5 weighings in order to improve sample analytical precision.

6.3.2 Anti-static Treatment. Commercially available gaseous anti-static rinses are recommended for low humidity situations that contribute to static charge problems.

7. Reagents and Standards.

7.1 Sampling Reagents. The reagents used in sampling are the same as Method 5 with the following exceptions:

7.1.1 Filters. The quality specifications for the filters are identical to those cited for Method 5. The only difference is the filter diameter of 47 millimeters.

7.1.2 Stopcock Grease. Stopcock grease cannot be used with this sampling train. We recommend that the sampling train be assembled with glass joints containing O-ring seals or screw-on connectors, or similar.

7.1.3 Acetone. Low residue type acetone, ≤0.001 percent residue, purchased in glass bottles is used for the recovery of particulate matter from the probe and nozzle. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers; thus, acetone blanks must be run prior to field use and only acetone with low blank values (≤0.001 percent residue, as specified by the manufacturer) must be used. Acetone blank correction is not allowed for this method; therefore, it is critical that high purity reagents be purchased and verified prior to use.

7.1.4 Gloves. Disposable, powder-free, latex surgical gloves, or their equivalent are used at all times when handling the filter housings or performing sample recovery.

7.2 Standards. There are no applicable standards commercially available for Method 5I analyses.

8. Sample Collection, Preservation, Storage, and Transport.

8.1 Pretest Preparation. Same as Method 5 with several exceptions specific to filter assembly and weighing.

8.1.1 Filter Assembly. Uniquely identify each filter support before loading filters into the holder assembly. This can be done with an engraving tool or a permanent marker. Use powder free latex surgical gloves whenever handling the filter holder assemblies. Place the O-ring on the back of the filter housing in the O-ring groove. Place a 47 mm glass fiber filter on the O-ring with the face down. Place a stainless steel filter holder against the back of the filter. Carefully wrap 5 mm (¼ inch) wide Teflon'' tape one timearound the outside of the filter holder overlapping the stainless steel filter support by approximately 2.5 mm (⅛ inch). Gently brush the Teflon tape down on the back of the stainless steel filter support. Store the filter assemblies in their transport case until time for weighing or field use.

8.1.2 Filter Weighing Procedures. a. Desiccate the entire filter holder assemblies at 20 ±5.6 °C (68 ±10 °F) and ambient pressure for at least 24 hours. Weigh at intervals of at least 6 hours to a constant weight, *i.e.,* 0.5 mg change from previous weighing. Record the results to the nearest 0.1 mg. During each weighing, the filter holder assemblies must not be exposed to the laboratory atmosphere for a period greater than 2 minutes and a relative humidity above 50 percent. Lower relative humidity may be required in order to improve analytical precision. However, low humidity conditions increase static charge to the sample media.

b. Alternatively (unless otherwise specified by the Administrator), the filters holder assemblies may be oven dried at 105 °C (220 °F) for a minimum of 2 hours, desiccated for 2 hours, and weighed. The procedure used for the tare weigh must also be used for the final weight determination.

c. Experience has shown that weighing uncertainties are not only related to the balance performance but to the entire weighing procedure. Therefore, before performing any measurement, establish and follow standard operating procedures, taking into account the sampling equipment and filters to be used.

8.2 Preliminary Determinations. Select the sampling site, traverse points, probe nozzle, and probe length as specified in Method 5.

8.3 Preparation of Sampling Train. Same as Method 5, section 8.3, with the following exception: During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until justbefore assembly or until sampling is about to begin. Using gloves, place a labeled (identified) and weighed filter holder assembly into the stainless steel holder. Then place this whole unit in the Method 5 hot box, and attach it to the probe. Do not use stopcock grease.

8.4 Leak-Check Procedures. Same as Method 5.

8.5 Sampling Train Operation.

8.5.1. Operation. Operate the sampling train in a manner consistent with those described in Methods 1, 2, 4 and 5 in terms of the number of sample points and minimum time per point. The sample rate and total gas volume should be adjusted based on estimated grain loading of the source being characterized. The total sampling time must be a function of the estimated mass of particulate to be collected for the run. Targeted mass to be collected in a typical Method 5I sample train should be on the order of 10 to 20 mg. Method 5I is most appropriate for total collected masses of less than 50 milligrams, however, there is not an exact particulate loading cutoff, and it is likely that some runs may exceed 50 mg. Exceeding 50 mg (or less than 10 mg) for the sample mass does not necessarily justify invalidating a sample run if all other Method criteria are met.

8.5.2 Paired Train. This Method requires PM samples be collected with paired trains.

8.5.2.1 It is important that the systems be operated truly simultaneously. This implies that both sample systems start and stop at the same times. This also means that if one sample system is stopped during the run, the other sample systems must also be stopped until the cause has been corrected.

8.5.2.2 Care should be taken to maintain the filter box temperature of the paired trains as close as possible to the Method required temperature of 120 ±14 °C (248 ±25 °F). If separate ovens are being used for simultaneously operated trains, it is recommended that the oven temperature of each train be maintained within ±14 °C (±25 °F) of each other.

8.5.2.3 The nozzles for paired trains need not be identically sized.

8.5.2.4 Co-located sample nozzles must be within the same plane perpendicular to the gas flow. Co-located nozzles and pitot assemblies should be within a 6.0 cm × 6.0 cm square (as cited for a quadruple train in Reference Method 301).

8.5.3 Duplicate gas samples for molecular weight determination need not be collected.

8.6 Sample Recovery. Same as Method 5 with several exceptions specific to the filter housing.

8.6.1 Before moving the sampling train to the cleanup site, remove the probe from the train and seal the nozzle inlet and outlet of the probe. Be careful not to lose any condensate that might be present. Cap the filter inlet using a standard ground glass plug and secure the cap with an impinger clamp. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger condenser and the filter holder, disconnect the line at the filter holder and let any condensed water or liquid drain into the impingers or condenser.

8.6.2 Transfer the probe and filter-impinger assembly to the cleanup area. This area must be clean and protected from the wind so that the possibility of losing any of the sample will be minimized.

8.6.3 Inspect the train prior to and during disassembly and note any abnormal conditions such as particulate color, filter loading, impinger liquid color, etc.

8.6.4 Container No. 1, Filter Assembly. Carefully remove the cooled filter holder assembly from the Method 5 hot box and place it in the transport case. Use a pair of clean gloves to handle the filter holder assembly.

8.6.5 Container No. 2, Probe Nozzle and Probe Liner Rinse. Rinse the probe and nozzle components with acetone. Be certain that the probe and nozzle brushes have been thoroughly rinsed prior to use as they can be a source of contamination.

8.6.6 All Other Train Components. (Impingers) Same as Method 5.

8.7 Sample Storage and Transport. Whenever possible, containers should be shipped in such a way that they remain upright at all times. All appropriate dangerous goods shipping requirements must be observed since acetone is a flammable liquid.

9. Quality Control.

9.1 Miscellaneous Field Quality Control Measures.

9.1.1 A quality control (QC) check of the volume metering system at the field site is suggested before collecting the sample using the procedures in Method 5, section 4.4.1.

9.1.2 All other quality control checks outlined in Methods 1, 2, 4 and 5 also apply to Method 5I. This includes procedures such as leak-checks, equipment calibration checks, and independent checks of field data sheets for reasonableness and completeness.

9.2 Quality Control Samples.

9.2.1 Required QC Sample. A laboratory reagent blank must be collected and analyzed for each lot of acetone used for a field program to confirm that it is of suitable purity. The particulate samples cannot be blank corrected.

9.2.2 Recommended QC Samples. These samples may be collected and archived for future analyses.

9.2.2.1 A field reagent blank is a recommended QC sample collected from a portion of the acetone used for cleanup of the probe and nozzle. Take 100 ml of this acetone directly from the wash bottle being used and place it in a glass sample container labeled ''field acetone reagent blank.'' At least one field reagent blank is recommended for every five runs completed. The field reagent blank samples demonstrate the purity of the acetone was maintained throughout the program.

9.2.2.2 A field bias blank train is a recommended QC sample. This sample is collected by recovering a probe and filter assembly that has been assembled, taken to the sample location, leak checked, heated, allowed to sit at the sample location for a similar duration of time as a regular sample run, leak-checked again, and then recovered in the same manner as a regular sample. Field bias blanks are not a Method requirement, however, they are recommended and are very useful for identifying sources of contamination in emission testing samples. Field bias blank train results greater than 5 times the method detection limit may be considered problematic.

10. Calibration and Standardization Same as Method 5, section 5.

10.1 Field Balance Calibration Check. Check the calibration of the balance used to weigh impingers with a weight that is at least 500g or within 50g of a loaded impinger. The weight must be ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 6 (or better). Daily, before use, the field balance must measure the weight within ±0.5g of the certified mass. If the daily balance calibration check fails, perform corrective measures and repeat the check before using balance.

10.2 Analytical Balance Calibration. Perform a multipoint calibration (at least five points spanning the operational range) of the analytical balance before the first use, and semiannually thereafter. The calibration of the analytical balance must be conducted using ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 2 (or better) tolerance weights. Audit the balance each day it is used for gravimetric measurements by weighing at least one ASTM E617–13 Class 2 tolerance (or better) calibration weight that corresponds to 50 to 150 percent of the weight of one filter or between 1g and 5g. If the scale cannot reproduce the value of the calibration weight to within 0.5 mg of the certified mass, perform corrective measures and conduct the multipoint calibration before use.

11. Analytical Procedures.

11.1 Analysis. Same as Method 5, sections 11.1–11.2.4, with the following exceptions:

11.1.1 Container No. 1. Same as Method 5, section 11.2.1, with the following exception: Use disposable gloves to remove each of the filter holder assemblies from the desiccator, transport container, or sample oven (after appropriate cooling).

11.1.2 Container No. 2. Same as Method 5, section 11.2.2, with the following exception: It is recommended that the contents of Container No. 2 be transferred to a 250 ml beaker with a Teflon liner or similar container that has a minimal tare weight before bringing to dryness.

12. Data Analysis and Calculations.

12.1 Particulate Emissions. The analytical results cannot be blank corrected for residual acetone found in any of the blanks. All other sample calculations are identical to Method 5.

12.2 Paired Trains Outliers. a. Outliers are identified through the determination of precision and any systemic bias of the paired trains. Data that do not meet this criteria should be flagged as a data quality problem. The primary reason for performing dual train sampling is to generate information to quantify the precision of the Reference Method data. The relative standard deviation (RSD) of paired data is the parameter used to quantify data precision. RSD for two simultaneously gathered data points is determined according to:

$$RSD = 100\% * \left|\left(C_a - C_b\right)\right| / \left(C_a + C_b\right)$$

where, Ca and Cb are concentration values determined from trains A and B respectively. For RSD calculation, the concentration units are unimportant so long as they are consistent.

b. A minimum precision criteria for Reference Method PM data is that RSD for any data pair must be less than 10% as long as the mean PM concentration is greater than 10 mg/dscm. If the mean PM concentration is less than 10 mg/dscm higher RSD values are acceptable. At mean PM concentration of 1 mg/dscm acceptable RSD for paired trains is 25%. Between 1 and 10 mg/dscm acceptable RSD criteria should be linearly scaled from 25% to 10%. Pairs of manual method data exceeding these RSD criteria should be eliminated from the data set used to develop a PM CEMS correlation or to assess RCA. If the mean PM concentration is less than 1 mg/dscm, RSD does not apply and the mean result is acceptable.

13. Method Performance [Reserved]

14. Pollution Prevention [Reserved]

15. Waste Management [Reserved]

16. Alternative Procedures. Same as Method 5.

17. Bibliography. Same as Method 5.

18. Tables, Diagrams, Flowcharts and Validation Data. Figure 5I–1 is a schematic of the sample train.

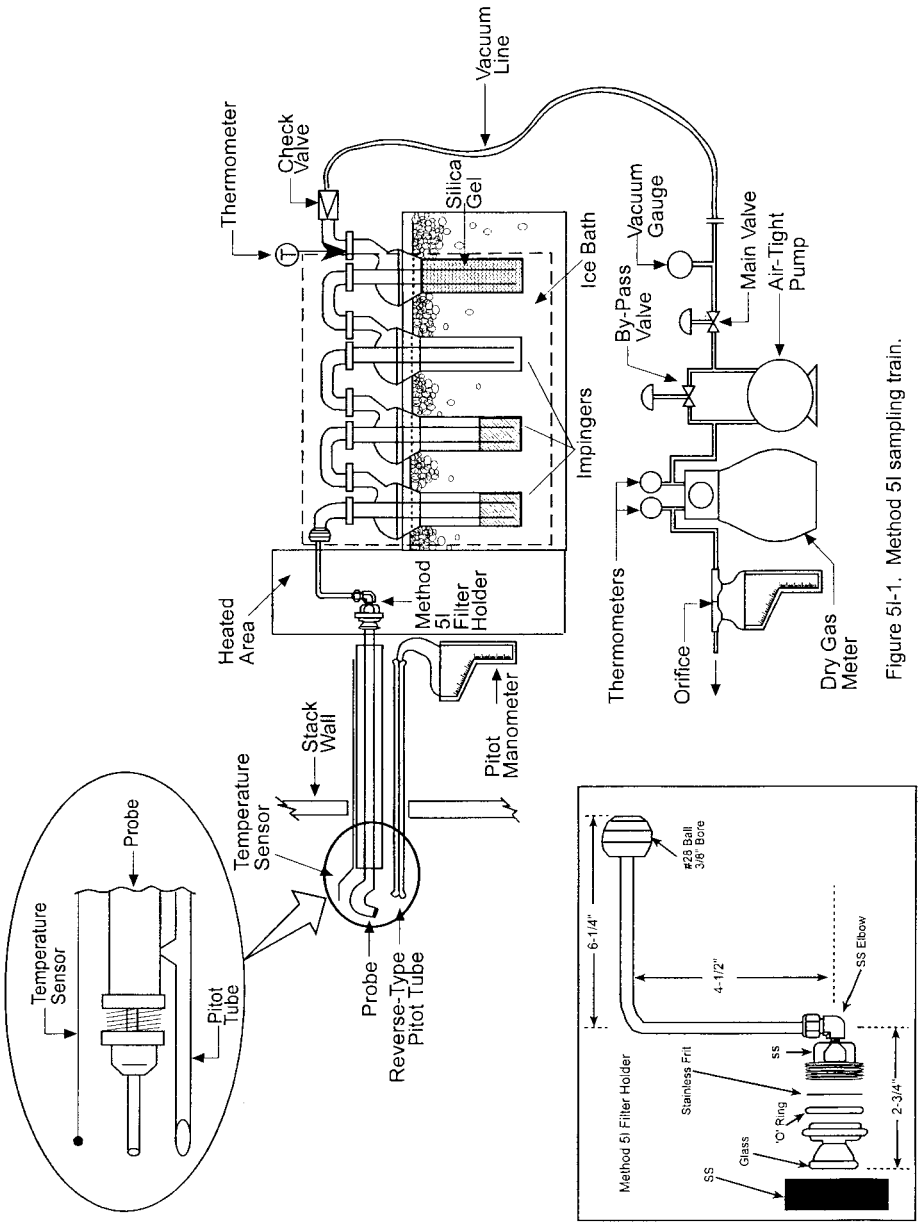


Figure 5I-1. Method 5I sampling train.

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–3 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at *www.fdsys.gov*.

State of Oregon Department of Environmental Quality

OAR 340-248-0270 Attachments

ASBESTOS and OTHER FIBERS by PCM 7400

FORMULA: Various MW: Various CAS: see Synonyms RTECS: Various

METHOD: 7400, Issue 2 **EVALUATION: FULL** **Issue 1: Rev. 3 on 15 May 1989**
Issue 2: 15 August 1994

OSHA: 0.1 asbestos fiber (> 5 µm long)/cc; 1 f/cc, 30 min excursion; carcinogen
MSHA: 2 asbestos fibers/cc
NIOSH: 0.1 f/cc (fibers > 5 µm long), 400 L; carcinogen
ACGIH: 0.2 f/cc crocidolite; 0.5 f/cc amosite; 2 f/cc chrysotile and other asbestos; carcinogen

PROPERTIES: solid, fibrous, crystalline, anisotropic

SYNONYMS [CAS #]: actinolite [77536-66-4] or ferroactinolite [15669-07-5]; amosite [12172-73-5]; anthophyllite [77536-67-5]; chrysotile [12001-29-5]; serpentine [18786-24-8]; crocidolite [12001-28-4]; tremolite [77536-68-6]; amphibole asbestos [1332-21-4]; refractory ceramic fibers [142844-00-6]; fibrous glass

SAMPLING

SAMPLER: FILTER (0.45- to 1.2-µm cellulose ester membrane, 25-mm; conductive cowl on cassette)

FLOW RATE*: 0.5 to 16 L/min

VOL-MIN*: 400 L @ 0.1 fiber/cc
-MAX*: (step 4, sampling)

*Adjust to give 100 to 1300 fiber/mm^2

SHIPMENT: routine (pack to reduce shock)

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 80 to 100 fibers counted

BIAS: see EVALUATION OF METHOD

OVERALL PRECISION ($\hat{S}_{rT}$): 0.115 to 0.13 [1]

ACCURACY: see EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE: LIGHT MICROSCOPY, PHASE CONTRAST

ANALYTE: fibers (manual count)

SAMPLE PREPARATION: acetone - collapse/triacetin - immersion method [2]

COUNTING RULES: described in previous version of this method as "A" rules [1,3]

EQUIPMENT:
1. positive phase-contrast microscope
2. Walton-Beckett graticule (100-µm field of view) Type G-22
3. phase-shift test slide (HSE/NPL)

CALIBRATION: HSE/NPL test slide

RANGE: 100 to 1300 fibers/mm^2 filter area

ESTIMATED LOD: 7 fibers/mm^2 filter area

PRECISION ($\bar{S}_r$): 0.10 to 0.12 [1]; see EVALUATION OF METHOD

APPLICABILITY: The quantitative working range is 0.04 to 0.5 fiber/cc for a 1000-L air sample. The LOD depends on sample volume and quantity of interfering dust, and is <0.01 fiber/cc for atmospheres free of interferences. The method gives an index of airborne fibers. It is primarily used for estimating asbestos concentrations, though PCM does not differentiate between asbestos and other fibers. Use this method in conjunction with electron microscopy (e.g., Method 7402) for assistance in identification of fibers. Fibers < ca. 0.25 µm diameter will not be detected by this method [4]. This method may be used for other materials such as fibrous glass by using alternate counting rules (see Appendix C).

INTERFERENCES: If the method is used to detect a specific type of fiber, any other airborne fiber may interfere since all particles meeting the counting criteria are counted. Chain-like particles may appear fibrous. High levels of non-fibrous dust particles may obscure fibers in the field of view and increase the detection limit.

OTHER METHODS: This revision replaces Method 7400, Revision #3 (dated 5/15/89).

REAGENTS:

1. Acetone,* reagent grade.
2. Triacetin (glycerol triacetate), reagent grade.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: field monitor, 25-mm, three-piece cassette with ca. 50-mm electrically conductive extension cowl and cellulose ester filter, 0.45- to 1.2-µm pore size, and backup pad.
   NOTE 1: Analyze representative filters for fiber background before use to check for clarity and background. Discard the filter lot if mean is ≥ 5 fibers per 100 graticule fields. These are defined as laboratory blanks. Manufacturer-provided quality assurance checks on filter blanks are normally adequate as long as field blanks are analyzed as described below.
   NOTE 2: The electrically conductive extension cowl reduces electrostatic effects. Ground the cowl when possible during sampling.
   NOTE 3: Use 0.8-µm pore size filters for personal sampling. The 0.45-µm filters are recommended for sampling when performing TEM analysis on the same samples. However, their higher pressure drop precludes their use with personal sampling pumps.
   NOTE 4: Other cassettes have been proposed that exhibit improved uniformity of fiber deposit on the filter surface, e.g., bellmouthed sampler (Envirometrics, Charleston, SC). These may be used if shown to give measured concentrations equivalent to sampler indicated above for the application.
2. Personal sampling pump, battery or line-powered vacuum, of sufficient capacity to meet flow-rate requirements (see step 4 for flow rate), with flexible connecting tubing.
3. Wire, multi-stranded, 22-gauge; 1″ hose clamp to attach wire to cassette.
4. Tape, shrink- or adhesive-.
5. Slides, glass, frosted-end, pre-cleaned, 25- × 75-mm.
6. Cover slips, 22- × 22-mm, No. 1½, unless otherwise specified by microscope manufacturer.
7. Lacquer or nail polish.
8. Knife, #10 surgical steel, curved blade.
9. Tweezers.

EQUIPMENT (continued):

10. Acetone flash vaporization system for clearing filters on glass slides (see ref. [5] for specifications or see manufacturer's instructions for equivalent devices).
11. Micropipets or syringes, 5-µL and 100- to 500-µL.
12. Microscope, positive phase (dark) contrast, with green or blue filter, adjustable field iris, 8 to 10× eyepiece, and 40 to 45× phase objective (total magnification ca. 400×); numerical aperture = 0.65 to 0.75.
13. Graticule, Walton-Beckett type with 100-µm diameter circular field (area = 0.00785 mm^2) at the specimen plane (Type G-22). Available from Optometrics USA, P.O. Box 699, Ayer, MA 01432 [phone (508)-772-1700], and McCrone Accessories and Components, 850 Pasquinelli Drive, Westmont, IL 60559 [phone (312) 887-7100].
    NOTE: The graticule is custom-made for each microscope. (see APPENDIX A for the custom-ordering procedure).
14. HSE/NPL phase contrast test slide, Mark II. Available from Optometrics USA (address above).
15. Telescope, ocular phase-ring centering.
16. Stage micrometer (0.01-mm divisions).

SPECIAL PRECAUTIONS: Acetone is extremely flammable. Take precautions not to ignite it. Heating of acetone in volumes greater than 1 mL must be done in a ventilated laboratory fume hood using a flameless, spark-free heat source.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. To reduce contamination and to hold the cassette tightly together, seal the crease between the cassette base and the cowl with a shrink band or light colored adhesive tape. For personal sampling, fasten the (uncapped) open-face cassette to the worker's lapel. The open face should be oriented downward.
    NOTE: The cowl should be electrically grounded during area sampling, especially under conditions of low relative humidity. Use a hose clamp to secure one end of the wire (Equipment, Item 3) to the monitor's cowl. Connect the other end to an earth ground (i.e., cold water pipe).
3. Submit at least two field blanks (or 10% of the total samples, whichever is greater) for each set of samples. Handle field blanks in a manner representative of actual handling of associated samples in the set. Open field blank cassettes at the same time as other cassettes just prior to sampling. Store top covers and cassettes in a clean area (e.g., a closed bag or box) with the top covers from the sampling cassettes during the sampling period.
4. Sample at 0.5 L/min or greater [6]. Adjust sampling flow rate, Q (L/min), and time, t (min), to produce a fiber density, E, of 100 to 1300 fibers/mm^2 (3.85×10^4 to 5×10^5 fibers per 25-mm filter with effective

collection area A_c = 385 mm^2) for optimum accuracy. These variables are related to the action level (one-half the current standard), L (fibers/cc), of the fibrous aerosol being sampled by:

$$t = \frac{A_c \times E}{Q \times L \times 10^3}.$$

NOTE 1: The purpose of adjusting sampling times is to obtain optimum fiber loading on the filter. The collection efficiency does not appear to be a function of flow rate in the range of 0.5 to 16 L/min for asbestos fibers [7]. Relatively large diameter fibers (>3 µm) may exhibit significant aspiration loss and inlet deposition. A sampling rate of 1 to 4 L/min for 8 h is appropriate in atmospheres containing ca. 0.1 fiber/cc in the absence of significant amounts of non-asbestos dust. Dusty atmospheres require smaller sample volumes (≤400 L) to obtain countable samples. In such cases take short, consecutive samples and average the results over the total collection time. For documenting episodic exposures, use high flow rates (7 to 16 L/min) over shorter sampling times. In relatively clean atmospheres, where targeted fiber concentrations are much less than 0.1 fiber/cc, use larger sample volumes (3000 to 10000 L) to achieve quantifiable loadings. Take care, however, not to overload the filter with background dust. If ≥50% of the filter surface is covered with particles, the filter may be too overloaded to count and will bias the measured fiber concentration.

NOTE 2: OSHA regulations specify a minimum sampling volume of 48 L for an excursion measurement, and a maximum sampling rate of 2.5 L/min [3].

5. At the end of sampling, replace top cover and end plugs.
6. Ship samples with conductive cowl attached in a rigid container with packing material to prevent jostling or damage.
   NOTE: Do not use untreated polystyrene foam in shipping container because electrostatic forces may cause fiber loss from sample filter.

SAMPLE PREPARATION:

NOTE 1: The object is to produce samples with a smooth (non-grainy) background in a medium with refractive index ≤ 1.46. This method collapses the filter for easier focusing and produces permanent (1–10 years) mounts which are useful for quality control and interlaboratory comparison. The aluminum "hot block" or similar flash vaporization techniques may be used outside the laboratory [2]. Other mounting techniques meeting the above criteria may also be used (e.g., the laboratory fume hood procedure for generating acetone vapor as described in Method 7400—revision of 5/15/85, or the non-permanent field mounting technique used in P&CAM 239 [3,7–9]). Unless the effective filtration area is known, determine the area and record the information referenced against the sample ID number [1,9–11].

NOTE 2: Excessive water in the acetone may slow the clearing of the filter, causing material to be washed off the surface of the filter. Also, filters that have been exposed to high humidities prior to clearing may have a grainy background.

7. Ensure that the glass slides and cover slips are free of dust and fibers.
8. Adjust the rheostat to heat the "hot block" to ca. 70 °C [2].
   NOTE: If the "hot block" is not used in a fume hood, it must rest on a ceramic plate and be isolated from any surface susceptible to heat damage.
9. Mount a wedge cut from the sample filter on a clean glass slide.
   a. Cut wedges of ca. 25% of the filter area with a curved-blade surgical steel knife using a rocking motion to prevent tearing. Place wedge, dust side up, on slide.
      NOTE: Static electricity will usually keep the wedge on the slide.
   b. Insert slide with wedge into the receiving slot at base of "hot block". Immediately place tip of a micropipet containing ca. 250 µL acetone (use the minimum volume needed to consistently clear the filter sections) into the inlet port of the PTFE cap on top of the "hot block" and inject the

acetone into the vaporization chamber with a slow, steady pressure on the plunger button while holding pipet firmly in place. After waiting 3 to 5 s for the filter to clear, remove pipet and slide from their ports.

CAUTION: Although the volume of acetone used is small, use safety precautions. Work in a well-ventilated area (e.g., laboratory fume hood). Take care not to ignite the acetone. Continuous use of this device in an unventilated space may produce explosive acetone vapor concentrations.

c. Using the 5-µL micropipet, immediately place 3.0 to 3.5 µL triacetin on the wedge. Gently lower a clean cover slip onto the wedge at a slight angle to reduce bubble formation. Avoid excess pressure and movement of the cover glass.

NOTE: If too many bubbles form or the amount of triacetin is insufficient, the cover slip may become detached within a few hours. If excessive triacetin remains at the edge of the filter under the cover slip, fiber migration may occur.

d. Mark the outline of the filter segment with a glass marking pen to aid in microscopic evaluation.

e. Glue the edges of the cover slip to the slide using lacquer or nail polish [12]. Counting may proceed immediately after clearing and mounting are completed.

NOTE: If clearing is slow, warm the slide on a hotplate (surface temperature 50 °C) for up to 15 min to hasten clearing. Heat carefully to prevent gas bubble formation.

CALIBRATION AND QUALITY CONTROL:

10. Microscope adjustments. Follow the manufacturer's instructions. At least once daily use the telescope ocular (or Bertrand lens, for some microscopes) supplied by the manufacturer to ensure that the phase rings (annular diaphragm and phase-shifting elements) are concentric. With each microscope, keep a logbook in which to record the dates of microscope cleanings and major servicing.
    a. Each time a sample is examined, do the following:
        (1) Adjust the light source for even illumination across the field of view at the condenser iris. Use Kohler illumination, if available. With some microscopes, the illumination may have to be set up with bright field optics rather than phase contract optics.
        (2) Focus on the particulate material to be examined.
        (3) Make sure that the field iris is in focus, centered on the sample, and open only enough to fully illuminate the field of view.
    b. Check the phase-shift detection limit of the microscope periodically for each analyst/microscope combination:
        (1) Center the HSE/NPL phase-contrast test slide under the phase objective.
        (2) Bring the blocks of grooved lines into focus in the graticule area.

        NOTE: The slide contains seven blocks of grooves (ca. 20 grooves per block) in descending order of visibility. For asbestos counting, the microscope optics must completely resolve the grooved lines in block 3 although they may appear somewhat faint, and the grooved lines in blocks 6 and 7 must be invisible when centered in the graticule area. Blocks 4 and 5 must be at least partially visible but may vary slightly in visibility between microscopes. A microscope which fails to meet these requirements has resolution either too low or too high for fiber counting.

        (3) If image quality deteriorates, clean the microscope optics. If the problem persists, consult the microscope manufacturer.
11. Document the laboratory's precision for each counter for replicate fiber counts.
    a. Maintain as part of the laboratory quality assurance program a set of reference slides to be used on a daily basis [13]. These slides should consist of filter preparations including a range of loadings and background dust levels from a variety of sources including both field and reference samples (e.g., PAT, AAR, commercial samples). The Quality Assurance Officer should maintain custody of the reference slides and should supply each counter with a minimum of one reference

slide per workday. Change the labels on the reference slides periodically so that the counter does not become familiar with the samples.

b. From blind repeat counts on reference slides, estimate the laboratory intra- and intercounter precision. Obtain separate values of relative standard deviation (S_r) for each sample matrix analyzed in each of the following ranges: 5 to 20 fibers in 100 graticule fields, >20 to 50 fibers in 100 graticule fields, and >50 to 100 fibers in 100 graticule fields. Maintain control charts for each of these data files.

NOTE: Certain sample matrices (e.g., asbestos cement) have been shown to give poor precision [9].

12. Prepare and count field blanks along with the field samples. Report counts on each field blank.

NOTE 1: The identity of blank filters should be unknown to the counter until all counts have been completed.

NOTE 2: If a field blank yields greater than 7 fibers per 100 graticule fields, report possible contamination of the samples.

13. Perform blind recounts by the same counter on 10% of filters counted (slides relabeled by a person other than the counter). Use the following test to determine whether a pair of counts by the same counter on the same filter should be rejected because of possible bias: Discard the sample if the absolute value of the difference between the square roots of the two counts (in fiber/mm^2) exceeds $2.77XS_r'$ where X = average of the square roots of the two fiber counts (in fiber/mm^2) and $S_r' = S_r / 2$ where S_r is the intracounter relative standard deviation for the appropriate count range (in fibers) determined in step 11. For more complete discussions see reference [13].

NOTE 1: Since fiber counting is the measurement of randomly placed fibers which may be described by a Poisson distribution, a square root transformation of the fiber count data will result in approximately normally distributed data [13].

NOTE 2: If a pair of counts is rejected by this test, recount the remaining samples in the set and test the new counts against the first counts. Discard all rejected paired counts. It is not necessary to use this statistic on blank counts.

14. The analyst is a critical part of this analytical procedure. Care must be taken to provide a non-stressful and comfortable environment for fiber counting. An ergonomically designed chair should be used, with the microscope eyepiece situated at a comfortable height for viewing. External lighting should be set at a level similar to the illumination level in the microscope to reduce eye fatigue. In addition, counters should take 10- to 20-minute breaks from the microscope every one or two hours to limit fatigue [14]. During these breaks, both eye and upper back/neck exercises should be performed to relieve strain.
15. All laboratories engaged in asbestos counting should participate in a proficiency testing program such as the AIHA-NIOSH Proficiency Analytical Testing (PAT) Program for asbestos and routinely exchange field samples with other laboratories to compare performance of counters.

MEASUREMENT:

16. Center the slide on the stage of the calibrated microscope under the objective lens. Focus the microscope on the plane of the filter.
17. Adjust the microscope (Step 10).

NOTE: Calibration with the HSE/NPL test slide determines the minimum detectable fiber diameter (ca. 0.25 µm) [4].

18. Counting rules: (same as P&CAM 239 rules [1,10,11]: see examples in APPENDIX B).

a. Count any fiber longer than 5 µm which lies entirely within the graticule area.
   (1) Count only fibers longer than 5 µm. Measure length of curved fibers along the curve.
   (2) Count only fibers with a length-to-width ratio equal to or greater than 3:1.
b. For fibers which cross the boundary of the graticule field:
   (1) Count as ½ fiber any fiber with only one end lying within the graticule area, provided that the fiber meets the criteria of rule a above.

(2) Do not count any fiber which crosses the graticule boundary more than once.
(3) Reject and do not count all other fibers.

c. Count bundles of fibers as one fiber unless individual fibers can be identified by observing both ends of a fiber.
d. Count enough graticule fields to yield 100 fibers. Count a minimum of 20 fields. Stop at 100 graticule fields regardless of count.

19. Start counting from the tip of the filter wedge and progress along a radial line to the outer edge. Shift up or down on the filter, and continue in the reverse direction. Select graticule fields randomly by looking away from the eyepiece briefly while advancing the mechanical stage. Ensure that, as a minimum, each analysis covers one radial line from the filter center to the outer edge of the filter. When an agglomerate or bubble covers ca. 1/6 or more of the graticule field, reject the graticule field and select another. Do not report rejected graticule fields in the total number counted.

NOTE 1: When counting a graticule field, continuously scan a range of focal planes by moving the fine focus knob to detect very fine fibers which have become embedded in the filter. The small-diameter fibers will be very faint but are an important contribution to the total count. A minimum counting time of 15 s per field is appropriate for accurate counting.

NOTE 2: This method does not allow for differentiation of fibers based on morphology. Although some experienced counters are capable of selectively counting only fibers which appear to be asbestiform, there is presently no accepted method for ensuring uniformity of judgment between laboratories. It is, therefore, incumbent upon all laboratories using this method to report total fiber counts. If serious contamination from non-asbestos fibers occurs in samples, other techniques such as transmission electron microscopy must be used to identify the asbestos fiber fraction present in the sample (see NIOSH Method 7402). In some cases (i.e., for fibers with diameters >1 µm), polarized light microscopy (as in NIOSH Method 7403) may be used to identify and eliminate interfering non-crystalline fibers [15].

NOTE 3: Do not count at edges where filter was cut. Move in at least 1 mm from the edge.

NOTE 4: Under certain conditions, electrostatic charge may affect the sampling of fibers. These electrostatic effects are most likely to occur when the relative humidity is low (below 20%), and when sampling is performed near the source of aerosol. The result is that deposition of fibers on the filter is reduced, especially near the edge of the filter. If such a pattern is noted during fiber counting, choose fields as close to the center of the filter as possible [5].

NOTE 5: Counts are to be recorded on a data sheet that provides, as a minimum, spaces on which to record the counts for each field, filter identification number, analyst's name, date, total fibers counted, total fields counted, average count, fiber density, and commentary. Average count is calculated by dividing the total fiber count by the number of fields observed. Fiber density (fibers/mm^2) is defined as the average count (fibers/field) divided by the field (graticule) area (mm^2/field).

CALCULATIONS AND REPORTING OF RESULTS

20. Calculate and report fiber density on the filter, E (fibers/mm^2), by dividing the average fiber count per graticule field, F / n_f, minus the mean field blank count per graticule field, B / n_b, by the graticule field area, A_f (approx. 0.00785 mm^2):

$$E = \frac{(F/n_f - B/n_b)}{A_f}, \text{ fibers/mm}^2.$$

NOTE: Fiber counts above 1300 fibers/mm^2 and fiber counts from samples with >50% of filter area covered with particulate should be reported as "uncountable" or "probably biased." Other fiber counts outside the 100–1300 fiber/mm^2 range should be reported as having "greater than optimal variability" and as being "probably biased."

21. Calculate and report the concentration, C (fibers/cc), of fibers in the air volume sampled, V (L), using the effective collection area of the filter, A_c (approx. 385 mm^2 for a 25-mm filter):

$$C = \frac{EA_c}{V \times 10^3}.$$

NOTE: Periodically check and adjust the value of A_c, if necessary.

22. Report intralaboratory and interlaboratory relative standard deviations (from Step 11) with each set of results.
    NOTE: Precision depends on the total number of fibers counted [1,16]. Relative standard deviation is documented in references [1,15–17] for fiber counts up to 100 fibers in 100 graticule fields. Comparability of interlaboratory results is discussed below. As a first approximation, use 213% above and 49% below the count as the upper and lower confidence limits for fiber counts greater than 20 (Figure 1).

EVALUATION OF METHOD:

Method Revisions:

This method is a revision of P&CAM 239 [10]. A summary of the revisions is as follows:

1. Sampling:
   The change from a 37-mm to a 25-mm filter improves sensitivity for similar air volumes. The change in flow rates allows for 2-m^3 full-shift samples to be taken, providing that the filter is not overloaded with non-fibrous particulates. The collection efficiency of the sampler is not a function of flow rate in the range 0.5 to 16 L/min [10].
2. Sample preparation technique:
   The acetone vapor-triacetin preparation technique is a faster, more permanent mounting technique than the dimethyl phthalate/diethyl oxalate method of P&CAM 239 [2,4,10]. The aluminum "hot block" technique minimizes the amount of acetone needed to prepare each sample.
3. Measurement:
   a. The Walton-Beckett graticule standardizes the area observed [14,18,19].
   b. The HSE/NPL test slide standardizes microscope optics for sensitivity to fiber diameter [4,14].
   c. Because of past inaccuracies associated with low fiber counts, the minimum recommended loading has been increased to 100 fibers/mm^2 filter area (a total of 78.5 fibers counted in 100 fields, each with field area = 0.00785 mm^2.) Lower levels generally result in an overestimate of the fiber count when compared to results in the recommended analytical range [20]. The recommended loadings should yield intracounter S_r in the range of 0.10 to 0.17 [21–23].

Interlaboratory Comparability:

An international collaborative study involved 16 laboratories using prepared slides from the asbestos cement, milling, mining, textile, and friction material industries [9]. The relative standard deviations (S_r) varied with sample type and laboratory. The ranges were:

Rules	Intralaboratory S_r	Interlaboratory S_r	Overall S_r
AIA (NIOSH A Rules)*	0.12 to 0.40	0.27 to 0.85	0.46
Modified CRS (NIOSH B Rules)†	0.11 to 0.29	0.20 to 0.35	0.25

*Under AIA rules, only fibers having a diameter less than 3 µm are counted and fibers attached to particles larger than 3 µm are not counted. NIOSH A Rules are otherwise similar to the AIA rules.
†See Appendix C.

A NIOSH study conducted using field samples of asbestos gave intralaboratory S_r in the range 0.17 to 0.25 and an interlaboratory S_r of 0.45 [21]. This agrees well with other recent studies [9,14,16].

At this time, there is no independent means for assessing the overall accuracy of this method. One measure of reliability is to estimate how well the count for a single sample agrees with the mean count from a large number of laboratories. The following discussion indicates how this estimation can be carried out based on measurements of the interlaboratory variability, as well as showing how the results of this method relate to the theoretically attainable counting precision and to measured intra- and interlaboratory S_r. (NOTE: The following discussion does not include bias estimates and should not be taken to indicate that lightly loaded samples are as accurate as properly loaded ones).

Theoretically, the process of counting randomly (Poisson) distributed fibers on a filter surface will give an S_r that depends on the number, N, of fibers counted:

$$S_r = 1/N^{1/2}.$$

Thus S_r is 0.1 for 100 fibers and 0.32 for 10 fibers counted. The actual S_r found in a number of studies is greater than these theoretical numbers [17,19–21].

An additional component of variability comes primarily from subjective interlaboratory differences. In a study of ten counters in a continuing sample exchange program, Ogden [15] found this subjective component of intralaboratory S_r to be approximately 0.2 and estimated the overall S_r by the term:

$$\frac{[N + (0.2 \times N)^2]^{1/2}}{N}.$$

Ogden found that the 90% confidence interval of the individual intralaboratory counts in relation to the means were +2 S_r and −1.5 S_r. In this program, one sample out of ten was a quality control sample. For laboratories not engaged in an intensive quality assurance program, the subjective component of variability can be higher.

In a study of field sample results in 46 laboratories, the Asbestos Information Association also found that the variability had both a constant component and one that depended on the fiber count [14]. These results gave a subjective interlaboratory component of S_r (on the same basis as Ogden's) for field samples of ca. 0.45. A similar value was obtained for 12 laboratories analyzing a set of 24 field samples [21]. This value falls slightly above the range of S_r (0.25 to 0.42 for 1984–85) found for 80 reference laboratories in the NIOSH PAT program for laboratory-generated samples [17].

A number of factors influence S_r for a given laboratory, such as that laboratory's actual counting performance and the type of samples being analyzed. In the absence of other information, such as from an interlaboratory quality assurance program using field samples, the value for the subjective component of variability is chosen as 0.45. It is hoped that the laboratories will carry out the recommended interlaboratory quality assurance programs to improve their performance and thus reduce the S_r.

The above relative standard deviations apply when the population mean has been determined. It is more useful, however, for laboratories to estimate the 90% confidence interval on the mean count from a single sample fiber count (Figure 1). These curves assume similar shapes of the count distribution for interlaboratory and intralaboratory results [16].

For example, if a sample yields a count of 24 fibers, Figure 1 indicates that the mean interlaboratory count will fall within the range of 227% above and 52% below that value 90% of the time. We can apply these percentages directly to the air concentrations as well. If, for instance, this sample (24 fibers counted) represented a 500-L volume, then the measured concentration is 0.02 fibers/mL (assuming 100 fields counted, 25-mm filter, 0.00785 mm^2 counting field area). If this same sample were counted by

a group of laboratories, there is a 90% probability that the mean would fall between 0.01 and 0.08 fiber/mL. These limits should be reported in any comparison of results between laboratories.

Note that the S_r of 0.45 used to derive Figure 1 is used as an estimate for a random group of laboratories. If several laboratories belonging to a quality assurance group can show that their interlaboratory S_r is smaller, then it is more correct to use that smaller S_r. However, the estimated S_r of 0.45 is to be used in the absence of such information. Note also that it has been found that S_r can be higher for certain types of samples, such as asbestos cement [9].

Quite often the estimated airborne concentration from an asbestos analysis is used to compare to a regulatory standard. For instance, if one is trying to show compliance with an 0.5 fiber/mL standard using a single sample on which 100 fibers have been counted, then Figure 1 indicates that the 0.5 fiber/mL standard must be 213% higher than the measured air concentration. This indicates that if one measures a fiber concentration of 0.16 fiber/mL (100 fibers counted), then the mean fiber count by a group of laboratories (of which the compliance laboratory might be one) has a 95% chance of being less than 0.5 fibers/mL; i.e., $0.16 + 2.13 \times 0.16 = 0.5$.

It can be seen from Figure 1 that the Poisson component of the variability is not very important unless the number of fibers counted is small. Therefore, a further approximation is to simply use +213% and −49% as the upper and lower confidence values of the mean for a 100-fiber count.

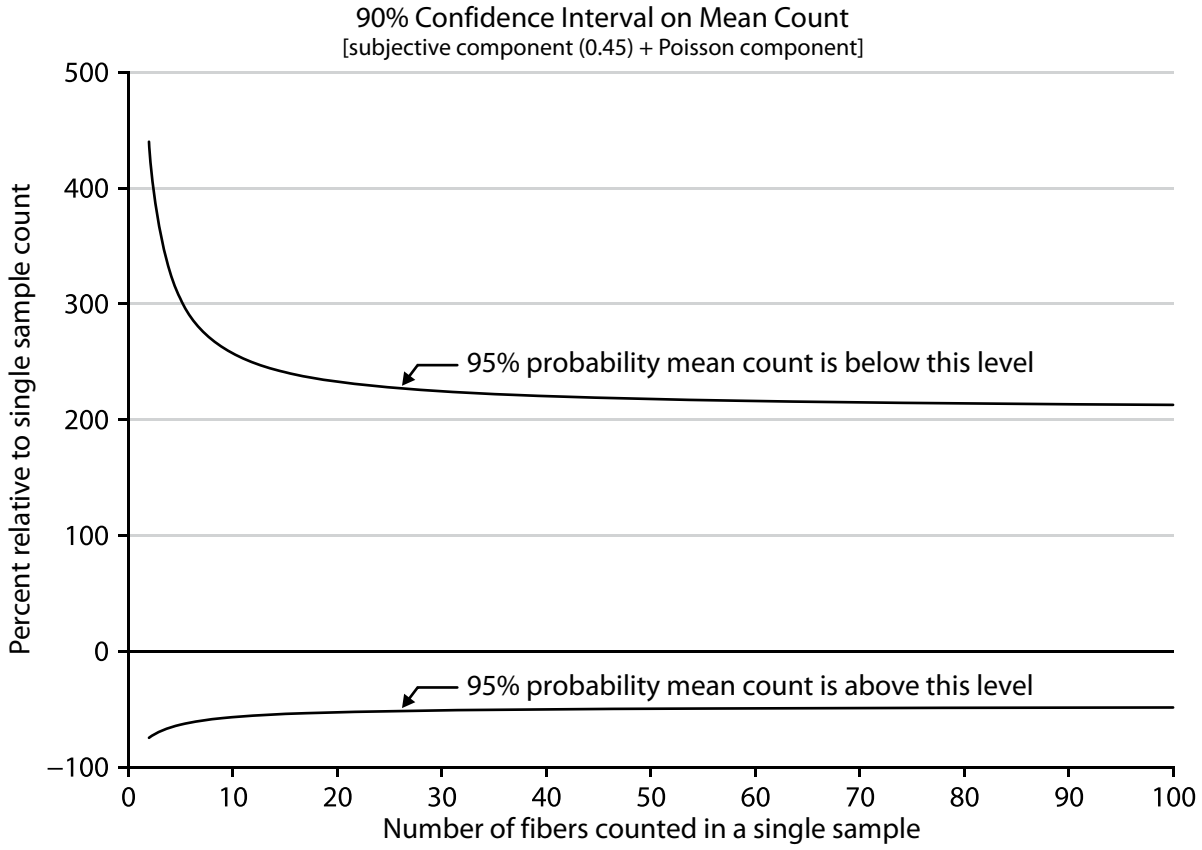


Figure 1. Interlaboratory precision of fiber counts.

The curves in Figure 1 are defined by the following equations:

$$U_{CL} = \frac{2X + 2.25 + [(2.25 + 2X)^2 - 4(1 - 2.25S_r^2)X^2]^{1/2}}{2(1 - 2.25S_r^2)} \text{ and}$$

$$L_{CL} = \frac{2X + 4 - [(4 + 2X)^2 - 4(1 - 4S_r^2)X^2]^{1/2}}{2(1 - 4S_r^2)},$$

where S_r = subjective interlaboratory relative standard deviation, which is close to the total interlaboratory S_r when approximately 100 fibers are counted,
X = total fibers counted on sample,
L_{CL} = lower 95% confidence limit, and
U_{CL} = upper 95% confidence limit.

Note that the range between these two limits represents 90% of the total range.

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APPENDIX A. CALIBRATION OF THE WALTON-BECKETT GRATICULE

Before ordering the Walton-Beckett graticule, the following calibration must be done to obtain a counting area (*D*) 100 µm in diameter at the image plane. The diameter, d_c (mm), of the circular counting area and the disc diameter must be specified when ordering the graticule.

1. Insert any available graticule into the eyepiece and focus so that the graticule lines are sharp and clear.
2. Set the appropriate interpupillary distance and, if applicable, reset the binocular head adjustment so that the magnification remains constant.
3. Install the 40 to 45× phase objective.
4. Place a stage micrometer on the microscope object stage and focus the microscope on the graduated lines.
5. Measure the magnified grid length of the graticule, L_o (µm), using the stage micrometer.
6. Remove the graticule from the microscope and measure its actual grid length, L_a (mm). This can best be accomplished by using a stage fitted with verniers.
7. Calculate the circle diameter, d_c (mm), for the Walton-Beckett graticule:

$$d_c = \frac{L_a}{L_o} \times D.$$

   Example: If L_o = 112 µm, L_a = 4.5 mm, and D = 100 µm, then d_c = 4.02 mm.
8. Check the field diameter, *D* (acceptable range 100 µm ± 2 µm) with a stage micrometer upon receipt of the graticule from the manufacturer. Determine field area (acceptable range 0.00754 mm^2 to 0.00817 mm^2).

APPENDIX B. COMPARISON OF COUNTING RULES

Figure 2 shows a Walton-Beckett graticule as seen through the microscope. The rules will be discussed as they apply to the labeled objects in the figure.

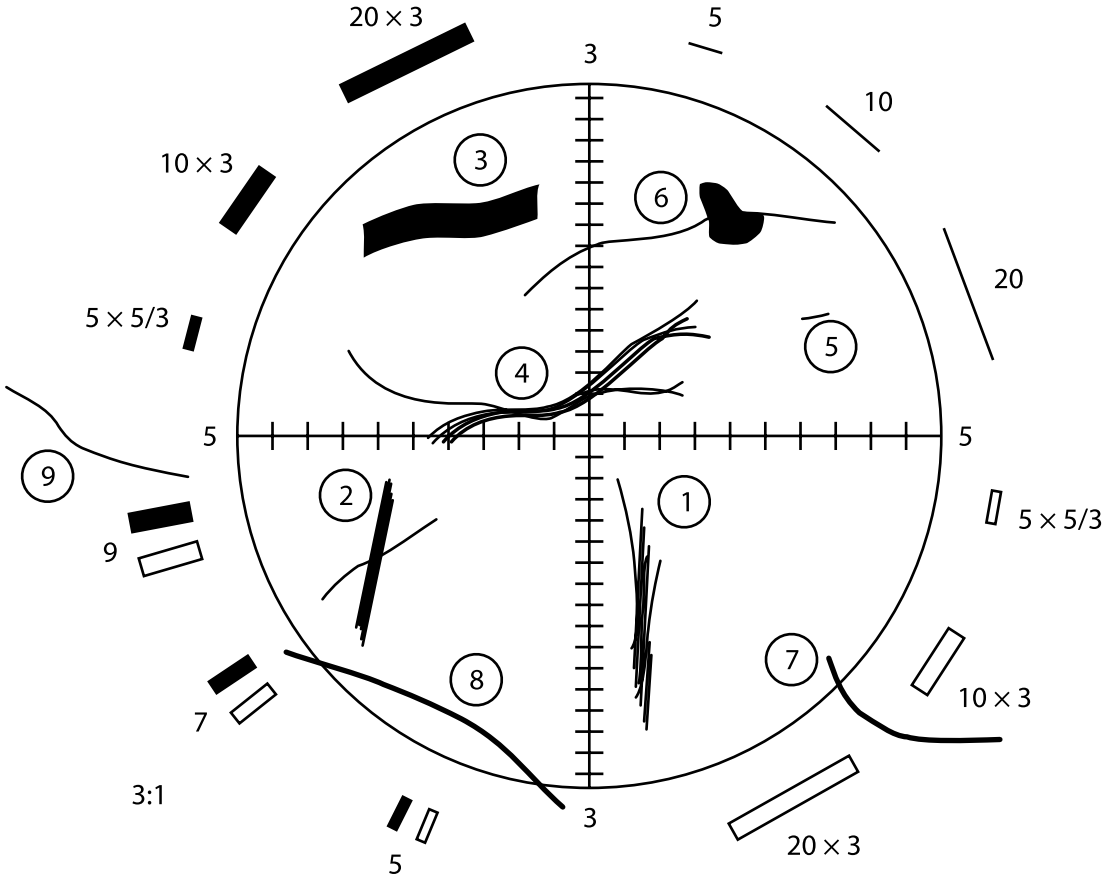

Figure 2. Walton-Beckett graticule with fibers.

These rules are sometimes referred to as the "A" rules:

Object	Count	Discussion
1	1 fiber	Optically observable asbestos fibers are actually bundles of fine fibrils. If the fibrils seem to be from the same bundle, the object is counted as a single fiber. Note, however, that all objects meeting length and aspect ratio criteria are counted whether or not they appear to be asbestos.
2	2 fibers	If fibers meeting the length and aspect ratio criteria (length >5 µm and length-to-width ratio > 3 to 1) overlap, but do not seem to be part of the same bundle, they are counted as separate fibers.
3	1 fiber	Although the object has a relatively large diameter (>3 µm), it is counted as fiber under the rules. There is no upper limit on the fiber diameter in the counting rules. Note that fiber width is measured at the widest compact section of the object.
4	1 fiber	Although long fine fibrils may extend from the body of a fiber, these fibrils are considered part of the fiber if they seem to have originally been part of the bundle.
5	Do not count	If the object is ≤ 5 µm long, it is not counted.
6	1 fiber	A fiber partially obscured by a particle is counted as one fiber. If the fiber ends emanating from a particle do not seem to be from the same fiber and each end meets the length and aspect ratio criteria, they are counted as separate fibers.
7	½ fiber	A fiber which crosses into the graticule area one time is counted as ½ fiber.
8	Do not count	Ignore fibers that cross the graticulate boundary more than once.
9	Do not count	Ignore fibers that lie outside the graticule boundary.

APPENDIX C. ALTERNATE COUNTING RULES FOR NON-ASBESTOS FIBERS

Other counting rules may be more appropriate for measurement of specific non-asbestos fiber types, such as fibrous glass. These include the "B" rules given below (from NIOSH Method 7400, Revision #2, dated 8/15/87), the World Health Organization reference method for man-made mineral fiber [24], and the NIOSH fibrous glass criteria document method [25]. The upper diameter limit in these methods prevents measurements of non-thoracic fibers. It is important to note that the aspect ratio limits included in these methods vary. NIOSH recommends the use of the 3:1 aspect ratio in counting fibers.

It is emphasized that hybridization of different sets of counting rules is not permitted. Report specifically which set of counting rules are used with the analytical results.

"B" Counting Rules

1. Count only *ends* of fibers. Each fiber must be longer than 5 µm and less than 3 µm diameter.
2. Count only ends of fibers with a length-to-width ratio equal to or greater than 5:1.
3. Count each fiber end which falls within the graticule area as one end, provided that the fiber meets rules 1 and 2 above. Add split ends to the count as appropriate if the split fiber segment also meets the criteria of rules 1 and 2 above.
4. Count visibly free ends which meet rules 1 and 2 above when the fiber appears to be attached to another particle, regardless of the size of the other particle. Count the end of a fiber obscured by another particle if the particle covering the fiber end is less than 3 µm in diameter.

5. Count free ends of fibers emanating from large clumps and bundles up to a maximum of 10 ends (5 fibers), provided that each segment meets rules 1 and 2 above.
6. Count enough graticule fields to yield 200 ends. Count a minimum of 20 graticule fields. Stop at 100 graticule fields, regardless of count.
7. Divide total end count by 2 to yield fiber count.

APPENDIX D. EQUIVALENT LIMITS OF DETECTION AND QUANTITATION

Fiber density on filter*			Fiber concentration in air, f/cc	
	Fibers per 100 fields	Fibers/mm^2	400-L air sample	1000-L air sample
	200	255	0.25	0.10
	100	127	0.125	0.05
LOQ	80.0	102	0.10	0.04
	50	64	0.0625	0.025
	25	32	0.03	0.0125
	20	25	0.025	0.010
	10	12.7	0.0125	0.005
	8	10.2	0.010	0.004
LOD	5.5	7	0.00675	0.0027

*Assumes 385 mm^2 effective filter collection area, and field area = 0.00785 mm^2, for relatively "clean" (little particulate aside from fibers) filters.

OAR 340-253-8010
Table 1
Oregon Clean Fuel Standard for Gasoline and Gasoline Substitutes

Calendar Year	Oregon Clean Fuel Standard (gCO2e per MJ)	Percent Reduction
2015	None (Gasoline Baseline is 98.62 for 2016-2017, 98.64 for 2018, and 98.06 for 2019 and beyond)	
2016*	98.37	0.25 percent
2017	98.13	0.50 percent
2018	97.66	1.00 percent
2019	96.59	1.50 percent
2020	95.61	2.50 percent
2021	94.63	3.50 percent
2022	93.15	5.00 percent
2023	91.68	6.50 percent
2024	90.21	8.00 percent
2025 and beyond	88.25	10.0 percent

*Initial compliance period is a two-year period for 2016 and 2017.

OAR 340-253-8020
Table 2
Oregon Clean Fuel Standard for Diesel Fuel and Diesel Substitutes

Calendar Year	Oregon Clean Fuel Standard (gCO2e per MJ)	Percent Reduction
2015	None (Diesel Baseline is 99.64 for 2016-2017, 99.61 for 2018, and 98.74 for 2019 and beyond)	
2016*	99.39	0.25 percent
2017	99.14	0.50 percent
2018	98.61	1.00 percent
2019	97.26	1.50 percent
2020	96.27	2.50 percent
2021	95.29	3.50 percent
2022	93.81	5.00 percent
2023	92.32	6.50 percent
2024	90.84	8.00 percent
2025 and beyond	88.87	10.00 percent
*Initial compliance period is a two-year period for 2016 and 2017.		

OAR 340-253-8030
Table 3
Oregon Clean Fuel Standard for Alternative Jet Fuel

Calendar Year	Oregon Clean Fuel Standard (gCO2e per MJ)
2015	None (Diesel Baseline is 99.64 for 2016-2017, 99.61 for 2018, and 98.74 for 2019 and beyond. The fossil jet baseline is 90.97.)
2019	90.80
2020	90.80
2021	90.80
2022	90.80
2023	90.80
2024	90.80
2025 and beyond	88.87

OAR 340-253-8040
Table 4
Oregon Carbon Intensity Lookup Table

Fuel	Pathway Identifier	Pathway Description	Carbon Intensity Values (gCO2e/MJ)
			Total Lifecycle Emissions
Gasoline	ORGAS001	Clear gasoline - based on a weighted average of gasoline supplied to Oregon	100.14
	ORGAS002	Imported blended gasoline (E10) – 90% clear gasoline & 10% corn ethanol based on Midwest average. Cannot be used to report exports except when the specific gallon was also imported under this fuel pathway code.	98.06
Diesel	ORULSD001	Clear diesel, based on a weighted average of diesel fuel supplied to Oregon	100.74
	ORULSD002	Imported blended diesel (B5) – 95% clear diesel & 5% soybean biodiesel. Cannot be used to report exports except when the specific gallon was also imported under this fuel pathway code.	98.74
	ORULSD003	Imported blended diesel (B20) – 80% clear diesel & 20% soybean biodiesel. Cannot be used to report exports except when the specific gallon was also imported under this fuel pathway code.	92.68
Compressed Natural Gas	ORCNG001	North American NG delivered via pipeline; compressed in OR	79.98
Liquefied Natural Gas	ORLNG001	North American NG delivered via pipeline; liquefied in OR using liquefaction with 80% efficiency	86.88
Liquefied Petroleum Gas	ORLPG001	Liquefied petroleum gas	80.88
Electricity	ORELEC100	Solar power, produced at or directly connected to the site of the	0

OAR 340-253-8040
Table 4
Oregon Carbon Intensity Lookup Table

Fuel	Pathway Identifier	Pathway Description	Carbon Intensity Values (gCO2e/MJ)
			Total Lifecycle Emissions
		charging station in Oregon, subject to OAR 340-253-0470 (3).	
	ORELEC101	Wind power, produced at or directly connected to the site of the charging station in Oregon, subject to OAR 340-253-0470 (3).	0
Hydrogen	ORHYF	Compressed H2 produced in Oregon from central steam methane reformation of North American fossil-based NG	120.68
	ORHYFL	Liquefied H2 produced in Oregon from central steam methane reformation of North American fossil-based NG	157.29
	ORHYB	Compressed H2 produced in Oregon from central steam methane reformation of biomethane (renewable feedstock) from North American landfills	116.76
	ORHYBL	Liquefied H2 produced in Oregon from central steam methane reformation of biomethane (renewable feedstock) from North American landfills	149.70
	ORHYEG	Compressed H2 produced in Oregon from electrolysis using Oregon average grid electricity	205.38
	ORHYEB	Compressed H2 produced in Oregon from electrolysis using BPA average grid electricity	31.65
	ORHYER	Compressed H2 produced in Oregon from electrolysis using solar- or wind-generated electricity	13.11

OAR 340-253-8050
Table 5
Summary Checklist of Quarterly Progress and Annual Compliance Reporting Requirements

Parameters to Report	Gasoline & Diesel Fuel	Ethanol, Biodiesel & Renewable Diesel	CNG, LNG & LPG	Electricity	Hydrogen & Hydrogen Blends
Company or organization name	x	x	x	x	x
Reporting period	x	x	x	x	x
Fuel pathway code	x	x	x	x	x
Transaction type	x	x	x	x	x
Transaction date	x	x	x	x	x
Business Partner	x	x	x	x	x
Production Company ID and Facility ID	n/a	x	n/a	n/a	x
Physical transport mode code	x	x	x	x	x
Aggregation	x	x	x	x	x
Application / EER	x	x	x	x	x
Amount of each fuel used as gasoline replacement	x	x	x	x	x
Amount of each fuel used as diesel fuel replacement	x	x	x	x	x
*Credits/deficits generated per quarter (MT)	x	x	x	x	x
For Annual Compliance Reporting (in addition to the items above)					
*Credits and Deficits generated per year (MT)	x	x	x	x	x

OAR 340-253-8050
Table 5
Summary Checklist of Quarterly Progress and Annual Compliance Reporting Requirements

Parameters to Report	Gasoline & Diesel Fuel	Ethanol, Biodiesel & Renewable Diesel	CNG, LNG & LPG	Electricity	Hydrogen & Hydrogen Blends
*Credits/deficits carried over from the previous year (MT), if any	x	x	x	x	x
*Credits acquired from another party (MT), if any	x	x	x	x	x
*Credits sold to another party (MT), if any	x	x	x	x	x
*Credits retired within LCFS (MT) to meet compliance obligation, if any	x	x	x	x	x

OAR 340-253-8060
Table 6
Oregon Energy Densities of Fuels

Fuel (unit)	MJ/unit
Gasoline (gallon)	122.48 (MJ/gallon)
Diesel fuel (gallon)	134.48 (MJ/gallon)
Compressed natural gas (therm)	105.5 (MJ/therms)
Electricity (kilowatt hour)	3.60 (MJ/kilowatt hour)
Denatured ethanol (gallon)	81.51 (MJ/gallon)
Clear biodiesel (gallon)	126.13 (MJ/gallon)
Liquefied natural gas (gallon)	78.83 (MJ/gallon)
Hydrogen (kilogram)	120.00 (MJ/kilogram)
Liquefied petroleum gas (gallon)	89.63 (MJ/gallon)
Renewable hydrocarbon diesel (gallon)	129.65 (MJ/gallon)
Undenatured anhydrous ethanol (gallon)	80.53 (MJ/gallon)
Alternative Jet Fuel (gal)	126.37 (MJ/gallon)

OAR 340-253-8070
Table 7
Oregon Energy Economy Ratio Values for Fuels

Light/Medium Duty Applications (Fuels used as gasoline replacements)		Heavy-Duty/Off-Road Applications (Fuels used as diesel replacements)		Aviation Applications (Fuels used as jet fuel replacements)	
Fuel/Vehicle Combination	**EER Value Relative to Gasoline**	**Fuel/Vehicle Combination**	**EER Value Relative to Diesel**	**Fuel/Vehicle Combination**	**EER Value relative to conventional jet**
Gasoline (including E10) or any other gasoline-ethanol blend	1	Diesel fuel (including B5) or any other blend of diesel and biodiesel or renewable hydrocarbon diesel	1	Alternative Jet Fuel	1
CNG Internal Combustion Engine Vehicle (ICEV)	1	CNG, LNG, or LPG (Spark-Ignition Engines)	0.9		
Electricity/Battery Electric Vehicle or Plug-In Hybrid Electric Vehicle	3.4	CNG,LNG, or LPG(Compression-Ignition Engines)	1		
Electricity/On-Road Electric Motorcycle	4.4	Electricity/Battery Electric Vehicle or Plug-In Hybrid Electric Vehicle	5		
Propane/Propane Forklift	0.9	Electricity/Battery Electric or Plug-in Hybrid Transit Bus	5		
Hydrogen/Fuel Cell Vehicle	2.5	Electricity/Fixed Guideway Light Rail	3.3		
		Electricity/Fixed Guideway Streetcar	2.1		
		Electricity/Fixed Guideway Aerial Tram	2.6		

OAR 340-253-8070
Table 7
Oregon Energy Economy Ratio Values for Fuels

Light/Medium Duty Applications (Fuels used as gasoline replacements)		Heavy-Duty/Off-Road Applications (Fuels used as diesel replacements)		Aviation Applications (Fuels used as jet fuel replacements)	
Fuel/Vehicle Combination	**EER Value Relative to Gasoline**	**Fuel/Vehicle Combination**	**EER Value Relative to Diesel**	**Fuel/Vehicle Combination**	**EER Value relative to conventional jet**
		Electricity/Electric Forklift	3.8		
		Electricity/Electric TRU (eTRU)	3.4		
		Hydrogen/Fuel Cell Vehicle	1.9		
		Hydrogen/Fuel Cell Forklift	2.1		

OAR 340-253-8080
Table 8
Oregon Substitute Fuel Pathway Codes

Fuel	Fuel Pathway code	CI (gCO2e/MJ)
Substitute CI for Ethanol. This pathway may only be used to report transactions that are sales or purchases without obligation, exports, loss of inventory, not for transportation use, and exempt fuel use.	ETH0116	40
Substitute CI for Biodiesel. This pathway may only be used to report transactions that are sales or purchases without obligation, exports, loss of inventory, not for transportation use, and exempt fuel use.	BIOD0116	15
Substitute CI for Renewable Diesel. This pathway may only be used to report transactions that are sales or purchases without obligation, exports, loss of inventory, not for transportation use, and exempt fuel use.	RNWD0116	15
Substitute CI for E10 Gasoline. This pathway may only be used to report transactions that are sales or purchases without obligation, exports, loss of inventory, not for transportation use, and exempt fuel use.	ORGAS0116	For 2019: 96.59 For 2020 and beyond: 96.00
Substitute CI for B5 Diesel. This pathway may only be used to report transactions that are sales or purchases without obligation,	ORULSD01165	For 2019: 97.26 For 2020 and beyond: 96.71

OAR 340-253-8080
Table 8
Oregon Substitute Fuel Pathway Codes

Fuel	Fuel Pathway code	CI (gCO2e/MJ)
exports, loss of inventory, not for transportation use, and exempt fuel use.		
Substitute CI for B20 Diesel. This pathway may only be used to report transactions that are sales or purchases without obligation, exports, loss of inventory, not for transportation use, and exempt fuel use.	ORULSD011620	84.45

OAR 340-253-8090
Table 9
Oregon Temporary Fuel Pathway Codes for Fuels with Indeterminate CIs

Fuel	Feedstock	Process Energy	FPC	CI (gCO_2e/MJ)
Ethanol	Corn	Grid electricity, natural gas, and/or renewables	ORETH100T	77.35
	Sorghum	Grid electricity, natural gas, and/or renewables	ORETH101T	93.35
	Sugarcane and Molasses	Bagasse and straw only, no grid electricity	ORETH102T	57.09
	Any starch or sugar feedstock	Any	ORETH103T	100.14
	Corn Stover, Wheat Straw, or Sugarcane Straw	As specified in OR-Greet 2.0	ORETH104T	41.05
Biodiesel	Any feedstock derived from animal fats, corn oil, or a waste stream	Grid electricity, natural gas, and/or renewables	ORBIOD200T	47.30
	Any feedstock derived from plant oils except for Palm-derived oils	Grid electricity, natural gas, and/or renewables	ORBIOD201T	65.03
	Any feedstock	Any	ORBIOD202T	100.74
Renewable Diesel	Any feedstock derived from animal fats, corn oil, or a waste stream	Grid electricity, natural gas, and/or renewables	ORRNWD300T	39.26
	Any feedstock derived from plant oils except for Palm-derived oils	Grid electricity, natural gas, and/or renewables	ORRNWD301T	56.55

OAR 340-253-8090
Table 9
Oregon Temporary Fuel Pathway Codes for Fuels with Indeterminate CIs

Fuel	Feedstock	Process Energy	FPC	CI (gCO_2e/MJ)
	Any feedstock	Any	ORRNWD302T	100.74
Biomethane CNG	Landfill or Digester Gas	Grid electricity, natural gas, and/or renewables	ORCNG500T	63.96
	Municipal Wastewater sludge, Food Waste, Green Waste, or Other Organic Waste	Grid electricity, natural gas, and/or parasitic load	ORCNG501T	50
Biomethane LNG	Landfill or Digester Gas	Grid electricity, natural gas, and/or renewables	ORLNG501T	80.44
	Municipal Wastewater sludge, Food Waste, Green Waste, or Other Organic Waste	Grid electricity, natural gas, and/or parasitic load	ORLNG502T	65
Biomethane L-CNG	Landfill or Digester Gas	Grid electricity, natural gas, and/or renewables	ORLCNG502T	84.65
	Municipal Wastewater sludge, Food Waste, Green Waste, or Other Organic Waste	Grid electricity, natural gas, and/or parasitic load	ORLCNG503T	70
Biomethane CNG, LNG, L-CNG	Dairy Manure	Grid electricity, natural gas, and/or parasitic load	ORLCNG504T	-150
Electricity	Coal, Natural Gas, Hydroelectric	Oregon average electricity mix	ORELEC600T	135.00

OAR 340-253-8090
Table 9
Oregon Temporary Fuel Pathway Codes for Fuels with Indeterminate CIs

Fuel	Feedstock	Process Energy	FPC	CI (gCO_2e/MJ)
	Dams, Wind Mills, etc.			
Any Gasoline Substitute Feedstock-Fuel Combination Not Included Above	Any	Any	ORSG800T	100.14
Any Diesel Substitute Feedstock-Fuel Combination Not Included Above	Any	Any	ORSD801T	100.74

OAR 340-253-8100

Table 10

Oregon Summary of Indirect Land-Use Change Values for Crop-Based Biofuels

Feedstock	ILUC Value (gCO_2e/MJ)
Corn Ethanol	7.60
Sorghum Ethanol	19.40
Sugarcane Ethanol	11.80
Soybean Biodiesel or Renewable Diesel	29.10
Canola Biodiesel or Renewable Diesel	14.50
Palm Biodiesel or Renewable Diesel	71.40

State of Oregon Department of Environmental Quality

OAR 340-257-0030
California Non-Methane Organic Gas Test Procedures

California Environmental Protection Agency
AIR RESOURCES BOARD

CALIFORNIA NON-METHANE ORGANIC GAS TEST PROCEDURES

Adopted:	July 12, 1991
Amended:	September 22, 1993
Amended:	June 24, 1996
Amended:	August 5, 1999
Amended:	July 30, 2002

Monitoring and Laboratory Division, Southern Laboratory Branch
Mobile Source Division
9528 Telstar Avenue
El Monte, California 91731

NOTE: Mention of any trade name or commercial product does not constitute endorsement or recommendation of this product by the Air Resources Board.

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Part A

GENERAL APPLICABILITY AND REQUIREMENTS

1. These test procedures shall apply to all 1993 and subsequent model-year transitional low-emission vehicles (TLEV), low-emission vehicles (LEV), ultra-low-emission vehicles (ULEV), and super-ultra-low-emission vehicles (SULEV) certifying to non-methane organic gas (NMOG) emission standards.

2. This document sets forth the analysis and calculation procedures that shall be performed to determine NMOG mass emissions. The document consists of the following parts:

   A. General Applicability and Requirements
   B. Determination of Non-Methane Hydrocarbon Mass Emissions by Flame Ionization Detection
   C. Determination of Alcohols in Automotive Source Samples by Gas Chromatography (Method No. 1001)
   D. Determination of C_2 to C_5 Hydrocarbons in Automotive Source Samples by Gas Chromatography (Method No. 1002)
   E. Determination of C_6 to C_{12} Hydrocarbons in Automotive Source Samples by Gas Chromatography (Method No. 1003)
   F. Determination of Aldehyde and Ketone Compounds in Automotive Source Samples by High Performance Liquid Chromatography (Method No. 1004).
   G. Determination of NMOG Mass Emissions

   Appendix 1 List of Light-End and Mid-Range Hydrocarbons
   Appendix 2 Definitions and Commonly Used Abbreviations
   Appendix 3 References

Alternative procedures may be used if shown to yield equivalent results and if approved in advance by the Executive Officer of the Air Resources Board.

3. The analyses specified in the table below shall be performed to determine mass emission rates of NMOG in grams per mile (g/mi) or milligrams per mile (mg/mi) for vehicles operated on the listed fuel:

Fuel	NMHC by FID	NMHC by GC	Alcohols	Carbonyls
Alcohol	X		X	X
CNG		X		X
Diesel	X			X
Gasoline	X			X
LPG	X			X

As Amended: July 30, 2002
Board Hearing: November 15, 2001

The specified analyses shall be performed in accordance with the following parts of this document:

NMHC by FID--	Part B.	Determination of Non-Methane Hydrocarbon Mass Emissions by Flame Ionization Detection
NMHC by GC--	Part D.	Determination of C_2 to C_5 Hydrocarbons in Automotive Source Samples by Gas Chromatography (Method No. 1002); and
	Part E.	Determination of C_6 to C_{12} Hydrocarbons in Automotive Source Samples by Gas Chromatography (Method No. 1003)
CARBONYLS--	Part F.	Determination of Aldehyde and Ketone Compounds in Automotive Source Samples by High Performance Liquid Chromatography (Method No. 1004)
ALCOHOLS --	Part C.	Determination of Alcohols in Automotive Source Samples by Gas Chromatography (Method No. 1001)

4. For those manufacturers that choose to develop reactivity adjustment factors unique to a specific engine family, exhaust NMOG emissions shall be fully speciated. NMHC emissions shall be analyzed in accordance with parts D and E (Method Nos. 1002 and 1003). In addition, aldehydes and ketones, alcohols, and ethers shall be analyzed according to parts F, C, and E (Method Nos. 1004, 1001, and 1003). Analysis for alcohols shall be required only for vehicles that are operated on fuels containing alcohols.

5. For natural gas-fueled vehicles, the methane concentration in the exhaust sample shall be measured with a methane analyzer. A GC combined with a FID is used for direct measurement of methane concentrations. SAE Recommended Practice J1151 is a reference on generally accepted GC principles and analytical techniques for this application. A density of 18.89 g/ft^3 shall be used to determine the methane mass emissions. The methane mass emissions shall be multiplied by the appropriate methane reactivity adjustment factor and then added to the reactivity-adjusted NMOG emissions as specified in the "California Exhaust Emission Standards and Test Procedures for 1988-2000 Model Passenger Cars, Light-Duty Trucks, and Medium-Duty Vehicles" and in the "California Exhaust Emission Standards and Test Procedures for 2001 and Subsequent Model Passenger Cars, Light-Duty Trucks, and Medium-Duty Vehicles."

6. The mass of NMOG emissions shall be calculated in accordance with part G, "Determination of NMOG Mass Emissions". The mass of NMOG emissions in g/mile or mg/mile shall be calculated by summing the mass of NMHC determined by the FID, the mass of aldehydes and ketones, and the mass of alcohols.

PART B

DETERMINATION OF NON-METHANE HYDROCARBON MASS EMISSIONS BY FLAME IONIZATION DETECTION

1. INTRODUCTION

1.1 This procedure describes a method for determining NMHC exhaust mass emissions from motor vehicles. Other applicable forms of instrumentation and analytical techniques which prove to yield equivalent results to those specified in this procedure may be used subject to the approval of the Executive Officer of the Air Resources Board.

1.2 All definitions and abbreviations are contained in Appendix 2 of these test procedures.

2. TOTAL HYDROCARBON MEASUREMENT

2.1 A FID is used to measure total hydrocarbon concentration in vehicle exhaust in accordance with the Code of Federal Regulations [Ref.1]. SAE Recommended Practices J254 [Ref. 2] and J1094a [Ref. 3] are references on generally accepted gas analysis and constant volume sampling techniques. For Beckman 400 FIDs only, implementation of the recommendations outlined in SAE paper 770141[Ref. 4] shall be required. Other FID analyzer models shall be checked and adjusted, if necessary, to minimize any non-uniformity of relative response to different hydrocarbons.

3. METHANE MEASUREMENT

3.1 A GC combined with a FID constitute a methane analyzer and shall be used for direct measurement of methane concentrations. The SAE Recommended Practice J1151[Ref. 5] is a reference on generally accepted GC principles and analytical techniques for this specific application.

4. TOTAL HC FID RESPONSE TO METHANE

4.1 The FID is calibrated to propane and therefore tends to over respond to the methane portion of the vehicle exhaust sample during hydrocarbon analysis. In order to calculate the NMHC concentration, a methane response factor must be applied to the methane concentration (as measured by the methane analyzer) before it can be deducted from the total hydrocarbon concentration. To determine the total hydrocarbon FID response to methane, known methane in air concentrations traceable to NIST shall be analyzed by the FID. Several methane concentrations shall be analyzed by the FID in the range of the exhaust sample concentration. The total hydrocarbon FID response to methane is calculated as follows:

$$r_{CH_4} = FID_{ppm}/SAM_{ppm}$$

where:

r_{CH_4}	=	FID methane response factor.
FID_{ppm}	=	FID reading in ppmC.
SAM_{ppm}	=	the known methane concentration in ppmC.

The FID response to methane shall be checked at each calibration interval.

5. NMHC MASS EMISSION PER TEST PHASE

5.1 The following calculations shall be used to determine the NMHC mass emissions for each phase of the Federal Test Procedure [Ref. 1].

5.2 **Non-Alcohol Fueled Vehicles**

5.2.1 $NMHC_e = FID\ THC_e - (r_{CH_4} * CH_{4e})$
NOTE: If $NMHC_e$ is calculated to be less than zero, then $NMHC_e = 0$.

5.2.2 $NMHC_d = FID\ THC_d - (r_{CH_4} * CH_{4d})$
NOTE: If $NMHC_d$ is calculated to be less than zero, then $NMHC_d = 0$.

5.2.3 $CO_e = (1 - (0.01 + 0.005 * HCR) * CO_{2e} - 0.000323 * R_a) * CO_{em}$
NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e.

a) For gasoline, $CH_{1.85}$, where HCR = 1.85:
$CO_e = (1 - 0.01925 * CO_{2e} - 0.000323 * R_a) * CO_{em}$

b) For Phase 2 gasoline, $CH_{1.94}$, where HCR = 1.94:
$CO_e = (1 - 0.01970 * CO_{2e} - 0.000323 * R_a) * CO_{em}$

c) For LPG, $CH_{2.64}$, where HCR = 2.64:
$CO_e = (1 - 0.02320 * CO_{2e} - 0.000323 * R_a) * CO_{em}$

d) For CNG, $CH_{3.78}$, where HCR = 3.78:
$CO_e = (1 - 0.02890 * CO_{2e} - 0.000323 * R_a) * CO_{em}$

5.2.4 $$DF = \frac{100 * \left(\frac{x}{x + y/2 + 3.76 * (x + y/4 - z/2)} \right)}{CO_{2e} + (NMHC_e + CH_{4e} + CO_e) * 10^{-4}}$$

(where fuel composition is $C_xH_yO_z$ as measured for the fuel used.)

a) For gasoline, $CH_{1.85}$, where x = 1, y = 1.85, and z = 0:
DF = 13.47 / [CO_{2e} + ($NMHC_e$ + CH_{4e} + CO_e) * 10^{-4}]

b) For Phase 2 gasoline, $CH_{1.94}$, x = 1, y = 1.94 and z = 0.017:
DF = 13.29 / [CO_{2e} + ($NMHC_e$ + CH_{4e} + CO_e) * 10^{-4}]

c) For LPG, $CH_{2.64}$, where x = 1, y = 2.64, and z = 0:
DF = 11.68 / [CO_{2e} + ($NMHC_e$ + CH_{4e} + CO_e) * 10^{-4}]

d) For CNG, $CH_{3.78}$, where x = 1, y = 3.78, and z = 0.016:
DF = 9.83 / [CO_{2e} + ($NMHC_e$ + CH_{4e} + CO_e) * 10^{-4}]

5.3 Vehicles Operating on Fuels Containing Methanol

5.3.1 $NMHC_e$ = FID THC_e - (r_{CH_4} * CH_{4e}) - (r_{CH_3OH} * CH_3OH_e)
NOTE: If $NMHC_e$ is calculated to be less than zero, then $NMHC_e$ = 0.

5.3.2 $NMHC_d$ = FID THC_d - (r_{CH_4} * CH_{4d}) - (r_{CH_3OH} * CH_3OH_d)
NOTE: If $NMHC_d$ is calculated to be less than zero, then $NMHC_d$ = 0.

5.3.3 CO_e = (1 - (0.01 + 0.005 * HCR) * CO_{2e} - 0.000323 * R_a) * CO_{em}
NOTE: If a CO instrument which meets the criteria specified in CFR 40 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e .

a) For M100 (100% methanol), CH_3OH, where HCR = 4:
CO_e = (1 - 0.03000 * CO_{2e} - 0.000323 * R_a) * CO_{em}

b) For M85 (85% methanol, 15% indolene), $CH_{3.41}O_{0.72}$, where HCR = 3.41:
CO_e = (1 - 0.02705 * CO_{2e} - 0.000323 * R_a) * CO_{em}

5.3.4 $$DF = \frac{100 * \left(\frac{x}{x + y/2 + 3.76 * (x + y/4 - z/2)} \right)}{CO_{2e} + (NMHC_e + CH_{4e} + CO_e + CH_3OH_e + HCHO_e) * 10^{-4}}$$

(where fuel composition is $C_xH_yO_z$ as measured for the fuel used.)

a) For M100 (100% methanol), CH_3OH, where x = 1, y = 4, and z = 1:
DF = 11.57 / [CO_{2e} + ($NMHC_e$+ CH_{4e} + CO_e + CH_3OH_e + $HCHO_e$) * 10^{-4}]

b) For M85 (85% methanol, 15% Indolene), $CH_{3.41}\ O_{0.72}$, where x = 1, y = 3.41, and z = 0.72:
DF = 12.02 / [CO_{2e} + ($NMHC_e$ + CH_{4e} + CO_e + CH_3OH_e + $HCHO_e$) * 10^{-4}]

5.4 Vehicles Operating on Fuels Containing Ethanol

5.4.1 $NMHC_e$ = FID THC_e - (r_{CH_4} * CH_{4e}) - ($r_{C_2H_5OH}$ * $C_2H_5OH_e$)
NOTE: If $NMHC_e$ is calculated to be less than zero, then $NMHC_e$ = 0

5.4.2 $NMHC_d$ = FID THC_d - (r_{CH_4} * CH_{4d}) - ($r_{C_2H_5OH}$ * $C_2H_5OH_d$)
NOTE: If $NMHC_d$ is calculated to be less than zero, then $NMHC_d$ = 0

5.4.3 CO_e = (1 - (0.01 + 0.005 * HCR) * CO_{2e} - 0.000323 * R_a) * CO_{em}
NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e .
a) For E100 (100% ethanol), C_2H_5OH, where HCR = 3:
CO_e = (1 - 0.02500 * CO_{2e} - 0.000323 * R_a) * CO_{em}

5.4.4 $$DF = \frac{100 * \left(\frac{x}{x + y/2 + 3.76 * (x + y/4 - z/2)} \right)}{CO_{2e} + (NMHC_e + CH_{4e} + CO_e + C_2H_5OH_e + HCHO_e) * 10^{-4}}$$

(where fuel composition is $C_xH_yO_z$ as measured for the fuel used.)

a) For E100 (100% ethanol), C_2H_5OH, where x = 1, y = 3, and z = 0.5:
DF = 12.29 / [CO_{2e} + ($NMHC_e$ + CH_{4e} + CO_e + $C_2H_5OH_e$ + $HCHO_e$) * 10^{-4}]

5.5 All Vehicles

5.5.1 $NMHC_{conc}$ = $NMHC_e$ - $NMHC_d$ * [1 - (1 / DF)]
NOTE: If $NMHC_{conc}$ is calculated to be less than zero, then $NMHC_{conc}$ = 0

5.5.2 $NMHC_{mass_n}$ = $NMHC_{conc}$ * $NMHC_{dens}$ * VMIX * 10^{-6}

6. TOTAL WEIGHTED NMHC MASS EMISSIONS

6.1 All Vehicles

6.1.1 $$NMHC_{wm} = 0.43 * \left(\frac{NMHC_{mass1} + NMHC_{mass2}}{D_{phase1} + D_{phase2}} \right) + 0.57 * \left(\frac{NMHC_{mass3} + NMHC_{mass2}}{D_{phase3} + D_{phase2}} \right)$$

7. SAMPLE CALCULATIONS

7.1 Given the following data for a gasoline vehicle, calculate the weighted NMHC mass emission.

Test Phase	FID THC_e (ppmC)	FID THC_d (ppmC)	CH_{4e} (ppmC)	CH_{4d} (ppmC)	CO_{em} (ppm)	CO_{2e} (%)	VMIX (ft^3)	$D_{phase\ n}$ (mile)	R_a (%)
1	41.8	8.6	7.53	5.27	147.2	1.19	2846	3.583	38
2	13.0	8.4	5.68	5.10	20.8	0.80	4856	3.848	38
3	15.4	8.9	6.16	5.20	36.7	1.04	2839	3.586	38

For Phase 1:

$NMHC_e$ = FID THC_e - (r_{CH_4} * CH_{4e})
= 41.8 ppmC - (1.04 * 7.53 ppmC)
= 33.97 ppmC

$NMHC_d$ = FID THC_d - (r_{CH_4} * CH_{4d})
= 8.6 ppmC - (1.04 * 5.27 ppmC)
= 3.12 ppmC

CO_e = (1 - 0.01925 * CO_{2e} - 0.000323 * R_a) * CO_{em}
NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e .

= (1 - 0.01925 * 1.19% - 0.000323 * 38%) * 147.18 ppm
= 142.0 ppm

DF = 13.47 ÷ [CO_{2e} + ($NMHC_e$ + CH_{4e} + CO_e) * 10^{-4}]

$$DF = \frac{13.47}{1.19\% + (33.97\ ppmC + 7.53\ ppmC + 142.0\ ppmC) * 10^{-4}}$$

= 11.15

$NMHC_{conc}$ = $NMHC_e$ - $NMHC_d$ * [1 - (1 ÷ DF)]

= 33.97 ppmC - 3.12 ppmC * [1- (1÷11.15)]
= 31.13 ppmC

$NMHC_{mass\ n}$ = $NMHC_{conc}$ * $NMHC_{dens}$ * VMIX * 10^{-6}
= 31.13 ppmC * 16.33 g/ft^3 * 2846 ft^3 * 10^{-6}

$NMHC_{mass\ 1}$ = 1.45 g

Similarly, for Phase 2: $NMHC_{mass\ 2}$ = 0.33 g
and for Phase 3: $NMHC_{mass\ 3}$ = 0.27 g

Therefore,

$$NMHC_{wm} = 0.43 * \left(\frac{NMHC_{mass1} + NMHC_{mass2}}{D_{phase1} + D_{phase2}} \right) + 0.57 * \left(\frac{NMHC_{mass3} + NMHC_{mass2}}{D_{phase3} + D_{phase2}} \right)$$

$$NMHC_{wm} = 0.43 * \left(\frac{1.45\,g + 0.33\,g}{3.583\ miles + 3.848\ miles} \right) + 0.57 * \left(\frac{0.27\,g + 0.33\,g}{3.586\ miles + 3.848\ miles} \right)$$

$NMHC_{wm}$ = 0.15 g/mile

7.2 Given the following data for a vehicle operating on 85% methanol and 15% gasoline (M85), calculate the weighted NMHC mass emission.

Test Phase	FID THC_e (ppmC)	FID THC_d (ppmC)	CH_{4e} (ppmC)	CH_{4d} (ppmc)	CH_3OH_e (ppm)	CO_{em} (ppm)	CO_{2e} (%)	VMIX (ft^3)	$D_{phase\ n}$ (mile)	R_a (%)	$HCHO_e$ (ppm)
1	88.5	5.5	17.76	2.82	72.9	303.2	1.28	2832	3.570	32	0.96
2	14.5	7.0	8.01	2.82	5.1	9.7	0.83	4827	3.850	32	0.10
3	21.8	7.7	10.13	2.93	7.4	18.2	1.13	2825	3.586	32	0.12

[For this example, CH_3OH_d was assumed to be 0.0 ppmC for all three background bag samples.]

For Phase 1:

$NMHC_e$ = FID THC_e - (r_{CH_4} * CH_{4e}) - (r_{CH_3OH} * CH_3OH_e)
= 88.5 ppmC - (1.04*17.76 ppmC) - (0.66*72.9 ppmC)
= 21.92 ppmC

$NMHC_d$ = FID THC_d - (r_{CH_4} * CH_{4d}) - (r_{CH_3OH} * CH_3OH_d)
= 5.5 ppmC - (1.04*2.82 ppmC) - (0.66*0.0 ppmC)
= 2.57 ppmC

CO_e = (1 - 0.02705 * CO_{2e} - 0.000323 * R_a) * CO_{em}
NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e
.

= (1 - 0.02705 * 1.28% - 0.000323 * 32%) * 303.2 ppm
= 289.6 ppm

DF = 12.02 ÷ [CO_{2e} + ($NMHC_e$ + CH_{4e} + CO_e + CH_3OH_e + $HCHO_e$) * 10^{-4}]

$$= \frac{12.02}{1.28\% + (21.92\,\text{ppmC} + 17.76\,\text{ppmC} + 289.6\,\text{ppmC} + 72.9\,\text{ppmC} + 0.96\,\text{ppmC}) * 10^{-4}}$$

= 9.10

$NMHC_{conc}$ = $NMHC_e$ - $NMHC_d$ * [1 - (1 / DF)]
= 21.92 ppmC - 2.57 ppmC * [1 - (1 / 9.10)]
= 19.63 ppmC

$NMHC_{mass\ n}$ = $NMHC_{conc}$ * $NMHC_{dens}$ * VMIX * 10^{-6}

$NMHC_{mass\ 1}$ = 0.91 g

Similarly, Phase 2: $NMHC_{mass\ 2}$ = 0.0 g
and for Phase 3: $NMHC_{mass\ 3}$ = 0.10 g

Therefore,

$$NMHC_{wm} = 0.43 * \left(\frac{NMHC_{mass1} + NMHC_{mass2}}{D_{phase1} + D_{phase2}} \right) + 0.57 * \left(\frac{NMHC_{mass3} + NMHC_{mass2}}{D_{phase3} + D_{phase2}} \right)$$

$$NMHC_{wm} = 0.43 * \left(\frac{0.91\,\text{g} + 0.00\,\text{g}}{3.570\ \text{miles} + 3.850\ \text{miles}} \right) + 0.57 * \left(\frac{0.10\,\text{g} + 0.00\,\text{g}}{3.586\ \text{miles} + 3.850\ \text{miles}} \right)$$

$NMHC_{wm}$ = 0.06 g/mile

Part C

DETERMINATION OF ALCOHOLS IN AUTOMOTIVE SOURCE SAMPLES BY GAS CHROMATOGRAPHY

METHOD NO. 1001

1. INTRODUCTION

1.1 This document describes a method of sampling and analyzing automotive exhaust for alcohols in the range of 1 to 1200 µg per 15 mL of solution. The "target" alcohols that shall be analyzed and reported by this method are methanol and ethanol. These alcohols, when measured in concentrations above the LOD, shall be reported.

1.2 This procedure is based on a method developed by the U. S. Environmental Protection Agency, (U.S. EPA) [Ref 6] which involves flowing diluted engine exhaust through deionized or purified water contained in glass impingers and analyzing this solution by gas chromatography .

1.3 All definitions and abbreviations are contained in Appendix 2 of these test procedures.

2. METHOD SUMMARY

2.1 The samples are received by the laboratory in impingers. Compound separation and analysis are performed using a GC. The sample is injected into the GC by means of a liquid autosampler. Separation of the sample mixture into its components is performed by a temperature-programmed capillary column. A FID is used for alcohol detection and quantification.

2.2 The computerized GC data system identifies the alcohol associated with each peak. The alcohol concentrations are determined by integrating the peak areas and using response factors determined from external standards.

3. INTERFERENCES AND LIMITATIONS

3.1 An interferent is any component present in the sample with a retention time similar to that of any target alcohol described in this method. To reduce interference error, proof of chemical identity may require periodic confirmations using an alternate method and/or instrumentation, e.g., GC/MS.

3.2 The concentration of the alcohols in the range of interest is stable for up to six days as long as the samples are sealed and refrigerated at a temperature below 40^{o}F.

4. INSTRUMENTATION AND APPARATUS

4.1 For each mode of the CVS test, two sampling impingers, each containing a known amount of deionized or purified water (e.g. 15 mL for this procedure), are used to contain the sample.

4.1.1 A temperature-programmable GC, equipped with a DB-Wax Megabore column (30 m, 0.53 mm ID, 1.0 µ film thickness) and FID, is used. Other columns may be used, provided the alternate(s) can be demonstrated to be equivalent or better with respect to precision, accuracy and resolution of all the target alcohols.

4.1.2 A liquid autosampler is required.

4.1.3 A PC-controlled data acquisition system for quantifying peak areas is required.

5. REAGENTS AND MATERIALS

5.1 Methanol shall have a purity of 99.9 percent, or be high performance liquid chromatography grade, EM Science or equivalent.

5.2 Ethanol shall be absolute, ACS reagent grade.

5.3 ASTM Type I purified or Type II deionized water shall be used.

5.4 Stock solutions are prepared gravimetrically or volumetrically by diluting methanol and ethanol with deionized or purified water, e.g., for this method a typical stock solution contains approximately 10 mg/mL of each target alcohol. Stock solutions must be replaced at least every six months.

5.4.1 A **calibration standard** within the expected concentration range of the samples is prepared by successive dilutions of the stock solution with deionized or purified water; 3 to 50 µg/mL is typical, depending on fuel type. Calibration standards must be replaced at least every week.

5.4.2 A **control standard** containing all target alcohols is prepared by successive dilutions of a stock solution different from that of Section 5.4.1. This standard, at an approximate concentration of the samples, is used to monitor the precision of the analysis of each target alcohol. Control standards must be replaced at least every week.

5.4.3 Standards used for linearity and LOD determinations (Section 8) are also prepared by successive dilutions of an appropriate level stock solution.

5.4.4 All standards should be refrigerated at a temperature below 40°F during storage.

5.5 Gas requirements.

5.5.1 Air shall be "Zero" grade (<1 ppmC total hydrocarbon contamination) or better.

5.5.2 Nitrogen shall have a minimum purity of 99.998 percent.

5.5.3 Helium shall have a minimum purity of 99.995 percent.

5.5.4 Hydrogen shall have a minimum purity of 99.995 percent.

6. PROCEDURE

6.1 Each of the graduated sampling impingers is filled with 15 mL of deionized or purified water.

6.2 The impingers are placed in an ice bath during the sample collection.

6.3 After sampling, the solution contained in each impinger is transferred to a vial and sealed.

6.3.1 Samples shall be refrigerated at a temperature below 40°F if immediate analysis is not feasible, or if reanalysis at a later date may be required.

6.4 One microliter aliquots of unmodified samples are injected via autosampler into a GC. Suggested standard operating conditions for the GC are:

Column:	DB-Wax, 30 m, 0.53 mm ID, 1.0µ film thickness
Carrier gas flow:	Helium at 5 mL/min
Make-up gas flow:	Nitrogen at 25 mL/min
Detector:	FID, hydrogen at 30 mL/min and air at 300 mL/min
Injector:	Packed column injector with Megabore adapter insert; on-column injection
Column temperature:	50°C (1 min), 50°C to 70°C (5°C/min), 70°C to 110°C (15°C/min), 110°C (4 min)
Data system:	PC-based data acquisition system

6.5 Samples containing compounds having concentrations above the documented range of instrument linearity must be diluted and reanalyzed.

6.6 The peak integrations are corrected as necessary in the data system. Any misplaced baseline segments are corrected in the reconstructed chromatogram.

6.7 The peak identifications provided by the computer are checked and corrected if necessary.

7. CALCULATIONS

7.1 The concentration of each target alcohol, in µg/mL, is determined by the following calculation that compares the sample peak area with that of an external standard:

$$\text{Concentration } (\mu g/mL)_{sample} = \text{ Peak Area}_{sample} \text{ x Response Factor}$$

where the response factor (RF) is calculated during the calibration by:

$$RF = \frac{\text{Concentration}_{\text{standard}\,(\mu g/mL)}}{\text{Peak Area}_{\text{standard}}}$$

7.2 This concentration is then used to calculate the total amount of alcohol in each impinger:

Mass (µg) = Concentration (µg/mL) x Impinger volume (mL)

7.3 An internal standard method may also be used.

8. QUALITY CONTROL

8.1 Blank Run - A deionized or purified water blank is run each analysis day. All target alcohol concentrations from the blank analysis must be below the LOD before the analysis may proceed.

8.1.1 If the blank shows a peak greater than the limit of detection (LOD) in the region of interest, the source of the contamination must be investigated and remedied.

8.2 Calibration Run - The calibration standard is analyzed each analysis day to generate the response factor used to quantify the sample concentrations.

8.3 Control Standard Run - The quality control standard is analyzed at least once each analysis day. Measurements of all target alcohols in the control standard must fall within the control limits to ensure the validity of the sample analyses that day. To

meet this requirement, it may be necessary to inspect and repair the GC, and rerun the calibration and/or control standards.

8.4 Control Charts - A quality control chart is maintained for each analyte in the control standard. The control charts, used on a daily basis, establish that the method is "in-control". The following describes how to construct a typical control chart:

1. Obtain at least 20 daily control standard results;
2. Calculate the control standard mean concentration and standard deviation for the target analyte; and
3. Create a control chart for the target analyte by placing the concentration on the Y-axis and the date on the X-axis. Establish upper and lower warning limits at either two standard deviations (2s) or 5 percent, whichever is greater, above and below the average concentration. Establish upper and lower control limits at either three standard deviations (3s) or 5 percent, whichever is greater, above and below the average concentration.
4. A control standard measurement is considered to be out-of-control when the analyzed value exceeds the control limit or two successive control standard measurements of the same analyte exceed the warning limit.
5. If 20 control standard results are not yet available to create a control chart (e.g., the control standard was expended and replaced with a different concentration standard prior to obtaining 20 points with the new standard), measurements must be within 10% of the theoretical concentration.

The measured concentrations of all target analytes contained in the control standard must be within the control limits ("in-control") for the sample results to be considered acceptable.

8.5 Duplicates - A duplicate analysis of one sample is performed at least once per analysis day. The relative percent difference (RPD) is calculated for each duplicate run:

$$\mathrm{RPD}(\%) = \frac{|\text{Difference between duplicate and original measurements}|}{\text{Average of duplicate and original measurements}} * 100$$

For each compound, the allowable RPD depends on the average concentration level for the duplicate runs, as shown in the following table:

Average Measurement for Duplicate Runs		Allowable RPD (%)
1 to 10	times LOD	100
10 to 20	" "	30
20 to 50	" "	20
Greater than 50	" "	15

If the results of the duplicate analyses do not meet these criteria for all target alcohols, the sample may be reanalyzed. If reanalysis is not feasible or if the criteria are still not met on reanalysis, all sample results for that analysis day are invalid.

8.6 Linearity - A multipoint calibration to confirm instrument linearity is performed for all target alcohols for new instruments, after making instrument modifications that can affect linearity, and at least once every year. The multipoint calibration consists of at least five concentration or mass loading levels, each above the LOD, distributed over the range of expected sample concentration. Each concentration level is measured at least twice. A linear regression analysis is performed using concentration and area counts to determine the regression correlation coefficient (r). The r must be greater than 0.995 to be considered sufficiently linear for one point calibrations.

8.7 Limit of Detection - The LOD for the target alcohols must be determined for new instruments, after making instrument modifications that can affect the LOD and at least once every year. To make the calculations, it is necessary to perform a multipoint calibration consisting of at least four "low" concentration levels, each above the expected LOD, with at least five replicate determinations of the lowest concentration standard. A linear regression is performed and the standard deviation (in area counts) of the lowest concentration standard determined. The standard deviation is converted to concentration units using the slope of the linear regression:

$$s = s_a \div m$$

where m is the slope of the linear regression, s is the standard deviation (in concentration units) of the lowest concentration standard and s_a is the standard deviation (in area counts) of the lowest concentration standard.

The LOD must be calculated using the following equation [Ref. 12]:

$$LOD = t * s$$

where s is the standard deviation (in concentration units) of at least five replicate determinations of the lowest concentration standard and t is the t-factor for 99 percent confidence for a one-sided normal (Gaussian) distribution. The number of

degrees of freedom is equal to the number of replicates, minus one. An abbreviated t–table is:

Degrees of Freedom	t-value
4	3.7
5	3.4
6	3.1
7	3.0

The lowest standard must be of a concentration of one to five times the estimated LOD.

8.7.1 The maximum allowable LOD for each alcohol is 0.10 µg/mL. The calculated laboratory LOD must be equal to or lower than the maximum allowable LOD. All peaks identified as target compounds that are equal to or exceed the maximum allowable LOD must be reported. If the calculated laboratory LOD is less than the maximum allowable LOD, the laboratory may choose to set its reporting limit at the maximum allowable LOD, the calculated laboratory LOD, or any level in between.

8.7.2 For the purpose of calculating the total mass of all species, the concentrations of the compounds below the LOD are considered to be zero.

Part D

DETERMINATION OF C_2 TO C_5 HYDROCARBONS IN AUTOMOTIVE SOURCE SAMPLES BY GAS CHROMATOGRAPHY

METHOD NO. 1002

1. INTRODUCTION

1.1 This document describes a gas chromatographic method of analyzing C_2 to C_5 hydrocarbons (light-end hydrocarbons) in the ppbC range from automotive source samples. This method does not include sample collection procedures [Ref. 8]. The "target" hydrocarbons that shall be analyzed and reported by this method and Method 1003 are listed in Appendix 1. All compounds on this list, when measured in concentrations above the LOD, shall be measured and reported ("targeted") by either Method 1002 or Method 1003. Each laboratory should divide the list into light-end (Method 1002) and mid-range (Method 1003) hydrocarbons in the manner that best suits the laboratory instrumentation. All compounds on the list not targeted by Method 1002 must be targeted by Method 1003.

1.2 All definitions and abbreviations are contained in Appendix 2 of these test procedures.

2. METHOD SUMMARY

2.1 This is a method intended for routine analysis.

2.2 The samples are received by the laboratory in Tedlar bags, which are sub-sampled into a GC for separation and analysis.

2.3 The gas chromatographic analysis is performed on an Alumina (Al_20_3) PLOT column temperature programmed from 0^oC to 200^oC. An FID is used for detection and quantification.

2.4 The sample is injected into the GC by means of gas sampling valves. Separation of the sample hydrocarbon mixture into its components takes place in the chromatographic column. The chromatographic column and the corresponding operating parameters described in this method normally provide complete resolution of most target compounds.

2.5 The computerized GC data acquisition system identifies the hydrocarbons associated with each peak. The hydrocarbon concentrations are determined by integrating the peak areas and using response factors determined from NIST-traceable standards.

3. INTERFERENCES AND LIMITATIONS

3.1 An interferent is any component present in the sample with a retention time very similar to that of any target hydrocarbon described in this method. To reduce interference error, proof of chemical identity may require periodic confirmations using an alternate method and/or instrumentation, e.g., GC/MS, PID, different column, etc.

3.2 To maximize sample integrity, sample bags should not leak or be exposed to bright light or excessive heat. Sampling bags must be shielded from direct sunlight to avoid photochemically induced reactions of any reactive hydrocarbons. The compound 1,3-butadiene, resulting mostly during cold-start testing is unstable. Therefore all cold-start samples must be analyzed within 8 hours; all other samples must be analyzed within 24 hours, although analysis within 8 hours is recommended.

4. INSTRUMENTS AND APPARATUS

4.1 Tedlar bags, 2 mil in thickness, nominally 5 to 10 liters in capacity and equipped with quick-connect fittings, are used to contain the samples.

4.2 For manual sub-sampling into a GC, a ground glass syringe is used to transfer gaseous samples from Tedlar bags to the GC sample inlet. For automated systems, a sample loop is used to transfer gaseous samples from the Tedlar bag to the sample inlet of the GC. Sample aliquot size is chosen based on considerations of instrument sensitivity and/or linearity.

4.3 A temperature-programmable GC equipped with a gas sampling valve system, a FID, and accessories is required.

4.4 An Alumina PLOT column (50 m x 0.32 mm) is used. A wax precolumn is recommended to prevent water damage to the PLOT column. Other columns may be used, provided the alternate(s) can be demonstrated to be equivalent or better with respect to precision, accuracy and resolution of all the target hydrocarbons.

4.5 A sample trap capable of being cryogenically cooled may be used.

4.6 Data acquisition software is used to integrate peak areas to determine hydrocarbon concentrations.

5. REAGENTS AND MATERIALS

5.1 Helium shall have a minimum purity of 99.995 percent. Higher purity helium may be required to achieve the LOD required by Section 8.7.1.

5.2 Hydrogen shall have a minimum purity of 99.995 percent.

5.3 Air shall be "Zero" grade (<1 ppmC total hydrocarbon contamination) or better.

5.4 Nitrogen shall have a minimum purity of 99.998 percent.

5.5 Calibration Standard - The quantitative calibration standard for all target hydrocarbons shall be propane at a concentration level between 0.25 and 1 ppm-mole and within the calculated linearity of the method. (See Section 8.6.) This propane standard must be a NIST-certified SRM or secondary NIST-traceable standard. A secondary standard is obtained by a comparison between a SRM and a candidate standard.

5.6 Control Standard - A quality control standard, containing at least ethene, propane, n-butane, and 2-methylpropene with concentrations between 0.2 and 3 ppmC based on a propane standard, is used for the following purposes:

1. Daily update of control charts, and
2. Daily determination of marker retention time windows.

5.7 A high concentration standard (higher than the calibration standard), containing the target hydrocarbons listed in Section 5.6, is used for linearity determinations. The high concentration standard must have concentrations verified against a NIST-traceable propane standard. (See Section 5.5 for the definition of NIST-traceable.) This verification can be performed at the laboratory performing the analysis.

5.8 A low concentration standard (one to five times the estimated LOD), containing the target hydrocarbons listed in Section 5.6, is used for LOD determinations. The low concentration standard must have concentrations verified against a NIST-traceable propane standard. (See Section 5.5 for the definition of NIST-traceable.) This verification can be performed at the laboratory performing the analysis.

5.8.1 In lieu of a low concentration standard, a higher concentration standard may be diluted.

5.9 Liquid nitrogen may be required to cool the cryogenic sample trap and column oven where applicable.

6. PROCEDURE

6.1 The gaseous sample is analyzed for the target hydrocarbons C_2 through C_5.

6.2 Suggested standard operating conditions for the gas chromatograph are:

Helium carrier gas velocity:	30 cm/sec at 200^0C
Nitrogen make-up gas flow:	sufficient such that the total flow of helium plus nitrogen is 30 mL/min
Hydrogen gas flow:	30 mL/min
Air flow:	300 mL/min
Sample valve temperature:	150^0C (PLOT column)
Column temperature:	0^0C (hold 7 min), 10^0C/min to 200^0C (hold 15 min)
Detector temperature:	250^0C
Injector temperature:	150^0C

6.3 For automated systems, connect the samples to the GC and begin the analytical process.

6.4 Introduce the sample into the carrier gas stream through the injection valve.

6.5 Each separated component exits from the column into the FID where a response is generated.

6.6 Concentrations of hydrocarbons are calculated using data acquisition/ processing software that uses calibration data from the NIST-traceable propane calibration standard.

6.7 For compounds having concentrations above the documented range of instrument linearity, a smaller aliquot must be taken (for manual systems, a smaller syringe or smaller loop; for automated systems, a smaller loop) or the sample must be diluted.

6.8 The peak integrations are corrected as necessary in the data system. Any misplaced baseline segments are corrected in the reconstructed chromatogram.

6.9 The peak identifications provided by the computer are checked and corrected if necessary.

6.10 Target compounds that coelute are reported as the major component, as determined by the analysis of several samples by GC/MS or other methods. An exception to this is m- and p-xylene, where GC/MS data and fuel profiles are used to determine the relative contribution of each component to the peak. This method was used to determine the m- and p-xylene MIR value given in Appendix 1.

6.11 The Alumina PLOT column is programmed to 200^{o}C to assure all compounds are eluted before the next run.

7. CALCULATIONS

7.1 The target hydrocarbon concentrations, in ppbC, are calculated by the data system using propane as an external standard.

$$\text{Concentration}_{\text{sample}}\ (\text{ppbC}) = \text{Peak Area}_{\text{sample}} \times \text{Response Factor}$$

where the response factor (RF) is calculated during daily calibration by:

$$\text{RF} = \frac{\text{Concentration of NIST-traceable propane standard, ppbC}}{\text{Area of propane peak}}$$

8. QUALITY CONTROL

8.1 Blank Run - A blank (pure nitrogen or helium) is run each analysis day. All target hydrocarbon concentrations from the blank analysis must be below the LOD before the analysis may proceed. As an alternative to a daily blank run, a daily partial blank check in tandem with a weekly blank run may be used. A partial blank check is defined as a check of the calibration standard run for contamination over all but the propane region of the chromatograph. The calibration standard must consist of only propane and make-up gas, with the concentration of all organic compounds except methane and propane below 2 percent of the propane standard concentration. The weekly blank run will provide a check on contamination in the propane region of the chromatograph.

8.1.1 If the blank shows a peak greater than the limit of detection (LOD) in the region of interest, the source of contamination must be investigated and remedied.

8.2 Calibration Run - The calibration standard is analyzed each analysis day to generate the response factor used to quantify the sample concentrations.

8.3 Control Standard Run - The quality control standard is analyzed at least once each analysis day. Measurements of all compounds specified in Section 5.6 must fall within the control limits to ensure the validity of the sample analyses that day. To meet this requirement, it may be necessary to inspect and repair the GC, and rerun the calibration and/or control standards.

8.4 Control Charts - A quality control chart is maintained for each component of the control standard listed in Section 5.6. The control charts, used on a daily basis, establish that the method is “in- control.” The following describes how to construct a typical control chart:

1. Obtain at least 20 daily control standard results;
2. Calculate the control standard mean concentration and standard deviation for the target hydrocarbon; and
3. Create a control chart for the target hydrocarbon by placing the concentration on the Y-axis and the date on the X-axis. Establish upper and lower warning limits at either two standard deviations (2s) or 5 percent, whichever is greater, above and below the average concentration. Establish upper and lower control limits at either three standard deviations (3s) or 5 percent, whichever is greater, above and below the average concentration.
4. A control standard measurement is considered to be out-of-control when the analyzed value exceeds the control limit or two successive control standard measurements of the same analyte exceed the warning limit.
5. If 20 control standard measurements are not yet available to create a control chart (e.g., the control standard was expended and replaced prior to obtaining 20 points with the new standard), measurements must be within 10% of the certified concentration. If the control standard is not a NIST standard, the cylinder should be certified by the laboratory against a NIST standard.

The measured concentrations of all target hydrocarbons contained in the control standard must be within the control limits (in-control) for the sample results to be considered acceptable.

8.5 Duplicates - A duplicate analysis of one sample is performed at least once per analysis day. The relative percent difference (RPD) is calculated for each duplicate run:

$$\text{RPD (\%)} = \frac{|\text{Difference between duplicate and original measurements}|}{\text{Average of duplicate and original measurements}} \times 100$$

For each compound specified in Section 5.6, the allowable RPD depends on the average concentration level for the duplicate runs, as shown in the following table:

Average Measurement for the Duplicate Runs			Allowable RPD (%)
1 to 10	times	LOD	100
10 to 20	"	"	30
20 to 50	"	"	20
Greater than 50	"	"	15

If the results of the duplicate analyses do not meet these criteria for all compounds specified in Section 5.6, the sample may be reanalyzed. If reanalysis is not feasible or if the criteria are still not met on reanalysis, all sample results for that analysis day are invalid.

8.6 Linearity - A multipoint calibration to confirm instrument linearity is performed for the target hydrocarbons in the control standard for new instruments, after making instrument modifications that can affect linearity, and at least once every year unless a daily check of the instrument response indicates that the linearity has not changed. To monitor the instrument response, a quality control chart is constructed, as specified in Section 8.4, except using calibration standard area counts rather than control standard concentrations. When the standard area counts are out-of-control, corrective action(s) must be taken before analysis may proceed. The multipoint calibration consists of at least five concentration or mass loading levels (using smaller or larger volume sample sizes of existing standards is acceptable), each above the LOD, distributed over the range of expected sample concentration. Each concentration level is measured at least twice. A linear regression analysis is performed using concentration and average area counts to determine the regression correlation coefficient (r). The r must be greater than 0.995 to be considered sufficiently linear for one-point calibrations.

8.7 Limit of Detection – The LOD for the target hydrocarbons in the control standard must be determined must be determined for new instruments and after making instrument modifications that can affect linearity and/or sensitivity and at least once every year unless a daily check of the instrument response indicates that the LOD has not changed. To monitor the instrument response, a quality control chart is constructed, as specified in Section 8.4, except using calibration standard area counts rather than control standard concentrations. When the calibration standard area counts are out-of-control, investigation and/or corrective action(s) must be taken. To make the calculations, it is necessary to perform a multipoint calibration consisting of at least four "low" concentration levels, each above the LOD, with at least five replicate determinations of the lowest concentration standard. A linear regression is performed and the standard deviation is converted to concentration units using the slope of the linear regression:

$$s = s_a \div m$$

where m is the slope of the linear regression, s is the standard deviation (in concentration units) of the lowest concentration standard and s_a is the standard deviation (in area counts) of the lowest concentration standard.

The LOD must be calculated using the following equation [Ref. 12]:

$$LOD = t * s$$

where s is the standard deviation (in concentration units) of at least five replicate determinations of the lowest concentration standard and t is the t-factor for 99 percent confidence for a one-sided normal (Gaussian) distribution. The number of degrees of freedom is equal to the number of replicates, minus one. An abbreviated t-table is:

Degrees of Freedom	t-value
4	3.7
5	3.4
6	3.1
7	3.0

The lowest standard must be of a concentration of one to five times the estimated LOD.

8.7.1 The maximum allowable LOD for each compound is 5 ppbC. The calculated laboratory LOD must be equal to or lower than the maximum allowable LOD. All peaks identified as target compounds that are equal to or exceed the maximum allowable LOD must be reported. If the calculated laboratory LOD is less than the maximum allowable LOD, the laboratory may choose to set its reporting limit at the maximum allowable LOD, the calculated laboratory LOD, or any level in between.

8.7.2 For the purpose of calculating the total mass of all species, the concentrations of all compounds below the LOD are considered to be zero.

8.8 Method No. 1002/Method No. 1003 Crossover Check - For each sample, a compound shall be measured by both Method No. 1002 and Method No. 1003. The crossover compound shall be a compound that can reasonably be expected to be found and measured by both methods in the laboratory performing the analysis. The results obtained by the two methods should be compared and an acceptance criteria set for the relative percent difference.

Part E

DETERMINATION OF C_6 TO C_{12} HYDROCARBONS IN AUTOMOTIVE SOURCE SAMPLES BY GAS CHROMATOGRAPHY

METHOD NO. 1003

1. INTRODUCTION

1.1 This document describes a gas chromatographic method of analyzing C_6 to C_{12} hydrocarbons (mid-range hydrocarbons) in the ppbC range from automotive source samples. This method does not include sample collection procedures [Ref. 7]. The target hydrocarbons that shall be analyzed and reported by this method and Method 1002 are listed in Appendix 1. All compounds on this list, when measured in concentrations above the LOD, shall be measured and reported ("targeted") by either Method 1002 or Method 1003. Each laboratory should divide the list into light-end (Method 1002) and mid-range (Method 1003) hydrocarbons in the manner that best suits the laboratory instrumentation. All compounds on the list not targeted by Method 1003 must be targeted by Method 1002.

1.2 All definitions and abbreviations are contained in Appendix 2 of these test procedures.

2. METHOD SUMMARY

2.1 This is a method intended for routine analysis.

2.2 The samples are received by the laboratory in Tedlar bags, which are sub-sampled into a GC for separation and analysis.

2.3 The gas chromatographic analysis is performed through a temperature-programmed capillary column. A FID is used for detection.

2.4 The sample is injected into the GC by means of gas sampling valves. Separation of the sample hydrocarbon mixture into its components takes place in the chromatographic column. The chromatographic column and the corresponding operating parameters described in this method normally provide complete resolution of most target hydrocarbons.

2.5 The computerized GC data acquisition system identifies the hydrocarbons associated with each peak. The hydrocarbon concentrations are determined by integrating the peak areas and using a response factor determined from NIST-traceable standards.

3. INTERFERENCES AND LIMITATIONS

3.1 An interferent is any component present in the sample with a retention time similar to that of any target hydrocarbon described in this method. To reduce interference error, proof of chemical identity may require periodic confirmations using an alternate method and/or instrumentation, e.g., GC/MS, PID, different column, etc.

3.2 The concentration of hydrocarbons in the range of interest is stable for at least 24 hours in the Tedlar sampling bags, provided the sample bags do not leak and are not exposed to bright light or excessive heat. Sampling bags must be shielded from direct sunlight to avoid photochemically induced reactions of any reactive hydrocarbons. Samples must be analyzed within 24 hours.

4. INSTRUMENTATION AND APPARATUS

4.1 Tedlar bags, 2 mil in thickness, nominally 5 to 10 liters in capacity and equipped with quick-connect fittings, are used to contain the samples.

4.2 For manual sub-sampling into a GC, a ground glass syringe is used to transfer gaseous samples from Tedlar bags to the GC sample inlet. For automated systems, a sample loop is used to transfer gaseous samples from the Tedlar bag to the sample inlet of the GC. Sample aliquot size is chosen based on considerations of instrument sensitivity and/or linearity.

4.3 The GC is equipped with a FID, and a gas sampling valve system.

4.4 A non-polar capillary column [e.g., J&W DB-1, 60 m x 0.32 mm ID, film thickness 1.0 µ] is used. Other columns may be used, provided the alternate(s) can be demonstrated to be equivalent or better with respect to precision, accuracy and resolution of all the target hydrocarbons.

4.5 A sample trap capable of being cryogenically cooled may be used.

4.6 A computer-controlled data acquisition system is required for quantifying peak areas.

5. REAGENTS AND MATERIALS

5.1 Helium shall have a minimum purity of 99.995 percent. Higher purity helium may be required to achieve the LOD required by Section 8.7.1.

5.2 Hydrogen shall have a minimum purity of 99.995 percent.

5.3 Air shall be “Zero” grade (<1 ppmC total hydrocarbon contamination) or better.

5.4 Nitrogen shall have a minimum purity of 99.998 percent.

5.5 Calibration Standard - The quantitative calibration standard for all target hydrocarbons shall be propane at a concentration level between 0.25 and 1 ppm-mole and within the calculated linearity of the method. (See Section 8.6.) This propane standard must be a NIST-certified SRM or secondary NIST-traceable standard. A secondary standard is obtained by a comparison between a SRM and a candidate standard.

5.6 Control Standard - A quality control standard, containing at least n-hexane, n-octane, n-decane, benzene, toluene, and m- or p-xylene with concentrations between 0.2 and 1 ppmC based on a propane standard, is used for the following purposes:

1. Daily update of control charts, and
2. Daily determination of marker retention time windows.

5.7 A high concentration standard (higher than the calibration standard), containing the target hydrocarbons listed in Section 5.6, is used for linearity determinations. The high concentration standard must have concentrations verified against a NIST-traceable propane standard. (See Section 5.5 for the definition of NIST-traceable.) This verification can be performed at the laboratory performing the analysis.

5.8 A low concentration standard (one to five times the estimated LOD), containing the target hydrocarbons listed in Section 5.6, is used for LOD determinations. The low concentration standard must have concentrations verified against a NIST-traceable propane standard. (See Section 5.5 for the definition of NIST-traceable.) This verification can be performed at the laboratory performing the analysis.

5.8.1 In lieu of a low concentration standard, a higher concentration standard may be diluted.

5.9 Liquid nitrogen may be required to cool the cryogenic trap and column oven where applicable.

6. PROCEDURE

6.1 Typical operating conditions.

6.1.1 Suggested operating conditions for the manual GC are:

Helium carrier gas velocity:	30 cm/sec at 200°C
Nitrogen make-up gas flow:	sufficient such that the total flow of helium plus nitrogen is 30 mL/min
Hydrogen gas flow (for FID):	30 mL/min
"Zero" air gas flow (for FID):	300 mL/min
Autozero FID at:	0.0 min
Range 11, Attenuation 8 (or another suitable value)	
Sample valve temperature:	150°C
Injector temperature:	150°C
Column entrance port temperature:	95°C
Detector temperature:	250°C
Column temperature:	Initial temperature 0°C; 10°C/min to 200°C

6.1.2 Suggested operating conditions for the automated GC are:

Helium carrier gas velocity:	30 cm/sec at 200°C
Nitrogen make-up gas flow:	sufficient such that the total flow of helium plus nitrogen is 30 mL/min
Hydrogen gas flow (for FID):	30 mL/min
"Zero" air gas flow (for FID):	300 mL/min
Range 12, attenuation 8 (or another suitable value)	
Sample valve temperature:	150°C
Detector temperature:	300°C
Injector temperature:	150°C
Column temperature:	Initial temperature -50°C (5 min), 5°C/min to 50°C, 10°C/min to 200°C

6.2 Data Reduction

6.2.1 The results are calculated from the FID responses.

6.2.2 The results are examined to see that the peaks are correctly integrated.

6.2.3 After running a particularly "dirty" sample, the analyst should run a blank before proceeding to the next sample as there may be sample carryover, or flush the sampling system with air.

6.2.4 The peak identifications provided by the computer are reviewed and, if necessary, corrected using the following procedure and criteria:

1. The relative retention indices from GC/MS analyses are used to help confirm peak identifications.
2. The primary peak identification is done by the computer using the relative retention times based on reference calibration runs.
3. Confirm that the relative peak heights of the sample run ("fingerprint") match the typical fingerprint seen in past sample runs.
4. Compare the relative retention times of the sample peaks with those of reference runs.
5. Any peak with a reasonable doubt is labeled 'Unidentified'.

6.2.5 For compounds having concentrations above the documented range of instrument linearity, a smaller aliquot must be taken (for manual systems, a smaller syringe or smaller loop; for automated systems, a smaller loop) or the sample must be diluted.

6.2.6 The concentrations of the hydrocarbons are calculated using data acquisition/ processing software which uses calibration data from a NIST-traceable propane calibration standard.

6.2.7 Target compounds that coelute are reported as the major component, as determined by the analysis of several samples by GC/MS or other methods. An exception to this is m- and p-xylene, where GC/MS data and fuel profiles are used to determine the relative contribution of each component to the peak. This method was used to determine the m- and p-xylene MIR value given in Appendix 1.

7. CALCULATIONS

7.1 The target hydrocarbon concentrations, in ppbC, are calculated by the data system using propane as an external standard.

$$\text{Concentration}_{\text{sample}}\ (\text{ppbC}) = \text{Peak Area}_{\text{sample}} * \text{Response Factor}$$

where the Response Factor (RF) is calculated during daily calibration by:

$$\text{RF} = \frac{\text{Concentration of NIST – traceable propane standard, ppbC}}{\text{Area of propane peak}}$$

8. QUALITY CONTROL

8.1 Blank Run - A blank (pure nitrogen or helium) is run each analysis day. All target hydrocarbon concentrations from the blank analysis must be below the LOD before the analysis may proceed. As an alternative to a daily blank run, a daily partial blank check in tandem with a weekly blank run may be used. A partial blank check is defined as a check of the calibration standard run for contamination over all but the propane region of the chromatograph. The calibration standard must consist of only propane and make-up gas, with the concentration of all organic compounds except methane and propane below 2 percent of the propane standard concentration. The weekly blank run will provide a check on contamination in the propane region of the chromatograph.

8.1.1 If the blank shows a peak greater than the limit of detection (LOD) in the region of interest, the source of the contamination must be investigated and remedied.

8.2 Calibration Run - The calibration standard is analyzed each analysis day to generate the response factor used to quantify the sample concentrations.

8.3 Control Standard Run - The quality control standard is analyzed at least once each analysis day. Measurements of all compounds specified in Section 5.6 must fall within the control limits to ensure the validity of the sample analyses that day. To meet this requirement, it may be necessary to inspect and repair the GC, and rerun the calibration and/or control standards.

8.4 Control Charts - A quality control chart is maintained for each component of the control standard listed in Section 5.6. The control charts, used on a daily basis, establish that the method is “in-control”. The following describes how to construct a typical control chart:

1. Obtain at least 20 daily control standard results,
2. Calculate the control standard mean concentration and standard deviation for the target hydrocarbon, and
3. Create a control chart for the target hydrocarbon by placing the concentration on the Y-axis and the date on the X-axis. Establish upper and lower warning limits at either two standard deviations (2s) or 5 percent, whichever is greater, above and below the average concentration. Establish upper and lower control limits at either three standard deviations (3s) or 5 percent, whichever is greater, above and below the average concentration.
4. A control standard measurement is considered to be out-of-control when the analyzed value exceeds the control limit or two successive control standard measurements of the same analyte exceed the warning limit.
5. If 20 control standard measurements are not yet available to create a control chart (e.g., the control standard was expended and replaced prior

to obtaining 20 points with the new standard), measurements must be within 10% of the certified concentration. If the control standard is not a NIST standard, the cylinder should be certified by the laboratory against a NIST standard.

The measured concentrations of all target hydrocarbons contained in the control standard must be within the control limits (in-control) for the sample results to be considered acceptable.

8.5 Duplicates - A duplicate analysis of one sample is performed at least once per analysis day. The relative percent difference (RPD) is calculated for each duplicate run:

$$\text{RPD}(\%) = \frac{|\text{Difference between duplicate and original measurements}|}{\text{Average of duplicate and original measurements}} * 100$$

For each compound specified in Section 5.6, the allowable RPD depends on the average concentration level for the duplicate runs, as shown in the following table:

Average Measurement for Duplicate Runs			Allowable RPD (%)
1 to 10	times	LOD	100
10 to 20	"	"	30
20 to 50	"	"	20
Greater than 50	"	"	15

If the results of the duplicate analyses do not meet these criteria for all compounds specified in Section 5.6, the sample may be reanalyzed. If reanalysis is not feasible or if the criteria are still not met on reanalysis, all sample results for that analysis day are invalid.

8.6 Linearity - A multipoint calibration to confirm instrument linearity is performed for all target hydrocarbons in the control standard for new instruments, after making instrument modifications that can affect linearity, and at least once every year unless a daily check of the instrument response indicates that the linearity has not changed. To monitor the instrument response, a quality control chart is constructed, as specified in Section 8.4, except using calibration standard area counts rather than control standard concentrations. When the standard area counts are out-of-control, corrective action(s) must be taken before analysis may proceed. The multipoint calibration consists of at least five concentration or mass loading levels (using smaller or larger volume sample sizes of existing standards is acceptable), each above the LOD, distributed over the range of expected sample concentration. Each concentration level is measured at least twice. A linear regression analysis is performed using concentration and average area counts to

determine the regression correlation coefficient (r). The r must be greater than 0.995 to be considered sufficiently linear for one point calibrations.

8.7 Limit of Detection - The LOD for the target hydrocarbons in the control standard must be determined for new instruments and after making instrument modifications that can affect linearity and/or sensitivity and at least once every year unless a daily check of the instrument response indicates that the LOD has not changed. To monitor the instrument response, a quality control chart is constructed, as specified in Section 8.4, except using calibration standard area counts rather than control standard concentrations. When the calibration standard area counts are out-of-control, investigation and/or corrective action(s) must be taken. To make the calculations, it is necessary to perform a multipoint calibration consisting of at least four "low" concentration levels, each above the LOD, with at least five replicate determinations of the lowest concentration standard. A linear regression is performed and the standard deviation (in area counts) of the lowest concentration standard determined. The standard deviation is converted to concentration units using the slope of the linear regression:

$$s = s_a \div m$$

where m is the slope of the linear regression, s is the standard deviation (in concentration units) of the lowest concentration standard and s_a is the standard deviation (in area counts) of the lowest concentration standard.

The LOD must be calculated using the following equation [Ref. 12]:

$$LOD = t * s$$

where s is the standard deviation (in concentration units) of at least five replicate determinations of the lowest concentration standard and t is the t-factor for 99 percent confidence for a one-sided normal (Gaussian) distribution. The number of degrees of freedom is equal to the number of replicates, minus one. An abbreviated t-table is:

Degrees of Freedom	t-value
4	3.7
5	3.4
6	3.1
7	3.0

The lowest standard must be of a concentration of one to five times the estimated LOD.

8.7.1 The maximum allowable LOD for each compound is 5 ppbC. The calculated laboratory LOD must be equal to or lower than the maximum allowable LOD. All peaks identified as target compounds that are equal to

or exceed the maximum LOD must be reported. If the calculated laboratory LOD is less than the maximum allowable LOD, the laboratory may choose to set its reporting limit at the maximum allowable LOD, the calculated laboratory LOD, or any level in between.

8.7.2. For the purpose of calculating the total mass of all species, the concentrations of all compounds below the LOD are considered to be zero.

8.8 Method No. 1002/Method No. 1003 Crossover Check - For each sample a compound shall be measured by both Method No. 1002 and Method No. 1003. The crossover compound shall be a compound that can reasonably be expected to be found and measured by both methods in the laboratory performing the analysis. The results of the two analyses should be compared and an acceptance criteria set for the relative percent difference.

Part F

DETERMINATION OF ALDEHYDE AND KETONE COMPOUNDS IN AUTOMOTIVE SOURCE SAMPLES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

METHOD NO. 1004

1. INTRODUCTION

1.1 This document describes a method of analyzing automotive engine exhaust for aldehyde and ketone compounds (carbonyls) using impingers, containing acidified 2,4-dinitrophenylhydrazine (DNPH)-absorbing solution, or DNPH-impregnated cartridges. Carbonyl masses ranging between 0.02 to 200 µg are measured by this method. The "target" carbonyls that shall be analyzed and reported by this method are listed in Appendix 1. All of these carbonyl compounds, when measured in concentrations above the LOD, shall be reported.

1.2 This procedure is derived from a method used by Hull [Ref. 10].

1.3 All definitions and abbreviations are contained in Appendix 2 of these test procedures.

2. METHOD SUMMARY

2.1 The samples are received by the laboratory in sample collection cartridges or impingers. (See Section 4.2.) The absorbing solution (2,4-DNPH) complexes the carbonyl compounds into their diphenylhydrazone derivatives. The cartridges are then eluted with 5 mL acetonitrile.

2.2 Separation and analysis are performed using a HPLC with an ultraviolet detector.

3. INTERFERENCES AND LIMITATIONS

3.1 An interferent is any detectable compound present in the sample with a retention time very similar to that of any target carbonyl described in this method. To reduce interference error, proof of chemical identity may require periodic confirmations using an alternate method and/or instrumentation, e.g., alternative HPLC columns or mobile phase compositions.

3.2 If samples are not analyzed the same day as received, they must be refrigerated at a temperature below 40^{o}F. Impinger solutions must first be transferred to glass bottles and sealed. Refrigerated samples are stable for up to 30 days.

3.3 When using the DuPont Zorbax or Supelco's Supelcosil columns described in Section 4.1.5, methyl ethyl ketone (MEK) and butyraldehyde tend to coelute.

3.4 When using the Delta Bond column described in Section 4.1.5, formaldehyde tends to coelute with an unknown, non-carbonyl compound, and the tolualdehyde isomers tend to coelute. The guard column for the Delta Bond column must also be changed frequently in order to prevent the coelution of butyraldehyde and methacrolein and to prolong the life of the column.

4. INSTRUMENT AND APPARATUS

4.1 The HPLC analytical system consists of the following:

4.1.1 Dual high pressure pumps.
4.1.2 Automated gradient controller or pump module controller.
4.1.3 Temperature controller module for the column oven.
4.1.4 A liquid autosampler.
4.1.5 The primary system incorporates two DuPont Zorbax ODS or Supelco's Supelcosil columns in tandem and a guard column, (2 cm long packed with LC18 5 µm pellicular beads). The secondary system incorporates a Delta Bond AK (4.6 mm ID x 200 mm) packed column with a guard column 2 cm long packed with LC18 5 µm pellicular beads or equivalent). Other columns may be used, provided the alternate(s) can be demonstrated to be equivalent or better with respect to precision, accuracy and resolution of all target carbonyls.
4.1.6 An ultraviolet/visible (UV/VIS) detector.
4.1.7 Data system for peak integration.

4.2 Sample collection containers are glass impingers or DNPH-impregnated cartridges.

5. REAGENTS AND MATERIALS

5.1 Acetonitrile, HPLC grade, (Burdick and Jackson or equivalent).

5.2 Water, HPLC grade, (Burdick and Jackson or equivalent).

5.3 2,4-DNPH, purified, Radian Corporation or equivalent. Unpurified DNPH must be recrystallized twice from acetonitrile. The recrystallized DNPH is checked for contaminants by injecting a dilute solution of DNPH in contaminant-free acetonitrile into the HPLC.

5.4 Sulfuric acid, or perchloric acid, analytical reagent grade, (Baker Analyzed or equivalent).

5.5 The carbonyl/2,4-dinitrophenylhydrazone (DNPH) complexes [Ref. 11] listed in Table F1 may be purchased (e.g., Radian Corporation, in 1.2 mL ampules) or prepared in the laboratory. In-house standards must be recrystallized at least three times from 95 percent ethanol.

TABLE F-1
PROPERTIES OF CARBONYL/2,4-DNPH COMPLEXES

Complex	Molecular Weight (g/mole)	Melting Point ^{o}C
formaldehyde	210.15	165-166
acetaldehyde	224.18	152-153
acrolein	236.19	165[1]
acetone	238.20	125-127
propionaldehyde	238.20	144-145
butyraldehyde	252.23	119-120
hexanaldehyde	280.28	106-107
benzaldehyde	286.25	240-242
methyl ethyl ketone	252.53	117-118
methacrolein	250.21	200-201
crotonaldehyde	250.21	185-188
valeraldehyde	266.26	107-108
m-tolualdehyde	300.27	212

5.6 Stock Calibration Standard - A stock calibration standard is prepared by diluting the target carbonyl/2,4-DNPH complexes with acetonitrile. A typical stock calibration standard contains 3.0 µg/mL of each target carbonyl compound. Stock calibration standards of other concentrations may also be used.

5.7 Working Standard - A working standard is prepared when required by diluting the stock calibration solution, making sure that the highest concentration of the standard is above the expected test level. Typically, the 3.0 µg/mL stock is diluted five times with acetonitrile in a volumetric flask to yield a 0.6 µg/mL solution.

5.8 Control Standard - A quality control standard, containing all target carbonyls/2,4-DNPH complexes within the typical concentration range of real samples, is analyzed to monitor the precision of the analysis of each target carbonyl. The control standard may be purchased, prepared in the laboratory from a stock solution different from the calibration standard, or prepared by batch mixing old samples, spiking it with a stock solution of target compounds, and

[1]This compound has been known to decompose.

stirring for a minimum of 2 hours. If necessary, the solution is filtered using filter paper to remove precipitation. All target compounds except acrolein have been found to be stable in the control standard.

5.9 Standards used for linearity and LOD determinations (Section 8) may be purchased or prepared by dilutions of an appropriate level stock solution.

6. PROCEDURE

6.1 For systems collecting the samples via impingers, an absorbing solution is prepared by dissolving 0.11 - 0.13 grams of recrystallized DNPH in 1 L of HPLC grade acetonitrile. The absorbing solution should be prepared at least every two weeks. Each batch of acetonitrile used in this procedure is checked for oxygenated impurities by adding it to a contaminant-free dilute solution of DNPH and analyzing by HPLC.

6.1.1 In the laboratory, pipette 15 mL of the DNPH absorbing solution into each of the 30 mL impingers for each emission test. Add 0.1 mL of 2.85 N sulfuric acid or 0.15 mL of 3.8 M perchloric acid to each impinger.

6.2 For systems collecting the samples via cartridges, DNPH-impregnated cartridges shall be sealed and refrigerated, at a temperature less than 40^{o}F, upon receipt from manufacturer, until ready for use.

6.2.1 At the exhaust volumes being sampled (1 L/min), a back-up cartridge may be required for CVS phase 1 but no back-up cartridge is needed for CVS phases 2 and 3.

6.3 After sampling uncap and place all impingers in preheated water at 70-80^{o}C for 30 minutes (min) to complete derivatization. Heating is not required when using perchloric acid.

6.3.1 For cartridges, remove the caps and extract with 5 mL acetonitrile, running the extract into glass storage bottles.

6.4 Remove the impingers from the water bath and cool to room temperature. Replace any lost solvent by adding acetonitrile to the 15-mL mark.

6.4.1 Replacing lost solvent is not required when using an internal standard method (Section 7.4).

6.5 Transfer the solution from each impinger/cartridge to glass vials and seal with new septum screw caps.

6.6 Place the vials containing blank, working standard, control standard, and samples into the autosampler for subsequent injection into an HPLC. Suggested standard operating conditions for the HPLC are:

Primary System:

Columns:	4.6 mm ID x 250 mm x 1/4 inches OD Dupont Zorbax ODS or Supelco Supelcosil - two columns in series, Guard column - 2 cm long packed with C18 5 µm pellicular	
Column temperature:	40°C	
Detector:	UV/VIS at 360 nm	
Sample volume:	10 µL	
Solvent A:	acetonitrile	
Solvent B:	10 percent (volume/volume) methanol in water	
Flow:	1 mL/min	
Program:	50 percent A, 50 percent B	0 (initial time)
	65 percent A, 35 percent B	0 to 2 min
	100 percent A, 0 percent B	2 to 22 min
	50 percent A, 50 percent B	22 to 37 min

Under the above configuration, methyl ethyl ketone and butyraldehyde tend to coelute. In order to report these compounds, it is necessary to analyze the samples using a secondary system. The tolualdehyde isomers (m-, p-, and o-) are separated using this configuration. The reporting of tolualdehyde is addressed in Section 7.4.

Secondary System:

Columns:	Delta Bond AK C18 (4.6 mm ID x 200 mm x 1/4 in OD) packed column, Guard column - 2 cm long packed with C18 5 µm pellicular	
Column temperature:	40°C	
Detector:	UV/VIS at 360 nm	
Sample volume:	10 µL	
Solvent A:	acetonitrile	
Solvent B:	acetonitrile in water, 35 percent (v/v)	
Flow:	1.5 mL/min	
Program:	0 percent A, 100 percent B	0 (initial time)
	23 percent A, 77 percent B	0 - 5.5 min
	46 percent A, 54 percent B	5.5 - 13 min
	0 percent A, 100 percent B	13 to 30 min

This secondary system is not used to report all compounds because formaldehyde tends to coelute with a non-carbonyl compound. If this coelution is resolved, the secondary system may be used alone to analyze all carbonyl compounds. The tolualdehyde isomers, however, are not separated with this configuration. The reporting of tolualdehyde is addressed in Section 7.4.

Data System: The outputs from the UV/VIS detector are sent to a PC-controlled data acquisition system.

6.7 The peak integrations are corrected as necessary in the data system. Any misplaced baseline segments are corrected in the reconstructed chromatogram.

6.8 Samples containing compounds having concentrations above the documented range of instrument linearity must be diluted and reanalyzed.

7. CALCULATIONS

7.1 For each target carbonyl, the carbonyl mass is calculated from its carbonyl/2,4-DNPH mass.

7.2 The mass of each carbonyl compound, per impinger or cartridge, is determined by the following calculation:

$$\text{Mass}_{\text{sample}} = \text{Peak Area}_{\text{sample}} * \text{Response Factor} * \text{Impinger}(\text{or Cartridge})\,\text{volume}(\text{mL}) * \text{B}$$

where B is the ratio of the molecular weight of the carbonyl compound to its 2,4-dinitrophenylhydrazone derivative and where the response factor (RF) for each carbonyl is calculated during the calibration by:

$$\text{RF} = \frac{\text{Concentration}_{\text{standard}}\ (\ \mu\text{g 2,4-DNPH species/mL})}{\text{Peak Area}_{\text{standard}}}$$

7.3 For tolualdehyde, the sum of all isomers present is reported as m-tolualdehyde.

7.3.1 Under the conditions of the primary system in Section 6.6, the isomers are separated. The m-tolualdehyde response factor is applied to each peak and the sum reported as m-tolualdehyde.

7.3.2 Under the conditions of the secondary system in Section 6.6, the isomers coelute. The m-tolualdehyde response factor is applied to the single tolualdehyde peak. This concentration is reported as m-tolualdehyde.

7.4 An internal standard method may also be used.

8. QUALITY CONTROL

8.1 Blank Runs

8.1.1 Reagent Blanks - The solvents used are of the highest HPLC grade and are tested for impurities when a new lot number is used. If this lot number is found to be acceptable, (no carbonyls present at concentrations at or above the LOD), daily blank analysis is not performed.

8.1.2 Carbonyl/2,4-DNPH Purity - The carbonyl/ 2,4- DNPHs are checked for purity by their melting points and their chromatograms (See Table F-1). Analysis of the solution of carbonyl/2,4-DNPH must yield only the peak of interest. No contaminant peaks above the LOD should be observed.

8.1.3 Field Blanks – One cartridge is analyzed as a field blank for each emission test. If the field blank shows a peak greater than the limit of detection (LOD) in the region of interest, the source of the contamination must be investigated and remedied.

8.1.4 Cartridge Blanks - At least one cartridge per batch is analyzed as a batch blank. If the cartridge blank shows a peak greater than the limit of detection (LOD) in the region of interest, the source of the contamination must be investigated and remedied.

8.2 Calibration Run - The calibration standard is analyzed each analysis day to generate the response factors used to quantify the sample concentrations.

8.3 Control Standard Run - The quality control standard is analyzed at least once each analysis day. Measurements of all target compounds in the control standard, except acrolein, must fall within the control limits to ensure the validity of the sample analyses that day. To meet this requirement, it may be necessary to rerun the calibration and control standards, and inspect and repair the HPLC.

8.4 Control Charts - A quality control chart is maintained for each component of the control standard. The control charts, used on a daily basis, establish that the method is “in- control.” The following describes how to construct a typical control chart:

1. Obtain at least 20 daily control standard results,
2. Calculate the control standard mean concentration, and standard deviation(s) for the target analyte, and
3. Create a control chart for the target analyte by placing the concentration on the Y-axis and the date on the X-axis. Establish an upper warning limit and a lower warning limit at two standard deviations (2s) above and below the average concentration. Establish an upper control limit and a lower

control limit at three standard deviations (3s) above and below the average concentration.

4. Due to the low variability of the carbonyl control standard measurements, a control standard measurement is considered to be out-of-control when the analyzed value exceeds either the 3s limit, or the range of ± 10% of the mean control measurement, whichever is greater, or if two successive control standard measurements of the same analyte exceed the 2s limit.
5. If 20 control standard measurements are not yet available to create a control chart (e.g., the control standard was expended and replaced prior to obtaining 20 points with the new standard), measurements must be within 10% of the assay (purchased) or theoretical (prepared in-house) concentration.

The measured concentrations of all target analytes contained in the control standard must be within the control limits (in-control) for the sample results to be considered acceptable. No control requirements have been established for acrolein, since it has been shown to degrade over time.

8.5 Duplicates - A duplicate analysis of one sample is performed at least once per analysis day. The relative percent difference (RPD) is calculated for each duplicate run:

$$\mathrm{RPD}(\%) = \frac{|\,\text{Difference between duplicate and original measurements}\,|}{\text{Average of duplicate and original measurements}} * 100$$

For each compound, the allowable RPD depends on the average concentration level for the duplicate runs, as shown in the following table:

Average Measurement for Duplicate Runs		Allowable RPD (%)
1 to 10	times LOD	100
10 to 20	" "	30
20 to 50	" "	20
Greater than 50	" "	15

If the results of the duplicate analyses do not meet these criteria for all target carbonyls, the sample may be reanalyzed. If reanalysis is not feasible or if the criteria are still not met on reanalysis, all sample results for that analysis day are invalid.

8.6 Linearity - A multipoint calibration to confirm instrument linearity is performed for all target analytes for new instruments, after making instrument modifications that can affect linearity, and at least once every year. The multipoint calibration consists of at least five concentration or mass loading levels (using smaller or larger volume sample sizes of existing standards is acceptable), each above the LOD, distributed over the range of expected sample concentration. Each concentration level is measured at least twice. A linear regression analysis is performed using concentration and average area counts to determine regression correlation coefficient (r). The r must be greater than 0.995 to be considered linear for one point calibrations.

8.7 Limit of Detection - The LOD for the target analytes must be determined for new instruments, after making instrument modifications which can affect the LOD and at least once per year. To make the calculations, it is necessary to perform a multipoint calibration consisting of at least four "low" concentration levels, each above the LOD, with at least five replicate determinations of the lowest concentration standard. A linear regression is performed and the standard deviation (in area counts) of the lowest concentration standard determined. The standard deviation is converted to concentration units using the slope of the linear regression:

$$s = s_a \div m$$

where m is the slope of the linear regression, s is the standard deviation (in concentration units) of the lowest concentration standard and s_a is the standard deviation (in area counts) of the lowest concentration standard.

The LOD must be calculated using the following equation [Ref. 12]:

$$LOD = t * s$$

where s is the standard deviation (in concentration units) of at least five replicate determinations of the lowest concentration standard and t is the t-factor for 99 percent confidence for a one-sided normal (Gaussian) distribution. The number

of degrees of freedom is equal to the number of replicates, minus one. An abbreviated t-table is:

Degrees of Freedom	t-value
4	3.7
5	3.4
6	3.1
7	3.0

The lowest standard must be of a concentration of one to five times the estimated LOD.

8.7.1 The maximum allowable LOD is 0.0075 µg/mL. The calculated laboratory LOD must be equal to or lower than the maximum allowable LOD. All peaks identified as target compounds that are equal to or exceed the maximum allowable LOD must be reported. If the calculated laboratory LOD is less than the maximum allowable LOD, the laboratory may choose to set its reporting limit at the maximum allowable LOD, the calculated laboratory LOD, or any level in between.

8.7.2 For the purpose of calculating the total mass of all species, the concentrations of the compounds below the LOD are considered to be zero.

Part G
DETERMINATION OF NMOG MASS EMISSIONS

1. INTRODUCTION

1.1 NMOG mass emissions consist of non-methane hydrocarbons and oxygenated hydrocarbons.

1.2 All definitions and abbreviations are set forth in Appendix 2 of these test procedures.

2. NMOG WEIGHTED MASS EMISSIONS

2.1 NMOG weighted mass (wm) emissions shall be calculated as follows:

$$NMOG_{wm} = \sum NMHC_{wm} + \sum ROH_{wm} + \sum RHO_{wm}$$

Non-methane hydrocarbon weighted mass emissions ($NMHC_{wm}$) can be determined by either FID or GC. If the FID method is used to calculate $NMHC_{wm}$, refer to Part B of these test procedures entitled, "Determination of Non-Methane Hydrocarbon Mass Emissions by Flame Ionization Detection." If the GC method is used to calculate $NMHC_{wm}$, refer to section 3, "Speciated Hydrocarbon Mass Emissions Calculation" contained herein. Carbonyl weighted mass emissions (RHO_{wm}) are to be calculated according to section 5 "Carbonyl Mass Emissions Calculation" contained herein. For alcohol fueled vehicles, alcohol weighted mass emissions (ROH_{wm}) are to be calculated according to section 4 "Alcohol Mass Emissions Calculation" contained herein.

3. SPECIATED HYDROCARBON MASS EMISSIONS CALCULATION

3.1 INTRODUCTION

Vehicular exhaust emissions are measured according to the FTP [Ref. 1]. For each of the three phases of the FTP, a tedlar bag of 0.5 ft^3 capacity is used to collect a dilute exhaust sample. A fourth 0.5 ft^3 tedlar bag is used to collect a composite dilution air (background) sample from all three phases of the FTP. All bag samples are analyzed according to Method No. 1002 (Part D of these test procedures) and Method No. 1003 (Part E of these test procedures) to determine the dilute exhaust and dilution air concentrations of individual hydrocarbon compounds. The measured hydrocarbon compound concentrations are used in the following equations to calculate the weighted mass emissions of each hydrocarbon compound.

3.2 HC MASS EMISSIONS CALCULATION PER TEST PHASE

3.2.1 $HC_{mass\ n} = (HC_{conc} * HC_{dens} * VMIX * 10^{-6}) / (Carbon\ No.)$

3.2.2 $HC_{conc} = HC_e - (HC_d * (1 - (1 / DF)))$
NOTE: If HC_{conc} is calculated to be less than zero, then $HC_{conc} = 0$.

3.3. WEIGHTED HC MASS EMISSIONS CALCULATION

3.3.1 $$HC_{wm} = 0.43 * \left(\frac{HC_{mass1} + HC_{mass2}}{D_{phase1} + D_{phase2}} \right) + 0.57 * \left(\frac{HC_{mass3} + HC_{mass2}}{D_{phase3} + D_{phase2}} \right)$$

3.4. SAMPLE CALCULATION

3.4.1 Exhaust emissions from a gasoline vehicle are collected in three dilute exhaust sample bags and one dilution air (background) sample bag during the FTP. Gas chromatography is used to determine the benzene concentration of each bag sample. Calculate the weighted benzene mass emissions based on the following data:

Test Phase	HC_e (ppbC)	HC_d (ppbC)	FID THC_e (ppmC)	CH_{4e} (ppmC)	CO_{2e} (%)	CO_{em} (ppm)	R_a (%)	VMIX (ft^3)	$D_{phase\ n}$ (mile)
1	500	25	98	6	1.20	280	28	2846	3.584
2	100	25	22	4	0.95	87	25	4854	3.842
3	120	25	29	5	1.07	101	24	2840	3.586

For Phase 1:

DF = $13.47 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e) * 10^{-4}]$
(see section 6, DF Calc.)

$NMHC_e$ = $FID\ THC_e - (r_{CH_4} * CH_{4e})$
= 98 ppmC - (1.04 * 6 ppmC)
= 92 ppmC

CO = $(1 - (0.01 + 0.005 * HCR) * CO_{2e} - 0.000323 * R_a) * CO_{em}$
NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e.
= (1 - (0.01925) * 1.2% - 0.000323 * 28%) * 280 ppm

= 271 ppm

DF = 13.47 / [1.2% + (92 ppmC + 6 ppmC + 271 ppm) * 10^{-4}]
= 10.89

HC_{conc} = HC_e - (HC_d * (1 - (1 / DF)))
= 500 ppbC - (25 ppbC * (1 - (1 / 10.89)))
= 477 ppbC

Mol. Wt. of C_6H_6 = (6 * 12.01115) + (6 * 1.00797)
= 78.11472 g/mole

HC_{dens} = (Mol. Wt. * conversion of liter to ft^3) / (Mol. Vol.)
= (78.11472 g/mole * 28.316 liter/ft^3) / 24.055 liter/mole
= 91.952 g/ft^3

$HC_{mass\ n}$ = (HC_{conc} * HC_{dens} * VMIX * 10^{-6}) / (Carbon No.)

$HC_{mass\ 1}$ = (477 ppbC * 91.952 g/ft^3 * 2846 ft^3 * 10^{-6}) / 6
= 20.8 mg

Similarly, for Phase 2: Hc_{mass} = 5.7 mg

and for Phase 3: Hc_{mass} = 4.2 mg

Therefore,

$$HC_{wm} = 0.43 * \left(\frac{HC_{mass1} + HC_{mass2}}{D_{phase1} + D_{phase2}} \right) + 0.57 * \left(\frac{HC_{mass3} + HC_{mass2}}{D_{phase3} + D_{phase2}} \right)$$

$$HC_{wm} = 0.43 * \left(\frac{20.8\,mg + 5.7\,mg}{3.584\ miles + 3.842\ miles} \right) + 0.57 * \left(\frac{4.2\,mg + 5.7\,mg}{3.586\ miles + 3.842\ miles} \right)$$

HC_{wm} = 2.3 mg/mile (benzene weighted mass emissions)

4. ALCOHOL MASS EMISSIONS CALCULATION

4.1. INTRODUCTION

Vehicular emissions are measured according to the (FTP [Ref. 1]. For each of the three phases of the FTP, a set of two impingers is used to collect alcohol emissions in the dilute exhaust. A fourth set of two impingers is used to collect a composite dilution air (background) alcohol sample from all three phases of the FTP. All impingers are analyzed according to Method No. 1001 to determine the alcohol concentration in each impinger. The measured alcohol concentrations are used in the following equations to calculate the weighted mass emissions of alcohol compounds.

4.2. ALCOHOL MASS EMISSIONS CALCULATION PER TEST PHASE

4.2.1 $ROH_{mass\ n} = (ROH_{conc} * ROH_{dens} * VMIX * 10^{-6}) / (Carbon\ No.)$

4.2.2 $ROH_{conc} = ROH_e - (ROH_d * (1 - (1 / DF)))$
NOTE: If ROH_{conc} is calculated to be less than zero, then $ROH_{conc} = 0$.

4.2.3 $ROH_e = (Imass_e / Ivol_e) * (Mol.\ Vol. / Mol.\ Wt.)$

4.2.4 $Imass_e = (Iconc_{e1} + Iconc_{e2}) * Dens_{ROH} * Ivol_r$

4.2.5 $Ivol_e = Ivol_{em} * (293.16^oK / Itemp_e) * (P_B / 760\ mm\ Hg)$

4.2.6 $ROH_d = (Imass_d / Ivol_d) * (Mol.\ Vol. / Mol.\ Wt.)$

4.2.7 $Imass_d = (Iconc_{d1} + Iconc_{d2}) * Dens_{ROH} * Ivol_r$

4.2.8 $Ivol_d = Ivol_{dm} * (293.16^oK / Itemp_d) * (P_B / 760\ mm\ Hg)$

4.3. WEIGHTED ALCOHOL MASS EMISSIONS CALCULATION

$$ROH_{wm} = 0.43 * \left(\frac{ROH_{mass1} + ROH_{mass2}}{D_{phase1} + D_{phase2}} \right) + 0.57 * \left(\frac{ROH_{mass3} + ROH_{mass2}}{D_{phase3} + D_{phase2}} \right)$$

4.4 SAMPLE CALCULATION

4.4.1 Alcohol emissions from an M85 fueled vehicle are collected in three sets of dilute exhaust impingers and one set of dilution air impingers during the FTP. Gas chromatography is used to determine the methanol concentration in each impinger. Calculate the weighted methanol mass emissions based on the following data:

Test Phase	$Ivol_r$ (mL)	$Iconc_{e1}$ (µg/mL)	$Iconc_{e2}$ (µg/mL)	$Ivol_{em}$ (liter)	$Iconc_{d1}$ (µg/mL)	$Iconc_{d2}$ (µg/mL)	$Ivol_{dm}$ (liter)	$Itemp_e$ (^oK)	$Itemp_d$ (^oK)
1	15	2.24	0.05	3.90	0.07	0.01	13.50	295	294
2	15	0.29	0.06	6.50	0.07	0.01	13.50	297	294
3	15	0.32	0.02	4.00	0.07	0.01	13.50	298	294

Test Phase	FID THC_e (ppmC)	CH_{4e} (ppmC)	CO_{2e} (%)	CO_{em} (ppm)	R_a (%)	VMIX (ft^3)	$D_{phase\ n}$ (mile)	P_B (mmHg)	$HCHO_e$ (ppm)
1	82	9	1.5	250	30	2834	3.581	760	0.81
2	19	5	0.7	20	32	4862	3.845	760	0.09
3	22	6	0.8	32	29	2835	3.583	760	0.10

For Phase 1:

$Imass_e$ = $(Iconc_{e1} + Iconc_{e2}) * Dens_{ROH} * Ivol_r$
= (2.24 µg/mL + 0.05 µg/mL) * 0.7914 g/mL * 15 mL * 10^6 µg/g
= 27.2 µg

Mol. Wt. of CH_3OH = (1 * 12.01115) + (4 * 1.00797) + (1 * 15.9994)
= 32.0428 g/mole

$Ivol_e$ = $Ivol_{em} * (293/16^o\ K / Itemp_e) * (P_B / 760\ mm\ Hg)$
= 3.90 liter * ($293.16^oK / 295^o$ K) * (760 mm Hg / 760 mm Hg)
= 3.88 liter

ROH_e = $(Imass_e / Ivol_e) * (Mol.\ Vol. / Mol.\ Wt.)$
= ($27.2*10^{-6}$ g / 3.88 liter) * (24.055 liter/mole / 32.0428 g/mole)
= 5.27 ppmC

$Imass_d$ = $(Iconc_{d1} + Iconc_{d2}) * Dens_{ROH} * Ivol_r$

= (0.07 µg/mL + 0.01 µg/mL) * 0.7914 g/ml *
15 ml * 10^6 µg/g
= 0.95 µg

$Ivol_d$ = $Ivol_{dm}$ * (293.16° K / $Itemp_d$) * (P_B / 760 mm Hg)
= 13.50 liter * (293.16°K / 294°K) * (760 mm Hg / 760 mm Hg)
= 13.46 liter

ROH_d = ($Imass_d$ / $Ivol_d$) * (Mol. Vol. / Mol. Wt.)
= ($0.95*10^{-6}$ g/ 13.46 liter) * (24.055 liter/mole / 32.0428 g/mole)
= 0.05 ppmC

$$DF = \frac{12.02}{CO_{2e} + (NMHC_e + CH_{4e} + CO_e + ROH_e + HCHO_e) * 10^{-4}}$$

(see section 6, DF Calc.)

$NMHC_e$ = FID THC_e - (r_{CH_4} * CH_{4e}) - (r_{CH_3OH} * ROH_e)
= 82 ppmC - (1.04 * 9 ppmC) - (0.66 * 5.27 ppmC)
= 69 ppmC

CO_e = (1 - (0.01 + 0.005 * HCR) * CO_{2e} - 0.000323 * R_a) * CO_{em}
NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e .

= (1 - (0.02705) * 1.5% - 0.000323 * 30%) * 250 ppm
= 237 ppm

$$DF = \frac{12.02}{1.5\% + (69\,\text{ppmC} + 9\,\text{ppmC} + 237\,\text{ppmC} + 5.27\,\text{ppmC} + 0.81\,\text{ppm}) * 10^{-4}}$$

ROH_{conc} = ROH_e - (ROH_d * (1 - (1 / DF)))
= 5.27 ppmC - (0.05 ppmC * (1 - (1 / 7.84)))
= 5.23 ppmC

ROH_{dens} = (Mol. Wt. * conversion of liter to ft^3) / (Mol. Vol.)
= (32.0428 g/mole * 28.316 liter/ft) / 24.055 liter/mole
= 37.719 g/ft^3

$ROH_{mass\ n}$ = (ROH_{conc} * ROH_{dens} * VMIX * 10^{-6}) / (Carbon No.)
$ROH_{mass\ 1}$ = (5.23 ppmC * 37.719 g/ft^3 * 2834 ft^3 * 10^{-6}) / 1
= 0.56 g

Similarly, for Phase 2: $ROH_{mass\ 2}$ = 0.08 g
and for Phase 3: $ROH_{mass\ 3}$ = 0.08 g

Therefore,

$$ROH_{wm} = 0.43 * \left(\frac{ROH_{mass1} + ROH_{mass2}}{D_{phase1} + D_{phase2}} \right) + 0.57 * \left(\frac{ROH_{mass3} + ROH_{mass2}}{D_{phase3} + D_{phase2}} \right)$$

$$ROH_{wm} = 0.43 * \left(\frac{0.56\,mg + 0.08\,mg}{3.581\ miles + 3.845\ miles} \right) + 0.57 * \left(\frac{0.08\,mg + 0.08\,mg}{3.583\ miles + 3.845\ miles} \right)$$

ROH_{wm} = 0.05 g (methanol weighted mass emissions)

5. CARBONYL MASS EMISSIONS CALCULATIONS

5.1. INTRODUCTION

Vehicular emissions are measured according to the FTP [Ref. 1]. For each of the three phases of the FTP, a set of two impingers (or cartridges) is used to collect carbonyl emissions in the dilute exhaust. A fourth set of two impingers (or cartridges) is used to collect a composite dilution air (background) carbonyl sample from all three phases of the FTP. All impingers (or cartridges) are analyzed according to Method No. 1004 to determine the mass of individual carbonyl compounds in each impinger (or cartridge). The measured carbonyl masses are used in the following equations to calculate the weighted mass emissions of each carbonyl compound.

5.2. CARBONYL MASS EMISSIONS CALCULATION PER TEST PHASE

5.2.1 $RHO_{mass\ n} = (RHO_{conc} * RHO_{dens} * VMIX * 10^{-6})$

5.2.2 $RHO_{conc} = RHO_e - (RHO_d * (1 - (1 / DF)))$
NOTE: If RHO_{conc} is calculated to be less than zero, then $RHO_{conc} = 0$.

5.2.3 $RHO_e = (Imass_e / Ivol_e) * (Mol.\ Vol. / Mol.\ Wt.)$

5.2.4 $Ivol_e = Ivol_{em} * (293.16^oK / Itemp_e) * (P_B / 760\ mm\ Hg)$

5.2.5 $RHO_d = (Imass_d / Ivol_d) * (Mol.\ Vol. / Mol.\ Wt.)$

5.2.6 $Ivol_d = Ivol_{dm} * (293.16^oK / Itemp_d) * (P_B / 760\ mm\ Hg)$

5.3. WEIGHTED CARBONYL MASS EMISSIONS CALCULATION

$$RHO_{wm} = 0.43 * \left(\frac{RHO_{mass1} + RHO_{mass2}}{D_{phase1} + D_{phase2}} \right) + 0.57 * \left(\frac{RHO_{mass3} + RHO_{mass2}}{D_{phase3} + D_{phase2}} \right)$$

5.4. SAMPLE CALCULATION

5.4.1 Carbonyl emissions from a CNG vehicle are collected in three sets of dilute exhaust impingers and one set of dilution air impingers during the FTP. HPLC is used to determine the formaldehyde mass in each impinger. Calculate the weighted formaldehyde mass emissions based on the following data:

Test Phase	$Ivol_r$ (mL)	$Imass_e$ (µg)	$Ivol_{em}$ (liter)	$Imass_d$ (µg)	$Ivol_{dm}$ (liter)	$Itemp_e$ (^oK)	$Itemp_d$ (^oK)
1	15	2.45	8.49	0.17	31.57	295	292
2	15	0.76	14.55	0.17	31.57	298	292
3	15	0.64	4.00	0.17	31.57	298	292

Test Phase	FID THC_e (ppmC)	CH_{4e} (ppmC)	CO_{2e} (%)	CO_{em} (ppm)	R_a (%)	VMIX (ft^3)	$D_{phase\ n}$ (mile)	P_B (mmHg)
1	132	108	0.9	8	68	2866	3.581	760
2	4	3	0.1	4	67	4841	3.845	760
3	22	9	0.5	5	65	2837	3.583	760

For Phase 1:

Mol. Wt. of HCHO = (1 * 12.01115) + (2 * 1.00797) + (1 * 15.9994)
= 30.0268 g/mole

$Ivol_e$ = $Ivol_{em}$ * (293/16^o K / $Itemp_e$) * (P_B / 760 mm Hg)
= 8.49 liter * (293.16^{o}K / 295^{o}K) * (760 mm Hg / 760 mm Hg)
= 8.44 liter

RHO_e = ($Imass_e$ / $Ivol_e$) * (Mol. Vol. / Mol. Wt.)
= ($2.45*10^{-6}$ g / 8.44 liter) * (24.055 liter/mole / 30.0268 g/mole)
= 233 ppb

$Ivol_d$ = $Ivol_{dm}$ * (293.16°K / $Itemp_d$) * (P_B / 760 mm Hg)
= 31.57 liter * (293.16°K / 292°K) * (760 mm Hg / 760 mm Hg)
= 31.70 liter

RHO_d = ($Imass_d$ / $Ivol_d$) * (Mol. Vol. / Mol. Wt.)
= ($0.17*10^{-6}$g / 31.70 liter)*(24.055 liter/mole / 30.0268 g/mole)
= 4 ppb

DF = $9.77 / [CO_{2e} + (NMHC_e + CH_{4e} + CO^e) * 10^{-4}]$
(see section 6, DF Calc.)

$NMHC_e$ = FID THC_e - (r_{CH_4} * CH_{4e})
= 132 ppmC - (1.04 * 108 ppmC)
= 20 ppmC

CO_e = (1 - (0.01 + 0.005 * HCR) * CO_{2e} - 0.000323 * R_a) * CO_{em}
NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e.

= (1 - 0.02890 * 0.9% - 0.000323 * 68%) * 8 ppm
= 7.6 ppm

DF = 9.77 / [0.9% + (20 ppmC + 108 ppmC + 7.6 ppm) * 10^{-4}]
= 10.69

RHO_{conc} = RHO_e - (RHO_d * (1 - (1 / DF)))
= 233 ppb - (4 ppb * (1 - (1 / 10.69)))
= 229 ppb

RHO_{dens} = (Mol. Wt. * conversion of liter to ft^3) / (Mol. Vol.)
= (30.0268 g/mole * 28.316 liter/ft^3) / 24.055 liter/mole
= 35.35 g/ft^3

$RHO_{mass\ n}$ = (RHO_{conc} * RHO_{dens} * VMIX * 10^{-6})
$RHO_{mass\ 1}$ = (229 ppb * 35.35 g/ft^3 * 2866 ft^3 * 10^{-6})
= 23.2 mg

Similarly, for Phase 2: $RHO_{mass\ 2}$ = 6.6 mg
and for Phase 3: $RHO_{mass\ 3}$= 12.7 mg

Therefore,

$$RHO_{wm} = 0.43 * \left(\frac{RHO_{mass1} + RHO_{mass2}}{D_{phase1} + D_{phase2}} \right) + 0.57 * \left(\frac{RHO_{mass3} + RHO_{mass2}}{D_{phase3} + D_{phase2}} \right)$$

$$RHO_{wm} = 0.43 * \left(\frac{23.2\,mg + 6.6\,mg}{3.581\,miles + 3.845\,miles} \right) + 0.57 * \left(\frac{12.7\,mg + 6.6\,mg}{3.583\,miles + 3.845\,miles} \right)$$

RHO_{wm} = 3.2 mg/mi (formaldehyde weighted mass emissions)

5.4.2 Carbonyl emissions from a gasoline vehicle are collected in three sets of dilute exhaust cartridges and dilution air cartridges during the FTP. HPLC is used to determine the formaldehyde mass in each cartridge. Calculate the weighted formaldehyde mass emissions based on the following data:

Test Phase	$Iconc_{ce}$ (μg/mL)	$Iconc_{cd}$ (μg/mL)	$Iconc_{blk}$ (μg/mL)	$Ivol_{dm}$ (liter)	$Ivol_{em}$ (liter)	$Itemp_e$ (^oK)	$Itemp_d$ (^oK)
1	1.212	0.028	0.0	8.61	8.57	294.26	294.26
2	0.334	0.043	0.0	14.91	13.83	294.26	294.26
3	0.172	0.026	0.0	8.68	8.74	294.26	294.26

Test Phase	FID THC_e (ppmC)	CH_{4e} (ppmC)	CO_{2e} (%)	CO_{em} (ppm)	R_a (%)	VMIX (ft^3)	$D_{phase\ n}$ (mile)	P_B (mmHg)
1	132	108	0.9	8	68	2866	3.581	760
2	4	3	0.1	4	67	4841	3.845	760
3	22	9	0.5	5	65	2837	3.583	760

For all three phases Ivolc = 4.4 mL

For Phase 1:

$Imass_d = (Iconc_{cd} - Iconc_{blk}) * Ivol_c$

$Imass_d = (0.028 - 0.0)$ μg/mL * 4.4 mL = 0.1232 μg

$Imass_e = (Iconc_{ce} - Iconc_{blk}) * Ivol_c$

$Imass_e$ = (1.212 – 0.0) μg/mL * 4.4 mL = 5.33 μg

Mol. Wt. of HCHO = (1 * 12.01115) + (2 * 1.00797) + (1 * 15.9994)
= 30.0265 g/mole

$Ivol_e$ = $Ivol_{em}$ * (293/16° K / $Itemp_e$) * (P_B / 760 mm Hg)
= 8.57 liter * (293.16°K / 294.26°K) * (760 mm Hg / 760 mm Hg)
= 8.54 liter

RHO_e = ($Imass_e$ / $Ivol_e$) * (Mol. Vol. / Mol. Wt.)
= ($5.33*10^{-6}$ g / 8.54 liter) * (24.055 liter/mole / 30.0265 g/mole)
= 500 ppb

$Ivol_d$ = $Ivol_{dm}$ * (293.16°K / $Itemp_d$) * (P_B / 760 mm Hg)
= 8.61 liter * (293.16°K / 294.26°K) * (760 mm Hg / 760 mm Hg)
= 8.58 liter

RHO_d = ($Imass_d$ / $Ivol_d$) * (Mol. Vol. / Mol. Wt.)
= ($0.1232*10^{-6}$g / 8.58 liter)*(24.055 liter/mole / 30.0265 g/mole)
= 11.5 ppb

DF = $9.77 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e) * 10^{-4}]$
(see section 6, DF Calc.)

$NMHC_e$ = $FID\ THC_e - (r_{CH_4} * CH_{4e})$
= 132 ppmC - (1.04 * 108 ppmC)
= 20 ppmC

CO_e = $(1 - (0.01 + 0.005 * HCR) * CO_{2e} - 0.000323 * R_a) * CO_{em}$
NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e.

= (1 - 0.02890 * 0.9% - 0.000323 * 68%) * 8 ppm
= 7.6 ppm

DF = $9.77 / [0.9\% + (20\ ppmC + 108\ ppmC + 7.6\ ppm) * 10^{-4}]$
= 10.69

RHO_{conc} = $RHO_e - (RHO_d * (1 - (1 / DF)))$
= 500 ppb - (11.5 ppb * (1 - (1 / 10.69)))
= 489.6 ppb (formaldehyde)

RHO_{dens} = (Mol. Wt. * conversion of liter to ft^3) / (Mol. Vol.)

= (30.0265 g/mole * 28.316 liter/ft^3) / 24.055 liter/mole
= 35.35 g/ft^3

$RHO_{mass\ n}$ = (RHO_{conc} * RHO_{dens} * VMIX * 10^{-6})

$RHO_{mass\ 1}$ = (489.6 ppb * 35.35 g/ft^3 * 2866 ft^3 * 10^{-6})
= 49.6 mg (formaldehyde)

Similarly, for Phase 2: $RHO_{mass\ 2}$ = 12.9 mg

and similarly for Phase 3: $RHO_{mass\ 3}$= 5.6 mg

Therefore,

$$RHO_{wm} = 0.43 * (\frac{RHO_{mass\,1} + RHO_{mass\,2}}{D_{phase\,1} + D_{phase\,2}}) + 0.57 * (\frac{RHO_{mass\,3} + RHO_{mass\,2}}{D_{phase\,3} + D_{phase\,2}})$$

$$RHO_{wm} = 0.43 * (\frac{49.6\,mg + 12.9\,mg}{3.581 miles + 3.845\,miles}) + 0.57 * (\frac{5.6\,mg + 12.9\,mg}{3.583\,miles + 3.845\,miles})$$

RHO_{wm} = 5.04 mg/mi (formaldehyde weighted mass emissions)

6. DILUTION FACTOR CALCULATION

6.1. **For Non-Alcohol Fueled Vehicles**:

6.1.1 $$DF = \frac{100 * \left(\frac{x}{x + y/2 + 3.76 * (x + y/4 - z/2)} \right)}{CO_{2e} + (NMHC_e + CH_{4e} + CO_e) * 10^{-4}}$$

(where fuel composition is $C_xH_yO_z$ as measured for the fuel used.)

6.1.2 CO_e = (1 - (0.01 + 0.005 * HCR) * CO_{2e} - 0.000323 * R_a) * CO_{em}
NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e .

a) For gasoline, $CH_{1.85}$, where x = 1, y = 1.85, and z = 0:
DF = 13.47 / [CO_{2e} + ($NMHC_e$ + CH_{4e} + CO_e) * 10^{-4}
CO_e = (1 - 0.01925 * CO_{2e} - 0.000323 * R_a) * CO_{em}

b) For Phase 2 gasoline, $CH_{1.94}$, where x = 1, y = 1.94 and z = 0.017,

$DF = 13.29 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e) * 10^{-4}$
$CO_e = (1 - 0.01970 * CO_{2e} - 0.000323 * R_a) * CO_{em}$

c) For LPG, $CH_{2.64}$, where x = 1, y = 2.64, z = 0:
$DF = 11.68 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e) * 10^{-4}$
$CO_e = (1 - 0.02320 * CO_{2e} - 0.000323 * R_a) * CO_{em}$

d) For CNG, $CH_{3.78}$, where x = 1, y = 3.78, and z = 0.016:
$DF = 9.83 / [[CO_{2e} + (NMHC_e + CH_{4e} + CO_e) * 10^{-4}]$
$CO_e = (1 - 0.02890 * CO_{2e} - 0.000323 * R_a) * CO_{em}$

6.2. **For Alcohol Fueled Vehicles**:

6.2.1 $$DF = \frac{100 * \left(\frac{x}{x + y/2 + 3.76 * (x + y/4 - z/2)} \right)}{CO_{2e} + (NMHC_e + CH_{4e} + CO_e + ROH_e + HCHO_e) * 10^{-4}}$$

(where fuel composition is $C_xH_yO_z$ as measured for the fuel used.)

6.2.2 $CO_e = (1 - (0.01 + 0.005 * HCR) * CO_{2e} - 0.000323 * R_a) * CO_{em}$
NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e.

a) For M100 (100% methanol), CH_3OH, where x = 1, y = 4, and z = 1:
$DF = 11.57 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e + ROH_e + HCHO_e) * 10^{-4}]$
$CO_e = (1 - 0.03000 * CO_{2e} - 0.000323 * R_a) * CO_{em}$

b) For M85 (85% methanol, 15% indolene), $CH_{3.41}O_{0.72}$, where x = 1, y = 3.41, and z = 0.72:
$DF = 12.02 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e + ROH_e + HCHO_e) * 10^{-4}]$
$CO_e = (1 - 0.02705 * CO_{2e} - 0.000323 * R_a) * CO_{em}$

c) For E100 (100% ethanol), C_2H_5OH, where x = 1, y = 3, and z = 0.5:
$DF = 12.29 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e + ROH_e + HCHO_e) * 10^{-4}]$
$CO_e = (1 - 0.02500 * CO_{2e} - 0.000323 * R_a) * CO_{em}$

APPENDIX 1

LIST OF COMPOUNDS

CAS #	COMPOUND	MIR
	Alcohols	
00067-56-1	methanol	0.71
00064-17-5	ethanol	1.69
	Light End and Mid-Range Hydrocarbons (Listed in approximate elution order)	
00074-85-1	ethene	9.08
00074-86-2	ethyne	1.25
00074-84-0	ethane	0.31
00115-07-1	propene	11.58
00074-98-6	propane	0.56
00463-49-0	1,2-propadiene	12.16
00074-99-7	1-propyne	6.45
00075-28-5	2-methylpropane	1.35
00115-11-7	2-methylpropene	6.35
00106-98-9	1-butene	10.29
00106-99-0	1,3-butadiene	13.58
00106-97-8	n-butane	1.33
00624-64-6	trans-2-butene	13.91
00463-82-1	2,2-dimethylpropane	1.68
00107-00-6	1-butyne	6.20
00590-18-1	cis-2-butene	13.22
00563-45-1	3-methyl-1-butene	6.99
00078-78-4	2-methylbutane	1.68
00503-17-3	2-butyne	16.33
00109-67-1	1-pentene	7.79
00563-46-2	2-methyl-1-butene	6.51
00109-66-0	n-pentane	1.54
00078-79-5	2-methyl-1,3-butadiene	10.69
00646-04-8	trans-2-pentene	10.23
00558-37-2	3,3-dimethyl-1-butene	6.06
00627-20-3	cis-2-pentene	10.24
00689-97-4	1-buten-3-yne	11.09
00513-35-9	2-methyl-2-butene	14.45
00542-92-7	1,3-cyclopentadiene	7.61
00075-83-2	2,2-dimethylbutane	1.33
00142-29-0	cyclopentene	7.38
00691-37-2	4-methyl-1-pentene	6.26

CAS #	COMPOUND	MIR
00760-20-3	3-methyl-1-pentene	6.22
00287-92-3	cyclopentane	2.69
00079-29-8	2,3-dimethylbutane	1.14
01634-04-4	1-methyl-tert-butyl-ether	0.78
00691-38-3	4-methyl-cis-2-pentene	8.44
00107-83-5	2-methylpentane	1.80
00674-76-0	4-methyl-trans-2-pentene	8.44
00096-14-0	3-methylpentane	2.07
00763-29-1	2-methyl-1-pentene	5.18
00592-41-6	1-hexene	6.17
00110-54-3	n-hexane	1.45
13269-52-8	trans-3-hexene	8.16
07642-09-3	cis-3-hexene	8.22
04050-45-7	trans-2-hexene	8.44
00616-12-6	3-methyl-trans-2-pentene	8.44
00625-27-4	2-methyl-2-pentene	12.28
01120-62-3	3-methylcyclopentene	8.65
07688-21-3	cis-2-hexene	8.44
00637-92-3	1-ethyl-tert-butyl-ether	2.11
00922-62-3	3-methyl-cis-2-pentene	8.44
00590-35-2	2,2-dimethylpentane	1.22
00096-37-7	methylcyclopentane	2.42
00108-08-7	2,4-dimethylpentane	1.65
00464-06-2	2,2,3-trimethylbutane	1.32
07385-78-6	3,4-dimethyl-1-pentene	4.56
00693-89-0	1-methylcyclopentene	13.95
00071-43-2	benzene	0.81
03404-61-3	3-methyl-1-hexene	4.56
00562-49-2	3,3-dimethylpentane	1.32
00110-82-7	cyclohexane	1.46
00591-76-4	2-methylhexane	1.37
00565-59-3	2,3-dimethylpentane	1.55
00110-83-8	cyclohexene	5.45
00589-34-4	3-methylhexane	1.86
01759-58-6	trans-1,3-dimethylcyclopentane	2.15
02532-58-3	cis-1,3-dimethylcyclopentane	2.15
00617-78-7	3-ethylpentane	1.63
00822-50-4	trans-1,2-dimethylcyclopentane	1.99
00592-76-7	1-heptene	4.56
00540-84-1	2,2,4-trimethylpentane	1.44
14686-14-7	trans-3-heptene	6.96
00142-82-5	n-heptane	1.28
02738-19-4	2-methyl-2-hexene	6.96
03899-36-3	3-methyl-trans-3-hexene	6.96

CAS #	COMPOUND	MIR
14686-13-6	trans-2-heptene	7.33
00816-79-5	3-ethyl-2-pentene	6.96
00107-39-1	2,4,4-trimethyl-1-pentene	3.45
10574-37-5	2,3-dimethyl-2-pentene	6.96
06443-92-1	cis-2-heptene	6.96
00108-87-2	methylcyclohexane	1.99
00590-73-8	2,2-dimethylhexane	1.13
00107-40-4	2,4,4-trimethyl-2-pentene	5.85
01640-89-7	ethylcyclopentane	2.27
00592-13-2	2,5-dimethylhexane	1.68
00589-43-5	2,4-dimethylhexane	1.80
02815-58-9	1,2,4-trimethylcyclopentane	1.75
00563-16-6	3,3-dimethylhexane	1.57
00565-75-3	2,3,4-trimethylpentane	1.23
00560-21-4	2,3,3-trimethylpentane	1.57
00108-88-3	toluene	3.97
00584-94-1	2,3-dimethylhexane	1.34
00592-27-8	2-methylheptane	1.20
00589-53-7	4-methylheptane	1.48
00589-81-1	3-methylheptane	1.35
15890-40-1	(1a,2a,3b)-1,2,3-trimethylcyclopentane	1.75
00638-04-0	cis-1,3-dimethylcyclohexane	1.72
02207-04-7	trans-1,4-dimethylcyclohexane	1.75
03522-94-9	2,2,5-trimethylhexane	1.33
02613-65-2	trans-1-methyl-3-ethylcyclopentane	1.75
16747-50-5	cis-1-methyl-3-ethylcyclopentane	1.75
00111-66-0	1-octene	3.45
14850-23-8	trans-4-octene	5.90
00111-65-9	n-octane	1.11
13389-42-9	trans-2-octene	5.90
02207-03-6	trans-1,3-dimethylcyclohexane	1.72
07642-04-8	cis-2-octene	5.90
01069-53-0	2,3,5-trimethylhexane	1.33
02213-23-2	2,4-dimethylheptane	1.48
02207-01-4	cis-1,2-dimethylcyclohexane	1.75
01072-05-5	2,6-dimethylheptane	1.25
01678-91-7	ethylcyclohexane	1.75
00926-82-9	3,5-dimethylheptane	1.63
00100-41-4	ethylbenzene	2.79
03074-71-3	2,3-dimethylheptane	1.25
00108-38-3	m-&p-xylene	8.49
02216-34-4	4-methyloctane	1.08
03221-61-2	2-methyloctane	0.96
02216-33-3	3-methyloctane	1.25

CAS #	COMPOUND	MIR
00100-42-5	styrene (ethenylbenzene)	1.95
00095-47-6	o-xylene	7.49
00124-11-8	1-nonene	2.76
00111-84-2	n-nonane	0.95
00098-82-8	(1-methylethyl)benzene	2.32
15869-87-1	2,2-dimethyloctane	1.09
04032-94-4	2,4-dimethyloctane	1.09
02051-30-1	2,6-dimethyloctane	1.27
00103-65-1	n-propylbenzene	2.20
00620-14-4	1-methyl-3-ethylbenzene	6.61
00622-96-8	1-methyl-4-ethylbenzene	6.61
00108-67-8	1,3,5-trimethylbenzene	11.22
00611-14-3	1-methyl-2-ethylbenzene	6.61
00095-63-6	1,2,4-trimethylbenzene	7.18
00124-18-5	n-decane	0.83
00538-93-2	(2-methylpropyl)benzene	1.97
00135-98-8	(1-methylpropyl)benzene	1.97
00535-77-3	1-methyl-3-(1-methylethyl)benzene	5.92
00526-73-8	1,2,3-trimethylbenzene	11.26
00099-87-6	1-methyl-4-(1-methylethyl)benzene	5.92
00496-11-7	2,3-dihydroindene (indan)	3.17
00527-84-4	1-methyl-2-(1-methylethyl)benzene	5.92
00141-93-5	1,3-diethylbenzene	5.92
00105-05-5	1,4-diethylbenzene	5.92
01074-43-7	1-methyl-3-n-propylbenzene	5.92
01074-55-1	1-methyl-4-n-propylbenzene	5.92
00135-01-3	1,2-diethylbenzene	5.92
01074-17-5	1-methyl-2-n-propylbenzene	5.92
01758-88-9	1,4-dimethyl-2-ethylbenzene	8.86
00874-41-9	1,3-dimethyl-4-ethylbenzene	8.86
00934-80-5	1,2-dimethyl-4-ethylbenzene	8.86
02870-04-4	1,3-dimethyl-2-ethylbenzene	8.86
01120-21-4	n-undecane (hendecane)	0.74
00933-98-2	1,2-dimethyl-3-ethylbenzene	8.86
00095-93-2	1,2,4,5-tetramethylbenzene	8.86
01595-11-5	1-methyl-2-n-butylbenzene	5.35
00527-53-7	1,2,3,5-tetramethylbenzene	8.86
01074-92-6	1-(1,1-dimethylethyl)-2-methylbenzene	5.35
00488-23-3	1,2,3,4-tetramethylbenzene	8.86
00538-68-1	n-pentylbenzene	1.78
00098-19-1	1-(1,1-dimethylethyl)-3,5-DMbenzene	7.33
00091-20-3	naphthalene	3.26
00112-40-3	n-dodecane	0.66

CAS #	COMPOUND	MIR
	Carbonyl Compounds	
00050-00-0	formaldehyde	8.97
00075-07-0	acetaldehyde	6.84
00107-02-8	acrolein	7.60
00067-64-1	acetone	0.43
00123-38-6	propionaldehyde	7.89
00123-72-8	butyraldehyde	6.74
00066-25-1	hexanaldehyde	4.98
00100-52-7	benzaldehyde	0.00
00078-93-3	methyl ethyl ketone (2-butanone)	1.49
00078-85-3	methacrolein	6.23
04170-30-3	crotonaldehyde	10.07
00110-62-3	valeraldehyde	5.76
00620-23-5	m-tolualdehyde	0.00

List of Compounds
(Listed by CAS number)

00050-00-0	formaldehyde
00064-17-5	ethanol
00066-25-1	hexanaldehyde
00067-56-1	methanol
00067-64-1	acetone
00071-43-2	benzene
00074-84-0	ethane
00074-85-1	ethene
00074-86-2	ethyne
00074-98-6	propane
00074-99-7	1-propyne
00075-07-0	acetaldehyde
00075-28-5	2-methylpropane
00075-83-2	2,2-dimethylbutane
00078-78-4	2-methylbutane
00078-79-5	2-methyl-1,3-butadiene
00078-85-3	methacrolein
00078-93-3	methyl ethyl ketone (2-butanone)
00079-29-8	2,3-dimethylbutane
00091-20-3	naphthalene
00095-47-6	o-xylene
00095-63-6	1,2,4-trimethylbenzene
00095-93-2	1,2,4,5-tetramethylbenzene
00096-14-0	3-methylpentane
00096-37-7	methylcyclopentane
00098-19-1	1-(1,1-dimethylethyl)-3,5-dimethylbenzene
00098-82-8	(1-methylethyl)benzene
00099-87-6	1-methyl-4-(1-methylethyl)benzene
00100-41-4	ethylbenzene
00100-42-5	stryrene (ethenylbenzene)
00100-52-7	benzaldehyde
00103-65-1	n-propylbenzene
00105-05-5	1,4-diethylbenzene
00106-97-8	n-butane
00106-98-9	1-butene
00106-99-0	1,3-butadiene
00107-00-6	1-butyne
00107-02-8	acrolein
00107-39-1	2,4,4-trimethyl-1-pentene
00107-40-4	2,4,4-trimethyl-2-pentene
00107-83-5	2-methylpentane
00108-08-7	2,4-dimethylpentane

00108-38-3	m- & p-xylene
00108-67-8	1,3,5-trimethylbenzene
00108-87-2	methylcyclohexane
00108-88-3	toluene
00109-66-0	n-pentane
00109-67-1	1-pentene
00110-54-3	n-hexane
00110-62-3	valeraldehyde
00110-82-7	cyclohexane
00110-83-8	cyclohexene
00111-65-9	n-octane
00111-66-0	1-octene
00111-84-2	n-nonane
00112-40-3	n-dodecane
00115-07-1	propene
00115-11-7	2-methylpropene
00123-38-6	propionaldehyde
00123-72-8	butyraldehyde
00124-11-8	1-nonene
00124-18-5	n-decane
00135-01-3	1,2-diethylbenzene
00135-98-8	(1-methylpropyl)benzene
00141-93-5	1,3-diethylbenzene
00142-29-0	cyclopentene
00142-82-5	n-heptane
00287-92-3	cyclopentane
00463-49-0	1,2-propadiene
00463-82-1	2,2-dimethylpropane
00464-06-2	2,2,3-trimethylbutane
00488-23-3	1,2,3,4-tetramethylbenzene
00496-11-7	2,3-dihydroindene (indan)
00503-17-3	2-butyne
00513-35-9	2-methyl-2-butene
00526-73-8	1,2,3-trimethylbenzene
00527-53-7	1,2,3,5-tetramethylbenzene
00527-84-4	1-methyl-2-(1-methylethyl)benzene
00535-77-3	1-methyl-3-(1-methylethyl)benzene
00538-68-1	n-pentylbenzene
00538-93-2	(2-methylpropyl)benzene
00540-84-1	2,2,4-trimethylpentane
00542-92-7	1,3-cyclopentadiene
00558-37-2	3,3-dimethyl-1-butene
00560-21-4	2,3,3-trimethylpentane
00562-49-2	3,3-dimethylpentane
00563-16-6	3,3-dimethylhexane
00563-45-1	3-methyl-1-butene

00563-46-2	2-methyl-1-butene
00565-59-3	2,3-dimethylpentane
00565-75-3	2,3,4-trimethylpentane
00584-94-1	2,3-dimethylhexane
00589-34-4	3-methylhexane
00589-43-5	2,4-dimethylhexane
00589-53-7	4-methylheptane
00589-81-1	3-methylheptane
00590-18-1	cis-2-butene
00590-35-2	2,2-dimethylpentane
00590-73-8	2,2-dimethylhexane
00591-76-4	2-methylhexane
00592-13-2	2,5-dimethylhexane
00592-27-8	2-methylheptane
00592-41-6	1-hexene
00592-76-7	1-heptene
00611-14-3	1-methyl-2-ethylbenzene
00616-12-6	3-methyl-trans-2-pentene
00617-78-7	3-ethylpentane
00620-14-4	1-methyl-3-ethylbenzene
00620-23-5	m-tolualdehyde
00622-96-8	1-methyl-4-ethylbenzene
00624-64-6	trans-2-butene
00625-27-4	2-methyl-2-pentene
00627-20-3	cis-2-pentene
00637-92-3	1-ethyl-tert-butyl-ether
00638-04-0	cis-1,3-dimethylcyclohexane
00646-04-8	trans-2-pentene
00674-76-0	4-methyl-trans-2-pentene
00689-97-4	1-buten-3-yne
00691-37-2	4-methyl-1-pentene
00691-38-3	4-methyl-cis-2-pentene
00693-89-0	1-methylcyclopentene
00760-20-3	3-methyl-1-pentene
00763-29-1	2-methyl-1-pentene
00816-79-5	3-ethyl-2-pentene
00822-50-4	trans-1,2-dimethylcyclopentane
00874-41-9	1,3-dimethyl-4-ethylbenzene
00922-62-3	3-methyl-cis-2-pentene
00926-82-9	3,5-dimethylheptane
00933-98-2	1,2-dimethyl-3-ethylbenzene
00934-80-5	1,2-dimethyl-4-ethylbenzene
01069-53-0	2,3,5-trimethylhexane
01072-05-5	2,6-dimethylheptane
01074-17-5	1-methyl-2-n-propylbenzene
01074-43-7	1-methyl-3-n-propylbenzene

01074-55-1	1-methyl-4-n-propylbenzene
01074-92-6	1-(1,1-dimethylethyl)-2-methylbenzene
01120-21-4	n-undecane (hendecane)
01120-62-3	3-methylcyclopentene
01595-11-5	1-methyl-2-n-butylbenzene
01634-04-4	1-methyl-tert-butyl-ether
01640-89-7	ethylcyclopentane
01678-91-7	ethylcyclohexane
01758-88-9	1,4-dimethyl-2-ethylbenzene
01759-58-6	trans-1,3-dimethylcyclopentane
02051-30-1	2,6-dimethyloctane
02207-01-4	cis-1,2-dimethylcyclohexane
02207-03-6	trans-1,3-dimethylcyclohexane
02207-04-7	trans-1,4-dimethylcyclohexane
02213-23-2	2,4-dimethylheptane
02216-33-3	3-methyloctane
02216-34-4	4-methyloctane
02532-58-3	cis-1,3-dimethylcyclopentane
02613-65-2	trans-1-methyl-3-ethylcyclopentane
02738-19-4	2-methyl-2-hexene
02815-58-9	1,2,4-trimethylcyclopentane
02870-04-4	1,3-dimethyl-2-ethylbenzene
03074-71-3	2,3-dimethylheptane
03221-61-2	2-methyloctane
03404-61-3	3-methyl-1-hexene
03522-94-9	2,2,5-trimethylhexane
03899-36-3	3-methyl-trans-3-hexene
04032-94-4	2,4-dimethyloctane
04050-45-7	trans-2-hexene
04170-30-3	crotonaldehyde
06443-92-1	cis-2-heptene
07385-78-6	3,4-dimethyl-1-pentene
07642-04-8	cis-2-octene
07642-09-3	cis-3-hexene
07688-21-3	cis-2-hexene
10574-37-5	2,3-dimethyl-2-pentene
13269-52-8	trans-3-hexene
13389-42-9	trans-2-octene
14686-13-6	trans-2-heptene
14686-14-7	trans-3-heptene
14850-23-8	trans-4-octene
15869-87-1	2,2-dimethyloctane
15890-40-1	(1a,2a,3b)-1,2,3-trimethylcyclopentane
16747-50-5	cis-1-methyl-3-ethylcyclopentane

APPENDIX 2

DEFINITIONS AND COMMONLY USED ABBREVIATIONS

I. The abbreviations and definitions set forth in this section apply to Parts A through G of these test procedures:

ASTM = American Society for Testing and Materials

Carbon No. = number of carbon atoms in the hydrocarbon or organic compound being measured.

CCR = California Code of Regulations

CH_3OH_d = the methanol concentration in the dilution air as determined from the dilution air methanol sample using the procedure specified in Method No. 1001, ppmC.

CH_3OH_e = the methanol concentration in the dilute exhaust as determined from the dilute exhaust methanol sample using the procedure specified in Method No. 1001, ppmC.

CH_{4d} = the methane concentration in the dilution air, ppmC.

CH_{4e} = the methane concentration in the dilute exhaust, ppmC.

$C_2H_5OH_d$ = the ethanol concentration in the dilution air as determined from the dilution air ethanol sample using the procedure specified in Method No. 1001, ppmC.

$C_2H_5OH_e$ = the ethanol concentration in the dilute exhaust as determined from the dilute exhaust ethanol sample using the procedure specified in Method No. 1001, ppmC.

CNG = compressed natural gas

CO_e = the carbon monoxide concentration in the dilute exhaust corrected for carbon dioxide and water removal, ppm.

CO_{em} = the carbon monoxide concentration in the dilute exhaust uncorrected for carbon dioxide and water removal, ppm.

CO_{2e} = the carbon dioxide concentration in the dilute exhaust, %.

CVS = constant volume sampler

$D_{phase\ n}$	=	the distance driven by the test vehicle on a chassis dynamometer during test phase n (where n is either 1, 2, or 3), mile.
$Dens_{ROH}$	=	density of alcohol, g/mL.
DF	=	dilution factor (see Dilution Factor Calculation).
FID	=	flame ionization detector
FID THC_d	=	the total hydrocarbon concentration including methane and methanol (for methanol-fueled engines) or ethanol (for ethanol-fueled engines) in the dilution air as measured by the FID, ppmC.
FID THC_e	=	the total hydrocarbon concentration including methane and methanol (for methanol-dueled engines) or ethanol (for ethanol-fueled engines) in the dilution exhaust as measured by the FID, ppmC.
FTP	=	Federal Test Procedure
GC	=	gas chromatograph
GC/MS	=	gas chromatography/mass spectrometry
HC_{conc}	=	net concentration of an HC compound in the dilute exhaust corrected for background per test phase, ppbC.
HC_d	=	composite concentration of an HC compound in the dilution air (background) for all three test phases as determined from the composite dilution air sample using the procedure specified in Method No. 1002 and Method No. 1003, ppbC.
HC_{dens}	=	mass per unit volume of an HC compound corrected to standard conditions (293.16 K and 760 mm Hg) g/ft^3.
HC_e	=	concentration of an HC compound in the dilute exhaust per test phase as determined from the dilute exhaust sample using the procedure specific in Method No. 1002 and Method No. 1003, ppbC.
$HC_{mass\ n}$	=	mass emissions of an HC compound per test phase n (where n is either 1, 2, or 3), mg.

HC_{wm}	=	total weighted mass of an HC compound per mile, g/mile.
$HCHO_e$	=	formaldehyde concentration in the dilute exhaust as determined from the dilute exhaust carbonyl sample using the procedure specified in Method No 1004, ppm.
HCR	=	the hydrogen-to-carbon ratio for the fuel used.
HPLC	=	high performance liquid chromatography
$Iconc_{blk}$	=	concentration of the blank cartridge, µg/mL
$Iconc_{cd}$	=	total concentration of carbonyl compound extracted from both cartridges for the dilution air, µg/mL
$Iconc_{ce}$	=	total concentration of carbonyl compound extracted from both cartridges for the diluted exhaust, µg/mL
$Iconc_{d1}$	=	dilution air (background) alcohol concentration in the primary impinger for all three test phases as determined by the procedure specified in Method No. 1001, µg/mL.
$Iconc_{d2}$	=	dilution air (background) alcohol concentration in the secondary impinger for all three test phases as determined by the procedure specified in Method No. 1001, µg/mL.
$Iconc_{e1}$	=	dilute exhaust alcohol concentration in the primary impinger per test phase as determined by the procedure specified in Method No. 1001, µg/mL.
$Iconc_{e2}$	=	dilute exhaust alcohol concentration in the secondary impinger per test phase as determined by the procedure specified in Method No. 1001, µg/mL.
$Imass_d$	=	total mass of an alcohol or carbonyl compound collected from the dilution air (background) in both primary and secondary impingers/cartridges for all three test phases as determined by the procedure specified in Method No. 1001 (alcohol) or Method No. 1004 (carbonyl), µg.
$Imass_e$	=	total mass of an alcohol or carbonyl compound collected from the dilute exhaust in both primary and secondary impingers/cartridges per test phase as determined by the procedure specified in Method No. 1001 (alcohol) or Method No. 1004 (carbonyl), µg.

$Itemp_d$	=	dilution air temperature at the flowmeter inlet for impinger/cartridge sampling, ^oK.
$Itemp_e$	=	dilute exhaust temperature at the flowmeter inlet for impinger/cartridge sampling, ^oK.
$Ivol_c$	=	elution volume of the cartridge, mL (The cartridge is extracted with 5 mL acetonitrile, but 0.6 mL is retained in the cartridge, so the elution volume is 4.4 mL.)
$Ivol_d$	=	total volume of dilution air (background) drawn through the impingers/cartridges for all three test phases corrected to standard conditions (293.16^oK and 760 mm Hg), liter.
$Ivol_{dm}$	=	total volume of dilution air (background) drawn through the impingers/cartridges for all three test phases as measured during testing, liter.
$Ivol_e$	=	total volume of dilute exhaust drawn through the impingers/cartridges per test phase corrected to standard conditions (293.16^oK and 760 mm Hg), liter.
$Ivol_{em}$	=	total volume of dilute exhaust drawn through the impingers/cartridges per test phase as measured during testing, liter.
$Ivol_r$	=	volume of the reagent used in an impinger, mL.
LOD	=	limit of detection
LPG	=	liquified petroleum gas
Mol. Vol.	=	molecular volume which is 24.055 liter/mole at standard conditions (293.16^oK and 760 mm Hg).
Mol. Wt.	=	molecular weight of the compound being measured, g/mole.
NIST	=	National Institute of Standards and Technology
NMHC	=	non-methane hydrocarbons
$NMHC_{conc}$	=	the non-methane hydrocarbon concentration in the dilute exhaust corrected for background, ppmC.
$NMHC_d$	=	the non-methane hydrocarbon concentration in the dilution air corrected for methane and alcohol removal, ppmC.

$NMHC_{dens}$	=	the mass per unit volume of non-methane hydrocarbon corrected to standard conditions (16.33 g/ft^3 at 293.16^{o}K and 760 mm Hg assuming a C:H ratio of 1:1.85 for gasoline; 16.78 g/ft^3 at 293.16^{o}K and 760 mm HG assuming a C:H ratio of 1:1.94 for Phase 2 reformulated gasoline; 19.52 g/ft^3 at 293.16^{o}K and 760 mm HG assuming a C:H ratio of 1:3.78 for natural gas; and 17.26 g/ft^3 for LPG at 293.16^{o}K and 760 mm Hg assuming a C:H ratio of 1:2.64), g/ft^3 .
$NMHC_e$	=	non-methane hydrocarbon concentration in the dilute exhaust corrected for methane and alcohol removal, ppmC.
$NMHC_{mass\ n}$	=	the mass emission of non-methane hydrocarbon per test phase n (where n is either 1, 2, or 3), g.
$NMHC_{wm}$	=	the total weighted mass of non-methane hydrocarbon per mile for all three phases of the FTP, g/mile.
NMOG	=	non-methane organic gases
P_B	=	barometric pressure during testing, mm Hg.
PID	=	photoionization detector
PLOT	=	porous layer open tubular
R_a	=	the relative humidity of the ambient air, %.
r_{CH_3OH}	=	the FID response factor to methanol (see CFR 40, 86.121-90(c)).
r_{CH_4}	=	the FID response factor to methane (see Part B, “Determination of NMHC by FID”).
$r_{C_2H_5OH}$	=	the FID response factor to ethanol (same procedure for methanol response factor, see CFR 40, 86.121-90(c)).
RHO	=	generic symbol representing a carbonyl compound such as formaldehyde, acetaldehyde, acetone, etc.
RHO_{conc}	=	net concentration of a carbonyl compound in the dilute exhaust corrected for background per test phase, ppm.

RHO_d	=	composite concentration of a carbonyl compound in the dilution air (background) for all three test phases, ppm.
RHO_{dens}	=	mass per unit volume of a carbonyl compound corrected to standard conditions (293.16°K and 760 mm Hg), g/ft^3.
RHO_e	=	concentration of a carbonyl compound in the dilute exhaust per test phase, ppm.
$RHO_{mass\ n}$	=	mass emissions of a carbonyl compound per test phase n (where n is either 1, 2, or 3), g.
RHO_{wm}	=	total weighted mass emissions of a carbonyl compound per mile, g/mile.
ROH	=	generic symbol representing an alcohol compound such as methanol or ethanol.
ROH_{conc}	=	net concentration of an alcohol compound in the dilute exhaust corrected for background per test phase, ppm.
ROH_d	=	composite concentration of an alcohol compound in the dilution air (background) for all three test phases, ppm.
ROH_{dens}	=	mass per unit volume of an alcohol compound corrected to standard conditions (293.16°K and 760 mm Hg), g/ft^3.
ROH_e	=	concentration of an alcohol compound in the dilute exhaust per test phase, ppmC.
$ROH_{mass\ n}$	=	mass emissions of an alcohol compound per test phase n (where n is either 1, 2, or 3), g.
ROH_{wm}	=	total weighted mass emissions of an alcohol compound per mile, g/mile.
SAE	=	Society of Automotive Engineers
SRM	=	Standard Reference Material
VMIX	=	the total dilute exhaust volume measured per test phase and corrected to standard conditions (293.16°K and 760 mm Hg), ft^3.

II. The following list is commonly used measurement abbreviations:

g	=	gram
µg	=	microgram
m	=	meter
cm	=	centimeter
µm	=	micrometer
µ	=	micron
L	=	liter
mL	=	milliliter
µL	=	microliter
ppb	=	parts per billion.
ppbC	=	parts per billion carbon equivalent.
ppm	=	parts per million.
ppmC	=	parts per million carbon equivalent.

APPENDIX 3

REFERENCES

[1] Code of Federal Regulations, Title 40, Part 86, Subpart B

[2] SAE J254, "Instrumentation and Techniques for Exhaust Gas Emissions Measurement"

[3] SAE J1094a, "Constant Volume Sampler System for Exhaust Emissions Measurement"

[4] SAE 770141, "Optimization of a Flame Ionization Detector for Determination of Hydrocarbons in Diluted Automotive Exhausts". G.D. Reschke, Vehicle Emissions Laboratory, General Motors Proving Ground

[5] SAE J1154, "Methane Measurement Using Gas Chromatography," (revised December 1991)

[6] U.S. Environmental Protection Agency, Characterization of Exhaust Emissions from Methanol and Gasoline Fueled Automobiles, EPA 460/3-82-004.

[7] U.S. Environmental Protection Agency, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, (Method T03-15) EPA-600/4-89-017 Research Triangle Park, North Carolina, June, 1989.

[8] Standard Test Method for C_1 through C_6 Hydrocarbons in the Atmosphere by Gas Chromatography, American Standards for Testing Materials (ASTM) Standards on Chromatography (1981).

[9] U.S. Environmental Protection Agency, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, (Method T03-15) EPA-600/4-84-041 Research Triangle Park, North Carolina, April, 1989.

[10] Hull, L.A., Procedures for 2,4-Dinitrophenylhydrazone Aldehyde-Ketone Air Analysis, Internal Report at U.S. EPA.

[11] Shriner, R.L. and Fuson, R.C., Identification of Organic Compounds, 2nd. Ed., John Wiley and Sons, Inc., 1940, p. 143.

[12] Keith, L. H., Taylor, J.K., et al, "Principles of Environmental Analysis", Analytical Chemistry, Vol. 55, No. 14, December 1983.

State of Oregon Department of Environmental Quality

OAR 340-257-0090
CARB Manufacturers' Advisory Correspondence – 2011-02

Air Resources Board

Mary D. Nichols, Chairman
9480 Telstar Avenue, Suite 4
El Monte, California 91731 • www.arb.ca.gov

Linda S. Adams
Acting Secretary for Environmental Protection

Edmund G. Brown Jr.
Governor

March 23, 2011

REVISED MANUFACTURERS ADVISORY CORRESPONDENCE (MAC) 2011-02

TO: ALL PASSENGER CAR MANUFACTURERS
ALL LIGHT-DUTY TRUCK MANUFACTURERS
ALL MEDIUM-DUTY VEHICLE MANUFACTURERS
ALL OTHER INTERESTED PARTIES

SUBJECT: Zero Emission Vehicle (ZEV) Credit Reporting and Tracking System

This letter transmits a Revised Manufacturers Advisory Correspondence (MAC) that provides vehicle manufacturers and other interested parties with the Air Resources Board's mechanism and format to be used for reporting and tracking ZEV deliveries and placements to determine ZEV credit compliance. This revised MAC corrects the applicable model year to 2010 and subsequent. This revised MAC supersedes MAC 2011-01 and MAC 2006-03. The primary purpose of modifying this MAC is to incorporate the amendments to the ZEV Regulation in 2008.

If you have any questions regarding this matter, please contact Ms. Krista Eley, Air Pollution Specialist, at (916) 322-2333, or via email at keley@arb.ca.gov .

Sincerely,

Robert H. Cross, Chief
Mobile Source Control Division

Attachments

cc: Ms. Krista Eley
Air Pollution Specialist
Sustainable Transportation Technology Branch

State of California
Air Resources Board

Revised Manufacturers' Advisory Correspondence (MAC) #2011-02

Subject: Format and policies for manufacturer Zero Emission Vehicle (ZEV) Reporting for 2010 and subsequent model-year ZEVs, Enhanced Advanced Technology Partial ZEVs (Enhanced AT PZEVs), AT PZEVs and Partial ZEVs (PZEVs). This MAC supersedes MAC 2011-01 and MAC 2006-03.

Applicability: Manufacturers of 2010 and subsequent model-year ZEVs, Enhanced AT PZEVs, AT PZEVs, and PZEVs certified for sale in California and any person or entity that transacts credits for these vehicles including, but not limited to, credit brokers and transportation project managers.

References: Section 1962.1, Title 13, California Code of Regulations (CCR), and the incorporated "California Exhaust Emission Standards and Test Procedures for 2009 and Subsequent Model Zero Emission Vehicles, and 2001 and Subsequent Model Hybrid Electric Vehicles, in the Passenger Car, Light-Duty Truck and Medium-Duty Vehicle Classes," adopted by the state board on December 17, 2008.

Background: The California ZEV regulations were originally adopted by the Air Resources Board (ARB or Board) in 1990, as part of the first generation California low-emission vehicle regulations. The ZEV program is an integral part of California's mobile source control efforts, and is intended to encourage the development of advanced technologies that will secure increasing air quality benefits and greenhouse gas reduction goals. The ZEV regulations nominally require that a certain percent of the passenger cars and light-duty trucks produced and delivered for sale in California by all but small volume manufacturers be ZEVs – vehicles with no emissions. However, there are mechanisms under which a manufacturer may satisfy part – or in some cases all – of its ZEV obligation with PZEV allowances generated from vehicles with extremely low emissions.

Discussion: This MAC provides a consistent format for reporting delivery and placement of ZEV program vehicles in California for demonstration of compliance with the regulation. Additionally, the process and format for submitting data related to other ZEV credit activities is provided.

ARB requests that manufacturers, and other interested parties provide both a hard copy and an electronic version of the appropriate forms and ZEV reports be submitted with an attached cover letter for all ZEVs,

Enhanced AT PZEVs, AT PZEVs and PZEVs. Vehicle manufacturers will continue to report production data as previously required.

ARB forms and specified electronic format for reporting credits and debits for ZEV reporting include: 1) an application form for opening a "ZEV account" with the ARB/Change of Company Representative or address, 2) a form for selecting the calculation method and Non-Methane Organic Gases (NMOG) production numbers, 3) credit and debit electronic format, 4) example data files, and 5) a form for transferring credits. These electronic forms are presented in the following Attachments:

Application for California Zero Emission Vehicle (ZEV) Account /Change of Company Representative or Address	Attachment A
Calculation Method for Zero Emission Vehicle (ZEV) Credit Requirement	Attachment B
Credits	Attachment C
Debits	Attachment D
Example Data files – Credits and Debits	Attachment E
Zero Emission Vehicle (ZEV) Credit Transfer Form	Attachment F

Guidance: **Credit Bank**

ARB will utilize the ZEV Bank to track ZEVs and the credits earned by vehicle manufacturers and transacted by credit traders. The system will also generate ZEV credit balance and summary statements.

Manufacturers of 2010 and subsequent model-year ZEVs, Enhanced AT PZEVs, AT PZEVs, and PZEVs certified for sale in California and any person or entity that holds ZEV credits for any length of time including, but not limited to, credit brokers and transportation project managers need to apply for a ZEV account with ARB. See Attachment A Application for Zero Emission Vehicle (ZEV) Account with the ZEV Bank.

ARB will record ZEVs in the ZEV Bank. The recording of vehicles is then subject to verification of the information substantiating delivery and placement of ZEVs. If ARB determines that discrepancies exist in any ZEV information submitted, staff will notify the appropriate party and will

accordingly adjust the ZEV Account. ARB may perform audits at any time.

Recorded ZEV credits will be multiplied by NMOG fleet average requirement for the appropriate model year. ZEV credits will be stored in the ZEV Bank in units of grams per mile (g/mi) NMOG. Please note that the g/mi NMOG units are only used as an index and do not represent actual values of g/mi NMOG.

Frequency of Reporting

ZEV account holders are to report ZEV data as indicated in Attachments B, C and D, annually by May 1st of the calendar year following the close of a model year. Attachment A must be resubmitted if there are any changes to the Company Representatives or the Company address, email or phone. Annual Reports may be updated by September 1 of the same year. ZEV account holders may choose to report more frequently, however, please contact the ZEV Bank Program Manager prior to transmittal. The schedule is as follows:

Annual

Report Date	Data Represents
May 1 of a given calendar year	preceding model year

Supplement to Annual

Report Date	Data Represents
September 1 of a given calendar year	preceding model year April 1 to June 30

Credit Statements

The ZEV Bank Program Manager will issue credit statements to ZEV account holders annually. Additional credit statements are available upon request.

Credit Types and Conditions

ZEVs

ZEVs may generate ZEV credits at several points in time including "Delivered for sale," "Placed in service" and "Extended service." Vehicles receive a base credit when "delivered for sale in California" and remaining ZEV credits based on applicable multipliers when "Placed in Service." ((§1962.1(d)(5)(C))

Placed in service – As defined in the ZEV regulation "means having been sold or leased to an end-user and not to a dealer or other distribution chain entity, and having been individually registered for on-road use by the California Department of Motor Vehicles (DMV)." (§1962.1(i)(7))

Vehicles sold en masse to another state by one person, entity or company shortly after registering at the California DMV do not meet the definition of "Placed in service" in the ZEV regulation. Specifically they do not meet the criteria of being sold or leased to an end-user and not to a dealer or other distribution chain entity. The person, entity or company in this situation would be a dealer or other distribution chain entity. Therefore vehicles in this circumstance do not qualify for ZEV credits.

All "Placed in service" vehicles will be verified with the California DMV with the exception of vehicles leased or sold to the government (see below). If any vehicles within a reported batch cannot be verified with the DMV, the ZEV Program Manager will contact the Account Holder and request that those records be corrected and resubmitted.

Vehicles Leased Or Sold To the Government - Vehicles sold to the federal government may or may not be registered at the California DMV. Indicate government agency name, agency contact and agency email when reporting credits.

Multiplier for Certain ZEVs – ZEVs produced in model years 2009 to 2011, excluding Neighborhood Electric Vehicles and Type 0 ZEVs, may receive a one time multiplier of 1.25 if it is either sold to a motorist or is leased for 3 or more years to a motorist who is given the option to purchase or re-lease the vehicle for 2 years or more at the end of the first term. (§1962.1(d)(5)(D))

Neighborhood Electric Vehicles (NEVs) and non-NEVs – For reporting and tracking purposes, a distinction is made between NEVs and ZEVs that are not NEVs regarding the limited use of banked NEV credits.

Enhanced AT PZEVs, AT PZEVs and PZEVs

Enhanced AT PZEVs, AT PZEVs and PZEVs may earn credits for having been "Delivered for sale" as described for ZEVs. No additional credits or multipliers are applied when the vehicles are placed. Thus, the ZEV Bank does not track placement for Enhanced AT PZEVs, AT PZEVs and PZEVs.

Phase-In Multiplier for Enhanced AT PZEVs

A PZEVs produced in model years 2009 through 2011 model year that earn zero-emission vehicle miles traveled allowance under §1962.1(c)(3) may receive a one time multiplier of 1.25 if it is either sold to a motorist or is leased for 3 or more years to a motorist who is given the option to purchase or re-lease the vehicle for 2 years or more at the end of the first term. (§1962.1(c)(7)(B))

Extended Service Multiplier

ZEVs and some AT PZEVs in model years 1997-2003 may earn ZEV credits for having been re-leased after an initial 3 years in accordance with the ZEV regulation. NEVs are not eligible to earn the credit for the Extended Service Multiplier. (§1962.1(f))

Advanced Technology Demonstration Programs

ZEVs and Enhanced AT PZEVs, excluding NEVs, placed in a California advanced technology demonstration program may earn ZEV credits even if it is not "delivered for sale" in accordance with the ZEV regulation. (§1962.1(g)(4)) Approval by the ARB's Executive Officer is required for Advance Technology Demonstration Program credits.

Transportation Systems

In model years 2009 and subsequent, a ZEV and Enhanced AT PZEV placed as part of a transportation system may earn ZEV credits in accordance with the ZEV regulation. In model years 2009 to 2011 AT PZEVs and PZEVs placed as part of a transportation system may also earn ZEV credits in accordance with the ZEV regulation. (§1962.1(g)(5)) Approval by the Executive Officer is required for transportation system credits. NEVs are not eligible to earn credit for transportation systems.

Transferring Credits

Credits may be transferred between parties and entities. Any party or entity that holds ZEV credits for any length of time including, but not limited to, credit brokers and transportation project managers, needs to have an account with the ARB ZEV Bank. Credit transfers can take place outside of the ZEV Bank at anytime. However, if credits are to be acknowledged for ZEV compliance, each transfer needs to be recorded in the ZEV Bank and all parties need to have an account with the ZEV Bank as indicated above. The ZEV Bank Program Manager will contact the Primary Account Holders and confirm the transfer request. See Attachment F for the Transferring ZEV Credit Form.

If a transferor double sells credits (sells the same credits to two or more parties or manufacturers), only the transferee to first record with the ZEV Bank will receive credit. The transferee that records with the ZEV Bank after the transferor's credits have been exhausted will not receive credit and will be notified of the shortfall. The ZEV Bank Program Manager will notify the appropriate parties of the discrepancy.

Confidentiality

Public Disclosure

Please see section 1962.1, Title 13, CCR for provisions of how records in the Board's possession for the vehicles subject to the requirements of section 1962.1 are subject to public disclosure.

Trade Secret

In accordance with Title 17, CCR, sections 91000 to 91022, and the California Public Records Act (Government Code Section 6250 et seq.), the information that a company provides to the ARB may be released (1) to the public upon request, except trade secrets which are not emissions data or other information which is exempt from disclosure or the disclosure of which is prohibited by law; and (2) to the Federal Environmental Protection Agency, which protects trade secrets as provided in Section 114(c) of the Clean Air Act and amendments thereto (42 USC 7401 et seq.) and in federal regulation; and (3) to other public agencies provided that those agencies preserve the protections afforded information which is identified as a trade secret, or otherwise exempt from disclosure by law (Government Code Section 6254.5 (e)).

Trade secrets as defined in Government Code Section 6254.7 are not public records and therefore will not be released to the public. However,

the California Public Records Act provides that air pollution emission data are always public records, even if data come within the definition of trade secrets. On the other hand, the information used to calculate emission data can be trade secret.

If any company believes that any of the information it may provide is trade secret or otherwise exempt from disclosure under any other provision of law, it must identify the confidential information as such at the time of submission to ARB and must provide the name, address, and telephone number of the individual to be consulted if ARB receives a request for disclosure or seeks to disclose the data. ARB may ask the company to provide documentation of its claim of trade secret or exemption at a later date. Data identified as confidential will not be disclosed unless ARB determines, in accordance with the above referenced regulations that the data do not qualify for a legal exemption from disclosure. In such a case the party claiming confidentiality will be notified at least 21 days before disclosure.

Guidance for Electronic Submittal of Data Files

Manufacturers and other persons or entities transacting ZEV credits need to submit ZEV data reports electronically using all applicable fields with the domains as defined in Attachment C and Attachment D. Note that all fields are required. The preferred electronic format is Microsoft Office Excel.

If an electronic submittal has incomplete or incorrectly formatted data, the data will take longer to process. In addition, the ZEV Bank Program Manager will contact the Account Holder and request that the records be corrected and a complete new data batch submitted. Only if the entire data batch is complete and correctly formatted will the data be recorded in the ZEV bank.

Each file should be named using the format, MMMM_MM_DD_YYYY.XXX, as defined below:

MMMM	=	Manufacturer code
MM_DD_YYYY	=	Date report sent for example March 25, 2011 = 03252011
XXX	=	file extension

The electronic file formats provided in Attachments C and D describe each field in detail. The columns are:

Sequence	Order of the data in the record
Data Name	Name of the data field
Type	Identifies type of the field C = Characters (i.e. Alpha-Numeric) N = Numeric D = Date - date format should be used
Length	Specifies the number of characters in each field. For numeric, specifies the number of digits including the decimal, if any.
Range or Domain	Lists the possible inputs or format for the field
Description	Describes the field

Attachment A

Application for California Zero Emission Vehicle (ZEV) Account/ Change of Company Representative or Address

Complete and Submit to:
Ms. Krista Eley, Program Manager, ZEV Bank
California Air Resources Board, MSCD/STTB
1001 "I" Street, P.O. Box 2815, Sacramento, California 95812

I hereby apply to open a new Zero Emission Vehicle Account with the ZEV Bank operated by the California Air Resources Board (ARB) in the administration of Section 1962.1, Title 13, California Code of Regulations.

ACCOUNT HOLDER

Company Name		*Account ID	**PURPOSE:** Information contained in this form will be used by ARB to process account initiation and carry out all necessary actions involving the account.
Company Mailing Address			
City	State	ZIP Code	
Company Phone Number		Type of Business	

A. PRIMARY REPRESENTATIVE (*please print.)*

Authorized Company Representative (First, Middle I., Last)		Title
Phone Number	Fax Number	Email Address

B. SECONDARY REPRESENTATIVE (*please print.)*

Authorized Company Representative (First, Middle I., Last)		Title
Phone Number	Fax Number	Email Address

I declare under penalty of perjury that all information provided herein are true and correct, to the best of my knowledge and belief. I understand only the undersigned company representatives can authorize transactions, and I represent that I am authorized to apply for this account.

Primary Authorized Company Representative Signature	Date
Secondary Authorized Company Representative Signature	Date

*Please contact the ZEV Bank Program Manager for an account ID.

FOR ARB USE ONLY:

Entered By (Please print name and title)	Initials	Date Received	Date Recorded

Attachment B

Calculation Method for ZEV Credit Requirement

Complete and Submit to:
Ms. Krista Eley, Program Manager, ZEV Credit Bank,
California Air Resources Board, MSCD/STTB
P.O. Box 2815, Sacramento, California 95812

As of _____ (mm / dd / yy) **I** _____ (Account Holder Representative *(please print)*)**, elect for vehicle manufacturer** _____ (Account Holder ID Code) **the following method to calculate the number of vehicles upon which the percentage ZEV requirements are based.**

A. CALCULATION METHOD

In accordance with policy letter dated April 3, 2009 and section 1962.1(b)(1)(B) manufacturers may select one method annually. A manufacturer need only select a method for the applicable model year of reporting.

Model Year	Method	
	Three Year Averaging	Same Year
2010	☐	☐
2011	☐	☐
2012	☐	☐
2013	☐	☐

B. NMOG PRODUCTION NUMBERS

The ZEV requirement will be based on the annual NMOG production report numbers below.

Passenger Car and LDT1 (light duty truck < 3751 lbs)

Model year	1997	1998	1999	2000	2001	2002	2003	2004	2005
Number of vehicles									
Model year	2006	2007	2008	2009	2010	2011	2012	2013	2014
Number of vehicles									

LDT2 (light duty truck 3751 lbs loaded vehicle weight - 8500 lbs gross vehicle weight)

Model year	1997	1998	1999	2000	2001	2002	2003	2004	2005
Number of vehicles	N/A	N/A	N/A						
Model year	2006	2007	2008	2009	2010	2011	2012	2013	2014
Number of vehicles									

I declare under penalty of perjury that all information provided herein are true and correct, to the best of my knowledge and belief.

Signature	Date

FOR ARB USE ONLY:

Entered By (Please print name and title)	Initials	Date Received	Date Recorded

Attachment C
Credits

ZEVs
Delivered

Sequence	Field Name	Type	Length	Range or Domain	Description
1	DATA_TYPE	C	2	ZD	ZEV delivered
2	ACC_ID	C	4	examples: GM, NISS, BENZ	Account ID of company
3	MOD_YR	N	4	example: 2011	Model year of vehicle
4	EX_ORDER	C	10	example: A-14-380-A	Executive order number
5	ZEV_TIER	C	6	NEV, 0XX, IXX, I.5XX, IIXX, IIIXX, IVXX, VXX (example IIICA, IIINY, IIINJ, IIIOR etc.)	Tier Type. Excluding NEVs, indicate California or Section 177 State where XX is the abbreviation of the Section 177 State.
6	VIN	C	17	example: JS112233344555667	Vehicle identification number
7	DATE_DEL	D	10	example: June 1, 2011 = 06/01/2011	Date vehicle delivered for sale

Placed in Service

Sequence	Field Name	Type	Length	Range or Domain	Description
1	DATA_TYPE	C	2	ZP	ZEV placed
2	ACC_ID	C	4	examples: GM, NISS, BENZ	Account ID of company
3	MOD_YR	N	4	example: 2011	Model year of vehicle
4	EX_ORDER	C	10	example: A-14-380-A	Executive order number
5	ZEV_TIER	C	6	0XX, IXX, I.5XX, IIXX, IIIXX, IVXX, VXX (example IIICA, IIINY, IIINJ, IIIOR etc.)	Tier Type. Excluding NEVs, indicate California or Section 177 State where XX is the abbreviation of the Section 177 State.
6	VIN	C	17	example: JS112233344555667	Vehicle identification number
7	DATE_PLACED	D	10	example: December 1, 2011 = 12/01/2011	Date vehicle placed in service
8	OPTION_PURLEA	C	1	Y or N	Yes or No option to purchase or lease. See 1962.1 (d)(5)(D) Multiplier for certain ZEVs.
9	GOV	C	1	Y or N	Yes or No government placement
10	AGENCY_NAME	C	30	example: City of Sacramento	If government, agency name
11	AGENCY_CONTACT_ NAME	C	30	example: Joe Smith	If government, agency contact name
12	AGENCY_CONTACT_ EMAIL	C	30	example: jsmith@sac.gov	If government, agency contact email

Delivered Enhanced AT PZEVs, AT PZEVs and PZEVs

Sequence	Field Name	Type	Length	Range or Domain	Description
1	DATA_TYPE	C	4	EnhATPZEV, ATPZEV or PZEV	Enhanced AT PZEV, AT PZEV or PZEV delivered
2	ACC_ID	C	4	examples: GM, NISS, BENZ	Account ID of company
3	MOD_YR	N	4	example: 2011	Model year of vehicle
4	EX_ORDER	C	10	example: A-14-380-A	Certification executive order number
5	TEST_GRP	C	12	example: 4TYXXV01.5MC1	Enter federal test group = CA test group
6	QUANTITY	C	7	example: 43550	Number of vehicles delivered

Attachment C
Credits

Extended Service Multiplier - Annual Reporting Only

Sequence	Field Name	Type	Length	Range or Domain	Description
1	DATA_TYPE	C	2	ES	Extended Service
2	ACC_ID	C	4	examples: GM, NISS, BENZ	Account ID of company
3	MOD_YR	N	4	example: 1999	Base model year of vehicle
4	EX_ORDER	D	10	example: A-14-380-A	Executive order number of base model year
5	ZEV_TIER	C	6	0, I, II, III	Tier Type excluding NEVs.
6	VIN	C	17	example: JS112233344555667	Vehicle identification number
7	START_DATE	D	10	example: February 1, 2011 = 02/01/2011	Date extended service begins for particular year applying for.

Advanced Technology Demonstration

Sequence	Field Name	Type	Length	Range or Domain	Description
1	DATA_TYPE	C	2	AD	Advanced Technology Demonstration
2	ACC_ID	C	4	examples: GM, NISS, BENZ	Account ID of company
3	YEAR	N	4	example: 2011	Year placed in program
4	EX_ORDER	C	10	example: Z-AD-78	Executive order number of project
5	VEH_TYPE	C	5	EnhATPZEV, 0XX, IXX, I.5XX, IIXX, IIIXX, IVXX, VXX (example IIICA, IIINY, IIINJ, IIIOR etc.)	Vehicle Type including: Enhanced AT PZEV and ZEVS, excluding NEVs;indicate California or Section 177 State where XX is the abbreviation of the State.
6	VIN	C	17	example: JS112233344555667	Vehicle identification number
7	DAYS_PLACED	D	4	example: 550	Days in program

Transportation System

Sequence	Field Name	Type	Length	Range or Domain	Description
1	DATA_TYPE	C	2	TS	Transportation System
2	ACC_ID	C	4	examples: GM, NISS, BENZ	Account ID of company
3	YEAR	N	4	example: 2011	Year placed in program
4	EX_ORDER	C	10	example: Z-TS-05	Executive order number of project
5	ZEV_TIER	C	5	0, I, I.5, II, III, IV, V, EnhATPZEV, ATPZEV, PZEV	Tier Type excluding NEVs. Enhanced AT PZEV, AT PZEV or PZEV.
6	VIN	C	17	example: JS112233344555667	Vehicle identification number
7	DAYS_PLACED	D	4	example: 750	Days in program

Attachment D
Debits

ZEV

Sequence	Field Name	Type	Length	Range or Domain	Description
1	DATA_TYPE	C	4	ZDbt	ZEV debit
2	ACC_ID	C	4	examples: GM, NISS, BENZ	Account ID of company
3	APP_YEAR	N	4	example: 2011	Year applying debit
4	FCV_BEV	C	3	FCV or BEV	Fuel cell vehicle or battery electric vehicle
5	ZEV_TIER	C	3	NEV, 0, I, I.5, II, III, IV, V	Tier Type
6	SUBSET	C	2	ES, AD, TS	Extended Service, Advance Demonstration, Transportation System
7	NUM	N	10	example: 184.210	Number of debits in g/mi NMOG
8	MOD_YR	N	4	example: 2002	Model year credit was earned.

Enhanced AT PZEV

Sequence	Field Name	Type	Length	Range or Domain	Description
1	DATA_TYPE	C	12	EnhATPZEVDbt	Enhanced AT PZEV debit
2	ACC_ID	C	4	examples: GM, NISS, BENZ	Account ID of company
3	APP_YEAR	N	4	example: 2011	Year applying debit
4	VEH_TYPE	C	6	NEV, 0, I, I.5, II, III, IV, V, EnhATPZEV, ATPZEV, PZEV	Vehicle Type
5	SUBSET	C	2	ES, AD, TS	Extended Service, Advance Demonstration, Transportation System
6	NUM	N	10	example: 184.210	Number of debits in g/mi NMOG
7	NEV_MODYR	N	4	example: 2002	If debit is a NEV enter model year. Enter null otherwise.

AT PZEV

Sequence	Field Name	Type	Length	Range or Domain	Description
1	DATA_TYPE	C	9	ATPZEVDbt	AT PZEV debit
2	ACC_ID	C	4	examples: GM, NISS, BENZ	Account ID of company
3	APP_YEAR	N	4	example: 2011	Year applying debit
4	VEH_TYPE	C	6	NEV, 0, I, I.5, II, III, IV, V, EnhATPZEV, ATPZEV, PZEV	Vehicle Type
5	SUBSET	C	2	ES, AD, TS	Extended Service, Advance Demonstration, Transportation System
6	NUM	N	10	example: 184.210	Number of debits in g/mi NMOG
7	NEV_MODYR	N	4	example: 2006	If debit is a NEV enter model year. Enter null otherwise.

PZEV

Sequence	Field Name	Type	Length	Range or Domain	Description
1	DATA_TYPE	C	7	PZEVDbt	PZEV debit
2	ACC_ID	C	4	examples: GM, NISS, BENZ	Account ID of company
3	APP_YEAR	N	4	example: 2011	Year applying debit
4	VEH_TYPE	C	6	NEV, 0, I, I.5, II, III, IV, V, EnhATPZEV, ATPZEV, PZEV	Vehicle Type
5	SUBSET	C	2	ES, TS	Extended Service, Transportation System
6	NUM	N	10	example: 552.632	Number of debits in g/mi NMOG
7	NEV_MODYR	C	1	example: 2006	If debit is a NEV enter model year. Enter null otherwise.

Example Data Files for Credits and Debits

Below are some example data files prescribed in Attachment C – Credits and Attachment D – Debits. Not all possible data types are presented.

Credits

DATA_TYPE	ACC_ID	MOD_YR	EX_ORDER	ZEV_TIER	VIN	DATE_DEL	OPTION_ PURLEA	GOV	AGENCY_ NAME	AGENCY_ CONTACT_ NAME	AGENCY_ CONTACT_ EMAIL
ZD	XXXX	2011	A-14-380	IIICA	JS1122333445556667	02/22/11	N	Y	Kings County	Joe Smith	Jsmith@king.gov
ZD	XXXX	2011	A-14-380	IIICA	JS1122333445554447	02/22/11	N	N			

DATA_TYPE	ACC_ID	MOD_YR	EX_ORDER	ZEV_TIER	VIN	DATE_PLACED	OPTION_ PURLEA	GOV	AGENCY _NAME	AGENCY CONTACT NAME	AGENCY CONTACT EMAIL
ZP	XXXX	2011	A-14-380	IIICA	JS1122333445556667	03/30/11	N	Y	Kings County	Joe Smith	Jsmith@king.gov
ZP	XXXX	2011	A-14-380	IIICA	JS1122333445554447	04/01/11	N	N			

DATA_TYPE	ACC_ID	MOD_YR	EX_ORDER	TEST_GRP	QUANTITY
EnhATPZEV	XXXX	2011	A-14-380	3TYAAV01.4MC1	1,000
ATPZEV	XXXX	2011	A-14-380	4TYXXV01.5MC1	5,000
PZEV	XXXX	2011	A-14-380	4SDDYY01.5QA1	20,000

DATA_TYPE	ACC_ID	MOD_YR	EX_ORDER	ZEV_TIER	VIN	START_DATE
ES	XXXX	2002	A-14-380	II	JS1122333445558887	03/25/10

Debits

DATA_TYPE	ACC_ID	APP_YEAR	FCV_BEV	ZEV_TIER	SUBSET	NUM	MODYR
ZDbt	XXXX	2011	FCV	III	AD	104.322	2005

DATA_TYPE	ACC_ID	APP_YEAR	VEH_TYPE	SUBSET	NUM	MODYR
ATPZEVDbt	XXXX	2011	NEV		24.322	2002
ATPZEVDbt	XXXX	2011	AT PZEV		100.12	null

DATA_TYPE	ACC_ID	APP_YEAR	VEH_TYPE	SUBSET	NUM	MODYR
PZEVDbt	XXXX	2011	AT PZEV		810.25	null

Attachment F

Zero Emission Vehicle (ZEV) Credit Transfer Form

Complete and Submit to:
Ms. Krista Eley, Program Manager, ZEV Bank
California Air Resources Board, MSCD/STTB
P.O. Box 2815, Sacramento, California 95812

Date of Transfer	**This document certifies that pursuant to Section 1962.1, Title 13, California Code of Regulations, an agreement executed between Company A and Company B on the Date of Transfer contains the following terms of transfer:**

I. TRANSFER OF ZERO-EMISSION VEHICLE CREDITS FROM TRANSFEROR (A) TO TRANSFEREE (B)

Model Year Earned	Type of Vehicle (NEV, 0CA, ICA, I.5CA, IICA, IIICA, IVCA, VCA, 0XX, IXX, I.5XX, IIXX, IIIXX, IVXX, VXX, Enhanced AT PZEV, AT PZEV and PZEV)	Number of Credits (g/mi NMOG)	Transportation System Credits (Y/N)

I declare under penalty of perjury that all information provided herein are true and correct, to the best of my knowledge and belief.

II. TRANSFEROR (A)

Account Holder – Company Name	*Account ID
Authorized Company Representative Name – First, Middle I., Last *(please print)*	Phone Number
Authorized Company Representative Signature (A)	Date

III. TRANSFEREE (B)

Account Holder – Company Name	*Account ID
Authorized Company Representative Name – First, Middle I., Last *(please print)*	Phone Number
Authorized Company Representative Signature (B)	Date

*Please contact the ZEV Bank Program Manager for your Account ID.

FOR ARB USE ONLY:

Entered By (Please print name and title)	Initials	Date Received	Date Recorded

Attachment F

Instructions and Definitions for the ZEV Credit Transfer Form

Definitions

Transferor	Party giving credits.
Transferee	Party receiving credits.
Account Holder/ Account ID	Account Holder/Account ID – Company Name and Account Holder Identification. Please contact the ZEV Bank Program Manager for an Account ID.
Model Year	Year in which ZEV credits were earned by manufacturer. For Enhanced Advanced Technology Partial ZEV (AT PZEVs), AT PZEVs and PZEVs enter null.
Type of Credit	ZEV Tier – Tier type including: NEV, 0CA, ICA, I.5CA IICA, IIICA, IVCA, VCA, 0XX, IXX, I.5XX IIXX, IIIXX, IVXX, VXX where XX is the abbreviation of 177 State. Enhanced Advanced Technology Partial ZEV (Enhanced AT PZEV) Advanced Technology Partial ZEV (AT PZEV) Partial ZEV (PZEV)
Number of Credits	Total number of credits transferring in grams/mile Non-Methane Organic Gas (g/mi NMOG).
Transportation System Credits	Credits earned in a Transportation System Project. These credits are only available for ZEVs (non-NEV), Enhanced AT PZEVs, AT PZEVs, and PZEVs.

Example

I. TRANSFER OF ZERO-EMISSION VEHICLE CREDITS FROM TRANSFEROR (A) TO TRANSFEREE (B)

	Model Year Earned	Type of Vehicle (NEV, 0CA, ICA, I.5CA, IICA, IIICA, IVCA, VCA, 0XX, IXX, I.5XX, IIXX, IIIXX, IVXX, VXX, Enhanced AT PZEV, AT PZEV, PZEV)	Number of Credits (g/mi NMOG)	Transportation System Credits (Y/N)
1	2008	IICA	15.3	Y
2	2008	IINJ	.39	N
3	2009	NEV	3.4	N
4	null	PZEV	6.8	N

Example

State of Oregon Department of Environmental Quality

OAR 340-258-0120
Table A
Oxygen Molecular Weight Contributions

Comparison of Specific Gravities and Oxygen Mass Fraction of Pure Oxygenates		
Specific Gravity	**Oxygen Mass 60/60 F**	**Fraction**
Methyl Alcohol	0.7963	0.4993
Ethyl Alcohol	0.7939	0.3473
n-Propyl Alcohol	0.8080	0.2662
Isopropyl Alcohol	0.7899	0.2662
n-Butyl Alcohol	0.8137	0.2158
Iso-Butyl Alcohol	0.8058	0.2158
Sec-Butyl Alcohol	0.8114	0.2158
Tertiary-Butyl Alcohol	0.7922	0.2158
Methyl tertiary-Butyl Ether	0.7460	0.1815
Ethyl tertiary-Butyl Ether	0.7452	0.1566
Tertiary Amyl Methyl Ether	0.7752	0.1566

State of Oregon Department of Environmental Quality

OAR 340-258-0290
Table B – Sample Size

Number in Population (N)	Sample Size
66 or larger	59
41 - 65	41
26 - 40	31
0 - 25	N or 24, whichever is smaller

State of Oregon Department of Environmental Quality

OAR 340-259-0030
EPA Protocols

US EPA ARCHIVE DOCUMENT

Revision No.: 07
Date: January 22, 2002

DRAFT

GENERIC VERIFICATION PROTOCOL FOR DIESEL EXHAUST CATALYSTS, PARTICULATE FILTERS, AND ENGINE MODIFICATION CONTROL TECHNOLOGIES FOR HIGHWAY AND NONROAD USE DIESEL ENGINES

EPA Cooperative Agreement No. CR826152-01-3
RTI Project No. 93U-7012-015

Prepared by:

RTI INTERNATIONAL

APPROVED BY:

APCTVC Director:	J. R. Farmer	*Signature on File*	Date: *1/24/02*
APCTVC Quality Manager:	R. S. Wright	*Signature on File*	Date: *1/24/02*
APCTVC Task Leader:	D. W. VanOsdell	*Signature on File*	Date: *1/24/02*
APCTVC Quality Leader:	C. E. Tatsch	*Signature on File*	Date: *1/24/02*
EPA Project Manager:	T. G. Brna	*Signature on File*	Date: *1/29/02*
EPA Quality Manager:	P. W. Groff	*Signature on File*	Date: *1/29/02*

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1.0 INTRODUCTION

1.1 Environmental Technology Verification

The U.S. Environmental Protection Agency (EPA) through its Office of Research and Development (EPA-ORD) has instituted the Environmental Technology Verification (ETV) Program to verify the performance of innovative and improved technical solutions to problems that threaten human health or the environment. EPA created the ETV Program to substantially accelerate the entrance of new and improved environmental technologies into the domestic and international marketplaces. It is a voluntary, non-regulatory program. Its goal is to verify the environmental performance characteristics of commercial-ready technologies through the evaluation of objective and quality-assured data so that potential purchasers and permitters are provided with an independent and credible assessment of what they are buying and permitting.

The ETV Program does not conduct technology research or development. ETV test results are always publically available, and the applicants are strongly encouraged to ensure, prior to beginning an ETV test, that they are satisfied with the performance of their technologies. Within the ETV Program, this state of development is characterized as "commercial-ready ," and the ETV test is conducted on production units or prototypes having the major characteristics of commercial units.

The provision of high-quality performance data on fully-developed commercial technology encourages more rapid implementation of those technologies and consequent protection of the environment with better and less expensive approaches. The ETV Program is conducted by six ETV centers that span the breadth of environmental technologies.

1.2 Air Pollution Control Technology Verification Center

EPA's partner in the Air Pollution Control Technology Verification Center (APCTVC) is RTI, a non-profit contract research organization with headquarters in Research Triangle Park, NC. The APCTVC verifies the performance of commercial-ready technologies used to control air pollutant emissions. The emphasis of the APCTVC is currently on technologies for controlling particulate matter, volatile organic compounds, nitrogen oxides (NO_x), and hazardous air pollutants from both mobile and stationary sources. The activities of the APCTVC are conducted with the assistance of stakeholders from various interested parties. Overall APCTVC guidance is provided by the Stakeholders Advisory Committee (SAC), while the detailed development of individual technology ETV protocols is conducted with input from Technical Panels (TP) focused on each technology area.

The APCTVC develops generic verification protocols and specific test/quality assurance (test/QA) plans, conducts independent testing of technologies, and prepares ETV test reports and statements for broad dissemination. Testing costs are ultimately borne by the technology applicants, although initial tests within a given technology area may be partially supported with government funds.

US EPA ARCHIVE DOCUMENT

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1.3 Mobile Sources Air Pollution Control Technologies

Control of emissions from mobile sources continues to be of great national importance. Several areas of the country are not able to attain ambient air quality standards. The mobile source provisions of the 1990 Clean Air Act Amendments (CAAA) are intended to reduce most vehicle-related air pollutants by more than 40 percent for 1996 and later model year vehicles and engines. Earlier engine models emit pollutants at higher levels, and as these engine are durable and have long useful lives, they will continue to emit pollutants at higher levels many years into the future. For these reasons, the EPA funded and the APCTVC SAC recommended inclusion of air pollution control technologies for mobile sources as a priority for ETV.

One important group of mobile source air pollution control initiatives is concerned with highway and nonroad use diesel engines. The diesel particulate standard for urban buses was reduced in 1993 by 60 percent, from 0.33 to 0.13 g/kWh (0.25 to 0.10 g/bhp-hr). The standard, which applies to urban transit buses, dropped to 0.094 g/kWh (0.070 g/bhp-hr) in 1994 and to 0.067 g/kWh (0.050 g/bhp-hr) in 1996. While existing engine technologies can meet these standards, future standards are expected to be increasingly stringent and will require the use of post-combustion emissions control technologies. New technologies are being developed to meet these goals. In addition, since a NO_x emission level below the level mandated allows the generation of credits through the Voluntary Diesel Retrofit Program (VDRP), pollution prevention becomes more cost effective, and innovations in less-polluting alternatives and control technologies are encouraged.

Retrofit mobile source control technologies are principally exhaust treatment emission control devices and engine modifications. Some require no mechanical changes to engines, while others will involve some modification of the engine or its control system.

Filters for particulate matter (PM) control and diesel exhaust catalysts (DECs) may make use of or require some integration with engines. Engine modifications, in the context of this protocol, refer to pollution reduction technologies integral to the engine or the engine control systems. All these technologies have the potential to affect engine performance, and the concurrence of the engine manufacturer that the changes are compatible with safe, efficient, and reliable operation in the engine is an important element in demonstrating commercial readiness and suitability for ETV. The technologies and their testing are discussed in more detail below.

Selective Catalytic Reduction (SCR) nitrogen oxides (NO_x) control technologies, fuels, fuel additives, reformulated fuels, and lubricants are specifically excluded from consideration under this protocol for testing as retrofit emissions control devices. Protocols for these technologies may be developed in the future.

1.4 The APCTVC Mobile Sources Verification Program

This generic verification protocol (GVP) provides the requirements for APCTVC's ETV of the performance of DEC, PM filter, and engine modification air pollution control technologies applied to highway and nonroad use diesel engines. Other technologies will be addressed

similarly. Other organizations [e.g., EPA's Office of Transportation and Air Quality (EPA-OTAQ) and the California Air Resources Board] also 'verify' the performance of mobile source emissions control devices under different protocols to meet the needs of those organizations. Specifically, EPA-OTAQ has established, for applicants who meet particular criteria, a generally parallel path that does not require the level of external QA that is required for APCTVC ETV. The technology applicant should discuss the intended application of the technology with the appropriate regulatory body to determine the most suitable path for "verification."

This GVP is intended to apply only to DECs, PM filters, and engine modifications and their combinations. The APCTVC reserves the right to evaluate each technology submitted for ETV and to determine the applicability of this protocol to that specific technology. Special testing may be required in some cases to maintain the integrity and credibility, and, therefore, the value of ETVs. The critical data quality objectives (DQOs) in this document were chosen to provide emissions measurements sufficient to support the VDRP and its emissions credit provisions. Emissions credit allowances will be set by the appropriate state regulatory authority or EPA-OTAQ. (As stated above, the VDRP approving agencies may have data requirements that are in addition to the ETV test report.)

This protocol was developed and has been reviewed by a technical panel composed of a broad group of stakeholders who have expertise in mobile source controls and come from the vendor, user, and regulatory spheres. Technical panel membership is dynamic, and its composition is expected to change over time as technical emphases change. The APCTVC will maintain membership balance on the panel.

The basic APCTVC ETV test will measure and report baseline emissions concentrations and rates for an engine prior to use of the retrofit technology and also the emissions concentrations and rates for this engine following retrofit. It will be conducted at an independent, third-party test laboratory. The data quality requirements of this generic protocol will be applied at approved test laboratories through the preparation of test-specific test/QA plans. Other laboratory-, application-, or technology-specific information may also need to be addressed in the test/QA plan, which is described in Section 10.0. In general, test/QA plans prepared by test laboratories will not be reviewed by the entire technical panel. However, because specific technology areas may require special expertise or emphasis, input and review will be obtained from an ad hoc subcommittee of the technical panel and/or outside experts when deemed appropriate by the APCTVC. Test results will be presented as ETV reports and statements.

1.5 Quality Management Documents

Management and testing in this APCTVC program are performed in accordance with procedures and protocols defined by the following:

1) EPA's ETV Quality and Management Plan (ETV QMP) (EPA, 1998a or the quality management plan current at the time of testing),
2) the APCT Quality Management Plan (QMP) (RTI, 1998),

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3) the Generic Verification Protocol for Diesel Exhaust Catalysts, Particulate Filters, and Engine Modification Control Technologies for Highway and Nonroad Use Diesel Engines (this document), and
4) the test/QA plan prepared for each specific test or group of tests.

EPA's ETV QMP lays out the definitions, procedures, processes, inter-organizational relationships, and outputs that will ensure the quality of both the data and the programmatic elements of the ETV Program. Part A of the ETV QMP contains the specifications and guidelines that are applicable to common or routine quality management functions and activities necessary to support the ETV Program. Part B of the ETV QMP contains the specifications and guidelines that apply to test-specific environmental activities involving the generation, collection, analysis, evaluation, and reporting of test data.

APCT's QMP describes the quality systems in place for the overall APCTVC. It was prepared by RTI and approved by EPA. Among other quality management items, it defines what must be covered in the GVPs and test/QA plans for technologies undergoing ETV testing.

Generic Verification Protocols (GVPs) are prepared to describe the general procedures to be used for testing a type of technology and define the critical data quality objectives (critical DQOs). The GVP for retrofit air pollution control technologies for highway and nonroad use diesel engines was written by the APCTVC with input from a technical panel and approved by EPA.

A test/QA plan is prepared for each test or group of tests. The test/QA plan describes, in detail, how the testing organization will implement and meet the requirements of the GVP. The test/QA plan also sets DQOs for any planned measurements that were not set in the GVP. The test/QA plan addresses issues such as the test organization's management structure, the test schedule, test procedures and documentation, analytical methods, record keeping requirements, and instrument calibration and traceability, and it specifies the QA and quality control (QC) requirements for obtaining ETV data of sufficient quantity and quality to satisfy the DQOs of the generic verification protocol. Section 10 of this GVP addresses requirements for the test/QA plan.

Because multiple testing organizations will be conducting the tests and the desirability to ensure comparability, the APCTVC will develop a prototype test/QA plan (not part of this GVP) for each type of technology. This prototype will be customized by the testing organization to meet its specific implementation of the Federal Test Procedures (FTPs) as defined in 40 CFR Parts 86 and 89, and the secondary measurements, subject to approval by the APCTVC and EPA-ORD. Testing arrangements that do not meet the requirements of the FTP will not be approved, and test instrumentation or test procedures that the APCTVC determines will compromise data reliability or comparability between testing organizations will not be approved.

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2.0 OBJECTIVE AND SCOPE

2.1 Objective

The objective of this GVP is to establish the parameters within which DECs, PM filters, and engine modification air pollution control technologies for highway and nonroad use diesel engines will be tested to verify their performance with uniform and consistent methodologies within the APCTVC. The protocol addresses the requirements for technology submission, outlines the test conditions and procedures to be used, and states the critical DQOs for ETV and states reporting requirements. The control technologies will be verified within a specified range of applicability, and ETV reports and statements will be produced for dissemination to the public.

2.2 Scope

APCTVC testing will be performed to quantify the effectiveness of commercially ready emissions control technologies that are intended for use on diesel engines considered mobile sources of air pollutants. Emissions testing under this ETV Program is based on the applicable FTPs for highway and nonroad engines. As performed by manufacturers to certify their engines, FTPs are fully defined by the regulations and consist of the engine-appropriate cold- and hot-start engine dynamometer tests conducted under specified load cycles. For purposes of this protocol, the number and type of FTP tests may be different from certification requirements, as determined by the applicant and the APCTVC to best verify the performance of the technology under consideration. However, the individual FTP test module -- the cold-start test or the hot-start test -- will be performed completely in accordance with the regulations. (The low NO_x and PM emissions from post-2001 engines are prompting development of new test procedures better suited to these emission levels. As these test procedures become standardized and acceptable to EPA, they will be acceptable for use in ETVs.) The pollutants of major interest are NO_x, hydrocarbons (HCs), PM, and carbon monoxide (CO). Other measurements will also be made of emissions (for instance, carbon dioxide[CO_2]) and operating parameters of the test engine and the control technology. Additional measurements may also be required if the technology might be reasonably expected to generate secondary emissions. Emissions will be measured along with other data useful for evaluating the performance of the technologies and the technologies' associated environmental and efficiency impacts. In this context, the effects of control technologies on fuel economy and engine performance and power will be of particular interest.

Also fundamental to this ETV protocol is providing emissions control efficiency information needed for applicants to participate in the EPA Voluntary Diesel Retrofit Program (VDRP). The VDRP is managed by EPA-OTAQ. The data quality objectives given in Section 2.3 were set to provide emissions control device performance data that can be used in submittals to the VDRP. VDRP determinations are made by EPA-OTAQ, which may require information not included in the ETV.

The APCTVC will consider applications for ETV of air pollution control technologies on test engines specified by the applicant. Depending on the expected application, the data collected,

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and the test design, the results obtained may be valid only for that single engine or to groupings of multiple engines. If application of single engine test results to an engine group is made by the regulatory body, the decision will be based on an expectation that the control device, if appropriately sized, will perform similarly on all the engines in that group. Generally, similar emissions control performance is expected from engines that have the same engine technology and use. The sensitivity of emissions control performance to engine type and usage is not known to be the same for all technologies, and the applicability decision will be made separately for each technology type and possibly for each technology. Previously obtained performance data may affect the decision. In all cases, the decision regarding applicability will be made by EPA-OTAQ, which should be contacted at the time a technology is submitted to obtain current information.

Implicit in the potential use of single engine ETV tests as predictive of performance over segments of the total engine population is the availability of non-proprietary application sizing information and that the technology be labeled. The purpose of this requirement is to allow the APCTVC and the potential technology user to evaluate the applicability of the verified technology to other applications. Applicants who utilize application sizing charts must verify their technologies on an engine at the most challenging end of the range of applicability. ETV reports and statements will report the results and the design guidance required to independently extend application of the technology to other engines in the same engine grouping.

To request ETV, the applicant applies to the APCTVC for the technology to be tested and proposes the test engine(s) to be used. The APCTVC will review the application and provide input as required to ensure that the engine(s) proposed are suitable and that the emission control equipment sizing is clear and correct. The equipment/technology will be applied to the engine(s) according to the applicant's instructions. ETV test results for the engine(s) will be reported in the ETV report and statement. The results will provide the emissions performance data required for the VDRP reviewing regulatory authority to determine the emission reduction capability of the technology.

2.2.1 Highway Engines

Applicants may choose to have their technologies verified on a single highway engine or multiple selected engines, depending on the applicant's intended use of the data. EPA-OTAQ will determine the extent of applicability of data from any given engine and should be consulted by the applicant for that purpose. Testing of emissions control technology intended to control emissions from highway diesel engines will be conducted generally under the provisions of 40 CFR, Part 86, Subpart N. The primary emissions measurements will be of NO_x, PM, HC, CO, and other FTP requirements. CO_2 and the engine operating parameters are required secondary measurements. Each engine in the test will be loaded by a dynamometer as described in the transient FTP. Each ETV test will consist of at least a single full FTP test (cold- and hot-start) and two additional hot-start tests (total of three hot-starts) on an emission-stabilized baseline engine and on the engine with the control technology in use. Additional hot-start tests may also be required to meet the number of test requirements described in Section 5, or the applicant may wish to run additional tests to narrow the confidence interval on the result. [An ETV

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requirement for multiple hot-start tests may be met using the hot-start results from full FTP test data (both cold- and hot-start), at the applicant's option.] Durability testing , which consists of ETV of aged control technology units as described in Section 5.2.9, is part of the ETV process. Emissions reductions will be computed relative to the baseline engine emissions.

2.2.2 Nonroad Engines

As with highway engines, applicants select the nonroad engines on which to test their technologies. The ETV testing of emissions from nonroad diesel engines will be conducted generally within the requirements of 40 CFR, Part 89, Subpart E. As for highway engines, the primary emissions measurements for nonroad engines will be of NO_x, PM, HC, CO, and other FTP requirements. CO_2 and engine operating parameters are required secondary measurements. The ETV testing will consist of three or more nonroad steady-state mode tests (40 CFR, Part 89, Subparts D and E), as described in Section 5. (Concerns about transient emissions from nonroad engines are prompting development of new test procedures. As these test procedures become standardized and are codified in the FTP, they will be included in the ETV test protocol.) The test must be conducted over all applicable modes of the test cycle appropriate to the engine (e.g., 8-mode test cycle for variable speed engines or 5-mode cycle for constant speed engines) or may be conducted over all modes at the applicant's request. The ETV report will reflect the extent of the test conducted. Each ETV test will consist of the same assemblage of FTP tests on the broken-in baseline engine and the engine with the control technology in use. Durability testing is required as described in Section 5.2.9. Composite emissions reductions are computed relative to the baseline engine emissions. In addition, the emissions results will be reported in composite and mode-by-mode to allow flexibility in use of the data for different engine applications.

2.2.3 Control Technologies

This GVP is specifically intended to include the following emissions control technologies:

1) DECs regenerated continuously or periodically,
2) PM filters, and
3) Engine modifications.

The basic ETV test remains the same for all emissions control technologies. However, the technologies interact differently with the various engines. Therefore, the engine grouping concept may be applied differently by EPA-OTAQ depending of the nature of the technology. In addition, where technologies require particular fuel characteristics or have other restrictions or interactions, applicants must specify these and any associated requirements in their ETV applications.

In all cases, the ETV test will be designed to reasonably isolate the effects of the retrofit technology from coincident engine adjustments and tune-ups. For example, a retrofit technology that required an engine tune-up following installation would be tested against a tuned-up baseline engine.

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Some technologies, by their nature, may reasonably require engine adjustments following installation. To be allowed, such adjustments must be part of the description of the technology, be included in the installation instructions, be described in the application, and be made by the laboratory technician and not by the applicant. They will be examined to determine the effect of those engine adjustments alone, and the baseline engine may be tuned to the same operating condition if the adjustments alone are considered to have a positive effect on emissions. This requires that the APCTVC and the testing laboratory be provided with a full disclosure of the working principles of the technology prior to developing the test. In these cases, the ETV report and statement will define the retrofit technology as consisting of both the device and the engine adjustments, with both required to achieve any emissions reduction observed.

2.2.4 Relationship of ETV Program to EPA-OTAQ VDRP Verified Technology List

EPA-OTAQ is charged with establishing a Verified Technology List of technologies capable of providing emissions reductions. The test results EPA-OTAQ will utilize to evaluate a technology may be generated following the ETV process, with the ETV report and verification statement serving as the data package to EPA-OTAQ. Other paths to the verified technology list also exist. The VDRP program is described and appropriate contacts are identified at http://www.epa.gov/otaq/retrofit/. The technology applicant should discuss the intended application of the technology with EPA-OTAQ to determine the most suitable evaluation path for the applicant's technology.

As of the date of this protocol, emissions test data from a full FTP test (whether highway or nonroad), that was generated by a manufacturer to obtain a certificate of conformity may be determined by EPA-OTAQ to constitute a valid data set for VDRP purposes. Certification data do not pass though the ETV Program. The certification and VDRP technology listing processes are independently performed by EPA-OTAQ. In addition, EPA-OTAQ has established for some applicants a technology evaluation pathway whose test requirements parallel those of this GVP, but with reduced QA requirements.

2.3 Data Quality Objectives (DQOs)

The data of primary interest in this ETV are the reduction in emissions of NO_x, HC, PM, and CO. (Numerous other measurements, including CO_2 emissions, will also be made as described in later sections. However, these are not considered critical, and the methods and data quality objectives will be stated in the test/QA plan for each technology.) The DQOs of this GVP are the requirements of the test methods specified in 40CFR Parts 86 or 89 for highway or nonroad diesel engines, respectively, when conducting the number and type of FTP tests called for by the approved test/QA plan for the technology. ETV tests that do not meet the FTP QA requirements must be repeated.

The number of and type of FTP tests (cold- and/or hot-start) required for ETV is determined from the following criteria:

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First, a minimum of three tests is required to provide the basic ETV result of a mean emission reduction and the 95% confidence interval on that mean based on measured variability for each of the measured emissions and test parameters. For highway engines this minimum is satisfied with one cold start test and three hot start tests. For nonroad engines three replicates of the appropriate test sequence (i.e., three 8-mode tests, or three 6-mode tests) are required. A three test minimum is currently the same as is required by the State of California for verification.

Second, additional tests may be required to meet the ETV requirement that the test/QA plan provide a 90% probability of detecting the expected emissions reductions when computed using the expected experimental errors for the various measurements. These criteria become controlling for low emissions reductions and/or high test variability. This is a planning requirement for the test/QA plan. The procedure to determine the appropriate number of tests is given in Section 5.

Third, additional tests may be desired by the applicant to reduce the width of the 95% confidence interval on the mean emission reduction. Section 5 provides additional explanation and example scenarios. This third criterion is a consequence of applying standard statistical procedures to the ETV test design and data analysis. At a fixed measurement variability, normal statistical procedures lead to a small number of tests giving a broader 95% confidence interval than a larger number of tests. To any regulator or potential technology user, an emission reduction of 40% ± 5% is better than 40% ± 20% and will be given more credence.

An applicant may conduct privately sponsored tests at a test laboratory for development purposes with the same test engine prior to and/or after conducting ETV tests. Such testing is understood to be common and important to ensure the technology is properly adjusted and tuned to the application. However, two important principles of ETV are that the verified technology be commercial ready when tested and that all data obtained under the ETV process be reported.

Therefore, preparation for the ETV test (submittal of the technology to the APCTVC, discussion of engine selection, and preparation of the test/QA plan) must be completed prior to conducting the ETV test itself. In particular, declaration of the test run which is to be the ETV test must be made prior to starting the test, the engine must be brought to a starting point in accordance with the test/QA plan, and the results of that test will be documented and reported in accordance with the test/QA plan. The data from all ETV tests will be retained and reported to the APCTVC, including invalid FTP test results. Data that meet the QA requirements of the FTP are considered valid and will be used to compute emissions reductions for ETV purposes. Section 8.0 addresses a technology applicant's options should the technology perform below expectations.

Tests conducted at qualified laboratories will be accepted as ETV tests provided the technology is submitted to the APCTVC and all requirements of this GVP are met, including approval of the test/QA plan prior to testing. This requires that the technology be submitted

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to the APCTVC, that a test/QA plan be prepared by the laboratory in conjunction with the APCTVC, and that the test/QA plan be approved by the APCTVC prior to testing. All QA requirements of the FTP methods must be met, and the test and test laboratory must meet the QA requirements of ETV as established in this GVP and the test/QA plan.

Engine emissions are expressed in grams of pollutant per kilowatt-hour (g/kWh) or in units of grams per brake horsepower-hour (g/bhp-hr). The primary measurement of HC and NO_x is normally concentration in the exhaust stream in parts per million by volume (ppmv), which is then converted to g/kWh in accordance with the FTP. For calculation of the technology's removal efficiency, the baseline emissions of the tested engine must also be known. The control technology performance will be reported as both absolute emissions in g/kWh and as percentage emissions reduction for a specific engine or engine family. The percentage emission reduction reported will be the mean emission reduction (relative to the baseline emission) with attendant upper and lower 95% confidence limits on that mean.

3.0 ETV TESTING RESPONSIBILITIES

This ETV program is conducted by the APCTVC under the sponsorship of the EPA-ORD and with the participation of technology applicants. The APCTVC is operated under a cooperative agreement by RTI, EPA's ETV partner. RTI's role as ETV partner is to provide technical and administrative leadership and either conduct or manage the conduct of ETV testing and reporting. Various subcontractors have roles in the APCTVC under RTI's management.

ETV tests are conducted by qualified test laboratories as contractors to RTI. Test laboratory-specific ETV test/QA plans are prepared by the testing laboratories to meet the requirements of the GVP.

The test/QA plan includes a chart that presents the test program organization and major lines of communication. The organizations involved in the ETV of mobile diesel engine air pollution control technologies are the EPA, RTI, testing laboratory, and technology applicant.

The primary responsibilities for each organization involved in the test program are:

1) The EPA-ORD, following its procedures for ETV, reviews and approves GVPs, test/QA plans, ETV reports and statements, and conducts QA audits.
2) The APCTVC prepares the GVP, provides oversight of the testing organization, provides a template for test/QA plans, and jointly with EPA-ORD reviews and approves the ETV reports and statements.
3) The testing organization prepares the test/QA plan in accordance with the GVP, coordinates test details and schedules with the applicants, conducts the tests, and prepares and revises draft ETV reports and statements. The testing organization QA staff is responsible for conducting internal QA on test results and reports.
4) EPA-ORD and/or APCTVC QA staff, at their discretion, will conduct assessments of the test organization's technical and quality systems.

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5) The technology applicant provides complete, commercial-ready equipment for ETV testing; provides logistical and technical support, as required; and assists the testing organization with operation and monitoring of the equipment during the ETV testing. The applicant's responsibilities are defined by a contract or letter of agreement with RTI..

4.0 TECHNOLOGY CAPABILITIES AND DESCRIPTION

This section outlines the information to be submitted by the ETV applicant, who is the basic source of the information regarding its mobile source air pollution control technology. This information is used by the test laboratory and APCTVC to prepare and review a test/QA plan that meets the requirements of the applicant and potential users of the ETV. No general outline can anticipate the data requirements for all possible technologies, so the applicant may be requested to supplement this outline when additional information is needed. This protocol has been developed with an awareness of the California Air Resources Board (CARB) "verification" program, and an application to CARB for retrofit "verification" is expected to provide adequate information. The basic application form to be used for ETV is that posted by EPA-OTAQ for the voluntary retrofit program, which can be found at:

http://www.epa.gov/otaq/retrofit/documents/forms.xls (as an Excel file)
http://www.epa.gov/otaq/retrofit/documents/forms.wk4 (as a Quattro file)

EPA-OTAQ has also posted application form guides, which can be found by replacing "forms" with "forms_guide" in the links above. The ETV test/QA plan will summarize this information in a form that clearly describes the technology being verified and states, for potential users of the technology, it's intended range of applicability as stated by the applicant. The test/QA plan will also include a draft ETV statement, based on Appendix A, customized to the specific technology being verified and measurements being made. The balance of this section independently describes the information requirements that led to development of these forms.

4.1 Basic Technology Identification and ETV Requirements

The basic technology identification should be a concise description of the technology that describes what is being verified and summarizes the emissions control performance expected. This information will be used to describe the technology in the ETV statement.

It should include such information as: technology name, model number, manufacturer's name and address, serial number or other unique identification, warning and caution statements, capacity or throughput rate, specific installation instructions, adjustments, limits on flow, temperature, pressure, and other information necessary to describe the specific technology and its intended use. Warranty information on the technology should be provided, including a sample warranty statement.

In addition, the applicant must state the goal of the ETV in terms of range of applicability

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(single or multiple engine, fuel requirements, equipment sizing, etc.), expected emissions reduction, and anticipated data use. This information will be used to develop the ETV test/QA plan.

4.2 Technology Descriptive Information

This section of the application is intended to describe the technology more fully. It will be used to prepare the test/QA plan and as a more complete description of the technology in the ETV report.

The applicant should describe the technology in a brief (300 word) statement, referring to the scientific principles of the technology's operation. Depending on the complexity of the technology, this may be followed by more extensive information. When applicable, the inclusion of schematic drawings explaining operation of the technology is encouraged. Examples of descriptive information that should be included are:

> Installation requirements. Space occupied, installation time, any physical modifications, placement issues, identification of ancillary equipment, if any, recommended duration of degreening as well as any special start-up procedures, and any other special requirements.
> Operation. Description to include identification of any favorable or unfavorable operating conditions and their effect on performance, fuel requirements (such as fuel sulfur limit), consequences of misfueling, identification of any chemicals or other consumable reactants, regeneration requirements, and expected engine back-pressure. Any requirement for energy sources (e.g., heat, electricity, compressed air, hydraulic fluid, pressure) external to the engine must be identified so they can be accounted for in the test/QA plan.
> Maintenance and warranty. Identification of recommended maintenance procedures, cleaning instructions, and spare parts and supplies. The warranty being offered should be stated.
> Operator or mechanic qualifications/training/safety. Qualifications needed to operate and service the technology, amount and type of training needed for operation and maintenance, and special safety considerations. Use of personal protective equipment (eyeglasses, hearing protection, etc.) should be noted.
> Secondary emissions. Identification of any secondary emission to the air that impacts water quality, or liquid or solid waste.
> Technology's life expectancy. Special attention should be given to the technology's regeneration requirements, if any, including a description of the regeneration process, any operating condition requirements for successful regeneration (e.g., temperature), and any manual or computer control of regeneration.

In the case of combinations of independent technologies that are being submitted for ETV, the description of the combined technology should completely identify and describe those technologies being combined and fully state the nature of the combined test and expected result.

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4.3 Technology Performance

The technology applicant must quantify the performance expected from the technology and support that expectation with background test data, including both initial performance and technology durability test descriptions and results. In general, these data will not be used to verify the performance of the technology, but will be used to develop an ETV test/QA plan that can adequately support the expected performance. The level of descriptive detail required for existing tests and their results cannot be generally stated because it is dependent on the ETV goals. Applicants are encouraged to supply pertinent data supporting their claims, which will include test facility descriptions, procedures, quality assurance and control, and any deviations from the FTP.

All aspects of the technology's performance should be addressed, beginning with performance during routine steady-state operation, but also including unsteady or unfavorable operation such as extended idling periods, uncontrolled regeneration, in-place maintenance, etc. Any known or expected impact the technology might have on the character of the emissions (gas composition, temperature, particle size or composition, etc.) should be identified.

4.4 Technology/Engine Interactions

The applicant must describe interactions between the proposed engine(s) and the technology, to include the known or expected effects of the technology on the engine(s). Backpressure, additional parasitic loads, fuel consumption, effects on engine durability, and oil consumption are of special concern. The relationship of the technology, engine control logic, and engine operation should be addressed for the engine(s) under consideration.

The applicant should defend the applicability of the technology to the applicable engine(s) by including exhaust temperature profiles, duty cycles, and other relevant performance information. The operating conditions that are favorable for the control technology should be compared with those of the engine.

The opinion of the engine(s)'s manufacturers regarding compatibility of the technology with their engine should be solicited, summarized, and the correspondence included in the application. Any known or anticipated impact of the technology on engine warranty is to be identified. The relationship between technology warranty and engine warranty should be discussed.

5.0 ETV TESTING

As stated in Section 2.3, Data Quality Objectives, an ETV test consists of a minimum of three FTP tests, and may include additional FTP tests to differentiate a low emission reduction technology from zero or to narrow the confidence limit on the mean emission reduction. Section 5.1 presents the methods that are used to design an ETV test to accomplish the applicant's goal, beginning from an expected emissions reduction for a

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particular pollutant and progressing through the methods used to generate the 95% confidence interval on the mean emission redutions. Section 5.2 presents other general ETV test considerations that apply to most retrofit air pollution control technologies. The remaining sections of this chapter are specific to the indicated types of technologies.

5.1 ETV Test Design

The data of primary interest in this ETV are the reduction in emissions of NO_x, HC, PM, and CO. (Numerous other measurements, including CO_2 emissions, will also be made as described in later sections. However, these are not considered critical, and the methods and data quality objectives will be stated in the test/QA plan for each technology.) NO_x emissions will be used to compute the number of tests required unless the applicant specifically requests that the reduction in another of the pollutants be used to control test design.

The number of and type of FTP tests required for ETV will be as follows:

A minimum of three tests is required to provide a mean emission reduction and the 95% confidence interval on that mean based on measured variability for each of the measured emissions and test parameters. For highway engines this minimum is satisfied with one cold start test and three hot start tests. For nonroad engines the minimum is satisfied with three replicates of the test sequence appropriate for the engine classification for which the technology is intended (i.e., three 8-mode tests for applicable engines, three 5-mode test for constant speed engines, three 6-mode test for variable speed engines under 19 kW.)

Additional tests may be required to meet the ETV requirement that the test/QA plan provide a 90% probability of detecting the expected emissions reductions when computed using the expected experimental errors for the various measurements. These criteria become controlling for low emissions reductions and/or high test variability for the controlling pollutant, which will be NO_x unless another pollutant is selected. This is a planning requirement for the test/QA plan. Section 5.1.1 describes the calculation procedure.

Relative to the minimum number, additional tests may be desired by the applicant to reduce the width of the 95% confidence interval on the mean emission reduction. Section 5.2 provides additional explanation and example scenarios.

5.1.1 Determination of Number of Tests Required to Meet ETV Requirements

Minimizing the cost of ETV testing is important, and reducing the number of tests conducted is one way to minimize cost. However, if too few tests are conducted, normal experimental variability could prevent the ETV from producing a useful outcome. For measurements having known variability and for stated expected reductions in emissions, the probability that a given number of tests can detect the expected reduction can be computed from statistical theory based on normal distributions. This ETV protocol requires that all ETV test/QA plans

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include sufficient tests to have a high probability of detecting the emissions reductions expected by the applicant. This requirement was implemented to ensure, as much as was practical, that the ETV test would accomplish the applicant's goals. This requirement will generally only be important to ETV test design for low emissions reductions and/or measurements having high variability. Specifically, the ETV test is to be designed such that there is 95% confidence that there is a 90% probability of detecting the emission reductions expected by the applicant, computed from the expected experimental variability for the various measurements. In this context, "detecting" means that the 95% confidence interval does not include zero emissions reduction. (This requirement is for test design purposes, and does not require that the test/QA plan be modified should actual test data show that the assumptions that went into the calculation were incorrect. However, as explained below, insufficient replication can result in inability to issue a verification and publication of an ETV report stating that a technology had no statistically significant benefit.)

An equation was derived to explicitly compute the number of tests required for normally distributed measurements having known standard deviations. Some results of applying that calculation are presented in Table 1 for PM and NO_x emission reductions. The equation used to compute the number of tests required is presented in Appendix B.

In Table 1 the baseline engine is assumed to be at a fixed emission value (the 1990 certification emission level for highway diesel engines) for PM (top of table) and NOx (bottom three rows). PM and NO_x measurements are used in Table 1 because the measurement standard deviations were known for one laboratory. The results in Table 1 are limited by the requirement in the derivation that the measurements be normally distributed with known variability. As will be shown in Section 5.1.2, the determination of the measurement variability from data, as will be done during the ETV data analysis, leads to a broadening of the confidence interval. Consequently, more tests than shown in Table 1 may be required under those conditions, and careful examination of the number of tests needed will be required during test/QA plan development.

The column headings in the first row of the PM and NO_x sections of the table give the assumption that installing the control technology gives emissions reductions of 5%, 20%, 50%, or 85% from the baseline emissions levels, which might be the applicant's estimate of emission reduction for different technologies. The second row gives the constant and known baseline engine (without control technology) variability when emitting at the 1990 certification level. The third row is the known measurement variability for the baseline engine after having been fitted with control technology that achieves the reduction shown in the column heading. (Variability is expressed as the known standard deviation at the emission level divided by the corresponding baseline engine mean emission and multiplied by 100%.) The variability increases as the emission reduction increases from left to right because the absolute error is roughly constant, while the magnitude is decreasing. The fourth row gives the calculated number of tests required to have 90% confidence that the 95% confidence interval about the mean expected emission reduction would not include zero.

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Table 1. Number of replicate tests (on both baseline and controlled engine) to achieve a 90% probability of detecting a PM emission reduction at a confidence level of 95%

Expected emission reduction (relative to the respective 1990 certification levels for PM and NO_x, respectively)	5%	20%	50%	85%
Variability for baseline engine PM measurement at 1990 levels	2%	2%	2%	2%
PM measurement variability at specified emission reduction	2%	2%	3%	10%
Number of tests required to have 90% probability (ETV requirement) of detecting expected PM emission reduction[a]	3	1	1	1
Variability for baseline engine NO_x measurement at 1990 levels	2%	2%	2%	2%
NO_x measurement variability at specified emission reduction	2%	2%	7%	NA[b]
Number of tests required to have 90% probability (ETV requirement) of detecting expected NOx emission reduction[a]	3	1	1	NA[b]

[a] Computed under the assumption of normally distributed measurements having known variability. Additional tests may be required for sample standard deviations obtained during ETV.

[b] NA = Not Available.

The fifth through the seventh rows (shaded) repeat the calculation for the NO_x measurement. No estimate of variability was available for the NO_x measurement at an 85% reduction from the 1990 level. Table 1 shows that, for both PM and NO_x, three tests are sufficient to distinguish between zero and emissions reductions as low as 5%, provided the estimates of measurement variability are met in the actual ETV. One test would be sufficient to detect the other emissions reductions, but three are required by ETV to provide a measured standard deviation. No specific estimates of variability for HC emissions were available, but at high emissions reductions (low absolute levels) the HC variability may be on the order of 30%. Three tests would not be sufficient in that case. In the development of the test/QA plan, the test laboratory will report its known measurement variability, and the expected number of tests required. This estimate will be reviewed by the APCTVC.

Appendix C presents a sensitivity analysis for additional levels of measurement variability. As explained in section 5.1.2, below, the number of tests may be increased further if an applicant desires to reduce the width of the confidence interval on the mean emission reduction.

5.1.2 Confidence Interval on the ETV Result

A consequence of the unavoidable variability in emissions measurements is that the mean of a small number of measurements has a small probability of giving the true emission reduction. In some cases it may not be possible to make a statistically-significant determination that the measured emission reduction is different from zero. The results of ETV measurements will be presented in verification statements and reports as the mean and

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95% confidence interval on that mean, calculated using the sample standard deviations determined from the ETV test data. Because sample standard deviations are available, the t-statistic is applied to compute the confidence intervals. This results in a broader error distribution than indicated in Table 1.

Table 2 illustrates the results that would be obtained for the PM emissions measurement variability numbers that were presented in Table 1 should those results be obtained during an ETV. Two additional 20% reduction columns have been added as examples of the effects of still higher variability at moderate reductions. (As was true in Table 1, the measurement variability in Table 2 is expressed as a measurement standard deviation divided by the baseline engine mean emission. However, relative to Table 1, the use of the t-distribution broadens the confidence interval.) The first three rows of Table 2 are the same as those in Table 1. Rows 5 through 7 give the two-sided 95% confidence intervals on the indicated mean percent emissions reduction from the 1990 certification emission value for three, six, and nine tests. For the 5% reduction column, Table 2 shows that the three test ETV minimum does not detect the 5% reduction in that a zero reduction is within the 95% confidence interval of -1.7 to 11.7% reduction. Six tests do detect the difference. Therefore, between three and six tests would be required.

The fourth and fifth columns of Table 2 illustrate the effects of higher variability levels for the controlled engine than were presented in Table 1 for a 20% emissions reduction, and more clearly show the potential benefits of additional testing. This hypothetical additional variability would arise from some interaction between the engine and the control device, because the variability of the test method is affected by modest changes in emissions levels such as are contemplated here. With 3 tests and an 8% test variability, the confidence interval on the mean reduction would be ± 16.4%. Obtaining the same mean from 6 tests, at the same variability, would give a confidence interval of ±6.9%, less than half the width of that with 3 tests.

Table 2. 95% confidence intervals on example mean emission reductions relative to baseline engine emissions at 1990 certification value.

Emission reduction, % of baseline engine emission	**5**	**20**	**20**	**20**	**50**	**85**
PM measurement variability for baseline engine, % of baseline engine emission	2	2	2	2	2	2
PM measurement variability for controlled engine, % of baseline engine emission	2	2	4	8	3	10
Number of replicate verification tests	**95% confidence intervals on emission reduction, % of baseline engine emission**					
3	5±6.7	20±5.6	20±8.9	20±16.4	50±4.5	85±3.8
6	5±2.8	20±2.4	20±3.8	20±6.9	50±1.9	85±1.6
9	5±2.1	20±1.7	20±2.8	20±5.1	50±1.4	85±1.2

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When planning a test, the ETV program will use the applicant's estimated emissions reduction, available test results, and experience with similar technologies to design an ETV that is capable of detecting the emission reduction expected and meeting the applicant's goals for confidence interval. However, the technology may not perform as expected. Section 8.0 addresses these circumstances.

5.2 General ETV Test Considerations

Unless specified otherwise, the general test considerations in this section will apply to all technologies covered by this protocol.

5.2.1 Submittal of Technologies and ETV Sequence

The ETV process begins with the applicant indicating to the APCTVC or to a test laboratory an interest in the ETV process. In either case, the second step is agreement between the APCTVC, the applicant, and the test laboratory regarding the general form of the ETV process and the responsibilities of all parties. This second step culminates with a formal application for ETV to the APCTVC, providing the information about the technology described in Section 4. The approximate cost of the ETV will be estimated and a contractual relationship between the APCTVC and the applicant will be started.

The test laboratory will then develop the ETV test/QA plan, reviewing it with the applicant and the APCTVC to ensure that it meets the requirements of the APCTVC, and, to the extent possible, accomplishes the applicant's goals for ETV. The test/QA plan will then be reviewed formally by the APCTVC and EPA. Test/QA plan development consists of a series of sequential activities, and the test/QA plan must be approved before testing begins.

The applicant will provide the technology to be tested. The applicant has the responsibility to arrange for provision of the engine on which the test will be conducted. Scheduling of the ETV test will be done by the test lab. De-greening of the technology is the applicant's responsibility, as is providing a de-greened unit and an aged unit for durability testing. The applicant must also provide any special ancillary equipment required for operation of the technology.

The applicant may choose to conduct private, proprietary test work at the test lab during the same time period the ETV is taking place. Such arrangements are between the test lab and the applicant. However, a clear differentiation is required between such private test work and the ETV test itself. In addition, the APCTVC must have adequate notice regarding an ETV test to be able to audit those tests if desired. The manner in which the start and end of the ETV test will be established and when the APCTVC will be notified must be specified in the test/QA plan. All ETV data must be reported.

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Following the ETV test, the test lab will report the data to the APCTVC, which will incorporate those data into the ETV report and statement. These documents will be reviewed with the test lab and the applicant to address comments and concerns as appropriate. The draft report will then be submitted to the multi-step EPA review and revised as needed. The ETV report and signed statement will be provided by the APCTVC to the applicant and EPA, and posted on the ETV and APCTVC websites.

5.2.2 Highway Engine ETV

Testing of technology intended to control emissions from highway diesel engines will be conducted generally under the provisions of 40 CFR Part 86 Subpart N. The primary emissions measurements will be of NOx, PM, HCs, CO, and other FTP specified emissions. CO_2 and other emissions and measurements described by this protocol are secondary measurements. Each ETV test will consist of the same number of tests on the baseline broken-in engine, the de-greened emission control technology, and the technology after aging. The number of tests will include a single cold- and hot-start highway transient FTP engine dynamometer test and may include additional hot-start tests in numbers determined using the test design procedure described above. The emissions reductions will be reported as the composite of the cold and mean of the hot starts, as required by the FTP, and as the mean and confidence interval on multiple hot-start tests. The smoke test is not required. The test parameters will be derived from the baseline engine mapping procedure. Emissions reductions will be computed relative to the baseline engine emissions using the same test cycle used during the baseline testing. As required by the FTP, tests that do not meet the FTP QA requirements must be repeated.

The test/QA plan for a specific technology will specify the engines that will be tested and any other aspects of the test that are specific to the technology or the test laboratory.

5.2.3 Highway Test Engines

The emissions characteristics of diesel engines of the same PM certification level are arguably similar because the engine technologies required to achieve those certification levels are likely to be similar. The emissions characteristics are also similar for engine families that have a breadth of technology similar to the tested engine. These similarities may provide an opportunity to group engines and reduce the ETV testing burden on applicants. As of the date of this protocol, EPA-OTAQ has proposed allowing the ETV test results from a single engine test to apply to multiple engines of different manufacturers. This is a decision that has been reserved by EPA-OTAQ, who should be consulted for details regarding the engines required to be tested as part of the ETV, the applicability of that ETV, and the magnitude of the associated emissions reduction credit under the VDRP.

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5.2.4 ETV Testing of Nonroad Engines - General

The basic ETV test for nonroad engines will consist of the nonroad steady-state mode tests as described in 40 CFR, Part 89, Subpart E. The primary emissions measurements will be of NO_x, PM, HC, CO and other FTP required measurements. CO_2 emissions and other measurements described by this protocol are required secondary measurements. Each ETV test will consist of one or more full steady-state multimode FTP test(s) on the baseline broken-in engine, the de-greened technology, and the technology after aging. The test condition will be derived from the baseline engine mapping procedure. The test may be conducted over all modes of the Part 89 test or over portions selected by the applicant. The emissions reductions will be reported as the composite mean and confidence interval of the multiple test modes, computed as stated in the FTP.

Composite emissions reductions are computed relative to the composite baseline engine emissions and will be reported in composite and mode-by-mode to allow flexibility in use of the data for different engine applications.

5.2.5 Nonroad Test Engines

Following an approach similar to that used for the highway engines, the results of ETVs conducted on individual nonroad engines may be applicable to broader groups of engines. Technology applicants may select the engines on which to test their technologies. Coordination with EPA-OTAQ is encouraged because the decision regarding acceptable engine grouping has been reserved by EPA-OTAQ, who should be consulted regarding the engines required to be tested as part of the ETV, the applicability of that ETV, and the magnitude of the associated emissions reduction credit under the VDRP.

5.2.6 De-greening

For many hardware technologies, a brief period of use (de-greening) is needed to achieve a stable emissions reduction that allows representative testing. For instance, the pressure drop across a continuously regenerating PM filter reaches an equilibrium value. The de-greening time period required varies for different technologies, but is on the order of 25 to 125 hours. In all cases, the technology applicant must propose and justify the extent of the de-greening process in the ETV application. The APCTVC office will review and comment on this proposal, advise regarding the documentation requirements, and append the de-greening process description to the technology test/QA plan. When complete, the actual process used must be documented. A description of the de-greening process will be included in the ETV report.

For purposes of this protocol, the de-greening time requirement will be specified by the technology applicant as indicated by either previous testing or the requirements of the data user. To allow flexibility for the applicant, de-greening is not required to be conducted at the test lab. It may be done and documented by the applicant or conducted by the test lab by arrangement with the applicant. In either case, the applicant will ensure that such de-

greening activity documentation as start and stop date and time, engine and fuel description, and operating conditions are available and signed by the person responsible for the activity.

De-greening may occur in a laboratory or during in-use field operations on an engine that is equivalent to the proposed ETV test engine, or another engine of the same size which utilizes the same engine technology (and thus falls within the range of the technology's stated applicability).

5.2.7 Regeneration

Emissions control devices whose normal operation includes a periodic regeneration will be tested over sufficient test cycles (described below) until a test cycle includes a "regeneration" event. The verified emissions rate and emissions reduction achieved will be computed as the time-weighted average of the emissions rate and reduction achieved over this complete operating cycle.

Technologies that are continuously regenerated in normal operation are not the subject of this paragraph. Continuous cleaning PM filters should reach a stable operating range (as evidenced by near constant pressure drop) before testing, which may be accomplished in the de-greening activity.

5.2.8 Device Scaling

The performance of most retrofit air pollution control technologies is affected by the relative sizes of the tested technologies and the engines. Therefore, the use of single engine ETV tests as predictive of performance over segments of the total engine population requires the availability of non-proprietary application sizing information and that the technology be labeled. Sizing information may be provided in sizing charts [e.g., model AA1 is suitable for 37 to 74 kW (50 to 100 hp) engines, model AA2 to 74 to 112 kW (100 to 150 hp) engines] or through the release of basic design information (e.g., space velocity, catalyst loading). The purpose of this requirement is to allow the APCTVC and the potential technology user (the public) to evaluate the applicability of the verified technology to other applications. Applicants who utilize application sizing charts must verify their technologies on an engine at the most challenging end of the range of applicability. ETV reports and statements will report the results and the design guidance required to independently extend application of the technology to other engines in the same engine grouping. Device scaling and engine selection decisions will be explained and documented in the test/QA plan to the extent possible and will be reported in the ETV report. The ETV report and statement will report the results and the design guidance required to independently extend application of the technology to other engines in the same engine grouping.

5.2.9 Durability

The emissions reductions measured for the de-greened air pollution control device will not account for changes in product performance that may occur as the device ages. For

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participation in the VDRP, additional testing of an "aged" control device is required by EPA-OTAQ. If done as part of the ETV program, the "aged" device test will meet the same data requirements as a new device test. This testing is followed by extrapolation of the "initial de-greened" and "aged" verified performance measurement to the end of the warranted life of the control technology using a method determined by EPA-OTAQ. The aging process details and the extrapolation of the data to an "end of life point" are not part of this protocol. Provided for information only, the description below is current as of December, 2001 and may change. The details should be confirmed prior to ETV.

1) Aging entails subjecting the control device to operating conditions that cause normal wear equivalent to at least 33% of the Minimum Durability Testing Period established in the California "verification" procedure for diesel retrofit systems (CARB, 2001). Table 3 provides the testing periods that were current as of the date of this protocol. The applicant should verify the testing period current at the date of ETV. The technology applicants must conduct the aging process on their technology. They have discretion to tailor this process to product requirements. Applicants may age an exhaust catalyst by using it during real-world operation, or through accelerated bench testing. It is expected that applicants will submit identical parts (one in a de-greened state, one aged to at least 33% expected full-life) so that testing with the baseline may occur sequentially. However, applicants may conduct the de-greened and aged technology tests as separate tests, in which case the baseline engine test must be repeated. All aging protocols must accompany the ETV application and explain the technical basis for stating the aging protocol results in at least 33% full-life aging. If real-world aging is performed, the application must describe and provide documentation of the usage and maintenance history of the aged unit as well as the engine with which it was aged.
2) Emissions testing using the aged device will be part of the ETV process and will follow the same procedures applied to the de-greened technology. First, baseline emissions testing shall be conducted, followed by testing with the de-greened device, and then finally testing the aged device with a re-test of the baseline engine if technically feasible. An applicant may elect to age a unit to its full useful life prior to testing and request ETV on that basis.

3) The full useful-life reduction capabilities will be estimated by EPA-OTAQ following procedures they will provide to applicants.

5.2.10 Standard Diesel Test Fuel

The standard diesel test fuel for highway engines should meet the EPA specifications outlined in 40 CFR Part 86.1313-98 with the exception of the sulfur content. For nonroad engines, the test fuel

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Table 3. Minimum durability testing periods (CARB, 2001)

Engine Type	Engine Size	Minimum Durability Testing Period	
Highway	Light heavy-duty, generally 70 to 170 hp, GVWR[a] normally less than 19,500 lb.	5 yr or 60,000 miles (or equivalent time in hours)	
	Medium heavy-duty, generally 170 to 250 hp, GVWR[a] normally from 19,500 to 33,000 lb.	5 yr or 100,000 miles (or equivalent time in hours)	
	Heavy heavy-duty, generally exceeds 250 hp, GVWR[a] normally exceeds 33,000 lb.	5 yr or 150,000 miles (or equivalent time in hours)	
Nonroad and Stationary	Under 25 hp and for constant speed engines rated under 50 hp with rated speeds greater than or equal to 3,000 rpm	3 yr	1,600 hr operation
	At or above 25 hp and under 50 hp	4 yr	2,600 hr operation
	At or above 50 hp	5 yr	4,200 hr operation

[a]GVWR = Gross Vehicle Weight Rating

should be that described in 40 CFR Part 89.330 or another fuel as specified by the control technology applicant. Because the performance and durability of many types of diesel retrofit technologies are affected by the sulfur content of the diesel fuel, applicants should specify the maximum sulfur level of the fuel for which their technologies are designed. The sulfur content of the ETV test fuel should be no less than 66% of the stated maximum sulfur content. (Because refinery and blending operations are such that very low sulfur content control is difficult, test fuel with a sulfur content of 15 ppm or below is not constrained to the "66% rule". The actual sulfur content of the test fuel batch is to be reported.) Other test fuels should meet the applicable EPA specifications outlined in 40CFR Part 86.1313. Adding sulfur to the fuel by the test laboratories is permissible if necessary to achieve the required fuel sulfur content for either baseline or controlled engine tests.
During ETVs, baseline engines should be fueled with the standard fuels that are representative of nominal in-use fuels and controlled engines with low sulfur versions of the standard fuels that are representative of the applicant's recommended or required fuel.

5.2.11 Engine Performance and Power

Engine performance and power will be measured and reported for both the baseline engine (without the control device installed) and the engine with the control technology. Engine performance measurements will be made with the engine operating at maximum power (rated conditions) and at peak torque as defined in the applicable FTP.

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5.2.12 Fuel Consumption

Fuel consumption will be measured for both the baseline engine (without the control device installed) and the engine with the control device installed to determine the effect of the technology on fuel consumption. The engine fuel consumption measurements will be made at maximum power at rated conditions and at peak torque at intermediate speed. Multiple tests, if available, will be averaged. The results will be reported as a fractional increase or decrease relative to the baseline engine. Also reported will be fuel economy and brake specific fuel consumption from testing by the applicable FTP.

5.2.13 Back-pressure

Within the test cell, baseline engine back-pressure will be set to the value required by the applicable FTP (highway or nonroad). Once installed for the ETV test, the back-pressure of the retrofit control technology may be greater than the FTP requirement. If so, the ETV test will be conducted without adding additional back-pressure; if not, the test cell will be adjusted to meet the FTP requirements. Because back-pressure of a retrofit control technology may affect the performance of an engine, the ETV test will measure and report back-pressure with the control device at full-load and rated speed. Back-pressure will be measured and reported for both the baseline engine (as set for the FTP test without the technology installed) and the engine with the de-greened or aged control technology installed.

5.2.14 Control Technology Operating Temperature

Inlet (engine exhaust) and discharge temperatures must be measured for technologies that are either dependent on specific operating temperature ranges or affected by engine or exhaust temperatures.

5.2.15 Other Measurements and Conditions

ETV of technologies that may produce secondary pollutants or have other secondary effects must include measurement of those pollutants in the ETV test. CO_2 emissions, while not primary, must be measured using instrumentation and/or estimated from a carbon balance from the fuel usage. ETV must include the appropriate measurements for technologies that require other specific operating conditions or affect emissions over only a limited range of a particular pollutant. For example, because the long-term operation of DECs and PM filters is affected by the soluble organic fraction (SOF) of the PM, SOF must be measured during ETV testing for these and similar technologies. The details of these non-critical measurements and their QA goals will be part of the test/QA plan.

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5.3 ETV of DECs and PM Filters

5.3.1 Technology Description

For the purposes of this GVP, DECs are defined as devices made of active catalyst material (often containing precious metal) deposited on a support medium. The engine exhaust passes through the device, where the pollutants catalytically react and more environmentally acceptable reaction products are exhausted. PM filters mechanically trap PM emissions and subsequently oxidize them. Filters may also employ a catalyst for gaseous emissions control and to enhance the oxidation of the collected PM.

Physically, DECs and PM filters have the general appearance of a large muffler and are placed in the engine exhaust at approximately the same location. They are therefore well-suited to retrofit applications. No external liquid or gaseous reactants are required for them to function.

DECs have been reported to decrease HC and CO emissions by over 50%. They decrease PM emissions by about 20%. PM filters have been reported to decrease PM and HC emissions by 80% or more and to decrease CO at about the level achieved by exhaust catalysts. NOx emissions may be decreased slightly by exhaust catalysts.

Operational issues with DECs and PM filters are primarily achieving or maintaining adequate temperature within the device to complete the reactions and functioning satisfactorily with an accumulation of catalyst poisons and/or non-combustible lubricant ash residue. Lubricant ash and wear metals can largely be removed by infrequent “blowing” with compressed air. Guidance on technique and frequency of such cleaning should be provided in the ETV application.

5.3.2 Test Considerations Specific to DECs and PM Filters

The general considerations in Section 5.2 apply to DEC and PM filter ETV testing. ETVs of DECs and PM filters require measurement of the SOF content of the exhaust stream prior to entering the DEC. (The SOF may be measured for PM collected during the baseline engine test. The method to be used is the *Test Method for Soluble Organic Fraction (SOF) Extraction* [CARB, 1989] or a equivalent method recognized by EPA-OTAQ.) Both DECs and PM filters require measurements of inlet and outlet temperatures.

5.4 ETV of Engine Modifications

5.4.1 Technology Description for Engine Modifications

Engine modifications are defined as a change integral to an engine (e.g., component modifications or change or engine control system calibration change) that is proposed as an emissions reduction technology.

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5.4.2 Test Considerations Specific to Engine Modifications

The general considerations in Section 5.2 apply to engine modification ETV. Baseline engine performance will be measured prior to modification, followed by modification of the baseline engine in accordance with the application instructions, operation for a de-greening/stabilization period, and then measurement of the de-greened technology's performance. An aged engine modification technology's emissions performance will be evaluated as described in Section 5.2.9. However, there is no requirement to re-run the baseline engine which was modified. It cannot be shown that a modified engine can be returned to its original state to again serve as a baseline.

Engine modifications whose use is warranted by engine manufacturers will be taken to have no adverse impact on engine durability, and that endorsement will be noted in the verification report (VR) and verification statement (VS) along with the verified emissions reductions for the aged engine. The lack of any verified knowledge regarding the impact on engine durability of technologies not warranted by the engine manufacturer will similarly be noted.

6.0 REPORTING AND DOCUMENTATION

This section describes the procedures for reporting data in the VR and VS. The specifics of what data must be included and the format in which the data must be included are addressed in this section (e.g., QA/QC summary forms, raw data collected, photographs/slides/video tapes). The VR for each technology will include near it's beginning the VS. The VS is a short summary of the ETV results. An example draft is attached as Appendix A. The VR, including the VS, will be written by the APCTVC based on the test report submitted by the testing organization. The VR and VS will be reviewed by the APCTVC and the technology applicant before being submitted to EPA for review and approval as specified in the ETV QMP.

6.1 Reports

Based on the test report from the laboratory, the APCTVC will prepare the draft VR, which includes the following topics:

1) VS;
2) Introduction;
3) Description and identification of product tested;
4) Procedures and methods used in testing;
5) Statement of operating range over which the test was conducted;
6) Summary and discussion of results as required to:
    a) Support the VS,
    b) Explain and document necessary deviations from test plan, and
    c) Discuss QA issues;
7) Conclusions and recommendations;
8) References; and

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9) Appendices:
   a) QA/QC activities and results,
   b) Raw test data, and
   c) Equipment calibration results.

The VS will include the following:

10) Technology applicant's name and technology's descriptive information,
11) Summary of ETV test program,
12) Results of the ETV test,
13) Any limitations of the ETV results, and
14) Brief QA statement.

Review and approval of the draft ETV report and statement are as described in Section 3.0. A draft VS is attached to this protocol as Appendix A.

6.2 Data Reduction

Data from measurements made as part of the ETV test will be reported as emissions rates in g/kWh (g/bhp-hr) and as percentage emission reductions from the baseline engine. The confidence limits will be presented as well as the mean emissions reduction, as discussed in Section 5.1.2. When they would be helpful to the mobile sources community because of established usage, the appropriate English Engineering units will be supplied parenthetically.

7.0 DISSEMINATION OF ETV REPORTS AND STATEMENTS

After a retrofit control technology has been tested and the draft VR and VS received from the testing organization, the APCTVC will send a draft of both to the applicant for review prior to submission to EPA-ORD and release of the approved report to the public. This gives the applicant opportunity to review the results, test methodology, and report terminology while the drafts remain working documents and are not publically accessible. The applicant may submit comments and revisions on the draft statement and report to the APCTVC. The APCTVC will consider these comments and may suggest revisions of its own.

After incorporating appropriate revisions, the draft final VR and VS will be submitted to EPA-ORD for review and approval. A signed original VS and VR will be filed and retained by the APCTVC, and signed originals will also be provided to the applicant and to EPA. Three additional paper copies of the ETV report will be provided to the applicant. Further distribution of the ETV report, if desired, is at the applicant's discretion and responsibility. However, approved VSs and VRs will be posted on the ETV web site for public access without restriction. The VR report appendices will not be posted on the website, but will be publically available from the APCTVC.

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8.0 APPLICANT'S OPTIONS SHOULD A TECHNOLOGY PERFORM BELOW EXPECTATIONS

ETV is not a technology research and development program; technologies submitted for ETV are to be commercial-ready and with well-understood performance. Tests that meet the ETV data quality requirements (a valid FTP test) are considered valid and suitable for publishing. However, a technology may fail to meet the applicant's expectations. Based on limited testing, for instance, the applicant might expect an emission reduction of 30% ± 7% result. However, the actual ETV result from the more complex FTP test cycle might be 20% ± 15%. The APCTVC will use its experience to avoid this situation, but it is possible. In this case, the applicant may choose to schedule additional tests, may accept the result and complete the verification, or may request that a VS not be issued. However, ETV reports are always in the public domain. VRs will be written and will be available from EPA-ORD for review by the public regardless of a request not to issue a verification statement, and summaries of the results of ETV testing may be published by ETV and/or EPA-OTAQ.

Another example of a technology not meeting expectations would be an expected result of a mean of 10% reduction with a confidence interval of ± 5% reduction, but an actual ETV mean reduction of 5% with a confidence interval of ± 7% reduction. In this case, the data are insufficient for ETV to verify that the technology does anything at all. Additional tests must be scheduled and a statistically significant reduction obtained for a VS to be issued. Inability to detect a statistically significant emission reduction (equivalently, failure to have sufficient tests) will prevent completion of the ETV, and the results of the ETV will be reported publically stating that performance could not be distinguished from 0% reduction. An ETV statement will not be issued in these cases.

In either of these cases, the applicant may improve the product and resubmit it under a new model identification for ETV testing. ETV Statements for acceptable tests of the new product will be issued as they are processed by the APCTVC and EPA-ORD (except that the results for several identical tests performed in rapid succession will all be released at the same time).

9.0 LIMITATIONS ON TESTING AND REPORTING

To avoid having multiple ETV reports for the same product and to maintain the ETV testing as a cooperative effort with the applicant, the following restrictions apply to ETV testing under this protocol:

1) Applicants may submit only products they manufacture or whose distribution they control. Applicants may not submit for ETV testing control devices whose use is not in their control except with the agreement of the manufacturer or vendor.
2) For a given product (e.g., brand and model), APCTVC policy is that only one ETV report and statement will be issued for any single application.
3) Air pollution control technology frequently performs differently in different

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applications. Applicants may request additional tests of essentially identical technology if it is being applied to pollution sources that are clearly different from those for which ETVs have been obtained.

10.0 REQUIREMENTS FOR TEST/QA PLAN

10.1 Quality Management

All testing organizations participating in this ETV Program must meet the QA/QC requirements defined below and have an adequate quality system to manage the quality of work performed. Documentation and records management must be performed according to the *ETV Quality and Management Plan for the Pilot Period (1995-2000)* (ETV QMP, EPA, 1998a). Testing organizations must also perform assessments and allow audits by the APCTVC (headed by the APCT QA Officer) and EPA corresponding to those in Section 11.

All testing organizations participating in the Retrofit Air Pollution Control Technologies for Highway and Nonroad Use Diesel Engines Program must have an ISO 9000-accredited (ISO, 1994) or ANSI E4-compliant (ANSI, 1994) quality system and an EPA- or APCTVC-approved QMP.

10.2 Quality Assurance (QA)

All ETV testing will be done following an approved test/QA plan that meets *EPA Requirements for Quality Assurance Project Plans* (EPA, 2001a) and Part B, Section 2.2.2 of EPA's ETV QMP (EPA, 1998a). These documents establish the requirements for test/QA plans and the common guidance document, *Guidance for Quality Assurance Project Plans* (EPA, 1998b), provides guidance on how to meet these requirements. The APCT Quality Management Plan (RTI, 1998) implements this guidance for the APCTVC.

ETVs conducted under this generic protocol utilize test procedures described in the FTP (40 CFR Part 86 for highway engines and 40 CFR Part 89 for nonroad engines). The test/QA plan must describe, in adequate detail, how the FTP test methods are implemented by the testing organization. Replication of the FTP text is neither expected nor desired. The test/QA plan should reference the FTP in detail, by section and subsection, as appropriate for the topic under consideration. Any deviations from the FTP must be identified and explained. Internal standard operating procedures (SOPs) may be referenced provided they are available for audit review. (SOPs need not be incorporated into the test/QA plan except by reference. If considered proprietary to the test organization, they should be clearly marked.) When the FTP offers alternative test procedures or equipment, the test/QA plan must identify the alternative implemented. Similarly, if a range of operating parameters is allowed by the FTP, the specifics of the particular implementation must be provided. For a test organization with multiple test cells, these details may be tabulated and incorporated by attaching a table and identifying the test cell on the test report. Steps the testing organization will take to ensure acceptable data quality in the test results are also identified in the test/QA plan. As above, detailed reference to SOPs, the calibration portions of the FTP, or other

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available documents is encouraged. Any needed SOPs will be developed in accordance with *Guidance for Preparing Standard Operating Procedures (SOPs)* (EPA, 2001b.)

The testing organization must prepare a test/QA plan and submit it for approval by the APCTVC. The test/QA plan must be approved before the test organization can begin ETV testing.

A test/QA plan contains the elements listed below, the contents of which may be stand alone or include references to the FTP or other widely distributed and publically available sources. Legible hand-notated diagrams from the FTP are acceptable. If specific elements are not included, an explanation for not including them must be provided.

1) Title and approval sheet;
2) Table of contents, distribution list;
3) Test description and test objectives;
4) Identification of the critical measurements, data quality objectives (DQOs) and indicators, test schedule, and milestones;
5) Organization of test team and responsibilities of members of that team;
6) Documentation and records;
7) Test design;
8) Sampling procedures;
9) Sample handling and custody;
10) Analytical procedures;
11) Test-specific procedures for assessing data quality indicators;
12) Calibrations and frequency;
13) Data acquisition and data management procedures;
14) Internal systems and performance audits;
15) Corrective action procedures;
16) Assessment reports to EPA;
17) Data reduction, data review, data validation, and data reporting procedures;
18) Reporting of data quality indicators for critical measurements;
19) Limitations of the data; and
20) Any deviations from methods from this generic verification protocol.

The APCTVC will provide a test/QA plan template that illustrates it's expectations.

10.3 Additional Requirements to be Included in the Test/QA Plan

The test/QA plan must include or reference a diagram and description of the extractive gaseous measurement system to be used for the testing and a list of the reference analyzers and measurement ranges to be used for quantifying the concentrations of all gaseous compounds to be measured, including both primary and ancillary pollutants.

The test/QA plan must include or reference a schematic drawing showing all sample and test locations, including the inlet and outlet to the technology sampling locations. The location of

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flow disturbances and the upstream and downstream distances from the sampling ports to those flow disturbances must be noted. The number of traverse points that will be sampled must be provided.

The test/QA plan must include or reference the appropriately detailed descriptions of all measuring devices that will be used during the test.

The test/QA plan must explain or reference the specific techniques to be used for monitoring process conditions appropriately for the source being tested. It must also note the techniques that will be used to estimate any other operational parameters.

The test/QA plan must include and document estimates of historical measurement variability that will be used, as discussed in Section 5.1.1, to compute the number of tests required and provide confidence intervals on single test ETVs.

11.0 ASSESSMENT AND RESPONSE

Each independent test laboratory must conduct internal assessments of its quality and technical systems and must allow external assessments of these systems by the APCTVC QA personnel and by EPA QA personnel. After an assessment, the test laboratory will be responsible for developing and implementing corrective actions in response to the assessment's findings.

As appropriate, the APCTVC and/or EPA will conduct assessments to determine the testing organization's compliance with its test/QA plan. The requirement to conduct assessments is specified in EPA's *Quality and Management Plan for the Pilot Period (1995 - 2000)* (EPA, 1998a), and in RTI's QMP (RTI, 1998). EPA will assess RTI's compliance with RTI's test/QA plans. RTI will assess the compliance of other organizations with their test/QA plans. The assessments will be conducted according to *Guidance on Technical Audits and Related Assessments for Environmental Data Operations* (EPA, 2000) and *Guidance on Assessing Quality Systems* (EPA, 2001.)

11.1 Assessment Types

Quality system assessment - Qualitative assessment of a particular quality system to establish whether the prevailing quality management structure, policies, practices, and procedures meet EPA requirements and are adequate for ensuring that the type and quality of measurements needed are obtained.

Technical systems audit - Qualitative on-site audit of the physical setup of the test. The auditors determine the compliance of testing personnel with the test/QA plan.

Performance evaluation audit - Quantitative audit in which measurement data are independently obtained and compared with routinely obtained data to evaluate the accuracy (bias and precision) of a measurement system.

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Audit of data quality - Qualitative and quantitative audit in which data and data handling are reviewed and data quality and data usability are assessed.

Surveillance audit - Observation of ongoing work to document conformance with specified requirements and/or procedures, such as those given in a test/QA plan or SOP.

11.2 Assessment Frequency

Activities performed during ETV performance operations that affect the quality of the data shall be assessed regularly and the findings reported to management to ensure that the requirements stated in the generic verification protocols and the test/QA plans are being implemented as prescribed.

The types and minimum frequency of assessments for the ETV Program are listed in Part A Section 9.0 of EPA's *Quality and Management Plan for the Pilot Period (1995 - 2000).* Tests conducted by the APCTVC will have at a minimum the following types and numbers of assessments:

1) Technical systems audits and surveillance audits: Self-assessments (qualitative) by test laboratory as provided for in the test/QA plans and at least one independent assessment of the test laboratory.
2) Performance evaluation audits: Self-assessments (quantitative) by test laboratory as provided for in the test/QA plans and at least one independent assessment of the test laboratory.
3) Audits of data quality: Self-assessments (quantitative and qualitative) by the test laboratory of at least 10% of all the ETV data with detailed reports of the audit results to be included in the data packages sent to the APCTVC for review.
4) Assessements of quality systems: Self-assessments by the test laboratory as provided for in the test/QA plans and at least one independent assessment of the test laboratory.

The independent assessments of tests conducted by RTI will be performed by EPA. The independent assessments of other organizations will be by RTI.

11.3 Response to Assessment

When needed, appropriate corrective actions shall be taken and their adequacy verified and documented in response to the findings of the assessments. Data found to have been taken from non-conforming technology shall be evaluated to determine its impact on the quality of the required data. The impact and the action taken shall be documented. Assessments are conducted according to procedures contained in the APCT QMP. Findings are provided in audit reports. Responses by the test laboratory to adverse findings are required within 10 working days of receiving the audit report. Follow up by the auditors and documentation of responses are required.

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12.0 SAFETY MEASURES

12.1 Safety Responsibilities

The test laboratory's project leader is responsible for ensuring compliance with all applicable occupational health and safety requirements. Each individual staff member is expected to follow the requirements and identify personnel who deviate from them and report such action to their supervisor.

12.2 Safety Program

The test company must maintain a comprehensive safety program and ensure that all test personnel are familiar with and follow it.

13.0 REFERENCES

ASQC. *AMERICAN NATIONAL STANDARD Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Programs*. ANSI/ASQC E4-1994. American Society for Quality Control. Milwaukee, WI. 1994.

CARB. *Proposed Regulation Order (DRAFT) Verification Procedure for Diesel Retrofit Systems*. http://www.arb.ca.gov/msprog/mailouts/msc0114/msc0114att1.pdf, California Air Resources Board, El Monte, CA. August, 2001.

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EPA. *Environmental Technology Verification Program, Quality and Management Plan for the Pilot Period (1995-2000).* EPA 600/R-98/064. http://www.epa.gov/etv/qmp.htm, National Risk Management Research Laboratory - National Exposure Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency. Cincinnati, OH. May 1998a.

EPA. *EPA Guidance for Quality Assurance Project Plans. EPA QA/G-5*, EPA/600/R-98/018, http://es.epa.gov/quality/qs-docs/g5-final.pdf, Office of Research and Development, U. S. Environmental Protection Agency. Washington, DC. February 1998b.

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EPA. *Guidance on Technical Audits and Related Assessments for Environmental Data Operations, EPA QA/G-7*, EPA/600/R-99/080, http://www.epa.gov/quality/qs-docs/g7-final.pdf, Office of Environmental Information, U.S. Environmental Protection Agency. Washington, DC. January 2000.

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EPA. *Guidance for the Preparing Standard Operating Procedures (SOPs). EPA QA/G-6*. EPA 240/B-01/004. http://www.epa.gov/quality/qs-docs/g6-final.pdf, Office of Environmental Information, U.S. Environmental Protection Agency. Washington DC. March, 2001.

EPA. Guidance on Assessing Quality Systems (Quality Staff Draft). EPA QA/G-3. Office of Environmental Information, U.S. Environmental Protection Agency. Washington, DC. August, 2001.

ISO. *ISO 9001-1994, Quality Systems Model for Quality Assurance in Design, Development, Production, Installation, and Servicing*. International Organization for Standardization. Geneva, Switzerland. In USA, American National Standards Institute, New York, NY. 1994.

RTI. *Verification Testing of Air Pollution Control Technology - Quality Management Plan*. Air Pollution Control Technology Program. J. R. Farmer, Program Director, Research Triangle Institute, Research Triangle Park, NC. 1998.

U.S. Government. Protection of Environment. Title 40, Part 86, Code of Federal Regulations, as of July 1, 1999. Federal Register. Washington, DC. 1999.

U.S. Government. Protection of Environment. Title 40, Part 89, Code of Federal Regulations, as of July 1, 1999. Federal Register. Washington, DC. 1999.

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APPENDIX A: EXAMPLE VERIFICATION STATEMENT

Appendix A is an example verification statement written for a generic PM filter control technology. The technology is assumed to be directed at a highway use engine. It is assumed to be an efficient control device, requiring only a single test by the minimum-number-of-tests calculation. The PM values in Table A-2 are taken from the 85% reduction column of Table 3, while the other values are completely hypothetical.

This generic verification statement is intended only to show the form of a verification statement. It will require modification for each technology verified, depending on the details of that technology's design, construction, and operation. The test/QA plan written for each test will include a draft verification statement customized for the technology actually being tested. The text of that specific verification statement will address the significant parameters that apply to the technology tested.

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THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

U.S. Environmental Protection Agency

ETV Joint Verification Statement

TECHNOLOGY TYPE:	**MOBILE DIESEL ENGINE AIR POLLUTION CONTROL**
APPLICATION:	**CONTROL OF EMISSIONS FROM MOBILE DIESEL ENGINES IN (*HIGHWAY*) (*NONROAD*) USE BY (*TECHNOLOGY TYPE*)**
TECHNOLOGY NAME:	**TECHNOLOGY NAME**
COMPANY:	**COMPANY NAME**
ADDRESS:	**ADDRESS** **PHONE: (000) 000-0000**
	CITY, STATE ZIP **FAX: (000) 000-0000**
WEB SITE:	**http://www.company.com**
E-MAIL:	**some.one@company.com**

The U.S. Environmental Protection Agency (EPA) has created the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative or improved environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high quality, peer reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized standards and testing organizations; stakeholder groups which consist of buyers, vendor organizations, permitters, and other interested parties; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The Air Pollution Control Technology Verification Center (APCTVC), one of six centers under the ETV Program, is operated by the RTI, in cooperation with EPA's National Risk Management Research Laboratory. The APCTVC has evaluated the performance of a *TYPE* emission control technology for mobile diesel engines, the *TECHNOLOGY* by *COMPANY NAME*.

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ETV TEST DESCRIPTION

All tests were performed in accordance with the APCTVC *Generic Verification Protocol for Diesel Exhaust Catalysts, PM Filters, and Engine Modification Technologies for Highway and Nonroad Use Diesel Engines* and the specific technology test plan "ETV Test/QA Plan for *TECHNOLOGY NAME*" These documents include requirements for quality management, quality assurance, procedures for product selection, auditing of the test laboratories, and test reporting format.

The mobile diesel engine air pollution control technology was tested at *TEST LABORATORY*. The performance verified was the percentage emission reduction achieved by the technology for particulate matter (PM), nitrogen oxides (NO_x), hydrocarbons (HCs), and carbon monoxide (CO) relative to the performance of the same baseline engine without the technology in place. Operating conditions were documented and ancillary performance measurements were also made. The basic modules of the test procedure are found in the federal test procedures (FTPs) for highway engines (40CFR, Part 86, Subpart N) and nonroad engines (40CFR, Part 89, Subpart E). For highway use, a single full FTP test was conducted, augmented by additional hot start transient tests as needed to meet the requirements of the generic verification protocol (GVP). For nonroad use, one or more multimode tests were conducted as described in the GVP. A summary description of the ETV test is provided in Table A-1.

Table A-1. Summary of the conditions for ETV test of *TECHNOLOGY NAME* on ENGINE DESCRIPTION.

Test Conducted	Highway Transient FTP
Engine Family	*ENGINE MFGR NAME* Series *XXXYYY*, ??? operating hours prior to test
Engine Size	YYY kW (XXX hp)
Technology	ACME Mark II PM Trap, Model AA1 for diesel engines up to 150 hp on standard fuel
Technology description	Honeycomb PM filter packaged in an muffler-sized can for retrofit installation by a moderately skilled mechanic. No engine modifications required.
Test cycle or mode description	1 full FTP test (1 cold start and 1 hot start)
Test fuel description	EPA standard diesel per 40 CFR Part 86.1313-98
Critical measurements	PM, NOx, HCs, and CO per the FTP
Ancillary measurements	CO_2, backpressure at engine exhaust port, exhaust temperature, fuel consumption, regeneration requirements

VERIFIED TECHNOLOGY DESCRIPTION

This verification statement is applicable to the *TECHNOLOGY NAME* (to include model number and other identifying information as needed), which is an cordierite-based PM filter manufactured by *MANUFACTURER NAME*. *TECHNOLOGY NAME* is packaged and marketed for particular engine families (for example, Model AA1 is properly sized for the A1A1 engine) or as a unit suitable for use on engines below a particular diesel power rating. The unit whose performance was verified was the Model AA1, which is rated for engines up to YYY kW (XXX hp) fueled by standard diesel fuel.

This verification statement describes the performance of *TECHNOLOGY NAME* on the diesel engine

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identified in Table A-1. The retrofit device, *TECHNOLOGY NAME*, is expected to provide similar emissions control performance on other engines having similar exhaust stream characteristics (similar fuel and engine technology) when properly sized for the application.

VERIFICATION OF PERFORMANCE

TECHNOLOGY NAME achieved the emissions reduction shown in Table A-2 at the stated conditions. The number of required ETV tests was estimated to be one complete FTP test, and this

Table A-2. Verified emissions reductions for hypothetical *TECHNOLOGY NAME*

Test Engine: **Manufacturer name Model No. AA1**	**Degreened (XX hours) Technology Test**			**Aged (XXXX hours) Technology Test**		
	Baseline Engine	Controlled Engine	Emissions Reduction %[a]	Baseline Engine	Controlled Engine	Emissions Reduction %[a]
Critical Measurements of Emissions						
Hot Start PM, g/bkWh (g/bhp-hr)	0.804 (0.600)	0.012 (0.090)	85±3	0.790 (0.590)	0.012 (0.091)	84.6±3
Composited PM, g/bkWh (g/bhp-hr)						
Hot Start NO_x, g/bkWh (g/bhp-hr)						
Composited NO_x, g/bkWh (g/bhp-hr)						
Composited HC, g/bkWh (g/bhp-hr)						
Composited CO, g/bkWh (g/bhp-hr)						
Ancillary Measurements						
Engine Power, kW (hp)						
Peak Torque, N-m (lb_f-ft)						
Composited CO_2, g/bkWh (g/bhp-hr)						
PM SOF, g/bkWh (g/bhp-hr)						
Exhaust Flow, L/min (ft^3/min)						
Exhaust Temperature, °C (°F)						
Backpressure, kPa (in. Hg)						
Fuel Usage, % reduction						
Technology In/Out Temp., °C (°F)						
Regeneration	brief description					
Maintenance Schedule	brief description					
Comments						

[a] units of rows as indicated except shaded columns in %

estimate was confirmed by the ETV test results. Table A-2 may include ETV results for both the initial operation (degreened) and for the technology following the stated period of aging. For the

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purposes of determining the status of the technology in regard to EPA's voluntary retrofit program, the prospective user is encouraged to contact EPA-Office of Transportation and Air Quality (OTAQ) or visit the retrofit program web site at http://www.epa.gov/otaq/retrofit/.

The APCT QA Officer has reviewed the test results and quality control data and has concluded that the data quality objectives given in the generic verification protocol and test/QA plan have been attained.

During the ETV tests, EPA or APCTVC quality assurance staff conducted technical assessments at the test laboratory. These confirm that the ETV tests were conducted in accordance with the test laboratory's EPA-approved test/QA plan.

This verification statement verifies the emissions characteristics of *TECHNOLOGY NAME* within the stated range of application. Extrapolation outside that range should be done with caution and an understanding of the scientific principles that control the performance of *TECHNOLOGY NAME*. This verification focused on emissions. Potential technology users may obtain other types of performance information from the manufacturer.

In accordance with the generic verification protocol, this verification statement is valid commencing on *DATE* indefinitely for application of *TECHNOLOGY NAME* within the range of applicability of the statement.

E. Timothy Oppelt Date
Director
National Risk Management Research Laboratory
Office of Research and Development
United States Environmental Protection Agency

Jack R. Farmer Date
Program Director
Air Pollution Control Technology Verification Center
RTI

NOTICE: ETV verifications are based on an evaluation of technology performance under specific, predetermined criteria and the appropriate quality assurance procedures. EPA and RTI make no expressed or implied warranties as to the performance of the technology and do not certify that a technology will always operate as verified. The end user is solely responsible for complying with any and all applicable federal, state, and local requirements. Mention of commercial product names does not imply endorsement.

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APPENDIX B: EXAMPLE CALCULATION OF NUMBER OF TESTS REQUIRED

This appendix presents example calculations to illustrate calculation of the minimum number of tests for ETV.

The calculation is based on:

1) PM and NO_x hot-start FTP emissions measurement variability experience for a diesel emissions laboratory, which is a function of both the type of measurement and the emissions level. The emissions variability is taken to be known for the population of measurements. Therefore the normal distribution value is appropriately used in the calculations. Eq. B-1 is not strictly applicable for a set of measurements for which only sample standard deviations are available;
2) A known baseline mean emission; and
3) A mean controlled emission (the product of the baseline emission and the expected emissions reduction).

The criterion being used is that the minimum number of hot-start FTP tests required for ETV is the number of tests required to have a 90% probability of detecting the specified emission reduction at the 95% confidence level. The basic equation being used for the calculation is:

$$n \approx (z_\alpha + z_\beta)^2 [\sigma^2_1 + (1 - \delta/100)^2 \cdot \sigma^2_2] / \delta^2 \qquad \text{(B-1)}$$

where:

n	=	sample size in each group, rounded up to the next integer;
z_α	=	normal distribution value corresponding to upper-tail probability of α; and
z_β	=	normal distribution value corresponding to upper-tail probability of β.
$1-\alpha$	=	confidence coefficient on comparison of means (0.95 minimum for ETV);
$1-\beta$	=	probability of detection of reduction (0.90 minimum for ETV);
σ^2_1	=	squared standard deviation of baseline-engine emission data, expressed as a percent of the baseline emission value;
σ^2_2	=	squared standard deviation of controlled-engine emission data, expressed as a percent of the baseline emission value;
δ	=	difference between baseline and controlled engine emissions mean, expressed as a percent of the baseline emission value;

Note that σ_1, σ_2, and δ, are expressed as percentages of the baseline emission. This transformation was used to simplify the equation and allow its use for Table 1. For Table 1, the baseline emission value was chosen as the 1990 EPA certification value. The parameter 'z' is tabulated under different names in statistics reference texts. It is the 'z' value corresponding to 'the tail area of the unit normal distribution' in Box, Hunter, and Hunter (1978). In the Standard Mathematical Tables (CRC, 1968), 'z' is known as 'x', and the tail area is labeled '1 - F(x)', where F(x) is the cumulative distribution function of a standardized normal random variable. To obtain the value of 'z' from the statistical tables, α (or β) is the probability (ranging from 0.5000 to 0.0000) in the body of the table, and 'z' is read (or interpolated) from the appropriate column and/or row, ranging from 0.00 to 4.00 over that

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range. The value 'z' can be calculated within an EXCEL® or QUATTRO PRO® spreadsheet as the absolute value of the function returning the inverse of the standard normal cumulative distribution, NORMSINV(probability), by setting probability equal to α or β, as appropriate.

Table B-1 gives a step-by-step calculation example drawn from Table 1 for a 90% probability ($\beta = 0.10$) of detecting a 5% and a 50% emission reduction at the 95% confidence level ($\alpha = 0.05$).

Table B-1. Example calculation of minimum number of ETV tests.

	Table 1, Col.1	Table 1, Col. 3
Emission reduction relative to baseline (certification) emission, δ, %	5	50
Known measurement variability at specified emission reduction, σ_2, %	2	3
Known measurement variability for baseline engine, σ_1, %	2	2
α	0.05	0.05
z_α	1.645	1.645
β	0.10	0.10
z_β	1.282	1.282
$(\sigma^2_1 + (1 - \delta/100)^2 \cdot \sigma^2_2) / \delta^2$	0.304	0.0016
$(z_\alpha + z_\beta)^2 (\sigma^2_1 + (1 - \delta/100)^2 \cdot \sigma^2_2) / \delta^2$	2.61	0.014
Number of tests required[a], n	3	1[a]

Note: [a] The minimum number of ETV tests is three. If 'n' is less than three, 'n' equals three.

Substitution of the t-statistic for z in Equation B-1 implicitly violates some of the assumptions made in the derivation and is therefore not strictly valid. An iterative calculation results, and it may not converge. However, it does provide a number of tests estimate that is larger and closer to the result of the population statistics confidence interval described in Section 5.1.2.

References for Appendix B

CRC. Standard Mathematical Tables, 16th Ed. S. Shelby, Ed. The Chemical Rubber Company, Cleveland, OH. 1968.

Box, G. E. P., W. G. Hunter, and J. S. Hunter. *Statistics for Experimenters*. John Wiley & Sons, New York, NY. 1978.

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APPENDIX C: SENSITIVITY OF NUMBER OF TESTS CALCULATION TO MEASUREMENT VARIABILITY

Table C-1 presents the results of a sensitivity analysis of the calculation of the required number of tests in the particular cases of high (85%) and low (10% and 5%) reductions in emissions. The number of tests reported in the final column is the number required to have a 90% probability of detecting the emissions reduction with 95% confidence. The equation in Appendix B was used to compute the required number of tests. As in these sections, all calculations utilize the normal distribution under the assumption that the test measurement error is known and constant.

Within Table C-1, the variability of the baseline engine measurement ranges from 2 to 30%, and the controlled engine measurement variability from 10 to 30%. All of the percentage numbers in the table are referenced to a baseline engine emission. To convert the percentages to an absolute emission rate, they must be multiplied by a baseline engine emission rate, and at 30% variability the standard deviations are twice the emission rate in g/bhp-hr. The emissions and standard deviations in Table C-1 have all been calculated for a baseline engine emitting PM at the 1990 certification level of 0.6 g/bhp-hr. For example, from the first row, an 85% reduction means an absolute PM emission of 0.09 g/bhp-hr. A 10% controlled engine measurement variability means the standard deviation for that measurement is 0.06 g/bhp-hr. For the baseline engine, the variability is 2%, so the baseline engine standard deviation is 0.012 g/bhp-hr. The same approach can be used to make a similar table for any other emission rate by multiplying the percentages by the desired baseline emission rate.

While the number of required tests increases as the test variability increases, Table C-1 shows that the increase is modest at high emissions reduction levels. While higher variability is expected at higher levels of control because the absolute emissions concentrations are low, the large reduction in emissions is easily detected.

On the other hand, lower variability is expected for low emissions reductions, but the smaller changes are harder to detect and more tests are required. Therefore even modest variability levels (relative to those in the top block of Table C-1) lead to very large numbers of tests.

As was discussed in Section 5.1.2, calculation of the confidence intervals on the mean emissions reduction will be based on population statistics and will utilize the t-distribution. Thus the number of tests calculated using Equation B-1 (population statistics) may be fewer than will be required by the data itself based on sample statistics. As mentioned in Appendix B, an approximate calculation can be made for sample variability utilizing the Student's t-distribution rather than the normal (z-distribution) in Equation B-1. This use of Equation B-1 is not strictly valid, but may be useful for low emission reduction and/or high variability test designs to make a better estimate of the number of tests required.

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Table C-1. Sensitivity of number of tests to measurement variability

Expected emissions reduction, %	Controlled engine emissions, g/bhp-hr, relative to a baseline engine at the 1990 PM certification emission limit	Controlled engine variability, % of baseline engine	Controlled engine standard deviation, g/bhp-hr for baseline emission of 0.6 g/bhp-hr	Baseline engine variability, %, with the 1990 certification limit as baseline	Baseline engine standard deviation, g/bhp-hr, for1990 emission limit baseline emission of 0.6 g/bhp-hr	Number[a] of tests to achieve 90% probability of detecting reduction with 95% confidence
85	0.09	10	0.06	2	0.012	1
85	0.09	15	0.09	2	0.012	1
85	0.09	20	0.12	2	0.012	1
85	0.09	30	0.18	2	0.012	1
85	0.09	10	0.06	10	0.060	1
85	0.09	15	0.09	10	0.060	1
85	0.09	20	0.12	10	0.060	1
85	0.09	30	0.18	10	0.060	1
85	0.09	10	0.06	30	0.150	2
85	0.09	15	0.09	30	0.150	2
85	0.09	20	0.12	30	0.150	2
85	0.09	30	0.18	30	0.150	2
10	0.54	2	0.012	2	0.012	1
10	0.54	4	0.024	4	0.024	3
10	0.54	6	0.036	6	0.036	6
10	0.54	8	0.048	8	0.048	10
10	0.54	10	0.06	10	0.060	16
5	0.57	2	0.012	2	0.012	3
5	0.57	4	0.024	4	0.024	11
5	0.57	6	0.036	6	0.036	24
5	0.57	8	0.048	8	0.048	42
5	0.57	10	0.06	10	0.060	66

Note: [a] For ETV, the minimum number of tests is three.

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September 2003

Environmental Technology Verification Protocol

DETERMINATION OF EMISSIONS REDUCTIONS OBTAINED BY USE OF ALTERNATIVE OR REFORMULATED LIQUID FUELS, FUEL ADDITIVES, FUEL EMULSIONS, AND LUBRICANTS FOR HIGHWAY AND NONROAD USE DIESEL ENGINES AND LIGHT DUTY GASOLINE ENGINES AND VEHICLES

Prepared by:

RTI INTERNATIONAL

Under a Cooperative Agreement with

U. S. Environmental Protection Agency

ETV ETV ETV

Revision No.: 03
Date: September 2003

GENERIC VERIFICATION PROTOCOL FOR DETERMINATION OF EMISSIONS REDUCTIONS OBTAINED BY USE OF ALTERNATIVE OR REFORMULATED LIQUID FUELS, FUEL ADDITIVES, FUEL EMULSIONS, AND LUBRICANTS FOR HIGHWAY AND NONROAD USE DIESEL ENGINES AND LIGHT DUTY GASOLINE ENGINES AND VEHICLES

EPA Cooperative Agreement No. CR829434-01-1
RTI Project No. 08281-001-003

Prepared by:

RTI INTERNATIONAL

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ABBREVIATIONS AND ACRONYMS

APCT	air pollution control technology
APCTVC	Air Pollution Control Technology Verification Center
BSFC	brake-specific fuel consumption
CARB	California Air Resources Board
CBI	confidential business information
CFR	Code of Federal Regulations
CI	confidence interval
CO	carbon monoxide
CO_2	carbon dioxide
CTM	conditional test method
DEC	diesel exhaust catalyst
DQO	data quality objective
EGR	exhaust gas recirculation
EPA	Environmental Protection Agency
ETV	Environmental Technology Verification Program
FM	fuel modification
FTIR	Fourier transform infrared
FTP	federal test procedure
g/bhp-hr	grams per brake horsepower-hour
g/kWh	grams per kilowatt-hour
GVP	generic verification protocol
HAP	hazardous air pollutant
HC	hydrocarbon
HHD	heavy-heavy duty
hp	horsepower
LDV	light duty vehicle
LHD	light-heavy duty
MHD	medium-heavy duty
MIL	maintenance indicator light
NH_3	ammonia
NMHC	non-methane hydrocarbon
NO_X	nitrogen oxides
OBD	on-board detection
OEM	original equipment manufacturer
ORD	Office of Research and Development
OTAQ	Office of Transportation and Air Quality
PCV	positive crankcase ventilation
PM	particulate matter
ppm	parts per million
QA	quality assurance
QC	quality control
QMP	quality management plan
RFG	reformulated gasoline
RTI	Research Triangle Institute
SAC	stakeholders advisory committee
SCR	selective catalytic reduction

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SET	Supplemental Emissions Test (40 CFR 86.1360)
SOP	standard operating procedure
ULSD	ultralow sulfur diesel
VDRP	Voluntary Diesel Retrofit Program
VOC	volatile organic compound

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1.0 INTRODUCTION

This protocol describes the Environmental Technology Verification (ETV) Program's considerations and requirements for verification of emissions reduction provided by fuel and lubricant technologies. For purposes of this protocol, all such technologies will be identified as fuel modifications (FMs). The basis of the verification will be comparison of the emissions and performance of well-maintained, conventionally fueled (or lubricated) engines or vehicles to the same engines or vehicles with FMs. The protocol applies to diesel- and gasoline-fueled engines and light-duty vehicles in mobile source applications and describes the requirements for a single engine or vehicle ETV having narrow application and for a multiple engine or vehicle ETV to evaluate fleet-wide emissions reductions.

ETV provides verified emissions reduction data for FM technologies. It may be part of an overall process that leads to inclusion of FMs on the U.S. Environmental Protection Agency (EPA) mobile sources retrofit emissions reduction verified technology list. This protocol describes the ETV portions of that process in detail. Table 1 provides an overview of mobile source FM ETV and its interface with the EPA retrofit emissions reduction program.

Table 1. Overview of Mobile Source ETV Process and Participants' Responsibilities

Step in Process	Applicant	ETV		EPA-OTAQ[b]	EPA-ORD[c]
		APCTVC[a]	Testing Org.		
Preparation of preliminary application (without ETV data)	Primary	None	None	Advise	Access
Preliminary test dialog	Participate	Organize & participate	Participate	Participate	Access
Test/quality assurance (QA) plan	Review	Shared preparation, APCTVC approve		Review	Review & approve
Acceptance of ETV test/QA plan, and terms and payment	Primary	Advise	Advise	Access	Access
Conduct ETV test	Access	Audit	Primary	Access	Audit
Prepare test report	Access	Review	Primary	Access	Access
Publish ETV report & statement	Review	Primary	Review	Access	Review & approve

[a] APCTVC = Air Pollution Control Technology Verification Center at RTI.
[b] EPA-OTAQ = EPA's Office of Transportation and Air Quality.
[c] EPA-ORD = EPA's Office of Research and Development, the ETV sponsor.

1.1 Environmental Technology Verification

EPA through its Office of Research and Development (EPA-ORD) has instituted the ETV Program to verify the performance of innovative and improved technical solutions to problems that threaten human health or the environment. EPA created the ETV Program to accelerate the entrance of new and improved environmental technologies into the marketplace. It is a voluntary, nonregulatory program. Its goal is to verify the environmental performance characteristics of commercially ready technologies through the evaluation of objective and quality-assured data so that potential purchasers and permitters are provided with an independent and credible assessment of what they are buying and permitting.

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The ETV Program does not conduct technology research or development. ETV test results are always publicly available, and the applicants are strongly encouraged to ensure prior to beginning an ETV test that they are satisfied with the performance of their technologies. Within the ETV Program, this state of development is characterized as "commercially ready."

The provision of high-quality performance data on a commercial technology encourages more rapid implementation of that technology and consequent protection of the environment with better and less expensive approaches. The ETV Program is conducted by seven ETV centers that span the breadth of environmental technologies.

1.2 Air Pollution Control Technology Verification Center

EPA's partner in the Air Pollution Control Technology Verification Center (APCTVC) is RTI International,[1] a nonprofit contract research organization with headquarters in Research Triangle Park, NC. The APCTVC verifies the performance of commercially ready technologies used to control air pollutant emissions. The emphasis of the APCTVC is currently on technologies for controlling particulate matter (PM), volatile organic compounds (VOCs), nitrogen oxides (NO_X), and hazardous air pollutants (HAPs) from both mobile and stationary sources. The activities of the APCTVC are conducted with the assistance of stakeholders from various interested parties. Overall, APCTVC guidance is provided by the Stakeholders Advisory Committee (SAC), whereas the detailed development of individual technology ETV protocols is conducted with input from technical panels focused on each technology area.

The APCTVC develops generic verification protocols and specific test/quality assurance (QA) plans, conducts independent testing of technologies, and prepares ETV test reports and statements for broad dissemination. Testing costs are ultimately borne by the technology applicants, although initial tests within a given technology area may be partially supported with government funds.

1.3 The APCTVC Mobile Sources Verification Program

The various retrofit technologies have been divided into three groups to facilitate ETV:

- Retrofit diesel mobile source control devices,
- FMs, and
- Selective catalytic reduction (SCR) devices.

Retrofit mobile diesel control devices include exhaust treatment emission control devices, other retrofit devices, and engine modifications. Some require no mechanical changes to engines, whereas others will involve some modification of the engine or its control system. Filters for PM control and diesel exhaust catalysts (DECs) may make use of or require some integration with engines. Engine modifications, in this context, refer to pollution reduction technologies integral to the engine or the engine control systems. All these technologies have the potential to affect engine performance, and the concurrence of the engine manufacturer that the changes are compatible with safe, efficient, and reliable operation in the engine is an important element in demonstrating commercial readiness and suitability for ETV. ETV of these technologies is guided by *Generic Verification Protocol for Diesel Exhaust Catalysts, Particulate*

[1]RTI International is a trade name of Research Triangle Institute.

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Filters, and Engine Modification Control Technologies for Highway and Nonroad Use Engines (RTI, 2002).

SCR NO_X control technologies are also retrofit technologies, but they require more integration with the controlled engine than most other retrofit devices and therefore are being treated as a separate category (for which a separate verification protocol is being developed).

This generic verification protocol (GVP) provides the requirements for APCTVC's verification of the performance of FMs applied to mobile source diesel and gasoline engines. Other organizations (e.g., EPA's Office of Transportation and Air Quality [EPA-OTAQ] and the California Air Resources Board) also verify the performance of FMs under different protocols to meet the needs of those organizations. The technology applicant should discuss the intended application of the FM with EPA-OTAQ to determine the most suitable path for verification.

This GVP is intended to apply only to FMs. The APCTVC reserves the right to evaluate each technology submitted for verification and to determine the applicability of this protocol to that specific technology. Regulatory authorities (EPA-OTAQ and others) may also have requirements. Special testing may be required in some cases to maintain the integrity and credibility and, therefore, the value of verifications. The critical data quality objectives (DQOs) in this document were chosen to provide emissions measurements sufficient to support the vendor's application for emissions credits under the Voluntary Diesel Retrofit Program (VDRP).

This protocol was developed and has been reviewed by a technical panel composed of a broad group of stakeholders who have expertise in mobile source controls and come from the vendor, user, and regulatory spheres. Technical panel membership is dynamic, and its composition is expected to change over time as technical emphases change. The APCTVC will maintain membership balance on the panel.

The basic FM verification will measure and report baseline emissions concentrations and rates using the Federal Test Procedures (FTPs) applicable to a particular engine or vehicle on a baseline fuel compared to that same engine or vehicle using the FM. The test requirements will differ depending on whether the FM provides its full emissions reduction immediately (immediate-effect FM) or requires operation for some period of time to reach full effect (cumulative-effect FM). The engines or vehicles required to be tested will depend on the intended use and applicability of the FM. The tests will be conducted at an independent, third-party testing organization that has been qualified and audited by the APCTVC. The data quality requirements of this GVP will be applied at approved testing organizations through the preparation of an FM-specific test/QA plan. Other laboratory-, application-, or technology-specific information may also need to be addressed in the test/QA plan, which is described in Section 10.0. Because specific technology areas may require special expertise or emphasis, input and review will be obtained from an ad hoc subcommittee of the technical panel and/or outside experts when deemed appropriate by the APCTVC. Test results will be presented as ETV reports and statements.

This generic protocol will be revised as necessary. Changes to the protocol will not affect products that have been verified. However, such changes will be reflected in test/QA plans not yet finalized regardless of the applicant's application status. Test/QA plans that are being carried out when a protocol change is enacted will be examined to determine whether any modifications must be made.

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1.4 Quality Management

Management and testing in the APCTVC program are performed in accordance with procedures and protocols defined by the following:

- EPA's ETV Quality and Management Plan (QMP) (U.S. EPA, 2002a or the QMP current at time of testing);
- APCTVC Quality Management Plan (RTI, 1998);
- *Generic Verification Protocol for Determination of Emissions Reductions Obtained by Use of Alternative or Reformulated Liquid Fuels, Fuel Additives, Fuel Emulsions, Lubricants, and Lubricant Additives for Highway and Nonroad Use Diesel Engines and Light Duty Gasoline Engines and Vehicles* (this document); and
- Test/QA plan prepared for each FM test or group of tests.

EPA's ETV QMP lays out the definitions, procedures, processes, interorganizational relationships, and outputs that will ensure the quality of both the data and the programmatic elements of the ETV Program. Part A of the ETV QMP contains the specifications and guidelines that are applicable to common or routine quality management functions and activities necessary to support the ETV Program. Part B of the ETV QMP contains the specifications and guidelines that apply to test-specific environmental activities involving the generation, collection, analysis, evaluation, and reporting of test data.

The APCTVC QMP describes the quality systems in place for the overall APCTVC. It was prepared by RTI and approved by EPA. Among other quality management items, it defines what must be covered in the GVPs and test/QA plans for technologies undergoing ETV testing.

Generic Verification Protocols are prepared to describe the general procedures to be used for testing a type of technology and to define the critical DQOs. The GVPs for retrofit air pollution control technologies for highway and nonroad use engines were written by the APCTVC with input from a technical panel and approved by EPA.

A test/QA plan is prepared for each test or group of tests. The test/QA plan describes, in detail, how the testing organization will implement and meet the requirements of the GVP. The test/QA plan also sets DQOs for any planned measurements that were not set in the GVP for a particular technology. The test/QA plan addresses issues such as the testing organization's management structure, the test schedule, test procedures and documentation, analytical methods, recordkeeping requirements, and instrument calibration and traceability, and it specifies the QA and quality control (QC) requirements for obtaining ETV data of sufficient quantity and quality to satisfy the DQOs of the GVP. Testing organizations will be audited by the APCTVC against the approved GVP and test/QA plan they are expected to follow. Section 10 of this GVP addresses requirements for the test/QA plan.

Because multiple testing organizations may be conducting the tests, the APCTVC will develop a prototype test/QA plan (not part of this GVP) for each type of technology to ensure comparability. This prototype will be customized by the testing organization to meet its specific implementation of the FTPs as defined in 40 Code of Federal Regulations (CFR) Parts 86 and 89, and the secondary measurements, subject to approval by the APCTVC and EPA-ORD. Testing arrangements that do not meet the requirements of the FTP will not be approved, and test instrumentation or test procedures that the APCTVC determines will compromise data reliability or comparability between testing organizations will not be approved.

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2.0 OBJECTIVE AND SCOPE

2.1 Objective

The objective of this GVP is to establish the parameters within which FMs to diesel or gasoline engines will be tested to verify their emissions control performance with uniform and consistent methods.

2.2 Scope

This protocol describes the considerations and requirements for ETV of emissions reduction by FMs. The FMs to which it applies are

- Alternative diesel and gasoline fuels,
- Reformulated diesel and gasoline fuels,
- Additives to standard diesel and gasoline fuels,
- Alternative lubricants for diesel- and gasoline-fueled engines, and
- Lubricant additives and systems for diesel- and gasoline-fueled engines.

Although FMs may achieve similar emissions reductions on many engines, each ETV test is conducted on and reported for the actual test conditions: engine (vehicle), base fuel, and FM test conditions. The base engine (vehicle) will be well maintained and will produce emissions at levels consistent with a well-maintained engine (vehicle) of its age and use. FMs may be combined with other technologies for verification testing as a single entity emissions control system. Before systems can be accepted for verification,

- the controlling interests in each technology must be in agreement to pursue ETV (in this context, low sulfur diesel fuels are considered commodities available to all, not technologies, and therefore no permission is required),
- the applicant must be a single organization with authority to pay for the applicant's cost, and
- the applicant must show that each component of the system has a credible impact on emissions.

Verification testing for a system will incorporate into the test/QA plan elements from the protocols applicable to the individual technologies. In general, the test for a system will include the more stringent aspects of each protocol where they differ. Each test may be different, and the APCTVC should be consulted for assistance.

For purposes of ETV, the emission reduction effects of FMs are classified as either of two types:

1. Immediate effect—FMs whose emissions reduction effect is immediate for a well-maintained, base-fueled engine. No long-term residual effect is expected from an immediate-effect FM. The applicant agrees and the test confirms that reproducible results can be obtained for both the base and FM fuels on the same engine with an alternating fuel test pattern, allowing only for fuel flushing and a brief stabilization period (as many as three preconditioning cycles [EPA Urban Dynamometer Driving Schedule 40 CFR 86.132-90] for a light duty vehicle (LDV) and 1 hour of engine operation for a diesel) between tests.
2. Cumulative effect—FMs that require more than 10 hours of engine operation for a diesel or 500 miles of driving for a LDV on the FM for the product to reach its full effectiveness. Cumulative-effect FMs are expected to have residual effects on the test engine, and repeated base-fueled tests

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separated by FM tests would not be meaningful. Return to base fuel emissions rates is expected only after an extended period of operation or manual cleaning and rebuild.

FMs may be evaluated based on either of these categories. The applicant's requests and the product's performance mechanism will be considered. For example, an applicant may have a fuel additive that reaches its full potential only after an extended period of time, but the applicant may prefer to evaluate the additive with the immediate-effect procedure. The applicant must recognize and accept the implied liability for selecting the appropriate test program.

Emissions testing under this protocol is based on the FTPs for emissions certification of diesel highway engines (40 CFR Part 86), diesel nonroad engines (40 CFR Part 89), and light duty gasoline engines (40 CFR Part 86). For diesel nonroad engines, emissions testing under this protocol will also include the nonroad transient test cycle as published in the NPRM (Notice of Proposed Rulemaking) for "Control Emissions of Air Pollution from Nonroad Diesel Engines and Fuel" on May 23, 2003. (New test procedures become standardized and are incorporated into the FTPs from time to time. Verifications are to be conducted under the current applicable FTP.)

2.3 Applicability

2.3.1 Applicability of ETV Results to Other Engines and Engine Families

The basic ETV test remains the same for all FMs and engines; however, the FMs may interact differently with the various engines. The extension of emissions reductions from one engine or engine family to another requires engineering analysis of the data and may require additional testing. Determination of the applicability of single-engine tests to other engines is an EPA-OTAQ decision and not part of ETV.

2.3.2 Relationship of ETV Program to EPA-OTAQ VDRP Verified Technology List

EPA-OTAQ is charged with establishing a verified list of technologies capable of providing emissions reductions. The test results EPA-OTAQ will use to evaluate a technology may be generated following the ETV process, with the ETV report and verification statement submitted by the vendor as the data package to EPA-OTAQ. Other paths to the verified technology list also exist. The VDRP program is described and appropriate contacts are identified at http://www.epa.gov/otaq/retrofit/. The technology applicant should discuss the intended application of the technology with EPA-OTAQ to determine the most suitable evaluation path for the applicant's technology.

2.3.3 Assignment of Emissions Benefits to FMs

The emissions from engines vary as engines age and progress through the cycle of routine maintenance. The intent of ETV under this GVP is to determine the emissions reductions provided by FMs, exclusive of oil and filter changes, engine tune-ups, and similar scheduled maintenance that, by themselves, may provide emissions benefits. Emissions benefits may also accrue from tuning an engine to lower power output or other operating points different from those recommended by the engine manufacturer. The ETV test will be designed to isolate the effects of the FMs from coincident engine adjustments and tune-ups to the extent possible. Baseline engines will be tuned and set to the engine manufacturer's recommendations, and the baseline emissions are expected to be consistent with the age and usage history of the engine (near certification levels for diesel engines; in conformance with the expected model year standard for gasoline vehicles).

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Engine modifications may be appropriate for particular FMs that have different energy contents than standard fuels, and these will be implemented on the required test engines provided they are part of the description of the FM as a single technology.

2.4 Data Quality Objectives

The data of primary interest in this verification are the reduction in emissions of the FTP primary pollutants: NO_X, hydrocarbons (HCs), PM, and carbon monoxide (CO). The DQOs of this GVP are the requirements of the test methods specified in 40 CFR Part 86 (light duty gasoline and diesel highway engines) or 89 (nonroad diesel engines) when conducting the number and type of FTP tests called for by the approved test/QA plan for the FM. ETV tests that do not meet the FTP QA requirements are invalid.

The number and type of FTP tests (cold- and/or hot-start) required for ETV is determined from the following criteria:

First, a minimum of three tests is required to provide the basic ETV result of a mean emission reduction and the 95% confidence interval on that mean based on measured variability for each of the measured emissions and test parameters. For highway engines this minimum is satisfied with one cold start test and three hot start tests. For nonroad engines three replicates of the appropriate test sequence (i.e., three 8-mode tests, or three 6-mode tests) are required. A three test minimum is currently the same as is required by the State of California for its program.

Second, additional tests may be required to meet the ETV requirement that the test/QA plan provide a 90% probability of detecting the expected emissions reductions when computed using the expected experimental errors for the various measurements. These criteria become controlling for low emissions reductions and/or high test variability. This is a planning requirement for the test/QA plan. The procedure to determine the appropriate number of tests is given in Appendix B.

Third, additional tests may be desired by the applicant to reduce the width of the 95% confidence interval on the mean emission reduction. Section 5 provides additional explanation and example scenarios. This third criterion is a consequence of applying standard statistical procedures to the ETV test design and data analysis. At a fixed measurement variability, normal statistical procedures lead to a small number of tests giving a broader 95% confidence interval than a larger number of tests. To any regulator or potential technology user, an emission reduction of 40% ± 5% is better than 40% ± 20% and will be given more credence.

Noncritical measurements, including carbon dioxide (CO_2) emissions, fuel utilization, and power, will also be made as described in later sections. These are not considered critical, and the methods and DQOs will be stated in the test/QA plan.

The FTP tests referenced above are conducted following test cycles specified in 40 CFR. As discussed in Section 5, other test cycles may also be required for verification of an FM. A single test data set would consist of a single FTP test cycle and any other special cycle required for the FM. The requirements for the emissions tests remain the same in both cases.

An applicant may conduct privately sponsored tests at a testing organization for development purposes with the same test engine prior to or after conducting verification tests. Such testing is understood to be

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common and important to ensure the technology is properly adjusted and tuned to the application. The ETV data quality objectives do not apply to privately sponsored testing. However, the applicant and testing organization must coordinate the entire testing effort with the APCTVC so that:

- Preparation for the ETV test (submittal of the technology to the APCTVC, discussion of engine selection, and preparation of the test/QA plan) is completed prior to conducting the ETV test itself;
- The APCTVC is notified of the ETV test dates in time to schedule QA activities at the discretion of the APCTVC; and
- Declaration of the test run that is to be the ETV test is made prior to starting the test, the engine must be brought to a starting point in accordance with the test/QA plan, and the results of that test are documented and reported in accordance with the test/QA plan.

An applicant may desire to run the base-fueled ETV test, conduct private developmental testing, and then complete the ETV tests following the private testing. This approach may be acceptable provided the base-fueled run is considered to remain valid for the duration of and for the activities that occur during the private testing. If not, the base-fuel case will have to be rerun.

The data from all ETV tests will be retained and reported to the APCTVC, including invalid FTP test results. Data that meet the QA requirements of the FTP are considered valid and will be used to compute emissions reductions for ETV purposes.

The FM emissions reduction performance will be reported as both absolute emissions in the appropriate units (per applicable FTP) for the base-fueled and FM-fueled cases, and as percentage emissions reduction for a specific engine or engine family. The percentage emissions reduction reported will be the mean emissions reduction (relative to the baseline emission) with attendant upper and lower 95% confidence limits on that mean.

3.0 ETV RESPONSIBILITIES

The primary responsibilities for each organization involved in the FM ETV verification program were summarized in Table 1. Additional comments are provided below:

- The technology applicant provides the complete, commercially ready product for ETV testing, and logistical and technical support, as required, during the ETV testing. The applicant's responsibilities are defined by a contract or letter of agreement with the APCTVC (RTI.) The preliminary application (Table 1, Row 1) provides relevant background data and technology information to facilitate test/QA plan development. The applicant must pay the portion of the verification cost required at the time its contractual relationship with the APCTVC begins.
- In addition to the items in Table 1, the APCTVC prepares the GVP (this document); qualifies, approves, and audits the testing organization; provides a template for test/QA plans; prepares the ETV reports and statements from the laboratory test reports; and, jointly with EPA-ORD, reviews and approves the ETV reports and statements.
- Qualified testing organizations conduct ETV verifications under contract to the APCTVC. The order of activities in Table 1 is mandatory, with the test/QA plan being prepared and approved before testing. The testing organization also conducts internal QA on test results and reports.

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4.0 APPLICATION AND TECHNOLOGY DESCRIPTION

The ETV applicant is the basic source of information regarding its technology, information which is provided to the APCTVC and EPA-OTAQ through an application form. This information is used by the testing organization and APCTVC to prepare and review a test/QA plan that meets the requirements of the applicant and by EPA-OTAQ and other users to verify data. In keeping with the voluntary nature of ETV, the applicant must control the technology within the United States to submit it for verification.

For the applicant's convenience, the application form used by the EPA-OTAQ retrofit program can also be used for ETV. The applicant should complete as much of the form as possible and submit it to OTAQ and the APCTVC. ETV will provide test data that will allow completion of the form for submission to EPA-OTAQ and participation in the VDRP. The form can be obtained from the APCTVC and is also posted on the EPA-OTAQ retrofit website at http://www.epa.gov/otaq/retrofit/retrofittech.htm. Both Microsoft Excel and Lotus 123 versions are provided. Alternatively, an applicant who is not participating in the VDRP can use the APCTVC's shorter general application form.

The VDRP application consists of four worksheets: (1) Manufacturer Information, (2) Product Information, (3) Test Information, and (4) Component Information. There is a separate spreadsheet containing directions and examples for completing the forms. This guidance document begins with a page of general instructions for the entire form. Since no general form can anticipate the data requirements for all possible FMs, the applicant should use the applicable portions of the form. Additional information will be requested to supplement this form if needed.

The mobile sources ETV program is intended to provide independent and quality-assured performance data to potential users of technologies through a documented public process. Existing data (whether Confidential Business Information [CBI] or not) cannot be used to substitute for ETV tests, although they can be used to help design the ETV test. The ETV documents (protocol, test/QA plans, reports, and verification statements) are publicly available. For these reasons, the submittal of CBI to the APCTVC is unlikely to be necessary. The application form **is not** intended to convey CBI to the APCTVC and none should be included in the form. Any applicant who believes that CBI is required to provide input to the ETV process should explain that belief in a cover letter to the APCTVC. It should be noted that all information submitted on the application is subject to the Freedom of Information Act.

4.1 Manufacturer Information

This first page of the application requests background and contact information for the applicant who is seeking product verification. Guidance and examples supporting its use are provided on the second page of the guidance form.

4.2 Fuel Modification Descriptive Information

The second page of the application is used to describe the FM fully and concisely. It will be used to prepare the test/QA plan and as a more complete description of the technology in the ETV report. It requires a concise (300-word or less) description of the FM being verified and requests a number of operating details that summarize the emissions control performance expected, along with the product's operation. All questions may not apply. Instructions for completing this page can be found in the "Explan_Prod" page of the guidance document.

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In the case where combinations of independent technologies are being submitted for verification, the description of the combined technology should completely identify and describe those technologies being combined and fully state the nature of the combined test and expected result.

4.3 Test Information

Results of verification testing on the applicant FM are to be detailed on the third sheet of the application form. Completion of this page is not required for application to the APCTVC for verification of a technology because the verification itself will be providing the test results. However, the applicant is encouraged to report all available test data, which can be used by the APCTVC to better plan the ETV test program for the applicant's technology. These existing test data will not be included in the verification report. The Explan_Tests page of the guidance document provides information for completing this page.

4.4 Component Information

The last page of the application form, Component Information, lists the major components of the technology system. For fuels and fuel additives, it is expected that few components will need to be listed here, although for combined systems this will be an important document. Directions are given in the Explan_Components page of the guidance.

5.0 ETV TESTING

This section gives the test requirements for verification of FMs. It also describes reduction of the data to produce the emissions reduction measures that are the product of the tests. Section 5.1 gives an overview of the testing and data analysis as it applies to all FMs. Section 5.2 gives ETV testing details for FMs intended for use in diesel engines. Section 5.3 gives the detailed test requirements for ETV of FMs intended for use in gasoline vehicles and engines. Section 5.4 gives detailed test requirements for ETV of lubricants.

5.1 Test Design and Data Analysis for ETV of FMs

5.1.1 Overview of Testing Requirements

The data of primary interest in this verification testing are the reduction in emissions of NO_X, HC, PM, and CO. Emissions reductions are defined as the percentage reduction obtained between a base case and the FM candidate case or the natural log equivalent. For all engine and vehicle types, emissions measurements are made using the FTP certification test cycles applicable to the engine or vehicle for which the FM is intended. Additional special test cycles are sometimes also required in addition to the FTP certification test. The details of the tests are different for different engines and vehicles and are given below.

A simple test of an engine without a control device installed followed by one with the device installed is not considered to be adequate for all FM ETVs. Emissions from engines or vehicles may increase over their service life, particularly for gasoline-fueled engines or vehicles. FMs may require significant service life to have their full effect. These characteristics require that the ETV test for FMs be designed to provide emissions reductions with a changing baseline emission.

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Testing conducted under this protocol utilizes individual FTP and special tests that measure emission rates, *E*, of various pollutants. Replicate tests are conducted at a particular test point in the service life of an engine or vehicle, fueled or lubricated by either the base or the FM candidate. The FTP and special tests are combined to give a combined emissions rate for each pollutant. The complete ETV test sequence includes several test points, each of which gives a combined emissions rate for either the base engine or the candidate FM engine. The combined emissions rates from all valid data are then used to estimate the emissions reduction, *ER*, for each pollutant.

The requirements for testing diesel and gasoline FMs for immediate and cumulative effects in highway and nonroad diesel applications will be discussed in greater detail in the following sections. Table 2 summarizes the tests required at each test point in the test sequence.

ETV provides engine emissions reductions from which EPA-OTAQ or others estimate fleet emissions reductions. Estimation of fleet-wide emissions reductions from single engine emissions reductions requires knowledge of the composition of the entire fleet, identification of the number and kind of representative engines or vehicles, and numerous other assumptions. All of these considerations factor into the experimental design. Making these assumptions is uniquely the responsibility of the agency evaluating the data.

Table 2. Summary of Tests Required at Each Test Point

Type	Effect	Engine	Sequence of Test Points[1]	Tests at Each Point[2]	Reference
Diesel FMs	Immediate	Highway	BCCB or BCBC	(Cold + 3 hots + SET)	5.2.3.4, 5.2.4.1
Diesel FMs	Immediate	Nonroad	BCCB or BCBC	3 (multi-mode steady-state) + NTTC[3]	5.2.3.4, 5.2.4.1
Diesel FMs	Cumulative	Highway	BBBBCCBB	(Cold + 3 hots + SET)	Fig. 1, 5.1.3.4
Diesel FMs	Cumulative	Nonroad	BBBBCCBB	3 (multi-mode steady-state) + NTTC	Fig. 1
Gasoline FMs	Immediate	Highway	BCCB	3 (Cold + hot + US06)[4]	5.3.3.2, 5.3.4
Gasoline FMs	Immediate	Nonroad	BCCB	3 (multi-mode steady-state)	5.3.3.2, 5.3.4
Gasoline FMs	Cumulative	Highway	BBBBCCBB	3 (Cold + hot + US06)[4]	5.3.3.2, 5.1.3.4
Gasoline FMs	Cumulative	Nonroad	BBBBCCBB	3 (multi-mode steady-state)	5.3.3.2, 5.1.3.4
Lubricant FM	*(diesel)*	Highway	BBBBCCCCBBBB	(Cold + 3 hots + SET)	Fig. 2, Table 7
Lubricant FM	*(diesel)*	Nonroad	BBBBCCCCBBBB	3 (multi-mode steady-state) + NTTC	Fig. 2, Table 7
Lubricant FM	*(gasoline)*	Highway	BBBBCCCCBBBB	3 (Cold + hot + US06)	Fig. 2, Table 7
Lubricant FM	*(gasoline)*	Nonroad	BBBBCCCCBBBB	3 (multi-mode steady-state)	Fig. 2, Table 7

[1] B = Baseline condition; C = Candidate technology.
[2] Minimum requirement. When emissions reductions are expected to be low, more tests may be required to achieve the 95% confidence interval.
[3] Nonroad transient test cycle.
[4] Highway fuel economy test, cold CO, and evaporative emissions testing will be required on any FM that may reasonably be expected to affect fuel volatility.

5.1.2 Test Design Requirement for Single Engine Verification

Minimizing the cost of ETV testing is important, and limiting the amount of testing required is one way to lower costs. However, if too few tests are conducted, normal experimental variability could prevent the ETV from finding a significant result. All ETV test/QA plans for FMs are required to include

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sufficient tests to have a high probability of detecting the emissions reductions expected by the applicant. In addition to other requirements, each FM ETV test plan is to be designed to have at least a 90% probability of detecting the emission reductions expected by the applicant. This requirement was adopted to ensure, as much as practical, that the ETV test would accomplish the applicant's goals.

In this context, detecting means that the 95% confidence interval on the emission reduction does not include zero. (This requirement is for test design purposes and does not require that the test/QA plan be modified should actual test data show that the assumptions that went into the calculation were incorrect. However, insufficient replication can result in the inability to verify any emissions reduction and publication of an ETV report stating that a technology had no statistically significant benefit.) The test/QA plan prepared for the FM will reflect this requirement, based on the applicant's knowledge of his product and the testing organization's estimates of test variability.

At each test point, a minimum of three tests are required. More may be necessary for low emission reduction technologies. The definition of a single test depends on the technology. For diesel engines, for instance, one FTP cold start, three FTP hot starts, and one additional cycle are considered three tests when combined. Depending on the FM technology and test engine or vehicle, a complete single engine ETV may require as few as two or as many as 12 base and FM test points. Sections 5.2 (diesel engines), 5.3 (gasoline vehicles), and 5.4 (lubricants) provide the details of these requirements.

5.1.3 Analysis of Combined Emissions Data

5.1.3.1 Data analysis for single engine tests of immediate effect FMs. Immediate effect FMs produce their emission reduction as soon as they are fully flushed through the fuel system and are expected to have no residual effect. The emissions reduction can therefore be determined without concern for test engine drift or deterioration. Verification of immediate effect FMs requires a single base case test point followed closely in time by a single candidate FM test point and is very similar to that used to test retrofit devices. This section describes the data analysis procedure that will be used to calculate the emission reductions for immediate effect FMs.

The first steps are the calculation of the combined test emission results for each test and each pollutant for the base and candidate FM tests. E_B and E_F are understood to refer to a single pollutant in the equations below. Calculation of E_B and E_F from individual test results differs for diesel and gasoline engines and for LDVs and is described in the respective sections below. Once the E values for the test points are available, the sample means and standard deviations (s_B and s_F) are computed using Equations 1 and 2.

$$\overline{E_B} = \frac{\sum_{1}^{n_B} E_{B,i}}{n_B} \qquad \textit{and} \qquad \overline{E_F} = \frac{\sum_{1}^{n_F} E_{F,i}}{n_F} \tag{1}$$

where:

$\overline{E_B}$ = mean emission rate for base for a single pollutant,
$\overline{E_F}$ = mean emission rate for FM for a single pollutant,
$E_{B,i}$ = emission results for a single base (B) test for a single pollutant,
$E_{F,i}$ = emission results for a single FM (F) test for a single pollutant,

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n_B and n_F = number of base (B) and FM (F) tests, and
s_B and s_F = standard deviations of base (B) and FM (F) tests.

$$s_B = \sqrt{\sum_1^{n_B}\left(E_{B,i} - \overline{E_B}\right)^2 \Big/ \left(n_B - 1\right)} \quad and \quad s_F = \sqrt{\sum_1^{n_F}\left(E_{F,i} - \overline{E_F}\right)^2 \Big/ \left(n_F - 1\right)} \tag{2}$$

The raw emission reduction for each pollutant, ER_{RAW}, is then computed as the difference between the combined emission results for the base and candidate FM case, divided by the base case emission, as shown in Equation 3.

$$ER_{RAW} = \left(\overline{E_B} - \overline{E_F}\right) \Big/ \overline{E_B} \tag{3}$$

The upper and lower bounds of the approximate confidence interval (*CI*) around ER_{RAW} are computed using Equations 4a and 4b.

$$CI\ (upper\ bound) = ER_{RAW} + \left\{ \left(t_{\alpha/2} \bullet \sqrt{\frac{s_B^2}{n_B} + \left(1 - ER_{RAW}\right)^2 \frac{s_F^2}{n_F}} \right) \Big/ \overline{E_B} \right\} \tag{4a}$$

$$CI\ (lower\ bound) = ER_{RAW} - \left\{ \left(t_{\alpha/2} \bullet \sqrt{\frac{s_B^2}{n_B} + \left(1 - ER_{RAW}\right)^2 \frac{s_F^2}{n_F}} \right) \Big/ \overline{E_B} \right\} \tag{4b}$$

where $t_{\alpha/2}$ is $t_{0.025}$ in tables of the critical values (alternatively, tail area probability) of the t-distribution, with degrees of freedom, *v*, given by Equation 5 (rounded down):

$$v = \frac{\left[s_B^2 / n_B + \left(1 - ER_{RAW}\right)^2 s_F^2 / n_F \right]^2}{\left[\left(s_B^2 / n_B \right)^2 / \left(n_B - 1\right) \right] + \left(1 - ER_{RAW}\right)^4 \left[\left(s_F^2 / n_F \right)^2 / \left(n_F - 1\right) \right]} \tag{5}$$

The fractional values of emission reduction and the confidence intervals are converted to percentages by multiplying by 100%.

Although ER_{RAW} is the observed value of the data for the single engine tested, there is significant potential for the true emission reduction achieved in the field to be lower due to measurement errors. Therefore, an environmentally conservative discounted single engine emission reduction, ER_{DSCT}, is also reported as the lower bound of the confidence interval using Equation 6.

$$ER_{DSCT} = 100\%\ CI\ (lower\ bound\ from\ Equation\ 4b) \tag{6}$$

For example, if ER_{RAW} was 0.15 (15% emissions reduction) with a confidence interval of ± 0.05 (± 5%), ER_{DSCT} would have a value of 0.1 (10%).

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5.1.3.2 Calculation of fleet-wide emissions reductions for immediate effect FMs. For immediate effect FMs, the fleet emissions reduction (ER_{FLEET}) is computed by EPA-OTAQ for gasoline engines as the unweighted (gasoline) mean or as the weighted mean (diesel engines) of the discounted single engine emissions reductions. Emissions reductions are computed separately for each pollutant.

5.1.3.3 General treatment of cumulative effect FMs. ETV of cumulative effect FMs requires additional testing. Because the technology must be in use for an extended period to take full effect, the total duration of the testing can be long. Therefore, the base engine emissions may change as the engine/vehicle ages, or because ambient conditions change, or because test cell instrumentation requires recalibration. This situation leads to uncertainty about the cause of a measured emission change. Cumulative effect technologies also have a residual effect after use ceases. This characteristic prevents immediately re-running the baseline at the end of the test to quantify any drift.

Figure 1 illustrates the expected FM performance and testing model used in this protocol to evaluate a cumulative effect FM having residual effects on emissions. Increasing emissions with increasing service is assumed based on the known behavior of gasoline vehicles and their catalytic emissions control systems. Over the life of the vehicle, the emissions steadily increase as shown by the solid line, which represents the base case. Some of the deterioration is caused by changes in the engine, and some is caused by the emissions control system's deterioration. The slope and intercept of the deterioration line varies from gasoline vehicle to gasoline vehicle and from within and across vehicle's type and manufacturer. For the purposes of this protocol, the deterioration factor is assumed to be linear and unknown. Over the service life of diesel engines (when not controlled by catalytic systems), the deterioration factor is low and may be zero within the time frame of ETV tests. After changing to the candidate FM, the emissions are assumed to become lower. The shape of the curve during the transition is not important to this analysis.

The goal of the cumulative effects testing and data analysis is to separate the change in emissions due to the FM from the other changes. The emission reduction is assumed to be proportional to total emissions. That is, regardless of total emissions, the percent emissions reduction is assumed constant as implied by the natural log transformation of the emissions rate (vertical scale in Figure 1). As shown in Appendix C, the use of a log-scale analysis produces results nearly identical to using a percentage change in the native units when the measurement errors and effects to be detected are relatively small. The analysis is thus conceptually consistent with that for an immediate-effect FM.

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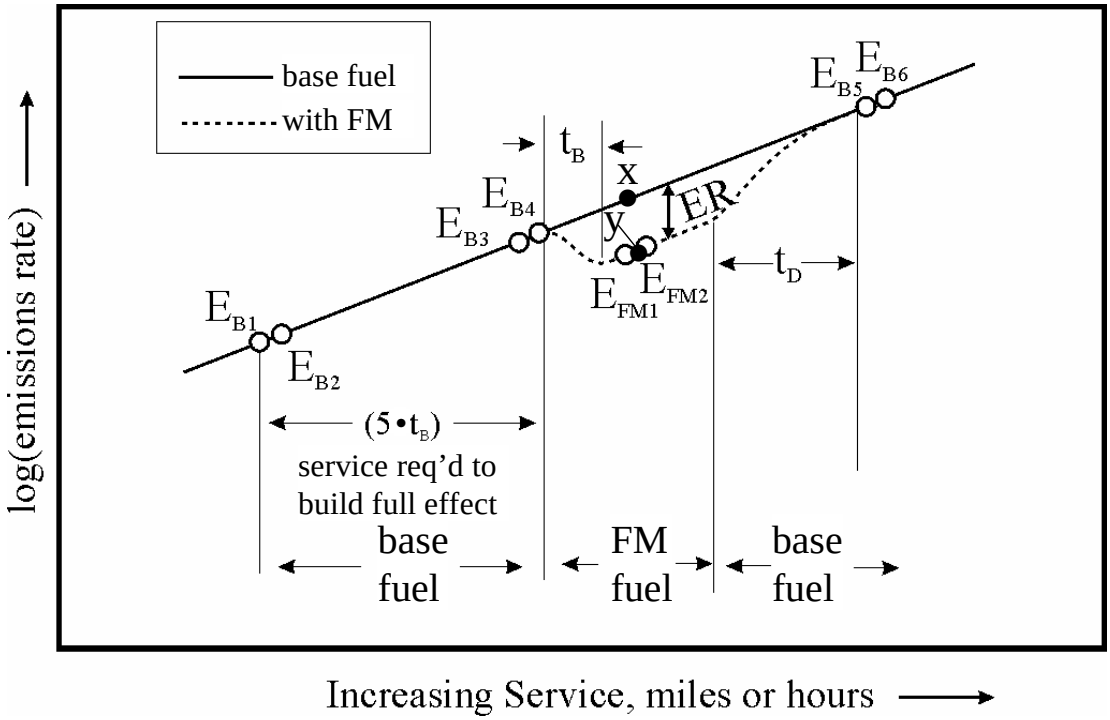

Figure 1. Performance Model and Testing for Cumulative Effects FMs

The candidate FM is assumed to be characterized by a known time for the emissions reduction to have full effect, t_B. Determining t_B is not part of this protocol and is assumed to be known and specified by the applicant. As shown in Figure 1, the test procedure requires a run-in period equal to five times t_B. The service accumulation cycle is required to be appropriate for the engine/vehicle (40 CFR 86.090-26), to be the same for both base fuel and candidate FM, and for an entire cycle to be completed before beginning a test sequence. Figure 1 shows two base case emissions test sequences carried out in duplicate at the beginning (E_{B1} and E_{B2}) and end (E_{B3} and E_{B4}) of the run-in period to provide a good estimate of the deterioration rate. FMs in diesel engines may not require both.

Following the completion of emissions test sequence E_{B4}, the FM fuel is flushed through the system, and a period of operation on candidate FM fuel begins. Use of candidate FM fuel continues for the period t_B, after which two FM test sequences, E_{FM1} and E_{FM2}, are carried out. Once E_{FM2} has been determined, the engine/vehicle is returned to base case fuel. The base fuel is used for the period required to return the engine to the base emission line. This time period, t_D, is also assumed to be known and specified by the applicant before ETV testing, and determination of t_D is not part of the ETV test. After operating on base fuel for the time required for the effect of the FM fuel's use to completely decay, the fifth and sixth base case emissions sequences are carried out to obtain E_{B5} and E_{B6}, which confirm the deterioration line.

Although the verification process does not require testing beyond point E_{B6}, the applicant may wish to generate additional data if the FM is expected to provide a benefit that would not be fully evaluated through a single FM test period, or to evaluate different pollutants or increase confidence in results. In keeping with ETV procedures, all verification testing must be planned and included in the test/QA plan.

The ETV test must be conducted in the order shown in Figure 1: base, candidate FM, base. Before all testing, the engine must be conditioned on the test fuel (base or candidate) to purge any remaining old

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fuel before each map or cold start procedure. The reference cycle map used for the candidate diesel fuel must be the same as determined for the base fuel. The oil and oil filter are to be changed immediately prior to test sequences E_{B1}, E_{FM1}, and E_{B5}.

The data analysis of the cumulative effect FMs described in the following sections is based on an assumption that Figure 1 represents the true behavior of FM, with t_B and t_D known so that there is no confounding between the base and FM fuel cases. These procedures are those recommended and preferred by EPA-OTAQ.

Because the data analysis approach in this protocol is specific to the technology performance and experimental design assumed in Figure 1, an applicant may propose a verification applying another experimental design. In this case, the applicant's proposal must include a detailed justification and demonstrate quantitatively its superiority to the ETV protocol's approach; the applicant's proposal will be evaluated and tested by ETV statisticians regarding the reasonableness of the design and the engine/vehicle selection. The test/QA plan will include an appendix describing development of the experimental design to be used for testing.

5.1.3.4 Data analysis for single engine cumulative effect FMs. The emission reduction is computed from the two FM measurements (E_{FM1} and E_{FM2}) and from the estimated base emissions at the same service (hours or miles). In Figure 1, this would be the intersection of a vertical line rising between E_{FM1} and E_{FM2} and the base case performance line (i.e., difference in rates at points X and Y). The base fueled emissions at that point are estimated from a linear least-squares regression of the natural logarithm of emissions [ln(E)] versus service accumulation for the six base case emissions measurements (E_{B1}, E_{B2}...E_{B6}). Appendix D develops this approach to analyzing the data, presents equations that allow calculation of the estimated effect of the FM and the variance of that estimate, and provides some suggestions to maximize the power of the experiment.

5.2 ETV Testing for Diesel FMs

This section applies to FMs used in compression-ignition engines.

5.2.1 Diesel Base Fuels

Applicants may choose from among the following two FM base fuel alternatives, which are described in more detail in Table 3:

1. The nationwide average base fuel for nationwide application of the FM.
2. FMs intended for California (or an area in which California-type fuel is the dominant available diesel fuel) may be tested using California-type fuel as the base fuel.

Applicants who intend to market FMs in specific markets (regional, specific, or other) may propose alternate base fuels for use during ETV testing. A proposal for an alternate base fuel must be accompanied by evidence that the fuel truly is a "base" that is in use and from which the candidate FM will reduce emissions. If acceptable, the fuel supplied by the applicant will be tested and reported as the base fuel in the ETV report and statement. ETV can make no representation regarding possible extension of the data to other base fuels.

In all these cases, the ETV report and statement will report the test conditions, the FM tested, and the results obtained.

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Note that the ranges given in Table 3 for the properties of the base fuels are not as broad as those for the fuel allowed in emissions certification tests, and that the sulfur level has been limited to 15 ppm. The ranges were narrowed to reduce test-to-test variations in the emissions reductions measurements, whereas the ultra-low sulfur diesel (ULSD) is proposed as the test case. Refinery diesel product streams must be used to produce the base fuels for tests. They cannot be blended from purified chemicals. Because oxygenates are rarely used in diesel, neither the California nor the national average fuel may contain oxygenates. Although additives are not used consistently in diesel, it is permissible for the California and/or the national average fuel to contain a registered additive or additives designed to maintain fuel quality during transport and storage, such as an antioxidant and/or corrosion inhibitor.

Table 3. Properties of Base Fuel for ETV of Diesel FMs

Property	Nationwide Average Fuel	California Fuel	Applicant-Choice Base fuel[a]	ASTM Test
Accepted by EPA-OTAQ	Yes	Yes	No[a]	
Cetane number	43 to 46	51 to 54		D 613
Aromatics, volume %	32 to 36	20 to 24		D 5186
Specific gravity	0.84 to 0.86	0.83 to 0.85		D 1298
Additives	minimal[b]	minimal[b]		
Sulfur, ppm				
Highway	0 to 15	0 to 15		D 6428
Nonroad	2500 to 3500[c]	100 to 160		D 2622
Distillation range				
10% point, °F	410 to 430	410 to 430		D 86
50% point, °F	490 to 520	490 to 520		D 86
90% point, °F	585 to 620	595 to 630		D 86

[a] Testing of FMs using a base fuel chosen by the applicant is possible within this protocol.
[b] Cetane improvers and some other additives cannot be avoided in refinery products. However, these are to be minimized, and no additional additives are to be used.
[c] Use of highway diesel sulfur levels allowed in accordance with 40 CFR part 89.330.

5.2.2 Selection of Engines for ETV Testing

The applicant may select one of three targets for the candidate diesel FM: (1) a specific engine family as represented by a single test engine, (2) the entire on-highway diesel fleet, or (3) some portion of the on-highway diesel fleet. A candidate FM ETV can be conducted on any single engine meeting the requirements of Section 5.2.2.1.

5.2.2.1 General criteria for diesel engine selection. Test engines must be in good operating condition and representative of in-use engines. Standard engines proposed for testing must be in a certified configuration. The engines are to be "as delivered, without any added technologies, and are to be tuned to the manufacturer's specifications. (Specially prepared engines [such as future technology engines that are not commonly available] may also be tested under this protocol, and will be identified as such. However, the acceptability of such a verification to EPA-OTAQ should be explored by the applicant prior to beginning verification if VDRP listing is desired.) For engines manufactured before implementation of emission standards, the engine must be representative of normal production engines.

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Engines must have a minimum of 125 hours of use before beginning an ETV test and exhibit stable operation. Emissions control components must be sufficiently broken in so that they exhibit stable operation over the course of the test program. Because residual effect FMs may have been used in an engine before its use in the ETV program, the engine owner (testing organization or applicant) must establish that the engine can be considered a reasonable baseline for the engine family of interest, either through replicate baseline tests showing a stable baseline or documentation of its fueling history. On the base fuel, the test engine must not exceed 110% of its applicable emission standards. For engines manufactured before emission standards, the engine must not exceed 150% of the first standards for that engine category.

Rebuilt engines will be allowed so long as they represent a certified configuration, produce emissions at the certification standard when fueled by the base fuel (within limits given above), and meet other applicable criteria.

5.2.3 Test Procedures—General Requirements

5.2.3.1 Engine maintenance. All equipment used in the testing must be maintained and operated in accordance with applicable FTP regulations. To the extent practical, the engine and test conditions should be maintained the same between the base and candidate FM tests. This consideration applies to all aspects of engine operation and maintenance. Routine engine maintenance must be performed before beginning a verification test and, once testing has started, routine engine maintenance is not allowed. If use of an FM requires that an engine be tuned for the fuel, this requirement must be detailed in the test/QA plan and will be included in the report as a requirement for use of the FM. Resumption of testing following engine or test stand breakdown and repair will be evaluated by the APCTVC on a case-by-case basis and will be allowable only for brief shutdowns for which no emissions impact is considered likely. A full fuel analysis is required on both base and candidate FM fuel.

5.2.3.2 Test data format and retention. Raw test results will be retained by the testing laboratory in the electronic format required for EPA certification tests and made available to the APCTVC on request. Results for cold and hot starts will be reported both independently and appropriately weighted. Emissions during steady-state testing are to be reported mode-by-mode as well as in the final weighted form. Torque curves will be provided electronically for each engine map. Brake-specific fuel consumption (BSFC) will be measured during each engine map and provided with the map.

5.2.3.3 Fuel conditioning. When switching fuels, a conditioning cycle will be run to purge old fuel and stabilize engine operation on the new fuel. The conditioning cycle must represent normal engine operation and will be specified in the test/QA plan. The engine must be mapped prior to performing a test sequence each time a new test fuel (base fuel or candidate fuel) is used. Engine mapping is conducted following conditioning. The most recently generated engine map on base fuel shall be used in transient testing. The supplemental emissions test (SET) will be performed with the most recently conducted map.

5.2.3.4 ETV test procedures. For on-highway engines, the FTP is described at 40 CFR Part 86. The minimum immediate effects FM emission reduction ETV on-highway engine test at a single test point consists of one cold start FTP test, three hot start FTP tests, and one SET. The weighted cold start results shall be applied to each of the weighted hot start results to provide three (3) transient sets of data for each regulated pollutant and BSFC. Additional testing at each test point may be required to detect the expected emissions reduction, as described in Section 5.1.2.

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The SET for on-highway engines is specified at 40 CFR 86.1360. The SET is a 13-mode steady-state test cycle. The test sequence shall consist of using the FTP to perform one cold start and three hot start transient tests followed by one SET.

For nonroad engines, the FTP is described at 40 CFR Part 89. In most cases, nonroad engines will be verified with both the applicable steady-state cycle and the nonroad transient cycle. However, constant speed engines, such as for generators, may be tested using only the steady-state cycles. For nonroad engines, the basic minimum immediate emission reduction ETV test requires triplicate multimode FTP tests plus the diesel nonroad transient cycle. Additional testing at each test point may be required to detect the expected emissions reduction, as described in Section 5.1.2.

For locomotive engines, the FTP is described at 40 CFR Part 92. The marine engine FTP is described in 40 CFR Part 94. Additional testing at each test point may be required to detect the expected emissions reduction, as described in Section 5.1.2.

Future revisions to the applicable FTP or new procedures adopted in applicable regulations are incorporated in this protocol. Unless otherwise described in this document or identified in the approved test/QA plan, the FTP is to be followed in its entirety. In accordance with this protocol, any deviations from the test/QA plan will be noted and throughly documented by the testing organization in its report.

Requests for the use of alternate or special test procedures to better predict emissions and/or engine operation will not be rejected without consideration. All data quality and QA requirements of this protocol must be met by any alternate test, and this protocol relies on the QA incorporated in the FTP. Significant modification of the FTP sampling and analysis system is unlikely to be acceptable. Changes in the FTP that amount to re-arrangement of existing portions of the test procedure and retain the existing QA steps are more likely to be acceptable.

With these constraints, alternate or special test procedures may be proposed in the application for the technology and will be reviewed with the APCTVC for conformance to this generic protocol before test/QA plan preparation.

Existing data of any kind and chassis and in-use field (e.g., on-road testing devices) data are not acceptable as the basis for ETV.

5.2.4 ETV of Diesel FMs Delivering Immediate Emission Reductions

5.2.4.1 ETV testing sequence. Emission testing on the base fuel must be conducted first. For an arbitrary engine choice for which no historical emissions performance information is available, the base/candidate test points may be conducted in either sequence of base/candidate/base/candidate (BCBC), or base/candidate/ candidate/ base (BCCB). Each test point (B or C) is to include the same number of tests. For the special case of an engine having a substantial documented emissions history (explained further below), a test sequence of BBCC is permitted.

Table 4 outlines the minimum single highway diesel engine test for an immediate emissions reduction FM using the BCCB sequence. The minimum number of tests required at each point in the test sequence is given in Equation B-3. For example purposes, the FM being evaluated in Table 4 is assumed to be one whose expected emissions reduction is large enough that the minimum test set (one cold test, three hot starts, and one SET) at each test point provides a sufficiently narrow confidence interval. Other diesel engine applications would run the appropriate FTP test sequence.

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After the base fuel is used to conduct the prescribed minimum number of tests for the expected emission reduction, candidate fuel testing should be performed. After conducting the minimum number of prescribed tests on the candidate fuel, emission results for each pollutant should be analyzed. If the emission reduction achieved is less than expected, the applicant may run additional tests to support fuel performance. If additional testing on the candidate fuel is desired by the applicant, all testing on the candidate fuel should be completed before switching fuels.

Diesel engines are not expected to exhibit emissions deterioration such as is shown in Figure 1. However, for an unknown FM in an arbitrary engine, it is possible. Potential drift by the test diesel engine (Table 4, Step 11) is to be evaluated as follows:

1. By comparing base fuel emissions at the beginning and end of the test program. Initial and final base fuel results that are not statistically different indicate no deterioration and a zero slope emissions line.
2. By choosing an engine with a documented test history for which at least two baseline emissions measurements show constant emissions over a period that exceeds the expected total ETV test duration. The FM application should propose the engine and provide the requisite evidence of constant emissions so that the test/QA plan can be properly prepared. If the initial ETV baseline emissions result (Table 4, Step 3) is not statistically different from the previous two measurements for the engine, the final baseline test (Table 4, Step 10) may be conducted, on a separate day, prior to use of the FM, and the average emissions of the two will serve as the base-fuel emissions. That is, Step 10 becomes a new Step 3a.

Table 4. Minimum ETV Test Program for Single On-highway Diesel Engine and Immediate Effect FM

1.	Select representative engine and stabilize operation on base fuel.
2.	Map engine on base fuel and practice cycles.
3.	Conduct cold start, three hot starts, and SET on base-fueled engine with base fuel map.
4.	Switch to candidate FM, purge base fuel, and operate and stabilize engine.
5.	Map engine with FM. Practice cycles using base fuel map.
6.	Conduct cold start, three hot starts (using base fuel map), and SET (with FM map) on FM-fueled engine.
7.	Repeat cold start, three hot starts (using base fuel map), and SET (with FM map) on FM-fueled engine.
8.	Switch back to base fuel, purge FM fuel, and operate and stabilize engine.
9.	Perform second map using base fuel. Perform practice cycles using new base map.
10.	Using new base fuel map, conduct cold start, three hot starts, and SET.
11.	Compare initial and final base fuel emissions results for statistical differences.

5.2.4.2 Data reduction for immediate effects diesel FM. For highway diesel engines, emissions tests results are recorded at each test point for HC, CO, NO_X, PM and the other measured pollutants. For each pollutant, the single cold start emissions measurement (e_C) is combined with each of up to three hot start emission measurements (e_H) to obtain up to three composite emissions rates [$(E_{COMP})_m$] following the normal fractional calculation for highway engines:

$$(E_{comp})_m = \frac{(1/7)(e_c) + (6/7)(e_H)_m}{(1/7)(W_c) + (6/7)(W_H)_m} \quad (7)$$

where:

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(E_{COMP}) = weighted mass emission level in grams per brake horsepower-hour and, if appropriate, the weighted mass total hydrocarbon equivalent, in grams per brake horsepower-hour,

m = hot start test 1, 2, or 3,

e_c = mass emission level in grams or grams carbon mass equivalent, measured during the cold start test,

e_H = mass emission level in grams or grams carbon mass equivalent, measured during the hot start test,

W_C = total brake horsepower-hour (brake horsepower integrated over time) for the cold start test,

W_H = total brake horsepower-hour (brake horsepower integrated over time) for the hot start test.

Hot start tests that are combined with a cold start test must be obtained sequentially following that cold start, and no more than three hot starts may be combined with a single cold start or single SET. The composited FTP highway transient emission for each pollutant, E_{COMP}, is combined with a single SET as follows to obtain the combined tests emission rate (E) for each pollutant for each of the n tests at the test point:

$$(E)_i = 0.85 \bullet (E_{COMP})_i + 0.15 \bullet E_{SET} \quad (8)$$

for i = 1 to n tests required at each test point.

As an example, suppose a total of five $(E)_k$ measurements were required to be calculated at each test point to provide enough data. As stated by Equation 8, $(E_{COMP})_1$, $(E_{COMP})_2$ and $(E_{COMP})_3$ would be computed from the first cold start and the first three valid hot starts following the cold start. $(E_{COMP})_4$ and $(E_{COMP})_5$ would be computed from the second cold start and next two valid hot starts, giving the required total of five E_{COMP} values. One SET would be required for the first three E_{COMP} values and a second SET for the last two E_{COMP} values. Then the SET results would be combined with the E_{COMP} values to obtain five E_T values according to Equation 9. (The APCTVC recognizes that the emissions results generated in this way are not fully independent. This approach is a compromise allowed to reduce cost.)

The same process would be applied to both the base case and the candidate FM case.

The same general approach is applied to nonroad engines. Instead of combining a cold and hot start test result, E_{COMP} for nonroad tests is obtained from the nonroad multimode test following the weightings in Appendix B to Subpart E of 40 CFR Part 89 as appropriate for the intended nonroad use as shown in Equation 10.

$$(E_{COMP})_i = \sum_{j=1}^{k} f_j \bullet E_j \quad (9)$$

where:

$(E_{COMP})_i$ = combined emissions rate for test i of n tests required at test point,

k = total number of modes for intended application per 40 CFR 89,

f_j = mode weighting factor from 40 CFR 89, Subpart E, Appendix B, for j = 1,2, …, k modes,

E_j = pollutant emissions rate for j=1,2,..., k modes.

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The nonroad transient test cycle takes the place of the SET for nonroad applications. Only a single nonroad transient test is required at each test point. The nonroad transient cycle emissions are combined with the combined multimode test emissions as follows:

$$E_i = \boldsymbol{X} \bullet (E_{COMP})_i + \boldsymbol{Y} \bullet E_{NTTC} \text{ for } i = 1 \text{ to } n \text{ tests required at each test point} \quad (10)$$

where: $\boldsymbol{X}$ = constant determined by EPA-OTAQ,
$\boldsymbol{Y}$ = constant determined by EPA-OTAQ,
E_{NTTC} = emissions from nonroad transient test cycle.

The emissions reductions for both highway and nonroad engines are then calculated using Equations 1 through 6 from Section 5.1.3.1.

5.2.5 FMs Delivering Cumulative Emission Reductions

5.2.5.1 ETV of single diesel engine tests of cumulative effect FMs. The general procedure discussed in Section 5.1.3.4 is applied for single engine tests.

5.3 ETV of Gasoline FMs

This section applies to fuels and fuel additives used in spark-ignition engines.

5.3.1 Base Fuels

The general requirement for a base gasoline fuel within ETV is that it be widely and consistently available within the region where the FM will be marketed and defined narrowly enough to give consistent test results. As part of the ETV test, the base fuel will be analyzed and the result reported in the ETV report and verification statement. The applicant will specify the desired base fuel in his application, with his choice based on the intended market.

5.3.2 Test Vehicles

5.3.2.1 General requirements. The gasoline FM applicant may select as the target of the verification results a specific engine family. The APCTVC specifies the general requirements for vehicles that will be used in the test and provides the single engine test protocol. General ETV requirements for gasoline test vehicles are as follows:

1. Test vehicles must be in their certified condition, have no obvious signs of tampering, and be in reasonably good repair. Vehicles may have no new emission control components.
2. Whether for single or multiple vehicle verification, the test/QA plan must specify the vehicle selection criteria and procurement method. Test vehicles must have at least 10,000 miles on their engines, be in good working condition, and not have been screened for sensitivity to the candidate FM.
3. All prior maintenance and repair information must be documented.
4. Rebuilt engines are not allowed.
5. Vehicles must not exceed 110% of the applicable emissions certification standard during baseline testing. Exceeding any emissions standard must be the result of the normal distribution of emissions; that is, the vehicle and emission control system must be operating properly, with no obvious reason for the non-compliance.

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5.3.2.2 Number of test vehicles. For single LDV family verification, the specific LDV is the applicant's choice. The application for the FM should state the desired vehicle, and the characteristics of that vehicle will be included in the test/QA plan. If eventually seeking full U.S. fleet verification, the applicant is required to coordinate with EPA-OTAQ.

5.3.2.3 Nonroad use gasoline engines for FM verification. Gasoline FMs may be verified for emissions reductions in nonroad gasoline engines. The applicant recommends the desired test engine, which must meet the general criteria in Section 5.3.2.1.

5.3.3 General Test Procedures

All equipment used in the ETV testing must be maintained and operated in accordance with applicable FTPs. Raw test results are to be retained by the testing organization in the electronic format required for certification tests and made available to the APCTVC if requested. Results for each test phase are to be reported separately as well as with final weighted FTP test results.

5.3.3.1 Vehicle preparation and maintenance. Prior to baseline testing, test vehicles must have normal maintenance performed such as oil and air filter changes. Other recommended maintenance, such as positive crankcase ventilation (PCV), spark plugs, crankcase filter, etc., shall be performed if the normally recommended interval is due or would become due during the test program. Vehicles will be checked for trouble codes and maintenance indicator lights (MILs) and repairs performed before beginning the ETV test. No trouble codes may be stored when beginning ETV testing. Trouble codes set during testing must be recorded and described in the test records.

To the extent practical, the engine and test conditions should be maintained the same between the base and candidate FM tests. This consideration applies to all aspects of engine operation and maintenance. Routine engine maintenance must be performed before beginning a verification test and, once testing has started, routine engine maintenance is generally not allowed. If use of an FM requires that an engine be tuned for the FM, this requirement must be detailed in the test/QA plan and will be included in the report as a requirement for use of the FM. Resumption of testing following engine or test stand breakdown and repair will be evaluated by the APCTVC on a case-by-case basis and will be allowable only for brief shutdowns for which no emissions impact is considered likely. A full fuel analysis is required on both base and candidate FM fuel.

Before initiating ETV testing, the fuel tank(s) shall be drained, base fuel added to the 40% full level, and a triple preparation (three 505-second hot-start tests per the EPA Dynamometer Procedure 40 CFR 86.135-90) performed.

5.3.3.2 Required test procedures. For on-road vehicles and engines, the FTP is described by 40 CFR Part 86. For nonroad engines, the FTP is described by 40 CFR Part 90. The FTP applicable at the time of the test is to be used. Whenever an FTP test is performed on a light duty vehicle or light duty truck, it will be followed by a US06 test (40 CFR 86.159-00). Heavy duty gasoline engines are tested on an engine dynamometer (40 CFR 86 Subpart N).

The highway fuel economy test, cold CO test, and evaporative emission testing will be required of any FM that may reasonably be expected to affect fuel volatility. When evaporative emission testing is not being performed, the heat build portion of the test will not be required after adding fuel.

Requests by applicants to use alternate or special gasoline vehicle or engine test procedures to better predict emissions and/or engine operation in use will not be rejected without consideration. They must

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be proposed in the application and will be discussed before preparing the test/QA plan, which must incorporate a complete description of the ETV test. The ETV testing data quality and QA requirements of this protocol must be met by any alternate test. Significant modification of the FTP sampling and analysis system is unlikely to be acceptable. Alternate test procedures that amount to rearrangements of existing portions of the FTP test for which the existing test descriptions and QA procedures remain valid are more likely to be acceptable. Specific modes of operation may be required to assess emission reductions for particular in-use operating conditions. Existing data may be used for test design.

5.3.4 Gasoline FMs Delivering Immediate Emission Effects

A single gasoline LDV test point consists of a complete composite FTP test (cold start test plus a valid hot start test) and the US06 test. In accordance with 40 CFR 86.137-94, emissions from the gasoline FTP tests are measured and recorded for all pollutants (HC, CO, NO_X, PM) for both phases of the cold start (transient and stabilized) and for the transient phase of the hot start. A minimum of three test points is required for both the base fuel and the candidate FM. After the base fuel is used to conduct the prescribed minimum number of tests for the expected emission reduction, candidate fuel testing should be performed. After conducting the minimum number of prescribed tests on the candidate fuel, emission results for each pollutant should be analyzed. If the emission reduction achieved is less than expected, the applicant may run additional tests to support better FM performance. If additional testing on the candidate fuel is desired by the applicant, all testing on the candidate fuel should be completed before switching fuels.

Additional testing may be conducted if the minimum testing requirements do not demonstrate the targeted emission reductions by continuing to test with the candidate fuel and then performing a corresponding number of tests with the base fuel.

The weighted FTP mass emission rate E_{comp} for each pollutant is obtained as described in 40 CFR 86.144-94 as the sum of 43% of the cold start emissions per mile (E_C) and 57% of the hot start emissions per mile (E_H).

$$E_{comp} = 0.43 \bullet E_C + 0.57 \bullet E_H \quad (11)$$

The combined emissions for each pollutant from a single test, E, are computed as follows:

$$E = 0.72 \bullet E_{comp} + 0.28 \bullet E_{US06} \quad (12)$$

where: E_{US06} = emission rate for the US06 test.

Each value of E_T is computed from separate FTP and US06 measurements. Therefore, if three tests are required to have sufficient data at a test point, a total of three full FTP tests and three US06 tests are required.

Calculation of the single engine emissions reduction is completed using Equations 1 through 6, with the combined emissions for each pollutant, E, for the base case being substituted for E_B, and E for the FM case being substituted for E_F.

The same general approach is applied to nonroad gasoline engines. Instead of combining a cold and hot start test result, E for nonroad tests is obtained from the multimode nonroad test following the weightings in 40 CFR Part 90 as appropriate for the intended nonroad use as shown in Equation 16.

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$$E_i = \sum_{j=1}^{k} f_j \bullet E_j \qquad (13)$$

where:

E_i = emissions rate for test *i* of *n* tests required at each test point,
k = total number of modes for intended application per 40 CFR 90, for j = 1,2, …, k modes,
f_j = mode weighting factor from 40 CFR 90,
E_j = pollutant emissions rate for j=1,2,...k modes.

5.3.5 ETV of Gasoline Cumulative Effect FMs

5.3.5.1 ETV of single gasoline vehicle with cumulative effect FMs. The general procedure discussed in Section 5.1.3.4 is applied for single engine tests.

5.3.5.2 ETV of multiple gasoline vehicles with cumulative effect FMs. For fleet-wide emissions reductions, the emissions reduction for each pollutant is computed from a linear regression on the data from the tested vehicles (as for diesel engines) as described in Appendix D.

5.4 ETV of Lubricant FMs

This protocol was developed to verify the performance of lubricant FMs that are straightforward replacements of conventional crankcase lubricants. Lubricant FMs tested are expected to provide equivalent or better performance than those recommended by the original equipment manufacturer (OEM) for the test engine(s). By providing emissions control and unchanged maintenance requirements, these FMs may provide a net emission reduction.

If a candidate lubricant is not a straightforward replacement for conventional crankcase lubricants or cannot meet the performance specifications required by the OEM, the applicant must provide an appropriate means to demonstrate that any emission reductions identified will be achieved in-use. For example, if the FM candidate lubricant cannot maintain the oil change interval recommended by the OEM, the applicant must provide a compliance and enforcement plan that will verify that the new interval will be followed in use to assure projected emission reductions are achieved in use. This plan will then be considered an integral part of the technology and the verification will be for the lubricant and its written plan for use.

If a candidate lubricant requires a special oil filter or other companion technology to function, the application must specify the requirement. The test will then be designed for both the FM lubricant and the companion technology, and the ETV verification will be for both technologies as a system.

As with the other FMs, verification of emissions reductions for lubricants is based on comparison of emissions during a base case test with those during a test using the candidate lubricant. For the base case and candidate lubricant test, the duration is approximately one oil change cycle, with emissions tests conducted periodically during that cycle. Tests done under this protocol do not evaluate the long term engine and emission control system deterioration/improvement from candidate lubricants; the applicant should be confident of and have conducted adequate tests to confirm the long term effects of the lubricant.

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The applicant is responsible for providing necessary information on candidate and base lubricants as well as OEM specifications for lubricants and their change intervals for each test engine. All applicable specifications and ratings must be fully referenced and documented by the applicant. All additives contained in the candidate lubricant must be fully described. Any exceptions to the applicable specifications must be noted for discussion with the APCTVC and/or EPA-OTAQ. Additionally, the application must describe the lubricant, its source, all additives, and provide information showing that the candidate lubricant does not contribute to increased engine or emission control system deterioration. Where procedures are not specified in this section, applicable procedures in the gasoline or diesel sections must be followed.

5.4.1 Candidate Lubricants

The suitability of candidate lubricants for the proposed application will be evaluated based on comparison of the candidate FM's properties to those of a base lubricant for the tests referenced in Table 5. The lubricant FM application must report results for the tests in Table 5 (or their latest revision) for all grades proposed for use in the ETV verification. This table suggests ranges of results for these tests. Because test procedures and property standards may change, the protocol will not require compliance with these ranges. Instead, a verification will indicate how a candidate lubricant compares with an expected performance standard. All additives in the candidate lubricant must be fully described. This includes measurements of all properties listed in Table 5. The presence of additives or of performance specifications related to emission control system deterioration (such as phosphorus) will be specifically noted in the verification report because these could cause decreased emission control system durability or a reduced emission benefit after long term use.

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Table 5. FM Lubricant Properties and Tests[a]

Test	ASTM Number	Description	Range of Result
Kinematic viscosity @ 100 °C	ASTM D 445	Measures flow resistance of fluid to gravity	3.5 (SAE 0W) to 16.5 cSt (SAE 50)
Pour point	ASTM D 97	Measures temperature at which fluid sample will no longer flow by gravity	-25 to - 45 °C
Noack volatility	ASTM D 5800	Measures evaporation of fluid at 250 °C for 1 hr	0 to 30%
Flash point	ASTM D 92 or D 93	Temperature at which a spark will ignite a flame in the vapor space over test fluid	120 °C minimum
Rotating bomb oxidation test (RBOT)	ASTM D 2272	Measures time for uptake of 100 psi oxygen gas (by pressure drop) of fluid at 100 °C in closed, rotating vessel	30 minutes minimum
Chemical analysis	ICP Spectra or XRF	Quantitative analysis of elements	No halogens, Pb, catalyst poisons
Phosphorus content	ICP Spectra or XRF	Quantitative analysis of elements	1500 ppm maximum
Copper corrosion	ASTM D 130	Grades color change of copper surface after immersion in fluid for 3 hr at 100 °C	1B maximum
Rust prevention	ASTM D 665 A&B	Counts size and number of rust spots on fluid-treated steel surface in fresh water (A) and sea water (B)	Pass A
Foam control	ASTM D 892 Sequence I-IV	Measures foam head on fluid into which air is sparged under various conditions (Sequence I-IV)	None after 10 minutes in all sequences
Four ball wear	ASTM D 4172	Measures diameter of spot worn on stationary ball bearings by a driven ball bearing under 20 kg load	0.5 mm maximum
Falex pin and vee block	ASTM D 3233	Measures friction and wear on a pin spinning between blocks under measured clamping load	Steady state coeff. of friction = 0.15 max

[a] Society of Automotive Engineers (SAE) Document J300, Viscosity Grades for Engine Oils, December, 1999.

The applicant must provide a single mixed batch of the candidate lubricant FM(s) in sufficient quantity for the entire program. The ETV report will list the lubricant grades tested and the emissions reduction obtained.

5.4.2 Base Lubricant and Test Fuel

The applicant must recommend potential base lubricating oils for the ETV verification. They are to be widely distributed, conventional technology lubricants, and are expected to be petroleum- based. The base lubricant must meet the most recent performance specifications for each engine or vehicle model. Where OEM specifications have been superseded by a new grade, the new grade must be used as the base lubricant. From the recommended list, the APCTVC will choose one brand of base lubricant for all ETVs, and the verification report will note emission reductions relative to that base lubricant.

If the applicant knows that the candidate lubricant may be affected by fuel properties, this should be described in the application, will be factored into the test design, and will be reported as characteristic of

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the FM. As described in more detail below, the ETV test includes periodic emissions test sequences separated by mileage (time) accumulation periods. Test fuels meeting the base fuel specifications in the gasoline or diesel sections must be used at each test sequence of the program. Commercial fuel may be used for mileage accumulation, provided it is used consistently throughout the entire test. The test/QA plan will identify specific fuel properties for all phases of the program, and the ETV will report the measured emissions reduction specifically for the gasoline or diesel fuel used during the test.

The base lubricant and the test fuel must be obtained and prepared as needed such that both are available in sufficient quantities for the entire program.

5.4.3 Highway Use Test Engines or Vehicles

Test vehicle(s) or engine(s) used in the lubricant FM tests must be stable as described in the applicable gasoline and diesel FM sections. The base and candidate lubricants must meet the lubricant specifications for the test vehicle(s) or engine(s). Documentation of these specifications must be provided for each vehicle or engine.

5.4.3.1 Types of vehicles. The types of test vehicles shall be selected in accordance with the gasoline and/or diesel FM sections. Where more than one vehicle or engine will be tested, an effort should be made to maximize the diversity of engine characteristics, such as engine speed and operating temperatures, that might affect oil performance.

5.4.4 Nonroad Engine Selection

The general requirements for engine selection for ETV of modified fuels remains applicable for lubricant FMs intended for nonroad applications. The applicant may propose test engines in his application, and these recommendations will be reviewed by the APCTVC.

5.4.5 General Test Procedures

To minimize carryover effects between the lubricants, a purge of the test vehicle (engine) shall be performed each time the oil type is changed. If the base or candidate oil is clearly labeled with a specific purge step as standard operating procedure (SOP), that SOP will be incorporated in the test/QA plan. If a purge SOP is not provided, the test vehicle or engine must be operated for a full oil change interval on the new lubricant before the oil change interval during which emission testing will occur. This operation will help insure that a normal residual amount of used oil (base or FM lubricant) is in the test vehicle when testing is conducted. Whenever the oil is changed or added, the volume of all oil added or removed must be recorded. Prior to making any oil changes (removal or addition), the crankcase oil level and condition must be recorded.

5.4.5.1 Vehicle preparation and maintenance. All test vehicles/engines are to be in good operating condition and to have been maintained in accordance with OEM requirements. Vehicle information must be recorded and maintenance documented through shop records. Prior to beginning the ETV test sequence, the crankcase oil level and condition must be recorded. After the engine/vehicle start condition has been noted, normally scheduled maintenance that is due or may become due during the test program should be performed; and, if so equipped, spark plugs, PCV valve, and air and breather filters are to be changed. The condition of the parts removed is to be noted and these parts are to be retained. An oil sample may be obtained to determine oil condition. No MIL/OBD fault codes are to be present. This vehicle information must be reviewed for acceptability prior to beginning testing.

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Similarly, at the end of the testing program, spark plugs, PCV valve, and air and breather filters will be removed, retained, and their condition noted. The vehicle/engine will be inspected, and any MIL/OBD faults noted. The condition of the vehicle/engine, indications of oil deposits, leaking, or any other oil-related potential concerns will be noted and described in detail in the verification report.

For replacement lubricant FMs, the same brand and part number of oil filters (as specified by the vehicle or engine original equipment manufacturer) must be used throughout the program. The number of filters required for the entire ETV program must be procured prior to its beginning, and the oil filter used at any time randomly selected from that stock.

Base and candidate oils must each be batch-mixed to have enough for the entire program. All special mixing and/or handling procedures must be consistent with good engineering judgment and fully described in the test/QA plan. All storage, mixing, and/or handling instructions for the candidate oil must be fully described in the application.

5.4.5.2 Required test procedures. The required emission tests are described in the applicable gasoline and diesel FM test sections. Equipment and reporting requirements, are specified in the applicable federal regulations. If an oil analysis is performed on any oil from a test vehicle, the results of that analysis will be included in the verification report.

5.4.5.3 Service accumulation. The test/QA plan will specify a service accumulation schedule for each vehicle to follow over the oil change interval. The OEM oil change interval should be used unless a longer interval is needed to evaluate changes over a longer period of operation such as if the oil were not changed in time. An applicant may request a shorter oil change interval. Where more than one vehicle or engine will be tested, the service accumulation schedules for different vehicles should include severe and normal operation to confirm performance of the candidate oil over a broad range of operation. In all cases, the service accumulation on the base oil and candidate oil must be the same over the oil change interval.

5.4.6 Lubricant FM ETV Test Sequences

Figure 2 shows the form of lubricant FM effects that are contemplated in the GVP data analysis in its most complex form with both short-term and long-term deterioration. The same analysis applies in cases exhibiting no deterioration in either the short term (over a single oil change) or the long term, and with different slopes for the base and FM cases. The estimated log (emission reduction) is the difference between the base case and FM case emissions at the midpoint of the FM case service. The analysis is simplest when the test points are symmetrical as shown in Figure 2.

The ETV test for a single vehicle/engine consists of a purge with the new lubricant and alternating test sequences and mileage/hours accumulation periods. As implied in Figure 2, it is assumed within this protocol that the emissions effect will be measurable during the first oil change of the candidate oil (following the purge step). If cumulative effects are expected, additional mileage accumulation may be incorporated into the test/QA plan and steps taken to return the vehicle/engine to baseline operation as described in Section 5.1. The applicant will be expected to provide the mileage/hours required for the FM to reach full effectiveness and the time required to return the vehicle/engine to baseline operation.

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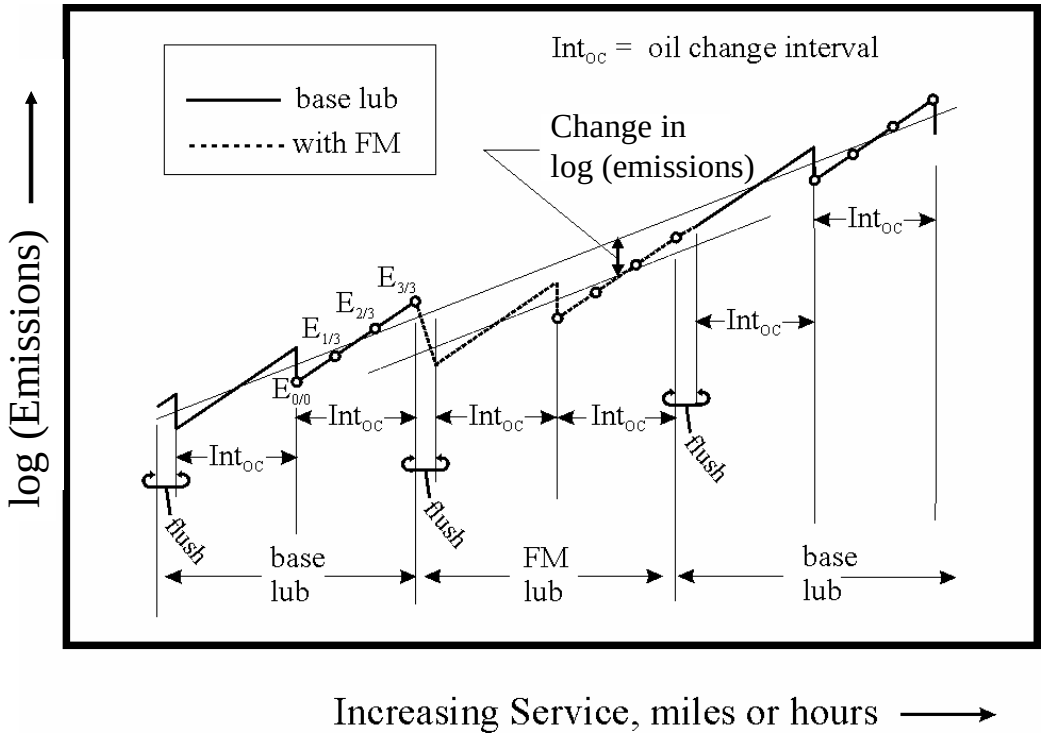

Figure 2. Lubricant FM Testing

The lubricant FM tests for light duty gasoline and all diesel engines are essentially the same as those described above for FMs. Figure 2 provides a graphic overview of the lubricant FM ETV test, and Table 6 gives the testing procedure for lubricant FMs. Details of the testing at the individual test points are as described in Sections 5.2 and 5.3 for diesel engines and gasoline vehicles, respectively.

5.4.7 Evaluating Results

Table 6. Lubricant FM Test Sequences

Light Duty Gasoline-Vehicle Test Sequence[a]
Fuel drain and 40% fill. Triple preparation
Fuel drain and 40% fill. Conduct FTP and US06 tests per Section 5.3.
Fuel drain and 40% fill. Conduct FTP and US06 tests per Section 5.3.
Fuel drain and 40% fill. Conduct FTP and US06 tests per Section 5.3.
Assign weight and combine results as described in Sections 5.3.5 and 5.3.6 to obtain the fully combined emission rates for each pollutant.
Heavy Duty Engine Test Sequence
Map engine.
Practice FTP cycles.
Run cold start test.
Run up to three hot start tests without running another cold start.
Run the SET.
Weight and combine emissions results as described in Sections 5.2.4 and 5.2.5 to obtain the fully composited emission rate for each pollutant.

[a] Highway fuel economy testing is optional; but, if used, it must be performed after required tests and consistently in each test sequence to maintain test uniformity.

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5.4.7.1 Single engine test data analysis. If there is no indication of emission system deterioration (the means of the base case test are the same), the single engine data may be analyzed applying Equations 1 through 6 as described in Section 5.1.3.1. All eight base case tests should be averaged to generate the base case mean. The resulting emission reduction for each pollutant will be reported.

If comparison of the two base case test series shows a measurable increase in emissions, a least-squares line should be fitted to the data applying the principles given in Appendix E. For an experiment in with a symmetrical design (Figure 2), the mean emission reduction, $\hat{\Delta}$, is

$$\hat{\Delta}_j = \overline{E2_j} - \frac{\overline{E1_j} + \overline{E3_j}}{2} \tag{14}$$

where:

$\overline{E1}$ = the mean of the first four base case tests (in log-scale units) for the pollutant of interest,

$\overline{E2}$ = the mean of the four FM tests (in log-scale units) for the pollutant of interest,

$\overline{E3}$ = is the mean of the second four base case tests (in log-scale units) for the pollutant of interest.

Equation 18 is a recast version of Equation E-5 in Appendix E. As a percentage, the emission reduction is computed as

$$ER = (1 - e^{\hat{\Delta}_j}) \times 100\% \tag{15}$$

For non-symmetrical designs, the general form of the analysis in Appendix D will be applied.

5.4.7.2 Cumulative effect lubricant FM data analysis. The analysis of cumulative effect lubricant FM emission reductions is highly dependent on the type of cumulative effect caused by the FM. As of the date of this protocol, no data or theory were available describing the probable effect of cumulative effect FMs. As is shown in Appendix E, the effect of a lubricant FM is totally confounded with a long-term quadratic effect for a 12-test experimental design such as is shown in Figure 2. Therefore, more complex data analyses are not likely to bear fruit. In addition, no cumulative effect lubricant FM vendor has applied to ETV and no such effects have been postulated to the APCTVC. Therefore, all lubricant FM technologies will be treated as providing an immediate effect for the purposes of this protocol.

Should an applicant propose a cumulative effect lubricant, the APCTVC and the testing organization will develop a specific experimental design that applies the test design criteria stated or implied in this protocol for the other technologies.

6.0 REPORTING AND DOCUMENTATION

This section describes the procedures for reporting data in the verification report and verification statement. The specifics of what data must be included and the format in which the data must be included are addressed in this section (e.g., QA/QC summary forms, raw data collected, photographs/slides/video tapes). The verification report for each technology will include near the

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beginning a verification statement that summarizes the ETV results. An example draft is attached as Appendix A. The verification report, including the verification statement, will be written by the APCTVC based on the test report submitted by the testing organization. The verification report and verification statement will be reviewed by the APCTVC and the technology applicant before being submitted to EPA for review and approval as specified in the ETV QMP.

6.1 Reports

Based on the test report from the laboratory, the APCTVC will prepare the draft verification report, which includes the following topics:

1. Verification statement;
2. Introduction;
3. Description and identification of product tested;
4. Procedures and methods used in testing;
5. Statement of operating range over which the test was conducted;
6. Summary and discussion of results as required to
    a. support the verification statement,
    b. explain and document necessary deviations from the test plan, and
    c. discuss QA issues;
7. References; and
8. Appendices:
    a. QA/QC activities and results,
    b. Raw test data, and
    c. Equipment calibration results.

The verification statement will include the following:

9. Technology applicant's name and technology's descriptive information,
10. Summary of ETV test program,
11. Results of the ETV test,
12. Notice of control device warranty and any limitations of the ETV results, and
13. Brief QA statement.

Review and approval of the draft ETV report and statement are described in Section 3.0.

6.2 Data Reduction

Data from measurements made as part of the ETV test will be reported as emissions rates in grams/kilowatt-hour (g/kW-h) (grams/brake horsepower-hour [g/bhp-hr]) or grams/mile (g/mi) and as percentage emission reductions from the baseline engine. The confidence limits will be presented as well as the mean emissions reduction, as discussed in Section 5.1.2. When they would be helpful to the mobile sources community because of established usage, the appropriate English engineering units will be supplied parenthetically.

7.0 DISSEMINATION OF ETV REPORTS AND STATEMENTS

After an FM technology has been tested and the draft verification report and verification statement prepared by the APCTVC, the APCTVC will send a draft of both to the applicant for review prior to

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submission to EPA and release of the approved report to the public. This gives the applicant the opportunity to review the results, test methodology, and report terminology while the drafts remain working documents and are not publicly accessible. The applicant may submit comments and revisions on the draft statement and report to the APCTVC. The APCTVC will consider these comments and may suggest revisions of its own.

After incorporating appropriate revisions, the draft final verification report and verification statement will be submitted to EPA for review and approval. A signed original verification statement within the verification report will be filed and retained by the APCTVC, and signed originals will also be provided in verification reports to the applicant and to EPA. Three additional paper copies of the ETV report will be provided to the applicant. Further distribution of the ETV report, if desired, is at the applicant's discretion and responsibility. However, approved verification statements and verification reports will be posted on the ETV Web site for public access without restriction. The verification report report appendices will not be posted on the Web site, but will be publicly available from the APCTVC.

8.0 APPLICANT'S OPTIONS SHOULD A TECHNOLOGY PERFORM BELOW EXPECTATIONS

ETV is not a technology research and development program; technologies submitted to ETV are to be commercially ready and with well-understood performance. Tests that meet the ETV data quality requirements (a valid FTP test) are considered valid and suitable for publishing; however, a technology may fail to meet the applicant's expectations. Based on limited testing, for instance, the applicant might expect an emission reduction of 30% ± 7% result. However, the actual ETV result from the more complex FTP test cycle might be 20% ± 15%. The APCTVC will use its experience to avoid this situation, but it is possible. In this case, the applicant may choose to schedule additional tests, may accept the result and complete the verification, or may request that a verification statement not be issued. However, ETV reports are always in the public domain and will be posted on the ETV Web site. Verification reports will be written and will be available from EPA for review by the public regardless of a request not to issue a verification statement.

As another example, an applicant might expect a mean of 10% reduction with a confidence interval of ±5%, but testing results in an actual verification shows a mean reduction of 5% with a confidence interval of ±7% reduction. In this case, the ETV data are insufficient to verify that the technology provided any reduction at all. Additional tests must be scheduled and a statistically significant reduction obtained for a verification statement to be issued. Inability to detect a statistically significant emission reduction (or failure to have sufficient tests) will prevent completion of the ETV, and the results of the ETV will be reported publicly stating that performance could not be distinguished from 0% reduction. A verification statement will not be issued in this case.

In either of the above cases, the applicant may improve the product and resubmit it under a new model identification for ETV testing. ETV reports and statements for acceptable tests of the new product will be issued as they are processed by the APCTVC and EPA (except that the results for several identical tests performed in rapid succession will be released simultaneously).

9.0 LIMITATIONS ON TESTING AND REPORTING

To avoid having multiple ETV reports for the same product and to maintain the ETV testing as a cooperative effort with the applicant, the following restrictions apply to ETV testing under this protocol:

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- Applicants may submit only products they manufacture or whose distribution they control. Applicants may not submit for ETV testing control systems whose use is not in their control except with the agreement of the manufacturer or vendor.
- For a given product (e.g., brand and model), APCTVC policy is that only one ETV report and statement will be issued for any single application.
- Air pollution control technology frequently performs differently in different applications. Applicants may request additional tests of essentially identical technology if it is being applied to pollution sources that are clearly different from those for which verifications have been obtained.

10.0 REQUIREMENTS FOR TEST/QA PLAN

10.1 Quality Management

All testing organizations participating in this ETV Program must meet the QA/QC requirements defined below and have an adequate quality system to manage the quality of work performed. Documentation and records management must be performed according to the ETV QMP (U.S. EPA, 2002a) or its superceding document. Testing organizations must also perform assessments and allow audits by the APCTVC (headed by the APCT QA Officer) and EPA corresponding to those in Section 11.

All testing organizations participating in the Retrofit Air Pollution Control Technologies for Highway and Nonroad Use Diesel Engines Program must have an ISO 9000-accredited (ISO, 1994) or ANSI E4-compliant (ANSI, 1994) quality system and an EPA- or APCTVC-approved QMP.

10.2 Quality Assurance

All ETV testing will be done following an approved test/QA plan that meets *EPA Requirements for Quality Assurance Project Plans* (U.S. EPA, 2001c) and Part B, Section 2.2.2 of EPA's ETV QMP (U.S. EPA, 2002a). These documents establish the requirements for test/QA plans and the common guidance document, *Guidance for Quality Assurance Project Plans* (U.S. EPA, 2002b), provides guidance on how to meet these requirements. The APCT Quality Management Plan (RTI, 1998) implements this guidance for the APCTVC.

ETVs conducted under this generic protocol utilize test procedures described in the FTP (40 CFR Part 86 for highway engines and 40 CFR Part 89 for nonroad engines). The test/QA plan must describe in adequate detail how the FTP test methods are implemented by the testing organization. Replication of the FTP text is neither expected nor desired. The test/QA plan should reference the FTP in detail, by section and subsection, as appropriate for the topic under consideration. Any deviations from the FTP must be identified and explained. Internal SOPs may be referenced provided they are available for audit review. (SOPs need not be incorporated into the test/QA plan except by reference. If considered proprietary to the testing organization, they should be clearly marked.) When the FTP offers alternative test procedures or equipment, the test/QA plan must identify the alternative implemented. Similarly, if a range of operating parameters is allowed by the FTP, the specifics of the particular implementation must be provided. For a testing organization with multiple test cells, these details may be tabulated and incorporated by attaching a table and identifying the test cell on the test report. Steps the testing organization will take to ensure acceptable data quality in the test results are also identified in the test/QA plan. Detailed reference to SOPs, the calibration portions of the FTP, or other available documents is encouraged. Any needed SOPs will be developed in accordance with *Guidance for Preparing Standard Operating Procedures (SOPs)* (U.S. EPA, 2001b.)

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The testing organization must prepare a test/QA plan and submit it for approval by the APCTVC. The test/QA plan must also be approved by EPA before the testing organization can begin ETV testing.

A test/QA plan contains the 24 elements listed below, the contents of which may be stand-alone or include references to the FTP or other widely distributed and publicly available sources. Legible hand-notated diagrams from the FTP are acceptable. If specific elements are not included, an explanation for not including them must be provided.

Group A Elements: Project Management

A1 Title and Approval Sheet
A2 Table of Contents
A3 Distribution List
A4 Project/Task Organization
A5 Problem Definition/Background
A6 Project/Task Description
A7 Quality Objectives and Criteria
A8 Special Training/Certifications
A9 Documentation and Records

Group B Elements: Data Generation and Acquisition

B1 Sampling Process Design (Experimental Design)
B2 Sampling Methods
B3 Sample Handling and Custody
B4 Analytical Methods
B5 Quality Control
B6 Instrument/Equipment Testing, Inspection, and Maintenance
B7 Instrument/Equipment Calibration and Frequency
B8 Inspection/Acceptance of Supplies and Consumables
B9 Non-direct Measurements
B10 Data Management

Group C Elements: Assessment and Oversight

C1 Assessments and Response Actions
C2 Reports to Management

Group D Elements: Data Validation and Usability

D1 Data Review, Verification, and Validation
D2 Verification and Validation Methods
D3 Reconciliation with User Requirements

The APCTVC will provide a test/QA plan template that illustrates its expectations.

10.3 Additional Requirements To Be Included in Test/QA Plan

The test/QA plan must include or reference a diagram and description of the extractive gaseous measurement system to be used for the testing and a list of the reference analyzers and measurement ranges to be used for quantifying the concentrations of all gaseous compounds to be measured, including both primary and ancillary pollutants.

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The test/QA plan must include or reference a schematic drawing showing all sample and test locations, including the inlet and outlet to the technology sampling locations. The location of flow disturbances and the upstream and downstream distances from the sampling ports to those flow disturbances must be noted. The number of traverse points that will be sampled must be provided.

The test/QA plan must include or reference the appropriately detailed descriptions of all measuring devices that will be used during the test.

The test/QA plan must explain or reference the specific techniques to be used for monitoring process conditions appropriately for the source being tested. It must also note the techniques that will be used to estimate any other operational parameters.

The test/QA plan must include and document estimates of historical measurement variability that will be used, as discussed in Section 5.1.1 and Appendix B, to compute the number of tests required and provide confidence intervals on single-test ETVs.

The test/QA plan must include a list of data quality indicator goals for individual measurements that conform to those specified in the relevant sections of the FTP and the corresponding acceptance criteria.

11.0 ASSESSMENT AND RESPONSE

Each independent testing organization must conduct internal assessments of its quality and technical systems and must allow external assessments of these systems by APCTVC QA personnel and by EPA QA personnel. After an assessment, the testing organization will be responsible for developing and implementing corrective actions in response to the assessment's findings.

As appropriate, the APCTVC and/or EPA will conduct assessments to determine the testing organization's compliance with its test/QA plan. The requirement to conduct assessments is specified in EPA's ETV QMP (U.S. EPA, 2002a), and in RTI's APCTVC QMP (APCTVC, 1998). EPA will assess RTI's compliance with APCTVC's test/QA plans. APCTVC will assess the compliance of other organizations with their test/QA plans. The assessments will be conducted according to *Guidance on Technical Audits and Related Assessments for Environmental Data Operations* (U.S. EPA, 2000) and *Guidance on Assessing Quality Systems* (U.S. EPA, 2001a.)

11.1 Assessment Types

Quality system assessment—Qualitative assessment of a particular quality system to establish whether the prevailing quality management structure, policies, practices, and procedures meet EPA requirements and are adequate for ensuring that the type and quality of measurements needed are obtained.

Technical systems audit—Qualitative on-site audit of the physical setup of the test. The auditors determine the compliance of testing personnel with the test/QA plan.

Performance evaluation audit—Quantitative audit in which measurement data are independently obtained and compared with routinely obtained data to evaluate the accuracy (bias and precision) of a measurement system.

Audit of data quality—Qualitative and quantitative audit in which data and data handling are reviewed and data quality and data usability are assessed.

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11.2 Assessment Frequency

Activities performed during verifications performance operations that affect the quality of the data will be assessed regularly and the findings reported to management to ensure that the requirements stated in the generic verification protocols and the test/QA plans are being implemented as prescribed.

The types and minimum frequency of assessments for the ETV Program are listed in Part A Section 9.0 of EPA's ETV QMP (U.S. EPA, 2002a). Tests conducted by the APCTVC will have, at a minimum, the following types and numbers of assessments:

- Quality system audit: Self-assessments by the testing organization at least once, and at least one independent assessment of the testing organization.
- Technical systems audits: Self-assessments (qualitative) by the testing organization at least once per test, and at least one independent assessment of the testing organization.
- Performance evaluation audits: Self-assessments (quantitative) by the testing organization on each test, and at least one independent assessment of the testing organization.
- Audits of data quality: Self-assessments (quantitative and qualitative) by the testing laboratory of at least 10% of all the ETV data with detailed reports of the audit results to be included in the data packages sent to the APCTVC for review.

The independent assessments of tests conducted by RTI for the APCTVC will be performed by EPA. The independent assessments of other organizations will be performed by the APCTVC.

11.3 Response to Assessment

When needed, appropriate corrective actions shall be taken and their adequacy verified and documented in response to the findings of the assessments. Data found to have been taken from nonconforming technology shall be evaluated to determine its impact on the quality of the required data. The impact and the action taken shall be documented. Assessments are conducted according to procedures contained in the APCT QMP. Findings are provided in audit reports. Responses by the testing organization to adverse findings are required within 10 working days of receiving the audit report. Followup by the auditors and documentation of responses are required.

12.0 SAFETY MEASURES

12.1 Safety Responsibilities

The testing organization's project leader is responsible for ensuring compliance with all applicable occupational health and safety requirements. Each individual staff member is expected to follow the requirements and identify personnel who deviate from them and report such action to their supervisor.

12.2 Safety Program

The testing organization must maintain a comprehensive safety program and ensure that all test personnel are familiar with and follow it.

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13.0 REFERENCES

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ASTM. *Standard Test Methods for Measurement of Extreme Pressure Properties of Fluid Lubricants (Falex Pin and Vee Block Methods)* ASTM D 3233. ASTM International, West Conshohocken, PA. 1998a.

ASTM. *Standard Test Method for Wear Preventive Characteristics of Lubricating Fluid (Four-Ball Method)* ASTM D 4172. ASTM International, West Conshohocken, PA. 1999.

ASTM. *Standard Test Method for Determination of Aromatic Content and Polynuclear Aromatic Content of Diesel Fuels and Aviation Turbine Fuels by Supercritical Fluid Chromatography* ASTM D 5186. ASTM International, West Conshohocken, PA. 1999a.

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ASTM. *Test Method for Total Sulfur in Liquid Aromatic Hydrocarbons and Their Derivatives by Oxidative Combustion and Electrochemical Detection* ASTM D 6428. ASTM International, West Conshohocken, PA. 1999c.

ASTM. *Standard Test Method for Evaporation Loss of Lubricating Oils by the Noack Method* ASTM D 5800. ASTM International, West Conshohocken, PA. 2000.

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ASTM. *Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure* ASTM D 86. ASTM International, West Conshohocken, PA. 2001.

ASTM. *Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (the Calculation of Dynamic Viscosity)* ASTM D 445. ASTM International, West Conshohocken, PA. 2001a.

ASTM. *Standard Test Method for Cetane Number of Diesel Fuel Oil* ASTM D 613. ASTM International, West Conshohocken, PA. 2001b.

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ASTM. *Standard Test Method for Foaming Characteristics of Lubricating Oils* ASTM D 892. ASTM International, West Conshohocken, PA. 2002d.

ASTM. *Standard Test Method for Oxidation Stability of Steam Turbine Oils by Rotating Pressure Vessel* ASTM D 2272. ASTM International, West Conshohocken, PA. 2002e.

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APPENDIX A: EXAMPLE VERIFICATION STATEMENT

Appendix A is an example verification statement written for a generic fuel modification intended to reduce engine emissions from mobile diesel engines. The technology is assumed to have an immediate effect and to be directed at a highway use engine. It is assumed to provide sufficiently large emissions reductions, requiring only the minimum number of tests by the minimum-number-of-tests calculation.

This generic verification statement is intended only to show the form of a verification statement. It will require modification for each technology verified, depending on the details of that technology's design, construction, and operation. The test/QA plan written for each test will include a draft verification statement customized for the technology actually being tested. The text of that specific verification statement will address the significant parameters that apply to the technology tested.

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U.S. Environmental Protection Agency

ETV Joint Verification Statement

TECHNOLOGY TYPE:	**MOBILE DIESEL ENGINE FUEL MODIFICATION INTENDED TO PROVIDE EMISSIONS REDUCTIONS**		
APPLICATION:	**CONTROL OF EMISSIONS FROM MOBILE DIESEL ENGINES IN (*HIGHWAY*) (*NONROAD*) USE BY (*TECHNOLOGY TYPE*)**		
TECHNOLOGY NAME:	**TECHNOLOGY NAME**		
COMPANY:	**COMPANY NAME**		
ADDRESS:	**ADDRESS**	**PHONE:**	**(000) 000-0000**
	CITY, STATE ZIP	**FAX:**	**(000) 000-0000**
WEB SITE:	**http://www.company.com**		
E-MAIL:	**some.one@company.com**		

The U.S. Environmental Protection Agency (EPA) has created the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative or improved environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high quality, peer reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized standards and testing organizations; stakeholder groups which consist of buyers, vendor organizations, permitters, and other interested parties; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The Air Pollution Control Technology Verification Center (APCTVC), one of six centers under the ETV Program, is operated by RTI, in cooperation with EPA's National Risk Management Research Laboratory. The APCTVC has evaluated the performance of a *TYPE* fuel modification for mobile diesel engines, the *TECHNOLOGY* by *COMPANY NAME*.

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ETV TEST DESCRIPTION

All tests were performed in accordance with the APCTVC ***Generic Verification Protocol for Determination of Emissions Reductions Obtained by Use of Alternative or Reformulated Liquid Fuels, Fuel Additives, Fuel Emulsions, and Lubricants for Highway and Nonroad Use Diesel Engines*** *and Light Duty Gasoline Engines* and the specific technology test plan "ETV Test/QA Plan for *TECHNOLOGY NAME*" These documents include requirements for quality management, quality assurance, procedures for product selection, auditing of the testing organizations, and test reporting format.

The mobile diesel engine air pollution control technology was tested at *TESTING ORGANIZATION*. The performance verified was the percentage emission reduction achieved by the fuel modification for particulate matter (PM), nitrogen oxides (NO_X), hydrocarbons (HCs), and carbon monoxide (CO) relative to the performance of the same engine on base fuel. Operating conditions were documented and ancillary performance measurements were also made. The basic modules of the test procedure are found in the Federal Test Procedures (FTPs) for emissions certification of diesel highway engines (40 CFR Part 86), diesel nonroad engines (40 CFR Part 89), and light-duty gasoline engines (40 CFR Part 86). Multiple replicate tests are required, depending on the type of fuel modification (FM) and the expected emissions reductions. A summary description of the ETV test is provided in Table A-1.

Table A-1. Summary of the Conditions for ETV Test of *TECHNOLOGY NAME* on ENGINE DESCRIPTION

Test conducted	Highway Transient Federal Test Procedure (FTP)
Engine family	*ENGINE MFGR NAME* Series *XXXYYY*, ??? operating hours prior to test
Engine size	YYY kW (XXX hp)
Technology	ACME Mark II Fuel Additive blended into CA 15 ppm ultra-low sulfur diesel fuel (ULSD)
Technology description	Additive is blended at the terminal with the base fuel at 0.02% by weight.
Test cycle or mode description	For both the base and FM-fueled tests, duplicate test sequences were run, each consisting of 1 cold start, 3 hot starts, and 1 highway steady-state (SET) cycle.
Base fuel description	EPA standard diesel per 40 CFR Part 86.1313-98
Critical measurements	PM, NO_X, HCs, and CO per the FTP
Ancillary measurements	CO_2, exhaust temperature, fuel consumption

VERIFIED TECHNOLOGY DESCRIPTION

This verification statement is applicable to the *TECHNOLOGY NAME* (to include model number and other identifying information as needed), which is a proprietary fuel additive manufactured by *MANUFACTURER NAME*. *TECHNOLOGY NAME* is distributed to fuel terminals and is blended into diesel fuel at the time all other additives are blended.

This verification statement describes the performance of *TECHNOLOGY NAME* on the diesel engine identified in Table A-1. The fuel additive, *TECHNOLOGY NAME*, is expected to provide similar emissions control performance on other engines having similar exhaust stream characteristics (similar fuel and engine technology) when properly sized for the application.

VERIFICATION OF PERFORMANCE

TECHNOLOGY NAME achieved the emissions reduction shown in Table A-2 at the stated conditions. The number of required ETV tests required was estimated to be the minimum test, consisting of one cold start, three hot starts, and one SET for each of six baseline tests and two candidate FM tests. This estimate was confirmed by the ETV test results. For the purposes of determining the status of the technology in regard to EPA's voluntary retrofit program, the prospective user is encouraged to contact EPA-Office of Transportation and Air Quality (OTAQ) or visit the retrofit program web site at http://www.epa.gov/otaq/retrofit/.

Table A-2. Verified Emissions Reductions for *TECHNOLOGY NAME*

Test Engine: Manufacturer's Name and Model No. AA1	Technology Test			
			Emissions Reduction, %[a]	
	Base Fuel	Candidate FM	Raw[b]	Discounted[c]
Critical Measurements of Emissions				
Hot start PM, g/bkWh (g/bhp-hr)or g/mi				
Composited PM, g/bkWh (g/bhp-hr)				
Hot start NO_X, g/bkWh (g/bhp-hr)				
Composited NO_X, g/bkWh (g/bhp-hr)				
Composited HC, g/bkWh (g/bhp-hr)				
Composited CO, g/bkWh (g/bhp-hr)				
Ancillary Measurements				
Engine power, kW (hp)				
Peak torque, N-m (lb_f-ft)				
Composited CO_2, g/bkWh (g/bhp-hr)				
Exhaust flow, L/min (ft^3/min)				
Exhaust temperature, °C (°F)				
Backpressure, kPa (in. Hg)				
Fuel usage,[d] % reduction				
Technology in/out temperature, °C (°F)				
Comments				

[a]Units of measure in rows are as indicated, except shaded columns in %.
[b]ER_{RAW} from Equation 3 of the GVP.
[c]ER_{DSCT} from Equation 6 of the GVP.
[d](Candidate PM-base fuel)/Base fuel x 100.

The APCT QA Officer has reviewed the test results and quality control data and has concluded that the DQOs given in the generic verification protocol and test/QA plan have been attained.

During the ETV tests, EPA or APCTVC QA staff conducted technical assessments at the testing organization. These confirm that the ETV tests were conducted in accordance with the testing organization's EPA-approved test/QA plan.

This verification statement verifies the emissions characteristics of *TECHNOLOGY NAME* within the stated range of application. Extrapolation outside that range should be done with

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caution and an understanding of the scientific principles that control the performance of *TECHNOLOGY NAME*. This verification focused on emissions. Potential technology users may obtain performance information from the manufacturer.

In accordance with the generic verification protocol, this verification statement is valid commencing on *DATE* indefinitely for application of *TECHNOLOGY NAME* within the range of applicability of the statement.

Hugh W. McKinnon, MD MPH Date
Director
National Risk Management Research Laboratory
Office of Research and Development
United States Environmental Protection Agency

Jack R. Farmer Date
Program Director
Air Pollution Control Technology Verification Center
RTI

NOTICE: ETV verifications are based on an evaluation of technology performance under specific, predetermined criteria and the appropriate quality assurance procedures. EPA and RTI make no expressed or implied warranties as to the performance of the technology and do not certify that a technology will always operate as verified. The end user is solely responsible for complying with any and all applicable federal, state, and local requirements. Mention of commercial product names does not imply endorsement.

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APPENDIX B: DETERMINING MINIMUM NUMBER OF TESTS REQUIRED AT EACH TEST POINT

The ETV program for mobile source emissions requires that a testing program for a given technology attempt to achieve the following for each vehicle tested:

- The emissions reduction (ER) is to be tested using a t-test with significance level of 0.05; the null hypothesis is that the FM produces no reduction, and the alternative is that it reduces emissions.
- For the applicant's expected ER, a statistical power of 0.90 is desired.

For FM, the t-test can be formulated in terms of a confidence interval as in equation (4) of the protocol document, or as the ratio (observed ER)/(square root of variance of ER). The goal of this appendix is to derive the sample size needed for this statistical test to achieve the desired level of power.

An approximate variance expression for the emissions reduction is embedded in eq. (4) of the protocol document. This variance is

$$Var(ER) \approx \left(\frac{1}{\bar{E}_B}\right)^2 \left[\frac{s_F^2}{n_F} + (1-ER)^2 \frac{s_B^2}{n_B}\right] \qquad \text{(B-1)}$$

where $\bar{E}_B$ = the mean of the baseline emissions
s_F^2 = the variance of the FM emissions
s_B^2 = the variance of the baseline emissions
n_F = the number of emissions measurements in the FM sample
n_B = the number of emissions measurements in the baseline sample

To get an initial sample size, assume that

$$n = n_B = n_F \text{ and } s_B^2 = s_F^2 = s^2 .$$

Then (B-1) becomes

$$Var(ER) = \frac{1}{n}\frac{s^2}{E_B{}^2}\left[1 + (1-ER)^2\right] \qquad \text{(B-2)}$$

Let μ_B and μ_F denote the true mean emissions level for the given vehicle under baseline and FM conditions, respectively. Assume that we want to have a probability of 1-β of declaring significance if the FM results in an emissions level equal to $k\mu_B$, where, for instance, k might be 0.95. The true ER would then be given by $\frac{\mu_B - \mu_F}{\mu_B} = 1-k,$ or 0.05. Then, if we want n to be

large enough to detect an true ER of (1-k) with power (1-β), an approximate formula for n would be given by,

$$n \geq \frac{\left(z_{1-\alpha} + z_{1-\beta}\right)^2 \left(\sigma^2 / \mu_B^2\right)\left[1+k^2\right]}{(1-k)^2} + \frac{z_{1-\alpha}^2}{2} \qquad \text{(B-3)}$$

where μ_B = the true population mean baseline emissions rate

σ^2 = the true population measurement-error variance (for both baseline and fuel additive emissions)

$Z_{1-\alpha}$ = the standard normal deviate associated with probability 1-α

$Z_{1-\beta}$ = the standard normal deviate associated with probability 1-β.

The n calculated in (B-3) is the sample size for both FM and baseline tests (i.e., the total number of tests is 2n); the calculated n should be rounded up to next highest integer. The first term in (B-3) is based on a modification of the standard sample size formula for a one sided z-test; note that it depends on the magnitude of the effect to be detected (k), the relative measurement-error variance (in the parentheses), and the specified error rates (α and β). The second term is a correction factor that accounts for the fact that a t-test rather than z-test (i.e., normal-distribution-based test) is used, since n will generally be small. A derivation of the correction factor is available in Appendix A of the EPA G-4 guidance document (*Guidance on the Data Quality Objectives Process* (EPA/600/R-96/055)).

As an example of applying (B-3), assume the following:
α=0.05, so $z_{1-\alpha}$=1.645;
β=0.10 when k=0.95, so $z_{1-\beta}$=1.282;
relative measurement error standard deviation = 0.02 (i.e., 2%).

Then substituting into (B-3) yields

$$n \geq \frac{(1.645+1.282)^2 (0.02)^2 [1+(0.95)^2]}{(1-0.95)^2} + \frac{(1.645)^2}{2} = 2.61 + 1.35 = 3.96 \qquad \text{(B-4)}$$

In this situation, 4 baseline and 4 FM tests would be sufficient to demonstrate the emissions reduction with the desired confidence.

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APPENDIX C: USE OF LOG SCALE TO TEST EMISSIONS REDUCTIONS

Let 100δ represent the true percentage reduction in emissions due to a candidate FM relative to the baseline emissions. That is, if there were no measurement error and no temporal variation associated with measurements, then we would expect the baseline emissions, E_B, and the FM-based emissions, E_F, to be related as

$$\delta = \frac{E_B - E_F}{E_B} \quad . \tag{C-1}$$

This implies that

$$E_B \delta = E_B - E_F \tag{C-2}$$

or

$$E_F = E_B (1 - \delta) \, . \tag{C-3}$$

Now suppose there is a series of n measurements for each type emission (E_{Bi} and E_{Fi}, $i=1,2,...,n$) and that these are summed. Then, from Equation C-3, the sums would be expected to be related as

$$\sum_{i=1}^{n} E_{Fi} = \left(\sum_{i=1}^{n} E_{Bi} \right) (1 - \delta) \, . \tag{C-4}$$

This suggests that a natural estimator for (1-δ) would be the ratio of the sums, or equivalently, that an estimator $\hat{\delta}$ for δ is

$$\hat{\delta} = 1 - \frac{\sum_{i=1}^{n} E_{Fi}}{\sum_{i=1}^{n} E_{Bi}} \quad . \tag{C-5}$$

This is the estimator described in Equation 3 of Section 5.1.3.1 of this generic verification protocol. It was proposed for use in simple before-versus-after analyses in which no residual effects were anticipated. In that context, confidence intervals for δ were developed which were used for testing the null hypothesis, H_0: δ = 0, versus the alternative hypothesis, H_A: δ > 0.

Elsewhere in this generic verification protocol, the use of a log-scale for assessing emission reductions is advocated. In particular, in testing fuel additives and lubricants where carry-over effects may occur and where phase-in periods are needed, it is not practical to test the baseline and FM conditions at essentially the same mileage or hours of engine operation. A log-scale

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model is proposed for estimating baseline emissions at that point where the FM tests are conducted. This is appropriate for several reasons.

First, the log-scale analysis is much easier to deal with statistically. Defining an estimator of δ in a manner analogous to Equation C-5 would result in complex variance formulas and complex formulas for approximate degrees of freedom because, in the original scale, measurement error variances are likely to change with varying emission levels. Use of the log scale, which presumes that standard deviations of measured emissions are approximately proportional to their magnitude, allows the relevant variances to be calculated in a simple fashion and for degrees of freedom to be determined exactly.

Second, when measurement errors are relatively small (e.g., relative standard deviations [RSDs] less than 20%) and when effects to be detected are relatively small (e.g., 5% or 10%, rather than 50%), the log-scale analysis will produce results nearly identical to that implied by Equation C-5. To see this, the log-scale equivalents of the above relationships are defined. Note that Equation C-3 implies (all logs are natural logarithms)

$$\ln(E_F) = \ln(E_B) + \ln(1-\delta). \tag{C-6}$$

For a series of measurements, then

$$\ln(1-\delta) = \mu_F - \mu_B \quad , \tag{C-7}$$

where μ_F and μ_B are the true ln-scale mean emissions for FM and base respectively.

A natural estimator of ln(1-δ) is therefore the difference in the observed ln-scale means from a series of measurements:

$$\ln(1-\delta) \cong \overline{Y}_F - \overline{Y}_B, \tag{C-8}$$

where $\overline{Y}_F$ and $\overline{Y}_B$ are the observed log-scale means. This implies that the $\tilde{\delta}$ can be estimated in terms of the ratio of the geometric means (GMs):

$$\tilde{\delta} = 1 - \frac{\exp(\overline{Y}_F)}{\exp(\overline{Y}_B)} \equiv 1 - \frac{GM_F}{GM_B} \quad . \tag{C-9}$$

Note that the hypotheses expressed in Equation C-6 can be equivalently stated in log-scale units as

$$H_0: \ln(1-\delta) = 0 \text{ versus } H_A: \ln(1-\delta) < 0 \tag{C-10}$$

or

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$$H_0: \mu_F = \mu_B \text{ versus } H_A: \mu_F < \mu_B \,. \qquad \text{(C-11)}$$

The similarity of the results obtained via the alternate approaches for estimating, and testing for, emission reductions is demonstrated by the simulation results given in Table C-1. Three different sample sizes were considered. In each case, a log-scale measurement error standard deviation of 0.1 (essentially a 10% RSD) was used. The true effects shown in column 2 were used to generate normally distributed "data." The estimated values of the effects and the results of the respective t tests are very similar, especially for the smaller effect sizes.

Table C-1. Summary of Simulation Results

	True Effects		Estimated Effects			Standard Errors (*s.e.*s) of Estimates		p Values from t Tests[b]	
Total *n*[a]	ln (1-δ)	δ	$\hat{\delta}$	$\hat{\mu}_F - \hat{\mu}_B$	$\tilde{\delta}$	$s.e.[\hat{\delta}]$	$s.e.[\hat{\mu}_F - \hat{\mu}_B]$	p_1	p_2
400	-0.03	0.030	0.027	-0.028	0.027	0.010	0.011	0.004	0.005
	-0.05	0.049	0.051	-0.053	0.052	0.010	0.010	0.000	0.000
	-0.10	0.095	0.086	-0.091	0.087	0.009	0.010	0.000	0.000
	-0.15	0.139	0.152	-0.164	0.152	0.008	0.010	0.000	0.000
	-0.20	0.181	0.166	-0.182	0.167	0.009	0.010	0.000	0.000
	-0.25	0.221	0.203	-0.227	0.203	0.008	0.010	0.000	0.000
	-0.30	0.259	0.260	-0.299	0.259	0.007	0.010	0.000	0.000
60	-0.03	0.030	0.014	-0.015	0.015	0.025	0.026	0.290	0.276
	-0.05	0.049	0.029	-0.028	0.028	0.024	0.025	0.116	0.135
	-0.10	0.095	0.056	-0.062	0.060	0.023	0.025	0.010	0.008
	-0.15	0.139	0.143	-0.155	0.144	0.021	0.024	0.000	0.000
	-0.20	0.181	0.158	-0.172	0.158	0.021	0.026	0.000	0.000
	-0.25	0.221	0.185	-0.206	0.186	0.017	0.021	0.000	0.000
	-0.30	0.259	0.273	-0.315	0.270	0.019	0.026	0.000	0.000
8	-0.03	0.030	0.108	-0.116	0.109	0.053	0.059	0.047	0.048
	-0.05	0.049	0.021	-0.019	0.019	0.058	0.059	0.368	0.381
	-0.10	0.095	0.135	-0.143	0.133	0.038	0.044	0.019	0.008
	-0.15	0.139	0.138	-0.148	0.138	0.045	0.052	0.014	0.015
	-0.20	0.181	0.289	-0.343	0.290	0.035	0.049	0.000	0.000
	-0.25	0.221	0.223	-0.253	0.223	0.017	0.021	0.000	0.000
	-0.30	0.259	0.111	-0.117	0.111	0.030	0.035	0.007	0.008

[a] $n/2$ observations each for FM and for baseline.

[b] p_1 is for t test based on $\hat{\delta}$. p_2 is for t test based on $\hat{\mu}_F - \hat{\mu}_B$.

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APPENDIX D: DATA ANALYSIS FOR CUMULATIVE EFFECT FMs

Assume that a series of emission measurements are made at each of four mileage points as indicated in Figure 1 of this generic verification protocol. In particular, assume that the third mileage point is for the candidate FM and that the other three points represent baseline measurements. Let X denote the mileage and let Y denote the natural log of the emissions for a given contaminant. Let $\overline{X}_{Fj}$ and $\overline{X}_{Bj}$ denote the average mileages associated with the FM measurements and baseline measurements, respectively, for vehicle *j*. For a single vehicle, the FM effect, Δ_j, is defined as the difference in ln(emissions) occurring at $\overline{X}_{Fj}$. The value $\hat{\Delta}_j$, which is an approximation of Δ_j, can be estimated as

$$\hat{\Delta}_j = \hat{Y}_{Fj}(\overline{X}_{Fj}) - \hat{Y}_{Bj}(\overline{X}_{Fj}) \tag{D-1}$$

where $\hat{Y}_{Fj}(\overline{X}_{Fj})$ is the predicted FM-based emissions at the (average) mileage associated with those measurements, and $\hat{Y}_{Bj}(\overline{X}_{Fj})$ is the predicted baseline emissions at that same mileage. With the measurement design indicated above, $\hat{Y}_{Fj}(\overline{X}_{Fj})$ is simply the average of the FM-based ln{emissions):

$$\hat{Y}_{Fj}(\overline{X}_{Fj}) = \overline{Y}_{Fj} = \frac{1}{n_F}\sum_{i=1}^{n_F} y_{ij} \tag{D-2}$$

where n_F is the number of FM-based measurements, y_{ij} = i^{th} observed ln(emission) for vehicle *j*, and the summation is over the FM-based measurements. On the other hand, $\hat{Y}_{Bj}(\overline{X}_{Fj})$ must be estimated based on the assumed baseline relationship between Y and X. If this relationship is assumed to be linear, then a statistical model for simultaneously estimating Δ_j and the parameters of the linear baseline relationship is the following:

$$y_{ij} = \alpha_j + \Delta_j Z_{ij} + \beta_j(x_{ij} - \overline{X}_{Fj}) + \varepsilon_{ij} \tag{D-3}$$

where

y_{ij} = i^{th} observed ln(emission) for vehicle *j*,
x_{ij} = mileage associated with i^{th} observation for vehicle *j*,
Z_{ij} = 1 if i^{th} observation for j^{th} vehicle is for FM-based condition,
= 0, otherwise,
ε_{ij} = random error for i^{th} observation for vehicle *j*, and

α_j, Δ_j, and $+\beta_j(x)$ are parameters to be estimated. With the model parameters defined in this way, the resulting estimates from a least squares regression are as follows:

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$\hat{\alpha}_j = \hat{Y}_{Bj}(\overline{X}_{Fj})$ = estimated baseline (ln-scale) emissions at the mileage where the FM-based tests are conducted,

$\hat{\Delta}_j$, as defined by Equation (D-1), is the estimated effect of the FM, and

$\hat{\beta}_j = \dfrac{\sum_{i=1}^{n_B} x_{ij} y_{ij} - n_B \overline{X}_{Bj} \overline{Y}_{Bj}}{\sum_{i=1}^{n_B} x_{ij}^2 - n_B \overline{X}_{Bj}^2}$ = estimated deterioration rate under baseline conditions,

where n_B is the total number of baseline measurements and $\overline{Y}_{Bj}$ is the mean of the n_B baseline measurements. It should be noted that this slope estimate is identical to the least squares estimate that would be obtained if only baseline data were included in the regression. Standard multiple regression software can therefore be used to produce both an estimate of the desired FM effect and of its standard error. Hence, confidence interval estimates for $\hat{\Delta}_j$ (or hypothesis tests) are straightforward. The variance of the estimated effect can be estimated as

$$Var[\hat{\Delta}_j] = s_j^2 \left[\frac{1}{n_F} + \frac{1}{n_B} + \frac{(\overline{X}_{Fj} - \overline{X}_{Bj})^2}{\sum_{i=1}^{n_B} x_{ij}^2 - n_B \overline{X}_{Bj}^2} \right] \quad \text{(D-4)}$$

where s_j^2 is the residual variance from the multiple regression performed on the vehicle *j* data. (If the model is accurate, then s_j^2 is an estimate of the measurement error variance of the emissions.) The degrees of freedom associated with Equation D-4 is $n_F + n_B - 3$.

The primary single-vehicle hypothesis of interest is the following:

$$H_0: \Delta_j = 0 \text{ vs. } H_A: \Delta_j < 0 \quad \text{(D-5)}$$

This is tested by computing a t statistic on the estimated effect, $\hat{\Delta}_j$,

$$t = \frac{\hat{\Delta}_j}{\sqrt{Var(\hat{\Delta}_j)}} \quad \text{(D-6)}$$

and comparing the result to t_C, the 5th percentage point of a t distribution with $n_F + n_B - 3$ degrees of freedom (e.g., if the total sample size is 24, then $t_C = -1.721$). The null hypothesis, H_0, is rejected if $t < t_C$.

To achieve the desired ETV confidence level (95%) and level of statistical power (90% at the applicant's anticipated effect level) for testing this hypothesis, one must ensure that the variance

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in Equation (D-4) is sufficiently small. Clearly, the magnitude on Equation (D-4) depends not only on the sample sizes and the underlying measurement error variance, but also on the design – namely, the spacing of the mileage points and the amount of replicate testing at each of those points. In general, smaller variance will be achieved by increasing the dispersion of the baseline mileage points used in the regression and/or by decreasing the absolute difference between $\overline{X}_{Fj}$ and $\overline{X}_{Bj}$. Note that all of the quantities appearing inside the brackets of Equation (D-4) depend solely on the particular design used. Hence, for any given design, the power of the test can be determined as follows.

- First determine the degrees of freedom and critical value, t_C, of the test, as defined above (e.g., select the 95th percentage point from a table of percentage points of the t distribution).

- Based on prior data, assume a value for the true underlying measurement error variance; denote this quantity as σ^2.

- Then compute a noncentrality parameter, *D*, as

$$D = \frac{\delta}{\sqrt{\sigma^2 K_j}} \qquad \text{(D-7)}$$

  where δ is the anticipated effect (in ln-scale units, or relative difference) and K_j is the quantity inside the brackets in Equation (C-4). (Given the formulation of the hypothesis test, δ should be negative.)

- The power (the probability of rejecting the null hypothesis when a true effect is equal to δ) is then determined as

$$\Pr[T(D) < t_C] \qquad \text{(D-8)}$$

  where T(D) denotes a random variable following a noncentral t distribution with noncentrality parameter D and $n_F + n_B - 3$ degrees of freedom. (Standard statistical software packages such as S-Plus or SAS have built-in functions for calculating such percentage points from noncentral t distributions.)

- By varying the design and/or the sample sizes, one can determine when Equation (D-8) exceeds 0.90, the desired power.

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APPENDIX E: SINGLE VEHICLE TESTS FOR LUBRICANTS

Assume that emission measurements are made at each of four mileage points within each of three phases, as indicated in Figure 2 of the generic verification protocol. In particular, assume that phase 2 consists of tests for the candidate FM and that phases 1 and 3 consist of baseline measurements. Note the following characteristics regarding the mileage scale of the design:

- The within-phase designs are the same for each phase. They can be characterized by a variable *U*, which is the mileage since oil change. Let U_{ijk} = the mileage since last oil change for measurement *i* within phase *k* for vehicle *j*, and let $\overline{U_{ik}}$ denote the average of these mileages for phase *k* of vehicle *j*. Let $u_{ijk} = U_{ijk} - \overline{U}_{jk}$ be the deviation of these mileages from their respective phase-specific means. (Nominally, the mileages within a phase are equally spaced, so that the four *U* values are proportional to 0, 1, 2, and 3; hence the deviations are proportional to -3, -1, 1, and 3.)

- In terms of the mileage scale, phase 2 is centered between phases 1 and 3. Hence, a continuous variable representing phase (with values of 1, 2, and 3) is in fact equivalent, apart from a scale factor and location factor, to a mileage variable. (That is, if the average mileages for the phases are denoted as $\overline{X}_{kj}$ and if deviations from the phase 2 mean are computed, then these deviations will be proportional to -1, 0, and 1, respectively, for phases 1, 2, and 3. This is the same variable as can be obtained by subtracting 2 from the phase indicator, *k*.)

An important consequence of the second bullet is that *the effect of the lubricant FM is totally confounded with a long-term quadratic deterioration effect*. To see this, *assume for the moment that phase 2 also involves baseline measurements* and assume that (a) within-phase deterioration effects are linear, and (b) that long-term (i.e., across phases or oil changes) deterioration effects are potentially quadratic. This corresponds to a saw-toothed curve with linear segments within phases that are connected at their midpoints by a second-order curve.

The statistical model for such a situation can be expressed as

$$y_{ijk} = \alpha_{jk} + \beta_{jk} u_{ijk} + \lambda_j L_{ijk} + \Delta_j Q_{ijk} + \epsilon_{ijk} \qquad \text{(E-1)}$$

where

y_{ijk} = i[th] observed ln(emission) for vehicle *j* and phase *k*,
u_{ijk} = within-phase mileage deviation (standardized, if desired [as described above], to take on values of -3, -1, +1, and +3),
L_{ijk} = -1 for phase 1 observations,
= 0 for phase 2 observations,
= +1 for phase 3 observations,
Q_{ijk} = -1/3 for phase 1 observations,
= +2/3 for phase 2 observations,
= -1/3 for phase 3 observations,
ε_{ijk} = random error for i[th] observation for phase *k* and vehicle *j*, and

α_{jk}, β_{jk}, λ_j, and Δ_j are parameters to be estimated.

With the model terms defined in this way, the resulting estimates, indicated by a ^, from a least-squares regression on the vehicle *j* data are as follows:

$$\hat{\alpha}_{jk} = \overline{Y}_{jk} = \text{average ln(emissions) for phase } k \text{ and vehicle } j, \quad \text{(E-2)}$$

$$\hat{\beta}_{jk} = \frac{\sum_{i=1}^{4} u_{ijk} y_{ijk}}{\sum_{i=1}^{4} u_{ijk}^2} = \text{within-phase deterioration factor for vehicle } j, \text{ phase k(expressed in thousand-mile [K] units, where 6K is the number of miles between the first and last tests within a phase),} \quad \text{(E-3)}$$

$$\hat{\lambda}_j = 0.5(\overline{Y}_{j3} - \overline{Y}_{j1}) = \text{linear component of long-term deterioration factor (expressed in phase units), and} \quad \text{(E-4)}$$

$$\hat{\Delta}_j = \overline{Y}_{j2} - \frac{\overline{Y}_{j1} + \overline{Y}_{j3}}{2} = \text{quadratic component of long-term deterioration factor (expressed in phase units).} \quad \text{(E-5)}$$

Now assume that the phase 2 measurements are for the lubricant FM rather than for baseline. Also assume that the long-term deterioration for baseline measurements is linear. This latter assumption is necessary if the effect of the FM for a given vehicle is to be defined as the "average FM emissions for phase 2 minus the baseline emissions that are predicted for phase 2," since we cannot isolate the effect of the FM from the quadratic component of the long-term baseline deterioration factor. For these assumptions, the model of Equation (E-1) still applies, but now Δ_j represents the effect of the FM and its estimate is given by Equation (E-5).

For the given design and the above model, fitting the model of Equation (E-1) to the data for a single vehicle will result in a variance for the estimated FM effect, $\hat{\Delta}_j$, as

$$Var[\hat{\Delta}_j] = 3s_j^2 / 8 \quad \text{(E-6)}$$

where s_j^2 is the residual variance from the multiple regression performed on the vehicle *j* data. (If the model is accurate, then s_j^2 is an estimate of the measurement error variance of the emissions.) The degrees of freedom associated with this variance is 4. The model of Equation (E-1) can also be fit using data from all tested vehicles; in that case, the variance of the estimated FM effect for vehicle *j* is

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$$Var[\hat{\Delta}_j] = 3s_P^2 / 8 \quad \text{(E-7)}$$

where s_P^2 is the (pooled) residual variance from the multiple regression performed on the *m* vehicles in the fleet. The degrees of freedom associated with Equation (E-7) is 4*m*.

Standard multiple regression software can therefore be used to produce both an estimate of the desired FM effect and of its standard error. Hence, confidence interval estimates for Δ_j (or hypothesis tests) are straightforward. The primary single-vehicle hypothesis of interest is the null hypothesis, H_0:$\Delta_j = 0$, versus the alternative hypothesis, H_A:$\Delta_j<0$.

This is tested by computing a t statistic, on the estimated effect, Δ_j,

$$t = \frac{\hat{\Delta}_j}{\sqrt{Var(\hat{\Delta}_j)}} \quad \text{(E-8)}$$

and comparing the result to t_C, the 5th percentage point of a t distribution with 4 or 4*m* degrees of freedom. The null hypothesis, H_0, is rejected if $t < t_C$.

To achieve the desired ETV confidence level (95%) and level of statistical power (90% at the applicant's anticipated effect level) for testing this hypothesis, one must ensure that the variance in Equations (E-6) or (E-7) is sufficiently small. The power of the test can be determined as follows:

- First determine the degrees of freedom and critical value, t_C, of the test, as defined above (e.g., select the 95th percentage point from a table of percentage points of the t distribution).
- Based on prior data, assume a value for the true underlying measurement error variance; denote this quantity as σ^2.
- Then compute a noncentrality parameter as

$$D = \frac{\delta}{\sqrt{\sigma^2 (3/8)}} \quad \text{(E-9)}$$

where δ is the anticipated effect (in ln-scale units, or relative difference). (Given the formulation of the hypothesis test, δ should be negative.)

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- The power, the probability of rejecting the null hypothesis when a true effect is equal to δ, is then determined as

$$\Pr[T(D) < t_C] \qquad \text{(E-10)}$$

where T(D) denotes a random variable following a noncentral t distribution with noncentrality parameter D and 4 or 4*m* degrees of freedom. (Standard statistical software packages such as S-Plus or SAS have built-in functions for calculating such percentage points from noncentral t distributions.)

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APPENDIX F: SENSITIVITY OF NUMBER OF TESTS CALCULATION TO MEASUREMENT VARIABILITY

Table F-1 presents the results of a sensitivity analysis of the calculation of the required number of tests in the particular cases of high (85%) and low (10% and 5%) reductions in emissions. The number of tests reported in the final column is the number required to have a 90% probability of detecting the emissions reduction with 95% confidence. Equation B-3 in Appendix B was used to compute the required number of tests. As in these sections, all calculations utilize the normal distribution under the assumption that the test measurement error is known and constant.

Within Table F-1, the variability of the baseline engine measurement ranges from 2 to 30%, and the controlled engine measurement variability from 10 to 30%. All of the percentage numbers in the table are referenced to a baseline engine emission. To convert the percentages to absolute emission rates, they must be multiplied by a baseline engine emission rate, and at 30% variability the standard deviations are twice the emission rates in g/bhp-hr. The emissions and standard deviations in Table F-1 have all been calculated for a baseline engine emitting PM at the 1990 certification level of 0.6 g/bhp-hr. For example, from the first row, an 85% reduction means an absolute PM emission of 0.09 g/bhp-hr. A 10% controlled engine measurement variability means the standard deviation for that measurement is 0.06 bhp-hr. For the baseline engine, the variability is 2%, so the baseline engine standard deviation is 0.012 bhp-hr. The same approach can be used to make a similar table for any other emission rate by multiplying the percentages by the desired baseline emission rate.

While the number of required tests increases as the test variability increases, Table F-1 shows that the increase is modest at high emissions reduction levels. While higher variability is expected at higher levels of control because the absolute emissions concentrations are low, the large reduction in emissions is easily detected.

On the other hand, lower variability is expected for low emissions reductions, but the smaller changes are harder to detect and more tests are required. Therefore even modest variability levels (relative to those in the top block of Table F-1) lead to very large numbers of tests.

As was discussed in Section 5.1.2, calculation of the confidence intervals on the mean emissions reduction will be based on population statistics and will utilize the t-distribution. Thus, the number of tests calculated using Equation B-3 (population statistics) may be fewer than will be required by the data itself based on sample statistics. As mentioned in Appendix B, an approximate calculation can be made for sample variability utilizing the Student's t-distribution rather than the normal (z-distribution) in Equation B-3. This use of Equation B-3 is not strictly valid, but may be useful for low emission reduction and/or high variability test designs to make a better estimate of the number of tests required.

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Table F-1. Sensitivity of Number of Tests to Measurement Variability

Expected emissions reduction, %	Controlled engine emissions, g/bhp-hr, relative to a baseline engine at the 1990 PM certification emission limit	Controlled engine variability, % of baseline engine	Controlled engine standard deviation, g/bhp-hr for baseline emission of 0.6 g/bhp-hr	Baseline engine variability, %, with the 1990 certification limit as baseline	Baseline engine standard deviation, g/bhp-hr, for1990 emission limit baseline emission of 0.6 g/bhp-hr	Number[a] of tests to achieve 90% probability of detecting reduction with 95% confidence
85	0.09	10	0.06	2	0.012	1
85	0.09	15	0.09	2	0.012	1
85	0.09	20	0.12	2	0.012	1
85	0.09	30	0.18	2	0.012	1
85	0.09	10	0.06	10	0.060	1
85	0.09	15	0.09	10	0.060	1
85	0.09	20	0.12	10	0.060	1
85	0.09	30	0.18	10	0.060	1
85	0.09	10	0.06	30	0.150	2
85	0.09	15	0.09	30	0.150	2
85	0.09	20	0.12	30	0.150	2
85	0.09	30	0.18	30	0.150	2
10	0.54	2	0.012	2	0.012	1
10	0.54	4	0.024	4	0.024	3
10	0.54	6	0.036	6	0.036	6
10	0.54	8	0.048	8	0.048	10
10	0.54	10	0.06	10	0.060	16
5	0.57	2	0.012	2	0.012	3
5	0.57	4	0.024	4	0.024	11
5	0.57	6	0.036	6	0.036	24
5	0.57	8	0.048	8	0.048	42
5	0.57	10	0.06	10	0.060	66

[a] For ETV, the minimum number of tests is three.

US EPA ARCHIVE DOCUMENT

State of Oregon Department of Environmental Quality

OAR 340-264-0078 - Figures

Figure 1 – Willamette Valley Open Burning Control Area

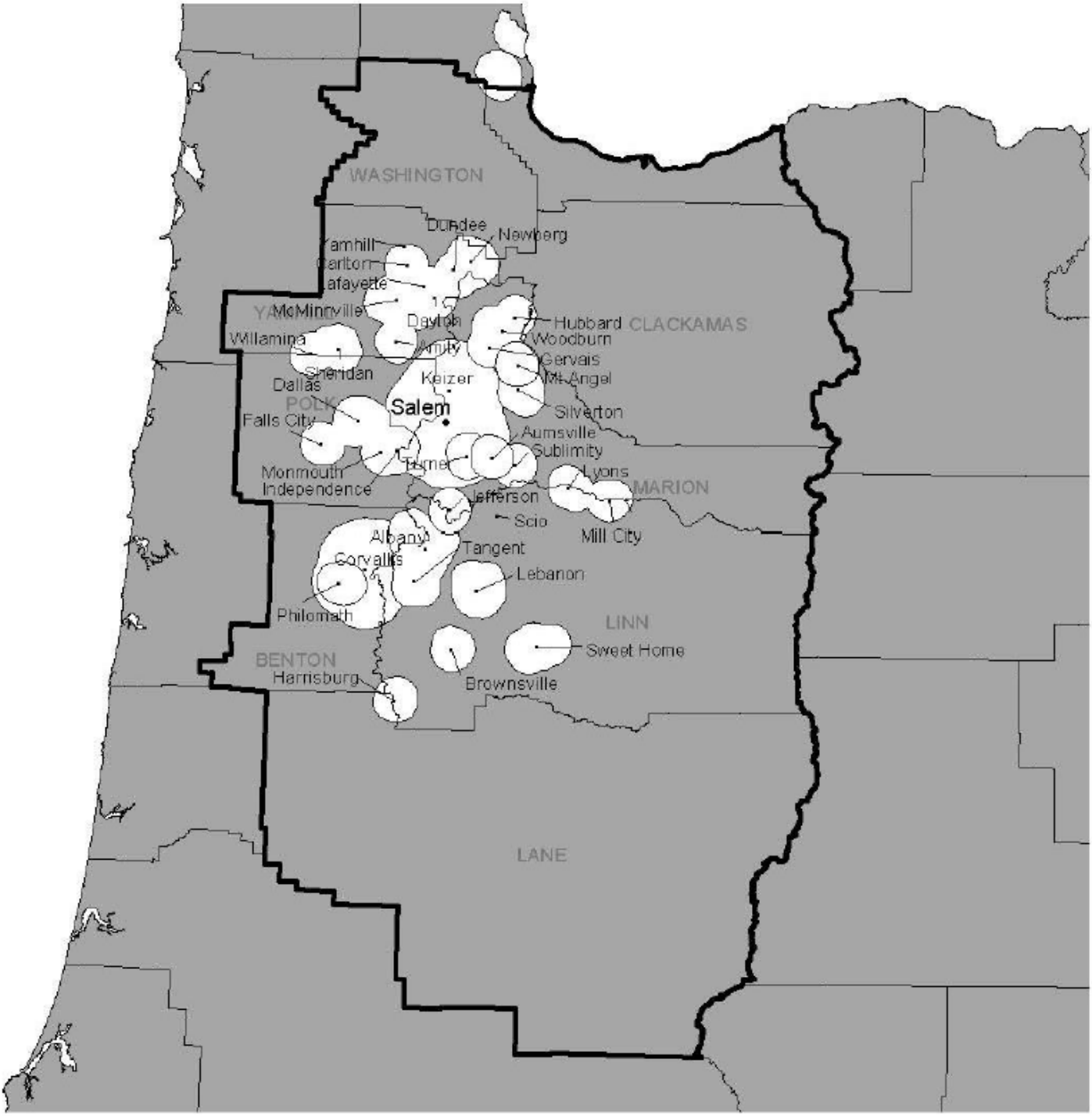

Figure 1A – Metropolitan Area Backyard Burning Boundaries

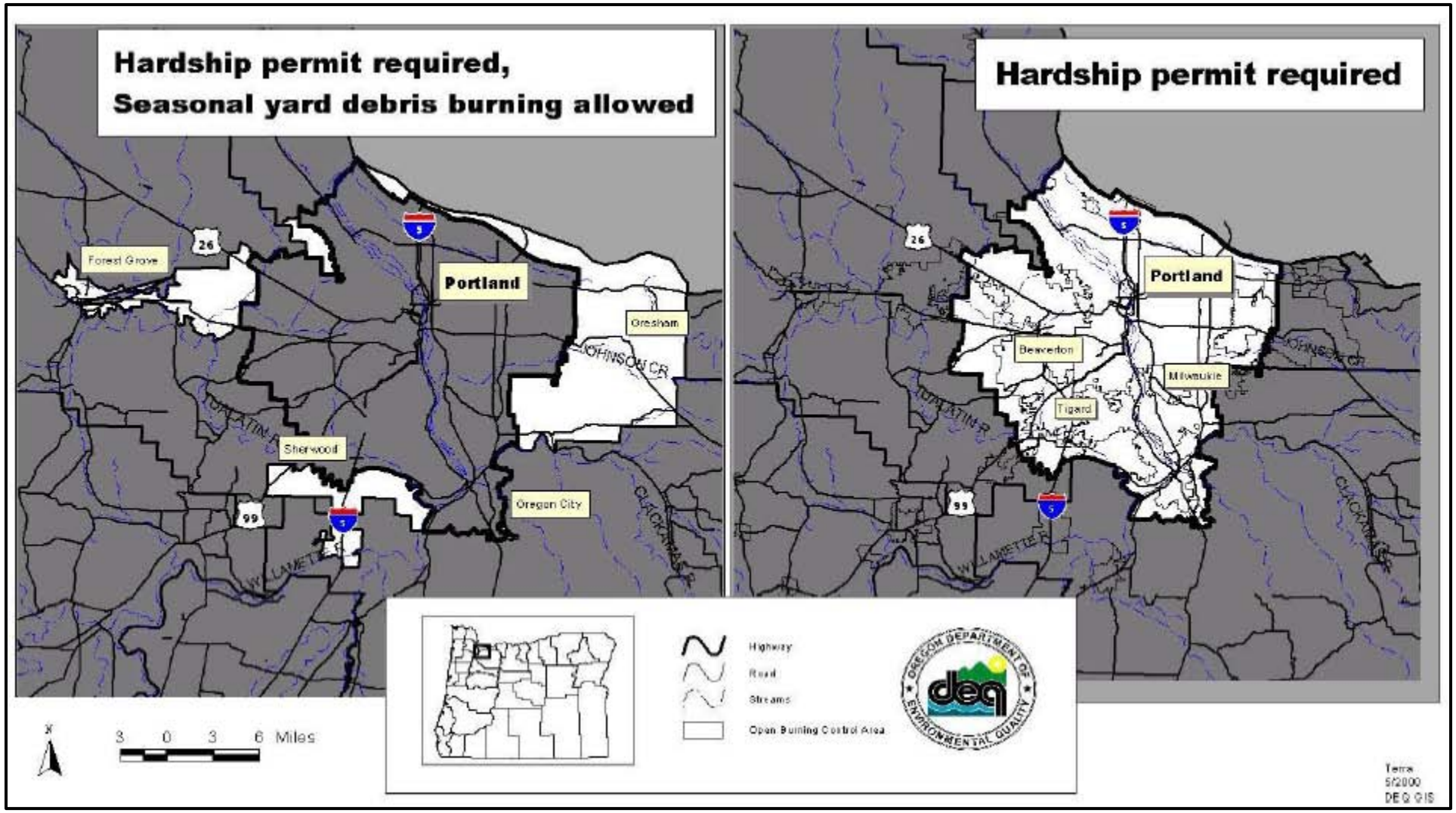

Figure 2 – Open Burning Control Areas

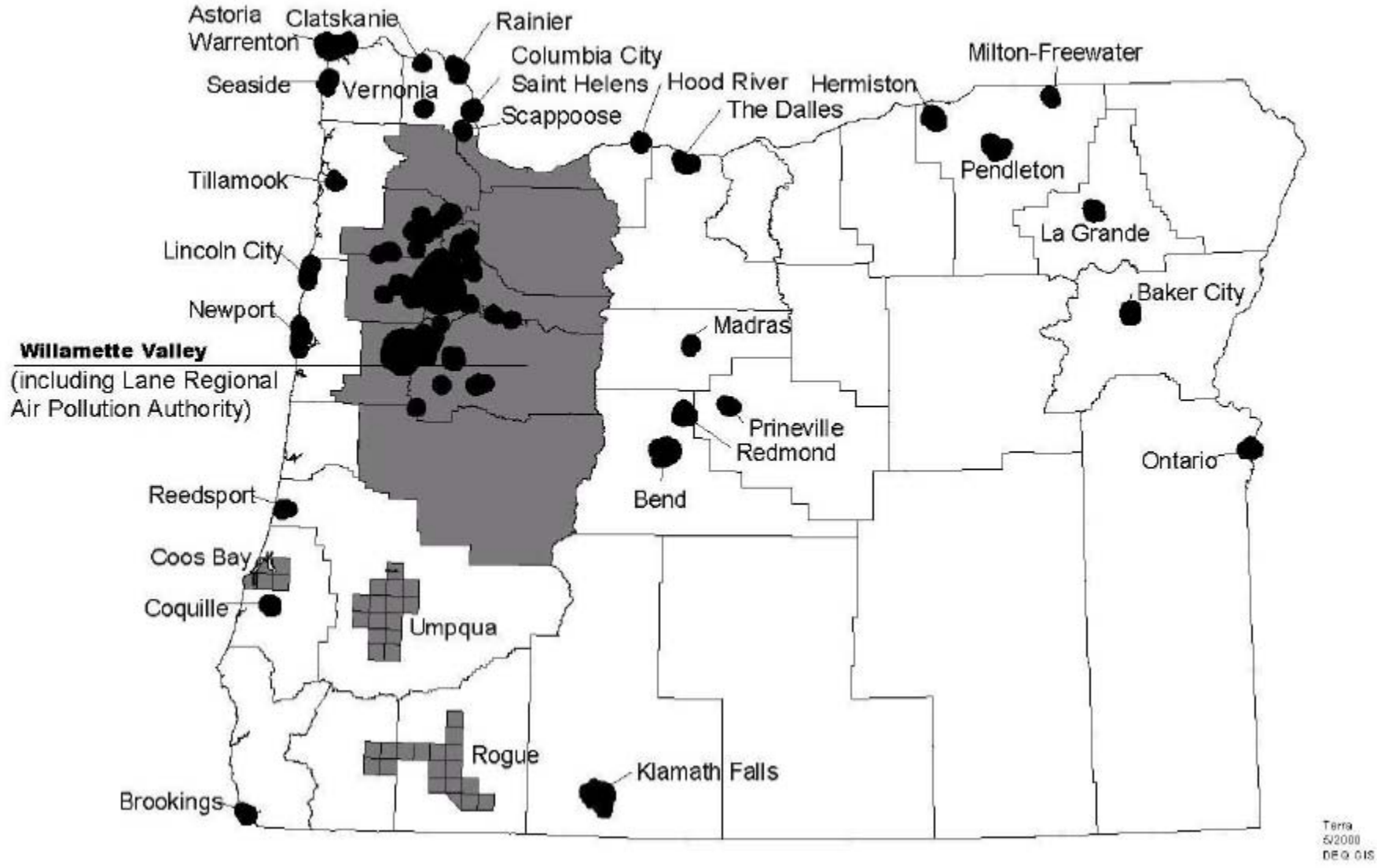

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Figure 3 – Coos Bay Open Burning Area

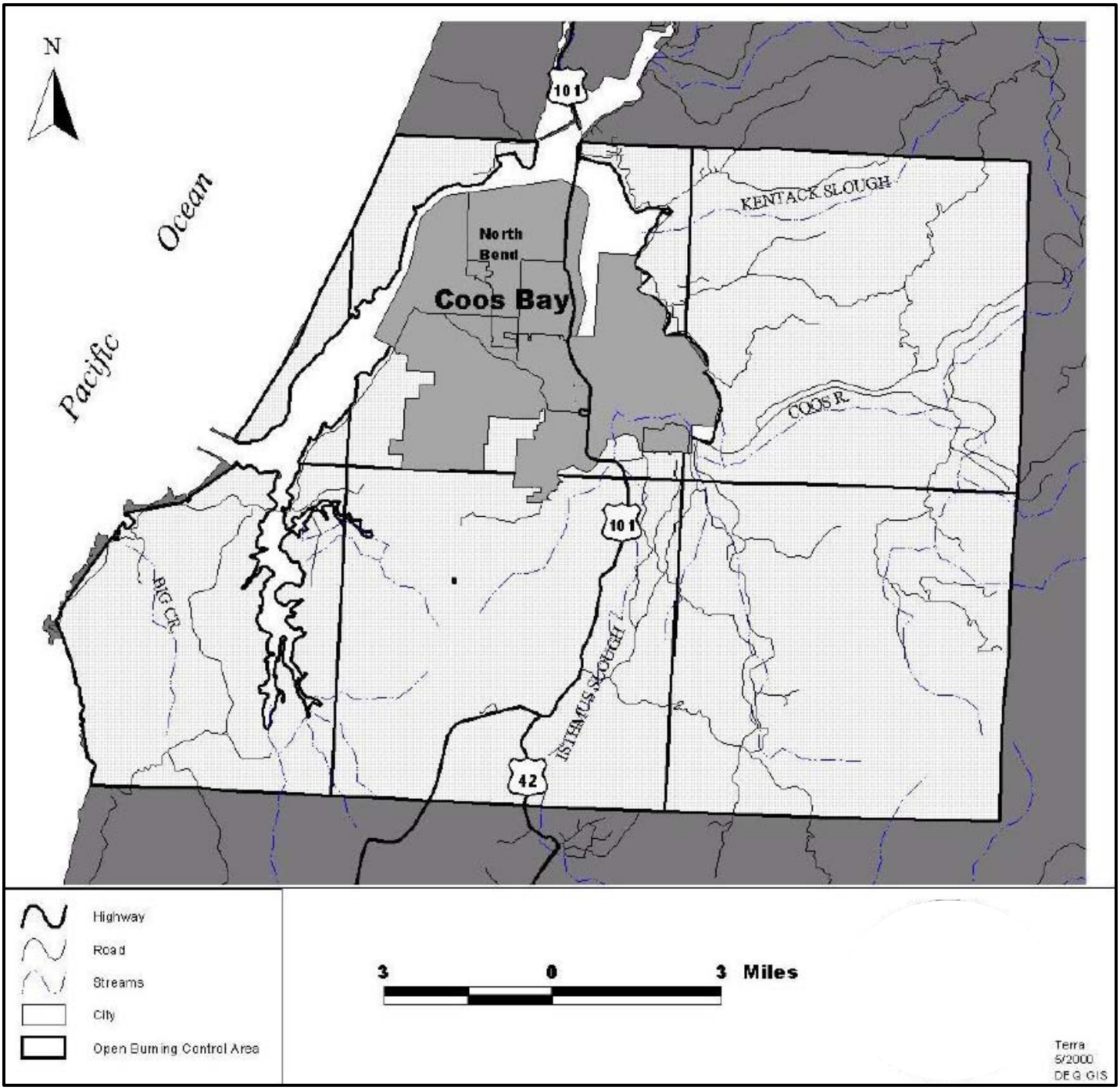


Figure 4 – Rogue Basin Open Burning Control Area

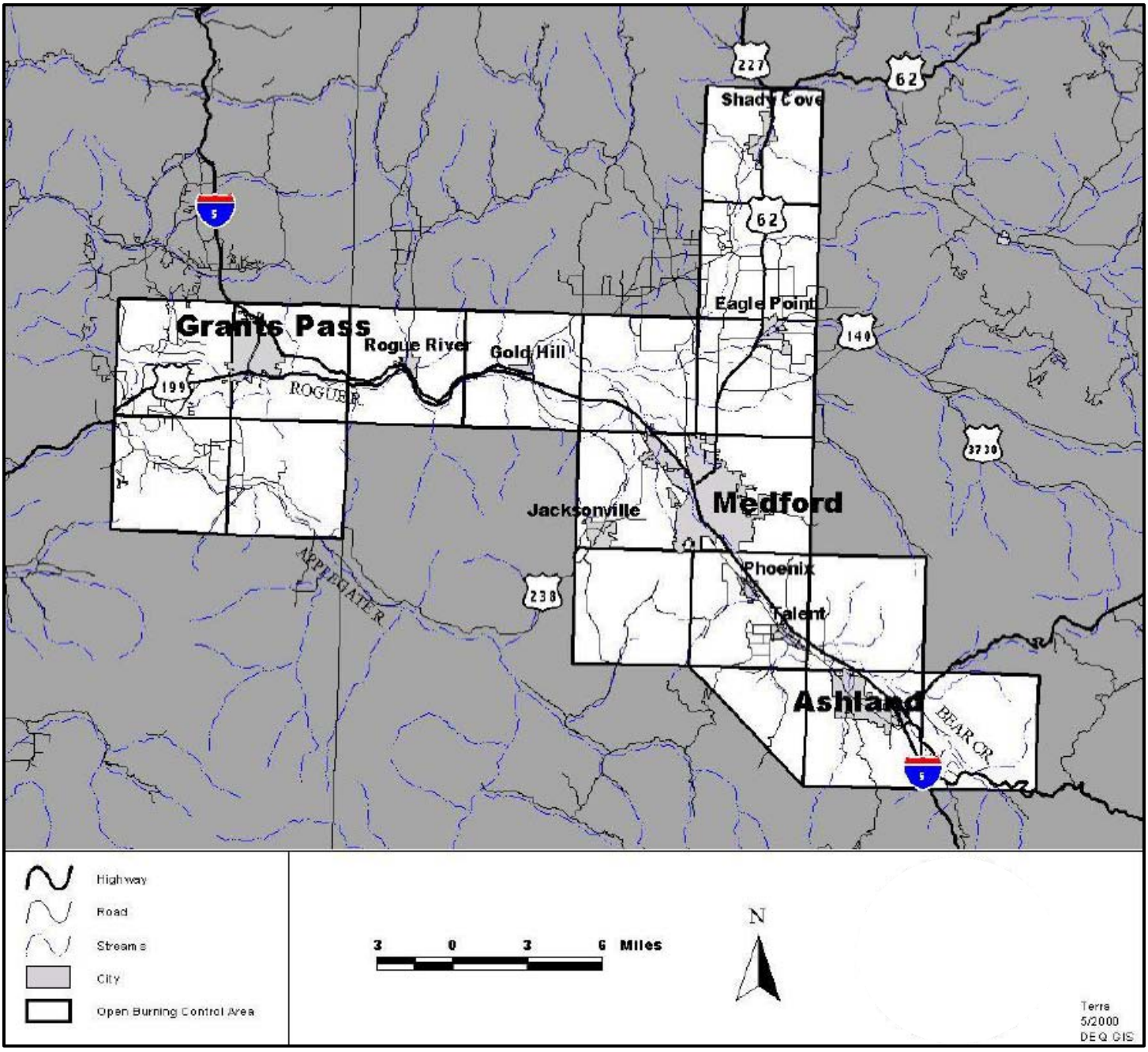


Figure 5 – Umpqua Basin Open Burning Control Area

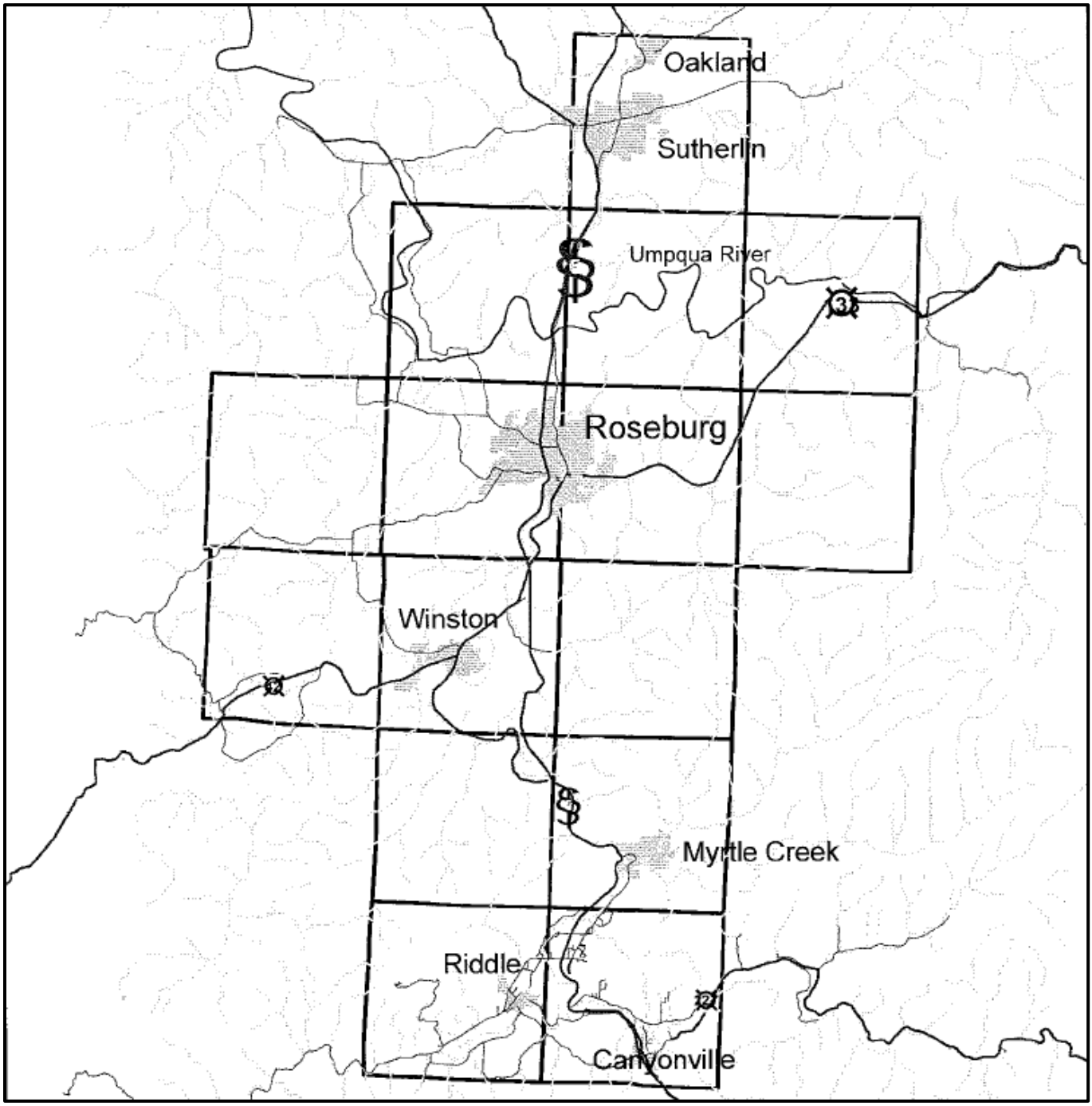
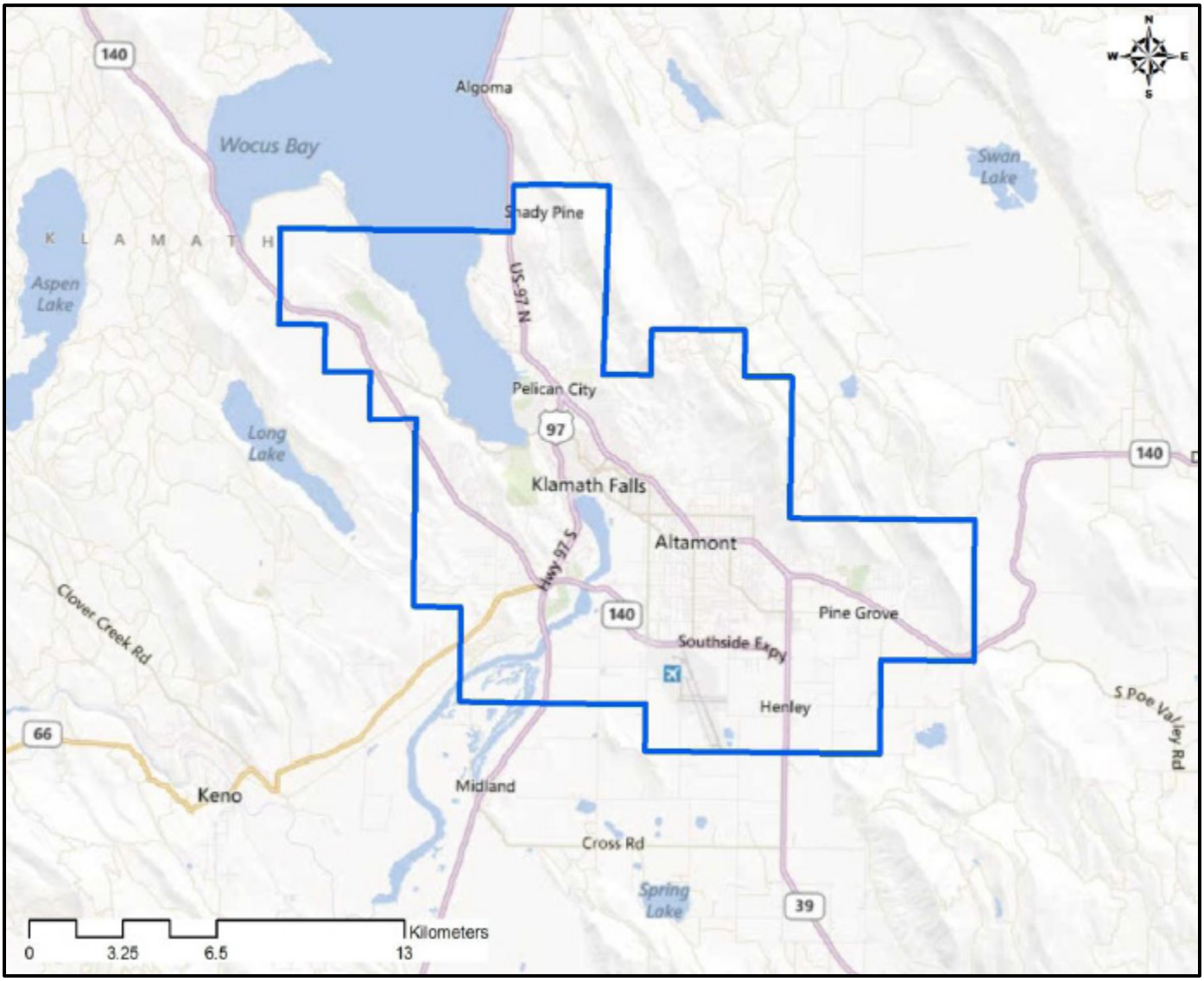


Figure 6 – Klamath Basin Open Burning Control Area



Klamath Basin Open Burning Control Area